

Supplementary Material to the article “Hidden metastable states, hysteresis and slow dynamics of silica–aqueous interface revealed with second harmonic microscopy”

S1. Second harmonic generation on the aqueous interfaces

Within the electric dipole approximation, the nonlinear optical polarization responsible for second harmonic generation (SHG) at an interface under laser excitation is given by [1]:

$$P^{(2)}(2\omega) = \chi_s^{(2)} E(\omega) E(\omega),$$

Where $\chi_s^{(2)}$ is the second-order surface susceptibility, and $E(\omega)$ is the optical electric field. The presence of surface charge and ions in solution induces an additional electric field $E_{DC}(z)$, which gives an extra contribution to the nonlinear polarization: $P_{NL}(2\omega) = P^{(2)}(\omega) + P^{(3)}(\omega)$, where $P^{(3)}(2\omega) = \chi^{(3)'} E(\omega) E(\omega) \int_0^{+\infty} E_{DC}(z) dz$.

Here $\chi^{(3)'}$ denotes the effective third-order nonlinear susceptibility tensor, which accounts for all processes leading to radiation at the double frequency through interaction with the $E_{DC}(z)$ field. These include, in particular, contributions from water molecules polarized by the interfacial electrostatic field. Integration over z yields:

$$P^{(3)}(2\omega) = \chi^{(3)'} E(\omega) E(\omega) \Phi_0$$

Where Φ_0 represents the surface potential. Thus, one arrives at an expression that relates the SHG intensity to different nonlinear contributions: $I(2\omega) \propto I(\omega)^2 |\chi_s^{(2)} + \chi^{(3)'} \Phi_0|^2$

In this relation $\chi_s^{(2)}$ describes the intrinsic symmetry-breaking response at the interface, while $\chi^{(3)'}$ accounts for the electroinduced contribution arising from polarized water molecules. In a more general case, when interference effects within the electrical double layer are taken into account, the dependence can be expressed as [2]:

$$I(2\omega) \propto I(\omega)^2 \left| \chi_s^{(2)} + \chi^{(3)'} \Phi_0 \frac{\kappa}{\kappa - i\Delta k_z} \right|^2,$$

Where κ is the Debye length of the double layer and Δk_z is the wave vector mismatch. These corrections are essential when SHG is measured in the reflection geometry. In our case, with SHG detected in transmission, the term $\frac{\kappa}{\kappa - i\Delta k_z}$ reduces to unity.

S2. SHG confirmation

To confirm that the observed signal corresponds to the second harmonic of the laser, the dependence of the SHG signal intensity on the excitation laser power was measured in the range from 40 to 120 mW. The resulting dependence is shown in Fig. S1 in logarithmic scale. As expected, the intensity exhibits a quadratic dependence on the laser power (intensity): $I(2\omega) \propto |E(\omega)E(\omega)|^2$. In the logarithmic representation, the data are well approximated by a straight line with a slope of 2.1 ± 0.5 , confirming the quadratic dependence.

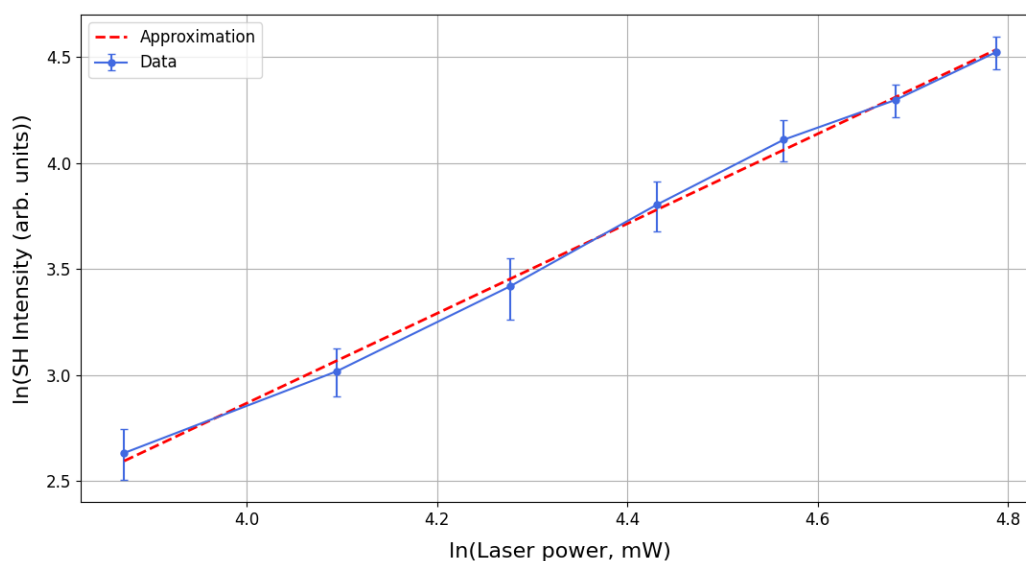


Fig. S1. Dependence of SHG signal intensity on laser power in logarithmic scale

Additionally, the SHG spectrum was measured, showing a single peak at twice the excitation laser frequency (Fig. S2). A polarization-dependent measurement was performed to investigate the variation of the SHG signal intensity at the interface as a function of the excitation laser polarization angle (Fig. S3). During the experiment, the excitation polarization was varied, while the detected signal polarization was kept fixed. As expected for interfacial SHG, the signal exhibits a maximum for polarization perpendicular to the interface (XX) and a minimum for polarization parallel to the interface (XY). This behavior arises because symmetry breaking at the interface occurs predominantly in the direction normal to the surface, whereas the parallel direction remains homogeneous. Furthermore, it is consistent with the preferential orientation of water molecular dipoles along the surface normal, providing additional evidence that the observed signal originates from second harmonic generation at the aqueous interface.

