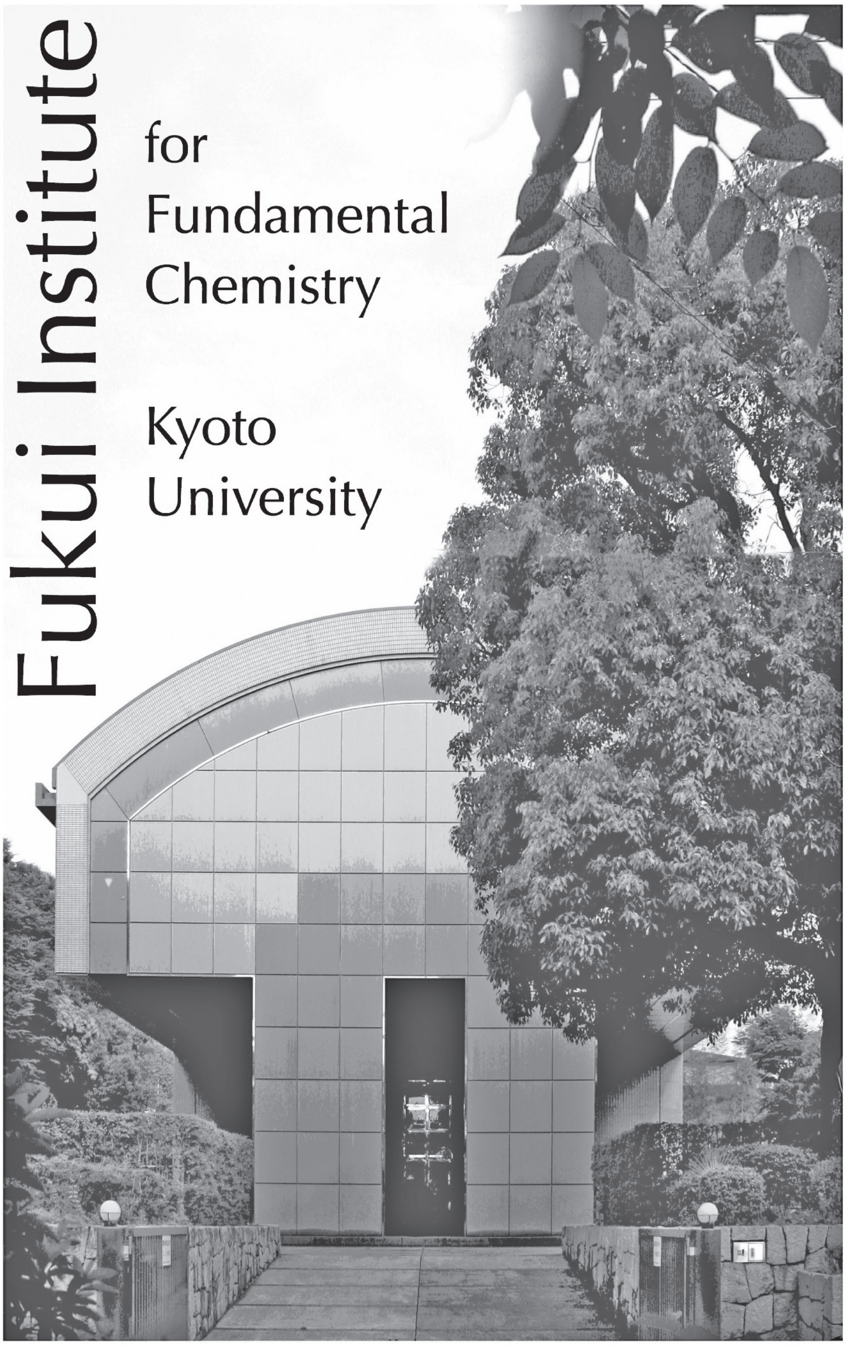
京都大学
福井謙一記念研究センター

Annual Report 2010

Fukui Institute for Fundamental Chemistry Kyoto University

年　報
2010



京都大学
福井謙一記念研究センター

はじめに

2010 年度 (平成 22 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．当センターは，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，2 名の副センター長と 10 名の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．この博士研究員のうち 9 名はセンターの雇用で，福井センターフェローと呼ばれ，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．また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 8 名の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（2011 年 (平成 23 年)11 月現在). 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，大峯巖先生は 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．

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方々が京都大学准教授，名古屋大学教授，Tartu 大学 (エストニア共和国) 教授，神戸大学准教授，分子科学研究所助教 (3 名)，Illinois 工科大学客員助教，早稲田大学准教授，九州大学助教，Northwestern 大学研究員等として活躍されております.

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．京都大学の部局となった後，森島 績，中辻 博，榊 茂好各先生にセンター長としてご指導を頂きました．

当センターは，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．日本学術振興会・若手研究者交流支援事業として，タイ，シンガポール，ベトナム ，マレーシア，フィリピンの東アジア首脳会議参加国からの若手研究者招聘，ベルギーおよびロシアとの2国間共同研究も行っております．当センターは，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，国際協力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，なら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．

当センターは，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，当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，当センターの順調な活動も，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23年11月

京都大学福井謙一記念研究センター長

田中　功

目　　　次

資料

（本冊子は下記アドレス（URL）にて、ウェブ上でも閲覧いただけます。
http://www.fukui.kyoto-u.ac.jp/publication/AnnualReport2010.pdf ）

Ⅰ専任教員・スーパーバイザー

1．教員組織

平成 22 年度

職名		氏名	備考
センター長		田中 功	工学研究科材料工学専攻
総合研究部門	副センター長	今堀 博	物質－細胞統合システム拠点 （工学研究科分子工学専攻）
理論研究部門	副センター長	太田 隆夫	理学研究科物理学・宇宙物理学専攻
協議員	工学研究科長	小森 悟	工学研究科機械理工学専攻
	理学研究科長	吉川 研一	理学研究科物理学・宇宙物理学専攻
	化学研究所長	時任 宣博	化学研究所物質創製化学研究系
総合研究部門 スーパーバイザー	教授	赤木 和夫	工学研究科高分子化学専攻
	教授	田中 勝久	工学研究科材料化学専攻
	教授	佐藤 直樹	化学研究所複合基盤化学研究系
	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	吉川 研一	理学研究科物理学・宇宙物理学専攻
理論研究部門 スーパーバイザー	教授	谷村 吉隆	理学研究科化学専攻
	教授	田中 一義	工学研究科分子工学専攻
	教授	山本 量一	工学研究科化学工学専攻
	准教授	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
総合研究部門	准教授	石田 俊正	専任 （工学研究科合成・生物化学専攻協力講座）
理論研究部門	准教授	佐藤 徹	専任：平成 16. 3. 1 － 22. 12. 31 （工学研究科分子工学専攻協力講座）
	准教授	中尾 嘉秀	専任：平成 23. 1. 1 － （工学研究科分子工学専攻協力講座）
福井謙一記念 研究部第一	リサーチ リーダー	諸熊 奎治	研究員（学術研究奨励）
	特定助教 （白眉）	前田 理	次世代研究者育成センター
福井謙一記念 研究部第二	リサーチ リーダー	（欠員中）	

２．教員プロフィール

（1）センター長

【氏名（ふりがな）】	田中　功　（たなか　いさお）
【職名】	センター長、教授
【所属】	工学研究科　材料工学専攻
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【研究分野】	材料科学
【現在の研究課題】	セラミックス基礎科学，計算材料科学
【研究内容キーワード】	量子材料設計，第一原理計算，電子ｴﾈﾙｷﾞｰ損失分光，Ｘ線吸収分光
【最終学歴】	1987年3月　大阪大学大学院基礎工学研究科物理系専攻博士後期課程修了
【学位】	1987年3月　大阪大学工学博士
【略歴】	1987年4月　日本学術振興会特別研究員(PD)、1987年6月大阪大学産業科学研究所・助手、1993年4月京都大学工学部・助手、1996年5月京都大学大学院エネルギー科学研究科・助教授、2001年7月京都大学大学院工学研究科・助教授、2003年12月京都大学大学院工学研究科・教授
【在外研究歴】	1992年4月-1993年3月　ドイツ マックスプランク金属研究所・客員研究員（アレキサンダー・フォン・フンボルト財団奨学研究員）
【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
【学会活動】	*Journal of American Ceramics Society* フェロー・編集委員、*World Academy of Ceramics* 会員、*Journal of Physics : Condensed Matter* 編集委員、日本金属学会評議員
【主な著書、学術論文】（過去5年以内）	1. A. Seko, F. Oba, I. Tanaka, Classification of spinel structures based on first-principles cluster expansion analysis, *Phys. Rev. B* **81** (2010) 054114 2. A. Matsumoto, Y. Koyama, I. Tanaka, Structures and energetics of Bi_2O_3 polymorphs in a defective fluorite family derived by systematic first-principles lattice dynamics calculations, *Phys. Rev. B* **81** (2010) 094117 3. M. Choi, F. Oba, I. Tanaka, Role of Ti Antisitelike Defects in SrTiO3, *Phys. Rev. Lett*. **103** (2009) 185502 4. First-principles investigation of atomic structures and stability of proton-exchanged layered sodium titanate M. Mori, Y. Kumagai, K. Matsunaga, and I. Tanaka, *Phys. Rev. B* ,**79** (2009) 144117 5. W. Olovsson, I. Tanaka, T. Mizoguchi, P. Puschnig, and C. Ambrosch-Draxl, All-electron Bethe-Salpeter calculations for shallow-core x-ray absorption near-edge structures *Phys. Rev. B* **79**, (2009) 041102. 6. K. Yuge, A. Seko, Y. Koyama, F. Oba, and I. Tanaka, First-principles-based phase diagram of the cubic BNC ternary system *Phys. Rev. B* **77**, (2008) 094121 7. I. Tanaka and F. Oba, First principles calculations for modern ceramic science and engineering *J. Phys: Condens. Matter* **20**, (2008) 064215 8. A. Seko, A. Togo, F. Oba, and I. Tanaka, Structure and stability of a homologous series of tin oxides *Phys. Rev. Lett.* **100,** (2008) 045702
【学術関係の受賞】	ドイツ政府　フィリップ･フランツ･フォン･シーボルト賞（2008年） ルーマニア科学アカデミー　ドラゴミール・フルムゼスコ賞（2006年） 米国セラミックス学会 リチャード・フルラース賞（2004年）

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【研究分野】	有機化学・光化学
【現在の研究課題】	人工光合成・有機太陽電池・ドラッグデリバリー
【研究内容キーワード】	ポルフィリン・フラーレン・ナノチューブ・自己組織化・電子移動
【最終学歴】	1990年3月　京都大学大学院理学研究科博士後期課程修了
【学位】	1990年3月　理学博士（京都大学）
【略歴】	1990年4月米国ソーク生物学研究所博士研究員、1992年4月大阪大学産業科学研究所助手、1999年11月大阪大学大学院工学研究科助教授、2001年12月科学技術振興機構さきがけ研究代表者（兼任）、2002年2月京都大学大学院工学研究科教授、2002年9月京都大学福井謙一記念研究センタースーパーバイザー（兼任）、2007年10月京都大学物質－細胞統合システム拠点教授
【所属学会】	日本化学会、光化学協会、米国化学会、米国電気化学会
【主な著書、学術論文】（過去5年以内）	1. T. Sagawa, S. Yoshikawa, and H. Imahori, “1-D Nanostructured Semiconducting Materials for Organic Photovoltaics,” *J. Phys. Chem. Lett*. (Perspective), **1**, 1020-1025 (2010). 2. H. Imahori, T. Umeyama, and S. Ito, “Large π Aromatic Molecules as Potential Sensitizers in Dye-Sensitized Solar Cells,” *Acc. Chem. Res.* **42**, 1809-1818 (2009). 3. Y. Matano and H. Imahori, “Phosphole-Containing Calixpyrroles, Calilxphyrins, and Porphyrins: Synthesis and Coordination Chemistry,” *Acc. Chem. Res.* **42,** 1193-1204 (2009). 4. H. Imahori, T. Umeyama, “Donor-Acceptor Nanoarchitecture on Semiconducting Electrodes for Solar Energy Conversion,” *J. Phys. Chem. C* (Feature Article), **113**, 9029-9039 (2009). 5. A. Kira, T. Umeyama, Y. Matano, K. Yoshida, S. Isoda, J.-K. Park, D. Kim, H. Imahori, “Supramolecular Donor-Acceptor Heterojunctions by Vectorial Stepwise Assembly of Porphyrins and Coordination-Bonded Fullerene Arrays for Photocurrent Generation,” *J. Am. Chem. Soc.*, **131**, 3198-3200 (2009).
【学術関係の受賞】	1. 2004年光化学協会賞 2. 2006年日本学術振興会賞 3. 2006年日本化学会学術賞 4. 2007年東京テクノ・フォーラム21ゴールド・メダル賞 5. 2007年大阪科学賞 6. 2007年ナイスステップ研究者

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【現在の研究課題】	非平衡ソフトマター物理学
【研究内容キーワード】	高分子共重合体・ミクロ相分離・共連結構造・パターン形成
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【学位】	1977年1月　理学博士（京都大学
【略歴】	1979年7月九州大学理学部助手、1987年8月お茶の水女子大学理学部助教授、1991年1月お茶の水女子大学理学部教授、1999年4月広島大学大学院理学研究科教授、2004年1月京都大学基礎物理学研究所教授、2006年7月京都大学大学院理学研究科教授
【在外研究歴】	1978年9月-1979年6月　米国Pittsburgh大学物理（David. Jansnow教授）（Mellon財団研究員）
【所属学会】	日本物理学会、中性子科学会、数理生物学会
【学会活動】	JPSJ Head Editor
【主な著書、学術論文】（過去5年以内）	1. T. Ohkuma and T. Ohta, Deformable self-propelled particles with a global coupling, *Chaos* **20**, 023101(1-13) (2010) 2. T. Hiraiwa and T. Ohta, Viscoelasticity of a Single Semiflexible Polymer Chain, *Macromolecules* **42**, 7553-7562 (2009) 3. T. Ohta, T. Ohkuma and K. Shitara, Deformation of a self-propelled domain in an excitable reaction-diffusion system, *Phys. Rev*. **E 80**, 056203 (2009) 4. T. Sakaue and T. Ohta, Probing Nonequilibrium Fluctuations through Linear Response, *Phys. Rev.* **E 77**, 050102R (2008) 5. Y. Tonosaki, H. Tokuda, V. Zykov and T. Ohta, Phase Dynamics for Nonlinear Dissipative Waves under Symmetric Feedback, *Europhysics Letters* **83** 50011-1-6 (2008) 6. R. Tamate, K. Yamada, J. Vinals, and T. Ohta, Structural rheology of microphase separated diblock copolymers, *J. Phys. Soc. Jpn.*,**77** 034802 (2008) 7. M. Yanagisawa, M. Imai, T. Masui, S. Komura, Takao Ohta, Growth Dynamics of Domains in Ternary Fluid Vesicles, *Biophysical Journal* **92**, 115-125 (2007) 8. H. Shoji, K. Yamada, D. Ueyama and Takao Ohta, Turing patterns in three dimensions, *Phys. Rev.* **E 75**, 046212(13) (2007)
【学術関係の受賞】	アレキサンダー・フォン・フンボルト賞（2008年）

(3) スーパーバイザー

【氏名（ふりがな）】	赤木　和夫　（あかぎ　かずお）
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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 18th Iketani Conference, International Conference on Control of Super-Hierarchical Structures and Innovative Functions of Next-Generation Conjugated Polymers (2008)、Chair of International Conference on Science and Technology of Synthetic Meatals (2010)
【主な著書、学術論文】（過去5年以内）	1. H. Hayasaka, T. Miyashita, K. Tamura, K. Akagi, "Helically π-Stacked Conjugated Polymers Bearing Photoresponsive and Chiral Moieties in Side Chains: Reversible Photoisomerization-Enforced Switching between Emission and Quenching of Circularly Polarized Fluorescence", *Adv. Func. Mater.*, **20**, 1243 (2010). 2. M. Goh, G. Piao, M. Kyotani, K. Akagi, "Cis-Rich Helical Polyacetylene Synthesized in Low-Temperature Chiral Nematic Liquid Crystal", *Macromolecules*, **42**, 8590 (2009). 3. K. Akagi, "Helical Polyacetylene - Asymmetric Polymerization in a Chiral Liquid Crystal Field", *Chem. Rev*., **109**, 5354 (2009). 4. T. Mori, T. Sato, M. Kyotani, K Akagi, "Macroscopically Aligned Helical Conjugated Polymers in Orientation-Controllable Chiral Nematic Liquid Crystal Field", *Macromolecules*, **42**, 1817 (2009). 5. M. Kyotani, S. Matsushita, T. Nagai, Y. Matsui, M. Shimomura, A. Kaito. K. Akagi, "Helical Carbon and Graphitic Films Prepared from Iodine-Doped Helical Polyacetylene Film using Morphology-Retaining Carbonization", *J. Am. Chem. Soc.*, **130**, 10880 (2008). 6. M. Goh, M. Kyotani, K. Akagi, "Highly Twisted Helical Polyacetylene with Morphology Free From Bundle of Fibrils Synthesized in Chiral Liquid Crystal Reaction Field", *J. Am. Chem. Soc.*, **129**, 8519 (2007).
【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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【研究分野】	無機固体化学
【現在の研究課題】	酸化物薄膜および非晶質酸化物の磁気的性質・表面プラズモンを利用した光機能材料の作製
【研究内容キーワード】	酸化物、薄膜、非晶質、表面プラズモン、磁気的性質、光学的性質
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【所属学会】	日本セラミックス協会、日本化学会、応用物理学会、日本物理学会、粉体粉末冶金協会、日本材料学会、Materials Research Society、Optical Society of America
【学会活動】	粉体粉末冶金協会 理事、日本材料学会 理事
【主な著書、学術論文】（過去5年以内）	1. Y. Hasegawa, T. Adachi, A. Tanaka, M. Afzaal, P. O’Brien, T. Doi, Y. Hinatsu, K. Fujita, K. Tanaka, and T. Kawai, “Remarkable Magneto-Optical Properties of Europium Selenide Nanoparticles with Wide Energy Gaps”, *Journal of the American Chemical Society* **130** (2008) 5710-5715. 2. 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. 3. 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. 4. 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. 5. 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.
【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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【研究内容キーワード】	有機半導体・有機薄膜・分子集合体・電子分光・界面物性・分子系構築
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【在外研究歴】	1989年5月-7月 スウェーデンLinköping大学物理学科（William R. Salaneck教授）（Visiting Scholar）
【所属学会】	日本化学会、日本物理学会、日本分光学会、分子科学学会
【学会活動】	日本化学会有機結晶部会長、日本化学会有機結晶ディビジョン主査、分子科学会運営委員
【主な著書、学術論文】（過去5年以内）	1. H. Yoshida, K. Inaba and N. Sato, X-ray diffraction reciprocal space mapping study of the thin film phase of pentacene, *Appl. Phys. Lett.* **90** (2007) 181930. 2. H. Yoshida and N. Sato, The crystallographic and electronic structures of three different polymorphs of pentacene, *Phys. Rev. B* **77** (2008) 235205. 3. R. Murdey, M. Bouvet, M. Sumimoto, S. Sakaki and N. Sato, Direct observation of the energy gap in lutetium bisphthalocyanine thin films, *Synth. Met.* **159** (2009) 1677-1681. 4. T. Hiramatsu, H.Yoshida and N. Sato, Solvent-dependent strutural and electronic behaviors of a push-pull molecule: {4-[4,5-bis(methylsufanyl)-1,3-dithiol-2-ylidene] cyclohexa-2, 5-dien-1-ylidene} malononitrile, *J. Phys. Chem. A* **113** (2009) 9174-9179. 5. J. Tsutsumi, H. Yoshida, R. Murdey, S. Kato and N. Sato, An accurate calculation of electronic contribution to static permittivity tensor for organic molecular crystals on the basis of the charge response kernel theory, *J. Phys. Chem. A* **113** (2009) 9207-9212. 6. J. Tsutsumi, H. Yoshida, R. Murdey and N. Sato, Decay mechanism of spontaneously built-up surface potential in a thin film of a zwitterionic molecule having noncentrosymmetric crystal structure, *J. Phys. Chem. C.* **115** (2011) 2356-2359. 7. H. Yoshida and N. Sato, The depth profile of core energy levels: Electronic structure of buried organic/metal interface examined by X-ray photoemission and target factor analysis, *Chem. Phys. Lett.* **511** (2011) 146-150.
【学術関係の受賞】	1985年4月日本化学会（第34回）進歩賞受賞

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【研究分野】	錯体化学、無機化学
【現在の研究課題】	新規多孔性材料の開拓とその応用
【研究内容キーワード】	多孔性配位高分子、金属有機構造体、光機能、超分子構造
【最終学歴】	1979年3月　京都大学大学院石油化学専攻博士課程修了
【学位】	1979年7月　工学博士（京都大学）
【略歴】	1979年4月近畿大学理工学部助手、1983年4月近畿大学理工学部講師、1988年4月近畿大学理工学部助教授、1992年4月東京都立大学理学部化学教室無機化学第一講座教授、1998年6月京都大学大学院工学研究科合成・生物化学専攻教授、2007年10月京都大学物質-細胞統合システム拠点・副拠点長および京都大学大学院工学研究科合成・生物化学専攻（兼任）教授
【在外研究歴】	1986年-1987年Texas A&M大学 Cotton研究室博士研究員
【所属学会】	日本化学会、錯体化学会、物理学会、高分子学会、米国学会
【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. "Selective sorption of oxygen and nitric oxide by an electron-donating flexible porous coordination polymer", S. Shimomura, M. Higuchi, R. Matsuda, K. Yoneda, Y. Hijikata, Y. Kubota, Y. Mita, J. Kim, M. Takata and S. Kitagawa, *Nature Chemistry,* **2010**, 2, 633-637. 3. "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. (Highlighted in News & Views in the same issue.).
【学術関係の受賞】	1. 2002年第19回日本化学会学術賞 2. 2007年Earl L. Muetterties Memorial Lectureship (University of California, Berkeley) 3. 2007年平成19年度錯体化学会賞 4. 2008年Humboldt Research Award, Germany 5. 2009年第61回日本化学会賞 6. 2010年トムソン・ロイター引用栄誉賞受賞 7. 2011年平成23年度科学技術分野の文部科学大臣表彰研究部門 8. 2011年平成23年度春の紫綬褒章受章

【氏名（ふりがな）】	吉川　研一　（よしかわ　けんいち）
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【研究分野】	非線形科学・生命物理学
【現在の研究課題】	1）非平衡開放系での時間的・空間的秩序の自発的生成に関する研究 2）生命現象の物理学
【研究内容キーワード】	非平衡開放系・時空間的秩序の自己生成・自己組織化・高分子物理学
【最終学歴】	1976年5月　京都大学大学院工学研究科博士課程修了
【学位】	1976年5月　工学博士（京都大学）
【略歴】	1976年10月徳島大学教養部講師、1979年4月徳島大学教養部助教授、1988年4名古屋大学教養部助教授、1990年11月名古屋大学教養部教授、1991年4月名古屋大学大学院人間情報学研究科教授、1998年4月京都大学大学院理学研究科教授、2002年9月京都大学福井謙一記念研究センター兼任教授（現在に至る）、1998年10月～1999年6月Universite Louis Pasteur 客員教授、2009年2月 ENS, Paris 客員教授
【在外研究歴】	長期のものはなし
【所属学会】	物理学会、日本化学会、生物物理学会など
【学会活動】	Vice Chair, Commission C-6, International Union of Pure and Applied Physics など
【主な著書、学術論文】（過去5年以内）	1. M.Horning, A.Isomura, K.Agladze, K.Yoshikawa, “Liberation of a pinned spiral wave by a single stimulus in excitable media”, *Phys. Rev. E,* 79, 026218(2009). 2. T.Saito, T.Iwaki, K.Yoshikawa, “Small anion with higher valency retards the compaction of DNA in the presence of multivalent cation”, *Biophys. J.*, 96, 1068(2009). 3. A. Estevez, C. Crozatier, A. Diguet, T. Hara, H. Saito, K. Yoshikawa and D. Baigl, “ Sequence-independent and reversible photocontrol of transcription/expression systems using a photosensitive nucleic acid binder”, *Proc.Natl.Acad. Sci.*, 106, 12219(2009). 4. M. Negishi, T. Sakaue and K. Yoshikawa,” Mismatch of bulk viscosity reduces interfacial diffusivity at an aqueous/oil system”, *Phys. Rev. E*, 81, 020901(2010). 5. M. Takinoue, Y. Atsumi and K. Yoshikawa, “Rotary motion driven by a direct current electric field”, *Appl. Phys. Lett.*, 96, 104105(2010).
【学術関係の受賞】	日本IBM科学賞（1991）

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【最終学歴】	Keio University
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【所属学会】	Japanese Physical Soc, American Physical Soc, 日本化学会、American Chemical Soc.
【学会活動】	2002-2004 日本物理学会理事
【主な著書、学術論文】（過去5年以内）	1. A. G. Dijkstra and Y. Tanimura, *Correlated fluctuations in the exciton dynamics and spectroscopy of DNA,* New J. of Phys. **12**, 055005 (19pages) (2010). 2. M. Tanaka and Y. Tanimura, *Multistate Electron Transfer Dynamics in the Condensed Phase: Exact Calculations from the Reduced Hierarchy Equations of Motion Approach,* J. Chem. Phys. **132,** 214502 (11pages) (2010) 3. A. G. Dijkstra and Y. Tanimura, *Non-Markovian entanglement dynamics in the presence of system-bath coherence,* Phys. Rev. Lett **104,** 250401 (4 pages) (2010). 4. A. Sakurai and Y. Tanimura, *Does hbar play a role in multidimensional spectroscopy? Reduced hierarchy equations of motion approach to molecular vibrations,* J. Phys. Chem. A **115**, 4009-4022 (2011) 5. T. Hasegawa and Y. Tanimura, *A polarizable water model for intramolecular and intermolecular vibrational spectroscopies,* J. Phys. Chem. B **115**, 5545-5553(2011).
【学術関係の受賞】	Morino Foundation Humboldt Research Award

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【研究分野】	物理化学・量子化学
【現在の研究課題】	分子ナノ工学、量子機能化学
【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
【最終学歴】	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. 分子エレクトロニクスの基盤技術と将来展望（共監修および共著, シーエムシー出版, 2009） 2. 物理化学（化学マスター講座）（共著, 丸善, 2010） （以上著書） 1. A. Ito, Y. Nakano, M. Urabe, T. Kato, and K. Tanaka, “Triradical Cation of p-Phenylenediamine Having Two Nitroxide Radical Groups: Spin Alignment Mediated by Delocalized Spin”, *J. Am. Chem. Soc.,* **128,** 2948-2953 (2006). 2. Y. Hirao, M. Urabe, A. Ito, and K. Tanaka, “Intramolecular Spin Transfer in a Spiro-Fused Bis(triarylamine)”, *Angew. Chem., Int. Ed.,* **46**, 3300-3303 (2007). 3. A. Ito, Y. Yamagishi, K. Fukui, S. Inoue, Y. Hirao, K. Furukawa, T. Kato, and K. Tanaka, “Trimacrocyclic Arylamine and Its Polycationic States”, *Chem. Commun.*, **2008**, Issue 48 (December 28), 6573-6575 (2008). 4. A. Ito, D. Sakamaki, H. Ino, A. Taniguchi, Y. Hirao, K. Tanaka, K. Kanemoto, and T. Kato, “Polycationic States of Oligoanilines Based on Wurster’s Blue”, *Eur. J. Org. Chem.*, **2009**, Issue 26 (September), 4441-4450 (2009). 5. A. Ito, Y. Yokoyama, R. Aihara, K. Fukui, S. Eguchi, K. Shizu, T. Sato, and K. Tanaka, “Preparation and Characterization of N-Anisyl-Substituted Hexaaza[16]paracyclophane”, *Angew. Chem. Int. Ed.*, **49**, 8205-8208 (2010). 6. K. Suzuki, T. Matsuo, D. Hashizume, H. Fueno, K. Tanaka, and K. Tamao, “A Planar Rhombic Charge-Separated Tetrasilacyclobutadiene”, *Science,* **331**, 1306-1309 (2011). （以上学術論文）
【学術関係の受賞】	該当なし

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【研究分野】	ソフトマターの移動現象
【現在の研究課題】	コロイド分散系の計算機シミュレーション
【研究内容キーワード】	ソフトマター、コロイド、計算機シミュレーション、ガラス転移
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【主な著書、学術論文】（過去5年以内）	1. S. Yasuda and R. Yamamoto, “Dynamic rheology of a supercooled polymer melt in nonuniform oscillating flows between rapidly oscillating plates”, *Phys. Rev. E* **84**, 031501 (2011). 2. H. Mizuno and R. Yamamoto, “Dynamical heterogeneity in a highly supercooled liquid: Consistent calculations of correlation length, intensity, and lifetime”, *Phys. Rev. E* **84**, 011506 (2011). 3. H. Kobayashi and R. Yamamoto, “Implementation of Lees-Edwards periodic boundary conditions for direct numerical simulations of particle dispersions under shear flow”, *J. Chem. Phys.* **134**, 064110 (2011). 4. S. Yasuda and R. Yamamoto, “Rheological properties of polymer melt between rapidly oscillating plates: an application of multiscale modeling”, *Europhys. Lett.* **86**, 18002 (2009). 5. Y. Nakayama, K. Kim and R. Yamamoto, “Simulating (electro) hydrodynamic effects in colloidal dispersions: smoothed profile method”, *Eur. Phys. J. E* **26**, 361 (2008).
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【主な著書、学術論文】（過去5年以内）	1. "Vibronic Coupling in Cyclopentadienyl Radical: A Method for Calculation of Vibronic Coupling Constant and Vibronic Coupling Density Analysis", Tohru Sato, Ken Tokunaga, and Kazuyoshi Tanaka, *J. Chem. Phys*. **124**, 024314 1-12(2006). 2. "Vibronic coupling in benzene cation and anion:Vibronic coupling and frontier electron density in Jahn-Teller molecules" Tohru Sato, Ken Tokunaga, and Kazuyoshi Tanaka, *J. Chem. Phys.* **124,** 154303 1-10(2006). 3. "Vibronic and spin-orbit coupling of a d 9 transition-metal ion encapsulated in an icosahedral cage: The (Γ_8+ Γ_9) × (g+2h) Jahn-Teller problem", Tohru Sato and Arnout Ceulemans, *J. Chem. Phys.* **126**, 184501 1-9(2007) . 4. "Vibronic coupling constant and vibronic coupling density", Tohru Sato, Ken Tokunaga, Naoya Iwahara, Katsuyuki Shizu, and Kazuyoshi Tanaka,in "The Jahn-Teller Effect: Fundamentals and Implications for Physics and Chemistry", Springer Series in Chemical Physics 97, H. Koeppel, H. Barentzen, and D. R. Yarkony (Eds) 5. "Vibronic coupling in naphthalene anion: Vibronic coupling density analysis for totally symmetric modes", Tohru Sato, Ken Tokunaga, and Kazuyoshi Tanaka, *J. Phys. Chem. A* **112**, 758-767 (2008). 6. "Electron-vibration interactions in carrier transport material: Vibronic coupling density analysis in TPD", Tohru Sato, Katsuyuki Shizu, Takako Kuga, Kazuyoshi Tanaka, Hironori Kaji, *Chem. Phys. Lett*. **458**, 152-156 (2008). 7. "A Boron-Containing Molecule as an Efficient Electron-Transporting Material with Low-Power Consumption", Katsuyuki Shizu, Tohru Sato, Kazuyoshi Tanaka, and Hironori Kaji, *Appl. Phys. Lett.* **97**, 142111 1-3(2010). 8. "Vibronic coupling in C 60 - anion revisited: Precise derivations from photoelectron spectra and DFT calculations", Naoya Iwahara, Tohru Sato, Kazuyoshi Tanaka, Liviu F. Chibotaru, *Phys. Rev. B*, **82**, 245409 1-10 (2010).
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【主な著書、学術論文】（過去5年以内）	1. Maeda, S.; Ohno, K.; Morokuma, K. Updated Branching Plane for Finding Conical Intersections without Coupling Derivative Vectors. *J. Chem. Theory Comput.* **2010**, *6*, 1538-1545. 2. Maeda, S.; Ohno, K.; Morokuma, K. A Theoretical Study on the Photodissociation of Acetone: An Insight into the Slow Intersystem Crossing and Exploration of Nonadiabatic Pathways to the Ground State. *J. Phys. Chem. Lett.* **2010**, *1*, 1841-1845. 3. Maeda, S.; Morokuma, K. Communications: A Systematic Method for Locating Transition Structures of A + B → X Type Reactions. *J. Chem. Phys*. **2010**, *132*, 241102/1-4. 4. Maeda, S.; Komagawa, S.; Uchiyama, M.; Morokuma, K. Finding Reaction Pathways for Multicomponent Reactions: The Passerini Reaction Is a Four-Component Reaction. *Angew. Chem. Int. Ed*. **2011**, *50*, 644-649. 5. Maeda, S.; Saito, R.; Morokuma, K. Finding Minimum Structures on Seam of Crossing in Reactions of Type A + B → X: Exploration of Nonadiabatic Ignition Pathways of Unsaturated Hydrocarbons. *J. Phys. Chem. Lett*. **2011**, *2*, 852-857.
【学術関係の受賞など】	2004年度－2006年度　日本学術振興会特別研究員（DC1） 2007年3月　青葉理学振興会賞 2007年3月　東北大学総長賞 2004年度－2006年度　日本学術振興会特別研究員（PD） 2008年10月　平成20年度分子科学討論会優秀講演賞 2010年度－現在　京都大学白眉研究者

Ⅱ 博士研究員

１．博士研究員組織

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	福井センターフェロー	平尾　一
	福井センターフェロー	Zhuofeng Ke
	福井センターフェロー	Joonghan Kim
	福井センターフェロー	Alister Page
	(JST) フェロー	Xin Li
	(JST) フェロー	K.R.S. Chandrakumar
	(JST) フェロー	Fengyi Liu
	(JST) フェロー	Parameswaran Pattiyil
	(JST) フェロー	Hong-Yan Xiao
	(JST) フェロー	Lina Ding
	(JST) フェロー	Haibei Li
	(JST) フェロー	Lung Wa Chung
	(JST) フェロー	Galina Petrova
福井センターフェロー		Wilfredo Credo Chung
福井センターフェロー		岩城　貴史
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【研究分野】	Computational Chemistry
【現在の研究課題】	Molecular dynamics (MD) simulations and electronic structure calculations of nano-materials
【研究内容キーワード】	Fullerene, nano-tube, metallofullerene, polycyclic aromatic hydrocarbon, DFTB
【学歴】	November 1998, Master of Science (M. Sc.), Calcutta University, India December 2003, Doctor of Science (Ph. D.), Indian Association for the Cultivation of Science (IACS), Jadavpur University, India
【学位】	Ph. D. (Science)
【略歴】	December 2003, Postdoctoral fellow, University of Kassel, Germany September 2004, JSPS postdoctoral fellow, Kyoto University, Japan November 2006, Postdoctoral fellow, FIFC, Kyoto University, Japan
【所属学会】	Life member, IACS, India Member, American Chemical Society
【主な著書、学術論文】（過去5年以内）	1. B. Saha, S. Irle, K. Morokuma, “Hot giant fullerenes eject and capture C_2 molecules: QM/MD simulations with constant density”, *J. Phys. Chem.* (Submitted) 2. B. Saha, S. Irle, K. Morokuma, “Formation mechanism of polycyclic aromatic hydrocarbons (PAHs) in benzene combustion: Quantum chemical molecular dynamics simulations” , *J. Chem. Phys.* **132**, 224303 (2010) 3. B. Saha, S. Shindo, S. Irle, K. Morokuma, “Quantum chemical molecular dynamics (QM/MD) simulations of fullerene from benzene” , *ACS Nano* **3**, 2241 (2009) 4. B. Saha, M. Ehara, H. Nakatsuji, “Investigation of electronic spectra and Excited-state geometries of poly-para-phenylene vinylene (PPV) and poly-para-phenylene by symmetry adapted configuration-interaction (SAC-CI) method” , *J. Phys. Chem. A* **111**, 5473, (2007)
【学術関係の受賞など】	JSPS postdoctoral fellowship, 2004-2006 Research fellowship, IACS, India, 1999 - 2003 National scholarship, Indian Government, 1990-1995

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【研究分野】	Computational bioinorganic chemistry, Metalloenzymes, Transition-metal catalysts
【現在の研究課題】	Computational studies of bioinorganic systems
【研究内容キーワード】	metalloenzymes, chemical reactions, electronic excited states, spectroscopy, ONIOM, QM/MM, medicinal chemistry, molecular interactions
【学歴】	Mar. 1998 BSc, Department of Engineering, Kyoto University Mar. 2000 MSc, Graduate School of Engineering, Kyoto University
【学位】	Nov. 2004, PhD, The University of Tokyo
【略歴】	Jan. 2002-Dec. 2004 Lab associate at Novartis Pharma K.K. Jan. 2005-Mar. 2007 Postdoc at The Hebrew University of Jerusalem Apr. 2007-Mar. 2009 JSPS Postdoctoral Fellow for Research Abroad (Hebrew University/Emory University) Apr. 2009-Oct. 2010 FIFC Fellow at Kyoto University Nov. 2010-Feb. 2011 Associate Professor Extraordinary at Kobe University Mar. 2011-present Assistant Professor at Nanyang Technological University
【所属学会】	American Chemical Society; The Chemical Society of Japan
【主な著書、学術論文】（過去5年以内）	1. H. Hirao, K. Morokuma, "Ferric Superoxide and Ferric Hydroxide Are Used in the Catalytic Mechanism of Hydroxyethylphosphonate Dioxygenase (HEPD): A Density Functional Theory Investigation," *J. Am. Chem. Soc*. **2010**, *132*, 17901-17909 2. H. Hirao, K. Morokuma, "What is the Real Nature of Ferrous Soybean Lipoxygenase-1? A New Two-Conformation Model Based on Combined ONIOM(DFT:MM) and Multireference Configuration Interaction Characterization," *J. Phys. Chem. Lett*. **2010**, *1*, 901-906. 3. H. Hirao, K. Morokuma, "Insights into the (Superoxo)Fe(III)Fe(III) Intermediate and Reaction Mechanism of myo-Inositol Oxygenase: DFT and ONIOM(DFT:MM) Study," *J. Am. Chem. Soc*. **2009**, *131*, 17206-17214. 4. O. Irie, T. Kosaka, T. Ehara, F. Yokokawa, T. Kanazawa, H. Hirao, A. Iwasaki, J. Sakaki, N. Teno, Y. Hitomi, G. Iwasaki, H. Fukaya, K. Nonomura, K. Tanabe, S. Koizumi, N. Uchiyama, S. J. Bevan, M. Malcangio, C. Gentry, A. J. Fox, M. Yaqoob, A. J. Culshaw, A. Hallett, "Discovery of Orally Bioavailable Cathepsin S Inhibitors for the Reversal of Neuropathic Pain," *J. Med. Chem*. **2008**, *51*, 5502-5505. 5. S. Shaik, H. Hirao, D. Kumar, "Reactivity Patterns of High-Valent Iron Oxo Species in Enzymes and Synthetic Reagents: A Tale of Many States," *Acc. Chem. Res*. **2007**, *40*, 532-542. 6. H. Hirao, D. Kumar, L. Que, Jr., S. Shaik, "Two-State Reactivity in Alkane Hydroxylation by Nonheme Iron-Oxo Complexes," *J. Am. Chem. Soc*. **2006**, *128*, 8590-8606. 7. H. Hirao, D. Kumar, W. Thiel, S. Shaik, "Two States and Two More in the Mechanisms of Hydroxylation and Epoxidation by Cytochrome P450," *J. Am. Chem. Soc*. **2005**, *127*, 13007-13018.
【学術関係の受賞など】	Oct. 2006-Mar. 2007 Golda Meir Fellowship Apr. 2007-Mar. 2009 JSPS Postdoctoral Fellowship for Research Abroad Oct. 2009-Mar. 2011 Kyoto Univ. Startup Grant for Young Researchers Mar. 2010 Kurata Grant Jul. 2010 Takeda Science Foundation Grant 2011 Nanyang Assistant Professorship 2010

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【現在の研究課題】	DNA-based asymmetric catalysis, pMMO enzymatic catalysis.
【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, Satoshi, Ueno, Takafumi, & Morokuma, Keiji, Rh-catalyzed Polymerization of Phenylacetylene: Theoretical Studies of the Reaction Mechanism, Regioselectivity and Stereoregularity. *J. Am. Chem. Soc*., Accepted. 2. Gao, H., Ke, Zhuofeng, DeYonker N. J., Wang J., Xu H., Mao Z.-W., Phillips, D.L., & Zhao C., Dinuclear Zn(II) Complex Catalyzed Phosphodiester Cleavage Proceeds via a Concerted Mechanism: A Density Functional Theory Study. *J. Am. Chem. Soc.*, **2011**, *133* (9), 2904-2915 3. Ke, Zhuofeng & Cundari, T.R., Palladium-Catalyzed C-H Activation/C-N Bond Formation Reactions: DFT Study of Reaction Mechanisms and Reactive Intermediates. Organometallics 29 (4), 821-834 (2010). (*Top10 Most Accessed Articles of Organometallics in 2010)* 4. Guo, Z.; Xue, Jiadan; Ke, Zhuofeng; Phillips, D. L.*; Zhao, C.Y.* "Influence of Water Hydrogen Bonding on the Reactions of Arylnitrenium Ions With Guanosine: Hydrogen-Bonding Effects Can Favor Reaction at the C8 Site" *J. Phys. Chem. B*, **2009,** *113*, 6528-6532. 5. Foley, N. A.; Lee, J. P.; Ke, Zhuofeng; Gunnoe, T. B.*; and Cundari, T. R.* "Ru(II) Catalysts Supported by Hydridotris(pyrazolyl)borate for the Hydroarylation of Olefins: Reaction Scope, Mechanistic Studies, and Guides for the Development of Improved Catalysts" *Acc. Chem. Res.* **2009,** *42*, 585-597 6. Lee, J. P.; Ke, Zhuofeng; Ramrez M. A.; Gunnoe, T. B.*; Cundari T. R.*; Boyle, P. D.; Petersen, J. L. "Six-, Five-, and Four-Coordinate Ruthenium(II) Hydride Complexes Supported by N-Heterocyclic Carbene Ligands: Synthesis, Characterization, Fundamental Reactivity, and Catalytic Hydrogenation of Olefins, Aldehydes, and Ketones" *Organometallics* **2009**, *28*, 1758-1775 7. Liu, Yan; Ke, Zhuofeng; Cui, Jianfang; Chen, Wen-Hua; Ma, Lin; Wang Bo*. "Synthesis, Inhibitory Activities and QSAR Study of Xanthone Derivatives as α-Glucosidase Inhibitors" *Bioorg. Med. Chem.* **2008**, *16*, 7185-7192. 8. Foley, Nicholas A.; Ke, Zhuofeng; Gunnoe, T. Brent*; Cundari, Thomas R.*; and Petersen, Jeffrey L. "Aromatic C-H Activation and Catalytic Hydrophenylation of Ethylene by TpRu{P(OCH2)3CEt}(NCMe)Ph" *Organometallics* **2008**, *27*, 3007-3017. 9. Guo, Zhen; Ke, Zhuofeng; Phillips, David Lee*; Zhao, Cunyuan*. "Intrinsic Reaction Coordinate Analysis of the Activation of CH4 by Molybdenum atoms: A Density Functional Theory Study of the Crossing Seams of the Potential Energy Surfaces" *Organometallics* **2008**, *27,* 181-188. 10. Gao, Haiyang; Ke, Zhuofeng; Pei, Lixia; Song, Keming; Wu, Qing*. "Drastic ligand electronic effect on anilidoeimino nickel catalysts toward ethylene polymerization" *Polymer* **2007**, *48*, 7249-7254. 11.Lin, Xufeng; Zhao, Cunyuan; Che, Chi-Ming*; Ke, Zhuofeng; Phillips, David Lee. "A DFT Study on the Mechanism of Rh2II,II-Catalyzed Intramolecular Amidation of Carbamates" *Chem. Asian J*. **2007**, *2*, 1101-1108 12.Ke, Zhuofeng; Zhou, Yubing; Gao, Hui; Zhao, Cunyuan*, Phillips, David Lee. "On the Mechanism and Stereochemistry of Chiral Lithium Carbenoid Promoted Cyclopropanation Reactions" *Chem. Eur. J.* **2007**, *13,* 6724-6731. 13.Fang, Ran; Ke, Zhuofeng; Shen, Yong; Zhao, Cunyuan*; Phillips, David Lee. "Concurrent Cyclopropanation by Carbenes and Carbanions? A Density Functional Theory Study on the Reaction Pathways" *J. Org. Chem.* **2007**, *72*, 5139–5145. 14.Ke, Zhuofeng; Zhao, Cunyuan*; Phillips, David Lee. "Methylene Transfer or Carbometalation? A Theoretical Study to Determine the Mechanism of Lithium Carbenoid Promoted Cyclopropanation Reactions in Aggregation and Solvation States." *J. Org. Chem.* **2007**, *72*, 848–860.
【学術関係の受賞など】	Sun Yat-sen University Fellow 2009 State Scholarship Funds, China Scholarship Council (CSC) 2007

【氏名】	Joonghan Kim
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【研究分野】	Computational Chemistry
【現在の研究課題】	DFTB-MD simulation of chirality controlled carbon nanotube growth, 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
【学位】	Doctor of Philosophy, KAIST, Daejeon, Korea
【略歴】	2010, Postdoctoral fellow, KAIST, Daejeon, Korea
【所属学会】	Korean Chemical Society
【主な著書、学術論文】 （過去5年以内）	1. Qingyu Kong, Michael Wulff, Savo Bratos, Rudolphe Vuilleumier, Joonghan Kim and Hyotcherl Ihee, "Structure of the Photodissociation Products of CCl_4, CBr_4 and CI_4 in Solution Studied by DFT and Ab Initio Calculations", *J. Phys. Chem. A* **110**, 11178-11187 (2006). 2. Joonghan Kim, Yoon Sup Lee and Hyotcherl Ihee, "Density Functional and Ab Initio Studies on Structures and Energies of the Ground State of CrCO", *Int. J. Quant. Chem.* **107**, 458 (2007). 3. Joonghan Kim, Tae Kyu Kim, Jangbae Kim, Yoon Sup Lee and Hyotcherl Ihee, "Density Functional and Ab Initio Study of $Cr(CO)_n$ (n = 1−6) Complexes", *J. Phys. Chem. A* **111**, 4697-4710 (2007). 4. 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). 5. 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). 6. 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). 7. 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). 8. 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). 9. 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). 10.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. Quant. Chem.* DOI : 10. 1002/qua. 23/47.

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【研究分野】	Computational Chemistry
【現在の研究課題】	Molecular Dynamics simulations and electronic structure calculations of nanoscale self-assembly processes (in particular, carbon nanotube nucleation and growth).
【研究内容キーワード】	Single-walled carbon nanotube, self-assembly, nucleation, growth, healing, (n,m) chirality, 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
【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. A. J. Page, K.R.S. Chandrakumar, S. Irle, K. Morokuma, “SWNT Nucleation from Carbon-Coated SiO2 Nanoparticles via a Vapor-Solid-Solid Mechanism” , *J. Am. Chem. Soc.*, **132**, 15699, (2011) 2. 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) 3. 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) 4. A. J. Page, B. Moghtaderi, “Molecular Dynamics Simulation of the Low-Temperature Partial Oxidation of CH_4”, *J. Phys. Chem. A,* **20**, 1539, (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】	Computational Chemistry
【現在の研究課題】	1. Radical Reaction Mechanism in B_{12}-Dependent Methylmalonyl-CoA Mutase 2. Reversibly Photoswitchable Fluorescent Protein: Dronpa 3. Irreversible Photoconversion Fluorescent Protein: Kaede
【研究内容キーワード】	Reaction mechanisms of metalloenzymes and photobiology
【学歴】	June 2005, Ph. D., College of Chemistry, Liaoning Normal University
【学位】	Ph. D. in Physical Chemistry from Liaoning Normal University
【略歴】	July 2005-May 2007, Postdoctoral Fellow, Peking University
【主な著書、学術論文】（過去5年以内）	1. Ling Xu, Xin Li, et al., “Ion-Specific Swelling of Poly (Styrene Sulfonic Acid) Hydrogel”, *J. Phys. Chem. B* **111**(13), 3391-3397 (2007). 2. Fu-Qiang Shi, Xin Li, et al., “DFT Study of the Mechanisms of In Water Au(I)-Catalyzed Tandem [3,3]-Rearrangement/Nazarov Reaction/[1,2]-Hydrogen Shift of Enynyl Acetates: A Proton-Transport Catalysis Strategy in the Water-Catalyzed [1,2]-Hydrogen Shift”, *J. Am. Chem. Soc.* **129**, 15503-15512 (2007). 3. Xin Li, Si-Yu Ye, Chuan He, and Zhi-Xiang Yu, “Mechanisms of Brønsted Acid Catalyzed Additions of Phenols and Protected Amines to Olefins: A DFT Study”, *Eur. J. Org. Chem.* 4296-4303 (2008). 4. Lung Wa Chung, Xin Li, Hiroshi Sugimoto, Yoshitsugu Shiro, Keiji. Morokuma, “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*. **131**, 12298 (2008). 5. Xin Li, Lung Wa Chung, Piotr Paneth, and Keiji Morokuma, “DFT and ONIOM(DFT:MM) Studies on Co-C Bond Cleavage and Hydrogen Transfer in B_{12}-Dependent Methylmalonyl-CoA Mutase. Stepwise or Concerted Mechanism?”, *J. Am. Chem. Soc*. **131**, 5115-5125 (2009). 6. Xin Li, Lung Wa Chung, Hideaki Mizuno, Atsushi Miyawaki, and Keiji Morokuma, “A Theoretical Study on the Nature of On- and Off-States of Reversibly Photoswitching Fluorescent Protein Dronpa: Absorption, Emission, Protonation and Raman”, *J. Phys. Chem. B* **114**, 1114-1126 (2010). 7. Xin Li, Lung Wa Chung, Hideaki Mizuno, Atsushi Miyawaki, and Keiji Morokuma, “Primary Events of Photodynamics in Reversible Photoswitching Fluorescent Protein Dronpa”, *J. Phys. Chem. Lett*. **1**, 3328-3333 (2010). 8. Xin Li, Lung Wa Chung, Hideaki Mizuno, Atsushi Miyawaki, and Keiji Morokuma, “Competitive Mechanistic Pathways for Green-to-Red Photoconversion in the Fluorescent Protein Kaede: A Computational Study”, *J. Phys. Chem. B* **114**, 16666-16675 (2010).
【学術関係の受賞など】	Postdoctoral Science Fund of China in Peking University, 2006.

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【研究分野】	Computational Chemistry
【現在の研究課題】	DFTB-MD simulation of carbon nanotube growth from the metal decorated carbon nanocones
【研究内容キーワード】	carbon nanotube, nanocones, self-assembly, nanocapsules, density-functional tight-binding
【学歴】	B.Sc., with distinction, Madurai Kamaraj University, (General Chemistry with Physics and Mathematics as ancillary subjects) 1994 M.Sc., with first class, Madurai Kamaraj University, (specialization in Physical Chemistry) 1996 Ph.D., Pune University, National Chemical Laboratory, 2003 Thesis Title: Theoretical studies on some aspects of chemical reactivity using density based descriptors.
【学位】	Doctor of Philosophy, Pune University, National Chemical Laboratory
【略歴】	Since 2004, working as a Scientific Officer at Bhabha Atomic Research Centre, India
【所属学会】	Chemical Research Society of India.
【主な著書、学術論文】 （過去5年以内）	1. A. J. Page, K. R. S. Chandrakumar, S. Irle, and K. Morokuma, "SWNT Nucleation from Carbon-Coated SiO2 Nanoparticles via a Vapor-Solid-Solid Mechanism", *J. Am. Chem. Soc.* **2011**, *133*, 621-628 2. A. J. Page, K. R. S. Chandrakumar, S. Irle, and K. Morokuma, "Do SiO_2 and Carbon-Doped SiO_2 Nanoparticles Melt? Insights from QM/MD Simulations and Ramifications Regarding Carbon Nanotube Growth", *Chem. Phys. Lett.* doi:10.1016/j.cplett.2011.01.075 3. N. K. Jena, K. R. S. Chandrakumar and S. K. Ghosh, "Theoretical Investigation on the Structure and Electronic Properties of Hydrogen- and Alkali-Metal-Doped Gold Clusters and Their Interaction with CO: Enhanced Reactivity of Hydrogen-Doped Gold Clusters", *J. Phys. Chem. C*, **2009**, *113*, 17885-17892. 4. K. R. S. Chandrakumar, K. Srinivasu and S. K. Ghosh, "Nanoscale Curvature Induced Hydrogen Adsorption in Alkali Metal Doped Carbon Nanomaterials", *J. Phys. Chem. C*, **2008**, *112*, 15670-15679. 5. K. R. S. Chandrakumar and S. K. Ghosh, "Alkali-Metal-Induced Enhancement of Hydrogen Adsorption in C_{60} Fullerene:An ab initio Study", *Nano Lett*. **2008**, *8*, 13-19.
【学術関係の受賞など】	**Indo-European Collaborative Project Grant (FP7);** Project Title: Modeling of Nano-scaled Advanced Materials Intelligently (MONAMI) **Young Scientist Award** in **2008** from Department of Atomic Energy **(DAE)** **Young Scientist Medal Award** in **2005** from the Indian National Science Academy **(INSA)**

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【現在の研究課題】	Theoretical calculation of molecular motor and 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, Rationalization of Light-Driven Rotary Molecular Motor: An Theoretical Study on the Photoisomerization of an Stiff Stilbene, *manuscript in preparation*. 2. 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. 3. 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 . 4. 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 . 5. Fengyi Liu, Lingpeng Meng, Shijun Zheng, Small Fullerenes with BN Belts: a Density Functional Theory Investigation, *J. Phys. Chem. B*, 2006, **110**, 6666-6672 . 6. Fengyi Liu, Lingpeng Meng, Zheng Sun, Shijun Zheng, Insights into the Mechanism of BN Generation via Boron Triazide Precursor: A Theoretical Study, *J. Phys. Chem. A*, 2006, **110**, 10591-10600.

