

**Vibrational relaxation time of OH stretch at the air/H<sub>2</sub>O interface: Reliable determination through the hot-band by time-resolved vibrational sum-frequency generation spectroscopy**

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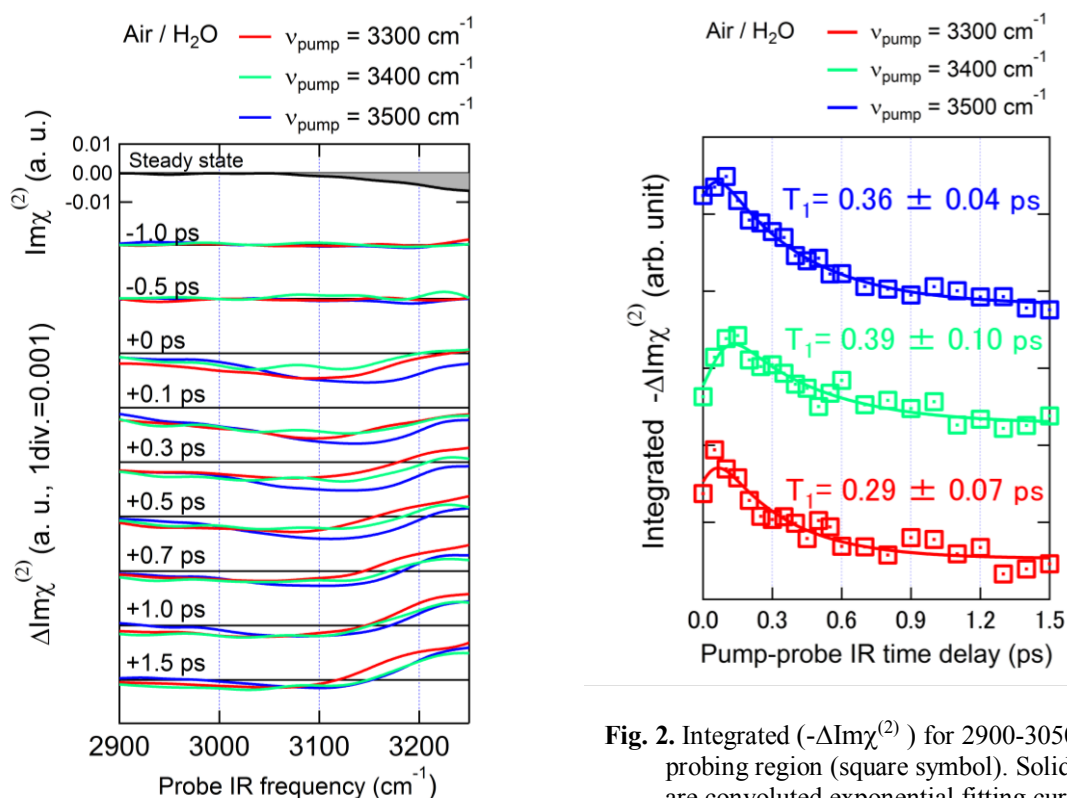
**[Abstract]** By using time-resolved heterodyne-detected vibrational sum-frequency generation (TR-HD-VSFG) spectroscopy, we examined the dynamics of the hot-band of the OH stretch mode at the air/H<sub>2</sub>O interface, and evaluated its vibrational relaxation ( $T_1$ ) time of interfacial water molecules. Compared to the bleach band, the hot band region is free from the thermalization signal and hence its analysis can provide more reliable  $T_1$  time. The interfacial  $T_1$  times obtained with three different pump IR frequencies at 3300, 3400, and 3500 cm<sup>-1</sup> were in the range of 0.3-0.4 ps, which are similar to those in bulk H<sub>2</sub>O. We concluded that there are no drastic pump frequency dependence in  $T_1$  time of hydrogen-bonded OH at the air/H<sub>2</sub>O interface although it was reported recently (van der Post et al. Nat. Commun. 6, 8384 (2015).)

