京都大学
福井謙一記念研究センター

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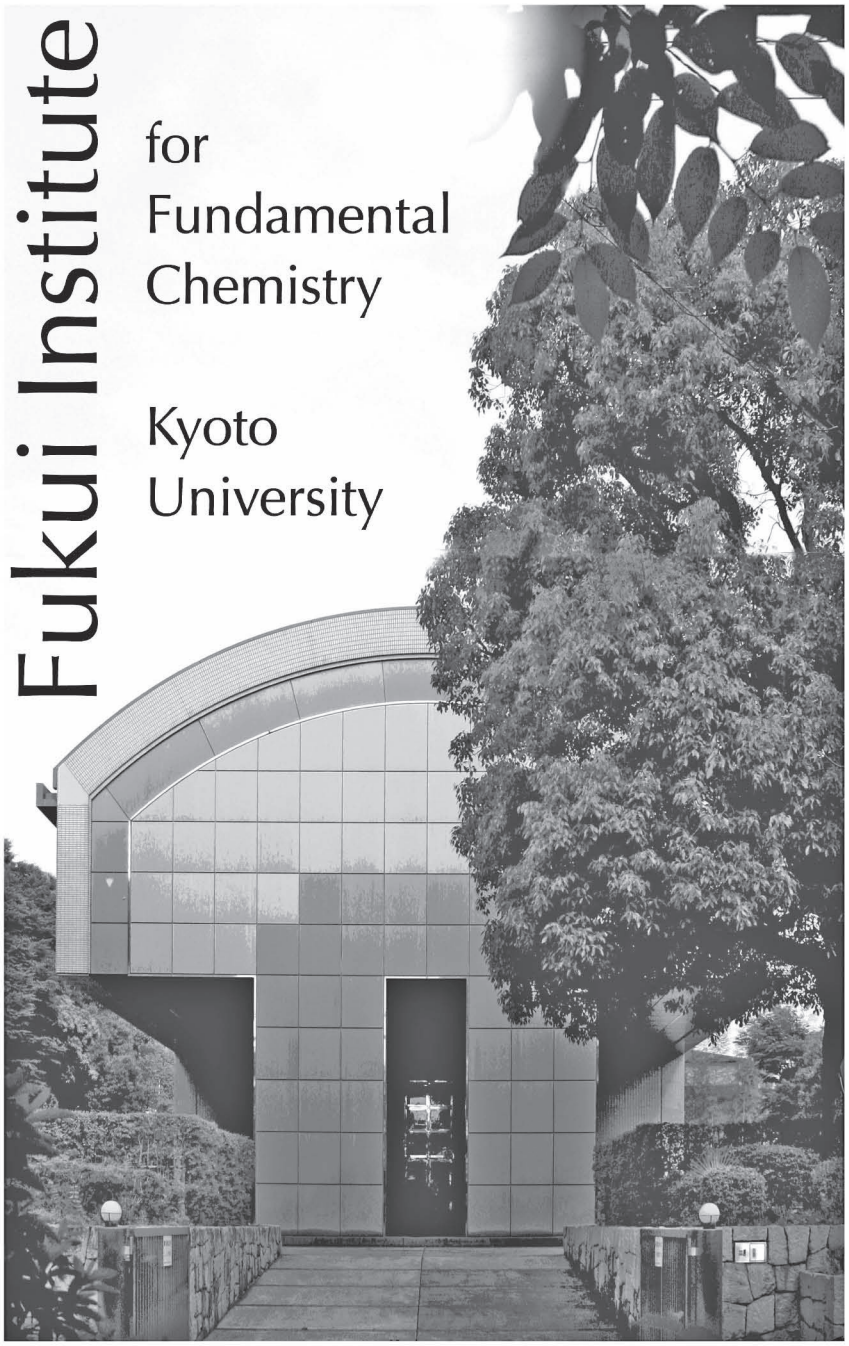
2012



京都大学
福井謙一記念研究センター

はじめに

2012 年度(平成 24 年度)の京都大学福井謙一記念研究センターの活動をまとめた年報をお届けします。本センターは、京都大学本部構内の北、約 1 キロの高野川沿いの静かな住宅街に独立して位置しております。専任教員は理論研究部門と総合研究部門に准教授各 1 名を持っているに過ぎませんが、センター長のほか副センター長とスーパーバイザーとして工学研究科、理学研究科、化学研究所所属の 11 名の教員にご協力頂いており、このメンバーが運営委員会を構成しています。そして優れた博士研究員に研究活動の機会を与える制度を持っており、若手研究者が国際的な雰囲気の中で日夜研究にいそしんでいます。福井センターフェローと呼ばれる博士研究員はセンターの雇用で、自分自身のアイデアで一定期間、自由闊達に研究できる身分を保証しています。

2006 年(平成 18 年)9 月に福井謙一記念研究部第一のリサーチリーダーとして世界的な理論化学者の諸熊奎治先生(分子科学研究所名誉教授)を米国エモリー大学から招聘し、研究面でのリーダーシップを発揮して頂いております。諸熊先生は，科学技術振興機構の戦略的創造研究推進事業の予算で博士研究員を採用され、全員がセンターで研究に励んでおられます。さらに 2009 年度(平成 21 年度)には福井謙一記念研究部第二も設置し、名古屋大学名誉教授（前副学長）の大峯巖先生をリサーチリーダーとして招聘し、研究体制を拡大しました。なお、大峯先生は 2010 年(平成 22 年)4 月に分子科学研究所長に転出されました。その後任として、2011 年(平成 23 年)4 月に京都大学物質―細胞統合システム拠点(iCeMS)特任教授の榊茂好先生を研究部第二のリサーチリーダーとして招聘しました。

榊先生は、遷移金属化合物や類縁化合物に関する研究で顕著な業績を挙げておられ、現在は科学研究費補助金「d－電子複合系の理論化学：新しい高精度大規模計算法による微視的理解と予測」を推進しておられます。榊先生は、この予算で博士研究員を採用され、そのメンバーはセンターで研究に励んでいます。私達は、センターが若手研究者の登竜門となることを期待しています。実際に、センターの博士研究員であった多くの方々が、現在、国内外の大学、研究機関で活躍しておられます。

当センターの歴史を簡単にご紹介します。ご承知のように故福井謙一京都大学名誉教授はフロンティア軌道理論を提案したご功績により、1981 年(昭和 56 年)にわが国で最初のノーベル化学賞を受賞されました。福井先生が京都大学ご退官後に研究を続けられるため、京都市と産業界などのご支援で 1985 年(昭和 60 年)に財団法人「基礎化学研究所」が設立されました。専任研究員数名の規模でしたが、研究のレベルは高く、当時の研究員は現在、東京大学、名古屋大学、分子科学研究所の教授になり、理論化学分野でトップクラスの研究者として活躍しています。この基礎化学研究所は 1998 年（平成 10 年）の福井先生のご逝去の後、2002 年(平成 14 年)に本学に寄贈され、福井謙一記念研究センターとなり、現在にいたっています。

本センターは、国際活動も活発で、2005 年(平成 17 年)よりチェコおよびスロバキアと

理論化学・計算化学シンポジウムを定期的に開催しております。2011 年(平成 23 年)には国内外(主にドイツ、東欧、中国、韓国)から第一線の研究者を招き、第 1 回福井センター理論化学・計算化学国際シンポジウムを開催しました。こうした国際連携活動をさらに活性化するという観点から、2011 年(平成 23 年)10 月に国際連携研究室を設置し、その運営上必要となるコーディネーター役として、特定准教授及び特定助教各 1 名を配置しました。2012 年度(平成 24 年度)には国際連携強化プロジェクトの一環として、センター教員が海外の研究機関を訪問し、研究所の運営に関して意見交換を行いました。本センターは、今後も、理論化学・計算化学分野におけるわが国の窓口の役割を果たし、国際連携活動を展開して行きたいと考えております。

例年晩秋に福井センターシンポジウムを開催しており、学外のトップクラスの研究者による特別講演、運営委員の講演、並びに京都大学内外からのポスター発表を行っております。研究発表のレベルは高く、特別講演に来られた講師からも毎年高い評価を得ております。

さらに社会貢献活動の一環として、2011 年(平成 23 年)が福井先生のノーベル化学賞受賞 30 周年にあたるため、これを節目として本センター玄関ロビーに先生ゆかりの文物の展示コーナーを設置しました。コーナーでは先生が使用された机、椅子、ノーベル賞メダル・賞状(複製)、研究ノート・メモ、写真などを展示し、常設展示として一般に公開しています。

また、本センターの諸熊奎治先生は、複雑分子系の理論研究の発展に多大な貢献をしたとして、2012 年(平成 24 年)11 月に文化功労者の顕彰を受けられました。これは、先生ご自身の栄誉はもとより、本センターの名を大いに高めて頂いたことでもあり、大変喜ばしいことでした。

本センターは、上述のように規模は大きくありませんが、研究活動は活発です。今後も、京都大学あるいは国内外との共同研究を積極的に進めて行きたいと考えております。とくに実験科学者との共同研究は重要であり、そのような連携研究をさらに活発化したいと考えております。

この年報により、本センターの活動に興味をお持ち頂ければ幸甚です。そして、それが共同研究の契機となり、時間をかけて大きな成果に結実していくことを念願しています。最後になりましたが、本センターの順調な活動はひとえに工学研究科、理学研究科、化学研究所のご協力、ご援助の賜物であり、ここに心から御礼申し上げる次第です。

平成 25 年 12 月

京都大学福井謙一記念研究センター長

田中　一義

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http://www.fukui.kyoto-u.ac.jp/publication/AnnualReport2012.pdf）

Ⅰ　専任教員・スーパーバイザー

１．教員組織

平成２４年度

職　　名		氏　名	備　考
センター長		田 中　一 義	工学研究科分子工学専攻
総合研究部門	副センター長	長谷川 淳 也	専任（平成 24 年 9 月 30 日まで）
理論研究部門	副センター長	赤 木　和 夫	工学研究科高分子化学専攻
協　議　員	工学研究科長	北 野　正 雄	工学研究科電子工学専攻
	理学研究科長	山 極　壽 一	理学研究科生物科学専攻
	化学研究所長	佐 藤　直 樹	化学研究所複合基盤化学研究系
総合研究部門 スーパーバイザー	教　　授	北 川　　進	物質－細胞統合システム拠点 （工学研究科合成・生物化学専攻）
	教　　授	田 中　勝 久	工学研究科材料化学専攻
	教　　授	田 中 耕一郎	物質－細胞統合システム拠点 （理学研究科物理学・宇宙物理学専攻）
	教　　授	時 任　宣 博	化学研究所物質創製化学研究系
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	教　　授	田 中　庸 裕	工学研究科分子工学専攻
	教　　授	谷 村　吉 隆	理学研究科化学専攻
	教　　授	山 本　量 一	工学研究科化学工学専攻
	教　　授	高 田　彰 二	理学研究科生物科学専攻
	准 教 授	林　　重 彦	理学研究科化学専攻
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理論研究部門	准 教 授	中 尾　嘉 秀	専任 （工学研究科分子工学専攻協力講座）
国際連携研究室	特定准教授	石 田　俊 正	専任
国際連携研究室	特定助教	池 野　豪 一	専任
永瀬グループ	シニアリサーチ フェロー	永 瀬　　茂	研究員（学術研究奨励）
諸熊グループ	シニアリサーチ フェロー	諸 熊　奎 治	研究員（学術研究奨励）
榊グループ	リサーチ リーダー	榊　　茂 好	研究員（学術研究奨励）

2．教員プロフィール

⑴ センター長

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【研究分野】	物理化学・量子化学
【現在の研究課題】	量子機能化学、物理化学
【研究内容キーワード】	単一分子スピン、単一分子発光、元素化学の量子論
【学歴】	1978 年 3 月　京都大学工学研究科石油化学専攻博士課程修了
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【所属学会】	日本化学会・日本物理学会・高分子学会
【学会活動】	フラーレン・ナノチューブ・グラフェン学会幹事
【主な著書、学術論文】（過去 5 年以内）	1. 物理化学（化学マスター講座）（共著 , 丸善 , 2010） 2. 炭素学（共編著 , 化学同人 , 2011） （以上著書） 1. A Stable Germanone as the First Isolated Heavy Ketone with a Terminal Oxygen Atom (L. Li, T. Fukawa, T. Matsuo, D. Hashizume, H. Fueno, K. Tanaka, and K. Tamao) *Nature Chem.*, **4**, 361-365 (2012). 2. 1,3,5-Benzenetriamine Double- and Triple-Decker Molecules (D. Sakamaki, A. Ito, K. Tanaka, K. Furukawa, T. Kato, and M. Shiro) *Angew. Chem. Int. Ed.*, **51**, 8281-8285 (2012). 3. Electronic Spectra of Cycl[3.3.2]azine and Related Compounds: Solvent Effect on Vibronic Couplings (Y. Shigemitsu, M. Uejima, T. Sato, K. Tanaka, and Y. Tominaga) *J. Phys. Chem. A*, **116**, 9100-9109 (2012). 4. A Triphenylamine Double-Decker: From a Delocalized Radical Cation to a Diradical Dication with an Excited Triplet State (Y. Yokoyama, D. Sakamaki, A. Ito, K. Tanaka, and M. Shiro) *Angew. Chem. Int. Ed.*, **51**, 9403-9406 (2012). 5. Mechanisms of Localization in Isotope-Substitutes Dynamical Jahn-Teller Systems (N. Iwahara, T. Sato, K. Tanaka, and L. F. Chibotaru) *Eur. Phys. Lett.*, **100**, 43001 1-6 (2012). 6. Chemical Reactivity in Nucleophilic Cycloaddition to C70: Vibronic Coupling Density and Vibronic Coupling Constants as Reactivity Indices (N. Haruta, T. Sato, and K. Tanaka) *J. Org. Chem.*, **77**, 9702-9706 (2012). 7. A Polymacrocyclic Oligoarylamine with a Pseudobeltane Motif: Towards a Cylindrical Multispin System (D. Sakamaki, A. Ito, K. Furukawa, T. Kato, M. Shiro, and K. Tanaka) *Angew. Chem. Int. Ed.*, **51**, 12776-12781 (2012). 8. Meta-Para-Linked Octaaza[18]cyclophanes and Their Polycationic States (D. Sakamaki, A. Ito, K. Furukawa, T. Kato, and K. Tanaka) *J. Org. Chem.*, **78**, 2947-2956 (2013). 9. Vibronic Couplings in Cycloadditions to Fullerenes (N. Haruta, T. Sato, N. Iwahara, and K. Tanaka) *J. Phys. C: Conf. Ser.*, **428**, 012003 1-7 (2013). 10.Vibronic Coupling Density and Related Concepts (T. Sato, M. Uejima, N. Iwahara, N. Haruta, K. Shizu, and K. Tanaka) *J. Phys. C: Conf. Ser.*, **428**, 012010 1-19 (2013). （以上学術論文）

⑵ 副センター長

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【現在の研究課題】	光機能性分子の励起状態と分子間相互作用、触媒反応機構
【研究内容キーワード】	励起状態理論、光機能性蛋白質、触媒反応機構
【最終学歴】	1998 年 3 月　京都大学工学研究科合成・生物化学専攻博士後期課程修了
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【略歴】	1999 年 11 月京都大学工学研究科合成・生物化学専攻助手、2007 年 4 月京都大学工学研究科合成・生物化学専攻助教、2008 年 12 月京都大学工学研究科合成・生物化学専攻講師、2011 年 10 月京都大学福井謙一記念研究センター准教授、2012 年 10 月北海道大学触媒化学研究センター教授
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【学会活動】	Chem. Lettters 編集委員、量子化学研究協会理事
【主な著書、学術論文】（過去 5 年以内）	1. J. Hasegawa, K. J. Fujimoto, and T. Kawatsu, “A Configuration Interaction Picture for a Molecular Environment Using Localized Molecular Orbitals: The Excited States of Retinal Proteins”, *J. Chem. Theo. Comp.* **8**(11), 4452-4461(2012). 2. T. Kawatsu and J. Hasegawa, “Sequentially Coupled Hole-Electron Transfer Pathways for Bridge-Mediated Triplet Excitation Energy Transfer”, *J. Phys. Chem. C* **116**(44), 23252-23256 (2012). 3. J. Hasegawa, T. Kawatsu, K. Toyoya, and K. Matsuda, “Chemical-intuition based LMO transformation simplifies excited-state wave functions of peptides”, Chem. Phys. Letters, **508**(1-3), 171-176 (2011). 4. J. Hasegawa, T. Ise, K. Fujimoto, A. Kikuchi, E. Fukumura, A. Miyawaki, and Y. Shiro, “Excited States of Fluorescent Proteins, mKO and DsRed: Chromophore-protein Electrostatic Interaction Behind the Color Variations”, *J. Phys. Chem. B*, **114**(8), 2971-2979 (2010). 5. K. Fujimoto, J. Hasegawa, and H. Nakatsuji, “Color tuning mechanism in human red, green, and blue cone visual pigments: SAC-CI theoretical study”, *Bull. Chem. Soc. Jpn.* **82**(9), 1140-1148 (2009).
【学術関係の受賞】	平成 9-11 年 日本学術振興会特別研究員、平成 21 年 9 月 分子科学会奨励賞、平成 23 年 9 月 QSCP Promising Scientist Prize of CMOA

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【研究分野】	高分子化学、液晶化学、物質化学
【現在の研究課題】	導電性、液晶性、発光性、階層らせん性の共役系高分子の合成と性質
【研究内容キーワード】	導電性高分子、液晶性共役高分子、不斉液晶反応場、階層構造制御
【最終学歴】	京都大工学研究科博士後期課程
【学位】	工学博士
【略歴】	福井大工助手、筑波大物質工講師、助教授、教授、同大学院数理物質科学研究科教授、学際物質科学研究センター長
【在外研究歴】	カリフォルニア大学サンタバーバラ校交換研究員、コーネル大学客員研究員
【所属学会】	日本化学会、高分子学会、日本液晶学会、アメリカ化学会
【学会活動】	文部科学省科研費（特定領域研究、2005-2008）「次世代共役ポリマーの超階層制御と革新機能」領域代表、Chair of International Conference onScience and Technology of Synthetic Metals (2010).
【主な著書、学術論文】（過去 5 年以内）	1. B. A. San Jose, S. Matsushita, K. Akagi, “Lyotropic Chiral Nematic Liquid Crystalline Aliphatic Conjugated Polymers Based on Di-Substituted Polyacetylene Derivatives that Exhibit High Dissymmetry Factors in Circularly Polarized Luminescence”, *J. Am. Chem. Soc.*, **134**, 19895 (2012). 2. K. Watanabe, H. Iida, K. Akagi, “Circularly Polarized Blue Luminescent Spherulites Consisting of Hierarchically Assembled Ionic Conjugated Polymers with a Helically π-Stacked Structure”, *Adv. Mater.*, **24**, 6451 (2012). 3. H. Hayasaka, T. Miyashita, M. Nakayama, K. Kuwada, K. Akagi, “Dynamic Photoswitching of Helical Inversion in Liquid Crystals Containing Photoresponsive Axially Chiral Dopants”, *J. Am. Chem. Soc.*, **134**, 3758 (2012). 4. S. Matsushita, M. Kyotani, K. Akagi, “Hierarchically Controlled Helical Graphite Films Prepared from Iodine-Doped Helical Polyacetylene Films Using Morphology-Retaining Carbonization”, *J. Am. Chem. Soc.*, **133**, 17977 (2011). 5. K. Akagi, “Helical Polyacetylene - Asymmetric Polymerization in a Chiral Liquid Crystal Field”, *Chem. Rev.*, **109**, 5354 (2009).
【学術関係の受賞】	日本化学会学術賞 (1999 年度)、日産科学賞 (2000 年度)、日本液晶学会賞論文賞 (2001 年度)、つくば賞 (2001 年度)、高分子学会賞 (2002 年度)、文部科学大臣表彰科学技術賞 (2005 年度)、筑波大学名誉教授称号授与（2009 年度)、日本液晶学会賞業績賞（2010 年度）

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【主な著書、学術論文】（過去 5 年以内）	1. “One-dimensional imidazole aggregate in aluminum porous coordination polymers with high proton conductivity”, S. Bureekaew, S. Horike, M. Higuchi, M. Mizuno, T. Kawamura, D. Tanaka, N. Yanai and S. Kitagawa, *Nature Materials*, **2009**, 8, 831-836. 2. “Photoactivation of a nanoporous crystal for on-demand guest trapping and conversion”, H. Sato, R. Matsuda, K. Sugimoto, M. Takata and S. Kitagawa, *Nature Materials*, **2010**, 9, 661-666. 3. “Mesoscopic architectures of porous coordination polymers fabricated by pseudomorphic replication”, J. Reboul, S. Furukawa, N. Horike, M. Tsotsalas, K. Hirai, H. Uehara, M. Kondo, N. Louvain, O. Sakata and S. Kitagawa, *Nature Materials*, **2012**, 11,717-723. (Cover Picture)
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【学会活動】	粉体粉末冶金協会 理事、日本化学会近畿支部 副支部長
【主な著書、学術論文】（過去 5 年以内）	1. X. Meng, K. Fujita, S. Murai, and K. Tanaka, “Coherent Random Lasers in Weakly Scattering Polymer Films Containing Silver Nanoparticles”, *Physical Review A* **79** (2009) 053817-1-7. 2. H. Akamatsu, S. Oku, K. Fujita, S. Murai, and K. Tanaka, “Magnetic Properties of Mixed-Valence Iron Phosphate Glasses”, Physical Review B 80 (2009) 134408-1-9. 3. H. Akamatsu, K. Fujita, S. Murai, and K. Tanaka, “Ferromagnetic Eu^{2+}-Based Oxide Glasses with Reentrant Spin Glass Behavior”, *Physical Review B* **81** (2010) 014423-1-9. 4. X. Meng, K. Fujita, S. Murai, T. Matoba, and K. Tanaka, “Plasmonically Controlled Lasing Resonance with Metallic-Dielectric Core-Shell Nanoparticles”, *Nano Letters* **11** (2011) 1374-1378. 5. H. Akamatsu, K. Fujita, H. Hayashi, T. Kawamoto, Y. Kumagai, Y. Zong, K. Iwata, F. Oba, I. Tanaka, and K. Tanaka, “Crystal and electronic structure and magnetic properties of divalent europium perovskite oxides $EuMO_3$ (M=Ti, Zr, and Hf): Experimental and first-principles approaches”, *Inorganic Chemistry* **51** (2012) 4560-4567. 6. X. Meng, U. Guler, A. V. Kildishev, K. Fujita, K. Tanaka, and V. M. Shalaev, “Breaking symmetry of plasmonic nanostructures: an efficient route towards unidirectional spaser”, *Scientific Reports* **3** (2013) 1241-1-5. 7. Y. Hasegawa, M. Maeda, T. Nakanishi, Y. Doi, Y. Hinatsu, K. Fujita, K. Tanaka, H. Koizumi, and K. Fushimi, “Effective optical Faraday rotations of semiconductor EuS nanocrystals with paramagnetic transition-metal ions”, *Journal of the American Chemical Society* **135** (2013) 2659-2666. 8. T. Kawamoto, K. Fujita, H. Akamatsu, T. Nakamura, T. Kinoshita, M. Mizumaki, N. Kawamura, M. Suzuki, Y. Kususe, S. Murai, and K. Tanaka, “Eu $M_{4,5}$- and $L_{2,3}$-edge x-ray magnetic circular dichroism of ferromagnetic amorphous oxides in EuO-TiO_2 system”, *Physical Review B* **88** (2013) 024405-1-9.
【学術関係の 受賞】	The Australasian Ceramic Society/Ceramic Society of Japan (ACS/CJS) Joint Ceramic Award (1997 年)、日本セラミックス協会学術賞 (2005 年)

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【所属学会】	Optical Society of America、日本物理学会、日本応用物理学会
【学会活動】	物理学会京都支部長
【主な著書、学術論文】（過去 5 年以内）	1. Tobias Kampfrath, Koichiro Tanaka and Keith A. Nelson, “Resonant and nonresonant control over matter and light by intense terahertz transients”, *Nature Photonics* **7**,680–690 (2013) 2. K. Shinokita, H. Hirori, K. Tanaka, T. Mochizuki, C. Kim, H. Akiyama, L. N. Pfeiffer and K. W. West, “Terahertz-Induced Optical Emission of Photoexcited Undoped GaAs Quantum Wells”, *Phys. Rev. Lett.* **111**, 067401 (2013) 3. F. Blanchard, A. Doi, T. Tanaka, and K. Tanaka, “Real-Time, Subwavelength Terahertz Imaging”, *Annu. Rev. Mater. Res.* **43**:11.1–11.23 (2013) 4. Shuntaro Tani, Francois Blanchard, and Koichiro Tanaka “Ultrafast Carrier Dynamics Under High Electric Field in Graphene”, *Phys. Rev. Lett.* **109**, 166603 (2012) 5. E. Collet, H. Watanabe, N. Bréfuel, L. Palatinus, L. Roudaut, L. Toupet, K. Tanaka, J.-P. Tuchagues, P. Fertey, S. Ravy, B. Toudic, H. Cailleau, “Aperiodic spin state ordering of bi-stable molecules and its photoinduced erasing”, *Phys. Rev. Lett.* **109**, 257206 (2012) 6. H. Hirori, K. Shinokita, M. Shirai, S. Tani, Y. Kadoya, K. Tanaka, “Extraordinary carrier multiplication gated by a picosecond electric field pulse”, *Nature Communications* **2**, 594/1-594/6, (2011)

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【研究分野】	Organoelement Chemistry
【現在の研究課題】	Synthesis and Characterization of Novel Low-coordinate Main Group Element Compounds
【研究内容キーワード】	Heavy Aromatics, Multiple-bond Compounds, d- π Conjugation
【学歴】	1979 B.S.; 1982 M.S.; 1985 Ph.D.; The University of Tokyo
【学位】	Doctor of Science from The University of Tokyo
【略歴】	Research Associate (1986) and then Assistant Prof. (1987) of Tsukuba Univ.; Assistant Prof. (1989) and Associate Prof. (1994) of The University of Tokyo; Professor of IFOC, Kyushu Univ. (1998-2000); Professor of ICR, Kyoto Univ. (2000-present); Visiting Prof. at Technische Universität Braunschweig, Germany (2004-2007); Vice-director of ICR (2006-2008); Director of ICR (2008-2012).
【所属学会】	Chemical Society of Japan, American Chemical Society, The Society of Physical Organic Chemistry, Japan, The Society of Silicon Chemistry, Japan, Kinki Kagaku Kyokai, The Society of Synthetic Organic Chemistry, Japan.
【学会活動】	1996- The Society of Silicon Chemistry, Japan, Standing Board Member; 2006- International Symposium on Inorganic Ring Systems, IAB Member; 2006- International Conference on Heteroatom Chemistry, IAB Member; 2009-2011 The Chemical Society of Japan, a Member of Board of Directors; 1998-2006 Journal of Physical Organic Chemistry, Associate Editor for Asia; 2006-2009 Organometallics, Advisory Board Member; 2011- The Society of Physical Organic Chemistry, Japan, Standing Board Member; 2012 10th International Conference on Heteroatom Chemistry, Chairman; 2012- International Symposium on Silicon Chemistry, IAB Member; 2013- International Conference on Organometallic and Coordination Chemistry of Germanium, Tin and Lead (ICCOC-GTL), IAB Member; 2013- Bulletin of the Chemical Society of Japan (CSJ), Editor-in-Chief
【主な著書、学術論文】（過去 5 年以内）	1. Syntheses and Structures of an “Alumole” and Its Dianion, Agou, T.: Wasano, T.; Jin, P; Nagase, S.; Tokitoh, N. *Angew. Chem. Int. Ed.* **2013**, *125*, 10215–10218. 2. Synthesis and Properties of 4,5,6-Triphospha[3]radialene, Miyake, H.; Sasamori, T.; Tokitoh, N. *Angew. Chem. Int. Ed.* **2012**, *51*, 3458-3461. 3. Synthesis of Kinetically Stabilized 1,2-Dihydrodisilenes, Agou, T.; Sugiyama, Y.; Sasamori, T.; Sakai, H.; Furukawa, Y.; Takagi, N.; Guo, J. D.; Nagase, S.; Hashizume, D.; Tokitoh, N. *J. Am. Chem. Soc.* **2012**, *134*, 4120-4123. 4. Fluorination Reaction of a Ditelluride Bearing Bulky Aryl Substituents: Formation of Mixed-Valent Te(IV)-Te(II) Ditelluride Difluoride, Sasamori, T.; Sugamata, K.; Tokitoh, N. *Chem-Asian J.* **2011**, *6*, 2301-2303. 5. Reactivity of an aryl-substituted silicon-silicon triple bond: 1,2-disilabenzenes from the reactions of a 1,2-diaryldisilyne with alkynes, Han, J. S.; Sasamori, T.; Mizuhata, Y.; Tokitoh, N. *Dalton Trans.* **2010**, *39*, 9238-9240.
【学術関係の受賞】	1992 Incentive Award of the Society of the Synthetic Organic Chemistry, Japan 1996 Incentive Award of the Society of Silicon Chemistry, Japan 1998 Japan IBM Science Award 2003 Chemical Society of Japan Award for Creative Work (CSJ) 2003 Alexander von Humboldt Research Award 2002, 2005, 2007, 2009, 2010 and 2013 BCSJ Awards (CSJ) 2007 Lectureship Award of National Science Council, Republic of China 2010 The 3rd Kim Yong Hae Lectureship Award (KAIST, Korea) 2010 Best Reviewer Commendation (Japan Society for the Promotion of Science)

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【研究内容キーワード】	液体、クラスター、分子、X 線自由電子レーザー、シンクロトロン放射光、金属・非金属転移、ナノプラズマ、プラズモン／エキシトン、超高速電荷・エネルギー移動、クーロン爆発、電子分光／イオン分光、密度汎関数法
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【所属学会】	日本金属学会、日本セラミックス協会、日本鉄鋼協会，応用物理学会、American Ceramic Society、Materials Research Society
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【主な著書、学術論文】（過去 5 年以内）	1. A. Togo and I. Tanaka, "Evolution of crystal structures in metallic elements", *Physical Review B*, **87** 184104 1-6 (2013). 2. H. Akamatsu, Y. Kumagai, F. Oba, K. Fujita, K. Tanaka, and I. Tanaka, "Strong Spin-Lattice Coupling Through Oxygen Octahedral Rotation in Divalent Europium Perovskites," *Advanced Functional Materials*, **23**[15] 1864-72 (2013). 3. M. Choi, F. Oba, Y. Kumagai, and I. Tanaka, "Anti-ferrodistortive-Like Oxygen-Octahedron Rotation Induced by the Oxygen Vacancy in Cubic SrTiO3," *Advanced Materials*, **25**[1] 86-90 (2013). 4. R. Ishikawa, N. Shibata, F. Oba, T. Taniguchi, S. D. Findlay, I. Tanaka, and Y. Ikuhara, "Functional Complex Point-Defect Structure in a Huge-Size-Mismatch System," *Physical Review Letters*, **110**[6] (2013). 5. D. Han, T. Uda, Y. Nose, T. Okajima, H. Murata, I. Tanaka, and K. Shinoda, "Tetravalent Dysprosium in a Perovskite-Type Oxide," *Advanced Materials*, **24**[15] 2051-53 (2012). 6. Y. Koyama, H. Arai, Z. Ogumi, I. Tanaka, and Y. Uchimoto, "Co K-edge XANES of LiCoO2 and CoO2 with a variety of structures by supercell density functional calculations with a core hole," *Physical Review B*, **85**[7] (2012). 7. Y. Kumagai, A. Seko, F. Oba, and I. Tanaka, "Ground-state search in multicomponent magnetic systems," *Physical Review B*, **85**[1] (2012). 8. B. Liu, A. Seko, and I. Tanaka, "Cluster expansion with controlled accuracy for the MgO/ZnO pseudobinary system via first-principles calculations," *Physical Review B*, **86**[24] (2012).
【学術関係の受賞】	ドイツ政府　ﾌｨﾘｯﾌﾟ・ﾌﾗﾝﾂ・ﾌｫﾝ・ｼﾞｰﾎﾞﾙﾄ賞（2008 年） ﾙｰﾏﾆｱ科学ｱｶﾃﾞﾐｰ　ﾄﾞﾗｺﾞﾐｰﾙ・ﾌﾙﾑｾﾞｽｺ賞（2006 年） 米国ｾﾗﾐｯｸｽ学会　ﾘﾁｬｰﾄﾞ・ﾌﾙﾗｰｽ賞（2004 年）

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【主な著書、学術論文】（過去 5 年以内）	1. Effects of Rreaction Temperature on the Photocatalytic Activity of Photo-SCR of NO with NH_3 over a TiO_2 Photocatalyst, Akira Yamamoto, Yuto Mizuno, Kentaro Teramura, Tetsuya Shishido and Tsunehiro Tanaka, *Catal. Sci. Technol.*, 2013, **3**, 1771-1775. 2. Characterization of Thermally Stable Brønsted Acid Sites on Alumina-Supported Niobium Oxide Calcined at High Temperature Tomoyuki Kitano, Tetsuya Shishido, Kentaro Teramura, and Tsunehiro Tanaka, *Chem. Phys. Chem.,* 2013, **14**(11), 2560-2564. 3. Development of Palladium Surface-Enriched Heteronuclear Au–Pd Nanoparticle Dehalogenation Catalysts in an Ionic Liquid, Xiao Yuan, Geng Sun, Hiroyuki Asakura, Tsunehiro Tanaka, Xi Chen, Dr. Yuan Yuan, Gabor Laurenczy, Yuan Kou, Paul J. Dyson, Ning Yan, *Chemistry –A European Journal*., 2013, **19**(4), 1227-1234. 4. Reaction Mechanism of Selective Photooxidation of Amines over Niobium Oxide: Visible Light-Induced Electron Transfer Between Adsorbed Amine and Nb_2O_5, Shinya Furukawa, Yasuhiro Ohno, Tetsuya Shishido, Kentaro Teramura, and Tsunehiro Tanaka, *J. Phys. Chem. C*., 2013, **117**(1), 442-450. 5. Insights into the Formation Mechanism of Rhodium Nanocubes, Siyu Yao, Yuan Yuan, Chaoxiab Xiao, Weizhen Li, Yuan Kou, Paul Dyson, Ning Yan, Hiroyuki Asakura, Kentaro Teramura, and Tsunehiro Tanaka, *J. Phys. Chem. C*., 2012, **116**(28), 15076-15086. 6. Artificial Photosynthesis Using Typical Clays: Photocatalytic Conversion of CO_2 in Water over Layered Double Hydroxides, Kentaro Teramura, Shoji Iguchi, Yuto Mizuno, Tetsuya Shishido, and Tsunehiro Tanaka, *Angew. Chem. Intern. Ed*.., 2012, **51**(32), 8008-8011. 7. Brønsted Acid Property of Alumina-Supported Niobium Oxide Calcined at High Temperatures: Characterization by Acid-Catalyzed Reactions and Spectro- scopic Methods, Tomoyuki Kitano, Tetsuya Shishido, Kentaro Teramura, and Tsunehiro Tanaka, *J. Phys. Chem. C*., 2012, **116**, 11615-11625

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【在外研究歴】	1995 年 5 月 -1998 年 3 月　米国イリノイ大学化学科（日本学術振興会研究員）
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【学会活動】	日本生物物理学会運営委員
【主な著書、学術論文】（過去 5 年以内）	1. M.J.McGrath, I.F.Kuo, S.Hayashi, and S.Takada, ATP hydrolysis mechanism in kinesin studied by combined quantum-mechanical molecular-mechanical metadynamics , *JACS*, **103**: 8908-8919, 2013. 2. X.Yao, N.Kimura, S.Murakami, and S.Takada, Drug Uptake Pathways of Multidrug Transporter AcrB Studied by Molecular Simulations and Site-Directed Mutagenesis Experiments, *JACS*, **135**: 7474-7485, 2013. 3. T.Terakawa, H.Kenzaki, & S.Takada, p53 searches on DNA by rotation-uncoupled sliding at C-terminal tails and restricted hopping of core domains , *JACS*, **134**: 14555-14562, 2012. 4. S.Takada, Coarse-grained molecular simulations of large biomolecules, *Curr Opinion in Struct Biol*, **22**: 130-137, 2012. 5. W.Li, P.G.Wolynes, & S.Takada, Frustration, specific sequence dependence, and nonlinearity in large-amplitude fluctuations of allosteric proteins, *Proc Nat Acad Sci USA*, **108**: 3504-3509, 2011. 6. X.Yao, H.Kenzaki, S.Murakami, & S.Takada, Drug export and allosteric coupling in a multidrug transporter revealed by molecular simulations, *Nature Comm*, **1**:117(8pages), 2010 7. *N.Koga, *T Kameda, K.Okazaki, & S.Takada, Paddling mechanism for the substrate translocation by AAA+ motor revealed by multiscale molecular simulations, *Proc Nat Acad Sci USA*, **106**: 18237-18242, 2009.

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【主な著書、学術論文】（過去 5 年以内）	1. Molecular mechanism of ATP hydrolysis in F1-ATPase revealed by molecular simulations and single molecule observations. Shigehiko Hayashi*, Hiroshi Ueno, Abdul Rajjak Shaikh, Myco Umemura, Motoshi Kamiya, Yuko Ito, Mitsunori Ikeguchi, Yoshihito Komoriya, Ryota Iino, and Hiroyuki Noji. *J. Am. Chem. Soc.* **134**, 8447-8454 (2012). 2. Crucial role of protein flexibility in formation of a stable reaction transition state in an a-amylase catalysis. Kosugi Takahiro and Shigehiko Hayashi*. *J. Am. Chem. Soc.* **134**, 7045-7055 (2012). 3. QM/MM reweighting free energy SCF for geometry optimization on extensive free energy surface of enzymatic reaction. Takahiro Kosugi and Shigehiko Hayashi*. *J. Chem. Theory Comput.* **8**, 322-334 (2012). 4. Protein collective motions coupled to ligand migration in myoglobin. Yasutaka Nishihara, Shigeki Kato, and Shigehiko Hayashi*, *Biophys. J.* **98**, 1649-1657 (2010). 5. Electronic coulombic coupling of excitation-energy transfer in xanthorhodopsin. Kazuhiro Fujimoto, and Shigehiko Hayashi*, *J. Am. Chem. Soc.* **131**, 14152-14153 (2009). 6. Photochemical reaction dynamics of the primary event of vision studied by a hybrid molecular simulation. Shigehiko Hayashi*, Emad Tajkhoshid, and Klaus Schulten, *Biophys. J.* **96**, 403-416 (2009).

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【主な著書、学術論文】（過去 5 年以内）	1. T. Akasaka, F. Wudl, and S. Nagase, Eds., Chemistry of Nanocarbons, John Wiley & Sons Ltd., Chichester (2010) 2. M. Yamada, T. Akasaka, and S. Nagase, Endohedral Metal Atoms in Pristine and Functionalized Fullerene Cages, *Acc. Chem. Res.*, **43**, 92-102 (2010). 3. X. Lu, L. Feng, T. Akasaka, and S. Nagase, Current Statues and Future Developments of Endohedral Metallofullerenes, *Chem. Soc. Rev.*, **41**, 7723-7760 (2012). 4. S. Nagase, Multiple Bonds between Lead Atoms and Short Bonds between Transition Metals, *Pure Appl. Chem.*, **85**, 649-659 (2013). 5. X. Lu, T. Akasaka, and S. Nagase, Carbide Cluster Metallofullerenes: Structure, Properties, and Possible Origin, *Acc. Chem. Res.*, in press. 6. M. Yamada, T. Akasaka, and S. Nagase, Carbene Additions to Fullerenes, *Chem. Rev.*, in press.
【学術関係の受賞】	2012 年 科学技術分野の文部科学大臣表彰科学技術賞（研究部門）、2012 年 福井メダル (Asia-Pacific Association of Theoretical & Computational Chemists) 、2013 年 日本化学会賞

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【学術関係の受賞など】	International Academy of Quantum Molecular Science (IAQMS) Medal, 1978;　日本化学会賞 , 1992; The Schrödinger Medal, The World Association of Theoretical Organic Chemists (WATOC), 1993; The Fukui Medal, Asian Pacific Association of Theoretical & Computational Chemists, 2005; 恩賜賞、日本学士院賞 , 2008; 瑞宝中綬章 , 2010; 文化功労者 , 2012

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【学術関係の受賞など】	第 1 回分子科学会賞 (2009 年 9 月)

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【主な著書、学術論文】（過去５年以内）	1. T. Saito, T. Iwaki, and K. Yoshikawa, “DNA compaction induced by neutral polymer is retarded more effectively by divalent anion than monovalent anion”, *Chemical Physics Letters* **465**(1-3), 40-44(2008) 2. T. Iwaki, “Effect of internal flow on the photophoresis of a micron-sized liquid droplet”, *Physical Review E* **81**, 066315 (13 pages) (2010) 3. 吉川研一、岩城貴史、“細胞の自己組織化”に物理の視点から迫る”, パリティ　2011年5月号 pp. 13-21 4. Y. Higuchi, K. Yoshikawa, T. Iwaki, “Stiffness causes opposite trend on the folding transition of a single polymer chain in a confined space”, *Physical Review E* **84**, 021924 (5 pages) 5. “Probability of double-strand breaks in genome-sized DNA by γ-ray decreases markedly as the DNA concentration increases”, S. F. Shimobayashi, T. Iwaki, T. Mori, and K. Yoshikawa, *The Journal of Chemical Physics, Accepted*.

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【主な著書、学術論文】（過去 5 年以内）	1. K. R. Brorsen, N. Minezawa, F. Xu, T. L. Windus, and M. S. Gordon, “Fragment molecular orbital molecular dynamics with the fully analytic energy gradient”, *J. Chem. Theory Comput.* **8**, 5008-5012 (2012). 2. N. Minezawa and M. S. Gordon, “Optimizing conical intersections of solvated molecules: The combined spin-flip density functional theory/effective fragment potential method”, *J. Chem. Phys.* **137**, article No. 034116 [12 pages] (2012). 3. A. Defusco, N. Minezawa, L. V. Slipchenko, F. Zahariev, and M. S. Gordon, “Modeling solvent effects on electronic excited states”, *J. Phys. Chem. Lett.* **2**, 2184-2192 (2011). 4. N. Minezawa and M. S. Gordon, “Photoisomerization of stilbene: A spin-flip density functional theory approach”, *J. Phys. Chem. A* **115**, 7901-7911 (2011). 5. N. Minezawa, N. De Silva, F. Zahariev, and M. S. Gordon, “Implementation of the analytic energy gradient for the combined time-dependent density functional theory/effective fragment potential method: Application to excited-state molecular dynamics simulations”, *J. Chem. Phys.* **134**, article No. 054111 [12 pages] (2011).

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【主な著書、学術論文】 （過去 5 年以内）	1. R. Okamoto and A. Onuki: “Ion distribution around a charged rod in one and two component solvents: Preferential solvation and first order ionization phase transition”, *J. Chem. Phys.* **131**, 094905 (2009). (Also in Virtual Journal of Nanoscale Science and Technology, September 14, 2009) 2. R. Okamoto and A. Onuki: “Precipitation in aqueous mixtures with addition of strongly hydrophilic or hydrophobic solute”, *Phys. Rev. E* **82**, 051501 (2010). (Also in Virtual Journal of Nanoscale Science and Technology, November 22, 2010) 3. R. Okamoto and A. Onuki: “Charged Colloids in an aqueous mixture with a salt”, *Phys. Rev. E* **84**, 051401 (2011) 4. R. Okamoto and A. Onuki: “Casimir amplitudes and capillary condensation of near-critical fluids between parallel plates: Renormalized local functional theory”, *J. Chem. Phys.* **136**, 114704 (2012)

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【研究分野】	Polymer Physics and Biophysics
【現在の研究課題】	Dynamics of Polymer Transportation
【研究内容キーワード】	Stretching dynamics, DNA compaction, Chromatin
【学歴】	March 2004, Master of Sci., Graduate School of Science, Kyoto University March 2007, Doctor of Sci., Graduate School of Science, Kyoto University
【学位】	Doctor of Science from Kyoto University
【略歴】	May 2007, The University of Tokyo Apr. 2010, Kyushu University
【所属学会】	The Physical Society of Japan
【主な著書、学術論文】（過去 5 年以内）	1. Takuya Saito, Takahiro Sakaue, “Process time distribution of driven polymer translocation”, *Phys. Rev. E*, **85**, 061803 (7 pages total) (2012). 2. Takahiro Sakaue, Takuya Saito, Hirofumi Wada, “Dragging a polymer in a viscous fluid: steady state and transient”, *Phys. Rev. E*, **86**, 011804 (8 pages total) (2012). 3. 坂上貴洋、齋藤拓也, 日本物理學會誌 **67**(10), 705-709, 2012-10-05.「紐状分子の非平衡ダイナミクス：細孔通過現象を中心に」 4. Takuya Saito, Takahiro Sakaue, Daiji Kaneko, Masao Washizu and Hidehiro Oana, “Folding dynamics of tethered giant DNA under strong flow”, *The Journal of Chemical Physics*, **135**, 154901 (5 pages total) (2011). 5. Takuya Saito and Takahiro Sakaue, “Driven Translocation of Semi-flexible Polymer under Strong Force”, *Progress of Theoretical Physics Supplement*, **191**, 210-214 (2011). 6. Takuya Saito and Kenichi Yoshikawa, “Finite-width bundle is most stable in a solution with salt”, *The Journal of Chemical Physics*, **133**, 045102 (6 pages total) (2010). 7. Takuya Saito, Takafumi Iwaki and Kenichi Yoshikawa, “Small Anion with Higher Valency Retards the Compaction of DNA in the Presence of Multivalent Cation”, *Biophysical Journal*, **96**, 1068-1075 (2009). 8. Takuya Saito, Takafumi Iwaki and Kenichi Yoshikawa, “DNA compaction induced by neutral polymer is retarded more effectively by divalent anion than monovalent anion”, *Chemical Physics Letters*, **465**, 40-44 (2008).
【学術関係の受賞など】	JSPS Research Fellowships for Young Scientists(DC2) 2005.4-2007.3

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【研究分野】	Theoretical Chemistry and Computational Chemistry
【現在の研究課題】	Reaction in excited state and molecular spectroscopy
【研究内容キーワード】	Exicted state, spectrum, reaction, bond break, DFT, TDDFT, MD
【学歴】	Jun. 2004, B.S. Major in Chemistry, College of Chemistry, Jilin University Jun. 2009, Ph.D. Major in Theoretical and Computational Chemistry, Institute of Theoretical Chemistry, State Key Laboratory of Theoretical and Computational Chemistry, Jilin University
【学位】	Ph.D. of Science from Jilin University Thesis: Quantum theoretical studies on the excited state and spectroscopic properties of transition metal complexes: Pt complexes
【略歴】	Jul. 2009, Research assistant, Jilin University Apr. 2012, FIFC Fellow, Kyoto University
【所属学会】	Chinese Chemical Society
【主な著書、学術論文】 （過去 5 年以内）	1. Qi Cao, Jing Wang, Zhao-Shuo Tian*, Zai-Feng Xie*, Fu-Quan Bai*, “Theoretical investigation on the photophysical properties of N-heterocyclic carbene Ir (III) complexes $(fpmb)_x Ir(bptz)_{3-x}$ (x=1-2)”. *Journal of Computational Chemistry*, (**2012**), 33(10), 1038-1046. 2. Fu-Quan Bai, Jian Wang, Bao-Hui Xia, Qing-Jiang Pan, Hong-Xing Zhang*, “DFT and TD-DFT study on the electronic structures and phosphorescent properties of 6-phenyl-2,2 '-bipyridine tridentate iridium(III) complexes and their isomer”. *Dalton Transactions*, (**2012**), 41(27), 8441-8446. 3. Juan Jin, Fu-Quan Bai, Ming-Jun Jia, Jie-Hui Yu*, Ji-Qing Yu*, “New monoacylhydrazidate-coordinated Mn2+ and Pb2+ compounds”. *Dalton Transactions*, (**2012**), 41(20), 6137-6147. 4. Jian Wang, Fu-Quan Bai, Bao-Hui Xia, Hong-Xing Zhang*, “Efficient blue-emitting ir(iii) complexes with phosphine carbanion-based ancillary ligand: a DFT study”. *Journal of Physical Chemistry A*, (**2011**), 115(42), 11689-11695. 5. Lei Sun, Fu-Quan Bai, Zeng-Xia Zhao, Hong-Xing Zhang*, “Design of new benzothiadiazole-based linear and star molecules with different functional groups as solar cells materials: A theoretical approach”. *Solar Energy Materials and Solar Cells*, (**2011**), 95(7), 1800-1810. 6. Fu-Quan Bai, Xin Zhou, Bao-Hui Xia, Tao Liu, Jian-Po Zhang, Hong-Xing Zhang*. “Electronic structures and optical properties of neutral substituted fluorene-based cyclometalated platinum(II) - acetylide complexes: A DFT exploration”. *Journal of Organometallic Chemistry*, (**2009**), 694(12), 1848–1860. 7. Guangjin Zhao, Guanglong Wu, Chang He, Fu-Quan Bai, Hongxia Xi, Hong-Xing Zhang, Yongfang Li*, “Solution-Processable Multiarmed Organic Molecules Containing Triphenylamine and DCM Moieties: Synthesis and Photovoltaic Properties”. *Journal of Physical Chemistry C*, (**2009**), 113(6), 2636-2642.
【学術関係の受賞など】	Teaching scheme design award, 2009 NSFC Young Scholar, 2010

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【現在の研究課題】	Theoretical studies of C-H Activation of Cycloalkenes by Dimetallynes (M=Ge, Sn)
【研究内容キーワード】	Reaction mechanism, heavier group 14 elements
【学歴】	2004, Doctor of Philosophy in Theoretical Chemistry, Royal Institute of Technology, Sweden
【学位】	Doctor of Philosophy, Royal Institute of Technology, Sweden
【略歴】	2007-2012,Postdoctoral Fellow, Institute for Molecular Science, Japan
【主な著書、学術論文】（過去 5 年以内）	1. Katsuhiko Takeuchi, Masaaki Ichinohe, Akira Sekiguchi, Jing-Dong Guo, and Shigeru Nagase, Reactivity of Disilyne RSiSiR (R=Si^{i}Pr[CH(SiMe$_3$)$_2$]$_2$) toward Nitriles: Unexpected Formation of Triaza-1,4-disilabicyclo-[2.2.2]octa-2,5,7-triene Derivatives, *Organometallics*, **28**, 2658-2660 (2009) 2. Katsuhiko Takeuchi, Masaaki Ichinohe, Akira Sekiguchi, Jing-Dong Guo, and Shigeru Nagase, Reactivity of the Disilyne RSiSiR (R=Si^{i}Pr[CH(SiMe$_3$)$_2$]$_2$) toward bis(silylcyanide) forming a 1,4-diaza-2,3-disilabenzene analog, *J. Phys. Org. Chem.*, **23**, 390-394 (2009) 3. Yang Peng, Jing-Dong Guo, Bobby D. Ellis, Zhongliang Zhu, James C. Fettinger, Shigeru Nagase, and Philip P. Power, Reaction of Hydrogen or Ammonia with Unsaturated Germanium or Tin Molecules under Ambient Conditions: Oxidative Addition versus Arene Ellmination, *J. Am. Chem. Soc.*, **131**, 16272-16282 (2009) 4. Xinping Wang, Yang Peng, Zhongliang Zhu, James C. Fettinger, Philip P. Power, Jingdong Guo, and Shigeru Nagase, Synthesis and Characterization of Two of the Three Isomers of a Germanium-Substituted Bicyclo[2.2.0]hexane Diradicaloid: Stretching the Ge-Ge Bond, *Angew. Chem. Int. Ed.*, **49**, 4593-4597 (2010) 5. Zachary D. Brown, Jing-Dong Guo, Shigeru Nagase, and Philip P. Power, Experimental and Computational Study of Auxiliary Molecular Effects on the Mechanism of the Addition of Hydrazines to a Low-Valent Germanium Complex, *Organometallics*, **31**, 3768-3772 (2012) 6. Satoru Sato, Yutaka Maeda, Jing-Dong Guo, Michio Yamada, Naomi Mizorogi, Shigeru Nagase, and Takeshi Akasaka, Mechanistic Study of the Diels-Alder Reaction of Paramagnetic Endohedral Metallofullerene: Reaction of La@C82 with 1,2,3,4,5-Pentamethylcyclopentadiene, *J. Am. Chem. Soc.*, **135**, 5582-5587 (2013)

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【現在の研究課題】	Fullerenes and related cluster chemistry
【研究内容キーワード】	Endohedral metallofullerenes, chemical functionalization of fullerenes
【学歴】	October 2010, Doctor of Eng., School of Chemical Engineering, Dalian University of Technology, China
【学位】	Doctor of Engineering from Dalian University of Technology
【主な著書、学術論文】（過去 5 年以内）	1. Peng Jin, Ce Hao, Zhanxian Gao, Shengbai B. Zhang, and Zhongfang Chen, “Endohedral Metalloborofullerenes $La_2@B_{80}$ and $Sc_3N@B_{80}$: A Density Functional Theory Prediction”, *J. Phys. Chem. A* **113**, 11613-11618(2009). 2. Peng Jin, Zhen Zhou, Ce Hao, Zhanxian Gao, Kai Tan, Xin Lu, and Zhongfang Chen, “NC Unit Trapped by Fullerenes: A Density Functional Theory Study on $Sc_3NC@C_{2n}$ (2n = 68, 78 and 80)”, *Phys. Chem. Chem. Phys.* **12**, 12442-12449(2010). 3. Peng Jin, Fengyu Li, Kevin Riley, Dieter Lenoir, Paul v. R. Schleyer, and Zhongfang Chen, “What is the Preferred Structure of the Meisenheimer-Wheland Complex between sym-Triaminobenzene and 4, 6-Dinitrobenzofuroxan?”, *J. Org. Chem.* **75**, 3761-3765(2010). 4. Peng Jin, Fengyu Li, and Zhongfang Chen, “Theoretical Design of Novel Trinuclear Sandwich Complexes with Central M3 Triangles (M = Ni, Pd, Pt)”, *J. Phys. Chem. A* **115**, 2402–2408(2011). 5. Peng Jin, Yongsheng Chen, Shengbai B. Zhang, and Zhongfang Chen, “Interactions between $Al_{12}X$ (X = Al, C, N and P) Nanoparticles and DNA Nucleobases/base Pairs: Implication to Nanotoxicity”, *J. Mol. Model.* **18**, 559-568(2012).

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【現在の研究課題】	Computational and experimental study on novel molecular transformation.
【研究内容キーワード】	Computational study of catalysis processes in organometallic systems and bio-systems
【学歴】	2002 B.Sc. in Chemistry, Sun Yat-sen University, 2005 M.Sc. in Polymer Chemistry and Physics, Sun Yat-sen University 2007 Jointly Educating Ph.D. in computational organometallic chemistry, University of North Texas, 2009 Ph.D. in Physical Chemistry (Theoretical and Computational Chemistry), Sun Yat-sen University
【学位】	Ph.D. in Physical Chemistry (Theoretical and Computational Chemistry), Sun Yat-sen University
【所属学会】	American Chemical Society
【学会活動】	241st ACS National Meeting in Anaheim, CA.
【主な著書、学術論文】（過去 5 年以内）	1. Ke, Zhuofeng, Abe, S., Ueno, T., & Morokuma, Keiji, Catalytic Mechanism in Artificial Metalloenzyme: QM/MM Study of Phenylacetylene Polymerization by Rhodium Complex Encapsulated in apo-Ferritin. *J. Am. Chem. Soc.* **134** (37), 15418–15429 (2012). 2. Ke, Zhuofeng, Abe, S., Ueno, T., & Morokuma, Keiji, *J. Am. Chem. Soc.* **133** (20), 7926-7941 (2011) (*JACS beta Select issue 13: Current Applications of Computational Chemistry in JACS - Molecules, Mechanisms and Materials*) 3. Liu, Y., Ke, Zhuofeng, Liu, Shuwen, Chen, Wen-Hua, Jiang, Shibo; Jiang, Zhi-Hong. *ChemMedChem* **6** (9), 1654- 1664 (2011).. 4. Gao, H., Ke, Zhuofeng, DeYonker N. J., Wang J., Xu H., Mao Z.-W., Phillips, D.L., & Zhao C. *J. Am. Chem. Soc.*, **2011**, 133 (9), 2904–2915 5. Ke, Zhuofeng & Cundari, T.R. *Organometallics* **29** (4), 821-834 (2010). (*Top10 Most Accessed Articles of Organometallics in 2010*)
【学術関係の受賞など】	Sun Yat-sen University Fellow 2009 State Scholarship Funds, China Scholarship Council (CSC) 2007

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【現在の研究課題】	DFTB-MD simulation of chirality-controlled carbon nanotube growth and determination of local chirality of carbon nanotube
【研究内容キーワード】	Carbon nanotube, density-functional tight-binding, chirality
【学歴】	2004 B. Sc., Hanyang University, Seoul, Korea 2010 Ph. D., KAIST, Daejeon, Korea
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【所属学会】	Korean Chemical Society
【主な著書、学術論文】 （過去 5 年以内）	1. Joonghan Kim, Sunhong Jun, Jeongho Kim, and Hyotcherl Ihee, “Density Functional and Ab Initio Investigation of CF_2ICF_2I and CF_2CF_2I Radicals in Gas and Solution Phases”, *J. Phys. Chem. A* **113**, 11059-11066 (2009). 2. Joonghan Kim, Tae Kyu Kim, and Hyotcherl Ihee, “Theoretical Study on the Reaction of Ti^+ with Acetone and the Role of Intersystem Crossing”, *J. Phys. Chem. A* **113**, 11382-11389 (2009). 3. Jeewon Kang, Joonghan Kim, Hyotcherl Ihee, and Yoon Sup Lee, “Molecular Structures, Energetics and Electronic Properties of Neutral and Charged Hgn Clusters (n= 2–8)", *J. Phys. Chem. A* **114**, 5630-5639 (2010). 4. Joonghan Kim, Hyotcherl Ihee, and Yoon Sup Lee, “Spin-Orbit Density Functional and Ab Initio Study of HgX_n (X=F, Cl, Br, and I; n=1, 2, and 4)”, *J. Chem. Phys.* **133**, 144309 (2010). 5. Joonghan Kim, Tae Kyu Kim, and Hyotcherl Ihee, “Density Functional and Spin-Orbit Ab Initio Study of CF_3Br: Molecular Properties and Electronic Curve-Crossing”, *J. Phys. Chem. A* **115**, 1264-1271 (2011). 6. Joonghan Kim, Hyotcherl Ihee, and Yoon Sup Lee, “Spin-orbit ab initio study of two low-lying states of chloroiodomethane cation”, *Theor. Chem. Acc.* **129**, 343-347 (2011). 7. Joonghan Kim, Stephan Irle, and Keiji Morokuma, “Determination of Local Chirality in Irregular Single-Walled Carbon Nanotubes Based on Individual Hexagons”, *Phys. Rev. Lett.* **107**, 175505 (2011) 8. Joonghan Kim and Hyotcherl Ihee, “Theoretical Study on the Reaction of Butadiynyl Radical (C_4H) with Ethylene (C_2H_4) to Form C_6H_4 and H”, *Int. J. Quantum Chem.* **112**, 1913-1925 (2012). 9. Joonghan Kim, Alister J. Page, Stephan Irle, and Keiji Morokuma, “Determination of Local Chirality in Irregular Single-Walled Carbon Nanotubes Based on Individual Hexagons”, *J. Am. Chem. Soc.* **134**, 9311-9319 (2012)

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【現在の研究課題】	Molecular Dynamics simulations and electronic structure calculations of nanoscale self-assembly processes (in particular, carbon nanotube & graphene nucleation and growth).
【研究内容キーワード】	Single-walled carbon nanotube, garphene self-assembly, nucleation, growth, healing, (n,m)chirality, functionalization density-functional tight-binding
【学歴】	2004, Bachelor of Mathematics (Honours Class I), The University of Newcastle, Australia 2004, Bachelor of Science (Honours Class I), The University of Newcastle, Australia 2008, Doctor of Philosophy, The University of Newcastle, Australia
【学位】	Doctor of Philosophy, The University of Newcastle, Australia
【略歴】	2008, Postdoctoral Research Associate, Priority Research Centre for Energy, Department of Chemical Engineering, The University of Newcastle, Australia 2009-2010, CREST Postdoctoral Research Fellow, Fukui Institute for Fundamental Chemistry, Kyoto University, Japan 2010-2012, Fukui Postdoctoral Research Fellow, Fukui Institute for Fundamental Chemistry, Kyoto University, Japan
【所属学会】	American Chemical Society, Royal Australian Chemistry Institute
【主な著書、学術論文】（過去 5 年以内）	1. Y. Wang, A. J. Page, H.-J. Qian, Y. Nishomoto, S. Irle, K. Morokuma, “Template Effect in the Competition Between Haeckelite and Graphene Growth on Ni(111): Quantum Chemical Molecular Dynamics Simulations.”, *J. Am. Chem. Soc.*, **133**, 18837, (2011) 2. A. J. Page, K.R.S. Chandrakumar, S. Irle, K. Morokuma, “SWNT Nucleation from Carbon-Coated SiO_2 Nanoparticles *via* a Vapor-Solid-Solid Mechanism”. *J. Am. Chem. Soc.*, **132**, 15699, (2011) 3. A. J. Page, Y. Ohta, S. Irle, K. Morokuma, “Mechanisms of Single-Walled Carbon Nanotube Nucleation, Growth and Healing Determined using QM/MD Methods”, *Acc. Chem. Res.*, **43**, 1375, (2010) 4. A. J. Page, Y. Ohta, Y. Okamoto, S. Irle, K. Morokuma, “Defect Healing During Single-Walled Carbon Nanotube Growth: A Density-Functional Tight-Binding Molecular Dynamics Investigation”, *J. Phys. Chem. C*, **113**, 20198, (2009) 5. A. J. Page, E. I. von Nagy-Felsobuki, “Rovibrational Spectra of LiH_2^+, $LiHD^+$ and LiD_2^+ Determined using FCI Property Surfaces”, *J. Phys. Chem. A*, **111**, 4478, (2007)
【学術関係の受賞など】	Australian Post-Graduate Award (2005-2008) RACI Chemistry Honours Prize (2004) Deans Medal, Faculty of Science and IT, The University of Newcastle (2004)

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【研究分野】	量子化学　理論化学
【現在の研究課題】	・ ランタノイド触媒を用いる向山アルドール反応の配位構造と立体選択性 ・ Gd(III)-MRI コントラスト剤の安定構造とその構造ゆらぎ ・ 人工力誘起反応 (AFIR) 法による IPNS 酵素の全反応経路探索 ・ 一酸化窒素還元酵素（cNOR、qNOR）の反応機構 ・ 密度行列繰り込み群 (DMRG) の方法を用いるアクチノイド二量体の電子状態と結合性
【研究内容キーワード】	ランタノイド触媒　酵素反応　反応自動経路探索法
【学歴】	2011 年 3 月　慶應義塾大学大学院理工学研究科 基礎理工学専攻後期博士課程修了
【学位】	2011 年 3 月　博士（理学）　慶應義塾大学
【略歴】	2009 年 4 月　慶應義塾大学大学院理工学研究科助教 (有期・研究奨励) 2011 年 4 月　京都大学福井謙一記念研究センターフェロー
【所属学会】	日本化学会、分子科学会
【主な著書、学術論文】 （過去 5 年以内）	1. M. Hatanaka, S. Maeda, K. Morokuma, “Sampling of Transition States for Predicting Diastereoselectivity Using Automated Search Method—Aqueous Lanthanide-Catalyzed Mukaiyama Aldol Reaction” *J. Chem. Theory Comput*. In press. 2. S. Maeda, E. Abe, M. Hatanaka, T. Taketsugu, K. Morokuma, “Exploring Potential Energy Surfaces of Large Systems with Artificial Force Induced Reaction Method in Combination with ONIOM and Microiteration” *J. Chem. Theory Comput*. **8**, pp5058-5063 (2012). 3. M. Hatanaka, S. Yabushita, “An ab initio study on the f–f hypersensitive transition intensities of lanthanide tribromide molecules”, *Chemical Physics Letters* **504**, pp 193-198 (2011). 4. M. Hatanaka, S. Yabushita, “Theoretical Study on the f–f Transition Intensities of Lanthanide Trihalide Systems”, *Journal of Physical Chemistry A* **113**, pp 12615-12625 (2009). 5. T. Ikeno, I. Iwakura, A. Shibahara, M. Hatanaka, A. Kokura, S. Tanaka, T. Nagata, T. Yamada, “Newly Designed Catalysts for the Enantioselective Borohydride Reduction: Prediction from the Theoretical Analysis”, *Chemistry Letters* **36**, pp 738-739 (2007). 6. I. Iwakura, M. Hatanaka, A. Kokura, H. Teraoka, T. Ikeno, T. Nagata, T. Yamada, “The Reactive Intermediate of Catalytic Borohydride Reduction by Schiff Base-Cobalt Comples”, *Chemistry – An Asian Journal* **1**, pp 656-663 (2006).
【学術関係の受賞など】	2009 年 3 月　日本化学会第 89 春季年会　学生講演賞 2010 年 4 月　公益信託　林女性自然科学者研究助成基金　林フェロー 2011 年 4 月　京都大学福井謙一記念研究センターフェロー

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【現在の研究課題】	Theoretical calculation of molecular motor and switch
【研究内容キーワード】	Artificial/biological molecular motor, molecular switch
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【主な著書、学術論文】（過去 5 年以内）	1. Fengyi Liu and Keiji Morokuma, Computational Study on the Working Mechanism of a Stilbene Light-Driven Molecular Rotary Motor: Sloped Minimal Energy Path and Unidirectional Nonadiabatic Photoisomerization, *J. Am. Chem. Soc.*, 2012, **134**, 4864–4876. 2. Shu-Feng Chen, Ya-Jun. Liu, Fengyi Liu, Luca De Vico, Roland Lindh, Multireference calculations on the chemical origin and mechanism of firefly bioluminescence, *Luminescence*, 2010, **25**, 89-90. 3. Fengyi Liu, Yajun liu, Luca De Vico, Roland Lindh, A CASSCF/CASPT2 Approach to the Decomposition of Thiazole-Substituted Dioxetanone: Substitution Effects and Charge-Transfer Induced Electron Excitation, *Chem. Phys. Lett.* 2009, **484**, 69-75. 4. Fengyi Liu, Yajun Liu, Luca De Vico, Roland Lindh, Theoretical Study of the Chemiluminescent Decomposition of Dioxetanone, *J. Am. Chem. Soc.*, 2009, **131**, 6181-6188. 5. Shu-Feng Chen, Feng-Yi Liu, Ya-Jun Liu, An ab initio investigation of the mechanisms of photodissociation in bromobenzene and iodobenzene, *J. Chem. Phys.*, 2009, **131**, 124304.

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【現在の研究課題】	Photodissociation mechanism of small molecules
【研究内容キーワード】	Photodissociation, excited state, conical intersection, nonadiabatic transition
【学歴】	Jun. 2002, B. Sc. in Chemistry, Liaoning Normal University, China Jun. 2005, M. Sc. in Physical Chemistry, Liaoning Normal University, China Jun. 2008, Ph. D. in Physical Chemistry, Beijing Normal University, China
【学位】	Ph. D. in Physical Chemistry, Beijing Normal University
【略歴】	July 2008-till now, assistant professor, associate professor, Technical Institute of Physics and Chemistry, Chinese Academy of Science July 2010-September 2012, Postdoctoral Fellow, Fukui Institute for Fundamental Chemistry
【主な著書、学術論文】 （過去 5 年以内）	1. Hong-Yan Xiao, Satoshi Maeda and Keiji Morokuma. Excited-state roaming dynamics in photolysis of a nitrate radical. *J. Phys. Chem. Lett.* **2**, 934-938 (2011) 2. Michael P. Grubb, Michelle L. Warter, Hong-Yan Xiao, Satoshi Maeda, Keiji Morokuma and Simon W. North. No straight path: roaming in both ground- and excited-state photolytic channels of $NO_3 \rightarrow NO + O_2$. *Science* **335**, 1075-1078 (2012) 3. Hong-Yan Xiao, Satoshi Maeda and Keiji Morokuma. Global ab initio potential energy surfaces for low-lying doublet states of NO_3. *J. Chem. Theory Comput.* **8**, 2600-2605 (2012) 4. Jie-Yun Wu, Shu-Hui Bo, Jia-Lei Liu, Ting-Ting Zhou, Hong-Yan Xiao, Ling Qiu, Zhen Zhen and Xin-Lou Liu. Synthesis of novel nonlinear optical chromophore to achieve ultrahigh electro-optic activity. *Chem. Commun.* **48**, 9637-9639 (2012) 5. Bi-Na Fu, Joel M. Bowman, Hong-Yan Xiao, Satoshi Maeda and Keiji Morokuma. Quasiclassical trajectory studies of the photodissociation dynamics of NO_3 from the D_0 and D_1 potential energy surfaces. *J. Chem. Theory Comput.* **9**, 893-900 (2013) 6. Hong-Yan Xiao, Satoshi Maeda and Keiji Morokuma. CASPT2 study of photodissociation pathways of ketene. *J. Phys. Chem. A* in press (DOI: 10.1021/jp312719a)
【学術関係の受賞など】	Qiu Shi Graduate Student Scholarship in Beijing Normal University (2007) National Natural Science Foundation of China (2010)

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【現在の研究課題】	photobiology
【研究内容キーワード】	Photo reaction mechanism of biochemical and metal-complexes systems
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【学位】	Ph.D. in Physical Chemistry, Beijing Normal University, China
【主な著書、学術論文】（過去 5 年以内）	1. Lina Ding, Lung Wa, Chung, Keiji Morokuma*, Excited-State Proton Transfer Controls Irreversibility of Photoisomerization in Mononuclear Ruthenium(II) Monoaquo Complexes: A DFT Study, submitted 2. Lina Ding, Naoki Ishida, Masahiro Murakami, and Keiji Morokuma*, sp^3–sp^2 vs sp^3–sp^3 C–C Activation in Rh-Catalyzed Ring Opening of Benzocyclobutenol: A DFT Study To be submitted 3. Lina Ding, Lung Wa Chung, Keiji Morokuma “Reaction Mechanism of Photoinduced Decarboxylation of the Photoactivatable Green Fluorescent Protein: An ONIOM(QM:MM) Study”, *J. Phys. Chem. B*, **2013**, 117 (4), 1075–1084. 4. Ganglong Cui, Lina Ding, Feng Feng, Yajun Liu, and Weihai Fang, “Insights into Mechanistic Photochemistry of Urea”, J. Chem. Phys. 2010, 132, 194308; 5. Lina Ding, Wei-Hai Fang, “Exploring Light-Induced Decarboxylation Mechanism of o-Acetylphenyl-Acetic Acid from the Combined CASSCF and DFT Studies”, *J. Org. Chem.* **2010**, 75, 1630-1636. 6. Lina Ding, Lin Shen, Xue-Bo Chen, Wei-Hai Fang, “Solvent Effects on photoreactivity of Valerophenone: A Combined QM and MM Study”, *J. Org. Chem.* Featured Article **2009**, 74, 8956-8962. 7. Lina Ding, Xue-Bo Chen, Wei-Hai Fang, “Ultrafast Asynchronous Concerted Excited-State Intramolecular Proton Transfer and Photodecarboxylation of o-Acetylphenylacetic Acid Explored by Combined CASPT2 and CASSCF Studies”, *Org. Lett.* **2009**, 11(7), 1495-1498.
【学術関係の受賞など】	Beijing Normal University, Academic Excellence Award, 2009. Beijing Normal University, Scientific Achievement Award, 2010.

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【研究分野】	Computational Chemistry
【現在の研究課題】	MD simulations of the formation and growth of carbon nanostructures: fullerenes, nanotubes, and graphene
【研究内容キーワード】	Fullerene, Hydrocarbon combustions, Self-assembly, Single-walled carbon nanotube, Chirality, Graphene growth, Density-functional tight-bingding
【学歴】	2004, Bachelor of Chemistry, Qufu Normal University, China 2007, Master of Chemical Physics, University of Science and Technology of China, China 2010, Doctor of Chemical Physics, University of Science and Technology of China, China
【学位】	Doctor of Philosophy, University of Science and Technology of China
【主な著書、学術論文】（過去 5 年以内）	1. Hai-Bei Li, Alister. J. Page, Stephan Irle and Keiji Morokuma, Single-walled Carbon Nanotube Growth from Chiral Carbon Nanorings: Prediction of Chirality and Diameter Influence on Growth Rates. *J. Am. Chem. Soc.* **134**, 15887, 2012 2. Hai-Bei Li, Alister. J. Page, Stephan Irle and Keiji Morokuma, Theoretical Insights into Chirality-Controlled SWCNT Growth from a Cycloparaphenylene Template. *ChemPhysChem*, **13**, 1479, 2012 3. Hai-Bei Li, Alister. J. Page, Ying Wang, Stephan Irle and Keiji Morokuma, Sub-surface nucleation of graphene precursors near a Ni(111) step-edge, *ChemComm*, **48**, 7937, 2012 4. Hai-Bei Li, Shanxi Tian, and Jinlong Yang. Propene oxidation on $V_4O_{11}^-$ cluster: reaction dynamics to acrolein, *J. Phys. Chem. A*, **114**, 6542, 2010 5. Hai-Bei Li, Shanxi Tian, and Jinlong Yang. Propene oxidation with anionic cluster $V_4O_{11}^-$: selective epoxidation, *Chem. Eur. J (communications)* **15**, 10747, 2009
【学術関係の受賞など】	Qiu Shi Graduate Student Scholarship (2009) Supported by the Scientific Research Foundation of Graduate School of USTC (2008)

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【研究分野】	Computational Chemistry, Biochemistry and Biophysics
【現在の研究課題】	Metalloenzymes, photobiology, multi-scale simulations
【研究内容キーワード】	Reaction mechanism of metalloenzymes, photobiology, bio-inspired systems and catalysis; multi-scale simulations development; strongly-correlated systems
【学歴】	Aug. 2000, B.Sc. in Chemistry (1st Hon.), The Hong Kong University of Science & Technology; Aug. 2003, M. Phil. in Chemistry, The Hong Kong University of Science & Technology; Aug. 2006, Ph. D. in Chemistry, The Hong Kong University of Science & Technology
【学位】	Ph. D. in chemistry, The Hong Kong University of Science & Technology
【主な著書、学術論文】 （過去 5 年以内）	1. Chung, L. W.; Li, X.; Sugimoto, H.; Shiro, Y.; Morokuma, K. “A DFT Study on a Missing Piece in Understanding of Heme Chemistry: The Reaction Mechanism for Indoleamine 2,3-Dioxygenase (IDO) and Tryptophan 2,3-Dioxygenase (TDO)” *J. Am. Chem. Soc.* **2008**, 130, 12298. 2. Chung, L. W.; Hayashi, S.; Lundberg, M.; Nakatsu, T.; Kato, H.; Morokuma, K. “Mechanism of Efficient Firefly Bioluminescence via Adiabatic Transition State and Seam of Sloped Conical Intersection” *J. Am. Chem. Soc.* **2008**, 130, 12880. 3. Li. X.; Chung, L. W.; Paneth, P.; Morokuma, K. “DFT and ONIOM(DFT:MM) Studies on Co-C Bond Cleavage and Hydrogen Transfer in B12-Dependent Methylmalonyl-CoA Mutase. Stepwise or Concerted Mechanism?” *J. Am. Chem. Soc.* **2009**, 131, 5115. 4. Li. X.; Chung, L. W.; Mizuno, H.; Miyawaki, A.; Morokuma, K. “A Theoretical Study on the Natures of On- and Off-States of Reversibly Photoswitching Fluorescent Protein Dronpa: Absorption, Emission, Protonation and Raman” *J. Phys. Chem. B* **2010**, 114, 1114 5. Chung, L. W.; Li, X.; Sugimoto, H.; Shiro, Y.; Morokuma, K. “ONIOM Study on a Missing Piece in Our Understanding of Heme Chemistry: Bacterial Tryptophan 2,3-Dioxygenase with Dual Oxidants”, *J. Am. Chem. Soc.* **2010**, 115, 11993. 6. Nakamura, A.; Munakata, K.; Ito, S.; Kochi, T.; Chung, L. W.; Morokuma, K.; Nozaki, K. “Pd-Catalyzed Copolymerization of Methyl Acrylate with Carbon Monoxide: Structures, Properties and Mechanistic Aspects toward Ligand Design” *J. Am. Chem. Soc.* **2011**, 133, 6761. 7. Li, X.; Chung, L. W.; Morokuma, K. “Primary Events of Photodynamics of All-trans Protonated Retinal Schiff Base in Bacteriorhodopsin, Methanol Solution and Gas Phase” *J. Chem. Theory Comput. (Lett.)* **2011**, 7, 2694. 8. Chung, L. W.; Li, X.; Hirao, H.; Morokuma, K. “Comparative Reactivity of Ferric-Superoxo and Ferryl-Oxo Species in Heme and non-Heme Complexes” *J. Am. Chem. Soc. (Commun.)* **2011**, 133, 20076. 9. Tanaka, R.; Yamashita, M.; Chung, L. W.; Morokuma, K.; Nozaki, K. “Hydrogenation of Carbon Dioxide Catalyzed by Ir-PNP Complex: Reversibility and Reaction Mechanism” *Organometallics* **2011**, 30, 6742. 10. Chung, L. W.; Hirao, H.; Li, X.; Morokuma, K. “The ONIOM Method: Its Foundation and Applications to Metalloenzymes and Photobiology”, *WIREs Comput. Mol. Sci.* **2012**, 2, 327. 11. Ding, L.; Chung, L. W.; Morokuma, K. “Reaction Mechanism of Photoinduced Decarboxylation of the Photoactivatable Green Fluorescent Protein: An ONIOM(QM:MM) Study” *J. Phys. Chem. B* **2013**, 117, 1075.

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【現在の研究課題】	Hetero- and homogeneous catalysis, Asymmetric organic catalysis
【研究内容キーワード】	metalloenzymes, DNA based asymmetric catalysis, reaction mechanisms
【学歴】	2009, Ph.D. degree in Organic chemistry, University of Sofia, Bulgaria 2003, B.Sc. in Chemistry (Theoretical and physical chemistry), University of Sofia, Bulgaria
【学位】	Ph.D. in Organic chemistry, University of Sofia, Bulgaria
【略歴】	05/2012-05/2013, JSPS Fellow at FIFC, Kyoto University, Kyoto, Japan 12/2010-04/2012, Postdoctoral Scholar at FIFC, Kyoto University, Kyoto, Japan 02-11/2010, Postdoctoral Scholar at the Faculty of Chemistry, University of Sofia 06/2009–01/2010, Postdoctoral Scholar at the Faculty of Chemistry, University of Sofia & Excellence Centre for Advanced Materials UNION 7/2008–5/2009, Research chemist at the Faculty of Chemistry, University of Sofia
【所属学会】	Bulgarian Catalytic Club, Bulgarian Zeolite Association
【主な著書、学術論文】（過去 5 年以内）	1. G. N. Vayssilov, G. P. Petrova, E. A. I. Shor, V. A. Nasluzov, A. M. Shor, P. S. Petkov, N. Rösch, “Reverse hydrogen spillover on and hydrogenation of supported metal clusters: Insights from computational model studies” *Phys. Chem. Chem. Phys.* **14**, 5879-5890 (2012). 2. G. N. Vayssilov, Y. Lykhach, A. Migani, T. Staudt, G. P. Petrova, N. Tsud, Tomáš Skála, A. Bruix, F. Illas, K. C. Prince, V. Matolín, K. M. Neyman, J. Libuda, “Support nanostructure boosts oxygen transfer to catalytically active platinum nanoparticles”, *Nature Materials*, **10**, 310–315 (2011). 3. G. P. Petrova, G. N. Vayssilov, N. Rösch, “Interaction of ethene and ethyne with bare and hydrogenated Ir4 clusters. A density functional study”, *Catalysis Science & Technology*, **1**, 958-970 (2011). 4. N. Rösch, G. P. Petrova, P. St. Petkov, A. Genest, S. Krüger, H. A. Aleksandrov, G. N. Vayssilov, “Impurity Atoms on Small Transition Metal Clusters. Insights from Density Functional Model Studies”, *Topics in Catalysis*, **54**, 363-377 (2011). 5. M. A. Rangelov, G. P. Petrova, V. M. Yomtova, G. N. Vayssilov, “Catalytic Role of Vicinal OH in Ester Aminolysis - Proton Shuttle versus Hydrogen-Bonds Stabilization”, *J. Org. Chem.*, **75**, 6782–6792 (2010).
【学術関係の受賞など】	Student award for high academic achievements of the Foundation for support of the Bulgarian Higher Education named after Prof. Michael Klett (2003)

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【研究分野】	Computational Chemistry
【現在の研究課題】	Computational studies of metalloenzymes and molecular magnets
【研究内容キーワード】	ferritin, ferroxidase, di-iron, DMRG, magnetic exchange coupling
【学歴】	2006, B.A. (summa cum laude), Willamette University, Salem, OR, USA 2011, Ph.D., Montana State University, Bozeman, MT, USA
【学位】	Doctor of Philosophy, Montana State University, Bozeman, MT, USA
【略歴】	2011, General Chemistry Lab TA, Montana State University 2007, Research Assistant, Montana State University 2006, Biochemistry Lab TA, Willamette University
【主な著書、学術論文】（過去 5 年以内）	1. Harris, T. V.; Morokuma, K. QM/MM Structural and Spectroscopic Analysis of the Di-iron(II) and Di-iron(III) Ferroxidase Site in M Ferritin *Inorg. Chem.*, submitted **2013**. 2. Harris, T. V.; Szilagyi, R. K. Comparative Assessment of the Composition and Charge State of Nitrogenase FeMo-Cofactor. *Inorg. Chem.,* **2011***, 50* (11), 4811. 3. Harris, T. V.; Szilagyi, R. K. Nitrogenase Structure and Function Relationships by Density Functional Theory. In *Nitrogen Fixation: Methods and Protocols*; Ribbe, M. W. Ed.; Humana Press: New York, 2011; pp 267-292. 4. Harris, T. V.; Szilagyi, R. K.; McFarlane Holman, K. L. Electronic Structural Investigations of Ruthenium Compounds and Anticancer Prodrugs. *J. Biol. Inorg. Chem.* **2009***, 14* (6), 891. 5. Pool, V. L.; Klem, M. T.; Holroyd, J.; Harris, T.; Arenholz, E.; Young, M.; Douglas, T.; Idzerda, Y. U. Site Determination of Zn Doping in Protein Encapsulated $Zn_xFe_{3-x}O_4$ Nanoparticles. *J. Appl. Phys.* **2009***, 105* (7), 07B515.
【学術関係の受賞など】	JSPS Fellowship, 2012 NSF Materials Computation Center Travel Grant, 2011 Kopriva Graduate Student Fellowship, 2009 Molecular Biosciences Fellowship, 2007–2011 Mildred Livingston Grant, 2007–2008

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【研究分野】	計算化学、理論化学
【現在の研究課題】	ニトロメタンの光解離、H_2NO の光解離、Carbocation の rearrangement に関する研究
【研究内容キーワード】	励起状態、光解離、遷移状態、有機化学反応
【学歴】	2009年10月　京都大学大学院理学研究科博士課程修了
【学位】	2009年10月 理学博士（京都大学）
【略歴】	2010年1月-2013年2月　Research scholar, University of Minnesota 2013年3 月- 研究員、福井謙一記念研究センター
【主な著書、学術論文】（過去 5 年以内）	1. Polarizable Force Field for protein with Charge Response kernel, M. Isegawa and S. Kato, *J. Chem. Theory Comput.* **5**, 2809 (2009). 2. Incorporation of charge transfer into the explicit polarization fragment method by grand canonical density functional theory, M. Isegawa, J. Gao, and D. G. Truhlar, *J. Chem. Phys.* **135**, 084107 (2011). 3. Polarized Molecular Orbital Model Chemistry 3. The PMO Method Extended to Organic Chemistry, M. Isegawa, L. Fieldler, H. R. Leverentz, Y. Wang, S. Nachimuthu, J. Gao, and D. G. Truhlar, *J. Chem. Theory Comput.* **9**, 33 (2013). 4. Performance of Recent Approximation Density functional for Time-Dependent Density Functional Theory Calculations of Valence and Rydberg Electronic Transition Energies, M. Isegawa, R. Peverati, and D. G. Truhlar, *J. Chem. Phys.* **137**, 244104 (2013). 5. Electrostatically Embedded Molecular Tailoring Approach and Validation for Peptide, M. Isegawa, B. Wang, and D. G. Truhlar, *J. Chem. Theory Comput.* **9**,1381(2013).

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【現在の研究課題】	有機化学反応における水素結合の役割
【研究内容キーワード】	反応経路、 軌道相互作用、 水素結合、プロトン移動
【学歴】	1969年3月京都大学　工学部燃料化学科　卒業、　1974年3月末　京都大学工学研究科　燃料化学専攻　博士課程　終了。
【学位】	工学博士
【略歴】	1974年4月-1975年9月末　米国　Rochester大学　博士研究員、 1975年10月-2012年3月末　奈良教育大学　教員。
【所属学会】	日本化学会
【主な著書、学術論文】（過去 5 年以内）	1. "How is the anionic tetrahedral intermediate involved in the isomerization of aspartyl peptides to iso-aspartyl ones? A DFT study on the tetra-peptide", Shinichi Yamabe, Wei Guan and Shigeyoshi Sakaki, *Org. Biomol. Chem.,* **2012***,10*, 8007-8015 DOI: 10.1039/C2OB26106E 2. "A new intermediate in the Prins reaction", Shinichi Yamabe, Takeshi Fukuda and Shoko Yamazaki, *Beilstein J. Org. Chem.* **2013***, 9*, 476-485. 3. "Presence or absence of a novel charge-transfer complex in the base-catalyzed hydrolysis of N-ethylbenzamide or ethyl benzoate", Shinichi Yamabe, Wei Guan and Shigeyoshi Sakaki, *Beilstein J. Org. Chem.* **2013***, 9*, 185-196. 4. "Three Competitive Transition States at the Glycosidic Bond of Sucrose in Its Acid-Catalyzed Hydrolysis", Shinichi Yamabe, Wei Guan and Shigeyoshi Sakaki, *J. Org. Chem.,* **2013***, 78* (6), pp 2527-2533. DOI: 10.1021/jo3027565 5. "An aniline dication-like transition state in the Bamberger rearrangement", Shinichi Yamabe, Guixiang Zeng, Wei Guan and Shigeyoshi Sakaki, *Beilstein J. Org. Chem.* **2013***, 9*, 1073-1082.doi:10.3762/bjoc.9.119

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【研究内容キーワード】	Gas Adsorption, Proton Conductivity
【学歴】	Mar 2008, Master of Eng., Graduate School of Engineering, Kyoto University May 2011, Ph.D. of Eng., Graduate School of Engineering, Kyoto University
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【略歴】	Oct. 2011- FIFC Fellow (Kyoto University) Apr. 2011-Sep. 2011 Specially Promoted Research Fellow (Kyoto University) Apr. 2008-Mar. 2011 JSPS Research Fellow (DC1) (Kyoto University)
【所属学会】	Chemical Society of Japan, Japan Society of Coordination Chemistry, Japan Society for Molecular Science
【主な著書、学術論文】 （過去 5 年以内）	1. Yuh HIJIKATA, Satoshi HORIKE, Masayuki SUGIMOTO, Munehiro INUKAI, Tomohiro FUKUSHIMA, and Susumu KITAGAWA, “Pore design of two-dimensional coordination polymers toward selective adsorption” *Inorg. Chem.* **52**, 3634-3642 (2013) 2. Nobuhiro YANAI, Koji KITAYAMA, Yuh HIJIKATA, Hiroshi SATO, Ryotaro MATSUDA, Yoshiki KUBOTA, Masaki TAKATA, Motohiro MIZUNO, Takashi UEMURA, and Susumu KITAGAWA, “Reporting structural transformation of soft porous crystals for detection of CO_2”, *Nat. Mater.*, **10**, 787-793 (2011) 3. Yuh HIJIKATA, Satoshi HORIKE, Daisuke TANAKA, Juergen GROLL, Motohiro MIZUNO, Jungeun KIM, Masaki TAKATA, and Susumu KITAGAWA, Differences of crystal structure and dynamics between soft porous nanocrystal and bulk crystal”, *Chem. Commun.*, **47**, 7632-7634 (2011) 4. Yuh HIJIKATA, Satoshi HORIKE, Masayuki SUGIMOTO, Hiroshi SATO, Ryotaro MATSUDA, and Susumu KITAGAWA, “Relationship between Channel and Sorption Properties in Coordination Polymers with Interdigitated Structures”, *Chem. Eur. J.*, **17**, 5138-5144 (2011) 5. Yuh HIJIKATA, Hiroyuki NAKASHIMA, and Hiroshi NAKATSUJI, “Solving non-Born-Oppenheimer Schrödinger equation for hydrogen molecular ion and its isotopomers using the free complement method”, *J. Chem. Phys.*, **130**, 024102-1-11 (2009)
【学術関係の受賞など】	JSPS Research Fellowships for Young Scientists (DC1) 2008-2011

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【現在の研究課題】	溶液化学・計算化学・理論化学
【研究内容キーワード】	溶液中の遷移金属錯体の化学反応の理論的解析
【学歴】	3D-RISM-SCF法、平均場QM/MM法、自由エネルギー解析、溶媒和構造解析、周期的結晶解析
【学位】	2010年3月 京都大学大学院理学研究科化学専攻博士後期課程研究指導認定退学
【略歴】	2010年4月 京都大学大学院理学研究科化学専攻 研修員 2010年5月 京都大学 物質-細胞統合システム拠点 教務補佐員 2010年10月 京都大学 物質-細胞統合システム拠点 特定研究員 2011年4月 京都大学 福井謙一記念研究センター 特定研究員
【主な著書、学術論文】（過去 5 年以内）	1. Aono S., Hosoya T., and Sakaki S., “A 3D-RISM-SCF method with dual solvent boxes for a highly polarized system: application to 1,6-anhydrosugar formation reaction of phenyl alpha- and beta-D-glucosides under basic conditions” *Phys. Chem. Chem. Phys.* **17** 6368 (2013) 2. Aono S. and Sakaki S., “Evaluation Procedure of Electrostatic Potential in 3D-RISM-SCF Method and Its Application to Hydrolyses of Cis- and Transplatin Complexes” *J. Phys. Chem. B* **116** 13045 (2012) 3. Aono S. and Sakaki S., “Proposal of new QM/MM approach for geometry optimization of periodic molecular crystal: Self-consistent point charge representation for crystalline effect on target QM molecule” *Chem. Phys. Lett.* **544** 77 (2012). 4. Aono S., Yamamoto T. and Kato S. “Solution reaction space Hamiltonian based on an electrostatic potential representation of solvent dynamics” *J. Chem. Phys.* **134** 144108 (2011). 5. Aono S. and Kato S. “Proton Transfer in Phenol-Amine Complexes: Phenol Electronic Effect on Free Energy Profile in Solution” *J. Comput. Chem.* **31** 2924-2931 (2010). 6. Aono S., Minezawa N. and Kato S. “Electronic spectra of coumarin-151 in polar solvents: Linear response free energy approach” *Chem. Phys. Lett.* **492** 193-197 (2010).

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【現在の研究課題】	遷移金属錯体の理論研究
【研究内容キーワード】	遷移金属
【学歴】	2010年九州大学大学院総合理工学府量子プロセス理工学専攻博士後期課程修了
【学位】	2010年3月博士 (理学) (九州大学)
【所属学会】	分子科学会、理論化学会、American Chemical Society
【主な著書、学術論文】（過去 5 年以内）	1. “CASSCF and CASPT2 calculations for lanthanide trihalides LnX3 using model core potentials” S. Tsukamoto, H. Mori, H. Tatewaki, and E. Miyoshi, *Chem. Phys. Lett.* **2009**, 474, 28. 2. “Theoretical Study of Pt(PR3)2(AlCl3)(R-H, Me, Ph, or Cy) Including an Unsupported Bond between Transition Metal and Non-Transition Metal Elements; Geometry, Bond Strength, and Prediction” S. Tsukamoto and S. Sakaki, *J. Phys. Chem. A*, **2011**, 115, 8520. 3. “A theoretical study of luminescent vapochromic compounds including an $AuCu_2(NHC)_2$ core” S. Tsukamoto and S. Sakaki, *Dalton Trans.* **2013**, 42, 4809.

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【研究分野】	Theoretical and Computational Chemistry
【現在の研究課題】	Gas Absorption in Metal Organic Framework, Non covalent Interactions and Activation of small molecule by transition metal complexes.
【研究内容キーワード】	Metal-Organic Framework, Potential Energy Surface, Catalysis
【学歴】	March 2001, Master of Sci., University of Pune, India October 2008, Doctor of Philosophy, University of Pune, India
【学位】	Doctor of Philosophy from Department of Chemistry, University of Pune, India
【略歴】	August 2008 to April 2010: Postdoctoral Research Fellow, Tata Institute of Fundamental Research, Mumbai, India June 2010 to present: Postdoctoral Research Fellow, Kyoto University, Japan
【主な著書、学術論文】（過去 5 年以内）	1. Milind M. Deshmukh, Masaaki Ohba, Susumu Kitagawa, and Shigeyoshi Sakaki "Absorption of CO_2 and CS_2 into the Hofmann-Type Porous Coordination Polymer: Electrostatic versus Dispersion Interactions" *J. Am. Chem. Soc.* **135**, 4840 (2013). 2. Milind M. Deshmukh, and Shigeyoshi Sakaki, "Two-step Evaluation of Potential Energy Surface and Binding Energy of van der Waals Complexes" *J. Comput. Chem.* **33**, 617 (2012). 3. Jayasree K. Kedkar, Milind M. Deshmukh, Shridhar R. Gadre. Shridhar P. Gejji, "Intramolecular Hydrogen Bonding and cooperative interactions in Calix[n]arenes (n = 4, 5)" *J. Phys. Chem. A.* **116**, 3739 (2012). 4. Milind M. Deshmukh and Shigeyoshi Sakaki, "Binding Energy of Gas Molecule with Two Pyrazine Molecules as Organic Linker in Metal-Organic Framework: Its Theoretical Evaluation and Understanding of Determining Factors" *Theo. Chem. Acc.* **130**, 475 (2011). 5. Milind M. Deshmukh, Bartolotti Libero Jr., and Shridhar R. Gadre, "Intramolecular Hydrogen Bond Energy and Cooperative Interactions in α-, β-, and γ-Cyclodextrin Conformers", *J. Comput. Chem.* **32**, 2996 (2011). 6. Milind M. Deshmukh and Shridhar R. Gadre, "Estimation of N-H···O=C Intramolecular Hydrogen Bond Energy in Polypeptides", *J. Phys. Chem. A.* **113**, 7927 (2009).
【学術関係の受賞など】	Senior Research Fellowship of CSIR, India, (2005-2008). Senior Research Fellowship of C-DAC, Pune, India (2004-2005).

