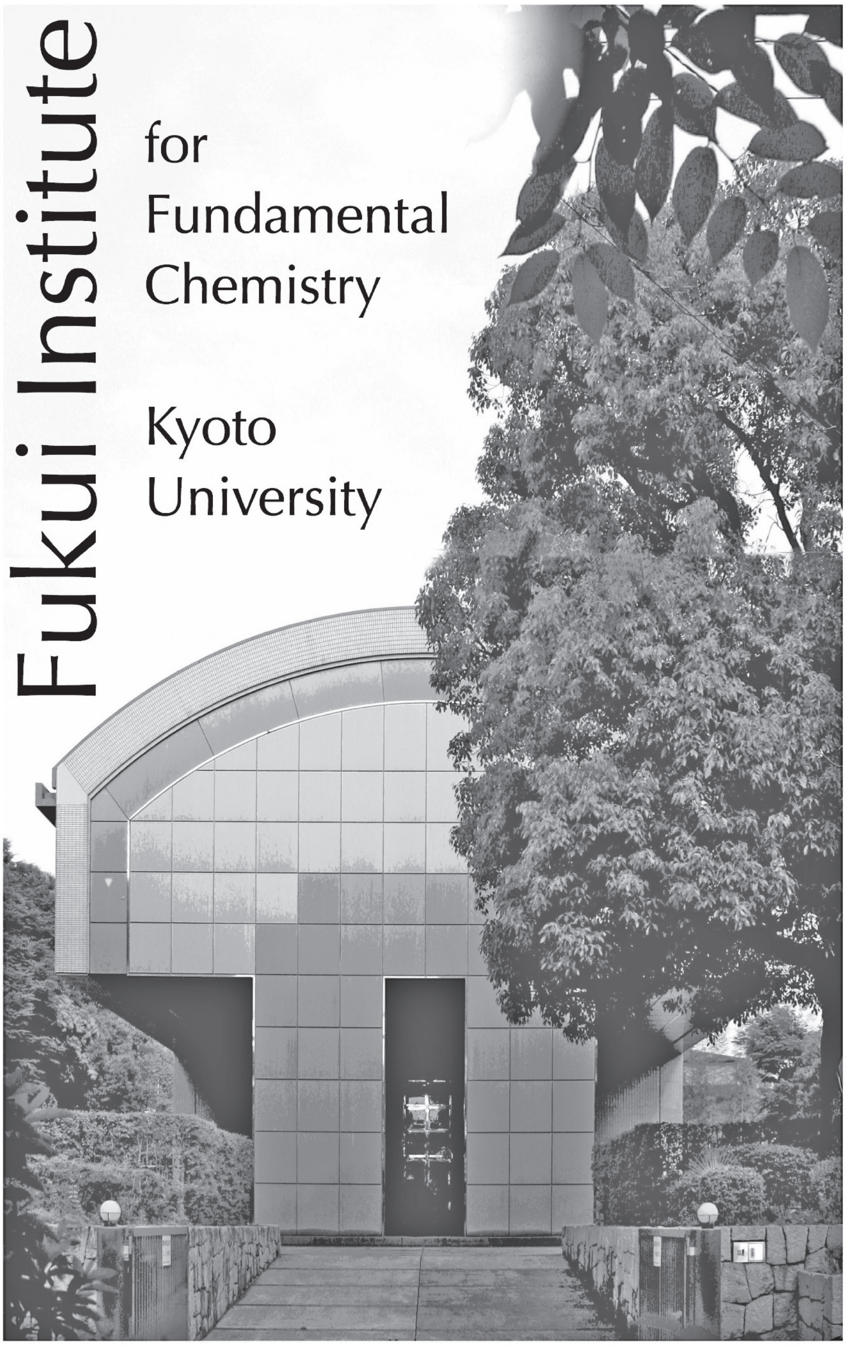
京都大学
福井謙一記念研究センター

Annual Report
2009

Fukui Institute for Fundamental Chemistry Kyoto University

年 報
2009



京都大学
福井謙一記念研究センター

はじめに

2009年度（平成21年度）の京都大学福井謙一記念研究センターの活動をまとめた年報をお届けします．当センターは，京都大学本部構内の北，約1キロの高野川沿いの静かな住宅街に独立して位置しております．専任教員は理論研究部門と総合研究部門に准教授各1名を持っているに過ぎませんが，センター長のほか，2名の副センター長と10名のスーパーバイザーとして工学研究科，理学研究科，化学研究所所属の教員にご協力頂いており，このメンバーが運営委員会を構成しています．そして優れた博士研究員に研究活動の機会を与える制度を持っており，若手研究者が国際的な雰囲気の中で日夜研究にいそしんでいます．この博士研究員のうち7名はセンターの雇用で，福井センターフェローと呼ばれ，自分自身のアイデアで一定期間，自由闊達に研究できる身分を保証しています．また福井謙一記念研究部第一のリサーチリーダーとして世界的な理論化学者の諸熊奎治先生（分子科学研究所名誉教授）を米国エモリー大学から招聘し，研究面でのリーダーシップを発揮して頂いております．諸熊先生は，科学技術振興機構の戦略的創造研究推進事業の予算で7名の博士研究員を採用され，全員がセンターで研究に励んでおられます（2010年（平成22年）7月現在）．さらに2009年度（平成21年度）には福井謙一記念研究部第二も設置し，名古屋大学名誉教授（前副学長）の大峯巖先生をリサーチリーダーとして招聘し，研究体制を拡大しました．私達は，センターが若手研究者の登竜門となることを期待しています．実際に，センターの博士研究員であった方々が京都大学准教授，名古屋大学特任准教授，Tartu大学（エストニア共和国）准教授，分子科学研究所助教（3名），Illinois工科大学客員助教，早稲田大学講師，九州大学助教，Northwestern大学研究員等として活躍されております．

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

福井謙一記念研究センターとなり，現在にいたっています．京都大学の部局となった後，森島 績，中辻 博，榊 茂好各先生にセンター長としてご指導を頂きました．

当センターは，国際活動も活発で，2005 年 (平成 17 年) よりチェコおよびスロバキアと理論化学・計算化学シンポジウムを定期的に開催しております．日本学術振興会・若手研究者交流支援事業として，タイ，シンガポール，ベトナム ，マレーシア，フィリピンの東アジア首脳会議参加国からの若手研究者招聘，ベルギーおよびロシアとの 2 国間共同研究も行っております．当センターは，今後も，理論化学・計算化学分野におけるわが国の窓口の役割を果たし，国際協力活動を展開して行きたいと考えております．

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

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

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

平成 22 年 7 月

京都大学福井謙一記念研究センター長
田中　功

目　　次

Ⅰ　専任教員・スーパーバイザー

Ⅱ　博士研究員

Ⅲ　研究広報活動

Ⅳ　研究業績

資料

Ⅰ専任教員・スーパーバイザー

１．教員組織

平成 21 年度

職名		氏名	備考
センター長		榊 茂好	工学研究科分子工学専攻
総合研究部門	副センター長	田中 功	工学研究科材料工学専攻
理論研究部門	副センター長	太田 隆夫	理学研究科物理学・宇宙物理学専攻
協議員	工学研究科長	大嶌 幸一郎	工学研究科材料化学専攻
	理学研究科長	吉川 研一	理学研究科物理学・宇宙物理学専攻
	化学研究所長	時任 宣博	化学研究所物質創製化学研究系
総合研究部門 スーパーバイザー	教授	赤木 和夫	工学研究科高分子化学専攻
	教授	今堀 博	物質－細胞統合システム拠点 （工学研究科分子工学専攻）
	教授	佐藤 直樹	化学研究所複合基盤化学研究系
	教授	杉野目 道紀	工学研究科合成・生物化学専攻
	教授	吉川 研一	理学研究科物理学・宇宙物理学専攻
理論研究部門 スーパーバイザー	教授	有賀 哲也	理学研究科化学専攻
	教授	加藤 重樹	理学研究科化学専攻 （平成 22 年３月 31 日逝去）
	教授	田中 文彦	工学研究科高分子化学専攻
	教授	山本 量一	工学研究科化学工学専攻
	准教授	高田 彰二	理学研究科生物科学専攻
総合研究部門	准教授	石田 俊正	専任 （工学研究科合成･生物化学専攻協力講座）
理論研究部門	准教授	佐藤 徹	専任 （工学研究科分子工学専攻協力講座）
福井謙一記念 研究部第一	リサーチ リーダー	諸熊 奎治	研究員（学術研究奨励）
福井謙一記念 研究部第二	リサーチ リーダー	大峯 巖	研究員（学術研究奨励）

２．教員プロフィール

（1）センター長

【氏名（ふりがな）】	榊　茂好　（さかき　しげよし）
【職名】	センター長、教授（平成21年度迄）
【所属】	工学研究科分子工学専攻
【研究室】	桂キャンパス　A4棟023号室
【直通電話】	075-383-2544
【FAX】	075-383-2799
【電子メールアドレス】	sakaki@moleng.kyoto-u.ac.jp
【ホームページ】	http://www.moleng.kyoto-u.ac.jp/~moleng_02/
【研究分野】	理論化学・計算化学
【現在の研究課題】	遷移金属元素を含む複合電子系の構造、電子状態、反応過程の理論化学
【研究内容キーワード】	電子状態理論・遷移金属錯体・反応解析・触媒作用・励起状態
【最終学歴】	1974年 3月　京都大学工学研究科燃料化学専攻博士課程単位取得退学
【学位】	1974年11月　工学博士（京都大学）
【略歴】	1975年4月　熊本大学工学部助手、1982年1月 同助教授、1990年4月　同教授を経て、2002年4月より京都大学工学研究科教授、現在に至る。
【在外研究歴】	1984年2月-1985年2月　仏国Strasbourg大学CNRS研究員
【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、American Chemical Society
【主な著書、学術論文】（過去5年以内）	1. A. Sugiyama, Y. -y. Ohnishi, M. Nakaoka, Y. Nakao, H. Sato, S. Sakaki, Y. Nakao, T. Hiyama, “Why Does Fluoride Anion Accelerate Transmetallation Between Vinylsilane and Palladium(II)-Vinyl Complex? Theoretical Study” J. Am. Chem. Soc., 130, 12975-12985 (2008). 2. Y. Ohnishi, Y. nakao, H. Sato, and S. Sakaki, “Frontier Orbital Consistent Quantum Capping Potential (FOC-QCP) for Bulky Ligand of Transition Metal Complexes”, J. Phys. Chem. A, 112, 1946-1955 (2008). 3. N. Nakatani, Y. Nakao, H. Sato, S. Sakaki, “Theoretical Study of Dioxygen Binding Process in Iron(III) Catechol Dioxygenase: “Oxygen Activation” vs. “Substrate Activation” J. Phys. Chem. B, 113, 4826-4836(2009). 4. N. Ochi, Y. Nakao, H. Sato, Y. Matano, H. Imahori, S. Sakaki, “New Palladium(II) Complex of P,S-Containing Hybrid Calixphyrin. Theoretical Study of Electronic Structure and Reactivity for Oxidative Addition”， J. Am. Chem. Soc., 131, 1955-10963 (2009). 5. A. Ishikawa, Y. Nakao, H. Sato, S. Sakaki, “Oxygen Atom Transfer Reactions of Iridium and Osmium Complexes: Theoretical Study of Characteristic Features and Significantly Large Differences Between These Two Complexes”, Inorg. Chem., 48, 8154-8163 (2009). 6. Y. Ohnishi, Y. Nakao, H. Sato, S. Sakaki, “A Theoretical Study of Nickel(0)-Catalyzed Phenylcyanation of Alkynes. Reaction Mechanism and Regioselectivity”， Organometallics, 28 (8), 2583-2594 (2009). 7. Y.-I. Korokawa, Y. nakao, S. Sakaki, “Bonding Nature of Open-Lantern-type Dinuclear Cr(II) Complexes. Theoretical Study with the MRMP2 Method” J. Phys. Chem. A, 113(13), 3202-3209 (2009).

(2) 副センター長

【氏名（ふりがな）】	田中　功（たなか　いさお）
【職名】	センター長、教授
【所属】	工学研究科　材料工学専攻
【研究室】	吉田キャンパス　工学部物理系校舎　量子材料学研究室
【直通電話】	075-753-5465
【FAX】	075-753-5447
【電子メールアドレス】	tanaka@cms.MTL.kyoto-u.ac.jp
【ホームページ】	http://cms.mtl.kyoto-u.ac.jp/tanaka.html
【研究分野】	材料科学
【現在の研究課題】	セラミックス基礎科学，計算材料科学
【研究内容キーワード】	量子材料設計，第一原理計算，電子ｴﾈﾙｷﾞｰ損失分光，Ｘ線吸収分光
【最終学歴】	1974年 3月　大阪大学大学院基礎工学研究科物理系専攻博士後期課程修了
【学位】	1987年 3月　大阪大学工学博士
【略歴】	1987年4月日本学術振興会特別研究員(PD)、1987年6月大阪大学産業科学研究所・助手、1993年4月京都大学工学部・助手、1996年5月京都大学大学院エネルギー科学研究科・助教授、2001年7月京都大学大学院工学研究科・助教授、2003年12月京都大学大学院工学研究科・教授
【在外研究歴】	1992年4月-1993年3月　ドイツ マックスプランク金属研究所・客員研究員（アレキサンダー・フォン・フンボルト財団奨学研究員）
【所属学会】	日本金属学会、日本セラミックス協会、日本鉄鋼協会，応用物理学会、American Ceramic Society、Materials Research Society
【学会活動】	*Journal of American Ceramics Society* フェロー・編集委員、*World Academy of Ceramics* 会員、*Journal of Physics : Condensed Matter* 編集委員、日本金属学会評議員
【主な著書、学術論文】（過去5年以内）	1. A. Seko, F. Oba, I. Tanaka, Classification of spinel structures based on first-principles cluster expansion analysis, *Phys. Rev. B* **81** (2010) 054114 2. A. Matsumoto, Y. Koyama, I. Tanaka, Structures and energetics of Bi_2O_3 polymorphs in a defective fluorite family derived by systematic first-principles lattice dynamics calculations, *Phys. Rev. B* **81** (2010) 094117 3. M. Choi, F. Oba, I. Tanaka, Role of Ti Antisitelike Defects in SrTiO3, *Phys. Rev. Lett*. **103** (2009) 185502 4. First-principles investigation of atomic structures and stability of proton-exchanged layered sodium titanate M. Mori, Y. Kumagai, K. Matsunaga, and I. Tanaka, *Phys. Rev. B* ,**79** (2009) 144117 5. W. Olovsson, I. Tanaka, T. Mizoguchi, P. Puschnig, and C. Ambrosch-Draxl, All-electron Bethe-Salpeter calculations for shallow-core x-ray absorption near-edge structures *Phys. Rev. B* **79**, (2009) 041102. 6. K. Yuge, A. Seko, Y. Koyama, F. Oba, and I. Tanaka, First-principles-based phase diagram of the cubic BNC ternary system *Phys. Rev. B* **77**, (2008) 094121 7. I. Tanaka and F. Oba, First principles calculations for modern ceramic science and engineering *J. Phys: Condens. Matter* **20**, (2008) 064215 8. A. Seko, A. Togo, F. Oba, and I. Tanaka, Structure and stability of a homologous series of tin oxides *Phys. Rev. Lett.* **100,** (2008) 045702
【学術関係の受賞】	ドイツ政府　フィリップ･フランツ･フォン･シーボルト賞（2008年） ルーマニア科学アカデミー　ドラゴミール・フルムゼスコ賞（2006年） 米国セラミックス学会 リチャード・フルラース賞（2004年）

【氏名（ふりがな）】	太田　隆夫　（おおた　たかお）
【職名】	教授
【所属】	福井謙一記念研究センター　理論研究部門
【研究室】	理学部5号館　422
【直通電話】	075-753-3740
【FAX】	075-753--3811
【電子メールアドレス】	takao@scphys.kyoto-u.ac.jp
【ホームページ】	http://www.ton.scphys.kyoto-u.ac.jp/nonlinear/
【研究分野】	相転移理論・非平衡系の統計物理学
【現在の研究課題】	非平衡ソフトマター物理学
【研究内容キーワード】	高分子共重合体・ミクロ相分離・共連結構造・パターン形成
【最終学歴】	1977年1月　京都大学大学院理学研究科物理学第一専攻博士課程修了
【学位】	1977年1月　理学博士（京都大学
【略歴】	1979年7月九州大学理学部助手、1987年8月お茶の水女子大学理学部助教授、1991年1月お茶の水女子大学理学部教授、1999年4月広島大学大学院理学研究科教授、2004年1月京都大学基礎物理学研究所教授、2006年7月京都大学大学院理学研究科教授
【在外研究歴】	1978年9月-1979年6月　米国Pittsburgh大学物理（David. Jansnow教授）（Mellon財団研究員）
【所属学会】	日本物理学会、中性子科学会、数理生物学会
【学会活動】	JPSJ Head Editor
【主な著書、学術論文】 （過去5年以内）	1. T. Ohkuma and T. Ohta, Deformable self-propelled particles with a global coupling, *Chaos* **20**, 023101(1-13) (2010) 2. T. Hiraiwa and T. Ohta, Viscoelasticity of a Single Semiflexible Polymer Chain, *Macromolecules* **42**, 7553-7562 (2009) 3. T. Ohta, T. Ohkuma and K. Shitara, Deformation of a self-propelled domain in an excitable reaction-diffusion system, *Phys. Rev*. **E 80**, 056203 (2009) 4. T. Sakaue and T. Ohta, Probing Nonequilibrium Fluctuations through Linear Response, *Phys. Rev.* **E 77**, 050102R (2008) 5. Y. Tonosaki, H. Tokuda, V. Zykov and T. Ohta, Phase Dynamics for Nonlinear Dissipative Waves under Symmetric Feedback, *Europhysics Letters* **83** 50011-1-6 (2008) 6. R. Tamate, K. Yamada, J. Vinals, and T. Ohta, Structural rheology of microphase separated diblock copolymers, *J. Phys. Soc. Jpn.*,**77** 034802 (2008) 7. M. Yanagisawa, M. Imai, T. Masui, S. Komura, Takao Ohta, Growth Dynamics of Domains in Ternary Fluid Vesicles, *Biophysical Journal* **92**, 115-125 (2007) 8. H. Shoji, K. Yamada, D. Ueyama and Takao Ohta, Turing patterns in three dimensions, *Phys. Rev.* **E 75**, 046212(13) (2007)
【学術関係の受賞】	アレキサンダー・フォン・フンボルト賞（2008年）

(3) スーパーバイザー

【氏名（ふりがな）】	赤木　和夫　（あかぎ　かずお）
【職名】	教授
【所属】	工学研究科高分子化学専攻
【研究室】	赤木研究室
【直通電話】	075-383-2595
【FAX】	075-383-2760
【電子メールアドレス】	akagi@fps.polym.kyoto-u.ac.jp
【ホームページ】	http://www.fps.polym.kyoto-u.ac.jp
【研究分野】	高分子化学、液晶化学、物質化学
【現在の研究課題】	導電性、液晶性、発光性、階層らせん性の共役系高分子の合成と性質
【研究内容キーワード】	導電性高分子、液晶性共役高分子、不斉液晶反応場、階層構造制御
【最終学歴】	京都大工学研究科博士後期課程
【学位】	工学博士
【略歴】	福井大工助手、筑波大物質工講師、助教授、教授、同大学院数理物質科学研究科教授、学際物質科学研究センター長
【在外研究歴】	カリフォルニ大学サンタバーバラ校交換研究員、コーネル大学客員研究員
【所属学会】	日本化学会、高分子学会、日本液晶学会、アメリカ化学会
【学会活動】	文部科学省科研費（特定領域研究、2005-2008）「次世代共役ポリマーの超階層制御と革新機能」領域代表、Chair of 18th Iketani Conference, International Conference on Control of Super-Hierarchical Structures and Innovative Functions of Next-Generation Conjugated Polymers (2008)、Chair of International Conference on Science and Technology of Synthetic Meatals (2010)
【主な著書、学術論文】 （過去5年以内）	1. H. Hayasaka, T. Miyashita, K. Tamura, K. Akagi, “Helically π-Stacked Conjugated Polymers Bearing Photoresponsive and Chiral Moieties in Side Chains: Reversible Photoisomerization-Enforced Switching between Emission and Quenching of Circularly Polarized Fluorescence”, *Adv. Func. Mater.*, **20**, 1243 (2010). 2. M. Goh, G. Piao, M. Kyotani, K. Akagi, “Cis-Rich Helical Polyacetylene Synthesized in Low-Temperature Chiral Nematic Liquid Crystal”, *Macromolecules*, **42**, 8590 (2009). 3. K. Akagi, “Helical Polyacetylene - Asymmetric Polymerization in a Chiral Liquid Crystal Field”, *Chem. Rev*., **109**, 5354 (2009). 4. T. Mori, T. Sato, M. Kyotani, K Akagi, “Macroscopically Aligned Helical Conjugated Polymers in Orientation-Controllable Chiral Nematic Liquid Crystal Field”, *Macromolecules*, **42**, 1817 (2009). 5. M. Kyotani, S. Matsushita, T. Nagai, Y. Matsui, M. Shimomura, A. Kaito. K. Akagi, “Helical Carbon and Graphitic Films Prepared from Iodine-Doped Helical Polyacetylene Film using Morphology-Retaining Carbonization”, *J. Am. Chem. Soc.*, **130**, 10880 (2008). 6. M. Goh, M. Kyotani, K. Akagi, “Highly Twisted Helical Polyacetylene with Morphology Free From Bundle of Fibrils Synthesized in Chiral Liquid Crystal Reaction Field”, *J. Am. Chem. Soc.*, **129**, 8519 (2007).
【学術関係の受賞】	日本化学会学術賞（1999年度）、日産科学賞（2000年度）、日本液晶学会賞論文賞（2001年度）、つくば賞（2001年度）、高分子学会賞（2002年度）、文部科学大臣表彰科学技術賞（2005年度）、筑波大学名誉教授称号授与（2009年度）、日本液晶学会賞業績賞（2010年度）

【氏名（ふりがな）】	今堀　博　（いまほり　ひろし）
【職名】	教授
【所属】	物質－細胞総合システム拠点（工学研究科　分子工学専攻）
【研究室】	桂キャンパス　A4棟　002号室
【直通電話】	075-383-2566
【FAX】	075-383-2571
【電子メールアドレス】	imahori@scl.kyoto-u.ac.jp
【ホームページ】	http://www.moleng.kyoto-u.ac.jp/~moleng_05/
【研究分野】	有機化学・光化学
【現在の研究課題】	人工光合成・有機太陽電池・ドラッグデリバリー
【研究内容キーワード】	ポルフィリン・フラーレン・ナノチューブ・自己組織化・電子移動
【最終学歴】	1990年3月　京都大学大学院理学研究科博士後期課程修了
【学位】	1990年3月　理学博士（京都大学）
【略歴】	1990年4月米国ソーク生物学研究所博士研究員、1992年4月大阪大学産業科学研究所助手、1999年11月大阪大学大学院工学研究科助教授、2001年12月科学技術振興機構さきがけ研究代表者（兼任）、2002年2月京都大学大学院工学研究科教授、2002年9月京都大学福井謙一記念研究センタースーパーバイザー（兼任）、2007年10月京都大学物質－細胞統合システム拠点教授
【所属学会】	日本化学会、光化学協会、米国化学会、米国電気化学会
【主な著書、学術論文】 （過去5年以内）	1. T. Sagawa, S. Yoshikawa, and H. Imahori, “1-D Nanostructured Semiconducting Materials for Organic Photovoltaics,” *J. Phys. Chem. Lett*. (Perspective), **1**, 1020-1025 (2010). 2. H. Imahori, T. Umeyama, and S. Ito, “Large π Aromatic Molecules as Potential Sensitizers in Dye-Sensitized Solar Cells,” *Acc. Chem. Res.* **42**, 1809-1818 (2009). 3. Y. Matano and H. Imahori, “Phosphole-Containing Calixpyrroles, Calilxphyrins, and Porphyrins: Synthesis and Coordination Chemistry,” *Acc. Chem. Res.* **42,** 1193-1204 (2009). 4. H. Imahori, T. Umeyama, “Donor-Acceptor Nanoarchitecture on Semiconducting Electrodes for Solar Energy Conversion,” *J. Phys. Chem. C* (Feature Article), **113**, 9029-9039 (2009). 5. A. Kira, T. Umeyama, Y. Matano, K. Yoshida, S. Isoda, J.-K. Park, D. Kim, H. Imahori, “Supramolecular Donor-Acceptor Heterojunctions by Vectorial Stepwise Assembly of Porphyrins and Coordination-Bonded Fullerene Arrays for Photocurrent Generation,” *J. Am. Chem. Soc.*, **131**, 3198-3200 (2009).
【学術関係の受賞】	1. 2004年光化学協会賞 2. 2006年日本学術振興会賞 3. 2006年日本化学会学術賞 4. 2007年東京テクノ・フォーラム21ゴールド・メダル賞 5. 2007年大阪科学賞 6. 2007年ナイスステップ研究者

【氏名（ふりがな）】	佐藤　直樹　（さとう　なおき）
【職名】	教授
【所属】	化学研究所　複合基盤化学研究系　分子集合解析研究領域
【研究室】	宇治キャンパス化学研究所本館 N-324C号室
【直通電話】	0774-38-3080
【FAX】	0774-38-3084
【電子メールアドレス】	naokis@e.kuicr.kyoto-u.ac.jp
【ホームページ】	http://www.kuicr.kyoto-u.ac.jp/labos/is2/scope_J.html
【研究分野】	有機物性化学
【現在の研究課題】	有機結晶・薄膜の構造・電子構造・電子物性の相関研究
【研究内容キーワード】	有機半導体・有機薄膜・分子集合体・電子分光・界面物性・分子系構築
【最終学歴】	1976年3月　東京大学大学院理学系研究科化学専門課程修士課程修了
【学位】	1983年3月　理学博士（東京大学）
【略歴】	1976年4月分子科学研究所分子集団研究系技官、1984年4月熊本大学理学部助手、1987年4月東京大学教養学部助教授、1992年5月京都大学化学研究所教授
【在外研究歴】	1989年5月-7月 スウェーデンLinköping大学物理学科（William R. Salaneck教授）（Visiting Scholar）
【所属学会】	日本化学会、日本物理学会、日本分光学会、分子科学学会
【学会活動】	日本化学会有機結晶部会長、日本化学会有機結晶ディビジョン主査、分子科学会運営委員
【主な著書、学術論文】 （過去5年以内）	1. R. Murdey, N. Sato and M. Bouvet, Frontier electronic structures in fluorinated copper phthalocyanine thin films studied using ultraviolet and inverse photoemission spectroscopies, *Mol. Cryst. Liq. Cryst.* **455** (2006) 211-218. 2. H. Yoshida, K. Inaba and N. Sato, X-ray diffraction reciprocal space mapping study of the thin film phase of pentacene, *Appl. Phys. Lett.* **90** (2007) 181930. 3. H. Yoshida and N. Sato, The crystallographic and electronic structures of three different polymorphs of pentacene, *Phys. Rev. B* **77** (2008) 235205. 4. T. Hiramatsu, T. Sasamori, H. Yoshida, N. Tokitoh and N. Sato, Reversible polymorphic crystalline transition of a push-pull-type molecule: {4-[4,5-bis(methylsulfanyl)-1,3-dithiol-2-ylidene]cyclohexa-2,5-dien-1-ylidene}malononitrile (BMDCM), *J. Mol. Struct.* **922** (2009) 30-34. 5. R. Murdey, M. Bouvet, M. Sumimoto, S. Sakaki and N. Sato, Direct observation of the energy gap in lutetium bisphthalocyanine thin films, *Synth. Met.* **159** (2009) 1677-1681. 6. J. Tsutsumi, H. Yoshida, R. Murdey, S. Kato and N. Sato, An accurate calculation of electronic contribution to static permittivity tensor for organic molecular crystals on the basis of the charge response kernel theory, *J. Phys. Chem. A* **113** (2009) 9207-9212. 7. J. Tsutsumi, H. Yoshida, R. Murdey and N. Sato, Spontaneous buildup of surface potential with a thin film of a zwitterionic molecule giving non-centrosymmetric crystal structure, *Appl. Phys. Lett.* **95** (2009) 182901.
【学術関係の受賞】	1985年4月日本化学会（第34回）進歩賞受賞

【氏名（ふりがな）】	杉野目　道紀　（すぎのめ　みちのり）
【職名】	教授
【所属】	工学研究科　合成・生物化学専攻
【研究室】	桂キャンパス　A4棟　306号室
【直通電話】	075-383-2723
【FAX】	075-383-2722
【電子メールアドレス】	suginome@sbchem.kyoto-u.ac.jp
【ホームページ】	http://www.sbchem.kyoto-u.ac.jp/suginome-lab/
【研究分野】	有機合成化学・有機元素化学・精密高分子合成
【現在の研究課題】	有機ホウ素化合物の新合成法開拓・光学活性らせん高分子の化学
【研究内容キーワード】	遷移金属触媒，有機ホウ素化合物，有機ケイ素化合物，不斉重合
【最終学歴】	1993年3月　京都大学大学院工学研究科合成化学専攻博士課程修了
【学位】	1993年3月　京都大学博士（工学）
【略歴】	1993年5月京都大学工学部助手、2002年6月京都大学大学院工学研究科助教授、2004年2月京都大学大学院工学研究科教授
【在外研究歴】	1998年9月-1999年8月　米国Massachusetts Institute of Technology（Gregory C. Fu教授）（文部省在外研究員（若手））
【所属学会】	日本化学会、高分子学会、有機合成化学協会，ケイ素化学協会、American Chemical Society
【主な著書、学術論文】（過去5年以内）	1. T. Yamamoto, M. Suginome, “High-Molecular-Weight Polyquinoxaline-Based Helically Chiral Phosphine (PQXphos) as Chirality-Switchable, Reusable, and Highly Enantioselective Monodentate Ligand in Catalytic Asymmetric Hydrosilylation of Styrenes,” *J. Am. Chem. Soc.* **132**, 7899 (2010). 2. N. Iwadate, M. Suginome, “Differentially Protected Diboron for Regio-selective Diboration of Alkynes: Internal-Selective Cross-Coupling of 1-Alkene-1,2-diboronic Acid Derivatives,” *J. Am. Chem. Soc.* **132**, 2548 (2010). 3. T. Ohmura, K. Masuda, I. Takase, M. Suginome “Palladium-Catalyzed Silylene-1,3-Diene [4+1] Cycloaddition with Use of (Aminosilyl)boronic Esters as Synthetic Equivalents of Silylene,” *J. Am. Chem. Soc.* **131,** 16624 (2009). 4. H. Ihara, M. Suginome, “Easily Attachable and Detachable ortho-Directing Agent for Arylboronic Acids in Ruthenium-Catalyzed Aromatic C-H Silylation,” *J. Am. Chem. Soc.* **131**, 7502 (2009). 5. M. Daini, A. Yamamoto, M. Suginome, “Palladium-Catalyzed trans- and cis-Carboboration of Alkynes Tethered to Chloroborane with Organozirconium Reagents: Ligand-Dependent Complementary Stereoselectivity,” *J. Am. Chem. Soc.* **130,** 2918 (2008). 6. H. Noguchi, K. Hojo, M. Suginome, “Boron-Masking Strategy for the Selective Synthesis of Oligoarenes via Iterative Suzuki-Miyaura Coupling,” *J. Am. Chem. Soc.* **129**, 758 (2007).
【学術関係の受賞】	平成10年度日本化学会進歩賞、平成13年度ケイ素化学協会奨励賞、平成17年Nagoya Silver Medal、平成17年Mukaiyama Award、平成21年度日本学術振興会賞

【氏名（ふりがな）】	吉川　研一　（よしかわ　けんいち）
【職名】	教授
【所属】	理学研究科　物理学・宇宙物理学専攻
【研究室】	理学研究科　吉川研究室
【直通電話】	075-753-3749
【FAX】	075-753-3779
【電子メールアドレス】	yoshikaw@scphys.kyoto-u.ac.jp
【ホームページ】	http://www.yklab.jp/
【研究分野】	非線形科学・生命物理学
【現在の研究課題】	1）非平衡開放系での時間的・空間的秩序の自発的生成に関する研究 2）生命現象の物理学
【研究内容キーワード】	非平衡開放系・時空間的秩序の自己生成・自己組織化・高分子物理学
【最終学歴】	1976年5月　京都大学大学院工学研究科博士課程修了
【学位】	1976年5月　工学博士（京都大学）
【略歴】	1976年10月徳島大学教養部講師、1979年4月徳島大学教養部助教授、1988年4名古屋大学教養部助教授、1990年11月名古屋大学教養部教授、1991年4月名古屋大学大学院人間情報学研究科教授、1998年4月京都大学大学院理学研究科教授、2002年9月京都大学福井謙一記念研究センター兼任教授（現在に至る）、1998年10月～1999年6月Universite Louis Pasteur客員教授、2009年2月 ENS, Paris 客員教授
【在外研究歴】	長期のものはなし
【所属学会】	物理学会、日本化学会、生物物理学会など
【学会活動】	Vice Chair, Commission C-6, International Union of Pure and Applied Physics など
【主な著書、学術論文】 （過去5年以内）	1. M.Horning, A.Isomura, K.Agladze, K.Yoshikawa, “Liberation of a pinned spiral wave by a single stimulus in excitable media”, *Phys. Rev. E,* 79, 026218(2009). 2. T.Saito, T.Iwaki, K.Yoshikawa, “Small anion with higher valency retards the compaction of DNA in the presence of multivalent cation”, *Biophys. J.*, 96, 1068(2009). 3. A. Estevez, C. Crozatier, A. Diguet, T. Hara, H. Saito, K. Yoshikawa and D. Baigl, “ Sequence-independent and reversible photocontrol of transcription/expression systems using a photosensitive nucleic acid binder”, *Proc.Natl.Acad. Sci.*, 106, 12219(2009). 4. M. Negishi, T. Sakaue and K. Yoshikawa,” Mismatch of bulk viscosity reduces interfacial diffusivity at an aqueous/oil system”, *Phys. Rev. E*, 81, 020901(2010). 5. M. Takinoue, Y. Atsumi and K. Yoshikawa, “Rotary motion driven by a direct current electric field”, *Appl. Phys. Lett.*, 96, 104105(2010).
【学術関係の受賞】	日本IBM科学賞（1991）

【氏名（ふりがな）】	有賀 哲也 （あるが てつや）
【職名】	教授
【所属】	理学研究科 化学専攻
【研究室】	理学研究科 6号館 271号室
【FAX】	075-753-4000
【電子メールアドレス】	aruga@kuchem.kyoto-u.ac.jp
【ホームページ】	www://kuchem.kyoto-u.ac.jp/hyoumen/
【研究分野】	表面物性化学
【現在の研究課題】	表面伝導電子のスピン軌道相互作用・表面相転移
【研究内容キーワード】	表面Peierls転移・Rashba効果・スピン流
【最終学歴】	1986年3月 東京大学大学院理学系研究科化学専門課程博士課程修了
【学位】	1986年3月 理学博士（東京大学）
【略歴】	1986年4月東京大学理学部助手、1992年10月東京大学理学部講師、1993年7月京都大学理学部助教授、2004年2月京都大学大学院理学研究科教授
【所属学会】	日本化学会、日本物理学会、日本表面科学会、真空協会
【学会活動】	1996-1997 日本化学会近畿支部幹事、2000-2001 日本物理学会領域9世話人
【主な著書、学術論文】（過去5年以内）	1. “Large Rashba spin splitting of a metallic surface-state band on a semiconductor surface”, K. Yaji, Y. Ohtsubo, S. Hatta, H. Okuyama, K. Miyamoto, T. Okuda, A. Kimura, H. Namatame, M. Taniguchi, and T. Aruga, Nat. Commun. 1:17 doi: 10.1038/ncomms1016 (2010). 2. “Large Rashba spin splitting of surface resonance bands on semiconductor surface”, S. Hatta, T. Aruga, Y. Ohtsubo and H. Okuyama, *Phys. Rev. B* **80,** 113309 (2009). 3. “Direct observation of hydrogen-bond exchange within a single water dimer”, T. Kumagai, M. Kaizu, S. Hatta, H. Okuyama, T. Aruga, I. Hamada, and Y. Morikawa, *Phys. Rev. Lett.* **100,** 166101 (2008). 4. “Band structure of Tl/Ge(111)-(3 × 1) : Angle-resolved photoemission and first-principles prediction of giant Rashba effect”, Shinichiro Hatta, Tetsuya Aruga, Chihiro Kato, Shin Takahashi, Hiroshi Okuyama, Ayumi Harasawa, Taichi Okuda, and Toyohiko Kinoshita, *Phys. Rev. B* 77, 245436 (2008) 5. “Surface Peierls transition on Cu(001) covered with heavier p-block metals”, T. Aruga, *Surf. Sci. Rep.* **61,** 283-302 (2006).

【氏名（ふりがな）】	加藤　重樹　（かとう　しげき）
【職名】	教授
【所属】	理学研究科　化学専攻
【研究室】	理学研究科
【直通電話】	075-753-4004
【FAX】	075-753-4000
【電子メールアドレス】	shigeki@kuchem.kyoto-u.ac.jp
【ホームページ】	http://kuchem.kyoto-u.ac.jp/riron/index.html
【研究分野】	理論化学、化学反応理論
【現在の研究課題】	化学反応ダイナミックスについての理論的研究
【最終学歴】	1976年　京都大学大学院工学研究科石油化学専攻博士課程修了
【学位】	1976年　工学博士（京都大学）
【略歴】	1977年分子科学研究所理論研究系助手、 1984年名古屋大学教養部助手、 1985年名古屋大学教養部講師、 1986年東京大学教養学部助教授、 1990年京都大学理学部教授
【所属学会】	日本化学会、高分子学会、日本液晶学会、日本MRS、アメリカ化学会
【主な著書、学術論文】 （過去5年以内）	1. Yamamoto, Takeshi; Kato, Shigeki. Ab initio calculation of proton-coupled electron transfer rates using the external-potential representation: A ubiquinol complex in solution. *Journal of Chemical Physics* (2007), **126**(22), 224514/1-224514/15. 2. Higashi, Masahiro; Hayashi, Shigehiko; Kato, Shigeki. Geometry optimization based on linear response free energy with quantum mechanical/molecular mechanical method: applications to Menshutkin-type and Claisen rearrangement reactions in aqueous solution. *Journal of Chemical Physics* (2007), **126**(14), 144503/1-144503/10. 3. Higashi, Masahiro; Hayashi, Shigehiko; Kato, Shigeki. Transition state determination of enzyme reaction on free energy surface: Application to chorismate mutase. *Chemical Physics Letters* (2007), **437**(4-6), 293-297. 4. Minezawa, Noriyuki; Kato, Shigeki. Efficient implementation of three-dimensional reference interaction site model self-consistent-field method: application to solvatochromic shift calculations. *Journal of Chemical Physics* (2007), **126**(5), 054511/1-054511/15. 5. Yamazaki, Shohei; Kato, Shigeki. Solvent Effect on Conical Intersections in Excited-State 9H-Adenine: Radiationless Decay Mechanism in Polar Solvent. *Journal of the American Chemical Society* (2007), **129**(10), 2901-2909.
【学術関係の受賞】	1992年日本IBM科学賞

【氏名（ふりがな）】	田中　文彦　（たなか　ふみひこ）
【職名】	教授
【所属】	工学研究科　高分子化学専攻
【研究室】	桂キャンパス　A3棟　113号室
【直通電話】	075-383-2705
【FAX】	075-383-2705
【電子メールアドレス】	ftanaka@phys.polym.kyoto-u.ac.jp
【ホームページ】	http://www.phys.polym.kyoto-u.ac.jp
【研究分野】	高分子物理学，統計力学
【現在の研究課題】	高分子溶液の相転移とレオロジー
【研究内容キーワード】	高分子水溶液・テレケリック会合高分子・ゾル-ゲル転移
【最終学歴】	1976年3月　東京大学理学系大学院物理学専攻博士課程修了
【学位】	1976年3月　理学博士（東京大学）
【略歴】	1976年4月東京大学理学部助手、1981年4月東京農工大学一般教育部助教授、1994年4月同教授、1995年4月同工学部教授、1997年4月京都大学工学研究科教授
【在外研究歴】	1978年10月-1980年3月英国Cambridge大学Cavendish研究所（S.F.Edwards教授）博士研究員、1990年4月-1991年3月　同（文部省在外研究員）
【所属学会】	高分子学会、日本物理学会、日本レオロジー学会、日本化学会、American Chemical Society
【主な著書、学術論文】（過去5年以内）	1. K. Kojima, F. Tanaka, *Cooperative Hydration Inuces Discontinuous Volume Phase Transition of Cross-Linked PolyNIPAM Gels in Water*, Macromolecules **43**(11), (2010) 5103-5113. 2. F. Tanaka, *Transient Network Theory of Wormlike Micelles: Topological Force Accelerates Relaxation,* Langmuir 26(8), (2010) 5374-5381. 3. T. Koga and F. Tanaka, T*heoretical Predictions on Normal Stresses under Shear Flow in Transient Networks of Telechelic Associating Polymers,* Macromolecules **43**(6), (2010) 3052-3060. 4. F.Tanaka, T.Koga H.Kojima and F.M.Winnik, *Temperature- and Tension-Induced Coil-Globule Transition of PolyNIPAM Chains*, Macromolecules, **42**(4) (2009) 1321-1330. 5. F.Tanaka, “Polymer Physics---Application to Molecular Association and Thermoreversible Gelation”, Cambridge Univ. Press (2011) pp.450
【学術関係の受賞】	高分子学会賞（科学）（平成13年度）

【氏名（ふりがな）】	山本　量一　（やまもと　りょういち）
【職名】	教授
【所属】	工学研究科　化学工学専攻
【研究室】	桂キャンパス　A棟118号室
【直通電話】	075-383-2661
【FAX】	075-383-2651
【電子メールアドレス】	ryoichi@cheme.kyoto-u.ac.jp
【ホームページ】	http://www-tph.cheme.kyoto-u.ac.jp/
【研究分野】	ソフトマターの移動現象
【現在の研究課題】	コロイド分散系の計算機シミュレーション
【研究内容キーワード】	ソフトマター、コロイド、計算機シミュレーション、ガラス転移
【最終学歴】	1992年3月　神戸大学大学院 工学研究科修士課程化学工学専攻修了
【学位】	1996年3月　博士（工学）京都大学
【略歴】	1994年9月 神戸大学大学院自然科学研究科物質科学専攻助手、1996年3月 京都大学大学院理学研究科物理学・宇宙物理学専攻助手、2000年1月 同講師、2004年10月 京都大学大学院工学研究科化学工学専攻助教授、2007年4月 同准教授、2008年10月 同教授
【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））
【所属学会】	日本物理学会、化学工学会、高分子学会、分子シミュレーション研究会、日本液晶学会、紛体工学会、日本レオロジー学会
【主な著書、学術論文】（過去5年以内）	1. H. Kobayashi and R. Yamamoto, Tumbling motion of a single chain in shear flow: a crossover from Brownian to non-Brownian behavior, *Phys. Rev. E,* **81**, 041807 (2010). 2. S. Yasuda and R. Yamamoto, Multiscale modeling and simulation for polymer melt flows between parallel plates, *Phys. Rev. E* **81,** 036308 (2010). 3. Shugo Yasuda and Ryoichi Yamamoto, Rheology of a supercooled polymer melt near an oscillating plate: an application of multiscale modeling, *Europhys. Lett. (EPL),* **86,** 18002 (2009). 4. Takuya Iwashita and Ryoichi Yamamoto, Short-time motion of Brownian particles in a shear flow, Phys. Rev. E, 79, 031401 (2009). 5. Shugo Yasuda and Ryoichi Yamamoto, A Model for Hybrid Simulations of Molecular Dynamics and Computational Fluid Dynamics, *Phys. Fluids,* **20**, 113101 (2008). 6. Kang Kim, Yasuya Nakayama and Ryoichi Yamamoto, Direct Numerical Simulations of Electrophoresis, *Phys. Rev. Lett.*, **96**, 208302 (2006).
【学術関係の受賞】	12007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

【氏名（ふりがな）】	高田　彰二　（たかだ　しょうじ）
【職名】	准教授
【所属】	理学研究科　生物科学専攻　生物物理学教室
【研究室】	理学部1号館205号室
【直通電話】	075-753-4220
【FAX】	075-753-4222
【電子メールアドレス】	takada@biophys.kyoto-u.ac.jp
【ホームページ】	http://theory.biophys.kyoto-u.ac.jp
【研究分野】	理論生物物理学
【現在の研究課題】	生体分子の構造機能についての理論およびコンピュータシミュレーション研究
【研究内容キーワード】	タンパク質、分子モーター、分子動力学、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
【学位】	1994年3月　理学博士（総合研究大学院大学）
【略歴】	1991年～ 1995年岡崎国立共同研究機構技官（分子科学研究所）、1995年～ 1998年日本学術振興会研究員（イリノイ大学化学科）、1998年～ 2001年神戸大学理学部化学科講師、2001年～ 2007年神戸大学理学部化学科助教授、2007年～京都大学理学研究科生物科学専攻生物物理教室准教授。
【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、日本物理学会
【主な著書、学術論文】 （過去5年以内）	1. Wenfei Li and Shoji Takada, Self-learning multiscale simulation for achieving high accuracy and high efficiency simultaneously, *Journal of Chemical Physics,* **130**: 214108(6 pages), 2009 2. Naoto Hori, George Chikenji, R. Stephen Berry, and Shoji Takada, Folding energy landscape and network dynamics of small globular proteins, *Proceedings of the National Academy of Sciences USA,* **106**: 73-78, 2009 3. Kei-ichi Okazaki, and Shoji Takada, Dynamic energy landscape view of coupled binding and protein conformational change: Induced-fit versus population-shift mechanisms, *Proceedings of the National Academy of Sciences USA,* **105**: 11182-11187, 2008. 4. Kei-ichi Okazaki, Nobuyasu Koga, Shoji Takada, Jose N Onuchic, and Peter G Wolynes, Multiple-basin energy landscapes for large amplitude conformational motions of proteins: Structure-based molecular dynamics simulations, *Proceedings of the National Academy of Sciences USA,* **103**(No.32):11844-11849, 2006. 5. Nobuyasu Koga and Shoji Takada, Folding-based molecular simulations reveal mechanisms of the rotary motor F1-ATPase, *Proceedings of the National Academy of Sciences USA,* **103**(No.14):5367-5372, 2006.

（4）専任教員

【氏名（ふりがな）】	石田　俊正　（いしだ　としまさ）
【職名】	准教授
【所属】	福井謙一記念研究センター　総合研究部門
【研究室】	福井記念研究センター 205
【直通電話】	075-711-7838
【FAX】	075-711-7838
【電子メールアドレス】	ishida@fukui.kyoto-u.ac.jp
【ホームページ】	http://www.fukui.kyoto-u.ac.jp/~ishida
【研究分野】	計算化学・理論化学
【現在の研究課題】	光機能分子の反応・ポテンシャル面生成法
【研究内容キーワード】	光機能分子・ポテンシャル面・非断熱遷移
【最終学歴】	1989年3月　東京大学理学系大学院相関理化学専攻博士課程修了
【学位】	1989年3月　理学博士（東京大学）
【略歴】	1989年4月　静岡大学教養部助手、1995年4月静岡大学教養部助教授、1995年10月静岡大学工学部助教授、2002年4月岡崎国立共同研究機構分子科学研究所助教授（流動部門）、2004年4月静岡大学工学部助教授、2004年10月京都大学福井謙一記念研究センター助教授、2007年4月同准教授
【在外研究歴】	1996年4月-1997年3月　米国Northwestern大学化学（George C. Schatz教授）（文部省在外研究員（若手））
【所属学会】	日本化学会、日本分子化学会、日本コンピュータ化学会、American Physical Society
【主な著書、学術論文】 （過去5年以内）	1. Toshimasa Ishida, Hideaki Kanno, Jun-ichi Aihara “Kinetic Stability of Gold Fullerenes and the $2(N+1)^2$ Rule”, *Bull. Chem. Soc. Jpn.,* **80**(11), 2145-2148(2007). 2. T. Ishida, H. Kanno and J. Aihara, “Magnetic Resonance Energies of Polycyclic Aromatic Hydrocarbon Molecular Ions”, *Polish J. Chem.*, **81**, 699-710 (2007). 3. Hiroshi Kohguchi, Toshinori Suzuki, Shinkoh Nanbu, Toshimasa Ishida, Gennady V. Mil’nikov, Ponmile Oloyede, Hiroki Nakamura, “Collision Energy Dependence of the O(^{1}D) + HCl → OH + Cl(^{2}P) Reaction Studied by Crossed Beam Scattering and Quasiclassical Trajectory Calculations on ab initio Potential Energy Surfaces”, *J. Phys. Chem. A* **112**(5), 818-825 (2008). 4. Toshimasa Ishida, Shinkoh Nanbu, and Hiroki Nakamura, Non-adiabatic ab initio dynamics of two models of Schiff base retinal J. *Phys. Chem. A,* **113**(16), 4356-4366 (2009). 5. Toshimasa Ishida and Jun-ichi Aihara, Aromaticity of neutral and doubly charged polyacenes, *Phys. Chem. Chem. Phys.* **11**, 7197 - 7201 (2009)

【氏名（ふりがな）】	佐藤　徹（さとう　とおる）
【職名】	准教授
【所属】	福井謙一記念研究センター　理論研究部門
【研究室】	桂キャンパス　A4棟　203号室
【電話】	075-383-2803
【FAX】	075-383-2555
【電子メールアドレス】	tsato@scl.kyoto-u.ac.jp
【ホームページ】	http://www.moleng.kyoto-u.ac.jp/~moleng_10/index_J.html
【研究分野】	理論化学・物理化学
【現在の研究課題】	振電相互作用、単一分子伝導、量子輸送現象
【研究内容キーワード】	Jahn-Teller 効果・フラーレン・ナノチューブ・有機EL
【最終学歴】	1997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】	1997年3月 京都大学博士（工学）
【略歴】	1998年1月 京都大学大学院工学研究科助手、 2004年1月 京都大学福井謙一記念研究センター助教授、 2007年4月 京都大学福井謙一記念研究センター准教授
【在外研究歴】	2003年10月-2004年9月ベルギー王国 Leuven カトリック大学化学（Arnout Ceulemans 教授）（文部省在外研究員（若手））
【所属学会】	日本化学会、日本物理学会、応用物理学会、フラーレンナノチューブ学会、日本コンピュータ化学会
【学会活動】	日本化学会、学会賞等支部推薦委員
【主な著書、学術論文】（過去5年以内）	1. Tohru Sato, Ken Tokunaga, and Kazuyoshi Tanaka, “Vibronic coupling in naphthalene anion: Vibronic coupling density analysis for totally symmetric modes”, *J. Phys. Chem. A* **112,** 758-767 (2008). 2. Tohru Sato and Arnout Ceulemans, “Vibronic and spin-orbit coupling of a d 9 transition-metal ion encapsulated in an icosahedral cage: The $(\Gamma_8+\Gamma_9)\times(g+2h)$ Jahn-Teller problem”, *J. Chem. Phys.* **126,** 184501 (2007) 3. Tohru Sato, Ken Tokunaga, and Kazuyoshi Tanaka, “Vibronic Coupling in Cyclopentadienyl Radica l: A Method for Calculation of Vibronic Coupling Constant and Vibronic Coupling Density Analysis”, *J. Chem. Phys.* **124**, 024314 1-12 (2006). 4. Tohru Sato, Liviu F. Chibotaru, and Arnout Ceulemans, “The E \otimes e dynamic Jahn-Teller problem: A new insight from the strong coupling limit”, *J. Chem. Phys.* **122,** 054104 1-12 (2005).. 5. Ken Tokunaga, Tohru Sato, and Kazuyoshi Tanaka,, “Vibronic coupling in benzene cation and anion:Vibronic coupling and frontier electron density in Jahn-Teller molecules”, *J. Chem. Phys.* **124***,* 154303 1-10 (2006).

(5) リサーチリーダー

【氏名（ふりがな）】	諸熊　奎治　（もろくま　けいじ）
【職名】	リサーチリーダー
【所属】	福井謙一記念研究センター　福井謙一記念研究部門第一
【研究室】	福井謙一記念研究センター 202
【直通電話】	075-711-7843
【FAX】	075-781-4757
【電子メールアドレス】	morokuma@fukui.kyoto-u.ac.jp
【ホームページ】	http://www.fukui.kyoto-u.ac.jp/~morokuma; http://kmweb.fukui.kyoto-u.ac.jp/
【研究分野】	理論化学・計算化学
【現在の研究課題】	複雑分子系の複合分子理論によるシミュレーション
【研究内容キーワード】	複合分子理論。複雑分子系、シミュレーション、ナノ構造、酵素反応
【最終学歴】	1962年3月　京都大学大学院工学研究科博士課程単位修得退学
【学位】	1963年3月　工学博士（京都大学）
【略歴】	1962年4月京都大学工学部助手、1964年9月Columbia大学客員助教授、1966年9月Harvard大学博士研究員、1967年9月Rochester大学助教授、1971年9月同教授、1976年12月分子科学研究所教授、1993年1月Emory大学William H. Emerson教授、2006年9月Emory大学William H. Emerson名誉教授、2006年9月京都大学福井謙一記念研究センターリサーチリーダー
【所属学会】	日本化学会、American Chemical Society、American Physical Society, 分子科学会
【主な著書、学術論文】 （過去5年以内）	過去５年間に約１２０報 1. S. Sekharan, A. Altun, and K. Morokuma, Photochemistry of Visual Pigment in a Gq-coupled GPCR-Insights from Structural and Spectral Tuning Studies on Squid Rhodopsin, *Chem. Eur. J.* **16**, 1744-1749 (2010). 2. X. Li, L. W. Chung, H. Mizuno, A. Miyawaki and K. Morokuma, A Theoretical Study on the Natures of the On- and Off-States of Reversibly Photoswitching Fluorescent Protein Dronpa: Absorption, Emission, Protonation and Raman, *J. Phys. Chem. B,* **114**, 1114-1126 (2010). 3. H. Hirao and K. Morokuma, Insights into the (Superoxo)Fe(III)Fe(III) Intermediate and Reaction Mechanism of myo-Inositol Oxygenase: DFT and ONIOM(DFT:MM) Study, *J. Am. Chem. Soc.* **131**,17206-17214 (2009). 4. A. J. Page, Y. Ohta, Y. Okamoto, S. Irle, and K. Morokuma, Defect Healing during Single-Walled Carbon Nanotube Growth: A Density-Functional Tight-Binding Molecular Dynamics Investigation. *J. Phys. Chem. C.* **113,** 20198-20207 (2009). 5. B. Saha, S. Shindo, S. Irle and K. Morokuma, Quantum Chemical Molecular Dynamics Simulations of Dynamic Fullerene Self-Assembly in Benzene Combustion, ACS Nano 3, 2241-2257 (2009). Errata, ACS Nano, 4, 583-583 (2010). 6. S. Maeda, K. Ohno, and K. Morokuma,, Automated Global Mapping of Minimal Energy Points on Seams of Crossing by the Anharmonic Downward Distortion Following Method: A Case Study on H_2CO, *J. Phys. Chem. A,* **113**, 1704-1710 (2009).
【学術関係の受賞】	Alfred P. Sloan Research Fellowship, 1970-72; International Academy of Quantum Molecular Science (IAQMS); 日本化学会賞, 1992; The Schr-dinger Medal, The World Association of Theoretical Organic Chemists (WATOC), 1993; The Fukui Medal, Asian Pacific Association of Theoretical & Computational Chemists, 2005; 恩賜賞、日本学士院賞、2008; 瑞宝中綬章、2010

【氏名（ふりがな）】	大峯　巖　（おおみね　いわお）
【職名】	所長
【所属】	大学共同利用機関法人自然科学研究機構分子科学研究所
【研究室】	
【直通電話】	0564-55-7103
【FAX】	0564-55-4386
【電子メールアドレス】	ohmine@ims.ac.jp
【ホームページ】	
【研究分野】	理論化学
【現在の研究課題】	理論化学,　水のダイナミクスと反応
【研究内容キーワード】	水、相転移、化学反応、水素結合、イオン輸送、生体高分子
【最終学歴】	1976年10月　ハーバード大学大学院博士課程(化学物理学)　修了
【学位】	1977年 3月　化学物理学博士（ハーバード大学）
【略歴】	1974年9月パリ第７大学研究員、1976年 10月MIT博士研究員、1977年4月日本学術振興会奨励研究員（分子科学研究所）、1980年4月MIT研究員、1981年6月慶応義塾大学助手、1982年12月分子科学研究所助教授、1994年4月名古屋大学教授、2006年4月同理事副総長、2009年4月京都大学福井謙一記念研究センターリサーチリーダー、2010年4月分子科学研究所長
【所属学会】	日本化学会、日本物理学会、米国化学会、米国物理学会
【主な著書、学術論文】（過去5年以内）	1. “Fifth-order two-dimensional Raman spectroscopy of liquid water, crystalline ice Ih and amorphous ices: Sensitivity to anharmonic dynamics and local hydrogen bond network structure”, *J. Chem. Phys* **125,** 084506 -1-12, (2006) S. Saito and I. Ohmine 2. “Mechanism of Ion permeation in a Model Channel; Free Energy Surface and Dynamics of K^+ Ion Transport in Anion-doped Carbon Nanotube” , *J. Phys. Chem. B,* **110,** 20671-20677 (2006), T. Sumikama, S. Saito and I. Ohmine. 3. “Proton Transfer and Associated Molecular Rearrangements in Photocycle of Photoactive Yellow Protein; Role of Water Molecular Migration on Proton Transfer Reaction” , *J. Phys. Chem. B,* **111**, 2948-2956 (2007), M. Kamiya, S. Saito and I. Ohmine 4. “Topological building blocks of hydrogen bond network in water” , *J. Chem. Phys.* **127,** 134504 1-9 (2007). M. Matsumoto, A. Baba and I. Ohmine 5. “A theoretical chemistry compares love to hydrogen bonds” in Nature Journal Club (Research Highlight), *Nature,* **447**, 511 (2007) 6. “Proton-transfer reactions in reaction center of photosynthetic bacteria Rhodobacter sphaeroides” , *J. Phys. Chem. B,* **113,** 8993-9003 (2009), Yu Kaneko, Shigehiko Hayashi and Iwao Ohmine 7. “A Molecular Dynamics Study for the Structure Determination of the “Signaling State in the Photocycle of Photoactive Yellow Protein”, *J. Phys. Chem. B,* **114** , 6594-6660 (2010), Motoshi Kamiya and Iwao Ohmine
【学術関係の受賞】	2003年中日文化賞、2008年日本化学会賞

３．教員研究紹介

センター長
工学研究科 分子工学専攻
教授　榊　茂好

本研究室では「化学事象の本質を理解・予測するための理論化学の展開」を目的に、「新しい理論の開発から現実の化学現象や化学反応（複雑な触媒反応や有機合成反応、金属酵素反応など）に密着した理論計算」などの取組みを行っている。

（１）**遷移金属元素を含む複合電子系の理論化学**：

複合電子系とは、遷移金属元素や有機官能基、ヘテロ元素、典型金属などを同一系内に持つものであり、複雑な電子状態や多様な構造、結合性、反応性を示し、基礎、応用双方で興味深い研究対象である。このような化合物や反応は有機化学反応に比べて、理論的解明も遅れている。我々は触媒的有機合成反応や有機金属化学反応、錯体触媒反応の反応機構、反応の電子的過程の理論的解明、分子論的理解を深め、反応予測と制御を目的とし、C-H 結合活性化反応、二酸化炭素の水素化反応、クロスカップリング反応などの反応機構を解明し、反応制御に必要な知見を得てきた。また、これらの物性にも興味を持ち、スピン転移錯体、りん光、蛍光発光特性、吸収スペクトルと構造揺らぎの関係などの理論的研究も行なっている。

（２）**大規模系の理論計算方法の開発**

ナノサイエンスの発展と共に、100 原子を越すような大規模分子系の高精度計算も必要である。本研究室ではそのような大きな分子系に適用可能な高精度大規模計算法を開発し、実在する分子や反応系の高精度理論計算に挑戦している。大きな系には密度汎関数理論が広く使用されているが、金属と π 電子系との相互作用が過小評価されるなどの欠点も見出されており、大規模系へ適用可能な post-Hartree-Fock 法の開発が求められている。遷移金属錯体では配位子の置換基が大きくなり、高精度計算が困難になる例が多い。本研究室では一電子演算子により置換基の電子効果を効果的に取り込み、高精度計算を行う方法を開発し、大規模系の CCSD(T)などの高精度計算へ応用し、化学的精度を達成した。

（３）**溶液、溶媒和理論の開発と応用**

多くの化学反応で溶媒和効果が大きな役割を果たしているが、従来その理論的な取り扱いは不十分であった。本研究室では、佐藤（啓）准教授を中心に、分子性液体の新規積分方程式理論の開発、それらと電子状態理論と組み合わせた理論方法の構築、溶媒和構造の解明や溶液内反応などへの応用を行っている。このような溶媒を考慮することで、分子の性質や反応のより正しい理解が可能になっている。最近では溶媒和構造の三次元分布を直接求められる新手法を開発し、これまで以上に精密な溶媒和構造を示すことが出来た。また、共鳴理論のように、分子軌道法の計算結果を原子価結合法の観点から解析する手法を開発した。これを溶媒和理論と組み合わせ、溶媒がイオン結合、共有結合にどう影響するか、を明らかにした。

