Preview

Electrical Double Layer Probed by Surface-Specific Vibrational Technique

Yuki Nagata[1,*] and Shaul Mukamel[2,*]

In this issue of *Chem*, Paesani and co-workers present a computational analysis of sum-frequency generation (SFG) spectra of water to disentangle the interfacial $\chi^{(2)}$ and bulk $\chi^{(3)}$ contributions. SFG line shapes are in good agreement with experimental results. The analysis reveals the molecular response of interfacial water, which is usually masked by the bulk water spectra at the water-charged surfactant interface.

The impact of surface charges on the structure of interfacial water near solids, lipid membranes, and surfactants is of great interest in biology, atmospheric chemistry, and electrochemistry. The (negatively) charged lipid membrane attracts proteins, thereby accelerating protein folding. Sea spray is a major source of aerosol particles, enhancing cloud growth. The electrodes in chemical cells are charged, leading to chemical reactions such as hydrogen production. Proteins approach the membrane in a stochastic manner and feel the electrostatic field due to the surface charge. These phenomena are often governed by the delicate balance between the ion accumulation near the surface and the permittivity of interfacial water.

Such a delicate balance has been well described by the electrical double-layer model. In this model, the interfacial water region is composed of layers parallel to the surface; in the first layer, known as the Stern layer, ions are adsorbed onto or accumulated near the charged surface with the opposite sign of charge to the ions through strong Coulomb interactions. In the second diffuse layer, the electric field is weakened by the charge cancellation as a result of the ions in the first layer, and thus the second layer is loosely associated with the charged surface. There, ions move freely under the influence of the electric field generated by the charged surface. Experimentally probing the double-layer structure and unveiling the molecular structure of solvent and ions in these layers separately has been a formidable challenge.

Surface-specific spectroscopies such as sum-frequency generation (SFG) and second-harmonic generation (SHG) are powerful tools for probing the molecular structure near surfaces. SFG can provide surface- and molecular-specific information through the vibrational modes of molecules. The SFG signal is generated by the spatial and temporal overlap between infrared radiation and a visible pulse. It is enhanced when the infrared frequency is resonant with the vibrational mode of molecules, making SFG chemically specific. The SFG signal is given by the second-order susceptibility $\chi^{(2)}$, which vanishes for a centrosymmetric medium (bulk), making SFG an ideal surface-specific probe of the molecular response in a non-centrosmmetric medium such as a surface. SFG resonances can also be generated in a bulk sample subjected to a static electric field E_0 through a $\chi^{(3)}$ process that is not surface specific. The two contributions can be described by an effective $\chi^{(2)}$:

$$\chi_{\text{eff}}^{(2)} = \chi^{(2)} + \int_{0^+}^{\infty} \chi^{(3)} \cdot \hat{z} E_0(z') e^{i\Delta k_z z'} dz'$$

(Equation 1)

Equation 1 is widely used in electric-field-induced second harmonic generation for obtaining SHG resonances in materials where $\chi^{(2)}$ vanishes.[1] In a double layer, the Stern layer contributes to the SFG signal via the first term, whereas the diffuse layer contributes via the second term, where the electric field, E_0, is generated by the surface charge.

It is not easy to disentangle these two contributions to the total SFG signal. For this reason, most studies of the interfacial water near a lipid and/or surfactant via vibrational surface-specific techniques have been so far limited to the water-neutral zwitterionic lipid and/or surfactant,[2–5] given that the net surface charge of the lipid is zero, and the diffuse layer is not present for these interfaces. The surface-specific signal of water can then be attributed solely to the water molecules in the Stern layer. A number of studies have addressed the molecular origin of the SFG signals of water at such interfaces; the positive SFG signatures in the SFG spectra are evidence that the net water orientation tends to point up to the lipid layer rather than to the bulk water at the zwitterionic lipid-water interface.[2,4] This specific orientation arises from the strong hydrogen bonding between water and the negatively charged lipid headgroup; normally, a positively charged lipid headgroup, such as the $-N(CH_3)^+$ group, cannot form a hydrogen bond with water because of the hydrophobic $-CH_3$ group.[2,4]

[1]Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

[2]Departments of Chemistry and Physics and Astronomy, University of California, Irvine, Irvine, CA, USA

*Correspondence:
nagata@mpip-mainz.mpg.de (Y.N.),
smukamel@uci.edu (S.M.)

