Theory and Computation of Liquids and Liquid Interfaces

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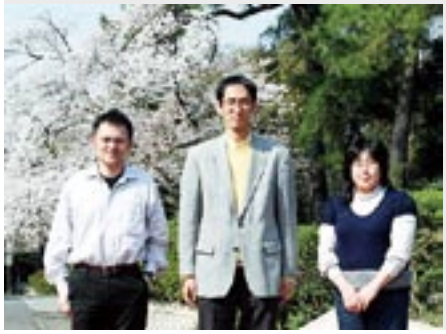

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The following projects 1–4 focus on the development of theory and computational analysis methods for interfacial sum frequency generation spectroscopy and its application to aqueous interfaces. The visible-infrared sum frequency generation spectroscopy is a powerful method to obtain interface-specific vibrational spectra. While this experimental technique is now widely used as an interface probe in a molecular level, reliable interpretation of the observed spectra is often lacking which significantly hinders the progress of this surface characterization method. We have proposed theoretical methods to compute the sum frequency spectra on the basis of ab initio molecular modeling and molecular dynamics simulation. These projects elucidated the sum frequency spectra of liquid interfaces, including aqueous salt and acid solutions, with the molecular modeling we have developed.

Projects 5 and 6 are mainly conducted by Dr. Ishida and his collaborators. Project 5 deals with the properties of room temperature ionic liquids in collaboration with Dr. Shirota at Chiba University. Project 6 is performed in collaboration with Dr. Yoshida and Prof. Hirata in the IMS about theoretical investigation of solvent effect on electron transfer reaction system.

1. Flexible and Polarizable Molecular Modeling for Describing Interfacial Properties of Gas-Liquid Aqueous Salt Solutions[1)]

Gas-liquid interfacial structures of NaCl and NaI aqueous solutions are investigated via molecular dynamics simulations using a flexible and polarizable water model we have developed. The new five-site model of water aims at suitably describing interfacial properties, including vibrational sum frequency spectroscopy where both flexibility and polarization are crucial. The performance of the water model is systematically examined and demonstrated by a number of properties of bulk and interface, including density, vaporization energy, dipole moment, diffusion coefficient, radial distribution function, infrared and Raman spectra of the O–H stretching region, surface potential, and surface excess of ions. The orientational structure of surface water is investigated in detail in connection with the issue of surface solvation of anions. These investigations will be utilized to analyze the sum frequency generation spectra in relation to the orientational structure at the molecular level.

2. Computation of Sum Frequency Generation Spectra of Aqueous Salt Solution Interfaces[2)]

The vibrational sum frequency generation (SFG) spectra of gas-liquid interfaces of NaCl and NaI aqueous solutions are computed and analyzed by molecular dynamics (MD) simulations using a flexible and polarizable molecular model. The MD calculations have reproduced the experimental features of SFG spectra, including observed perturbation on the NaI spectra in contrast to little perturbation on NaCl. Analysis of the nonlinear susceptibility revealed that the intermolecular correlation has a significant contribution to the vibrationally resonant amplitude, which largely distorts the generally accepted relationship between the SFG intensity and orientation of individual molecules. In NaI solutions, modest enhancement of ssp intensity in the 3400 cm^{-1} region is thereby elucidated by this mechanism. Regarding the sps spectra, three spectral components are assigned and elucidated. Calculated remarkable enhancement in the 3400–3800 cm^{-1} region for NaI solutions is found to be sensitive to the electric double layer structure. It is also revealed that the sps intensity is augmented by the intermolecular water-water correlation effect.

3. Molecular Dynamics Analysis of Sum Frequency Generation Spectra of Aqueous Acid Solution Interfaces[3)]

Molecular dynamics simulation for gas/liquid interfaces of aqueous hydrochloric (HCl) and hydroiodic (HI) acid solutions is performed to calculate and analyze their sum frequency generation (SFG) spectra. The present MD simulation supports strong preference of hydronium ions at the topmost surface layer and a consequent formation of ionic double layers by the hydronium and halide ions near the interface. Accordingly, the orientational order of surface water in the double layers is reversed in the acid solutions from that in the salt (NaCl or NaI). The calculated SFG spectra of O–H stretching region well reproduce the experimental spectra of ssp and sps polarizations. In the ssp spectra, the strong enhancement in the hydrogen bonding region for the acid solutions is elucidated by two mechanisms, ordered orientation of water in the double layer and symmetric OH stretching of the surface hydronium ions. In the sps spectra, reversed orientation of surface water is evidenced in the spectral lineshapes, which are quite different from those of the salt solutions.

4. Modeling of C–H Vibrations for Alkyl Chain Molecules and Related Interfaces

The present work aims at applying our computational methods to the interfaces including alkyl chains. Alkyl chains have ubiquitous importance in organic films and polymer interfaces, and their C–H stretching vibration has been extensively studied by SFG and IR spectra. Their spectral structure in C–H stretching vibration is often complicated by those of CH_3 and CH_2 moieties and Fermi resonance with the CH bending overtone. As the first step to deal with such systems, we construct an appropriate model of methanol for describing interfacial vibrational spectra.

The present model of methanol is flexible and polarizable, and all the ingredient parameters are determined by density functional calculations. The present intramolecular force field appropriately includes the contribution of the Fermi resonance. For modeling of electrostatic interaction and polarization, we used the Charge Response Kernel (CRK) method. The present model takes account of geometry dependence of the partial charges and CRK, so that it is able to describe the dipole moment vector and polarizability tensor accurately as a function of molecular vibrational configuration. This molecular model of methanol will be extended to other molecules with alkyl chains for use of MD simulation.

5. Theoretical Investigation of Characteristics of Components of Room Temperature Ionic Liquids and Its Effect on Interplay between Cation and Anion Units

Room temperature ionic liquids (RTILs) show a wide variety of interesting physical and chemical properties, different from so-called molten salts. It is considered that many of them can be attributed to the character of both cation and anion which consist of RTILs. From these viewpoints, we can expect that the size of cation and anion, their geometric shapes, remarkable characteristics of elements in the cation and anion and so on, determine and explain some of essential properties and inside details. In particular, we focus on the characteristics of elements in the anion component in ionic liquids, 1-Butyl-3-Methylimidazolium cation (BMIM) with XF_6^-: PF_6^-, AsF_6^- and SbF_6^-. We compared important physical properties among them, referring to experimental data by molecular dynamics simulation procedures.

6. Theoretical Study of Temperature and Solvent Dependence of the Free Energy Surface of the Intramolecular Electron Transfer based on the RISM-SCF Theory; Application to 1,3-Dinitrobenzene Radical Anion in Acetonitrile and Methanol[4)]

The free energy surfaces along the intramolecular electron transfer reaction of 1,3-dinitrobenzen radical anion in acetonitrile and methanol are investigated with the reference interaction site model self-consistent field theory. Although acetonitrile and methanol have similar values of the dielectric constant, the free energy profiles are quite different. The electronic coupling strength exhibits an intriguing behavior in the temperature dependence: it increases with increasing temperature in acetonitrile, while that in methanol exhibits the opposite trend.

References

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3) T. Ishiyama and A. Morita, *J. Phys. Chem. A* **111**, 9277–9285 (2007).
4) N. Yoshida, T. Ishida and F. Hirata, submitted to *J. Phys. Chem. B* (2007).

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