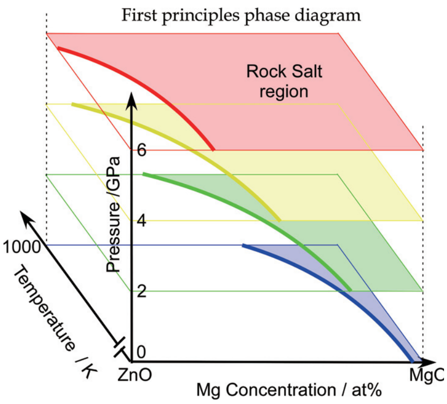
総合研究部門　副センター長

工学研究科 材料工学専攻

教授　田中　功

（1）　第一原理統計熱力学法の開発と材料科学への応用

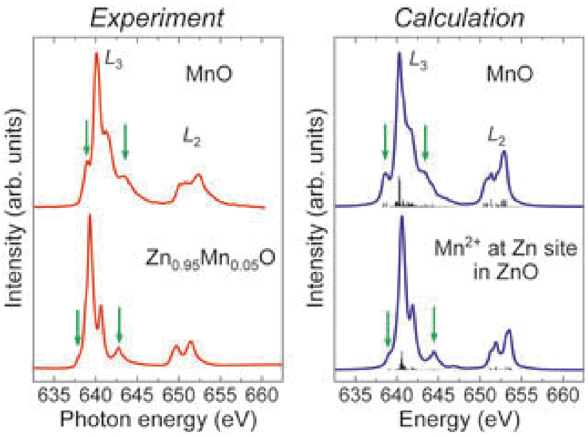
密度汎関数法に基づいたバンド計算を材料研究に応用する試みは1980年代に開始し，その後の計算機と計算技術の進歩により着実な成果を上げてきた．21世紀に入ったころから，格子振動を擬調和近似の範囲で精度よく計算できるようになり，物質の比熱や自由エネルギーのような熱力学関数が第一原理的に求められるようになってきた．また，網羅的な第一原理計算をクラスター展開法やモンテカルロ法などの統計力学手法と組み合わることにより，固溶体や化合物の原子配列を議論することが可能となってきた．われわれは，これらの手法を第一原理統計熱力学法と呼び，計算手法の開発と，それを材料開発に応用する研究を進めている．エネルギー変換材料や半導体材料，光学材料や生体材料のように材料工学として興味ある物質を対象とし，その状態図や相転移，拡散のような基本現象にアプローチしている．



MgO-ZnO 擬2元系の岩塩型構造固溶体領域の温度および圧力依存性の第一原理計算結果．実験結果をよく再現している．

（2）　XANES と ELNES のナノ材料科学への応用

X線吸収スペクトルの吸収端近傍微細構造（XANES）は，内殻軌道から非占有軌道への電子励起に起因することから，注目する材料のナノ構造を反映する．実験方法を工夫すれば，ppmオーダーの不純物や，材料の表面，界面を修飾している機能元素の局所環境を評価することができる．これと同様の情報を与える分光法に，電子顕微鏡を利用した電子エネルギー損失分光励起端近傍微細構造（ELNES）法がある．この手法は，X線を利用した実験と異なり，微細組織と対応させた状態分析ができるというユニークな特長を持つ．最先端の電子顕微鏡を用いれば，電子ビーム径0.1nmでの原子カラム毎の測定も可能である．われわれは，このXANESやELNESの計算手法を開発すると同時に，放射光や電子顕微鏡を用いた実験を行い，これらの分析法を材料科学の様々な問題に適用すべく研究を進めている．



MnO 及び Mn 添加 ZnO からの Mn $L_{2,3}$ 端 XANES および，その相対論 DFT-CI 法による理論計算結果．この比較により，ZnO 中の Mn は形式電荷 2+で，高スピン状態，4配位環境にあることがわかる．

理論研究部門　副センター長
理学研究科 物理学・宇宙物理学専攻
教授　太田　隆夫

（１） 非平衡系の統計物理学

熱平衡近傍での線形非平衡系についてはアインシュタインのブラウン運動に始まり、前世紀中頃には揺動散逸定理、線形応答理論の形に理論がまとめられた。一方、熱平衡から大きく離れた非平衡系の構造形成、ダイナミクスの系統的研究は１９７０年代に始まった。これまでに、現象を表現する方法については縮約理論などの優れた成果が得られているが、熱平衡統計力学のエントロピー最大の原理のような普遍法則は未知であり、非平衡系の観測量を第一原理的に計算する理論体系も未発達である。熱平衡近傍の揺動散逸定理を特別な場合として含み、より一般的な状況で成立する、いわゆる、揺らぎの定理が最近注目されている。これらをさらに発展させ、非平衡開放系の統計物理学の構築を目指した研究を行っている。このような問題は長い間、純学問的な見地からのみ語られてきたが、近年の材料科学や生命科学における実験的進歩は非線形非平衡系研究に質的変革が起ころうとしていることを指摘したい。生体細胞内の１分子計測や光ピンセット法で得られたデータがミクロ非平衡系のどのような情報を含んでいるのか、あるいは、ナノスケールでの非平衡構造を効率よく制御するにはどうしたらよいかなどは一見、応用的であるが、実際は非平衡系の基本問題と直結している。これらを解決するために、数理モデルの導入とその解析、実験データから背後の法則性を見抜く現象論の展開などによる研究を遂行している。

（２） 非平衡ソフトマター物理学

ソフトマターの特徴の一つは構成する(高)分子が自己集合し 1～100nm のナノまたはメソスコピックな内部構造を形成することである。さらに、ソフトマターは力学的に「ソフト」な応答を示し、同時に非常にゆっくりとしたダイナミクスを発現する。すなわち、ソフトマターは小さな外場で大きな構造変化を示す非線形性と、熱平衡への緩和での著しく遅いダイナミクスを兼ね備えている。我々はこのようなソフトマターの特徴をふまえ、外場によるソフトマターの非平衡ダイナミクスの研究を行っている。メソスコピック構造からの非線形応答の計算機シミュレーションと理論解析を行い、階層性をもつ系の普遍な動的性質を明らかにするが目的である。メソ構造形成と外場との相互作用を調べることで、新しい非平衡構造を探求すると同時にその制御に対する知見を得ることができる。基礎物理学的な原理に基づいて非平衡ソフトマターの階層構造形成のメカニズムを理解することは、長期的には、分子の持つ自己組織化能力を用いて、様々なスケールの構造を自在に設計することにつながり、さらには、究極のボトムアップ手法のナノテクノロジーとなり得る。その成果は、光デバイス、有機・高分子材料、薬品、化粧品、食品などの高機能材料の設計・試作・プロセスといった産業応用に波及するであろうし、同時に、生体構造、生命現象への理解へと研究が発展拡大していくと期待できる。

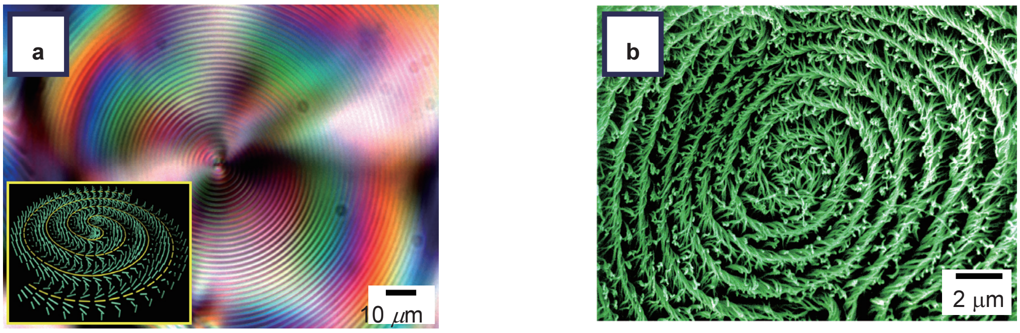
総合研究部門　スーパーバイザー
工学研究科　高分子化学専攻
教授　赤木　和夫

共役ポリマーの超階層性らせん構造の制御と機能創出

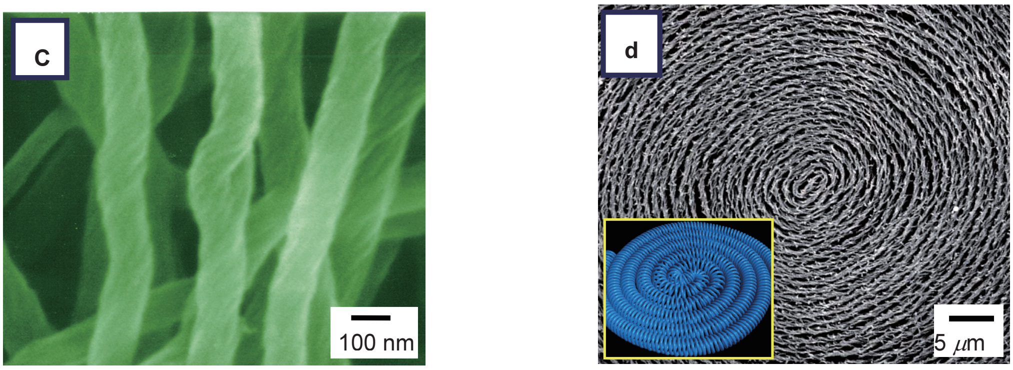
これまで、液晶のもつ自発配向性や外場応答性を利用して、共役ポリマーの不斉反応場の構築や、液晶性の直接付与を展開してきた。これにより、階層性らせん構造を有するヘリカルポリアセチレンを合成することに成功した。また、電気的異方性や発光二色性をもつ液晶性共役ポリマーや、高速電場応答性を有する強誘電型液晶性共役ポリマーを開発した。

本研究では、液晶を用いた特殊反応場を構築し、階層性が制御された巨視的配向や渦巻き状などの特異な構造や形態を有する導電性・発光性・液晶性高分子を合成することを目標とする。不斉液晶場での重合を展開・確立し、一次構造から高次構造に至るまで、らせん構造を自在に制御した超階層性らせん状共役ポリマーを合成する。外部摂動を不斉液晶場に印加することで、ポリマーのらせん形態を配向させ、誘起ソレノイド磁性などの革新的な電磁気的性質を導出する。次に、液晶性とらせん構造を併せ持つ次世代共役ポリマーを創成し、発光時での直線偏光性や円偏光性を創出する。

π 電子が鎖上に非局在化した共役高分子に新たな機能を発現させることで、次代の電子・光ポリマー材料を開発するとともに、「高分子と液晶が融合した新しい学域の創成」を目指す。



Science (1998), *JACS* (2004), *PRL* (2004), *PRB* (2005), *JACS* (2005), *Chem. Rev.* (2009)



JACS (2007), Highlight in *Science* (2007)　　*JACS* (2008), Highlight in *Nature Mater.* (2008)

不斉液晶反応場（a）で合成したらせん状導電性高分子，ヘリカルポリアセチレン（H−ＰＡ）の階層的スパイラル形態（b），極限的ねじれ液晶場で合成したバンドルフリーのシングルH−ＰＡフィブリル（c），形態保持炭素化法で調製したヘリカルグラファイト（d）

総合研究部門　スーパーバイザー

物質－細胞統合システム拠点（工学研究科　分子工学専攻）

教授　今堀　博

(1)人工光合成系の構築

天然の光合成では色素分子が高度に配列することで、高効率な光捕集や電荷分離の機能を発現しています。我々は光機能性分子を合理的に設計することで、それらの分子を高度に配列させ、光合成の機能を人工的に再現することを目指しています。

(2)有機太陽電池の開発

近年、エネルギー・環境問題の観点から、太陽エネルギーの有効利用に注目が集まっています。有機太陽電池は、柔軟性、着色性、軽量性、低コストなどの長所を有していますが、現在のところ、エネルギー変換効率は十分とは言えず、さらなる向上が必要です。本研究室では、合理的な分子設計・有機合成により、電極上に色素分子を望み通りに自己組織化させることで、高効率有機太陽電池の開発を目指しています。具体的には、色素増感太陽電池、バルクヘテロ接合太陽電池、両電池の特性を有する新規有機太陽電池に関する研究を行っており、エネルギー変換効率で最高8%程度を達成しています。

(3)カーボンナノチューブ（CNT）の基本物性の解明と光機能化

CNT は、炭素原子でできたナノスケールの超微細管というユニークな構造をとっています。そのため、半導体にも金属にもなり得る電子的性質を有し、引っ張りや曲げに対する機械的強度が極めて高くなっています。本研究では、その CNT に対し、有機化学反応による色素分子との結合形成や、共役系分子とのナノレベルでの複合化を行うことで、光機能性が付与された新しいナノカーボン材料を開発しています。さらに、その光物性や電子・エネルギー移動特性などの基本物性の評価、および太陽電池への応用を行っています。

(4)典型元素の特性を活かした機能性有機材料の開発

炭素、窒素、酸素などの第二周期元素を中心に発展してきた有機化学の流れに第三周期以降の典型元素が加わることで、有機化学という学問はその間口を広げ、物理化学、材料化学、錯体化学など他の学問領域と深く結びついてきました。 本研究では、リンや硫黄の特性を活かした発光、電子輸送機能を示す有機材料や触媒の開発を念頭に置いて、ホスホール環やチオフェン環を骨格に含む新しい複素環化合物やポルフィリン金属錯体の合成、構造解析、および物性・反応性の評価を系統的に行っています。

(5) 新規な薬物送達システム（DDS）の創製

本研究では京都大学物質−細胞統合システム拠点（アイセムス）と共同で、ナノカーボン材料、ナノ粒子などを用いる新規な薬物送達システム(DDS)の創製を目指しています。

総合研究部門　スーパーバイザー
化学研究所　複合基盤化学研究系
教授　**佐藤　直樹**

（1）有機固体・薄膜とその表面・界面の電子構造解析

有機化合物、金属錯体や高分子の、主に薄膜とその表面・界面の電子構造について、価電子状態を紫外光電子分光法（UPS）、空状態を逆光電子分光法（IPES）により観測しています。特に注目しているのはそれらの有機半導体としての特性ですが、それを決定づけるエネルギーギャップ上下の（フロンティア）電子構造を直接的にとらえることがこれらの測定の目的です。図 1 は、開殻分子のルテチウムフタロシアニン（LuPc$_2$）の薄膜についてそのフロンティア電子構造を実測した結果で、計算によるシミュレーションスペクトルとの比較から、スピン偏極した半占軌道が（SOMO-SUMO）エネルギーギャップを与えている様子が明らかになりました。

基本的には分子の電子構造が導く凝集相の電子構造を、分子の集合構造との相関から明らかにするとともに、基礎・応用の両面から重要な表面・界面が関わる問題にも注目しています。また、一般には弱い分子間相互作用で結合する有機固体でも、分子や集合形態により示す顕著な付加的相互作用も重視しています。

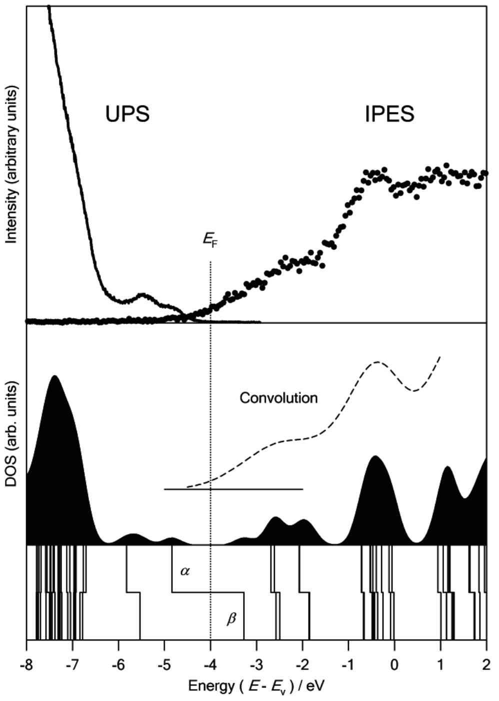


図 1. LuPc$_2$ のフロンティア電子構造（UPS と IPES による実測と DFT 計算によるシミュレーション）

（2）新奇な電子物性を示す分子集合系の創出

注目すべき電子物性の発現が期待できる分子集合体を創り出すため、(1)の電子構造研究で得られる知見を活用し、初めから集合形態を考えて新分子の設計を行ったり、既知の分子でも集合化を制御して新しい物質を創出したりする研究も進めています。とくに、特異な結合や構造をもつ分子の設計・合成、既存分子の中でもそのような特徴をもつ分子を選び、それらの特異な集合構造に導いて新しい分子集合系を構築しようとしています。一例として、電子供与性と電子受容性の二つの基を抑制の効いた非局在性をもつ結合でつないで両性と極性の高い分子を創り、分子内と分子間の電荷移動相互作用の調和に基づき顕著な電子的特性が期待できる系の実現を目指しています。

（3）動的物性の発現を導きうる有機固相反応の探索

分子内／分子間の結合や電子構造の著しい変化が電子物性の端的な発現・制御を招く分子集合系（固相反応系）を探しています。固相中のプロトンやイオンの移動などに注目し、光や熱による互変異性や転位・付加・重合などが起こる有機固相反応について、機構解明から臨んでいます。

総合研究部門　スーパーバイザー

工学研究科　合成・生物化学専攻

教授　杉野目　道紀

（１）　有機化合物の精密合成に資する遷移金属触媒反応の開発

多様な有機化合物群を精密，効率的，かつ迅速に合成する新しい方法論の確立を目指し，典型金属元素や遷移金属元素を効果的に用いた新しい触媒反応の開発を行っている。特に，ホウ素やケイ素を含んだ有機メタロイド化合物の触媒的精密合成，遷移金属触媒によるC-H結合官能基化を含む新しい合成反応の開拓，新しいキラル触媒系の創出を通じた不斉合成反応の開発等に焦点を絞って研究を展開している。具体的な研究項目と参考文献を以下に示す。

・シリルホウ素化：遷移金属触媒を用いた有機不飽和化合物とシリルボランの反応［*J. Am. Chem. Soc.* **129**, 3518 (2007); *J. Am. Chem. Soc.* **130**, 1526 (2008); *Bull. Chem. Soc. Jpn.* **82**, 29 (2009) (Account)]

・遷移金属触媒を用いたアルキンへのシアノボランの付加反応 [*Angew. Chem., Int. Ed.* **44**, 2380 (2005)]

・Ni触媒を用いたアルキンへのアルキニルボランの付加反応 [*J. Am. Chem. Soc.* **128**, 14438 (2006)]

・遷移金属触媒によるB-Cl結合活性化を鍵とするアルキンのカルボホウ素化反応 [*J. Am. Chem. Soc.* **130**, 2918 (2008)]

・アミノボランをイミニウムイオン発生剤として用いるアミノ化反応 [*Org. Lett.* **9**, 4407 (2007)]

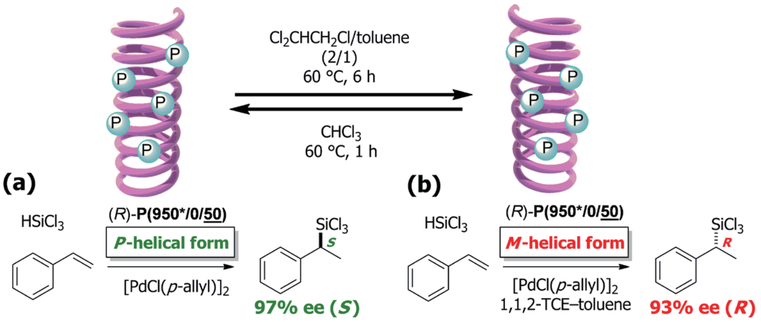
・ホウ素のマスキングを鍵とするオリゴアレーン類の繰り返しカップリング合成法の開発 [*J. Am. Chem. Soc.* **129**, 758 (2007)]

・アルキンC-H結合の炭素-炭素二重結合への触媒的付加 [*J. Am. Chem. Soc.* **130**, 5410 (2008); *J. Am. Chem. Soc.* **131**, 5060 (2009); 不斉付加 *Angew. Chem., Int. Ed.* **49**, 3827 (2010)]

・触媒的C-Hボリル化反応 [*J. Am. Chem. Soc.* **131**, 6070 (2009); *Angew. Chem., Int. Ed.* **48**, 2372 (2009)]

（２）らせん高分子の不斉合成法の開発と機能化

有機合成化学の21世紀のターゲットのひとつは、巨大分子の精密合成と機能化である。特に、立体構造の制御を伴う合成法の開拓は、有機化学者にとって最も興味深い研究課題であり、新しい機能開拓が期待される。我々はその中でも、安定ならせん構造を持つ高分子に注目し、その右巻および左巻体の不斉合成法の開発に取り組んでいる。これらの知見に基づき，らせんキラリティーを不斉源とする「キラル高分子触媒」を創製し，高選択的不斉触媒反応に応用した。溶媒効果によってらせんキラリティーが可逆的に反転するらせんポリマーを見出し，右巻体と左巻体とがそれぞれ逆のエナンチオマーの選択的（それぞれ93%ee以上）生成の触媒となる新しい不斉触媒系を開発した。（参考文献 *Angew. Chem., Int. Ed.* **48**, 539 (2009); *J. Am. Chem. Soc.*, **132**, 7899 (2010); *Chem. Commun.*, **46**, 4914 (2010)）



総合研究部門　スーパーバイザー

理学研究科　物理学・宇宙物理学専攻

教授　吉川　研一

1）DNA の高次構造相転移と遺伝子活性の on/off スイチング

100 キロ塩基対以上のサイズの長鎖 DNA に関して、その折り畳み転移が不連続転移であることを明らかにしてきている。また、数値計算による研究も援用して、より一般的に単一高分子レベルの構造転移の研究を進めてきた。高分子物理、統計力学に立脚した理論的研究により、持続長が大きな高分子（硬い高分子）や荷電高分子では、多様なナノ秩序構造体が、環境パラメーターに依存して、自己組織的に生成することとする仮説を提唱し、実際の実験で実証してきている。さらに、DNA の折り畳み転移により、鋳型 DNA 上での RNA 合成反応（転写反応）に厳密な on/off スイッチングが起きることを、1 分子 DNA レベルで明らかにしてきている。このような研究を通して明らかになってきた長鎖 DNA 特有の物性と活性は、生命体における遺伝子活性の自己制御の機構に深くかかわっているものと期待される。さらに、DNA 分子に限らず、半剛直性(semi-flexible)の高分子鎖、一般について、折り畳み転移は、無秩序―秩序の構造相転移を起こすことを、実験・理論両面から明らかにしてきている。

2) 生物における時空間の自己組織化

生命の基本単位である細胞は、リン脂質 2 分子膜による閉鎖空間を固有の反応場としており、それがゆえに多様でかつ特異な機能を創り出していると考えられる。このナノメータスケールの構造は、脂質と溶液との相互作用により自発的に形成される（熱力学的安定構造)。一方、マイクロメーターのスケールでは、速度論的な効果が重要となり、時間に依存した相空間上の経路が最終的な構造を規定している。このことを、理論的に考察することにより、リン脂質を用いて細胞サイズのベシクルを作製するための実験手法を確立することに成功している。この細胞サイズリポソームを用いて、細胞の人工的なモデルを作り出すといった、構成論的な研究を進めている。具体的には、DNA を含む転写反応溶液をリン脂質の多層膜と接触させると、反応液を取り込んだ細胞サイズのリポソームが自発的に形成されることを見出した。さらに、RNA にとどまらずタンパク質を合成するリポソーム系を作り出すことにも成功している。

3）非平衡開放条件下で働く分子機械

生命現象の中で“生命らしい”特徴をもつものとして、その実空間上の運動があげられる。しかし、そのメカニズムは不明な点が多く残されている。すなわち、生物では、ATP などの化学エネルギーから運動を生み出していることは知られているが、実際にどのようにして、等温条件のもと、高いエネルギー変換効率で運動を生み出しているかといった問題は、いまだ解明されていない。生命現象は本来的に、散逸系、すなわち、非平衡開放系とみなすことができ、その条件下で分子機械は働いていると考えられる。散逸構造に関する研究の重要性は、Prigogine 教授らにより 30 年以上前から指摘されてきたが、現実の実験的研究による進展は遅々としたものであった。吉川らは、レーザーによる分子複合系の時空間構造の自己形成や、化学ポテンシャルによって駆動される等温条件下での液滴の秩序運動の実現など、非平衡条件下の散逸構造に関する研究を展開してきている。

総合研究部門　スーパーバイザー

理学研究科　化学専攻

教授　有賀　哲也

（１）　結晶表面におけるPeierls転移

金属カルコゲナイド、有機伝導体などの低次元金属においては電荷密度波(CDW)相転移（Peierls 転移）の存在が良く知られている。単純な平均場描像によると、低次元フェルミ面のネスティングによる電子系エネルギーの減少により低温の CDW 相が実現する一方、高温では電子エントロピーの寄与により金属相へと相転移する。固体表面においても、例えば W(001)表面における相転移について、CDW 描像の当否を巡って 1970-90 年頃に精力的に研究が展開され、平均場描像とは異なる強結合 CDW 相転移として理解された。すなわち、強い電子格子結合のために、金属相への転移が起こるよりはるかに低温で CDW の位相揺らぎ（秩序無秩序転移）が起こり、これが回折法での超構造の消失や、フォノン異常として観測される、と結論されたのである。これらの研究を通して、強結合/弱結合という CDW 相転移の分類法が確立されて来た。

我々は、In/Cu(001)系で観測される CDW 相転移の機構を調べた。角度分解光電子分光(ARPES)により、CDW ギャップの温度依存性を調べたところ、いわゆる BCS の式とほぼ一致する挙動が見られ、一見すると弱結合的 CDW 転移であるように見える。ところが、SPring-8 BL-13XU の高輝度アンジュレータを用いて X 線臨界散乱の測定を行ったところ、T=345 K において 2 次元 Ising ユニバーサリティ・クラスに属する秩序-無秩序転移が起きていることがわかった。これは、この系で弱結合描像が成り立たないことを明確に示している。他方、電子系のギャップ-非ギャップ転移の低い転移温度は、強結合描像と明らかに矛盾する。つまり、弱結合/強結合という二分法が成立していない。

この系における CDW 相関長は ARPES のギャップ付近のバンド構造から ξ_{CDW} = 6 nm と見積もられる。一方、X 線臨界散乱で決定された格子相関長 ξ_l の温度依存性を見ると、400-420 K 付近で格子相関長が CDW 相関長とほぼ同程度にまで短くなっていることがわかる。つまり、秩序無秩序転移に伴って格子相関長が短くなるとともに CDW の波束が壊れはじめ、400-420 K 以上では完全に CDW が破壊されてしまう（金属相に転移する）と考えることができる。この転移温度は ARPES で観測されたギャップ-非ギャップ転移のそれとほぼ一致する。

これまで、強結合 CDW は非常に短い CDW 相関長を伴うものと仮定されてきた。実際、W(001)や *2H*-TaSe2 では CDW 相関長が 0.5 nm 程度であってこの仮定を満たしている。しかし、In/Cu(001)のように強結合であっても ξ_{CDW} が大きい系が存在すること、さらに、このような系では弱結合/強結合描像は成り立たず、格子エントロピーに起因してギャップ-非ギャップ転移が進むという、新しいタイプの CDW 相転移が起こることが分かった。

(２) 巨大 Rashba 効果

表面や界面においては、反転対称性の破れのためスピン縮退が解ける（$E(k,\uparrow) \neq E(k,\downarrow)$、ただし、$E(k,\uparrow) = E(-k,\downarrow)$）。スピン軌道分裂の大きさはkに比例し、その比例定数をRashba定数と呼ぶ。自由電子的描像では、スピン軌道分裂の大きさは界面垂直方向のポテンシャル勾配により決まるはずだが、実際には、原子ポテンシャルの寄与が大きく、例えばAu(111)表面の2次元自由電子的表面状態バンドでは、ポテンシャル勾配から予測されるものの数倍にスピン軌道分裂が観測される。これまで最大のスピン軌道分裂はBi単結晶表面で観測されている。

我々は、Ag(100)表面上にBi単原子層が吸着した系において、Bi(111)、Bi(110)などと比較して1桁近く大きなRashbaスピン軌道分裂を観測した。伝導バンドを構成するp的な原子波動関数がBi/Ag界面によって強く影響を受け、Rashba定数の異常をもたらしていると思われる。このような大きなスピン軌道分裂は、スピン偏極電流などの実現にも繋がるものである。現在は、半導体スピントロニクスの実現に向けて重要な、半導体表面における巨大Rashba効果の研究を進めている。

総合研究部門　スーパーバイザー

理学研究科　化学専攻

教授　加藤　重樹

1 気相における化学反応ダイナミックス

気相における比較的簡単な分子の反応ダイナミックスの研究は、化学反応理論の最も基礎的な研究として位置づけられるとともに、燃焼過程や大気化学において重要な役割を果たしている。当研究室では、反応分子の電子状態はもとより原子核の運動も量子論に基づいて取り扱うことにより、反応のダイナミックスを第一原理から理解することを目指している。化学反応には、遷移状態理論やRRKM理論のような統計的な理論が広範に用いられていますが、それらが適用できる条件は必ずしも明らかになっていません。私たちの研究は、例えば、単分子反応を共鳴性散乱として捉え、反応が起こるエネルギー領域での分子運動の量子状態を調べることにより反応ダイナミックスに新たな知見をもたらそうとするもので、化学反応ダイナミックスの理論の進展に基礎的な情報を与えるものと位置づけることができます。また、励起状態における化学反応には複数のポテンシャル面間の遷移を伴うものも多くありますが、このような反応を理解するため、非断熱遷移を引き起こすスピン軌道相互作用や振電相互作用の行列要素の計算法を開発し、量子動力学の方法と組み合わせることにより速度過程の第一原理からの理論的取り扱いを行ってきました。従来の近似的な理論では、説明することができなかった多原子分子の無輻射遷移速度の理論計算などに適用し、成功を収めています。現在では、分子とレーザー場との相互作用により引き起こされる反応のダイナミックスの研究を行っています。

2 溶液内における化学反応のダイナミックス

溶液内における化学反応は事実上無限個の溶媒分子が関与する複雑な過程で、反応のポテンシャル面を求めることも極めて難しい課題であると云われてきました。当研究室では、分子の電子状態理論と分子性液体の統計力学理論である積分方程式理論を組み合わせたRISM-SCF法を提案し、溶液内反応の自由エネルギー面の理論計算を行ってきました。この方法は、従来の溶媒を誘電連続体と見なす方法に比べて、溶媒分子の微視的な性質を反映させることができるモデルとして注目を浴びています。これまでは、水溶液中の反応を取り上げてきましたが、最近、非プロトン性の有機溶媒にもこの方法を拡張し、経験的な溶媒パラメーターの理論的説明を行いました。現在では、溶媒の熱揺らぎの効果や反応速度の理論計算を行っています。

分子動力学法などの計算機シミュレーションの方法は、溶液内での化学反応のダイナミックスを研究する有力な手段として発展してきました。当研究室では、電子状態理論を用いて分子動力学計算のための理論モデルの精密化に取り組んできました。溶液内での反応分子の電荷分布は、周りの溶媒分子の熱揺らぎにより変化を被ることが考えられます。私たちは、溶媒分子の揺らきに対する溶質分子の電荷分布の応答を記述するモデルを分子軌道理論に基づいて定式化し、そのモデルを用いた分子動力学計算により光化学反応の中間体ラジカルの拡散係数の異常性や振動緩和の新しい機構の解明に成功を収めてきました。また、電子移動反応などの溶液内反応のダイナミックスを記述するハミルトニアンを理論的に導き、その中に含まれるパラメーターを分子動力学計算から求める方法を確立しました。この方法は、ポルフィリンとキノン間の長距離電子移動反応の機構の解明に用いられました。

今後、溶液内反応に対して開発してきた理論的手法を更に発展させ、酵素反応などの生体内反応の機構の解明に取り組もうと考えています。

3 不均質大気化学における理論化学

近年、大気化学においてエアロゾルと呼ばれる液体・固体の微粒子が、化学的およびエネルギー収支の両面において大気環境に大きな役割を果たすことが知られるようになり、現在非常にホットな分野となっています。これらの問題は、物理化学としても、従来の気相化学と凝集相化学の両面にまたがる新しい分野で、理論化学的にも重要で面白い問題が数多く残されています。本研究室では、電子状態計算や分子シミュレーションなどの手法を用いて、(i)エアロゾル表面構造の解析、(ii)気液界面での物質移動の理論、および (iii)不均質化学反応機構の解明に取り組んでいます。

理論研究部門　スーパーバイザー

工学研究科　高分子化学専攻

教授　田中　文彦

（１） 高分子系のゾル-ゲル転移

高分子溶液（融液）のゾル-ゲル転移現象を分子間相互作用の理論解析に基づいて解明し制御する研究を行っている。 疎水化された水溶性高分子，水素結合性高分子，可逆反応性の高分子のゲル化現象を典型３タイプの研究対象とし，１）ゲル化温度T_gやゲル化濃度c_gが官能基の数，鎖上配置，結合強度にどのように依存するかについて統計熱力学を基礎にした理論解析を行い，その予測を実験的に検証する方法を考案する。２）ゲル化点で弾性率がどのような鋭さで立ち上がるかを，複素弾性率（弾性的に有効な鎖の数）の理論計算で予測する。3）任意の初期条件からゲル化点に到達するまでの時間，ゲルの融解に要する時間を分子ダイナミックスの視点から研究を行い，架橋反応経路や反応速度を温度や蒸気圧でコントロールする分子機構の研究を行っている。

（２）疎水化水溶性高分子（会合高分子）の相転移とレオロジー

水溶性の感熱高分子であるポリイソプロピルアクリルアミド（PNIPAM）は，コイル・グロビュール転移点が生理温度に近いため医学や薬学に広く応用されている。PNIPAMの感熱性の物理的原因は永く謎であったが，我々は最近PNIPAMのシャープな転移が水和の協同性（水分子の高分子への水素結合が連鎖状に形成される現象）に由来することを指摘し，高分子の協同水和の理論モデル化を行って特異なLCST現象を説明するのに成功した。また， PNIPAMの両末端をアルキル鎖（$-C_{18}H_{37}$）で疎水化したテレケリックPNIPAMの会合構造（花型ミセルの形成，曇点曲線，高温で現れるメソグロビュール（100nm程度の巨大会合体））の光および中性子散乱実験，凝縮温度のDSC測定，蛍光測定の解析と理論モデルの構築を行っている。準濃厚領域では末端鎖の疎水凝集によるミセルで架橋されたネットワーク構造が形成され，ゾル-ゲル転移現象と高温相分離（LCST）型のマクロ相分離現象が観測される。末端鎖の組替え可能な高分子ネットワークのレオロジー的性質に関しては，「組換え網目理論」を用いて流動・緩和現象の解析や非線形粘弾性のシックニング現象の研究を行い，水溶性高分子の新展開を試みている。

（３） 高分子系における水素結合の生成機構

高分子溶液系において水素結合の連鎖性を制御することにより，新規な架橋構造をもつ熱可逆性ゲルの設計原理を理論的に探索している。連鎖性水素結合とは，高分子鎖上で相隣る水素結合ボンドが強い相関をもって形成される結果生じるジッパー状の水素結合集団のことであり，高分子系特有の非線型増幅作用（ドミノ効果）の主たる原因となるものである。重要な例は，2重鎖ヘリックスによる架橋（バイオポリマーのゲル），はしご型水素結合（高分子コンプレックスPEO+PAA），連鎖性水和（PNIPAM水溶液のLCST），低分子ゲル化剤，微結晶性架橋ゲル（PVA，セルロース誘導体のゲル）などである。連鎖性の強度は協同性パラメータで表現することができ，非線型増幅によるマジョリティ効果や相転移の鋭さを推定するために重要であることが判明した。

理論研究部門　スーパーバイザー
工学研究科　化学工学専攻
教授　山本　量一

（１）　コロイド系の計算機シミュレーション

マルチスケール（ミクロnm～メソμm～マクロmm)の複雑な階層構造を持つソフトマターでは、各階層を単一の計算手法でカバーすることは不可能である。ソフトマター科学において計算機シミュレーションがさらに有効活用されるためには、このマルチスケール問題の克服が不可欠である。候補者は、独自のアイディアで分子動力学(MD)法と連続体モデルを組み合わせたシミュレーション手法の開発に取り組み、世界で初めて液晶コロイド多粒子分散系のシミュレーションに成功した。その後JST-PRESTO研究を実施し、流体力学と統計力学に基づいてミクロ階層の情報を取り込みながら効率よくメソスケールのシミュレーションを実行するSmoothed Profile (SP)法と、それに基づくコロイドシミュレータKAPSELの開発を行った。この成果を典型的なマルチスケール問題を有する荷電コロイド粒子系に応用し、多粒子分散系の電気泳動のシミュレーション（図１）に世界で初めて成功した。

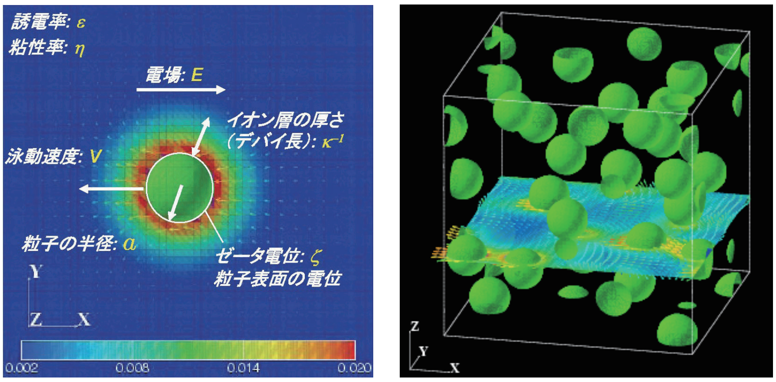


図１．荷電コロイド粒子の電気泳動のシミュレーション

（２）　複雑流体・ソフトマターの移動現象に有効なマルチスケールシミュレーションの開発

JST-CREST研究の一環として、計算流体力学（CFD）法と分子動力学（MD）法の組み合わせによる新しい「マルチスケールシミュレーション法」を開発し、高速振動する平板間の高分子溶液の複雑な流動挙動（図２）の解析に成功した。ニュートン流体とは異なり、高分子溶液では振動板から遠ざかると急激に振動が減衰する。これは振動板近傍の速度勾配の大きな領域で粘性率の急激な減少が起こり、振動板の運動が流体内部へ浸透せずに板近傍にとどまることが原因であることを突き止めた。さらに、振動板からの距離に応じて、高分子溶液の局所的な力学特性が空間的に変化することを世界ではじめて明らかにした。

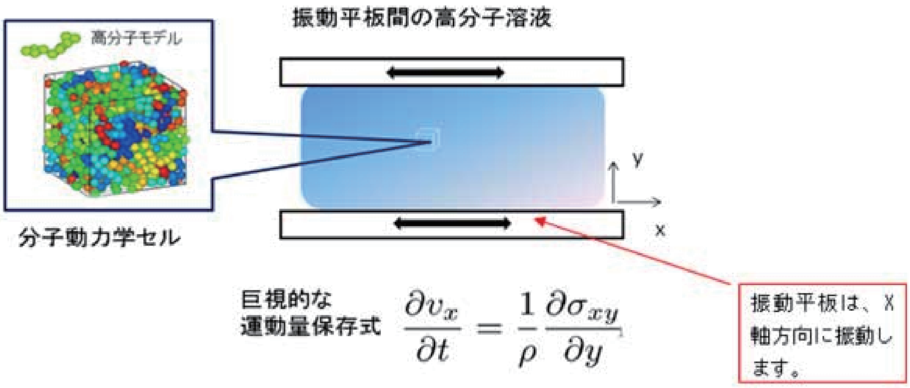


図２．平板間の高分子溶液のマルチスケールシミュレーション

理論研究部門　スーパーバイザー

理学研究科　生物科学専攻

准教授　高田　彰二

（1） 蛋白質のフォールディング理論と立体構造予測

広い意味での蛋白質フォールディング問題にさまざまな角度から取り組んでいます。とくに、「ランダムコイルとして合成される蛋白質がいかにして自発的に、それぞれ独自の3次元構造にフォールディングできるのか」というフォールディング機構の研究、および、「アミノ酸配列が与えられたときに、その蛋白質がとる3次元天然構造が、計算機によって予測できるのか」という立体構造予測問題が主要な課題です。

フォールディング機構の研究では、エネルギー地形の統計理論に基づく、粗視化モデルによる分子シミュレーションから、フォールディング反応の遷移状態アンサンブルの特徴や、フォールディング速度のスケーリング則などを明らかにしました。

立体構造予測研究では、物理化学に基づく経験的エネルギー関数を自作し、それに基づく経験的モンテカルロシミュレーションによって、構造予測を行う方法を開発しています。2 年に一度世界規模で行われる構造予測のコンテストにおいて、2004年、06年に世界トップレベルの成績を収めています。

(2) 分子シミュレーションによる生体分子機械の作動原理研究

フォールディング研究で威力を発揮した粗視化分子モデルを拡張し、それを利用して、分子モーターなどの巨大な生体分子機械の作動原理のシミュレーション研究を行っています。生体分子モーターは、ATPの加水分解によって開放されるわずか12kcal/mol程度の自由エネルギーを利用して、力学的な仕事を取り出すことが出来ます。熱揺らぎとほとんど同程度のエネルギー源からいかにして、効率よく、力学的な運動を取り出せるのか、という問は原理探求として興味深いだけでなく、新しい人工機械の設計原理のためにも重要です。

回転分子モーターF1-ATPase では、粗視化分子モデルによって、実験とつじつまの合う回転運動を再現し、さらに、それから化学力学共役機構について新しい提案を行いました。また、歩く分子モーターであるミオシンVでは、シミュレーション研究から、ブラウン運動の利用の仕方、歩幅を決める機構などを見出しました。そのほか、AAA+ATPase、シャペロニンなどさまざまな分子モーターの作動原理を横断的に研究し、生体分子機械の作動原理を追求しています。

（3） 生体分子シミュレーション方法論の研究

生体分子は柔らかい高分子であり、その機能発現には、しばしば非常に大規模のコンフォーメーション変化を伴います。従って機能発現研究のためには、大規模コンフォーメーション変化を実現することが不可欠ですが、それは容易なことではありません。そこで、大規模ダイナミクスを実現するためのさまざまなシミュレーション方法論の研究も行っています。

ハミルトニアンレプリカ法、自己学習マルチスケールシミュレーション法などのアルゴリズムから、スイッチング郷モデルや多谷モデルなど新しい粗視化モデルの提案まで、さまざまな方法論を開発してきました。

総合研究部門 専任教員

准教授　石田　俊正

（１）　レチナールのab initio動力学計算

ab initio 動力学計算をSchiff塩基11-cisレチナールに対して適用した。電子状態計算にCASSCF/6-31Gを用い、励起状態から基底状態への遷移については、Zhu-Nakamura 公式で見積もった。周囲のタンパク質の影響は考慮していない。

全 trans 型、9-cis 型、11-cis 型(反応物)が生じる場合の時間変化を調べると、どの場合でも C11=C12 角が反時計回りに捩れる（捩れ角の減少）につれて、C9=C10 捩れ角が時計回りに捩れる（捩れ角の増加）がわかる。これはは Fruto ら、Weingart の指摘している「クランク軸運動」をしていることを示している。Fruto らはこのクランク軸運動は、周囲のタンパク質の影響であるとしたが、今回の in vacuo の計算でも現れることから、Weingart の指摘どおり、retinal 固有の運動であることがわかった。また、C9=C10 捩れがどのような場合でも起こることから、気相で 9-cis 型が生成する理由も理解できる。また、全 trans 型と 11-cis 型の間の円錐交差および 9-cis 型と 11-cis 型の間の円錐交差のいずれもが、11-cis 型励起状態から到達可能のであることがわかっており、その事実とも整合的である。

（２）光スイッチ機能分子の反応制御

ジアリールエテンのように、光照射により可逆的に構造が変化する分子はフォトクロミック分子と呼ばれ、光記録、スイッチなどとしての利用が可能である。ジアリールエテンは光照射によって開環・閉環反応を起こすことが知られており、光スイッチとして利用するために光異性化の反応収率の制御に関心が集まっている。このような過程では、ポテンシャルエネルギー曲面間の交差による非断熱遷移が重要な役割をしていることが多い。ジアリールエテンの反応中心と類似の光化学的特性を持つシクロヘキサジエン(CHD、閉環)ーヘキサトリエン(HT、開環)系における反応制御を2次元波束動力学により調べた。図1に座標系を、図2にS1上での波束の運動を模式的に示した。ポテンシャルの決定にはCASSCF/MRCI計算を用いている。5員環構造の円錐交差がCHD,HTの生成に重要な役割を果たすことがわかった。

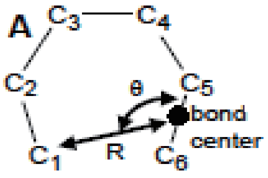


図１　用いた座標系 R，θ

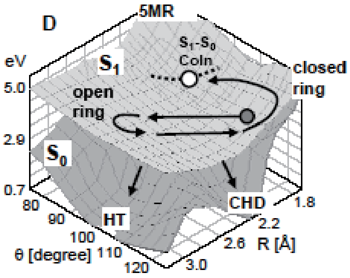


図２　反応制御のないときの S_1 上での波束の運動

さらに、非断熱遷移を制御することによって、機能の効率を高めることが可能となる。二次チャープパルスおよびある方向への運動量付加により、ジアリールエテンの反応中心と類似の光化学的特性を持つシクロヘキサジエン(CHD、閉環)ーヘキサトリエン(HT、開環)系における反応制御を波束動力学により調べた。その結果、（１）二次チャープレーザーパルスを用いると、初期光励起およびポンプーダンプ過程において効率よく遷移を起こして開環型のHTを多く生成可能なこと、（２）閉環型のCHDの五員環への変形方向に大きな運動量を与えると、開環型のHTへの遷移を促進することができることを示した。

(3)少数多体系の反応の計算と実験との比較

O+HCl→OH+Cl反応について、古典トラジェクトリ計算を行い、基底状態$1^1A'$と励起状態$1^1A''$, $2^1A'$に関して微分断面積を計算し、衝突エネルギー依存性を調べ、交差分子線のイオンイメージング法による実験結果と比較を行い、実測とよい一致をみ、衝突エネルギーが6kcal以下の場合には、励起状態の寄与が小さいことを明らかにした。

理論研究部門 専任教員

准教授 佐藤 徹

(1) Jahn-Teller効果の基礎に関する研究

電子状態に縮退がない場合、Born-Oppenheimer近似はよい近似であるが、縮退が有る場合、Born-Oppenheimer近似は破綻する。電子状態が2重に縮退している場合、電子状態は2重縮退している振動モードと相互作用し、分子構造の対称性を低下させ縮退を解消させる。これをE x e Jahn-Teller効果という。このような系において核振動の運動エネルギーを無視することなく取り扱う基礎方程式がE x e 動的Jahn-Teller方程式であるが、1957年にLonguet-Higginsらにより数値解が与えられて以来、現在まで一般の相互作用定数に対する厳密解は得られていない(特定の有理数の相互作用定数に対する解はJuddにより得られている)。近似解析解については、これまで強結合極限においても得られていなかったが、最近、われわれは原点での漸近挙動を正しく取り扱うことにより、強結合極限における解析解を得ることに成功した。

(2) 単一分子伝導における非弾性電流に関する研究

一般に電子が単一分子中を流れるとき、電子は分子振動と相互作用し、非弾性散乱を受けると考えられる。分子ワイヤーにおいては、この非弾性散乱によって電気伝導度が低下し、ジュール熱が発生する。したがって、分子デバイスを設計する際、非弾性散乱の影響を考慮する必要がある。一方で、振動励起による非弾性電流の発生は、単分子をスイッチングデバイスとして利用できる可能性を示している。

近年、Ho らによって Inelastic electron tunneling spectroscopy (IETS) を用いた測定技術が確立され、電極表面に吸着した単分子を流れる非弾性電流を直接観測できるようになった。 以来、様々な分子について非弾性電流の測定が行われ、特にπ共役系では C=C 伸縮振動が鋭いピークを示すことが知られている。非弾性電流は分子の固有振動を反映しており、IETS は電極表面に吸着した分子の同定に役立つと考えられている。 また、 IETS は電子輸送におけるエネルギーの散逸過程を直接観測していることから、ナノサイエンスの立場からも注目されている。

本研究では電極を金電極、分子ワイヤーをチオフェンジチオールとして、振電相互作用定数を第一原理から計算した。さらに、その結果を電子輸送理論を記述できる非平衡グリーン函数理論と組み合わせることで非弾性電流を計算し、振電相互作用の電気伝導に対する影響を考察した。

他に以下のようなテーマで研究を行っている。

(3) 振電相互作用定数の評価に関する研究

(4) 新炭素材料の電子物性ならびに光物性に関する研究

(5) 有機EL材料におけるキャリア輸送に関する研究

Fukui Kenichi Memorial Research Group 1 福井謙一記念研究部門第一

Research Leader Keiji MOROKUMA リサーチリーダー 諸熊 奎治

The central theme of research of our group is “simulation of complex systems”, with a special emphasis on theories of chemical reactions. The goals of the research of this group are 1. to develop further the hybrid theoretical methods (such as ONIOM) already proposed by us, 2. to demonstrate that such hybrid methods can be used for simulations of structures, reactions and dynamics and 3. to solve some of the important problems in each field. Our research is supported in part by the Institute and in large fraction by a 5-year grant in the area of High Performance Computing for Multi-Scale and Multi-Physics Phenomena from CREST (Core Research for Evolutional Science and Technology) program of JST (Japan Science and Technology Agency) until March 2012. With ten to twelve postdoctoral fellows (both Fukui fellows and JST fellows) and other staff as well as in collaboration with my group at Emory University and the group of Prof. Stephan Irle of Nagoya University, we have a strong team of theoretical/computational chemists working together toward a common goal.

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

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

III. Method Development. Several method development projects are also in progress.

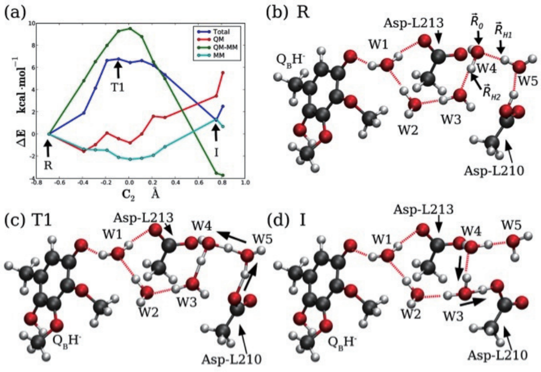
福井謙一記念研究部門第二

リサーチリーダー　大峯　巖

水のダイナミックスの研究、氷の融解過程の分子的機構を調べるとともに、以下のような、光によっておこる生体高分子反応機構の理論的解明を行った。

(1) 光合成中心におけるプロトン移動

光合成細菌Rhodobacter sphaeroides由来の反応中心で生じる光駆動プロトン取り込み機構に関して研究を行った。このタンパク質は、二個の光子によって誘起される二個の電子と二個のプロトンの長距離移動反応を生じさせる事により、secondary ubiquinone(QB)を還元する。還元されたキノン(QBH2)は反応中心から乖離し、チトクロムb/c1複合体で酸化され、膜の反対側にプロトンを放出する。この一連の反応によって膜に対するプロトン濃度勾配が生じる。本研究は、理論化学的手法でQBへのプロトン移動過程の詳細なメカニズムを明らかにするものである。分子動力学計算（MD法）を用いて自由エネルギー計算とプロトン移動経路の探索を行い、また、ハイブリッド型の第一原理分子動力学計算（QM/MM法）を用いて各プロトン移動経路に沿ったポテンシャル面解析を行った。QB-が二個のプロトンを受け取る直前の状態（第二電子移動前）において、プロトン化したGlu-L212とAsp-L210がプロトンドナーである事を示した。Glu-L212からのプロトン移動経路（経路１）はQB-とGlu-L212間の安定な単一の水素結合であること、Asp-L210からの長距離プロトン移動経路（経路２）は幾つかの水分子を介した水素結結合ネットワークによって形成される事などを、MDによる探索で明らかにした。経路１の電子移動前後のプロトン移動ポテンシャル面をQM/MM法などを用いて解析し、経路１は第二電子移動と強くカップルしたプロトン経路であること、経路２では、タンパク質内部の水分子の熱揺らぎ運動によって水素結合ネットワークが組み替わり、プロト移動経路は生成と消滅を繰り返すことなどを示した。経路２を通るAsp-L210からQBH-へのプロトン移動ポテンシャル面を解析した結果、その活性化エネルギーから推定される反応のタイムスケールはFTIR実験によるQBH-のプロトン化反応のタイムスケールと一致した。また、プロトン化したAsp-L210と水分子の強い相互作用から、負に帯電した酸性残基に囲まれたhydroniumイオンが存在すると示唆された。

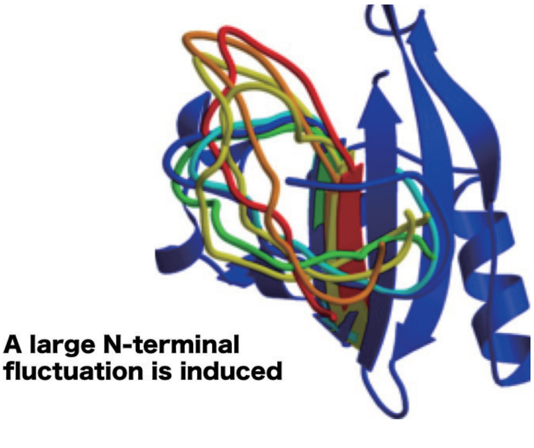


(2) Photoactive Yellow Protein (PYP)の光反応サイクルの研究

紅色光合成細菌の photoactive yellow protein(PYP)は細菌の光センサーと考えられており、p-クマル酸を発色団によって青色光を吸収し、光サイクルを行う。この PYP の光サイクル過程では、光吸収による発色団の trans-cis 異性化に続いて、Glu46 から発色団へのプロトン移動反応、さらに N 末端領域とその近傍のアンフォールドが起こる。本研究において、このプロトン移動反応に続く大きな蛋白質の構造変化の分子論的機構を明らかにする理論研究を行った。

まず、QM/MM 法(Quantum Mechanics と Molecular Mechanics を組み合わせた電子状態記述法) と自由エネルギー摂動法を用いプロトン移動反応に伴う自由エネルギー変化を計算し、分子動力学(MD)計算とアンブレラ法を用いてプロトン移動反応を促進するような構造変化を探索した。その結果、プロトン移動に伴い大量の水分子が蛋白質に取り込まれ、アニオン化した Glu46 を水和し安定化することで、プロトン移動反応を起こりやすくしていること、また Met100 を含むターンや Glu46 を含むヘリックスの構造変化が誘起されていることなどを明らかにした。即ち、PYP の光サイクルで起こるゆっくりとしたプロトン移動反応や、その水和状態への強い依存性は、タンパク質内部への水の取り込みとそれに伴う蛋白質構造や水和構造の変化に起因することを明らかにした。

このようにプロトン移動反応に続いて、N 末端領域のアンフォールドを伴うタンパク質全体に渡る大規模な構造変化が数ミリ秒の長時間をかけて起こるが、この機構を明らかにするために Steered MD 計算を行い、N 末端領域がアンフォールドすることによって Glu46 と N 末端領域の間にある b-シートが部分的に不安定化すること、及び Glu46 の水和が強められていることを明らかにした。プロトン移動後に起こる N 末端領域の構造変化はアニオン化した Glu46 が引きつけた水分子が b-シートを部分的に壊し、それによって b-シートと N 末端領域の間の相互作用が乱され、最終的に N 末端領域がベータシートから切り離されて不安定化、アンフォールドするという機構であることを示した。すなわち PYP の光サイクルの鍵となるステップの分子機構を解明し、タンパク質の周囲に存在する水分子の役割、即ち発色団の光異性化によって誘起されるプロトン移動反応過程や N 末端領域のアンフォールドに於ける、水分子移動・水和構造の変化の詳細、を明らかにした。



Ⅱ 博士研究員

１．博士研究員組織

平成 21 年度

職　名		氏　名
福井謙一記念 研究部第一	福井センターフェロー	Lung Wa Chung
	福井センターフェロー	Biswajit Saha
	福井センターフェロー	平尾　一
	福井センターフェロー	Zhuofeng Ke
	(JST) フェロー	河津　励
	(JST) フェロー	岡本　佳子
	(JST) フェロー	Xin Li
	(JST) フェロー	Safwat Abdel-Azeim
	(JST) フェロー	Alister Page
	(JST) フェロー	K.R.S. Chandrakumar
	(JST) フェロー	Fengyi Liu
	(JST) フェロー	Parameswaran Pattiyil
福井センターフェロー		田代　基慶
福井センターフェロー		Wilfredo Credo Chung
福井センターフェロー		坂上　貴洋
福井センターフェロー		岩城　貴史

２．博士研究員プロフィール

【氏名（ふりがな）】	Lung Wa Chung（るん　わ　ちゅん）
【職名】	FIFC Fellow
【所属】	Fukui Kennichi Memorial Research Group 1, Fukui Institute For Fundamental Chemistry
【研究室】	Room 212
【直通電話】	075-711-7631
【電子メールアドレス】	chung@fukui.kyoto-u.ac.jp
【研究分野】	Computational Chemistry
【現在の研究課題】	Metalloenzymes, photobiology, multi-scale simulations
【研究内容キーワード】	Reaction mechanism of metalloenzymes and photobiologies
【学歴】	Aug. 2000, B.Sc. in Chemistry (1st Hon.), The Hong Kong University of Science & Technology; Aug. 2003, M. Phil. in Chemistry, The Hong Kong University of Science & Technology; Aug. 2006, Ph. D. in Chemistry, The Hong Kong University of Science & Technology
【学位】	Ph. D. in chemistry, The Hong Kong University of Science & Technology
【主な著書、学術論文】 （過去5年以内）	1. A. Chung, L. W.; Li, X.; Sugimoto, H.; Shiro, Y.; Morokuma, K. "A DFT Study on a Missing Piece in Understanding of Heme Chemistry: The Reaction Mechanism for Indoleamine 2,3-Dioxygenase (IDO) and Tryptophan 2,3-Dioxygenase (TDO)", *J. Am. Chem. Soc.* **2008***, 130,* 12298. 2. Chung, L. W.; Hayashi, S.; Lundberg, M.; Nakatsu, T.; Kato, H.; Morokuma, K. "Mechanism of Efficient Firefly Bioluminescence via Adiabatic Transition State and Seam of Sloped Conical Intersection", *J. Am. Chem. Soc. (Communication)* **2008***, 130,* 12880. 3. Wu, Y.-D.; Chung, L. W.; Zhang, X.-H. "*Hydrosilylation Reactions Discovered in the Last Decade: Combined Experimental and Computational Studies on the New Mechanisms,*" In: "Computational Modeling for Homogeneous and Enzymatic Catalysis" Morokuma, K.; Musaev, D. G. Eds. WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, **2008,** pp285-316. 4. Li. X.; Chung, L. W.; Paneth, P.; Morokuma, K. "DFT and ONIOM(DFT:MM) Studies on Co-C Bond Cleavage and Hydrogen Transfer in B12-Dependent Methylmalonyl-CoA Mutase. Stepwise or Concerted Mechanism?", *J. Am. Chem. Soc.* **2009,** *131,* 5115. 5. Li. X.; Chung, L. W.; Mizuno, H.; Miyawaki, A.; Morokuma, K. "A Theoretical Study on the Natures of On- and Off-States of Reversibly Photoswitching Fluorescent Protein Dronpa: Absorption, Emission, Protonation and Raman", *J. Phys. Chem. B* **2010,** *114,* 1114 6. Chung, L. W.; Li, X.; Morokuma, K. "*Modeling Enzymatic Reactions in Metalloenzymes and Photobiology by Quantum Mechanics (QM) and Quantum Mechanics/Molecular Mechanics (QM/MM) Calculations,*" In "Quantum Biochemistry" Matta, C. Eds. WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, **2010,** pp85-130. 7. Noda, S.; Nakamura, A.; Kochi, T.; Chung, L. W.; Morokuma, K.; Nozaki, K. "Mechanistic Studies on the Formation of Linear Polyethylene Chain Catalyzed by Palladium Phosphine-Sulfonate Complexes: Experiment and Theoretical Studies", *J. Am. Chem. Soc.* **2009,** *131,* 14088 8. Li, X.; Chung, L. W.; Morokuma, K. "Modeling Photobiology Using Quantum Mechanics (QM) and Quantum Mechanics/Molecular Mechanics (QM/MM) Calculations," In "Computational Methods for Large systems: Electronic Structure Approaches for Biotechnology and Nanotechnology" Reimers, *J. R. Eds. Wiley,* **2010,** pp342-373. 9. Chung, L. W.; Li, X.; Sugimoto, H.; Shiro, Y.; Morokuma, K. "ONIOM Study on a Missing Piece in Our Understanding of Heme Chemistry: Bacterial Tryptophan 2,3-Dioxygenase (TDO)", *J. Am. Chem. Soc.* 2010, **132**, 11993

【氏名（ふりがな）】	Biswajit Saha（びすわじと　さは）
【職名】	FIFC Fellow
【所属】	Morokuma Group, Fukui Institute for Fundamental Chemistry
【研究室】	Room 203
【直通電話】	075-711-7834
【FAX】	075-781-4757
【電子メールアドレス】	saha@fukui.kyoto-u.ac.jp
【ホームページ】	http://www.fukui.kyoto-u.ac.jp/~saha
【研究分野】	Computational Chemistry
【現在の研究課題】	Molecular dynamics (MD) simulations and electronic structure calculations of nano-materials
【研究内容キーワード】	Fullerene, nano-tube, metallofullerene, polycyclic aromatic hydrocarbon, DFTB
【学歴】	November 1998, Master of Science (M. Sc.), Calcutta University, India December 2003, Doctor of Science (Ph. D.), Indian Association for the Cultivation of Science (IACS), Jadavpur University, India
【学位】	Ph. D. (Science)
【略歴】	December 2003, Postdoctoral fellow, University of Kassel, Germany September 2004, JSPS postdoctoral fellow, Kyoto University, Japan November 2006, Postdoctoral fellow, FIFC, Kyoto University, Japan
【所属学会】	Life member, IACS, India Member, American Chemical Society
【主な著書、学術論文】（過去5年以内）	1. B. Saha, S. Irle, K. Morokuma, “Formation mechanism of polycyclic aromatic hydrocarbons (PAHs) in benzene combustion: Quantum chemical molecular dynamics simulations”, *J. Chem. Phys.* **132**, 224303(2010) 2. B. Saha, S. Shindo, S. Irle, K. Morokuma, “Quantum chemical molecular dynamics (QM/MD) simulations of fullerene from benzene”, ACS Nano 3, 2241 (2009) 3. B. Saha, M. Ehara, H. Nakatsuji, “Investigation of electronic spectra and Excited-state geometries of poly-para-phenylene vinylene (PPV) and poly-para-phenylene by symmetry adapted configuration-interaction (SAC-CI) method”, *J. Phys. Chem. A* **111**, 5473, (2007) 4. B. Saha, S. Fritzsche, “Influence of dense plasma on the low lying transitions in Be-like ions: relativistic multiconfiguration Dirac-Fock calculation”, J. Phys. B: At. Mol. Opt. Phys. 40, 259 (2007) 5. B. Saha, M. Ehara, H. Nakatsuji, “Singly and doubly excited states of butadiene, acrolein and glyoxal: geometries and electronic spectra”, *J. Chem. Phys.* **124,** 014316 (2006)
【学術関係の受賞など】	JSPS postdoctoral fellowship, 2004-2006 Research fellowship, IACS, India, 1999 - 2003 National scholarship, Indian Government, 1990-1995

