RESEARCH ACTIVITIES VII
Department of Computational Molecular Science

VII-A Computer Simulation

VII-A-1 Path Integral Influence Functional Theory of Dynamics of Coherence between Vibrational States of Solute in Condensed Phase

MIKAMI, Taiji; OKAZAKI, Susumu

[*J. Chem. Phys.* **121**, 10052 (2004)]

Path integral influence functional theory has been applied to the dynamics of coherence between vibrational states of solute in condensed phase. First, time evolution of the off-diagonal term of the reduced density matrix $\rho_{mn}(t)$ was algebraically described by the cumulant expansion of the perturbative influence functional. Then, the theory is compared with the Redfield theory, rearranging the present description in a familiar way to that found in the Redfield theory. A numerical example of the theory is presented for the vibrational dynamics of cyanide ion in water assuming a coherent state $\left(1+\sqrt{2}\right)\left(|0\rangle+|1\rangle\right)$ at $t = 0$. We find that $\mathrm{Re}\rho_{10}(t)$ oscillates with high frequency and shows a fast damping. Relaxation time of the oscillation amplitude is estimated to be 5.1 ps for a certain configuration of the solution. Then, secular approximation often used in the Redfield theory is found to work well, at least, in the present system. Population relaxation time for the first excited state and pure dephasing time may also be calculated from the component of $\mathrm{Re}\rho_{10}(t)$ to be 7.9 ps and 7.5 ps, respectively. Further, many-particle measurement for $\mathrm{Re}\rho_{10}(t)$ gives the relaxation rate about three times faster than the single-measurement above. This comes from the inhomogeneity of the solute environment. We also calculated $\mathrm{Re}\rho_{11}(t)$ and found the fast oscillation in the diagonal part of the density matrix $\mathrm{Re}\rho_{11}(t)$. This oscillation is generated only when the initial density matrix includes the coherence.

VII-A-2 Mixed Quantum-Classical Molecular Dynamics Study of Vibrational Relaxation of CN^- Ion in Water: An Analysis of Coupling as a Function of Time

SATO, Masahiro; OKAZAKI, Susumu

[*J. Mol. Liq.* in press]

Mixed quantum-classical molecular dynamics method has been applied to vibrational relaxation of CN^- in water, where coulombic force is predominant in the interaction. The calculation demonstrated that time-dependent interaction between the solute vibrational degree of freedom and the solvent water shows random-noise-like behavior, no collisional or stationary coupling observed in gas or solid, respectively, being found. This is in contrast to short-ranged-force system where the collision plays a dominant role in the relaxation. The interaction has been analyzed in detail as a function of time defining the effective coupling for the relaxation.

VII-A-3 Vibrational Relaxation Time of CN^- Ion in Water Studied by Mixed Quantum-Classical Molecular Dynamics: Comparison with Fermi's Golden Rule and Influence Functional Theory

SATO, Masahiro; OKAZAKI, Susumu

[*Mol. Sim.* in press]

Mixed quantum-classical molecular dynamics method has been applied to vibrational relaxation of CN^- in water. The calculated relaxation time was compared with those based upon Fermi's golden rule with classical interaction and influence functional theory with classical bath. They are in good agreement with each other. Flexible water model adopted here enhanced the relaxation rate by a factor of about 5 compared with the rigid rotor model. This supports our previous result of path integral influence functional theory that intramolecular bending of water plays an essential role in the relaxation.

VII-B Molecular Dynamics Study of Classical Complex Systems

VII-B-1 Molecular Dynamics Studies of Self-Organization of Amphiphilic Molecules in the Aqueous Solution

YOSHII, Noriyuki; IWAHASHI, Kensuke; YAMADA, Atsushi; OKAZAKI, Susumu

Self-organization of amphiphilic molecules in water such as micelles and lipid bilayers is investigated. Potential of mean force between amphiphilic molecules is a target of this investigation. In order to accomplish this, general purpose program for large-scale molecular dynamics calculation has been coded in a suitable way for very highly parallel computing and grid computing. The program can be used to execute a calculation for the system of a million of atoms with arbitrary molecular configurations. Preliminary calculations have been done for many-body effect on the potential of mean force among small hydrophobic solutes.

