Ultrafast vibrational dynamics of water at the hydrophobic ion/water interface revealed by time-resolved heterodyne-detected vibrational sum frequency generation (TR-HD-VSFG)

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Introduction
Water at hydrophobic interfaces plays an important role in various chemical and biological processes such as protein folding, membrane formation, enzyme–substrate binding, etc [1]. Aromatic hydrocarbons are the building blocks of many hydrophobic surfaces and interact with water through delocalized π-electrons. The interaction of π-electrons of aromatic hydrocarbons with water hydrogen is known as π-hydrogen bonding [2]. Since these π-hydrogen bonds are believed to play crucial roles in biological processes, molecular level insight into the hydrogen bond dynamics of such π-hydrogen bonded water is important for understanding those phenomena. Here we report the hydrogen bond dynamics of the interfacial π-hydrogen bonded water at the tetra phenyl borate (TPB) ion/water interface by time-resolved heterodyne-detected vibrational sum frequency generation (TR-HD-VSFG) spectroscopy.

Experimental
The optical setup for TR-HD-VSFG measurements was described in detail previously [3]. Briefly, a narrow-band visible $\omega_1$ pulse (center wavelength: 795 nm, bandwidth: 24 cm$^{-1}$, pulse width: 0.5 ps, s-polarized) and a broadband infrared $\omega_2$ pulse (center frequency: 3450 cm$^{-1}$, bandwidth: 300 cm$^{-1}$, pulse width: 0.1 ps, p-polarized) were first focused into a y-cut quartz crystal and then onto the sample surface to generate sum frequency ($\omega_1 + \omega_2$, s-polarized). The former SFG generated from the quartz was used as a local oscillator (LO) and passed through a glass plate (2 mm) to be delayed with respect to the latter SFG generated from the sample interface. The time-resolved measurements were carried out with pump pulse (bandwidth: 100 cm$^{-1}$, pulse width: 0.2 ps, p-polarized, 20 µJ) centered at 3600 cm$^{-1}$ for the selective excitation of high frequency region of the OH stretch mode of interfacial water.

Results and Discussion
Figure 1A shows the $\text{Im}\chi^{(2)}$ spectrum of the TPB ion/water interface in the OH stretch frequency region. The sign of the $\text{Im}\chi^{(2)}$ of the OH stretch band of the TPB/ HOD-D$_2$O interface is positive, indicating that the water has the hydrogen (H-) up orientation at the anionic TPB interface. Moreover, $\text{Im}\chi^{(2)}$ spectrum of the OH stretch band is wider than other negatively charged interfaces and shows significant intensity around 3600 cm$^{-1}$, which is possibly due to existence of weak π-hydrogen bonds between phenyl rings of TPB and interfacial water. In order to further explore the nature of OH vibrations of water appearing at 3600 cm$^{-1}$, we carried out TR-HD-VSFG measurements for the OH stretch region at TPB/ HOD-D$_2$O interface with 3600 cm$^{-1}$ excitation to selectively probe the dynamics of water hidden in this region.
Figure 1. (a) Steady-state $\text{Im} \chi^{(2)}$ spectra of the TPB/ HOD-D$_2$O interfaces in the OH stretch region. (b) Schematic of the TPB/water interface. (c) TR-HD-VSFG spectra with 3600 cm$^{-1}$ excitation. Steady-state (SS) and pump spectra are also shown at the top.

Figure 1C shows time-resolved $\Delta \text{Im} \chi^{(2)}$ spectra at different time delays. The $\Delta \text{Im} \chi^{(2)}$ spectrum at 0 fs shows a narrow negative bleach (spectral hole) centered around 3550 cm$^{-1}$ accompanied by positive hot band centered around 3325 cm$^{-1}$. One important observation from the data in Figure 1C is that the band width of the spectral hole remains almost constant up to 700 fs. At the later time scales ($\geq$300 fs), the intensity of negative bleach at 3550 cm$^{-1}$ decreases and lower frequency region becomes negative due to bleach recovery and subsequent thermalization process: the pump energy absorbed by the water is converted to the thermal energy, which increases local temperature and weakens the H-bond and causes blue shift of the OH stretch band. The constant band width of the spectral hole up to longer delay times suggest very slow/ negligible spectral diffusion (loss of $\omega_{\text{pump}}$ excitation memory) of high frequency OH stretch vibrations. This observation implies that water hidden in the high frequency OH stretch region (presumably $\pi$-hydrogen bonded water) is energetically isolated from the remaining H-up oriented H-bonded water molecules and interconversion between these two configurations is very slow or negligible. These results are quite different from other lipid-water interfaces.

References