【氏名（ふりがな）】	Hajime Hirao（はじめ　ひらお）
【職名】	FIFC Fellow
【所属】	Fukui Kenichi Memorial Research Group 1, Fukui Institute for Fundamental Chemistry
【研究室】	Room 212
【直通電話】	075-711-7647
【FAX】	075-781-4757
【電子メールアドレス】	hirao@fukui.kyoto-u.ac.jp
【研究分野】	Computational bioinorganic chemistry, Metalloenzymes, Transition-metal catalysts
【現在の研究課題】	Computational studies of bioinorganic systems
【研究内容キーワード】	metalloenzymes, chemical reactions, electronic excited states, spectroscopy, ONIOM, QM/MM, medicinal chemistry, molecular interactions
【学歴】	Mar. 1998 BSc, Department of Engineering, Kyoto University Mar. 2000 MSc, Graduate School of Engineering, Kyoto University
【学位】	Nov. 2004, PhD, The University of Tokyo
【略歴】	Jan. 2002-Dec. 2004 Lab associate at Tsukuba Research Institute, Novartis Pharma K.K. Jan. 2005-Mar. 2007 Postdoc at The Hebrew University of Jerusalem Apr. 2007-Mar. 2009 JSPS Postdoctoral Fellow for Research Abroad (Hebrew University/Emory University) Apr. 2009- FIFC Fellow at Kyoto University
【所属学会】	American Chemical Society; The Chemical Society of Japan; The Pharmaceutical Society of Japan; Japan Society for Molecular Science; Chem-Bio Informatics Society; Japan Society of Coordination Chemistry; Society of Computer Chemistry, Japan; The Biophysical Society of Japan
【主な著書、学術論文】 （過去5年以内）	1. H. Hirao, K. Morokuma, "What is the Real Nature of Ferrous Soybean Lipoxygenase-1? A New Two-Conformation Model Based on Combined ONIOM(DFT:MM) and Multireference Configuration Interaction Characterization," *J. Phys. Chem. Lett.* **2010**, *1*, 901-906. 2. H. Hirao, K. Morokuma, "Insights into the (Superoxo)Fe(III)Fe(III) Intermediate and Reaction Mechanism of *myo*-Inositol Oxygenase: DFT and ONIOM(DFT:MM) Study," *J. Am. Chem. Soc.* **2009**, *131,* 17206-17214. 3. O. Irie, T. Kosaka, T. Ehara, F. Yokokawa, T. Kanazawa, H. Hirao, A. Iwasaki, J. Sakaki, N. Teno, Y. Hitomi, G. Iwasaki, H. Fukaya, K. Nonomura, K. Tanabe, S. Koizumi, N. Uchiyama, S. J. Bevan, M. Malcangio, C. Gentry, A. J. Fox, M. Yaqoob, A. J. Culshaw, A. Hallett, "Discovery of Orally Bioavailable Cathepsin S Inhibitors for the Reversal of Neuropathic Pain," *J. Med. Chem.* **2008**, *51*, 5502-5505. 4. S. Shaik, H. Hirao, D. Kumar, "Reactivity Patterns of High-Valent Iron Oxo Species in Enzymes and Synthetic Reagents: A Tale of Many States," *Acc. Chem. Res.* **2007**, *40*, 532-542. 5. H. Hirao, D. Kumar, L. Que, Jr., S. Shaik, "Two-State Reactivity in Alkane Hydroxylation by Nonheme Iron-Oxo Complexes," *J. Am. Chem. Soc*. **2006**, *128*, 8590-8606. 6. H. Hirao, D. Kumar, W. Thiel, S. Shaik, "Two States and Two More in the Mechanisms of Hydroxylation and Epoxidation by Cytochrome P450," *J. Am. Chem. Soc.* **2005**, *127*, 13007-13018.
【学術関係の受賞など】	Oct. 2006-Mar. 2007 Golda Meir Fellowship Apr. 2007-Mar. 2009 JSPS Postdoctoral Fellowship for Research Abroad Oct. 2009-Mar. 2011 Kyoto Univ. Startup Grant for Young Researchers Mar. 2010 Kurata Grant

【氏名（ふりがな）】	Zhuofeng Ke （ちょーふん くー）
【職名】	FIFC Fellow
【所属】	Morokuma Group, Fukui Institute For Fundamental Chemistry
【研究室】	Room 207
【直通電話】	075-711-7893
【FAX】	
【電子メールアドレス】	zhuofeng.ke@fukui.kyoto-u.ac.jp
【研究分野】	Computational Chemistry
【現在の研究課題】	Rh-Catalyzed Polymerization of Phenylacetylene in Nano-Cavity of apo-Ferritin
【研究内容キーワード】	Computational study of catalysis processes in organometallic systems and bio-systems
【学歴】	2002 B.Sc. in Chemistry, Sun Yat-sen University, 2005 M.Sc. in Polymer Chemistry and Physics, Sun Yat-sen University 2007 Jointly Educating Ph.D. in computational organometallic chemistry, University of North Texas, 2009 Ph.D. in Physical Chemistry (Theoretical and Computational Chemistry), Sun Yat-sen University
【学位】	Ph.D. in Physical Chemistry (Theoretical and Computational Chemistry), Sun Yat-sen University
【主な著書、学術論文】 （過去5年以内）	1. Zhuofeng Ke and Thomas R. Cundari* “Palladium-Catalyzed C–H Activation/C–N Bond Formation Reactions: DFT Study of Reaction Mechanisms and Reactive Intermediates” *Organometallics* 2010, **29** (4), 821-834. 2. Guo, Z.; Xue, Jiadan; Ke, Zhuofeng; Phillips, D. L.*; Zhao, C.Y.* “Influence of Water Hydrogen Bonding on the Reactions of Arylnitrenium Ions With Guanosine: Hydrogen-Bonding Effects Can Favor Reaction at the C8 Site” *J. Phys. Chem. B,* 2009, **113**, 6528- 6532. 3. Foley, N. A.; Lee, J. P.; Ke, Zhuofeng; Gunnoe, T. B.*; and Cundari, T. R.* “Ru(II) Catalysts Supported by Hydridotris(pyrazolyl)borate for the Hydroarylation of Olefins: Reaction Scope, Mechanistic Studies, and Guides for the Development of Improved Catalysts” *Acc. Chem. Res.* 2009, **42**, 585-597. 4. Lee, J. P.; Ke, Zhuofeng; Ramrez M. A.; Gunnoe, T. B.*; Cundari T. R.*; Boyle, P. D.; Petersen, J. L. “Six-, Five-, and Four-Coordinate Ruthenium(II) Hydride Complexes Supported by N-Heterocyclic Carbene Ligands: Synthesis, Characterization, Fundamental Reactivity, and Catalytic Hydrogenation of Olefins, Aldehydes, and Ketones” *Organometallics* 2009, **28**, 1758-1775 5. Liu, Yan; Ke, Zhuofeng; Cui, Jianfang; Chen, Wen-Hua; Ma, Lin; Wang Bo*. “Synthesis, Inhibitory Activities and QSAR Study of Xanthone Derivatives as α-Glucosidase Inhibitors” *Bioorg. Med. Chem.* 2008, **16**, 7185-7192. 6. Foley, Nicholas A.; Ke, Zhuofeng; Gunnoe, T. Brent*; Cundari, Thomas R.*; and Petersen, Jeffrey L. “Aromatic C-H Activation and Catalytic Hydrophenylation of Ethylene by $\mathrm{TpRu\{P(OCH_2)_3CEt\}}$ (NCMe)Ph” *Organometallics* 2008, **27**, 3007-3017. 7. Guo, Zhen; Ke, Zhuofeng; Phillips, David Lee*; Zhao, Cunyuan*. “Intrinsic Reaction Coordinate Analysis of the Activation of CH4 by Molybdenum atoms: A Density Functional Theory Study of the Crossing Seams of the Potential Energy Surfaces” *Organometallics* 2008, **27**, 181-188. 8. Gao, Haiyang; Ke, Zhuofeng; Pei, Lixia; Song, Keming; Wu, Qing*. “Drastic ligand electronic effect on anilidoeimino nickel catalysts toward ethylene polymerization” *Polymer* 2007, **48**, 7249-7254. 9. Lin, Xufeng; Zhao, Cunyuan; Che, Chi-Ming*; Ke, Zhuofeng; Phillips, David Lee. “A DFT Study on the Mechanism of Rh2II,II-Catalyzed Intramolecular Amidation of Carbamates” *Chem. Asian J*. 2007, **2**, 1101-1108 10.Ke, Zhuofeng; Zhou, Yubing; Gao, Hui; Zhao, Cunyuan*, Phillips, David Lee. “On the Mechanism and Stereochemistry of Chiral Lithium Carbenoid Promoted Cyclopropanation Reactions” *Chem. Eur. J.* 2007, **13**, 6724-6731. 11.Fang, Ran; Ke, Zhuofeng; Shen, Yong; Zhao, Cunyuan*; Phillips, David Lee. “Concurrent Cyclopropanation by Carbenes and Carbanions? A Density Functional Theory Study on the Reaction Pathways” *J. Org. Chem.* 2007, **72**, 5139–5145. 12.Ke, Zhuofeng; Zhao, Cunyuan*; Phillips, David Lee. “Methylene Transfer or Carbometalation? A Theoretical Study to Determine the Mechanism of Lithium Carbenoid Promoted Cyclopropanation Reactions in Aggregation and Solvation States.” *J. Org. Chem.* 2007, **72**, 848–860. 13.Li, Zhao-Hui; Ke, Zhuofeng; Zhao, Cunyuan*; Geng, Zhi-Yuan; Wang, Yong-Cheng; Phillips, David Lee*. “A Density Functional Theory Study of Aluminum Carbenoid $\mathrm{(CH_3)_2AlCH_2X}$ (X = Cl, Br, I) Promoted Cyclopropanation Reactions Compared to IMCH2I (M = Li, Sm, Zn) Carbenoids. “ *Organometallics* 2006, **25,** 3735–3742. 14.Zhang, Junkai; Ke, Zhuofeng; Bao, Feng; Long, Jieming; Gao, Haiyang; Zhu, Fangming; Wu, Qing*. “Ethylene polymerization and oligomerization catalyzed by bulky β-diketiminato Ni(II) and β-diimine Ni(II) complexes/methylaluminoxane systems.” *J. Mol. Catal. A: Chem*. 2006, **249**, 31–39. 15.Ye, Guodong; Ke, Zhuofeng; Yang, Jianwen; Zhao, Tianyi; Zeng, Zhaohua*; Chen, Yonglie. “Low VOC bifunctional photoinitiator based on a-hydroxyalkylphenone structure.” *Polymer* 2006, **47**, 4603–4612. 16.Zhou, Yu-Bing; Ke, Zhuo-Feng; Zhao, Cun-Yuan*. “A theoretical study on the mechanism of ruthenium(II)-catalyzed reaction of organic azide with alkyne.” *Acta Chimica Sinica* 2006, **64**, 2071–2078.
【学術関係の受賞など】	Sun Yat-sen University Fellow 2009 State Scholarship Funds, China Scholarship Council (CSC) 2007 SSSAP Scholar, Univeristy of North Texas 2007

【氏名（ふりがな）】	河津　励（かわつ　つとむ）
【職名】	JSTフェロー
【所属】	福井謙一記念研究センター　福井記念研究部第一
【研究室】	福井謙一記念研究センター　212号室
【直通電話】	075-711-7631
【FAX】	075-781-4757
【電子メールアドレス】	kawatsu@fukui.kyoto-u.ac.jp
【ホームページ】	http://kmweb.fukui.kyoto-u.ac.jp/top/member/kawatsu/index.html
【研究分野】	蛋白質シミュレーション
【現在の研究課題】	酵素反応の自由エネルギー計算
【研究内容キーワード】	蛋白質、反応、自由エネルギー、分子動力学、量子化学
【学歴】	2002年2月 名古屋大学理学研究科物質理学専攻博士後期課程修了
【学位】	2002年2月 理学博士 (名古屋大学)
【略歴】	2002年 3月 デューク大学化学科ポスドク、 2005年 9月 ジョージア工科大学化学生化学科ポスドク、 2006年11月 京都大学福井謙一記念研究センター JSTフェロー
【所属学会】	American Physical Society、American Biophysical Society、日本生物物理学会
【主な著書、学術論文】 （過去5年以内）	1. M. Lundberg, T. Kawatsu, T. Vreven, M. J. Frisch and K. Morokuma, “Transition states in the protein environment-ONIOM QM:MM modeling of isopenicillin N synthesis,” *J. Chem. Theory Comput.* **2009**, *5,* 222-234. 2. T. Kawatsu, V. Coropceanu, A. Ye, J.-L. Brédas, “A Quantum-Chemical Approach to Electronic Coupling: Application to Charge Separation and Charge Recombination Pathways in a Model Molecular Donor-Acceptor System for Organic Solar Cells,” *J. Phys. Chem. C* **2008**, *112,* 3429-3433. 3. T. Kawatsu, D. N. Beratan, T. Kakitani, “Conformationally averaged score functions for electronic propagation in proteins,” *J. Phys. Chem. B* **2006**, *110,* 5747. 4. T. Kawatsu, D. N. Beratan, “Electron transfer between cofactors in protein domains linked by a flexible tether,” *Chem. Phys.* **2006**, *326*, 259. 5. S. S. Skourtis, I. A. Balabin, T. Kawatsu, D. N. Beratan, “Protein dynamics and electron transfer: electronic decoherence and non-Condon effects,” *Proc. Natl. Acad. Sci. USA* **2005**, *102,* 3552. 6. H. Nishioka, A. Kimura, T. Yamato, T. Kawatsu, T. Kakitani, “Interference, fluctuation and alternation of electron tunneling in protein media. 2. Non-Condon theory for the energy gap dependence of electron transfer rate,” *J. Phys. Chem. B* **2005,** *109,* 15621. 7. H. Nishioka, A. Kimura, T. Yamato, T. Kawatsu, T. Kakitani, “Interference, fluctuation and alternation of electron tunneling in protein media. 1. Two tunneling routes in photosynthetic reaction center alternate due to thermal fluctuation of protein conformation,” *J. Phys. Chem. B* **2005**, *109,* 1978

【氏名（ふりがな）】	岡本　佳子（おかもと　よしこ）
【職名】	JSTフェロー
【所属】	福井謙一記念研究センター　福井謙一記念研究部第一
【研究室】	福井謙一記念研究センター　203号室
【直通電話】	075-711-7831
【FAX】	075-781-4757
【電子メールアドレス】	okamoto@fukui.kyoto-u.ac.jp
【研究分野】	理論物理、計算科学、理論化学
【現在の研究課題】	単層カーボンナノチューブ生成における遷移金属触媒の役割の解明
【研究内容キーワード】	カーボンナノチューブ，遷移金属触媒、分子動力学計算
【学歴】	京都大学大学院理学研究科物理学・宇宙物理学専攻　博士課程中退
【学位】	京都大学博士（理学）
【略歴】	三菱総合研究所研究員 外務省在ウィーン日本政府代表部専門調査員 京都大学大学院理学研究科 研究生 福井謙一記念研究センター　研究補助 2007年3月より　福井謙一記念研究センター　JSTフェロー
【所属学会】	日本物理学会、日本化学会
【主な著書、学術論文】 （過去5年以内）	1. Y. Okamoto, Spin Wave and Sound in High-Field Phase of Solid Helium-3, *J. Phys. Soc. Jpn.* **75**, 094601/1-16 (2006). 2. S. Irle, Y. Okamoto, G. Zheng and K. Morokuma, NCC-DFTB Molecular Dynamics Study of Fe/Co/Ni Catalyst Particle Melting and Carbide Formation During SWCNT Nucleation, in “DFT calculations on fullerenes and carbon nanotubes”, ed. V.A. Basiuk and S. Irle, Research Signpost, 413-434 (2009). 3. Y. Ohta, Y. Okamoto, S. Irle, and K. Morokuma, Density-functional tight-binding molecular dynamics simulations of SWCNT growth by surface carbon diffusion on an iron cluster, *Carbon,* **47**, 1270-1275 (2009). 4. Y. Ohta, Y, Okamoto, S, Irle, and K. Morokuma, Temperature dependence of SWNT growth process on an iron cluster: density functional tight-binding molecular dynamics, *J. Phys. Chem. C,* **113,** 159-169, (2009). 5. Y. Ohta, Y. Okamoto, S. Irle, and K. Morokuma, Rapid growth of a single-walled carbon nanotube on an iron cluster: Density-functional tight-binding molecular dynamics simulations, ACS nano 2, 1437-1444 (2008).

【氏名（ふりがな）】	Xin Li （しん　り）
【職名】	JST Fellow
【所属】	Fukui Institute for Fundamental Chemistry
【研究室】	Room 212
【直通電話】	075-711-7647
【電子メールアドレス】	lixin@fukui.kyoto-u.ac.jp
【研究分野】	Computational Chemistry
【現在の研究課題】	1. Radical Reaction Mechanism in B12-Dependent Methylmalonyl-CoA Mutase 2. Reversibly Photoswitchable Fluorescent Protein: Dronpa 3. Irreversible Photoconversion Fluorescent Protein: Kaede
【研究内容キーワード】	Reaction mechanisms of metalloenzymes and photobiology
【学歴】	June 2005, Ph. D., College of Chemistry, Liaoning Normal University
【学位】	Ph. D. in Physical Chemistry from Liaoning Normal University
【略歴】	July 2005-May 2007, Postdoctoral Fellow, Peking University
【主な著書、学術論文】（過去5年以内）	1. Xin Li and Zhong-Zhi Yang, "An Ab initio Study of Proton-Transfer Reaction in Be^{2+}(H$_2$O)$_n$ and the Spatial Changing Feature in the Formation Process of Hydroxide" , *J. Theor. Comp. Chem*. **5**(1), 75-85 (2006). 2. Xin Li and Zhong-Zhi Yang, "ABEEM/MM-based Pair Potential for Molecular Dynamics Simulation of Fe^{2+}(aq) and Fe^{3+}(aq)" , *J. Theor. Comp. Chem.* **5**(1), 341-353 (2006). 3. Ling Xu, Xin Li, et al., "Ion-Specific Swelling of Poly (Styrene Sulfonic Acid) Hydrogel", *J. Phys. Chem. B* **111**(13), 3391-3397 (2007). 4. Fu-Qiang Shi, Xin Li, et al., "DFT Study of the Mechanisms of In Water Au(I)-Catalyzed Tandem [3,3]-Rearrangement/Nazarov Reaction/[1,2]-Hydrogen Shift of Enynyl Acetates: A Proton-Transport Catalysis Strategy in the Water-Catalyzed [1,2]-Hydrogen Shift", *J. Am. Chem. Soc.* **129,** 15503-15512 (2007). 5. Xin Li, Si-Yu Ye, Chuan He, and Zhi-Xiang Yu, "Mechanisms of Br-nsted Acid Catalyzed Additions of Phenols and Protected Amines to Olefins: A DFT Study", *Eur. J. Org. Chem.* 4296-4303 (2008). 6. Lung Wa Chung, Xin Li, Hiroshi Sugimoto, Yoshitsugu Shiro, Keiji. Morokuma, "A DFT Study on a Missing Piece in Understanding of Heme Chemistry: The Reaction Mechanism for Indoleamine 2,3-Dioxygenase (IDO) and Tryptophan 2,3-Dioxygenase (TDO)", *J. Am. Chem. Soc.* **131**, 12298 (2008). 7. Xin Li, Lung Wa Chung, Piotr Paneth, and Keiji Morokuma, "DFT and ONIOM(DFT:MM) Studies on Co-C Bond Cleavage and Hydrogen Transfer in B12-Dependent Methylmalonyl-CoA Mutase. Stepwise or Concerted Mechanism?", *J. Am. Chem. Soc.* **131**, 5115-5125 (2009). 8. Xin Li, Lung Wa Chung, Hideaki Mizuno, Atsushi Miyawaki, and Keiji Morokuma, "A Theoretical Study on the Nature of On- and Off-States of Reversibly Photoswitching Fluorescent Protein Dronpa: Absorption, Emission, Protonation and Raman", *J. Phys. Chem. B* **114**, 1114-1126 (2010).
【学術関係の受賞など】	Postdoctoral Science Fund of China in Peking University, 2006.

【氏名（ふりがな）】	Safwat Abdel-Azeim （さふわっと　あぶでる　あじーむ）
【職名】	JST fellow
【所属】	Fukui Institute for Fundamental Chemistry
【研究室】	Room 212
【直通電話】	075-711-7647
【電子メールアドレス】	safwat.abdel-azeim@fukui.kyoto-u.ac.jp
【ホームページ】	http://kmweb.fukui.kyoto-u.ac.jp/top/eng/member2.html#safa
【研究分野】	Computational Chemistry
【現在の研究課題】	Enzymatic catalysis
【研究内容キーワード】	Metalloenzyme, QM/MM methods, MetH, MetE and homocysteine activation
【学歴】	June 2004, Master of Sci., physical chemistry University of Paris-XI July 2008, Doctor of Sci., Molecular modeling University of Paris-XI
【学位】	Doctor of Science from Paris-XI University
【略歴】	Oct. 2008, Postdoctoral Fellow, Kyoto University Japan, Oct. 2009 Postdoctoral fellow, Ecole Normale Supérieure de Cachan, France
【所属学会】	SFBBM, société française de biochimie et biologie moléculaire
【主な著書、学術論文】（過去5年以内）	1. **Abdel-Azeim, S.**, Van Der Rest, G. (2005). Thermochemical properties of the ammonia-water ionized dimmer probed by ion-molecule reactions. *J. Phys. Chem. A* **109**, 2505-2513. 2. Mouawad, L., Tétreau, C., **Abdel-Azeim, S.**, Perahia, D. and Lavalette, D. (2007). CO Migration in cytochrome P450cam studied by molecular dynamics simulations. *Prot. Sci.*, **16,** 781-794 3. Darra, E., **Abdel-Azeim, S.**, Manara, A., Shoji, K., Maréchal, J-D., Mariotto, S., Cavalieri, E., Perbellini, L., Pizza, C., Perahia, D., Crimi, M., and Suzuki, H., (2008). Insight into the apoptosis-induced action of α-bisabolol towards malignant tumour cells: involvement of lipid rafts and bid. *Arch. Biochem. Biophys.*, **476**, 113-123. 4. **Abdel-Azeim, S.**, Mouawad, L., Perahia, D., and Maréchal, J-D, (2008). Study of the molecular basis of the unusual calcium binding properties of the Human centrin-2 by a combined MD and QM/MM approach. Poster in the International Symposium - Theoretical Biochemistry - Methods and Applications Wenner-Gren Center, Stockholm-Sweden, May 14-17, 2008. 5. Scarabelli, T., Mariotto, S., **Abdel-Azeim, S.**, Shoji, K., Darra, E., Stephanou, A., Chen-Scarabelli, C., Marechal, J-D., Knight, R., Ciampa, A., Carcereri, de Prati, A., Z., Yuan, E., Cavalieri, Allebban, Z., Menegazzi, M., Latchman, D., Pizza, C., Perahia, D. , and Suzuki, H. (2009). Targeting STAT1 by myricetin and delphinidin provides efficient protection in the heart from ischemia/reperfusion-induced injury. *FEBS Lett.* , 531-541. 6. **Abdel-Azeim, S.**, Mouawad, L., Perahia, D., and Maréchal, J-D. QM/MM study of calcium binding properties of the human centrin-2, (to be submitted). 7. Romeo, S., **Abdel-Azeim, S.**, Mariotto, S., Pizza, C., Shoji, K., Darra, E., Marechal, J-D., Ciampa, A., Cavalieri, Allebban, Z., Menegazzi, Perahia, D. , and Suzuki, H. Structural features of catechins responsible for inhibitory action on signal transducer and activator of transcription 1 (to be submitted). 8. Homocysteine activation in Cobalamin-dependent methyltransferase: DFT and ONIOM study. **S. Abdel-Azeim**, X. Li, L. W. Chung and K. Morokuma, to be submitted
【学術関係の受賞など】	Sidaction Postdoctoral fellow for young researcher, Oct. 2009-2011

【氏名（ふりがな）】	Alister Page（ありすたー　ぺいじ）
【職名】	JST Fellow
【所属】	Fukui Kenichi Memorial Research Group 1, Fukui Institute for Fundamental Chemistry
【研究室】	Room 203
【直通電話】	075-711-7831
【FAX】	095-781-4757
【電子メールアドレス】	alisterpage@fukui.kyoto-u.ac.jp
【研究分野】	Computational Chemistry
【現在の研究課題】	Molecular Dynamics simulations and electronic structure calculations of nanoscale self-assembly processes (in particular, carbon nanotube nucleation and growth).
【研究内容キーワード】	Single-walled carbon nanotube, self-assembly, nucleation, growth, healing, (n,m) chirality, density-functional tight-binding
【学歴】	2004, Bachelor of Mathematics (Honours Class I), The University of Newcastle, Australia 2004, Bachelor of Science (Honours Class I), The University of Newcastle, Australia 2008, Doctor of Philosophy, The University of Newcastle, Australia
【学位】	Doctor of Philosophy, The University of Newcastle, Australia
【略歴】	2008, Postdoctoral Research Associate, Priority Research Centre for Energy, Department of Chemical Engineering, The University of Newcastle, Australia
【所属学会】	American Chemical Society, Royal Australian Chemistry Institute
【主な著書、学術論文】 （過去5年以内）	1. A. J. Page, S. Irle, K. Morokuma, “Polyyne Extension and Ring Collapse Drives Ni-Catalyzed SWNT Growth” , *J. Phys. Chem. C,* **114**, 8206, (2010) 2. A. J. Page, Y. Ohta, Y. Okamoto, S. Irle, K. Morokuma, “Defect Healing During Single-Walled Carbon Nanotube Growth: A Density-Functional Tight-Binding Molecular Dynamics Investigation”, *J. Phys. Chem. C*, **113**, 20198, (2009) 3. A. J. Page, B. Moghtaderi, “Molecular Dynamics Simulation of the Low-Temperature Partial Oxidation of CH_4” , *J. Phys. Chem. A,* **20,** 1539, (2009) 4. A. J. Page, E. I. von Nagy-Felsobuki, “Ab Initio Rovibrational Spectrum of the NaH_2^{2+} Ion-Quadrupole Complex” , Theor. *Chem. Acc.*, **120**, 87, (2009) 5. A. J. Page, E. I. von Nagy-Felsobuki, “Ab Initio Study of Ground State MH_2, $HMHe^+$ and MHe_2^{2+}, M = Mg, Ca”, Phys. Chem. Chem. Phys., 10, 1285, (2008) 6. A. J. Page, E. I. von Nagy-Felsobuki, “Rovibrational Spectra of LiH_2^+, $LiHD^+$ and LiD_2^+ Determined using FCI Property Surfaces”, *J. Phys. Chem. A*, **111**, 4478, (2007)
【学術関係の受賞など】	Australian Post-Graduate Award (2005-2008) RACI Chemistry Honours Prize (2004) Deans Medal, Faculty of Science and IT, The University of Newcastle (2004)

【氏名（ふりがな）】	K. R. S. Chandrakumar （ちゃんどらくまーる）
【職名】	JST Fellow
【所属】	Fukui Kenichi Memorial Research Group 1, Fukui Institute for Fundamental Chemistry
【研究室】	Room 203
【直通電話】	075-711-7834
【FAX】	075-781-4757
【電子メールアドレス】	krsc@fukui.kyoto-u.ac.jp; krschandrakumar@gmail.com
【研究分野】	Computational Chemistry
【現在の研究課題】	DFTB-MD simulation of carbon nanotube growth from the metal decorated carbon nanocones
【研究内容キーワード】	carbon nanotube, nanocones, self-assembly, nanocapsules, density-functional tight-binding
【学歴】	B.Sc., with distinction, Madurai Kamaraj University, (General Chemistry with Physics and Mathematics as ancillary subjects) 1994 M.Sc., with first class, Madurai Kamaraj University, (specialization in Physical Chemistry) 1996 Ph.D., Pune University, National Chemical Laboratory, 2003 Thesis Title: Theoretical studies on some aspects of chemical reactivity using density based descriptors.
【学位】	Doctor of Philosophy, Pune University, National Chemical Laboratory
【略歴】	Since 2004, working as a Scientific Officer at Bhabha Atomic Research Centre, India
【所属学会】	Chemical Research Society of India.
【主な著書、学術論文】 （過去5年以内）	1. N. K. Jena, K. R. S. Chandrakumar and S. K. Ghosh, “Theoretical Investigation on the Structure and Electronic Properties of Hydrogen- and Alkali-Metal-Doped Gold Clusters and Their Interaction with CO: Enhanced Reactivity of Hydrogen-Doped Gold Clusters” *J. Phys. Chem. C,* **2009**, *113*, 17885-17892. 2. K. Srinivasu, K. R. S. Chandrakumar and S. K. Ghosh, “Computational Studies on Hydrogen Adsorption in Organic Molecular systems: Role of Aromatics” *Chem Phys Chem.* **2009**, *10*, 427-435. 3. K. R. S. Chandrakumar, K. Srinivasu and S. K. Ghosh, “Nanoscale Curvature Induced Hydrogen Adsorption in Alkali Metal Doped Carbon Nanomaterials” *J. Phys. Chem. C,* **2008**, *112,* 15670-15679. 4. K. Srinivasu, K. R. S. Chandrakumar and S. K. Ghosh, “Quantum Chemical Studies on Hydrogen Adsorption in Carbon Based Model Systems: Role of Charged Surface and the Electronic Induction Effect” *Phys. Chem. C. Phys.,* **2008**, *10,* 5832-5839. 5. K. R. S. Chandrakumar and S. K. Ghosh, “Alkali-Metal-Induced Enhancement of Hydrogen Adsorption in C_{60} Fullerene: An *ab initio* Study” *NanoLett.* **2008,** *8*, 13-19.
【学術関係の受賞など】	Indo-European Collaborative Project Grant (FP7); Project Title: Modeling of Nano-scaled Advanced Materials Intelligently (MONAMI) Young Scientist Award in 2008 from Department of Atomic Energy (DAE) Young Scientist Medal Award in 2005 from the Indian National Science Academy (INSA)

【氏名（ふりがな）】	Fengyi Liu （ふぉんい　りお）
【職名】	JST Fellow
【所属】	Fukui Institute for Fundamental Chemistry
【研究室】	Room 207
【直通電話】	075-711-7893
【FAX】	
【電子メールアドレス】	fengyiliu@fukui.kyoto-u.ac.jp
【研究分野】	Computational Chemistry
【現在の研究課題】	Theoretical calculation of molecular motor and switch
【研究内容キーワード】	Artificial/biological molecular motor, molecular switch
【学歴】	Jun. 1998, B. Sc. in Chemistry, Hebei Normal University, China Jun. 2001, M. Sc. in Chemistry, Hebei Normal University, China Dec. 2005, Ph.D. in Chemistry, Beijing University of Chemical Technology, China
【学位】	Ph. D. in Applied Chemistry, Beijing University of Chemical Technology
【略歴】	Sep. 2007-Jun. 2009, Postdoctoral researcher, Lund University, Sweden
【主な著書、学術論文】（過去5年以内）	1. Fengyi Liu, Lingpeng Meng, Shijun Zheng, Small Fullerenes with BN Belts: a Density Functional Theory Investigation, *J. Phys. Chem. B,* 2006, **110**, 6666-6672. 2. Fengyi Liu, Lingpeng Meng, Zheng Sun, Shijun Zheng, Insights into the Mechanism of BN Generation via Boron Triazide Precursor: A Theoretical Study, *J. Phys. Chem. A,* 2006, **110,** 10591-10600. 3. Jie Ren, Fengyi Liu, et al., Initial reaction of HfO2 atomic layer deposition on silicon surfaces with different oxygen levels: A density functional theory study, *Thin Solid Film,* 2007, **515,** 4702-4708. 4. Fengyi Liu, Yajun Liu, Luca De Vico, Roland Lindh, Theoretical Study of the Chemiluminescent Decomposition of Dioxetanone, *J. Am. Chem. Soc.*, 2009, **131**, 6181-6188. 5. Shu-Feng Chen,Feng-Yi Liu, Ya-Jun Liu, An ab initio investigation of the mechanisms of photodissociation in bromobenzene and iodobenzene, *J. Chem. Phys.,* 2009, **131,** 124304. 6. Fengyi Liu, Yajun liu, Luca De Vico, Roland Lindh, A CASSCF/CASPT2 Approach to the Decomposition of Thiazole-Substituted Dioxetanone: Substitution Effects and Charge-Transfer Induced Electron Excitation, *Chem. Phys. Lett.* 2009, **484**, 69-75. 7. Fengyi Liu and Keiji Morokuma, Rationalization of Light-Driven Rotary Molecular Motor: An Theoretical Study on the Photoisomerization of an Stiff Stilbene, *manuscript in preparation.*

【氏名（ふりがな）】	Parameswaran Pattiyil （ぱらめすわらん　ぴったいる）
【職名】	JST Fellow
【所属】	Fukui Institute for Fundamental Chemistry
【研究室】	Room 214
【直通電話】	080-61487634
【FAX】	075-781-4757
【電子メールアドレス】	param@fukui.kyoto-u.ac.jp
【ホームページ】	http://kmweb.fukui.kyoto-u.ac.jp/top/eng/member2.html#patt
【研究分野】	Computational Chemistry
【現在の研究課題】	Electronic structure calculations and molecular dynamics simulations of molecules, clusters and solids
【研究内容キーワード】	Dynamics, DFTB, nanowire, growth, DFT
【学歴】	1998, Bachelor of Sci., St. Thomas’ College, Thrissur, University of Calicut 2000, Master of Sci., St. Thomas’ College, Thrissur, University of Calicut
【学位】	Ph. D in Chemistry from University of Hyderabad
【略歴】	Mar. 2007 - Oct. 2007 : Research Associate, Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore Nov. 2007 - Sept. 2009 : Alexander von Humboldt Research Fellow, Philipps-Universit- Marburg, Germany Oct. 2009 - to-date : Postdoctoral Research Fellow, Fukui Institute for Fundamental Chemistry, Kyoto University
【主な著書、学術論文】（過去5年以内）	1. Melaimi, M.; Parameswaran, P.; Donnadieu, B.; Frenking, G.; Bertrand. G. “Synthesis and Ligand Properties of a Persistent All-Carbon Four-Membered Ring Allene”, *Angew. Chem. Int. Ed.* **48**, 4792-4795 (2009). 2. Parameswaran, P.; Frenking, G. “Transition Metal Complexes $[(PMe_3)^2Cl_2M(E)]$ and $[(PMe_3)^2(CO)^2M(E)]$ with Naked Group 14 Atoms (E = C - Sn) as Ligands; Part 1: Parent Compounds”, *Chem. Eur. J.* **15**, 8807-8816 (2009). 3. Parameswaran, P.; Frenking, G. “Transition Metal Complexes $[(PMe_3)^2Cl_2M(E)]$ and $[(PMe_3)^2(CO)^2M(E)]$ with Naked Group 14 Atoms (E = C - Sn) as Ligands; Part 2: Complexation with $W(CO)^5$”, *Chem. Eur. J.* **15**, 8817-8824 (2009). 4. Aldeco-Perez, E.; Rosenthal, A.; Donnadieu, B.; Parameswaran, P.; Frenking, G.; Bertrand. G.. “Isolation of a C-5-Deprotonated Imidazolium, a Crystalline Abnormal N-Heterocyclic Carbene”, *Science,* **326**, 556-559 (2009). 5. Back, O.; Donnadieu, B.; Parameswaran, P.; Frenking, G.; Bertrand. G. “Isolation of Crystalline Carbene-Stabilized P2-Radical Cations and P2-Dication”, *Nature Chemistry,* **2**, 369-373 (2010).
【学術関係の受賞など】	Alexander von Humboldt Research Fellow 2007-2009

【氏名（ふりがな）】	田代基慶　（たしろ　もとみち）
【職名】	センターフェロー
【所属】	福井謙一記念研究センター
【研究室】	福井記念研究センター　213号室
【直通電話】	075-711-7902
【FAX】	075-781-4757
【電子メールアドレス】	tashiro@fukui.kyoto-u.ac.jp
【研究分野】	計算化学・理論化学
【現在の研究課題】	電子・分子衝突、分子の光電離
【研究内容キーワード】	R行列法、散乱理論、共鳴、光電離
【最終学歴】	2002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
【学位】	2002年3月博士（理学）（京都大学）
【略歴】	2002年 4月 京都大学理学部研修員、 2002年 5月 独マックス・プランク研究所ポスドク研究員、 2003年11月 米カリフォルニア大学デービス校ポスドク研究員、 2004年11月 米エモリー大学ポスドク研究員、 2005年 4月 本学術振興会海外特別研究員、 2006年10月 京都大学福井謙一記念研究センター・センターフェロー
【在外研究歴】	2002年 5月-2003年11月 独マックス・プランク研究所（R. Schinke博士）、 2003年11月-2004年11月 米カリフォルニア大学デービス校化学（A.A.Stuchebrukhov教授）、 2004年11月-2006年10月 米エモリー大学化学（諸熊奎治教授） （2005年4月-2006年10月は日本学術振興会海外特別研究員）
【所属学会】	日本物理学会
【主な著書、学術論文】（過去5年以内）	1. Motomichi Tashiro, “Application of the R-matrix method to photoionization of molecules”, *Journal of Chemical Physics,* **132**, 134306 (2010) 2. Motomichi Tashiro, “Electron scattering from gas-phase glycine molecules”, *Journal of Chemical Physics,* 129, 164308 (2008) 3. Motomichi Tashiro, “Electron impact excitations of S2 molecules”, *Chemical Physics Letters,* **453**, 145 (2008) 4. Motomichi Tashiro, “Exchange effects in elastic collisions of spin-polarized electrons with open-shell molecules with ${}^3\Sigma_g$- symmetry”, *Physical Review A* **77**, 012723 (2008) 5. Motomichi Tashiro and Keiji Morokuma, “R-matrix calculation of integral and differential cross sections for low-energy electron-impact excitations of the N_2 molecule”, *Physical Review A* **75,** 012720 (2007). 6. Motomichi Tashiro, Keiji Morokuma and Jonathan Tennyson, “R-matrix calculation of differential cross sections for low-energy electron collisions with ground and electronically excited state O_2 molecules”, *Physical Review A* **74**, 022706 (2006). 7. Motomichi Tashiro, Keiji Morokuma and Jonathan Tennyson, “R-matrix calculation of electron collisions with electronically excited O_2 molecules”, *Physical Review A* **73**, 052707 (2006). 8. Motomichi Tashiro and Alexei A. Stuchebrukhov, “Thermodynamic Properties of Internal Water Molecules in Hydrophobic Cavity around Catalytic Center of Cytochrome c Oxidase”, *Journal of Physical Chemistry B* **109**, 1015 (2005).
【学術関係の受賞など】	日本学術振興会海外特別研究員（2005年4月-2006年10月）

【氏名（ふりがな）】	Wilfredo Credo Chung （うぃるふれーど くれーど ちゅん）
【職名】	FIFC Fellow
【所属】	Fukui Institute for Fundamental Chemistry
【研究室】	Room 213
【直通電話】	075 711 7902
【FAX】	075 781 4757
【電子メールアドレス】	wchung@fukui.kyoto-u.ac.jp
【研究分野】	Computational Chemistry
【現在の研究課題】	Theoretical elucidation of reaction mechanisms and dynamics of important molecules in the electronic ground and excited states
【研究内容キーワード】	potential energy surface, wave packet dynamics, conical intersection, diabatic representation, QM/MM
【学歴】	March 1991, Bachelor of Science in Chemical Engineering, University of San Carlos, Cebu City, Philippines October 1999, Master of Science in Chemistry, Mindanao State University–Iligan Institute of Technology, Iligan City, Philippines March 2007, Doctor of Science, Graduate School of Science, Tohoku University
【学位】	Doctor of Science, Tohoku University
【略歴】	March 1992 – June 1993 Research and Development Chemist, Treasure Island Industrial Corporation, Cebu City, Philippines June 1994 – October 1996 Lecturer, Colleges of Arts, Sciences and Engineering, Saint Joseph Institute of Technology, Butuan City, Philippines November 1996 – March 2003 Lecturer, Department of Chemistry, Northern Mindanao State Institute of Science and Technology, Butuan City, Philippines August 2007 – September 2007 Postdoctoral Fellow, Laboratory of Theoretical Chemistry, Tohoku University October 2007 – present Center Fellow, Fukui Institute for Fundamental Chemistry, Kyoto University
【所属学会】	Chemical Society of Japan, Japan Society for Molecular Science
【主な著書、学術論文】（過去5年以内）	1. W. M. I. Hassan, W. C. Chung, N. Shimakura, S. Koseki, H. Kono and Y. Fujimura Ultrafast radiationless transition pathways through conical intersections in photo-excited 9H-adenine, *Phys. Chem. Chem. Phys.*, **12**, 5317-5328 (2010). 2. M. Yamaki, K. Hoki, T. Teranishi, W. C. Chung, F. Pichierri, H. Kono and Y. Fujimura, Theoretical design of an aromatic hydrocarbon rotor driven by a circularly polarized electric field, *J. Phys. Chem. A,* **111**, 9374-9378 (2007). 3. W. C. Chung, Z. Lan, Y. Ohtsuki, N. Shimakura, W. Domcke and Y. Fujimura, Conical intersections involving the dissociative $^1\pi\sigma^*$ state in 9H-adenine: a quantum chemical ab initio study, *Phys. Chem. Chem. Phys.* **9**, 2075-2084 (2007). 4. W. C. Chung and E. W. Ignacio, A DFT study on the intramolecular dissociation pathways of ethyl fluoroformate radical cation in the gas phase; II. Keto path, J. Mol. Struct. (THEOCHEM) 713 , 153-159 (2005).

【氏名（ふりがな）】	Takahiro Sakaue（たかひろ　さかうえ）
【職名】	Assistant Professor
【所属】	Department of Physics, Kyushu University
【研究室】	Room 2646, Faculty of Science Building 2
【直通電話】	092-642-2567
【FAX】	
【電子メールアドレス】	sakaue@phys.kyushu-u.ac.jp
【研究分野】	Statistical physics
【現在の研究課題】	Nonequilibrium phenomena in softmatter and biological systems
【研究内容キーワード】	Polymer, biopolymer, fluctuation and response
【学歴】	March 2001, Master of Sci., Graduate School of Science, Kyoto University March 2004, Doctor of Sci., Graduate School of Science, Kyoto University
【学位】	Doctor of science from Kyoto university
【略歴】	Apr, 2003, JSPS Fellow (DC2), Kyoto University Apr. 2004, JSPS Fellow (PD), College de France Apr. 2005, JSPS Fellow (PD), Kyoto University Apr. 2008, FIFC Fellow, Kyoto University May. 2009, Assistant Professor, Kyushu University
【所属学会】	Physical society of japan
【主な著書、学術論文】 （過去5年以内）	1, Takahiro Sakaue, Kenichi Yoshikawa, “Water and Biomolecules- Physical Chemistry of Life Phenomena” (edited by K. Kuwajima, Springer-Verlag, 2009) Chapter 3 “Transition in the higher-order structure of DNA in aqueous solutions” 2, Takahiro Sakaue, Natsuhiko Yoshinaga, “Dynamics of Polymer Decompression: Expansion, Unfolding and Ejection”, *Physical Review Letters*, **102**, 14832:1-4 (2009). 3, Takahiro Sakaue, Takao Ohta, “Probing Nonequilibrium Fluctuations through Linear Response”, *Physical Review E*, **77**, 050102:1- 4(R) (2008). 4, Takahiro Sakaue, “Nonequilibrium Dynamics of Polymer Translocation and Straightening”, *Physical Review E*, **76**, 021803:1- 7 (2007). 5, Takahiro Sakaue, “Semiflexible Polymer Confined in Closed Spaces”, *Macromolecules,* **40**, 5206-5211 (2007).
【学術関係の受賞など】	Inoue Research Award for Young Scientists (2004) JSPS Research Fellowships for Young Scientists(DC2) 2003-2004 JSPS Research Fellowships for Young Scientists(PD) 2004-2008

【氏名（ふりがな）】	Takafumi Iwaki（たかふみ　いわき）
【職名】	FIFC Fellow
【所属】	Fukui Institute for Fundamental Chemistry
【研究室】	Room 213
【直通電話】	075-711-7902
【FAX】	
【電子メールアドレス】	iwaki@fukui.kyoto-u.ac.jp
【研究分野】	Soft Matter, Biological Physics
【現在の研究課題】	Interfacial Phenomena, Simulation Method
【研究内容キーワード】	Polyelectrolyte, DNA folding transition, Thermofluid, Photophoresis
【学歴】	March 2001, Master of Sci., Graduate School of Science, Kyoto University March 2004, Doctor of Sci., Graduate School of Science, Kyoto University
【学位】	Doctor of Science from Kyoto University
【略歴】	Apr. 2004, Postdoctoral Fellow at The City University of New York, USA Apr. 2005, Okayama Institute for Quantum Physics
【所属学会】	The Physical Society of Japan
【主な著書、学術論文】 （過去5年以内）	1. T. Iwaki, N. Makita and K. Yoshikawa, “Folding transition of a single semi-flexible polyelectrolyte chain through toroidal bundling of loop structures”, *The Journal of Chemical Physics* **129**(6), 065103 (13 pages) (2008) 2. T. Saito, T. Iwaki, and K. Yoshikawa, “DNA compaction induced by neutral polymer is retarded more effectively by divalent anion than monovalent anion”, *Chemical Physics Letters* **465**(1-3), 40-44(2008) 3. T. Saito, T. Iwaki, and K. Yoshikawa, “Small anion with higher valency retards the compaction of DNA in the presence of multivalent cation”, *Biophysical Journal* **96**(3), 1068-1075 (2009) 4. A. Khoo, T. Iwaki, C-Y. Shew, and K. Yoshikawa, “Preferential Positioning of a Nanoparticle Bound to a Polymer: Exact Enumeration of a Self-avoiding Walk Chain Model”, *Journal of Chemical Physics* **131**, 104904 (9 pages) (2009) 5. S Araki, K. Hizume, T. Iwaki, Y. Suzuki, K. Takeyasu, and K. Yoshikawa, “Nucleosomal arrays reconstituted from ring and linear DNA”, *Chemical Physics Letters* **479**, 284-289 (2009)

Ⅲ 研究広報活動

１．福井謙一記念研究センターシンポジウム

第7回センターシンポジウム (2009/12/4　9:30-17:40)

日　　時　平成21年12月4日（金）

場　　所　京都大学福井謙一記念研究センター　（３Ｆ　大会議室）

開会の辞　榊　茂好　（センター長）　9:30- 9:40

ご挨拶　大嶌　幸一郎　（京大・工学研究科長）　9:40- 9:50

講　　演

中村　栄一　（東大・理）　9:50-10:50

「単一有機分子の動きを見るー化学物理学の新しい世界ー」

大峯　　巖　（京大・福井センター）　11:00-12:00

「水、その豊かな世界：ミクロの水の性質」

石田　俊正　（京大・福井センター）　13:30-14:20

「光化学反応のシミュレーションー非断熱遷移反応動力学」

佐藤　　徹　（京大・福井センター）　14:30-15:20

「振電相互作用とJahn-Teller効果」

ポスターセッション　15:40-17:40

懇親会（１Ｆ多目的ルーム）　18:00-19:30

２．センターセミナー

第７回福井センターセミナー (2010 年 2 月 4 日 (木)　15:00-17:00)

15:00 〜 15:30　Zhuofeng Ke　（福井センター）
"Theoretical Study of the Rh-Catalyzed Polymerization of Phenylacetylene"
15:30 〜 16:00　Hajime Hirao　（福井センター）
"QM/MM Computational Studies of Metalloenzymes: Characterization of Elusive Intermediates and Elucidation of Reaction Mechanisms"
16:00 〜 17:00　Arnout Ceulemans (Catholic University of Leuven)
"Frustration in Jahn-Teller systems"

３．CREST International Symposium on Theory and Simulations of Complex Molecular Systems & International Symposium on Theory of Molecular Structure, Function and Reactivity, Celebrating Prof. Morokuma's 75th Birthday

July 19 (Sun): CREST Symposium

9:00 Shigeyoshi Sakaki, FIFC　Director Opening Remarks

Chair: Shigehiko Hayashi
9:10 Richard A. Friesner C-01 Density functional based QM/MM studies of metalloprotein active sites
9:40 Kazunari Yoshizawa C-02 QM/MM Study on Oxygenation Enzymes
10:10 Todd Martinez C-03 Photobiology and mechanochemistry from first principles
10:40 Break

Chair: Toshiaki Matsubara
11:00 Junya Hasegawa C-04 Excited states of photofunctional molecules in protein environments
11:30 Qiang Cui C-05 Multi-scale models of biomolecular processes: developments and applications

12:00 Weitao Yang C-06

Free energies and mechanism of chemical reactions in solution and in enzymes with ab initio QM/MM method

12:30-13:30 Lunch

Chair: Djamaladdin G. Musaev

13:30 Feliu Maseras C-07 Cross-coupling reactions: calculations do help mechanistic understanding

14:00 Chantal Daniel C-08 From small to large transition metal complexes: quantum theory of electronic excited states

14:30 Christophe Bichara C-09 Modeling Nickel-Carbon alloys to study the catalytic synthesis of Carbon Nanotubes

15:00 Break

Chair: Alister Page

15:30 Gustavo E. Scuseria C-10 Carbon nanotubes and grapheme nanoribbons

16:00 Kim Bolton C-11 Computational studies of single-walled carbon nanotube growth

16:30 Susumu Saito C-12 Abundance of C60 revisited: A microscopic formation process of fullerenes

17:00 Stephan Irle C-13 Density-functional tight-binding molecular dynamics simulations of carbon nanotube formation

17:30 Shigeo Maruyama C-14 Nucleation of a Single-Walled Carbon Nanotube inside a Nanotube

18:00 Keiji Morokuma Welcome Reception

July 20 (Mon): "Birthday" Symposium

*Chair: Seiji Mor*i

9:00 Shigeyoshi Sakaki B-01 CCSD(T) Study of Large Transition Metal Complexes with Frontier-Orbital-Consistent Effective Potential

9:30 Suehiro Iwata B-02 Perturbation Expansion Based on Absolutely Local Excited Molecular Orbitals and Application to Molecular Clusters

Chair: Alexander Mebel

10:00 Masanori Tachikawa B-03 Nuclear Quantum Effect on Hydrogen Bonded Systems

1030 Break

11:00 Michael J. Frisch B-04 Recent Advances in the Exploration of Potential Energy Surfaces and the Prediction of Vibrational Spectra

Chair: Ulf Ryde

11:30 Seiji Mori B-05 Important insight into Reaction Mechanisms of Organic Syntheses and Biosyntheses from View of Computational Chemistry
12:00 Kazuo Kitaura B-06
Quantum-chemical calculations of large biomolecules with the fragment molecular orbital method

12:30-13:30 Group Picture & Lunch
13:30-15:30 2hr poster session

Chair: Junya Hasegawa

15:30 Djamaladdin G. Musaev B-07 Computation aided catalyst design:
visible lightdriven water oxidation
16:00 Koichi Yamashita B-08 Quantum transport of single molecules and solid interfaces
16:30 Alexander M. Mebel B-09 Growth mechanisms of large organic molecules in
low-temperature conditions of Titan's atmosphere: from polyynes to PAH
17:00 Break

17:20 Toshiaki Matsubara B-10 Application of the ONIOM-molecular dynamics method to the chemical reactions. A new theory of chemical reactivity
17:50 Satoshi Yabushita B-11 Theoretical study on the f-f transition intensities of
lanthanide trihalide systems

18:20 Mori, Tachikawa Poster Award Ceremony
19:00-21:00 Kazuo Kitaura, Stephan Irle Birthday Party

July 21 (Tue): CREST Symposium

Chair: Stephan Irle

9:00 Boris I. Yakobson C-15 Relaxation mechanisms in nanostructures through theory and computations
9:30 Henryk A. Witek C-16 When finite becomes infinite...
10:00 Atsushi Oshiyama C-17 Nanometer-scale shapes that produce unusual properties of carbon nanomaterials

10:30 Break

11:00 Younghee Lee C-18 Engineering electronic structures of carbon nanotubes: Theory and experiment
11:30 Shigeru Nagase C-19 Structures and reactions of endohedral metallofullerenes

Chair: Masanori Tachikawa
12:00 Shinichiro Nakamura C-20 Theoretical Chemistry in Chemical industrial researches
12:30-13:30 Lunch

Chair: Kazunari Yoshizawa
13:30 Ulf Ryde C-21 A comparison of different methods to calculate reaction energies in proteins
14:00 Shigehiko Hayashi C-22 Molecular mechanisms of enzymatic activities in motor and photoreceptor proteins
14:30 Shigenori Tanaka C-23 Large-scale biomolecular simulations based on the fragment molecular orbital method
15:00 Lung Wa Chung C-24 Our ONIOM journey of metalloenzymes and photobiology
15:30 Walter Thiel C-25 QM/MM studies of enzymatic reactions
16:00 Adjourn

４．若手研究者交流支援事業ー東アジア首脳会議参加国からの招へいー

分子理論による複雑分子のシミュレーションに関する共同研究と研究者交流

（Collaboratory Research and Exchange of Researchers in Simulations of Complex Molecules Using Molecular Theoretical Methods）

コーディネーター　諸熊奎治
（資料編 178 ページの実施報告書参照）

Detailed schedule of JENESYS program

Wednesday, July 8
by noon; Group C participants arrive at Seifu Kaikan hotel in Kyoto
1230 Walk to FIFC, led by Ms. Liu
1300 Registration at FIFC
1400 (Group B members also join at this point)
1400 Welcome to JENESYS and logistics (Dr. Morokuma)
1500 Introduction to FIFC and activity of Ishida Group (Prof. Ishida)
1530 Activity of Morokuma group I (Dr. Alister –nano projects)
1600 Activity of Morokuma group 2 (Dr. Chung- bio projects)
1630 Reception (JENESYS participants and FIFC members)
1800 adjourn

Thursday, July 9
930 Presentation of JENESYS participants (10 min from each participant)
1130 Activity of Ohmine group (Dr. Kamiya)
1200 Final logistics (Dr. Morokuma)
1230 Walk to Kyoto University north campus and have lunch
1400 Visit Kato-Hayashi-Tanimura Group at Faculty of Science (science faculty bidg 2, room 218)
1400 Overview of theoretical groups
1420 Seven presentations of Jenesys participants
1540 Presentations of theoretical groups
1620 Visit labs
1700 End visit. Walk to the main campus and confirm the shuttle bus stop in front of the clock tower
1730 Adjourn

Friday, July 10
850 Gather at the bus stop in front of the clock tower of the main campus
910 Shuttle bus to Katsura campus leaves punctually (If you miss the bus, the next bus leaves at 1035)

1010 Bus arrives at Katsura campus. Get off at the first stop (A-cluster). Nakatsuji group picks up at the bus stop.
1020 Presentation of research of Nakatsuji group at Quantum Chemistry Research Institute(QCRI)
1120 Seven presentations of JENESYS participants
1230 Box lunch at QCRI
1330 Walk to Sakai Lab, Kyoto University
1345 Seven presentations of JENESYS participants
1500 Presentation of research of Sakaki group, Faculty of Engineering, Kyoto University
1620 Visit laboratories
1700 Dinner at Coop dining room
1820 Shuttle bus leaves
1915 Arrive at clock tower of the main campus and adjourn

Saturday, July 11
Free. Enjoy visiting sights in Kyoto.

Sunday, July 12
~800 Group C Leave Seifu Kaikan hotel
~830 All gather at the main gate of Kyoto Station
902 at Kyoto station take Nozomi #220 train
1116 Arrive at Shinagawa station. Change train
~1140 arrive at Takadanobaba station
~1200 arrive at Hotel Sunroute Takadanobara
~1300 Students from Prof. Nakai group will come to the hotel and take for sightseeing

Monday, July 13
1030 Students from Nakai group pick up at the hotel
1045 Arrive at Nakai group, Waseda University
1100- Discussion 1 (group B and Nakai group presentations)
1300- Lunch
1500- Discussion 2 (group C and Nakai group presentations)
1700- Reception
2000- ??

Tuesday, July 14
730 Check out hotel
740 Leave Takadanobaba station
820 Arrive at Hamamatsucho station
900 Hato Bus tour (half-day tour of Tokyo) leaves
1200 Tour ends. Lunch
~1300 Leave Hamamatsucho station for Shinagawa station
1334 Kodama#650 leaves Shinagawa
1542 arrive at Toyohashi. Change train to Meitetsu line
1553 Metetsu leaves Toyohashi
1618 Arrive at Higashi-Okazaki// Walk to Mishima lodge of IMS

Wednesday, July 15
845 Walk from Mishima Lodge to IMS (Prof. Nagase's office)
900 Overview of theo/comp research area of IMS
915 Presentations of JENESYS participants
1115 research presentation of theory groups 1230 lunch
1330 visit UVSOR facility
1415 presentations of computational groups.
1500 visit research center for computational science
~1600 leave Higashi-Okazaki by Meitetu line
~1730 Arrive at the guest house, Nagoya university

Thursday, July 16
1000 Visit Irle group meeting, IAR, Nagoya University
1040 Seven presentations by JENESYS participants
1150 Presentations of Irle group members
1250 lunch
1350 Presentations by chemistry GCOE
1420 Visit of Prof. Hisanori Shinohara lab (Science)
1500 Visit of Prof. Eiji Yashima's lab (Engineering)
1600 Leave Nagoya University by subway
~1700 Take Shinkansen from Nagoya to Kyoto
~1800 Arrive at Kyoto, adjourn

Friday, July 17
Gion Festival in Kyoto, enjoy

Saturday, July 18
free

Sunday, July 19
900 International symposium at FIFC
1800 Reception

Monday, July 20
900 International symposium at FIFC
1900 Banquet

Tuesday, July 21
900 International symposium at FIFC
1600 Adjourn

Wednesday, July 22
900 Final discussions at FIFC

Thursday, July 23
Group C members head back to home
Group B members continue research

Ⅳ　研究業績（2009）

1．専任教員

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

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

1. Summary of the research of the year

(1) Ab initio non-adiabatic trajectory calculations for 9-cis Schiff base retinal

Isorhodopsin is an analogue of rhodopsin that contains a 9-cis retinal chromophore instead of 11-cis retinal embedded in the same opsin environment. Light-induced isomerization of the 9-cis retinal chromophore to the all-trans form is known to occur at a longer timescale (600 fs) and at a reduced quantum yield (0.22) resulting in a weaker visual response whereas isomerization of 11-cis retinal to the all-trans form is essentially completed in 200 fs with a 0.67 quantum yield.

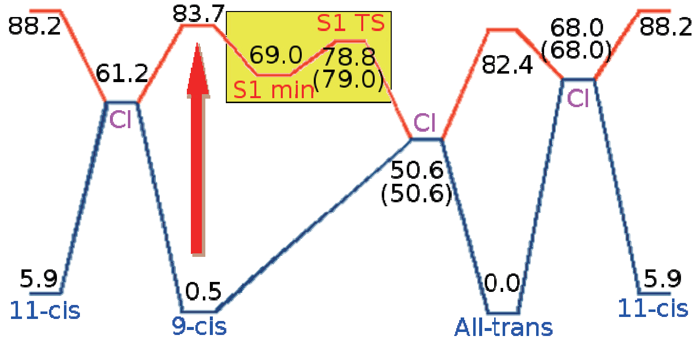


Figure 1 Energy diagram for the cis-trans isomerization of retinal. Energy is in kcal mol^{-1}. At the conical intersections, numbers without/in parentheses indicate energy when the C8-C9=C10-C11 torsion is twisted in the clockwise/counterclockwise direction. CI = conical intersection. TS = transition state (saddle point). Min = minimum.

We investigate the dynamics of the photoisomerization of a model PSB of 9-cis retinal in a similar fashion in the previous research to seek the origin of the difference of reaction time and quantum yield between rhodopsin and isorhodopsin.

One minimum is found in the excited state in addition to the one in the ground state of protonated Schiff base of 9-cis retinal, as shown in Figure 1. Two similar saddle points are found between the S$_1$ minimum and two minimal energy conical intersection points, which bifurcates to the all-trans product and the 9-cis reactant. One of the two saddle points as well as one of the conical intersection points are twisted from the S$_1$ minimum in the clockwise direction with respect to the -C8-C9=C10-C11- dihedral angle (ϕ_9). The other ones are twisted in the counterclockwise directions. Both the two saddle points give ~10 kcal mol^{-1} barrier along a mixed coordinate of a twist in the ϕ_9 dihedral and complementary bond-order alteration of the C9-····-C13 polyene chain. At the S$_1$ saddle points, the ϕ_9 dihedral is twisted from 0° at the S$_1$ minimum well to around 26°.

Figure 2 shows the population of the 9-cis, all-trans and 11-cis photoproducts as well as the still-unreacted residual of the starting material. the quantum yield of the all-trans photoproduct is found to be 0.13. If the 9-trans (11-cis) products are counted as a trans product, the ratio is 0.18, which is in excellent agreement with the experimentally measured quantum yield of 0.22. This is significantly lower than the one obtained by Ishida et al. for 11-cis PSB retinal of 0.27 (or 0.49 if the 11-trans (9-cis) form is counted as a trans form). Experimentally, the all-trans quantum yield for rhodopsin is 0.67 around three times more than that for isorhodopsin. The rhodopsin/isorhodopsin quantum yield ratio for the two simulations is 2.1 to 2.7, in good agreement with the experimental ratio.