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【現在の研究課題】	1. Cooperative catalysis through new metal-Ligand cooperation modes 2. H-H and C-H bond activations 3. Dehydrogeanation and hydrogenation reactions
【研究内容キーワード】	Cooperation catalysis, C-H bond, H-H bond, main group catalyst
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【主な著書、学術論文】（過去 5 年以内）	1. Guixiang Zeng, Yong Guo, Shuhua Li, “H2 activation by a (PNP)Ir(C6H5) complex via the dearomatization/aromatization process of the PNP ligand: A computational study” *Inorg. Chem.* **48**, 10257 (2009). 2. Guixiang Zeng, Shuhua Li, “Mechanistic insight on the hydrogenation of conjugated alkenes with H2 catalyzed by early main-group metal catalysts” *Inorg. Chem.* **49**, 3361 (2010). 3. Guixiang Zeng, Shuhua Li, “Insights on Dehydrogenative Coupling of Alcohols and Amines catalyzed by a (PNN)–Ru(II) Hydride Complex: Unusual Metal–Ligand Cooperation” *Inorg. Chem.* **50**, 10572 (2011). 4. Guixiang Zeng, Shigeyoshi Sakaki, “Noble Reaction Features of Bromoborane in Oxidative Addition of B–Br σ–Bond to [M(PMe3)2] (M= Pt or Pd): Theoretical Study” *Inorg. Chem.* **50**, 5290 (2011). 5. Guixiang Zeng, Shigeyoshi Sakaki, “Theoretical Study on the Transition-Metal Oxoboryl Complex: M–BO Bonding Nature, Mechanism of the Formation Reaction, and Prediction of a New Oxoboryl Complex” *Inorg. Chem.* **51**, 4597 (2012) 6. Guixiang Zeng, Shigeyoshi Sakaki, “Unexpected Electronic Process of H2 Activation by a New Nickel Borane Complex: Comparison with the Usual Homolytic and Heterolytic Activations” *Inorg. Chem.* **52**, 2844 (2013)

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【現在の研究課題】	d- 電子複合系および高周期典型元素化合物の理論化学
【研究内容キーワード】	遷移金属元素、高周期典型元素、分子軌道計算
【学歴】	1997年3月　立教大学理学部化学科　卒業 1999年3月　東京都立大学大学院理学研究科化学専攻修士士課程　修了 2002年3月　東京都立大学大学院理学研究科化学専攻博士課程　修了
【学位】	2002年 3月　理学博士（東京都立大学）
【略歴】	2002年4月　日本学術振興会　特別研究員(PD) 2005年4月　自然科学研究機構・分子科学研究所　専門研究職員 2007年5月　ドイツ・フィリップス=マールブルク大学　博士研究員 2011年4月　京都大学・福井謙一記念研究センター　特定研究員
【在外研究歴】	2007年5月-2010年12月　ドイツ・フィリップス=マールブルク大学　博士研究員（Gernot Frenking教授）
【所属学会】	日本化学会、理論化学研究会
【主な著書、学術論文】（過去 5 年以内）	1. "Theoretical Study of Reactivity of Ge(II)-hydride Compound: Comparison with Rh(I)-hydride Complex and Prediction of Full Catalytic Cycle by Ge(II)-hydride" N. Takagi, S. Sakaki, *J. Am. Chem. Soc., in press*. 2. "A Theoretical Study of Unusual Y-Shaped Three-coordinate Pt Complex: Pt(0) σ-Disilane Complex or Pt(II) Disilyl Complex?" N. Takagi, S. Sakaki, *J. Am. Chem. Soc.*, **134**, 11749-11759 (2012). 3. "Carbodiphosphorane-Analogues $E(PPh_3)_2$ with E = C - Pb. A Theoretical Study with implications for ligand design" N. Takagi, R. Tonner, G. Frenking, *Chem. Eur. J.*, **18**, 1772-1780 (2012). 4. "Bonding Situation in "Early-Late" Transition Metal Complexes $Cl_3M\text{-}M'(PCl_3)_4$ (M = Ti, Zr, Hf; M' = Co, Rh, Ir) - Theoretical Study for a Ligand Fine Tuning of M-M' Bonds -" N. Takagi, A. Krapp, G. Frenking, *Z. Anorg. Alleg. Chem.* **637**, 1728-1735 (2011). 5. "Divalent Pb(0) Compounds" N. Takagi, G. Frenking, *Theor. Chem. Acc.*, **129**, 615-623 (2011). 6. "Bonding Analysis for Metal-Metal Multiple bonds in $R_3M\text{-}M'R_3$ (M, M' = Cr, Mo, W; R = Cl, NMe_2)" N. Takagi, A. Krapp, G. Frenking, *Inorg. Chem.*, **50**, 819-826 (2010). 7. "On the nature of homo- and heterodinuclear metal-metal quadruple bonds – Analysis of the bonding situation and benchmarking DFT against wavefunction methods" N. Takagi, A. Krapp, G. Frenking, *Can. J. Chem.*, **88**, 1079-1093 (2010). 8. "Divalent E(0) Compounds (E = Si - Sn)" N Takagi, T. Shimizu, G. Frenking, *Chem. Eur. J.*, **15**, 8593-8604 (2009). 9. "Divalent Si(0) Compounds" N Takagi, T. Shimizu, G. Frenking, *Chem. Eur. J.*, **15**, 3448-3456 (2009). 10. "Do Lead Analogues of Alkynes Take a Multiply Bonded Structure? " N. Takagi, S. Nagase, *Organometallics*, **26**, 3627-3629 (2007). 11. "Tin Analogues of Alkynes. Multiply Bonded Structures vs Singly Bonded Structures" N. Takagi, S. Nagase, *Organometallics*, **26**, 469-471 (2007). 12. "Effects of Bulky Substituent Groups on the Si-Si Triple Bonding in RSi≡SiR and the Short Ga-Ga Distance in Na_2[RGaGaR]. A Theoretical Study" N. Takagi, and S. Nagase, *J. Organomet. Chem.* **692**, 217-224 (2007).
【学術関係の受賞など】	2002年-2005年　日本学術振興会　特別研究員(PD)

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【研究分野】	Computational Chemistry
【現在の研究課題】	Electronic Structure of Inverted Sandwich Type Complexes
【研究内容キーワード】	Electronic Structure of Metal Complex, Multireference Theory
【学歴】	March 2005, Master of Sci., Graduate School of Science, Kyushu University March 2009, Doctor of Sci., Graduate School of Science, Kyushu University
【学位】	Doctor of Science from Kyushu University
【略歴】	Apr. 2009, Postdoctoral Fellow, Kyushu University
【所属学会】	Japan Society for Molecular Science
【主な著書、学術論文】 （過去 5 年以内）	1. K. Sakota, Y. Komoto, M. Nakagaki, W. Ishikawa, H. Sekiya “Observ- ation of a catalytic proton/hydrogen atom relay in microsolvated 7-azaindole-methanol cluster enhanced by a cooperative motion of the hydrogen-bonded network” *Chem. Phys. Lett.* **435**, 1-4 (2007) 2. X. Zhang, Y. Komoto, K. Sakota, M. Nakagaki, H. Nakano, T. Shinmyozu, H. Sekiya “Heavy mass effect on excited-state double-proton transfer in 7-azaindole dimer by Cl substitution” *Chem. Phys. Lett.* **441**, 176-180 (2007) 3. X. Zhang, Y. Komoto, K. Sakota, N. Masayuki, T. Shinmyozu, S. Nanbu, H. Nakano, H. Sekiya “Remarkable suppression of the excited-state double-proton transfer in the 7-azaindole dimer due to substitution of the dimethylamino group studied by electronic spectroscopy in the gas phase” *Chem. Phys. Lett.* **443**, 194-198 (2007)

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【研究内容キーワード】	NMR, DFT, Douglas–Kroll–Hess method, Transition metal complexes
【学歴】	March 2006, Master of Sci., Graduate School of Science, Tokyo Metropolitan University March 2009, Doctor of Sci., Graduate School of Science and Engineering, Tokyo Metropolitan University
【学位】	Doctor of Science from Tokyo Metropolitan University
【略歴】	Apr. 2009, Postdoctoral Fellow, Kyushu University Jan. 2010, Postdoctoral Fellow, RIKEN Apr. 2011, (SPR) Fellow, Kyoto University
【主な著書、学術論文】（過去 5 年以内）	1. T. Yoshizawa and M. Hada, “Calculations of Frequency-Dependent Molecular Magnetizabilities with Quasi-Relativistic Time-Dependent Generalized Unrestricted Hartree-Fock Method”, *J. Comput. Chem.* **28**, 740–747, (2007) 2. T. Yoshizawa and M. Hada, “Relativistic quantum-chemical calculations of magnetizabilities of noble gas atoms using the Douglas–Kroll–Hess method”, *Chem. Phys. Lett.* **458**, 223–226, (2008) 3. T. Yoshizawa and M. Hada, “Relativistic and Electron–Correlation Effects on Magnetizabilities Investigated by the Douglas–Kroll–Hess Method and the Second-Order Møller–Plesset Perturbation Theory”, *J. Comput. Chem.* **30**, 2550–2566, (2009) 4. T. Yoshizawa and T. Nakajima, “Second-order generalized unrestricted Moller–Plesset perturbation theory for the spin–orbit part of zero-field splitting tensors”, *Chem. Phys. Lett.* **515**, 296–301, (2011) 5. T. Yoshizawa and T. Nakajima, “A new computational scheme for the spin–orbit part of zero-field splitting tensor” *Chem. Phys. Lett.* **549**, 108–112, (2012) 6. T. Yoshizawa and S. Sakaki, “NMR shielding constants of CuX, AgX, and AuX (X = F, Cl, Br, and I) investigated by density functional theory based on the Douglas–Kroll–Hess Hamiltonian” *J. Comput. Chem.* **34**, 1013–1023, (2013)
【学術関係の受賞など】	JSPS Research Fellowships for Young Scientists(DC) 2007-2009

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【研究内容キーワード】	Decarboxylaton, Cycloaddition, Charge Transfer, Nickel
【学歴】	June 2008, Faculty of Chemistry, Northeast Normal University, P.R. China
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【所属学会】	Chinese Chemical Society membership
【主な著書、学術論文】（過去 5 年以内）	1. Guan, W.; Yamabe, S.; Sakaki, S. *Dalton Trans*. **2013**, *42*, 8717−8728. 2. Yamabe, S.; Guan, W.; Sakaki, S. *J. Org. Chem*. **2013**, *78*, 2527−2533. 3. Yamabe, S.; Guan, W.; Sakaki, S. *Beilstein J. Org. Chem*. **2013**, *9*, 185–196. 4. Yamabe, S.; Guan, W.; Sakaki, S. *Org. Biomol. Chem*. **2012**, *10*, 8007−8015. 5. Guan, W.; Wu, Z. J.; Su, Z. M. *Dalton Trans*. **2012**, *41*, 2798−2803.
【学術関係の受賞など】	China Postdoctoral Science Special Foundation 2010-2011

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【研究分野】	Computational Chemistry
【現在の研究課題】	Electronic Structure of Transition Metal Dioxygen Complex
【研究内容キーワード】	Electronic Structure of Transition Metal and Lanthanide Complexes
【学歴】	June 2012, College of Chemistry, Beijing Normal University
【学位】	Doctor of Physical Chemistry from Beijing Normal University
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【主な著書、学術論文】（過去 5 年以内）	1. Chen, Yue; Liu, Shubin; Lei, Ming "Nature of Asynchronous Hydrogen Transfer in Ketone Hydrogenation Catalyzed by Ru Complex" *J. Phys. Chem. C*, **112**, 13524-13527 (2008) 2. Chen, Yue; Tang, Yanhui; Lei, Ming "A comparative study on the hydrogenation of ketones catalyzed by diphosphine-diamine transition metal complexes using DFT method" *Dalton Trans.*, 2359-2364 (2009) 3. Chen, Yue; Tang, Yanhui; Liu, Shubin; Lei, Ming; Fang, Weihai "Mechanism and Influence of Acid in Hydrogenation of Ketones by η^{6}-Arene/N-Tosylethylenediamine Ruthenium(II)" *Organometallics*, **28**, 2078-2084 (2009) 4. Chen, Yue; Fang, Wei-Hai "Mechanism for the Light-Induced O_2 Evolution from H_2O Promoted by Ru(II) PNN Complex: A DFT Study" *J. Phys. Chem. A*, **114**, 10334-10338 (2010) 5. Yue Chen, Juan Han, Wei-Hai Fang "Mechanism of Water Oxidation to Molecular Oxygen with Osmocene as Photocatalyst: A Theoretical Study" *Inorg. Chem.*, **51**, 4938–4946 (2012) 6. Juan Han, Xuebo Chen, Lin Shen, Yue Chen, Weihai Fang, Haobin Wang "Energy Transfer Tunes Phosphorescent color if single-Dopant White OLED" *Chem. -Eur. J.*, **17**, 13971-13977 (2011)

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【現在の研究課題】	Organometallic reactions
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【主な著書、学術論文】 （過去 5 年以内）	1. Suresh, C. H.; Sayyed, F. B. “Resonance Enhancement via Imidazole Substitution Predicts New Cation Receptors”. *J. Phys. Chem. A, 2013* (accepted for publication). 2. Sayyed, F. B.; Suresh, C. H. “Accurate Prediction of Cation-π Interaction Energy Using Substituent Effects”. *J. Phys. Chem. A 2012*, **116**, 5723–5732. 3. Sayyed, F. B.; Suresh, C. H. “Quantitative Assessment of Substituent Effects on Cation-π Interactions Using Molecular Electrostatic Potential Topography”. *J. Phys. Chem. A 2011*, **115**, 9300–9307. 4. Sayyed, F. B.; Suresh, C. H. “Substituent Effects in Cation-π Interactions: A Unified View from Inductive, Resonance, and Through-Space Effects”. *J. Phys. Chem. A 2011*, **115**, 5660–5664. 5. Sayyed, F. B.; Suresh, C. H.; Gadre, S. R. “Appraisal of Through-Bond and Through-Space Substituent Effects via Molecular Electrostatic Potential Topography”. *J. Phys. Chem. A 2010*, **114**, 12330–12333.

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【現在の研究課題】	酸化還元電位の計算
【研究内容キーワード】	酸化還元電位・溶媒和モデル・金属クラスター
【学歴】	2009年3月 東京大学大学院工学系研究科応用化学専攻博士課程修了
【学位】	2009年 工学博士 (東京大学)
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【所属学会】	日本化学会、日本分子科学会
【主な著書、学術論文】（過去 5 年以内）	1. T. Matsui, Y. Kitagawa, M. Okumura, Y. Shigeta and S. Sakaki, "Consistent Scheme for Computing Standard Hydrogen Electrode and Redox Potentials", *Journal of Computational Chemistry*, **34**, p. 21-26 (2013). 2. T. Matsui, T. Baba, K. Kamiya and Y. Shigeta, “An accurate density functional theory based estimation of pK_a values of polar residues combined with experimental data: from amino acids to minimal proteins”, *Physical Chemistry Chemical Physics*, **14**, p. 4181-4187 (2012). 3. T. Matsui, H. Miyachi, T. Baba and Y. Shigeta, “A Theoretical Study on Reaction Scheme of Silver (I) Containing 5-Substituted Uracils Bridge Formation”, *The Journal of Physical Chemistry A*, **115**, p.8504-8510 (2011). 4. Y. Nakanishi, T. Matsui, Y. Kitagawa, Y. Shigeta, T. Saito, Y. Kataoka, T. Kawakami, M. Okumura and K. Yamaguchi, “Electron Conductivity in Modified Models of Artificial Metal-DNA Using Green's Function-Based Scattering Theory”, *Bulletin of Chemical Society of Japan*, **84**, p.366-375 (2011). 5. T. Matsui, A. Oshiyama and Y. Shigeta, “A Simple Scheme for pK_a of 5-substituted Uracils” *Chemical Physics Letters*, **502**, p.238-242 (2011). 6. Y. Nakanishi, T. Matsui, Y. Shigeta, Y. Kitagawa, T. Saito, Y. Kataoka, T. Kawakami, M. Okumura and K. Yamaguchi, “Sequence dependent proton-transfer reaction in stacked GC pair III: The Influence of Proton Transfer to Conductivity“, *International Journal of Quantum Chemistry*, **110**, p. 2221-2230 (2010). 7. K. Kamiya, T. Matsui, T. Sugimura and Y. Shigeta, “Theoretical Insight into Stereoselective Reaction Mechanisms of 2,4-Pentanediol-Tethered Ketene-Olefin [2+2] Cycloaddition”, *The Journal of Physical Chemistry A*, **116**, p.1168-1175 (2012). 8. T. Matsui, H. Miyachi, Y. Shigeta and K. Hirao (2012) “Metal-Assisted Proton Transfer in Guanine-Cytosine Pair: An Approach from Quantum Chemistry”, in Some Applications of Quantum Mechanics, ISBN 978-953-51-0059-1, edited by Mohammad Reza Pahlavani, InTech, p. 167-188.
【学術関係の受賞など】	日本学術振興会 特別研究員 (DC2) 2008-2010, 日本学術振興会 特別研究員 (PD) 2011-2013, 日本化学会第93春季年会　優秀講演賞(学術)

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【現在の研究課題】	革命的ハイパフォーマンス・コンピューティング・インフラ (HPCI) の構築
【研究内容キーワード】	電子移動、励起エネルギー移動、蛋白質科学、自由エネルギー計算
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【略歴】	2002年3月　デューク大学化学科 ポスドク 2005年9月　ジョージア工科大学化学生化学科 ポスドク 2006年11月　京都大学福井謙一記念研究センター JSTフェロー 2010年4月　京都大学工学研究科合成・生物専攻 特定研究員 2011年10月　自然科学研究機構分子科学研究所 専門研究職員 2012年4月　自然科学研究機構分子科学研究所 特任研究員
【所属学会】	American Physical Society、日本生物物理学会
【主な著書、学術論文】（過去 5 年以内）	1. T. Kawatsu, “Review: Pathway analysis for peptide-mediated electronic coupling in the super-exchange mechanism of ET and EET,” *Pep. Sci.* **2013**, *100*, 100-113. 2. T. Kawatsu, J. Hasegawa, “Sequentially Coupled Hole–Electron Transfer Pathways for Bridge-Mediated Triplet Excitation Energy Transfer,” *J. Phys. Chem. C* **2012**, *116*, 23252–23256. 3. T. Kawatsu, J. Hasegawa, K. Matsuda, “Singlet Excitation Energy Transfer Mediated by Local Exciton Bridges,” *J. Phys. Chem. C* **2012**, *116*, 13865-13876. 4. T. Kawatsu, J. Hasegawa, “Excitation energy transfer in GFP-X-CFP model peptides (X = amino acids): Direct Versus through-bridge energy transfers,” *Int. J. Quantum Chem.* **2013**, *113*, 563-568 . 5. T. Kawatsu, J. Hasegawa, K. Matsuda, “Bridge-mediated excitation energy transfer pathways through protein media: a Slater determinant-based electronic coupling calculation combined with localized molecular orbitals,” *J. Phys. Chem. A* **2011**, *115*, 10814-10822. 6. J. Hasegawa, T. Kawatsu, K. Toyota, K. Matsuda, “Chemical-intuition based LMO transformation simplifies excited-state wave functions of peptides,” *Chem. Phys. Lett.* **2011**, *508*, 171-176. 7. T. Kawatsu, M. Lundberg, K. Morokuma, “Protein free energy corrections in ONIOM QM:MM modeling: A case study for isopenicillin N synthesis (IPNS),” *J. Chem. Theory Comput.* **2011**, *7*, 390-401. 8. M. Lundberg, T. Kawatsu, T. Vreven, M. J. Frisch and K. Morokuma, “Transition states in the protein environment – ONIOM QM:MM modeling of isopenicillin N synthesis,” *J. Chem. Theory Comput.* **2009**, *5*, 222-234.

Ⅲ　研究広報活動

１．福井謙一記念研究センターシンポジウム

第 10 回京都大学福井謙一記念研究センターシンポジウム

日　　時　2012 年（平成 24 年）11 月 30 日

場　　所　京都大学福井謙一記念研究センター（3F　大会議室）

講　　演　Weston T. Borden (University of North Texas)
“Why Does Cyclobutane-1,2,3,4-tetraone
Have a Triplet Ground State？”
10:15―11:15

赤木　和夫（京都大学工学研究科 教授）
「不斉液晶反応場での高分子合成：
ヘリカル共役ポリマーのらせん制御と形態保持炭素化 」
11:30―12:30

榊　茂好（京都大学福井謙一記念研究センター リサーチリーダー）
「金属錯体の分子物性と反応：電子状態に基づく微視的理解」　14:00―15:00

ポスターセッション　15:15―17:15

― コーヒーブレイク ―

懇親会（１F 多目的ルーム）　17:30―19:00

２．センターセミナー

第 10 回福井センターセミナー

日　　時　2012 年（平成 24 年）3 月 1 6 日　14:30－17:30

場　　所　京都大学福井謙一記念研究センター（3F　大会議室）

14:30～14:35　Opening by Professor Shigeyoshi Sakaki
(Fukui Institute for Fundamental Chemistry)

14:35～15:30　Assistant Professor Satoshi Maeda (Hokkaido Univ.)
"Development and Applications of Automated Reaction Path Search Methods: The Global Reaction Route Mapping (GRRM) Strategy"

15:30 ～16:00　Dr. Miho Hatanaka　(Fukui Institute for Fundamental Chemistry)
"Mechanism of Mukaiyama Aldol Reaction Catalyzed by Water-Tolerant Lanthanide Lewis Acid - An Artificial Force Induced Reaction Study"

Break

16:15～17:30　Professor Pradipta Bandyopadhyay　(Jawaharlal Nehru Univ. India)
"New Development in Monte Carlo Based Methods: Large Water Cluster Optimization and Efficient Sampling"

３．国際交流

当センター国際連携強化プロジェクトの一環として、教員が海外の研究機関を訪問し、研究所の運営に関して意見交換を行った。（資料編 6 を参照）

４．アウトリーチ活動

高等学校への出張講義

（1）畑中美穂 特定研究員
兵庫県立北摂三田高等学校　2012 年（平成 24 年）9 月 13 日
京都府立宮津高等学校　2012 年（平成 24 年）11 月 5 日

タイトル「コンピュータで見る化学反応の世界」

(2) 榊 茂好リサーチリーダー
京都府立南陽高等学校　2012 年(平成 24 年) 11 月 8 日
タイトル「理論化学、計算化学の面白さ」

(3) 諸熊　奎治シニアリサーチフェロー
京都府立洛北高等学校　2012 年(平成 24 年) 11 月 16 日
タイトル「コンピュータで化学反応の世界を探る」

5．栄　誉

諸熊　奎治シニアリサーチフェローは、複雑分子系の理論研究の発展に多大な貢献をしたとして、平成 24 年 11 月 5 日に文化功労者の顕彰を受けた。
（資料編８を参照）

Ⅳ　研究業績

１．専任教員

長谷川　淳也

総合研究部門　准教授
（平成 24 年 9 月 30 日まで）

1. 今年度の研究の要約

生体関連分子の励起状態と機能に関する理論的研究

【始めに】 これまで、アミノ酸などの周辺環境（以下、溶媒と呼ぶ）に応じて光吸収・発光エネルギーを大きく変化させる光機能性蛋白質について、理論化学計算を用いてメカニズムを解析してきた。色素や発色団を取り囲む溶媒分子の電子状態との相互作用、即ち量子化学的相互作用が、励起状態の準位に無視できない影響を与えることを見出している。溶媒との協同効果による化学現象の制御は、化学における基本的かつ重要なテーマであり、これを記述する理論化学を発展させる必要がある。我々は、励起状態における分子間相互作用の起源を解析するために、分子軌道の局在化手法を提案している。今年度は、局在化分子軌道を用いた解析を行い、エネルギー準位に大きな変化を与える幾つかのレチナール蛋白質における特異的な分子間相互作用を見出した。更には、溶媒効果を定量的に記述できる波動関数の構造についても明らかにした。

また、励起エネルギーのトンネル移動経路の解析を行っており、特にブリッジを経由して起きる励起エネルギー移動について、様々なブリッジを用いてトンネル確率の大きさを決定する要因を求めた。更に、一重項移動と三重項移動のトンネル移動経路の差異を理論的に明らかにした。

【光機能性蛋白質の励起状態と分子間相互作用】 周辺環境に応じて分子の励起エネルギー準位が変化する現象はソルバトクロミズムとして良く研究されてきた。我々はレチナール蛋白質、蛍光蛋白質、蛍ルシフェリンなどの光機能性蛋白質におけるカラー・チューニングの起源について、QM(SAC-CI)/MM(AMBER)計算に基づく研究を行い、周辺環境の静電ポテンシャルが重要な役割を果たすことを明らかにしたが、他方で、周辺環境の電子状態が無視できない影響を与えることも見出している。バクテリオロドプシン(bR)及びメタノール溶液中におけるレチナール色素の第一励起状態について、約 6 Å 程度の距離にあるアミノ酸までを考慮した励起状態計算を行うと、周辺環境を点電荷モデルで記述した結果と比較して、bR では約 0.3 eV、MeOH では約 0.1 eV 励起エネルギーが減少する。この差 0.2 eV は、ソルバトクロミズムの物理化学的原理を議論する上では無視できない寄与を与える。

我々は周辺環境の電子状態に由来する効果を解析するために局在化分子軌道を計算する手法を提案した。一電子軌道をフラグメント（アミノ酸残基やペプチド結合）へと帰属できるので、励起状態の波動関数の解析が明確になった。本研究の目的は、同局在化軌道を用いた解析を行い、凝集系における分子の励起状態の波動関数の構造を明らかにすることである。

周辺環境の効果が最も顕著であった bR について、局在化軌道を用いた解析結果について説明する。図 1 には第一励起状態の主配置に関与する分子軌道の一部を示す。最も主要な配置はレチナール色素の HOMO（図 1a）から LUMO（図 1b）への一電子遷移であり、これに Tyr185 の HOMO（図 1c）

からレチナールの LUMO への CT 遷移が副配置として混合することが明らかになった。この結果は、レチナールの HOMO が Tyr の HOMO と相互作用し、非局在化することにより励起エネルギーが低下したことを意味する。

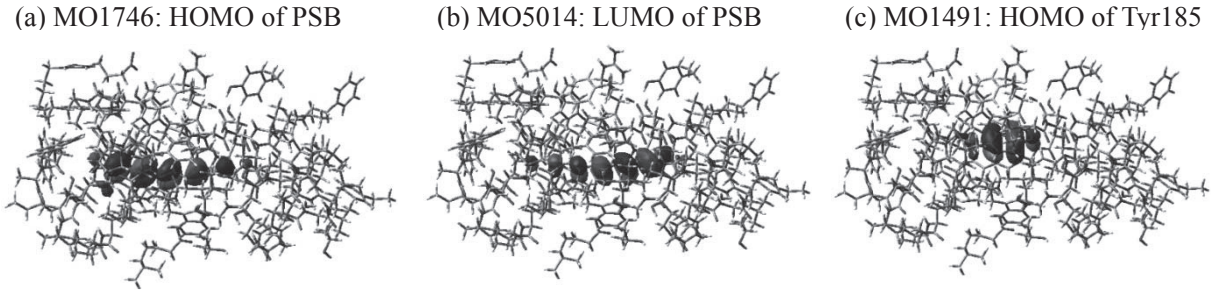

図 1. bR の第一励起状態の波動関数に関与する局在化分子軌道。(a)Protonated retinal Schiff base (PSB)の HOMO 及び (b) LUMO。(c) Tyr185 の HOMO。

各フラグメントにおいて最大の CI 係数を抽出した。結果を図 2 に示す。bR では主配置である PSB における励起に加えて、Tyr185 から PSB への CT（及び逆 CT）励起、Tyr185 における局所励起が比較的大きな係数を持っている。他方で、MeOH 溶液中の場合は、レチナールから溶媒分子への CT 励起が見られるが、bR ほど顕著な寄与が無いことが特徴的である。また、図 2a と 2b では、電子励起の寄与がレチナールから溶媒分子への CT 励起、その逆の CT 励起、エキシトン励起を表わす３つの直線上に偏って分布することが明確に分かる。この状況は他の系でも共通であり、周辺環境の励起波動関数の構造を示唆している。

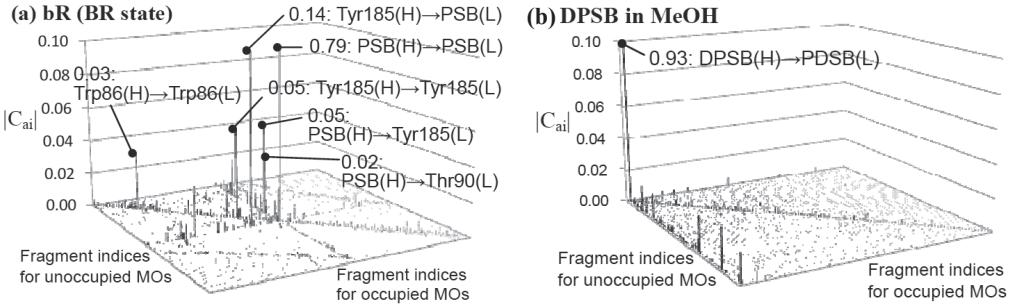

図 2.　(a)bR 及び(b)MeOH 中のレチナール色素について、第一励起状態の波動関数をアミノ酸残基毎に分類し、最大の係数をプロットした。

図 3 には、各フラグメントについて励起波動関数のノルムを計算し、PSB からの距離に関して、プロットしたものを示す。bR において、距離約 4 Å 程度の第一溶媒和圏では CT 等の効果が顕著に見られ、軌道間相互作用の重要さが示唆された。それを超える領域では CT の寄与は減衰し、エキシトンの寄与が相対的に重要になる。遷移双極子モーメント間相互作用の長距離性が反映していると考えられる。

更に、励起エネルギーの分割解析を行った。結果は波動関数の解析の時と同様であり、色素ーアミノ酸の CT 励起と局所励起が重要であり、アミノ酸間 CT の寄与は無視できる程度であった。また、Tyr185

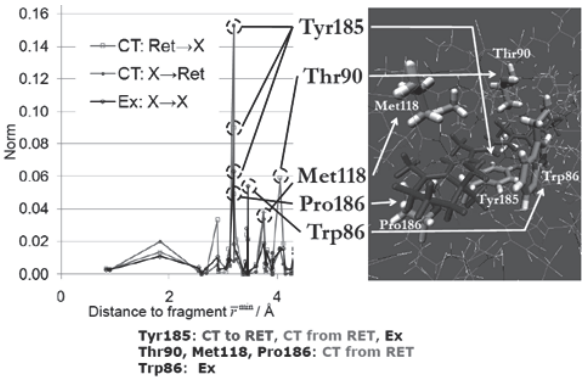

図 3. 各フラグメントの局所励起配置、色素との CT 励起配置のノルムを、フラグメント―色素間距離についてプロットした。（右）第一溶媒和圏において主要な寄与を与えるフラグメント。

が主要な寄与をすることも確認することができた。

【ソルバトクロミズムの起源を考慮するための AO 駆動CIプログラムの開発】 周辺環境の溶媒効果を考慮するために必要な波動関数の構造について、上述のように解析を行った。本研究では、新たに、水溶液中における s-trans-acrolein の n-π*励起状態と π-π*励起状態についても同様の解析を行った。気相中の実験結果と比較すると、水溶液中では n-π*励起で 0.3 eV の青方シフト、π-π*励起で 0.5 eV もの赤方シフトを示す。解析の結果、これまでの研究で得られた蛋白質中や溶液中のレチナール色素での結果と同様に、周辺環境－色素間の CT 励起配置と周辺環境における局所励起配置が波動関数に寄与している。前者は色素波動関数が近傍のアミノ酸の領域へと非局在化する効果であり、後者は周辺環境の波動関数の分極効果を表している。また、周辺のアミノ酸間の CT 励起配置の寄与は非常に小さいことが明らかになった。ONIOM 法を用いて、SAC-CI 法により計算した s-trans-acrolein の励起エネルギーに CIS 法による環境効果を補正したところ、n-π*、π-π*ともスペクトルシフトに関する実験結果を良好に再現した。

次に、このような構造を持つ波動関数がソルバトクロミックシフトを再現できることを確認する必要がある。そこで、本研究では AO 駆動 CI プログラムを開発した。周辺環境を含んだ励起状態の波動関数における電子励起を制限し、算出される励起エネルギーへの影響を検討した。周辺のアミノ酸間の CT 励起配置は、数において全波動関数の大部分を占めるにも関わらず、0.02 eV 程度の誤差しか与えない。局在化軌道を用いた結果、アミノ酸間 CT 励起が数値的な意味で first-order interacting space から外れたことを示している。

【ブリッジを経由する三重項励起エネルギー移動の電子的メカニズム】 三重項励起状態におけるエネルギー移動は、光合成系における余剰エネルギーを散逸するための経路や、光力学療法における一重項酸素生成過程に含まれる。エキシトン・カップリングにより駆動される一重項励起エネルギー移動とは異なり、Dexter 機構で示されたように、三重項励起エネルギー移動においては交換相互作用により駆動されると考えられている。従って、三重項励起エネルギー移動では、ブリッジの電子状態の寄与によりドナー(D)とアクセプター(A)の電子的カップリング(H_{DA})が増大するものと期待される。

本研究では、三重項エネルギー移動のトンネル経路を明らかにするために、局在化分子軌道を用いた解析手法を開発した。これを応用することより、三重項の場合のエネルギー移動経路の特徴を一重項の場合との比較の観点から明らかにした。

前述したように、ブリッジを経由する一重項励起エネルギー移動は、Förster 型の相互作用が主要であるため、D-A 間の直接移動やブリッジ状態を一つ経由する移動経路が主要であった (図 4a)。つまり、hole と electron 対が同時に移動する。これに対して三重項の場合では、Förster 型の相互作用が小さくなるため、複数のブリッジ状態を経由する super-exchange 機構が主要となることが分かった。これは行列要素の表式

$$\left\langle \Phi_i^a \middle| \hat{H} \middle| \Phi_j^b \right\rangle = \delta_{i,j} F_{a,b} - \delta_{a,b} F_{i,j} + (ia|jb) - (ab|ij)$$

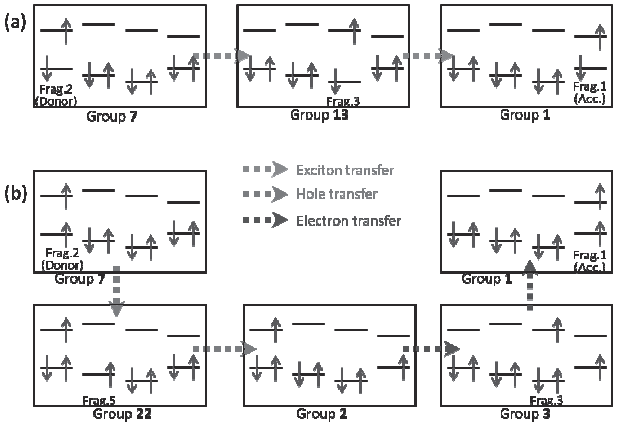

図 4. 励起エネルギー移動におけるトンネル経路の概念図。(a) 一重項において主要であるエキシトン経由機構。(b) ホールと電子移動が逐次的にカップルする三重項励起エネルギー移動(CHET 機構)。

において、軌道 i と a のスピンが異なるため、(ia|jb)=0 となるからである。図 6b に示したように、三重項移動において特徴的であるのは、ホール移動と電子移動が逐次的に起きる点である。これは、上式において a=b や i=j のときに(ab|ij)の値が増大するからである。我々はこのメカニズムを、sequentially coupled hole and electron transfer (CHET) 機構として提案した。電子移動やホール移動との関連性から、分子軌道を用いて三重項励起エネルギー移動を制御できる可能性がある。

論文

(1) J. Hasegawa,
"Fragment-Based Configuration Interaction Wave Function to Calculate Environmental Effect on Excited States in Proteins and Solutions"
Chem. Phys. Lett. 571(*), 77-81 (2013).

(2) S. Nishizawa, J. Hasegawa, K. Matsuda,
"Theoretical Investigation of the β Value of the Phenylene and Phenylene Ethynylene Units by Evaluating Exchange Interaction between Organic Radicals"
Chem. Phys. Lett. 555(*), 187-190 (2013).

(3) T. Kawatsu and J. Hasegawa,
"Excitation Energy Transfer in GFP-X-CFP Model Peptides (X=amino acids): direct vs. through-bridge energy transfers"
Intern. J. Quantum. Chem. 113(4), 563-568 (2013).

(4) T. Kawatsu and J. Hasegawa,
"Sequentially Coupled Hole-Electron Transfer Pathways for Bridge-Mediated Triplet Excitation Energy Transfer"
J. Phys. Chem. C 116(44), 23252-23256 (2012).

(5) J. Hasegawa, K. J. Fujimoto, and T. Kawatsu
"A Configuration Interaction Picture for a Molecular Environment Using Localized Molecular Orbitals: The Excited States of Retinal Proteins"
J. Chem. Theo. Comp. 8(11), 4452-4461 (2012).

(6) T. Kawatsu, K. Matsuda, and J. Hasegawa
"Singlet Excitation Energy Transfer Mediated by Local Exciton Bridges"
J. Phys. Chem. C 116(26), 13865-13876 (2012).

(7) J. Hasegawa, K. Fujimoto, and H. Nakatsuji
"Color tuning in human cone visual pigments: the role of the protein environment"
Progress in Theoretical Chemistry and Physics 26, 489-502 (2012).

(8) T. Sakano, J. Hasegawa, K. Higashiguchi, and K. Matsuda,
"Chronological Change from Face-On to Edge-On Ordering of Zinc Tetraphenylporphyrin at Phenyloctane-HOPG Interface"

Chem. Asian J. 7(2), 394-399 (2012).

(9) Y. Yamamoto, J. Hasegawa, and Y. Ito,
"Kinetic investigation on carbamate formation from the reaction of carbon dioxide with amino acids in homogeneous aqueous solution"
J. Phys. Org. Chem. 25(3), 239-247 (2012).

2. 学会発表

(1) J. Hasegawa,
"Computational Chemistry for Complex Systems: Environmental Effect in Proteins and Solutions"
The Fourth Joint Symposium of PCOSS-CRC, Hokkaido University, 2013.5.9

(2) J. Hasegawa
"Theoretical Study on the Color Tuning Mechanism of Photo-functional Proteins: Excited States and Molecular interactions"
2012 HU - NU - SNU - NIMS/MANA Joint Symposium, "Challenges in Advanced Chemistry of Asia", Hokkaido University, 2012.12.6-7

(3) J. Hasegawa
"Configuration Interaction in Quantum Chemistry"
MAterial Simulation in Petaflops era (MASP2012), Institute for Solid State Physics, Univ. Tokyo, 2012.6.25

(4) J. Hasegawa
"Color-tuning in Photo-functional Proteins: Electronic Structure and Interactions"
The 17-th International Symposium on Bioluminescence and Chemiluminescence, Guelph, Canada, 2012.5.28-6.2

(5) 長谷川淳也
「視物質・蛍光蛋白質におけるカラーチューニング：分子間相互作用の理論解析」
岡山（岡山大学）　2013/3/15

(6) 長谷川淳也
「光機能性生体分子の励起状態に関する量子化学」
第2回量子化学ウインタースクール～基礎理論と生体系の理論～TCCIウインターカレッジ：量子化学　岡崎（分子科学研究所）　2012/12/17-18

(7) 長谷川淳也
"Excited states and molecular interactions in photo-functional proteins"
シンポジウム"Photochemistry of Supra Functional Molecular Systems"光化学討論会　東京（東京工業大学）2012/9/12-14

中尾 嘉秀

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1. 今年度の研究の要約

今年度は遷移金属元素を含んだ機能性金属錯体の物性と梯子型π共役分子の固体中の光物性について研究を行った。

【始めに】

遷移金属元素を含んだ金属錯体は様々な配位子との組み合わせで、多様な構造や電子状態をとることができ、様々な機能が発現することがある。高スピン状態を保つ錯体は記憶素子に、発光性錯体は発光素子などに応用できる可能性がある。これらの機能が発現する仕組みを理解することは機能性金属錯体の制御や設計に繋がるため、機能の発現機構の理論的解明が求められている。今年度はシアノ架橋した1次元多核金属錯体の磁気異方性と多核金属錯体の固体中の発光を量子化学計算により明らかにした。

【シアノ架橋した1次元多核金属錯体の磁気異方性に関する研究】

1 次元鎖錯体は金属中心のスピン同士の強磁性的な相互作用により、大きなスピン角運動量を持つ可能性がありメモリなどへの応用が期待されている。Figure 1 に示したシアノ架橋1次元鎖錯体 {$ReCl_4(CN)M(DMF)_4(NC)$} (M = Mn(**1**), Fe(**2**), Co(**3**)) は遷移金属の種類に依存して磁気的性質が大きく異なり、Fe 錯体では低温で磁気ヒステリシスを示す[1]。本研究では磁気的な性質の予測を目指し、1 次元鎖錯体を構成する単一ユニットの磁気異方性の原因を明らかにすることを目的とした。

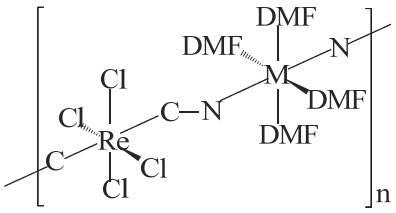


Figure 1. 1 次元鎖錯体

X 線解析から1次元鎖錯体は対称中心を持っており、配位子の配向の異なる2種類の構造があることが分かっている。1 次元鎖錯体から金属二核部分を抜き出した計算モデル[$(NC)ReCl_4(CN)M(DMF)_4(NC)$]を用いて理論計算を行った。2つの構造(**A**、**B**)の初期構造として X 線解析の構造を用いて、水素原子の位置のみを構造最適化した。遷移金属の基底関数には Christiansen による基底関数と ECP、その他の原子には cc-pVDZ を用いた。スピン結合定数 J 値の計算は DFT(B3LYP)法、CASSCF 法と MCQDPT 法で行った。スピン軌道相互作用(SOC)と外部磁場の効果を考慮した計算も行い、磁気異方性を予測した。全ての計算は Gaussian 09 と GAMESS を使用した。

Table 1 に各錯体の J 値を示した。DFT 法では Mn 錯体の J 値は実験結果と良い一致を示した。しかし、Fe 錯体に関しては実験値の 1/7 程度の値しか示さず、Co 錯体に関しては 2 つの構造で異なる磁性を示した。また、CASSCF 法と MCQDPT 法では実験値を再現しなかった。擬縮退状態を持つ Fe 錯体と Co 錯体に対して、CASSCF 波動関数を用いてスピン-軌道相互作用(SOC)と磁場の効果を加味した計算を行った。Fe 錯体の **A** 構造(**2A**)の外部磁場 0.1T 下での温度磁化率曲線は Figure 2

に示す結果となった。**2A** はシアノ配位子方向である y 軸から磁場を印加した時に y 軸方向のスピン角運動量期待値を持つ電子状態が安定化されることで、低温で温度磁化率曲線が上昇することが分かった。逆に、**2B**, **3A**, **3B** は DMF 配位子から磁場を印加した時に低温で温度磁化率曲線が上昇することが分かった。磁気異方性の原因となる電子状態を調べたところ、擬縮退状態間の相互作用から予想される磁気異方性の方向と、温度磁化率曲線の上昇をもたらす磁場の印加方向はほとんど一致した。従って、CASSCF 法の結果を解析することで、磁気異方性の方向をあらかじめ予測することができることが本研究によって明らかになった。

Table 1. スピン結合定数 J(cm^{-1})

		DFT法	CASSCF法	MCQDPT法	実験値[1]
Mn錯体	**1A**	-5.52	-0.46	-1.78	-5.4
	1B	-7.56	-0.59	-2.31	
Fe錯体	**2A**	0.58	-0.17	-0.91	4.8
	2B	0.68	-0.14	-0.87	
Co錯体	**3A**	1.65	0.16	1.05	2.4
	3B	-1.39	0.28	-1.18	

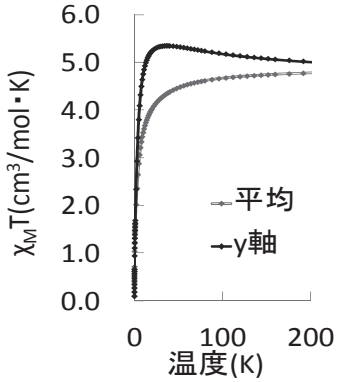
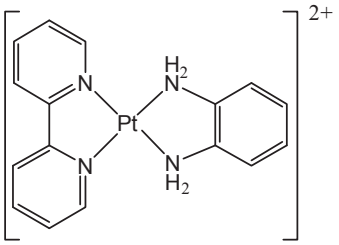


Figure 2. **2A** の磁化率曲線

【白金錯体の固体中の発光に関する研究】

燐光性錯体は量子収率が高いため、発光デバイスへの応用が期待されている。最近、実験で報告された白金(II)錯体は Scheme 1 に示すような構造を持ち、固体中で特異な発光を示す[1]。本研究では、周囲の錯体やカウンターアニオンによる静電場の影響を点電荷と Buckingham ポテンシャルで表現した固体モデルを用いて、気相中及び固体中の励起エネルギーと構造変化について理論的に検討した。



Scheme 1

Pt の基底関数には Christiansen による基底関数と有効内殻ポテンシャル、その他の原子については cc-pVDZ を用いた。BLYP 法、B3LYP 法、B3PW91 法、O3LYP 法、LC-BLYP 法、CAM-B3LYP 法を用いて、Mulliken と自然軌道解析(NAO)と静電ポテンシャル(ESP)フィッティングの 3 つの方法により点電荷を決定した。固体モデルの汎関数と点電荷の依存性を調べるために、中心錯体の点電荷を X 線データ構造で分かっている隣接する錯体やカウンターイオンの位置に配置して、点電荷が自己無撞着するまで繰り返し計算を行った。固体中の基底状態と三重項励起状態の構造を予測するために、固体モデルに Buckingham ポテンシャルも加えて構造最適化した。以上の計算は Gaussian 09 を用いて行った。

系の全エネルギーから点電荷同士の静電エネルギーを引いたものを、固体中の静電場による中心錯体の安定化エネルギーと考えて固体モデルを評価した。個々のモデルでは、点電荷と安定化エネルギーは 5 回程度の繰り返し計算で収束した。固体モデルのサイズによって中心錯体の安定化エネルギーと軌道エネルギー準位は大きく変化し、モデルの選択が重要であることが分かった。次に、汎関数と点電荷の種類に対する依存性を調べる

Table 1. 固体中の錯体の安定化エネルギー(kcal mol^{-1})

計算方法	Mulliken	NAO	ESP
BLYP	567.4	569.8	567.6
B3LYP	568.8	570.6	568.4
CAM-B3LYP	569.0	571.7	568.8

ために、中心錯体 1 分子の周りに 49 個の錯体と 100 個の Cl^-を配置した固体モデルを用いた。Table 1 に示したように、安定化エネルギーの汎関数と点電荷依存性は非常に小さいことが分かった。B3LYP 法と NAO 電荷を用いた固体モデルで最適化した基底状態の安定構造は、Figure 3 に示すように気相中の構造と比較して折れ曲がり、X 線構造と良く一致した。

真空中　　固体モデル

Figure 3. 基底状態の最適化構造

【文献】

[1] Harris, T. D.; Bennett, M.V.; Clérac R.; Long J. R. J. Am. Chem. Soc. 2010, 132, 3980-3988.

[2] K. Umakoshi (private communication).

[3] H. Yamada, C. Xu, A. Wakamiya, S. Yamaguchi, Macromol *Chem. Phys*. **210**, 904-916 (2009).

2. 論文

(1) S. Akatsu, Y. Kanematsu, T. Kurihara, S. Sueyoshi, Y. Arikawa, M. Onishi, S. Ishizaka, N Kitamura, Y. Nakao, S. Sakaki, K. Umakoshi,
"Syntheses and Luminescent Properties of 3,5-Diphenylpyrazolato-Bridged Heteropolynuclear Platinum Complexes. The Influence of Chloride Ligands on the Emission Energy Revealed by the Systematic Replacement of Chloride Ligands by 3,5-Dimethylpyrazolate"
Inorg. Chem. 51, 7977-7992, (2012).

(2) Y. Nakajima, S. Sakaki, Y. Nakao, H. Suzuki,
"Theoretical Study of Dihydrogen Activation by a Trinuclear Ruthenium μ3-Imido Complex"
Organometallics, 31, 5342–5348, (2012).

(3) Y. Hayashi, Y. Matano, K. Suda, Y. Kimura, Y. Nakao, H. Imahori,
"Effects of Carbon–Metal–Carbon Linkages on the Optical, Photophysical, and Electrochemical Properties of Phosphametallacycle-Linked Coplanar Porphyrin Dimers"
Chem. Eur. J. 18, 15972-15983 (2012).

3. 学会発表

(1) 野口純樹、佐藤啓文、中尾嘉秀
「オキサラト架橋した多核金属錯体の磁気異方性に関する理論的研究」
第15回理論化学討論会, 仙台市福祉プラザ, 2012年5月24日～26日, 1C2b

(2) 野口純樹、佐藤啓文、中尾嘉秀
「有機ラジカルを配位子とするCo(II)錯体の磁性に関する理論的研究」
第6回分子科学討論会, 東京大学本郷キャンパス, 2012年9月18日～21日, 2P120

(3) 成田真弘、佐藤啓文、中尾嘉秀

「CPMDを用いた梯子型π共役化合物の発光に関する理論的研究」
第6回分子科学討論会, 東京大学本郷キャンパス, 2012年9月18日～21日, 4P089

(4) 中尾嘉秀、山田哲士、馬越啓介
「ピラゾラト架橋した白金二核金二核錯体の固体中の発光に関する理論的研究」
第62回錯体化学討論会, 富山大学五福キャンパス, 2012年9月21日～23日, 2Ba-01

(5) 野口純樹、中尾嘉秀、佐藤啓文
「Cr(III)、Co(II)のオキサラト架橋錯体の磁気異方性に関する理論的研究」
第62回錯体化学討論会, 富山大学五福キャンパス, 2012年9月21日～23日, 2Ba-07

(6) 中尾嘉秀、竹中裕喜雄、佐藤啓文
「第一原理分子動力学法によるサーモクロミック銅(II)錯体に関する理論的研究」
第62回錯体化学討論会, 富山大学五福キャンパス, 2012年9月21日～23日, 2Ba-08

(7) 枡井基典、佐藤啓文、中尾嘉秀
「第1周期遷移金属からなるシアノ架橋1次元鎖型錯体の磁気的性質に関する理論的研究」
日本化学会第93春季年会, 立命館大学, 2013年3月22日～25日, 1G3-54

(8) 加藤諒佑、佐藤啓文、中尾嘉秀
「燐光性白金(II)錯体の結晶中の発光に関する理論的研究」
日本化学会第93春季年会, 立命館大学, 2013年3月22日～25日, 1G3-55

国際連携研究室　International Relationship Office

特定准教授　石田　俊正　Program-specific Associate Professor　Toshimasa ISHIDA

1. Summary of the research of the year

(1) A Nonadiabatic Ab Initio Dynamics Study on Rhodopsin and its Analog Isorhodopsin

Rhodopsin (Rh) has 11-cis retinal as chromophore and is the photosensitive chemical found on the outer segment of rod-like cells in the retina, the light-sensing structure of the eye. Isorhodopsin (isoRh) is an Rh analogue that contains 9-cis retinal embedded in the same opsin environment. Both are known to yield bathorhodopsin (bathoRh), a photoisomer that contains all-trans retinal, via cis-trans isomerization of the 11 or 9 position upon absorption of a photon. Despite their similarity, the photoisomerization period and quantum yield is largely different. Rhodopsin photoisomerization is experimentally known to be faster (t_{Rh} = 200 fs, t_{isoRh} = 600 fs) and more efficient (quantum yield: Φ_{Rh} = 0.65, Φ_{isoRh} = 0.22). We carried out non-adiabatic ab initio dynamics calculations on the two molecules. We have already reported that the reaction times and quantum yields are qualitatively reproduced.

Rhodopsin is reported to give bathorhodopsin only while isorhodopsin yields a byproduct. The rigorous selectivity in rhodopsin would be another reason why rhodopsin is selected biologically. Comparison with our previous opsin-free investigations reveals that opsin tends to confine the twist of the active dihedral to only one direction and funnels transitions into the vicinity of minimum energy conical intersections (MECI). The twist-confinement totally blocks simultaneous twisting of ϕ9 and ϕ11 (=C10–C11=C12–C13=) and enhance the quantum yields. The opposite rotation of ϕ9 and ϕ11 (‘wring-a-wet-towel’ motion) takes place upon photoexcitation, which also does without opsin. The wring-a-wet-towel motion is dynamically enhanced in comparison with the one expected from locations of the MECI.

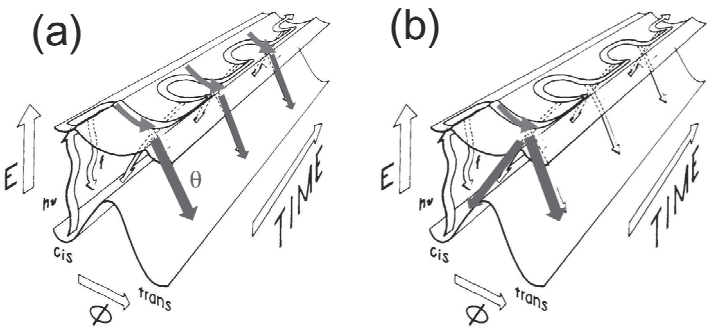


Figure 1 Isomerization schemes in (a) Weiss-Warshel Model and (b) from the analysis of actural trajectories.

Weiss and Warshel proposed a model for cis-trans photoisomerization in 1979. They assumed that a trajectory goes back and forth around the crossing point in the excited state. In their scheme, if the transition takes place when the trajectory goes forth, the product is generated and if it does

when the trajectory go back, the ground state reactant is regenerated. In order to check if their scheme is applicable to the present systems, we counted how many trajectories make turns before transitions for Rh. If their argument is correct, the number of turns should be strongly correlated to the compound generated: if the number of turns is even (odd), it should results in the product (reactant). It is found, however, that the ratio of the generated compounds expected from the number of turns were 58.3%, which means that the correlation is weak because 50% corresponds to no correlation. Moreover, it is found that the transition probability for the first passing over the transition region (corresponding to no turns) is 0.95. Thus, the first access to the crossing point almost determines the fate of the trajectory. Thus, the present simulation reveals that the Weiss-Warshel model for cis-trans photoisomerization is not applicable for rhodopsin because the branching ratio after transition is crucial.

(2) Photochemical dynamics of indolylmaleimide derivatives

On-the-fly nonadiabatic ab initio molecular dynamics simulations have been carried out for three ionic species of indolylmaleimides (3-(1H-3-indolyl)-2,5-dihydro-1H-2,5-pyrroledione, IM) to clarify the mechanisms of photochemical reactions. The results are obtained for (i) a monovalent anion with a deprotonated indole NH group (**IM**$^{-'}$), (ii) a monovalent anion with a deprotonated maleimide NH group (**IM**$^{-''}$) and (iii) a divalent anion with doubly deprotonated indole and the maleimide NH groups (**IM**$^{2-}$). Quantum chemical calculations are treated at the three state averaged complete-active space self-consistent field level for 6 electrons in 5 orbitals with the cc-pVDZ basis set (CAS (6, 5) SCF/cc-pVDZ). Molecular dynamics simulations are performed with electronically nonadiabatic transitions included using the Zhu–Nakamura version of the trajectory surface hopping (ZN-TSH) method. It is found that the nonadiabatic transitions occur accompanied by the stretching and shrinking motions of the N(7)–C(8) bond in the case of **IM**$^{-'}$ and the C(11)–N(12) bond in **IM**$^{2-}$ rather than the twisting motion of the dihedral angle. We also found that the ultrafast $S_2 \rightarrow S_1$ nonadiabatic transitions occur through the conical intersection (CoIn) right after photoexcitation to S_2 in **IM**$^{-'}$ and **IM**$^{2-}$. Furthermore, the $S_1 \rightarrow S_0$ nonadiabatic transitions are found to take place in **IM**$^{-'}$. It is concluded that **IM**$^{2-}$ would mainly contribute to the photoemission, because the $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ transitions of **IM**$^{-''}$ are dipole-forbidden transitions and, moreover, **IM**$^{2-}$ is found to be the only species to stay in the S1 state without non-radiative decay.

(3) A model theoretical study on ligand exchange reactions of CooA

Rr-CooA is a CO-sensor heme protein, where binding of CO with the heme group stimulates a transcriptional activator activity of CooA. In this process, the heme undergoes a series of ligand exchanges. In the ferric form, the heme has Cys75 and Pro2 as the axial ligands. In the reduced ferrous form, the heme has His77 instead of Cys75 as an axial ligand with Pro2. Only in the reduced form, CooA can bind CO that replaces Pro2. Model calculations are carried out to elucidate the ligand exchange reactions of CooA.

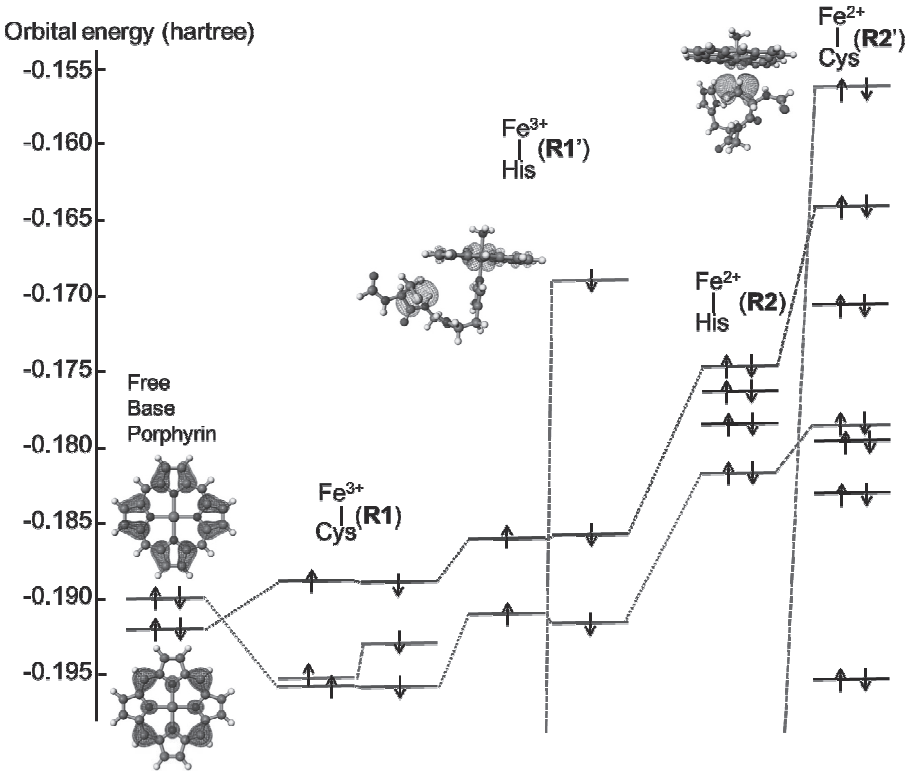


Figure 2 Kohn-Sham orbital energy diagram for free base porphyrin, **R1**, **R1'**, **R2**, and **R2'** in the smaller model of Rr-CooA along with isodensity surface maps[55] for key orbitals. Only occupied orbitals are shown in the diagram. The red horizontal line corresponds to non-bonding orbital localized at the sulfur atom of Cysteine (n(S(Cys)). The blue and light blue lines correspond to highest occupied Kohn-Sham orbital (HOKSO) (a_{1u}) and the next HOKSO (a_{2u}) in the free base porphyrin. The black lines stand for other orbitals. **R1** and **R1'** have α- and β-orbitals with different energies because the species have the open shell. Note that the energies of the α-orbital in **R1'** and doubly-occupied orbital in **R2** are -0.249 and -0.221 hartree, therefore, below the range of energy shown.

We used cluster models that include the center iron and the proximate ligand portions. The whole CooA protein was not dealt with in the present study because the present modeling would give the characteristic of ligand exchange reactions more clearly. Geometry optimization for reactants and products were carried out. We employed the ONIOM (our own N-layered integrated molecular orbital and molecular mechanics) scheme, a quantum mechanics/molecular mechanics (QM/MM) approach, for some computations. For the others, quantum mechanical (QM) computations alone were performed. QM calculations were done at the B3LYP hybrid functional level. We used the B3LYP scheme in the present computation because many calculations have been carried out at this level and accuracy/error at this level has been established. The basis set used is the Hay-Wadt set and the corresponding effective core potential

for iron and the 6-31G(d) basis set for the other elements. For MM calculations, universal force field was employed.

The coordinated proline is found to be the neutral, protonated form. The ligand exchange of cysteine for histidine is reproduced by a relatively small model. This exchange would be mainly due to difference in stability of non-bonding sulfur *p*-orbital in Cys75 between the ferric and ferrous states, which is shown in Figure 2.

The selectivity of gas molecules among CO, NO, and O_2 in the proteins are explained by relative stability of products for Rr-CooA. This is the case also for Ch-CooA, where the amino group of the N-terminus and a histidine are coordinated to the iron ion both in the ferric and ferrous state. The ability to bind the gas molecules is a little stronger in Rr-CooA than in Ch-CooA. In the ferric form of Rr-CooA, heme is deformed to a ruffled from whereas heme is planar in the ferrous form, which leads to red-shifted Q-band in the former.

2. Original papers

(1) Wilfredo Credo Chung, Shinkoh Nanbu, and Toshimasa Ishida
"A QM/MM Trajectory Surface Hopping Approach to Photoisomerization of Rhodopsin and Isorhodopsin. The Origin of Faster and More Efficient Isomerization for Rhodopsin",
J. Phys. Chem. B 2012, 116, 8009−8023.

(2) Tatsuhiro Murakami, Manabu Nakazono, Alexey Kondorskiy, Toshimasa Ishida and Shinkoh Nanbu
"Photochemical dynamics of indolylmaleimide derivatives"
Phys. Chem. Chem. Phys., 2012, 14, 11546–11555

(3) Toshimasa Ishida and Shigetoshi Aono,
"A model theoretical study on ligand exchange reactions of CooA"
Phys. Chem. Chem. Phys. **15**, 6139-6148 (2013).

(4) Jun-ichi Aihara, Masakazu Makino, Toshimasa Ishida, and Jerry R. Dias
Analytical Study of Superaromaticity in Cycloarenes and Related Coronoid Hydrocarbons
J. Phys. Chem. A. in press dx.doi.org/10.1021/jp4016678

3. Presentation at academic conferences

(1) Wilfredo C. Chung、南部 伸孝、石田 俊正
A Nonadiabatic Ab Initio Dynamics Study on Rhodopsin and its Analog Isorhodopsin
第 9 回福井謙一記念研究センターシンポジウム(P42) 2012 年 1 月 6 日 京都

(2) 村上龍大、石田俊正、南部伸孝、

「インドリルマレイミドの光物理過程の非断熱力学」
日本化学会第 92 春季年会　(4A4-01)　2012 年 3 月 28 日　日吉

(3) CHUNG, Wilfredo Credo; ISHIDA, Toshimasa; NANBU, Shinkoh; NAKAMURA, Hiroki,
"A non-adiabatic QM/MM trajectory approach to photoisomerization of rhodopsin and isorhodopsin. The origin of faster and more efficient isomerization in rhodopsin",
28th Symposium on Chemical Kinetics and Dynamics (2E4), Kasuga, Fukuoka, June 7, 2012

(4) KOBAYASHI, Osamu; ISHIDA, Toshimasa; NANBU, Shinkoh,
"Theoretical study of charge transfer and deactivation process of donor-acceptor type thiophene derivatives",
28th Symposium on Chemical Kinetics and Dynamics (2P16), Kasuga, Fukuoka, June 7, 2012

(5) OHTA, Ayumi; ISHIDA, Toshimasa; NANBU, Shinkoh
"Theoretical study of selectivity mechanism on photoisomerization reaction between cyclohexadiene and hexatriene"
28th Symposium on Chemical Kinetics and Dynamics (2P19), Kasuga, Fukuoka, June 7, 2012

(6) Wilfredo Credo Chung, Toshimasa Ishida,Shinkoh Nanbu and Hiroki Nakamura,
"A QM/MM Trajectory Surface Hopping Approach to Photoisomerization of Rhodopsin and Isorhodopsin",
The 14th International Congress of Quantum Chemistry　(ICQC2012)　(I.62), Boulder, Colorado, USA.　Jun. 25-30(2012)

(7) 太田亜由美、石田俊正、南部伸孝、
「シクロヘキサジエン、ヘキサトリエン間の光異性化反応における選択制の理論的研究」
第 6 回分子科学討論会 2012　3P088　東京、2012 年 9 月 20 日

(8) 小林理、赤間知子、石田俊正、南部伸孝
ドナーアクセプター型ポリチオフェン誘導体の電荷移動と失活過程」
第 6 回分子科学討論会 2012　3P111　東京、2012 年 9 月 20 日

(9) Wilfredo Credo Chung, 南部伸孝、石田俊正
「ロドプシンとイソロドプシンの光応答性に関する非断熱 ab initio トラジェクトリ法による理論的研究」
第 6 回分子科学討論会 2012　4A04　東京、2012 年 9 月 21 日

(10) 村上龍大、Kondorskiy　Alexey、石田俊正、南部伸孝
「蛍光性分子の光化学動力学」
第 6 回分子科学討論会 2012　4E16　東京、2012 年 9 月 21 日

(11) 北淑宏、南部伸孝、石田俊正
「緑色蛍光タンパク質の光励起動力学：QM/MM 法による非断熱 ab initio 分子動力学」
第 6 回分子科学討論会 2012　4P124　東京、2012 年 9 月 21 日

(12) Wilfredo Credo Chung, Shinkoh Nanbu, and Toshimasa Ishida,

“A Non-adiabatic Trajectory Approach to Photoisomerization for Rhodopsin and Isorhodopsin. The Origin of Faster and More Efficient Isomerization in Rhodopsin”
Congress on Computational Physics 2012, Kobe, Oct. 15-18, 2012

(13)石田俊正、Wilfredo C. Chung、南部伸孝、青野重利
”Theoretical studies on reactions in biomolecules: photoisomerization of rhodopsins and ligand exchange in CooA”
第１０回福井謙一記念研究センターシンポジウム　2012 年 11 月 30 日　京都

Hidekazu IKENO

Assistant Professor

1. Summary of the research of the year

Systematic *ab-initio* Multiplet Calculations of Transition Metal $L_{2,3}$ XANES

Molecules and molecular systems which consist of transition metal element, organic moiety, The spectral shape 3*d* transition metal (*M*) $L_{2,3}$ x-ray absorption near-edge structure (XANES) is dominated by the multiplet structures, since the strong electronic correlations among spatially localized 3*d* electrons and the 2*p* core-hole play a central role. In order to simulate the multiplet structures in M-$L_{2,3}$ XANES, we have developed an *ab initio* charge transfer multiplet (CTM) method for XANES[2,3,4]. This method is based on the restricted active space configuration interaction (RASCI) method in quantum chemistry using fully relativistic (four-component) molecular spinors. All relativistic effects, including the spin-orbit coupling at the *M*-2p levels, are taken into account by solving Dirac equation. All possible Slater determinants, corresponding to the electronic configurations, $2p^6 3d^n$ and $2p^5 3d^{n+1}$ which will dominate the initial and final states, respectively, are considered. In addition, the electronic excitation from molecular spinors mainly composed of O-2*p* to those of *M*-3*d*, that is, charge transfer, are also taken into account by taking O-2*p* spinors as another RAS space with max hole number is 1 or 2.

In this study, the M-$L_{2,3}$ XANES for divalent, trivalent and tetravalent *M* oxides (*M*=Ti-Ni) with various crystalline structures are calculated systematically the *ab initio* CTM method. The effects of the *M*-O covalent bonding and charge transfer oxygen to *M* ions on the M-$L_{2,3}$ XANES are investigated in detail.

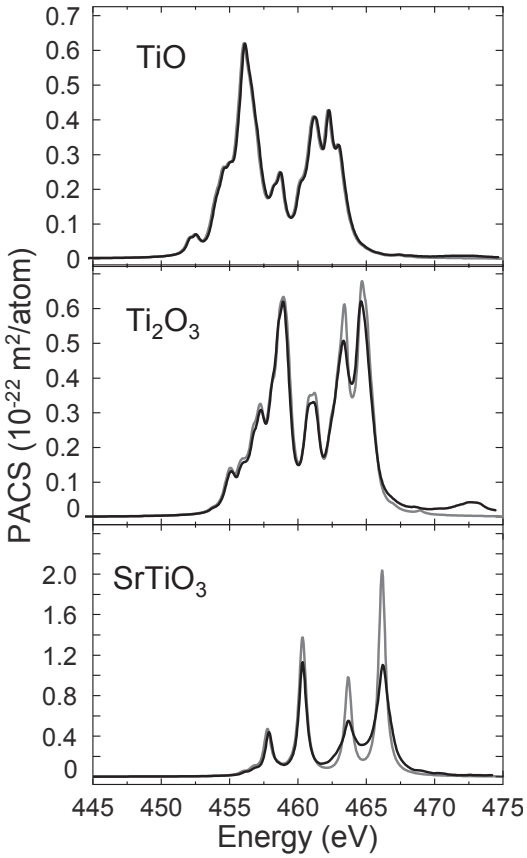


Fig. 1 Theoretical Ti-$L_{2,3}$ XANES with (black line) and without (gray line) charge transfer effects

First, we have clearly specified that the *M* 2*p*-3*d* and 3*d*-3*d* inter-electron interaction energies are reduced by the covalent bonding between the M and oxygen ions, because the spatial distributions of *M*-3*d* spinors are increased by the covalent bonding. This affects the multiplet structures and the transition probabilities in the M-$L_{2,3}$ XANES. Then the effects of charge transfer on *M* $L_{2,3}$-edges have discussed. In the *ab initio* CTM approach, the contribution of the charge-transferred configuration increased with increasing

atomic number and valency of *M* ions in the oxides. This tendency is similar to that of the covalent bonding between *M*-3*d* and O-2*p* spinors. The stronger the covalency, the larger the influence of the CT on M-$L_{2,3}$ XANES/ELNES.

Finally, The M-$L_{2,3}$ XANES of *M* oxides were calculated systematically by the *ab initio* CTM approaches. Figure 1 shows the theoretical Ti-$L_{2,3}$ XANES spectra for Ti oxides, for instance. In the case of divalent oxides of Ti, V, Cr, Mn, and Fe, the spectral shapes were hardly affected by the CT; it was only necessary to take the CT into account for divalent Ni oxides. The effects of the CT on $L_{2,3}$-edges became larger when the valency of the TM increased. The CT mainly contributed to the changes in peak intensities and peak broadness and to the formation of satellite peaks.

Variations of Zr-$L_{2,3}$ XANES in Zr oxides

Zr is an important element in the ceramic science. Many zirconium-bearing phases are used, e.g. for transformation toughening of structural ceramics, in bioceramics, and as nucleation agents for the fabrication of glass ceramics. The identifications of the local atomic environment of Zr in ceramics is important for the new development of materials. Among many techniques, X-ray absorption near-edge structure (XANES) is a powerful technique to selectively observe the local environment of specific element in materials. In this work, Zr-$L_{2,3}$ XANES of tetravalent zirconium oxides are studied both theoretically and experimentally. The influences of the coordination number and local symmetry of Zr on the spectral shapes are investigated.

Three polymorphs of ZrO_2, namely, cubic ZrO_2 (*c*-ZrO_2), tetragonal ZrO_2 (*t*-ZrO_2), monoclinic ZrO_2 (*m*-ZrO_2), and orthorhombic $SrZrO_3$ (*o*-$SrZrO_3$) are examined. The coordination numbers and symmetries of Zr sites are different in these four compounds. The crystal structures of these four oxidic Zr compounds are drawn in Fig. 2(a). The Zr-$L_{2,3}$ XANES for these four Zr oxides were computed using the *ab initio* charge transfer multiplet (CTM) method. The results obtained are shown in Fig. 2 (b). One can see that both L_3- and L_2-edges are mainly composed of two peaks as indicated by A and B Fig. 2 (b). In every compound, the spectral shapes of L_3- and L_2-edges are different. In particular, the difference in the A/B intensity ratios is clearly visible at both edges. As can be seen, the A/B intensity ratio is much smaller at the L_3-edge than at the L_2-edge. This can be ascribed to the larger multiplet effects at the L_3-edge.

In Fig. 2(b), clear differences in spectral shapes among the four compounds are evident, reflecting the difference in the coordination number and in the symmetry around the Zr sites. The A/B intensity ratio is also found to be very sensitive to the coordination number of Zr. As the coordination number of Zr decreases, the A/B intensity ratio increases. The A/B intensity ratio at the Zr L_3- and L_2-edge XANES can therefore be used to roughly estimate the coordination number of Zr in such oxides. The Zr-$L_{2,3}$ XANES of Zr oxides were also measured using synchrotron light sources. The experimental results confirms our theoretical prediction that the A/B intensity ratio at Zr L_3- and L_2-edges is sensitive to the coordination number of Zr.

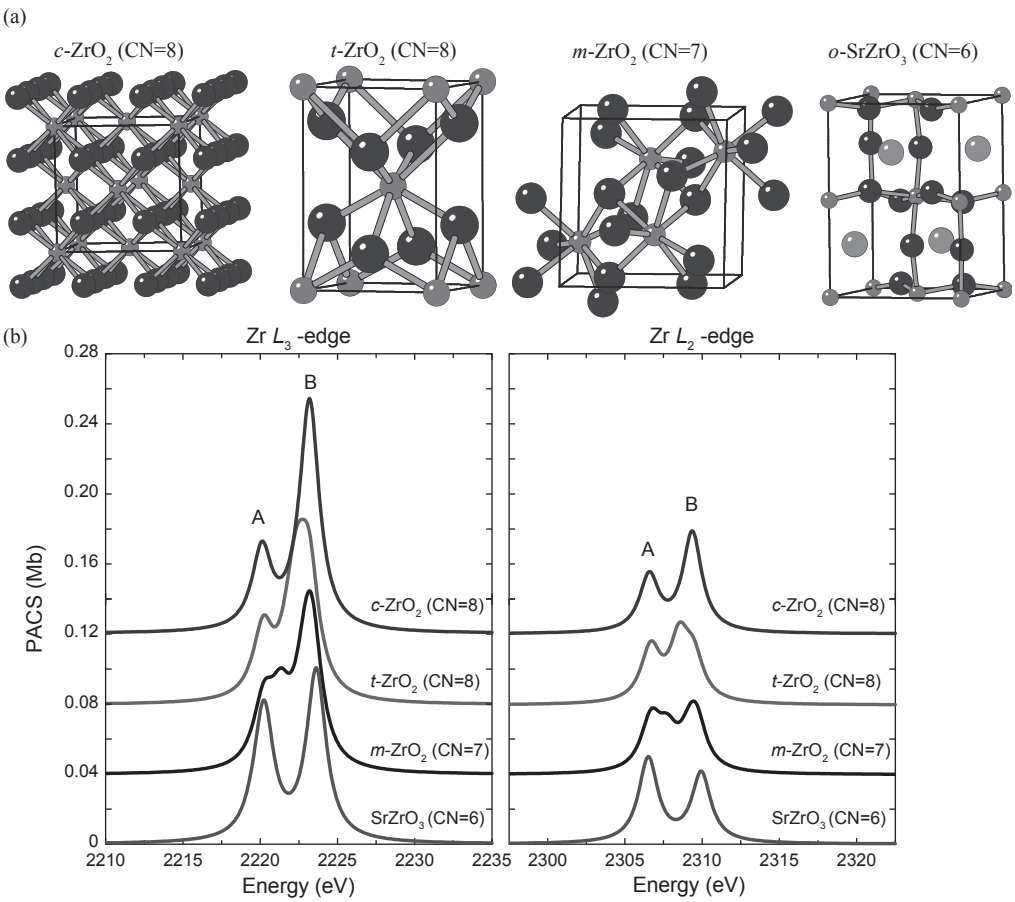


Figure 2 (a) Crystalline structures of Zr-oxides. (b) Theoretical Zr-$L_{2,3}$ XANES of tetravalent Zr-oxides.

2. Original papers

(1) Thomas Höche, and Hidekazu Ikeno, Marisa Mäder, Grant S. Henderson, and Robert I.R. Blyth, Brian C. Sales, and Isao Tanaka
Vanadium $L_{2,3}$ XANES experiments and first-principles multielectron calculations: Impact of second-nearest neighboring cations on vanadium-bearing fresnoites
Am. Mineral. **98,** 665-670 (2013).

(2) Hidekazu Ikeno, Michael Krause, Thomas Hoöhe, Christian Patzig, Yongfeng Hu, Antje Gawronski, Isao Tanaka and Christian Rüssel
Variation of Zr-$L_{2,3}$ XANES in tetravalent zirconium oxides
J. Phys.: Condens. Matter **25,** 165505 (2013).

3. Presentation at academic conferences

(1) Hidekazu Ikeno

"Systematic *ab initio* multiplet calculations for $L_{2,3}$ XAS of 3*d* transition metal compounds"
Workshop on Fundamental Aspects of X-ray Spectroscopies, (Feb. 21-22, 2013, Utrecht, the Netherlands)

(2) Hidekazu Ikeno and Teruyasu Mizoguchi
"Theory of XANES/ELNES: from quasi-particle to many-particle"
19th WIEN2k WORKSHOP, (Sep 3-7, 2012, Tokyo, Japan)

(3) Hidekazu Ikeno, Teruyasu Mizoguchi, and Isao Tanaka
"Systematic Calculations of $L_{2,3}$ x-ray absorption spectra for 3d Transition Metal Oxides by *Ab Initio* Charge Transfer Multiplet Method"
The 15th International Conference on X-ray Absorption Fine Structure (XAFS15), (Jul 22-28, 2012, Beijing, China)

(4) Hidekazu Ikeno, Teruyasu Mizoguchi, and Isao Tanaka
"Relativistic Configuration Interaction Calculations under the External Magnetic Field: Application to XMCD"
XAFS theory workshop: XAFS theory and nano particles, (July 18-20, 2012, Chiba, Japan)

(5) Hidekazu Ikeno, Teruyasu Mizoguchi, Yukinori Koyama, Zenpachi Ogumi, Yoshiharu Uchimoto, and Isao Tanaka
"Theoretical Fingerprints of M-$L_{2,3}$ XANES and ELNES for LiMO$_2$ (M=Mn,Fe,Co,Ni) by *ab initio* Multiplet Calculations"
The 3rd International Symposium on Advanced Microscopy and Theoretical Calculations (AMTC3), (May 9-11, 2012, Gifu, Japan)

(6) 池野豪一
「遷移金属 $L_{2,3}$ white line の第一原理計算」
日本顕微鏡学会第 68 回学術講演会(2012 年 5 月 14 日～16 日，つくば)

(7) 池野豪一
「3*d* 遷移金属化合物における $L_{2,3}$ 端 X 線吸収スペクトルの第一原理計算」
第 3 回 CMSI 研究会(2012 年 12 月 3 日～5 日)

4. Others

(1) 池野豪一，田中功
「六方晶フェライトにおけるMössbauerパラメータの第一原理計算」
第10回福井センターシンポジウム (2012年11月30日，京都)

２．シニアリサーチフェロー　Shigeru NAGASE

Senior Research Fellow

1. Summary of the research of 2012

(a) Lead-Lead Double Bonds Stabilized by Dative Carbene Ligands

Carbon-carbon double bonds play an important role in many fields of chemistry. As a new type of double bonds between the heavier atoms, diatomic molecules stabilized by the coordination of dative N-heterocyclic carbenes (:L) are of interest currently. The synthesis and isolation have been performed for L:→Si=Si←:L and L:→Ge=Ge←:L (:L = :C[N(2,6-^{i}Pr$_2$-C$_6$H$_3$)CH]$_2$). The Si and Ge atoms are regarded as being in a formal zero-oxidation state. The Si-Si and Ge-Ge bond distances compare well with typical double bond distances of $R_2Si=SiR_2$ and $R_2Ge=GeR_2$. Because the heaviest Pb case remains unknown, theoretical calculations were performed.

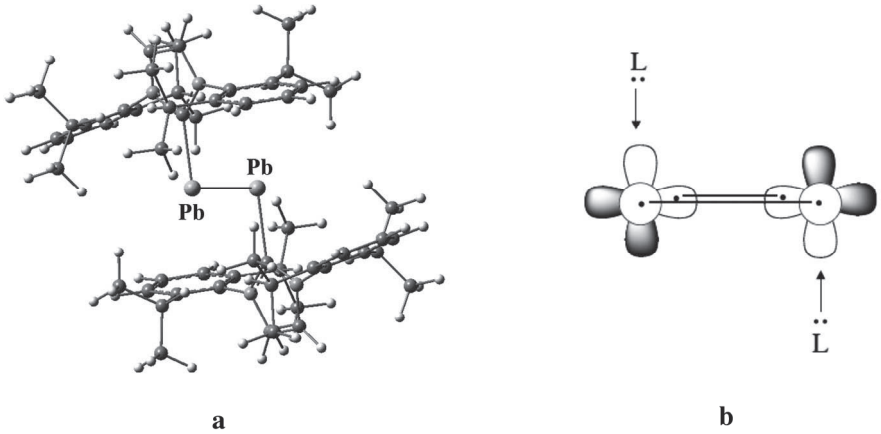


Fig. 1. (a) Optimized structure of L:→Pb=Pb←:L. (b) Donation of the lone pair of :L into the vacant 6p orbital of the Pb atom (for simplicity, the 6s orbital of Pb is omitted).

The optimized structure of L:→Pb=Pb←:L is presented in Fig. 1a, which has C_{2h} symmetry. Molecular orbital analysis shows that one σ bond and one π bond exist clearly between the Pb atoms, the Pb atoms being doubly bonded. It is notable that the Pb-Pb bond distance of 2.833 Å is considerably shorter than the shortest Pb-Pb double bond distance of 2.903 Å known to date and differs little from the Pb-Pb bond distance of Pb_2. As Fig. 1b shows, L:→Pb=Pb←:L is formed by the donation of the lone pair of L: into the vacant 6p orbital on Pb. Therefore, the Pb-Pb-L bond angle of 93.0° is close to 90°. The electron donation from L: makes the Pb atom negatively charged slightly (the charge on Pb is -0.17). The binding energy between Pb_2 ($^3\Sigma_g^-$) and 2L: is calculated to be 45.6 kcal/mol. It is expected that L:→Pb=Pb←:L is an interesting synthetic target.

(b) Heaviest Analogues of Alkynes

The heavier analogues of alkynes, REER (E = Si, Ge, Sn, Pb), have attracted special interest in

main-group element chemistry. Therefore, all the heavier analogues have been synthesized and isolated up to now: $R^{Si}SiSiR^{Si}$ (R^{Si} = $Si^{i}Pr\{CH(SiMe_3)_2\}_2$), BbtSiSiBbt (Bbt = C_6H_2-2,6-$\{CH(SiMe_3)_2\}_2$-4-$C(SiMe_3)_3$), Ar'GeGeAr' (Ar' = C_6H_3-2,6-(C_6H_3-2,6-$^{i}Pr_2)_2$), BbtGeGeBbt, Ar'SnSnAr', and Ar*PbPbAr* (Ar* = C_6H_3-2,6-(C_6H_2-2,4,6-$^{i}Pr_3)_2$). However, X-ray crystal analysis and theoretical calculations revealed that the Pb-Pb bond distance of the heaviest analogue, Ar*PbPbAr*, is much longer than typical Pb-Pb single bond distances and no π bond exists between the Pb atoms. Therefore, it has been accepted that the heaviest Pb analogues of alkynes take a singly bonded structure, unlike the Si, Ge, and Sn cases.

It is convenient to view REER as consisting of two ER components. ER has ground doublet and excited quartet states. As E becomes heavier, the ground doublet state becomes more stable than the quartet state. Therefore, the doublet-doublet interaction is most preferred for the heaviest case (E = Pb). Two interaction modes (**a** and **b**) between two PbR components in the ground doublet state are presented in Fig. 2. Mode **a** engenders a triply bonded structure because the donor-acceptor interaction of lone-pair electrons is allowed to form two dative bonds between Pb atoms. Mode **b** engenders a singly bonded structure because the lone pair of PbR does not participate in bonding. The lone-pair orbital of PbR is mostly composed of the 6s orbital of Pb. Because of the so-called relativistic effect, the 6s orbital shrinks and is stabilized. Therefore, mode **a** may be expected to be less favorable than mode **b**.

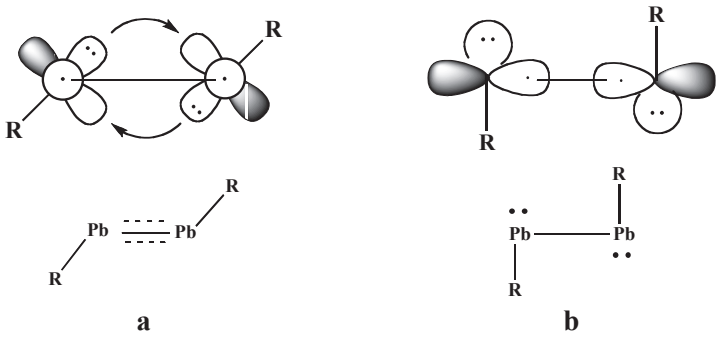


Fig. 2. Two interaction modes between the doublet PbR

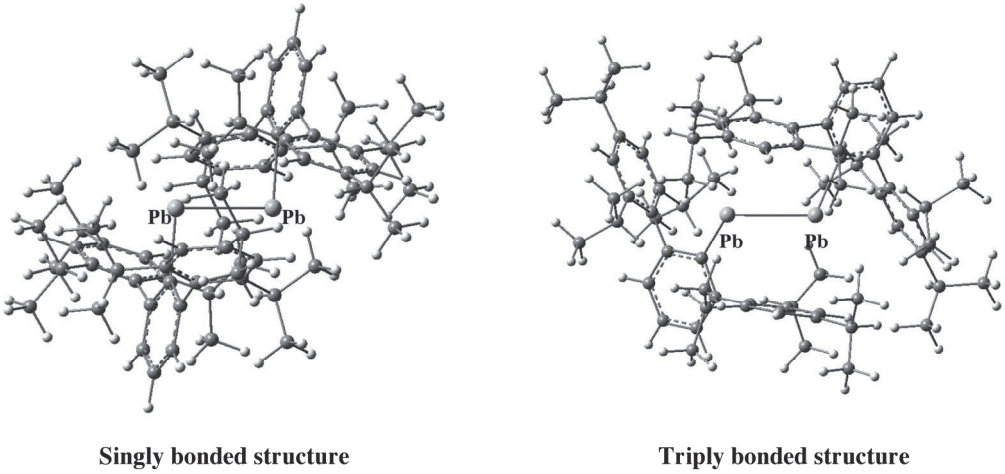


Fig. 3. Singly and triply bonded structures optimized for Ar*PbPbAr*

The singly bonded structure of Ar*PbPbAr* determined by X-ray crystal analysis was optimized using density functional theory calculations, as shown in Fig. 3 The optimized Pb-Pb bond distance agrees reasonably well with the experimental value in the crystal structure, despite packing forces. The HOMO and LUMO of the singly bonded structure respectively correspond to in-plane antibonding π_{in}* and out-of-plane bonding π_{out} orbitals. Interestingly, it was found that a triply bonded structure is located as an energy

minimum by switching the HOMO and LUMO, which is more stable than the singly bonded structure. The observed UV-vis spectrum is well reproduced by calculations on the triply bonded structure, which confirm that Ar*PbPbAr* takes a triply bonded structure in solution.

The Pb-Pb bond distance of 3.071Å calculated for the triply bonded structure of Ar*Pb-PbAr* is longer than the Pb-Pb single bond distance of 2.844 Å in $Ph_3PbPbPh_3$. For REER, we have suggested that electropositive silyl groups shorten the E-E bond distance. Several bulky silyl groups were tested using density functional calculations. It was found that the Pb-Pb bond distance of 2.696Å calculated for $R^{Si}PbPbR^{Si}$ (R^{Si} = $Si^iPr\{CH(SiMe_3)_2\}_2$) is remarkably shorter than the Pb-Pb single bond distance of 2.844 Å in Ph_3Pb-$PbPh_3$. In addition, the Pb-Pb bond distance is considerably shorter than the shortest Pb-Pb double bond distance of 2.903 Å known to date for $Si(SiMe_3)_3MesPb{=}PbSi(SiMe_3)_3Mes$ (Mes = C_6H_2-2,4,6-Me_3). However, the triply bonded structure was calculated to be 4.3 kcal/mol less stable than the singly bonded structure (Pb-Pb = 3.080Å). We are still searching for good substituent groups that stabilize a triply bonded structure with a sufficiently short Pb-Pb bond.

(c) Short Bonds between Transition Metals

The most common coordination numbers for transition metal complexes are four, five, and six. As novel transition metal complexes with an unsupported two-coordinate metal, R*MFe(η^5-C_5H_5)$(CO)_2$ (M = Fe, Mn, Cr; R* = C_6H-2,6-Ar_2-3,5-$^iPr_2$ where Ar = C_6H_2-2,5,6-$^iPr_3$) were synthesized and isolated. As is shown in Fig. 4, the bulky R* group surrounds the two-coordinate M atom and blocks the formation of any third bond to M. The metal-metal bond distances are much shorter than those of the known unsupported complexes.

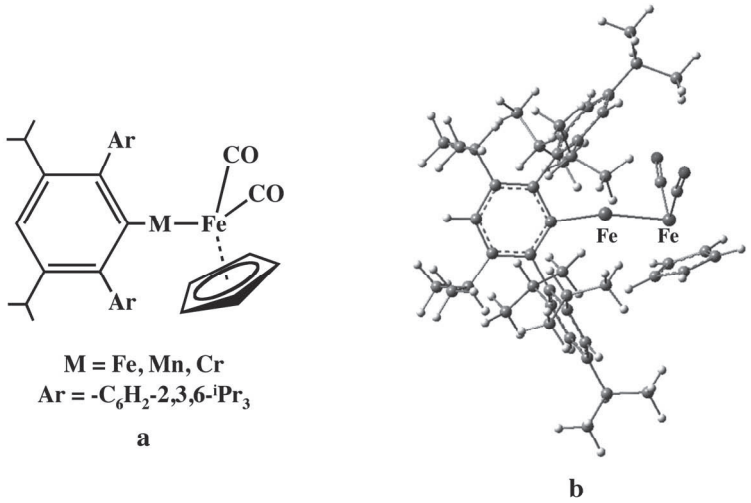


Fig. 4. (a) R*MFe(η^5-C_5H_5)$(CO)_2$. (b) Optimized structure for M = Fe.

We have predicted that, for example, the Fe-Fe bond distance is greatly shortened in the bicyclic four-membered ring presented in Fig. 5a. It is remarkable that the Fe-Fe bond distance of 2.045 Å is much shorter than the currently known shortest Fe-Fe bond distance of 2.127 Å. This bond shortening assisted by two heavier main group atoms such as Sn was very recently corroborated in the joint research with experiment for the bicyclic four-membered Ru_2Sn_2 ring complex presented in Fig. 5b. The Ru-Ru bond distance of 2.343 Å determined by X-ray crustal analysis agrees well with the calculated value of 2.363 Å. It is shorter than the Ru-Ru distance of 2.449-2.469 Å in the

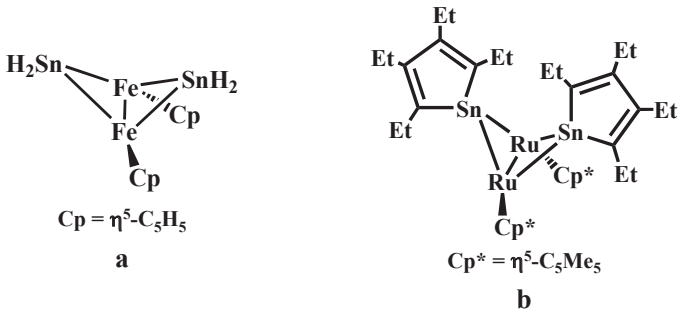
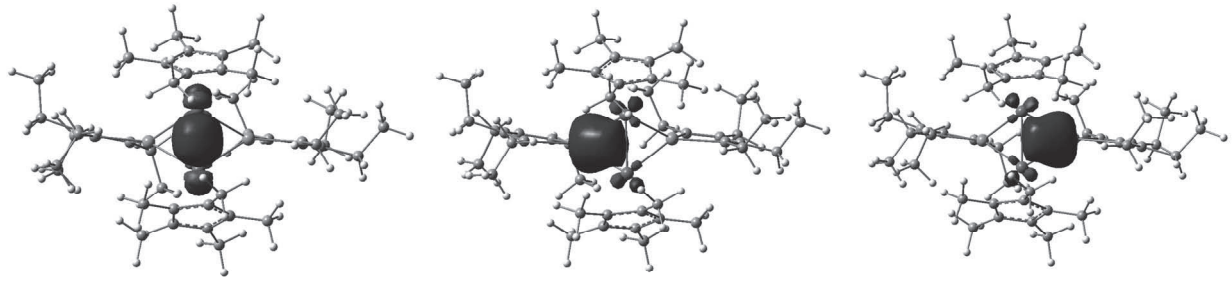


Fig. 5. Bicyclic four-membered ring complex.

related bridge complexes, for which it is assumed that the two Ru atoms are triply bonded. As shown in Fig. 6, localized molecular orbital analysis reveals that one clear σ bond exists between the Ru atoms, while two three-centered σ orbitals are delocalized over each of the three-membered Ru_2Sn rings, which make an important contribution to Ru-Ru bonding. As a result, the Ru-Ru bond has a somewhat multiple-bond character, as indicated by the bond order of 1.3. It is also predicted that the Ru-Ru bond distance in the bicyclic four-membered ring is shortened further in the bicyclic six-membered Ru_2Sn_4 ring, although the shortening does not take place for the corresponding Ru_2C_4 ring.



σ (Ru-Ru) orbital **Three-centered σ orbitals**

Fig. 6. One σ orbital between Ru atoms and two three-centered σ orbitals delocalized over the three-membered rings for the complex presented in Fig. 5.

As interesting compounds with heavier main group atoms and transition metals in their frameworks, anionic iron complexes with a clear bond between an ate-type pentacoordinate Ge atom and an Fe Atom were investigated. Since silicon versions of olefin metathesis are unknown, 18-electron titantium silylene complexes were investigated, which have loosely bound and readily removable Lewis base ligands that are classified as the Schrock-type silydenes.

(d) Nanocarbon Systems

We have performed theoretical calculations for tunable charge-transport properties of I_h-C_{80}, linking $Lu_3N@C_{80}$ to electron acceptors, metal-promoted restoration of defective graphene, fullerene genetic code, silylene-bridged $Lu_3N@I_h$-C_{80}, $La@C_{82}$/π-extended tetrathiafulvalene conjugate, violation of the isolated pentagon rule for endohedral metallic carbide fullerenes, three $Yb@C_{82}$ isomers cocrystallized with Ni^{II} (octaethylporphyrin), intramolecular electron transfer in donor-acceptor conjugates of $La_2@C_{80}$ and TCAQ, coordinative interactions between porphyrins and C_{60}, $La@C_{82}$, and $La_2@C_{80}$, MCD spectroscopy of endohedral metallofullerenes, and Diels-Alder reactions of $La@C_{82}$.

2. Original papers

(1) H. Zheng, X. Zhao, W. -W. Wang, T. Yang, and S. Nagase, "$Sc_2@C_{70}$ Rather Than $Sc_2C_2@C_{68}$: Density Functional Theory Characterization of Metallofullerene Sc_2C_{70}", *J. Chem. Phys.,* **137**, 014308 (5 pages) (2012).

(2) S. Sato, S. Seki, G. Luo, M. Suzuki, J. Lu, S. Nagase, and T. Akasaka, "Tunable Charge-Transport Properties of I_h-C_{80} Endohedral Metallofullerenes: Investigation of $La_2@C_{80}$, $Sc_3N@C_{80}$, and $Sc_3C_2@C_{80}$", *J. Am. Chem. Soc.*, **134**, 11681-11686 (2012).

(3) L. Feng, M. Rudolf, S. Wolfrum, A. Troeger, Z. Slanina, T. Akasaka, S. Nagase, N. Martin, T. Ameri, C. J. Brabec, and D. M. Guldi, "A Paradigmatic Change: Linking Fullerenes to Electron Acceptors", *J. Am. Chem. Soc.*, **134**, 12190-12197 (2012).

(4) W. -W. Wang, J. -S. Dang, J. -J. Zheng, X. Zhao, E. Osawa, and S. Nagase, "Metal-Promoted Restoration of Defective Graphene", *J. Mater. Chem.*, **22**, 16370-16375 (2012).

(5) J. -S. Dang, W. -W. Wang, J. -J. Zheng, X. Zhao, E. Osawa, and S. Nagase, "Fullerene Genetic Code: Inheritable Stability and Regioselective C_2 Assembly", *J. Phys. Chem. C*, **116**, 16233-16239 (2012).

(6) K. Sato, M. Kako, M. Suzuki, N. Mizorogi, T. Tsuchiya, M. M. Olmstead, A. L. Balch, T. Akasaka, and S. Nagase, "Synthesis of Silylene-Bridged Endohedral Metallofullerene $Lu_3N@I_h$-C_{80}", *J. Am. Chem. Soc.*, **134**, 16033-16039 (2012).

(7) Y. Takano, S. Obuchi, N. Mizorogi, R. Carcia, M. A. Herranz, M. Rudolf, S. Wolfrum, D. M. Guldi, N. Martin, S. Nagase, and T. Akasaka, "Stabilizing Ion and Radical Ion Pairs States in a Paramagnetic Endohedral Metallofullerene/π-Extended Tetrathiafulvalene Conjugate", *J. Am. Chem. Soc.*, **134**, 16103-16106 (2012).

(8) T. Yang, X. Zhao, and S. Nagase, "Structural Determination on $Yb@C_{78}$ Reveals an Unexpected Relationship of $Yb@C_{2n}$ (2n = 74-78)", *J. Phys. Chem. C*, **116**, 21640-21645 (2012).

(9) T. Yang, X. Zhao, S. -T. Li, and S. Nagase, "Is the Isolated Pentagon Rule Always Satisfied for Metallic Carbide Endohedral Fullerenes?", *Inorg. Chem.,* **51**, 11223-11225 (2012).

(10) Z. Slanina, F. Uhlik, S. -L. Lee, L. Adamowicz, T. Akasaka, and S. Nagase, "Stability Computations for Isomers of $La@C_n$ (n = 72, 74, 76)", *Molecules,* **17**, 13146-13156 (2012).

(11) M. Suzuki, Z. Slanina, N. Mizorogi, X. Lu, S. Nagase, M. M. Olmstead, A. L. Balch, and T. Akasaka, "Single-Crystal X-ray Diffraction Study of Three $Yb@C_{82}$ Isomers Cocrystallized with Ni^{II} (octaethylporphyrin)", *J. Am. Chem. Soc.*, **134**, 18772-18778 (2012).

(12) Y. Takano, S. Obuchi, N. Mizorogi, R. Garcia, M. A. Herranz, M. Rudolf, D. M. Guldi, N. Martin, S. Nagase, and T. Akasaka, "An Endohedral Metallofullerene as a Pure Electron Donor: Intramolecular Electron Transfer in Donor-Acceptor Conjugates of $La_2@C_{80}$ and 11,11,12,12-Tetracyano-9,10-anthra-p-quinodimethane (TCAQ)", *J. Am. Chem. Soc.*, **134**, 19401-19408 (2012).

(13) T. Tanikawa, M. Saito, J. -D. Guo, S. Nagase, and M. Minoura, "Synthesis, Structures, and Optical Properties of Heterasumanenes Containing Group 14 Elements and Their Related Compounds", *Eur. J. Org. Chem.,* 7135-7142 (2012).

(14) K. Sato, M. Kako, N. Mizorogi, T. Tsuchiya, T. Akasaka, and S. Nagase, "Bis-Silylation of $Lu_3N@I_h$-C_{80}: Considerable Variation in the Electronic Structures", *Org. Lett.*, **14**, 5908-5911 (2012).

(15) N. Kano, N. Yoshinari, Y. Shibata, M. Miyachi, T. Kawashima, M. Enomoto, A. Okazawa, N. Kojima, J. -D. Guo, and S. Nagase, "Anionic Iron Complexes with a Bond between an Ate-Type Pentacoordinated Germanium and an Iron Atom", *Organometalics,* **21**, 8059-8062 (2012).

(16) T. Tsuchiya, M. Rudolf, S. Wolfrum, S. G. Radhakrishnan, R. Aoyama, Y. Yokosawa, A. Oshima, T. Akasaka, S. Nagase, and D. M. Guldi, "Coordinative Interactions between Porphyrins and C_{60}, La@C_{82}, and La_2@C_{80}", *Chem. -Eur. J.*, **19**, 558-565 (2013).

(17) L. Feng, M. Suzuki, N. Mizorogi, X. Lu, M. Yamada, T. Akasaka, and S. Nagase, "Mapping the Metal Positions inside Spherical C_{80} Cages: Crystallographic and Theoretical Studies of Ce_2@D_{5h}-C_{80} and Ce_2@I_h-C_{80}", *Chem. -Eur. J.,* **19**, 988-993 (2013).

(18) W. -W. Wang, J. -S. Dang, J. -J. Zheng, X. Zhao, and S. Nagase, "Selective Growth of Fullerenes from C_{60} to C_{70}: Inherent Geometrical Connectivity Hidden in Discrete Experimental Evidence", *J. Phys. Chem. C*, **117**, 2349-2357 (2013).

(19) T. Yang, X. Zhao, and S. Nagase, "Quantum Chemical Insight of the Dimetallic Sulfide Endohedral Fullerene Sc_2S@C_{70}: Does It Possess the Conventional D_{5h} Cage?", *Chem. Eur. J.,* **19**, 2649-2654 (2013).

(20) M. Yamada, Z. Slanina, N. Mizorogi, A. Muranaka, Y. Maeda, S. Nagase, T. Akasaka, and N. Kobayashi, "Application of MCD Spectroscopy and TD-DFT to Endohedral Metallofullerenes for Characterization of their Electronic Transitions", *Phys. Chem. Chem. Phys.,* **15**, 3593-3601 (2013).

(21) V. Y. Lee, S. Aoki, T. Yokoyama, S. Horiguchi, A. Sekiguchi, H. Gornitzka, J. –D. Guo, and S. Nagase, "Toward a Silicon Version of Metathesis: From Schrock-Type Titanium Silylidenes to Silatitanacyclobutenes", *J. Am. Chem. Soc.*, **135**, 2987-2990 (2013).

(22) Y. Morinaka, S. Sato, A. Wakamiya, H. Nikawa, N. Mizorogi, F. Tanabe, M. Murata, K. Komatsu, K. Furukawa, T. Kato, S. Nagase, T. Akasaka, and Y. Murata, "X-Ray Observation of a Helium Atom and Placing a Nitrogen Atom inside He@C_{60} and He@C_{70}", *Nat. Commun.*, **4**, 1554 (5 pages) (2013).

(23) T. Kuwabara, M. Saito, J. –D. Guo, and S. Nagase, "Unexpected Formation of Ru_2Sn_2 Bicyclic Four-Membered Ring Complexes with Butterfly and Inverse-Sandwich Structures", *Inorg. Chem.,* **52**, 3585-3587 (2013).

