

RESEARCH ACTIVITIES VII

Department of Computational Molecular Science

VII-A Computer Simulation of Quantum Systems in Condensed Phase

VII-A-1 A Study of Molecular Vibrational Relaxation Mechanism in Condensed Phase Based upon Mixed Quantum-Classical Molecular Dynamics: I. A Test of IBC Model for the Relaxation of a Nonpolar Solute in Nonpolar Solvent at High Density

SATO, Masahiro; OKAZAKI, Susumu

[*J. Chem. Phys.* **123**, 124508 (2005)]

In order to investigate vibrational relaxation mechanism in condensed phase, a series of mixed quantum-classical molecular dynamics calculations have been executed for non-polar solute in non-polar solvent and polar solute in polar solvent. In the first paper (Paper I), relaxation mechanism of I_2 in Ar, where Lennard-Jones force is predominant in the interaction, is investigated as a function of density and temperature, focusing our attention on the isolated binary collision (IBC) model. The model was originally established for the relaxation in gas phase. A key question, here, is "Can we apply the IBC model to the relaxation in the high-density fluid?" Analysing the trajectory of solvent molecule as well as its interaction with the solute, we found that collisions between them may be defined clearly even in the high-density fluid. Change of the survival probability of the vibrationally first excited state on collision was traced. The change caused by collisions with a particular solvent molecule was also traced together with the interaction between them. Each collision makes a contribution to the relaxation by a stepwise change in the probability. The analysis clearly shows that the relaxation is caused by collisions even in the high-density fluid. Difference between stepwise relaxation and continuous one found for the total relaxation in the low-density fluid and in the high-density one, respectively, was clarified to come from just the difference in frequency of the collision. The stronger the intensity of the collision is, the greater the relaxation caused by the collision is. Further, the shorter the collision time is, the greater the resultant relaxation is. The discussion is followed by the succeeding paper (Paper II), where we report that molecular mechanism of the relaxation of a polar molecule in supercritical water is significantly different from that assumed in the IBC model despite that the

density dependence of the relaxation rate showed a linear correlation with the local density of water around the solute, the linear correlation being apparently in good accordance with the IBC model. The puzzle will be solved in Paper II.

VII-A-2 A Study of Molecular Vibrational Relaxation Mechanism in Condensed Phase Based upon Mixed Quantum-Classical Molecular Dynamics: II. Non-Collisional Mechanism for the Relaxation of a Polar Solute in Supercritical Water

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[*J. Chem. Phys.* **123**, 124509 (2005)]

Mixed quantum-classical molecular dynamics method has been applied to vibrational relaxation of a hydrophilic model NO in supercritical water at various densities along an isotherm above the critical temperature. The relaxation rate was determined based on the Fermi's golden rule at each state point and showed an inverse S-shaped curve as a function of bulk density. The hydration number was also calculated as a function of bulk density based on the calculated radial distribution function, which showed a good correlation with the relaxation rate. Change of the survival probability of the solute vibrational state was analyzed as a function of time together with the trajectory of the solvent water and the interaction with it. We will show that the solvent molecule resides near the solute molecule for a while and the solvent contributes to the relaxation by the random-noise-like coulombic interaction only when it stays near the solute. After the solvent leaves the solute, it shows no contribution to the relaxation. The relaxation mechanism for this system is significantly different from the collisional one found for a nonpolar solute in nonpolar solvent in Paper I. Then, the relaxation rate is determined, on average, by the hydration number or local density of the solvent. Thus, the density dependence of the relaxation rate for the polar solute in supercritical water is apparently similar to that found for the nonpolar solute in nonpolar solvent, although the molecular process is quite different from each other.

