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

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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
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 $\omega_1$ and $\omega_2$ 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 $\chi^{(2)}$ spectrum of the silica/water interface. This spectrum was normalized by $\chi^{(2)}_{\text{silica/air}}$ 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 $\omega_1$, and IR $\omega_2$ lights were S-, S-, and P-polarized, respectively.](image)

References: