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

We focus 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 focuses on the development of a theoretical method to describe electron energy transfer including solvent motion and dynamics with the theoretical treatment we have developed. On the other hand, ILs' projects concentrate the study of specific interionic dynamics in ILs and the investigation of a new perspective on the physically and chemically unique characteristics of ILs.

1. The Theoretical Study of Photoinduced Electron Energy Transfer Processes in the Excited State in Solution

We have 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 solvent motion 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 indicated that the coupling between solvation dynamics and a fast intramolecular electron energy transfer is likely to play an important role in the emergence of photoinduced unique functionalities in biochemical and metal complex systems.

2. The Unique Physical and Chemical Properties of Ionic Liquids through Interionic Interactions: Theoretical Investigation with Molecular Dynamics Simulations1)

Ionic liquids (ILs) have been found to possess a wide potential variety of interesting physical and chemical properties. We consider the unique properties of ILs which owe to the specific interionic interaction between ionic species. In particular, we study the importance of both the cross-correlation between cation and anion species, and the effect of polarization in ILs. On the basis of recent theoretical studies on ILs employing molecular dynamics simulations, how the collective dynamics through interionic interactions cause the unique physical and chemical properties of ILs and how electronic polarizability effects modify interionic dynamics have been investigated. Those include the investigation of the contribution of ionic motions with velocity cross-correlation functions and the study of many-body polarization effects on the cage effect in ILs.

3. Investigations of New Perspectives on the Characteristics of Ionic Liquids: Microscopic Aspects in Dicationic Ionic Liquids2)

The interionic vibrations in imidazolium-based dicationic ionic liquids (ILs) containing the bis(trifluoromethylsulfonyl)-amide ($[NTf_2]^-$) counteranion were investigated using femtosecond optical-heterodyne-detected Raman-induced Kerr effect spectroscopy. The microscopic nature of the dicationic ILs ($[C_n(MIm)_2][NTf_2]_2$, where n = 6, 10, and 12; MIm = *N*-methylimidazolium) was compared with that of the corresponding monocationic ILs ($[C_nMIm][NTf_2]$, where n = 3, 5, and 6) used as reference samples. Low-frequency Kerr spectra within the frequency range 0–200 cm^{-1} of the ILs revealed that the spectral profile of the dicationic ILs as well as that of the corresponding monocationic ILs is bimodal. The distinguished line-shape of the low-frequency Kerr spectrum of $[C_3MIm][NTf_2]$ from the other ILs can be accounted for by the homogeneous nature in the microstructure of the IL, but the other ILs indicate microsegregation structures due to the longer nonpolar alkylene linker or alkyl group in the cations.

References

1) T. Ishida, in *Handbook of Ionic Liquids: Properties, Applications and Hazards*, J. Mun and H.Sim, Eds., Nova Science Publishers Inc.; Hauppauge, NY, pp. 395–417 (2012).
2) H. Shirota and T. Ishida, *J. Phys. Chem. B* **115**, 10860–10870 (2011).