

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

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Abstract: The behavior of hydroxide and hydrated protons, the auto-ionization products of water, at surfaces is important for a wide range of applications and disciplines. However, it is unknown at which bulk concentration these ions start to become surface active at the water–air interface. Here, we report changes in the D₂O–air interface in the presence of excess D⁺_{hyd}/OD⁻_{hyd} determined using surface-sensitive vibrational sum-frequency generation (SFG) spectroscopy. The onset of the perturbation of the D₂O surface occurs at a bulk concentration as low as 2.7 ± 0.2 mM D⁺_{hyd}. In contrast, a concentration of several hundred mM OD⁻_{hyd} is required to change the D₂O surface. The hydrated proton is thus orders of magnitude more surface-active than hydroxide at the water–air interface.

The auto-ionization of water (H₂O ⇌ H⁺_{hyd} + OH⁻_{hyd}) produces hydrated protons and hydroxide ions. Their relative concentrations depend on the pH of the medium. The likelihood of surface adsorption of either of those two ions is yet to be accurately determined.^[1] As reviewed recently,^[1] both from experimental and theoretical points of view contradictory results have been obtained regarding the surface affinity of both ions. Part of this inconsistency may originate from comparing results from different methods that have unequal probing depths at the aqueous surface.

However, also different results are reported by using the nonlinear, surface-specific optical spectroscopies, second-harmonic generation (SHG) and sum-frequency generation (SFG). These methods have been used to extract molecular level information from these interfaces. Symmetry breaking at the water surface results in an SHG/SFG response from interfacial water molecules. The presence of ions adsorbed at the surface affects the interfacial arrangement of water molecules and subsequently enhances or reduces the SFG

intensity. SHG studies of the strongly acidic and basic solution conclude surface adsorption of the hydrated proton and surface depletion of hydroxide, respectively.^[2] However, a previous phase-resolved SFG study of highly concentrated (> 1 M) hydrated proton and hydroxide solutions showed that for high concentrations, both ions are surface-active.^[3] Moreover, conventional SFG intensity studies on concentrated acid^[4] and base^[4b] solutions (≥ 0.55 M) also established surface adsorption of hydrated protons and hydroxide. In contrast, a very recent study, combining SFG with molecular dynamics, found no adsorption of either H⁺_{hyd} or OH⁻_{hyd} at an air–water interface over a range of pH 2–11.^[5] Combined, these studies indicate that hydrated protons adsorb at the water–air interface. However, it is not apparent at which bulk concentration the surface adsorption of the hydrated proton starts to influence the nonlinear response. Less seems to be known about the surface propensity of hydroxide.

Here we use SFG spectroscopy to study the modulation in the vibrations of the interfacial D₂O molecules at the D₂O–air interface, in the presence of D⁺_{hyd}/OD⁻_{hyd} ions for different concentrations in the subphase. We note that the hydrated proton can exist in various conformations including hydronium (D₃O⁺), Eigen (D₅O₂⁺), and Zundel (D₉O₄⁺). Here, we represent all those moieties as D⁺_{hyd}. We find that both D⁺_{hyd} and OD⁻_{hyd} perturb interfacial water at the water–air interface. However, D⁺_{hyd} affects the water surface already at a few mM bulk concentration, whereas for OD⁻_{hyd} the surface remains unperturbed beyond 100 mM concentration. The surface adsorption of OD⁻_{hyd} becomes prominent at a bulk concentration that is two orders of magnitude higher than that of D⁺_{hyd}.

Figure 1 shows the SFG intensity (*I*_{SFG}), from the D₂O–air interface with different concentrations of a) DCI, b) NaCl, and c) NaOD in the subphase as a function of the infrared frequency in SSP polarization (S: SFG, S: VIS, P: IR). Each spectrum has a broad response from ≈ 2000 cm⁻¹ to ≈ 2600 cm⁻¹ due to hydrogen-bonded D₂O molecules at the D₂O–air interface^[6] and a sharp response centered at ≈ 2700 cm⁻¹ from the vibration of OD groups “dangling” in the air.^[7] With increasing acid concentration (Figure 1 a), *I*_{SFG} in the hydrogen-bonded region increases, and that of the dangling OD groups decreases, implying interfacial adsorption of hydrated protons: free OD groups are displaced by the hydrated protons at the interface, and the presence of charges at the surface aligns water molecules, thereby increasing the signal in the hydrogen-bonded region. The surface is affected already at 0.01 M acid concentration, suggesting hydrated protons have adsorbed to the D₂O–air interface already at 10 mM.

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<https://doi.org/10.1002/anie.201908420>.

