

VII-D Development of Polarizable Molecular Modeling for Simulation Studies

Accuracy and reliability of molecular models are crucial for theoretical understandings of condensed phase chemistry. This year we have developed molecular models which incorporate both intramolecular vibration and electronic polarization. Such flexible and polarizable models have a number of applications to condensed phase chemistry, including electron transfer reactions. Another important purpose of the flexible and polarizable models is to describe the sum frequency generation spectroscopy by molecular dynamics simulation, as discussed in the next section.

VII-D-1 Polarizable Solute in Polarizable and Flexible Solvents: Simulation Study of Electron Transfer Reaction Systems

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[*J. Phys. Chem. B* **109**, 18558–18564 (2005)]

A polarizable solute model, based on the empirical valence bond approach, is developed and applied to electron transfer (ET) reactions in polarizable and flexible water solvents. The polarization effect is investigated in comparison with a nonpolarizable solute and solvent model. With free energy curves constructed by a molecular dynamics simulation, the activation energy barrier and the reorganization energy related to ET processes are investigated. The simulation results show that the activation energy barrier becomes larger in the polarizable model than in the nonpolarizable model and that this makes the ET rate slower than that with the nonpolarizable model. It is shown that the effect of the electronic energy difference of solute molecule on free energy profiles is remarkable and that, corresponding to this effect, the reorganization energy is significantly modified. These results indicate that the process of solvent polarization by the polarized solute to enhance the solute-solvent interaction is a key factor and that treating the polarization of both solute and solvent at the same time is essential. Also, the polarization effect on the diffusive motion of the solute molecule in the polarization solvent is studied. The polarized solute molecule shows slower diffusive motion compared with that in the

nonpolarizable model.

VII-D-2 Extended Treatment of Charge Response Kernel Comprising the Density Functional Theory and Charge Regulation Procedures

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[*J. Chem. Phys.* **125**, 074112 (2006)]

We propose an extended treatment of the charge response kernel (CRK), $\partial Q_a / \partial V_b$, which describes the response of partial charges on atomic sites to external electrostatic potential, on the basis of the density functional theory (DFT) via the coupled perturbed Kohn-Sham equations. The present CRK theory incorporates regulation procedures in the definition of partial charges to avoid unphysical large fluctuation of the CRK on “buried” sites. The CRKs of some alcohol and organic molecules, methanol, ethanol, propanol, butanol, dimethylsulfoxide (DMSO) and tetrahydrofuran (THF) were calculated, demonstrating that the new CRK model at the DFT level has greatly improved the performance of accuracy in comparison with that at the Hartree-Fock level previously proposed. The CRK model was also applied to investigate spatial nonlocality of the charge response through alkyl chain sequences. The CRK model at the DFT level enables us to construct a non-empirical strategy for polarizable molecular modeling, with practical reliability and robustness.

VII-E Computational Analysis of Sum Frequency Generation Spectroscopy

This project aims at developing theoretical and computational methods of visible-infrared Sum Frequency Generation (SFG) spectroscopy for interface characterization. While SFG is recognized as a powerful experimental technique to optically probe a variety of interface structure, experimental spectra are not often amenable to straightforward fitting or interpretation. We have proposed theoretical methods to compute SFG directly via molecular modeling and molecular dynamics simulation, without resorting to empirical parameterization. This year, we have developed a general polarizable and flexible molecular model, called charge response kernel, on the basis of the density functional theory for the purpose of the SFG calculation. SFG spectra of aqueous electrolyte solutions are also analyzed by molecular dynamics simulation.

VII-E-1 Intermolecular Correlation Effect in Sum Frequency Generation Spectroscopy of Electrolyte Aqueous Solution

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[*Chem. Phys. Lett.* **431**, 78–82 (2006)]

Molecular dynamics analysis of the sum frequency generation (SFG) spectroscopy was performed to solve the recent controversial problem about liquid-vapor interface of electrolyte aqueous solution [Garrett, *Science* **303**, 1146 (2004)]. The present MD analysis revealed a crucial role of ion-water dipolar correlation in the vibrational SFG spectroscopy, which significantly distorts the general relationship between SFG intensity and surface orientational order. The experimental SFG spectra were thereby elucidated from the local structure of interface.