Water Structure at the "Buried" Silica Interface Studied with Heterodyne-Detected Vibrational Sum-Frequency Generation

Anton MYALITSIN[1], Shu-hei URASHIMA[1], Satoshi NIHONYANAGI[1,2], Shoichi YAMAGUCHI[3], Tahei TAHARA[1,2]

[1] *Molecular Spectroscopy Laboratory, RIKEN*
[2] *Ultrafast Spectroscopy Research Team, RIKEN Center for Advanced Photonics*
[3] *Department of Applied Chemistry, Faculty of Engineering, Saitama University*

Heterodyne-detected vibrational sum-frequency generation (HD-VSFG) spectroscopy is a powerful tool to study the interfacial boundary between two materials. Over the last years, we have employed HD-VSFG in a variety of experiments to investigate the molecular properties at liquid surfaces exposed to the air by measuring the complex second-order nonlinear susceptibility $\chi^{(2)}$ [1]. The imaginary part of the $\chi^{(2)}$ spectrum is directly comparable to the linear absorption spectrum in the bulk. Furthermore, the sign of the imaginary $\chi^{(2)}$ provides information about the up/down orientation of the interfacial molecules. However, application of HD-VSFG to the buried solid/liquid interface over a wide frequency range has not been achieved so far.

In a previous study, we measured the $\chi^{(2)}$ spectrum of silica/water interface in the CH stretch region using the CH resonance as a phase reference [2]. A 150 nm thick gold film, evaporated on a part of the fused silica substrate was used as an intermediate reference. The phase of the silica/gold reference was determined by comparing the resonant $\chi^{(2)}$ spectrum from the silica/ODS/air interface with the air/ODS/silica interface. However, this approach is applicable only to the CH stretch frequency region. In this study, we report a method to obtain complex $\chi^{(2)}$ spectra from the "buried" solid/liquid interface in a wide frequency region without relying on a resonant signal.

The spectra were recorded in a home-built fluid cell (Figure 1). Water can be filled and exchanged with a syringe, without opening the cell. To
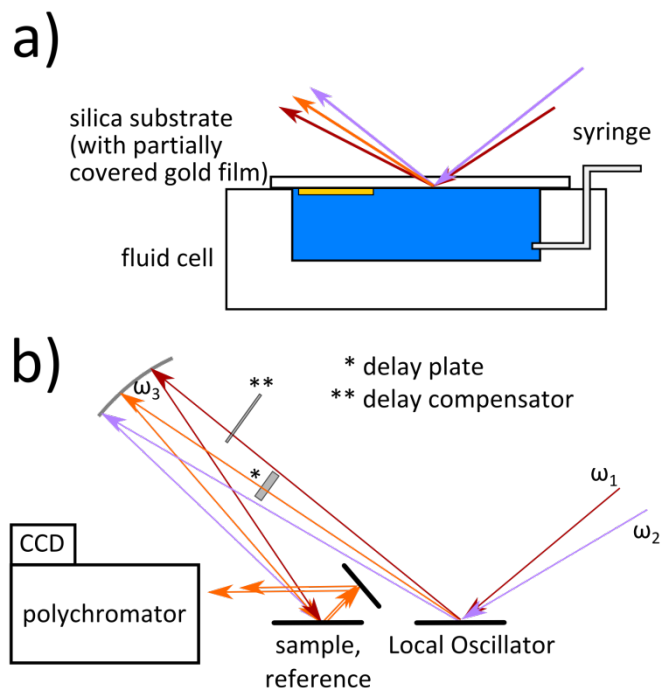

Figure 1: a) Schematic of the fluid cell. b) Schematic of the VSFG setup.

obtain the correct phase of the complex $\chi^{(2)}$, we used the nonresonant SFG signal from the "buried" silica/air interface as a reference, i.e. focusing the ω_1 and ω_2 beams at the lower surface of the silica substrate in the empty cell. To avoid the effect of OH resonance due to adsorbed water, SFG spectra of silica/air were measured in D$_2$O saturated air. Therefore the silica/air signal is completely nonresonant and real.

To confirm the validity of the use of silica/air interface as a reference, we used perfluorohexane (C$_6$F$_{14}$) as a sample. Since C$_6$F$_{14}$ shows no absorption near the OH stretch region, we can reasonably expect $\chi^{(2)}$ of the silica/C$_6$F$_{14}$ interface is nonresonant. The observed $\chi^{(2)}$ spectrum of C$_6$F$_{14}$ was real and constant, verifying the validity of the measurement.

As a model "buried" interface, we measured the silica/water interface. We observed a positive imaginary $\chi^{(2)}$, indicating an up-orientation of the water molecules (figure 2). This is consistent with a partially negatively charged silica surface.
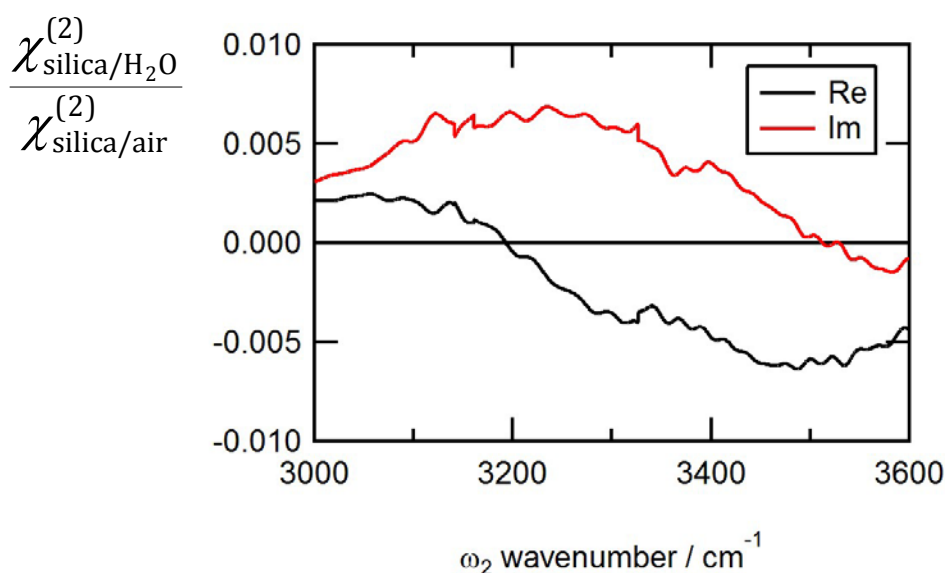
Figure 2: Complex $\chi^{(2)}_{\text{eff}}$ spectrum of the silica/water interface. This spectrum was normalized by $\chi^{(2)}_{\text{eff}}$ of the silica/air interface, because it is a positive real constant in the present wavenumber range. The sum-frequency $\omega_1 + \omega_2$, visible ω_1, and IR ω_2 lights were S-, S-, and P-polarized, respectively.

References:

[1] Nihonyanagi, S.; Mondal, J.; Yamaguchi, S.; Tahara, T., Ann. Rev. Phys. Chem., **2013**, *64,* 579.
[2] Myalitsin, A.; Nihonyanagi, S.; Yamaguchi, S.; Tahara, T., 7th JSMS Meeting, **2013**, (1P069).