Theoretical Investigation of Dielectric Constant at Monolayer Interfaces by Polarizable Molecular Dynamics Simulation

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Due to its highly surface selectivity and sensitivity, sum frequency generation (SFG) spectroscopy has an excellent potential to study interfaces, such as electrode-electrolyte interfaces and monolayer interfaces. It is particularly useful for the *in situ* detection of electrode interfaces in electrochemically working conditions. We have developed the computational analysis of SFG spectroscopy, and calculated microscopic structure and nonlinear susceptibility of various interfaces including electrodes and batteries.[1-3] However, one of the remaining difficulties to advance our computational analysis is how to deal with uncertainties associated to the interfacial dielectric constant (ε'). As an optical probe of interfaces, the dielectric constant of the interface is a critical factor, though it has been treated as an empirical parameter so far. The measurement of ε' is not straightforward for a monolayer region. Lack of reliable determination of ε' hinders our quantitative analysis of SFG spectra in organic interfaces.

In this work, we extended our theory of SFG to deal with the interfacial dielectric constant besides the nonlinear susceptibility of the interfaces. We propose a general modeling and theory to evaluate the interfacial dielectric constant by *ab initio* polarizable model and molecular dynamics (MD) simulations. The proposed method is able to calculate the frequency-dependent dielectric constant, including the static and optical ones, as a function of the depth position. The present work revealed the local dielectric profile with spatial and frequency decomposition near the interface. To validate our theory of ε', the calculated local dielectric constants of dodecanol-water monolayer are examined. It is noteworthy that the interfacial dielectric constant show anisotropy as well as complicated structure as a function of depth position, which reflects the inhomogeneous structure of the interface. The detailed results of the dielectric profile and its implication to the analysis of SFG spectroscopy will be shown in the presentation. The reliable information of interfacial dielectric profile is necessary to apply the SFG spectroscopy to complex interfaces, such as those at batteries.

References

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