Theory and Computation of Reactions and Properties in Solutions and Liquids

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Our researches are focused on the projects both on ultrafast photoinduced electron energy transfer in the excited state in solution and on ionic liquids (ILs). The project on photoinduced electron energy transfer processes in the excited state in solution concentrates the development of a theoretical method to describe solvent motion and dynamics accompanying electron energy transfer with the theoretical treatment to solvation processes and excited-state intramolecular electron transfer processes in solution we have developed. On the other hand, the purpose of ILs projects is to study specific interionic dynamics in ILs and to extract a new perspective on the physically and chemically unique characteristics of ILs.

1. Photoinduced Electron Energy Transfer Processes in the Excited State in Solution

We have proposed and developed a procedure for describing 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 around a solute molecule in the formalism of an interaction site model. We extend this prescription for studying electron energy transfer processes in the excited state in solution. It is shown that the coupling between fast solvation dynamics and a fast intramolecular electron energy transfer is likely to play an important role in the emergence of photoinduced various and unique functionalities in biochemical and metal complex systems.

2. Molecular Dynamics Study of the Unique Dynamical Behavior in Ionic Liquids through Interionic Interactions[1)]

We have focused on the interionic dynamics of an IL, 1-Butyl-3-Methylimidazolium cation with the anion, $[PF_6]^-$, $[BMIm][PF_6]$, and have investigated the interionic interaction in the IL and the polarization effects on the system. From the results by Molecular dynamics simulations, it has been concluded that the cage effect in ILs could be reduced by many-body polarization effects.

3. Investigations of New Perspectives on the Characteristics of Ionic Liquids[2)]

We investigated the ultrafast dynamics in 1-butyl-3-methylimidazolium-based ionic liquids with two series of anions: (1) cyano-group substituted anions ($[SCN]^-$, $[N(CN)_2]^-$, and $[C(CN)_3]^-$) and (2) trifluoromethylsulfonyl group substituted anions ($[OTf]^-$, $[NTf_2]^-$, and $[CTf_3]^-$) by femtosecond Raman-induced Kerr effect spectroscopy. From the Fourier-transform Kerr spectra of the ionic liquids, the low-frequency spectrum of 1-butyl-3-methylimidazolium tricyanomethide indicates a low-frequency shift compared to the ILs with the other cyano-group substituted anions, due to the planar structures of the cation and the anion. The relative amplitude of the low-frequency band at approximately 20 cm^{-1} to the entire broad spectrum for the ionic liquids with trifluoromethylsulfonyl-group substituted anions is larger with the order $[OTf]^- < [NTf_2]^- \sim [CTf_3]^-$. These results can be attributed to the librational motion of anions and/or the coupling of the translational and reorientational motions.

Also, we have carried out the study of dicationic ILs with typical counter anions. (DOI 10.1021/jp206266e) The molecular dynamics simulations for dicationic ILs systems have been proceeded. The interionic interactions dependent on the unique spatial distribution of ionic species have been investigated including the analysis of velocity autocorrelation and polarizability time correlation functions and various dynamical properties based on the detailed analyses of collective motion of ionic molecules.

References

1) T. Ishida, *J. Non-Cryst. Solids* **357**, 454–462 (2011).
2) H. Fukazawa, T. Ishida and H. Shirota, *J. Phys. Chem. B* **115**(16), 4621–4631 (2011).