

Partially Hydrated Electrons at the Air Water Interface Observed by UV-Excited Time-Resolved Heterodyne-Detected Vibrational Sum Frequency Generation Spectroscopy

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ABSTRACT: Hydrated electrons are the most fundamental anion species, consisting only of electrons and surrounding water molecules. Although hydrated electrons have been extensively studied in the bulk aqueous solutions, even their existence is still controversial at the water surface. Here, we report the observation and characterization of hydrated electrons at the air/water interface using new time-resolved interface-selective nonlinear vibrational spectroscopy. With the generation of electrons at the air/water interface by ultraviolet photoirradiation, we observed the appearance of a strong transient band in the OH stretch region by heterodyne-detected vibrational sum-frequency generation. Through the comparison with the time-resolved spectra at the air/indole solution



interface, the transient band was assigned to the vibration of water molecules that solvate electrons at the interface. The analysis of the frequency and decay of the observed transient band indicated that the electrons are only partially hydrated at the water surface, and that they escape into the bulk within 100 ps.

Experimental set up

UV-Excited Time-Resolved HD-VSFG Spectroscopy



□Neat water surface without pump power



3000

3200

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3400 3600

3800

 Positive peak 3700 assigned to free OH
Negative peak 3450 assigned to hydrogenbonded OH group
The positive peak below 3200 cm⁻¹ is not seen as previous report because of artifact due to inaccurate phase calibration.



FIG. 1. Real (black) and imaginary (red) parts of $\chi^{(2)}_{eff,SSP}$ spectra of the air/H₂O interface normalized by (a) z-cut quartz and (b) D₂O. In (a), the real (blue) and imaginary (green) parts of $\chi^{(2)}_{eff,SSP}$ spectrum of the air/D₂O interface normalized by z-cut quartz are also shown. The blue arrow indicates the low frequency positive band discussed in the text.

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The present study shows that the normalization procedure using quartz generates a positive feature in the Im $\chi^{(2)}$ spectra around 3000 cm⁻¹. The shape and magnitude of this feature vary day to day but in most cases, the features observed for the H_2O and D_2O surfaces are very similar to each other. We found that this positive feature very often decreases with cleaning the quartz surface by wiping with acetone or being soaked in hot sulfuric acid (Figure $S2^{33}$). This strongly indicates that the positive feature that appears in the $\chi^{(2)}$ spectrum normalized by quartz (Figure 1(a)) is attributable, at least partly, to the issues related to the quartz surface such as contamination and/or adsorbed water on the quartz surface. This can explain the day-to-day variation in the shape and amplitude of the



$$H_2O \xrightarrow{2h\nu, H_2O} OH^{\bullet} + H_3O^{+} + e^{-}$$
 (1)

Figure 3 shows the UV-pumped time-resolved interfaceselective spectra, Im $\Delta \chi^{(2)} = \text{Im}[\chi^{(2)}(t) - \chi^{(2)}_{0}]$, in the OH stretch region at the air/water interface. $(\chi^{(2)}(t) \text{ and } \chi^{(2)}_{0})$ are the second-order nonlinear susceptibilities in the presence of UV light at delay *t* and in the absence of UV light, respectively.)

■ Measure separately between 3050-3400 and 3400-3800 and join the same scale

The positive peak at 3260 appeared when delayed the pump power from 0.2 ps to 100 ps, after that it disappeared.



□ The peak at 3260 could not contribute of the hydronium cation (H₃O⁺)

□ 3260 peak is the OH from hydrated electron



Figure 4. Analysis of the transient spectra at the air/water interfact (a) Spectrum averaged over all the delay time, (b) temporal change, and (c) assignment of the observed transient species. Pump power / mW

□ The intensity of the 3260 cm⁻¹ band at the delay of 0.2 ps was evaluated and fitted with by fitting the complex $\chi(2)$ spectrum with a complex Lorentzian function.

Air/indole surface without pump power



Positive and broadening peak at 3600 assigned to weak interaction between OH group and indole

A sharp negative band at 3065 assigned to an

aromatic CH stretch mode of indole



□ Surface pressure of indole



$$=\frac{c_M}{RT}\frac{\partial\Pi}{\partial c_M}$$

~5 indole molecules exist within every 1 nm^2





indole $\xrightarrow{h\nu}$ S₁ indole \rightarrow (indole cation)⁺ + e⁻

Positive peak at 3430 cm⁻¹ and negative peak at 3230 cm⁻¹
Positive peak 3430 disappeared after 100 ps (short-lifetime transient) and negative peak 3230 cm⁻¹ does not change after 300 ps (long-time transient).

□ Short-life time positive peak assignment

Air/indole (3430 cm⁻¹)



□ Air/water (3260 cm⁻¹)



Air/indole (3430 cm⁻¹)

One photon ionization of indole

indole $\xrightarrow{h\nu}$ S₁ indole \rightarrow (indole cation)⁺ + e⁻

Not only water molecules but also indole molecules that aligned by electron which could shift to higher frequency



Air/water (3260 cm⁻¹)

□ Two-photon ionization of water

$$H_2O \xrightarrow{2h\nu, H_2O} OH^{\bullet} + H_3O^{+} + e^{-}$$

□ Only water molecules aligned by electron



□long-life time negative peak assignment



Negative peak at 3230 cm⁻¹ is assigned to OH band from indole cation as similar negative peak as CTAB interface



□Hydrated electron at gas phase, surface, and bulk water





