

RESEARCH ACTIVITIES I

Department of Theoretical Studies

I-A Theoretical Study and Design of Functional Molecular Systems: New Bonding, Structures, and Reactions

In theoretical and computational chemistry, it is an important goal to develop functional molecules with novel bonding and structures before or in cooperation with experiment. Thus, novel bonds and structures provided by heavier atoms are investigated. In addition, unique spaces and flexible structures provided by large molecules and clusters are investigated. Efficient computational methods are investigated to perform reliable quantum chemistry calculations of large molecular systems.

I-A-1 Effect of the Axial Cysteine Ligand on the Electronic Structure and Reactivity of High-Valent Iron (IV) Oxo-Porphyrins (Compound I): A Theoretical Study

CHOE, Yoong-Kee¹; NAGASE, Shigeru
(¹AIST)

[*J. Comput. Chem.* **26**, 1600–1611 (2005)]

The effects of axial ligands on the alkane hydroxylation of high-valent iron (IV) oxo-porphyrins (Compound I) are investigated using hybrid density functional theory at the B3LYP level. As axial ligands, thiolate, imidazole, phenolate, and chloride anions are investigated; the first three are the models of cysteinate, histidine, and tyrosinate, respectively. The alkane hydroxylation proceeds *via* several steps. A remarkable effect of axial ligands is found in the final product release step. The thiolate ligand weakens a bond between heme and an alcohol. In contrast, the imidazole ligand significantly increases the interaction between heme and an alcohol, which causes the catalytic cycle to be less efficient.

I-A-2 Sc₃N@C₈₀: Computations on the Two-Isomer Equilibrium at High Temperatures

SLANINA, Zdenek; NAGASE, Shigeru

[*ChemPhysChem* **6**, 2060–2063 (2005)]

The relative concentrations of the two isomers (I_h and D_{5h}) of Sc₃N@C₈₀, are investigated by calculating Gibbs free energies at the B3LYP level. When a relatively free motion of Sc₃N inside C₈₀ is allowed, the observed populations of 10 and 17% for the minor D_{5h} isomer are reached at 2100 and 2450 K, respectively. The entropy term plays an essential role, since, if it is neglected, the D_{5h} population at 2100 K is only 1%, owing to the relatively large interisomeric separation potential energy of 19 kcal/mol.

I-A-3 The Aromaticity of the Stannole Dianion

SAITO, Masaichi¹; HAGA, Ryuta¹; YOSHIOKA,

Michikazu¹; ISHIMURA, Kazuya; NAGASE, Shigeru
(¹Saitama Univ.)

[*Angew. Chem., Int. Ed.* **44**, 6553–6556 (2005)]

Neither monoanions nor dianions of stannoles have been well characterized, unlike the cases of the silole and germole anions. Thus, the lithium salt of a stannole dianion is isolated and investigated by NMR, X-ray crystal analysis, and theoretical calculations as the first tin-containing carbocyclic aromatic compound. The aromaticity of the stannole dianion is characterized by calculating charge delocalization and NICS (nucleus-independent chemical shift) values.

I-A-4 Reversible and Regioselective Reaction of La@C₈₂ with Cyclopentadiene

MAEDA, Yutaka¹; MIYASHITA, Jun¹;
HASEGAWA, Tadashi¹; WAKAHARA, Takatsugu²;
TSUCHIYA, Takahiro²; NAKAHODO, Tsukasa²;
AKASAKA, Takeshi²; MIZOROGI, Naomi;
KOBAYASHI, Kaoru; NAGASE, Shigeru; KATO,
Tatsuhisa³; BAN, Noritaka⁴; NAKAJIMA, Hiroshi⁴;
WATANABE, Yoshihito⁴
(¹Tokyo Gakugei Univ.; ²Univ. Tsukuba; ³Josai Univ.;
⁴Nagoya Univ.)

[*J. Am. Chem. Soc.* **127**, 12190–12191 (2005)]

The reversible and regioselective reaction of La@C₈₂ with cyclopentadiene is demonstrated in comparison with the corresponding reaction of C₆₀. Theoretical calculations show that La@C₈₂ reacts faster with cyclopentadiene than C₆₀, because La@C₈₂ has a lower LUMO than C₆₀. The low yield of the adduct of La@C₈₂ and cyclopentadiene is due to the presence of the fast retro-reaction. The rate constant for the consumption of La@C₈₂ is 2200 times slower than that of C₆₀ at 293 K.

I-A-5 Structural Determination of Metallofullerene Sc₃C₈₂ Revisited: A Surprising Finding

IIDUKA, Yuko¹; WAKAHARA, Takatsugu¹; NAKAHODO, Tsukasa¹; TSUCHIYA, Takahiro¹; SAKURABA, Akihiro²; MAEDA, Yutaka³; AKASAKA, Takeshi¹; YOZA, Kenji⁴; HORN, Ernst⁵; KATO, Tatsuhisa⁶; LIU, Michael T. H.⁷; MIZOROGI, Naomi; KOBAYASHI, Kaoru; NAGASE, Shigeru
(¹Univ. Tsukuba; ²Niigata Univ.; ³Tokyo Gakugei Univ.; ⁴Bruker AXS K.K.; ⁵Rikkyo Univ.; ⁶Josai Univ.; ⁷Univ. Prince Edward Island)

[*J. Am. Chem. Soc.* **127**, 12500–12501 (2005)]

It is widely accepted that the maximum-entropy-method (MEM)/Rietveld analysis of synchrotron X-ray powder diffraction data is powerful for structural determination of endohedral metallofullerenes. For example, the MEM/Rietveld analysis of Sc₃C₈₂ has shown that three Sc atoms are encapsulated inside a C_{3v} isomer of C₈₂ as a trimer with extremely short Sc–Sc distances. For Sc₃C₈₂, however, theoretical calculations reveal that two C atoms as well as three Sc atoms are encapsulated inside the I_h-C₈₀ (not C₈₂) fullerene, this Sc₂C₂@C₈₀ structure being much more stable than the Sc₃@C₈₂ structure determined by MEM/Rietveld analysis. The Sc₂C₂@C₈₀ structure is also verified by the NMR analysis of the anion and X-ray crystal analysis of a Sc₂C₂@C₈₀ derivative. It is suggested that the widely used MEM/Rietveld analysis is not reliable enough to determine the structures of endohedral metallofullerenes.

I-A-6 Electronic Structures of Semiconducting Double-Walled Carbon Nanotubes: Important Effect of Interlayer Interaction

SONG, Wei¹; NI, Ming¹; LU, Jing¹; GAO, Zhengxiang¹; NAGASE, Shigeru; YU, Dapeng¹; YE, Hengqiang¹; ZHANG, Xinwei²
(¹Peking Univ.; ²Inst. Appl. Phys. Comput. Math.)

[*Chem. Phys. Lett.* **414**, 429–433 (2005)]

Electronic structures of zigzag (7, 0)@(15, 0), zigzag (7, 0)@(18, 0), zigzag (8, 0)@(16, 0), and chiral (4, 2)@(10, 5) double-walled carbon nanotubes (DWNTs) are investigated by using first-principle calculations. The π and π^* states of inner (7, 0) and (4, 2) single-walled carbon nanotubes (SWNTs) exhibit a larger downward shift with respect to those of the outer (15, 0), (18, 0) and (10, 5) SWNTs. For (7, 0)@(15, 0), (8, 0)@(16, 0), and (4, 2)@(10, 5) DWNTs, it is notable that the interlayer π - π stacking interaction causes a significant band reconstruction of the inner SWNT.

I-A-7 Positional Control of Encapsulated Atoms inside a Fullerene Cage by Exohedral Addition

YAMADA, Michio¹; NAKAHODO, Tsukasa¹;

WAKAHARA, Takatsugu¹; TSUCHIYA, Takahiro¹; MAEDA, Yutaka²; AKASAKA, Takeshi¹; KAKO, Masahiro³; YOZA, Kenji⁴; HORN, Ernst⁵; MIZOROGI, Naomi; KOBAYASHI, Kaoru; NAGASE, Shigeru

(¹Univ. Tsukuba; ²Tokyo Gakugei Univ.; ³Univ. Electro-Communications; ⁴Bruker AXS K.K.; ⁵Rikkyo Univ.)

[*J. Am. Chem. Soc.* **127**, 14570–14571 (2005)]

Theoretical calculations shows that the three-dimensional random motion of two La atoms in La₂C₈₀ can be restricted to the circular motion in a plane by attaching an electron-donating molecules such as disilirane on the outer surface of the C₈₀ cage. Thus, the exohedral chemical functionalization of Ce@C₈₂ by disilirane is performed to fix the random motion of two Ce atoms at specific positions. The exohedral attachment of disilirane regulates the Ce positions under the equator of the C₈₀ cage.

I-A-8 A Singly Bonded Derivative of Endohedral Metallofullerene: La@C₈₂CBr(COOC₂H₅)₂

FENG, Lai¹; NAKAHODO, Tsukasa¹; WAKAHARA, Takatsugu¹; TSUCHIYA, Takahiro¹; MAEDA, Yutaka²; AKASAKA, Takeshi¹; KATO, Tatsuhisa³; HORN, Ernst⁴; YOZA, Kenji⁵; MIZOROGI, Naomi; NAGASE, Shigeru
(¹Univ. Tsukuba; ²Tokyo Gakugei Univ.; ³Josai Univ.; ⁴Rikkyo Univ.; ⁵Bruker AXS K.K.)

[*J. Am. Chem. Soc.* **127**, 17136–17137 (2005)]

A novel singly bonded derivative of La@C₈₂ is obtained by the reaction with diethyl bromomalonate. Theoretical calculations show that the reaction center of La₂@C₈₂ is most positively charged and has the second largest local strain, which is most reactive toward a nucleophilic attack. This suggests that a nucleophilic reaction takes place at the first step, followed by the oxidation of an intermediate, [La@C₈₂CBr(COOC₂H₅)₂], to afford the singly-bonded adduct.

I-A-9 S-Heterocyclic Carbene with a Disilane Backbone

NIKAWA, Hidefumi¹; NAKAHODO, Tsukasa¹; TSUCHIYA, Takahiro¹; WAKAHARA, Takatsugu¹; RAHMAN, G. M. Aminur¹; AKASAKA, Takeshi¹; MAEDA, Yutaka²; LIU, Michael T. H.³; MEGURO, Akira⁴; KYUSHIN, Soichiro⁴; MATSUMOTO, Hideyuki⁴; MIZOROGI, Naomi; NAGASE, Shigeru
(¹Univ. Tsukuba; ²Tokyo Gakugei Univ.; ³Univ. Prince Edward Island; ⁴Gunma Univ.)

[*Angew. Chem., Int. Ed.* **44**, 7567–7570 (2005)]

Heterocyclic carbenes have attracted considerable interest as ligands, catalysis, and spin sources. It is found that S-heterocyclic carbene can be generated by the [2 + 3] addition of cyclotetrasilene with CS₂, which is trapped by C₆₀ as a chemical probe. The structure and

electronic state of the S-heterocyclic carbene are determined by density functional calculations. It is calculated that the singlet state is 23.4 kcal/mol stable than the triplet state, and has a high nucleophilicity.

I-A-10 Ab Initio and DFT Study of the ^{29}Si NMR Chemical Shifts in $\text{RSi}\equiv\text{SiR}$

KARNI, Miriam¹; APELOIG, Yitzhak¹; TAKAGI, Nozomi; NAGASE, Shigeru
(¹Technion-Israel Inst. Tech.)

[*Organometallics* **24**, 6319–6330 (2005)]

The first DFT and ab-initio calculations of the ^{29}Si NMR chemical shifts of triply bonded silicon atoms are reported for $\text{RSi}\equiv\text{SiR}$ ($\text{R} = \text{H}, \text{CH}_3, \text{SiH}_3, \text{SiMe}(\text{SiH}_3)_2, \text{SiMe}(\text{SiMe}_3)_2, \text{SiMe}(\text{Si}t\text{Bu}_3)_2, \text{and Si}i\text{Pr}[\text{CH}(\text{SiMe}_3)_2]_2$). Small changes in geometries (the central Si–Si bond distance, the RSiSi bond angle and the RSiSiR twisting angle) strongly affect the chemical shifts. Inclusion of electron correlation by using MP2 and CCSD methods is found to be very important for reliable chemical shift calculations of $\text{RSi}\equiv\text{SiR}$. The chemical shifts calculated using the HCTH407 GGA functional are in good agreement with those calculated at the MP2 and CCSD levels. In contrast, a poor agreement is obtained when the popular B3LYP functional is used. The chemical shift of the triply-bonded silicon atoms in $\text{RSi}\equiv\text{SiR}$ ($\text{R} = \text{SiMe}(\text{Si}t\text{Bu}_3)_2$) is calculated to be in the range of 88 ± 5 ppm, this agreeing well with the observed chemical shift.

I-A-11 A New Parallel Algorithm of MP2 Energy Calculations

ISHIMURA, Kazuya; PULAY, Peter¹; NAGASE, Shigeru
(¹Univ. Arkansas)

[*J. Comput. Chem.* **27**, 407–413 (2006)]

A new parallel algorithm is developed for second order Møller-Plesset perturbation theory (MP2) energy calculations. Its main projected applications are for large molecules, for instance for the calculation of dispersion interaction. Tests on a moderate number of processors (2–16) show that the program has high CPU and parallel efficiency. Timings are presented for two relatively large molecules, taxol ($\text{C}_{47}\text{H}_{51}\text{NO}_{14}$) and luciferin ($\text{C}_{11}\text{H}_8\text{N}_2\text{O}_3\text{S}_2$), the former with the 6-31G* and 6-311G** basis sets (1032 and 1484 basis functions, 164 correlated orbitals), and the latter with the aug-cc-pVDZ and aug-cc-pVTZ basis sets (530 and 1198 basis functions, 46 correlated orbitals). An MP2 energy calculation on $\text{C}_{130}\text{H}_{10}$ (1970 basis functions, 265 correlated orbitals) completes in less than 2 hours on 128 processors.

I-A-12 Synthesis and Properties of a New Kinetically Stabilized Digermyne: New Insights for a Germanium Analogue of an Alkyne

SUGIYAMA, Yusuke¹; SASAMORI, Takahiro¹; HOSOI, Yoshinobu¹; FURUKAWA, Yukio²; TAKAGI, Nozomi; NAGASE, Shigeru; TOKITOH,

Norihiko¹
(¹Kyoto Univ.; ²Waseda Univ.)

