RESEARCH ACTIVITIES VII
Department of Computational Molecular Science

VII-A Computer Simulation of Quantum Systems in Condensed Phase

VII-A-1 A Surface Hopping Method for Chemical Reaction Dynamics in Solution Described by Diabatic Representation: An Analysis of Tunneling and Thermal Activation

YAMADA, Atsushi; OKAZAKI, Susumu

[*J. Chem. Phys.* **124**, 094110 (11 pages) (2006)]

We present a surface hopping method for chemical reaction in solution based on diabatic representation, where quantum mechanical time evolution of the vibrational state of the reacting nuclei as well as the reaction-related electronic state of the system are traced simultaneously together with the classical motion of the solvent. The method is effective in describing the system where decoherence between reactant and product states is rapid. The diabatic representation can also give a clear picture for thereaction mechanism, *e.g.* thermal activation mechanism and tunneling one. An idea of molecular orbital theory has been applied to evaluate the solvent contribution to the electronic coupling which determines therate of reactive transition between the reactant and product potential surfaces. We applied the method to a model system which can describe complex chemical reaction of the real system. Two numerical examples are presented in order to demonstrate the applicability of the present method, where the first example traces a chemical reaction proceeded by thermal activation mechanism and the second examines tunneling mechanism mimicking a proton transfer reaction.

VII-B Molecular Dynamics Study of Classical Complex Systems

VII-B-1 A Molecular Dynamics Study of Sodium Chenodeoxycholate in an Aqueous Solution

NAKASHIMA, Toshio; IWAHASHI, Kensuke; OKAZAKI, Susumu

[*Chem. Phys. Lett.* **420**, 489–492 (2006)]

Hydration structure and dynamics of sodium chenodeoxycholate (CDC) in water are studied by a long-time molecular dynamics calculation. Strong hydration shell around the hydrophobic region of this large solute and strong hydrogen bonds of water with both hydroxyl and carboxyl oxygen atoms have been identified. The rotation of CDC around its longitudinal axis is found to be particularly active in comparison with that around other axes of the molecule. The diffusion coefficient of CDC calculated from the slope of the meansquaredisplacement, 0.95×10^{-9} m^2/s, is only 1/6 of that for water in the solution, 5.4×10^{-9} m^2/s.

VII-B-2 A Molecular Dynamics Study of Free Energy of Micelle Formation for Sodium Dodecyl Sulfate in Water and Its Size Distribution

YOSHII, Noriyuki; IWAHASHI, Kensuke; OKAZAKI, Susumu

[*J. Chem. Phys.* **124**, 184901 (6 pages) (2006)]

Free energy of micelle formation has been evaluated for spherical sodium dodecyl sulfate (SDS) in water by a thermodynamic integration method combined with a series of large-scale molecular dynamics calculations following the chemical species model. In particular, free energy change $\Delta\mu_{n+1}{}^0$ with respect to the addition of one surfactant molecule to the spherical micelle of size n was obtained as a function of n. The free energy profile showed a minimum followed by a maximum, which corresponds to a peak in the size distribution. The calculated peak size $n = 57$ near its critical micelle concentration is in good agreement with the experimental averaged aggregation number $n = 55$–75 of the SDS micelle. The distribution showed a rather sharp peak, indicating that the size is almost a monodisperse one. The size is likely to be insensitive to the total concentration of the surfactant.

VII-B-3 A Molecular Dynamics Study of Structural Stability of Spherical SDS Micelle as a Function of Its Size

YOSHII, Noriyuki; OKAZAKI, Susumu

[*Chem. Phys. Lett.* **425**, 58–61 (2006)]

In order to investigate stability of spherical sodium dodecyl sulfate micelle in water, molecular dynamics calculations have been performed for the micelle of various sizes. Size-dependence of the micelle structure such as asphericity, Voronoi polyhedron, and radial density profile has been analyzed in detail from a viewpoint of geometrical instability found in it, *i.e.*, direct exposition of the hydrophobic group to water observed for small micelles and cavity formation in the center of large micelles.

VII-B-4 A Molecular Dynamics Study of Surface Structure of Spherical SDS Micelles

YOSHII, Noriyuki; OKAZAKI, Susumu

[*Chem. Phys. Lett.* **426**, 66–70 (2006)]

A series of molecular dynamics calculations have been carried out for spherical sodium dodecyl sulfate micelle of various sizes in order to investigate surface structure of the micelle as a function of its size. Two-dimensional surface pair correlation function of the hydrophilic head group projected on the sphere of the micelle showed a gas-like structure for small micelle, *e.g.* $N = 31$, and a liquid-like one for large micelles, *e.g.* $N \geq 61$, depending on the surface density of the head group. Coordination structure of the sodium ion near the surface has been analyzed in detail, too.

