Complete picture of vibrational relaxation of OH stretch at the air/H2O interface: From hydrogen-bonded OH to free OH

(^{1}*Molecular Spectroscopy Laboratory, RIKEN*, ^{2}*Ultrafaqst Spectroscopy Research Team, RIKEN Center for Advanced Photonics*)

○Woongmo Sung,[1] Ken-ichi Inoue,[1] Satoshi Nihonyanagi,[1,2] Tahei Tahara[1,2]

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It has been a long-lasting question how the vibrational dynamics of water at the interface differs from that of bulk water. Until now, even a very fundamental quantity such as the vibrational relaxation (T_1) time of the OH stretch at the air/water interface has been controversial.[1,2] In the present study, we used time-resolved heterodyne-detected vibrational sum-frequency generation (TR-HD-VSFG) to determine the T_1 time of the OH stretch of water at the air/water interface. For obtaining reliable T_1 values, we monitored the temporal evolution of the hot band ($1\rightarrow2$ transition) in the hydrogen-bonded (HB) OH stretch. By tuning the pump frequency, we selectively excited the OH stretch vibration at different frequencies, in a wide range covering both the HB OH and non-hydrogen-bonded OH (free-OH). When the HB OH was excited with the pump of 3200-3500 cm^{-1}, the T_1 time in the range of 200-400 fs was obtained directly through the decay of the hot band of HB OH. Upon excitation of the free-OH (3700 cm^{-1}), in contrast, we observed a delayed rise and a decay of the hot band of the HB OH, reflecting the conversion from the excited free OH to the excited HB OH ($T_{1,free}\sim840\pm80$ fs)[3] and the subsequent vibrational relaxation of the converted HB OH ($T_{1,HB}\sim340\pm60$ fs). The present TR-HD-VSFG study successfully provides reliable and consistent T_1 time of the OH stretch at the air/H2O interface, as well as a coherent view of the vibrational relaxation dynamics of the interfacial OH stretch.
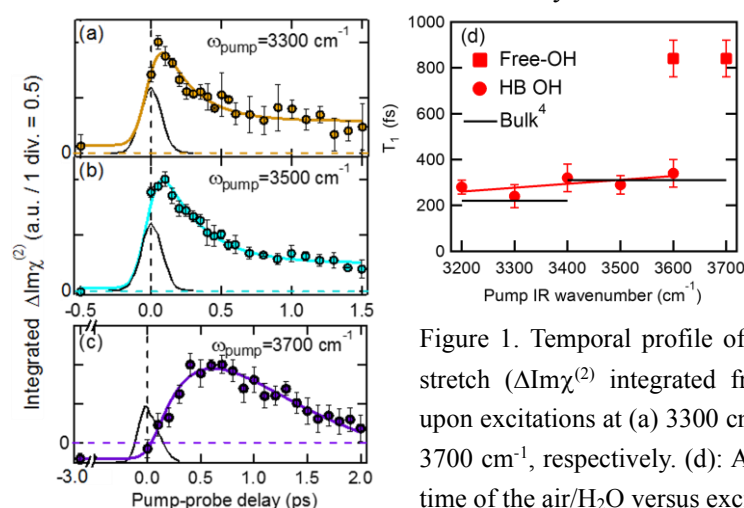

Figure 1. Temporal profile of the hot band of HB OH stretch ($\Delta Im\chi^{(2)}$ integrated from 2900 to 3050 cm^{-1}) upon excitations at (a) 3300 cm^{-1}, (b) 3500 cm^{-1}, and (b) 3700 cm^{-1}, respectively. (d): A graph of summary on T_1 time of the air/H2O versus excitation frequencies.

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