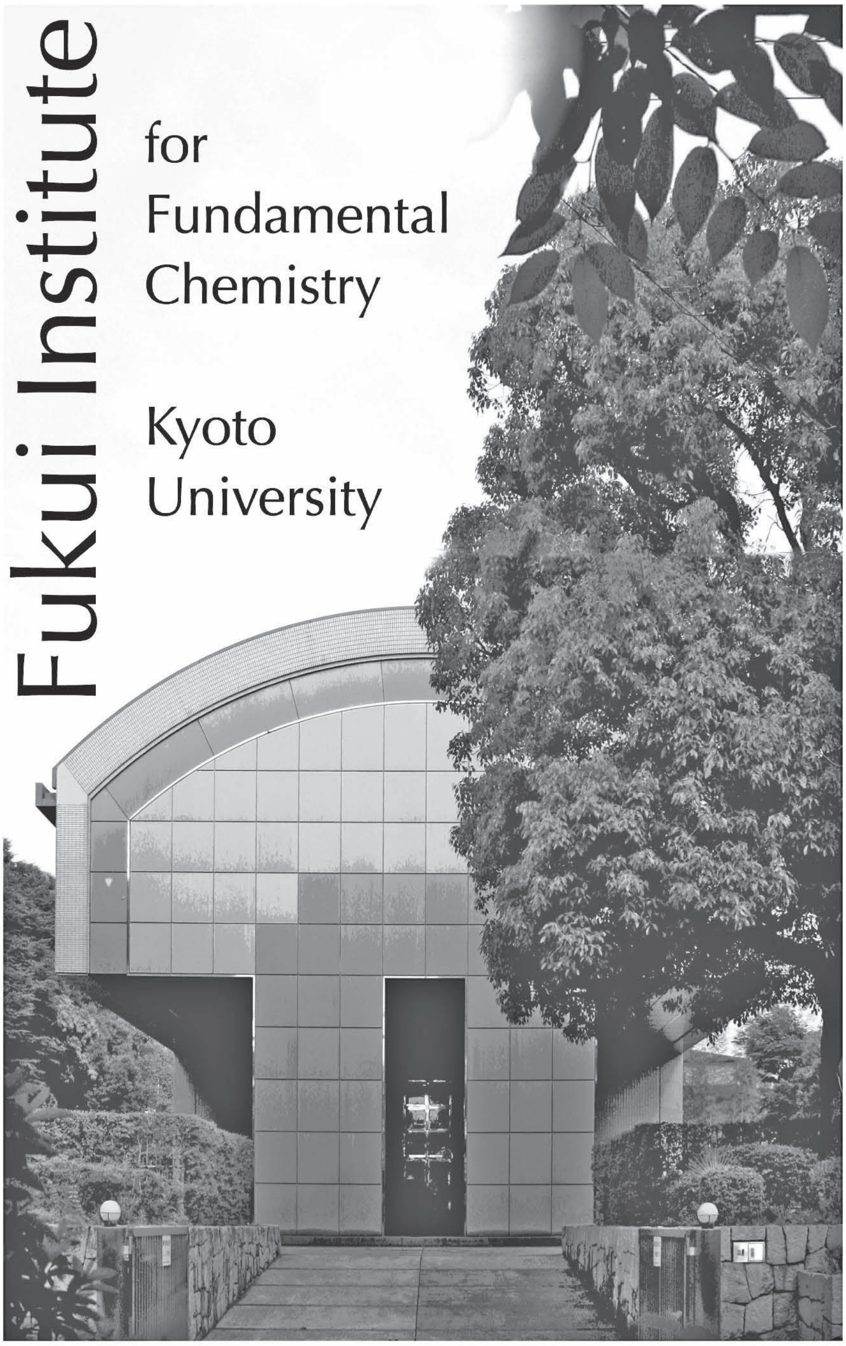
年　報
2018



京都大学
福井謙一記念研究センター

はじめに

2018年度の京都大学福井謙一記念研究センターの活動をまとめた年報をお届けします。本センターは、京都大学本部構内の北、約１キロの高野川沿いの静かな住宅街に独立して位置しております。専任教員は理論研究部門と総合研究部門に１名ずつを持っているに過ぎませんが、センター長のほか副センター長とスーパーバイザーとして工学研究科、理学研究科、化学研究所所属の12名の教員にご協力頂いており、このメンバーが運営委員会を構成しています。そして優れた博士研究員に研究活動の機会を与える制度を持っており、若手研究者が国際的な雰囲気の中で日夜研究にいそしんでいます。福井センターフェローと呼ばれる博士研究員はセンターの雇用で、自分自身のアイデアで一定期間、自由闊達に研究できる身分を保証しています。

2018年度は福井謙一先生の生誕百年にあたる大きな節目となりました。前年より実施委員会を中心に準備を進め、2018年10月12日には彬子女王殿下御臨席のもと、メモリアルシンポジウム及び記念式典を百周年時計台記念館百周年記念ホールにおいて挙行しました。メモリアルシンポジウムでは、福井謙一先生とノーベル化学賞を同時受賞された米国コーネル大学のロアルド・ホフマン先生、筑波大学名誉教授の白川英樹先生、化学史学会前会長の古川安先生にご講演頂き、多数の参加者を迎え盛況のうちに開催することができました。翌13日には、本センターにてサテライトシンポジウムを開催しました。2018年10月３日～12月９日には京都大学総合博物館にて「京都大学総合博物館2018年度企画展　応用をやるには、基礎をやれ　ノーベル賞化学者を育んだ教室」を開催し、多数の来場者を迎えることができました。

さらに　記念事業の一環として、企業研究者のための基礎化学研修プログラム（喜多－福井プロジェクト）を開設しました。喜多源逸先生は、福井謙一先生が“終生の師”と呼び、「応用をやるなら、基礎をやれ」、「数学が得意なら化学をやれ」という言葉で福井先生が化学の道に進むきっかけを作られた方であり、また本学工学部化学系における基礎重視の学風を築かれた方です。このプロジェクトは、喜多先生に源を発するこの伝統を再認識し、産業への応用も見据えた基礎化学・理論化学を広く展開できる技術者・研究者の育成に貢献しようとするものです。

本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、東京大学、名古屋大学、分子科学研究所の教授になるなど、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年の福井先生のご逝去の後、2002年に京都大学に寄贈され、福井謙一記念研究センターとなり、現在に至っております。本学の部局となった後、森島　績、中辻　博、榊　茂好、田中　功、田中　一義、赤木　和夫、田中　勝久の各先生にセンター長としてご指導を頂きました。

本センターでは、2006年９月に福井謙一記念研究部第一のリサーチリーダーとして諸熊奎治先生を米国エモリー大学から招聘しました。諸熊先生は、2012年にシニアリサーチフェローに就任され、この年の11月には、複雑分子系の理論研究の発展に多大な貢献をしたとして、文化功労者の顕彰を受けられました。また、2015年からはFIFCリサーチフェローとして研究ならびに若手人材育成にご尽力下さいました。諸熊先生は理論化学・計算化学の領域で多くの学術的業績を挙げられるとともに、我が国の量子化学の分野を牽引され、多数の研究者を育成されました。2009年度には福井謙一記念研究部第二を設置し、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。大峯先生は2010年４月に分子科学研究所長に転出され、その後任として、2011年４月に京都大学物質―細胞統合システム拠点（iCeMS）特任教授の榊茂好先生を研究部第二のリサーチリーダーとして招聘しました。榊先生は、遷移金属化合物や類縁化合物に関する研究で顕著な業績を挙げておられ、現在はｄ電子複合系の理論化学に関する研究を推進しておられます。

2012年にはシニアリサーチフェローとして永瀬茂先生（分子科学研究所名誉教授）を招聘しました。永瀬先生は、望む構造、物性、機能を持つ分子を自在に組み立てて思うように反応させる理論と計算およびコンピューターシミュレーションの開発において顕著な業績を挙げられました。2015年からはFIFCリサーチフェローとして高周期典型元素と遷移金属元素化学種の理論化学に関する研究を進めておられます。同じ年に、シニアリサーチフェローとして田中一義先生（京都大学名誉教授）を招聘しました。田中一義先生は導電性や磁性を有する有機化合物など量子機能材料に関する物理化学的研究において優れた多くの業績を挙げておられ、現在は元素ブロックを有する分子・高分子の理論化学に関する研究を展開されています。さらに2016年には、化学反応電子動力学の基礎理論研究において著名な高塚和夫先生（東京大学名誉教授）をリサーチリーダーとして招聘しました。センターでは非断熱電子動力学理論による化学反応の解析に関する研究を推進しておられます。

2018年２月には理論研究部門の専任教授として、佐藤徹先生が着任されました。佐藤徹先生は振電相互作用に関する研究、特に動的ヤーンテラー効果や振電相互作用を解析・制御する振電相互作用密度を用いた有機EL素子などの機能性分子材料の理論設計を行っています。佐藤徹先生の研究室は、工学研究科分子工学専攻の協力講座（分子材料科学講座　量子分子科学分野）としても位置付けられ、大学院生、学部４回生が配属されて、研究を進めています。10月には、リサーチダイレクターとして平尾公彦先生（国立研究開発法人理化学研究所計算科学研究センター上級研究員）を招聘いたしました。

私共は、センターが若手研究者の登竜門となることを期待しています。実際に、センターの博士研究員であった多くの方々が、現在、国内外の大学、研究機関で活躍しておられます。2016年には、化学の将来の発展のために若手研究者の育成の大切さを説いておられた福井博士の遺志を汲み、基礎化学・理論化学の分野で顕著な研究業績を挙げた若手研究者を顕彰する「福井謙一奨

励賞」を創設し、「理論化学研究に立脚した量子干渉現象の分子エレクトロニクスへの展開に関する研究」に対して辻雄太先生（九州大学分子システムデバイス国際リーダー教育センター助教）に第１回同奨励賞が授与されました。第２回(2017年)は､「第一原理波動関数理論の固体への展開：量子化学と固体電子論の融合」で越智正之先生（大阪大学大学院理学研究科助教）に、第３回（2018年）は「縮退と擬縮退の包括的理解に向けた新たな数理科学の開拓に関する研究」で春田直樹先生（東京工業大学化学技術創成研究特任助教）に授与されました。また次世代を担う若手研究者の育成を図るため、福井センター基金も開設いたしました。

本センターは、国際活動も活発で、2005年よりチェコおよびスロバキアと理論化学・計算化学シンポジウムを定期的に開催しております。2011年には国内外（主にドイツ、東欧、中国、韓国）から第一線の研究者を招き､第１回福井センター理論化学･計算化学国際シンポジウムを開催しました。こうした国際連携活動をさらに活性化するという観点から、2016年２月に国際学術連携研究室（2016年12月に国際連携インターディシプリナリー研究推進室と改組）を設置し、その運営上必要となるコーディネーター役として、特定助教１名を配置しました。本センターは、今後も理論化学・計算化学分野におけるわが国の研究拠点の役割を果たし、国際連携活動を展開して行きたいと考えております。

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

さらに社会貢献活動の一環として、2011年が福井先生のノーベル化学賞受賞30周年にあたるため、これを節目として本センター玄関ロビーに先生ゆかりの文物の展示コーナーを設置しました。コーナーでは先生が使用された机、椅子、ノーベル賞メダル・賞状（複製)、研究ノート・メモ、写真などを展示し、常設展示として一般に公開しています。2018年には、前年ご逝去された諸熊先生のゆかりの文物の展示コーナーも加わりました。

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

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

2019年12月

京都大学福井謙一記念研究センター長
佐藤啓文

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Ⅴ　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/AnnualReport2018.pdf）

Ⅰ　専任教員・スーパーバイザー

1．教員組織

平成３０年度

職名		氏名	備考
センター長		田中勝久	工学研究科 材料化学専攻
副センター長		佐藤啓文	工学研究科 分子工学専攻
副センター長		林重彦	理学研究科 化学専攻
副センター長		(欠員中)	
協議員	工学研究科長	大嶋正裕	工学研究科 化学工学専攻
	理学研究科長	平野丈夫	理学研究科 生物科学専攻
	化学研究所長	辻井敬亘	化学研究所 材料機能化学研究系
総合研究部門 スーパーバイザー	教授	古賀毅	工学研究科 高分子化学専攻
	教授	跡見晴幸	工学研究科 合成・生物化学専攻
	教授	佐々真一	理学研究科 物理学・宇宙物理学専攻
	教授	山本潤	理学研究科 物理学・宇宙物理学専攻
	教授	渡辺宏	化学研究所 分子レオロジー
理論研究部門 スーパーバイザー	教授	宇田哲也	工学研究科 材料工学専攻
	教授	田中庸裕	工学研究科 分子工学専攻
	教授	谷村吉隆	理学研究科 化学専攻
	教授	山本量一	工学研究科 化学工学専攻
	教授	高田彰二	理学研究科 生物科学専攻
総合研究部門	准教授	(欠員中)	
理論研究部門	教授	佐藤徹	専任 (工学研究科分子工学専攻協力講座)
国際連携インターディシプリナリー研究推進室	特定助教	西本佳央	専任
平尾グループ	リサーチダイレクター	平尾公彦	研究員：平成 30. 10. 1-
永瀬グループ	FIFC リサーチフェロー	永瀬茂	研究員
田中グループ	FIFC リサーチフェロー	田中一義	研究員
榊グループ	シニアリサーチフェロー	榊茂好	研究員
高塚グループ	リサーチリーダー	高塚和夫	研究員
榊グループ	研究員	北浦和夫	研究員

２．教員プロフィール

⑴　センター長

【氏名（ふりがな）】	田中　勝久　（たなか　かつひさ）
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【研究分野】	無機固体化学
【現在の研究課題】	新規無機固体・材料の合成と磁気的・誘電的・光学的性質
【研究内容キーワード】	酸化物、金属、磁気的性質、誘電的性質、光学的性質
【学歴】	1984 年 3 月　京都大学工学部工業化学科卒業 1986 年 3 月　京都大学大学院工学研究科工業化学専攻修士課程修了
【学位】	1991 年 3 月　京都大学工学博士
【略歴】	1986 年 4 月　三重大学工学部助手 1989 年 4 月　京都大学工学部助手 1999 年 7 月　京都工芸繊維大学工芸学部助教授 2004 年 4 月 京都大学大学院工学研究科教授 2019 年 4 月 京都大学国際高等教育院教授（工学研究科併任）
【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、日本金属学会、Materials Research Society、Optical Society of America
【学会活動】	日本セラミックス協会理事、粉体粉末冶金協会理事
【主な著書、学術論文】 （過去５年以内）	(1) T. Yajima, F. Takeiri, K. Aidzu, H. Akamatsu, K. Fujita, M. Ohkura, W. Yoshimune, S. Lei, V. Gopalan, K. Tanaka, C. M. Brown, M. A. Green, T. Yamamoto, Y.i Kobayashi, and H. Kageyama, “A labile hydride strategy to synthesize heavily nitridized BaTiO$_3$”, *Nat. Chem.* **7** (2015) 1017. (2) K. Fujita, T. Kawamoto, I. Yamada, O. Hernandez, N. Hayashi, H. Akamatsu, W. Lafargue-Dit-Hauret, X. Rocquefelte, M. Fukuzumi, P. Manuel, A. J. Studer, C. Knee, and K. Tanaka, “LiNbO$_3$-type InFeO$_3$: Room-temperature polar magnet without second-order Jahn-Teller active ions”, *Chem. Mater.* **28** (2016) 6644. (3) Y. Nakatsuka, K. Pollok, T. Wieduwilt, F. Langenhorst, M. A. Schmidt, K. Fujita, S. Murai, K. Tanaka, and L. Wondraczek, “Giant Faraday rotation through Fe^{0}_{n} states in superparamagnetic FeO-SiO$_2$ vitreous films”, *Adv. Sci.* (2017) 1600299. (4) T. Sawai, Y. Yamaguchi, N. Kitamura, T. Date, S. Konishi, K. Taga, and K. Tanaka, “Pulse-based electron spin transient nutation measurement of BaTiO$_3$ fine particle: Identification of controversial signal around g=2.00”, *Appl. Phys. Lett.* **112** (2018) 202902. (5) S. Yoshida, H. Akamatsu, R. Tsuji, O. Hernandez, H. Padmanabhan, A. S. Gupta, A. Gibbs, K. Mibu, S. Murai, J. M. Rondinelli, V. Gopalan, K. Tanaka, and K. Fujita, “Hybrid improper ferroelectricity in (Sr,Ca)$_3$Sn$_2$O$_7$ and beyond: universal relationship between ferroelectric transition temperature and tolerance factor in n = 2 Ruddlesden−Popper phases”, *J. Am. Chem. Soc.* **140** (2018) 15690. (6) R. Kamakura, S. Murai, Y. Yokobayashi, K. Takashima, M. Kuramoto, K. Fujita, and K. Tanaka, “Enhanced photoluminescence and directional white light generation by plasmonic array”, *J. Appl. Phys.* **124** (2018) 213105. (7) H. Akamatsu, K. Fujita, T. Kuge, A. S. Gupta, J., M Rondinelli, I. Tanaka, K. Tanaka, and V. Gopalan, “Unexpected A-site cation size effect on oxygen octahedral rotations in acentric Ruddlesden-Popper alkaline rare-earth titanates”, *Phys. Rev. Mater.* **3** (2019) 065001. (8) 田中勝久，固体化学 第２版，東京化学同人 (2019).
【学術関係の受賞など】	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)、Award of the Outstanding Papers Published in the JCerSJ in 2013（2013 年）

⑵　副センター長

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【研究分野】	理論化学・量子化学・統計力学
【現在の研究課題】	理論化学・物理化学
【研究内容キーワード】	化学反応・自己集合・溶媒和
【最終学歴】	1996 年 5 月京都大学理学研究科化学専攻博士後期課程修了
【学位】	1996 年 5 月京都大学博士（理学）
【略歴】	1996 年 8 月　岡崎国立共同研究機構分子科学研究所助手 2002 年 5 月京都大学工学研究科講師 2004 年 5 月京都大学工学研究科助教授 2010 年 7 月京都大学工学研究科教授
【在外研究歴】	2004 年 6 月 -2004 年 12 月　連合王国 Oxford 大学 PTCL 訪問研究員（Paul A. Madden 教授）
【所属学会】	日本化学会、分子科学会、理論化学会、溶液化学研究会
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【主な著書、学術論文】 （過去 5 年以内）	1. Satoshi Takahashi, Yuya Sasaki, Shuichi Hiraoka, and Hirofumi Sato, “A stochastic model study on the self-assembly process of a Pd”, Phys. Chem. Chem. Phys., 21, 6341-6347 (2019). 2. Yoshihiro Matsumura, Satoru Iuchi, Shuichi Hiraoka, and Hirofumi Sato, “Chiral effects on the final step of an octahedron-shaped coordination capsule self-assembly” Phys. Chem. Chem. Phys., 20, 7383-7386 (2018). 3. Maxim Shishkin, Shinichi Kumakura, Syuhei Sato, Kei Kubota, Shinichi Komaba, and Hirofumi Sato, “Unraveling the Role of Doping in Selective Stabilization of $NaMnO_2$ Polymorphs: Combined Theoretical and Experimental Study” Chem. Materials, 30, 1257 (2018). 4. Kento Kasahara and Hirofumi Sato, “Dynamics theory for molecular liquids based on an interaction site model” Phys. Chem. Chem. Phys. 19, 27917-27929 (2017). 5. Hirofumi Sato, “A modern solvation theory: quantum chemistry and statistical chemistry” Phys. Chem. Chem. Phys. 15(20), 7450-7465 (2013).
【学術関係の受賞】	日本化学会・進歩賞（2002 年） 分子構造総合討論会奨励賞（2006 年） 公益信託分子科学研究奨励森野基金（2008 年） 溶液化学研究会学術賞（2009 年）

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【主な著書、学術論文】（過去 5 年以内）	1. An atomistic model of a precursor state of light-induced channel opening of channelrhodopsin. Cheng Cheng, Motoshi Kamiya, Mizuki Takemoto, Ryuichiro Ishitani, Osamu Nureki, Norio Yoshida*, and Shigehiko Hayashi*, *Biophys. J.*, **115**, 1281-1291 (2018). 2. Atomistic modeling of alternating access of a mitochondrial ADP/ATP membrane transporter with molecular simulations. Koichi Tamura and Shigehiko Hayashi*, *PLOS ONE*, **12**, e0181489 (2017). 3. Photoactivation intermediates of a G-protein coupled receptor rhodopsin investigated by a hybrid molecular simulation. Motoshi Kamiya and Shigehiko Hayashi*, *J. Phys. Chem. B,* **121**, 3842-3852 (2017). 4. Molecular mechanism of wide photoabsorption spectral shifts of color variants of human cellular retinol binding protein II. Cheng Cheng, Motoshi Kamiya, Yoshihiro Uchida, Shigehiko Hayashi*, *J. Am. Chem. Soc.*, **137**, 13362-13370 (2015) 5. Atomistic design of microbial opsin-based blue-shifted optogenetics tools. Hideaki E. Kato, Motoshi Kamiya, Seiya Sugo, Jumpei Ito, Reiya Taniguchi, Ayaka Orito, Kunio Hirata, Ayumu Inutsuka, Akihiro Yamanaka, Andres D. Maturana, Ryuichiro Ishitani, Yuki Sudo, Shigehiko Hayashi*, and Osamu Nureki*, *Nat. Commun.*, **6**, 7177 (2015)

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【主な著書、学術論文】（過去 5 年以内）	1. Molecular simulation of structures and mechanical properties of nanocomposite networks consisting of disk-shaped particles and polymers, T. Furuya, T. Koga, *SOFT MATTER*, **41**, 8293-8305 (2018) 2. Molecular simulation of structure formation and rheological properties of mixtures of telechelic and monofunctional associating polymer, T. Furuya, T. Koga, *JOURNAL OF POLYMER SCIENCE, PART B: POLYMER PHYSICS*, **56**, 1251-1264 (2018) 3. Theoretical study of inclusion complex formation of cyclodextrin and single polymer chain, T. Furuya, T. Koga, *POLYMER*, **131**, 193-201 (2017) 4. Physical gelation of supramolecular hydrogels cross-linked by metal-ligand interactions: Dynamic light scattering and microrheological studies, H. Ozaki, T. Indei, T. Koga, T. Narita, *POLYMER*, **128**, 363-372 (2017) 5. Statistical Thermodynamic Theory of Heat-Induced Gelation of Aqueous Methylated Polyrotaxane Solutions, H. Kojima, T. Koga, *MACROMOLECULES*, **49**, 7015-7024 (2016)

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【主な著書、学術論文】 （過去 5 年以内）	1. Nagata R, Fujihashi M, Sato T, Atomi H, Miki K. “Identification of a pyrophosphate-dependent kinase and its donor selectivity determinants”, *Nature Commun*. **9**, 1765, (2018). 2. Nunoura T, Chikaraishi Y, Izaki R, Suwa T, Sato T, Harada T, Mori K, Kato Y, Miyazaki M, Shimamura S, Yanagawa K, Shuto A, Ohkouchi N, Fujita N, Takaki Y, Atomi H, Takai K. “A primordial and reversible TCA cycle in a facultatively chemolithoautotrophic thermophile”, *Science* **359**, 559-563, (2018). 3. Zheng RC, Hachisuka SI, Tomita H, Imanaka T, Zheng YG, Nishiyama M, Atomi H. “An ornithine ω-aminotransferase required for growth in the absence of exogenous proline in the archaeon Thermococcus kodakarensis”. *J. Biol. Chem.* **293**, 3625-3636, (2018). 4. Makino Y, Sato T, Kawamura H, Hachisuka SI, Takeno R, Imanaka T, Atomi H. “An archaeal ADP-dependent serine kinase involved in cysteine biosynthesis and serine metabolism”, *Nature Commun*. **7**, 13446, (2016). 5. Aono R, Sato T, Imanaka T, Atomi H. “A pentose bisphosphate pathway for nucleoside degradation in Archaea”, *Nature Chem. Biol.* **11**(5):355-360, 2015. 6. Watanabe S, Kawashima T, Nishitani Y, Kanai T, Wada T, Inaba K, Atomi H, Imanaka T, Miki K. “Structural basis of a Ni acquisition cycle for [NiFe] hydrogenase by Ni-metallochaperone HypA and its enhancer”. *Proc. Natl. Acad. Sci. USA* **112**(25), 7701-7706, (2015).
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【学会活動】	2017.4-2018.3 日本物理学会領域１１代表
【主な著書、学術論文】 （過去 5 年以内）	1.Liquid-gas transitions in steady heat conduction_ Naoko Nakagawa, Shin-ichi Sasa Phys. Rev. Lett. 119, 260602/1-6(2017) 2. Thermodynamic entropy as a Noether invariant S.-I. Sasa, Yuki Yokokura Phys. Rev. Lett 116 140601/1-140601/6（2016） 3.Replica symmetry breaking in trajectories of a driven Brownian particle Masahiko Ueda, S.-I. Sasa Phys. Rev. Lett 115 080605/1-080605/5（2015） 4.Derivation of Hydrodynamics from the Hamiltonian Description of Particle Systems S.-I. Sasa Phys. Rev. Lett 112 100602/1-100602/5（2014） 5. Computation of large deviation statistics via iterative measurement-and-feedback procedure T. Nemoto, S.-I. Sasa Phys. Rev. Lett 112 090602/1-090602/5（2014）

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【主な著書、学術論文】（過去 5 年以内）	S. L. Morelly, L. Palmese, H. Watanabe, and N. J. Alvarez, “Effect of Finite Extensibility on Nonlinear Extensional Rheology of Polymer Melts”, *Macromolecules*, *52*, 915-922 (**2019**). Y. Matsumiya, H. Watanabe, Y. Masubuchi, Q. Huang, and O. Hassager, “Nonlinear Elongational Rheology of Unentangled Polystyrene and Poly(p-tert-butyl styrene) Melts”, *Macromolecules*, *51*, 9710-9729 (**2018**). H. Watanabe, Y. Matsumiya, and Y. Kwon, “Viscoelastic and Dielectric Relaxation of Reptating Type-A Chains Affected by Reversible Head-to-Head Association and Dissociation”, *Macromolecules*, *51*, 6476-6496 (**2018**). S. Wu, X. Cao, Z. Zhang, Q. Chen, Y. Matsumiya, and H. Watanabe, “Molecular Design of Highly-Stretchable Ionomers”, *Macromolecules*, *51*, 4735-4746 (**2018**). K. I. S. Mongcopa, M. Tyagi, J. P. Mailoa, G. Samsonidze, B. Kozinsky, S. A. Mullin, D. A. Gribble, H. Watanabe and N. P. Balsara, “Relationship between Segmental Dynamics Measured by Quasi-Elastic Neutron Scattering and Conductivity in Polymer Electrolytes”, *ACS Macro Lett.*, *7*, 504-508 (**2018**).

H. Watanabe, Y. Matsumiya, and Y. Kwon, “Dynamics of Rouse Chains undergoing Head-to-Head Association and Dissociation: Difference between Dielectric and Viscoelastic Relaxation”, *J. Rheol.*, *61*, 1151-1170 (**2017**).

Y. Doi, A. Matsumoto, T. Inoue, T. Iwamoto, A. Takano, Y. Matsushita, Y. Takahashi, and H. Watanabe, “Re-examination of terminal relaxation behavior of high-molecular-weight ring polystyrene melts”, *Rheol. Acta*, *56*, 567-581 (**2017**).

O. M. Kwon, H. Watanabe, K. H. Ahn, and S. J. Lee, “Interplay between structure and property of graphene nanoplatelet networks formed by an electric field in a poly(lactic acid) matrix”, *J. Rheol.*, *61*, 291-303 (**2017**)

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S. Ankiewicz, H. Orbey, H. Watanabe, H. Lentzakis, and J. Dealy, On the use of continuous relaxation spectra to characterize model polymers”, *J. Rheol.*, *60*, 1115-1120 (**2016**)

Y. Matsumiya and H. Watanabe , “Nonlinear Stress Relaxation of Miscible Polyisoprene/Poly(p-tert-butyl Styrene) Blends in Pseudo-monodisperse State”, *Macromolecules*, *49*, 4544-4556 (**2016**).

Youngdon Kwon, Yumi Matsumiya, and Hiroshi Wtanabe, Viscoelastic and Orientational Relaxation of Linear and Ring Rouse Chains undergoing Reversible End-Association and Dissociation”, *Macromolecules*, *49,* 3593-3607 (**2016**).

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H. Watanabe, Y. Matsumiya , Y. Masubuchi ,O. Urakawa, and T. Inoue, “Viscoelastic Relaxation of Rouse Chains undergoing Head-to-Head Association and Dissociation: Motional Coupling through Chemical Equilibrium”, *Macromolecules, 48, 3014–3030* (**2015**).

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【在外研究歴】	2002年5月 -2005年3月　米国カリフォルニア工科大学（Sossina M. Haile教授）
【所属学会】	資源・素材学会、日本金属学会、電気化学会、日本固体イオニクス学会
【学会活動】	資源・素材学会 会報誌 編集幹事長など
【主な著書、学術論文】（過去5年以内）	Thermodynamic maximum of Y doping level in Barium Zirconate in co-sintering with NiO,Katsuhiro Ueno, Naoyuki Hatada, Donglin Han, and Tetsuya Uda *Journal of Materials Chemistry A*, **7**, (2019), 7232-7241 Characteristic Microstructure Underlying the Fast Hydration-dehydration Reation of β-La$_2$(SO$_4$)$_3$:”Fine Platy Joints” with “Loose Grain Boundaries”, Kunihiko Shizume, Naoyuki Hatada, Kazuaki Toyoura, Tetsuya Uda *Journal of Materials Chemistry A*, **6**, (2018), 24956-24964 The Best Composition of an Y-doped BaZrO$_3$ Electrolyte: Selection Criteria from Transport Properties, Microstructure,and Phase Behavior, Donglin Han and Tetsuya Uda, *Journal of Materials Chemistry A*, **6**, (2018), 18571-185824 Preferential Proton Conduction along Three-Dimensional Dopant Network in Yttrium-Doped Barium Zirconate:A First-Principles Study,Kazuaki Toyoura, Weijie Meng, Donglin Han, and Tetsuya Uda,*Journal of Materials Chemistry A*, **6**, (2018), 22721-22730 Discovery of Rapid and Reversible Water Insertion in Rare Earth Sulfates: A New Process for Thermochemical Heat Storage,Naoyuki Hatada, Kunihiko Shizume, Tetsuya Uda, *Advanced Materials*, **2**9, (2017), 1606569
【学術関係の受賞】	2014　第10回（平成25年度）日本学術振興会賞　など

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【現在の研究課題】	固体と接触したナノ粒子・光触媒による人工光合成
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【所属学会】	触媒学会，日本化学会，石油学会，アメリカ化学会，日本 XAFS 研究会，英国王立化学会
【主な著書、学術論文】（過去 5 年以内）	1. NO_x Oxidation and Storage Properties of a Ruddlesden-Popper Type $Sr_3Fe_2O_{7-\delta}$ Layered Perovskite Catalyst K. Tamai, S. Hosokawa, H. Okamoto, H. Asakura, K. Teramura, T. Tanaka, *ACS Appl. Mater. Interfaces,* 2019, **11(30)**, 26985-26993. 2. In Situ Spectroscopy-guided Engineering Rhodium Single-Atom Catalysts for CO Oxidation M. J. Hülsey, B. Zhang, Z. Ma, H. Asakura, D. N. Do, W. Chen, T. Tanaka, P. Zhang, Z. Wu, N. Yang, *Nature Communications,* 2019,**10**:1330. 3. Efficient Oxygen Storage Property of Sr-Fe Mixed Oxide as Automotive Catalyst Support K. Beppu, S. Hosokawa, H. Asakura, K. Teramura, T. Tanaka *J. Mater. Chem. A,* 2019, **7**, 1013-1021. 4. Photocatalytic Conversion of Carbon Dioxide by $A_2BTa_5O_{15}$ (A= Sr, Ba; B= K, Na) Using Ammonia as an Efficient Sacrificial Reagent Z. Huang, S. Yoshizawa, K. Teramura, H. Asakura, S. Hosokawa, T. Tanaka *ACS Sustainable Chem. Eng.,* 2018, **6(7),** 8247-8255. 5. Catalytic Amino Acid Production from Biomass-derived Intermediates W. Deng, Y. Wang, S. Zhang, K. M. Gupta, M. J. Hülsey, H. Asakura, L. Liu, Y. Han, E. M. Karp, G. T. Beckham, P. J. Dyson, J. Jiang, T. Tanaka, Y. Wang, N. Yan, *PNAS,* 2018, **115(20)**, 5093-5098. 6. Dynamic Behavior of Rh Species in Rh/Al_2O_3 Model Catalyst during Three-Way Catalytic Reaction: An Operando Xray Absorption Spectroscopy Study H.Asakura, S. Hosokawa, T. Tanaka *et al.*, *J. Am. Chem. Soc.,* 2018, **140**, 176-184. 7. Efficient Photocatalytic Carbon Monoxide Production from Ammonia and Carbon Dioxide by the Aid of Artificial Photosynthesis Z. Huang, K. Teramura, H. Asakura, S. Hosokawa, T. Tanaka *Chemical Science,* 2017, **8**, 5797-5801. 8. Strong Metal-Support Interaction between Pt and SiO_2 Following High-Temperature Reduction: A Catalytic Interface for Propane Dehydrogenation L. Deng, H. Miura, T. Shishido, S. Hosokawa, K. Teramura, T. Tanaka *Chemical Communications,* 2017, **53**, 6937-6940. 9. Thermally Stable Single Atom Pt/m-Al_2O_3 for the Selective Hydrogenation and CO Oxidation Z. Zhang, Y. Zhu, H. Asakura, B. Zhang, J. Zhang, M. Zhou, Y. Han, T. Tanaka, A.-Q. Wang, T. Zhang, N. Yan, *Nature Communications*, 2017, 8:16100.

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【学術関係の受賞】	2002 年　分子科学研究奨励森野基金 2012 年　フンボルト賞　（ドイツ） 2015 年　アメリカ物理学会フェロー

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【在外研究歴】	2000 年 9 月 -2001 年 8 月　英国ケンブリッジ大学化学教室（J-P. Hansen 教授）（文部省在外研究員（若手））
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【学会活動】	化学工学会理事
【主な著書、学術論文】 （過去 5 年以内）	1. M. Campo, S. K. Schnyder, J. J. Molina, T. Speck and R. Yamamoto, Spontaneous Spatiotemporal Ordering of Shape Oscillations Enhances Cell Migration, ***Soft Matter*** 15, 4939-4946 (2019). 2. J. J. Molina, and R. Yamamoto, Mechanosensitivity of Crawling Cells under Periodically Stretching Substrates, ***Soft Matter*** 15, 683 (2019). 3. C. Shih, J.J. Molina, and R. Yamamoto, Field-induced dipolar attraction between like-charged colloids, ***Soft Matter*** 12, 914-924 (2018). 4. N. Oyama, K. Teshigawara, J.J. Molina, R. Yamamoto, and T. Taniguchi, Hydrodynamic synchronization of externally driven colloids, ***Phys. Rev. E*** **97**, 032611 (2018). 5. Gregory Lecrivain, Yuki Kotani, Ryoichi Yamamoto, Uwe Hampel, and Takashi Taniguchi, A diffuse interface model to simulate the rise of a fluid droplet across a cloud of particles, Physical Review Fluids 3, 094002 (2018). 6. S. K. Schnyder, J. J. Molina, Y. Tanaka, and R. Yamamoto, Collective motion of cells crawling on a substrate: roles of cell shape and contact inhibition, ***Sci. Rep.*** **7**, 5163 (2017). 7. J. J. Molina, K. Otomura, H. Shiba, H. Kobayashi, M. Sano, and R. Yamamoto, Rheological evaluation of colloidal dispersions using the smooth profile method: formulation and applications, ***J. Fluid Mech.*** **792**, 590-619 (2016).
【学術関係の受賞】	2007 年 1 月 ホソカワ研究奨励賞、2002 年 12 月 分子シミュレーション研究会学術賞

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【研究内容キーワード】	タンパク質フォールディング、分子モーター、遺伝子動態、生体分子モデリング
【最終学歴】	1991 年 9 月総合研究大学院大学数物科学研究科機能分子科学専攻博士後期課程退学
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【在外研究歴】	1995 年 5 月 -1998 年 3 月　米国イリノイ大学化学科（日本学術振興会研究員）
【所属学会】	日本生物物理学会
【学会活動】	日本生物物理学会副会長
【主な著書、学術論文】（過去 5 年以内）	1. M. Shimizu, Y. Noguchi, Y. Sakiyama, H. Kawakami, T. Katayama*, S. Takada*, Near-atomic structural model for bacterial DNA replication initiation complex and its functional insights, ***Proc. Nat. Acad. Sci. USA***, 113・E8021-E8030・2016 2. C. Tan, T. Terakawa, S. Takada*, Dynamic Coupling among Protein Binding, Sliding, and DNA Bending Revealed by Molecular Dynamics, ***JACS.***, 138・8512-8522・2016 3. S. Takada*, R. Kanada, C. Tan, T. Terakawa, W. Li, H. Kenzaki, Modeling Structural Dynamics of Biomolecular Complexes by Coarse-Grained Molecular Simulations, **Acc. Chem. Res.**, 48・3026-3035・2015 4. W. Li, W. Wang, and S. Takada, Energy landscape views for interplays among folding, binding, and allostery of calmodulin domain, ***Proc. Nat. Acad. Sci. USA***, 111: 10550-10555, 2014. 5. M.J.McGrath, I.F.Kuo, S.Hayashi, and S.Takada, ATP hydrolysis mechanism in kinesin studied by combined quantum-mechanical molecular-mechanical metadynamics, ***JACS***, 103: 8908-8919, 2013. 6. X.Yao, N.Kimura, S.Murakami, and S.Takada, Drug Uptake Pathways of Multidrug Transporter AcrB Studied by Molecular Simulations and Site-Directed Mutagenesis Experiments, ***JACS***, 135: 7474-7485, 2013. 7. T.Terakawa, H.Kenzaki, & S.Takada, p53 searches on DNA by rotation-uncoupled sliding at C-terminal tails and restricted hopping of core domains , ***JACS***, 134: 14555-14562, 2012.

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【研究分野】	理論化学
【現在の研究課題】	振電相互作用理論、機能性分子の理論設計
【研究内容キーワード】	振電相互作用 , 有機 EL, Jahn-Teller 効果
【学歴】	平成 9 年 3 月 京都大学大学院工学研究科 分子工学専攻博士後期課程修了
【学位】	博士 (工学)
【略歴】	平成 9 年 4 月日本学術振興会特別研究員 (PD)(財団法人基礎化学研究所) 平成 10 年 1 月 京都大学大学院工学研究科分子工学専攻助手 平成 15 年 10 月 文部科学省在外研究員 (若手)(ルーヴァンカトリック大学) 平成 16 年 3 月 京都大学福井謙一記念研究センター理論研究部門助教授 平成 23 年 1 月 京都大学大学院工学研究科分子工学専攻准教授 平成 30 年 2 月京都大学福井謙一記念研究センター理論研究部門教授 現在に至る
【所属学会】	日本コンピュータ化学会， 日本化学会， フラーレン・ナノチューブ・グラフェン学会， 日本物理学会， 応用物理学会 , 有機 EL 討論会 , 化学史学会
【学会活動】	Jahn-Teller Steering Committee (2009-)
【主な著書、学術論文】（過去 5 年以内）	“Fluorescence via Reverse Intersystem Crossing from Higher Triplet States in a Bisanthracene Derivative”, Tohru Sato*, Rika Hayashi, Naoki Haruta, Yong-Jin Pu, *Sci. Rep.* **7** 4820 1-9 (2017). “Thermodynamical vibronic coupling constant and density: Chemical potential and vibronic coupling in reactions”, Tohru Sato*, Naoki Haruta, and Kazuyoshi Tanaka, *Chem. Phys. Lett.* **652**, 157-161 (2016). “A Light-Emitting Mechanism for Organic Light-Emitting Diodes: Molecular Design for Inverted Singlet-Triplet Structure and Symmetry-Controlled Thermally Activated Delayed Fluorescence”, Tohru Sato*, Motoyuki Uejima, Kazuyoshi Tanaka, Hironori Kaji, and Chihaya Adachi, *J. Mater. Chem. C* **3**, 870-878 (2015). “Quantum Yield in Blue-Emitting Anthracene Derivatives: Vibronic Coupling Density and Transition Dipole Moment Density”, Motoyuki Uejima, Tohru Sato*, Daisuke Yokoyama, Kazuyoshi Tanaka, and Jong-Wook Park, *Phys. Chem. Chem. Phys.* **16**, 14244-14256 (2014) . “Jahn-Teller Instability of Icosahedral $[\mathrm{W@Au}_{12}]^{-}$”, Tohru Sato*, Erwin Lijnen, Arnout Ceulemans, *J. Chem. Theo. Comput.* **10**, 613-622 (2014).
【学術関係の受賞など】	2016 年度日本コンピュータ化学会学会賞 平成 23 年 3 月 欧州委員会 Erasumus Mundus Scholar

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【所属学会】	日本化学会・理論化学研究会・分子科学会
【主な著書、学術論文】（過去5年以内）	1. Nishimoto, Y. “Analytic first-order derivatives of partially contracted *n*-electron valence state second-order perturbation theory (PC-NEVPT2)”, *J. Chem. Phys.* **2019**, *151*, 114103. 2. Nishimoto, Y. “Time-Dependent Long-Range-Corrected Density-Functional Tight-Binding Method Combined with the Polarizable Continuum Model”, *J. Phys. Chem. A* **2019**, *123*, 5649–5659. 3. Vuong, V. Q.; Nishimoto, Y.; Fedorov, D. G.; Sumpter, B. G.; Niehaus, T. A.; Irle, S. “The Fragment Molecular Orbital Based on Long-Range Corrected Density-Functional Tight-Binding”, *J. Chem. Theory Comput.* **2019**, *15*, 3008–3020. 4. Nishimoto, Y.; Fedorov, D. G. “Adaptive frozen orbital treatment for the fragment molecular orbital method combined with density-functional tight-binding”, *J. Chem. Phys.* **2018**, *148*, 064115. 5. Kitoh-Nishioka, H.; Welke, K.; Nishimoto, Y.; Fedorov, D. G.; Irle, S. “Multi-Scale Simulations on Charge Transport in Covalent Organic Frameworks: Including Dynamics of Transfer Integrals from FMO-DFTB/LCMO”, *J. Phys. Chem. C* **2017**, *121*, 17712–17726.
【学術関係の受賞など】	日本学術振興会特別研究員（DC1）　2012.4–2015.3

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【所属学会】	日本化学会、アメリカ化学会
【主な著書、学術論文】 （過去5年以内）	1.　The reHISS Three-Range Exchange Functional with an Optimal Variation of Hartree–Fock and Its Use in the reHISSB-D Density Functional Theory Method, Bun Chan, Yukio Kawashima and Kimihiko Hirao *J.Comput.Chem.(Memorial Festschrift for Keiji Morokuma),* **40**, 29-38 (2019) 2. Accelerated Long-range Corrected Exchange Functional Using a Two-Gaussian Operator combined with One-parameter Progressive Correlation Functional [LC-BOP(2Gau)], Jong-Won Song and Kimihiko Hirao *J.Comput.Chem.(Memorial Festschrift for Keiji Morokuma),* **40**, 104-112 (2019) 3. Time-Dependent Density Functional Theory, T.Tsuneda and K.Hirao *Theoretical and Quantum Chemistry at the 21st Century Dawn End*, Eds. T. Chakraborty and R. Carbo (Apple Academic Press, 2017). 4. Correlation Functional in Screened-Exchange Density Functional Theory Procedures, Chan, Bun; Kawashima, Yukio; Hirao, Kimihiko, *J.Comput.Chem.,* **38**, 2307-2315 (2017) 5. Singularity Correction for Long Range Corrected Density Functional Theory with Plane-Wave Basis Sets, Kawashima, Yukio; Hirao, Kimihiko, *J.Phys.Chem.* **A 121,** 2035–2045 (2017) 6. Assessment of Range-separated Functionals in the Presence of Implicit Solvent: Computation of Oxidation Energy, Reduction Energy and Orbital Energy, Abhijit Boruah, Manash Protim Borpuzari,Yukio Kawashima, Kimihiko Hirao and Rahul Kar, *J.Chem.Phys.*, **146**, 164102 (2017) 7. Best of density-functional-based methods on intermolecular interaction energies. DeCarlos E. Taylor, János G. Ángyán, Giulia Galli, Cui Zhang, Francois Gygi, Kimihiko Hirao, Jong Won Song, Kar Rahul, O. Anatole von Lilienfeld, Rafał Podeszwa, Ireneusz W. Bulik, Thomas M. Henderson, Gustavo E. Scuseria, Julien Toulouse, Roberto Peverati, Donald G. Truhlar and Krzysztof Szalewicz, *J. Chem. Phys.* **145,** 124105 (2016) 8. From C_{60} to Infinity: Large-Scale Quantum Chemistry Calculations of the Heats of Formation of Higher Fullerenes, Bun Chan, Yukio Kawashima, Michio Katouda, Takahito Nakajima, and Kimihiko Hirao J. Am. Chem. Soc., **138** 1420–1429 (2016) (Award, Fellowship) 2002 International Academy of Quantum Molecular Science (Menton, France) 2005 Chemical Society of Japan Award 2007 Fukui Medal, Asia Pacific Association of Theoretical & Computational Chemists 2008 Mukai Award 2008

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【所属学会】	日本化学会、理論化学会、ケイ素化学協会、アメリカ化学会
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15. 化学つれづれ草　第十回　理論化学と計算化学 (単著) 化学 73, No. 2, 29 (2018).
16. 化学つれづれ草　第十一回　分割統治と化学 (単著) 化学 73, No. 3, 24 (2018).
17. 化学つれづれ草　第十二回　論文不正 (単著) 化学 73, No. 4, 19 (2018).
18. 化学つれづれ草　第十三回　教育と研究 (単著) 化学 73, No. 5, 39 (2018).
19. 化学つれづれ草　第十四回　無用の用 (単著) 化学 73, No. 6, 20 (2018).
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21. 化学つれづれ草　第十六回　頭がよいということ？ (単著) 化学 73, No. 8, 41 (2018).
22. 化学つれづれ草　第十七回　面白そうな研究テーマ？ (単著) 化学 73, No. 9, 27 (2018).
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24. 化学つれづれ草　第十九回　海外留学のすゝめ (単著) 化学 73, No. 11, 40 (2018).
25. 化学つれづれ草　第二十回　ロアルド・ホフマンさん（前編）(単著) 化学 73, No. 12, 37 (2018).
26. 化学つれづれ草　第二十一回　ロアルド・ホフマンさん（後編）(単著) 化学 74, No. 1, 25 (2019).
27. 化学つれづれ草　第二十二回　伝統と効率 (単著) 化学 74, No. 2, 28 (2019).
28. 化学つれづれ草　第二十三回　思い出の研究 (単著) 化学 74, No. 3, 55 (2019)
29. ロアルド・ホフマン博士に聞く　分野を超えて挑み続けるには (単著) 現代化学 No. 1, 24-27 (2019).
30. シミュレーションか理解か　ー量子化学分野だけにとどまらない緊張関係—　Roald Hoffmann (訳) 現代化学 No. 1, 28-32 (2019)

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14. Enhanced Electroluminescence from a Thermally Activated Delayed-Fluorescence Emitter by Suppressing Nonradiative Decay (K. Shizu, M. Uejima, H. Nomura, T. Sato, K. Tanaka, H. Kaji, and C. Adachi) Phys. Rev. Appl., 3, 014001 1-7 (2015).
15. Strategy for Designing Electron Donors for Thermally Activated Delayed Fluorescence Emitters (K. Shizu, H. Tanaka, M. Uejima, T. Sato, K. Tanaka, H. Kaji, and C. Adachi) J. Phys. Chem., C, 119, 1291-1297 (2015).
16. Reactivity Index for Diels-Alder Cycloadditions to Large Polycyclic Aromatic Hydrocarbons Using Vibronic Coupling Density (N. Haruta, T. Sato, and K. Tanaka) Tetrahedron Lett., 56, 590-594 (2015).
17. Synthesis and Characterization of Heterofluorenes Containing Four-coordinated Group 13 Elements: Theoretical and Experimental Analyses and Comparison of Structures, Optical Properties and Electronic States (T. Matsumoto, K. Tanaka, K. Tanaka, and Y. Chujo) Dalton Trans., 44, 8697-8707 (2015).
18. Luminescent Coordination Glass: Remarkable Morphological Strategy for Assembled Eu (III) Complexes (Y. Hirai, T. Nakanishi, Y. Kitagawa, K. Fushimi, T. Seki, H. Ito, H. Fueno, K. Tanaka, T. Satoh, and Y. Hasegawa) Inorg. Chem., 54, 4364-4370 (2015).
19. Multiscale Simulation of Charge Transport in a Host Material, N, N’-Dicarbazole-3,5-benzene (mCP), for Organic Light-Emitting Diodes (F. Suzuki, K. Shizu, H. Kawaguchi, S. Furukawa, T. Sato, K. Tanaka, and H. Kaji) J. Mater. Chem. C, 3, 5549-5555 (2015).
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21. New Tris- and Pentakis-Fused Donors Containing Extended Tetrathiafulvalenes: New Positive Electrode Materials for Reachargeable Batteries (S. Iwamoto, Y. Inatomi, D. Ogi, S. Shibayama, Y. Murakami, M. Kato, K. Takahashi, K. Tanaka, N. Hojo, and Y. Misaki) Beilstein J. Org. Chem., 11, 1136-1147 (2015).
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24. para-Bisvinylhexaisobutyl-Substituted T_8 Caged Monomer: Synthesis and Hydrosilylation Polymerization (T. Maegawa, Y. Irie, H. Imoto, H. Fueno, K. Tanaka, and K. Naka) Polym. Chem., 6, 7500-7504 (2015).
25. Coplanar Oligo(p-phenylenedisilenylene)s as Si=Si Analogues of Oligo(p-phenylenevinylene)s: Evidence for Extended π-Conjugation through the Carbon-Silicon π-Frameworks (L. Li, T. Matsuo, D. Hashizume, H. Fueno, K. Tanaka, and K. Tamao) J. Am. Chem. Soc., 137, 15026-15035 (2015).

	26. Isolation and Characterization of Persistent Radical Cation and Dication of 2,7-Bis(dianisylamino)pyrene (R. Kurata, K. Tanaka, and A. Ito) J. Org. Chem., 81, 137-145 (2016). 27. (Z)-1,2-Di(1-pyrenyl)disilene: Synthesis, Structure, and Intramolecular Charge-Transfer Emission (M. Kobayashi, N. Hayakawa, T. Matsuo, B. Li, T. Fukunaga, D. Hashizume, H. Fueno, K. Tanaka, and K. Tamao) J. Am. Chem. Soc., 138, 758-761 (2016). 28. Synthesis and Characterization of 6,13-Diamino-Substituted Pentacenes (A. Ito, M. Uebe, K. Takahashi, H. Ishikawa, D. Sakamaki, H. Sato, T. Matsumoto, and K. Tanaka) Chem. Eur. J., 22, 2165-2170 (2016). 29. O_2-Triggered Directional Switching of Photocurrent in Self-Assembled Monolayer Composed of Porphyrin- and Fullerene-Terminated Helical Peptides on Gold (H. Uji, K. Tanaka, and S. Kimura) J. Phys. Chem. C, 120, 3684-3689 (2016). 30. Synthesis and Magnetic Properties of Linear Two-coordinate Monomeric Diaryliron(II) Complexes Bearing Fused-ring Bulky “Rind” Groups (S. Goda, M. Nikai, M. Ito, D. Hashizume, K. Tamao, A. Okazawa, N. Kojima, H. Fueno, K. Tanaka, Y. Kobayahsi, and T. Matsuo) Chem. Lett., 45, 634-636 (2016). 31. Thermodynamical Vibronic Coupling Constant and Density: Chemical Potential and Vibronic Coupling in Reactions (T. Sato, N. Haruta, and K. Tanaka) Chem. Phys. Lett., 652, 157-161 (2016). 32. Color Tuning of Alternating Conjugated Polymers Composed of Pentaazaphenanthrene by Modulating Their Unique Electronic Structures Involving Isolated-LUMOs (H. Watanabe, M. Hirose, K. Tanaka, K. Tanaka, and Y. Chujo) Polym. Chem., 7, 3674-3680 (2016). 33. Arsole-Containing π-Conjugated Polymer by the Post-Element-Transformation Technique (Y. Matsumura, M. Ishidoshiro, Y. Irie, H. Imoto, K. Naka, K. Tanaka, S. Inagi, and I. Tomita) Angew. Chem. Int. Ed., 55, 15040-15043 (2016). 34. Radical Cation of an Oligoarylamine Having a Nitroxide Radical Substituent: A Coexistent Molecular System of Localized and Delocalized Spins (A. Ito, R. Kurata, Y. Noma, Y. Hirao, and K. Tanaka) J. Org. Chem., 81, 11416-11420 (2016). 35. Borophosphonate Cages as Element-blocks: Ab Initio Calculation of the Electronic Structure of a Simple Borophosphonate, $[HPO_3BH]_4$, and Synthesis of Two Novel Borophosphonate Cages with Polymerizable Groups (J. Zapico, M. Shirai, R. Sugiura, N. Idota, H. Fueno, K. Tanaka, and Y. Sugahara) Chem. Lett., 46, 181-184 (2017). 36. Stereoisomerization of 1,4-Dihydroarsinetetracarboxylic Acid Diimides under Non-acidic Condition from cis- to trans-Forms (K. Naka, T. Kato, K. Abe, M. Ishidoshiro, S. Nishiyama, S. Tanaka, H. Imoto, S. Watase, K. Matsukawa, H. Fueno, and K. Tanaka) Heterocycles, 94, 923-937 (2017). 37. Studies of Spherically Distributed LUMO and Electron-Accepting Properties of Caged Hexakis(germasesquioxanes) (J. Ohshita, T. Tsuchida, K. Komaguchi, K. Yamamoto, Y. Adachi, Y. Ooyama, Y. Harima, and K. Tanaka) Organometallics, 36, 2536-2540 (2017). 38. Induced-Dipole-Directed, Cooperative Self-Assembly of a Benzotrithiophene (T. Ikeda, H. Adachi, H. Fueno, K. Tanaka, and T. Haino) J. Org. Chem., 82, 10062-10069 (2017). 39. A Stable Free Tetragermacyclobutadiene Incorporating Fused-ring Bulky EMind Groups (K. Suzuki, Y. Numata, N. Fujita, N. Hayakawa, T. Tanikawa, D. Hashizume, K. Tamao, H. Fueno, K. Tanaka, and T. Matsuo) Chem. Commun., 54, 2200-2203 (2018). **（以上学術論文）**
【学術関係の受賞など】	2002-2007年　科学技術振興機構(JST)の戦略的創造研究推進事業(CREST)「精密分子設計に基づくナノ電子デバイス構築」研究代表者 2004-2005年　文部科学省知的クラスター創成事業「京都ナノテククラスター」のナノテク共同研究テーマ「mRNAの数理学的特異性抽出ソフトの開発と解析サービスの事業化展開」研究代表者

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【研究内容キーワード】	電子状態・遷移金属錯体・反応解析・触媒作用・金属微粒子・無限系
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【所属学会】	日本化学会、触媒学会、近畿化学協会、ケイ素化学協会、錯体化学会
【主な著書、学術論文】（過去5年以内）	1. How Can We Understand Au$_8$ Cores and Entangled Ligands of Selenolate- and Thiolate-Protected Gold Nanoclusters Au$_{24}$(ER)$_{20}$ and Au$_{20}$(ER)$_{16}$ (E = Se, S; R = Ph, Me)? A Theoretical Study, N. Takagi, K. Ishimura, M. Matsui, R. Fukuda, T. Matsui, T. Nakajima, M. Ehara, and S. Sakaki, *J. Am. Chem. Soc.*, **137**, 8593−8602 (2015). 2. CASPT2 study of inverse sandwich-type dinuclear 3d transition metal complexes of ethylene and dinitrogen molecules: similarities and differences in geometry, electronic structure, and spin multiplicity, M. Nakagaki and S. Sakaki, *Phys. Chem. Chem. Phys.*, 17, 16294-16305 (2015). 3. Theoretical Study of Hydrogenation Catalysis of Phosphorus Compound and Prediction of Catalyst with High Activity and Wide Application Scope, G. Zeng, S. Maeda, T. Taketsugu, S. Sakaki, *ACS Cat*., 6, 4859-4870 (2016). 4. Catalytic Hydrogenation of Carbon Dioxide with Ammonia-Borane by Pincer-Type Phosphorus Compounds: Theoretical Prediction, GX. Zeng, S. Maeda, T. Taketsugu, S. Sakaki, *J. Am. Chem. Soc.*, 138, 13481-13484 (2016). 5. Theoretical study of one-electron-oxidized salen complexes of group 7 (Mn(III), Tc(III), and Re(III)) and group 10 metals (Ni(II), Pd(II), and Pt(II)) with the 3D-RISM-GMC-QDPT method: localized vs. delocalized ground and excited states in solution, S. Aono, M. Nakagaki, S. Sakaki, *Phys. Chem. Chem. Phys.*, 19, 16831-16849 (2017). 6. How to Control Inversion vs. Retention Transmetallation between Pd^{II}-Phenyl and Cu^{I}-Alkyl Complexes: Theoretical Insight, H. Zheng, K. Semba, Y. Nakao, S. Sakaki, *J. Am. Chem. Soc.*, 139, 14065-14076 (2017). 7. A coordination strategy to realize a sextuply-bonded complex Y. Chen, J.-ya Hasegawa, K. Yamaguchi, S. Sakaki, *Phys. Chem. Chem. Phys.*, 2017, 19, 14947-14954. 8. Theoretical Insight into Core−Shell Prefernce for Bimetallic Pt−M (M = Ru, Rh, Os, and Ir) Cluster and Its Electronic Structure J. Lu, K. Ishimura, and S. Sakaki, *J. Phys. Chem. C* 122, 9081−9090 (2018). 9. QM/MM Approach to Isomerization of Ruthenium(II) Sulfur Dioxide Complex in Crystal; Comparison with Solution and Gas Phases, S. Aono and S. Sakaki, *J. Phys. Chem. C.*, 122, 20701−20716 (2018). 10. Theoretical Insight into Gate-Opening Adsorption Mechanism and Sigmoidal Adsorption Iso therm into Porous Coordination Polymer, J.-J. Zheng, S. Kusaka, R. Matsuda, S. Kitagawa, and S. Sakaki, *J. Am. Chem. Soc.*, 140, 13958−13969 (2018).
【学術関係の受賞など】	第1回分子科学会賞 (2009年9月)　第66回日本化学会賞 (2014年3月) Fukui Medal (2015年 ; from APATCC)

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【研究内容キーワード】	化学動力学・電子波束動力学・非断熱現象の科学・レーザー化学
【学歴】	1978年3月　大阪大学大学院基礎工学研究科化学系専攻学位取得卒業
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【略歴】	1978年8月　ノースダコタ州立大学　博士研究員 1979年9月　カルフォルニア工科大学博士研究員 1982年1月　岡崎国立共同研究機構分子科学研究所理論研究系助手 1987年4月　名古屋大学教養部助教授（名古屋大学大学院工学研究科および理学研究科を担当） 1992年4月　名古屋大学大学院人間情報学研究科教授 1997年10月－2016年3月　東京大学大学院総合文化研究科教授 1998年4月－2016年3月　東京大学教授　理学系研究科化学専攻（兼担） 2001年4月－2016年3月　自然科学研究機構分子科学研究所教授（兼任） 2016年4月－　現職
【所属学会】	日本化学会，日本物理学会，アメリカ化学会，分子科学会，理論化学会
【学会活動】	計算分子科学研究拠点長（2016年3月まで）．各種評価委員会委員（非公開），Chem. Phys. 誌等編集委員
【主な著書、学術論文】 （過去5年以内）	論文 1. K. Takatsuka, “Electron wavepacket dynamics of photoionizing states”, J. Phys. B, **47**, 124038 (6pages) (2014). 2. K. Takatsuka, S. Takahashi “Towards many-dimensional real-time quantum theory for heavy particle dynamics. II. Beyond semiclassics by quantum smoothing of singularity in quantum-classical correspondence” *Phys. Rev. A* **89**, 012109 (12 pages) (2014). 3. Kazuo Takatsuka “Lorentz-like force emerging from kinematic interactions between electrons and nuclei in molecules. A quantum mechanical origin of symmetry breaking that can trigger molecular chirality.” J. Chem. Phys. **146**, 084312 (10 pages) (2017). 4. Kazuo Takatsuka “Theory of molecular nonadiabatic electron dynamics in condensed phases.” J. Chem. Phys. **147**, 174102 (13 pages) (2017). 5. Kentaro Yamamoto and Kazuo Takatsuka “Collision induced charge separation in ground-state water splitting dynamic” PCCP, **20**, 12229 (2018) 単行本 1. Kazuo Takatsuka, Takehiro Yonehara, Kota Hanasaki, and Yasuki Arasaki “Chemical Theory beyond the Born-Oppenheimer Paradigm: Nonadiabatic Electronic and Nuclear Dynamics in Chemical Reactions”, (World Scientific, Singapore, 2014) 2. 高塚和夫，田中秀樹「分子熱統計力学」（東京大学出版会，2014）
【学術関係の受賞など】	分子科学会賞（2013年），日本化学会賞（2014年），Mizushima-Raman Lectureship Award (2016年)，Fukui メダル（2019年)

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【所属学会】	日本化学会、日本薬学会
【主な著書、学術論文】 （過去 5 年以内）	1. Tomomi Shimazaki, Kazuo Kitaura, Dmitri G. Fedorov, Takeshi Nakajima, “Gropup molecular orbital approarch to solve Huzinaga subsystem self-consistent-field equations”, J. Chem. Phys. 146(8) 084109(2017). 2. Dmitri G. Fedorov, Kazuo Kitaura, "Many-body expansion of the Fock matrix in the fragment molecular orbital method", J. Chem. Phys. 147(10) 104106 (2017). 3. Abe, Yukihiro; Shoji, Mitsuo; Nishiya, Yoshiaki; Aiba, Hiroshi; Kishimoto, Takahiro; Kitaura, Kazuo , “The reaction mechanism of sarcosine oxidase elucidated using FMO and QM/MM methods”, PhysChemChemPhys. 19, 9811-9822 (2017). 4. Fedorov, Dmitri G.; Kitaura,Kazuo; “Pair Interaction Energy Decomposition Analysis for Density Functional Theory and Density-Functional Tight-Binding with an Evaluation of Energy Fluctuations in Molecular Dynamics”, J. Phys. Chem. A 122, 1781-1795(2018).