VII-C Development of Simulation Algorithms for Quantum Many-Body Systems

VII-C-1 Path Integral Hybrid Monte Carlo Study on Structure of Small Helium-4 Clusters Doped with a Linear Molecule

MIURA, Shinichi

[*J. Low Temp. Phys.* in press]

Microscopic structure of small helium-4 clusters doped with a carbonyl sulfide molecule, $\mathrm{OCS}(^4\mathrm{He})_N$, at 0.37 K is studied by the path integral hybrid Monte Carlo method; the size of the cluster N ranges from $N = 2$ to $N = 5$. In all the cases examined in the present study, the helium atoms are localized around the carbon atom of the OCS molecule, forming a doughnut-type structure around the molecular axis. Bosonic exchange among the helium atoms is found to be promoted in the doughnut region, showing an anisotropic “superfluid” response of the clusters.

VII-D Development of Polarizable Molecular Modeling for Simulation Studies

Accuracy and reliability of molecular models are crucial for theoretical understandings of condensed phase chemistry. This year we have developed molecular models which incorporate both intramolecular vibration and electronic polarization. Such flexible and polarizable models have a number of applications to condensed phase chemistry, including electron transfer reactions. Another important purpose of the flexible and polarizable models is to describe the sum frequency generation spectroscopy by molecular dynamics simulation, as discussed in the next section.

VII-D-1 Polarizable Solute in Polarizable and Flexible Solvents: Simulation Study of Electron Transfer Reaction Systems

ISHIDA, Tateki

[*J. Phys. Chem. B* **109**, 18558–18564 (2005)]

A polarizable solute model, based on the empirical valence bond approach, is developed and applied to electron transfer (ET) reactions in polarizable and flexible water solvents. The polarization effect is investigated in comparison with a nonpolarizable solute and solvent model. With free energy curves constructed by a molecular dynamics simulation, the activation energy barrier and the reorganization energy related to ET processes are investigated. The simulation results show that the activation energy barrier becomes larger in the polarizable model than in the nonpolarizable model and that this makes the ET rate slower than that with the nonpolarizable model. It is shown that the effect of the electronic energy difference of solute molecule on free energy profiles is remarkable and that, corresponding to this effect, the reorganization energy is significantly modified. These results indicate that the process of solvent polarization by the polarized solute to enhance the solute-solvent interaction is a key factor and that treating the polarization of both solute and solvent at the same time is essential. Also, the polarization effect on the diffusive motion of the solute molecule in the polarization solvent is studied. The polarized solute molecule shows slower diffusive motion compared with that in the nonpolarizable model.

VII-D-2 Extended Treatment of Charge Response Kernel Comprising the Density Functional Theory and Charge Regulation Procedures

ISHIDA, Tateki; MORITA, Akihiro

[*J. Chem. Phys.* **125**, 074112 (2006)]

We propose an extended treatment of the charge response kernel (CRK), $\partial Q_a/\partial V_b$, which describes the response of partial charges on atomic sites to external electrostatic potential, on the basis of the density functional theory (DFT) via the coupled perturbed Kohn-Sham equations. The present CRK theory incorporates regulation procedures in the definition of partial charges to avoid unphysical large fluctuation of the CRK on “buried” sites. The CRKs of some alcohol and organic molecules, methanol, ethanol, propanol, butanol, dimethylsulfoxide (DMSO) and tetrahydrofuran (THF) were calculated, demonstrating that the new CRK model at the DFT level has greatly improved the performance of accuracy in comparison with that at the Hartree-Fock level previously proposed. The CRK model was also applied to investigate spatial nonlocality of the charge response through alkyl chain sequences. The CRK model at the DFT level enables us to construct a non-empirical strategy for polarizable molecular modeling, with practical reliability and robustness.

VII-E Computational Analysis of Sum Frequency Generation Spectroscopy

This project aims at developing theoretical and computational methods of visible-infrared Sum Frequency Generation (SFG) spectroscopy for interface characterization. While SFG is recognized as a powerful experimental technique to optically probe a variety of interface structure, experimental spectra are not often amenable to straightforward fitting or interpretation. We have proposed theoretical methods to compute SFG directly via molecular modeling and molecular dynamics simulation, without resorting to empirical parameterization. This year, we have developed a general polarizable and flexible molecular model, called charge response kernel, on the basis of the density functional theory for the purpose of the SFG calculation. SFG spectra of aqueous electrolyte solutions are also analyzed by molecular dynamics simulation.

