



RESEARCH ACTIVITIES

Theoretical and Computational Molecular Science

It is our ultimate goal to develop theoretical and computational methodologies that include quantum mechanics, statistical mechanics, and molecular simulations in order to understand the structures and functions of molecules in gasses and condensed phases, as well as in bio and nano systems.

Theoretical Study and Design of Functional Molecules: New Bonding, Structures, and Reactions

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In theoretical and computational chemistry, it is an important goal to develop functional molecules prior to or in cooperation with experiment. Thus, new bonds and structures provided by heavier atoms are investigated together with the reactivities. In addition, chemical modification and doping of cage-like molecules and clusters including fullerenes and carbon nanotubes are investigated to develop functional nano-molecular systems. Efficient computational methods are also developed to perform reliable quantum chemistry calculations even for large molecular systems.

1. New Parallel Algorithm of Energy Gradient Calculations for Second-Order Møller-Plesset Perturbation (MP2) Theory¹⁾

It is an important subject to determine molecular geometries and reaction paths. For this purpose, density functional theory (DFT) is widely used because of its low computational cost. However, the generally used DFT methods fail to describe non-covalent interactions that play an important role in supramolecules, host-guest interactions, self-assembly, molecular recognition, and the folding of proteins, and they tend to underestimate reaction barriers.

Second-order Møller-Plesset perturbation theory (MP2) is the simplest method that includes electron correlation important for non-covalent interactions and reaction barriers. MP2 is also helpful for checking DFT results. Despite these advantages, MP2 calculations are much more time-consuming than DFT calculations and require very large memory and hard disk. These make MP2 geometry optimization difficult for large molecules. Therefore, a new parallel algorithm of MP2 energy gradient calculations is developed using the MP2 energy algorithm that we have developed recently, which is

essential for the determination of molecular geometries and reaction paths. The algorithm decreases highly the FLOP (floating point operation) count as well as memory and disk sizes. Test parallel calculations are performed for taxol (C₄₇N₁₄H₅₁) and luciferin (C₁₁N₂O₃S₂H₈) with the 6-31G, 6-31G(d) and aug-cc-pVDZ basis sets. The results demonstrate the high parallel efficiency of the algorithm. In addition, the computational speed per CPU is considerably higher than that of other representative programs. Obviously, these make MP2 calculations feasible for considerably large molecules, and enriches the important applications, especially for molecular systems where DFT is inferior to MP2 in accuracy and reliability.

2. Accuracy of the Fragment Molecular orbital (FMO) Method Based MP2 Theory²⁾

The fragment molecular orbital (FMO) method permits high-speed *ab initio* calculations of large molecular systems by dividing them into small fragments. Since the MP2 code applicable to large molecules is developed, it is interesting to calibrate the accuracy of the MP2-based FMO method. Therefore, three-body interactions as well as two-body interactions are considered in the FMO method. These are named FMO2 (two-body) and FOM3 (three-body). Test calculations are carried out with the 6-31G(d) and 6-311G(d) basis sets for (H₂O)_n (*n* = 16, 32, 64), (alanine)_n (*n* = 10, 20, 40), and a small synthetic protein. FMO3-MP2 energies are closer to full MP2 energies than FMO2-MP2 energies. For example, the energy errors for the protein shown in Figure 1 are 4.61 (FMO2-MP2) and 0.81 (FMO3-MP2) mH for the 6-311G (d) basis set.

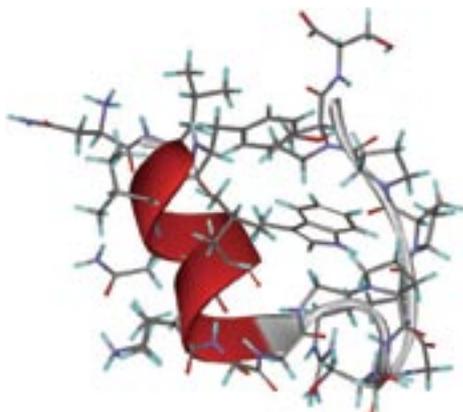


Figure 1. The synthetic protein IL2Y containing 304 atoms.

3. Multiple Bonds between Heavier Group 14 Elements: Structure and Reactivity^{3,4)}

Multiple bonds between heavier elements are of wide interest in main-group chemistry. Among these, heavier group 14 element analogues of alkynes, RMMR (M = Si, Ge, Sn, Pb), have attracted special interest as challenging synthetic targets. We have theoretically predicted that bulky substituent groups play an important role in making RMMR synthetically accessible and isolable as stable compounds. Accordingly, the Si, Ge, Sn, and Pb analogues of alkynes have been synthesized and isolated by introducing very bulky aryl and silyl groups. As shown by X-ray crystal structural analysis, the Si, Ge, and Sn analogues of alkynes have a multiply bonded structure, while the heaviest Pb analogue, Ar^{*}PbPbAr^{*} (Ar^{*} = C₆H₃-2,6-(C₆H₂-2,4,6-*i*Pr₃)₂), takes a singly bonded structure. Form theoretical calculations, however, we have revealed that even the heaviest analogue has a multiply bonded structure in solution, unlike the singly bonded structure found by X-ray crystal analysis. The different structures in solution and the crystal state are ascribed to packing forces. In addition, it is general that crystallization is significantly affected by the bulk of substituent groups. These have been also demonstrated for the recently synthesized tin analogues, Ar^{*}SnSnAr^{*} and Ar^{**}SnSnAr^{**} (Ar^{**} = C₆H₂-2,6-(C₆H₃-2,6-*i*Pr₂)₂-4-SiMe₃).

To provide insight to the unique reactivity of the silicon–silicon triple bond, the reactions of R^{Si}SiSiR^{Si} (R^{Si} = Si^{*i*}Pr [CH(SiMe₃)₂]₂) with 2-butenes (cis and trans) and alkynes are investigated. The cycloaddition of R^{Si}SiSiR^{Si} to 2-butenes proceeds in a stereospecific way, while its cycloaddition to phenylalkyne leads to an isolable aromatic 1,2-disilabenzene derivative. The reaction mechanisms are disclosed by theoretical calculations.

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4. Structures and Functionalization of Endohedral Metallofullerenes^{5,6)}

From MEM/Rietveld analysis of synchrotron X-ray powder diffraction data of Sc₂C₈₄, it was once believed that two Sc atoms are encaged inside the C₈₄ fullerene. From theoretical calculations and experiment, however, we have disclosed that two C atoms as well two Sc atoms are encapsulated inside the C₈₂ fullerene, forming Sc₂C₂@C₈₂.

We have predicted theoretically that the three-dimensional random motion of two La³⁺ cations in La₂@C₈₀ can be restricted to the circular motion in a plane by attaching an electron-donating molecule such as disilirane on the outer surface of the C₈₀ cage. This has been beautifully verified, as shown in Figure 2. Such circular motion in a plane is expected to induce unique electronic and magnetic fields in the direction perpendicular to the plane.

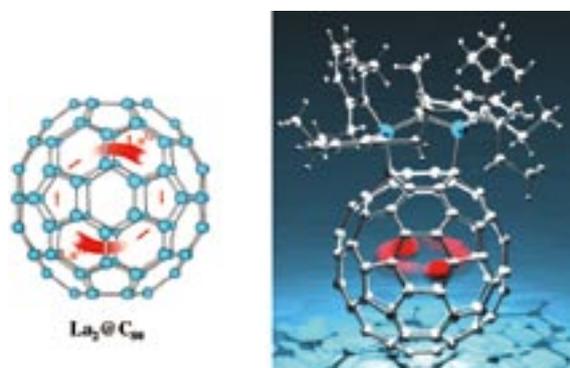


Figure 2. Random and two-dimensional circular motions of two La³⁺ cations in La₂@C₈₀ and its derivative.

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Theoretical Studies of Electron Dynamics

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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, electrical conduction, and also chemical reaction. Despite their 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 elucidated the dynamics.