[*J. Am. Chem. Soc.* **128**, 1023–1031 (2006)]

The reduction of an overcrowded (E)-1,2-dibromodigermyne, $\text{Bbt}(\text{Br})\text{Ge}=\text{Ge}(\text{Br})\text{Bbt}$ [$\text{Bbt} = 2,6$ -bis[bis(tri methylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl], with KC_8 affords a stable digermene, $\text{BbtGe}\equiv\text{GeBbt}$. The Ge–Ge triple bond distance of $\text{BbtGe}\equiv\text{GeBbt}$ is significantly shorter than that in the previously reported digermene, $\text{Ar}'\text{Ge}\equiv\text{GeAr}'$ ($\text{Ar}' = 2,6$ -Dip₂C₆H₃, Dip = 2,6-diisopropylphenyl). The nature of the Ge–Ge triple bond in $\text{BbtGe}\equiv\text{GeBbt}$ is disclosed by density functional calculations with large basis sets.

I-A-13 Computational Modelling for the Clustering Degree in the Saturated Steam and the Water-Containing Complexes in the Atmosphere

SLANINA, Zdenek; UHLIK, Filip¹; LEE, Shyi-Long²; NAGASE, Shigeru
(¹Charles Univ.; ²Natl. Chung-Cheng Univ.)

[*J. Quant. Spectrosc. Radiat. Transfer* **97**, 415–423 (2006)]

Recent computational findings of temperature increase of clustering degree in several different saturated vapors are analyzed further. A thermodynamic proof is presented, showing that this event should be rather common, if not general. Illustrations are based on the saturated steam and consequences for the atmosphere are discussed with both homo- and hetero-clustering. The best stabilization energies of $\text{H}_2\text{O}\cdot\text{N}_2$, $\text{H}_2\text{O}\cdot\text{O}_2$, and $(\text{O}_2)_2$ are reported. The water-dimer thermodynamics is recomputed in an anharmonic regime and a remarkable agreement with experiment is found. The results have some significance for the atmospheric greenhouse effect.

I-A-14 Analysis of Lanthanide-Induced NMR Chemical Shifts of the $\text{Ce}@C_{82}$ Anion

YAMADA, Michio¹; WAKAHARA, Takatsugu¹; LIAN, Yongfu¹; TSUCHIYA, Takahiro¹; AKASAKA, Takeshi¹; WAELCHLI, Markus²; MIZOROGI, Naomi; NAGASE, Shigeru; KADISH, Karl M.³
(¹Univ. Tsukuba; ²Bruker Biospin K.K.; ³Univ. Houston)

[*J. Am. Chem. Soc.* **128**, 1400–1401 (2006)]

From paramagnetic NMR spectra analysis and density functional calculations, it is found that the Ce atom in $\text{Ce}@C_{82}$ as well as $[\text{Ce}@C_{82}]^-$ is located at an off-centered position near a hexagonal ring of the C_{2v} - C_{82} cage along the C_2 axis, as found for $\text{M}@C_{82}$ ($\text{M} = \text{Sc}, \text{Y}, \text{and La}$). This is in sharp contrast with the Eu and Gd positions determined recently by the MEM/Rietveld method for $\text{Eu}@C_{82}$ and $\text{Gd}@C_{82}$.

I-A-15 Synthesis and Structural Characterization of Endohedral Pyrrolidinodimetallfullene: $\text{La}_2@C_{80}(\text{CH}_2)_2\text{NTrt}$

YAMADA, Michio¹; WAKAHARA, Takatsugu¹; NAKAHODO, Tsukasa¹; TSUCHIYA, Takahiro¹; MAEDA, Yutaka²; AKASAKA, Takeshi¹; YOZA, Kenji³; HORN, Ernst⁴; MIZOROGI, Naomi; NAGASE, Shigeru
(¹Univ. Tsukuba; ²Tokyo Gakugei Univ.; ³Bruker AXS K.K.; ⁴Rikkyo Univ.)

[*J. Am. Chem. Soc.* **128**, 1402–1403 (2006)]

The reaction of $\text{La}_2@C_{82}$ with 3-triphenylmethyl-5-oxazolidinone leads to the 6,6- and 5,6-adducts, $\text{La}_2@C_{80}(\text{CH}_2)_2\text{NTrt}$ (Trt = triphenylmethyl). The structure of the 6,6 adduct is determined by X-ray crystal structure and density functional calculations. As suggested by the electrostatic potential maps calculated for $[\text{C}_{80}(\text{CH}_2)_2\text{NH}]^-$, the two La atoms in $\text{La}_2@C_{80}(\text{CH}_2)_2\text{NTrt}$ are fixed, unlike the random motion in $\text{La}_2@C_{80}$, and can be regulated by addition positions.

I-A-16 $\text{La}_2@C_{72}$ and $\text{Sc}_2@C_{72}$: Computational Characterizations

SLANINA, Zdenek; CHEN, Zhongfang¹; SCHLEYER, Paul v. R.¹; UHLIK, Filip²; LU, Xin³; NAGASE, Shigeru
(¹Univ. Georgia; ²Charles Univ.; ³Xiamen Univ.)

[*J. Phys. Chem. A* **110**, 2231–2234 (2006)]

The $\text{La}_2@C_{72}$ and $\text{Sc}_2@C_{72}$ metallofullerenes are characterized by systematic density functional computations. On the basis of the most stable geometry of 39 C_{72} hexaanions and the computed energies of the best endofullerene candidates, the experimentally isolated $\text{La}_2@C_{72}$ has the structure coded #10611 that invalidates the so-called isolated pentagon (IPR) rule. The good agreement between the computed and the experimental ¹³C chemical shifts for $\text{La}_2@C_{72}$ further supports the literature assignment. The geometry, IR vibrational frequencies, and ¹³C chemical shifts of $\text{Sc}_2@C_{72}$ are predicted to assist its future experimental characterization.

I-A-17 Reactivity of 1-Hydro-5-Carbaphosphatane Based on Tautomerization between Pentavalent Phosphorane and Trivalent Cyclic Phosphonite

KOBAYASHI, Junji¹; GOTO, Kei¹; KAWASHIMA, Takayuki¹; SCHMIDT, Michael W.²; NAGASE, Shigeru
(¹Univ. Tokyo; ²Iowa State Univ.)

[*Chem. Eur. J.* **12**, 3811–3820 (2006)]

Several reactions of 1-hydro-5-carbaphosphatane based on tautomerization to the trivalent *t* cyclic phosphonite, not definitively observed by spectroscopic

methods, are investigated experimentally and analyzed by ab initio theoretical calculations. The calculated potential energy surfaces (reaction intermediates and transition states) provide insight into the reaction mechanism.

I-A-18 Evolution of the Electronic Properties of Metallic Single-Walled Nanotubes with the Degree of CCl_2 Covalent Functionalization

LU, Jing¹; WANG, Dan²; NAGASE, Shigeru; NI, Ming¹; ZHANG, Xinwei³; MAEDA, Yutaka⁴; WAKAHARA, Takatsugu⁵; NAKAHODO, Tsukasa⁵; TSUCHIYA, Takahiro⁵; AKASAKA, Takeshi⁵; GAO, Zhengxiang¹; YU, Dapeng¹; YE, Hengqiang¹; ZHOU, Yunsong²; MEL, W. N.⁶
(¹Peking Univ.; ²Capital Normal Univ.; ³Inst. Appl. Phys. Comput. Math.; ⁴Tokyo Gakugei Univ.; ⁵Univ. Tsukuba; ⁶Univ. Nebraska)

[*J. Phys. Chem. B* **110**, 5655–5658 (2006)]

The changes in energetic, structural, and electronic properties of the metallic (5, 5) single-walled carbon nanotube (SWNT) with the degree of sidewall covalent functionalization of CCl_2 are investigated by using density functional calculations. The saturation concentration of CCl_2 covalent functionalization is predicted to be 33.3%. The cycloadducts always adopt an open structure. A band gap opens as the functionalization concentration reaches 11% and then basically increases with increasing functionalization concentration. These results are in agreement with available experiments and can be applied to predict the band gap of metallic SWNTs produced by the HiPco method at a given CCl_2 functionalization concentration.

I-A-19 Stability Computations for $\text{Ba}@C_{74}$ Isomers

SLANINA, Zdenek; NAGASE, Shigeru

[*Chem. Phys. Lett.* **422**, 133–136 (2006)]

Relative concentrations of six isomers of $\text{Ba}@C_{74}$ are evaluated: one cage with isolated pentagons, three isomers with a pentagon–pentagon junction, two structures with one pentagon–pentagon pair and one heptagon. The density functional calculations of Gibbs free energies show that $\text{Ba}@C_{82}$ has a D_{3h} - C_{74} cage that satisfies the isolated pentagon rule. The stability computations are in agreement with recent observations.

I-A-20 Comment on Disproving a Silicon Analog of an Alkyne with the Aid of Topological Analyses of the Electronic Structure and Ab Initio Molecular Dynamics Calculations

FRENKING, Gernot¹; KRAPP, Andreas¹; NAGASE, Shigeru; TAKAGI, Nozomi; SEKIGUCHI, Akira²
(¹Philipps-Univ.; ²Univ. Tsukuba)

[*ChemPhysChem* **7**, 799–800 (2006)]

As the first example of the silicon analogues of alkynes, $\text{RSi}\equiv\text{SiR}$ ($\text{R} = \text{SiPr}[\text{CH}(\text{SiMe}_3)_2]_2$) has been isolated. From the topological analysis of electron density distributions, it is recently claimed that only two electron pairs participate in the Si–Si bonding. In view of donor-acceptor interactions, however, it is commented that the Si–Si bond can be described as a triple bond.

I-A-21 Selective Interaction of Larger or Charge-Transfer Aromatic Molecules with Metallic Single-Wall Carbon Nanotubes: Critical Role of the Molecular Size and Orientation

LU, Jing¹; NAGASE, Shigeru; ZHANG, Xinwei²; WANG, Dan³; NI, Ming¹; MAEDA, Yutaka⁴; WAKAHARA, Takatsugu⁵; NAKAHODO, Tsukasa⁵; TSUCHIYA, Takahiro⁵; AKASAKA, Takeshi⁵; GAO, Zhengxiang¹; YU, Dapeng¹; YE, Hengqiang¹; MEI, W. N.⁶; ZHOU, Yunsong³
(¹Peking Univ.; ²Inst. Appl. Phys. Comput. Math.; ³Capital Normal Univ.; ⁴Tokyo Gakugei Univ.; ⁵Univ. Tsukuba; ⁶Univ. Nebraska)

[*J. Am. Chem. Soc.* **128**, 5114–5118 (2006)]

Using first principles calculations, we report for the first time that large nearly neutral aromatic molecules, such as naphthalene and anthracene, and small charge-transfer aromatic molecules, such as TCNQ and DDQ, interact more strongly with metallic single-walled carbon nanotubes (SWNTs) *vs.* their semiconducting counterparts as the molecular orientation of DDQ is taken into account. Two new mechanisms for separating metallic and semiconducting SWNTs *via* noncovalent π - π stacking or charge-transfer interaction are suggested.

I-A-22 Excited Electronic States and Relative Stabilities of C_{80} Isomers

SLANINA, Zdenek; LEE, Shyi-Long¹; UHLIK, Filip²; ADAMOWICZ, Ludwik³; NAGASE, Shigeru
(¹Natl. Chung-Cheng Univ.; ²Charles Univ.; ³Univ. Arizona)

[*Int. J. Quantum Chem.* **106**, 2222–2228 (2006)]

The synthesis of fullerenes at very high temperatures allows for a significant population of excited electronic states and thus for non-negligible electronic partition functions. This issue is studied for seven isomers of C_{80} that satisfy the isolated pentagon rule. It is calculated that the effects of electronic excited states are larger than those in the previously tested examples. For the special conditions of fullerene synthesis/isolation, the electronic partition function based on the singlet excited states only reflect better the experimental population findings.

I-A-23 Synthesis and Characterization of a Bisadduct of La@C_{82}

FENG, Lai¹; TSUCHIYA, Takahiro¹; WAKAHARA, Takatsugu¹; NAKAHODO, Tsukasa¹; PIAO, Qiuyue¹; MAEDA, Yutaka²; AKASAKA, Takeshi¹; KATO, Tatsuhisa³; YOZA, Kenji⁴; HORN, Ernst⁵;

MIZOROGI, Naomi; NAGASE, Shigeru
(¹Univ. Tsukuba; ²Tokyo Gakugei Univ.; ³Josai Univ.; ⁴Bruker AXS K.K.; ⁵Rikkyo Univ.)

[*J. Am. Chem. Soc.* **128**, 5990–5991 (2006)]

Up to now, no direct evidence has been reported for the dimerization of endohedral metallofullerenes. By synthesizing the bisadduct of La@C_{82} , it is demonstrated that the bisadduct forms a dimer in the single crystal. From the density functional calculations, it is evaluated which carbons in the bisadduct have large spin densities and POAV (p orbital axis vector) values to predict the most favorable position for dimerization. The intermolecular C–C distance of 1.635 Å calculated at the B3LYP level for the dimer agrees very well with the value of 1.638 (9) Å determined by the X-ray crystal analysis.

I-A-24 ¹³C NMR Spectroscopic Study of Scandium Dimetallofullerene, $\text{Sc}_2\text{@C}_{84}$ vs. $\text{Sc}_2\text{C}_2\text{@C}_{82}$

IIDUKA, Yuko¹; WAKAHARA, Takatsugu¹; NAKAJIMA, Koji¹; TSUCHIYA, Takahiro¹; NAKAHODO, Tsukasa¹; MAEDA, Yutaka²; AKASAKA, Takeshi¹; MIZOROGI, Naomi; NAGASE, Shigeru
(¹Univ. Tsukuba; ²Tokyo Gakugei Univ.)

[*Chem. Commun.* 2057–2059 (2006)]

It has been widely believed that the typical dimetallofullerene, Sc_2C_{84} , takes the form of $\text{Sc}_2\text{@C}_{84}$ in which two Sc atoms are encaged inside the C_{84} fullerene. However, it is found that the endohedral structure is not $\text{Sc}_2\text{@C}_{84}$ but $\text{Sc}_2\text{C}_2\text{@C}_{80}$. This finding is in sharp contrast with the previous NMR and power X-ray MEM/Rietvelt analysis.

