

Theory and Computation of Liquids and Liquid Interfaces

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The following projects 1 and 2 focus on the development of theory and computational analysis methods for interfacial sum frequency generation (SFG) 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. The following project 1 summarized the theoretical methods of SFG analysis that we have developed. Project 2 is a collaborative work with experimental groups of Drs. Miyamae at AIST and Dr. Ouchi at Nagoya. Collaboration of SFG experiments and the theoretical analysis will be a powerful way to study liquid interfaces. Project 3 summarizes theoretical study of mass transfer dynamics and kinetics at liquid-water interfaces.

Projects 4, 5, and 6 are mainly conducted by Dr. Ishida and his collaborators.

1. Theory of Sum Frequency Generation Spectroscopy¹⁾

Gas-liquid interfacial structures of NaCl and NaI aqueous solutions. This article summarizes computational analysis of the vibrational Sum Frequency Generation (SFG) spectroscopy with molecular dynamics simulation. The analysis allows direct comparison of experimental SFG spectra and microscopic interface structure obtained by molecular simulation, and thereby obviates empirical fitting procedures of observed spectra. In the theoretical formulation, the frequency-dependent nonlinear susceptibility of an interface is calculated in two ways, based on the energy representation and time-dependent representation. The application to aqueous interfaces revealed a number of new insights into the local structure of electrolyte interfaces and interpretation of the SFG spectroscopy.

2. Sulfuric Acid Aqueous Solution Surfaces Studied by a Combination of Sum Frequency Generation and Molecular Simulation²⁾

This project is a collaborative work with experiment of SFG spectroscopy. The vibrational sum frequency generation spectra of the air-liquid interface of H₂SO₄-H₂O solutions over the wide range of concentration are measured in the SO stretch region (1000–1300 cm⁻¹). This is the first measurement of sulphur species at the surface region with distinguishing their ionization state. The analogy of the concentration dependence of Raman and SFG is indicative of a nearly identical behavior of the first acid dissociation at the air-liquid interface as in the bulk.

3. Theoretical Investigation of Aqueous Surface Structure and Mass Transfer Dynamics³⁾

The mass transfer mechanism across gas/water interface is studied with molecular dynamics (MD) simulation. The MD results provide a robust and qualitatively consistent picture to previous studies about microscopic aspects of mass transfer, including interface structure, free energy profiles for the uptake, scattering dynamics and energy relaxation of impinging molecules. These MD results are quantitatively compared with experimental uptake measurements, and we find that the apparent inconsistency between MD and experiment could be partly resolved by precise decomposition of the observed kinetics into elemental steps. Remaining issues and future perspectives toward constructing a comprehensive multi-scale description of interfacial mass transfer are summarized.

4. Theoretical Study of Temperature and Solvent Dependence of the Free-Energy Surface of the Intramolecular Electron-Transfer Based on the RISM-SCF Theory⁴⁾

The free-energy surfaces along the intramolecular electron-transfer reaction path of the 1,3-dinitrobenzene 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. In the methanol solution, the charge is strongly localized on one of the nitrile substituents due to a strong hydrogen bond between 1,3-dinitrobenzene and the solvent, while the polarization is not so large in the case of acetonitrile. The temperature dependence of the reorganization energy, the coupling strength, and the activation barrier decrease with increasing temperature for both cases. The electronic coupling strength also shows a similar tendency in the temperature dependence; it increases with increasing temperature in both solvents but with different rates. The behavior is explained in terms of the strong polarization induced by the hydrogen bond between the solute and solvent in the methanol solution.

5. Optimal Charge and Charge Response Determination through Conformational Space: Global Fitting Scheme for Representative Charge and Charge Response Kernel⁵⁾

We propose global fitting scheme derived in least-square sense to estimate optimal partial charge and charge response kernel (CRK), $\partial Q_a / \partial V_b$, with the data collected from conformational space sampling. We applied the global fitting method to 1-butanol system and the performance and accuracy of our global fitting procedure are shown. In addition, we choose 1-pentanol as the test system with the electronic structure change via conformational change and applied the global fitting method to it. From our study, it is indicated that intramolecular polarization can be influenced by intramolecular hydrogen bonding, and it is shown that our global fitting method can correspond to such situation. Also, the global fitting procedure is tested in a large molecular system, 1-dodecanol. We show the results of the availability of our fitting method for the system needed to sample large sets of data over large conformational space. It is indicated that the nonlocality in intramolecular polarization in alkyl chain sequence can be observed and that the large fluctuation of CRKs via nonbonded interaction such as intramolecular hydrogen bonding, as seen

in the 1-pentanol case, can appear in common. The global fitting scheme we proposed is available for building molecular modeling considering polarization effect explicitly even in the case that target systems include a lot of conformers.

6. Theoretical Study of Strong Coupling between Solvation and Electronic Structure in the Excited State of a Betaine Dye⁶⁾

The electronic ground and excited state structures of the betaine dye molecule pyridinium-N-phenoxide [4-(1-pyridinio) phenolate] are investigated both in the gas phase and in aqueous solution, using the reference interaction site model self-consistent-field (RISM-SCF) procedure within a CASSCF framework. We obtain the total free energy profiles in both the ground and excited states with respect to variation in the torsion angle between the phenoxide and pyridinium rings. We analyze the effect of solvent on the variation of the solute dipole moment and on the charge transfer character in the excited state. In the gas phase, it is shown that the potential energy profile in the excited state decreases monotonically toward a perpendicular ring orientation and the dipole moment decreases along with decreasing charge localization. In water, the free energy surface for twisting is better characterized as nearly flat along the same coordinate for sterically accessible angles. These results are analyzed in terms of contributions of the solvation free energy, the solute electronic energy, and their coupling. Correspondingly, the dependence of the charge transfer character on solute geometry and solvation are analyzed, and the important roles in the excitation and subsequent relaxation processes for the betaine dye are discussed. It is found that there is considerable solute electronic reorganization associated with the evolution of solvation in the excited state, and it is suggested that this reorganization may contribute significantly to the early time evolution of transient spectra following photoexcitation.

References

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