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

VII-C-1 On the Solvation Structure of a Rare-Gas Solute in Superfluid Helium-4

MIURA, Shinichi

[*J. Mol. Liq.* in press]

Path integral hybrid Monte Carlo calculations have been performed for a system consisting of a single neon atom in the superfluid helium. An expression of the local superfluid density around the solute atom is introduced to analyze the microscopic density fluctuation around the solute in detail. We show that the superfluid component in the sovaltion shell dramatically increases with lowering temperature, although the radial number density profile itself is almost independent of temperature. We also compare the local superfluid density calculated by our expression with that by another commonly used one. Although both local superfluid densities show similar trend as a function of the radial distance from the solute atom, quantitative differences are found; the superfluid component is underestimated by the commonly used one. This is due to the fact that the commonly used definition of the local superfluid density does not give the bulk superfluid density by integrating it over whole space. New expression introduced in the present study is free from such a deficiency.

VII-D Theory of Sum Frequency Generation Spectroscopy

Sum Frequency Generation (SFG) spectroscopy in combination of infrared and visible lights has a wide range of applications to study interfacial structure, including ambient and buried surfaces not accessible by most other techniques. In contrast to the recent experimental progress, however, theoretical study of SFG is still in a relatively primitive stage. We recently proposed two theories which allow us to calculate SFG spectra via ab initio molecular orbital theory and molecular dynamics simulation, and applied them to the experimental SFG spectrum of water surface with considerable success. This project aims at extending this theory in two ways: (1) development of fundamental SFG theory toward quantitative interpretation of the experiments, and (2) application to other interfacial structures of interest using large-scale computation.

VII-D-1 Toward Computation of Bulk Quadrupolar Signals in Vibrational Sum Frequency Generation Spectroscopy

MORITA, Akihiro

[*Chem. Phys. Lett.* **398**, 361–366 (2004)]

Although SFG is regarded as a surface-sensitive spectroscopy, bulk contribution *via* quadrupole and other higher-order terms should not be negligible. Relative importance of surface and bulk signals has been a long standing issue, although quantitative discussion is rather scarce. This study provides theoretical expressions of the bulk signals, which are extension of our previous SFG theories and are readily implemented in molecular dynamics calculations.

VII-E Theory of Mass Transfer Kinetics at Liquid-Vapor Interfaces

Mass transfer kinetics at liquid-vapor interface is of fundamental importance in heterogeneous atmospheric chemistry, as it governs rates of heterogeneous reactions and nucleation. Observed uptake kinetics, however, is quite difficult to interpret in molecular level, since it is related to many kinetic factors including gas diffusion, liquid solubility and diffusion, interfacial mass accommodation, *etc.* We have demonstrated with the help of molecular dynamics and computational fluid dynamics calculations that those elemental kinetic resistances can be accurately decoupled in actual experimental conditions.

VII-E-1 Revised Kinetics in the Droplet Train Apparatus Due to a Wall Loss

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[*J. Phys. Chem. A* **108**, 3739–3744 (2004)]

Heterogeneous uptake experiments become further complicated when a wall loss effect is involved in addition to the interfacial mass transfer. In most experimental analyses of the droplet train flow reactor, the wall loss rate is simply subtracted as a constant background, assuming that it is independent from the uptake rate constant into droplets. However, we showed that this usual assumption is flawed because of radial concentration gradient in the flow tube. Accurate treatment of the wall loss effect is demonstrated using computational fluid dynamics calculations.