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【研究内容キーワード】	Dynamics, DFTB, nanowire, growth, DFT
【学歴】	1998, Bachelor of Sci., St. Thomas' College, Thrissur, University of Calicut 2000, Master of Sci., St. Thomas' College, Thrissur, University of Calicut
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【略歴】	Mar. 2007 - Oct. 2007 : Research Associate, Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore Nov. 2007 - Sept. 2009 : Alexander von Humboldt Research Fellow, Philipps-Universität Marburg, Germany Oct. 2009 - June 2010 : Postdoctoral Research Fellow, Fukui Institute for Fundamental Chemistry, Kyoto University July 2010- Till date : Assistant Professor, Department of Chemistry, NIT Calicut
【主な著書、学術論文】（過去5年以内）	1. Melaimi, M.; Parameswaran, P.; Donnadieu, B.; Frenking, G.; Bertrand. G. "Synthesis and Ligand Properties of a Persistent All-Carbon Four-Membered Ring Allene", *Angew. Chem. Int. Ed.* **48**, 4792-4795 (2009). 2. Parameswaran, P.; Frenking, G. "Transition Metal Complexes $[(PMe_3)^2Cl_2M(E)]$ and $[(PMe_3)^2(CO)^2M(E)]$ with Naked Group 14 Atoms (E = C - Sn) as Ligands; Part 1: Parent Compounds", *Chem. Eur. J.* **15**, 8807-8816 (2009). 3. Parameswaran, P.; Frenking, G. "Transition Metal Complexes $[(PMe_3)^2Cl_2M(E)]$ and $[(PMe_3)^2(CO)^2M(E)]$ with Naked Group 14 Atoms (E = C - Sn) as Ligands; Part 2: Complexation with $W(CO)^5$", *Chem. Eur. J.* **15**, 8817-8824 (2009). 4. Aldeco-Perez, E.; Rosenthal, A.; Donnadieu, B.; Parameswaran, P.; Frenking, G.; Bertrand. G.. "Isolation of a C-5-Deprotonated Imidazolium, a Crystalline Abnormal N-Heterocyclic Carbene", *Science,* **326**, 556-559 (2009). 5. Back, O.; Donnadieu, B.; Parameswaran, P.; Frenking, G.; Bertrand. G. "Isolation of Crystalline Carbene-Stabilized P2-Radical Cations and P2-Dication", *Nature Chemistry,* **2**, 369-373 (2010).
【学術関係の受賞など】	Alexander von Humboldt Research Fellow 2007-2009

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【主な著書、学術論文】（過去5年以内	1. Hong-Yan Xiao, Jun Cao, Ya-Jun Liu, Wei-Hai Fang, Hiroto Tachikawa, Masaru Shiotani. Structures and cis-to-trans photoisomerization of hexafluoro-1,3-butadiene radical cation: electron spin resonance and computational studies. *J. Phys. Chem. A* **111**, 5192-5200 (2007) 2. Hong-Yan Xiao, Ya-Jun Liu, Wei-Hai Fang. Multireference theoretical investigation on selectivity of the bond fissions in photodissociation of acetyl cyanide. *J. Chem. Phys*. **127**, 244313-1~244313-7 (2007) 3. Ya-Jun Liu, Hong-Yan Xiao, Meng-Tao Sun, Wei-Hai Fang. Spin-orbit ab initio investigation of the photodissociation of dibromomethane in the gas and solution phases. *J. Comput. Chem*. **29**, 2513-2519 (2008) 4. Isabelle Navizet, Ya-Jun Liu, Nicolas Ferré, Hong-Yan Xiao, Wei-Hai Fang and Roland Lindh. Color-tuning mechanism of firefly investigated by multi-configurational perturbation method. *J. Am. Chem. Soc*. **132**, 706-712 (2010) 5. Hong-Yan Xiao, Zhen Zhen, Huan-Quan Sun, Xu-Long Cao, Zhen-Quan Li, Xin-Wang Song, Xiao-Hong Cui and Xin-Hou Liu. Molecular dynamics simulation of anionic surfactant at the water/n-alkane interface. *Acta Phys. -Chim. Sin*. **26**, 422-428 (2010) 6. 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)
【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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【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, 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. 2. 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. 3. 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. 4. Ganglong Cui, Lina Ding, Feng Feng, Yajun Liu, and Weihai Fang, Insights into Mechanistic Photochemistry of Urea, *J. Chem. Phys*. **2010**, *132*, 194308;
【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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【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
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【主な著書、学術論文】（過去5年以内）	1. Haibei Li, Shanxi Tian, and Jinlong Yang. Theoretical study of the stepwise protonation of the dioxo Manganese (V) porphyrin, *J. Phys. Chem. B,* **112**, 15807, 2008 2. Haibei Li, Shanxi Tian, and Jinlong Yang. Chemical bonds and electronic strucures of the methonium cations CH_6^{2+} and CH_7^{3+}, J. Theor. Comp. *Chem.* **7**, 139, 2008 3. Haibei Li, Yubin Bai, Shanxi Tian, and Jinlong Yang. Electron topological and energetic study of the intermolecular non-hydrogen bonding interactions in complexes H_2O　M (M=F_2, ClF, and CF_4), J. Theor. Comp. *Chem*. **8**, 615, 2009 4. Haibei Li, Shanxi Tian, and Jinlong Yang. Propene oxidation with anionic cluster $V_4O_{11}^-$: selective epoxidation, *Chem. Eur. J* (communications) **15**, 10747, 2009 5. Haibei Li, Shanxi Tian, and Jinlong Yang. Propene oxidation on $V_4O_{11}^-$ cluster: reaction dynamics to acrolein, *J. Phys. Chem. A,* **114**, 6542, 2010
【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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【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
【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. Noda, S.; Nakamura, A.; Kochi, T.; Chung, L. W.; Morokuma, K.; Nozaki, K. “Mechanistic Studies on the Formation of Linear Polyethylene Chain Catalyzed by Palladium Phosphine-Sulfonate Complexes: Experiment and Theoretical Studies”, *J. Am. Chem. Soc*. **2009**, *131*, 14088 6. 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. 7. Nozaki, K.; Kusumoto, S.; Noda, S.; Kochi, T.; Chung, L. W.; Morokuma, K.; “Why Did Incorporation of Acrylonitrile to a Linear Polyethylene Become Possible? Comparison of Phosphine−Sulfonate Ligand with Diphosphine and Imine−Phenolate Ligands in the Pd-Catalyzed Ethyelene/Acrylonitrile Copolymerization”, *J. Am. Chem. Soc*. **2010,** *132*, 16030. 8. Li, X.; Chung, L. W.; Mizuno, H.; Miyawaki, A.; Morokuma, K. “Primary Events of Photodynamic in Reversibly Photoswitching Fluorescent Protein Dronpa”, *J. Phys. Chem. Lett.* **2010**, *1*, 3328. 9. 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. 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*. **2011**, doi: 10.1002/wcm. 85

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【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. 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). 2. 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). 3. G. P. Petrova, G. N. Vayssilov, N. Rösch, “Redox behavior of small metal clusters with respect to hydrogen. The effect of the cluster charge from density functional results”, *Phys. Chem. Chem. Phys*., **12**, 11015-11020 (2010). 4. G. P. Petrova, G. N. Vayssilov, N. Rösch, “Hydrogen Adsorption on Zeolite-Supported Tetrairidium Clusters. Thermodynamic Modeling from Density Functional Calculations”, *J. Phys. Chem. C*, **112**, 18572-18577 (2008). 5. G. N. Vayssilov, H. A. Aleksandrov, G. P. Petrova, P. St. Petkov, “Computational Modelling of Nanoporous Materials”, Chapter 8 in Ordered Porous Solids; Valtchev, Mintova, Tsapatsis (Eds.), Elsevier, Amsterdam, pp. 209-236 (2008). 6. G. P. Petrova, G. N. Vayssilov, N. Rösch, “Density Functional Modeling of Reverse Hydrogen Spillover on Zeolite-Supported Tetrairidum Clusters”, *Chem. Phys. Lett.*, **444**, 215-219 (2007).
【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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【現在の研究課題】	Theoretical elucidation of reaction mechanisms and dynamics of important molecules in the electronic ground and excited states
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【主な著書、学術論文】（過去5年以内）	1. W. C. Chung, Z. Lan, Y. Ohtsuki, N. Shimakura, W. Domcke and Y. Fujimura, Conical intersections involving the dissociative 1 $\pi\sigma^*$ state in 9H-adenine: a quantum chemical ab initio study, Phys. Chem. Chem. Phys. 9, 2075-2084 (2007). 2. M. Yamaki, K. Hoki, T. Teranishi, W. C. Chung, F. Pichierri, H. Kono and Y. Fujimura, Theoretical design of an aromatic hydrocarbon rotor driven by a circularly polarized electric field, J. Phys. Chem. A, 111, 9374-9378 (2007). 3. W. M. I. Hassan, W. C. Chung, N. Shimakura, S. Koseki, H. Kono and Y. Fujimura Ultrafast radiationless transition pathways through conical intersections in photo-excited 9H-adenine, Phys. Chem. Chem. Phys., 12, 5317-5328 (2010). 4. W. C. Chung, S. Nanbu and T. Ishida, Nonadiabatic ab initio dynamics of a model protonated Schiff base of 9-cis retinal, J. Phys. Chem. A 114, 8190-8201 (2010).

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【主な著書、学術論文】（過去5年以内）	1. T. Iwaki, N. Makita and K. Yoshikawa, “Folding transition of a single semi-flexible polyelectrolyte chain through toroidal bundling of loop structures”, *The Journal of Chemical Physics* **129**(6), 065103 (13 pages) (2008) 2. 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) 3. T. Saito, T. Iwaki, and K. Yoshikawa, “Small anion with higher valency retards the compaction of DNA in the presence of multivalent cation”, *Biophysical Journal* **96**(3), 1068-1075 (2009) 4. S Araki, K. Hizume, T. Iwaki, Y. Suzuki, K. Takeyasu, and K. Yoshikawa, “Nucleosomal arrays reconstituted from ring and linear DNA”, *Chemical Physics Letters* **479**, 284-289 (2009) 5. T. Iwaki, “Effect of internal flow on the photophoresis of a micron-sized liquid droplet”, *Physical Review E* **81**, 066315 (13 pages) (2010)

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【現在の研究課題】	電子分光法の理論および第一原理計算による解析
【研究内容キーワード】	X線分光・電子線エネルギー損失分光・多重項・強相関
【学歴】	京都大学大学院工学研究科材料工学専攻博士後期課程修了
【学位】	2007年3月 京都大学 博士（工学）
【略歴】	2007年4月 - 2009年3月 京都大学大学院工学研究科 博士研究員 2009年4月 - 2010年3月ユトレヒト大学（オランダ）博士研究員 2010年4月 - 現在 福井謙一記念研究センター フェロー
【所属学会】	日本物理学会，日本金属学会
【主な著書、学術論文】（過去5年以内）	1. Hidekazu Ikeno, Teruyasu Mizoguchi and Isao Tanaka, “*Ab initio* charge transfer multiplet calculations on the $L_{2,3}$ XANES and ELNES of 3d transition metal oxides”, *Phys. Rev. B* **83**, 155107 (2011). 2. Teruyasu Mizoguchi, Weine Olovsson, Hidekazu Ikeno and Isao Tanaka, “Theoretical ELNES using one-particle an multi-particle calculations”, *Micron* **41**, 695-709, (2010). 3. Hidekazu Ikeno , Frank M.F. de Groot, Eli Stavitski and Isao Tanaka, “Multiplet calculations of $L_{2,3}$ x-ray absorption near-edge structures for 3d transition-metal compounds”, J. Phys.: Condens. Matter 21, 104208 (2009). 4. Hidekazu Ikeno, Teruyasu Mizoguchi, Yukinori Koyama, Yu Kumagai and Isao Tanaka, “First-principles calculations for $L_{2,3}$ ELNES/XANES of 3d transition metal monooxides, *Ultramicroscopy* **106**, 970-975 (2006). 5. Hidekazu Ikeno, Isao Tanaka, Yukinori Koyama, Teruyasu Mizoguchi and Kazuyoshi Ogasawara, “First-principles calculations of Ni $L_{2,3}$ NEXAFS for $LiNiO_2$ and related compounds”, *Phys. Rev. B* **72**, 075123 (2005).
【学術関係の受賞など】	日本学術振興会特別研究員(DC2) 2005-2006

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【研究分野】	ソフトマター物理、生物物理
【現在の研究課題】	Self-propulsion and deformation of reactive droplet
【研究内容キーワード】	Self-propulsion, free boundary problem, hydrodynamics, thermophoresis
【学歴】	2007年3月京都大学理学研究科　物理学・宇宙物理学専攻　博士課程修了
【学位】	2007年3月理学博士（京都大学）
【略歴】	2007年4月東京大学理学系研究科　日本学術振興会特別研究員PD 2010年4月京都大学福井謙一記念研究センター特定研究員
【所属学会】	日本物理学会
【主な著書、学術論文】（過去5年以内）	1. Hong-Ren JIANG, Natsuhiko YOSHINAGA, and Masaki SANO, “Active Motion of Janus Particle by Self-thermophoresis in Defocused Laser Beam”, *Physical Review Letters,* **105,** 268302 (2010)　Editor’s suggestion and Viewpoint in Physics, 3, 108 (2010) Debut of a hot “fantastic voyager” 2. Natsuhiko YOSHINAGA, Jean-Francois JOANNY, Jacques PROST and Pilippe MARCQ, “Polarity patterns of stress fibers”, *Physical Review Letters*, **105**, 238103 (2010) 3. Takahiro SAKAUE and Natsuhiko YOSHINAGA, “Dynamics of Polymer Decompression: Expansion, Unfolding and Ejection”, *Physical Review Letters,* **102**, 148302 (2009). 4. Hong-Ren JIANG, Hirofumi WADA, Natsuhiko YOSHINAGA, and Masaki SANO, “Manipulation of Colloids by Nonequilibrium Depletion Force in Temperature Gradient”, *Physical Review Letters*, **102**, 208301 (2009). 5. Natsuhiko YOSHINAGA, Efim KATS and Avraham HALPERIN, “On the Adsorption of Two-State Polymers”, *Macromolecules*, **41**, 7744-7751 (2008) 6. Natsuhiko YOSHINAGA, “Folding and unfolding transition in a single semi-flexible polymer”, *Physical Review E*, **77**, 061805 (2008)

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 8 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　平成 22(2010) 年 12 月 3 日 (金)　10:00 ― 19:00

場　　所　京都大学福井謙一記念研究センター （３Ｆ　大会議室）

開会の辞　田中　功（センター長）　10:00-10:05

ご 挨 拶　小森　悟　（京大・工学研究科長）　9:40- 9:50

講　　演

中村　宏樹 (国立交通大学（台湾)、前分子科学研究所長)　10:15-11:15

「非断熱化学動力学―分子科学に新次元を」

谷村　吉隆　（京大・院理）　11:30-12:30

「散逸系の階層型量子運動方程式と多次元分光」

山本　量一　（京大・院工）　14:00-15:00

「粗視化モデリングのすすめ：分子科学とソフトマター科学の接点」

ポスターセッション　15:15-17:15

懇親会（１Ｆ多目的ルーム）　17:30-19:00

２．センターセミナー

第８回福井センターセミナー(2010 年 6 月 21 日 (月)　15:00-17:00)

15:00 ～ 15:30　Satoshi Maeda (Hakubi Center, FIFC)

"Systematic Exploration of Photochemical Reaction Pathways:
Applications to Ketones and Aldehydes" "

15:30 ～ 16:00　Alister Page (FIFC)

"Carbon Nanotube Nucleation on Traditional and Non-Traditional Catalysts:
Insights from QM/MD Simulations"

16:00 ～ 17:00　Alexey Timoshkin (St. Petersburg State University)

"From Donor-Acceptor Complexes to Nanorods"

Ⅳ　研究業績（2010）

１．専任教員

総合研究部門　専任教員　General Division Fulltime Faculty

准教授　石田　俊正　Associate Professor **Toshimasa Ishida**

1. Summary of the research of the year

(1) Theoretical study on reaction of CooA protein with carbon monoxide

Heme-containing gas sensor proteins have a new function for heme. The heme acts as an active site for sensing gas molecules such as O_2, CO and NO. CooA is one of the proteins, and is a CO-sensing transcriptional activator found in a photosynthetic bacterium. The binding of CO to the heme group stimulates the transcriptional activator activity of CooA. CooA has a ferrous form with histidine (His^{77}) and prorine (Pro^{2} in the other subunit) amino acids as axial ligands before the protein binds to CO instead of Pro although, in the rest state, it has a ferric form with Pro^{2} and Cys^{75}. Figure 1 shows the ligand exchanges for various forms. Here, we investigate the reaction during CO-sensing theoretically.

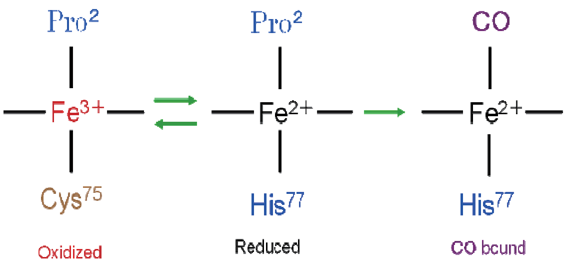


Figure 1. Ligand exchanges for various forms of CooA reaction center

We carried out quantum chemical calculations on a model system of this reaction. Several models are employed, but essentially includes porphyrin ring, imidazole and pyrrolidine, where the two latter compounds are models for His and Pro. We used the Hay-Wadt basis set and effective core potential for iron and the 6-31G(d) basis set at the B3LYP level. We used neutral model and anion model where proton is removed from pyrrolidine in the single as well as triplet states. Figure 2 is the optimized geometry of the product in the neutral singlet state of the model compound.

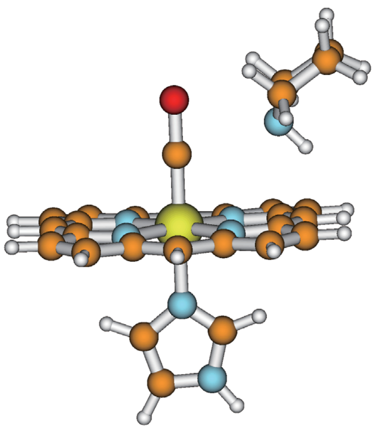


Figure 2. The optimized geometry of the product in the neutral singlet state of the model compound.

The distances for Fe-N(Pro) and Fe-N(His) in the optimized geometry are 2.19 and 2.02 Å in the neutral model and 2.04 and 2.15 Å in the anion model whereas the experimental values from EXAFS analyses are 2.16 and 2.02 Å. Table 1 shows the distances for singlet and triplet states. The neutral model is, thus, favorable from this comparison. The products is lower than the reactants in the neutral and anion models by 4.1 and 28.7 kcal mol^{-1}. CO is attached to Fe with the carbon atom in the products and the Fe-C-O angle is almost 180°, which is in agreement with the previous theoretical study. The transition state is not found so far: the reaction probably proceeds with no barrier on the single surface. Table 2 shows the Charges, multiplicities energy differences, bond distances for ferrous and ferric compounds. For the ferrous form, the His-coordination is more stable than the Cys-coordination, which is in agreement with experimental observations. For the ferric form, however, the His coordination is more stable again, which is not consistent with experiments. A QM/MM treatment would be needed to reproduce the experimental result.

Table 1 The distances between Fe-N for Prolin and Histidine ligands and energy differences for singlets and triplets.

	R(Fe−N(Pro))(Å)	R(Fe−N(His))(Å)	ΔE(kcal/mol)
1Neutral	2.188	2.016	0
3Neutral	2.493	2.484	7.1
1Deprotonated	2.040	2.152	0
3Deprotonated	1.839	2.124	−2.1
EXAFS	2.16	2.02	−

Table 2 Charges, multiplicities energy differences, bond distances for ferrous and ferric compounds

	Charge	Multiplicity	ΔE(kcal/mol)	Fe−N(His)	Fe−S(Cys)
Fe(2+)−His−Gly−Cys	0	singlet	0.0	2.04	6.68
Fe(2+)−Cys−Gly−His	0	singlet	21.7	5.41	2.53
Fe(3+)−His−Gly−Cys	1	doublet	0.0	1.97	10.35
Fe(3+)−Cys−Gly−His	1	doublet	11.9	4.94	2.29
X−ray(Fe(2+)−His)			−	2.19	4.86
EXAFS(Fe(2+)−His)			−	2.02	−
EXAFS(Fe(3+)−Cys)			−	−	2.25

(2) Nonadiabatic ab initio dynamics of a model protonated Schiff base of 9-cis retinal

The dynamics of the photoisomerization of a model protonated Schiff base of 9-cis retinal in isorhodopsin is investigated using nonadiabatic molecular dynamics simulation combined with ab initio quantum chemical calculations on-the-fly. The quantum chemical part is treated at the complete-active space self-consistent field level for six electrons in six active π orbitals with the 6-31G basis set (CASSCF(6,6)/6-31G). The probabilities of nonadiabatic transitions between the S_1 ($^1\pi\pi^*$) and S_0 states are estimated in light of the Zhu-Nakamura theory. The photoinduced cis-trans isomerization of 9-cis retinal proceeds slower than that of its 11-cis analogue and at a lower quantum yield, confirming experimental observations. An energetic barrier in the excited state impedes the elongation and twist of the C9=C10 stretch and torsion coordinates, respectively, resulting in the trapping of trajectories before transition. Consequently, the isomerization takes longer time and the transition more often occurs at smaller twist angle of =C8-C9=C10-C11=, which leads to regeneration of the 9-cis reactant. Thus, neither the smaller twist observed in the x-ray crystal nor the slower movement of nuclei in the transition region would be the main reason for the longer reaction time and lower yield. A well-known space-saving asynchronous bicycle pedal or crankshaft photoisomerization mechanism is found to be operational in 9-cis retinal. The simulation *in vacuo* suggests that the excited-state barrier and the photoisomerization itself are intrinsic properties of the visual chromophore and not triggered mainly by the protein environment that surrounds the chromophore.

(3) Syntheses, crystal structures and DFT calculations of 2-[4,5-bis(ethylsulfanyl)-1,3-dithiol-2-ylidene]-5- (4,5-diiodo-1,3-dithiol-2-ylidene)-1,3-dithiolan-4-thione and -one

Iodine substituted 2,5-di(1,3-dithiol-2-ylidene)-1,3-dithiolan-4-thione and –one derivatives, namely 2-[4,5-bis(ethylsulfanyl)-1,3-dithiole-2-ylidene]-5-(4,5-diiodo-1,3-dithiol-2-ylidene)-1,3-dithiolan-4-thione (**1a**) and -one (**1b**), were synthesized. **1a** was obtained from the reaction of bis(tetraethylammonium)bis[2-[4,5-bis(ethylsulfanyl)-1,3- dithiol-2-ylidene]-1,3-dithiole-4,5-bis(thiolato)]zinc and 4,5-diiodo-2-methylsulfanyl-1,3- dithiole-2-ylium tetrafluoroborate. **1b** was obtained from the reaction of **1a** and mercury(II) acetate. Recrystallization of **1a** and **1b** from carbondisulfide/*n*-hexane gave single crystals suitable for X-ray structure analysis. In the crystals, both **1a** and **1b** were stacked to form one-dimensional columns and the interplanar distances in the columns were greater than a π-cloud thickness. Some effective side-by-side contacts were observed between molecules of adjacent columns. The interactions were accomplished through S…I contacts for **1a**, and S…I and O…I contacts for **1b**. The interesting features of these structures are the intermolecular C=S…I contacts for **1a** and the intermolecular C=O…I contacts for **1b** which are respectively 16% and 17% shorter than the sum of van der Waals radii of corresponding atoms. DFT calculations suggest that the effective geometry of **1a** molecules for charge transfer from the moiety interacting with sulfur to the moiety interacting with iodine plays an important role for molecular packing through in the crystal system.

(4) Unusually High Aromaticity and Diatropicity of Bond-Alternate BenzeneBenzene

Enormous effort has been devoted to the elucidation of possible effects of bond-length alternation on the benzene *π*-system. Benzene tends to stay highly aromatic and highly diatropic even if strong bond-length alternation is introduced artificially into the *π*-system. Such peculiar aromatic and magnetic characters of benzene were justified consistently and unambiguously within a single theoretical framework. From all physically sound points of view, bond-alternate benzene is highly aromatic with a large aromatic stabilization energy. We confirmed that in the annulene family benzene is least sensitive in aromaticity to bond-length alternation.

2. Original papers

(1) Aihara, Jun-ichi; Ishida, Toshimasa,
"Unusually High Aromaticity and Diatropicity of Bond-Alternate Benzene"
J. Phys. Chem. A, *114* (2), 1093–1097 (2010).

(2) K. Ueda, K. Suzuki, K. Suzuki, K. Yoza, T. Ishida,
"Syntheses, crystal structures and DFT calculations of
2-[4,5-bis(ethylsulfanyl)-1,3-dithiol-2-ylidene]-5-(4,5-diiodo-1,3-dithiol-2-ylidene)-1,3-dithiolan-4-thione and –one"
Physica B 405, S69–S74 (2010).

(3) Wilfredo C. Chung, Shinkoh Nanbu, and Toshimasa Ishida,
"Nonadiabatic ab Initio Dynamics of a Model Protonated Schiff Base of 9-cis Retinal",
J. Phys. Chem. A, 114 (32), 8190–8201 (2010).

3. Presentation at academic conferences

(1) Wilfredo C. Chung, Shinkoh Nanbu, Toshimasa Ishida
9-cis レチナールの光異性化の理論的研究
第 13 回理論化学討論会 1P03　札幌　2010/5/23

(2) Ishida, Toshimasa and Aono, Shigetoshi,
"Theoretical study on reaction of CooA protein with carbon monoxide",
第 26 回化学反応討論会 1P46　東広島　2010/6/2

(3) Wilfredo Credo Chung, Shinkoh Nanbu, Toshimasa Ishida,
"Nonadiabatic ab initio dynamics of an isorhodopsin model system based on the Zhu-Nakamura theory"
第 26 回化学反応討論会　2P45　東広島　2010/6/3

(4) 石田　俊正、青野　重利
「CooA タンパク質の CO との一連の反応に関する理論的研究」
第 4 回分子科学討論会 2010　2P089　豊中　2010/9/15

(5) Chung Wilfredo Credo，南部 伸孝，石田 俊正
"Hindered cis-trans isomerization in 9-cis retinal: a two-state model dynamics simulation"
第 4 回分子科学討論会 2010　4P092　豊中　2010/9/17

(6) Ishida, Toshimasa; Chung, Wilfredo Credo; Nanbu, Shinkoh,
"Nonadiabatic ab initio dynamics of 11-cis retinal"

The international Chemical Congress of Pacific Basin Societies (Pacifichem2010), Honolulu, Hawaii, USA. Dec. 17, 2010.

(7) Chung, Wilfredo Credo; Nanbu, Shinkoh, Ishida, Toshimasa
"Nonadiabatic ab initio dynamics of a model protonated Schiff base of 9-cis retinal",
The international Chemical Congress of Pacific Basin Societies (Pacifichem2010), Honolulu, Hawaii, USA. Dec. 18, 2010.

4. Others

(1) 石田　俊正
「ペニングイオン化の理論的研究」
化学反応のポテンシャル曲面とダイナミックス～加藤重樹先生の足跡をたどって～　京都　2010/6/19

(2) Toshimasa Ishida,
"Theoretical Study on Photoionization",
Colloquium on Computational Chemistry, Mindanao State University-Iligan Institute of Technology, Iligan, Philippines, Sep. 6, 2010 (Invited)

(3) Toshimasa Ishida,
"Theoretical Study on Photoionization",
Mindanao State University of Science and Technology, Cagayan de Oro, Philippines, Sep. 7, 2010 (Invited)

(4) 石田 俊正、青野 重利
CooA タンパク質と CO との反応に関する理論的研究
第 8 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　2010/12/3

(5) Wilfredo Credo Chung and Toshimasa Ishida
On the mechanism of the structural decoy action of LMP1 over CD40 in relation to Epstein-Barr virus infection: an essential dynamics approach
第 8 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　2010/12/3

(6) Wilfredo C. Chung1, Shinkoh Nanbu2, Toshimasa Ishida1
Comparison of the 9-cis retinal photoisomeriation with the 11-cis counterpart
文部科学省「最先端・高性能汎用スーパーコンピュータの開発利用」プロジェクト　次世代ナノ統合シミュレーションソフトウェアの研究開発　第５回　公開シンポジウム P102　2011/2/23　神戸

(7) 南部伸孝，石田俊正，徳江郁雄、関谷 博，中園 博
非断熱遷移を利用した分子設計
文部科学省「最先端・高性能汎用スーパーコンピュータの開発利用」プロジェクト　次世代ナノ統合シミュレーションソフトウェアの研究開発　第５回　公開シンポ

ジウム P103　2011/2/23　神戸

(8) 日本国特許

「光学活性分子の絶対配置決定方法、絶対配置決定装置、及びプログラム 」

公開日　2006/10/19

出願人　国立大学法人　静岡大学

発明者　田中康隆・石田俊正

出願番号　特願 2005-105319

出願日　2005/3/31

公開番号　特開 2006-284390

登録番号　特許 4547499

登録日　2010/7/16

佐藤　徹

理論研究部門　准教授

1. 今年度の研究の要約

今年度は振電相互作用密度の概念を用いて、新規な電子輸送材料の分子設計を行った。

【はじめに】高効率な有機 EL 素子の開発のために、高い移動度を有するキャリア輸送材料が必要とされている。現在知られている電子輸送材料の移動度は、多くの場合、ホール輸送材料のそれよりも小さく、移動度の違いに起因するキャリアバランスの問題が高効率化の妨げとなっている[1]。

分子レベルで設計可能な因子として、フロンティア軌道準位とともに振電相互作用をあげることができる。振電相互作用が小さいことは、高移動度・低エネルギー散逸の必要条件である。

我々は、最近、振電相互作用密度の概念を提案している[2,3]。振電相互作用密度解析によれば、振電相互作用を電子構造と振動構造との関係から理解することが可能となり、さらには、振電相互作用を制御することができる。

ここでは、既知である 3TPYMB の振電相互作用密度解析を通じて、キャリア輸送分子の設計指針を示し、設計した新規な電子輸送分子を示す。

【方法】振電相互作用密度 η_α は、イオン化状態と中性状態の間の差電子密度 $\Delta\rho$ とポテンシャル導関数 υ_α の積で定義される。

$$\eta_\alpha = \Delta\rho \times \upsilon_\alpha \qquad (1)$$

ここで、ポテンシャル導関数は、ひとつの電子に全ての核から作用する核-電子ポテンシャル u の規準座標 Q_α に関する導関数である。

$$\upsilon_\alpha = \frac{\partial u}{\partial Q_\alpha} \qquad (2)$$

振電相互作用定数 V_α は、振電相互作用密度の積分に等しい。

$$V_\alpha = \int \eta_\alpha(r) d^3 r \qquad (3)$$

従って、電子構造から求められる $\Delta\rho$ と振動構造から定まる υ_α の関係から振電相互作用定数を理解することができる。

振電相互作用密度 η_α は、正負の値を取る。原子核近傍では、υ_α は対称的に正負の値を持って分布する。したがって、$\Delta\rho$ が原子上に局在すると η_α は、正負の値に対称的に分布し、相殺がおこる。このような系では、小さな振電相互作用を与える。

【分子設計指針】図 1 に示す 3TPYMB は、電子輸送材料としてよく知られる Alq_3 よりも高い電子移動度を有することが知られている。図 2 と図 3 は、それぞれ Alq3 と 3TPYMB の計算された振電相互作用定数である。3TPYMB の方が小さな振電相互作用を有することがわかる。3TPYMB の差電子密度を図 2 に示す。差電子密度がホウ素原子上に局在していることがわかる。このため、原子ごとの寄与を表す原子振電相互作用定数はホウ素原子上では、0 となっている。また、3 回対称軸を有するため、選択則により相互作用モードの数も少ない。

従って、以下のような設計指針が得られる[4]。(1)差電子密度が原子上に局在した(2)対称性の高い

分子がキャリア輸送分子として望ましい。
このような設計指針に基づき図 5 に示す HBCP を設計した[5]。計算された最適化構造は、6 回対称軸を持ち、差電子密度もホウ素原子上に局在している。
図 6 に計算した振電相互作用定数を示す。3TPYMB よりも小さな振電相互作用を有することが示された。

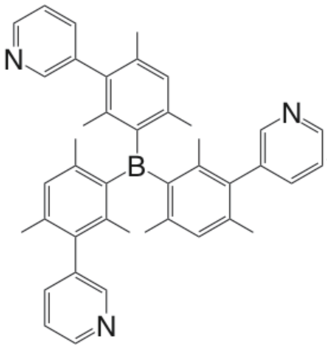


図 1. 3TPYMB

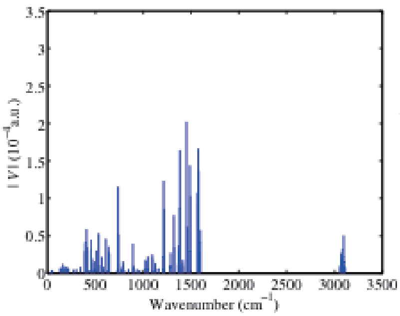


図 2. Alq3 の振電相互作用定数

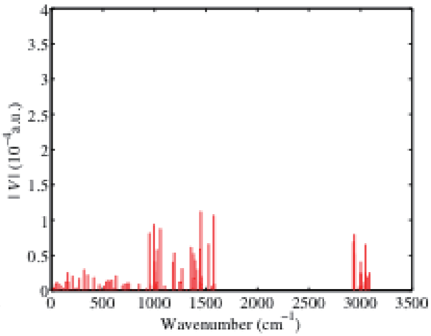


図 3. 3TPYMB の振電相互作用定数

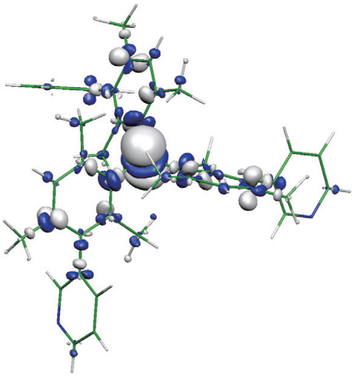


図 4. 3TPYMB の差電子密度

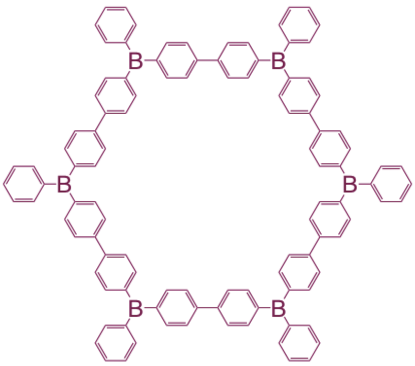


図 5.新規に設計した HCBP

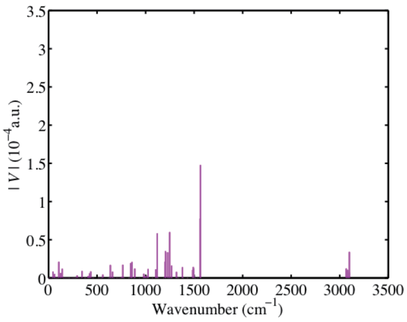


図 6. HCBP の振電相互作用定数

【文献】

[1] Chopra, N., Lee, J., Zheng, Y., Eom, S.-H., Xue, J., and So, F., “Effect of the charge balance on high-efficiency blue-phosphorescent organic light-emitting diodes," *Appl. Mater. Interfaces* 1, 1169 (2009).

[2] Sato, T., Tokunaga, K., and Tanaka, K., “Vibronic coupling in naphthalene anion: Vibronic coupling density analysis for totally symmetric vibrational modes," *J. Phys. Chem. A* 112, 758-767 (2008).

[3] Sato, T., Tokunaga, K., Shizu, K., and Tanaka, K., “Vibronic coupling constant and vibronic coupling density," in [The Jahn-Teller Effect: Fundamentals and Implications for Physics and Chemistry], K oppel, H., Barentzen, H., and Yarkony, D. R., eds., *Springer Series in Chemical Physics* 97, 99-129, Springer-Verlag, Heidelberg Berlin (2009).

[4] Shizu, K., Sato, T., Ito, A., Kaji, H., and Tanaka, K., "Theoretical design of a hole-transporting molecule: Hexaaza[16]parabiphenylophane," *J. Mater. Chem.* **21**, 6375-6382 (2011).
[5] Shizu, K., Sato, T., Tanaka, K., and Kaji, H., "A boron-containing molecule as an efficient electron-transporting material with low-power consumption," *Appl. Phys. Lett.* **97**, 142111 1-3 (2010).

2. 論文

(1) "Vibronic Coupling Density Analysis of Hole-Transporting Materials: Electron-Density Difference in DFT and HF Methods", Katsuyuki Shizu, Tohru Sato, Kazuyoshi Tanaka, Hironori Kaji, Organic Electronics 11, 1277-1287(2010).
(2) "Inelastic Electron Tunneling Spectra and Vibronic Coupling Density Analysis of 2,5-Dimercapto-1,3,4-thiadiazole and Tetrathiafulvalene Dithiol", Katsuyuki Shizu, Tohru Sato, Kazuyoshi Tanaka, Nanoscale 2, 2186-2194(2010).
(3) "N-Anisyl-Substituted Hexaaza[1_6]paracyclophane", A. Ito, Y. Yokoyama, R. Aihara, K. Fukui, S. Eguchi, K. Shizu, T. Sato, K.Tanaka, Angew. Chem. Int. Ed. 49, 8205-8208(2010).
(4) "Revealing Bipolar Charge-Transport Property of 4,4'-N,N'-dicarbazolylbiphenyl (CBP) by Quantum Chemical Calculations", Tomonori Yamada, Furitsu Suzuki, Atsushi Goto, Tohru Sato, Kazuyoshi Tanaka, Hironori Kaji, Organic Electronics 12, 169-178(2010).
(5) "A Boron-Containing Molecule as an Efficient Electron-Transporting Material with Low-Power Consumption", Katsuyuki Shizu, Tohru Sato, Kazuyoshi Tanaka, and Hironori Kaji, Appl. Phys. Lett. 97, 142111 1-3(2010).
(6) "Vibronic coupling in C_{60}^- anion revisited: Precise derivations from photoelectron spectra and DFT calculations", Naoya Iwahara, Tohru Sato, Kazuyoshi Tanaka, Liviu F. Chibotaru, Phys. Rev. B 82, 245409 1-10(2010).
(7) "Molecular design for high-spin molecules in view of vibronic couplings", Naoya Iwahara, Tohru Sato, Kazuyoshi Tanaka, Polyhedron 印刷中.
(8) "Vibronic Coupling Density Analysis for Free-Base Porphin Cation", Katsuyuki Shizu Tohru Sato, Kazuyoshi Tanaka, Chem. Phys. Lett. 505, 42-46 (2010).
(9) "Theoretical Design of a Hole-Transporting Molecule: Hexaaza[1_6]parabiphenylophane", Katsuyuki Shizu Tohru Sato, Akihiro Ito, Hironori Kaji, Kazuyoshi Tanaka, J. Mater. Chem. 21, 6375-6382(2011).
(10) "Vibronic Interactions in Hole-Transporting Molecules: An Interplay with Electron-Hole Interactions", Tohru Sato, Katsuyuki Shizu; Keisuke Uegaito; Naoya Iwahara; Kazuyoshi Tanaka; Hironori Kaji, Chem. Phys. Lett. 507, 151-156(2011).

3. 総説

該当なし

4. 著書

該当なし

5. 学会発表

(1) [招待講演] “Vibronic coupling density analysis”, 20th International Symposium on the Jahn-Teller Effect, 2010年8月16日-20日, University of Fribourg Campus Perolles II, Fribourg, Switzerland

(2) Naoya Iwahara, Tohru Sato, Kazuyoshi Tanaka, Liviu F. Chibotaru, “Vibronic coupling in C60 monoanion”, フラーレンナノチューブ学会 第 39 回フラーレン・ナノチューブ総合シンポジウム, 2010 年 9 月 5 日-7 日, 京都大学百周年記念ホール, 京都市

(3) 佐藤徹, Arnout Ceulemans, “Ih 対称における振電相互作用とスピン-軌道相互作用: (Gamma8 + Gamma9) X (g + 2h) Jahn-Teller 問題”, 日本コンピュータ化学会　２０１０秋季年会, 2010 年 10 月 22-23 日, 長岡技術科学大学, 新潟県長岡市

(4) 上島基之, 佐藤徹, 田中一義, “二原子分子における結合次数と振電相互作用密度”, 日本コンピュータ化学会　２０１０秋季年会, 2010 年 10 月 22-23 日, 長岡技術科学大学, 新潟県長岡市

(5) 新井友春, 岩原直也, 佐藤徹, 田中一義, 田中庸裕, “アルカリ金属イオン添加バナジウム酸化物における光触媒作用と振電相互作用”, 日本コンピュータ化学会　２０１０秋季年会, 2010 年 10 月 22-23 日, 長岡技術科学大学, 新潟県長岡市

(6) 春田直毅, 佐藤徹, 田中一義, “Cyclopentadienyl radical における振電相互作用”, 日本コンピュータ化学会 2010 秋季年会, 2010 年 10 月 22-23 日, 長岡技術科学大学, 新潟県長岡市

(7) 岩原直也、佐藤徹、田中一義、Liviu F. Chibotaru, “C_{60}^{-}における光電子スペクトルと振電相互作用”, 京都大学工学研究科　桂インテックセンター高等研究院 第 3 回　融合ナノ基盤工学研究部門　若手研究者交流会 2010 年 7 月 2 日, 京都大学桂キャンパス、

京都市

(8) Naoya Iwahara, Tohru Sato, Kazuyoshi Tanaka, Liviu F. Chibotaru
Photoelectron spectrum and vibronic couplings in C_{60}^-
20th International Symposium on the Jahn-Teller Effect
2010年8月16日-20日
University of Fribourg Campus Perolles II, Fribourg, Switzerland

(9) 岩原直也、佐藤徹、田中一義、Liviu F. Chibotaru,“C_{60}^-における光電子スペクトルと振電相互作用”, 日本物理学会2010年秋季大会, 2010年9月23日-26日, 大阪府立大学中百舌鳥キャンパス、大阪市

(10) Naoya Iwahara, Tohru Sato, Kazuyoshi Tanaka, “Vibronic Couplings in High- and Low-Spin States of Phenylene Diamines”, The 12th International Conference on Molecule-Based Magnets, 2010年10月8日-12日, Four Points by Sheraton Beijing, Haidian、北京、中国

(11)志津功将、佐藤徹、田中一義、梶弘典,”電子輸送材料Alq3ならびに3TPYMBにおける振電相互作用の理論解析”, 有機EL討論会第10回例会, 2010年6月17-18日, 日本科学未来館、みらいCANホール（東京）

(12)上島基之, 佐藤徹, 田中一義,“CO^+の基底状態における振電相互作用定数”, 日本コンピュータ化学会 年会：2010春季年会, 2010年5月20日(木)-21日(金), 東京工業大学大岡山キャンパス

(13)上島基之, 佐藤徹, 田中一義, 梶弘典, “Alq3 の励起状態における振電相互作用密度解析:構造異性と振電相互作用”, 有機ＥＬ討論会 第11回例会, 2010年11月2日（火-3日(水), 名古屋大学 豊田講堂,

6.その他

特許

(1) 新規な環状化合物、電子輸送材料および有機エレクトロルミネッセンス素子
出願番号： 特願２０１１−４８７２５
発明者: 佐藤　徹、志津　功将、俣野　善博、田中　一義、梶　弘典
権利者: 京都大学、九州大学

中尾 嘉秀

理論研究部門 准教授

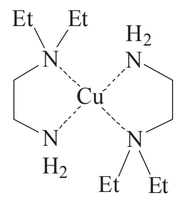
1. 今年度の研究の要約

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。発光性錯体は発光素子に、高スピン状態を保つ錯体は記憶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。今年度はサーモクロミック銅(II)錯体の色変化に対して、量子化学計算と分子動力学法により解明を行った。また、メカノクロミズムを示す金(I)錯体の発光機構について、金-金間相互作用に着目して発光色の変化を理論的に解明した。

【サーモクロミック銅(II)錯体に関する研究】

温度変化により物質の色が変化する現象はサーモクロミズムと呼ばれ、インキやディスプレイ材料への応用が期待されている。Scheme 1 に示した銅(II)錯体 Cu(dieten)$_2$ [dieten = *N*,*N*-diethylethylenediamine]の ClO_4 塩は温度を上昇させると、316 K で赤色から青紫色へと可逆的に色が変化することが報告されている[1]。低温相(293 K)、高温相(329 K)の X 線構造解析から、低温相では銅に対して四つの窒素原子が平面四配位しているのに対して、高温相ではわずかに四面体歪みした配位構造をとることが分かっている[2]。本研究では、量子化学計算により高温相と低温相構造の安定性を評価し、吸収スペクトルの解析を行った。次に、第一原理分子動力学法である Car-Parrinello Molecular Dynamics (CPMD)を用いて温度による構造変化の解析を行って、錯体の色変化と相転移の関係を明らかにした。



Scheme 1. Cu(dieten)$_2$ 錯体

構造最適化及びエネルギー評価、振動計算には B3LYP 法を用い、吸収スペクトルの評価には TD-B3LYP 法を用いた。Cu の内殻電子は Stuttgart-Dresden-Bonn の有効内殻ポテンシャル(ECP)で置き換え、原子価軌道は triple zeta の基底関数を用いた。N, H, C の基底関数は cc-pVDZ を、O,Cl の基底関数は aug-cc-pVDZ を用いた。以上の計算には Gaussian 03 を用いた。相転移のダイナミクスを明らかにするために、CPMD 法を用いて 50 K, 150 K, 250 K, 350 K の温度で結晶状態の構造変化の解析を行った。CPMD 計算では、擬ポテンシャルと平面波(cutoff = 90 Ry.)を基底に、汎関数は BLYP、時間の刻み幅は 0.1 fs、仮想電子質量を 400 a.u.として、CPMD 3.13 を用いた。

X 線構造解析で得られた構造から Cu(dieten)$_2$ 錯体のみを B3LYP 法で構造最適化すると、低温相(**L**)と高温相構造(**H**)のそれぞれに 4 通りの安定構造が得られた。各構造の相対安定性と、配位子と金属のなす 2 つの面の角度 *d* を平面からのずれとして、Table 1 に示した。TD-B3LYP 計算から、平面からのずれが大きい $\mathbf{H_c}$ 構造のみが 490 nm 付近に *d-d* 遷移が存在することが分かった。周期的境界条件を考慮して、これらの結晶状態の構造を最適化すると、低温相構造では $\mathbf{L_a}$ 構造だけが、高温

相構造では 4 つ全てが安定に存在した。10 ps の CPMD 計算から得られた平面からのずれ *d* の分布を Figure 1 に示した。50 K では低温相構造は 3.6 度、高温相構造では 13.9 度と平面からのずれは小さいが、350 K では 17.7 度と 24.3 度と大きな値をとる。Cu(dieten)$_2$ 錯体は高温では四面体歪が大きくなり、*d-d* 遷移が許容となり色変化が起こることが明らかになった。Figure 2 に $\mathbf{L_a}$ 構造を初期構造とした 350K での CPMD 計算から得られた二面角 CuNCC と二面角 NCCN と *d* 値の時間変化を示した。6 ps までは $\mathbf{L_a}$ 構造を保持し、16 ps から $\mathbf{H_d}$ 構造へと構造変化が起こった。50K, 150K, 250K では高温構造への変化は見られなかった。

Table 1. 各構造の相対安定性(kcal mol^{-1})と平面からのずれ *d*(括弧内、degree)

	B3LYP	BLYP	BLYP+PBC
$\mathbf{L_a}$	0.00(0.0)	0.00(0.0)	0.00(1.8)
$\mathbf{L_b}$	2.35(0.1)	2.14(0.0)	—
$\mathbf{L_c}$	1.15(5.0)	1.04(5.6)	—
$\mathbf{L_d}$	1.15(5.0)	1.04(5.2)	—
$\mathbf{H_a}$	1.35(8.5)	1.26(7.9)	0.04(12.9)
$\mathbf{H_b}$	1.35(8.5)	1.26(7.9)	0.05(13.1)
$\mathbf{H_c}$	2.18(22.3)	2.10(14.7)	0.21(8.8)
$\mathbf{H_d}$	0.40(3.5)	0.33(9.2)	0.01(16.7)

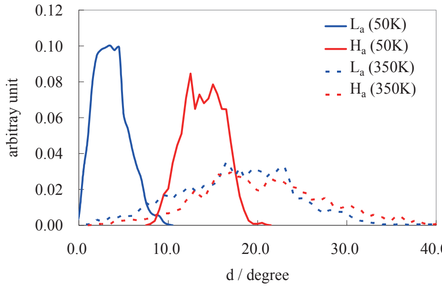


Figure 1. 平面からのずれ *d* の分布

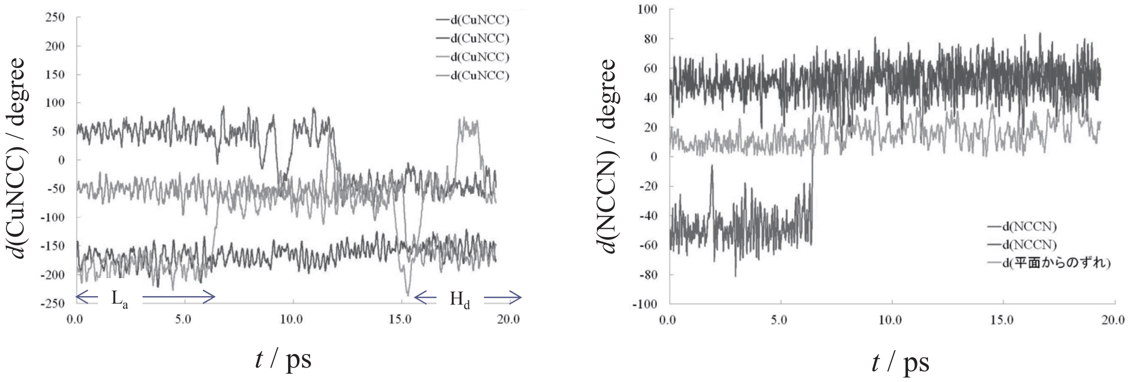
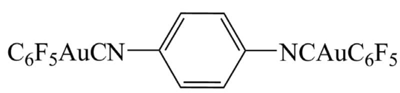


Figure 2. 350K での二面角 CuNCC と二面角 NCCN と *d* 値の時間変化

【金(I)二核錯体およびその集積錯体の吸収・発光スペクトルに関する研究】

量子収率が高いリン光性の金属錯体は、変換効率の高い発光素子への応用が期待され、興味が持たれている。中でも一価の金錯体の発光現象に関しては数多くの興味深い報告例が存在する。例えば、三核金属錯体 [$M_3(R_2pz)_3$] (M = Au; R = CH_3, CF_3) では金属-金属間の相互作用に由来する温度や溶媒に依存する発光が報告されている[3]。最近、金(I)二核錯体 [$(C_6F_5Au)_2$(dicb)] (dicb = 1,4-diisocyanobenzene) (Scheme 2) の発光現象に関する興味深い報告がなされた[4]。この分子は結晶および CH_2Cl_2 溶液中でそれぞれ 415, 418 nm の発光を示し、結晶をスパチュラで擦りつぶすなどの機械的刺激を加えることで、長波長側の 533 nm に発光が変化する非常に珍しいメカノクロミズムを示す。また、類似の単核錯体では短波長側の発光のみ観測され、類似の三核錯体では長波長側の発光のみ観測される。メカノクロミズムなどの特殊な発光現象に関する理論計算の報告例は非常に少なく、発光機構の理論的解明は新規錯体の発光を制



Scheme 2. [$(C_6F_5Au)_2$(dicb)] 錯体

御・設計する上でも重要である。

S_0状態及びT_1状態の構造最適化と振動解析はB3LYP法で、吸収スペクトルの検討はTD-B3LYP法で行った。Auの内殻電子はChristiansenの有効内殻ポテンシャルで置き換え、価電子には(541/551/211)基底を用いた。H, C, N, FにはDunningのcc-pVDZを基底関数として用いた。B3LYP法ではAu-Au間の分子間力を再現できないため、MP2法を用いてAu-Au間距離に対するポテンシャルエネルギー曲線(PEC)の計算を行い、Au-Au間の相互作用を評価した。溶液中の吸収・発光エネルギーの計算ではPolarizable Continuum Model(PCM)法を用いた。二核錯体の単量体および二量体の発光エネルギー評価には、交換汎関数に長距離補正を取り込んだLC-BLYP法も用いた。LC-BLYP法による計算にはGAMESSを用いて、それ以外の計算にはGaussian 03を用いた。

金二核錯体の単量体のT_1状態ではFigure 3に示したπ, π^*軌道が一電子占有軌道となっており、S_0状態では上の軌道がLUMOに相当する。リン光は$\pi^* \rightarrow \pi$遷移に帰属され、リン光エネルギーはB3LYP法では2.37 eVと計算され、短波長側の実験値2.99 eVに比べて小さくなった。B3LYP法では大きなπ共役系を含む分子の長距離相関をうまく表すことができないため、長距離補正を組み込んだLC-BLYP法を用いて計算を行ったところ、リン光エネルギーは2.73 eVとなり、短波長側の実験値とよく一致した(Table 2)。次に、金二核錯体の二量体の構造とリン光エネルギーの検討を行った。S_0状態ではAu-Au間距離が4.752 Åと離れておりAu-Au間に相互作用は存在しないが、H-F間距離が2.307, 2.419 Åと短いので、水素結合のみで二量体が安定化している。一方、T_1状態ではAu-Au間距離が2.853 Å、H-F間距離はS_0状態よりわずかに長く2.520, 2.918 Åで、Au-Au間の金属間結合および水素結合により系が安定化していると考えられる。Figure 4に金二核錯体の単量体の最低励起三重項状態(T_1)の一電子占有軌道を示した。T_1状態における一電子占有軌道はAu-Au間の$5d_{\sigma^*}$軌道と中心の-C_6H_4-NC-Au-のπ^*軌道であり、S_0状態では上の軌道がLUMOに相当する。リン光は$\pi^* \rightarrow 5d_{\sigma^*}$遷移に帰属され、リン光エネルギーは2.50 eVとなり実験値とよく一致した。つまり、機械的刺激後の長波長側の発光はAu-Au間の金属間結合に起因することが明らかになった。TD-B3LYP法で吸収スペクトルを求めると、単量体、二量体ともに4.0～5.0 eV付近の吸収は、π(dicb) → π^*(dicb), π(C_6F_5) → $(5d_\pi\text{-}\pi)^*$(-Au-C-N-)遷移に帰属された。

Table 2. 二核錯体の単量体および二量体のリン光エネルギー(eV)

	B3LYP	LC-BLYP	Expt
単量体	2.37	2.73	2.99
二量体	2.50	3.18	2.33

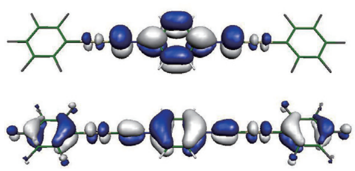


Figure 3. 二核錯体の単量体のT_1状態の一電子占有軌道

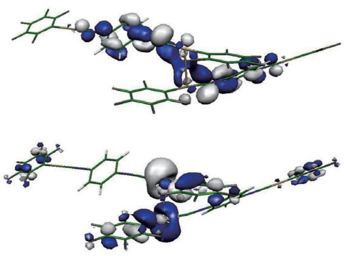


Figure 4. 二核錯体の二量体のT_1状態の一電子占有軌道

【文献】

(1) L. Fabbrizzi, M. Micheloni, and P. Paoletti, *Inorg. Chem.* 13, 3019-3021 (1974).