1. Photoinduced Electric Currents in Ring-Shaped Molecules by Circularly Polarized Laser Pulses¹⁾

We have theoretically demonstrated that circularly polarized laser pulses induce electric currents and magnetic moments in ring-shaped molecules Na_{10} and benzene. The time-dependent adiabatic local density approximation is employed for this purpose, solving the time-dependent Kohn-Sham equation in real-space and real-time. It has been found that the electric currents are induced efficiently and persist continuously even after the laser pulses were switched off provided the frequency of the applied laser pulse is in tune with the excitation energy of the electronic excited state with the dipole strength for each molecular system. The electric currents are definitely revealed to be a second order nonlinear optical response to the magnitude of the electric field. The magnetic dipole moments inevitably accompany the ring currents, so that the molecules are magnetized. The production of the electric currents and the magnetic moments in the present procedure is found to be much more efficient than that utilizing static magnetic fields.

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

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 (FCC2) 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 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.

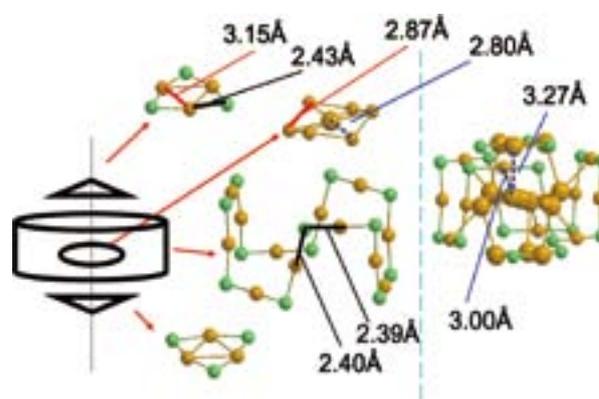


Figure 1. Fractionalized subsystems of FCC2 and their bond distances.²⁾

3. Efficient Numerical Method for Calculating Exciton States in Quantum Boxes³⁾

We have developed an efficient numerical method for exciton states confined in quantum boxes. The exciton wave function is expanded in terms of discrete variable representation basis functions. Our numerical approach has proved to be computationally much less demanding in comparison with the conventional configuration-interaction one.

4. Open-Boundary Cluster Model for Calculation of Adsorbate-Surface Electronic States

We have developed a simple embedded-cluster model approach to investigate adsorbate-surface systems. In our approach, the physically-relevant subsystem is described as an open-quantum system by considering a model cluster subject to an outgoing-wave boundary condition at the edge. This open-boundary cluster model (OCM) is free from artificial waves reflected at the cluster edge, and thus the adsorbate properties computed with the OCM are almost independent of the model cluster size. The exact continuous density of states (DOS) of a 1D periodic potential model is shown to be precisely reproduced with the OCM. The accurate DOS leads to an appropriate description of adsorbate-surface chemical bonding. Moreover, the open-boundary treatment of the OCM allows us to evaluate the electron-transfer rate from the adsorbate to the surface, whereas the conventional cluster model (CCM) does not give any information about such a dynamical process.

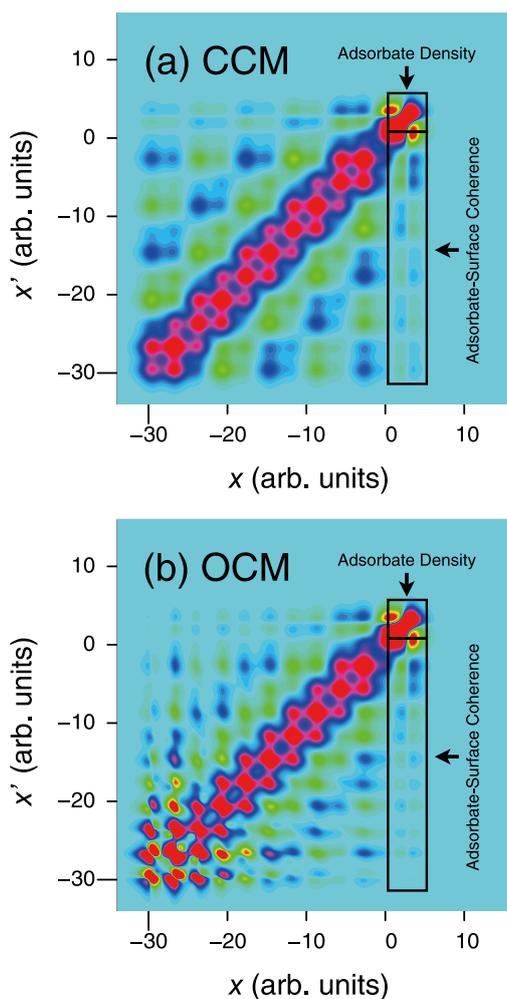


Figure 2. One-body reduced density matrix in the real space representation obtained with (a) CCM and (b) OCM. The adsorbate density and the adsorbate-surface coherence are illustrated in the square and rectangle regions, respectively. The adsorption distance and the chemical potential are set to be 2.5 and -1.3 , respectively.

5. Finite-Temperature Density Functional Calculation with Polarizable Continuum Model in Electrochemical Environment

We present a numerical methodology to calculate electronic structures of a molecule in electrochemical environment. The methodology is based on the finite temperature density functional theory (FTDFT) and allows us to study electronic properties of a molecule at a fixed chemical potential. The approach is applied to a reaction of $\text{NO}^+ + e^- \rightleftharpoons \text{NO}$ in chemical equilibrium. The solvent effect is taken into account by a conductor-like polarizable continuum model (C-PCM), and the size of the cavity in C-PCM is given in terms of the molecular charge so as to reproduce the experimental solvation energy of the cation. We demonstrate that the method combined with C-PCM (FTDFT/C-PCM) successfully describes the electronic structures of the molecule in electrochemical environment. Applicability of the present method to electrochemical properties is discussed in comparison with an alternative approach of statistically averaged DFT calculations.

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Advanced Electronic Structure Theory in Quantum Chemistry

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Aimed at predictive computational modelings of molecular electronic structures with *ab initio* quantum chemistry calculations, our scientific exploration is to establish a cutting-edge theoretical methodology that allows one to compute accurately and efficiently the complex electronic structures where the substantial multireference character in the wave functions has to be handled for the qualitative and quantitative descriptions. Our resultant works to be reported here are (1) to develop a new type of the multireference correlation model named Canonical Transformation (CT) theory, which can efficiently describe short-range dynamic correlation on top of the multi-configurational starting wave function, and (2) to construct the extensive complete active space self-consistent field (CASSCF) method combined with *ab initio* density matrix renormalization group (DMRG) method for making unprecedentedly larger active spaces available for the CASSCF calculations. These two pivotal developments are tailored to eventually be incorporated for solving large-scale multi-reference electronic structure problems.

1. Canonical Transformation (CT) Theory from Extended Normal Ordering¹⁾

We have presented a canonical transformation (CT) theory which is based on an exponential ansatz, is rigorously size extensive, and which may easily be combined with any multi-reference starting wave function such as CASSCF or DMRG wave functions. This study has derived a new formulation of the theory based on the extended normal ordering procedure of Mukherjee and Kutzelnigg.

Assuming that a reference wave function Ψ_0 is available that describes the nondynamic correlation in the problem, we incorporate the remaining dynamic correlation on top of the reference wave function Ψ_0 via an exponential operator that generates excitations between the active and external spaces, yielding

$$\Psi = e^A \Psi_0 \quad (\text{eq. 1})$$

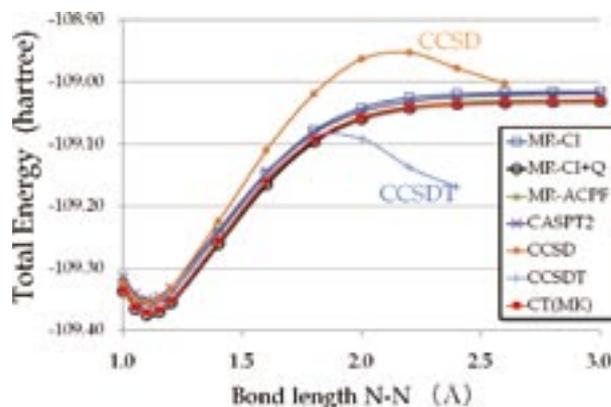


Figure 1. Bond-breaking curve of N_2 molecule with CAS(6e,6o) and cc-pVTZ Gaussian basis sets.