VII-E-2 Uptake of the HO_2 Radical by Water: Molecular Dynamics Calculations and Their Implications to Atmospheric Modeling

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[*J. Geophys. Res.* **109**, D09201, 10.1029/2003JD004240 (2004)]

HO_2 plays many critical roles in radical-chain oxidation reactions in the troposphere. Although a substantial sink of HO_2 has been suggested to be the uptake into aerosols, its efficiency is largely uncertain. Therefore, we performed molecular dynamics calculations of HO_2 uptake into water surface, and found that the mass accommodation coefficient of HO_2 is close to unity. Implications of this result in the troposphere are examined by photochemical box model calculations for typical two cases of tropospheric boundary layers; remote marine air and polluted urban air. It is shown that HO_2 concentration is particularly sensitive to the heterogeneous uptake in the urban case.

VII-E-3 Mass Accommodation Coefficient of Water: Molecular Dynamics Simulation and Revised Analysis of Droplet Train/Flow Reactor Experiment

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[*J. Phys. Chem. B* **108**, 9111–9120 (2004)]

Mass accommodation coefficient of water α has been studied for a century, in relation to the cloud formation kinetics and many other implications. Most recent experiment using droplet train flow reactor reported $\alpha = 0.23$ at room temperature, which appears inconsistent to molecular dynamics value, $\alpha \sim 1$. This study resolved this discrepancy by reanalyzing the gas diffusion and flow conditions in the experimental reactor. Accurate calculations of the gaseous diffusion resistance yielded a value of α close to unity, which is fully consistent to the molecular dynamics and some other experiments.

VII-F Theoretical Studies on Electronic Structure and Dynamics of Electronically Excited States

VII-F-1 Millimeter-Wave Spectroscopy of the Internal-Rotation Band of the X-HCN Complex (X = He, Ne, and Ar) and the Intermolecular Potential Energy Surface

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Millimeter-wave absorption spectroscopy combined with a pulsed-jet expansion technique was applied to the measurement of the internal-rotation band of the X-HCN (X = He, Ne, and Ar) in the frequency region of 95–125 GHz. The observed transition frequencies were analyzed including their hyperfine splitting to yield an intermolecular potential energy surface, as improved from the one given by a coupled-cluster single double (triple) ab initio calculation. Regarding the He complex, the surface has a global minimum in the linear configuration (He···H–C–N) with a well depth of 30.2 cm^{-1}, and the saddle point located in the anti-linear configuration (H–C–N···He) is higher by 8.174 cm^{-1} in energy than the global minimum. The distance R_m between the He atom and the center of mass of HCN along the minimum energy path shows a strong angular dependence; R_m = 4.169 Å and 4.040 Å in the linear and anti-linear forms, respectively, while it is 3.528 Å in a T-shaped configuration. The energy level diagram is consistent with the millimeter-wave observation. And now, we are trying to measure the stretching motion located just below the dissociation limits.

VII-F-2 Ab Initio Study of the Complexation Behavior of *p*-Tert-Butylcalix[5]arene Derivative toward Alkyl Ammonium Cations

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[*Bull. Korean. Chem. Soc.* **25**, 190–194 (2004)]

The structures and complexation energies of penta-O-tert-butyl ester of *p*-tert-butylcalix[5]arene toward a series of alkyl ammonium guests have been optimized by ab initio HF/6-31G method. The calculated complexation efficiencies of the ester for alkyl ammonium guests have been found to be similar to the values of previously reported debutylated-calix[5]arene. Calculation results show that both of the calyx[5]aryl alkyl ammonium guests. The structural characteristics of the calculated complexes are discussed as a function of the nature of the alkyl substituents of the ammonium guests.