(2) P. Naumov, K. Sakurai, T. Asaka, A. A. Belik, S. Adachi, J. Takahashi, and S. Koshihara, P. Naumov, *Inorg. Chem.* 45, 5027-5033 (2006).

(3) Omary, M. A.;Rawashdeh-Omary, M. A.; Gonser, M. W. A.; Elbjeirami, O.; Grimes, T.; Cundari, T. R.; Diyabalanage, H. V. K.; Gamage, C. S. P.; Dias, H. V. R. *Inorg. Chem.* 44, 8200-8210 (2005).

(4) Ito, H.; Saito, T.; Oshima, N.; Kitamura, N.; Ishizaka, S.; Hinatsu, Y.; Wakeshima, M.; Kato, M.; Tsuge, K.; Sawamura, M. J. Am. Chem. Soc., 130, 10044-10045 (2008).

2. 論文

(1) T. Umeyama, N. Tezuka, S. Seki, Y. Matano, M. Nishi, K. Hirao, H. Lehtivuori, N. V. Tkachenko, H. Lemmetyinen, Y. Nakao, S. Sakaki, H. Imahori,
Selective formation and efficient photocurrent generation of [70] fullerene-single-walled carbon nanotube composites
Adv. Mater. 22, 1767-1770 (2010).

(2) H. Ando, Y. Nakao, H. Sato, S. Sakaki,
Comparison of Electronic Structures and Light-induced Excited Spin State Trapping between $[Fe(2\text{-picolylamine})_3]^{2+}$ and Its Iron(III) Analogue
Dalton Trans. 39, 3279-3289 (2010).

(3) Y. Nakajima, Y. Nakao, S. Sakaki, Y. Tamada, T. Ono, F. Ozawa,
Electronic structure of four-coordinate iron(I) complex supported by a bis(phosphaethenyl)pyridine ligand
J. Am. Chem. Soc. 132, 9934-9936 (2010).

(4) K. Saito, Y. Nakao, K. Umakoshi, S. Sakaki,
Theoretical study of excited states of pyrazolate- and pyridinethiolate-bridged dinuclear platinum(II) complexes: relationship between geometries of excited states and phosphorescence spectra.
Inorg. Chem. Soc. 49, 8977-8985 (2010).

3. 学会発表

(1) 中尾嘉秀，山田裕，榊茂好，伊藤肇，澤村正也
「金(I)二核錯体およびその集積錯体の吸収・発光スペクトルに関する理論的研究」
第 60 回錯体化学討論会，大阪国際交流センター，2010 年 9 月 27 日～30 日，2B-07

(2) 竹中裕喜雄，黒川悠索，中尾嘉秀，佐藤啓文，榊茂好
「逆サンドイッチ型二核金属錯体に関する理論的研究」
第4回分子科学討論会，大阪大学豊中キャンパス，2010年9月14日～17日，2P108

(3) 中尾嘉秀，山田裕，榊茂好，伊藤肇，澤村正也
「金(I)二核錯体およびその集積錯体の吸収・発光スペクトルに関する理論的研究」
第 4 回分子科学討論会，大阪大学豊中キャンパス，2010 年 9 月 14 日～17 日，1P116

(4) 吉本亜矢，石川敦之，佐藤啓文，中尾嘉秀
「リンや硫黄を含んだ梯子型π共役化合物の光物性の理論的研究」
日本化学会第91春季年会，神奈川大学横浜キャンパス，2011年3月26日～29日，
2PC-167

２．リサーチリーダー

Keiji MOROKUMA

Research Leader, Kenichi Fukui Memorial Research Group 1

1. Summary of the research of the year

Multi-level Simulation of Complex Molecular Systems

The goals of the research of this group are 1. to develop further the hybrid theoretical methods (such as ONIOM) already proposed by us, 2. to demonstrate that such hybrid methods can be used for simulations of structures, reactions and dynamics 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) until March 2012. With ten to twelve postdoctoral fellows (both Fukui fellows and JST fellows), a few visiting graduate students and several research assistants in the group, as well as in collaboration with my group at Emory University, the group of Prof. Stephan Irle (a CREST collaborator) of Nagoya University as well as Prof. Satoshi Maeda, Assistant Professor at Hakubi Center, Kyoto 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 Biomolecular Systems

In the area of **multi-level simulation of biomolecular systems**, in recent years we have studied structures and reactions of metalloenzyme systems mainly using the active site models in which only the active site atoms are explicitly included in the QM calculations. In the last few years we have explicitly included the effects of protein employing the ONIOM QM/MM scheme. We optimized the structures of intermediates and transition states of enzymatic reactions, and in some cases included the statistical effects of protein by QM/MM molecular dynamics, In a few examples we have found that the protein effects completely changed the mechanism of reaction, compared to the active-site models. We also perform direct dynamics calculations using QM and QM/MM methods to study the primary events of photochemical processes of biomolecular chromophore. We recently expanded our theoretical studies of catalytic reactions that take place in the nano cavity created by the protein.

a) **Density Functional Theory Investigation of the Catalytic Mechanism of Hydroxyethylphosphonate Dioxygenase** (See research activities of Dr. Hirao)
b) **Theoretical Study of the Mechanism of Oxoiron(IV) Formation from H_2O_2 and a Nonheme Iron(II) Complex: O–O Cleavage Involving Proton-Coupled Electron Transfer** (See research activities of Dr. Hirao)
c) **Comparative Reactivity of Ferric-Superoxo and Ferryl-Oxo Species in Heme and non-Heme Complexes** (See research activities of Dr. Chung)
d) **Towards understanding the HppE catalytic mechanism** (See research activities of Dr. Petrova)
e) **Theoretical Studies of the Reaction Mechanism, Regioselectivity and Stereoregularity** (See research activities of Dr. Ke)
f) **Theoretical Study of Artificial Metalloenzymes** (See research activities of Dr. Ke)
g) **Theoretical Investigation on Light-Driven Molecular Rotary Motors** (See research activities of Dr. Liu)
h) **Ring-Opening and Ring-Closure Mechanism of Spiropyran-Merocyanine Photochromic Reaction** (See research activities of Dr. Liu)
i) **Photodynamics of All-trans Retinal Protonated Schiff Base in Bacteriorhodopsin and Methanol Solution** (See research activities of Dr. Xing Li)
j) **Mechanistic study on photo-induced decarboxylation of the Photoactivable Green Fluorescent**

Protein: A theoretical ONIOM(QM:MM) calculation (See research activities of Dr. Ding)

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 and other nanostructure formation based on density functional tight binding (DFTB). Single-walled carbon nanotubes (SWNTs) have been one of representative nanotechnology materials and their various potential applications. Although SWNTs are known to be efficiently synthesized using metal catalyst, its growth mechanism is still not well understood. In order to understand interplay among feedstock carbon, nanotube, and metal, we have implemented growth simulations of metal-catalyzed SWNT using DFTB MD simulations. Previously we succeeded in simulating continued growth SWNT on Fe cluster in our simulation studies. Since then we have successfully simulated SWNT growth from scratch (without seed SWNT) under a variety of conditions and our understanding of the growth process has given insight to its mechanism which has not been seen previously from either experimental or theoretical studies. We also studied the nucleation of SWNT cap from Si-bases materials.

a) **Annealing of hot giant fullerenes: DFTB MD simulations** (See research activities of Dr. Saha)
b) **Determination of Local Chirality in Irregular Single-Walled Carbon Nanotube Based on Individual Hexagons** (See research activities of Dr. Kim)
c) **QM/MD Investigation of Single-Walled Carbon Nanotube Nucleation from Si-Based Catalysts: A Vapor-Solid-Solid Mechanism** (See research activities of Dr. Page)
d) **DFT QM/MD Investigation of the Nucleation of Single-walled Carbon nanotubes on the Nonmetallic Silicon Nanoparticles** (See research activities of Dr. Chandrakumar)
e) **Is SWNT Nucleation on Silicon Nanoparticles Preceded by a Carbide Phase or a Carbon-Coated Surface?** (See research activities of Dr. Chandrakumar)
f) **Melting Behavior of the Pure and carbon-doped Silicon Nanoparticles: Carbon Induced Liquid-to-Solid Phase Transition in Silicon Nanoparticles** (See research activities of Dr. Chandrakumar)
g) **Fullerene formation from hydrocarbon combustions: Quantum chemical molecular dynamics study** (See research activities of Dr. Haibei Li)
h) **Armchair-type SWCNT growth from bottom-up organic synthesis** (See research activities of Dr. Haibei Li)
i) **QM/MD Investigation of Haeckelite and Graphene Growth on Transition Metal Surfaces synthesis** (See research activities of Dr. Page)

III. Method Developments and Applications

Last year we have extended the Global Reaction Route Mapping (GRRM) method developed previously by Ohno and Maeda to automatic search of the minimum of seam of crossing (MSX) including the conical intersection. This year we further developed the MSX search method based on the updating of the branching plane without calculating derivative coupling vector. Further more, this method was applied to elucidation of the mechanism of photodissociation reactions of acetone and methyl ethyl ketone.

A new method, artificial force-induced reaction (AFIR) method, suitable to determining the transition and intermediates of reactions of two or more molecules A + B (+C…) → X, has been developed based on imposing an artificial attractive force between the reactant molecules. The application of this method to the Passerini reaction, which has been known in textbooks as an example of three-molecule reaction, showed that it actually involved four molecules in the reaction. Application to other multicomponent reactions is in progress.

(Work in collaboration with Prof. Maeda, who is Assistant Professor at Hakubi Center of Kyoto University and Visiting Assistant Professor at FIFC. See also his Research Activities)

a). Theoretical Study of NO_3 Photodissociation (See research activities of Dr. Xiao)

2. Original papers

1. A. J. Page, K. R. S. Chandrakumar, S. Irle, and K. Morokuma, Do SiO_2 and Carbon-Doped SiO_2 Nanoparticles Melt? Insights from QM/MD Simulations and Ramifications Regarding Carbon Nanotube Growth, Chem. Phys. Lett. 508, 235–241 (2011).
2. A. Nakamura, K. Munakata, S. Ito, T. Kochi, L. W. Chung, K. Morokuma and K. Nozaki, Pd-Catalyzed Copolymerization of Methyl Acrylate with Carbon Monoxide: Structures, Properties and Mechanistic Aspects toward Ligand Design, J. Am. Chem. Soc. 133, 6761-6779 (2011).
3. H. Xiao, S. Maeda and K. Morokuma, Excited State Roaming Dynamics in Photolysis of Nitrate Radical. J. Phys. Chem. Lett. *2*, 934–938 (2011). DOI: 10.1021/jz2003364; featured in S. North, Natue Chem. 3, 504-504 (2011).
4. S. Maeda, R. Saito, and K. Morokuma, Finding Minimum Structures on Seam of Crossing in Reactions of Type A + B → X: Exploration of Nonadiabatic Ignition Pathways of Unsaturated Hydrocarbons. J. Phys. Chem. Lett. 2, 852–857 (2011).
5. S. Sekharan and K. Morokuma, QM/MM Study of the Structure, Energy Storage and Origin of the Bathochromic Shift in Vertebrate and Invertebrate Bathorhodopsins. J. Am. Chem. Soc, 133, 4734-4737 (2011).
6. Kawatsu, M. Lundberg and K. Morokuma. Protein Free Energy Corrections in ONIOM QM:MM Modeling: A Case Study for Isopenicillin N Synthase (IPNS) J. Chem. Theo. Comp. 7, 390-401 (2011).
7. S. Maeda, S. Komagawa, M. Uchiyama, and K. Morokuma. Finding Reaction Pathways for Multicomponent Reactions: The Passerini Reaction Is a Four-Component Reaction. Angew, Chem. Int. Ed. 50, 644-649. (2011).
8. A. J. Page, K. R. S. Chandrakumar, S. Irle, and K. Morokuma, SWNT Nucleation from Carbon-Coated SiO_2 Nanoparticles via a Vapor-Solid-Solid Mechanism. J. Am. Chem. Soc. 133, 621-628 (2011).
9. H. Hirao and K. Morokuma, Ferric Superoxide and Ferric Hydroxide Are Used in the Catalytic Mechanism of Hydroxyethylphosphonate Dioxygenase (HEPD): A Density Functional Theory Investigation, J. Am. Chem. Soc. 132, 17901-17909 (2010).
10. N. Bera, S. Maeda, K. Morokuma and A. A. Viggiano, Theoretical study of proton affinity and fluoride affinity of nerve agent VX. J. Phys. Chem. A 114, 13189-13197 (2010).
11. R. Nádasdi, G. L. Zügner, M. Farkas, S. Dóbé, S. Maeda, and K. Morokuma, Photochemistry of Methyl Ethyl Ketone: Quantum Yields and S_1/S_0-Diradical Mechanism of Photodissociation, Phys. Chem. Phys. 11, 3883–3895 (2010).
12. X. Li, L. W. Chung, A. Miyawaki and K. Morokuma, Primary Events of Photodynamics in Reversibly Photoswitching Fluorescent Protein Dronpa, J. Phys. Chem. Lett. 1, 3328–3333 (2010).
13. X. Li, L.W. Chung, A. Miyawaki, and K. Morokuma, Competitive Mechanistic Pathways for Green-to-Red Photoconversion in the Fluorescent Protein Kaede: A Computational Study, J. Phys. Chem. B, 114, 16666-16675 (2010).
14. K. Nozaki, S. Kusumoto, S. Noda, T. Kochi, L. W. Chung, and K. Morokuma, Why Did Incorporation of Acrylonitrile to a Linear Polyethylene Become Possible? Comparison of Phosphine-Sulfonate Ligand with Diphosphine and Imine-Phenolate Ligands in the Pd-Catalyzed Ethyelene/Acrylonitrile Copolymerization; J. Am. Chem. Soc. 132, 16030-16042 (2010).
15. S. Sekharan, A. Altun, and K. Morokuma, Retinal QM/MM Study of Dehydro and Dihydro β-Ionone Retinal Analogues in Squid and Bovine Rhodopsins: Implications for Vision in Salamander Rhodopsin, J. Am. Chem. Soc. 132, 15856-15859 (2010),
16. A. J. Page, H. Yamane, Y. Ohta, S. Irle, and K. Morokuma, QM/MD Simulation of SWNT Nucleation from Transition-Metal Carbide Nanoparticles, J. Am. Chem. Soc. 132, 15699–15707 (2010
17. A. J. Page, Y. Ohta, S. Irle and K. Morokuma, Mechanisms of Single-Walled Carbon Nanotube Nucleation, Growth and Healing Determined Using QM/MD Methods, Acc. Chem. Res. 43. 1375-1385 (2010).
18. J. Jakowski, S. Irle and K. Morokuma, Collision-induced fusion of two C60 fullerenes: quantum chemical molecular dynamics simulations, Phys. Rev. B 82, 125443/1-8 (2010).
19. P. V. Avramov, S.Minami, S. Irle, L. A. Chernozatonskii, and K. Morokuma. Atomic Structure and Energetic Stability of Complex Chiral Silicon Nanowires, J. Phys. Chem. C, 114, 16692-14696 (2010).
20. L. W. Chung, X. Li, H. Sugimoto, Y. Shiro, and K. Morokuma, ONIOM Study on a Missing Piece in Our Understanding of Heme Chemistry: Bacterial Tryptophan 2,3-Dioxygenase with Dual Oxidants. J. Am. Chem. Soc. 132, 11993-12005 (2010).
21. S. Maeda and K. Morokuma, Communications: A Systematic Method for Locating Transition Structures of A + B → X Type Reactions, J. Chem. Phys. 24, 241102/1-4 (2010).
22. S. Maeda, K. Ohno, and K. Morokuma, A Theoretical Study on the Photodissociation of Acetone: An Insight into the Slow Intersystem Crossing and Exploration of Nonadiabatic Pathways to the Ground State,

J. Phys. Chem. Lett. 1, 1841-1845 (2010).
23. A. J. Page, S. Minami, Y. Ohta, S. Irle and K. Morokuma, Comparison of Single-Walled Carbon Nanotube Growth from Fe and Ni Nanoparticles using quantum chemical molecular dynamics methods, Carbon, 48, 3014-3026 (2010).
24. B. Saha, S. Irle and K. Morokuma, Formation mechanism of polycyclic aromatic hydrocarbons (PAH) in the benzene flame: Density functional tight binding molecular dynamics simulations, J. Chem. Phys. 132, 224303/1-11 (2010)
25. V. P. Ananikov, D. G. Musaev, and K. Morokuma, Real size of ligands, substrates and catalysts: studies of structure, reactivity and selectivily by ONIOM and other hybrid computational approaches, J. Mol. Cat. A. 24, 104–119 (2010).
26. S. Maeda, K. Ohno, and K. Morokuma, Updated Branching Plane for Finding Conical Intersections without Derivative Coupling Vectors. J. Chem. Theo. Comp. 6, 1538–1545 (2010).

3. Review article

J. Jakowski, S. Irle and K. Morokuma, Quantum Chemistry: Propagation of Electronic Structure on a GPU, in “GPU Compute Gems Emerald Edition” ed. W. W. Hwu, Morgan Kaufmann (Elsevier), 59-74 (2011).

4. Books

None

5. Presentation at academic conferences

1. May 10, 2010, Harry King symposium, University of Buffalo, NY, USA, Exciting World of Theoretical Studies of Chemical Reactions – From Gas Phase Reactions to Nano Structures, Catalysts, and Enzymatic Reactions.
2. May 26, 2010, Molecular Quantum Mechanics conference, Berkeley, CA, USA, ONIOM Studies of Photochemical Processes and Chemical Reactions of Biomolecular Systems in Protein
3. July 20,2010, Gordon Conf- Atomic and Molecular Interaction, Colby Sawyer college, New London, USA: Theoretical studies of excited state structure, spectroscopy and dynamics of some gas phase and biomolecular systems
4. November 29, 2010, invited seminar at Oak Ridge National Laboratory, Oak Ridge, TN USA, Exciting World of Theoretical Studies of Chemical Reactions – From Gas Phase Reactions to Nano Structures, Catalysts, and Enzymatic Reactions
5. December 1, 2010, invited seminar at University of Tennessee, TN, Nashville, USA, Exciting World of Theoretical Studies of Chemical Reactions – From Gas Phase Reactions to Nano Structures, Catalysts, and Enzymatic Reactions
6. December 17, 2010, Pacifichem 2010, Symposium on Computational Quantum Chemistry: Theory and Interactions with Experiment, Honolulu, HI, USA, History and Overview of Quantum Chemistry in Japan, on the Occasion of Honoring Profs. Hiroshi Nakatsuji, Kimihiko Hirao, and Shigeru Nagase
7. December 18, 2010, Pacifichem 2010, Symposium on Challenges and Solutions to Accurate Calculations on Large Molecular Systems and Condensed Phases, Honolulu, HI, USA, ONIOM Studies of Photochemical Processes and Chemical Reactions of Biomolecular Systems in Protein
8. 2011 年２月７日原子力科学研究所 金曜セミナー、複雑分子系の分子理論によるシミュレーション
9. March 30, 2011, Fatih University, Department of Physics, Istanbul, Turkey, Exciting World of Theoretical Studies of Chemical Reactions – From Gas Phase Reactions to Nano Structures, Catalysts, and Enzymatic Reaction,

３．特定助教（白眉）

Satoshi MAEDA

Visiting Assistant Professor (The Hakubi Center, Kyoto University),
Kenichi Fukui Memorial Research Group 1

1. Summary of the research of the year

1-0. Introduction

The mechanism of chemical reactions can be elucidated by exploring quantum chemical potential energy surfaces (PESs) for reaction pathways [1,2]. Search for transition state (TS) structures is the primal task in such studies, since a reaction path can be computed easily by the intrinsic reaction coordinate (IRC) method [3] once a corresponding TS structure is found. Reaction mechanisms of numerous chemical reactions have been elucidated by calculations of TS structures and corresponding reaction pathways.

One TS structure can be found by a geometry optimization starting from an initial guess structure. However, an initial guess structure leads only to a TS structure anticipated from it. For finding unexpected pathways as well as anticipated ones, systematic search is necessary using an automated reaction path search method.

There had been no general method which can explore chemical reaction pathways automatically on quantum mechanical PESs until very recently. Hence, we have developed two such methods: the global reaction route mapping (GRRM) method [4-6] and the artificial force induced reaction (AFIR) method [original paper 9]. These two are independent but complementally to each other. Reaction pathways of type A → X (isomerization) and A → X + Y (dissociation) can be explored by GRRM, while AFIR can search for A + B → X (+ Y) type synthetic pathways.

We applied these methods to some complex chemical reactions: photolysis of atmospheric molecules [original papers 1, 7, and 10], combustion reactions of unsaturated hydrocarbons [original paper 2], an organic multicomponent reaction [original paper 4], a photoionization reaction in a hydrogen-bond cluster [original paper 6], and a surface oxidation reaction [original paper 8].

We also investigated on the infrared spectra of benzene [original paper 3] and ion-molecule reactions of nerve-agent VX [original paper 5] to make analyses of experimental data.

Works in original papers 4, 5, 6, 7, and 8 were conducted with experimental groups.

[1] Schlegel, H. B. *J. Comput. Chem.* **2003**, *24*, 1514.
[2] Jensen, F. *Introduction to Computational Chemistry, 2nd edn.*, Wiley, Chichester, **2007**.
[3] Fukui, K. *Acc. Chem. Res.* **1981**, *14*, 363.
[4] Ohno, K.; Maeda, S. *Chem. Phys. Lett.* **2004**, *384*, 277.
[5] Maeda, S.; Ohno, K. *J. Phys. Chem. A* **2005**, *109*, 5742.
[6] Ohno, K.; Maeda, S. *J. Phys. Chem. A* **2006**, *110*, 8933.

1-1. Excited-State Roaming Dynamics in Photolysis of a Nitrate Radical *(original paper 1)*

Roaming dynamics has been recognized as one of the key mechanisms in atmospheric and combustion processes. In this Letter, we report the first example of roaming dynamics that occurs on an excited-state potential energy surface. In the photodissociation of a nitrate radical, systematic CASPT2 reaction path search and DFT dynamics calculations show that the roaming dynamics occurs on the first excited doublet state (D_1). The direct dissociation on D_1 gives the minor vibrationally cold O_2, while the indirect dissociation after the nonadiabatic transition to the ground doublet state (D_0) produces the major vibrationally hot O_2; this proposal explains the recent experimental results. (This article was highlighted in News & Views of Nature Chemistry: see, S. W. North, Roaming in the Dark., *Nat. Chem.*, **2011**, *3*, 504-505.)

2-2. Finding Minimum Structures on the Seam of Crossing in Reactions of Type A + B → X: Exploration of Nonadiabatic Ignition Pathways of Unsaturated Hydrocarbons *(original paper 2)*

A new theoretical approach is proposed for finding automatically minimum structures on the seam of crossing (MSX) in reactions of type A + B → X, where the artificial-force-induced reaction (AFIR) method is combined with the seam model function (SMF) approach. Its application to reactions between triplet dioxygen and unsaturated hydrocarbons provided many MSX structures. In addition to known ignition pathways, we discovered a pathway through a new type of MSX in the reaction of dioxygen with aromatic hydrocarbons; for benzene, this new pathway requires a lower energy than those of three known ignition pathways and is likely to be the most important. This demonstrates that the AFIR-SMF approach has the ability to discover unknown/unexpected MSX structures without prejudice for presumed pathways or mechanisms.

2-3. Ab Initio Anharmonic Calculations of Vibrational Frequencies of Benzene by Means of Efficient Construction of Potential Energy Functions *(original paper 3)*

An efficient technique constructing anharmonic potential energy functions was applied to ab initio vibrational analysis of benzene. Anharmonic potentials including the 6-order terms, much higher than the full quartic force field, were automatically generated by a second-order algorithm using the scaled hypersphere search method, and vibrational calculations were performed at the level of VQDPT[1+2]. In comparison with previously reported anharmonic calculations, the present approach gave an excellent ab initio result for in-plane modes including the b_{2u} so called Kekulé mode. Characteristic properties of various approaches were discussed in connection with the anharmonic effects and the strong vibronic effects.

2-4. Finding Reaction Pathways for Multicomponent Reactions: The Passerini Reaction Is a

Four-Component Reaction *(original paper 4)*

The Passerini three-component reaction of a carboxylic acid, an aldehyde (or ketone), and an isocyanide to give an α-acyloxycarboxamide actually follows a four-component mechanism involving an additional molecule of carboxylic acid (see scheme). The discovery was made by applying a new "reaction route explorer" to the simplest Passerini reaction ($HCOOH+HCHO+CH_3NC$).

2-5. Theoretical Proton Affinity and Fluoride Affinity of Nerve Agent VX *(original paper 5)*

Proton affinity and fluoride affinity of nerve agent VX at all of its possible sites were calculated at the RI-MP2/cc-pVTZ//B3LYP/6-31G* and RI-MP2/aug-cc-pVTZ//B3LYP/6-31+G* levels, respectively. The protonation leads to various unique structures, with H^+ attached to oxygen, nitrogen, and sulfur atoms; among which the nitrogen site possesses the highest proton affinity of $-\Delta E \sim 251$ kcal/mol, suggesting that this is likely to be the major product. In addition some H_2, CH_4 dissociation as well as destruction channels have been found, among which the CH_4 + [Et−O−P(═O)(Me)−S−$(CH_2)_2$−N^+(*i*Pr)═CHMe] product and the destruction product forming Et−O−P(═O)(Me)−SMe + CH_2═$N^+$$(i\mathrm{Pr})_2$ are only 9 kcal/mol less stable than the most stable N-protonated product. For fluoridization, the S−P destruction channel to give Et−O−P(═O)(Me)(F) + $[S{-}(CH_2)_2{-}N{-}(i\mathrm{Pr})_2]^-$ is energetically the most favorable, with a fluoride affinity of $-\Delta E \sim 44$ kcal. Various F^- ion−molecule complexes are also found, with the one having F^- interacting with two hydrogen atoms in different alkyl groups to be only 9 kcal/mol higher than the above destruction product. These results suggest VX behaves quite differently from surrogate systems.

2-6. Long-Range Migration of a Water Molecule To Catalyze a Tautomerization in Photoionization of the Hydrated Formamide Cluster *(original paper 6)*

The dynamics on the vacuum-ultraviolet one-photon ionization of a formamide−water cluster is investigated by a combination of theoretical reaction-path search and infrared spectroscopic methods. A keto−enol tautomerization of the formamide moiety occurs after photoionization by a catalytic action of the water molecule accompanied with its long-distance migration; the water molecule in the cluster migrates almost one turn around the formamide moiety. During the migration, the water molecule abstracts the proton of CH in the formamide moiety and carries it to the O atom side in the carbonyl group through a "catch and release"-type catalytic action.

2-7. Photochemistry of Methyl Ethyl Ketone: Quantum Yields and S_1/S_0-Diradical Mechanism of Photodissociation *(original paper 7)*

Pulsed laser photolysis (PLP) at λ = 248 and 308 nm coupled with gas-chromatographic analysis is applied to determine the photodissociation quantum yield (QY) of methyl ethyl ketone (MEK).

Temperature dependent UV absorption cross-sections [$\sigma_{MEK}(\lambda,T)$] are also determined. At 308 nm, the QY decreases with decreasing temperature (T = 323–233 K) and with increasing pressure (P = 67-998 mbar synthetic air). Stern–Volmer (SV) analysis of the T and P dependent QYs provides the experimental estimate of E_{S1} = 398 ± 9 kJ mol^{-1} (= 300 ± 6 nm) for the barrier of the first excited singlet state (S_1). The QY at 248 nm is close to unity and independent of pressure (T = 298 K). Theoretical reaction pathways are examined systematically on the basis of CASPT2/6-31+G* calculations. Among three possible pathways, a S_1/S_0-diradical mechanism, which involves H atom transfer on the S_1 surface, followed by a nonadiabatic transition at a diradical isomer of MEK, explains the experimental data very well. Therefore, this unusual mechanism, which is not seen in any smaller carbonyl compounds, is proposed as an important pathway for the MEK dissociation. Our study supports the view that both the absorption cross-sections and the QYs of carbonyls have significant temperature dependences that should be taken into account for accurate modeling of atmospheric chemistry. (This article was featured on the inside cover.)

2-8. Theoretical Investigation of the Reaction Pathway of O Atom on Si(001)-(2 × 1) *(original paper 8)*

Structural, energetic, and mechanistic features of the initial steps of the reaction of an O atom with Si(001)-(2 × 1) were modeled by the use of a Si_9H_{12} + O system. Transition state structures (TSs) and equilibrium structures (EQs) as well as dissociation channels (DCs) were systematically searched using a global reaction route mapping (GRRM) technique on the potential energy surface (PES) based on the scaled hypersphere search (SHS) algorithm. The first six low-energy structures were consistent with known structure models for oxygen adsorption on the dimer of Si(001)-(2 × 1). Other structures with higher energies could be well interpreted as intermediates leading toward reaction paths for migration/dissociation occurring at high temperatures.

2-9. A Systematic Method for Locating Transition Structures of A + B → X Type Reactions *(original paper 9)*

Search for transition structures (TSs) as first-order saddles is one of the most important tasks in theoretical study of chemical reaction. Although automated search has been established either by starting from a local minimum (MIN) or by connecting two MINs, there is no systematic method which can locate TSs of A + B → X (+ Y) type reactions starting from separated reactants. We propose such an approach for the first time; it was demonstrated to work very well in the SN2, Diels–Alder, and Wittig reactions.

2-10. A Theoretical Study on the Photodissociation of Acetone: An Insight into the Slow Intersystem Crossing and Exploration of Nonadiabatic Pathways to the Ground State *(original* *paper 10)*

Structures of transition states (TSs) and minima on seam of crossing (MSXs) for potential energy surfaces (PESs) of acetone of the S_0, S_1, and T_1 states were explored. On the basis of the results, we propose a new mechanism, slow intersystem crossing from S_1 to T_1 without seam of crossing, followed by CH_3 dissociation via a TS on T_1; this slow pathway will be overtaken by a more efficient S_1 pathway for higher energy. This is consistent with the observed long lifetime of the S_1 species. Moreover, four channels, including three new ones, were found to regenerate the ground state acetone from the S_1 PES, and they all may be involved in the roaming channel that has been proposed recently as a new route of CO generation in a 230 nm photolysis. There are significant differences in MSX structures and energies between the present CASPT2 results and previous CASSCF results.

2. List of original papers

(1) H. Xiao, S. Maeda, K. Morokuma, Excited State Roaming Dynamics in Photolysis of Nitrate Radical., *J. Phys. Chem. Lett.*, **2011**, *2*, 934-938.

(2) S. Maeda, R. Saito, K. Morokuma, Finding Minimum Structures on the Seam of Crossing in Reactions of Type A + B → X: Exploration of Nonadiabatic Ignition Pathways of Unsaturated Hydrocarbons., *J. Phys. Chem. Lett.*, **2011**, *2*, 852-857.

(3) K. Ohno, S. Maeda, Ab Initio Anharmonic Calculations of Vibrational Frequencies of Benzene by Means of Efficient Construction of Potential Energy Functions., *Chem. Phys. Lett.*, **2011**, *503*, 322-326.

(4) S. Maeda, S. Komagawa, M. Uchiyama, K. Morokuma, Finding Reaction Pathways for Multicomponent Reactions: The Passerini Reaction Is a Four-Component Reaction., *Angew. Chem. Int. Ed.*, **2011**, *50*, 644-649.

(5) N. C. Bera, S. Maeda, K. Morokuma, A. A. Viggiano, Theoretical Proton Affinity and Fluoride Affinity of Nerve Agent VX., *J. Phys. Chem. A*, **2010**, *114*, 13189-13197.

(6) S. Maeda, Y. Matsuda, S. Mizutani, A. Fujii, K. Ohno, Long-Range Migration of a Water Molecule To Catalyze a Tautomerization in Photoionization of the Hydrated Formamide Cluster., *J. Phys. Chem. A*, **2010**, *114*, 11896-11899.

(7) R. Nadasdi, G. L. Zugner, M. Farkas, S. Dobe, S. Maeda, K. Morokuma, Photochemistry of Methyl Ethyl Ketone: Quantum Yields and S_1/S_0-Diradical Mechanism of Photodissociation., *ChemPhysChem*, **2010**, *11*, 3883-3895.

(8) S. Ohno, K. Shudo, M. Tanaka, S. Maeda, K. Ohno, Theoretical Investigation of the Reaction Pathway of O Atom on Si(001)-(2 × 1)., *J. Phys. Chem. C*, **2010**, *114*, 15671-15677.

(9) S. Maeda, K. Morokuma, Communication: A Systematic Method for Locating Transition Structures of A + B → X Type Reactions., *J. Chem. Phys.*, **2010**, *132*, 241102/1-4.

(10) S. Maeda, K. Ohno, K. Morokuma, A Theoretical Study on the Photodissociation of Acetone: An Insight into the Slow Intersystem Crossing and Exploration of Nonadiabatic Pathways to the Ground State., *J. Phys. Chem. Lett.*, **2010**, *1*, 1841-1845.

3. List of review articles

(1) 前田理・大野公一・諸熊奎治、「分子の反応経路の自動探索が可能になった」、現代化学、**2011**, *478*, 32-37.

4. List of books

5. List of presentations at meetings

(1) (Oral) S. Maeda, K. Ohno, K. Morokuma, Theoretical Studies on Gas-Phase Photochemical Reaction Mechanisms of Small Organic Molecules Using the Global Reaction Route Mapping Method., The 2010 International Chemical Congress of Pacific Basin Societies (Pacifichem), Honolulu, Hawaii, USA, December 15-20, 2010

(2) (Poster) S. Maeda, K. Ohno, K. Morokuma, Efficient Optimizations of Conical Intersection Geometries Using New Algorithms., The 2010 International Chemical Congress of Pacific Basin Societies (Pacifichem), Honolulu, Hawaii, USA, December 15-20, 2010

(3) (Invited talk) S. Maeda, Development of Automated Reaction Path Search Methods and Applications to Hydrogen-bonded Clusters., Molecular Photoscience Research Center International Symposium "New Horizons of Cluster Chemistry", Kobe University, Japan, October 9-10, 2010

(4) (招待講演)「反応経路探索法の新展開」、シンポジウム「化学反応経路探索のニューフロンティア 2010」、京都大学福井謙一記念研究センター、2010 年 9 月 13 日

(5) (口頭発表)前田理・駒川晋輔・内山真伸・諸熊奎治、「多成分反応の遷移構造の自動的な系統探索」、第 4 回分子科学討論会、大阪大学豊中キャンパス、2010 年 9 月 14-17 日

(6) (Oral) S. Maeda, Systematic Exploration of Photochemical Reaction Pathways: Applications to Ketones and Aldehydes., The 8th FIFC Seminar, Fukui Institute for Fundamental Chemistry, Kyoto University, June 21, 2010

(7) (Oral) S. Maeda, K. Ohno, K. Morokuma, Photodissociation Mechanisms of Aldehydes and Ketones., 26th Symposium on Chemical Kinetics and Dynamics, Hiroshima University Satake Memorial Hall, June 2-4, 2010

6. Others

４．博士研究員

Biswajit SAHA

FIFC Fellow, Fukui kenichi Memorial Research Group 1
（To 30 Apr. 2010）

1. Summary of the research of the year FY2010

(A) Annealing of hot giant fullerenes: DFTB MD simulations

To understand the fullerene formation process, Irle, Morokuma, and coworkers had performed earlier a series of density-functional tight-binding (DFTB)-based quantum chemical molecular dynamics (QM/MD) simulations. These extensive nonequilibrium MD studies led to the formulation of the “Shrinking Hot Giant” (SHG) road of fullerene formation, according to which at first giant fullerenes (GFs) C_n with $n > 80$ self-assemble through irreversible interactions and autocatalytic reactions of polyyne chains or macrocycles (‘size up’), which then shrink in size down to smaller, kinetically more stable fullerenes such as C_{70} and C_{60}, initially by polyyne “antenna” ‘fall-off’ and later by continued and irreversible C_2 evaporation (‘size down’). The latter cage shrinking process resembles Smalley’s ‘shrink-wrap’ mechanism of laser-induced C_2 elimination from C_{60}, and occurs under the effect of thermal excitation in the case of defect-bearing fullerene cages, even though the shrinking process itself is endothermic.

Although thermal shrinking has been established as a widely accepted mechanism, recent HRTEM observations of direct fullerene formation from a graphene flake and of catalyst-free fullerene growth inside nanotubes, as well as the symmetric smooth size distributions of fullerene laser coalescence products around main BF dimer (C_{118}), trimer (C_{178}), *etc.* peaks are seemingly at odds with the SHG road. We note however that in the cage growth and coalescence experiments a *tightly sealed environment* is required, and that C_2 can presumably not escape in such an experimental setup. It therefore appears that in addition to C_2 evaporation, the reverse process, namely C_2 capture, should occur as well, consistent with the principle of microscopic reversibility.

In the present study we therefore revisit the size-down shrinking process of hot GFs as well as the growth mechanism by maintaining constant carbon density in a QM/MD simulation with periodic boundary conditions, to simulate the effect of an environment where C_2 cannot escape. We explicitly include noble gas (Ng) atoms in the model system to increase the pressure. Interactions with Ng atoms were included using nonbonded molecular mechanics Lennard-Jones potentials, resulting in the use of a mixed QM/MM potential. We describe details of isokinetic, high-temperature QM/MD trajectories for C_2 ejection and capture processes of GFs that were self-assembled in previous simulations, and focus on the structure and energetics of “antenna fall-off”, “C_2 pop out” and “C_2 incorporation” events under the constant density conditions. Our study is qualitative and not aimed at quantitatively evaluating shrinking and growth rates and their dependence on fullerene cage isomer, carbon density, buffer gas pressure, and temperature, as such a study would exceed present computational capabilities.

Molecular dynamics (MD) simulations were performed using the density-functional tight-binding (DFTB) method within non-charge-consistent (NCC) approximation. The Gamma-point approximation was employed in the periodic boundary calculations. C-Ng and Ng-Ng interactions were evaluated using Lennard-Jones (LJ) pair potentials. The C-He, He-He, C-Ar, and Ar-Ar LJ parameters were taken from literature.

Shrinking Mechanism

We describe the shrinking mechanism in the present simulations briefly by giving examples in Figure 1. At first stage antenna fall-off event occurred very fast where polyyne chains are detached from the cage. The second stage of the shrinking process is C_2 pop-out. Figure 1 shows a sequence of events leading up to C_2 elimination from a divalent carbon (in the following named “carbene”) defect. There are four rings participating in this ejection, marked in blue: a heptagon, two hexagons, and a pentagon. At first, the seven-membered ring containing the carbene produced a kink at 36.33 ps. The kink site and the four participating rings converted to two joint 10-membered ring openings, with the carbene defect being converted to a C_3 bridge at 36.34 ps. At 36.39 ps these 10-membered rings converted to two abutting pentagons and two fused 7-membered rings in which the bridge was shortened to two carbons. Around 37.07 ps the bridge broke and a wobbling C_2 unit was formed. Much later, at around 90.19 ps, this wobbling C_2 broke off, leaving behind a carbene-bearing octagon joint to the two abutting pentagons. Further ring transforms occurred at 108.03 ps when this structure transformed into a carbene-containing 7/5/6 structure. Overall, this process corresponds to a carbene-containing 7/6/6/5 structure transforming into a carbene-containing 7/5/6 structure where one C_2 unit was ejected. The periodic boundary conditions allow future reactions with the fullerene cage and the ejected C_2 molecules, resulting in C_2 capture as described in the next paragraph.

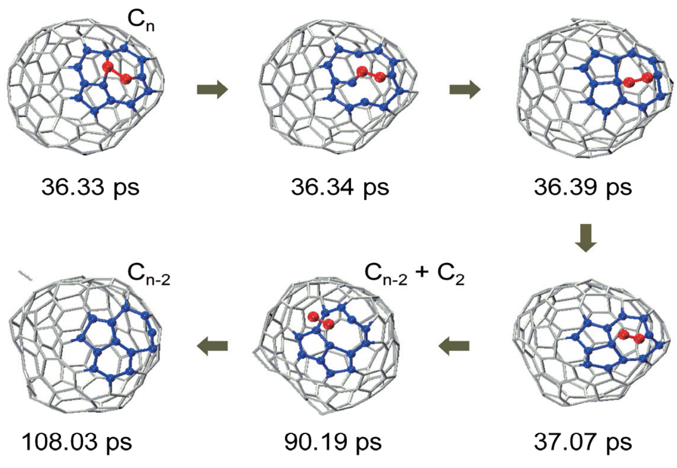


Figure 1. C_2-fragment emission and shrinking mechanism.

Growth Mechanism

Cage growth only occurs in trajectories where a sufficient number of carbon fragments were present in the system, allowing reactions of C_n fragments with the giant fullerene during the simulation time. Representative snapshots of C_2 capture processes are shown in Figure 2. No significant difference is observed in simulations using different thermal control conditions (VS, He or Ar). In this Figure, the newly added C atoms are indicated by red color while the C atoms of the participating ring structures are indicated by blue color. We note that C_2 incorporation can occur either via breaking of the original C_2 bond, or the captured C_2 molecule becomes subsequently “swallowed whole”, leaving its original C-C bond intact as shown in Figure 2. It is observed that in general the C_2 unit is incorporated via three distinct stages: (i) reaction of C_2 with a cage C which is shared by adjacent five-and six-membered rings/five- and seven membered rings/six- and seven-membered rings (chemisorptions), (ii) large ring formation in which C_2 is attached to form a bridge, and (iii) C_2 is consumed by the cage via ring transformation and thus forming five- and six-membered rings. In some cases the two C’s of the C_2 unit are consumed in two steps.

The growth mechanism proceeds in our simulations exclusively by the more probable edge-on attack of C_2 and subsequent cage incorporation. The reorganization of the exothermic reaction energy due to GF-C_2 bond formation in the carbon network is crucial to achieve a lifetime long enough to proceed via the cage ingestion processes described above. Our simulations show that the cage ingestion occurs on the order of several tens of picoseconds after initial C_2 capture.

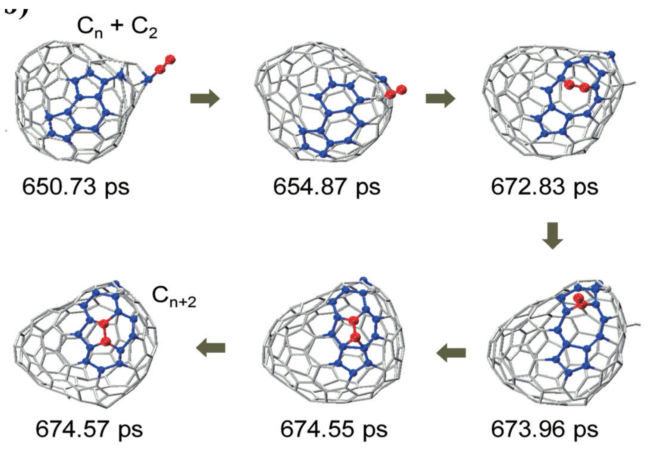


Figure 2 C_2-fragment incorporation events.

Constant temperature/constant density direct quantum chemical/molecular mechanics (QM/MM) molecular dynamics (MD) simulations of dynamically self-assembled, hot giant fullerenes (GFs) with their attached polyyne antennas were performed on the nanosecond timescale to investigate the C_2 ejection and cage incorporation rates associated with GF cage shrinking and growth. It was found that hot GFs are able to shrink as well as grow during continued high temperature simulations, on the order of several carbon atoms per nanosecond.

It was observed that larger GFs (>100 cage carbons) have a tendency to shrink whereas smaller GFs (<100 cage carbons) tend to grow. However, the C_2 ejection and insertion rates depend strongly on the concentration of available carbon outside the cages: A larger number of free carbons increases the growth rate, whereas a smaller number increases the shrinking rate.

2. Original papers

1. B. Saha, S. Irle, K. Morokuma, “Formation mechanism of polycyclic aromatic hydrocarbons (PAHs) in benzene combustion: Quantum chemical molecular dynamics simulations”, J. Chem. Phys. *132*, 224303 (2010)

3. Presentation at academic conferences

4. Others

Hajime HIRAO

FIFC Fellow, Fukui Kenichi Memorial Research Group 1
（To 31 Oct. 2010）

1. Summary of the research of the year: Computational studies of bioinorganic chemistry

Metalloenzymes are finely tuned catalytic machines that drive energetically unfavorable reactions under mild conditions, often with surprisingly high selectivity. Detailed understanding of the catalytic functions of metalloenzymes is of considerable importance in the sense that it would open up new avenues for practical applications such as rational design of potent enzyme inhibitors and development of powerful biomimetic catalysts. A fundamental prerequisite for that is a full understanding of the enzymatic reaction mechanism, and quantum mechanical (QM) calculations and hybrid QM/MM methods such as ONIOM(QM:MM) have useful roles to play in such efforts. Another approach to elucidate the catalytic machineries of metalloenzymes should be to investigate mechanisms of simpler synthetic complexes that have some resemblance to metalloenzymes. Studies of biomimetic systems may provide us with clues as to how enzymes operate in physiological conditions, as well as how enzyme-like competent catalysts could rationally be designed. This year, the author studied both metalloenzymes and transition-metal complexes actively.

1-1. Density Functional Theory Investigation of the Catalytic Mechanism of Hydroxyethylphosphonate Dioxygenase

Hydroxyethylphosphonate dioxygenase (HEPD) is a mononuclear nonheme iron enzyme that utilizes an O_2 molecule to cleave a C−C bond in 2-hydroxyethylphosphonate and produce hydroxymethylphosphonate (HMP) and formic acid. Density functional theory calculations were performed on an enzyme active-site model of HEPD to understand its catalytic mechanism. The reaction starts with H-abstraction from the C2 position of 2-HEP by a ferric superoxide-type (Fe(III)-OO•$^-$) intermediate, in a similar manner to the H-abstraction in the reaction of the dinuclear iron enzyme *myo*-inositol oxygenase. The resultant Fe(II)-OOH intermediate may follow either a hydroperoxylation or hydroxylation pathway, the former process being energetically more favorable. In the hydroperoxylation pathway, a ferrous-alkylhydroperoxo intermediate is formed, and then its O−O bond is homolytically cleaved to yield a complex of ferric hydroxide with a gem-diol radical. Subsequent C−C bond cleavage within the gem-diol leads to formation of an R-CH_2• species and one of the two products (i.e., formic acid). The R-CH_2• then intramolecularly forms a C−O bond with the ferric hydroxide to provide the other product, HMP. The overall reaction pathway does not require the use of a high-valent ferryl intermediate but does require ferric superoxide and ferric hydroxide intermediates.

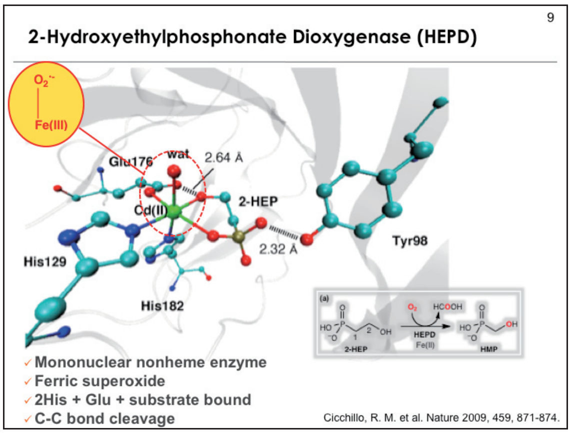


Figure 1. X-ray crystal structure of HEPD.

1-2. Theoretical Study of the Mechanism of Oxoiron(IV) Formation from H_2O_2 and a Nonheme Iron(II) Complex: O–O Cleavage Involving Proton-Coupled Electron Transfer

It has recently been shown that the nonheme oxoiron(IV) species supported by the 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane ligand (TMC) can be generated in near-quantitative yield by reacting $[Fe^{II}(TMC)(OTf)_2]$ with a stoichiometric amount of H_2O_2 in CH_3CN in the presence of 2,6-lutidine (Li, F.; England, J.; Que, L., Jr. J. Am. Chem. Soc. 2010, 132, 2134─2135). This finding has major implications for O–O bond cleavage events in both Fenton chemistry and nonheme iron enzymes. To understand the mechanism of this process, especially the intimate details of the O–O bond cleavage step, a series of density functional theory (DFT) calculations and analyses have been carried out. Two distinct reaction paths (A and B) were identified. Path A consists of two principal steps: (1) coordination of H_2O_2 to Fe(II) and (2) a combination of partial homolytic O–O bond cleavage and proton-coupled electron transfer (PCET). The latter combination renders the rate-limiting O–O cleavage effectively a heterolytic process. Path B proceeds via a simultaneous homolytic O–O bond cleavage of H_2O_2 and Fe–O bond formation. This is followed by H abstraction from the resultant Fe(III)–OH species by an •OH radical. Calculations suggest that path B is plausible in the absence of base. However, once 2,6-lutidine is added to the reacting system, the reaction barrier is lowered and more importantly the mechanistic path switches to path A, where 2,6-lutidine plays an essential role as an acid–base catalyst in a manner similar to how the distal histidine or glutamate residue assists in compound I formation in heme peroxidases. The reaction was found to proceed predominantly on the quintet spin state surface, and a transition to the triplet state, the experimentally known ground state for the TMC-oxoiron(IV) species, occurs in the last stage of the oxoiron(IV) formation process.