I-A-25 H_2 , Ne, and N_2 Energies of Encapsulation into C_{60} Evaluated with the MPWB1K Functional

SLANINA, Zdenek; PULAY, Peter¹; NAGASE, Shigeru
(¹Univ. Arkansas)

[*J. Chem. Theory Comput.* **2**, 782–785 (2006)]

The recently suggested MPWB1K functional is tested on $\text{H}_2\text{@C}_{60}$, Ne@C_{60} , and $\text{N}_2\text{@C}_{60}$ as a tool for evaluations of stabilization energies upon encapsulation of nonmetallic species into fullerenes. It is found that the MPWB1K (modified Perdew-Wang and Becke functionals) values can be within a few kilocalories per mole from the MP2 or SCS-MP2 (spin-component scaled MP2) values so that further applications of the functional are clearly encouraged. The best estimates of the encapsulation-energy gains found for $\text{H}_2\text{@C}_{60}$, Ne@C_{60} , and $\text{N}_2\text{@C}_{60}$ are at least 4 kcal/mol, slightly less than 4 kcal/mol, and about 9 kcal/mol, respectively.

I-A-26 Host-Guest Complexation of Endohedral Metallofullerene with Azacrown Ether and Its Application

TSUCHIYA, Takahiro¹; SATO, Kumiko¹;
 KURIHARA, Hiroki¹; WAKAHARA, Takatsugu¹;
 NAKAHODO, Tsukasa¹; MAEDA, Yutaka²;
 AKASAKA, Takeshi¹; OHKUBO, Kei³;
 FUKUZUMI, Shunich³; KATO, Tatsuhisa⁴;
 MIZOROGI, Naomi; KOBAYASHI, Kaoru;
 NAGASE, Shigeru
 (¹Univ. Tsukuba; ²Tokyo Gakugei Univ.; ³Osaka Univ.;
⁴Josai Univ.)

[*J. Am. Chem. Soc.* **128**, 6699–6703 (2006)]

Complexation of La@C₈₂-A with macrocyclic compounds, such as 1,4,7,10,13,16-hexaazacyclooctadecane, 1,4,7,10,13,16-hexamethyl-1,4,7,10,13,16-hexaazacyclooctadecane, mono-aza-18-crown-6 ether, 18-crown-6 ether, and p-*tert*-butylcalix[*n*]arenes (*n* = 4–8) is investigated.

I-A-27 Synthesis of Stannaindenyl Anions and a Dianion

SAITO, Masaichi¹; SHIMOSAWA, Masakazu¹;
 YOSHIOKA, Michikazu¹; ISHIMURA, Kazuya;
 NAGASE, Shigeru
 (¹Saitama Univ.)

[*Organometallics* **25**, 2967–2971 (2006)]

Reduction of 1,1-diphenylstannaindene with lithium gives the 1-phenyl-1-stannaindenyl anion, which is further reduced to provide the 1-stannaindenyl dianion. The remarkable upfield ⁷Li NMR resonance in the dianion and theoretical calculations suggest that the 1-stannaindenyl dianion has considerable aromatic character, as is observed in the sila- and germaindenyl dianions. The structure, charge distribution, NMR chemical shifts of the unsolvated and solvated 1-stannaindenyl dianion are calculated at the B3LYP level.

I-A-28 The Bingel Monoadducts of La@C₈₂: Synthesis, Characterization, and Electrochemistry

FENG, Lai¹; WAKAHARA, Takatsugu¹;
 NAKAHODO, Tsukasa¹; TSUCHIYA, Takahiro¹;
 PIAO, Qiuyue¹; MAEDA, Yutaka²; LIAN, Yongfu¹;
 AKASAKA, Takeshi¹; HORN, Ernst³; YOZA,
 Kenji⁴; KATO, Tatsuhisa⁵; MIZOROGI, Naomi;
 NAGASE, Shigeru
 (¹Univ. Tsukuba; ²Tokyo Gakugei Univ.; ³Rikkyo Univ.;
⁴Bruker AXS K.K.; ⁵Josai Univ.)

[*Chem. Eur. J.* **12**, 5578–5586 (2006)]

The reaction of La@C₈₂ with diethyl bromomalonate provides five monoadducts. Four of the five adducts are ESR inactive and singly bonded regioisomers, while the remaining adduct is ESR active and possesses a cyclic moiety between the malonate group and the C₈₂ cage.

Addition sites, thermal stabilities, and electrochemical properties are investigated with the help of density functional calculations.

I-A-29 Syntheses, Structures, and Reactions of Heptacoordinate Trihalogermanes Bearing a Triarylmethyl-Type Tetradentate Ligand

IWANAGA, Kohei¹; KOBAYASHI, Junji¹;
 KAWASHIMA, Takayuki¹; TAKAGI, Nozomi;
 NAGASE, Shigeru
 (¹Univ. Tokyo)

[*Organometallics* **25**, 3388–3393 (2006)]

Heptacoordinate trihalogermanes are synthesized by the reaction of the (triarylmethyl)lithium species and with tetrachlorogermane. The bonding nature of the central heptacoordinate Ge atom and the surrounding O atoms is investigated by the AIM (atoms-in-molecules) analysis at the B3PW1 level. The small electron density ($\rho(r_c)$) value and the small positive Laplacian ($\nabla^2\rho(r_c)$) value at the bond critical point (r_c) value suggest that the Ge–O bonds are weak and have ionic character.

I-A-30 Structural and Electronic Properties of Fluorinated Boron Nitride Nanotubes

LAI, Lin¹; SONG, Wei¹; LU, Jing¹; GAO,
 Zhengxiang¹; NAGASE, Shigeru; NI, Ming¹; MEI,
 W. N.²; LIU, Jianjun²; YU, Dapeng¹; YE,
 Hengqiang¹
 (¹Peking Univ.; ²Univ. Nebraska)

[*J. Phys. Chem. B* **110**, 14092–14097 (2006)]

The effects of F doping on the structural and electronic properties of the (5,5) single-walled boron nitride nanotube (BNNT) are investigated by using the density functional theory method. The chemisorption of F maintains the hexagonal BN network, increases the lattice constant, and introduces acceptor impurity states. On the other hand, substitutional doping of F destroys the hexagonal BN network, decreases the lattice constant, but does not alter the insulating feature of the BNNT. The observed insulator-to-semiconducting transition, a lattice contraction, and a highly disordered atom arrangement in the sidewall of BNNTs upon F doping are most reasonably attributed to a codoping of dominating substitutional F over chemisorbed F, which can induce deep donor impurity states, a lattice contraction, and a destruction of the hexagonal BN network simultaneously.

I-A-31 Characterization of the Bis-Silylated Endofullerene Sc₃N@C₈₀

WAKAHARA, Takatsugu¹; IIDUKA, Yuko¹;
 IKENAGA, Ozora¹; NAKAHODO, Tsukasa¹;
 SAKURABA, Akihiro²; TSUCHIYA, Takahiro¹;
 MAEDA, Yutaka³; KAKO, Masahiro⁴; AKASAKA,
 Takeshi¹; YOZA, Kenji⁵; HORN, Ernst⁶;
 MIZOROGI, Naomi; NAGASE, Shigeru
 (¹Univ. Tsukuba; ²Niigata Univ.; ³Tokyo Gakugei Univ.;

⁴Univ. Electro-Communications; ⁵Bruker AXS K.K.;
⁶Rikkyo Univ.)

[*J. Am. Chem. Soc.* **128**, 9919–9925 (2006)]

The photochemical reaction of Sc₃N@C₈₀ with 1,1,2,2-tetramesityl-1,2-disilirane affords the bis-silylated adduct. This adduct was characterized by NMR spectroscopy and single-crystal X-ray structure analysis. The dynamic behavior of the disilirane moiety and the encapsulated Sc₃N cluster were also investigated. The unique redox property of the adduct is reported by means of CV and DPV. Experimental results were confirmed by density functional calculations.

I-A-32 Synthesis and Characterization of Dimetallostannafluorenes

SAITO, Masaichi¹; SHIMOSAWA, Masakazu¹;
 YOSHIOKA, Michikazu¹; ISHIMURA, Kazuya;
 NAGASE, Shigeru
 (¹Saitama Univ.)

[*Chem. Lett.* 940–941 (2006)]

There has been considerable interest in the chemistry of anions and dianions of group 14 metalloids as heavier congeners of cyclopentadienyl anions. The reaction of 9,9-bis(*p*-methoxyphenyl)-9-stannafluorene with lithium or potassium gives the corresponding dimetallostannafluorene. The structure and aromaticity are characterized by density functional calculations.

I-A-33 Carbon Monoxide inside an Open-Cage Fullerene

IWAMATSU, Sho-ichi¹; STANISKY, Christopher M.²;
 CROSS, R. James²; SAUNDERS, Martin²;
 MIZOROGI, Naomi; NAGASE, Shigeru; MURATA,
 Shizuaki¹
 (¹Nagoya Univ.; ²Yale Univ.)

[*Angew. Chem., Int. Ed.* **45**, 5337–5340 (2006)]

It is of considerable interest to store a molecule inside cage molecules by making an orifice on the cage surface. Thus, an orifice is made on C₆₀ by chemical modification, which is the largest known to date for fullerenes, and CO is inserted through the orifice. The binding energy and dynamic behaviors are investigated by density functional calculations. It is suggested that the stored CO molecule rotates rapidly on the NMR time scale but not on the IR time scale.

I-B Applications of the Zhu-Nakamura Theory to Nonadiabatic Chemical Dynamics

I-B-1 Generalized Trajectory Surface Hopping Method Based on the Zhu-Nakamura Theory

OLOYEDE, Ponnile¹; MIL'NIKOV, Gennady V.¹; NAKAMURA, Hiroki
(¹SOKENDAI)

[*J. Chem. Phys.* **124**, 144110 (2006)]

We present a generalized formulation of the trajectory surface hopping method applicable to a general multidimensional system. The method is based on the Zhu-Nakamura theory of a nonadiabatic transition and therefore includes the treatment of classically forbidden hops. The method uses a generalized recipe for the conservation of angular momentum after forbidden hops and an approximation for determining a nonadiabatic transition direction which is crucial when the coupling vector is unavailable. This method also eliminates the need for a rigorous location of the seam surface, thereby ensuring its applicability to a wide class of chemical systems. In a test calculation, we implement the method for the DH_2^+ system, and it shows a remarkable agreement with the previous results of C. Zhu, H. Kamisaka, and H. Nakamura, [*J. Chem. Phys.* **116**, 3234 (2002)]. We then apply it to a diatomic-in-molecule model system with a conical intersection, and the results compare well with exact quantum calculations. The successful application to the conical intersection system confirms the possibility of directly extending the present method to an arbitrary potential of general topology.

I-B-2 Semiclassical Treatment of Thermally Activated Electron Transfer in the Intermediate to Strong Electronic Coupling Regime under the Fast Dielectric Relaxation

ZHAO, Yi¹; LIANG, Wanzhen²; NAKAMURA, Hiroki
(¹IMS and Univ. Sci. Tech. China; ²Univ. Sci. Tech. China)

[*J. Phys. Chem. A* **110**, 8204 (2006)]

The generalized nonadiabatic transition-state theory (NA-TST) (Zhao, Y.; *et al. J. Chem. Phys.* **121**, 8854 (2004)) is used to study electron transfer with use of the Zhu-Nakamura (ZN) formulas of nonadiabatic transition in the case of fast dielectric relaxation. The rate constant is expressed as a product of the well-known Marcus formula and a coefficient which represents the correction due to the strong electronic coupling. In the case of general multidimensional systems, the Monte Carlo approach is utilized to evaluate the rate by taking into account the multidimensionality of the crossing seam surface. Numerical demonstration is made by using a model system of a collection of harmonic oscillators in the Marcus normal region. The results are naturally coincident with the perturbation theory in the weak

electronic coupling limit; while in the intermediate to strong electronic coupling regime where the perturbation theory breaks down the present results are in the good agreement with those from the quantum mechanical flux-flux correlation function within the model of effective one-dimensional mode.

I-B-3 Electron Transfer Rate Uniformly Valid from Nonadiabatic to Adiabatic Regime Based on the Zhu-Nakamura Theory

ZHAO, Yi¹; NAKAMURA, Hiroki
(¹IMS and Univ. Sci. Tech. China)

[*J. Theor. Comput. Chem.* **5**, Special Issue 1–8 (2006)]

On the basis of the generalized nonadiabatic transition state theory recently introduced to remedy the crucial deficiencies of the conventional transition state theory, we have presented a new formula for electron transfer rate, which can cover the whole range from adiabatic to nonadiabatic regime in the absence of solvent dynamics control. The rate is expressed as a product of the well-known Marcus theory and a new coefficient that represents the effects of nonadiabatic transition at the crossing seam surface. The numerical comparisons are performed with different approaches and the present approach shows an excellent agreement with the quantum mechanical numerical solutions from weak to strong electronic coupling. The explanation of the experimental data of Nelson *et al.* manifests the potential applicability of the present theory.

I-B-4 Incorporation of Nonadiabatic Transition into Wave-Packet Dynamics

MIL'NIKOV, Gennady V.; ZOU, Shiyang; NAKAMURA, Hiroki

[*J. Chem. Phys.* **123**, 141101 (2005)]

Nonadiabatic wave-packet dynamics is factorized into purely adiabatic propagation and instantaneous localized non-adiabatic transition. A general formula is derived for the quantum-mechanical local nonadiabatic operator which is implemented within the framework of the R- matrix method. The operator can be used for incorporating the nonadiabatic transition in semiclassical wave-packet dynamics.

I-B-5 Dynamics of Nonadiabatic Chemical Reactions

NAKAMURA, Hiroki

[*J. Phys. Chem. A* **110**, 10929 (2006)]

New methods are proposed to treat nonadiabatic chemical dynamics in realistic large molecular systems

by using the Zhu-Nakamura (ZN) theory of curve-crossing problems. They include the incorporation of the ZN formulas into the Herman-Kluk type semiclassical wave packet propagation method and the trajectory surface hopping (TSH) method, formulation of the nonadiabatic transition state theory, and its application to the electron transfer problem. Since the nonadiabatic coupling is a vector in multi-dimensional space, the one-dimensional ZN theory works all right. Even the classically forbidden transitions can be correctly treated by the ZN formulas. In the case of electron transfer, a new formula which can improve the celebrated Marcus theory in the case of normal regime is obtained so that it

can work nicely in the intermediate and strong electronic coupling regimes. All these formulations mentioned above are demonstrated to work well in comparison with the exact quantum mechanical numerical solutions and are expected to be applicable to large systems which cannot be treated quantum mechanically numerically exactly. In order to take into account another quantum mechanical effect, namely, tunneling effect, an efficient method to detect caustics from which tunneling trajectories emanate is proposed. All the works reported here are the results of recent activities carried out in the author's research group. Finally, the whole set of ZN formulas is presented in Appendix.