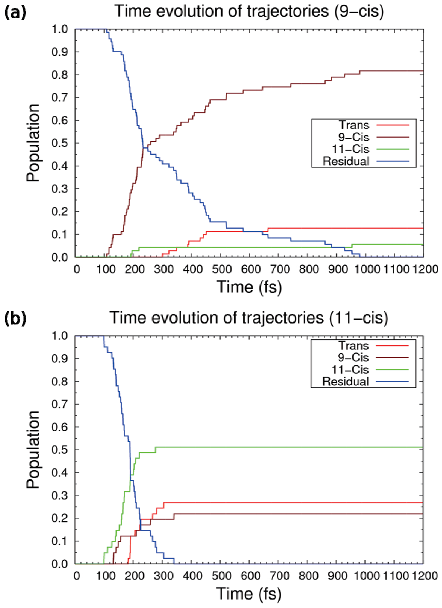


Figure 2. Population change calculated for all the trajectories in the (a) isorhodopsin (9-cis) and (b) rhodopsin (11-cis) model systems.

On the average, it takes 441 fs to form the all-trans isomer from the 9-cis form; the time scale of isomerization is shorter than, but in reasonable agreement with the experimental reaction time of 600 fs. We examine the time-dependence of the active dihedral angle and C9=C10 bond length to understand the origin of the oscillation of the torsion angle around the 9-cis conformation before a larger torsion angle is attained.

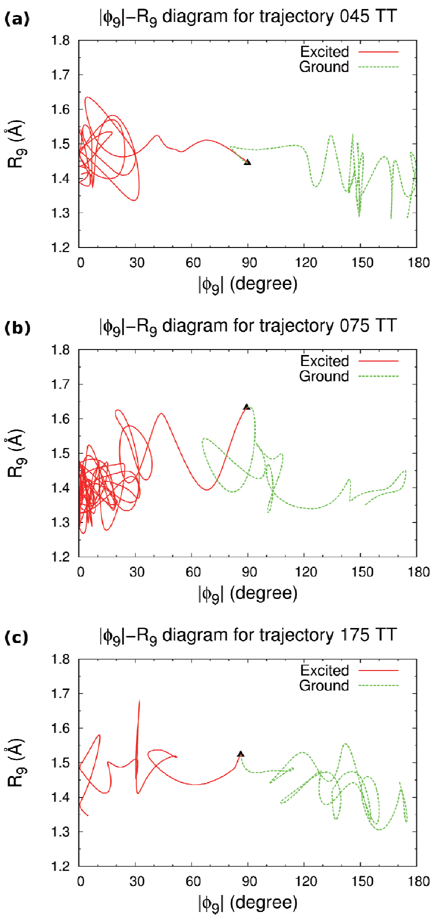


Figure 3. The correlation of R_9 and $|\phi_9|$ for three typical trajectories.

Shown in Figure 3 are the diagram for C9=C10 (R_9) and dihedral angle ϕ_9 to present time evolution of three typical trajectories generating the all-trans form. Figures 3a and 3b shows that the trajectories are trapped where the torsion angle $|\phi_9|$ is confined to 0-30° before the angle increases in a continuous and monotonous fashion with time in some cases whereas the trajectory shown in Figure 3c is a representative for the other trajectories which relatively straightforwardly give the product. The trajectory trapping with the twist angle of less than 30° is consistent with the existence of the saddle point with $|\phi_9|\sim 26°$. Thus, the delay in the excited-state dynamics would be mainly due to an energetic barrier in the excited state associated mainly with the ϕ_9 torsion coordinate.

Cis-trans isomerization is an intrinsic property of 9-cis retinal that is not triggered although it may be altered by the opsin environment in isorhodopsin. The processes that occur from photoexcitation to ground-state relaxation of the PSB of isorhodopsin in the gas phase are summarized as follows:

1. The C9=C10 bond R_9 is stretched to a single bond and the torsion coordinate ϕ_9 is twisted to as far as ±30° after photoexcitation.
2. The bond oscillates between single- and double-bond character while ϕ_9 also oscillates within ±30° while being trapped in the S_1 well.
3. The barrier is surmounted and crank shaft motion of the two angles of ϕ_9 and ϕ_{11} occurs toward the transition point to the ground state. The R_9 bond is predominantly single bond in character during transition. When $|\phi_9|$ is greater than about 70° at the transition point, an all-trans photoproduct is likely to result.
4. The molecule relaxes in the ground state as R_9 shrinks back to a double bond and $|\phi_9|$ approaches 0° and 180° depending on the resulting photoproduct.

(2) **Aromaticity of neutral and doubly charged polyacenes**

Aromatic character of polycyclic aromatic hydrocarbon (PAH) molecules has been investigated extensively using energetic, magnetic, and geometric indicators of global and local aromaticity. Clar's concept of an 'aromatic sextet' is also useful for intuitively grasping the global aromaticity of PAH molecules. Here, aromatic character of neutral and doubly charged polyacenes was explored in terms of the harmonic oscillator model of aromaticity (HOMA) and bond resonance energy (BRE). Doubly charged species of polyacenes are different in global and local aromaticity from the neutral species. Neutral species are fairly uniform in local aromaticity, whereas doubly charged species are more aromatic in the edge rings than in the central rings. Higher polyacenes have been predicted to exist as singlet-state diradicals. It was found that these polyacene diradicals are quite similar in global and local aromaticity to the closed-shell molecular dications. The possible instability of higher polyacenes in closed-shell electronic configuration is associated with the high-lying highest occupied molecular orbital (HOMO) that contributes little to global aromaticity.

(3) **Aromaticity and Diatropicity of Bond-Alternate Benzene**

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

(4) Geometries of MCN (M=Cu, Ag, and Au) in comparison with a microwave experiment and the previous calculations

Calculations were carried out at the level of B3PW91 for MCN (M=Cu, Ag, and Au). The basis set employed is the 6-311++G(3df) set for C and N and the LanL2DZ set for Cu, Ag and Au. The calculation results reproduced the experimental internuclear distances of MCN. Recent accurate CCSD(T) calculations with the large cc-pVQZ basis set by Zaleski-Ejgierd et al. also provided consistentvalues. Most of the other M-C distances calculated using a fairly large basis set were also close to the experimental lengths. Early MP2/I work where the basis set I was essentially the DZP basis set with relativistic effective core potential, supplied poorer estimates.

2. Original papers

(1) Toshimasa Ishida and Jun-ichi Aihara,
Aromaticity of neutral and doubly charged polyacenes, Phys. Chem. Chem. Phys. **11**, 7197 - 7201 (2009)

(2) Toshiaki Okabayashi, Emi Y. Okabayashi, Fumi Koto, Toshimasa Ishida, and Mitsutoshi Tanimoto
Detection of Free Monomeric Silver(I) and Gold(I) Cyanides,AgCN and AuCN: Microwave Spectra and Molecular Structure
J. Am. Chem. Soc. *131* (33), 11712–11718 (2009).

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

3. Presentation at academic conferences

(1) 石田 俊正、Chung Wilfredo Credo、南部　伸孝、中村 宏樹
レチナールの非断熱遷移 ab initio トラジェクトリ計算
第 12 回理論化学討論会 1P25　東京　2009/5/28

(2) Toshimasa Ishida, Wilfredo C. Chung, Shinkoh Nanbu, and Hiroki Nakamura
“Analysis of ab initio trajectories in retinal photoisomerization”
第 25 回化学反応討論会 1E01　大宮　2009/6/1

(3) Wilfredo Credo Chung and Toshimasa Ishida,
“Comparative Essential Dynamics of the Interaction of Human TRAF3 with Human CD40 and Epstein-Barr Virus LMP1 proteins“
第25回化学反応討論会 1P17　大宮　2009/6/1

(4) 石田　俊正、Wilfredo Credo Chung、南部　伸孝、中村 宏樹
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第7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　2009/12/4

(2) Wilfredo Credo Chung, Shinkoh Nanbu and Toshimasa Ishida
Non-adiabatic ab initio dynamics of a model protonated Schiff base of 9-cis retinal
第7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　2009/12/4

(3) 石田　俊正、南部　伸孝、中村　宏樹
「レチナールの光異性化の理論的研究ー二面角の変化ー」
文部科学省「最先端・高性能汎用スーパーコンピュータの開発利用」プロジェクト 次世代ナノ統合シミュレーションソフトウェアの研究開発 第4回公開シンポジウム　岡崎　2010/3/4

佐藤　徹

理論研究部門　准教授

1. 今年度の研究の要約

今年度は簡約振電相互作用密度を定義し、それを BEDT-TTF に適用した。

【始めに】振電（電子-振動）相互作用は超伝導や電荷輸送において重要である。振電相互作用の強さは振電相互作用定数（Vibronic Coupling Constant, VCC）により支配される。したがって、新規な材料を設計する上で VCC の大小の起源を理解することは重要な意味を持つ。最近我々は振電相互作用密度（Vibronic Coupling Density, VCD）解析に基づいて、様々な分子における VCC の大小の起源を明らかにしてきた[1-7]。VCC の大小の起源は VCD 解析により理解することができるが、VCD の空間分布は特に原子核の近傍で複雑であり、振電相互作用の局所的な描像について誤った解釈を与えることがある。この複雑さは VCD に含まれる、空間積分が 0 となる要素に由来する。本研究では、空間積分が 0 となる要素を VCD から差し引いた簡約 VCD を定義し、それに基づいた解析を有機超伝導体として知られている Bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF)[8,9]に適用した。

【結果と考察】BEDT-TTF のカチオン状態では C=C 伸縮振動モード（a(32)モード）が最大の VCC を持つ。図 1 に a(32)モードについての振電相互作用密度，簡約振電相互作用密度および相殺する成分の計算結果を示す。S1 原子は TTF 部位のイオウ原子であり、その AVCC は負(-1.13X10^{-6} a.u.)である。ところが図 1(a)の振電相互作用密度の分布からは AVCC の正負さえ判別できない。これは空間積分が 0 となる要素（図 1 (c)）の値が振電相互作用密度と同程度に大きいためである。このことは図 1(a)と(c)を比較すると理解できる。一方、簡約振電相互作用密度の分布（図 1(b)）からは S1 原子の AVCC が負であることを容易に理解できる：振電相互作用密度が負である領域（青色の領域）の方が、振電相互作用密度が正である領域（グレーの領域）よりも大きく分布している。この例から分かるように、簡約振電相互作用密度は振電相互作用密度よりも振電相互作用の局所的な描像をより明確に記述する。

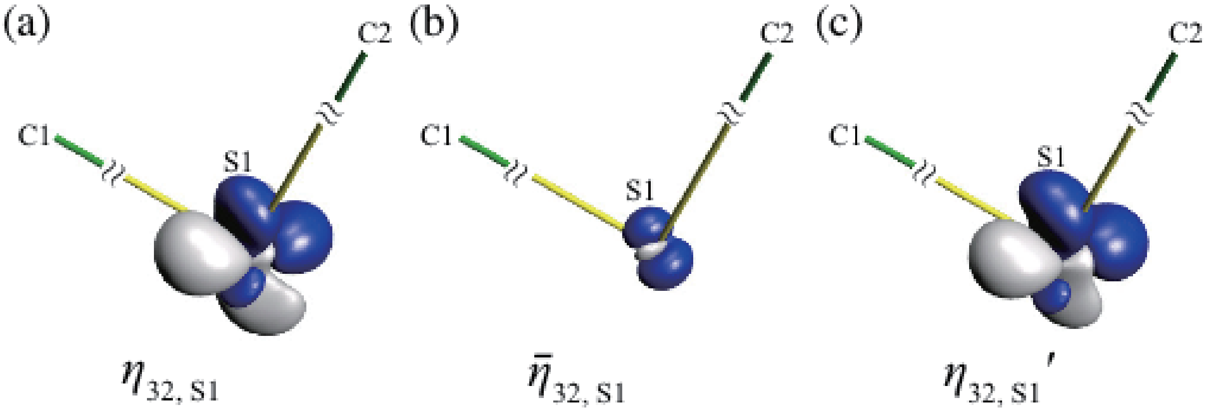

図 1. a(32)モードの S1 原子についての(a) 振電相互作用密度 (b) 簡約振電相互作用密度,および(c)

相殺する成分の等値面。グレーの領域は正の領域を、青色の領域は負の領域を表す。

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(3)佐藤徹,上垣内啓介,志津功将,岩原直也,田中一義,梶弘典,ホール輸送材料における振電相互作用と軌道緩和,第 12 回 理論化学討論会,東京大学本郷キャンパス 武田先端知ビル 武田ホール,平成21年5月28-30日

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(8)志津　功将，佐藤　徹，田中　一義，梶弘典，振電相互作用密度解析による電子輸送材料の分子設計，有機ＥＬ討論会 第 9 回例会,京都大学 宇治キャンパス おうばくプラザ,平成 21 年 11 月 12 日（木)、13 日（金）

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4. 招待講演

(1)Tohru Sato, Vibronic coupling density analysis and its applications, The 3rd Japan-Czech-Slovak Symposium on Theoretical and Computational Chemistry, Bratislava, Slovak, 9-12 September, 2009

(2) 佐藤　徹，"振電相互作用密度解析によるキャリア輸送材料の分子設計",特別講演会,富山大学理学部２階多目的ホール 2010年1月22日

２．リサーチリーダー

Keiji MOROKUMA

Research Leader, Kenichi Fukui Memorial Research Group 1

1. Summary of the research of the year

Multi-level Simulation of Complex Molecular Systems

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

I. Simulation of Biomolecular Systems

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

A. **Insights into the (superoxo)Fe(III)Fe(III) intermediate and reaction mechanism of *myo*-inositol oxygenase: DFT and ONIOM(DFT:MM) study** (See research activities of Dr. Hirao)

B. **What is the real nature of ferrous soybean lipoxygenase-1? A new two-conformation model based on combined ONIOM(DFT:MM) and multireference configuration interaction characterization** (See research activities of Dr. Hirao)

C. **Zinc-homocysteine displacement in cobalamin-dependent methionine synthase and its role in substrate activation: DFT and ONIOM study** (See research activities of Dr. Abdel-Azeim)

D. The effect of thermal fluctuation of the protein environment on the free energy reaction diagram of isopenicillin-N synthase (See research activities of Dr. Kawatsu)

E. Free energy gradient optimization in the ONIOM QM:MM scheme (See research activities of Dr. Kawatsu)

F. The photodynamic mechanism of GFP chromophores in water and reversibly photoswitchable fluorescent protein: Dronpa. (See research activities of Dr. L. W. Chung and Dr. Li)

G. The mechanisms of irreversible photoconversion of fluorescent protein: Kaede (See research activities of Dr. Li)

H. Toward understanding light-driven rotary (bio)molecular motor systems: a theoretical study of photoisomerization of a stiff stilbene (See research activities of Dr. Liu)

I. Theoretical study of catalysis in bio-nano cavity of protein and in solution(See research activities of Dr. Ke)

II. Simulation of Nanomaterials

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

A. Density-functional tight-binding molecular dynamics simulations of nucleation and growth of a single-walled carbon nanotube on a metal cluster (See Dr. Page's report for details)

B. Carbon nanotube growth from metal decorated carbon nanocones: density functional tight-binding based molecular dynamics (DFTB-MD) approach (See Dr. Chandrakumar's report for details)

C. Shrinking of hot giant fullerenes in presence of buffer gas: DFTB MD simulations (See Dr. Saha's report for details)

D. Formation mechanism of polycyclic aromatic hydrocarbons (PAHs) during benzene combustions: DFTB MD simulations (See Dr. Saha's report for details)

E. Growth mechanism for aluminum-catalyzed silicon nanowires: density functional tight binding molecular dynamics simulations (See Dr. Parameswaran's report for details)

III. Method Developments

A. Generalized ONIOM: Truncation and extrapolation of many-body expansion for large systems

(See research activities of Dr. L. W. Chung)

B. Automated and systematic transition-structure explorer in large flexible molecular systems based on combined global reaction route mapping (GRRM) and microiteration methods (See Original paper 16 below, in collaboration with Dr. Satoshi Maeda, who was visiting FIFC as JSPS Postdoctoral Fellow)

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4. Books

None

5. Presentation at academic conferences

Keiji Morokuma, invited, “Density Functional Tight-Binding Molecular Dynamics Simulation of Growth of Single-Walled Carbon Nanotubes from Metal Cluster”, The Fourth NASA – Rice University – Air Force Workshop on Nucleation and Growth Mechanisms of Single Wall Carbon Nanotube, Guadalupe, Texas, April 18, 2009

Keiji Morokuma, Invited, “Theoretical studies of chemical reactions – gas phase to nano structure growth”. AFOSR Contractors’ meeting, San Diego, CA, May 19. 2009.

Keiji Morokuma, invited, “Theoretical studies of chemical reactions: carbon nanotube growth reaction and enzymatic reactions”. iCeMS International Symposium, Kyoto, Japan, May 29, 2009.

Keiji Morokuma, invited, “Exciting World of Theoretical Studies of Chemical Reactions – From Gas Phase Reactions to Nano Structures, Catalysts, and Enzymatic Reactions”. Fourth Japan-Czech-Slovakia Theoretical Chemistry Symposium, Bratislava, Slovakia, September 10, 2009

諸熊奎治、招待、“GRRM Method – A New Paradigm of Potential Energy Surface Exploration. A Few New Developments”, 豊田理化学研究所 研究討論会「化学反応経路探索のニューフロンティア，長久手、2009.9.24

6. Presentation at Institutional/Departmental Seminars

Keiji Morokuma, invited, “Exciting World of Theoretical Studies of Chemical Reactions – From Gas Phase Reactions to Nano Structures, Catalysts, and Enzymatic Reactions”. Seminar for computational chemists in Ho Chi Minh City. Ho Chi Minh City University of Technology, Vietnam, June 3, 2009

Keiji Morokuma, invited, “Exciting World of Theoretical Studies of Chemical Reactions – From Gas Phase Reactions to Nano Structures, Catalysts, and Enzymatic Reactions”. Seminar for computational chemists in Danang. Danang University of Technology, Vietnam, June 4, 2009

Keiji Morokuma, invited, “Exciting World of Theoretical Studies of Chemical Reactions – From Gas Phase Reactions to Nano Structures, Catalysts, and Enzymatic Reactions”. Seminar for computational chemists in Hanoi, Hanoi University of Science, Vietnam, June 5, 2009

Keiji Morokuma, invited, “Exciting World of Theoretical Studies of Chemical Reactions – From Gas Phase Reactions to Nano Structures, Catalysts, and Enzymatic Reactions”. Seminar at St. Petersburg State University, Russia, June 18, 2009

Keiji Morokuma, invited, “Theoretical Studies of Chemical Reactions – From Gas Phase Reactions to Nano Structures, Catalysts, and Enzymatic Reactions”, Seminar at Air Force Laboratory, Wright Patterson Air Force Laboratory. Dayton, USA, July 27, 2009

Keiji Morokuma, invited, “Exciting World of Theoretical Studies of Chemical Reactions – From Gas Phase Reactions to Nano Structures, Catalysts, and Enzymatic Reactions”. Seminar at L.V. Kirensky Institute of Physics, Krasnoyarsk, Russia, September 7, 2009.

Keiji Morokuma, invited, “Exciting World of Theoretical Studies of Chemical Reactions – From Gas Phase Reactions to Nano Structures, Catalysts, and Enzymatic Reactions”. Iligan Institute of Technology, Iligan, Philippines, November 25, 2009

Keiji Morokuma, invited, “Exciting World of Theoretical Studies of Chemical Reactions – From Gas Phase Reactions to Nano Structures, Catalysts, and Enzymatic Reactions”. Xavier University, Cagayan de Oro, Philippines, November 26, 2009

Keiji Morokuma, invited, “Exciting World of Theoretical Studies of Chemical Reactions – From Gas Phase Reactions to Nano Structures, Catalysts, and Enzymatic Reactions”. University of Santo Tomas, Manila, Philippines, November 27, 2009

Keiji Morokuma, invited, “Exciting World of Theoretical Studies of Chemical Reactions – From Gas Phase Reactions to Nano Structures, Catalysts, and Enzymatic Reactions”. Aeteneo de Manila University, Manila, Philippines, November 27, 2009

Keiji Morokuma, invited, “Exciting World of Theoretical Studies of Chemical Reactions – From Gas Phase Reactions to Nano Structures, Catalysts, and Enzymatic Reactions”. University of Technology Malaya, Johor, Malaysia, November 30, 2009

Keiji Morokuma, invited, “Exciting World of Theoretical Studies of Chemical Reactions – From Gas Phase Reactions to Nano Structures, Catalysts, and Enzymatic Reactions”. University of Malaya, Kuala Lumpur, Malaysia, December 1, 2009

諸熊奎治、招待，”複雑分子系の化学反応のシミュレーション”，マテリアルズテーラリング研究会、京都、2009.12.26

大峯　巖

福井謙一記念研究センター　福井謙一記念研究部門第二

1. Summary of the research of the year

In addition to our study on water dynamics, e.g. melting dynamics of ice, we have made two studies on biomolecular reactions initiated by photon excitation, namely, the proton transfer in Reaction Center (RC) and the reaction cycle of Photoacive Yellow Protein (PYP). (1) Mechanism of proton uptakes by the secondary ubiquinone (Q_B) in the reaction center of the photosynthetic bacteria, *Rhodobacter sphaeroides*, is investigated theoretically. Two protons are transferred to the secondary ubiquinone (Q_B) upon two electron transfers to it. The pathways of the proton transfers are explored through molecular dynamics and free energy calculations by a molecular mechanical method and potential energy surface calculations by a hybrid ab initio quantum mechanical/molecular mechanical method. Initial locations of donor protons are identified at Glu-L212 and at Asp-L210. It is shown that the first proton transfer takes place from Glu-L212 to Q_B through their direct hydrogen-bond, only when the second electron is transferred to Q_B. The second proton transfer from Asp-L210 to Q_B proceeds through long-range hydrogen-bond network bridges connecting them. The hydrogen-bond network bridges are occasionally formed with several water molecules in the water molecular structural fluctuation dynamics of “proton channel”. The activation energy barrier along the second proton transfer path thus formed is consistent with the experimental rate. It is also found that there exist very strong interactions among water molecules and a protonated carboxyl group of Asp-L210, suggesting formation of a hydronium ion in the surrounding of negatively charged acidic groups in the proton channel. (2) Photocycle of photoactive yellow protein (PYP) is investigated. Upon the photo absorption, the deprotonated p-coumaric acid chromophore undergoes the isomerization. The protonation of the chromophore and the deprotonation of Glu46 then occur, and the pB' state is formed. In the previous study (JPCB 111, 2948(2007)), we have shown that not only the alternation of the protonation state of the chromophore and Glu46, but also the water molecular migration into the protein interior take place during the formation of pB'. PYP in the pB' state undergoes a wide structural change of the protein structure, and the putative signaling state pB is then formed. Since this process is very slow and involves large structural changes, the structure of the pB state and the cause of the structural change has not been explored. This structural change is investigated by means of MD, steered MD, and new free energy calculation techniques. We enforce the structural change on the N-terminal region using steered MD calculations to obtain the structure of pB. We then evaluate the free energy change of the structural change and show that the displacement of the alpha-helix and the corresponding elongation of the beta-strand induce the translational displacement of the N-terminal region.

2. Original papers

(1) “Proton-transfer reactions in reaction center of photosynthetic bacteria Rhodobacter sphaeroides”, *J. Phys. Chem.* B, **113**, 8993-9003 (2009), Yu Kaneko, Shigehiko Hayashi and Iwao Ohmine

(2) “A Molecular Dynamics Study for the Structure Determination of the “Signaling State in the Photocycle of Photoactive Yellow Protein”, *J. Phys. Chem.* B, **114** , 6594–6660 (2010), Motoshi Kamiya and Iwao Ohmine

３．博士研究員

Lung Wa CHUHG

FIFC Fellow, Fukui Kenich Memorial Research Group 1

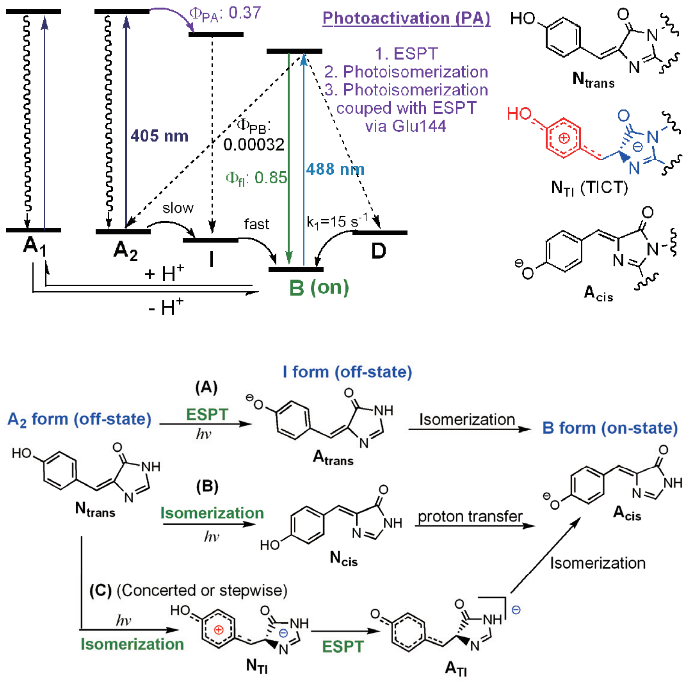
1. Summary of the research of the year

I. Photobiology

The Primary Events of Photodynamics in GFP Chromophores in Water and Dronpa. Application of green fluorescent protein (GFP) and its variants are vital in biological imaging and analysis. A new class of photoactivatable fluorescent proteins (FPs), e.g. reversible photoswitching fluorescent proteins (RPFPs), were developed. Remarkably, fluorescent on-state and non-florescent off-state in RPFPs can be reversibly switched by irradiating two radiations. Such photochromism in RPFPs advances FP technology and can potentially become nano applications, e.g. optical data storage.

However, the reaction mechanism for the reversibly photoswitching is unclear, and proposed to be dictated by protonation state, conformation or non-planarity of the chromophore, as well as intersystem crossing. On the basis of a kinetic isotope study and crystal structures, two mechanisms were proposed for photoactivation for Dronpa (Scheme 1). Our recent calculations supported the proposed on- and off-states (A_2 and B) and proposed another feasible pathway via photoisomerization coupled with excited-state proton transfer (ESPT) to the nearby residue Glu144 (Path C in Scheme 1). Contrast with Dronpa, the neutral and anionic GFP chromophores undergoes ultrafast internal conversion in solutions.

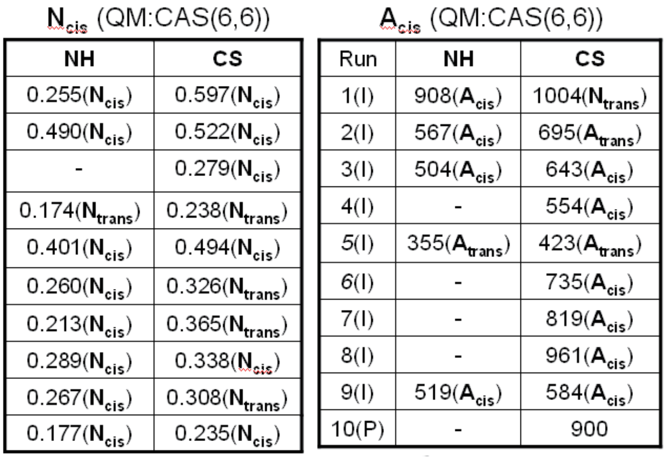
Scheme 1. The proposed mechanisms for Dronpa



Recently, Li Xin (JST fellow) and I proposed and developed non-adiabatic ONIOM molecular dynamics (MD) with a fast and efficient approximated surface hopping scheme for two different electronic transitions, i.e. non-adiabatic crossing (NC) and crossing seam (CS). Accordingly, the primary events of photodynamics of GFP chromophores in water and in Dronpa have been studied by our non-adiabatic MD at ONIOM(SA2-CASSCF(6e,6o)/3-21G:Amber) and ONIOM(SA2-CASSCF(10e,10o)/6-31G:Amber) levels.

As shown in Table 1, the neutral and anionic GFP chromophores undergo ultrafast internal conversion in water. In addition, the excited-state life-time for the anionic GFP chromophore is generally longer than the neutral chromophore, which is consistent with the experiment. Moreover, as indicated in Table 2, electrostatic and polarization stabilization from the MM point charges significantly reduce the energy gap and thus promote the crossings. In particularly, the neutral chromophore has a larger electrostatic and polarization stabilization than the anionic chromophore.

Table 1. The computed excited-state life-time (ps) and photoproduct of GFP chromophores ($\mathbf{N_{cis}}$ and $\mathbf{A_{cis}}$) in water by ONIOM(SA2-CASSCF(6e,6o:MM) MD



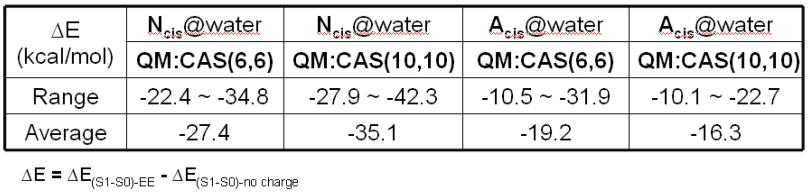
N_{cis} (QM:CAS(6,6))

NH	CS
0.255($\mathbf{N_{cis}}$)	0.597($\mathbf{N_{cis}}$)
0.490($\mathbf{N_{cis}}$)	0.522($\mathbf{N_{cis}}$)
-	0.279($\mathbf{N_{cis}}$)
0.174($\mathbf{N_{trans}}$)	0.238($\mathbf{N_{trans}}$)
0.401($\mathbf{N_{cis}}$)	0.494($\mathbf{N_{cis}}$)
0.260($\mathbf{N_{cis}}$)	0.326($\mathbf{N_{trans}}$)
0.213($\mathbf{N_{cis}}$)	0.365($\mathbf{N_{trans}}$)
0.289($\mathbf{N_{cis}}$)	0.338($\mathbf{N_{cis}}$)
0.267($\mathbf{N_{cis}}$)	0.308($\mathbf{N_{trans}}$)
0.177($\mathbf{N_{cis}}$)	0.235($\mathbf{N_{cis}}$)

A_{cis} (QM:CAS(6,6))

Run	NH	CS
1(I)	908($\mathbf{A_{cis}}$)	1004($\mathbf{N_{trans}}$)
2(I)	567($\mathbf{A_{cis}}$)	695($\mathbf{A_{trans}}$)
3(I)	504($\mathbf{A_{cis}}$)	643($\mathbf{A_{cis}}$)
4(I)	-	554($\mathbf{A_{cis}}$)
5(I)	355($\mathbf{A_{trans}}$)	423($\mathbf{A_{trans}}$)
6(I)	-	735($\mathbf{A_{cis}}$)
7(I)	-	819($\mathbf{A_{cis}}$)
8(I)	-	961($\mathbf{A_{cis}}$)
9(I)	519($\mathbf{A_{cis}}$)	584($\mathbf{A_{cis}}$)
10(P)	-	900

Table 2. The solvent stabilization (kcal/mol) at the crossings at ONIOM(CAS:MM) level.



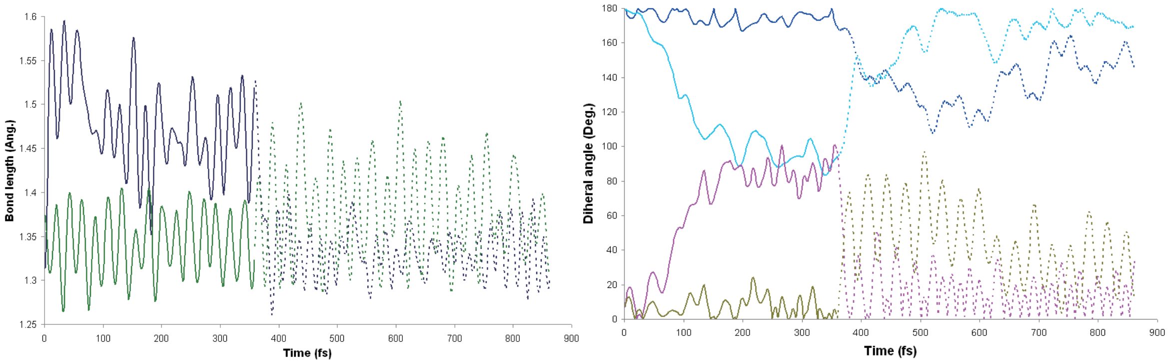
ΔE (kcal/mol)	N_{cis}@water	N_{cis}@water	A_{cis}@water	A_{cis}@water
	QM:CAS(6,6)	**QM:CAS(10,10)**	**QM:CAS(6,6)**	**QM:CAS(10,10)**
Range	-22.4 ~ -34.8	-27.9 ~ -42.3	-10.5 ~ -31.9	-10.1 ~ -22.7
Average	-27.4	-35.1	-19.2	-16.3

$\Delta E = \Delta E_{(S1\text{-}S0)\text{-}EE} - \Delta E_{(S1\text{-}S0)\text{-}no\ charge}$

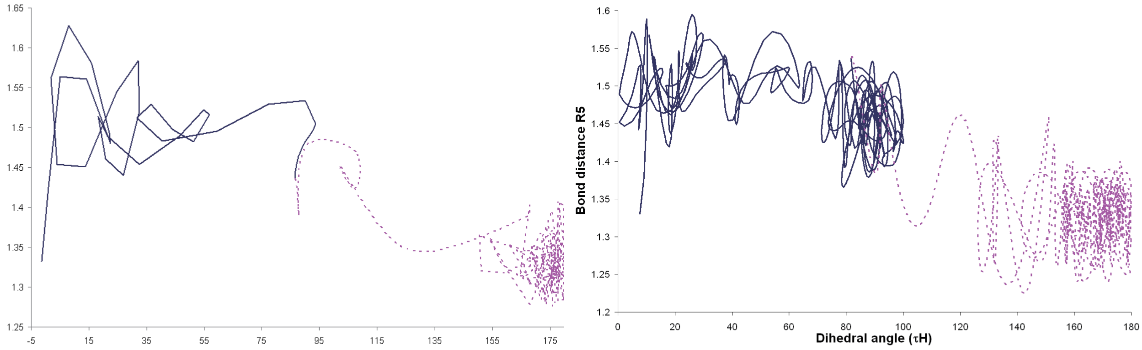
Upon the excitation, for the neutral chromophore, the formal C=C bond is elongated and thus weakened, while the formal C-C bond is strengthened. Therefore, rotation along the imidazolinone ring takes place only

(Scheme 2). Moreover, the internal conversion processes can be regarded as two-state two-model, in which the bond stretching/compression of the two bridging C-C bonds occurs first, followed by changes of torsions relating to rotation of the imidazolinone ring (Scheme 3).

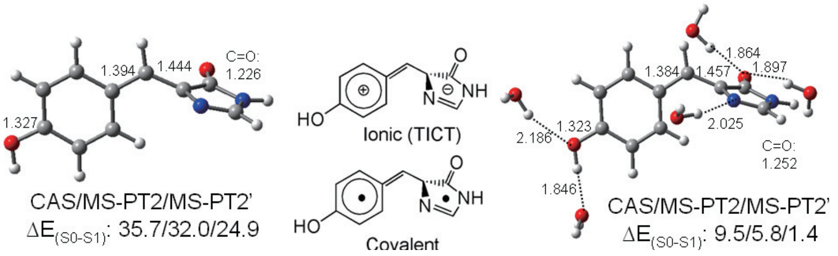
Scheme 2. Time evolution of the bond distances (left) and dihedral angles related to the two bridging C-C bonds for the neutral GFP chromophore in water at ONIOM(SA2-CASSCF(6e,6o)/3-21G:MM) level.

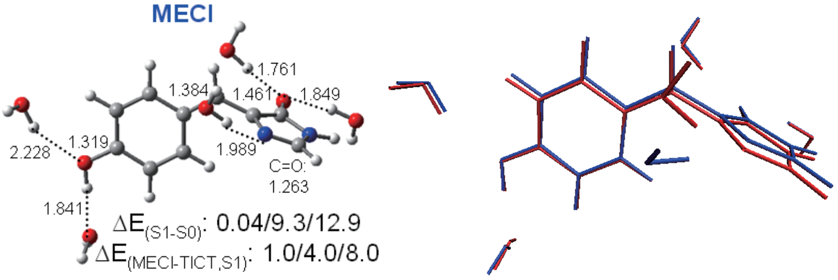


Scheme 3. Structural changes of the key bond distance and dihedral angle for photoisomerization of the neutral GFP chromophore in water (left) and Dronpa (right)



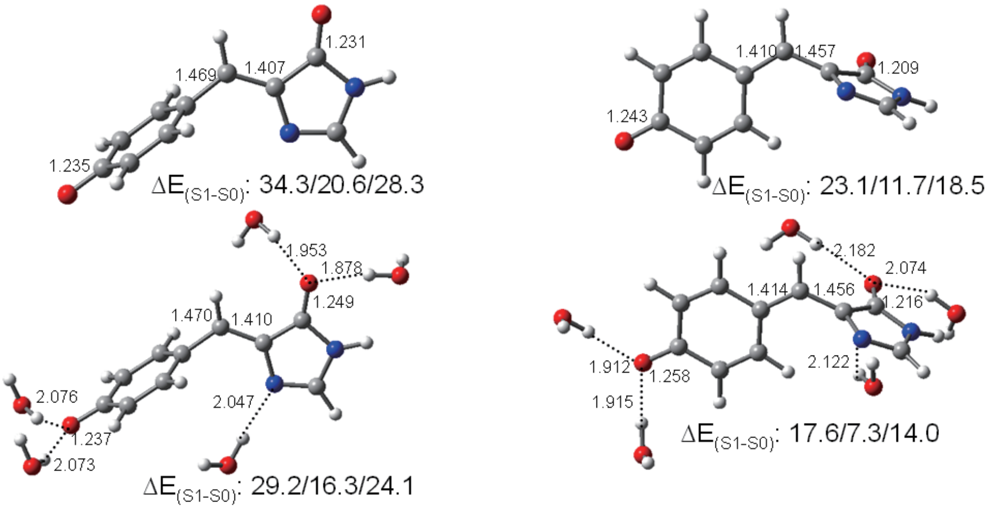
Scheme 4. Optimized twisted intermediates (top) and minimum energy conical intersection (bottom) for the neutral GFP chromophores by CASSCF(12e,12o)/6-31G* level.



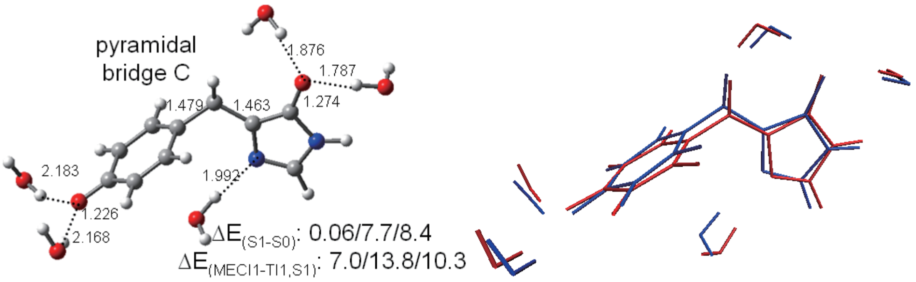


Faster internal conversion for the neutral chromophore than the anionic chromophore is also supported by geometry optimization in the presence of the explicit water molecules at CASSCF(12e,12o)/6-31G* level (Schemes 4-6). The presence of the water molecules lowers the energy gap, especially for the neutral chromophore (Scheme 4). In addition, in the presence of the water molecules, energy difference between the minimum energy conical intersection (MECI) and the twisted intermediate is much smaller for the neutral chromophore (Scheme 4) than the anionic chromophore (Schemes 5-6). Therefore, the neutral chromophore should easily reach the intersection and this has a shorter excited-state life time.

Scheme 5. Optimized twisted intermediates (top) and minimum energy conical intersection (bottom) for the anionic GFP chromophores by CASSCF(12e,11o)/6-31G* level.



Scheme 6. Optimized minimum energy conical intersection for the anionic GFP chromophores by CASSCF(12e,11o)/6-31G*



II. Extension of ONIOM

Generalized ONIOM: Truncation and Extrapolation of Many-Body Expansion for Large systems: Evaluating reliable energetic and geometry for large systems are computationally challenging and demanding. Treatment of the complex systems are generally approximated by two common means: hybrid QM/MM method (including Morokuma’s ONIOM, see Eqs. 1-3) and fragmentation methods (e.g. FMO). Both approaches have their own merits and disadvantages. For example, computational cost for hybrid QM/MM method is smaller, in which one key part of the system is described by the high-accurate QM method. However, more than one part (transition metals or molecules in different electronic states) of the system can sometimes play an important role in some metalloenzymes and photobiologies, but they are too computationally expensive to be described by the high-accurate QM method in the current hybrid QM/MM method. On the other hand, the common fragmentation approaches is generally based on many-body expansion approximation. Unfortunately, computational cost for large systems by the high-accurate QM method via many-body expansion is also high, and dramatically increases with the sizes and numbers of the fragments.

Extrapolated schemes (ONIOM)

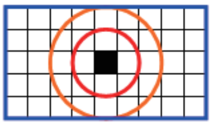
$$\Delta E_{\mathrm{ONIOM(QM:MM)}} = \Delta E_{\mathrm{QM,model}} + \Delta E_{\mathrm{MM,real}} - \Delta E_{\mathrm{MM,model}} \qquad (1)$$

$$\Delta E_{\mathrm{ONIOM(QM:QM')}} = \Delta E_{\mathrm{QM,model}} + \Delta E_{\mathrm{QM',real}} - \Delta E_{\mathrm{QM',model}} \qquad (2)$$

$$\Delta E_{\mathrm{ONIOM(QM:QM':MM)}} = \Delta E_{\mathrm{QM,model}} + \Delta E_{\mathrm{QM',int}} - \Delta E_{\mathrm{QM',model}} + \Delta E_{\mathrm{MM,real}} - \Delta E_{\mathrm{MM,int}} \qquad (3)$$

Remarkably, the success of hybrid ONIOM method is constructed and approximated from extrapolation of energies/gradients for the major parts via less expensive MM or lower QM method. Unfortunately, MM and lower QM method may not treat transition metals or excited-states for large systems properly. In this connection, we combined advantages of the extrapolation ONIOM method and many-body expansion approximation: generalized ONIOM (Scheme 7). In this case, the large systems can be divided into many units. The (2- or higher-body) interactions of the units in short-range distances are treated by high-accurate method (such as DFT and MP2). Whereas, the interactions of the units in medium- or long-range distances are approximated by extrapolation with the lower QM method or/and MM method. Our preliminary testing showed that our proposed generalized ONIOM can give very similar geometries at a lower computational cost than the normal full QM method (Schemes 8-9).

Scheme 7. Schematic layer-separated interactions in generalized ONIOM

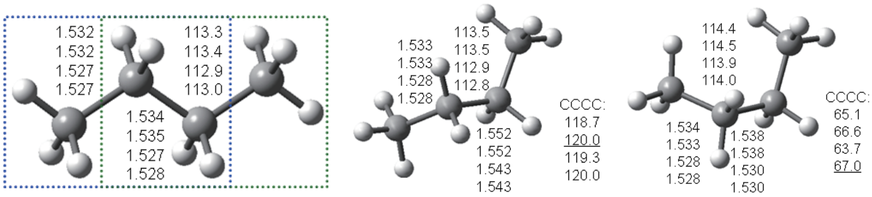


Short-range: *2 (or higher) body* terms by higher QM method with ***electron correlation*** (e.g. DFT, MP2)

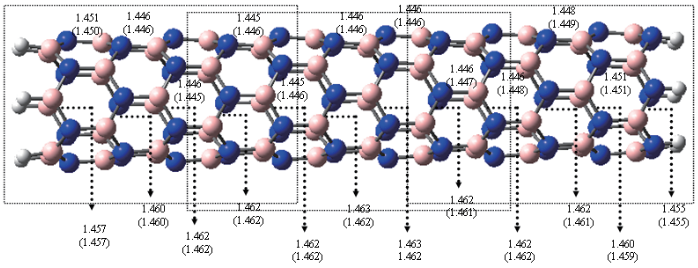
Medium-range: extrapolated by lower QM method (e.g. HF, semi-empirical)

Long-range: extrapolated by lowest QM method (semi-empirical) or MM method

Scheme 8. Optimized butane (right: anti; middle: rotation TS; gauche: right) by full QM and generalized ONIOM(QM:HF/3-21G). (QM: B3LYP/6-31G* for 1st and 2nd rows; MP2/6-31G for 3rd and 4th rows).



Scheme 9. Optimized boron-nitrogen nano-tube by full QM (top) and generalized ONIOM(QM:HF/3-21G) (bottom). (QM: B3LYP/6-31G*).



2. Original papers

(1) Chung, L. W.; Li, X.; Sugimoto, H.; Shiro, Y.; Morokuma, K. "ONIOM Study on a Missing Piece in Our Understanding of Heme Chemistry: Bacterial Tryptophan 2,3-Dioxygenase (TDO)", submitted.

(2) Li, X.; Chung, L. W.; Miyawaki, A.; Morokuma, K. "The Primary Events of Photodynamic in Reversibly Photoswitching Fluorescent Protein Dronpa" Manuscript in preparation.

(3) Li. X.; Chung, L. W.; Miyawaki, A.; Morokuma, K. "Photoisomerization of GFP Chromphores in Water" Manuscript in preparation.

(4) Chung, L. W.; Li, X.; Morokuma, K. "Generalized ONIOM for Large System: Truncation and Extrapolation of Many-Body Expansion" Manuscript in preparation.

(5) Li. X.; Chung, L. W.; Mizuno, H.; Miyawaki, A.; Morokuma, K. "A Theoretical Study on the Natures of On- and Off-States of Reversibly Photoswitching Fluorescent Protein Dronpa: Absorption, Emission, Protonation and Raman" *J. Phys. Chem. B* **2010**, *114*, 1114.

3. Presentation at academic conferences

(1) Chung, L. W.; Hayashi, S.; Nakatsu, T.; Kato, H.; Morokuma, K. “Mechanism of Efficient Firefly Bioluminescence via Adiabatic Transition State and Seam of Sloped Conical Intersection”, American Chemical Society 237th National Meeting, Salt Lake City, Utah, March 2009.

(2) Lung Wa Chung, Xin Li, Keiji Morokuma, “*Our ONIOM Journey of Metalloenzymes and Photobiology*” CREST International Symposium on Theory and Simulations of Complex Molecular Systems, Kyoto, Japan, July 21, 2009.

(3) Lung Wa Chung, Shigehiko Hayashi, Toru Nakatsu, Hiroaki Kato, Keiji Morokuma “*Mechanism of Efficient Firefly Bioluminescence Via Adiabatic Transition State and Seam of Sloped Conical Intersection*” (poster) Simulations and Dynamics for Nanoscale and Biological Systems, Tokyo, March 5, 2009.

(4) Lung Wa Chung, Shigehiko Hayashi, Toru Nakatsu, Hiroaki Kato, Keiji Morokuma “*Mechanism of Efficient Firefly Bioluminescence Via Adiabatic Transition State and Seam of Sloped Conical Intersection*” (poster) Reaction Dynamics of Many-Body Chemical Systems, Kyoto, June 23, 2009.

(5) Lung Wa Chung, Xin Li, Hiroshi Sugimoto, Yoshitsugu Shiro, Keiji Morokuma “*DFT and ONIOM Studies on a Missing Piece in Our Understanding of Heme Chemistry: Bacterial Tryptophan 2, 3-dioxygenase*” 14th International Conference on Biological Inorganic Chemistry, Nagoya, July 26-29, 2009.

(6) Lung Wa Chung, Xin Li, Hiroshi Sugimoto, Yoshitsugu Shiro, Keiji Morokuma “*DFT and ONIOM Studies on a Missing Piece in Our Understanding of Heme Chemistry: Bacterial Tryptophan 2, 3-dioxygenase*” Molecular Theory for Real Systems, Kyoto, January, 7-9, 2010.

4. Book Chapter

(1) Chung, L. W.; Li, X.; Morokuma, K. “Modeling Enzymatic Reactions in Metalloenzymes and Photobiology by Quantum Mechanics (QM) and Quantum Mechanics/Molecular Mechanics (QM/MM) Calculations,” In “Quantum Biochemistry” Matta, C. Eds. WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, 2010, pp85-130.

(2) Li, X.; Chung, L. W.; Morokuma, K. “*Modeling Photobiology Using Quantum Mechanics (QM) and Quantum Mechanics/Molecular Mechanics (QM/MM) Calculations,*” In “Computational Methods for Large systems: Electronic Structure Approaches for Biotechnology and Nanotechnology ” Reimers, J. R. Eds. Wiley, 2010, pp342-373.

Biswajit SAHA

FIFC Fellow, Fukui Kenichi Memorial Research Group 1

1. Summary of the research of the year FY2009

(A) Formation mechanism of polycyclic aromatic hydrocarbons (PAHs) during benzene combustions: DFTB MD simulations

High temperature quantum chemical molecular dynamics simulations on the polycyclic aromatic hydrocarbons (PAHs) formation during combustion of benzene were performed using the density-functional tight-binding (DFTB) method. Systems with varying H/C of 0.8, 0.6, 0.4 and 0.2 and temperatures T_n = 2500 K and T_n = 3000 K were employed for the study of the PAH formation and growth mechanism, and trajectories were analyzed by recording average C:H compositions, common elementary reactions and molecular species, ring count, and other characteristic quantities as functions of time. We found that at H/C = 0.8 mostly short polyacetylenic hydrocarbons were formed, and no significant PAH growth was found. At lower H/C ratio, longer polyacetylenic chains started to form and new 5-, 6-membered rings were created due to chain entanglement. Significant PAH growth forming only peri-condensed PAHs was observed at lower H/C ratios of 0.4 and 0.2. In addition, smaller hydrocarbon species, such as C_2H_2, C_2H, and C_2, are constantly produced by fragmentation of hydrocarbons (unimolecular reactions) and remain common species, although they are simultaneously consumed by HACA growth mechanism. Hydrogen is found to have a clear inhibitive effect on PAH and carbon cluster growth in general, in agreement with recent experimental observations.

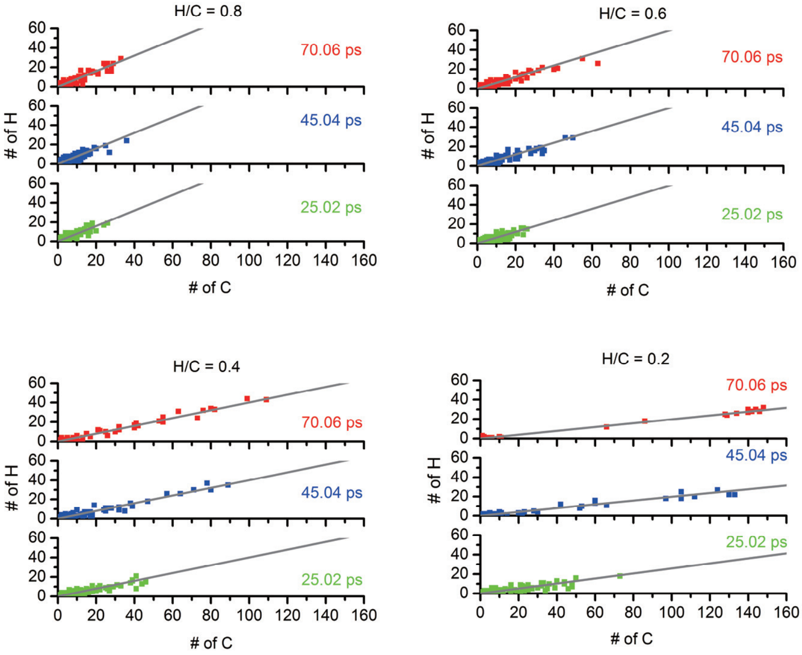


Fig. 1 Hydrocarbon formation and growth with time for T_n = 2500 K. Each point corresponds to a species of the form C_xH_y. The (red) line corresponds to the H/C ratio of over all system. Data points plotted for 10 simulations.

The oxidation of benzene molecules was modeled by removing 30 randomly selected hydrogen atoms every 5.00 ps until desired H/C ratios were reached, and the systems were then allowed to propagate up to a total simulation time of 70.06 ps. The effects of H/C ratio by considering H/C = 0.8, 0.6, 0.4 and 0.2 and temperatures using T_n = 2500 K and T_n =

3000 K on the formation and growth mechanism were analyzed by recording average C:H compositions, most common elementary reactions and molecular species, ring count, and other quantities as a function of time. The effect of H/C ratio on the PAH growth process is shown in Fig. 1. We found no significant PAH growth at an H/C ratio of 0.8. At this ratio, only linear small hydrocarbons were formed at T_n = 3000 K although small PAH with two or three rings are present for T_n = 2500 K. Hydrogen is found to have a clear inhibitive effect on PAH and carbon cluster growth in general, in agreement with recent experimental observations. Faster growth occurs at lower H/C ratios. At the end of the simulations, larger PAH with fused 5/6/7-membered rings were formed, with polyacetylyne-like structures attached. In agreement with the HACA reaction mechanism, C_2 and C_2H are the most abundant species for all H/C ratios, however, this is not the only route for PAH growth. Other, more complex reaction mechanisms were found to contribute to the growth process.

A significant amount of sp-hybridized polyyne-like carbon species remains present up until all hydrogen atoms are removed. The C:H composition of the growing PAH radical species from polyacetylene-like open-chain radical species differs rather little from the H/C ratio of the system, and no tendency towards formation of maximally condensed PAH systems was observed. This finding stands in remarkable contrast to the hypothesis of ordered PAH growth following thermodynamically most favorable species, and emphasizes the necessity to consider growth mechanisms that involve open-chain and pentagon-containing intermediate species. It can be expected that upon continuation the presented simulations for longer time with same H/C ratio, the cluster will not grow significantly since the largest cluster has already consumed nearly all available carbon atoms. Continuation of the simulations for longer time should also lead to further ring condensation processes, specifically for H/C = 0.4 and 0.2. To study the equilibrium composition at a given H/C system ratio, we are currently performing longer simulations with more benzene molecules.

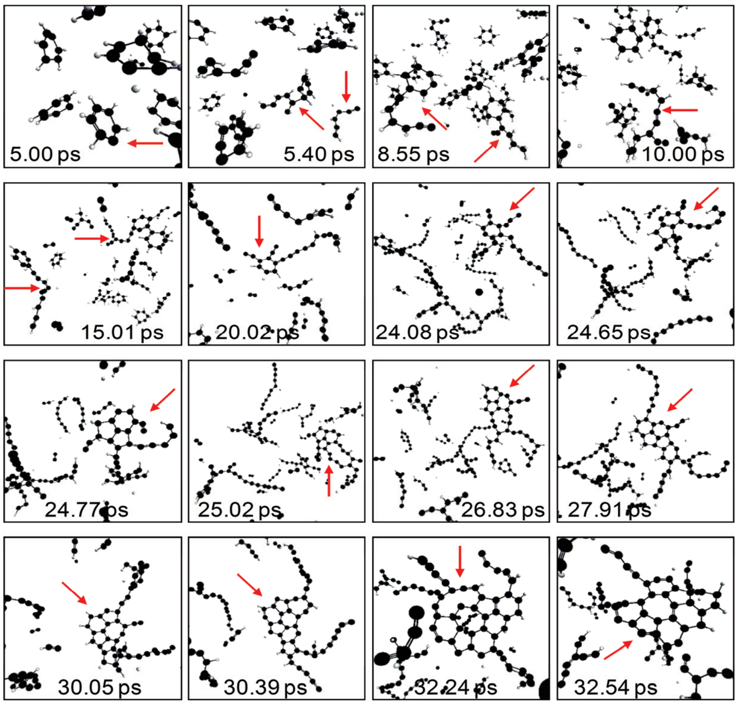


Fig.2 Snapshots of PAH formation and growth mechanism. Arrows denote region where the mentioned event is observed.

Formation and growth mechanism of a PAHs are shown using selected snapshots from a representative trajectory with T_n = 2500 K with H/C = 0.2 in Fig. 2. We observe that the created radical species (either due to thermal decomposition or due the programmed H removal) with ring structure easily forms polyacetylene-like structures (5.00 ps, 5.40 ps, 8.55 ps, 10.00 ps). These polyacetylene-like structures may grow further by reacting with other polyacetylene-like structures, radical species or benzene molecules present in the system (15.01 ps, 20.02 ps, 24.08 ps). Usually most of the rings open to form polyacetylene-like structures, and only very few ring could survive (20.02 ps, 24.08 ps). Thus these polyacetylene-like structures assemble themselves to form larger and branched polyacetylene-like structures (24.08 ps). Therefore in some cases an original 6-membered ring can be attached to a polyacetylene-like structure. In the situation where there is no original 6-membered ring, the polyacetylene-like structures can catch each other to form new ring 5-, 6-, or 7-membered rings (24.65 ps). Once a ring (usually 5- or 6-membered) is formed, the further ring condensation proceeds quite fast (24.65 ps, 24.77 ps, 25.02 ps, 26.33 ps, 27.91 ps, 30.05 ps, 30.39 ps, 32.24 ps, 32.54 ps). The formation of the first aromatic ring is a crucial event in the formation process of PAH and soot in flame. The snapshot shown at 32.54 ps consists of two 5-membered rings, five 6-membered rings and one 7-membered ring and polyacetylyne-like structures attached with this. These polyacetylene-like structures (may) help further ring condensation and growth processes. Thus a pre-formed PAH may catch a polyacetylene-like structure at high temperatures. The above-mentioned stages can be presented as follows. In the first stage C_6H_n ($n < 6$) radical species are created and subsequently polyacetylenic chains form. In the next stage, these linear chains occasionally react to form branched polyacetylene-like structures, typically initiated by radical centers present somewhere on the chain of carbon atoms. In the third stage these branched polyacetylene-like structures form new 5-, 6-, 7-membered or larger rings due to ring condensation, depending on the availability of the free valences. In the fourth stage, further ring condensation growth occurs around this newly formed condensed ring system to form peri-condensed rings, and the size of the π-system increases while sp-type carbon converts to sp^2-type. At higher temperature, we notice a preference for hexagon creation over pentagons, resulting from annealing transformations that occur simultaneously with ring condensation.

(B) Shrinking of hot giant fullerenes in presence of buffer gas: DFTB MD simulations

Density functional tight binding (DFTB) molecular dynamics simulations have been performed by annealing hot giant fullerenes in presence of buffer gases, such as Helium and Argon. The interaction potential (L-J) for carbon and buffer gas are taken from literature. Cluster size and structural changes are analyzed and discussed. It is observed that the explicit use of buffer gas helps to shrink the giant fullerenes faster and eventually may form smaller fullerenes, e.g., C_{60}, C_{70} etc. The shrinking process occurs almost exclusively via emission of C2 unit from the giant fullerenes. Ring transformations are occurred following general Stone-Walls (GSW) type transformation and thus the defects due to 7-, 8-membered, or higher membered rings are healed up. These simulations show that the explicit use of buffer gas during annealing is helpful for formation of smaller fullerenes.

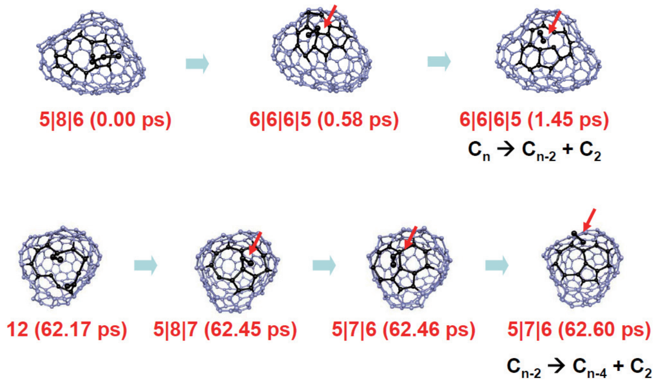


Fig.3 C2 fragmentation mechanism from giant fullerenes. Arrows denote region where the mentioned event is observed. Different colors are used to present C atoms for clarity.

It is observed that the shrinking of giant fullerenes due to annealing at high temperature occurs in two stages: (i) fall of side chain and (ii) C2/C4 pop-out. Shrinking process occurs almost exclusively via C2 emission from the giant fullerenes. Ring transformations and subsequent C2 fragmentations are occurred following general Stone-Walls (SW) or non-SW type transformation and thus the defects due to 4-, 7- or higher membered rings are healed up and hence π-conjugation increases. Snapshots representing C2 fragmentation mechanism is shown in Fig. 3 which shows subsequent C2 fragmentations from a giant fullerene. It is also observed that the appearance of sp^3 carbon has important role in the fragmentation process. It appears that simulations with buffer gas show faster shrinking compared to simulations using velocity scaling thermostat.

