# **Electronic supplementary information:**

The Surface Roughness, But Not the Water Molecular Orientation Varies with Temperature at the Water-Air

# Interface

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## **1. SIMULATION DETAILS**

#### **1.1. MD simulation protocols**

We performed MD simulations of the water-air interface with an *ab initio* based force field model.<sup>1</sup> We set the simulation cell size as 26.6 Å  $\times$  26.6 Å  $\times$  160 Å with periodic boundary conditions with the cell containing 500 water molecules. The electrostatic forces were calculated with the Ewald method. The time step for integrating the equations of motion was set to 0.4 fs. For the comparison with different temperatures, we generated 32 independent samples for the five subgroups with each target temperature by rescaling the atom velocities in the MD simulation. Following the 100 ps MD runs for equilibrating the system in the NVE ensemble, we performed 550 ps MD runs, where we recorded the MD trajectories every 4 fs. The resulting average temperatures of the five subgroups were 282.0 K, 293.5 K, 304.9 K, 318.1 K, and 330.8 K, respectively. Obtained temperature distributions for the 32 samples are plotted in Fig. S1.



**Figure S1.** System temperature distribution of the independent samples. The five subgroups are colored differently.

### 1.2. Calculation of SFG spectra

The methodology to obtain the SFG susceptibility from the simulation has been reported in ref<sup>2</sup>. Here, we describe the simulation details briefly. The resonant part of the second-order susceptibility at the *xxz* direction (*x*: SFG, *x*: visible, *z*: IR) can be calculated with the truncating response function formalism as<sup>2,3</sup>

$$\chi_{xxz}^{\text{res},(2)}(\omega;r_t) = iQ(\omega) \int_0^\tau dt R_{xxz}^{(2)}(t;r_t) f(t) e^{-i\omega t} , \qquad (S1)$$

where the *z*-axis denotes the surface normal and the *xy* plane denotes the interface.

$$Q(\omega) = \beta \hbar \omega / (1 - \exp(-\beta \hbar \omega))$$
(S2)

is the quantum correction factor,  $^{4}\beta = 1/kT$  is the inverse temperature of the system. f(t) is the Hann window function,

$$f(t) = \begin{cases} \cos^2(\pi t/2\tau) & \text{for } 0 < t < \tau \\ 0 & \text{for } t > \tau \end{cases}$$
(S3)

where  $\tau$  is the limit of the time for Fourier transformation. We used  $\tau = 1$  ps. The time correlation function  $R_{xxz}^{(2)}(t; r_t)$  is given by

$$R_{xxz}^{(2)}(t;r_{t}) = \left\langle \sum_{i} g_{sc}^{3}(z_{i}(0))\mu_{zi}(0)\alpha_{xxi}(t) + \sum_{i} \sum_{j\neq i} g_{sc}(z_{i}(0))g_{sc}^{2}(z_{j}(0))\mu_{zi}(0)\alpha_{xxj}(t)g_{t}(r_{ij}(0);r_{t}) \right\rangle,$$
(S4)

where  $\mu_{ai}(t)$  ( $\alpha_{abi}(t)$ ) is the *a* component of the molecular dipole moment (the *ab* component of the molecular polarizability) of water molecule *i* at time *t*.  $g_t(r; r_t)$  is the function to control the cross-correlation terms with the cross-correlation cutoff of  $r_t$  and is given by

$$g_t(r;r_t) = \begin{cases} 1 & \text{for } r \le r_t \\ 0 & \text{for } r > r_t \end{cases}.$$
(S5)

To avoid the cancellation of the molecular dipole moments at the two interfaces where the net orientation of the water molecules are exactly opposite, we multiplied the dipole moment by the screening function of

$$g_{sc}(z) = \operatorname{sign}(z) \times \begin{cases} 0 & \text{if } |z| \le z_{c1} \\ \cos^2 \left( \frac{\pi(|z| - z_{c2})}{2(z_{c1} - z_{c2})} \right) & \text{if } z_{c1} < |z| \le z_{c2} \\ 1 & \text{if } z_{c2} < |z| \end{cases}$$
(S6)

where *z* denotes the *z*-coordinate of the center of mass of a water molecule.<sup>3</sup> Here, we set  $z_{c1} = 2$ Å and  $z_{c2} = 3$  Å, where the origin point was set to the center of mass of the system.