We will be concerned with a *unitary* formulation, where $A^\dagger = -A$. The excitations are understood to be both of external and semi-internal forms of up to two-particle operators. In a related picture, we can also view e^A as generating an effective *canonically transformed* Hamiltonian H^{CT} that acts only in the active space, but which has dynamic correlation folded in from the external space, where

$$H^{CT} = e^{-A} H e^A \quad (\text{eq. 2})$$

$$H^{CT} \Psi = E \Psi \quad (\text{eq. 3})$$

A central feature of the canonical transformation theory is the use of an *operator decomposition*, both to close the infinite expansions associated with an exponential ansatz and to reduce the complexity of the energy and amplitude equations that arise when working with a complicated reference function. Starting from the Baker-Campbell-Hausdorff expansion of the exact effective Hamiltonian, we replace each commutator by an approximate *decomposed* commutator to yield an approximate effective Hamiltonian,

$$H_{1,2}^{CT} = H_{1,2} + [H, A]_{1,2} + \frac{1}{2} [[H, A]_{1,2}, A]_{1,2} + \dots \quad (\text{eq. 4})$$

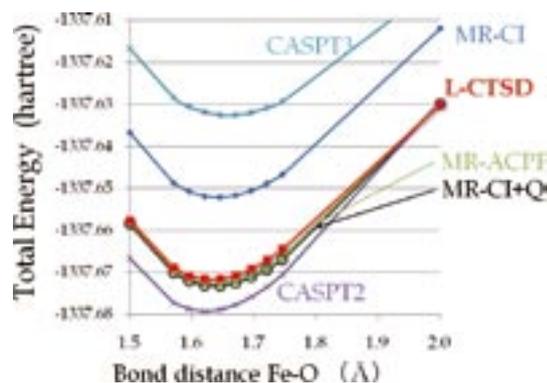


Figure 2. Bond-breaking curve of FeO molecule with CAS(12*e*,12*o*) and ANO-DZP Gaussian basis sets.

Table 1. Timings for different multireference methods for a single point calculation on the FeO curve. The time for the CASSCF calculation is not included. L-CTSD (present work) did not exploit the point-group symmetry of the molecule in the calculation.

	Time (sec)
CASPT2	5,900
CASPT3	17,000
MR-CT+Q	158,000
MR-ACPF	168,000
L-CTSD (present)	4,500

Each subscript denotes a decomposition, and the numbers “1,2” denote the particle ranks of the operators that remain after the decomposition. In this study, we have introduced a new-type operator decomposition, with some formal advantages, that is based on the concept of *extended normal ordering* as introduced by Mukherjee and Kutzelnigg. The study presented and exploited a form of the extended normal-ordered decomposition for three-particle operators. In the form implemented in the work, the computational cost is $O(a^2e^4)$, which is essentially the same as that of the single-reference coupled-cluster single and double (CCSD) model, where a is the number of active orbitals and e is the number of external orbitals.

A second focus of this work is to investigate in detail the behavior of the canonical transformation theory in a variety of chemical problems. For example, we study, with a range of basis sets, the bond-breaking potential energy curves of water, nitrogen, and iron oxide and compare our results against state-of-the-art multireference configuration interaction and perturbation theories. In addition, we examine numerically the size-extensivity and density-scaling properties of the canonical transformation energies. The results in the present study are much improved, in large part, because of improvements we have made to our numerical algorithms, and we describe in detail the numerical aspects of efficiently implementing and converging the CT equations.

Figure 1 shows the bond-breaking curve of the nitrogen molecule, which is a prototype multireference problem where the complication of breaking a triple bond occurs. For this application, the prevalent single-reference methods CCSD or

CCSDT are known to typically fail to describe the bond breaking. Figure 2 presents the potential curves of FeO computed by various multireference methods. The overall performance of our linearized CT method with single and double substitutes (L-CTSD) for these potential curves was competitive with the best multireference methods such as MR-ACPF. It is found that, for the FeO calculations, the multireference perturbation series CASPT2 and CASPT3 seemed to break down. Timings for the multireference calculations, which are listed in Table 1, reveal that CT method is two to three orders of magnitude faster than the most accurate MR-ACPF method, which though the CT is competitive with in accuracy.

2. Extensive Complete Active Space Self-Consistent Field (CASSCF) with *ab initio* Density Matrix Renormalization Group (DMRG)

To perform the large-scale multireference calculations with CT or other multireference methods, the extensive active-spaced reference wave functions where a large number of active electrons are highly (or fully) correlated within the active orbitals must be found. The CASSCF method provides the most desirable, optimal reference wave functions, in which the static correlations are effectively captured with the relaxed active orbitals that are optimized self-consistently at a high computational cost. We have developed a parallelized CAS optimization method that enables to handle unprecedentedly larger CAS with high-quality basis sets. Figure 3 shows timings for the orbital optimization steps of a single CASSCF iteration for all-trans $C_{12}H_{14}$ chain with a full π active space and cc-pVTZ Gaussian basis sets. The timings were measured on Pentium 4 2.2 GHz PC clusters connected within 100 MB bandwidth network. We have again performed the CASSCF calculation on the $C_{20}H_{22}$ chain with *ab initio* DMRG for an exact diagonalization of CAS(20*e*,20*o*). A single iteration of the extensive CASSCF calculation took just a couple of hours.

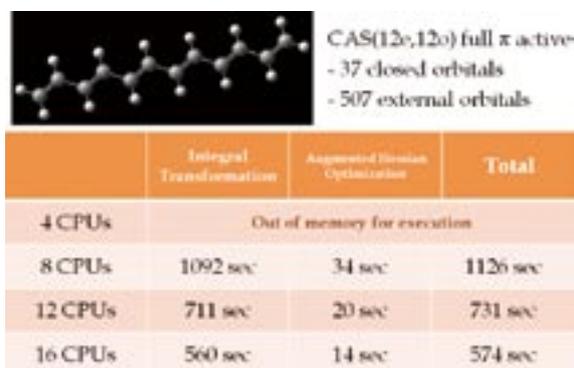


Figure 3. Timings for the parallelized CASSCF method with full π active space CAS(12*e*,12*o*) and cc-pVTZ basis.

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Developing the Statistical Mechanics Theory of Liquids in Chemistry and Biophysics

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We have been exploring the chemical and biological processes in solutions, based on the statistical mechanics of liquids, especially, on the integral equation theory of molecular liquids or the “RISM” and “3D-RISM” theories.¹⁻³⁾ Such exploration can be realized by combining the statistical mechanics theories with the other theoretical methods in the molecular science, which describes the different aspects of the physics such as the quantum processes and the liquid dynamics.

Our recent attention is focused on the “molecular recognition” and “fluctuation” of bio-molecules, which are the two key-processes in the living system. For examples, for an enzymatic reaction to take place, substrate molecules should be accommodated by the enzyme. The process is nothing but the molecular recognition which is regulated by the solvation free energy of the enzyme-substrate (ES) complex, and by the structural fluctuation of the protein.

1. Selective Ion-Binding by Protein Probed with the Statistical Mechanical Integral Equation Theory^{4,5)}

Molecular recognition is the most fundamental and important function of biomolecules. It is regarded as a process in which a host molecule makes a complex with a guest molecule through non-covalent chemical bonds including electrostatic, hydrophobic, and other interactions.

One of the most elementary processes of molecular recognition is the selective ion binding by protein. A variety of functions of protein is related to the ion binding: ion channels, ligand binding by a receptor, enzymatic reactions, and so on.