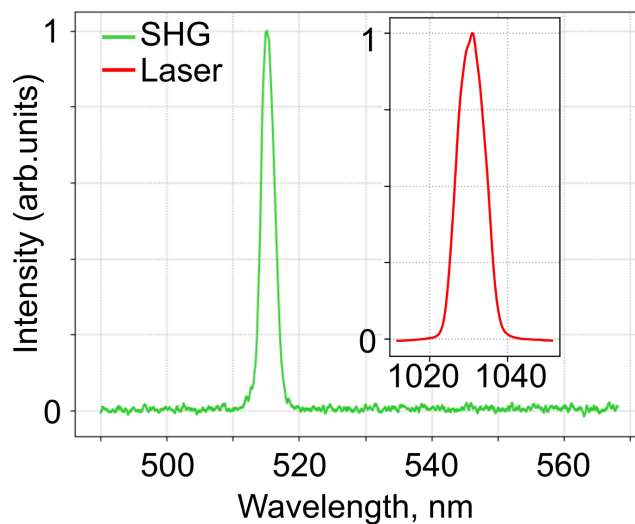


Fig. S2. Measured spectrum of the glass–water interface (inset shows the laser spectrum).

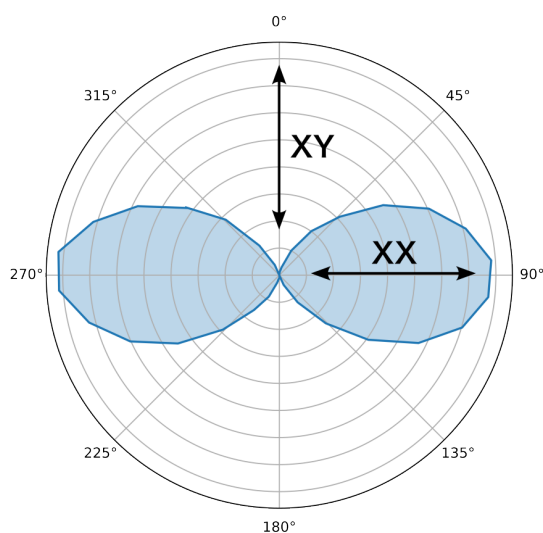


Fig. S3. Dependence of the SHG signal on the polarization angle of the excitation laser. The first letter denotes the polarization of the detected signal, and the second letter denotes the polarization of the excitation laser. During the measurement, the signal was detected in a fixed X polarization, while the excitation polarization was varied.

S3. Obtaining surface potential values from the intensity of the SHG signal

At pH values above 2, the surface of amorphous silica acquires a negative charge, which induces polarization of water molecules in the interfacial double layer through interaction with the electrostatic field. Polarized water molecules contributes to interfacial SH signal through third order nonlinear susceptibility: $I(2\omega) \propto I(\omega)^2 |\chi_s^{(2)} + \chi^{(3)'} \Phi_0|^2$, where Φ_0 is the surface potential value,

$\chi_s^{(2)}$ is the second-order surface susceptibility and $\chi^{(3)}$ is the effective third-order surface susceptibility of the water. This implies that with increasing surface charge density, the SHG intensity grows quadratically. The maximum signal is observed at pH 12, as the degree of surface deprotonation is assumed to reach its maximum under these conditions. The surface concentration of siloxide groups at this pH reaches approximately 15% [3], corresponding to a surface charge density of about 14 $\mu\text{C}/\text{cm}^2$ [4].

For calibration, a linear relationship between the square root of the SHG signal intensity and the surface potential was employed: $\sqrt{I(2\omega)} \propto I(\omega)(\chi_s^{(2)} + \chi^{(3)}\Phi_0)$

SHG intensities were experimentally measured at pH 2 and pH 12, while the corresponding surface potentials were taken from the literature. As the point of zero charge of silica occurs at pH 2, this condition was assigned a potential of 0 mV, whereas at pH 12 an average literature value of 158 mV was used. Accordingly, a linear function was established that relates the surface potential values to the corresponding square roots of the SHG signal intensity.

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3. Y. Duval, J. A. Mielczarski, O. S. Pokrovsky, E. Mielczarski, and J. J. Ehrhardt, “Evidence of the Existence of Three Types of Species at the Quartz-Aqueous Solution Interface at pH 0-10: XPS Surface Group Quantification and Surface Complexation Modeling,” *J. Phys. Chem. B*, vol. 106, no. 11, pp. 2937–2945, 2002.
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