2. Original papers

1. B. Saha, S. Irle, K. Morokuma, "Formation mechanism of polycyclic aromatic hydrocarbons (PAHs) in benzene combustion: Quantum chemical molecular dynamics simulations", J. Chem. Phys. 132, 224303 (2010)
2. B. Saha, S. Shindo, S. Irle, K. Morokuma, "Quantum chemical molecular dynamics (QM/MD) simulations of fullerene from benzene", ACS Nano *3*, 2241 (2009)

3. Presentation at academic conferences

1. 239th ACS National Meeting, San Francisco, CA, USA, March 21-26, 2010 - Fullerene self-assembly in benzene flame: Density functional tight-binding (DFTB) MD Simulations (poster) - B. Saha, S. Irle, K. Morokuma
2. International Symposium on Molecular Theory for Real Systems, Fukui Institute for Fundamental Chemistry, Kyoto University, Japan 7-9 Jan., 2010 - Shrinking of hot giant fullerene in presence of buffer gas: DFTB MD simulations (poster) - B. Saha, S. Irle and K. Morokuma
3. CREST International Symposium on Theory and Simulations of Complex Molecular Systems, Fukui Institute for Fundamental Chemistry, Kyoto University, Japan, 19-21 July, 2009 – Annealing of giant fullerene in presence of buffer gas: DFTB/MM MD simulations (poster) - B. Saha, S. Irle, K. Morokuma

4. Others

Hajime HIRAO

FIFC Fellow, Fukui Kenichi Memorial Research Group 1

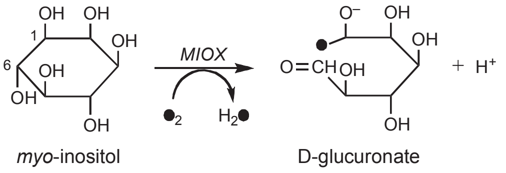
1. Summary of the research of the year

Hybrid Quantum Mechanical and Molecular Mechanical Studies of Metalloenzymes: Characterization of Elusive Intermediates and Elucidation of Reaction Mechanisms

Metalloenzymes are finely tuned catalytic machines that drive energetically unfavorable reactions under mild conditions, often with surprisingly high selectivity. Understanding the catalytic functions of metalloenzymes is of considerable scientific importance, and the knowledge gained from fundamental studies would open up new avenues for practical applications such as rational design of potent enzyme inhibitors and development of powerful biomimetic transition-metal catalysts. My long-term research goal is to contribute to both of these scientific and practical aspects of bioinorganic chemistry via computational studies. Two prerequisites for understanding metalloenzyme functions are full characterization of intermediates in their catalytic cycles and elucidation of the catalytic reaction mechanisms at the atomic level. Hybrid quantum mechanical (QM) and molecular mechanical (MM) methods such as ONIOM(QM:MM) have useful roles to play in these efforts. With this in mind, I have been applying hybrid methods to a wide range of metalloenzymes. This year, my research focus was on two metalloenzymes, *myo*-inositol oxygenase (MIOX) and soybean lipoxygenase-1 (SLO-1), both of which are physiologically important iron enzymes.

1-1. Insights into the (Superoxo)Fe(III)Fe(III) Intermediate and Reaction Mechanism of *myo*-Inositol Oxygenase: DFT and ONIOM(DFT:MM) Study

myo-Inositol (MI) is a structural component of inositol phosphates and phosphoinositides that are known to serve as second messengers to mediate important cellular processes including insulin action. Accumulated evidence indicates that depletion of the intracellular level of MI is associated with various diabetic complications such as nephropathy, retinopathy, neuropathy, and cataract. MI is degraded via conversion to D-glucuronate (DG), which is the first committed step in MI catabolism (Scheme 1). This MI-to-DG oxidative conversion was found to proceed predominantly in the kidney catalyzed by MIOX, and it was also shown that MIOX is expressed, albeit at much lower levels, in extra-renal tissues where diabetic complications occur. It is therefore conceivable that the MIOX function somehow regulates the MI level and thereby plays a critical role in the pathogenesis of diabetic complications. Despite the apparent biomedical and chemical significance of MIOX, its molecular details are still largely unclear, although recent experiments showed that MIOX is a diiron enzyme and utilizes a (superoxo)Fe(III)Fe(III) intermediate as a reactive species. In this study, the (superoxo)Fe(III)Fe(III) reactive species and the catalytic



Scheme 1. MIOX catalyzed reaction.

reaction mechanism of a diiron enzyme, *myo*-inositol oxygenase (MIOX), were theoretically investigated by means of density functional theory (DFT) and ONIOM quantum mechanical/molecular mechanical (QM/MM) approaches. The ground state of the (superoxo)Fe(III)Fe(III) intermediate was shown to have a side-on coordination geometry and an $S = 1/2$ spin state, wherein the two iron sites are antiferromagnetically coupled while the superoxide site and the nearest iron are ferromagnetically coupled. The initial step of the reaction, namely H-abstraction (Fig. 1), was theoretically characterized in detail, through the computations of the reaction pathway and kinetic isotope effect. Furthermore, subsequent steps leading to a D-glucuronate product were proposed based on ONIOM computational results. It was found that the enzyme surrounding plays an essential role in the catalysis. The unique role of the bridging hydroxide ligand as a catalytic base was also identified.

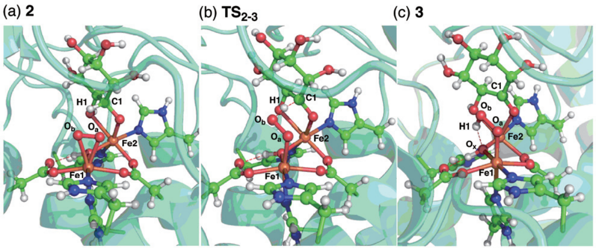


Fig. 1. Initial step of the reaction (H-abstraction).

1-2. What is the Real Nature of Ferrous Soybean Lipoxygenase-1? A New Two-Conformation Model Based on Combined ONIOM(DFT:MM) and Multireference Configuration Interaction Characterization

Soybean lipoxygenase-1 (SLO-1) is a nonheme iron enzyme that oxidizes linoleic and linolenic acids to yield the corresponding hydroperoxides. SLO-1 has served as a model for dissecting the structure and function of lipoxygenases, which are ubiquitously distributed in plant and animal kingdoms. Past studies have demonstrated that SLO-1 exhibits a variety of intriguing features and phenomena, including a unique coordination sphere around the Fe(II) site. Crystallographic studies have converged onto the view that ferrous SLO-1 has six ligands, with one of the ligands, Asn694, being only loosely bound. However, the circular dichroism (CD) and magnetic circular dichroism (MCD) studies indicated that ferrous SLO-1 exists as an almost equal mixture of two distinct forms, which are most probably five-coordinate and six-coordinate forms. Thus, discrepancies remain among the previous experimental results, concerning the nature of ferrous SLO-1. Therefore, we have theoretically characterized ferrous SLO-1 by means of the ONIOM(DFT:MM), TDDFT, and CASSCF/SORCI methods, taking explicitly into account the effect of the protein environment. Two

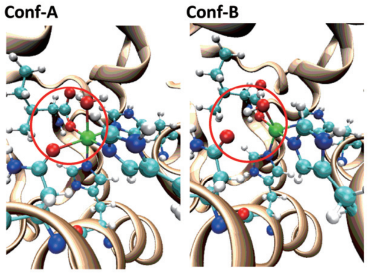


Fig. 2. Two conformations of SLO-1 found in this study.

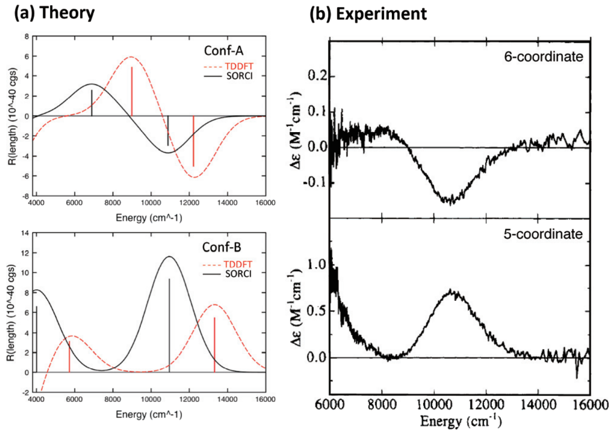


Fig. 3. Theoretical and experimental CD spectra.

conformations found theoretically in this study, Conf-A and Conf-B (Fig. 2), were shown to have almost equal stability but have quite different geometries, with short and long Fe-O_{694} distances, respectively. While neither of the geometries agreed well with the crystal structure of the enzyme, an averaged geometry showed excellent agreement. This result indicates that the crystal structure reflects a mixture of these two conformations. Furthermore, the calculated circular dichroism (CD) spectra for Conf-A and Conf-B were found to agree well with the two experimental spectra obtained previously for putative "six-coordinate" and "five-coordinate" forms of ferrous SLO-1, respectively (Fig. 3). We thus propose that, in both the crystal for X-ray analysis and the solution for CD analysis, Conf-A and Conf-B coexist.

2. Original papers

(1) Hajime Hirao and Keiji Morokuma
Insights into the (Superoxo)Fe(III)Fe(III) Intermediate and Reaction Mechanism of *myo*-Inositol Oxygenase: DFT and ONIOM(DFT:MM) Study
J. Am. Chem. Soc. **2009**, *131*, 17206-17214.

(2) Hajime Hirao and Keiji Morokuma
What is the Real Nature of Ferrous Soybean Lipoxygenase-1? A New Two-Conformation Model Based on Combined ONIOM(DFT:MM) and Multireference Configuration Interaction Characterization
J. Phys. Chem. Lett. **2010**, *1*, 901-906.

3. Presentation at academic conferences

(1) Hajime Hirao and Keiji Morokuma (Poster: 2P46)
"DFT 法と ONIOM(DFT:MM)法を用いた *myo*-inositol oxygenase に関する研究"
第 12 回理論化学討論会 (Theoretical Chemistry Symposium), Tokyo, May 29, 2009.

(2) Hajime Hirao and Keiji Morokuma (Poster: P6)
"ONIOM studies of biological molecules: *myo*-inositol oxygenase"
International Symposium on Reaction Dynamics of Many-Body Chemical Systems (RDMCS2009), Kyoto, June 23, 2009.

(3) Hajime Hirao and Keiji Morokuma (Poster: P-12)
"DFT and ONIOM(DFT:MM) studies of *myo*-inositol oxygenase"
CREST International Symposium on Theory and Simulations of Complex Molecular Systems & International Symposium on Theory of Molecular Structure, Function and Reactivity, Celebrating Prof. Morokuma's 75th Birthday, Kyoto, July 20, 2009.

(4) Hajime Hirao and Keiji Morokuma (Poster: P526)
"DFT and ONIOM(DFT:MM) studies of *myo*-inositol oxygenase"
ICBIC 14, Nagoya, July 27, 2009 (*J. Biol. Inorg. Chem.* **2009**, *14 (Suppl 1)*, S526).

(5) Hajime Hirao and Keiji Morokuma (Oral: COMP-020)

"DFT and ONIOM(DFT:MM) computational studies of *myo*-inositol oxygenase: Insights into the (superoxo)diiron(III/III) intermediate and reaction mechanism"
238th ACS National Meeting, Washington, DC, August 16, 2009.

(6) Hajime Hirao and Keiji Morokuma (Oral: 1E-03)
"*myo*-Inositol oxygenase に関する理論的研究"
第 59 回錯体化学討論会 (59th JSCC Annual Meeting), Nagasaki, September 25, 2009.

(7) Hajime Hirao and Keiji Morokuma (Poster: 48)
"DFT and ONIOM(DFT:MM) studies of *myo*-inositol oxygenase"
International Symposium on "Molecular Theory for Real Systems", Kyoto, January 7, 2010.

(8) Hajime Hirao (Oral: INV-1, Invited)
"QM/MM computational studies of metalloenzymes: Characterization of elusive intermediates and elucidation of reaction mechanisms"
14th International Annual Symposium on Computational Science and Engineering (ANSCSE14), Chiang Rai (Thailand), March 24, 2010.

4. Others

4-1. Other presentations

(1) Hajime Hirao and Keiji Morokuma (Poster: 3)
"DFT and ONIOM(DFT:MM) studies of *myo*-inositol oxygenase"
7th FIFC Symposium, Kyoto, December 4, 2009.

(2) Hajime Hirao (Oral)
"QM/MM computational studies of metalloenzymes: Characterization of elusive intermediates and elucidation of reaction mechanisms"
7th FIFC Seminar, Kyoto, February 4, 2010.

4-2. External research grants

(1) Startup Grant for Young Researchers (Kyoto University)
(2) Kurata Grant (The Kurata Memorial Hitachi Science and Technology Foundation)

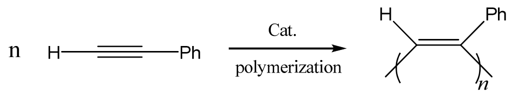
Zhuofeng KE

FIFC Fellow, Fukui Kenichi Memorial Research Group 1
(From 7 Jul. 2009)

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

I. Theoretical Study of Catalysis in Organometallic Systems

Scheme 1. *Catalyzed Polymerization of Phenylacetylene*



Polyenes with π-conjugated backbones are important materials with potential applications in photoconductivity, optical nonlinear susceptibility, and magnetic susceptibility *etc*. The Rh-catalyzed polymerization is one of the most powerful methods to synthesize polyenes (Scheme 1).

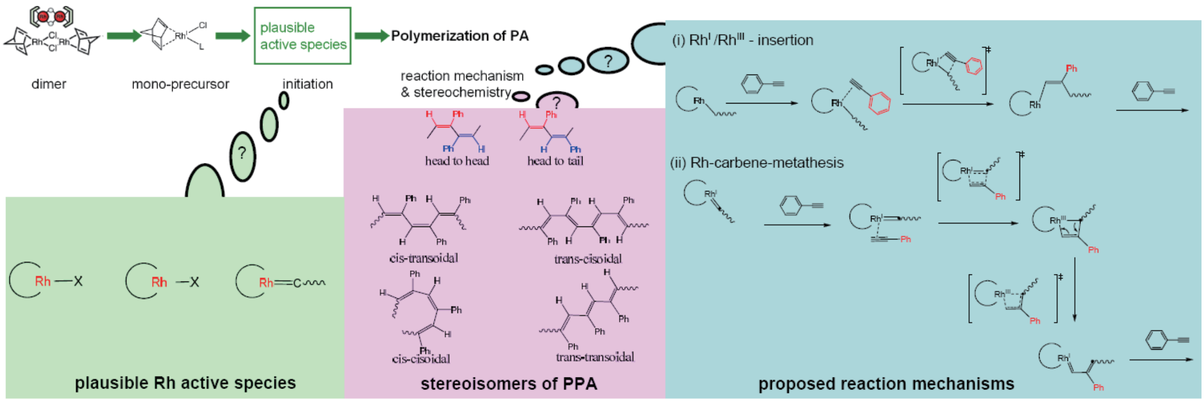
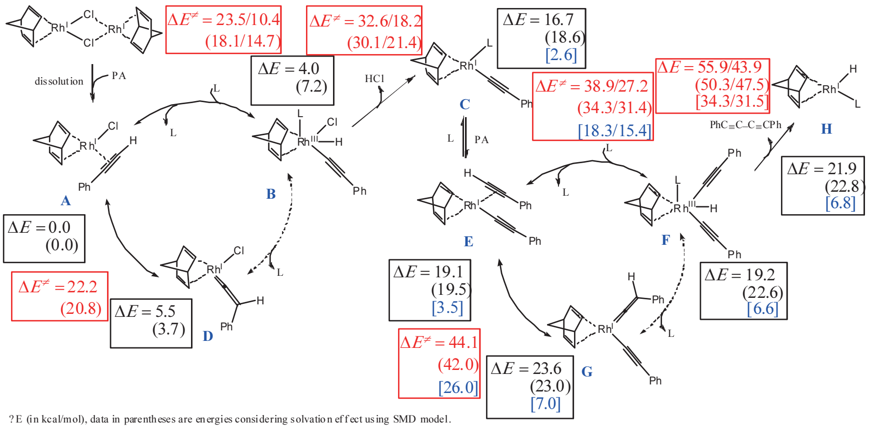


Fig 1. *Backgroup of Mechanistic Problems in Rh-Catalyzed Polymerization of Phenylacetylene.*

In contrast to numerous experimental efforts in the past decades, the polymerization mechanism still remains a subject of discussion (Fig. 1). The Rh^I/Rh^{III}-insertion, and metathesis mechanism involving a Rh^I-carbene species were both proposed in the literature. The relationship between the reaction mechanism and the stereochemistry for the polymerization is still less known. DFT studies were carried out to reveal the whole picture for the Rh-catalyzed polymerization of phenylacetylene, to provide detailed

Scheme 2. *Transformations between Different Plausible Active Species in the Solution.*



?E (in kcal/mol), data in parentheses are energies considering solvation effect using SMD model.
L: water, Data in square brackets are corrected with exp. HCl solvation energy (-16.7 kcal/mol)

mechanistic information which is helpful for advancing the design of new efficient and stereospecific catalysts for polyenes.

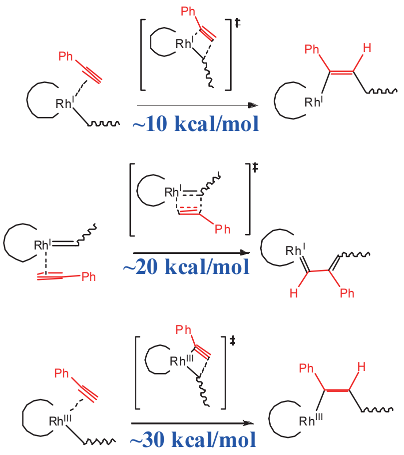


Fig 2. *Reaction Mechanisms for the Rh-Catalyzed Polymerization of Phenylacetylene.*

Our studies have revealed that Rh^{I}-insertion is the most feasible mechanism for the Rh-catalyzed polymerization of phenylacetylene, although the formation of Rh^{I}, Rh ^{III} and Rh^{I}-carbene species are all thermodynamically and kinetically feasible in the reaction solution (Scheme 2). The barriers of the propagation steps for Rh^{I}-insertion, Rh^{III}-insertion and Rh^{I}-carbene metathesis are calculated to be around 10 kcal/mol, 30 kcal/mol and 20 kcal/mol, respectively (Fig. 2). For the RhI-insertion mechanism, monomer phenylacetylene prefers a 2,1-insertion rather than a 1,2-insertion, leading to a head-to-tail cis-transoidal poly-phenylacetylene, in good agreement with experimental observations. The origin of the selectivity is from the electronic effect and steric Effect in the transition state (Fig. 3). The former favors an electrophilic attack of π* orbital of phenylacetylene to the π electrons of alkenyl group; the latter dislikes the steric repulsion between phenyl group in phenylacetylene and the propagation chain.

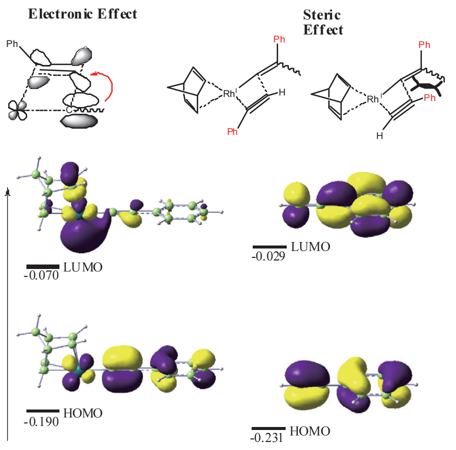


Fig 3. *Origin of the Selectivity in Rh-Catalyzed Polymerization of Phenylacetylene.*

II. Theoretical Study of Catalysis in Bio-Nano Cavity of Protein

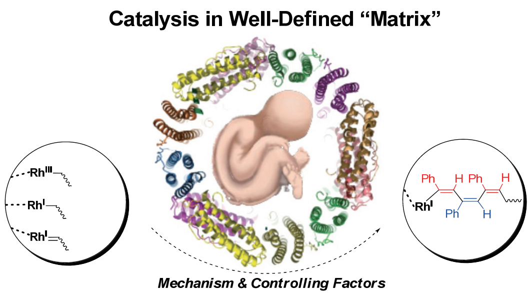


Fig 4. *Rh-catalyzed Polymerization of Phenylacetylene in Nano-Cavity of apo-Ferritin*

The interface between bio and nano chemistry has become one of the most promising fields for its application in biology and nano-materials. Proteins are able to form different cavities with size ranging from tens to hundreds of nanometers. One of the significant applications is to make a confined reaction space for catalysis by encapsulating catalyst into these protein cavities. It has the potential to become a promising strategy to develop novel catalysis in well-defined “matrix”. Recently, Abe et al. reported that the spherical protein, apo-Ferritin, immobilized with rhodium complexes are able to catalyze the polymerization of phenylacetylene, providing polymers with restricted molecular weight and a narrow molecular weight distribution in the reaction space of the protein. Around 60 molecules of rhodium complexes are suggested to be immobilized on the interior surface of the protein. These binding sites can be roughly divided into three types. However, it is still unknown which bind sites of the rhodium complexes are the active sites for the polymerization, and how they initiate the polymerization. To provide insight into the polymerization behavior in the bio-nano reaction space and to reveal the factors that controlling the selectivity and the restricted molecular weight of the polymerization, QM/MM studies were carried out on the Rh-catalyzed polymerization of phenylacetylene in nano-cavity of Ferritin (Fig. 4).

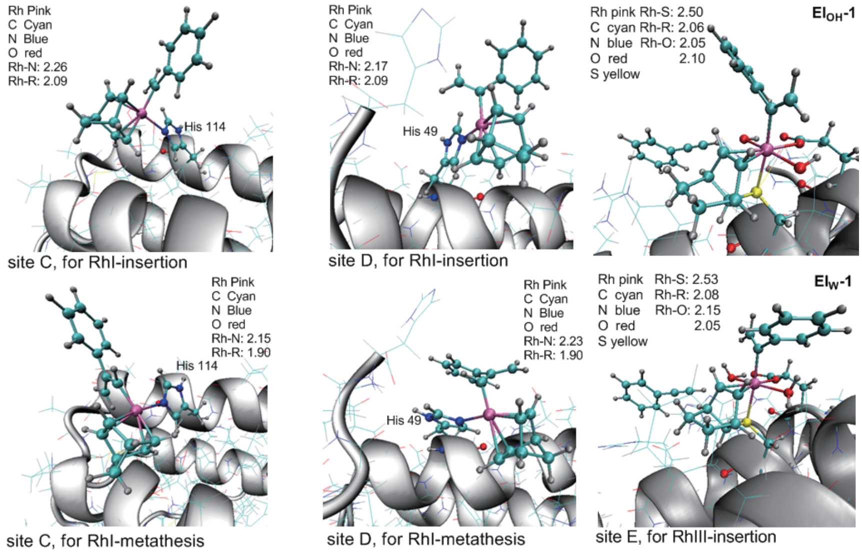


Fig. 5. *Rh^{I}, Rh^{III} and Rh^{I}-Carbene Binding Sites in apo-Ferritin*

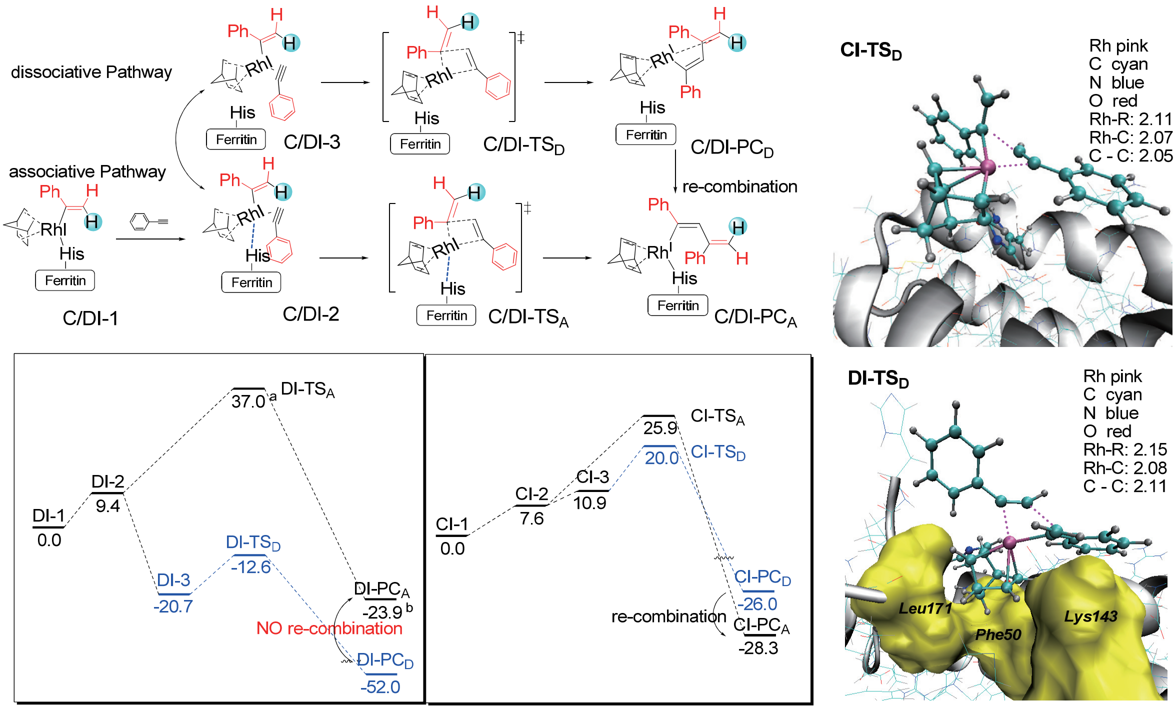


Fig 6. *Rh^{I}-Insertion Mechanism for the Rh-Catalyzed Polymerization of Phenylacetylene in apo-Ferritin (both site C and D).*

Different plausible active sites were constructed for the polymerization in binding site C, D and E (Fig. 5). Site C and D should be four-coordinated Rh^{I} and Rh^{I}-carbene centers, Site E should be a six-coordinated Rh^{III} center. Our studies suggested that Site D is the most possible active site for the polymerization. As shown in Fig. 6, dissociative Rh^{I}-insertion from site D is the most feasible mechanism with an insertion barrier of ~ 9 kcal/mol. There is no recombination of the active center back to the histidine residue after the insertion. The abstraction of Rh-complex from histidine to a hydrophobic pocket (Phe50, Lys143 and Leu171) nearby plays an important role in the dissociative Rh^{I}-insertion polymerization in site D. The ejection of Rh-complex from site D during the coordination of phenylacetylene monomer releases a true active site for the polymerization. On the contrast, Rh^{I}-carbene metathesis polymerization in site D has to overcome a barrier of ~ 35 kcal/mol. In Site C, Both Rh^{I}-insertion polymerization (barrier, ~ 20 kcal/mol) and Rh^{I}-carbene metathesis polymerization (barriers ~ 22 kcal/mol) are less favorable than Rh^{I}-insertion polymerization in site D. Rh^{III}-insertion in site E is calculated to be the least possible polymerization mechanism. The coordination of phenylacetylene to the crowded Rh^{III} center is difficult, and the insertion barrier is higher than 45 kcal/mol. Rh^{I}-insertion polymerization in site D favors a 2,1-insertion, producing stereospecific polymers, consistent well with the experimental observations.

2. Original papers

(1) Zhuofeng Ke, Keiji Morokuma, “Rh-Catalyzed Polymerization of Phenylacetylene: a Panoramic View on the Reaction Mechanism and Stereochemistry by DFT” manuscript in preparation.

3. Presentation at academic conferences

(1) Zhuofeng Ke, Keiji Morokuma. "On the Mechanism and Stereochemistry of the Rh-Catalyzed Polymerization of Phenylacetylene" The International Symposium on “Molecular Theory for Real Systems”, Kyoto, Japan. Jan 7-9. 2010. (poster)

4. Others

(1) Zhuofeng, Ke "Theoretical Study of the Rh-Catalyzed Polymerization of Phenylacetylene: Insight into the Construction of a Single Polymer Molecule in Nano-Cavity of Protein" The 7th Seminar of Fukui Institute for Fundamental Chemistry, FIFC, Kyoto University, Kyoto, Japan. Feb. 4. 2010. (talk)

(2) Zhuofeng, Ke "Applications of Theoretical Chemistry in Medicine and Synthesis" Southern Medicinal University, China. May. 12th. 2010. (talk)

(3) Zhuofeng, Ke "Twins in Chemistry: Story about the Conjunction of Theory and Experiment" Sun Yat-sen University, China. May. 13th. 2010. (talk)

(4) Zhuofeng Ke, Keiji Morokuma. "On the Mechanism and Stereochemistry of the Rh-Catalyzed Polymerization of Phenylacetylene" The 7th Symposium of Fukui Institute for Fundamental Chemistry, FIFC, Kyoto University, Kyoto, Japan. Dec. 13. 2009. (poster)

Tsutomu KAWATSU

JST Fellow, Fukui Kenichi Memorial Research Group 1

1. Summary of the research of the year

The effect of thermal fluctuation of the protein environment on the free energy reaction diagram of isopenicillin N synthase

The protein environment can have significant effects on the enzyme catalysis even though the reaction occurs locally at the reaction center. The effect includes the static and dynamic contributions. Compared to a single configuration description, the dynamical contribution changes the potential diagram. We have analyzed two origins of the dynamic contribution named statistical and geometric effects. First, the average protein geometry has changed in the room temperature with the solvent compared to the static structure. Second, environmental interactions fluctuate and certain geometries mainly contribute to free energy in the statistical effect. For some reaction steps, the most important dynamical contribution is caused by such statistical effect, while for other steps the most important factor is a change in geometry compared to the optimized structure. In present study, we have estimated the contributions of each protein residue on the statistical and geometric effects.

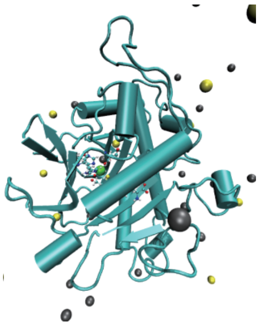


Fig.1: Structure of IPNS

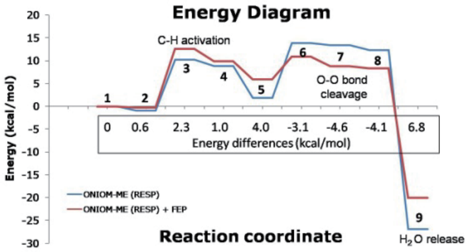


Fig.2: First half of the Free energy reaction diagram of IPNS. Bold numbers indicate stationary states.

In our former study, we have computed an efficient scheme that includes the dynamic contribution of the protein, as a complement to the static effect obtained from static ONIOM QM:MM calculations. This is done by applying an MM-level (classical) free-energy perturbation (FEP) correction to the potential energy diagram of the non-heme iron enzyme isopenicillin N synthase (IPNS). The FEP method is used to evaluate the protein effect for eight different reaction steps, from the initial O_2 bound state to formation of a high-valent ferryl-oxo intermediate. IPNS (Fig.1) is an important enzyme for catalyzing penicillin in biological system. Lundberg et al. have determined its reaction diagram using quantum chemical approach and ONIOM(QM:MM) method (Fig.2, blue line)[1]. ONIOM(QM:MM) includes high level quantum chemical (QM) calculation for the reaction center and low level molecular mechanics (MM) calculation for the interaction between the reaction center and its protein environment. We have added the free energy contribution from thermal fluctuation of the protein environment on the reaction diagram using free energy perturbation (FEP) method. Figure 3 redline shows the results of the free energy diagram (ONIOM-ME+FEP) with static energy diagram (ONIOM-ME). Significant difference is at a barrier from **5**th to **6**th states for O-O bond cleavage. Computed free energy corrections include several kinds of physical effect.

We have analyzed the statistical and geometric effects comparing three types of interaction differences between the reaction center and others. The statistical effect is caused by the geometry fluctuation. The geometric effect on the change of the potential energy is caused by the temperature and solvent. ΔF is the free energy difference between two states that includes both types of above effects. ΔE is the potential energy difference that excludes these. And <ΔH> that is an average value of the interaction difference between two states over the MD simulation. <ΔH> includes the geometric effect but not the statistical effect. We could estimate the statistical and geometric effects, substituting <ΔH> from ΔF and ΔE, respectively (see Fig.3). When |ΔE-<ΔH>| is large, the geometric effect is strong. The average geometry of MD simulation energetically changes from ONIOM optimized geometry. When |ΔF-<ΔH>| is large, the statistical effect is strong. Even though the average interaction between reaction center and bulk is similar to ONIOM optimized geometry, the thermal fluctuation can present large free energy shift caused by the statistical effect. First case appears at state pairs of **12**, **23**, **34**, **67** and **78** (bold numbers indicate stationary states). Second case is at state pairs of **45** and **56**.

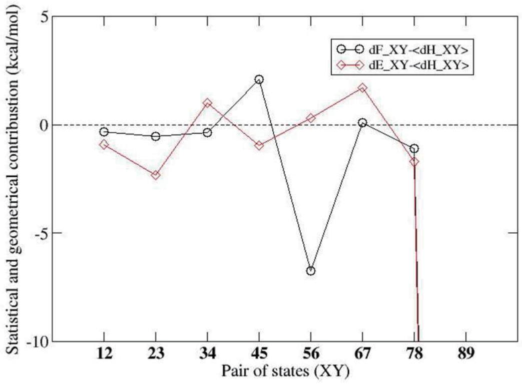


Fig.3: Comparison of statistic and geometric effects in the free energy corrections.

The geometric effect is caused by the difference between the average geometry in the MD simulation and optimized static geometry of the protein. We estimated the contribution from each residue calculating the difference of the interaction change $\Delta\Delta H^{i}_{XY}(X) \equiv \Delta H^{i}_{XY}(X) - \Delta E^{opt,i}_{XY}$ in the enzymatic reaction step (see Fig.2). Where $\Delta\Delta H^{i}_{XY}(X)$ and $\Delta E^{opt,i}_{XY}$ are the change from reaction step X to Y of the interaction between the reaction center and protein environment at average protein geometry in X state, and at optimized geometries, respectively. The superscript *i* indicates contribution of residue number *i*. Namely, $\Delta\Delta H^{i}_{XY}(X)$ indicates the how much each residue contributes to the free energy potential barrier from X to Y in the geometric effect. Figure 4 shows $\Delta\Delta H^{i}_{XY}(X)$ at the reaction steps XY=**23** and XY=**56**. Free energy contributions of the reaction barrier at these reaction steps are dominated by geometric and statistical effects, respectively. Numbers indicate dominant residues. However, amplitudes of significant

$\Delta\Delta H^{i}_{XY}(X)$ are not much different between these two cases.

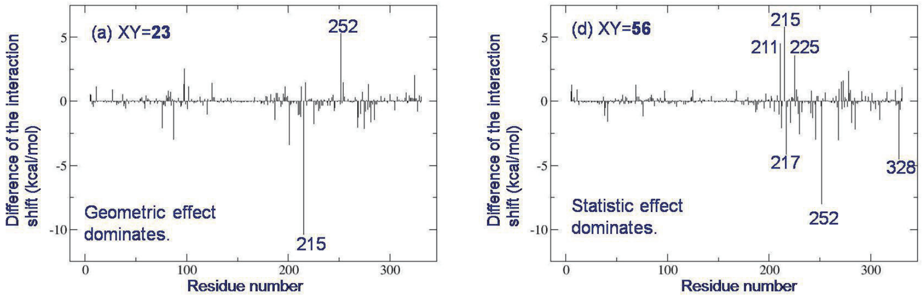


Fig.4: Difference of the interaction shift $\Delta\Delta H^{i}_{XY}(X)$ in residue *i*. X and Y are stationary points of IPNS enzymatic reaction steps.

On the other hand, the statistical effect is caused by the geometric fluctuation around the average geometry of the protein environment. When the interaction shift between the reaction center and the protein environment from a stationary point to another fluctuates strongly, the statistical effect becomes large. We estimate the largeness of the contribution calculating the standard deviation of the interaction shift s^{i}_{XY} contributed by residue *i* at the reaction potential barrier from stationary point X to Y. Where,

$$s^{i}_{XY} \equiv \sqrt{\langle (\Delta H^{i}_{XY}(X)^{2} \rangle - \langle \Delta H^{i}_{XY}(X) \rangle^{2}} .$$

s^{i}_{XY} indicates the largeness of the statistical effect. Figure 5 shows values of s^{i}_{XY} at two reaction steps XY=**23** and **56** as well as Fig.4 above. In XY=23 of the geometric effect dominant case, s^{i}_{XY} is significantly smaller than the case of the statistical effect dominant case, XY=**56**. We notice that most contribution of s^{i}_{XY} is caused by VDW interaction between the reaction center and the protein environment.

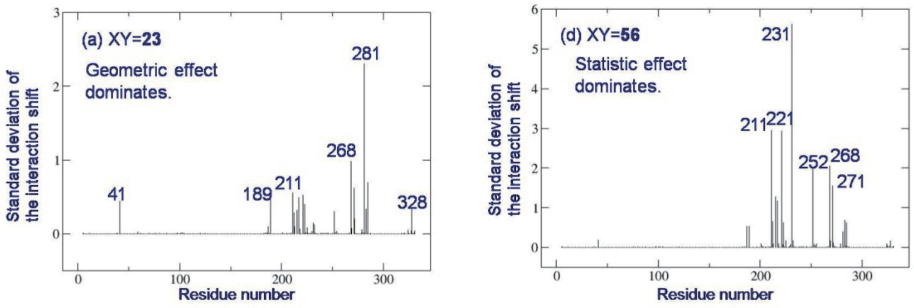


Fig.5: Standard deviation of the interaction shift s^{i}_{XY}. Notations are the same as in Fig. 4.

Comparing two results of Fig.4 and 5, the geometric effect is stable and the strength of the statistical effect determines which effect dominates the dynamic contribution on the free energy reaction barrier.

[1] Lundberg, M. et al., *JCTC* **2009**, *5*, 220.

Free energy gradient optimization in the ONIOM QM:MM scheme

In the above study, the geometric effect is free energy difference between zero Kelvin and room temperature. We have developed programs for free energy gradient optimization method [2] to obtain the free energy minimized geometry in ONIOM QM:MM scheme. Free energy gradient is computed as canonical average of potential gradients,

$$\frac{\partial F}{\partial r} = \left\langle \frac{\partial V}{\partial r} \right\rangle_B .$$

We have also tested sequential sampling method [3] to save the sampling time in the simulation. The method applies the multi-canonical sampling using the same MM sampling set with different potential made by the QM part. The multi-canonical sampling is,

$$\langle A(R,r)\rangle_R = \frac{\left\langle A(R,r)\exp\left(-\beta\left(E(R,r)-E\left(R^{ref},r\right)\right)\right)\right\rangle_{R^{ref}}}{\left\langle \exp\left(-\beta\left(E(R,r)-E\left(R^{ref},r\right)\right)\right)\right\rangle_{R^{ref}}}$$

Where R and r are QM and MM part coordinates. E is the potential energy. The superscript of ref describes the reference coordinate.

We have benchmarked free energy optimization for a water molecule in water sphere r=16 angstrom (see Fig.6). The target molecule is computed in 3BLYP/6-31G(d) level QM calculation and solvent molecules are in TIP3P MM level. The MD simulation is controlled in 300K temperature using Langevin thermostat with frozen QM molecule.

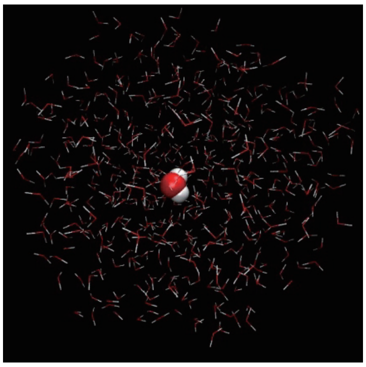


Fig.6: Test system of the free energy optimization.

Optimized results for a water molecule in MM water box are shown in Table 1 (notation is described in Fig. 7). Because a water molecule has C_2 symmetry, R_1 and R_2 optimized to the same length in gas phase calculation. However, when surrounding MM water is optimized together, the symmetry can break and R_1 and R_2 become different. On the other hand, during free energy optimization, potential made by surrounding water is counted as an average value of canonical ensemble and R_1 and R_2 become similar values again. We have also tested the sequential sampling (SS) and obtained reasonable result. We note that the MM water force field may not good for such small molecular system because we used TIP3P water. That is, the angle of HOH is much inconsistent between QM and MM molecules in these calculations.

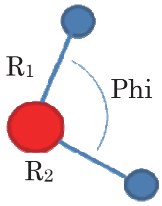


Fig.7: Water model

Table1: Geometries of free energy optimized water molecule.

	Phi (degree)	R1 (angstrom)	R2 (angstrom)	R2-R1(angstrom)
Vacuum	103.6487	0.96875	0.96875	0
ONIOM(QM:MM)	103.4697	0.98087	0.98416	0.00429
FEG	102.5059	0.98583	0.98628	0.00045
FEG(SS)	102.6162	0.98533	0.98633	0.00100

[2] N. Okuyama-yoshida, M. Nagaoka, T. Yamabe, *Int. J. Quantum Chem.,* 1998, *70*, 95., H. Hu, Z. Lu, W. Yang, *JCTC*, 2007, *3*, 390

[3] Hao et al. *JCP* **2008**, *128*, 034105.

2. Presentation at academic conferences

(1) CREST International Symposium on Theory and Simulations of Complex Molecular Systems & International Symposium on Theory of Molecular Structure, Function and Reactivity ~Celebrating Prof. Morokuma's 75th Birthday 2009: Poster title: "Thermal fluctuation of the protein environment influences the potential diagram."

3. Others

(1) The 7th Symposium of Fukui Institute for Fundamental Chemistry 2009: Poster title: "Free energy optimization in ONIOM scheme."

Yoshiko OKAMOTO

JST Fellow, Fukui Kenichi Memorial Research Group 1
(To 31 May 2009)

1. Summary of the research of the year

QM/MD Molecular Dynamics study concerning the states of transition metal catalysis during Single-walled carbon nanotube formation

In spite of more than a decade of scientific struggles, the formation mechanisms of single-walled carbon nanotubes (SWCNTs) have not been fully understood yet. Meanwhile, their application spreads to various technologies such as electronic devices and novel materials, and the understanding of formation mechanisms is highly expected.

Until now, vapor-liquid-solid (VLS) model is considered to be the most possible candidate to explain their formation mechanisms, however, even within the scheme of this model, there still remains some controversies as to the diffusion of carbons (Is it surface/bulk diffusion? What are the driving force?), states of the transition metal catalysis (are they metal or carbide? Are they in liquid or in solid state?) etc. Some experimental observation suggests that they are in carbide[1,2], some suggests fluctuating crystals[3], while Harutyunyan et al. observed solid-liquid-solid transition during the SWCNTs growth[4], and concluded that liquid state is favored for the nanotube growth. However, there are strong arguments whether the catalyst can be in liquid state when its eutectic point is much higher than the reaction temperatures, and this large decrease in melting point (Tm) of transition metal catalysts does not seem to be caused by cluster size effect[5].

We carried out mechanical molecular dynamic study of a system of transition metal (TM) catalysts (Co/Fe/Ni) with the existence of C_2, as well as the study of phase diagrams of Fe catalysts, in order to obtain some hints for the formation mechanisms of SWCNTs.. QM/MD are carried out using self-consistent-charge (SCC) density functional tight-binding (DFTB) method developed by Frauenheim et al. [6,7,8]. In this report we will present main findings of the studies.

1. Solid-Liquid-Solid transition of TM catalysts

We conducted DFTB simulations to study the states of TM catalysts during the carbon ring formations. Details of the simulation are as follows. Transition metal catalysts (Co/Fe/Ni) of 38 atoms (truncated octahedron, Fig.1) are placed in a cubic box of 40 Å a side. After annealing about 70ps, one or two C_2 molecules are added every 3 to 30 ps. Simulations are continued until total of 110 C_2 are added. To realize the anti-bonding character and Fermi broadning, we introduced electric temperature (Te) of Te=Tn and of 10,000K in the DFTB simulations. We present here the results of Te=Tn case and adding rate of

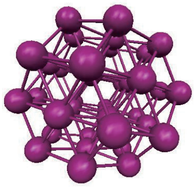


Fig.1 TM38 cluster (Truncated octahedron)

$2C_2$/3ps. Lindemann criteria [9] is used to analyze the status of TM clusters. Ten trajectories of the same parameters were simulated. Results of different C_2 adding rates are given below. In each case, carbon ring formations and ring condensations were observed for Fe and Ni clusters. However, in contrast to Ni and Fe clusters, maximum of several rings are observed to be created on Co clusters.

(1) Ring formation statistics

Ring formation statistics are given in Fig.2. Usually, on Fe and Ni clusters, more than 10-30 rings are found to be formed. Ring condensation starts at about 100ps, after about 60 C_2 are added in the system. At higher temperatures, this ring condensation can start earlier, because of the high diffusion rate of carbon atoms on the TM clusters. Co clusters form only carbides, only up to several rings are observed to be formed.

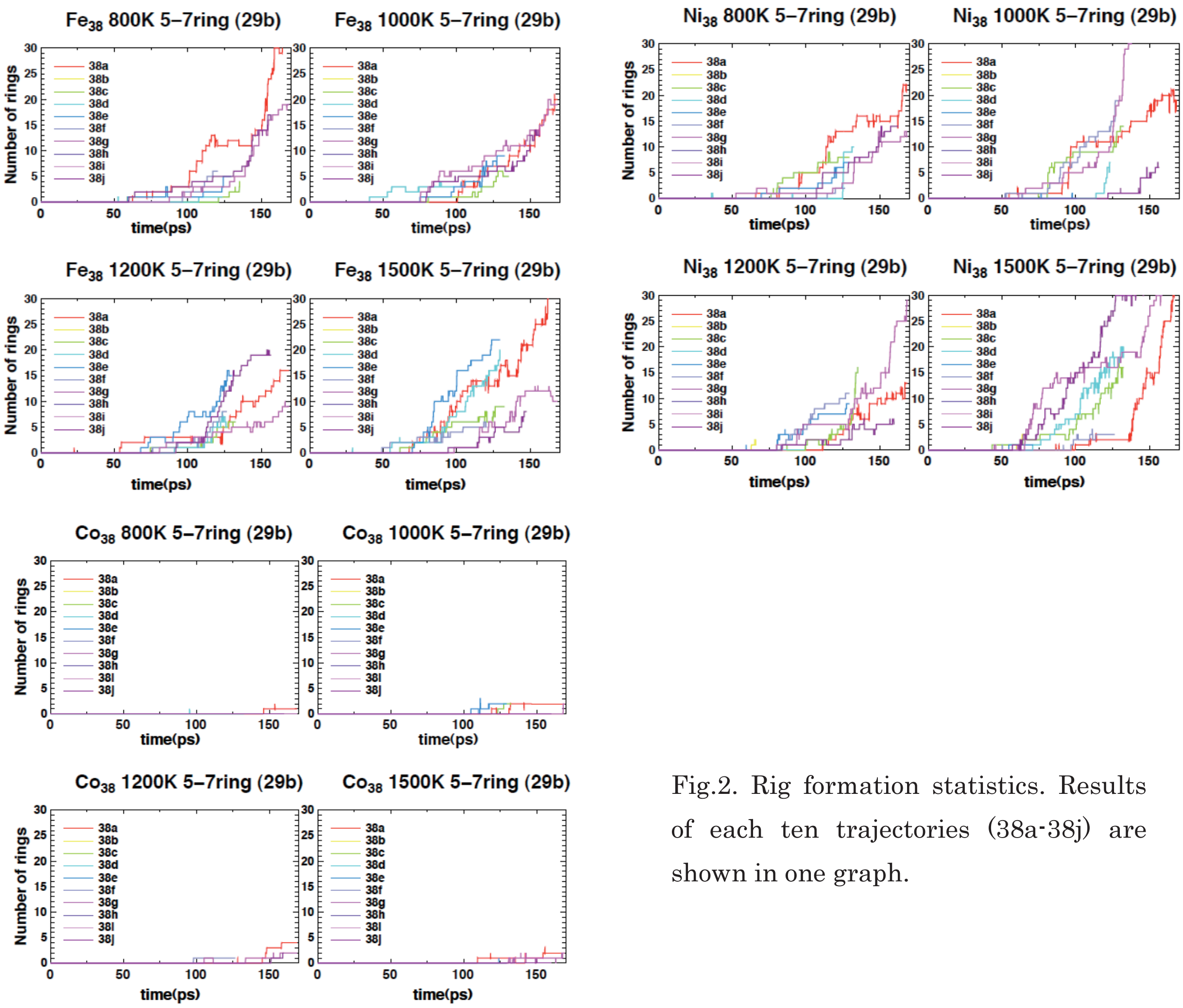


Fig.2. Rig formation statistics. Results of each ten trajectories (38a-38j) are shown in one graph.

(2) Time variations of Lindemann index and correlation between ring formations

In Fig.3 we present the Lindemann index obtained from the snapshots from several time slots. Since Lindemann index depends on the number of sampling point, it should be obtained from several time slots in order to ensure that it has sufficient sampling points to obtain the stable value. In Fig.3, we arranged the figures in the way that the Lindemann index at each time slots almost corresponds to the time in the above figures. Usually Lindemann index of 0.1 indicates high mobility of the atoms. The results suggests that as more carbon atoms are added, initially Fe/Ni atoms start to show higher mobility until the encapsulation of the catalysts by the carbon atoms. As the encapsulation of TM catalysts occurs, the mobility of the transition metals go down. These results show exactly the same tendencies as in the Harutunyan's experiments. This solid-liquid-solid transition of the catalyst metals might be the ground for the contradicting observations by many experimentalists. Actually, these C_2 adding rate are found to be too high in order to form a nanotube, our study with lower adding rate show similar tendencies in the time variations of Lindemann index.

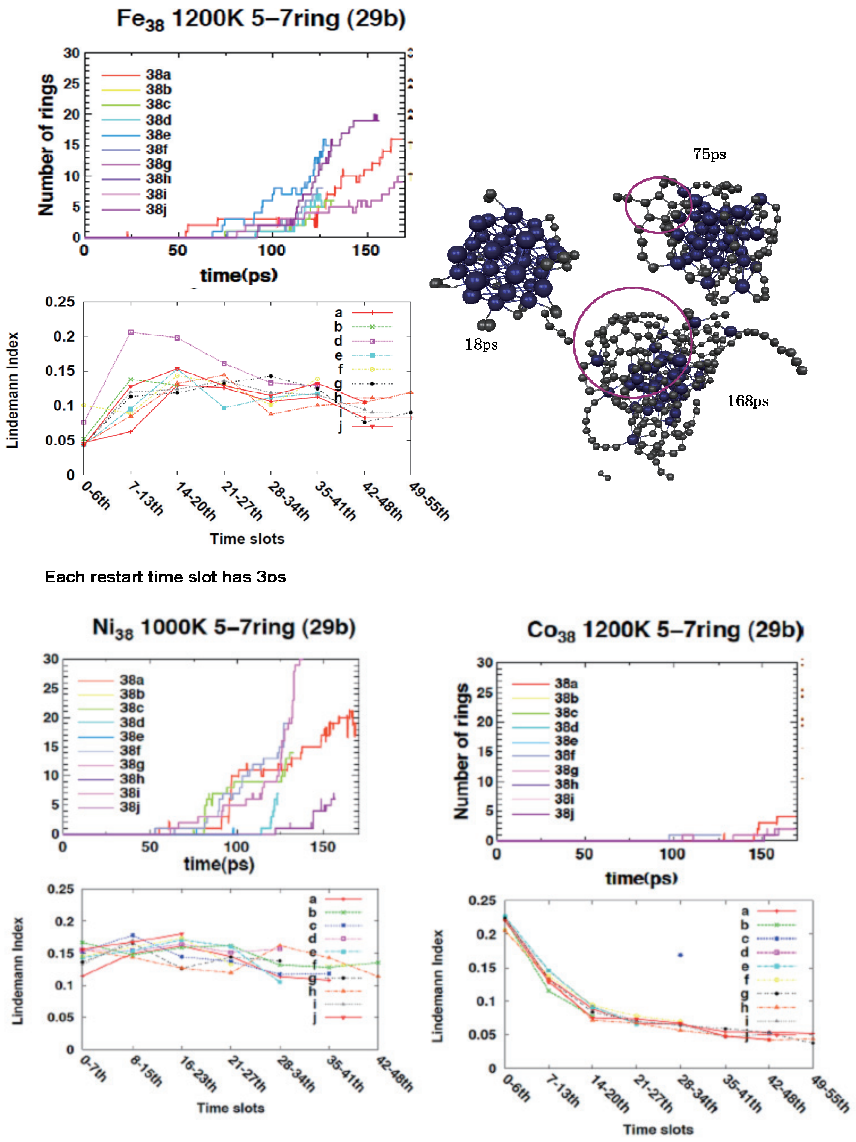


Fig.3. Graphs show time variations of Lindemann indices of each metals. For Fe/Ni clusters, at the beginning, as more carbons are added, Lindemann index becomes larger and TM atoms have higher mobilities, like in liquid. After the encapsulation of the cluster, value of the index becomes smaller and TM clusters turn to be in solid states. Co seems to have completely different characters. Top right figures show representative snapshots of one trajectory of Fe cluster at various times.

2. New phase diagrams of Fe cluster.

As in the Harutyunyan's experiments, catalysts in liquid state are observed in many experiments. However, the significant decrease of melting temperatures of these clusters have not been successfully explained by their size effect. Some discussed the possibility of lowering of the melting point by carbon existence.

In many experiments, cementite iron is observed, but in some experiments, they observe high C concentration on the catalysts up to 60%. Phase diagram of iron which is widely accepted show cementite iron as the highest C concentrated complex. Jiang et al. recently suggested a new phase diagram of Fe-C complex, which has another eutectic points and discussed that the formation of SWCNTs can be explained by this phase diagram[5]. This new phase diagram might solve some controversial questions concerning the states of TM catalysts, however, it have been never validated.

Here, we show the result of QM/MD studies on the melting points of small Fe cluster at various C concentrations. The simulation method is as follows. We prepared a Fe cluster of 70 atoms. Of those 70 atoms, some number of Fe atoms are replaced with C atoms randomly to prepare a cluster of $Fe_{70-x}C_x$. These clusters are annealed for about 48ps, and simulated up to 178 ps at various temperatures. Lindemann indices of these $Fe_{70-x}C_x$ clusters were examined at various temperatures, and melting point Tm was determined as the temperatures where lindemann index equals 0.2. Nose-Hoover chain thermostat was used to control the temperature during the simulations. Obtained phase diagram of Fe cluster is given in Fig.5. As is obvious from the Fig.5, as the Fe has more carbon concentration than cementite iron (Fe_3C), which is about 7 weight %, we see dramatic decrease in the melting point, by 100-300 degrees. These decreases are much larger than the decrease of melting point caused by cluster size effect, and seem to explain the liquid state of Fe catalyst during the nanotube formation.

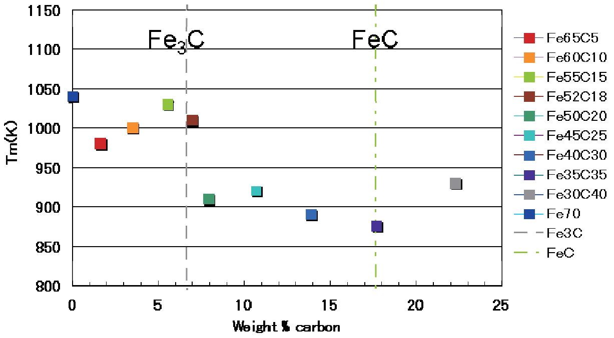


Fig.5. Fe-C phase diagram obtained by QM/MD simulations.

In Fig.5, we see somewhat like another eutectic point, which also support the Jiang's suggestion that segregation of graphitic structure can be explained by this eutectic point. The phase diagrams of Ni and Co clusters are now under simulation. In the future, we need to check Jiang's other two suggestions concering the driving force of C and rate limiting step.

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[9] Lindemann, E. A., *Phys. Z.* 1910, *11*, 609.
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2. Original papers

[1]Ohta, Y.; Irle, S.; Okamoto, Y.; Morokuma, K., Rapid growth of a single-walled carbon nanotube on an iron cluster: Density-functional tight-binding molecular dynamics simulations. *ACS NANO* 2008, *2*, 1437-1444

[2]Ohta, Y.; Okamoto, Y.; Irle, S.; Morokuma, K., Density-functional tight-binding molecular dynamics simulations of SWCNT growth by surface carbon diffusion on an iron cluster. *Carbon* 2009, in press

[3]Ohta, Y.; Okamoto, Y.; Irle, S.; Morokuma, K., Single-walled carbon nanotube growth from a cap fragment on an iron nanoparticle: Density-functional tight-binding molecular dynamics simulations. *Phys. Rev. B* 2009, in press

[4]Ohta, Y.; Okamoto, Y.; Irle, S.; Morokuma, K., Temperature Dependence of Iron-Catalyzed Continued Single-Walled Carbon Nanotube Growth Rates: Density Functional Tight-Binding Molecular Dynamics Simulations. *Journal of Physical Chemistry C* 2009, *113* (1), 159-169.

3. Presentation at academic conferences

(1) Yoshiko Okamoto, Yasuhito Ohta,, Stephan Irle, Keiji Morokuma
“Theoretical Study on the roles of transition metal (Fe/Ni/Co) catalyst clusters at the early stage of Single-Walled Carbon nanotube formation”
Molcular Science Symposium, Fukuoka, Sep., 2008

(2) Yoshiko Okamoto, Yasuhito Ohta,, Stephan Irle, Keiji Morokuma
“**Quantum chemical molecular dynamics studies on the formation mechanism of single-walled carbon nanotubes during initial stages**”
Fukui Symposium, Kyoto, Dec, 2008

(3) Yoshiko Okamoto, Yasuhito Ohta,, Stephan Irle, Keiji Morokuma
Theoretical Study on the roles of transition metal (Fe/Ni/Co) catalyst clusters at the early stage of Single-Walled Carbon nanotube formation, Hirao Symposium, Tokyo, Mar., 2009

Xin LI

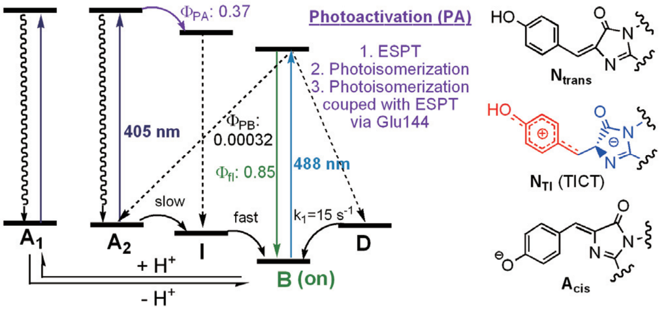
JST Fellow, Fukui Kenichi Memorial Research Group 1

1. Summary of the research of the year

Reversibly Photoswitchable Fluorescent Protein: Dronpa

A GFP-like fluorescent protein, Dronpa, which was engineered from a coral Pectiniidae, was found to display perfect photochromic properties; the fluorescent “on”-state and non-fluorescent “off”-state of Dronpa can be reversibly switched by irradiation of two different wavelengths of light. To understand the detailed mechanism of the reversibly photoswitching process at the atomic level, we performed non-adiabatic CASSCF/AMBER molecular dynamics (MD) simulations to study the primary events of photodynamics of Dronpa (Scheme 1). $\mathbf{N_{trans}}$ in the off-state Dronpa undergoes ultrafast radiativeless decay via rotation along the imidazolinone ring. The computed mean lifetime of S_1 is about 0.66 and 0.87 ps via non-adiabatic crossing and crossing seam, respectively, which is shorter than the experiment. The calculated quantum yield for the photoisomerization is about 0.40-0.67, depending on the crossing modes. Whereas, $\mathbf{N_{cis}}$ in the on-state Dronpa takes longer time for the decay via the imidazolinone ring rotation and has smaller quantum yield for the photoisomerization. In contrast, the chromophore remains roughly planar for about 20 ps in most of the trajectories for $\mathbf{A_{cis}}$ in the on-state Dronpa. Remarkably, fast decay of $\mathbf{A_{cis}}$ via either rotation along the phenol or imidazolinone ring was found in the on-state mutant Dronpa (H193T), which shows the important role of H193 in the on-state *wt*-Dronpa. Overall, these non-adiabatic QM/MM MD results are qualitatively consistent with the experiments.

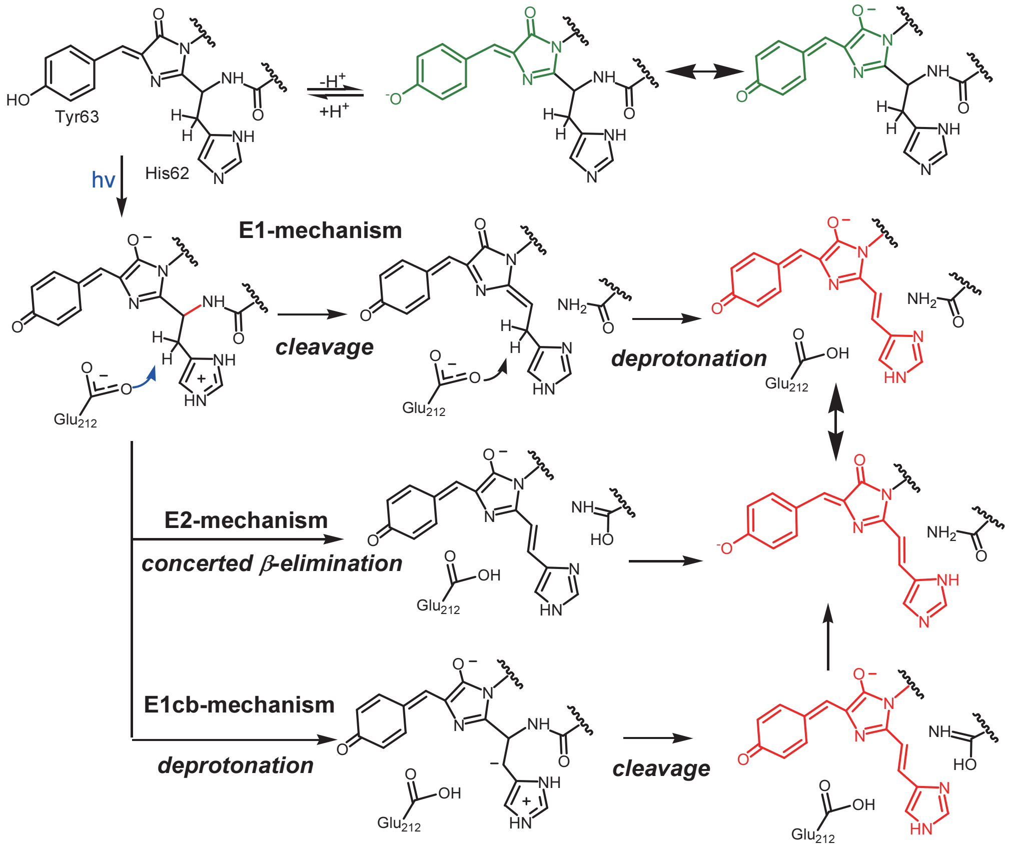
Scheme 1



Irreversible Photoconversion Fluorescent Protein: Kaede

In Kaede, a new class of fluorescent protein, dramatic changes of photo-physical and chemical properties by UV illumination have been observed in which color of fluorescence is irreversibly altered from green to red. Unusual photo-induced peptide backbone cleavage resulting in extending π-conjugation of the chromphore takes place. Accordingly, two mechanistic pathways (E1 and E2 mechanisms) involving the N-C_α bond cleavage at His62 and deprotonation at the C_β by Glu212 have been proposed. Here several possible pathways (Scheme 2) are explored by ONIOM(B3LYP:AMBER) calculations. The results reject the concerted E2-type pathway. Instead, the stepwise E1 and new E1cb mechanisms are suggested to occur and may compete in the electronic ground state. Absorption for the green- and red-type chromophore in vacuum and the proteins was also studied.