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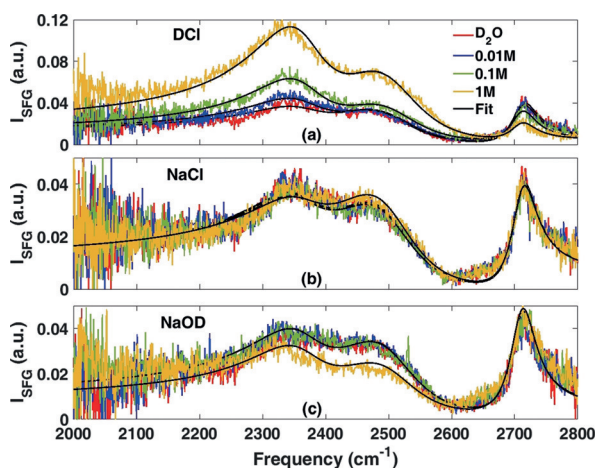


Figure 1. SFG spectra in SSP polarization from the D₂O–air interface at different bulk concentrations of a) DCl, b) NaCl, and c) NaOD. The red spectrum is a pure D₂O spectrum. The black lines on each experimental spectrum are the fits with a Lorentzian lineshape model (details in the text).

To exclude effects due to counterions, we have monitored I_{SFG} from an interface containing NaCl in the subphase. I_{SFG} is independent of bulk NaCl concentration, as shown in Figure 1b, providing evidence that neither Na⁺ nor Cl⁻ adsorb at the interface at 0.01M ionic strength. At 1M ionic strength, according to literature,^[8] Cl⁻ can adsorb, but Na⁺ does not. Therefore, the spectral changes occurring already in the presence of 10 mM DCl can be attributed entirely to D⁺_{hyd} adsorbed at the surface. Control experiments to rule out impurities as the cause for the increase in the I_{SFG} with increasing acid concentration are detailed in the Supporting Information. Measurements on H⁺_{hyd} in H₂O give similar results as for D₂O, and experiments using comparable angles of incidence for infrared and visible pulses as those used by Tyrode et al.,^[5] reproduce the results of Tyrode et al. These results showed no effect of protons on interfacial response up to 10 mM, implying that the threshold for observing protons at the interface depends on the experimental geometry (details in the Supporting Information).

Upon addition of base into the subphase, I_{SFG} in the hydrogen-bonded region remains unchanged up to and including 0.1M bulk concentration (Figure 1(c)). Only upon the addition of 1M base, the I_{SFG} in the hydrogen-bonded region decreases, while in the dangling OD region the spectrum remains unchanged: OD⁻_{hyd} seems to adsorb at the D₂O–air interface significantly only around 1M ionic strength. Surfactant studies have shown that the presence of positive and negative charges at the surface affects the magnitude of the SFG response in the H-bonded region very similarly.^[9] Hence, for a given surface concentration, both D⁺_{hyd} and OD⁻_{hyd} are expected to perturb the D₂O–air interface response equally strongly. However, OD⁻_{hyd} adsorption requires a bulk concentration that is two orders of magnitude higher than that of D⁺_{hyd}.

D⁺_{hyd} and OD⁻_{hyd} have opposite effects on I_{SFG} in the H-bonded region: with increasing D⁺_{hyd} (OD⁻_{hyd}) concentration, I_{SFG} increases (decreases). This difference can be explained, in line with ref. [10] as follows: at a nominally neutral D₂O

surface, on average the hydrogen-bonded D₂O molecules orient with their deuterium atoms pointing towards the bulk.^[10] Due to adsorption of D⁺_{hyd} at the surface, the preferential alignment of the D₂O molecules with deuterium towards bulk increases, giving rise to a higher I_{SFG} . In contrast, the adsorption of OD⁻_{hyd} at the surface causes a decrease in the orientation of D₂O molecules with their deuterium atoms pointing towards bulk, resulting in a lower I_{SFG} compared to that of neutral D₂O interface. The presence of charges at the interface can also give rise to a $\chi^{(3)}$ signal that is equally consistent with the observed signal variations.^[11]

To determine the onset of D⁺_{hyd}/OD⁻_{hyd} adsorption at the interface, we quantify the amplitudes of the different resonances in the SFG spectra using an established fitting procedure.^[4b] According to this fitting procedure, the I_{SFG} is proportional to the square of the second-order susceptibility $\chi^{(2)}$ of the sample and intensity of the incoming IR and visible (Vis) light [Eq. (1)].

$$I_{\text{SFG}} = |\chi^{(2)}|^2 I_{\text{IR}} I_{\text{Vis}} \quad (1)$$

$\chi^{(2)}$ is a sum of a nonresonant term, $\chi_{\text{nr}}^{(2)}$ (comprising of a nonresonant amplitude A_{nr} and a nonresonant phase ϕ_{nr}) and resonant ($\chi_{\text{r}}^{(2)}$) contribution(s). Each $\chi_{\text{r}}^{(2)}$ is expressed as a Lorentzian line shape with area A_{n} , central frequency ω_{n} , and bandwidth Γ_{n} (half-width at half maximum) [Eq. (2)].

