

Supporting Information

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SI Text

Rate Equation Model for Vibrational Relaxation of Free OH and H-Bonded OH. The rate equation model for vibrational relaxation of interfacial water molecules follows the definition presented before (1). The free OH groups are denoted as F , the hydrogen-bonded counterparts are denoted as HB , and the subsequent relaxation process from the hydrogen-bonded state into a state at somewhat elevated temperature is denoted as T . The vibrational modes transfer from free OH to H-bonded OH occurs at rate k_{VR}^f , whereas k_{VR}^b is the vibrational modes transfer rate for the inverse process (from H-bonded OH to free OH). f denotes the forward process and b denotes the backward process. We assume that vibrational relaxation with rate k_{HB} occurs from the HB state, rather than from the F state, into the T state. The occupation of each of the states is denoted as $N_X^{0,1}$, where $X = F, HB, \text{ or } T$, and the superscript denotes ground (0) or excited (1) state.

When the free OH groups are excited, the excitation pulse, characterized by the time-dependent intensity $I(t)$, gives rise to population of N_F^1 , and the time-dependent occupation numbers of states N_X follows the rate equations

$$\begin{aligned}\frac{\partial N_F^1}{\partial t} &= \sigma_{01} I(t) [N_F^0 - N_F^1] - k_{VR}^f N_F^1 + k_{VR}^b N_{HB}^1 \\ \frac{\partial N_{HB}^1}{\partial t} &= k_{VR}^f N_F^1 - k_{VR}^b N_{HB}^1 - k_{HB} N_{HB}^1 \\ \frac{\partial N_T^0}{\partial t} &= k_{HB} N_{HB}^1.\end{aligned}$$

1. Zhang Z, Piatkowski L, Bakker HJ, Bonn M (2011) Ultrafast vibrational energy transfer at the water/air interface revealed by two-dimensional surface vibrational spectroscopy. *Nat Chem* 3(11):888–893.
2. Nagata Y, et al. (2013) Water bending mode at the water–vapor interface probed by sum-frequency generation spectroscopy: A combined molecular dynamics simulation and experimental study. *J Phys Chem Lett* 4(11):1872–1877.

When the H-bonded OH groups are excited, the equation leads to

$$\begin{aligned}\frac{\partial N_F^1}{\partial t} &= -k_{VR}^f N_F^1 + k_{VR}^b N_{HB}^1 \\ \frac{\partial N_{HB}^1}{\partial t} &= \sigma'_{01} I(t) [N_{HB}^0 - N_{HB}^1] + k_{VR}^f N_F^1 - k_{VR}^b N_{HB}^1 - k_{HB} N_{HB}^1 \\ \frac{\partial N_T^0}{\partial t} &= k_{HB} N_{HB}^1,\end{aligned}$$

where σ_{01} and σ'_{01} represent the absorption cross-section for the 0–1 transition of free OH and H-bonded OH stretching mode, respectively.

Density Ratio Between Free OH and H-Bonded OH. To determine the ratio of the rate for the reorientational motion of free OH to rotate down to the bulk and become hydrogen bonded (k_{REOR}^f) and the H-bonded OH to break the hydrogen bond and become free OH (k_{REOR}^b), the relative populations of the free OH and H-bonded OH groups must be estimated. Fig. S1 shows the axial distributions of water molecules at the water–vapor interface from the molecular dynamics simulation (2). The 0-, 1-, and 2-DH water denote the water with two free O–H groups; one free O–H group and one H-bonded donating H (DH) atom; and two DH atoms, respectively. The hydrogen bond definition is based on the electric structure (3). The gray rectangle represents the area we defined as interfacial water, starting from 10% to 90% of the bulk density. By integrating the amount of OH groups in this area, we get the ratio of 1.7 between the H-bonded OH and free OH groups.

3. Kumar R, Schmidt JR, Skinner JL (2007) Hydrogen bonding definitions and dynamics in liquid water. *J Chem Phys* 126(20):204107.

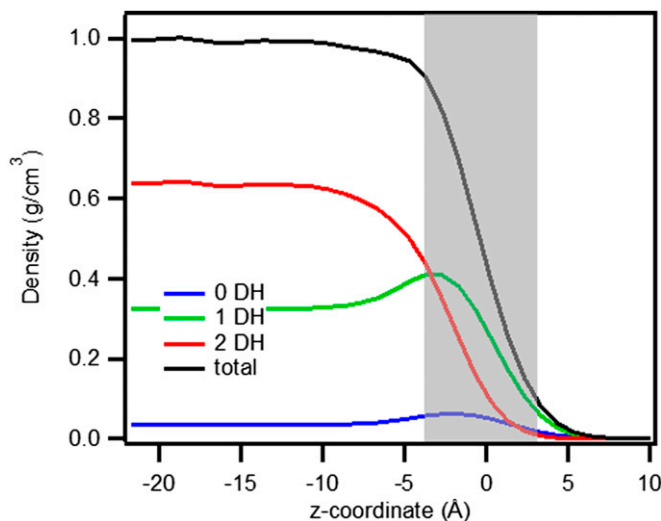


Fig. S1. Axial distribution for the density of water with different numbers of donor hydrogen atoms. The blue, green, red, and black traces denotes the axial distributions of water molecules with two free O–H groups; one free O–H group and one DH atom; two DH atoms; and the total water molecules, respectively.