I-C Theory of Multi-Dimensional Tunneling

I-C-1 Tunneling Splitting of Energy Levels and Rotational Constants in the Vinyl Radical C_2H_3

MIL'NIKOV, Gennady V.; ISHIDA, Toshimasa¹;
NAKAMURA, Hiroki
(¹Kyoto Univ.)

[*J. Phys. Chem. A* **110**, 5430–5435 (2006)]

The instanton theory newly implemented by two of

the authors (G. V. M. and H. N.) is applied to hydrogen tunneling transfer in a vinyl radical. The converged instanton trajectory is found on the CCSD(T)/aug-cc-pVTZ level of an ab initio potential energy surface. The calculated ground-state energy splitting agrees with the recent high-resolution experimental data within 3% of discrepancy. The semiclassical wave function is used to estimate the splitting of the principal rotational constants of the radical.

I-D Laser Control of Molecular Processes and Development of Molecular Functions

I-D-1 Semiclassical Guided Optimal Control of Molecular Dynamics

KONDORSKIY, Alexey; MIL'NIKOV, Gennady V.;
NAKAMURA, Hiroki

[*Phys. Rev. A* **72**, 041401(R) (2005)]

An efficient semiclassical optimal control theory applicable to multidimensional systems is formulated for controlling wave packet dynamics on a single adiabatic potential energy surface. The approach combines advantages of different formulations of optimal control theory: quantum and classical on one hand and global and local on the other. Numerical applications to the control of NCH-CN₂ isomerization demonstrate that this theory can provide an efficient tool to manipulate molecular dynamics of many degrees of freedom by laser pulses.

I-D-2 Selective Transition to the Closely-Lying States $Cs(7D_{3/2})$ and $Cs(7D_{5/2})$ by Femtosecond Laser Pulses

YAMADA, H.²; YOKOYAMA, K.¹; TERANISHI,

Y.¹; SUGITA, A.¹; SHIRAI, T.¹; AOYAMA, M.¹;
AKAHANE, Y.¹; INOUE, N.¹; UEDA, H.¹;
YAMAKAWA, K.¹; YOKOYAMA, A.¹; KAWASAKI,
M.³; NAKAMURA, Hiroki
(¹Japan Atomic Energy Research Inst.; ²Japan Atomic
Energy Research Inst. and Kyoto Univ.; ³Kyoto Univ.)

[*Phys. Rev. A* **72**, 063404 (2005)]

A demonstration of coherent quantum control for ultrafast precise selection of closely-lying states is reported. A phase-locked pair of femtosecond laser pulses is generated through a pulse shaper to excite the ground-state cesium atom to the $Cs(7D_{3/2})$ and $Cs(7D_{5/2})$ states by two-photon absorption. The excited state population is measured by detecting fluorescence from each spin-orbit state. By controlling the phase-difference of the pulse pair, an ultrafast precise selection is accomplished. The contrast ratio of the maximal to minimal selection ratio exceeds 10^3 with the delay less than 400 fs.

I-D-3 Ab Initio Nonadiabatic Quantum Dynamics of Cyclohexadiene/Hexatriene Ultrafast Photoisomerization

TAMURA, Hiroyuki; NANBU, Shinkoh¹; ISHIDA, Toshimasa²; NAKAMURA, Hiroki
(¹Kyushu Univ.; ²Kyoto Univ.)

[*J. Chem. Phys.* **124**, 084313 (2006)]

Reaction mechanisms of the ultrafast photoisomerization between cyclohexadiene and hexatriene have been elucidated by the quantum dynamics on the *ab initio* potential energy surfaces calculated by multi-reference configuration interaction method. In addition to the quantum wave-packet dynamics along the two-dimensional reaction coordinates, the semiclassical analyses have also been carried out to correctly estimate the nonadiabatic transition probabilities around conical intersections in the full-dimensional space. The reaction time durations of radiationless decays in the wave-packet dynamics are found to be generally consistent with the femtosecond time-resolution experimental observations. The nonadiabatic transition probabilities among the ground (S_0), first (S_1), and second (S_2) excited states have been estimated by using the semiclassical Zhu-Nakamura formula considering the full-dimensional wave-packet density distributions in the vicinity of conical intersections under the harmonic normal mode approximation. The cyclohexadiene (CHD) ring-opening process proceeds descending on the $S_1(1^1B)$ potential after the photoexcitation. The major part of the wave-packet decays from $S_1(1^1B)$ to $S_1(2^1A)$ by the first seam line crossing along the C_2 -symmetry-breaking directions. The experimentally observed ultrafast S_1 - S_0 decay can be explained by the dynamics through the S_1 - S_0 conical intersection along the direction toward the five-membered ring. The CHD: hexatriene (HT) branching ratio is estimated to be approximately 5:5, which is in accordance with the experiment in solution. This branching ratio is found to be mainly governed by the location of the five-membered ring S_1 - S_0 conical intersection along the ground state potential ridge between CHD and HT.

I-D-4 Atomic Hydrogen Transmission through Five-Membered Carbon Ring by the Mechanism of Non-Adiabatic Tunneling

NANBU, Shinkoh¹; ISHIDA, Toshimasa²; NAKAMURA, Hiroki
(¹Kyushu Univ.; ²Kyoto Univ.)

[*Chem. Phys.* **324**, 721–732 (2006)]

A novel usage of the non-adiabatic effects is proposed. In this proposal, atomic hydrogen penetrates through a five-membered carbon ring with the help of the non-adiabatic tunneling phenomenon. The cyclopentadienyl radical (C_5H_5) and pentaboron-substituted corannulene radical ($C_{15}H_{10}B_5$) are used to illustrate the mechanism. To demonstrate the proposal, first principles calculations are performed for the non-adiabatic dynamics on potential energy surfaces determined by

multi-reference configuration interaction method. The results show that the non-adiabatic transitions between the ground and excited states essentially control the hydrogen atom transmission through the five-membered ring of a pentaboron-substituted corannulene radical. It is found that the transmission occurs more than once out of four incidences when an appropriate initial wave packet is chosen. The phenomenon can be interpreted in terms of the Zhu-Nakamura semiclassical theory of non-adiabatic transitions.

I-D-5 Laser Control of Reactions of Photoswitching Functional Molecules

TAMURA, Hiroyuki; NANBU, Shinkoh¹; ISHIDA, Toshimasa²; NAKAMURA, Hiroki
(¹Kyushu Univ.; ²Kyoto Univ.)

[*J. Chem. Phys.* **125**, 034307 (2006)]

Laser control schemes of reactions of photoswitching functional molecules are proposed based on the quantum mechanical wave-packet dynamics and the design of laser parameters. The appropriately designed quadratically chirped laser pulses can achieve nearly complete transitions of wave packet among electronic states. The laser parameters can be optimized by using the Zhu-Nakamura theory of nonadiabatic transition. This method is effective not only for the initial photoexcitation process but also for the pump and dump scheme in the middle of the overall photoswitching process. The effects of momentum of the wave packet crossing a conical intersection on the branching ratio of products have also been clarified. These control schemes mentioned above are successfully applied to the cyclohexadiene/hexatriene photoisomerization (ring-opening) process which is the reaction center of practical photoswitching molecules such as diarylethenes. The overall efficiency of the ring opening can be appreciably increased by using the appropriately designed laser pulses compared to that of the natural photoisomerization without any control schemes.

I-D-6 Laser Control of Chemical Dynamics: Control of Electronic Transitions by Quadratic Chirping

ZOU, Shiyang; KONDORSKIY, Alexey¹; MIL'NIKOV, Gennady V.; NAKAMURA, Hiroki
(¹IMS and Lebedev Phys. Inst.)

[*Progress in Ultrafast Intense Laser Science*, Springer-Verlag (2006)]

An effective scheme of the laser control of wave packet dynamics applicable to the systems of many degrees of freedom is discussed. It is demonstrated that by using specially designed quadratically chirped pulses fast and nearly complete excitation of wave packet can be achieved without significant distortion of its shape. The parameters of the laser pulse can be estimated analytically from the Zhu-Nakamura (ZN) theory of nonadiabatic transition. The scheme is applicable to various processes such as simple electronic excitation,

pump-dump, and selective bond breaking, and it is actually numerically demonstrated to work well by taking diatomic and triatomic molecules as examples.

I-D-7 Laser Control of Chemical Dynamics: Control of Wave Packet Motion

**KONDORSKIY, Alexey¹; MIL'NIKOV, Gennady V.;
NAKAMURA, Hiroki**

(¹IMS and Lebedev Phys. Inst.)

[Progress in Ultrafast Intense Laser Science, Springer-Verlag (2006)]

An efficient semiclassical optimal control theory for controlling wave packet dynamics on a single adiabatic potential energy surface applicable to the systems of many degrees of freedom is discussed with all the details. The approach combines advantages of different formulations of optimal control theory: quantum and classical on one hand and global and local on the other. The efficiency and reliability of the method is demonstrated by taking the systems of two and four dimensions as examples.

I-E Theoretical Studies of Electron Dynamics

Electron dynamics in nanometer-sized molecules and nanostructured materials is an intrinsic process related to a number of interesting phenomena such as linear and nonlinear optical response, electric conduction, and also chemical reaction. Despite the importance, the electron dynamics has not been understood in detail. We have developed a computational method simulating the electron dynamics in real time and real space, and revealed the dynamics in detail.

I-E-1 Photoinduced Electric Currents in Ring-Shaped Molecules by Circularly Polarized Laser Pulses

NOBUSADA, Katsuyuki; YABANA, Kazuhiro¹
(¹Univ. Tsukuba)

[*Phys. Rev. A* submitted]

We have theoretically demonstrated that circularly polarized laser pulses induce electric currents and magnetic moments in ring-shaped molecules Na₁₀ and benzene. The photoinduced electric currents are simulated in real space and real time within a time-dependent local density approximation. It has been found that the electric currents are induced efficiently and persist continuously even after the laser pulses were switched off provided the applied laser frequency is in tune with the dipole resonance frequency for each molecular system. The electric currents are definitely revealed to be a second order nonlinear optical response. The ring currents inevitably cause the magnetic dipole moment, so that the molecules are magnetized. The circularly polarized laser pulses induce the electric currents and the magnetic moment much more effectively than by using static magnetic fields.

I-E-2 An Efficient Numerical Method for Exciton States in Quantum Boxes

KUBOTA, Yoji; NOBUSADA, Katsuyuki

[*Phys. Lett. A* submitted]

We have developed an efficient numerical method for exciton states in thin quantum boxes. In our numerical method, the exciton wave function is expanded in terms of coordinate eigenstates on each grid point. This method is found to be much more efficient and promising for calculating the exciton states than the standard configuration-interaction (CI) approach. In the CI approach, the wave function is expanded in terms of single-particle electron and hole eigenfunctions. Then, the computations of the matrix elements of the Hamiltonian (Coulomb potential) require multidimensional numerical integrals. Thus, the CI approach needs huge computational costs due to the multidimensional integrals. It is practically difficult to apply the CI approach to the studies of multi-exciton states, dynamics of excitons, and excitons in complex microstructures. To overcome the drawback, we alternatively use the discrete variable representation (DVR) as the basis set for the wave function. The DVR is a coordinate eigenfunction localized on each grid point associated with the Gaussian quadrature rule. Taking the advantage of the DVR, the matrix of the multidimensional Coulomb integrals can be reduced to the diagonal matrix with single point values. Consequently, the computational time for the matrix elements decreases sharply. The matrix of the kinetic energy is also sparse. Then, we can deal with a large number of bases by using the Lanczos diagonalization. We obtained energy, eigenfunction, and electron-hole separation of the exciton for various widths L of the quantum box. Our numerical method has high potentialities for studying properties of bi- and tri-excitons in various microstructures.

I-F Electronic Structure Theory of Quantum Dissipative Systems

I-F-1 Electronic Structure Theory of Adsorbate-Surface Systems

YASUIKE, Tomokazu; NOBUSADA, Katsuyuki

In the conventional cluster model, the model cluster, which is constructed by subtracting a subsystem from the whole adsorbate-surface system, is isolated. The isolated cluster implicitly has the artificial boundary condition that the wave function should be zero at the edge of the cluster. Such an inaccurate boundary condition leads to discrete energy spectra, although adsorbate-

surface systems must have continuous ones. In the present work, we circumvent this problem by introducing the absorbing boundary condition (ABC) into the model cluster. The ABC model cluster was found to precisely reproduce the exact density of states (DOS) of a 1D periodic potential model. The improvement of DOS leads to an appropriate description for the adsorbate-surface chemical bonding. Moreover, it was also shown that the ABC model cluster allows us to reveal the dynamical properties such as an adsorbate-surface electron transfer rate and a lifetime of adsorbate electronic states.

I-F-2 Electronic Structure Calculations at Constant Chemical Potential toward the Application to Electrochemistry

SHIRATORI, Kazuya; NOBUSADA, Katsuyuki

We have developed the method of quantum chemistry calculations based on Mermin's finite temperature density functional theory (FT-DFT) to describe the electronic structures of molecular systems interacting with an electron reservoir. On the basis of the Kohn-Sham (KS) formalism of FT-DFT, the FT-KS equation is derived in a very similar form to the equation at zero-temperature. In the FT-KS equation, the exchange-correlation potential is intrinsically a function of temperature, and the occupation numbers are associated

with the Fermi-Dirac distribution. We practically approximate the exchange-correlation potential by the hybrid B3LYP functional given at zero-temperature. Then, the FT-KS equation can be solved by exploiting the same algorithm in the standard DFT calculations except that the effects of the temperature and the chemical potential are taken into account through the fractional occupation numbers. The numerical scheme for solving the FT-KS equation mentioned above was implemented in the quantum chemistry program GAMESS and applied to the reaction, $\text{Ag}^{2+} + e^- \rightleftharpoons \text{Ag}^+$ in aqueous solution. To estimate the effects of the aqueous solvent, the polarizable continuum model (PCM) was employed. The radii R of the cavities in PCM were adjusted to reproduce the experimental data of the hydration free energies.

I-G Electronic Structures and Photochemical Properties of Nanometer-Sized Metal Clusters

Nanometer-sized metal clusters provide interesting physicochemical properties such as optical response, catalysis, and reactivity, which are significantly different from those in corresponding bare metal clusters or bulk metals. We have investigated the electronic structures and the photochemical properties of monolayer-protected metal clusters with special emphasis on describing metal-molecule interactions.