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		Zheng, Jiajia
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【主な著書、学術論文】（過去 5 年以内）	T. Ohta, M. Tarama and M. Sano, “Simple model of cell crawling”, Physica D 318-319, 3-11 (2016). M. Tarama and T. Ohta, “Reciprocating motion of active deformable particles”, Europhys. Lett. 114, 30002 (2016). M. Tarama, “Swinging motion of active deformable particles in Poiseuille flow”, Phys. Rev. E **96**, 022602 (2017). M. Tarama, “Dynamics of Deformable Active Particles under External Flow Field”, J. Phys. Soc. Jpn. **86**, 101011 (2017). M. Tarama and R. Yamamoto, “Mechanics of cell crawling by means of force-free cyclic motion”, J. Phys. Soc. Jpn. **87**, 044803 (2018). Mitsusuke Tarama, “Nonlinear Dynamics of Active Deformable Particles” Chapter 12. of “Self-organized Motion: Physicochemical Design based on Nonlinear Dynamics” (S. Nakata, V. Pimienta, I. Lagzi, H. Kitahata, N. J. Suematsu, eds.) The Royal Society of Chemistry e-book (2019).
【学術関係の受賞など】	Presentation Awards for Young Scientist (International Conference on Advances of Emergent orders in Fluctuations (APEF2018)) ポスター発表 優秀賞（平成 24 年度未踏科学サマー道場、Aug. 2014） the Richard M. Noyes Fund Fellowship (Jul. 2014)

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【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. Masato Itami and Shin-ichi Sasa, “Singular behaviour of time-averaged stress fluctuations on surfaces” J. Stat. Mech. **2018**, 123210 (2018). 2. Masato Itami and Shin-ichi Sasa, “Universal Form of Stochastic Evolution for Slow Variables in Equilibrium Systems” J. Stat. Phys. **167**, 46–63 (2017). 3. Masato Itami and Shin-ichi Sasa, “Derivation of Stokes’ Law from Kirkwood’s Formula and the Green-Kubo Formula via Large Deviation Theory” J. Stat. Phys. **161**, 532–552 (2015). 4. Masato Itami and Shin-ichi Sasa, “Nonequilibrium Statistical Mechanics for Adiabatic Piston Problem” J. Stat. Phys. **158**, 37–56 (2015). 5. Masato Itami and Shin-ichi Sasa, “Macroscopically measurable force induced by temperature discontinuities at solid-gas interfaces” Phys. Rev. E **89**, 052106 (2014).

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【現在の研究課題】	選択的溶媒和効果を取り入れた電気二重層のダイナミクスの研究、アクティブ流体力学
【研究内容キーワード】	選択的溶媒和効果、電気二重層、アクティブマター
【学歴】	2014年3月京都大学大学院理学研究科物理学宇宙物理学専攻博士後期課程修了
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【略歴】	2012年4月　JSPS Research Fellow (DC) 2014年4月　JSPS Research Fellow (PD) 2016年12月　京都大学福井謙一記念研究センターフェロー
【所属学会】	日本物理学会
【主な著書、学術論文】 （過去5年以内）	1. “Collision between chemically-driven self-propelled drops”, Shunsuke Yabunaka and Natsuhiko Yoshinaga, Journal of Fluid Mechanics, November 2016, Pages 205-233 2. “Structure formation due to antagonistic salts”, Akira Onuki, Shunsuke Yabunaka, Takeaki Araki and Ryuichi Okamoto Current Opinion in Colloid & Interface Science Volume 22, April 2016, Pages 59–64 3. “Functional renormalization group approach to noncollinear magnets”, B. Delamotte, M. Dudka, D. Mouhanna, and S. Yabunaka, Phys. Rev. B 93, 064405 4. “Electric double layer composed of an antagonistic salt in an aqueous mixture: Local charge separation and surface phase transition”, Shunsuke Yabunaka,and Akira Onuki, Physical review letters 119, 118001, (2017) 5. “Surprises in O (N) Models: Nonperturbative Fixed Points, Large N Limits, and Multicriticality”, Shunsuke Yabunaka and Bertrand Delamotte, Physical review letters 119, 191602 (2017)
【学術関係の受賞など】	JSPS Research Fellowships for Young Scientists(DC) 2012-2014 JSPS Research Fellowships for Young Scientists(PD) 2014-2017 Journal of Chemical Physics Editors’ choice 2015

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【研究分野】	Soft matter physics, Biophysics, Computational physics
【現在の研究課題】	Structure and dynamics of cellular tissues, anomalous transport in heterogeneous media
【研究内容キーワード】	Cell migration, Epithelial tissues, Lorentz model, Porous media, Percolation, Anomalous diffusion
【学歴】	January 2010, Diploma in Physics, University of Konstanz, Konstanz, Germany May 2014, Doctor of Science , University of Düsseldorf, Düsseldorf, Germany
【学位】	Doctor of Science from University of Düsseldorf
【略歴】	Jun. 2014 – Nov. 2014, Postdoc, University of Düsseldorf Dec. 2014 – Dec. 2016, Postdoc, Chemical Engineering, Kyoto University Jan. 2017 – now, FIFC Fellow, Fukui Institute for Fundamental Chemistry, Kyoto University
【所属学会】	German Physical Society (DPG)
【主な著書、学術論文】 （過去 5 年以内）	1. A. L. Thorneywork, S. K. Schnyder, D. G. A. L. Aarts, J. Horbach, R. Roth, and R. P. A. Dullens, “Structure factors in a two-dimensional binary colloidal hard sphere system”, Molecular Physics, 116(21-22), 3245-3257 (2018) 2. S. K. Schnyder, & J. Horbach, “Crowding of interacting fluid particles in porous media through molecular dynamics: breakdown of universality for soft interactions”, Physical Review Letters, 120(7), 78001 (2018). 3. J. Horbach, N. H. Siboni, & S. K. Schnyder, “Anomalous transport in heterogeneous media“, The European Physical Journal Special Topics, 226(14), 3113–3128 (2017). 4. S. K. Schnyder, J. J. Molina, Y. Tanaka, R. Yamamoto, “Collective motion of cells crawling on a substrate: roles of cell shape and contact inhibition“, Scientific Reports 7, 5163 (2017). 5. S. K. Schnyder, T. O. E. Skinner, A. Thorneywork, D. G. A. L. Aarts, J. Horbach, R. P. A. Dullens, “Dynamic heterogeneities and non-Gaussian behaviour in 2D randomly confined colloidal fluids”, Physical Review E (2017). 6. M. Heinen, S. K. Schnyder, J. F. Brady, H. Löwen, “Classical liquids in fractal dimension”, Physical Review Letters 115, 097801 (2015). 7. S. K. Schnyder, M. Spanner, F. Höfling, T. Franosch, J. Horbach, “Rounding of the localization transition in model porous media”, Soft Matter 11, 701 (2015).

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【研究分野】	理論化学　計算化学
【現在の研究課題】	蛍光分子の円錐交差探索
【研究内容キーワード】	励起状態、項間交差
【学歴】	2014 年 3 月　九州大学理学府　化学専攻修了
【学位】	2014 年 3 月　博士（理学）　九州大学
【略歴】	2014 年 4 月　福井謙一記念研究センター
【所属学会】	分子科学会、理論化学研究会
【主な著書、学術論文】 （過去 5 年以内）	1. T. Tsuneda, J.-W. Song,S. Suzuki, and K. Hirao ”On Koopmans’theorem in density functional theory” J. Chem. Phys. 133, 174101 (2010). 2. S.Suzuki, S. Maeda, K. Morokuma Exploration of Quenching Pathways of Multiluminescent Acenes Using the GRRM Method with the SF-TDDFT Method *J. Phys. Chem. A*, **119** pp 11479–11487 (2015) 3. S.Sasaki, S.Suzuki, W.M.C. Sameera, K. Igawa, K. Morokuma, G. Konishi, Highly twisted N,N-dialkylamines as a design strategy to tune simple aromatic hydrocarbons as steric environment-sensitive fluorophores J. Am. Chem. Phys., **138**, 8194-8206 (2016)
【学術関係の受賞など】	2012 年 9 月　Best Poster Awardsat the Annual Meeting of the Japan Society for Molecular Science

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【現在の研究課題】	Mechanistic study of organic and organometalic reactions
【研究内容キーワード】	DFT, AFIR, Reaction Mechanism, Stereoselectivity
【学歴】	May 2006, Master of Science, Himachal Pradesh University, Shimla, India
【学位】	August 2014, Ph.D., Indian Institute of Technology (IIT), Bombay, Mumbai, India
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【主な著書、学術論文】 （過去５年以内）	1. A. K. Sharma, W. M. C. Sameera, Y. Takeda, S. Minakata, “A Computational Study on the Mechanism and Origin of the Reigioselectivity and Stereospecificity in Pd/SIPr-Catalyzed Ring-Opening Cross-Coupling of 2-Arylaziridines with Arylboronic Acids” ACS Catal., 9, 4582-4592 (2019). 2. Y. Takeda, T. Matsuno, A. K. Sharma, W. M. C. Sameera, S. Minakata, “Asymmetric Synthesis of β^2-Aryl Amino Acids through Pd-Catalyzed Enantiospecific and Regioselective Ring-Opening Suzuki-Miyaura Arylation of Aziridine-2-carboxylates” Chem. Eur. J., 25, 10226-10231 (2019). 3. M. Isegawa, A. K. Sharma “CO2 reduction by a Mn electrocatalyst in the presence of a Lewis acid: a DFT study on the reaction mechanism” Sustainable Energy Fuels, 3, 1730-1738 (2019). 4. M. Isegawa, A.K. Sharma, S. Ogo, K. Morokuma, “Electron and Hydride Transfer in a Redox-Active NiFe Hydride Complex: A DFT Study” ACS Catal., 8, 10419-10429 (2018). 5. Akhilesh K. Sharma, W. M. C. Sameera, Masayoshi Jin, Laksmikanta Adak, Chiemi Okuzono, Takahiro Iwamoto, Masako Kato, Masaharu Nakamura, and Keiji Morokuma “DFT and AFIR Study on the Mechanism and the Origin of Enantioselectivity in Iron-Catalyzed Cross-Coupling Reactions” J. Am. Chem. Soc., 139, 16117-16125 (2017).
【学術関係の受賞など】	1. “2014 Eli Lilly and Company Asia Outstanding Thesis Award” for Best Ph.D. Thesis. 2. “Junior and Senior Research Fellowship” from Council of Scientific & Industrial Research (CSIR), India; (2007-2012).

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【現在の研究課題】	溶液中の遷移金属錯体の化学反応の理論的解析
【研究内容キーワード】	3D-RISM-SCF 法、平均場 QM/MM 法、自由エネルギー解析、溶媒和構造解析、周期的分子結晶解析
【学歴】	2010 年 3 月　京都大学大学院理学研究科化学専攻博士後期課程研究指導認定退学
【学位】	2010 年 9 月　理学博士（京都大学）
【略歴】	2010 年 4 月　京都大学大学院理学研究科化学専攻 研修員 2010 年 5 月　京都大学 物質 - 細胞統合システム拠点 教務補佐員 2010 年 10 月　京都大学 物質 - 細胞統合システム拠点 特定研究員 2011 年 4 月　京都大学 福井謙一記念研究センター 特定研究員 2015 年 4 月　京都大学 福井謙一記念研究センター フェロー（榊研） 2019 年 4 月　高度情報科学技術研究機構 計算技術部 研究員
【所属学会】	分子科学会、理論化学会、錯体化学会
【主な著書、学術論文】（過去 5 年以内）	1. Aono S., Nakagaki M., Kurahashi T., Fujii H., and Sakaki S., “Theoretical Study of One-Electron Oxidized Mn(III)− and Ni(II)−Salen Complexes: Localized vs Delocalized Ground and Excited States in Solution” *J. Chem. Theory Comput.* 10, 1062, (2014). 2. Aono S., Mori T., and Sakaki S., “3D-RISM-MP2 Approach to Hydration Structure of Pt(II) and Pd(II) Complexes: Unusual H−Ahead Mode vs Usual O−Ahead One” *J. Chem. Theory Comput.* 12, 1189-1206, (2016). 3. Aono S., Nakagaki M., and Sakaki S. “Theoretical Study of One-Electron Oxidized Salen Complexes of Group 7 (Mn(III), Tc(III), and Re(III)) and Group 10 Metals (Ni(II), Pd(II), and Pt(II)) with 3D-RISM-GMC-QDPT Method: Localized vs. Delocalized Ground and Excited States in Solution” *Phys. Chem. Chem. Phys.* 19, 16831-16849, (2017). 4. Aono S. and Sakaki S. “QM/MM Approach to Isomerization of Ruthenium(II) Sulfur Dioxide Complex in Crystal; Comparison with Solution and Gas Phases” *J. Phys. Chem. C* 122, 20701-20716, (2018). 5. Aono S., Seki T., Ito H., and Sakaki S. “Dependence of Absorption and Emission Spectra on Polymorphs of Gold(I) Isocyanide Complexes: QM/MM Approach” *J. Phys. Chem. C* 123, 4773−4794, (2018).
【学術関係の受賞など】	(Award, Fellowship)

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【研究分野】	Computational Chemistry
【現在の研究課題】	Electronic Structure of Inverted Sandwich Type Complexes
【研究内容キーワード】	Electronic Structure of Metal Complex, Multireference Theory
【学歴】	March 2005, Master of Sci., Graduate School of Science, Kyushu University March 2009, Doctor of Sci., Graduate School of Science, Kyushu University
【学位】	Doctor of Science from Kyushu University
【略歴】	April 2009, Postdoctoral Fellow, Kyushu University April 2011, FIFC Fellow, Kyoto University
【所属学会】	The Chemical Society of Japan Japan Society for Molecular Science Japan Society of Theoretical Chemistry
【主な著書、学術論文】 （過去 5 年以内）	1. N Takagi, M Nakagaki, K. Ishimura, R Fukuda, M Ehara, and S Sakaki "Electronic Processes in NO Dimerization on Ag and Cu Clusters: DFT and MRMP2 Studies" J. Comput. Chem., 40, 181–190 (2019). 2. M Nakagaki, A. Baceiredo, T. Kato, and S. Sakaki "Reversible Oxidative Addition/Reductive Elimination of a Si-H Bond with Base-Stabilized Silylenes: A Theoretical Insight" Chem. Eur. J. 24, 11377 – 11385 (2018). 3. T. Muraoka, H. Kimura, G. Trigagema, M. Nakagaki, S. Sakaki, and K. Ueno "Reactions of Silanone(silyl)tungsten and -molybdenum Complexes with MesCNO, $(Me_2SiO)_3$, MeOH, and H_2O: Experimental and Theoretical Studies" Organometallics, 36, 1009–1018(2017). 4. M Nakagaki and S. Sakaki "Hetero-dinuclear complexes of 3d metals with a bridging dinitrogen ligand: theoretical prediction of the characteristic features of geometry and spin multiplicity" Phys. Chem. Chem. Phys., 18, 26365-26375 (2016) 5. M. Nakagaki and S. Sakaki "CASPT2 study of inverse sandwich-type dinuclear 3d transition metal complexes of ethylene and dinitrogen molecules: similarities and differences in geometry, electronic structure, and spin multiplicity" Phys. Chem. Chem. Phys. 17, 16294-16305(2015). 6. M. Nakagaki and S. Sakaki "CASPT2 Study of Inverse Sandwich-Type Dinuclear Cr(I) and Fe(I) Complexes of the Dinitrogen Molecule: Significant Differences in Spin Multiplicity and Coordination Structure between These Two Complexes" J. Phys. Chem. A, 118, 1247-1257 (2014) 7. S. Aono, M. Nakagaki, T. Kurahashi, H. Fujii, and S. Sakaki, J. Chem. Theory Comput., 10 1062-1073 (2014)

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【研究分野】	Computational Chemistry
【現在の研究課題】	Theoretical study of bimetallic alloyed nanoclusters/particles
【研究内容キーワード】	Bimetallic alloyed nanoclusters/particles, core-shell structure, oxygen reduction reaction
【学歴】	June 2016, Doctor of Sci., Faculty of Chemistry, Northeast Normal University, P.R. China
【学位】	Doctor of Science from Northeast Normal University
【略歴】	Aug. 2016 – Sept. 2018, Postdoctoral Fellow, FIFC, Kyoto University
【主な著書、学術論文】 （過去5年以内）	1. Lu, J.; Ishimura, K.; Sakaki, S., Theoretical Insight into Core–Shell Preference for Bimetallic Pt-M (M = Ru, Rh, Os, and Ir) Cluster and Its Electronic Structure. J. Phys. Chem. C 122, 9081-9090 (2018). 2. Lu, J.; Zheng, Y.; Zhang, J., Computational design of benzo [1,2-b:4,5-b′] dithiophene based thermally activated delayed fluorescent materials. *Dyes and Pigments* 127, 189-196 (2016). 3. Lu, J.; Zheng, Y.; Zhang, J., Rational design of phenoxazine-based donor-acceptor-donor thermally activated delayed fluorescent molecules with high performance. Phys. Chem. Chem. Phys. 17, 20014-20020 (2015). 4. Lu, J.; Yao, Y.; Shenai, P. M.; Chen, L.; Zhao, Y., Elucidating the enhancement in optical properties of low band gap polymers by tuning the structure of alkyl side chains. Phys. Chem. Chem. Phys. 17, 9541-9551 (2015). 5. Lu, J.; Zheng, Y.; Zhang, J., Tuning the color of thermally activated delayed fluorescent properties for spiro-acridine derivatives by structural modification of the acceptor fragment: a DFT study. RSC Adv. 5, 18588-18592 (2015).

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【研究分野】	Computational Chemistry
【現在の研究課題】	Theoretical Study of Complex Systems Including d-electrons
【研究内容キード】	Palladium catalysis, oxidative addition, reaction mechanism
【学歴】	June 2010, bachelor of Chemistry Education, Faculty of Chemistry, Northeast Normal University June 2015, Doctor of Physical Chemistry, Institute of Functional Material Chemistry, Faculty of Chemistry, Northeast Normal University
【学位】	Doctor of Physical Chemistry from Northeast Normal University
【略歴】	Oct. 2016, Lecturer, Jilin University
【主な著書、学術論文】（過去5年以内）	1. Zhong, R.-L.; and Sakaki, S., J. Am. Chem. Soc., 2019, *141*, 9854-9866. 2. Zhong, R.-L.; Nagaoka, M.; Nakao, Y.; and Sakaki, S., *Organometallics*, 2018, *37*, 3480-3487. 3. Yadav, R. M.; Nagaoka, M.; Kashihara, M.; Zhong, R.-L.; Miyazaki, T.; Sakaki, S.; Nakao, Y. J. Am. Chem. Soc., 2017, 139, 9423-9426. 4. R.-L. Zhong, H.-L. Xu,* Z.-R. Li* and Z.-M. Su*. Role of Excess Electrons in Nonlinear Optical Response. J. Phys. Chem. Lett. 2015, 6, 612−619 5. Zhong, R.-L.; Zhang, M.; Xu, H-L.; and Su, Z.-M.; *Chem. Sci.*, 2016, *7*, 1028-1032.

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【研究分野】	Computational Chemistry
【現在の研究課題】	Gas Adsorption by Porous Coordination Polymers
【研究内容キーワード】	Porous Coordination Polymer,
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【学位】	Doctor of Engineering from Xi’an Jiaotong University
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【所属学会】	Japan Society of Coordination Chemistry
【主な著書、学術論文】 （過去５年以内）	1. C. Gu, N. Hosono, J.-J. Zheng, Y. Sato, S. Kusaka, S. Sakaki, S. Kitagawa, “Design and Control of Gas Diffusion Process in a Nanoporous Soft Crystal”, Science 363, 387-391 (2019). 2. J.-J. Zheng, S. Kusaka, R. Matsuda, S. Kitagawa, S. Sakaki, “Theoretical Insight into Gate-Opening Adsorption Mechanism and Sigmoidal Adsorption Isotherm into Porous Coordination Polymer”, J. Am. Chem. Soc. 140, 13985-13969 (2018). 3. S. Sen, N. Hosono, J.-J. Zheng, S. Kusaka, R. Matsuda, S. Sakaki, S. Kitagawa, “Cooperative Bond Scission in a Soft Porous Crystal Enables Discriminatory Gate Opening for Ethylene over Ethane”, J. Am. Chem. Soc. 139, 18313-18321 (2017). 4. J.-J. Zheng, S. Kusaka, R. Matsuda, S. Kitagawa, S. Sakaki, “Characteristic Features of CO_2 and CO Adsorptions to Paddle-Wheel-type Porous Coordination Polymer”, J. Phys. Chem. C 121, 19129-19139 (2017). 5. J. Duan, M. Huguchi, J.-J. Zheng, S. Noro, I-Ya Chang, K. Hyeon-Deuk, S. Mathew, S. Kusaka, E. Sivaniah, R. Matsuda, S. Sakaki, S. Kitagawa, “Density Gradation of Open Metal Sites in the Mesospace of Porous Coordination Polymers” J. Am. Chem. Soc. 139, 11576-11583 (2017).

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【研究分野】	Computational Chemistry
【現在の研究課題】	Porous Materials
【研究内容キーワード】	Gas adsorption, reaction in porous materials
【学歴】	June 20012, Doctor of Phys Chem., Faculty of Chemistry, Northeast Normal University
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【略歴】	Aug. 2018-Jan. 2019, Resear Fellow, FIFC, Kyoto University
【主な著書、学術論文】（過去5年以内）	1. A Nano-Sized [MnII18] Metallamacrocycle as a Building Unit to Construct Stable Metal-Organic Frameworks: Effective Gas Adsorption and Magnetic Properties，CHEM-EUR J，2018 2. Mechanistic Insight on Water and Substrate Catalyzed the Synthesis of 3-(1H-indol-3-yl)-2-(4-methoxybenzyl) isoindolin-1-one: Driving by Noncovalent Interactions，J COMPUT CHEM，2018 3. Mechanistic Insights Into N-Bromosuccinimide-Promoted Synthesis of Imidazo[1,2-a]pyridine in Water: Reactivity Mediated by Substrates and Solvent，J COMPUT CHEM，2018 4. Anionic Lanthanide Metal-Organic Frameworks: Selective Separation of Cationic Dyes, Solvatochromic Behavior, and Luminescent Sensing of Co(II) Ion，INORG CHEM，2018 5. Bifunctional Separator Coated with Hexachlorocyclotriphosphazene/Reduced Graphene Oxide for Enhanced Performance of Lithium-Sulfur Batteries，CHEM-EUR J，2018

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【現在の研究課題】	Coordination feature and chemical reactivity of Rh(PAlP) complex
【研究内容キーワード】	Transition metal complex, Binding ability, Reaction mechanism
【学歴】	07/2013 Bachelor of Science, Shanxi Normal University, China 09/2018 Doctor of Engineering, Xi’an Jiaotong University, China
【学位】	Doctor of Engineering from Xi’an Jiaotong University
【主な著書、学術論文】 （過去 5 年以内）	1. Li QZ, Zheng JJ, He L, Nagase S, Zhao X. La–La bonded dimetallofullerenes $[La_2@C_{2n}]^-$: species for stabilizing C_{2n} (2n = 92~96) besides $La_2C_2@C_{2n}$. *Physical Chemistry Chemical Physics*, 2018, 20 (21): 14671-14678. 2. Li QZ, Zheng JJ, He L, Zhao X, Nagase S. Epoxy and oxidoannulene oxidation mechanisms of fused-pentagon chlorofullerenes: oxides linked by a pirouette-type transition state. *Journal of Organic Chemistry*, 2017, 82 (13): 6541-6549. 3. Li QZ, Zheng JJ, He L, Nagase S, Zhao X. Stabilization of a chlorinated $^{\#4348}C_{66}$:C_{2v} cage by encapsulating monometal species: coordination between metal and double hexagon-condensed pentalenes. *Inorganic Chemistry*, 2016, 55 (15): 7667-7675. 4. Li QZ, Zheng JJ, Zhao X. Bingel–Hirsch reaction on $Sc_2@C_{66}$: a highly regioselective bond neighboring to unsaturated linear triquinanes. *Journal of Physical Chemistry C*, 2015, 119 (46): 26196-26201. 5. Li QZ, Zheng JJ, Zhao X. Azide addition to $Sc_2@C_{66}$: favorable activity on unsaturated linear triquinanes and dramatic reactivity difference compared with the free C_{66} cage. *Physical Chemistry Chemical Physics*, 2015, 17 (32): 20485-20489.

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【電子メールアドレス】	matsuzaki_rei@cyberagent.co.jp
【学歴】	2017 年 3 月　慶應義塾大学大学院基礎理工学専攻博士課程修了
【学位】	2017 年 3 月　博士（理学）
【略歴】	2015 年 4 月　慶應義塾大学助教（有期・研究奨励） 2016 年 4 月　日本学術振 興会特別研究員 DC2 2017 年 4 月　日本学術振興会特別研究員 PD 2018 年 4 月　福井謙一記念研究センター フェロー 2019 年 1 月　現職
【主な著書、学術論文】（過去 5 年以内）	1. R.Matsuzaki, S.Asai, C.W.McCurdy, S.Yabushita, Theoretical Chemistry Accounts, **133**, 1521 (2014) 2. R.Matsuzaki, S.Yabushita, J.Comput.Chem. **38**, 910 (2017) 3. R. Matsuzaki, S.Yabushita, J.Comput.Chem. **38**, 2030 (2017) 4. R. Matsuzaki, K. Takatsuka, J. Comput. Chem. **40**, 148 (2018) 5. R. Matsuzaki, K. Takatsuka, JCP **150**, 014103 (2019)
【学術関係の受賞など】	Journal of Physics B Atomic, Molecular and Optical Physics Best Poster Award 2013

【氏名（ふりがな）】	山本　憲太郎（やまもと　けんたろう）
【職名】	研究フェロー
【所属】	福井謙一記念研究センター　高塚グループ
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【ホームページ】	http://mns2.fukui.kyoto-u.ac.jp/~kyamamoto/
【研究分野】	理論化学
【現在の研究課題】	非断熱電子動力学理論による化学反応の研究
【研究内容キーワード】	非断熱遷移，電荷分離
【学歴】	2015年3月東京大学大学院理学系研究科化学専攻博士過程修了
【学位】	2015年3月博士（理学）（東京大学）
【略歴】	2014年東京大学技術補佐員 2015年東京大学特任研究員
【所属学会】	分子科学会，理論化学研究会
【主な著書、学術論文】 （過去5年以内）	[1] K. Yamamoto and K. Takatsuka, “On the Elementary Chemical Mechanisms of Unidirectional Proton Transfers: A Nonadiabatic Electron-Wavepacket Dynamics Study” J. Phys. Chem. A, 2019, 123, 4125-4138. [2] K. Yamamoto and K. Takatsuka, “Collision induced charge separation in ground-state water splitting dynamics”, Phys. Chem. Chem. Phys., 2018, 20, 12229-12240. [3] K. Yamamoto and K. Takatsuka, “On the photocatalytic cycle of water splitting with small manganese oxides and the roles of water clusters as direct sources of oxygen molecules”, Phys. Chem. Chem. Phys., 2018, 20, 6708-6725. [4] K. Yamamoto and K. Takatsuka, “Photoinduced Charge Separation Catalyzed by Manganese Oxides onto a Y-Shaped Branching Acceptor Efficiently Preventing Charge Recombination”, ChemPhysChem, 2017, 18, 537-548. [5] K. Yamamoto and K. Takatsuka, “Dynamical mechanism of charge separation by photoexcited generation of proton–electron pairs in organic molecular systems. A nonadiabatic electron wavepacket dynamics study” (perspective), Chem. Phys. 2016, 475, 39-53.

【氏名（ふりがな）】	新崎　康樹　（あらさき　やすき）
【職名】	研究フェロー
【所属】	福井謙一記念研究センター　高塚グループ
【研究室】	東京大学駒場キャンパス 16 号館 408
【研究分野】	理論化学
【現在の研究課題】	非断熱動力学理論による化学反応
【研究内容キーワード】	非断熱相互作用、クラスター、励起状態動力学
【学歴】	2000 年 9 月　東京大学大学院総合文化研究科博士課程修了
【学位】	2000 年 9 月　博士（学術）（東京大学）
【略歴】	2000 年 10 月　東京大学インテリジェント・モデリング・ラボラトリー研究員 2002 年 10 月　東京大学大学院総合文化研究科　研究員
【所属学会】	分子科学会
【主な著書、学術論文】（過去 5 年以内）	1. Y. Arasaki, Y. Mizuno, S. Scheit, and K. Takatsuka, Induced photoemission from driven nonadiabatic dynamics in an avoided crossing system, J. Chem. Phys. 141, 234301 (2014, 14 pages). 2. Y. Arasaki, Y. Mizuno, S. Scheit, and K. Takatsuka, Stark-assisted quantum confinement of wavepackets. A coupling of nonadiabatic interaction and CW-laser, J. Chem. Phys. 144, 044107 (2016, 10 pages). 3. Y. Arasaki and K. Takatsuka, Time-resolved photoelectron signals from bifurcating electron wavepackets propagated across conical intersection in path-branching dynamics, Chem. Phys. 493, 42-48 (2017). 4. Y. Arasaki and K. Takatsuka, Chemical bonding and nonadiabatic electron wavepacket dynamics in densely quasi-degenerate excited electronic state manifold of boron clusters, J. Chem. Phys. 150, 114101 (2019, 18 pages). 5. K. Takatsuka, T. Yonehara, K. Hanasaki, and Y. Arasaki, *Chemical Theory Beyond the Born-Oppenheimer Paradigm: Nonadiabatic Electronic and Nuclear Dynamics in Chemical Reactions* (World Scientific, Singapore, 2014).

【氏名（ふりがな）】	花崎　浩太（はなさき　こうた）
【職名】	研究フェロー
【所属】	福井謙一記念研究センター
【研究室】	高塚研究室
【直通電話】	075-711-7907
【電子メールアドレス】	hanasaki@fukui.kyoto-u.ac.jp
【研究分野】	計算化学・理論化学
【現在の研究課題】	分子における相対論的電子動力学の定式化
【研究内容キーワード】	非断熱動力学、電子動力学、相対論効果
【学歴】	2014年3月東京大学大学院総合文化研究科博士課程修了
【学位】	2014年3月学術博士　（東京大学）
【略歴】	2014年　博士研究員（Deutches Elektronen Synchrotron (DESY), The Hamburg Centre for Ultrafast Imaging (CUI), Center for Free-electron Laser Science (CFEL) theory group） 2016年　研究支援者（東北大学大学院理学研究科化学専攻物理化学講座数理化学研究室） 2018年　研究フェロー（京都大学福井謙一記念研究センター）
【所属学会】	分子科学会
【学会活動】	
【主な著書、学術論文】 （過去5年以内）	1. Y. Hao, L. Inhester, K. Hanasaki, S.-K. Son and R. Santra, “*Efficient electronic structure calculation for molecular ionization dynamics at high x-ray intensity*”, Struct. Dyn. **2** 041707 (2015). 2. A. Rudenko, L. Inhester, K. Hanasaki, *et al.* “*Femtosecond response of polyatomic molecules to ultra-intense hard X-rays*”, Nature **546**, 129 (2017). 3. K. Hanasaki, M. Kanno, T. A. Niehaus and H. Kono, “*An efficient approximate algorithm for nonadiabatic molecular dynamics*”, J. Chem. Phys. **149**, 244117 (2018).

Ⅲ　研究広報活動

１．京都大学福井謙一博士生誕百年記念行事　メモリアルシンポジウム・記念式典・祝賀会

1981年にアジア初のノーベル化学賞を受賞された福井謙一博士の生誕百年を記念する行事として、彬子女王殿下ご臨席のもと、メモリアルシンポジウム、記念式典及び祝賀会を開催した。メモリアルシンポジウムには、学術関係機関・学会・産業界、教職員からの参加者、一般参加者等あわせて350名余りが、引き続き行われた記念式典・祝賀会には、約160名の参加があった。

⑴　メモリアルシンポジウム

日　　時　2018年10月12日（金）13:30 ― 16:15

場　　所　京都大学百周年時計台記念館 百周年記念ホール
司会　　佐藤　啓文　副センター長

13:30 ― 13:35　田中　勝久　福井謙一記念研究センター長挨拶

13:35 ― 14:25　記念講演１
Roald Hoffmann（コーネル大学教授　1981年ノーベル化学賞福井謙一博士と同時受賞）
「Simulation vs Understanding: A Tension, and Not Just in Our Profession」

14:25 ― 15:15　記念講演２
白川　英樹（筑波大学 名誉教授　2000年ノーベル化学賞受賞）
「高分子合成を志して」

15:25 ― 16:15　記念講演３
古川　安（化学史学会前会長）
『応用をやるなら基礎をやれ』― 福井謙一のたどった道、拓いた世界 ―

⑵　記念式典

日　　時　2018年10月12日（金）16:25 ― 16:55

場　　所　京都大学百周年時計台記念館 百周年記念ホール
司会　　佐藤　徹　福井謙一記念研究センター教授

16:25 ― 16:30　式辞　山極　壽一　京都大学総長

16:30 ― 16:35　おことば　彬子女王殿下

16:35 ― 16:55　祝辞　山脇　良雄　文部科学省文部科学審議官
西脇　隆俊　京都府知事　山下　晃正
門川　大作　京都市長　岡田　憲和
里見　進　日本学術振興会理事長

⑶　祝賀会

日　　時　2018年10月12日（金）17:10 ― 18:30

場　　所　京都大学百周年時計台記念館 2階　国際交流ホール
司会　　林　重彦　副センター長

17:10 ― 17:15　挨拶　山極　壽一　京都大学総長
17:15 ― 17:20　祝辞　森迫　清貴　京都工芸繊維大学長
17:20 ― 17:25　乾杯　曽我　直弘　京都大学名誉教授、元工学研究科長、元京都大学工化会会長
17:25 ― 18:30　歓談

⑷　サテライトシンポジウム

福井博士の研究理念を継承し、基礎化学分野の発展に貢献することを目的に設立された福井謙一記念研究センターのこれまでの研究活動を再確認するとともに、基礎化学・理論化学とその周辺分野における最新の研究成果を発表し、議論を深める目的で開催した。

国内外からの研究者、学生など約60名が参加した。

日　　時　2018年10月13日（土）

場　　所　京都大学 福井謙一記念研究センター

10:05 ― 11:05　講演1
西本 佳央（京都大学福井謙一記念研究センター）
「FMO-DFTB法：100万原子に適用可能な量子化学計算の実証」

11:05 ― 12:05　講演2
John J.Molina（京都大学工学研究科化学工学専攻）
「クロール細胞の感受性」

13:30 ― 15:00　ポスターセッション

15:00 ― 16:00　講演３
畑中　美穂（奈良先端科学技術大学院大学マテリアルズ・インフォマティクス研究室）
「自動反応経路探索の応用：メカニズム研究を超えて」

16:00 ― 17:00　講演４
長谷川　淳也（北海道大学触媒科学研究所）
「制御力による計算科学」

17:30 ― 19:00　ディスカッションミーティング

⑸　京都大学総合博物館2018年度企画展　福井謙一博士生誕百年記念展示「ノーベル化学者を育んだ教室　応用をやるには、基礎をやれ」

本学が輩出した世界的な研究者である福井謙一博士の偉大な研究業績「フロンティア軌道理論」や、本理論が現在の化学や産業の発展に大きな貢献をしていることを広く社会に紹介し、学術研究に対する関心を高める機会を提供した。

企画展には約9,000名が来館した。

日　　時　2018年10月3日（水）～12月9日（日）

場　　所　京都大学総合博物館

２．福井謙一記念研究センターシンポジウム

第16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　2019年2月8日（金）9:50 — 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）

講　　演　10:05 — 11:05
佐藤　徹（京都大学 福井謙一記念研究センター）
「振電相互作用密度とその応用ー発光、キャリア輸送、化学反応ー」

11:20 — 12:20
平尾　公彦（京都大学 福井謙一記念研究センター・理化学研究所）
「長距離補正密度汎関数法（LC-DFT）の最近の進展」

— 休　憩 —

13:50 ー 14:50
跡見　晴幸（京都大学 大学院工学研究科）
「第3の生物アーキアの特異な代謝」

15:00 ー 15:30　　福井謙一奨励賞表彰式

15:30 ー 17:20　　ポスターセッション

17:30 ー 19:00　　懇親会（1階多目的ルーム）

３．セミナー

(1)　第 16 回福井センターセミナー

日　　時　2018（平成 30）年 11 月 20 日（火）15：00 ― 17：20

場　　所　京都大学福井謙一記念研究センター（１階 106 室）

15：00 ― 15：40
Satoshi Suzuki (Kyoto Univ.)
“Theoretical understanding and rational design of aggregation induced emission molecule”

15：40 ― 16：20
Masato Itami (Kyoto Univ.)
“Singular behavior of time-averaged stress fluctuations on surfaces”

― Break ―

16：30 ― 17：20
Hiroshi Watanabe (Keio University)
“Development and applications of molecular dynamics simulation with the quantum chemical effect of solvent””

(2)　その他のセミナー

Contact	Speaker	Title	Affiliation	Date
Shigeyoshi Sakaki	Oscar Jimenez-Halla	Selective reaction routes in multicomponent reactions: A Computational study	University of Guanajuato	April 2 (Mon.), 2018
	Rong Shang	Facile reactions of Gold(I) complexes with Tri(tert-butyl) azadiboriridine	Hiroshima University	
	Alexey Y. Timoshkin	Donor-acceptor stabilized phosphany Iboranes and Alanes: stabitlity and reactivity	St. Petersburg State University	June 8(Mon.), 2018
	Takefumi Yamashita	Theoretical study of molecular recognition mechanisms in the life and pharmaceutical sciences	University of Tokyo	December 11(Tue.), 2018
Kimihiro Hirao	Roland Lindh	Implementation of the exact semi-classical light-matter interaction: an easy way beyond the multipole expansion	Uppsala University	January 22 (Tue.), 2019

４．国際交流

当センター教員が海外の研究機関を訪問し、研究所の運営に関して意見交換を行った。（資料編を参照）

５．社会へのアウトリーチ活動

＜研究紹介＞

（１）京都大学アカデミックデイへ参加　　　　2018（平成29）年９月22日（土）
榊　茂好　シニアリサーチフェローが「ちゃぶ台囲んでひざ詰め対話」コーナーへ参加
話　題：「縁の下の力持ち『触媒』と『計算化学』」
場　所：京都大学百周年時計台記念館

＜学術講演＞

（２）多羅間 充輔 福井センターフェロ　　　　2018（平成30）年５月25日（金）
演　題：Mechanics of cell crawling by means of force-free cyclic motion
行事名：BDR セミナー
場　所：理化学研究所　生命機能科学研究センター　フィジカルバイオロジー研究チーム

（３）田中　一義　シニアリサーチフェロー　　2018（平成30）年11月６日（火）
演　題：計算化学はどのように役立つか
行事名：京都グリーンケミカル・ネットワーク人材育成事業
場　所：京都市成長産業創造センター

６．福井謙一奨励賞の創設及び奨励賞の授与

福井謙一博士の生誕百年を控え、日頃から、化学の将来の発展のためには若手研究者の育成の大切さを説いておられた福井博士の意志を汲み、基礎化学、理論化学の分野で顕著な研究業績を挙げた若手研究者を顕彰する福井謙一奨励賞を平成29年度に創設した。

平成30年秋に公募し、応募のあった中から委員会で選考の結果、次のとおり選考された。表彰式は、平成31年２月２日（金）に開催の福井謙一記念研究センターシンポジウムの中で行い受賞者に表彰状と記念楯が授与され、続いて受賞題目に関した講演が行われた。

受 賞 者：春田　直毅（東京工業大学　科学技術創成研究員　特任助教）
受賞題目：縮退と擬縮退の包括的理解に向けた新たな数理化学の開拓

Ⅳ　研究業績

１．専任教員

Tohru Sato

Professor

1. Summary of the research of the year

Origin of Aggregation-Induced Enhanced Emission: Role of Pseudo-Degenerate Electronic States of Excimers Formed in Aggregation Phases

We have reported that, in fluorescent dopants employed in organic light-emitting diodes (OLEDs), radiative and non-radiative transitions from a triplet excited state T_n ($n > 1$) to all the lower triplet excited states can be suppressed due to the pseudo-degenerate electronic states [1-3]. The pseudo-degeneracy leads to cancellation of the overlap density between the excited states, which generates T_n excitons with long life-times. This enables the fluorescence via higher triplets (FvHT) mechanism for OLEDs, that is fluorescence utilizing the reverse intersystem crossing (RISC) from T_n to singlets.

Aggregation-induced enhanced emission (AIEE) yields strong luminescence in the aggregation phases. A cyano-substituted 1,2-bis(pyridylphenyl)ethene (CNPPE) has been reported to exhibit the AIEE behavior in solid phase [4]. Some cofacial CNPPE molecules have *Ci* symmetry in the crystal structure. This suggests the possibility of pseudo-degenerate electronic states delocalized over the cofacial molecules. These indicate that the internal conversion can be more suppressed in solid phase than in solution phase as long as excimer formation occurs in solid phase. In this study, based on the vibronic coupling density (VCD) analysis [5-7], we investigated the role of pseudo-degeneracy in the appearance of AIEE considering CNPPE as an example [8].

We modeled the CNPPE solid as a dimer with a cofacial configuration, Dimer Model, where the cofacial dimer was calculated by the QM method and the surrounding molecules were

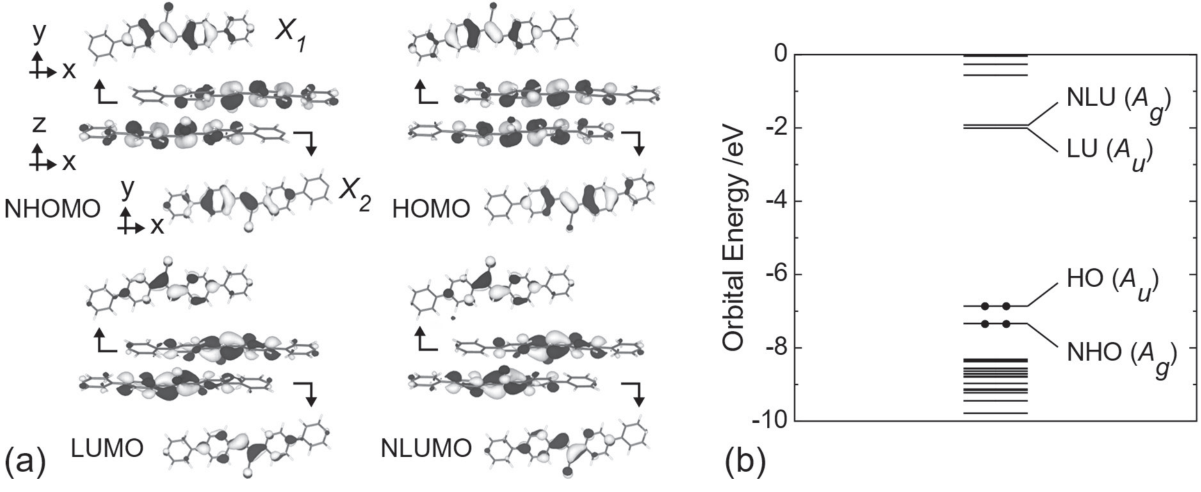

Fig. 1 (a) Frontier orbitals and (b) orbital levels of Dimer Model in solid phase. Isosurface values are 3×10^{-2} a.u.

calculated by the MM method based on the ONIOM approach The CNPPE in CH_2Cl_2 solution was modeled as a single molecule, Monomer Model, with C_1 symmetry.

From the selection rule of the electric dipole transition, S_1 (A_g) is symmetry-forbidden and S_2(A_u) is symmetry-allowed (Laporte rule) for Dimer Model. Although, according to Kasha's rule, an emission does not occur from the second excited states, the fluorescence from S_2 is possible if all the transitions from S_2 to S_1 are suppressed. Figures 1 (a) and (b) present the frontier orbitals and orbital levels at the S_2 optimized structure, respectively. The adiabatic wave functions are delocalized over the molecules, thereby indicating the excimer formation in solid phase. In the present case, the delocalized electronic states are obtained because Dimer Model belongs to C_i symmetry even in the adiabatic excited state. The NHOMO and HOMO as well as the LUMO and NLUMO of the excimer are pseudo-degenerate. Figure 2 (a) and (b) show the electron density differences of $S_2@S_2$-$S_0@S_2$, $\Delta\rho_{20}$, and $S_1@S_2$-$S_0@S_2$, $\Delta\rho_{10}$, respectively. $\Delta\rho_{20}$ and $\Delta\rho_{10}$ exhibit similar distributions. On the contrary, the electron density difference of $S_2@S_2$-$S_1@S_2$, $\Delta\rho_{21}$ (Fig. 2 (c)) exhibits an extremely small distribution. This leads to the small diagonal VCD of $S_1@S_2$, resulting in the small diagonal VCCs of $S_1@S_2$. Figures 2 (d) and (e) show the overlap densities of $S_2@S_2$-$S_0@S_2$, ρ_{20}, and $S_2@S_2$-$S_1@S_2$, ρ_{21}, respectively. ρ_{21} exhibits a smaller distribution than that of ρ_{20}. The small ρ_{21} contributes to the small off-diagonal VCCs of $S_1@S_2 \leftarrow S_2@S_2$. It should be noted, because of the small electron density difference and overlap density between S_1 and S_2, that the internal conversion from S_2 to S_1 is suppressed, thereby enabling the fluorescence from S_2.

Figures 3 (a) and (b) show the diagonal VCCs of Monomer Model in the FC S_1 state and Dimer Model in the FC S_2 state, respectively. The diagonal VCCs are greatly reduced due to the

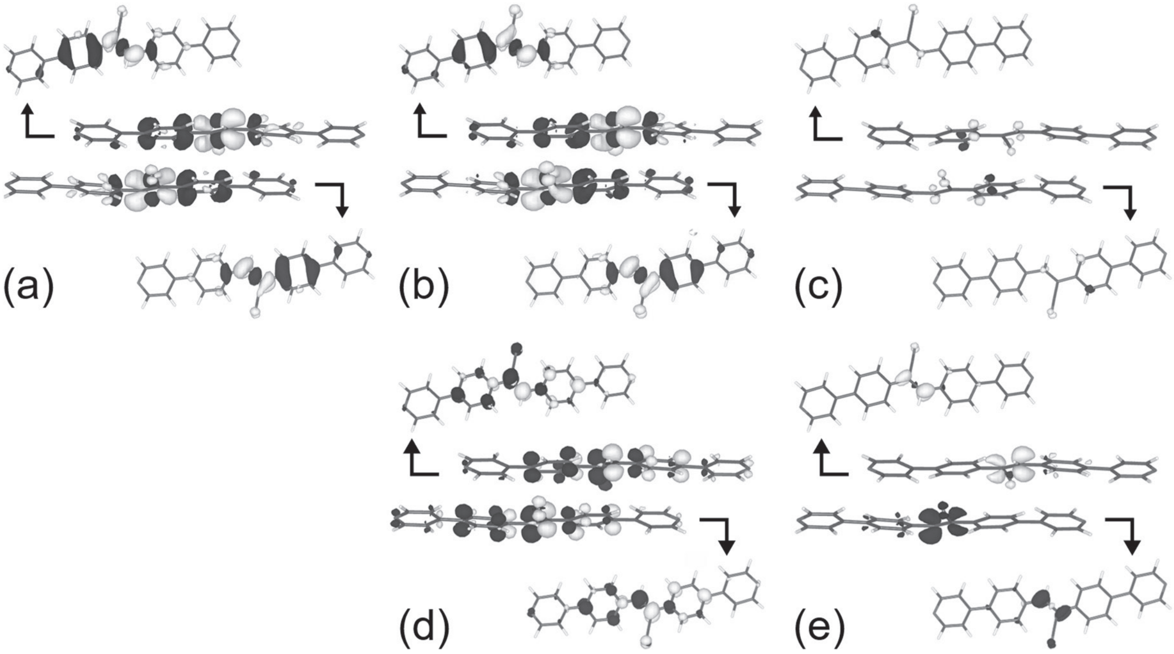

Fig. 2 Electron density differences of (a) $S_1@S_2$-$S_0@S_2$, (b) $S_2@S_2$-$S_0@S_2$, and (c) $S_2@S_2$-$S_1@S_2$. Isosurface values are 1×10^{-3} a.u. Overlap densities of (d) $S_2@S_2$-$S_0@S_2$ and (e) $S_2@S_2$-$S_1@S_2$. Isosurface values are 2×10^{-3} a.u.

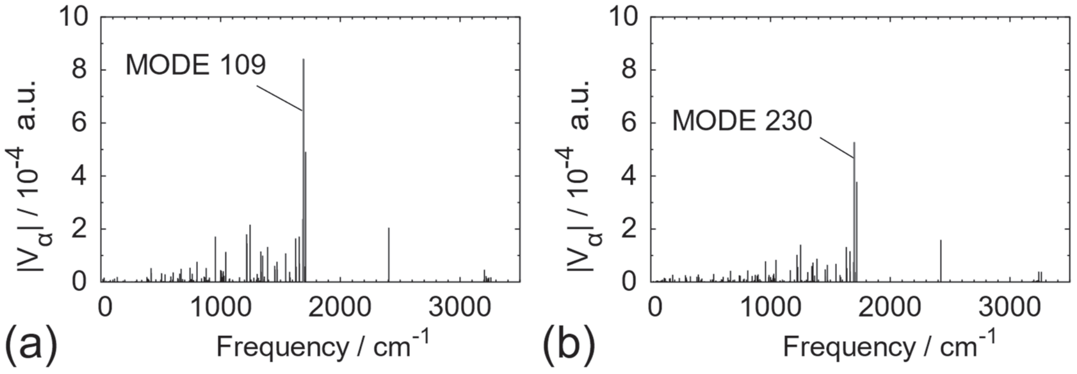

Fig. 3 Diagonal VCCs (a) of Monomer Model in the FC S_1 state and (b) of Dimer Model in the FC S_2 state.

excimer formation where the largest VCC of mode 109 in Monomer Model is 8.42×10^{-4} a.u. and that of mode 230 in Dimer Model is 5.27×10^{-4} a.u. This result indicates that the internal conversion from S_2 to S_0 in Dimer Model is suppressed in comparison with the one from S_1 to S_0 in Monomer Model because the rate constant of the internal conversion is strongly correlated with the diagonal VCCs. The electronic states delocalized over the molecules reduce the diagonal VCCs in solid phase to approximately $1/\sqrt{2}$ times those in solution phase [9]. Thus, the internal conversions from excited to ground states are more suppressed in solid phase than in solution phase.

