

Theory and Computation of Reactions and Properties in Solutions and Liquids

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We focus on the projects both on ultrafast photoinduced reaction and on ionic liquids. The project on photoinduced 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. Also, it includes the application of the developed theoretical treatment to solvation processes and excited-state intramolecular processes in Betaine dye molecule solution. On the other hand, the project on ionic liquids is collaborating work with the experimental studies by Prof. Shirota at Chiba University.

1. Solvent Motions and Solvation Processes in a Short-Time Regime: Effects on Excited-State Intramolecular Processes in Solution¹⁾

We propose a method for treating equation of motions for atoms taking into account 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 show a prescription for solving the equation which governs the development of the fluctuation of solvent number density with the inertial term, and, also, the procedure is applied to the study of solvation dynamics of the simplest betaine dye molecule pyridinium *N*-phenoxide in water 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.

2. Atom Substitution Effects of $[XF_6]^-$ in Ionic Liquids. 1. Experimental Study²⁾

We have investigated the interionic vibrational dynamics of 1-butyl-3-methylimidazolium cation ($[BMIm]^+$) based ionic liquids with the anions of $[PF_6]^-$, $[AsF_6]^-$, and $[SbF_6]^-$ as well as the static physical properties, such as shear viscosity and

liquid density. Shear viscosity for the ionic liquids becomes lower with the heavier atom anion: $[BMIm][PF_6] > [BMIm][AsF_6] > [BMIm][SbF_6]$. Femtosecond optically heterodyne-detected Raman-induced Kerr effect spectroscopy has been used to observe the interionic vibrational dynamics of ionic liquids. The interionic vibration in the frequency region of less than 50 cm^{-1} clearly shows the heavy atom substitution effect; that is, the heavy atom substitution of $[XF_6]^-$ critically affects the interaction-induced motion.

3. Atom Substitution Effects of $[XF_6]^-$ in Ionic Liquids. 2. Theoretical Study³⁾

We have carried out the molecular dynamics simulations for 1-butyl-3-methylimidazolium cation based ILs ($[BMIm][PF_6]$, $[BMIm][AsF_6]$, and $[BMIm][SbF_6]$) including the calculations of density of state (DOS) profiles, polarizability time correlation function (TCF), and Kerr spectra (with the development of the force fields of $[AsF_6]^-$ and $[SbF_6]^-$ by an ab initio calculation). From these computational studies, we find that the contribution of the reorientation of cations and anions mainly governs the Kerr spectrum profile in all three ILs, while the contribution of the collision-induced and cross terms, which are related to translational motions including coupling with librational motion, is not large at higher frequencies than 50 cm^{-1} . In addition, it is emphasized in this study that atomic mass effects in ILs are accessible through a complementary approach of both experimental and theoretical approaches.

References

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- 3) T. Ishida, K. Nishikawa and H. Shirota, *J. Phys. Chem. B* **113**, 9840–9851 (2009).