VII-F-3 Theoretical Transition Probabilities for the $\tilde{A}\ ^2A_1$–$\tilde{X}\ ^2B_1$ System of H_2O^+ and D_2O^+ and Related Franck-Condon Factors Based on Global Potential Energy Surfaces

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In order to elucidate the ionization dynamics, in particular the vibrational distribution, of $H_2O^+(\tilde{A})$ produced by the photoionization and the Penning ionization of H_2O and D_2O with He*(2^3S) atoms, the Franck-Condon factors (FCFs) were presented for the $H_2O(\tilde{X}) \rightarrow H_2O^+(\tilde{X},\tilde{A})$ ionization and the transition probabilities were presented for the $H_2O^+(\tilde{A}–\tilde{X})$ system. The FCFs were obtained by quantum vibrational calculations using the three-dimensional potential energy surfaces (PESs) of $H_2O(\tilde{X}\,^1A_1)$ and $H_2O^+(\tilde{X}\,^2B_1,\ \tilde{A}\,^2A_1,\ \tilde{B}\,^2B_2)$ electronic states. The global PESs were determined by the multi-reference configuration interaction calculations with the Davidson correction and the interpolant moving least squares method combined with the Shepard interpolation. The obtained FCFs exhibit that the $H_2O^+(\tilde{X})$ state primarily populates the vibrational ground state since its equilibrium geometry is almost equal to that of $H_2O(\tilde{X})$, while the bending mode (ν_2) is strongly enhanced for the $H_2O^+(\tilde{A})$ state; the maximums in the population of H_2O^+ and D_2O^+ are around ν_2 = 11–12 and 15–17, respectively. These results are consistent with the distributions observed by photoelectron spectroscopy. Transition probabilities for the $\tilde{A}–\tilde{X}$ system of H_2O^+ and D_2O^+ show that the bending progressions consist of the great part of the $\tilde{A}–\tilde{X}$ emission and that combination bands from the (1, ν_2' = 4–8, 0) state are next important.

VII-F-4 Analysis of the Ultraviolet Absorption Cross Sections of Six Isotopically Substituted Nitrous Oxide Specie Using 3D Wavepacket Propagation

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[*J. Phys. Chem. A* **108**, 8905–8913 (2004)]

The ultraviolet absorption cross sections of six isotopically substituted nitrous oxide species ($^{14}N^{14}N^{16}O$, $^{14}N^{14}N^{17}O$, $^{14}N^{14}N^{18}O$, $^{14}N^{15}N^{16}O$, $^{15}N^{14}N^{16}O$, and $^{15}N^{15}N^{16}O$) were computed using the wavepacket propagation technique to explore the influence of excited state dynamics, transition dipole surface and initial vibrational state. Three-dimensional potential energy surfaces for the electronic states of N_2O related to the experimentally observed photoabsorption between 170 and 220 nm were calculated using the *ab initio* molecular orbital (MO) configuration interaction (CI) method. The transition dipole moment surfaces between these states were also calculated. Numerous wave packet simulations were carried out and used to calculate the temperature-dependent photodissociation cross sections of the six isotopically substituted species. The photolytic isotopic fractionation constants determined using the calculated cross sections are in good agreement with recent experiments. The results show that in addition to the effect of the changed shape of the ground state vibrational wavefunction with isotopic substitution, photodissociation dynamics play a central role in determining isotopic fractionation constants.

VII-F-5 Coarse-Grained Picture for Controlling Quantum Chaos

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[*Adv. Chem. Phys.* in press]

We propose a coarse-grained picture to analyze control problems for quantum chaos systems. Using optimal control theory, we first show that almost perfect control is achieved for random matrix systems and a quantum kicked rotor. Second, under the assumption that the controlled dynamics is well described by a Rabi-type oscillaion between unperturbed states, we derive an analytic expression for the optimal field. Finally we numerically confirm that the analytic field can steer an initial state to a target state in random matrix systems.

VII-F-6 Coarse-Grained Picture for Controlling Complex Quantum Systems

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[*J. Phys. Soc. Jpn.* **73**, 3215–3216 (2004)]

We propose a coarse-grained picture to control complex quantum dynamics, *i.e.*, multi-level-multi-level transition with a random interaction. Introducing a Rabi-like-oscillating state between two time-dependent states, we derive an analytic optimal field as a solution to optimal control theory. For random matrix systems, we numerically confirm that the analytic optimal field actually steers an initial state to a target state, which both contain many eigenstates.