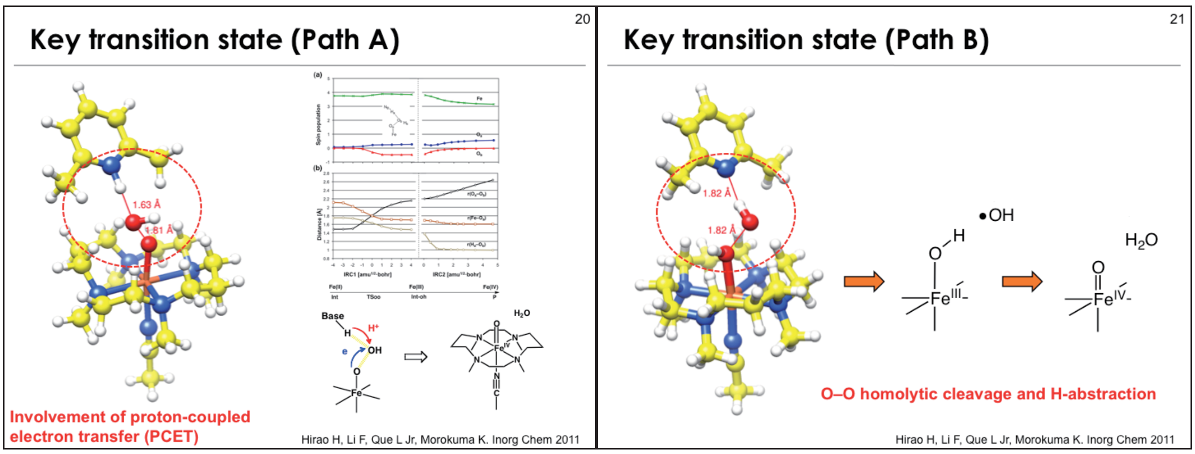


Figure 2. Key transitions states for paths A and B.

2. Original papers

(1) Hajime Hirao and Keiji Morokuma

Ferric Superoxide and Ferric Hydroxide Are Used in the Catalytic Mechanism of Hydroxyethylphosphonate Dioxygenase (HEPD): A Density Functional Theory Investigation

J. Am. Chem. Soc. **2010**, *132*, 17901-17909.

(2) Hajime Hirao
Correlation Diagram Approach as a Tool for Understanding Chemistry: An Introductory Overview
WIREs: Computational Molecular Science, **2011**, *1*, 337-349.

(3) Lung Wa Chung, Hajime Hirao, Xin Li, and Keiji Morokuma
The ONIOM Method: Its Foundation and Applications to Metalloenzymes and Photobiology
WIREs: Computational Molecular Science, in press.

(4) Hajime Hirao and Keiji Morokuma
Recent Progress in the Theoretical Studies of Structure, Function, and Reaction of Biological Molecules
Yakugaku Zasshi-J. Pharm. Soc. Jpn. **2011**, *131*, 1151-1161.

(5) Hajime Hirao, Feifei Li, Lawrence Que, Jr., and Keiji Morokuma
Theoretical Study of the Mechanism of Oxoiron(IV) Formation from H_2O_2 and a Nonheme Iron(II) Complex: O–O Cleavage Involving Proton-Coupled Electron Transfer
Inorg. Chem. **2011**, *50*, 6637-6648.

(6) Hajime Hirao
Energy Decomposition Analysis of the Protein Environmental Effect: The Case of Cytochrome P450cam Compound I
Chem. Lett. in press.

(7) Witcha Treesuwan, Hajime Hirao, Supa Hannongbua and Keiji Morokuma
Characteristic Vibration Patterns and Protein Binding of Odor Compounds
from Bread Baking Volatiles: Density Functional and ONIOM Study and Principle Component Analysis (PCA)
J. Mol. Model. in press.

3. Presentation at academic conferences

(1) Hajime Hirao, Lawrence Que, Jr., Keiji Morokuma (Oral: 5T02)
How is Fe(IV)=O Formed from H_2O_2 and a Nonheme Fe(II) Complex? A Density Functional Theory Study
ICTAC-13: 13th International Conference on Computational Catalysis, Matsushima (Miyagi, Japan), June 25, 2010.

(2) Hajime Hirao, Keiji Morokuma (Poster: 3P125)
シトクロム P450cam の化学反応における環境効果のエネルギー分割解析
4th Annual Meeting of Japan Society for Molecular Science (2010), Osaka University (Osaka), September 16, 2010.

4. Others

4-1. Other presentations

(1) Hajime Hirao (Oral)
計算量子化学による鉄酵素の反応メカニズムの理解
70th Colloquium of Computational Sciences. University of Tsukuba (Tsukuba), April 8, 2010.

(2) Hajime Hirao (Oral)
Biology-Related Activities at the Morokuma Group (Part 1)
JENESYS meeting, Kyoto University (Kyoto), June 17, 2010.

(3) Hajime Hirao (Oral)
Computational Studies of Molecular Interactions and Chemical Reactions: From Simple Molecules to Complex Systems
An open seminar, Nanyang Technological University (Singapore), July 27, 2010.

(4) Hajime Hirao (Oral)
Valence-shell electron pair repulsion (VSEPR) theory and molecular shape
An open lecture, Nanyang Technological University (Singapore), July 28, 2010.

4-2. Competitive external research grants

(1) The Kyoto University Foundation Grant (Travel stipend to attend Pacifichem2010, Declined because I left Kyoto University)
(2) Takeda Science Foundation Grant (Life Science)

4-3. Competitive external computer resources

(1) Collaborative Research Program for Young Scientists of ACCMS and IIMC, Kyoto University.

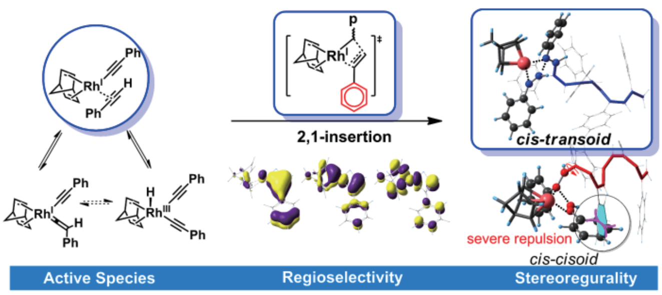
Zhuofeng KE

FIFC Fellow, Fukui kenichi Memorial Research Group 1

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

I. Theoretical Studies of the Reaction Mechanism, Regioselectivity and Stereoregularity.

Scheme 1. Rh-*Catalyzed Polymerization of Phenylacetylene*



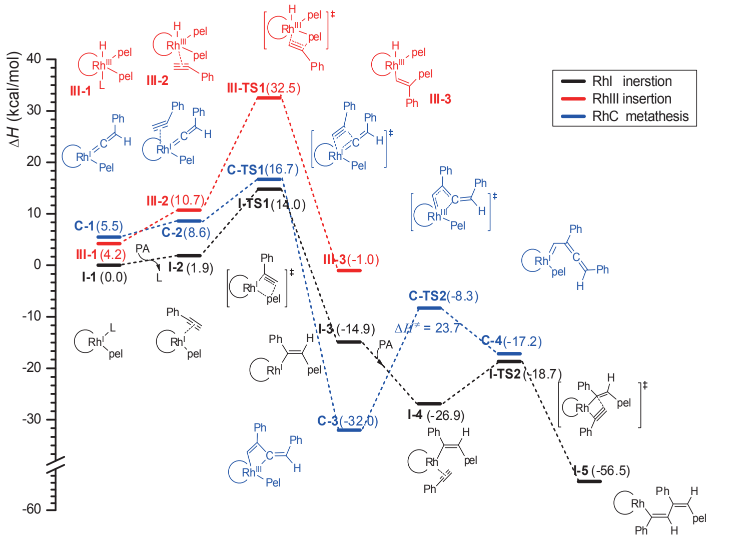


Figure 1. *Potential energy surfaces of the RhI/RhIII-insertion, and metathesis mechanisms for the Rh-Catalyzed Polymerization of*

Poly(phenylacetylene) (PPA) is a conducting polymer with especially intriguing properties. Its stability, solubility in organic solvents, helical conformation, and unique magnetic and electrical properties have prompted development of PPA-derived materials for numerous high-tech applications, including optical polarizing films and asymmetric electrodes. The properties of PPA depend much on its structure. To tailor the PPA structure, it is necessary to understand the exact mechanisms of the polymerization process. However, it has remained a challenge to selectively produce PPA materials with desired structures, partially due to the mechanism is not well known yet. Rh-based catalysts offer numerous advantages over other transition metal catalysts for the synthesis of PPA-derived materials. The Rh-catalyzed polymerization is tolerant toward polar functionalized PA derivatives, can be used to construct screw-sense, helical materials. Herein, we used sophisticated computational methods - density functional theory, ONIOM method, and molecular dynamics - to gain insight into the rhodium-catalyzed polymerization process and the factors that control the regiochemistry and stereochemistry of the resulting polymer. The computational findings have possible applications in the design of catalysts tailored for PPA polymerizations.

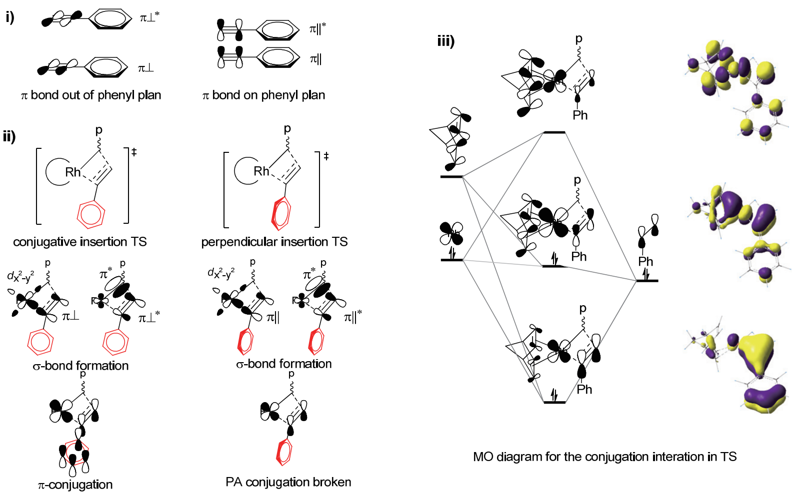


Figure 2. *Regioselectivity origin: electronic characteristics of the conjugative insertion transition state and its molecular orbital diagram.*

We found that the Rh-catalyzed polymerization of PA proceeds via the Rh^{I} insertion mechanism, although all the Rh^{I}, Rh^{III}, and Rh-carbene types of intermediates are calculated to be thermodynamically and kinetically feasible at room temperature in solution. The Rh^{I} insertion mechanism is calculated to have a propagation activation enthalpy of ~9 kcal/mol, much lower than those of the Rh-carbene metathesis mechanism ($\Delta H^{\neq} \approx 25$ kcal/mol for the rate-determining step) and the Rh^{III} insertion mechanism ($\Delta H^{\neq} \approx 22$ kcal/mol).

The Rh^{I} insertion mechanism prefers a 2,1-insertion, leading to head-to-tail regioselective PPA. The preference for 2,1-insertion over 1,2-insertion increases with increasing bulk of the propagated chain. The 2,1-insertion is favored over 1,2-insertion by up to 7.9 kcal/mol with the ONIOM models. Our study found a unique π-conjugative characteristic for the insertion transition state, in which a conjugative network is formed by the conjugative PA, the Rh d_{π} orbital, and the π acceptor nbd ligand, to gain extra stabilization energy. This conjugative characteristic of the insertion transition state always causes steric repulsion between the phenyl group of PA and the bulky propagation chain, probably exclusively preferring the 2,1-insertion. This provides a new understanding for tuning 2,1-/1,2-selectivity during polymerization of PA.

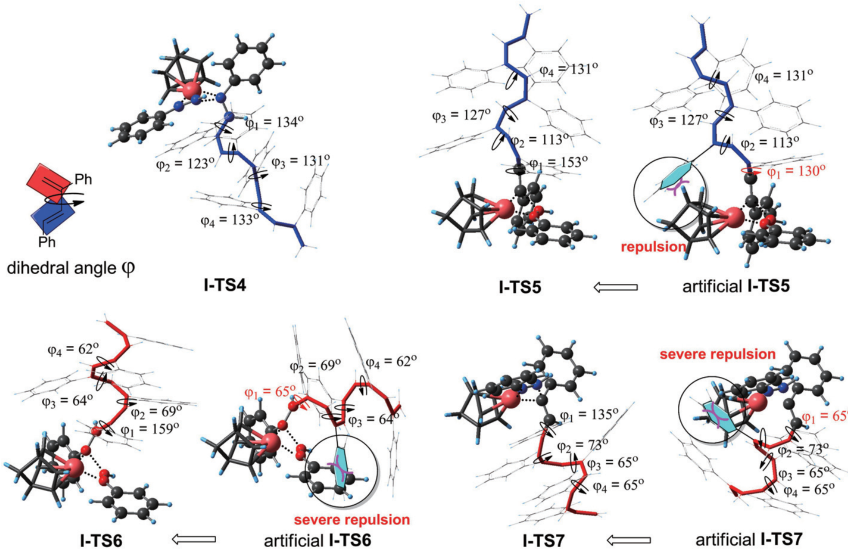


Figure 3. *Stereoregularity origin: Steric repulsion in the transition states leading to different stereoconformers of PPA.*

Kinetic factors play a key role in the stereoconformational selectivity. PA monomer highly prefers to insert into a parent propagation chain in a cis-transoidal conformer rather than a cis-cisoidal conformer ($\Delta\Delta H^{\neq} \geq 4.8$ kcal/mol). The propagation chain can easily adopt a cis-transoidal conformation via single bond rotation before the next insertion. The kinetic difference mainly originates from steric repulsion caused by the conformational constraint of the parent propagation chain during insertion. To tailor the stereoregularity of the PPA catalyzed by Rh catalysts, it is important to distinguish kinetic control from thermodynamic control.

II. Theoretical Study of Artificial Metalloenzymes.

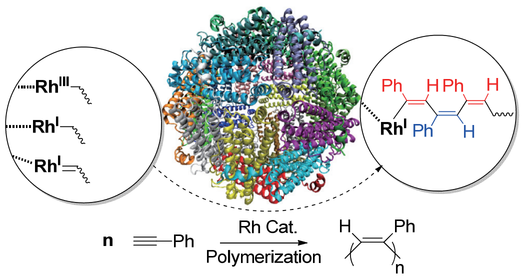


Figure 4. *Rh-catalyzed Polymerization of Phenylacetylene in Nano-Cavity of apo-Ferritin*

The efficiency and specify of enzymes in nature inspire scientists to design and construct artificial enzyme to reproduce their catalytic function or to develop novel enzyme-like catalysis. One of the promising strategies is to incorporate a catalytic metal complex into a host protein to construct an artificial metalloenzyme with novel catalytic features in the well-defined "womb" of protein. However, the design of new artificial metalloenzyme is rather challenging. The structures of metal complexes are much variable and the interaction between metal complex and protein is rather tricky leading to complicated binding sites for the catalysis inside artificial metalloenzyme. Understanding the active site and the catalysis process inside artificial metalloenzyme is extremely important to advance its rational design and development. However, the characterization of the structural details of artificial metalloenzyme is very difficult. Even with some structural snapshots of the catalytic precursor or intermediates, we are still far from understanding the active site and the reaction mechanism inside artificial metalloenzymes. In this study, we demonstrated an example with QM/MM studies to illustrate the complicated mechanism in artificial metalloenzyme based on our recently developed artificial metalloenzyme for polymerization.

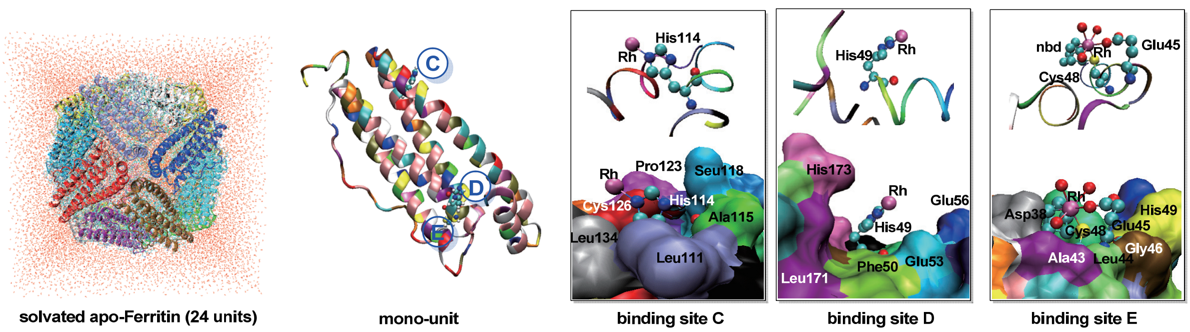
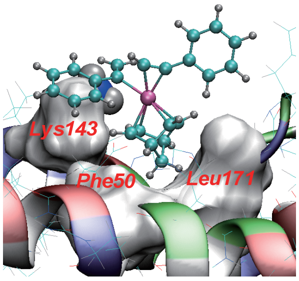


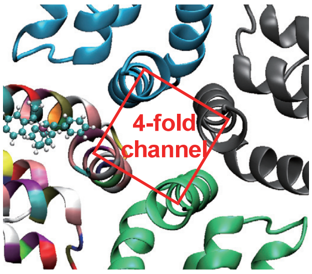
Figure 5. *The solvated apo-Ferritin structures with 24 sub-units, the mono-unit structure with immobilized rhodium complexes, and the structures for binding site C, D and E on each mono-unite*

We have evaluated the possible mechanisms for all binding sites suggested by X-ray crystal structure, i.e. site C, D and E. We found that site C, D and E themselves are only precursors, not the true active site for the polymerization of PA. The active site should be a Rh^{I}-center located at a hydrophobic pocket near site D. The Rh^{I}-insertion is the most plausible polymerization mechanism. The active site is first generated by the abstraction of rhodium-PA complex from site D. After the insertion, the metal center doesn't recombine to His49 of site D, remaining in the hydrophobic pocket for the propagation.

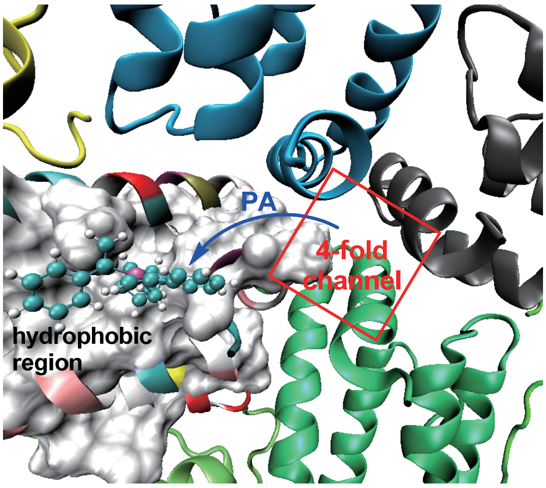
The hydrophobic pocket, which composed of residues Phe50, Lys143, and Leu170, plays a key role for the polymerization behavior in the studied artificial metalloenzyme. The active site, the nonpolar 4-fold channel of Ferritin, and other hydrophobic resides nearby compose a hydrophobic region for the transportation, coordination and insertion of PA during the polymerization. Notably, this hydrophobic pocket can maintain the stereoselectivity feature of the Rh-catalyzed polymerization. This study highlights the importance of theoretical study in mechanistic understanding and rational design of artificial metalloenzyme, and indicates that even though with the X-ray crystal structure in hand, the active site and the catalytic mechanism are still far from fully understanding.



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



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



(iii) Transportation of PA monomers through 4-fold channel to the active site during polymerization. Hydrophobic residues are highlighted with grey surface.

Figure 6. *The plausible active site in hydrophobic pocket near site D and the 4-fold channel.*

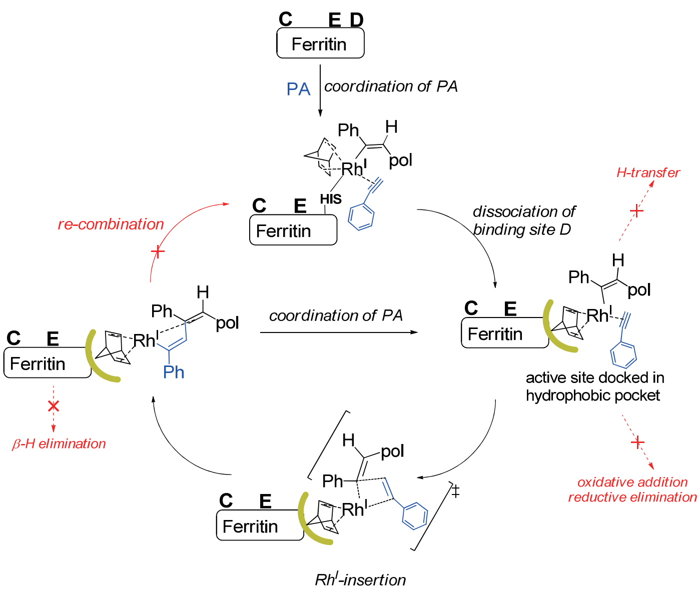


Figure 7. *The overview mechanism of the polymerization of PA in the studied artificial metalloenzyme system.*

2. Original papers

(1) Ke, Zhuofeng, Abe, S., Ueno, T., & Morokuma, Keiji, Understanding the Complicated Mechanism in Artificial Metalloenzymes: QM/MM study of catalyzed polymerization by Rhodium Complex Encapsulated in apo-Ferritin. *In preparation*.

(2) 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.* 133 *(20)*, 7926-7941 (2011). (***JACS beta Select issue 13: Current Applications of Computational Chemistry in JACS - Molecules, Mechanisms and Materials***)

3. Presentation at academic conferences

(1) Ke, Zhuofeng, Morokuma, K. "Catalyzed polymerization in Bio-Nano Cavity of Protein". *The 4th Annual Meeting of Japan Society for Molecular Science*, Osaka University, Osaka, Japan. Sep. 14-17, 2010. (talk)

(2) Ke, Zhuofeng, Abe,S., Ueno, T., Morokuma, K., Rh-catalyzed polymerization in bionano cavity of apo-ferritin. *the 241st American Chemical Society National Meeting*, Anaheim, CA, USA. Mar. 27-31,2011. (poster)

4. Others

(1) Yan, Y., Ke, Zhuofeng, Liu, Shuwen, Chen, Wen-Hua, Jiang, Shibo; Jiang, Zhi-Hong. "Betulinic Acid-Polyphenol Conjugates as HIV Inhibitors Targeting gp41". *ChemMedChem* 6 (9), 1654-1664 (2011)

(2) Gao, H., Ke, Zhuofeng, DeYonker N.J., Wang J., Xu H., Mao Z.-W., Phillips, D.L., Zhao C., Dinuclear Zn(II) Complex Catalyzed Phosphodiester Cleavage Proceeds via a Concerted Mechanism: A Density Functional Theory Study. *J. Am. Chem. Soc.* 133 *(9)*, 2904–2915 (2011).

Joonghan KIM

FIFC Fellow, Fukui kenichi Memorial Research Group 1
（From 8 Nov. 2010）

1. Summary of the research of the year

Determination of Local Chirality in Irregular Single-Walled Carbon Nanotube Based on Individual Hexagons

The chirality of single-walled carbon nanotubes (SWCNTs) has great importance since their physical and electronic properties strongly depend on it. In this respect the chirality-controlled SWCNT growth is an essential prerequisite for useful applications in nanotechnology. For the chirality-controlled growth, the preservation of predefined chirality of initial structures such as cap and seed SWCNTs is essential during the growth process. However, the chirality of irregular structures of SWCNTs, especially, those formed during the growth process, was difficult to define in contrast to the definition of the chirality of ideal SWCNTs, usually done using a graphene sheet with the direction of roll-up vector. For example, as shown in Fig. 1, if an incoming C_2 (magenta in Fig. 1(b)) is attached and a new hexagon is formed on a preexisting armchair (AC)-type SWCNT in Fig. 1(a), the determination of chirality of SWCNT that involves the newly added hexagon is ambiguous; the black line in Fig. 1(b) indicates that the chirality of SWCNT is still AC-type while the red line shows that the chirality is zigzag (ZZ)-type. This means that a new method is urgently required to define the chirality based not on the whole tube structure but on the individual hexagons that are formed during the growth process. Thus, we propose a robust theoretical method for the determination of the chirality of arbitrary SWCNT structures that does not rely on the edge structure. This method extracts information of the chirality based on individual hexagons that compose SWCNT. Thus, the chirality of SWCNT can be determined by the local information, viz. the local chirality of individual hexagons.

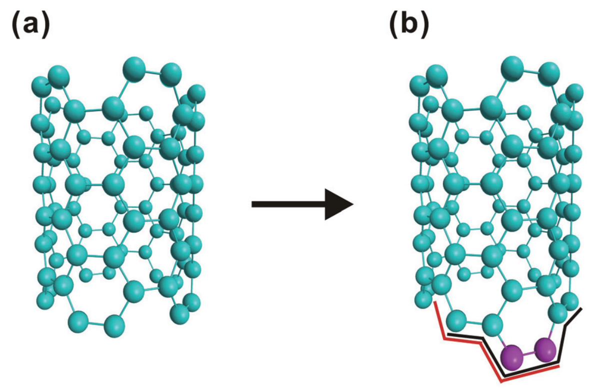


Fig. 1 (a) Ideal AC(5,5) SWCNT (cyan). (b) Incoming C_2 (magenta) is attached to SWCNT and one new hexagon forms. The black and red lines show AC and ZZ edges, respectively.

The scheme for the calculation of the local chiral angles is shown in Figs. 2(a)-(e). Firstly, all Cartesian coordinates of C atoms in SWCNT are extracted and all other atoms (Fe and H atoms in this case) are removed from the original structure. Secondly the principal axes (PAs) X, Y, Z of the whole SWCNT structure, which we call the global PAs (GPAs) (called GPAX, GPAY, and GPAZ axes in Fig. 2 (b), are calculated, with the standard order of momenta of inertia, $I_Z \geq I_X, I_Y$. The Cartesian coordinates of all the carbon atoms are then transformed into this XYZ coordinate system for easy representation in the following calculations. In particular, the Z axis of GPA (GPAZ) plays a crucial role in the calculations of the chiral angles. In a regular, or almost regular, long SWCNT, GPAZ is (almost) equal to the growth axis of SWCNT. In the next step, all hexagons with their Cartesian coordinates in the nanostructure are found. The PAs with the standard order of momenta of inertia, $I_z \geq I_x, I_y$, of each individual hexagon (for instance the magenta hexagon in Fig. 2(b)), called the local principal axes (LPAs), are also calculated (see Fig. 2(c)). The directional cosines of LPAs in the GPA system are LPAx (l_x, m_x, n_x), LPAy (l_y, m_y, n_y) and LPAz (l_z, m_z, n_z). LPAz shown in Fig. 2(c) plays an important role in distinguishing between *suitable* and *ill-suited* hexagons or in determining the *suitable* and *ill-suited* hexagon components of a given hexagon, as will be discussed later. Other PAs of a hexagon, viz. LPAx and LPAy are not used in the analysis because of the degeneracy of hexagon-like structures: the values of the principal moment of inertia of LPAx and LPAy are almost equal to each other.

In an ideal SWCNT, the planes of all the hexagons that make up the sidewall are parallel to Z, and the tilt angle ϕ as defined between GPAZ and LPAz (see Fig. 2(c)) is exactly 90° for all hexagons. These hexagons may be called *suitable* hexagons. However, in irregular SWCNTs or SWCNT fragments such as a cap structure, the angle ϕ of a hexagon can deviate substantially from 90°. For instance, the angle ϕ of a hexagons located near the top site of the C_{40} cap is deviated from 90°. In an extreme case of ϕ = 0°, namely when the hexagon plane is perpendicular to GPAZ or the LPAz is parallel to GPAZ (the directional cosine n_z=1), the calculation of the chiral angle loses its meaning completely, i.e. the distinction between AC and ZZ is totally lost; the hexagon with ϕ = 0° may be called an *ill-suited* hexagon. Between these two extremes, (90°– ϕ) is an indicator of the suitability of a hexagon, namely how much the plane of the hexagon is deviated from being parallel to GPAZ. We actually

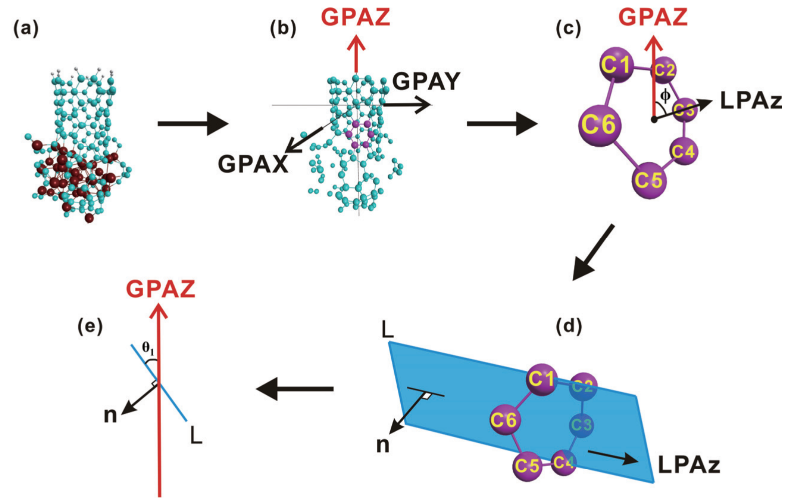


Fig. 2 Schematic description for the calculation of the local chiral angle. (a) An example of an irregular SWCNT (C: cyan, Fe: brown, and H: white). (b) Irregular SWCNT after removal of other atoms except C atom from the structure in (a) in XYZ coordinate system. (c) One of the individual hexagons from the structure in (b) with LPAz and the definition of the angle (ϕ) between GPAZ and LPAz. (d) The plane L with its normal unit vector **n**. (e) The definition of the angle (θ_1) between the plane L and GPAZ.

use $\sin^2\phi$ and $\cos^2\phi$ (which is equal to $(n_z)^2$) as the magnitude of the *suitable* and *ill-suited* tilt components, respectively, of a hexagon. A *suitable* hexagon ($\phi = 90°$) has 100% of the *suitable* component and the other extreme case of the hexagon ($\phi = 0°$) has 100% of the *ill-suited* component. Between the two extremes, the components change smoothly. In the succeeding calculations of the local chiral angles, we have chosen to remove any hexagon with the ill-suited component larger than 75 %, in other words, if the suitable component is less than 25 %; the local chirality of this hexagon is considered indefinable.

In the next step, we calculate the local chiral angles only of the hexagons that have more than 25 % of the suitable component. Firstly, the center of mass of a chosen hexagon is moved to the origin of the XYZ Cartesian coordinate. Next, the coordinates of the hexagon are transformed from the GPA system to the LPA system. This transformation, represented by the matrix of directional cosines, can be accomplished by the Euler formula with two consecutive rotations. As shown in Fig. 2(d), next we choose two C atoms in the para position of the hexagon (for instance, C1 and C4). The plane L is defined to be parallel to LPAz and also to contain C1 and C4. The angle θ_1 in Fig. 2(e) between GPAZ (red arrow) and the plane L is calculated using a simple inner product between GPAZ and the normal unit vector **n** of plane L. For the same hexagon, two more angles, θ_2 and θ_3, are also calculated using the C3-C6 pair and the C2-C5 pair, respectively. The three angles (θ_1, θ_2, and θ_3) were averaged effectively using Eq. (1).

$$\theta = \frac{\theta_1 + \theta_2 + \theta_3}{3} - 60°. \qquad (1)$$

The ranges of the three angles are $0° \le \theta_1 \le 30°$, $60° \le \theta_2 \le 90°$, and $120° \le \theta_3 \le 150°$, respectively, and the range of the average angle is $0° \le \theta \le 30°$. For a regular hexagon in an ideal SWCNT, θ_2 and θ_3 are equal to $\theta_1 + 60°$ and $\theta_1 + 120°$, respectively, and thus, the average angle θ should be equal to θ_1 using Eq. (1). For example, the above formula gives θ to be 30° (= (30 + 90 + 150)/3 − 60) and 0° (= (0 + 60 + 120)/3 − 60) as θ for ideal AC and ZZ SWCNT, respectively. They are exactly equivalent to the chiral angle α (with $0° \le \alpha \le 30°$) of AC ($n, m = n$) and ZZ ($n, m = 0$) SWCNT given by Eq. (2).

$$\sin\alpha = \frac{\sqrt{3}m}{2\sqrt{n^2 + m^2 + nm}}. \qquad (2)$$

This average angle θ can be defined clearly also for irregular hexagons with different bond lengths and/or different bond angles. Thus, just one angle θ represents the critical information concerning the chirality of a hexagon in SWCNT and will be called the local chiral angle. We named the present method, the analysis according to the local chiral angle, LOcal Chirality Index (LOCI). The analysis for various examples including ideal nanotubes as well as irregular SWCNTs is in progress.

2. Original papers

(1) Joonghan Kim, Stephan Irle, and Keiji Morokuma,
"Determination of Local Chirality in Irregular Single-Walled Carbon Nanotube Based on Individual Hexagons", *manuscript in preparation*.

Alister PAGE

FIFC Fellow, Fukui kenichi Memorial Research Group 1

1. Summary of the Research of the Year

(A) QM/MD Investigation of Single-Walled Carbon Nanotube Nucleation from Si-Based Catalysts: A Vapor-Solid-Solid Mechanism

The ability of non-metal catalysts, notably SiO_2, to assist the nucleation and growth of single-walled carbon nanotubes (SWNTs) *via* chemical vapour decomposition (CVD) has been established experimentally within the last decade. Recent speculation indicated that the traditional vapour-liquid solid mechanism (established for transition-metal catalysts) is possibly responsible for SWCNT nucleation on silica nanoparticles also. However, the exact mechanism by which this new breed of catalysts assists the nucleation and growth of SWNTs remains unknown. We have addressed this issue by investigating the atomistic mechanism of SWNT nucleation on SiO_2 catalyst nanoparticles, based on QM/MD simulations of CH_4 CVD. In agreement with experiment, we found that CO was produced as the main chemical product of this CH_4 CVD process (Fig. 1). The production of CO in this case, and the nucleation of CNTs in general, necessitate the abstraction of atomic hydrogen from the CO carbon. We have therefore observed the mechanism by which this removal takes place in the case of SiO_2 catalysts. The production of CO during CH_4 CVD resulted in the carbothermal reduction of the SiO_2 nanoparticle, resulting in a catalyst nanoparticle consisting of a SiO_2 'core' surrounded by an amorphous SiC 'shell'. The first stage of the SWNT nucleation process featured the coalescence of carbon atoms on the SiO_2 surface, resulting in the formation of extended polyyne chains. At higher carbon concentrations, the isomerization of these polyyne chains resulted in the formation of isolated sp^2-carbon networks on the SiO_2 surface, and ultimately, the formation of a SWNT cap structure (Fig. 2). The surface saturation of the SiO_2 nanoparticle was a necessary prerequisite for SWNT nucleation. This is consistent with the experimental hypothesis of a 'carbon-coated' nanoparticle precursor (Homma *et al*. *Nano Res.*, **2**, 793 (2009)). The SiO_2/SiC nanoparticle remained in the solid phase throughout the nucleation process. Moreover, QM/MD thermal annealing simulations of SiO_2 and carbon-doped SiO_2 nanoparticles between temperatures of 1000 and 3000 K revealed that these nanoparticles did not undergo a solid – liquid phase transition. Instead, sublimation of the solid phase nanoparticle, yielding SiO and CO vapor was observed. Such phenomena are irreconcilable with those of a VLS-type mechanism. It was thus concluded that SiO_2-catalyzed SWNT nucleation proceeds according to a VSS mechanism, and so is comparable to the growth of a number of other inorganic nanostructures. Consequently, it is evident that the processes of SWNT nucleation on SiO_2 and 'traditional' catalysts (such as Fe and Ni[27,28]) differ at the most fundamental level. This VSS proposal has since been corroborated experimentally (Liu *et al*., *J. Am. Chem. Soc*., **133**, 197 (2011)).

Following the observation of the surface reduction of SiO_2 nanoparticles discussed above, the role of oxygen on the SWNT nucleation mechanism on SiO_2 catalysts was further elucidated. To this end, QM/MD thermal annealing simulations of SiC nanoparticles were performed between 1200 and 2500 K. SWNT nucleation in

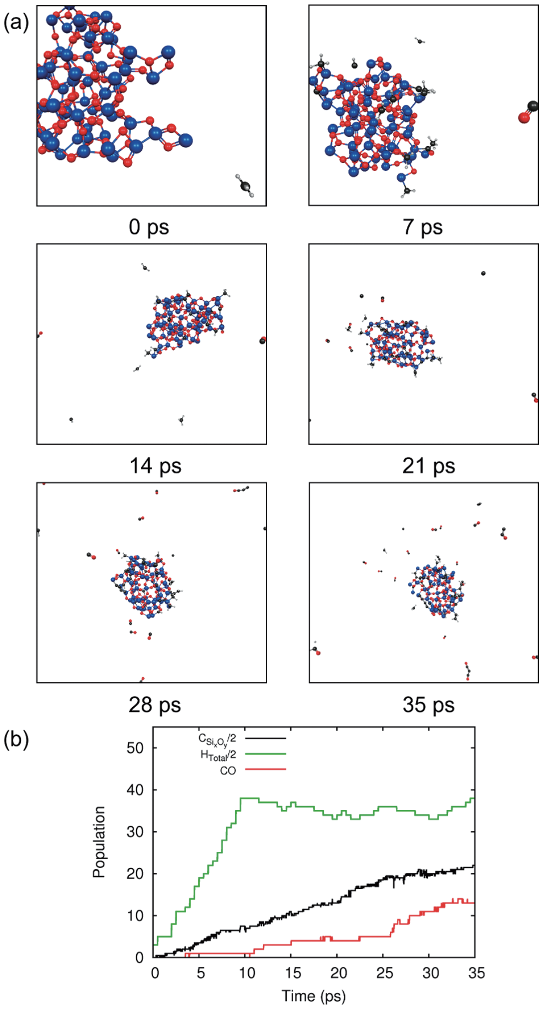


Fig. 1. SCC-DFTB/MD simulation of CH_4 CVD on SiO_2 nanoparticles (following 35 ps of simulation). Blue, red, cyan and white spheres represent Si, O, C and H atoms, respectively.

this case is preceded by a change of the SiC structure from a crystalline one to one in which silicon and carbon atoms became segregated (Fig. 3). This structural transformation ultimately resulted in the formation of extended polyyne chains on the SiC nanoparticle surface. These polyyne chains subsequently coalesced, forming an extended sp^2-hybridized carbon cap on the SiC nanoparticle. The kinetics of this process were enhanced significantly at higher temperatures (2500 K), compared to lower temperatures (1200 K) and so directly correlated to the surface premelting behavior of the nanoparticle structure. Analysis of the SiC nanoparticle Lindemann index between 1000 and 3000 K indicated that SWNT nucleation at temperatures below 2600 K occurred in the solid, or quasi-solid, phase. Thus, the traditional vapor-liquid-solid mechanism of SWNT nucleation once more did not apply in the case of SiC nanoparticles, with a VSS mechanism appearing to dictate the SWNT nucleation process Such a marked similarity between the atomistic SWNT nucleation mechanisms on SiC and SiO_2 catalysts provided the first evidence of a catalyst-independent SWNT nucleation mechanism with respect to ‘non-traditional’ SWNT catalyst species.

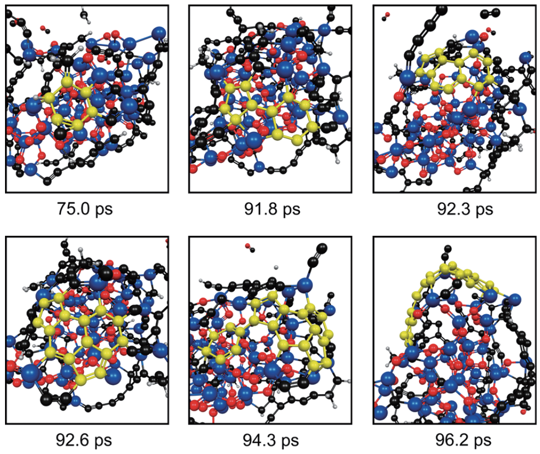


Fig. 2. SiO_2-catalyzed SWNT nucleation following CH_4 CVD simulation using SCC-DFTB/MD. Colour conventions as in Figure 1.

(B) QM/MD Investigation of Haeckelite and Graphene Growth on Transition Metal Surfaces

Graphene exhibits remarkable electronic, optical, and mechanical properties. This phenomenal nanomaterial has therefore been ascribed a number of potential applications in electronic, spintronic, sensor, and mechanical devices. Its electronic properties depend explicitly on the edge structure, which provides an additional control parameter for the purpose of electronic or spintronic property tuning. Haeckelite, on the other hand, is a hypothetical planar carbon compound that is intrinsically metallic, irrespective of its edge structure. Haeckelite’s

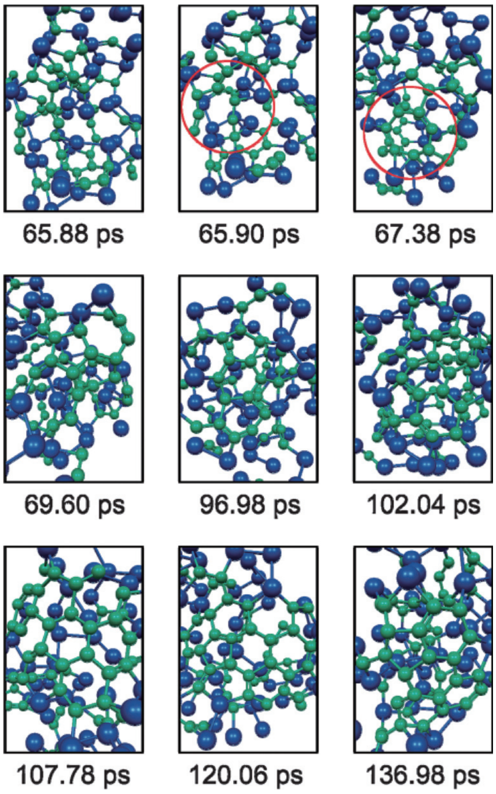


Fig. 3. Thermal annealing of SiC nanoparticles yields SWNT nucleation, as shown by SCC-DFTB/MD simulations. Blue and cyan spheres represent Si and C atoms, respectively.

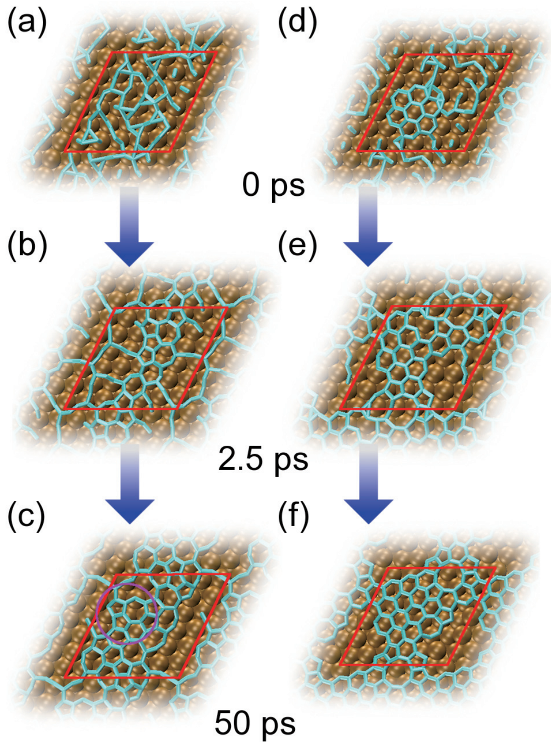


Fig. 4. Comparison of Haeckelite and graphene nucleation on a Ni(111) terrace. In the absence of a molecular template, Haeckelite forms as a structure rich in pentagon and heptagon defects from a random ensemble of C_2 fragments. Brown and cyan spheres represent Ni and C atoms, respectively.

structure can be formally derived from graphene by periodical replacement of hexagon pairs with pentagon/heptagon defects. At present, it is only a hypothetical structure, having never been experimentally synthesized and characterized. Its formation mechanism is therefore unknown.

To this end, QM/MD simulations of ensembles of C_2 molecules on a Ni(111) terrace (Fig. 4) show that, in the absence of a hexagonal template or step edge, Haeckelite is preferentially nucleated over graphene. The nucleation process is dominated by the swift transition of long carbon chains towards a fully connected sp^2 carbon network. Starting from a pentagon as nucleus, pentagons and heptagons condense during ring collapse reactions, which results in zero overall curvature. To the contrary, in the presence of a coronene-like C_{24} template, hexagonal ring formation is clearly promoted, in agreement with recent suggestions from experiments. Neverthless, analysis of the free energy of Haeckelite and graphene systems during nucleation shows the former structure to be *ca.* 0.1 eV/carbon atom higher in energy compared to the latter. This suggests that Haeckelite is a metastable intermediate formed during graphene nucleation in the absence of molecular templates. In such a scenario, graphene nucleation follows Ostwald's 'rule of stages' cascade of metastable states, from linear carbon chains, *via* Haeckelite islands that finally anneal to form the pristine hexagonal carbon lattice of graphene.

2. Original Papers

(1) A. J. Page, S. Minami, Y. Ohta, S. Irle and K. Morokuma, "Comparison of Single-Walled Carbon Nanotube Growth from Fe and Ni Nanoparticles using QM/MD Simulations", *Carbon*, **48**, 3014 (2010).
(2) A. J. Page, S. Irle, Y. Ohta and K. Morokuma, "Metal-Catalyzed Single-Walled Carbon Nanotube Nucleation, Growth and Healing Mechansims Determined Using QM/MD Methods", *Acc. Chem. Res.*, **43**, 1375 (2010).
(3) A. J. Page, D. J. D. Wilson, E. I. von Nagy-Felsobuki, "Trends in MH_2^{n+} Ion-Quadrupole Complexes (M = Li, Na, K, Be, Mg, Ca; *n* = 1, 2) using *Ab Initio* Methods", *Physical Chemistry Chemical Physics*, **12**, 13788 (2010).
(4) A. J. Page, H. Yamane, Y. Ohta, S. Irle and K. Morokuma, "QM/MD Simulation of SWNT Nucleation from Transition-Metal Carbide Nanoparticles", *Journal of the American Chemical Society*, **132**, 15699 (2010).
(5) 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", *Journal of the American Chemical Society*, **133**, 621 (2011).
(6) A. J. Page, K. R. S. Chandrakumar, S. Irle, K. Morokuma, "Do SiO_2 and Carbon-Doped SiO_2 Nanoparticles Melt? Insights From QM/MD Simulations, and Ramifications Regarding Carbon Nanotube Growth", *Chemical Physics Letters*, **508**, 235 (2011).
(7) A. J. Page, K. R. S. Chandrakumar, S. Irle, K. Morokuma, "Thermal Annealing of SiC Nanoparticles Induces SWNT Nucleation: Evidence for a Catalyst-Independent SWNT Nucleation Mechanism", *Physical Chemistry Chemical Physics*, **13**, 15673 (2011).
(8) Y. Okamoto, Y. Ohta, A. J. Page, S. Irle, K. Morokuma, "QM/MD Study of Transition Metal Catalyst Particle Melting and Carbide Formation During SWCNT Nucleation", *Journal of Theoretical and Computational Nanoscience*, **8**, 1755, (2011).
(9) Y. Wang, A. J. Page, H.-J Qian, Y. Nishimoto, S. Irle, K. Morokuma, "Template Effect in the Competition Between Haeckelite and Graphene Growth on Ni(111): Quantum-Chemical Molecular Dynamics Simulations", *Journal of the American Chemical Society*, In press.

3. Presentations at Academic Conferences

(1) "Methane CVD on SiO_2 Nanoparticles Investigated using QM/MD Methods". (Poster) A. J. Page, S. Irle, K. Morokuma, *NT2010 - The 11th International Conference on the Science and Application of Nanotubes*, Abstract Page 141, Montreal, Canada (2010).
(2) "QM/MD Simulations of Single-Walled Carbon Nanotube Nucleation on Transition Metal Catalysts". (Poster) A. J. Page, H. Yamane, S. Irle, K. Morokuma, *NT2010 - The 11th International Conference on the Science and Application of Nanotubes*, Abstract Page 109, Montreal, Canada (2010).
(3) "QM/MD Investigation of SWNT Nucleation on SiO_2 via CH_4 CVD". (Oral) A. J. Page, S. Irle, K. Morokuma, *The 39th Fullerenes-Nanotubes General Symposium, Abstract Page 1-13*, Kyoto University, Japan (2010).
(4) "SWNT Nucleation on Si-Based Catalysts via a Vapor-Solid-Solid Mechanism". (Poster) A. J. Page, K. R. S. Chandrakumar, S. Irle, K. Morokuma, *The Fifth NASA – Air Force Research Laboratory and Rice University Workshop on Nucleation and Growth Mechanisms of Single Wall Carbon Nanotubes*, Abstract Page 50, San Antonio, Texas, USA (2011).
(5) "Modelling Carbon Nanotube Growth with Quantum-Mechanical Molecular Dynamics". (Poster) A. J. Page, K. R. S. Chandrakumar, S. Irle, K. Morokuma, *Theoretical Modelling of Materials*, Abstract Page 67, Barcelona, Spain (2011).
(6) "Understanding Nanoscale Self-Assembly Processes Using QM/MD: Mechanisms of Carbon Nanotube Nucleation and Growth". (Talk) A. J. Page, K. R. S. Chandrakumar, S.

Irle, K. Morokuma, *2011 World Congress of WATOC*, Abstract Page OC098, Santiago de Compostela, Spain (2011).

(7) "Mechanisms of Carbon-Based Nanostructure Self-Assembly: Insights from Density-Functional Tight-Binding Molecular Dynamics". (Talk) A. J. Page, K. R. S. Chandrakumar, S. Irle, K. Morokuma, *7th Congress of the International Society for Theoretical Chemical Physics*, Abstract Page 6A2-2C, Tokyo, Japan (2011).

4. Book Chapters

(1) "Mechanisms of Single-Walled Carbon Nanotube Nucleation, Growth and Chirality-Control: Insights from QM/MD Simulations" in *Electronic Properties of Carbon Nanotubes*, A. J. Page, Y. Wang, K. R. S. Chandrakumar, S. Irle and K. Morokuma, ed. Jose Mauricio Marulanda. InTech, Vienna, Austria, p. 521-558. ISBN: 978-953-307-499-3.

(2) "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.

Xin LI

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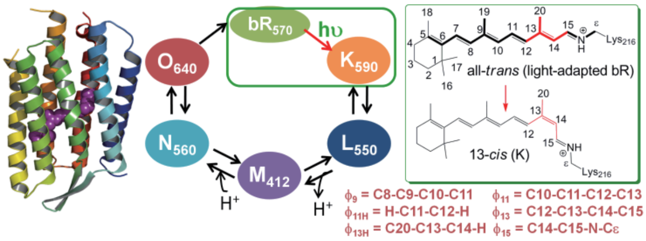
1. Summary of the research of the year

Photodynamics of All-trans Retinal Protonated Schiff Base in Bacteriorhodopsin and Methanol Solution

Bacteriorhodopsin (bR) is a transmembrane protein in the purple membrane of *Halobacterium salinarium*. All-*trans* retinal protonated Schiff base (RPSB) is covalently linked to Lys216 of the protein in the light-adapted bR. Absorption of a photon by RPSB can trigger a photocycle with several photostationary states (see Scheme 1). Photodynamics of light-induced all-*trans* RPSB is sharply different in bR and in homogeneous solutions, leading to different photoproducts and excited-state lifetimes. Primary events of photodynamics of all-*trans* RPSB in bR and methanol solution were elucidated by non-adiabatic ONIOM(QM:MM) molecular dynamics simulations. Our simulations showed that the photoisomerization in bR is bond-specific (leading to the 13-*cis* form) and unidirectional, as well as the photoisomerization along the C11=C12 bond is suppressed. Comparatively, the photoisomerization is not bond-specific and unidirectional in methanol solution, in which the rotation along the C11=C12 bond is dominant. As shown in Figure 1, photo-excited RPSB underwent ultrafast radiationless decay ($S_1 \rightarrow S_0$) exclusively via a torsional change along ϕ_{13} in bR. In methanol, however, the nearly planar RPSB takes a longer time to decay via one of three torsional changes: ϕ_9, ϕ_{11} or ϕ_{13}. Therefore, bR catalyzes the photoisomerization to afford the meta-stable 13-*cis* form, which should efficiently store energy and thus promote the subsequent proton pumping and protein conformational change processes. In addition, a bicycle-pedal like mechanism was found to be the major decay pathway in bR and methanol solution. The reaction mechanism and environmental effects on the photodynamics have been extensively investigated.