I-G-1 Theoretical Investigation of Optimized Structures of Thiolated Gold Cluster $[\text{Au}_{25}(\text{SCH}_3)_{18}]^+$

IWASA, Takeshi; NOBUSADA, Katsuyuki

[*J. Phys. Chem. C* in press]

Geometric and electronic structures of a gold-methanethiolate $[\text{Au}_{25}(\text{SCH}_3)_{18}]^+$ are investigated by using density functional theory. Three types of optimized structures are derived from two different Au_{25} core clusters protected by 18 methanethiolates. The most probable optimized structure consists of a Au_7 core cluster and Au-S complex-like ring clusters, $\text{Au}_{12}(\text{SCH}_3)_{12}$ and $\text{Au}_3(\text{SCH}_3)_3$. The Au_7 core cluster is enclosed by the $\text{Au}_{12}(\text{SCH}_3)_{12}$ ring cluster and then the $\text{Au}_7\text{-Au}_{12}(\text{SCH}_3)_{12}$ core-ring subsystem is capped with the two $\text{Au}_3(\text{SCH}_3)_3$ ring clusters from both sides of the top and the bottom. This structural feature is in contrast to a general notion of gold-thiolate clusters that a core gold cluster is superficially protected by thiolate molecules. The optimized structure provides a large HOMO-LUMO gap, and its X-ray diffraction and absorption spectra successfully reproduce the experimental results.

plexes $\text{Au}_n(\text{SCH}_3)_n$. The complexes were found to be stable structures in the form of a circular ring. The characteristic Au-S interaction plays an important role in forming such a unique ring structure. The ring structure also provides interesting photochemical properties that are rather different from those of similar-sized gold-methanethiolate clusters.

I-G-2 Gold-Thiolate Nanoring: Electronic Structure and Photochemical Properties

NOBUSADA, Katsuyuki

We have studied the electronic structure and the photochemical properties of gold-methanethiolate com-

I-H Electronic Structure of a Molecule in Solution

Chemical reaction is undoubtedly the most important issue in the theoretical chemistry, and the electronic structure is a key to solve the problem. As long as molecules in the gas phase are concerned, the theory for the electronic structure has been enjoying its great success. However, when it comes to molecules in solution, the stage of theory is still an infant. Thirteen years ago, we have proposed a method referred to as RISM-SCF based on the integral equation theory of molecular liquids (RISM) and the *ab initio* electronic structure theory (SCF).¹⁾ The method was applied successfully to a variety of chemical processes in solution including a number of different types of chemical reactions, S_N2 , acid-base, redox, and so on.

More recently, we have revised the theory so that the theory can account for the three dimensional distribution of solvent around solute.²⁾ (3D-RISM) This revision turns out to be essential when one tries to treat the solvent distribution around the native state of protein. The new theory allows us to handle the electronic structure of protein in water with appropriate theories for quantum chemistry.

One of the most complicated chemical reactions is that taking place in protein, or the enzymatic reaction. The reaction involves not only the electronic structure change of chemical species, but also recognition of substrates by host protein. The latest progress in our group is to develop a new approach for molecular recognition in host-guest systems. The progress is reported in the section I-I. Combining the approach with the 3D-RISM/SCF type theory will enable us to treat enzymatic reactions.

References

- 1) S. Ten-no, F. Hirata and S. Kato, *Chem. Phys. Lett.* **214**, 391 (1993); *J. Chem. Phys.* **100**, 7443 (1994); H. Sato, F. Hirata and S. Kato, *J. Chem. Phys.* **105**, 1546 (1996).
- 2) H. Sato, A. Kovalenko and F. Hirata, *J. Chem. Phys.* **112**, 9463 (2000).

I-H-1 A New Method to Determine Electrostatic Potential around a Macromolecule in Solution from Molecular Wave Function

YOSHIDA, Norio; HIRATA, Fumio

[*J. Comput. Chem.* **27**, 453 (2006)]

The three dimensional reference interaction site model integral equation theory (3D-RISM) combined with the *ab initio* molecular orbital method (3D-RISM-SCF) is applied to a solvated macro molecular system. The solvation structure around a solute molecule is obtained from the 3D-RISM integral equation under the electrostatic potential of the solute molecule, calculated by the *ab initio* molecular orbital theory.

The electrostatic potential should be calculated on each grid point in the three dimensional real space. Therefore, the calculation of the electrostatic potential is the most time consuming part in this method. In this paper, we propose a new procedure to save the computational cost for calculating the electrostatic potential and the solvated fock matrix.

I-H-2 Ab Initio Theoretical Study of Temperature and Density Dependence of Molecular and Thermodynamic Properties of Water in the Entire Fluid Region: Autoionization Processes

YOSHIDA, Norio; ISHIZUKA, Ryosuke; SATO, Hirofumi¹; HIRATA, Fumio
(¹Kyoto Univ.)

[*J. Phys. Chem.* **110**, 8451 (2006)]

The temperature and density dependence of the molecular and thermodynamic properties of water is investigated theoretically by means of the *ab initio*

electronic structure theory combined with the reference interaction site model method, so called as RISM-SCF. We consider the autoionization process ($H_2O + H_2O = H_3O^+ + OH^-$) by regarding H_2O , H_3O^+ and OH^- as "solute" molecules in an aqueous solution and evaluate molecular geometries, electronic structure, solvation structure, and ionic product of water (pK_w) of these species as functions of thermodynamical conditions. In our previous paper, we calculated these properties by using essentially the same method in a wide range of density (0.6–1.4 g/cm³). However, the calculation was limited in rather higher density (> 0.6 g/cm³) due to the difficulty of convergence, which is inherent to the hyper-netted chain (HNC) closure. The problem is overcome in this study by employing the Kovalenko-Hirata (KH) closure which hybridizes the HNC and mean spherical approximation (MSA). Here, we present the results for the thermodynamic range 0.025 g/cm³ to 1.0 g/cm³ and from 300 K to 800 K including a supercritical point.

I-H-3 Conformational Equilibrium of 1,2-Dichloroethane in Water: Comparison of PCM and RISM-SCF Methods

LEE, Jin Yong¹; YOSHIDA, Norio; HIRATA, Fumio
(¹Sungkyunkwan Univ.)

[*J. Phys. Chem. B* **110**, 16018 (2006)]

The RISM-SCF and polarizable continuum model (PCM) approaches have been applied to study the conformational equilibrium of 1,2-dichloroethane (DCE) in water. Both the electron correlation effect and basis sets play an important role to the relative energies of the gauche and trans conformers in gas and solution phases. Both PCM and RISM-MP2 methods resulted in the consistent trend with the previous experimental and theoretical studies that the population of the gauche

conformer increases in going from the gas phase to the aqueous solution. However, the PCM treatment could not describe the solvent effect completely in that the sign of relative free energy of the gauche and trans forms is opposite to the most recent experimental and theoretical data, while it is in good agreement by the RISM-MP2 method. We found that the larger excess chemical potential gain (by ~ -4.1 kcal/mol) for the gauche conformer is large enough to result in the gauche

preference of DCE in water, though it has to compensate the more solute reorganization energy (~ 1.7 kcal/mol) and overcome the energy difference (~ 1.6 kcal/mol) in the gas phase. The radial distribution functions between DCE and the nearest water shows that the electrostatic repulsion between chlorine and oxygen atoms is higher in trans conformer than gauche one, while the attractive interaction between chlorine and hydrogen of water is higher in gauche conformer.

I-I Solvation Thermodynamics of Protein and Related Molecules

Concerning biomolecules such as protein, it is a final goal for the biochemistry and biophysics to explore the relation between conformations and biological functions. The first important step toward the goal would be to explain the conformational stability of biomolecules in terms of the microscopic structure of the molecules in solvent. It is an extremely difficult problem by any means due to the overwhelmingly large degrees of freedom to be handled, including protein and solvent.

In the past 11 years, we have been developing a method to attack the problem based on the statistical mechanics of liquids, especially, on the RISM theory.¹⁾ Recently, we put forward our effort to apply the three dimensional (3D) RISM theory to biomolecules, and have succeeded for the first time to obtain thermodynamic quantities of "real" protein, which is in agreement with experiments not only qualitatively but also quantitatively in case of the partial molar volume.²⁾ The 3D-RISM theory turns out to be even more powerful to explore water molecules trapped in a cavity of protein.³⁾

References

- 1) M. Kinoshita, Y. Okamoto and F. Hirata, *J. Am. Chem. Soc.* **120**, 1855 (1998).
- 2) T. Imai, A. Kovalenko and F. Hirata, *Chem. Phys. Lett.* **395**, 1 (2004).
- 3) T. Imai, R. Hiraoka, A. Kovalenko and F. Hirata, *J. Am. Chem. Soc.* **127**, 15334 (2005).

I-I-1 Locating Missing Water Molecules in Protein Cavities by the Three-Dimensional Reference Interaction Site Model (3D-RISM) Theory of Molecular Solvation

IMAI, Takashi¹; HIRAOKA, Ryusuke¹;
KOVALENKO, Andriy F.²; HIRATA, Fumio
(¹Ritsumeikan Univ.; ²NRC, Canada)

[Protein in press]

Water molecules confined in protein cavities are of great importance in understanding the protein structure and functions. However, it is a nontrivial task to locate such water molecules in protein by ordinary molecular simulation and modeling techniques as well as experimental methods. The present study proves that the three-dimensional reference interaction site model (3D-RISM) theory, a recently developed statistical-mechanical theory of molecular solvation, has an outstanding advantage in locating such water molecules. In this paper, we demonstrate that the 3D-RISM theory was able to reproduce the structure and the number of water molecules in cavities of hen egg-white lysozyme observed commonly in the X-ray structures of different resolutions and conditions. Furthermore, it is shown that the theory successfully identified a water molecule in a cavity, even the existence of which had been ambiguous from the X-

ray results. In contrast, it was confirmed that molecular dynamics simulation is helpless to find such water molecules because the results substantially depend on the initial coordinates of water molecules. Possible applications of the theory to problems in the field of molecular biology are also discussed.

I-I-2 Conformational Equilibria in Liquids Consisting of Small Chain Molecules

ISHIZUKA, Ryosuke; HIRATA, Fumio

[*Chem. Phys. Lett.* **420**, 135 (2006)]

The conformational equilibrium in neat liquids consisting of small chain molecules, *n*-butane and 1,2-dichloroethane, are studied by means of a RISM-type integral equation theory formulated by Yoshida, Munakata and Hirata. Conformational shift toward the *gauche* isomer was observed upon transferring from gas to liquid phases in the both fluids in harmony with experiments. The equilibrium constant for 1,2-dichloroethane shows very small temperature dependence. The pressure dependence of the equilibrium constant indicates that the *gauche* isomer is in favor at higher temperature. The theoretical results are consistent with the experimental observations.

I-I-3 Theoretical Study of Volume Changes Accompanying Xenon-Lysozyme Binding: Implication for Molecular Mechanism of Pressure Reversal of Anesthesia

IMAI, Takashi¹; ISOGAI, Hideto¹; SETO, Tomoyoshi²; KOVALENKO, Andriy F.³; HIRATA, Fumio

(¹Ritsumeikan Univ.; ²Shiga Univ.; ³NRC, Canada)

[*J. Phys. Chem. B* **110**, 12149 (2006)]

The change in partial molar volume (PMV) accompanying the xenon-lysozyme binding was investigated for elucidating the molecular mechanism of the pressure reversal of general anesthesia, using the three-dimensional reference interaction site model (3D-RISM) theory. An increase of the PMV from xenon binding to the substrate binding site of lysozyme was found, and the binding is suppressed by pressure, while the internal site binding did not change the PMV. From the decomposition of the PMV change, combined with the analysis of the hydration change due to the binding, we propose a molecular mechanism of the PMV increase from anesthetic-protein binding, that is the mechanism of pressure reversal of general anesthesia.

I-I-4 A Theoretical Analysis on Hydration Thermodynamics of Proteins

IMAI, Takashi¹; HARANO, Yuichi²; KINOSHITA, Masahiro²; KOVALENKO, Andriy F.³; HIRATA, Fumio

(¹Ritsumeikan Univ.; ²Kyoto Univ.; ³NRC, Canada)

[*J. Chem. Phys.* **125**, 024911 (2006)]

The hydration free energy (HFE) is calculated for several proteins using the three-dimensional reference interaction site model (3D-RISM) theory, a recently developed integral equation theory of molecular solvation, combined with the all-atom potentials. The HFE is decomposed into the energetic and entropic components under the isochoric condition. The former comprises the protein-water interaction energy and the water reorgani-

zation energy (the energy arising from the structural changes induced in water). Each component is further decomposed into the non-electrostatic and electrostatic contributions. It is found that the HFE is governed by the non-electrostatic hydration entropy and the electrostatic hydration energy. The non-electrostatic hydration entropy is almost exclusively ascribed to the translational entropy loss of water upon the protein insertion. It asymptotically becomes proportional to the excluded volume (EV) for water molecules with increasing the protein size. The hydration energy is determined by the protein-water interaction energy which is half compensated by the water reorganization energy. These energy terms are approximately proportional to the water-accessible surface area (ASA). The energetic and entropic contributions are balanced with each other, and the HFE has no apparent linear relation with the EV and ASA.

I-I-5 Selective Ion-Binding by Protein Probed with the 3D-RISM Theory

YOSHIDA, Norio; PHONGPHANPHANEE, Saree; MARUYAMA, Yutaka; IMAI, Takashi¹; HIRATA, Fumio

(¹Ritsumeikan Univ.)

[*J. Am. Chem. Soc.* in press]

Selective ion-binding by human lysozyme and its mutants is probed with the three-dimensional interaction site model theory, which is the statistical mechanical integral equation theory. The three-dimensional distribution of ions as well as water molecules was calculated for aqueous solutions of three different electrolytes CaCl₂, NaCl and KCl, and for four different mutants of the human lysozyme: wild type, Q86D, A92D, Q86D/A92D that have been studied experimentally. For the wild type of the protein in the aqueous solutions of all the electrolytes studied, there are no distributions observed for the ions inside the active site. The A92D and Q86D/A92D mutants show a large peak of Na⁺ in the recognition site. Especially, holo-Q86D/A92D, one of the mutants, shows conspicuous peak of Ca²⁺. These behaviors are in accord with the experimental results.