We have presented theoretical results for the ion binding by human lysozyme based on the 3D-RISM theory. The ion distribution around the wild type, Q86D, A92D and Q86D/A92D mutants in the several electrolyte solutions, KCl, NaCl and CaCl₂, has been evaluated. The doubly substituted mutant, Q86D/A92D, has two isomers distinguished with whether it has a Ca²⁺ ion or not: apo, without Ca²⁺; holo, with Ca²⁺. Since the difference between wild type and mutants lies only

in their active site, the discussion are focused on the active site, which consists of amino acid residues from Q83 to A92. The wild type and the Q86D mutant show no cation binding ability in accord with the experimental results. The 3D-RISM theory indicates that the A92D and Q86D/A92D mutants have cation binding ability. Na⁺ and Ca²⁺ ions are bound by the active site of the A92D and Q86D/A92D mutants, though K⁺ ions are not found in the active site. (see Figure 1)

The results are quite encouraging indicating the possibility of predicting protein functions by the theory. For example, it may become possible to find and/or design a protein, which has an ion binding ability. Such studies by means of the 3D-RISM theory are in progress.

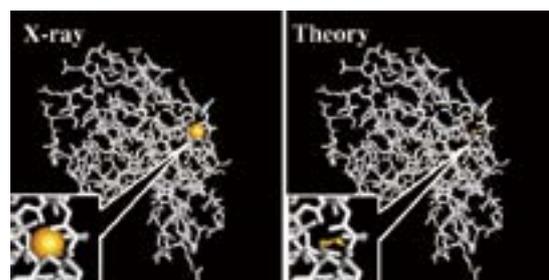


Figure 1. Comparison of Ca²⁺ position in holo-Q86D/A92D mutant between x-ray result and theoretical estimation. Threshold of 3D-DF is 25.0 for Ca²⁺ in the right hand side figure.

2. The Molecular Mechanism of the Pressure Denaturation of Protein Is Clarified by the 3D-RISM Theory⁶⁾

It has been well regarded that protein denatures by applying pressure, but nothing is known to date about the molecular mechanism. The key to solve the question is the “partial molar volume (PMV)” of protein, because the volume should “shrink” in the denatured state of the molecule due to the Le Chatelier law. Therefore, the question “why and how does pressure change the structure of protein” can be rephrased as “why and how is the PMV of the high pressure structure (HPS)

less than that of the low pressure structure (LPS).”

In order to answer the question, we have calculated the PMV of a protein called “ubiquitin,” associated with the transition from the low to high pressure structures, based on the 3D-RISM theory. The theory predicts that the PMV decreases upon the structural transition, which is consistent with the experimental observation. It is found from further analysis that the PMV reduction is ascribed substantially to the penetration of water molecules into a specific part of the protein. Based on the thermodynamic relation, this result implies that the water penetration causes the pressure-induced structural transition.

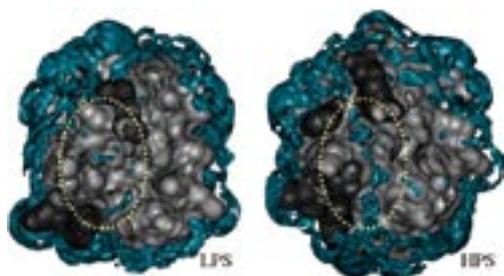


Figure 2. Isosurface representation of the three-dimensional distribution function of water oxygen around low-pressure (3 MPa) and high-pressure (300 MPa) structures (LPS and HPS, respectively) of ubiquitin. The blue surfaces show the area where the distribution function is larger than 2. The penetration of water molecules in the HPS is clearly seen in the area circled by the yellow dots.

3. Combination of Molecular Dynamics Method and 3D-RISM Theory for Conformational Sampling of Large Flexible Molecules in Solution⁷⁾

It has been a common understanding that the solvent plays an essential role in the thermodynamic stability of large molecules in solutions through, for instance, the hydrophobic and Coulomb interactions. In order to incorporate the solvent effects into the molecular simulations, we have developed a combination method of the molecular dynamics (MD) simulation with 3D-RISM theory. Using the proposed method, conformations of large flexible molecules in solution can be sampled along the free energy surface.

The solvent-induced force acting on solute atoms was evaluated as the gradient of the solvation free energy with respect to the solute-atom coordinates, which is obtained from 3D-RISM theory. In order to enhance the speed of computation, we have applied a multiple timestep algorithm based on the RESPA (Reversible System Propagator Algorithm) to the combined MD/3D-RISM method. To illustrate the present MD/3D-RISM simulation, we applied the method to a model of acetylacetone in aqueous solution, as a simple example of flexible solute.

To examine the validity of multiple timesteps, the dependence of energy conservation on timesteps was studied. Figure 3 shows the “time series” of the Hamiltonian H , where Δt_{RISM} denotes the timestep for performing the 3D-RISM calculation. The conformations of solute molecules were renewed with the

timestep of 1 fs. For $\Delta t_{\text{RISM}} = 1$ and 5[fs], H is conserved within a tolerable accuracy. For $\Delta t_{\text{RISM}} = 10$ and 20[fs], however, the values of H deviate from their initial values, with “time” elapsing. The result indicates that we can choose the timestep $\Delta t_{\text{RISM}} = 5$ [fs] without losing numerical accuracy: that is, the calculation of solvent-induced force once in 5 fs is sufficient for an accurate conformational sampling. This choice enhances the speed of computation by 3.4 times compared to a single timestep method, *i.e.* $\Delta t_{\text{RISM}} = 1$ [fs].

Acetylacetone possesses an intramolecular hydrogen bonding capability between the hydroxyl group and the carbonyl oxygen atom, and the molecule is significantly stabilized due to this hydrogen bond, especially in gas phase. The intramolecular hydrogen bond was kept intact during almost entire course of the MD simulation in gas phase, while in the aqueous solutions the bond is disrupted in a significant number of conformations. This result qualitatively agrees with the behavior on a free energy barrier lying upon the process for rotating a torsional degree of freedom of the hydroxyl group, where it is significantly reduced in aqueous solution by a cancellation between the electrostatic interaction and the solvation free energy.

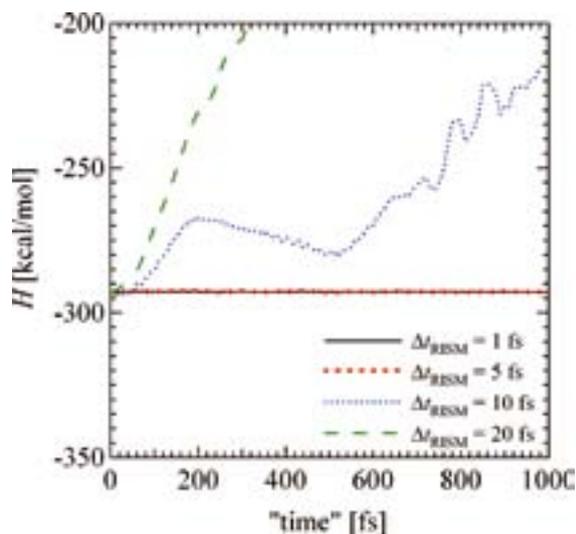


Figure 3. “Time series” of the Hamiltonian H . Δt_{RISM} denotes the timestep for performing the 3D-RISM calculation.

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Theory of Photoinduced Phase Transitions

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Photoirradiation of materials usually creates electrons and holes, which are often accompanied by local structural deformation. With the help of cooperativity, the electronic and/or structural deformation can proliferate to change the physical property such as conductivity, permittivity, and magnetic susceptibility. The resultant nonequilibrium phase may not be reached by changing temperature or pressure because the energy of a photon is much higher than thermal energies. Our theoretical researches are focused on the mechanisms and dynamics of photoinduced phase transitions, how they are controlled, and how the photoinduced electron-lattice states are different from those which are realized in thermal equilibrium.

1. Relaxation Processes in Photoinduced Neutral-Ionic Pseudoferroelectric-Ferroelectric Phase Transitions¹⁾

To find characteristic properties of relaxation processes in the neutral-ionic, pseudoferroelectric-ferroelectric phase transition in the charge-transfer complex, tetrathiafulvalene-*p*-chloranil, we investigate stochastic processes in the classical spin-1 anisotropic Blume-Emery-Griffith model. Spins are assumed to obey the Markov process that is described by the master equation with the Arrhenius-type transfer probability. Time-evolution equations are derived from two standpoints. One is the mean-field approximation and the other is an extension of the Saito-Kubo treatment to the spin-1 and anisotropic case, which improves the mean-field approximation. Solving the equations numerically, we have found highly anisotropic relaxations during the neutral-to-ionic (thus, pseudoferroelectric-to-ferroelectric) transition: The interchain ordering develops much more slowly than the intrachain one. In contrast, the ionic-to-neutral (thus, ferroelectric-to-pseudoferroelectric) phase transition proceeds in a rather isotropic manner. This finding is relevant to the experimentally realized transition induced by intramolecular photoexcitations.