(24) S. Sato, Y. Maeda, J. –D. Guo, M. Yamada, N. Mizorogi, S. Nagase, and T. Akasaka, "Mechanistic Study of the Diels-Alder Reaction of Paramagnetic Endohedral Metallofullerene: Reaction of La@C_{82} with 1,2,3,4,5-Pentamethylcyclopentadiene", *J. Am. Chem. Soc.*, **135**, 5582-5587 (2013).

2. Review articles

(1) X. Lu, L. Feng, T. Akasaka, and S. Nagase, "Current Statues and Future Developments of Endohedral Metallofullerenes", *Chem. Soc. Rev.*, **41**, 7723-7760 (2012).

(2) Y. –P. Xie, X. Lu, T. Akasaka, and S. Nagase, "New Features in Coordination Chemistry: Valuable Hints from X-Ray Analyses of Endohedral Metallofullerenes", *Polyhedron*, **52**, 3-9 (2013).

(3) S. Nagase, "Multiple Bonds between Lead Atoms and Short Bonds between Transition Metals", *Pure Appl. Chem.*, **85**, 649-659 (2013).

Keiji MOROKUMA

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1. Summary of the Research of the Year

Theoretical and Computational Studies of Complex Molecular Systems

The goals of the research of this group are 1. to develop theoretical methods (such as ONIOM, GRRM) for complex systems, 2. to demonstrate that such methods can be used for simulations of structures, reactions and dynamics of complex systems and 3. to solve some of the important problems in each field. Our research is supported in part by the Institute and in large fraction by a 5-year grant in the area of High Performance Computing for Multi-Scale and Multi-Physics Phenomena from CREST (Core Research for Evolutional Science and Technology) program of JST (Japan Science and Technology Agency) that ended on March 31, 2012. With several postdoctoral fellows and a few research assistants, as well as in collaboration with my group at Emory University, the group of Prof. Stephan Irle of Nagoya University as well as Prof. Satoshi Maeda, Assistant Professor at Hokkaido University, we have a strong team of theoretical/computational chemists working together toward a common goal. Since detailed description on individual projects can be found in the reports of postdoctoral fellows, here the areas of studies and titles of individual projects are summarized.

I. Simulation of Reactions and Dynamics of Complex and Biomolecular Systems

In the area of **simulation of complex and biomolecular systems**, in recent years we have studied structures and reactions of complex molecular and biomolecular systems. For complex molecular systems, our emphasis has been catalyses, both transition metal catalysis and organic catalysis, with special attention to selectivity. In addition to the standard TS optimization method, we extensively used the GRRM strategy (see research area III below) to find reaction pathways. We expanded our theoretical studies of catalytic reactions that take place in the nano cavity created by the protein and nucleic acids. In our studies of the structures of intermediates and transition states of enzymatic reactions, we explicitly included the effects of protein employing the ONIOM QM/MM scheme.

Another research topic in complex systems is chemical reactions in excited electronic states. We have studied potential energy surfaces of low-lying excited states for some organic and inorganic photochemical reactions, and elucidated rather complex reaction mechanisms involving different electronic states. Recently a most advanced multiconfigurational ab initio method called DMRG (density matrix renormalization group) method, has been used in collaboration with its developer, Prof. Yanai of Institute of Molecular Science, for calculations of potential energy surfaces of excited states of complex molecular systems.

a) **Sp^3–sp^2 vs sp^3–sp^3 C–C Activation in Rh-Catalyzed Ring Opening of Benzocyclobutenol: A DFT Study** (See research activities of Dr. Ding)
b) **Theoretical Studies of ACDC: Asymmetric Counteranion Directed Catalysis** (See research activities of Dr. Petrova)
c) **Theoretical Studies of PTC: Enentioselective Base-Free Phase-Transfer Catalysis** (See research activities of Dr. Petrova)
d) **Theoretical Modeling of Stereochemistry Control of Copper Catalysts Based on the Chirality of DNA** (See research activities of Dr. Petrova)
e) **Theoretical Study of Asymmetric Hydration Catalyzed by DNA-based Artificial Enzyme**

Metalloenzymes (See research activities of Dr. Ke)

f) **Theoretical Study of Polymerization Catalyzed by Artificial Metalloenzymes** (See research activities of Dr. Ke)

g) **QM/MM Structural and Spectroscopic Analysis of the Di-iron(II) and Di-iron(III) Ferroxidase Site in M Ferritin** (See research activities of Dr. Harris)

h) **Theoretical Studies of Reduction of NO in qNOR Enzyme** (See research activities of Dr. Hatanaka)

i) **Reactivity of Hydrogen Atom Transfer (HAT) with Metal-Oxo and How Enzymes Facilitates the Reaction** (See research activities of Dr. Chung)

j) **Reaction Mechanism of Spiropyran-Merocyanine Photochromic Reaction** (See research activities of Dr. Liu)

k) **Theoretical Study on the Deactivation Path of Fluorescence** (See research activities of Dr. Liu)

l) **Reaction Mechanism of Photo-induced Decarboxylation of the Photoactivatable Green Fluorescent Protein: An ONIOM(QM:MM) Study**

m) **Excited-State Proton Transfer Controls Irreversibility of Photoisomerization in Mononuclear Ruthenium(II) Monoaquo Complexes: A DFT Study** (See research activities of Dr. Ding)

n) **Chemiluminescence and Bioluminescence of Dioxetanones** (See research activities of Dr. Chung)

II. Simulation of Nanomaterials

In the area of **simulation of nanomaterials**, we continued our research efforts on quantum chemical molecular dynamics (QM/MD) computations of carbon nanostructure formation based on density functional tight binding (DFTB). Our focus in the last few years has been on the growth dynamics of single-walled carbon nanotube (SWCNT) and graphene, for which the growth mechanism is still poorly understood. The chirality control in the CNT growth is one of the most important pending issues. We invented a theoretical method to define the local chirality of irregular carbon nanotubes and used this to analyze mechanism of retention and loss of chirality during the growth of carbon nanotubes on transition metal clusters. We also addresses on the chirality control in the CNT growth from organic templates. The nucleation and growth of graphenes on transition metal surfaces have also been studied using a variety of model systems.

a) **Effects of Molecular Dynamics Thermostats on Descriptions of Chemical Non-Equilibrium** (See research activities of Dr. Page)

b) **Optimization of a Genetic Algorithm for the Functionalization of Fullerenes**

c) **The Dynamics of Local Chirality during SWCNT Growth: Armchair versus Zigzag Nanotubes**

d) **Quantum Chemical Molecular Dynamics Simulations for Chirality-Controlled SWCNT Growt**h (See research activities of Dr. Kim)

e) **SWCNT Growth from Chiral Carbon Nanorings: Prediction of Chirality and Diameter Influence on Growth Rates**

f) **Theoretical Insights into Chirality-Controlled SWCNT Growth from a Cycloparaphenylene Template**

g) **Temperature Dependence of Catalyst-Free Chirality-Controlled Single-Walled Carbon Nanotube Growth from Organic Templates** (See research activities of Dr. Haibei Li)

h) **Revealing the Dual Role of Hydrogen for Growth Inhibition and Defect Healing in Polycyclic Aromatic Hydrocarbon Formation: QM/MD Simulations** (See research activities of Dr. Haibei Li)

i) **Coupled Cluster and Density Functional Theory Calculations of Atomic Hydrogen Chemisorption on Pyrene and Coronene as Model Systems for Graphene Hydrogenation**

j) **Sub-Surface Nucleation of Graphene Precursers near a Ni(111) Step Edge**

k) **Graphene Nucleation on Transition Metal Surfaces (S**ee research activities of Dr. Page)

l) **Simulated IR/Raman Spectra of Graphene and Graphene Oxide** (See research activities of Dr. Page)

III. Method Developments and Applications

In collaboration with Profs. Koichi Ohno and Satoshi Maeda, combining the two methods of potential energy search we have developed before, the ADDF (adiabatic downward distortion following) method and the AFIR (artificial force-induced reaction (AFIR) method, we have developed **the Global Reaction Route Mapping (GRRM) strategy.** These methods allow determination of all the reaction pathways, including intermediates and transition states as well as minim energy conical intersections and seam of crossing, of complex reaction systems without any guess. The strategy includes expanding the applicability to complex molecular systems by using micro-iteration techniques. The GRRM strategy has been actively applied to homogenous catalysis systems such as transition metal catalysts and organic catalysts without transition metals, for which the research area I above should also be referred to. The GRRM strategy has been particularly powerful in finding reaction pathways of photo-activated molecules, in which multiple pathways involving various electronically excited sates and crossings between them can effectively be located using the GRRM strategy.

a) **Systematic Exploration of the Mechanism of Chemical Reactions: the Global Reaction Route Mapping (GRRM) Strategy by the ADDF and AFIR Methods**

b) **Exploring Potential Energy Surfaces of Large Systems with Artificial Force Induced Reaction in Combination with ONIOM and Microiteration**

c) **Automated Exploration of Photolytic Channels of HCOOH: Conformational Memory via Excited State Roaming**

d) **Global Ab Initio Potential Energy Surfaces for Low-lying Doublet States of NO_3**

e) **Theoretical Study on the Photodissociation of Methylamine Involving S_1, T_1, and S_0 States** (See research activities of Dr. Xiao)

f) **Photodissociation of CH_3NO_2** (See research activities of Dr. Isegawa)

g) **Aqueous Mukaiyama-Aldol Reaction Catalyzed by Lanthanide Trication** (See research activities of Dr. Hatanaka)

Original papers

1. P. S. Krstic, J. P. Allain, C. N. Taylor, J. Dadras, S. Maeda, K. Morokuma, J. Jakowski, A. Allouche, and C. H. Skinner, Deuterium Uptake in Magnetic Fusion Devices with Lithium Conditioned Carbon Walls, Phys. Rev. Lett., 110, 105001/1-5, 2013.
2. B. Fu, J. M. Bowman, H. Xiao, S. Maeda, and K. Morokuma, Quassiclassical Trajectory Studies of the Photodissociation Dynamics of NO_3 from the D_0 and D_1 Potential Energy Surfaces, J. Chem. Theo. Comp., 9, 893-900, 2013.
3. K. R. S. Chandrakumar, A. J. Page, S. Irle and K. Morokuma, Carbon Coating Precedes SWCNT Nucleation on Silicon Nanoparticles: Insights from QM/MD Simulations, J. Phys. Chem. C, 117, 4238-4244, 2013.
4. S. Maeda, K. Ohno and K, Morokuma, Systematic Exploration of the Mechanism of Chemical Reactions: the Global Reaction Route Mapping (GRRM) Strategy by the ADDF and AFIR Methods, Phys. Chem. Chem. Phys., 15, 3683-3701, 2013.
5. A. J. Page, C.-P. Chou, B. Q. Pham, H. Witek, S. Irle and K. Morokuma, Quantum Chemical Investigation of Epoxide and Ether Groups in Graphene Oxide and Their Vibrational Spectra, Phys. Chem. Chem. Phys., 15, 3725-3735, 2013.
6. L. Ding, L. W. Chung, K. Morokuma, Reaction Mechanism of Photo-induced Decarboxylation of the Photoactivatable Green Fluorescent Protein: An ONIOM(QM:MM) Study, J. Phys. Chem. B, 117, 1075-1084, 2013.

7. K. R. S. Chandrakum ar, A. Puretzky, C. Rouleau, J. D. Readle, D. B. Geohegan, K. More, V. Krishnan, G. Duscher, B. Sumpter, S. Irle, and K. Morokuma, High-Temperature Transformation of Fe-Decorated Single-Wall Carbon Nanohorns to Nanooysters: A Combined Experimental and Theoretical Study, Nanoscale, 5, 1849-1857, 2013.
8. S. Maeda, E. Abe, M. Hatanaka, T. Taketsugu, and K. Morokuma, Exploring Potential Energy Surfaces of Large Systems with Artificial Force Induced Reaction in Combination with ONIOM and Microiteration, J. Chem. Theo. Comp., 5, 5058-5063, 2012.
9. A. J. Page, T. Isomoto, J. Knaup, S. Irle, and K. Morokuma, Effects of Molecular Dynamics Thermostats on Descriptions of Chemical Non-Equilibrium, J. Chem. Theo. Comp., 8, 4019-4028, 2012.
10. A. Y. Timoshkin, and K. Morokuma, Novel group 13 Lewis superacids and 13-15 donor-acceptor cryptands for hydrogen activation: a theoretical study, Phys. Chem. Chem. Phys., 14, 14911-14916, 2012.
11. H.-B. Li, A. J. Page, S. Irle, and K. Morokuma, SWCNT Growth from Chiral Carbon Nanorings: Prediction of Chirality and Diameter Influence on Growth Rates, J . Am. Chem. Soc., 134, 15887-15896, 2012.
12. P. S. Krstic, J. P. Allai, A. Allouched, J, Jakowski, J. Dadras, C. N. Taylor, Z. Yang, K. Morokuma, and S. Maeda, Dynamics of deuterium retention and sputtering of Li-C-O surfaces, Fusion Eng. Design, 87, 1732-1736, 2012.
13. Z. Ke, S. Abe, T. Ueno, and K. Morokuma, Catalytic Mechanism in Artificial Metalloenzyme: QM/MM Study of Phenylacetylene Polymerization by Rhodium Complex Encapsulated in apo-Ferritin, J. Am. Chem. Soc., 134, 15418-15429, 2012.
14. H. Xiao, S. Maeda and K. Morokuma, Global Ab Initio Potential Energy Surfaces for Low-lying Doublet States of NO3, J. Chem. Theo. Comp., 8, 2600-2605, 2012.
15. S. Sekharan, K. Katayama, H. Kandori and K. Morokuma, The “OH-Site” Rule for Seeing Red and Green, J. Am. Chem. Soc., 134, 10706-10712, 2012.
16. W. Treesuwan, H. Hirao, K. Morokuma, and S. Hannongbua, Characteristic vibration patterns and protein binding of odor compounds from bread baking volatiles: Density functional, ONIOM study and principal component analysis (PCA), J. Mol. Model., 18, 2227-2240, 2012.
17. Y. Wang, H.-J. Qian, K. Morokuma, and S. Irle, Coupled Cluster and Density Functional Theory Calculations of Atomic Hydrogen Chemisorption on Pyrene and Coronene as Model Systems for Graphene Hydrogenation, J. Phys. Chem. A, 116, 7154-7160, 2012
18. K. P. O’Halloran, C. Zhao, N. S. Ando, A. J. Schultz, T. F. Koetzle, P. M. B. Piccoli, B. Hedman, K. O. Hodgson, E. Bobyr, M. L. Kirk, S. Knottenbelt, E. C. Depperman, B. Stein, T. M. Anderson, R. Cao, Y. V. Geletii, K. I. Hardcastle, D. G. Musaev, W. A. Neiwert, X. Fang, K. Morokuma, S. Wu, P. Koegerler and C. L. Hill, Revisiting the Polyoxometalate-Based Late-Transition-Metal-Oxo Complexes: The “Oxo Wall” Stands, Inorg. Chem., 51, 7025-7031, 2012.
19. S. Maeda, T. Taketsugu and K. Morokuma, Automated Exploration of Photolytic Channels of HCOOH: Conformational Memory via Excited State Roaming, J. Phys. Chem. Lett., 3, 1900-1907, 2012.
20. H.-B. Li, A. J. Page, Y. Wang, S. Irle, and K. Morokuma, Sub-Surface Nucleation of Graphene Precursers near a Ni(111) Step Edge, Chem. Comm., 48, 7937-7939, 2012.
21. J. Kim, A. J. Page, S. Irle, and K. Morokuma, The Dynamics of Local Chirality during SWCNT Growth: Armchair versus Zigzag Nanotubes, J. Am. Chem. Soc., 134, 9311-9319, 2012J.
22. Jakowski, S. Irle, B. Sumpter, and K. Morokuma, Modeling charge transfer in fullerene collisions via real time electron dynamics simulations, J. Phys. Chem. Lett., 3, 1536-1542, 2012.
23. M. A. Addicoat, A. J. Page, Z. E. Brain, L. Flack, K. Morokuma and S. Irle, Optimization of a Genetic Algorithm for the Functionalization of Fullerenes, J. Chem. Theo. Comp., 8, 1841-1851, 2012.
24. J. Jakowski. S. Irle and K. Morokuma, Time-dependent quantum dynamical simulations of C2 condensation under extreme conditions, Phys. Chem. Chem. Phys., 14, 6266-6272, 2012.
25. V. P. Ananikov, N. V. Orlov, S. S. Zalesskiy, I. P. Beletskaya,.V. N. Khrustalev, K. Morokuma and D. G. Musaev, Catalytic Adaptive Recognition of Thiol (SH) and Selenol (SeH) Groups Towards Synthesis of Functionalized Vinyl Monomers, J. Am. Chem. Soc., 134, 6637-3349, 2012.
26. H.-B. Li, A. J. Page, S. Irle, and K. Morokuma, Theoretical Insights into Chirality-Controlled SWCNT Growth from a Cycloparaphenylene Template, ChemPhysChem, 13, 1479-1485, 2012.
27. M. N. Ryanzantsev A. Altun and K. Morokuma, Color Tuning in Rhodopsins: The Origin of the Spectral Shift between the Chloride-bound and Anion-free Forms of Halorhodopsin, J. Am. Chem. Soc., 134, 5520-5523, 2012.

2. Review articles

1. S. Irle, A. J. Page, B. Saha, Y. Wang, K. R. S. Chandrakumar, Y. Nishimoto, H.-J. Qian, K. Morokuma, Atomistic mechanism of carbon nanostructure self-assembly as predicted by QM/MD simulations, in eds. J. Leszczynski and M. Shukla, “Practical Aspects of Computational Chemistry: An Overview of the Last Two Decades and Current Trends”, 103-172 (2012): Springer-European Academy of Sciences. ISBN 978-94-007-0922-5

4. Presentation at academic conferences and universities

1. Keiji Morokuma, “Fascinating World of Theory of Chemical Reactions”, Keynote Speaker, CRC International Symposium in Strasbourg: Chemical Theory of Complex Systems, Strasbourg, France, March 7-8, 2013.
2. Keiji Morokuma, “Exciting World of Theoretical Studies of Chemical Reactions – From Gas Phase Reactions to Nano Structures, Catalysts, and Enzymatic Reactions”, Departmental Invited Seminar, Department of Chemistry, Miami University, Miami, FL, USA, February 15, 2013.
3. Keiji Morokuma. “Automatic Search of Potential Energy Surfaces for Saddles and Intersection”, Invited Speaker, 2013 Mesilla Chemistry Workshop on Dynamics for Chemical Reaction Pathways. Role of Non-Statistical Effects, Las Cruces, NM, USA, February 10-12, 2013.
4. Keiji Morokuma, “Exciting World of Theoretical Studies of Chemical Reactions – From Gas Phase Reactions to Nano Structures, Catalysts, and Enzymatic Reactions”, Special Departmental Seminar for 65th Birthday Celebration of Prof. J. M. Bowman, Department of Chemistry, Emory University, Atlanta, GA, USA, February 8, 2013.
5. K. Morokuma, “Multilevel simulations of biomolecular reactions”, Invited lecture, The second international symposium on large-scale computational sciences: Nnao- and bio-simulations. Japan Society and Technology Agency, Tokyo, November 8, 2012.
6. K. Morokuma, “New Fascinating World of Theory of Chemical Reactions”, Plenary Speaker, the 3rd International Symposium of Theoretical Chemistry, USTHB, Alger, Algeria, October 14-17, 2012.
7. K. Morokuma, “New Paradigm in Exploration of Reaction Paths in Organometallic Catalysis”, Plenary Speaker, International Conference "Catalysis in Organic Synthesis", (ICCOS-2012). Zelinsky Institute of Organic Chemistry, Moscow, Russia, September 15-20, 2012.
8. Keiji Morokuma, “How much became understood about chemical reaction mechanisms of complex molecular systems by theoretical and computational chemistry?”, Special seminar, Hokkaido Section, Chemical Society of Japan, Hokkaido University, Japan, August 30, 2012.
9. Keiji Morokuma, “Exploring reaction pathways using automated reaction route finders”, Invited Speaker, 244th American Chemical Society National Meeting, Philadelphia, PA, USA. August 19-23, 2012.
10. Keiji Morokuma, “Exciting World of Theoretical Studies of Chemical Reactions – From Gas Phase Reactions to Nano Structures, Catalysts, and Enzymatic Reactions”, Plenary Speaker, International Symposium on Computational Sciences (ISCS) shanghai, China, August 13-14, 2012.
11. Keiji Morokuma, “Exciting World of Theoretical Studies of Chemical Reactions – From Gas Phase Reactions to Nano Structures, Catalysts, and Enzymatic Reactions”, Departmental Invited Seminar, Institute of Theoretical Chemistry, Nanjing University, Nanjing, China, August 10, 2012.
12. K. Morokuma, “Exciting World of Theoretical Studies of Chemical Reactions – From Gas Phase Reactions to Nano Structures, Catalysts, and Enzymatic Reactions, Departmental Invited Seminar, Department of Chemistry, Sun Yat-sen University, Guangzhou, China, August 7, 2012.
13. K. Morokuma, “Exploration of reaction pathways using automatic search methods; Quantum mechanical molecular dynamics simulations of formation of carbon nano structures; ONIOM(QM:MM) approaches to chemical reactions in protein environment”, Invited Speaker, 2012 Summer School on Theoretical Chemistry, South China Normal University, Guangzhou, China, August 6, 2012.
14. K. Morokuma, “Mechanisms of Chemical Reactions of Organic and Biomolecular Systems”, Invited Speaker, International Symposium on Quantum Mechanics and Molecular Dynamics of Organic and Biological Reactivity, UCLA, USA, June 20-23, 2012.
15. K. Morokuma, “Exciting World of Theoretical Studies of Chemical Reactions – From Gas Phase Reactions to Nano Structures, Catalysts, and Enzymatic Reactions”, Invited Speaker, International Symposium on Theoretical Chemistry in Rio: Nascimento Conference, Rio de Janeiro, BR, June 11-12, 2012.
16. K. Morokuma, “Theoretical Studies on Dynamics, Mechanism and Active Species in Luminescence and Photoconversion of Chromophores in Protein”, Invited Speaker, the 17th International Symposium on Bioluminescence and Chemiluminescence, Guelph, Canada, May 28 - June 2, 2012.
17. K. Morokuma, “Two Stories of Chemical Reactions. 1. Exploring Reaction Pathways Using Automated Reaction Route Finders. 2. Nucleation, Growth and Healing Processes of Single-Walled Carbon Nanotubes”, Invited Speaker, AFOSR Contractors’ Meeting on Molecular Dynamics and Theoretical Chemistry, Arlington, VA, USA, May 23-25, 2012.

5. Public talks

1. Let’s Explore the World of Chemical Reactions Using Computer (in Japanese), University Moc Lectures, Rakuhoku High School, Kyoto, November 16, 2012.

３．リサーチリーダー　Shigeyoshi SAKAKI

Research Leader, Kenichi Fukui Memorial Research Groups II

1. Summary of the research of 2012

Molecules and molecular systems which consist of transition metal element, organic moiety, non-transition metal element, and hypervalent species are attractive research targets in wide areas of chemistry. Actually, some of those molecules play important roles as metal enzymes, molecular catalysts, and molecular devices such as photo-sensitizer, molecular switch, luminescence material etc. Their functions deeply relate to their electronic structures. In this regard, we need to know the electronic structure of the complex system including transition metal element.

At the same time, those complex systems are interesting and challenging research targets from the point of view of theoretical/computational chemistry, because their electronic structures are not simple but complicated in many cases. In particular, transition metal complexes bearing large correlation effects are challenging research target even nowadays. Also, the post Hartree-Fock calculations of very big systems like metal-organic-framework and molecular crystal are still challenging. Our group is theoretically investigating those complex systems bearing complicated electronic structure.

This year, we theoretically investigated (i) two-step evaluation method of binding energy and potential energy surface of van der Waals complexes, (ii) proposal of QM/MM approach to molecular crystal, (iii) CASPT2 study of inverted sandwich complexes of 4d metals, (iv) theoretical study of abnormal three-coordinate Pt disilyl complexes, and (v) 3D-RISM-SCF study of hydrolysis of cis- and trans-platine. We wish to report summary of them.

(i) Two-Step Evaluation Method of Binding Energy and Potential Energy Surface of van der Waals Complexes

Evaluation of intermolecular distance and binding energy of van der Waals complex/cluster at ab initio level of theory are computationally demanding when many monomers are involved. Starting from MP2 energy, we reached a two-step evaluation method of binding energy of van der Waals complex/cluster through reasonable approximations;

$$BE(MP2) = BE(HF) + \Sigma_{Mi}\,\Sigma_{Mj}\,\{BE_{(Mi\text{-}Mj)}(MP2) - BE_{(Mi\text{-}Mj)}(HF)\} \quad (1)$$

$$BE(MP2.5) = BE(HF) + \Sigma_{Mi}\,\Sigma_{Mj}\,\{BE_{(Mi\text{-}Mj)}(MP2.5) - BE_{(Mi\text{-}Mj)}(HF)\} \quad (2)$$

$$BE(MP2.5) = BE(MP2) + \Sigma_{Mi}\,\Sigma_{Mj}\,\{BE_{(Mi\text{-}Mj)}(MP2.5) - BE_{(Mi\text{-}Mj)}(MP2)\} \quad (3)$$

where HF represents the Hartree-Fock calculation and Mi, Mj etc. are interacting monomers. The first term is the usual binding energy of the complex/cluster evaluated at the HF level. The second term is the sum of the differences in two-body binding energy between the correlated and HF levels of theory. This equation can be obtained by taking an reasonable approximation that the three-center and four-center two-electron integrals are small. This equation was applied to

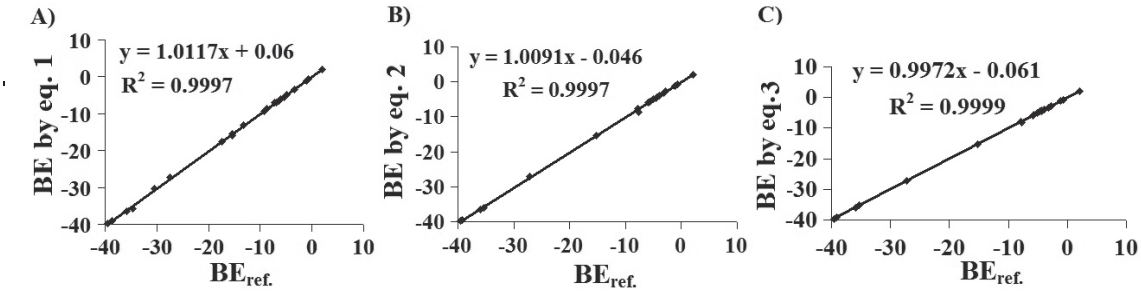
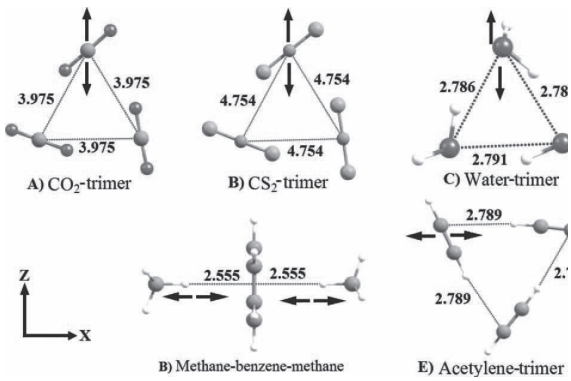


Figure 1. Comparison of Binding energy between reference value and the approximated value with eqs. 1 to3

various van der Waals complexes consisting of up-to-four monomers at MP2 and MP2.5 levels of theory. We found that this method is capable of providing precise estimate of the binding energy and reproducing well the potential energy surface of van der Waals complexes/clusters; the maximum error of the binding energy is less than 1 kcal/mol and 1% in most cases except for several limited cases.



Scheme 1. Cluster complexes examined here.

These equations are also useful for geometry optimization of molecular clusters shown in Scheme 1. The intermolecular distance is reproduced well by these approximate equations, as shown in Figure 2.

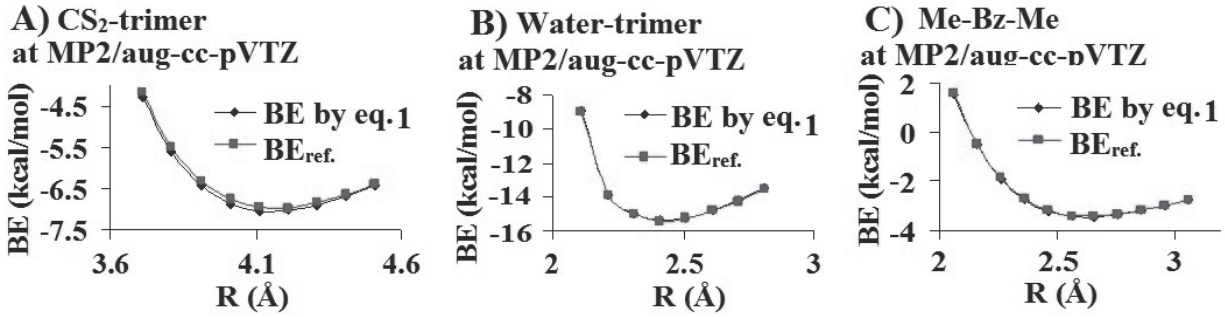
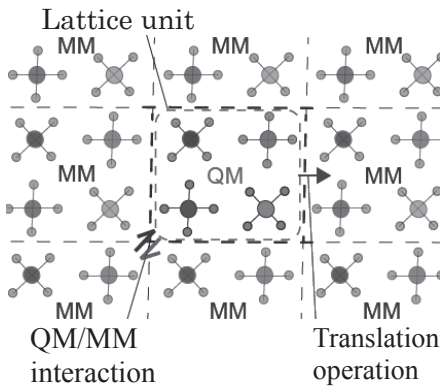


Figure 2. Comparison between optimized inter-molecular distance calculated with the approximate methods and the usual MP2 to MP2.5 methods.

(ii) Proposal of new QM/MM approach for geometry optimization of periodic molecular crystal: Self-consistent point charge representation for crystalline effect on target QM molecule

Post Hartree-Fock calculation of molecular crystal is one of the important targets for theoretical/computational study now, because many chemical issues have been reported in molecular crystals; for instance, spin transition of transition metal complex, photo-absorption and photo-emission of molecules in crystal, chemical reaction in crystal and so on. Usually, periodic calculation with DFT method is applied to such infinite systems. However, the use of functional is limited and also plane-wave basis sets are used in many calculations. Considering that we need to use various functional in DFT calculation and also the post Hartree-Fock method, we wish to propose a QM/MM method to analytically optimize structure of periodic molecular crystal. Considering that the whole crystal consists of equivalent subunits, we construct the Fock matrix and evaluate the energy derivatives under the condition that the MM charge distribution is self-consistently determined by the corresponding QM subunit. The idea is schematically shown in Scheme 2.



Scheme 2. QM and MM parts in the calculation of molecular crystal

This QM/MM approach is applied to the periodic molecular crystals of the traditional O-coordinated system, $Pt(CN)_4\,2(H_2O)$, and the untraditional H-interacted one, trans-$PtCl_2(NH_3)$(N-glycine) H_2O. The obtained molecular structures in crystal much better agree with the experimental ones than the optimized ones of the isolated cluster calculation. Here, we wish to report computational results about trans-$PtCl_2(NH_3)$(N-glycine) H_2O because

the water molecule interacts with the Pt center through H atom. This is against our expectation that water molecule interacts with the metal center through the O lone pair orbital. MP2-calculated geometry of isolated system does not agree with the experimental Pt-H distance. On the other hand, the present QM/MM approach of molecular crystal reproduces well the Pt-H distance.

(iii) Theoretical Study of Inverted Sandwich Type Complexes of 4d Transition Metal Elements: Interesting Similarities to and Differences from 3d Transition Metal Complexes

Inverted sandwich type complexes (ISTCs) of 4d metals, $(\mu\text{-}\eta^6{:}\eta^6\text{-}C_6H_6)[M(DDP)]_2$ (DDPH = 2-{(2,6-diisopropylphenyl)amino}-4-{(2,6-diisopropylphenyl)imino}pent- 2-ene; M = Y, Zr, Nb, Mo, and Tc), were investigated with DFT and MRMP2 methods, where a model ligand AIP (AIPH = (Z)-1-amino-3-imino-prop-1-ene) was mainly employed. When going to Nb (group V) from Y (group III) in periodic table, the spin multiplicity of the ground state increases in the order singlet, triplet, and quintet for M = Y, Zr, and Nb, respectively, like 3d ISTCs reported recently. This is interpreted with orbital diagram and number of d electrons. However, the spin multiplicity decreases to either singlet or triplet in ISTC of Mo (group VI) and triplet in ISTC of Tc (group VII), where MRMP2 method is employed because the DFT method is not useful here. These spin multiplicities are much lower than the septet of ISTC of Cr and the nonet of that of Mn. It is noted that when going from 3d to 4d the position providing the maximum spin multiplicity shifts to group V from group VII. These differences arise from the size of the 4d orbital. Because of larger size of 4d orbital, the energy splitting between two d_δ orbitals of M(AIP) and that between the d_δ and d_π orbitals are larger in the 4d complex than in the 3d complex. Thus, when occupation on the d_δ orbital starts, the low spin state becomes ground state, which occurs at group VI. Hence, the ISTC of Nb (group V) exhibits the maximum spin multiplicity.

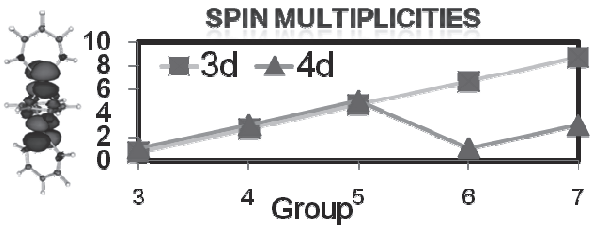
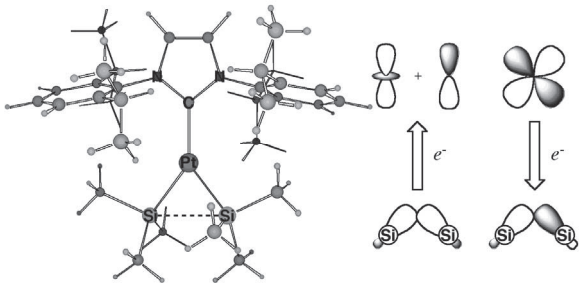


Figure 3. Changes in spin multiplicity along the periodic table in the 3d and 4d metals.

(iv) A Theoretical Study of Unusual Y-Shaped Three-coordinate Pt Complex: Pt(0) σ-Disilane Complex or Pt(II) Disilyl Complex

The unusual Y-shaped structure of recently reported three-coordinate Pt complex $Pt[NHC(Dip)_2](SiMe_2Ph)_2$ (NHC = *N*-heterocyclic carbene, Dip = 2,6-diisopropylphenyl) was considered a snapshot of reductive elimination of disilane. DFT study indicates that this structure arises from strong *trans*-influence of extremely σ-donating carbene and silyl ligands. Though this complex can be understood to be a Pt(II) disilyl complex bearing a distorted geometry due to the Jahn-Teller effect, its ^{195}Pt NMR chemical shift is considerably different from those of Pt(II) complexes but close to those of typical Pt(0) complexes. Its Si···Si bonding interaction is about 50% of the usual Si-Si single bond energy. The interaction between the Pt center and the $(SiMe_2Ph)_2$ moiety can be understood in terms of donation and back-donation



Scheme 3. Schematical representation of the interaction of the Si-Si σ-bond with the Pt d orbitals.

interactions of the Si-Si σ-bonding and σ*-anti-bonding MOs with the Pt center. Thus, it is likely concluded that this is a Pt(0) σ-disilane complex and a snapshot after the charge-transfer considerably occurs from two silyl groups to the Pt center. Phenyl anion, Ph^- and $[R\text{-}Ar]^-$ (R-Ar = C_6H_3-2,6(C_6H_3-2,6-*i*Pr_2)$_2$), and divalent carbon(0) ligand $C(NHC)_2$ also provide the similar unusual Y-shaped structure. Three-coordinate digermyl, diboryl, and silyl-boryl complexes of Pt and a disilyl complex of Pd are theoretically predicted to take the similar unusual Y-shaped structure, when a strongly donating ligand coordinates with the metal center. In a trigonal bipyramidal Ir disilyl complex $Ir(SiR_3)_2(NHC)(PH_3)_2$, the equatorial plane takes the similar unusual Y-shaped structure. These results suggest that various snapshots can be shown for the reductive eliminations of the Ge-Ge, B-B, and B-Si σ-bonds.

(v) **Evaluation Procedure of Electrostatic Potential in 3D-RISM-SCF Method and Its Application to Hydrolyses of cis- and trans-Platin　Complexes**

In 3D reference interaction site model self-consistent field (3D-RISM-SCF) method, switching function was introduced to evaluate electrostatic potential (ESP) around solute to smoothly connect the ESP directly calculated with solute electronic wavefunction and that approximately calculated with solute point charges. Hydrolyses of cis- and trans-platins, cis- and trans-PtCl2(NH3)2, were investigated with this method. Solute geometries were optimized at DFT level with the M06-2X functional and free energy changes were calculated at CCSD(T) level. In the first hydrolysis, the calculated activation free energy is 20.8 kcal/mol for cis-platin and 20.3 kcal/mol for trans-platin, which agree with the experimental and recently reported theoretical results. A Cl anion, which is formed by the first hydrolysis, somehow favorably exists in the first solvation shell as a counter anion. The second hydrolysis occurs with similar activation free energy (20.9 kcal/mol) for cis-platin but somewhat larger energy (23.2 kcal/mol) for trans-platin to afford cis- and trans-diaqua complexes. The Cl counter anion in the first solvation shell little influences the activation free energy but somewhat decreases the endothermicity in both cis- and trans-platins. The present 3D-RISM-SCF method clearly displays the microscopic solvation structure and its changes in the hydrolysis, which are discussed in detail.

2. Original papers

(1) Hisako Hashimoto, Fukuda Tetsuya, Hitomi Tobita, Mausumi Ray, and Shigeyoshi Sakaki
"Formation of a Germylyne Complex: Dehydrogenation of a Hydrido(hydrogermylene)tungsten Complex with Mesityl Isocyanate"
Angew. Chem., Int. Ed., 51, 2930-2933 (2012).

(2) Kentaro Kido, Hirofumi Sato, Shigeyoshi Sakaki
"Systematic Assessment on Aqueous pK(a) and pK(b) of an Amino Acid Base on RISM-SCF-SEDD Method: Toward First Principles Calculations"
Int. J. Quant. Chem., 112, 103-112 (2012).

(3) Milind Deshmukh, Shigeyoshi Sakaki,
"Two-step evaluation of binding energy and potential energy surface of van der Waals complexes"
J. Compt. Chem.., 33, 617-628 (2012).

(4) Yusaku I. Kurokawa, Shigeysohi Sakaki,
"Theoretical Study of Inverted Sandwich Type Complexes of 4d Transition Metal Elements: Interesting Similarities to and Differences from 3d Transition Metal Complexes"
J. Phys. Chem. A, 116, 2292-2299 (2012).

(5) Guixiang Zeng, S. Sakaki,
"Theoretical Study on the Transition-Metal Oxoboryl Complex: M-BO Bonding Nature, Mechanism of the Formation Reaction, and Prediction of a New Oxoboryl Complex"
Inorg. Chem., 51, 4597-4605 (2012).

(6) Ken Saito, Yoshinori Eishiro, Yoshihide Nakao, Hirofumi Sato, Shigeyoshi Sakaki,
"Oscillator Strength of Symmetry-Forbidden d-d Absorption of Octahedral Transition Metal Complex: Theoretical Evaluation"
Inorg. Chem., 51, 2785-2792 (2012).

(7) Noboru Takagi, Shigeyoshi Sakaki,
"A Theoretical Study of an Unusual Y-Shaped Three-Coordinate Pt Complex: Pt(0) sigma-Disilane Complex or Pt(II) Disilyl Complex?"
J. Am. Chem. Soc., 134, 11749-11759 (2012).

(8) Seiji Akatsu, Yasunori Kanematsu, Taka-aki Kurihara, Shota Sueyoshi, Yasuhiro Arikawa, Masayoshi Onishi, Shoji Ishizaka, Noboru Kitamura, Yoshihide Nakao, Shigeyoshi Sakaki, Keisuke Umakoshi,
"Syntheses and Luminescent Properties of 3,5-Diphenylpyrazolato-Bridged Heteropolynuclear Platinum Complexes. The Influence of Chloride Ligands on the Emission Energy Revealed by the Systematic Replacement of Chloride Ligands by 3,5-Dimethylpyrazolate"
Inorg. Chem., 51, 7977-7992 (2012).

(8) Yumiko Nakajima, Shigeyoshi Sakaki, Yoshihide Nakao, HIroharu Suzuki
"Theoretical Study of Dihydrogen Activation by a Trinuclear Ruthenium mu(3)-Imido Complex"
Organometallics, 31, 5342-5348 (2012).

(9) Shinji Aono, Shigeyoshi Sakaki,
"Proposal of new QM/MM approach for geometry optimization of periodic molecular crystal: Self-consistent point charge representation for crystalline effect on targetQM molecule"
Chem. Phys. Lett. 544, 77-82 (2012).

(10) Shinji Aono, Shigyeoshi Sakaki,
"Evaluation Procedure of Electrostatic Potential in 3D-RISM-SCF Method and Its Application to Hydrolyses of Cis- and Transplatin Complexes"
J. Phys. Chem. B, 116, 13045-13062 (2012).

(11) Atsushi Ishikawa, Yudai Tamura, Yoshihide Nakao, Hirofumi Sato, Shigeyoshi Sakaki,
"Complicated Electronic Process of C-C sigma-Bond Activation of Cyclopropene by Ruthenium and Iridium Complexes: Theoretical Study"
Organometallics, 31, 8189-8199 (2012).

3. Presentation at academic conferences

(1) Shinya Tsukamoto, Shigeyoshi Sakaki,
"A Theoretical Study for Solid-state Spin crossoverr of Ni(II) in N3S2 ligand field", 14th ICQC, Boulder, Corolad, USA, June 2012.

(2) Masayuki Nakagaki, Yusaku I. Kurokawa, Shigeyoshi Sakaki
"CAS-PT2 and LMO-CAS Study of Spin States and Coordination Modes of N2 bridged Inverted Sandwich Type Complexes", 14th ICQC, Boulder, Corolad, USA, June 2012.

4. Others

(1) 榊　茂好
"理論化学・計算化学は化学研究にどう役に立ったか？"
近畿化学協会第34期研修塾、2012年8月　大阪（大阪科学技術センター）

(2) 榊　茂好
"理論化学・計算化学と実験化学のインタープレイ
Riken-Spring-8 放射光連携研究ワークショップ　平成２５年１月　東京(東京大学)

(3) 榊　茂好
"巨大分子系の計算化学　超大型計算機時代の理論化学の新展開　日本化学会編　10 章 錯体触媒反応ー魅力に満ちた遷移金属化学種の世界　pp.113-122 (2012).

(4) Shigeyoshi Sakaki
"Practical Aspects of Computational Chemistry II, ED. by Jerzy Leszczynski, Moj K. Shukla, Splinger, Chap. 11, Theoretical Study of s-Bonf Activation Reactions and Catalytic Reactions by Transition Metal Complexes, pp.391-470. (2012).

４．博士研究員

Takafumi IWAKI

FIFC Fellow

1. Summary of the research of the year

Study of DNA Double Strand Breaking Produced by Ionizing Radiations

Naked DNA suffers damage from various environmental triggers. Intense light is one of such triggers, which causes breaking of DNA strands directly or through free radical production. When a pair of single-strand breakings occurs within 10 base pair distance, double-strand DNA is cut into two pieces thoroughly. It is much more difficult to repair the double strand breaks than the single-strand breaks. Thus, the double-strand breaking is regarded as a more serious problem in medical and life science. Since DNA double-strand breaks (DSBs) represent a serious source of damage for all living things, there have been many quantitative studies of DSBs both in vivo and in vitro. Despite this fact, the processes that lead to their production have not yet been clearly understood, and there is no established theory that can account for the statistics of their production, in particular, the number of DSBs per base pair per unit Gy, here denoted by P1, which is the most important parameter for evaluating the degree of risk posed by DSBs.

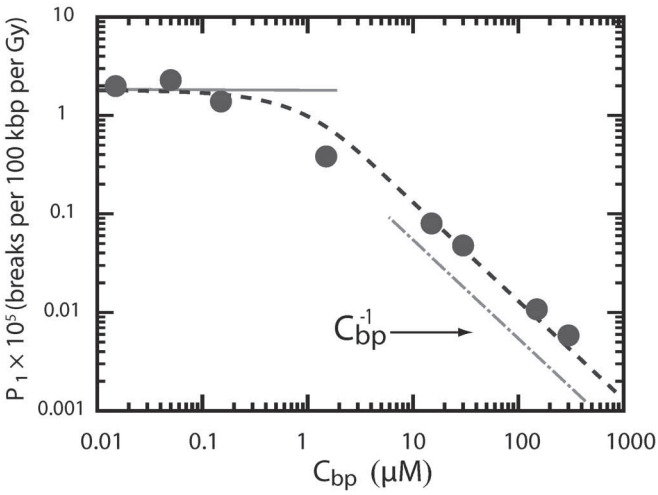


Figure 1: The number of double-strand breaks per 100 kbp per unit Gy versus base-pair concentration of DNA.

Using the single-molecule observation method with giant DNA molecules (166 kbp), we evaluated the number of DSBs caused by γ-ray irradiation for wide ranges of γ-ray intensity and DNA concentration. In an investigated region, double-strand breaking linearly scales to γ-ray intensity, which is not general in a much higher intensity region of γ-ray where double strand breaking scales to the square of the intensity. From the experiment, we found that, in the dependence of P1 to the DNA concentration, there are two characteristic regions (See Fig. 1). In a low DNA concentration region, P1 is nearly constant to the DNA concentration. On the other hand, P1 is nearly inversely proportional to the DNA concentration above a certain threshold. We calculate the probability to occur double strand breaking on the basis of a simple model, which well accounts for the marked profile of P1 over all measured region. Based on this argument, we show that it is necessary to consider the characteristics of giant DNA molecules as semiflexible polymers to interpret the intrinsic mechanism of DSBs. This work was accepted as a regular article in The Journal of Chemical Physics.

Numerical Fluid Dynamics Study of a Heated Oil Droplet on Air-Water Interface

A centimeter-sized droplet of liquid paraffin on water can be accelerated by a laser irradiation. In this scale of experiments, the origin of the migration force is attributable to the Marangoni effect: a surface force arising from a local difference of surface tensions. For example, as shown in Fig. 2, irradiation of the laser induces flows outside and inside the droplet by thermal Marangoni effect, which in turn influences a temperature distribution of the heated droplet. In actual experiments, we found that the presence/absence of surfactant (SDS) changes the migration direction to the opposite side. Since this system has a low symmetry, we performed a CFD simulation to analyze an essential mechanism of this change in the acceleration direction.

Here, we performed a numerical simulation of thermal fluid on an irregular lattice with a finite volume method. Several causes were assumed for the above-mentioned effect of SDS. For example, the difference in the shape of the droplet might have induced a different flow mode inside the droplet. Nonlinear effect of the hydrodynamics might have promoted the appearance of the different modes in similar experimental systems. These expectations were, however, denied by a sequence of simulations. We found that the migration direction changes due to the temperature coefficients of surface tensions changed by the presence/absence of SDS. The Marangoni effect on an oil droplet on an air-water interface caused by local heating induces two types of actions on the droplet. One is the viscous friction force from an external flow induced by caterpillar-like action of the droplet surface. This force always accelerates the droplet to approach a heating spot. The other is the Young force arising from a dynamical breaking of a surface tension balance in a periphery of the droplet. This force is determined by the weight of the temperature coefficient of surface tension in each of interfaces. When the magnitude relation of the temperature coefficients between air-water interface and oil surfaces reverses, the Young force changes its direction.

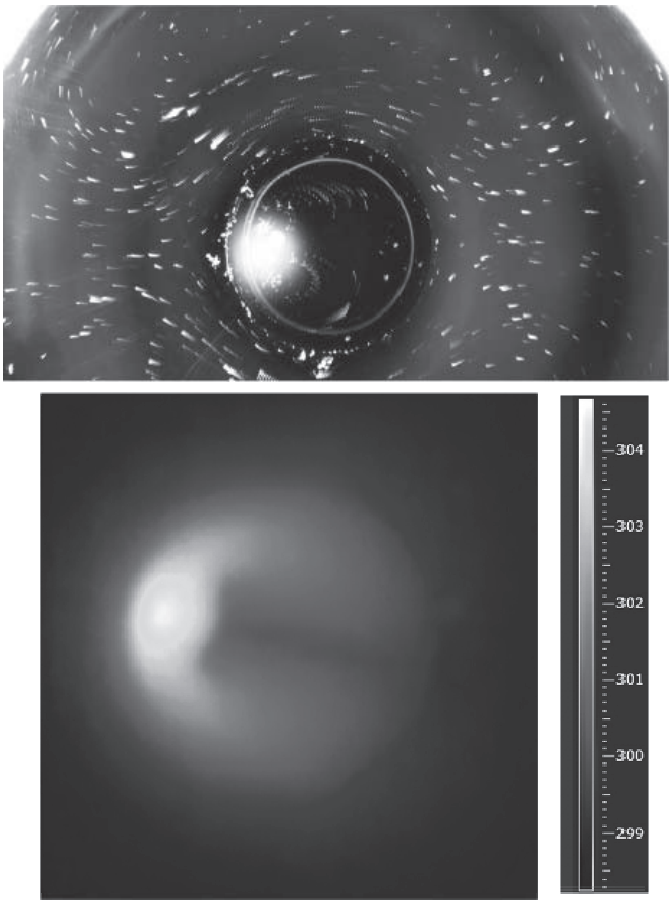


Figure 2: Flow pattern and temperature distribution of a paraffin droplet on pure water heated by a laser irradiation.

Thus, we simulated a thermal flow for two typical sets of temperature coefficients of surface tensions. Consequently, we obtained flow patterns and temperature distributions very similar to experimentally obtained ones in the presence/absence of SDS, respectively, which rationalize that the

above-mentioned mechanism is applicable to the interpretation of the experimentally observed effect of SDS. This work is now submitted to a scientific journal through several revisions.

Study of the Dynamical Mechanism of the Self-Organization of the Tooth Germ

In a development process of a tooth germ, an epithelial layer grows resulting in its invagination. A formation of an enamel knot is accompanied with this process. The enamel knot is considered to be deeply involved with the development process, but a detailed mechanism of a shape formation of the tooth germ has not been clarified. We started from a very simple numerical model of cell growth, and studied to what extent the simple physical process can control the shape of the cell system.

We performed Brownian dynamics simulations of a coarse-grained system of cell particles stochastically increasing with time. In the simulations, we found that according to the proliferation rates of the surface layer and the interior of the dental epithelial, the buckling formation undergoes several courses (See Fig. 3). In particular, when the proliferation rate of the surface layer is considerably larger than that of the interior, the bending is not uniform, and the plural buds are formed similarly to the actual development process. This fact suggests that the formation of the enamel knot is governed by a rather simple mechanical process.

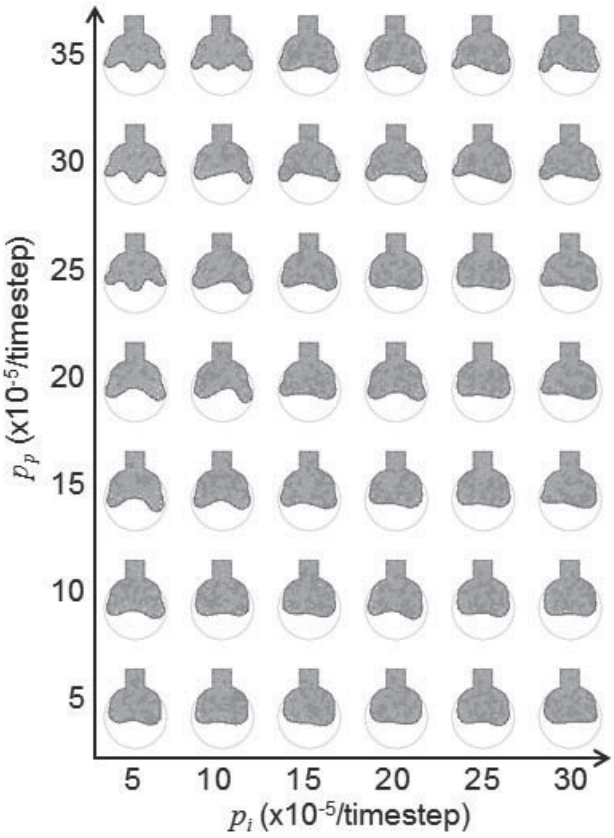


Figure 3: Diagram of final state of a growing numerical model teeth germ on a plane of inner proliferation rate and peripheral proliferation rate.

To get a further insight, we calculate the “free energy of time course” of the buckling process of an elastic continuous segment for the several given paths, and found that the shrinking speed of the end-to-end distance determines the favored type of buckling. In fact, when this speed is faster, buckling along with a growth of plural peaks is more favored. This well corresponds to the simulation result and also the actual development process. At present, we continue a discussion about interpretation of these results and applicability to an actual tooth development process. The manuscript is under preparation, which is to be submitted to a scientific journal.

2. Original papers

(1) Shunsuke F. Shimobayashi, Takafumi Iwaki, Toshiaki Mori, and Kenichi Yoshikawa, "Probability of double-strand breaks in genome-sized DNA by g-ray decreases markedly as the DNA concentration increases"
J. Chem. Phys. Accepted.

3. Presentation at academic conferences

(1) 岩城 貴史、"Path-Ensemble sampling for a folding transition of semiflexible polymer" (poster), 岩城貴史, 日本物理学会 2012 年秋季大会, Yokohama, Sep. 21, 2012

嶺澤　範行

センターフェロー

1. 今年度の研究の要約

今年度は溶液内における分子の光化学反応を解析するために、電子励起状態の自由エネルギー面を構築する新しい方法論の開発を行った。そして、時間依存密度汎関数法と積分方程式を組み合わせた計算手法を導入した。

【始めに】

光化学反応を理論的に理解するためには、電子励起状態におけるポテンシャルの極小点、遷移状態、および複数のポテンシャル面の交差点を同定する必要がある。例えば、ポテンシャル極小点の分子構造は蛍光スペクトル、ポテンシャルの交差点は無輻射遷移に関する重要な情報を含んでいる。したがって、反応機構に関する重要な知見を得るためには、これらの位置関係を求める必要がある。特に電子励起状態を記述するためには、電子相関を考慮した精密な電子状態計算の手法が求められる。

溶液内分子の記述には、溶媒効果を取り入れた電子状態計算が不可欠である。極性溶媒はイオン型の電荷分布をより安定化するため、気相中とは定性的に異なる反応機構を示すことがある。溶液内分子の記述には、ポテンシャル面よりも自由エネルギー面による議論が便利である。それは、溶媒分子の自由度が莫大なものとなり、また局所的なポテンシャル極小点も多数存在するためである。したがって自由エネルギーの計算では、溶媒分子の配置空間について十分な統計平均をとらなければならない。

【溶液内における電子励起状態の自由エネルギー面の構築】

本研究では、溶液内光化学反応を解析するために、電子励起状態の自由エネルギー面の計算手法を確立した。それは、時間依存密度汎関数法 (TDDFT) と溶媒和構造を分子論的に記述できる積分方程式 (RISM) を組み合わせた方法である (TDDFT/RISM-SCF)。RISM-SCF 法[1][2]は、溶質分子の電子状態と溶媒の動径分布関数を self-consistent になるように決定するが、分子動力学シミュレーションのような統計サンプリングが必要ないため計算コストが低くおさえられる。線形応答の枠内で

定式化することで、基底状態の平衡溶媒和の情報 (RISM-DFT) だけで励起状態の自由エネルギーが求められるようにした (図 1)。さらに、電子励起状態の自由エネルギー及びその解析的微分法により自由エネルギー面の構築を図った。enol → keto 励起状態プロトン移動反応の例として、*ortho*-hydroxybenzaldehyde (OHBA) のエネルギープロファイルを示す (図 2)。1A″ (nπ*) 状態では、溶媒効果はほとんど見られないのに対し、2A′ (ππ*) 状態では~0.1 eV の安定化が見られた。

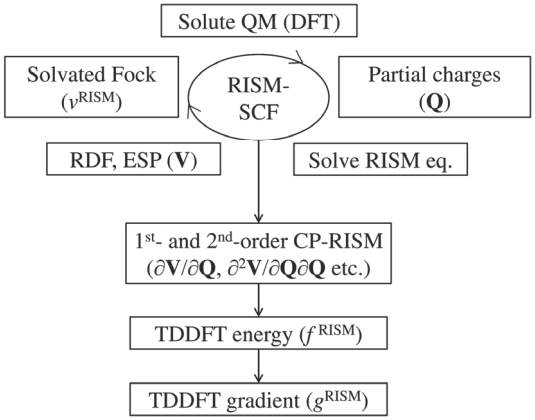


図 1 RISM-TDDFT 法の計算スキーム

今後の予定として、線形応答近似の妥当性の検証が求められる。上で述べたように、線形応答の枠組みでは励起状態の電子状態が溶媒和構造に反映されない。例えば、光誘起電子移動反応のような溶媒和構造が大きく変化する場合、基底状態の溶媒和構造は良い参照系ではなくなる可能性がある。この問題を回避するため、励起状態の電子分布を溶媒和構造に反映させる計算手法を開発中である。

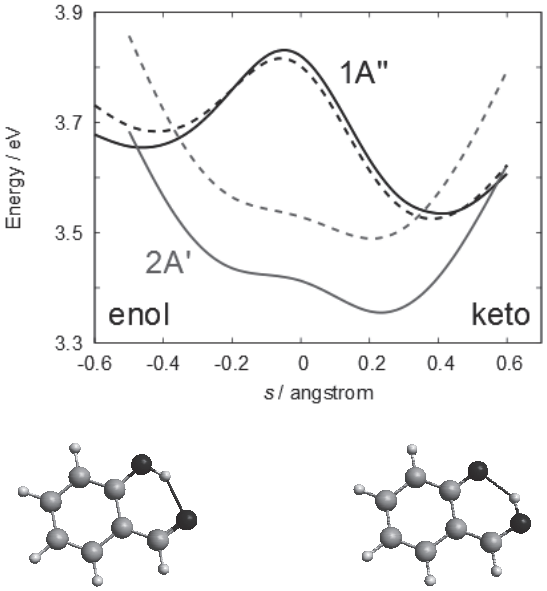


図 2 OHBA のエネルギープロファイル
実線: アセトニトリル溶液　点線: 孤立系

【溶液内における自由エネルギー面の交差領域】

本研究では、溶液内における自由エネルギーの交差点を決定する手法を確立した。自由エネルギーの交差領域は、溶液内における無輻射過程だけでなく、電子移動反応の活性化自由エネルギーを求めるうえでも重要である。今回、計算手法として spin-flip TDDFT (SFDFT) 法[3]と RISM-SCF 法を組み合わせた。SFDFT 法は、スピン反転励起に基づく TDDFT 法であり、静的電子相関を部分的にではあるが取り入れることができる。そのため、この方法は気相中における円錐交差の探索に用いられてきた[4][5]。溶液内での自由エネルギーの交差は、自由エ

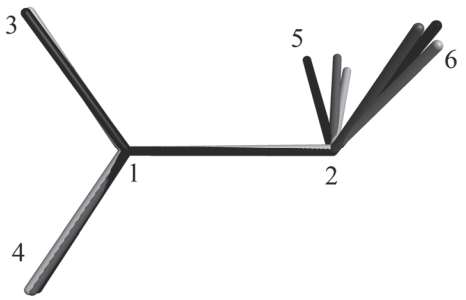


図 3 エチレンの分子構造
(黒)孤立系、(灰)アセトニトリル溶液、(薄灰)水溶液

ネルギーの極小点 (すなわち平衡溶媒和) から離れた非平衡領域でおこる。したがって、あらわに溶媒和座標に依存する、非平衡自由エネルギーを採用した[6][7]。孤立系で用いられている交差点の探索法を拡張して、溶液内での自由エネルギー交差点の分子構造を決定した。テスト計算として、交差領域でのエチレンの分子構造を求めた (図 3 および表 1)。溶媒効果により、C1-C2-H5 の角度が増加していることがわかる。これは、極性溶媒との相互作用により、分子内における大きな構造変化が溶液中では必要ないことを示唆している。

	Gas	Acetonitrile	Water
r(C1-C2)	1.388	1.394	1.410
r(C2-H5)	1.144	1.120	1.109
∠C1-C2-H5	92	103	109
∠C1-C2-H6	112	104	109
∠H5-C2-H6	91	92	101

表 1 交差領域におけるエチレンの分子構造。
結合距離(Å)、結合角(度)。

【文献】

[1] S. Ten-no, F. Hirata, and S. Kato, J. Chem. Phys. **100**, 7443 (1994).

[2] H. Sato, F. Hirata, and S. Kato, J. Chem. Phys. **105**, 1546 (1996).

[3] Y. Shao, M. Head-Gordon, and A. I. Krylov, J. Chem. Phys. **118**, 4807 (2003).

[4] N. Minezawa and M. S. Gordon, J. Phys. Chem. A **113**, 12749 (2009).

[5] N. Minezawa and M. S. Gordon, J. Phys. Chem. A **115**, 7901 (2011).

[6] S. Yamazaki and S. Kato, J. Chem. Phys. **123**, 114510 (2005).

[7] T. Mori, K. Nakano, and S. Kato, J. Chem. Phys. **133**, 064107 (2010).

2. 論文

(1) N. Minezawa and M. S. Gordon, “Optimizing conical intersections of solvated molecules: The combined spin-flip density functional theory/effective fragment potential method”, J. Chem. Phys. **137**, 034116 (2012).

(2) K. R. Brorsen, N. Minezawa, F. Xu, T. L. Windus, and M. S. Gordon, “Fragment molecular orbital molecular dynamics with the fully analytic energy gradient”, J. Chem. Theory Comput. **8**, 5008 (2012).

(3) N. Minezawa, “Excited-state free energy surfaces in solution: Time-dependent density functional theory/reference interaction site model self-consistent field method”, J. Chem. Phys., *accepted*.

(4) N. De Silva, N. Minezawa, and M. S. Gordon, “Excited state hydrogen atom transfer reaction in solvated 7-hydroxy-4-methylcoumarin”, J. Phys. Chem. B, *submitted*.

3. 学会発表

(1) 嶺澤 範行
「電子励起状態における自由エネルギー面の構築: RISM-TDDFT法」
第６回分子科学討論会　東京 2012/09/18

(2) 原渕　祐・前田　理・武次　徹也・嶺澤　範行・諸熊　奎治
「GRRM法とSF-TDDFT法を組み合わせた最小エネルギー円錐交差構造自動探索: 大きな分子への適用へ向けて」
日本化学会第９３春季年会　滋賀 2013/03/23

4. その他

(1) 嶺澤 範行
「電子励起状態における自由エネルギー面: RISM-TDDFT法」
第10回京都大学福井謙一記念研究センターシンポジウム　京都 2012/11/30

Ryuichi OKAMOTO

FIFC Fellow

1. Summary of the research of the year (3-5 pages, includes appropriate figures and tables)

Phase separation in a near-critical binary fluid mixture confined between symmetric parallel plates

We investigate phase separation of near-critical binary mixtures between parallel symmetric walls in the strong adsorption regime. We take into account the renormalization effect due to the critical fluctuations using the recent local functional theory [Okamoto and Onuki, J. Chem. Phys. 136, 114704 (2012)]. In statics, a van der Waals loop is obtained in the relation between the average order parameter □ψ□ in the film and the chemical potential when the temperature T is lower than the film critical temperature T^{c}_{ca} (See Fig. 1). In dynamics, we lower T below the capillary condensation line from above T^{c}_{ca}. We calculate the subsequent time development assuming no mass exchange between the film and the reservoir. In the early stage, the order parameter ψ changes only in the direction perpendicular to the walls. For sufficiently deep quenching, such one-dimensional profiles become unstable with respect to the fluctuations varying in the lateral d-irections. The late-stage coarsening is then accelerated by the hydrodynamic interaction. A pancake domain of the phase disfavored by the walls finally appears in the middle of the film (Fig. 2).

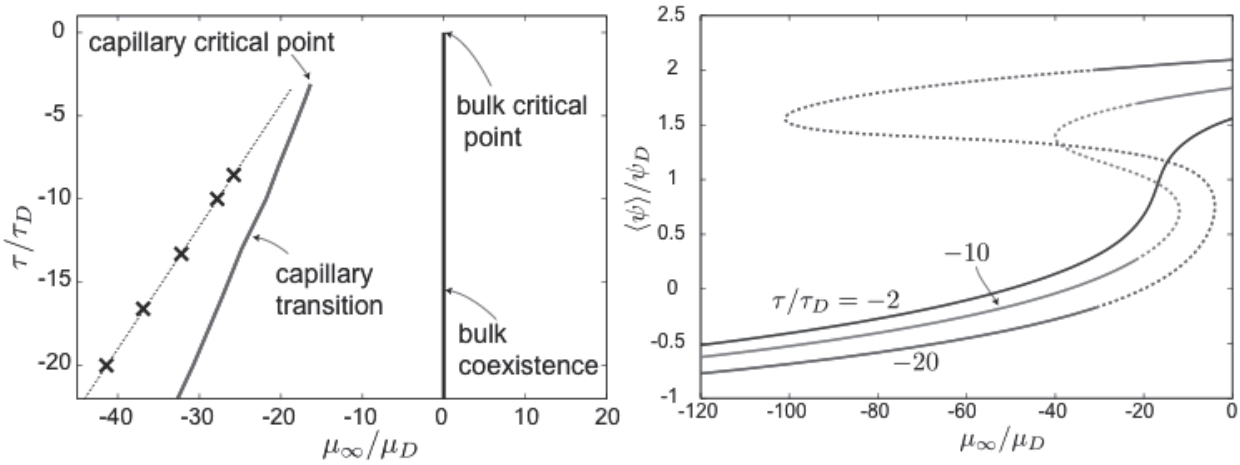


Fig. 1 (Left) Phase diagram of a near-critical fluid in a film in the temperature (τ)-chemical potential (μ_∞) plane. The bulk coexistence line is given by $\tau < 0$ and $\mu_\infty = 0$. On its left, there appears a capillary transition line (red bold line) ending at the capillary critical point, which is calculated from 1D profile. Displayed also are values of μ_∞ in steady two phase coexistence (in the film) in our 3D simulations. (Right)Isothermal curves in the μ_∞-$\langle\psi\rangle$ plane, which are calculated for 1D profiles at $\tau/\tau_D = -2$, −10, and −20. For τ less than its film critical value ($= -3.14\tau_D$), a van der Waals loop appears. Dotted parts of the curves for $\tau/\tau_D = -10$ and −20 are not stable in contact with a reservoir.

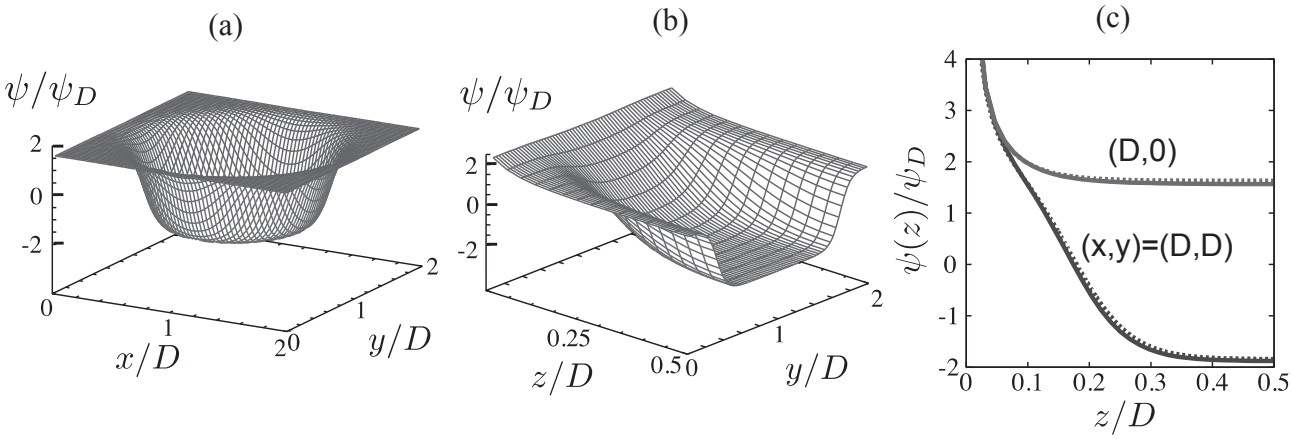


Fig. 2 Equilibrium two-phase state at $\tau/\tau_D = -20$ in a 2D × 2D × D system: Scaled order parameter ψ/ψ_D (a) in the xy plane at z=D/2 and (b) in the yz plane at x=D. (c) Scaled order paramter ψ/ψ_D along the z axis for (x,y) = (D,D) (blue bold line) and (D,0) (red bold line).

Drag coefficient of a rigid spherical particle in a binary fluid mixture: Effect of preferential adsorption on the particle surface

We calculate the drag coefficient of a rigid spherical particle in an incompressible binary fluid mixture. A weak preferential attraction is assumed between the particle surface and one of the fluid components, and the difference in the viscosity between the two components is neglected. Using the Gaussian free-energy functional, we solve the hydrodynamic equation explicitly under the condition that the particle moves with constant velocity. Near the particle surface, there appears an “adsorption layer” of the preferred component of the mixture owing to the preferential attraction. We find that the adsorption layer reduces the hydrodynamic flow near the particle from that in a one-component fluid having the same viscosity. As a result, the drag coefficient becomes larger in a binary fluid mixture. Furthermore, we can show that the preferential attraction makes the drag coefficient larger as the bulk correlation length becomes longer. The dependence of the deviation from the Stokes law on the correlation length, when it is short, turns out to be much steeper than the previous estimates.

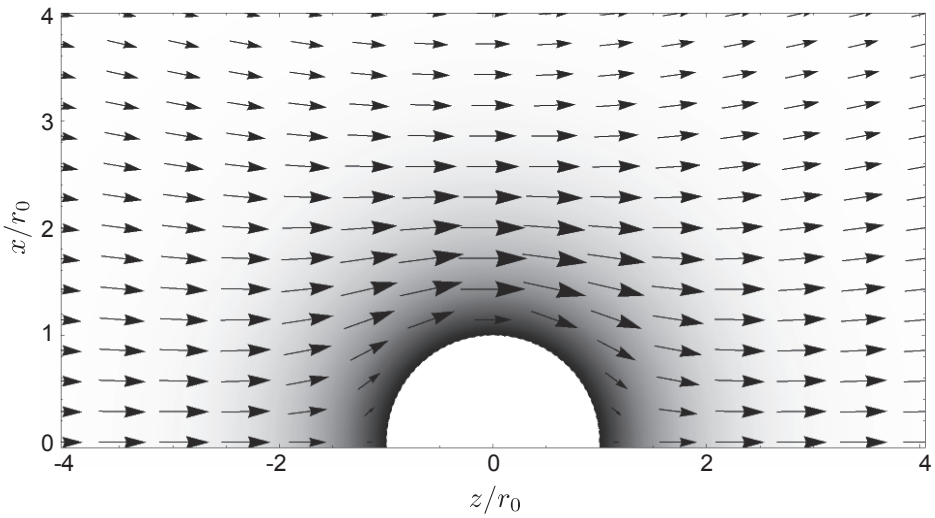


Fig. 3 The order paramter profile (gray gradation) and the deviation of the flow field from that in one-component fluid (arrows) on x-z plane. The spherical particle moves along the z-axis in negative direction.

2. Original papers

(1) Shunsuke Yabunaka, Ryuichi Okamoto and Akira Onuki
"Phase separation in a binary mixture confined between symmetric parallel plates: Capillary condensation transition near the bulk critical point"
Phys. Rev. E 87(3), 032405 (2008).

(2) Ryuichi Okamoto, Youhei Fujitani and Shigeyuki Komura
"Drag coefficient of a rigid spherical particle in a near-critical binary fluid mixture"
J. Phys. Soc. Jpn. accepted for publication.

3. Review article

(1) R. Okamoto and A. Onuki: "Solvation effects in soft matters", Physical Society of Japan **67**, 566 (2012) (in Japanese).

4. Presentation at academic conferences

(1) Ryuichi Okamoto and Akira Onuki,
"Solvation effects in soft matters" (oral)
18th Symposium on Thermophysical Properties, Boulder, CO, USA, June 25, 2012

(2) Ryuichi Okamoto and Akira Onuki
"Solvation effects on wetting on an ionizable surface" (oral, in Japanese)
Physical Society of Japan 2012 autumn meeting, Yokohama, September 20, 2012

(3) Ryuichi Okamoto and Akira Onuki
"Colloid interaction in a binary mixture solvent near criticality" (poster)
The 10th symposium of Fukui Institute for Fundamental Chemistry, Kyoto, Nov. 30, 2012.

(4) Ryuichi Okamoto and Akira Onuki
"Nanobubble stabilized by a strongly hydrophobic solute" (poster)
Self-Organization and Emergent Dynamics in Active Soft Matter, Kyoto, February 19, 2013

(5) Ryuichi Okamoto and Akira Onuki
"Stable nanobubbles induced by hydrophobic impurities" (oral, in Japanese)
Physical Society of Japan 2013 annual meeting, Higashi-Hiroshima, March 27, 2013

Takuya SAITO

FIFC Fellow
(From 1 Nov. 2012)

1. Summary of the research of the year

1. Stretching and Compression in driven polymer translocation

A single polymer transportation induced by local stimuli is a fundamental process found in technology as well as biology. One of the most studied transport processes is “driven translocation”, which is polymer passage through the pore with driving force from the cis- to the trans-sides.

In the weak force regime, the polymeric chain essentially retains the equilibrium shape in the both sides. A large asymmetric deformation, however, takes place under the strong force, so that the cis- or trans-side segments are governed by different kinds of dynamics. In the cis-side, all the chain does not respond to local stimulus at once, and a portion of those segments is largely stretched. In the course of the dynamics, the moving stretching domain grows through tension propagation along the polymeric chain. On the other hand, in the trans-side, the passed segments are compressed owing to the pushing by the force around pore so that those get decompressed outward. While the tension propagation dynamics has been recently investigated, the non-equilibrium dynamics in the trans-side is still elusive.

We investigated the driven translocation, taking account of asymmetric dynamics in the cis-/trans- sides with the help of the scaling argument.

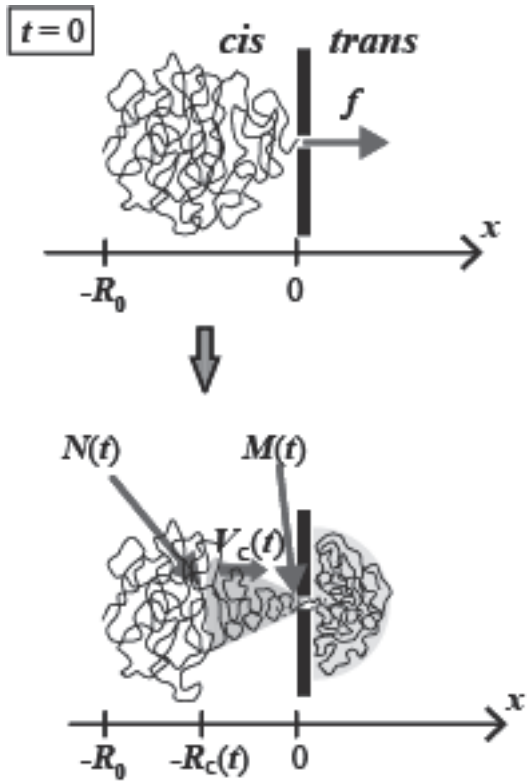


Fig. 1 Schematic representation of driven polymer translocation.

Fast/ slow diffusion

The blob picture is used as a powerful method to describe a large polymeric deformation. From the analysis based on the blob, the segment currents are found to be standardized as

$$j(\vec{x}) = -L(\vec{x})\phi_d(\vec{x})\vec{\nabla}_d\left(\frac{\partial f_d}{\partial \phi_d}\right) = -D_0\phi_d(\vec{x})^{-p_z/p_{v,d}}\vec{\nabla}_d\phi_d(\vec{x}). \qquad (1)$$

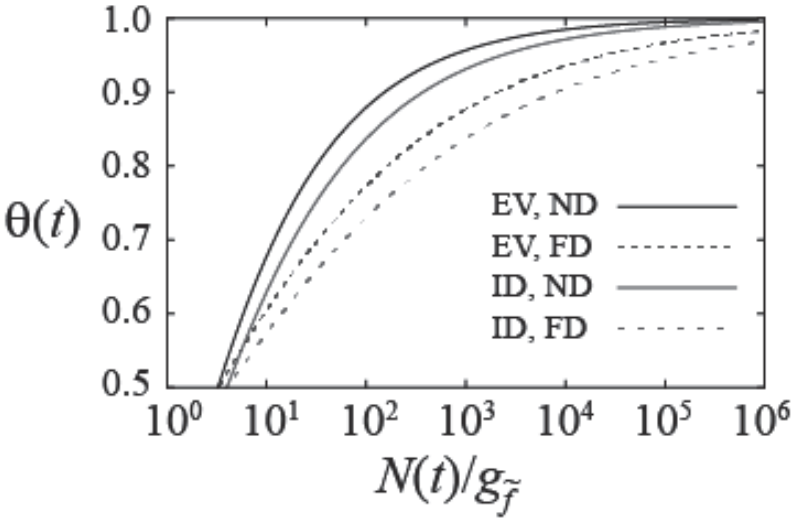


Fig. 2 Plot of a fraction of pulling force in the course of translocation $\vartheta(t) \equiv f_c(t)/[f_c(t)+f_t(t)]$ (ID: ideal chain, EV: excluded volume chain, ND: non-draiining, FD: free-draining)..

The flow form suggests the remarkable difference, i.e., the dynamics in the cis- or trans-sides are identified as fast or slow diffusion, respectively. Capturing the dominant contribution yields the dynamical equation of state for each side, which represents asymmetric transport characteristics. Using this, we obtain the force fraction $\theta(t)$ in the course of the translocation as shown in Fig. 2. This indicates the pushing force in the trans-side gets smaller with time, i.e., the cis-side dynamics eventually dominates.

2. Temporal distribution in driven polymer transportation

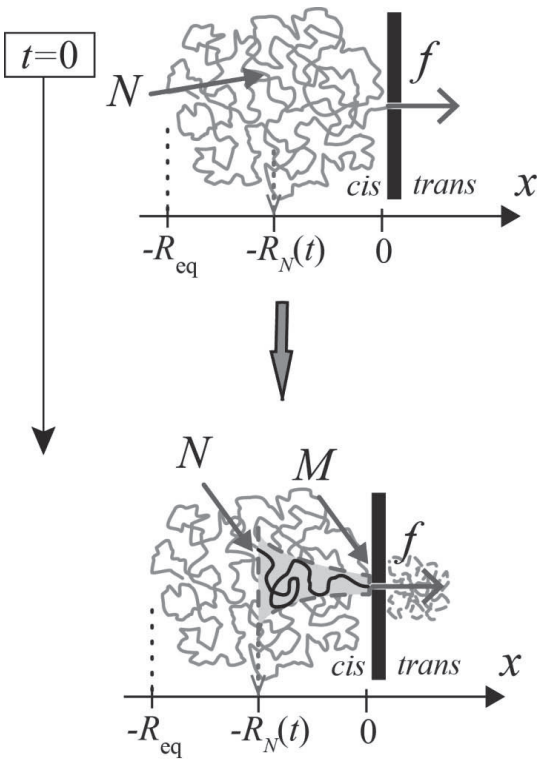


Fig. 3 Schematic representation of stochastic tension propagation along the chain.

We investigate the temporal distribution of dynamic processes in driven polymer transportation through stochastic tension propagation along polymeric chain. An entire chain does not respond to local stimulus at once, but a part of it does. The moving domain grows accompanied with the tensile force propagation along the random coiled chain so that the tension path is stochastic (Fig. 3). The stochastic tension path results in the temporal distribution of the polymer transport.

We consider the process time for two cases; (1) translocation occurs across a fixed pore and (2) stretching occurs by pulling one of the chain ends. A scaling argument for the mean and standard deviation of the process time are given by employing the two-phase picture combined with stochastic propagation. The two cases show remarkably different results. The temporal distribution of the translocation remains even in the long-chain limit, unlike that found for the dynamics of polymer stretching.

3. Stretching dynamics

We study transient dynamics of a single polymer chain, whose one chain end is suddenly pulled by a constant force. A rapidly developing technology of single macromolecule manipulation requires a paradigm research for probing far-from-equilibrium responses of long flexible polymers.

We first obtain the exact analytical results through the Rouse model. To capture more realistic situations, the excluded volume and the hydrodynamic interactions are taken into account with the help of scaling arguments, which provides various nontrivial predictions such as the force-dependent friction constants. We further find generalized dynamical equations of state to describe extension/friction laws in steady-state and the tension propagation laws during the transient process. Our results predict that the manipulation protocols make a crucial difference in the time evolutions of the dynamic friction. These remarkable results could be verified in experiments by manipulating macromolecules such as giant DNAs.

2. Original papers

(1) Takuya Saito and Takahiro Sakaue, *Phys. Rev. E* **85**, 061803 (2012).
"Process time distribution of driven polymer transport".

(2) Takahiro Sakaue, Takuya Saito and Hirofumi Wada, *Phys. Rev. E* **86,** 011804 (2012).
"Dragging a polymer in a viscous fluid: Steady state and transient".

(3) 坂上貴洋、齋藤拓也, 日本物理學會誌67(10), 705-709, 2012-10-05.
「紐状分子の非平衡ダイナミクス：細孔通過現象を中心に」

3. Presentation at academic conferences

(1) 齋藤拓也、坂上貴洋
"高分子鎖輸送過程の時間分布:分布の広がりのスケーリング"
日本物理学会 2012 年秋季大会, 横浜国立大学 2012 年 9 月 18 日.

(2) 齋藤拓也、坂上貴洋
"微細孔を通り抜ける高分子鎖のダイナミクス: 通り抜け時間の分布のスケーリング"
第十回京都大学福井謙一記念研究センターシンポジウム, 京都, 2012年11月30日.

(3) 齋藤拓也、坂上貴洋
"微細孔を通り抜ける高分子鎖のダイナミクス: 通過前後における鎖の伸張と圧縮"
日本物理学会第 68 回年次大会, 広島大学 東広島キャンパス, 2013 年 3 月 26 日.

Fu-Quan BAI

FIFC Fellow
(From 16 Apr. 2012)

1. Summary of the research of the year

electronic spectra, photophysical properties and potential energy surface conical intersection of free-base porphyrin and meso-subsitituted free-base tetratertiary-butylporphyrin

Besides planar porphyrins, nonplanar porphyrins are synthesized and also commonly found in biological systems. The out-of-plane distortion in a series of sterically-crowded porphyrins results in unusual optical properties and enhanced radiationless decay of the $^1(\pi, \pi^*)$ excited state. In particular, macrocycle distortions increase the rates of both the internal conversion and intersystem crossing decay pathways. The distortion is induced either by linking steric interactions using peripheral substitution or by the introduction of central metal ions of suitable size into the porphyrin core. This raises the possibility that the excited-state properties of the porphyrin may be adjusted step by step through introducing distortions into this tetrapyrroles skeleton. Not as the normal planar porphyrins with a minor difference in Q bands optical absorption (around 2.0 eV), fluorescence spectra as well as the $^1(\pi, \pi^*)$ lifetime of 10-15 ns, the perturbed porphyrins, such as free-base tetratertiary-butylporphyrin (**H_2T(t-Bu)P**), its absorption spectra are broader, and there is bathochromic shifts by over 0.2~0.3 eV for absorptions and emissions following the conspicuous Stokes shift. The $^1(\pi, \pi^*)$ lifetime are also extremely short based on its very low fluorescence quantum yield. The Knowledge of spectroscopic behavior and the molecular structures is needed for a deeper understanding of the inherent processes in essence to find a cause-and-effect relationship. Recently, Marian group studied the radiationless deactivation of lowest excited singlet state of planar free-base porphyrin (**H_2P**) from opening of unprotonated single pyrrole, excited-state proton transfer and vibronic spin-orbit coupling matrix elements (SOCMEs) points of view. The out-of-plane distortion of the first excited singlet state of the **H_2P** caused a significant increase of the $<T_2 |Hso| S_1>$, $<T1 |Hso| S_1>$, and $<T_1 |Hso| S_0>$ spin－orbit coupling matrix elements was concluded.

It is well known that the electronic spectra of **H_2P** have two major absorption bands, namely the weak Q band in the visible region (500–650 nm) and the strong B band (or Soret band) in the near-UV region (350–400 nm). The vertical excited state calculation from CAM-B3LYP ground state geometry by TD-CAM-B3LYP, there is an overvaluation for the B band and higher band energies for **H_2P**. Meanwhile, the TD-B3LYP based on the B3LYP ground state geometry can give rather reasonable results. From B3LYP geometry of **H_2P**, few *ab initio* methods, SAC/SAC-CI (with different levels), Configuration Interaction-singles (CIS) and with perturbative doubles correction (CIS(D)), second-order approximated Coupled-Cluster model with the resolution of identity approximation (RICC2) and spin-component scaled RICC2 (SCS-RICC2), were also adopted for achieving most accurate results. A summary of the singlet state excitation energies for **H_2P** was listed in Table 1.

Table 1. The singlet state excitation energies under different methods and the experimental spectra results of **H_2P**.

CAM-B3LYP	B3LYP	SACCI(Level 1)	SACCI(Level 3)	CIS	CIS(D)	RICC2	SCS-RICC2	Exptl. (eV)
2.20	2.26	1.67	1.69	2.39	2.46	2.30	2.13	Q_x : 1.98
2.42	2.42	2.06	2.18	2.50	2.61	2.50	2.51	Q_y : 2.42
3.55	3.30	3.41	3.41	4.44	4.13	4.38	3.45	B : 3.33
3.65	3.44	3.57	3.53	4.62	4.45	4.72	3.78	N : 3.65
4.26	3.79	4.13	4.19	5.23	4.97	5.23	4.38	L : 4.25~4.67
4.79	4.05	4.68	4.75	5.60	5.30	6.54	4.66	

The photoabsorption, fluorescence, and phosphorescence energies and related π→π* states of **H_2P** and **H_2T(t-Bu)P** and the corresponding transitions with dominant electric dipole oscillator strength values using TD-DFT and SCS-RICC2 are reported in Table 2 and 3. From Table 2 and 3, one can see that the experimental spectra are well reproduced by the present calculations but with some red shifts in wavelength for the lowest energy absorption bands (ca. 0.10~0.15 eV for RICC2 result and 0.20~0.25 eV for TDDFT). The differences between calculations and experimental data, especially the lowest excited states, not only come from methods limitations, but also include the minor deviation between the optimized molecular geometry and the experimentally observed results. Furthermore, the gratifying results have been achieved for the fluorescence, especially the phosphorescence energies with almost reproduced completely (< 0.05 eV error). Comparing with RICC2 results, the B3LYP is good at geometry optimization and same-spin state (S-S or T-T) transition calculations but more underestimate the S-T states transition energies. Since the fluorescence and the lowest-absorption have the same symmetry and transition character for **H_2P** and **H_2T(t-Bu)P**, the fluorescence may come from the lowest-energy absorptions. But the phosphorescence transition character has changed greatly comparing with the lowest-T_1-absorption for **H_2T(t-Bu)P**. The persistence of the substantial stokes shift and the transition character transformation for the **H_2T(t-Bu)P** suggests that an additional reorganization in the excited state dominates the behavior of **H_2T(t-Bu)P**.

Table 2. Photoabsorption, fluorescence, and phosphorescence energies and related π→π* states of **H_2P**.

State	TD-B3LYP/6-31+G(d,p)// TD-B3LYP/6-31+G(d,p)		SCS-CC2/def-SV(P) // TD-B3LYP/6-31+G(d,p)		
	Main configurations (|C| > 0.25)	EE(eV)	Main configurations (|C| > 0.25) [a]	EE(eV)	Exptl.
Photo absorption at the S_0 minimum structure					
S_1	+0.54 (81($5b_{1u}$)→83 ($4b_{3g}$)) +0.46 (80($2a_u$)→82($4b_{2g}$))	2.26 (<1.0×10^{-5})	+0.78 (80($5b_{1u}$)→83 ($4b_{3g}$)) +0.58 (81($2a_u$)→82($4b_{2g}$))	2.13 (1.67×10^{-3})	1.98 (Q_x) in vapor 2.02 in $CHCl_3$
T_1	+0.64 (81($5b_{1u}$)→82($4b_{2g}$)) -0.32 (80($2a_u$)→83 ($4b_{3g}$))	1.48	+0.93 (80($5b_{1u}$) →82($4b_{2g}$))	1.94	
Fluorescence at the S_1 minimum structure					
S_1	+0.55(81($5b_{1u}$)→82($4b_{2g}$)) +0.44 (80($2a_u$)→83 ($4b_{3g}$))	2.23 (1.10×10^{-3})	+0.78 (80($5b_{1u}$)→83 ($4b_{3g}$))-0.62 (81($2a_u$)→82($4b_{2g}$))	2.09 (2.09×10^{-4})	2.03 in EPA
Phosphorescence at the T_1 minimum structure					
T_1	+0.71(81($5b_{1u}$)→82($4b_{2g}$))	1.12	+0.97 (80($5b_{1u}$) →82($4b_{2g}$))	1.55	1.58 in EPA:EtI

Table 3. Photoabsorption, fluorescence, and phosphorescence energies and related π→π* states of **H_2T(t-Bu)P.**

State	TD-B3LYP/6-31+G(d,p) // TD-B3LYP/6-31+G(d,p)		SCS-CC2/def-SV(P) // TD-B3LYP/6-31+G(d,p)		
	Main configurations (|C| > 0.25)	EE(*f*)	Main configurations (|C| > 0.25) [a]	EE(*f*)	Exptl.
Photo absorption at the S_0 minimum structure					
S_1	+0.44 (145→146) +0.35 (145→147)	2.00	+0.53 (144→146) +0.46 (145→147)	1.89	1.78 (Q_x)
	-0.32 (144→147)	(9.30×10^{-3})	+0.52 (144→147) +0.44 (145→146)	(1.22×10^{-3})	
T_1	+0.50 (145→146) -0.45 (145→147)	1.13	+0.83 (144→146) -0.45 (144→147)	1.65	
			+0.26 (145→146)		
Fluorescence at the S_1 minimum structure					
S_1	-0.49 (145→146) +0.31 (145→147)	1.92	0.63 (144→146) +0.64 (145→147)	1.81	1.72
	-0.32 (144→147)		+0.34 (145→146)	(4.68×10^{-3})	
Phosphorescence at the T_1 minimum structure					
T_1	-0.71 (145→146)	-0.54	0.97 (145→146)	0.49	

Respect to the dihedral angles of N4-C9-C10-C11 in **H_2T(t-Bu)P** geometry are varied altered remarkably at different electronic states, we calculated the vertical excitation potential energies change curves in singlets and triplets for S_0, S_1 and T_1 states along the alteration of the dihedral angles of N4-C9-C10-C11. The Partial geometry optimization in each state was performed by DFT based on the fixed (N4-C9-C10-C11) in some degree. The vertical excitation energies calculations are under SCS-RICC2 level. The results are drew in Figure 1-3.

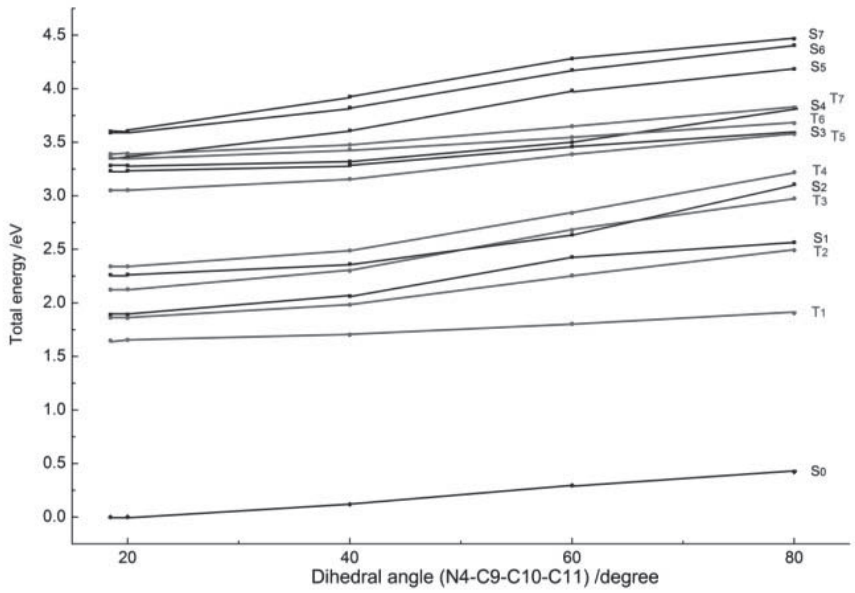


Fig. 1 the vertical excitation energy profiles of **H_2T(t-Bu)P** calculated at the ground state geometry as function of the fixed different dihedral angle (N4-C9-C10-C11).

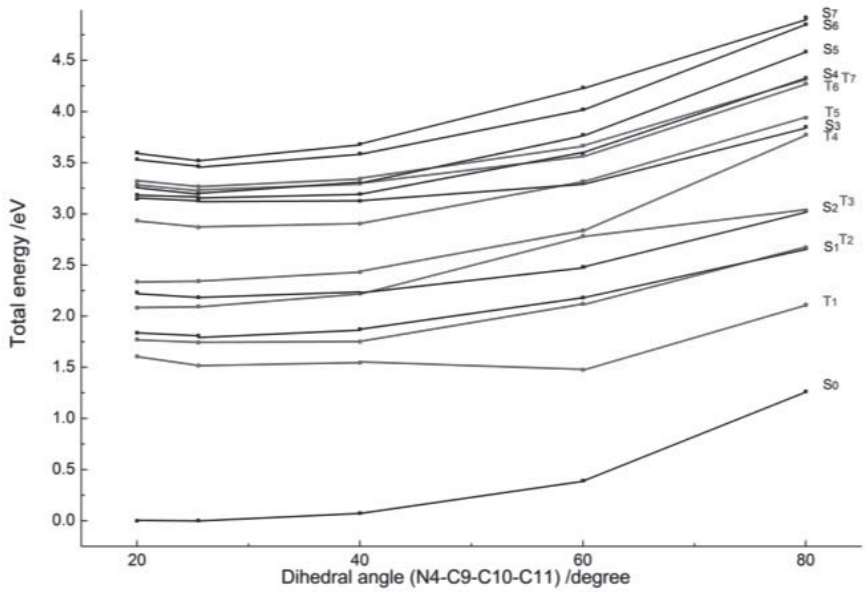


Fig. 2 the vertical excitation energy profiles of **H_2T(t-Bu)P** calculated at the S_1 geometry as function of the fixed different dihedral angle (N4-C9-C10-C11).

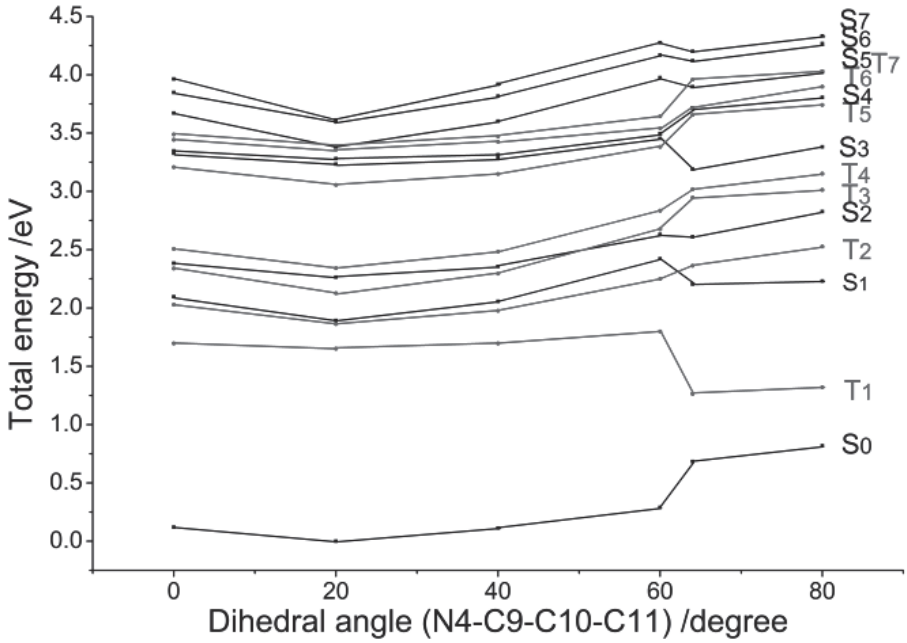


Fig. 3 the vertical excitation energy profiles of **H_2T(t-Bu)P** calculated at the T_1 geometry as function of the fixed different dihedral angle (N4-C9-C10-C11).

The various absorption bands of **H_2T(t-Bu)P** have an bathochromic shift compared to those of **H_2P.** The Stokes shift in the spectrum of **H_2T(t-Bu)P** is 2 times larger than that form **H_2P** spectrum results due to the obvious distortion of the **H_2T(t-Bu)P** geometry in the ground state and lowest excited state. The lowest triplet state excitation energy form RICC2 calculation is ca. 0.45 eV larger than the TD-B3LYP result and agree well with the spectra measurement for FBP, whereas the corresponding RICC2 value for triplet state excitation energy of **H_2T(t-Bu)P** under the TD-B3LYP first triplet excited state geometry is completely different from the TD-B3LYP excitation energy, the RICC2 value is 0.49 eV at middle infra-red region, while

the TD-B3LYP value is -0.54 eV meaning the lowest triplet state energy level lower than ground state energy level on this molecular geometry. (Require further explanation). At the excited state relaxation process of **H_2T(t-Bu)P** molecule, there are more complicated intersections of potential energy surface between their ground state and excited state as well as between different excited states. The phosphorescence of **H_2T(t-Bu)P** is ultrafast and a poor competition with nonradiative course (for example: S1→T2→T1→S0). The state-averaged multi-configurational self-consistent field (SA-MCSCF) was used for finding the conical intersection point geometry. The results of these studies indicate that the substantial bulky substituent decorated at the porphyrin periphery has an innegligible effect on the geometries and electronic spectra of **H_2P** and **H_2T(t-Bu)P** through the central porphyrin plan ruffling.

2. Original papers

(1) Qi Cao, Jing Wang, Zhao-Shuo Tian*, Zai-Feng Xie*, Fu-Quan Bai*,
"Theoretical investigation on the photophysical properties of N-heterocyclic carbene Ir (III) complexes $(fpmb)_xIr(bptz)_{3-x}$ (x=1-2)".
Journal of Computational Chemistry, 33(10), 1038-1046 (**2012**)

(2) Fu-Quan Bai, Jian Wang, Bao-Hui Xia, Qing-Jiang Pan, Hong-Xing Zhang*,
"DFT and TD-DFT study on the electronic structures and phosphorescent properties of 6-phenyl-2,2 '-bipyridine tridentate iridium(III) complexes and their isomer".
Dalton Transactions, 41(27), 8441-8446 (**2012**).