In this MD simulation we did not include the nuclear quantum effects. The nuclear quantum effects lead to the red shift of vibrational signatures.<sup>1,5</sup> Because the simulated IR peak frequency of the bulk water above 2800 cm<sup>-1</sup> and below 2800 cm<sup>-1</sup> is blue shifted by ~4 % for  $\omega$  > 2800 cm<sup>-1</sup> region and by ~2 % for  $\omega$  < 2800 cm<sup>-1</sup> region, respectively, compared with the IR experimental spectra,<sup>1</sup> we multiplied the frequency by 0.96 and 0.98 in order to reproduce the corresponding vibrational SFG signature.<sup>2</sup>

#### **1.3. Simulation of bulk IR and Raman spectra**

The systems were initially prepared in a 3D periodic cubic box of side length 18.639 Å with 216 water molecules at the temperature of 282 K, 293 K, 305 K, 318 K and 331 K by running 300 ns NVT MD simulations. Then we carried out 1.5 ns NVE MD simulations at each temperature. The first 300 ps trajectories were discarded to assure equilibrium conditions. Finally, the IR and Raman spectra were calculated from the 1.2 ns MD trajectories at each temperature. The average temperatures of the NVE MD simulations were 282.8 K, 294.8 K, 305.0 K, 318.1 K and 330.8 K. The other simulation details were the same as in the previous MD simulations in ref. 1.

### 1.4. Calculation of the averaged orientation of the OH groups

We used the definition of the hydrogen bond given by ref. 6. In this definition, the hydrogen bond is formed between the OH group and the other water molecule, when the intermolecular oxygen-oxygen atom distance is less than 3.5 Å and the O-H...O angle is less than 30°. For these hydrogen-bonded OH groups, we calculated the angle  $\theta$  which is formed by the surface normal and the OH vector. Sequentially, we calculated the total orientations of the hydrogen-bonded OH groups of the interfacial water molecules per unit area of nm<sup>2</sup> ( $\sum \cos \theta$ ). Note that this quantity is zero in the isotropic bulk and the non-zero contributions arise from the interfacial regions. We calculated the orientation of the water molecules in the region  $|z| > z_{c1} = 2$  Å, where *z* denoted the *z*-coordinate of the center of mass of the water molecule. The origin point was set to the averaged center of mass of the 500 water molecules. The numerical data is displayed in Table S1.

**Table S1.** Simulated total orientations of hydrogen-bonded OH groups of the interfacial water molecules per unit area  $\langle \sum \cos \theta \rangle$ .

Average temperature (K)	Average orientation (/nm <sup>2</sup> )
282.0	-1.923
293.5	-1.918
304.9	-1.910
318.1	-1.887
330.8	-1.865

## 2. SIMULATION RESULTS

#### 2.1. Simulated density profiles of water at the water-air interface

We explored the Gibbs dividing surfaces at the water-air interfaces and the widths of the interfacial regions with different temperatures. The axial distributions of the density profiles of water ( $\rho(z)$ ) were fit to the hyperbolic tangent function<sup>7</sup>

$$\rho(z) = a \left( 1 - \tanh\left(-\frac{z - z_G}{\delta}\right) \right), \tag{S7}$$

where *a* and  $\delta$  correspond to half the average bulk density and the thickness of the interfacial region, respectively, and  $z_{\rm G}$  denotes the position of the Gibbs dividing surface with respect to the center of mass of the system. The calculated 2a,  $\delta$ ,  $z_{\rm G}$  are listed in Table S2 together with the experimental data. The thickness of 1.75 Å is in good agreement with the previous polarizable force field model calculations<sup>8,9</sup> and first-principles MD simulation.<sup>10</sup> Our MD simulations

indicate that the thickness of the interfacial water ( $\delta$ ) by 17% increases by increasing the temperature from 282 K to 331 K.

**Table S2.** Simulated bulk density (2*a*), position of the Gibbs dividing surface ( $z_G$ ) and thickness of the interfacial region ( $\delta$ ) with different temperatures.