2. Charge-Transfer Excitations in One-Dimensional Dimerized Mott Insulators^{2,3)}

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 from the decoupled-dimer limit 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 (Figure 1). We propose a purely electronic origin of midgap states that are observed in a latest photoexcitation experiment of an organic spin-Peierls compound, potassium-tetracyanoquinodimethane (K-TCNQ).

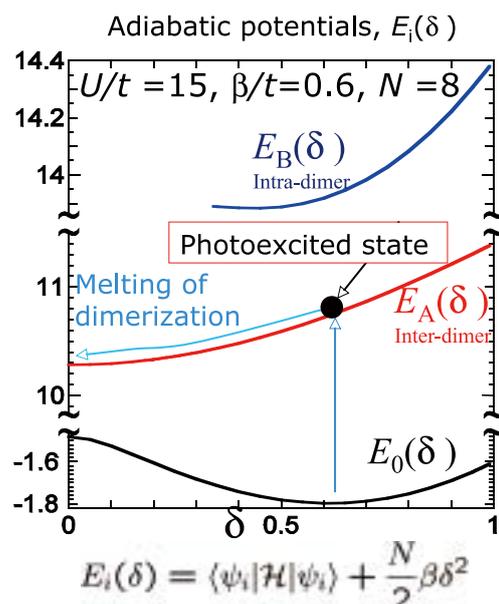


Figure 1. Adiabatic potentials of the ground state, the inter-dimer charge-transfer state, and the intra-dimer charge-transfer state.

The optical properties of one-dimensional dimerized Mott insulators are investigated further by using the one-dimensional dimerized extended Hubbard model, which contains nearest-neighbor interaction. Numerical calculations and a perturbative analysis from the decoupled-dimer limit clarify that there are three relevant classes of charge-transfer (CT) states generated by photoexcitation: interdimer CT unbound states, interdimer CT exciton states, and intradimer CT exciton states (Figure 2). This classification is applied to understanding the optical properties of an organic molecular material, 1,3,5-trithia-2,4,6-triazapentalenyl (TTTA), which is known for its photoinduced transition from the dimerized spin-singlet phase to the regular paramagnetic phase. We conclude that the lowest photoexcited state of TTTA is the interdimer CT exciton state and the second lowest state is the intradimer CT exciton state.

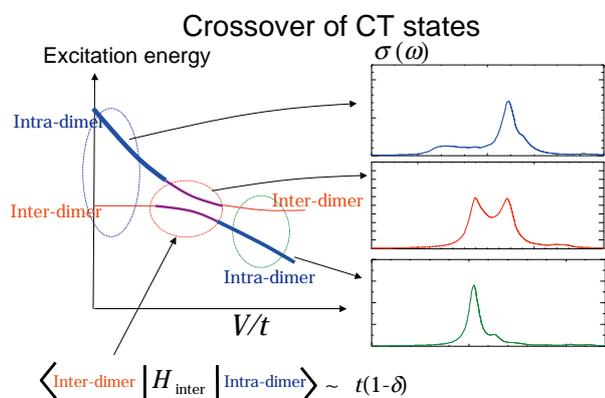


Figure 2. Energy diagram of relevant excited states. The solid (dotted) lines show the exciton (unbound) states, and the width of the lines indicate the strength of the spectral weight.

3. Effects of Electron Correlations and Lattice Distortions on Charge Order in Two-Dimensional Organic Salts^{4,5)}

Charge ordering accompanied by lattice distortion in quasi-two dimensional organic conductors θ -(BEDT-TTF)₂X [BEDT-TTF = bis(ethylenedithio)-tetrathiafulvalene] is studied by using a two-dimensional 3/4-filled extended Hubbard model with Peierls-type electron-lattice couplings first within the Hartree-Fock approximation. It is found that the horizontal-stripe charge-ordered state, which is experimentally observed in θ -(BEDT-TTF)₂RbZn(SCN)₄, is stabilized by the self-consistently determined lattice distortion. Furthermore, in the presence of the anisotropy in nearest-neighbor Coulomb interactions, the horizontal charge order becomes more stable than any other charge patterns such as diagonal, vertical, and three-fold-type states. At finite temperatures, we compare the free energies of various charge-ordered states and find a first-order transition from a metallic state with three-fold charge order to the insulating state with the horizontal charge order. The role of lattice degrees of freedom in the realization of the

horizontal charge order and the relevance to experiments on θ -(BEDT-TTF)₂X are clarified.

These combined effects of electron correlations and lattice distortions on the charge ordering in θ -(BEDT-TTF)₂RbZn(SCN)₄ are further investigated by means of the exact-diagonalization method. The findings are explained by the third-order perturbation theory from the strong-coupling limit. Electron-phonon interactions are found to be crucial to stabilize the horizontal-stripe charge order and to realize the low-symmetry crystal structure at low temperatures. Especially, modulations of transfer integrals not only by *c*- and *a*-axis molecular translations but also by molecular rotations are demonstrated to be important (Figure 3).

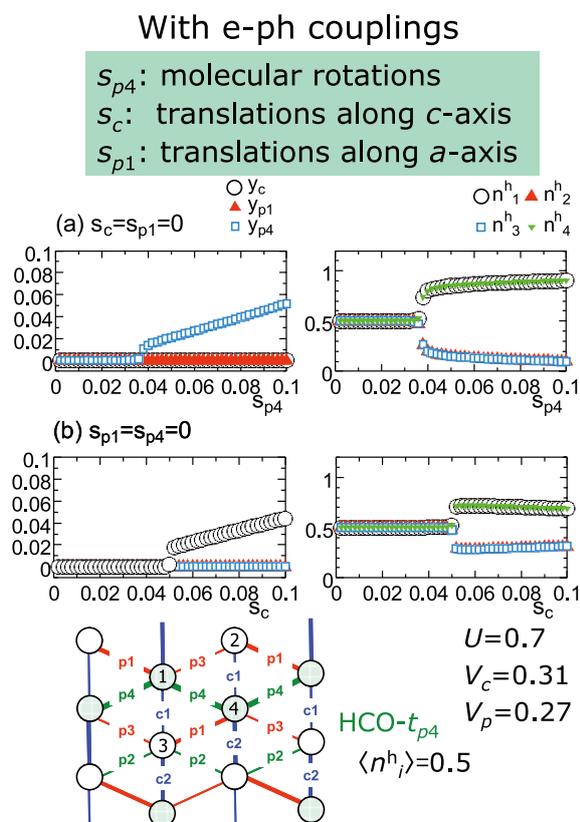


Figure 3. Electron-phonon coupling strength dependence of modulations of transfer integrals (left) and hole densities (right).

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Molecular Dynamics Study of Classical Complex Systems and Quantum Systems in Condensed Phase

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1. Free Energy of Water Permeation into Hydrophobic Core of Sodium Dodecyl Sulfate Micelle by Molecular Dynamics Calculation¹⁾

In our previous analysis of the structural stability of sodium dodecyl sulfate (SDS) micelle based on molecular dynamics calculation, vacancies were found in the center of the micelles (*Chem. Phys. Lett.* **425**, 58 (2006)). It is very interesting to clarify whether a water molecule is expected in the vacancy in thermodynamic equilibrium at room temperature. In order to investigate the stability of water in the core of micelle, free energy of transfer of water from bulk to the core has been calculated for the SDS micelle in water for two micelle sizes, $N = 61$ and 121 , at temperature $T = 300$ K and pressure $P = 1$ atm. The calculated free energy of transfer, $\Delta G_{c \leftarrow b}$, from the bulk to the core is about 28 ± 4 and 26 ± 4 kJ/mol for the micelle of size $N = 61$ and 121 , respectively, where the corresponding Boltzmann factor, $\exp(-\Delta G_{c \leftarrow b}/kT)$, is in the order of one over several ten thousand. Thus, water molecule hardly permeates into the core of the micelle.