$$|\chi^{(2)}|^2 = |\chi_{\text{nr}}^{(2)} + \chi_{\text{r}}^{(2)}|^2 = \left| A_{\text{nr}} e^{i\phi_{\text{nr}}} + \sum_{\text{n}} \frac{A_{\text{n}}}{\omega_{\text{n}} - \omega_{\text{IR}} + i\Gamma_{\text{n}}} \right|^2 \quad (2)$$

First, the spectrum for pure D₂O is fitted with three resonant peaks and a frequency-independent nonresonant response. The peak positions (2367, 2498, and 2710 cm⁻¹) and FWHM bandwidths (140, 170, and 50 cm⁻¹ respectively) of the bands, as well as the phase (0.0 rad) from this fit, are subsequently used in the fits of the spectra containing different electrolytes. The resonant areas are the only free parameters for a specific dataset. The obtained values of the nonresonant amplitude are enlisted in Table S-2 in the Supporting Information. The fits are shown as black lines in Figure 1. Please note that the $\chi^{(2)}$ is an effective $\chi^{(2)}$ also including possible contributions from the electrostatic potential driven $\chi^{(3)}$.^[12]

Figure 2 depicts the areas (A_{n}) of the different vibrations as a function of DCl, NaCl, and NaOD concentration, obtained from the fits to the data in Figure 1. Panel (a) shows that the 2710 cm⁻¹ resonant contribution practically does not change in the presence of up to 1M NaCl and NaOD, yet decreases by $\approx 15\%$ in the presence of 1M D⁺_{hyd}. Assuming that the free OD orientation does not change in line with ref. [4a] the 15% area reduction implies a $\approx 15\%$ decrease in the number of “dangling” ODs due to the displacement of free OD groups by D⁺_{hyd} ions. Panel (b) shows that the signal at 2498 cm⁻¹ increases by $\approx 45\%$ for 1M D⁺_{hyd}, marginally increases for 1M NaCl, and decreases weakly for 1M OD⁻_{hyd}. The 2367 cm⁻¹ resonant contribution (panel (c)) does not change significantly for 1M NaCl and NaOD and increases by $\approx 250\%$ for 1M D⁺_{hyd}. These changes in the signal intensity of the low-frequency features report on

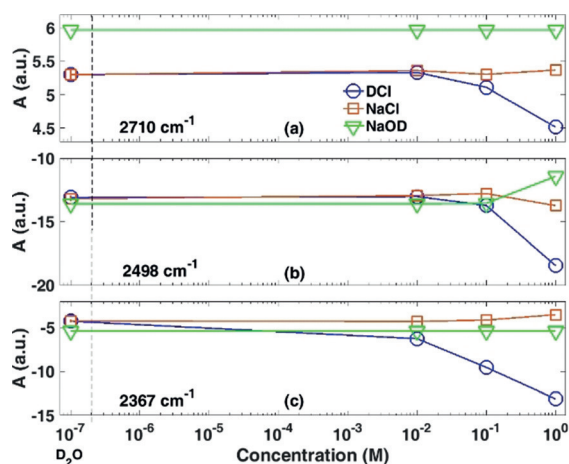


Figure 2. Areas (A_n) of different OD vibrations as a function of ionic strength of the solution. A positive sign of the OD stretching vibration indicates that the D atoms of D_2O molecules are pointing towards air. A negative sign means the opposite. The connecting lines are to guide the eyes. The differences of the A_n values for D_2O (most prominent in panel (a)) arise from variations between data sets.

a change of the response of the water molecules due to a change in the interfacial charge distribution. Similar to the structure of H^+_{hyd} , at least in part present as H_3O^+ at the interface^[13,8b] of H_2O , the “tripod” structure of D_3O^+ orients at the water–air interface pointing its D-atoms towards the bulk, donating three strong hydrogen bonds. The increase in the hydrogen-bonded OD signal can, therefore, originate from hydronium-OD groups, the enhanced downward orientation of the interfacial D_2O molecules, or a bulk $\chi^{(3)}$ contribution.^[12]