Scheme 1



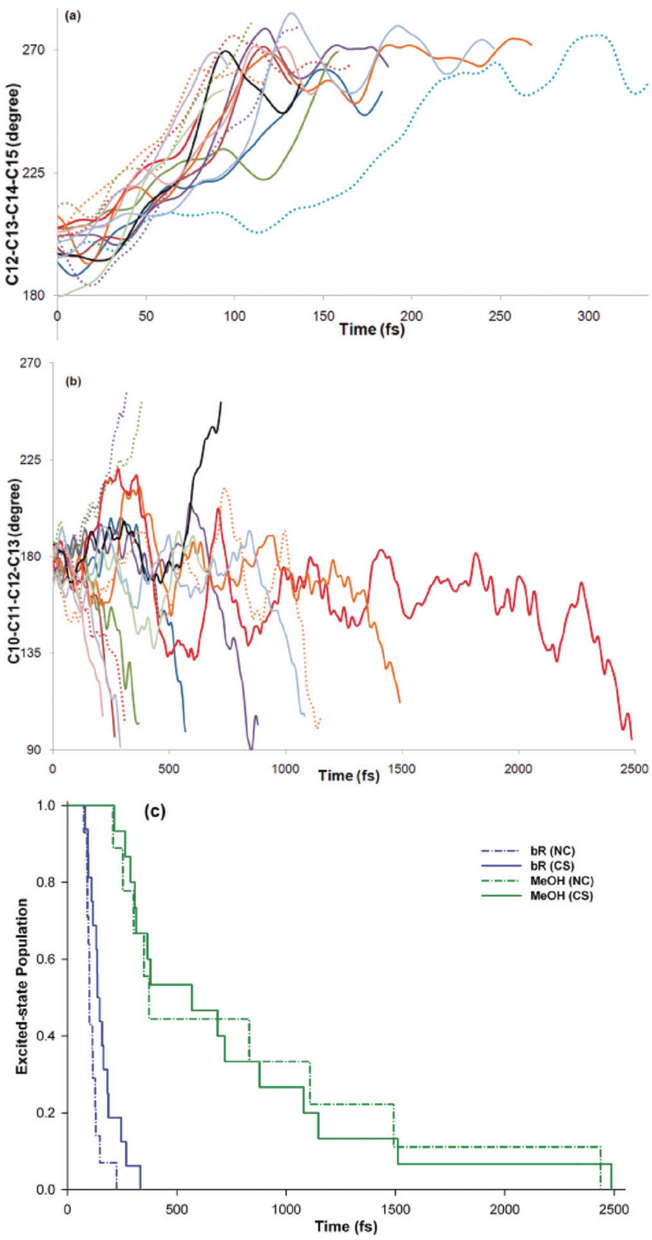


Figure 1. Changes of the rotating dihedral in S_1 until CS: (a) ϕ_{13} in bR and (b) ϕ_{11} in methanol. (c) Excited-state population for photoisomerization in bR and methanol.

2. Original papers

(1) Xin Li, Lung Wa Chung, Hideaki Mizuno, Atsushi Miyawaki, and Keiji Morokuma, “Primary Events of Photodynamics in Reversible Photoswitching Fluorescent Protein Dronpa”, J. Phys. Chem. Lett. 1, 3328-3333 (2010).

(2) Xin Li, Lung Wa Chung, Hideaki Mizuno, Atsushi Miyawaki, and Keiji Morokuma, “Competitive Mechanistic Pathways for Green-to-Red Photoconversion in the Fluorescent Protein Kaede: A Computational Study”, J. Phys. Chem. B 114, 16666-16675 (2010).

(3) Xin Li, Lung Wa Chung, and Keiji Morokuma, “Photodynamics of All-trans Retinal Protonated Schiff Base in Bacteriorhodopsin and Methanol Solution”, J. Chem. Theory Comp. (letter) 7, 2694-2698 (2011).

3. Presentation at academic conferences

(1) Xin Li, Lung Wa Chung, Hideaki Mizuno, Atsushi Miyawaki, and Keiji Morokuma, “*Primary Events of Photodynamics in Reversible Photoswitching Fluorescent Protein Dronpa*”, American Chemical Society 241th National Meeting, Anaheim, California, March 27-31, 2011.

(2) Xin Li, Lung Wa Chung, Hideaki Mizuno, Atsushi Miyawaki, and Keiji Morokuma, “*Primary Events of Photodynamics of GFP Chromophores in Proteins, Solution, and Gas-phase*”, 9th Triennial Congress of the World Association of Theoretical and Computational Chemists, Santiago de Compostela, Spain, July 17-22, 2011.

(3) Xin Li, Lung Wa Chung, and Keiji Morokuma, “*Primary Events of Photodynamics of All-trans Retinal Protonated Schiff Base in Bacteriorhodopsin, Methanol Solution and Gas Phase*”, 5th Asia and Oceania Conference on Photobiology, Nara, Japan, July 30-August 1, 2011.

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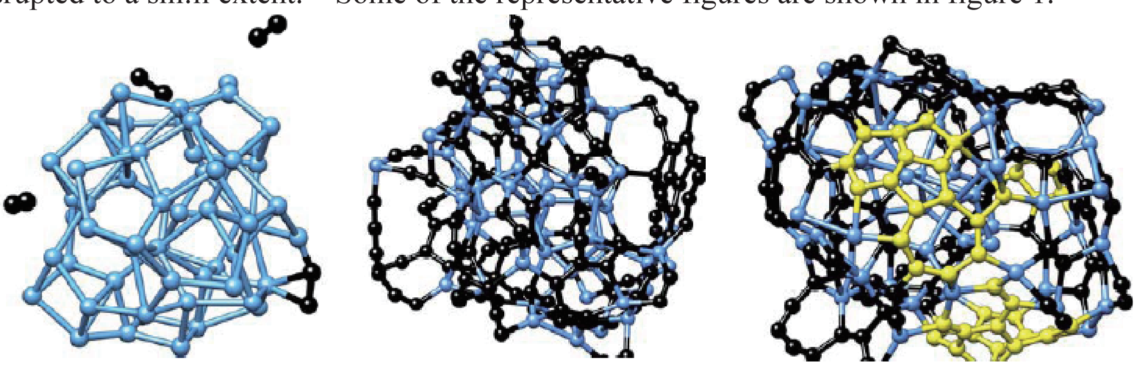
1. Summary of the research of the year 2010

DFT QM/MD Investigation of the Nucleation of Single-walled Carbon nanotubes on the Nonmetallic Silicon Nanoparticles

Carbon nanotubes (CNTs) and single-walled CNTs (SWNTs) have attracted great interest in recent years due to their unique physical and chemical properties, and their range of potential applications. Many of these applications require the physical properties of CNTs (*i.e.* chirality, diameter and density) to be precisely controlled. In recent years, much progress has been made regarding the synthesis *via* the chemical vapor deposition (CVD) method. Significant progress has also been achieved in obtaining large yields of CNTs by the optimization of CVD catalysts, substrates, experimental conditions, *etc.* Despite these advances, a method by which a SWNT of a specific chirality, diameter *etc.* may be synthesized remains elusive to date. This is largely due to the difficulty in observing nucleation and growth processes *in situ*. A detailed understanding of the nucleation and growth mechanisms on various catalyst particles is therefore crucial. With respect to traditional, transition metal catalysts (such as Fe, Co, Ni *etc.* and alloys thereof), the vapor-liquid-solid (VLS) mechanism is one such mechanism. Although the nucleation and growth processes of single-walled carbon nanotubes have been experimentally and theoretically studied, the precise atomistic mechanism explaining SWNT growth on nontraditional catalysts, such as silicon, has not yet been reported. In this work, we will present a systematic study of the SWNT nucleation mechanism on Si nanoparticles using quantum mechanical molecular dynamics (QM/MD) simulations. SWNT nucleation here is induced using a model CVD process, in which gas phase C_2 moieties are adsorbed onto a model Si_{58} nanoparticle 1250 K. We have considered the nucleation of SWNT induced by the low and high carbon concentration ($Si_{58}C_{100}$ and $Si_{58}C_{150}$). Our results indicate that the catalyst is stable upon the addition of C_2 species and the outer layer of the catalyst surface is disrupted to a sm:ll extent. Some of the representative figures are shown in figure 1.



CVD on Si Catalyst sp^2-Carbon-Network CNT Nucleation

Figure 1: Nucleation of SWCNT on silicon nanoparticles

Following the adsorption of C_2 onto the Si_{58} nanoparticle surface, the resultant surface structure resembled an amorphous SiC phase, while the core of the Si nanoparticle remained pristine. As shown in Figure 1, most of these carbon units are found to be at the silicon surface and only few carbon atoms are found to penetrate inside the cluster. The incident carbon species supplied to the silicon catalysts mostly form the linear and short/long polyyne chains with the number of carbon atoms extending up to ~3-6. Both the ends of the polyyne chains are connected to the silicon particles and they are found to be very stable for a long period of time. It is also noted that since the silicon particles act like clamped surface for the carbon polyyne chains, the flexibility or mobility of these chains are restricted. The resulting final structures, as shown in Figure 1, are thus typically characterized by the formation of amorphous SiC structure at the surface along with carbon polyyne chains and the core of the nanoparticle is continued to exist with the Si atoms. These results reveal certain interesting features, especially on the mechanism of the CNT cap-nucleation, which are found to be strikingly different from the traditional catalysts. In particular, our simulation results indicate that the growth of the sp^2-carbon network is exclusively dependent on the dynamics of the vibrational/translational motion of the polyyne chains formed at the catalyst surface. The process of nucleation stage begins only after the saturation of such carbon networks (sufficiently higher carbon based ring networks) at the catalysts surface.

Is SWNT Nucleation on Silicon Nanoparticles Preceded by a Carbide Phase or a Carbon-Coated Surface?

A detailed understanding of the mechanism of the formation of CNT, especially through the CVD method is very crucial for obtaining precisely controlled the physical and chemical properties of the carbon nanotubes (chirality, density and metallic or nonmetallic property). In this regard, one pertinent question often asked is on the nature of the intermediate stage for the nucleation of the CNTs. Few experimental and theoretical studies have been carried out in the past and some of the results are conspicuously different from each other. The important intermediate stage for the CNT cap-nucleation with the traditional catalyst is either the carbide phase and/or the precipitation of carbon at the catalyst surface through the bulk/surface diffusion of the carbon adatoms to the boundary of the catalyst. However, for the case of non-traditional catalysts, the detailed mechanism for each stage of the nucleation/growth mechanism is yet to be established. In particular, we will address the question of whether or not a Si-carbide phase precedes the SWNT nucleation process. To this end, we have monitored the radial distribution of carbon within the Si_{58} catalyst (with respect to the Si_{58} center of mass) throughout the thermal annealing period, averaged over intervals of 20 ps. It is noted here that the radius of the cluster is approximately 4.5 Å. These data are shown in **Figure 2a**. It is evident that the populations of carbon atoms at the core and surface of the Si_{58} nanoparticle are very distinct from each other. For example, only two carbon atoms are found 4 Å from the Si_{58} center of mass at 20 ps, a population which is maintained until 200 ps. At a distance of 4.5 Å from the Si_{58} center of mass (*i.e.* the catalyst surface), this population increases to five carbon atoms, whereas a maximum of 14 carbon atoms are observed at 7 Å. At larger distances, the number of carbon atoms decreases.

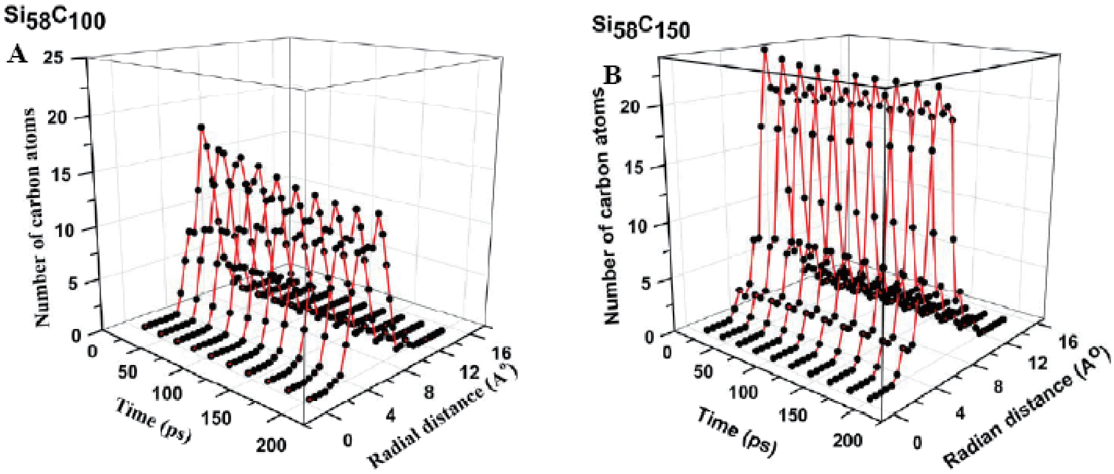


Figure 2: Solubility of carbon species inside the silicon cluster for (A) low[C] and (B) high[C]. Number of carbon atoms present inside a sphere of radius equivalent to the distance of each carbon atom from the center-of-mass of the cluster.

A similar pattern is also found for the high [C] case (F**igure 2b)**. For example, at distances of 4, 4.5 and 7.5 Å from the Si_{58} center of mass, the populations of carbon atoms is two, three and 21, respectively, are observed. Interestingly, no significant change in this general pattern is observed even after a further 200 ps, for both carbon concentrations. Approximately 97% of all carbon atoms are found to be at the Si nanoparticle surface. The remaining carbon atoms penetrate the surface and reside in the Si nanoparticle subsurface. The possibility of the diffusion of carbon within the nanoparticle bulk is therefore very unlikely, and the catalyst surface is uniformly covered by sp- and sp^2-hybridized carbon. These results demonstrate that *the formation of a carbide phase, and the subsequent diffusion of carbon to the catalyst surface, are not necessary conditions for the SWNT nucleation for Si catalysts.* On the other hand, these two stages are generally accepted to precede SWNT nucleation and growth on transition metal catalysts. Indeed, such diffusion of carbon from the catalyst bulk to the catalyst surface is central to the traditional VLS mechanism of SWNT nucleation and growth. This is consistent with the activation energy for the diffusion of carbon in iron (0.75 eV), compared to that of carbon in Si (2.93 eV) in the temperature range of 1200-1650 K. From these results, one can unquestionably argue that, contrary to established phenomena using transition metal catalysts: (i) carbon atoms neither dissolve nor diffuse through Si nanoparticles, hence, a Si-carbide phase is not observed; (ii) SWNT nucleation is driven by the formation of a carbon network through the linear polyyne carbon chains on the Si nanoparticle surface; and (iii) the polyyne chains are exceptionally stable and their constrained rotational/translational motion impedes the formation of sp^2-carbon networks (and thus SWNT nucleation) on the Si surface. An important consequence of these facts is that the SWNT yield on Si-catalysts should be much lower than for iron group metal catalysts. These observations also suggest that the VLS type of mechanism may not be applicable in the case of Si nanoparticles. Two prerequisites for VLS growth of CNTs are that carbon is soluble in the catalyst nanoparticles, and that the growth temperature should be above the eutectic melting point. As shown above, the solubility of carbon inside the Si catalyst is essentially negligible.

Melting Behavior of the Pure and carbon-doped Silicon Nanoparticles: Carbon Induced Liquid-to-Solid Phase Transition in Silicon Nanoparticles

Since the phase of the catalyst determines the dynamics and kinetics of CNT nucleation, herein, our objective is to investigate the nature of the phase of the silicon catalyst during the nucleation/growth of the CNT. It is well known that the mechanism for the CNT growth with the transition metal catalyst is shown to be vapor-Liquid-Solid (VLS), i.e. the state of the catalyst is in the molten state and the carbon species are dissolved from vapor phase into the molten "liquid-like" catalyst particle and forms the carbide phase. The carbon super saturation in these metal-carbide precursors subsequently induces precipitation of carbon from the nanoparticle bulk to the surface, at which point the solid phase CNTs nucleate and grow. Conversely, CNT growth on a diverse range of covalent catalysts (such as Al_2O_3, SiC, Si, Ge or SiO_2) proposed that during CNT growth the catalyst exists as a solid nanoparticle. During the chemical vapor decomposition (CVD) process, a high carbon density builds upon the surface of this nanoparticle resulting in a 'carbon-coated' particle. This ultimately results in the formation of an sp^2- hybridized carbon patch (i.e. a 'graphene island'). Continued CNT growth from this solid structure then ensues. Thus, it would be interesting to verify the experimental hypothesis on the nature of the phase of the silicon catalyst and the CNT nucleation/growth mechanism .

The melting phenomena of pristine and carbon-doped Si nanoparticles have been investigated using the Lindemann Index.

$$\delta = \frac{1}{N(N-1)} \sum_{i \le N} \sum_{i \ne j} \frac{\sqrt{\left\langle r_{ij}^2 \right\rangle_T - \left\langle r_{ij} \right\rangle_T^2}}{\left\langle r_{ij} \right\rangle_T}$$

where N is the number of atoms, r_{ij} is the instantaneous distance between atoms i and j, and T denotes thermal averaging at temperature T. In this work, all thermal averaging has been performed using 1 ps periods. The Lindemann criterion, introduced in 1910, measures the atomic vibrational amplitude in units of the lattice constant of a crystal. If this ratio, which is defined as the disorder parameter reaches a certain value, it is presumed that fluctuations cannot increase without damaging or destroying the lattice. Experiments and simulations show that the critical value of this index for simple solids is in the range of 0.10–0.15. The critical value has been found to be relatively independent of the types of substance, the nature of the interaction potential, and the crystal structure.

The melting pattern for the Si_{58} cluster obtained from the DFTB based QM/MD method is represented in Figure 3a. It is evident from the above figure that the Si_{58} cluster starts melting at 900 K and above1600 K it exists as liquid. The experimental melting point for the bulk silicon is 1687 K and for the cluster with different sizes, the calculated melting point is in the range of 900–1400 K. It may be noted that the CNT growth experiment with Si nanoparticle was performed at 1250 K and hence, it can be mentioned that the silion nanocluster is in the liquid state. Does that mean VLS mechanism can explain the growth of CNT? Although it appears that VLS mechanism can explain the CNT growth, the answer for this question can be provided if we also analyze the melting pattern for the carbon-doped silicon nanocluster system. Accordingly, we have systematically considered 3 different carbon-doped silicon clusters, namely $Si_{58}C_{100}$ (Low), $Si_{58}C_{150}$ (Medium), $Si_{58}C_{208}$ (High) and the corresponding melting pattern curves are given in Figure 3b, 3c and 3d, respectively.

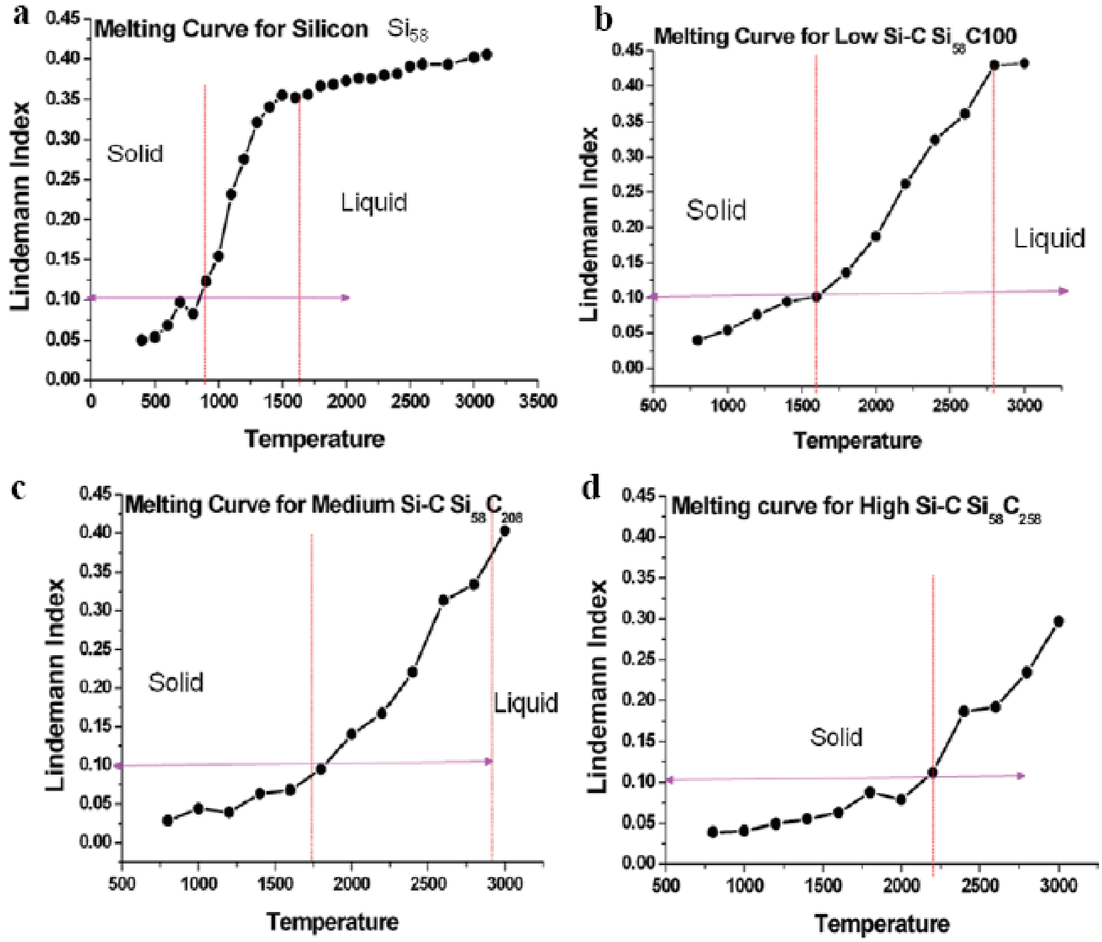


Figure 3: Melting curve for the silicon and carbon-doped silicon clusters

It is clear from the above figures that addition of carbon into the silicon cluster substantially increases the melting temperature of the carbon-doped silicon nanoclusters. For instance, $Si_{58}C_{100}$ starts melting at 1600 K and above 2600 K, it may exist as liquid and for the case of $Si_{58}C_{150,}$ the melting temperature is ~1750 K and existence of liquid region is estimated to be above 3000 K. More interestingly, it appears that the higher level doping of carbon into the silicon cluster increases their stability and the melting of the cluster starts above 2250 K. It is also interesting to note that both the medium and high-carbon-doped silicon clusters are observed to disintegrate into smaller fragments at above 3000 K and hence, it can be mentioned that these clusters sublimes directly without having the liquid phase. Our simulations show that no liquid phase catalyst carbide precursor can exist during CNT synthesis on Si nanoparticles, since the experimental/simulation temperature is 1250 K. In other words, the VLS mechanism can be ruled out for the Si-catalyzed SWNT nucleation and growth and our results point to a VSS mechanism. Thus, the mechanisms of SWNT nucleation and growth on traditional and non-traditional catalysts are therefore of fundamentally different natures. Based on the above discussions, we conclude that although the mechanism at the initial stage appears to be VLS, once the chemical vapor deposition process begins (as the concentration of carbon increases in silicon nanocluster), the mechanism changes from VLS to VSS. These results can have important implications for the CNT nucleation and growth mechanism with silicon catalyst.

DFTB based QM/MD Investigation on the Formation of Fullerene Molecule from Graphene Sheet

Although fullerenes have been synthesized by different methods especially from the graphite based starting materials, the recent experiment has opened up another interesting venue for generating fullerenes from graphene sheets. The mechanism of fullerene formation from graphene sheets has been investigated using the DFTB QM/MD methods with different graphene models of finite sizes. Our findings reveal that the creation of the defects in the model graphene sheets is identified as an important step, which facilitates the transformation of sheet into fullerene. At the lower temperature (less than 3000 K), the sheet is found to be stable except at the peripheral regions and leads to the structure with small curvature. The effect of temperature is observed to be very substantial and the successful transformation occurs at 3000 K accompanying by the loss of few C_2 units from the peripheral regions and the formation of polyyne chains. In most of the cases, the pentagons are formed either by the interaction of these polyyne chains or reorganization of the deformed 6m-rings. In addition, the pentagons are never formed at the center of the sheet and they are rather formed by pushing from outer most layers to penultimate inner layer of the hexagonal sheet. The time scale for this transformation is found to be around 200-400ps depends on the size of the sheets as well as the temperature.

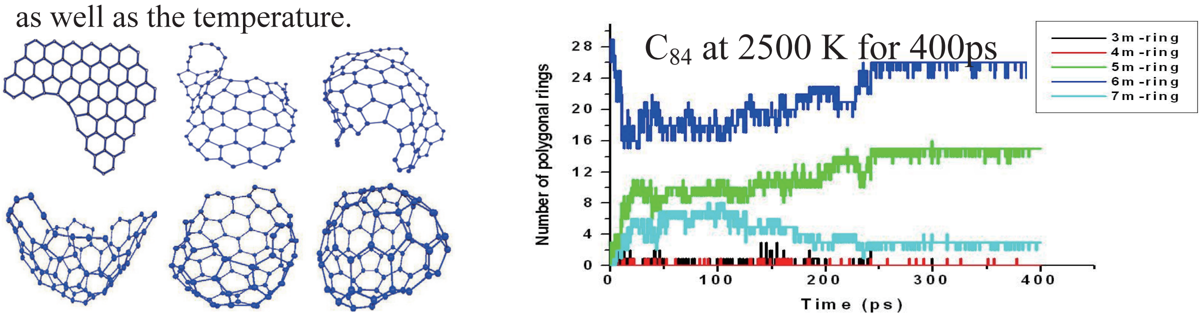


Figure 4: (a) Snapshots for the formation of fullerene molecule from the C_{84} graphene sheet and (b) the polygonal ring formation dynamics

2. Original Papers

1. Do SiO_2 and carbon-doped SiO_2 nanoparticles melt? Insights from QM/MD simulations and ramifications regarding carbon nanotube growth; Alister J. Page, K.R.S. Chandrakumar, Stephan Irle and Keiji Morokuma; *Chem. Phys. Lett.* 508 (**2011**) 235-241.
2. SWNT Nucleation from Carbon-Coated SiO2 Nanoparticles via a Vapor−Solid−Solid Mechanism Alister J. Page, K. R. S. Chandrakumar, Stephan Irle, and Keiji Morokuma; *J. Am. Chem. Soc.,* 133 (**2011**) 621–628.
3. Thermal Annealing of SiC Nanoparticles Induces SWNT Nucleation: Evidence for a Catalyst-Independent VSS Mechanism; Alister J. Page, K. R. S. Chandrakumar, Stephan Irle, and Keiji Morokuma; *Phys. Chem. Chem. Phys.* 13 (**2011**) 15673-15680

3. Presentations at Academic Conferences

1. K. R. S. Chandrakumar, S. Irle and K. Morokuma “Carbon Nanotube Growth from Carbon Nanocones catalyzed by Iron Nanoparticles” (Poster) Presented in International Symposium on "Molecular Theory for Real Systems" Kyoto University, Kyoto, Japan (2010).
2. K. R. S. Chandrakumar, S. Irle and K. Morokuma “DFTB-MD simulation of carbon nanotube growth from metal decorated carbon nanocones” (Poster) presented in, 50th Sanibel Symposium, St.Simons Island, Georgia, USA, (2010).
3. K. R. S. Chandrakumar, S. Irle and K. Morokuma "Growth of Nanotubes/ Nanocapsules from Metal Decorated Carbon Nanocone Aggregates: Insights from DFTB-MD Simulations" (Oral Presentation) Presented in, 39th Fullerenes-Nanotubes General Symposium, Kyoto University, Kyoto, Japan. Oral Presentation (2010).
4. K. R. S. Chandrakumar, A. J. Page, S. Irle and K. Morokuma”QM/MD Investigation of the Nucleation of Carbon Nanotube on the Nonmetallic Silicon Nanocluster: Is the Intermediate Stage Carbide or Carbon Coated Surface?” (Poster) Presented in 8th Fukui Institute for Fundamental chemistry Symposium, FIFC, Kyoto University, Kyoto. (2010).

Fengyi LIU

JST Fellow, Fukui kenichi Memorial Research Group 1

1. Summary of the research of the year

a) Theoretical Investigation on Light-Driven Molecular Rotary Motors

Light-driven molecular rotary motors undergoing repetitive and unidirectional rotation (in similar manner to that of their biological counterparts, *e.g.*, the bacterial flagella motor and ATPase) have been recently synthesized and attracted wide interest. The photophysics and photochemistry behind these genius designs are crucial in fully understanding the working mechanism of the currently synthesized rotary molecular motors and in designing promising nanoscale molecular devices. However, the necessary information of the photo-initiated ultrafast processes of the involved molecules, for instance the reaction paths on the ground- and excited state potential energy surface (PES), the nonadiabatic decay governed by the interactions between the PESs (*i.e.*, conical intersections (CIs) or avoided crossings) , is not sufficient. In order to understand their working mechanism, we investigated the light-driven molecular rotary motors by using the CASPT2//CASSCF methods.

Driving Force—the Engine Powers the Rotation: Driving forces are perquisite for molecular motors. It stimulates the relative mechanistic movement of one component of the molecule with respect to the other. According to quantum mechanistic theory, stable molecules are trapped in the well on their fundamental-state potential energy surface (PESs), with all nuclei in optimal distributions. Upon external perturbation, the molecule is promoted off the equilibrium state (either geometrically or electronically) to another high-energy, nonequilibrium state. In order to regain the equilibrium, the molecule adjusts the nuclei coordinates until it finds the optimal distribution again. In this process, the re-stabilization along with the geometry relaxation will act as the driving force.

Among the many ways to create such nonequilibrium state, light is an ideal source of energy input. In light-initiated processes, the nonequilibrium state is electronic excited state (ES), more specifically, the FC structure on ES PES. It has demonstrated in numerous cases that the landscape of excited-state (ES) PESs can evidently differ from the ground-state (GS) ones; therefore the ES FC structure (with the same geometry to the GS minimum) could be highly unstable compared with the actual relaxed ES minimum. Along the adiabatic ES decay path started from the region (to ES intermediate or other crucial region such as conical intersection (CI), avoided crossing and intersecting seams, etc.), the energy change drives the geometry relaxation, namely the relative mechanistic movement. This is also valid for the consequent GS decay process, which is connected with the ES decay by possible ES→GS nonadiabatic transition, though the nonadiabatic decay through CI could be more complicated. For instance, excited from either the *cis*- or t*rans*-isomer of free-stilbene (FS) which are more or less with planar geometries, the ES FC points are geometrically far from and energetically less stable than the perpendicular ES intermediate. These differences generate the bond rotation around the central C-C bond.

Without considering the dynamics of the atoms, the minimal geometry relaxation path corresponds to the minimal reaction path (MEP). Therefore, the sloppiness of the PES along MEP could qualitatively predict the rotary potential of a given molecule. The steeper the slope is, the larger the driving force is and the faster relaxation takes place. The shape of the ES PES in the vicinity of the FC region, which generates the initial momentum of the molecule, is the most important and fundamental one. The sloped PES near FC region fascinates large initial momentum, while well-shape PES more or less hinders (or at least slows down) the rotation. The latter case may be overcome by carefully chosen the excitation wavelength (i.e., exciting molecule to higher electronic state or "hot" vibrational state, etc.), but which is beyond the scope of this discussion. Another major factor is the overall potential energy change against the whole reaction path, which reflects the average driving force of the geometry relaxation. In general, large driving force is can be achieved by increase the stability of the final state or decrease the stability of the initial state. In stilbene motor (SR), the ES FC structures are actually strongly decreased by the methyl-methyl repulsion between the substituents in the "*fjord*" region.

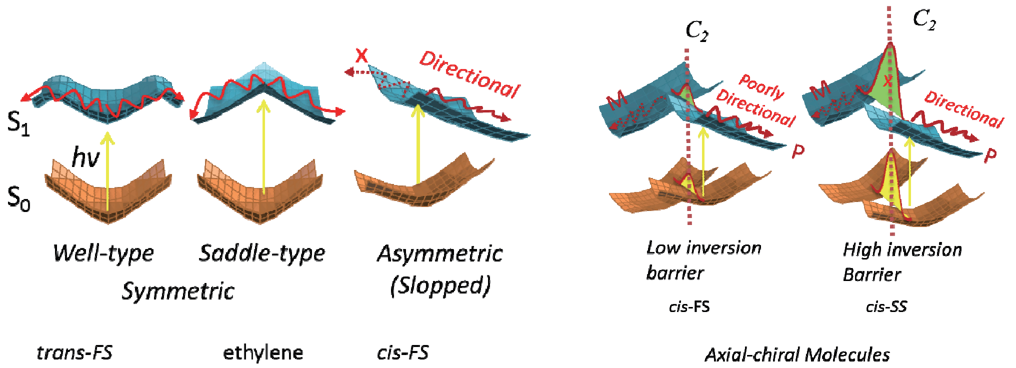


Figure 1. The different shape of PESs in the vicinity of the ES FC region. (**FS**: free-stilbene; **SS**: stiff stilbene; **SR**: stilbene rotary motor)

Directionality of Rotation: Nondirectional-(Bidirectional-), Directional- and Unidirectional Rotation: Though bond rotation is an abundant phenomenon in stereochemistry, the direction of bond rotation is generally ignored in nonchiral chemistry (because the two rotation processes, clockwise- and anticlockwise-rotation and their resulting products are undistinguishable). For instance, the simplest photo-active C-C bond rotary system is ethylene. From the concept of the molecular rotary motor, the rotor part (with respect to the stator part) of the molecule can rotate clockwise or anticlockwise towards to the *perp**(-90) and *perp**(90) ES intermediate, however, these two *perp** structures are stereochemical the same. The excited FC ethylene is located on the ridge of the two intersected rotation PES, therefore the rotation opportunities towards the clockwise- and anticlockwise- directions are equal. Such kind of the bond rotation is thus ***no direction-preferential*** (***nondirectional***), or ***bidirectional***. Similar situations are found in the photoisomerization of *trans*-FS. Commonly, the nondirectional/bidirectional rotations are governed by the high symmetric PES resulted from the high symmetry of the molecule. In order to initiate directional movement, the symmetry of the molecule (as well as the PES) has to be lowered (or broken) and two paths have to be distinguishable. This can be achieved by introducing asymmetric substitutions, secondary structure (helicity), or both.

Strictly speaking, any asymmetric rotary PESs could generate rotation with more or less directionality. However, only in the case that one direction is evidently more favorable than the other could be regarded as

directional rotation. *cis*-**FS** will be good example representing a directional rotation on ES PES. The *cis*-FS molecule is weakly heical-twisted by the repulsion between the near edges of the two benzene moieties. Started from one of the two helically chiral enantiomers (for instance, right-hand or *P,P'*- *cis*-FS) to *perp**(90) intermediate, the anticlockwise rotation is energetically favorable, while the reversed direction is unfavorable due to the uphill PES caused by the repulsion. Meantime, the M,M'- enantiomer prefers clockwise rotation to the anticlockwise one. Though for each of them the ES decay follows a directional way, the overall decay doesn't show directionality due to the barrier between these two enantiomers are rather low and one could easily isomerization to the other. Only if the helical inversion barrier is high enough to hinder the thermal isomerization of the *P*- and *M*- enantiomers, they could be separated and a light-driven directional decay is possible. In *cis*-3, the methyl- substituents on the "*fjord*" region significantly increase the barrier height, which makes the separation of the *P*- and *M*- conformers possible. Similarly, on *trans*-SR-3, the repulsion forces the two benzene moieties twisted along the *P*- or *M*- directions (The ideal planar structure as in free stilbene now actually corresponds to the helical-inversion barrier between *P*- and *M*-conformer). The directional rotation started from FC-*trans*-**SR** is also expected, though the MEPs are not totally downhill.

Unidirectionality, which is one of the ultimate goals of artificial molecular rotary motor, can be achieved by the couple of several directional rotations. A series of the directional along the same direction (clockwise or anticlockwise) compose ***unidirectional rotation*** as showed in **SR**; while two or more directional rotation in reversed direction is possible to be utilized as molecular switch (and similar fancy concepts of functional molecular devices such as molecular elevator, molecular truck, *etc.*).

Directional Rotation in Nonadiabatic Decay: The above discussions of directionality only focus on adiabatic PES. In fact, the photo-induced process is more complicated since they involve in the nonadiabatic transitions. For instance, the decay through nonadiabatic coupling region strongly depends on the nature and location of crucial points (or seam). In stilbene, the ES decay does not terminated at ES intermediate; instead, the molecule goes further though CIs and relaxes on GS PES. In **SR 3**, t wo types of crossings are found in the rotary process: 1) the 1B/2A seams, which are located along the 1B-MEP and the slope of the interesting seam is roughly in parallel with that of the decay path. They are classified as ***directional nonadiabatic decay***. 2) The 2A/1A CIs, which are off the reaction path along the orthogonal C_1/C_1' pyramidalization coordinate and also high in energy, therefore are classified as ***poorly directional nonadiabatic decay***. In the latter case, the pyramidalization- rather than the primary C-C rotation coordinate controls the 2A→1A decay, it could slows down the rotation

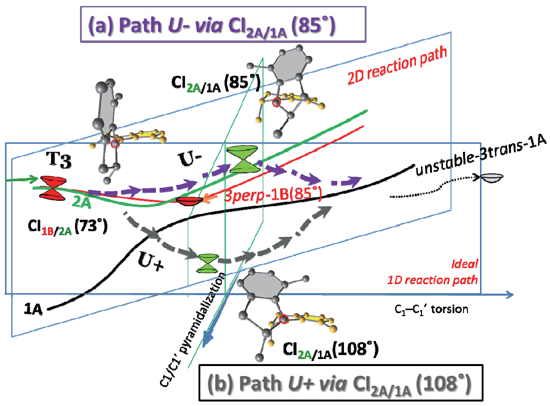


Figure 2. The 2A/1A nonadiabatic decays (a) **U-** *via* **CI$_{2A/1A}$(85)**, (b)U+ via CI$_{2A/1A}$(108) in ***cis-SR→unstable-trans-SR*** photoisomerization. **U-** is the more favorable pathway.

and eliminates the directionality of rotation. Therefore, the 2A/1A nonadiabatic decay is the key issue in stilbene rotary motor. In order to design unidirectional rotary motor based on stilbene, the directionality of the 2A/1A decay has to be improved. Our CASPT2//CASSCF calculations reveal that the 2A/1A CIs in motor **3** is, though not as comparable with 1B/2A seams, still directional. These are because: 1) The helical torsional MEP approaches the 2A/1A CIs along non-perpendicular direction; 2) The repulsions (between the crowded substituents) push the reaction path close to one of the CIs against the other. These will to largest extend, maintain the direction of the rotation and the inertial velocity of the molecular.

b) Ring-Opening and Ring-Closure Mechanism of Spiropyran-Merocyanine Photochromic Reaction

The photochromic reaction of spiropyran (SP)-Merocyanine(MC) photochromic reaction has been widely used in molecular devices. However, due to the complicity of the potential energy surface of this reaction (conical intersections of the ground- and excited-state potential energy surfaces, excited singlet and triplet state reactions and unusual intersystem crossing properties of spiropyrans), the details of the reaction have not been well understood. We carried out CASPT2//CASSCF calculation to explore the ground- and excited-state PESs of the model molecule (especially the excited-state PES which has been poorly described) and to uncover the conical intersection based internal conversation processes in this reaction.

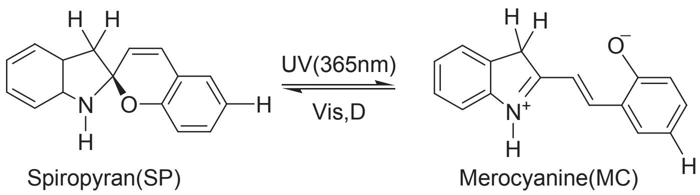


Figure 3. SP-MC photochromic reaction (Unsubstituted-SP)

The SP-MC ring-opening reaction takes place in two steps: 1) Photocleavage of C-O bond. Two parallel C-O cleavage paths were found on the S_1 PES (to S_0 C-O cleavage). Starting from the FC(S_0-SP), the molecules follow two primary reaction paths, *S_1-SP→ S_1-TCC* and *S_1-SP →S_1-CCC*, both are barrierless downhill MEP. Along the S_1-MEP, the S_0 and S_1 curve intersect with each other and form extensive state-interacting regions (S_1-S_0 gaps lower than 10 kcal/mol). The torsional modes (especially the N3—C1—C4—C7) corresponding to dihedral angle α, β and γ regulate the branching ratio in the initio step, and are responsible for the strong state-interacting region along the reaction path. 2) Isomerization between MC Isomers. In principle,

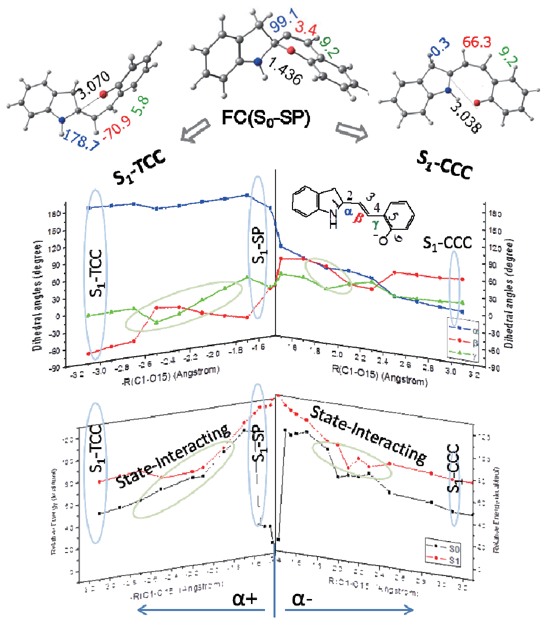


Figure 2. The variation of dihedral angles α, β and γ (in degree) along the S_1-MEP.

OBF, HT and BP can take place in MC photoisomerization. Considering of their relative long life time (~10ps), low isomerization barriers and flexible reaction paths, all MC conformers can be generated from the CCC and TCC. Several CIs were located at the CASSCF level and are responsible to produce ground-state MC isomers, though CASPT2 show large discrepancy with CASSCF results.

The ring-closure mechanism of MC chromic reaction is studied. It is found the bond rotations around β are crucial for ring-closure, γ less important, and α bond are highly unfeasible. The most efficient reaction path corresponds to FC-TTC(S_2)→ CI (S_2/S_1,β2)→ TS(β2,S_1) → TCC(S_1) → $CI2_{S1/S0}$→SP(S_0). These results agree with the experimental findings.

2. Original papers

(1) Fengyi LIU, Keiji MOROKUMA,
"A CASSCF/CASPT2 Study on the Working Mechanism of Stilbene Light-Driven Molecular Rotary Motor: Sloped Minimal Energy Path and Unidirectional Nonadiabatic Decay"
to be submitted.

(2) Fengyi LIU, Keiji MOROKUMA,
"Photochemistry and Photophysics behind Light-Driven Molecular Rotary Motor: What We Learnt from Stiff Stilbene Rotary Motor"
manuscript in preparation.

(3) Fengyi LIU, Keiji MOROKUMA,
"Ring-Opening and Ring-Closure Mechanism of the Spiropyran-Merocyanine Photochromic Reaction: A CASSCF/CASPT2 Study"
manuscript in preparation.

3. Presentation at academic conferences

(1) Fengyi LIU, Keiji MOROKUMA, Poster on:
"A Theoretical Study on the Photoisomerization of Stiff Stilbene: A Model of Light-Driven Rotary Molecular Motor"
Annual Meeting of Japan Society for Molecular Science (2010), Osaka, Sept 14-17, 2010.

(2) Fengyi LIU, Keiji MOROKUMA, Poster on:
"Mechanism of Spiropyran-Merocyanine Photochromic Reaction: A CASPT2//CASSCF Study"
第 8 回 京都大学福井謙一記念研究センターシンポジウム, Kyoto, Dec 3, 2010.

Parameswaran PATTIYIL

JST Fellow, Fukui kenichi Memorial Research Group 1
(To 15 Jun. 2010)

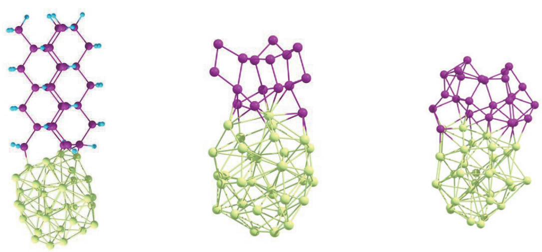
1. Summary of the research of the year

Growth Mechanism for Aluminum-Catalyzed Silicon Nanowires : Density Functional Tight Binding Molecular Dynamics Simulations

Silicon nanowires are identified as one of the important components for future micro electronic revolution. Several metal-catalyzed silicon nanowires have been reported in the literature. The metal catalyst is believed to play an essential role in the nucleation and growth of silicon nanowires. The control over the growth of nanowires is nevertheless essential for various technological applications. Recent report of Al-catalyzed Si-nanowire growth demonstrated that the tip is mainly consists of Al atoms whereas nanowire part is mainly consisting of Si atoms. It is to be noted that these Al-catalyzed Si-nanowires are grown in the lower temperature range of 430°C to 490°C.

It is well known that Si-Si π-bond (≈ 25kcal/mol) is rather weak as compared to C-C. π-bond (≈ 60kcal/mol). This in turn destabilizes planar coordination in silicon and hence planar, tabular and fullerene type nano scale structures are less stable as compared to carbon. Thus nanoclusters and nanowires are suitable candidates for nanoscale properties for silicon. In this study, we are investigating the nucleation and growth of the silicon nanowire using aluminum catalyst at different temperatures by self-consistent-charge density functional tight binding molecular dynamics simulations (SCC-DFTB).

Three model systems have been used to understand the mechanism of growth of Si-nanowire (Figure 1). Al_{34} cluster was used as a cap to Si-nanowires. All the dangling valencies of Si atoms are satisfied by hydrogen atoms in model-I (Al_{34}-$Si_{28}H_{33}$), where as model-II (Al_{34}-Si_{16}) and model-III (Al_{34}-Si_{42}) do not have any hydrogen atoms. The nuclear temperature of the system was controlled by the Nose Hoover chain thermostat and electronic temperature is set to 1500K. Periodic boundary conditions were imposed with a cubic box of side 100Å. The simulation involving model-I was carried out two different temperature 500K and 750K to study the effect of temperature.



I II III

Figure 1: SCC-DFTB optimized geometries of model Al-capped Si-nanowires. Green, pink and blue spheres represent Al, Si and H-atoms respectively.

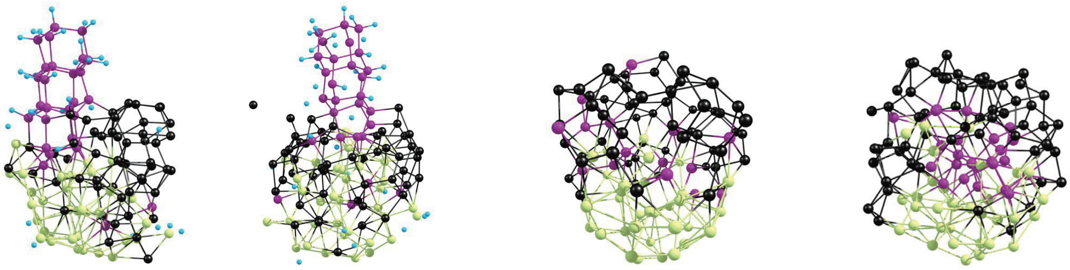


Figure 2: Snapshots after supplying 50 Si atoms on model-I at temperature (a) 500K and (b) 750K and snapshots after supplying 60 Si atoms on (c) model-II and (d) model-III at 500K. Green, pink and blue spheres represent Al, Si and H-atoms respectively and black spheres represent newly added Si-atoms.

Si atoms were supplied at the interval of 0.5ps at the interface of Al-Si cluster in model-I. Our simulations at 500K and 750K showed the formation of several 3-7 membered rings which finally leads to Si-nanoclusters (Figures 2a and 2b). Some of the hydrogen atoms attached to Si-atoms has migrated to Al-cluster and form Al-H bonds. The number of Si-rings increases with time and the number of six membered rings is always greater than other rings (Figures 3a and 3b). A few of the added Si-atoms have diffused into Al-cluster. The simulation at two different temperatures shows that mixing between Al and Si as a result of diffusion of added Si-atoms is higher at 750K as compared to 500K. It is to be noted that Si-Si bond strength is only a little higher than Al-Si bond strength. The Si-Si bond strength in Si_2H_6 is 96.0kcal/mol while Al-Si bond strength in H_3SiAlH_2 is 85.6kcal/mol. It can be concluded from this simulation that lower temperature shows more cluster formation, however even after supplying 50 Si atoms no significant uni-directional growth has been observed. On the other hand a Si-nanocluster growth has been observed (Figure 2a). This might be due to the hydrogen atoms on Si-nanowire which prevent uni-directional growth. In order to understand this factor we supplied silicon atoms at the centre of mass of Si-atoms in models-II and III.

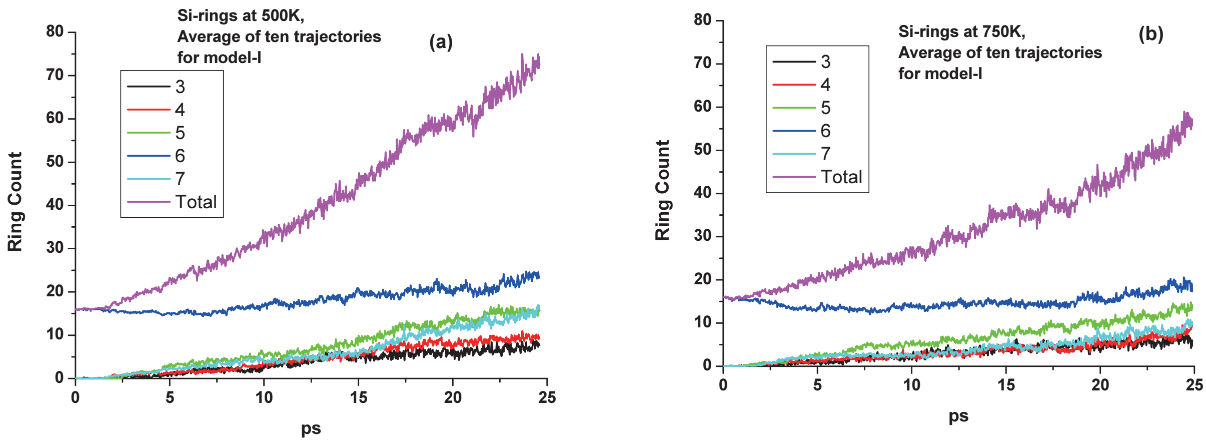


Figure 3: The plots of average ring count for ten trajectories versus time in ps at (a) 500K and (b) 750K for model-I.

Addition of Si-atoms on model-II and model-III results in mixed Al-Si nanocluster formation with lower part mainly consists of Al-atoms where as upper part is mainly Si-atoms (Figures 2c and 2d). Here also a few of the added Si-atoms have diffused into Al-cluster. The number of Si-ring increases with time; however the formations of 3-membered rings are lesser as compared to other rings (Figures 4a and 4b). The number of ring formation is more for the model-II than the model-III.

A general conclusion observed from these simulations is that a few of the supplied Si-atoms are diffused into Al-cluster, while other Si-atoms form nanocluster on the surface of Al-cluster.

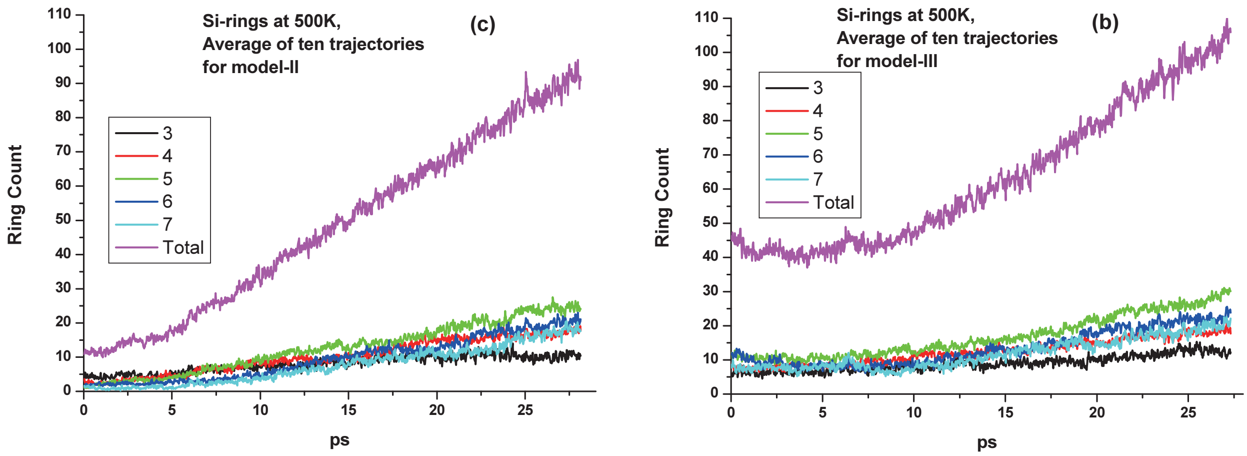


Figure 4: The plots of average ring count for ten trajectories versus time in ps at 500K for (a) model-II and (b) model-III.