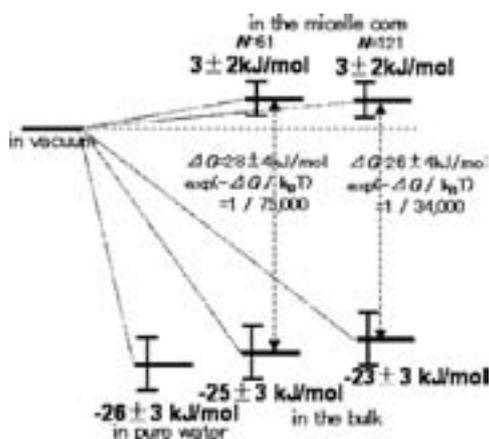


Figure 1. The calculated free energy of transfer of water molecule from vacuum to the core and to the bulk water for the micelle of the size $N = 61$ and 121 . The hydration free energy of water in pure water itself is also presented.

2. A Molecular Analysis of the Vibrational Energy Relaxation Mechanism of the CN^- Ion in Water Based upon Path Integral Influence Functional Theory Combined with a Dipole Expansion of the Solute–Solvent Interaction²⁾

The molecular mechanism of vibrational energy relaxation of the CN^- ion in water has been investigated using path integral influence functional theory combined with a dipole expansion of the solute–solvent interaction. First, in order to find out which solvent water molecules contribute most to the absorption of the solute excess vibrational energy, the normal modes of the solution, adopted for the harmonic oscillators

in the influence functional theory, have been back-transferred to the molecular coordinates and a contribution to the relaxation has been assigned to each water molecule according to the transformation matrix. Then, the coupling intensity $C^{(i)2}$ between solute and solvent molecules playing a major role in the relaxation, has been analyzed by dipole expansion of the solute–solvent interaction, where bending, rotational and translational degrees of freedom were all represented by the standard variables μ_1 , μ_2 , R , θ_1 , θ_2 , and ϕ for the dipole expansion. From these analyses, it is clarified that (1) the contribution of the solvent water to the relaxation decreases rapidly in proportion to $1/R^6$, such that only water molecules in the first hydration shell take part in the relaxation, (2) water molecules located in the direction of C–N bond contribute much to the relaxation, and (3) the excess energy is transferred to the bending of the relevant water molecule and its rotational libration represented by the variable θ_2 .

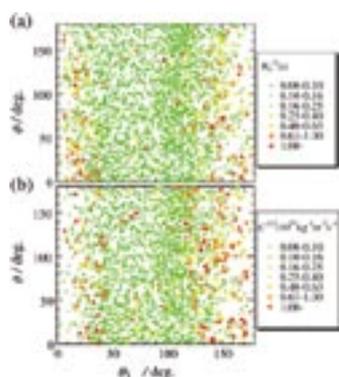


Figure 2. Actual (a) molecular relaxation $R^{(i)}$ and (b) molecular coupling intensity $C^{(i)2}$ for the water molecules in the first hydration shell.

3-1. Rotational Fluctuation of Molecules in Quantum Clusters. I. Path Integral Hybrid Monte Carlo Algorithm³⁾

We present a path integral hybrid Monte Carlo (PIHMC) method for rotating molecules in quantum fluids. This is an extension of our PIHMC for correlated Bose fluids [S. Miura and J. Tanaka, *J. Chem. Phys.* **120**, 2160 (2004)] to handle the molecular rotation quantum mechanically. A novel technique referred to be an effective potential of quantum rotation is introduced to incorporate the rotational degree of freedom in the path integral molecular dynamics or hybrid Monte Carlo algorithm. For a permutation move to satisfy Bose statistics, we devise a multilevel Metropolis method combined with a configurational-bias technique for efficiently sampling the permutation and the associated atomic coordinates. Then, we have applied the PIHMC to a helium-4 cluster doped with a carbonyl sulfide molecule. The effects of the quantum rotation on the salvation structure and energetics were examined. Translational and rotational fluctuations of the dopant in the superfluid cluster were also analyzed.

3-2. Rotational Fluctuation of Molecules in Quantum Clusters. II. Molecular Rotation and Superfluidity in OCS-Doped Helium-4 Clusters⁴⁾

Helium-4 clusters are studied as a function of cluster size N in a small-to-large size regime ($2 \leq N \leq 64$). The molecular rotation of the dopant shows nonmonotonic size dependence in the range of $10 \leq N \leq 20$, reflecting the density distribution of

the helium atoms around the molecule. The size dependence on the rotational constant shows a plateau for $N \geq 20$, which is larger than the experimental nanodroplet value. Superfluid response of the doped cluster is found to show remarkable anisotropy especially for $N \leq 20$. The superfluid fraction regarding the axis perpendicular to the molecular axis shows a steep increase at $N = 10$, giving the significant enhancement of the rotational fluctuation of the molecule. On the other hand, the superfluid fraction regarding the axis parallel to the molecular axis reaches 0.9 at $N = 5$, arising from the bosonic exchange cycles of the helium atoms around the molecular axis. The anisotropy in the superfluid response is found to be the direct consequence of the configurations of the bosonic exchange cycles.

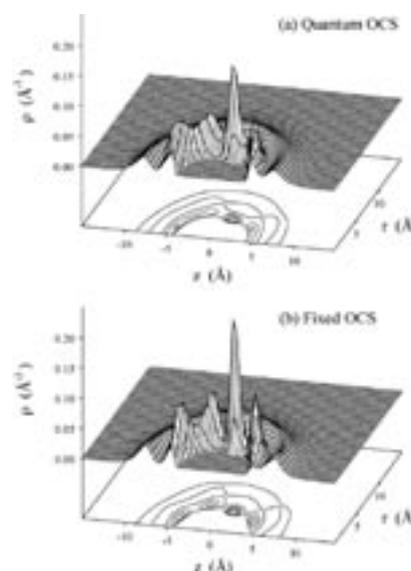


Figure 3. The total helium density distribution around the OCS molecule $\rho(z,r)$ in the OCS(^4He)₆₄ cluster [top: $\rho(z,r)$ for the quantum OCS case; bottom: $\rho(z,r)$ for the fixed OCS case]. z is the molecular axis and r the radial distance from the z axis. The OCS center of mass is located at the origin and the molecule is oriented as O–C–S from $+z$ to $-z$. All distances are in units of angstrom.

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Theoretical Studies on Condensed Phase Dynamics

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Liquids and biological systems show complicated dynamics because of their structural flexibility and dynamical hierarchy. Understanding these complicated dynamics is indispensable to elucidate the chemical reactions in solutions and the functions of proteins. We have been investigating liquid dynamics and chemical reactions in biological systems using molecular dynamics and electronic structure calculations. In addition, we have been analyzing complicated dynamics in terms of multi-dimensional spectroscopy.

1. Glass Transition in Porous Media: Test of Mode-Coupling Theory via Molecular Dynamics Simulation

When a liquid is supercooled below its freezing temperature, it becomes a metastable supercooled state. When the temperature is lowered further and crystallization could be avoided, the supercooled liquid undergoes the glass transition. In the glass transition region a drastic slowing-down occurs in dynamical properties, *e.g.* structural relaxation time, diffusion constant, and viscosity, whereas the static structure is almost the same as that of normal liquids.

The dynamics of glass forming liquids under confinement has attracted attention for its unusual thermodynamic properties; the glass transition temperature in a spatially confined system, *i.e.* a thin film or a porous media, is different from that in the bulk. A theoretical study for glass forming liquids confined in disordered immobile particles has been recently reported. In the study, the liquid-glass transition points for various densities of fluid and immobile particles were determined by using the mode-coupling theory (MCT).