Model building of metal oxide surfaces and vibronic coupling density as a reactivity index

To design heterogeneous catalysts and understand of their mechanisms, the sites for molecular adsorption on the solid catalyst must be clarified. The VCD as a function of a position identifies the reactive sites as those where the vibronic coupling is large. Therefore, VCD can be utilized as a reactivity index for systems with various reactive sites, such as solid surfaces. Reactivity indices, such as the frontier orbital density or VCD, strongly depend on the electronic structure of the frontier level. When building a model for the surface reactions of metal oxides based on a bulk crystal structure, the treatment of dangling bonds strongly affects the electronic structure. For instance, because hydrogen termination for dangling bonds involves electron doping, the frontier level is shifted by hydrogen termination. In this study, to build a model for the subsequent calculations, we employed a step-by-step hydrogen-terminated (SSHT) approach to reproduce the experimental observations. We applied VCD to the Ag-loaded Ga_2O_3 surface to show the effectiveness of VCD as a reactivity index for CO_2 adsorption on the surface [10].

Fig. 4 shows the calculated orbital levels of the bare cluster. The band gap of Ga_2O_3 has been experimentally estimated to be 4.6 eV [11]. However, the energy gap of the bare cluster is 0.8 eV, which is much smaller than the experimental value. This is because the occupied molecular orbitals become unoccupied when the cluster is cut from the crystal structure. The bare cluster has reactive dangling bonds arising from the cleavage of O atoms. The dangling bonds at the O atoms are terminated by H atoms because it has been experimentally observed that H atoms are adsorbed on the Ga_2O_3 surface [12]. The hydrogen termination, which involves electron doping, shifts the frontier level. The 16 unoccupied molecular orbitals must be occupied for the model to have a reasonably wide energy gap. Thus, the 32 H atoms, i.e., 2 H atoms for each unoccupied molecular orbital, are step-by-step bonded to O atoms with large molecular orbital coefficients. As a result, we obtained the hydrogen-terminated cluster with an energy gap of 5.4 eV after geometry optimization.

Fig. 5 shows the VCD of the SSHT cluster model, which is localized on the O atoms without hydrogen termination. This result indicates that these O atoms donate electrons to the reactants, and act as the Lewis bases. The stabilization arising from the structural relaxation after charge transfer is large at the sites where the VCD is localized. Therefore, the Ag-loaded Ga_2O_3 surface is modeled by placing a single Ag atom on one of the Lewis basic O atoms in the SSHT cluster model. Geometry optimization is performed after the initial position of CO_2 is set above the Ag atom. After the electron transfer, CO_2 undergoes structural relaxation from the linear structure to the bent structure. We found that CO_2 with a bent structure, which is advantageous for photocatalytic reduction, is adsorbed on the Ag atom.

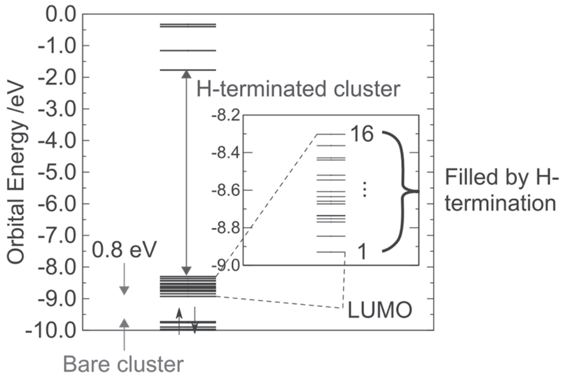

Fig. 4 Orbital levels of the non-hydrogen terminated cluster model.

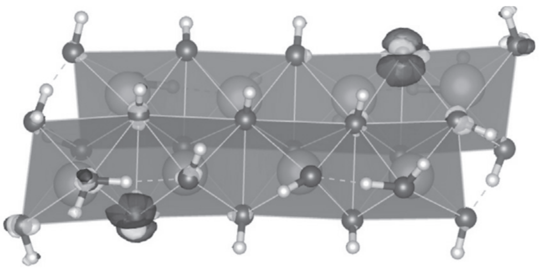

Fig .5 VCD of hydrogen terminated Ga_2O_3 cluster model.

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「振電相互作用密度解析に基づく(6,5)カーボンナノチューブの成長機構」
第55回フラーレン・ナノチューブ・グラフェン総合シンポジウム，仙台, 2018/9/11-13, 3P-20 ポスター

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日本コンピュータ化学会2018年春季年会，東京, 2018/6/7-8, 2O 04

(4) 大田航，佐藤徹
「半無限固体表面上における吸着分子の有効電子ハミルトニアン」
日本コンピュータ化学会2018秋季年会 ，弘前,　2O02 2018/11/3-4 2O 02

(5) 西川智裕，佐藤徹，春田直毅，兒玉健，阿知波洋次
Growth Mechanism of (6,5) Carbon Nanotube: Edge Structures and their Regioselectivities
第56回フラーレン・ナノチューブ・グラフェン総合シンポジウム，東京, 2019/3/2-4, 2P-20 ポスター

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(1) 佐藤　徹
「福井謙一博士生誕百年記念特別展示 ギャラリートーク」
京都大学総合博物館　京都　2018/12/2, 8

(2) 佐藤　徹

「振電相互作用密度とその応用ー発光、キャリア輸送、化学反応ー」

第１６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（京都大学）
2019/2/8

Yoshio Nishimoto

Program-Specific Assistant Professor

1. Summary of the research of the year

Development of TD-LC-DFTB/PCM

The development of large-scale quantum mechanical (QM) methods is one of the hottest topics in computational chemistry. Although standard single-reference QM methods, such as density functional theory (DFT), is much more economical than electron correlation methods, but are still time-consuming, and it is difficult to evaluate large systems. Modeling excited states is even more computationally demanding. QM methods can be drastically simplified by applying various approximations or employing fitted parameters, giving rise to semiempirical QM methods. For instance, the self-consistent charge density-functional tight-binding (DFTB) method was derived by introducing tight-binding approximations and applying a Taylor expansion to the density fluctuation of DFT.

In this fiscal year, the time-dependent long-range corrected second-order DFTB (TD-LC-DFTB2) method was implemented in conjunction with an implicit solvent model, the polarizable continuum model (PCM), namely TD-LC-DFTB/PCM [1], in a local version of the GAMESS-US software package based on an earlier implementation of the LC-DFTB2 method. The long-range correction employed in this study closely followed the work by Lustker *et al.* [2] Analytic first-order derivatives were also implemented by employing the Z-vector method as in the well-known TD-DFT with long-range corrections. The exchange-type term, which exhibited an unfavorable computational requirement, was computed via efficient matrix multiplications, and thus, the scaling of the (TD-)LC-DFTB method was expected to be cubic as in the conventional (TD-)DFTB. Compared with the conventional DFTB2, LC-DFTB2 for the ground state was 1.4 times more computationally expensive, whereas TD-LC-DFTB2 for excited states was approximately 3 times more computationally expensive. However, a single-point gradient calculation for a system consisting of 1000 atoms took only 30 min (without PCM) with one CPU core, demonstrating the advantage of the TD-LC-DFTB2 method. Adding PCM increased the computation time significantly.

As a pilot example, in the calculations for 3-hydroxyflavone (3HF), which exhibits dual emission, TD-LC-DFTB2 predicted similar absorption and enol-form emission energies as TD-LC-BLYP/aug-cc-pVDZ; however, the predicted emission energy of the keto form deviated significantly from the experiment and from TD-LC-BLYP. Further benchmark calculations were performed using the other TD-DFTB methods implemented in GAMESS-US, TD-DFTB2, TDDFTB3, and TD-LC-DFTB2 for a set of molecules that were previously collected and theoretically evaluated by Jacquemin et al. Even though TD-LC-DFTB2 clearly overestimated the absorption and 0−0 transition energies when compared with the experimentally measured values, they agreed well with the results obtained by CAM-B3LYP and significantly reduced the computational cost. Further, when the range separation parameter ω was decreased from 0.30 to 0.15, the results agreed even more closely with CAM-B3LYP (Fig. 1). Therefore, based on these benchmark calculations, TD-LC-DFTB2 can be considered a computationally cost-effective approximation of DFT with long-range corrections.

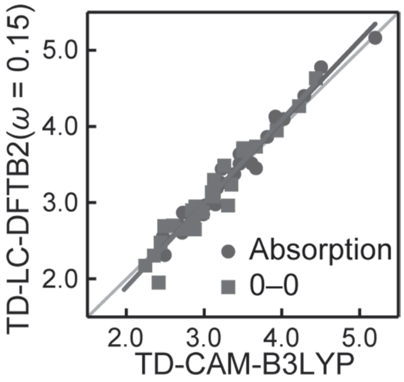

Fig. 1 Comparison of absorption and 0–0 transition energies calculated with CAM-B3LYP and LC-DFTB with ω = 0.15.

It should be noted that the currently available parameter set is rather limited and only includes various combinations of H, C, N, and O elements. In addition, the extension to include the third-order Taylor expansion, namely (TD-)LC-DFTB3, is also important. The extension to TD-LC-DFTB3 should be rather straightforward as long as the LC-DFTB3 energy is formulated and appropriate parameters are developed because TD-DFTB3 has been developed in GAMESS-US. Hence, further development and improvement are essential for practical application studies. The developed method is expected to be publicly available in GAMESS-US in the future.

Development of Analytic Derivatives of PC-NEVPT2

A balanced treatment of dynamic and static electron correlation is important in computational chemistry, and multireference perturbation theory (MRPT) is able to do this at a reasonable computational cost. In addition to the above study, analytic first-order derivatives, specifically gradients and dipole moments, are developed for a particular MRPT method, state-specific partially contracted *n*-electron valence state second-order perturbation theory (PC-NEVPT2) [3,4].

Looking at MRPT methods, such as NEVPT2 and complete active space second-order perturbation theory (CASPT2), in terms of analytic derivative techniques, the first challenge is posed by the fact that most MRPT energies are not variationally optimized with respect to wavefunction parameters (molecular orbital and configuration coefficients). This necessitates the evaluation of derivatives of nonvariational parameters, which are orbital and configuration interaction (when internally contracted) coefficients. A straightforward approach is to evaluate these derivatives directly by solving the coupled-perturbed equations. Despite the simplicity of this strategy, the number of coupled-perturbed equations to be solved increases linearly with the number of atoms in the system, so it is not suitable for treating even medium-sized systems. Another, more practical, approach relies on the Z-vector or Lagrangian methods. The advantage of these methods is the reduced computational requirement: solving only one perturbation-independent equation is sufficient to evaluate response contributions for the first-order derivatives. In this study, first-order derivatives are computed by exploiting the Z-vector method, so the additional computational cost is not explicitly dependent on the number of atoms. Furthermore, the derived expressions do not involve any vanishing denominators resulting from orbital degeneracies (in contract to the strongly contracted variant).

The methodology has been implemented in a local version of GAMESS-US and applied to typical systems: the geometrical parameters of O_3 and O^-_3 and the 0–0 transition energies of methylpyrimidines and a series of *trans*-polyacetylenes. The results show the importance of perturbative corrections and the necessity for development of analytic derivatives. A comparison with experiment suggests that the accuracies of NEVPT2 and CASPT2 are roughly comparable: CASPT2 with the IPEA shift outperforms other wavefunction methods for methylpyrimidine derivatives, while NEVPT2 does so for *trans*-polyacetylene.

CASPT2 calculations for the state-averaged CASSCF reference required a shift technique84 to ensure convergence of the amplitude equation. The 0–0 transition energies computed using the extended multistate (XMS) CASPT2 method with and without the IPEA shift indicated that the impact of the IPEA shift is as large as 0.3 eV. The ionization potential–electron affinity (IPEA) shift improved the agreement with experiment for methylpyrimidine derivatives, but slightly degraded it for the larger transpolyacetylene. These two shift techniques may impart a slight arbitrariness to multistate CASPT2 calculations, but NEVPT2 is an intruder-state-free method, and no such empirical parameters are required as long as an appropriate active space is used. In addition, since NEVPT2 is size-consistent, it can be applied to chemical reactions.

Extension to quasidegenerate NEVPT2 and the computation of derivative coupling are essential tasks for the future, in particular in the study of photochemical processes, for example, in the identification of conical intersections. Algorithmic improvements are also highly desirable; for instance, CASSCF in GAMESS-US does not utilize any matrix decomposition techniques, which severely restricts the number of orbitals that can be employed in CASSCF and NEVPT2 calculations.

Development of Analytic Derivatives of FMO-LC-DFTB

In the study of the fragment molecular orbital-based (FMO) LC-DFTB method [5], I implemented analytic first-order derivatives of the FMO-LC-DFTB method. As in earlier FMO-DFTB studies, the analytic derivatives are computed by solving the self-consistent Z-vector equation. The accuracy of the implementation was evaluated by comparing the difference between the analytic and numerical gradients for a $(H_2O)_{64}$ cluster. The maximum deviations are only 1.5×10^{-6} and 9.8×10^{-6} hartree/bohr for FMO2-LC-DFTB and FMO3-LC-DFTB, respectively. The accuracy was also verified by analyzing the energy conservation in NVE molecular dynamics simulations for a $(H_2O)_{64}$ cluster with varying time integration intervals. For the slope of the energy fluctuations versus the time step, ideally, the fully analytic gradient would yield a slope of 2 when plotted on a double-logarithmic scale due to our use of a second-order velocity Verlet time integration algorithm. The actual calculation showed that the obtained slopes were very close to the theoretical slope: 1.99 for FMO2 and 1.98 for FMO3.

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(1) Vuong, V. Q.; Nishimoto, Y.; Fedorov, D. G.; Sumpter, B. G.; Niehaus, T. A.; Irle, S.
“The Fragment Molecular Orbital Based on Long-Range Corrected Density-Functional Tight-Binding”
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3. Presentation at academic conferences

(1) 西本　佳央
「密度汎関数強束縛法と周期的境界条件を組み合わせる実装」
第21会理論化学討論会（P56）、愛知県、2018年5月16日

(2) 西本　佳央、フェドロフ　ドミトリ
「ナノ材料への応用へ向けたフラグメント分子軌道法と密度汎関数強束縛法を用いた理論開発」
第12回分子科学討論会（3E05）、福岡県、2018年9月12日

(3) 西本　佳央
「時間依存密度汎関数強束縛法を用いた理論開発」
日本コンピュータ化学会2018秋季年会（2P17）、青森県、2018年11月4日

(4) 西本　佳央
「長距離補正時間依存密度汎関数強束縛法を用いた理論開発」
日本化学会第９９春季年会（1D6-42）、兵庫県、2019年3月16日

4. Others

(1) Yoshio Nishimoto
“FMO-DFTB: A Semi-Empirical Quantum Chemical Method Applicable to One-Million-Atom Systems”
FUKUI 2018 Satellite Symposium, Kyoto, October 13, 2018

２．リサーチダイレクター

Kimihiko Hirao

Research Director

1. Summary of the research of the last 6 months (3-5 pages, includes appropriate figures and tables)

(a) Excitation Energies Expressed as Orbital Energies of KS-DFT with LC Functionals

Density functional theory (DFT) is as a powerful computational tool for the chemical systems. Conceptually, it is appealing because, with the one-electron Kohn-Sham (KS) DFT, all properties are in principle obtainable directly from an observable that is the electron density. A major obstacle to the application of KS-DFT is that the form of the exact functional is yet unknown. As a result, there have been continuous developments of approximate DFT methods. These methods represent a useful way for tackling many chemical problems with adequate accuracy.

Despite the success of approximate functionals, they are not without problem. Two major causes for these failures are the incorrect long-range behavior (at tails of the density) and self-interaction errors associated with the local character of approximate functionals. While a DFT-based cure for these drawbacks remains elusive, non-DFT strategies have been developed to alleviate the symptoms. Some of these approaches, e.g., the use of Hartree–Fork (HF) exchange in hybrid-DFT, have been demonstrated to be useful and widely applicable.

To tackle these problems the long-range corrected (LC) functionals have been proposed by us and many others. In the LC scheme, the electron repulsion operator, $1/r_{12}$, is divided into short-range (SR) and long-range (LR) components using a standard error function:

$$\frac{1}{r_{12}} = \frac{1 - erf(\mu r_{12})}{r_{12}} + \frac{erf(\mu r_{12})}{r_{12}}$$

The parameter μ determines the weight of the two ranges as a function of r_{12}. DFT exchange functional is included in the first term for SR interactions, while LR orbital–orbital exchange interaction is described by the second term using the HF exchange integral. In most cases, LC functionals have common features, especially in the high reproducibility of van der Waals bonds, electronic spectra, optical response properties. A striking feature of LC-DFT that is of particular relevance to the present study, which focuses on electronic excitation energies, is that LC-DFT satisfies Koopmans-type theorem. The LC orbital energy $-\varepsilon_i$ of HOMO corresponds to accurate vertical ionization potentials (IP), and likewise $-\varepsilon_a$ of LUMO corresponds to accurate vertical electron affinities (EA). In other words, ε_i is the energy for a correlated electron moving in orbital *i* and ε_a is that for an attached electron in the unoccupied orbital *a*.

A new theoretical scheme is proposed for estimating excitation energies using Kohn-Sham (KS) solutions calculated with long-range corrected (LC) functionals. It is simple and conceptual. Reasonable excitation energies are obtained with only orbital energies. There is no need for integral evaluation or matrix diagonalization.

An electronic transition can be expressed in two steps, the first being the removal of an electron from the occupied orbital and the second being attachment of an electron to the unoccupied orbital. The former process corresponds to the ionization energy of the neutral system while the latter corresponds to the electron affinity of its cation. The solution of the exact KS equation satisfies Koopmans-type theorem due to the Janak's theorem and the energy linearity theorem. Thus, the vertical ionization potential and electron affinity can be obtained from KS solutions and one electron excitation energies are expressed as the differences between occupied orbital energies of a neutral molecule and corresponding unoccupied orbital energies of its cation.

Conventional approximate functionals do not satisfy the Koopmans-type theorem since the energy linearity theorem is not satisfied due to the delocalization errors. On the contrary LC satisfies the energy linearity theorem and therefore satisfies the Koopmans-type theorem. The total electronic energy of LC varies almost linearly as a function of its fractional occupation number. LC orbital energies reproduce the ionization energies and electron affinities with high accuracy. One electron excitation energies are expressed as the difference between LC occupied orbital energies and unoccupied orbital energies. Two such expressions can be used, with one employing the orbital energies for the neutral and cationic systems, while the other utilizes orbital energies of just the cation. The electron affinity of a molecule is the ionization energy of its anion. If we utilize this identity two expressions coincide and give the same excitation energies. This identity can also be used for improving DFT functionals.

When the present scheme is used in conjunction with LC-type functionals we obtain promising results for valence and core excitations. Illustrative calculations are performed for H2O, C2H4, H2CO, polyenes, five-membered ring compounds, DNA bases etc.

Orbitals provide an intuitive language for the complex reality of molecules. In addition, they are not merely a convenient concept but, through Koopmans' theorem, they provide a simple and natural connection between orbital energies and an experimental observable, namely ionization energies. The solutions of KS equation with LC functionals satisfy Koopmans-type theorem and they thus have a strict physical meaning. We will further demonstrate the physical significance of KS orbitals.

(b) The reHISS Three-Range Exchange Functional with an Optimal Variation of Hartree-Fock and Its Use in the reHISSB-D Density Functional Theory Method,

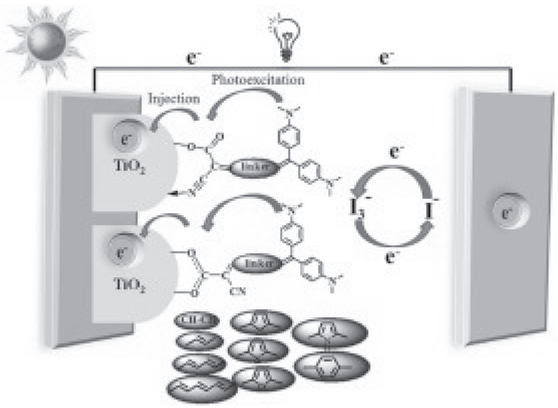
In the present study, we have reparametrized the HISS exchange functional. The new "reHISS" exchange provides a balance between short- and mid-range Hartree–Fock exchange (HFX) and a large total HFX coverage, with a fast convergence to zero HFX in the long range. The five parameters in this functional (according to equations 3 and 4 in the main text) are $c_{SR} = 0.15$, $c_{MR} = 2.5279$, $c_{LR} = 0$, $\omega_{SR} = 0.27$, and $\omega_{LR} = 0.2192$. The combination of reHISS exchange with a reparametrized B97c-type correlation functional (Chan et al., *J. Comput. Chem*. **2017**, *38*, 2307) and a D2 dispersion term ($s_6 = 0.6$) gives the reHISSB-D method. We find it to be more accurate than related screened-exchange methods and, importantly, its accuracy is more uniform across different properties. Fundamentally, our analysis suggests that the good performance of the reHISS exchange is related to it capturing a near-optimal proportion of HFX in the range of interelectronic distance that is important for many chemical properties, and we propose this range to be approximately 1–4Å.

(c) Accelerated Long-range Corrected Exchange Functional Using a Two-Gaussian Operator combined with One-parameter Progressive Correlation Functional [LC-BOP(2Gau)],

Recently, we proposed a simple yet efficient method for the computation of a long-range corrected (LC) hybrid scheme [LC-DFT(2Gau)], which uses a modified two-Gaussian attenuating operator instead of the error function for the long-range HF exchange integral. This method dramatically reduced the computational time while maintaining the improved features of the LC density functional theory (DFT). Here, we combined an LC hybrid scheme using a two-Gaussian attenuating operator with one-parameter progressive correlation functional and Becke88 exchange functional with varying range-separation parameter values [LC-BOP(2Gau) with various μ values of 0.16, 0.2, 0.25, 0.3, 0.35, 0.4, and 0.42] and demonstrated that LC-BOP(2Gau) reproduces well the thermochemical and frontier orbital energies of LC-BOP. Additionally, we revised the scaling factors of the Gaussian multipole screening scheme for LC-DFT(2Gau) to correspond to the angular momentum of orbitals, which decreased the energy deviations from the energy with the no-screening scheme.

(d) DFT/TD-DFT Calculations of the Electronic and Optical Properties of Bis-*N*,*N*- Dimethylaniline-Based Dyes for Use in Dye-Sensitized Solar Cells

Using density functional theory (DFT) and time-dependent DFT (TD-DFT) methods, the current study reports the role of inserting acyclic and cyclic conjugated π-linkers in bis-*N*,*N*-dimethylaniline-based dyes as sensitizers in the dye-sensitized solar cells (DSSCs). Some optical and electron transfer parameters are calculated to accomplish our objective. The results show that increasing number of ethylene π-linker (–CH[dbnd]CH–) enhances light harvesting efficiency but decreases the driving force for electron injection and possibility of dye regeneration with encouraging dye aggregation on the surface of the electrode. Extending the conjugation length of the linker decreases the efficiency, while incorporating some cyclic conjugated linkers has a positive effect on the efficiency through effective coexistence of both direct and indirect mechanisms of electron injection. A comparison with experiment and previous theoretical studies on NKX-2554 (**P1**) and NKX-2569 (**P2**) is considered.



2. Original papers

The reHISS Three-Range Exchange Functional with an Optimal Variation of Hartree-Fock and Its Use in the reHISSB-D Density Functional Theory Method,
B Chan, Y Kawashima, K Hirao,
J..Comput.Chem.(Memorial Festschrift for Keiji Morokuma), 40, 29-38 (2019)

Accelerated Long-range Corrected Exchange Functional Using a Two-Gaussian Operator combined with One-parameter Progressive Correlation Functional [LC-BOP(2Gau)],
JW Song and K Hirao,
J.Comput.Chem.(Memorial Festschrift for Keiji Morokuma), 40, 104-112 (2019)

DFT/TD-DFT Calculations of the Electronic and Optical Properties of Bis-*N*,*N*- Dimethylaniline-Based Dyes for Use in Dye-Sensitized Solar Cells
Asmaa B. El-Meligy, Nobuaki Koga, Satoru Iuchi, Kumi Yoshida, Kimihiko Hirao, Ahmed H. Mangood, and Ahmed M. El-Nahas
J.Photochem. & Photobio. A: Chemistry, 367 332-346 (2018)

３．FIFC リサーチフェロー

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1. Summary of the Research of the Year

(a) Salvaging Reactive Fullerenes from Soot by Exohedral Derivatization

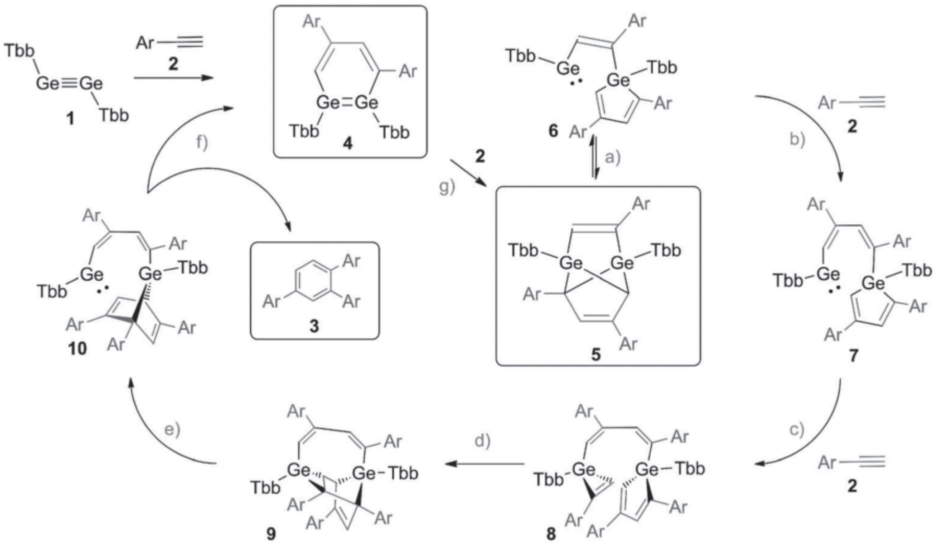
Fullerenes comprise a large family of molecular carbon allotropes, which possess different numbers of carbon atoms and cage frameworks of different geometries. The spherical shapes of the molecules enable the encapsulation of guest atoms, clusters, or even small molecules. Particularly, fullerenes encaging metal atoms, which are known as endohedral metallofullerenes, constitute another fullerene family that is substantially different from empty fullerenes. Nowadays, macroscopic amounts of empty fullerenes and endohedral metallofullerenes are produced experimentally by using the standard arc-discharge method with a Krätschmer–Huffman arc reactor. By arc-discharging graphite electrodes, fullerene-containing soot is grown during the diffusion of carbon vapor and subsequent cooling in the reactor. For the production of endohedral metallofullerenes, metal-containing graphite electrodes are used instead of pure graphite electrodes, where encapsulation of metal atoms occurs simultaneously with the carbon cage formation. Because of the high temperature (2000–3000 K) conditions, it is believed that only thermodynamically favorable fullerene species survive among innumerable, topologically possible fullerene structures. To generate macroscopic amounts of pure-form empty fullerenes and endohedral metallofullerenes, extraction with organic solvents followed by high-performance liquid chromatography separation has been recognized as an effective and reliable approach. Therefore, their availability is reliant largely on their solubility in organic solvents. To date, several stable and soluble empty fullerenes and endohedral metallofullerenes have been prepared and isolated. Their structures have been characterized with various techniques including NMR spectroscopy and single-crystal X-ray diffractometry. However, it needs to be emphasized that many other unidentified fullerene species, which must be reactive and insoluble in their pristine forms, remain in soot. These nonextractable fullerene species are also termed “missing fullerenes”. In this respect, one might say that there are still plenty of treasures in soot. These missing species must have extremely small HOMO–LUMO gaps and might have unconventional cage structures, which would fascinate not only chemists but also physicists and materials scientists.

How can these reactive (missing) fullerenes be salvaged from soot? Recent advances have shown that reactive fullerenes can be stabilized and extracted from soot by exohedral derivatization. In this review, we have presented a summary of the most significant progress in studies of salvaging reactive fullerenes, most of which have been reported during the last decade. By salvaging reactive fullerenes by exohedral derivatization, a means of preparing macroscopic amounts of unconventional fullerenes as their derivatives has been provided. Structural elucidation of the stabilized derivatives has revealed that various anomalous carbon cages are already within our reach. The most significant findings are related to the fact that pyrolytic high-temperature derivatizaion promotes cage skeletal transformations involving Stone-Wales rearrangement and/or C_2 elimination processes, which are otherwise difficult to observe under reasonable experimental conditions without additional stabilization. These transformations are regarded as important fullerene formation processes. Their mechanisms remain of considerable fundamental interest, and unveil remarkable carbon allotropy. In this respect, in situ derivatization by carbon arc fullerene formation and structural elucidation of the resultant derivatives has also provided structural insight into the key intermediates of the formation of stable structures satisfying the so-called isolated pentagon rule. Consequently, the salvaged cage frameworks can be a missing link for long-standing considerations of the fullerene formation mechanism. Furthermore, in situ derivatization of endohedral metallofullerenes during extraction enables the stabilization and solubilization of endohedral metallofullerenes with high radical character. These salvaged derivatives stand as their stabilized forms with enlarged HOMO–LUMO gaps. In this respect, defunctionalization of such exohedrally stabilized fullerenes to obtain bare small-band-gap fullerenes remains a challenging task to unveil their intrinsic properties.

(b) Regioselective Cyclotrimerization of Terminal Alkynes Using Digrmynes

Academically and industrially, the catalytic activation of neutral organic molecules, followed by the formation of C-C bonds, is highly important to increase the complexity and/or value of simple starting materials. For example, cyclotrimerization reactions of alkynes that afford aromatic compounds represent very important C-C bond formation reactions because of the versatility of the resulting aromatic products. Traditionally, transition metal catalysts have been used for this purpose, as some transition metal complexes based on, for example, cobalt, efficiently activate alkynes for oxidative additions, ring expansions, and reductive eliminations with concomitant formation of C-C bonds. The reaction mechanism underlying the transition metal-catalyzed cyclotrimerization of alkynes has been well established. Several transition metal-based catalysts have been developed and they are highly efficient with respect to both chemical yields and selectivity, and these are superior to catalysts based on main group elements, although such transition metal-free catalytic systems are highly desirable to avoid the use of precious metals. The reason behind why similar C-C coupling reactions of neutral small organic molecules, in the absence of transition metal catalysts, remain largely unknown could be due to difficulties associated with the reductive elimination process of main group elements as a result of the strong covalent bonds between the main group atoms and carbon atoms.

It is therefore hardly surprising that only few cyclotrimerizations of alkynes, catalyzed by main group elements, have been accomplished and proceed by redox process of the main group elements. For example, in the Si_2Cl_6-catalyzed cyclotrimerization of alkynes, $SiCl_3$ radicals initiate the radical trimerization. Because such radical reactions usually require high temperatures, the regioselectivity is easily compromised. Yet, the creation of main group element-based catalysts for C-C coupling reactions that proceed by redox processes, similar to those in transition metal-based catalysts, remain challenging. Herein, we report a new transition metal-free catalytic system for the cyclotrimerization of terminal arylalkynes, and include a germanium-centered redox process. It is discovered that a substoichiometric amount of a previously reported isolable digermyne promotes the regioselective cyclotrimerization of several arylacetylenes in high yield. The present results demonstrate that bespoke main group element compounds



Reaction mechanism for the cyclotrimerization of arylacetylene promoted by digermyne (TbbGe≡GeTbb, Tbb = 2,6-[CH(SiMe$_3$)$_2$]2-4-t-Bu-phenyl)

activate catalytically small neutral organic molecules and induce the formation of C-C bonds. For example, digermynes (RGe≡GeR, R=organic groups) act as a precatalyst for the formation of C-C bonds in the absence of a transition metal catalyst, specifically for the perfectly regioselective cyclotrimerization of terminal arylacetylenes. In these reactions, the two Ge atoms undergo mild redox processes between Ge^{II} and Ge^{IV}, which ultimately enables them to transform small organic molecules with a performance that rivals that of transition metal catalysts. The absolute stereoselectivity of the germanium catalyst is probably due to kinetically controlled reactions of such main group element compounds, while transition metal based reactions are usually controlled thermodynamically. Transition metal catalysts for Reppe reactions promote the cyclotrimerization based on their flexibility to switch between oxidation states, while the combination of Ge^{II} (germylene) and Ge^{IV} (germole) species stabilizes the redox process during the cyclotrimerization. Low-coordinate main group element compounds such as digermynes (RGe≡GeR) thus represent promising prospectives for transition metal-free catalysts for C-C coupling reactions.

(c) Control of Near Infrared Photoluminescence Properties of Single-Walled Carbon Nanotubes by Functionalization with Dendrons

Single-walled carbon nanotubes (SWNTs) have generated considerable interest as promising nanocarbon materials for practical applications because of their outstanding mechanical, electrical, and optical properties.1,2 Photoluminescence (PL) properties of SWNTs observed in the near-infrared (NIR) region are studied keenly for applications in bio-imaging, energy conversion, sensing, and optoelectronics. The E_{11} and E_{22} energies are known as the first and second transitions between the van Hove singularities. Observation of the E_{11} PL of SWNTs needs the E_{22} excitation owing to the small Stokes shift. Thus, PL measurements are a strong tool for the characterization of the chiral index of SWNTs using the two factors based on the E_{11} and E_{22} energies. One of the advantages is that the excitation and emission wavelengths can be selected from a wide range as they are based on the SWNT structure. Recently, it has been revealed that the functionalization of SWNTs is an effective means to exert control over their NIR PL properties. It has been reported that new red-shifted PL peaks are observed by the reaction of individually dispersed SWNTs in D_2O solution containing a surfactant with ozone or benzene diazonium compounds. The Stokes shift of the red-shifted PL of functionalized SWNTs is sufficient and allows excitation with both E_{22} and E_{11} energies. Excitation with NIR light improves the PL performance of SWNTs in biological imaging materials because NIR light has high transparency in biological tissues and reduces phototoxicity and autofluorescence.

For such practical applications, it is very important to develop methods to control the PL properties of SWNTs on a bulk scale. Therefore, we clarified the steric effect of the reagent used in the reductive alkylation of SWNTs and demonstrated the control of PL properties of SWNTs using dendrons of different generations. The degree of functionalization of the SWNTs decreased with the increasing bulkiness of the dendrons used. After functionalization, new red-shifted PL peaks could be observed around 1110 nm (E_{11}* PL) and 1210 nm (E_{11}** PL), where the intensities were drastically enhanced by the thermal treatment. The relative peak intensity of E_{11}* PL to that of E_{11}** PL increased with the increasing bulkiness of the dendrons. Density functional theory calculations of the functionalized SWNTs with dendrons suggest that the adducts with less bulky hydroalkylated substitution are stable in Clar structures and the addition positions predominantly determine the PL peak positions. The tuning of the functionalization degree by manipulating the bulkiness is advantageous because this method can be utilized regardless of the thermal stability of the functionalized SWNTs. The selective emergence of the red-shifted PL peak and control of the PL efficiency by sidewall functionalization contribute to our understanding of the intrinsic nature of SWNTs and the practical application of SWNTs as NIR PL materials.

(d) La-La Bonded Dimetallofullerenes $[La_2@C_{2n}]^-$: Species for Stabilizing C_{2n} (2n = 92–96) besides $La_2C_2@C_{2n}$

Recent reports pointed out that the formal La_2C_{2n} (2n = 92–106) series can exist stably as carbide cluster metallofullerenes $La_2C_2@C_{2n}^{-2}$ with their successful crystallographic characterization. We suggested that the corresponding dimetallofullerenes $La_2@C_{2n}$ possessing the lowest potential energies are also plausible candidates because of their favorability in statistical thermodynamics. This can be demonstrated on La_2C_{94} and previously reported other La_2C_{2n} (2n = 92, 96–100) series by density functional theory calculations and statistical mechanics analyses. It was found that these thermodynamically favorable $La_2@C_{2n}$ isomers turned out to be kinetically unstable radicals due to the presence of one unpaired electron on the carbon cage, making them missing fullerenes and difficult to be captured in their pristine forms, except for the experimentally obtained $La_2@D_5(450)\text{-}C_{100}$ that has no unpaired electron. Such kinetic instability could be modified by electron reduction (the products were denoted as $[La_2@C_{2n}]^-$) or other similar exterior functionalization with CF_3 and benzyl radicals, resulting in La–La bonded and paramagnetic species capable of being captured. On the basis of these approaches, carbon cages $D_3(85)\text{-}C_{92}$, $C_s(120)\text{-}C_{94}$, $D_2(186)\text{-}C_{96}$, and $C_2(157)\text{-}C_{96}$ are predicted to be feasibly captured as both pristine carbide cluster metallofullerenes and electron reduced dimetallofullerenes derivatives.

2. Original Papers

(1) T. Sugahara, J. –D. Guo, T. Sasamori, S. Nagase, and N. Tokitoh,
"Reversible Addition of Terminal Alkenes to Digermynes"

Chem. Commun., **54**, 519-522 (2018).

(2) Z. Slanina, F. Uhlík, S. Nagase, T. Akasaka, X. Lu, and L. Adamowicz,
"Cyclic Water-Trimer Encapsulation into D_2(22)-C_{84} Fullerene"
Chem. Phys. Lett., **695**, 245-248 (2018).

(3) T. Sugahara, J. –D. Guo, T. Sasamori, S. Nagase, and N. Tokitoh,
"Regioselective Cyclotrimerization of Terminal Alkynes Using a Digermyne"
Angew. Chem. Int. Ed., **57**, 3499-3503 (2018).

(4) Q. –Z. Li, J. –J. Zheng, L. He, S. Nagase, and X. Zhao,
"La-La Bonded Dimetallofullerenes $[La_2@C_{2n}]^-$: Species for Stabilizing C_{2n} (2n = 92-96) besides $La_2C_2@C_{2n}$"
Phys. Chem. Chem. Phys., **20**, 14671-14678 (2018).

(5) T. Sugahara, J. –D. Guo, D. Hashizume, T. Sasamori, S. Nagase, and N. Tokitoh,
"The Selective Formation of a 1,2-Disilabenzene from the Reaction of a Disilyne with Phenylacetylene"
Dalton Trans., **47**, 13318-13322 (2018).

(6) Y. Maeda, Y. Konno, M. Yamada, P. Zhao, X. Zhao, M. Ehara, and S. Nagase,
"Control of Near Infrared Photoluminescence Properties of Single-Walled Carbon Nanotubes by Functionalization with Dendrons"
Nanoscale, **10**, 23012-23017 (2018).

3. Review

(1) M. Yamada, T. Akasaka, and S. Nagase,
"Salvaging Reactive Fullerenes from Soot by Exohedral Derivatization"
Angew. Chem. Int. Ed., **57**, 13394-13405 (2018).

田中　一義

FIFC リサーチフェロー

1. 今年度の研究の要約

有機金属錯体における水素貯蔵の可能性探索は、燃料電池の水素源確保に向けて重要である。この考えに沿って2017年度はPH_3を配位子とするメタロセン錯体 (M = Ti^{III}, Cr^{III}, Sc^{III} および V^{III}) における水素分子との反応と吸着について、遠距離および分散力補正を含めたDFT計算(ωB97XD/aug-cc-pVDZ)解析に基づく理論的検討を行った。特にKubas錯体の形成と余剰の水素分子の吸着に着目して反応および吸着エンタルピーの算出を行い、それぞれの金属錯体における水素吸蔵能の評価を行った。これにより$[Cp_2Ti^{III}(PH_3)]^+$, $[Cp_2Sc^{III}(PH_3)]^+$ および$[Cp_2V^{III}(PH_3)]^+$については１分子当たり２個の水素分子吸着能が発現することを明らかにした。しかしこれらは重金属で分子量も大きい欠点もある。したがって2018年度には軽金属であるMgを用いて軽量化に向けた有機金属錯体分子を設計し、同時により多量の水素分子の吸着を実現することを目指した理論的検討を行った。

なおこの要約はトヨタ自動車と豊田中研との共同研究の一部であり、平成31年3月の日化春季年会で発表済みの部分である。また実験的な研究部分は省略した。

【始めに】燃料電池を搭載した自動車(FCV)における水素ガス供給法としては、通常の航続距離等を考慮した場合700気圧程度に加圧充填した水素タンクを積載する必要がある。その安全性は一応担保されて市販のFCV車種に搭載されているが、高圧に耐える容器の重量および体積軽減などさらに改善すべき点をいくつか含んでおり、これに向けた可能性を探ることが重要な課題となっている。したがって有機金属錯体における水素分子貯蔵の可能性を明らかにすることは意味があると考えられる。

本研究では有機金属錯体への水素分子付加反応についての理論的解析を行っている。2017年度には図１に示すような付加体(Kubas錯体)[1]においてRをホスフィン(PH_3)とし、MをTi^{III}, Sc^{III}, Cr^{III}およびV^{III}とするメタロセン錯体について水素分子吸着に関する解析を行い、吸着されうる水素分子数やその電子状態に関する解析を行ったが、これらにおける吸着水素分子数は２であった。Mの

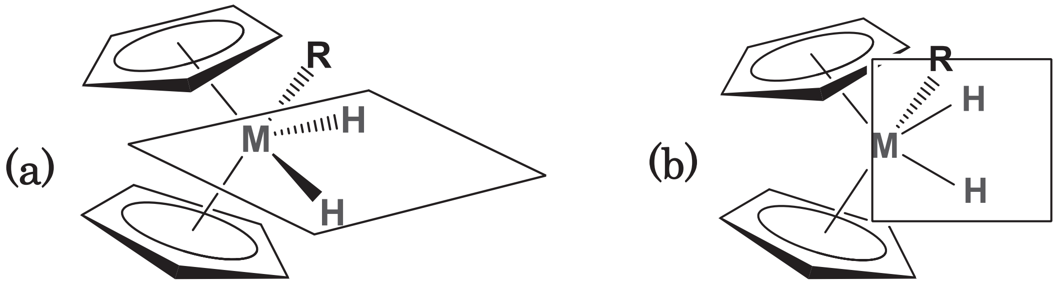


Fig. 1　Two kinds of Kubas complexes: (a) horizontal Kubas complex, and (b) vertical Kubas complex, where M stands for a transition metal of valence III state and R for an appropriate ligand.

うちでCr^{III}については安定な解が得られなかった。

これに引き続いて2018年度には金属錯体分子の軽量化および吸着水素分子数の向上を目指して、図2に示す3種類のMg有機分子錯体を設計し、これらの錯体における水素分子吸着に関する計算を行い、吸着しうる水素分子数やその電子状態に関する解析を行った。

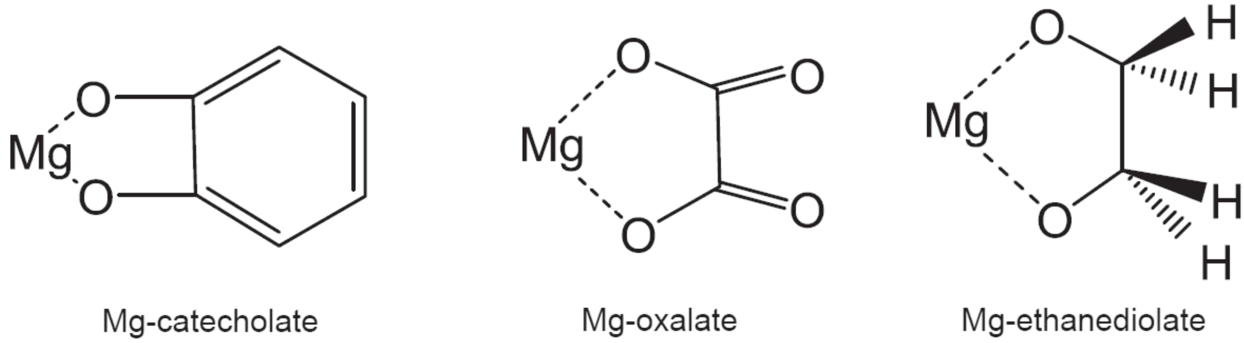
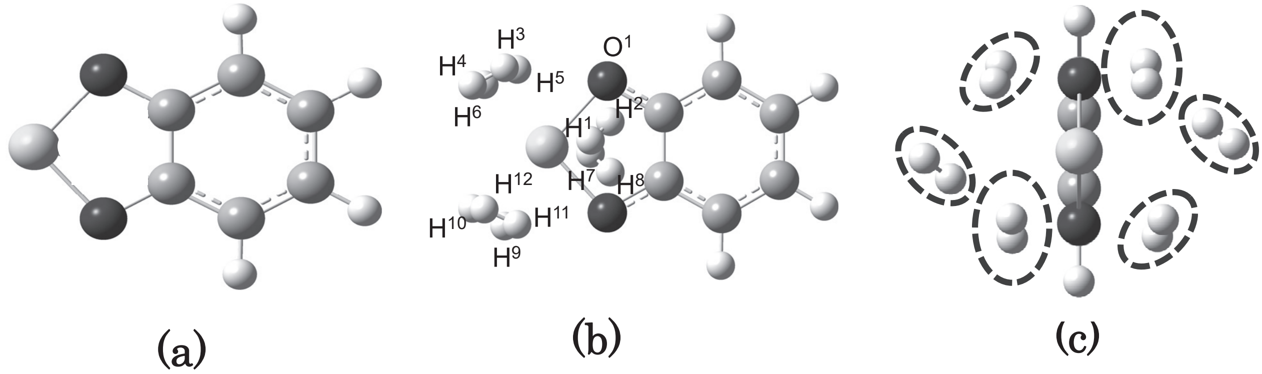


Fig. 2　Three kinds of organomagnesium complexes examined in this study.

【計算方法】計算にはGaussian09ソフトを使用し[2)]、密度汎関数理論(DFT)に基づくωB97XD法を用いた。基底としてはcc-pVDZを使用した。具体的には図2に示すMg有機金属錯体の構造最適化を行い、これらに対する水素分子吸着の可能性、最大吸着数、吸着した状態の錯体の構造最適化、さらに吸着された水素分子の電子状態等に関する知見を得るための解析を行った。

【Mg-catecholateの解析結果】

水素分子が吸着される前のこの錯体の構造は図3(a)のようで、この錯体には水素分子が結合することなくすぐに吸着を開始して、最高で水素6分子が吸着されることが明らかとなった(図3(b),(c))。



(a)　(b)　(c)

Fig. 3　Optimized structures of (a) Mg-catecholate complex and (b) that with six absorbed H_2 molecules.　In (c) is indicated the same with (b) from a different angle with indication of adsorbed H_2 molecules by red-broken ovals.

最初の水素分子吸着によるエンタルピー安定化は19.09 kJ/mol(298.15 K, 1 atm; 以下同じ)、第2、第3および第4の水素分子吸着によるエンタルピー安定化の増分はそれぞれ17.00, 13.57, 10.43 kJ/molであった。さらに第6の水素分子吸着による安定化の増分は、第4分子吸着からすれば12.04 kJ/molで1分子当たりの増分は6.02 kJ/molであった。このように吸着水素分子数が増えるほど、エ

ンタルピー安定化の増分は漸減するが、少なくとも第 6 水素分子まで吸着されることが明らかとなった。なお Tsivion らは、Mg-catecholate に水素分子が３分子まで吸着されうることを報告している[3)]。

この第 6 水素分子まで吸着した構造における H^1-H^2 距離は 0.762 Å（WBI = 0.986）で、孤立水素分子の結合距離 0.758 Å (WBI = 1.000)に比較して少し緩むものの、吸着された状態であることが分かる。Mg からの H^1 と H^2 への距離は 3.097 Å と 2.838 Å である。一方、H^3-H^4 および H^5-H^6 の結合距離は 0.767 Å (WBI = 0.959)および 0.768 Å (WBI = 0.957)で、同じく孤立水素分子からの変化はほとんどなく、また Mg からの距離もかなり遠い（2.276～2.455 Å 程度）など、この錯体に吸着されていると見てよいことが分かる。したがって、これらの吸着水素分子は燃料電池の水素源として使用できる可能性があることになる。

【Mg-oxalate の解析結果】

水素分子が吸着される前のこの錯体の構造は図 4(a)のようで、この錯体でも水素分子が結合することなくすぐに吸着を開始して、最高で水素 7 分子が吸着されうることが明らかとなった（図 4(b),(c)）。

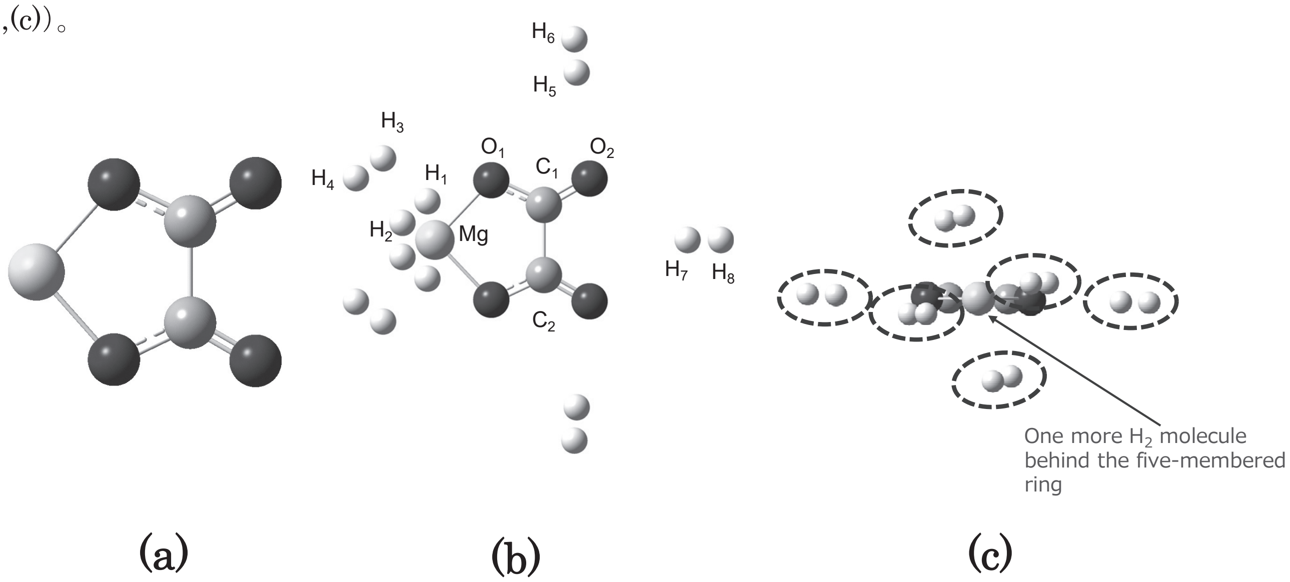


Fig. 4　Optimized structures of (a) Mg-oxalate complex and (b) that with seven absorbed H_2 molecules.　In (c) is indicated the same with (b) from a different angle with indication of adsorbed H_2 molecules by red-broken ovals.

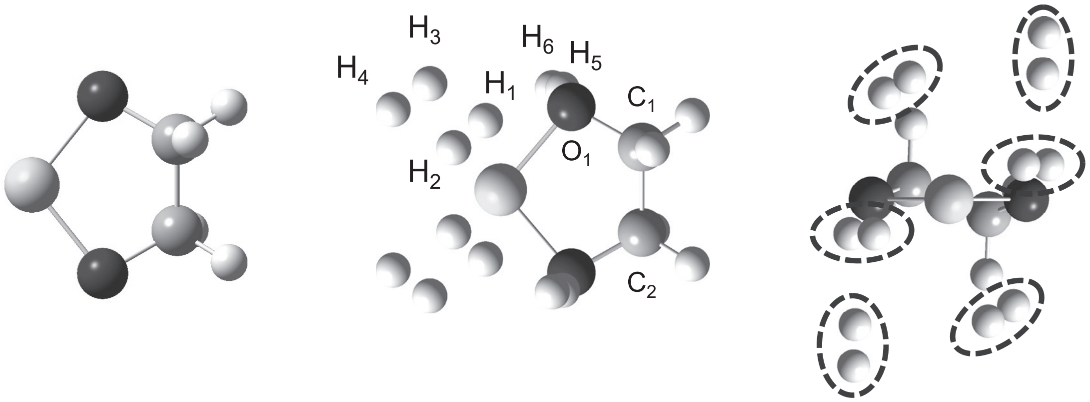
Mg-oxalate では最初の水素分子吸着によるエンタルピー安定化は 21.33 kJ/mol、第 2、第 3 および第 4 の水素分子吸着によるエンタルピー安定化の増分はそれぞれ 18.94, 16.86, 13.82 kJ/mol であった。さらに第 6 の水素分子吸着による安定化の増分は、第 4 分子吸着からすれば 7.11 kJ/mol で 1 分子当たりの増分は 3.56 kJ/mol であった。Oxalate の場合にはさらに 7 分子まで吸着されうることが明らかになり、第 6 分子吸着からの増分は 4.08 kJ/mol となった。このように吸着水素分子数が増えるほど、エンタルピー安定化の増分は漸減するが、少なくとも第 7 水素分子まで吸着されることが明らかとなった。

この第 7 水素分子まで吸着した構造における H^1-H^2 距離は 0.766 Å（WBI = 0.961）で、孤立水素

分子の結合距離 0.758 Å (WBI = 1.000)に比較して少し緩むものの、吸着された状態であることが分かる。Mg からの H^1 と H^2 への距離は 2.277 Å と 2.379 Å である。一方、H^3-H^4 および H^5-H^6 の結合距離は 0.768 Å (WBI = 0.960)および 0.762 Å (WBI = 0.986)で、同じく孤立水素分子からの変化はほとんどなく、また Mg からの距離もかなり遠い（2.277～2.379 Å 程度）など、この錯体に吸着されていると見てよいことが分かる。したがって安全を見ると、Mg-oxalate でも第 6 番目の吸着水素分子までは燃料電池の水素源として使用できる可能性があることになる。

【Mg-ethanediolate の解析結果】

水素分子が吸着される前のこの錯体の構造は図 5 (a)のようで、この錯体には水素分子が結合することなくすぐに吸着を開始して、最高で水素 6 分子が吸着することが明らかとなった（図 5(b),(c)）。



(a)　(b)　(c)

Fig. 5　Optimized structures of (a) Mg-ethanediolate complex and (b) that with six absorbed H_2 molecules.　In (c) is indicated the same with (b) from a different angle with indication of adsorbed H_2 molecules by red-broken ovals.

