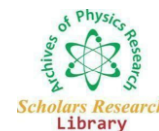




Extended Abstract

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Ab initio theory for computing sum frequency generation spectra at aqueous interfaces

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Understanding aqueous interfaces at the molecular level is not only fundamentally important, but also highly relevant for a variety of disciplines. For instance, electrode–water interfaces are relevant for electrochemistry, as mineral–water interfaces for geochemistry and air–water interfaces for environmental chemistry; lipid–water interfaces constitute the boundaries of the cell membrane, and are thus relevant for biochemistry. One of the major challenges in these fields is to link macroscopic properties such as interfacial reactivity, solubility, and permeability as well as macroscopic thermodynamic and spectroscopic observables to the structure, structural changes, and dynamics of molecules at these interfaces. Simulations, by themselves, or in conjunction with appropriate experiments, can provide such molecular-level insights into aqueous interfaces. We study aqueous interfaces, by assessing computations of the sum-frequency generation (SFG) spectra, which selectively detect the interfacial molecules, at aqueous interfaces. To avoid bias in the computational results and interpretation originating from the choices of the details of FF models, applying a parameter-free ab initio molecular dynamics (AIMD) simulation technique to the SFG calculation seems to be a promising route. However, the huge computational cost required for AIMD simulation has prohibited the widespread use of AIMD simulations

for computing the SFG spectra. We have recently presented an efficient calculation algorithm for computing the SFG spectra of the water O–H stretch mode based on the surface-specific velocity–velocity correlation function, by separating degrees of freedom of the nuclei from solvation effects such as the induced dipole and polarizability. This methodology has been applied to the fundamental water–air, water–lipid, and aqueous solution–air interfaces. We are going to extend our method to solid–liquid interfaces. Interfacial water structures have been studied intensively by probing the O–H stretch mode of water molecules using sum-frequency generation (SFG) spectroscopy. This surface-specific technique is finding increasingly widespread use, and accordingly, computational approaches to calculate SFG spectra using molecular dynamics (MD) trajectories of interfacial water molecules have been developed and employed to correlate specific spectral signatures with distinct interfacial water structures. Such simulations typically require relatively long (several nanoseconds) MD trajectories to allow reliable calculation of the SFG response functions through the dipole moment–polarizability time correlation function. These long trajectories limit the use of computationally expensive MD techniques such as ab initio MD and centroid MD simulations. Here, we present an efficient algorithm determining the SFG response from the surface-specific velocity–velocity correlation function (ssVVCF). This ssVVCF formalism allows us to calculate SFG spectra using a MD trajectory of only ~ 100 ps, resulting in the substantial reduction of the computational costs, by almost an order of magnitude. We demonstrate that the O–H stretch SFG spectra at the water–air interface calculated by using the ssVVCF formalism well reproduce those calculated by using the dipole moment–polarizability time correlation function. Furthermore, we applied this ssVVCF technique for computing the SFG spectra from the ab initio MD trajectories with various density functionals. We report that the SFG responses computed from both ab initio MD simulations and MD simulations with an ab initio based force field model do not show a positive feature in its imaginary component at 3100 cm^{-1} . The surface structure of aqueous sulfuric acid solution at $0.02x$ (x is the mole fraction) concentration is investigated by molecular dynamics (MD) simulation with newly developed flexible and polarizable molecular models. The models are applied to calculate the SFG spectrum on the assumption that the acid dissociation of sulfuric acid at the surface is the same as in the bulk. The calculated SFG spectrum well reproduces the experimental one, indicating that the assumption on the acid dissociation is valid in a relatively low concentration range. The density profiles of the constituent ions at the surface region show distinct surface preference in the order of the hydronium cation, bisulfate anion, and sulfate dianion, which thereby forms an electric double layer and strongly perturbs the orientational structure of surface water. The enhancement of the SFG intensity at the hydrogen-bonding OH stretching region and the depletion at the dangling (free) OH region are elucidated from the interfacial structure. We use density functional theory molecular dynamics simulations to investigate the structure, dynamics, and vibrational sum frequency generation (vSFG) spectra at the $\text{Al}_2\text{O}_3(0001)\text{--H}_2\text{O}$ and $\text{Al}_2\text{O}_3(11\bar{2}0)\text{--H}_2\text{O}$ interfaces. We find that the differences in the vSFG spectra between the two interfaces can be explained by significantly weaker surface–water interactions at the (0001) vs (11 $\bar{2}$ 0) interface. The weaker interactions at the (0001) surface are caused by the flat surface plane and high density of OH groups, leading to a decoupling of the vibrational modes of the surface OH groups and H₂O molecules.

Bottom Note: This work is partly presented at 4th International Conference on Physical and Theoretical Chemistry September 18–19, 2017, Dublin, Ireland