2. Original papers

(1) Back, O.; Donnadieu, B.; Parameswaran, P.; Frenking, G.; Bertrand. G. "Isolation of Crystalline Carbene-Stabilized P_2-Radical Cations and P_2-Dications"
Nature Chemistry, 2, 369-373 (2010).

(2) Parameswaran P.; Frenking, G.
"Chemical Bonding in Transition Metal Complexes with Beryllium Ligands $[(PMe_3)_2M\text{-}BeCl_2]$, $[(PMe_3)_2M\text{-}BeClMe]$ and $[(PMe_3)_2M\text{-}BeMe_2]$ (M = Ni, Pd, Pt)"
J. Phys. Chem. A, 114, 8529-8535 (2010).

Hongyan XIAO

JST Fellow, Fukui kenichi Memorial Research Group 1

（From 1 Jul. 2010）

1. Summary of the research of the year

I. Theoretical Study of NO_3 Photodissociation

The nitrate radical (NO_3) is known to play an important role in the atmospheric chemistry, and has been extensively investigated both experimentally and theoretically. Photodissociation of NO_3 has two product channels in the visible region.

$$NO_3 + h\nu \rightarrow NO + O_2 \quad (1)$$

$$\rightarrow NO_2 + O \quad (2)$$

The thresholds for both channels are very close in energy. In a narrow wavelength range of 585–595 nm channel (1) occurs, while in the higher energy channel (2) dominates. Recently, the product energy distribution of channel (1) at 588 nm photolysis was measured by North and coworkers. They showed a clear evidence of existence of two dissociation pathways: (1A) a path generating vibrationally hot O_2 molecules and (1B) a path giving vibrationally cold O_2 molecules. They postulated that the former path involves dynamics of a roaming oxygen-atom. There is no clear interpretation of the latter path.

Based on PES characterization and *ab initio* dynamics, we propose that both (1A) and (1B) involve roaming dynamics of an oxygen atom on the first excited doublet state PES, and that the branching between the two paths occurs during the roaming dynamics in the partially dissociated (NO_2…O) region through a conical intersection (CI).

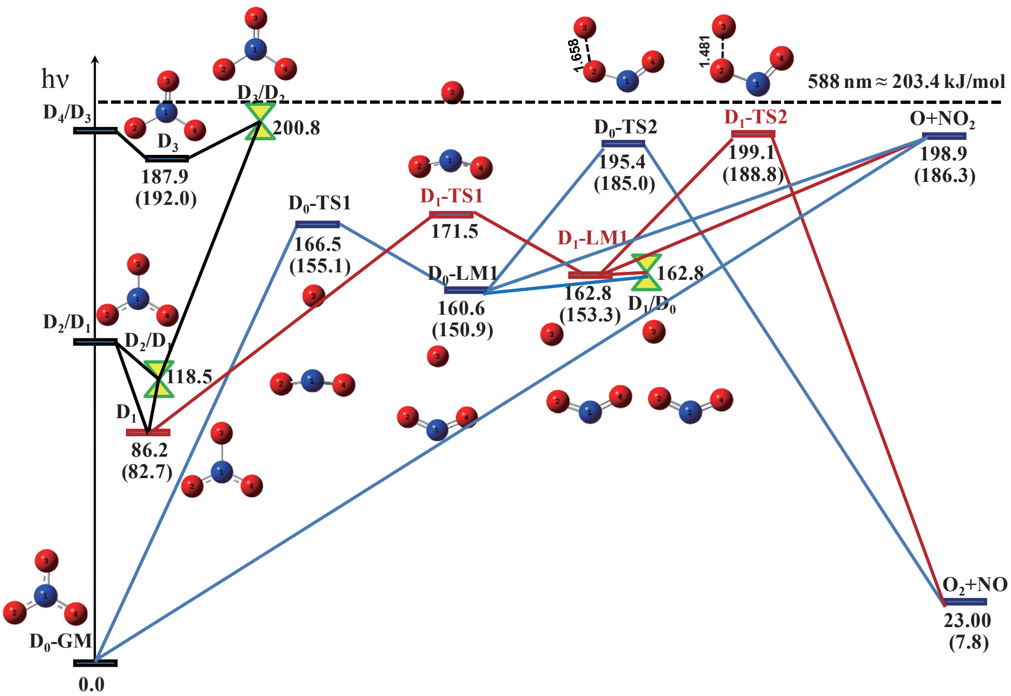


Figure 1 The photodissociation processes of NO_3 by MS-CAS(11,8)PT2/6-31+G*

As shown in Figure 1, upon excitation of NO_3 at 588 nm, it reaches D_4/D_3 crossing point at the Franck Condon region, then a series of radiationless decay follows $D_4/D_3 \rightarrow D_3 \rightarrow D_3/D_2 \rightarrow D_2/D_1 \rightarrow D_1$, and at final the roaming pathways of decomposition of NO_3 to NO + O_2 occur on the D_1 and D_0 surfaces. *Ab initio* classical trajectory calculation further differentiates product O_2 vibrational states in the different dissociation pathways, see Figure 2. The O—O vibration range in the D_0 curve is larger than that in the D_1 curve. That is to say, elimination of O_2 on the D_0 surface gave a vibrationally hot O_2 product, while elimination of O_2 on the D_1 surface gave a cold one.

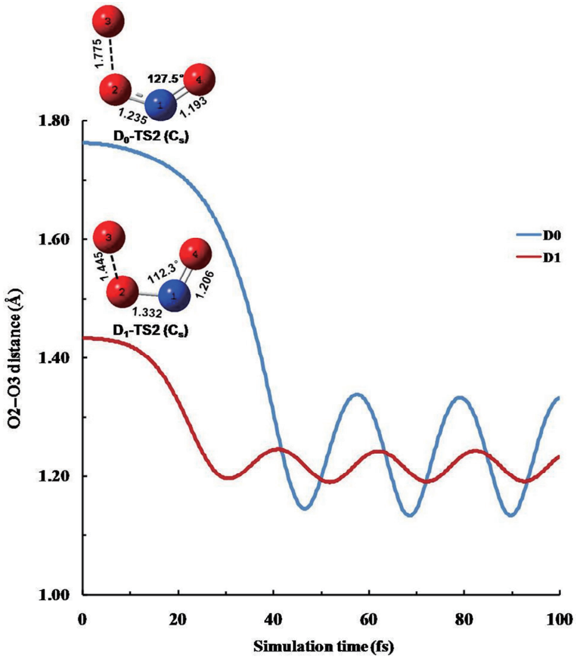


Figure 2. The classical trajectory of O_2 elimination at the (TD)UB3LYP/6-31+G* level

In conclusion, both of the two O_2 elimination pathways observed in a recent experiment originate from the excited state roaming dynamics. The branching into two products occurs during the D_1 roaming dynamics through a D_1/D_0 conical intersection; the indirect dissociation after the nonadiabatic transition to D_0 produces the major vibrationally hot O_2 product, while the direct dissociation on the D_1 PES gives the minor vibrationally cold O_2 product.

II. Theoretical Study of HNO_3 Photodissociation

Nitric acid (HNO_3) molecule plays an important role in the atmospheric chemistry. Depending on the irradiation wavelength, the photodissociation of HNO_3 has rich photochemical decay channels.

$$\begin{aligned}
\mathrm{HNO_3} + h\nu &\rightarrow \mathrm{OH}(X\,^2\Pi) + \mathrm{NO_2}(X\,^2\mathrm{A}_1) \quad \Delta H^0 = 200\ \mathrm{kJ/mol} \quad (1)\\
&\rightarrow \mathrm{OH}(X\,^2\Pi) + \mathrm{NO_2}(A\,^2\mathrm{B}_2) \quad \Delta H^0 = 315\ \mathrm{kJ/mol} \quad (2)\\
&\rightarrow \mathrm{O}(^1\mathrm{D}) + \mathrm{HONO}(X\,^1\mathrm{A}') \quad \Delta H^0 = 490\ \mathrm{kJ/mol} \quad (3)\\
&\rightarrow \mathrm{O}(^3\mathrm{P}) + \mathrm{HONO}(a\,^3\mathrm{A}'') \quad \Delta H^0 = 550\ \mathrm{kJ/mol} \quad (4)\\
&\rightarrow \mathrm{O}(^3\mathrm{P}) + \mathrm{HONO}(X\,^1\mathrm{A}') \quad \Delta H^0 = 300\ \mathrm{kJ/mol} \quad (5)
\end{aligned}$$

Experimental observed results are that pathway (1) is dominant at 308 nm (388.4 kJ/mol), pathway (2) is dominant at 248 nm (482.3 kJ/mol), and pathway (3) is open at 222 nm (538.8 kJ/mol) and is primary at 193 nm (619.8 kJ/mol). Till now, there is no clear theoretical explanation on HNO_3 photodissociation.

Therefore, we undertook a systematic study on the dissociation pathways of HNO_3 involving S_3, S_2, S_1 and S_0 states. Some new structures and pathways were reported and the dissociation thresholds were explained.

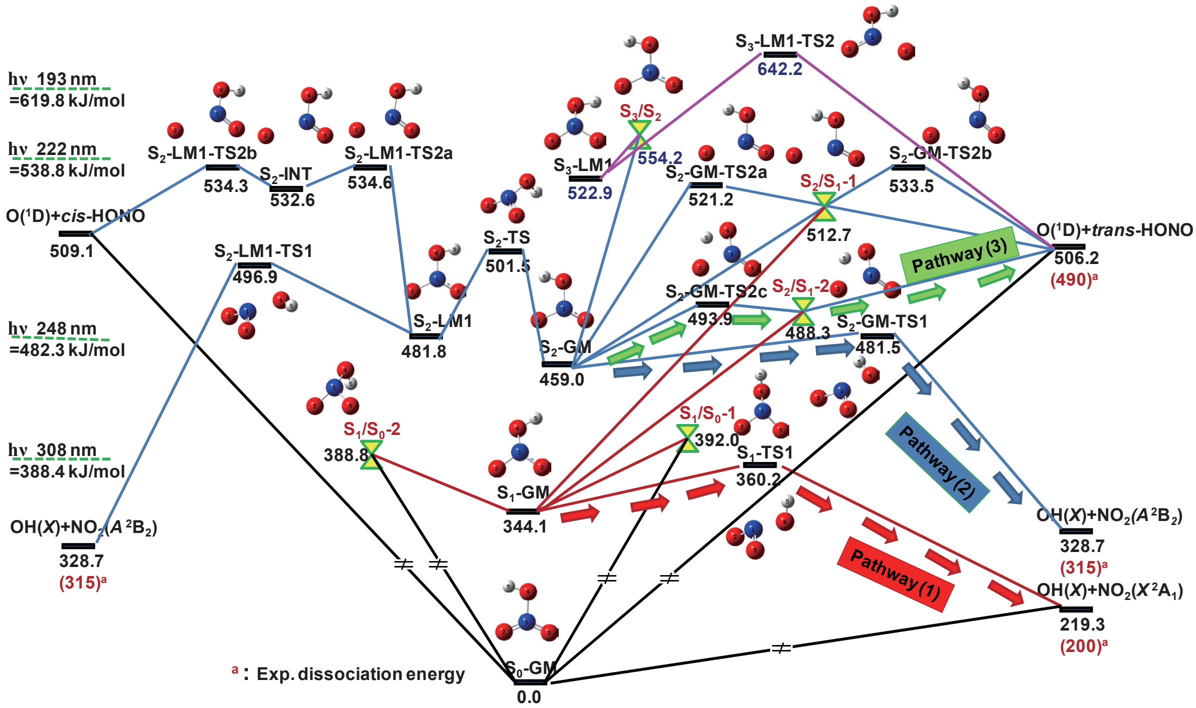


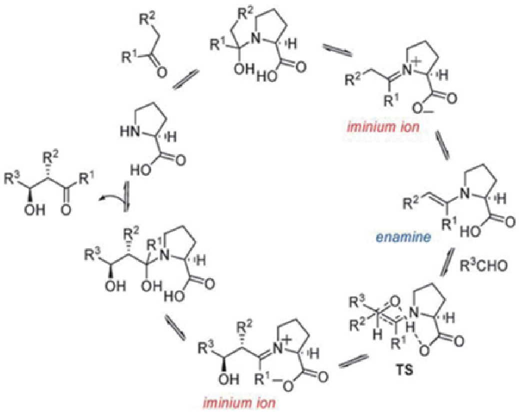
Figure 3. The potential energy (kJ/mol) profiles of photodissociation of HNO_3 by 3S-CASPT2(12,8)/6-31+G* (except for those involving S_3 by 4S-CASPT2(12,8)/6-31+G*)

The $S_0 \rightarrow S_1(n\pi^*)$, $S_0 \rightarrow S_2(n\pi^*)$ and $S_0 \rightarrow S_3(\pi\pi^*)$ translations strongly localized on the NO_2 group of HNO_3. As shown in Figure 3, at the short wavelength (193 nm), S_3 has a strong absorption (oscillator strength: 0.193). Pathway (3) is impossible on the S_3 state due to a very high barrier. S_3 may decay to S_2 via S_3/S_2 conical intersection, and then pathway (3) occurring on the S_2 state becomes the primary pathway with an increase of photon energy. At longer wavelengths, S_2 and S_1 have weak absorption (oscillator strengths: $1.03 \times 10^{-4}$and 1.72×10^{-6}). Pathway (1) takes place on the S_1 state and pathway (2) occurs on the S_2 state.

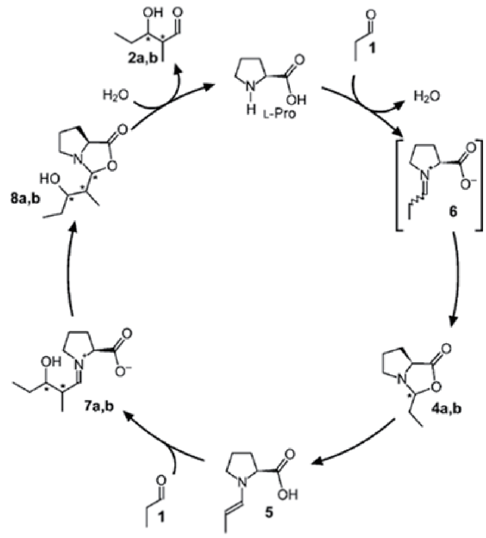
III. Proline-catalyzed Direct Asymmetric Aldol Reactions

Small organic molecules recently emerged as a third class of broadly useful asymmetric catalysts that direct reactions to yield predominantly one chiral product, complementing enzymes and metal complexes. The amino acid proline and its derivatives are useful for the catalytic activation of carbonyl compounds and forming carbon-carbon bond in Aldol and Mannich reactions. Scheme 1 shows the generally accepted mechanism of the proline-catalyzed asymmetric aldol reaction (single proline enamine mechanism). Recently, some studies reported a new role of the oxazolidinones in the proline-catalyzed asymmetric aldol reaction. In order to have an insight into the whole processes of the proline-catalyzed asymmetric aldol reaction, first we used the AFIR method to follow the previously proposed mechanism. Our calculated results indicate that the previously proposed mechanism does not explain the experimental results well and has some problems such that (i) how to form enamine intermediate from oxazolidinone; (ii) terminate reactions at the intermediate with lower energy other than the products; (iii) the function (M06) or SCRF model (PCM and CPCM) are suitable for the aldol reaction or not. From the present results we think that the proline-catalyzed asymmetric aldol reaction has another new lower energy reaction pathway and we will further explore the reaction mechanism.

Scheme 1



List B., *Chem.Comm.*, *2006*, *819-824*.



Gschwind R. M., et al. *Angew. Chem. Int. Ed.*, *2010*, *49*, *4997-5003*.

2. Original papers

(1) Hongyan Xiao, Satoshi Maeda and Keiji Morokuma
"Excited-state roaming dynamics in photolysis of a nitrate radical"
J. Phys. Chem. Lett. 2, 934-938 (2011).

3. Presentation at academic conferences

4. Others

(1) Hongyan Xiao, Satoshi Maeda and Keiji Morokuma (Poster)
"A theoretical study on the photodissociation of NO_3"
The 8th FIFC symposium, Kyoto, December 3, 2010.

Lina DING

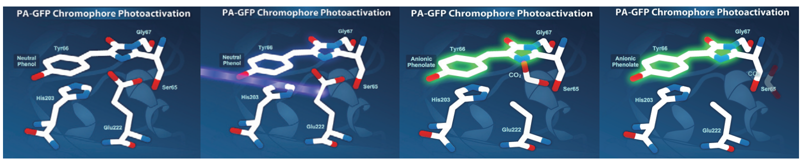
JST Fellow, Fukui kenichi Memorial Research Group 1

(Form 1 Jul. 2010)

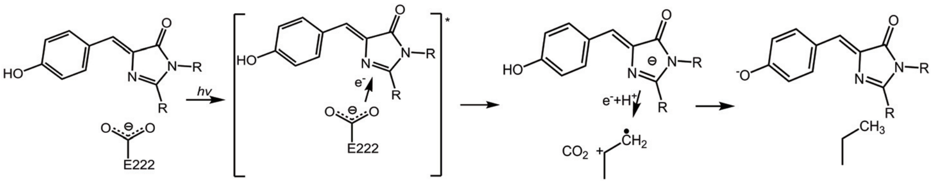
1. Summary of the research of the year

Mechanistic study on photo-induced decarboxylation of the Photoactivable Green Fluorescent Protein: A theoretical ONIOM(QM:MM) calculation

The Photo-induced decarboxylation of the green fluorescent protein (GFP) and its variants have received wide attention since GFP has revolutionized GFP-technology to visualize the molecular events that occur within living cells, which marks the improvement in biological imaging and analysis, as recently honored by Nobel Prize in chemistry to three pioneers in the field. The reported quantum yield 0.03~0.002 for this irreversible photo-decarboxylation is much lower than that 0.8 for reversible process in WT-GFP which indicates that both irreversible and reversible process are involved in GFP photo-transformation with different kinetics and quantum yields. Recently, X-ray crystal structures of native and photoactivated states of PA-GFP were also reported. Rate measurements for photoactivation in WT and PA-GFP reveal similar kinetics in both proteins.



http://zeiss-campus.magnet.fsu.edu/tutorials/fluorescentproteins/pagfpchroma/index.html



Scheme 1 Proposed Klobe-mechanism

However, the photo-decarboxylation mechanism is still mystery and the detailed study at the atomic level remains unresolved up to now despite Kolbe mechanism is well-accepted (**Scheme 1**).

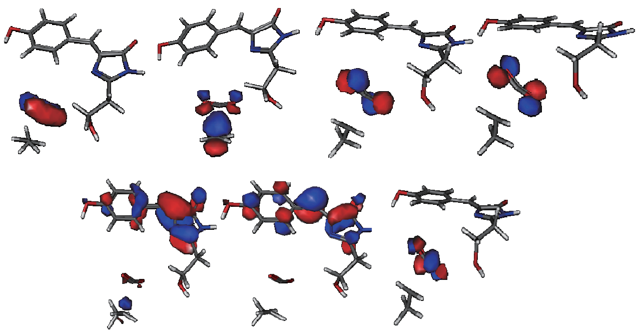


Fig. 1 Seven active orbitals

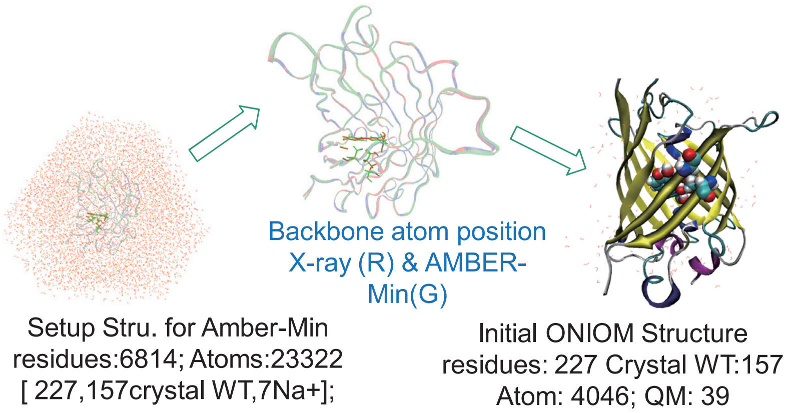
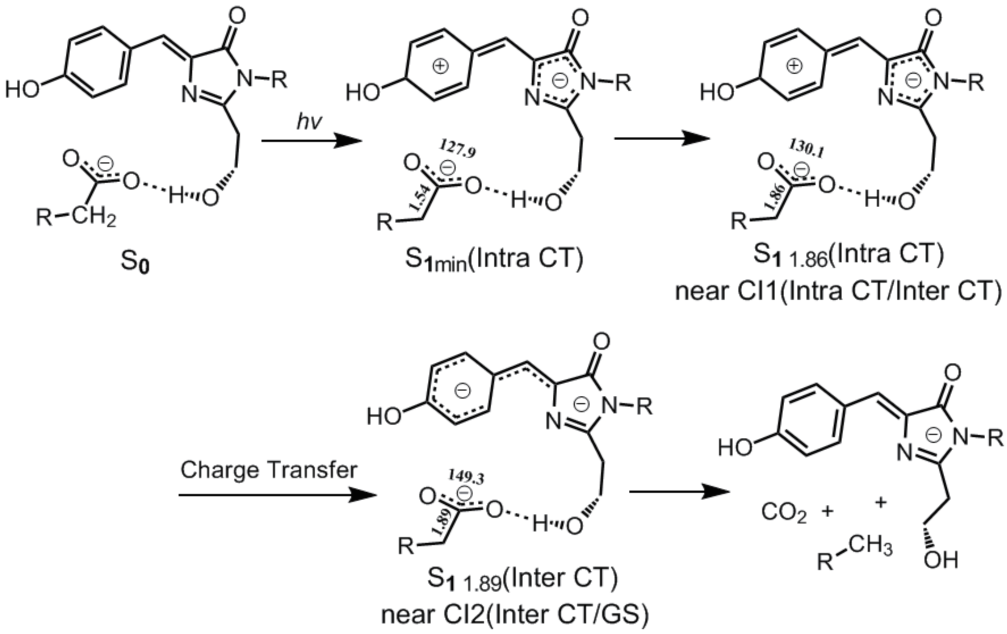


Fig. 2 Structures in MD and ONIOM setup(PDB:3GJ1(1.80 Å))

In this work, we report the first theoretical mechanistic study on the photo-induced decarboxylation of GFP by using ONIOM(SA6-CASSCF(10e,7o)/6-31G*:Amber)-MEUC and ONIOM(SS-CASPT2(10e,7o)/6-31G*:Amber)//ONIOM(SA6-CASSCF(10e,7o)/6-31G* :Amber)-MEUC methods. The active space includes two n, one p, π and π^* orbitals (8e/5o) of COO^- in Glu219, one pair π and π^* orbitals (2e/2o) of chromophore (**Fig**. 1). All the structures involved in molecular dynamics and initial ONIOM setup are given in **Fig**. 2. All calculations were performed by Molcas74 and Gaussian09. It was found that the decarboxylation process is initiated on an intra-molecular charge transfer excited state (Intra CT) PES, which then triggers an ultrafast decarboxylation process via an avoided conical intersection (CI) of an intra-molecular charge transfer excited state (Intra CT) and an inter-molecular charge transfer excited state(Inter CT). The inter CT excited state plays a key important role in the photo-induced irreversible process, and finally decays to the ground state via the second avoided conical intersection (CI) of Inter CT excited state and ground state. The initial process on the Intra CT PES is rate-determined step while on the Inter CT PES is ultrafast.



2. 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

Hai-Bei LI

JST Fellow, Fukui kenichi Memorial Research Group 1
（From 27 Jul. 2010）

1. Summary of the research of the year

(A) Fullerene formation from hydrocarbon combustions: Quantum chemical molecular dynamics study

The formation of polycyclic aromatic hydrocarbon (PAH) and fullerenes have been investigated in great detail. Combustion of hydrocarbon fuels in lean oxygen flame offers advantages for large-scale fullerene production. Saha *et al.* performed high temperature simulations of benzene combustion by gradually reducing hydrogen atoms randomly using density-functional tight-binding (DFTB)-based quantum chemical molecular dynamics (QM/MD). In this work, we simulate fullerene formation from naphthalene combustion at 1500 K and 2500 K. All QM/MD simulations were performed by employing a Nose Hoover chain thermostat, and carbon densities of 0.119 and 0.026 g/cm^3, respectively. A Monte Carlo-based hydrogen removal strategy was devised where we calculate the probability factor for each candidate structure after removing two hydrogen atoms in randomly selected positions, and select the candidate hydrogen pair randomly under consideration of Boltzmann weights for the environmental temperature. One hydrogen pair is removed every 0.235 ps and 0.470 ps at 1500 K and 2500 K, respectively, until all hydrogen is removed from the system. One selected trajectory is shown in the Figure 1. Although the mechanism of fullerene formation is similar to previous results, in our simulation, lower carbon density and lower temperature favor the formation of smaller size fullerenes (Figure 2). Our new hydrogen removal scheme tends to produce more cage structures than the random removal scheme in Saha’s work.

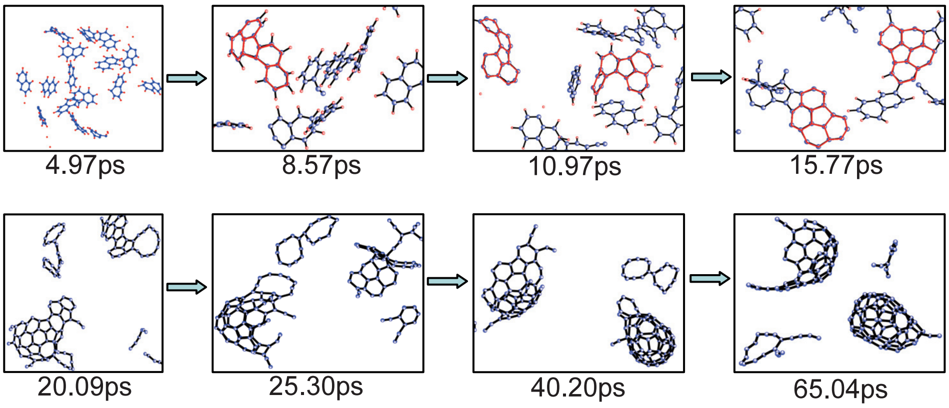


Figure 1. Snapshots from one trajectory showing the key events during the hydrogen removal and self-assembly processes.

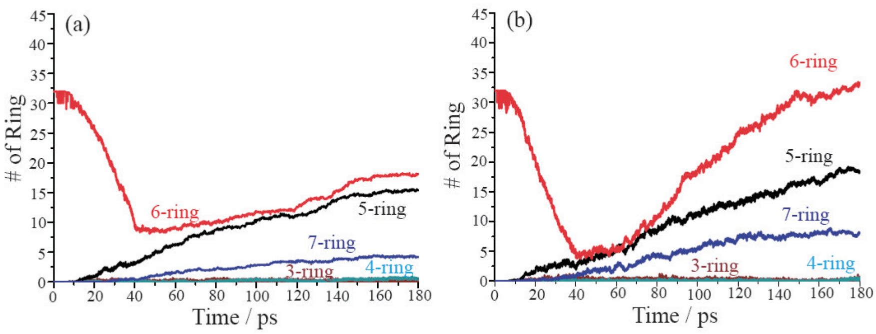


Figure 2. Formation statistics of average rings counting at different temperature as a function of simulation time. (a) Tn=1500K, (b) Tn=2500K.

(B) AC SWCNT growth from bottom-up organic synthesis

Cycloparaphenylenes(CPPs) as the shortest units of armchair SWCNTs have been used as the promising precursors to produce the controllable SWCNT in diameter and orientation. (6,6) SWCNT growth has been modeled using quantum chemical molecular dynamics (QM/MD) in conjunction with feeding of C_2H radicals to [6]CPP seed at low temperature 500K. About 7.5-Å-long (6,6) SWCNT with almost 5 belts is produced within 500 ps. The present QM/MD simulations have shown that C_2H radicals can facilitate the H abstraction, and act as sidewall growth agent, that is, the successful growth of (6,6) SWCNT is proposed by H-abstraction and C_2H insertion mechanism, as shown in Figure 3. From our QM/MD simulation, it has been demonstrated that uniform armchair SWCNTs in fixed diameter could grow in a controlled way by adding C_2H radical species. Figure 4 shows the six-membered ring counting statistics as a function of simulation times. In comparison to previously proposed SWCNT growth mechanisms based on repeated DA cycloadditions, such a radical addition based mechanism exhibits extremely competitive energetics. The addition of C_2H_2 to the growing SWCNT fragment, following hydrogen abstraction by C_2H, is also a much more energetically favorable process compared to DA cycloaddition. However, in both cases, the rate of reaction is determined by the presence of terminating hydrogen atoms at the 'bay' area of the nanotube sidewall.

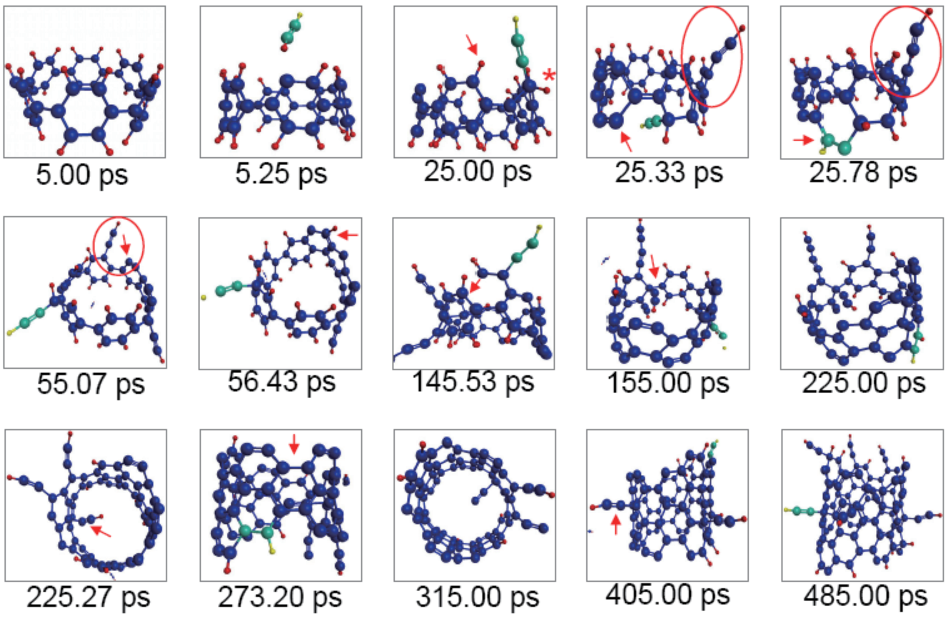


Figure 3. The snapshots of SCC-DFTB/MD simulations of (6,6)-SWCNT growth.

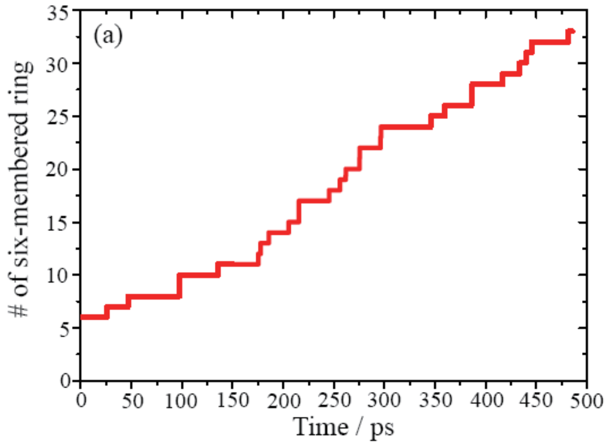


Figure 4. Six-membered ring counting statistics as a function of simulation times.

2. Original papers

(1) H. B. Li, S. Irle, A. M. Mebel and K. Morokuma, “Fullerene Formation from Hydrocarbon Combustions: Quantum Chemical Molecular Dynamics Study” Manuscript in preparation.

(2) H. B. Li, A. J. Page, S. Irle and K. Morokuma, “(6,6) SWCNT Growth from a [6]Cycloparaphenylene Seed Molecule: Nonequilibrium Quantum Chemical Molecular Dynamics Simulations”, Submitted.

(3) H. B. Li, S. Irle and K. Morokuma, “The Roles of Hydrogen in the Fullerene Formation” Manuscript in preparation.

3. Presentations at Academic Conferences

H. Li, S. Irle and K. Morokuma, “Fullerene Formation from Hydrocarbon Combustions: Quantum Chemical MD Study”, *7th Congress of the International Society for Theoretical Chemical Physics*, Abstract page 4PP-78, Tokyo, Japan (Septemper 2~8, 2011)

Lung Wa CHUNG

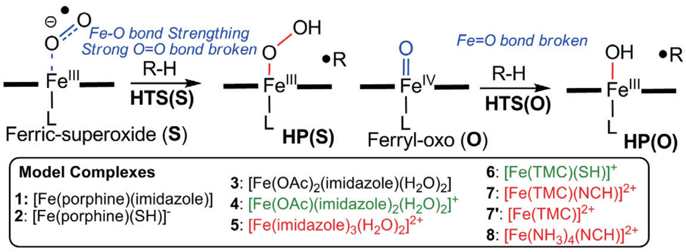
JST Fellow, Fukui kenichi Memorial Research Group 1

1. Summary of the research of the year

Comparative Reactivity of Ferric-Superoxo and Ferryl-Oxo Species in Heme and non-Heme Complexes

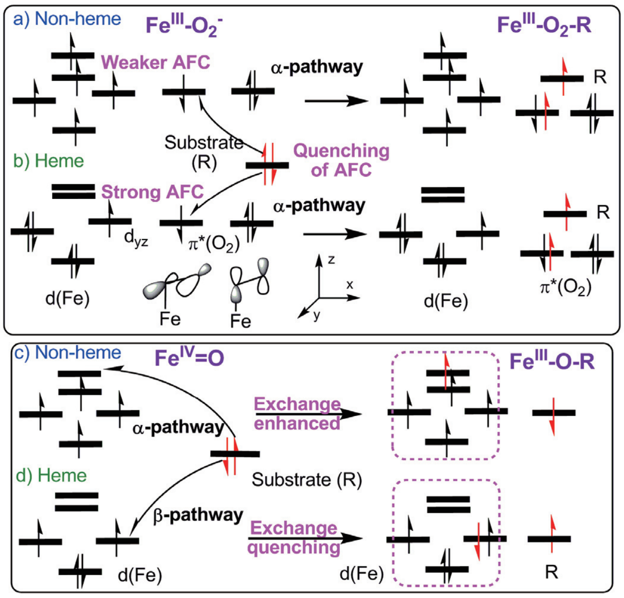
Heme- and non-heme-containing oxygenases and oxidases play vital roles in many selective and efficient biochemical oxidation. Several species including ferryl-oxo, ferric-hydroperoxo and ferric-peroxy were proposed or found to act as oxidants in these enzymes. In addition to the well-known high-valent ferryl-oxo species, not-well-characterized lower-valent ferric-superoxo species have recently been suggested or observed to be an alternative electrophilic oxidant, e.g. in isopenicillin N synthase (IPNS), hydroxyethylphosphonate dioxygenase (HEPD), and tryptophan 2, 3-dioxygenase (TDO). Furthermore, some recent synthetic ferric-superoxo and other metal superoxo complexes were reported to be capable of catalyzing oxidation, including C-H bond activation. Notably, many non-heme enzymes can use ferric-superoxo species as an oxidant, but only few heme enzymes (TDO, IDO and NOD so far) use ferric-superoxo species! In this study, we theoretically and systematically compare reactivity of several key ferric-superoxo and ferryl-oxo model complexes (Scheme 1).

Scheme 1



Our calculations show that different ferric-superoxo species can adopt different O_2 coordination and/or spin state. For instance, ground-state heme ferric-superoxo complexes ^{1}**1S** and ^{1}**2S** favor low-spin and end-on O_2 coordination, whereas ground-state non-heme or synthetic model complexes ^{7}**3S**, ^{7}**4S**, ^{7}**5S** and ^{7}**8S** prefer high-spin and side-on mode. However, ^{5}**7S** is computed to be similar in energy to less-bulky 5-coordinate complex ^{7}**7′S** in the gas phase and even ^{7}**7′S** becomes the most stable form in solution ($\Delta\Delta E$ = 3.0 (gas) and -16.5~-18.0 (acetonitrile, ACN) kcal/mol). Driven further by entropy, the 5-coordinate complex ^{7}**7′S** should be the resting state of the recent not-yet-characterized synthetic model, whereas the corresponding ferryl-oxo complex was observed to be 6-coordinate. The ferric-superoxo can be stabilized by an anti-ferromagnetic coupling (AFC) between the Fe d electrons and superoxo radical in the singlet heme and quintet non-heme complexes, or by a ferromagnetic coupling (FC) in the triplet heme and septet non-heme complexes (Scheme 2). Electronic structures for most of the end-on ferric-superoxo complexes are schematically illustrated in Scheme 2. Surprisingly, key electronic structures of complexes **6S-8S** are different, in which the out-of-plane $\pi^*(O_2)$ orbital becomes fully occupied and the in-plane $\pi^*(O_2)$ orbital is singly occupied. Additionally, compared to the low-spin heme ferric-superoxo complexes, a much smaller coupling was found in a non-heme end-on ferric-superoxo dioxygenase experimentally ($J \sim 6$ cm^{-1}) and in our model complexes. In comparison, geometry and electronic configuration of the ferryl-oxo complexes are much simpler and generally favor the triplet state.

Scheme 2.



Scheme 2 conceptually illustrates the oxidative processes of the ferric-superoxo and ferryl-oxo complexes. For the former ones, one electron is formally transferred from the substrate to the half-filled π*(O_2) orbital (reduction of the superoxo), but not to the metal, and thus, the strong π(O_2) bond is broken as well as the Fe-O bond is strengthened. Therefore, the coupling (AFC or FC) between the ferric metal and superoxo parts is quenched partly in transition states and completely in products. Since the electronic configuration of the metal does not change, the effect of exchange interactions of the metal on the reaction should be small. In contrast, for the ferryl-oxo oxidants, one electron is formally transferred from the substrate to the ferryl metal (reduction of the metal) to weaken the Fe=O bond via a ferric-oxo transition state. Hence, the reactivity of the ferryl-oxo complexes can be affected by the spin state to change the exchange interactions.

Our key results for the reactivity of the ferric-superoxo and ferryl-oxo oxidants towards a model substrate propene are summarized as follows. First, the neutral or anionic heme ferric-superoxo and ferryl-oxo oxidants (**1**-**2**) are usually less reactive than the non-heme oxidants (**3**-**8**): the reactivity qualitatively in-creases with increasing positive charge of the oxidants and stability of the products (i.e. thermodynamic driving force). Remarkably, a good linear correlation (Figure 1) between the computed barrier and reaction energy of hydrogen atom transfer (HAT) is found for various ferric-superoxo oxidants with different charges and spin states. A similar linear correlation is also observed for the ferryl-oxo oxidants. Second, the higher-valent ferryl-oxo oxidants generally have higher reactivity of HAT and radical addition (RA) than the corresponding ferric-superoxo oxidants. Third, the reaction barrier for an intramolecular HAT in ^{7}**7′S** is high (about 26-30 kcal/mol), and higher than the intermolecular HAT with propene (by 26.0 (gas) and 6.3 (ACN) kcal/mol). Hence, self-decay of ^{7}**7′S** is less feasible, due to larger strain in the transition state.

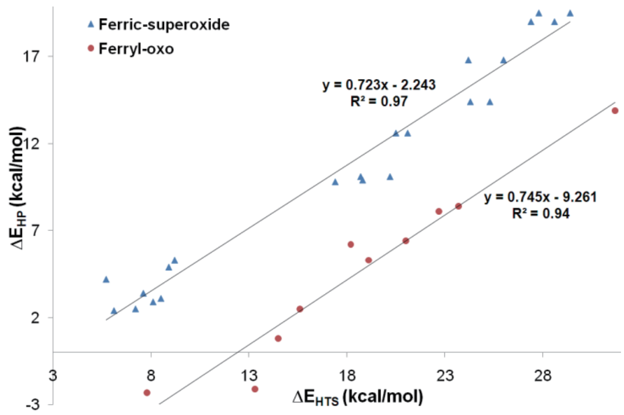


Figure 1. Correlations between the calculated barrier and reaction energy (relative to the most stable reactant) for HAT with the ferric-superoxo and ferryl-oxo species.

These oxidation reactions involve an electron transfer from the substrate to the iron oxidants. The more electrophilic complex with a lower-lying electron-accepting orbital (e.g. the half-filled π*(O2) orbital of the ferric-superoxo complexes) can enhance both the reactivity and thermodynamic driving force. As shown in Table 1, the cationic non-heme complexes have higher electron affinity, which can promote the reactivity, especially for the di-cationic complexes **7S**, ^{7}**7′S** and **7O**. Importantly, even for the neutral complexes **1S** and **3S**, the electron-accepting half-filled π*(O2) orbital for the reactions in ^{1,5}**3S** is lower-lying than ^{1}**1S**. Therefore, the lower reactivity and driving force of the neutral and anionic heme ferric-superoxo complexes is partly attributed to their lower electrophilicity. Moreover, as discussed previously, the more pronounced quenching of anti-ferromagnetic coupling in the low-spin heme ferric-superoxo complexes than the high-spin non-heme superoxo complexes should further decrease the reactivity and thermodynamic driving force of the heme ferric-superoxo complexes.

Table 1. Calculated adiabatic electron and proton affinity of the key FeIII-O2- and FeIV=O species (kcal/mol, with ZPE) in gas phase and acetonitrile solution and barrier for HAT.

	EA_{ad}	PA_{ad}
1S	24.5/75.5^{a,b}	-242.8/-14.2^{a,c}
4S	121.8/94.1^{a,b}	-140.2/2.4^{a,c}
7S	213.3/110.2^{a,b}	-67.8/0.0^{a,c}
7′S	218.8/106.3^{a,b}	-52.1/16.5^{a,c}
1O	19.6/63.3^{a,b}	-254.1/-22.8^{a,c}
4O^{c}	120.4/93.7^{a,b}	-144.2/-3.3^{a,c}
7O	206.5/103.1^{a,b}	-65.8/0.0^{a,c}

a. DFT(PCM)//DFT. b. no solvation energy of an electron c. the solvation free energy of a proton (-260.2) from ref. 10d.

Surprisingly, the lower-valent ferric-superoxo oxidants are calculated to have higher electron affinity than the high-valent ferryl-oxo species. However, besides electrophilicity of the oxidants, the high-valent ferryl-oxo species is found to have higher proton affinity (and basicity), which is another key factor for the higher reactivity than the ferric-superoxo species. In addition, as found by different groups, the additional gain of large exchange stabilization for the high-spin non-heme ferryl-oxo species further contributes to the higher reactivity and driving force (exchange-enhanced reactivity and thermodynamic driving force).

The importance of the driving force on the reactivity makes us further investigate effects of the ligand or metal on HAT. Bond dissociation energy of the new O-H bond (BDE_{O-H}) can offer “qualitative understanding” of HAT reactivity. Therefore, BDE_{O-H} of the key ferric-superoxo, ferryl-oxo (including high-spin ferryl-oxo in TauD and cationic ferryl-oxo in P450) and other common oxidants were evaluated and compared (Table 2) to understand different mechanistic strategies as well as to help rationally design reactive heme ferric-superoxo oxidants.

Table 2. Calculated bond dissociation energy (BDE_{O-H}, kcal/mol, with ZPE) of the O-H bond forming.

MO_2-H	BDE_{O-H}	MOH	BDE_{O-H}
1S	66.2/65.9[b]	**1O**	78.0
2S	63.9	**2O**	79.4
3S	68.7[c]	Compound I	86.8
4S	70.6[d]	**4O**	85.6[e]/77.3[f]
5S	71.2		
6S	70.3	**6O**	77.8[e]/72.1[f]
7S	75.4	**7O**	81.0[e]/76.5[f]
7′S	74.0		
8S	72.5	**8O**	93.4[e]/79.9[f]
1S(Ru)[a]	69.3[b]	tmcsFeO	76.9[e]
1S(Os)[a]	70.1[b]	TauD	87.8[e]/78.7[d]
1S(V)[a]	68.0		
1S(Cr)[a]	65.0	$[MnO_4]^-$	68.8
1S(Mn)[a]	65.6	RuO_4	70.7
1S(Co)[a]	60.8	OsO_4	53.9

a. Fe in **1S** is replaced by the other metal (in parenthesis). b. SDD basis sets and ECP used. c. 71.1 kcal/mol for ^{1}**3S**. d. 73.2 kcal/mol for ^{1}**4S**. e. sextet state. f. quartet state.

A trend of the computed BDE_{O-H} is consistent with the above-discussed reactivity and driving force. The less reactive heme oxidants are endowed with the smaller BDE_{O-H} than the non-heme oxidants (even for low-spin ^{1}**3S** and ^{1}**4S**). Also, the ferric-superoxo oxidants intrinsically give smaller BDE_{O-H} than the ferryl-oxo oxidants, presumably due to the strong π(O2) bond broken and AFC quenching in the former ones and the exchange stabilization gain for the latter ones. Comparatively, a very reactive cationic low-spin ferryl-oxo oxidant (Compound I) employed in P450 heme enzymes is driven by the very large BDE_{O-H} (86.8 kcal/mol) so that it can react with inert substrates. On the other hand, the extra exchange stabilization gained in the high-spin ferryl-oxo oxidants in TauD or synthetic model complexes increases the BDE_{O-H} (81.0-87.8 kcal/mol) and, thus, increases the reactivity. The highest-valent metal-oxo oxidants $[MnO_4]^-$ and MO_4 (M = Ru or Os) give rather small BDE_{O-H} (53.9-70.7 kcal/mol), explaining why stepwise HAT is less favorable than the concerted [3+2] pathway. As to the heme ferric-superoxo, replacing Fe in **1S** by other first-row transition metals gives only smaller or similar $BDE_{O\text{-}H}$, while using Ru or Os affords a slightly higher $BDE_{O\text{-}H}$. Based on these results, we finally used a mono-anionic 21-oxaporphyrin ligand to generate a cationic heme-like ferric-superoxo complex $\mathbf{1S_{oxa}}$. We are pleased to find that $\mathbf{1S_{oxa}}$ gives a lower HAT barrier with propene (19.3 vs. 24.2 kcal/mol for **1S**), as well as higher $BDE_{O\text{-}H}$.

In summary, the reactivity of several key ferric-superoxo and ferryl-oxo model complexes are found to correlate well with the driving force and can be enhanced by using more electrophilic complexes. Moreover, the ferryl-oxo complexes with the higher driving force are usually more reactive than the ferric-superoxo ones. Compared to the non-heme ferric-superoxo oxidants, the lower electrophilicity and more pronounced quenching of anti-ferromagnetic coupling in the heme ferric-superoxo complexes lower the reactivity. In addition, the non-heme Fe center is often coordinately-unsaturated and flexible: the substrate can be directly activated through ligation for intramolecular reactions (and even forms a strong C=S or C=O bond after HAT). These may be the reasons why nature prefers to use the transient non-heme ferric-superoxo species for oxidation, to a larger extent than the heme superoxo species. The latter may be tailored to function mainly as oxygen storage or carrier, and be activated by electron and/or proton transfer to generate more powerful oxidants. Having various oxidants with different reactivity in nature, the milder ferric-superoxo oxidants should render the oxidation more selective with the reactive substrates and atomically-economic. The reactivity and driving force of the ferric-superoxo species could be further enhanced in enzymes by stronger electrostatic interactions with the reacting (more charged and polar) O-H moieties. Our comparative results may help design more reactive ferric-superoxo oxidants or artificial heme enzymes.

2. Original papers

(1) 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.

(2) Li, X.; Chung, L. W.; Mizuno, H.; Miyawaki, A.; Morokuma, K. "Primary Events of Photodynamic in Reversibly Photoswitching Fluorescent Protein Dronpa" *J. Phys. Chem. Lett.* **2010**, *1*, 3328.

(3) Li, X.; Chung, L. W.; Mizuno, H.; Miyawaki, A.; Morokuma, K. "Competitive Mechanistic Pathways for Green-to-Red Photoconversion in the Fluorescent Protein Kaede: A Computational Study" *J. Phys. Chem. B* **2010**, *114*, 16666.

(4) 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.* **2011**, doi: 10.1002/wcms.85.

(5) Abdel-Azeim, S.; Li, X.; Chung, L. W.; Morokuma, K. "Zinc-Homocysteine Displacement in Cobalamin-Dependent Methionine Synthase and its Role in Substrate Activation: DFT and ONIOM Study", *J. Comput. Chem.* **2011**, *32*, 3154.

(6) 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.

(7) 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**, (doi:10.1021/ja2084898).

3. Presentation at academic conferences

(1) Lung Wa Chung, Xin Li, Hiroshi Sugimoto, Yoshitsugu Shiro, Keiji Morokuma “*ONIOM Study on a Missing Piece in Our Understanding of Heme Chemistry: Bacterial Tryptophan 2,3-Dioxygenase with Dual Oxidants*”, (oral) ACS 240th National Meeting, Boston, Massachusetts, August 22, 2010.

(2) Xin Li, Lung Wa Chung, Hideaki Mizuno, Atsushi Miyawaki, Keiji Morokuma “*Reaction Mechanisms of Novel Fluorescent Proteins*”, (oral) the seventh Congress of the International Society for Theoretical Chemical Physics, Tokyo, September 4, 2011.

(3) Xin Li, Lung Wa Chung, Hideaki Mizuno, Atsushi Miyawaki, Keiji Morokuma “*Reaction Mechanisms of Photophysics and Photochemistry of New Fluorescent Proteins*”, 5th Asia and Oceania Conference for Photobiology, Nara, July, 31, 2011.

Galina PETROVA

JST Fellow, Fukui kenichi Memorial Research Group 1
（From 1 Dec. 2010）

1. Summary of the research of the year

Towards understanding the HppE catalytic mechanism

The hydroxypropylphosphonic acid epoxidase (HppE) is a non-heme redox-active iron containing enzyme involved into the biosynthesis of (1*R*,2*S*)-epoxypropylphosphonic acid also referred to as fosfomycin – a clinically applied antibiotic inhibiting the first committed step of bacterial cell wall biosynthesis. By this reason the enzyme has been an object of many experimental studies aiming at defining its properties and understanding the detailed mechanism of its catalytic action. Though most of the natural epoxides are biosynthesized from alkanes via oxygen insertion by α-ketoglutarate dependant non-heme monooxygenases or by the heme cytochrome P450 enzymes, HppE does not require the presence of α-ketoglutarate to function as the substrate itself (2-hydroxypropylphosphonic acid) activates the metal center for O_2-binding. On the other hand, the enzyme is not selective with respect to the enantiomeric form of the substrate but does convert stereospecifically each enantiomer into a specific product; thus, only fosfomycin is obtained from 2*S*-form of the substrate while the reaction with (*R*)-2-hydroxypropylphosphomic acid results in ketone product (Fig. 1a).

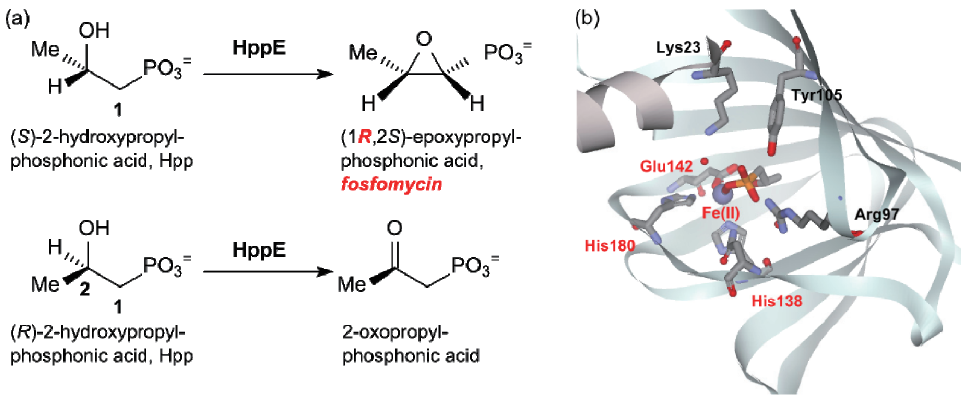


Figure 1. (a) Reaction products depending on the enantiomeric form of the substrate. (b) Structure of the active center of HppE as the isolated model includes Glu142, His180 and His138 residues.