Mg-ethanediolate では最初の水素分子吸着によるエンタルピー安定化は 16.55 kJ/mol、第 2、第 3 および第 4 の水素分子吸着によるエンタルピー安定化の増分はそれぞれ 14.97, 14.31, 12.89 kJ/mol であった。さらに第 6 の水素分子吸着による安定化の増分は、第 4 分子吸着からすれば 11.25 kJ/mol で 1 分子当たりの増分は 5.63 kJ/mol であった。このように吸着水素分子数が増えるほど、catecholate や oxalate と同様にエンタルピー安定化の増分は漸減するが、少なくとも第 6 水素分子まで吸着されると言える。

この第 6 水素分子まで吸着した構造における H^1-H^2 距離は 0.768 Å（WBI = 0.954）で、孤立水素分子の結合距離 0.758 Å (WBI = 1.000)に比較して少し緩むものの、吸着された状態であることが分かる。Mg からの H^1 と H^2 への距離は 2.283 Å と 2.467 Å である。一方、H^3-H^4 および H^5-H^6 の結合距離は 0.767 Å (WBI = 0.963)および 0.766 Å (WBI = 0.973)で、同じく孤立水素分子からの変化はほとんどなく、また Mg からの距離もかなり遠い（2.268～2.467 Å 程度）など、この錯体に吸着されていると見てよいことが分かる。したがって catecholate のようにベンゼン環がなく軽量な Mg-ethanediolate でも第 6 番目の吸着水素分子までは燃料電池の水素源として使用できる可能性があることになる。

【まとめ】

以上の理論的解析から明らかになった知見は以下のようにまとめられる。

(1) Mg-catecholate, Mg-oxalate, Mg-ethanediolate ともに図 1 の Kubas 様の錯体は作らず、最初の水素分子からすぐに吸着状態に入る。今回の解析では少なくとも 6 分子まで吸着される（特に oxalate では 7 分子まで吸着される）。

(2) Mg-catecholate の水素分子吸着においては、水素 1 分子あたりの吸着安定化エネルギーと同エンタルピーの増分は以下のようである。

$\Delta\Delta E$ = 25.83〜11.39 kJ/mol, $\Delta\Delta H$ = 19.09〜6.02 kJ/mol

(3) Mg-oxalate の水素分子吸着においては Mg 側に吸着するのがエネルギー的に有利で、水素 1 分子あたりの吸着安定化は

$\Delta\Delta E$ = 28.06〜8.10 kJ/mol, $\Delta\Delta H$ = 21.33〜4.08 kJ/mol

(4) Mg-ethanediolate の水素分子吸着においては同じく Mg 側に吸着するのがエネルギー的に有利で、水素 1 分子あたりの吸着安定化は

$\Delta\Delta E$ = 23.64〜11.76 kJ/mol, $\Delta\Delta H$ = 16.55〜5.63 kJ/mol

(5) 以上の結果からすると水素分子吸着にとってベンゼン環の有無、もっと言えばπ電子の有無は関係ないようにみえる。したがって低分子化しても水素分子吸着が担保されることが分かる。

(6) 以上の水素分子吸着ではいわゆる結合的な兆候は認められず、詳細なデータは省略したが吸着によって Mg-O 結合の分極が僅かに変化するのみであった。水素分子と Mg-catecholate, Mg-oxalate, Mg-ethanediolate 間の共有結は生成しておらず、電子の授受もほとんどない（1 分子目の水素分子吸着では、この水素分子からごくわずかな電子移動があるのみであり、水素分子の側にわずかな電子移動が起こっているケースもあった）。

(7) このような水素分子の遠距離相互作用的な吸着はあるいは普遍的なものであり、むしろ 2017 年度に解析した Kubas 錯体生成などの方が特殊なケースかも知れない。

以上の知見は燃料電池における水素源の開発にとって有用なものと期待できる。ここで解析した金属錯体の実際の使用法としては粉体状態での利用などを含めて今後考慮すべき点が多くあり、それらに関する検討も必要である。また同時に金属種や分子骨格のさらなる軽量化に向けても検討を広げる予定である。

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(2)　田中一義
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(3)　田中一義
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４．シニアリサーチフェロー

Shigeyoshi Sakaki

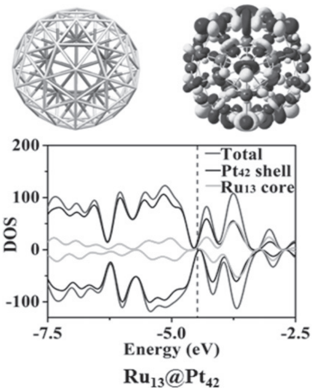
Senior Research Fellow, Kenichi Fukui Memorial Research Group II

1. Summary of the research of 2018

The complex systems consisting of transition metal element(s), heavy main-group element(s), and organic group(s) play important roles as metal enzymes, industrial catalysts, catalysts for fine organic synthesis, photo-sensitizer, molecular switch, luminescence material and so on. Also, they are important research target in physical chemistry and molecular science, because they exhibit a variety of new geometry, new chemical bond, rich molecular property, rich reactivity, and useful catalysis. All these features arise from their flexible electronic structures. In this regard, theoretical and computational studies of the electronic structures of the complex systems are indispensable for correct understanding of various chemical issues, finding new functions and prediction of new useful material.

Also, these complex systems are challenging research targets from the point of view of theoretical/computational chemistry, because their electronic structures are not simple but complicated in many cases. One good example is multi-nuclear transition metal complexes which need the application of multi-reference wave-function theory in theoretical calculation. Another example is significantly large coupling of electronic structure with surrounding atmosphere such as solvation effects, molecular crystal effects and so on. Infinite systems such as metal-organic-framework (MOF) is new challenging target because of its flexible structure and various new functions.

Our group is theoretically investigating the complex systems bearing complicated electronic structure with electronic structure theory. In 2018, we performed various theoretical studies, as follows: (i) Ni(I)-Hydride Catalyst for Hydrosilylation of Carbon Dioxide and Dihydrogen Generation: Theoretical Prediction and Exploration of Full Catalytic Cycle, (ii) Theoretical Insight into Core−Shell Preference for Bimetallic Pt‑M (M = Ru, Rh, Os, and Ir) Cluster and Its Electronic Structure, (iii) Rhodium Complexes Bearing PAlP Pincer Ligands, (iv) Reversible Oxidative Addition/Reductive Elimination of a Si-H Bond with Base-Stabilized Silylenes: A Theoretical Insight, (v) Mechanism of NO–CO reaction over highly dispersed cuprous oxide on γ-alumina catalyst using a metal–support interfacial site in the presence of oxygen: similarities to and differences from biological systems, (vi) How To Perform Suzuki-Miyaura Reactions of Nitroarene or Nitrations of Bromoarene Using a Pd^0 Phosphine Complex: Theoretical Insight and Prediction, (vii) QM/MM Approach to Isomerization of Ruthenium(II) Sulfur Dioxide Complex in Crystal; Comparison with Solution and Gas Phases, (viii) Theoretical Insight into Gate-Opening Adsorption Mechanism and Sigmoidal Adsorption Iso therm into Porous Coordination Polymer, and so on. We wish to report some of them, below.



Scheme 1. Structure of Pt-Ru core-shell particle with Pt shell and its DOS.

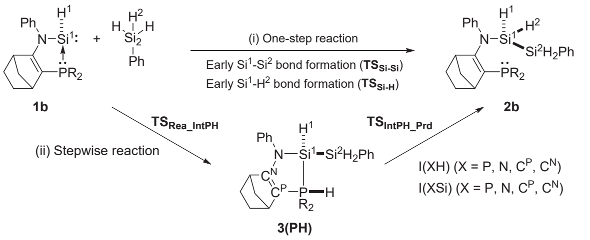
(i) Theoretical Insight into Core−Shell Preference for Bimetallic Pt‑M (M = Ru, Rh, Os, and Ir) Cluster and Its Electronic Structure[2]

Pt_mM_n (M = Ru, Rh, Os, and Ir; m+n = 38 and 55) clusters are systematically investigated using DFT calculations. In octahedral 38-atom cluster, core-shell structure $M_6@Pt_{32}$ with M_6 core and Pt_{32} shell is stable for Pt-Rh and Pt-Ir combinations but is not for Pt-Ru and Pt-Os combinations. In 55-atom cluster, icosahedral $M_{13}@Pt_{42}$ structure is stable for all Pt-M combinations, indicating that large cluster is more preferable to stabilizing the core-shell structure than small cluster. The difference in cohesive energy (E_{coh}) between M_{13} and Pt_{13} and the distortion energy

{$E_{dis}(M_{13})$} of M_{13} are parallel to the segregation energy (E_{seg}), indicating that these are important factors for stabilizing M_{13}@Pt_{42}. One more crucially important factor is the interaction energy (E_{int}) between M_{13} core and Pt_{42} shell, because E_{int} is parallel to E_{seg} and its absolute value is much larger than those of $E_{dis}(M_{13})$ and $E_{dis}(Pt_{42})$. The E_{int} depends on energy gap between LUMO of M_{13} core and HOMO of Pt_{42} shell, indicating that LUMO energy of M_{13} and HOMO energy of Pt_{42} are good properties for understanding and predicting stability of core-shell structure. Pt atom is more positively charged in M_{13}@Pt_{42} than in Pt_{55}, and the HOMO energy of M_{13}@Pt_{42} is higher than that of Pt_{55}. The presence of these two contrary factors for O_2 binding suggests that M_{13}@Pt_{42} is not bad for O_2 binding.

(ii) Reversible Oxidative Addition/Reductive Elimination of a Si-H Bond with Base-Stabilized Silylenes[4]

Although oxidative addition (O.A.) and reductive elimination (R.E.) are exceedingly important processes in organometallic chemistry, such processes are still extremely rare for main group element species. Here we report a theoretical study on the reaction of phosphine-stabilized silylenes with silanes which proceeds via reversible O.A./R.E. at room temperature, as shown in Scheme 2. Of particular interest, this theoretical approach highlights the important role of the ligand, which can greatly affect kinetics and energy balance of the reaction. Indeed, in contrast to the case of free aminosilylenes, the reaction of ligand-supported silylenes proceeds in an unsynchronized manner and starts with the silylene→silane charge transfer (CT). Suitably electron-donating ligands such as phosphines or *N*-heterocyclic carbenes, enhancing the CT at the transition state (TS), significantly decrease the Gibbs activation energy and the exergonic nature of the reaction (Figure 1), which promote the O.A./R.E. processes. In the same way, silanes with electron-withdrawing groups also favor the CT and thus stabilize the TS. It was also computationally predicted that phosphine-stabilized silylenes should be able to activate the C-Si bond of trimethoxy(ethynyl)silane (HC≡C-Si(OMe)$_3$) and that the reaction should proceed in a reversible manner under mild conditions.



Scheme 2. Two kinds of reaction course of oxidative addition and reductive elimination.

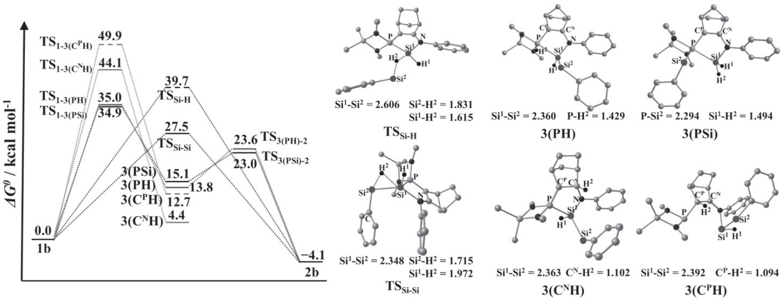
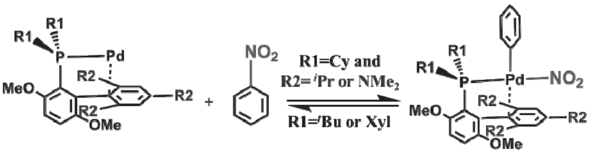


Figure 1. Gibbs energy profile (kcal mol^{-1}) in one step and stepwise oxidative additions

(iii) How To Perform Suzuki-Miyaura Reactions of Nitroarene or Nitrations of Bromoarene Using a Pd0 Phosphine Complex[7]

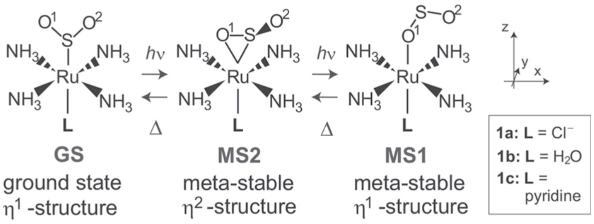
Pd^0(BrettPhos) **1** was experimentally applied to Suzuki-Miyaura reaction of nitroarenes which occurs through oxidative addition of nitroarene (ArNO$_2$) to Pd^0. On the other hand, Pd^0(^{t}Bu-BrettPhos) **2** was experimentally applied to nitration of bromoarenes which occurs through reductive elimination of nitroarene (Scheme 3). DFT calculations disclosed that oxidative addition of 4-nitroanisole to **1** was exergonic but that to **2** was endergonic, indicating that **1** is useful for oxidative addition of Ar-NO_2 bond but **2** is useful for reductive elimination of Ar-NO_2 bond. This difference in reactivity between **1** and **2** is explained in terms that bulky ^{t}Bu groups on ^{t}Bu-BrettPhos destabilize Pd^{II} complex $Pd^{II}(Ar)(NO_2)$(^{t}Bu-BrettPhos) due to large steric repulsion between Ar and ^{t}Bu-BrettPhos but less bulky cyclohexyl groups on BrettPhos do not. It is theoretically predicted here that NMe_2-substituted BrettPhos is better for Ar-NO_2 bond cleavage than BrettPhos but xyl-BrettPhos is good for Ar-NO_2 formation like ^{t}Bu-BrettPhos, where NMe_2 and 2,6-dimethylphenyl groups are introduced to BrettPhos instead of isopropyl and cyclohexyl groups, respectively.



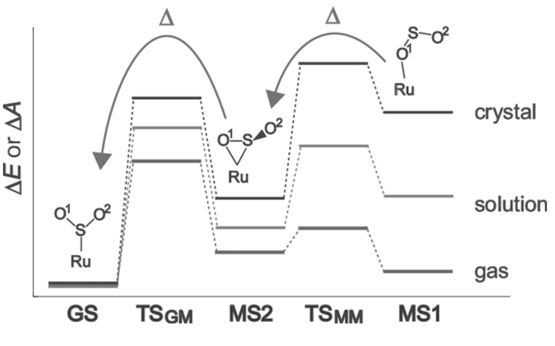
Scheme 3. Oxidative addition and reductive elimination of Ph-NO_2 bond on Pd^0 complex

(iv) QM/MM Approach to Isomerization of Ruthenium(II) Sulfur Dioxide Complex in Crystal; Comparison with Solution and Gas Phases[8]

The theoretical study of chemical reactions in molecular crystals is a challenging research target. To optimize the transition state in a crystal, we have improved the crystal model and modified the quantum mechanics/molecular mechanics (QM/MM) method based on the periodic MM crystal model. We applied this method to the ruthenium(II) sulfur dioxide complex $[Ru^{II}(NH_3)_4(SO_2)Py]^{2+}$ **1Py** which is potentially useful for optical data storage systems in crystal because this Ru complex has two isolable metastable structures, η^1-O-bound **MS1** and η^2-S,O-bound **MS2**, in addition to η^1-S-bound ground state **GS** in crystal. **MS2** and **MS1** are formed from **GS** by photoirradiation at low temperature (10−100 K) and thermal isomerization occurs from **MS2** to **MS1** and from **MS2** to **GS** by raising the temperature (Scheme 4). For comparison, the thermal isomerization of $[Ru^{II}(NH_3)_4(SO_2)L]^{n+}$ (L = Cl^-, W (water), and Py) was investigated in gas and aqueous phases, where the three-regions 3D reference site interaction model self-consistent field (RISM-SCF) method was employed to incorporate solvation effects in the aqueous phase. In the gas phase, **MS2** is more stable than **MS1** for L = Cl^- but less stable for L = W and Py. Thermal isomerization occurs with similar changes in geometry and charge distribution among L = Cl^-, W, and Py, whereas the energy profile of L = Cl^- differs very much from those of L = W and Py. In the aqueous phase, MS1 becomes much less stable than MS2 and the Ru^{II} complex becomes lower in energy following the order **MS1** > **MS2** > **GS** for L = Cl^-, W, and Py because of the small solvation free energy for MS1. In crystal, 1Py also becomes lower in energy following the order **MS1** > **MS2** > **GS**. The **MS1** → **MS2** isomerization occurs with much smaller activation energy than the **MS2** → **GS** in crystal phase, which is consistent with the experimental observations. In crystal, the short-range steric repulsion between the SO_2 of the target QM molecule and the neighboring Ru complex and the



Scheme 4. Photo and thermal isomerization of Ru(II) SO_2 complex.

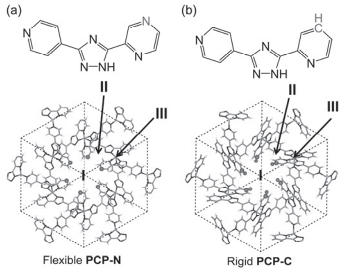


Scheme 5. Schematical presentation of isomerization of Ru(II) SO_2 complex in gas, solution, and crystal phases

long-range ES interaction between the target molecule and the MM crystal play crucially important roles in determining the relative stabilities of **MS1** and **MS2** and the energy barrier of the thermal isomerization.

(v) Theoretical Insight into Gate-Opening Adsorption Mechanism and Sigmoidal Adsorption Iso therm into Porous Coordination Polymer[9]

Gate-opening adsorption mechanism and sigmoidal adsorption isotherm were theoretically investigated taking CO_2 adsorption into porous coordination polymers, $[Fe(ppt)_2]_n$ (**PCP-N,** Hppt = 3-(2-pyrazinyl)-5-(4-pyridyl)-1,2,4-triazole) and $[Fe(dpt)_2]_n$ (**PCP-C**, Hdpt = 3-(2-pyridinyl)-5-(4-pyridyl)-1,2,4-triazole) as example (Scheme 6), where hybrid method consisting of dispersion-corrected DFT for infinite PCP and post-Hartree-Fock (SCS-MP2 and CCSD(T)) method for cluster model was employed. **PCP-N** has site I (one-dimensional channel), site II (small aperture to the site I), and site III (small pore) useful for CO_2 adsorption. CO_2 adsorption at site I occurs one by one with Langmuir adsorption isotherm. CO_2 adsorption at sites II and III occurs through gate-opening adsorption mechanism, because crystal deformation energy (E_{DEF}) at these sites is induced largely by the first CO_2 adsorption but induced much less by the subsequent CO_2 adsorption. Interestingly, nine CO_2 molecules are adsorbed simultaneously at these sites because large E_{DEF} cannot be overcome by adsorption of one CO_2 molecule but can be by simultaneous adsorption of nine CO_2 molecules. For such CO_2 adsorption, Langmuir-Freundlich sigmoidal adsorption isotherm was derived from equilibrium equation for CO_2 adsorption (Figure 2). Very complicated CO_2 adsorption isotherm, experimentally observed, is reproduced by combination of Langmuir and Langmuir-Freundlich adsorption isotherms. In **PCP-C**, CO_2 adsorption occurs only at site I with Langmuir adsorption isotherm. Sites II and III of **PCP-C** cannot be used for CO_2 adsorption because very large E_{DEF} cannot be overcome by simultaneous adsorption of nine CO_2 molecules. Factors necessary for gate-opening adsorption mechanism are discussed based on the basis of differences between **PCP-N** and **PCP-C**.



Scheme 6. Fe(II)-based two PCPs, flexible PCP-N and rigid PCP-N

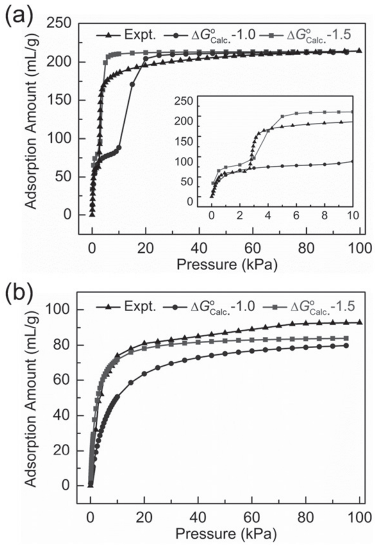


Figure 2. Sigmoidal Langmuir-Freundlich-type (a) and non-sigmoidal Langmuir type (b) CO_2 adsorption isotherm

2. Original Papers

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Organometallics, 37, 3480−3487 (2018).
(8) Shinji Aono and Shigeyoshi Sakaki,
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J. Phys. Chem. C., 122, 20701−20716 (2018).
(9) Jia-Jia Zheng, Shinpei Kusaka, Ryotaro Matsuda, Susumu Kitagawa, and Shigeyoshi Sakaki,
“Theoretical Insight into Gate-Opening Adsorption Mechanism and Sigmoidal Adsorption Iso therm into Porous Coordination Polymer”,
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(1) S. Sakaki,
Theoretical Approach toward d-Electron System: From Molecular Catalysts to Molecular Crystals and MOFs,
The 7-th Japan-Czech-Slovakia Joint Symposium for Theoretical and Computational Chemistry, Prague, May 21-24, 2018.
(2) S. Aono, S. Sakaki
QM/MM study of thermal isomerization of Ru(II) sulfur dioxide complex in crystal; comparison with gas and solution phases
16th International Congress of Quantum Chemistry, June 18-23, 2018, Menton, France.
(3) M. Nakagaki, S. Sakai,
Electronic Structure and Bonding Nature of Trinuclear Cr(II) Complex: Remarkably Small Cr-Cr Bond Order and Large Spin Polarization
16th International Congress of Quantum Chemistry, June 18-23, 2018, Menton, France.

５．リサーチリーダー

Kazuo Takatsuka

Research Leader

Summary of the research of the year

The main objective of our research here in FIFC is developing a basic framework of theoretical chemistry, which we call the theory of nonadiabatic electron wavepacket dynamics, or time-domain quantum chemistry, to explore new realm of theoretical chemistry beyond the framework of the Born-Oppenheimer approximation. Outcomes of such theoretical developments in the academic year of 2018 include; (1) Theoretical analyses on nonadiabatic electron-nuclear dynamics in terms of their fluxes (currents) in molecules [3,4]. Analysis of electron current in molecules is extremely powerful and vivid view of real-time dynamics of chemical reactions. (2) Nature of chemical bonds having densely quasi-degenerate electronic states, which undergoes very frequent nonadiabatic transitions among many adiabatic state, which is thereby called chemistry without notion of potential energy surface [5]. This is a theory of nature of chemical bond in second or third generation, which was never considered before by Pauling, Ruedenberg, Fukui and other great quantum chemists. (3) Coupled proton and electron-wavepacket transfer (CPEWT) in the system of water splitting by Mn oxides both in photo-excited and ground states. We have been finding several basic chemical principles involved in the series of reactions, beginning from charge-separation dynamics to oxygen molecule generation therefrom [6]. (4) Various theoretical attempts to extend the beyond-Born-Oppenheimer theoretical scheme have been made, with a particular example being development of a formalism of nuclear and electronic simultaneous full-quantum dynamics [1]. We will proceed to this aspect more technically. (5) In this year I have started a theoretical project with Dr. Hanasaki about relativistic theory of nonadiabatic electron dynamics in intense laser fields. Two very long papers are already published in C. Chem. Phys. A and Phys. Rev. A as of November 2019.

Thus our research group has been making a progress in very characteristic yet fundamental field of theoretical chemistry.

(i) Nonadiabatic nuclear and electronic quantum wavepacket dynamics [1]

In this study, the path-branching theory as a nonadiabatic electron wavepacket theory (Yonehara et al., 2012), in which nonadiabatic electron wavepackets are propagated in time along branching nuclear paths, has been extended so that Gaussian nuclear wavepackets are to be evolved in time along the variational quantum paths, which are determined consistently with the electron dynamics.

ii) Ab-initio calculation of femtosecond-time-resolved photoelectron spectra of NO_2 after excitation to the A-band [2]

We have presented calculations of time-dependent photoelectron spectra of NO_2 after excitation to the A-band for comparison with extreme-ultraviolet (XUV) time-resolved photoelectron spectroscopy. We have calculated potential energy surfaces of the two lowest-lying coupled $2A_0$ states obtained from multi-reference configuration-interaction calculations to propagate the photo-excited wave packet using a split-step-operator method. The propagation includes the nonadiabatic coupling of the potential surfaces as well as the explicit interaction with the pump pulse centered at 3.1 eV (400 nm). A semiclassical approach to calculate the time-dependent photoelectron spectrum arising from the ionization to the eight energetically lowest-lying states of the cation allows us to reproduce the static experimental spectrum up to a binding energy of 16 eV and enables direct comparisons with XUV time-resolved photoelectron spectroscopy. This work is a result of collaboration with Professor Hans Wörner and his group at ETH.

iii) Electronic and nuclear flux analysis on nonadiabatic electron transfer reaction: A view from single-configuration adiabatic Born-Oppenheimer representation [3]

A detailed flux analysis on nonadiabatically coupled electronic and nuclear dynamics in the intramolecular electron transfer of LiF has been investigated. Full quantum dynamics both of electrons and nuclei within two-state model has uncovered interesting features of the individual fluxes (current of probability density) and correlation between them. In particular, a spatiotemporal oscillatory pattern of electronic flux has been revealed, which reflects the coherence coming from spatiotemporal differential overlap between nuclear wavepackets running on covalent and ionic potential curves. In this regard, a theoretical analogy between the nonadiabatic transitions and the Rabi oscillation is surveyed. We also present in this paper a flux–flux correlation between the nuclear and electronic motions, which quantifies the extent of deviation of the actual electronic and nuclear coupled dynamics from the Born–Oppenheimer adiabatic limit, which is composed only of a single product of the adiabatic electronic and nuclear wavefunctions.

iv) Electronic and nuclear fluxes induced by quantum interference in the adiabatic and nonadiabatic dynamics in the Born-Huang representation [4]

This work is the second part, the first one being the above item (iii), of our series of study on an electronic and nuclear flux analysis for nonadiabatic dynamics. The corresponding adiabatic counterpart, both of the wavefunctions of which are represented in the Born-Huang expansion. It is well known that the electronic-nuclear configurations (terms) in the expansion of the total wavefunction interfere each other through the nonadiabatic interactions and give birth to electronic and nuclear fluxes. Interestingly, even in the adiabatic dynamics without such nonadiabatic interactions, a wavefunction composed of more than one adiabatic state can undergo interference among the components and give the electronic and nuclear fluxes. That is, the individual pieces of the wavepacket components associated with the electronic wavefunctions in the adiabatic representation can propagate in time independently with no nonadiabatic interaction, and yet they can interfere among themselves to generate the specific types of electronic and nuclear fluxes. We refer to the dynamics of this class of total wavefunction as multiple-configuration adiabatic

Born-Huang dynamics. A systematic way to distinguish the electronic and nuclear fluxes arising from nonadiabatic and the corresponding adiabatic dynamics is discussed, which leads to the deeper insight about the nonadiabatic dynamics and quantum interference in molecular processes. The so-called adiabatic flux has been also discussed.

v) Chemical bonding and nonadiabatic electron wavepacket dynamics in densely quasi-degenerate excited state manifold of boron clusters [5]

Formation of chemical bonds is theoretically discerned by the presence of static nuclear configuration on a potential energy surface given within the Born–Oppenheimer framework. We here have studied dynamical chemical bonding for molecules residing in the electronic excited states that are in a densely quasi-degenerate electronic state manifold and thereby keep undergoing extremely frequent nonadiabatic transitions. For this type of the states, the notion of global potential energy surfaces based on the adiabatic representation loses the usual sense. Nonetheless, chemical bonding exists and associated chemical reactions certainly proceed, for which we call chemistry without potential surfaces. As such, we investigate the highly excited states of boron clusters, which have extraordinarily long lifetimes with neither ionization nor dissociation. The dynamical chemical bonds keep rearranging themselves without converging to a static structure, the vivid electron dynamics of which is tracked by means of the nonadiabatic electron wavepacket dynamics theory. To characterize the dynamical bonding theoretically, we have proposed the notion of hyper-resonance.

vi) On the Elementary Chemical Mechanisms of Directional Proton Transfers: A Nonadiabatic Electron-Wavepacket Dynamics Study [6]

We have proposed a set of chemical reaction mechanisms of unidirectional proton transfers, which may possibly work as an elementary process in chemical and biological systems. Being theoretically derived based on our series of studies on charge separation dynamics in water splitting by Mn oxides, the present mechanisms have been constructed after careful exploration over the accumulated biological studies on cytochrome c oxidase (CcO) and bacteriorhodopsin. In particular, we have focused on the biochemical findings in the literature that unidirectional transfers of approximately two protons are driven by one electron passage through the reaction center (binuclear center) in CcO, whereas no such dissipative electron transfer is believed to be demanded in the proton transport in bacteriorhodopsin. The proposed basic mechanisms of unidirectional proton transfers were further reduced to two elementary dynamical processes, namely, what we call the coupled proton and electron-wavepacket transfer (CPEWT) and the inverse CPEWT. To show that the proposed mechanisms can indeed be materialized in a molecular level, we constructed model systems with possible molecules that are rather familiar in biological chemistry, for which we have performed the ab initio calculations of full-dimensional nonadiabatic electron-wavepacket dynamics coupled with all nuclear motions including proton transfers.

2. Original papers

[1] Nonadiabatic nuclear and electronic quantum wavepacket dynamics
Kazuo Takatsuka, Chem. Phys. **515**, 52-59 (2018).
https://doi．org/10．1016/j．chemphys．2018．07．006

[2] Ab-initio calculation of femtosecond-time-resolved photoelectron spectra of NO_2 after excitation to the A-band
Andres Tehlar, Aaron von Conta, Yasuki Arasaki, Kazuo Takatsuka, and Hans Jakob Woerner, J. Chem. Phys. 149, 034307 (2018). (13 pages)
https://doi．org/10．1063/1．5029365

[3] Electronic and nuclear flux analysis on nonadiabatic electron transfer reaction: A view from single-configuration adiabatic Born-Oppenheimer representation
Rei Matsuzaki and Kazuo Takatsuka, J. Comput. Chem. (Morokuma memorial issue), **40** 148-163 (2019). DOI: http://dx．doi．org/10．1002/jcc．25557

[4] Electronic and nuclear fluxes induced by quantum interference in the adiabatic and nonadiabatic dynamics in the Born-Huang representation.
Rei Matsuzaki and Kazuo Takatsuka, J. Chem. Phys. **150**, 014103 (2019). (22 pages)
DOI: https://doi．org/10．1063/1．5066571

[5] Chemical bonding and nonadiabatic electron wavepacket dynamics in densely quasi-degenerate excited state manifold of boron clusters.
Yasuki Arasaki and Kazuo Takatsuka, accepted for publication, J. Chem. Phys. **150**, 114101 (18 pages) (2019)
DOI: https://doi．org/10．1063/1．5094149

[6] On the Elementary Chemical Mechanisms of Directional Proton Transfers: A Nonadiabatic Electron-Wavepacket Dynamics Study.
Kentaro Yamamoto and Kazuo Takatsuka, J. Phys. Chem. A **123**, 4125-4138

3. Presentation at academic conferences

［国際研究集会］

“Recent Progress in Nonadiabatic Electron Wavepacket Dynamics”

Kazuo Takatsuka,
Mini-workshop on nonadiabatic chemistry,
Peking Universtity,　May 19-20,　2018

“Nonadiabatic phenomena: From wavepacket bifurcation to machinery behind biochemical dynamics”
Kazuo Takatsuka,
International Conference on Nonadiabatic Dynamics (ICND 2018)
21-23,　2018 at Peking University Shenzhen Graduate School,　China

［国内研究集会］

“Jahn-Teller,　Hellmann-Feynman,　多次元非断熱動力学”
高塚和夫　理論化学討論会，岡崎，2018．5．15-17

“Hyper-resonance あるいは動的化学結合；　新しい化学結合様態”
新崎康樹，高塚和夫　分子科学討論会，福岡(福岡国際会議場)，9．10-9．13/2018

“非断熱過程における電子と原子核のフラックス”
松崎 黎，高塚 和夫　第２１回 理論化学討論会　２０１８年５月１５日，岡崎コンフェレンスセンター

″一方向的なプロトン移動の化学的な機構について：非断熱電子動力学による研究″,
山本憲太郎, 高塚和夫　第 16 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 2019/2/8 P15.

″生物系に見られる一方向的なプロトンおよび電子移動の化学的な機構について″
山本憲太郎，高塚和夫　第 12 回分子科学討論会，福岡 2018/9/10-13 2D19.

″電子の往復運動に駆動されるプロトンポンプの化学的な機構について：非断熱電子動力学による解析″
山本憲太郎，高塚和夫　第 21 回理論化学討論会，岡崎 2018/5/15-17 3L01.

６．研究員

Kazuo Kitaura

Research Fellow

1. Summary of the research of the year

Pair Interaction Energy Decomposition Analysis For Density Functional Theory

Pair interaction energy decomposition analysis in the fragment molecular orbital (FMO) method is extended to treat density functional theory (DFT). Energy components obtained from the DFT levels are compared to the values obtained with Hartree-Fock, second order Møller-Plesset (MP2) and coupled cluster methods.

In the FMO method[1)], the total energy of entire system E is computed using energies of fragments and fragment pairs,

$$E = \sum_{I}^{N} E_I' + \sum_{I>J}^{N} \Delta E_{IJ} \qquad (1)$$

where N, E_I' and ΔE_{IJ} are the number of fragments, the internal energy of monomer I, and the interaction energy between fragments I and J(Pair Interaction Energy; PIE), respectively. PIEDA[2)] is a method to divide PIE into components, according to an energy decomposition method for molecular interactions[4)]; intermolecular interaction energy at the Hartree-Fock level is decomposed into electrostatic(ES), exchange-repulsion(EX), polarization(PL), and charge-transfer+mix(higher order coupling energy)(CT-MIX). The computation of PL is optional in PIEDA. Correlation energy contribution(DI) is calculated separately. Solvation energy contribution(SOLV)[5)] can be evaluated using polarizable continuum solvent model(PCM).

PIE is represented as a sum of these components,

$$\Delta E_{IJ} = \Delta E_{IJ}^{\mathrm{ES}} + \Delta E_{IJ}^{\mathrm{EX}} + \Delta E_{IJ}^{\mathrm{CT+mix}} + \Delta E_{IJ}^{\mathrm{DI}} + \Delta E_{IJ}^{\mathrm{SOLV}} \qquad (2)$$

CT+MIX energy in DFT is defined as,

$$\Delta E_{IJ}^{\mathrm{CT+MIX}} = \Delta E_{IJ} - \Delta E_{IJ}^{\mathrm{ES}} - \Delta E_{IJ}^{\mathrm{EX}} - \Delta E_{IJ}^{\mathrm{c}} - \Delta E_{IJ}^{\mathrm{SOLV}} \qquad (3)$$

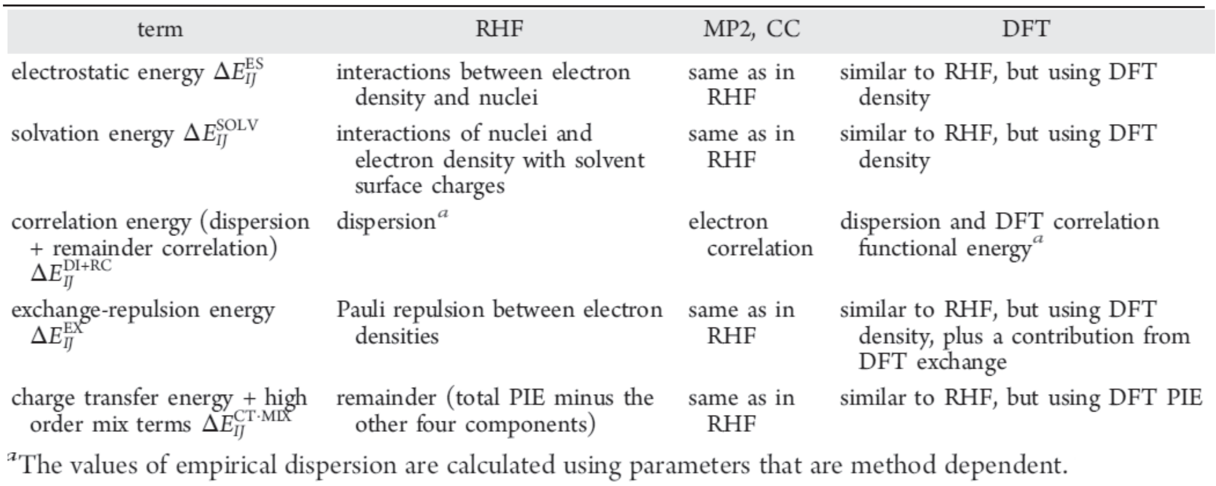
where ΔE_{IJ}^{c} is pair correlation energy defined as,

$$\Delta E_{IJ}^{\mathrm{c}} = E_{IJ}^{\mathrm{c}} - E_{I}^{\mathrm{c}} - E_{J}^{\mathrm{c}} \qquad (4)$$

where E^c is correlation energy in DFT.[6)]

Correspondence between pair interaction energy components for several electronic structure theories is summarized in Table 1.

Table 1. Correspondence between pair interaction energy (PIE) contributions.



term	RHF	MP2, CC	DFT
electrostatic energy ΔE_{IJ}^{ES}	interactions between electron density and nuclei	same as in RHF	similar to RHF, but using DFT density
solvation energy ΔE_{IJ}^{SOLV}	interactions of nuclei and electron density with solvent surface charges	same as in RHF	similar to RHF, but using DFT density
correlation energy (dispersion + remainder correlation) ΔE_{IJ}^{DI+RC}	dispersion[a]	electron correlation	dispersion and DFT correlation functional energy[a]
exchange-repulsion energy ΔE_{IJ}^{EX}	Pauli repulsion between electron densities	same as in RHF	similar to RHF, but using DFT density, plus a contribution from DFT exchange
charge transfer energy + high order mix terms $\Delta E_{IJ}^{CT \cdot MIX}$	remainder (total PIE minus the other four components)	same as in RHF	similar to RHF, but using DFT PIE

[a]The values of empirical dispersion are calculated using parameters that are method dependent.

PIEDA calculations were performed for $(H_2O)_n$ (n=3,4,8) at RHF, DFT, MP2 and CCSD(T) levels (Figure 1). The basis function used is aug-cc-pVTZ. The DFT functionals, PBE, B3LYP, CAM-B3LYP, and M11 were used. All FMO calculations were performed with GMAESS[7)].

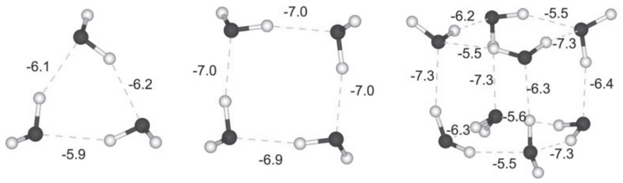
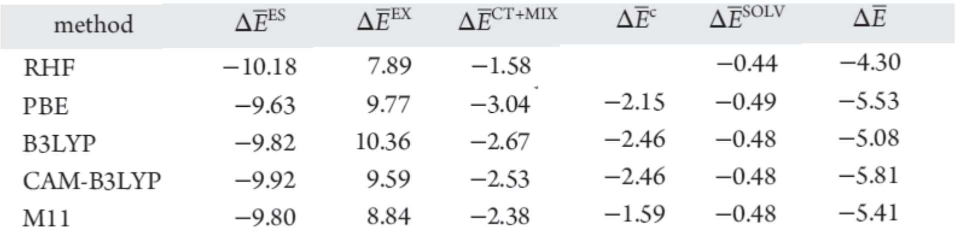


Figure 1. Structures of water clusters. Pair interaction energies are shown in kcal/mol at the CCSD(T)/aug-cc-pVTZ level.

Table 1. Averaged interaction energies for hydrogen bonds (kcal/mol) in $(H_2O)_8$, and their components: electrostatic $\Delta\overline{E}^{ES}$, exchange-repulsion $\Delta\overline{E}^{EX}$, charge transfer + mix terms $\Delta\overline{E}^{CT+MIX}$, correlation $\Delta\overline{E}^{c}$ and solvent screening $\Delta\overline{E}^{SOLV}$ energies[a].



method	$\Delta\overline{E}^{ES}$	$\Delta\overline{E}^{EX}$	$\Delta\overline{E}^{CT+MIX}$	$\Delta\overline{E}^{c}$	$\Delta\overline{E}^{SOLV}$	$\Delta\overline{E}$
RHF	−10.18	7.89	−1.58		−0.44	−4.30
PBE	−9.63	9.77	−3.04	−2.15	−0.49	−5.53
B3LYP	−9.82	10.36	−2.67	−2.46	−0.48	−5.08
CAM-B3LYP	−9.92	9.59	−2.53	−2.46	−0.48	−5.81
M11	−9.80	8.84	−2.38	−1.59	−0.48	−5.41

[a] The aug-cc-pVTZ basis set used.

Figure 8 shows the eight hydrogen bond energies in $(H_2O)_8$. Since the structure is not a perfect cubic, hydrogen bond energies are just a little different. Table 2 shows the averaged interaction energies per hydrogen bond $\Delta\overline{E}$ and their components (results of n = 3, 4 are not shown). The electrostatic component (ES) is quite similar for all methods (about -10 kcal/mol). The exchange-repulsion(EX) energy of 8-10 kcal/mol shows more variation than ES. DFT has a larger EX than RHF, by 1-2 kcal/mol. The charge transfer and mix component (CT+MIX) is from -1.6 to -3.0 kcal/mol for RHF and DFT. The DFT correlation energies (c) are between -1.6 to -2.5 kcal/ mol. The averaged correlation energies per hydrogen bond at MP2 and CCSD (T) are -1.97 and -2.08 kcal/mol, respectively (not shown). The solvation energy component (SOLV) are almost the same for all the theories (-0.44 to -0.49 kcal / mol).

PIEDA results depend on electronic structure theory and basis set used. In a comparison of molecular interactions between a series of molecular systems, the same theory and basis set should be employed. In this study, various theories were compared and their characteristics were clarified.

Reference 1) Kitaura, K.; Ikeo, E.; Asada, T.; Nakano, T.; Uebayasi, M. , Chem. Phys. Lett. 1999, 313, 701–706. 2) Fedorov, D. G.; Kitaura, K., J. Comput. Chem. 2007, 28, 222–237. 3) Alexeev, Y.; Mazanetz, M. P.; Ichihara, O.; Fedorov, D. G. , Curr. Top. Med. Chem. 2012, 12, 2013–2033. 4) Kitaura, K.; Morokuma, K., Int. J. Quant. Chem. 1976, 10, 325–340. 5) Fedorov, D. G.; Kitaura, K., J. Phys. Chem. A 2012, 116, 704–719. 6) Parrish, R. M.; Parker, T. M.; Sherrill, C. D., J. Chem. Theory Comput. 2014, 10, 4417–4431. 7) Fedorov, D. G., WIREs: Comp. Mol. Sc., WIREs, 2017, 7, e1322.

2. Original papers

(1) Fedorov, Dmitri G.; Kitaura,Kazuo
"Pair Interaction Energy Decomposition
Analysis for Density Functional Theory and Density-Functional Tight-Binding with an Evaluation of Energy Fluctuations in Molecular Dynamics
J. Phys. Chem. A 122, 1781-1795(2018)

７．博士研究員

Mitsusuke Tarama

Special Postdoctoral Researcher

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

Mechanochemical model of crawling cells

Active matter refers to objects that exhibit spontaneous motion, which results from the force that they generate by consuming potential energy, e.g. chemical energy. Such force should vanish in total due to the law of action and reaction. In order to achieve active motion, such as spontaneous translational motion, under the force-free condition, active matter should break corresponding symmetry. For active matter that swims in a low Reynolds number fluid, this fact is known as Purcell's scallop theorem. One simple model to test how microswimmers can achieve a net migration is a model swimmer that is composed of three particles connected linearly by cyclically stretching bonds.

Most biological systems are examples of active matter. The simplest unit of living system is a cell, which already shows a variety of complicated dynamics. In the case of cell migration, we can classify cells into two groups; one is swimming cells such as bacteria that swim in a fluidic environment. The other group is crawling cells, which migrate by adhering to a substrate. The basic mechanism of cell crawling motion consists of four processes (Fig. 1):

① Protrusion of the leading edge due to actin polymerization
② Adhesion of the leading edge to the substrate
③ De-adhesion of the trailing edge from the substrate
④ Contraction of the trailing edge due to the actomyosin contraction

In our previous study [M. Tarama and R. Yamamoto, JPSJ 2018], we introduced a simple model of a crawling cell that is composed of two particles (subcellular elements) connected by a viscoelastic spring. The spring also possesses a linear actuator that cyclically elongates the cell, representing the protrusion and the contraction. The cell can also change the characteristics of the substrate adhesion of the two elements, corresponding to the adhesion and de-adhesion processes. We assumed a perfect cyclic actuator elongation of sinusoidal form and a two-state transition of the substrate interaction between the adhered stick state and the de-adhered slip state. We also assume that the frequencies of these intracellular activities are the same for simplicity, but the phase of the substrate adhesion is shifted by a given constant. This phase shift can be different for the two elements since they represent different position of the cell. In fact, these two phase shifts

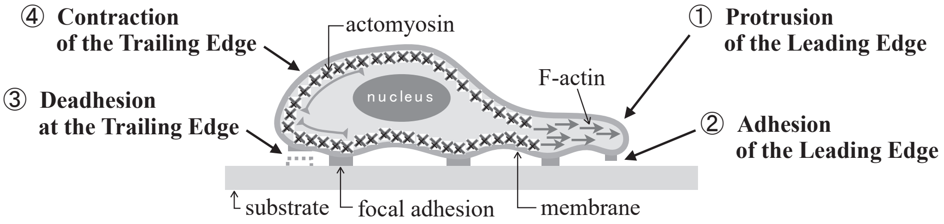


Fig. 1　The four basic processes of cell crawling mechanism.

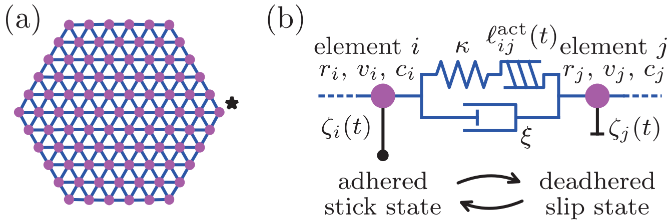


Fig. 2　Schematics of the mechanochemical model.

are the key parameters. If they are in phase, the cell undergoes symmetric oscillation with its centre-of-mass position stationary. Since we assumed perfect intracellular activities, if the two phase shifts are in anti-phase, the model cell can exhibit the most efficient migration. However, things are not that simple; even for the anti-phase case, in the worst case, the model cell cannot achieve a net migration if it undergoes reciprocating motion. Therefore, the cellular scale regulation of the four processes is important for efficient crawling.

However, the two-element (dumbbell) model is intrinsically one dimensional, although real cells are three dimensions. Then, we need to scale up the model. Here, we try to extend the model to two dimensions considering a cell crawling on a flat substrate. The extension is simply achieved by representing a single cell by many elements connected by viscoelastic springs including linear actuators, as depicted in Fig. 2. In this network model, the substrate adhesion characteristic of each element again changes in time. The time evolution equation of the element *i* is given by

$$\zeta_i(t)\,v_i + \sum_{j\in\Omega_i} \xi\left(v_i - v_j\right) = \sum_{j\in\Omega_i} \frac{\kappa}{l_0}\,\widehat{r_{ij}}\left\{ r_{ij} - l_0 - l_{ij}(t) \right\}$$

Here, the inertia term is omitted since the typical size of cells are tens of microns. However, unlike the dumbbell model, if there are many elements, it is not feasible to control all the phases, i.e., the time evolution of the actuator elongation and the substrate interaction of all the elements, “by hand”. Therefore, we need to include a mechanism that regulates the elongation of the bonds and substrate adhesion characteristic of all elements. Here, we consider intracellular chemical reactions. For simplicity, we employ the reaction-diffusion equations proposed by Sawai and his coworkers that models the intracellular PIP2 and PIP3 chemical wave observed on the membrane of Dictyostelium cells:

$$\frac{\partial U_i}{\partial t} = D_U \nabla^2 U_i - \frac{\alpha U_i V_i^2}{K_K + \langle V^2 \rangle} + \frac{\beta U_i V_i}{K_P + \langle U \rangle} + S - \gamma U_i$$

$$\frac{\partial V_i}{\partial t} = D_V \nabla^2 V_i + \frac{\alpha U_i V_i^2}{K_K + \langle V^2 \rangle} - \frac{\beta U_i V_i}{K_P + \langle U \rangle} - \mu V_i$$

where U_i and V_i represent PIP2 and PIP3 concentration on the element *i*, and <x> stands for the mean value of x over the entire cell.

Now we couple the mechanical model and the chemical reaction-diffusion model. In order to do that, we change the actuator elongation $l_{ij}(t)$ and the substrate adhesion characteristics $\zeta_i(t)$ depending on the intracellular chemical concentrations (U_i, V_i). Since the PIP3 accumulation coincides with the actin accumulation, we assume the elongation occurs depending on the PIP3 concentration:

$$l_{ij}(t) = dl\,tanh\left[\sigma V_{ij}(t)\right]$$

where $V_{ij}(t) = \left(V_i(t) + V_j(t)\right)/2$. On the other hand, we assume that the substrate adhesion characteristics show transition between the adhered stick state ζ_{stick} and de-adhered slip state ζ_{slip}:

$$\tau_\zeta \frac{d\zeta_i}{dt} = g_\zeta(\zeta_i) - A_v g_v(v_i) - (1 - A_v) g_V(V_i)$$

where

$$g_\zeta(\zeta\} = -\frac{1}{2} tanh\left(\frac{\zeta - \zeta_{\mathrm{stick}}}{\epsilon_\zeta}\right) - \frac{1}{2} tanh\left(\frac{\zeta - \zeta_{\mathrm{slip}}}{\epsilon_\zeta}\right)$$

However, it is not well-understood what controls the adhesion characteristics. Here we consider two controlling mechanisms; One is mechanical cue, for which we consider dependence on the local velocity:

$$g_v(v) = \frac{(v/v^*)^2}{1 + (v/v^*)^2} - \frac{1}{2}$$

which prefers the adhered stick state when the velocity is below the critical value $v < v^*$, whereas the de-adhered slip state is preferable for $v > v^*$. The other cue is chemical one. However, the regulating chemistry of the substrate adhesion is far less understood. Therefore, here, we assume the dependence on the PIP3 concentration, just as the actuator elongation:

$$g_V(V) = \frac{1}{2} tanh\big(\sigma_V (V - V^*)\big)$$

However, it is not clear if the PIP3 concentration enhances the stick state or the slip state, which are realized by the sign of the coefficient σ_V (the stick state is preferable for high PIP3 concentration if $\sigma_V < 0$, while the slip state is more likely for high PIP3 concentration if $\sigma_V > 0$).

Therefore, we tested both positive and negative σ_V. Interestingly, we obtained qualitatively opposite results as in Fig. 3. If $\sigma_V > 0$, the cell migrates in the opposite direction to the chemical wave (Fig. 3(a)), whereas it crawls in the same direction if $\sigma_V < 0$ (Fig. 3(b)).

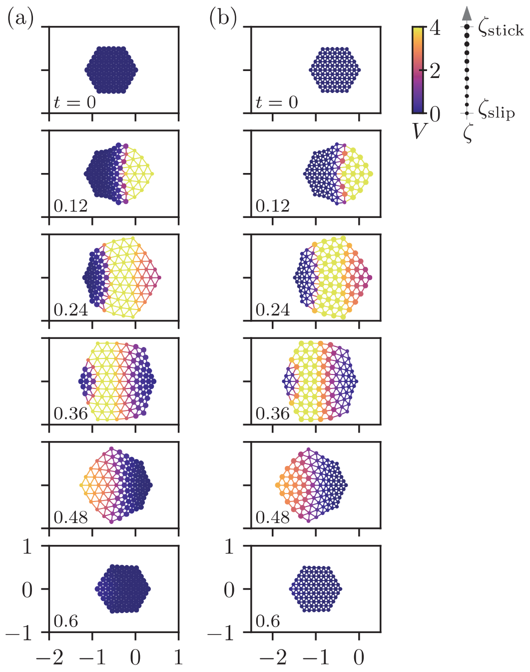


Fig. 3　Cell crawling for (a) positive and (b) negative σ_V.

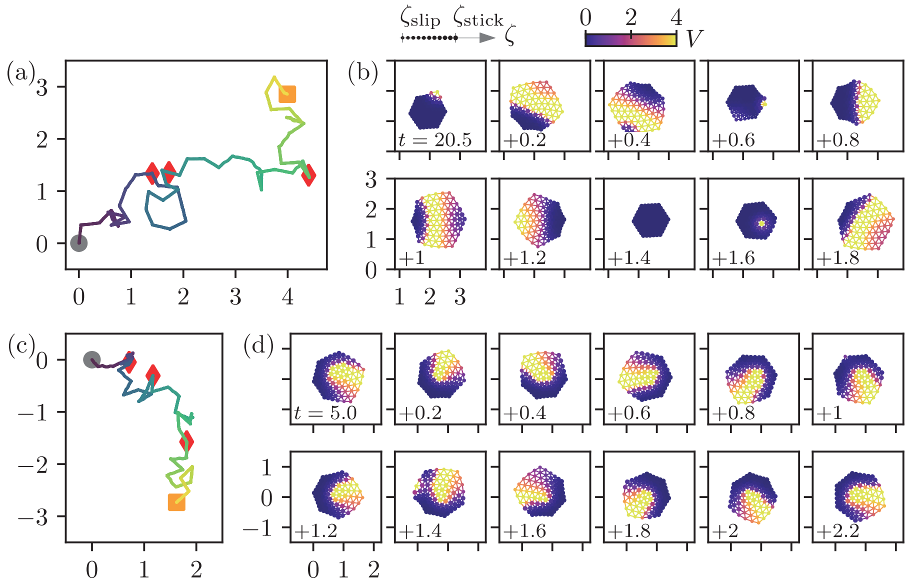


Fig. 4　(a) Trajectory of the centre-of-mass position of randomly crawling cell and (b) the time series of its snapshots. (c) Trajectory of the centre-of-mass position for the cell that switches between random migration and spinning motion and (d) the time series of the snapshots of spinning cell.

Moreover, under the existence of intracellular chemical randomness, the cell crawls randomly in a two-dimensional space (Figs. 4(a) and 4(b)). Depending on the parameters, in addition to the random translational motion, it also exhibits spinning motion as depicted in Figs. 4 (c) and 4(d).

Finally, we also measure the traction force that the cell exerts on the substrate. To analyse it, we calculate the multipole expansion of the traction force. The traction force monopole is vanishing as in Fig. 5(a), which confirms the force-free condition. On the other hand, the diagonal components of the traction force dipole are oscillating between the positive and negative values as in Fig. 5(a), which correspond to the extensile and contractile traction force, respectively. However, in most experiments, the traction force of crawling cells is measured to be contractile, which our current model fails to reproduce.

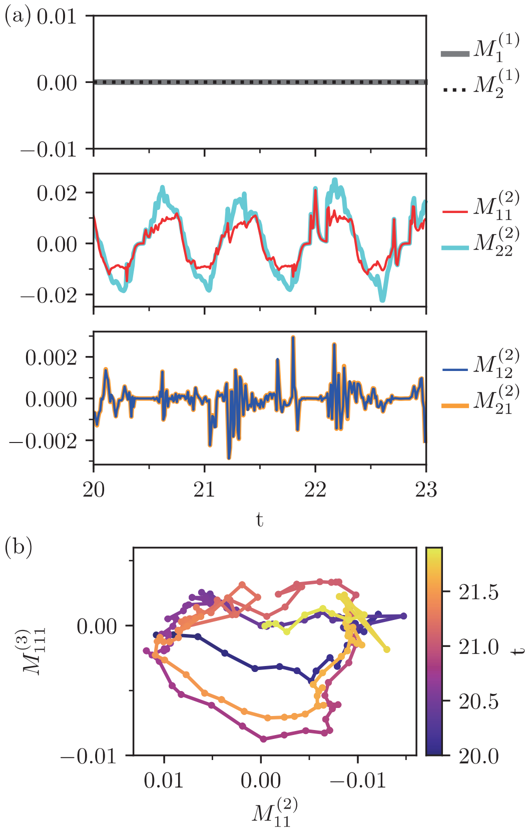


Fig. 5　(a) Time series of the traction force monopole ($M_1^{(1)}$ and $M_2^{(1)}$), and the diagonal ($M_{11}^{(2)}$ and $M_{22}^{(2)}$) and off-diagonal components ($M_{12}^{(2)}$ and $M_{21}^{(2)}$) of the traction force dipole. (b) Time evolution of the major components of the traction force dipole $M_{11}^{(2)}$ and quadrupole $M_{111}^{(3)}$.

Still, the off-diagonal components of the traction force dipoles coincide with each other as in Fig. 5(a), which is consistent with the experimental result by Tanimoto and Sano. What this means is that the model cell is torque free, since the torque monopole is equaled to the difference of the two off-diagonal components of the traction force dipole. Finally, Tanimoto and Sano measured the trajectory of the major components of the traction force dipole and quadrupole, which results in the counterclockwise rotation. We, thus, also measured the same force curve. Then, interestingly, we also obtained the same counterclockwise rotation as in Fig. 5(b), although its meaning is not clear yet.

In summary, we constructed mechanochemical model for crawling cells based on the subcellular elements connected by the network of the viscoelastic springs. The mechanical model includes two intracellular activities, the actuator elongation and the stick-slip transition of the substrate adhesiveness. Since the force that the cell generates is represented by the actuator elongation, it acts symmetrically to the pairs of the subcellular elements. Therefore, the model apparently satisfies the force-free condition. The mechanical model is coupled to intracellular chemistry, which is modelled by the reaction-diffusion equations of the phosphorylation and de-phosphorylation of PIP2 and PIP3; the actuator elongation and the stick-slip transition of the substrate adhesion characteristics depend on the intracellular PIP3 concentration. The dependence of the substrate characteristics on the PIP3 concentration, i.e., if the adhered stick state or the de-adhered slip state is preferred for high PIP3 concentration, qualitatively changes the cell migration. If the slip state is preferred for the high PIP3 concentration, the cell migrates in the opposite direction to the intracellular chemical wave. On the other hand, if the stick state is preferable for high PIP3 concentration, the cell crawls in the same direction as the intracellular chemical wave. Finally, we also measured the traction force multipoles to compare with the experimental observation. Then, although our model failed to reproduce the only contractile traction force dipoles, it confirms the force-free migration and the torque-free spinning motion. In addition, we obtained counterclockwise force curve in the space of the major components of the traction force dipole and quadrupole, which consists with the experimental observation.