We carried out molecular dynamics simulations of soft-sphere supercooled liquids in order to examine the above theoretical predictions, because the MCT is considered to be violated in the limit of low density for fluid particles. We confirmed that the structural relaxation becomes slow with the

increase in immobile particles. It is also found that the relaxation profile of the intermediate scattering function changes from the type B to the type A with the decrease in the density of fluid particles. In the type B, dynamics for high density of fluid particles, the well-known two-step relaxation is found and gradually stretched with increasing density of immobile particles. On the other hand, in the type A, dynamics for low density of fluid particles, the dynamics is significantly different from that of the type B, where the single-step relaxation decay with the long time tail has been observed. This long time tail is thought to be due to the diffusion localization, *i.e.* the fluid particles are trapped by the immobile obstacle particles for a long time. Moreover, we revealed that the system shows a reentry in the limit of low density for fluid particles at a certain high density for immobile particles as the prediction of the theoretical study. In the reentrant phenomenon, some delocalization is expected to occur due to fluid-fluid collisions. We are now examining this scenario and investigating the physical mechanism of the reentrant phenomenon using simulations.

2. Conformational Changes Associated with GTP Hydrolysis in Ras

Ras superfamily is a well-known signal transduction protein. Ras is activated by binding of GTP and binds to some effectors for regulation of cell proliferation, whereas it is inactivated by the hydrolysis of Ras-bound GTP. The hydrolysis rate is accelerated by five orders of magnitude by binding of GTPase-activating protein, GAP. Therefore, it is essential to investigate the binding effect of GAP on Ras for understanding the reaction.

We analyze the hydrolysis by dividing into the following four states; (i) active (reactant), (ii) GAP-bound, (iii) intermediate of hydrolysis, and (iv) inactive (product) states. We performed molecular dynamics (MD) calculation for the four states and analyzed the conformational changes and fluctuation.

tuations of Ras and GAP in these states. We also carried out QM/MM calculation to examine the details of structures.

In the step from the active to GAP-bound state, salt bridges between acidic residues in Ras and basic residues in GAP are formed. These bonds between Ras and GAP change the HB network structure around the active site and the structures in the switches I and II. In addition, the exchange of a water molecule near GTP is significantly suppressed by the binding of GAP to RAS. The present result implies that the bound water molecule near GTP makes the hydrolysis reaction facile.

GTP is converted to GDP and Pi by the hydrolysis. With MD and QM/MM methods we successfully constructed a stable intermediate state which was found in a recent experimental study. We found that the HB network structure around the active site and the conformation between Ras and GAP in the intermediate state are almost the same as those in the GAP-bound state. We clarified that the invasion of water required for the release of Pi and GAP does not take place in this state. We are also investigating how Pi and GAP are released from Ras in the last step.

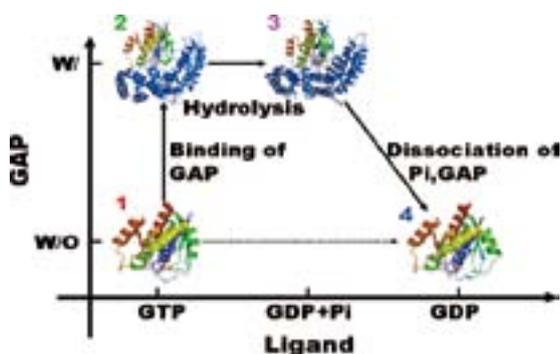


Figure 1. Conformational changes associated with GTP hydrolysis in Ras.

3. Two-Dimensional Infrared Spectroscopy of Intermolecular Modes in Liquid Water

Liquid water is an interesting system with a number of anomalous thermodynamic and dynamic properties. Its complicated dynamics has been analyzed with various kinds of spectroscopies. Great progresses have been achieved in developing multi-dimensional spectroscopies since late 90 s.

We have been investigating intermolecular water dynamics using two-dimensional (2D) infrared (IR) spectroscopy which is a powerful technique to provide detailed information on dynamics. In the 2D IR spectroscopy, the system interacts with electric fields at $t = 0$, t_1 , and $t_1 + T$, and the signal is detected at $t = t_1 + T + t_3$ and thus the response function is expressed in terms of a three-time correlation function. The so-called hybrid method in which equilibrium and non-equilibrium molecular

dynamics simulations are combined is employed in the calculation of 2D IR spectroscopy.

The peak width along the diagonal line in the 2D IR spectroscopy provides a measure of inhomogeneous broadening. The present result shows that the libration motion of water has inhomogeneous contribution. In addition, the present analysis shows that the initial inhomogeneity rapidly decays with ~ 100 fs, by analyzing the waiting time, T , dependence of the diagonal line shape. The loss of initial inhomogeneity slows down about three times, when the intermolecular translation motion which couples with the libration motion is removed. Consequently, we revealed the significant effect of the translation motion on the fast loss of initial inhomogeneity of the libration motion in liquid water.

We can obtain useful information about relaxation dynamics by analyzing off-diagonal peaks of the 2D IR spectroscopy. We found a strong off-diagonal peak located at $(\omega_1, \omega_3) = (\sim 700 \text{ cm}^{-1}, \sim 150 \text{ cm}^{-1})$. The cross peak arises from the coupling between the libration motion during t_1 and the intermolecular translation motion during t_3 . The intensity of the peak decreases for $T < 40$ fs and then it increases for $T > 40$ fs. The increase in the signal intensity can be attributed to the relaxation from the libration motion to intermolecular translation motion during t_2 . The present result shows that the time constant of the relaxation is about 150 fs.

Feynman diagrams for the 2D IR spectroscopy are usually classified into three kinds of Liouville pathways, S_I , S_{II} , and S_{III} : S_I represents rephasing pathways, on the other hand, S_{II} and S_{III} represent non-rephasing ones. We found that the third-order 2D IR response function of water contains several Feynman diagrams which cannot be classified into the above three pathways. The new pathways, S_{IV} , are related to the second overtone of the libration motion due to a three-quantum transition. The existence of the three-quantum transition shows the anharmonic dynamics in the libration motion. It is conceivable that S_{IV} can be observed by the intermolecular 2D IR experiment of water with two colors.

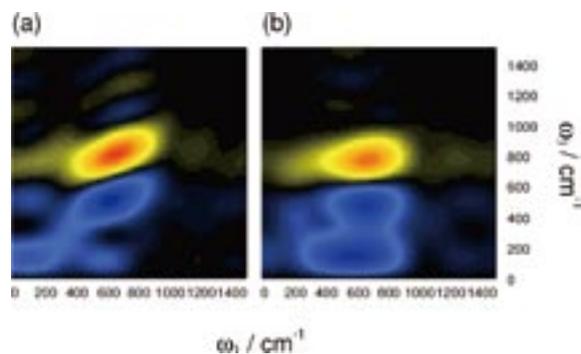


Figure 2. 2D IR spectra of water at (a) $T = 20$ and (b) 200 fs, respectively.

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Theory and Computation of Liquids and Liquid Interfaces

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The following projects 1–4 focus on the development of theory and computational analysis methods for interfacial sum frequency generation spectroscopy and its application to aqueous interfaces. The visible-infrared sum frequency generation spectroscopy is a powerful method to obtain interface-specific vibrational spectra. While this experimental technique is now widely used as an interface probe in a molecular level, reliable interpretation of the observed spectra is often lacking which significantly hinders the progress of this surface characterization method. We have proposed theoretical methods to compute the sum frequency spectra on the basis of *ab initio* molecular modeling and molecular dynamics simulation. These projects elucidated the sum frequency spectra of liquid interfaces, including aqueous salt and acid solutions, with the molecular modeling we have developed.

Projects 5 and 6 are mainly conducted by Dr. Ishida and his collaborators. Project 5 deals with the properties of room temperature ionic liquids in collaboration with Dr. Shiota at Chiba University. Project 6 is performed in collaboration with Dr. Yoshida and Prof. Hirata in the IMS about theoretical investigation of solvent effect on electron transfer reaction system.