The current project is focused on the theoretical modeling of the different reaction mechanisms in order to understand and explain the catalytic role of HppE in the formation of fosfomycin as well as the differences observed in the enzyme behavior towards different substrates. The first stage of the study is based on isolated gas-phase model of the active center including the iron ion, the substrate and the first shell of amino acid residues of the peptide (see Fig. 1b) as two different reactive species were considered – ferric superoxo, Fe(III)$OO^{\bullet-}$, and ferryl oxo, Fe(IV)=O. At the next step of the modeling a QMMM computational scheme will be applied in order to estimate the influence of the enzyme surrounding.

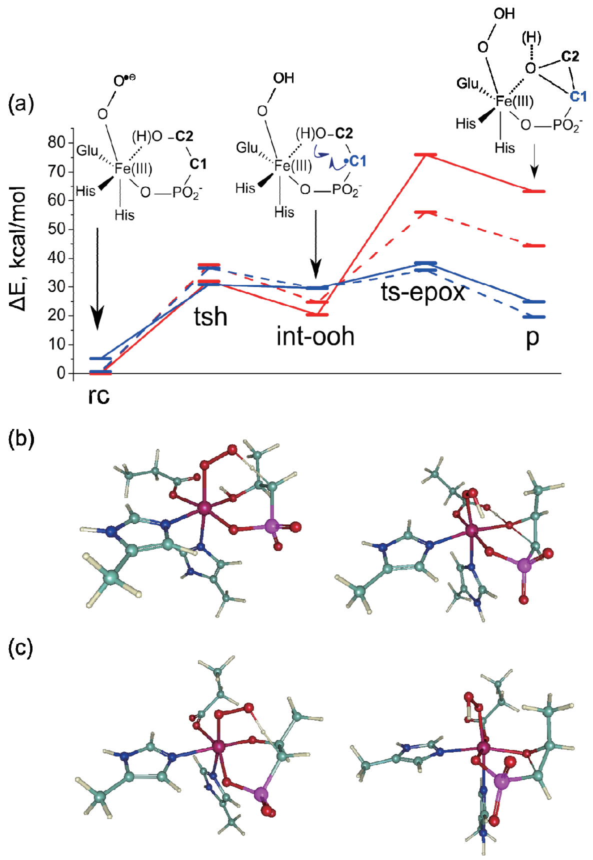


Figure 2. (a) Energy diagram of the reaction in case of (*S*)-2-hydroxypropylphosphonic acid: blue/red for quintet/septet state, solid/dashed lines for hydrogenated/ dehydrogenated substrate. Examples of structures for tsh and ts-epox states for hydrogenated (b) and dehydrogenated (c) substrate. Relative energy (ZPE corrected) is estimated with respect to the most stable reaction complex.

The formation of fosfomycin from the initial (*S*)-2-hydroxypropyl-phosphomic acid could proceed into two main steps: (*i*) H-abstraction from C1 atom of the substrate, and (*ii*) further cyclization of the radical intermediate to epoxide structure. The energy profile of the reaction in the case of ferric superoxo active species for quintet and septet state of the system is presented on Fig. 2a as the structures of the corresponding transition states are provided in panels b and c for the hydrogenated (i.e. the hydroxyl group at C2 is considered intact) and dehydrogenated substrate, respectively.

According to the obtained results, the reaction barrier for hydrogen abstraction from C1 atom is quite high, above 25 kcal/mol. Significant decrease of the energy barrier for H abstraction by ca. 10 kcal/mol was observed in case of ferryl-oxo active species.

The reaction was modeled also with (*R*)-2-hydroxypropylphosphomic acid as reactant in which case the hydrogen atom at the C2 atom is also available for abstraction. For ferric superoxo species the abstraction from C2 is preferred by 5-10 kcal/mol while the energy barriers for the ferryl oxo structures are very similar for both C1 and C2 abstraction.

Wilfredo Credo CHUNG

FIFC Fellow

1. Summary of research for the year

A Nonadiabatic Ab Initio Dynamics Study on Rhodopsin and its Analog Isorhodopsin: Chemical Dynamics Reasons Behind Selection of Rhodopsin by Life

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.[1] Isorhodopsin (isoRh) is an Rh analogue that contains 9-cis retinal embedded in the same opsin environment.[2, 3] 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[4, 5], t_{isoRh} = 600 fs[6]) and more efficient (quantum yield: Φ_{Rh} = 0.65[7], Φ_{isoRh} = 0.22[8]).

We carried out a Quantum Mechanics/Molecular Mechanics (QM/MM) trajectory surface hopping (TSH) direct dynamics calculations in order to understand the origin of the discrepancy. Comparison is also made with our previous calculations[9, 10] The transition probability is estimated using the Zhu-Nakamura (ZN) theory[11] of nonadiabatic transitions. We call the present scheme the ZN-QM/MM-TSH scheme. The QM region is essentially a protonated Schiff base of retinal (see Figure 1 of reference 9 and Figure 2 of reference 10). The rest of the molecules were treated with MM using mechanical embedding. The QM treatment was the 6-electron-6-orbital complete active space self-consistent field (CASSCF) technique[12, 13] with the 6-31G basis set[14]. The MM part was described by AMBER parameters[15] in Gaussian 03[16]. 162 trajectories were calculated in total for both Rh and isoRh starting material at 300 K. Geometries of minima in the ground state and minimum energy conical intersections (MECI) are identified to analyze the dynamics results.

We have already shown[9, 10] that retinal molecule without opsin leads to rotations of ϕ_{11} and ϕ_9 rotates in a direction opposite to each other. Thus, the essential feature of isomerization motion after photo-excitation is intrinsic in retinal itself.

The experimental photoisomerization period and bathoRh quantum yield are reproduced reasonably (see Table 1). The slight discrepancy between the simulation and experiments are due to the failure of the chosen QM/MM treatment to reproduce a barrier[8, 17] in the excited state in isoRh reported in experiments. Even a tiny barrier would have slowed down the photoisomerization by trapping the trajectories in the excited state and yield a quantitatively accurate timescale and quantum yield.

Table 1 also shows that photoexcitation of Rh gives bathoRh (and the reactant) whereas the isoRh excitation yields a 9,11-dicis analog in addition to bathoRh (and the reactant). This byproduct formation in isoRh photoisomerization is another reason why life uses Rh rather than isoRh. Shown in Figure 1 are the plots of the time

Table 1. The ratio of photo products, quantum yield and photoisomerization period of rhodopsin in comparison with isorhodopsin. The values in square brackets are taken from the corresponding gas-phase PSB calculations[a].

		reactants	
		Rh(11-cis)	isoRh(9-cis)
photoproducts (%)	bathoRh(all-trans)	52 [27]	31 [13]
	isoRh(9-cis)	0 [22]	65 [82]
	Rh(11-cis)	48 [51]	0 [5]
	9,11-dicisRh	0 [0]	4 [0]
quantum yield	calc.	0.52	0.31
	expt.	0.65[7]	0.22[8]
photoisomerization period (fs)	calc.	187[185]	344[665]
	expt.	200[4, 5]	600[6]

[a] References 9 and 10.

evolution of the active dihedral angles (=C_{10}-C_{11}=C_{12}-C_{13}= or ϕ_{11} and =C_8-C_9=C_{10}-C_{11}= or ϕ_9, respectively) for the (a) Rh and (b) isoRh trajectories. Clearly seen in Figure 1a is, for Rh, the lack of access of trajectories to a clockwise twist in ϕ_{11} in addition to rapid change in ϕ_{11} to -90°, where an MECI is located. Figure 1a shows that most of trajectories are in a similar and simultaneous way in the excited state, consistent with vibrational coherence revealed in an experiment on Rh[18] although the present treatment of the nuclei is classical except for transitions. In the case of isoRh (Figure 1b), a few trajectories are initiated by a clockwise twist of ϕ_9 in the excited state although the twist is unsuccessful and isoRh is regenerated in the ground state (S_0). Thus, all bathoRh photoproducts are formed via counterclockwise twist of the active dihedral ϕ_9 or ϕ_{11}. This obviously hindered isomerization is due to the constraints offered by the opsin environment especially by amino acid residues close to the binding pocket. In contrast, in our previous gas-phase PSB simulations, twists in both directions take place (cf. Figure 6, reference 10). The slower twist in isoRh is in the excited state. This is another consequence of the slower isoRh excited-state dynamics.

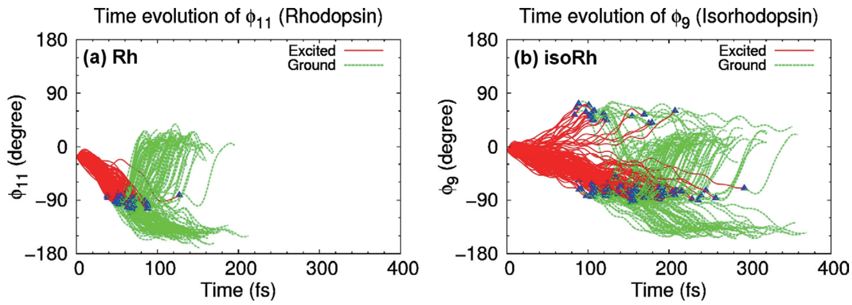


Figure 1. Time evolution of the dihedral angle of the twisting bond for the (a) Rh and (b) isoRh systems. Blue triangles are transition points from the excited state to the ground state.

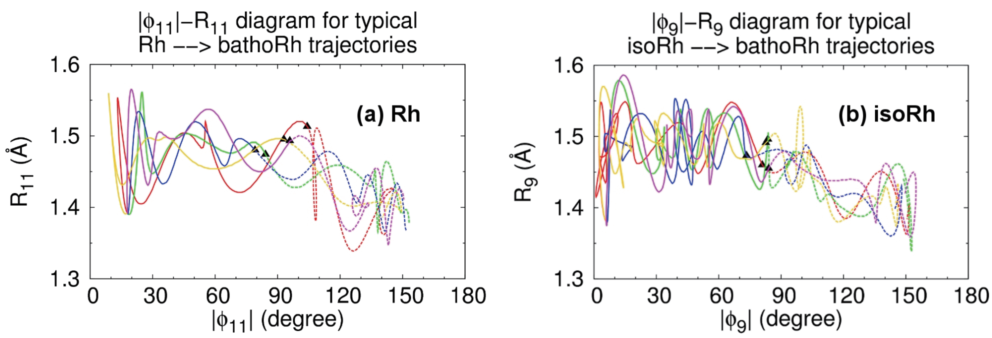


Figure 2. Change in length of the active bond -Cn-Cn+1- against the absolute value of the dihedral angle Cn-1-Cn-Cn+1-Cn+2 for typical (a) Rh (n = 11) and (b) isoRh (n = 9) trajectories leading to the all-trans form. The solid and dashed lines shows that trajectories are in the excited and ground states and the black triangles correspond to transition from the excitated state to the ground state.

Figure 2 shows the diagram of the active twist angle and the length of the active bond for five typical trajectories for Rh and isoRh. Fast and straightforward dynamics in Rh is shown in Figure 2a whereas complicated excited-state dynamics is evident in the isoRh case in Figure 2b.

Why is the isoRh photoisomerization more difficult compared to that of Rh? One reason is the atomic displacements required by the chromophore at the excited state potential energy surface to reach the conical intersection region. Shown in Figure 3 is a superimposed image of the S_0 optimized geometry and the geometry adapted by the chromophore at the crossing region. The pocket that contains the retinal chromophore is similar in shape for both the Rh and isoRh case. Opsin residues Thr118 and Tyr268 create a narrow gap near the -C_9=C_{10}-C_{11}= region of the retinal chain with the two residues coming as close as 7 Å to each other. The isoRh photoisomerization is more difficult compared to that of Rh because of at least two reasons: (1) the isoRh isomerization requires more space than that of Rh and (2) the dihedral that needs to be twisted in the isoRh case (-C_9=C_{10}-) is situated within the narrow gap between Thr118 and Tyr268.

Another reason is the initial acceleration of retinal atoms induced by surrounding residues. The initial force between two atoms for a few retinal-opsin atom pairs is listed in Table 2. Cys187, Thr118 and Tyr268 are close enough to the chromophore to significantly influence the isomerization. For example, for the atomic distance between the C_{12} hydrogen in retinal and the oxygen in Cys187, the projected inter-atomic force for Rh is about 15 times larger than the counterpart for isoRh. Also, a five-fold difference is found for the force between retinal C_{10} and Tyr268. Such differences partially explain the discrepancy in the speed and efficiency of the cis-trans isomerization between the Rh and isoRh chromophores.

Table 2. Initial interatomic forces between most relevant chromophore-opsin atom pairs

	Force (hartree-bohr^{-1})	
	Rh	isoRh
Ret C_{12}-H-Cys187 O	2.5×10^{-3}	1.7×10^{-4}
Ret C_{10}-Tyr268 CE2	2.2×10^{-3}	4.5×10^{-4}
Ret C_{11}-Thr118 N	1.8×10^{-3}	1.6×10^{-3}

CE2 = Tyr's second ε-carbon.

Comparison with the previous gas-phase simulations reveals three other consequences shown below.

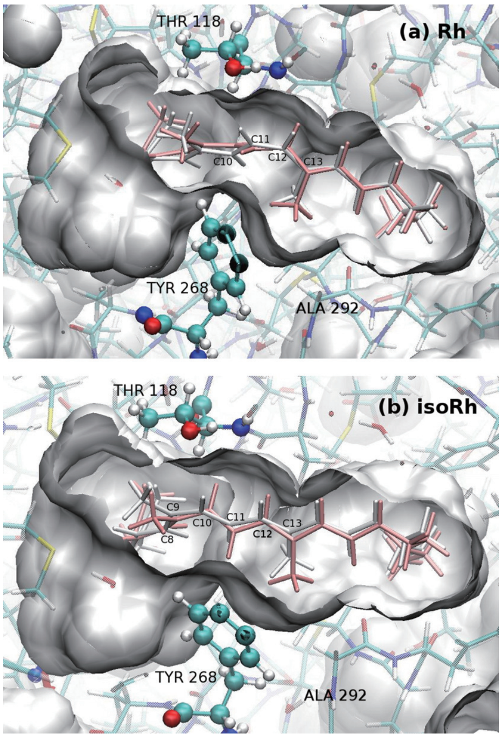


Figure 3. Superimposed structures of the S0 optimized geometry (gray) and geometry at the MECI (pink) for the (a) Rh and (b) isoRh case. Also shown is the opsin pocket that contains the chromophore. The pocket surface is the overlapped envelope of amino residues surrounding the retinal chromophore, which is generated using the S0 optimized geometry wherein the retinal chromophore is artificially removed.

The protein causes (almost) one-way twist of the active angle. In Figure 4, the values of the active dihedral angles ϕ_9 and ϕ_{11} at the time of hopping are plotted (compare with Figure 11, reference 9 and Figure 10, reference 10). All Rh trajectories go though only one MECI region with clockwise-twisted ϕ_9 and counterclockwise-twisted ϕ_{11} (Figure 4a). This MECI branches towards the

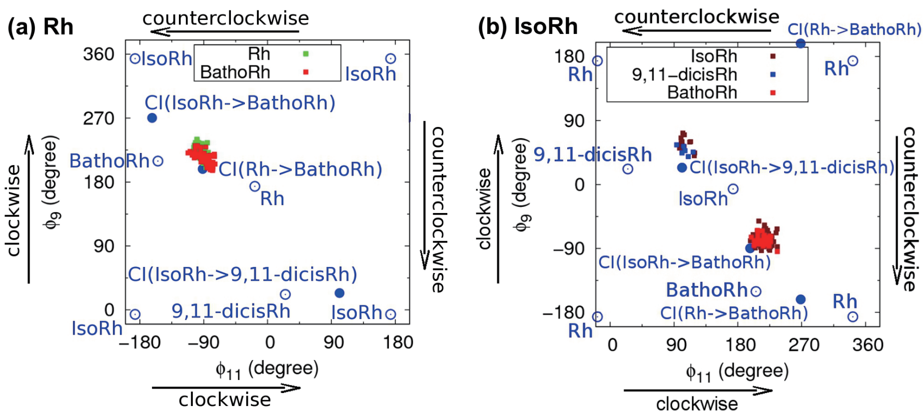


Figure 4. Diagram of the twist angles of -C_{11}=C_{12}- (ϕ_{11}) and -C_9=C_{10}- (ϕ_9) at the transition points. The minima in the ground state (open blue circles) and conical intersections (filled blue circles) obtained in the present calculations are plotted in the diagram. Rh = rhodopsin, isoRh = isorhodopsin, bathoRh = bathorhodopsin, 9,11-dicisRh = 9,11-dicis rhodopsin, CI=minimum energy conical intersection.

formation of bathoRh and the regeneration of the reactant. The relaxation of the excited state of isoRh, on the other hand, goes through two MECI regions. Most of trajectories from isoRh go through the MECI region with ϕ_9 ~ -90° and clockwise-twisted ϕ_{11}, which is shown as CI(isoRh->BathoRh) in Figure 4b. This MECI is responsible for all of bathoRh generation. A few trajectories go through another MECI region (CI(isoRh->9,11-dicisRh)), which is responsible for the generation of a photoproduct with 9,11-dicis retinal as chromophore (we call this as 9,11-dicisRh hereafter). Thus, photoexcitation of Rh only gives bathoRh as a product whereas isoRh yields 9,11-dicisRh in addition to bathoRh, as shown in Table 1. Note that the reaction speeds through the two MECI in isoRh are significantly different. The reaction time is longer through CI(isoRh->BathoRh) (τ_{ave}=233 fs) than that through CI(isoRh->9,11-dicisRh) (τ_{ave}=188 fs). The difference is revealed in the dissimilarity in the twist speed of ϕ_9 in Figure 1(b).

Secondly, the protein environment enhances the production of bathoRh. When the opsin environment was totally ignored, the calculated bathoRh (all-trans PSB) quantum yield was only 0.27 and 0.13, respectively (in square brackets of Table 1). Explicit consideration of the opsin residues that envelop the chromophore significantly improves the theoretical quantum yield to 0.51 and 0.31, respectively. This is partly due to the unidirectional rotation in opsin environment.

The third effect of the opsin on the dynamics is to cause transitions to take place near MECIs. Comparison of transition points in Figure 4 with those in Figure 11 in reference 9 and Figure 10 in reference 10 reveals that the present transition points with the opsin environment are nearer the MECI points than the points without the opsin. In our previous opsin-free simulations, it was observed that inefficient, premature hops (excited-to-ground state hops that occur far from the MECI region) occur often especially in the isoRh case. The opsin environment enhances the dynamics by drastically reducing the probability of premature hopping, in particular in the isoRh case with transitions occurring near the MECI region. The protein may keep large energy gaps between the excited state and S_0 except for the MECI region.

In conclusion, the faster and more efficient photoisomerization of Rh than of isoRh is due to a straightforward and fast excited-state dynamics for Rh in contrast with a complicated dynamics in a back and forth fashion especially in the excited state for isoRh. The dynamics is governed by the differences (1) in volume-saving motions of retinal molecules, (2) in space gaps formed by surrounding residues, and (3) in the initial acceleration by repulsive force from the surrounding amino residues. The formation of 9,11-dicis Rh byproduct from isoRh photoisomerization is another reason why organisms adopt rhodopsin rather than isorhodopsin. The other effects of the opsin environment are (1) to cause the active dihedral angle in retinal to rotate one way, (2) to enhance the bathoRh quantum yield and (3) to cause transitions to take place near the MECIs. The present ZN-QM/MM-TSH scheme is found to be applicable to photoreactions of biomolecules.

References

1 F. Boll, *Am. J. Med. Sci.* **1878**, *151*, 190.
2 F. D. Collins, R. A. Morton, *Biochem. J.* **1950**, *47*, 18.
3 G. Wald, P. K. Brown, R. Hubbard, *Proc. Natl. Acad. Sci. U. S. A.* **1955**, *41*, 438.
4 R. W. Schoenlein, L. A. Peteanu, R. A. Mathies, C. V. Shank, *Science* **1991**, *254*, 412.
5 L. A. Peteanu, R. W. Schoenlein, Q. Wang, R. A. Mathies, C. V. Shank, *Proc. Natl. Acad. Sci.* **1993**, *90*, 11762.
6 R. W. Schoenlein, L. A. Peteanu, Q. Wang, R. A. Mathies, C. V. Shank, *J. Phys. Chem.* **1993**, *97*, 12087.
7 J. E. Kim, M. J. Tauber, R. A. Mathies, *Biochemistry (Mosc).* **2001**, *40*, 13774.
8 J. B. Hurley, T. G. Ebrey, B. Honig, M. Ottolenghi, *Nature* **1977**, *270*, 540.
9 T. Ishida, S. Nanbu, H. Nakamura, *J. Phys. Chem. A* **2009**, *113*, 4356.
10 W. C. Chung, S. Nanbu, T. Ishida, *J. Phys. Chem. A* **2010**, *114*, 8190.
11 H. Nakamura, *Nonadiabatic Transition: Concepts, Basic Theories and Applications*, World Scientific Publishing Co. Pte. Ltd., Singapore, **2002**, pp. 376.

12 H.-J. Werner, P. J. Knowles, *J. Chem. Phys.* **1985**, *82*, 5053.
13 P. J. Knowles, H.-J. Werner, *Chem. Phys. Lett.* **1985**, *115*, 259.
14 W. J. Hehre, R. Ditchfield, J. A. Pople, *J. Chem. Phys.* **1972**, *56*, 2257.
15 W. D. Cornell, P. Cieplak, C. I. Bayly, I. R. Gould, K. M. Merz, D. M. Ferguson, D. C. Spellmeyer, T. Fox, J. W. Caldwell, P. A. Kollman, *J. Am. Chem. Soc.* **1995**, *117*, 5179.
16 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. C. M. Head-Gordon, E. S. Replogle, J. A. Pople, *Gaussian 03 (Revision D.01)*, Gaussian, Inc., Pittsburgh, PA, **2003**.
17 R. R. Birge, C. M. Einterz, H. M. Knapp, L. P. Murray, *Biophys. J.* **1988**, *53*, 367.
18 R. M. Weiss, A. Warshel, *J. Am. Chem. Soc.* **1979**, *101*, 6131.

2. Original Paper

1. W. C. Chung, S. Nanbu and T. Ishida, Nonadiabatic ab initio dynamics of a model protonated Schiff base of 9-cis retinal, J. Phys. Chem. A 114, 8190–8201 (2010).

3. Presentation at academic conferences

1. W. C. Chung, S. Nanbu and T. Ishida *Nonadiabatic ab initio dynamics of an isorhodopsin model system based on the Zhu-Nakamura theory* 第26回化学反応討論会 平成22(2010)年6月2-4日広島大学東広島キャンパス (Poster)
2. W. C. Chung *Computational Studies on Some Important Molecules* In-House Seminar on Computational Chemistry, MSU-IIT (Iligan City) and MUST (Cagayan de Oro City) Philipines, September 7-8, 2010 (Invited Talk)
3. W. C. Chung, S. Nanbu and T. Ishida *Hindered cis-trans isomerization in 9-cis retinal: a two-state model dynamics simulation* 第4回分子科学討論会　大阪大学豊中キャンパス 2010年9月14日〜17日(Poster)
4. W. C. Chung and T. Ishida *On the mechanism of the structural decoy action of LMP1 over CD40 in relation to Epstein-Barr virus infection: an essential dynamics approach* 第8回福井謙一記念研究センターシンポジウム 京都大学福井謙一記念研究センター3 December 2010 (Poster)
5. W. C. Chung, S. Nanbu and T. Ishida *Nonadiabatic ab initio dynamics of a model protonated Schiff base of 9-cis retinal* The 2010 International Chemical Congress of Pacific Basin Societies (Pacifichem) Honolulu, Hawaii, USA, December 15-20, 2010 (Poster)

Takafumi IWAKI

FIFC Fellow

1. Summary of the research of the year

Theoretical Study of Nonlinear Photophoretic Motion of a Micro Droplet

When a temperature has a gradient, it sometimes induces a convectional flow, coupled with a body force such as the gravity. This type of convection is called a natural convection, which is commonly recognized in our daily life. On the other hand, there are convections of which mechanisms rely on a more delicate effect upon a surface of the object. One example of this is the Marangoni convection arising from a gradient in surface energy, and another is the radiometric effect arising from an inelastic reflection of gas molecules at the solid surface with a temperature different from ambient gas (Fig. 1).

So far, the photophoresis caused by the inelastic reflections of gas molecules has been studied for a solid colloidal object, and yet there have been not so much consideration on the photophoresis of the liquid droplet. According to the research in the preceding year, we have advanced a theoretical analysis for this case on the basis of the linearized Boltzmann equation with Maxwell-type kinetic boundary condition, which was summarized as one original paper in this year.

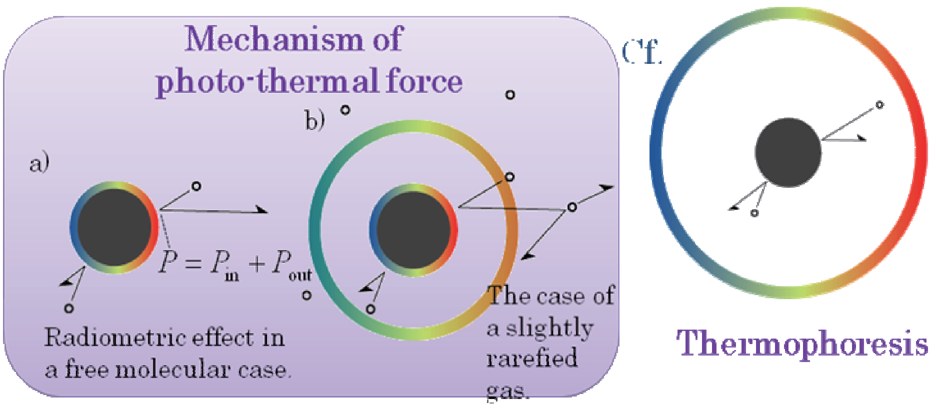


Figure 1: A schematic representation of the radiometric effect. The Maxwell temperature of impinging gas particles is different from that of outgoing gas particles influenced by a surface temperature of an object. On the other hand, the densities of gas particles are same before and after the reflection. This induces the difference of the pressure according to the temperature difference. For the case of a slightly rarefied gas, interactions between gas molecules heats

the impinging particles, and the temperature difference between impinging and outgoing particles decreases as compared with the free molecular case. For comparison, schematic of thermophoresis is also sketched.

The solution for the linearized Boltzmann equation coupled with the Navier-Stokes equation for a spherical liquid droplet was obtained by a spectral method for the system with an axial symmetry. It is notable that the photophoretic velocity and the Peclet number are linearly dependent on the surface temperature gradient, respectively. When light intensity becomes larger, the system shifts from a temperature diffusion dominant region to a temperature advection dominant region. According to this shift, the scaling exponent of the photophoretic velocity shifts from 1 to about 0.5.

Response functions for $P_1(\cos\ \theta)$ heat sources monotonically decrease as the Peclet number increases. On the other hand, response functions for other modes of heat source functions show a peak at around the Peclet number of 10. For a small Peclet number, an advection carries energy from other modes. For a large Peclet number, stirring by the advection becomes too strong and the temperature distribution is equalized in all modes. When internal flow is slow, a temperature distribution inside the droplet is determined by the diffusion equation. In this case, the photophoretic velocity linearly scales to the radiation intensity. Only difference with the case of a solid sphere is its coefficient. When internal flow is fast, the temperature advection changes the behavior of the system in a qualitative manner. The most characteristic point is the occurrence of an asymmetric flow field induced by a homogeneous mode of the radiation intensity distribution inside the droplet. Figure 2 is a schematic representation of the mechanism of the occurrence of this flow. When there is a small flow, it carries heat and makes a surface temperature gradient. The surface temperature gradient results in the photophoretic motion of the droplet. The drag force between air and droplet then strengthen the internal flow. This positive feed-back process induces the spontaneous breaking of symmetry.

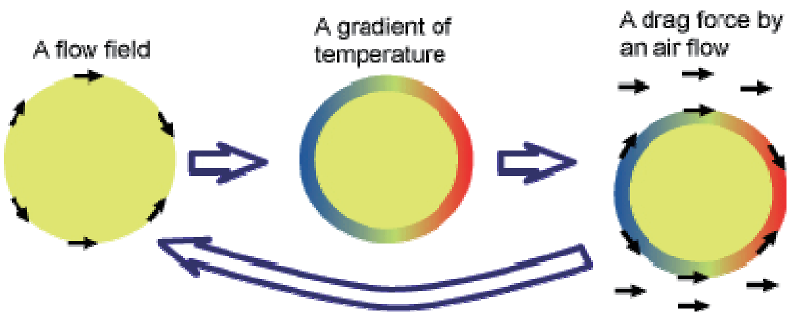


Figure 2: Positive feed-back process between internal flow and a photophoretic

motion for a micron-sized droplet.

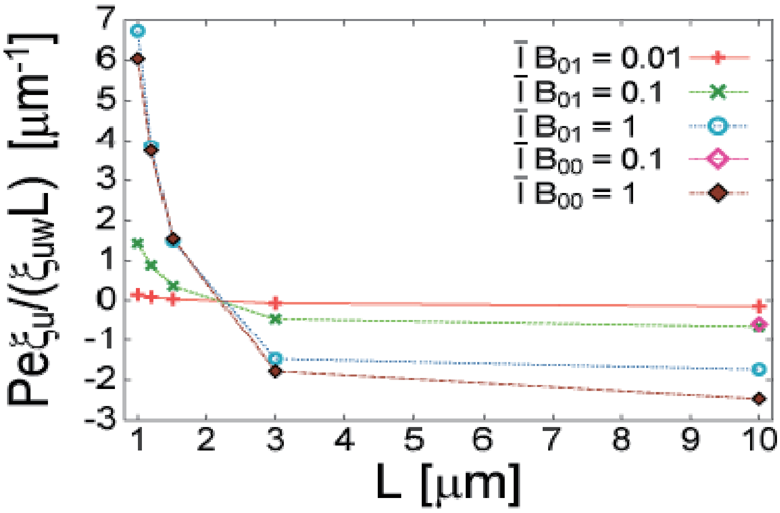


Figure 3: The Peclet number at a steady state divided by the size of the droplet versus the size of the droplet. ξ_u and ξ_{uw} are nondimensional coefficients relating to each flow modes. $\bar{I}$ is an intensity of an irradiated laser, and B_{0x} indicates a homogeneous mode and the first Legendre mode for the heat source distribution inside the droplet.

Figure 3 shows the size-dependence of the Peclet number at a steady state divided by the radius of a droplet. In the present analysis, the photophoretic velocity linearly depends on the Peclet number. The figure shows that the direction of a photophoretic motion reverses as the size of the droplet increases. This reverse of the direction indicates that the dominant effect to the motion of the whole droplet changes from a radiometric force to the Marangoni convection. In principle, the Marangoni convection moves a droplet toward the warm side of the droplet just like a breast stroke. However, when the droplet is very small, this effect is invisible behind the radiometric force. When the size of the droplet increases, the Knudsen number becomes smaller. The system then gets far from the rarefied gas. The radiometric force vanishes rapidly in this continuous limit of the ambient gas.

In relation to this work, we advance two researches. One is the analysis of the actual experiment for the photophoretic velocity of the aerosol particles under micro-gravity. In the beginning, the experiment seemed to show the nonlinear dependence of the photophoretic velocity on a light intensity. Unfortunately, a detailed analysis showed that this was wrong.

Theoretical analysis based on the Boltzmann equation well explains a linear relation found in the experiment including its coefficient. From the comparison with the experiment on the ground, we clarified that the microgravity experiment essentially reduces the “noise” of the natural convection, which enables to obtain a clear result.

In addition we built CFD software on an irregular lattice as an implicit solver of the finite volume method to simulate a Marangoni convection of thermo-fluid droplet. For Marangoni convection, an advection term sometimes plays an essential role. The shape of the droplet is also important factor. To consider such a problem, computer simulation is very useful. As concerns this research, an important result was not obtained in this year, and the research is now continued.

Theoretical Study of a Linear Polymer Morphology Confined in a Sphere

Biopolymers are normally confined in a very tiny space. For example, DNA in vivo is usually confined in a nucleus of which size is extremely smaller than the contour length of DNA. Readout of gene information is done in such a narrow confinement. However, with a very dense condition, it is not known how DNA unfolds its expedient part selectively to offer a transcription reaction. Moreover, the structure and the statistical property of a confined linear polymer have not yet fully understood.

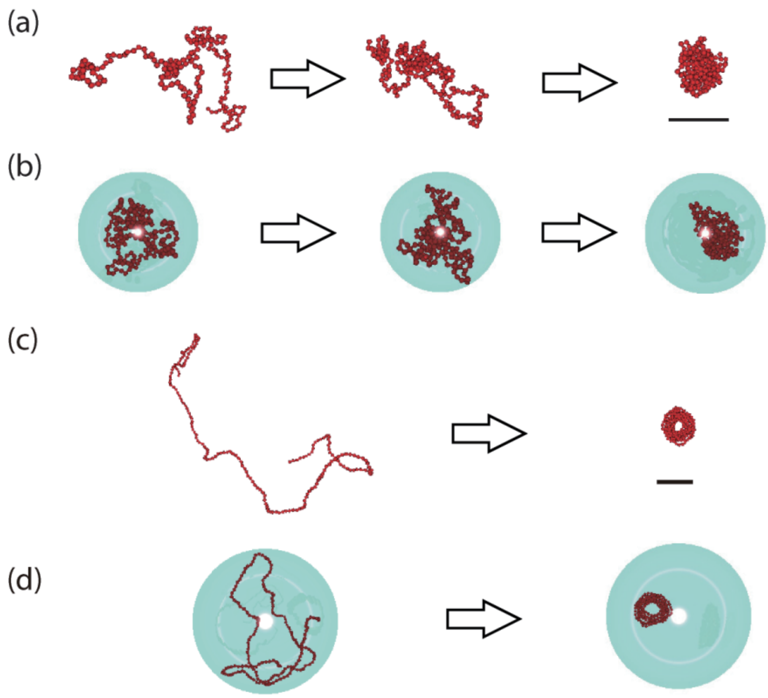


Figure 4: Snapshots of the folding transition of linear polymer chains. (a) A flexible polymer in a free solution. (b) A confined flexible polymer. (c) A

semiflexible polymer in a free solution. (d) A confined semiflexible polymer.

We performed a Langevin dynamics simulation of a simplified model polymer confined in a spherical cavity to get insight into this problem. Figure 4 shows typical snapshots of polymeric chain undergoing a folding transition. Folding transition of a flexible polymer is a continuous transition, and the folded structure is in a liquid-like or amorphous state. On the other hand, a semiflexible polymer undergoes a discontinuous transition, and the folded structure is in an ordered state. From a sequence of simulations, the confinement was found to shift transition point of a linear polymer folding in the opposite direction between a flexible polymer and a semiflexible polymer. We successfully explained this qualitative difference of the confinement effect by a simple scaling argument. These results are summarized in a paper coming next year.

2. Original Papers

(1) Takafumi Iwaki,
"Effect of internal flow on the photophoresis of a micro liquid droplet",
PRE 81(6),066315-(1-13) (2010)

3. Presentation at academic conferences

(1) "液滴の光泳動におけるサイズ依存性" ("Size-dependence of photophoretic velocity of a micro droplet"), (poster), Takafumi Iwaki, 2010 Autumn meeting of Japan physical society, Osaka, September 23-26, 2010

(2) "レーザーによる熱流体駆動の数値解析" ("Numerical analysis of thermo-fluid driven by laser irradiation"), (poster), Takafumi Iwaki, The 20-th workshop of nonlinear reaction and cooperative phenomena, Kagoshima, January 8-9, 2011

(3) "Transportation of a micro droplet by light irradiation: The influence of an advection and the Marangoni effect." (invited), T. Iwaki, Optics in the Life Science Congress, Monterey, USA (April 4-6, 2011)

4. Others

(1) ""細胞の自己組織化"に物理の視点から迫る" ("Physical approach toward a "self-organization of a biological cell""), Kenichi Yoshikawa and Takafumi Iwaki, パリティ (parity), vol. 26, No. 05, pp. 13-21 (issued on Apr. 25, 2011)

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FIFC Fellow

1. Summary of the research of the year

Ab initio multiplet calculation for 3*d* transition metal $L_{2,3}$ x-ray absorption and electron energy loss spectroscopy

Both x-ray absorption near-edge structure (XANES) and electron energy-loss near-edge structure (ELNES) are powerful techniques to observe the electronic structure of selected elements in materials. They monitor the electronic transition from core states to unoccupied states. Thus, they reflect information about the oxidation states, spin states, chemical bonding, and atomic coordinates of the element of interest. To extract such information from experimental spectra, however, a good theoretical tool that has predictive performance without using adjustable parameters is indispensable.

Density functional calculations using a large periodic supercell with inclusion of a core-hole are widely used to compute XANES/ELNES theoretically. Most of *K* XANES/ELNES, which corresponds to the electronic transition from 1*s* to unoccupied *p* orbitals, are reproduced well following the "recipe"[1,2]. However, in the case of 3d transition metal (TM) $L_{2,3}$ XANES/ELNES, which are dominated by the 2*p*-3*d* transition, the independent particle approximation breaks down. Because of the strong interactions among core TM-2*p* and 3*d* electrons, the shape of $L_{2,3}$ XANES/ENLES is strongly modified from the empty 3*d* density of states: this is known as multiplet effects. In order to treat the electronic transition from core levels, relativistic effects should also be considered. The most prevalent and conventional theoretical approach for the analysis of TM-$L_{2,3}$ XANES/ELNES is the semi-empirical charge transfer multiplet method, where crystal field effects are incorporated into an atomic multiplet calculation using the group theoretical formalism. In this approach, the ligand field effects are considered using the empirical parameters. Hence it has little predictive performance of the multiplet structures *a priori*. An *ab initio* calculation that takes multiplet effects into account is therefore strongly desirable.

For this purpose, we have developed an *ab initio* multiplet method based on the relativistic configuration interaction (CI) theory. As the first step, the Dirac-Kohn-Sham equation was solved using a model cluster within the framework of local density approximation (LDA). Then, Slater determinants were constructed as the basis of many-electron wavefunctions using four-component molecular spinors. All possible determinants corresponding to $(\phi_{3d})^n$ and $(\phi_{2p})^5(\phi_{3d})^{n+1}$ configurations were considered for rigorously taking the exchange-correlation interaction among the 2*p* core-hole and 3*d* electrons, where ϕ_{3d} (ϕ_{2p}) denotes the molecular spinors mainly composed of 3*d* (2*p*) atomic spinors. The many-electron eigenvalues and eigenfunctions for all possible initial and final states were computed by fully diagonalizing the many-electron Hamiltonian matrix. Then the oscillator strength of the electric dipole transition is evaluated as where Ψ_i and Ψ_f are the many-electron wavefunctions for the initial and final states, while E_i and E_f are their energies, respectively. A theoretical spectrum was obtained by convolving the oscillator strength of electric dipole transition with a Lorentzian function.

Figure 1 shows experimental and theoretical Ni-$L_{2,3}$ XANES of NiO and Ni-doped ZnO. Excellent agreement between the experimental and theoretical spectra is found. The differences of the experimental spectra due to the difference of the coordination number and symmetry around Ni ions, such as the presence or absence of the splitting at L_3 main peaks and difference of L_2 line-shapes, are well reproduced. The results demonstrate that the oxidation states, spin states and local coordination of TM ions in materials can be revealed using *theoretical fingerprinting* obtained by the *ab initio* CI method. The present method is also useful for characterizing TM ions in more complex hosts, such as in interface, surface and amorphous structures.

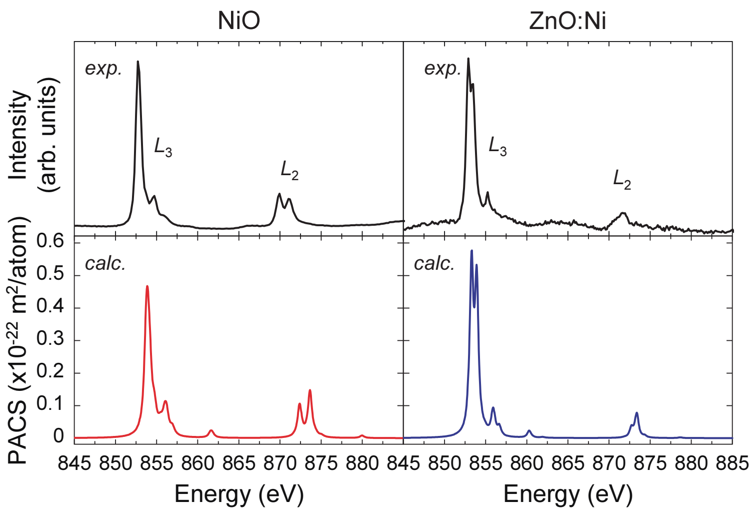

Fig. 1 Theoretical Ni-$L_{2,3}$ XANES of NiO (Mn^{2+}, CN=6) and Ni dopant in ZnO (Mn^{2+}, CN=4) obtained by the relativistic CI method. Experimental spectra are also shown for comparison.

In many 3*d* TM compounds, neighboring ligand atoms contribute to the spectral shapes of $L_{2,3}$ XANES/ELNES. In the case of 3*d* TM oxides, The charge transfer (CT) from ligand oxygen ions to the TM ions plays an important role in the spectral shapes of the TM-$L_{2,3}$ XANES/ELNES. In the *ab initio* CI method described above, part of this charge transfer through the covalent bonding between TM-3*d* and O-2*p* is automatically included by using molecular spinors. The other part of the CT effect can be included by considering the additional configurations (Slater determinants) with a hole(s) on the $\phi_{O\text{-}2p}$ levels in the CI. In order to quantitatively understand the effects of CT on spectra, TM-$L_{2,3}$ XANES/ELNES for 3d TM oxides with various d-electron numbers and symmetries are systematically calculated using the *ab inito* CI method. In these calculations, the additional single electron excitation from $\phi_{O\text{-}2p}$ to ϕ_{3d} spinors is explicitly included in the CI. The results are summarized in ref. [4].

First, the influences of the covalency on TM $L_{2,3}$-edges were discussed. The important consequence of the covalent bonding between O-2p and TM-3d is the reduction of inter-electron interactions. The covalent bonding between TM elements and oxygen increased the spatial distribution of TM-3d spinors, which resulted in the reduction of inter-electron interaction energies among TM-2p and 3d electrons. Hence, it changed the multiplet structures (eigenvalues and eigenfunctions) and the transition probabilities in the TM-$L_{2,3}$ XANES/ELNES. Then, the influences of the from $\phi_{O\text{-}2p}$ to ϕ_{3d} on TM $L_{2,3}$-edges have been discussed. We found that the contribution of $\phi_{O\text{-}2p}\rightarrow\phi_{3d}$ excitation to the initial state eigenfunction increased with increasing atomic number and valency of TM ions in the oxides. This tendency is similar to that of the covalent bonding between TM-3d and O-2p spinors. The stronger the covalency, the larger the $\phi_{O\text{-}2p}\rightarrow\phi_{3d}$ excitation becomes. We also found that the $\phi_{O\text{-}2p}\rightarrow\phi_{3d}$ excitation significantly modify the spectral features of TM-$L_{2,3}$ XANES/ELNES for strongly covalent systems. In the case of Ti-$L_{2,3}$ XANES/ELNES of $SrTiO_3$, for instance, the Ti-L_2 peaks are much broadened by considering $\phi_{O\text{-}2p}\rightarrow\phi_{3d}$ excitation in the CI as shown in Fig. 2. One can also find that the intensity ratio between the two L_3 main peaks is changed. In addition, small satellite peaks appears around 470-472 eV. It should be noted that the extra broadening of the L_2 peaks in $SrTiO_3$ has been explained by the shorter lifetime of the core hole in 2$p_{1/2}$ than in 2$p_{3/2}$ and by Coster-Kronig Auger decay. The present result clearly shows that the CT from the ligand oxygen to the Ti ion also contributes to the broadening of the L_2 peaks in $SrTiO_3$.

Through this work, the power of the *ab initio* CI method to quantitatively reproduce the spectra is demonstrated.

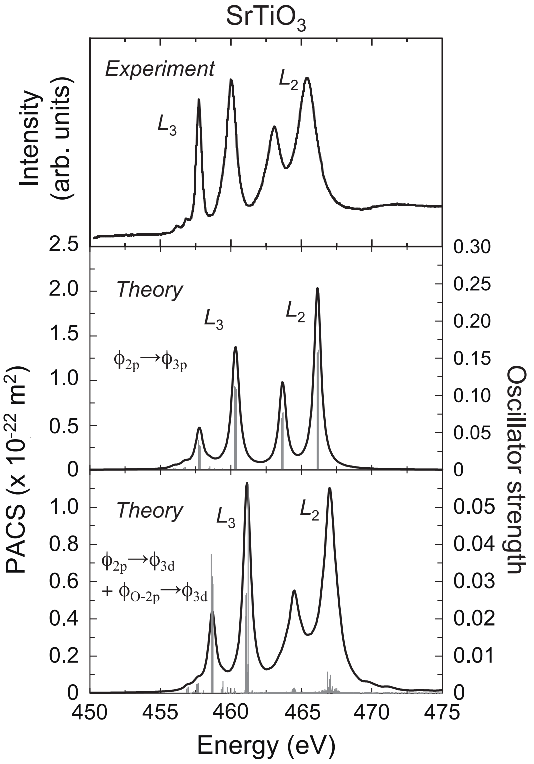

Fig. 2 Theoretical Ti-$L_{2,3}$ XANES of $SrTiO_3$ compared with the experimental spectrum[6].

References

[1] I. Tanaka *et al.*, J. Am. Ceram. Soc.

[2] T. Mizoguchi *et al.*, Micron 41, 695 (2010).

[3] H. Ikeno *et al.*, J. Phys.: Condens. Matter **21,** 104208 (2009).

[4] H. Ikeno *et al.*, Phys. Rev. B **83,** 155107 (2011).

[5] F.M.F. de Groot *et al.*, Phys. Rev. B **41,** 928 (1990).
[6] Y. Uehara *et al.*, Appl. Phys. A **65**, 179 (1997).

2. Original papers

(1) Mizoguchi Teruyasu, Weine Olovsson, Hidekazu Ikeno and Isao Tanaka
"Theoretical ELNES using one-particle, and multi-particle calculations"
Micron **41,** 695-709 (2010).

(2) P.S. Miedema, H. Ikeno, and F.M.F. de Groot
"First principles multiplet calculations of the calcium $L_{2,3}$ x-ray absorption spectra of CaO and CaF_2"
J. Phys.: Condens. Matter 23, 144501 (2011).

(3) Hidekazu Ikeno, Teruyasu Mizoguchi and Isao Tanaka
"*Ab initio* charge transfer multiplet calculations on the $L_{2,3}$ XANES and ELNES of 3*d* transition metal oxides"
Phys. Rev. B **83,** 155107 (2011).

3. Presentation at academic conferences

(1) Hidekazu Ikeno
"Relativistic Configuration Interaction Approach to the 3*d* Transition Metal $L_{2,3}$ X-ray Absorption Spectra"
The Electronic Structure of Transition Metal Systems (Oct 21, 2010, Utrecht, the Netherlands)

4. Others

(1) 池野豪一
「相対論CI法によるX線吸収分光の理論計算」
第8回 福井謙一記念研究センターシンポジウム (2010年12月3日，京都)

(2) Hidekazu Ikeno
"Introduction of *Ab-initio* Multiplet Method for X-ray Absorption Spectroscopy"
Institut de minéralogie et de physique des milieux condensés CNRS, Université Pierre et Marie Curie (Feb 11, 2011, Paris)

Natsuhiko YOSHINAGA

FIFC Fellow

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

Self-propulsion of a drop driven by Marangoni flow

Spontaneous motion or self-propulsion have been attracting attention in last decades for its potential application to biological problems such as cell motility and wound healing. Recently several model experiments showing spontaneous motion have been proposed. The systems in these works consist of relatively simple ingredients for instance oil drops in water nevertheless the motion is as if the drops are alive. The key questions are why the particle moves without external force and why it breaks symmetry and chooses one direction.

The first point has been discussed in hydrodynamics of the Marangoni effect in which a liquid droplet is driven by a gradient of surface tension. The mechanism is that the gradient induces convective flow inside and outside of a drop, which leads to swimming motion of the drop itself. The second point was less discussed, but has been discussed in the field of nonlinear dynamics as drift instability. In fact, the mode equations of drift instability and deformation have been derived with symmetry consideration and from specific reaction diffusion equations.

Thus far there are only few attempts to discuss the spontaneous symmetry breaking from hydrodynamics points of view. In this work, we derive the nonlinear equations exhibiting drift instability. This is of importance because all the coefficients are determined with physical quantities.

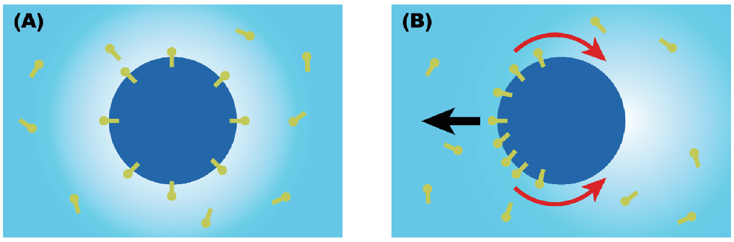

Fig. 1: Schematics of our system. Surfactants dissolve in the outer bulk and are absorbed onto the interface, resulting in reduction of the surface tension. (A) Isotropic distribution of the surfactants when a drop is stationary. (B) When the distribution breaks symmetry the flow (the red thin arrow) occurs and the drop starts to move (the black thick arrow).

Polarity patterns of stress fibers

Stress fibers are bundles of actin filaments made contractile by interaction with myosin minifilaments and elastic by cross-linking with α-actinin and other proteins. They are formed in the cytoskeleton of nonmuscle animal cells that need either to exert or to resist a mechanical force. Their biological function is exemplified in vivo by myofibroblasts that use the contractility of stress fibers to remodel the extracellular matrix during wound healing or by vascular endothelial cells in blood vessels that align stress fibers parallel to the direction of flow to resist shear forces. Actin filaments are polar structures, with a plus (or barbed) end and a minus (or pointed) end. The polarity of actin filaments inside a bundle is determined by decoration of actin with myosin subfragment-1 and electron microscopy imaging. Noncontractile (or passive) actin bundles often present uniform polarity, with barbed ends predominantly facing the same direction along the bundle, as seen in filopodia or in the retraction fibers of postmitotic cells. The polarity profile of stress fibers is alternating, with a majority of barbed ends successively pointing in opposite directions. This periodic structure, with a wavelength of the order of 1 um, is reminiscent of the sarcomeric organization of muscle cells. The actomyosin filament bundles of motile fibroblasts, however, exhibit a graded polarity profile: The proportion of barbed ends in the bundle facing one direction varies gradually and monotonically between 0 and 100% from one end to the other. The direction of the bundle sets the orientation of locomotion: The formation of graded polarity bundles is an early event in the polarization of fibroblasts prior to migration. The spatial dependence of polarity in contractile actomyosin bundles contrasts with the uniform polarity observed in structures such as cilia, filopodia, and retraction fibers, in which motors do not play an organizing role.

In this work, we aim at identifying the physical mechanisms responsible for the existence of variable polarity patterns in elastic actin bundles. We show that active contractility, the chemomechanical transduction from ATP hydrolysis to motion by myosin motors “pulling” on actin, can generate periodic, sarcomerelike polarity patterns provided that it exceeds a well-defined threshold. We focus our attention on ventral stress fibers that span the cell ventral surface and transmit force to the underlying substrate through end-point focal adhesions. We consider existing actomyosin bundles, with constant total material content, and ignore the intriguing questions raised by their assembly.

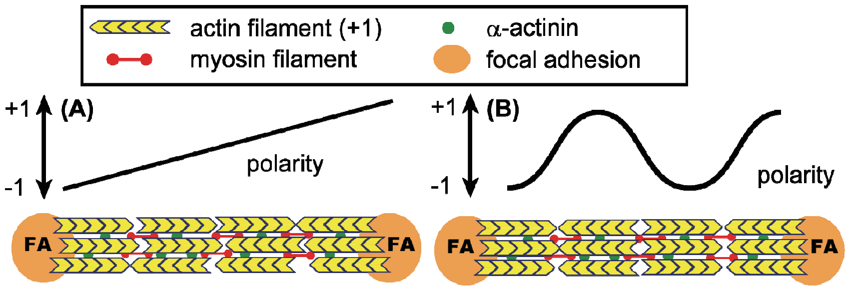

Fig. 2: Schematic representation of an actomyosin bundle with graded (a) and periodic (b) filament polarity profile.