Of course, our mechanochemical model is a course-grained model and the chemical reaction of the real cells are more complicated and may differ depending on the condition and for different cell types. In this sense, the employed intracellular chemical reaction is just one example. Thus, we believe our current model can give one standard mechanochemical model that can be applied to many other conditions and cell types by replacing the intracellular chemistry to the appropriate ones for each specific system.

2. Books

(1) Mitsusuke Tarama,
“Nonlinear Dynamics of Active Deformable Particles”
Chapter 12 of "Self-organized Motion: Physicochemical Design based on Nonlinear Dynamics"
(S. Nakata, V. Pimienta, I. Lagzi, H. Kitahata, N. J. Suematsu, eds.)
The Royal Society of Chemistry e-book (2019).

3. Presentation at academic conferences

(1) Mitsusuke Tarama and Ryoichi Yamamoto
Mechanics of cell crawling by means of force-free cyclic motion
Designer Soft Matter 2018, PARKROYAL Hotel on Beach Road, Singapore, 6-8 Jun., 2018.

(2) Mitsusuke Tarama and Ryoichi Yamamoto
Mechanics of cell crawling under force-free condition
27th International Liquid Crystal Conference (ILCC2018), Kyoto International Conference Center, Kyoto, 22-27 (27) Jul., 2018.

(3) Mitsusuke Tarama and Ryoichi Yamamoto
Modeling of cell crawling by means of force-free intracellular motion
International Conference on Advances of Emergent orders in Fluctuations (APEF2018), Ito International Research Center Symposium, The University of Tokyo, Tokyo, 12-15 (14-15) Nov., 2018.

(4) 多羅間充輔
Cell crawling on elastic substrate
札幌非線形現象研究会 2018，北海道大学　電子科学研究所, 27-29 (29) Aug., 2018.

(5) Mitsusuke Tarama、Ryoichi Yamamoto
Mechanics of cell crawling with force-free cyclic motion
A Satellite Symposium to celebrate Prof. Kenichi Fukui's 100th birthday, FIFC, Kyoto University, 13 Oct., 2018.

(6) Mitsusuke Tarama、Ryoichi Yamamoto
Mechanochemical modeling of crawling cells
Active Matter Workshop 2019, Meiji University, 10-11 (10) Jan., 2019 (oral).

(7) Mitsusuke Tarama、Kenji Mori, and Ryoichi Yamamoto
Modelling crawling cells: From simple mechanical model to mechano-chemical model
第 16 回京都大学福井謙一記念研究センターシンポジウム，京都大学　福井謙一記念研究センター, 8 Feb., 2019.

4. Others

(1) Mitsusuke Tarama, Kenji Mori, Ryoichi Yamamoto
Mechano-chemical subcellular-element model of crawling cells
Seminar in Sawai Lab, Univ. of Tokyo, 18 Sep, 2018.

(2) Mitsusuke Tarama
Mechanics of cell crawling by means of force-free cyclic motion
BDR Seminar in Kobe, RIKEN Center for Biosystems Dynamics Research, 25 May, 2018.

Masato Itami

Program-Specific Researcher

1. Summary of the research of the year

Stochastic order parameter dynamics for phase coexistence in heat conduction

Phase coexistence, such as liquid-gas coexistence, is ubiquitous in nature. As the most idealized situation, phase coexistence under equilibrium conditions has been studied. For example, the liquid-gas coexistence temperature is determined by equality of the chemical potential of liquid and gas at constant pressure. The pressure dependence of the coexistence temperature is related to the latent heat and the volume jump at the transition point, which is known as the Clausius–Clapeyron equation. These are important consequences of thermodynamics.

In addition to equilibrium systems, phase coexistence gives rise to a rich variety of phenomena out of equilibrium such as flow boiling heat transfer, pattern formation in crystal growth, and motility-induced phase separation. Moreover, as an interesting phenomenon, it has been reported that heat flows from a colder side to a hotter side in a transient regime for continuous heating. One may expect that a deterministic hydrodynamic equation incorporating interface thermodynamics, which is referred to as generalized hydrodynamics or dynamical van der Walls theory, could describe such dynamical phenomena. The first message of the present study is that contrary to this expectation, stochastic dynamics is inevitable if one wants to quantitatively predict thermodynamic properties even in steady heat conduction.

We discuss the reason why deterministic equations are not appropriate for phase coexistence in heat conduction. In general, a deterministic macroscopic equation emerges from a microscopic description as a result of the law of large numbers, which is applied to systems with the separation of two scales: a microscopic length ℓ, such as the size of atoms, and the system size L. By introducing the ratio of the two scales as

$$\eta \equiv \frac{\ell}{L}, \tag{1}$$

we express the separation of the scales as $\eta \to 0$, which corresponds to the thermodynamic limit in equilibrium statistical mechanics. A deterministic description of the time evolution is obtained in an appropriate limit involving the scale separation $\eta \to 0$, while small fluctuations come into the description when η is small but finite. With this in mind, we study the simplest case, which is phase coexistence in steady heat conduction near equilibrium. We assume that the system is divided into two phases by a macroscopic planer interface across which the heat flows in a simple cuboid geometry. More microscopically, the interface is identified as a deformed surface of an intrinsic width w which is at most 10^{-7} cm. This width w is of the same order as the microscopic length ℓ, and the deformation of the surface is described by a capillary wave theory or fluctuation theory. By averaging density profiles in the equilibrium ensemble, one has an effective interface of the width w_{eff} which is estimated as $\mathrm{w}_{\mathrm{eff}} \simeq \ell\sqrt{\log(\mathrm{L}/\ell)}$for three-dimensional systems. We note here that $w_{\mathrm{eff}}/L \to 0$ in the limit $\eta \to 0$. That is, the interface in the deterministic hydrodynamic equation is a singular surface where the interface motion may not be properly defined. When we keep the finiteness of the interface width in the dynamics, the noise intensity also remains finite. Therefore, the limit $\eta \to 0$ should be taken after thermodynamic quantities are determined in stochastic dynamics with small but finite η.

The description with small but finite η is formulated as follows. We define mesoscopic quantities by the average over a region of a length scale Λ satisfying

$$\ell \ll \Lambda \ll L, \tag{2}$$

so as to apply local thermodynamics to the region. For simplicity in the later argument, we set $\Lambda = L\sqrt{\eta}$ for small η. One may take a different exponent satisfying (2), such as $\Lambda = L\eta^{a}$ with $0 < a < 1$. The final result is independent of the choice of a in the limit $\eta \to 0$. In this mesoscopic description, the interface width of the spatially averaged configuration is approximately Λ. We call this interface a mesoscopic interface.

In this description, the effective noise intensity for mesoscopic fluctuations vanishes in the limit $\eta \to 0$, while the interface motion, which is the slowest process in equilibration, ceases in the limit $\eta \to 0$. In this sense, the weakness of the noise is connected to the slowness of the motion. This non-trivial combination may yield a surprising phenomenon. In this study, we formulate such a noise effect for phase coexistence in heat conduction.

Among many first-order transitions, we specifically study the order-disorder transition associated with the Z_2 symmetry breaking. This is clearly the simplest case of the symmetry breaking, and it is easily generalized to other complicated symmetry breakings, such as the nematic-isotropic transition in liquid crystals, which may be relevant in experiments. Although the liquid-gas transition may be most popular in the first-order transition, we study this phenomenon in another study.

For the order-disorder transition associated with the Z_2 symmetry, one may recall a Ginzburg-Landau equation that includes the interface thermodynamics as a gradient term. However, because this model describes the order parameter dynamics with the isothermal condition, it cannot be used for heat conduction systems. We must at least consider a coupled equation of the order parameter density field and the energy density field. Such a model was proposed as a phase field model that describes crystal growth. From this direction of research, one may interpret the stochastic model as a phase field model with noise.

When we consider a stochastic model as a generalization of the Ginzburg-Landau model, it is best to use the concept of the Onsager theory as follows. First, we specify a set of dynamical variables. Then, under the assumption of local thermodynamics, we consider the minimum form of dissipation and noise with the detailed balance condition at equilibrium. Concretely, the variables are the order parameter density field m, associated momentum density field v, and energy density field ϕ. Starting from the Ginzburg-Landau free energy, we obtain the entropy density s as a function of the internal energy density u and m. By using the relation among ϕ, u, v, and ∇m, we obtain equations for (m, v, ϕ) following the Onsager theory with the entropy functional. The equations are essentially equivalent to the so-called Model C.

In this manner, a formal expression of the stochastic model is immediately obtained. However, due to the multiplicative nature of the noise, the formal model exhibits a singular behavior. Therefore, we must perform a careful analysis of the stochastic process by appropriately choosing the short-length cut-off of the noise. It should be noted that the singularity is specific to the dynamics of non-conserved quantities and that it does not appear in the standard fluctuating hydrodynamics. By a theoretical argument using the separation of scales, we obtain a consistent stochastic model. We do not find references that mention this remark, but this is not surprising even if it was well-recognized by specialists in the 1970's.

The theory for stochastic models related to thermodynamics has developed significantly over the last two decades. This mainly comes from the discovery of simple and universal relations: the fluctuation theorem and Jarzynski equality. Even for the theoretical calculation of quantities, these formulas can simplify the derivation of macroscopic evolution such as the Navier–Stokes equation and the order parameter dynamics of coupled oscillators. In the present problem, we start by deriving the stationary distribution for the system out of equilibrium. It has been known that the stationary distribution is formally expressed in terms of the time integration of the excess entropy production rate. We attempt to derive a potential function of the interface position for the phase coexistence in the heat conduction by contracting the stationary distribution of configurations. When we obtain the potential function, the most probable position of the interface is determined as an extremal point of the potential. This is simply a variational principle. We may say that our theoretical challenge is the derivation of such a new variational principle.

This problem is too difficult to solve for a general setup. Because the expectation value of a thermodynamic quantity is determined from the time correlation between this quantity and the excess entropy production, derivation of the potential function requires analysis of such time-dependent statistical quantities, which is a difficult task. Here comes a key concept of this study. We consider a special boundary condition, where the constant energy flux is assumed at boundaries so that the energy of the system is conserved. We refer to this as the non-equilibrium adiabatic condition. In equilibrium cases, this boundary condition is the standard adiabatic condition, where the total energy is conserved in the time evolution without an external operation. The variational principle for determining thermodynamic properties here is well-established as the maximal principle of the total entropy. Thus, for the non-equilibrium adiabatic condition in the linear response regime, we can develop a perturbation theory for extending this variational principle.

Towards the derivation of the variational principle, we calculate the time integration of excess entropy production rate for the configuration with a single interface. Explicitly, we consider the relaxation to the equilibrium state from this configuration. In the ordered and disordered regions, because the process may be described by the deterministic equation, we can solve it for small η. We can then estimate this contribution to the excess entropy production. Physically, the latent heat is generated at the moving interface in the relaxation process. This heat diffuses into both regions, and as the result, the entropy production is observed. Moreover, a macroscopic temperature gap appears in the moving interface, as observed in experiments. This is another source of entropy production. We estimate this contribution with some approximation.

By using these results for the particular setup, we derive a potential function of the interface position in the limit $\eta \to 0$. That is, the interface position is uniquely determined by the variational principle for the phase coexistence in heat conduction. The variational function is a modified entropy of the steady state profile for a given interface position, where the modified entropy contains a correction term expressed in terms of the excess entropy, which is produced in slow interface motion. It should be noted that the expectation value of a thermodynamic quantity would be independent of boundary conditions if the energy flux and energy are specified. We thus expect that our result is available even for cases where two heat baths contact at boundaries, which is a standard setup for heat conduction.

From a theoretical viewpoint, the variational principle for determining thermodynamic properties out of equilibrium has never been considered in previous studies. For example, it has been known that the minimum entropy production principle may characterize the steady state in the linear response regime. However, in the most general form, the variational principle is formulated for determining the statistical ensemble in the linear response regime as that minimizes the entropy production as a function of probability density. Although one may expect that the variational principle for thermodynamic properties is obtained from the variational principle for the statistical ensemble, this remains too formal to calculate thermodynamic values explicitly. As another example of recent activities in the variational principle, we recall those coming from the large deviation theory. In these theories, the main concern is fluctuation properties, while thermodynamic values are assumed to be obtained immediately.

The most important physical result in our theory is that the interface temperature θ deviates from the equilibrium transition temperature T_c. That is, a super-heated ordered state or a super-cooled disordered state stably appears locally near the interface. It should be noted that this phenomenon was predicted by an extended framework of thermodynamics for heat conduction systems, which we call global thermodynamics [N. Nakagawa and S. Sasa, Liquid-gas transitions in steady heat conduction, Phys. Rev. Lett. **119**, 260602, (2017)]. Remarkably, despite the difference of theoretical frameworks, our result on $\theta - T_c$ qualitatively agrees with the prediction of this thermodynamic framework up to a multiplicative numerical constant.

Here, we briefly introduce the global thermodynamics. The theory describes spatially inhomogeneous systems by a few global quantities, such as the global temperature, which is defined such that the fundamental relation in thermodynamics is satisfied. This idea is simple and natural but has never been considered in previous studies seeking an extended framework of thermodynamics. More importantly, this framework naturally leads to a quantitative prediction of the interface temperature different from T_c. Therefore, experiments can judge the validity of the fundamental hypothesis on which global thermodynamics is built.

The deviation of the interface temperature θ from T_c leads us to reconsider the local equilibrium state. We may assume that thermodynamic relations hold locally in each phase, while it is not obvious how to connect the local equilibrium states at the interface. No deviation of the interface temperature from T_c can be concluded from the assumption of the continuity of the local free energy density (or the local chemical potential for liquid-gas transitions). This assumption seems reasonable and indeed was adopted as one of the basic equations for non-equilibrium thermodynamics for systems with interfaces. From our viewpoint, this assumption can be derived from the deterministic order parameter equation with the interface thermodynamics. However, the deterministic equation is not justified, as we have already discussed. Therefore, we do not assume the continuity of the local free energy density for connecting the local equilibrium states at the interface. We also discuss previous studies on molecular dynamic simulations.

This is joint work with Shin-ichi Sasa, Naoko Nakagawa, and Yohei Nakayama [arXiv:1908.03029].

2. Original Papers

(1) Masato Itami and Shin-ichi Sasa
“Singular behaviour of time-averaged stress fluctuations on surfaces”
J. Stat. Mech. **2018**, 123210 (2018).

3. Presentation at academic conferences

(1) Masato Itami and Shin-ichi Sasa
“Singular behavior of time-averaged stress fluctuations on surfaces”
Advances in Physics of Emergent orders in Fluctuations, Tokyo, Japan, 12–15 November 2018 (poster)

(2) 伊丹將人、佐々真一
「流体中で固定壁に働く熱誘起力」
日本物理学会第74回年次大会、九州大学、2019年3月14-17日（口頭）

4. Others

(1) Masato Itami
“Singular behavior of time-averaged stress fluctuations on surfaces”
The 16th Fukui Center Seminar, Kyoto, 20 November 2018 (oral)

(2) Masato Itami and Shin-ichi Sasa
“Singular behaviour of time-averaged stress fluctuations on surfaces”
The 16th symposium of Fukui Institute for Fundamental Chemistry, Kyoto, 8 February 2019 (poster)

Shunsuke Yabunaka

FIFC Fellow

1. Summary of the research of the year

Breakdown of the standard large analysis in the O(N) model: The role of cusps in the fixed point potentials

The large-N expansion plays a fundamental role in quantum and statistical field theory. We showed on the example of the O(N) model that at infinity N, its traditional implementation misses in all dimensions below four some fixed points of the renormalization group. These new fixed points show singularities at in their effective potential that become a boundary layer at finite N as shown in Fig. 1. We showed that they have a physical impact on the multicritcal physics of the O(N) model at finite N. We also showed that the mechanism at play holds also for the O (N)* O (2) model and is thus probably generic.

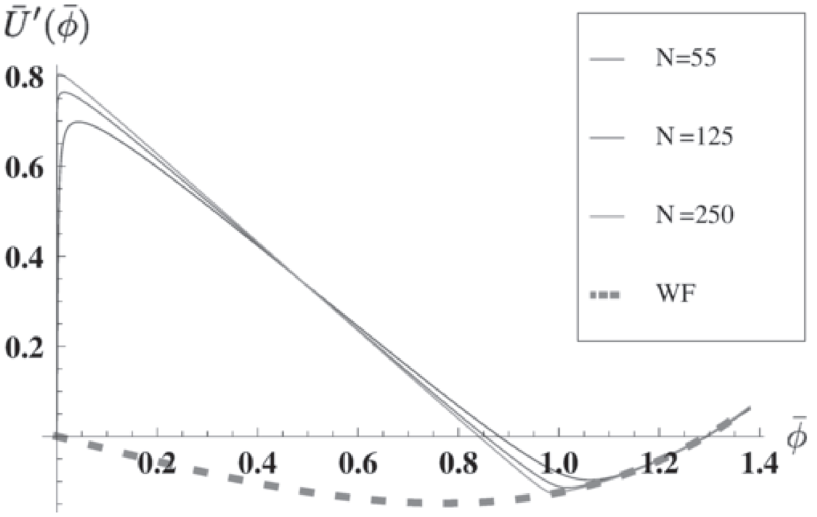


Fig. 1 The derivative of the effective potential for a nonperturbative FP called C_2 for different values of N and the Wilson-Fisher FP for N=100 in d=3.2

Drag Coefficient of a Rigid Spherical Particle in a Near-Critical Binary Fluid Mixture beyond the Regime of the Gaussian Model

The drag coefficient of a rigid spherical particle deviates from the Stokes law when it is put into a near-critical fluid mixture in the homogeneous phase with the critical composition. The deviation is experimentally shown to depend approximately linearly on the correlation length far from the particle, and is suggested to be caused by the preferential attraction between one component and the particle surface. In contrast, the dependence was shown to be much steeper in the previous theoretical studies based on the Gaussian free-energy density. In the vicinity of the particle, especially when the adsorption of the preferred component makes the composition strongly off-critical, the correlation length becomes very small as compared with the bulk correlation length.

This spacial inhomogeneity, not considered in the previous theoretical studies, can influence the dependence of the drag coefficient on the bulk correlation length. To examine this possibility, we here apply the local renormalized functional theory, which was previously proposed to explain the interaction of walls immersed in a (near-) critical binary fluid mixture, describing the preferential attraction in terms of the surface field. The free-energy density in this theory, coarse-grained up to the local correlation length, has much complicated dependence on the order parameter, as compared with the Gaussian free-energy density. Still, a concise expression of the drag coefficient, which was derived in one of the previous theoretical studies, turns out to be available in the present formulation. We show that, as the bulk correlation length becomes larger, the dependence of the drag coefficient on the bulk correlation length becomes distinctly gradual and close to the linear dependence.

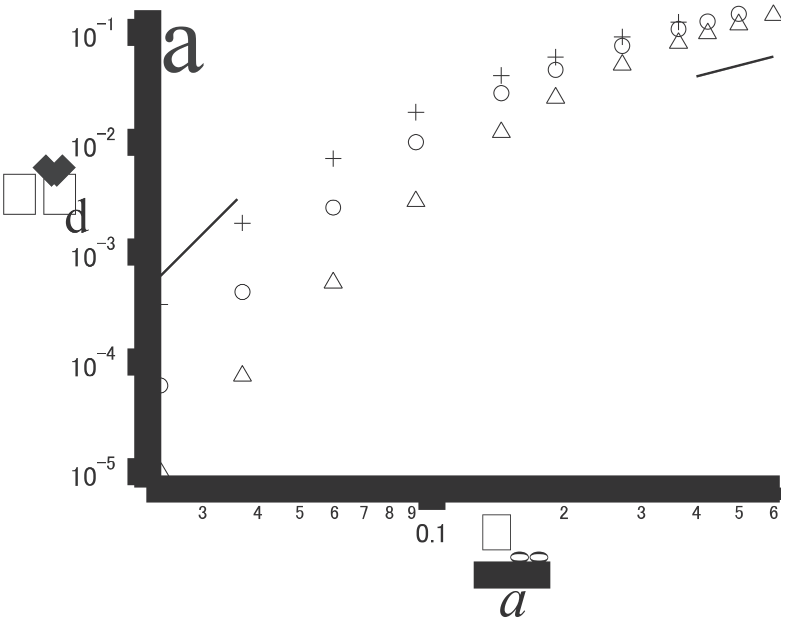


Fig. 2 The logarithmic plot of the deviation of the drag coefficient from the Stokes' law as a function of the bulk correlation length for various values of the adsorption parameter on the particle surface. Lines represent the slopes of one and four.

2. Original papers

(1) Shunsuke Yabunaka and Delamotte Bertrand
"Why Might the Standard Large N Analysis Fail in the O(N) Model: The Role of Cusps in Fixed Point Potentials"
Phys. Rev. Lett. 121, 231601(2018).

3. Presentation at academic conferences

(1) Shunsuke Yabunaka and Akira Onuki
“Electric double layer composed of an antagonistic salt in an aqueous mixture: Local charge separation and surface phase transition”
Soft Matter Physics: from the perspective of the essential heterogeneity Fukuoka, Dec. 10-12, 2018

4. Others

(1) Shunsuke Yabunaka
“Surprises in O(N) Models: Nonperturbative Fixed Points, Large N Limits, and Multicriticality”
Keio University, Yokohama, August 3, 2018

(2) Shunsuke Yabunaka
“Cell growth, division, and death in cohesive tissues: A thermodynamic approach” 九大前多研セミナー, Fukuoka, May 17, 2018.

(3) Shunsuke Yabunaka
“細胞組織における細胞増殖、極性、変形の連続体記述” UBI seminar (20th), Tokyo, May 7, 2018.

Simon K. Schnyder

FIFC Fellow

1. Summary of the research of the year

Structure factors in a two-dimensional binary colloidal hard sphere system

Most materials of practical interest consist of more than a single component, yet elucidating the physical behaviour of multicomponent systems is challenging. Nevertheless, these systems, which include metallic alloys, polymer blends and glasses are important for a range of applications, making this detailed understanding crucial for the development of more sophisticated materials. Here, a key difficulty is that multicomponent systems often display markedly different properties from those of their pure components, with precise details of the interactions and cross-correlations between species leading to a range of subtle effects. The simplest multicomponent system to consider is a binary mixture, i.e. a system consisting of only two components. However, even these 'simple' binary mixtures already display a rich range of physical behaviour beyond that seen in a single component system. This includes different phase transitions, such as fluid–solid phase separation, and glass formation, with binary solids forming alloys or glasses depending upon the structural order of the individual particles. Even in a single fluid phase the correlation functions display a much richer behaviour than a one-component system, as the unique wavelength of oscillation in a mixture can either be set by the size of the smaller or the large particles of a mixture. The transition from one to the other lengthscale is called structural crossover, which can be observed not only in bulk correlation functions but also in several inhomogeneous distributions. Structural crossover has been observed experimentally in binary colloidal fluids and ionic liquid–solvent mixtures.

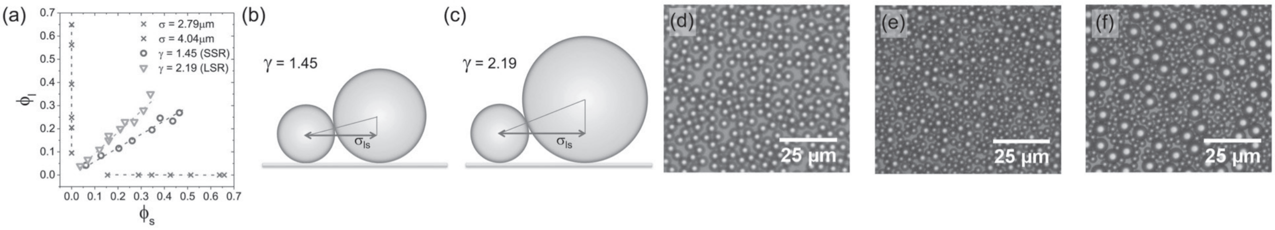


Figure 1. (a) State diagram indicating the different colloidal systems studied. The in-plane geometry of the (b) SSR and (c) LSR systems. Panels (d) to (f) show experimental images of the (d) monodisperse system with $\sigma = 4.04\mu m$, (e) the SSR system ($\gamma = 1.45$) and (f) the LSR system ($\gamma = 2.19$) at $\varphi_t \approx 0.6$.

The simplest interacting binary system is that of a mixture of large and small hard spheres with diameters $\sigma l,s$. The behaviour of binary hard spheres is governed by the total packing fraction, $\varphi t = \varphi l + \varphi s$, with $\varphi l,s$ the packing fractions of the large and small hard spheres, the composition $q = \varphi l/\varphi t$ and the size ratio $\gamma = \sigma l/\sigma s$. However, for binary hard sphere mixtures at relatively large size ratios, non-additivity effects can give rise to complex behaviour, as is evident from the vast amount of theoretical and simulation studies. Experimentally, hard sphere model systems can be realised using colloids, and previous work on three-dimensional (3D) binary colloidal hard sphere systems has included studies of phase separation, crystallisation and glass formation. In 2D, the situation is markedly different with the phase behaviour of monodisperse hard disks only recently having been established in simulations and in experiments on 2D colloidal hard spheres. In these experiments the colloidal hard spheres are confined to a monolayer and can – in the plane of the centres of the spheres – be considered as an excellent experimental hard disk system. For hard disks in particular, the increased complexity in the behaviour of binary mixtures is nicely illustrated by the fact that the melting behaviour of monodisperse hard disks qualitatively changes with the addition of a second component.

While a comprehensive study of the radial distribution functions in both single component and binary hard disk systems was reported previously, its counterpart in Fourier space, the (partial) static structure factor $S_{ij}(k)$, has received much less attention, despite the fact that there is a direct link between the zero-wavevector ($k \to 0$) limit of the static structure factor and thermodynamic quantities. For monodisperse systems, for example, this link directly leads to the isothermal compressibility, χ_T, which quantifies macroscopic fluctuations in the number of particles. For binary systems determining the isothermal compressibility is much more challenging. In fact, a full description of a binary mixture requires the knowledge of multiple thermodynamic quantities that follow from specific linear combinations of the partial static structure factors, known as Bhatia–Thornton structure factors.

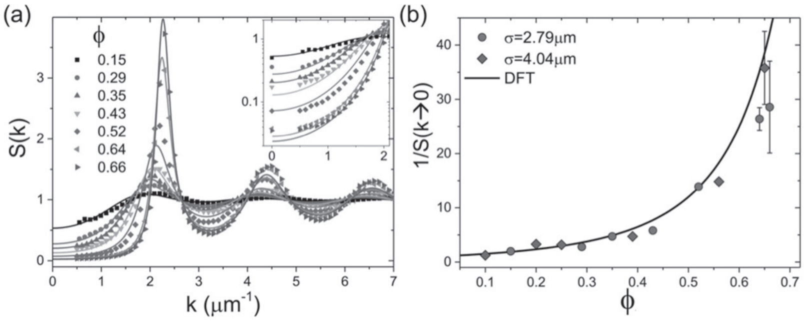


Figure 3. (a) The static structure factors, $S(k)$, for the monodisperse, $\sigma = 2.79$ μm, system for a range of packing fractions. The symbols denote data from experiments, while lines correspond to the theoretical structure factor based on DFT. Inset is the small k limit of $S(k)$ for the same system where points at $k = 0$ are those determined by an analysis of number fluctuations. (b) A comparison of the theoretical expression for the $1/S(k \to 0)$ limit with the experimentally determined limit from an analysis of number fluctuations for both monodisperse systems with σ = 2.79 and 4.04 μm.

The isothermal compressibility for binary mixtures is analogous to that for single component systems; however, as the $k \to 0$ limits of the Bhatia–Thornton structure factors are all interdependent, χ_T for mixtures cannot be obtained from the limit of a single static structure factor. As such, the determination of χ_T for mixtures requires that multiple limits are obtained to a high degree of accuracy. The thermodynamic factor Φ□, which follows from $S_{cc}(0)$ and is directly related to the second derivative of the molar Gibbs free energy, plays a key role in transport processes like mutual diffusion or interdiffusion as the variation of the thermodynamic factor is directly linked to the nature of the concentration fluctuations. Importantly, the thermodynamic factor accounts for the tendency of concentration fluctuations to relax over large length scales and these concentration fluctuations are indicative of the overall stability of the mixture. For example, the long-range concentration fluctuations characteristic of a phase separating system close to the critical point thus lead to a large $S_{cc}(0)$ and a correspondingly small Φ. For binary systems that tend to order rather than phase separate, the opposite behaviour is seen and the thermodynamic factor becomes large. Once Φ is known, the dilatation factor, δ, which describes the relationship between system size and composition, follows from $S_{nc}(0)$ and the compressibility χ_T then results from $S_{nn}(0)$.

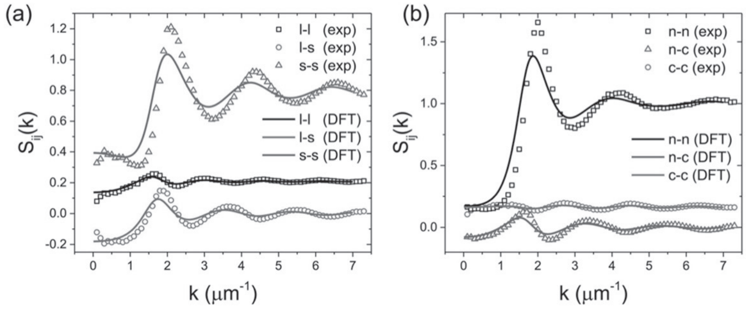


Figure 5. (a) A comparison between theory (lines) and experiments (symbols) of the partial structure factors $S_{ss}(k)$, $S_{ls}(k)$ and $S_{ll}(k)$ for the SSR with φ_t=0.54. The results agree qualitatively; but, due to the high concentration of the small disks there are clear deviations between theory and experiments found in $S_{ss}(k)$. This deviation can also be found in the Bhatia–Thornton structure factors, as shown in (b).

We analyse in detail the static structure factors for quasi-2D monodisperse and binary colloidal hard spheres and compare these to those calculated using density functional theory (DFT). We determine the $k \to 0$ limits of the structure factors from the analysis of the number and concentration fluctuations. For the compressibility of monodisperse systems, we find good agreement between results of the fluctuation analysis, DFT and the previously determined equation of state. We next consider the Bhatia–Thornton structure factors as a function of the total packing fraction for binary systems at two different size ratios. We again find that an analysis of the relevant fluctuations provides a good estimate for the $S(k \to 0)$ limit for these mixtures, allowing us to obtain the key thermodynamic quantities, such as the variation of the isothermal compressibility, the dilatation factor and the thermodynamic factor as a function of the total packing fraction.

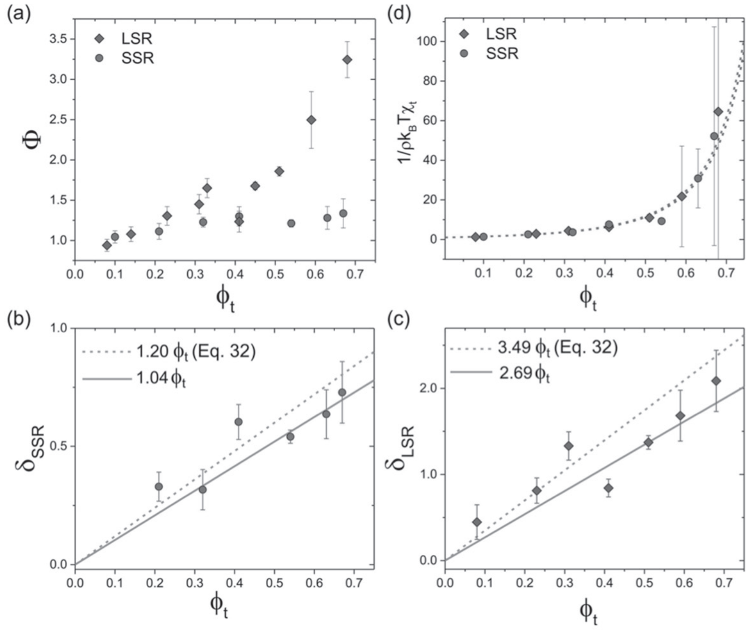


Figure 6. (a) The thermodynamic factor □as a function of total packing fraction φ_t for both binary colloidal fluids. (b, c) The dilatation factors δ as a function of total packing fraction for the SSR (b) and LSR (c) systems. Solid lines show the linear fit to the data used to approximate δ and dashed lines show the prediction. (d) The isothermal compressibility expressed as $1/\rho k_B T \chi_T$ for the colloidal binary systems at LSR and SSR as a function of φ_t. The dashed lines show the predictions for the equation of state from scaled particle theory.

2. Original papers

(1) A. L. Thorneywork, S. K. Schnyder, D. G. A. L. Aarts, J. Horbach, R. Roth, and R. P. A. Dullens
"Structure factors in a two-dimensional binary colloidal hard sphere system",
Molecular Physics, 116:21-22, 3245-3257 (2018)

3. Presentations at academic conferences

(1) S. K. Schnyder, J. J. Molina, and R. Yamamoto,
"Control of cell colony growth by contact inhibition",
Active Matter Workshop 2019, Meiji University, Tokyo, Japan (11/01/2019).

(2) S. K. Schnyder, J. J. Molina, and R. Yamamoto,
"Collective motion of cells on a substrate",
International Conference on Advances in Physics of Emergent orders in Fluctuations (APEF), Tokyo, Japan (12-13/11/2018).

(3) S. K. Schnyder, J. J. Molina, and R. Yamamoto,
"Collective motion of cells on a substrate",

Fukui 2018 Satellite Symposium, Kyoto, Japan (13/10/2018).

(4) S. K. Schnyder, J. J. Molina, and R. Yamamoto,
"Coherent migration and colony growth of cells on a substrate",
Conference "Active and collective motion: from cells to organisms", University of Warwick, UK (16/07/2018).

(5) S. K. Schnyder, J. J. Molina, and R. Yamamoto,
"Colony growth of cells on a substrate",
8th World Congress of Biomechanics, Dublin, Ireland (09/07/2018).

(6) S.K. Schnyder and J. Horbach,
"Anomalous transport in heterogenous media",
Workshop on Rheology of disordered particles: suspensions, glassy and granular materials, YITP, Kyoto University (19/06/2018).

4. Others

(1) Seminar: S.K. Schnyder and J. Horbach,
"Anomalous transport in heterogenous media",
Group of Roel Dullens, Oxford University, UK (18/07/2018).

(2) Seminar: S. K. Schnyder, J. J. Molina, and R. Yamamoto,
"Colony growth of cells on a substrate",
Group of Chiu Fan Lee, Imperial College London, UK (06/07/2018).

(3) S. K. Schnyder, J. J. Molina, and R. Yamamoto,
"Collective motion of cells on a substrate",
The 16th Symposium of Fukui Institute for Fundamental Chemistry, Kyoto (08/02/2018).

Satoshi Suzuki

1. Summary of the research of the year

小分子の励起状態ダイナミクスは分光法による観測が行えるようになってきており、光物理過程、光化学過程について実験・理論の両面から興味が持たれている。我々は機能性色素の発光性について、円錐交差の構造を決定し、励起状態のポテンシャル面を議論することで理解できるのではないかと考え、研究を行なっている。凝集誘起発光(Aggregation induce emission: AIE)は、希薄溶液では非発光性の色素が凝集により発光性を持つようになる現象である。油滴、アモルファス、ポリマー中など、不規則な構造であっても発光を示すようになることから、特定の分子間相互作用で発光性を生じるのではなく、主にメカニカルな原因によって発光性を生じるということが示唆される。内部転換の速度が周辺の環境により遅くなることにより蛍光量子収率が大きくなると考えられ、円錐交差がどの程度立体的な制約を受けるかを考えれば AIE の原理は理解できることになる。これまでにアルキルアミノアントラセンについての AIE の原理を解明し[1,2]、また、ONIOM 法により立体制約の大きさを見積もる方法も提案した[3]。

テトラフェニルエチレン(TPE)とスチルベン類の AIE の原理について、テトラフェニルエチレンの AIE の起源として、フェニル基の回転が重要だと言われている[4]。一方で、TPE の円錐交差は二重結合の回転に由来するという計算がされている[5]。それらを踏まえて、TPE 及び trans-スチルベンとその誘導体について円錐交差の構造を計算し、どのような構造変化が内部転換を促進するのかを考察する。二重結合の回転が内部転換を促進しているのだとすれば、AIE を示す trans-スチルベン誘導体も可能に違いない。実際、一部の trans-スチルベン誘導体は AIE を示す。そこで、TPE とスチルベン誘導体のポテンシャルエネルギー面を比較し、AIE を示すもの、示さないものとで特徴を調査する。また、架橋や置換基の導入により構造、電子状態を制御することで分子設計ができるのではないかと考え、物性の予測を目指す。

エチレンの円錐交差として Twisted Pyramid 型, Hydrogen Migration 型のものが知られているので、その構造を出発として、TPE、trans-スチルベンの円錐交差の構造を最適化した。Becke Half&Half LYP 汎関数、6-31G(d)基底関数による Spin-Flip TDDFT により一重項基底状態と第一励起状態の間の円錐交差を分岐面更新法により最適化した。電子状態計算と構造最適化には GAMESS を用いた。

まず、trans-スチルベンに対し、Twisted Pyramid 型, Hydrogen Migration 型の二種類の円錐交差を見つけることができた。SFTDDFT のレベルでは Twisted Pyramid 型の円錐交差の方が 2kJ/mol 低エネルギーであった。SFTDDFT はスピン固有関数を与えないので、多参照摂動法である MCQDPT による一点計算も行った。MCQDPT による計算でも Twisted Pyramid 型の円錐交差の方が Hydrogen Migration 型よりも 13kJ/mol 低エネルギーであるため、Twisted Pyramid 型の円錐交差を経由して内部転換が起こると考えられる。TPE についても同様の Twisted Pyramid 型円錐交差が得られ(Fig.1.)、ここから内部転換が起こると考えられる。

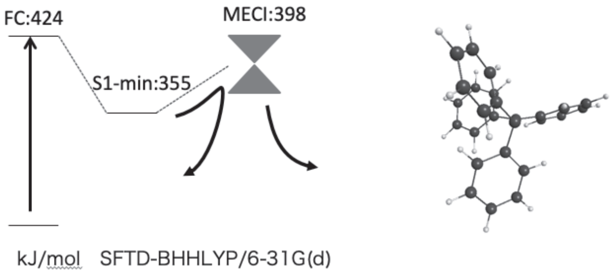


Fig. 1. TPE の円錐交差

Twisted Pyramid 型の円錐交差は架橋により妨げることが可能であるから、この円錐交差を構造あるいは電子状態により制御することで発光性を制御できる可能性がある。そこで、以下の Fig.2 のような架橋スチルベン分子の円錐交差を考察した。Twisted Pyramid 型円錐交差は二重結合のねじれを必要とするため、剛直な鎖長の短い架橋分子では円錐交差は高くなると予想される。

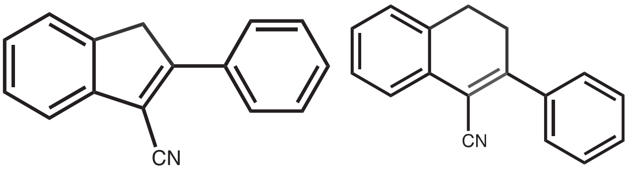


Fig.2. 検討した架橋スチルベン

実際、得られた円錐交差を比較すると、五員環架橋の方が高エネルギーであることがわかった(Fig.3)。現在、実験グループにより、架橋スチルベンを動作部位とする AIE 分子の合成準備が進められており、五員環架橋では液相でも強く発光し、七員環程度の緩い架橋では液相で発光しなくなることが確かめられた。理論的に提案された「架橋により Twisted Pyramid 型円錐交差をコントロールすることにより発光強度のコントロールする」という分子設計指針の有用性が確かめられたといえる。

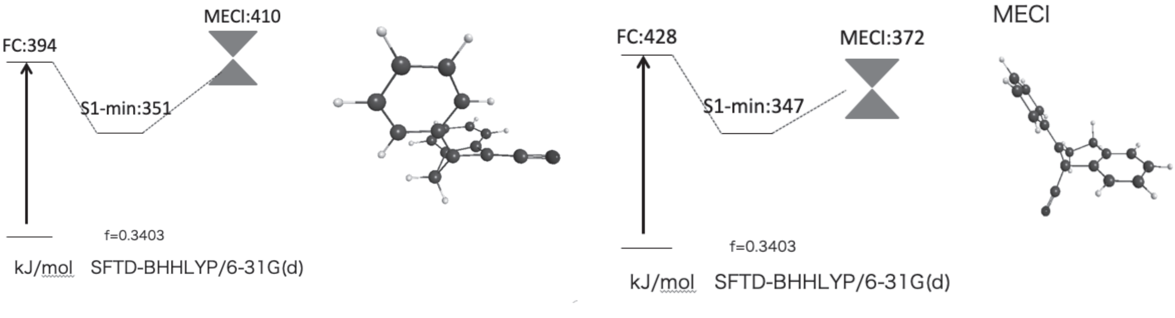


Fig.3 検討した架橋スチルベンの potential energy surface と円錐交差の構造

[1] S. Sasaki, S. Suzuki, W. M. C. Sameera, K. Igawa, K. Morokuma, G. Konishi *J. Am. Chem. Soc.*, **138,** 8194 (2016).

[2] S. Sasaki, S. Suzuki, K. Igawa, K. Morokuma, G. Konishi *J. Org. Chem.*, **82,** 6865 (2017).

[3] 鈴木，諸熊, 第 19 回理論化学討論会，(2016).

[4] Z. Yang *et al., J. Mater. Chem. C,* **4**,99,(2016)
[5] K. Kokado, T. Machida, T. Iwasa, T. Taketsugu, K. Sada, *J. Phys. Chem. C*, **122,** 245 (2018).

2. Original papers

(1) S.Suzuki, S. Maeda, K. Morokuma
Exploration of Quenching Pathways of Multiluminescent Acenes Using the GRRM Method with the SF-TDDFT Method
J. Phys. Chem. A, **119**, 11479–11487 (2015)

(2) S.Sasaki, S.Suzuki, W.M.C. Sameera, K. Igawa, K. Morokuma, G. Konishi,
Highly twisted N,N-dialkylamines as a design strategy to tune simple aromatic hydrocarbons as steric environment-sensitive fluorophores
J. Am. Chem. Soc., **138**, 8194-8206

(3) S.Sasaki, S.Suzuki, K. Igawa, K. Morokuma, G. Konishi,
“The K-Region in Pyrenes as a Key Position to Activate Aggregation-Induced Emission: Effects of Introducing Highly Twisted N,N-Dimethylamines”
J. Org. Chem., 2017, 82 (13), pp 6865–6873

3. Presentation at academic conferences

(1) “凝集誘起発光分子の原理解明と理論的分子設計”
○鈴木聡　諸熊奎治　分子科学討論会 2018

4. Others

Akhilesh Kumar Sharma

Postdoctoral Fellow

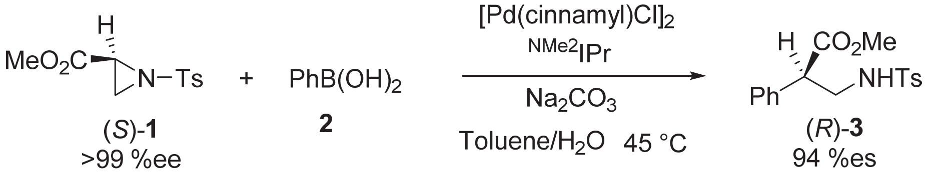
1. Summary of the Research of FY2018

1.1 Mechanism and Selectivity in PdSIPr-Catalyzed Ring-Opening and Cross-Coupling of Aziridine-2-carboxylates with Arylboronic Acids: A Computational Study

The strained small ring compounds such as oxiranes, aziridine, are being utilized in organic synthesis for variety of transformations. The aziridines are important synthons for formation of variety of N-containing compounds of synthetic importance, such as β–amino-functionalized motifs. The organometalic catalysts are effective for regioselective and stereospecific ring-opening of aziridines. The formed adducts after ring-opening can be further functionalized or used to generate products with regio- or chemo- or stereo-selectively.

Recently, we reported DFT study on the mechanism of Pd/SIPr-catalyzed enantiospecific and regioselective ring-opening and cross-coupling of 2-arylaziridines with arylboronic acids in collaboration with experimental group of Y. Takeda. In a new study, Y. Takeda and coworkers have developed cross-coupling of aziridine-2-carboxylates with arylboronic acids, which lead to generation of β-aryl amino acids. In current study we have explored mechanism and origin of selectivity in this reaction through DFT method.

To obtain insights on the mechanism and selectivity B3LYP-D3BJ functional was used. The PCM implicit solvation model was employed. The SDD basis sets and associated effective core potentials were applied for Pd, the 6-31G(d) basis sets were employed for remaining atoms. Final potential energies of stationary points were calculated using $\mathrm{PCM}_{\mathrm{Toluene}}$/B3LYP-D3/SDD(Pd),cc-pVTZ(other atoms). The best experimental catalyst $^{\mathrm{NMe2}}$IPr-Pd and (*S*)-substrate was used for the study (Scheme 1). The Free energy profile is given in Figure 1.



Scheme 1. Stereospecific and regioselective coupling of aziridine-2-carboxylates with phenylboronic acid.

The first step involve regioselective and stereoinvertive aziridine ring opening and occurs with a low barrier (6.6 kcal/mol, Figure 1). The water in reaction is important to stabilize the anionic intermediate **I2** (by 3.4 kcalmol). Further water is helpful in the proton transfer through **TS2**, which is almost barrierless. The formed intermediate **I3** (without H_2O) is only 0.4 kcal/mol above **I3.2H$_2$O**. It indicates that water molecules may not stabilize the neutral molecules. Then, coordination of the $PhB(OH)_2$ to **I3** lead to formation of lower energy intermediate **I4**. After rearrangement in **I4** through **TS3**, transmetalation occurs through **TS4** to give **I5**. Finally, reductive elimination takes place with a barrier of 19.2 kcal/mol (**TS5**), and the coupling product (*R*)-**3** (**P** in Figure 2) is formed. The rate determining step in the reaction is reductive elimination. The aziridine ring opening in S_N2 fashion at the carboxylic-carbon is responsible for enantioselectivity. The optimized TS for ring opening at methylene carbon is 3.3 kcal/mol higher in energy, which explain the high regioselectivity in the reaction. The energy decomposition analysis (EDA) suggests that interaction between substrate and catalyst is the key to regioselectivity. Further, the low yield with SIPr-ligand (instead of $^{\mathrm{NMe2}}$IPr-Pd) might be due to the higher barrier for reductive elimination (Figure 1), which would lead to slow reaction with the SIPr-Pd0 catalyst and give a lower yield. From our calculations it is concluded that water is necessary for aziridine ring opening step, which reduces the byproduct formation from zwitterionic intermediate **I2** and the reductive elimination is the rate limiting step.

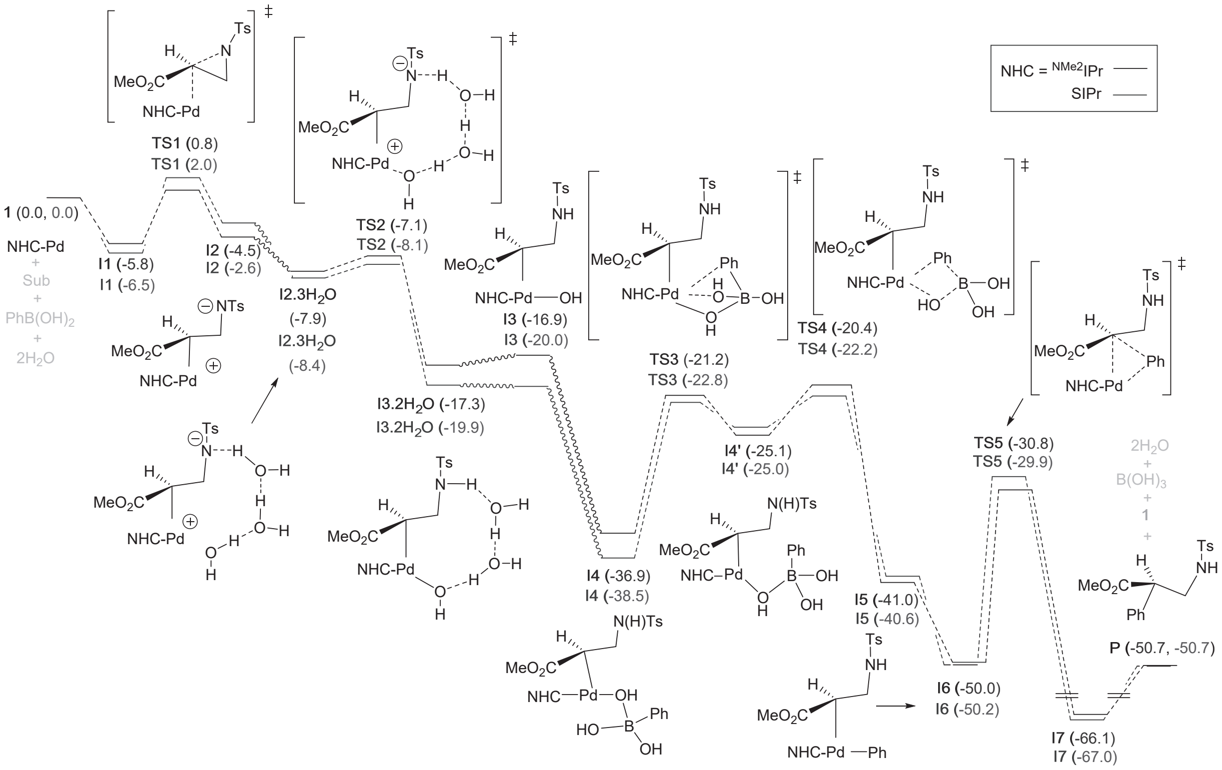
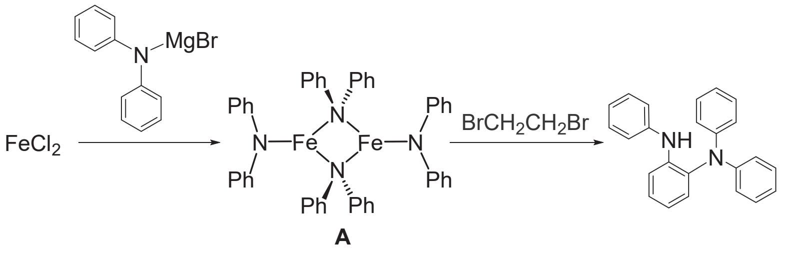


Figure 1. Free energy profiles (kcal/mol) for the mechanism of the Cross-Coupling of Aziridine-2-carboxylates with Arylboronic Acids.

1.2 Theoretical Study on the Mechanism of Fe-catalyzed C–H amination

Nitrogen containing molecules are ubiquitous in nature. Formation of many natural products, pharmaceutical compounds and functional materials require formation of C–N bond. The C–N bond formation is generally performed through transition metal catalyzed amination reaction, which involve C–X (X=halide) and C–H amination strategy. Since, C–H amination involve direct fictionalization and does not require pre-synthesis of reactive group, this method is atom economic and highly preferred. Pd-catalyzed amination reactions are well developed. However, due to economic and environmental friendly nature of Fe-Complexes, these are increasingly probed and used for variety of reactions. Fe-catalyzed reactions are in developmental stage, and the mechanism of Fe-catalysis will be helpful for further advancement. The group of M. Nakamura has been involved in development of Fe-catalyzed reactions. Recently, C–H amination of biphenyl amine is being developed in their group (Scheme 2). The detailed mechanistic understanding of reaction will be helpful in development and widening the scope of this reaction.



Scheme 2. Fe-catalyzed C–H amination of diaryl amine

The reaction was studied using DFT methods (PCM/B3LYP-D3BJ/6-31G*) to obtain mechanistic insights. First the active species involved in the reaction was explored. The transmetalation of $FeCl_2$ will give Fe^{II}-amide species. The Fe^{II}-amide species is known to exist in dimeric form and DFT results agree with it. The geometry optimized at PCM/B3LYP-D3BJ/6-31G* method match well with crystal structure in broken-symmetry singlet spin state. Hence, this method is used for further calculations. The ether is found to coordinate to Fe^{II}-amide and coordination of two ether molecules lead to ~12 kcal/mol lower energy complex. The Fe^{II}-amide dimers with two ethers molecules in high spin state and broken-symmetry singlet spin state are close in energy. Whereas, other spin states are very high in energy.

First the Fe^{II}-amide dimeric species react with dibromoethane. The reaction is found to occur in stepwise manner. The dibromoethane reaction with one Fe of dimer leads to the formation of higher energy $Fe^{III}Fe^{II}$ species and bromoethane radical. In next step the radical react with second-Fe leading to formation of $Fe^{III}Fe^{III}$ species and ethene. The activation barrier for these steps is ~22 kcal/mol.

In next step the formed $Fe^{III}Fe^{III}$ species undergo rearrangement to form lower energy complex **C** (Figure 2). Similar to Fe^{II}-dimer, for $Fe^{III}Fe^{III}$ complex **C**, the high spin state and broken symmetry spin state are close in energy and other spin states are >4 kcal/mol higher in energy.

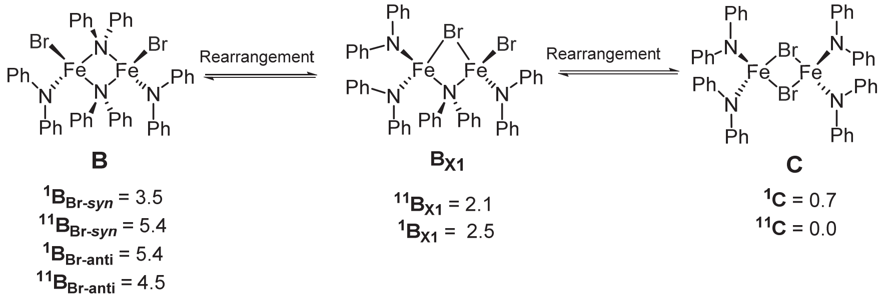
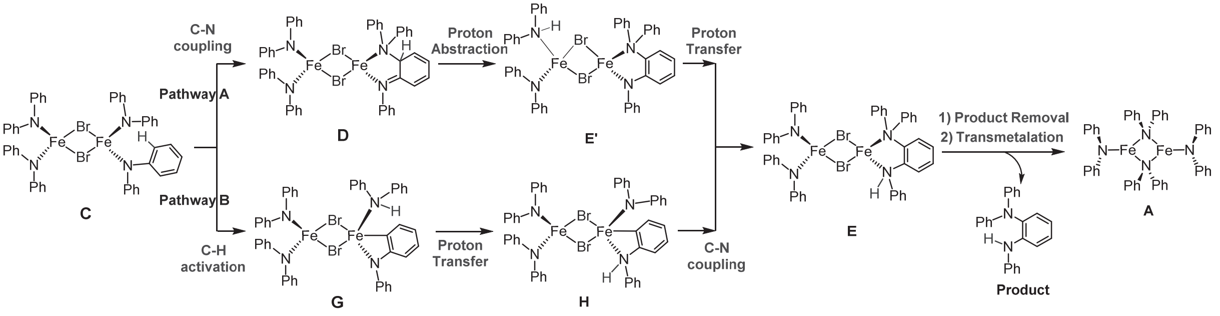


Figure 2. Energies of Fe^{III} intermediates at PCM_{DBE}/B3LYP-D3BJ/6-31G* level of theory.

After formation of Fe^{III}-dimer the next step is C–N coupling. Two different pathways were explored for the reaction. Pathway A involve C–N coupling through S_NAr type of mechanism whereas, the pathway B involve first C–H activation followed by coupling. Preliminary results show that the S_NAr type of mechanism is favorable. Detailed analysis of these steps is currently in progress.



Scheme 3. Proposed pathways form C–N coupling from Fe^{III} dimeric species.

The DFT study involving open shell dimeric metal complexes are very challenging; as it involve many spin states and broken symmetry spin states. In the current study we have investigated the different spin states and found that the reaction involves multiple spin-crossings. We identified the lowest energy Fe^{III} species. Further we found that reaction proceed through S_NAr type of mechanism.