Scheme 2



2. Original papers

(1) Xin Li, Lung Wa Chung, Hideaki Mizuno, Atsushi Miyawaki and Keiji Morokuma "*A Theoretical Study on the Nature of On- and Off-States of Reversibly Photoswitching Fluorescent Protein Dronpa: Absorption, Emission, Protonation and Raman*" J. Phys. Chem. B 114, 1114-1126 (2010).

3. Presentation at academic conferences

(1) Xin Li, Lung Wa Chung, Atsushi Miyawaki, and Keiji Morokuma, "*A Theoretical Study on the Nature of On- and Off-States of Reversibly Photoswitching Fluorescent Protein Dronpa*", American Chemical Society 237th National Meeting, Salt Lake City, Utah, March 2009.

(2) Xin Li, Lung Wa Chung, Piotr Paneth, and Keiji Morokuma "*DFT and ONIOM(DFT:MM) Studies on Enzymatic Mechanism in B_{12}-Dependent Methylmalonyl-CoA Mutase*", 14th International Conference on Biological Inorganic Chemistry, Nagoya, July 26-29, 2009.

3. Book Chapter

(1) Xin Li, Lung Wa Chung, Keiji Morokuma "*Modeling Photobiology Using Quantum Mechanics (QM) and Quantum Mechanics/Molecular Mechanics (QM/MM) Calculations,*" In "Computational Methods for Large systems: Electronic Structure Approaches for Biotechnology and Nanotechnology " Reimers, J. R. Eds. Wiley, 2010, pp342-373.

Safwat ABDEL-AZEIM

JST Fellow, Fuikui Memorial Research Group 1
（To 30 Sep. 2009）

1) Research summary of the year

Homocysteine activation by methyltransferase enzymes.

The process of homocysteine (Hcy) activation is a crucial step in the synthesis of methionine. Three different types of metalloenzyme catalyze the transfer of methyl group to (Hcy) to produce methionine: 1) Cobalamin-dependent Methionine synthase (MetH), 2) cobalamin-independent Methionine synthase (MetE), both enzymes catalyze the transfer of methyl from tetrahydrofolate to Hcy (Banerjee and Matthews 1990, FASEB J., ***4,*** 1450) eq. 1. The third one is the Betaine-Hcy Methyltransferase (BHM) which uses betaine (tri-methylglaycine) as a methyl donor eq. 2.

CH3-H4folate + Homocysteine -----> H4folate + Methionine (1)

Betaine (N,N,N trimethylglaycine) + Homocysteine --->Methionine + N, N dimethylglycine (2)

The three enzymes require zinc for activation and binding of Hcy. MetH and BHM enzymes share the overall scaffold of the Hcy binding domain and also they share the metal ligands (Cys)3OZn: in case of MetH the oxygen donor is asparagin residue and is tyrosine in case of BHM. While MetE does not share any detectable sequence similarity with MetH and BHM furthermore the active site lies between the tops of the two $(\beta\alpha)_8$ barrels domains and the metal ligands are Cys2HisGluZn.

Extended X-ray absorption fine structure (EXAFS) spectra of native MetE and MetH confirmed that Zn ions switched from ZnS2NO and ZnS3O to ZnS3N and ZnS4 for MetE and MetH ligation state respectively upon Hcy binding. (Pearson et al. 1998, J. Am. Chem. Soc., 120, 8410, and 2001 Biochem., 40, 989).

In MetH and MetE, Hcy binds at the face of the metal opposite to the oxygen-donor ligand, which moves away from the zinc in the binary Enzyme.Hcy complex.

Based on the available pdb structures, M. Koutmos et al 2008, Proc Natl Acad Sci U S A. 105, 3286, proposed large zinc displacement in the catalytic cycles of both MetE and MetH, resulting in inversion of metal geometry as Hcy binds and displaces away the oxygen-donor ligand from the protein. They also interpreted the pdb structure 1XDJ of MetE enzyme which was obtained under acidic conditions (PH=5.2) is the possible transition-state mimic structure. In this structure the Zn coordination is a distorted trigonal–bipyramidal with Zn positioned approximately halfway between Glu642 and Hcy.

We focus here on MetH and MetE enzymes as they use the same substrate (Hcy and folates) in their catalytic cycle. The main objective is to investigate the protein effects on the Hcy-Zn binding process and its role in the substrate activation. The computational details are the same of the annual report of 2008, therefore we jump it here.

A) MetH enzyme

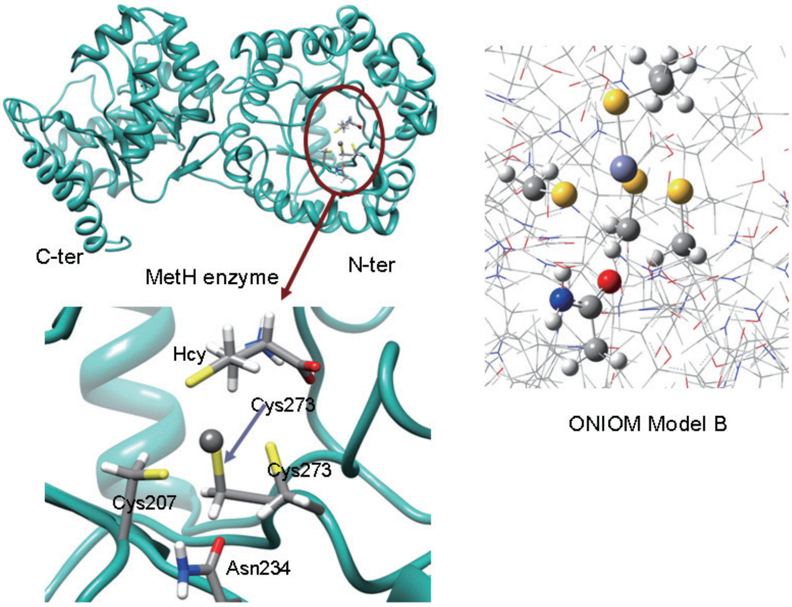
1) Active site calculations.

The overall process is highly unfavorable in the gas phase with a barrier around 44.6 kcal/mol and the reaction is very endothermic (27.1 kcal/mol). Our results of the active site model of Zn-S (Hcy) association reaction are agree well with D. Picot et al, *Chem Asian J.*

2010 (in press), who studied the dissociation of phenylthiolate (Zn-SPh) from Zn $(SC6H5)_4{}^{2-}$ complex. They located a transition state at 42.8 kcal/mol from the dissociated products ($SC6H5^-$ + Zn $(SC6H5)_3{}^{2-}$) and at 12.4 kcal/mol from the reactant. Also, our results are in good agreement with the earlier studies done by Todor Dudev, and Carmay Lim 2002 *J. Am. Chem. Soc.*, 124, 6759, which demonstrate the effect of the high dielectric constant in the stability of the $Zn\text{-}S^-_4$ complex.

2) Protein effects on the Zn-Hcy binding

In the protein environment, the calculations were performed on two models A and B (model A in which the QM regions is exactly the same as the active site model but including entire Hcy, model B in which the QM region is exactly as the gas phase model) (see Fig. 1) the aim of model B calculations is to compare with the active site calculations). The calculations confirmed the barrier disappear and the reaction is highly drift toward the product with exthothermity of -35.5 and -33.4 (ZPC) kcal/mol in case of model A and model B respectively.



ONIOM Model B

ONIOM Model A

Fig .1: Overview of MetH enzyme and its active site in ONIOM model A and B.

To understand the enzyme effect on the Zn-Hcy displacement, we compared the QM energy of the QM part for the ONIOM-ME optimized reactants and product in the model B with that in the active site model calculations (without ZPC). The QM energy of the model B in the ONIOM optimized structure for the reactant is 80.7 kcal/mol less stable than the energy in the fully optimized (gas phase) structure of model B (see Figure 2). The corresponding energy difference for the product is 36.1 kcal/mol. The reaction energy in the gas phase is 26.2 kcal/mol (endothermic), becomes -19.2 kcal/mol (exothermic) in the QM part in protein. The MM part (including QM-MM interaction) further stabilizes the product by -12.6 kcal/mol, to make the ONIOM energy of reaction to be -31.7.

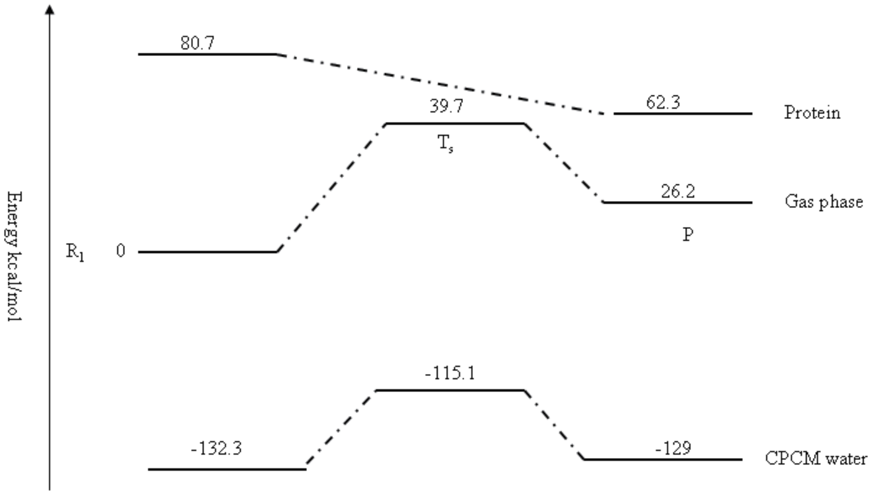


Figure 2: Schematic representation of the Hcy addition step reaction profile in gas phase, in PCM model and enzyme for modelA. The energies reported in this figure were calculated using molecular embedding without charges update.

3) Mutations effect on the Zn-Hcy displacement

Recently, Prasannan *et al. Biochem. Biophys. Research commu.* **2009**, 382, 730, experimentally studied directed mutations of some selected residues in the homocysteine and folate binding sites. These authors mutated two residues, Asp614 (which forms ion-pair with the ammonium group of Hcy) by Ala and Ser448 by Ala, in the binding site of Hcy in the cobalamin-independent methionine synthase from *Candida albicans*. They found that the mutant Asp614Ala did not show any enzymatic activity, while Ser448Ala mutant exhibited 67% of the wild type activity. We have performed directed mutations for the selected residues computationally to investigate the effect of those residues on the reaction energetics for the Zn displacement, paying special attention whether mutant enzymes do the same overall reaction as the wild type. The considered mutants are Asn234Glu, Cys272His, Thr147Ala, Glu146Ala and Phe66Ala. A mutant Asn234Glu is interesting to test the effect of the Glu which is in MetE. Mutations of Glu146Ala, Thr147Ala and Phe66Ala investigate the importance of the salt-bridge interaction, hydrogen bond and the hydrophobic interactions on the reaction profile. We did not consider the mutation of Gly23Ala in MetH which is equivalent to the experimental Ser448Ala in cobalamin-independent methionine synthase from *Candida albicans.* This residue interacts with Hcy through the backbone NH, and the structural difference between Gly and Ala is very small and should not change the reaction energetic. It was found that for all considered mutants, Zn is spontaneously displaced toward the substrate except for one mutant Asn234Glu, which passes with transition state of 1.1 kcal/mol energy barrier (see Figure 3). The analysis of the optimized structures of the considered mutants can explain different effects of the mutations. In case of Asn234Glu, the high electrostatic repulsion in the reactant (charge = -4) prefers that Glu moves away from Zn and interacts with water molecules to minimize this repulsion. Therefore, the product in which Glu is dissociated is more stable than the reactant. In the reactant complex of Cys272His, steric hindrance prevents Zn from being ligated to His272. While in the product Zn is coordinated to His272 and the complex is more stabilized by interactions with Asn206. The mutations of Thr147Ala and Glu146Ala have very little effect on the reaction energy. The absence of the hydrophobic interactions between Phe and the substrate decreases the reaction energy from -36.8 to -28.4 kcal/mol. The reaction energies were -37.1 and -28.5 kcal/mol for the wild and Phe66Ala mutant respectively, when the calculations were done using B3LYP-D (the B3LYP functional corrected for the dispersion term). It was found that mutations of the above-mentioned residues have a little effect on the Zn-Hcy displacement process. The experimental observations of Asp614Ala and Ser488Ala mutations effect from

Candida albicans should relate to the other steps in the methyl transfer reaction, e.g. the pre-binding of the substrate in the active site.

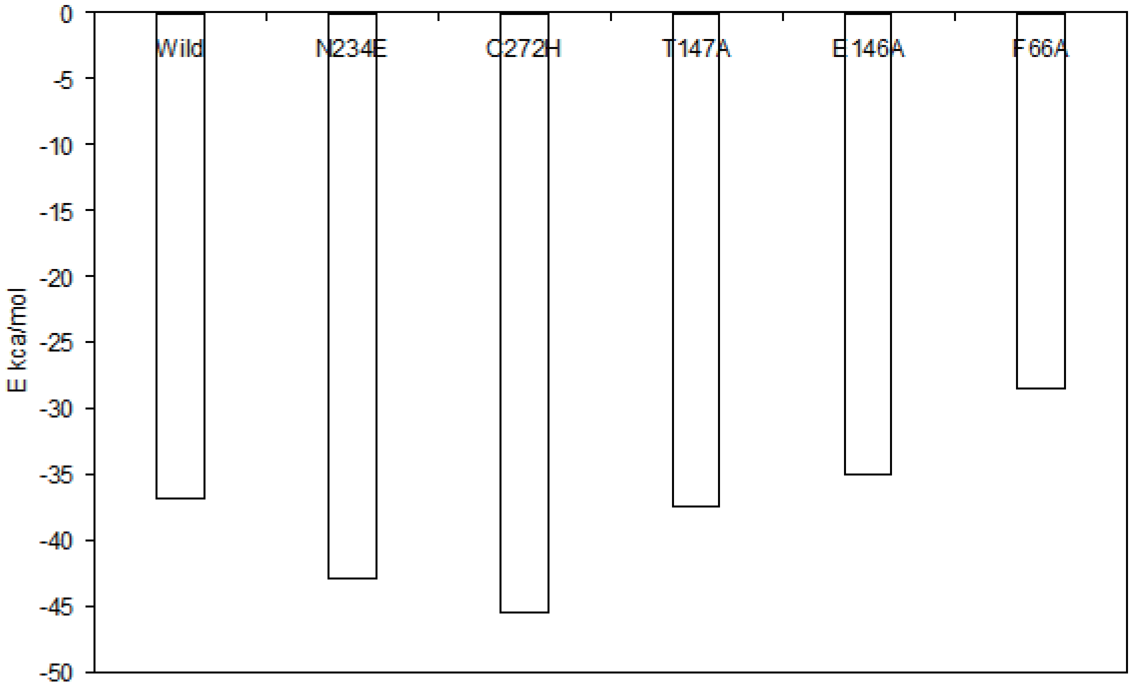


Figure 3: The histogram of ONIOM-EE Zn-Hcy displacement energy for the considered mutants

4) Conclusion

Our results do not support the experimental zinc five-coordinate intermediate or transition state hypothesis of the Zn-substrate switch reaction. In the active site, the reaction is stepwise starts by Zn-O (Asn) dissociation followed by unfavorable step of Hcy addition. Our calculations suggest that Zn dissociates quickly from Asn to give the Hcy-bound state without barrier in the protein. The calculated reaction energy is a favorable chemical process, which is qualitatively in good agreement with the experimental observation: at the physiological conditions, MetH is always saturated with Hcy and the experimental Michaelis constant K_M of Hcy =0.6 μM. Our calculations support the proposed role of Zn which acts as lewis acid; it activates the substrate by stabilizing its thiolate form. Furthermore, the calculations support the associative methyl transfer mechanism from cobalamin to Hcy substrate and the methyl transfer should takes place to the bound Zn-Hcy followed by product release. Also, the anchored of the substrate in the active site is necessary for the appropriate orientation of Hcy for the methyl transfer from the cobalamin co-factor and should proceed Zn-Hcy binding. In our static calculations, the Zn displacement toward the substrate (Hcy) should not be the rate-determining step in the substrate activation process. The substrate binding in the active site may be the rate-determining step. The directed mutations of the binding site residues have not shown large effect on the Zn-Hcy displacement.

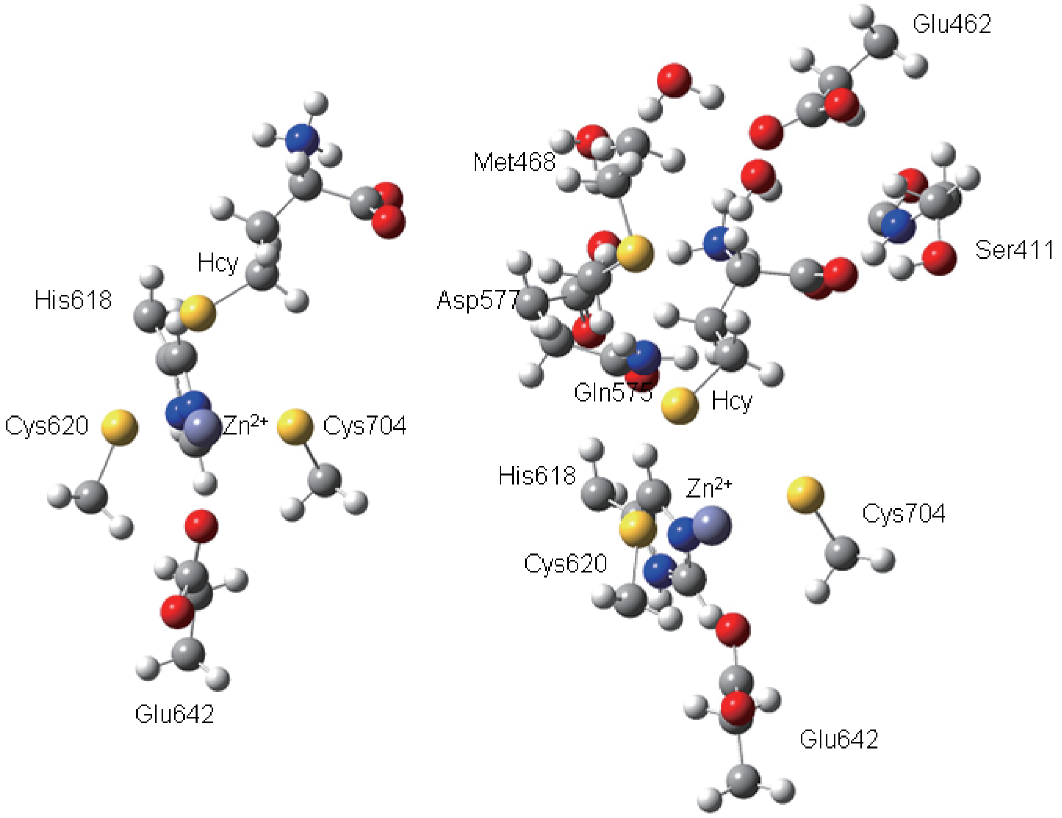
B) MetE enzyme.

1) The active site model performed in MetE enzyme showed the same pathway as MetH in the gas phase, firstly the Zn-Glu dissociates followed by addition of homocysteine with barrier of 30 kcal/ml. While in PCM environment MetH takes another pathway to bind Hcy: it takes SN2 mechanism passing with transition state of barrier 16 kcal/mol which is different from MetH.

2) ONIOM calculations on MetE enzyme showed that the enzyme keeps the SN2 pathway and the optimized transition state is very similar to the PCM one. Finding transition state explains the Zn active site geometry of the 1XDJ pdb structure, in which the Zn is in between Hcy and the glutamate. However the barrier of the Ts in the enzyme environment (47 kcal/mol), is higher than in PCM (16 kcal/mol).

2.1) Refining ONIOM energy with larger QM region

To test the effect of the QM size on the calculation results, another ONIOM model with larger QM region (109 atoms) is used to for single point calculations (see Figure 4).



Ts in partition1 (P1, 49 atom) Ts in partition2 (P2, 109 atom)

Figure 4: Two ONIOM models used in the calculations, P1 (partition 1) used for the location of the stationary points and P2 (partition 2) for the refining of the energy.

Using ONIOM model with larger QM region shifts the location of the transition state to one of lower barrier (23.34 kcal/mol) see Figure 5. These calculations demonstrate the big effect of the protein environment and the importance of using large QM region to accurately estimate this effect.

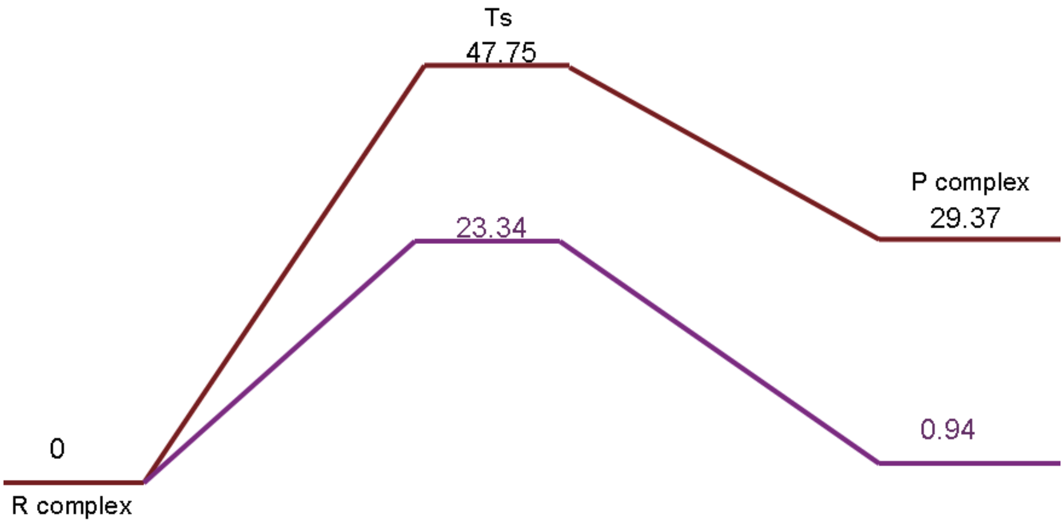


Figure 5: Represents the QM size on the reaction profile, in brown the results of P1 and in violet the results of P2.

3) Directed mutations in Hcy binding site MetE

Similar to MetH, the mutation effect on the Zn-Hcy binding is a little; we take here the Ts barrier as comparing criteria between wild type and the mutants for the Zn-Hcy binding process. All the mutants showed the feasibility of the reaction and the energy barriers ranging from 13.7 for D577A to 28.8 for H618C see figure 6. We have to keep in mind the conformational changes causes by the modeling protocol of the mutant structures, which may be produces some energy changes in the reaction profile. The produced structure model of the mutants need to be relaxed with long molecular dynamics, therefore these results are more qualitative than quantities as we need more conformations used in the calculation to be statistically meaning. However, these results are in agreement of Prasannan *et al. Biochem. Biophys. Research commu*. **2009**, 382, 730 experimental data of concerning the mutants D577 and S411.

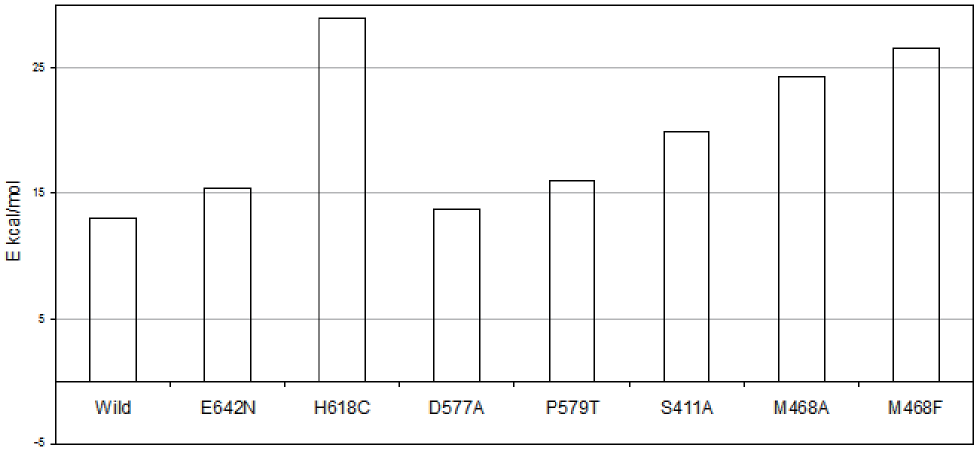


Figure 6: Represents the mutation effects on the Ts barrier in MetE, the calculations were performed using larger QM P2 with ONIOM-EE method.

2) Original Papers

1- Homocysteine activation in Cobalamin-dependent methyltransferase: DFT and ONIOM study. S. Abdel-Azeim, X. Li, L. W. Chung and K. Morokuma, to be submitted.

2- Homocysteine activation in Cobalamin-independent methyltransferase: DFT and ONIOM study. S. Abdel-Azeim and K. Morokuma, manuscript in preparation

3) Presentation at academic conferences

July 19-21, 2009: CREST International Symposium on Theory and Simulations of Complex Molecular Systems and International Symposium on Theory of Molecular Structure, Function and Reactivity, Celebrating Prof. Morokuma’s 75th Birthday, Kyoto University, Japan.

Poster: S. Abdel-Azeim, X. Li, L. W. Chung., K. Morokuma “ Zinc-Homocysteine binding in cobalamin-dependent methionine synthase”.

Alister PAGE

JST Fellow, Fukui Kenichi Memorial Research Group 1

1. Summary of the Research of the Year

(A) Transition-Metal-Catalyzed SWNT Nucleation, Growth & Healing: Dependence on Temperature, Catalyst Composition and Size

Since their initial discovery late last century, single-walled carbon nanotubes (SWNTs) have stimulated myriad experimental and theoretical investigations due to their extraordinary physicochemical, mechanical, and electrical properties. However, complete understanding, or consensus, on many important structural and energetic aspects of SWNT synthesis is yet to be attained. A pertinent illustration of this fact is the current lack of control over the diameter and (*n*,*m*) chirality of SWNTs produced using current synthetic techniques. This is also the case with respect to the control and quantification of SWNT growth rates in CCVD experiments. The effect(s) of pertinent environmental factors (such as catalyst particle size and composition) on the mechanism and kinetics of SWNT nucleation and growth remain therefore, largely unexplored.

The self-consistent-charge density-functional tight-binding molecular dynamics (SCC-DFTB/MD) method has been employed in order to elucidate these effects with respect to SWNT growth. SWNT growth was simulated using model C_{40}-M_x 'cap-catalyst' complexes, where M = Fe & Ni, and x = 38 & 55 (Figure 1). The effect of different catalyst composition and sizes on the mechanism and kinetics of SWNT growth could therefore be observed directly. The ultimate conclusions of this investigation are outlined in Table 1. The kinetics of SWNT growth was observed to depend acutely on the size of the supporting catalyst nanoparticle. In particular, the rate of SWNT growth was inversely proportional to the diameter of the catalyst nanoparticle. In addition, Table 1 indicates that Ni_x nanoparticles are 'better' catalysts (in the context of SWNT growth rates) than Fe_x nanoparticles, since SWNT growth proceeded more quickly using Ni, as compared to Fe (for an equivalent catalyst size). This is consistent with conclusions from laser evaporation and carbon-arc experiments.

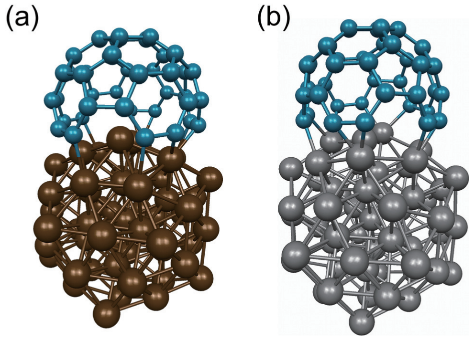


Figure 1. Model $C_{40}M_{55}$ systems employed for SCC-DFTB/MD investigations of SWNT growth. (a) M = Fe, (b) M = Ni. Cyan, brown and grey spheres represent C, Fe and Ni atoms, respectively.

The mechanism of SWNT growth was observed to depend critically on the composition of the catalyst nanoparticle. Ni_x-catalyzed growth was preceded by the formation of extended polyyne chains at the base of the SWNT, and so differed fundamentally from Fe_x-catalyzed growth. These polyyne chains usually persisted for 10-30 ps. Polygonal ring formation, and hence SWNT growth itself, was driven by the continual, simultaneous extension of these polyyne chains and subsequent 'ring collapse' (*i.e.* self-isomerization/interaction of the

Table 1. Dependence of C_{40} cap growth on catalyst size and composition: Average growth rate, numbers of added carbon and polygonal ring after 50 ps of simulation using Fe_{38}, Fe_{55}, Ni_{38} and Ni_{55} catalysts (all data averaged over 10 trajectories).

Catalyst	Growth rate ($\times 10^{-2}$ Å ps^{-1})	Number of carbons added to SWNT	Number of *n*-membered rings added to SWNT		
			n=5	*n*=6	*n*=7
Fe_{55}	2.879	51.0	6.2	6.5	4.4
Fe_{38}	3.542	55.2	6.2	9.2	4.3
Ni_{55}	4.874	62.4	9.0	9.0	5.9
Ni_{38}	7.299	64.8	9.2	10.2	6.5

polyyne chains resulting in ring formation). The rate of the former exceeded that of the latter, and so this mechanism was self-perpetuating (Figure 2). The relative stabilities of the polyyne moieties on the Fe_x and Ni_x surfaces were consistent with the relative strengths of the Fe-C, Ni-C and C-C interactions. The presence of smaller carbon moieties on the Fe_x surface led to the dissemination of surface iron atoms, and subsequent diffusion of short C_n units through the subsurface region of the catalyst particle. Conversely, the Ni_x catalyst particles were observed to be more stable, remaining intact to a greater extent during SWNT growth. The Ni-catalyzed SWNT growth mechanism established in this investigation was the first to be reported in the literature based upon quantum mechanics.

The mechanism and kinetics of SWNT nucleation from model M_cC_y (M = Fe, Ni) nanoparticle precursors, and their dependence(s) on simulation temperature, have also been investigated using SCC-DFTB/MD. These model carbides were constructed from M_{116} clusters, by randomly replacing M atoms with C (Figure 3). It was observed that SWNT nucleation occurred via three distinct stages, *viz.* the precipitation of the carbon from the metal-carbide, the formation of a “surface/sub-surface” carbide intermediate species and finally the formation of a nascent sp^2-hybdrized carbon structure supported by the metal catalyst. This investigation constituted the first quantum mechanics-based investigation into the mechanism of Ni-catalyzed SWNT nucleation reported in the literature (Figure 4). Ultimately, it was found that the metal-carbide carbon concentration and simulation temperature had little influence over the SWNT nucleation mechanism itself. However, the kinetics of SWNT nucleation exhibited distinct dependences on these same factors. In particular, SWNT nucleation from Ni_xC_y nanoparticles proceeded more favorably compared to nucleation from Fe_xC_y nanoparticles. Although SWNT nucleation from Fe_xC_y and Ni_xC_y nanoparticle precursors occurred *via* an identical route, the ultimate outcomes of these processes also differed substantially.

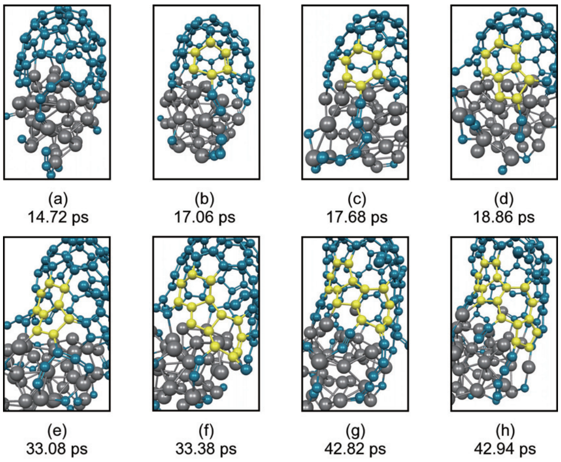

(a) 14.72 ps
(b) 17.06 ps
(c) 17.68 ps
(d) 18.86 ps
(e) 33.08 ps
(f) 33.38 ps
(g) 42.82 ps
(h) 42.94 ps

Figure 2. Typical polygonal ring addition mechanism observed during SCC-DFTB/MD simulation of Ni_{38}-catalyzed SWNT growth. In this case, the alternating extension and collapse of a single polyyne chain results in the formation of a 6-5-7-6 ring system. Colour conventions as in Figure 1; yellow spheres represent carbon atoms in newly formed polygonal rings. (a), (c), (e) and (g) represent polyyne extension, (b), (d), (f) and (h) represent ring formation. Times are given with respect to the beginning of the simulation.

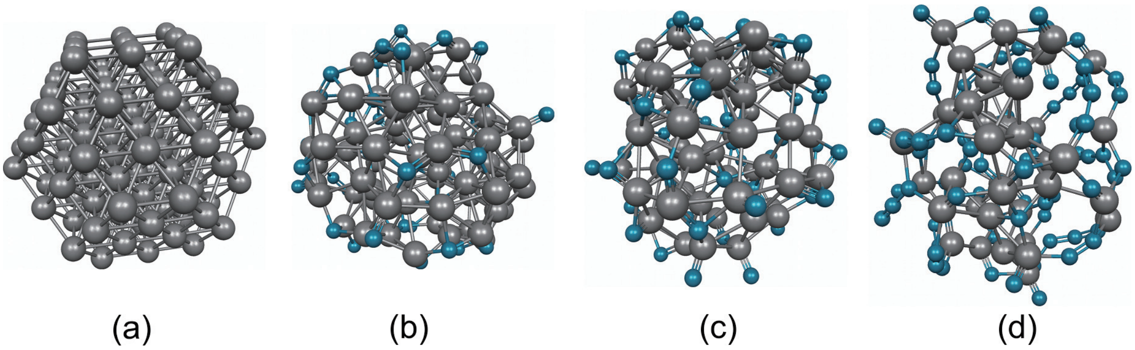


Figure 3. Optimized geometries of the (a) Ni_{116}, (b) $Ni_{77}C_{39}$, (c) $Ni_{58}C_{58}$ and (d) $Ni_{39}C_{77}$ model systems. Grey and cyan spheres represent Ni and C atoms, respectively.

Explicitly, the Ni_x-supported sp^2-hybridized carbon structures tended to encapsulate the catalyst particle itself, whereas the Fe_x-supported structures tended to "lift-off" from the catalyst surface, resulting in more well-defined SWNT cap structures. These differences in SWNT nucleation kinetics were attributed directly to the relative strengths of the metal-carbon interaction. The strength of the metal-carbon interaction was also observed to play a dominant role in dictating the precipitation of carbon from the nanoparticle bulk, and the longevity of the resultant surface/sub-surface carbide species. The mechanism and kinetics of both SWNT nucleation and growth therefore appear to be controlled primarily by the same factor, *viz.* the strength of the carbon-catalyst interaction. The stability of the metal-carbide bulk, however, was determined by the interplay of this metal-carbon interaction strength and the phase (*i.e.* solid/liquid) of the nanoparticle itself.

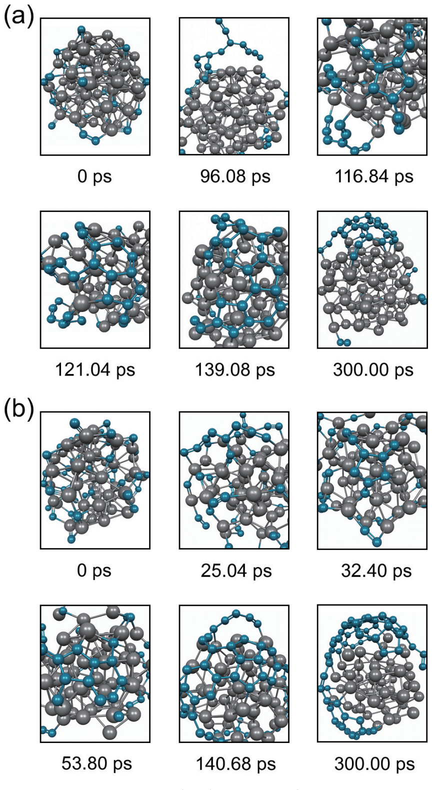


Figure 4. Evolution of SCC-DFTB/MD simulations of SWNT nucleation at 1400 K from (a) $Ni_{77}C_{39}$ and (b) $Ni_{58}C_{58}$ nanoparticle precursors. Colour conventions as in Figure 1.

(B) SCC-DFTB/MD Investigation of CH_4 Chemical Vapour Decomposition and SWNT Nucleation on SiO_2 Nanoparticles

The ability of non-metal catalysts, notably SiO_2, to assist the nucleation and growth of single-walled carbon nanotubes (SWNTs) *via* chemical vapour decomposition (CVD) has been established experimentally within the last decade. Recent speculation indicated that the traditional vapour-liquid solid mechanism (established for transition-metal catalysts) is possibly responsible for SWCNT nucleation on silica nanoparticles also. However, the exact mechanism by which this new breed of catalysts assists the nucleation and growth of SWNTs remains unknown.

We have addressed this issue using SCC-DFTB/MD simulations of CH_4 CVD on a SiO_2 nanoparticle at 1200 K.

CH_x radicals, chosen at random, were initially deposited on the SiO_2 surface at regular intervals. In contrast to CVD using traditional transition-metal catalysts, a complex chemical process was observed, as shown in Figure 5. Most notably, CO was produced as the primary chemical product *via* the carbothermal reduction of the SiO_2 nanoparticle, a fact that is consistent with recent experimental observations. The production of each CO molecule first required hydrogen-abstraction from neighbouring C, Si or O atoms. Ultimately, the insertion of carbon into/removal of oxygen from the SiO_2 nanoparticle resulted in the local formation of amorphous SiC. However, this carbothermal reduction was limited to the outer regions of the catalyst, with the core of the particle remaining “oxygen rich”. In addition, the amorphous SiC regions, are composed predominantly of extended polyyne chains “anchored” in place by native Si atoms. Consequently, these polyyne chains exhibit restricted vibrational and translational mobility, compared to the equivalent precursor structures observed during transition-metal catalysed SWNT nucleation. On this basis, we suggest that the extension of the traditional VLS model of SWNT nucleation to SiO_2-catalysts may by inadequate. Compared to transition-metal catalysed SWNT nucleation, SiO_2-catalyzed SWNT nucleation is a far slower process because of these considerations. Nevertheless, the formation of five-membered carbon rings (generally considered to be the “moment of nucleation”) has been observed following extended annealing at 1200 K (Figure 6). Further ring condensation from this SWNT “nucleus” (as observed for Fe- and Ni-catalyzed SWNT nucleation) is expected to follow.

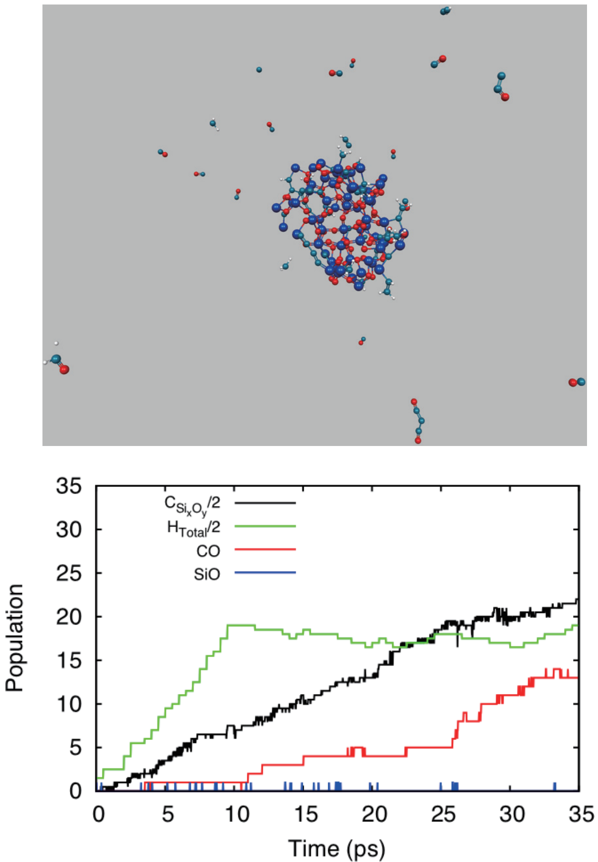


Figure 5. SCC-DFTB/MD simulation of CH_4 CVD on SiO_2 nanoparticles (following 35 ps of simulation). Blue, red, cyan and white spheres represent Si, O, C and H atoms, respectively.

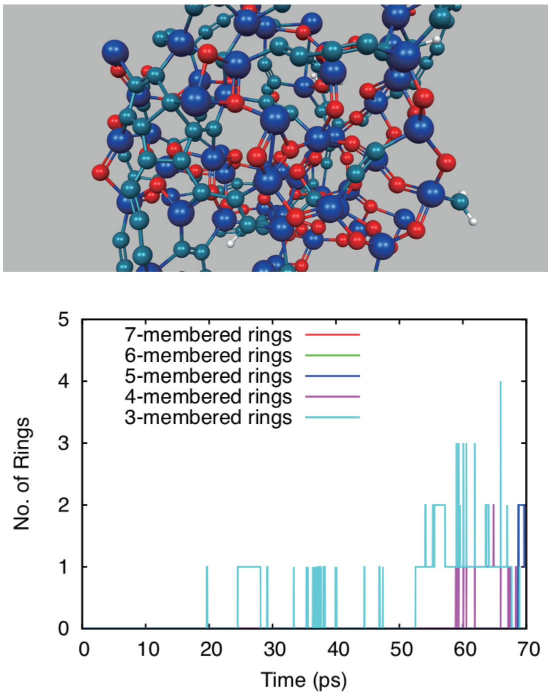


Figure 6. The beginnings of SiO_2-catalyzed SWNT nucleation following 70 ps of CH_4 CVD simulation using SCC-DFTB/MD. Colour conventions as in Figure 5.

2. Original Papers

(1) Y. Ohta, Y. Okamoto, A. J. Page, S. Irle and K. Morokuma, “Quantum Chemical Molecular Dynamics Simulation of Single-Wall Carbon Nanotube Cap Nucleation on an Iron Particle”, *ACS Nano*, **3**, 3413-3420, (2009).
(2) A. J. Page, Y. Ohta, Y. Okamoto, S. Irle and K. Morokuma, “Defect Healing during Single-Walled Carbon Nanotube Growth: A Density-Functional Tight-Binding Molecular Dynamics Investigation”, *J. Phys. Chem. C*, **113**, 20198-20207, (2009).
(3) A. J. Page, S. Irle and K. Morokuma, “Polyyne Extension and Contraction Drives Ni-Catalyzed SWNT Growth: A QM/MD Investigation”, *J. Phys. Chem. C*, **114**, 8206-8211, (2010).
(4) A. J. Page, S. Minami, Y. Ohta, S. Irle and K. Morokuma, “Comparison of Single-Walled Carbon Nanotube Growth from Fe and Ni Nanoparticles using QM/MD Simulations”, *Carbon*, (In press).
(5) A. J. Page, S. Irle, Y. Ohta and K. Morokuma, “Metal-Catalyzed Single-Walled Carbon Nanotube Nucleation, Growth and Healing Mechansims Determined Using QM/MD Methods”, *Acc. Chem. Res.*, (Submitted).
(6) A. J. Page, H. Yamane, S. Irle and K. Morokuma, “QM/MD Simulation of SWNT Nucleation from Transition-Metal Carbide Nanoparticles”, *ACS Nano*, (Submitted).

3. Presentations at Academic Conferences

(1) A. J. Page, Y. Ohta, S. Irle and K. Morokuma, “Healing of SWNTs During Growth *via* Ring Isomerisation: Towards (*n*,*m*) Chirality Control”, *CREST International Symposium on Theory and Simulations of Complex Molecular Systems*, Abstract page P-19, Kyoto, Japan, (2009).
(2) A. J. Page, Y. Ohta, S. Irle and K. Morokuma, “Quantum Mechanical Molecular-Dynamics Simulations of Single-Walled Carbon Nanotube Nucleation, Growth and Healing on Transition-Metal Catalysts”, *The 6th Korea-Japan Symposium on Carbon Nanotubes*, Abstract page 1P-2, Ginowan, Okinawa, Japan, (2009)
(3) A. J. Page, Y. Ohta, S. Irle and K. Morokuma, “Quantum Mechanical Molecular-Dynamics Simulations of Single-Walled Carbon Nanotube Nucleation, Growth and Healing on Transition-Metal Catalysts”, *International Symposium on Molecular Theory for Real Systems*, Abstract page 25, Kyoto, Japan, (2010).
(4) A. Udomvech, A. J. Page, K. Morokuma, “Theoretical Study of Li and Li^+ Intercalated in Double-Walled Carbon Nanotubes”, *ANSCSE14 – 14th International Annual Symposium on Computational Science and Engineering*, Abstract page B00034, Chiang Rai, Thailand, (2010).
(5) Y. Ohta, Y. Okamoto, A. J. Page, Z. Wang, S. Irle, K. Morokuma, “Nucleation and Growth Processes of Single-Walled Carbon Nanotubes from Metal Clusters: Density-Functional Tight-Binding Molecular Dynamics Simulation”, *13th International Congress of Quantum Chemistry*, Abstract page A.88, Helsinki, Finland, (2009).
(6) A. J. Page, S. Irle, Y. Ohta, Y. Okamoto, G. Zheng, Z. Wang, Y. Wang and K. Morokuma, “Nucleation, Growth and Healing Processes of Single-Walled Carbon Nanotubes from Metal Clusters: Density Functional Tight-Binding Molecular Dynamics Studies”, *The 50th Sanibel Symposium*, Abstract page 2-3, St Simons Island, USA, (2010).
(7) A. J. Page, S. Irle and K. Morokuma, “SWNT Nucleation, Growth and Healing: Insights from Density-Functional Tight-Binding Molecular Dynamics Simulations”, *The 38th Fullerenenes-Nanotubes General Symposium*, Abstract page 3P-14, Nagoya, Japan, (2010).

4. Others

(1) A. J. Page, “Density-Functional Tight-Binding Molecular Dynamics Simulations of Growth Mechanisms of Carbon Nanoclusters”, *L. V. Kirensky Institute of Physics, Siberian Federal University, Krasnoyarsk, Russia*, September 9, 2009, Invited Lecture.

K. R. S. CHANDRAKUMAR

JST Fellow, Fukui Kenichi Memorial Research Group 1,
（From 11 May 2009）

1. Summary of the research of the year 2009

Carbon Nanotube Growth from Metal Decorated Carbon Nanocones: Density Functional Tight-Binding based Molecular Dynamics (DFTB-MD) Approach

Carbon nanotubes and other related nanomaterials are now well-known in the literature and have been identified as one of the practically applicable nanomaterials by different experimental and theoretical groups. Owing to these unique properties, they have been found potential applications in the area of hydrogen storage materials, electronic device components, nanoscale biosensors, etc. The introduction of pentagon in the hexagonal carbon lattice leading to a formation of conical shaped materials, now known as carbon nanohorns or nanocones. Unlike the well-known carbon nanotubes, carbon nanohorns can be made simply without the use of a catalyst and their aggregates can be produced with a yield of more than 90% through laser vaporization of carbon at room temperature. These aggregates have a dahlia-like shape with a large number of horn-shaped short single layered nanotubes that stick out in all directions. The tips of these short nanotubes are capped with five-membered rings. One of the key characteristics of these carbon nanohorns is high adsorbability, due to their large surface area. In view of the importance of this relatively new material, carbon nanocone, an extensive study has been undertaken to study their electronic structure and properties. The catalyst-free self-assembly mechanism of single-walled carbon nanohorns (SWNHs) from vaporized carbon is currently little understood. It is of great importance to achieve understanding of the restructuring processes occurring in the single-walled carbon material at high temperatures in the presence of the transition metal catalyst.

A. Structural Transformation of Carbon Nanocone into Nanotube:

Herein, we have made an attempt to study the structural transformation of carbon nanocone into nanotube in the presence of iron and nickel nanoclusters as catalyst using the density functional based tight binding approach. In the present DFTB/MD simulations, we employed the self-consistent-charge DFTB (SCC-DFTB) method in combination with a finite electronic temperature approach with T_e = 10000 K to evaluate the quantum chemical Born-Oppenheimer potential on the fly. In the molecular dynamics simulations the velocity Verlet integrator was used with a time step of 1 fs, and the nuclear temperature was controlled by connecting the Nose−Hoover chain thermostat to the degrees of freedom of the present model system. We have annealed the initial starting structure at different temperatures 1500, and 2500 K for 10 ps, and ten such trajectories have been considered at the respective temperature for 30-40ps. Thus, the investigation in this work is comprised of a total of 50 trajectories plus a large number of less systematic supplementary simulations. Out initial structure comprises of the nanocone with definite length along with the iron nanocluster of size Fe_{38} (Figure 1).

Our initial results at 2500K reveal that different possible structures are possible when the two nanocones interact each other in the presence of iron catalyst. In all the cases, part of the metal cluster is covered by one cone and the other cone either covers the metal cluster or it is in the suspended position. However, at 1500 K, in most of cases, one end of the cones is attached with the metal cluster and the other part is found to be in the suspended position.

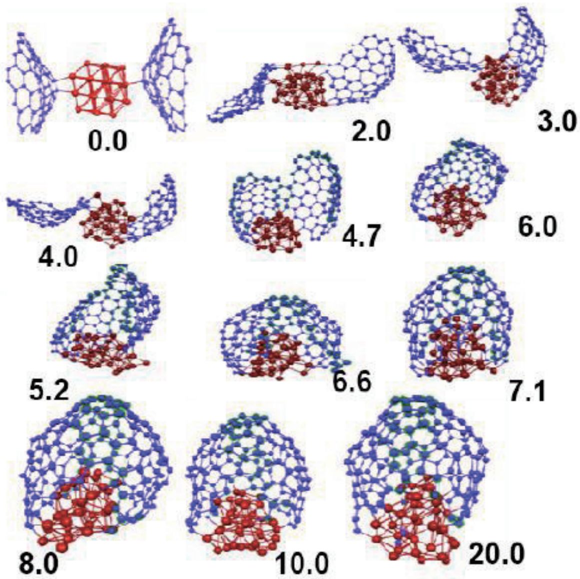


Figure 1: Snapshots of the nanotube growth process at 2500K showing some important key steps. The number denotes time in pico seconds

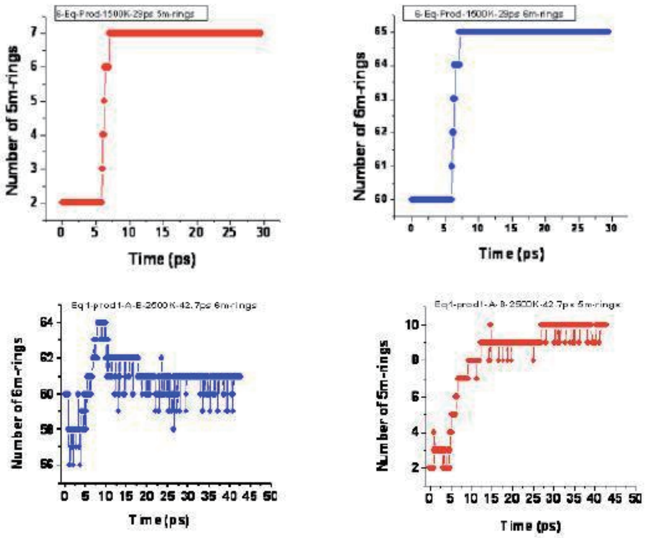
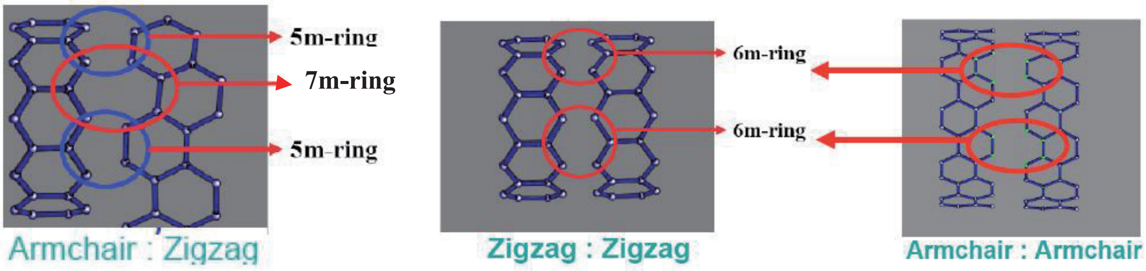


Figure 2: Statistics of the ring formation for one of the trajectories at 1500 (top) and 2500K (below)

The effect of temperature appears to be very significant in these cases. In some cases, the structural transformation of cone into tube-like transformation is indeed observed and the tube starts degrading at 2500K while the tube is observed to be very stable at 1500K. From the Figure 1, it is evident that initially, both the cones have to flip from the tip position to the edge and thereafter, both the cones are zipped together. The entire process is leading to the formation new 5m and 6m-rings as it is shown in Fig. 2. Considering the time scale, it can be mentioned that the flipping of the cones and the formation of the tube-like structure takes place in the time range of 3-4ps and 7-9ps, respectively. In addition, our simulation results illustrate that the transformation process is faster at 2500K compared to that of 1500K. It can be seen from Fig.2 that the growth process at 1500K is quite smoother and the increment in the number of new 5m and 6m-rings in the nanotube is quite sharp, indicating the growth process is quite fast with threshold time period. We have also observed that the 3m, 4m and 7m-rings are not formed and the number of 5m-rings present in the tube are less compared to that of the tube obtained at 2500K and the 6m-rings are higher in the earlier case. The rings, which are directly connected to the metal cluster, are affected significantly. More strikingly, the structure of the tube is not changed after annealing the structure up to 34ps, which is also evident from the ring count (From Fig. 2).

B. Nature of the tube-like structure: The transformed tube-like structure has many defects and the shape of the tube is also found to be very irregular, in particular at the edges where the two cones are joined together. The irregular shape of the tube can be attributed due to the presence of 5m-rings. In general, one 5m-ring is present at the capping region, which is surrounded by the five 6m-rings in the normal cones. However, the number of 5m-rings is increased to 8-10, during the growth of the tube along with few 6m-rings. This type of arrangement of the rings causes the curved types of structure. Since the nanocone has the zigzag as well as armchair types of edges, the formation of 5m, 6m and 7m rings is expected when two cones joins together especially at the interface region, as shown in Fig. 3.



Armchair : Zigzag Zigzag : Zigzag Armchair : Armchair

Figure 3: Formation of different combination of rings during the growth process of the tube

In the present case, the peripheral part of the cones are normally composed of both the armchair and zigzag types of structure and hence, the interface or bridge position at the intramolecular junctions of the two cones can define the nature of the nanotube (defect or perfect nanotube). The Fig. 4, describes that the combination of armchair - zigzag types of structure can lead to the formation of 5m-rings at the interface or bridge region of the intramolecular junctions where the two cones meet each other. The additional 5m-rings cause the tube to have the curved or

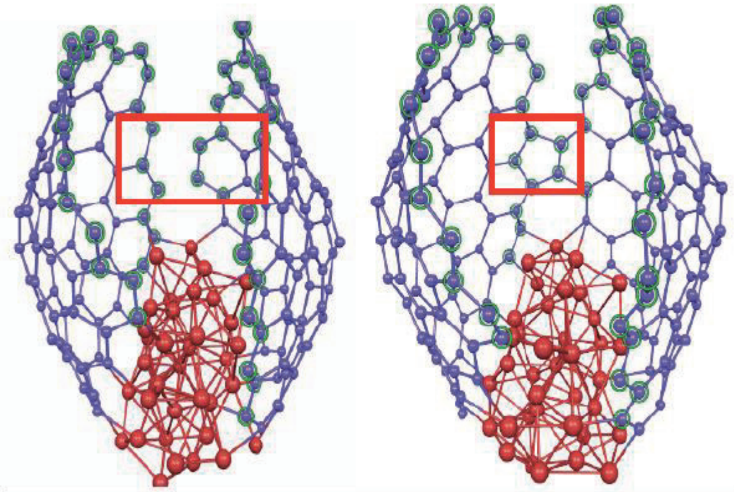


Figure 4: Armchair-Zigzag combination leading to the formation of 5m-rings during the growth process of the tube

irregular shapes with defective sites as well.

C. Structural Transformation of Carbon Nanocone into Nanotube: Some Differences between the Nickel and Iron Catalyst

As a sequel to the earlier study, we have investigated the transformation mechanism in the presence of nickel catalyst. The size of the catalyst has been the same as iron catalyst and the simulation has been carried out different temperatures, 1000K, 1500 K and 2500K. As explained earlier, we have followed the same methodology, DFTB-MD approach in this case also. More strikingly, the present results as shown in Fig.5, demonstrate that one of the cones is observed to be non-interactive, implying that only one cone is interacting with the nickel catalyst and in some cases, both the nanocones are found to be leave the catalyst. In some cases, the cone covers either the metal cluster or it is in the suspended position. This feature is not observed in case of iron catalyst. Another important difference is that one of the cones interacting with the nickel cluster is inversed, as shown in Fig.6, which takes place in 400fs without breaking 5m or 6m-rings of the cones. Only in two cases, the formation of the nanotubes like structure is favored at 2500K. Another important observation as shown in Fig.7, is that at higher temperature, 2500K, when the two nanocones interact each other, the first ring at the bridge position of the two nanocones is formed at 8.6ps (*in case of iron, at 7ps the tube is formed*) and it takes 16ps to form the tube-like structure. In addition, the 8m-rings as well as several 5m-rings are also formed and the number of 5m-rings is found to be approximately ~10-12 (much more than that of iron case). This feature is different from the case of iron cluster-induced nanotube

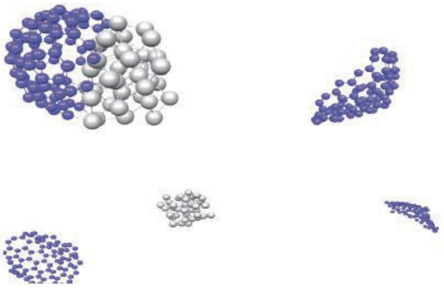


Figure 5: Nature of the interaction of cones with nickel cluster

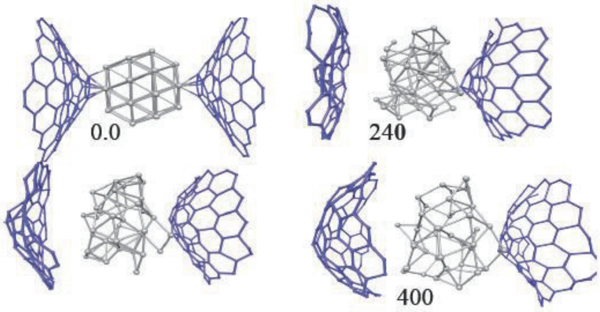


Figure 6: Inversion of the cone attached to nickel cluster. The number denotes time in femto seconds

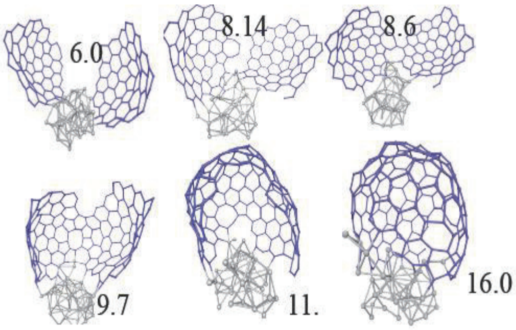


Figure 7: Snapshots of the nickel catalyzed nanotube growth process at 2500K showing some important key steps. The number denotes time in pico seconds

formation. Interestingly, the similar trajectories at 1500K, found to be very different from what has been observed at higher temperature. In this case, one of the nanocone is observed to be effectively interacting with the catalyst surface and one of the nanocones is found to be away from the surface. In addition, out of 10 trajectories, we did not observe any nanotube like transformation at 1500K. On comparing with the iron-catalyzed reaction, the mechanism of the formation of the tube-like structure by nickel catalyst is found to be profoundly different from the iron-catalyzed tube formation. In case of iron-catalyst, the basic structure of the zigzag as well as armchair types of edges are not destroyed and hence, the mechanism of the formation of the tube has been explained in terms of the interface or bridge region at the intra-molecular junctions of the two cones which can have the 5m-rings around the tube. However, in case of nickel cluster-induced tube formation, the mechanism is not very apparent from the trajectories. The zigzags as well as armchair types of edges are found to have no role. Thus, although there are some similarities with the interaction of single nanocone with the catalysts, the interaction of the two cones with the iron and nickel cluster is very different from each other.

2. Original Papers

(1) K. R. S. Chandrakumar, S. Irle and K. Morokuma, “*Carbon Nanotube Growth from Metal Decorated Carbon Nanocones: Density Functional Tight-Binding based Molecular Dynamics (DFTB-MD) Approach”* Manuscript in Preparation

(2) K. R. S. Chandrakumar, S. Irle and K. Morokuma, “DFTB-MD simulations on the Growth of Carbon Nanotubes M*etal Doped Nanocones: Effect of Catalysts, Catalysts Size and Reaction Temperature”* Manuscript in Preparation

3. Presentations at Academic Conferences

(1) K. R. S. Chandrakumar, S. Irle and K. Morokuma, *“DFTB-MD simulation of carbon nanotube growth from metal decorated carbon nanocones”* (poster) presented in, “50th Sanibel Symposium, Celebrating the Past, Present and Future of the Quantum Theory”, St. Simons Island, Georgia, USA (2010).