To quantify the onset of surface activity for the two ions, we use the resonance most sensitive to that particular ion: that at 2367 cm^{-1} for the hydrated proton and 2498 cm^{-1} for the hydrated hydroxide. The areas of these two resonances are plotted in Figure 3. As the amplitude of the 2498 cm^{-1} mode for hydroxide changes between 0.1 (no apparent reorganization of the water molecules at the surface) and 1M, we determine the threshold of surface activity at $\approx 0.5 \pm 0.4\text{ M}$. As the amplitude enhancement of the 2367 cm^{-1} resonance for hydrated proton shows a linear behavior on a log scale from 10^{-2} M onwards, we linearly extrapolate the concentration-dependent signals to the signal intensity observed for pure water (Figure 3) and find the onset of surface adsorption at $\approx 2.7 \pm 0.2\text{ mM}$ for hydronium. Given the estimated detection efficiency of surface charge of around 0.1–1% (see the Supporting Information), we conclude that we could detect surface concentrations as low as 0.05–0.5M of $D^+_{\text{hyd}}/OD^-_{\text{hyd}}$ ions. From the observed onset of surface adsorption of the hydrated proton at $\approx 2.7\text{ mM}$, we conclude that the partition coefficient of the hydrated proton is larger than 1, that is, the protons are attracted to the water–air surface. For hydroxide, the partition coefficient seems to be in the range of 1.

Although it has often been argued that the surface of neat water in contact with air has an excess negative charge, that is, the hydroxide formed through the autoionization of water adsorbs more than hydronium,^[14] this seems to be unlikely

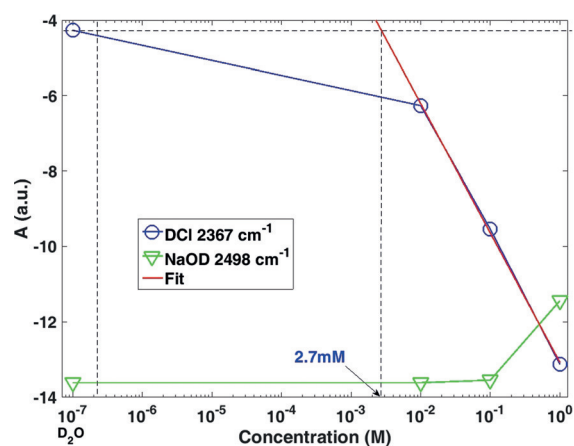


Figure 3. Fitted areas of the 2367 cm^{-1} peak in the presence of DCl and 2498 cm^{-1} peak in the presence of NaOD. The blue dotted horizontal line represents the A_n value for the 2367 cm^{-1} resonance band of pure D_2O . The vertical dotted blue line represents the onset concentration of the surface propensity of hydronium.

based on our SFG results. The SFG spectra in Figure 1 show that the OD^-_{hyd} concentration at the surface at thermodynamic equilibrium is apparently very small in the range $pD(H) = 7\text{--}13$; that is, only above $pD(H) = 13$ the SFG spectrum changes.

In summary, we have determined the onset concentrations of surface adsorption at the water–air surface of hydrated protons and hydroxide ions. Protons adsorb at the D_2O –air interface at a bulk concentration around $2.7 \pm 0.2\text{ mM}$. For OD^- , the interfacial water structure remains unaffected until a significantly higher bulk concentration of $0.5 \pm 0.4\text{ M}$ is reached. Given our estimated detection limit for charges present at a surface, we conclude that the partition coefficient for D^+_{hyd} is higher than 1, meaning that D^+_{hyd} is expelled from the bulk. For OD^-_{hyd} we estimate a partition coefficient around 1. The surface adsorption ability likely anti-correlates with the hydrogen-bond-formation ability of the two species,^[15] especially within the first solvation shell.^[16] As D_3O^+ is a very weak hydrogen-bond acceptor,^[8b] it prefers to stay close to the surface^[15,17] where the number of neighboring species to make a hydrogen bond with, specifically at the immediate water–air interface, is naturally scarce.^[18] However, the most recent multistate empirical valence bond model-based calculation comparing the instantaneous air–water interfacial structure and the Gibbs dividing surface shows that also the second solvation shell structure can influence surface affinity.^[17] The free energy minimum very close to the interface ($\approx 1\text{ \AA}$) is similar for hydrated proton and hydroxide. However, the hydroxide has a higher maximum in free energy than the hydrated proton at 2–3 \AA away from the instantaneous surface, increasing the barrier for hydroxide to come to the interface.

Experimental Section

Sample preparation: The electrolyte solutions were made by dissolving HCl (37%) and/or NaCl in D_2O and H_2O . H^+ instantly reacts with D_2O to produce D^+ . Since 37% HCl has a concentration of 12M (in

H₂O), 1M and 0.1M HCl solutions in D₂O will have 10% and 1% H₂O in it, respectively.

SFG spectroscopy: Details on SFG spectroscopy are included in the Supporting Information.

Acknowledgements

This work is funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation; BA 5008/3).

Conflict of interest

The authors declare no conflict of interest.

Keywords: hydronium ions · hydroxide ions · water interface · sum-frequency generation

How to cite: *Angew. Chem. Int. Ed.* **2019**, *58*, 15636–15639
Angew. Chem. **2019**, *131*, 15783–15786

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Manuscript received: July 7, 2019

Accepted manuscript online: August 16, 2019

Version of record online: September 24, 2019