2. Original papers

1. A. K. Sharma, W. M. C. Sameera, Y. Takeda, S. Minakata
   "A Computational Study on the Mechanism and Origin of the Reigioselectivity and Stereospecificity in Pd/SIPr-Catalyzed Ring-Opening Cross-Coupling of 2-Arylaziridines with Arylboronic Acids"
   ACS Catal., 9, 4582-4592 (2019).
2. Y. Takeda, T. Matsuno, A. K. Sharma, W. M. C. Sameera, S. Minakata
   "Asymmetric Synthesis of β^2‐Aryl Amino Acids through Pd‐Catalyzed Enantiospecific and Regioselective Ring‐Opening Suzuki‐Miyaura Arylation of Aziridine‐2‐carboxylates"
   Chem. Eur. J., 25, 10226-10231 (2019).
3. M. Isegawa, A. K. Sharma
   "CO2 reduction by a Mn electrocatalyst in the presence of a Lewis acid: a DFT study on the reaction mechanism"
   Sustainable Energy Fuels, 3, 1730-1738 (2019).
4. M. Isegawa, A.K. Sharma, S. Ogo, K. Morokuma,
   "Electron and Hydride Transfer in a Redox-Active NiFe Hydride Complex: A DFT Study"
   ACS Catal., 8, 10419-10429 (2018).

青野 信治

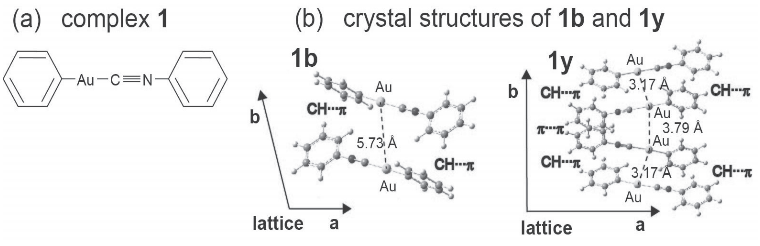
センターフェロー（榊研）

1. 今年度の研究の要約

今年度は金(I)-イソシアニド錯体によって構成される多型結晶の相対安定性および吸収・発光スペクトルの研究を行った。

【序】　金(I)-イソシアニド錯体は複数の単結晶構造を持ち、熱や光照射でなく機械的刺激によって相転移を起こし、各々の単結晶構造で異なる発光色を示す事から分子科学的にも、また材料化学的にも興味深い系である。 phenyl(phenyl-isocyanide) Gold(I)錯体 **1** は、溶媒中から高速で結晶化させると単結晶構造 **1b** が、ゆっくり結晶化させると単結晶構造 **1y** が生成する事が実験的に報告されている（Scheme 1）[1]。**1b** では最小単位格子が２個の分子から構成されているのに対して、**1y** では１６個の分子（Scheme 1b において c 軸方向に更に３層が方向性を各々90 度変えて存在する。）から構成されている。特に **1b** では PhNC 基と Ph 基の平面角τが 70 度ほど捻じれた単量体から構成されるのに対し、**1y** では PhNC 基と Ph 基がほぼ並行な単量体から構成されている。また **1b** では隣り合う分子間の Au-Au 距離は 4.7～5.7Å と長く、PhNC 基と Ph 基は CH-π相互作用しているのに対し、**1y** では隣り合う分子間の Au-Au 距離は 3.2～3.7Å と短く、PhNC 基と Ph 基の CH-π相互作用に加えて、PhNC 基のπ-π相互作用も存在している。

吸収・発光スペクトルのピーク位置は、これらの単結晶構造の間で大きく異なり、吸収スペクトルにおいて **1y** は **1b** よりも 1.0 eV、発光スペクトルにおいて **1y** は **1b** よりも 0.3 eV 以上低エネルギー側へのシフトが観測されている[1]。本研究では、QM/MM 法で結晶効果を考慮し、気相、溶液、結晶中での比較・検討を行い、この原因の究明を試みた。



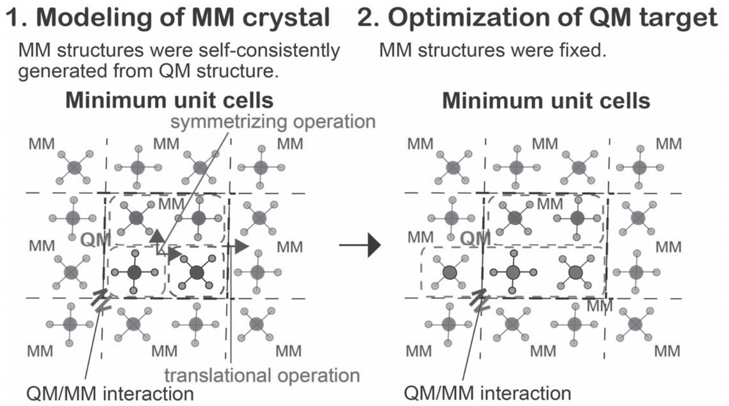
Scheme 1: 金(I)-イソシアニド錯体の構造

【方法】構造最適化には B3LYP-D3 汎関数による DFT 法を用い、吸収エネルギーは B3LYP 汎関数による TDDFT 法で求め、発光エネルギーは B3LYP-D3 汎関数を用いた３重項-１重項のエネルギー差で求めた。Au の原子価電子には(2111111/411/2111/1)基底を用い、内殻電子は Stuttgart グループの ECP で置き換え、f 軌道の分極関数を１つ加えた。他の原子については 6-31++G**基底を用いた。$CHCl_3$ 中の溶媒効果は 3D-RISM 法、結晶効果は周期境界条件に基づく QM/MM 法によって考慮した[2]。

本研究の QM/MM 法に基づく結晶中の構造決定は、次のように構築されている（Scheme 2）。まず、基底状態結晶を点電荷と LJ パラメータを用いてモデル化した。ここで、対称操

作と格子ベクトルによる並進操作を用いる事で全結晶部分を再構成できる領域をQM領域に選び、計算されたRESP電荷をMM領域に再分布させる事で自己無撞着的にMM領域の点電荷と構造を決めた^{2}。これによって得られた基底状態結晶中での吸収エネルギーを求めた。

基底状態結晶のMMモデルは固定したまま、式(1)のエネルギーE_{crystal}が最少となるように反応中心部分の３重項状態の構造を決定して、発光エネルギーを求めた。



Scheme 2: QM/MM法による結晶中３重項構造の決定

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

本研究では、格子ベクトルと基底状態結晶のAu原子の位置を実験結果に固定した。

またスペクトルに対する結晶内部と結晶表面の結果を調べるため、結晶内部で定めた構造について、スラブモデルを適用し、結晶表面での吸収・発光スペクトルを求めた。

【結果と考察】　基底状態の単量体では、Ph基とPhNC基の分子内平面角τ に対する気相中のエネルギー、$CHCl_3$中の自由エネルギーはB3LYP-D3汎関数を用いたDFT計算レベルでほぼ一定であり、CCSD(T)計算レベルでも平面角τ＝90度のねじれ構造がτ＝0度の平行構造に比べて0.5 kcal/molだけ安定であるという結果から、常温では自由回転していると考えられる。（図１）

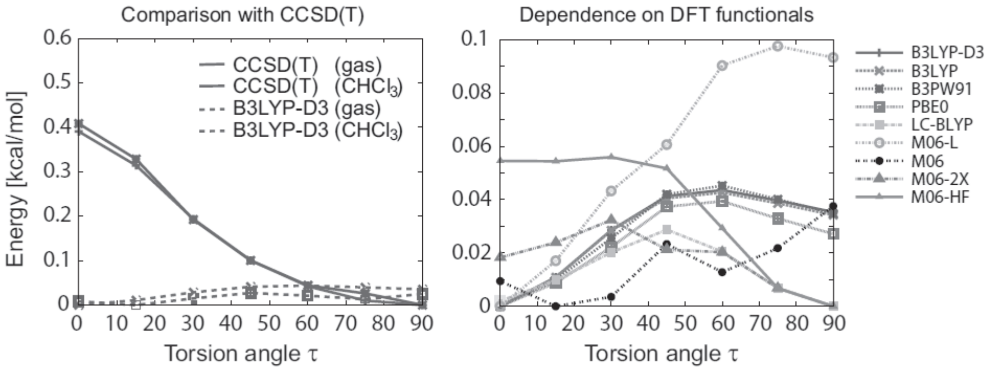


図１：分子内平面角τ に対するエネルギー安定性

そこで、吸収スペクトルと平面角τの関係性をみる為、τ＝0、30、60、90度の構造についてTDDFT計算を行った結果､Ph基のπ軌道からPhNC基のπ*軌道へのLLCT励起が最低励起状態となるが、その振動子強度は平面角τに強く依存する事が分かった（図２）。また最低励起エネルギーは気相中で3.2-3.3 eV、$CHCl_3$中で3.7-3.8 eVと後者の方が0.5 eV高い。また、第二ピークはPh基のπ軌道からPhNC基の面内π_{in}*軌道へのLLCT励起であり、第一ピークが平面角τ=0度で大きな強度を持つのに対して、第二ピークは平面角τ=90度で大きな強度を持つ。この第二ピークについても、気相中で4.2 eV、$CHCl_3$中で4.6 eVと後者の

方が 0.4 eV 高い。この溶媒中における励起エネルギーの増加は、錯体 **1** の PhNC 基は中性であるのに対して Ph 基はアニオン性であるので、より強い CH-π相互作用の溶媒和が Ph 基に生じ、この溶媒和によって Ph 基のπ軌道が相対的に安定化するため、Ph 基のπ軌道から PhNC 基のπ*軌道への LLCT 励起などの励起エネルギーは $CHCl_3$ 中でより高くなる事が原因である。

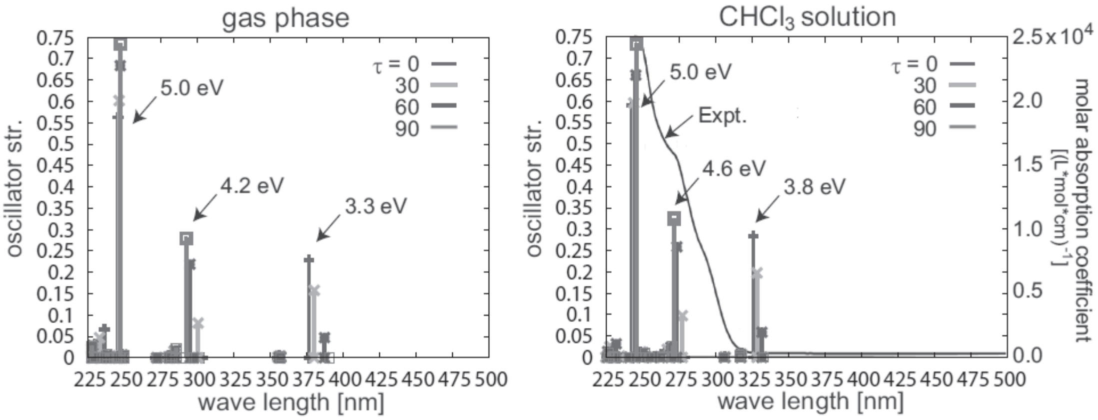


図２：気相、液相の励起エネルギーと振動子強度

結晶中の **1b** と **1y** についても、四量体を QM 領域に選び、自己無撞着点電荷を用いた QM/MM 計算によって構造を決定した。計算された単量体当りの結晶エネルギーは **1b** よりも **1y** の方が約 1 kcal/mol ほど安定であり、この傾向は実験において **1b** から **1y** への単結晶-単結晶相転移を不可逆的に起こす事が出来る事に合致する。また、得られた結晶構造における四量体について TDDFT 計算を行う事で吸収スペクトルを計算した（図３）。

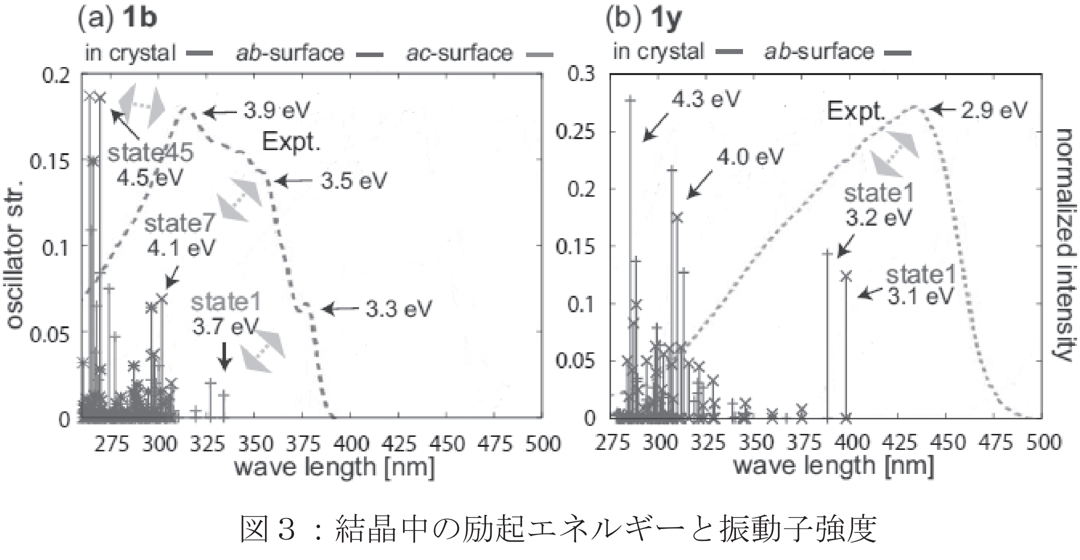


図３：結晶中の励起エネルギーと振動子強度

1b で計算された 4.1 eV の第一ピークは Ph 基のπ軌道から PhNC 基のπ*軌道への分子内および分子間 LLCT 励起であり、気相中の分子内 LLCT 励起に比べて 0.8 eV ほど高く、また 4.5 eV の第二ピークは Ph 基のπ軌道から PhNC 基の面内π_{in}*軌道への LLCT 励起であり、起草中の分子内 LLCT 励起に比べて 0.3 eV ほど高い。これらの増加は、Ph 基が隣り合う２つの分子の PhNC 基と CH-π相互作用している事が原因である。実際、CH-π相互作用が１つ

しかない結晶表面の場合は、特にこの前者のLLCT励起は3.7 eVに計算される。実験結果では3.9 eVに大きなピークがある他、3.5 eVにショルダーと3.2 eVに小さな吸収が観測されているが、これらは各々、結晶内分子のPh基のπ軌道からPhNC基の面内π_{in}*軌道へのLLCT励起、結晶内分子のPh基のπ軌道からPhNC基のπ*軌道へのLLCT励起、結晶表面の分子のPh基のπ軌道からPhNC基のπ*軌道へのLLCT励起に対応すると帰属できる。

一方、**1y**での結晶中と結晶表面で計算された3.2 eV、3.1 eVの第一ピークはAuのd軌道からPhNC基のπ*軌道へのMLCT励起であり、実験値2.9 eVのピークに対応している。**1y**では隣り合う分子のAu-Au距離が短いので、anti-bonding combination型のd軌道が生じ、そのエネルギーが相対的に高くなるため、π-π*型LLCT励起よりもMLCT励起が低く、**1b**の第一ピークとは異なる励起状態となる。**1b**から**1y**への単結晶-単結晶相転移による吸収スペクトルのレッドシフトについて、実験値1.0 eVに対して計算値1.4 eVであり、傾向を再現している。

また、気相、$CHCl_3$中の単量体の３重項状態は、PhNC基のπ-π*局所的励起構造が求まった。このπ-π*局所的励起は基底状態と電荷分布が大きく変化しておらず、発光エネルギーは気相、$CHCl_3$中ともに2.72 eVであり、環境の影響を受けない。二量体も検証したが、π-π*局所的励起よりもanti-bonding combination型Auのd軌道からbonding combination型PhNC基のπ*軌道へのMLCT励起構造が安定であった（図４）。π-π相互作用構造は、CH-π相互作用構造よりも気相中で3 kcal/mol安定であり、発光エネルギーも前者が1.95 eV、後者が2.45 eVとなり、発光エネルギーはAu-Au距離だけでなく、２つのPhNC基の向きにも大きく依存する。

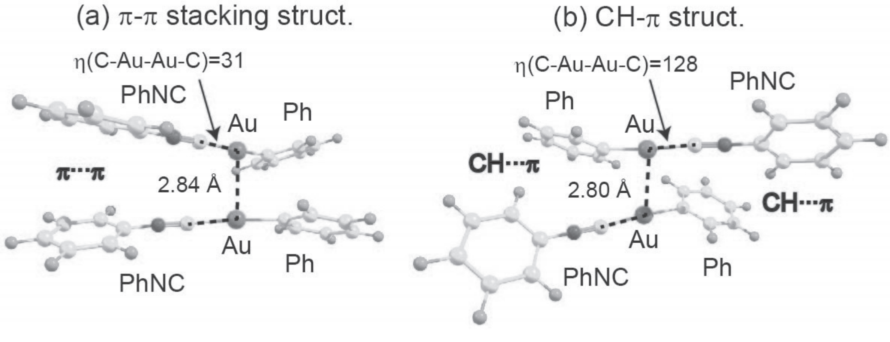


図４：MLCT型３重項の２つの安定構造

1bでは、周囲の分子の配向性のためMLCT型３重項構造を二量体間で作る事ができず、PhNC基のπ-π*局所的励起構造からの発光エネルギーが2.72 eVに求まった。一方、**1y**ではMLCT型３重項のCH-π相互作用構造を二量体間で作り、両側の隣り合う二量体も近付く事で、その発光は2.38 eVに求まった。これは実験値2.19 eVに比べて高い結果になっているが、**1b**から**1y**への単結晶-単結晶相転移による発光スペクトルのレッドシフトについて、実験値0.34 eVに対して計算値0.35 eVであり、良い一致を与えている。

更に１の**PhNC**にジメチル化を行った金(I)イソシアニド系では緑の発光色を示す**2g**から黄色の発光色**2y**へ単結晶-単結晶相転移を起こす事が知られている。これは**1b**から**1y**への単結晶-単結晶相転移とは発光色変化の逆の傾向であり、この**2g**と**2y**の間の相対安定性や吸収・発光スペクトルに違いについても同様の計算を行い、理論的な見識を広げた。[3]

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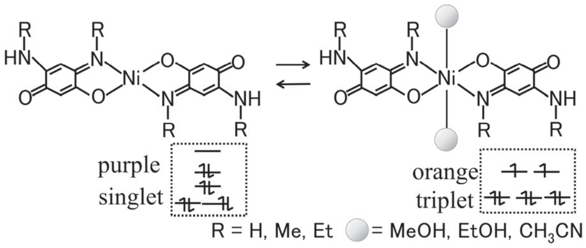
中垣雅之

FIFC フェロー

1. 今年度の研究の要約

【緒言】近年、加藤らのグループによりキノノイドを配位子として持つ Ni 錯体にメタノール分子が吸着することで結晶が変色するベイポクロミズム現象が報告された(Scheme 1) [1]。これはメタノール分子が配位することにより Ni 原子が 1 重項から 3 重項へスピン転移を起こすためであり、磁性化学の点からも興味深い。このスピン転移はメチルアミノ基(NHR; R=Me)をもつキノノイド錯体で起こるが、エチルアミノ基(R=Et)をもつ錯体では観測されない。また、メタノール以外の揮発性分子(VOC)ではスピン転移は起こらない。本研究では結晶効果を取り込んだ電子状態計算により、ベイポクロミズムを誘起する因子について検討を行い、吸収スペクトル及びその変化について定量的な再現を試みた。



Scheme 1

【モデル及び計算方法】側鎖の異なるアミノ基を持つ 3 つのキノノイドの Ni 錯体に関して、キノノイド配位子のみの場合と VOC 2 分子が配位した場合について結晶構造及び分子構造の最適化を行った。結晶構造の最適化は平面波基底と PBE-D3 汎関数を用いた密度汎関数法で行った。気相及び QM/MM 法を用いた結晶中の Ni 錯体の構造最適化には B3LYP*-D3 汎関数を用いた。励起エネルギーの計算には CASPT2 法を用いた。活性軌道にはσ型の 2 電子占有軌道である $d_{x2\text{-}y2}$ 軌道を除く Ni 原子の 4 つの d 軌道と 10 個のπ軌道を用いた(18 電子 14 軌道)。Ni 原子の内殻電子は Stuttgart-Dresden-Bonn の ECP で置き換え、原子価軌道には triple zeta 基底関数を用いた。その他の原子には cc-pVDZ を用いた。

【結果及び考察】孤立系の計算では、アミノ基の違いに関わらず Ni 原子とメタノール及びエタノール 1 分子あたりの結合エネルギーは 12.4-14.0 kcal/mol であり大きな違いは見られなかった(Table 1)。一方、結晶中においては構造や結合エネルギーに顕著な違いが見られた。メチルアミノ基とメタノールの組み合わせでは、Ni 原子は孤立系と同様の 6 配位構造をとる。このメタノール分子は同時に隣接する錯体のキノノイド配位子と水素結合を形成する(Figure 1a)。エタノール分子では配位子との水素結合は形成されるが、Ni-O の距離は 2.73Å と非常に長く(Figure 1b)、結合エネルギーは 3.0 kcal/mol と弱く、Ni のスピン状態は 1 重項のままである。この結果は、エタノールではベイポクロミズム現象が観測されなかった実験結果と一致する。

Table 1. Energy difference (kcal/mol) between 1et of [Ni(HL^R)$_2$]and 3et of [Ni(HL^R)$_2$]・2ROH

R	H		Me		Et	
VOC	MeOH	EtOH	MeOH	EtOH	MeOH	EtOH
ΔE	−35.7	−36.8	−35.1	−39.5	−33.9	−36.3
ΔG	−13.1	−14.5	−14.8	−13.4	−9.9	−12.3

エチルアミノ基錯体では、メタノールが Ni に配位した構造と配位子と水素結合を形成した構造の２つが得られたが、後者の方がより安定であった(Figure 1c)。

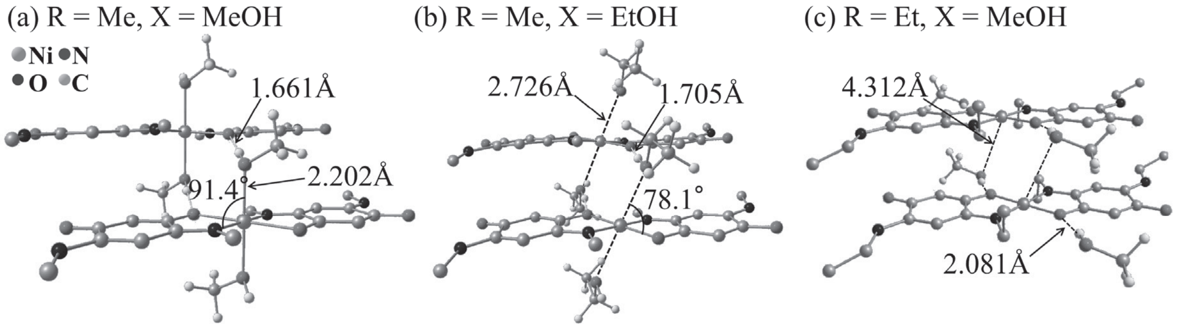


Figure 1 . Optimized structure in crystal calculated by QM/MM method.[3]

結晶中の分子間相互作用を評価するため、結晶構造における相対位置を基に Ni 錯体及び配位子の二量体の相互作用エネルギーを求めた(Figure 2)。R = Me 錯体と R = Et 錯体を比較すると、MeOH 配位後の構造では、MeOH 分子の Ni への配位結合及び配位子への水素結合、酸素原子の配位子-配位子相互作用のいずれも大きな違いは見られなかった。一方、VOC を含まない結晶においては、R=Et 錯体では隣接錯体間の配位子-配位子間の分子間相互作用が大きく、R=Me 錯体との明確な違いが見られた。このことから、R=Et 錯体では、Ni 原子への配位による構造変化はその相互作用を減少させてしまうため不利になると考えられる。

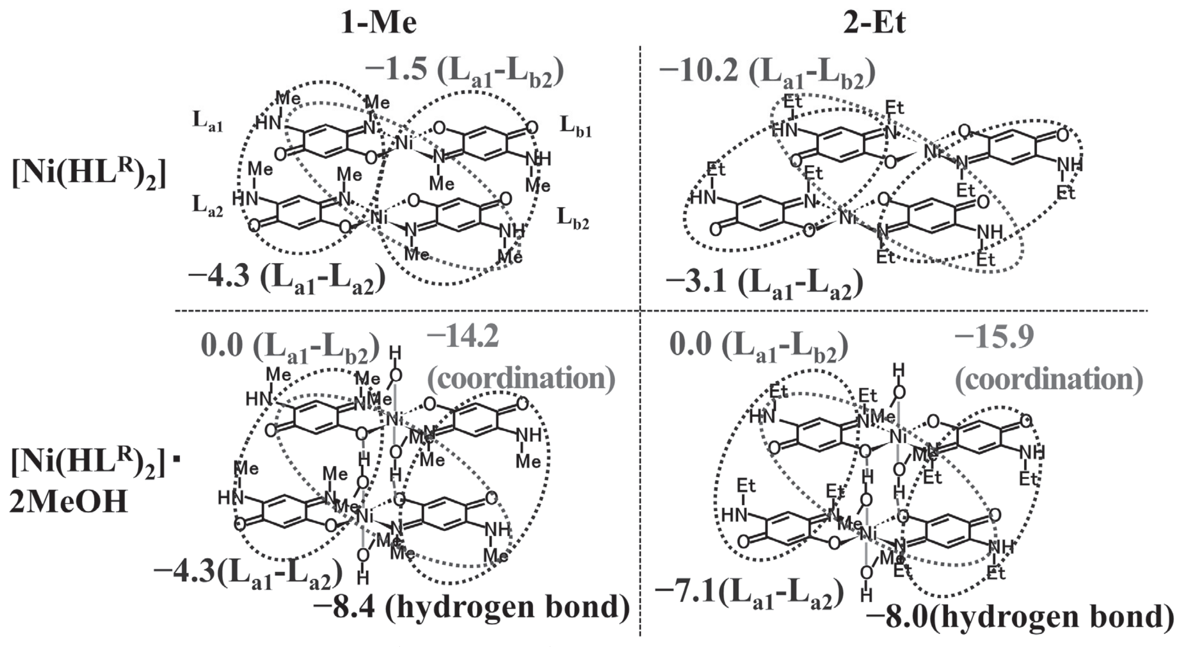
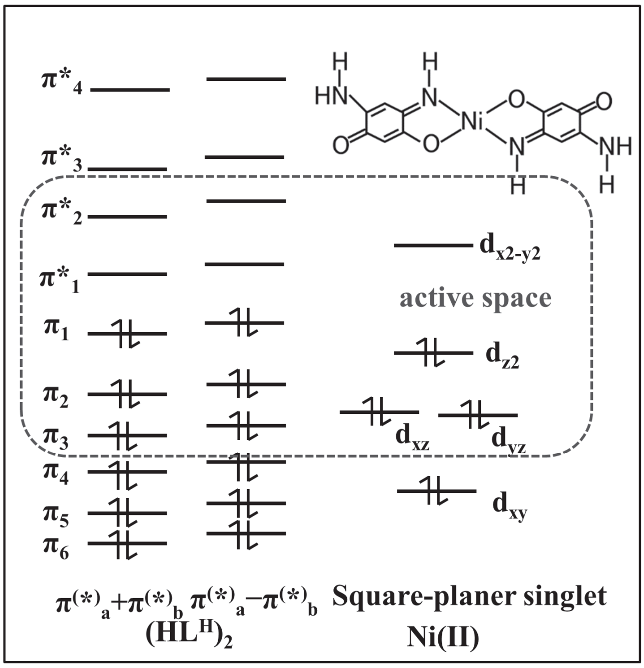


Figure 2. Interaction energy (in kcal/mol) of surrounding complexes calculated by model.

吸収波長に関して結晶中でのスペクトルの測定は行われていないが、平面４配位錯体及び配位子自身のジクロロメタン溶液中での吸収スペクトルが報告されている[2]。DFT 法では用いる汎関数によって結果が大きく異なる。励起エネルギーについては BLYP 等の Pure functional は過小評価する傾向が見られるが、実験値に比較的近い。配位子と Ni 錯体の励起エネルギーの差は Hybrid functional がよい結果を与えた(Table 2)。4配位構造における配位子のπ軌道とNi原子のd軌道の電子配置をScheme 1に示す。計算コストの面から、多配置性により重要であると考えられる赤枠内の18電子14軌道を活性空間に選びCASPT2法を行い、孤立系、溶液中及び結晶中の遷移エネルギーを計算した。CASPT2法は、配位子とNi錯体共に0.15eV以内の誤差で励起エネルギーを再現した。結晶中の励起エネルギーはメタノール配位により2.56 eVから2.66 eVへと短波長側にシフトした。これは結晶の色から予想されるシフトの方向と一致する。結晶効果は4配位錯体(0.02 eV)よりも6配位錯体で大きい(0.11 eV)。6配位錯体では隣接するNi錯体に配位するメタノールが配位子と水素結合するためと考えられる。



Scheme 1　Ni d and ligand π electron configuration at singlet state.

本研究では、Ni-キノノイド錯体のベイポクロミズム反応に関して、QM/MM法を用いた結晶中の構造最適化及び高精度な電子状態計算であるCASPT2法を用いて遷移エネルギーの計算を行った。結晶構造に関しては孤立系では見られないVOCの違いや配位子置換基の違いを明らかにした。遷移エネルギーについては、DFT法では汎関数の依存性が極めて大きいNi錯体の遷移エネルギーに関して、溶液中の実験結果を0.15eV以内の誤差で再現し、結晶中の色調変化に関してもその傾向を再現した。

Table 2. Excitation energies (eV) to the lowest excited state with large oscillator strength[a)] calculated by DFT method with various functionals and CASPT2 method.

	H_2L^{Me}		$[Ni(HL^H)_2]$			$[Ni(HL^H)_2]$・(2MeOH)		
	gas	solution	gas	solution	crystal	gas	solution	crystal
B3LYP	4.037	3.811	2.896	2.802	2.833	3.425	3.350	3.379
BLYP	3.716	3.470	2.017	1.937		2.445	2.383	
LC-BLYP	4.620	4.432	4.159	3.990		4.511	4.325	
M06	4.120	3.908	3.097	3.032		3.674	3.584	
M06L	3.959	3.704	2.191	2.100		2.697	2.651	
CASPT2	3.325	3.637	2.535	2.516	2.556	2.553	2.450	2.662
exp.[2]		3.54		2.38				

a) f > 0.1 for DFT and f > 0.01 for CASPT2

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4. その他

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「結晶中でのニッケル(II)-キノノイド錯体のスピン転移を伴うベイポクロミズムの理論研究」
ソフトクリスタル 第2回公開シンポジウム, 北海道, 2018/5/25-26 ポスター

(2) 中垣雅之，青野信治，吉田将己，小林厚志，加藤昌子，榊茂好
「Theoretical study of vapochromism and spin transition of Nickel(II)-quinonoid complex using hybrid method of QM(CASPT2)/MM and DFT」
福井謙一博士生誕百年記念サテライトシンポジウム, 京都, 2018/10/13 ポスター

(3) 中垣雅之，青野信治，吉田将己，小林厚志，加藤昌子，榊茂好
「ニッケル(II)-キノノイド錯体のスピン転移を伴うベイポクロミズムの理論研究：結晶中の分子選択性」
第16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, 2019/2/8 P10

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1. Summary of the research of the year

Catalytic ability of $Ru_{13}@Pt_{42}$ and Pt_{55} toward oxygen reduction reaction: a DFT study

Proton exchange membrane fuel cells (PEMFCs) are regarded as a leading candidate of clean and sustainable energy source to cope with the growing energy need and environmental concern. Pt-based clusters/particles have attracted immense interest in catalysis for oxygen reduction reaction (ORR, $1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O$) at the cathode in PEMFCs. Pt alloys with core-shell structure (M@Pt) are expected to be useful for the new generation ORR catalyst due to their higher activity and lower cost than pure Pt. In our previous work, the icosahedron-like core-shell structure ($Ru_{13}@Pt_{42}$) exhibited much higher stability than the non-core-shell structures ($Pt^{core-1}Ru_{12}@Pt_{41}Ru^{edge}$ and $Pt^{core-1}Ru_{12}@Pt_{41}Ru^{vertex}$). Furthermore, the potential of $Ru_{13}@Pt_{42}$ as less expensive catalyst for ORR was predicted. However, the current knowledge of catalytic performance of $Ru_{13}@Pt_{42}$ and Pt_{55} for ORR and corresponding reaction mechanism remains rather limited. In this work, the preferential sites on the Pt_{42} surface for interaction with oxygen species (O_2, OH, O, and OOH), as well as geometry and energy change in each important elementary step of ORR catalyzed by $Ru_{13}@Pt_{42}$ and Pt_{55} were studied using first-principle calculations.

All spin-polarized calculations were performed with the Vienna Ab initio Simulation Package (VASP). The PBE-D3 method was employed for geometry optimizations with an energy cutoff of 400 eV. The clusters were placed in a sufficiently large supercell (25 Å × 25 Å × 25 Å) to ensure enough separation by vacuum. The thresholds for energy and force were set to 0.0001 eV and 0.01 eV/Å, respectively. Reaction barrier was calculated using Nudged Elastic Band (NEB) method.

O_2 Adsorption The first important intermediate is η^2-O_2/b1-binding species **2**. The Pt-O bond distances R(Pt-O) are 1.997 Å and 1.969 Å for Pt_{55}-η^2-O_2/b1, which are shorter than those for $Ru_{13}@Pt_{42}$-η^2-O_2/b1 (2.073 Å and 1.977 Å). The O-O bond distances are 1.384 Å and 1.374 Å for Pt_{55}-η^2-O_2/b1 and $Ru_{13}@Pt_{42}$-η^2-O_2/b1, respectively, which are consistent with the moderately shorter R(Pt-O) for Pt_{55}-η^2-O_2/b1 than that for $Ru_{13}@Pt_{42}$-η^2-O_2/b1. The Mulliken charge of O_2 moiety $q(O_2)$ for Pt_{55}-η^2-O_2/b1 is slightly more negative than that of $Ru_{13}@Pt_{42}$-η^2-O_2/b1, indicating that the charge transfer (CT) occurs from the Pt shell to the O_2 moiety for both O_2-binding species and the CT is stronger in Pt_{55}-η^2-O_2/b1 than in $Ru_{13}@Pt_{42}$-η^2-O_2/b1. The calculated *d*-band center for $Ru_{13}@Pt_{42}$ (-2.18 eV) is lower than that for Pt_{55} (-2.02 eV), indicating that $Ru_{13}@Pt_{42}$ has a weaker binding ability for O_2 than Pt_{55}. This result could also verify the stronger interaction of O_2 with Pt_{55} than that with $Ru_{13}@Pt_{42}$.

O-O Bond Activation To date, there are two kinds of widely accepted mechanisms for O-O bond activation in ORR: one is direct O-O bond cleavage after O_2 molecular adsorption; the other is OOH formation followed by O-OH bond cleavage, O_2+H → OOH → OH+O, and this reaction is denoted as O-OH bond cleavage hereinafter. In the direct O-O bond activation, the activation barriers are calculated to be 0.33 eV and 0.49 eV for

Pt_{55} and $Ru_{13}@Pt_{42}$, respectively, in gas phase, as shown in Table 1. In water, the activation barriers decrease to 0.31 eV and 0.35 eV for Pt_{55} and $Ru_{13}@Pt_{42}$, respectively.

In the initial species of OOH formation process, O_2 is adsorbed at the b1 and H is adsorbed at the neighboring b1 site, which is named (O_2)(H)/b1b1 (**3**), because the b1 is the best position for both O_2 for H binding. The final state of OOH formation process is the most favorable OOH/t2 (**4**) species. The activation barriers are calculated to be 0.72 eV and 0.50 eV for Pt_{55} and $Ru_{13}@Pt_{42}$, respectively, in gas phase. These barriers slightly decrease to 0.70 eV and 0.49 eV in water solution for Pt_{55} and $Ru_{13}@Pt_{42}$, respectively. The other possibility is direct H addition to O_2. In this scenario, the proton is likely to attach to O_2, simultaneously with electron transfer to O_2; this is called proton-coupled electron transfer. It should be easy to occur because the proton concentration is very high and the electrode is continuously supplying electrons. Though this proton-coupled electron transfer is likely to occur as important process, this step is difficult to simulate with conventional DFT method. We tried to optimize the OOH species at the b1 site because O_2 is adsorbed at the b1 site in an η^2-form. For the (OOH)/b1 species, the OOH bond cleavage to afford the O and OH at the t2 and t1 sites, respectively, in the case of Pt_{55}. On the other hand, the OOH moves from b1 to t2 site during geometric optimization in the case of $Ru_{13}@Pt_{42}$. We also investigated the O-OH bond cleavage of the (OOH)/t2 species, which is the most stable OOH-binding species on Pt_{55} and $Ru_{13}@Pt_{42}$. This reaction occurs with very small activation barriers of 0.12 eV (0.12 eV) and 0.18 eV (0.17 eV) for Pt_{55} and $Ru_{13}@Pt_{42}$, respectively, in gas phase (water) to afford (O)(OH)/t2t1 species. Thus, it is clearly concluded that the O-OH bond cleavage occurs with nearly no barriers on Pt_{55} and $Ru_{13}@Pt_{42}$ and much easier than the O-O bond cleavage of O_2 species.

For Pt_{55}, the R(Pt-O) slightly increases from 1.940 Å for **4** to 1.958 Å for $\mathbf{TS_{4/5a}}$, and the R(Pt-OH/t1) and R(Pt-O/t2) in **5a** are 1.949 Å and 1.780 Å. For $Ru_{13}@Pt_{42}$, the R(Pt-O) increases from 1.957 Å for **4** (**IS**) to 1.968 Å for $\mathbf{TS_{4/5a}}$. In **5a,** O(OH)/t2t1-binding species (**FS**), the R(Pt-OH/t1) and R(Pt-O/t2) for $Ru_{13}@Pt_{42}$ are 1.986 Å and 1.777 Å, respectively. The charge of OOH moiety [*q*(OOH)] for $Pt_{55}/Ru_{13}@Pt_{42}$ becomes more negative from **4** (-0.286 *e*/-0.329 *e*) to $\mathbf{TS_{4/5a}}$ (-0.313 *e* /-0.376 *e*) and then to **5a** (-0.930 *e* /-0.994 *e*). The CT occurs from the Pt shell to the (OOH) moiety.

Table 1 Activation barriers for ORR mechanisms with $Ru_{13}@Pt_{42}$ and Pt_{55} in gas phase and solution.

	$\mathbf{Pt_{55}}$	$\mathbf{Ru_{13}@Pt_{42}}$	$\mathbf{Pt_{55}}$	$\mathbf{Ru_{13}@Pt_{42}}$
	Gas Phase		**Solution**	
O-O bond cleavage	0.33	0.49	0.31	0.35
OOH^{Pt} formation	0.72	0.50	0.70	0.49
OOH^{O} formation	0.00	0.00	0.00	0.00
O-OH bond cleavage	0.12	0.18	0.12	0.17

(OH)(OH) and (O)(OH_2) Formation Reactions Because (O)(OH)/h1t2 (**5**) is the most stable species, and the best position for H is the bridge b1 site for both Pt_{55} and $Ru_{13}@Pt_{42}$, the (O)(H)(OH) /h1b1t2 species (**6**) was optimized here. Starting from **6**, the H attacks the O atom and OH group to form (OH)(OH)/h1t2 (**7a**) and (O)(OH_2)/h1t2 (**7b**) species. The species **7b** was calculated to be slightly more stable than **7a**. However, the energy difference between them is small (7.24 kcal/mol and 5.74 kcal/mol for Pt_{55} and $Ru_{13}@Pt_{42}$, respectively), indicating that both of them should be considered as possible product of this step. The barriers for (OH)(OH) formation from **6** to **7a** are 1.38 eV and 0.86 eV in water for Pt_{55} and $Ru_{13}@Pt_{42}$, respectively. On the other hand, the barriers for $O(OH_2)$ formation from **6** to **7b** species 0.86 eV and 0.88 eV in water for Pt_{55} and $Ru_{13}@Pt_{42}$, respectively.

$(OH)(OH_2)$ Formation Reaction Because the H tends to bind with Pt_{55} at the b1 site, the (H)(OH)(OH)/b1t2t2 species (**8**) was optimized as the starting intermediate for $(OH)(OH_2)$ formation. The product of this step is $(OH)(OH_2)$/t2t2 species (**9**). The activation barrier is 1.09 eV and of 0.76 eV in gas phase for Pt_{55} and $Ru_{13}@Pt_{42}$, respectively, where the activation barrier is different litter in water, 1.10 eV and 0.76 eV for Pt_{55} and $Ru_{13}@Pt_{42}$, respectively. These results indicate that the $(OH)(OH_2)$ formation can occur much easier in $Ru_{13}@Pt_{42}$ than in Pt_{55}.

OH Formation from the O Species Different from the reaction for Pt_{55}, the $O(OH_2)$ formation is possible for $Ru_{13}@Pt_{42}$. The next step is the reaction of OH group with H atom in $Ru_{13}@Pt_{42}$. The reaction starts from the (O)(H)/h1b1 to form (OH)/h1. The activate barrier is calculated to be 1.16 eV in gas phase. This barrier is much larger than that of the $(OH)(OH_2)$ formation (0.76 eV, as discussed above). Thus, the $(O)(OH_2)$ formation should be excluded from the catalytic cycle; and this process will be not discussed further.

H_2O Formation from the OH Species After H_2O dissociates from the $(OH)(OH_2)$ species, (OH)/t2 intermediate (**10**) could form. From this species, one H_2O molecule is generated to complete the whole catalytic cycle. This reaction occurs from the (H)(OH)/b1t2 species (**11**) to form (OH_2)/t2 (**12**). The activation barriers are calculated to be 0.90 (0.91) eV and 0.90 (0.89) eV for the reaction catalyzed by Pt_{55} and $Ru_{13}@Pt_{42}$ in gas (water) phase. The R(H-OH) are 2.749 Å (2.665 Å), 1.574 Å (1.589 Å), and 0.977 Å (0.972 Å) for **11**, $TS_{11/12}$, and **12** in the case of Pt_{55} ($Ru_{13}@Pt_{42}$), respectively. For Pt_{55}/ $Ru_{13}@Pt_{42}$ the q(H) becomes more positive from **11** (0.043/0.004 e) to $TS_{11/12}$ (0.248/0.238 e), and then to **12** (0.722/0.760 e). The q(O) becomes more negative from **11** (-1.055/-0.977 e) to $TS_{11/12}$ (-1.002/-0.925 e), and then to **12** (-1.258/-1.659 e). The Bader charges of H_2O moiety $q(H_2O)$ in **12** are 0.147 e and 0.101 e for Pt_{55} and $Ru_{13}@Pt_{42}$, respectively. Also, the Mulliken charges of H_2O moiety in **12** are 0.281 e and 0.232 e for Pt_{55} and $Ru_{13}@Pt_{42}$ using B3LYP functional, respectively. In the other word, the $q(H_2O)$ in $Ru_{13}@Pt_{42}$ is less positive than that in Pt_{55}, indicating that the H_2O is easier to desorb in the former case.

This work has demonstrated the favorable reaction cycle mechanism catalyzed by $Ru_{13}@Pt_{42}$, which is similar to that by pure Pt_{55}, revealing the potential of $Ru_{13}@Pt_{42}$ as promising ORR catalyst with lower cost.

2. Original papers

(1) Jing LU, Kazuya ISHIMURA, and Shigeyoshi SAKAKI,
“Theoretical Insight into Core–Shell Preference for Bimetallic Pt-M (M = Ru, Rh, Os, and Ir) Cluster and Its Electronic Structure.”
J. Phys. Chem. C 122 (16), 9081-9090 (2018).

3. Presentation at academic conferences

(1) Jing LU, Kazuya ISHIMURA, and Shigeyoshi SAKAKI,
"Capability of Pt55 and Ru13@Pt42 Catalysts toward the Oxygen Reduction Reaction: A First-Principle Study"
第21回理论化学研讨会，岡崎，2018年5月15日-17日

Rong-Lin Zhong

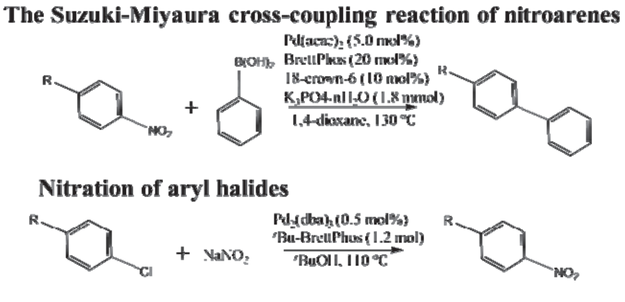
Research Fellow

1. Summary of the research of the year

How to Perform Suzuki-Miyaura Reaction of Nitroarene or Nitration of Bromoarene Using Pd^0(Phosphine) Complex: Theoretical Insight and Prediction

The Pd-catalyzed Suzuki-Miyaura reaction is one of the most efficient and versatile methods for constructing carbon-carbon bond. Aryl halides are employed as electrophilic coupling reagent in this reaction. To broaden its application scope, a lot of efforts have been made to use alternative compounds such as aryl ethers, aryl esters, and arenols. However, the use of nitroarenes has not been succeeded for a long time despite of weak Ar-NO_2 (Ar = aryl) bond. Notably, the Suzuki-Miyaura reaction of nitroarenes was very recently succeeded by us using Pd^0(BrettPhos) as a catalyst, as shown in Scheme 1. Usual monodentate phosphine could not be used in this reaction. On the other hand, Fors and Buchwald succeeded Pd-catalyzed nitration of aryl halides using a similar Pd^0(^{t}Bu-BrettPhos) as a catalyst. In this reaction, the last step should be reductive elimination of nitroarene from Pd^{II}(Ar)(NO_2)(^{t}Bu-BrettPhos). This is reverse to the oxidative addition of Ar-NO_2 which is the first step of the Suzuki-Miyaura reaction. Considering these two reports by Buchwald group and us, we address following points; (1) why the Ar-NO_2 bond cleavage is more difficult than the Ar-Br bond cleavage, (2) why usual monodentate phosphine could not be used for the Suzuki-Miyaura reaction of nitroarenes but BrettPhos could be, (3) why BrettPhos was used for the Suzuki-Miyaura reaction of nitroarenes but the similar ^{t}Bu-BrettPhos was used for the nitration of aryl halides despite of tiny difference between these two phosphines, and (4) how we can control the Ar-NO_2 bond cleavage and Ar-NO_2 bond formation by using Pd^0(BrettPhos) and analogues.

Scheme 1. The Suzuki-Miyaura reaction of nitroarenes and nitration of aryl halides.



In this work, we theoretically investigated the oxidative addition of nitrobenzene to Pd^0(BrettPhos) to elucidate characteristic features of the oxidative addition of nitroarenes and to provide clear answers to the above-mentioned questions. Also, we wish to propose theoretical prediction what ligand is more effective for oxidative addition and reductive elimination of nitroarene. Because the transformation of nitroarenes has been limited so far, such knowledge provides us with new idea how to utilize nitroarenes and how to synthesize them.

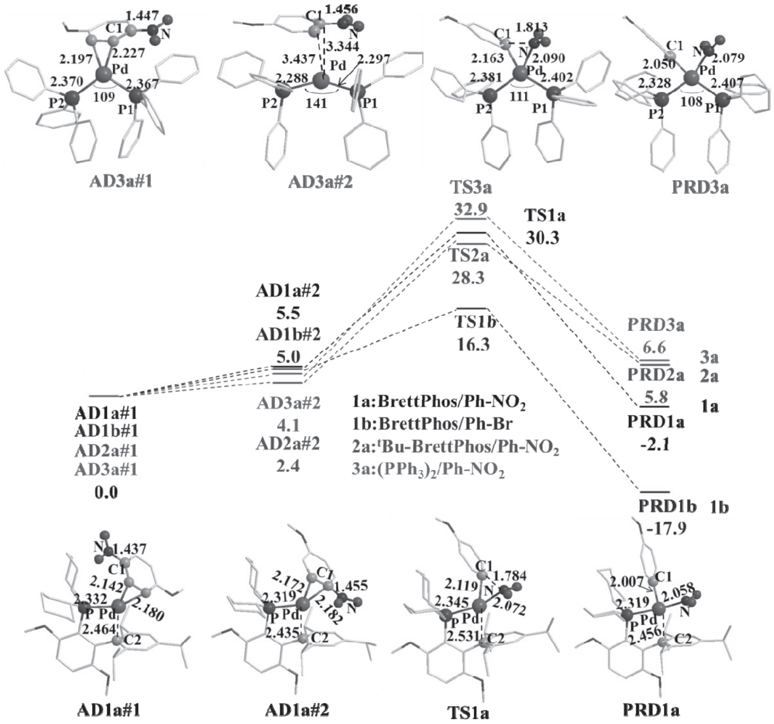


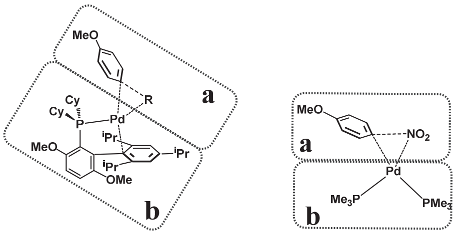
Figure 1. Optimized geometries in oxidative addition of 4-nitroanisole to Pd^0(BrettPhos) complex.

Results and Discussion

Oxidative Addition of 4-nitroanisole (Rea) and its Bromo derivative to Pd^0(BrettPhos) and $Pd^0(PMe_3)_2$. The geometry and energy change of oxidative addition of **Rea** to Pd^0(BrettPhos) **1** is shown in Figure 1. **Rea** approaches **1** to form stable η^2-coordinated adducts, **AD1a#1** and **AD1a#2**, in which the C^2-C^3 and C^1-C^2 bonds coordinate with the Pd, respectively. The oxidative addition occurs through a three-membered transition state **TS1a** to afford a palladium(II) complex $Pd^{II}(NO_2)(C_6H_4\text{-}OMe^p)$(Brettphos) (**PRD1a**). The Gibbs activation energy ($\Delta G^{o\ddagger}$) is 30.3 kcal mol^{-1} and the Gibbs reaction energy ($\Delta G^o_{(R)}$) is -2.1 kcal mol^{-1} relative to the most stable reactant adduct **AD1a#1**. This oxidative addition needs rather large activation energy but it is exergonic.

Oxidative addition of 4-bromoanisole (**Reb**) to **1** occurs through similar η^2-coordinated adducts and transition state to afford a palladium(II) complex $Pd^{II}(Br)(C_6H_4OMe^p)$(Brettphos). The $\Delta G^{o\ddagger}$ (16.3 kcal mol^{-1}) is much smaller and the $\Delta G^o_{(R)}$ (-15.0 kcal mol^{-1}) is much more negative than those of the oxidative addition of **Rea**. Therefore, the oxidative addition of nitroarene is much more difficult than that of bromoarene kinetically and thermodynamically. To investigate the difference in $\Delta G^{o\ddagger}$ between these two oxidative additions, we separated the reaction system into Pd^0(BrettPhos) and substrate moieties, as shown in Scheme 3, and made deformation/interaction energy analysis. As shown in Table 1, the potential energy barrier (E_a) is much larger for **TS1a** than for **TS1b**, indicating that the analysis of E_a provides the reason why the oxidative addition of **Rea** is more difficult than that of **Reb**. In **TS1a**, the deformation energy (E_{Def} = 33.2 kcal mol^{-1}) of **Rea** is much larger than that (6.2 kcal mol^{-1}) of **Reb** in **TS1b**. Interaction energy E_{Int} is defined as a stabilization energy provided by the interaction between reagent (**Rea** or **Reb**) and Pd^0 complex, where both have deformed geometries like in TS. The E_{Int} (-42.1 kcal mol^{-1}) between **Rea** and Pd^0(BrettPhos) in **TS1a** is much larger than that (-24.6 kcal mol^{-1}) in **TS1b** by 17.5 kcal mol^{-1}, where a negative value means the stabilization energy. However, this large E_{Int} of **TS1a** cannot overcome the overly large E_{Def} of **Rea** at **TS1a**. As a result, **TS1a** becomes higher in energy than **TS1b**. These results lead to a conclusion that the large E_{Def} of **Rea** is the origin of larger E_{a} and larger $\Delta G^{\circ\ddagger}$ for Ar-NO_2 bond cleavage than those for Ar-Br bond cleavage. In **TS1a**, the NO_2 group changes its direction toward the Pd because the sp^2 orbital of NO_2 must change its direction to form a bonding interaction with the Pd, which gives rise to the large E_{Def} value of **Rea**. On the other hand, Br has a spherical valence orbital which can start to form the bonding interaction with the Pd, keeping the Ar-Br bonding interaction. Therefore, **Reb** can reach **TS1b** without significant distortion. This is the reason why bromoarene is more reactive for the oxidative addition than nitroarene.

Scheme 3. Definition of fragments a and b in TS1a (R=NO_2), TS1b (R=Br), and TS3a.



TS1a/TS1b　　**TS3a**

Table 1. Activation barrier (E_{a}), deformation energy (E_{Def}) of each moiety and interaction energy (E_{int}) between them in transition state (in kcal mol^{-1}).

	TS1a	**TS1b**	**TS2a**	**TS3a**
ΔE	-4.2	-14.1	-2.4	15.9
E_{a}	31.3	16.9	30.1	30.2
$E_{\mathrm{Def\text{-}a}}$	33.2	6.2	33.0	35.5
$E_{\mathrm{Def\text{-}b}}$	4.7	4.3	5.4	19.9

Oxidative addition of **Rea** to $Pd^0(PMe_3)_2$ **3** was investigated for making comparison between BrettPhos and usual monodentate phosphine PMe_3. This reaction occurs with $\Delta G^{\circ\ddagger}$ of 29.1 kcal mol^{-1}. Though this value does not differ very much from that of the reaction with **1**, its transition state **TS3a** is at much higher energy than the sum of reactants, **3** + **Rea**, indicating that **Rea** more easily dissociates from **3** than it completes the oxidative addition via **TS3a**. Thus, it is concluded that the oxidative addition of **Rea** to **3** does not occur.

The deformation/interaction energy analysis clearly shows that the higher energy transition state **TS3a** arises from the larger E_{Def} value (19.0 kcal mol^{-1}) of $Pd^0(PMe_3)_2$ in **TS3a** (Table 1). The large $E_{\mathrm{Def\text{-}a}}$ value arises from significantly small P-Pd-P angle in **TS3a** (Figure 1). It is of importance to elucidate the reason why such large distortion is needed in **TS3a**. In the oxidative addition, CT from metal moiety to substrate is important. In **TS1a**, charge-transfer (CT) occurs from the HOMO of Pd ($\phi_{\text{Pd-HOMO}}$) to the LUMO and LUMO+1 of **Rea**, as shown in Figure 2. The $\phi_{\text{Pd-HOMO}}$ at high energy can form large CT. As shown in Figure 3(a), the $\phi_{\text{Pd-HOMO}}$ of $Pd^0(PMe_3)_2$ in equilibrium geometry is calculated at much lower energy (-7.81 eV) than that (-5.82 eV) of Pd^0(BrettPhos). To raise the $\phi_{\text{Pd-HOMO}}$ energy, $Pd^0(PMe_3)_2$ must be distorted by decreasing the P-Pd-P angle; as shown in Figure 3(a), the $\phi_{\text{Pd-HOMO}}$ energy certainly becomes higher (-5.73 eV) in the distorted geometry of **TS3a**.

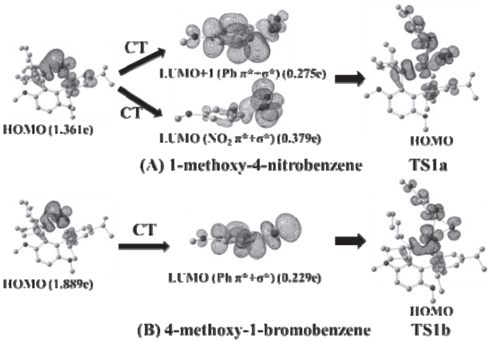


Figure 2. Orbital interactions in the transition state of the oxidative addition of 4-nitroanisole (a) and 4-bromoanisole (b) to Pd^0(BrettPhos).

