

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

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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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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

KOMATSU, Takahiro; YOSHII, Noriyuki; MIURA, Shinichi; OKAZAKI, Susumu

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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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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.