

Theory and Computation of Reactions and Properties in Solutions and Liquids

Department of Theoretical and Computational Molecular Science
Division of Computational Molecular Science



ISHIDA, Tateki

Assistant Professor

Our researches are focused on the projects both on ultrafast photoinduced excited state reaction in solution and on ionic liquids (ILs). The project on photoinduced excited state reaction processes in solution focuses on the development of a theoretical method to describe solvent motion and dynamics around a solute molecule in short-time region, including the application of the developed theoretical treatment to solvation processes and excited-state intramolecular electron transfer processes in Betaine dye molecule solution. On the other hand, the aim of ILs projects is to pursue specific interionic dynamics in ILs through many-body polarization effects and to study a new perspective on the characteristics of ILs using dicationic ILs.

1. Photoinduced Excited State Reaction Processes: Effects of Solvent Motions and Solvation Processes on Excited-State Intramolecular Processes in Solution

We propose a procedure for describing equation of motions for atoms considering the inertial term with an interaction site model for capturing solvent dynamics attributed to solvent motions in a short-time regime, $t < 100$ fs. We present a method for calculating the time-dependent evolution of the electronic structure of a solute molecule in solution coupling an electronic structure theory with a solution of the equation which governs the development of the fluctuation of solvent number density with the inertial term. The prescription is applied to the study of solvation dynamics of the simplest betaine dye molecule pyridinium *N*-phenoxide in acetonitrile and methanol in the excited state. It is shown that the coupling between solvation and a fast intramolecular reaction such as charge transfer is likely to play an important role in solvation dynamics of the simplest betaine. Also, it is indicated that intramolecular electron transfer processes in the present dye system could be promoted by solvation dynamics rather than solute structural relaxation such as in twisted intramolecular

charge transfer (TICT) processes.

2. Molecular Dynamics Study of the Dynamical Behavior in Ionic Liquids through Interionic Interactions

We have focused on the interionic dynamics of an IL, 1-Butyl-3-Methylimidazolium cation with the anion, $[\text{PF}_6]^-$, $[\text{BMIm}][\text{PF}_6]$, and have investigated the interionic interaction in the IL and the polarization effects on the system. Molecular dynamics simulations have been carried out to pursue the understanding of interionic properties in ILs at molecular level. The analyses of velocity cross-correlation functions have been performed to study the interionic interactions. We have computed the momentum correlation functions between ionic species. From simulation results, it is suggested that, at the short time region up to 1 ps, the velocity cross-correlation is predominantly governed by the longitudinal contribution. It is found out that, compared with the longitudinal correlation in the nonpolarizable model, the longitudinal motions are further influenced in the polarizable model. It is indicated that the behavior of mean-squared displacement of the cation at a long-time region is not influenced by polarization effects, while the anion shows important difference. Also, it is concluded that the cage effect in ILs could be reduced by many-body polarization effects. (DOI 10.1016/j.jnoncrysol.2010.05.086)

3. New Perspective on the Characteristics of Ionic Liquids

We focus on dicationic ILs with typical counter anions. The molecular dynamics simulations for dicationic ILs systems have been performed. The interionic interactions and the properties dependent on the specific distribution of ionic species are investigated including the analysis of velocity autocorrelation and polarizability time correlation functions.