VII-B Molecular Dynamics Study of Classical Complex Systems

VII-B-1 A Large-Scale Molecular Dynamics Study of Dynamic Structure Factor and Dispersion Relation of Acoustic Mode in Liquid and Supercritical Water

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[*Fluid Phase Equilib.* **226**, 345–350 (2004)]

Large-scale and long-time molecular dynamics calculations have been performed using a fluctuating charge model TIP4P-FQ in order to investigate structure

and dynamics of supercritical water near the critical point. The calculated Ornstein-Zernike behavior of the structure factor $S(k)$ in the small wave number region was in satisfactory agreement with experiment. The intermediate scattering function $F(k, t)$ showed much slower decay in the supercritical water than that found in the ambient water. Further, the calculated dynamic structure factor $S(k, \omega)$ clearly showed the existence of acoustic mode for both systems. The calculated dispersion relation for the liquid water is in good agreement with the IXS data. In the supercritical water near the critical point, the acoustic excitation propagates with a speed of about 420 m/s.

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

VII-C-1 Quantum Rotation of Carbonyl Sulfide Molecules in Superfluid Helium Clusters: A Path Integral Hybrid Monte Carlo Study

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[*J. Phys.: Condens. Matter* **17**, S3259 (2005)]

Carbonyl sulfide (OCS) molecules in superfluid helium-4 clusters have been studied by path integral hybrid Monte Carlo methods. A new technique was developed to treat quantum rotational degree of freedom of the molecules in the hybrid Monte Carlo methods, which is referred to be a “Legendre potential technique.” Then, our method was applied to the OCS-doped helium clusters. It was found that although the molecule is solvated inside the cluster, the calculated orientational correlation function exhibits free-rotor-type behavior. The estimated effective rotational constant was in good agreement with the experimental value.

VII-D Theory of Sum Frequency Generation Spectroscopy

Visible-Infrared Sum Frequency Generation (SFG) spectroscopy has been recognized as a powerful experimental technique to optically probe a variety of interface structure. In spite of the recent technical progress in experimental measurement, its analysis remains a challenging issue in general, since 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 work aims at developing our methods for practical applications.

VII-D-1 Improved Computation of Sum Frequency Generation Spectrum of Water Surface

MORITA, Akihiro

The SFG spectrum of water surface was calculated with significantly improved accuracy *via* the time-

dependent formalism we have recently proposed. The revisions include molecular modeling of OH stretching region, sampling statistics, and treatment of boundary conditions. The computation was performed by fully exploiting the massive parallel environment of the NAREGI supercomputers. The calculated spectra show excellent agreement with the recent experiments, allowing us fairly detailed comparison and analysis.

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

Mass transfer kinetics at liquid-vapor interfaces is of fundamental significance in atmospheric chemistry or fluid engineering, and accordingly it has been studied over a century. Understanding of the mass transfer kinetics ranges from phenomenological macroscopic or thermodynamic description to molecular-scale dynamics, and precise comparison between laboratory experiments and molecular-level simulation poses conflicting, unresolved problems. This study tries to obtain a unified picture of mass transfer kinetics, including bulk transport and surface accommodation.

VII-E-1 Mass Accommodation Coefficient of Water

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[*J. Phys. Chem. B* **109**, 14747–14749 (2005)]

The mass accommodation coefficient α of water into liquid water has been a controversial issue for a long time, whether α is essentially unity or smaller than one. We have recently argued that the molecular dynamics study yield an α value very close to one, and the droplet train experiments, which insists a significantly smaller than one, is in fact not inconsistent to the unit α , after accurate analysis of the experimental uptake kinetics. This study strengthens our argument, and showing possible directions to resolve this conflict.

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

VII-F-1 Encapsulation of Hydrogen Atoms by Fullerenes and Carbon Nanotubes with the Use of Nonadiabatic Transition

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An aggressive usage of the non-adiabatic phenomenon is proposed. In this proposal, atomic hydrogen is encapsulated by the transmission through five-membered rings of fullerenes with the help of the non-adiabatic tunneling phenomenon. Cyclopentadienyl radical (C₅H₅) and corannulene (C₂₀H₁₀) are used to model a pentagonal moiety of fullerenes. To demonstrate the proposal, the first principles calculations are performed for the non-adiabatic dynamics on the potential energy surfaces determined by multi-reference configuration interaction (MRCI) method. The results show that the non-adiabatic transitions between ground and excited states essentially control the hydrogen atom transmission through the five-membered ring of corannulene. This transmission is found to occur more than once out of four incidences when the five carbons which surround the five-membered ring are replaced by borons. This phenomenon can be interpreted in terms of the Zhu-Nakamura semiclassical theory of non-adiabatic transition.