(3) Danming Chao, Xiaoteng Jia, Fu-Quan Bai, Hongtao Liu, Lili Cui, Erik B. Berda*, Ce Wang*,
"An efficient fluorescent sensor for redox active species based on novel poly(aryl ether) containing electroactive pendant".
Journal of Materials Chemistry, 22(7), 3028-3034 (**2012**).

(4) Fu-Quan Bai, Jun-ya Hasegawa,
"Computational studies of electronic spectra, photophysical properties and potential energy surface conical intersection of free-base porphyrin and meso-subsitituted free-base tetratertiary-butylporphyrin"
Manuscript in preparation.

3. Others (Participation)

(1) The 2nd International Conference on Computational and Theoretical Nanoscience -ICCTN 2013. Hong Kong, China, Mar. 1~3, 2013.
(2) The 10th Fukui Center Seminar, Kyoto, Japan, Mar. 21, 2013.
(3) Supercomputer Workshop, Okazaki, Japan, Jan.22~23, 2013.
(4) The 10th Symposium of Fukui Institute for Fundamental Chemistry, Kyoto, Japan, Nov. 30, 2012.

Jing-Dong GUO

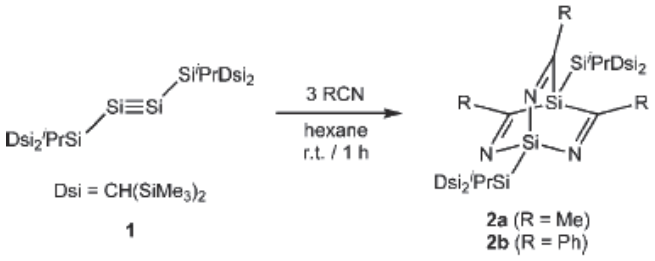
SPR Fellow

1. Summary of the research of the year

I. Theoretical study of the reaction of Disilyne with RCN (R=Me, Ph).

The silicon-silicon triple-bond disilyne **1** was reported on Science journal in 2004 by Prof. Sekiguchi group. To understand the nature of the pi bonds of the triple bond, the reactivity of the disilyne toward nitrile (Scheme 1) was investigated in experiments by the same group.

Scheme 1. Reaction of Disilyne with RCN (R=Me, Ph).



To gain a mechanistic insight, we have performed density functional calculations for the reaction of disilyne using a SiH3 group instead of $Si^iPr[CH(SiMe_3)_2]_2$ with acetonitrile by using the Gaussian 03 program.

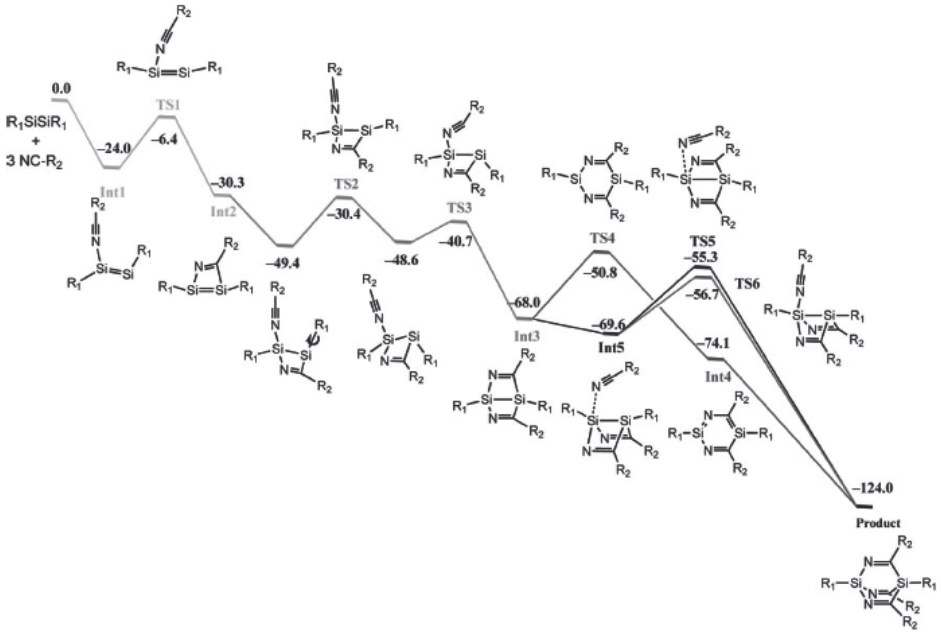


Figure 1. Potential energy profile for reaction of a simplified disilyne with acetonitrile (energy in kcal/mol; R_1=SiH_3, R_2=CH_3).

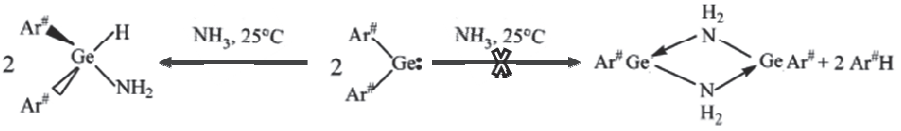
Figure 1 shows the energy profile along the reaction path calculated at the B3PW91 level using the 6-311+G(2df) basis set for Si and 6-31G(d) for all other atoms. The first step in the reaction is the interaction between the in-plane LUMO (πin*) of disilyne and the HOMO (lone pair) of the nitrile, resulting in σ-coordination to produce the disilyne-nitrile complex intermediate (**Int1**), in which the nitrile is coordinated to one of the Si centers, with a C-N bond length of 1.163 Å, which lies in the typical N-C triple-bond range (1.160 Å). Following this, intramolecular nucleophilic attack of the anionic silicon atom on the nitrile carbon atom affords the imine-bridged disilene intermediate (**Int2**), which is the result of a formal [2 + 2] cycloaddition between disilyne and nitrile. The addition of a second nitrile proceeds via a similar formal [2 + 2] cycloaddition to give a 2,6-diaza-1,4-disila-Dewar benzene-type intermediate (**Int3**), in which the regiochemistry is reflected by the polarization of the Si-Si bond of **Int2** as a result of the difference in electronegativities of the N atom and the C atom. On the other hand, a concerted pathway via [2 + 2] cycloaddition was not found.

From the 2,6-diaza-1,4-disila-Dewar benzene-type intermediate (**Int3**) to the final product, triaza-1,4-disilabicyclo[2.2.2]octa-2,5,7-triene derivatives, there are three possible pathways for the last step: path A (blue), where the pathway starts with a skeletal Si-Si bond splitting to give a 1,3-diaza-2,5-disilabenzene intermediate, followed by addition of a third nitrile; path B (black), where the pathway starts with a skeletal Si-Si bond being split with a coordinated nitrile as a ligand in the transition state; path C (purple), where the pathway starts with a skeletal Si-Si bond being split by the attack of a nitrile from above. As shown in Figure 1, the pathway involving the 1,3-diaza-2,5-disilabenzene-type intermediate (**Int4**) is less likely. Pathways B and C, which both include a complex intermediate(**Int5**), would be possible; pathway C is the most probable because the energy barrier of 12.9 kcal/mol is the lowest of the three (path A 17.2 kcal/mol, path B 14.3 kcal/mol), although the other two possibilities cannot be excluded.

II. Theoretical study of the reaction of $GeAr^{\#}_2$ with NH_3.

The reactivity of germanium (II) carbene analogue ($GeAr^{\#}_2$, $Ar^{\#}=C_6H_3$-2,6-(C_6H_2-2,4,6-$Me_3)_2$, Me: methyl group) toward NH_3 (Scheme 2) was investigated by Prof. Power group. The reaction afforded Ge(IV) tetravalent product but not Ge(II) arene eliminated product.

Scheme 2. Reaction of $GeAr^{\#}_2$ with NH_3.



To understand the phenomena observed in experiments, we carried out the calculations with the density functional theory (DFT) in the Gaussian 03 program.

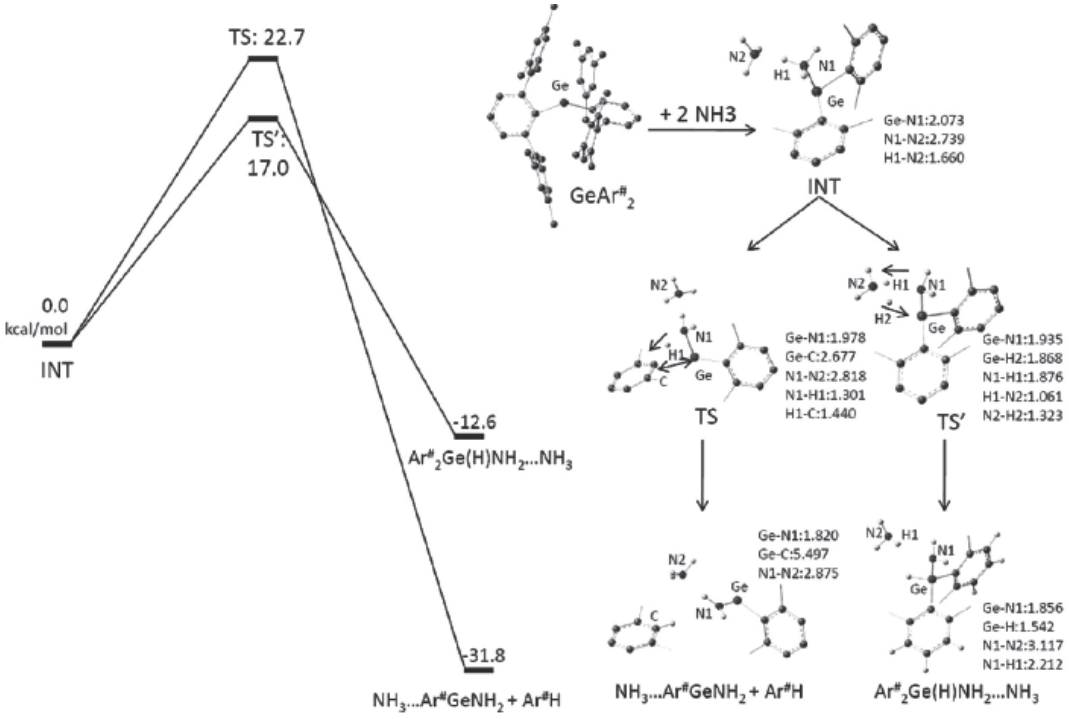


Figure 2. Calculated energy and drawings of intermediates and transition states with selected distances (Å) and angles (deg) for the reaction of $GeAr^{\#}_2$ with NH_3 at the B3PW91 level.

The DFT calculations for the reaction of $GeAr^{\#}_2$ with NH_3 indicate that the pathway involving a single NH_3 molecule had a high energy barrier. Since excess NH_3 was used in the experiment, the alternative pathway involving the participation of a second NH_3 molecule was considered in the calculations. Calculated reaction pathways for the reactions of $GeAr^{\#}_2$ and drawings of the intermediates and transition state structures are provided in Figure 2. The initial step is the interaction of a lone pair on the nitrogen of an NH_3 molecule with the 4p orbital of Ge to form the intermediate (INT) $Ar^{\#}_2GeNH_3$ complex. In the presence of excess ammonia, a second NH_3 molecule solvates the complexed NH3 via intermolecular N--

H interactions. The INT then transforms via either TS or TS' to $Ar^{\#}H$ eliminated or oxidative addition product respectively. The oxidative pathway (TS') is considerably (5.7 kcal mol-1) lower in energy than the alternative elimination pathway even though the eliminated product $Ar^{\#}GeNH_2$ + $Ar^{\#}H$ is much more energetically favored than $Ar^{\#}_2Ge(H)NH_2$. Therefore, the reaction of $Ar^{\#}_2Ge$ with NH_3 is kinetically controlled by TS' to form the Ge(IV) tetravalent product.

2. Original papers:

(1) Katsuhiko Takeuchi, Masaaki Ichinohe, Akira Sekiguchi, Jing-Dong Guo, and Shigeru Nagase,
"Reactivity of Disilyne RSiSiR (R=Si^{i}Pr[CH(SiMe$_3$)$_2$]$_2$) toward Nitriles: Unexpected Formation of Triaza-1,4-disilabicyclo-[2.2.2]octa-2,5,7-triene Derivatives"
Organometallics 28, 2658-2660(2009).

(2) Yang Peng, Jing-Dong Guo, Bobby D. Ellis, Zhongliang Zhu, James C. Fettinger, Shigeru Nagase, and Philip P. Power,
"Reaction of Hydrogen or Ammonia with Unsaturated Germanium or Tin Molecules under Ambient Conditions: Oxidative Addition versus Arene Ellmination"
J. Am. Chem. Soc. 131, 16272-16282(2009).

Peng JIN

SPR Fellow
(From 16 Apr. 2012)

1. Summary of the research of the year (3-5 pages, includes appropriate figures and tables)

Density functional theory study of fullerene–carbene Lewis acid–base adducts

When a Lewis base (LB) is combined with a Lewis acid (LA), a neutralization reaction takes place to yield a Lewis adduct by the interaction of the HOMO of LB and the LUMO of LA. Various carbon-based LBs have been reported; examples are enamines, ylides, and N-heterocyclic carbenes (NHCs). In contrast, carbon-based LAs have remained limited to date.

A recent experiment by Bazan and co-workers shows that C_{60} can act as an all-carbon LA in the reaction with a strongly dative NHC, 1,3-bis(diisopropylphenyl)imidazol-2-ylidene (IDipp), to yield the Lewis IDipp–C_{60} adduct (Fig. 1a). X-ray structural data and B3LYP density functional calculations show that the adduct has a C–C single bond between C_{60} and IDipp, in sharp contrast to the cyclopropanation reaction that usually occurs between fullerenes and carbenes or carbene surrogates. Charge distribution analysis reveals that almost one electron is transferred from IDipp to C_{60}, representing the formation of a zwitterionic adduct. Moreover, C_{70} can react with IDipp to form a single-bonded Lewis adduct in a highly selective manner (Fig. 1b). In this context, ascertaining the major driving force for the formation of the novel Lewis adducts is important.

Here, we carried out density functional theory (DFT) calculations for IDipp–C_{60} and IDipp–C_{70} adducts to expand the chemistry of fullerene-based LAs. The B3LYP/6-31G* optimized structure of IDipp–C_{60} almost has C_s symmetry. The bridging C–C bond length (R_{CC}) is 1.542 Å, indicating the formation of a typical σ single bond between IDipp and C_{60} (Fig. 1a). Intramolecular electron transfer (0.84 e) takes place from IDipp to C_{60}.

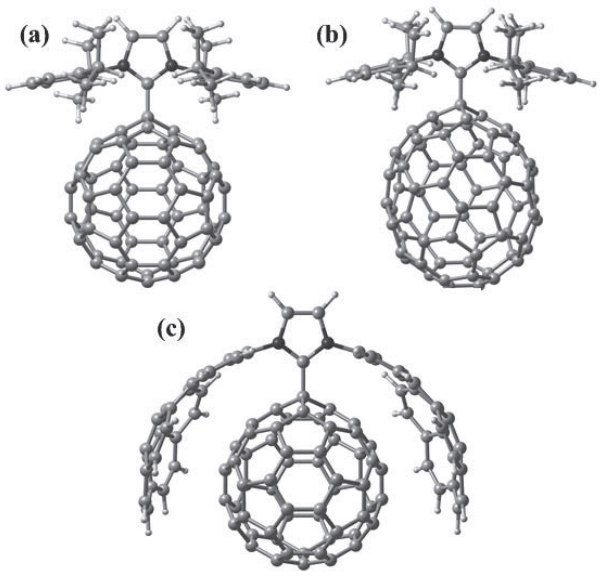
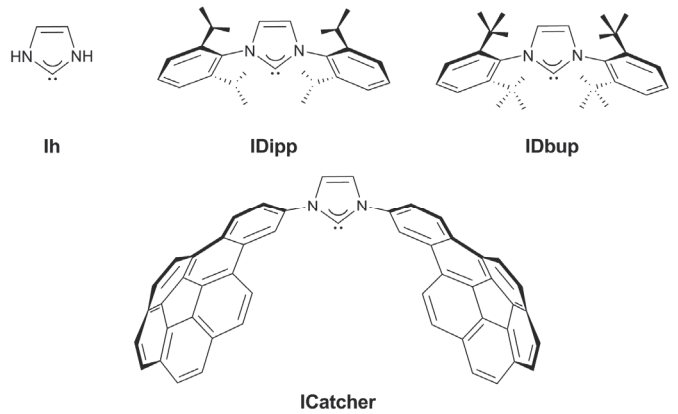


Fig. 1 Optimized structures of (a) IDipp–C_{60}, (b) IDipp–C_{70}, and (c) ICatcher–C_{60}.

Apparently, donor–acceptor interaction between IDipp and C_{60} is responsible for the binding of the adduct. Surprisingly, the energy of formation (E_f) is only 1.6 kcal/mol at the B3LYP/6-31G* level. This small E_f value might be attributed to the dominance of the steric repulsion between the bulky IDipp (especially the diisopropylphenyl groups) and C_{60}. To verify this point, the much smaller Ih in Scheme 1 was tested as LB. The R_{CC} distance of 1.504 Å calculated for Ih–C_{60} becomes shorter than that of 1.542 Å for IDipp–C_{60}. However, the calculated E_f



Scheme 1 Carbon-based Lewis bases studied in this work.

value of 10.8 kcal/mol is too small to explain the irresistible formation of LB–fullerene adducts.

Therefore, we further performed calculations using the dispersion-corrected B3LYP-D3 method. The E_f value of Ih–C_{60} was increased by 7.0 kcal/mol at the B3LYP-D3/6-31G* level. In contrast, the E_f value of IDipp–C_{60} is much more increased with the dispersion correction, which is as large as 30.6 kcal/mol at the B3LYP-D3/6-31G* level and 27.8 kcal/mol at the B3LYP-D3/6-311G(2d)//B3LYP-D3/6-31G* level. These results show the importance of dispersion attractions between IDipp and C_{60}. The R_{CC} distance of 1.527 Å calculated for IDipp–C_{60} at the B3LYP-D3/6-31G* level is closer to the distance of 1.502 Å observed for the crystal structure. The nearest distance of 3.372 Å between the two phenyl ring centers of IDipp and C_{60} suggests π–π interactions between IDipp and C_{60}. In addition, the shortest CH–C_{60} distance of 2.680 Å suggests CH–π(C_{60}) interactions.

Fig. 2 shows the energy profile for direct formation of the IDipp–C_{60} adduct by donation of the electron pair of IDipp to C_{60}. In the initial step for the addition of IDipp to C_{60}, an intermediate complex of IDipp and C_{60} is formed, which is more stabilized at the B3LYP-D3 level. The energy barrier from the intermediate to the final adduct is only 4.1 kcal/mol at the B3LYP-D3 level, indicating that the direct addition of IDipp to C_{60} proceeds much easily. The energy barrier (12.9 kcal/mol) and exothermicity (1.6 kcal/mol) calculated at the B3LYP level are considerably larger and smaller, respectively, suggesting that dispersion attractions play an important role in reducing the reaction barrier and in making the reaction much more exothermic.

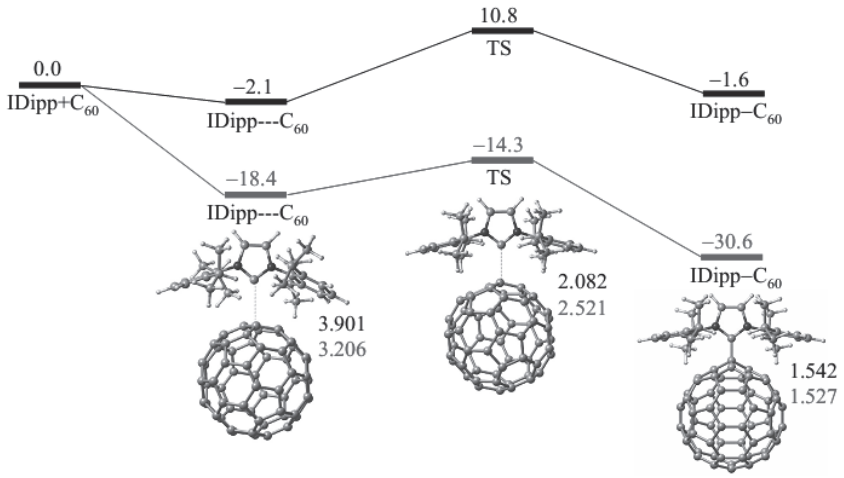


Fig. 2 Energy profiles (kcal/mol) and R_{CC} distances (Å) calculated for the addition of IDipp to C_{60} at the B3LYP/6-31G* (black) and B3LYP-D3/6-31G* (red) levels.

In an attempt to check substituent groups surrounding the imidazole ring, the bulkier IDbup in Scheme 1 was considered. The E_f value calculated for the IDbup–C_{60} adduct was only 6.8 kcal/mol at the B3LYP-D3/6-31G* level because of the steric repulsion caused by the bulkier *t*-Bu group.

To design stable LB–fullerene adducts, it is important to enhance dispersion attractions. Therefore, we considered ICatcher in Scheme 1. The R_{CC} distance calculated for ICatcher–C_{60} is 1.550 Å (Fig. 1c). The shortest distance of 3.103 Å between the corannulene carbon atoms and C_{60} suggests the presence of important π–π interactions. The electron transfer of 0.89 *e* from ICatcher to C_{60} reflects that the ICatcher–C_{60} adduct is zwitterionic, as is IDipp–C_{60}. It is interesting that the E_f value of 39.1 kcal/mol for ICatcher–C_{60} is larger than that of 30.6 kcal/mol for IDipp–C_{60} because of more effective dispersion attractions.

The C_{70} (D_{5h}) cage has five types of nonequivalent carbon atoms (denoted as 1–5 in Fig. 3). Therefore, five adducts can be formed for the addition of IDipp to C_{70}. It has been observed that IDipp attacks carbon-1 selectively to yield adduct-1 (see Fig. 3). The R_{CC} distance of 1.528 Å calculated for adduct-1 at the B3LYP-D3 level is closer to the distance of 1.503 Å observed in the crystal structure. Total electron transfer of 0.86 *e* from IDipp to C_{70} indicates that the IDipp-C_{70} adduct is zwitterionic, as is IDipp–C_{60}. As Table 1 shows, dispersion attractions are responsible for the binding of all IDipp–C_{70} adducts. However, both B3LYP and B3LYP-D3 calculations show that adduct-1 is the most stable, followed by the almost isoenergetic adduct-2, adduct-3, and adduct-4, with adduct-5 being the most unstable. These results suggest that dispersion attractions make no important contribution to the relative stability of the adducts. It is interesting to note that the LUMO distribution of C_{70} is the largest on carbon-1. In addition, carbon-1 is the most highly locally strained, as measured by the largest pyramidal angle of 11.9 °.

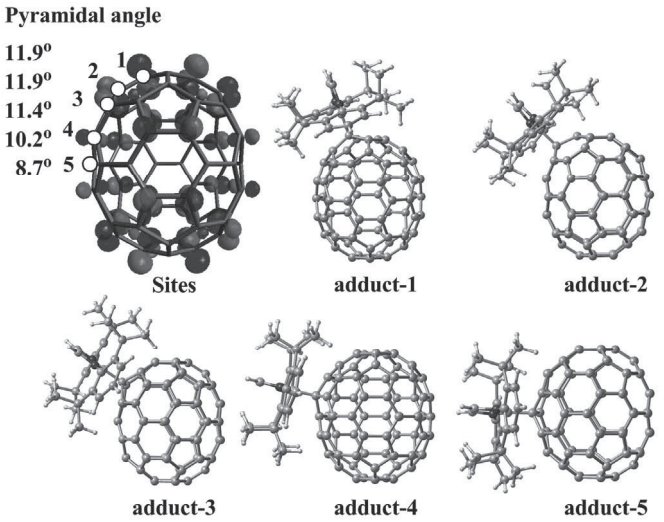


Fig. 3 Carbon sites, twofold degenerate LUMO, and pyramidal angles of C_{70} (D_{5h}) as well as five IDipp–C_{70} adducts.

Table 1 R_{CC} distances (Å) and energies of formation (E_f, kcal/mol) of five IDipp−C_{70} adducts calculated at the B3LYP/6-31G* and B3LYP-D3/6-31G* levels. Values in parentheses are relative energies.

	R_{CC}		E_f	
	B3LYP	B3LYP-D3	B3LYP	B3LYP-D3
adduct-1	1.540	1.528	5.4 (0.0)	33.9 (0.0)
adduct-2	1.542	1.530	−0.2 (5.6)	28.1 (5.8)
adduct-3	1.549	1.537	−0.4 (5.8)	28.3 (5.6)
adduct-4	1.549	1.535	−1.6 (7.0)	29.2 (4.8)
adduct-5	1.562	1.547	−13.0 (18.4)	17.8 (16.1)

In summary, we found that dispersion attractions are critical for the formation of novel carbon-based LB−fullerene adducts (IDipp−C_{60} and IDipp−C_{70}) synthesized recently, although they play no important role in the selective formation. Results suggest that a double concave catcher with a tweezers structure (ICatcher) is an interesting carbon-based LB, which embraces fullerenes. The electronic properties, geometries, and reactivities of ICatcher−fullerene adducts can be controlled by introducing substitution groups on the corannulene carbons. Introduction of bulky substituent group may lead to new carbon-based frustrated Lewis pairs. Further developments in the chemistry of carbon-based LA/LB pairs are expected.

2. Original papers

(1) Peng Jin and Shigeru Nagase
"Density Functional Theory Study of Fullerene-Carbene Lewis Acid-Base Adducts: Critical Role of Dispersion Interactions"
RSC Adv. 3(26), 10177-10180(2013).

Zhuofeng KE

FIFC Fellow, Fukui Kenchi Memorial Research Group 1

(To 31 Aug. 2012)

1. Summary of the research of the year (3-5 pages, includes appropriate figures and tables)

I. Theoretical Study of Polymerization Catalyzed by Artificial Metalloenzymes.

One of the promising strategies is to incorporate a catalytic metal complex into a host protein to construct an artificial metalloenzyme to achieve novel catalytic features in the well-defined "womb" of protein. Through genetic evolution of the protein component and chemical screening of the metal complex component, artificial metalloenzymes will provide a new horizon for application and development of catalysis. However, it is highly challenging to unveil the active site and exact reaction mechanism inside artificial metalloenzyme, due to the complicated interactions between metal complex and protein, especially when the metal complexes have variable geometries in binding sites, which is the bottleneck in its rational design. Even with some X-ray crystal structures of catalytic precursors or intermediates we are still far from understanding the catalysis process inside artificial metalloenzyme. In this study, we will clarify, with QM/MM calculations, an example of the intricate reaction mechanism of the recently developed artificial metalloenzyme system (**Rh(nbd)·*apo*-Fr**) for polymerization (Figure 1).

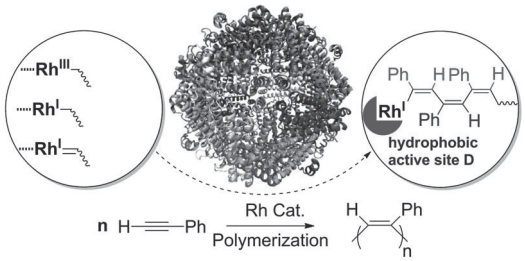


Figure 1. *The overview mechanism of the polymerization of PA in the studied artificial metalloenzyme system.*

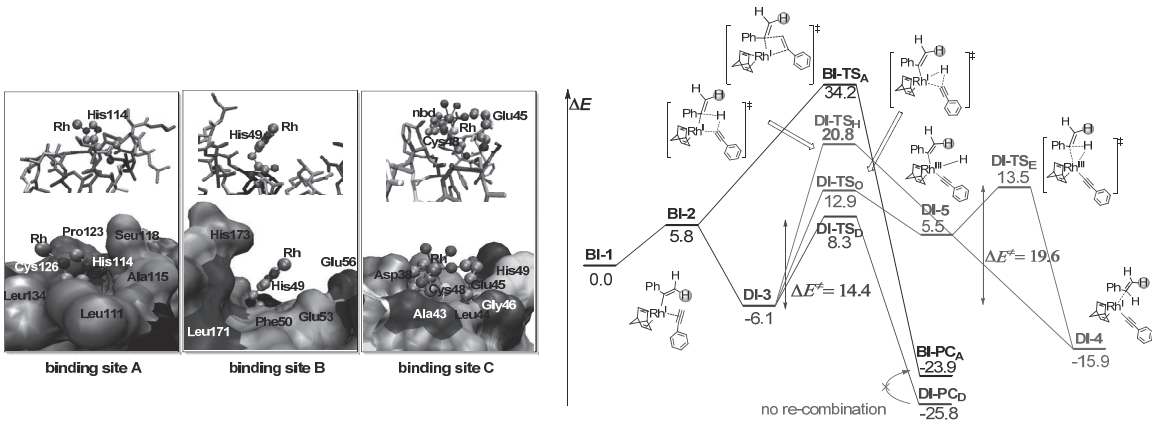


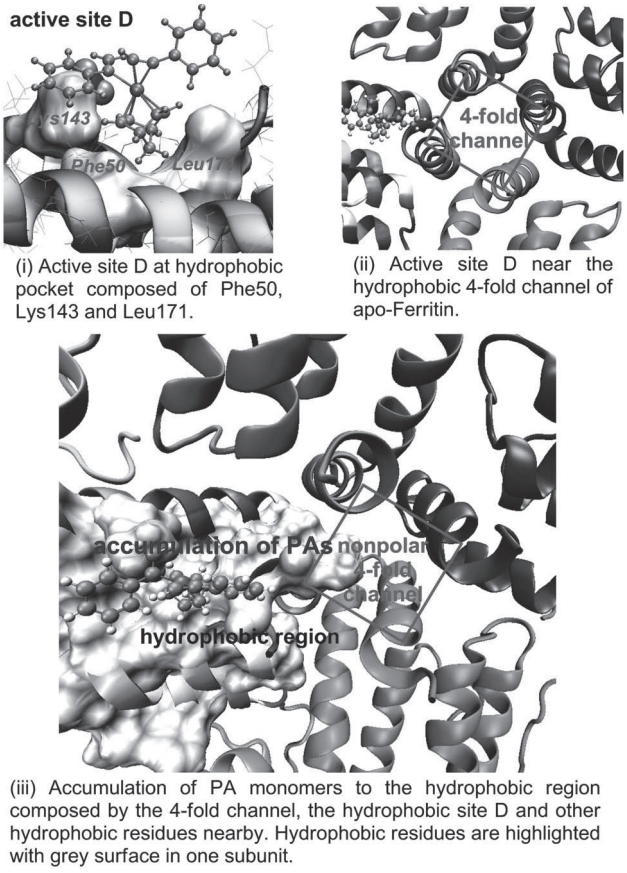
Figure 2. *The binding sites and plausible active site that promote the polymerization in **Rh(nbd)·apo-Fr**.*

Inspired by our previously studies computationally the detailed mechanism of polymerization of PA catalyzed by the homogenous catalyst $[Rh(nbd)Cl]_2$ without protein environment. (J. Am. Chem. Soc. **2011**, 133, 7926-7941), we evaluated various possible mechanisms for all binding sites suggested by the X-ray crystal structure, i.e., sites A, B, and C (Figure 2). Our QM/MM studies found that sites A, B, and C themselves are only precursors/intermediates, not true active sites for

polymerization of PA inside Rh(nbd)·apo-Fr. A new site D is suggested to be the most plausible active site for polymerization. This active site D is generated by extrusion of the RhI(PA) complex to a hydrophobic pocket near site B after coordination of first monomer PA. RhI insertion is the most plausible polymerization mechanism. The metal center does not recombine to His49 of site B even after olefin insertion, remaining in the hydrophobic pocket for further propagation. Further ONIOM calculations with 5Å solvated water shell guaranteed the reliability of former optimized results and conclusions.

The hydrophobic pocket of site D, which is composed of hydrophobic types of residues, Phe50 and Leu170, and the hydrocarbon side chain of Lys143, plays a key role for the polymerization behavior inside **Rh(nbd)·apo-Fr** (Figure 3). The hydrophobic active site D, nonpolar 4-fold channel, and other hydrophobic residues nearby constitute a specific "hydrophobic region" for accumulation, coordination, and insertion of PA during polymerization.

Notably, The ONIOM-EE calculation predicts a preference of 2,1-insertion over 1,2-insertion by 2.3 kcal/mol (Figure 4), leading to head-to-tail cis–trans PPA, suggesting that this hydrophobic active site D in the artificial



(i) Active site D at hydrophobic pocket composed of Phe50, Lys143 and Leu171.

(ii) Active site D near the hydrophobic 4-fold channel of apo-Ferritin.

(iii) Accumulation of PA monomers to the hydrophobic region composed by the 4-fold channel, the hydrophobic site D and other hydrophobic residues nearby. Hydrophobic residues are highlighted with grey surface in one subunit.

Figure 3. *The plausible active site in hydrophobic pocket near site D and the 4-fold channel.*

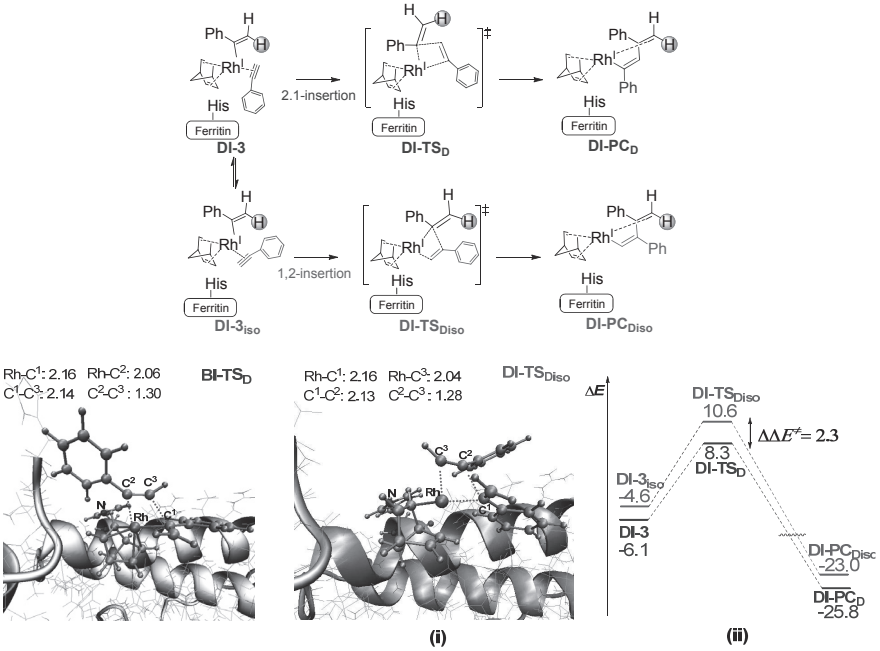


Figure 4. *The regioselectivity of the polymerization of PA in the hydrophobic active site D of Rh(nbd)·apo-Fr.*

metalloenzyme, **Rh(nbd)·apo-Fr**, well retains the regio- and stereoselectivity feature of Rh-catalyzed polymerization of PA found without the protein, which was observed in the experimental studies.

The analysis of energy changes and their major components arising from protein environment for the extrusion of Rh(PA) complex from site B (BI-2) to site D (DI-3), suggests that that the electrostatic effect contributes the most (−25.0 kcal/mol) and the vdW effect contributes the second, while polarization has some negative effect (11.5 kcal/mol) when the Rh(PA) complex moves from site B to site D (Figure 5). The vdW, electrostatic, and polarization effects from the protein environment to the selectivity are relatively small, that is why the regioselectivity can be maintained inside protein.

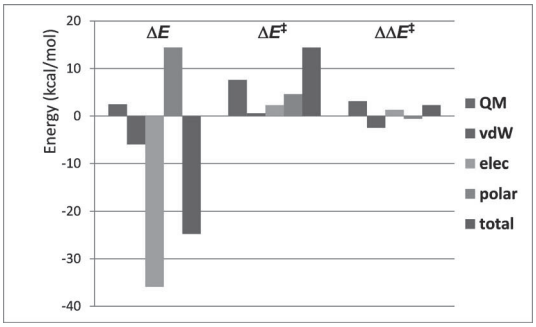
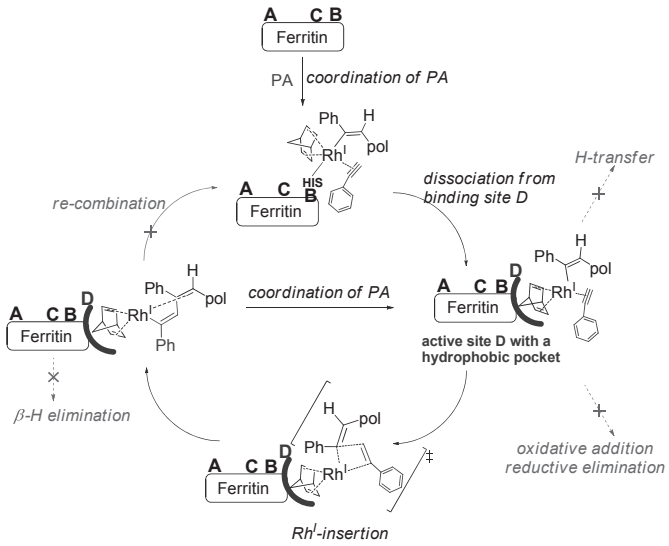


Figure 5. *The analysis of energy changes and their major components arising from protein enviroment: energy changes (ΔE) for the extrusion of Rh(PA) complex from site B (BI-2) to site D (DI-3); reaction barrier ($\Delta E^{\ddagger}$) of the RhI-insertion at DI-TSD in the active site D (relative to DI-3); the selectivity ($\Delta\Delta E^{\ddagger}$) between 2,1-insertion and 1,2-insertion in site D. QM is the deformation energy of the QM part. vdW, elect and polar are the van der Waals, electrostatic and polarization energies of the protein environment, respectively.*

Scheme 1. *The overview mechanism of the polymerization of PA in the studied artificial metalloenzyme system.*



The overall reaction mechanism is shown in Scheme 1. This study highlights the importance of theoretical study in mechanistic understanding and rational design of artificial metalloenzymes, indicating that even with X-ray crystal structures at hand we may still be far from fully understanding the active site and the catalytic mechanism of artificial metalloenzymes.

Our QM/MM study demonstrates an example of a complicated reaction mechanism of artificial metalloenzymes. Binding sites from X-ray crystal structures do not always guarantee the true active site for catalytic reaction of artificial metalloenzyme, especially when binding interactions of the metal complexes and protein can highly vary. Theoretical studies are essential in providing deeper insights to the active site and the catalytic behavior of artificial metalloenzymes. The binding and active sites are not always the same, which inspires us to believe that reactivity should be tuned based on the true active site and binding sites, on the other hand, may serve as a useful tool in improving the loading amount of catalyst. Furthermore, the hydrophobic or hydrophilic region of

the protein may have a significant influence on catalysis design.

II. Theoretical Study of Asymmetric Hydration Catalyzed by DNA-based Artificial Enzyme.

Biomacromolecule, like DNA, based catalysts recently emerges as an attractive strategy to the synthesis of enantiomerically pure compounds. Through recombination of DNA and metal complexes with a specific ligand, high stereoselectivity and rate enhancement had been achieved in several important applications, such as Diels–Alder, Michael addition, Friedel–Crafts reactions and hydration reactions. A novel non-enzymatic catalytic enantioselective hydration of enones was recently published by Ben L. Feringa, Gerard Roelfes and co-workers. The chiral beta-hydroxy ketone product was obtained in up to 82% enantiomeric excess. Importantly, this diastereospecific and enantioselective reaction had no equivalent in conventional homogeneous catalysis. Herein, our theoretical study aims to understand the mechanism and the factors that controlling the enantioselectivity, which is of fundamental important to the development of these types hybrid catalysis with DNA (Figure 6).

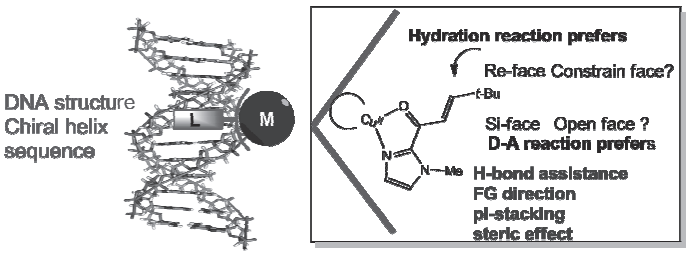


Figure 6. *The hypothesis for the origin of asymmetric hydration catalyzed by DNA-based artificial enzyme.*

Previously, our results suggested that the Cu^{II} complexes prefer five and six-coordinated structures with additional axial solvent ligands, rather than a four-coordinated square planar structure. The combination of docking and MD simulation of the binding modes and binding energies of Cu^{II} complexes to DNA molecules suggested that the intercalations insertion should be more favorable than the minor groove aggregations, and the intercalations prefer specific layer of the base pairs (Figure 7).

Figure 7. *The suggested binding modes of Cu^{II} complexes to DNA molecules.*

As for the mechanism of hydration of enones, our calculation suggested both the 1,4-addition and the 1,2-addition assisted by coordinated water are less feasible (barriers, about 30 kcal/mol), However, the hydration reaction barrier is only about 16 kcal/mol with the assistance of a deprotonated water. We constructed the initial structures on the basis of binding modes form Docking and MD simulations. Waters around the metal complex were removed, while water shell around the DNA was remained.

As shown in Figure 8, red part & one key phosphate, two additional water molecules were included as reactants, also in QM part (DFT/SDD&6-31G*); Black part, MM (gaff); DNA helix & 5A water shell MM(amber).

Our preliminary QM/MM results found that in the DNA microenvironment, the hydration of enone undergoes a mechanism similar to that of a deprotonated aqueous copper complex, with a reaction barrier of around 20 kcal/mol. Our studies imply that the acidity/basicity of the coordinated ligand or the base-pair/phosphodiester linkage may play an important role in the stereoselectivity, which is still under progress.

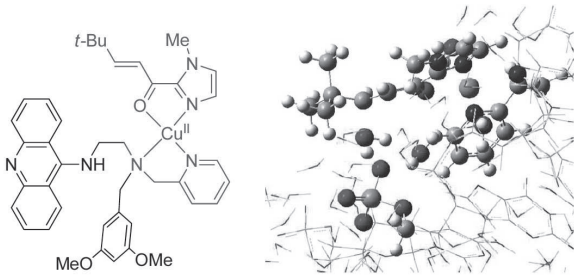


Figure 8. *Modles in ONIOM calculations..*

2. Original papers

(1) Ke, Zhuofeng, Abe, S., Ueno, T., & Morokuma, Keiji. Catalytic Mechanism in Artificial Metalloenzyme: QM/MM Study of Phenylacetylene Polymerization by Rhodium Complex Encapsulated in apo-Ferritin. *J. Am. Chem. Soc.* **2012**, 134, 15418−15429.

(2) Ye, R.-R., Ke Zhuofeng, Tan C.-P., He L., Ji L.-N. & Mao Z.-W. Histone-Deacetylase-Targeted Fluorescent Ruthenium(II) Polypyridyl Complexes as Potent Anticancer Agents. Chem. Eur. J. 19, 10160 – 10169 (2013)

(3) Liu Y., Ma L., Chen W.-H.*, Park H., Ke Zhuofeng*, & Wang B.* Binding Mechanism and Synergetic Effects of Xanthone Derivatives as Non-competitive α-Glucosidase Inhibitors: a Theoretical and Experimental Study. *J. Phys. Chem. B.* Accepted.

3. Presentation at academic conferences

(1) Ke, Zhuofeng, Abe,S., Ueno, T., Morokuma, K. "Structural control mechanism in Rh-catalyzed synthesis of pi-conjugated polymer in the nano cavity of apo-Ferritin ". *International Conference for Leading and Young Materials Scientists (IC-LYMS 2012)*, Zhuhai, China. Dec. 16-20, 2012.

(2) Liu, Z., Liu, Y., Yang, C., Zhao, C., Ke, Zhuofeng*, The Strong Effect of Weak Interaction in Asymmetric Organocatalysis. *International Symposium on Organic Reaction Mechanism*, University Town Library of Shenzhen UTSZ, China. May. 8-9, 2013.

Joonghan KIM

FIFC Fellow, Fukui Kenichi Memorial Research Group 1
(To 17 Aug. 2012)

1. Summary of the research of the year

Quantum Chemical Molecular Dynamics Simulations for Chirality-Controlled SWCNT Growth

Single-walled carbon nanotube (SWCNT) has attracted much attention for electronic and optical applications due to its fascinating physical and chemical properties. SWCNT's unique properties solely depend on its chirality. Therefore, the control of the chirality is a prerequisite condition for further applications. However, the chirality-controlled growth of SWCNT experimentally and theoretically has not been achieved yet due to its chaotic nature. Quantum chemical molecular dynamics (QM/MD) simulations based on the self-consistent-charge density-functional tight-binding (SCC-DFTB) method to investigate the chirality-controlled growth of SWCNT have been performed. All simulated trajectories are analyzed using recently developed time evolution local chirality index (TE-LOCI) method; the dynamics of local SWCNT chirality have been monitored during the growth process. The final structures of all simulated trajectories at 1 ns are shown in Figure 1. As can be seen in Figure 1, the added C atoms are adsorbed onto the Fe_{38} surface or located at the interface between SWCNT and Fe_{38} as the ingredient of SWCNT. Here we focus general growth mechanism of AC SWCNT in the case of shooting C_2 to the Fe_{38} surface. First, the added C_2 is anchored onto the Fe_{38} surface. Since the electronic temperature (T_e) is high (10000 K), the diffusion of C_2 on the Fe_{38} surface is readily takes place. Generally, C_2 remains with diffusion on the Fe_{38} surface for a long

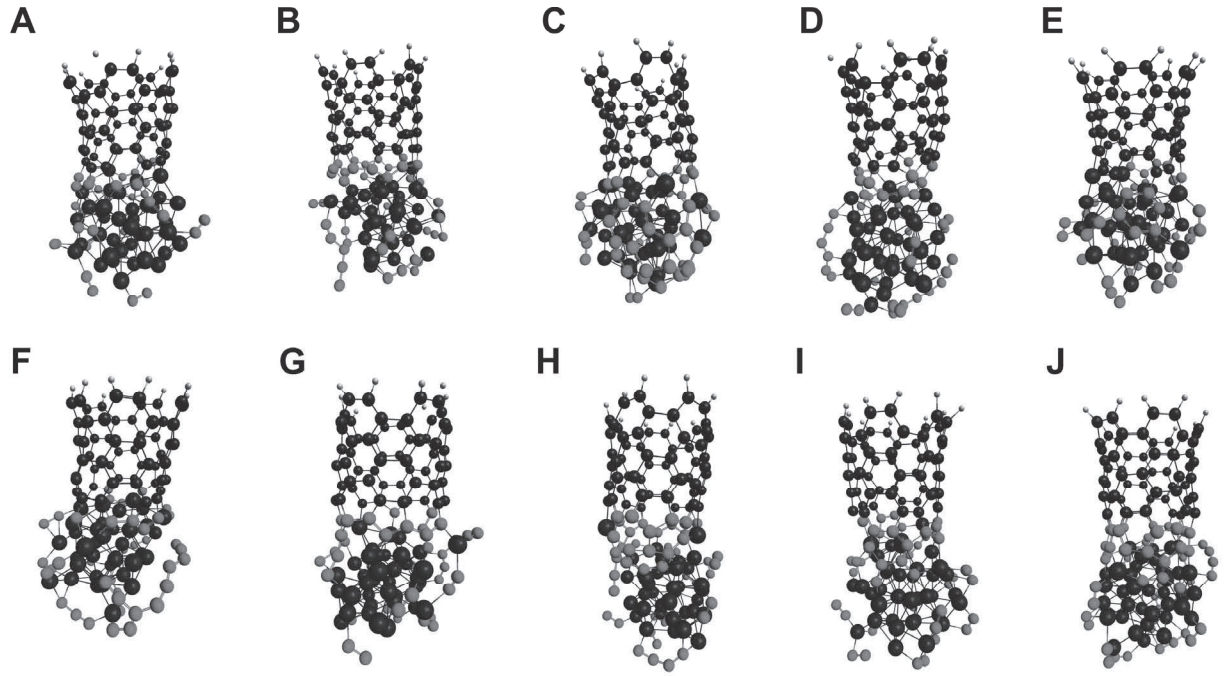


Figure 1. Snapshots of trajectories from A to J following 1 ns (1000 ps) of QM/MD growth simulations. Brown, black, white, and green spheres represent Fe, C, H, and added C atoms, respectively.

time. The diffusing C_2 molecules meet another C_2 on the Fe_{38} surface and subsequently make short polyyne chains. In another case, the diffusing C_2 is attached to the interface between SWCNT and Fe_{38}; the one side of C_2 is connected to one of Fe atom of Fe_{38} and the other is connected to one of C atom of the hexagon edge. Finally, the bond between C and Fe is broken and then a hexagon on the edge is formed. This is a basic mechanism of forming hexagon in all simulated trajectories (see Figure 2); almost all hexagons have been formed *via* this simple mechanism.

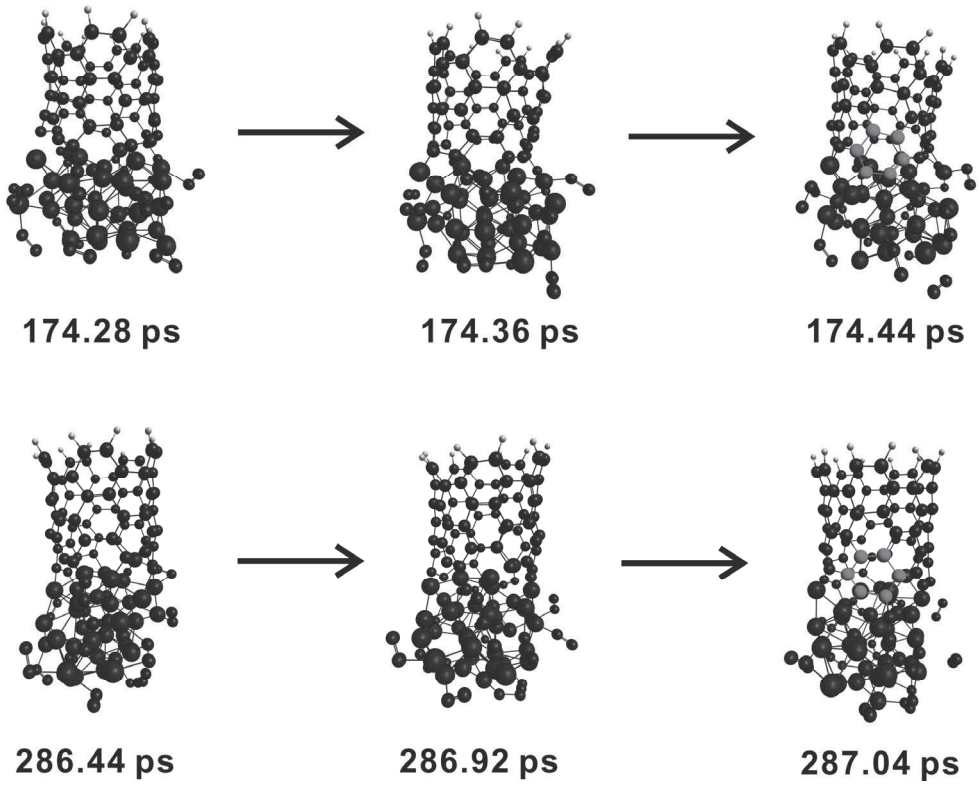


Figure 2. Reaction mechanism of formation of hexagon. The snapshots were extracted from the trajectory J.

The added C_2 molecule remains on Fe_{38} surface for a long time and frequently polyyne chains are formed. The retention time of polyyne chain on the surface is prolonged as the chain length of polyyne increases. Hence, the concentration of carbon is accumulated on Fe_{38} surface. If it is over some threshold value, a nucleation process on the catalyst surface takes place; long polyyne chains change to the polygons, in particular pentagon, *via* self-isomerization. As time passes, other polyyne chain or C_2 unit are attached to the pentagon; it eventually grows as another “cap”, carbon encapsulation. Another cap in the trajectory C (TrajC) have been reflected to increases of pentagons and hexagons. In addition, hexagon in the cap can possesses the local chirality which differs from the original one (armchair, AC in this case). TE-LOCI analysis of TrajC shows sudden broadness of standard deviation of the local chiral angles. The change of chirality (broadening standard deviation) in TrajC is ascribed to the formation of hexagons in the cap. These results indicate that occurring nucleation process hinders achievement of the chirality-controlled growth. To prevent forming new cap structure or occurring nucleation process, the concentration of carbon on the catalyst surface should be controlled. Continuous adding C_2 on the Fe_{38} surface increase the concentration of carbon and eventually leads to occurrence of nucleation and growth of another cap. Therefore, we developed

the method to maintain the concentration of carbon on the Fe_{38} surface to circumvent the occurrence of nucleation and formation of another. These two unwanted occurrence have been greatly reduced using this method; only one trajectory, TrajC with another cap structure has been observed. According to these results, keeping proper concentration of carbon on the catalyst surface should be one of prerequisites for a success of the chirality-controlled SWCNT growth.

In the earlier studies where C atom has been shot as a feedstock, formations of heptagon are considerable; the simulated all trajectories contains heptagons even using slow supply. The formation of heptagon at the edge region makes the chirality-controlled growth be more complex because heptagon at the edge changes the original chirality of SWCNT. The new added hexagon after formation of heptagon can possess other chirality. The mechanism of formation heptagon in the supplying C atom is very simple. The added C atom can readily be inserted into a hexagon due to very high reactivity of C atom. Thereby one number of the preexisted hexagon decreases, in contrast, one number of heptagon increases. Thus, total number of hexagons is smaller than that of starting SWCNT (20 in this case). This indicates that SWCNT actually does not grow in the case of supplying C atom. In contrast, formations of heptagon are not considerable in this work where C_2 has been added. In addition, it is note that no trajectory observed where the number of hexagon is less than twenty which is the number of hexagon in the starting structure of

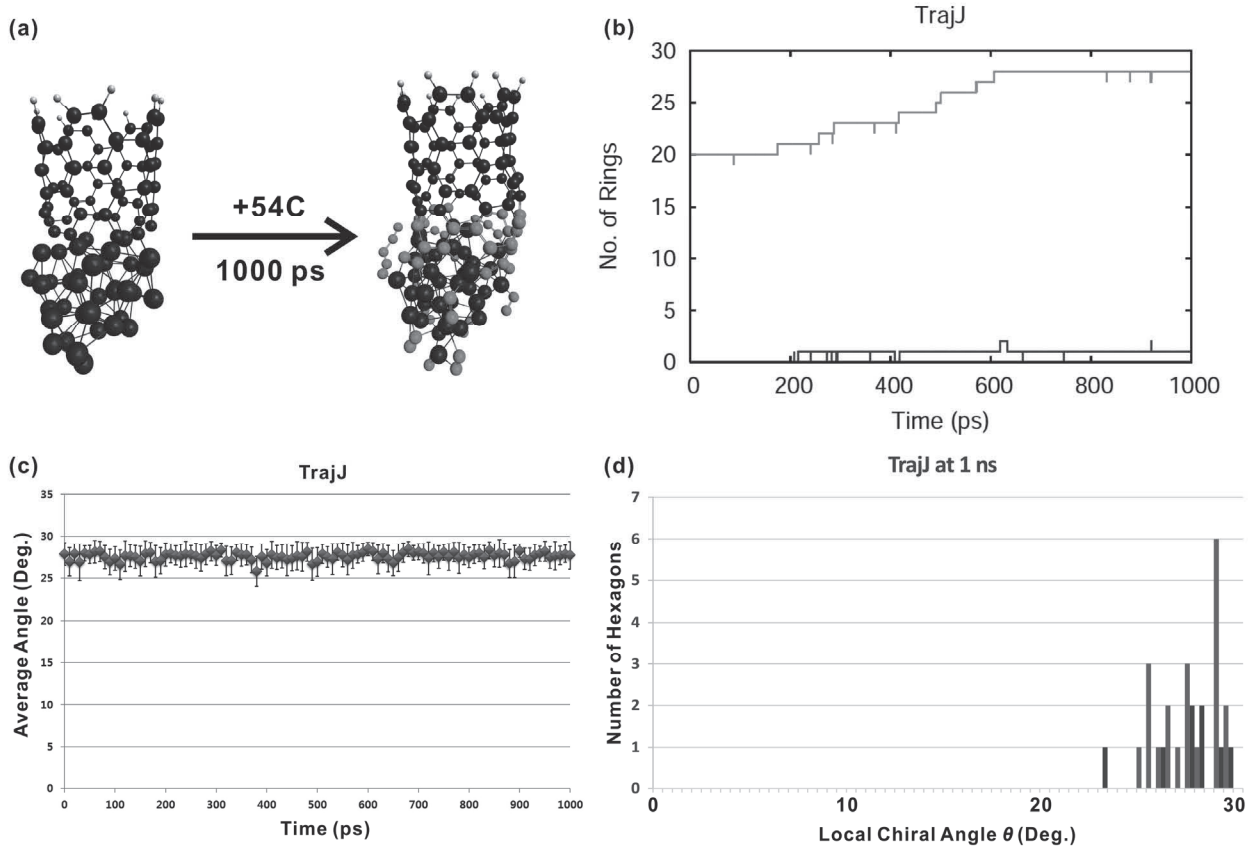


Figure 3. (a) SWCNT growth from (5,5) armchair fragment in trajectory J (TrajJ). Color scheme as in Figure 1. (b) Polygonal carbon ring populations of TrajJ. Blue, green, and red lines are pentagon, hexagon, and heptagon, respectively. (c) TE-LOCI analysis of SWCNT growth in TrajJ. The red dot is average of local chiral angle and error bar denotes its standard deviation. (d) Local chiral angles of all hexagons in TrajJ at 1 ns. Red and blue bars denote original and added hexagons, respectively.

SWCNT. These results indicate that the supplementing C_2 rather than C atom greatly reduce the formations of heptagon and it can facilitate the actual growth of SWCNT. In addition, C_2 was directed to the Fe_{38} surface instead of the edge region between nanotube and Fe_{38}. It also contribute to less formation of heptagon. If adding C_2 is directed to the edge where the reactions frequently occur, the possibility of defects formation significantly increases. These results have been already observed in the preliminary simulations of the previous study. According to these results, supplying C_2 to the catalyst surface is more appropriate for reducing defects formations, especially heptagon, thereby it will lead to achieve the chirality-controlled growth.

Polygonal carbon ring populations of TrajJ in Figure 3(b) shows that the eight new hexagons have been added to the seed nanotube; total number of hexagons is twenty eight. In addition, no fluctuation is observed in TE-LOCI plot (see Figure 3(c)). This indicates that the chirality is maintained during the growth process up to 1 ns. Indeed, as can be seen in Figure 3(d), the local chiral angles of both preexisting and newly added hexagons in the SWCNT at 1 ns are close to 30°, chiral angle of AC SWCNT. It is noteworthy that SWCNT in TrajJ shows a root growth. The five hexagons of the new eight hexagons formed from five C_2 make a new one ring of SWCNT. The proper five new hexagons provide a new one ring of AC(5,5) SWCNT. This result has not been ever achieved in the previous QM/MD simulations. In summary, TrajJ shows actual growth of SWCNT with maintaining its original AC chirality *viz*. the chirality-controlled growth. Therefore, TrajJ in this work strongly suggests the evidence that the chirality-controlled growth can be achieved. Unfortunately, the SWCNT structure of TrajJ at 1 ns contains one pentagon at the edge region between SWCNT and the Fe_{38} catalyst as shown in Figure 3(b). This pentagon formed at 215.72 ps and maintained for ~400 ps. It eventually has been removed at 633.08 ps (it does not mean the healing because the number of hexagon did not increase). However, the same kind of pentagon also formed at 618.64 ps and it remained up to 1 ns. This result implies that a removal of this kind of pentagon at the edge is very difficult task. However, consequentially, one of two these pentagons has been removed due to the catalytic effect of Fe_{38}. Therefore, if the QM/MD simulation is performed persistingly, another remained pentagon at the edge can be removed. Thereby SWCNT can grow without defects and change its original chirality, the chirality-controlled growth. According to these results, TrajJ shows the evidence of achieving the chirality-controlled SWCNT growth.

2. Original papers

(1) Joonghan Kim, Alister J. Page, Stephan Irle, and Keiji Morokuma,
"Dynamics of Local Chirality during SWCNT Growth: Armchair versus Zigzag Nanotubes", J. Am. Chem. Soc. 134, 9311 (2012)

3. Presentation at academic conferences

(1) Joonghan Kim, Alister J. Page, Stephan Irle, and Keiji Morokuma
"LOCI (Local Chirality Index) Method for Chirality-Controlled Growth of Single-Walled

Carbon Nanotubes”
14th International Congress of Quantum Chemistry (ICQC), Boulder, Colorado, USA, June 26, 2012

Alister PAGE

Fukui Fellow, Fukui Kenichi Memorial Research Group 1
(To 30 Jun. 2012)

1. Summary of the Research of the Year

(A) Graphene Nucleation on Transition Metal Surfaces

Graphene is heralded as 'the ultimate material', due to its remarkable electronic, thermal and mechanical properties. It is these properties that are the basis for many proposed graphene-based devices on the nanoscale. Earlier reports of graphene synthesis consisted of techniques such as mechanical exfoliation of highly oriented pyrolytic graphite (the 'scotch-tape method'). However, chemical-vapor deposition (CVD) synthesis of graphene, typically using transition or noble metal catalysts, is increasingly becoming the most likely candidate by which large-area graphene will be manufactured on a commercial scale. In this respect, the Ni(111) surface exhibits particular notoriety, with a number of experimental demonstrations of graphene growth on Ni(111) reported in the literature. Cu is also an increasingly popular catalyst, due to the fast growth rates and large domain sizes that can be obtained by its use. Presumably the latter phenomena are driven by the relatively weak carbon-metal interaction strength and poor bulk carbon solubility in the case of Cu. The former is also true, although to a lesser extent, in the case of Ni. On the other hand, metal surfaces such as Fe(111) exhibit notably less catalytic activity in the context of graphene nucleation, and also yield smaller domain sizes. The effect of the carbon-metal interaction strength on the mechanism and kinetics of graphene growth is therefore implicated by these CVD studies. Similar relationships have previously been observed in the context of carbon nanotube growth on transition metal catalysts. The mechanism by which discrete graphene precursor islands are converted into large-area graphene is itself unknown at present. We performed quantum chemical simulations demonstrating graphene precursor formation on bcc (111) transition metal surfaces during the chemical vapor deposition process. We observe that the experimentally reported positive curvature of graphene precursors is a consequence of the natural tendency towards pentagon formation during the precursor self-assembly process. Density functional theory calculations reveal that the stability of these precursors is driven by the dominance of metal-carbon σ bonding over metal-carbon π bonding at the precursor edge (Table 1). These simulations show that Fe(111) catalysts facilitate precursor formation at lower carbon densities, and increase precursor stabilities. However, the stronger catalyst-carbon interaction strength in the case of Fe(111) significantly promotes catalyst surface degradation. The use of more weakly interacting catalysts, such as Ni(111) and Cu(111), circumvents this issue. However, QM/MD simulations of Ni(111) catalyzed CVD show that graphene nucleation requires a significantly higher carbon density, compared to the case of Fe(111). We propose that the performance of different transition metals with respect to catalyzing graphene growth, akin to carbon nanotube growth, correlates with the catalyst-carbon interaction strength.

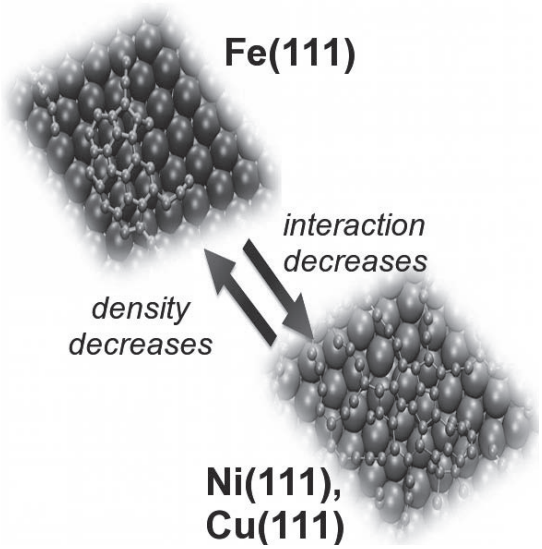


Figure 1. Quantum chemical simulations show that the mechanism of graphene growth is determined by the strength of the catalyst-carbon interaction, akin to carbon nanotube growth.

Table 1. Comparison of σ- and π- bonding between graphene and Fe(111), Ni(111) and Cu(111) surfaces in terms of binding energy (eV/carbon atom) and metal-carbon bond distances (Å, in parentheses). Binding energy is defined here as (E[M(111)-graphene] – E[M(111)] – E[graphene])/nC, for n C atoms.

	σ			π		
	Fe	Ni	Cu	Fe	Ni	Cu
DFT	2.94 (1.91)	2.76 (1.86)	2.13 (1.95)	0.27 (2.04)	0.00 (3.58)	0.00 (3.76)
DFTB	2.68 (2.13)	2.96 (2.10)	1.82 (2.26)	0.14 (2.75)	0.05 (3.03)	0.06 (3.11)

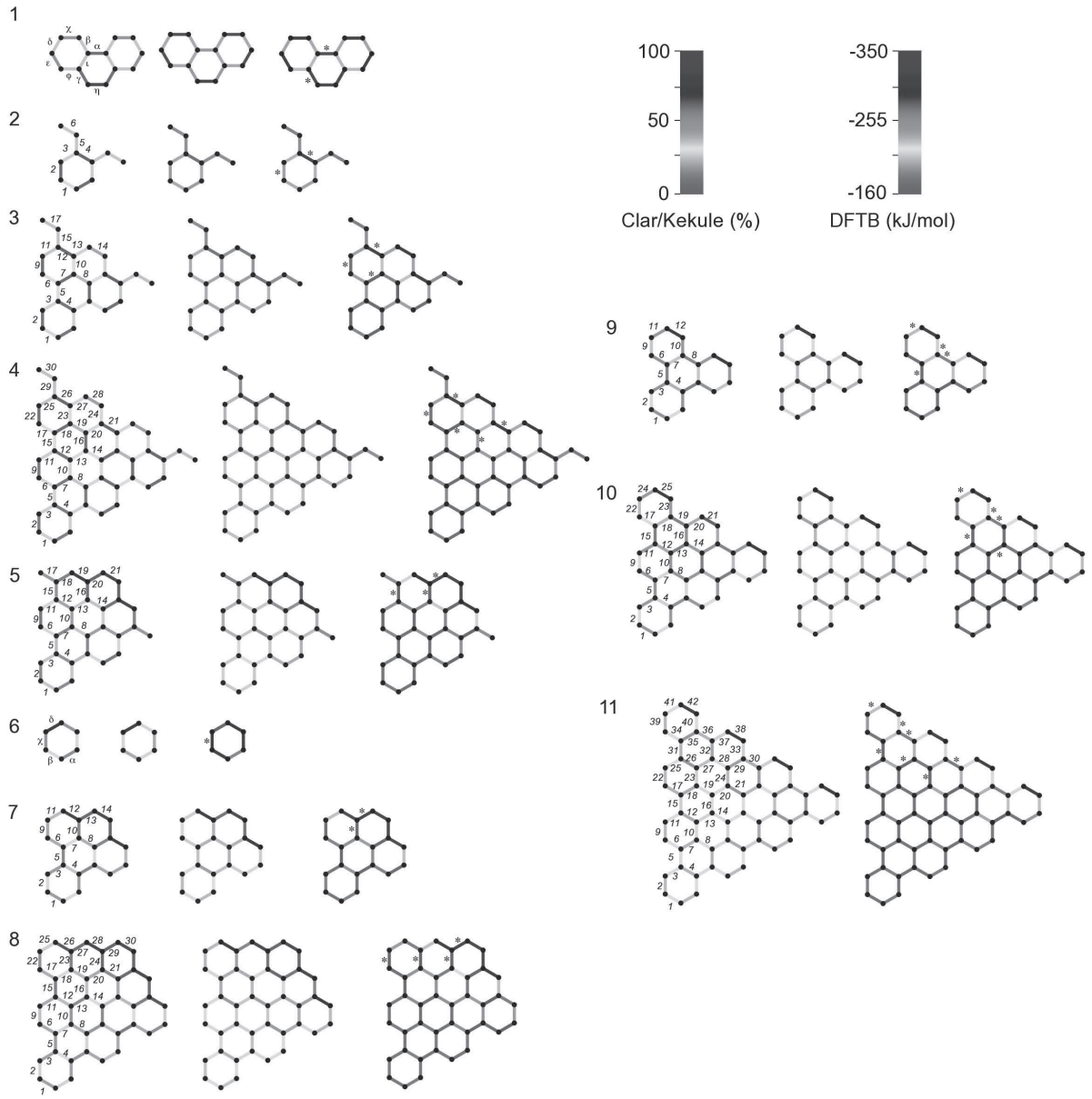


Figure 2. Comparison of Clar (left), Kekule (middle) and DFTB (right) descriptions of oxidation of HGFs **1-11**. Bonds are color-coded according to the % of conjugation remaining in the structure (Clar/Kekule) or ΔE(DFTB); DFTB data correspond to singlet-state HGF oxides. Asterisks on DFTB structures denote those positions at which oxidation leads to ether formation. No triplet-state HGF oxide **1o-11o** featured ether formation, for any oxygen position (*i.e.* oxidation at all positions resulted in epoxide formation).

(B) Simulated IR/Raman Spectra of Graphene and Graphene Oxide

Graphene and graphene oxide (GO) are currently at the forefront of modern materials science and technology. Yet it was over a century ago, in 1859, that Benjamin Brodie isolated GO for the first time *via* the exfoliation of graphite oxide. The popularity of graphene and GO today stems from their outstanding physicochemical properties, which make their application in nanoscale electronic and optical devices a potential reality. Proposed GO structures and their dynamic and chemical behavior remain controversial. Perhaps the most popular structural proposal is that by Lerf and Klinowski, which assumes epoxides and alcohols to be the main features in the graphene basal plane, leaving the carbon σ□bond network intact. Conversely, the GO structure proposed by Dekany *et al*. is dominated by ether and keto functional groups in the GO basal plane, assuming partial damage to the carbon σ□bond network. Recent experiments suggest that oxidation results in both ether and epoxy groups in the GO basal plane, with the ratio of epoxy and ether groups being dependent on the extent of functionalization. Molecular dynamics simulations suggest that epoxide groups are able to migrate on the surface even at 300 K, while other investigations point to a 'kinetically constrained' GO structure. Oxidative linear unzipping of graphenes has been deemed possible, but could not directly be confirmed in quantum chemical molecular dynamics simulations.

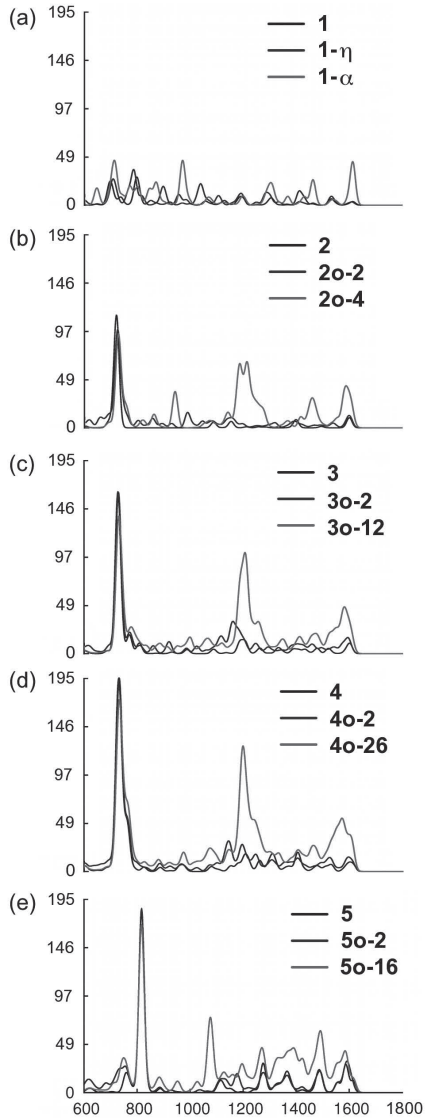


Figure 3.(a) – (e) IR spectra of isolated Clar-sextet species **1** – **5** and **1o** – **5o** between 600 – 1800 cm^{-1}. The IR spectra of species with oxygen near the edge and center of the HGF are depicted in red and blue, respectively. Spectra in black are those of the respective pristine HGFs. Position numbers are defined in Fig.1. Peak intensities (vertical axis) given in KM/mol, vibrational wavenumbers (horizontal axis) given in cm^{-1}.

We performed a detailed analysis of the factors influencing the oxidation of graphene nanoflakes using conventional density functional theory (DFT), the density-functional tight-binding (DFTB) method, graph theoretical invariants, and π□Hückel theory. The relative thermodynamic stability associated with the chemisorption of oxygen atoms at various positions on hexagonal graphene flakes (HGFs) of D_{6h}-symmetry is determined by two factors – *viz.* the disruption to the π-conjugation of the HGF, and the geometrical deformation of the HGF structure. The most thermodynamically stable structure is achieved when the former factor is minimized, and the latter factor is simultaneously maximized (Figure 2). Infrared (IR) spectra computed using DFT and DFTB reveal a close correlation between the relative thermodynamic stabilities of the oxidized HGF structures and their IR spectral activities. The most stable oxidized structures exhibit greatest IR activity between 600 – 1800 cm^{-1}, whereas less stable oxidized structures exhibit little to no activity in this region (Figure 3). This in itself reflects experimental trends in the structural evolution during the thermal reduction of GO. Finally, we note that when geometrical deformation was minimal, Hückel method and graph-theory based topological invariants effectively predicted the results gained from density functional based methods, which are more computationally expensive by two or three orders of magnitude. We believe this fact should remind the community of the physical insights that are made possible by the use of such conceptually simple techniques in the context of graphene/SWCNT functionalization.

(C) Effects of Molecular Dynamics Thermostats on Descriptions of Chemical Non-Equilibrium

The performance of popular molecular dynamics (MD) thermostat algorithms in constant temperature simulations of equilibrium systems is well known. This is not the case, however, in the context of non-equilibrium chemical systems, such as chemical reactions or nanoscale self-assembly processes. We have investigated the effect of popular thermostat algorithms on the natural dynamics of a non-equilibrium, chemically reacting system. By comparing constant-temperature quantum mechanical MD (QM/MD) simulations of carbon vapor condensation using velocity scaling, Berendsen, Andersen, Langevin and Nosé-Hoover Chain thermostat algorithms with 'natural' NVE simulations, we have shown that efficient temperature control and reliable reaction dynamics are mutually exclusive under conditions of chemical non-equilibrium, see Fig. 5. This problem may be circumvented, however, by placing the reactive system in an inert He atmosphere which is itself described using NVT MD, see Fig. 6. We have demonstrated that both realistic temperature control and dynamics consistent with natural NVE dynamics can then be obtained simultaneously. In essence, the thermal energy created by the natural dynamics of the NVE subsystem is drained by the thermostat acting on the NVT atmosphere, without adversely affecting the dynamics of the reactive system itself.

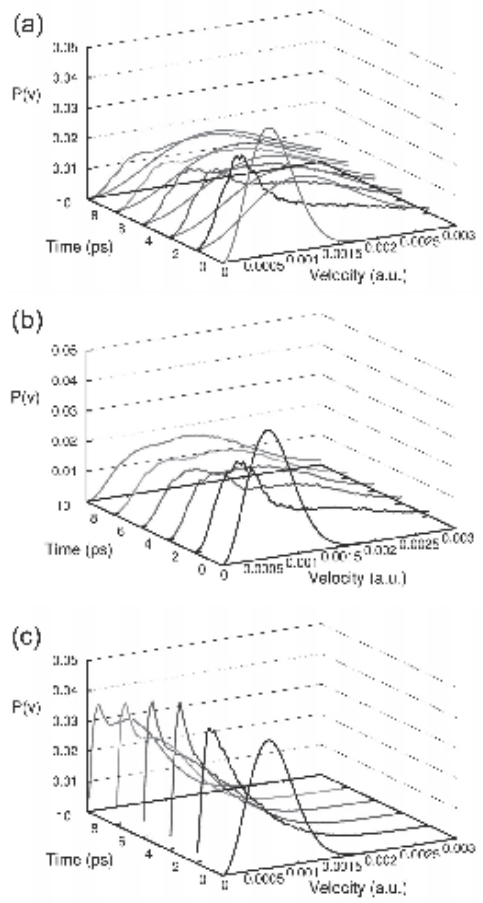


Fig 5. Comparison of time-dependent velocity distributions of a reactive C_2 system using (a) NVE C_2 and a Nosé-Hoover Chain thermostat coupled (b) strongly (ω = 188.37 ps^{-1}) and (c) weakly (ω = 0.19 ps^{-1}) to the degrees of freedom of the system. For reference, time-dependent Maxwell-Boltzmann velocity distributions at the corresponding NVE MDsimulation temperatures are included in (a) (grey lines). Temperature control comes at the cost of sacrificing a reliable description of the 'natural' reaction dynamics.

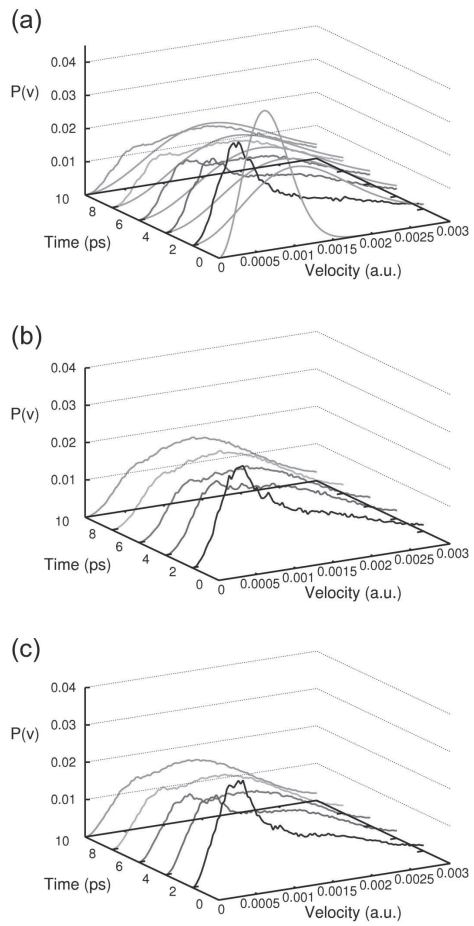


Fig 6. Comparison of time-dependent velocity distributions of a reactive C_2 system using (a) NVE C_2, (b) NVE C_2+He, and (c) NVE(C)-NVT(He) ensembles. For reference, time-dependent Maxwell-Boltzmann velocity distributions at the corresponding NVE MD simulation temperatures are included in (a) (grey lines). NVE/NVE(C)-NVT(He) simulations use C:He=1:1. P(v) shown only take into account carbon atom velocities.

2. Original Papers

(1) H.-B. Li, A. J. Page, Y. Wang, S. Irle, K. Morokuma, "Sub-Surface Nucleation of Graphene Precursors near a Ni(111) Step-Edge", *Chemical Communications*, **48**, 7937-7939 (2012).
(2) A. J. Page, T. Isomoto, J. Knaup, S. Irle, K. Morokuma, "Effects of Molecular Dynamics Thermostats on Non-Equilibrium Systems.", *Journal of Chemical Theory and Computation*, **8**, 4019-4028 (2012).
(3) H.-B. Li, A. J. Page, S. Irle, K. Morokuma, "SWCNT Growth from Chiral Carbon Nanorings: Prediction of Chirality and Diameter Influence on Growth Rates", *Journal of the American Chemical Society*, **134** 15887-15896 (2012).
(4) A. J. Page, C.-P. Chou, P. Q. Buu, H. Witek, S. Irle, K. Morokuma, "Quantum Chemical Investigation of Epoxide and Ether Groups in Grpahene Oxide and their Vibrational Spectra", *Physical Chemistry Chemical Physics*, **15**, 3725-3735 (2012).
(5) K. R. S. Chandrakumar, A. J. Page, S. Irle, K. Morokuma, "Carbon Coating Precedes SWCNT Nucleation on Silicon Nanoparticles: Insights from QM/MD Simulations", *Journal of Physical Chemistry C*, **117**, 4238-4244 (2012).
(6) A. J. Page, Y. Wang, H.-B. Li, S. Irle, K. Morokuma, "Nucleation of Graphene Island Precursors on Transition Metal Surfaces: Insights from Theoretical Simulations", *Journal of Physical Chemistry C*, Submitted.
(7) H.-B. Li, A. J. Page, S. Irle, K. Morokuma, "Revealing the Dual Role of Hydrogen for Defect Healing and Growth Inhibition in Polycyclic Aromatic Hydrocarbon Formation with QM/MD Simulations", *Journal of Physical Chemistry Letters*, Submitted.

3. Book Chapters

(1) "Atomistic Mechanism of Carbon Nanostructure Self-Assembly as Predicted by QM/MD Simulations" in *Practical Aspects of Computational Chemistry: An Overview of the Last Two Decades and Current Trends*. S. Irle, A. J. Page, B. Saha, Y. Wang, K. R. S. Chandrakumar, Y. Nishimoto, H.-J. Qian, K. Morokuma, Springer, New York, USA, In press. ISBN: 978-94-007-0918-8.

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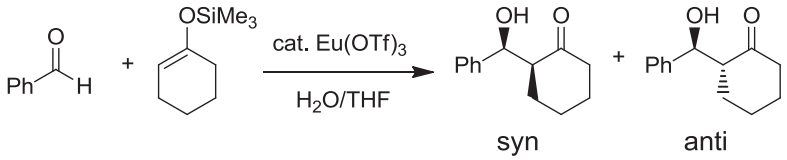
1. Summary of the research of the fiscal year

1.1 Aqueous Mukaiyama Aldol reaction catalyzed by lanthanide tri cation

Organic chemical reactions in aqueous solution are getting much attention as a green chemistry for the next generation. Among them, carbon-carbon bond forming reactions catalyzed by water-tolerant Lewis acid is one of the most attractive reactions. Usually, Lewis acid catalysts have to be used under strictly anhydrous conditions because they are unstable and inactive with water. However, lanthanide triflates $Ln(OTf)_3$ can catalyze many carbon-carbon bond forming reactions, such as Mukaiyama Aldol reaction (Scheme 1). However, these reactions achieved only for limited substrates because of the lack of information about the reaction mechanism.

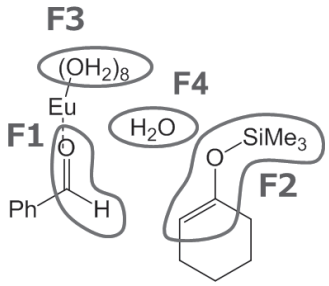


Scheme 1. Lanthanide triflate-catalyzed Mukaiyama Aldol reaction in aqueous media

To design more efficient and high stereoselective reactions, we need to understand the detailed reaction mechanism, especially the role of lanthanide cation and water. Though several experimental studies were reported to discuss the mechanism, there are remaining questions about the role of water. First question is why the yield of Mukaiyama Aldol reaction catalyzed by Ln^{3+} in organic solvent dramatically increases by addition of water. Second question is why diastereoselectivity changes from *anti*-preference to *syn*-preference by addition of water. To answer these questions, the reaction mechanism as well as hydrous structures of Eu^{3+} and their stability is discussed using dispersion corrected B3LYP-D3 theory.

The most stable Eu^{3+} species in aqueous media is Eu^{3+} coordinated by eight or nine water molecules and that coordinated by eight water molecules and a benzaldehyde. Therefore, Eu^{3+} coordinated by eight water molecules and an aldehyde is considered as a reactant below. The whole reaction pathways are explored by using automated explore

method, called the artificial force induced reaction (AFIR) method. To consider all the reaction pathways, reactions between all the combinations of fragments shown in Scheme 2 are considered.



Scheme 2. Fragmentation for AFIR calculation

The obtained reaction pathway is a step-by-step reaction which starts from C-C bond formation followed by proton transfer from water to benzaldehyde and trymethyl silyl (TMS) dissociation promoted by nucleophilic attack of bulk water molecules. The first question can be explained by the shape of reaction energy surface. The product of C-C bond formation (Cmp2) is less stable than the reactant (Cmp1) and the backward reaction barrier is only 1.2 kcal/mol, which means that the backward reaction proceeds easily. The complex is well stabilized only after the TMS dissociation by nucleophilic attack of water molecules. Therefore, TMS dissociation displaces the equilibrium between Cmp1 and Cmp2 and promotes the forward reaction. This TMS dissociation does not proceed without water, which results in the low yield under the anhydrous condition.

Next, we focus on the C-C bond formation step to discuss the diastereoselectivity. Because of the structural fluctuation around Eu^{3+} and different torsion around reactive C-C bond, many TSs are expected for the same C-C bond formation step and a method for search of all possible TSs is required. The AFIR method seems to be ideally suited for determination of many possible stereoselective TSs of complex and flexible organic reactions. As shown in Figure 1, 91 and 74 unique TSs are obtained which produce *syn* and *anti*-products, respectively by using AFIR method starting from random 437 initial structures. Among them, the lower 17 TSs contribute to the diastereomeric ratio (*syn*:*anti* = 75%:25%) which shows a good agreement with the experimental ratio of 73%:27%. The second question mentioned above can be understood by comparison of the lowest *syn* and *anti*-TSs. Though the lowest *anti*-TS has the lowest potential energy because of the smallest steric repulsion, the destabilization by entropic effect for the lowest *anti*-TS is larger than that for the lowest *syn*-TS because of the less structural fluctuation caused by hydrogen bond between TMS enol ether and coordination water.

That results in the higher Gibbs free energy of the *anti*-TS than that of the *syn*-TS. In other words, *anti*-TS is destabilized because of coordination water molecules.

As shown above, the roles of water for this reaction are to stabilize the product by promoting TMS dissociation by nucleophilic attack, and to supply a proton to aldehyde. In addition, the entropic effect caused by coordination water around Eu^{3+} changes the diastereoselectivity.

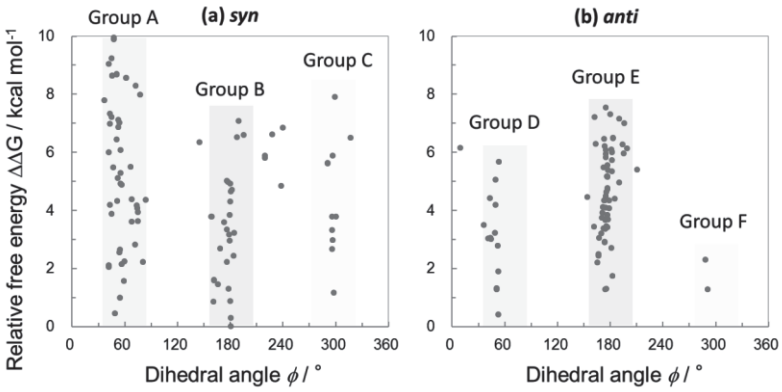


Figure 1. The relative Gibbs free energy $\Delta\Delta G$ (in kcal/mol) and dihedral angle ϕ (in °) of TSs for C-C bond forming step. TSs producing *syn* and *anti*-products are shown in (a) and (b), respectively.

1.2. Enantio-selective Ln^{3+} catalyzed Aqueous Mukaiyama Aldol reaction

The demerit of the reaction above is low diastereoselectivity mainly caused by structural fluctuation of coordination water around Eu^{3+}. To solve this problem, Allen and coworkers designed a new C_2 symmetric ligand for Eu^{3+} which achieved a high diastereoselective and enantioselective Mukaiyama Aldol reaction in aqueous media.

However, our optimized geometry of C_2 symmetric catalyst did not seem to control the stereoselectivity. Therefore, to find other stable structures for the catalyst, another automated explore method, called the anharmonic downward distortion following (ADDF) method was carried out which results in 26 unique geometries for local minima. As

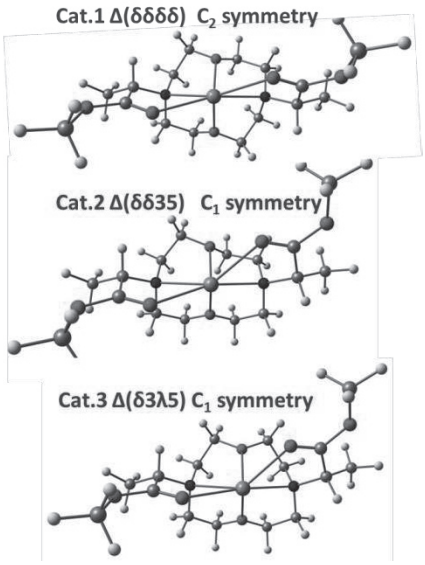


Figure 2. The three most stable geometries of the catalyst.

shown in Figure 2, we found not only C_2 symmetric geometry but also distorted C_1 symmetric geometries whose energetics were quasi-degenerated. As discussed in the previous section, aldehyde coordinates to Eu^{3+} firstly and the following C-C bond formation is the diastereo and enantio-determining step. Firstly, we focus on the coordination geometry of aldehyde and two water molecules, where the coordination number of water is measured by luminescence-decay. Surprisingly, the coordination structure can be categorized into only two groups regardless of different geometries of the catalyst. The structural sampling of TSs for C-C bond is still calculating, so we cannot conclude the mechanism of the stereoselectivity. However, we can say two important keys for this reaction. The first point is that asymmetric environments, such as Cat2 and Cat3 in Figure 2, are generated by the structural fluctuation around Eu^{3+}. The second point is that what control the coordination structure of aldehyde are the oxygen atoms in the macro cyclic ring part and the carbonyl part by hydrogen bonds.

1.3. Reduction of NO in qNOR enzyme

Nitrous oxide reductase (NOR) is a key enzyme for the reduction of NO which is a step in anaerobic respiration process. Recently, the X-ray structure of a new type of NOR, called quinol-dependent NOR (qNOR), was reported, whose geometry around two Fe centers are slightly different from another NOR (cNOR). Figure 3 shows the obtained reaction pathways calculated by B3LYP method using a model complex. The most favorable path is the *cis*:b_3 mechanism whose rate determining step is the rotation of five- membered ring step (Cmp6→Cmp9). In the case of the NO reduction mechanism in cNOR, the reaction barrier of the rotation of five-membered ring is too high because of the smaller space of the active site. In other words, the coordination structure around two Fe centers controls the reaction even if they do not participate in the reaction itself.

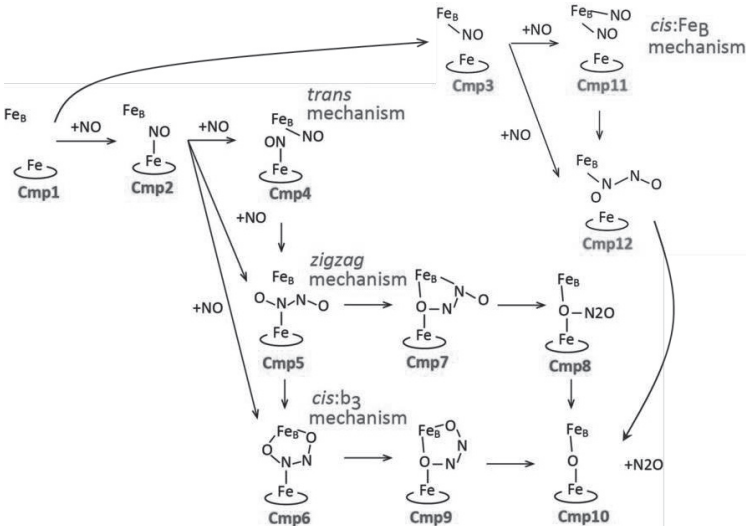


Figure 3. Reaction pathways for NO reduction

2. Original Papers

1. S. Maeda, E. Abe, M. Hatanaka, T. Taketsugu, K. Morokuma, "Exploring Potential Energy Surfaces of Large Systems with Artificial Force Induced Reaction Method in Combination with ONIOM and Microiteration" *J. Chem. Theory Comput*. **8**, pp5058-5063 (2012).
2. M. Hatanaka, S. Maeda and K. Morokuma, "Sampling of Transition States for Predicting Diastereoselectivity Using Automated Search Method–Aqueous Lanthanide- Catalyzed Mukaiyama Aldol Reaction", *J. Chem. Theory Comput*. In press.
3. M. Hatanaka and K. Morokuma, "Role of water in Mukaiyama Aldol Reaction Catalyzed by Lanthanide Lewis Acid", Manuscript in preparation.
4. M. Hatanaka and K. Morokuma, "The mechanism of reduction of nitric oxide in cytochrome c-dependent nitric oxide reductase (cNOR): A DFT study", Manuscript in preparation.

3. Presentations at meetings

1.畑中美穂, 諸熊奎治, "DFT 法および ONIOM 法を用いた一酸化窒素還元酵素の反応機構に関する理論的", 第 15 回理論化学討論会 2012 仙台, 2012/05/25.

2. Miho Hatanaka, Keiji Morokuma, "The mechanism of the reduction of nitric oxide in bacterial nitric oxide reductase: A DFT and ONIOM study" 14th International Congress of Quantum Chemistry, Boulder, 2012/06/27.

3. 畑中美穂, 諸熊奎治, "一酸化窒素還元酵素 cNOR 及び qNOR における一酸化窒素還元反応機構の理論的研究", 第 6 回分子科学討論会 2012 東京, 2012/09/21.

4. Others

1.畑中美穂, "コンピュータで見る化学反応の世界", 理系インスパイアー講演会, 北摂三田高等学校, 2012/09/13.

2.畑中美穂, "コンピュータで見る化学反応の世界", 子どもの知的好奇心をくすぐる体験授業, 京都府立宮津高等学校, 2012,11/05.

3.畑中美穂, "新薬ができるまで―「化学」はこんなふうに新薬開発に関わっています―", 人間科学類型特別授業, 北摂三田高等学校, 2013/01/10.

4. Miho Hatanaka, "Mechanism of Mukaiyama Aldol Reaction Catalyzed by Water-Tolerant Lanthanide Lewis Acid - An Artificial Force Induced Reaction Study", The 10th Fukui Center Seminar, 2013/03/21

Fengyi LIU

Research Fellow, Fukui Kenichi Memorial Research Group 1

1. Summary of the research of the year

Reaction Mechanism of Spiropyran-Merocyanine Photochromic Reaction

The photochromic reaction of Spiropyran-Merocyanine(SP-MC) photochromic reaction has been a hot but challenging subject for theoretical chemists. Due to the dramatic changes of electronic structure during the ring-open and ring-closure processes and highly flexible geometry of MC isomers, the potential energy surfaces of SP-MC are complex. The efficient nonadiabatic path from excited- to ground state, including crucial structures such as conical intersections and unusual intersystem crossing, have not been well understood.

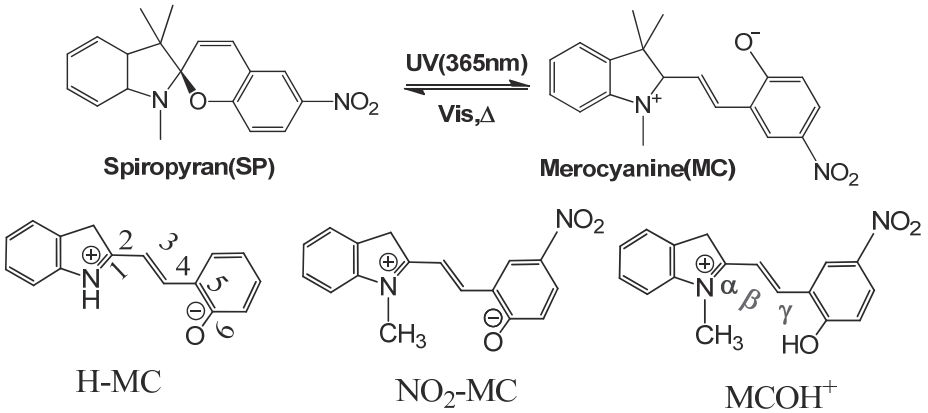


Figure 1. Spiropyran-Merocyanine photochromic reaction path and unsubstituted MC(H-MC), 6-NO_2 MC(NO_2-MC) and protonated MC($MCOH^+$).

Multiple reaction path explored in H-SP Photochromic reaction:

In this project, we carried out high-level multireference CASSCF and CASPT2 calculations to investigate the reaction mechanism of the photochromic ring-opening process of a spiropyran (BIPS).

The possible excited-state C-O (and C-N) bond cleavage pathways and efficient nonadiabatic path from excited- to ground state have been revealed. (1) The C–O bond dissociation in SP does not follow a conical-intersection mechanism that has been proposed in a model study with a simplified benzopyran. The CASSCF-optimized crossing points are actually avoided crossings with large S_1-S_0 energy gap at the CASPT2 level; thus, they could not act as efficient S_1-to-S_0 funnels. (2) C–O bond cleavage paths on S_1 leading to both the CCC (with respect to the configuration around α, β, γ in Figure 2) and TCC intermediates of merocyanine (MC) are barrierless, in line with the experimentally observed ultrafast formation of MC.

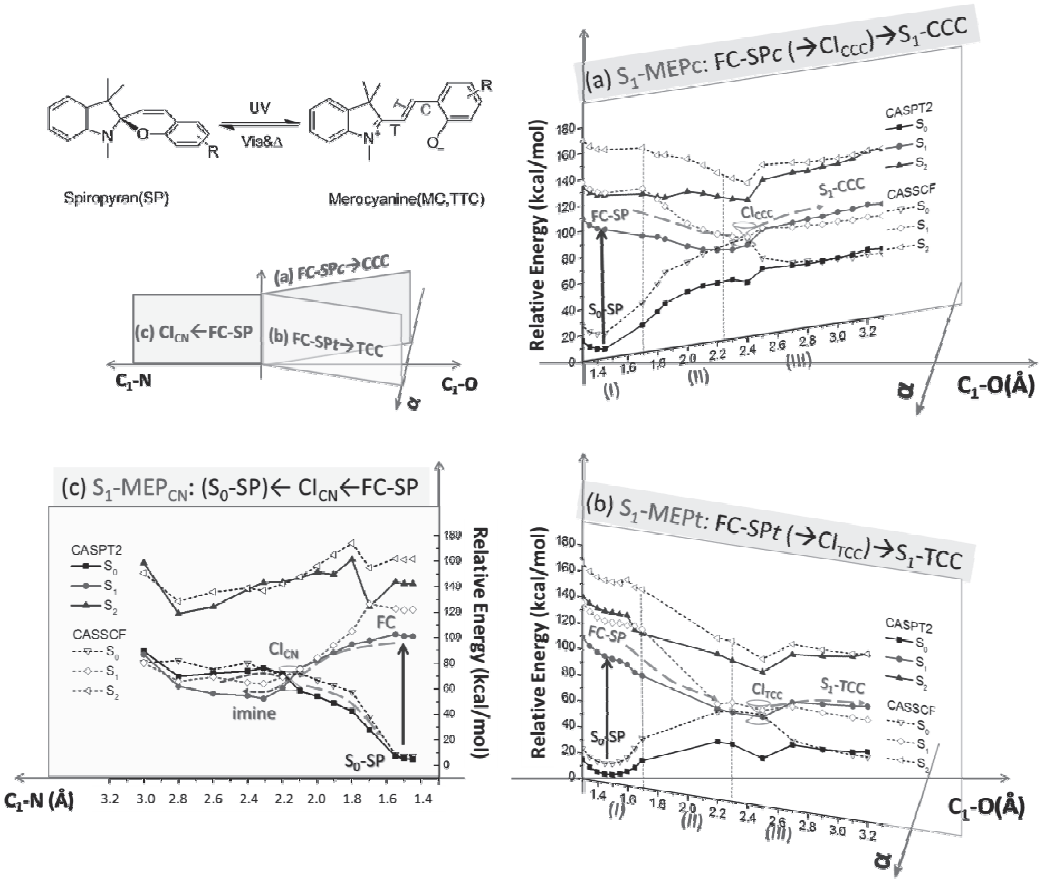


Figure 2. The MS-CASPT2//CASSCF (solid curve and symbols) and CASSCF (dash line with hollow symbols) S_1-MEP's for ring-opening reaction of: (a) S_1-MEPc: FC-SPc→ CCC(S_1) path; (b) S_1-MEPt: FC-SPt →TCC(S_1) path and (c) S_1-MEP_{CN}: FC-SP → CI_{CN} path.