Furthermore, a 3,600 cm^{-1} peak signifies that the O–H group of water is weakly hydrogen bonded to the carbonyl group.[2,4,5] As such, SFG has provided detailed information on the hydration structure of water near zwitterionic lipids. However, once the balance between negative charge and positive charge is broken and thus the surface has explicit charges, the contribution of the diffuse layer to the surface-specific signal is non-negligible;[6] even for a surface with a charge density of $\pm$ 0.01 C/m^2, the SFG signal contributed from the Stern layer is masked by the contribution from the diffuse layer. Disentangling the contribution of the diffuse layer from that of the Stern layer has thus been a formidable challenge for understanding the strength and impact of the electric double layer near charged interfaces.

In 2016, Tian and co-workers proposed a route for disentangling these contributions experimentally.[1] By varying the surface charge density and then subtracting the SFG signal at the slightly charged interface from that at a non-charged interface, one can estimate the SFG signal contributed by the diffuse layer ($\chi^{(3)}$ term). Once this is known, the contribution of the Stern layer ($\chi^{(2)}$ term) can be readily extracted from the total spectrum $\chi^{(2)}_{eff}$ via Equation 1. That study had demonstrated that the contributions of the diffuse layer and Stern layer could be comparable.

In this issue of *Chem*, Paesani and co-workers[7] compared the simulated $|\chi^{(2)}_{eff}|^2$ spectrum at the charged interface with new experimental data and were able to decompose the SFG spectrum into the $\chi^{(2)}$ and $\chi^{(3)}$ contributions. The authors calculated the SFG response of water at the water-palmitic-acid monolayer interface by using the molecular dynamics simulation technique and computed the $\chi^{(2)}$ and $\chi^{(3)}$ contributions separately. The calculated $|\chi^{(2)}_{eff}|^2$ spectral shape was in good agreement with

their experiments. This study suggests that the bulk contribution can dominate the SFG spectrum of the O–H stretch mode of interfacial water. Indeed, the 3,570 cm^{-1} positive peak contributed from the Stern layer in the Im($\chi^{(2)}$) was completely masked by a very broad 3,200–3,600 cm^{-1} positive peak contributed by the bulk at the palmitic-acid-water interface. Furthermore, the sign of the peaks in the Im($\chi^{(2)}$) was also masked by the $\chi^{(3)}$ contribution, making the $\chi^{(2)}_{eff}$ spectrum positive and featureless. Once the $\chi^{(2)}$ signal was extracted from the $\chi^{(2)}_{eff}$ spectrum, the authors could investigate the molecular conformation of water neighboring the lipid and/or surfactant and relate these with the $\chi^{(2)}$ spectrum, again from the computational approach. By categorizing water molecules into specific surfactant motifs, Paesani and co-workers were able to separate the contribution of water near the C=O group and C–O–H group, as well as the water molecules that were not neighboring the surfactant headgroups.[7] This computational protocol can directly connect the microscopic structure in the simulation with the SFG features.

This approach could be further extended to understanding the ultrafast dynamics of water in the Stern and diffuse layers. In fact, the interfacial water dynamics near charged lipids has been measured by the time-resolved SFG technique or two-dimensional SFG technique,[9,10] whereas the observed dynamics of water cannot be clearly attributed to the contributions of water in the Stern layers. As discussed above and in previous reports,[1,6,8] the bulk contribution to the SFG signal is not negligible. This seems to suggest that comparing the dynamics near charged interfaces (which are largely contaminated by the bulk contribution) with the dynamics near the zwitterionic interface (which arises solely from the Stern layer) is not straightforward. Applying the computational approach to time-resolved

SFG simulation is a promising direction for future study.

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