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, $OCS(^4He)_N$, 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.