A low-energy hydrogen-out-of-plane (HOOP) valley on the (π→σ*) surface was located not far from the C–O bond cleavage path and was suggested to be an efficient S_1-to-S_0 nonadiabatic decay channel. Triggered by the active HOOP mode, the molecule can easily access the S_1-HOOP valley and then make transition to S_0 surface through the narrow S_1-S_0 gap that exists in an extended region. Nonadiabatic decay through a conical intersection on C–N dissociation path as well as the HOOP funnel is responsible for high internal conversion yields of SP.

These findings shedding light on the complex mechanism of SP-MC interconversion provide fundamental information for design spiropyran-based photochromic devices.

H-SP Photochromic reaction: High Accuracy Refinement by Multiconfigurational DensityMatrix Renormalization Group Approach

Many problems in photochemistry, e.g., the spectroscopy and ground- and excited-state reaction of large conjugated systems, demand large multireference active space, which are always beyond the reach of convertional complete active space correlation methods. Recently, the density matrix renormalization group (DMRG) method has been able to solve many problems with active spaces much larger than are possible

with traditional active space techniques, and can obtain near-exact solutions.

In this study, we applied the DMRG methods to the reaction mechanism of HSP with large active space (22*e*-in-20*o*, the active orbitals include all π/π* orbitals and σ/σ* of C–O and C–N). The DMRG-CASSCF and DMRG-CASPT2 energies are obtained on top of the reaction path optimized by conventional CASSCF and (12*e*-in-10*o*) active space, to accurately evaluate the energies of photo excitation, dissociation path and nonadiabatic crossing region.

Table 1. DMRG-CASSCF & CASPT2 Energies of Key Structures.

	DMRG-SA3-CASSCF			DMRG-SS-CASPT2		
Structures	S_0	S_1	S_2	S_0	S_1	S_2
		S_0-SPc				
CAM-B3LYP	1.4	111.4	115.1	**0.0**	106.8	109.9
B3LYP	1.5	109.7	113.7	0.0	104.9	108.7
CASSCF(12e,10o)	1.5	112.3	115.4	2.0	109.6	112.8
DMRG-SS-CASSCF	**0.0**	108.9	112.8	0.8	106.5	110.5
Ref: MOLCAS	*0.0*	*129.7*	*131.8*	*0.0*	*111.6*	*113.1*
		S_0-SPt				
CAM-B3LYP	2.5	112.2	116.4	**0.3**	105.8	111.6
CASSCF(12e,10o)	2.6	113.2	116.7	2.2	109.0	113.8
DMRG-SS-CASSCF	**1.1**	109.6	114.0	1.3	105.2	112.1
Ref: MOLCAS	*0.0*	*129.0*	*131.9*	*0.3*	*111.1*	*113.9*
		S_1/S_0 CIs				
CI(TSc)	**63.8**	**67.3**	101.5	**68.7**	**53.2**	94.0
Ref: MOLCAS	***66.0***	***67.3***	*102.0*	***45.2***	***68.8***	*99.4*
CI(TSt)	**63.2**	**64.0**	107.6	**57.1**	**60.6**	98.5
Ref: MOLCAS	***72.4***	***72.6***	*116.7*	***42.4***	***69.1***	*105.8*
CI(CN)	**65.7**	**68.3**	118.5	**70.4**	**59.6**	119.0
Ref: MOLCAS	***70.2***	***68.7***	*141.6*	***72.2***	***60.6***	*143.6*

In general, it is found the calculation results at the DMRG-CASSCF and DMRG-CASPT2 level are in good agreement with the ones obtained with (12*e*-in-10*o*) active space. The only evident differences are seen at the Frank-Condon region; the DMRG-CASSCF and DMRG-CASPT2 decrease the relative energies of excited-state PES, suggesting inadequate size of active space by conventional CASSCF (12*e*-in-10*o*). While the relative energies along the reaction path, e.g., at the three crucial MECIs (Table 1) are very similar (at different approaches), confirming the reasonability of our "truncated" active space. In addition, the dynamic effects in the HSP reaction are significant, at both the conventional- and DMRG approaches. The findings here supported the reaction mechanism proposed in our conventional CASSCF/CASPT2 study.

Theoretical Study on the Deactivation Path of Fluorescence

From photophysical and photochemical textbooks, it is well known that in a unimolecular process, the excess energy taken up by photo excitation can be dissipated either as emission (fluorescence for $S_1 \rightarrow S_0$)

or by radiationless transition. The rate of the radiationless transition depends not only on the energy gap (therefore if the potential energy surfaces (PES) of the corresponding states intersect or are very close to each other, the probability of radiationless transition is high), but also on the equilibrium geometries of the states involved (i.e., in rigid π systems, the ground state and first excited state differ so little that the PESs are nearly parallel, radiationless transition is less likely). These two processes, in many systems, compete with each other and determining the fluorescent/nonfluorenscent feature of the excited molecule.

Theoretical calculation of such systems involving multiple potential energy surfaces (PESs) and seams of intersection among the PESs are often complicate. Recently, the global reaction route mapping (GRRM) method has successfully been applied to automatically explore multiple PESs and tested to be a powerful tool to discovery nonadiabatic pathways. In this study, we explored the radiationless deactivation pathway of some fluorescent compound by combining GRRM with spin-flipping density functional methods. The results are useful in explaining experimental findings as well as designing new high-yield fluorescent materials.

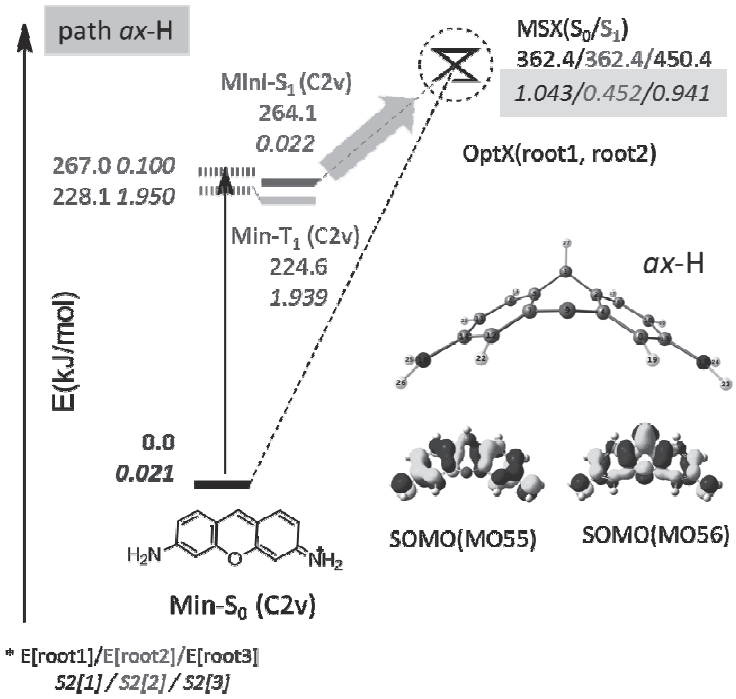


Figure 3. A unfavorable S_1-to-S_0 radiationless path revealed at SF-B3LYP/6-31G* level.

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2. Original papers

(1) Fengyi LIU, Keiji MOROKUMA,

"Multiple Pathways for Primary Step of Spiropyran Photochromic Reaction: A

CASPT2//CASSCF Study”,

J. Am. Chem. Soc., *submitted*.

(2) Fengyi LIU, Keiji MOROKUMA,

" Density Matrix Renormalization Group Study on Spiropyran Photochromic reaction”

manuscript in preparation.

Hongyan XIAO

Research Fellow, Fukui Kenichi Memorial Research Group 1
(To 30 Sep. 2012)

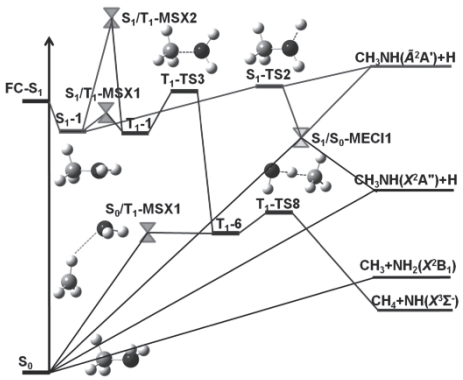
1. Summary of the research of the year

I. Theoretical Study on the Photodissociation of Methylamine Involving S_1, T_1, and S_0 States

Methylamine (CH_3NH_2) is the simplest primary amine, which plays an important role in various fields of chemical science. Because of its simplicity and importance, the structural and spectroscopic properties, photodissociation dynamics and pathways have been widely investigated. Furthermore, the photodissociation of CH_3NH_2 might provide helpful insights and implications in understanding photoinduced processes of various compounds containing amine moieties.

$$CH_3NH_2 \rightarrow H + CH_3NH \quad (1)$$
$$\rightarrow H + CH_2NH_2 \quad (2)$$
$$\rightarrow CH_3 + NH_2 \quad (3)$$
$$\rightarrow H_2 + CH_3N \quad (4)$$
$$\rightarrow CH_4 + NH\ (X^3\Sigma^-) \quad (5)$$

However, till now some questions remain: whether pathway (4) goes through a four-center transition state, which form of the product ($CHNH_2$, CH_2NH, or CH_3N) pathway (4) mainly gives, whether pathway (5) is a primary channel occurring on the triplet state, whether pathway (5) undergoes roaming-mediated intersystem crossing, and so on. To answer these questions further theoretical evidences are needed. Therefore we performed a systematic CASPT2 reaction path search on the three lowest electronic states (S_1, T_1, and S_0) by the global reaction route mapping (GRRM) strategy utilizing the anharmonic downward distortion following (ADDF) and artificial force induced reaction (AFIR) methods.

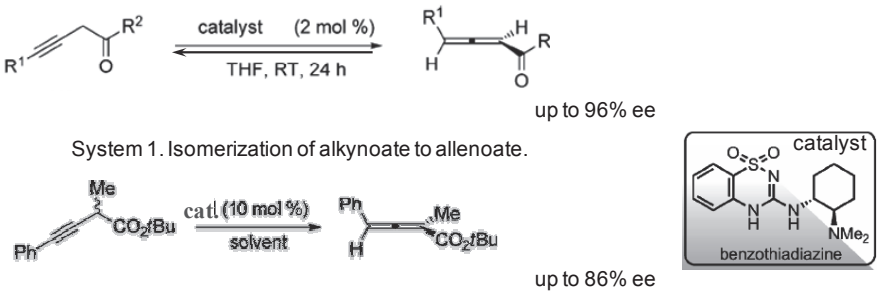


On the basis of obtained structures, we discuss the photodissociation mechanism of methylamine in the experimental excitation wavelength range of 222-240 nm in detail. Especially, the T_1 potential energy surface was explored systematically for the first time. The N-H bond rupture is a primary channel on the S_1 state. Along the N-H dissociation path on S_1, there is a low-energy conical intersection (CI), and through this CI the system can go back to the S_0 state; from the CI the system can directly dissociate to CH_3NH + H or

reproduce the original CH_3NH_2 on S_0. There is a seam of crossing between S_0 and T_1 in a partially dissociated CH_3---NH_2 geometry, and through this seam the system may go up to the T_1. On the T_1 state, a roaming-like pathway giving CH_4 + NH ($X^3\Sigma^-$) products was found, which would explain the recently proposed intersystem crossing mediated roaming dynamics. In addition, H_2 elimination pathways, channel (4), on the S_0 and T_1 PESs were searched systematically. Three forms of CH_3N, i.e., $CHNH_2$, CH_2NH, and CH_3N, can be generated by H_2 elimination on the T_1 state via roaming-like pathways, although these paths are expected to play a minor role due to high energy barriers. On the S_0 state, there are two preferential paths giving CH_2NH + H_2 and $CHNH_2$ + H_2 through stepwise and concerted mechanisms, respectively.

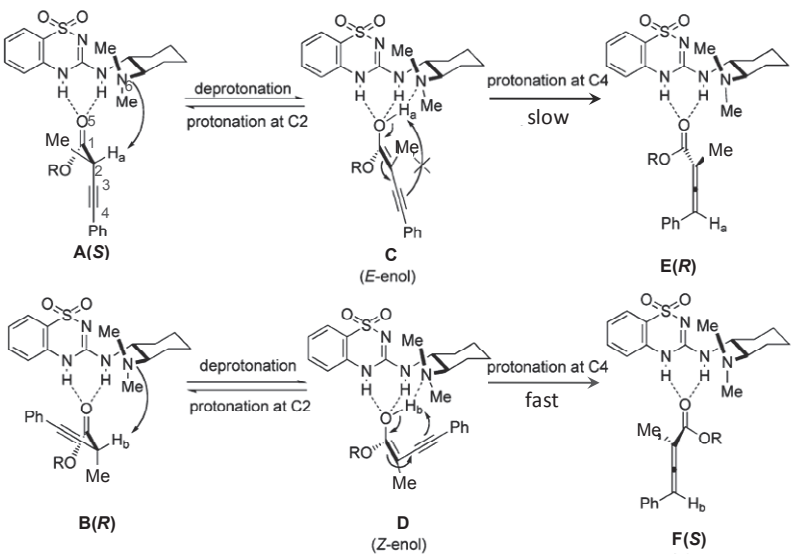
II. Theoretical Study on Organocatalyzed Isomerization of Alkynoate to Allenoate

Chiral allenes are interesting chiral building blocks in synthetic organic chemistry. The development of the catalytic enantioselective synthesis of chiral allenes has received considerable attention in the field of organic synthesis. Enantioselective isomerization of alkynoates is one of the most atom-economical ways to access this motif. In experiment Prof. Takemoto group reported the isomerization of α-nonsubstituent (System 1) and α-substituent (System 2) of alkynoates into allenoates using benzothiadiazine organocatalyst, respectively. It was found that the reaction in System 1 is reversible, while the reaction in System 2 is irreversible; the isomerization from (*R*)-alkynoate to (*S*)-allenoate is a fast path. They proposed the reaction mechanism as follows.



System 1. Isomerization of alkynoate to allenoate.

System 2. Isomerization of α-substituted alkynoate to trisubstituted allenoate.



The proposed reaction mechanism by Prof. Takemoto and co-workers.

In this study we used the B3LYP/6-31G* method to investigate the mechanisms of organocatalyzed isomerization of alkynoate to allenoate. We also considered the solvent effect using PCM model, where THF is as a solvent. Here, we take System 2 as example to elucidate reaction mechanism. Beginning from the four initial complexes (substitute and catalyst) below, four pathways were explored, see Figure 2.

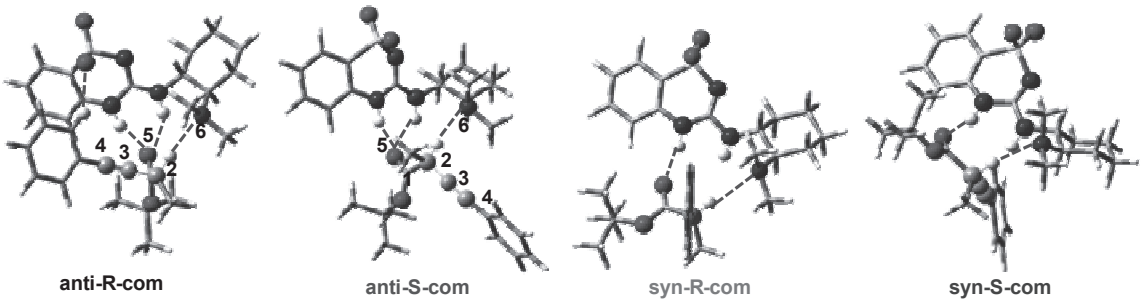


Figure 1. Four initial complexes in System 2.

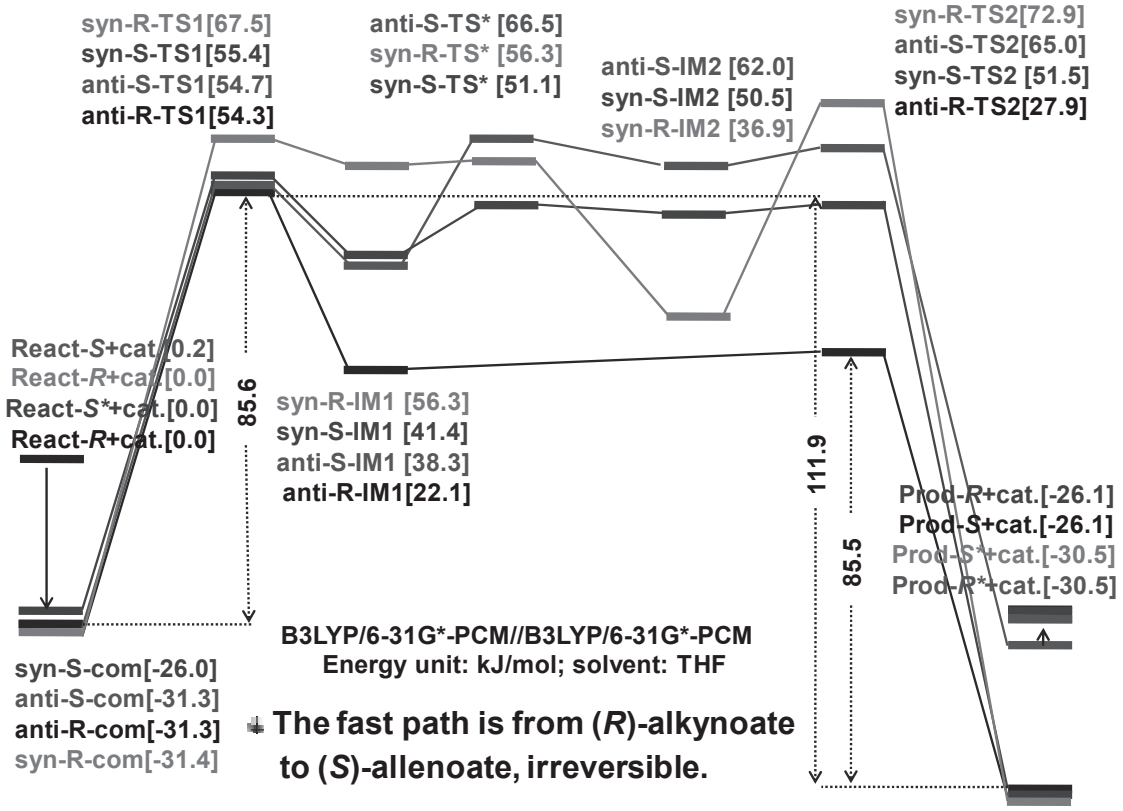


Figure 2. The potential energy surface of alkynoate to allenoate in System 2.

The results show that the isomerization process includes two hydrogen-transfer steps and one conformational change. The fast path from *R*-alkynoate (anti-R-com) to *S*-allenoate (prod-S + cat) only involves two hydrogen-tranfer steps mediated by benzothiadiazine catalyst. As shown in Figure 2, the path from IM1 to TS2 is very import, so we in detail analyse the structures, molecular orbital overlap integrals, charge distributions of IM1 and TS, and do energy decoposition analysis from IM1 to TS2. Hydrogen bond interactions between substrate and catalyst play an important role in the overall reaction. Using the similar method, we also studied the isomerization process in Systme I. On the whole, our computational results are in agreement with the experimental observations, proposed the isomerization mechanism of alkynoate to

allenoate mediated by benzothiadiazine from theory.

2. Original papers

(1) Hongyan Xiao, Satoshi Maeda and Keiji Morokuma
"Global *ab initio* potential energy surfaces for low-lying doublet states of NO_3"
J. Chem. Theory Comput. 8, 2600-2605 (2012)

(2) Bina Fu, Joel M. Bowman, Hongyan Xiao, Satoshi Maeda and Keiji Morokuma
"Quasiclassical trajectory studies of the photodissociation dynamics of NO_3 from the D_0 and D_1 potential energy surfaces"
J. Chem. Theory Comput. 9, 893-900 (2013)

(3) Hongyan Xiao, Satoshi Maeda and Keiji Morokuma
"CASPT2 study of photodissociation pathways of ketene"
J. Phys. Chem. A in press (DOI: 10.1021/jp312719a)

(4) Hongyan Xiao, Satoshi Maeda and Keiji Morokuma
"Theoretical study on the photodissociation of methylamine involving S_1, T_1, and S_0 states"
Submitted.

(5) Hongyan Xiao, Satoshi Maeda and Keiji Morokuma
"Theoretical study on the photodissociation mechanism of nitric acid involving S_3, S_2, S_1 and S_0 states"
Manuscript in preparation.

(6) Hongyan Xiao, Satoshi Maeda and Keiji Morokuma
"Theoretical study on catalytic enantioselective mechanism of Passerini reaction"
Manuscript in preparation.

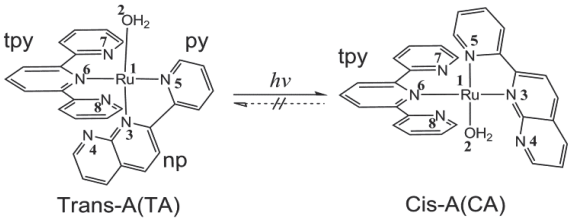
Lina DING

Research Fellow, Fukui Kenichi Memorial Research Group 1

1. Summary of the research of the year

P1. Excited-State Proton Transfer Controls Irreversibility of Photoisomerization in Mononuclear Ruthenium(II) Monoaquo Complexes: A DFT Study

Photo-induced or photo-triggered isomerization can utilize photonic energy for selective bond-breaking and bond-making reactions. This type of reactions between two or more optically and electronically distinct isomers or meta-stable species have been observed in a broad variety of molecules, including stilbene and its derivatives, rhodopsins, and fluorescence proteins, as well as transition metal complexes including photochromic ruthenium(II) polypyridine sulfoxide and polypyridyl mononuclear ruthenium(II) aquo (PMRA) and other ruthenium(II) complexes. Except for ruthenium polypyridine sulfoxide complexes, mechanistic studies on PMRA are scarce. The importance of photoisomerization in PMRA lies in the fact that the two isomers have different potential catalytic abilities for water oxidation into molecular oxygen, one of the key reactions involved in solar energy conversion.



Scheme 1. Photoisomerization of *trans*-[Ru(tpy)(pynp)(OH_2)]$^{2+}$ (TA) to *cis*-[Ru(tpy)(pynp)(OH_2)]$^{2+}$ (CA), with atom and group labels.

Recently, an irreversible photo-isomerization of *trans*-[Ru(tpy)(pynp) (OH_2)]$^{2+}$ (TA) to *cis*-[Ru(tpy)(pynp)(OH_2)]$^{2+}$ (CA) complex (tpy = 2,2′:6′,2″-terpyridine; pynp = 2-(2-pyridyl)-1,8-naphthyridine, **Scheme 1**) has been observed and characterized by experimental techniques, such as such as X-ray crystallographic analysis, NMR spectroscopy and cyclic voltammetry. Importantly, the redox and water oxidation reactions were reported to be significantly controlled by the photoisomerization. Yagi proposed a mechanism for the

photoisomerization: visible-light irradiation of TA can generate a metal-ligand charge-transfer (MLCT) state which is followed by a metal-centered (MC) states, on which an aquo ligand could dissociate to form a five-coordinate $[Ru(tpy)(pynp)]^{2+}$ intermediate, and then a water molecule re-coordinates to the metal center of the intermediate from the opposite side of the tpy plane to form the CA isomer. The proposed Ru–O bond cleavage involved in the water dissociation was implicated by the observed activation energy of the photoisomerization (41.7 kJ mol^{-1}), which is similar to that for the water exchange in ruthenium aquo complexes (50.6-87.8 kJ mol^{-1}). However, it is still a puzzle why the isomerization is irreversible.

In this study, we explored the photo-induced non-adiabatic isomerization paths between *trans*-$[Ru(tpy)(pynp)(H_2O)]^{2+}$ (TA) and *cis*-$[Ru(tpy)(pynp)(H_2O)]^{2+}$ (CA) on the lowest triplet and singlet states by density functional theory (DFT) calculations. Several minimum energy crossing points (MSX) were located and characterized to connect the two adiabatic potential energy surfaces (PESs) for non-adiabatic pathways. Interestingly, excited-state proton transfer (ESPT) occurred only in the minimum of $T_{MLCT\text{-}CA}$ with a stronger Ru(II)-OH bond suppress the transition to $T_{MC\text{-}CA}$ and, thus, the adiabatic triplet pathway from CA to TA. The findings of the present study should shed light on the working mechanism of the irreversible isomerization processes of PMRA.

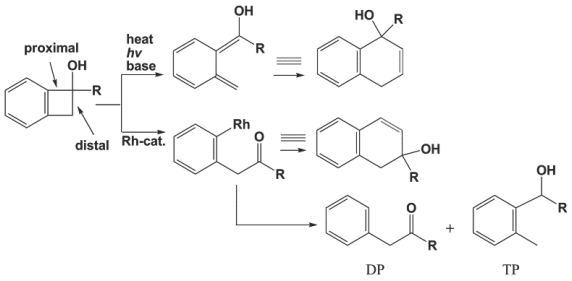
P2. sp^3–sp^2 vs sp^3–sp^3 C–C Activation in Rh-Catalyzed Ring Opening of Benzocyclobutenol: A DFT Study

Transition metal catalysis has made significant and continual contributions to the development of synthetic organic chemistry, which has opened the wide synthetic applications of non-polar and highly inert σ-bonds such as C–H bonds. The recent evolution has rendered it possible to cleave C–C single bonds in a catalytic manner and utilize them in organic synthesis. However, the available means to cleave C–C bonds are still in its infancy and generally rely on substrate-specific strategies such as ring strain, aromatization, chelating or coordinating assistance to induce C−C bond cleavage.

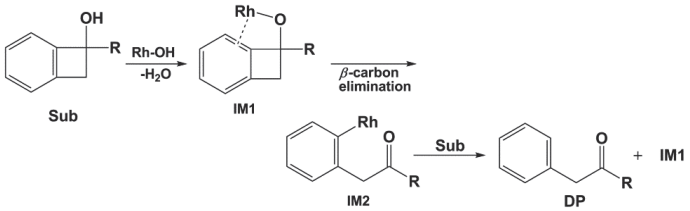
Murakami has reported that a rhodium catalyst induces ring opening of cyclobutanols. The ring-opening process has been extended to various reactions to restructure carbon frameworks. Very recently, ring opening of benzocyclobutenols with site-selective cleavage

of the C_{sp3}–C_{sp2} ("proximal" bond) (Scheme 1) was reported. The site-selective C_{sp3}–C_{sp2} ring opening is complementary to the C_{sp3}–C_{sp3} bond ("distal" bond) ring opening induced by heating, photo irradiation, and treatment with a base to furnish reactive *o*-quinodimethanes. Experimentally, the site-selectivity is significantly influenced by the ligands on the Rh(I) and the solvent. A proposed mechanism for the ring-opening of benzocyclobutenols is via proton transfer followed by β-carbon elimination, as shown in Scheme 2.

Scheme 1. Ring opening of benzocyclobutenols



Scheme 2. Plausible mechanism



Further investigations on the mechanism are highly desired to understand these reactions in detail. Up to now, mechanistic investigations on the carbon−carbon bond activation by the transition metal are quite square. To clarify the factors that influence carbon−carbon bond cleavage could be helpful for deeper understanding of the general area of carbon−carbon activation and may lead to new methodology for restructuring carbon frameworks. Theoretical studies would be very profitable toward this goal. Mechanistic picture including the potential energy surfaces, energetic and the nature of equilibrium structures is very important to describe the nature of reaction pathways. Unfortunately theoretical studies on the field of carbon−carbon activation have been limited to the C–CN bond and some special substrate.

In the present work, we systematically investigated the mechanism of Rh-catalyzed ring

opening of benzocyclobutenol by a density functional theory. The catalytic cycle has been found to include three steps: deprotonation of benzocyclobutenol to form Rh(I) alkoxide, C–C bond cleavage (β-carbon elimination), and water dissociation to form the product and to regenerate active catalyst. The present results successfully depict the mechanism of the site-selectivity and explain well its ligands-dependency and solvent influence, which should be useful for designing new catalysts and improving site-selectivity. The mechanistic picture described by the present computational study provides deeper insight into understanding of C–C bond cleavage.

2. Original Papers

(1) **Lina Ding**, Lung Wa, Chung, Keiji Morokuma*,
Excited-State Proton Transfer Controls Irreversibility of Photoisomerization in Mononuclear Ruthenium(II) Monoaquo Complexes: A DFT Study, submitted

(2) **Lina Ding**, Naoki Ishida, Masahiro Murakami, and Keiji Morokuma*,
sp^3–sp^2 vs sp^3–sp^3 C–C Activation in Rh-Catalyzed Ring Opening of Benzocyclobut--enol: A DFT Study, To be submitted

(3) **Lina Ding**, Lung Wa Chung, Keiji Morokuma
"Reaction Mechanism of Photoinduced Decarboxylation of the Photoactivatable Green Fluorescent Protein: An ONIOM(QM:MM) Study", *J. Phys. Chem. B,* ***2013****, 117 (4), 1075–1084.*

3. Presentation at academic conferences

(1) Lina Ding, Lung Wa Chung, Keiji Morokuma
"QM/MM study on the Photoinduced decarboxylation mechanism of Photoactivable Green Fluorescent Protein"
7th Congress of the International Society for Theoretical Chemical Physics (4PP-62), Tokyo, Sep. 2-8. 2011

(2) Lina Ding, Lung-Wa Chung, Keiji Morokuma.
"Theoretical Study on the Photoisomerization of Mononuclear Ruthenium(II) Monoaquo Complex,"
福井謙一博士ノーベル賞受賞 30 周年記念 京都, 2012, Jan.01

(3) Lina Ding, Naoki Ishida, Masahiro Murakami, and Keiji Morokuma*,
"Ligands and Solvent Effects on the Site-Selectivity of Rh-Catalyzed-Ring-Opening of Benzocyclobutenol: A Computational Study,"
The 10th FIFC Symposium, 2012, Nov. 30.

Hai-Bei LI

Research Fellow, Fukui Kenichi Memorial Research Group 1

1. Summary of the Research of the Year

(A) Temperature Dependence of Catalyst-Free Chirality-Controlled Single-Walled Carbon Nanotube Growth from Organic Templates

Traditional CNT growth methods, such as carbon-arc, laser evaporation, and catalytic chemical vapor deposition (CCVD) are incapable of *in situ* control of (*n*, *m*) chirality during CNT synthesis, primarily due to the high temperatures employed. Recently proposed bottom-up strategy based upon organic synthetic methods represents a more realistic approach towards chirality-controlled SWCNT growth. We have recently revealed the potential role of the ethynyl (C_2H) radical in low-temperature templated SWCNT growth. In the current work, we investigate the role of temperature on chirality-controlled SWCNT growth from organic templates. We have taken [6]CPP → (6,6)-SWCNT growth as a model system, and SWCNT growth was induced by C_2H radical addition to the [6]CPP template at the temperatures of 300, 500, and 800 K. Figure 1 depicts the hexagon addition distributions for growth at 300, 500 and 800 K, respectively, following 245 ps. It is evident that SWCNT growth, as measured by hexagon addition, at 300 K is noticeably slower compared to that at 500 and 800 K. In 90% of 300 K trajectories between four and seven new hexagons were added. Conversely, hexagon addition distributions at 500 and 800 K shift noticeably towards higher hexagon populations: the number of trajectories with four new hexagons decreases sharply, while the number of trajectories with 8 ~ 10 new hexagons increases. On average, 5.8, and 6.8 and 6.7 hexagons are added during this period at 300, 500 and 800 K, respectively. While the average growth rates at 500 and 800 K are essentially equal, hexagon addition distributions at these temperatures differ significantly, suggesting a difference in growth mechanism. At higher temperature, terminating polyyne chains and their supporting hexagonal rings exhibit larger vibrational and torsional motion. This on the one hand, could potentially promote ring formation; this is certainly what a comparison of hexagon addition distributions between 300 and 500 K suggests. On the other hand, this can potentially promote instability in the SWCNT structure itself, which in turn results in irregular growth rates and more defect formation.

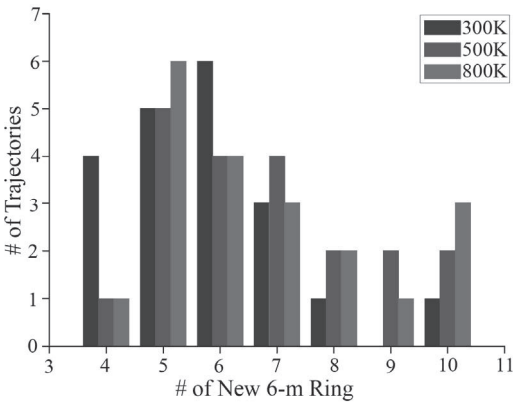


Figure 1. Hexagon addition distributions at 300K, 500K, and 800K.

We have calculated reaction rate constants for the hexagon and pentagon addition during [6]CPP →(6,6)SWCNT growth as a function of temperature according to the well-known transition state theory. Figure 2 shows that reaction rates for pentagon defect formation exceed those for hexagon formation. The kinetic advantage that defect formation holds over hexagon formation is greatest at lower temperatures – presumably this has ramifications for low-temperature strategies for chirality-controlled growth. While pentagon defect formation is more favorable than hexagon formation, the thermodynamic stability of the latter product is significantly greater than that for pentagon defect formation. Hexagon and pentagon formation during SWCNT growth are therefore competitive processes. Reaction rate constants of hexagon and pentagon formation (Figure 2b) increase with increasing temperature, and this is consistent with QM/MD results showing faster growth at higher temperatures. Figure 2 also indicates that, higher temperature results in more pentagon defect formation during growth, which is consistent with trends observed in QM/MD simulations.

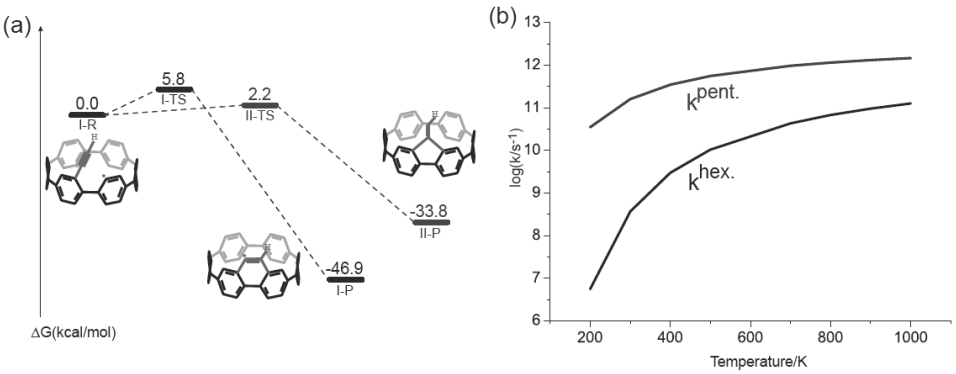


Figure 2. (a) Reactive potential energy surface for hexagon and pentagon addition to [6]CPP precursor *via* C_2H insertion, energies presented are at 300K. (b) Temperature dependence of

reaction rate constants k for hexagon and pentagon.

(B) Revealing the Dual Role of Hydrogen for Growth Inhibition and Defect Healing in Polycyclic Aromatic Hydrocarbon Formation: QM/MD Simulations

There is increasing concern about the formation of polycyclic aromatic hydrocarbons (PAHs) during the combustion and pyrolysis of hydrocarbons, due to their harmful environmental effects. We have previously performed quantum mechanical molecular dynamics (QM/MD) simulations of PAH formation from high-temperature benzene combustion, varying the H/C ratios between 0.8 and 0.2. In the current work, we report the dual role played by hydrogen atoms during PAH growth via the combustion or pyrolysis of hydrocarbons. Very high hydrogen densities lead to the inhibition of PAH growth. On the other hand, high hydrogen densities facilitate defect healing in the growing PAH fragments and promote hexagon formation. We present the evolution of the largest PAH fragments observed using H/C ratios of 0.6, 0.4, and 0.2 in Figure 1. The effect of hydrogen density on both the ring condensation of edge carbon chains and enhanced defect healing in the PAH structure is immediate. For the case of trajectory T1 at H/C=0.6 (Figure 1(a)), at 131.8 ps the PAH structure exhibits a one-to-one mix of hexagons and defects (8 hexagons and 5/3 pentagons/heptagons); small polyacetylene- or polyyne chains and methyl groups are also bound to the edge of the PAH. By 590 ps, all ring defects have been healed in the PAH structure, which now exhibits a hexagon-only structure. Defect healing is driven by the diffusion of hydrogen atoms on the plane of the PAH structure; this diffusion correlates with repeated C-H bond formation and cleavage. This healing role of hydrogen is clearly visible in Figure 1(a) for the case of pentagon-heptagon pair defects. Four hydrogen atoms are initially bonded to carbon atoms of the fused pentagon/heptagon pair, alternately with respect to the plane of the PAH (275.5 ps). The diffusion of one of these hydrogen atoms then induces the cleavage of C-C bond common to the heptagon and pentagon (275.6 ps). Consequently, this leads to the local reorganization of the PAH and the formation of an additional hexagon within the following 0.3 ps. A CH_2 edge defect is also formed during this period. On the other hand, all edge carbon atoms are terminated by at least one hydrogen atom, in some cases some edge carbon atoms are doubly or even triply hydrogenated. This gives rise to edge C-C single bonds; defects at the periphery of PAH are

therefore more easily reconstructed compared to double or triple bonds. At H/C=0.4, the situation is very similar to that at H/C=0.6; after approximately 590 ps, the PAH fragments are dominated by hexagons, as depicted in Figure 1(b). Indeed, in trajectory T2 only one pentagon exists in the largest PAH fragment (denoted by the arrow). It is interesting to note that most defect rings reside at the periphery of the PAH at H/C=0.6 and 0.4, whereupon there is a high possibility of them being converted into hexagons with the assistance of terminating hydrogen.

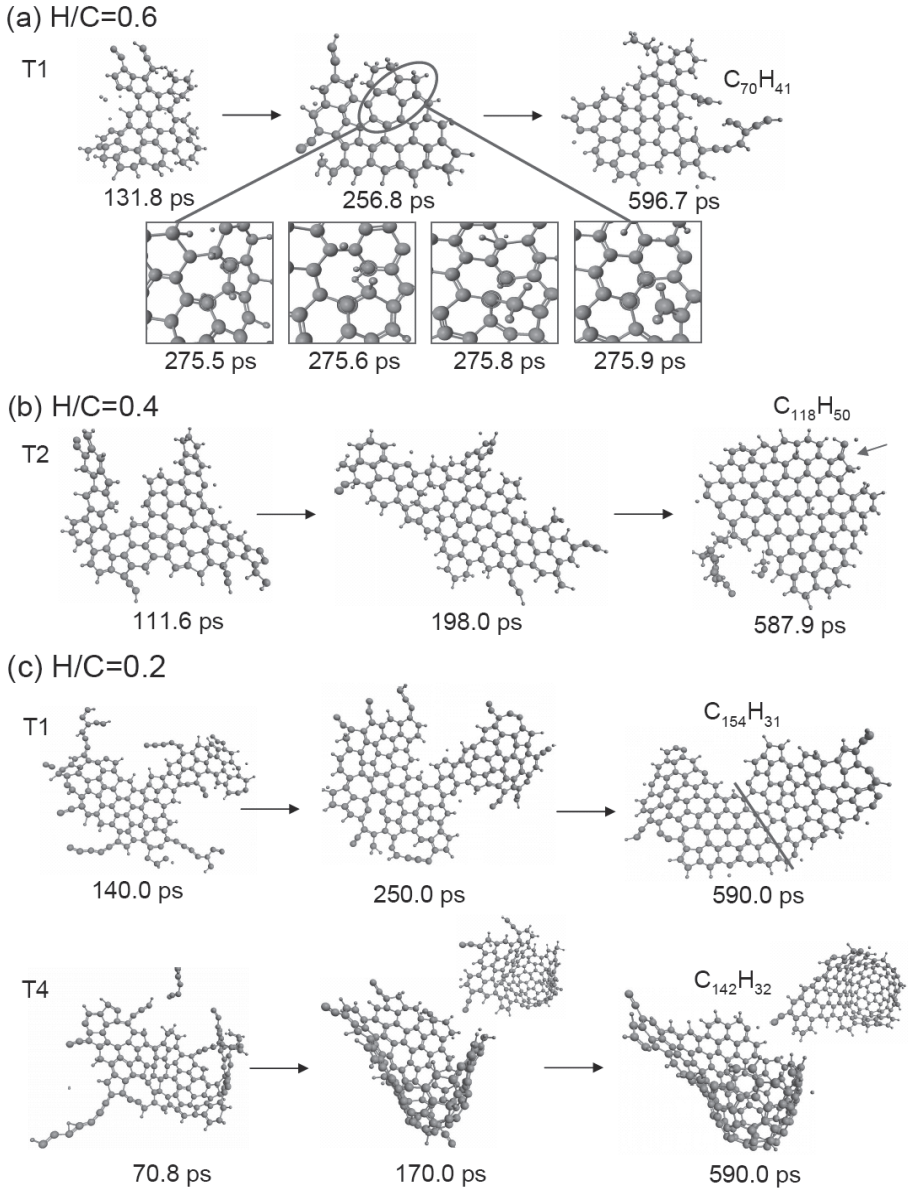


Figure 1. The evolution of the largest fragment in representative PAH formation trajectories at H/C ratios of (a) 0.6, (b) 0.4, and (c) 0.2.

2. Original papers

(1) H. B. Li, A. J. Page, A. M. Mebel, S. Irle, and K. Morokuma, "SWCNT Growth from Chiral Carbon Nanorings: Prediction of Chirality and Diameter Influence on Growth Rates", *J. Am. Chem. Soc.* 134**,** *15887***,** 2012.

(2) H. B. Li, A. J. Page, A. M. Mebel, S. Irle, and K. Morokuma, "Revealing the Dual Role of Hydrogen for Growth Inhibition and Defect Healing in Polycyclic Aromatic Hydrocarbon Formation: QM/MD Simulations", *under revision*.

(3) H. B. Li, A. J. Page, S. Irle and K. Morokuma, "Temperature Dependence of Catalyst-Free Chirality-Controlled Single-Walled Carbon Nanotube Growth from Organic Templates", *to be submitted*.

3. Presentations at Academic Conferences

H. Li, S. Irle and K. Morokuma, "Nucleation of Graphene on Ni(111) Surface with low subsurface carbon concentration", *10th* FIFC Symposium, Kyoto, Japan (Nov. 30, 2012)

Lung Wa CHUNG

Research Fellow, Fukui Kenichi Memorial Research Group 1

1. Summary of the research of the year

1a. Reactivity of Hydrogen Atom Transfer (HAT) with Metal-Oxo and How Enzymes Facilitates the Reaction. Heme- and non-heme oxygenases and oxidases catalyze many important and efficient biochemical oxidations. Several transient species, such as ferryl-oxo, ferric-hydroperoxo, ferric-peroxy and ferric-superoxo, have been proposed or found to act as oxidants. In comparison, the reported HAT reactivity in enzymes (such as sMMO) is much higher than synthetic model Fe=O complexes. Previously, I theoretically and systematically compare reactivity of several key ferric-superoxo and ferryl-oxo model complexes. Reactivity was found to correlate well with thermodynamic driving force and can increase with higher electrophilicity of the oxidant. In addition, reactivity of the ferric-superoxo oxidants generally is not stronger than the ferryl-oxo ones.

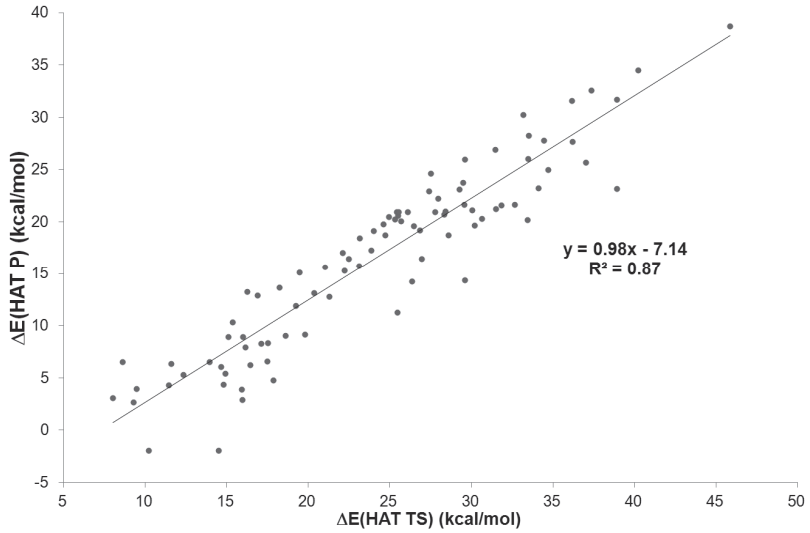
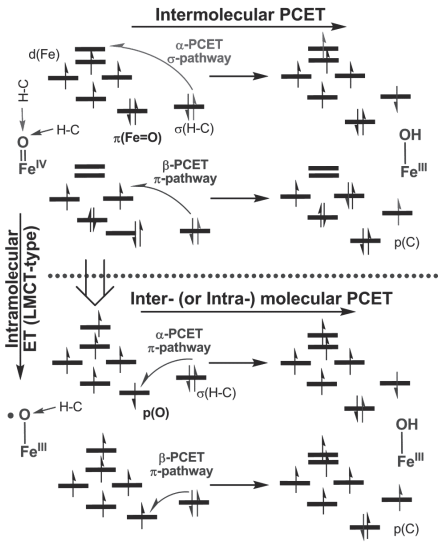


Figure 1.

To further understand why enzymes can catalyze HAT much faster than the synthetic model complexes, I designed and performed more extensive calculations by including many synthetic model complexes and several important metal-oxo species in enzymes (Figure 1). Again, the HAT reactivity was found to qualitatively correlate with thermodynamic driving force and BDE(FeO-H). Also, I generalized two mechanistic pathways (Fe(IV)-oxo or Fe(III)-oxy) for HAT in these metal complexes (Scheme 1). However, the computed HAT barrier for the important metal-oxo species in enzymes is similar to or even higher than some of the reactive ferryl-oxo model complexes, which is seemingly not consistent with the observed reactivity. Different from the model complexes, the substrate usually enters the active site of the enzymes before formation of the high-valent reactive metal-oxo species (e.g. TauD in Scheme 2). Therefore, entropy effect for the formation of a precursor complex in the enzymes should be minor, while that in the model

complexes becomes important and thus the HAT reactivity is reduced. As a result, combination of the reactive ferryl-oxo model complexes with supra-molecule which stabilizes the formation of the precursor complexes could enhance HAT reactivity. On the other hand, since HAT reactivity is known to qualitatively correlate with thermodynamic driving force and BDE(FeO-H), I proposed a decomposition scheme to understand origin of the driving force in more details (Table 1), in which exchange interactions of Fe is also found to play a role in the reactivity.

Scheme 1.



Scheme 2.

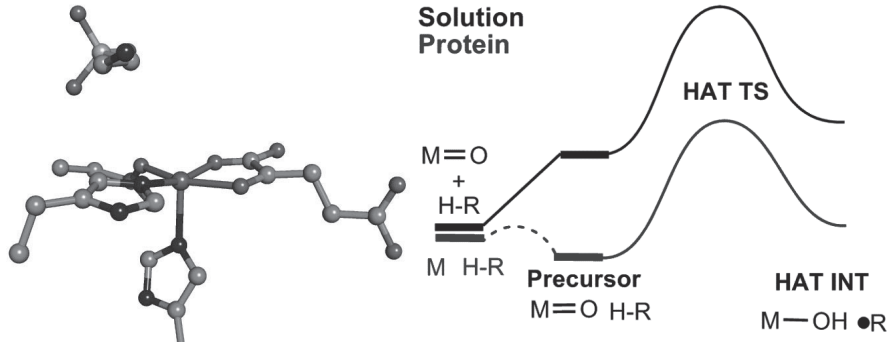
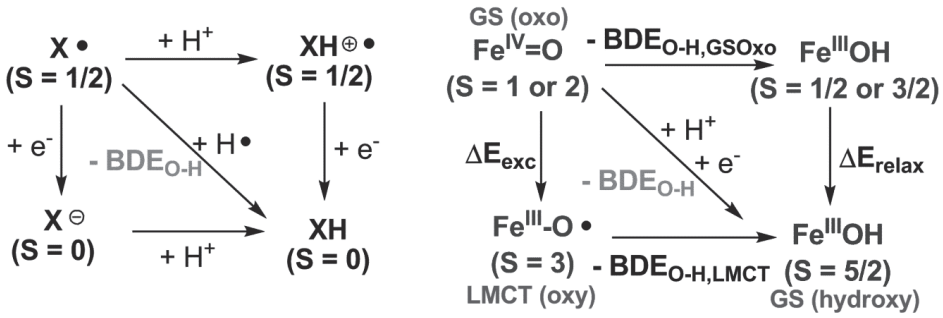


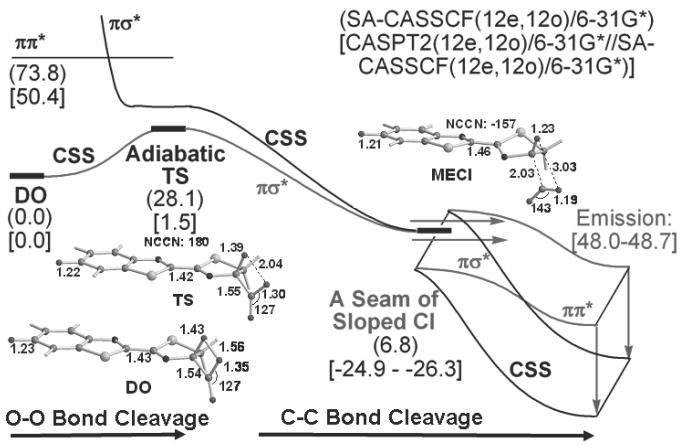
Table 1



BSIII	BDE_{OH}	$BDE_{OH,LMCT}$	ΔE_{exc}	$BDE_{OH,GSOxo}$	ΔE_{relax}
$[Fe^{IV}O(TMC)(NCMe)]^{+2}$	80.3	105.6	25.3	72.4	-7.9
$[Fe^{IV}O(N_4Py)]^{+2}$	81.2	116.2	35.0	80.1	- 1.1
$[Fe^{IV}O(NTB)(NCMe)]^{+2}$	90.1	108.6	18.5	79.9	-10.2
$[Fe^{IV}O(buea)]^{-1}$	77.5	98.5	21.0	68.6	-8.9
$[Fe^{IV}O(TPA)]^{-1}$	79.7	106.9	27.3	70.8	-8.9
(2*N ligand → 2*CO_2^-)	85.2	106.8	20.6	73.9	-11.3
$[Fe^{IV}O(TMG_2)(NCMe)]^{+2}$	81.0	108.2	27.3	76.8	-4.2
$[Fe^{IV}O(TauD)]$	*87.8*	*105.2*	*17.3*	*78.7*	*-9.1*
$[Fe^{IV}O(P2DA)]$	91.5	110.1	18.6	79.4	-12.1
$[Fe^{IV}O(por)(His)]$ (heme)	***78.0***	-	-	***78.0***	***0.0***

1b. Chemiluminescence and Bioluminescence of Dioxetanones: Firefly emission is a well-known efficient bioluminescence. However, mystery of the efficient thermal generation of electronic excited states still remains unclear. Previously, I performed SA2-CASSCF and CASPT2 calculations with a computationally feasible active space (12,12) to uncover an adiabatic transition state followed by a seam of sloped conical intersection in the gas phase (Scheme 3). Recently, Liu used a slightly larger active space (16,13) or (18,15), and six-state CASSCF averaging (DZ basis sets) based on the CAM-B3LYP IRC pathway. They proposed an additional conical intersection during the O-O bond cleavage. Unfortunately, complicated electronic structures involved in the reaction requires a much larger active space, which can only be treated by new methods (e.g. density matrix renormalization group method (DMRG)). We collaborated with Prof. Yanai (IMS) for his efficient DMRG code. I performed DMRG-CASSCF and DMRG-CASPT2 calculations with very large active spaces (e.g. (30,26)) and TZ basis sets. These very high-level results qualitatively support my previous proposed mechanism, but not support a recent proposed mechanism the additional conical intersection (partly due to a too small active space). Geometry optimization of the reaction path with novel DMRG-CASSCF analytic gradient is in progress.

Scheme 3.



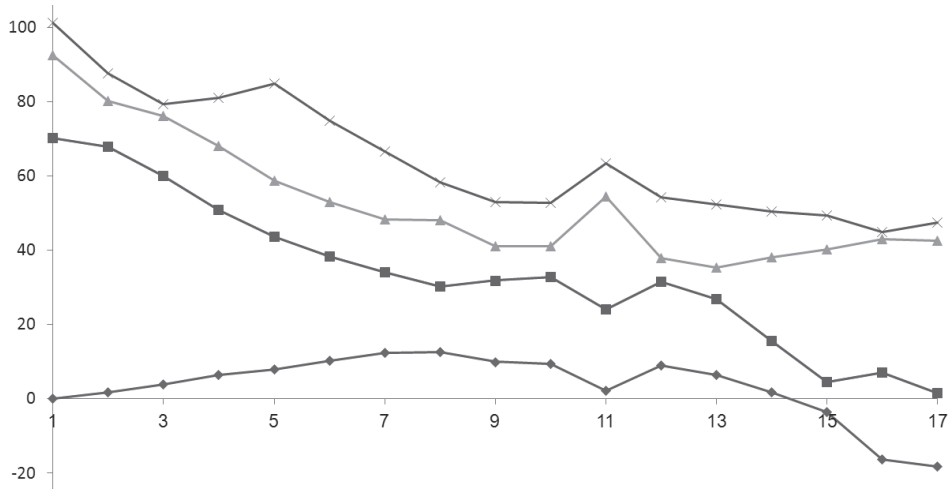


Figure 2.

2. Original papers

(1) Chung, L. W.; Hirao, H.; Li, X.; Morokuma, K. “The ONIOM Method: Its Foundation and Applications to Metalloenzymes and Photobiology”, *Wiley Interdisciplinary Reviews: Comput. Mol. Sci.* **2012**, *2*, 327.

(2) Ding, L.; Chung, L. W.; Morokuma, K. “Reaction Mechanism of Photoinduced Decarboxylation of the Photoactivatable Green Fluorescent Protein: An ONIOM(QM:MM) Study” *J. Phys. Chem. B* **2013**, *117*, 1075.

(3) Ding, L.; Chung, L. W.; Morokuma, K.* “Excited-State Proton Transfer Controls Irreversibility of Photoisomerization in Mononuclear Ruthenium(II) Monoaquo Complexes: A DFT Study”, Revision.

(4) “Reaction Mechanisms of Diversified Reactions in Hydroxypropylphosphonic Acid Epoxidase (HppE): Effect of Conformations of the Substrates”, Manuscript in preparation.

3. Presentation at academic conferences

(1) Xin Li, Lung Wa Chung, Keiji Morokuma "Primary Events of Photodynamics of All-trans Retinal Protonated Schiff Base in Bacteriorhodopsin, Methanol Solution and Gas Phase", JST International Symposium on Multi-scale Simulation of Condensed-phase Reacting Systems, Nagoya, May, 10, 2012.

Galina PETROVA

Research Fellow, Fukui Kenichi Memorial Research Group 1

1. Summary of the research of the year

All the topics discussed in the current report are proposed by experimental groups interested in gaining better understanding on the mechanism of catalyzed reactions from different spheres of asymmetric organic catalysis. The available experimental data are not sufficient or ambiguous in order to define the complicated reaction cycles and thus, theoretical modeling of the systems can provide essential information about the reaction mechanisms and the nature of the enantio(stereo) selectivity allowing further modifications of the catalysts and the experimental conditions. The last two subjects despite the relatively early stage of the theoretical studies are good example of the advantages of using the AFIR approach for transition state search for systems with flexible structures, more than one active center and potential assisting groups and species easily available in vicinity to the reaction center.

Theoretical modeling of stereochemistry control of copper catalysts based on the chirality of DNA

At the first stages of this investigation we have been concentrated on gaining information about the detailed structure of the supramolecular catalyst consisting of DNA fragment, Cu(II)-based complex and the reacting species [Sugiyama et al. Chem. Commun. 2012]. We have applied a combination of docking, MD, and QMMM simulations being able at the last stage to define the difference in the stability of the possible complexes and the reasons for these differences. Comparing the available for the moment structures at QMMM level (e.g. Fig. 1), it can be concluded that the stability of the reactant complexes depends on several factors: (i) deformation of the DNA double strand at the intercalation of the metal complex and rearrangement of the water surrounding, (ii) deformation of the metal complex due to changes in its initially π-π stacked structure, and (iii) the stabilizing effect of interaction between the DNA and the complex originating from both electrostatical and dispersion interactions. The structure with highest binding energy is pro-*S*1 complex intercalated between 6-7 base pairs of the DNA with reactant oriented towards the major groove of the DNA. The high BE of the structure, -60.7 kcal/mol, is a result of relatively low deformation of the DNA (compared with most of the other structures) and high interaction energy. Interestingly the reactant molecule preserved its local stacking and the structure is a good candidate for a transition state search. Next in stability with BE around -40 kcal/mol are pro-*S*2 from the 6-7 bp/MajG series and pro-*S*2 and pro-*R*2 from the 5-6 bp/MinG series and while in the pro-*S*2 the metal complex deviates from its initial intramolecular stacking structures which results in quite high interaction energy, the pro-*R*2 structure from the 5-6 bp/MinG is characterized with deformational changes similar to those observed in the most stable conformer, pro-*S*1 in 6-7 bp/MajG but with much lower energy of interaction. The performed analysis also shows that intercalation of the metal complex in the 6-7 base pairs layer with the reactant moiety located in the minor groove of the DNA strand is basically unfavorable as two of the conformers of the complex, pro-*S*2 and pro-*R*1, induce severe deformation of the DNA strand while in the case of pro-*S*1 structure the interaction energy is insufficient to compensate the energy lost due to deformation of the sub-systems.

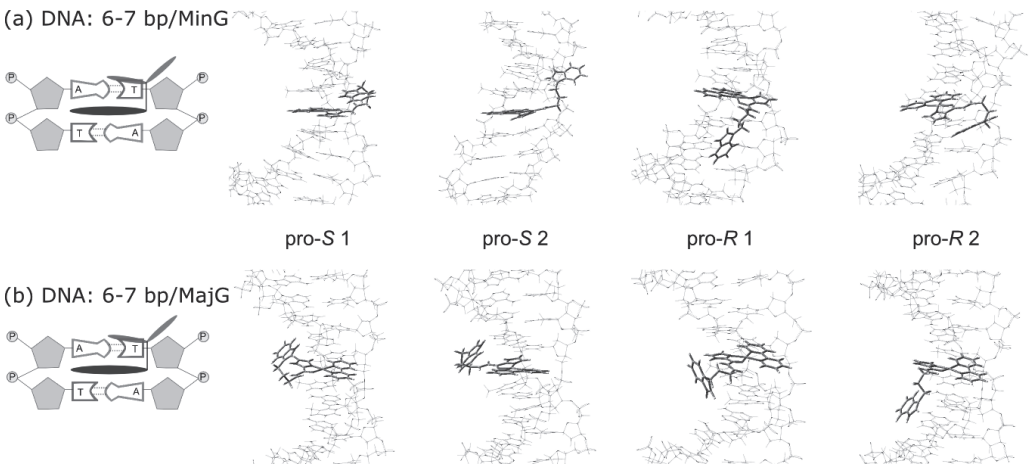


Figure 1. Structure of the supramolecular Cu/DNA complexes in case of intercalation between base pairs 6-7 with reactant located in the minor (a) or major (b) groove.

In order to check the effect of the DNA on the reaction mechanism we modeled transition states for the C-C bond formation for 5-6 MinG structures and the results confirm the high catalytic effect of DNA, lowering the barriers for this stage by ca. 10 kcal/mol for both pro-*R* and pro-*S* species compared to the reaction catalyzed by the Cu(II) in the absence of DNA. The energy barriers for the formation of *S* or *R* intermediates remain very similar and it is difficult to distinguish which structure will prevail. On the other hand, calculations both with and without DNA show that the next step of the process, the H-transfer stage, is more complicated and more energy demanding. In order to check the possibilities for direct participation of the DNA fragment in the reaction we intend to use AFIR - a novel theoretical approach for automated search of transitions states [Maeda, Ohno, Morokuma, Phys. Chem. Chem. Phys. 2013].

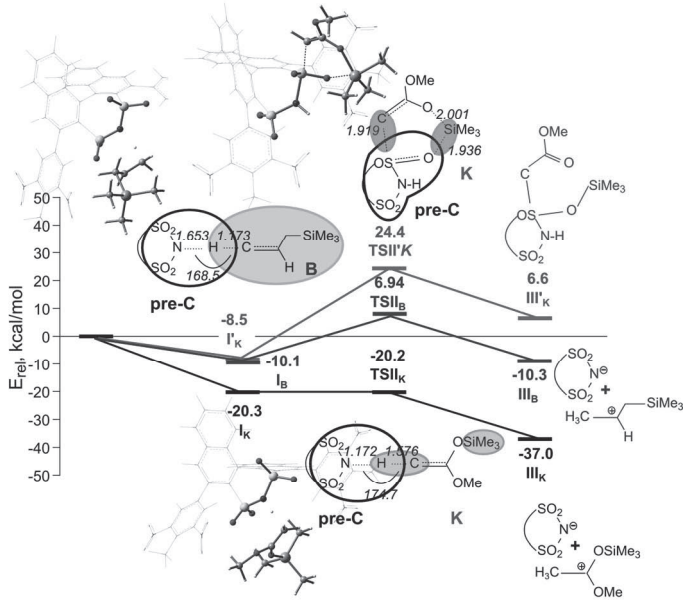


Figure 2. First step of the reaction cycle of ACDC Hosomi-Sakurai reaction obtained by AFIR (pre-C: pre-catalyst, K – ketene, B – allyltrimethyl silane which is also the second reactant in the Hosomi-Sacurai reaction).

ACDC: Asymmetric counteranion directed catalysis

Another interesting problem also related to organic catalysis is the asymmetric counteranion directed catalytic Hosomi-Sakurai reaction applying chiral disulfonamide catalyst [List et al. Angew. Chem. Int. Ed. 2013; Chem. Eur. J. 2012]. Except for the reaction cycle itself and the experimentally predicted TMS group shifting, it is also interesting to understand the mechanism of formation of the silylated form of the asymmetric catalyst. By this reason we applied AFIR for

automatic search of transitions states for the interaction between the pre-catalyst in its H-form and the possible silylating agents in the system – the catalyst activator silyl ketene acetal and one of the reactants in the Hosomi-Sakurai reaction, allyltrimethylsilane (See Figure 2). The AFIR approach combined with random orientation of the reacting species allowed us to locate TS structures deferring on the conformation and on the nature of the interaction. The H-transfer from N atom of the pre-catalyst to the CH_2 group of the silylating agents is the most favorable path in both cases and for the ketene structure this process is barrierless while for the reactant allyltrimethylsilane it would require ca. 20 kcal/mol. The last observation is in good agreement with the experimental observations according to the reaction can proceed enantioslectively with only allyltrimethylsilane to silylate the catalyst but is very slow.

PTC: Enentioselective base-free phase-transfer catalysis

The conformational interconversion between homo- and heterochiral forms of a asymmetric phase transfer quaternary ammonium bromide catalysts have been studied [Maruoka, Tetrahedron 2006]. In agreement with the experimental data, the homo-form of the catalyst which shows better catalytic performance is found by 3.4 kcal/mol less stable than the heteroform. The barrier for conversion is estimated to 16.8 kcal/mol. Simple docking experiments followed by QMMM optimization of the predicted structures have shown that the differences in the catalytic activity of the two species can not be explained only on their structural specifics. By this reason, we are working on modeling the reaction mechanism via AFIR in attempt to understand the effect of the water necessary for the reaction to proceed.

2. Original papers

Galina Petrova, Zhuofeng Ke, Keiji Morokuma, Theoretical modeling of DNA-based copper catalysts: structure and performance in intramolecular Friedel-Crafts reaction. *In preparation*.

3. Presentation at academic conferences

Galina P. Petrova, Lung Wa Chung, Keiji Morokuma
"DFT and ONIOM modeling of fosfomycin biosynthesis catalyzed by HppE" (Poster presentation)
XIVth International Congress of Quantum Chemistry, Boulder, Colorado, USA (June 25-30, 2012)

Galina Petrova, Zhuofeng Ke, Keiji Morokuma (FIFC)
"Theoretical modeling of DNA-based copper catalysts performance in intramolecular Friedel-Crafts reaction" (Poster presentation)
10th FIFC Symposium, Kyoto, Japan (November 30, 2012)

Travis HARRIS

Research Fellow, Fukui Kenichi Memorial Research Group 1

1. Summary of the research of the year

I. QM/MM Structural and Spectroscopic Analysis of the Di-iron(II) and Di-iron(III) Ferroxidase Site in M Ferritin

Ferritins are cage-like proteins composed of 24 subunits that take up iron(II) and store it as an iron(III) oxide mineral core. A critical step is the ferroxidase reaction, in which oxygen reacts with a di-iron(II) site to form μ-oxo/hydroxo-bridged di-iron(III) products:

$$2Fe^{2+} + O_2 + H_2O \rightarrow [Fe(III)–O–Fe(III)] + H_2O_2$$

Recently, crystal structures of copper(II)- and iron(III)-bound frog M ferritin at 2.8 Å resolution (active sites shown in Figure 1) provided an opportunity for theoretical modeling of the reactant state and products. The moderate resolution, partial occupancy of ferroxidase sites, and use of Fe(II) analogues in ferritin crystal structures precludes a detailed description of the positions, binding modes, and protonation states of protein- and water-derived ligands by crystallography alone; complementary spectroscopic and theoretical studies are necessary to define the structures of the Fe(II), Fe(III), and intermediate states.

QM/MM calculations were carried out using B3LYP/Amber using single subunit models. The QM layer included the side chains of Glu23, Glu58, His61, Glu103, Gln137, Asp140, and, in the Fe(II)-containing models, His54. The C_β-C_α bond was the QM-MM boundary for each of these residues. Atoms beyond 9 Å from either Fe center were fixed. To identify the structure of the 2Fe(II)-bound ferroxidase site, we examined a series of models (**R1-R11**) shown in Figure 1. We found that no single model can be definitively described as having the experimentally determined one square pyramidal and one trigonal bipyramidal site. The distorted geometries and, in some cases, weak metal-ligand interactions present difficulties in assigning the environments. However, models **R4** and **R6-R8** clearly have two five-coordinate iron centers, and are thus good candidates for the Fe(II)-bound state. These models have Fe-Fe distance of 4.95 Å, 4.48 Å, 4.63 Å, and 4.35 Å, respectively; thus, **R6-R8** are most consistent with the crystallographic distance of 4.3 ± 0.4 Å.

The CD/MCD spectra of the Fe(II)-bound state, taken at 1.7 K, show features at 5025 cm^{-1}, 7600 cm^{-1}, 9900 cm^{-1}, and 11150 cm^{-1} (see Figure 2), attributed to two d-d transitions at each iron center.[1] The calculated spectra of four models, **R1** and **R6-R8**, are also plotted in Figure 2. None of the calculated spectra have the correct signs for all three features, but this is not unexpected; incorrect signs were also obtained in a study of another di-iron enzyme, Δ^9 desaturase, using the same computational method. Based on the relative energies of all four transitions, the spectrum of **R6** agrees best with the experiment. A constant shift of -1000 cm^{-1} would result in very good energetic agreement for **R6**, as each transition would be within 500 cm^{-1} of the corresponding experimental transition. Similar corrections for systematic error have been applied previously for TD-DFT-based CD calculations

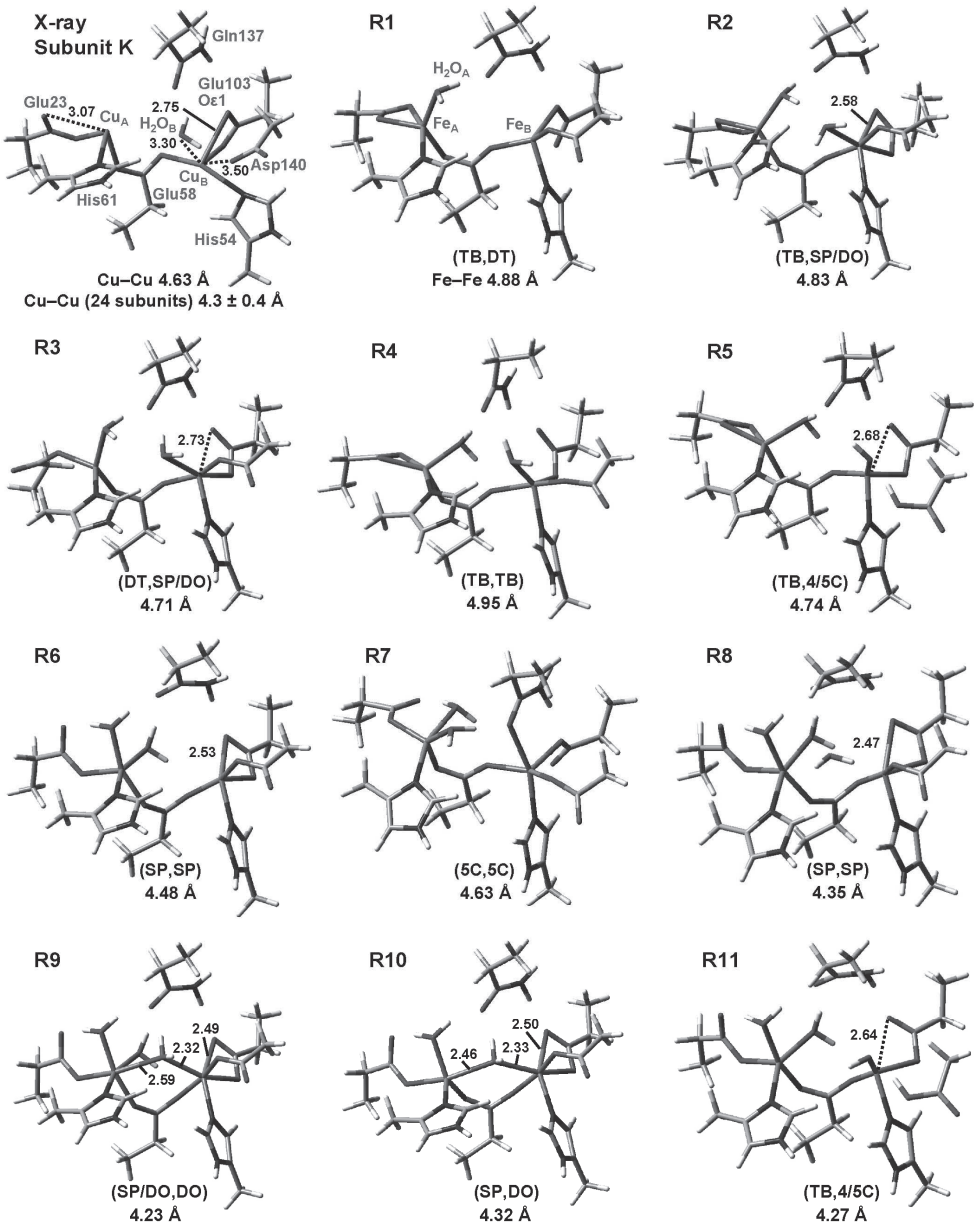


Figure 1. (top) QM/MM-optimized di-Fe(II) models and initial crystallographic structure, including metal-metal distances. Only the QM layer is shown. Ligand field geometries are given for (Fe_A,Fe_B) as follows: TB, trigonal bipyramidal; SP, square pyramidal; DO, distorted octahedral; DT, distorted tetrahedral; 4/5C, four or five coordinate.

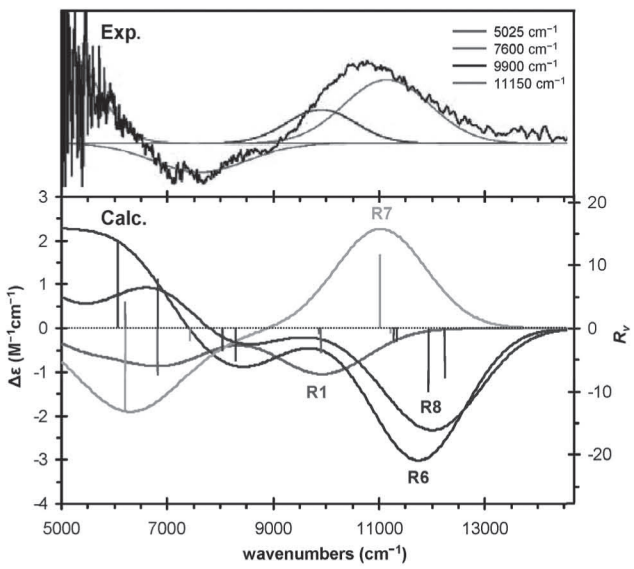


Figure 2. (right) Calculated CD spectra for four di-Fe(II) models compared to the 1.7 K experimental spectrum and deconvolution.[1] The right axis (rotatory strength) corresponds to the line spectra.

The di-Fe(III) products of the ferroxidase reaction have a short Fe-Fe distance of 3.05 Å that suggests the presence of a bridging oxo or hydroxo ligand obscured by the electron density of the iron centers. The Fe-Fe distances and Mössbauer parameters provide the best link to experiment, enabling the di-Fe(III) site (i.e., ferroxidase reaction products) to be identified. The experimental Mössbauer spectrum is broad, and the fitting analysis required at least four quadrupole doublets, indicating variable ligand environments of the products. Optimizations of a series of models led to four groups of structures, which were categorized by the nature of the bridging ligand(s): (1) single μ-hydroxo, (2) single μ-oxo, (3) double μ-hydroxo, or (4) double μ-oxo/hydroxo. Table 1 shows that our models with various bridging ligands have distinct sets of Mössbauer parameters, with differences on the order of 0.05 mm/s in δ, and/or 1 mm/s in ΔE_Q. By contrast, the additional hydrogen bonds and changes in protonation state of the H_2O_{B1} ligand due to the additional water in models denoted **(2)** cause only small perturbations of ~0.01 mm/s in δ and 0.3 mm/s or less in ΔE_Q. Thus, the experimental quadrupole doublets (Table 1, exp(1-4)) can be attributed to species with different bridging ligands.

Table 1. Calculated and experimental Mössbauer parameters and Fe-Fe distances for di-Fe(III) products

model	Fe-Fe	$\delta(Fe_A)$	$\delta(Fe_B)$	$\lvert\Delta E_Q(Fe_A)\rvert$	$\lvert\Delta E_Q(Fe_B)\rvert$
μ-OH^-	3.50	0.50	0.50	0.43	1.12
μ-O^{2-}(1)	3.32	0.51	0.50	1.95	1.56
μ-O^{2-}(2)	3.35	0.51	0.50	1.77	1.43
2μ-OH^-(1)	3.07	0.56	0.51	0.49	1.25
2μ-OH^-(2)	3.05	0.56	0.52	0.23	0.97
2μ-O^{2-}/OH^-(1)	2.88	0.54	0.47	1.25	1.23
2μ-O^{2-}/OH^-(2)	2.88	0.55	0.47	1.33	0.94
2μ-OH^-/O^{2-}	2.85	0.57	0.51	1.21	1.26
exp(1)[a]		0.48		1.95	
exp(2)[a]		0.55		1.63	
exp(3)[a]		0.48		1.17	
exp(4)[a]		0.52		0.63	
crystallography	3.1 ± 0.1				
EXAFS	2.99–3.00[b]				

[a]1-4 in parentheses refer to the four quadrupole doublets used to fit the experimental spectrum. They are not assigned specifically to Fe_A or Fe_B. [b]2.99 and 3.00 Å were found using two independent samples.

Based on the Mössbauer parameters in Table 1, exp(1) is assigned to a single di-Fe(III) model, **μ-O^{2-}(1)**, while exp(2-4) are assigned to individual iron centers of **2μ-O^{2-}/OH^-(2)** and **2μ-OH^-(1)**. The Fe-Fe distances are 3.32, 3.07, and 2.88 Å for **μ-O^{2-}(1)**, **2μ-OH^-(1)**, and **2μ-O^{2-}/OH^-(2)**, respectively, and the experimental distances, 3.1 ± 0.1 Å (crystallography) and 2.99-3.00 Å (EXAFS), are in the middle of this range. The EXAFS results represent an average over the products, while in the crystal structure some of the

variation in Fe-Fe distances between subunits may be due to the various products.

In this work, we identified the most likely structure of the di-Fe(II) site, and three Fe(III) dimers that are produced simultaneously in different subunits of ferritin. These structures will be the basis of future mechanistic studies aimed at understanding biomineralization in ferritin. Currently, we are applying the methods used here to identify a spectroscopically consistent structure of the peroxo intermediate. With the key structures in hand we will be in position to explore the pathway connecting the di-Fe(II) state to the peroxo intermediate, and the branching mechanisms that lead to the multiple products found in this work.

II. Density Matrix Renormalization Group Calculations of Magnetic Exchange Coupling in Dinuclear Transition Metal Complexes

Theoretical calculations of exchange couplings are indispensable in the fields of molecular magnet and metalloenzyme research. The most accurate methods that are typically employed include complete active space second-order perturbation theory (CASPT2) and difference dedicated configuration interaction (DDCI), but for larger systems and those containing metals with high spin moment (e.g., iron), it is common to resort to density functional theory. A promising approach is to use the density matrix renormalization group (DMRG) method, which can treat larger active spaces than in conventional CASSCF calculations. The antiferromagnetically coupled (S = 0) oxo-bridged $[Fe_2OCl_6]^{2-}$ anion was selected as a model system to test the applicability of DMRG for calculating magnetic interactions.

The exchange coupling constant, J, of the Heisenberg spin-Hamiltonian $H = -2JS_AS_B$ can be determined from the spin-ladder of the following form:

$E(S) - E(S\text{-}1) = -2JS$

The J value derived from the lowest spin states, S = 0 and 1 are the most appropriate for comparison to the -117 cm^{-1} experimental value determined from temperature-dependent magnetic susceptibility, as the higher spin states are not significantly populated. Furthermore, deviations from this Heisenberg behavior can occur for higher spin states of antiferromagnetically coupled systems.

Table 2. J values for $[Fe_2OCl_6]^{2-}$ calculated with various methods

method	act. space	M	J/cm^{-1}
CASSCF	(16,13)		-58.6
MRCI	(16,13)		-96.3
DMRG	(16,16)	512	-58.0
DMRG	(10,20)	256	-49.0
DMRG	(16,26)	1000	-116.8
exp.			-117

DMRG-CASSCF J values presented in Table 1 were calculated using a triple-zeta ANO-RCC basis set with various active spaces and M, which is the number of renormalized states. DMRG calculations approach the CASSCF limit for the employed active space as M increases, but they also become more computationally demanding. For comparison, conventional CASSCF and multi-reference configuration interaction (MRCI) calculations were performed using the smallest active space, (16,13). This active space consists of 16 e in 10 Fe(3d) and 3 O(2p) orbitals. DMRG allows inclusion of "double shells," which are the O(3p) or Fe(4d) virtual orbitals that are important for correlation. The (16,16) active space adds the oxygen double shell to (16,13), while (10,20) includes just the Fe(3d,4d). The largest active space, (16,26), is composed of Fe(3d,4d) and O(2p,3p). DMRG calculations converge at lower M for smaller active spaces;

thus, 256 and 512 for (10,20) and (16,16) are sufficiently converged. The *J* value for DMRG-CASSCF(16,26) (-116.8 cm^{-1}) accurately reproduces the experimental value, -117 cm^{-1}, while the conventional CASSCF(16,13) result is -58.6 cm^{-1}. MRCI(16,13) (-96.3 cm^{-1}) approaches the experiment, but it is still less accurate than the large active space DMRG calculation. Addition of either the O(3p) or Fe(4d) double-shell orbitals alone does not improve the result; they both must be included.

DMRG pushes the theoretical boundaries for the study of multi-reference systems, allowing unprecedented accuracy in the case described here. In future work this method will be applied to other molecular magnets and metal-containing systems of biological significance.

2. Original papers

(1) Harris, T. V.; Morokuma, K.
"QM/MM Structural and Spectroscopic Analysis of the Di-iron(II) and Di-iron(III) Ferroxidase Site in M Ferritin"
Inorg. Chem. Submitted (2013).

5. Others

(1) Harris, T. V.; Morokuma, K.
"ONIOM Study of the Ferritin Ferroxidase Reaction" (Poster)
10th FIFC Symposium (2012).

伊勢川　美穂
研究員（2013 年 3 月 1 日から）

ニトロメタンの光解離

ニトロメタンは最も単純なニトロ化合物であるが、その複雑な電子構造のため、紫外線照射により始まるその解離過程は単純ではない。

実験においては、これらの光解離の生成物として、CH_3, NO_2, HNO, NOH, CH_2O, CH_3NO, CH_3O, NO, OH があげられている。しかしこれらの生成物は、実験者により、検出されたか否の結果が異なり、明確な反応機構を含めた実験における一致点は、まず、C-N 結合の解離により CH_3 および NO_2 が生成されるということのみである。

理論計算に関して、これまで、基底状態の熱的解離については多くの研究がなされてきたが、励起状態についての研究はその解離極限における遷移状態の求めることが容易ではないことから、いまだその解離機構は部分的にしか知られていない。特に、このような、複雑な電子構造系に対し、異なる同一スピン励起状態への遷移が可能な、conical intersection また、異なるスピン状態への遷移が可能な seam of crossing の役割を明らかにすることは重要である。近年では Arenas らにより、その励起状態を含めた解離（$CH_3NO_2 \rightarrow CH_3 + NO_2$, $CH_3NO_2 \rightarrow CH_3NO + O$）について調べられているが、[a] 彼らは、分子対称性を C_s に制約しているため、実像とは多少異なると考えられる。

また近年、この系の基底状態においては非常に興味深い解離過程として、Homayoon らが、Roaming 過程のある異性化反応を経由した、解離過程を半古典的動力学計算により示した。[b] 分子解離における Roaming 過程はいくつかの分子で検証されており、たとえば、H_2CO では基底状態 [e]、 NO_3 においては励起状態で [f] みられることがこれまで立証されている。

私たちの研究の目的は、193nm (148.1kcal/mol)の紫外線照射により始まる光解離過程をより詳細な記述とともにその解離機構を明らかにすることである。上記の Roaming 過程が励起状態において見られるかも検証する。　解離機構を示すには、多くの critical points、すなわち、平衡状態、遷移状態(一次の鞍点)、conical intersection, 及び seam of crossing を求め、それらの相関を intrinsic reaction coordinate (IRC) により明示することが必要である。　近年、Maeda, Morokuma, Ono らは遷移状態 を核座標に対する、電子のエネルギーの一次、二次微分を大量に計算することにより、リストアップするアルゴリズムを提案した。[c] すなわち、ある大域、もしくは局所的な最小値を出発点とし、派生的に遷移状態、そのほかの最小値を探索する方法である。また、彼らは artificial な力を、もとのフラグメント間の力に加え、フラグメント A—フラグメント B (ここで、フラグメントは、分子、原子である。) の反応における、遷移状態を求める方法も提案している。[d] 前者については、まったく未知の dissociation channel を導出する場合、後者は、前者において限られた計算時間の中で、得られなかった状態を推測とともに得るために用いられる。両者を、有効に応用することで、電子エネルギーにおいて有利な分子解離の反応経路を探る。

【文献】[a] J. F. Arenas, J. C. Otero, D. Pelaez, J. Soto, *J. Chem. Phys.* **122**, 084324 (2005).
[b] Z. Homayoon, J. M. Bowman, *J. Phys. Chem.* A, **XXX**, XXXX (XXXX).
[c] S. Maeda, K. Ohno, *J. Phys. Chem.* A, **109**, 5742 (2005).
[d] S. Maeda, K. Morokuma, *J. Chem. Phys*, **132**, 241102 (2010).
[e] D. Townsend, S. A. Lahankar, S. K. Lee, S. D. Chambreau, A. G. Suits, X. Zhang, J. Rheinecker, L. B. Harding, J. M. Bowman, Science, **306**, 1158 (2004).
[f] H. Xiao, S. Maeda, K. Morokuma, *J. Phys. Chem. Lett*, **2**, 934 (2011).

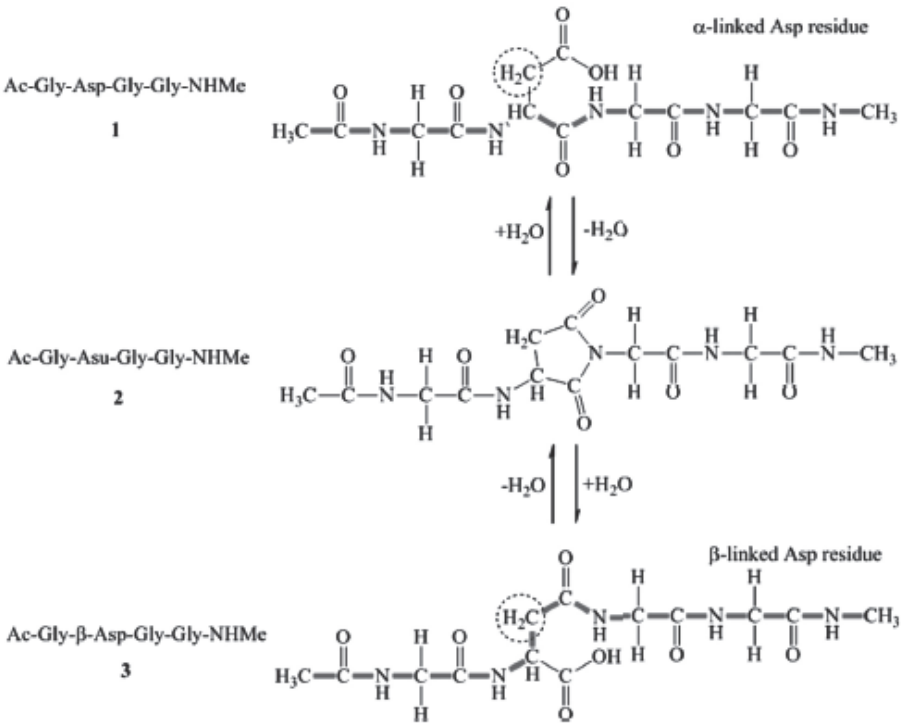
Shinichi YAMABE

SPR Fellow, Fukui Kenichi Memorial Research Group 2

1. Summary of the research of the year

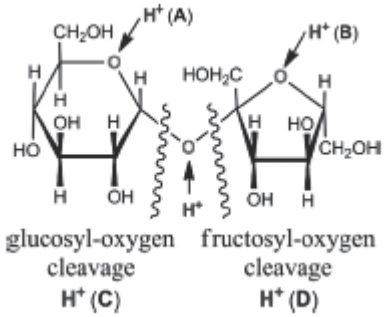
(1-1) A DFT study on the isomerization of aspartyl peptides to iso-aspartyl ones

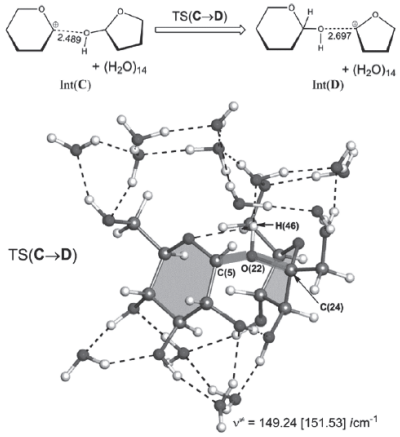
The isomerization reaction of a tetra-peptide, Ac-Gly-Asp-Gly-Gly-NHMe -> Ac-Gly-isoAsp-Gly-Gly-NHMe, was investigated by DFT calculations.
Thirteen water molecules were added to the peptide for simulating proton transfers during the isomerization. As a staring analysis, the number (m) of water molecules participating in ready proton transfers was examined by the use of a small model system, $H_3C.NH.C(=O).CH_2.CH_2.COOH$ and $(H_2O)_m$. The m=2 stepwise path found to be of the smallest activation free energy. On the basis of this result, the first isomerization path of the tetra-peptide was obtained with four elementary processes. The m=2 proton transfer is involved in them. A different proton transfer gives the second isomerization path with six elementary processes. The second path (with ionization) is more likely than the first one (without ionization). Formation of the five membered rings of the aminosuccinimidyl-residue and anionic tetrahedral intermediates enhances the encapsulation of H_3O^+ through the wound tetra-peptide ring. The role of the hydrogen bonds on the encapsulation was discussed in terms of the optimized geometries of proton-transfer transition states and intermediates.



(1-2) A　DFT study on the acid-catalyzed hydrolysis of sucrose to glucose and fructose

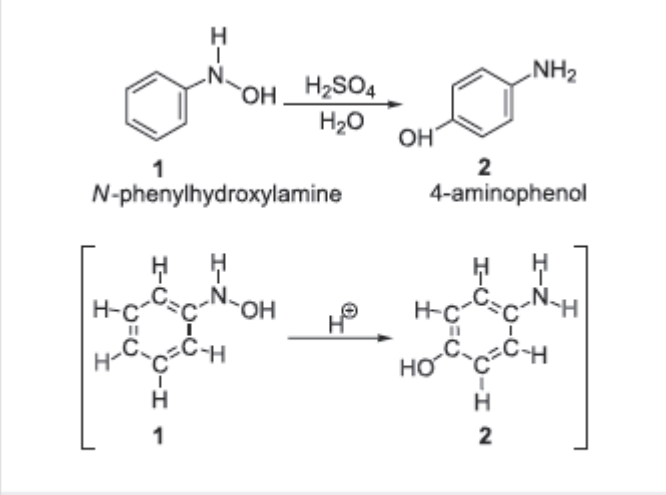
The acid-catalyzed hydrolysis of sucrose to glucose and fructose was investigated by DFT calculations. Protonations to three etheroxygen atoms of the sucrosemolecule,A,B,and C,D),were compared. Three(B, the fructosyl-ringoxygen protonation;, C that to the bridge oxygen of the glycosidic bond for the glucosyl-oxygen cleavage; and D,protonation to that for the fructosyl-oxygen cleavage) gave the fragmentation.　Paths B, C, and D were examined by the use of the sucrose molecule and $H_3O^+(H_2O)_{13}$. The path B needs a large activation energy, indicating that it is unlikely.　The fragmentation transition state(TS1) of path C needs almost the same activation energy as that of path D.　The isomerization TS of Int(C)→Int(D), TS(C→D), was also obtained as a bypass route.　The present calculations showed that the path via the fructosyl-oxygen cleavage(D) is slightly(not absolutely) more favorable than that via the glucosyl-oxygen cleavage(C).



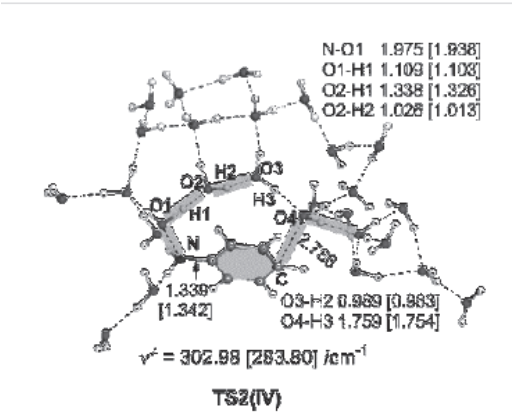


(1-3) Analysis of the reaction paths in the Bamberger rearrangement

A Bamberger rearrangement of N-phenylhydroxylamine, Ph.N(OH)H, to p-aminophenol was investigated by DFT calculations for the first time.　There has been a significant question as to why in some cases, for example where the nucleophile　is water,　only the 4(para)-isomer product is formed from phenylhydroxylamine, whereas in other cases, e.g., when chloride ion is present, both 2- and 4-chloro isomers are　formed.　By the present calculations,　the nitrenium ion, $C6H5.NH^+$, suggested and seemingly established as an intermediate , was　found to be absent owing to the high nucleophilicity of the water cluster around it.　A　reaction of the monoprotonated system, Ph.N(OH)H + $H_3O^+(H_2O)_n$ (n = 4 and 14) was examined. However, the rate-determining transition states involving proton transfers were calculated to have much larger activation energies than the experimental one.　Netx, a reaction of the diprotonated system, Ph.N(OH)H + $(H_3O^+)_2(H_2O)_{13}$,　was traced.　An activation energy similar to the experimental one was obtained.　A　new　mechanism of　the rearrangement including the aniline dication-like transition state was proposed.



Scheme 1: The Bamberger rearrangement. In the square bracket, the apparent exchange of H and OH is shown.



2 Original Papers

(1) "How is the anionic tetrahedral intermediate involved in the isomerization of aspartyl Peptides to iso-aspartyl ones? A DFT study on the tetra-peptide",
Shinichi Yamabe, Wei Guan and Shigeyoshi Sakaki
Org. Biomol. Chem., 2012,10, 8007-8015

(2) "Presence or absence of a novel charge-transfer complex in the base-catalyzed hydrolysis of N-ethylbenzamide or ethyl benzoate",
Shinichi Yamabe, Wei Guan and Shigeyoshi Sakaki,
Beilstein J. Org. Chem. 2013, 9, 185-196.

(3) "Three Competitive Transition States at the Glycosidic Bond of Sucrose in Its Acid-Catalyzed Hydrolysis",
Shinichi Yamabe, Wei Guan and Shigeyoshi Sakaki
J. Org. Chem., 2013, 78 (6), 2527-2533.

(4) "An aniline dication-like transition state in the Bamberger rearrangement",
Shinichi Yamabe, Guixiang Zeng, Wei Guan and Shigeyoshi Sakaki
Beilstein J. Org. Chem. 2013, 9, 1073-1082.