(2) K. R. S. Chandrakumar, S. Irle and K. Morokuma, *“Structural Transformation of Carbon Nanocones into Nanotubes: Role of Iron and Nickel Nanoparticles”*(poster) presented in “International Symposium□on□“ Molecular Theory for Real Systems”, Fukui Institute for Fundamental Chemistry, Kyoto, Japan (2010).

(3) K. R. S. Chandrakumar, N. K. Jena and S. K. Ghosh, *“Structure, Property and Reactivity Correlations in Carbon Nanomaterials: A Simple and Novel Concept of Nanoscale Curvature”* (Poster) presented in “International Symposium on Theory and Simulations of Complex Molecular Systems”, Fukui Institute for Fundamental Chemistry, Kyoto, Japan (2010).

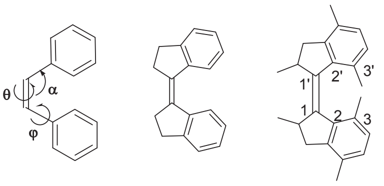
Fengyi LIU

JST Fellow, Fukui Kenichi Memorial Research Group 1
（From 15 Sep. 2009）

1. Summary of the research of the year

Rationalization of Light-Driven Rotary Molecular Motor: An Theoretical Study on the Photoisomerization of an Stiff Stilbene

Molecular rotary motors, though common in nature, were synthesized rather recently. One of the most promising categories of artificial light-driven rotary molecular motors allowing for optical control is based on helical overcrowded alkenes. For instance, light-driven rotary molecular motors (**3** in Chart 1) based on stilbene **1** have been synthesized by Feringa's group. By introducing helical substitutions into these overcrowded alkenes, the authors have successfully harnessed the nondirectional motion to achieve an unidirectional, 360º rotation around the central carbon-carbon double bond (Fig. 1). The rotational process consists of four steps, two of which occur in the electronically excited state and involve *cis–trans* isomerization of the central carbon-carbon bond. Though the mechanisms of these photo-initiated processes are important in rationalization of the chemical nature of the currently synthesized rotary molecular motor and to design new promising motors, they have not been well understood yet. In the present study, we carried out complete active space self-consistent field (CASSCF) calculations to explore the rotary potential-energy surface (PES) of stiff-stilbene-based molecular motor **3** in order to understand the reaction mechanism of the phoisomierzation reaction and rationalize the unidirectionality of the rotation.



1 Stilbene **2** Stiff-stilbene **3** Molecular motor

Chart 1

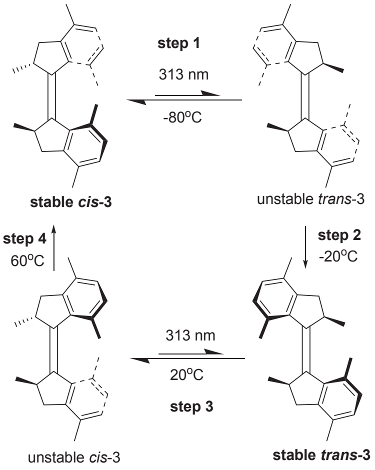
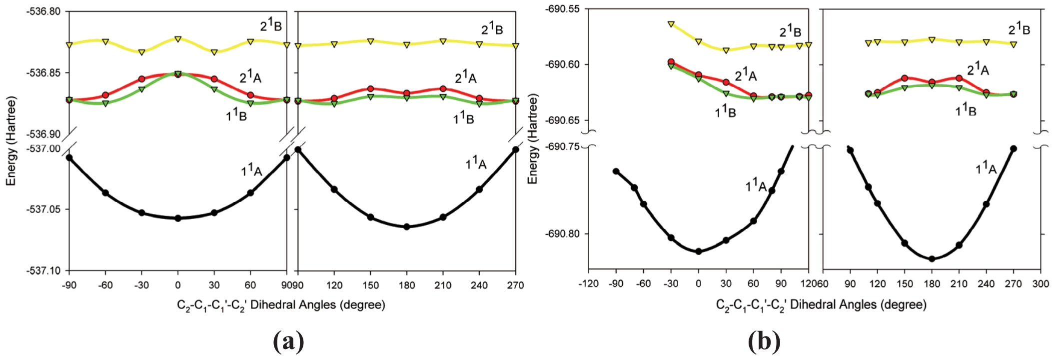


Figure 1. Four-step rotation in stiff-stilbene-based molecular motor **3**.

The *cis-trans* photoisomerization of stilbene is one of the most extensively investigated subjects in photochemistry. It is known that for free stilbene both *trans→cis* and *cis→trans* isomerization can take place. Though their dynamics are evidently different, the wave packet from both isomers can access a conical intersection (CI) with perpendicular conformation near the minimum of the S$_1$ state. The ideal branching ratio of the *cis-* and *trans-* products is 50:50. Thus the primary torsional motion during this process is nondirectional and reversible. As shown in Fig. 2a, the one-dimensional PESs are symmetric around θ =0 and 180º for the *cis-* and *trans*-**1**, respectively. The introduction of two 5-membered rings into free stilbene produces stiff stilbene **2** (Chart 1). The 5-membered ring in **2** not only prohibits the photocyclization side reaction (which is the predominant side process in free stilbene **1**) but also more or less fixes C$_1$–C$_2$ bond thus makes hula-twist mechanism unfeasible. From Fig. 2b it is seen that compared with that of free stilbene

1, the symmetry of the excited-state PESs around the Frank-Condon (FC) region of *trans*-**2** remains, while the one around *cis*-**2** has been removed. This is caused by the steric compulsion between the two benzene moieties which is only significant in the *cis*-isomer. In order to avoid the high cross-plane rotational barrier, the C_2–C_1–C_1'–C_2' and C_3–C_2–C_1–C_1' dihedral angles increase (or decrease) simultaneously, resulting in the helically twisted conformation and asymmetric excited-state PESs.



(a) **(b)**

Figure 2. SA-CASSCF energy profile of (a) free stilbene **1** and (b) stiff-stilbene **2**.

Further introducing methyl group into stiff-stilbene **2** slightly changed the geometry of the *cis*-**3**, while put significant effects on *trans*-**3**. The SA-CASSCF optimized θ,φ are 162.5 and –37.3°, respectively. The strong methyl-methyl compulsions alternate both the ground- and excited-state PESs around *trans*-minimum into slopped. Tracking the geometry variation along the rotational coordinates suggests that after the photoexcitation the molecule follows the twist motion to reach the perpendicular excited-state intermediate, which represents a conformation better matching the product than the reactant. Therefore, the steric effects of 5-membered rings and the methyl groups which evidently slope the excited-state 1B surface, could partially account for the unidirectionality rotation of molecular motor **3**.

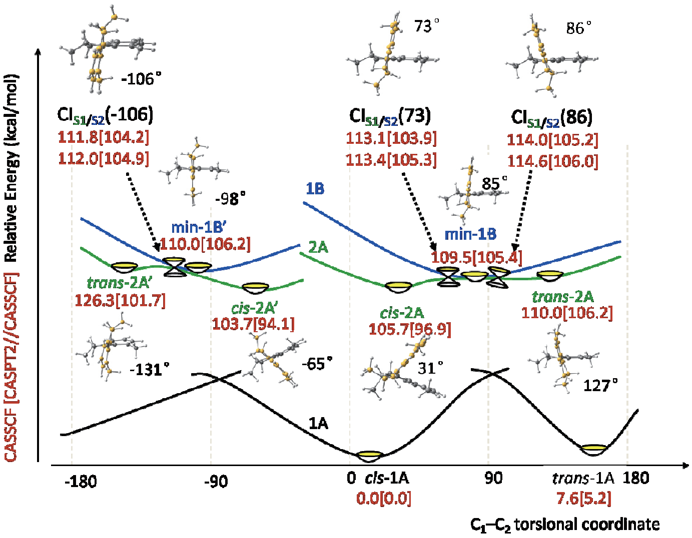


Figure 3. The SA-CASSCF//SA-CASSCF and CASPT2//SA-CASSCF (in square brackets) schematic energy profiles of molecular motor **3** along the C_1-C_1' torsional coordinate.

In addition to the topology of the excited-state PES, it is also important to understand the radiationless relaxation of the excited-state molecules to the ground-state PES in these two photoisomerization steps (step 1 and 3 in Fig. 1). Along the primary reaction coordinate, several excited-state intermediates, on both the 1B and 2A states, were located. It is found the 1B and 2A PESs approach each other from the FC region of *cis*-**3** (or *trans*-**3**) to the perpendicular intermediate region and finally intersect with each other in the vicinity of the 1B minimum (*min*-1B or *min*-1B′). The located MECPs on the 1B/2A seams has "peak" nature and are almost identical in energy with the 1B intermediates, thus they provide opportunities for the molecules on the 1B PESs to barrierlessly access the energetically more favorable 2A surface. Moreover, with the torsional angle increasing from planar to perpendicular, the double-bond character of the central C_1-C_1' bond is weakened, correspondingly the C_1 and C_1' have high mobility along the carbon pyramidalization coordinate. Indeed, two S_0/S_1 MECPs can be found on either directions of the pyramidalization coordinate (shown in Fig. 4). Before the excited-state molecule could cross the $CI_{S0/S1}$ to reach 1A surface, they have to overcome 10~30 kcal/mol energy barrier. In short, the photoisomerziation process undergoes a 3-state, 2-coordinate mechanism: The excited molecules in 1B state first decay to 2A state though the 1B/2A seams along the primary C_1-C_1' torsional coordinate, and then follow the C_1/C_1' pyramidalization to cross the 2A/1A conical intersection and return the ground-state PES. In summary, our calculations rationalize the undirectionality of the rotation and suggest a possible reaction mechanism for the stiff-stilbene based rotary molecular motor.

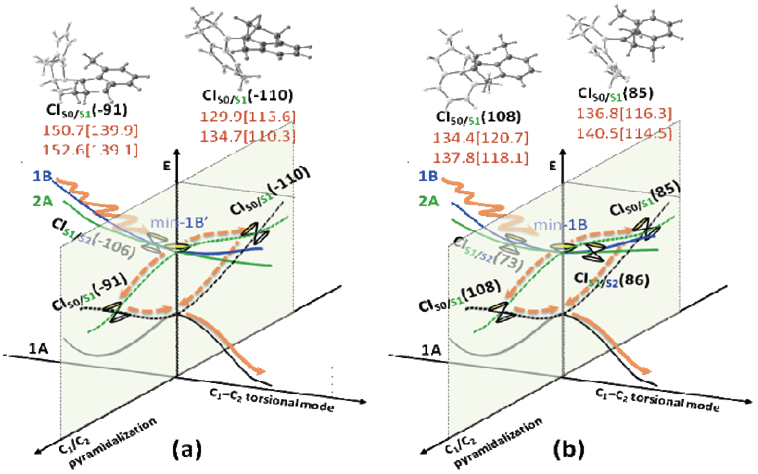


Figure 4. The reaction paths around 1B intermediates: (a) **min-1B′**(θ = -98°) in photoisomerization step 1 and (b) **min-1B** (θ = 85°) in photoisomerization step 3.

2. Original papers

(1) Fengyi Liu and Keiji Morokuma,
Rationalization of Light-Driven Rotary Molecular Motor: An Theoretical Study on the Photoisomerization of an Stiff Stilbene, *manuscript in preparation*.

3. Presentation at academic conferences

(1) Fengyi Liu and Keiji Morokuma, Poster on:
"Rationalization of Light-Driven Rotary Molecular Motor: An Theoretical Study on the Photoisomerization of an Stiff Stilbene"
International Symposium on "Molecular Theory for Real Systems", Kyoto, Jan 7-9, 2010

Parameswaran PATTIYIL

JST Fellow, Fukui Kenichi Memorial Research Group 1
（From 12 Oct. 2009）

1. Summary of the research of the year

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

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

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

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

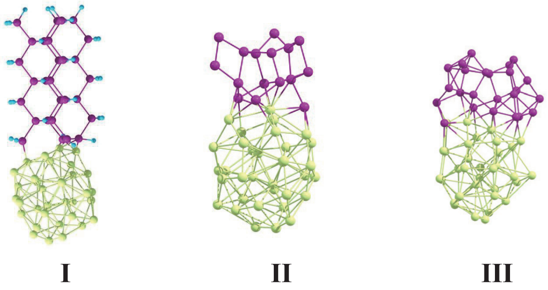
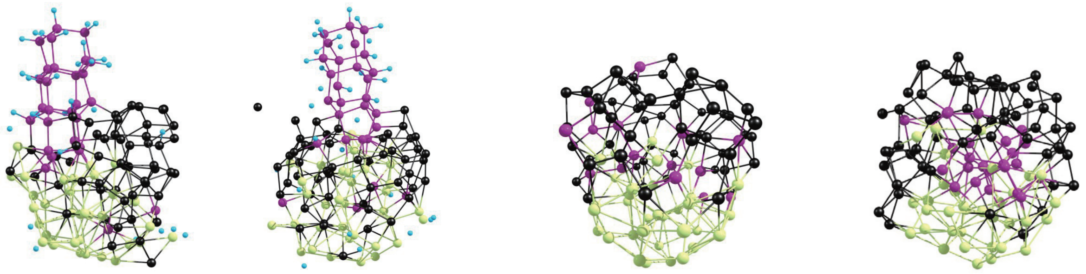


Figure 1: SCC-DFTB optimized geometries of model Al-capped Si-nanowires. Green, pink and blue spheres represent Al, Si and H-atoms respectively.



(a) (b) (c) (d)

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

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

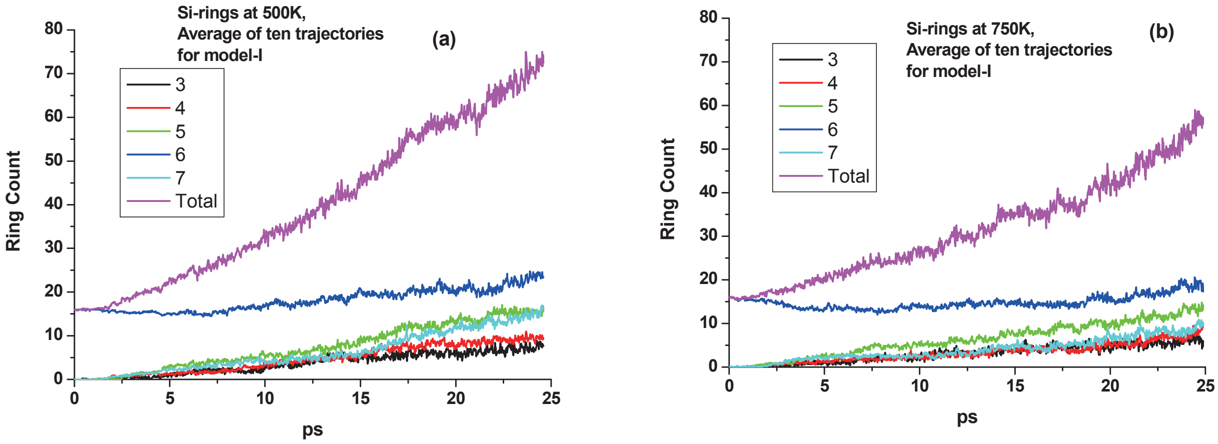


Figure 3: The plots of average ring count for ten trajectories versus time in ps at (a) 500K and (b) 750K for model-I.

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

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

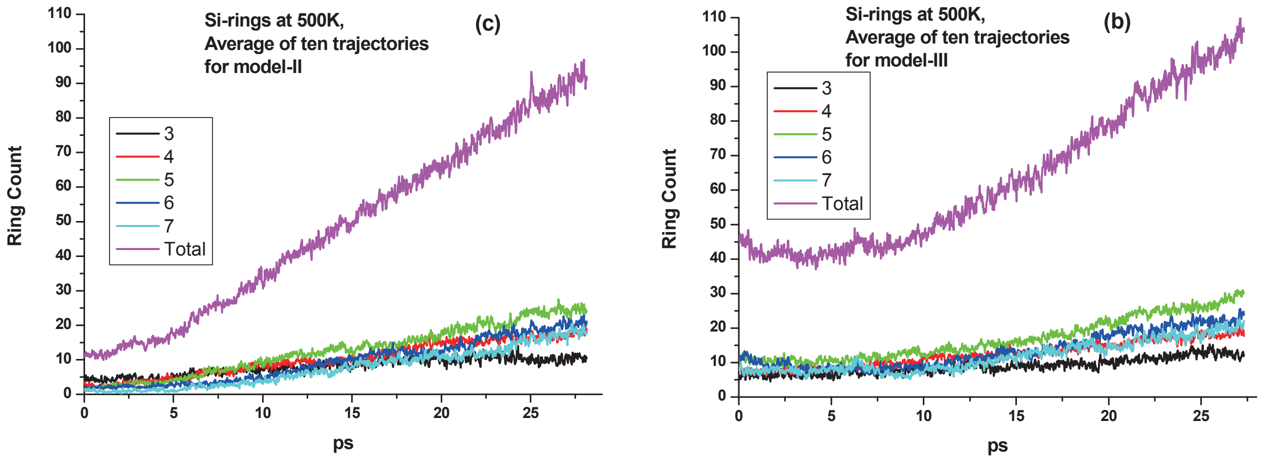


Figure 4: The plots of average ring count for ten trajectories versus time in ps at 500K for (a) model-II and (b) model-III.

2. Original papers

(1) Melaimi, M.; Parameswaran, P.; Donnadieu, B.; Frenking, G.; Bertrand. G.
“Synthesis and Ligand Properties of a Persistent All-Carbon Four-Membered Ring Allene”
Angew. Chem. Int. Ed. 48, 4792-4795 (2009).

(2) Prabusankar, G.; Gemel, C.; Parameswaran, P.; Flener, C.; Frenking, G.; Fischer, R. A.
“A Short Bi=Bi Bond Supported by a Metalloid Group 13 Ligand”
Angew. Chem. Int. Ed. 48, 5526-5529 (2009).

(3) Parameswaran, P.; Frenking, G.
“Transition Metal Complexes $[(PMe_3)_2Cl_2M(E)]$ and $[(PMe_3)_2(CO)_2M(E)]$ with Naked Group 14 Atoms (E = C – Sn) as Ligands; Part 1: Parent Compounds”
Chem. Eur. J. 15, 8807-8816 (2009).

(4) Parameswaran, P.; Frenking, G.
“Transition Metal Complexes $[(PMe_3)_2Cl_2M(E)]$ and $[(PMe_3)_2(CO)_2M(E)]$ with Naked Group 14 Atoms (E = C – Sn) as Ligands; Part 2: Complexation with $W(CO)_5$”
Chem. Eur. J. 15, 8817-8824 (2009).

(5) Aldeco-Perez, E.; Rosenthal, A.; Donnadieu, B.; Parameswaran, P.; Frenking, G.;

Bertrand. G.
"Isolation of a C-5-Deprotonated Imidazolium, a Crystalline Abnormal N-Heterocyclic Carbene"
Science, 326, 556-559 (2009).

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

(7) Parameswaran P.; Frenking, G.
“Chemical Bonding in Transition Metal Complexes with Beryllium Ligands $[(PMe_3)_2M\text{-}BeCl_2]$, $[(PMe_3)_2M\text{-}BeClMe]$ and $[(PMe_3)_2M\text{-}BeMe_2]$ (M = Ni, Pd, Pt)”
J. Phys. Chem. A　ASAP (2010), DOI: 10.1021/jp910181q.

3. Presentation at academic conferences

(1) Parameswaran P.; Frenking, G..
“Chemical Bonding in Transition Metal Complexes with Beryllium Ligands” (Poster Presentation)
The 7th symposium of Fukui Institute for Fundamental Chemistry, Kyoto, 4th December, 2009.

(2) Parameswaran P.; Frenking, G..
“Chemical Bonding in Transition Metal Complexes with Beryllium Ligands” (Poster Presentation)
International Symposium on “Molecular Theory for Real Systems” 7th-9th January, 2010.

田代　基慶

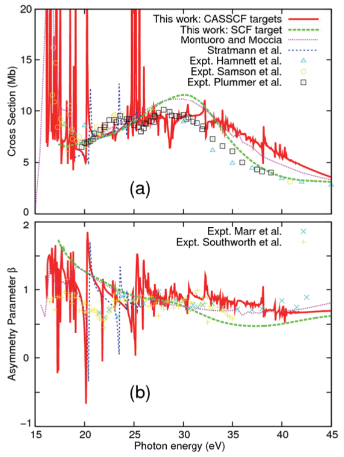
センターフェロー
（平成 21 年 7 月 15 日まで）

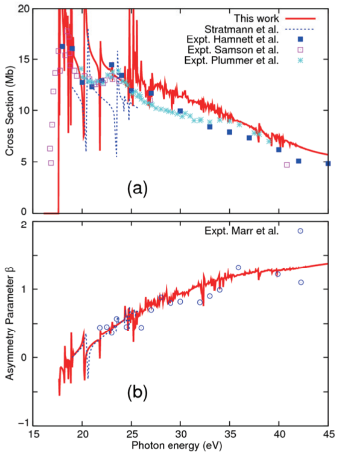
1. 今年度の研究の要約

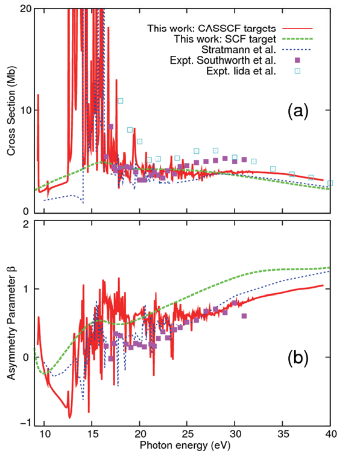
2009年度は分子の光電離過程に関する理論的取扱いを進めた。光電離過程の終状態には電子が無限遠に飛び去る過程を含んでいるために、通常の量子化学的手法による理論的取扱いは困難である。しかし、いくつかの理論グループは電子−分子の散乱理論を利用し、乱雑位相近似を用いたK行列法、Schwinger variational principle理論、時間依存密度汎関数理論などによって光電離過程の計算を行ってきた。第一原理R行列法は低エネルギー電子と分子の衝突過程を取り扱う理論手法のひとつであり、原子・分子の光電離過程にも適用できることが知られている。しかし、今までの所、原子系への応用がほとんどであり分子系への応用例はあまりない。我々はこのR行列法を用いた分子の光電離計算手法の開発を進めてきた（R行列法などの詳細は前年度年次報告を参照）。

今回我々はR行列法による光電離の取扱いで、電離する中性分子・電離で生じる分子イオンの記述にCI型波動関数を用いることができるようにした。従来の多くの理論手法では分子・分子イオンの記述は単一配置によるものであり、多電子励起共鳴のような過程の記述は不可能であった。今回の我々の手法では多電子励起配置の効果を調べることができることに加え、静的電子相関を始・終状態に含めることが可能となっている。

窒素分子（N_2）・一酸化窒素分子（NO）を対象にした計算結果を以下に示す。一番左の図はN_2基底状態の電離によって$N_2^+(X^2\Sigma_g^+)$が生じる過程、中央の図は$N_2^+(A^2\Pi)$が生じる過程、一番右の図は$NO(X^2\Pi)$の光電離によって$NO^+(X^1\Sigma^+)$が生じる過程である。上のパネル(a)は光電離断面積、下のパネル(b)は光電子の放出方向非等方性を表すパラメータβの結果である。赤線で示す我々の結果は点で表してある実験結果を良く再現しており、R行列による光電離の取扱いが効果的であることを示している。







2. 論文

（1） Motomichi Tashiro
Application of the R-matrix method to photoionization of molecules
Journal of Chemical Physics **132** 134306 (2010)

3. 学会発表

(1) 第12回理論化学討論会（東京大学 2009年5月29日）
題名 「R行列法を用いた分子の光電離過程の理論的取扱い」
ポスター発表・2P20
田代基慶

(2) 13th International Congress of Quantum Chemistry（ヘルシンキ 2009年6月25日）
題名 「Electron collision with gas-phase amino acid molecules」
ポスター発表・C-134
田代基慶

(3) 日本物理学会2009年秋季大会（熊本大 2009年9月27日）
題名 「光電離過程に対するR行列理論の応用：CI標的による取扱い」
口頭発表・27pZB-1
田代基慶

Wilfredo Credo CHUNG

FIFC Fellow

1. Summary of research for the year

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

Rhodopsin is the photosensitive chemical found on the outer segment of rod-like cells in the retina, the light-sensing structure of the eye. The 11-cis retinal chromophore in rhodopsin is changed to all-trans retinal upon exposure of rhodopsin to light. Isomerization of retinal to the all-trans form is essentially completed in 200 fs with a 0.67 quantum yield.[1] Isorhodopsin is an analogue of rhodopsin that contains a 9-cis retinal chromophore instead of 11-cis retinal embedded in the same opsin environment. Light-induced isomerization of the 9-cis retinal chromophore to the all-trans form is known to occur at a longer timescale (600 fs)[2] and at a reduced quantum yield (0.22)[3] resulting in a weaker visual response.

The dynamics of the photoisomerization of a model protonated Schiff base of 9-cis retinal in isorhodopsin is investigated using nonadiabatic molecular dynamics simulation combined with ab initio quantum chemical calculations on-the-fly. The classical time-evolution of the trajectories employ the velocity Verlet algorithm while the quantum chemical part is treated at the complete-active space self-consistent field level for six electrons in six active π orbitals with the 6-31G basis set (CASSCF(6,6)/6-31G). Initial atomic velocity was generated using random numbers subject to the Wigner distribution and the molecule was excited onto the S_1 state. Seventy-one trajectories were calculated in total with a 0.5 fs time step. The probabilities of nonadiabatic transitions between the S_1 ($^1\pi\pi^*$) and S_0 states are estimated in light of the Zhu-Nakamura theory.

Figure 1 shows the population of the 9-cis, all-trans and 11-cis photoproducts as well as the still-unreacted residual of the starting material. Generation of each form is counted only after the product region in the ground state (the dihedral angle C_8–C_9–C_{10}–C_{11} reaches $0 \pm 10^\circ$ or $180 \pm 10^\circ$). Thirteen percent of the trajectories yield the all-trans isomer in this simulation: the quantum yield of the all-trans photoproduct is 0.13. If the 9-trans (11-cis) products are counted as a trans product, the ratio is 0.18, which is in excellent agreement with the experimentally measured quantum yield of 0.22. This is significantly lower than the one obtained by Ishida et al. for 11-cis PSB retinal of 0.27 (or 0.49 if the 11-trans (9-cis) form are counted as a trans form).[4] Experimentally, the all-trans quantum yield for rhodopsin is 0.67,[1] around three times more than that for isorhodopsin. The rhodopsin/ isorhodopsin quantum yield ratio for the two simulations is 2.1 to 2.7, in good agreement with the experimental ratio.

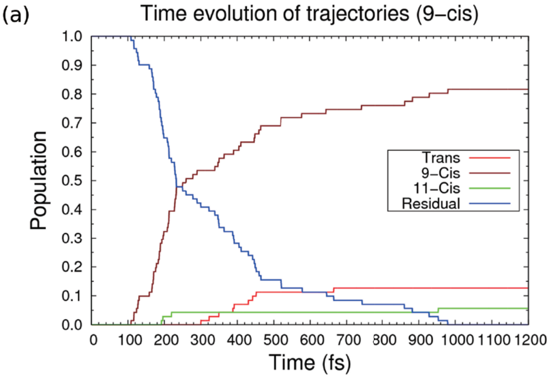


Figure 1. Population change calculated for all the trajectories in the isorhodopsin (9-cis) model systems.

On the average, it takes 441 fs to form the all-trans isomer from the 9-cis form; the time scale of isomerization is shorter than, but in reasonable agreement with the experimental reaction time of 600 fs.[2] The shorter time scale of the isomerization may be due to the total neglect of the influence of the protein environment that surrounds the chromophore in a biological medium. Inside the binding pocket, the cis-trans isomerization is slowed down by steric interactions with nearby amino acid residues and counterions. In the gas phase, on the other hand, the active dihedral rotates freely with little impediment.

Formation of the all-trans product begins about 280 fs and peaks around 660 fs after photoexcitation in the case of the 9-cis model trajectory calculation. If the 11-cis (9-trans) form is counted as a trans photoproduct, formation of the said product starts around 200 fs in this simulation. This is consistent with Schoenlein et al.'s observation that “measurements on isorhodopsin show an initial photoproduct absorption by 200 fs, which continues to grow-in until 600 fs”[2] reinforcing the validity of our model simulation.

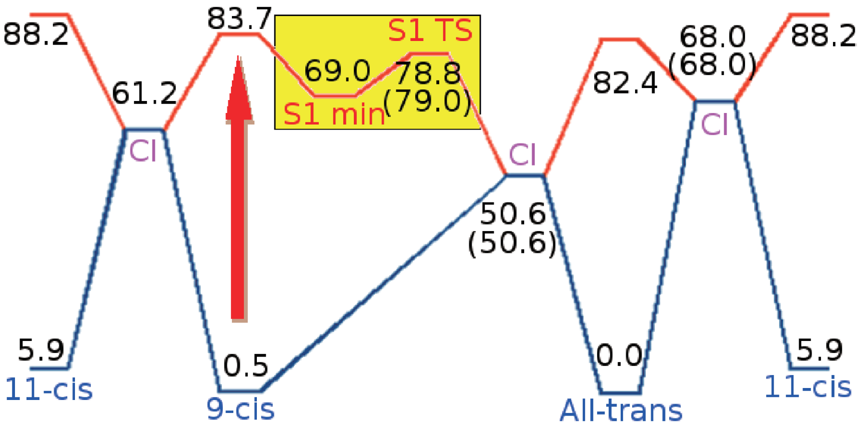


Figure 2. Energy diagram for the cis-trans isomerization of retinal. Energy is in kcal mol^{-1}.

Our simulation confirms the experimental observation that the photoisomerization to the all-trans chromophore is slower than that of rhodopsin and at a lower quantum yield. We point out the existence of an energetic barrier to the C_9–C_{10} twist coordinate in the excited state as the main reason for the delay and reduction in the generation of the all-trans isomer from isorhodopsin. Since these features are captured in a gas-phase simulation, it appears that these are intrinsic properties of the chromophore that may be altered, but not necessarily triggered by the surrounding environment of the retinal chromophore in the process of vision.

The energetics shown in Figure 2 suggests that once the barrier in the excited state is surmounted, the molecule has access to the conical intersection region that presumably controls the branching ratio between the 9-cis and all-trans photoproducts. At the conical intersection, the reactive ϕ_9 torsion coordinate is twisted further to ~90° from ~0° at the S_1 minimum and ~26° at the S_1 saddle point.

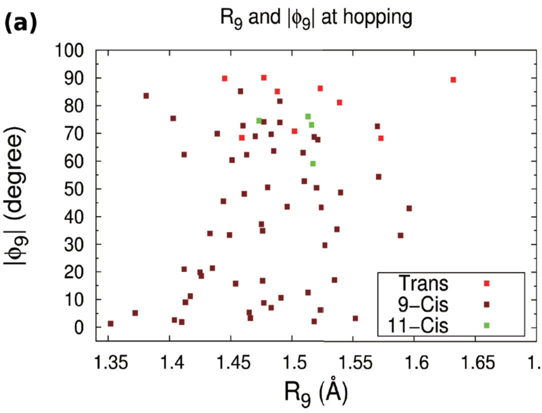


Figure 3. The diagram for the bond length and the absolute value of the dihedral angle of the dihedral angle C_8–C_9–C_{10}–C_{11} ($|\phi_9|$) at the instance of transition from the excited state to the ground state.

Figure 3(a) shows the diagram of the bond distance C_9–C_{10} and the absolute value of the dihedral $|\phi_9|$ of twisted bond at the instance of hopping for all the trajectories. We note that at smaller values of $|\phi_9|$, the trajectories show strong tendency to return to the starting reagent, the 9-cis form. It appears that it is necessary for $|\phi_9|$ to be greater than ~70° at the time of hopping for successful photoisomerization to the all-trans form. Many of trajectories make transition prematurely before reaching the conical intersection region which connects to the all-trans form. The premature transition would be caused by the trajectory trap in the well in the excited state. This mechanism explains the smaller quantum yield of 9-cis retinal.

The type of photoproduct generated is weakly dependent on the C_9–C_{10} bond length with all sorts of photoproducts generated within a region of $R_9 > 1.45$ Å and $R_9 < 1.6$ Å. On the other hand, at bond lengths shorter than 1.45 Å, photoisomerization to the all-trans form is unlikely to succeed. That is, the C_9–C_{10} bond needs to be stretched for successful photoisomerization. A sole trajectory where $R_9 > 1.6$ Å at transition resulted in the formation of the all-trans form. While it is necessary for the R_9 coordinate to be stretched, this is not necessarily a guarantee that formation of the all-trans form will succeed when this condition is met. The branching ratio at the 9-cis-all-trans conical intersection is more likely to be controlled by ϕ_9 rather than R_9.

In line with the analyses of Strambi[5] and Ishida[4] on the mechanism of retinal photoisomerization in terms of the ϕ_9 and ϕ_{11} dihedrals, the topology map of isorhodopsin, rhodopsin, bathorhodopsin and conical intersections and other stationary points that interconnect these photoisomers is shown in Figure 4. The transition points in terms of ϕ_9 and ϕ_{11} are plotted using squares in the map. The transitions of trajectories leading to successful cis-trans isomerization of ϕ_9 tend to occur within a very limited region in the ϕ_9–ϕ_{11} space. Transition at failed photoisomerization occurs on a much wider range of ϕ. Nevertheless, the plot shows that only the second and fourth quadrants are populated, reflecting successful photoisomerization as well as failed one proceeds with the crankshaft or asynchronous bicycle-pedal photoisomerization mechanism. Transition from the excited state to the ground state during isomerization toward the 11-cis photoproducts clearly occurs near the conical intersection that connects the photoisomers. In the case of all-trans isomer formation, on the other hand, transition occurs near the 9-cis-all-trans conical intersection but with the ϕ_{11} dihedral heavily twisted as a consequence of a cooperative nonlocal motion of the carbon backbone in a crankshaft-like motion.

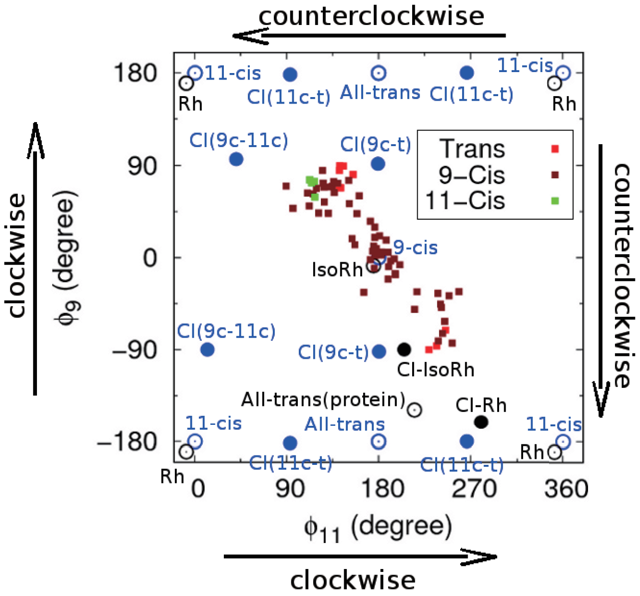


Figure 4. Diagram of the twist angle of $-C_{11}{=}C_{12}-$ (ϕ_{11}) and $-C_9{=}C_{10}-$ (ϕ_9) at the transition points. The minima and conical intersections obtained in the present and previous[4] calculations in vacuo are plotted in the diagram. The corresponding points in protein obtained by Strambi[5] are also plotted in open and filled circles.

An on-the-fly ab initio molecular dynamics simulation based on the Zhu-Nakamura theory is carried out on the cis-trans photoisomerization of a model protonated Schiff base of 9-cis retinal *in vacuo*. We have found an energy barrier with the $-C_8-C_9{=}C_{10}-C_{11}-$ angle (ϕ_9) twisted in the $^1\pi\pi^*$ S_1 state (see Figure 1). Many trajectories are trapped by the barrier and make transition prematurely before reaching the conical intersection region which connects to the all-trans form. This mechanism would explain the experimentally observed slower photoisomerization and lower quantum yield of isorhodopsin compared to rhodopsin (see Figure 2). The smaller pretwist of isorhodopsin would not be main reason for the slower reaction and the lower yield.

Dihedral angle ϕ_9 needs to be twisted to at least ~70° and the $C_9{=}C_{10}$ (R_9) intermolecular distance needs to be stretched to at least 1.45 Å in the excited state before nonadiabatic transition for successful photoisomerization to the all-trans form. The type of photoproduct formed is controlled by the degree of twist in the ϕ_9 dihedral where the transition to the ground state occurs. The slower velocity of the twist angle at the crossing region would be irrelevant to the lower yield in isorhodopsin because the products are not dependent on the velocity.

Cis-trans isomerization is an intrinsic property of 9-cis retinal that is not triggered although it may be altered by the opsin environment in isorhodopsin. A widely-accepted crankshaft or asynchronous bicycle-pedal photoisomerization mechanism of the retinal chromophore in rhodopsin is also found to be operative in isorhodopsin.

The processes that occur from photoexcitation to ground-state relaxation of the PSB of isorhodopsin in the gas phase are summarized as follows:

1. The $C_9{=}C_{10}$ bond R_9 is stretched to a single bond and the torsion coordinate ϕ_9 is twisted to as far as ±30° after photoexcitation.
2. The bond oscillates between single- and double-bond character while ϕ_9 also oscillates within ±30° while being trapped in the S_1 well.
3. The barrier is surmounted and crank shaft motion of the two angles of ϕ_9 and ϕ_{11} occurs toward the transition point to the ground state. The R_9 bond is predominantly single bond in character during transition. When $|\phi_9|$ is greater than about 70° at the transition point, an all-trans photoproduct is likely to result.
4. The molecule relaxes in the ground state as R_9 shrinks back to a double bond and $|\phi_9|$ approaches 0° and 180° depending on the resulting photoproduct.

It is suggested that lower efficiency of photoisomerization and slower response to photons in Schiff-base 9-cis retinal itself would be one of important reasons for human to evolve to choose 11-cis retinal in retinal. The effect by surrounding protein would not be a major one.

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2. Original Papers

1. W. M. I. Hassan, W. C. Chung, N. Shimakura, S. Koseki, H. Kono and Y. Fujimura Ultrafast radiationless transition pathways through conical intersections in photo-excited 9H-adenine, Phys. Chem. Chem. Phys., 2010, 12, 5317–5328.

3. Presentation at academic conferences

1. Wilfredo Credo Chung, Andreas Markmann, Noriyuki Shimakura, Hirohiko Kono, Wolfgang Domcke and Yuichi Fujimura Time-dependent quantum dynamics simulation of the $^1\pi\sigma^*$ photochemical relaxation of 9H-adenine 11th SPVM National Physics Conference and Workshop October 22-24,2009 Fr. Saturnino Urios University, Butuan City, Philippines. (Oral)

2. Wilfredo Credo Chung, Shinkoh Nanbu and Toshimasa Ishida Nonadiabatic ab initio dynamics of a model protonated Schiff base of 9-cis retinal 第7回 京都大学福井謙一記念研究センターシンポジウム 2009年12月4日 京都大学福井謙一記念研究センター 京都市 (Poster)
3. Chung Wilfredo Credo, 石田 俊正 Comparative Essential Dynamics of Protein-Protein Interactions 分子科学討論会2009 名古屋市 2009年9月21日～24日 (Poster)

4. Others

第69回岡崎コンファレンス 量子化学動力学の最先端 2010年2月21日(日)－23日(火) 岡崎コンファレンスセンター 愛知県岡崎市

Takahiro SAKAUE

FIFC Fellow
(To 15 May 2009)

1. Summary of the research of the year

A) Diffusion at interfaces

Consider a surface-active small particle at an interface (say, oil-water). This molecule, while staying around the interface, exhibits a (two-dimensional) lateral diffusion (Fig. 1). The main question here is "how is such a Brownian motion at the interface affected by the viscosities of surrounding fluids, $\eta_{\rm oil}$ and $\eta_{\rm water}$?"

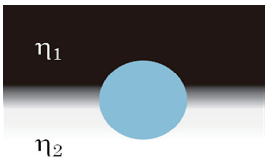


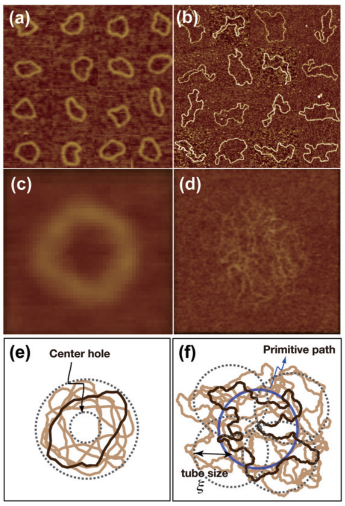
Fig. 1: A particle at interface

A naïve theory predicts that the diffusivity decreases with the increase in either $\eta_{\rm oil}$ or $\eta_{\rm water}$ (more precisely, with the increase in the average viscosity), which may well correspond to our natural intuition. However, a recent experiment has demonstrated that it is really not the case, and the diffusion coefficient as a function of $\eta_{\rm water}$ (with fixed $\eta_{\rm oil}$) exhibits a maximum! We point out the crucial role of out-of-interface fluctuation of the particle, and propose a generic scenario that the maximum corresponds to the iso-viscosity point ($\eta_{\rm oil} = \eta_{\rm water}$).

B) Statistical Physics of Planer Ring

Circular chains represent an important class of macromolecules found in living organisms as well as in modern biotechnologies. Although expected to be much different from those of linear polymers, their properties are not yet fully understood. The combined effect of topology and flexibility is for example dramatic on the shape of DNA minicircles and has raised important questions about the structure of DNA.

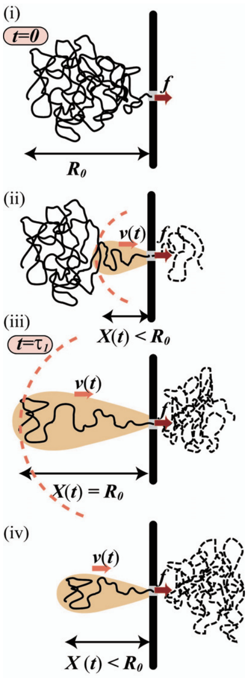
Here, using analytical and numerical approaches, we aim at unraveling the functional form of bond correlation function (BCF) of a circular chain confined in two dimensions over the entire range of flexibility $\chi \equiv L/l_p$, where L and l_p are the contour length and the persistence length of the chain. We first formulate a Gaussian theory by assuming that a ring takes a nearly circular shape with small fluctuations around it. Such a description is accurate in the ***stiff*** regime characterized by small χ. We then estimate the onset point χ^* at which this approximation breaks down. Finally, we argue that, in the ***flexible*** regime, the polymer adjusts its structure to a particular universal one as a result of the excluded volume and the topological constraints. The scaling properties in that universal regime are discussed based on the



self-confinement picture. The analytic BCF formulas are confirmed by extensive Lanvevin Dynamics simulations, and quantitatively agree with recent experimental data of DNA rings of various lengths adsorbed on a mica surface in two dimensions

Fig. 2: Images of DNA plasmids and simulation snapshots. (a) DNA mini-circles ($L \approx 230$ nm). (b) pSH1 plasmids ($L \approx 2016$ nm). (c) and (d) Superposition in the center-of-mass frame of pictures of (a) and (b), respectively. (e) and (f) Superposition in the center-of-mass frame of chain configurations from our simulations for $\chi \approx 7$, and $\chi \approx 110$.

C) Driven translocation of DNA



Flexible polymers, such as long DNA, RNA molecules and proteins, can pass through a narrow pore whose size is comparable to their molecular thickness. We highlight the richness and complexity involved in the dynamics of this unique mode of molecular transport, called ***translocation***, actively driven by external forces . In particular, the process takes place in the condition far-from-equilibrium accompanying of large conformational distortion in line with the propagation of the tensile force along the chain backbone. A general framework is proposed, which captures such essential features, whereby can account for reported various experimental data from a unified viewpoint.

Fig. 3: Schematics of the translocation process driven by the action of a moderate force. The front (represented by a dashed curve) separates the steady state region under tension (designated by the colored area) and the rear part as yet at rest.

2. Original papers

(1) A. Kato, E. Shindo, T. Sakaue, A. Tsuji and K. Yoshikawa,
"Conformational transition of giant DNA in a confined space surrounded by a phospholipid membrane",
Biophysical Journal, vol. 97, 1678-1686 (2009).

(2) M. Negishi, T. Sakaue and K. Yoshikawa,

"Mismatch of bulk viscosity reduces interfacial diffusivity at an aqueous/oil system",
Phys. Rev. E, vol. 81, 020901(R) (2010).

(3) T. Sakaue,
"Sucking genes into pores: Insight into driven translocation",
Phys. Rev. E, vol. 81, 041808 (2010)

(4) T. Sakaue, A. Mikhailov, R. Kapral,
"Nanoscale Swimmers: Hydrodynamic Interactions and Propulsion of Molecular Machines",
The European Physical Journal B, vol. 75, 381 (2010)

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3. Books

4. Presentation at academic conferences

(1) Takahiro Sakaue
"Diffusion at interfaces"
JPSJ Autumn meeting,Kumamoto, Sep. 2009

(2) Takahiro Sakaue
"Two topics on diffusion"
The 5th Kyushu University–Pukyong Natl University Joint Symposium on Sciences, Pukyong, Nov. 2009.

(3) Takahiro Sakaue
"Asymmetric response and fluctuation in nonequilibrium steady state"
Open Statistical Physics, Open University, Mar. 2010.

(4) Takahiro Sakaue, Takao Ohta
"Electro-rheology of immiscible blend under shear"
JPSJ annual meeting, Okayama, March, 2010.

5. Others

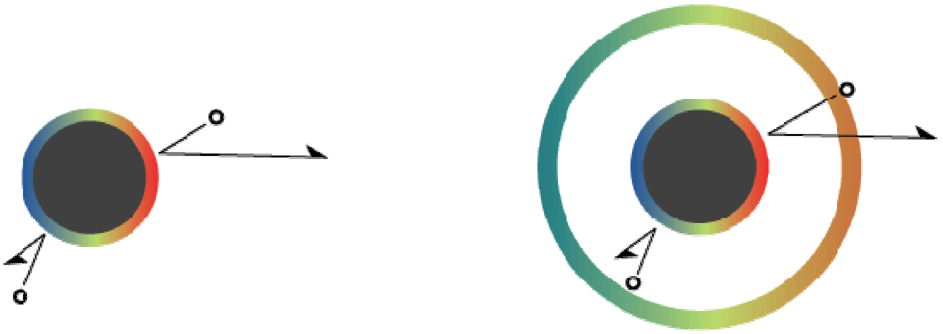
Takafumi IWAKI

FIFC Fellow
(From 1 Mar. 2010)

1. Summary of the research of the year (from March 1 to March 31, 2010)

Theoretical study of photophoresis of a liquid droplet

When a temperature has a gradient, it sometimes induces a convectional flow, coupled with a body force such as the gravity. This type of convection is called a natural convection, which is commonly recognized in our daily life. On the other hand, there are convections of which mechanisms rely on a more delicate effect upon a surface of the object. One example of this is the Marangoni convection arising from a gradient in surface energy, and another is the radiometric effect arising from an inelastic reflection of gas molecules at the solid surface with a temperature different from a gas. These two types of convection are really highlighted in mesoscopic systems, and their behaviors are not fully understood as compared with the natural convection. These convectional phenomena are particularly important in conjunction with the transportation of a micro object. When the object is transported through the radiometric effect from a temperature gradient induced by light absorption, this transportation phenomenon is called photophoresis.



a) Radiometric effect in a free molecular case.

b) The case of a slightly rarefied gas.

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

Since the discovery of the photophoresis a century ago, theoretical studies of photophoresis have focused on the photophoresis of a solid particle. On the other hand, the photophoresis of a liquid droplet is also important in a practical application. For the case of a droplet, the main difference from the case of a particle is an internal flow induced by two effects; a viscous stress from an external air flow and a Marangoni effect by a temperature gradient. Here, we theoretically analyzed the Navier-Stokes equation for a liquid region with the (linearized) Boltzmann equation (Eq.1) for a gas region coupled through a Maxwell-type boundary condition (Eq.2) with an accommodation coefficient $\alpha=1$ (complete condensation).

$$\partial_t f + \xi \cdot \nabla_{\mathbf{X}} f + \nabla_{\xi}(\mathbf{F}f) = J(f,f) \qquad (1)$$

$$f(\mathbf{X},\xi,t) = (1-\alpha) f(\mathbf{X},\xi - 2((\xi - \mathbf{v}_w)\cdot\mathbf{n})\mathbf{n},t) + \frac{\alpha\sigma_w}{(2\pi R T_w)^{3/2}} \exp\left(-\frac{\left|\xi - \mathbf{v}_w\right|^2}{2RT_w}\right)$$

$$[(\xi - \mathbf{v}_w)\cdot\mathbf{n} > 0] \qquad (2)$$

The solution for the linearized versions of Eqs.1 and 2 coupled with the Navier-Stokes equation for a liquid sphere was obtained by a spectral method in the second order and 5-th order for the system with an axial symmetry. The second-order solution (Fig.2) is not necessarily accurate, but stable with a large Peclet number, and is convenient for capturing a general behavior of the solution. When the Peclet number is less than 1, the Green function almost linearly increases with a normalized radial distance r', in which the temperature distribution is almost determined by heat conduction. As the Peclet number increases, the advection becomes to influence the temperature distribution. In this case, the surface temperature gradient is determined mainly by the heat source in the shell region near the surface of a droplet. It is notable that the photophoretic velocity and the Peclet number are linearly dependent on the surface temperature gradient, respectively. When light intensity becomes larger, the system shifts from a temperature diffusion dominant region to a temperature advection dominant region. According to this shift, the scaling exponent of the photophoretic velocity shifts from 1 to about 0.5.

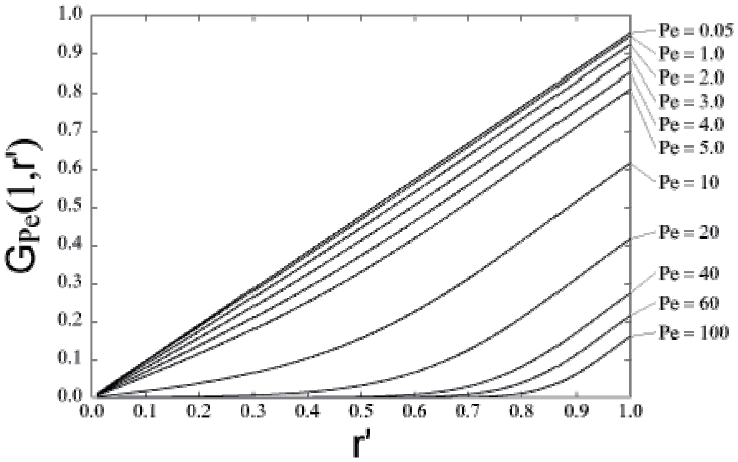


Figure 2: Green function of the surface temperature ($P_1(\cos\theta)$ component, where $P_n(x)$ is the Legendre polynomial of the n-th order) for a heat source function (P_1 component) of a radial distance r'. The Peclet number Pe corresponds to the magnitude of the internal flow.

Figure 3 is the 5-th order solution of the response function of the surface temperature (P_1 component) to a various heat source function in the form of $P_m(1-2r')P_n(\cos\ \theta)$. These response functions can be substituted for the Green function if the complete set of the response function for functional bases are given. A finite set of the response functions, however, is also useful to discuss an approximate behavior. Response functions for $P_1(\cos\ \theta)$ heat sources monotonically decrease as the Peclet number increases. On the other hand, response functions for other modes of heat source functions show a peak at around the Peclet number of 10. For a small Peclet number, an advection carries energy from other modes. For a large Peclet number, stirring by the advection becomes too strong and the temperature distribution is equalized in all modes.

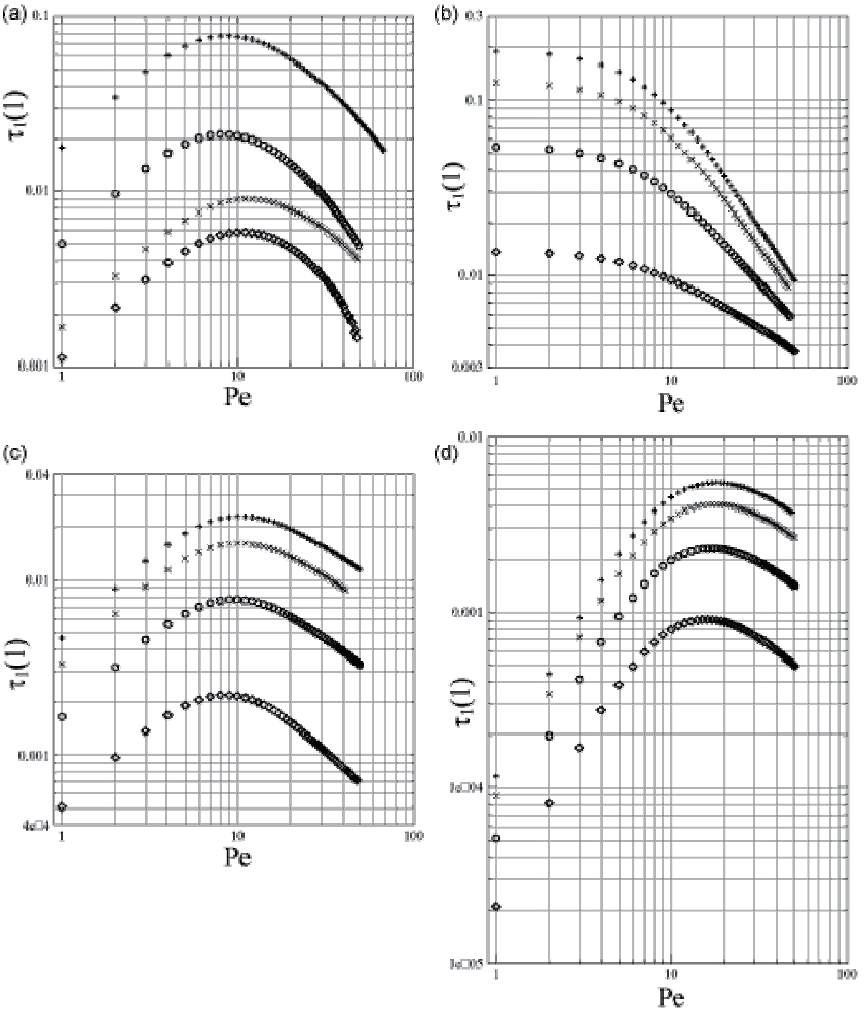


Figure 3: Temperature response functions at the surface in $P_1(\cos\ \theta)$ component for the heat-source function in the form of a) $P_m(1-2r')P_0(\cos\ \theta)$, b) $P_m(1-2r')P_1(\cos\ \theta)$, c) $P_m(1-2r')P_2(\cos\ \theta)$, and d) $P_m(1-2r')P_3(\cos\ \theta)$. The plus symbols are for m=0, the cross symbols are for m=1, the circles are for m=2, and the diamonds are for m=3.

In summary, when internal flow is slow, a temperature distribution inside the droplet is determined by the diffusion equation. In this case, the photophoretic velocity linearly scales to the radiation intensity. Only difference with the case of a solid sphere is its coefficient. When internal flow is fast, the temperature advection changes the behavior of the system in a qualitative manner. We observed an asymmetric flow field induced by a homogeneous mode of the radiation intensity distribution inside the droplet. While such a mixing of modes is a characteristic of nonlinear phenomena, this case has a much simpler explanation. A homogeneous mode is not an eigenmode for this system even if the hydrodynamic equation is linearized. On the other hand, since nonlinear coupling exists between the flow field and temperature field through the boundary condition, a nonlinear relation appears between the photophoretic velocity and the radiation intensity. For a sufficiently strong radiation intensity, the photophoretic velocity scales to the intensity with a scaling exponent of about 0.4, and the actual value depends on the intensity distribution inside the droplet. In addition, the radiation intensity can switch the dominant mode of the radiation distribution, and a threshold behavior is anticipated for the photophoretic velocity.

Original papers

(1) Takafumi Iwaki,
“Effect of internal flow on the photophoresis of a micro liquid droplet”,
in submission.