I-J Collective Density Fluctuations in Polar Liquids and Their Response to Ion Dynamics

As to the model for molecular diffusion in polar liquids, there are two quite different points of view. One is the conventional rot-translation model, and the other the interaction-site description which sees the diffusion of a molecule as a correlated motion of each atom (site).¹⁾ It is clearly advantageous to use the interaction-site description compared to the rot-translation model to account for chemical characteristics of solvent as well as solute dynamics. However, the interaction-site description has its own disadvantage in interpreting physical meaning of the results, since it does not give an explicit picture for the rotational relaxation of molecules, which can be directly probed by many experimental means including the dielectric and NMR relaxation. We have solved the problem by extracting collective modes of the density fluctuation from the site-site density correlation functions. In our recent study for dynamics of molecular liquids based on the interaction-site model, we have succeeded to abstract the collective excitations in liquids, which can be identified as optical and acoustic modes, by diagonalizing the collective

frequency matrix appearing in the generalized Langevin equation. The two modes arise essentially from the rotational and translational motions of molecules.²⁾ We applied the method to the ion dynamics in a dipolar liquid, and could have explained successfully the peculiar size dependence of friction of alkali and halide ions in terms of response of the collective excitations in solvent to the solute displacement.³⁾

In the past year, we have elaborated the memory kernel in our generalized Langevin equation base on the mode coupling theory. We have also extended our treatment to dynamics of water and hydrated ions. Those studies as well as other related topics are reviewed below.

References

- 1) F. Hirata, *J. Chem. Phys.* **96**, 4619 (1992).
- 2) S. Chong and F. Hirata, *Phys. Rev. E* **57**, 1691 (1998).
- 3) S. Chong and F. Hirata, *J. Chem. Phys.* **108**, 7339 (1998).

I-J-1 Study of Anomalous Mobility of Polar Molecular Solutions by Means of the Site-Site Memory Equation Formalism

KOBRYN, Alexander; YAMAGUCHI, T.¹; HIRATA, Fumio

(¹Fukuoka Univ.)

[*J. Mol. Liq.* **125**, 14 (2006)]

In this work, the memory equation approach is applied for theoretical study of dynamics of polar molecular liquids described by the interaction site model. The study includes the temperature-density (pressure) dependence of the translational diffusion coefficients D and orientational relaxation times τ for infinitely dilute solutions of acetonitrile and methanol in water, and methanol in acetonitrile. Calculations are performed over the range of temperatures and densities employing

the SPC/E model for water and optimized site-site potentials for acetonitrile and methanol. Despite an approximate character of the model potentials and closure relation used, the theory is able to reproduce qualitatively all main features of temperature and density dependences of D and τ observed in computer and real experiments. In particular, anomalous behavior, *i.e.*, the increase in mobility with density (pressure), is obtained for D and τ of methanol in water, while acetonitrile in water or methanol in acetonitrile do not show deviations from the usual. The observed enhancement in the molecular mobility is interpreted in accordance with the concept by Yamaguchi *et al.* [*J. Chem. Phys.* **119**, 1021 (2003)], *i.e.*, in terms of two competing origins of friction, which interplay with each other as density increases: the collisional and dielectric frictions that have tendency, respectively, to strengthen and weaken with increasing density.

I-K Statistical Mechanics of Interfacial Fluids

Microscopic structure of fluid interfaces has been drawing a lot of attention due to recent development in the experimental techniques devised particularly to probe the interface. However, there are many open questions remained unanswered. For example, how wide is the interfacial region, how does it depend on the chemical species consisting the solution? Is the interface more or less homogeneous in terms of density or concentration of the two fluids, or is it spatially inhomogeneous? If it is inhomogeneous, what is the spatial extent of the inhomogeneity? Answering those questions is the most difficult and challenging tasks for theoretical physics and chemistry, and not much progress has been made in the past, especially from a molecular view point. We have been developing statistical mechanics for two different types of interfacial fluids: fluid-fluid interface and fluids in porous media. Following are the latest achievement in that direction.

I-K-1 Criticality of a Liquid-Vapor Interface from an Inhomogeneous Integral Equation Theory

OMELYAN, Igor¹; HIRATA, Fumio; KOVALENKO, Andriy F.²

(¹ICMP, Ukraine; ²NRC, Canada)

[*Phys. Chem. Chem. Phys.* **7**, 4132 (2005)]

A microscopic theory is developed to study the liquid-vapor interfacial properties of simple fluids with *ab initio* treatment of the inhomogeneous two-body

correlation functions, without any interpolation. It consists of the inhomogeneous Ornstein-Zernike equation coupled with the Duh-Henderson-Verlet closure and the Lovett-Mou-Buff-Wertheim equation. For the liquid-vapor interface of the Lennard-Jones fluid, we obtained the density profile and the surface tension, as well as their critical behaviour. In particular, we identified non-classical critical exponents. The theory accurately predicts the phase diagram and the interfacial properties in a very good agreement with simulations. We also showed that the method leads to true capillary-wave asymptotics in the macroscopic limit.

I-L Photoinduced Phase Transitions in Molecular Materials

Photoirradiation may create electrons, holes or excitons, which are often accompanied by local structural deformation. Sometimes it causes spatially large structural transformations with the help of cooperativity possessed by interacting electrons and molecules. Thus, a nonequilibrium phase can be generated, which may not be reached by simply changing temperature or pressure because the energy of a photon is much higher than thermal energies. Such photoinduced phase transitions have been studied extensively, both experimentally and theoretically. Thanks to the great progress in laser spectroscopy techniques, charge and lattice dynamics are being clarified in many molecular materials on different time scales including ultrafast and/or coherent dynamics. Now we need to treat relevant itinerant-electron models, whose transfer integrals give transition amplitudes. This is in contrast to stochastic dynamics in classical statistical models, where transition probabilities are determined by the Boltzmann factors at finite temperatures.

I-L-1 Interchain Coupling Effects on Photoinduced Phase Transitions between Neutral and Ionic Phases in an Extended Hubbard Model with Alternating Potentials and an Electron-Lattice Coupling

[*Synth. Met.* **154**, 257–260 (2005)]

YONEMITSU, Kenji

[*Phys. Rev. B* **73**, 155120 (7 pages) (2006)]

Dynamics of ionic-to-neutral and neutral-to-ionic phase transitions induced by intrachain charge-transfer photoexcitations are studied in a quasi-one-dimensional extended Hubbard model with alternating potentials and an electron-lattice coupling for mixed-stack charge-transfer complexes. For interchain couplings, we use electron-electron interactions previously estimated for TTF-CA. Photoexcitation is introduced by a pulse of oscillating electric field. The TDHF approximation is used for the electronic part, and the classical approximation for the lattice part. In the ionic-to-neutral transition, the transferred charge density is a strongly nonlinear function of the photoexcitation density, which is characterized by the presence of a threshold. With substantial interchain couplings comparable to those in TTF-CA, the interchain correlation is strong during the transition. Neutral domains in nearby chains simultaneously grow even if their nucleation is delayed by reducing the amplitude of the electric field. With weaker interchain couplings, the growing processes are in phase only when the amplitude of the electric field is large. Thus, the experimentally observed, coherent motion of a macroscopic neutral-ionic domain boundary is allowed to emerge by such substantial interchain couplings. In the neutral-to-ionic transition, by contrast, the transferred charge density is almost a linear function of the photoexcitation density. Interchain electron-electron interactions make the function slightly nonlinear, but the uncooperative situation is unchanged and consistent with the experimental findings.

I-L-2 Inter-Chain Coulomb-Lattice Relaxation and Multicriticality in Charge Transfer Organic Complexes

KISHINE, Jun-ichiro¹; OHARA, Tomoaki¹; LUTY, Tadeusz²; YONEMITSU, Kenji

(¹*Khushu Inst. Tech.*; ²*Tech. Univ. Wroclaw*)

We discuss the neutral-to-ionic phase transition and the emergence of multi-criticality in the quasi-one-dimensional charge-transfer salt TTF-CA under pressure. We stress that subtle interplay of Coulomb and lattice processes may be quite sensitive to pressure. Emergence or disappearance of the multi-critical point in a series of charge-transfer salts is understood through this interplay. What's behind is coexistence and coupling of non-symmetry-breaking and symmetry-breaking order parameters.

I-L-3 Quantum Paraelectricity near the Neutral-Ionic Critical Point

YAMASHITA, Yasufumi; YONEMITSU, Kenji

In a series of organic charge-transfer complexes DM-TTF-QBr_nCl_{4-n}, the neutral-ionic (NI) phase transition is observed in the chlorine rich complexes for $n < 2.1$. The neutral ground state of DM-TTF-QBr₄ is destabilized by applying hydrostatic pressure P , and the NI transition emerges when P exceeds P_c where $T_c = 0$; so-called the quantum critical point (QCP). In the vicinity of the QCP, the dielectric permittivity in the neutral phase follows the Barrett formula characteristic of quantum paraelectricity, which probably originates from charge-transfer fluctuations. In the present study, we have phenomenologically dealt with the NI phase transition by a quantum version of the Blume-Emery-Griffiths (QBEG) model. Applying the mean-field approximation to the QBEG model, the magnitude of ferroelectricity and ionicity as well as the dielectric permittivity are calculated with changing P . The paraelectric ground state with a finite ionicity is realized with the Barrett-type permittivity, which is consistent with the experimental results. In addition, the calculated permittivity agrees well with that of DM-TTF-QBr₄ under various pressures including the ionic phase. What we found is that the quantum dipole-flipping term is indispensable to reproduce the experimental results within our model. Therefore, it is highly suggested that charge transfer fluctuations due to the quantum tunneling allow a finite ionicity even in the neutral phase, which realizes the quantum paraelectric ground state near the quantum critical point.

I-L-4 Dynamics of Photoexcited States in One-Dimensional Dimerized Mott Insulators

MAESHIMA, Nobuya¹; YONEMITSU, Kenji
(¹IMS and Tohoku Univ.)

[*Phys. Rev. B* **74**, 155105 (11 pages) (2006)]

Dynamical properties of photoexcited states are theoretically studied in a one-dimensional Mott insulator dimerized by the spin-Peierls instability. Numerical calculations combined with a perturbative analysis have revealed that the lowest photoexcited state without nearest-neighbor interaction corresponds to an interdimer charge transfer excitation that belongs to dispersive excitations. This excited state destabilizes the dimerized phase, leading to a photoinduced inverse spin-Peierls transition. We discuss the purely electronic origin of midgap states that are observed in a latest photoexcitation experiment of an organic spin-Peierls compound, K-TCNQ.

I-L-5 Charge Ordering in θ -(BEDT-TTF)₂RbZn(SCN)₄: Cooperative Effects of Electron Correlations and Lattice Distortions

MIYASHITA, Satoshi¹; YONEMITSU, Kenji
(¹IMS and Tohoku Univ.)

We investigate combined effects of electron correlations and lattice distortions on the charge ordering (CO)

in θ -(BEDT-TTF)₂RbZn(SCN)₄ theoretically by the two-dimensional extended Hubbard model at 1/4-filling. It is well known that this material undergoes a phase transition from the high-symmetry to the low-symmetry structure by lowering temperature. The ground state is an insulator with the horizontal-stripe CO along t_{p4} (HCO- t_{p4}). The importance of long-range electron-electron interactions is well recognized and the mechanism for stabilizing the HCO- t_{p4} has been argued mainly on the basis of the low-symmetry structure. Because the lattice distortions are coupled with the electron system, giving rise to the first-order transition sensitive to the crystal structure, electron-phonon interactions are also important. Then, by means of the exact diagonalization, we have calculated the ground-state energy and local density of holes by adopting both electron-electron and electron-phonon couplings on the basis of the high-symmetry structure. For electron-phonon couplings, we consider three kinds of distortions: displacements along the c -direction (s_c), those along the a -direction (s_{p1}) and molecular rotations (s_{p4}), leading to linear modulations in the respective transfer integrals. The s_c -dependence of the local density of holes demonstrates that the coupling s_c induces the HCO- t_{p4} . The coupling s_{p4} also induces this CO, though s_{p1} does not. In this salt, the effects of displacements along the c -direction and molecular rotations are stronger than those along the a -direction. Thus, electron-phonon interactions are crucial to stabilize both the HCO- t_{p4} and the low-symmetry structure in θ -(BEDT-TTF)₂RbZn(SCN)₄.

I-M Collective Transport through Metal-Insulator Interfaces

Molecular materials are used in many device structures. Charge transport is always through an interface between two materials with different electronic states and work functions. In field-effect transistors fabricated on an insulating material with coherent charge transport under electric fields, the insulator-(source/drain) electrode interface barrier potentials, known as Schottky barriers, play an important role. For band insulators, the Schottky barriers indeed govern the current-voltage characteristics. Quite recently, ambipolar characteristics are found in field-effect transistor device structures based on organic single crystals of a quasi-one-dimensional Mott insulator. Thus, we need to take correlation effects into account in dealing with charge transport through electrostatic potentials that originate from the long-range Coulomb interaction.

I-M-1 Mechanism of Ambipolar Field-Effect Transistors on One-Dimensional Organic Mott Insulators

YONEMITSU, Kenji

[*Proc. Pacificchem* (2005) in press]

The characteristics of a field-effect transistor (FET) fabricated on a crystal of an organic charge-transfer complex depend on the electronic state of the crystal. Ambipolar characteristics are observed for Mott insulators, while unipolar ones for band insulators. We study them in one-dimensional models of electrons. The Hubbard model for a Mott insulator is attached to the tight-binding model for metallic electrodes. We solve

the Poisson equation and add its solution for the electrostatic potential to these models in order to reproduce Schottky barriers at the interfaces. We use both the mean-field approximation and the Lanczos exact-diagonalization method in solving the time-dependent Schrödinger equation to obtain essentially the same result. Mott insulators show the ambipolar FET characteristics irrespective of the difference between the work function of the channel and that of the metallic electrodes. In order to exclude the ambiguity introduced in the one-dimensional modeling of the effect of the gate electrode and to allow the direct observation of the correlation between the electronic state in the channel and that at the interfaces, we have removed the gate electrode and employ different metals for the electrodes among which only one interface possesses a large work-

function difference. In this case, the current-voltage characteristics are almost anti-symmetric for Mott insulators and very asymmetric for band insulators. These results are also consistent with recent experiments by T. Hasegawa and coworkers. The characteristics for Mott insulators are again caused by the correlation between the electronic state in the channel and that at the interface.

I-N Polyamorphism in Molecular Liquids

So far the only quantity known as the order parameter that distinguishes liquids from gases is density. However, a recent experimental confirmation of the very existence of the pressure-induced “structural” transition between stable liquids of black phosphorus lends strong impetus to reconsideration on the concepts of liquids. Recently, we have succeeded, through *in situ* synchrotron x-ray diffraction measurements under high pressures and temperatures, in unveiling the presence of a liquid-to-liquid structural phase transition in a molecular liquid SnI₄. This discovery offers the first evidence of the thermodynamically stable transition found in general compounds other than elements. The purpose of the present project is on the basis of theoretical, computational as well as experimental investigations to construct the statistical-mechanical model for the transition from which local order parameters characterizing the polyamorphism can be extracted.