3.Presentation at academic conference

“Mechanism of the Nozoe azulene reaction“(B10),
S. Yamabe, T.Machiguchi, T. Hasegawa, T. Minato, S. Yamazaki,
and S. Sakaki, Sept. 19, 2012,
The 23-rd Symposium on Physical Organic Chemistry, at Kyoto

土方　優

FIFC フェロー

1. 今年度の研究の要約

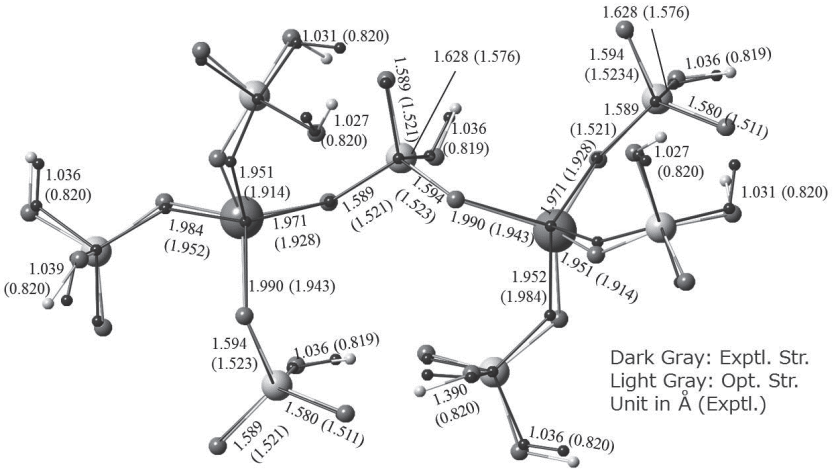
今年度は配位高分子におけるプロトン伝導性に関する研究を行った。

【始めに】

多孔性配位高分子と呼ばれる物質群が近年注目を集めている。この物質群は、金属イオンと有機配位子からなる空孔を有した多孔性材料であり、そのガス吸着能、選択的吸着、光応答性、ゲスト応答性、触媒、磁性など多岐にわたる機能が注目を集め研究が行われている。最近、このような配位高分子は輸送システムとしての応用も注目を集め始めた。特にプロトン伝導に関する研究は、電極材料などデバイスなどへの応用が期待され、この数年で活発に研究が展開されている。このような伝導性に関する研究では、用いる骨格やプロトンのキャリアとなる化学種の組み合わせなどの探求とその伝導性の測定が活発である一方で、そのメカニズム、特に伝導経路については多くの場合は未解明な部分が多い。その理由としては、X 線などの実験測定ではプロトンの位置決定や、そのダイナミクスを追跡することが困難なためと考えられる。そこで、本研究ではそのような化合物として、最近報告された配位高分子、$\{[Zn(HPO_4)(H_2PO_4)]\cdot 2ImH_2]\}_n$ (**1**)（ImH: イミダゾール）に注目した。錯体 **1** 中には 2 種類のイミダゾールが存在する。一方のイミダゾール（dynamic ImH_2^+）は温度上昇に伴い回転運動が誘起されることが X 線および固体 NMR から確認されている。その回転運動の発現とプロトン伝導度の上昇が同期していることも確認されている。もう一方のイミダゾール（static ImH_2^+）ではこのような回転運動の誘起などは起きない。そこで本研究では、この二つのイミダゾールにおける挙動の違いの原因、プロトン伝導経路の解明、イミダゾールの回転と伝導との相関の解明を目的とした。

【計算、結果、考察】

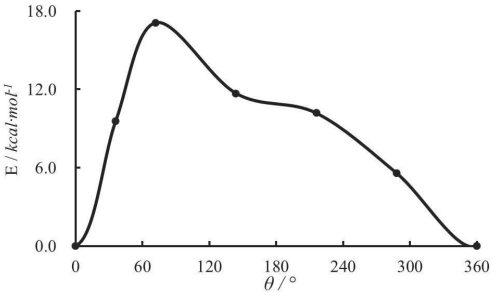
本研究では錯体 **1** の無限骨格に対する検討および、無限骨格から切り出したモデル構造における検討を行った。無限骨格の計算には SIESTA プログラムを用い、汎関数として PBE、基底関数として DZP を用いて構造最適化を行った。最適化構造をもとに切り出した構造について Gaussian 09 を用いて、同様に PBE 汎関数で検



（図１）無限骨格における最適化構造と実験構造の比較

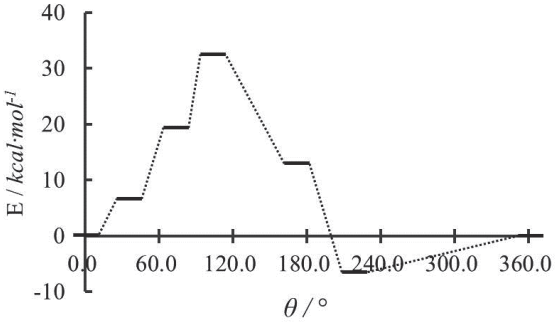
討を行った。基底関数は、Zn については LAN2DZ を用い内核電子は ECP で置き換え、O については 6-31+G*、その他の原子については 6-31G**を用いた。

図１に無限骨格の最適化構造と実験構造の比較を示す。リン酸と亜鉛からなる骨格を構成する一次元鎖については実験値と良い一致を示した一方で、末端の水素および、一次元鎖から伸びる末端リン酸については実験構造とのズレが大きい。これは、水素結合や dynamic ImH_2^+の運動の影響と考えられる。この構造をもとに、static ImH_2^+の回転障壁をモデル構造における計算から見積もった。得られたポテンシャルカーブを図２に示す。最適化構造から static ImH_2^+は二つの水素結合を形成しており、この二つの水素結合を切断するエネルギーが回転障壁（約 17kcal/mol）と考えられる。Dynamic ImH_2^+も二つの水素結合で捕捉されているが、水素結合を形成している酸素の電荷が static ImH_2^+の場合は-0.66 e であるのに対し、dynamic ImH_2^+では-0.60 e であった。また、形成している水素結合の角度も 180 度から大きくずれており、この電荷の違いと水素結合角度の違いが運動性の違いを生み出していると考えられる。Static ImH_2^+と同様に Dynamic ImH_2^+の回転によるエネルギーの変化を確認したところ、その回転障壁は 22 kcal/mol であったが、いくつかの局所安定構造が得られた。この事から、dynamic ImH_2^+では骨格の構造緩和が寄与していることが示唆された。

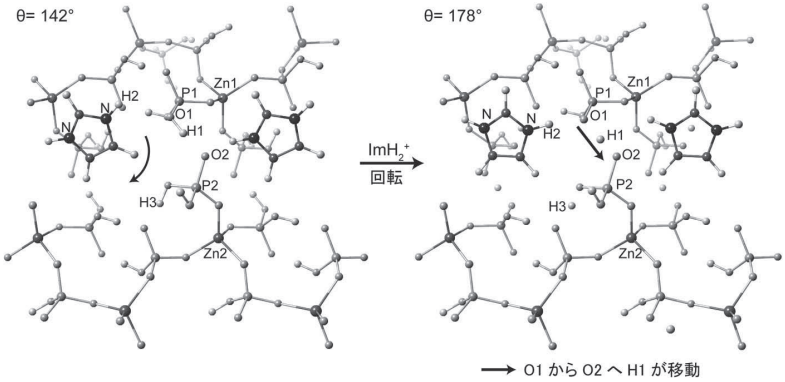


（図２）Static ImH_2^+の回転障壁

そこで、無限骨格において、dynamic ImH_2^+の回転させた状態から構造最適化を行った。その結果を図３に示す。図３に示すように、いくつかの局所安定構造が得られた。さらに、報告されている結晶構造とは異なる状態に最安定構造が存在している可能性が示唆された。この最安定構造からの回転角度が 142 度（実験構造に近い角度）と 178 度の位置での構造を図４に示す。イミダゾールの回転に伴い、イミダゾール上の H2 が O1 に接近すると、O1 と H1 の距離が 1.036 Å から 1.282 Å へと変化し、向かいのリン酸上の酸素 O2 と H1 の距離が 1.148 Å へと変化していることが明らかとなった。このことから dynamic ImH_2^+の回転によってリン酸間のプロトン移動が誘起されることが明らかとなった。この次のステップとしては dynamic ImH_2^+からリン酸へのプロトンの移動が考えられ、このプロセスに関する検討を現在進めている。



（図３）無限骨格中における dynamic ImH_2 の回転に伴うエネルギー変化



（図４）Dynamic ImH_2^+の回転に伴うプロトンの移動

2. 論文

(1) Masakazu Higuchi, Kohei Nakamura, Satoshi Horike, Yuh Hijikata, Nobuhiro Yanai, Tomohiro Fukushima, Jungeun Kim, Kenichi Kato, Masaki Takata, Daisuke Watanabe, Shinji Ohshima, and Susumu Kitagawa
"Design of flexible Lewis acidic sites in porous coordination polymers by using the viologen"
Angew. Chem. Int. Ed., 51, 8369-8372 (2012)

(2) Maw Lin Foo, Satoshi Horike, Tomohiro Fukushima, Yuh Hijikata, Yoshiki Kubota, Masaki
"Ligand-based solid solution approach to stabilization of sulphonic acid groups in porous"
Dalton Trans., 41, 13791-13794 (2012)

(3) Munehiro Inukai, Satoshi Horike, Daiki Umeyama, Yuh Hijikata, and Susumu Kitagawa
"Investigation of post-grafted groups of a porous coordination polymer and its proton conduction behavior"
Dalton Trans., 41, 13261-13263 (2012)

(4) Shin-ichiro Noro, Yuh Hijikata, Munehiro Inukai, Tomohiro Fukushima, Satoshi Horike, Masakazu Higuchi, Susumu Kitagawa, Tomoyuki Akutagawa, and Takayoshi Nakamura
"Highly selective CO_2 adsorption accompanied with low-energy regeneration in a two-dimensional Cu(II) porous coordination polymer with inorganic fluorinated PF^{6-} anions"
Inorg. Chem., 52, 280-285 (2013)

(5) Satoshi Horike, Masayuki Sugimoto, Kanokwan Kongpatpanich, Yuh Hijikata, Munehiro Inukai, Daiki Umeyama, Shinji Kitao, Makoto Seto, and Susumu Kitagawa
"Fe^{2+} layered porous coordination polymers and soft encapsulation of guest via redox activity"
J. Mater. Chem. A, 1, 3675-3679 (2013)

(6) Yuh Hijikata, Satoshi Horike, Masayuki Sugimoto, Munehiro Inukai, Tomohiro Fukushima, and Susumu Kitagawa
"Pore design of two-dimensional coordination polymers toward selective adsorption"
Inorg. Chem., 52, 3634-3642 (2013)

3. 学会発表

(1) 土方　優，榊　茂好
「プロトン伝導性配位高分子の電子状態に関する理論的研究」
日本化学会第 93 春季年会　滋賀　2013/3/22-25

(2) 土方　優，榊　茂好
「配位不飽和サイトにおける静電相互作用に関する理論的研究」
錯体化学会第 62 回討論会　富山　2012/9/21-23

(3) 土方　優，榊　茂好
「プロトン伝導性配位高分子の電子状態に関する理論的研究」
第 4 回協定講座シンポジウム「計算生物学と材料化学の融合」　兵庫　2012/12/19

青野 信治

特推研究フェロー

1. 今年度の研究の要約

本年度は遷移金属錯体に対する周期的結晶効果や溶媒和効果を中心に研究を行った。

【序論】　理論化学における重要な課題の１つに、溶媒や結晶といった周囲の環境からの影響を考慮して注目する分子の構造や電子状態を検討する事が挙げられる。特に近年、分子デバイスの開発に対する要請を背景に、結晶およびアモルファスなど固体中での電子励起や発光、スピン状態などの分子的性質が実験と理論の双方で研究対象として多くの興味を持たれている。特に、様々な分子性結晶の構造がＸ線や中性子散乱実験によって明らかにされているものの気相中での孤立系計算による理論予測とは異なる事も多く、注目する分子に対する周囲の分子集団からの影響の考慮は必要不可欠である。

固体中に含まれる無数の分子を独立に扱い計算をする事は事実上不可能であるが、分子集団の周期的構造性を仮定する事による自由度の削減により計算可能なものとする。周期的分子性結晶を扱う際に有用な手法として、主に次の２つの理論的手法が挙げられる。１つは周期的密度汎関数理論であり、もう１つはQM/MM法である。前者においては、注目する分子に周期的並進操作を施す事で無限サイズの結晶を直接計算する事ができ、特に注目する分子とその周囲からの集団的な影響を等価な計算レベルで記述できる点が長所に挙げられる。しかしながら密度汎関数理論に基づくため、多参照性が求められる電子励起状態などの記述において原理的に限界がある。一方、後者は周囲の分子集団を古典的モデルによって記述する点において、注目する分子に掛る結晶効果の記述精度に限界があるが、注目する分子の励起状態に対して高精度な電子状態計算を適用する事が原理的に可能である点が長所として挙げられる。

本研究では周期的分子性結晶中での励起状態の理論化学研究を目標として、今回まずQM/MM法の枠組みにおいて、結晶中における基本単位格子同士が全て等しい状態にある場合における結晶分子の構造および格子ベクトルの最適化法を開発した[1]。この周期的分子性結晶の最適化方法を、水分子がOサイト向きでPt金属に配位した典型的なO配向構造を持つ$Pt(CN)_4 \cdot 2H_2O$[2]と、水分子がHサイト向きでPt金属へと水素結合した珍しいH配向構造を持つtrans- $PtCl_2(NH_3)$(N-glycine)・H_2O[3]という２つの水素結合性結晶系へ適

用し（図１）、また孤立系計算で得られる最適化構造と比較する事で周囲の分子集団からの影響による分子構造と電子状態の違いについて検討した。

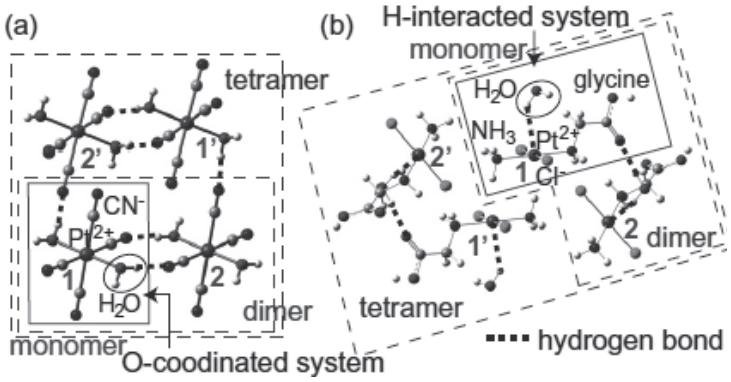


図１基本単位格子内の分子構造

(a) $Pt(CN)_4 \cdot 2H_2O$ (C_2 対称性)　(b) trans-PtCl2(NH3)(N-glycine)・H2O (Ci 対称性)

【計算方法】 本研究における QM/MM 法は周期的分子性結晶の基本単位格子を QM 領域、あるいは基本単位格子内に対称性がある場合は対称操作を行う事で基本単位格子を再現できるような最小構成ユニットを QM 領域に選ぶ事とした。これは注目する QM 領域に対して並進および対称操作を行う事で周期的分子性結晶全体を再現できるからである。また QM 領域以外の結晶部分を MM 領域と見做し、QM エネルギーE_{QM}と QM/MM 相互作用エネルギー$E_{QM/MM}$の 1/2 の和（式(1)）を変分原理によって最小化するように、注目する QM 領域の電子波動関数Φ_{QM}を決定する。

$$E_{\mathrm{crystal}} \propto E_{\mathrm{QM}} + \frac{1}{2}E_{\mathrm{QM/MM}} = \left\langle \Phi_{\mathrm{QM}} \middle| \hat{H}^{\mathrm{gas}} \middle| \Phi_{\mathrm{QM}} \right\rangle + \frac{1}{2}\left(E_{\mathrm{ES}} + E_{\mathrm{LJ}}\right) \qquad \text{式(1)}$$

本研究は式(1)において QM/MM 相互作用を静電項と Lennard-Jones 項の和で表現し、特に静電項に含まれる MM 分子電荷に関しては QM 分子における電荷解析値と並進操作T_{trans}および対称操作T_{sym}を介して等価になるように定めた（式(2)、(3)）。

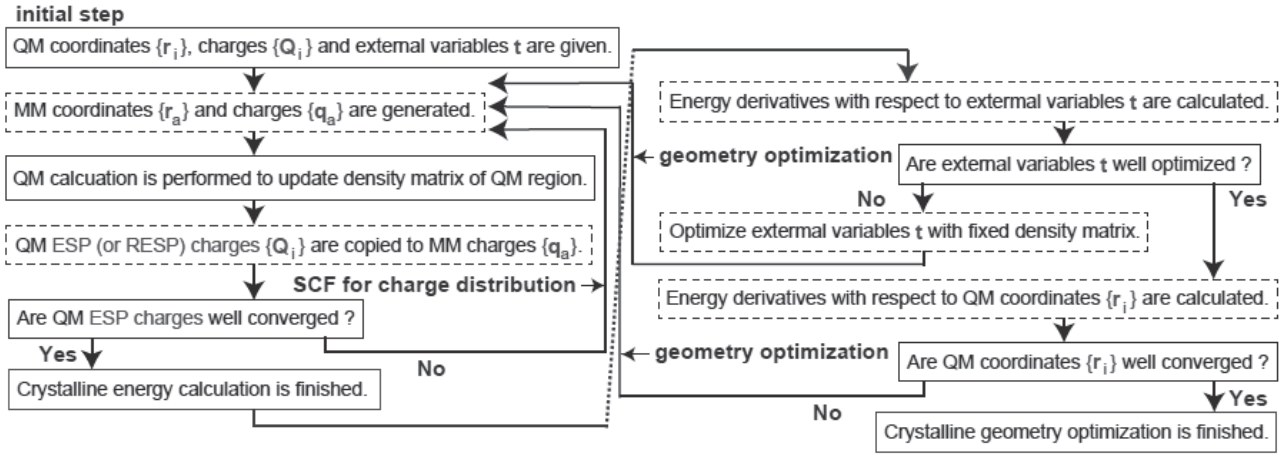
$$E_{\mathrm{ES}} = \sum_{a\in\mathrm{MM}} q_a \left[\left\{ -\sum_{\mu\nu} P_{\mu\nu} \int d\mathbf{r}' \frac{\chi_\mu^*(\mathbf{r}')\chi_\nu(\mathbf{r}')}{|\mathbf{r}_a - \mathbf{r}'|} + \sum_{i\in\mathrm{QM}} \frac{Z_i}{|\mathbf{r}_a - \mathbf{r}_i|} \right\} w(\mathbf{r}_a) + \sum_{i\in\mathrm{QM}} \frac{q_i}{|\mathbf{r}_a - \mathbf{r}_i|}\left(1 - w(\mathbf{r}_a)\right) \right] \qquad \text{式(2)}$$

$$q_a = q_{a'} = q_i \equiv \sum_{\mu\nu} \left\langle \chi_\mu \middle| \hat{Q}_i \middle| \chi_\nu \right\rangle + Z_i \qquad \text{for} \begin{cases} {}^{\exists}\mathbf{n} : T_{\mathrm{trans}}(a') = a \\ {}^{\exists}\alpha : T_{\mathrm{sym}}(i) = a' \end{cases} \qquad \text{式(3)}$$

ここで$\chi_\mu(\mathbf{r})$は原子軌道関数、$P_{\mu\nu}$は一電子密度行列、q_aとq_iは MM 分子サイト i および QM 分子サイト a の有効電荷、$\hat{Q}_i$は QM 分子サイト i における電荷演算子、$w(\mathbf{r})$は Switching 関数。これにより変分原理を用いて式(1)を最小化する事で Fock 行列を導出した（式(4)）。

$$F_{\mu\nu}^{\mathrm{crystal}} = F_{\mu\nu}^{\mathrm{gas}} + \frac{1}{2}\sum_{a\in\mathrm{MM}} q_a \left[\left\{ -\int d\mathbf{r}' \frac{\chi_\mu^*(\mathbf{r}')\chi_\nu(\mathbf{r}')}{|\mathbf{r}_a - \mathbf{r}'|} \right\} w(\mathbf{r}_a) + \sum_{i\in\mathrm{QM}} \frac{Q_{i,\mu\nu}}{|\mathbf{r}_a - \mathbf{r}_i|}(1 - w(\mathbf{r}_a)) \right]$$
$$+ \frac{1}{2}\sum_{a\in\mathrm{MM}} Q_{a,\mu\nu} \left[\left\{ -\sum_{\mu\nu} P_{\mu\nu} \int d\mathbf{r}' \frac{\chi_\mu^*(\mathbf{r}')\chi_\nu(\mathbf{r}')}{|\mathbf{r}_a - \mathbf{r}'|} + \sum_{i\in\mathrm{QM}} \frac{Z_i}{|\mathbf{r}_a - \mathbf{r}_i|} \right\} w(\mathbf{r}_a) + \sum_{i\in\mathrm{QM}} \frac{q_i}{|\mathbf{r}_a - \mathbf{r}_i|}(1 - w(\mathbf{r}_a)) \right] \quad \text{式(4)}$$

式(4)は第一項の孤立系での Fock 行列と残る周囲の分子集団からの一電子補正項により構成されるが、一電子補正項には無限周期からの長距離効果が含まれており、今回 Ewald 和により評価するようプログラム化した。更に解析的な gradient を導出する事で、MM 分子の経験的な分子内ポテンシャルを定める事なく分子構造と格子ベクトルおよび対称操作に関する最適化を行った[1]。（Scheme）



Scheme：周期的分子性結晶における電荷 **Q**、分子座標 **r**、格子と対称操作 **t** の決定

この基底状態下の結晶分子および格子の構造最適化法を B3PW91 汎関数による DFT レベルで上記の Pt 錯体へ適用した。Pt は 60 個の内殻電子を Hay-Wadt ECP に置き換えて（11111/11111/111/1）基底を、その他の原子には 6-31++G**基底を用いた。Lennard-Jones 変数には AMBER および SPC モデルの値を用いた。

【結果】　テトラシアノ錯体、グリシン錯体での基本単位格子は４分子により構成されているものの、対称性を持つため独立な分子は、図１に示した **1**、**2** の２分子である。またテトラシアノ錯体の **1**、**2** 間には水配位子の H サイトと CN 配位子の N サイトを介した水素結合が２つ、**1**、**2'** 間には１つ存在し（図２）、グリシン錯体の分子間では水分子の H サイトとグリシンの COOH 基の O サイトおよび水分子の O サイトとグリシンの COOH 基の H サイトを介した水素結合が存在する（図３）。孤立したテトラシアノ錯体の単量体では最適化構造は結晶構造中と一致するが、二量体、四量体では Ow(1A)-Hw 距離（図２）が伸び、プロトン移動性が現れる。一方、結晶を考慮した QM/MM 計算ではプロトン移動性は

現れない。この点は周囲分子から掛かる静電ポテンシャルが水分子の Ow サイトから CN 配位子の N サイトへ向かうにつれ増大している点により、正電荷に誘起された Hw サイトが受ける力が N→O 向きである事が理由であると分かった。また、孤立したグリシン錯体の単量体では水分子が Cl 配位子と NH_3 配位子の間で水素結合を作り、結晶構造中と大きく異なる。二量体、四量体となるに従って結晶構造に近付くが、水分子の相対位置や Pt(1)-Pt(1’) 距離は依然として結晶構造中とは異なる。

周囲の結晶分子を考慮した QM/MM 計算によって得られた最適化構造はこれら２つの錯体共に実験結果を再現し、構造最適化の定量性に関して Lennard-Jones 変数の大きさや RESP 変数の使用に関する QM/MM 相互作用の評価方法に更なる議論と改善が必要なものの、QM/MM 法に基づき今回構築した計算方法は周期的分子結晶中での基底状態など、基本単位格子同士が全て等しい状態にある結晶環境についてのモデル化に有用であると考えられる。

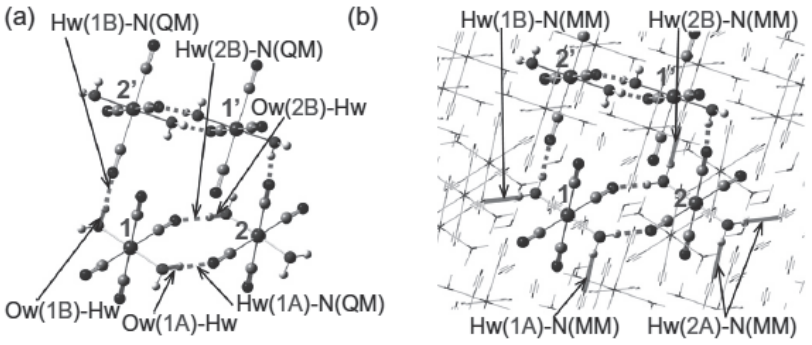


図２：テトラシアノ錯体（a）基本セル内（b）基本セル間水素結合

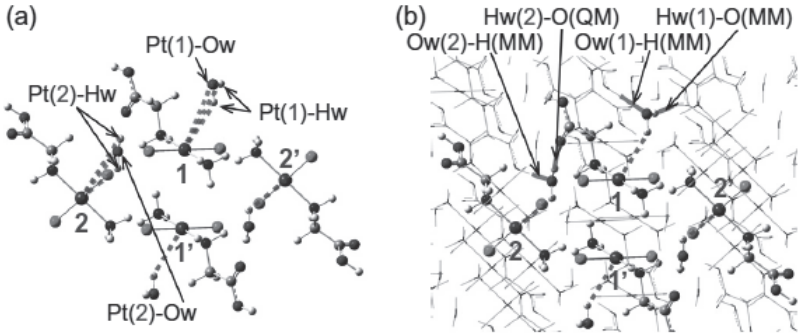


図３：グリシン錯体（a）水分子の相対位置（b）分子間水素結合

[1]：S. Aono, S. Sakaki, Chem. Phys. Lett. **2012**, 544, 77

[2]：C. Mühle, J. Nuss, M. Jansen, Z. Kristallogr. New Cryst, Struct. **2009**, 224, 9.

[3]：S. Rizzato, J. Berges, S. A. Mason, A. Albinati, J Kozelka, Angew. Chem. **2010**, 49, 7443.

2. 論文

(1) Shinji Aono, Takashi Hosoya, and Shigeyoshi Sakaki, “A 3D-RISM-SCF method with dual solvent boxes for a highly polarized system: application to 1,6-anhydrosugar formation reaction of phenyl alpha- and beta-D-glucosides under basic conditions” Phys. Chem. Chem. Phys. 17 6368 (2013)

(2) Shinji Aono and Shigeyoshi Sakaki, “Evaluation Procedure of Electrostatic Potential in 3D-RISM-SCF Method and Its Application to Hydrolyses of Cis- and Transplatin Complexes” J. Phys. Chem. B 116 13045 (2012)

(3) Shinji Aono and Shigeyoshi Sakaki, “Proposal of new QM/MM approach for geometry optimization of periodic molecular crystal: Self-consistent point charge representation for crystalline effect on target QM molecule” Chem. Phys. Lett. 544 77 (2012).

3. 学会発表

(1) 青野信治、榊茂好
「周期的分子性結晶に対するQM/MM法の開発：SCF点電荷による結晶効果のモデル化」
分子科学討論会2012　東京　2012/9/19　2E04

4. その他

(1) 青野信治、細谷隆史、榊茂好
「塩基性条件下におけるグルコシドからのレボグルコサン生成機構：α体とβ体の反応性の相違に関する 3D-RISM-SCF法による理論的研究」
京都大学福井謙一記念研究センターシンポジウム2012 京都 2012/11/30　P53

塚本　晋也

特推研究フェロー

1. 今年度の研究の要約

五配位 Ni(II)錯体の結晶中でのスピンクロスオーバー現象の理論的考察

【背景及び目的】遷移金属錯体の結晶中でのスピンクロスオーバー現象は、工業的な応用が期待される。近年、五配位 Ni(II) スピンクロスオーバー (SCO) 錯体 $Tp^{Ph,Me}Ni(S_2CNMe_2)$[$Tp^{Ph,Me}$=hydrotris(3-phenyl-5methyl-1-pyrazolyl)borate]が、結晶中で二つの独立な構造 Ni1, Ni2 を持ち (Scheme1, Fig1)、磁気的性質が異なることが、X 線構造と磁化率の測定によって明らかにされた [1]。Ni1 の構造は 123K と 293K で大きな違いがないが、Ni2 では 123K と 293K で構造が大きく異なる。このことは SCO が Ni1 で起こらず、Ni2 で起きていることを示している。

本研究では、単量体の構造と電子状態、及び結晶化の影響を考慮した場合の違いを電子状態計算から議論し、分子性結晶中のスピンクロスオーバー現象の理由を説明した。

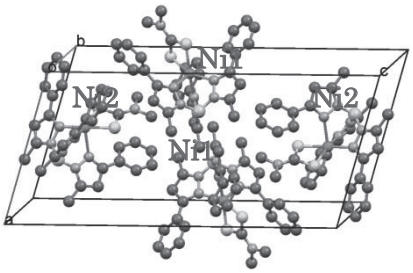
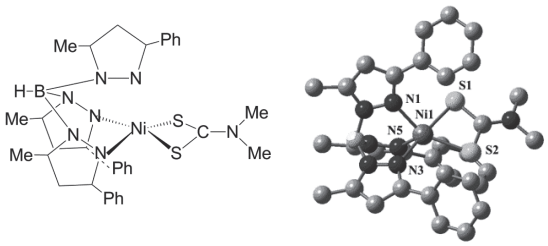


Fig.1 X-ray structure of $Tp^{Ph,Me}Ni(S_2CNMe_2)$ in 123K



Scheme 1 $Tp^{Ph,Me}Ni(S_2CNMe_2)$

【計算方法】単量体の構造最適化を行い X 線構造と比較した。Ph, Me を H 原子に置換したモデル錯体で電子状態と一重項、三重項の相対安定性を議論した。結晶の効果を取り入れるため、周囲の置換基の一部を考慮したモデルで、置換基の位置を X 線構造で固定した構造最適化 Embedded model と QM/MM 計算を行った。ここで MM の電荷は QM と MM の電荷が等しくなるように決定し、QM/MM 間の相互作用はレナードジョーンズポテンシャルで記述した。基底関数は BSI (Ni: SDD ECP plus 2*f* polarization functions, C, H, N, B, S: 6-31G(d)), BSII (Ni: C, H, N, B, S: cc-pVDZ) を用い、構造最適化は B3PW91/BSI, 相対エネルギーは B3LYP*/BSII で計算した。結晶の a,b,c 軸方向の影響は X 線構造から構築したクラスターモデルで評価した。結晶の a,b,c 軸方向の分子間力は金属の電子状態を S=0 に固定し、ωB97XD で評価した。

[結果と考察]　単量体の最適化構造から Ni1 は 123K, 293K ともに triplet 構造、Ni2 は 123K で singlet, 293K で triplet 構造に対応している(Table 1)。このことから SCO は Ni1 で起こらず、Ni2 で起きていることを示している。しかし、Ni2 の 123K の実験構造と単量体の最適化構造の一致は悪い。Embedded model と QM/MM を導入すると Ni2 の最適化構造が改善され(0.25 から 0.05, 0,04)、結晶の影響が Ni2 で大きい。一方で Ni1 は単量体、embedded model, QM/MM で標準誤差に大きな違いがなく且つ値も小さいので、結晶化の影響が小さい。

Table 1. $Tp^{Ph,Me}Ni(S_2CNMe_2)$の最安定化構造

Ni1	embedded	QM/MM	expl.	embedded	QM/MM	expl.	isolated	
T (K)		123K			293K			
multiplicity	triplet	HS		triplet	HS		singlet	triplet
Ni-N1 (Å)	2.027	2.095	2.038	2.035	2.111	2.048	2.927	2.069
Ni-N3 (Å)	2.123	2.160	2.111	2.119	2.151	2.111	1.929	2.128
Ni-N5 (Å)	2.074	2.003	2.048	2.071	2.005	2.058	1.913	2.063
Ni-S2 (Å)	2.379	2.366	2.342	2.381	2.374	2.344	2.219	2.379
Ni-S1 (Å)	2.448	2.419	2.401	2.447	2.421	2.393	2.227	2.436
RMS	0.03	0.04		0.03	0.04			

Ni2	embedded	QM/MM	expl.	embedded	QM/MM	expl.	isolated	
multiplicity	singlet	LS		triplet	HS		singlet	triplet
Ni-N1 (Å)	2.478	2.386	2.401	2.050	2.170	2.149	2.927	2.069
Ni-N3 (Å)	1.934	2.025	1.972	2.138	2.031	2.046	1.929	2.128
Ni-N5 (Å)	1.945	1.953	2.003	2.055	2.090	2.083	1.913	2.063
Ni-S2 (Å)	2.249	2.302	2.272	2.387	2.425	2.361	2.219	2.379
Ni-S1 (Å)	2.234	2.292	2.257	2.451	2.367	2.323	2.227	2.436
RMS	0.05	0.04		0.07	0.04		0.25	0.03

Table 2. HS-LS 相対安定性ΔE(HS-LS)の a,b,c 軸方向依存

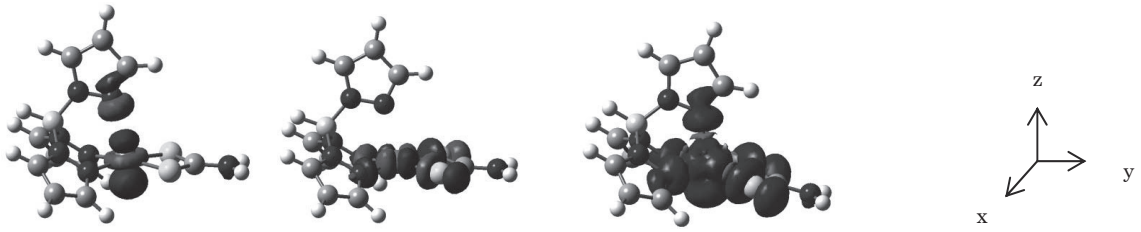
Packing direction	123K	293K
Ni1-Ni2	15.9	-4.1
c	20.6	-3.0
a two blocks	15.3	-5.4
a three blocks	15.1	-5.8
b	15.9	-4.6

次に a, b, c 方向の影響を調べるため X 線構造から構築したモデルクラスターで HS-LS 相対安定性と分子間相互作用を調べた。結晶構造から一つの単位格子の中に Ni1-Ni2 二量体が存在するので、この二量体を最小単位として a,b,c 方向に伸長したモデルで評価した。123K では Ni1-Ni2 二量体は LS が安定で、293K では HS が安定と計算され、実験の傾向を再現した、c 方向では 123K でΔE(HS-LS)の値に変化が見られたが、a,b 方向ではΔE(HS-LS)の値に変化がほとんどない (Table 2)。このことから c 方向の影響がΔE(HS-LS)の値に大きな影響を与えることが分かった。分子間力の a, b, c 方向の影響を調べると、a,b 方向依存性より Ni1-Ni2 二量化と c 方向依存性が大きい (Table 3)。以上の結果から、Ni1-Ni2 の c 方向の二量化が Ni2 の相対安定性に影響を与えることが示唆された。

Table 3.分子間力の a,b,c 軸方向依存

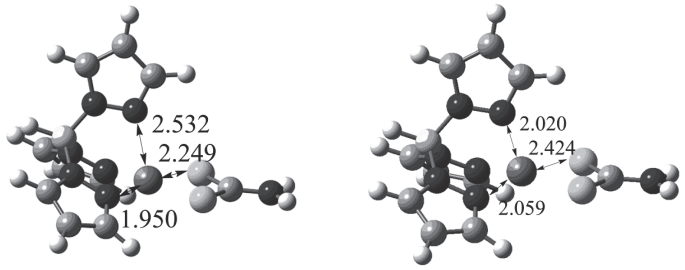
Packing direction	123K		293K	
ΔE(real)	LS	HS	LS	HS
a	–27.9	–27.9	–26.9	–27.9
b	–28.8	–26.1	–28.6	–26.9
c	–24.4	–21.0	–20.3	–23.0
Ni1-Ni2	–24.9	–20.4	–20.9	–22.7

ここで、錯体の Ph, Me 基を H 原子に置き換えたモデル錯体で singlet と triplet の電子状態と構造を調べた。Singlet の HOMO は Ni dz2-Nax lone pair の反結合性軌道で LUMO は Ni dxy –Neq lone pair の反結合性軌道である（Fig.2)。一方、triplet ではこれらの軌道が SOMO である。最適化構造を比較すると、Singlet の最適化構造は triplet 構造より Ni-S, Ni-Neq 距離が短く、Ni-Nax 距離が長い（Fig.2)。singlet と triplet の構造の違いは電子状態を反映している。singlet の Ni-Nax 距離が長い理由は二重占有の dz2-Nax lone pair anti-bonding orbital に由来し、triplet では dz2-Nax lone pair と dxy –Neq lone pair が SOMO になることで、Ni-Nax 距離が短く Ni-S, Ni-Neq 距離が長い。



d_{z2}(HOMO)　　d_{xy}(LUMO)　　spin density of triplet

Fig.2　singlet の HOMO と LUMO. Triplet のスピン密度



Singlet　　triplet

Fig.3　モデル錯体の最適化構造

モデル錯体及びリアル錯体でΔE(HS-LS)を評価すると、triplet が singlet より安定であるため、結晶化により Ni2 は 123K で singlet が安定になっていると言える。実際、123K ではΔE(HS-LS)は singlet が安定、LS 構造では分子間力が大きい(Table 2, 3)。この理由は singlet と triplet の分子構造の違いと結晶中での分子の配向に由来している。123K と 293K の単位格子を比較すると結晶群は共に $P\bar{1}$ で、293K の単位格子は 123K の単位格子より a,b,c 方向にそれぞれ 0.14, 0.13, 0.38Å 長い。c 方向の単位格子の伸長が大きいことと(Table2)、c 方向のΔE(HS-LS)と分子間力が大きいことから(Table3)、c 方向に影響する分子に着目すると、Ni1 と Ni2 の二量体が c 軸方向に整列していることが見て取れる（Fig.1)。

Ni1 の Ni-S 分子面は a 軸方向、Ni2 の分子面は c 軸方向を向いている。モデル錯体で見た通り、singlet は Ni-Neq, Ni-S 距離が短く、triplet は逆に長い。そのため 123K では Ni2 が singlet 構造を取る方が c 軸方向の Ni1-Ni2 二量体が空間的に小さく立体反発を避けることが出来るため二量化エネルギーが大きい(Table 3)。結晶化による構造変化も 123K での Ni2 の相対安定性に重要である。最適化構造を用いるとΔE(HS-LS) は–8.3 kcal/mol で triplet が安定であるが、X 線構造を用いるとΔE(HS-LS)は 5.7 kcal/mol で singlet が安定であり、実験結果を支持する。以上の結果から、Ni2 が 123K で singlet を取る理由は、1. Ni-Neq, Ni-S 距離が短く c 軸方向の Ni1-Ni2 二量化エネルギーが大きくなるため 2. 結晶化による構造変化により singlet が有利になるため、と結論付けられる。123K → 293K で Ni2 が singlet→triplet へ SCO を起こす理由は、振動エントロピーで説明出来る。Triplet の振動エントロピーは singlet より大きいため、ギブスの自由エネルギーを考慮すると、高温で triplet の自由エネルギーが安定になる。

【文献】 1) Huaibo M. *et al. JACS*, **2011**, 133, 5644.

2. 論文

(1) “A theoretical study of luminescent vapochromic compounds including an $AuCu_2(NHC)_2$ core” S. Tsukamoto and S. Sakaki, *Dalton Trans.* **2013,** 42, 4809.

3. 学会発表

(1) 塚本　晋也、榊　茂好「Au(I)-Cu(I)相互作用を含む多核金属錯体の発光メカニズムと金属間相互作用」第15回理論化学討論会　仙台福祉プラザ 2012/5/24(木)-26(土) ポスター　1P07

(2) Shinya Tsukamoto、Shigeyoshi Sakaki「A Theoretical Study for Solid-state Spin crossoverr of Ni(II) in N3S2 ligand field」14th ICQC Interactional Congress of Quantum Chemistry, Boulder, Colorado, USA, June 25-30, Poster　IV.48

(3) 塚本　晋也、榊　茂好「五配位 Ni(II)-N3S2 錯体の理論研究:スピン状態と結晶構造の関連」第 6 回分子科学討論会 東京 2012/9/18(火)-21(金)　ポスター　2P-095

(4) 塚本　晋也、榊　茂好 「五配位 Ni(II)錯体の結晶中でのスピンクロスオーバー現象の理論的考察: A Theoretical study of Spin Cross Over (SCO) in solid state of five coordinated Ni(II) Complex - the reason of SCO in solid state」錯体化学会第 62 回討論会　富山大学　五福キャンパス 2012/9/21(金)-23 日(日) 口頭 2Ba-05

4. その他

(1) 「五配位　d8 Ni(II) 錯体 の構造と電子状態及び結晶中でのスピンクロスオーバーについての理論的考察: A Theoretical study of geometry and electronic

structure of Spin Cross Over (SCO) in solid state of five coordinated Ni(II) Complex」福井謙一京都大学第9回京都大学福井謙一記念研究センターシンポジウム 京都　2012/3/16

Milind Madhusudan DESHMUKH
SPR Fellow, Fukui Kenichi Memorial Research Group 2

1. Summary of the research carried out during April 2012 to March 2013.

A) Absorption of Gas Molecules into the Porous Coordination Polymer: Understanding of the Determining Factors for Absorption position and Energy

We recently proposed a two step evaluation method for evaluation of binding energy (BE) of van der Waals complex/cluster through reasonable approximations (Deshmukh M. M. and Sakaki S. *J. Comput. Chem.***2012***,* 33, 617). This approximation was shown to be useful for number of systems. This developed strategy was extremely useful in of our study of absorption/adsorption of CO_2 and CS_2 into porous coordination polymers (PCPs).

PCPs recently attract much attention to the potential application to gas storage, gas separation, and catalysis and these desired properties were well investigated in past. Recently, optical and magnetic properties and their responses to inclusion of a guest molecule have started to draw new attention in the chemistry of PCP. Recently the chemo-responsive switching of spin-state was recently shown to occur by gas absorption in the Hofmann-type three-dimensional PCP $\{Fe^{II}(Pz)[Pt^{II}(CN)_4]\}_n$ (Pz=pyrazine). For instance, the absorption of such bulky molecules as benzene, pyrazine, water, methanol etc. stabilizes the high spin state; note that though water and methanol are not bulky, they forms bulky cluster in PCP. Of particular interest is the absorption of CS_2 molecule; despite of its small size, CS_2 absorption induces the spin transition from the high-spin to the low-spin state. This is the reverse to the spin transition by bulky molecules. On the other hand, the absorption of similar CO_2 does not induce any spin transition.

In this work, we theoretically investigated the interactions of CS_2 and CO_2 molecules with a realistic model (**RM**) consisting of a unit cell of the Hofmann-type PCP $\{Fe(Pz)[Pt(CN)_4]\}_n$ as shown in Figure 1.

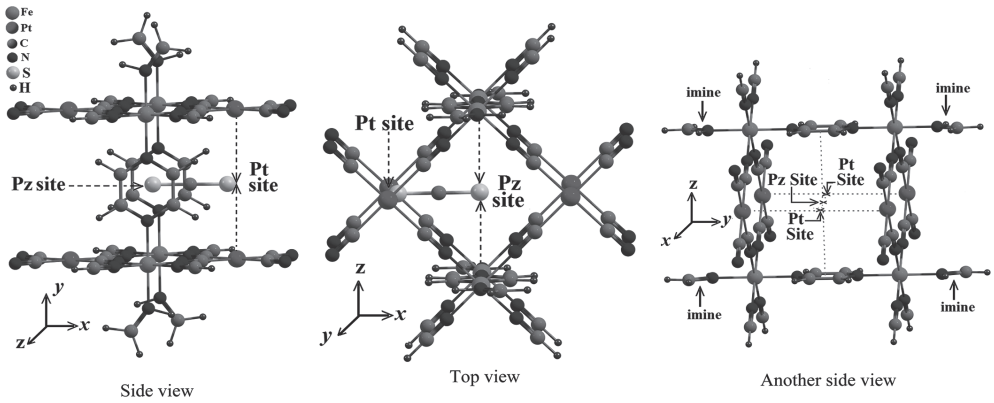


Figure 1: Realistic model (**RM**) of CS_2-absorbed PCP; Fe (green), Pt (pink), N (blue), C (gray), and S (yellow).

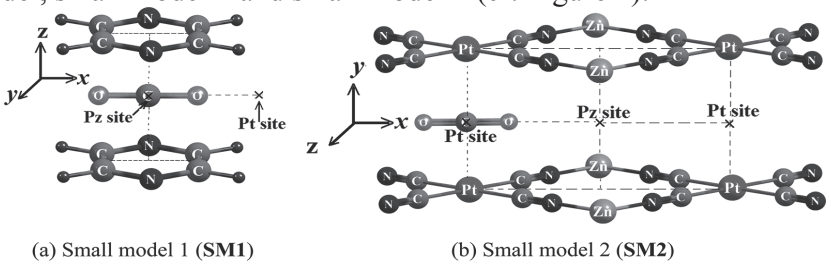
The purposes of the present work are to find the binding sites of these gases in the Hofmann-type PCP, to evaluate their BE, and to clarify the determining factors for absorption site and absorption energies of these gases with the PCP. We believe that the knowledge of such determining factors is indispensible to understanding the gas

absorption with PCP and finding a gas molecule which induces the spin transition between high and low spin states.

The BE of gas molecule with was evaluated with ONIOM scheme, as shown in Eq. 1.

$$BE_{RM}^{ONIOM} = BE_{RM}^{Low} + \left\{ BE_{SM1}^{High} - BE_{SM1}^{Low} \right\} + \left\{ BE_{SM2}^{High} - BE_{SM2}^{Low} \right\} \quad (1)$$

where superscripts "High" and "Low" represents the high quality calculation and low quality calculation, respectively and subscripts, "RM", "SM1", and "SM2" represents realistic model, small model 1 and small model 2 (cf. Figure 2).



(a) Small model 1 (**SM1**) (b) Small model 2 (**SM2**)

Figure 2: Small models (a) SM1 and (b) SM2 representing the Pz and Pt interaction sites respectively. These models were used in ONIOM calculations.

The first term on the right hand side of Eq. 1 is BE of gas molecule with realistic model, **RM**. This is a "real low" component of the ONIOM equation. The second term represents, BE of gas molecule with small model **SM1** and the third term represent BE with small model **SM2**. The M06-2X level of theory was employed with cc-pVTZ basis sets for low quality calculation and scaled MP2 methods[21] were used with aug-cc-pVTZ basis sets for high quality calculation. The calculated potential energy surfaces (PES) for CS_2 and CO_2 absorption in Hofmann-type PCP, are shown in Figure 3

(a) CS_2 absorption (b) CO_2 absorption

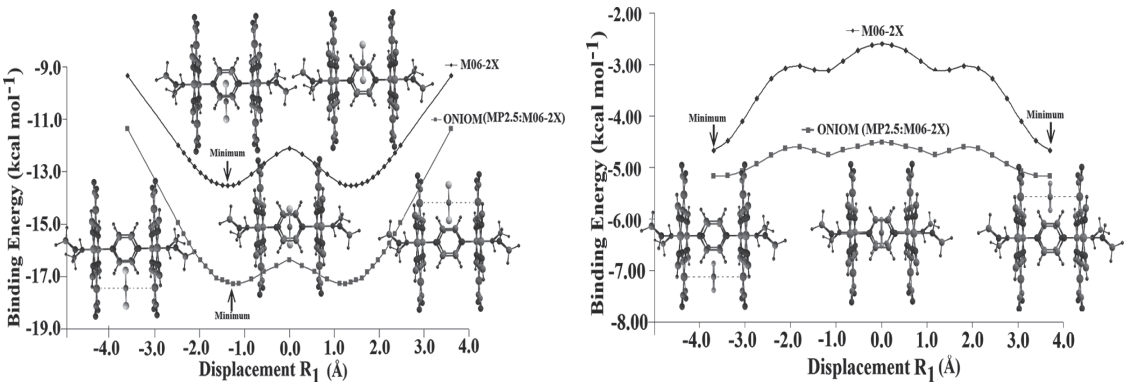


Figure 3: Potential energy surface for absorption of (a) CS_2 and (b) CO_2 into PCP.

As seen in Figure 3, BE of CS_2 and CO_2 are evaluated to be -17.3 kcal mol^{-1} and -4.0 kcal mol^{-1}, respectively at the ONIOM(MP2.5:M06-2X) level, indicating that CS_2 strongly absorbs in PCP but CO_2 weakly. The absorption positions of these molecules are completely different between CO_2 and CS_2; CO_2 molecule exists between two Pt sites. To the contrary, one S atom of CS_2 exists between two Pz ligands and the other S atom is between two Pt sites. The optimized position of CS_2 agrees with experimentally reported

X-ray structure. Based on energy decomposition analysis and electrostatic potential of the PCP framework, it is concluded that both of the large binding energy and absorption position of CS_2 arise from large dispersion interaction between CS_2 and Pz. The different absorption position of CO_2 arises from large electrostatic interactions between CO_2 and Pt site, and small binding energy of CO_2 comes from weak dispersion interaction with both Pz and Pt site.

B) Theoretical study of Molecular Hydrogen and Carbon Dioxide Functionalization with Zinc Hydride: Insights into Interesting Catalytic Cycle

The discovery of catalytic methods is important for (i) the rapid generation of H_2 as use a fuel source and (ii) utilization of CO_2 as an effective C-source. Transition metal complexes are shown by number of studies that they can act as effective catalyst for variety of conversion of chemical entities into desired products. Recent experimental study reported that [tris(2-pyridylthio)methyl] zinc hydride **1** is an effective catalyst for H_2 generation from methanol or water and for CO_2 utilization (*J. Am. Chem. Soc.* **2011**, *133*, 9708). However, no detailed mechanistic insights have been presented.

In this work, we theoretically investigated the reaction mechanism and proposed a complete catalytic cycle for CO_2 functionalization and also for the H_2 generation process. The CO_2 functionalization occurs via CO_2 insertion into the Zn-H bond of **1** (cf. Figure 4) followed by a metathesis of Zn-OCOH compound with hydrosilane to generate silyl formate (cf. Figure 5.)

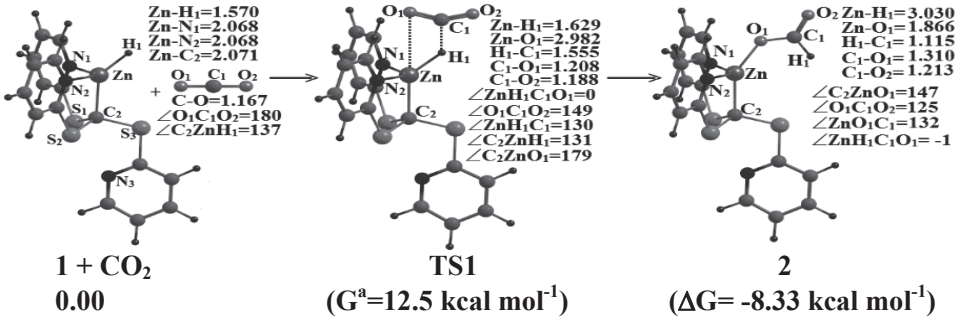


Figure 4: Detailed mechanism for the reaction of CO_2 with catalyst 1.

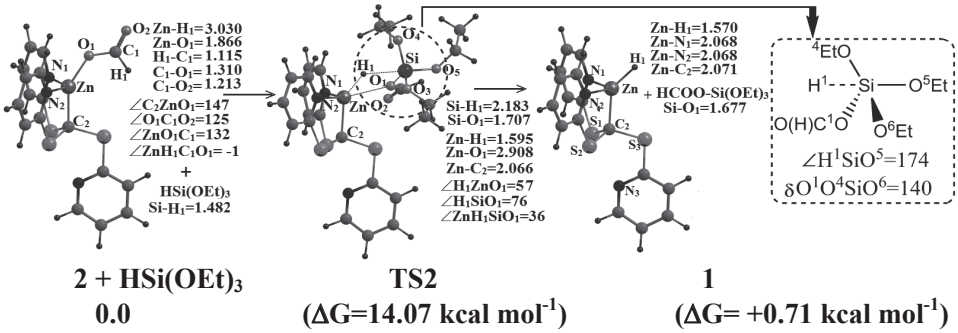


Figure 5: The reaction mechanism for the regeneration of catalyst **1** from **2** and $HSi(OEt)_3$

In CO_2 insertion, the second step (TS2) is rate determining step, wherein silicon moiety takes hypervalent structure. The formation of hypervalent silicon is seems to be important for the formation of silyl formate.

The reaction of **1** with methanol occurs through a metathesis between the Zn-H and the O-H bond of methanol to obtain molecular hydrogen and the Zn-OMe compound. The next step is the metathesis between the Zn-OMe bond and hydrosilane to regenerate **1** and silylether (cf. Figure 6). Here, on going from **TS4** to **TS5** via **Int 1**, the silicon center gradually changes its structure from tetrahedral to trigonal bipyramidal.

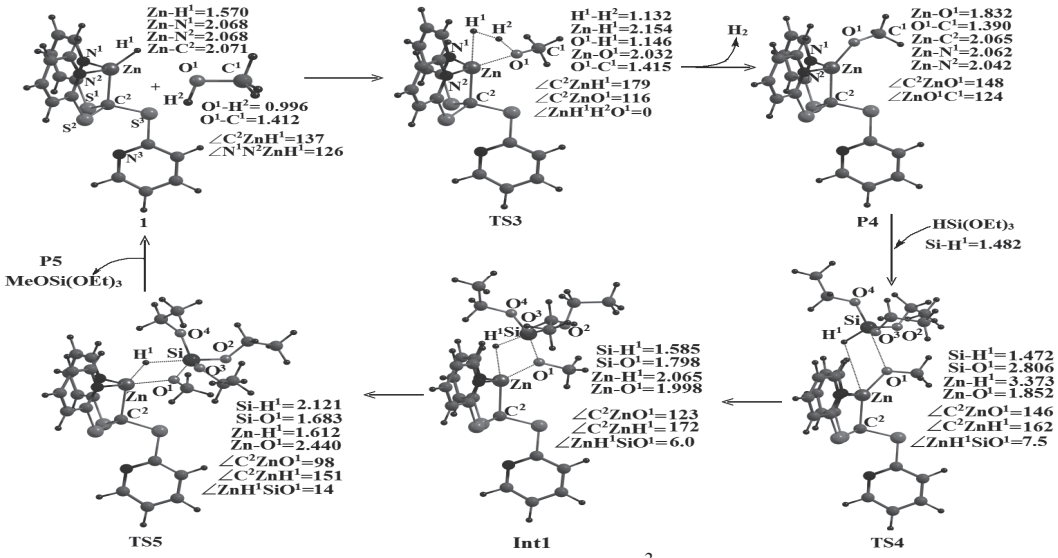


Figure 6: Catalytic cycle for H_2 generation using [K^3-Tptm]ZnH catalyst, **1.**

The small activation barrier and large exothermicity for the H_2 generation and CO_2 insertion reaction indeed suggest that **1** is effective catalyst and produces product **P4** and **P1**, respectively. The analysis of electronic structures suggests a strong charge transfer (CT) from the valence s- and p-orbital of Zn to the CO_2 moiety which stabilizes **TS1** for CO_2 insertion. Also, the rapid generation molecular hydrogen is facilitated by a strong CT from metal center to hydride hydrogen of **1** and also to the hydrogen of methanol through oxygen moiety.

For the regeneration of catalyst **1** and formation of silyl formate or silyl ether, the formation of respective hypervalent silicon structures are found to be important. For instance, the small activation barrier and exothermicity of these reactions is shown to nicely correlate with the stability of hypervalent structure.

Table 1: The reaction energy (ΔG) and the activation barrier (G^a) for regeneration of **1** using **P1** or **P4** and along with the stabilization energy of hypervalent silicon species.

		Reaction of P1 and Silane	
Silane	**G^a (kcal/mol)**	**ΔG (kcal/mol)**	**$\Delta E_{Stabilization}$ (kcal/mol)**
$HSi(OEt)_3$	4.23	0.71	-17.87
$PhSiH_3$	16.59	20.97	-16.61
		Reaction of P4 and Silane	
$HSi(OEt)_3$	+0.37	-14.13	-51.22
$PhSiH_3$	+6.84	-7.11	-44.11

Based on Table 1, the higher reactivity of **$HSi(OE)_3$** than **$PhSiH_3$** and also the higher reactivity of **P4** than **P1** is explained.

It is concluded that catalytic cycle for CO_2 functionalization and H_2 generation reactions indeed occurs rapidly and (i) the above discussed strong CT interaction and (ii) the stability of hypervalent silicon in the transition states are the two important factors for these rapid catalytic cycles.

2. Original Papers

(1) Deshmukh Milind M. and Sakaki Shigeyoshi
"Two-step Evaluation of Potential Energy Surface and Binding Energy of van der Waals Complexes"
J. Comput. Chem., 33, 617 (2012).

(2) Deshmukh Milind M.; Ohba Masaaki, Kitagawa Susumu, and Sakaki Shigeyoshi,
"Absorption of CO_2 and CS_2 into the Hofmann-Type Porous Coordination Polymer: Electrostatic versus Dispersion Interactions."
J. Am. Chem. Soc. 135, 4840 (2013).

(3) Deshmukh Milind M. and Sakaki Shigeyoshi
"Rapid Generation of Molecular Hydrogen and Carbon Dioxide Functionalization with Zinc Hydride: Theoretical Insights into Interesting Catalytic Cycle"
To be submitted (2013).

3. Presentations at academic conferences

(1) Deshmukh Milind M. and Sakaki Shigeyoshi,
"Absorption of CO2 and CS2 into the Hofmann-type Porous Coordination Polymer: ONIOM(MP2.5:DFT) Study of Absorption Position and Energy"
Challenges in Organic Materials & supramolecular Chemistry (ISACS 10), Kyoto University, Japan, June 18-21, 2013.

(2) Deshmukh Milind M. and Sakaki Shigeyoshi,
"Reaction between CO2 and Zinc Hydride: Interesting Theoretical Insights"
The 7th Annual Meeting of Japan Society for Molecular Science, Kyoto University, Kyoto Terrsa, Japan, September 24-27, 2013.

4. Others

(1) Deshmukh Milind M. and Sakaki Shigeyoshi
"Comparative Theoretical Study of Reactivities of Pd(II), Pd(III), and Pd(IV) Complexes towards the C-C Bond Reductive Elimination Reaction"
The 6th Annual Meeting of Japan Society for Molecular Science, University of Tokyo, Japan, September 18-21, 2012.

(2) Deshmukh Milind M. and Sakaki Shigeyoshi
"Absorption of I2 in Hofmann-type Porous Coordination Polymer: Unusual Absorption Position and Determining Factors"
The 10th symposium of Fukui Institute for Fundamental Chemistry, Kyoto University, Kyoto, November. 30, 2012.

Guixiang ZENG

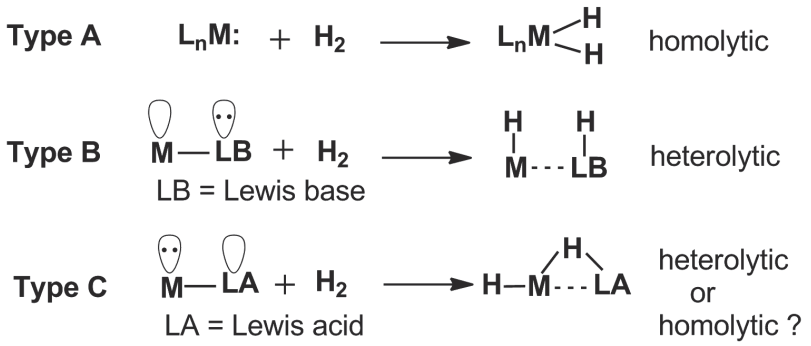
SPR Fellow, Fukui Kenichi Memorial Research Group 2

1. Summary of the research of the year

Unexpected Electronic Process of H_2 Activation by a New Nickel Borane Complex: Comparison with the Usual Homolytic and Heterolytic Activations. [1]

H-H σ-bond activation promoted by transition-metal catalysts is of great importance not only in fundamental chemistry [2] but also in the hydrogen storage technology [3]. Usually, the H−H σ-bond is either homolytically or heterolytically cleaved by transition-metal complexes, as displayed in Scheme 1.[4]

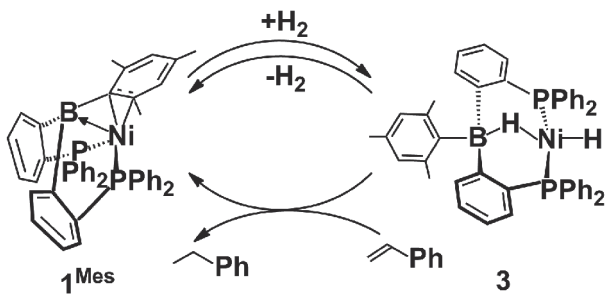
Scheme 1. H−H σ-Bond Activation.



The former cleavage occurs through the oxidative addition of the H−H σ-bond to a metal center to form a dihydride complex (type A in Scheme 1), where the oxidation state of the metal center increases by 2. This kind of reaction is possible for electron-rich late transition metals. The latter reaction generally occurs under the cooperative functions of an electron-deficient transition-metal center and an electron-rich Lewis base (LB) ligand, where the metal center and the ligand accept a hydride and a proton, respectively (type B in Scheme 1). In this type of reaction, the oxidation state of the metal center does not change at all. However, the H−H σ-bond cleaved by the cooperation of an electron-rich transition-metal center and an electron-deficient Lewis acid (Z) ligand is rarely reported (type C in Scheme 1).

To elucidate the electronic process of the type C reaction in Scheme 1, we investigated the H_2 activation by a nickel-borane complex $\mathbf{1}^{Mes}$, as shown in Scheme 2. [5] First, one H2 molecule coordinates with the nickel center to form a dihydrogen complex, **2**, which induces an increase in the nickel 3d and 4p orbital populations and thus a decrease in the nickel

Scheme 2. H−H σ-Bond Activation by $\mathbf{1}^{Mes}$.



oxidation state, as shown in Figure 1. Then, the H−H σ-bond is cleaved under the cooperation of the electron-rich nickel center and the electron-deficient borane ligand in a polarized manner, leading to an unprecedented trans-nickel(II) hydridoborohydrido complex, **3**. In the transition state, charge transfer (CT) occurring from the H_2 moiety to the $\mathbf{1}^{Mes}$ moiety (0.683 e) is much larger than the reverse CT (0.284 e); see Scheme 3. As a result, cleavage of the H−H σ-bond affords two positively charged hydrogen atoms. In this process, the boron atomic population and the nickel 4p orbital population increase, but the nickel 3d orbital population decreases. After the H−H σ-bond cleavage, CT from the nickel 4p orbital to these positively charged hydrogen atoms occurs to afford **3**, where the oxidation state of the nickel center increases to +2.

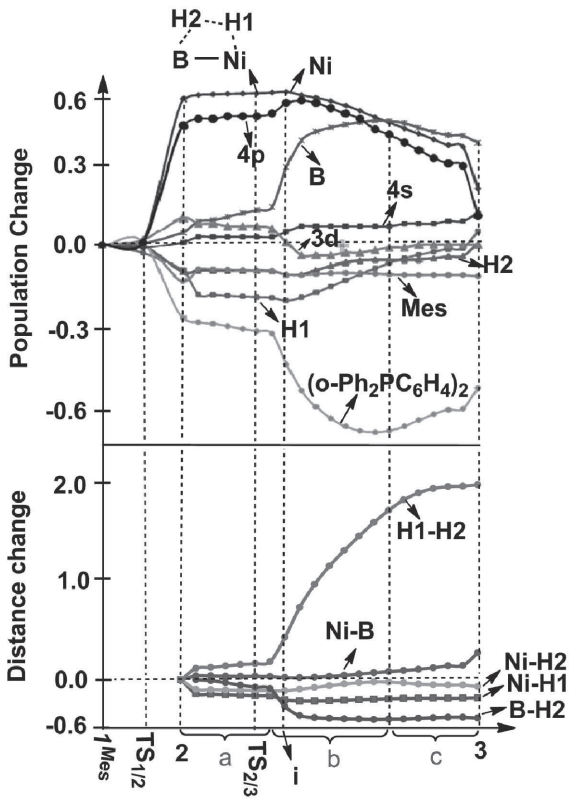
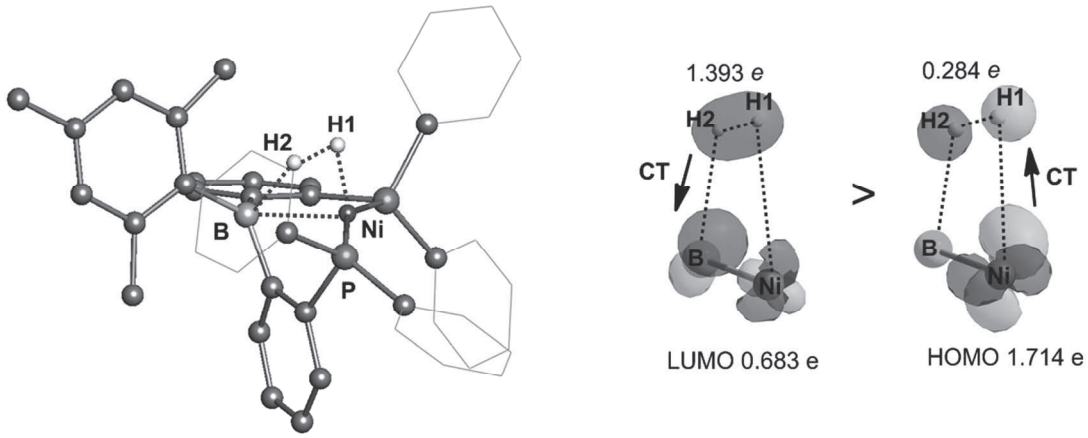


Figure 1. Changes in bond distance (in Å) and electron populations (in *e*) along the intrinsic reaction coordinate (IRC) of the H−H σ-bond activation by the nickel-borane unit. .



Scheme 3. The geometry of the $\mathbf{TS_{1/2}}$ for the H–H σ–bond activation and the charge transfer (CT) between the H_2 and nickel-borane moieties in $\mathbf{TS_{1/2}}$.

Original papers

[1] Guixiang ZENG and Shigeyoshi SAKAKI

"Unexpected Electronic Process of H2 Activation by a New Nickel Borane Complex: Comparison with the Usual Homolytic and Heterolytic Activations" *Inorg. Chem.* 52, 2844-2853 (2013).

[2] Sean E. Clapham, Alen Hadzovic, and Robert H. Morris "Mechanisms of the H_2-Hydrogenation and Transfer Hydrogenation of Polar Bonds Catalyzed by Ruthenium Hydride Complexes" *Coord. Chem. Rev.* 248, 2201-2237, (2004).

[3] Charles W. Hamilton, R. Tom Baker, Anne Staubitz and Ian Manners, "B-N Compound for Chemical Hydrogen Storage." *Chem. Soc. Rev.* 38, 279-293 (2009).

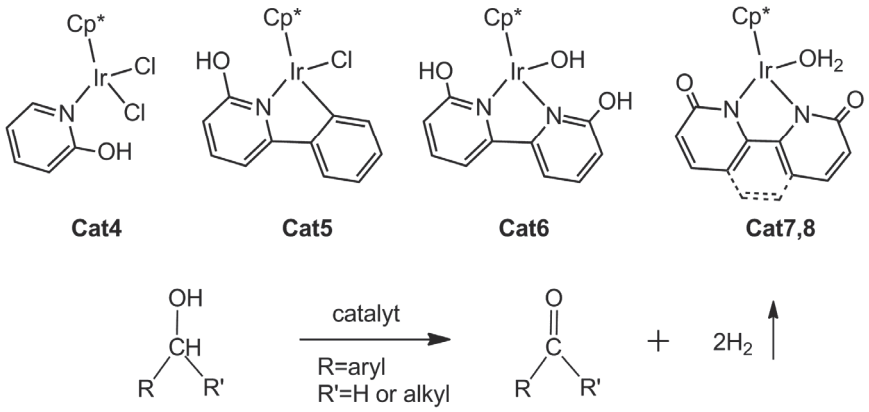
[4] Jesse W. Tye, Marcetta Y. Darensbourg and Michael B. Hall "In Activation of Small Molecules: Organometallic and Bioinorganic Perspectives" Tolman, W. B., Ed.; Wiley-VCH: Weinheim, Germany, 2006; p 121.

[5] Harman, W. H.; Peters, J. C. "Reversible H_2 Addition across a Nickel–Borane Unit as a Promising Strategy for Catalysis " *J. Am. Chem. Soc.* 134, 5080-5082 (2012).

Iridium-catalyzed Acceptorless Alcohol Dehydrogenation: Interplay Between Theoretical and Experimental Studies for Understanding Reaction Mechanism and Finding New Efficient Catalysts

Promoterless AAD reactions are desirable for the requirement of green chemistry, which has attracted extensive interests in the past decade. Since 2008, Yamaguchi, Fujita, and their coworkers have successfully applied a series of efficient iridium complexes (**Cat 4** to **Cat 6**) to the AAD reaction; see Scheme 1. These iridium catalysts work efficiently under relatively mild conditions (<100ºC).

Scheme 1. Iridium Complexes Efficient for AAD Reaction.



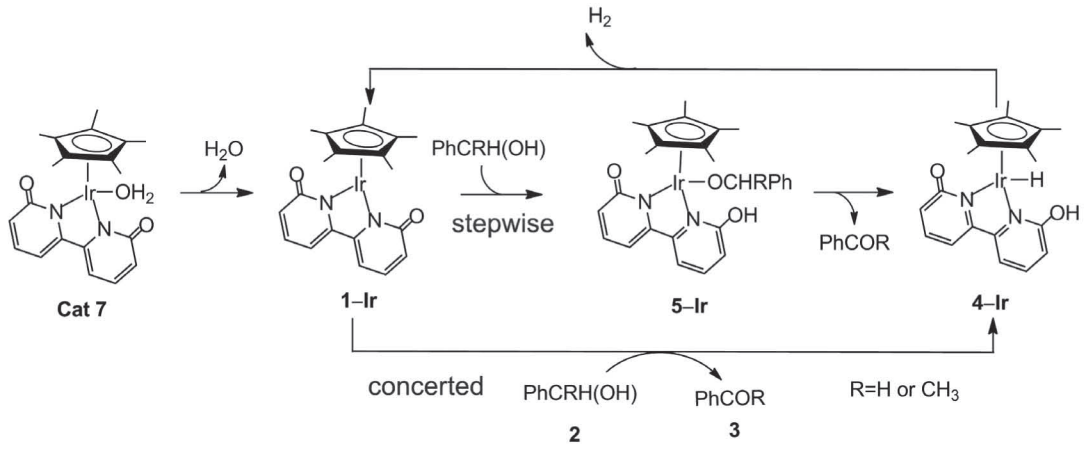
Recently, they synthesized a new iridium complex Cp*Ir(bipyridonate) **Cat 7** (Cp*= pentamethylcyclopentadienyl); see Scheme 1. **Cat 7** is much more active than **Cat 4** to **Cat 6** and works well not only in the AAD of aromatic alcohols but also in the AAD of the aliphatic alcohol under mild conditions. This is interesting because the acceptorless AAD of aliphatic alcohol has been limited, compared with that for the aromatic alcohols. The sole difference between **Cat 7** and **Cat 4** to **Cat 6** is the functional bipyridonate ligand (bpyO). Furthermore, if the bpyO is substituted for a phenanthroline-based functional ligand (phenO), the reactivity of the catalyst (**Cat 8**) decreases very much; see Scheme 2 for the

phenO ligand. These results suggest that the reactivity of the Cp*Ir catalyst is sensitive to the ligand, and the bpyO ligand is the best ligand now. But, the reason is not clear. Also, it is unclear whether the mechanism is the same as that of the previous catalysts such as **Cat 4** or not.

First, we explored the reaction mechanism, where two possible pathways are investigated, as shown in Scheme 2. Our computational results demonstrated that that concerted pathway is much more favorable than the stepwise pathway. This is different from the AAD mechanism mediated by **Cat 4**, where these two reaction pathways are comparable.

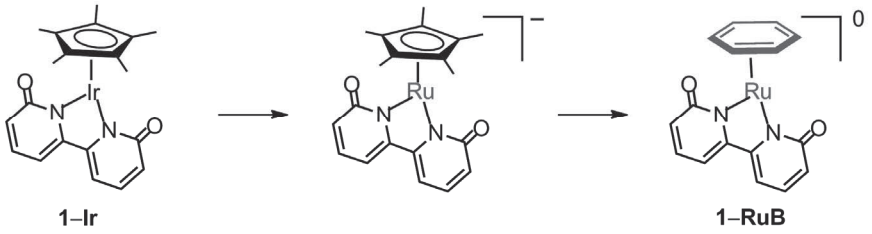
Next, the electronic process of the AAD reaction was examined. In this process, we found that the Cp* ligand receives electrons from the iridium center in the dehydrogenation step, but it donates electrons to the iridium center in the dihydrogen complex formation step. Because the dihydrogen complex formation step is the rate-determining step, therefore, the electron donating ligand is more favorable for the AAD reaction.

Scheme 2. Proposed reaction pathways of the AAD reaction mediated by **Cat 7**.



Then, a new efficient AAD catalyst (Ben)Ru(bpyO) **1–RuB** with a cheaper and abundant 4d ruthenium element was predicted both theoretically and experimentally. The construction procedure is shown in Scheme 3. **1-RuB** exhibits good reactivity in the AAD reaction according to our computational results, which is verified by the experimental work. Experimental results also demonstrated that when the benzene ligand is substituted for a hexyl methyl benzene ligand, the reactivity of the catalyst is enhanced. This is consistent with our computational result that the electron donating ligand is more favorable the AAD reaction.

Scheme 3. Prediction of a New Catalyst.



Original paper

Guixiang Zeng, Kenichi Fujita, Ryohei Yamaguchi, and Shigeyoshi Sakaki "Iridium-catalyzed Acceptorless Alcohol Dehydrogenation: Interplay Between Theoretical and Experimental Studies for Understanding Reaction Mechanism and Finding New Efficient Catalysts" in preparation.

2. Presentation at academic conferences

Guixinag Zeng, Shigeyoshi Sakaki

"Unexpected Electronic Process of the H2 Activation by a New Nickel(0)−Borane Complex: Comparison with the Usual Homolytic and Heterolytic Activations"

The 60th Symposium of Organometallic Chemistry, Osaka, September 14, 2012

3. Others

Guixinag Zeng, Shigeyoshi Sakaki

"Unexpected Electronic Process of the H2 Activation by a New Nickel(0)−Borane Complex: Comparison with the Usual Homolytic and Heterolytic Activations" The 9th symposium of Fukui Institute for Fundamental Chemistry, Kyoto, Nov. 30, 2012.

Nozomi TAKAGI

SPR Fellow, Fukui Kenichi Memorial Research Group 2

1. Summary of the research of the year

A Theoretical Study of Unusual Y-Shaped Three-coordinate Pt Complex: Pt(0) σ-Disilane Complex or Pt(II) Disilyl Complex?

The unusual Y-shaped structure of the recently reported three-coordinate Pt complex $Pt[NHC(Dip)_2](SiMe_2Ph)_2$ (NHC = N-heterocyclic carbene; Dip = 2,6-diisopropylphenyl) was considered a snapshot of the reductive elimination of disilane (Figure 1). A density functional theory study indicates that this structure arises from the strong trans-influence of the extremely σ-donating carbene and silyl ligands. Though this complex can be understood to be a Pt(II) disilyl complex bearing a distorted geometry due to the Jahn-Teller effect, its ^{195}Pt NMR chemical shift is considerably different from those of Pt(II) complexes but close to those of typical Pt(0) complexes. Its Si···Si bonding interaction is <50% of the usual energy of a Si-Si single bond. The interaction between the Pt center and the $(SiMe_2Ph)_2$ moiety can be understood in terms of donation and back-donation interactions of the Si-Si σ-bonding and σ*-antibonding molecular orbitals with the Pt center (Scheme 1). Thus, we conclude that this is likely a Pt(0) σ-disilane complex and thus a snapshot after a considerable amount of the charge transfer from the two silyl groups to the Pt center has occurred. Phenyl anion (Ph^-) and $[R\text{-}Ar]^-$ [R-Ar = 2,6-(2,6-iPr$_2$C$_6$H$_3$)$_2$C$_6$H$_3$] as well as the divalent carbon(0) ligand

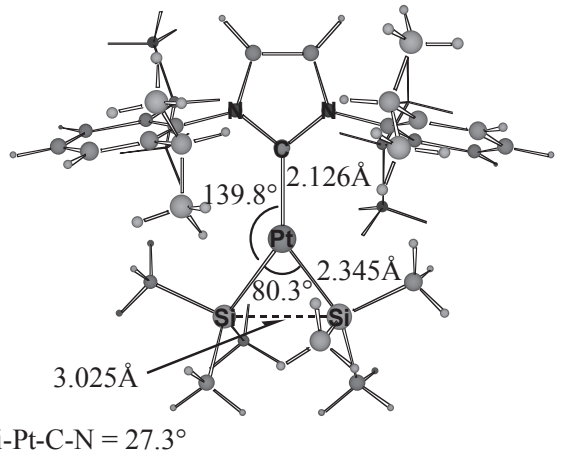
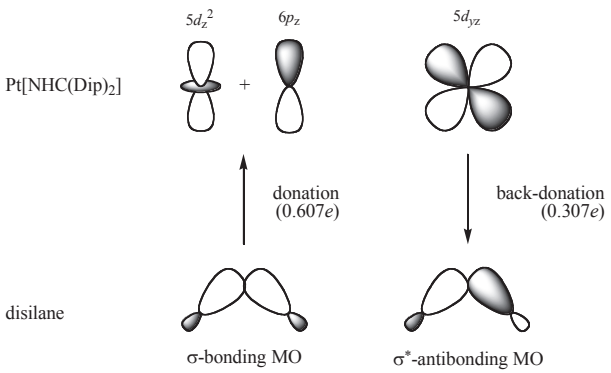


Figure 1. Optimized structure of $Pt[NHC(Dip)_2](SiMe_3)_2$ at the B3PW91 level.



Scheme 1

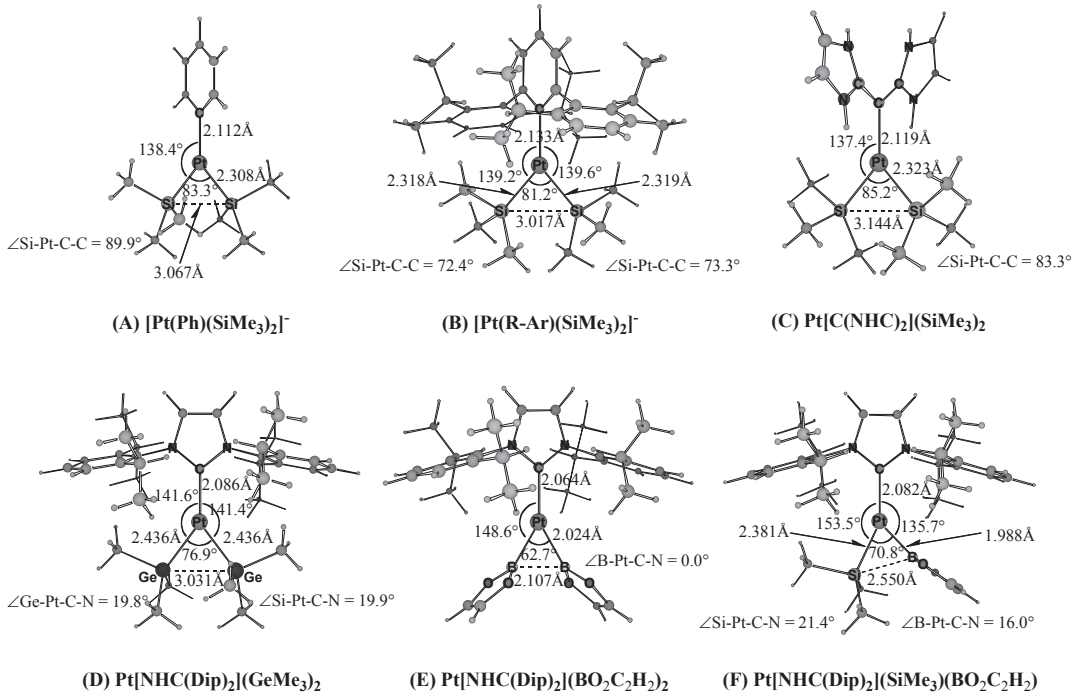


Figure 2. Various snapshots for reductive elimination of Si-Si, Ge-Ge, B-B, and B-Si bonds calculated at the B3PW91 level.

$C(NHC)_2$ also provide similar unusual Y-shaped structures. Three-coordinate digermyl, diboryl, and silyl-boryl complexes of Pt and a disilyl complex of Pd are theoretically predicted to have similar unusual Y-shaped structures when a strongly donating ligand coordinates to the metal center. In a trigonal-bipyramidal Ir disilyl complex $Ir(SiR_3)_2(NHC)(PH_3)_2$, the equatorial plane has a similar unusual Y-shaped structure. These results suggest that various snapshots can be shown for the reductive eliminations of the Ge-Ge, B-B, and B-Si σ-bonds (Figure 2).

Theoretical Study of Reactivity of Ge(II)-hydride Compound: Comparison with Rh(I)-hydride Complex and Prediction of Full Catalytic Cycle by Ge(II)-hydride

The reaction of a Ge(II) hydride compound $HC\{CMeArN\}_2GeH$ (Ar = 2,6-*i*$Pr_2C_6H_3$) **1** with 2,2,2-trifluoroacetophenone (CF_3PhCO) is theoretically investigated with DFT and SCS-MP2 methods. This reaction easily occurs with moderate activation barrier and considerably large exothermicity, to afford a Ge(II) alkoxide **2** through a four-membered metathesis-like transition state (Figure 3). In the transition state, the charge-transfer (CT) from the Ge-H σ-bonding molecular orbital (MO) to the C=O π*-antibonding MO of CF_3PhCO plays an important role. Acetone ($(CH_3)_2CO$) and benzophenone (Ph_2CO) are not reactive for **1**, because their π*-antibonding MOs exist at higher energy than that of CF_3PhCO. Though **2** is easily formed, the

catalytic hydrogenation of CF_3PhCO by **1** is difficult because the reaction of **2** with a dihydrogen molecule needs a large activation energy (Figure 4). On the other hand, our calculations clearly show that the catalytic hydrogenation of ketone by *cis*-$RhH(PPh_3)_2$ **4** easily occurs, as expected. The comparison of catalytic cycle between **1** and **4** suggests that the strong Ge-O bond of **2** is the reason of the very large activation energy for the hydrogenation by **1**. To overcome this defect, we investigated various reagents and found that the catalytic cycle can be completed with the use of SiF_3H. The product is silylether $CF_3PhCHOSiF_3$, which is equivalent to alcohol because it easily undergoes hydrolysis to afford $CF_3PhCHOH$. The similar catalytic cycles are also theoretically predicted for hydrosilylations of CO_2 and imine. This is the first theoretical prediction of the full catalytic cycle with a heavier main-group element compound.

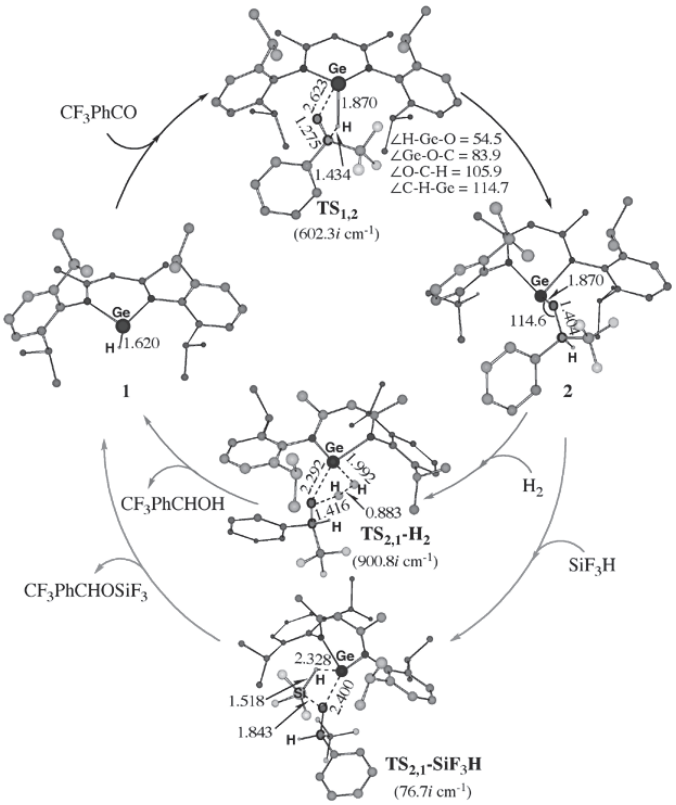


Figure 3. Geometry changes in hydrogenation and hydrosilylation of CF_3PhCO by the Ge(II) hydride **1** calculated at the B3PW91 level.

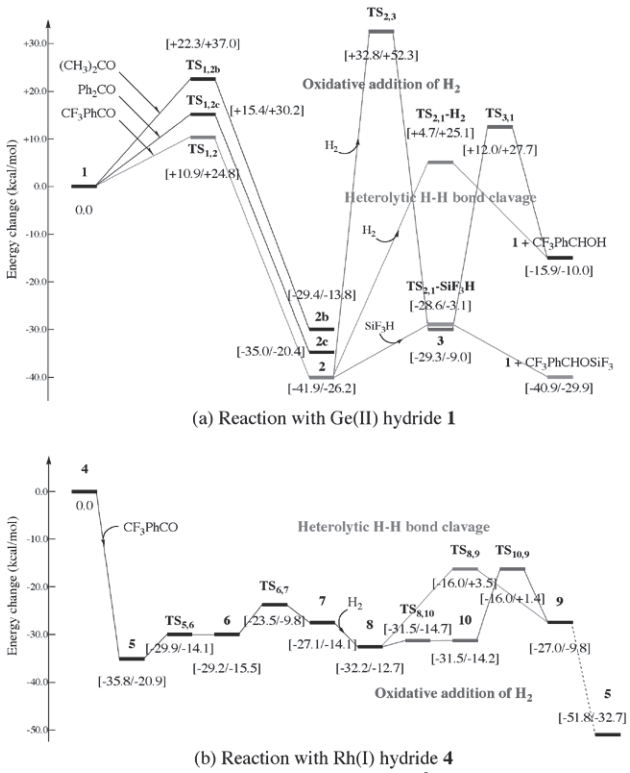


Figure 4. Potential (ΔE) and Gibbs (ΔG^0) energy changes (in kcal/mol) in (a) the hydrogenation and hydrosilylation of CF_3PhCO by the Ge(II) hydride **1** and (b) the hydrogenation of CF_3PhCO by the Rh(I) hydride **4** at the SCS-MP2//B3PW91 level, where ΔE and ΔG^0 are shown before and after the slash, respectively.

2. Original papers

(1) "A Theoretical Study of Unusual Y-Shaped Three-coordinate Pt Complex: Pt(0) σ-Disilane Complex or Pt(II) Disilyl Complex?"
N. Takagi, and S. Sakaki, *J. Am. Chem. Soc.*, **2012**, *134*, 11749-11759.

(2) "Theoretical Study of Reactivity of Ge(II)-hydride Compound: Comparison with Rh(I)-hydride Complex and Prediction of Full Catalytic Cycle by Ge(II)-hydride"
N. Takagi, and S. Sakaki, *J. Am. Chem. Soc.*, *in press*.

3. Presentation at academic conferences

(1) "Theoretical Study of Ketone Insertion into Ge(II)-H Bond: Comparison with that into Rh(I)-H Bond"
N. Takagi, and S. Sakaki, Annual Meeting of Japan Society for Molecular Science, Tokyo, September, 18 – 21, 2012.

(2) "A Theoretical Study of Unusual Y-Shaped Three-coordinate Pt Complex: Pt(0) σ-Disilane Complex or Pt(II) Disilyl Complex?"
N. Takagi, and S. Sakaki, The 62nd Japan Society of Coordination Chemistry Symposium, Toyama, September, 21 – 23, 2012.

(3) "A Theoretical Study of Activation of Ketone by Ge(II) Hydride: Reaction Mechanism, Comparison with Rh(I) Hydride, and Prediction as a Main-group-based Catalyst"
N. Takagi, and S. Sakaki, The 10th Fukui Institute for Fundamental Chemistry Symposium, Kyoto, November 30, 2012.

(4) "A theoretical study of ketone activation by a Ge(II) hydride compound and prediction of a full cycle."
N. Takagi, and S. Sakaki, The 93rd Annual Meeting of the Chemical Society of Japan, Shiga, March 22-25, 2013.

Masayuki NAKAGAKI

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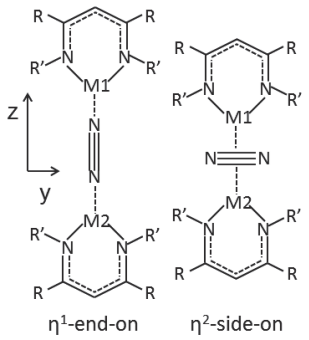
1. Summary of the research of the year

Spin state of inverted sandwich type complexes of hetero transition metals bridged by N_2

β-diketiminate ligands make low-valent and low-coordinate transition metal complexes and form the inversed sandwich type complexes (ISTCs). Especially, ISTCs bridged by dinitrogen molecule are interesting for its spin states and coordination mode of N_2. The $(\mu\text{-}N_2)[Fe(DDP)]_2$ (DDPH = 2-{(2,6-diisopropyl-phenyl)imino}pent-2-ene, which is refer to "nacnac" in several works) takes septet spin state. On the other hand, $(\mu\text{-}N_2)[Cr(DDP)]_2$ takes singlet spin state. Furthermore, the coordination modes of N_2 in Cr and Fe complexes are different; the Fe complex takes η^1-end-on mode, though the Cr complex takes η^2-side-on mode. Previously, we could explain these differences of spin state and coordination mode by the difference of bonding interaction between metal atoms and N_2.

In this study, we investigated the electronic structure of the dinitrogen bridged ISTCs of hetero transition metals; the combination of chromium(I), manganese(I), and iron(I) atoms, to expect the unique character.

Scheme 1 $(\mu\text{-}N_2)[M1(AIP)][M2(AIP)]_2$ ([M1,M2]=[Mn,Fe], [Cr,Mn], [Cr,Fe]; DDP: R=Me, R'=2,6-^{i}Pr$_2$C$_6$H$_3$; AIP: R=H, R'=H)



We replaced the DDP ligands with AIP (AIPH = 1-amino-3-imino-prop-1-ene; Scheme 1) for brevity. Geometry optimizations were carried out for each spin states by the complete active space self-consistent field (CASSCF) method. The active space consists of the d-orbitals of two metals and two π* orbitals of dinitrogen molecule. The second-order perturbation theory with a CASSCF reference function (CASPT2) calculations were carried out at CASSCF optimized structures. CASCI calculations with the orbitals were carried out to obtain the occupation number and spin density of each localized orbitals

The relative energies of various spin states of $(\mu\text{-}N_2)[Mn(AIP)][Fe(AIP)]$ and $(\mu\text{-}N_2)[Cr(AIP)][Mn(AIP)]$ with η^1-end-on and η^2-side-on structures calculated by CASPT2 methods are listed in Table 1. In the $(\mu\text{-}N_2)[Mn(AIP)][Fe(AIP)]$, the A_2 state with η^1-end-on structure corresponds to the

B_2 state with η^2-side-on structure. In these states, the octet state is the most stable spin state but the quartet and the sextet states are also relatively stable than the singlet state. The $^8A_2$ state with η^1-end-on is 1.7 kcal/mol more stable than the $^8B_2$ state with η^2-side-on, which is the medium value between that of $(\mu\text{-}N_2)[Mn(AIP)]_2$ and $(\mu\text{-}N_2)$ $[Fe(AIP)]_2$. The A_1 state with η^2-side-on structure is similar to the grand state of Cr complex, in which the doublet state is the most stable spin state but the energy differences among the doublet state to the dectet state are very small, though the B_1 sate is energetically quite higher than the B_2 state.

In the $(\mu\text{-}N_2)[Cr(AIP)][Mn(AIP)]$, the B_1 state with η^2-side-on structure is the electronic grand state, which corresponds to the B_1 state with η^1-end-on structure. In these states, the dectet state is the most stable spin state but the energy differences among the doublet to the dectet are very small. The A_2 state with η^2-side-on structure corresponds to the B_2 state with η^1-end-on structure. In these states, among the doublet to the octet states are close each other. In η^2-side-on structure, doublet state is the most stable spin state. On the other hand, the octet state is the most stable spin state in the η^1-end-on structure. Different from the B_1 state, the relative energies between the η^2-side-on and the η^1-end-on structures are close. The $^2A_2$ state with η^2-side-on is 3.2 kcal/mol more stable than the $^8B_2$ state with η^2-side-on but 4.4kcal/mol less stable than the $^{10}B_1$ state with η^2-side-on. The result of the $(\mu\text{-}N_2)[Cr(AIP)][Fe(AIP)]$, is similar to that of the $(\mu\text{-}N_2)[Cr(AIP)][Mn(AIP)]$. Due to the doubly occupied d_{x2} orbital in Fe, the most stable spin state of B_1 and A_2 states are nonet and triplet, respectively. And the energy difference of these states is only 1.4 kcal/mol.

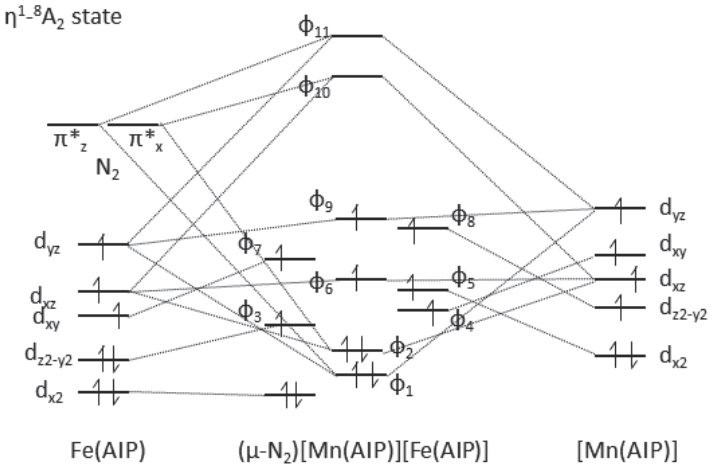
Table 1 Relative energies of various spin states of $(\mu\text{-}N_2)[M1(AIP)][M2(AIP)]$ calculated by CASPT2 methods (in kcal/mol).

	$(\mu\text{-}N_2)[Mn(AIP)][Fe(AIP)]$			$(\mu\text{-}N_2)[Cr(AIP)][Mn(AIP)]$			
	η^1-end	η^2-side		η^1-end		η^2-side	
multiplicity	A_2 state	B_2 state	A_1 state	B_2 state	B_1 state	A_2 state	B_1 state
10tet	26.5	12.1	30.7	13.5	14.1	18.3	0.0
8tet	0.0	1.7	29.8	7.6	15.5	6.2	1.4
6tet	5.7	6.4	28.3	8.2	16.0	5.7	2.3
4tet	9.6	9.7	27.1	9.5	16.2	5.5	2.8
2let	20.2	16.8	26.3	11.4	16.1	4.4	3.0

Molecular orbital (MO) interaction diagram of $(\mu\text{-}\eta^1\text{:}\eta^1\text{-}N_2)[Mn(AIP)][Fe(AIP)]_2$ is shown in Scheme 2. The Mn(AIP) moiety has six d-electrons and the d_{x2} orbital is doubly occupied in the ground state of isolated Mn(AIP); see the right hand of Scheme 2. The Fe(AIP) moiety has seven d-electrons and the $d_{x2\text{-}y2}$ and d_{z2} orbitals are doubly occupied and other three d-orbitals are singly occupied in the grand state; see the left hand of Scheme 2. In the η^1-end-on structure, the d_{xz} and d_{yz} orbitals overlap with N_2 π^*_x and π^*_y MOs to from bonding ψ_1 and ψ_2 MOs and anti-bonding ψ_{10} and ψ_{11} MOs, as shown in Scheme 2. The CASSCF(11,11) natural orbitals of $(\mu\text{-}\eta^1\text{:}\eta^1\text{-}N_2)[Mn(AIP)][Fe(AIP)]_2$ are shown in Figure 1. Numbers in

parentheses represent occupation numbers in the octet state. In this complex, the d_{x2} orbital of Fe was excluded from the active space to avoid the convergence problem. In these orbitals, the ψ_1 and ψ_2 are doubly occupied in the main electron configuration, which mainly consist of d_{xz}-π^*_x and d_{yz} -π^*_y bonding interaction, respectively. However, their occupation numbers are much smaller than 2.00. On the other hand, the occupation numbers of their anti-bonding counterparts are considerably large. These results indicate that the one- and two- electron from φ_1 and φ_2 to φ_{10} and φ_{11} considerably contribute to the wavefunction. Two d_{z2-y2}, d_{xy} orbitals, dx_2 orbital of Mn and non-bonding d_{xz}, d_{yz} orbitals are singly occupied. Because these MOs are either purely non-bonding or nearly non-bonding, the highest spin multiplicity of octet is the grand state.

Scheme 2 MO diagram of (μ-η^1:η^1-N_2)[Mn(AIP)][Fe(AIP)]



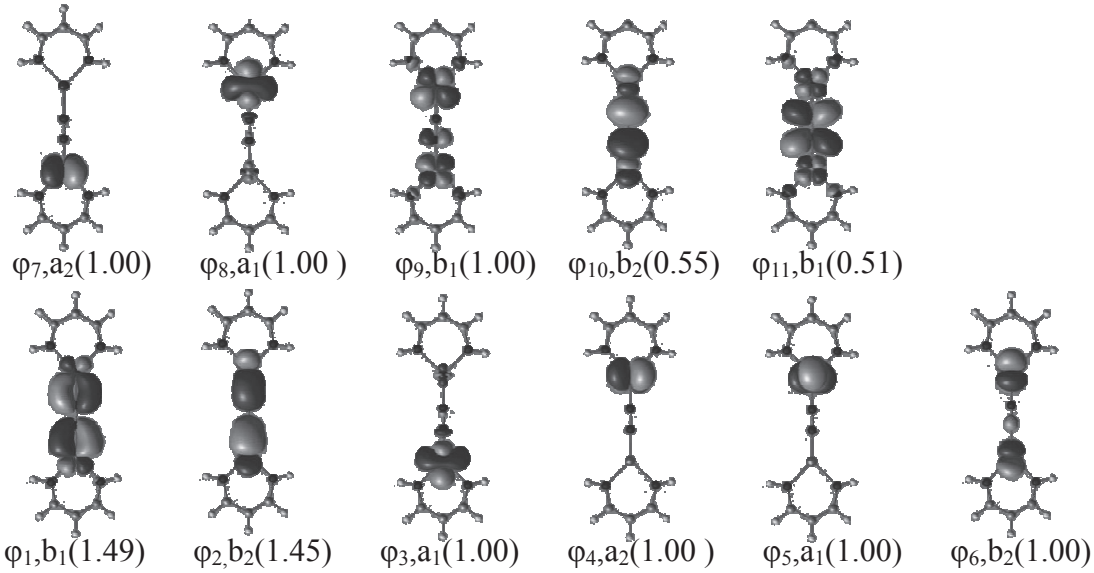
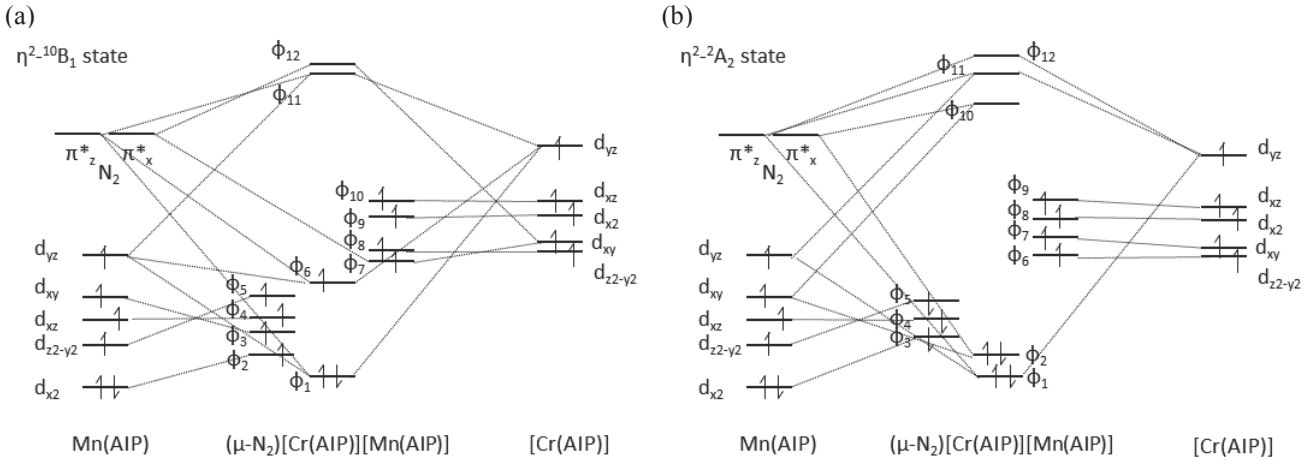


Figure 1. CASSCF(11,11) optimized orbitals of $^8A_2$ state of (μ-η^1:η^1-N_2)[Mn(AIP)] [Fe(AIP)]. Upper side is Mn(AIP) and lower side is Fe(AIP).

The MO diagrams of (μ-η^2:η^2-N_2)[Cr(AIP)][Mn(AIP)] are shown in Scheme 3. In isolated Cr(AIP) moiety, five d orbitals are singly occupied; see the right hand of Scheme 3. In the $^{10}B_1$ state, the d_{yz} orbitals of Cr and Mn overlap with N_2 π^*_z orbital to form bonding MO φ_1, anti-bonding MO φ_{11} and SOMO φ_6; see Scheme 3(a). The φ_2 to the φ_5 MOs are non-bonding d orbital of Mn, and the φ_7 to the φ_{10} MOs are that of Cr.

The N_2 π^*_x orbital is week interact to Cr d_{xy} orbital. As the results, the anti-bonding MO φ_{12} is formed, though it seems 4d-type orbital of Cr. The CASSCF(10,11) optimized orbitals and occupation numbers in B_1 state are shown in Figure 2(a). The φ_1 is very stable and almost doubly occupied. The φ_6 is bonding interaction between Cr and N_2 but anti-bonding interaction between Mn and N_2. The other 9 d-orbitals, φ_2 to φ_{10} including φ_6, are essentially singly occupied and the φ_{11} and φ_{12} MOs are unoccupied in Hartree-Fock configuration.

