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Ultrafast Vibrational Dynamics of Water at a Charged Interface Revealed by Two Dimensional Heterodyne-Detected Vibrational Sum-Frequency Generation (2D HD-VSFG) Spectroscopy

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[Introduction]

The water dynamics in the bulk has been intensively studied by various time-resolved (TR-) spectroscopies, and the ultrafast dynamics relating to the spectral diffusion, inhomogeneity, energy transfer etc. have been observed. Especially, two-dimensional infrared (2D-IR) spectroscopy is a powerful tool and it has been playing a key role.[1] On the other hand, the dynamics of water at interfaces is much less understood because an interface-selective spectroscopy is needed to probe only interfacial water in the presence of bulk water behind. The 2nd-order nonlinear spectroscopy, in particular vibrational sum-frequency generation (VSFG), has intrinsic interface specificity and has been widely utilized to study steady-state properties of water at various interfaces. Recently, TR-VSFG measurements (i.e., pump-probe and 2D-VSFG) have been realized at aqueous interfaces.[2] Since heterodyne detection (HD-) enables us to directly measure $\chi^{(2)}$ spectra, it is very crucial to realize heterodyne detection in TR-VSFG measurements to elucidate true vibrational dynamics of interfacial water.[3] Here, we report the extension of our TR-HD-VSFG method to two-dimensional spectroscopy, which enabled us to observe 2D-HD-VSFG spectra at an aqueous interface for the first time.

[Experiamental Setup]

Figure 1 shows the TR-HD-VSFG setup which is the combination of IR pump and HD-VSFG probe. A narrow band visible (ω_1) and broadband IR (ω_2) beams are used for the HD-VSFG probe. In the TR-HD-VSFG setup, a pump IR pulse (ω_{pump}) was obtained by splitting ca. 80% of the energy from the IR output of the different frequency generator.

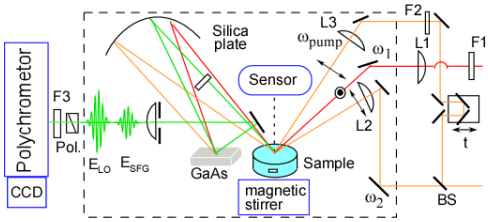

Figure 1: The optical Scheme of the 2D HD-VSFG setup.

The ω_{pump} pulse was passed through a band pass filter to narrow the bandwidth down to ~100 cm^{-1}. In order to make 2D HD-VSFG, the ω_{pump} dependence of $\Delta Im\chi^{(2)}$ was measured for the five different pump whose center wavenumber was at 3300, 3340, 3400, 3475, and 3500 cm^{-1}. The SF, ω_1, ω_2, ω_{pump} beams were s-, s-, p-, and p-polarized, respectively.

[Results and Discussion]

Figure 2 shows the 2D HD-VSFG spectra in the OH stretch region of HOD in D_2O at an interface positively charged by cetyltrimethylammonium bromide (CTAB) measured at the delay times of 0, 100, and 300 fs after IR photoexcitation. In the 2D HD-VSFG spectra, the horizontal and vertical axes represent pump and probe wavenumbers, respectively. The red lobe of the spectra represents positive $\Delta \mathrm{Im}\chi^{(2)}$ associated with ground-state bleaching of the 0–1 transition, and the blue represents negative $\Delta \mathrm{Im}\chi^{(2)}$ associated with the 1–2 transition. The 2D HD-VSFG spectra clearly represent the overall feature of ultrafast vibrational dynamics in the OH stretch region at the charged water interface. In fact, the spectrum at 0 fs is diagonally elongated, which indicates the memory of the pump wavenumber and the initial inhomogeneous frequency distribution on the 0–1 and 1–2 transitions. At 100 fs, the elongation becomes less prominent, because the initial frequency distribution is getting randomized by spectral diffusion. At 300 fs, the elongation almost disappears, and the slope of the node separating the 0–1 and 1–2 transitions becomes nearly parallel with the horizontal axis. This demonstrates that the memory of the pump wavenumber is nearly lost and the spectral diffusion is almost completed at 300 fs. Inhomogeneity and spectral diffusion of water at the charged interface is clearly exhibited by the 2D HD-VSFG technique, which shows the novelty of this technique.

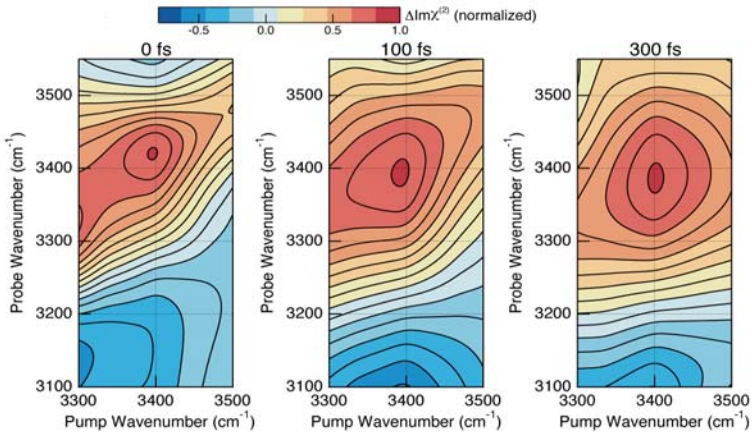

Figure 2. 2D HD-VSFG spectra of the OH stretch of HOD in D_2O at the CTAB interface for 0, 100, and 300 fs delay times after photoexcitation. The concentration of CTAB is 0.5 mM and water isotope ratio is H_2O: HOD: D_2O = 1:8:16. In the 2D HD-VSFG spectra red color represent bleaching of the 0–1 transition, whereas negative peaks blue color indicate the hot band due to the 1–2 transition. The color scales are shown at the top of the figures.

[References]

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