On the other hand, Pd^0(BrettPhos) is distorted little at **TS1a**. The reason can be easily found by seeing Figure 3(b). In the case of BrettPhos, the lone pair orbital on the P atom and the π orbital on the phenyl group overlap with the Pd d_π orbital in an antibonding way to afford the $\phi_{\text{Pd-HOMO}}$ of **1**. As a result, the $\phi_{\text{Pd-HOMO}}$ orbital energy is -5.82 eV in Pd^0(BrettPhos) even with equilibrium geometry. It indicates that the 2,4,6-tris-isopropylphenyl group plays crucially important role to raise the d_π orbital energy like usual chelating diphosphine. It is concluded that the oxidative addition of $Ar\text{-}NO_2$ to $Pd^0(PR_3)_2$ is difficult because the transition state suffers from two large deformation energies of $Ar\text{-}NO_2$ and $Pd^0(PR_3)_2$ moieties. On the other hand, Pd^0(Brettphos) is reactive for the oxidative addition of $Ar\text{-}NO_2$ because the d_π orbital is at high energy even without distortion of Pd^0(Brettphos) and the transition state suffers from only one deformation energy of the $Ar\text{-}NO_2$ moiety. This means that the presence of 2,4,6-tris-isopropylphenyl group is crucially important in BrettPhos because its π orbital interacts with the Pd d_π orbital to raise the $\phi_{\text{Pd-HOMO}}$ energy (Figure 3b). It is a strong point of BrettPhos-type ligand for the oxidative addition that both of phosphine lone pair and π orbital of 2,4,6-tris-isopropylpheny participate in raising the $\phi_{\text{Pd-HOMO}}$ energy.

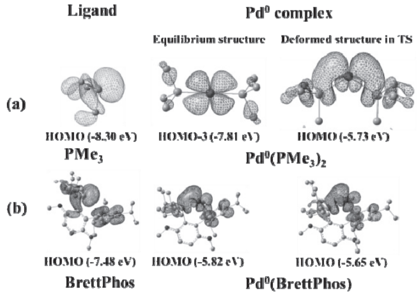


Figure 3. HOMOs of PPh_3, BrettPhos, and their Pd^0 complexes with deformed structure in TS.

Effects of Various BrettPhos Derivatives on the Reactivity of Pd^0 Complexes. Because Pd^0(BrettPhos) and Pd^0(^{t}Bu-BrettPhos) can be applied to the oxidative addition of nitroarene and reductive elimination of nitroarene, respectively, we investigated various BrettPhos derivatives in the oxidative addition of **Rea**, as shown in Scheme 2. Among them, Pd^0(BrettPhos-NMe$_2$) is the best for the oxidative addition because the $\Delta G^{o}_{(R)}$ is the most negative, the $\Delta G^{o\ddagger}$ value is the smallest, and the $\Delta G^{o}_{(D)}$ is larger than $\Delta G^{o\ddagger}$, as shown in Table 1. These features arise from the high energy HOMO ($\phi_{Pd\text{-}HOMO}$) of Pd^0(BrettPhos-NMe$_2$) to which the high energy HOMO ($\phi_{L\text{-}HOMO}$) of BrettPhos-NMe$_2$ contributes (Table 1). The next is Pd^0(BrettPhos), because the $\Delta G^{o}_{(R)}$ is negative and the $\Delta G^{o\ddagger}$ does not differ very much from the $\Delta G^{o}_{(D)}$ (the difference is 2.4 kcal mol^{-1}) despite of the slightly larger $\Delta G^{o\ddagger}$ value than those of some other BrettPhos derivatives. In the oxidative addition to Pd^0(Me-BrettPhos) and Pd^0(XPhos), the $\Delta G^{o}_{(R)}$ is negative and the $\Delta G^{o\ddagger}$ value is moderately smaller than that of Pd^0(BrettPhos) but the $\Delta G^{o\ddagger}$ is somewhat larger than the $\Delta G^{o}_{(D)}$ by 4.5 and 4.0 kcal mol^{-1}, respectively. These two complexes could be applied to the oxidative addition of nitroarene but they are not useful very much because the nitroarene dissociation from the Pd occurs much more easily. Actually, the experimental results showed that the Suzuki-Miyaura reaction of **Rea** was succeeded with Pd^0(XPhos) but the yield was much lower than that by Pd^0(BrettPhos). In Pd^0(CF$_3$-BrettPhos) and Pd^0(C$_6$F$_5$-BrettPhos), the $\Delta G^{o}_{(R)}$ is considerably positive and the $\Delta G^{o\ddagger}$ is considerably larger than the $\Delta G^{o}_{(D)}$ by 10.8 and 9.1 kcal mol^{-1}, respectively, indicating that these two complexes are not good for oxidative addition. Their low reactivity arises from the presence of $\phi_{Pd\text{-}HOMO}$ at lower energy than that of Pd^0(BrettPhos).

2. Original papers

(1) **Rong-Lin Zhong**, Masahiro Nagaoka,Yoshiaki Nakao, and Shigeyoshi Sakaki, How To Perform Suzuki−Miyaura Reactions of Nitroarene or Nitrations of Bromoarene Using a Pd0 Phosphine Complex: Theoretical Insight and Prediction *Organometallics*, 2018, *37*, 3480-3487.

3. Presentation at academic conferences

(1) **Rong-Lin Zhong**, and Shigeyoshi Sakaki, “Regioselectivity of SP^3 C-H activation of N-hetrocycles by iridium(III) boryl complexes”, 21th Annual Meeting of Theoretical Chemistry Society, Okazaki, May 15-17, 2018.

(2) **Rong-Lin Zhong**, Yoshiaki Nakao, and Shigeyoshi Sakaki “”, “Regioselective sp3C−H borylation of cyclic ethers catalyzed by iridium(III) boryl complex: Theoretical Study”,12th Annual Meeting of Japan Society for Molecular Science, Fukuoka, Sep.9-13, 2018.

Jia-Jia Zheng

SPR Fellow

1. Summary of the research of the year

(a) Oxidative Addition of Nitroarene to Pd(0)-NHC Complex

The Pd-catalyzed Suzuki-Miyaura coupling (SMC) reaction is an important process to create carbon-carbon bonds in organic synthesis. The use of nitroarenes, which are versatile and common aromatic building blocks, is very limited in the SMC reaction and has succeeded recently, using a special Pd-BrettPhos complex (Figure 1a). It is interesting to explore useful ligand to extend the scope of this reaction. Herein, we theoretically investigated the Pd-catalyzed C-N bond cleavage of nitroarene, which is the rate-determining step for the full catalytic cycle (Figure 1a), using a kind of good electro-donating ligand, namely, N-heterocyclic carbene (NHC). Results show that the Pd-NHC1 complex can indeed cleave the C-N bond of nitroarene with moderate barrier (26.1 kcal mol^{-1}) and negative reaction energy (–4.1 kcal mol-1). Further investigations on the influence of substituent (R) of N and NHC skeleton (S) (Figure 1b) on the reaction process suggest that the NHC ligands with less bulky electro-denoting R group (NHC3) and saturated skeleton S (NHC7) are good candidates to moderately lower the reaction barrier and increase the reaction energy.

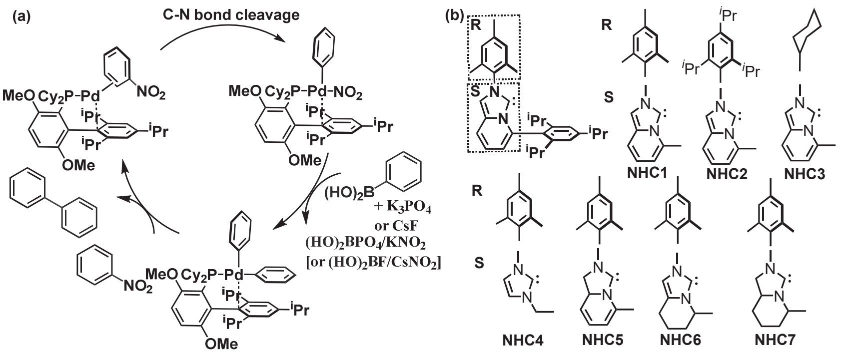
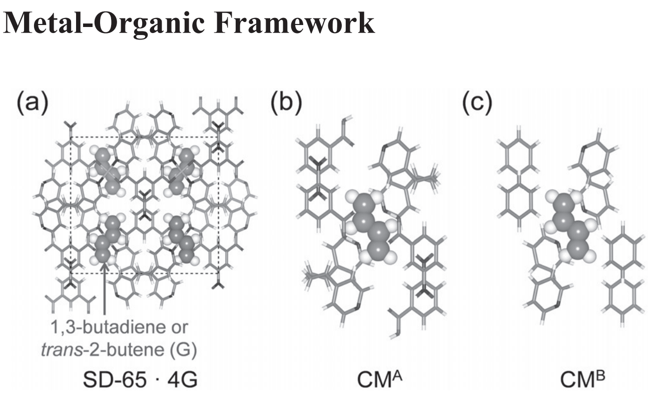


Figure 1. (a) Full catalytic cycle of SMC reaction of nitroarenes. (b) N-heterocyclic carbene ligands investigated in this work.

(b) C4-Hydrocarbon Separation by a Soft Metal-Organic Framework

Gas separation by soft metal-organic frameworks (MOFs), which undergo structural transformations in response to external stimuli such as gas adsroption, has attracted great attention in recent years. Soft Zn(II)-based MOF, [Zn(NO$_2$ip)(dpe)]$_n$, (SD-65, NO$_2$ip = 5-nitroisophalate, dpe = 1,2-di(4-pyridyl)ethylene), was synthesized and demonstrated to selectively adsorb 1,3-butadiene over *trans*-2-butene.



SD-65 · 4G　CM^A　CM^B

Figure 1. Optimized gas (G) adsorption structures and cluster models used in post-HF calculations.

Theoretical study on gas adsorption in this MOF is important to understand the selectivity of one gas molecule to other similar ones. Also, it is challenging to estimate accurately the interaction energy between gas molecule and MOF, because the post-HF calculation must be employed to incorporate dispersion interaction but its application to MOF is difficult. In this work, we theoretically investigated 1,3-butadiene and *trans*-2-butene adsorptions in this soft MOF using ONIOM-type method combining periodic DFT (PBE-D3) for infinite system and MP2.5 and CCSD(T) for cluster models to disclose the reasons for the difference in adsorption between 1,3-butadiene and *trans*-2-butene.

Four symmetrical adsorption positions were found for both 1,3-butadiene and *trans*-2-butene (Figure 1) in SD-65. The PBE-D3 method overestimates the 1,3-butadiene adsorption enthalpy but the CCSD(T):MP2.5:PBE-D3-calculated value (–10.91 kcal mol^{-1}) agrees well with the experimental one (–9.56 kcal mol^{-1}). These results suggest that CCSD(T) and MP2.5 corrections are of considerabe importance to investigate correctly the adsorption behaviour. The calculated binding energies (BEs) for 1,3-butadiene and *trans*-2-butene are –12.10 and –11.55 kcal mol^{-1}, respectively, suggesting that SD-65 has a higher affinity to 1,3-butadiene than to *trans*-2-butene. The smaller BE of *trans*-2-butene arises mainly from the larger deformation energy of framework, because of the larger molecular size of *trans*-2-butene and thus a larger structural transformation of SD-65 upon adsorption of *trans*-2-butene than that of 1,3-butadiene. The sigmoidal adsorption isotherm was well reproduced by the Langmuir-Freundlich model using the calculated adsorption Gibbs energy changes ($\Delta G°$). The performance of this MOF for separation of 1,3-butadiene from *trans*-2-butene was discussed in relation to the difference between their adsorption Gibbs energy changes ($\Delta\Delta G°$). Two MOFs showing better separation performance (with larger $\Delta\Delta G°$ between 1,3-butadiene and *trans*-2-butene adsorptions) than SD-65 are computationally predicted in this work.

2. Original papers

(1) Jia-Jia Zheng, Shinpei Kusaka, S. Ryotaro Matsuda, Susumu Kitagawa, Shigeyoshi Sakaki,
“Theoretical insight into gate-opening adsorption mechanism and sigmoidal adsorption isotherm into porous coordination polymer”
J. Am. Chem. Soc. 140, 13958-13969 (2018).

(2) Haijun Wang, Haifei Cao, Jia-jia Zheng, Simon Mathew, Nobuhiko Hosono, Bihang Zhou, Hongliang Lyu, Shinpei Kusaka, Wanqin Jin, Susumu Kitagawa, Jingui Duan,
“Finely Controlled Stepwise Engineering of Pore Environments and Mechanistic Elucidation of Water-Stable, Flexible 2D Porous Coordination Polymers”
Chem. Eur. J. 24, 6412-6417 (2018).

(3) Qiao-Zhi Li, Jia-Jia Zheng, Ling He, Shigeru Nagase, Xiang Zhao,
“La–La bonded dimetallofullerenes $[La_2@C_{2n}]^-$: species for stabilizing C_{2n} (2n = 92–96) besides $La_2C_2@C_{2n}$”
Phys. Chem. Chem. Phys. 20, 14671-14678 (2018).

(4) Cheng Gu, Nobuhiko Hosono, Jia-Jia Zheng, Yohei Sato, Shinpei Kusaka, Shigeyoshi Sakaki, Susumu Kitagawa,

"Design and control of gas diffusion process in a nanoporous soft crystal"
Science 363, 387-391 (2019).

3. Presentation at academic conferences

(1) Jia-Jia Zheng, Shinpei Kusaka, S. Ryotaro Matsuda, Susumu Kitagawa, Shigeyoshi Sakaki,
"Separation of 1,3-Butadiene and trans-2-Butene by a Soft Metal-Organic Framework: A Three-Layer ONIOM-type Computational Investigation"
The 21th Symposium for Theoretical Chemistry, Okazaki, May 15-17, 2018

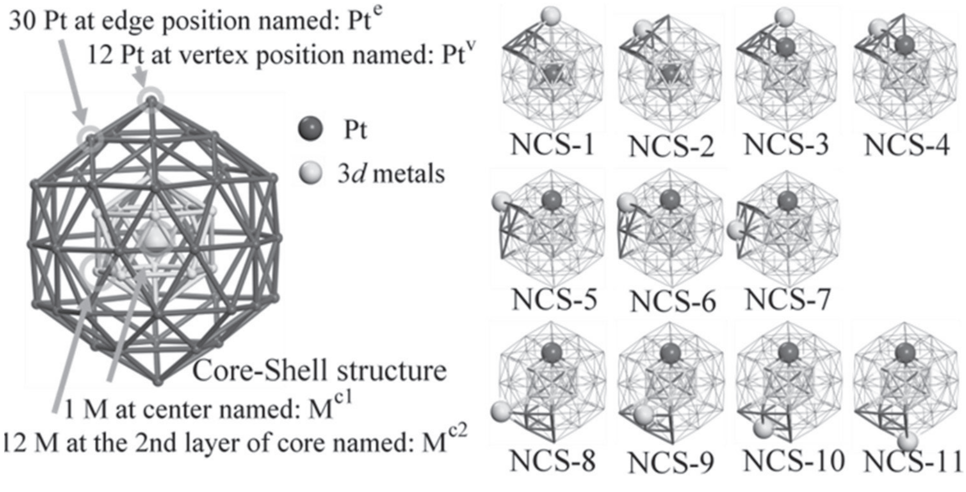
LI Wenliang

Research Fellow

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

Theoretical Insight into $M_{13}@Pt_{42}$($M=3d$ Transition Metals) Core-Shell Clusters

For Pt clusters to be effective oxygen reduction reaction (ORR) catalysts, an approach involving core-shell (CS) clusters with Pt shell is beneficial in stabilizing Pt and reducing costs while maintaining high catalytic activity. The icosahedron (Ih) $M_{13}@Pt_{42}$ ($M=3d$ transition metals) clusters are systematically investigated respecting their stability, electronic properties, ORR catalytic activity with the aid of the DFT-D3 method. The CS $Cu_{13}@Pt_{42}$, $Co_{13}@Pt_{42}$, and $Ni_{13}@Pt_{42}$ clusters are found to be stable with positive segregation energy (E_{seg}), which is defined as the energy difference between CS clusters and the corresponding non-core-shell (NCS) clusters with a 3*d* metal atom in the core exchanged by Pt atom in the shell in the present work. While for other 3*d* metals cases, a negative E_{seg} is observed indicating the CS cluster is less stable than the NCS cluster. Several factors including core/shell deformation energy, the interaction energy between core and shell, and cohesive energy are considered to find the important one for stabilizing the CS cluster. The electronic structure of CS clusters in comparison with Pt_{55} was systematically investigated to provide theoretical insight into the CS clusters. Moreover, O_2 adsorption to the stable CS $M_{13}@Pt_{42}$ (M=Co, Ni, and Cu) and Pt_{55} clusters shows the tunable catalytic activity for ORR, making the CS $M_{13}@Pt_{42}$ (M=Co, Ni, and Cu) promising candidates as catalysis for ORR.



Scheme 1. Icosahedral $M_{13}@Pt_{42}$ clusters with core-shell (CS) structures and 11 non-core-shell (NCS) structures investigated in this work.

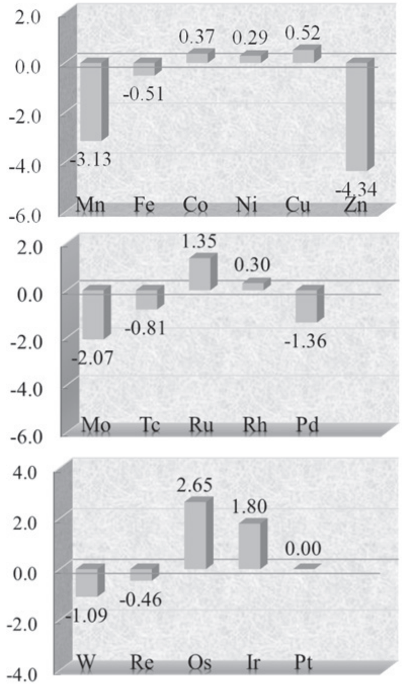


Figure 1. Comparison of the segregation energy of $M_{13}@Pt_{42}$ (M=3*d* metals) clusters with that of $M_{13}@Pt_{42}$ (M=4*d* and 5*d* metals) clusters.

The comparison of the segregation energy of $M_{13}@Pt_{42}$ (M=3*d* metals) clusters with that of $M_{13}@Pt_{42}$ (M=4*d* and 5*d* metals) clusters is demonstrated in Figure 1. The NCS structures for the cases of Mn, Fe, and Zn show -3.13. -0.51, and -0.80 eV more stable than the corresponding CS structure, while the core-shell structures of Co, Ni, and Cu cases are more stable than all the segregated ones. The similar arch can be easily found for all 3*d*, 4*d* and 5*d* metals. In details, three stable CS clusters for 3*d* metal ($Cu_{13}@Pt_{42}$, $Co_{13}@Pt_{42}$, and $Ni_{13}@Pt_{42}$) can be found with E_{seg} from 0.29 to 0.52 eV. And two stable CS clusters for 4*d* and 5*d* metals ($Ru_{13}@Pt_{42}$, $Rh_{13}@Pt_{42}$, $Os_{13}@Pt_{42}$ and $Ir_{13}@Pt_{42}$) can be found with E_{seg} from 0.29 to 0.52 eV and from 1.80 to 2.65 eV, respectively.

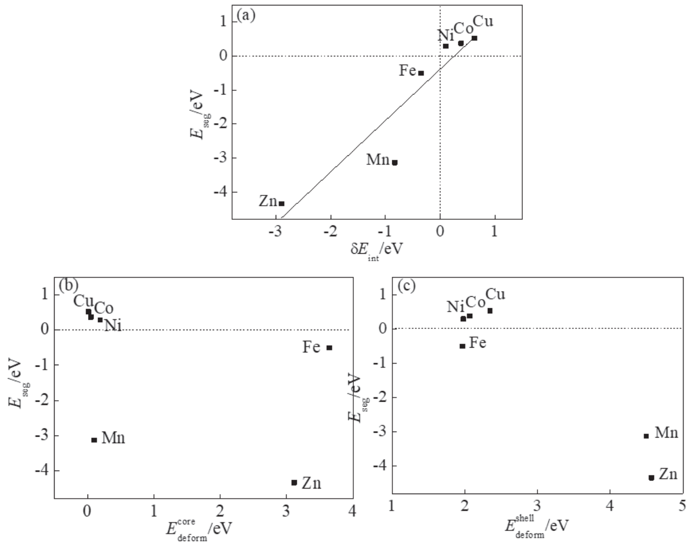


Figure 2. The relationship of segregation energy with (a) difference in interaction energy (δE_{int}), (b) core deformation energy ($E^{\text{core}}_{\text{deform}}$), and (c) shell deformation energy ($E^{\text{shell}}_{\text{deform}}$).

Figure 2 is drawn to clearly show the relationship of segregation energy with difference in interaction energy ($\delta E_{\mathrm{int}} = E_{\mathrm{int}}^{\mathrm{NCS}} - E_{\mathrm{int}}^{\mathrm{CS}}$), core deformation energy ($E_{\mathrm{deform}}^{\mathrm{core}}$), and shell deformation energy ($E_{\mathrm{deform}}^{\mathrm{shell}}$). Good linear correlation between E_{seg} and δE_{int} can be observed from Figure 4a, indicating the δE_{int} may be a key factor in determining a stable CS cluster. Although no linear correlation between E_{seg} and $E_{\mathrm{deform}}^{\mathrm{core}}$ or $E_{\mathrm{deform}}^{\mathrm{shell}}$ can be observed, the large E_{deform} for Fe and Zn core, as well as Mn and Zn shell, can be found to make the CS cluster unstable.

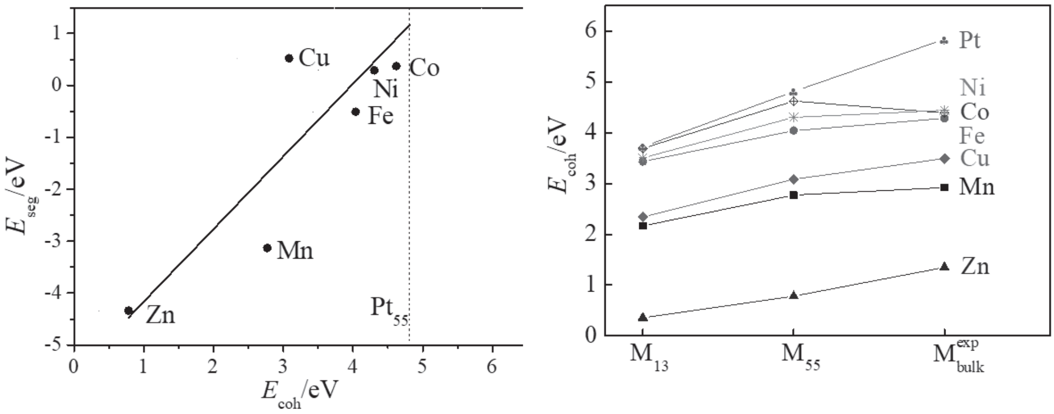


Figure 3. Segregation energy vs cohesive energy of cluster M_{55} with Pt_{55} shown as dash line, and the comparison of cohesive energy for M_{13}, M_{55} and experimental data for metal crystal.

Cohesive energy, E_{coh}, maybe another key factor for the stability of the bimetallic CS cluster, because metals with large E_{coh} tend to be bound together with as many as possible to form a core moiety as found in CS M_{13}@Pt_{42} clusters (M=4*d* or 5*d* transition metals)[10]. However, the situation changes for 3*d* metals cases as displayed in Figure 3a. For all 3*d* transition metals, the M_{55} clusters show smaller E_{coh} than Pt_{55}, including the stable CS clusters, M_{13}@Pt_{42}, (M=Cu, Ni, and Cu), indicating the E_{coh} is not the determining factor for the stable CS cluster, at, least, for 3*d* metal cases. By comparing the E_{coh} for M_{13} and M_{55} with the experimental data for metal crystal in Figure 3b, one can confirm the accuracy of the E_{coh} calculation. Also, the E_{coh} increases as cluster size increases from M_{13} to M_{55}, and then to the experimental values of bulk metal, except the Co case.

Li Qiaozhi

Research Fellow

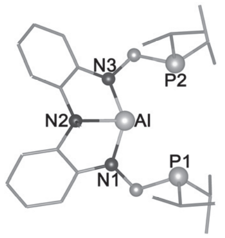
1. Summary of the research of the year

Reactivity of New Unique Rh(PXP) Complexes (X = B, Al, Ga): Theoretical Insight

Recently synthesized rhodium complex Rh(PAlP) (PAlP = pincer-type diphosphino-aluminyl ligand) has a unique Rh-Al direct bond. This complex has been reported to cleave the *sp*^{2} C-H σ-bond of pyridine. We theoretically investigated the reactivity of Rh(PAlP) and its two analogues, Rh(PBP) and Rh(PGaP), to elucidate the origin of its interesting new reactivity using DFT and CCSD(T). We found that the C-F bond of fluorobenzene (PhF) is cleaved by Rh(PXP) in σ-bond metathesis manner and X (X = B, Al, Ga) center participates well in the activation process. For this reaction, Rh(PAlP) is better than the B and Ga analogues in both kinetically and thermodynamically.

Transition metal complexes of phosphine-based pincer ligands have attracted recent attentions because of their successful applications to various organometallic and catalytic reactions. Recently, rhodium complex Rh(PAlP) (PAlP = $\{Al[N(C_6H_4)]_2NMe\}[PCH_2({}^iPr)_2]_2$; Scheme 1) bearing X-type aluminyl moiety was synthesized. The Rh-Al bond of Rh(PAlP) was characterized as the unusual $Rh^{\delta-}$-$Al^{\delta+}$ polarized covalent bond by DFT calculations. In addition, this complex was reported to successfully activate the *sp*^{2} C-H σ-bond of pyridine, where the N atom of pyridine coordinates to the Al center and the C-H bond cleavage occurs on the Rh center. One important open question is whether this rhodium complex can activate other σ-bonds such as stronger C-F and C-O bonds or not. Another question is if other group 13 elements can be applied to this complex and σ-bond activation. In this work, we investigated the activation performance of Rh(PAlP) and two analogues Rh(PBP) and Rh(PGaP) for C-F σ-bond of fluobenzene (PhF).

Scheme 1. PAlP ligand.



Geometries were optimized using DFT method with the B3PW91-D3 functional, where LANL2DZ basis sets were used for Al, P, Ga, and Rh with effective core potentials (ECPs) and 6-31G(d) for other atoms; this basis set system is named BS-I. Energy change was evaluated using the B3PW91-D3 functional and better basis set system (BS-II), in which Stuttgart-Dresden-Bonn basis sets were used for Ga and Rh with ECPs and 6-311G(d) for other atoms. Solvation effect of toluene was considered using PCM model. The B3PW91-D3 functional was selected for these calculations because (i) the geometry of Rh(PAlP) complex could be reproduced well using this functional and (ii) the energy change in the model C-F bond activation calculated by this functional was similar to that by CCSD(T). Gaussian 16 program was used.

In the reaction of Rh(PXP) (X = B, Al, Ga) with PhF, we employed 2,5-norbornadiene (nbd) complex of Rh(PXP) as starting material, considering the experimental result. In nbd complex of Rh(PAlP) **Rea-Al**, nbd coordinates to Rh in a bidentate manner, as shown in Figure 1. After the ligand substitution for nbd with PhF, Rh(PAlP)(PhF) **Ad-Al** is formed, in which the C=C bond of PhF coordinates to the Rh center. Three possible coordination modes were found in **Ad-Al**: (i) coordination of PhF at the position trans to Al to form a planar (PL) structure **Ad-a-Al**, (ii) coordination at the perpendicular (PE) position to form **Ad-b-Al**, and (iii) coordination at the seesaw position (between PL and PE) to form **Ad-c-Al**. Starting from **Ad-b-Al**, the C-F bond cleavage occurs in σ-bond metathesis manner keeping Al-F bonding interaction, suggesting that the Al center plays important role in the C-F bond activation process. In the σ-bond activation, the Al moiety is converted to Z-type aluminum ligand. Finally, the product **P-a-Al** and its isomer **P-b-Al** are located, where the Ph group is bound with the Rh center at the position cis to the F in **P-a-Al** but at the position trans to the F in **P-b-Al**.

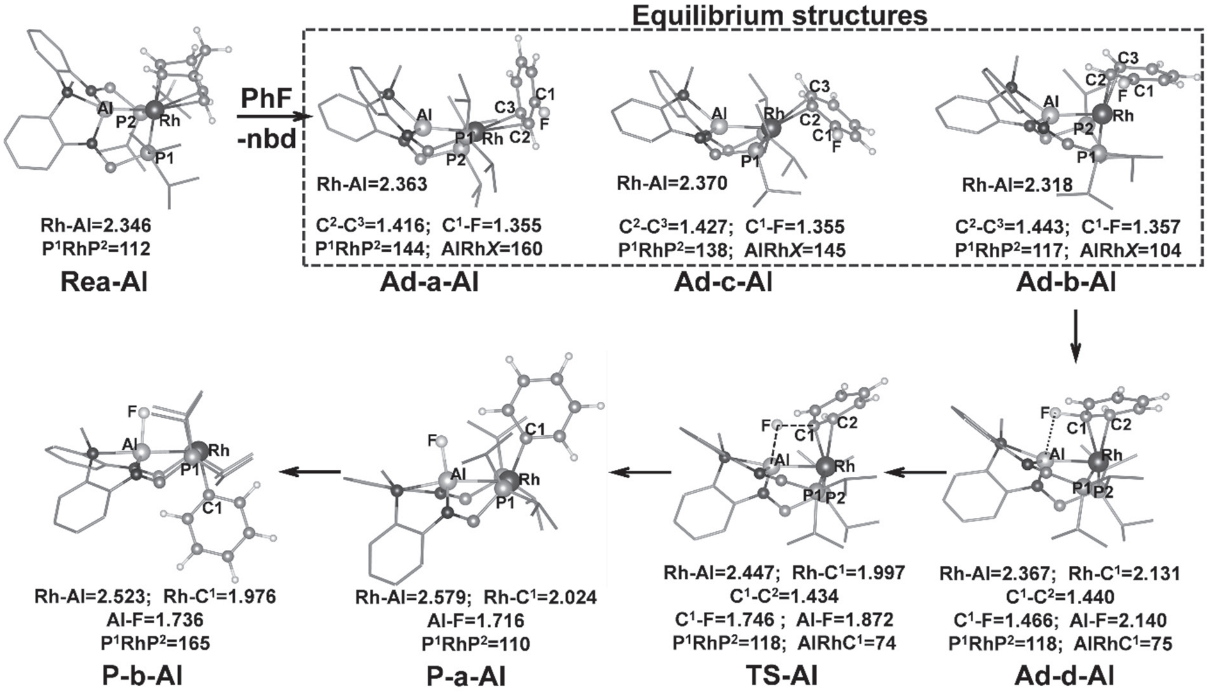


Fig. 1. Geometry changes in C-F bond activation process by Rh(PAlP).

Table 1. Relative Gibbs energies (kcal mol^{-1}) in C-F bond activation process by Rh(PXP).

Rh(PXP)	**Rea-X**	**Ad-a-X**	**Ad-c-X**	**Ad-b-X**	**Ad-d-X**	**TS-X**	**P-a-X**	**P-b-X**
X = Al	0.0	25.3	21.6	19.2	21.4	22.1	-26.4	-33.6
X = B	0.0	22.6	22.9	25.5	32.1	52.6	-8.0	-9.2
X = Ga	0.0	24.1	21.7	21.8	23.8	34.8	-8.2	-15.9

As shown in Table 1, the Gibbs activation energy $\Delta G^{o\ddagger}$ (**Rea-Al** to **TS-Al**) and the Gibbs reaction energy ΔG^{o} are 22.1 and -33.6 kcal mol^{-1}, respectively. These results indicate that this activation reaction can occur easily by moderate heating. The ligand substitution process from **Rea-Al** to the most stable adduct **Ad-b-Al** shows a very positive ΔG^{o} value of 19.2 kcal mol^{-1}. However, the C-F σ-bond cleavage occurs with marginal energy barrier from **Ad-b-Al**. The isomerization of **P-a-Al** to **P-b-Al** is exothermic with the ΔG^{o} of -7.2 kcal mol^{-1}. For B and Ga analogues, the $\Delta G^{o\ddagger}$ is 52.6 and 34.8 kcal mol^{-1} (**Rea-X** to **TS-X**) and the total ΔG^{o} is -9.2 and -15.9 kcal mol^{-1} for X = B and X = Ga, respectively; these $\Delta G^{o\ddagger}$ values are much larger and ΔG^{o} are less negative than those for X = Al. It is concluded that Rh(PAlP) is the best for C-F bond activation both thermodynamically and kinetically.

2. Original papers

3. Presentation at academic conferences

4. Others

(1) Qiaozhi Li and Shigeyoshi Sakaki
“Theoretical study on C−X σ-bond activation by Rh(PAlP) complexes”
The 16th symposium of Fukui Institute for Fundamental Chemistry, Kyoto, Feb. 08, 2019.

Rei Matsuzaki

FIFC Fellow

1. Summary of the research of the year

Electronic and nuclear fluxes induced by quantum interference

We perform an electronic and nuclear flux analysis for nonadiabatic dynamics and its corresponding adiabatic counterpart, both of the wavefunctions of which are represented in the Born-Huang expansion. It is well known that the electronic-nuclear configurations (terms) in the expansion of the total wavefunction interfere each other through the nonadiabatic interactions and give birth to electronic and nuclear fluxes. Interestingly, even in the adiabatic dynamics without such nonadiabatic interactions, a wavefunction composed of more than one adiabatic state can undergo interference among the components and give the electronic and nuclear fluxes. That is, the individual pieces of the wavepacket components associated with the electronic wavefunctions in the adiabatic representation can propagate in time independently with no nonadiabatic interaction, and yet they can interfere among themselves to generate the specific types of electronic and nuclear fluxes. We refer to the dynamics of this class of total wavefunction as multiple-configuration adiabatic Born-Huang dynamics. A systematic way to distinguish the electronic and nuclear fluxes arising from nonadiabatic and the corresponding adiabatic dynamics is discussed, which leads to the deeper insight about the nonadiabatic dynamics and quantum interference in molecular processes. The so-called adiabatic flux will also be discussed.

As usual, we begin with the time-dependent Schrödinger equation with the Born-Huan expansion

$$\Psi(\boldsymbol{q},\boldsymbol{R},t)=\sum_{I}\chi_{I}(\boldsymbol{R},t)\Phi_{\mathrm{I}}(\boldsymbol{q};\boldsymbol{R}). \tag{1}$$

We do not have to specify $\Phi_{\mathrm{I}}(\boldsymbol{q};\boldsymbol{R})$ at this point. We consider the conservation of the quantum probability and finally obtain electronic flux $\boldsymbol{j}_{\mathrm{el}}$ and nuclear flux $\boldsymbol{J}_{\mathrm{nu}}+\boldsymbol{J}_{nu}^{el}$. Here, derivative operator for nuclear position is operated on nuclear wavefunctions in $\boldsymbol{J}_{\mathrm{nu}}$ and on electronic wavefunctions in $\boldsymbol{J}_{nu}^{el}$. To facilitate the intuitive understanding of the physical properties of these fluxes, we will use the following reduced ones

$$\mathbf{f}_{\mathbf{R}}(\mathbf{R},\boldsymbol{t})=\int\mathbf{j}_{\boldsymbol{el}}(\mathbf{r},\mathbf{R},\boldsymbol{t})\mathrm{d}\mathbf{r}\mathrm{dt}, \tag{2}$$

$$\mathbf{f}_{\mathbf{r}}(\mathbf{r},\boldsymbol{t})=\int\mathbf{j}_{\boldsymbol{el}}(\mathbf{r},\mathbf{R},\boldsymbol{t})\mathrm{d}\mathbf{R}\mathrm{dt}, \tag{3}$$

$$\mathbf{F}_{nu}(\mathbf{R},\mathrm{t})=\int\mathbf{J}_{\boldsymbol{nu}}(\mathbf{r},\mathbf{R},\boldsymbol{t})\mathrm{d}\mathbf{r}\mathrm{dt}, \tag{4}$$

$$\mathbf{F}_{nu}^{el}(\mathbf{R},\mathrm{t})=\int\mathbf{J}_{\boldsymbol{nu}}^{\boldsymbol{el}}(\mathbf{r},\mathbf{R},\boldsymbol{t})\mathrm{d}\mathbf{r}\mathrm{dt}. \tag{5}$$

Table 1. Components of the electronic and nuclear fluxes and their properties.

	Nonadiabatic	BO multi-configuration	BO single-configuration
$\mathbf{j}_{el}(\mathbf{r},\mathbf{R},t)$	Finite value, beat+ Rabi-like	Finite value, beat	0
$\mathbf{f}_{\mathbf{r}}(\mathbf{r},t)$	Finite value	Finite value	0
$\mathbf{f}_{\mathbf{R}}(\mathbf{R},t)$	Finite value, beat+Rabi-like	Finite value, beat	0
$\mathbf{J}_{nu}(\mathbf{r},\mathbf{R},t)$	Finite value, beat+Rabi-like	Finite value, beat	Finite value, no beat
$\mathbf{F}_{nu}(\mathbf{R},\mathrm{t})$	Finite value, no beat	Finite value, no beat	Finite value, no beat
$\mathbf{J}_{nu}^{el}(\mathbf{r},\mathbf{R},t)$	Finite value, beat+Rabi-like	0 or very small	0
$\mathbf{F}_{nu}^{el}(\mathbf{R},\mathrm{t})$	Finite value, beat+Rabi-like	0	0

We analyzed these fluxes for three types of total wavefunctions: (i) nonadiabatic wavefunctions (ii) BO(Born-Oppenheimer) multi-configuration wavefunctions (iii) BO single-configuration wavefunctions. Table I summarizes the conclusions.

We perform numerical studies to see how we can or cannot distinguish the nonadiabatic dynamics and the multiple configuration adiabatic dynamics in terms of the quantum flux components. To do so, we perform the full quantum mechanical calculations over the electronic and nuclear degrees of freedom for the two-state model of the spin-singlet LiF molecule. We obtained the adiabatic ground state and first excited state with the GAMESS quantum chemistry package using two-state averaged complete active space self-consistent field calculation of the level of a six electron six orbital active space with aug-cc-pVDZ basis sets at every 0.1 angstrom to 11.0 angstrom. We have numerically calculated the nonadiabatic coupling elements by means of the finite difference method. Since all the quantum wavepackets dynamics calculations are performed in the diabatic representation, we adopt the standard method using the adiabatic-to-diabatic transformation angle obtained from the non-adiabatic coupling constant. The nuclear wavepackets in the diabatic representation are obtained by integrating the coupled Schrödinger equations with the split-operator FFT method.

The main subject of the present study is the quantum interference effect arising in two dynamics: one undergoing nonadiabatic transition and the other being adiabatic all the way through, but they commonly have the multiple configuration. To prepare the initial conditions from them, a Gaussian wavepacket (C) in Fig. 1 is made to run according to the coupled Schrödinger equation towards the Franck-Condon region. In the passing through the avoiding crossing, it bifurcates into two pieces, each arriving at the position (A) and (B) at some time on the individual adiabatic potential curve. As a pair of two initial wavepackets, we let them move back numerically to the reserved direction with the inverse momenta. The nonadiabatic version of this total wavefunction consisting of (A) and (B) proceeds towards the asymptotic region and two wavepackets merged into a single piece like the packet (C). On the other hand, each of the components of wavepackets (A) and (B) proceeds individually on their adiabatic potential curves without merged.

Fig. 2 shows that the calculation result of reduced electron flux $f_Q(Q,t)$ defined in Eq. (2) where Q is atomic distance of LiF. In the present dynamics, the initial two wavepackets reach the crossing region at $t = 30$ fs. In the nonadiabatic case (left panel of Fig. 2.), the electron flux disappears after this time. This is because the wavepackets merge and become single configuration and the electron flux for such a wavefunction is nullified as shown in Table 1. Remarkably through, the electron flux in the adiabatic wavefunction (right panel of Fig. 2.) does not disappear after reaching crossing region. This is because adiabatic wave function doesn't merge into single configuration and multiple-configuration adiabatic wavefunction have a finite value in the electron flux (see Table 1).

In the present research, we study the property of multi-configuration adiabatic wavefunctions in terms of flux. Especially, we show that the quantum interference can induce the electronic flux even if the system is adiabatic. We also discussed the correlation between electron flux and nuclear flux.

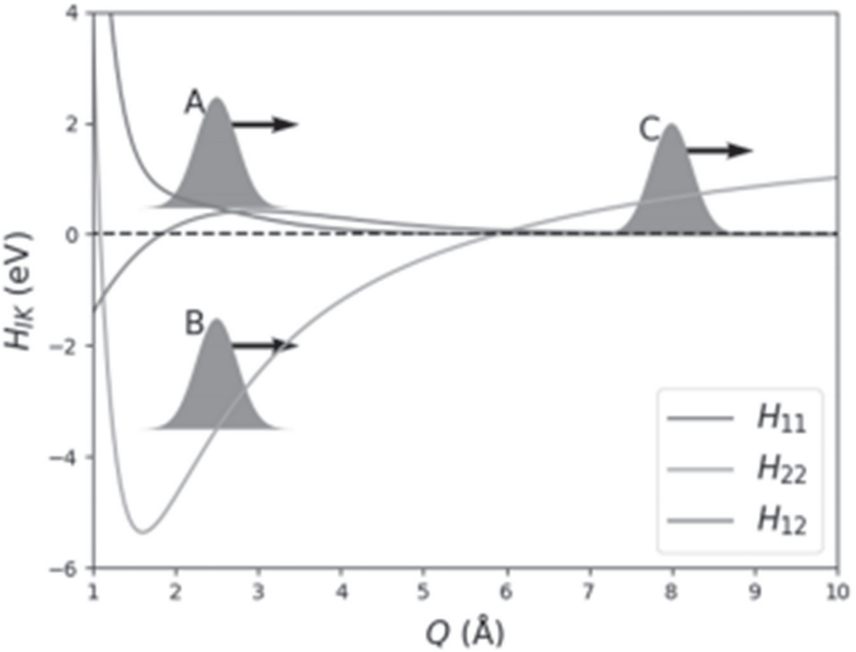
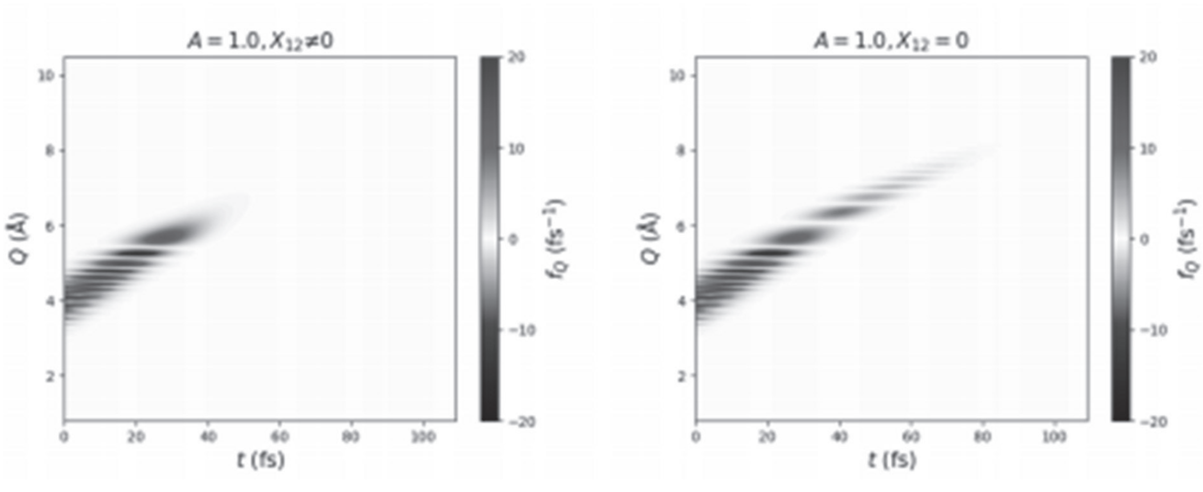


Fig. 1. Schematic illustration of the potential curves in the diabatic representation and the associated electronic Hamiltonian matrix element. Two wavepackets (A) and (B) constitute an initial local wavefunction both for the adiabatic and nonadiabatic dynamics.


$A = 1.0, X_{12} \neq 0$

$A = 1.0, X_{12} = 0$

Fig. 2. Distribution of the reduced electronic flux $f_Q(Q,t)$. The left(right) panel shows the nonadiabatic(adiabatic) dynamics.

2. Original papers

(1) Rei MATSUZAKI and Kazuo TAKATSUKA,
"Electronic and nuclear flux analysis on nonadiabatic electron transfer reaction: A view from single configuration adiabatic Born-Huang representation"
J. Comput. Chem. 40(1), 148-163 (2019).

(2) Rei MATSUZAKI and Kazuo TAKATSUKA, "Electronic and nuclear fluxes induced by quantum interference in the adiabatic and nonadiabatic dynamics in the Born-Huang representation", J. Chem. Phys. 150(1), 014103(2019)

3. Presentation at academic conferences

(1) 松崎 黎、高塚 和夫、非断熱過程に置ける電子と原子核フラックス、第21理論化学討論会、岡崎、2018年5月15-17日

4. Others

山本 憲太郎
研究フェロー（高塚グループ）

１．今年度の研究の要約

今年度は，非断熱電子動力学的な一方向的プロトン移動の機構の理論的研究を行った．

【序】プロトンポンプは生化学における基本的な機構のひとつである．たとえば，bacteriorhodopsin (BR) や cytochrome *c* oxidase (CcO) はそのような機能を持ち，生じたプロトン勾配をATPの合成に利用する．このプロトンポンプは，電子状態の変化と何らかの形でカップルしているため，proton-coupled electron transfer (PCET) として理解されている．実際には，BRでは retinal の光励起に伴う，CcO では一連の酸化還元反応伴う PCET によって, proton pumping がそれぞれ駆動される．どちらの場合も，electron と proton の動力学的な関係は単純ではなく，基本的な機構は明らかではない．本研究は，非対称性を持つタンパクの動作機構によるものではなく,「化学反応的な」原理による一方向的なプロトン移動の機構を提案する．この仕組みを実現する簡単な分子システムの構築とその非断熱電子動力学ダイナミクスの詳細を示す.

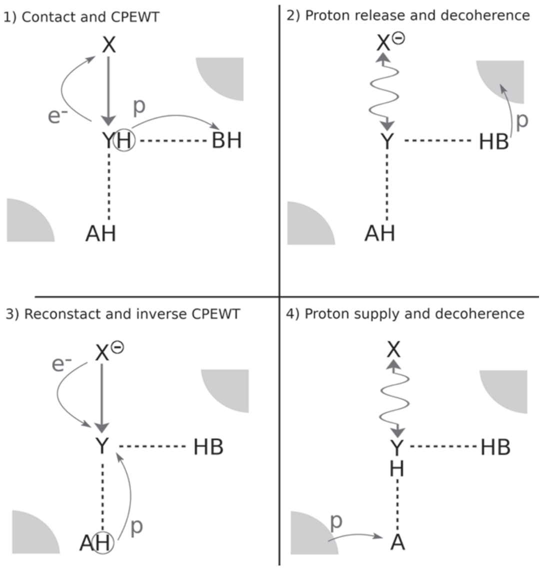


Fig. 1. Schematic representation of the mechanism of unidirectional proton transportation, which proceeds sequentially from Panel (1) to (4).

【方法論】Fig. 1 は，一方向的な電子移動の機構 [1]の類推から構築された，一方向的なプロトン移動の機構の概念図である．ここで AH = 酸, BH = 塩基, YH =弱酸，そして X = (Y に対する酸化および還元剤) である．Y は X に酸化されることによって強酸に変化する． 破線は水素結合を示す．AH は proton supplying units (PS, Fig. 1 の各パネルの左下の領域) と，BH は proton accepting unit (PA, 同右上の領域) にそれぞれ水素結合している． そして以下に示すスキームによって実質的に，PS から PA に proton が移動する(= proton pumping): (1) X が YH に近づくことによって，電子状態的なコヒーレンスが生じ，そこで coupled proton electron-wavepacket transfer (CPEWT) が起こって HB^{+}H, X^{-}，そして Y$^{\bullet}$が生じる．(2) X^{-}が Y$^{\bullet}$から離れてコヒーレンスが切れるため，逆反応がブロックされ

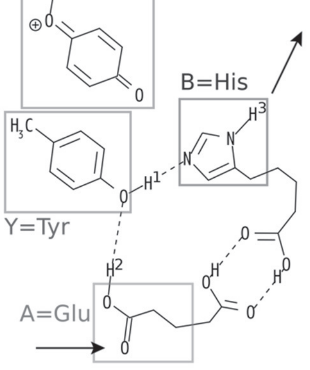


Fig. 2. Model system.

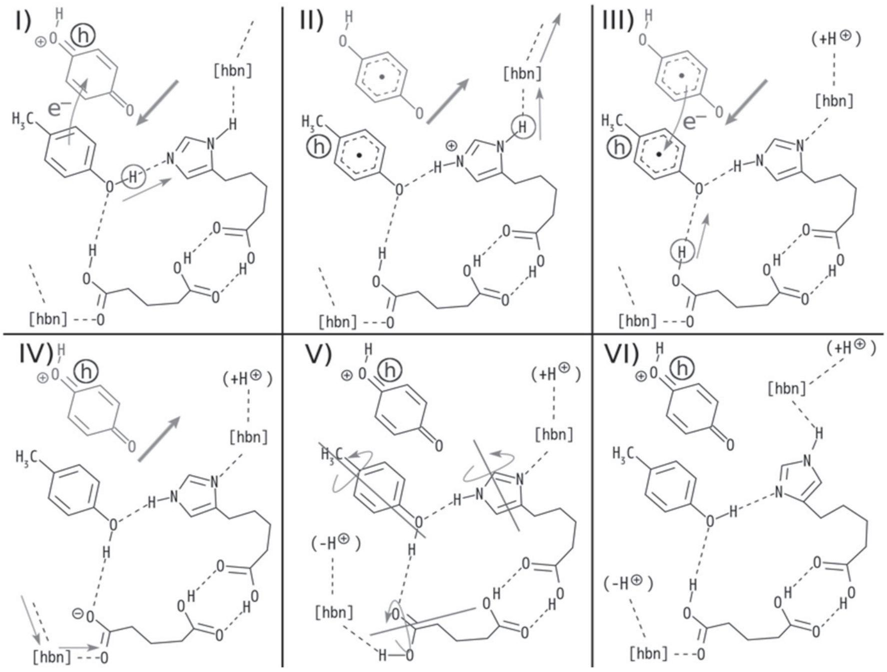


Fig. 3. Schematic snapshots of the one-way proton transfer dynamics; proceeding from panel I to VI. “h denotes hole position.

る．同時に，HB$^+$H の proton が PS に渡される．(3) ある程度の時間が経ってから，X$^-$ が Y$^\bullet$の方に戻ることで再びコヒーレンスが生じ，inverse CPEWT によって X, YH の組が再生される．このとき，AH の方の proton が使われる. (4) X が YH から再び離れるときに，A$^-$が PS から proton をもらうことで，AH が再生する．よって，core の部分が最初の状態に戻る．このような機構が実現可能であることを示すために，Fig. 2 に示すような具体的なモデル系を構築する．そしてプロセス全体 (Fig. 3) に対して energetics を計算し，重要な部分について全自由度の非断熱電子動力学 [2] を計算する.

【結果・考察】 Fig. 3 に示す I から VI の間の全てのモデル系について，概念的に示す電子状態が，基底状態として得られた．これらの中で，I→II および III→IV は，proton pumping の機構の鍵となるプロセスである. Proton transfer の一方向性を理解する上で重要なのは，X = SQ$^+$と Y = Tyr の距離によって，電子のコヒーレンスの on/off が切り替えられることである．これによって，proton transfer の一方向性がもたらされる．計算結果から，非断熱遷移がこのような役割を担うことわかる．これらの機構は，サイト間のコヒーレンスの on/off，および CPEWT によって，統一的に理解することができる.