Scheme 3 MO diagram of (μ-η^2:η^2-N_2)[Cr(AIP)][Mn(AIP)]



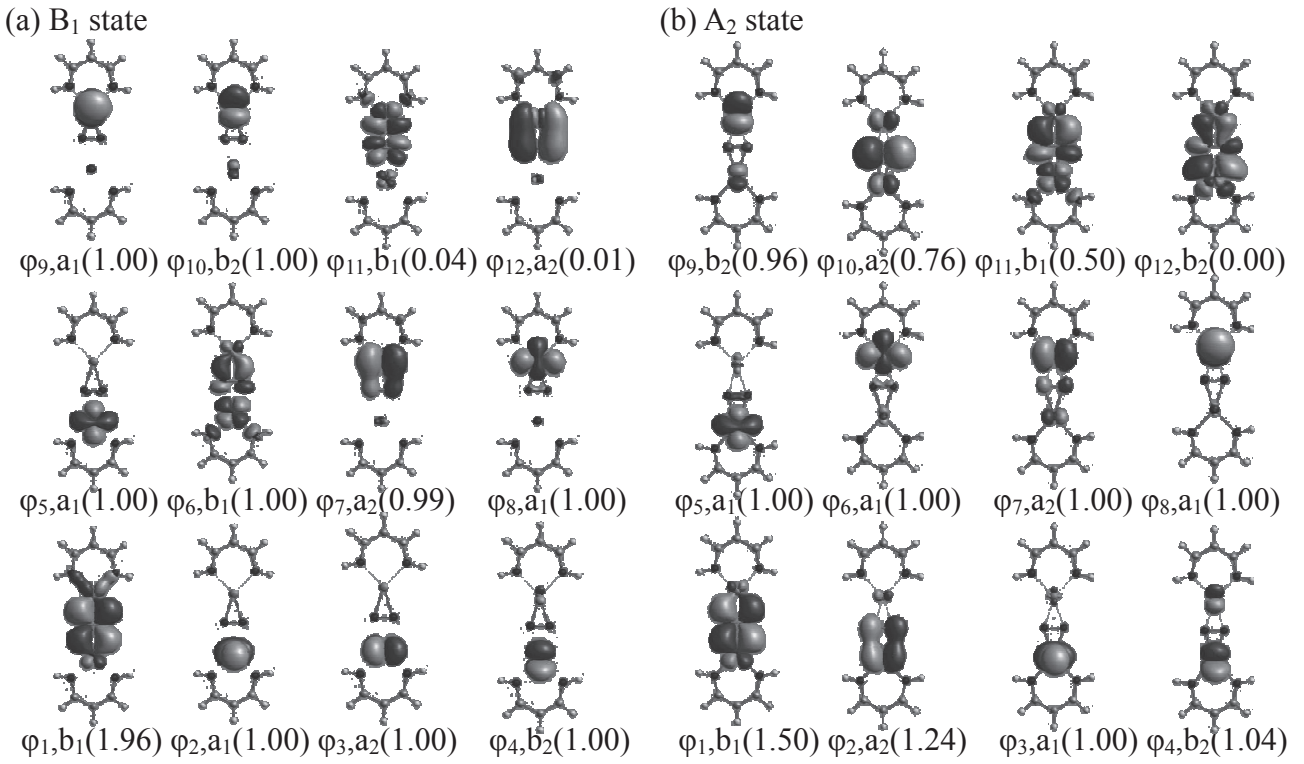


Figure 2 CASSCF(11,12) optimized orbitals of (a)B_1 and (b)A_2 states of (μ-η^2:η^2-N_2)[Cr(AIP)][M(AIP)] (M=Mn, Fe). Upper side is Cr(AIP) and lower side is Mn(AIP).

In the $^2A_2$ state, the d_{yz} orbitals of Cr and Mn overlap N_2 π^*_z orbital to form bonding MO φ_1, anti-bonding MO φ_{11} and φ_{12}. The Mn d_{xy} orbital overlaps with π^*_x orbital to form bonding MO φ_2 and anti-bonding MO φ_{10}. On the other hand, Cr d_{xy} orbital seems to be non-bonding MO φ_7. The Cr(AIP) moiety has four non-bonding d orbitals and the Mn(AIP) moiety has three non-bonding d orbitals. The electron spins in these orbitals are opposite each other; see Scheme 3(b). The CASSCF(10,11) optimized orbitals and occupation numbers in A_2 state are shown in Figure 2(b).

Table 2 shows the spin density of N_2 and two M(AIP) moieties calculated by CASCI method with localized molecular orbitals. In the (μ-N_2)[Mn(AIP)][Fe(AIP)], large negative spin density is obtained on N_2. The single occupation of non-bonding orbitals causes the spin polarization of bonding orbitals, α-electron localizes to metal side moieties and β-electron localizes to N_2 side, and the high-spin state is favorable. This electronic structure is similar to that of the (μ-N_2)[Mn(AIP)]$_2$ and the (μ-N_2)[Fe(AIP)]$_2$. In the (μ-N_2)[Cr(AIP)][Mn(AIP)], the spin polarization does not occur in B_1 state. However, in A_2 state, N_2 and Cr have same spin density but Mn has opposite spin density. In the $^{10}B_1$ state, the main configuration has doubly occupied N_2 π^*_z orbital and singly occupied Mn d_{yz} orbital. In the second reading terms, a single electron moves from N_2 π^*_z orbital to Cr d_{yz} orbital compared to the main configuration. It suggests that the dπ-π* bonding interaction between Cr and N_2 is stronger than that between Mn and N_2. On the other hand, in the A_2 state, the dπ-π* bonding interaction between Mn and N_2 is stronger, though the highest b_1 orbital was excluded from active space because the Cr d_{yz} and N_2 π^*_y orbitals could not be separated.

Table 2 Spin densities calculated by LMO-CASCI method

	(Mn,Fe)	(Cr,Mn)	
	η^1-$^8A_2$	η^2-$^{10}B_1$	η^2-$^2A_2$
M1(AIP)	4.80	4.01	1.99
M2(AIP)	3.49	4.98	−1.45
N_2	−1.28	0.02	0.47
Total	7.00	9.00	1.00

Summary

In the (μ-N_2)[Mn(AIP)][Fe(AIP)], the spin states of two metal atoms take strong high-spin coupling, the octet states is the most stable spin state. They form two bond between N_2 and two M(AIP) moieties; $\pi(d_{yz})$-bond and $\delta(d_{xy})$-bond in η^2-side-on and $\pi(d_{yz})$-bond and $\pi(d_{xz})$-bond in η^1-end-on. There is large negative spin density on N_2 and the high-spin state is favorable, which is similar to that of the (μ-N_2)[Mn(AIP)]$_2$ and the (μ-N_2)[Fe(AIP)]$_2$.

In the (μ-N_2)[Cr(AIP)][Mn(AIP)], we found two electronic states which has different electronic structure from the (μ-N_2)[Cr(AIP)]$_2$ and the (μ-N_2)[Mn(AIP)]$_2$. The B_1 state takes dectet spin state which has$\pi(d_{yz})$-bond. On the other hand, the A_2 state takes doublet state. Though the A_2 state has $\pi(d_{yz})$-bond and $\delta(d_{xy})$-bond, the $^2A_2$ state is 4.4 kcal/mol higher than the $^{10}A_1$ state.

2. Presentation at academic conferences

(1) 中垣 雅之，黒川 悠索，榊 茂好
「窒素分子を挟んだ逆サンドイッチ型二核金属錯体の特異的なスピン状態に関する理論的研究」
第１５回理論化学討論会 2012 仙台 仙台 2012/5/24-26 1B5b 口頭

(2) Masayuki Nakagaki, Yusaku I. Kurokawa, Shigeyoshi Sakaki
“CAS-PT2 and LMO-CAS Study of Spin States and Coordination Modes of N2 bridged Inverted Sandwich Type Complexes”
14th ICQC Interactional Congress of Quantum Chemistry (Boulder, Colorado, USA) 2012/6/25-30 I15 poster

(3) 中垣 雅之、黒川 悠索、榊 茂好
「異種金属原子による窒素分子を挟んだ逆サンドイッチ型錯体の電子構造に関する理論的研究」
第６回分子科学討論会 2012 東京　東京　2012/9/18-21 3P130 ポスター

(4) 中垣 雅之，黒川 悠索，榊 茂好
「窒素分子を挟んだ逆サンドイッチ型二核金属錯体の特異的なスピン状態に関する理論的研究」
錯体化学会第６２回討論会　富山 2012/9/21-23 2Ba-06 口頭

3. Others

(1) 中垣 雅之、榊 茂好
「異種金属原子による窒素分子を挟んだ逆サンドイッチ型錯体の電子構造に関する理論的研究」
第10回京都大学福井謙一記念研究センターシンポジウム　京都 2012/11/30

Terutaka YOSHIZAWA

SPR Fellow, Fukui Kenichi Memorial Research Group 2

(To 30 Sep. 2012)

1. Summary of the research of the year

NMR shielding constants of CuX, AgX, and AuX (X = F, Cl, Br, and I) investigated by density functional theory based on the Douglas–Kroll–Hess Hamiltonian

Introduction

NMR shielding constants of heavy metal elements are of considerable interest in molecular science and theoretical chemistry, because those shielding constants reflect characteristic electronic structure, in particular, relativistic effects in the system including heavy elements. Actually, David and Restrepo recently reported that the paramagnetic term of the Au nuclear magnetic resonance (NMR) shielding constant of AuF molecule is more than three times as large as those of AuCl, AuBr, and AuI. They discussed that this result arises from spin-orbit (SO) effect enhanced by the high electronegativity of F atom. Since their report, the relation between the SO effect and the electronegativity attracts a lot of interests, because the SO effect does not seem to directly relate to electronegativity. However, the mechanism of the relation has not been elucidated yet.

In the present study, we combined the DFT method with the second-order DKH (DKH2) one-electron Hamiltonian and applied it to the calculation of the NMR shielding constant. Then, we applied this method to the NMR shielding constant of the metal in CuX, AgX, and AuX (X = F, Cl, Br, and I), investigated relativistic effects on the NMR shielding constant, and discussed the reasons why the electronegativity of halogen influences the NMR shielding constant.

Results and discussion

Second-order magnetically relativistic (MR2) effect on metal shielding constant in MX

The MR2 effects on the Cu, Ag, and Au shielding constants are summarized in Table 1 and Supporting Information Table S5 [1], where they were defined as the difference between the DKH2 magnetic operators and the Breit-Pauli magnetic operators. As shown in Table 1, the MR2 effect considerably decreases the DKH2(SR+SO) value. Interestingly, the MR2 effect in CuF is considerably larger than those for other halides. This result is consistent with the understanding that the MR2 effect is not always large only for the heavier system. The largest MR2 effect for CuF is attributed to the overestimation of the SD+FC term (= 2783 ppm) by the Breit-Pauli magnetic operators, while the MR2 effect is moderate in the paramagnetic and diamagnetic terms.

The MR2 effect in AgX is not large; see Table 1 and Supporting Information Table S5 [1]. The moderate MR2 effect in AgF to AgBr arises from the cancellation of the MR2 effects between the diamagnetic term and the sum of the paramagnetic and SD+FC terms. In AuX, the MR2 effect is remarkably large because of the extremely large overestimation of the SD+FC term and the somewhat large overestimation of the paramagnetic term by the Breit-Pauli magnetic operators, as shown in Table 1. This result indicates that the Breit-Pauli magnetic operators cannot be applied to the NMR study of Au compounds.

Table 1. Second-order magnetically relativistic (MR2) effects on Cu, Ag, and Au shielding constants estimated by the full DKH2-BP86 method containing the scalar relativistic (SR), SO, and MR2 effects and the DKH2-BP86 method containing only the SR and SO effects.

Molecule	σ	DKH2 (SR+SO)	DKH2 (SR+SO+MR2)	Trend[a]	MR2%
CuF	Dia	2510	2285	Down	–8.9
	Para	–2548	–2512	Down	–1.4
	SD+FC	2783	1525	Down	–45.2
	Total	2745	1298	Down	–52.7
CuCl	Dia	2539	2314	Down	–8.9
	Para	–1413	–1381	Down	–2.2
	SD+FC	813	647	Down	–20.4
	Total	1939	1580	Down	–18.6
AgF	Dia	5000	4373	Down	–12.5
	Para	–816	–690	Down	–15.5
	SD+FC	1202	1314	Up	9.3
	Total	5386	4997	Down	–7.2
AgCl	Dia	5027	4409	Down	–12.3
	Para	–778	–646	Down	–17.0
	SD+FC	153	1046	Up	584.3
	Total	4402	4809	Up	9.3
AuF	Dia	11093	9647	Down	–13.0
	Para	–6076	–5176	Down	–14.8
	SD+FC	173376	19276	Down	–88.9
	Total	178393	23747	Down	–86.7
AuCl	Dia	11123	9766	Down	–12.2
	Para	–3203	–2482	Down	–22.5
	SD+FC	15771	6912	Down	–56.2

Total	23691	14196	Down	–40.1

[a] ”Down” means that absolute value decreases by the MR2 effects.

Conclusions

We developed the two-component relativistic method for NMR shielding constant based on the DKH2 one-electron Hamiltonian. Important results are summarized, as follows:

(1) The shielding constant considerably depends on the basis set in the DKH2 method like the 4c relativistic theory only with the restricted kinetic balance, viz., without an explicit diamagnetism.

(2) The DKH2-DFT method presents the shielding constant of heavy atom (up to Xe) comparable to the 4c-DFT-calculated value and reproduces well the experimental I shielding constant of CuI and AgI and the experimental Xe shielding constant of XeF_2.

(3) The DKH2-DFT-calculated increasing order of the Ag shielding constant AgF < AgBr < AgI agrees with the experimental result, but the DKH2-HF-calculated order does not.

(4) AuF exhibits extremely large Au shielding constant, which is the largest in AuX, but CuF and AgF do not exhibit very large Cu and Ag shielding constants.

(5) The FC term in the sd_σ+p_σ → sd_σ–p_σ transition is responsible for the large SD+FC term of AuF. One important reason is the small orbital energy separation between the sd_σ+p_σ and sd_σ–p_σ MOs in AuF.

(6) The large paramagnetic term of AuF arises from the large metal *d*-orbital components in the d_π–p_π and sd_σ–p_σ MOs. This large paramagnetic term compensates the positive SD+FC term in AuF to some extent.

(7) For all these compounds, the MR2 effect decreases the diamagnetic term, the absolute value of the paramagnetic term, and the SD+FC term which is overestimated by the Breit-Pauli magnetic operators except for the SD+FC terms of AgF and AgCl.

(8) The MR2 effect is important even for CuF. The relatively small MR2 effect in AgF to AgBr is attributed to the cancellation of the MR2 effect for the diamagnetic term by that for the paramagnetic and SD+FC term.

Considering all these results, we believe that the DFT method based on the DKH2 Hamiltonian is useful for calculating NMR shielding constant of heavy metal element.

Reference

[1] T. Yoshizawa, S. Sakaki, J. Comput. Chem. 34, 1013, (2013).

2. Original papers

(1) T. Yoshizawa and T. Nakajima “A new computational scheme for the spin–orbit part of zero-field splitting tensor” Chem. Phys. Lett. 549, 108–112, (2012)

(2) T. Yoshizawa and S. Sakaki “NMR shielding constants of CuX, AgX, and AuX (X = F, Cl, Br, and I) investigated by density functional theory based on the Douglas–Kroll–Hess Hamiltonian” J. Comput. Chem. 34, 1013–1023, (2013)

3. Presentation at academic conferences

T. Yoshizawa and S. Sakaki “NMR shielding constants of CuX, AgX, and AuX (X = F, Cl, Br, and I) investigated by density functional theory based on the Douglas–Kroll–Hess Hamiltonian” Annual Meeting of Japan Society for Molecular Science, 3P099, September 18-21, 2012, the University of Tokyo, Tokyo (Japan).

Wei GUAN

SPR Fellow, Fukui Kenichi Memorial Research Group 2

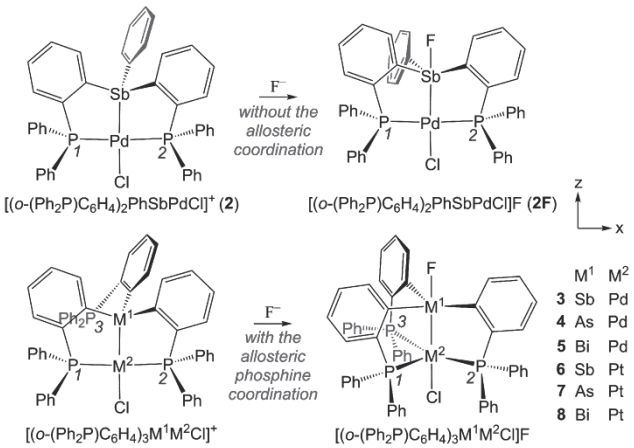
1. Summary of the research of the year

Interest in new heterodinuclear transition-metal/main-group-metal complexes: DFT study of electronic structure and mechanism of fluoride sensing function

Fluoride anion plays a crucial role in biological process and daily life. However, excessive intake will lead to dental and skeletal fluorosis and even osteosarcoma. Taking into account these adverse effects of fluoride anion, the recognition and sensing of fluoride anions are necessary. For a potential fluoride chemosensor, such factors as large ion affinity, high selectivity, visible photophysical response, and hydrolytic stability must be satisfied.

In this work, the colorimetric fluoride sensing property of the heterodinuclear main-group/transition-metal complexes $[(o\text{-}(Ph_2P)C_6H_4)_3M^1\text{-}M^2Cl]^+$ (M^1 = As, Sb, or Bi; M^2 = Pd or Pt) was systematically investigated with the DFT method (**Scheme 1**).

Scheme 1



(1) Not only the larger F^- capturing ability of the Lewis acidic M^1 center but also the allosteric coordination of the third phosphine with the M^2 center is indispensable for the colorimetric sensing of the fluoride anion. The stabilization energy by the fluoride adduct formation is −15.5 and −16.2 kcal mol^{-1} for **3** (M^1 = Sb; M^2 = Pd) and **6** (M^1 = Sb; M^2 = Pt), respectively. The formation of the hypervalent M^1–F bond induces the allosteric coordination of the P3 with the M^2 center. Accordingly, the coordination geometry of the M^2 center changes from a four-coordinate planar structure in **3**–**8** to a five-coordinate trigonal-bipyramid in fluoride adducts (**3F**–**8F**).

(2) The calculated absorption spectra agree with the experimental ones (**Figure 1**). For instance, the two absorption bands at 383 and 315 nm (**2**) disappear but a new strong peak appears at 332 nm (**2F**), when **2** converts to **2F**. These absorptions are mainly assigned to LFT/LMCT. The addition of fluoride anion to **3** quenches the absorption

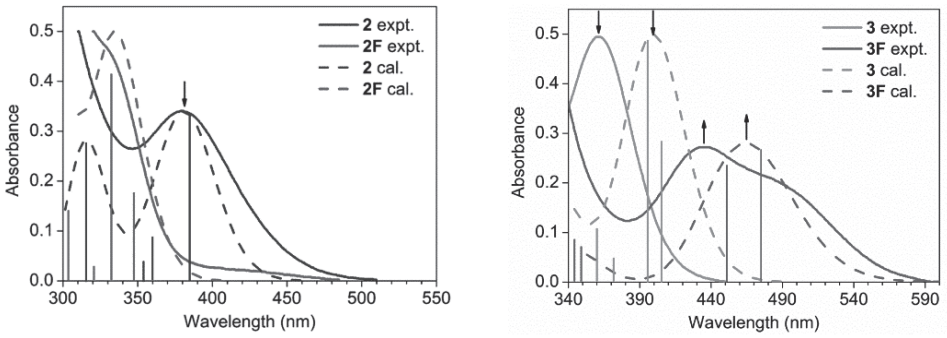


Figure 1. Comparisons of experimental and calculated absorption spectra[b] of **2**, **2F**, **3**, and **3F**. *a* PCM(CH_2Cl_2)/TD-PBE0/BS-II level.

band around 400 nm but newly produces two absorption peaks (475 and 451 nm) in the long wavelength region in **3F**. They are assigned to the Pd-based LFT, $d_{xy} \rightarrow d_{z^2}$ and $d_{x^2-y^2} \rightarrow d_{z^2}$ including LMCT character. The allosteric coordination of the P3 with the Pd center plays a crucial role in decreasing the d-d orbital energy separation and hence the resultant spectrum appears in the visible region in the fluoride adduct.

(3) This kind of heterodinuclear complex **3** exhibits high selectivity for fluoride anion. In the anion-capturing process of **3** for such other anions as chloride, bromide and thiocyanide anions, the Pd center does not change to a trigonal-bipyramidal structure and their binding energies with those anions are only 6.0, 4.3, and 3.1 kcal mol^{-1}, respectively. The binding energy for cyanide adduct (–9.9 kcal mol^{-1}) is moderately smaller than that for the fluoride adduct, but it is enough to bind the cyanide anion. The allosteric coordination is not stable in the cyanide adduct of the Sb-Pd combination, however, in the cyanide adduct of the Sb-Pt the allosteric coordination form is more stable than the other structure without the allosteric coordination. Actually, the cyanide adduct **6CN** provides a large absorption in visible region. Thus, the Sb-Pt combination is suggested to be useful for detecting cyanide anion.

(4) In the absence of fluoride anion, the strain energy of the bridging (o-$(Ph_2P)C_6H_4)_3Sb$ moiety of **3'** is much larger than the stabilization induced by the coordination of the third phosphine. In the fluoride adduct, on the contrary, the moderate strain energy is overcome by the Pd-P3 coordinate bond. Hence, the chelating structure of (o-$(Ph_2P)C_6H_4)_3Sb$ is the origin of the absence of the P3 allosteric coordination in **3** but the presence of the P3 coordination in **3F**; in other words, this ligand plays a crucial role in the allosteric coordination.

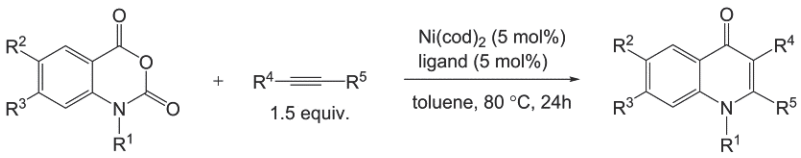
The Bi-Pd (**5**) and Bi-Pt (**8**) combinations provide a moderately smaller binding energies (–10.5 and –10.9 kcal mol^{-1}) than that of **3**, and the Sb-Pt combination (**6**) presents a bit larger binding energy (–16.2 kcal mol^{-1}) than **3**. Also, **5**, **6**, and **8** exhibit similar spectral changes to those of the **3** → **3F** conversion because of the allosteric coordination on the Pd/Pt center in the fluoride adduct. The Bi-Pd combination is recommended for fluoride sensing material without interference from cyanide anion.

Mechanism Investigation of Nickel-Catalyzed Decarboxylative [4 + 2] Cycloaddition of Isatoic Anhydrides with Alkynes

Heterocyclic compounds play a vital role in life processes due to their biological activities in agrochemical and pharmaceutical applications. As the demand for these chemicals increases, it is very essential for developing novel and efficient synthetic methods to prepare heterocyclic compounds. Among a variety of synthetic transformations, intermolecular cycloadditions catalyzed by transition-metal complexes are powerful methodologies for constructing structurally diverse heterocyclic compounds in modern synthetic organic chemistry.

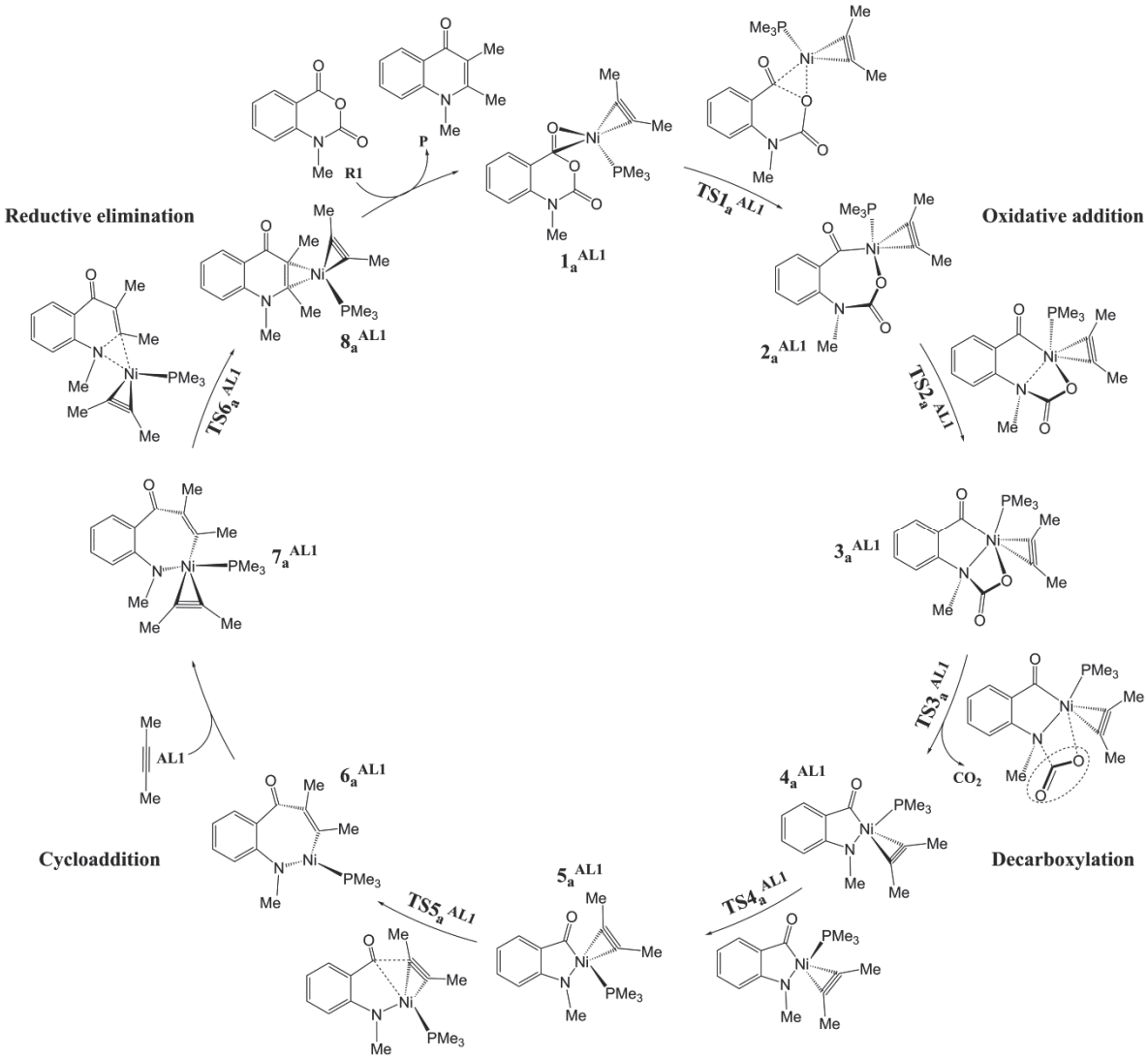
Here, Ni-catalyzed decarboxylative [4 + 2] cycloaddition of isatoic anhydrides with alkynes to quinolones was theoretically investigated with the DFT method (**Scheme 2**).

Scheme 2



(1) The overall catalytic cycle is found to consist of four basic processes: oxidative addition, decarboxylation, cycloaddition, and reductive elimination (**Scheme 3**). The interesting selectivity between the C−O, C−C, and C−N bond activations of the isatoic anhydride **R1** is examined first. Calculations suggest that the anhydride C(=O)−O bond is preferentially activated in either the bis-ligand (phosphine and alkyne) pathway or the alternative monophosphine pathway. Comparatively, although there is competition between the two mechanisms through equilibrium reaction, the bis-ligand (phosphine and alkyne) pathway is more favorable ($\Delta G^{\circ\ddagger}$ = 14.31 kcal/mol) (**Figure 2**). It means that the alkyne participates into the reaction in the initial catalytic stage. FMO analyses of $\mathbf{TS1_a^{AL1}}$ indicate that the CT from the $3d_\pi$-Ni MO to the antibonding LUMO of isatoic anhydrides contributes to a weakening of the anhydride C(=O)−O bond in the oxidative addition process. The replacement of strong electron-donating ligand enhances the degree of CT, accordingly promote the anhydride C(=O)−O bond cleavage.

Scheme 3



(2) The exothermic decarboxylation proceeds through two steps, the formation of Ni−N bond and CO_2 elimination, with a $\Delta G^{\circ\ddagger}$ value of 12.92 and 9.71 kcal/mol, respectively. Wherein, the donation from

p-electrons of N to empty acceptor Ni orbital contributes the Ni–N bond formation, which essentially promotes the following CO_2 elimination. In view of this point, other heteroatom (O and S) and C atom effect on the decarboxylation process was examined. The substitution of N by C signficantly increases the $\Delta G°^{\ddagger}$ value of decarboxylation to 41.91 kcal/mol, even though the oxidative addition becomes easier with $\Delta G°^{\ddagger}$ value of 11.05 kcal/mol. The substitutions of N by O and S with more valence electron pairs facilitate the oxidative addtion and decarboxylation processes, especially the later step. The O and S substitutions signficantly decrease the $\Delta G°^{\ddagger}$ value of decarboxylation to 2.17 and –9.17 kcal/mol, respectively.

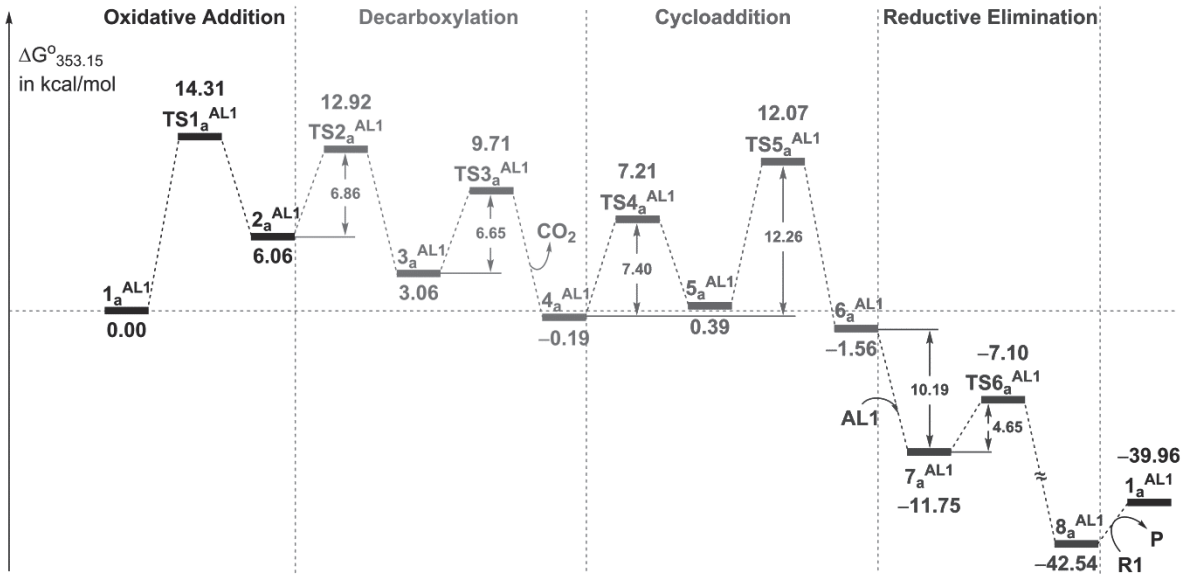


Figure 2. Energy Profile ($\Delta G°_{353.15}$) for the Full Catalytic Cycle in Scheme 3.

(3) Cycloaddition process also undergoes two steps: the ligands (**AL1** and PMe_3) rotation and the but-2-yne (**AL1**) insertion. The former step requires a $\Delta G°^{\ddagger}$ value of 7.40 kcal/mol. Then, **AL1** more readily inserts into the acyl-nickel (Ni−CO) bond instead of the Ni−N bond after CO_2 elimination with a $\Delta G°^{\ddagger}$ value of 12.26 kcal/mol. In the ligands rotation step, the gradually bending **AL1** ligand decreases its unoccupied π* orbital energy, which favors the accumulation of electrons on the **AL1** by π_{Ni} back donation, and then makes C10 become an active nucleophilic site to interact with electrophilic C2 center in the following the **AL1** insertion step. Additionally, regioselectivity of the alkynes insertion was investigated when the polarized alkynes, 1-(silyl)propyne (**AL3**) and 1-(trimethylsilyl)propyne (**AL4**), are utilized. It is found that both electronic effect and steric effect influence the regioselectivity, but the latter play a major role.

(4) The last and facile reductive elimination is found to be promoted by the addition of a second electron-donating **AL1** ligand with a very facile step a $\Delta G°^{\ddagger}$ value of 4.65 kcal/mol.

The present mechanism investigations on this efficient and complicated Ni-catalyzed intermolecular decarboxylative cycloaddition reaction should be not only improve our understanding of the observed experimental facts but also shed important light on how to further expand their scope and utility.

2. Original papers

(1) Wei Guan, Shinichi Yamabe, Shigeyoshi Sakaki
"Interest in new heterodinuclear transition-metal/main-group-metal complexes: DFT study of electronic structure and mechanism of fluoride sensing function"
Dalton Trans. 42, 8717–8728(2013).

(2) Shinichi Yamabe, Wei Guan, Shigeyoshi Sakaki
"Three Competitive Transition States at the Glycosidic Bond of Sucrose in Its Acid-Catalyzed Hydrolysis"
J. Org. Chem. 78, 2527−2533(2013).

(3) Shinichi Yamabe, Wei Guan, Shigeyoshi Sakaki
"Presence or absence of a novel charge-transfer complex in the base-catalyzed hydrolysis of N-ethylbenzamide or ethyl benzoate"
Beilstein J. Org. Chem. 9, 185–196(2013).

(4) Shinichi Yamabe, Gui-Xiang Zeng, Wei Guan, Shigeyoshi Sakaki
"An aniline dication-like transition state in the Bamberger rearrangement"
Beilstein J. Org. Chem. 9, 1073–1082(2013).

(5) Shinichi Yamabe, Wei Guan, Shigeyoshi Sakaki
"How is the anionic tetrahedral intermediate involved in the isomerization of aspartyl peptides to iso-aspartyl ones? A DFT study on the tetra-peptide"
Org. Biomol. Chem. 10, 8007−8015(2012).

(6) Zhong-Ling Lang, Wei Guan, Li-Kai Yan, Shi-Zheng Wen, Zhong-Min Su, Li-Zhu Hao
"The self-assembly mechanism of the Lindqvist anion $[W_6O_{19}]^{2-}$ in aqueous solution: a density functional theory study"
Dalton Trans. 41, 11361–11368(2012).

(7) Wei Guan, Zhi-Jian Wu, Zhong-Min Su
"DFT study of ionic peapod structures from single-walled carbon nanotubes and Lindqvist tungstates"
Dalton Trans. 41, 2798–2803(2012).

3. Presentation at academic conferences

(1) Wei Guan, Shinichi Yamabe, Shigeyoshi Sakaki
"DFT study of colorimetric fluoride ion sensing by the heterodinuclear main-group/transition-metal complexes through allosteric coordination"
The 6th Annual Meeting of Japan Society for Molecular Science (2P-126) Tokyo, Sep. 19, 2012.

Yue CHEN

SPR Fellow, Fukui kenichi Memorial Research Group 2

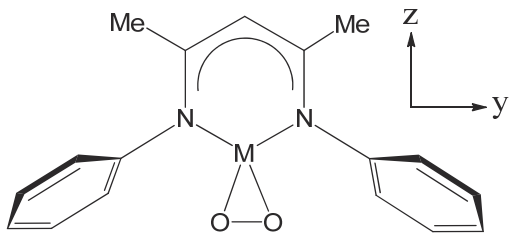
(From 16 Jul. 2012)

1. Summary of the research of the year

Theoretical Study of Mononuclear Nickel(I), Nickel(0), Copper(I), and Cobalt(I) Dioxygen Complexes: New Insight into Differences and Similarities in Geometry and Bonding Nature

Activation of dioxygen by such first row transition metals as Mn, Fe, Co, Ni, and Cu plays crucial roles in biological oxidation. However, the nickel-dioxygen interaction and the role of the nickel center in the relevant dioxygen complexes have been much less investigated than those of copper-dioxygen complexes despite the importance of the nickel-dioxygen species in superoxide dismutase. It is of considerable importance to know how much and why the electronic structure and bonding interaction of the nickel dioxygen complex are different from and/or similar to those of the copper dioxygen complex.

In the present work, we theoretically investigated (N^N)Ni(O_2), its cobalt(I) and copper(I) analogues, and $(Ph_3P)_2Ni(O_2)$ by DFT and multi-state restricted active space multi-configurational second-order perturbation (MS-RASPT2) method with large active space; see Scheme 1. We selected these complexes in expectation that we can clarify the differences and/or similarities among cobalt(I), nickel(I), and copper(I) and between nickel(I) and nickel(0). Our purposes here are (1) to elucidate the electronic structures of these complexes, in particular, to elucidate which understanding of peroxo and superoxo is correct in these complexes, (2) to disclose the metal and ligand effects on the M-O_2 interaction, and (3) to find the determining factors for the M-O and the O-O bond lengths and their bonding natures. During this work, we found that pseudo-Jahn-Teller distortion occurs only in (N^N)Ni(O_2) but does not in other three complexes. We wish to emphasize that this new finding deeply relates to the electronic structures of these dioxygen complexes interestingly.



$(N^N)_mM(O_2)$
M= Ni, Cu, Co

Model complex $(N^N)_mM(O_2)$

Scheme 1. The real and model complexes of (N^N)Ni(O_2) and (N^N)Cu(O_2)

Both DFT and MS-RASPT2 calculations clearly show that (N^N)Ni(O_2) is not C_{2V} but C_S symmetrical with different Ni-O bond lengths. On the other hand, $(N^N)_mCu(O_2)$, $(N^N)_mCo(O_2)$, and $(Me_3P)_2Ni(O_2)$ all have a C_{2V} symmetrical structure in the ground state.

In $(N^{\wedge}N)_mNi(O_2)$ with a C_{2V} symmetry, the main configuration of the ground state is $\pi^2_{\pi^*_z+d_{yz}}\delta^2_{\pi^*_x+d_{xy}}d^2_{y^2-z^2}d^2_{x^2}d^2_{xz}\delta^1_{d_{xy}-\pi^*_x}\pi^0_{\pi^*_z-d_{yz}}$; see Table 1. The first excited state exists near the ground state, where the energy difference is only 1.8 kcal·mol^{-1}. On the other hand, the energy

Table 1. The relative energies of the ground and low lying excited states of model complexes.

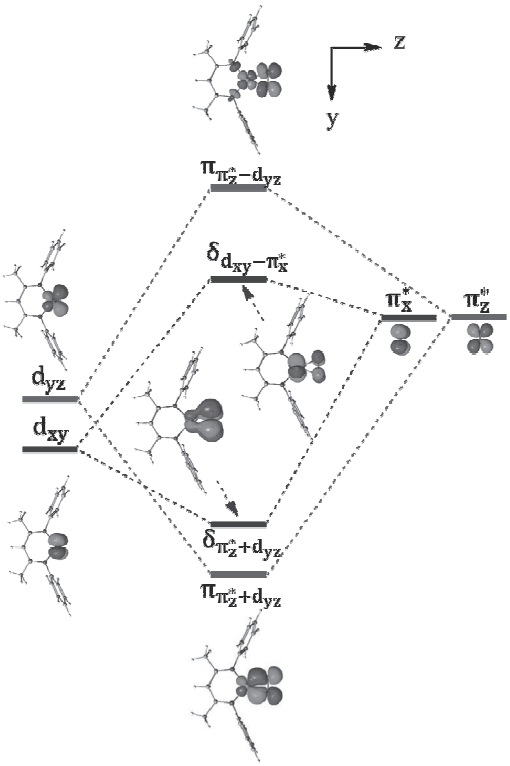
State (symmetry)	Configurations	Weight (%)	Relative Energy (kcal·mol^{-1})
	$(N^{\wedge}N)_mNi(O_2)$ (C_{2V})		
Ground state (^{2}A")	$\pi^2_{\pi^*_z+d_{yz}}\delta^2_{\pi^*_x+d_{xy}}d^2_{y^2-z^2}d^2_{x^2}d^2_{xz}\delta^{*1}_{d_{xy}-\pi^*_x}\pi^{*0}_{\pi^*_z-d_{yz}}$	61.4	0.0
First excited state (^{2}A")	$\pi^2_{\pi^*_z+d_{yz}}\delta^2_{\pi^*_x+d_{xy}}d^2_{y^2-z^2}d^2_{x^2}d^1_{xz}\delta^{*2}_{d_{xy}-\pi^*_x}\pi^{*0}_{\pi^*_z-d_{yz}}$	62.9	1.8
	$(N^{\wedge}N)_mNi(O_2)$ (C_S)		
Ground state (^{2}A")	$\pi^2_{\pi^*_z+d_{yz}}\delta^2_{\pi^*_x+d_{xy}}d^2_{y^2-z^2}d^2_{x^2}d^2_{xz}\delta^{*1}_{d_{xy}-\pi^*_x}\pi^{*0}_{\pi^*_z-d_{yz}}$	44.1	-1.0
First excited state (^{2}A")	$\pi^2_{\pi^*_z+d_{yz}}\delta^2_{\pi^*_x+d_{xy}}d^2_{y^2-z^2}d^2_{x^2}d^1_{xz}\delta^{*2}_{d_{xy}-\pi^*_x}\pi^{*0}_{\pi^*_z-d_{yz}}$	45.2	3.3
	$(N^{\wedge}N)_mCu(O_2)$		
Ground state (^{1}A')	$\pi^2_{\pi^*_z+d_{yz}}\delta^2_{\pi^*_x+d_{xy}}d^2_{y^2-z^2}d^2_{x^2}d^2_{xz}\delta^{*2}_{d_{xy}-\pi^*_x}\pi^{*0}_{\pi^*_z-d_{yz}}$	54.1	0.0
First excited state (^{1}A")	$\pi^2_{\pi^*_z+d_{yz}}\delta^1_{\pi^*_x+d_{xy}}d^2_{y^2-z^2}d^2_{x^2}d^2_{xz}\delta^{*2}_{d_{xy}-\pi^*_x}\pi^{*1}_{\pi^*_z-d_{yz}}$	54.6	14.4
	$(N^{\wedge}N)_mCo(O_2)$		
Ground state (^{3}A')	$\pi^2_{\pi^*_z+d_{yz}}\delta^2_{\pi^*_x+d_{xy}}d^2_{y^2-z^2}d^2_{x^2}d^1_{xz}\delta^{*1}_{d_{xy}-\pi^*_x}\pi^{*0}_{\pi^*_z-d_{yz}}$	66.6	0.0
First excited state (^{3}A")	$\pi^2_{\pi^*_z+d_{yz}}\delta^2_{\pi^*_x+d_{xy}}d^2_{y^2-z^2}d^1_{x^2}d^1_{xz}\delta^{*2}_{d_{xy}-\pi^*_x}\pi^{*0}_{\pi^*_z-d_{yz}}$	30.9	4.0
	$(Me_3P)_2Ni(O_2)$		
Ground state (^{1}A')	$\pi^2_{\pi^*_z+d_{yz}}\delta^2_{\pi^*_x+d_{xy}}d^2_{y^2-z^2}d^2_{x^2}d^2_{xz}\delta^{*2}_{d_{xy}-\pi^*_x}\pi^{*0}_{\pi^*_z-d_{yz}}$	64.5	0.0
First excited state (^{1}A")	$\pi^2_{\pi^*_z+d_{yz}}\delta^1_{\pi^*_x+d_{xy}}d^2_{y^2-z^2}d^2_{x^2}d^2_{xz}\delta^{*2}_{d_{xy}-\pi^*_x}\pi^{*1}_{\pi^*_z-d_{yz}}$	55.9	19.1

gap in $(N^{\wedge}N)_mCu(O_2)$, $(N^{\wedge}N)_mCo(O_2)$, and $(Me_3P)_2Ni(O_2)$ are 14.4, 4.0, and 19.1 kcal·mol^{-1}, respectively, which are larger than in $(N^{\wedge}N)_mNi(O_2)$. More important is the symmetry of the electronic state; in $(N^{\wedge}N)_mNi(O_2)$, both of the ground and the first excited states belong to A" irreducible representation under C_S symmetry, while they belong to different irreducible representation in other complexes (Table 1).

The d_{yz} forms a bonding orbital $\pi_{\pi^*_z+d_{yz}}$ and an anti-bonding orbital $\pi_{\pi^*_z-d_{yz}}$ with the O_2 π^*_z orbital; see Scheme 2. Though the d_{yz} is singly occupied in $(N^{\wedge}N)_mNi$, the $\delta_{d_{xy}-\pi^*_x}$ becomes singly occupied in $(N^{\wedge}N)_mNi(O_2)$. The reason is easily understood by Scheme 2. Because the d_{yz} overlaps well with the O_2 π^*_z orbital, its bonding MO becomes more stable in energy than the $\delta_{\pi^*_z+d_{xy}}$ and its anti-bonding MO becomes more unstable than the $\delta_{d_{xy}-\pi^*_x}$. Hence, the $\delta_{d_{xy}-\pi^*_x}$ becomes singly occupied. The presence of one singly occupied $\delta_{d_{xy}-\pi^*_z}$ provides the low-lying first excited state in $(N^{\wedge}N)_mNi(O_2)$, which is responsible for the symmetry lowering. This is one

of the interesting features of (N^N)Ni(O_2).

The O_2 moiety strongly interacts with the metal moiety in the $\pi_{\pi_z^*+d_{yz}}$, as seen in Scheme 2. In the other natural orbitals, the d orbitals of the metal moiety and the □* orbitals of the O_2 moiety are well localized. It is noted that the π_x^* orbital of the O_2 moiety is doubly occupied in all these complexes. Thus, the character of the O_2 moiety is mainly determined by the $\pi_{\pi_z^*+d_{yz}}$. Because the d_{yz} participates in the anti-bonding counterpart $\pi_{\pi_z^*-d_{yz}}$, we evaluated the population of the d_{yz} considering all the natural orbitals. Also, we calculated the electron population ($q_{\pi_z^*}$) of the π_z^* orbital of the O_2 moiety. The $q_{\pi_z^*}$ is found between 0.96 and 1.14. The total d orbital population is about 7 in (N^N)$_m$Co(O_2), 8 in the Ni analogue, 9 in the Cu analogue, and 9 in (Me_3P)$_2$Ni(O_2).



Scheme 2. The interactions between metal orbitals (d_{yz} and d_{xy}) and O_2 π*orbitals (π_x^* and π_z^*) in

One of the important factors to determine which is correct understanding, peroxo or superoxo, is the O-O □-bond order; the □-bond order should be zero for peroxo and 0.5 for superoxo. The □ bond order BO_{O-O} is defined by eq. (1);

$$BO_{O-O} = (q_{\pi_x} + q_{\pi_z} - q_{\pi_x^*} - q_{\pi_z^*})/2 \quad (1)$$

where q_{π_x} is the occupation number of the□π_x orbital. The □ bond order of the O_2 moiety is evaluated to be 0.38 to 0.50. Based on these results, it is likely concluded that these complexes exhibit a considerable superoxo nature rather than a peroxo nature from the viewpoint of electron distribution.

Here, all four complexes exhibit considerable superoxo nature in the O_2 moiety, but the M-O bond and O-O distance are considerably different among them. The M-O bond length becomes shorter in the order (N^N)$_m$Cu(O_2) > (N^N)$_m$Ni(O_2) > (Me_3P)$_2$Ni(O_2) > (N^N)$_m$Co(O_2).

In these dioxygen complexes, the charge transfer mainly occurs from the d_{yz} to the π_z^* orbital of the O_2 moiety via the π-type interaction (Scheme 2). One can expect that the M-O_2 bonding interaction becomes stronger and the R_{M-O} becomes shorter, as the CT from the metal

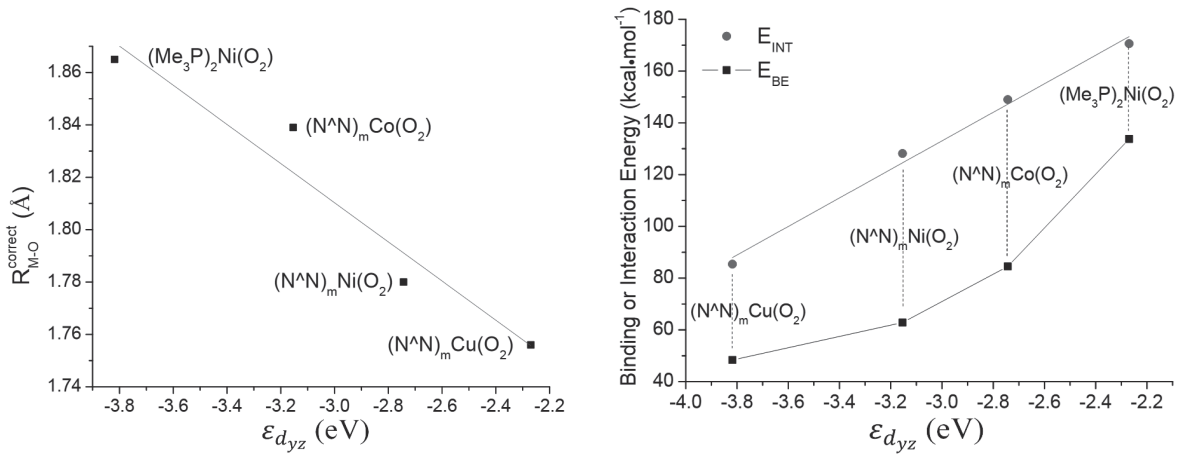
d orbital to the O_2 π_z^* increases. The CT strength is determined by the d_{yz} orbital energy ($\varepsilon_{d_{yz}}$) in the valence state. We employed another parameter to take the difference in ionic radius into account, as shown in eq (2).

$$R_{M-O}^{correct} = R_{M-O} - \Delta R_{M^{n+}} \qquad (2)$$

where R_{M-O} is the M-O bond length in the complex and $\Delta R_{M^{n+}}$ is the difference of ionic radius of M^{n+} from that of Ni^{2+}, as defined by eq (3).

$$\Delta R_{M^{n+}} = R_{M^{n+}} - R_{Ni^{2+}} \qquad (3)$$

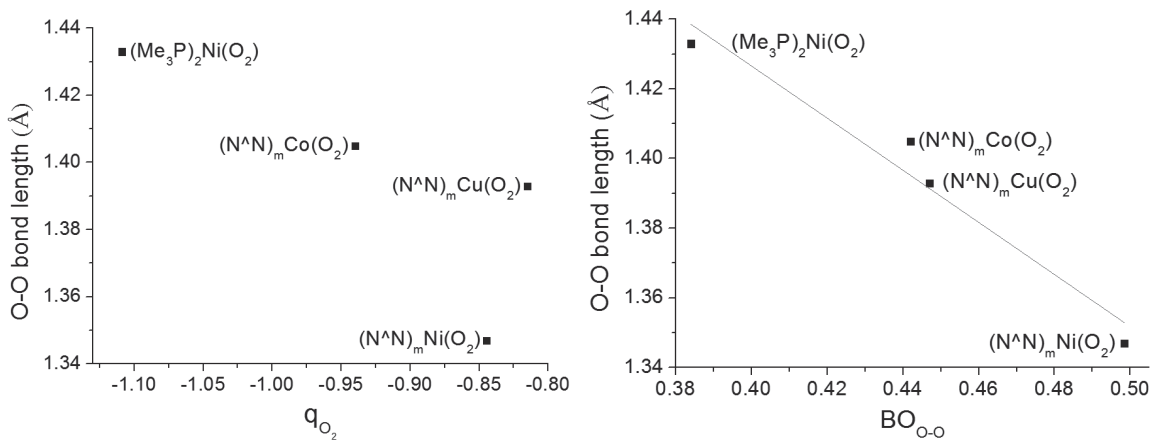
where "n+" is the oxidation state. We found a good linear relationship between the $\varepsilon_{d_{yz}}$ and the $R_{M-O}^{correct}$, as shown in Figure 1A. Also, we examined the relationship between the $\varepsilon_{d_{yz}}$ and the binding energy (E_{BE}). As expected, the calculated ΔE_{INT} value linearly increases as the $\varepsilon_{d_{yz}}$ increases; see the red line in Figure 1B. The parabolic-like relation between the $\varepsilon_{d_{yz}}$ and the E_{BE} (black line in Figure 1B) can be understood with the d_{yz} orbital energy in the valence state and the promotion energy of the metal moiety to the valence state.



(A) (B)

Figure 1. The correlations of (A) $R_{M-O}^{correct}$ vs. $\varepsilon_{d_{yz}}$ and (B) E_{BE} and E_{INT} vs. $\varepsilon_{d_{yz}}$.

One can expect that the O-O distance depends on the electron population of the O_2 moiety (q_{O_2}), because the O-O distance becomes longer as the electron population increases in the π_x^* and π_z^* orbitals. However, this relationship is not successful, as shown in Figure 2A. Because of the presence of various CTs, the electron population of the O_2 moiety is not a good index for the O-O bond distance. For instance, the CT from the metal d_{yz} to the O_2 π_z^* increases both the q_{O_2} value and the O-O distance, as expected. However, the O_2 moiety has a $\pi_x^{*2}\pi_z^0$ conifiguration in the valence state. This means that the CT can occur from the O_2 π_x^* to the M d_{xy} when the d_{xy} is not doubly occupied. This CT decreases the q_{O_2} value and decreases the O-O distance. When the d_{xz} is



(A) (B)

Figure 2. The correlations of the O-O bond length vs. (A) Mulliken charge of O_2, and (B) O-O bond order BO_{O-O}.

unoccupied or singly occupied, the CT occurs from the O_2 π_x to the d_{xz}. Such CT decreases the q_{O_2} but increases the O-O distance, because the electron population decreases in the bonding MO. Finally, we employed the O-O □ bond order (BO_{O-O}), which is defined above. Apparently, a good relationship is presented between the BO_{O-O} and the O-O bond distance, as shown in Figure 2B.

2. Original papers

(1) Yue Chen, Shigeyoshi Sakaki
"Theoretical Study of Mononuclear Nickel(I), Nickel(0), Copper(I), and Cobalt(I) Dioxygen Complexes: New Insight into Differences and Similarities in Geometry and Bonding Nature" (submitted).

3. Presentation at academic conferences

(1) Yue Chen, Shigeyoshi Sakaki
"Electronic State and Bonding Nature of Nickel(I)- and Copper(I)- Dioxygen complexes: MS-RASPT2 Study"
10th FIFC Symposium, Fukui Institute for Fundamental Chemistry, Kyoto Unviersity, Nov. 30, 2012

Sayyed Fareed BHASHA
SPR Fellow, Fukui Kenichi Memorial Research Group 2
(From 1 Feb. 2013)

Theoretical study of CO_2 Insertion into Ni(I)-Alkyl and Ni(II)-Alkyl Bonds

The conversion of carbon dioxide (CO_2) to useful chemicals is one of the most escalating areas of research. Aryl halide is one of the best substrates for the synthesis of carboxylic acid from CO_2. However, a direct CO_2 insertion into aryl halide bond is not easy. In this context, the recently reported Ni-catalyzed direct carboxylation of $PhCH_2Cl$ with CO_2 is considered efficient CO_2 transformation reaction, where $Ni(PCp_3)_2$ (Cp = cyclopentyl) is employed as a catalyst. Experimental results suggest that the Ni(I) species participates in the CO_2 insertion, as shown in Eq. (1), but the evidence has not been provided.

We theoretically investigated this reaction to unravel the reason why Ni(I) species is crucial for this reaction and why Ni(II) is not suitable for the CO_2 insertion; see Eq. (2).

$$(Cp_3P)_2Ni^{I}(CH_2Ph) + CO_2 \rightarrow (Cp_3P)_2Ni^{I}(OOCCH_2Ph) \quad (1)$$

$$(Cp_3P)_2Ni^{II}(CH_2Ph)Cl + CO_2 \rightarrow (Cp_3P)_2Ni^{II}(OCOCH_2Ph)Cl \quad (2)$$

All geometries were optimized with the dispersion corrected B3LYP-D functional with BS-I basis set system. In BS-I, Lanl2Tz(f) basis set for Ni, 6-31G(d) for H, C, O, P, and 6-31+G(d) for Cl were employed. The solvent effect of *N*,*N*-dimethylformamide (DMF) was estimated by conductor-like polarizable continuum model (CPCM). A better basis system (BS-II) was used for evaluation of solvent effect. In BS-II, we employed Lanl2Tz(f) basis set for Ni, cc-pVDZ for H, C, O, P, and aug-cc-pVDZ for Cl. The reliability of the B3LYP-D functional is verified here with the oxidative addition to a model complex $Ni(PH_3)_2$; $Ni(PH_3)_2 + PhCH_2Cl \rightarrow Ni(PhCH_2)(Cl)(PH_3)_2$. The calculated activation energy agrees well with that of CCSD(T).

Geometry and energy changes for the CO_2 insertion into the Ni(I)-CH_2Ph bond of $(Cp_3P)_2Ni^{I}(CH_2Ph)$ are shown in Figure 1. First, CO_2 coordinates to the Ni(I) centre to form η^2-coordinated CO_2 complex **2**, from which CO_2 insertion occurs to afford a carboxylate complex **3** through a four-member transition state $\mathbf{TS_{2\text{-}3}}$ with an activation barrier of 6.6 kcal/mol. Complex **3** isomerises to the most stable η^2-coordinated carboxylate complex $(Cp_3P)_2Ni^{I}(\eta^2\text{-}O_2CCH_2Ph)$ **4**. The CO_2 insertion into the Ni(II)-CH_2Ph of $(Cp_3P)_2Ni^{II}(CH_2Ph)Cl$ **5** occurs through a four-member transition state without the formation of a Ni(II)-CO_2 complex, as shown in Figure 2. The

activation barrier is 38.8 kcal/mol, which is substantially larger than that into the Ni(I)-CH_2Ph bond. These results indicate that the Ni(II)-CH_2Ph is not reactive for CO_2 insertion but the Ni(I)-CH_2Ph is reactive.

We investigated the reasons from the bond energy and the interaction in the transition state. By the CO_2 insertion reaction, the Ni-C bond is broken and the Ni-OCOR bond (R=CH_2Ph)

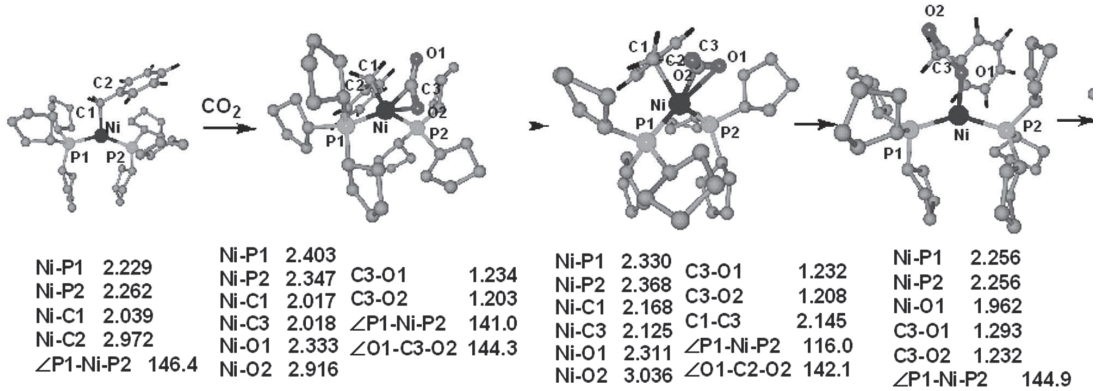


Figure 1. Geometry and energy changes in the CO_2 insertion of Ni(I)-CH_2Ph bond of $(Cp_3P)_2Ni^I(CH_2Ph)$. Gibss free energies are provided in parenthesis. All the bond lengths are in angstroms and angles are in degrees.

is formed. The Ni(I)-CH_2Ph bond is calculated to be stronger (42.5 kcal/mol) than the Ni(II)-CH_2Ph bond (32.1 kcal/mol) but the Ni(I)-OCOR bond (103.3 kcal/mol) is much stronger than the Ni(II)-OCOR bond (79.7 kcal/mol). NBO population analysis of $\mathbf{TS_{2\text{-}3}}$ and $\mathbf{TS_{5\text{-}6}}$ suggest that charge transfer (CT) from the Ni(I)-benzyl moiety to CO_2 much more strongly occurs than that from the Ni(II)-benzyl. The is because the benzyl group is more negatively charged in the Ni(I)-benzyl complex than in the Ni(II)-benzyl group.

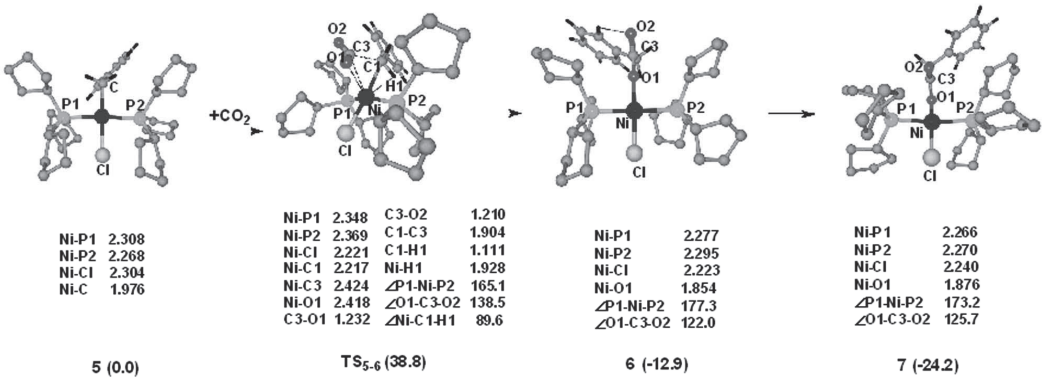


Figure 2. Geometry and energy changes in the CO_2 insertion of Ni(II)-CH_2Ph bond of $(Cp_3P)_2Ni^{II}(CH_2Ph)(Cl)$. Gibss free energies are provided in parenthesis. All the bond lengths are in angstroms and angles are in degrees.

Thus, it is concluded that the CO_2 insertion into Ni(I)-alkyl bond is thermodynamically and kinetically favourable.

松井　亨

日本学術振興会 特別研究員(大阪大学) 訪問研究員（2012 年 12 月 31 日まで）

1. 今年度の研究の要約

今年度は酸化還元電位の算出に関する計算スキームの開発を行った。

1.1 標準水素電極ポテンシャルと酸化還元電位の算出

【序】物質の酸化還元反応は分子内の電子のやり取りによって生じる。この反応の起こりやすさは分子に固有な酸化還元電位によって定量化され、物質のみならず生体内においても非常に重要な役割を担うことが多い。しかし、酸化還元電位は絶対値の測定が不可能であるため、基準となる電極(標準水素電極(SHE)ポテンシャル)を用いた相対値で測定されている。量子化学計算を用いて酸化還元電位を算出するには、後で示すように酸化状態と還元状態のギブスエネルギーを計算して SHE ポテンシャルを引くこととなる。だが、これまでの計算ではプロトンのギブスエネルギーに関する情報がなく、実験値として報告されている 4.44 V を計算手法に関わらず採用していたため、酸化還元電位の計算において大きな誤差が生じていた。本発表では、新しく SHE ポテンシャルを計算手法に依存する形で求める方法を提案し、生体内での電子移動に用いられる小分子(ビタミン c 等)から NADH, ユビキノン, 核酸塩基まで様々な大きさの分子における酸化還元電位の計算へ応用することを目的とする。

【方法】SHE ポテンシャル(E_{SHE})は、気相中の水素分子のギブスエネルギーとプロトンのギブスエネルギーの 2 つにより計算できる。ここで、F はファラデー定数である。

$$E_{SHE}=\{G(H^+, aq)-1/2G(H_2, gas)\}/F. \quad (1)$$

(1)式により SHE ポテンシャルが求まると、酸化還元電位(E_{redox})は反応に寄与する電子数 n とギブスエネルギーΔG_{redox} を用いて次式により導出できる。

$$E_{redox}= \Delta G_{redox}/nF - E_{SHE}. \quad (2)$$

ただ、量子化学計算により水中でのプロトンのギブスエネルギーを導出することはできない。それに対して本研究においては、数種類のアルコールの pK_a 値(実験値)と各分子における脱プロトン化に必要なギブスエネルギー(計算値)をプロットして線形近似を用いて、近似した直線の切片から水中でのプロトンのギブスエネルギーを導出する方法[1]を採用した。本研究では溶媒モデル(C-PCM)を用いて、量子化学で頻繁に用いられる B3LYP 法を中心として計算を行った。また、比較のために高精度に自由エネルギーを算出する Gaussian-3 B3LYP (G3B3)法や HF, MP2 での基底関数極限を外挿的に求め、CCSD(T)などの高精度な計算手法によって補正する手法を採用した。

【結果】pK_a 値(実験値)と計算の脱プロトンエネルギーの相関を図 1 に示す。図にあるように、アルコール分子においては線形関係にあることが分かった。Gaussian-3(G3)法で-265.5 kcal/mol と文献値(-265.9 kcal/mol)に極めて近い結果が得られた。

SHE ポテンシャルは、計算手法によって大きく変化するが、高精度な計算では実験値として採用されている 4.44 V に極めて近い値を算出している。一方で、HF では 3.83 V と実験値よりも 0.6 V 程度低い値を出しているが、これは $G(H_2)$が電子相関の欠如のために低く見積もられているためである。MP2 においても TZ から QZ に増やしたが、若干 E_{SHE} が大きく評価されたために、補外された CBS-limit では少し過大評価されてしまう。CCSD(FE, T)/aDZ の計算を行った所、frozen core での結果とそこまで大きな変化はなかった。そのため、今回は Frozen core と Full electron で大きな差はないと思われる。一方で、CCSD(T, full)/aTZ の計算を実行すると E_{SHE} が 4.48 V となって改善され global standard な SHE potential に近づく。その時の G(H+, aq)が-265.41 kcal/mol となり、それから得られるプロトンの水に対する溶媒和エネルギーが-259.13 kcal/mol と得られた。

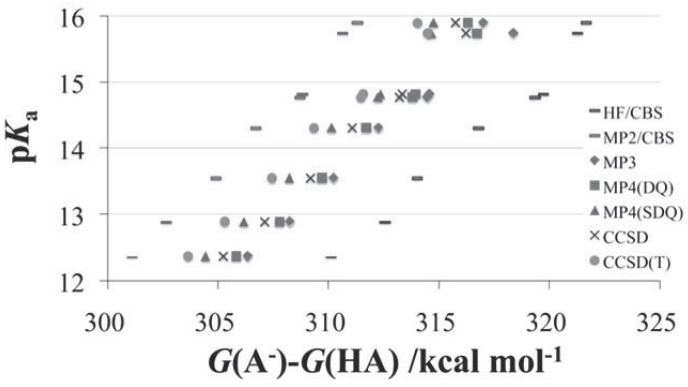


図 1: HF, post HF 法による脱プロトン化エネルギーの計算値と実験による pK_a 値の相関

これを利用して、小分子における 8 種類の酸化還元反応電位の実験値との平均誤差は表 1 のようになった。SHE ポテンシャルを調整しなければ、B3LYP や HF においては大きな誤差が生じている。一方で、CCSD(T)や G3B3 などでは平均誤差が 0.1V 程度とこの時点でも正確な値が出ている。ここで、得られた SHE ポテンシャルを適用すると B3LYP での平均誤差は 0.08 V となり、CCSD(T)などの高精度な計算と同程度の誤差に収まることが分かった。また、HF においても誤差は大幅に減っていることから、HF や DFT を用いて酸化還元電位を算出する場合、SHE ポテンシャルの補正が不可欠となることがこの結果からも明らかとなった。

表 1: 小分子における酸化還元電位の平均絶対誤差(V)の SHE ポテンシャル調整前後での変化

	調整前	調整後
B3LYP/6-31++G(d,p)	0.26	0.08
HF/CBS-Limit	0.48	0.17
CCSD(T)/aug-cc-pVDZ	0.10	0.08
G3B3	0.09	0.06

現在は、この SHE ポテンシャルを調整した計算スキームを用いて、ビタミン類・核酸塩基の酸化還元電位の算出を行っている。

1. 2 溶媒和モデルでの電荷補正を加えた金属錯体の酸化還元電位計算

遷移金属イオンを含む電子伝達タンパク質は構造や周りの環境に応じて電子伝達の性質、すなわち酸化還元電位を変化させることができる。そのような効果を検証する一つの手法として、量子化学計算に基づいた正確な電位の計算手法の確立が求められている。しかしながら、密度汎関数法を用いた金属錯体の電位計算においては

(1)電位の零点となる標準水素電極(SHE)ポテンシャルの扱い

(2)溶媒和モデルによる大きい価数を持つ錯体の溶媒和エネルギーの算出が難しい

などの困難を伴うことから、これまでに正確な計算は多く報告されてこなかった。そこで本研究では、特に(2)の問題に対してカウンターイオンを擬似的に置き、その溶媒和エネルギーを補正する手法を提案し、実際にヘム系に適用することを目的とする。本研究においては、Generalized-Born の式を基にして(3)式のような近似を提案する。

$$E\mathrm{redox}=1/F(E\mathrm{ox}-E\mathrm{red})-\mathrm{A}\,(1-1/\varepsilon\mathrm{r})\{\,q|q|\,\mathrm{erf}(\mu\mathrm{r}q)\,-\mathrm{B}(q-1)|q-1|\,\mathrm{erf}(\mu\mathrm{r}(q-1))\}/r-E_{\mathrm{SHE}} \qquad (3)$$

ここで、Eox, Eredは酸化状態、還元状態の最適化構造でのエネルギーを、Fはファラデー定数、q は酸化状態の錯体の電荷、εr は測定に用いられた溶媒の誘電率を表す。r は溶媒和モデルにおいて、最初に生成する空洞を球とみなしたときの半径である。また、Aは擬似的に置いたカウンターイオンの半径に対応し、E_{SHE} は先程と同様SHEポテンシャルである。本研究ではこれらのパラメータをテスト分子によりフィッティングして求めることとする。一連の計算はGaussian09 を用い、溶媒和モデルはC-PCM 法、密度汎関数はB3LYP を採用した。

フィッティングの結果、B3LYP/6-31++G(d,p)レベルの計算においては、テストの39 種類の錯体における平均誤差は0.14 V となった。特に酸化状態において+3 価, -3 価と大きな電荷を持つ10 種の錯体においては、一定のSHE ポテンシャルを用いた場合では平均誤差は0.78 V となるのに対して、(3)式を用いた場合は0.16 V まで大幅に減少する。また、この系は一度パラメータを決めた場合、どの金属錯体にも適用が可能となる。M1(bpy)3 (M1=Fe, Ru, Os)やM2(mnt)2 (M2=Ni, Pd,Pt)などの重金属を含む錯体の酸化還元電位も実験値と0.2 V 以下の誤差で算出することに成功した。最後に、ヘムc のモデル錯体で誘電率依存性を算出したところ、1/εr と酸化還元電位に線形関係があり、タンパク質の環境とされるεr =4-20 の間で符号の変化が生じることが分かった。

【参考文献】[1] Matsui, T.; Baba, T.; Kamiya, K.; Shigeta, Y. *Phys. Chem. Chem. Phys.* **2012**, 14, 4181. [2] Matsui, T.; Kitagawa, Y.; Okumura, M.; Shigeta, Y.; Sakaki, S. *J. Comput. Chem.***2013***,* 34*,* 21. [3] Matsui, T.; Kitagawa, Y.; Shigeta, Y.; Okumura, M. *J. Chem. Theory Comput. in press*.

2. 論文

(1) Y. Kitagawa, N. Yasuda, H. Hatake, T. Saito, Y. Kataoka, **T. Matsui**, T. Kawakami, S. Yamanaka, M. Okumura and K. Yamaguchi, “Combination of approximate spin-projection and spin-restricted calculations based on ONIOM method for geometry optimization of large biradical systems”, International Journal of Quantum Chemistry, 113, p.290-295 (2013).

(2) **T. Matsui**, Y. Kitagawa, M. Okumura, Y. Shigeta and S. Sakaki, "Consistent Scheme for Computing Standard Hydrogen Electrode and Redox Potentials", Journal of Computational Chemistry, 34, p. 21-26 (2013).

3. 学会発表

(1) 松井 亨，馬場 剛史，安田 奈都美，神谷 克政，北河 康隆，重田 育照，奥村 光隆
「タンパク質内アミノ酸側鎖の酸解離定数の新規算出法と応用」
第15回 理論化学討論会 仙台　2012/5/25

(2) Toru Matsui, Takeshi Baba, Katsumasa Kamiya, Mitsutaka Okumura, and Yasuteru Shigeta
“Density functional theory based estimation of pK_a value of polar residues: from amino acids to

minimal proteins”
14th International Congress of Quantum Chemistry, Colorado University, 2012/6/26

(3) 松井 亨，北河 康隆，重田 育照，奥村 光隆，榊　茂好
「標準水素電極ポテンシャルと酸化還元電位の算出法」
第6回 分子科学討論会 東京 2012/9/19

(4) 松井 亨，北河 康隆，重田 育照，奥村 光隆，榊　茂好
「標準水素電極ポテンシャルと酸化還元電位の新規算出法」
第23回基礎有機化学討論会 京都 2012/9/19

(5) 松井 亨，北河 康隆，重田 育照，奥村 光隆
「溶媒和モデルを利用した金属錯体の酸化還元電位の算出法と応用」
第93回 日本化学会春季年会、草津 2013/3/25

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（2012 年 6 月 30 日まで）

1. 今年度の研究の要約

ブリッジ経由三重項励起エネルギー移動[1]

【始めに】

光合成系では、直接反応に寄与しない副産物として三重項励起状態が生成されることがあり、この三重項状態を励起エネルギー移動によって輸送し処理する過程の存在が確認されている。また、有機 LED ではその原理上、発行に寄与しない大量の三重項励起状態が生成される。このような三重項励起状態の輸送は三重項ゆえに禁制遷移であり、中間状態をはさんだ二次以上の相互作用によって行われる。本研究では、そのような中間状態として、ブリッジを含む様々な電荷分離状態や励起状態を導入し、それぞれの状態の寄与を調べることで、三重項励起エネルギー移動のしくみを明らかにした。

【方法】

以前一重項励起エネルギー移動について計算した GFPc-ブリッジ-CFPc のモデルシステム[2]（図１）の X=Tyr の構造を用いて、さらに、以前開発したプログラムを三重項励起エネルギー状態に拡張して同様の計算を行った。計算には以前と同様に CIS/D95 を用いており、計算手順も同様に、参照分子として GFPc（両端に CH3 を含む）、CFPc（両端に CH3 を含む）および、X（側鎖及びα炭素を含む）の３つを用いた MOD 法[3]により、それぞれのフラグメントに局在化した分子軌道を作り、残りのペプチド部分を Pipek-Mezey 法で局在化するというハイブリッド局在化法[4]を行いてモデル全域における局在化分子軌道を得ている。分子軌道は GFPc-pep1-X-pep2-CFPc の 5 か所のフラグメントに局在化しており、これらの局在分子軌道から今回は三重項 Slater determinant を基底として、EET トンネル経路を計算した。電子トンネル経路の計算にはグリーン関数法、トンネルエネルギーは CFPc と GFPc のそれぞれの最低三重項状態と基底状態のエネルギー差の平均値を用いた(0.0724au)。

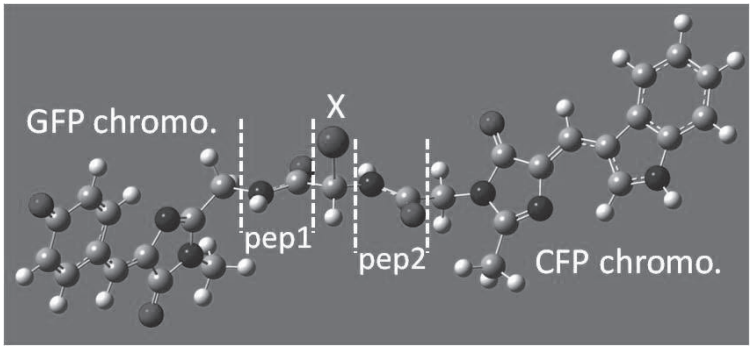

図 1. GFPc-X-CFPc モデル。

【結果】

以前計算した一重項励起エネルギー移動では、フェルスター機構に基づく双極子共鳴相互作用の直接項が主体であり、ブリッジ経由の項についても、同様の双極子共鳴による局在励起状態経由の

トンネル経路が主体となる(図 2 上段)。このような相互作用は長距離力であり、トンネル経路は少ないステップで構成されていた。一方で今回計算した三重項励起エネルギー移動では、上記の双極子相互作用は禁制であり、結果として、より弱く短距離でしか効かない電子移動、ホール移動型の相互作用が主体となった。その結果、ドナー、アクセプター状態間の直接項の寄与は小さいものになり、ブリッジ経由項は図 2 下段に示したような複数ステップの電位移動とそれとカップルしたホール移動の組み合わせによる多段階ステップのトンネル経路を持つことがわかった。

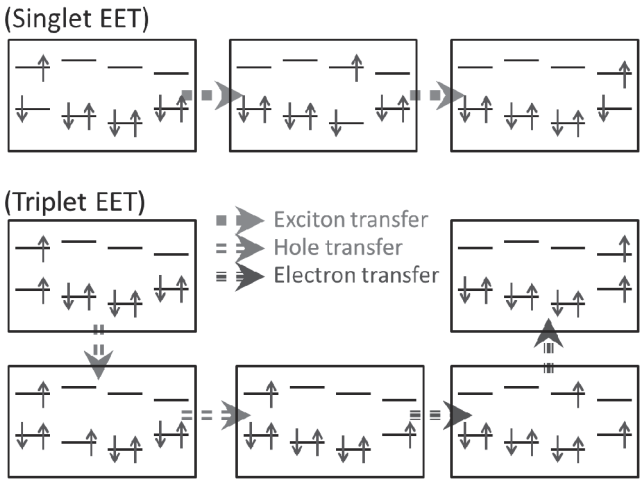

図 2. 一重項および三重項ブリッジ経由励起エネルギー移動トンネル経路模式図

[1] T. Kawatsu, J. Hasegawa, *J. Phys. Chem. C 116* 23252-23256(**2012**).
[2] T. Kawatsu, J. Hasegawa, *Int. J. Quantum Chem. 113*, 563-568(**2013**).
[3] K. Toyota, M. Ehara, H. Nakatsuji, *Chem. Phys. Lett. 356,* 1-6(**2002**).
[4] J. Hasegawa, T. Kawatsu, K. Toyota, K. Matsuda, *Chem. Phys. Lett. 508*, 171-176(**2011**).

2. 論文

(1) Tsutomu Kawatsu, “Review: Pathway analysis for peptide-mediated electronic coupling in the super-exchange mechanism of ET and EET,” Pep. Sci. 100, 100-113(2013).

(2) Tsutomu Kawatsu, and Jun-ya Hasegawa, “Sequentially Coupled Hole-Electron Transfer Pathways for Bridge-Mediated Triplet Excitation Energy Transfer,” J. Phys. Chem. C 116, 23252-23256(2012).

(3) Tsutomu Kawatsu, Jun-ya Hasegawa, and Kenji Matsuda, “Singlet Excitation Energy Transfer Mediated by Local Exciton Bridges,” J. Phys. Chem. C 116, 13865-13876(2012).

3. 学会発表

(1) 河津励、長谷川淳也
「三重項励起エネルギー移動のトンネル経路」
第 15 回理論化学討論会　仙台　2012/5/25　2P14

(2) 長谷川淳也、河津励
「凝集系における分子の励起状態：局在化軌道を用いた分子間相互作用の解析」
第 15 回理論化学討論会　仙台　2012/5/24　1P30

V　資料

1．外国人共同研究者受入れ状況（平成 24 年度）

氏名	受入れ身分	受入れ期間	所属機関・職	受入れ教員	研究内容
Vayssilov Georgi	外国人 共同研究者	平成24年7月21日～ 平成24年8月18日	University of Sofia （ブルガリア）・教授	諸熊奎治	複雑分子系の シミュレーション
Petkov Petko	外国人 共同研究者	平成24年7月23日～ 平成24年8月2日	University of Sofia （ブルガリア）・助手	諸熊奎治	複雑分子系の シミュレーション
Rangelov Miroslav	外国人 共同研究者	平成24年7月23日～ 平成24年8月2日	Bulgarian Academy of Sciences （ブルガリア）・助手	諸熊奎治	複雑分子系の シミュレーション
Predrag Krstic	外国人 共同研究者	平成25年2月17日～ 平成25年3月2日	Oak Ridge National Laboratory （アメリカ）Senior Research Staff Member	諸熊奎治	複雑分子系の シミュレーション

２．海外渡航一覧（平成 24 年度）

職　　名	氏　　名	期間（自）	期間（至）	目　的　地
研究員（学術研究奨励）	諸熊　奎治	2012.5.21	2012.7.1	アメリカ合衆国
准教授	長谷川　淳也	2012.5.29	2012.6.3	カナダ
研究員（学術研究奨励）	KIM CHUNGHAN	2012.6.24	2012.7.2	アメリカ合衆国
准教授	長谷川　淳也	2012.6.25	2012.7.2	アメリカ合衆国
特任准教授	石田　俊正	2012.6.24	2012.7.2	アメリカ合衆国
特定研究員	畑中　美穂	2012.6.24	2012.7.2	アメリカ合衆国
JSPS 外国人特別研究員	PETROVA, Galina	2012.6.24	2012.7.2	アメリカ合衆国
研究員（学術研究奨励）	榊　　茂好	2012.6.25	2012.7.2	アメリカ合衆国
研究員（科学研究）	中垣　雅之	2012.6.25	2012.7.2	アメリカ合衆国
研究員（科学研究）	塚本　晋也	2012.6.24	2012.6.30	アメリカ合衆国
特定研究員	岡本　隆一	2012.6.23	2012.6.30	アメリカ合衆国
助教	池野　豪一	2012.7.22	2012.7.28	中国
特定研究員	岩城　貴史	2012.7.27	2012.8.7	ロシア
研究員（学術研究奨励）	諸熊　奎治	2012.8.4	2012.8.15	中国
研究員（学術研究奨励）	榊　　茂好	2012.8.9	2012.8.12	中国
研究員（学術研究奨励）	諸熊　奎治	2012.8.17	2012.8.25	アメリカ合衆国
教授	田中　一義	2012.9.4	2012.9.8	アメリカ合衆国
研究員（学術研究奨励）	Li, Haibei	2012.9.17	2012.10.1	ドイツ
研究員（学術研究奨励）	諸熊　奎治	2012.9.14	2012.9.22	ロシア
センター長	田中　一義	2012.10.10	2012.10.15	ドイツ連邦共和国
研究員（学術研究奨励）	榊　　茂好	2012.10.2	2012.10.6	フランス
研究員（学術研究奨励）	諸熊　奎治	2012.10.12	2012.10.18	アルジェリア
センター長	田中　一義	2012.11.22	2012.11.26	イギリス
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特定研究員	畑中　美穂	2013.3.5	2013.3.10	フランス
助教	池野　豪一	2013.2.17	2013.2.24	オランダ
特任准教授	石田　俊正	2013.2.24	2013.2.28	台湾
研究員（学術研究奨励）	Bai Fu-Quan	2013.3.1	2013.3.4	中国

３．研究業績一覧（平成 24 年度）

№	Authors	Title	Journal	Volume (Number), first page to last page	year
長谷川　淳也					
1	J. Hasegawa	Fragment-Based Configuration Interaction Wave Function to Calculate Environmental Effect on Excited States in Proteins and Solutions	*Chem. Phys. Lett.*	571, 77–81	2013
2	S. Nishizawa, J. Hasegawa, K. Matsuda	Theoretical Investigation of the β Value of the Phenylene and Phenylene Ethynylene Units by Evaluating Exchange Interaction between Organic Radicals	*Chem. Phys. Lett.*	555, 187–190	2013
3	T. Kawatsu and J. Hasegawa	Excitation Energy Transfer in GFP-X-CFP Model Peptides (X=amino acids): direct vs. through-bridge energy transfers	*Intern. J. Quantum. Chem.*	113(4), 563-568	2013
4	T. Kawatsu and J. Hasegawa	Sequentially Coupled Hole-Electron Transfer Pathways for Bridge-Mediated Triplet Excitation Energy Transfer	*J. Phys. Chem. C*	116(44), 23252–23256	2012
5	J. Hasegawa, K. J. Fujimoto, and T. Kawatsu	A Configuration Interaction Picture for a Molecular Environment Using Localized Molecular Orbitals: The Excited States of Retinal Proteins	*J. Chem. Theo. Comp.*	8(11), 4452-4461	2012
6	T. Kawatsu, K. Matsuda, and J. Hasegawa	Singlet Excitation Energy Transfer Mediated by Local Exciton Bridges	*J. Phys. Chem. C*	116(26), 13865-13876	2012
7	J. Hasegawa, K. Fujimoto, and H. Nakatsuji	Color tuning in human cone visual pigments: the role of the protein environment	*Progress in Theoretical Chemistry and Physics*	26, 89-502	2012
8	T. Sakano, J. Hasegawa, K. Higashiguchi, and K. Matsuda	Chronological Change from Face-On to Edge-On Ordering of Zinc Tetraphenylporphyrin at Phenyloctane-HOPG Interface	*Chem. Asian J.*	7(2), 394-399	2012
9	Y. Yamamoto, J. Hasegawa, and Y. Ito	Kinetic investigation on carbamate formation from the reaction of carbon dioxide with amino acids in homogeneous aqueous solution	*J. Phys. Org. Chem.*	25(3), 239-247	2012
中尾　嘉秀					
10	S. Akatsu, Y. Kanematsu, T. Kurihara, S. Sueyoshi, Y. Arikawa, M. Onishi, S. Ishizaka, N Kitamura, Y. Nakao, S. Sakaki, K. Umakoshi	Syntheses and Luminescent Properties of 3,5-Diphenylpyrazolato-Bridged Heteropolynuclear Platinum Complexes. The Influence of Chloride Ligands on the Emission Energy Revealed by the Systematic Replacement of Chloride Ligands by 3,5-Dimethylpyrazolate	*Inorg. Chem.*	51, 7977-7992	2012
11	Y. Nakajima, S. Sakaki, Y. Nakao, H. Suzuki	Theoretical Study of Dihydrogen Activation by a Trinuclear Ruthenium μ3-Imido Complex	*Organometallics*	31, 5342–5348	2012
12	Y. Hayashi, Y. Matano, K. Suda, Y. Kimura, Y. Nakao, H. Imahori	Effects of Carbon–Metal–Carbon Linkages on the Optical, Photophysical, and Electrochemical Properties of Phosphametallacycle-Linked Coplanar Porphyrin Dimers	*Chem. Eur. J.*	18, 15972-15983	2012

№	Authors	Title	Journal	Volume (Number), first page to last page	year
石田　俊正					
13	Wilfredo Credo Chung, Shinkoh Nanbu, and Toshimasa Ishida	A QM/MM Trajectory Surface Hopping Approach to Photoisomerization of Rhodopsin and Isorhodopsin. The Origin of Faster and More Efficient Isomerization for Rhodopsin	*J. Phys. Chem. B*	116, 8009−8023	2012
14	Tatsuhiro Murakami, Manabu Nakazono, Alexey Kondorskiy, Toshimasa Ishida and Shinkoh Nanbu	Photochemical dynamics of indolylmaleimide derivatives	*Phys. Chem. Chem. Phys.*	14, 11546–11555	2012
15	Toshimasa Ishida and Shigetoshi Aono	A model theoretical study on ligand exchange reactions of CooA	*Phys. Chem. Chem. Phys.*	15, 6139-6148	2013
16	Jun-ichi Aihara, Masakazu Makino, Toshimasa Ishida, and Jerry R. Dias	Analytical Study of Superaromaticity in Cycloarenes and Related Coronoid Hydrocarbons	*J. Phys. Chem. A*	in press	2013
池野　豪一					
17	Thomas Höche, and Hidekazu Ikeno, Marisa Mäder, Grant S. Henderson, and Robert I.R. Blyth, Brian C. Sales, and Isao Tanaka	Vanadium $L_{2,3}$ XANES experiments and first-principles multielectron calculations: Impact of second-nearest neighboring cations on vanadium-bearing fresnoites	*Am. Mineral.*	98, 665-670	2013
18	Hidekazu Ikeno, Michael Krause, Thomas Hoöhe, Christian Patzig, Yongfeng Hu, Antje Gawronski, Isao Tanaka and Christian Rüssel	Variation of Zr-$L_{2,3}$ XANES in tetravalent zirconium oxides	*J. Phys.: Condens. Matter*	25, art. no. 165505	2013
永瀬　茂					
19	H. Zheng, X. Zhao, W. -W. Wang, T. Yang, and S. Nagase	$Sc_2@C_{70}$ Rather Than $Sc_2C_2@C_{68}$: Density Functional Theory Characterization of Metallofullerene Sc_2C_{70}	*J. Chem. Phys.*	137, 014308 (5 pages)	2012
20	S. Sato, S. Seki, G. Luo, M. Suzuki, J. Lu, S. Nagase, and T. Akasaka	Tunable Charge-Transport Properties of I_h-C_{80} Endohedral Metallofullerenes: Investigation of $La_2@C_{80}$, $Sc_3N@C_{80}$, and $Sc_3C_2@C_{80}$	*J. Am. Chem. Soc.*	134,11681-11686	2012
21	L. Feng, M. Rudolf, S. Wolfrum, A. Troeger, Z. Slanina, T. Akasaka, S. Nagase, N. Martin, T. Ameri, C. J. Brabec, and D. M. Guldi	A Paradigmatic Change: Linking Fullerenes to Electron Acceptors	*J. Am. Chem. Soc.*	134, 12190-12197	2012
22	W. -W. Wang, J. -S. Dang, J. -J. Zheng, X. Zhao, E. Osawa, and S. Nagase	Metal-Promoted Restoration of Defective Graphene	*J. Mater. Chem.*	22, 16370-16375	2012
23	J. -S. Dang, W. -W. Wang, J. -J. Zheng, X. Zhao, E. Osawa, and S. Nagase,	Fullerene Genetic Code: Inheritable Stability and Regioselective C_2 Assembly	*J. Phys. Chem. C*	116, 16233-16239	2012
24	K. Sato, M. Kako, M. Suzuki, N. Mizorogi, T. Tsuchiya, M. M. Olmstead, A. L. Balch, T. Akasaka, and S. Nagase	Synthesis of Silylene-Bridged Endohedral Metallofullerene $Lu_3N@I_h$-C_{80}	*J. Am. Chem. Soc.*	134,16033-16039	2012
25	Y. Takano, S. Obuchi, N. Mizorogi, R. Carcia, M. A. Herranz, M. Rudolf, S. Wolfrum, D. M. Guldi, N. Martin, S. Nagase, and T. Akasaka	Stabilizing Ion and Radical Ion Pairs States in a Paramagnetic Endohedral Metallofullerene/π-Extended Tetrathiafulvalene Conjugate	*J. Am. Chem. Soc.*	134, 16103-16106	2012

№	Authors	Title	Journal	Volume (Number), first page to last page	year
26	T. Yang, X. Zhao, and S. Nagase	Structural Determination on Yb@C_{78} Reveals an Unexpected Relationship of Yb@C_{2n} (2n = 74-78)	*J. Phys. Chem. C*	116, 21640-21645	2012
27	T. Yang, X. Zhao, S. -T. Li, and S. Nagase	Is the Isolated Pentagon Rule Always Satisfied for Metallic Carbide Endohedral Fullerenes?	*Inorg. Chem.*	51, 11223-11225	2012
28	Z. Slanina, F. Uhlik, S. -L. Lee, L. Adamowicz, T. Akasaka, and S. Nagase	Stability Computations for Isomers of La@C_n (n = 72, 74, 76)	*Molecules*	17, 13146-13156	2012
29	M. Suzuki, Z. Slanina, N. Mizorogi, X. Lu, S. Nagase, M. M. Olmstead, A. L. Balch, and T. Akasaka,	Single-Crystal X-ray Diffraction Study of Three Yb@C82 Isomers Cocrystallized with NiII (octaethylporphyrin)	*J. Am. Chem. Soc.*	134, 18772-1877	2012
30	Y. Takano, S. Obuchi, N. Mizorogi, R. Garcia, M. A. Herranz, M. Rudolf, D. M. Guldi, N. Martin, S. Nagase, and T. Akasaka	An Endohedral Metallofullerene as a Pure Electron Donor: Intramolecular Electron Transfer in Donor-Acceptor Conjugates of La_2@C_{80} and 11,11,12,12-Tetracyano-9,10-anthra-p-quinodimethane (TCAQ)	*J. Am. Chem. Soc.*	134, 19401-19408	2012
31	T. Tanikawa, M. Saito, J. -D. Guo, S. Nagase, and M. MinouraSynthesis, Structures, and Optical Properties of Heterasumanenes Containing Group 14 Elements and Their Related Compounds	Synthesis, Structures, and Optical Properties of Heterasumanenes Containing Group 14 Elements and Their Related Compounds	*Eur. J. Org. Chem.*	7135-7142	2012
32	K. Sato, M. Kako, N. Mizorogi, T. Tsuchiya, T. Akasaka, and S. Nagase	Bis-Silylation of Lu_3N@I_h-C_{80}: Considerable Variation in the Electronic Structures	*Org. Lett.*	14, 5908-5911	2012
33	X. Lu, L. Feng, T. Akasaka, and S. Nagase	Current Statues and Future Developments of Endohedral Metallofullerenes	*Chem. Soc. Rev.*	41, 7723-7760	2012
34	N. Kano, N. Yoshinari, Y. Shibata, M. Miyachi, T. Kawashima, M. Enomoto, A. Okazawa, N. Kojima, J. -D. Guo, and S. Nagase	Anionic Iron Complexes with a Bond between an Ate-Type Pentacoordinated Germanium and an Iron Atom	*Organometalic*	21, 8059-8062	2012
35	T. Tsuchiya, M. Rudolf, S. Wolfrum, S. G. Radhakrishnan, R. Aoyama, Y. Yokosawa, A. Oshima, T. Akasaka, S. Nagase, and D. M. Guldi,	Coordinative Interactions between Porphyrins and C_{60}, La@C_{82}, and La_2@C_{80}	*Chem. -Eur.*	19, 558-565	2013
36	L. Feng, M. Suzuki, N. Mizorogi, X. Lu, M. Yamada, T. Akasaka, and S. Nagase	Mapping the Metal Positions inside Spherical C_{80} Cages: Crystallographic and Theoretical Studies of Ce_2@D_{5h}-C_{80} and Ce_2@I_h-C_{80}	*Chem. -Eur. J*	19, 988-993	2013
37	W. -W. Wang, J. -S. Dang, J. -J. Zheng, X. Zhao, and S. Nagase	Selective Growth of Fullerenes from C_{60} to C_{70}: Inherent Geometrical Connectivity Hidden in Discrete Experimental Evidence	*J. Phys. Chem. C*	117, 2349-2357	2013
38	T. Yang, X. Zhao, and S. Nagase	Quantum Chemical Insight of the Dimetallic Sulfide Endohedral Fullerene Sc_2S@C_{70}: Does It Possess the Conventional D_{5h} Cage?	*Chem. Eur.*	19, 2649-2654	2013
39	M. Yamada, Z. Slanina, N. Mizorogi, A. Muranaka, Y. Maeda, S. Nagase, T. Akasaka, and N. Kobayashi	Application of MCD Spectroscopy and TD-DFT to Endohedral Metallofullerenes for Characterization of their Electronic Transitions	*Phys. Chem. Chem. Phys.*	15, 3593-3601	2013

№	Authors	Title	Journal	Volume (Number), first page to last page	year
40	V. Y. Lee, S. Aoki, T. Yokoyama, S. Horiguchi, A. Sekiguchi, H. Gornitzka, J. –D. Guo, and S. Nagase	Toward a Silicon Version of Metathesis: From Schrock-Type Titanium Silylidenes to Silatitanacyclobutenes	*J. Am. Chem. Soc.*	135, 2987-2990	2013
41	Y. Morinaka, S. Sato, A. Wakamiya, H. Nikawa, N. Mizorogi, F. Tanabe, M. Murata, K. Komatsu, K. Furukawa, T. Kato, S. Nagase	X-Ray Observation of a Helium Atom and Placing a Nitrogen Atom inside He@C_{60} and He@C_{70}	*Nat. Commun.*	4, 1554 (5 pages)	2013
42	T. Kuwabara, M. Saito, J. –D. Guo, and S. Nagase	Unexpected Formation of Ru_2Sn_2 Bicyclic Four-Membered Ring Complexes with Butterfly and Inverse-Sandwich Structures	*Inorg. Chem.*	52, 3585-3587	2013
43	S. Sato, Y. Maeda, J. –D. Guo, M. Yamada, N. Mizorogi, S. Nagase, and T. Akasaka	Mechanistic Study of the Diels-Alder Reaction of Paramagnetic Endohedral Metallofullerene: Reaction of La@C_{82} with 1,2,3,4,5-Pentamethylcyclopentadiene	*J. Am. Chem. Soc.*	135, 5582-5587	2013
44	Y. –P. Xie, X. Lu, T. Akasaka, and S. Nagase	New Features in Coordination Chemistry: Valuable Hints from X-Ray Analyses of Endohedral Metallofullerenes	*Polyhedron*	52, 3-9	2013
45	S. Nagase	Multiple Bonds between Lead Atoms and Short Bonds between Transition Metals	*Pure Appl. Chem.*	85, 649-659	2013
諸熊　奎治					
46	P. S. Krstic, J. P. Allain, C. N. Taylor, J. Dadras, S. Maeda, K. Morokuma, J. Jakowski, A. Allouche, and C. H. Skinner	Deuterium Uptake in Magnetic Fusion Devices with Lithium Conditioned Carbon Walls	*Phys. Rev. Lett.*	110, 105001/1-5	2013
47	B. Fu, J. M. Bowman, H. Xiao, S. Maeda, and K. Morokuma	Quassiclassical Trajectory Studies of the Photodissociation Dynamics of NO_3 from the D0 and D1 Potential Energy Surfaces	*J. Chem. Theo. Comp.*	9, 893–900	2013
48	K. R. S. Chandrakumar, A. J. Page, S. Irle and K. Morokuma	Carbon Coating Precedes SWCNT Nucleation on Silicon Nanoparticles: Insights from QM/MD Simulations	*J. Phys. Chem. C*	117, 4238–4244	2013
49	S. Maeda, K. Ohno and K, Morokuma	Systematic Exploration of the Mechanism of Chemical Reactions: the Global Reaction Route Mapping (GRRM) Strategy by the ADDF and AFIR Methods	*Phys. Chem. Chem. Phys.*	15, 3683-3701	2013
50	A. J. Page, C.-P. Chou, B. Q. Pham, H. Witek, S. Irle and K. Morokuma	Quantum Chemical Investigation of Epoxide and Ether Groups in Graphene Oxide and Their Vibrational Spectra	*Phys. Chem. Chem. Phys.*	15, 3725-3735	2013
51	L. Ding, L. W. Chung, K. Morokuma	Reaction Mechanism of Photo-induced Decarboxylation of the Photoactivatable Green Fluorescent Protein: An ONIOM(QM:MM) Study.	*J. Phys. Chem. B*	117, 1075-84	2013
52	K. R. S. Chandrakum ar, A. Puretzky, C. Rouleau, J. D. Readle, D. B. Geohegan, K. More, V. Krishnan, G. Duscher, B. Sumpter, S. Irle, and K. Morokuma	High-Temperature Transformation of Fe-Decorated Single-Wall Carbon Nanohorns to Nanooysters: A Combined Experimental and Theoretical Study,	*Nanoscale*	5, 1849–1857	2013
53	S. Maeda, E. Abe, M. Hatanaka, T. Taketsugu, and K. Morokuma	Exploring Potential Energy Surfaces of Large Systems with Artificial Force Induced Reaction in Combination with ONIOM and Microiteration	*J. Chem. Theo. Comp.*	5, 5058–5063	2012