I-N-1 Murnaghan’s Equation of Motion Revisited

FUCHIZAKI, Kazuhiro
(IMS and Ehime Univ.)

[*J. Phys. Soc. Jpn.* **75**, 034601 (4 pages) (2006)]

The expression known as Murnaghan’s equation of state in high-pressure research community is mathematically a correct solution to the equation of bulk modulus but is valid only within a very limited parameter space. Moreover, the equation of state in question exhibits a peculiar behavior at high pressures when fitted to compression data. An alternative expression with a much wider range of validity is given. No peculiarity appears in the resultant compression curve. The latter expression thus provides a new tool as an infinitesimal-strain equation of state for quick estimate of compression characteristics of substances.

I-N-2 Polyamorphism in Tin Tetraiodide

FUCHIZAKI, Kazuhiro¹; **HASE, Takaki**²;
YAMADA, Akihiro²; **HAMAYA, Nozomu**³;
KATAYAMA, Yoshinori⁴; **FUNAKOSHI, Ken-ichi**⁵
(¹IMS and Ehime Univ.; ²Ehime Univ.; ³Ochanomizu Univ.; ⁴JAEA; ⁵JASRI)

[*Science* submitted]

The experimental evidence for a thermodynamically stable liquid-to-liquid transition to occur has been given thus far only for liquid phosphorus. This transition is regarded as an allotropic transition in noncrystalline states. Then, one might ask whether there can be a general polymorphic transition in noncrystalline states. Such polyamorphism in equilibrium states has been searched for a long time. Here, we present firm evidence that there exist two types of phases in a molecular liquid SnI₄ below and above about 1.5 GPa, where the melting curve of the crystalline phase has an apparent break. Structure factors of the liquids were obtained through *in situ* synchrotron x-ray diffraction measurements performed under pressures from 1 atm up to 3.4 GPa. At lower pressures below 1.5 GPa higher-wavenumber components of the structure factor can be well explained by an ideal gas structure consisting of molecules with regular tetrahedral symmetry. The presence of molecules is also confirmed by the fact that the positions of the two

principal peaks in the reduced radial distribution functions inverted from the structure factors, which corresponds to two kinds of intramolecular separation, are almost independent of pressures applied as far as the pressure is below 1.5 GPa. However, with increasing pressure beyond 1.5 GPa, the two peaks are going to merge, the situation having been found in high-pressure amorphous structure in which molecular dissociation proceeds. We conclude from these observations that the lower-pressure liquid is a molecular liquid, whereas polymerization takes place on the higher-pressure side.

I-N-3 New Method for Inversion from Structure Factors to Radial Distributions

FUCHIZAKI, Kazuhiro
(IMS and Ehime Univ.)

[*J. Chem. Phys.* submitted]

Although one of the advantages of using synchrotron radiation is its wide energy range available to scattering experiments, the situation is a bit different in the energy-dispersive type of measurements employed upon high-pressure experiments utilizing a multi-anvil type apparatus. The effective energy range is restricted by scattering angles; it is limited down to several degrees to avoid strong forward scattering on the one hand while an upper bound is limited up to ~16 degrees to obtain scattered intensities with reasonable S/N ratio on the other. The actual wavenumber window, Λ , is thus limited both in low and high k directions. If the structure factors with a finite window Λ is naively Fourier transformed to obtain radial distribution functions, G , they will suffer from spurious peaks originated from this finite truncation. Applying some window functions to reduce the truncation effects is not recommended because it severely modifies the peak height of G . Hence, a new method has been devised in which no Fourier inversion is invoked. The method relies on the maximum entropy principle to yield G according to the relation involving an observed structure factor and a Lagrange’s multiplier, λ , as input. G determined based on the relation agrees well with that obtained through the reverse Monte Carlo calculations of the structure factor, and found to be robust against a choice of the value for λ .

I-N-4 Changes in Orientational Correlations in a Molecular Liquid on Compression

FUCHIZAKI, Kazuhiro¹; NEZBEDA, Ivo²;
KALYUZHNYI, Y. V.³

(¹IIMS and Ehime Univ.; ²Czech Acad. Sci.; ³Natl. Acad. Sci. Ukraine)

[*J. Chem. Phys.* submitted]

Evolution in local molecular configuration in a molecular liquid, especially in orientational correlations, with increasing pressure is of primary interest. This aspect was investigated conducting molecular dynamics simulations for a molecular liquid SnI₄. The method of the simulations is basically the same as that employed previously¹⁾ except that the shape of the MD cell was fixed to be cubic with only its size allowed to vary.

The structure factor, S , obtained at ambient pressure attains remarkable agreement with the experimental result. Moreover, its components with wavenumbers beyond $\sim 2.7 \text{ \AA}^{-1}$ are hardly affected by thermodynamic conditions applied as well as the precise nature of the intermolecular interactions. The region beyond $k \sim 2.7 \text{ \AA}^{-1}$ corresponds to the lengths within the intramolecular distance. In fact, the behavior of S over this length scale is quantitatively explained by the ideal gas model consisting of freely rotating tetrahedral molecules. However, the behavior in the low- k region is strongly affected by the intermolecular correlations. The primary peak shifts in higher- k direction upon compression, reflecting the shrinkage of the system as a whole, whereas the height of the peak increases, implying that the spatial correlation develops due to, mainly, hard-core repulsion between the molecules. The first small peak located at $\sim 1 \text{ \AA}^{-1}$, which diminishes in height, is from the spatial correlation between the central tins; in the structure factors obtained through RISM calculations with no interactions between tin atoms, the corresponding peak never appears. A unique orientational order parameter that can capture the intermolecular orientational correlation is discussed. We found on the basis of the behavior of the order parameter that population of nearest neighbor molecular pairs which are in vertex-to-face configuration increases on compression.

References

- 1) K. Fuchizaki and K. Nagai, *Solid State Commun.* **132**, 305–308 (2004).

I-O Molecular Dynamics Simulations of Proteins

Molecular functions of proteins are investigated by molecular dynamics (MD) simulations. Using parallel computing, the present-day computer resources allow us to simulate a dynamical process of a protein system consisting of $\sim 10^6$ atoms over $\sim 10^2$ ns. The studies go one step further to develop the method of deriving biologically significant information from the MD trajectories. Here, we report a result of such simulation study. Each specific protein function requires its specific way of description. The following example is a problem of the stationary transport process of water through narrow channels formed by proteins and lipid molecules. The results of the analysis stress the importance of the single-file characteristics for the efficient transport.

I-O-1 Determinants of Water Permeability in Aquaporin Family: A Comparative Simulation Study

HASHIDO, Masanori¹; IKEGUCHI, Mitsunori¹; KIDERA, Akinori²
(¹Yokohama City Univ.; ²IMS and Yokohama City Univ.)

Water permeation through the water channel, aquaporin (AQP), was studied by comparative molecular dynamics (MD) simulations of five members of the AQP family, AQP1, AQP4, AQPZ, GlpF, and AQP0, in the explicit membrane environment. Water permeability of the AQPs was determined from the MD trajectories in the form of the single-channel osmotic permeability p_f using the linear response formula. Comparing the p_f values of the five homologous proteins, we found several structural determinants of water permeability. First, the

wider channel containing more water simply appeared to transport more water. Second, water permeability through the AQP channel is related to the frequency of the jumping motion determined by the free-energy barrier height for water to jump between two adjacent preferential hydrogen bonding sites. The third factor is the correlation in the motions of the channel waters. In the analysis of the newly developed p_f matrix, we found that the water motion in AQPs was a perturbed single-file permeation, in which the two NPA motifs appear to interrupt the correlation in water motions, referring to the ideal single-file permeation in a carbon nanotube. This means that a smaller perturbation in the NPA region results in larger permeation. The importance of the single-file nature of water permeation was confirmed in MD simulations of three mutants of AQPZ mimicking AQP1.

I-P Bioinformatics Studies of Proteins

Database work on biological information, bioinformatics, is another important part of the theoretical studies of proteins. Molecular simulation focuses on each specific protein function. On the other hand, the database study treats the ensemble of proteins in the database. Here, we report two different types of bioinformatics study developing a new method. The first is about a method describing protein dynamics using the protein structure database and the elastic network model. This treats a problem of classical mechanics, or the separation of the internal and external degrees of freedom. The second is a method comparing two proteins using an analogy between dynamic programming and Ising model. Using the partition function of Ising model, we can further improve the conventional dynamic programming to detect remote homology in amino acid sequences.

I-P-1 Normal Mode Analysis Fixing the External Degrees of Freedom for Any Portion of a System

FUCHIGAMI, Sotaro¹; OMORI, Satoshi¹; IKEGUCHI, Mitsunori¹; KIDERA, Akinori²
(¹Yokohama City Univ.; ²IMS and Yokohama City Univ.)

Normal mode analysis, including the coarse-grained version of elastic network model, is most widely used to illustrate protein fluctuations. In the system with no external field, the external degrees of freedom are defined as the six normal modes with zero frequency. This definition is equivalent to those of the Eckart condition, or the Eckart frame. However, it has been recognized that the Eckart condition is not the best way to represent protein motions, but a relative motion to a

certain fixed part of the protein gives a more transparent representation. We call it the fixed-domain frame. Here, we derived the formula converting the Hessian matrix, or the covariance matrix, defined in the Eckart frame into the one in the fixed-domain frame. This formula was derived by imposing fictitious external forces to the molecule so as to eliminate the external motions of the domain without affecting the internal degrees of freedom. The validity of the formula was confirmed by a comparison with the superposition of many snapshots obtained from a molecular dynamics simulation.

I-P-2 Probabilistic Alignment Detects Remote Homology in a Pair of Protein Sequences without Homologous Sequence Information

KOIKE, Ryotaro¹; KINOSHITA, Kengo²; KIDERA,

Akinori³

(¹Tokyo Tech; ²Univ. Tokyo; ³IMS and Yokohama City Univ.)

Dynamic programming (DP) and its heuristic algorithms are the most fundamental methods for similarity searches of amino acid sequences. Their detection power has been improved by including supplemental information, such as homologous sequences in the profile method. Here, we describe a method, probabilistic alignment (PA) that gives improved detection power, but similarly to the original DP, uses only a pair of amino acid sequences. Receiver operating characteristic (ROC) analysis demonstrated that the PA method is far superior to BLAST, and that its sensitivity and selectivity approach to those of PSI-BLAST. Particularly for orphan proteins having few homologues in the database, PA exhibits much better performance than PSI-BLAST. Based on this observation, we applied the PA method to a homology search of two orphan proteins, Latexin and Resuscitation-promoting factor domain. Their molecular functions have been described based on structural similarities, but sequence homologues have not been identified by PSI-BLAST. PA successfully detected sequence homologues for the two proteins and confirmed that the observed structural similarities are the result of an evolutionary relationship.

I-Q Theoretical Studies on Dynamical Foundation of Chemical Reactions and Proteins

Recent experimental developments in single molecule spectroscopy have shed light on the distinct nonergodic features and the heterogeneity of the state space and non-Markovian process of biomolecules. This project focuses on the dynamical foundation of chemical reactions, *i.e.*, why and how the reacting systems climb through the saddle, and on the developments of new time series analyses to extract the dynamical information regarding the underlying state space structure from single molecule time series.

I-Q-1 Dynamical Hierarchy in Transition States of Reactions

LI, Chun Bui^{1,2}; SHOUJIGUCHI, Akira³; TODA, Mikito³; KOMATSUZAKI, Tamiki⁴
(¹Kobe Univ.; ²JST/CREST; ³Nara Women's Univ.; ⁴IMS, Kobe Univ. and JST/CREST)

[*Few-Body Systems* **38**,173–179 (2006)]

Recent theoretical developments^{1–4}) in chemical reactions have greatly improved our understanding of the definability of the no-return dividing hypersurface and the reaction path along which all reacting species follow. We present a partial normalization procedure of Lie canonical perturbation theory to elucidate the phase space geometry of the transition state in the multi-dimensional phase space for a wide range of energy above the threshold. State selectivity and dynamical correlation along the evolution of reactions are also discussed.

References

- 1) T. Komatsuzaki and R. S. Berry, *Proc. Natl. Acad. Sci. U.S.A.* **98**, 7666 (2001).
- 2) T. Komatsuzaki and R. S. Berry, *J. Chem. Phys.* **130**, 4105 (2001).
- 3) T. Komatsuzaki and R. S. Berry, *Adv. Chem. Phys.* **123**, 79 (2002).
- 4) M. Toda, T. Komatsuzaki, T. Konishi, R. S. Berry and S. A. Rice, Eds., "Geometrical Structures of Phase Space in Multidimensional Chaos: Applications to Chemical Reaction Dynamics in Complex Systems," *Adv. Chem. Phys.* **130A**, **130B** (2005).

I-Q-2 Definability of No-Return Transition States in High Energy Regime above Reaction Threshold

LI, Chun Bui^{1,2}; SHOUJIGUCHI, Akira³; TODA, Mikito³; KOMATSUZAKI, Tamiki⁴
(¹Kobe Univ.; ²JST/CREST; ³Nara Women's Univ.; ⁴IMS, Kobe Univ. and JST/CREST)

[*Phys. Rev. Lett.* **97**, 028302 (4 pages) (2006)]

No-return transition states (TSs) defined in multi-dimensional phase space, where *recrossing* trajectories through the commonly used "configuration" TS pass only *once*, robustly exist up to moderately high energy regime above the reaction threshold even when nonlinear resonances among the bath degrees of freedom perpen-

dicular to the reaction coordinate result in local chaos. However, at much higher energy when global chaos appears in the bath space, the separability of the reaction coordinate from the bath degrees of freedom ceases to hold locally. In the phase space near the saddles, it is found that the slower the system passes the TS, the more recrossing trajectories reappear. Their implications and mechanisms are discussed concerning to what extent one can define no-return TSs in high energy regime above the reaction threshold.

I-Q-3 Wavelet Analysis and Arnold Web Picture for Detecting Energy Transfer in a Hamiltonian Dynamical System

SHOUJIGUCHI, Akira¹; BABA, Akinori²; LI, Chun Bui²; KOMATSUZAKI, Tamiki³; TODA, Mikito¹
(¹Nara Women's Univ.; ²Kobe Univ.; ³IMS and Kobe Univ.)