Active Motion of a Janus Particle by Self-Thermophoresis

Self-propulsion arouses interest among scientists because of its interesting dynamics, associated theoretical challenges to nonequilibrium transport phenomena, and possible applications, including microswimmers, nanomachines, and drug delivery. Biological self-propelled molecules or biomotors, such as

ATPase and myosin, convert chemical energy to mechanical motion through chemomechanical coupling. Such thermodynamic coupling also causes self-propulsion in physical systems as exemplified by nanorods' motion in hydrogen peroxide solutions. In contrast to self-propulsion, phoretic motions, such as electrophoresis, dielectrophoresis, and thermophoresis, generally described by the linear response theory, are the directional motions of material in given external fields. Making a bridge between a phoresis and a self-phoretic motion would give more insight into the mechanisms for self-propulsion. In this work, we produced Janus particles (the particle containing two different surfaces on its two sides), by evaporating gold coat on the hemisphere of silica or polystyrene spheres, and analyzed self-propulsive motion under the laser irradiation. The Janus particle moves along a local temperature gradient which is generated by absorption of laser at the metal-coated hemisphere. The local driving gradient and flow near a micro-scale Janus particle are experimentally observed. To clarify the mechanism, temperature distribution and a thermal slip flow field around a micro-scale Janus particle are measured. With measured temperature drop across the particle, the speed of self-propulsion is corroborated with the prediction based on accessible parameters.

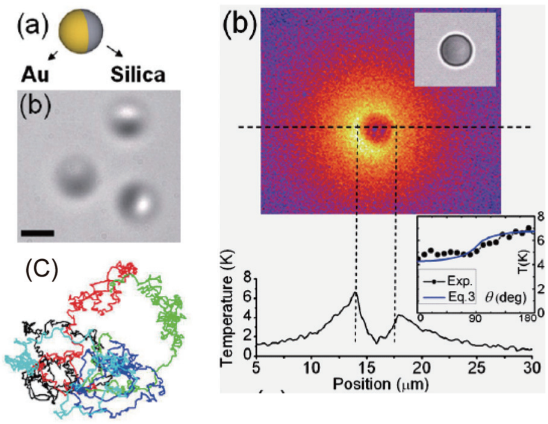

Fig. 3: Janus particle and its bright field image under microscope. The dark sides of the particles shown in (b) are the Au coatings (scale bar: 1 μm). The temperature distribution around the particle and the path of the propelled particle are also shown.

2. Original papers

(1) Natsuhiko Yoshinaga, Jean-Francois Joanny, Jacques Prost and Pilippe Marcq,
"Polarity patterns of stress fibers"
Phys. Rev. Lett. 105, 238103 (2010).

(2) Hong-Ren Jiang, Natsuhiko Yoshinaga, and Masaki Sano
" Active Motion of Janus Particle by Self-thermophoresis in Defocused Laser Beam"
Phys. Rev. Lett. 105, 268302 (2010).
Editor's suggestion and introduced in Viewpoint in Physics, 3, 108 (2010) Debut of a hot "fantastic voyager"

3. Presentation at academic conferences

(1) Natsuhiko Yoshinaga, Ken Nagai, and Yutaka Sumino, and Hiroyuki Kitahata
"Self-propulsion of a drop driven by Marangoni flow"
Far-from-Equilibrium Dynamics 2011
RIMS Kyoto University,　Kyoto, Japan, (4-8 Jan, 2011)

(2) Natsuhiko Yoshinaga, Ken Nagai, and Yutaka Sumino, and Hiroyuki Kitahata
"Self-propulsion of a drop driven by Marangoni flow"
International Symposium on Non-Equilibrium Soft Matter 2010
Nara, Japan, (17-20 Aug., 2010)

(3) Natsuhiko Yoshinaga, Ken Nagai, and Yutaka Sumino, and Hiroyuki Kitahata
"Self-propulsion of a drop driven by Marangoni flow"
International Soft Matter Conference 2010
Granada, Spain, (5-8 July, 2010)

(4) Natsuhiko Yoshinaga, Ken Nagai, and Yutaka Sumino, and Hiroyuki Kitahata
"Spontaneous deformation of a reactive droplet"
Annual meeting of Japan Physical Society
Osaka, (23-26 September, 2010)

(5) Natsuhiko Yoshinaga, Jean-Francois Joanny, Jacques Prost and Pilippe Marcq
"Polarity patterns of stress fibers"
Annual meeting of Biophysical Society of Japan
Sendai, (20-22 September, 2010)

(6) Natsuhiko Yoshinaga,
"Two-state polymers: Folding transition and adsorption"
Memorial Symposium Toyoichi Tanaka
Kyoto, (19-20 November, 2010)

4. Others

(1) Natsuhiko Yoshinaga
"Drift instability of a drop driven by Marangoni flow"

Seminar in Kyoto University, Kyoto, April 16, 2010

(2) Natsuhiko Yoshinaga
"Polarity patterns of stress fibers"
Seminar in the University of Tokyo, Tokyo, April 28, 2010

招へい外国人学者・外国人共同研究者受入れ状況（平成22年度）

氏　　名	受入れ身分	受入れ期間	所属機関・職名	受入れ責任者	研 究 内 容
Sivakumar Sekharan	外国人共同研究者	平成22年4月3日～平成22年4月24日	Emory University（アメリカ）・研究員	諸熊 奎治	複雑分子系のシミュレーション
Hasmerya Maarof	招へい外国人学者	平成22年4月4日～平成22年7月3日	Universitiy Teknologiy Malaysia（マレーシア）・講師	諸熊 奎治	分子理論による複雑分子のシミュレーションに関する共同研究と研究者交流
Thanyarat Udommaneethanakit	外国人共同研究者	平成22年4月16日～平成22年7月15日	Chulalongkorn University（タイ）・研究員	諸熊 奎治	分子理論による複雑分子のシミュレーションに関する共同研究と研究者交流
Chatchawal Wongchoosuk	外国人共同研究者	平成22年6月15日～平成22年9月13日	Mahidol University（タイ）・D2	諸熊 奎治	分子理論による複雑分子のシミュレーションに関する共同研究と研究者交流
Marvin Jose F. Fernandez	外国人共同研究者	平成22年6月3日～平成22年8月31日	Ateneo de Manila University（フィリピン）・大学院生	諸熊 奎治	分子理論による複雑分子のシミュレーションに関する共同研究と研究者交流
Hoa My Nguyen	外国人共同研究者	平成22年6月7日～平成22年9月4日	HaNoi University of Science（ベトナム）・研究員	諸熊 奎治	分子理論による複雑分子のシミュレーションに関する共同研究と研究者交流
Pham Quoc Buu	外国人共同研究者	平成22年6月7日～平成22年9月4日	HCMCInsititute for Computational Science & Tech.（ベトナム）・研究員	諸熊 奎治	分子理論による複雑分子のシミュレーションに関する共同研究と研究者交流
Panita Decha	招へい外国人学者	平成22年6月15日～平成22年6月30日	Thaksin University（タイ）・講師	諸熊 奎治	分子理論による複雑分子のシミュレーションに関する共同研究と研究者交流
Darinee Sea-tang	招へい外国人学者	平成22年6月15日～平成22年6月30日	College of KMITL Nanotechnology（タイ）・講師	諸熊 奎治	分子理論による複雑分子のシミュレーションに関する共同研究と研究者交流
Thang Ho Viet	外国人共同研究者	平成22年6月16日～平成22年6月30日	Danang University of Technology,（ベトナム）・講師	諸熊 奎治	分子理論による複雑分子のシミュレーションに関する共同研究と研究者交流
Bokun Cho	外国人共同研究者	平成22年6月16日～平成22年6月30日	シンガポール国立大学(シンガポール)・大学院生	諸熊 奎治	分子理論による複雑分子のシミュレーションに関する共同研究と研究者交流
Rozana Othman	招へい外国人学者	平成22年6月16日～平成22年6月30日	Universiti Malaya（マレーシア）・上級講師	諸熊 奎治	分子理論による複雑分子のシミュレーションに関する共同研究と研究者交流
Higinio R. Barros, Jr.	外国人共同研究者	平成22年6月16日～平成22年6月30日	Ateneo de Manila University（フィリピン）・大学院生	諸熊 奎治	分子理論による複雑分子のシミュレーションに関する共同研究と研究者交流
Benjoe Rey B. Visayas	外国人共同研究者	平成22年9月20日～平成22年12月18日	MSU-Illigan Institute of Technology（フィリピン）・大学院生	諸熊 奎治	分子理論による複雑分子のシミュレーションに関する共同研究と研究者交流
Natercia Fernandes Bras	外国人共同研究者	平成22年10月17日～平成22年12月18日	The University of Porto（ポルトガル）・大学院生	諸熊 奎治	複雑分子系のシミュレーション

海外渡航一覧（平成 22 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	2010/5/4	2010/5/30	アメリカ合衆国
研究員（学術研究奨励）	Ke, Zhoufeng	2010/5/8	2010/5/14	中国
特任助教授	Stephan Irle	2010/6/3	2010/6/10	ロシア
特定研究員	KRS Chandrakumar	2010/6/3	2010/6/10	ロシア
特定研究員	義永　那津人	2010/6/16	2010/7/9	フランス、スペイン
特定研究員	Alister Page	2010/6/26	2010/7/7	カナダ
研究員（学術研究奨励）	諸熊　奎治	2010/7/13	2010/8/17	アメリカ合衆国
特定研究員	平尾　一	2010/7/26	2010/7/29	シンガポール
研究員（学術研究奨励）	Lung Wa Chung	2010/8/20	2010/8/28	アメリカ合衆国
准教授	石田　俊正	2010/9/5	2010/9/8	フィリピン
研究員（学術研究奨励）	Wilfredo C. Chung	2010/9/5	2010/9/8	フィリピン
特定研究員	Alister Page	2010/10/9	2010/10/15	タイ
特任准教授	Stephan Irle	2010/10/8	2010/10/15	タイ
研究員（学術研究奨励）	諸熊　奎治	2010/11/15	2010/12/21	アメリカ合衆国
研究員（学術研究奨励）	Wilfredo C. Chung	2010/12/16	2010/12/22	アメリカ合衆国
准教授	石田　俊正	2010/12/16	2010/12/22	アメリカ合衆国
特命准教授	平尾　一	2010/12/19	2010/12/23	ベトナム
特定助教	前田　理	2010/12/16	2010/12/21	アメリカ合衆国
特任准教授	Stephan Irle	2011/3/9	2011/3/18	ロシア
外国人特別研究員	Matt Addicoat	2011/3/9	2011/3/18	ロシア
研究員（学術研究奨励）	諸熊　奎治	2011/2/21	2011/3/16	アメリカ合衆国
産学官連携研究員	Li Xin	2011/3/26	2011/4/2	アメリカ合衆国
研究員（学術研究奨励）	Ke, Zhoufeng	2011/3/26	2011/4/2	アメリカ合衆国


第８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
2010年12月3日（金）　10:00-19:00
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
京都市左京区高野西開町34－4
Tel : 075-711-7708,　Fax : 075-781-4757,　Web : www.fukui.kyoto-u.ac.jp

第8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　2010(平成 22)年 12 月 3 日(金)

場所　京都大学福井謙一記念研究センター （3F　大会議室）

・　開会の辞　　田中　功　（センター長）　10:00-10:05

・　ご挨拶　　小森　悟　（京大・工学研究科長）　10:05-10:15

・　中村　宏樹(国立交通大学（台湾）、前分子科学研究所長)　10:15-11:15

「非断熱化学動力学—分子科学に新次元を」

・　谷村　吉隆　（京大・院理）　11:30-12:30

「散逸系の階層型量子運動方程式と多次元分光」

－昼休み－

・　山本　量一　（京大・院工）　14:00-15:00

「粗視化モデリングのすすめ：分子科学とソフトマター科学の接点」

・ポスターセッション　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(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. CooA タンパク質と CO との反応に関する理論的研究
（京大福井セ、統合バイオ[2]）○石田　俊正[1]、青野　重利[2]

2. 有機 EL 素子の新規電子輸送材料の分子設計
（京大福井セ[1]、京大院工[2]）○佐藤　徹[1]、志津功将[2]、田中一義[2]、梶　弘典[2]）

3. Theoretical analysis of photo-thermal force coupled with internal flow field
（FIFC）○Takafumi Iwaki

4. Vapor-Liquid-Solid versus Vapor-Solid-Solid: How do Single-Walled Carbon Nanotubes Nucleate on SiO_2 Catalysts?
（FIFC, IAR Nagoya Univ.）○Alister J. Page, K. R. S. Chandrakumar, Stephan Irle, Keiji Morokuma

5. 相対論 CI 法による X 線吸収分光の理論計算
（FIFC）○池野豪一

6. 反応性界面活性剤を用いた液滴の自発的運動
（京大福井センター[1]、お茶の水大アカプロ[2]、東大院工[3]、千葉大理[4]、JST[5]）
○義永　那津人[1]、永井　健[2]、住野　豊[3]、北畑　裕之[4,5]

7. Polymerization in the Bio-Nano Cavity of Apoferritin
（FIFC）○Zhuofeng KE, Keiji MOROKUMA, Takafumi UENO, Satoshi ABE

8. A New Paradigm for Finding Reaction Pathways for Multicomponent Reactions
（Hakubi, FIFC, RIKEN, Univ. of Tokyo, Emory Univ.）
○Satoshi Maeda, Shinsuke Komagawa, Masanobu Uchiyama, and Keiji Morokuma

9. On the mechanism of the structural decoy action of LMP1 over CD40 in relation to Epstein-Barr virus infection: an essential dynamics approach
（FIFC）○Wilfredo Credo Chung and Toshimasa Ishida

10. Computational Studies on Enzymatic Catalytic Mechanisms
（FIFC） ○Natércia F. Brás, Óscar Chung, Pedro A. Fernandes, Maria J. Ramos and Keiji Morokuma

11. A theoretical study on the photodissociation of NO_3.
（FIFC, Hakubi Kyoto Univ.）○Hongyan Xiao, Satoshi Maeda, Keiji Morokuma

12. ONIOM Study on a Missing Piece in Our Understanding of Heme Chemistry: Bacterial Tryptophan 2,3-Dioxygenase with Dual Oxidants
（FIFC & Sping8）○Lung Wa Chung, Xin Li, Hiroshi Sugimoto, Yoshitsugu Shiro, and Keiji Morokuma

13. QM/MD Investigation of the Nucleation of Carbon Nanotube on the Nonmetallic Silicon Nanocluster: Is the Intermediate Stage Carbide or Carbon Coated surface?
（FIFC, IAR Nagoya Univ.）○K. R. S. Chandrakumar, Alister J. Page, Stephan Irle, and Keiji Morokuma

14. Competitive Mechanistic Pathways for Green-to-Red Photoconversion in the Fluorescent Protein Kaede: A Computational Study
（FIFC）○Xin Li, Lung Wa Chung, Hideaki Mizuno, Atsushi Miyawaki, and Keiji Morokuma

15. Mechanism of the Spiropyran-Merocyanine Photochromic Reacion: A CASSCF/CASPT2 Study
（FIFC）○Fengyi Liu, Keiji Morokuma

16. The fullerene formation mechanism from combustion: quantum chemical MD study
（FIFC, IAR Nagoya Univ.）○Haibei Li, Stephan Irle, Keiji Morokuma

17. 高分子電解質の水中形状解析
（東亞合成(株)[1]、名古屋大院工[2]）
○飯田優羽[1]、佐々木裕[1]、藤本和士[2]、岡崎進[2]

18. 分子動力学シミュレーションによる水蒸気の均一核生成過程の速度論的研究
（海洋研究開発機構）○河野明男　河村洋史　草野完也

19. Ab initio MO 量子マスター方程式法に基づく動的第一超分極率の計算および実空間解析法の開発
（阪大院基礎工）○藤井　宏旭，岸　亮平，南　拓也，重田　育照，中野　雅由

20. Dicyclopenta-fused acene 系の芳香族性、開殻性に対する分子間相互作用効果と非線形光学特性についての理論的研究
（阪大院基礎工）○元村脩人、米田京平、福井仁之、重田育照、岸亮平、中野雅由

21. フェナレニルユニット連結型一次元グラフェンナノフレークの開殻性と第二超分極率についての理論研究
（阪大院基礎工）○米田京平　福井仁之　南拓也　岸亮平　重田育照　中野雅由

22. スピン非制限型 TDDFT 法に基づく量子マスター方程式法による開殻分子系の動的分極率の理論的研究
（阪大院基礎工）○岸亮平、南拓也、藤井宏旭、重田育照、中野雅由

23. ペンタセン／C_{60}ダイマーモデルの励起状態に関する理論的研究
（阪大院基礎工[1]、ボルドー大学[2]）○南拓也[1]、Frédéric Castet[2]、重田育照[1]、中野雅由[1]

24. 半古典ガウス波束伝播法による励起状態動力学—大自由度系への適用
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25. Kick: Constraining a Stochastic Search Procedure with Molecular Fragments
○Matthew A. Addicoat, and Greg F. Metha

26. A Theoretical study of $Pt(PR_3)_2(AlCl_3)$ (R=H, Me, Ph, or Cy); Why does $Pt(PR_3)_2(AlCl_3)$ take T-shaped structure unlike Y-shaped $Pt(PR_3)_2(C_2H_4)$?
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27. Absorption of Gases into Metal Organic Framework: A theoretical Investigation
（ICeMS, Kyoto University）○Milind M.Deshmukh and Shigeyoshi Sakaki

28. Theoretical Study of the Oxoboxyl Complex Formation Reaction and M-BO Bonding Nature
（ICeMS, Kyoto University）○Guixiang Zeng and Shigeyoshi Sakaki

29. 局在化分子軌道を用いた励起エネルギー移動の研究
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30. SAC-CI:CIS による脱プロトン化レチナールのオプシンシフトの理論解析
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31. 鉄触媒クロスカップリング反応における触媒活性種のスピン状態と反応性に関する理論的研究
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32. 14, 15, 16, 17 族高周期ヘテロ元素化合物と炭素ラジカルとの置換反応の理論化学的研究
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33. Folding Pathways of Human Telomeric Type G-quadruplex Structures
（京大院理） ○眞下知子、三戸祐太、杉山　弘

34. 脂質マイクロチューブのブラウン運動と形状揺らぎ
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35. 高分子溶液のミクロ相分離パターン：疑似二次元系に対する三次元的効果の検証
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36. テレケリック会合高分子のレオロジーの分子機構
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37. 水/ メタノール混合溶媒中における架橋ポリ N イソプロピルアクリルアミドゲルの再帰的体積相転移理論
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38. すり抜け環モデルを用いた紐状ミセルの分子シミュレーション
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39. 水素結合による有機ゲル化剤の超分子構造とダイナミクス
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40. Ir(I)および Ru(II)三員環環状オレフィン錯体と C-C 結合活性化反応の理論的研究
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41. たんぱく質の水和水、内部水の揺らぎに関する定量的な解析法の開発:
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42. 金(I)二核錯体およびその集積錯体の吸収・発光スペクトルに関する理論的研究
（京大院工，京大 iCeMS，北大院理）○中尾嘉秀，山田裕，榊茂好，伊藤肇，澤村正也

43. 逆サンドイッチ型二核金属錯体に関する理論的研究
（京大院工，京大 iCeMS）○竹中裕喜雄，黒川悠索，中尾嘉秀，佐藤啓文，榊　茂好

44. 水中におけるフッ化マグネシウム錯体の理論的研究
-フッ素配位数、溶媒和エネルギー及び溶媒和構造-
○（京大院工，京大 iCeMS）柴田尚人、横川大輔、佐藤啓文、榊茂好

45. Symmetric Band Structures and Asymmetric Ultrafast Electron and Hole Relaxations in Silicon and Germanium Quantum Dots
（京大院理[1]、Univ. of Washington[2]、University of Rochester[3]）
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46. A stochastic model of neon-liquid surface scattering
○Daniel M. Packwood and Leon F. Phillips

47. 複雑な環境における励起子：DNA の不等方緩和
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48. フッ化カーボンナノチューブの構造と振動様態の研究：
分子動力学シミュレーションによる赤外応答の解析
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49. QM/MD 法による分子性液体の IR・RAMAN スペクトルの直接計算
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50. 多次元振動分光における散逸と緩和の影響についての理論的研究
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51. フェノール誘導体の溶液内電子・プロトン移動反応
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52. 7-アザインドール2量体の励起状態ダブルプロトン移動反応における反応ダイナミクスの量子動力学法を用いた解析
（京大院理）○安藤耕平、加藤重樹

53. 第一原理計算によるセレンの鎖間相互作用の研究
（京大院理）○松井正冬

54. 溶媒接触表面効果を考慮した pH 一定 MD 法による Melittin の膜挿入過程の研究
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55. 気相中でのピリジンの超高速緩和過程に関する理論的研究
（京大院理[1]、スタンフォード大[2]） ○中野勝博[1]、森俊文[2]、加藤重樹[1]

56. アルミナテンプレートを用いた有機／無機複合ナノロッドの作製と光電気特性
（京大院工） ○北浦真司、張哲、松重和美、梅山有和、俣野善博、今堀博

57. Synthesis and Optical Properties of Chemically Converted Graphene Covalently Linked with Pyrene
（京大院工）〇三原潤也、手塚記庸、梅山有和、俣野善博、今堀博

58. 3次元興奮性反応拡散系における自己推進ドメインの運動
（京大院理）〇設楽恭平、平岩徹也、太田隆夫

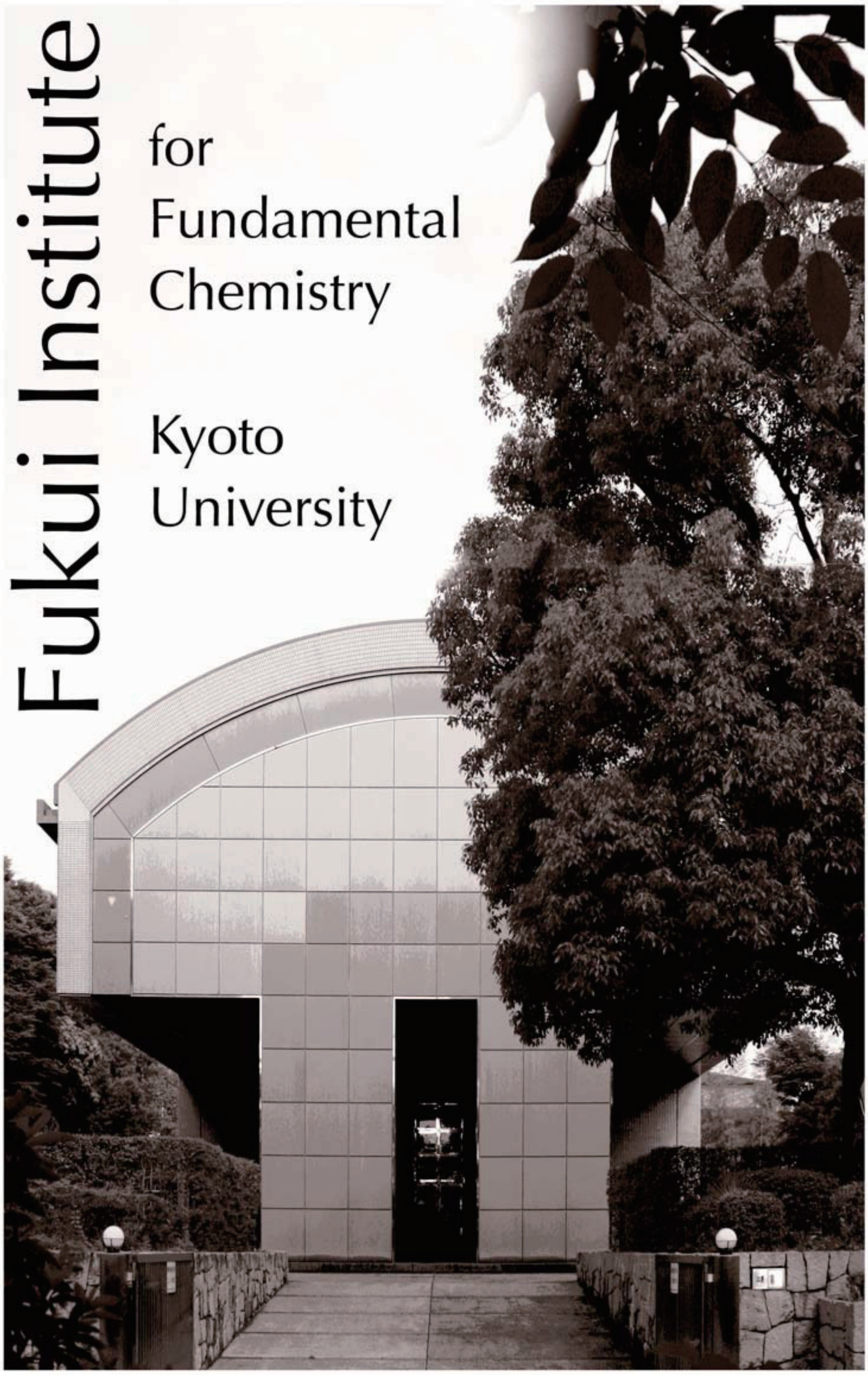
59. 磁性化合物における構造探索手法の開発
（京大院工）〇熊谷悠, (京大 PRU)世古敦人, (京大工)大場史康, 田中功

60. ハイブリッド密度汎関数法による Eu^{2+}ペロブスカイト酸化物の磁性と電子状態
（京大院工）〇赤松寛文, 熊谷悠, 大場史康, 藤田晃司, 田中勝久, 田中功

61. First principles study on Ti antisites and O vacancies in perovskite titanates
（Graduate School of Eng., Kyoto Univ.）〇Minseok Choi, Fumiyasu Oba, and Isao Tanaka

62. 水溶液環境下における層状チタン酸化物の構造安定性の第一原理計算
（京大院工）〇森　正弘

63. プロトン移動性分子結晶 5-ブロモ-9-ヒドロキシフェナレノンの誘電物性に関する理論的研究
（京大院理）〇大滝大樹、安藤耕司



第8回福井謙一記念研究センターシンポジウム

2010年(平成22年)12月3日(金)

京都大学福井謙一記念研究センター


第8回
福井センターセミナー
The 8th FIFC Seminar
2010年6月21日(月)　15:00-17:00
京都大学福井謙一記念研究センター 3F 大会議室
〒606-8103 京都市左京区高野西開町34-4
（TEL075-711-7708）
http://www.fukui.kyoto-u.ac.jp/
(at FIFC, Kyoto Univ. on June, 21(Mon.), 2010)
15:00～15:30 Satoshi Maeda (Hakubi Center, FIFC)
“Systematic Exploration of Photochemical Reaction Pathways: Applications to Ketones and Aldehydes"
15:30～16:00 Alister Page (FIFC)
“Carbon Nanotube Nucleation on Traditional and Non-Traditional Catalysts: Insights from QM/MD Simulations”
16:00～17:00 Alexey Timoshkin (St. Petersburg State University)
“From Donor-Acceptor Complexes to Nanorods”
多数の方のご来場を歓迎いたします
We welcome all of you to join.

研究業績一覧（2010 年度）

№	Authors	Title	Journal	Volume(Number), first page to last page	year
石田　俊正					
1	K. Ueda, K. Suzuki, K. Suzuki, K. Yoza, T. Ishida	Syntheses, crystal structures and DFT calculations of 2-[4,5-bis (ethylsulfanyl) -1,3-dithiol-2-ylidene]-5- (4,5-diiodo-1,3-dithiol-2-ylidene) -1,3-dithiolan-4-thione and -one	*Physica B*	405, S69-S74	2010
2	Wilfredo C. Chung, Shinkoh Nanbu, and Toshimasa Ishida	Nonadiabatic ab Initio Dynamics of a Model Protonated Schiff Base of 9-cis Retinal	*J. Phys. Chem. A*	114 (32), 8190-8201	2010
3	Shinkoh Nanbu, Toshimasa Ishida and Hiroki Nakamura	Future Perspectives of Nonadiabatic Chemical Dynamics	*Chemical Science*	1(6), 663-674	2010
佐藤　徹					
4	Katsuyuki Shizu, Tohru Sato, Kazuyoshi Tanaka, Hironori Kaji	Vibronic Coupling Density Analysis of Hole-Transporting Materials: Electron-Density Difference in DFT and HF Methods	*Organic Electronics*	11, 1277-1287	2010
5	Katsuyuki Shizu, Tohru Sato, Kazuyoshi Tanaka	Inelastic Electron Tunneling Spectra and Vibronic Coupling Density Analysis of 2,5-Dimercapto-1,3,4-thiadiazole and Tetrathiafulvalene Dithiol	*Nanoscale*	2, 2186-2194	2010
6	A. Ito, Y. Yokoyama, R. Aihara,K. Fukui, S. Eguchi, K. Shizu, T. Sato, K.Tanaka	N-Anisyl-Substituted Hexaaza[16] paracyclophane	*Angew. Chem. Int. Ed.*	49(44), 8205-8208	2010
7	Tomonori Yamada, Furitsu Suzuki, Atsushi Goto,Tohru Sato, Kazuyoshi Tanaka, Hironori Kaji	Revealing Bipolar Charge-Transport Property of 4,4'-N, N'-dicarbazolylbiphenyl (CBP) by Quantum Chemical Calculations	*Organic Electronics*	12, 169-178	2010
8	Katsuyuki Shizu, Tohru Sato, Kazuyoshi Tanaka,and Hironori Kaji	A Boron-Containing Molecule as an Efficient Electron-Transporting Material with Low-Power Consumption	*Appl. Phys. Lett.*	97, 142111 1-3	2010
9	Naoya Iwahara, Tohru Sato, Kazuyoshi Tanaka, Liviu F. Chibotaru	Vibronic coupling in C_{60} - anion revisited: Precise derivations from photoelectron spectra and DFT calculations	*Phys. Rev. B*	82, 245409 1-10	2010
10	Naoya Iwahara, Tohru Sato, Kazuyoshi Tanaka	Molecular design for high-spin molecules in view of vibronic couplings	*Polyhedron*	In Press	
11	Katsuyuki Shizu Tohru Sato, Kazuyoshi Tanaka	Vibronic Coupling Density Analysis for Free-Base Porphin Cation	*Chem. Phys. Lett.*	505, 42-46	2011
12	Katsuyuki Shizu Tohru Sato, Akihiro Ito, Hironori Kaji, Kazuyoshi Tanaka	Theoretical Design of a Hole-Transporting Molecule:Hexaaza[1_6]parabiphenylophane	*J. Mater. Chem.*	21, 6375-6382	2011
13	Tohru Sato, Katsuyuki Shizu; Keisuke Uegaito; Naoya Iwahara; Kazuyoshi Tanaka; Hironori Kaji	Vibronic Interactions in Hole-Transporting Molecules: An Interplay with Electron-Hole Interactions	*Chem. Phys. Lett.*	507, 151-156	2011
中尾　嘉秀					
14	T. Umeyama, N. Tezuka, S. Seki, Y. Matano, M. Nishi, K. Hirao, H. Lehtivuori, N. V. Tkachenko, H. Lemmetyinen, Y. Nakao, S. Sakaki, H. Imahori	Selective formation and efficient photocurrent generation of [70] fullerene-single-walled carbon nanotube composites	*Adv. Mater.*	22, 1767-1770	2010

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15	H. Ando, Y. Nakao, H. Sato, S. Sakaki	Comparison of Electronic Structures and Light-induced Excited Spin State Trapping between [Fe(2-picolylamine)$_3$]$^{2+}$ and Its Iron(III) Analogue	*Dalton Trans.*	39, 3279-3289	2010
16	Y. Nakajima, Y. Nakao, S. Sakaki, Y. Tamada, T. Ono, F. Ozawa	Electronic structure of four-coordinate iron(I) complex supported by a bis (phosphaethenyl) pyridine ligand	*J. Am. Chem. Soc.*	132, 9934-9936	2010
17	K. Saito, Y. Nakao, K. Umakoshi, S. Sakaki	Theoretical study of excited states of pyrazolate- and pyridinethiolate-bridged dinuclear platinum(II) complexes: relationship between geometries of excited states and phosphorescence spectra.	*Inorg. Chem. Soc.*	49, 8977-8985	2010
諸熊　奎治					
18	S. Sekharan and K. orokuma	QM/MM Study of the Structure, Energy Storage and Origin of the Bathochromic Shift in Vertebrate and Invertebrate Bathorhodopsins	*J. Am. Chem. Soc*	133, 4734-4737	2011
19	T. Kawatsu, M. Lundberg and K. Morokuma	Protein Free Energy Corrections in ONIOM QM:MM Modeling: A Case Study for Isopenicillin N Synthase (IPNS)	*J. Chem. Theo. Comp.*	7, 390-401	2011
20	S. Maeda, S. Komagawa, M. Uchiyama, and K. Morokuma	Finding Reaction Pathways for Multicomponent Reactions: The Passerini Reaction Is a Four-Component Reaction	*Angew, Chem. Int. Ed.*	50, 644-649	2011
21	A. J. Page, K. R. S. Chandrakumar, S. Irle, and K. Morokuma	SWNT Nucleation from Carbon-Coated SiO_2 Nanoparticles via a Vapor-Solid-Solid Mechanism	*J. Am. Chem. Soc.*	133, 621-628	2010
22	H. Hirao and K. Morokuma	Ferric Superoxide and Ferric Hydroxide Are Used in the Catalytic Mechanism of Hydroxyethylphosphonate Dioxygenase (HEPD): A Density Functional Theory Investigation	*J. Am. Chem. Soc.*	132, 17901-17909	2010
23	N. Bera, S. Maeda, K. Morokuma and A. A. Viggiano	Theoretical study of proton affinity and fluoride affinity of nerve agent VX	*J. Phys. Chem. A*	114, 13189-13197	2010
24	R. Nádasdi, G. L. Zügner, M. Farkas, S. Dóbé, S. Maeda, and K. Morokuma	Photochemistry of Methyl Ethyl Ketone: Quantum Yields and S1/S0-Diradical Mechanism of Photodissociation	*Phys. Chem. Phys.*	11, 3883–3895	2010
25	X. Li, L. W. Chung, A. Miyawaki and K. Morokuma	Primary Events of Photodynamics in Reversibly Photoswitching Fluorescent Protein Dronpa	*J. Phys. Chem. Lett.*	1, 3328–3333	2010
26	X. Li, L.W. Chung, A. Miyawaki, and K. Morokuma	Competitive Mechanistic Pathways for Green-to-Red Photoconversion in the Fluorescent Protein Kaede: A Computational Study	*J. Phys. Chem. B*	114, 16666-16675	2010
27	K. Nozaki, S. Kusumoto, S. Noda, T. Kochi, L. W. Chung, and K. Morokuma	Why Did Incorporation of Acrylonitrile to a Linear Polyethylene Become Possible? Comparison of Phosphine-Sulfonate Ligand with Diphosphine and Imine-Phenolate Ligands in the Pd-Catalyzed Ethyelene/Acrylonitrile Copolymerization	*J. Am. Chem. Soc*	132, 16030-16042	2010
28	S. Sekharan, A. Altun, and K. Morokuma	Retinal QM/MM Study of Dehydro and Dihydro β-Ionone Retinal Analogues in Squid and Bovine Rhodopsins: Implications for Vision in Salamander Rhodopsin	*J. Am. Chem. Soc*	132, 15856-15859	2010

№	Authors	Title	Journal	Volume(Number), first page to last page	year
29	A. J. Page, H. Yamane, Y. Ohta, S. Irle, and K. Morokuma	QM/MD Simulation of SWNT Nucleation from Transition-Metal Carbide Nanoparticles	*J. Am. Chem. Soc.*	132, 15699–15707	2010
30	A. J. Page, Y. Ohta, S. Irle and K. Morokuma	Mechanisms of Single-Walled Carbon Nanotube Nucleation, Growth and Healing Determined Using QM/MD Methods	*Acc. Chem. Res.*	43. 1375-1385	2010
31	J. Jakowski, S. Irle and K. Morokuma	Collision-induced fusion of two C_{60} fullerenes: quantum chemical molecular dynamics simulations	*Phys. Rev. B*	82, 125443/1-8	2010
32	P. V. Avramov, S.Minami, S. Irle, L. A. Chernozatonskii, and K. Morokuma	Atomic Structure and Energetic Stability of Complex Chiral Silicon Nanowires	*J. Phys. Chem. C*	114, 16692-14696	2010
33	L. W. Chung, X. Li, H. Sugimoto, Y. Shiro, and K. Morokuma	ONIOM Study on a Missing Piece in Our Understanding of Heme Chemistry: Bacterial Tryptophan 2,3-Dioxygenase with Dual Oxidants	*J. Am. Chem. Soc.*	132, 11993-12005	2010
34	S. Maeda and K. Morokuma	Communications: A Systematic Method for Locating Transition Structures of A + B → X Type Reactions	*J. Chem. Phys.*	24, 241102/1-4	2010
35	S. Maeda, K. Ohno, and K. Morokuma	A Theoretical Study on the Photodissociation of Acetone: An Insight into the Slow Intersystem Crossing and Exploration of Nonadiabatic Pathways to the Ground State	*J. Phys. Chem. Lett*	1, 1841-1845	2010
36	A. J. Page, S. Minami, Y. Ohta, S. Irle and K. Morokuma	Comparison of Single-Walled Carbon Nanotube Growth from Fe and Ni Nanoparticles using quantum chemical molecular dynamics methods	*Carbon*	48, 3014-3026	2010
37	B. Saha, S. Irle and K. Morokuma	Formation mechanism of polycyclic aromatic hydrocarbons (PAH) in the benzene flame: Density functional tight binding molecular dynamics simulations	*J. Chem. Phys.*	132, 224303/1-11	2010
38	V. P. Ananikov, D. G. Musaev, and K. Morokuma	Real size of ligands, substrates and catalysts: studies of structure, reactivity and selectivily by ONIOM and other hybrid computational approaches	*J. Mol. Cat. A*	24, 104–119	2010
39	S. Maeda, K. Ohno, and K. Morokuma	Updated Branching Plane for Finding Conical Intersections without Derivative Coupling Vectors	*J. Chem. Theo. Comp.*	6, 1538–1545	2010
前田　理					
40	S. Maeda, K. Ohno, K. Morokuma	A Theoretical Study on the Photodissociation of Acetone: An Insight into the Slow Intersystem Crossing and Exploration of Nonadiabatic Pathways to the Ground State	*J. Phys. Chem. Lett.*	1, 1841-1845	2010
41	S. Maeda, K. Morokuma	Communication: A Systematic Method for Locating Transition Structures of A + B → X Type Reactions	*J. Chem. Phys.*	132, 241102/1-4	2010
42	S. Ohno, K. Shudo, M. Tanaka, S. Maeda, K. Ohno	Theoretical Investigation of the Reaction Pathway of O Atom on Si(001)-(2 × 1)	*J. Phys. Chem. C*	114, 15671-15677	2010
43	R. Nadasdi, G. L. Zugner, M. Farkas, S. Dobe, S. Maeda, K. Morokuma	Photochemistry of Methyl Ethyl Ketone: Quantum Yields and S_1/S_0-Diradical Mechanism of Photodissociation	*ChemPhysChem*	11, 3 883-3895	2010
44	S. Maeda, Y. Matsuda, S. Mizutani, A. Fujii, K. Ohno	Long-Range Migration of a Water Molecule To Catalyze a Tautomerization in Photoionization of the Hydrated Formamide Cluster	*J. Phys. Chem. A*	114, 11896-11899	2010

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45	N. C. Bera, S. Maeda, K. Morokuma, A. A. Viggiano	Theoretical Proton Affinity and Fluoride Affinity of Nerve Agent VX	*J. Phys. Chem. A*	114, 13189-13197	2010
46	S. Maeda, S. Komagawa, M. Uchiyama, K. Morokuma	Finding Reaction Pathways for Multicomponent Reactions: The Passerini Reaction Is a Four-Component Reaction	*Angew. Chem. Int. Ed.*	50, 644-649	2011
47	S. Maeda, R. Saito, K. Morokuma	Finding Minimum Structures on Seam of Crossing in Reactions of Type A + B → X: Exploration of Nonadiabatic Ignition Pathways of Unsaturated Hydrocarbons	*J. Phys. Chem. Lett.*	2, 852-857	2011
48	H. Xiao, S. Maeda, K. Morokuma	Excited-State Roaming Dynamics in Photolysis of a Nitrate Radical	*J. Phys. Chem. Lett.*	2, 934–938	2011
Biswajit Saha					
49	B. Saha, S. Irle, K. Morokuma	Formation mechanism of polycyclic aromatic hydrocarbons (PAHs) in benzene combustion: Quantum chemical molecular dynamics simulations	*J Chem Phys*	132, 224303_1-224303_11	2010
平尾　一					
50	Hajime Hirao and Keiji Morokuma	Ferric Superoxide and Ferric Hydroxide Are Used in the Catalytic Mechanism of Hydroxyethylphosphonate Dioxygenase (HEPD): A Density Functional Theory Investigation	*J. Am. Chem. Soc.*	132(48), 17901–17909	2010
51	Hajime Hirao	Correlation Diagram Approach as a Tool for Interpreting Chemistry: An Introductory Overview	*WIREs Computational Molecular Sciences*	In Press	2011
Zhuofeng Ke					
52	Ke Zhuofeng , Abe, Satoshi, Ueno, Takafumi, & Morokuma, Keiji	Rh-catalyzed Polymerization of Phenylacetylene: Theoretical Studies of the Reaction Mechanism, Regioselectivity and Stereoregularity.	*J. Am. Chem. Soc.*	In Press	2011
53	Gao, H., Ke, Zhuofeng, DeYonker N. J., Wang J., Xu H., Mao Z.-W., Phillips, D.L.,& Zhao C.,	Dinuclear Zn(II) Complex Catalyzed Phosphodiester Cleavage Proceeds via a Concerted Mechanism: A Density Functional Theory Study.	*J. Am. Chem. Soc.*	133 (9), 2904–2915	2011
Joonghan Kim					
54	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
55	Sunhong Jun, Jae Hyuk Lee, Jeongho Kim, Joonghan Kim, Kyung Hwan Kim, Qingyu Kong, Tae Kyu Kim, Manuela Lo Russo, Michael Wulff, and Hyotcherl Ihee	Photochemistry of $HgBr_2$ in methanol investigated using time-resolved liquidography	*Phys. Chem. Chem. Phys.*	12, 11536-11547	2010
56	Joonghan Kim, Hyotcherl Ihee, and Yoon Sup Lee	Spin-orbit density functional and ab initio study of HgXn (X=F, Cl, Br, and I; n=1, 2, and 4)	*J. Chem. Phys.*	133, 144309	2010
57	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

№	Authors	Title	Journal	Volume(Number), first page to last page	year
Alister Page					
58	A. J. Page, S. Irle, K. Morokuma	Polyyne Extension and Ring Collapse Drives Ni-Catalyzed SWNT Growth: A QM/MD Investigation	*J. Phys. Chem. C*	114(18), 8206-8211	2010
59	A. J. Page, S. Minami, S. Irle, K. Morokuma	Comparison of Single-Walled Carbon Nanotube Growth from Fe and Ni Nanoparticles using QM/MD Simulations	*Carbon*	48(11), 3014-3026	2010
60	A. J. Page, D. J. D. Wilson and E. I. von Nagy-Felsobuki	Trends in MH_2^{n+} Ion-Quadrupole Complexes (M = Li, Be, Na, Mg, K, Ca; n = 1,2)	*Phys. Chem. Chem. Phys.*	12(41), 13788-13797	2010
61	A. J. Page, S. Irle, Y. Ohta, K. Morokuma	Metal-Catalyzed Single-Walled Carbon Nanotube Nucleation, Growth and Healing Mechanisms Determined using QM/MD Methods	*Acc. Chem. Res.*	43(10), 1375-1385	2010
62	A. J. Page, H. Yamane, S. Irle, K. Morokuma	QM/MD Simulation of SWNT Nucleation from Transition-Metal Carbide Nanoparticles	*J. Am. Chem. Soc.*	132(44), 15699-15707	2010
63	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.*	133(3), 621-628	2011
64	A. J. Page, K. R. S. Chandrakumar, S. Irle, K. Morokuma	Do SiO_2 and Carbon-Doped SiO_2 Nanoparticles Melt? Insights from QM/MD Simulations, and Ramifications Regarding Carbon Nanotube Growth	*Chem. Phys. Lett.*	In Press	
65	Y, Okamoto, Y.Ohta, A. J. Page, S. Irle, K. Morokuma	QM/MD Study of Transition Metal Catalyst Particle Melting and Carbide Formation During SWCNT Nucleation	*J. Comp. Theor. Nanoscience*	In Press	
Xin Li					
66	Xin Li, Lung Wa Chung, Hideaki Mizuno, Atsushi Miyawaki, and Keiji Morokuma	A Theoretical Study on the Nature of On- and Off-States of Reversibly Photoswitching Fluorescent Protein Dronpa: Absorption, Emission, Protonation and Raman	*J. Phys. Chem. B*	114, 1114-1126	2010
67	Xin Li, Lung Wa Chung, Hideaki Mizuno, Atsushi Miyawaki, and Keiji Morokuma	Primary Events of Photodynamics in Reversible Photoswitching Fluorescent Protein Dronpa	*J. Phys. Chem. Lett.*	1, 328-3333	2010
68	Xin Li, Lung Wa Chung, Hideaki Mizuno, Atsushi Miyawaki, and Keiji Morokuma	Competitive Mechanistic Pathways for Green-to-Red Photoconversion in the Fluorescent Protein Kaede: A Computational Study	*J. Phys. Chem. B*	114, 16666-16675	2010
K.R.S. Chandrakumar					
69	Alister J. Page, K. R. S. Chandrakumar, Stephan Irle, and Keiji Morokuma	SWNT Nucleation from Carbon-Coated SiO_2 Nanoparticles via a Vapor-Solid-Solid Mechanism	*J. Am. Chem. Soc.*	133 (3), 621–628	2011
70	Alister J. Page, K. R. S. Chandrakumar, Stephan Irle, and Keiji Morokuma	Do SiO_2 and Carbon-Doped SiO_2 Nanoparticles Melt? Insights from QM/MD Simulations and Ramifications Regarding Carbon Nanotube Growth	*Chem. Phys. Lett.*	In Press	2011
Parameswaran Pattiyil					
71	Back, O.; Donnadieu, B.; Parameswaran, P.; Frenking, G.; Bertrand. G.	Isolation of Crystalline Carbene-Stabilized P2-Radical Cations and P2-Dications	*Nature Chemistry*	2, 369-373	2010

№	Authors	Title	Journal	Volume(Number), first page to last page	year
72	Parameswaran, P.; Frenking, G.	Chemical Bonding in Transition Metal Complexes with Beryllium Ligands $[(PMe_3)^2M\text{-}BeCl_2]$, $[(PMe_3)^2M\text{-}BeClMe]$ and $[(PMe_3)^2M\text{-}BeMe_2]$ (M = Ni, Pd, Pt)	*J. Phys. Chem. A*	114, 8529-8535	2010
Hong-yan Xaio					
73	Hongyan Xiao, Atoshi Maeda and Keiji Morokuma	Excited-state roaming dynamics in photolysis of a nitrate radical	*J. Phys. Chem. ett.*	2, 934-938	2011
Lina Ding					
74	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.*	75, 1630-1636	2010
75	Ganglong Cui, Lina Ding, Feng Feng, Yajun Liu, and Weihai Fang	Insights into Mechanistic Photochemistry of Urea	*J. Chem. Phys.*	132, 194308	2010
Lung Wa Chung					
76	Lung Wa Chung, Xin Li, Hiroshi Sugimoto, Yoshitsugu Shiro and Keiji Morokuma	ONIOM Study on a Missing Piece in Our Understanding of Heme Chemistry: Bacterial Tryptophan 2,3-Dioxygenase with Dual Oxidants	*J. Am. Chem. Soc.*	132(34), 11993-12005	2010
77	Kyoko Nozaki, Shuhei Kusumoto, Shusuke Noda, Takuya Kochi, Lung Wa Chung, and Keiji Morokuma	Why Did Incorporation of Acrylonitrile to a Linear Polyethylene Become Possible? Comparison of Phosphine−Sulfonate Ligand with Diphosphine and Imine−Phenolate Ligands in the Pd-Catalyzed Ethylene/ Acrylonitrile Copolymerization	*J. Am. Chem. Soc.*	132(45), 16030-16042	2010
78	Xin Li, Lung Wa Chung, Hideaki Mizuno, Atsushi Miyawaki, and Keiji Morokuma	Primary Events of Photodynamics in Reversible Photoswitching Fluorescent Protein Dronpa	*J. Phys. Chem. Lett.*	1(23), 3328-3333	2010
79	Xin Li, Lung Wa Chung, Hideaki Mizuno, Atsushi Miyawaki, and Keiji Morokuma	Competitive Mechanistic Pathways for Green-to-Red Photoconversion in the Fluorescent Protein Kaede: A Computational Study	*J. Phys. Chem. B*	114 (49), 16666-16675	2010
80	Akifumi Nakamura, Kagehiro Munakata, Shingo Ito, Takuya Kochi, Lung Wa Chung, Keiji Morokuma, and Kyoko Nozaki	Pd-Catalyzed Copolymerization of Methyl Acrylate with Carbon Monoxide: Structures, Properties and Mechanistic Aspects toward Ligand Design	*J. Am. Chem. Soc.*	133 (17), 6761-6779	2011
Galina Petrova					
81	Galina P. Petrova, Georgi N. Vayssilov, Notker Rösch	Redox behavior of small metal clusters with respect to hydrogen. The effect of the cluster charge from density functional results	*Phys. Chem. Chem. Phys.*	12, 11015-11020	2010
82	Petko St. Petkov, Galina P. Petrova, Georgi N. Vayssilov, Notker Rösch	Saturation of Small Supported Metal Clusters by Adsorbed Hydrogen. A Computational Study on Tetrahedral Models of Rh_4, Ir_4, and Pt_4	*J. Phys. Chem. C*	114, 8500-8506	2010
83	Miroslav A. Rangelov, Galina P. Petrova, Vihra M. Yomtova, Georgi N. Vayssilov	Hierarchical Approach to Conformational Search and Selection of Computational Method in Modeling the Mechanism of Ester Ammonolysis	*J. Mol. Graph. Modelling*	29, 246–255	2010

№	Authors	Title	Journal	Volume(Number), first page to last page	year
84	Miroslav A. Rangelov, Galina P. Petrova, V ihra M. Yomtova, Georgi N. Vayssilov	Catalytic Role of Vicinal OH in Ester Aminolysis - Proton Shuttle versus Hydrogen-Bonds Stabilization	*J. Org. Chem.*	75, 6782-6792	2010
85	Notker Rösch, Galina P. Petrova, Petko St. Petkov, Alexander Genest, Sven Krüger, Hristiyan A. Aleksandrov, Georgi N. Vayssilov	Impurity Atoms on Small Transition Metal Clusters. Insights from Density Functional Model Studies	*Topics in Catalysis*	54, 363-377	2011
Wilfredo Credo Chung					
86	Wilfredo Credo Chung, Shinkoh Nanbu, Toshimasa Ishida	Nonadiabatic ab Initio Dynamics of a Model Protonated Schiff Base of 9-cis Retina	*J. Phys. Chem. A*	114(32), 8190-8201	2010
岩城　貴史					
87	Takafumi Iwaki	Effect of internal flow on the photophoresis of a micron-sized liquid droplet	*Phys. Rev. E*	81(6), 066315-(1-13)	2010
池野　豪一					
88	Mizoguchi Teruyasu, Weine Olovsson, Hidekazu Ikeno and Isao Tanaka	Theoretical ELNES using one-particle, and multi-particle calculations	*Micron*	41, 695-709	2010
89	P. S. Miedema, H. Ikeno, and F. M. F. de Groot	First principles multiplet calculations of the calcium $L_{2,3}$ x-ray absorption spectra of CaO and CaF_2	*J. Phys.: Condens. Matter*	23, 145501	2011
90	Hidekazu Ikeno, Teruyasu Mizoguchi, and Isao Tanaka	Ab initio charge transfer multiplet calculations on the $L_{2,3}$ XANES and ELNES of 3d transition metal oxides	*Phys. Rev. B*	83, 155107	2011
義永　那津人					
91	Hong-Ren Jiang, Natsuhiko Yoshinaga, and Masaki Sano	Active Motion of Janus Particle by Self-thermophoresis in Defocused Laser Beam	*Physical Review Letters*	105, 268302(1-4)	2010
92	Natsuhiko Yoshinaga, Jean-Francois Joanny,. Jacques Prost, and Philippe Marcq	Polarity patterns of stress fibers	*Physical Review Letters*	105, 238103(1-4)	2010

京都大学福井謙一記念研究センター　年報　2010

2011 年 12 月 発行

発行人　田中　　功

編　者　石 田 俊 正

発行所　京都大学福井謙一記念研究センター
（京都市左京区高野西開町 34-4）

印刷所　有限会社　津田印刷
（京都市左京区岩倉中大鷺町 14）

Fukui Institute for Fundamental Chemistry Kyoto University

Annual Report 2010