

Supporting Information

The Surface Activity of the Hydrated Proton Is Substantially Higher than That of the Hydroxide Ion

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SFG spectroscopy:

Two different experimental set-ups for SFG spectroscopy have been used for this work. The setup that was used to collect the data shown in Fig. 1 in the main text and S1 in section ‘Check of surface-active impurities’ and S2 in section ‘Spectra in OH region’ in this SI consisted of a mode-locked Ti:sapphire laser (Mai Tai SP, Spectra-Physics) and a regenerative amplifier (Spitfire Ace, Spectra-Physics) pumped with a Nd:YLF laser (Empower 45, Spectra-Physics). The amplifier produced 800 nm pulses with 4.5 mJ power, ~ 45 fs pulse width, at a 1 kHz repetition rate. From its output, ~ 1.7 mJ was used to pump a commercial OPA (TOPAS-C, Light conversion) that mixes signal and idler in a AgGaS₂ crystal and produced tunable broadband IR pulses. The IR pulses, centered around ~ 2500 cm⁻¹, had a full width at half maximum (FWHM) of ~ 450 cm⁻¹ and ~ 5 μ J pulse energy. The remainder of the amplifier output was spectrally narrowed to ~ 15 cm⁻¹ FWHM using a Fabry-Perot etalon (SLS optics ltd.). The output energy was ~ 20 μ J. The diameters of the beams focused onto the sample were ~ 0.2 mm.

The other setup, used to collect the data shown in S3 in this SI was comparable to the one described before, but with ~ 9.5 mJ output power from the amplifier, of which ~ 3 mJ was used to pump a commercial OPA to produce IR pulses of ~ 20 μ J energy, with an FWHM spectral width of ~ 350 cm⁻¹ centered at ~ 2500 cm⁻¹.

In both of the above cases, the signal was collected by a spectrograph (Acton, Princeton Instruments) and detected with an electron multiplied charge coupled device (emCCD) camera (Newton, Andor Instruments). The acquisition time was typically 5 to 10 minutes depending on the signal strength. All spectra in the presented work were collected in SSP polarization (S: SFG, S: Vis, P: IR). The data were normalized by the non-resonant signal from z-cut quartz. The details of incident angles are presented in table S-1 in the section: ‘Spectra at different geometries’ below.

Check of surface-active impurities:

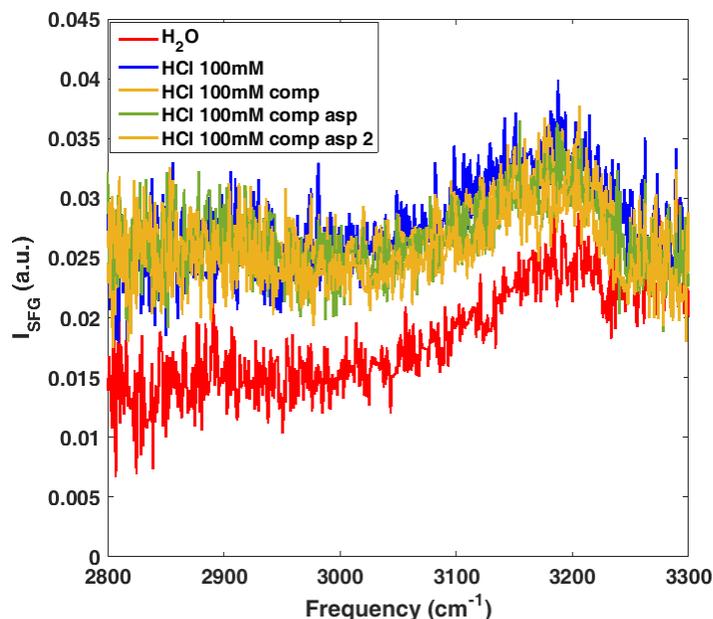


Figure S-1: Comparison of SFG intensity of pure H_2O and 0.1M HCl. The spectra are collected using a Langmuir trough. 'HCl comp' corresponds to the spectrum taken from a compressed HCl surface immediately after compression. 'HCl comp asp' corresponds to the spectrum taken after aspirating the compressed HCl surface. 'HCl comp asp2' corresponds to the spectrum taken after (de-)compression and aspiration of the surface three times subsequently.

Figure S-1 shows the comparison of the spectra obtained from the surfaces of pure H_2O and 0.1 M HCl solutions, the latter being checked for the presence of any surface active impurity in a Langmuir trough. First, the spectrum of a 0.1 M HCl sample is recorded. Then the surface is compressed to $\sim 1/4$ th of its initial surface area in order to compress the surface-active impurities, if any, inside the smaller area. An SFG spectrum is recorded immediately ('HCl 100 mM comp' in figure S-1). Some amount of sample from the surface is sucked out using an Eppendorf pipette (aspiration) in order to remove potentially present surface active impurities, and immediately another SFG spectrum is taken that is referred to as 'HCl 100 mM comp asp' in figure S-1. The surface area is further decompressed, compressed and aspirated three times subsequently and another SFG spectrum is recorded at the end that is referred to as 'HCl 100 mM comp asp 2' in figure S-1. None of the four HCl spectra shows any CH vibration response or differs from each other in either intensity or spectral shape implying that there is no surface-active impurities present and we probe a clean HCl surface.