**[Introduction]** Water is one of the most common and important substances we can encounter on the earth, and it mediates many of biological and atmospheric phenomena. Heterodyne-detected sum-frequency generation (HD-VSFG) spectroscopy has successfully revealed microscopic structure of interfacial water distinct from bulk by directly providing spectra of second-order susceptibility,  $\chi^{(2)}$  [1]. Dynamics of interfacial water molecules such as vibrational relaxation and spectral diffusion are also important in the fundamental aspect, and they can be different from bulk water dynamics because the truncated geometry of interface may significantly affect vibrational energy relaxation process. Previously, the Bonn group and we reported remarkably different vibrational relaxation time ( $T_1$ ) of hydrogen-bonded OH at the air/H<sub>2</sub>O interface based on the analysis of the recovery of the bleaching of the OH stretch mode: The Bonn group reported substantially large  $T_1$  time (~0.7 ps) for the high-frequency side (weakly hydrogen-bonded water) excitation [2] while we reported  $T_1$  time to be ~0.4 ps with no drastic excitation frequency dependence [3]. In order to solve this discrepancy, we evaluated the  $T_1$  time of the OH stretch vibration of interfacial water by measuring the decay of the vibrationally excited state (i.e., hot band) of the OH stretch vibration in this study. This measurement is complementary to that in the bleach band region but the analysis can be more straightforward because the hot band appears in the lower frequency region where the ground-state OH stretch band does not give any signal so that it can be separated from the signal due to thermalization (hot ground state).

**[Methods]** Our setup of TR-HD-VSFG has been described elsewhere [3]. Briefly, two probe beams:  $\omega_1$ ~795 nm NIR (~24 cm<sup>-1</sup> in bandwidth) and  $\omega_2$ ~3  $\mu$ m IR (~300 cm<sup>-1</sup> in bandwidth), are focused on 10  $\mu$ m thickness y-cut quartz generating the local oscillator. Then,  $\omega_1$ ,  $\omega_2$  and local oscillator are refocused on the sample surface. In addition, the pump IR beam ( $\omega_{\text{pump}}$ ) having bandwidth of ~150 cm<sup>-1</sup> is focused and spatially overlapped with the  $\omega_1$  and  $\omega_2$  probe beams on the surface. The time delay between IR pump and probe beams is scanned by a motorized mechanical stage. The generated SF signal is filtered by 750-nm shortpass filter and sent to a nitrogen-cooled CCD (10:2KB-dll) through polychromator (SP-2300i) for

obtaining time-resolved spectra. Polarization of incident and SF lights are S-, S-, P-, and P-polarization for SF,  $\omega_1$ ,  $\omega_2$ , and  $\omega_{\text{pump}}$ , respectively.

**[Results and Discussion]** Figure 1 shows  $\Delta\text{Im}\chi^{(2)}$  spectra of the air/H<sub>2</sub>O interface in the frequency region corresponding to the hot band of the OH stretch mode. At 0.0 ps, the band center of the hot band (negative sign) observed by 3500-cm<sup>-1</sup> excitation is more blue-shifted compared to the bands obtained with other two pump frequencies, due to the inhomogeneity of hydrogen bonding of interfacial water. After 0.5 ps, the spectral features in the  $\Delta\text{Im}\chi^{(2)}$  spectra measured with three different  $\omega_{\text{pump}}$  frequencies almost converge to each other in the frequency region of <3050 cm<sup>-1</sup> due to effective spectral diffusion [4], although the spectra are different in the region of >3050 cm<sup>-1</sup> because of different magnitude of the thermalization signal. To avoid this thermalization contribution, we integrated the  $-\Delta\text{Im}\chi^{(2)}$  from 2900 to 3050 cm<sup>-1</sup> in the  $\omega_2$  frequency region to evaluate the  $T_1$  time (Figure 2). For the three  $\omega_{\text{pump}}$  frequencies, the  $T_1$  times deduced from the fitting analysis lies between 0.3 and 0.4 ps, showing no significant  $\omega_{\text{pump}}$  dependence within the error. This result is fully consistent with our previous analysis in the bleaching region. Therefore, we concluded that the  $T_1$  time of hydrogen-bonded OH stretch mode at the air/water interface is 0.3-0.4 ps with no drastic  $\omega_{\text{pump}}$  dependence.



**Fig. 1.** TR-HD-VSFG spectra of air/H<sub>2</sub>O interface in the region of OH stretch hot-band including the tail thermalization region.

**Fig. 2.** Integrated ( $-\Delta\text{Im}\chi^{(2)}$ ) for 2900-3050 cm<sup>-1</sup> probing region (square symbol). Solid lines are convoluted exponential fitting curves. Offset is applied for clear visibility of curves.

## [References]

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