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

*Molecular Spectroscopy Laboratory, RIKEN, Japan* MYALITSIN, Anton;  
NIHONYANAGI, Satoshi; YAMAGUCHI, Shoichi; TAHARA, Tahei

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.

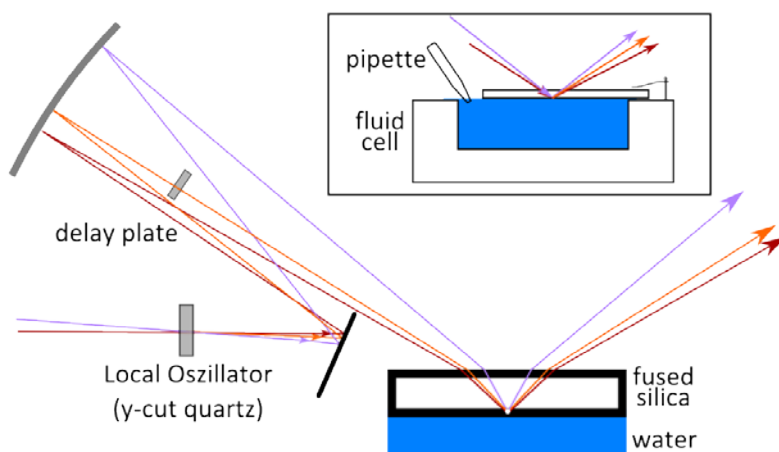
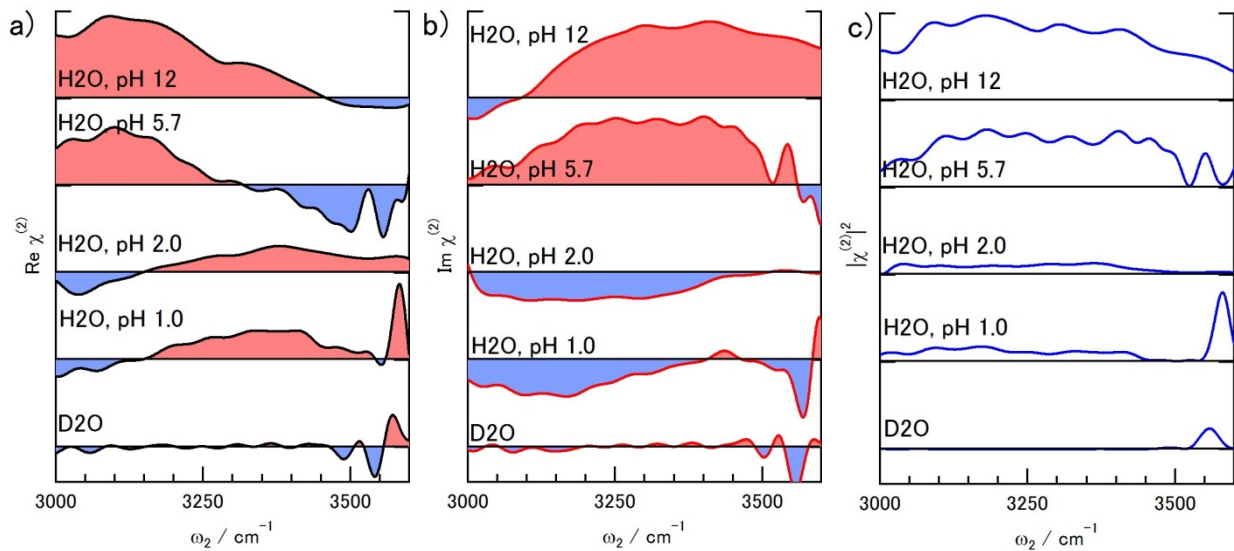


Figure 1: Schematic of the VSFG setup for buried interface.

$\chi^{(2)}$  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<sup>-</sup> 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<sub>2</sub>O at different pH and D<sub>2</sub>O: a) real, b) imaginary, c) magnitude square. Flip-flop of interfacial water is observed in the imaginary  $\chi_{\text{eff}}^{(2)}$ .**

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- [3] Yamaguchi, S.; Tahara, T., *J. Chem. Phys.* **2008**, *129*, 101102.