Spectra in OH region:

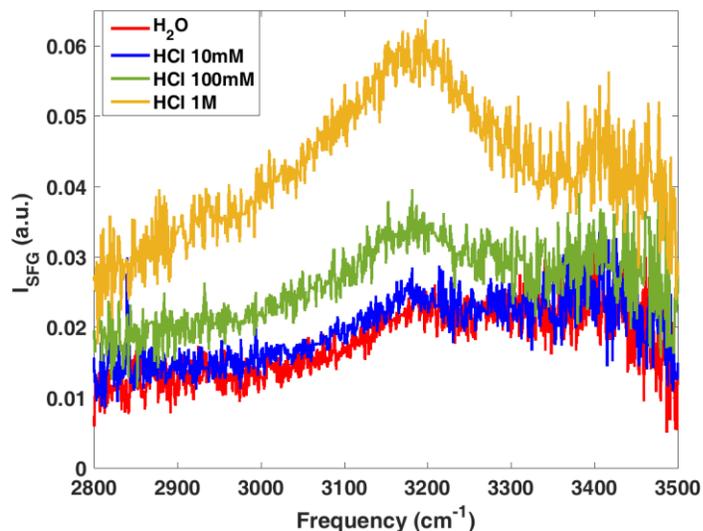


Figure S-2: The SFG intensity in SSP polarization from H₂O-air interface containing HCl at different concentrations in the subphase.

Figure S-2 shows the SFG response in SSP polarization from an air-H₂O interface for pure H₂O and H₂O containing acid in the subphase as a function of frequency in the H-bonding region of H₂O. The intensity of the H-bonding region increases in the presence of 10mM acid, indicating significant adsorption of hydrated protons at the surface.

Spectra at different geometries:

To verify if the difference between our work and the work by Tyrode *et al.*^[1] can be explained by the different experimental geometries, we have obtained spectra in SSP polarization from the D₂O-air interface in two different experimental geometries. The incoming angles of IR and VIS pulses in these two geometries are tabulated below (Table S1) along with the geometry used by Tyrode *et al.*^[1] for comparison. The spectra shown in Fig S-3 in this SI are recorded in Geometry 2. The spectra shown in Fig 1 in the main text and Fig S(1,2) in this SI are recorded in Geometry 1.

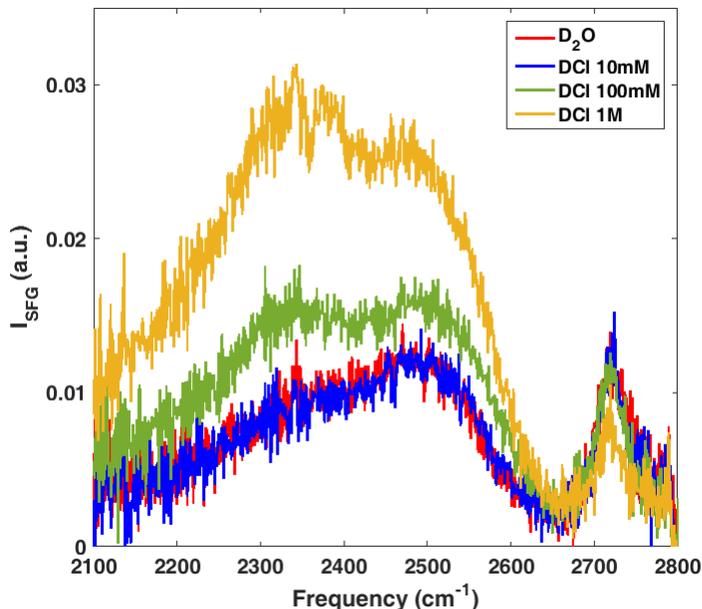


Figure S-3: SFG spectra in SSP polarization from the D₂O-air interface from pure D₂O and at different concentrations of DCI in the subphase, recorded in geometry 2 (details in Table S1).

Figure S-3 represents the SFG intensity spectra as a function of frequency for pure D₂O and at different concentrations of DCI in the subphase. The SFG intensity remains unchanged in the presence of 10 mM DCI. However, the intensity in the hydrogen-bonded region (~ 2100 - 2600 cm^{-1}) increases and that of the free OD region (~ 2710 cm^{-1}) decreases with increasing concentration of acid.

Table S-1: Incoming angles of IR and VIS pulses in different experimental geometries.

	Geometry 1	Geometry 2	Tyrode <i>et al.</i> ^[1]
IR	36	40	55
VIS	34	70	70

Non-resonant SFG response obtained from the fits with eq. 2 in the main text:

Table S-2: Non-resonant amplitudes obtained from the fits with eq. 2 in the main text.

	DCl	NaCl	NaOD
0.00M (D ₂ O)	-0.10	-0.10	-0.095
0.01M	-0.10	-0.10	-0.095
0.1M	-0.10	-0.10	-0.095
1M	-0.12	-0.10	-0.095

The small variations in the non-resonant SFG response for pure D₂O arise from different data sets.

Calculation of the SFG sensitivity for surface charge at the water-air interface:

To estimate how sensitive SFG is to a charge density at the air-water interface, we use SFG spectra for the lipid-water interface. We estimate that a lipid density of 1 charged lipid per 1000-10000 Å² will result in a noticeable change of the water spectrum, based on the observation of a clear change in water signal for the zwitterionic lipid DPPC at 300 Å² per lipid^[2]. Therefore, we set our detection limit to one charge at 1000-10000 Å², which equals 10¹⁴-10¹⁵ charges per dm². Assuming a surface concentration of water molecules of 10¹⁷ molecules per dm² (55 M x 3 Å thick surface layer), we can conclude that we have a detection limit of about 0.1-1%. Given the water concentration of 55 M, we estimate that we could see an interfacial concentration as low as 0.05-0.5 mol – i.e., we have a detection threshold of 50 mM at best.

References:

- [1] S. Sengupta, D. R. Moberg, F. Paesani, E. Tyrode, *The Journal of Physical Chemistry Letters* **2018**, 9, 6744-6749.
- [2] E. H. G. Backus, D. Bonn, S. Cantin, S. Roke, M. Bonn, *Journal of Physical Chemistry B* **2012**, 116, 2703-2712.