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新崎　康樹

研究フェロー（高塚グループ）

1. 今年度の研究の要約

今年度はホウ素クラスター系における、個々の断熱状態が意味をなくすほど強く非断熱相互作用する電子状態に発生する「超共鳴状態」の動力学的性質およびそのような系での結合様式の時間発展の理論研究を行った。

【概要】 これまで電子状態の断熱描像、その描像における非断熱相互作用は化学反応の解釈に重要な役割を果たしてきた。一方で分子に内在する非断熱相互作用や外場によるその制御の研究が進むにつれて、従来の断熱電子状態という描像ではとらえきれないような状態を考える可能性が出てきた。特に、ポテンシャル面上の静的な原子核配置ととらえられる通常の化学結合とは全く異なる、電子状態が密集する高電子励起状態において原子核が運動し続けることによる非断熱相互作用によって維持される結合状態、「超共鳴状態」が本研究によって見いだされた。そのような電子状態の動的性質を検討するとともに、このような状態を反応場として利用する新規な化学反応の開発に繋げたい。

【方法論】 原子核の時間発展と同時に、多くの断熱電子状態が強く相互作用する電子状態が時間発展する系を理論計算により取り扱いたい。まずはそのような扱いを最も簡単に実現できる半古典エーレンフェスト理論による動力学計算を行う。ここでは断熱電子状態ではなく、電子の配置状態関数（CSF）を基底として電子状態を展開し、その展開係数$\{C_I(t)\}$ を時間発展させることで非断熱相互作用の強い系を必ずしも断熱状態で記述することなく扱う。

$$i\hbar\frac{\partial}{\partial t}C_I(t)=\sum_{J=1}^{N_\mathrm{S}}\left[H^{(\mathrm{el})}_{IJ}(\boldsymbol{R}(t))-i\hbar\sum_{k=1}^{3N_\mathrm{N}}\dot{R}_k(t)X^k_{IJ}(\boldsymbol{R}(t))\right]C_J(t) \tag{1}$$

原子核座標$\boldsymbol{R}(t)$ はその電子状態の平均場フォースに駆動されるとする。

$$m_k\ddot{R}_k(t)=-\sum_{I=1}^{N_\mathrm{S}}\sum_{J=1}^{N_\mathrm{S}}C_I^*(t)F^k_{IJ}(\boldsymbol{R}(t))C_J(t) \tag{2}$$

平均場フォースは

$$F^k_{IJ}(\boldsymbol{R}(t))=\sum_{K=1}^{N_\mathrm{S}}\left[X^k_{IK}(\boldsymbol{R}(t))H^{(\mathrm{el})}_{KJ}(\boldsymbol{R}(t))-H^{(\mathrm{el})}_{IK}(\boldsymbol{R}(t))X^k_{KJ}(\boldsymbol{R}(t))\right]+\bar{F}^k_{IJ}(\boldsymbol{R}(t)) \tag{3}$$

によって計算される（最後の項は CSF 基底ハミルトニアンの空間微分）。このとき電子、原子核の時間発展はともに CSF 間の相互作用行列要素

$$X^k_{IJ}(\boldsymbol{R}(t)) = \left\langle \Phi_I(\boldsymbol{R}(t)) \middle| \frac{\partial}{\partial R_k} \middle| \Phi_J(\boldsymbol{R}(t)) \right\rangle_{\boldsymbol{r}} \tag{4}$$

の影響を受ける。電子状態、核座標の時間発展は $H^{(\mathrm{el})}_{IJ}$、X^k_{IJ} 非対角項による CSF 間の混合の影響を強く受ける。

【ホウ素クラスターによる電子混合状態の検討】 ホウ素原子は電子が 5 つであり、2p 軌道に電子が 1 つの基底配置をとる。そのためホウ素クラスターでは多数の安定な励起状態が密に存在し、電子励起状態では原子核の運動にともない非断熱相互作用により電子状態が強く混合される。そのような励起状態での動力学は少数の断熱状態とその間の相互作用と解釈するよりは、個々の断熱状態が区別できない混合状態と解釈することが妥当であることが先行研究で示唆されている[1,2]。本研究ではこの特異な状態の特徴を動力学計算から探った。B_6、B_{12} クラスターでの非断熱相互作用を含む時間発展と仮想的な断熱時間発展との比較により、非断熱相互作用がなければ解離する条件の軌跡であっても、頻繁に強く非断熱相互作用することによって解離が阻害される場合のあることが確認できた（図１）。これは実効的には強い非断熱相互作用が存在する場合にのみ、原子核運動によって維持される「結合状態」ととらえることができる[3]。

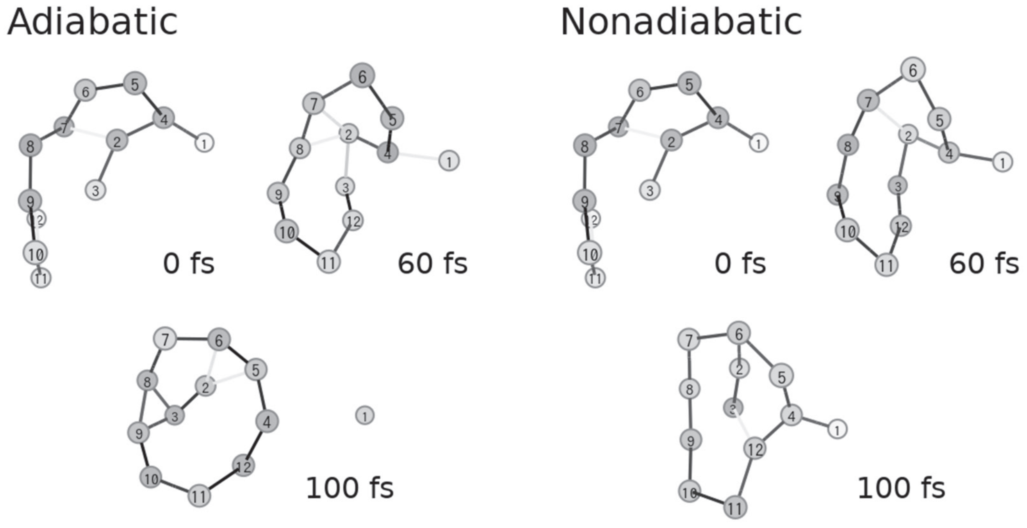

図１　B_{12} クラスターで断熱時間発展では解離する（左）が非断熱相互作用により束縛される（右）例。

【結合状態の時間発展の検討】 今年の研究では、高励起状態における結合領域の不対電子密度が結合エネルギーに及ぼす役割に解釈を与えることができ[3]、原子核基底に情報を集約することが、多数の断熱電子状態を含む状態の結合様式の時間発展を特徴付けることに有益である示唆を得た。例えば原子核基底での電子エネルギー行列を構成すると、その非対角要素は原子核間の結合領域のエネルギーと解釈できるので、分子内の結合様式を反映すると期待できる。現在、結合様式の時間発展の指標として、原子核基底行列、例えば原子核基底電子エネルギー行列の固有値と固有関数を検討している（図２）。電子状態がいかに複雑に記述されようとも原子核数に応じた量に情報を集約できて好都合である。

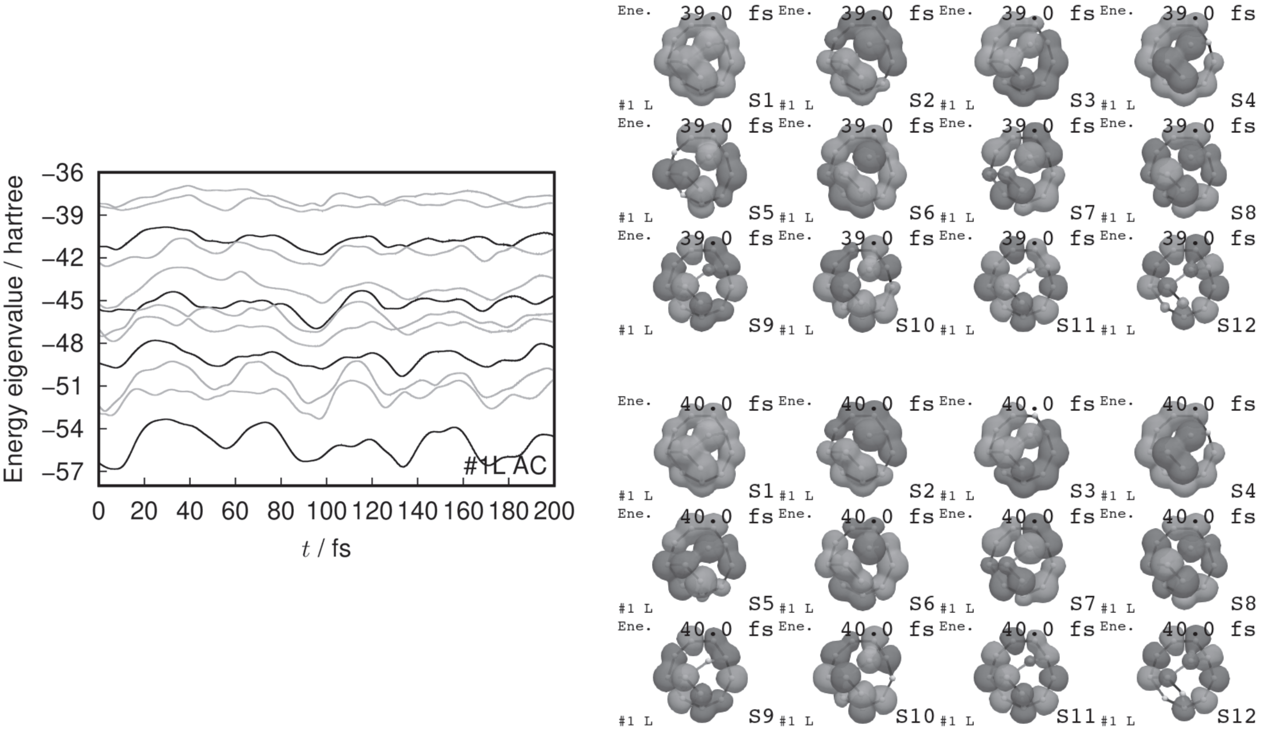

図２ (左) B_{12}（原子核数 12）の原子核基底電子エネルギー行列の固有値の時間発展。(右上) 39.0 fs、(右下) 40.0 fs での原子核基底電子エネルギー固有関数の符号の空間分布（赤: 正、青: 負）。多体の複雑な変化をさらに少数の変数（ここでは固有状態 5、6 間の交差）に縮約する。

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第12回分子科学討論会　福岡　2018/9/13　4E3

Kota Hanasaki

Research fellow (Takatsuka group)

1. Summary of the research of the year

Formulation of relativistic electron dynamics in molecules

Rapid progress in the laser technology has realized ultraintense laser fields of intensity exceeding 10^{20} W/cm^2, ultrashort pulses of attosecond duration and new X-ray laser sources [1-4], opening up a new avenue for direct observation and manipulation of electron dynamics [5,6]. Analysis of unconventional dynamics in such extremal conditions requires novel theoretical tools based on deep understanding on the underlying physics and an efficient *ab initio* calculation scheme of many-body electronic wavefunctions. Here we explore one of the most challenging types of unconventional electronic dynamics and develop a theory of relativistic electron dynamics in molecules.

Relativistic electrons have long been known to exist in heavy atoms [7] where the strong Coulombic field accelerates electrons close to the speed of light. The static relativistic effects, including relativistic orbital shrinkage (s and p orbitals) or diffusion (d and f orbitals) and the spin-orbit coupling, have been revealed to have distinct effects on the static chemical properties [7]. *Ab initio* calculations of those electrons have been successfully realized in the framework of the relativistic quantum chemistry [8-10]. On the other hand, ultrastrong laser techniques have realized new types of relativistic electrons of dynamical nature [11,12] by direct acceleration of electrons in ultraintense ($\gtrsim 10^{18}$ W/cm^2) infrared laser fields or by excitation of relativistic electronic orbitals in heavy atoms using X-ray laser pulses.

In contrast to static properties affected by above-listed single-particle relativistic effects, analysis of relativistic dynamics requires careful consideration of electron-radiation coupling enhanced by large electronic velocity. We therefore constructed a new theoretical framework for electron-nucleus-radiation coupled dynamics based on quantum electrodynamics [13,14].

We first derived a formal quantum electrodynamical expressions of a general dynamical observables. After a formal path-integral decoupling of the nuclear degrees of freedom [15,16], the problem reduces to electron-radiation coupled time evolution along an arbitrary given nuclear trajectory $\boldsymbol{R}_\tau$. We can then construct a formal perturbation expansion by combining the mean-field electronic Hamiltonian and non-interacting radiation field Hamiltonian to form the zeroth order single-body Hamiltonian $H_0(\boldsymbol{R}_\tau)$ and putting the remaining part into the interaction Hamiltonian $H_{\mathrm{int}}(\boldsymbol{R}_\tau)$. A formal perturbation series for a general dynamical observable O_A along such time evolution reads

$$M_{fi}^{\mathrm{el,rad}}[\boldsymbol{R}_\tau] = \lim_{\eta\to 0} \frac{\langle \Phi_f{:}\boldsymbol{R}_f | \mathcal{T}\{U(\infty,-\infty;\boldsymbol{R}_\tau) O_A(x_A)\} | \Phi_i{:}\boldsymbol{R}_i \rangle}{N_i N_f \langle \Phi_f{:}\boldsymbol{R}_f | U(\infty,0) | \Phi_f{:}\boldsymbol{R}_f \rangle \langle \Phi_i{:}\boldsymbol{R}_i | U(0,-\infty) | \Phi_i{:}\boldsymbol{R}_i \rangle}, \qquad (1)$$

with $\Phi_i,\boldsymbol{R}_i$ ($\Phi_f,\boldsymbol{R}_f$) representing the initial (final) electronic state and nuclear coordinates, $\mathcal{T}$ representing the time-ordering operator, $U_\eta(t,t')$ being the radiation-corrected perturbative propagator in the interaction representation with a small damping factor $e^{-\eta|\tau|}$[17], and $N_i(N_f)$ being a normalization factor associated to the initial (final) state. Although being formally exact, evaluation of the formal perturbation series, Eq. (1) is out of reach of conventional techniques because of the explicit time-dependence of $H_0(\boldsymbol{R}_\tau)$ and $H_{\text{int}}(\boldsymbol{R}_\tau)$.

In order to obtain a more feasible calculation scheme, we first consider a calculation scheme based on an effective Hamiltonian, which is a radiation-corrected energy operator acting on a d dimensional model space $\mathcal{V}$ (an invariant subspace of $H_0(\boldsymbol{R}_t)$). The generalized Gell-Mann-Low theorem [18] shows that one can construct such an effective Hamiltonian in a perturbative manner as $H_{\text{eff}}^{\text{el,rad}} = \mathcal{P}H\Omega\mathcal{P}$ with $\mathcal{P}$ being the projection operator on $\mathcal{V}$ and $\Omega = U_\eta(0,-\infty)\frac{1}{\mathcal{P}U_\eta(0,-\infty)\mathcal{P}}$ being the (perturbative) wave operator. We can then rewrite Eq. (1) as

$$M_{fi}^{\text{el,rad}}[\boldsymbol{R}_\tau] \approx \langle \tilde{F}_f | e^{i\epsilon\left(H_{\text{eff}}^{\text{el,rad}}(\boldsymbol{R}_n)+\dot{\boldsymbol{R}}_n\cdot(\frac{q_e}{c}\boldsymbol{A}(\boldsymbol{R}_n)-i\hbar\boldsymbol{X})\right)/\hbar} \cdots O_A^{\text{eff}}(x_A) \cdots e^{i\epsilon\left(H_{\text{eff}}^{\text{el,rad}}(\boldsymbol{R}_1)+\dot{\boldsymbol{R}}_1\cdot(\frac{q_e}{c}\boldsymbol{A}(\boldsymbol{R}_1)-i\hbar\boldsymbol{X})\right)/\hbar} | F_i \rangle, \tag{2}$$

with $\boldsymbol{X}$ being the derivative coupling, $\boldsymbol{A}$ being the transversal radiation field and O_A^{eff} being the effective operator defined in an analogous manner as $O_A^{\text{eff}} = \mathcal{P}O_A\Omega\mathcal{P}$. The initial (final) state, represented by $|F_i\rangle$ ($\langle\tilde{F}_f|$), is (the conjugate of) the model-space projection of the radiation-corrected initial (final) adiabatic state. Equation (2) is correct up to the basis set expansion. The effective Hamiltonian $H_{\text{eff}}^{\text{el,rad}}$ can be constructed using the standard perturbation expansion techniques in the quantum field theory [14], but more efficiently using advanced techniques introduced in Refs. 19 and 20. We can further show that, within this effective Hamiltonian approach, the full electron-nucleus coupled dynamics, with the non-relativistic approximation on the nuclear degrees of freedom, can be represented by an effective non-adiabatic Schrödinger dynamics of the nuclear wavepacket using the effective Hamiltonian. Details of this research can be found in our forthcoming publication [21].

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The 21st Annual Meeting of Japan Society of Theoretical Chemistry, May 17, 2018

4. Others

(1) Kota Hanasaki and Kazuo Takatsuka
"Formulation of relativistic electron dynamics"
The 16th symposium of Fukui Institute for Fundamental Chemistry, Kyoto, Feb. 8, 2019.

V　資料

1．研究業績一覧（平成 30 年度）

№	Authors	Title	Journal	Volume(Number), first page to last page	year
佐藤　徹					
1	W. Ota, K. Teramura, S. Hosokawa, T. Tanaka, T. Sato	Regioselectivity of H2 Adsorption on Ga2O3 Surface Based on Vibronic Coupling Density Analysis	*J. Comput. Chem. Jpn.*	17, 138-141	2018
2	Z. Lian, M. Sakamoto, H. Matsunaga, J.J.M. Vequizo, A. Yamakata, Mi. Haruta, H. Kurata, W. Ota, T. Sato, T. Teranishi	"Near infrared light induced plasmonic hot hole transfer at a nano-heterointerface"	*Nature Commun.*	9, 2314 1-7	2018
3	D. Liu, Y. Niwa, N. Iwahara, T. Sato, L. F. Chibotaru	Quadratic Jahn-Teller effect of fullerene anions	*Phys. Rev. B*	98, 035402 1-9	2018
4	S. Kimura, A. Tanushi, T. Kusamoto, S. Kochi, T. Sato, H. Nishihara	A luminescent organic radical with two pyridyl groups: high photostability and dual stimuliresponsive properties, with theoretical analyses of photophysical processes	*Chem. Sci.*	9, 1996-2007	2018
西本　佳央					
1	Van Quan Vuong, Yoshio Nishimoto, Dmitri G. Fedorov, Bobby G. Sumpter, Thomas A. Niehaus, and Stephan Irle	The Fragment Molecular Orbital Method Based on Long-Range Corrected Density-Functional Tight-Binding	*J. Chem. Theory Copmut.*	15(5), 3008-3020	2019
永瀬　茂					
1	T. Sugahara, J. –D. Guo, T. Sasamori, S. Nagase, and N. Tokitoh	Reversible Addition of Terminal Alkenes to Digermynes	*Chem. Commun.*	54, 519-522	2018
2	Z. Slanina, F. Uhlík, S. Nagase, T. Akasaka, X. Lu, and L. Adamowicz	Cyclic Water-Trimer Encapsulation into D2(22)-C84 Fullerene	*Chem. Phys. Lett.*	695, 245-248	2018
3	T. Sugahara, J. –D. Guo, T. Sasamori, S. Nagase, and N. Tokitoh	Regioselective Cyclotrimerization of Terminal Alkynes Using a Digermyne	*Angew. Chem. Int. Ed.*	57, 3499-3503	2018
4	Q. –Z. Li, J. –J. Zheng, L. He, S. Nagase, and X. Zhao	La-La Bonded Dimetallofullerenes [La2@C2n]-: Species for Stabilizing C2n (2n = 92-96) besides La2C2@C2n	*Phys. Chem. Chem. Phys.*	20, 14671-14678	2018
5	T. Sugahara, J. –D. Guo, D. Hashizume, T. Sasamori, S. Nagase, and N. Tokitoh	The Selective Formation of a 1,2-Disilabenzene from the Reaction of a Disilyne with Phenylacetylene	*Dalton Trans.*	47, 13318-13322	2018
6	M. Yamada, T. Akasaka, and S. Nagase	Salvaging Reactive Fullerenes from Soot by Exohedral Derivatization	*Angew. Chem. Int. Ed.*	57, 13394-13405	2018
7	Y. Maeda, Y. Konno, M. Yamada, P. Zhao, X. Zhao, M. Ehara, and S. Nagase	Control of Near Infrared Photoluminescence Properties of Single-Walled Carbon Nanotubes by Functionalization with Dendrons	*Nanoscale*	10, 23012-23017	2018

№.	Authors	Title	Journal	Volume(Number), first page to last page	year
榊　茂好					
1	Vijay Singh, Shigeyoshi Sakaki, Milind M. Deshmukh	Ni(I)-Hydride Catalyst for Hydrosilylation of Carbon Dioxide and Dihydrogen Generation: Theoretical Prediction and Exploration of Full Catalytic Cycle	*Organometallics*	37, 1258-1270	2018
2	Jing Lu, Kazuya Ishimura, and Shigeyoshi Sakaki	Theoretical Insight into Core−Shell Preference for Bimetallic Pt-M (M = Ru, Rh, Os, and Ir) Cluster and Its Electronic Structure	*J. Phys. Chem. C.*	122, 9081−9090	2018
3	Naofumi Hara, Teruhiko Saito, Kazuhiko Semba, Nishamol Kuriakose, Hong Zheng, Shigeyoshi Sakaki, and Yoshiaki Nakao	Rhodium Complexes Bearing PAlP Pincer Ligands	*J. Am. Chem. Soc.*	140, 7070−7073	2018
4	Masayuku Nakagaki, Antoine Baceiredo, Tsuyoshi Kato,* and Shigeyoshi Sakaki*	Reversible Oxidative Addition/Reductive Elimination of a Si-H Bond with Base-Stabilized Silylenes: A Theoretical Insight	*Chem. Eur. J.*	24, 11377 – 11385.	2018
5	Tomohiro Higashino, Atsushi Kumagai, Shigeyoshi Sakaki and Hiroshi Imahori	Reversible π-system switching of thiophene-fused thiahexaphyrins by solvent and oxidation/reduction	*Chem. Sci*	9, 7528 - 7539.	2018
高塚　和夫					
1	Kazuo Takatsuka	Nonadiabatic nuclear and electronic quantum wavepacket dynamics	*Chem. Phys.*	515, 52-59	2018
2	Andres Tehlar, Aaron von Conta,Yasuki Arasaki, Kazuo Takatsuka, and Hans Jakob	Ab-initio calculation of femtosecond-time-resolved photoelectron spectra of NO2 after excitation to the A-band	*J. Chem. Phys.*	149, 034307 (13 pages)	2018
3	Rei Matsuzaki and Kazuo Takatsuka	Electronic and nuclear flux analysis on nonadiabatic electron transfer reaction: A view from single-configuration adiabatic Born-Oppenheimer representation	*J. Comput. Chem. (Morokuma memorial issue)*	40, 148-163	2019
4	Rei Matsuzaki and Kazuo Takatsuka	Electronic and nuclear fluxes induced by quantum interference in the adiabatic and nonadiabatic dynamics in the Born-Huang representation	*J. Chem. Phys.*	150, 014103 (22 pages)	2019
5	Yasuki Arasaki and Kazuo Takatsuka	Chemical bonding and nonadiabatic electron wavepacket dynamics in densely quasi-degenerate excited state manifold of boron clusters.	*J. Chem. Phys.*	150, 114101 (18 pages)	2019
6	Kentaro Yamamoto and Kazuo Takatsuka	On the Elementary Chemical Mechanisms of Directional Proton Transfers: A Nonadiabatic Electron-Wavepacket Dynamics Study	*J. Phys. Chem. A*	123, 4125-4138	2019
北浦　和夫					
1	Dmitri G. Fedorov, Kazuo Kitaura	Pair Interaction Energy Decomposition Analysis for Density Functional Theory and Density-Functional Tight-Binding with an Evaluation of Energy Fluctuations in Molecular Dynamics	*J. Phys. Chem. A*	122(6), 1781-1795	2018

№.	Authors	Title	Journal	Volume(Number), first page to last page	year
多羅間　充輔					
1	Mitsusuke Tarama	Nonlinear Dynamics of Active Deformable Particles	*The Royal Society of Chemistry e-book*	Chapter 12. of "Self-organized Motion: Physicochemical Design based on Nonlinear Dynamics" (S. Nakata, V. Pimienta, I. Lagzi, H. Kitahata, N. J. Suematsu, eds.)	2019
伊丹　將人					
1	Masato Itami and Shin-ichi Sasa	Singular behaviour of time-averaged stress fluctuations on surfaces	*J. Stat. Mech.*	2018(12), 123210	2018
藪中　俊介					
1	(1) Shunsuke Yabunaka and Bertrand Delamotte	Why Might the Standard Large-N Analysis Fail in the O(N) Model: The Role of Cusps in Fixed Point Potentials	*Physical review letters*	23, 23161 1-5	2018
Schnyder, Simon K.					
1	Alice L. Thorneywork, Simon K. Schnyder, Dirk G. A. L. Aarts, Jürgen Horbach, Roland Roth, and Roel P. A. Dullens	Structure factors in a two-dimensional binary colloidal hard sphere system	*Molecular Physics*	111(36), 8873-8876	2018
鈴木　聡					
1	S.Suzuki, S. Maeda, K. Morokuma	Exploration of Quenching Pathways of Multiluminescent Acenes Using the GRRM Method with the SF-TDDFT Method	*J. Phys. Chem. A*	119, 11479–11487	2015
2	S.Sasaki, S.Suzuki, W.M.C. Sameera, K. Igawa, K. Morokuma, G. Konishi,	Highly twisted N,N-dialkylamines as a design strategy to tune simple aromatic hydrocarbons as steric environment-sensitive fluorophores	*J. Am. Chem. Phys.*	138, 8194-8206	2016
3	S.Sasaki, S.Suzuki, K. Igawa, K. Morokuma, G. Konishi,	The K-Region in Pyrenes as a Key Position to Activate Aggregation-Induced Emission: Effects of Introducing Highly Twisted N,N-Dimethylamines	*J. Org. Chem.*	82, 6865–6873	2017
Sharma, Akhilesh Kumar					
1	A. K. Sharma, W. M. C. Sameera, Y. Takeda, S. Minakata	A Computational Study on the Mechanism and Origin of the Reigioselectivity and Stereospecificity in Pd/SIPr-Catalyzed Ring-Opening Cross-Coupling of 2-Arylaziridines with Arylboronic Acids	*ACS Catal.*	9(5), 4582-4592	2019

№.	Authors	Title	Journal	Volume(Number), first page to last page	year
2	Y. Takeda, T. Matsuno, A. K. Sharma, W. M. C. Sameera, S. Minakata	Asymmetric Synthesis of β^2-Aryl Amino Acids through Pd-Catalyzed Enantiospecific and Regioselective Ring-Opening Suzuki-Miyaura Arylation of Aziridine-2-carboxylates	*Chem. Eur. J.*	25(43), 10226-10231	2019
3	M. Isegawa, A. K. Sharma	CO2 reduction by a Mn electrocatalyst in the presence of a Lewis acid: a DFT study on the reaction mechanism	*Sustainable Energy Fuels*	3(7), 1730-1738	2019
4	M. Isegawa, A.K. Sharma, S. Ogo, K. Morokuma	Electron and Hydride Transfer in a Redox-Active NiFe Hydride Complex: A DFT Study	*ACS Catal.*	8(11), 10419-10429	2018
青野　信治					
1	Shinji Aono, Tomohiro Seki, Hajime Ito, and Shigeyoshi Sakaki	Dependence of Absorption and Emission Spectra on Polymorphs of Gold(I) Isocyanide Complexes: QM/MM Approach	*J. Phys. Chem. C*	123, 4773−4794	2018
2	Shinji Aono and Shigeyoshi Sakaki	QM/MM Approach to Isomerization of Ruthenium(II) Sulfur Dioxide Complex in Crystal; Comparison with Solution and Gas Phases	*J. Phys. Chem. C*	122, 20701-20716	2018
中垣　雅之					
1	Masayuki Nakagaki, Antoine Baceiredo, Tsuyoshi Kato, and Shigeyoshi Sakaki	Reversible Oxidative Addition/Reductive Elimination of a Si-H Bond with Base-Stabilized Silylenes: A Theoretical Insight	*Chem. Eur. J.*	24, 11377 – 11385	2018
2	Nozomi Takagi, Masayuki Nakagaki, Kazuya Ishimura, Ryoichi Fukuda, Masahiro Ehara, and Shigeyoshi Sakaki	Electronic Processes in NO Dimerization on Ag and Cu Clusters: DFT and MRMP2 Studies	*J. Comput. Chem.*	40, 181–190	2019
3	Kazushi Fujimoto, Rajadeep Singh Payal, Tomonori Hattori, Wataru Shinoda, Masayuki Nakagaki, Shigeyoshi Sakaki, Susumu Okazaki	Development of dissociative force field for all-atomistic molecular dynamics calculation of fracture of polymers	*J. Comput. Chem.*	40, 2571–2576	2019
Lu, Jing					
1	Jing Lu, Kazuya Ishimura, and Shigeyoshi Sakaki	Theoretical Insight into Core–Shell Preference for Bimetallic Pt-M (M = Ru, Rh, Os, and Ir) Cluster and Its Electronic Structure	*J. Phys. Chem. C*	122 (16), 9081-9090	2018
Zhon, Ronglin					
1	Rong-Lin Zhong, Masahiro Nagaoka,Yoshiaki Nakao, and Shigeyoshi Sakaki	How To Perform Suzuki.Miyaura Reactions of Nitroarene or Nitrations of Bromoarene Using a Pd0 Phosphine Complex: Theoretical Insight and Prediction	*Organometallics*	37, 3480−3487	2018
Zheng, Jia-Jia					
1	Jia-Jia Zheng, Shinpei Kusaka, S. Ryotaro Matsuda, Susumu Kitagawa, and Shigeyoshi Sakaki	Theoretical Insight into Gate-Opening Adsorption Mechanism and Sigmoidal Adsorption Isotherm into Porous Coordination Polymer	*J. Am. Chem. Soc.*	140(42), 13958-13969	2018

№.	Authors	Title	Journal	Volume(Number), first page to last page	year
2	Haijun Wang, Haifei Cao, Jia-jia Zheng, Simon Mathew, Nobuhiko Hosono, Bihang Zhou, Hongliang Lyu, Shinpei Kusaka, Wanqin Jin, Susumu Kitagawa, and Jingui Duan	Finely Controlled Stepwise Engineering of Pore Environments and Mechanistic Elucidation of Water-Stable, Flexible 2D Porous Coordination Polymers	*Chem. Eur. J.*	24(24), 6412-6417	2018
3	Qiao-Zhi Li, Jia-Jia Zheng, Ling He, Shigeru Nagase, and Xiang Zhao	La–La Bonded Dimetallofullerenes [La2@C2n]−: Species for Stabilizing C2n (2n = 92–96) besides La2C2@C2n	*Phys. Chem. Chem. Phys.*	20(21), 14671-14678	2018
4	Cheng Gu, Nobuhiko Hosono, Jia-Jia Zheng, Yohei Sato, Shinpei Kusaka, Shigeyoshi Sakaki, and Susumu Kitagawa	Design and Control of Gas Diffusion Process in a Nanoporous Soft Crystal	*Science*	363(6425), 387-391	2019
松崎　黎					
1	Rei Matsuzaki and Kazuo Takatsuka	Electronic and nuclear flux analysis on nonadiabatic electron transfer reaction: A view from single-configuration adiabatic born–huang representation	*J. Comput. Chem.*	40(1), 148-163	2019
2	Rei Matsuzaki and Kazuo Takatsuka	Electronic and nuclear fluxes induced by quantum interference in the adiabatic and nonadiabatic dynamics in the Born-Huang representation	*J. Chem. Phys.*	150(1), 014103	2019
山本　憲太郎					
1	Kentaro Yamamoto and Kazuo Takatsuka	"On the Elementary Chemical Mechanisms of Unidirectional Proton Transfers: A Nonadiabatic Electron-Wavepacket Dynamics Study	*J. Phys. Chem. A*	123(19), 4125-4138	2019
新崎　康樹					
1	Andres Tehlar, Aaron von Conta, Yasuki Arasaki, Kazuo Takatsuka, and Hans Jakob Wörner	Ab initio calculation of femtosecond-time-resolved photoelectron spectra of NO2 after excitation to the A-band	*J. Chem. Phys.*	149, 034307 (13 pages)	2018
2	A. von Conta, A. Tehlar, A. Schletter, Y. Arasaki, K. Takatsuka, and H. J. Wörner	Conical-intersection dynamics and ground-state chemistry probed by extreme-ultraviolet time-resolved photoelectron spectroscopy	*Nat. Comm.*	9, 3162 (10 pages)	2018
3	Yasuki Arasaki and Kazuo Takatsuka	Chemical bonding and nonadiabatic electron wavepacket dynamics in densely quasi-degenerate excited electronic state manifold of boron clusters	*J. Chem. Phys.*	150, 114101 (18 pages)	2019
花崎　浩太					
1	K. Hanasaki, M. Kanno, T. A. Niehaus and H. Kono	An efficient approximate algorithm for nonadiabatic molecular dynamics	*J. Chem. Phys.*	149, 244117	2018

２．共同研究者受入れ状況（平成 30 年度）

受入れ教員	共同研究者名	受入れ身分	受入れ期間	所属機関・職	研究内容
榊　茂好	REN, Xuefeng	招へい 外国人学者	平成28年６月18日～ 平成30年６月17日	中国鉱山技術大学 （中国）・准教授	光機能性分子の発行阻害機構の理論化学的研究
榊　茂好	MENG, Qingxi	招へい 外国人学者	平成31年３月６日～ 令和２年３月５日	中国山東農業大学 （中国）・准教授	金属微粒子や MOFs の理論化学研究

３．海外渡航一覧（平成 30 年度）

職　　名	氏　　名	期間（自）	期間（至）	目　的　地
研　究　員	高塚　和夫	5/18/2018	5/21/2018	中国
特定研究員	多羅間　充輔	6/5/2018	6/9/2018	シンガポール
特定研究員	藪中　俊介	7/12/2017	7/27/2017	ドイツ、スロベニア
特定研究員	SCHNYDER, Simon Kaspar	7/16/2017	7/28/2017	スロベニア、ドイツ
特定研究員	藪中　俊介	6/17/2018	7/18/2018	フランス
特定研究員	中垣　雅之	6/18/2018	6/25/2018	フランス
特定研究員	伊丹　將人	9/3/2017	9/10/2017	ポーランド
教　　授	佐藤　　徹	6/23/2018	7/1/2018	スペイン
特定研究員	SCHNYDER, Simon Kaspar	7/4/2018	7/20/2018	イギリス
研　究　員	高塚　和夫	9/21/2018	9/24/2018	中国
特定研究員	藪中　俊介	10/28/2018	12/9/2018	フランス
特定研究員	多羅間　充輔	2/26/2019	3/21/2019	ドイツ

4．福井謙一博士生誕百年記念メモリアルシンポジウム・記念式典・祝賀会（予告）ポスター

予告

FUKUI INSTITUTE FOR FUNDAMENTAL CHEMISTRY

Kenichi Fukui 100th Birthday Anniversary

福井謙一博士生誕百年記念

Memorial Symposium & Ceremony

メモリアルシンポジウム・記念式典・祝賀会

2018/10/12（金）午後

講演者

Roald Hoffmann 教授（米国コーネル大学　1981年ノーベル化学賞 福井謙一博士と同時受賞）

白川 英樹 博士（2000年 ノーベル化学賞受賞）、**古川 安 教授**（日本大学）

会場：京都大学百周年時計台記念館（京都市左京区吉田本町）

記念展示

2018/10/3（水）**－12/9**（日）

会場：京都大学総合博物館（京都市左京区吉田本町）

福井謙一博士（当時・京都大学教授）は、フロンティア軌道理論の業績により、1981年に日本人として初めてノーベル化学賞を受賞しました。福井謙一博士の生誕百年を記念し、メモリアルシンポジウム、記念式典を開催するとともに、京大総合博物館で、記念展示を開催いたします。

主催　京都大学福井謙一記念研究センター
　　　京都大学福井謙一博士生誕百年記念事業実施委員会

5．福井謙一博士生誕百年記念メモリアルシンポジウム　ポスター

FUKUI INSTITUTE FOR FUNDAMENTAL CHEMISTRY

福井謙一博士生誕百年記念

Kenichi Fukui 100th Birthday Anniversary

メモリアルシンポジウム

Memorial Symposium

1918.10.04–1998.01.09　2018.10.12　13:30–16:15　135.7808171　35.0262378

福井謙一博士（当時・京都大学教授）は、フロンティア軌道理論の業績により、1981年に日本人として初めてノーベル化学賞を受賞しました。福井謙一博士の生誕百年を記念し、メモリアルシンポジウムを開催いたします。

date.　**2018年10月12日（金）**

place.　**京都大学百周年時計台記念館 百周年記念ホール**（京都市左京区吉田本町）

参加無料（以下のwebサイトをご覧ください）

http://www.fukui.kyoto-u.ac.jp/memorial/mem_sympo/

program.

13:30-13:35	挨拶	**田中 勝久**　京都大学福井謙一記念研究センター長・工学研究科教授
13:35-14:25	記念講演Ⅰ	**Roald Hoffmann**　コーネル大学教授｜1981年ノーベル化学賞福井謙一博士と同時受賞 *Simulation vs Understanding: A Tension, and Not Just in Our Profession*
14:25-15:15	記念講演Ⅱ	**白川 英樹**　筑波大学名誉教授｜2000年ノーベル化学賞受賞 *高分子合成を志して*
15:25-16:15	記念講演Ⅲ	**古川 安**　化学史学会前会長 *『応用をやるなら基礎をやれ』ー福井謙一のたどった道、拓いた世界ー*

KYOTO UNIVERSITY FOUNDED 1897

主催：京都大学｜運営 福井謙一記念研究センター｜協力 理学研究科、工学研究科、化学研究所｜共催：京都大学学際融合教育研究推進センター・スーパーグローバルコース化学系ユニット｜協賛：京都大学工化会

問合せ先：京都大学福井謙一記念研究センター　電話：075-711-7708　Mail：fukui-sympo@mail2.adm.kyoto-u.ac.jp

６．福井謙一博士生誕百年記念事業サテライトシンポジウム　プログラム

福井謙一博士生誕百年記念事業サテライトシンポジウム

■開催日：２０１８年１０月１３日（土）

■プログラム
９：３０～受付
１０：００～１０：０５
　開会挨拶（田中勝久・福井謙一記念研究センター長）
（司会：山本　量一教授）

１０：０５～１１：０５
講演①西本 佳央（京都大学福井謙一記念研究センター）
「FMO-DFTB 法：100 万原子に適用可能な量子化学計算の実証」

１１：０５～１２：０５
講演②John J.Molina（京都大学工学研究科化学工学専攻）
「クロール細胞の感受性」

１２：１５～１３：３０　昼休憩

１３：３０～１５：００　ポスターセッション（司会：林　重彦教授）

１５：００～１６：００
講演③畑中　美穂（奈良先端科学技術大学院大学ﾏﾃﾘｱﾙｽﾞ･ｲﾝﾌｫﾏﾃｨｸｽ研究室）
「自動反応経路探索の応用：メカニズム研究を超えて」

１６：００～１７：００
講演④長谷川　淳也（北海道大学触媒科学研究所）
「制御力による計算科学」

１７：３０～１９：００　ディスカッションミーティング

7．京都大学総合博物館 2018 年度企画展　福井謙一博士生誕百年記念展示　ポスター

応用をやるには、基礎をやれ

ノーベル賞化学者を育んだ教室

京都大学総合博物館2018年度企画展
福井謙一博士生誕百年記念展示

2018年10月3日（水）－12月9日（日）

京都大学総合博物館

開館時間：9:30～16:30（入館は16:00まで）　**休館日：月曜日、火曜日**（平日・祝日にかかわらず）

入館料：一般400円／高校・大学生300円／小・中学生200円

※20名以上の場合は団体観覧料を適用　※障害者手帳をお持ちの方とその付き添いの方１名、70歳以上の方、京都大学学生・教職員、京都府下の大学在籍の学生は無料（要証明証）

主催：京都大学総合博物館、京都大学福井謙一記念研究センター
共催：京都大学大学院理学研究科、京都大学大学院工学研究科、京都大学化学研究所／後援：京都府教育委員会、京都市教育委員会

MUSEUM
THE KYOTO UNIVERSITY MUSEUM

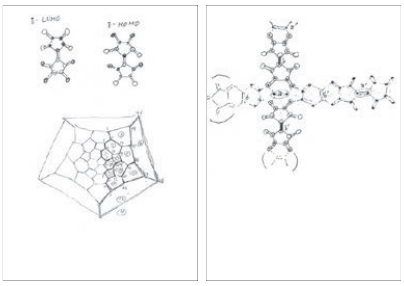
FUKUI INSTITUTE FOR FUNDAMENTAL CHEMISTRY

京都大学総合博物館2018年度企画展／福井謙一博士生誕百年記念展示

ノーベル賞化学者を育（はぐく）んだ教室

― 応用をやるには、基礎をやれ ―

2018年10月3日（水）― 12月9日（日）



「応用をやるには、基礎をやれ」アジア人として初めてノーベル化学賞を受賞した福井謙一博士が、終生の師・喜多源逸教授より受け継いだ言葉です。この言葉は、当時はまだ経験がものをいう職人肌の学問と言われた化学の世界で、物理学や数学など基礎理論で化学反応過程を説明可能であることを示す偉業に結実します。

本企画展示は、福井博士の生誕百年にあたる2018年に開催されます。福井博士の業績はもとより、博士が研究と思索を深めた京都大学の工業化学教室や燃料化学教室の歴史と系譜をひも解くことで、理論化学の拠点形成を支えた最高峰の研究環境が偶然ではなく必然として周到に整備されてきた経緯を知ることができます。

所縁の資料　化学者・福井謙一を知る

思索を深めた膨大なメモ紙と鉛筆、ノーベル賞受賞を報せた電報など、福井謙一ゆかりの資料を紹介します。ファーブル昆虫記をこよなく愛した福井少年が、化学の常識を覆した「もっとも化学者らしくない化学者」と呼ばれるまで、サイエンスの探検家であり続けた福井の足跡をたどります。

教室の歴史　化学の京都学派その歴史と系譜

福井が学び、研究し、そして教鞭をとった京都帝国大学の工業化学、燃料化学の教室は、喜多門下の児玉信次郎、新宮春男らが切磋琢磨した研究拠点でした。喜多源逸から現在に至るまで脈々と受け継がれてきた京都学派とも称される化学研究の系譜をひもときます。

知己の記憶　福井謙一をよく知る人々へのインタビュー映像

理論だけでなく実験も大切にした福井研究室からは、次々に新たな分野を開拓していった数多くの研究者や技術者が輩出されました。このコーナーでは、福井の日頃の研究姿勢や授業風景、ノーベル賞受賞前の雰囲気など、福井から薫陶を受けた研究者や当時に直接言葉を交わした人々の言葉から、福井像に迫ります。

理論の体験　難解な理論の一端を体験

写経ワークショップにより難解な理論を構成する数式や化学式を無心で写しとる体験をします。また、折り紙や3Dプリンタで構成された複雑な分子模型や分子軌道模型、最先端の理論化学計算のデモなどをご覧いただけます。

期間中、企画担当者らによるギャラリートークやワークショップなど、展示内容を多面的に楽しんでいただける企画を予定しています。詳しくは、期間中に京都大学総合博物館Webサイトに随時掲載、関連チラシを館内に掲示してまいりますので、注目ください。

1. 福井謙一博士（提供：京都大学福井謙一記念研究センター）
2. 絶筆研究メモ（フラーレン分子の軌道相互作用の解析）／1997年（提供：京都大学福井謙一記念研究センター）
3. 学士院賞受賞の祝賀講演会／1962年（福井家所蔵）
4. ノーベル化学賞受賞を祝って教授室に集まった石油化学教室の教官と学生／1981年（提供：株式会社化学同人）
5. 旧石油化学教室本館（提供：京都大学総務部広報課）

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	5

表面写真：工業化学科の喜多教授グループ／1937年（近土家所蔵）

メモリアルシンポジウム

日時：2018年10月12日（金）午後
会場：京都大学百周年時計台記念館（京都市左京区吉田本町）

サテライトシンポジウム

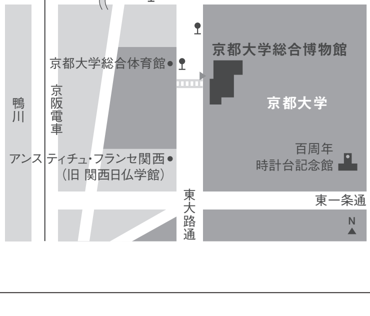
日時：2018年10月13日（土）
会場：京都大学福井謙一記念研究センター（京都市左京区高野西開町34-4）

メモリアルシンポジウム、サテライトシンポジウムへの問い合わせ先：
京都大学福井謙一記念研究センター
TEL. 075-711-7708
E-MAIL. fukui-sympo@mail2.adm.kyoto-u.ac.jp
www.fukui.kyoto-u.ac.jp/memorial/

京都大学総合博物館

〒606-8501 京都市左京区吉田本町
TEL. 075-753-3272
FAX. 075-753-3277
www.museum.kyoto-u.ac.jp

アクセス
市バス停留所「百万遍」より徒歩約2分
京阪電車「出町柳駅」より徒歩約15分
※駐車場はございません。
公共交通機関をご利用ください。



8．福井謙一記念研究センターシンポジウム　ポスター・プログラム

KYOTO UNIVERSITY
KYOTO JAPAN
FOUNDED 1897

FUKUI INSTITUTE FOR
FUNDAMENTAL CHEMISTRY

第16回

京都大学
福井謙一
記念研究センター
シンポジウム

開会式（Opening）

［開会の辞］田中 勝久（センター長）　09:50–09:55
［ご挨拶］大嶋 正裕（工学研究科長）　09:55–10:05

講演会（Lecture Session）

佐藤 徹（京都大学 福井謙一記念研究センター）　10:05–11:05
「振電相互作用密度とその応用
－発光、キャリア輸送、化学反応－」

平尾 公彦（京都大学 福井謙一記念研究センター）　11:20–12:20
「長距離補正密度汎関数法（LC-DFT）の最近の進展」

－ 昼食 －　12:20–13:50

跡見 晴幸（京都大学 大学院工学研究科）　13:50–14:50
「第3の生物アーキアの特異な代謝」

「福井謙一奨励賞」表彰式
（Ceremony of Kenichi Fukui Encouragement Award）　15:00–15:30
ポスターセッション（Poster Session）　15:30–17:20
懇親会（Banquet）　17:30–19:00

平成31年2月8日㊎
会場：京都大学 福井謙一記念研究センター
2019.2.8　Fukui Institute for Fundamental Chemistry（FIFC）, Kyoto University

京都大学福井謙一記念研究センター
〒606-8103　京都市左京区高野西開町34-4
お申し込みは下記ホームページをご参照ください（2019年1月25日締め切り）
問合せ先：西本佳央／E-mail: sympo2018@fukui.kyoto-u.ac.jp
　　　　　事務室／Tel: 075-711-7708　Fax: 075-781-4757
http://www.fukui.kyoto-u.ac.jp

第16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　　2019年2月8日（金）　9:50~19:00
場所　　京都大学 福井謙一記念研究センター

開会式 (Opening)：　3階大会議室

[開会の辞]　田中 勝久（京都大学 福井謙一記念研究センター長）　9:50 – 9:55
[ご 挨 拶]　大嶋 正裕（京都大学 工学研究科長）　9:55 – 10:05

講演会 (Lecture Session)：　3階大会議室

- **佐藤 徹**（京都大学 福井謙一記念研究センター）　10:05 – 11:05
  「振電相互作用密度とその応用－発光、キャリア輸送、化学反応－」
  座長：　田中 一義（福井センター）

- **平尾 公彦**（京都大学 福井謙一記念研究センター・理化学研究所）　11:20 – 12:20
  「長距離補正密度汎関数法(LC-DFT)の最近の進展」
  座長：　高塚 和夫（福井センター）

― 昼食 ―

- **跡見 晴幸**（京都大学 大学院工学研究科）　13:50 – 14:50
  「第3の生物アーキアの特異な代謝」
  座長：　林 重彦（京大院理）

「福井謙一奨励賞」表彰式 (Ceremony of Kenichi Fukui Encouragement Award)：

3階大会議室　15:00 – 15:30

受賞者：**春田 直毅**　（東京工業大学 科学技術創成研究院）
「縮退と擬縮退の包括的理解に向けた新たな数理化学の開拓」

ポスターセッション (Poster Session)：　3階大会議室　15:30 – 17:20

懇親会 (Banquet)：　1階多目的ルーム　17:30 – 19:00

ポスターリスト (3階大会議室 15:30～17:20)

- ✓ 番号が奇数の方は前半（15:30–16:25）、番号が偶数の方は後半（16:25–17:20）には、ポスターボードの前で発表するようにしてください。
- ✓ Authors with odd and even poster numbers should be present at the poster during the first half (15:30–16:25) and the second half (16:25–17:20) of the session, respectively.

1. **Quantitative analysis of QM/MM artifacts and its correction in adaptive QM/MM**
   ◯Hiroshi C. Watanabe[1,2] (Quantum Computing Center, Keio University[1], JST PRESTO[2])

2. **DABNAを用いたOLEDの発光機構に関する理論的研究**
   ◯伊藤 俊介[1]、佐藤 徹[2,3]、畠山 琢次[4]（京大工[1]、京大院工[2]、京大ESICB[3]、関西学院理工[4]）

3. **Theoretical study on the fluorescence of azaperylenes derivatives.**
   Akitsu Hirono[1], Hayato Sakai[1], ◯Shuntaro Kochi[2,3], Tomo Sakanoue[5], Taishi Takenobu[5], Tohru Sato[2,3,4] and Taku Hasobe[1] (Faculty of Science and Technology, Keio University[1], FIFC[2], Grad. School. of Eng. Kyoto Univ.[3], ESICB, Kyoto Univ.[4], Department of Chemistry, Department of Applied Physics, Nagoya University[5])

4. **Growth Mechanism of (6,5) Carbon Nanotube: Edge Structures and their Regioselectivities**
   ◯Tomohiro Nishikawa[1,2], Tohru Sato[1,2,3], Naoki Haruta[2], Takeshi Kodama[4] and Yohji Achiba[4] (FIFC[1], Grad. School. of Eng. Kyoto Univ.[2], ESICB[3], Grad. School. of Sci. Tokyo Metropolitan Univ.[4])

5. **Vibronic Coupling Density and Fragment Analyses of NO on Cu/γ-alumina Using Hydrogen Terminated Models**
   ◯Wataru Ota[1,2], Yasuro Kojima[2], Saburo Hosokawa[2,3], Kentaro Teramura[2,3], Tsunehiro Tanaka[2,3], and Tohru Sato[1,2,3] (FIFC [1], Grad. School. of Eng. Kyoto Univ. [2], ESICB [3])

6. **自己無撞着点電荷QM/MM法に基づく分子結晶構造の最適化**
   ◯青野 信治、榊 茂好（京大福井セ）

7. **相対論的な電子動力学理論の定式化**
   ◯花崎 浩太、高塚 和夫（京大福井セ）

8. **Singular behaviour of time-averaged stress fluctuations on surfaces**
   ○Masato Itami[1] and Shin-ichi Sasa[2] (FIFC[1], Dept. of Phys. Kyoto Univ.[2])

9. **Theoretical Study on C–X σ-Bond Activation by Rh(PAIP) Complexes**
   ○Qiao-Zhi Li[1], Yoshiaki Nakao[2] and Shigeyoshi Sakaki[1] (FIFC[1], iCeMS, Kyoto Univ.[2])

10. **ニッケル(II)-キノノイド錯体のスピン転移を伴うベイポクロミズムの理論研究:結晶中の分子選択性**
    ○中垣 雅之[1]、青野 信治[1]、吉田 将己[2]、小林 厚志[2]、加藤 昌子[2]、榊 茂好[1]（京大福井セ[1]、北大院理[2]）

11. **時間依存長距離補正密度汎関数強束縛法と分極誘電体モデルを用いた理論開発（TD-LC-DFTB/PCM）**
    ○西本 佳央（京大福井セ）

12. **Collective motion of cells on a substrate**
    ○Simon K. Schnyder, John J. Molina, Ryoichi Yamamoto

13. **Theoretical understanding and rational design of aggregation induced emission molecule**
    ○Satoshi Suzuki (FIFC)

14. **Modelling crawling cells: From simple mechanical model to mechano-chemical model**
    ○M Tarama, K Mori, and R Yamamoto

15. **一方向的なプロトン移動の化学的な機構について: 非断熱電子動力学による研究**
    ○山本 憲太郎、高塚 和夫（京大福井セ）

16. **Theoretical Study on Diffusion-Regulated Gas Adsorption into Porous Coordination Polymer**
    ○Jia-Jia Zheng[1,2], Susumu Kitagawa[2] and Shigeyoshi Sakaki[1] (FIFC[1], iCeMS, Kyoto Univ.[2])

17. **Borylation of sp3 C–H Bond Catalyzed by Ir(III) Complex: Theoretical Study of Regioselectivity**
    ○Rong-Lin Zhong, Shigeyoshi Sakaki (FIFC)

18. **Mechanistic Study of Hydrocarbon Oxidation on M_{55} Cluster (M = Pt, Pd, Rh)**
    ○Bo Zhu, Shigeyoshi Sakaki (FIFC)

19. **ナノシリンダーアレイにおける紫外領域での協同プラズモニックモード励起と希土類錯体の発光増強**
○河内谷 佑季[1]、村井 俊介[1,2]、田中 勝久[1]（京大院工[1]、JST さきがけ[2]）

20. **Coarse-grained model of nanocube based on the analysis of all atom molecular dynamics simulation**
○Kosuke Imamura[1] and Hirofumi Sato[2,3] (Fac. of Eng. Kyoto Univ.[1], Grad. School. of Eng. Kyoto Univ.[2], ESICB, Kyoto Univ.[3])

21. **Free energy calculation of a proton transfer reaction in condensed phase including nuclear quantum effects**
○Kento KOSUGI[1], Hiroshi NAKANO[1,2], Hirofumi SATO[1,2] (Department of Molecular Engineering, Kyoto University[1], ESICB, Kyoto University[2])

22. **DFTB3 parametrization for Pt(II) complexes**
○Jun OSHIKI[1], Kento KOSUGI[2], Hiroshi NAKANO[2,3] and Hirofumi SATO [2,3] (Kyoto Univ.[1], Grad. School. of Eng. Kyoto Univ.[2], ESICB. Kyoto Univ. [3])

23. **広域的構造探索法を用いた含炭素アルミニウムアニオンクラスターの理論的研究**
○勅使河原 翔[1]、吉田 悠一郎[1]、佐藤 啓文[1,2] (京大院工[1]、京大 ESICB[2])

24. **ハロロドプシン Cl-イオンポンプの光活性化の分子機構に関する理論的研究**
○小山 糧、長谷川 太佑、林 重彦（京大院理）

25. **分子シミュレーションによる AsLOV2 光受容タンパク質の光活性化中間状態**
○田口 真彦、成 鉱、東村 智佳、内田 芳裕、林 重彦（京大理）

26. **液体ピレンの MD シミュレーションと理論的解析**
○山本 裕生[1]、中西 尚志[2]、林 重彦[3]（京大院理[1]、物質・材料研究機構[2]）

27. **ヨウ素結合、水素結合を利用した電荷移動錯体における分子間相互作用と物性**
○石田 耕大[1]、髙橋 佑輔[1]、中野 義明[1,2]、石川 学[2]、大塚 晃弘[1,2]、矢持 秀起[1,2]、賣市 幹大[3]、春木 理恵[4]、熊井 玲児[4]、足立 伸一[4]（京大院理[1]、京大環安保[2]、分子研[3]、高エネ研[4]）

28. **Dissociative Adsorption or Dimerization? A Theoretical Study for Reaction of NO on M*n* Cluster (M = Ru, Rh, Pd, Ag; *n* = 13, 55)**
◯Nozomi TAKAGI[1], Ryoichi FUKUDA[1], Masahiro EHARA[1,2], Shigeyoshi SAKAKI[1,3] (ESICB, Kyoto Univ. [1], IMS [2], FIFC Kyoto Univ.[3])

29. **[2Fe–2S] Ferredoxin における活性中心周囲の水素結合とタンパク場がイオン化ポテンシャルに及ぼす影響**
◯江良 伊織[1]、多田 隼人[1]、藤井 琢也[1]、池永 和輝[1]、北河 康隆[1]、中野 雅由[1,2]（阪大院基礎工[1]、分子研[2]）

30. **ピラゾール架橋二核金属錯体における金属イオン間の磁気的相互作用の理論研究**
◯藤井 琢也[1]、江良 伊織[1]、多田 隼人[1]、池永 和輝[1]、北河 康隆[1]、中野 雅由[1,2]（阪大院基礎工[1]、分子研[2]）

31. **2 層積層型イットリウム(III)－フタロシアン錯体の磁気的な分子間相互作用に関する理論研究**
◯池永 和輝[1]、北河 康隆[1]、加藤 恵一[2]、山下 正廣[2]、中野 雅由[1,3]（阪大院基礎工[1]、東北大院理[2]、分子研[3]）

32. **配位子で保護された 25 核金クラスターの電子状態についての理論研究**
◯川尻 真広[1]、藤井 琢也[1]、北河 康隆[1]、中野 雅由[1,2]（阪大基礎工[1]、分子研[2]）

33. **開殻分子からなる一次元周期系の電子構造と非線形光学特性についての理論研究**
◯岸 亮平[1]、鎌田 賢司[2]、久保 孝史[3]、中野 雅由[1,4]（阪大院基礎工[1]、産総研[2]、阪大院理[3]、分子研[4]）

34. **五員環および六員環からなるカーボンナノベルトの開殻性、芳香族性、第二超分極率のリングサイズ依存性の理論研究**
山根 正暉[1]、◯岸 亮平[1]、當波 孝凱[1]、岡田 健治[1]、永海 貴識[1]、中野 雅由[1,2]（阪大院基礎工[1]、分子研[2]）

35. **一次元３核ならびに５核ニッケル錯体の分子構造・電子状態と電気伝導性の相関に関する理論研究**
◯北河 康隆[1]、多田 隼人[1]、江良 伊織[1]、藤井 琢也[1]、池永 和輝[1]、中野 雅由[1,2]（阪大院基礎工[1]、分子研[2]）

36. 対称および非対称ビアントロン誘導体の開殻性、電荷の非対称性、非線形光学特性の立体構造依存性についての理論研究

◯北野　奨実[1]、岸　亮平[1]、平尾　泰一[2]、久保　孝史[2]、中野　雅由[1,3]（阪大院基礎工[1]、阪大院理[2]、分子研[3]）

37. テリレン二量体のシングレットフィッションにおける振電相互作用の理論的研究

◯永海　貴識[1]、當波　孝凱[1]、岡田　健治[1]、伊藤　聡一[2]、中野　雅由[1,2]（阪大院基礎工[1]、分子研[2]）

38. 摂動論的アプローチと量子マスター方程式アプローチによるペンタセン二量体モデルのシングレットフィッション速度配置依存性の比較

◯岡田　健治[1]、當波　孝凱[1]、永海　貴識[1]、中野　雅由[1,2]（阪大院基礎工[1]、分子研[2]）

39. 反芳香族環状縮環共役分子テトラシクロペンタテトラフェニレンの中性および二電子酸化還元状態における芳香族性、開殻性、非線形光学特性の理論研究

◯杉浦　亮介[1]、岸　亮平[1]、戸部　義人[2,3]、中野　雅由[1,4]（阪大院基礎工[1]、阪大産研[2]、台湾国立交通大[3]、分子研[4]）

40. 多変量解析に基づいたビピリジン配位子のフロンティア軌道エネルギー設計指針の構築とルテニウム(II)錯体への適用

○冨永　萌[1]、寺本　玲奈[1]、青木　笙悟[1]、北河　康隆[1]、中野　雅由[1,2]（阪大基礎工[1]、分子研[2]）

41. 超重元素 Rf の化学研究に向けた Zr, Th を含む錯体の量子化学計算

○渡邉　瑛介[1]、北河　康隆[2]、中野　雅由[2,3]、笠松　良崇[1]、篠原　厚[1]（阪大院理[1]、阪大院基礎工[2]、分子研[3]）

９．福井センターセミナー　ポスター・プログラム

第16回
福井センターセミナー
The 16th Fukui Center Seminar

2018年11月20日(火) 15:00–17:20
京都大学福井謙一記念研究センター1F 多目的室（Room: 1F 106)
http://www.fukui.kyoto-u.ac.jp/
〒606-8103 京都市左京区高野西開町34-4（℡075-711-7708)
(at FIFC, Kyoto Univ. on November, 20 (Tues.), 2018)

15:00–15:40　Satoshi Suzuki (FIFC)

“Theoretical understanding and rational design of aggregation induced emission molecule”

15:40–16:20　Masato Itami (FIFC)

“Singular behavior of time-averaged stress fluctuations on surfaces”

Break (10 min.)

16:30–17:20　Hiroshi Watanabe (Keio University)

“Development and applications of molecular dynamics simulation with the quantum chemical effect of solvent”

多数の方のご来場を歓迎いたします
We welcome all of you to join.

京都大学福井謙一記念研究センター　年報　2018

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