第７回
京都大学福井謙一記念研究センター シンポジウム

2009年12月4日（金）

- 開会の辞　榊　茂好（センター長）　9:30- 9:40
- ご挨拶　大嶌　幸一郎（京大・工学研究科長）　9:40- 9:50
- 中村　栄一（東大・理）　9:50-10:50
  「単一有機分子の動きを見る－化学物理学の新しい世界－」
- 大峯　巖（京大・福井センター）　11:00-12:00
  「水、その豊かな世界：ミクロの水の性質」

－昼休み－

- 石田　俊正（京大・福井センター）　13:30-14:20
  「光化学反応のシミュレーション－非断熱遷移反応動力学」
- 佐藤　徹（京大・福井センター）　14:30-15:20
  「振電相互作用とJahn-Teller効果」
- ポスターセッショ　15:40-17:40
- 懇親会（1F多目的ルーム）　18:00-19:30

京都大学福井謙一記念研究センター　3F大会議室
Fukui Institute for Fundamental Chemistry, Kyoto University
京都市左京区高野西開町３４－４
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問い合わせ先　石田　俊正（ishida@fukui.kyoto-u.ac.jp）

第７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　平成21年12月4日（金）

場所　京都大学福井謙一記念研究センター（３Ｆ　大会議室）

- 開会の辞　　榊　茂好　（センター長）　9:30- 9:40
- ご挨拶　　大嶌　幸一郎　（京大・工学研究科長）　9:40- 9:50
- 中村　栄一（東大・理）　9:50-10:50

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- ポスターセッション　15：40-17：40
- 懇親会（1F多目的ルーム）　18：00-19：30

ポスターセッション　15:40-17:40(大会議室)

※ 番号が奇数の方は前半(15:40-16:40)に、番号が偶数の方は後半(16:40-17:40)にポスターの場所にて発表を行ってください。

1. ONIOM Study on a Missing Piece in Our Understanding of Heme Chemistry: Bacterial Tryptophan 2,3-Dioxygenase (TDO)
   (FIFC, Spring8) ○Lung Wa Chung, Xin Li, Hiroshi Sugimoto, Yoshitsugu Shiro and Keiji Morokuma*

2. Annealing of Hot Giant Fullerene in presence of buffer gas: DFTB/MM MD simulations
   (FIFC) ○B. Saha, S. Irle, K. Morokuma

3. DFT and ONIOM(DFT:MM) studies of *myo*-inositol oxygenase
   (FIFC) ○Hajime Hirao and Keiji Morokuma

4. On the mechanism and stereochemitry of the Rh-catalyzed polymerization of phenylactylene
   (FIFC) ○Zhuofeng Ke

5. Free Energy optimization in ONIOM scheme.
   (FIFC) ○Tsutomu Kawatsu, Keiji Morokuma

6. QM/MD Simulations of Single-Walled Carbon Nanotube Nucleation, Growth and Healing on Transition-Metal Catalysts
   ○Alister J. Page (FIFC), Yasuhito Ohta (Nara Women's University), Stephan Irle (Nagoya University), Keiji Morokuma (FIFC)

7. Chemical Bonding in Transition Metal Complexes with Beryllium Ligands
   (FIFC) ○Pattiyil Parameswaran and Gernot Frenking

8. mno Rule for Condensed Boranes vs. Mingos' Rule for Condensed Transition Metal Clusters: The Missing Link
   (FIFC) ○Susmita De and Eluvathingal D. Jemmis

9. Non-adiabatic ab initio dynamics of a model protonated Schiff base of 9-cis retinal
   ○Wilfredo Credo Chung (FIFC), Shinkoh Nanbu (Sophia U) and Toshimasa Ishida (FIFC)

10. 原子分子集合体の構造変化運動の超球モード解析
（早大基幹理工）○柳尾朋洋

11. Ras-GAP 内での GTP 加水分解反応に関する理論的研究
（分子研）○東　雅大、小林　千草、斉藤　真司

12. Double core-hole states of small molecules
（分子研）○田代基慶、江原正博、福澤宏宣、上田潔、 C.Buth、L.S.Cederbaum

13. A theoretical study on the structural change of the N-terminal domain of PYP
(FIFC, Chem. Dept., Nagoya Univ.) ○Motoshi Kamiya, Iwao Ohmine

14. Density-Functional Tight-Binding Studies of Pristine and N-Vacancy Defects in Hexagonal Graphene Flakes
Lili Liu,[1] Francisco J. Martín-Martínez,[2] Jose A. Dobado,[2] Stephan Irle[1] [1]Nagoya University, Japan [2]Universidad de Granada,

15. Early Stages in the Nucleation Process of Carbon Nanotubes: Density Functional Tight Binding Molecular Dynamics Simulations on Acetylene Polymerization on Fe_{38} Cluster
（Nagoya University）Ying Wang, Yosgiko Ohta, Hu-jun Qian, Stephan Irle, Keiji Morokuma

16. ReaxFF simulation of fullerene formation in benzene combustion
（Nagoya University）Hu-Jun Qian, Stephan Irle.

17. DNA 中の核酸塩基の励起状態に関する理論的研究
（1.量子化学研究協会、2.京大院理）○宮原友夫[1]、杉山弘[2]、中辻博[1]

18. 有機高スピン分子の零磁場分裂テンソルの第一原理計算
（阪市大院理）○杉崎研司・豊田和男・佐藤和信・塩見大輔・工位武治

19. 零磁場分裂のスピン-スピン項の理論計算について
（大阪市立大理）○豊田和男、杉崎研司、佐藤和信、塩見大輔、工位武治

20. CW・パルス ESR 分光法による弱交換相互作用ビラジカルの電子構造に関する研究
○文部一希、佐藤和信、伊瀬智章、杉崎研司、中澤重顕、森田靖、豊田和男、塩見大輔、北川勝浩、工位武治

21. 正方対称テトラニトロキシドラジカルの交換相互作用の決定 －2次元量子ビットモデル系の構築を目指して－

(阪市大院理) ○野﨑 幹人, 中澤 重顕, 杉﨑 研司, 佐藤 和信, 塩見 大輔, 豊田 和男, Aaron S. Micallef, Graeme R. Hanson, 北川 勝浩, 工位 武治

22. Weakly Exchange-Coupled Biradicals as Electron Two-Qubit Systems: Determination of the Spin Dipolar and Exchange Interactions by Single-Crystal Pulse-ELDOR Experiments

（[1] 阪市大院理・[2] 近大理工・[3] 阪大院理・[4] 阪大院基礎工・[5] ブルカーバイオスピン・[6]JST-CREST）○中澤重顕[1,6]・藤和信[1,6]・吉野共広[1]・伊瀬智章[1,6]・西田辰介[1,6]、森展之[1]・Robabeh Rahimi[2]・森田靖[3,6]・豊田和男[1]・塩見大輔[1]・北川勝浩[4,6]・中筋一弘[3]・原英之[5]・Patrick Carl[5]・Peter Hofer[5]・工位武治[1,6]

23. パルス電子-電子二重共鳴法によるクラウンエーテル置換ビラジカルの超分子構造の研究

(阪市大院理) ○神崎祐貴, 塩見大輔, 沢井隆利, 中澤重顕, 佐藤和信, 岡田惠次, 工位武治

24. パルス ENDOR 法を用いた分子スピンバス量子コンピュータモデル系 $\mathrm{DP^{15}NO}$-d_8 の Bell 状態の生成と評価

（[1] 阪市大院理・[2] 近大理工・[3] 阪大院理・[4] 阪大基礎工・[5]JST-CREST）○吉野共広[1,5]・西田辰介[1,5]・中澤重顕[1,5]・佐藤和信[1,5]・Robabeh RAHIMI[2]・豊田和男[1,5]・塩見大輔[1,5]・森田靖[3,5]・北川勝浩[4,5]・工位武治[1,5]

25. 開殻分子系の非線形光学効果とジラジカル因子の実験的推定

○中野雅由（阪大院基礎工）、米田京平（阪大院基礎工）、鎌田賢司（産総研関西センター）、太田浩二（産総研関西センター）、久保孝史（阪大院理）

26. LC-UDFT 法による開殻一重項分子系の静的第二超分極率の計算

（阪大院基礎工）○岸 亮平、Sean Bonness、米田 京平、高橋 英明、中野 雅由

27. 三角形グラフェンナノフレークからなる開殻分子系のスピン状態とジラジカル性の構造依存性

（阪大院基礎工）○米田京平 永井広梓 岸亮平 高橋英明 中野雅由

28. 二重環状分子集合体モデルにおけるエキシトン回帰運動の環径依存性に関する研究

（阪大院基礎工）○南拓也、岸亮平、高橋英明、中野雅由

29. 一重項ジラジカル分子とそのラジカルイオンの第二超分極率に関する理論的研究

（阪大院基礎工） ○福井仁之、米田京平、岸亮平、高橋英明、中野雅由

30. 四角形グラフェンナノフレークのジラジカル因子とスピン分極の理論的研究

（阪大院基礎工）○永井広梓、米田京平、岸亮平、高橋英明、中野雅由

31. 非断熱化学動力学における半古典理論

（九大院理・上智大理工・レブデフ物理研）○斉田謙一郎、Alexey D. Kondorskiy、南部伸孝

32. Binding free energy calculation of β-lactam inhibitors in the covalent complex with methicillin-resistance S.Aureus

（Ha Noi University of Science）○Nguyen Hoa My, Dang Ung Van, Truong Nguyen Thanh

33. Folding pathways of human telomeric type-1 and type-2 G-quadruplex structures

（京大院理[1]、NEC ソフト[2]） ○眞下知子[1]、三戸祐太[1]、八木博隆[2]、杉山弘[1]

34. 鎖状構造結晶セレンの電子・振動物性の理論的研究

(京大・院) ○松井正冬

35. 15,16,17 族ジヘテロ元素化合物と炭素ラジカルのホモリティク置換反応に関する研究

（[1]京大化研, [2]京大福井センター）○茅原 栄一[1]、山子茂[1]、Lung Wa Chung[2]、諸熊奎治[2]

36. 場の理論によるガラス転移の研究 -結合角秩序変数の役割について-

(京都大学基礎物理学研究所)○黒岩健, 早川尚男

37. 氷の真空紫外光分解による振動回転励起した水素分子の生成

（京大院・工）羽馬哲也、横山正明、岡田加奈、藪下彰啓、○川﨑昌博 （北大・低温研）渡部直樹 （Univ.of Bristol）Michael N.R. Ashfold （Queen's Univ.）Hans-Peter Loock

38. アモルファス氷の光分解により生成したOHラジカルの直接検出

（京大院・工）○横山正明、岡田加奈、羽馬哲也、藪下彰啓、川﨑昌博 （Leiden Univ.）Stefan Andersson

39. アモルファス氷からの水分子の真空紫外光脱離機構

（京大院・工）○岡田加奈、横山正明、羽馬哲也、藪下彰啓、川﨑昌博 （北大・低温研）渡部直樹 （Leiden Univ.）Stefan Andersson （Univ. of Bristol）Richard N. Dixon, Michael N.R. Ashfold

40. 光化学系 II における光合成反応中心の励起状態に関する理論的研究

(京大院・工) ○北川裕也、長谷川淳也、松田建児

41. 半屈曲性高分子一本鎖の線形粘弾性

（京大理） ○平岩徹也、太田隆夫

42. 蛋白質の揺らぎを考慮した自由エネルギー計算
（京大院理） ○小杉貴洋、林重彦

43. 溶液内励起状態反応の理論的研究 ～動的電子相関の重要性について～
(京大院理)○森俊文、中野勝博、加藤重樹

44. 氷表面における化学反応の理論研究
(京大院理)○安部 賢治 、加藤 重樹

45. 7-アザインドール２量体の励起状態ダブルプロトン移動反応の反応ダイナミクスに対する理論的研究
（京大院・理) ○安藤耕平、加藤重樹

46. QM/MM 法による溶液内化学反応の自由エネルギー計算
（京大理）○山本武志

47. ポルフィリン連結フラーレン・単層カーボンナノチューブ複合３元クラスター修飾半導体電極の膜構造と光電気化学特性/Film Morphology and Photoelectrochemical Properties of Semiconducting Electrodes Modified with Ternary Composite Clusters of Porphyrin- Fullerene Linked Dyads and Single-Walled Cabon Nanotubes
（京大院工・iCeMS） ○河島史明、手塚記庸、梅山有和、俣野善博、今堀 博

48. Synthesis, Structures, and electrochemical properties of Naphthalene-fused phosphole derivatives
(京大院工・京大 iCeMS・京大化研)○A. Saito, T. Miyajima, Y. Matano T. Fukushima, H. Kaji, H. Imahori

49. ホウ素－塩素結合の触媒的活性化：アルケンを有機基供与源とするパラジウム触媒環化カルボホウ素化反応
（京大院工）○中田加那予、杉野目道紀

50. イソインドリンの触媒的脱水素化／C-H ボリル化によるボリルイソインドールの合成
（京大院工） 大村智通、○木嶋昭仁、杉野目道紀

51. 電子状態計算によるセルロースオリゴマーの熱分解におけるレボグルコサン生成機構の解明
（京大院工）○細谷隆史、中尾嘉秀、佐藤啓文、榊 茂好

52. Bonding Nature and Electronic Structure of New Ethynediyl-Bridged Bis(Silylene) Dinuclear Tungsten Complex: A Theoretical Study
（京大院工）○Mausumi Ray, Yoshihide Nakao, Hirofumi Sato, Shigeyoshi Sakaki

53. 吸収・発光スペクトルに関する理論的研究:温度を取り込んだ短時間ダイナミクス法によるピーク幅の評価

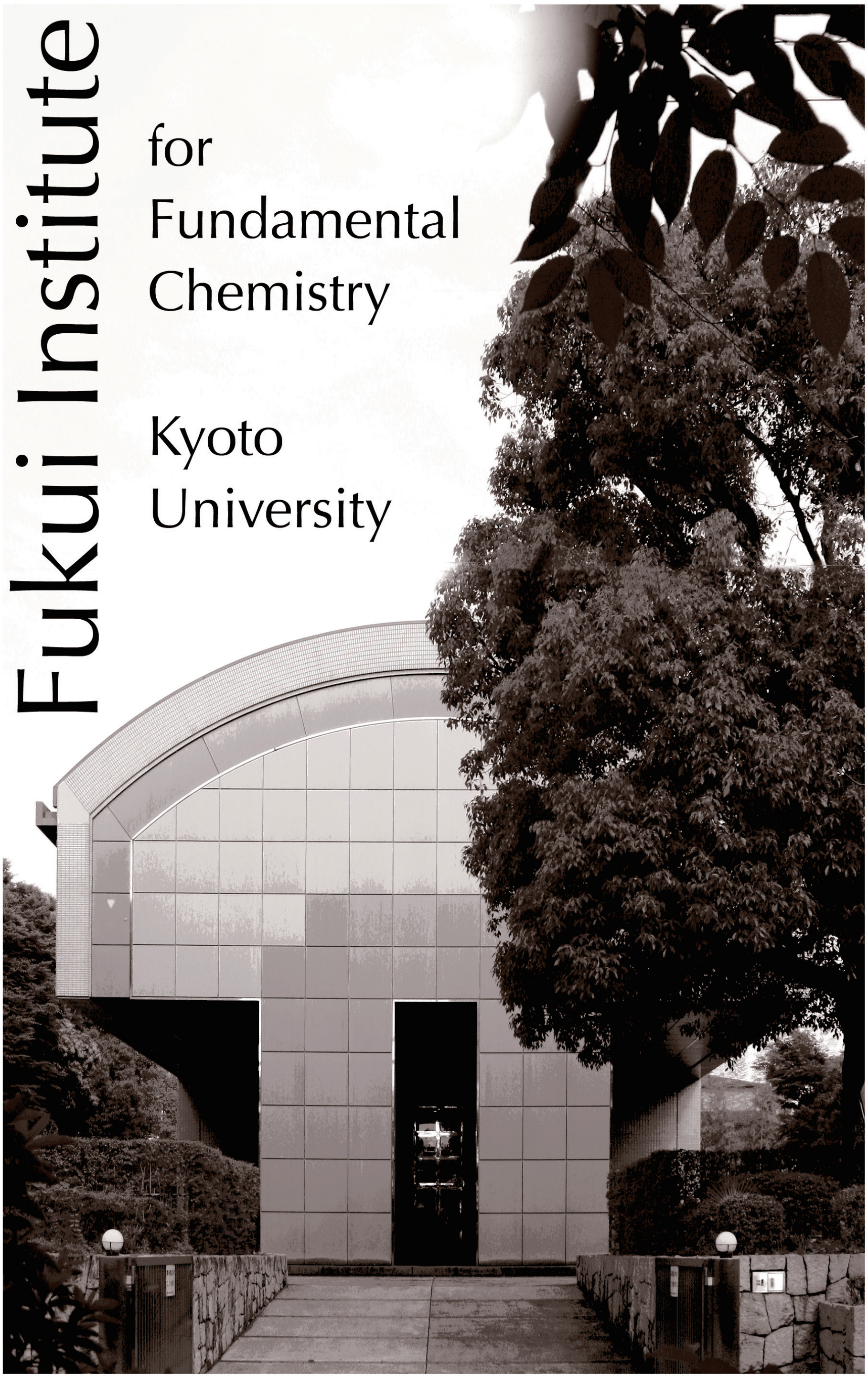
(京大院工[1]、京大福井センター[2])　○齋藤 健[1]、中尾 嘉秀[1]、佐藤 啓文[1]、榊 茂好[1,2]

54. カテコールジオキシゲナーゼ機能モデル錯体の LMCT 吸収に関する理論的研究

（京大院工・京大福井セ）○中谷直輝、中尾嘉秀、佐藤啓文、榊茂好

55. ジメチルピラゾラト架橋六核錯体の発光現象に関する理論的研究

（京大院工）○中尾 嘉秀、榊 茂好



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第7回福井謙一記念研究センターシンポジウム
2009年（平成21年）12月4日（金）
京都大学福井謙一記念研究センター

第7回
福井センターセミナー

2010年2月4日(木)　15:00-17:00
〒606-8103　京都市左京区高野西開町34-4
京都大学福井謙一記念研究センター（℡075-711-7708)
3F 大会議室
http://www.fukui.kyoto-u.ac.jp/

15:00～15:30　**Zhuofeng Ke**　（福井センター）

"Theoretical Study of the Rh-Catalyzed Polymerization of Phenylacetylene"

15:30～16:00　**Hajime Hirao**　（福井センター）

"QM/MM Computational Studies of Metalloenzymes: Characterization of Elusive Intermediates and Elucidation of Reaction Mechanisms"

16:00～17:00　**Arnout Ceulemans**
(Catholic University of Leuven)

"Frustration in Jahn-Teller systems"

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Program

July 19 (Sun): CREST Symposium

9:00	Shigeyoshi Sakaki, FIFC Director		Opening Remarks

CREST Bio Session
Chair: Shigehiko Hayashi

9:10	Richard A. Friesner	C-01	Density functional based QM/MM studies of metalloprotein active sites
9:40	Kazunari Yoshizawa	C-02	QM/MM Study on Oxygenation Enzymes
10:10	Todd Martinez	C-03	Photobiology and mechanochemistry from first principles
10:40	Break		

Chair: Toshiaki Matsubara

11:00	Junya Hasegawa	C-04	Excited states of photofunctional molecules in protein environments
11:30	Qiang Cui	C-05	Multi-scale models of biomolecular processes: developments and applications
12:00	Weitao Yang	C-06	Free energies and mechanism of chemical reactions in solution and in enzymes with ab initio QM/MM method
12:30-13:30	Lunch		

CREST Transition Metal Session
Chair: Djamaladdin G. Musaev

13:30	Feliu Maseras	C-07	Cross-coupling reactions: calculations do help mechanistic understanding
14:00	Chantal Daniel	C-08	From small to large transition metal complexes: quantum theory of electronic excited states
14:30	Christophe Bichara	C-09	Modeling Nickel-Carbon alloys to study the catalytic synthesis of Carbon Nanotubes
15:00	Break		

CREST Nano Session
Chair: Alister Page

15:30	Gustavo E. Scuseria	C-10	Carbon nanotubes and grapheme nanoribbons
16:00	Kim Bolton	C-11	Computational studies of single-walled carbon nanotube growth
16:30	Susumu Saito	C-12	Abundance of C60 revisited: A microscopic formation process of fullerenes
17:00	Stephan Irle	C-13	Density-functional tight-binding molecular dynamics simulations of carbon nanotube formation
17:30	Shigeo Maruyama	C-14	Nucleation of a Single-Walled Carbon Nanotube inside a Nanotube
18:00	Keiji Morokuma		Welcome Reception

July 20 (Mon): "Birthday" Symposium

Molecular Structure & Functions Session

Chair: Seiji Mori

9:00	Shigeyoshi Sakaki	B-01	CCSD(T) Study of Large Transition Metal Complexes with Frontier-Orbital-Consistent Effective Potential
9:30	Suehiro Iwata	B-02	Perturbation Expansion Based on Absolutely Local Excited Molecular Orbitals and Application to Molecular Clusters

Chair: Alexander Mebel

10:00	Masanori Tachikawa	B-03	Nuclear Quantum Effect on Hydrogen Bonded Systems
1030	Break		
11:00	Michael J. Frisch	B-04	Recent Advances in the Exploration of Potential Energy Surfaces and the Prediction of Vibrational Spectra

Chemical Reactions and Dynamics Session

Chair: Ulf Ryde

11:30	Seiji Mori	B-05	Important insight into Reaction Mechanisms of Organic Syntheses and Biosyntheses from View of Computational Chemistry
12:00	Kazuo Kitaura	B-06	Quantum-chemical calculations of large biomolecules with the fragment molecular orbital method
12:30-13:30	Group Picture & Lunch		

13:30-15:30 2hr poster session

Chair: Junya Hasegawa

15:30	Djamaladdin G. Musaev	B-07	Computation aided catalyst design: visible light-driven water oxidation
16:00	Koichi Yamashita	B-08	Quantum transport of single molecules and solid interfaces
16:30	Alexander M. Mebel	B-09	Growth mechanisms of large organic molecules in low-temperature conditions of Titan's atmosphere: from polyynes to PAH
17:00	Break		
17:20	Toshiaki Matsubara	B-10	Application of the ONIOM-molecular dynamics method to the chemical reactions. A new theory of chemical reactivity
17:50	Satoshi Yabushita	B-11	Theoretical study on the f-f transition intensities of lanthanide trihalide systems
18:20	Mori, Tachikawa		Poster Award Ceremony
19:00-21:00	Kazuo Kitaura, Stephan Irle		Birthday Party

July 21 (Tue): CREST Symposium

CREST Nano Session
Chair: Stephan Irle

9:00	Boris I. Yakobson	C-15	Relaxation mechanisms in nanostructures through theory and computations
9:30	Henryk A. Witek	C-16	When finite becomes infinite...
10:00	Atsushi Oshiyama	C-17	Nanometer-scale shapes that produce unusual properties of carbon nanomaterials
10:30	Break		
11:00	Younghee Lee	C-18	Engineering electronic structures of carbon nanotubes: Theory and experiment
11:30	Shigeru Nagase	C-19	Structures and reactions of endohedral metallofullerenes

CREST Comp Chem in Industry Session
Chair: Masanori Tachikawa

12:00	Shinichiro Nakamura	C-20	Theoretical Chemistry in Chemical industrial researches
12:30-13:30	Lunch		

CREST Bio Session
Chair: Kazunari Yoshizawa

13:30	Ulf Ryde	C-21	A comparison of different methods to calculate reaction energies in proteins
14:00	Shigehiko Hayashi	C-22	Molecular mechanisms of enzymatic activities in motor and photoreceptor proteins
14:30	Shigenori Tanaka	C-23	Large-scale biomolecular simulations based on the fragment molecular orbital method
15:00	Lung Wa Chung	C-24	Our ONIOM journey of metalloenzymes and photobiology
15:30	Walter Thiel	C-25	QM/MM studies of enzymatic reactions
16:00			Adjourn

International Symposium on Theory of Molecular Structure, Function and Reactivity
and
CREST International Symposium on Theory and Simulations of Complex Molecular Systems
1:30-3:30 pm on July 20, 2009

Ver.6 (July 7,2009)

Poster Program
JENESYS participants (including award applicants)

P-01	**Effect of hydrogen bonds to the OH stretching mode of bicarbonate in aqueous solution** Viwat Vchirawongkwin and Saowapak Kasemsook *Faculty of Science, Chulalongkorn University*	general
P-02	**Computational Study of a Bicyclic Cyclophane Nitrate Receptor** Huifang Xie and Ming Wah Wong *National University of Singapore*	general
P-03	**Reliable DFT Method for Determining Bond Dissociation Enthalpies: The Case of Green Inhibitors (Poster)** Pham Cam Nam, Le Minh Duc, Minh Tho Nguyen *Danang University of Technology*	young award
P-04	**Systematic investigation on the methodology in the binding of GW420867X as NNRTI by using quantum chemical calculations** Patchreenart Saparpakorn, Peter Wolschann, Alfred Karpfen, Pornpan Pungpo, Supa Hannongbua *Kasetsart University*	young award
P-05	**How does single water play a role in the binding pocket of wild type and Y181C HIV-1reverse transcriptase with nevirapine, examined by molecular dynamics simulations and MM-PBSA calculations** Witcha Treesuwan and Supa Hannongbua *Kasetsart University*	young award
P-06	**First-Principle Studies of Straight Armchair//Zigzag Carbon Nanotube Junctions for Molecular Device Architectures** Anurak Udomvech and Teerakiat Kerdcharoen *Faculty of Science, Thaksin University*	young award
P-07	**Effects of Tube Diameter and Boron-Nitrogen Doping on Electronic Structure of single-walled carbon nanotubes** Arthit Vongachariya,Vudhichai Parasuk, and Thiti Bovornratanaraks *Chulalongkorn University*	student award

Poster Program
Award applicants

P-08 **Zinc-Homocysteine binding in Cobalamin-dependent methionine synthase** young award
S. Abdel-Azeim, X. Li, L. W. Chung., K. Morokuma
Fukui Institute for Fundamental Chemistry, Kyoto University

P-09 **Structural and electronic properties of chiral SiC nanotubes** young award
G. Alfieri, T. Kimoto
Kyoto University

P-10 **Molecular Single-Bond Covalent Radii for Elements 1 - 118** young award
Pekka Pyykko, Michiko Atsumi
University of Helsinki

P-11 **Reaction Mechanism for the Formation of Pyridine-2-one and Pyridine-2-thione from Cobaltacyclopentadiene with Isocyanate and Isothiocyanate. A Theoretical Study** young award
AbdelRahman A. Dahy and Nobuaki Koga
Nagoya University

P-12 **DFT and ONIOM(DFT:MM) Studies of myo-Inositol Oxygenase** young award
Hajime Hirao and Keiji Morokuma
Kyoto University

P-13 **Hydrogen atom and graphite surfaces interaction by molecular dynamics, Monte-Carlo and ab-initio calculations** young award
Atsushi Ito, Takahiro Kenmotsu, Kaoru Ohya, Kenmotsu Inai, Ying Wang, Stephan Irle, Keiji Morokuma, and Hiroaki Nakamura
National Institute for Fusion Science

P-14 **Palladium-Catalyzed C-H Bond Amination: Mechanistic Study and Computer-Aided Catalyst Design** young award
Zhuofeng Ke, Thomas R. Cundari
Fukui Institute for Fundamental Chemistry, Kyoto University

P-15 **Symmetric Band Structures and Asymmetric Ultrafast Electron and Hole Relaxations in Silicon and Germanium Quantum Dots: Time-Domain Ab Initio Simulation** young award
Kim Hyeon-Deuk, Angeline B. Madrid, and Oleg V. Prezhdo
Kyoto University

P-16 **Quantum Monte Carlo Study of Positronic Hydrogen Cyanide Molecule** young award
Yukiumi Kita, Ryo Maezono, and Masanori Tachikawa
Yokohama-City University

P-17 **A Theoretical Study on the Nature of On- and Off-States of Reversibly Photoswitching Fluorescent Protein Dronpa** young award
Xin Li, Lung Wa Chung, Hideaki Mizuno, Atsushi Miyawaki and Keiji Morokuma
Kyoto University

P-18 **DFT Calculations of the CN and NH_2 Substitutional Effects on the Geometrical and Optical Properties of Vinyl-Fluorenes Model** young award
Wichanee Meeto, Songwut Suramitr, Vladimír Lukeš, Peter Wolschann, Supa Hannongbua
Kasetsart University

P-19 **Healing of SWNTs During Growth via Ring Isomerization: Towards (n,m) Chirality Control** young award
Alister J. Page, Yasuhito Ohta, Yoshiko Okamoto, Stephan Irle, Keiji Morokuma
Kyoto University

P-20 **Surface Diffusion Dynamics of a Single Polymer Chain in Dilute Solution** young award
Hu-Jun Qian, Zhong-Yuan Lu
Institute for Advanced Research

P-21 **Neutral vs. Zwitterionic forms of SAH ? Comparison Interaction of the Mycolic Acid Cyclopropane Synthase as Tuberculosis Targets with SAH Cofactors: An ONIOM Study** young award
Darinee Sae-Tang and Supa Hannongbua
Kasetsart University

P-22 **Density functional method including weak interactions: dispersion coefficients based on the local response approximation** young award
Takeshi Sato, Hiromi Nakai
Waseda University

P-23 **Chemisorption of Hydrogen on Graphite (0001): Spin-Polarized** young award

Density-Functional Tight-Binding Molecular Dynamics Simulations Using G2MS-Derived C-H Parameters
Ying Wang, Atsushi Ito, Hiroaki Nakamura, Stephan Irle,and Keiji Morokuma
Nagoya University, Kyoto University

P-24 **Molecular and Electronic Structures of Di-erbium and Di-erbium-carbide Metallofullerenes $Er_2(C_2)@C_{82}$: Density Functional Theory Calculations** young award
Jian Wang, Stephan Irle, and Keiji Morokuma
Nagoya University, Kyoto University

P-25 **Ab Initio Studies on the Nonradiative Decay Mechanisms of Guanine and Xanthine** young award
Shohei Yamazaki, Andrzej L. Sobolewski, and Wolfgang Domcke
Technical University of Munich

P-26 **Development of efficient computational scheme for four-component relativistic GMC-QDPT and application to molecular systems** student award
Ryo Ebisuzaki, Yoshihiro Watanabe, Haruyuki Nakano
Kyushu university

P-27 **Density-functional tight-binding molecular dynamics simulations of the self-capping process in open-ended (n,n) SWCNTs (n=3 to 10)** student award
Hironori Hara, Genki Ichinose, Stephan Irle
Nagoya University

P-28 **The analysis of sodium hydroxide water cluster by using ab initio path integral molecular dynamics** student award
Akihito Koizumi, Motoyuki Shiga, Masanori Tachikawa
Graduate School of Nanobioscience, Yokohama-City University

P-29 **Density-Functional Tight-Binding Studies of Pristine and N-Vacancy Defects in Hexagonal Graphene Flake** student award
Lili Liu, Francisco J. Martin-Martinez, Jose A. Dobado, Stephan Irle
Institution of Advanced Research, Nagoya University

P-30 **Study of amino acid models for coarse graining of protein.** student award
Shunsuke Mieda, Misako Aida
Hiroshima University

P-31 **Two-Mode Circular-Polarized Laser Control of Exciton Recurrence Motion on Double-Ring-Shaped Aggregate Model** student award
Takuya Minami,Hitoshi Fukui, Hiroshi Nagai, Kyohei Yoneda, Ryohei Kishi, Hideaki
Osaka University

P-32 **Development and Application of ab initio Docking Procedure Based on the FMO-ONIOM Method** student award
Sayaka Motoyoshi, Kenji Yamagishi, Sachiko Yamada and Hiroaki Tokiwa
Rikkyo University

P-33 **Alternating Copolymerization of Polar Vinyl Monomers with Carbon Monoxide** student award
Akifumi Nakamura, Kagehiro Munakata, Takuya Kochi, Lung Wa Chung, Keiji Morokuma, Kyoko Nozaki
School of Engineering, The University of Tokyo

P-34 **Dioxygen Binding Mechanism of the Iron(III) Catechol Dioxygenase: A CASPT2 Study** student award
Naoki Nakatani, Yoshihide Nakao, Hirofumi Sato, and Shigeyoshi Sakaki
Graduate School of Engineering, Kyoto University

P-35 **Benchmark Studies of Acetone Interaction on Graphite Surface** student award
Yoshifumi Nishimura, Takao Tsuneda, and Stephan Irle
Nagoya University

P-36 **Theoretical Studies on Endoperoxide O-O Bond Cleavage Catalyzed by Iron Porphyrin Complexes** student award
Jun Ochiai, Tetsuya K. Yanai, Seiji Mori, and Tsunehiko Higuchi
Ibaraki University, Nagoya City University

P-37 **Theoretical Study of Tungsten Dihydride Silyl Complex: Non-Classical Bonding Nature and Novel Fluxional Behavior** student award
Mausumi Ray, Yoshihide Nakao, Hirofumi Sato, Shigeyoshi Sakaki
Kyoto University

P-38 **Unusual Reaction Catalyzed by Cytochrome P450: Density Functional Studies on Prostacyclin Biosynthesis** student award
Tetsuya K. Yanai, Seiji Mori
Ibaraki University

P-39 **Nonlinear optical properties of rhombic and bow-tie shaped graphene nanoflakes in open-shell singlet states** student award

Kyohei Yoneda,Hiroshi Nagai, Hitoshi Fukui, Takuya Minami, Ryohei Kishi,
Hideaki Takahashi, Takashi Kubo, Masayoshi Nakano
Osaka University

Poster Program for General Participants

P-40 **Theoretical study on the S_1-S_0 relaxation pathways of realistic diphosphenes**
Yoshiaki Amatatsu
Akita University

P-41 **Theoretical study on the gold catalyzed C-S bond formation of α-thioallenes**
Kaori Ando
Gifu University

P-42 **Quantum Cluster Theory for the Polarizable Continuum Model.**
Roberto Cammi
University of Parma

P-43 **Structure, property and reactivity correlations in carbon nanomaterials: A simple and novel concept of nanoscale curvature**
K. R. S. Chandrakumar, Naresh K. Jena and Swapan K. Ghosh
Kyoto University

P-44 **Computational modeling of polymer electrolyte membrane, sulfonated polyethersulfone**
Yoong-Kee Choe, Eiji Tsuchida, Tamio Ikeshoji, Akihiro Ohira, Koh Kidena
National Institute of Advanced Industrial Science and Technology

P-45 **High Precision Core-Level SAC-CI Spectroscopy**
Masahiro Ehara
Institute for Molecular Science

P-46 **A Theoretical Study on the Aromaticity and Excitation Spectra of Phosphorus-Containing Hybrid Porphyrins**
Shinya Fujishige, Haruyuki Nakano, Takashi Nakabuchi, Makoto Nakashima, Yoshihiro Matano
Kyushu University

P-47 **ONIOM Prediction of the Gas Phase Acidities of Polyfluoroalkanes**
Haruhiko Fukaya, Taizo Ono, Takaaki Sonoda, and Masaaki Mishima
National Institute of Advanced Industrial Science and Technology (AIST)

P-48 **Electronic spectra and excited state properties of extended porphyrins**
Ryoichi Fukuda, Hiroshi Nakatsuji
Institute for Molecular Science

P-49 **FMO calculations associated with Influenza Hemagglutinin**
Kaori Fukuzawa, Kazutomo Takematsu, Tatsunori Iwata, Katsuhisa Nakajima, Yuji Mochizuki, Tatsuya Nakano, and Shigenori Tanaka
Mizuho Information & Research Institute, Inc.

P-50 **Non-adiabatic ab initio dynamics simulations of retinal**
Toshimasa Ishida, Shinkoh Nanbu, and Hiroki Nakamura
Kyoto University

P-51 **Study on the reaction mechanism of adenylate kinase with ONIOM method**
Kenshu Kamiya
School of Science, Kitasato University

P-52 **Thermal fluctuation of the protein environment influences the potential diagram**
Tsutomu Kawatsu, Marcus Lundberg, Keiji Morokuma
Kyoto University

P-53 **Spin Projected Hessian of Broken-Symmetry Method**

Yasutaka Kitagawa, Toru Saito, Yasuyuki Nakanishi, Yusuke Kataoka, Toru Matsui,Takashi Kawakami, Mitsutaka Okumura and Kizashi Yamaguchi

Osaka University

P-54 **Cluter Model DFT Study for Hydrogen Evolution Reaction and Oxygen Reduction Reaction:Comparison of Reversible Potential among Electrode Metals**

Hisayoshi Kobayashi
Kyoto Institute of Technology

P-55 **Synthesis of Optically Active Green Fluorescent π-Conjugated Fluorene Polymers Having Chiral Schiff Base in the Side Chain**
Gen-ichi Konishi, Kengo Asai, Susumu Kawauchi
Tokyo Institute of Technology

P-56 **Bonding Nature of Dinuclear Cr Complexes: Theoretical Study with MRMP2 Method**
Yusaku I. Kurokawa, Yoshihide Nakao, Shigeyoshi Sakaki
Graduate School of Engineering, Kyoto University

P-57 **Large-scale correlated calculations with FMO scheme**
Yuji Mochizuki, Katsumi Yamashita, Tatsuya Nakano, Shigenori Tanaka
Rikkyo University, Faculty of Science

P-58 **Monte Carlo study of the pressure-induced liquid-solid phase transition of Lennard-Jones fluid system**
Chizuru Muguruma
Chukyo University

P-59 **Third-order nonlinear optical properties of hexagonal graphene nanoflakes**
Hiroshi Nagai,Kyouhei Yoneda, Hitoshi Fukui,
Takuya Minami, Ryohei Kishi, Hideaki Takahashi, Takashi Kubo,
Osaka University

P-60 **Molecular Orbital Calculation for Large Molecule with Sakurai-Sugiura Method on Grid Computing Environment**
Umpei Nagashima, Yuichi Inadomi, Hiroaki Umeda, Toshio Watanabe,
Takayoshi Ishimoto and Tetsuya Sakurai
National Institute of Advanced Industrial Science and Technology

P-61 **A theoretical study on the π-π^*/π-σ^* conical intersection along the amino stretching and inversion coordinates of aminonaphthalene**
Masayuki Nakagaki and Haruyuki Nakano
Kyushu University

P-62 **Theoretical Study on the Reaction Mechanism of Carboxypeptidase A**
Setsuko Nakagawa
Kinjo Gakuin University

P-63 **Cholesky decomposition approach for the integral approximations in the fragment molecular orbital method**
Y. Okiyama, T. Nakano, K. Yamashita, Y. Mochizuki, S. Tanaka
The University of Tokyo

P-64 **Ab initio molecular dynamics simulation with internal constraint on photoisomerization of azobenzene in nπ^* state**
Y. Ootani, K. Satoh, A. Nakayama, T. Noro and T. Taketsugu
Hokkaido University

P-65 **Theoretical Study for the Possibility of the Bimetallic Activation**
Masato Oshima, Masaharu Ito, Shin-ya Suzuki, Kazuhide
Matsumura, Hiroharu Suzuki
Tokyo Polytechnic University

P-66 **Insight into important inhibitor-enzyme interactions of anti-tuberculosis agents using molecular docking and quantum chemical**
Pornpan Pungpo, Auradee Punkvang, Patchreenart Saparpakorn, and
Supa Hannongbua
Ubonratchathani University

P-67 **On the mechanism of reversible phosphorylation catalyzed by Phosphoserine Phosphatase**
Suyong Re, Jaewoon Jung, Seiichiro Ten-no, Yuji Sugita
RIKEN Advanced Science Institute, Kobe University, JST-CREST

P-68 **Effect of annealing on the dynamics and structure of hot giant**

fullerenes in presence of buffer gas: DFTB/MM MD simulations
Biswajit Saha, Stephan Irle, Keiji Morokuma
Kyoto University

P-69 **Theoretical study of emissive iridium complexes: Molecular geometries, electronic structures, and quantum efficiencies**
Ken Saito, Yoshihide Nakao, Shigeyoshi Sakaki
Kyoto University

P-70 **Theoretical Studies on the structures and the aromaticity for condensed cyclobutadienoids series.**
Shogo Sakai, Taro Ydagawa, and Yuki Kita
Gifu University

P-71 **Evaluating ONIOM (QM:QM) method on the electronic excited-states**
Yoko Sasakura, Lung Wa Chung, Xin Li, Ahmet Altun, Keiji Morokuma
Kyoyo University

P-72 **Development of Computational Methods for Solvated Molecules**
Hirofumi Sato, Atsushi Ikeda, Daisuke Yokogawa, Kenji Iida, Seigo Hayaki, Kentaro Kido, and Shigeyoshi Sakaki
Kyoto University

P-73 **Calculated Structural and Electronic Properties of the Ruthenium Dye N3 and Derivatives**
Songwut Suramitr, Prapimporn Thammawich, Supa Hannongbua
Faculty of Science, Kasetsart University

P-74 **Electron collision with gas-phase amino acid molecules**
Motomichi Tashiro
Kyoto University

P-75 **Ab initio fragment molecular orbital study on the inhibitory effect of NAD glycohydrolase by glycosphingolipids**
Kaori Ueno-Noto, Keiko Takano, Dmitri G Fedorov, and Kazuo Kitaura
Ochanomizu University

P-76 **Instability in Chemical Bonds: UNO CASCC, Resonating UCC and Approximately Projected UCC Methods to Quasi-degenerate Electronic Systems.**
S. Yamanaka, S. Nishihara, K. Nakata, Y. Yonezawa, Y. Kitagawa, T. Kawakami, M. Okumura, T. Takada, H. Nakamura and K. Yamaguchi
Osaka University, TOYOTA Physical & Chemical research institute

P-77 **Benchmark Studies of Acetone Interaction on Graphite Surface**
Yoshifumi Nishimura, Takao Tsuneda, and Stephan Irle
Nagoya University

（様式４）

若手研究者交流支援事業－東アジア首脳会議参加国からの招へい－
平成２１年度　第１回実施報告書

１．基本データー

【事業課題名】

課題名（和文は 40 字以内。）
（和文）分子理論による複雑分子のシミュレーションに関する共同研究と研究者交流
（英文）Collaboratory Research and Exchange of Researchers in Simulations of Complex Molecules Using Molecular Theoretical Methods

【実施期間】

平成　21 年 4 月 1 日～平成　21 年　12 月 31 日

【受入機関】

機関名	（和文）	京都大学
	（英文）	Kyoto University
機関代表氏名		総長　　　　松本　紘

【実施の中心となる部局】（受入機関内の研究科、附置研、研究センター等）

部局名	（和文）	福井謙一記念研究センター			
	（英文）	Fukui Institute for Fundamental Chemistry			
部局代表者	職名（和文）	センター長	氏名（和文）	榊　茂好	
	（英文）	Director	（英文）	Shigeyoshi SAKAKI	

【コーディネーター】

所属部局（和文）	福井謙一記念研究センター	職名（和文）	リサーチリーダー	氏名（和文）	諸熊奎治
（英文）	Fukui Institute for Fundamental Chemistry	（英文）	Research Leader	（英文）	Keiji Morokuma
電話番号 075-711-7843		ﾌｧｯｸｽ番号 075-781-4757		Email morokuma@fukui.kyoto-u.ac.jp	

【事務責任者】（変更申請書等の提出者となる責任者）

所属部局	職名	氏名
工学研究科 学術協力課	課長	田村　京市

【本会との連絡窓口となる事務担当者】（担当が複数人いる場合は枠を追加して、記述してください。）

所属部局	職名	氏名（フリガナ）
工学研究科 学術協力課	専門職員	幸　俊烈　（ユキ　トシタケ）
電話番号 075-383-2058	ﾌｧｯｸｽ番号 075-383-2061	Email toshitake.yuki@mail2.adm.kyoto-u.ac.jp

住所　（〒 615-8530）
京都市西京区京都大学桂

【受入機関内のその他の部局等】（該当がある場合のみ記述してください。部局等が複数ある場合は、すべて記述してください。）

部局名	（和文）	大学院工学研究科
	（英文）	Graduate School of Engineering
部局名	（和文）	大学院理学研究科
	（英文）	Graduate School of Science

【受入機関以外の協力機関】（該当がある場合のみ記述してください。部局等が複数ある場合は、すべて記述してください。）

機関名	（和文）	名古屋大学
	（英文）	Nagoya University
部局等名	（和文）	高等研究院
	（英文）	Institute for Advanced Research
機関名	（和文）	自然科学研究機構
	（英文）	National Institutes of Natural Sciences
部局等名	（和文）	分子科学研究所
	（英文）	Institute for Molecular Science
機関名	（和文）	早稲田大学
	（英文）	Waseda University
部局等名	（和文）	先進理工学部
	（英文）	Faculty of Science and Engineering
機関名	（和文）	特定非営利活動法人量子化学研究協会
	（英文）	NPO Quantum Chemistry Research Institute
部局等名	（和文）	研究所
	（英文）	Research Institute

【交流相手機関】（該当がある場合のみ記述してください。部局等が複数ある場合は、すべて記述してください。）

機関名	（和文）	チュラロンコーン大学	国名	タイ
	（英文）	Chulalongkorn University	（英文）	Thailand
部局名	（和文）	化学科		
	（英文）	Department of Chemistry		
機関名	（和文）	カセツァート大学	国名	タイ
	（英文）	Kasetsart University	（英文）	Thailand
部局名	（和文）	化学科		
	（英文）	Department of Chemistry		
機関名	（和文）	タクシン大学	国名	タイ
	（英文）	Thaksin University	（英文）	Thailand
部局名	（和文）	化学科		
	（英文）	Department of Chemistry		
機関名	（和文）	シンガポール国立大学	国名	シンガポール
	（英文）	National University of Singapore	（英文）	Singapore
部局名	（和文）	化学科		
	（英文）	Department of Chemistry		
機関名	（和文）	ダナン大学	国名	ベトナム
	（英文）	University of Danang	（英文）	Viet Nam
部局名	（和文）	ダナン工科大学		
	（英文）	Danang University of Technology		

（平成 21 年度）

【交流相手機関】（該当がある場合のみ記述してください。部局等が複数ある場合は、すべて記述してください。）

機関名	（和文）	ホーチミン市立計算科学工学研究所	国名	ベトナム
	（英文）	Ho Chi Minh City Institute for Computational Science and Technology	（英文）	Viet Nam
部局名	（和文）			
	（英文）			
機関名	（和文）	ホーチミン市立工科大学	国名	ベトナム
	（英文）	Ho Chi Minh City University of Technology	（英文）	Viet Nam
部局名	（和文）	科学技術石油学部		
	（英文）	Faculty of Chemical Technology and Petroleum		
機関名	（和文）	ベトナム国立大学ハノイ校	国名	ベトナム
	（英文）	Vietnam National University, Hanoi	（英文）	Viet Nam
部局名	（和文）	ハノイ理科大学		
	（英文）	Hanoi University of Science		

【受入研究者】（派遣のみの研究者も記入してください。）

氏　名	所属機関	所属部局等	職　名	備考
諸熊　奎治	京都大学	福井謙一記念研究センター	リサーチリーダー	
榊　茂好	京都大学	大学院工学研究科	教授	
Stephan IRLE	名古屋大学	高等研究院	特任准教授	
中辻　博	NPO 法人 量子化学研究協会	研究所	理事長	
林　重彦	京都大学	大学院理学研究科	准教授	
永瀬　茂	自然科学研究機構	分子科学研究所	教授	
中井　浩巳	早稲田大学	先進理工学部	教授	

２．事業目標の達成状況

理論化学・計算化学は理論とそれに基づいた計算によって化学の諸問題を研究しようとする学問であり、理論的方法論の発展と超高速計算機の普及によって最近その重要性をおおいに増してきた。今後、新触媒、新材料（ナノ物質など）、生体物質（蛋白、核酸）等といった複雑な分子系の構造、機能、反応の解明とその設計にますます重要な役割を果たすと期待されている。しかし、これらの複雑分子は数百個から数万個の原子からなる系であり、その解明には種々の理論的方法を組み合わせた複合分子理論の開発と応用が不可欠である。福井謙一記念研究センターでは、諸熊リサーチリーダーを中心に、複雑分子の複合分子理論によるシミュレーションを一つの旗印として、独立行政法人科学技術振興機構戦略的創造推進事業 CREST のマルチスケール・マルチフィジックス現象の統合シミュレーション研究領域のもと『複雑分子系の複合分子理論シミュレーション』という課題で、複合分子理論の開発とその複雑分子系への応用の研究を推進している。

東アジア諸国、とくにタイおよびシンガポールでは、複雑分子系のシミュレーションは極めて盛んで、今後これらの国での新しい科学技術の発展の基礎を担うものと位置づけられている。　たとえばタイでは、若手の大学教官養成のため数多くの博士課程学生が研究に励んでいるが、計算化学の盛況は、年一回開かれるタイ計算化学学会には２００人を超える教官、大学院生、学部研究生が参加し、複雑分子系を中心に幅広い高レベルの研究結果が発表され、熱心な討論が行われていることにも見ることが出来る。これらの博士課程学生のうちごく一部はタイ国政府の奨学金や外国の援助によって外国で研究の経験を積む機会があるが、未だその機会は乏しいのが現状である。　シンガポールも事情はよく似ており、諸熊博士が２００６年１２月に参加したシンガポール化学会では、１００件を超す計算化学のポスター発表があり、レベルも高く、その熱気に圧倒される感があった。　この両国の若手研究者に必要なのは、外国の研究状況を直接自分の目で見る機会を持つこと、さらにできれば外国で実際に研究に従事する機会を持つことで、本計画はその希望の一部を満たすことになる。

ベトナムではこの数年、新しい研究環境の整備が進み大学での研究も活発化しはじめたが、計算化学の分野でも外国で大学院教育を受けた若手研究者が帰国して大学での教育研究に参加するケースが見られる様になった。また、外国で確立したベトナム人研究者が自国で新しい研究機関（大学院教育にも参画）の設立に関与しその長となるケースも見いだされている。これらの若手研究者や大学院学生に、日本訪問および共同研究参加の機会を与えることは、やっと芽を出し始めたベトナムの学術の発展に大いに寄与すると考えられる。

本交流計画は、若手研究員の長期受入と短期受入ならびに国内受入研究者の派遣の３つの柱からなっている。

１。若手研究員の長期受け入れ
２。若手研究員の短期期受け入れ
３。国内受入研究者の派遣

下記５に詳述するように、いずれもほぼ計画通りに事業は進行し、事業目標は達成された。全体の印象でいえば、シンガポールの研究のレベルは突出しており、今後対等な共同研究の相手としての可能性が大きい。タイについても、この１０年ほどの研究の進歩は質量ともに眼を見張るものが有り、今後研究協力をおおいに進めて行くべき相手であると言える。ベトナムについて言えば、研究の芽がやっと出てきたという段階にあり、若い研究者に本プログラムのような研究機会を与えることは今後の研究の発展に大きな寄与をすると考えられる。幸い平成２１年度第２回の本事業の申請が認められ、これらの国にさらにフィリピンとマレーシアを加えて、若手招聘が継続できることになった。東アジア若手研究者に共同研究の場を提供すると言う本事業の目標の達成に更なる寄与が出来ると思う。

（平成 21 年度）

３．事業実施概要

本交流計画は、若手研究員の長期受入と短期受入ならびに国内受入研究者の派遣の３つの柱からなっていおり、いずれもほぼ計画 (当初計画および２回にわたる交流相手機関の追加) 通り実施した。

１。若手研究員の長期受け入れ：タイから３人、ベトナムから３人、合計６人の研究者（京大福井センターに４名、京大工学研究科に１名、名大高等研究院に１名）をそれぞれ３０－９０日ずつ受け入れ、共同研究に従事させた。これらの受け入れ部署では、それぞれ既に外国人研究者を含む活発な研究グループが活動しており、研究に必要な計算機時間も充分に確保されたので、ここで実際に計算化学の共同研究に従事したことは研究者の研究発展上大変大きなインパクトがあったと考えられる。いずれも、招聘研究者たちは夜遅くまでまた週末も研究に没頭し、受け入れ側の教官あるいは研究員が研究進行を充分にサポートしたこともあって、研究はおおいに進行した。実質的な共同研究は研究者の帰国後もインターネットを通じて継続しており、招聘研究者それぞれが共同研究論文１編の作成を目指している。早いものは近く投稿が可能とおもわれ、他のものも１年以内の完成を予定している。また、５人は滞在期間のうち１４日は、６．で述べる理論化学・計算化学研究室訪問旅行に参加した。

２。 若手研究員の短期期受け入れ：上記１と別の４人 (シンガポール１名、タイ２名、ベトナム１名) を７月８日から２３日まで１６日間京大福井センターをベースに受け入れ、下記６．で述べる理論化学・計算化学研究室訪問旅行を実施した。この間、福井センター、京大理学研究科、京大工学研究科、量子化学研究協会、名古屋大学、分子研、早稲田大学を訪問し、討論と交換セミナーを行った。受け入れグループはいずれもこの分野で日本をリードする研究を行っており、また若手研究者も数多くいるので、活発な討論、交流が行われた。さらに京大福井センターで複雑分子のシミュレーションに関する国際会議に出席し、ポスター発表を行った。詳細は下記６．を参照されたい。

３。国内受入研究者の派遣；国内受入研究者の中から中井教授が５月に、榊教授が１１月に (5 月の予定が新型インフルエンザで延期を余儀なくされた) それぞれ７日、６日の旅程でタイおよびシンガポールの３大学を訪問した。両教授ともこれらの国を訪問するのははじめてであったが、各訪問先でセミナーを行うとともに、各国の研究状況の調査と研究指導者および若手研究者との交流を行った。これらの両国は、理論化学・計算化学の研究者の数も多く研究のレベルも高いので、本課題の終了後にも、大学院留学生の受け入れや若手教官との共同研究の企画など、これらの国との交流が大いに進むものと期待される。中井教授（早稲田大学）は、2009 年 5 月 6 日（水）から 5 月 12 日（火）にかけて、タイとシンガポールに出張した。タイでは、Chulalongkorn 大学（Parasuk 教授）および Kasetsart 大学（Hannongbua 准教授）を訪問した。それぞれの大学において、"Linear-Scaling Divide-and-Conquer (DC) Method: Implementation of GAMESS09" という演題でセミナーを行った。質疑応答も活発に行われ、多くの聴講者が発表内容に興味を持ったようである。また、両大学において受入れ研究室の研究内容に関しても、所属メンバーと議論を交わした。後日、Parasuk 教授から、DC 法に関するワークショップをバンコクで開催する可能性について検討を始めたとの報告を受けた。シンガポールでは、シンガポール国立大学 S(Chun 教授) を訪問し、"Development of linear-scaling electronic-structure calculation based on the dived-and-conquer approach" という演題でセミナーを行った。Chun 教授は物理学科所属であり、多少バックグラウンドが異なっていたが、講演内容のみならず、量子化学という分野自体にも強い関心が寄せられた。また、榊教授 (京大) も１１月にタイとシンガポールを訪問し。講演および研究討論を行った

諸熊リサーチリーダーは６月にベトナムを訪問した。ベトナム訪問ははじめてであり、理論化学・計算化学の研究者に関する情報は日本では極めて少なく、唯一旧知の仲であるアメリカユタ大学の教授でホーチミン市立計算科学工学研究所所長を兼ねている Thang Truong 教授に紹介を依頼して訪問先を推薦してもらった。その結果、ホーチミン市、ダナン、ハノイの３都市をまわり、ホーチミン市立計算科学工学研究所、ホーチミン市立工科大学、ダナン大学ダナン工科大学、ベトナム国立大学ハノイ校ハノイ理科大学でセミナーを行うとともに、研究者と 理論化学・計算化学の研究事情等について討論した。ベトナムでは、理論化学・計算化学の研究者の研究者の数はまだ少なく、ホーチミン市で大学院生や若い研究員が１０名近く、ダナンでは若手講師ら２－３名位、ハノイでもベテラン若手合わせて３－４名が、それぞれ限られた研究環境で頑張っているとの印象を受けた、しかし、研究者の熱意は大変高くまたハングリー精神にみちており、今後研究協力の機会を提供していけば、将来大きな発展が期待される。

（平成 21 年度）

4．若手研究者の受入実績

受入研究者氏名	招へい若手研究者氏名	国籍	所属機関	部局	身分	博士号有無	招へい開始日	招へい終了日	招へい日数
諸熊奎治	Witcha Treesuwan	タイ	Kasetsart University	Department of Chemistry	講師	有	平成21年7月1日	平成21年9月28日	90
諸熊奎治	Pham Cam Nam	ベトナム	University of Danang	Danang University of Technology	講師	有	平成21年7月1日	平成21年9月28日	90
Stephan IRLE	Nguyen Tien Hung	ベトナム	HoChiMinh City Institute for Computational Science & Technology		大学院生	無	平成21年7月2日	平成21年9月28日	89
榊　茂好	Viwat Vchirawongkwin	タイ	Chulalongkorn University,	Department of Chemistry	講師	有	平成21年7月1日	平成21年9月28日	90
諸熊奎治	Anurak Udomvech	タイ	Thaksin University	Department of Chemistry	講師	有	平成21年7月1日	平成21年9月28日	90
諸熊奎治	Patchreenart Saparpakorn	タイ	Kasetsart University	Department of Chemistry	講師	有	平成21年7月8日	平成21年7月23日	16
諸熊奎治	Arthit Vongachariya	タイ	Chulalongkorn University	Department of Chemistry	大学院生	無	平成21年7月8日	平成21年7月23日	16
諸熊奎治	Xie Huifang	シンガポール	National University of Singapore	Department of Chemistry	大学院生	無	平成21年7月8日	平成21年7月23日	16
諸熊奎治	Le Min Duc	ベトナム	University of Danang	Danang University of Technology	上級講師	有	平成21年7月8日	平成21年7月23日	16
諸熊奎治	Nguyen Hoa My	ベトナム	Vietnam National University, Hanoi,	Hanoi University of Science	研究員	無	平成21年11月8日	平成21年12月7日	30
	計10人								

（平成21年度）

5．日本側研究者等の派遣実績

派遣者 氏　名	派遣先機関	部　局	国名	派遣開始日	派遣終了日	派遣日数	派遣目的
中井 浩巳	チュラロンコーン大 カセツァート大学 シンガポール国立大学	いずれも 化学科	タイ・シンガポール	平成 21 年 5 月 6 日	H21 年 5 月 12 日	7	各国の研究状況の調査を行うとともに、研究指導者および若手研究者との人脈の育成を図る
諸熊 奎治	ホーチンミン市立 計算科学工学研究所 ホーチミン市立工科大学 ダナン大学 ベトナム国立大学 ハノイ校	科学技術石油 学部 ダナン工科大学 ハノイ理科大学	ベトナム	平成 21 年 6 月 1 日	平成 21 年 6 月 8 日	8	各国の研究状況の調査を行うとともに、研究指導者および若手研究者との人脈の育成を図る
榊　茂好	チュラロンコーン大 カセツァート大学 シンガポール国立大学	いずれも 化学科	タイ・シンガポール	平成 21 年 11 月 2 日	平成 21 年 11 月 7 日	6	各国の研究状況の調査を行うとともに、研究指導者および若手研究者との人脈の育成を図る
計３人						計 21 日	

（平成 21 年度）

6．招へい若手研究者を対象とした企画等の実施状況

<table>
<tr><td colspan="2" rowspan="2">企　　画　　名</td><td colspan="2">（和文）日本の理論化学・計算化学研究室訪問旅行</td></tr>
<tr><td colspan="2">（英文）Tour of Japanese theoretical and computational chemistry laboratories</td></tr>
<tr><td colspan="2">開　催　期　間</td><td colspan="2">平成21年7月9日　～　平成21年7月22日（14日間）</td></tr>
<tr><td colspan="2">開　　催　　地</td><td colspan="2">京都、東京、岡崎、名古屋</td></tr>
<tr><td rowspan="4">開催責任者</td><td rowspan="2">氏　　　名</td><td colspan="2">（和文）　諸熊　奎治</td></tr>
<tr><td colspan="2">（英文）　Keiji morokuma</td></tr>
<tr><td rowspan="2">所属機関・職名</td><td colspan="2">（和文）　京都大学　リサーチリーダー</td></tr>
<tr><td colspan="2">（英文）　Kyoto University, Research Leader</td></tr>
<tr><td rowspan="5">参加者数</td><td>国　　　籍</td><td>当該事業で招へいした若手研究者の人数</td><td>その他の研究者の人数（スタッフを除く）</td></tr>
<tr><td>日本</td><td>0</td><td>約50。この中には外国人の大学院生(中国, インド)や研究者(エジプト、インド、オーストラリア、中国、韓国)を15人程度含む。</td></tr>
<tr><td>タイ</td><td>5</td><td>2</td></tr>
<tr><td>シンガポール</td><td>1</td><td>0</td></tr>
<tr><td>ベトナム</td><td>3</td><td>0</td></tr>
</table>

概要及び成果

【目的・概要】 日本の計算化学を代表する受け入れ教官の研究者を7カ所訪問し、その研究の実情に直接触れまた自分たちの研究を紹介するとともに、研究者(教官、研究員、大学院生など)との交流を深めることを目的に、本課題で招待した若手研究者10名のうち時期が合わなかった1名を除く9名がこのツアーに参加した。日程は次の通りである。 7/9午前京大福井センター、午後京大理学研究科加藤•林研究室、7/10午前量子化学研究協会、午後京大工学研究科榊•佐藤研究室、7/13早稲田大中井研究室、7/15分子科学研究所理論•計算分子科学領域、7/16名大高等研イレ研究室をそれぞれ訪問してセミナーおよび討論を行ったほか、研究者たちとの交流の懇親会を持った。東京都内のはとバスツアーや散策なども、日本の理解に大いに寄与したと思われる。また、7/19-21に京大福井センターで開催されたCREST International Symposium on Theory and Simulations of Complex Molecular Systems and International Symposium on Theory of Molecular Structure, Function and Reactivity, Celebrating Prof. Morokuma's 75th Birthdayにこのツアーの一環として参加し、3日間世界一流の研究者の講演を聞くとともに、ポスターセッションで7件のポスター発表を行った。最後に7/22京大福井センターにて本旅行の総括討論を行った。さらに、7/17の祇園祭には全員が出かけ、日本の伝統文化に触れる機会を持った。

【成果】 総括討論の際、招へい若手研究者の多くから、このツアーによって理論化学計算化学のなかで、自分の今までに知らなかったようなテーマの研究に出会ったり、自分の研究に有用なコメントが聞けたりして、今後の研究の発展に大きな刺激になったとの意見が数多く出された。又、日本の計算機事情も、シンガポールを除く国の研究者には羨望の的であった。また、このツアーを通じて、日本の若手研究者との交流も始まり、今後の日本と東南アジア各国とのネットワークの形成にいい影響を与えると思われる。また、3カ国からの9人がまとまって旅行したことによって、招聘研究者の間の情報交換など交流も盛んに行われ、今後の東アジア諸国の若手の間の接触も推進されたことは特記していいと思う。今回16日間の短期招聘でこのツアーに参加した研究者の1人は、長期招聘であらためて来日して研究したいとの希望を強く表明し、実際次回（H21年度第2期）に推薦され、早稲田大学に90日滞在することが決まった。

（平成21年度）

７．経費使用額

日本学術振興会からの交付経費：7,000,000　円

Detailed schedule of JENESYS program

Wednesday, July 8

by noon; Group C participants arrive at Seifu Kaikan hotel in Kyoto
1230 Walk to FIFC, led by Ms. Liu
1300 Registration at FIFC
1400 (Group B members also join at this point)
1400 Welcome to JENESYS and logistics (Dr. Morokuma)
1500 Introduction to FIFC and activity of Ishida Group (Prof. Ishida)
1530 Activity of Morokuma group I (Dr. Alister –nano projects)
1600 Activity of Morokuma group 2 (Dr. Chung- bio projects)
1630 Reception (JENESYS participants and FIFC members)
1800 adjourn

Thursday, July 9

930 Presentation of JENESYS participants (10 min from each participant)
1130 Activity of Ohmine group (Dr. Kamiya)
1200 Final logistics (Dr. Morokuma)
1230 Walk to Kyoto University north campus and have lunch
1400 Visit Kato-Hayashi-Tanimura Group at Faculty of Science (science faculty bidg 2, room 218)
1400 Overview of theoretical groups
1420 Seven presentations of Jenesys participants
1540 Presentations of theoretical groups
1620 Visit labs
1700 End visit. Walk to the main campus and confirm the shuttle bus stop in front of the clock tower
1730 Adjourn

Friday, July 10

850 Gather at the bus stop in front of the clock tower of the main campus
910 Shuttle bus to Katsura campus leaves punctually (If you miss the bus, the next bus leaves at 1035)
1010 Bus arrives at Katsura campus. Get off at the first stop (A-cluster). Nakatsuji group picks up at the bus stop.
1020 Presentation of research of Nakatsuji group at Quantum Chemistry Research Institute(QCRI)
1120 Seven presentations of JENESYS participants
1230 Box lunch at QCRI
1330 Walk to Sakai Lab, Kyoto University
1345 Seven presentations of JENESYS participants
1500 Presentation of research of Sakaki group, Faculty of Engineering, Kyoto University
1620 Visit laboratories
1700 Dinner at Coop dining room
1820 Shuttle bus leaves
1915 Arrive at clock tower of the main campus and adjourn

Saturday, July 11
Free. Enjoy visiting sights in Kyoto.

Sunday, July 12
~800 Group C Leave Seifu Kaikan hotel
~830 All gather at the main gate of Kyoto Station
902 at Kyoto station take Nozomi #220 train
1116 Arrive at Shinagawa station. Change train
~1140 arrive at Takadanobaba station
~1200 arrive at Hotel Sunroute Takadanobara
~1300 Students from Prof. Nakai group will come to the hotel and take for sightseeing

Monday, July 13
1030 Students from Nakai group pick up at the hotel
1045 Arrive at Nakai group, Waseda University
1100- Discussion 1 (group B and Nakai group presentations)
1300- Lunch
1500- Discussion 2 (group C and Nakai group presentations)
1700- Reception
2000- ??

Tuesday, July 14
730 Check out hotel
740 Leave Takadanobaba station
820 Arrive at Hamamatsucho station
900 Hato Bus tour (half-day tour of Tokyo) leaves
1200 Tour ends. Lunch
~1300 Leave Hamamatsucho station for Shinagawa station
1334 Kodama#650 leaves Shinagawa
1542 arrive at Toyohashi. Change train to Meitetsu line
1553 Metetsu leaves Toyohashi
1618 Arrive at Higashi-Okazaki// Walk to Mishima lodge of IMS

Wednesday, July 15
845 Walk from Mishima Lodge to IMS (Prof. Nagase’s office)
900 Overview of theo/comp research area of IMS
915 Presentations of JENESYS participants
1115 research presentation of theory groups 1230 lunch
1330 visit UVSOR facility
1415 presentations of computational groups.
1500 visit research center for computational science
~1600 leave Higashi-Okazaki by Meitetu line
~1730 Arrive at the guest house, Nagoya university

Thursday, July 16
1000 Visit Irle group meeting, IAR, Nagoya University
1040 Seven presentations by JENESYS participants
1150 Presentations of Irle group members
1250 lunch
1350 Presentations by chemistry GCOE
1420 Visit of Prof. Hisanori Shinohara lab (Science)
1500 Visit of Prof. Eiji Yashima’s lab (Engineering)
1600 Leave Nagoya University by subway
~1700 Take Shinkansen from Nagoya to Kyoto
~1800 Arrive at Kyoto, adjourn

Friday, July 17
Gion Festival in Kyoto, enjoy

Saturday, July 18
free

Sunday, July 19
900 International symposium at FIFC
1800 Reception

Monday, July 20
900 International symposium at FIFC
1900 Banquet

Tuesday, July 21
900 International symposium at FIFC
1600 Adjourn

Wednesday, July 22
900 Final discussions at FIFC

Thursday, July 23
Group C members head back to home
Group B members continue research

（平成 21 年度）

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発行人　田中　　功

編　者　石田俊正

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