Towards Heterodyne-Detected Sum-Frequency Generation from Buried Glass-Water Interface

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Solid-liquid interfaces are ubiquitous in material science and are utilized for a wide variety of applications, such as wetting, catalysis and electrochemistry. To understand and control processes at the surface of the material, it is necessary to observe the interfacial molecules in situ. However, due to their buried nature, solid-liquid interfaces are surrounded by bulk material and thus make it difficult to characterize with conventional spectroscopic methods. In contrast, Sum-Frequency Generation (SFG) can selectively probe the surface of a material without contribution from the bulk and is therefore suitable for this purpose.

Here we report for the first time the measurement of the complex second order non-linear susceptibility $\chi^{(2)}$ from the buried glass/water interface, using the recently developed heterodyne-detected vibrational SFG (HD-VSFG) spectroscopy (Figure 1a). This is of particular interest, since the imaginary part of the $\chi^{(2)}$ spectrum is directly comparable to the linear absorption spectrum of the water molecules in the bulk [1]. Additionally, the sign of the imaginary $\chi^{(2)}$ provides us with information about the absolute orientation of the interfacial molecules [2,3]. However, the measurement of the complex $\chi^{(2)}$ spectrum requires a careful consideration of the phase. Typically, for air/liquid and air/solid surfaces, this is achieved by using the non-resonant signal from a quartz crystal as a reference. The phase shift $\Psi$ between air/sample and air/quartz is straightforward, if both samples are kept at the same height. For the silica/water interface the phase shift, introduced by the glass itself, has to be considered as well. Therefore, we evaporated a 150 nm gold film at one side of the fused silica substrate and used the sum-frequency signal from the glass/gold interface to normalize the glass/water spectrum.

Figure 1: Schematic of the VSFG setup for buried interface.
$\chi^{(2)}$ spectra from the buried silica surface were recorded in a home-built fluid cell (Figure 1, inset). The gold film at the bottom of the glass was used as a reference. Water with different pH could be added and exchanged with a pipette, without touching the sample. This configuration ensured high stability of the setup.

A gold film in air shows only an electronically resonant, very broad and mostly imaginary, $\chi^{(2)}$. Under the assumption that the silica/gold $\chi^{(2)}$ follows the same shape, it was used to normalize the silica/water spectra. The amplitude of the SFG spectra $|\chi_{\text{eff}}^{(2)}|^2$, measured under homodyne and heterodyne conditions, gave the same results, even though some ambiguity about the phase correction for the buried interface remains. This point is currently under investigation.

Figure 2 a) and b) show the real and imaginary $\chi_{\text{eff}}^{(2)}$ of the glass/water interface for different pH, using glass/gold as reference. The magnitude square $|\chi_{\text{eff}}^{(2)}|^2$ is plotted in Figure 2c). By changing the pH of the solution from basic to acidic, we observed an inversion of the sign of the imaginary $\chi^{(2)}$ spectrum of the -OH stretch region, which indicates re-orientation of interfacial water at the glass interface. This flip-flop of the water molecules is explained by the de-protonation of the terminal Si-OH hydroxyl groups to Si-O$^-$ of the fused silica at high pH. Thereby the silica surface becomes negatively charged. This in turn leads to an inversion of the orientation of the water molecules which re-align with the local electric field.

Figure 2: Complex $\chi_{\text{eff}}^{(2)}$ for H$_2$O at different pH and D$_2$O: a) real, b) imaginary, c) magnitude square. Flip-flop of interfacial water is observed in the imaginary $\chi_{\text{eff}}^{(2)}$.