VII-F-2 Ab Initio Calculated Structures of Conformers for 1,3-Dimethoxy-p-tert-Butylcalix[4] Crown-5-Ether Complexed with Potassium Cation

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[THEOCHEM 722, 117–123 (2005)]

Stable molecular conformations were calculated for the 1,3-dimethyl ether of p-tert-butylcalix[4]crown-5-ether (**1**) in the various conformers and their potassium-ion complexes. The structures of three distinct conformation have been optimized using ab initio RHF/6-31G methods. After geometry optimizations, B3LYP/6-31+G(d,p) single point calculations of the final structures are done to include the effect of electron correlation and basis set with diffuse function and polarization function. Relative stability of free host **1** is in following order: cone (most stable) > partial-cone > 1,3-alternate conformer. For two different kinds of complexation mode, the potassium cation in the crown-5-ether moiety (*cr*) has much better complexation efficiency than in the benzene-rings (*bz*) pocket for all three kinds of conformation of host molecule **1**. The relative stability of complex (**1** + K⁺) in the *cr*-binding mode is in following order: cone ~ 1,3-alternate > partial-cone conformer.

VII-F-3 Theoretical Transition Probabilities for the A ²A₁-X ²B₁ System of H₂O⁺ and D₂O⁺ and Related Franck-Condon Factors Based on Global Potential Energy Surfaces

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[J. Theor. Comput. Chem. 4, 225–245 (2005)]

In order to elucidate the ionization dynamics, in particular the vibrational distribution, of H₂O⁺($\tilde{A}$) produced by the photoionization and the Penning ionization of H₂O and D₂O with He*(2³S) atoms, the Franck-Condon factors (FCFs) were presented for the H₂O($\tilde{X}$) → H₂O⁺($\tilde{X}$, $\tilde{A}$) ionization and the transition probabilities were presented for the H₂O⁺($\tilde{A}$ - $\tilde{X}$) system. The FCFs were obtained by quantum vibrational calculations using the three-dimensional potential energy surfaces (PESs) of H₂O($\tilde{X}$ ¹A₁) and H₂O⁺($\tilde{X}$ ²B₁, $\tilde{A}$ ²A₁, $\tilde{B}$ ²B₂) 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 H₂O⁺($\tilde{X}$) state primarily populates the vibrational ground state since its equilibrium geometry is almost equal to that of H₂O($\tilde{X}$), while the bending mode (ν_2) is strongly enhanced for the H₂O⁺($\tilde{A}$) state; the maximums in the population of H₂O⁺ and D₂O⁺ are around $\nu_2 = 11$ –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 H₂O⁺ and D₂O⁺ show that the bending progressions consist of the great part of the $\tilde{A}$ - $\tilde{X}$ emission and that combination bands from the (1, $\nu_2' = 4$ –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 (¹⁴N¹⁴N¹⁶O, ¹⁴N¹⁴N¹⁷O, ¹⁴N¹⁴N¹⁸O, ¹⁴N¹⁵N¹⁶O, ¹⁵N¹⁴N¹⁶O, and ¹⁵N¹⁵N¹⁶O) 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 N₂O 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 Theoretical Study of the Oxidation Reaction for the H Atom-Induced Water-Terminated Si Surface $2\text{H}+\text{H}_2\text{O}/\text{Si}(100)\text{-(}2\times 1\text{)}$

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[*Chem. Phys. Lett.* **412**, 347–352 (2005)]

The reported oxidation reaction observed by BML-IRRAS spectra on the silicon surface system, $2\text{H} + \text{H}_2\text{O}/\text{Si}(100)$, has been studied by an *ab initio* molecular orbital method. The highest transition state is found at $\approx +25$ kJ/mol from the reactant energy level, and the oxidation occurs easily under the experimental condition. The present study also accounts for the reactivity deduced from the absorption bands in the IR spectra. It is noted that the quenching of the reaction by thermal relaxation is impossible because the surface is not trapped into the meta-stable states located much lower in energy than the reactant.