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

SAITO, Shinji; OHMINE, Iwao[1]
(*[1]Nagoya Univ.*)

[*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 mo-tions, 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

SUMIKAMA, Takashi[1]; SAITO, Shinji; OHMINE, Iwao[1]
(*[1]Nagoya Univ.*)

[*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, $-5.4e$ 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

SHUDO, Akira[1]; ICHIKI, Kouichiro[1]; SAITO, Shinji
(*[1]Tokyo Metropolitan Univ.*)

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

We study slow relaxation in dynamics of liquid water at room temperatures and propose a consistent inter-

pretation 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.