VII-E-1 Intermolecular Correlation Effect in Sum Frequency Generation Spectroscopy of Electrolyte Aqueous Solution

ISHIYAMA, Tatsuya; MORITA, Akihiro

[*Chem. Phys. Lett*. **431**, 78–82 (2006)]

Molecular dynamics analysis of the sum frequency generation (SFG) spectroscopy was performed to solve the recent controversial problem about liquid-vapor interface of electrolyte aqueous solution [Garrett, *Science* **303**, 1146 (2004)]. The present MD analysis revealed a crucial role of ion-water dipolar correlation in the vibrational SFG spectroscopy, which significantly distorts the general relationship between SFG intensity and surface orientational order. The experimental SFG spectra were thereby elucidated from the local structure of interface.

VII-F Theoretical Study of Condensed Phase Dynamics by Using Multi-Dimensional Spectroscopy

VII-F-1 Fifth-Order Two-Dimensional Raman Spectroscopy of Liquid Water, Crystalline Ice Ih and Amorphous Ices: Sensitivity to Anharmonic Dynamics and Local Hydrogen Bond Network Structure

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[*J. Chem. Phys.* **125**, 084506 (12 pages) (2006)]

Theoretical study of off-resonant fifth-order two-dimensional (2D)-Raman spectroscopy is made to analyze the intermolecular dynamics of liquid and solid water. The 2D-Raman spectroscopy is susceptible to the nonlinear anharmonic dynamics and local hydrogen bond structure in water. It is found that the distinct 2D-Raman response appears as the negative signal near the t_2 axis. The origin of this negative signal for $t_2 < 15$ fs is from the nonlinear polarizability in the librational motions, whereas that for 30 fs $< t_2 <$ 150 fs is attributed to the anharmonic translational motions. It is found that the mechanical anharmonicity and nonlinear polarizability couplings among modes clearly can be observed as the sum- and difference-frequency peaks in the 2D-Raman spectrum (that is, Fourier transforms of the responses). The 2D-Raman spectroscopies of ice Ih and amorphous ices, low-density, high-density, and very high-density amorphous ices, are also investigated. It is found that the 2D-Raman spectroscopy is very sensitive to the anisotropy of the structure of ice Ih. The strong HB stretching band is seen in the 2D-Raman spectroscopy of the polarization directions parallel to the *c*-axis, whereas the contributions of the librational motion can be also seen in the spectrum with the polarization directions parallel to the *a*-axis. The 2D-Raman spectroscopy is also found to be also very sensitive to the differences in local hydrogen bond network structures in various amorphous phases.

VII-G Theoretical Study of Dynamics in Biological Systems

VII-G-1 Mechanism of Ion Permeation in Model Channel; Free Energy Surface and Dynamics of K^+ Ion Transport in Anion-Doped Carbon Nanotube

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[*J. Phys. Chem. B* **110**, 20671–20677 (2006)]

The mechanism of the ion permeation is investigated for an anion-doped carbon nanotube, as a model of the K^+ channel, by analyzing the free energy surface and the dynamics of the ion permeation through the model channel. It is found that the main rate-determining step is how an ion enters the channel. The entrance of the ion is mostly blocked a water molecule locating at this entrance. Only a few percent of K^+ ions which reach the mouth of the channel can really enter the channel. The rejection rate sensitively depends on the location of this water molecule, which is easily controlled by the charge of the carbon nanotube; for example, the maximum permeation is obtained when the anion charge is at a certain value, –5.4*e* in the present model. At this charge, the facile translocation of the ion inside the channel is also induced due to the number fluctuation of the ions inside the channel. Therefore, the so-called “Newton’s balls,” a toy model, combined with a simple ion diffusion model for explaining the fast ion permeation should be modified. The present analysis thus suggests that there exists an optimum combination of the length and the charge of the carbon nanotube for the most efficient ion permeation.

VII-H Theoretical Study of Origin of Slow Relaxation in Liquid Water

VII-H-1 Origin of Slow Relaxation in Liquid Water Dynamics: A Possible Scenario for the Presence of Bottleneck in Phase Space

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[*Europhys. Lett.* **73**, 826–832 (2006)]

We study slow relaxation in dynamics of liquid water at room temperatures and propose a consistent interpretation explaining why liquid-water dynamics exhibits power law relaxation behavior and can form the bottleneck in phase space even though it is a many dimensional and strongly chaotic system. Our idea is inspired by recent developments of perturbation theories of Hamiltonian systems, and is reminiscent of the so-called Boltzmann-Jeans conjecture. Within this scenario, it is natural to expect that slow relaxation is not limited to liquid-water dynamics. We found that our hypothesis works well in predicting the relaxation properties of other molecules. The relation to the potential landscape picture is also discussed.