№	Authors	Title	Journal	Volume (Number), first page to last page	year
54	A. J. Page, T. Isomoto, J. Knaup, S. Irle, and K. Morokuma	Effects of Molecular Dynamics Thermostats on Descriptions of Chemical Non-Equilibrium	*J. Chem. Theo. Comp.*	8, 4019–4028	2012
55	A. Y. Timoshkin, and K. Morokuma	Novel group 13 Lewis superacids and 13-15 donor-acceptor cryptands for hydrogen activation: a theoretical study	*Phys. Chem. Chem. Phys.*	14, 14911-14916	2012
56	H.-B. Li, A. J. Page, S. Irle, and K. Morokuma	SWCNT Growth from Chiral Carbon Nanorings: Prediction of Chirality and Diameter Influence on Growth Rates	*J. Am. Chem. Soc.*	134, 15887–15896	2012
57	P. S. Krstic, J. P. Allai, A. Allouched, J, Jakowski, J. Dadras, C. N. Taylor, Z. Yang, K. Morokuma, and S. Maeda	Dynamics of deuterium retention and sputtering of Li–C–O surfaces	*Fusion Eng, Design*	87, 1732-1736	2012
58	Z. Ke, S. Abe, T. Ueno, and K. Morokuma	Catalytic Mechanism in Artificial Metalloenzyme: QM/MM Study of Phenylacetylene Polymerization by Rhodium Complex Encapsulated in *apo*-Ferritin	*J. Am. Chem. Soc.*	134, 15418–15429	2012
59	H. Xiao, S. Maeda and K. Morokuma	Global Ab Initio Potential Energy Surfaces for Low-lying Doublet States of NO_3	*J. Chem. Theo. Comp.*	8, 2600–2605	2012
60	S. Sekharan, K. Katayama, H. Kandori and K. Morokuma	The “OH-Site” Rule for Seeing Red and Green	*J. Am. Chem. Soc.*	134, 10706–10712	2012
61	W. Treesuwan, H. Hirao, K. Morokuma, and S. Hannongbua	Characteristic vibration patterns and protein binding of odor compounds from bread baking volatiles: Density functional, ONIOM study and principal component analysis (PCA)	*J. Mol. Model.*	18, 2227–2240	2012
62	Y. Wang, H.-J. Qian, K. Morokuma, and S. Irle	Coupled Cluster and Density Functional Theory Calculations of Atomic Hydrogen Chemisorption on Pyrene and Coronene as Model Systems for Graphene Hydrogenation	*J. Phys. Chem. A*	116, 7154–7160	2012
63	K. P. O’Halloran, C. Zhao, N. S. Ando, A. J. Schultz, T. F. Koetzle, P. M. B. Piccoli, B.Hedman, K. O. Hodgson, E. Bobyr, M. L. Kirk, S. Knottenbelt, E. C. Depperman, B. Stein, T. M. Anderson, R. Cao, Y. V. Geletii, K. I. Hardcastle, D. G. Musaev, W. A. Neiwert, X. Fang, K. Morokuma, S. Wu, P. Kögerler and C. L. Hill	Revisiting the Polyoxometalate-Based Late-Transition-Metal-Oxo Complexes: The “Oxo Wall” Stands	*Inorg. Chem.*	51, 7025–7031	2012
64	S. Maeda, T. Taketsugu and K. Morokuma	Automated Exploration of Photolytic Channels of HCOOH: Conformational Memory via Excited State Roaming	*J. Phys. Chem. Lett.*	3, 1900-1907	2012
65	H.-B. Li, A. J. Page, Y. Wang, S. Irle, and K. Morokuma	Sub-Surface Nucleation of Graphene Precursers near a Ni(111) Step Edge	*Chem. Comm.*	48, 7937-7939	2012
66	J. Kim, A. J. Page, S. Irle, and K. Morokuma	The Dynamics of Local Chirality during SWCNT Growth: Armchair versus Zigzag Nanotubes	*J. Am. Chem. Soc.*	134, 9311–9319	2012
67	Jakowski, S. Irle,. B. Sumpter, and K. Morokuma	Modeling charge transfer in fullerene collisions via real time electron dynamics simulations	*J. Phys. Chem. Lett.*	3, 1536–1542	2012
68	M. A. Addicoat, A. J. Page, Z. E. Brain, L. Flack, K. Morokuma and S. Irle	Optimization of a Genetic Algorithm for the Functionalization of Fullerenes	*J. Chem. Theo. Comp.*	8, 1841−1851	2012

№	Authors	Title	Journal	Volume (Number), first page to last page	year
69	J. Jakowski. S. Irle and K. Morokuma	Time–dependent quantum dynamical simulations of C2 condensation under extreme conditions,	*Phys. Chem. Chem. Phys.*	14, 6266-6272	2012
70	V. P. Ananikov, N. V. Orlov,.S. S. Zalesskiy, I. P. Beletskaya,. V. N. Khrustalev, K. Morokuma and D. G. Musaev	Catalytic Adaptive Recognition of Thiol (SH) and Selenol (SeH) Groups Towards Synthesis of Functionalized Vinyl Monomers	*J. Am. Chem. Soc.*	134, 6637-3349	2012
71	H.-B. Li, A. J. Page, S. Irle, and K. Morokuma	Theoretical Insights into Chirality-Controlled SWCNT Growth from a Cycloparaphenylene Template	*ChemPhysChem*	13, 1479-1485	2012
72	M. N. Ryanzantsev A. Altun and K. Morokuma	Color Tuning in Rhodopsins: The Origin of the Spectral Shift between the Chloride-bound and Anion-free Forms of Halorhodopsin	*J. Am. Chem. Soc.*	134, 5520-5523	2012
榊　茂好					
73	Hisako Hashimoto, Fukuda Tetsuya, Hitomi Tobita, Mausumi Ray, and Shigeyoshi Sakaki	Formation of a Germylyne Complex: Dehydrogenation of a Hydrido(hydrogermylene)-tungsten Complex with Mesityl Isocyanate	*Angew. Chem., Int. Ed.*	51 (12), 2930-2933	
74	Kentaro Kido, Hirofumi Sato, Shigeyoshi Sakaki	Systematic Assessment on Aqueous pK(a) and pK(b) of an Amino Acid Base on RISM-SCF-SEDD Method: Toward First Principles Calculations	*Int. J. Quant. Chem.*	112(1), 103-112	
75	Milind Deshmukh, Shigeyoshi Sakaki,	Two-step evaluation of binding energy and potential energy surface of van der Waals complexes	*J. Compt. Chem..*	33(6), 617-628	
76	Yusaku I. Kurokawa, Shigeysohi Sakaki	Theoretical Study of Inverted Sandwich Type Complexes of 4d Transition Metal Elements: Interesting Similarities to and Differences from 3d Transition Metal Complexes	*J. Phys. Chem. A*	116(9), 2292-2299	
77	Guixiang Zeng, S. Sakaki	Theoretical Study on the Transition-Metal Oxoboryl Complex: M-BO Bonding Nature, Mechanism of the Formation Reaction, and Prediction of a New Oxoboryl Complex	*Inorg. Chem.*	51(8), 4597-4605	
78	Ken Saito, Yoshinori Eishiro, Yoshihide Nakao, Hirofumi Sato, Shigeyoshi Sakaki	Oscillator Strength of Symmetry-Forbidden d-d Absorption of Octahedral Transition Metal Complex: Theoretical Evaluation	*Inorg. Chem.*	51(5), 2785-2792	
79	N. Takagi, S. Sakaki	A Theoretical Study of an Unusual Y-Shaped Three-Coordinate Pt Complex: Pt(0) sigma-Disilane Complex or Pt(II) Disilyl Complex?	*J. Am. Chem. Soc.*	134(28), 11749-11759	
80	Seiji Akatsu, Yasunori Kanematsu, Taka-aki Kurihara, Shota Sueyoshi, Yasuhiro Arikawa, Masayoshi Onishi, Shoji Ishizaka, Noboru Kitamura, Yoshihide Nakao, Shigeyoshi Sakaki, Keisuke Umakoshi	Syntheses and Luminescent Properties of 3,5-Diphenylpyrazolato-Bridged Heteropolynuclear Platinum Complexes. The Influence of Chloride Ligands on the Emission Energy Revealed by the Systematic Replacement of Chloride Ligands by 3,5-Dimethylpyrazolate	*Inorg. Chem.*	51(15), 7977-7992	
81	Yumiko Nakajima, Shigeyoshi Sakaki, Yoshihide Nakao, Hiroharu Suzuki	Theoretical Study of Dihydrogen Activation by a Trinuclear Ruthenium mu(3)-Imido Complex	*Organometallics*	31(15), 5342-5348	

№	Authors	Title	Journal	Volume (Number), first page to last page	year
82	S. Aono, S. Sakaki	Proposal of new QM/MM approach for geometry optimization of periodic molecular crystal: Self-consistent point charge representation for crystalline effect on target QM molecule	*Chem. Phys. Lett.*	544, 77-82	
83	S. Aono, S. Sakaki	Evaluation Procedure of Electrostatic Potential in 3D-RISM-SCF Method and Its Application to Hydrolyses of Cis- and Transplatin Complexes	*J. Phys. Chem. B*	116(43), 13045-13062	
84	Atsushi Ishikawa, Yudai Tamura, Yoshihide Nakao, Hirofumi Sato, Shigeyoshi Sakaki	Complicated Electronic Process of C-C sigma-Bond Activation of Cyclopropene by Ruthenium and Iridium Complexes: Theoretical Study	*Organometallics*	31 (23), 8189-8199	
85	Shinichi Yamabe, Wei Guan, Shigeyoshi Sakaki	How is the anionic tetrahedral intermediate involved in the isomerization of aspartyl peptides to iso-aspartyl ones? A DFT study on the tetra-peptide	*Org. Biomol. Chem.*	10(39), 8007-8015	
岩城　貴史					
86	Shunsuke F. Shimobayashi, Takafumi Iwaki, Toshiaki Mori, and Kenichi Yoshikawa	Probability of double-strand breaks in genome-sized DNA by g-ray decreases markedly as the DNA concentration increases	*J. Chem. Phys.*	Accepted	2013
嶺澤　範行					
87	Noriyuki Minezawa and Mark S. Gordon	Optimizing Conical Intersections of Solvated Molecules: The Combined Spin-Flip Density Functional Theory/Effective Fragment Potential Method	*J. Chem. Phys.*	137(3), 034116 [12 pages]	2012
88	Kurt R. Brorsen, Noriyuki Minezawa, Feng Xu, Theresa L. Windus, and Mark S. Gordon	Fragment Molecular Orbital Molecular Dynamics with the Fully Analytic Energy Gradient	*J. Chem. Theory Comput.*	8, 5008-5012	2012
岡本　隆一					
89	Shunsuke Yabunaka, Ryuichi Okamoto, and Akira Onuki	Phase separation in a binary mixture confined between symmetric parallel plates: Capillary condensation transition near the bulk critical point	*Phys. Rev. E*	87(3),032405 (10 pages)2013	2007
齋藤　拓也					
90	Takuya Saito and Takahiro Sakaue	Process time distribution of driven polymer transport	*Phys. Rev. E*	85, 061803(7)	2012
91	Takahiro Sakaue, Takuya Saito and Hirofumi Wada	Dragging a polymer in a viscous fluid: Steady state and transient	*Phys. Rev. E*	86, 011804(8)	2012
F-Quan Bai					
92	Qi Cao, Jing Wang, Zhao-Shuo Tian, Zai-Feng Xie and Fu-Quan Bai	Theoretical investigation on the photophysical properties of N-heterocyclic carbene iridium (III) complexes (fpmb) xIr(bptz)3-x (x=1-2)	*J. Comput. Chem.*	33(10), 1038-1046	2012
93	Juan Jin, Fu-Quan Bai, Guang-Hua Li, Ming-Jun Jia, Jin-Jing Zhao, Hong-Li Jia, Jie-Hui Yu and Ji-Qing Xu	Synthesis, structural characterization and photoluminescence property of four di(mono)acylhydrazidate-coordinated Cd2+ and Zn2+ compounds	*CrystEngComm*	14(23), 8162-8172	2012

№	Authors	Title	Journal	Volume (Number), first page to last page	year
94	Fu-Quan Bai, Jian Wang, Bao-Hui Xia, Qing-Jiang Pan and Hong-Xing Zhang	DFT and TD-DFT study on the electronic structures and phosphorescent properties of 6-phenyl-2,2'-bipyridine tridentate iridium(III) complexes and their isomer	*Dalton Trans.*	41(27), 8441-8446	2012
95	Danming Chao, Xiaoteng Jia, Fu-Quan Bai, Hongtao Liu, Lili Cui, Erik B. Berda and Ce Wang	An efficient fluorescent sensor for redox active species based on novel poly(aryl ether) containing electroactive pendant	*J. Mater. Chem.*	22(7), 3028-3034	2012
Guo Jingdon					
96	Zachary D. Brown, Jing-Dong Guo, Shigeru Nagase, and Philip P. Power	Experimental and Computational Study of Auxiliary Molecular Effects on the Mechanism of the Addition of Hydrazines to a Low-Valent Germanium Complex	*Organometallics*	31, 3768-3772	2012
97	Satoru Sato, Yutaka Maeda, Jing-Dong Guo, Michio Yamada, Naomi Mizorogi, Shigeru Nagase, and Takeshi Akasaka	Mechanistic Study of the Diels-Alder Reaction of Paramagnetic Endohedral Metallofullerene: Reaction of La@C82 with 1,2,3,4,5-Pentamethylcyclopentadiene	*J. Am. Chem. Soc.*	135, 5582-5587	2013
Jin Peng					
98	Peng Jin and Shigeru Nagase	Density functional theory study of fullerene–carbene Lewis acid–base adducts: critical role of dispersion interactions	*RSC Adv.*	3(26), 10177–10180	2013
Zhuofeng Ke					
99	Ke, Zhuofeng, Abe, S., Ueno, T., & Morokuma, Keiji*	Rh-catalyzed Polymerization of Phenylacetylene: Theoretical Studies of the Reaction Mechanism, Regioselectivity and Stereoregularity	*J. Am. Chem. Soc.*	134 (37), 15418–15429	2012
100	R.-R. Ye, ZhuoFeng Ke, C.-P. Tan, L. He, L.-N. Ji and Z.-W. Mao.	Histone Deacetylases Targeted Fluorescent Ruthenium(II) Polypyridyl Complexes as Potent Anticancer Agents.	*Chem. Eur. J.*	19, 10160 – 10169	2013
101	Liu Y., Ma L., Chen W.-H.*, Park H., Ke Zhuofeng*, & Wang B.*	Binding Mechanism and Synergetic Effects of Xanthone Derivatives as Non-competitive α-Glucosidase Inhibitors: a Theoretical and Experimental Study.	*J. Phys. Chem. B.*	Just Accepted	2013
Joonghan Kim					
102		Dynamics of Local Chirality during SWCNT Growth: Armchair versus Zigzag Nanotubes	*J. Am. Chem. Soc*	134(22), 9311	2012
Alister Page					
103	H.-B. Li, A. J. Page, S. Irle, K. Morokuma	Theoretical Insights into Chirality-Controlled SWCNT Growth from a Cycloparaphenylene Template	*ChemPhysChem*	13,6. 1479-1485	2012
104	M. A. Addicoat, A. J. Page, Z. Brain, L. Flack, S. Irle, K. Morokuma	Optimisation of a Genetic Algorithm for the Functionalisation of Fullerenes	*J. Chem. Theor. Comp.*	8,5. 1841-1851	2012
105	J. Kim, A. J. Page, S. Irle, K. Morokuma	The Dynamics of Local Chirality during SWCNT Growth: Armchair versus Zigzag Nanotubes	*J. Am. Chem. Soc.*	134,22. 9311-9319	2012
106	H.-B. Li, A. J. Page, Y. Wang, S. Irle, K. Morokuma	Sub-Surface Nucleation of Graphene Precursors near a Ni(111) Step-Edge	*Chem. Comm.*	48,64. 7937-7939	2012

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107	A. J. Page, T. Isomoto, J. Knaup, S. Irle, K. Morokuma	Effects of Molecular Dynamics Thermostats on Non-Equilibrium Systems	*J. Chem. Theor. Comp.*	8,11. 4019-4028	2012
108	H.-B. Li, A. J. Page, S. Irle, K. Morokuma	SWCNT Growth from Chiral Carbon Nanorings: Prediction of Chirality and Diameter Influence on Growth Rates	*J. Am. Chem. Soc.*	134,38. 15887-15896	2012
109	A. J. Page, C.-P. Chou, P.-Q Buu, H. Witek, S. Irle, K. Morokuma	Quantum Chemical Investigation of Epoxide and Ether Groups in Graphene Oxide and their Vibrational Spectra	*Phys. Chem. Chem. Phys.*	15,11. 3725-3735	2013
110	K. R. S. Chandrakumar, A. J. Page, S. Irle, K. Morokuma	Carbon Coating Precedes SWCNT Nucleation on Silicon Nanoparticles: Insights from QM/MD Simulations	*J. Phys. Chem. C*	117,8. 4238-4244	2013
畑中　美穂					
111	Miho Hatanaka, Satoshi Maeda, and Keiji Morokuma	Sampling of Transition States for Predicting Diastereoselectivity Using Automated Search Method—Aqueous Lanthanide-Catalyzed Mukaiyama Aldol Reaction	*J. Chem. Theory Comput.*	in press	2013
112	Satoshi Maeda, Erika Abe, Miho Hatanaka, Tetsuya Taketsugu, and Keiji Morokuma	Exploring Potential Energy Surfaces of Large Systems with Artificial Force Induced Reaction Method in Combination with ONIOM and Microiteration	*J. Chem. Theory Comput.*	8(12), 5058-5063	2012
Hongyan Xiao					
113	Hongyan Xiao, Satoshi Maeda and Keiji Morokuma	Global *ab Initio* Potential Energy Surfaces for Low-Lying Doublet States of NO_3	*J. Chem. Theory Comput.*	8(8),2600-2605	2012
114	Bina Fu, Joel M. Bowman, Hongyan Xiao, Satoshi Maeda and Keiji Morokuma	Quasiclassical Trajectory Studies of the Photodissociation Dynamics of NO_3 from the D_0 and D_1 Potential Energy Surfaces	*J. Chem. Theory Comput.*	9(2),893-900	2013
115	Hongyan Xiao, Satoshi Maeda and Keiji Morokuma	CASPT2 Study of Photodissociation Pathways of Ketene	*J. Phys. Chem. A*	in press (DOI: 10.1021/jp312719a)	2013
Haibei Li					
116	Hai-Bei Li, Aister. J. Page, Sthephan. Irle and K. Morokuma,	SWCNT Growth from Chiral Carbon Nanorings: Prediction of Chirality and Diameter Influence on Growth Rates	*J. Am. Chem. Soc.*	134, 15887-15896,	2012
Lung Wa Chung					
117	Lung Wa Chung, Hajime Hirao, Xin Li and Keiji Morokuma	The ONIOM method: its foundation and applications to metalloenzymes and photobiology	*WIREs Comput. Mol. Sci.*	2 (2), 327–350	2012
118	Lina Ding, Lung Wa Chung and Keiji Morokuma	Reaction Mechanism of Photoinduced Decarboxylation of the Photoactivatable Green Fluorescent Protein: An ONIOM(QM:MM) Study	*J. Phys. Chem. B*	117 (4), 1075-1084	2013
Galina Petrova					
119	G. V. Vayssilov, G. P. Petrova, E. A. I. Shor, V. A. Nasluzov, A. M. Shor, P. S. Petkov, N. Rösch	Reverse hydrogen spillover on and hydrogenation of supported metal clusters: Insights from computational model studies	*Phys. Chem. Chem. Phys.*	14 (17), 5879-5890	2012

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山邊　信一					
120	Yamabe, Shinichi; Fukuda, Takeshi; Yamazaki, Shoko	Proton Transfers Along Hydrogen Bonds in the Tautomerization of Purine	*J. Phys. Chem. A*	116 (4), 1289-1297	2012
121	T. Machiguchi, T. Hasegawa, S. Yamabe, T. Minato, S. Yamazaki, and T. Nozoe	Experimental and Theoretical Analyses of Azulene Synthesis from Tropones and Active Methylene Compounds: Reaction of 2-Methoxytropone and Malononitrile	*J. Org. Chem.*	77, 5318-5330	2012
122	Shinichi Yamabe, Wei Guan and Shigeyoshi Sakaki	How is the anionic tetrahedral intermediate involved in the isomerization of aspartyl peptides to iso-aspartyl ones? A DFT study on the tetra-peptide	*Org. Biomol. Chem.*	10, 8007-8015	2012
123	Shinichi Yamabe, Takeshi Fukuda and Shoko Yamazaki	A new intermediate in the Prins reaction	*Beilstein J. Org. Chem.*	9, 476-485	2013
124	Shinichi Yamabe, Wei Guan and Shigeyoshi Sakaki	Presence or absence of a novel charge-transfer complex in the base-catalyzed hydrolysis of N-ethylbenzamide or ethyl benzoate	*Beilstein J. Org. Chem.*	9, 185-196	2013
125	Shinichi Yamabe, Wei Guan and Shigeyoshi Sakaki	Three Competitive Transition States at the Glycosidic Bond of Sucrose in Its Acid-Catalyzed Hydrolysis	*J. Org. Chem.*	78 (6), 2527-2533	2013
126	Shinichi Yamabe, Guixiang Zeng, Wei Guan and Shigeyoshi Sakaki	An aniline dication-like transition state in the Bamberger rearrangement	*Beilstein J. Org. Chem.*	9, 1073-1082	2013
土方　優					
127	Masakazu Higuchi, Kohei Nakamura, Satoshi Horike, Yuh Hijikata, Nobuhiro Yanai, Tomohiro Fukushima, Jungeun Kim, Kenichi Kato, Masaki Takata, Daisuke Watanabe, Shinji Ohshima, and Susumu Kitagawa	Design of flexible Lewis acidic sites in porous coordination polymers by using the viologen moiety	*Angew. Chem. Int. Ed.*	51, 8369-8372	2012
128	Maw Lin Foo, Satoshi Horike, Tomohiro Fukushima, Yuh Hijikata, Yoshiki Kubota, Masaki Takata, and Susumu Kitagawa	Ligand-based solid solution approach to stabilization of sulphonic acid groups in porous coordination polymer $Zr_6O_4(OH)_4(BDC)_6$ (UiO-66)	*Dalton. Trnas.*	41, 13791-13794	2012
129	Munehiro Inukai, Satoshi Horike, Daiki Umeyama, Yuh Hijikata, and Susumu Kitagawa	Investigation of post-grafted groups of a porous coordination polymer and its proton conduction behavior	*Dalton. Trnas.*	41, 13261-13263	2012
130	Shin-ichiro Noro, Yuh Hijikata, Munehiro Inukai, Tomohiro Fukushima, Satoshi Horike, Masakazu Higuchi, Susumu Kitagawa, Tomoyuki Akutagawa, and Takayoshi Nakamura	Highly selective CO_2 adsorption accompanied with low-energy regeneration in a two-dimensional Cu(II) porous coordination polymer with inorganic fluorinated PF_6^- anions	*Inorg. Chem.*	52, 280-285	2013
131	Satoshi Horike, Masayuki Sugimoto, Kanokwan Kongpatpanich, Yuh Hijikata, Munehiro Inukai, Daiki Umeyama, Shinji Kitao, Makoto Seto, and Susumu Kitagawa	Fe^{2+} based layered porous coordination polymers and soft encapsulation of guests via redox activity	*J. Mater. Chem. A*	1, 3675-3679	2013

№	Authors	Title	Journal	Volume (Number), first page to last page	year
132	Yuh Hijikata, Satoshi Horike, Masayuki Sugimoto, Munehiro Inukai, Tomohiro Fukushima, and Susumu Kitagawa	Pore design of two-dimensional coordination polymers toward selective adsorption	*Inorg. Chem.*	52, 3634-3642	2013
青野　信治					
133	Shinji Aono, Takashi Hosoya, and Shigeyoshi Sakaki	A 3D-RISM-SCF method with dual solvent boxes for a highly polarized system: application to 1,6-anhydrosugar formation reaction of phenyl alpha- and beta-D-glucosides under basic conditions	*Phys. Chem. Chem. Phys.*	17 6368	2013
134	Shinji Aono and Shigeyoshi Sakaki	Evaluation Procedure of Electrostatic Potential in 3D-RISM-SCF Method and Its Application to Hydrolyses of Cis- and Transplatin Complexes	*J. Phys. Chem. B*	116 13045	2012
135	Shinji Aono and Shigeyoshi Sakaki	Proposal of new QM/MM approach for geometry optimization of periodic molecular crystal: Self-consistent point charge representation for crystalline effect on target QM molecule	*Chem. Phys. Lett.*	544 77	2012
塚本　晋也					
136	Shinya Tsukamoto and Shigeyoshi Sakaki	A theoretical study of luminescent vapochromic compounds including an $AuCu_2(NHC)_2$ core	*Dalton Transactions*	42, 4809-4821	2013
Milind Deshmukh					
137	Deshmukh, Milind. M.; Sakaki Shigeyoshi	Two-step Evaluation of Potential Energy Surface and Binding Energy of van der Waals Complexes	*J. Comput. Chem.*	33, 617-628	2012
138	Khedkar, J. K.; Deshmukh, Milind M.; Gejji, S. P.; Gadre, S. R."	Intramolecular Hydrogen Bonding and cooperative interactions in Calix[n]arenes (n = 4, 5)	*J. Phys. Chem. A*	116, 3739-3744.	2012
139	Deshmukh, Milind M.; Ohba, Massaki.; Kitagawa, Susumu.; Sakaki Shigeyoshi	Absorption of CO2 and CS2 into the Hofmann-type Porous Coordination Polymer:Electrostatic versus Dispersion	*J. Am. Chem. Soc.*	135, 4840-4849	2013
髙木　望					
140	N. Takagi, S. Sakaki	A Theoretical Study of Unusual Y-Shaped Three-coordinate Pt Complex: Pt(0) σ-Disilane Complex or Pt(II) Disilyl Complex?	*J. Am. Chem. Soc.*	134, 11749-11759	2012
141	N. Takagi, S. Sakaki	Theoretical Study of Reactivity of Ge(II)-hydride Compound: Comparison with Rh(I)-hydride Complex and Prediction of Full Catalytic Cycle by Ge(II)-hydride	*J. Am. Chem. Soc.*	in press	
吉澤　輝高					
142	T. Yoshizawa, S. Sakaki	NMR shielding constants of CuX, AgX, and AuX (X = F, Cl, Br, and I) investigated by density functional theory based on the Douglas–Kroll–Hess Hamiltonian	*J. Comput. Chem.*	34, 1013–1023	2013
143	T. Yoshizawa, T. Nakajima	A new computational scheme for the spin–orbit part of zero-field splitting tensor	*Chem. Phys. Lett.*	549, 108–112	2012

№	Authors	Title	Journal	Volume (Number), first page to last page	year
Guan Wei					
144		Interest in new heterodinuclear transition-metal/main-group-metal complexes: DFT study of electronic structure and mechanism of fluoride sensing function	*Dalton Trans.*	42, 8717–8728	2013
145		Three Competitive Transition States at the Glycosidic Bond of Sucrose in Its Acid-Catalyzed Hydrolysis	*J. Org. Chem.*	78, 2527−2533	2013
146		Presence or absence of a novel charge-transfer complex in the base-catalyzed hydrolysis of N-ethylbenzamide or ethyl benzoate	*Beilstein J. Org. Chem.*	9, 185–196	2013
147		An aniline dication-like transition state in the Bamberger rearrangement	*Beilstein J. Org. Chem.*	9, 1073–1082	2013
148		How is the anionic tetrahedral intermediate involved in the isomerization of aspartyl peptides to iso-aspartyl ones? A DFT study on the tetra-peptide	*Org. Biomol. Chem.*	10, 8007−8015	2012
149		The self-assembly mechanism of the Lindqvist anion [W6O19]2− in aqueous solution: a density functional theory study	*Dalton Trans.*	41, 11361–11368	2012
150		Building blocks and formation thermodynamics of a-Keggin-type [PW12O40]3- anion	*Comput. Theor. Chem.*	999, 66–73	2012
151		DFT study of ionic peapod structures from single-walled carbon nanotubes and Lindqvist tungstates	*Dalton Trans.*	41, 2798-2803	2012
松井　亨					
152	Toru Matsui, Yasutaka Kitagawa, Mitsutaka Okumura Yasuteru Shigeta and Shigeyoshi Sakaki	Consistent Scheme for Computing Standard Hydrogen Electrode and Redox Potentials	*Journal of Computational Chemistry*	34, 21-26	2013
153	Y. Kitagawa, N. Yasuda, H. Hatake, T. Saito, Y. Kataoka, T. Matsui, T. Kawakami, S. Yamanaka, M. Okumura and K. Yamaguchi	Combination of approximate spin-projection and spin-restricted calculations based on ONIOM method for geometry optimization of large biradical systems	*International Journal of Quantum Chemistry*	13, 290-295	2013
河津　励					
154	Tsutomu Kawatsu	Pathway analysis for peptide-mediated electronic coupling in the super-exchange mechanism of ET and EET	*Peptide Science*	100, 100-113	2013
155	Tsutomu Kawatsu, Jun-ya Hasegawa	Sequentially Coupled Hole–Electron Transfer Pathways for Bridge-Mediated Triplet Excitation Energy Transfer	*J. Phys. Chem. C*	116, 23252–23256	2012
156	Tsutomu Kawatsu, Jun-ya Hasegawa, Kenji Matsuda	Singlet Excitation Energy Transfer Mediated by Local Exciton Bridges	*J. Phys. Chem. C*	116, 13865-13876	2012

４．福井謙一記念研究センター　シンポジウム　ポスター・プログラム

第10回
京都大学福井謙一記念研究センター
シンポジウム

日　時 2012年11月30日(金)10時～

会　場 京都大学福井謙一記念研究センター　３F大会議室
Fukui Institute for Fundamental Chemistry, Kyoto University

プログラム

●10:00-10:05
開会の辞　田中 一義(センター長)

●10:05-10:15
ご 挨 拶　北野 正雄(京大・工学研究科長)

●10:15-11:15
Weston T. Borden(University of North Texas)
“Why Does Cyclobutane-1,2,3,4-tetraone
Have a Triplet Ground State?”

●11:30-12:30
赤木 和夫(京大・院工)
「不斉液晶反応場での高分子合成：
ヘリカル共役ポリマーのらせん制御と形態保持炭素化」

－昼休み－

●14:00-15:00
榊　茂好(福井センター)
「金属錯体の分子物性と反応：電子状態に基づく微視的理解」

●15:15-17:15
ポスターセッション

●17:30-19:00
懇親会(１F多目的ルーム)

問い合わせ先
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第10回京都大学福井謙一記念研究センターシンポジウム
プログラム

日時　2012(平成 24)年 11 月 30 日(金)
場所　京都大学福井謙一記念研究センター

講演会

(3F 大会議室 10:00-15:00)

- 開会の辞　田中 一義(京都大学 福井謙一記念研究センター長)　・・・・・・10:00-10:05
- ご挨拶　北野 正雄(京都大学 工学研究科長)　・・・・・・10:05-10:15
- Weston T. Borden (University of North Texas)
  "Why Does Cyclobutane-1,2,3,4-tetraone Have a Triplet Ground State?"
  ・・・・・・10:15-11:15
- 赤木 和夫(京都大学大学院 工学研究科)
  「不斉液晶反応場での高分子合成:ヘリカル共役ポリマーのらせん制御と形態保持炭素化」
  ・・・・・・11:30-12:30

― 昼休み ―

- 榊 茂好(福井謙一記念研究センター)
  「金属錯体の分子物性と反応:電子状態に基づく微視的理解」　・・・・・・14:00-15:00

ポスターセッション

(3F 大会議室 15:15-17:15)

懇親会

(1F 多目的ルーム 17:30-19:00)

ポスターセッション　15:15−17:15 (3F 大会議室)

※ 番号が奇数の方は前半(15:15-16:15)に、番号が偶数の方は後半(16:15-17:15)にポスターの場所にて発表を行ってください。

※ Please present your poster at the first half (15:15-16:15) when your poster number is odd and do it at the second half (16:15-17:15) when the number is even.

1. **インスタントン法によるトンネル分裂計算**
(分子研[1]、金大院自然[2]、金大院理工[3]) ○河津　励[1,2]、三浦伸一[3]

2. Temperature effect in the fluorescence blueshift of [n]cycloparaphenylenes with increasing molecular size
(Department of Chemistry, Graduate School of Science, Nagoya University) ○Cristopher Camacho and Stephan Irle

3. ΔSCF(2): a balanced, economical approach to multireference perturbation theory
(Massachusetts Institute of Technology[1] and Nagoya University[2]) Shane Yost[1], ○Tim Kowalczyk[1,2] and Troy Van Voorhis[1].

4. Theoretical Study on Cycloreversion Reaction of Diarylethene Derivatives: Relation between Optimized Geometry on Excited State and Cycloreversion Quantum Yield
（阪大院基礎工）○奥野　克樹、重田　育照、岸　亮平、宮坂　博、中野　雅由

5. The Diradical Characters and Third-Order Nonlinear Optical Properties of Bucky Ferrocenes Systems
(Department of Materials Engineering Science, Osaka University) ○Shabbir Muhammad, Takuya Minami, Ryohei Kishi, Yasuteru Shigeta, Masayoshi Nakano

6. **アシル化反応に対するアミノ酸変異の効果**
(阪大院基礎工[1]、筑波大院数理[2]、阪大院理[3]、兵庫県立大学院工学[4]、ストラスブール大[5]) ○馬場剛史[1]、神谷克政[2]、松井亨[3]、根来誠司[4]、Mauro Boero[5]、中野雅由[1]、重田育照[1]

7. **時間依存密度汎関数法に基づくドナー・アクセプタ2置換ベンゼンの電子遷移特性と第一超分極率の理論的研究**
（阪大院基礎工）○村田裕介、岸本真悟、岸亮平、中野雅由

8. **実空間密度汎関数法による2次元無限系の光学応答量の計算手法の実装**
(阪大院基礎工) ○乾　智也、奥野　克樹、馬場　剛史、米田　京平、福田　幸太郎、重田　育照、中野雅由

9. 一次元開殻一重項縮環共役分子系の線形吸収ピークのジラジカル因子依存性についての理論的研究
(阪大院基礎工)○岸本 真悟、岸 亮平、南 拓也、伊藤 聡一、村田 裕介、福田 幸太郎、中野 雅由

10. オリゴリレンにおけるシングレットフィッションの理論的研究
(阪大院基礎工)○南拓也、伊藤聡一、中野雅由

11. 開殻一重項ジフェナレニルジラジカル分子の電子構造と二光子吸収特性についての理論研究
(阪大院基礎工[1]、産総研ユビキタス[2]、阪大院理[3]) ○岸 亮平[1]、岸本 真悟[1]、南出 秀[1]、村田 裕介[1]、福田 幸太郎[1]、鎌田 賢司[1]、太田 浩二[2]、久保 孝史[3]、重田 育照[1]、中野 雅由[1]

12. 一般化多配置参照擬縮重摂動法および時間依存密度汎関数法によるオリゴアセンの励起状態の研究
(阪大院基礎工) ○伊藤 聡一、南 拓也、福田 幸一郎、岸 亮平、中野 雅由

13. 遷移金属二核錯体の開殻性と第二超分極率に対するエクアトリアル配位子が及ぼす効果の理論的研究
(阪大院基礎工) ○井上雄大、山田大志、福田幸太郎、松井啓史、重田育照、中野雅由

14. 一重項開殻性をもつゼトレン類の非線形光学特性:ドナー／アクセプター置換基効果
(阪大院基礎工[1]、産総研ユビキタスエネルギー[2]) ○南出 秀[1]、福田 幸太郎[1]、米田 京平[1]、伊藤 聡一[1]、岸 亮平[1]、鎌田 賢司[2]、中野 雅由[1]

15. ヘテロ二核遷移金属系のジラジカル因子と三次非線形光学物性の相関についての理論研究
(阪大院基礎工[1]、阪大基礎工[2]) ○山田 大志[1]、 井上 雄大[1]、福田 幸太郎[1]、 松井 啓史[2]、 重田 育照[1]、中野 雅由[1]

16. ヘキサセン分子の開殻性と第二超分極率に対する置換基効果の理論的研究
(阪大院基礎工)○米田京平、福田幸太郎、南出秀、中野雅由

17. 標準水素電極ポテンシャルと酸化還元電位の新規算出法
(阪大院理[1]・京大福井謙一記念研究セ[2]・阪大院基礎工[3])○松井 亨[1,2], 北河 康隆[1], 奥村 光隆[1], 重田 育照[3], 榊 茂好[2]

18. 環状$(VO)_7$錯体における磁気的相互作用の汎関数および基底関数依存性
(阪大院理)○北河康隆・松井亨・安田奈都美・畑ヶ宇宙・川上貴資・山中秀介・奥村光隆

19. 平面波 DFT 法による鎖状構造結晶セレンの電荷移動とバンド構造の研究
(京大院理[1]、京大 ESICB[2]) ○松井 正冬[1][2]

20. 導電性金属酸化物を用いたプラズモニックデバイスの設計と作製
（京大院工） ○安原 隆一郎、藤田 晃司、村井 俊介、田中 勝久

21. FMO-LCMO 法を用いた蛋白質中の電子移動経路解析
(京大院理) ○鬼頭(西岡) 宏任、安藤 耕司

22. ラジカルカチオンプール法による非対称ビアリール化合物の直接合成
(京大院工) ○清水 章弘、諸藤 達也、吉田 潤一

23. 分子動力学シミュレーションによるアルカリ金属ハライド水溶液の1次元振動分光スペクトル解析
(京大院理) ○伊藤 広伸、 谷村 吉隆

24. 平均場 QM/MM 法による溶液・酵素反応の自由エネルギー計算
（京大院理）○中農 浩史、山本 武志

25. 溶液内におけるフェノール誘導体の電子・プロトン移動反応の理論的研究: 非断熱性とトンネリング効果
(京大院理) ○稲垣泰一、山本武志

26. QM/MM 法のための ESP 多重極子演算子の開発
(京大院理[1]、ワシントン大[2]) ○井上 雄介[1]、小杉 貴洋[2]、中農 浩史[1]、山本 武志[1]、林 重彦[1]

27. 古典 MD と QM/MM 法によるロドプシンの光反応中間体の理論研究
(京大院理) ○神谷 基司, 林 重彦

28. MS-CASPT2 法を応用したピリジンの超高速緩和過程についての理論的研究
(京大院・理[1], スタンフォード大[2]) ○中野勝博[1], 森俊文[2], 林重彦[1], 加藤重樹[1]

29. Enhanced green fluorescent protein の蛍光状態に関する理論的研究
(京大院理[1]、分子研[2]) ○内田 芳裕[1]、東 雅大[2]、林 重彦[1]

30. Ras-GAP の GTP 加水分解触媒作用に関する理論的研究
(京大院理[1]、分子研[2]) ○公文 啓瑛[1]、 林 重彦[1]、 東 雅大[2]、斎藤 真司[2]

31. poly(quinoxaline-2,3-diyl)s の螺旋構造と安定性に関する理論的研究
(京大院工) ○本田 龍之介、城戸健太朗、佐藤啓文

32. Ru 触媒による水の分解反応に関する理論的研究
(京大院工) ○横井 勇人、佐藤 啓文

33. 水溶液中でのアニリンのイオン化に関する理論的研究
(京大院工) ○松村 祥宏、 飯田 健二、佐藤 啓文

34. A molecular level study of selective cation capture by a host-guest mechanism for 25, 26, 27, 28-tetramethoxycalix[4]arene in $MClO_4$ solution (M=Na, K)
(京大院工[1], 京大福井セ[2]) 城戸　健太朗[1], ○笠原　健人[1], 佐藤　啓文[1], 榊　茂好[2]

35. ホール輸送材料における振電相互作用と多体効果
（京大院工[1]、京大化研[2]）○三村　貴信[1]、 佐藤　徹[1]、田中　一義[1]、梶　弘典[2]

36. 反応性指標としての振電相互作用密度:フラーレンへの応用
(京大院工[1]) ○春田　直毅[1]、佐藤　徹[1]、岩原　直也[1]、田中　一義[1]

37. 電解液中におけるリチウム塩と有機溶媒分子の配位状態に関する理論解析
（京大院工[1]、福井セ[2]、富士重工スバル技研[3]）○梶　章浩[1]、伊藤　彰浩[1]、田中　一義[1,2]、波戸崎　修[3]

38. 人工筋肉に向けた導電性高分子アクチュエーターの理論的研究
（京大院工[1]、京大福井セ[2]）○木村　正弥[1]、笛野　博之[1]、田中　一義[1][2]

39. CPMD を用いた梯子状 π 共役分子の励起状態に関する理論的研究
(京大院工[1], 京大福井セ[2]) ○成田　真弘[1], 佐藤　啓文[1], 中尾　嘉秀[2]

40. 有機ラジカルを配位子とする Co(II)錯体の磁性に関する理論的研究
(京大院工[1]、京大福井セ[2]) ○野口　純樹[1]、 佐藤　啓文[1]、中尾　嘉秀[2]

41. Theoretical studies on reactions in biomolecules: photoisomerization of rhodopsins and ligand exchange in CooA
(京大福井セ[1]、DLSU[2]、上智大理工[3]、分子研[4]) ○石田俊正[1]、Wilfredo C. Chung[1,2]、南部伸孝[3]、青野重利[4]

42. Cr(III)、Co(II)のオキサラト架橋錯体の磁気異方性に関する理論的研究
(京大福井セ[1]、京大院工[2]) ○中尾　嘉秀[1]、 野口　純樹[2]、佐藤　啓文[2]

43. Three competitive transition states at the glycosidic bond of sucrose in the acid-catalyzed hydrolysis.
(FIFC) ○Shinichi Yamabe, Wei Guan and Shigeyoshi Sakaki

44. 六方晶フェライトにおける Mössbauer パラメータの第一原理計算
(京大福井セ[1], 京大院工[2]) ○池野　豪一[1], 田中　功[2]

45. The Mechanism of Lanthanide-Catalyzed Mukaiyama Aldol Reaction in Water Solution
(FIFC[1],Emory univ[2]) ○Miho Hatanaka[1], Keiji Morokuma[1,2]

46. Revisiting the Mechanisms of Spiropyran Photochromic Ring-Opening Reaction: a CASPT2//CASSCF Study
(FIFC) ○Fengyi Liu, Keiji Morokuma

47. Mechanistic investigation on the site selectivity on C(sp^3)-C(sp^3) and C(sp^3)-C(sp^2) cleavage by Rh-catalyst: A DFT study
(FIFC[1], Kyoto University[2]) ○Lina Ding[1], Naoki Ishida[2], Keiji Morokuma[1]

48. Subsurface Nucleation of Uniform Graphene Precursors on Ni(111) Surface
(FIFC) ○Hai-Bei Li, Alister J. Page, Ying Wang, Stephan Irle, and Morokuma Keiji

49. Strong Correlations in Decomposition and Chemiluminescence of Dioxetanones
(FIFC[1], IMS[2]) ○Lung Wa Chung [1], Yuki Kurashige [2], Takeshi Yanai [2] and Keiji Morokuma [1]

50. Theoretical modeling of DNA-based copper catalysts performance in intramolecular Friedel-Crafts reaction
(FIFC [1], [2]) ○Galina Petrova [1], Zhuofeng Ke [2], Keiji Morokuma [1]

51. ONIOM study of the ferritin ferroxidase reaction
(FIFC) ○Travis V. Harris and Keiji Morokuma

52. プロトン伝導性配位高分子の電子状態に関する理論的研究
(京大福井セ) ○土方　優、榊　茂好

53. 塩基性条件下におけるグルコシドからのレボグルコサン生成機構:α体とβ体の反応性の相違に関する 3D-RISM-SCF 法による理論的研究
(京大福井セ[1]、京大 iCeMS[2]) ○青野　信治[1]、細谷　隆史[2]、榊　茂好[1]

54. 五配位　d^8 Ni(II) 錯体 の構造と電子状態及び結晶中でのスピンクロスオーバーについての理論的考察
(京大福井セ) ○塚本　晋也、榊　茂好

55. Absorption of Gas Molecules in Metal Organic Framework: A Theoretical Study
(FIFC[1], Grad. School. of Sci. Kyushu Univ.[2]) ○Milind Deshmukh[1], Masaaki Ohba[2], Shigeyoshi Sakaki[1]

56. Unexpected Electronic Process of the H_2 Activation by a New Nickel(0)−Borane Complex: Comparison with the Usual Homolytic and Heterolytic Activations
(FIFC) ○Guixiang Zeng and Shigeyoshi Sakaki

57. A Theoretical study of Hydrogenation of Ketone by Ge(II) Hydride. Reaction Mechanism, Comparison with Rh(I) Hydride, and Prediction in Expectation of a Main-Group-Based Catalyst
(FIFC) ○Nozomi Takagi, Shigeyoshi Sakaki

58. 異種金属原子による窒素分子を挟んだ逆サンドイッチ型錯体の電子構造に関する理論的研究
(京大福井セ) ○中垣 雅之、榊 茂好

59. Heterodinuclear main-group/transition-metal complexes and their fluoride sensing function: DFT study
(FIFC) ○Wei Guan, Shinichi Yamabe, Shigeyoshi Sakaki

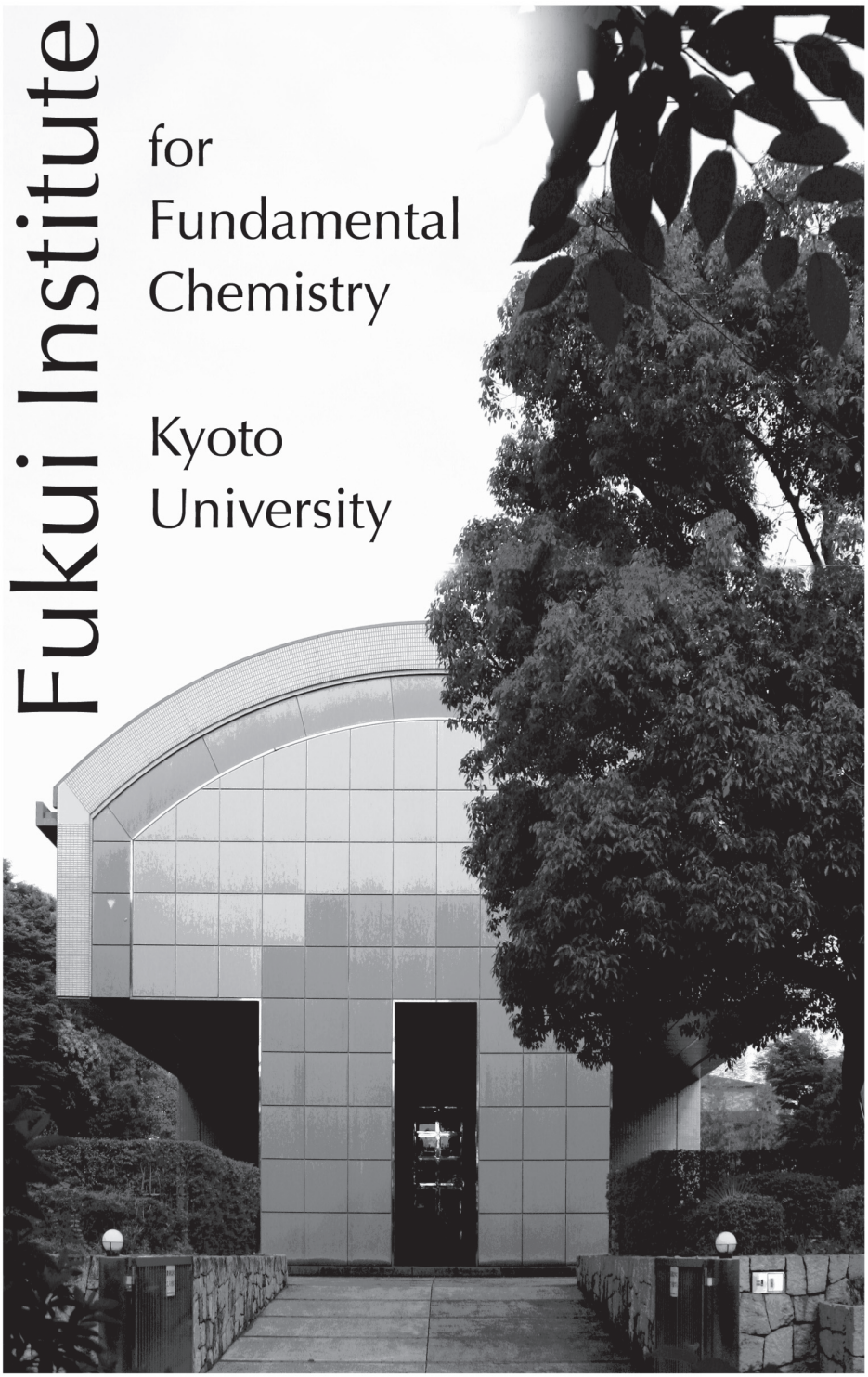
60. Electronic State and Bonding Nature of Nickel(I)- and Copper(I)- Dioxygen Complexes: RASPT2 Study
(FIFC) ○Yue Chen, Shigeyoshi Sakaki

61. 歯胚形成過程の Langevin Dynamics によるモデリングと経路遷移確率の計算
(京大福井セ[1]、京大医[2]、同大生命医[3]) ○岩城 貴史[1]、 今村 寿子[2]、吉川 研一[3]

62. 電子励起状態の自由エネルギー面: RISM-TDDFT 法
(京大福井セ) ○嶺澤 範行

63. 臨界溶液中のコロイド間相互作用の普遍的振る舞い
(京大福井セ[1]、京大理[2]) ○岡本隆一[1]、小貫明[2]

64. 微細孔を通り抜ける高分子鎖のダイナミクス: 通り抜け時間の分布のスケーリング
(京大福井セ[1]、九大理[2])、○齋藤 拓也[1]、坂上 貴洋[2]



第10回福井謙一記念研究センターシンポジウム

2012年（平成24年）11月30日（金）

京都大学福井謙一記念研究センター

５．福井謙一記念研究センター　セミナー　ポスター・プログラム

第10回
福井センターセミナー
The 10th Fukui Center Seminar

2013年3月21日(木) 14:30-17:30

京都大学福井謙一記念研究センター1F 多目的室 (Room: 1F 106)
http://www.fukui.kyoto-u.ac.jp/
〒606-8103 京都市左京区高野西開町34-4（TEL075-711-7708)
(at FIFC, Kyoto Univ. on March, 21(Thu.), 2013)

14:30～14:35 Opening by Professor Shigeyoshi Sakaki
(Fukui Institute for Fundamental Chemistry)

14:35～15:30 Assistant Professor Satoshi Maeda
(Hokkaido Univ.)
“Development and Applications of Automated Reaction Path Search Methods: The Global Reaction Route Mapping (GRRM) Strategy”

15:30 ～16:00 Dr. Miho Hatanaka
(Fukui Institute for Fundamental Chemistry)
“Mechanism of Mukaiyama Aldol Reaction Catalyzed by Water-Tolerant Lanthanide Lewis Acid - An Artificial Force Induced Reaction Study”

Break

16:15～17:30 Associate Professor Pradipta Bandyopadhyay
(Jawaharlal Nehru Univ., India)
“New Development in Monte Carlo Based Methods: Large Water Cluster Optimization and Efficient Sampling”

多数の方のご来場を歓迎いたします
We welcome all of you to join.

６．国際交流

― 海外の研究機関との研究所運営に関する意見交換のための出張報告書 ―

福井謙一記念研究センター長　田中一義

平成２４年９月５日、６日訪問
カリフォルニア大学サンタバーバラ分校　カブリ理論物理学研究所(UCSB, KITP)：　Kavli は財団の名称で、KITP は Kavli 研究所ネットワークの一つ。

Lars Bildsten 所長（今年６月から）

・KITP には５つの Faculty （研究室）があり、５人の Permanent Member（教授）がいる。院生、PD18 名もいるが、学部生はいない。しかし学部講義は行う。
・ほかに１２名のスタッフ（計算機、Money, House 関連など）
・UC が土地・建物・職員の給与を負担。
・所長と UCSB の分校長(Chancellor)との関係は大事。UC 自身は巨大すぎる。
・研究資金は NSF から年に４６０万ドル（もとは５００万ドルあったが、不況のため減額）。５年毎に見直し。ほか Simons Foundation などからも補助。
・結局、合計６００万ドル／年で運営している。
・研究所の対外活動として非常に重要と位置づけているのは、”Program”である。これはあるテーマのもとに研究者がグループを組んで KITP に滞在して研究に専念するためのもの。
・志願者グループは申請書を書く。
・志願者は全世界から（40%が米国外）。中国からはまだ多くない。
・KITP の Advisory Board（所外研究者１５～１７名：米国、カナダ、欧州在）が申請書を審査する。採用に当たっては Coordinator３～４名を決める（志願者グループの自薦から選ぶことも、Advisory Board が適切な人を持ってくることもある）。
・ちなみにこの Advisory Board Members は年１回開催の Steering Committee @KITP にやってくる。
・採用倍率は 1.5～2 倍
・志願者は PD～シニア教授までいろいろ。
・ホテル滞在はあまり精神的にもよくないようなので、貸家、アパートを見つけて斡旋する。(House Coordinator の仕事)
・滞在期間は３週間～３ヶ月。滞在中に１回は 100 名規模の Conference を開くことが義務。

・１年に１０～１２個の Program が走る。並走することもある。
・給料はなし。KITP からの補助は所内の居場所確保: Allocate space、渡航・滞在費の補助程度のみ。家族を連れてくることも可能。とはいえ、いろいろな世話を実施。Simons Foundation などから補助を貰うための申請もする。
・この Program を走らせることは、結局、KITP の活性化につながるメリットあり。
・http://www.kitp.ucsb.edu/for-scientists
・http://www.kitp.ucsb.edu/for-scientists/suggestions/guidelines

Walter Kohn 元所長（KITP 設立者: 1998 年度ノーベル化学賞）
・1990 年に福井先生に会ったときに、彼の研究所（旧基礎化学研究所）を世界水準にするにはどうしたら良いか聞かれたので、global に考えたときには英語使用が不可避であるため、「活動」を英語中心にすべきと言った。
Cf: おおげさに言えば、Kohn さんはもともと田中の知己。

David Gross 前所長（2004 年度ノーベル物理学賞）
・Asymptotic Freedom in Quantum Chromodynamics (QCD)により受賞。
・東大の国際高等研究所のカブリ数物連携宇宙研究機構（@柏キャンパス）は何かの参考になると思うので、調べることを勧める（Gross 氏も関与している）。
・北京に KITP との連携研究機構が２つある。ひとつは北京大学、もう一つは中国科学院との合弁。
・現在の京大湯川記念館（基礎物理研）の所長は？という質問もあった（当時は九後先生であると回答）。

Program 関連スタッフからの聞き取り
Marty Einhorn (Deputy Director)
+ Michelle Keuper (MSO; Management and Service Officer)
Housing Coordinator（この人は不動産屋でもあるらしい）はこの日不在（休暇？）。
・北野先生（工学研究科長）は 2002 年に走ったうちの Program で２週間 KITP に滞在されたとのこと。
・年に１２個の Program が走り、週当たり２３名（のべ８００名／年）の参加者がいる。
・予算、場所とも制限があるので、この数程度が限界か。
・Program のテーマには理論物理のほかに、数学、生物学、物理化学まで含む。
・基本は、参加者どうし、さらに KITP とも新しい Collaboration が始まること

を強く期待している。
・Program の参加者は、通常、車を持っていない。レンタカーも高いので、自転車使用が多い。ダウンタウンからのバスも便利（２０分程度)。
・Program の参加者は４５％が非米国人。
・H1（労働）ビザは不要。
・日・独には研究所も多く、講義義務がないので、そういうところからは Program に参加しやすいのではないだろうか。
・Program の参加者のためのアパートとしては、２Bed Rooms + Common Kitchen などを使う。常に１室は余分に確保。他にレンタルハウス、下宿なども活用。下宿なら食事も作ってくれるメリットあり。
・ほかに West Cottage（と称する短期滞在型宿泊所？）を（たぶん）UCSB が持っている。２８室あり。
・参加者のアパートにスタッフが出向いて、書類を書かせることもある（細かい気配り)。金銭的なやりとり・交渉を手伝うことも必要。
・参加者の滞在は平均して４週間程度。
・所内各室には基本的に黒板を多く設置。理論家にとっては必須のアイテム。
・建物内部の色はオレンジを基調としている（暖色系：雰囲気つくり)。
・理論物理学者は、気分的には開放的な人が多い。
・午後３時頃にクッキータイム／日を設ける。このような場所にも黒板を置いている。
・そのほかにもピクニック、海水浴、共同晩御飯（割り勘)、ビアパーティなどの行事を多くして（１週間に一度くらい)、全員が溶け込む仕掛けを作っている。
・この意味では、格式ばった Gordon Conference とは違う。
・小規模の Discussion が非常に大事。２０名程度の参加者の Program ではこれが可能。この人数を超えると、「Social Dynamics」が変わってくる。

以上のような質疑で時間切れ。Conference のこと（ネットで、ある程度分かる）はあまり聞けなかったが、上記 Program が最重要と見える。

ほかに KITP の所謂 Outreach 活動としては、
Friends of KITP：　外から著名な学者を呼んで、一晩 Discussion など。
Public Lecture Series：年に３～４回。
Art, Image, Science：非専門家向けのアピール。物理と芸術との関連
Writers & Science：年に最大５カ月程度、科学ライターを呼ぶ。
High School Physics：年に１日、高校の先生を呼んで Conference を行う。
などがある。

田中の個人的感想：
・これまでの６名の所長のうち、３名がノーベル賞を受賞している。
・大きな研究ダイナミズムは、残念ながら日本の各研究所とはケタが違う感あり。
・それでもこのたび田中が訪問できていろいろな人が会ってくれたのは、福井センターのネームバリューによるのであろう（つまり福井センターにはそういう意味のステータスがある）。

福井謙一記念研究センター長　田中一義

平成２４年１０月１２日、１３日訪問
マックス・プランク固体化学物理学研究所（MPfS）:　Dresden 市にある。
MPfS = Max-Planck-Institut für Chemische Physik fester Stoffe

Liu-Hao Tjeng 所長（Managing Director）
・この人は在欧の中国人の２（あるいは３）世で、中国語は話せない。オランダで教育を受けている。ドイツ語・英語は当然堪能。専門は固体物理学で、無機物の分光学・強相関現象を研究。管理者というよりは、端正な学者のイメージを受ける。
・MPfS には４つの研究室があり、それを担当する４人の Permanent Member (Director) がいる。
・そのうち２名は固体化学、２名は固体物理学専門。この Director というのはマックス･プランク研究所（MPI）独特の呼称か。大学でいう Professor に相当。
・Director は、J. Grin 氏（固体化学）, C. Felser 氏（固体化学）, F. Steglich 氏（固体物理）, L.-H. Tjeng 氏（固体物理）の４名。通常は Prof. Dr.と呼ぶ。これは近隣の大学（Dresden 市内か）の教授をも兼ねていて(Honorary Professor)、学生（４回生、大学院生）を受け入れて研究をさせているため。
・大学での講義義務はない（Tjeng 氏はあった方がよいと少し思っている)。
・Director は人事管理と研究の両方を行う。(Tjeng 氏によると、例えば韓国の研究所ではスタッフ２００名くらいのところに Director１名という体制でやっているが、これでは人事管理が行き届かないと思うとのこと)
・MPfS にはもう一人くらい、固体理論専門の Director が欲しいと思っている。
・MPfS には約２００人が在籍し、Scientist, Technician, Assistant（秘書)、ポスドク、院生、学部生などを含む。Scientist は１００人以上。うちポスドクは４０名。院生（修士課程１０名、博士課程４０名の計５０名）と学部生は、ドレスデン市内の大学から預かっている。
・諮問委員（Scientific Advisory Board）は７名おり、うち４名がドイツ以外。
・予算は、基本的にドイツ国家が（90-95 %以上）保証していて恵まれており、財団申請などによる外部資金を積極的に取りに行くことは必要ない（テーマが合えば、取りに行くことがある程度)。
・MPfS 自身の自己資産はない。
・研究所の土地は州政府、建物はマックス・プランク協会(Max-Planck Gesellschaft; MPG)所有。
・各 MPI の Director の選考は、MPG が当該 MPI とは完全に独立した人事委

員会を作って行う（これが重要と強調していた）。
・世界的に興味深い研究施設があればすぐにそこに行って、測定をしたり共同研究を行っている。Director 自身が研究には大変アクティブである印象。Tjeng 氏も SPring 8 に測定に数週間来たり、広島大学（先端物質科学研究科：田中 新教授）と共同研究をしている。

資金の流れ

ドイツ連邦政府＋州政府（半々ぐらい出資）

↓ 年間１５億ユーロ＝約１６００億円

マックス・プランク協会(Max-Planck Gesellschaft; MPG)＠ミュンヘン

↓

ドイツ全国に８０ある研究所(MPI：合計約２６０名の Directors がいる)と、協会本部運営＋新しい研究所の計画などにすべて予算を配付。これによって各 MPI の人件費や研究費はほぼすべて賄える。

・ドイツ政府と MPG の間には強い関係がある。このことは非常に重要。
・産業の生産部門をドイツで持っていると高額である。ルーマニア等の賃金の安い国で行う方が遥かに効率がよい。従ってドイツでは、基本的な研究知見を貯める方が得策。ただし製品のデザイン的なプロセスは行う。
・博士一人を養成するのにかかる費用は膨大であり、これを多く輩出するのがドイツの国力に繋がる。
・以上のように、ドイツ国内で基礎科学を進展させることは国是でもあり、これが欧州不況のおりでも政府が MPG に大量に資金投下をする理由である。
（日本も見習うべきか）
・MPfS も基本的には無機固体物理の基礎研究がメイン。しかし無機固体化学の Director は企業と共同研究をして、特許などを取得することもある。
・MPfS と他研究機関との共同研究は平均９機関ぐらいと（Partner Group と呼称。ドイツ以外の国も多くある。日本では物材機構など。アジアでは中国、台湾、韓国の研究機関などとも展開)。
・ロシアからのポスドクは一人２～３年間滞在させている。彼らがロシアに帰国してからも、２～３万ユーロ／年を「仕送り」して、研究助成をしている。
・外国からの訪問研究者(Visitor)は MPI と契約をし、１年間くらい滞在できる

（実際に決裁するのは各 Director)。月２５００ユーロくらいを支給（近隣のアパートには月５００ユーロくらいで入れる)。
・近々、東大・理・物理の高木英典教授が Stuttgart の MPI の Director に着任される。
・対外活動としては、年４～５回のワークショップ開催、コンファレンス開催、ユーロスクール（若手院生向けか？）など。田中の滞在期間にも超伝導のワークショップ(LEMSUPER)が開かれていたので、勧められて部分的に出席した。
・社会へのアウトリーチ活動としては、ドレスデン市共催で、年に１回 Long Night of Science という催しを行っている（７月の第１金曜の夜の時から深夜まで)。これは MPfS だけではなく、在ドレスデンの大学・研究所がほぼすべて参加して、演示実験や科学イベントを行う。一般市民が３５００人程度参加。

参考：
ドイツには４つの協会があって、相補的に動いている。
① マックス・プランク協会(Max-Planck Gesellschaft)はほぼ基礎研究専一。
② フラウンホーファ協会（Fraunhofer Gesellschaft）（年間予算１２億ユーロ）は応用研究専門。起業向け。
③ ヘルムホルツ協会（Helmholtz Gemeinschaft）（年間予算２８億ユーロ）は工業化前段階の技術開発など。ここの機器設備は充実している。
④ ライプニッツ協会（Leibniz Gemeinschaft）は社会科学専門。

田中の個人的感想：
・自分自身にとっては全く初めてのマックス・プランク研究所(MPI)訪問であったが、その財務・管理・研究体制の大枠が理解できた。
・前回に訪問した米国 UCSB のカブリ理論物理学研究所とは全く異なった印象。ドイツの国力を感じさせる研究所で、恐らく他の MPI もこのようなイメージかと思える。
・改めて基礎研究の重要さに対する国家あげてのバックアップ精神の認識ができた感あり。「研究かくあるべし」
・この Tjeng 所長は大変研究好きな人であり、上記の話のほかに、無機物質の構造と磁性の関係、強相関現象、マルチフェロイック現象、多体効果、動的平均場理論、トポロジカル絶縁体、マヨラナ場、などの議論をいっぱいさせられた（かなりの時間を費やした)。これはあまり期待しなかったことであるが、良い頭の体操になりました。

福井謙一記念研究センター長　田中一義

平成２４年１１月２３日、２４日訪問
キャベンディッシュ研究所：　Cambridge 市にある。

総論：キャベンディッシュ研究所はケンブリッジ大学の物理学教室と１００％同じである。その意味で、通常の研究所の概念とは異なっており、むしろ大学の一学科と理解する方が当たっている。

なぜことさらに「キャベンディッシュ研究所」という名称を冠するかと言うと、当該物理学教室の発祥が 1871 年に H. Cavendish を記念して作られたキャベンディッシュ研究所（初代所長は J. C. Maxwell）にあるため、この名称を頑なに守っていることが理由である。

これまでに２９名のノーベル賞受賞者を輩出しており、このことを非常に誇りとしているように見える。なおすべてが物理学賞受賞者ではなく、Rutherford, Aston のように化学賞受賞者が６名、Watson, Crick のように医学・生理学賞受賞者が３名含まれていることは興味深い。

James Stirling 所長（Head of the Cavendish）

・上記の意味で、Stirling 所長は物理学教室の主任を兼ねている。この人の専門は高エネルギー物理学である。典型的な英国人紳士で好感が持てる。

・キャベンディッシュ研究所は 1871 年～1974 年まではケンブリッジ旧市内の中心部分にあったが、その後同市の西郊外の広大な牧草地近隣のキャンパスに移り、現在も建物を増築中である。しかしケンブリッジ旧市街中心地までは乗換なしの市バス１本で繋がっていて便利である。

・本研究所（学科）の研究スタッフは約１７０名（教員＋博士研究員）で、教員（教授、講師など）では約７０名が在籍している。その他事務スタッフ、技術スタッフが在籍。

学部学生は約１０００名（１年生４５０名、２年生２００名、３年生２００名、４年生１５０名）で、大学院には年間に６０～７０名が進学する。このうち英国外からの学生は約１０％であり、そのうちの半数は中国人学生でかなりよくできるが、彼らの主たる興味は Engineering 寄りである。なお日本人学生は非常に少ない。上記の学生数規模は、ちょうど本学の工学部工業化学科およびその上部の化学系専攻を合わせたものと似ているとも言える。

・本研究所（学科）の総予算は 2200 万ポンド／年（日本円で 28 億 6 千万円／年）であり、かなり潤沢と言える。その内訳は、学生からの授業料（一人 9000 ポンド／年（日本円で 117 万円／年））、私学としてのインフラ・人件費予算、

国(Research Council)からのプロジェクト研究費予算、さらに同窓会組織からの寄附などである。
・以前の Cambridge 大学生は物理学にあまり興味がなかったが、最近の国策および研究所自身のアウトリーチ活動（後述）の効果が出てきて、物理学をやりたい学生が増えてきている。なおご多分に漏れず、英国でも子供数が減ってきているので、今後良い素質を持つ物理学志望の学生獲得にはなお注力する予定とのこと。
・本研究所（学科）の物理学研究は多岐に亘るが、特色は、通常の物理学のほかに、宇宙物理学、高エネルギー物理学、薬理物理学、原子・メソスコピック・光物理学、および計算物理学などにある。薬理物理学を含むのは Watson, Crick などからの伝統、また原子系を含むのは化学的な Rutherford, Aston, Hodgkin, Klug などからの伝統であるらしい。
・９月に訪問した、米国カリフォルニア大学サンタバーバラ分校のカブリ理論物理学研究所と同じカブリ財団が寄与して作ったカブリ宇宙学(Cosmology)研究所もある（広大な敷地ならでは)。
・日本の日立や東芝ともコラボ研究契約を結んで研究室を設置し、前者とはマイクロエレクトロニクス・オプトエレクトロニクス、後者とは半導体物理学・量子情報理論の共同研究を展開している。
・高校生および高校教員に対して、Educational Outreach という高大連携活動を頻繁に実施していて、そのための専任スタッフを置いている(Lisa Jardine-Wright 博士)。年間６００名程度の高校生を受け入れて、物理学についての分かりやすい講義や体験実験を受講させるようにしている。また各高校への出前講義も行っている。これらのためのグッズ（パンフレットやテキストを始めとする種々のコンファレンスキットのようなものまで）も充実している。

田中の個人的感想：
・自分自身にとっては全く初めての Cavendish 研究所訪問であり、ケンブリッジ大学の物理学教室と同一であることや、その財務・管理・研究体制の大枠が理解できた。
・この意味では、これまでに訪問した米国 UCSB のカブリ理論物理学研究所やドイツのマックス・プランク研究所とは全く異なった印象であり、むしろ大学の一学科の運営方針の勉強になった面が強い。
・自然科学全般に関する英国の誇りと、その教育・研究持続のための具体例として Cavendish 研究所は充分興味深い意味を持つと思えた。
・特に優秀な研究者の予備軍としての高校生への物理学の啓蒙の徹底には瞠目

すべきものがあり、これぐらい積極的な高大連携をとるべきかと考えさせられた。

・田中自身が工学のなかの化学系所属であるということが、Stirling 所長には非常に奇異に映ったと見える。彼らのマインドからすると、恐らく工学は一段低いものであり、そこで化学をやっていることはあり得ないことのようである。かつて福井先生がノーベル賞をとられたときに、欧米の多くの研究者は福井先生の所属が理・物理であると思ったらしいことと一脈通じるものがある。

平成 25 年 3 月 6 日

台湾の研究機関との交流報告書

福井謙一記念研究センター国際連携研究室
石田俊正

平成 25 年 2 月 25 日から 27 日まで、当センター国際連携強化プロジェクトの一環として、台湾大学擬態科学研究中心・中央研究院原子與分子科学研究所・台湾交通大学分子科学研究所の３研究所で、将来の共同研究への可能性を探るために実験家との交流を行った。それぞれの英語名は、台湾大学擬態科学研究中心が Center for Condensed Matter Sciences, National Taiwan University、中央研究院原子與分子科学研究所が Institute of Atomic and Molecular Sciences, Academia Sinica、台湾交通大学分子科学研究所が Institute of Molecular Science, National Chiao Tung University である。今回の交流に際して、台湾大学擬態科学研究中心の林倫年研究員に仲介をお願いした。

1. 国立台湾大学擬態科学研究中心

林研究員から、台湾大学擬態科学研究中心に概略を説明いただいた。ファカルティメンバーは 12 名であり、林研究員を除いて、全員が実験研究を行っている。そのため、実験と理論研究の共同研究が盛んに行われている。3 人の実験研究員を紹介いただき、お話を伺うとともにディスカッションを行った。

(1) Juen-Kai Wang（王俊凱）研究員

研究分野は多岐で、基礎的な高速分光から、実用に近い有機太陽電池までにわたっている。

現在、実験からわからないこととして具体的に２つのことを提起された。一つは、有機太陽電池でのモーフォロジーの変化によって反応性がどのように変化するかについてである。（有機太陽電池では、ドナーとアクセプターが平面の境界面を構成せず、表面積を稼ぐため入り組んだ界面を構成する）

もう一つは、表面増強ラマン分光の実験において大腸菌 E. Coli によるピークがいくつか出現するが、そのピークが E. Coli のどの部分構造によるものかということであった。

どちらも応用に大きく結びついた実験に関連する解釈であり、よい共同研究ができれば、理論の価値が大きく高まる可能性があると思われる。

(2) F. C. Chou（周方正）研究員

スピンに興味をもつ固体物理の実験家。物理では、バンド計算が多用されているが、実験の解釈には、化学で使われている混成や共鳴などの概念が重要に思えると語っていた。混成・共鳴などの概念を周期系または固体の電子構造にどのような形で生かしうるかを知りたがっていた。

(3) Woei-Wu Pai（白偉武）研究員

走査プローブ顕微鏡を用いた表面の実験をしている。固体表面での反応に興味をもっているが、反応により周期性境界条件が成り立たなくなっているため、固体物理で用いるバンド計算を適用するのが難しいとのことであり、化学で用いるクラスター計算手法に興味を持っていた。

2. 中央研究院原子與分子科學研究所

台湾大学の中にあるが、大学とは別組織で政府直轄の研究所である。29 名のファカルティメンバーを有している。ファカルティには、台湾で唯一のノーベル賞受賞者である Yuan-She Lee(李遠哲)氏も特聘研究員(Distinguished Research Fellow)として名を連ねている。

(1) Kopin Liu（劉國平）特聘研究員

配向を制御した CDH_2 と Cl 原子との衝突実験から、配向の違いにより生成物が異なり、それが CD の振動励起、回転励起に依存することを見いだした最近の研究（Science, Nature Chemistry に掲載）、さらには、CH_4 と Cl 原子の場合、CDH_2+Cl とは全く異なる機構であることを見いだしたことを伺った。CH_4 と CDH_2 では、H と D の違いがあるだけだが、分子が正四面型から対象コマ分子に変化することで大きな変化が起こるようで理論の寄与が期待されるところである。

(2) Jim Jr-Min Lin（林志民）研究員

オゾン層破壊に関わる ClOOCl の関わる反応の分子線を使った精密実験のほか、いくつかの気相分子の反応の結果を伺った。実験室で研究内容の説明をいただき、実験装置（真空チェンバー、レーザー、装置構成）の説明もしていただいた。

(3) Chi-Kung Kenny Ni（倪其焜）教授

３つのテーマについてお話しいただいた。振動・回転エネルギーが運動エネルギーへ移行する過程の研究、水素結合の励起状態のポテンシャル面への影響の研究、MALDI(マトリックス支援レーザー脱離イオン化法)の機構の解明についてである。MALDI はノーベル賞を受賞した田中耕一氏の貢献が大きい手法であるが、機構に未解明なところが多かったのが Ni 教授らによって解明されつつあるとのことであった。

昼食をご一緒させていただいたが、日本の科学だけでなく、政治にも興味を持っておられるようで、最近できた第二次安倍政権のことをよく訊かれた。

(4)　高橋開人助研究員

専門は理論計算で、原子與分子科學研究所にどのような人がいてどのような研究が行われているかの話をしてくださった。理論家は 3 名で、ほかの 26 名は実験研究を行っているとのことであった。そののち、高橋助研究員自身の研究、$OH^-(H_2O)_n$ クラスターの構造の話等を伺った。

3.　国立交通大学分子科学研究所

国立交通大学に関しては、Yuan-Pern Lee（李遠鵬）応用化学科長が窓口になってくださり、実験研究者 3 名、理論研究者 3 名のお話を伺うとともに、ディスカッションを行った。分子科学研究所には、20 人のファカルティが所属している。Lee 教授には、車で駅まで迎えに来てくださった際、学内を車で案内くださった。交通大学は理科系中心の大学であり、日本で言うと東京工業大学に当たるような大学のようである。また、隣接して総合大学的な清華大学があり、そちらの方が一般的には有名である。しかし、最近の論文数などを示すグラフを用いて、最近は研究面で清華大学をしのぐ成果を分子科学研究所では出しているとの説明をしていただいた。（これは、あとで話を伺った中村教授によると、Lee 学科長のてこ入れによるものであるとのことであった。）この Lee 教授はノーベル賞受賞者の Yuan Tseh Lee 氏の弟に当たる。

(1)　Yuan-Pern Lee（李遠鵬）教授（応用化学科研究科長）

実験室を案内していただき、レーザー誘起蛍光を使ったラジカル種の動力学的研究、マトリックスの影響の非常に少ないスペクトルのとれる、パラ水素を使ったマ

トリックス単離実験、通常のフーリエ変換赤外分光と異なり高速な測定が可能な、ステップスキャン時間分解フーリエ変換法の説明とその応用を説明いただいた。

(2)　重藤真介副教授

水クラスター、ラマン顕微分光による細胞構造のイメージングの話を伺った。ラマン顕微分光では、波数成分に対して主成分分析のような手法を適用することにより、細胞の内部構造に特徴的なイメージングができることを見せていただき、個人的にとても印象的であった。

(3)　Eric, Wei-Guang Diau （刁維光）教授

実験も理論計算も行う研究者であるが、現在は色素増感太陽電池の実験を行っている。色素からの酸化チタン電極への電子移動に理論的な問題があり、取り組んでいるとのことであった。以前教授が行っていたアゾベンゼンの光異性化の計算についても意見を交換し、理論家と実験家の間で論争になっている点、すなわち、異性化の時に、ベンゼン環が平面に沿って動くか回転して動くかについて議論を行うことができて有意義であった。

ほかに、3 人の理論研究者と交流した。反応動力学が専門の中村宏樹教授は分子科学研究所長当時、特別推進研究を行い、石田も参加させていただいていた。同じく反応動力学が専門の Chaoyuan Zhu （朱超原）教授は以前からの知己であり、最近の研究成果を紹介いただいた。3 人目は、Sheng Hsien Lin （林聖賢）教授である。Lin 教授は計算機を使わず、密度行列に興味を持って純粋的な理論研究を行っている。

以上台湾の 3 研究所、台湾大学擬態科学研究中心・中央研究院原子與分子科学研究所・台湾交通大学分子科学研究所をまわっての印象は、いずれも実験研究者のレベルは、理論研究者とともに高く、国際連携研究にふさわしい研究所であるということである。今回の交流が今後の共同研究につながっていけば幸いである。

平成 25 年 3 月 6 日

ユトレヒト大学訪問

国際連携研究室 池野豪一

平成 25 年 2 月 18 日から 2 月 22 日の間, オランダにあるユトレヒト大学化学科, Debye ナノ材料科学研究センター，無機化学・触媒研究グループ (Inorganic Chemistry and Catalysis, Debye Institute for Nanomaterials Science, Utrecht University) の Frank de Groot 教授を訪問した. 今回の訪問の目的は国際連携機能強化プロジェクトの活動の一環として，将来的な共同研究の可能性を探ることにある．また，2 月 21，22 日の両日は同教授の呼び掛けにより，”Workshop on Fundamental Aspects of X-ray Spectroscopies: the role of the 2p core hole in XAS and RIXS (FXS2013)” が開催された．本ワークショップには主にヨーロッパ，アメリカの X 線分光実験，理論の研究者が集まり活発な議論が行われた．私も本ワークショップに参加し，各国の研究者と交流を行った.

Debye ナノ材料科学研究センター (Debye Institute for Nanomaterials Science)

同センターは 1936 年にノーベル化学賞を受賞したオランダ人物理化学者，Peter J. M. Debye の名を冠する研究センターであり，1989 年に設立された．同センターは化学科 (Department of Chemistry)，および物理・天文学科(Department of Physics & Astronomy)に属する 6 つの研究グループによって構成されている.

無機化学・触媒研究グループ

前述の Debye ナノ材料科学研究センターに属する研究グループの 1 つである. 同グループは Krijn de Jong 教授，Bert Weckhuysen 教授，Frank de Groot 教授 3 名のフルプロフェッサーが中心となり，パーマネント教員 5 名，技術職員 6 名，ポスドク 18 名，Ph.D 学生 40 名，他学部学生合わせて約 80 名からなる巨大な研究グループである．その名が表す通り，無機触媒の合成と特性評価，さらに分光法を用いた触媒反応プロセスの解析に関する研究を中心に行っている．研究資金はオランダ政府，EU からの競争的資金の他に, 石油エネルギー企業との共同研究プロジェクトを実施することで獲得しているとのこと.

Frank de Groot 教授

Frank de Groot 教授の専門は触媒科学ではなく，無機化学である．特に放射光を用いた X 線分光の分野においては世界をリードする研究者の一人であり, 世界各地の実験・

理論研究者と繋がりがある．無機化学・触媒グループにおいて，同教授のグループは少人数であるが, X 線分光を利用した触媒反応プロセスの解析に関する重要な役割を担っている．それ以外にも，X 線分光の理論の確立，新しい X 線分光実験の開発といった基礎的な研究も行っている．

―― 研究テーマについて ――

現在，Frank de Groot 教授のグループで行われている研究テーマについて伺った．

(1) X 線吸収分光(XAS)の理論解析

XAS は X 線と物質の相互作用により，内殻軌道から非占有軌道へ電子が遷移することに対応するスペクトルである，その解釈には量子論に基づく理論計算が欠かせない．同グループではスペクトル測定と同時に時間依存密度汎関数理論(TD-DFT)を用いたスペクトルの理論計算を行っている．3d 遷移金属化合物の L 端(2p→3d 遷移)や希土類元素の M 端(3d→4f 遷移)においては，強い電子相関をあらわに取り扱う必要がある．その場合には，配位子場理論に基づく半経験的な手法を用いた理論計算を利用している．

(2) 共鳴非弾性 X 線散乱(RIXS)法の開発

RIXS は，元素の吸収端に近いエネルギーの X 線で内殻の電子が励起させ，その緩和過程で放出される蛍光 X 線を分光する測定法である．遷移金属化合物においては，格子振動，d-d 遷移から内殻励起過程まで，硬 X 線を用いたでバルク敏感な測定が可能である．同グループでは，測定法とその解析理論の開発といった基礎的な研究，触媒科学への応用研究の両方を行っている．

(3) ナノ粒子の化学吸着過程の解析

遷移金属ナノ粒子の合成，および X 線分光と理論計算を利用したナノ粒子の電子状態の解析を行っている．化学吸着による電子状態の変化やナノ粒子のサイズ効果，合金効果について系統的な研究を行っているとこと．また，顕微 X 線分光を利用した化学吸着過程の動的観察も行っているとのこと．

(4) 走査型透過型 X 線顕微鏡(STXM)の開発

集光した X 線を走査プローブとして X 線吸収スペクトルの測定を行う方法で, 約 20nm の空間分解能で試料内部の化学種のマッピングが可能である. これまでに反応中の触媒のナノスケールイメージングに成功している．

―― 量子化学計算に対するニーズ ――

上記の研究テーマと別に X 線分光実験の研究者としての立場から，量子化学計算に対するニーズについてお話を伺った．

(1) 遷移金属化合物における XAS, RIXS の第一原理計算

配位子場理論に基づく半経験的計算は有用ではあるが，対称性の低い系や表面，界面といった系を解析するにはフィッティングパラメータが多くなり，解釈が困難となる問題がある．実際の原子構造と電子状態，スペクトルを直接結びつけることができる第一原理計算からのアプローチが望ましい．本テーマについては，池野と共同研究を実施しているが今後も継続することで合意した．

(2) 遷移金属錯体/遷移金属タンパク質の X 線分光と電子状態

複数原子からなる配位子を持つ遷移金属錯体において，中心金属の電子状態を X 線分光と理論計算から解明する．特に遷移金属のスピン状態や，配位子と金属原子間の電荷移動について関心があるとのこと．また遷移金属元素を含む金属タンパク質の電子状態について，幾つかの研究グループが測定を行っているが，理論計算はまだまだ不十分とのこと．

(3) 自由電子レーザー(FEL)を用いた励起状態の解明

分光用の X 線と同時にレーザー光を同時に入射させて行う XAS,RIXS 法が開発されている．通常の XAS, RIXS 測定において，遷移の始状態は系の基底状態であるが，レーザー光を照射することで，系を基底状態から励起させ，その準位を始状態としたスペクトルを測定することができる．しかし，スペクトルの解析には励起状態の高精度計算が必要となると考えられる．

(4) パルスレーザーを用いた分子のダイナミクス

測定方法としては(3)と類似のものである．分子に対し，フェムト秒パルスレーザーを入射し，時間分解のスペクトルを測定することで，分子のダイナミクス(解離，拡散，化学反応)を追跡することが目的とのこと．スペクトルの時間発展をシミュレートした計算ができるかどうか知りたいとのこと．

Pieter Glatzel (Dr.)

FXS2013 ワークショップ参加者の一人．現在はフランスのグルノーブルにある放射光施設, European Synchrotron Radiation Facility (ESRF), ID26 ビームライン責任者．Frank de Groot 教授とはよく共同研究を行っている．最近は．硬 X 線を用いた RIXS 実験を主に行っている. 講演内容は硬 X 線 RIXS の原理についての説明と最近の研究成果についてである．講演後他の理論研究者も交えて議論を交わした．特に物性物理で長年議論の対象となっている Ce 酸化物の価数について興味があるようで，RIXS 実験結果を理論的にどう解釈すれば良いか, 特に Ce の 4f 電子数はどうなっているのか知りたがっていた.

Amelie Juhin (Dr.)

FXS2013 ワークショップ参加者の一人．フランスのピエール・マリー・キュリー大学(パリ第 6 大学)の研究員．RIXS の磁気円二色性(MCD)の実験を行っている．MCD は磁化させた磁性体に左右偏光方向の異なる円偏光 X 線を用いて得られるスペクトルの差として定義され，磁気構造に関する情報が得られる．様々な Fe 化合物の RIXS-MCD 結果と sum-rule を用いた解析結果について話を伺った.

Philippe Wernet (Dr.)

FXS2013 ワークショップ参加者の一人. Helmholtz Zentrum Berlin (HZB)の研究員. HZB にある放射光施設 BESSY II で自由電子レーザーを利用した RIXS 測定から遷移金属を含む分子のダイナミクスの観察を行っている. 反応パスの解析を始めとする分子のダイナミクスに興味があるとのこと．遷移金属を含む分子の L2,3 端 XAS,RIXS の理論計算について相談を受けた.

Piter Miedema (Dr.)

FXS2013 ワークショップ参加者の一人．de Groot 教授の下で Ph.D を取得した．3d 遷移金属錯体の電子状態と触媒反応について研究を行っていた．現在はドイツの Helmholtz Zentrum Berlin (HZB)のポスドク研究員．HZB にある放射光施設 BESSY II で自由電子レーザーを利用した固体の RIXS 測定から物質の素励起過程を調べる研究を行っているとのこと．理論計算も自身で行っており，他の実験研究員からも良く相談を受けるとか. 使い易いインターフェイスを持った計算プログラムの重要性について語ってくれた.

Matti M. van Schooneveld (Ph.D 学生)

FXS2013 ワークショップ参加者の一人．de Groot 教授の学生で，ナノ粒子の合成と X 線分光を用いた解析に関する研究を行っている．現在の所属は Max Planck 研究所 (Mulheim)である．2 月 25 日ユトレヒト大学において学位論文の公聴会が開催されたとのこと．学位論文の内容から特に Co 化合物における RIXS の測定結果とその解釈について説明を受け，議論を交わした．Co ナノ粒子のスペクトルの第一原理計算について知りたがっていた．

Josh Vura-Weis (Dr.)

FXS2013 ワークショップ参加者の一人．アメリカ，UC Berkley のポスドク研究員．テーブルトップのパルス X 線源を開発し，低エネルギー(30-100eV)の光子を利用して X 線分光実験を行う装置を開発したとの説明を受けた．遷移金属化合物の $M_{2,3}$ 端(3p→3d 遷移)の測定結果について紹介された．その後，$M_{2,3}$ 端の理論解析をしたいとのことで，第一原理計算による計算について相談を受けた．

FXS2013 ワークショップにおいては，実験研究者の他，理論計算の専門家も多数集まっており，活発な議論が行われた．

池野の個人的感想：

近年の X 線分光実験の技術の進歩は目覚しいものがある．最近は，RIXS 法と自由電子レーザーを利用した励起状態，分子ダイナミクスの探索が流行っているようである．一方で，スペクトルを解析する理論計算手法の進展はまだまだこれから，といった印象である．理論面でのキーワードとしては，電子相関，巨大な活性空間，beyond Born-Oppenheimer 近似，フォノン，マグノン，電子・格子相互作用，巨大分子などが挙げられるであろうか．いずれも計算分野において挑戦的な内容であるが，同時に X 線分光のコミュニティにおいて量子化学研究者が貢献する余地は大いに存在すると感じた．実験研究者からのスペクトルの理論計算に関する要求は非常に強く，今回の訪問においても多数の実験研究者から同様の相談を受けた．研究対象となる物質についても理論研究者と共通する部分が多く，スムーズに共同研究を行うことができると期待される．

７．社会へのアウトリーチ活動紹介記事

出張講義

福井謙一記念研究センターでは出張講義を承っております。

現在の講師

諸熊奎治（リサーチリーダー）

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lecture@fukui.kyoto-u.ac.jp （@を@に変えて下さい）

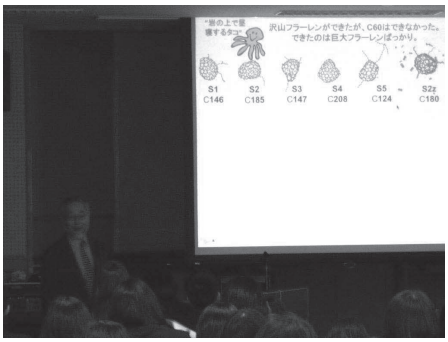
075-711-7708（事務室）

までお願いいたします。

コンピュータで化学反応の世界を探る

京都大学福井謙一記念研究センター　リサーチリーダー　諸熊奎治

福井謙一先生のフロンティア軌道理論が出て６０年経ちました。手回し計算機で化学反応の容易さを明らかにされた先生の慧眼には感嘆するばかりです。コンピュータの進歩によって今ではその１兆倍の速さで計算ができるようになり、化学反応がどのようにして起っているかを明らかにすることができるようになりました。60サッカーボール分子はどのように生成されるのか、触媒反応はどのように進むのか、クラゲの緑色蛍光タンパクはなぜ光るのかなど、化学反応が起る様子を、コンピュータを使って“眼で見たように”追跡したいと思います。



滋賀県立守山高等学校での講義風景

京都府立南陽高等学校での講義風景

諸熊奎治　略歴

京都大学福井謙一研究室出身。分子科学研究所、アメリカエモリー大学教授などを経て、平成１８年から福井謙一記念研究センターリサーチリーダー。

8．諸熊奎治シニアリサーチフェローに文化功労者の顕彰に関する記事

京都新聞　平成24年10月30日 夕刊

京都大福井謙一記念研究センターシニアリサーチフェロー

諸熊奎治さん

「人がしないことにチャレンジして道を開いてほしい」と若手研究者にエールを送る諸熊さん

理論・計算で本質に迫る

材料の反応設計などに用いる理論や計算手法を開発。「化学の本質に迫る基礎研究が、幅広く科学技術に寄与するようになった。多くの研究者の努力が認められた」といい、理論化学・計算化学への評価と受け止め、笑顔を見せる。

「見えないところで何が起こっているのか知りたかった」。化学反応に引かれ京都大工学部に入学。ノーベル化学賞を受賞する福井謙一教授の研究室で化学反応の計算に取り組んだ。

1964年に米国に留学。1万倍、10万倍の計算速度のコンピューターが使える米国の環境に魅了され、「1年で戻る予定が13年間いることになった」と振り返る。

今は世界最高水準のスーパーコンピューター「京」もあり、日米の環境に差はないが、「世界にはいろいろな発想を持った研究者がいる。刺激やエネルギーを受け取ってほしい」と、国内にとどまりがちな若手にエールを送る。

（梶井進）

文化功労者

朝尾直弘（あさお・なおひろ）京大名誉教授。日本近世史の分野、特に幕藩制前期の研究において、実証的で斬新な論稿を数多く発表。80歳。大阪府出身。京都市。

甘利俊一（あまり・しゅんいち）東大名誉教授。世界に先駆けて情報幾何学を創始し、神経回路網理論研究でも卓越した業績。76歳。東京都出身。東京都江東区。

安野光雅（あんの・みつまさ）画家・絵本作家。優れたイラストレーターとして、画期的な絵本や叙情性豊かな絵本を発表。86歳。島根県出身。東京都小金井市。

飯守泰次郎（いいもり・たいじろう）指揮者。日本を代表する指揮者として広く国内外で活躍し、オーケストラの育成に尽力。72歳。東京都出身。東京都港区。

大村智（おおむら・さとし）北里大名誉教授。数々の有用な微生物由来の生理活性物質を発見し、人類の健康に貢献。77歳。山梨県出身。東京都世田谷区。

岡野俊一郎（おかの・しゅんいちろう）日本サッカー協会最高顧問。豊富な競技経験と学識で、日本サッカーの隆盛の基礎を築いた。81歳。東京都出身。東京都文京区。

金子宏（かねこ・ひろし）東大名誉教授。日本で初めて課税要件中心の研究を推し進め、租税法を独立した法分野として体系化した。81歳。長野県出身。東京都文京区。

竹西寛子（たけにし・ひろこ）小説家・古典評論家。小説とエッセイ・論評で文筆活動を展開。長年にわたり優れた作品を数多く発表。83歳。広島県出身。川崎市。

辻井喬（つじい・たかし、本名堤清二＝つつみ・せいじ）詩人・小説家。時代と自らを厳しく見つめる優れた詩や小説を多数発表。85歳。東京都出身。東京都港区。

中路融人（なかじ・ゆうじん）日本画家。日展を中心に優れた作品を発表。後進の育成にも力を入れ、日本美術界の振興発展に寄与した。79歳。京都府出身。京都市。

西田篤弘（にしだ・あつひろ）宇宙科学研究所名誉教授。宇宙空間でのプラズマ物理現象の解明に数多くの業績を挙げた。76歳。三重県出身。東京都町田市。

松本幸四郎（まつもと・こうしろう、本名藤間昭暁＝ふじま・てるあき）俳優。歌舞伎やミュージカル、テレビドラマで活躍した。70歳。東京都出身。東京都港区。

別府輝彦（べっぷ・てるひこ）東大名誉教授。微生物利用学の領域に分子生物学的知見と手法を導入し、多様な研究成果を挙げた。78歳。東京都出身。東京都杉並区。

宮崎駿（みやざき・はやお）アニメ映画監督。「となりのトトロ」など優れたアニメ映画を次々に発表し、観客に感動を与えた。71歳。東京都出身。埼玉県所沢市。

諸熊奎治（もろくま・けいじ）京大福井謙一記念研究センターシニアリサーチフェロー。複雑分子系の理論研究の発展に多大な貢献。78歳。大阪府出身。京都市。

京大広報　2012.12　No. 684

朝尾直弘名誉教授，諸熊奎治福井謙一記念研究センターシニアリサーチフェローが文化功労者に選ばれる

このたび，朝尾直弘名誉教授，諸熊奎治 福井謙一記念研究センターシニアリサーチフェロー(研究員(学術研究奨励))が平成24年度文化功労者に選ばれ，11月5日(月)に東京都内で顕彰式が行われた。以下に各氏の略歴，業績等を紹介する。

諸熊奎治福井謙一記念研究センターシニアリサーチフェロー(研究員(学術奨励))は，昭和32年3月京都大学工学部を卒業，同34年3月同大学大学院工学研究科修士課程修了，同37年3月同大学大学院工学研究科博士課程単位取得退学(同38年3月修了，工学博士の学位授与)，同37年4月から同41年5月まで同大学工学部助手，その後米国のコロンビア大学，ハーバード大学，ロチェスター大学での勤務等を経て，同51年12月分子科学研究所教授，同56年4月改組により岡崎国立共同研究機構分子科学研究所教授，平成5年1月から米国エモリー大学教授，同18年9月京都大学福井謙一記念研究センターリサーチリーダー，次いで同24年4月に同センターのシニアリサーチフェローに就任し，現在に至っている。この間，平成5年4月岡崎国立共同研究機構分子科学研究所名誉教授，同7年4月総合研究大学院大学名誉教授，同18年9月米国エモリー大学名誉教授の称号を授与された。さらに平成12年より国際量子分子科学アカデミー会長を2期6年間にわたって務められた。

同シニアリサーチフェローは永年にわたって世界的なスケールで理論化学・計算化学の教育と研究に努められ，また教育研究関係の人材育成を行ってきた。特に分子の電子論とその複雑分子系の構造，反応，機能の理論的研究の世界的権威としてこの分野の発展に多大で重要な貢献をされており，以上の功績によって昭和53年にInternational Academy of Quantum Molecular Science (IAQMS) Medal，平成4年に日本化学会賞，同5年にThe World Association of Theoretical Organic Chemists (WATOC)からThe Schrödinger Medal，同17年にAsian Pacific Association of Theoretical & Computational ChemistsからThe Fukui Medal，同20年に恩賜賞，日本学士院賞，さらに同22年に瑞宝中綬章を受けられた。

これらに続いて今回の文化功労者の顕彰を受けられたことは誠に喜ばしい。

(福井謙一記念研究センター)

(京大広報　No.684　2012.12より転載)

諸熊奎治先生文化功労者顕彰祝賀会

ご承知のように、諸熊奎治先生（現 京大福井謙一記念研究センター シニアリサーチフェロー、分子研名誉教授）におかれましては、この度、平成24年度文化功労者の顕彰を受けられました。

諸熊先生は、昭和32年京都大学工学部工業化学科をご卒業後、同大学院工学研究科燃料化学専攻博士課程を経て、同大学工学部燃料化学科福井謙一先生の研究室に助手として採用され、同38年に京都大学より工学博士の学位を授与されました。昭和39年米国コロンビア大学客員助教授、博士研究員、ハーバード大学博士研究員、ロチェスター大学助教授、准教授を経て、昭和46年から同大学教授に昇進されました。同51年には分子科学研究所教授に着任され、強力な研究グループを直ちに立ち上げられると共に、同研究所計算センター長を兼務され、我国の理論化学・計算化学の発展に多大な功績を残されました。平成5年より米国エモリー大学教授に転じられ、化学科教授、チェリー・エマーソン科学計算センター長としてご活躍の後、平成18年には京都大学福井謙一記念研究センターにリサーチリーダーとして着任され、本年度からはシニアリサーチフェローとして、現在も活発な研究活動を展開していらっしゃいます。この間、平成12年より国際量子分子科学アカデミー会長を二期六年間に渡って務められ、文字通り世界レベルで量子化学、理論・計算化学の発展に大きな足跡を残してこくられました。

今回の文化功労者のご栄誉は、諸熊先生の永年にわたる「複雑分子系の理論研究の発展に対する多大な貢献」に対するもので、量子化学および統計力学に基づく理論化学・計算化学における世界的な業績が認められたものでございます。先生は独創的な考えにより、新しい理論的方法を開発・提案され、それに基づいて理論化学・計算化学を力強く推進され、分子の構造・機能、化学反応過程の微視的理解と予測を達成されました。これらのご研究に対し、平成4年日本化学会賞、平成5年世界理論有機化学会のシュレーディンガーメダル、平成17年アジア・太平洋理論および計算化学会の福井メダル、平成20年恩賜賞・日本学士院賞、平成22年瑞宝中綬章のご受賞に続く、今回の文化功労者のご栄誉は、私ども福井謙一記念研究センターにとりましても、大変喜ばしいことでございます。

諸熊奎治先生のご受賞にあたってのお言葉

「このたび、文化功労者に選ばれましたことは、大変名誉なことであります。今までご支援いただきました国内外の多くの方々に心から感謝申し上げます。50年間励んできた理論化学・計算化学という基礎研究の分野が、多くの研究者の努力によって、化学結合の本質を明らかにするにとどまらず、化学の幅広い問題の解決に役立つとともに、科学技術にも大きな寄与をするようになったことは、大変喜ばしいことであります。これからも研究者として、基礎研究を通じて社会のために尽くしたいと思います。」

日時：平成25年4月13日(土)
　　午後4時 諸熊先生記念講演会
　　午後5時 記念写真撮影
　　午後5時半 祝宴開始
場所：京都ブライトンホテル 京都市上京区新町通中立売（御所西）
　　ご招待状を2月上旬にお送り申し上げます。
　　（届かなかった場合やご住所変更の場合は、センター事務室へご連絡頂ければ幸いです。）

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