[*Laser Phys.* **16**, 1097–1106 (2006)]

Our motivation is to understand how, in chemical reactions, the reaction coordinate effectively gains dynamical energy from the other degrees of freedom (*i.e.*, bath coordinates) avoiding thermalization of the redistributed energy. In such a system, the phase space structure should be not homogeneous; *i.e.*, the system is never ergodic. In this study, we introduce a way to capture the inhomogeneity of the phase space and to monitor energy transfers among their partial degrees of freedom in nonergodic systems using wavelet analysis and a picture of the Arnold web. First, we examine several simple energy transfer processes, *i.e.*, a motion on a resonance line, between resonance lines, and around a resonance junction in a simple three-degree-of-freedom (DOF) system and show how the elemental processes of the intramolecular vibrational energy redistribution (IVR) are detected by our tools. We especially note that the structure of the higher order resonance of the system can be detected by wavelet analysis and motion in the action space. Next, we analyze a reaction process in a simple Hamiltonian system of 3 DOF with a double-well potential, *i.e.*, a system with a transition state of the center-saddle-center type, and detect energy transfers in the reactive process. The aim of the study is to propose a way to characterize the inhomogeneity of the phase space, *e.g.*, the reactive doorway, which leads to controllability of the chemical reaction by light, *i.e.*, control of the reaction by selectively preparing an initial state in the reactive doorway by optical excitation.

I-Q-4 Foundation and Limitations of Statistical Reaction Theory

SHOUJIGUCHI, Akira¹; LI, Chun Biu²;
KOMATSUZAKI, Tamiki³; TODA, Mikito¹

(¹Nara Women's Univ.; ²Kobe Univ.; ³IMS and Kobe Univ.)

[Commun. Nonlinear Sci. Numerical Simulation in press]

We study the foundation and limitations of the statistical reaction theory. In particular, we focus our attention to the question of whether the rate *constant* can be defined for nonergodic systems. Based on the analysis of the Arnold web in the reactant well, we show that the survival probability exhibits two types of behavior: one where it depends on the residential time as the power-law decay and the other where it decays exponentially. The power-law decay casts a doubt on definability of the rate *constant* for nonergodic systems. We indicate that existence of the two types of behavior comes from subdiffusive motions in remote regions from the primary resonances. Moreover, based on the analysis of non-stationary features of the trajectories, we can understand how Normally Hyperbolic Invariant Manifolds (NHIM) is connected with the Arnold web. We propose that the following two features play a key role in understanding the reactions where ergodicity is broken, i.e., whether the Arnold web is nonuniform and how the NHIM is connected with the Arnold web.

I-Q-5 Bifurcation of Transition States in Many-Degrees of Freedom Chemical Reactions: Non-Collinear H₂+H Exchange Reaction

LI, Chun Biu^{1,2}; TODA, Mikito³; KOMATSUZAKI, Tamiki⁴

(¹Kobe Univ.; ²JST/CREST; ³Nara Women's Univ.; ⁴IMS, Kobe Univ. and JST/CREST)

A new method is presented to scrutinize the bifurcation of no-return transition states (TSs) at potential saddles for many degrees of freedom (dof) systems. The bifurcation can give rise to a short-lived intermediate state at the saddle resulting in the overestimation of the reaction rate from the TS. As an illustrative example of the method, the H₂+H exchange reaction is investigated. It is shown that the new action variable of bath dof defined in the multidimensional phase space also serves as a bifurcation control parameter for the no-return TS besides the total energy. This enables us to determine analytically when and how the no-return TS is ruined through the bifurcation. The definability of no-return TSs after the occurrence of bifurcation above the reaction threshold is also discussed.

I-Q-6 Fractional Behavior in Nonergodic Reaction Processes of Isomerization

SHOUJIGUCHI, Akira¹; LI, Chun Biu²;
KOMATSUZAKI, Tamiki³; TODA, Mikito¹

(¹Nara Women's Univ.; ²Kobe Univ.; ³IMS and Kobe Univ.)

We present numerical manifestation of fractional behavior in reaction processes for a prototype model of three-degree-of-freedom (3DOF) isomerization. Survival probability in the well exhibits two distinct ranges of time scale: One when it decreases in time with power-law and the other when it does exponentially. Trajectories with power-law decay exhibit $1/f$ spectra and subdiffusion in action space, and those with exponential decay do Lorentzian spectra and normal diffusion. The existence of these two types of behavior is explained based on nonergodicity on the network of nonlinear resonances (Arnold web) in the well, and connection between the saddle and the Arnold web. Implications of the fractional dynamics are discussed in terms of Maxwell's demon in molecules.

I-Q-7 Mechanism of Fast Energy Exchange between Two NO Vibrations in a Short Lifetime Path of O(1D)+N₂O→NO+NO: Analyses by the Normal Form Theory

KAWAI, Shinnosuke¹; FUJIMURA, Yo¹;
KAJIMOTO, Okitsugu¹; YAMASHITA, Takefumi²;
LI, Chun Biu³; KOMATSUZAKI, Tamiki⁴; TODA, Mikito⁵

(¹Kyoto Univ.; ²Univ. Tokyo; ³Kobe Univ.; ⁴IMS and Kobe Univ.; ⁵Nara Women's Univ.)

Normal form theory is applied to analyze classical dynamics of a short lifetime path in the reaction O(¹D) + N₂O → NO + NO, which was found to exhibit efficient energy exchange between the vibrational modes in spite of the short lifetime of the reaction intermediate as shown in our previous paper [S. Kawai *et al.*, *J. Chem. Phys.* **124**, 184315 (2006)]. The normal form procedure simplifies the analysis of the dynamics near the saddle point by significantly reducing the number of coupling terms in the Hamiltonian. By assessing the contribution of the remaining coupling terms, we reduce the system to a subsystem of two degrees of freedom, which describes the basic mechanism of the energy transfer near the saddle. The motion of the subsystem preserves the "normal mode picture" in spite of its high energy. Then the vibrational energy, which is initially localized in the new NO bond, is transferred to the old NO bond through the beat between the symmetric and antisymmetric stretching modes. Moreover, the period of the "beat" between the two normal modes is short enough for the energy transfer to take place near the saddle. Thus, the essence of the efficient energy transfer is explained by the robust preservation of the "normal mode picture" and the relatively large difference between the frequencies of the two modes.

I-Q-8 Topographical Complexity of Multidimensional Energy Landscapes

RYLANCE, Gareth J.¹; JOHNSTON, Roy L.¹;
MATSUNAGA, Yasuhiro²; LI, Chun Biu^{2,3}; BABA, Akinori^{2,3}; KOMATSUZAKI, Tamiki⁴

(¹Univ. Birmingham; ²Kobe Univ.; ³JST/CREST; ⁴IMS, Kobe Univ. and JST/CREST)

A new scheme for visualizing and quantifying the

complexity of multidimensional energy landscapes and multiple pathways is presented employing Principal Component (PC)-based disconnectivity graphs and the Shannon entropy of relative 'sizes' of superbasins. The PC-based disconnectivity graphs incorporate a metric relationship between the stationary points of the system, which enable us to capture not only the actual assignment of the superbasins but also the size of each superbasin in the multidimensional configuration space. The landscape complexity measure quantifies the degree of topographical complexity of a multidimensional energy landscape and tells us at which energy regime branching of a main path becomes significant, making the system more likely to be kinetically trapped in local minima. The path complexity measure quantifies the difficulty encountered by the system to reach a connected local minimum by the path in question, implying that the more significant the branching points along the path are the more difficult it is to end up with the desired local minimum. As an illustrative example, we apply this analysis to two kinds of small model protein systems exhibiting a highly frustrated, and an ideal funnel-like energy landscape.

I-Q-9 A New Scheme to Construct Multidimensional Effective Free Energy Landscape from Single Molecule Time Series

BABA, Akinori^{1,2}; KOMATSUZAKI, Tamiki³
(¹Kobe Univ.; ²JST/CREST; ³IMS, Kobe Univ. and
JST/CREST)

The questions "How can one learn from an ensemble of short single molecule time series about the underlying multidimensional free energy landscape or, in general, state space?" and "How can one differentiate molecular memory along several reaction paths, if it exists?" are among the most important and central subjects for analyzing single molecule time series. Here we present a concept of local ergodic state (LES) to explore free energy landscape picture. We introduce a working hypothesis on a given single molecule time series concerning LES: if LES exists, a unique distribution (not necessarily Gaussian) function for the observable can be assigned for the LES. To assign LESs from single molecule time series, we focus on the hierarchy of time scales, $t_{\text{cor}} \ll t_{\text{eq}} \ll t_{\text{obs}} \ll t_{\text{esc}}$, where t_{cor} is the time scale of the system to possess dynamic memory, t_{eq} the time scale to be "equilibrated" within each LES, t_{obs} the observation time, and t_{esc} the time scale of the system to escape from a LES to the other LES on multidimensional free energy landscape. Our methodology naturally leads to a free energy landscape whose topography depends on which time scale the system experiences the underlying landscape. For example two metastable states will be unified as one if the time scale of observation is longer than the escape time scale for which the system can visit mutually these two states. We present our recent analyses on time series of the end-to-end distance of 46-bead model protein.

I-R Analysis Method of Electronic Structure

Understanding of chemical bond has been one of the main subjects in physical chemistry since its foundation. Nowadays, it is easy for the modern quantum-chemical technique to compute bond energy, length or detailed information on wave functions. However, it is difficult to directly bridge between these results and traditional chemical concepts (or chemical intuition), because the wave function of a molecule is usually described in terms of molecular orbitals (MO) being de-localized over whole molecule. Even obtaining the wave function of the molecule, it is numerical description of the molecule, and is often far from chemical intuition. Various methods have been developed to make up for the deficiencies in MO method. One good example is population analysis, which provides the information on an atom in a molecule. In this project, we have developed new analysis methods abstracting chemical concepts from computational results of standard MO.

I-R-1 Analysis on Solvated Molecule with a New Energy Partitioning Scheme for Intra- and Intermolecular Interactions

SATO, Hirofumi¹; SAKAKI, Shigeyoshi²
(¹IMS and Kyoto Univ.; ²Kyoto Univ.)

[*J. Phys. Chem. B* **110**, 12714–12720 (2006)]

A new partitioning scheme for the total energy of molecules is presented. In the scheme, the Hartree-Fock total energy of a molecular system is represented as the sum of one- and two-center terms exactly. The present method provides physically reasonable behavior for a wide range of interactions, and intermolecular interaction is treated equivalently with intramolecular interaction. The method is applied to analysis on the inter- and intramolecular interactions of molecular complexes both in gas phase and in aqueous solution. The results strongly indicate that the present method is a powerful tool to understand not only the bonding nature of molecules but also interaction between molecules.

I-R-2 A New Analysis of Molecular Orbital Wavefunctions Based on Resonance Theory

IKEDA, Atsushi¹; NAKAO, Yoshihide¹; SATO, Hirofumi²; SAKAKI, Shigeyoshi¹
(¹Kyoto Univ.; ²IMS and Kyoto Univ.)

[*J. Phys. Chem. A* **110**, 9028–9030 (2006)]

A new method to evaluate the weights of resonance

structures from molecular orbital wave function is proposed, which is based on the second quantization of singlet-coupling. The present method is useful to analyze molecules of which the electronic structures are well localizable. The evaluation is carried out through localization of molecular orbitals followed by algebraic calculation of density matrices. This method is applied to H₂O, H₃O⁺, and BH₃. The calculated weights of covalent and ionic structures are in excellent agreement with those of the previous works and our chemical intuition.

I-R-3 Solvation Effect on Resonance Structure. Extracting Valence Bond-Like Character from Molecular Orbitals

IKEDA, Atsushi¹; YOKOGAWA, Daisuke¹; SATO, Hirofumi²; SAKAKI, Shigeyoshi¹
(¹Kyoto Univ.; ²IMS and Kyoto Univ.)

[*Chem. Phys. Lett.* **424**, 449–452 (2006)]

We have analyzed the resonance structure in the electronic structure for solvated molecules, which are computed by the RISM-SCF method. The analysis offers a bridge between modern quantum computational results and chemical intuitions. As expected, the contribution from the ionic structure tends to be enhanced in aqueous solutions on the electronic structure polarization due to solvation. The present procedure offers understanding of the nature of chemical bonds in a solvated molecule.

I-S Solvation Structure and Its Effect on Electronic Structure

It is well known that the electronic structure of a molecule considerably changes when the molecule is dissolved in solvent. Understanding the essential of this complex event requires three points of view, namely, the electronic structure of the molecule, solvation structure around it and these coupling. In this project, we have developed various types of methods to describe solvation processes and applied them to real systems.

I-S-1 A New Method to Reconstruct Three-Dimensional Spatial Distribution Function from Radial Distribution Function in Solvation Structure

YOKOGAWA, Daisuke¹; SATO, Hirofumi²; SAKAKI, Shigeyoshi¹
(¹Kyoto Univ.; ²IMS and Kyoto Univ.)

[*J. Chem. Phys.* **123**, 211102 (5 pages) (2005)]

Three-dimensional spatial distribution function SDF of solvent is a fundamental quantity for analysis of solvation. However, its calculation has been very limited because long computational time is required. We here developed a novel and robust method to construct approximated SDFs of solvent sites from radial distribution functions. In this method, the expansion of SDFs in real solid harmonics around atoms of solute leads to a linear equation, from which SDFs are evaluated with reasonable computational time. This method is applied to the analysis of the solvation structure of liquid water, as an example. The successful results clearly show that this method is very powerful to investigate solvation structure.

I-S-2 New Evaluation of Reconstructed Spatial Distribution Function from Radial Distribution Functions

**YOKOGAWA, Daisuke¹; SATO, Hirofumi²;
SAKAKI, Shigeyoshi¹**

(¹Kyoto Univ.; ²IMS and Kyoto Univ.)

[*J. Chem. Phys.* **125**, 114102 (2006)]

Although three dimensional (3D) solvation structure is much more informative than one dimensional structure, its evaluation is difficult experimentally and theoretically. In our previous communication [Yokogawa *et al. J. Chem. Phys.* **123**, 211102 (2005)], we proposed a new method to present reconstructed spatial distribution function (RC-SDF) from a set of radial distribution functions (RDFs). In this article, we successfully extended the method more accurately with new basis sets. This new method was applied to two liquid solvation structures, methanol and DMSO, as examples. Their RC-SDFs evaluated here clearly show that the former solvation structure is well-defined while the latter one is broad, which agrees well with the SDFs calculated directly from MD simulations. These results indicate that the method can reproduce well these 3D solvation structures in reasonable computational cost.