1. Flexible and Polarizable Molecular Modeling for Describing Interfacial Properties of Gas-Liquid Aqueous Salt Solutions¹⁾

Gas-liquid interfacial structures of NaCl and NaI aqueous solutions are investigated via molecular dynamics simulations using a flexible and polarizable water model we have developed. The new five-site model of water aims at suitably describing interfacial properties, including vibrational sum frequency spectroscopy where both flexibility and polarization are crucial. The performance of the water model is system-

atically examined and demonstrated by a number of properties of bulk and interface, including density, vaporization energy, dipole moment, diffusion coefficient, radial distribution function, infrared and Raman spectra of the O–H stretching region, surface potential, and surface excess of ions. The orientational structure of surface water is investigated in detail in connection with the issue of surface solvation of anions. These investigations will be utilized to analyze the sum frequency generation spectra in relation to the orientational structure at the molecular level.

2. Computation of Sum Frequency Generation Spectra of Aqueous Salt Solution Interfaces²⁾

The vibrational sum frequency generation (SFG) spectra of gas-liquid interfaces of NaCl and NaI aqueous solutions are computed and analyzed by molecular dynamics (MD) simulations using a flexible and polarizable molecular model. The MD calculations have reproduced the experimental features of SFG spectra, including observed perturbation on the NaI spectra in contrast to little perturbation on NaCl. Analysis of the nonlinear susceptibility revealed that the intermolecular correlation has a significant contribution to the vibrationally resonant amplitude, which largely distorts the generally accepted relationship between the SFG intensity and orientation of individual molecules. In NaI solutions, modest enhancement of ssp intensity in the 3400 cm^{-1} region is thereby elucidated by this mechanism. Regarding the sps spectra, three spectral components are assigned and elucidated. Calculated remarkable enhancement in the $3400\text{--}3800\text{ cm}^{-1}$ region for NaI solutions is found to be sensitive to the electric double layer structure. It is also revealed that the sps intensity is augmented by the intermolecular water-water correlation effect.

3. Molecular Dynamics Analysis of Sum Frequency Generation Spectra of Aqueous Acid Solution Interfaces³⁾

Molecular dynamics simulation for gas/liquid interfaces of aqueous hydrochloric (HCl) and hydroiodic (HI) acid solutions is performed to calculate and analyze their sum frequency generation (SFG) spectra. The present MD simulation supports strong preference of hydronium ions at the topmost surface layer and a consequent formation of ionic double layers by the hydronium and halide ions near the interface. Accordingly, the orientational order of surface water in the double layers is reversed in the acid solutions from that in the salt (NaCl or NaI). The calculated SFG spectra of O–H stretching region well reproduce the experimental spectra of ssp and sps polarizations. In the ssp spectra, the strong enhancement in the hydrogen bonding region for the acid solutions is elucidated by two mechanisms, ordered orientation of water in the double layer and symmetric OH stretching of the surface hydronium ions. In the sps spectra, reversed orientation of surface water is evidenced in the spectral lineshapes, which are quite different from those of the salt solutions.

4. Modeling of C–H Vibrations for Alkyl Chain Molecules and Related Interfaces

The present work aims at applying our computational methods to the interfaces including alkyl chains. Alkyl chains have ubiquitous importance in organic films and polymer interfaces, and their C–H stretching vibration has been extensively studied by SFG and IR spectra. Their spectral structure in C–H stretching vibration is often complicated by those of CH₃ and CH₂ moieties and Fermi resonance with the CH bending overtone. As the first step to deal with such systems, we construct an appropriate model of methanol for describing interfacial vibrational spectra.

The present model of methanol is flexible and polarizable, and all the ingredient parameters are determined by density functional calculations. The present intramolecular force field appropriately includes the contribution of the Fermi resonance. For modeling of electrostatic interaction and polarization, we used the Charge Response Kernel (CRK) method. The present model takes account of geometry dependence of the partial charges and CRK, so that it is able to describe the dipole moment vector and polarizability tensor accurately as a function of molecular vibrational configuration. This molecular model of methanol will be extended to other molecules with alkyl chains for use of MD simulation.

5. Theoretical Investigation of Characteristics of Components of Room Temperature Ionic Liquids and Its Effect on Interplay between Cation and Anion Units

Room temperature ionic liquids (RTILs) show a wide variety of interesting physical and chemical properties, different from so-called molten salts. It is considered that many of them can be attributed to the character of both cation and anion which consist of RTILs. From these viewpoints, we can expect that the size of cation and anion, their geometric shapes, remarkable characteristics of elements in the cation and anion and so on, determine and explain some of essential properties and inside details. In particular, we focus on the characteristics of elements in the anion component in ionic liquids, 1-Butyl-3-Methylimidazolium cation (BMIM) with X⁻: PF₆⁻, AsF₆⁻ and SbF₆⁻. We compared important physical properties among them, referring to experimental data by molecular dynamics simulation procedures.

6. Theoretical Study of Temperature and Solvent Dependence of the Free Energy Surface of the Intramolecular Electron Transfer based on the RISM-SCF Theory; Application to 1,3-Dinitrobenzene Radical Anion in Acetonitrile and Methanol⁴⁾

The free energy surfaces along the intramolecular electron transfer reaction of 1,3-dinitrobenzene radical anion in acetonitrile and methanol are investigated with the reference interaction site model self-consistent field theory. Although acetonitrile and methanol have similar values of the dielectric constant, the free energy profiles are quite different. The electronic coupling strength exhibits an intriguing behavior in the temperature dependence: it increases with increasing temperature in acetonitrile, while that in methanol exhibits the opposite trend.

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Visiting Professors



Visiting Professor

ASAI, Yoshihiro (from *National Institute of Advanced Industrial Science and Technology*)

Theory of Electron Transport through Single Molecular Bridge Junctions

Theories of transport properties through single molecular bridges and atomic wires between the two electrodes have been investigated.¹⁻³⁾ Special attentions will be paid on heat dissipations accompanying the electron transport. Both fundamental theories and their implementations in terms of first principle electronic structure methods⁴⁾ have been studied, as well as their applications to real non-equilibrium open systems.

Both the physical reality and the chemical reality have been taken into account in the calculations.

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Visiting Associate Professor

AKIYAMA, Ryo (from *Kyushu University*)

Interaction between Like-Charged Colloidal Particles Immersed in Electrolyte Solution

Study of mesoscopic structure constructed by colloidal particles is important to discuss stability of cytoplasm, formation of rennet gel, and so on. The effective interaction between colloidal particles is necessary to calculate those systems using simulation method, because the molecular simulation with explicit solvent molecule and colloidal particle model is very hard. On the other hand, Kinoshita *et al.* are suggesting the importance of translational motion of solvent molecules to discuss the interaction. Then, we pay attention to the solvent granularity in this study.

We calculate the interaction between like-charged colloidal particles immersed in electrolyte solution using the OZ-HNC theory. Solvent molecules are modeled as neutral hard spheres, and ions and colloidal particles are modeled as charged hard spheres. The Coulomb potentials for ion-ion, ion-colloidal particle, and colloidal particle-colloidal particle pairs are divided by the dielectric constant of water. The van der Waals attraction between the colloidal particles, which is an essential constituent of the DLVO theory, is omitted in our model. Nevertheless, attractive regions appear in the interaction, when the electrolyte concentration is sufficiently high. Then the colloidal particles can adhere each other and can form aggregations or gels in spite of like-charged particles. In our model, the attraction arises from the granularity of solvent molecules. (R. Akiyama, N. Fujino, K. Kaneda, and M. Kinoshita, *Cond. Matt. Phys.* accepted.) We start in to study of Brownian dynamics simulation with the effective interaction and some related chemical reactions.



Visiting Associate Professor

HAYASHI, Michitoshi (from *National Taiwan University*)

Development of a Molecular Theory for Time-Resolved Sum-Frequency Generation and Its Applications to Vibrational Dynamics of Water

We developed a molecular theory for time-resolved sum-frequency generation (SFG). The molecular model for vibrational dynamics of water is constructed using the coupled-oscillator model in the adiabatic approximation. This model allows us to calculate vibrational energy transfer rate constants with two different ways; one is with the dipole-dipole interaction scheme and another is the anharmonicity scheme. An application of this theory is also provided for estimation of the time constants of the intermolecular vibrational energy transfer between water molecules using density functional theory method. This approach can provide a clue of a molecular mechanism as to how vibrational dynamics of water at the surface takes place.