Average temperature [K]	Simulated bulk density (2 <i>a</i> ) [g/cm <sup>3</sup> ]	<i>z</i> <sub>G</sub> [Å]	$\delta$ [Å]
282.0	$0.998 \pm 0.002$	$10.59\pm0.01$	$1.62\pm0.02$
293.5	$0.992 \pm 0.002$	$10.66 \pm 0.01$	$1.64 \pm 0.02$
304.9	$0.988 \pm 0.002$	$10.71\pm0.01$	$1.75\pm0.02$
318.1	$0.979 \pm 0.002$	$10.80\pm0.02$	$1.82\pm0.03$
330.8	$0.971 \pm 0.002$	$10.89 \pm 0.01$	$1.90\pm0.03$

## 2.2 SFG spectra with different cross-correlation cutoffs

The truncating response function formalism provides an efficient route to calculate the vibrational responses by neglecting the cross-correlation terms geometrically, which is particularly useful for SFG calculation because the number of molecules contributing to the signal is limited compared with the bulk. For the bending mode, we have clarified that the cross-correlation terms does not affect the lineshape of the SFG spectra.<sup>2</sup>

We examined the dependence of the SFG signals on the cutoff distances for the OH stretching mode with different temperatures, which has been displayed in Fig. S2. As expected,

the amplitude of the free OH (~3700 cm<sup>-1</sup>) is not affected by the cross-correlation terms, indicating that the intermolecular coupling between the free OH groups is very limited. In contrast to the free OH peaks, we could see that the water molecules within the 5 Å cutoff sphere contributes to the significant enhancement of the SFG band at ~3300 cm<sup>-1</sup>, indicating that the intermolecular couplings contribute to this SFG band. This is consistent with the IR spectra in liquid water.<sup>11</sup> Also Fig. S2 indicates that the correlation length of 5 Å is insensitive to the system temperature.

Here, we note that the Im[ $\chi^{(2)}$ ] spectra simulated here do not reproduce the positive 3100 cm<sup>-1</sup> band reported in experiments.<sup>12,13</sup> Recent MD simulations reported by the Morita and Skinner groups reproduced this feature independently by refining the dipole moment calculation<sup>14</sup> or the water force field model.<sup>15</sup> Although the modeling of 3100 cm<sup>-1</sup> SFG feature is still challenging,<sup>1</sup> we could obtain good agreement between simulated and experimental SFG spectra variation in the region of 3200 cm<sup>-1</sup> <  $\omega$  < 3750 cm<sup>-1</sup>, indicating that the force field model used here is adequate to study the molecular mechanism of the SFG signal variation at the water-air interface.



Figure S2. SFG spectra of OH stretching frequency with various cross-correlation cutoffs.

## 2.3 Melting point of the force field model

We simulated the phase transition from ice to liquid water with the slab model. The cell size was set to 31.626 Å × 31.302 Å × 60 Å, in which 1344 water molecules were contained. The initial ice configuration was generated by using the  $7 \times 4 \times 6$  unit cells of the ice Ih structure (the unit cell size was 4.518 Å × 7.8255 Å × 7.3780 Å). The basal plane formed the ice-air interface. Here, the initial slab structure generated had the vacuum space with thickness more than 15 Å.

We generated a system of the water-ice mixture in the slab model, where the water faces the vacuum region. The snapshot of the initial configuration is shown in Fig. S3. Note that the melting point of the ice was also checked in the coexistence of ice-water system by Fernandez *et*  *al.*<sup>16</sup> By using this initial structure, we ran the MD simulation at 260, 265, 270, 275, 280, and 285K in the NVT ensemble and recorded the potential energy of the whole system.

The total potential energies of the systems are plotted in Figure S4. The increase in the potential energy means that the ice has melted and has changed to the liquid water by absorbing the latent heat. Since the total potential energy apparently increases with time above 270 K and it is almost constant at 260 K after 1.5 ns, this result indicates that the melting point of this water model<sup>1</sup> is  $265 \pm 5$  K.



**Figure S3.** Snapshots of (left) initial structure, (middle) final structure at 260 K and (right) the final structure at 285 K.



**Figure S4.** Time evolutions of the total potential energies for whole systems at different temperatures.

## 2.4 Temperature Dependence of Self-diffusion Coefficient

Self-diffusion coefficients were calculated at the temperatures of 300, 333, and 363 K to check the temperature dependent properties of the bulk water. Five independent NVE simulations were performed for each temperature. We used the same conditions as the previous study except for the temperatures and volumes of the system. The experimental densities of 0.9832 and 0.965 g/cm<sup>3</sup> were used for the simulations at 333 K and 363 K, respectively, while the details of the simulation at the temperature of 300 K are given in Ref. 1. The self-diffusion coefficients were calculated from the slopes of the mean square displacements of the center of mass of a water molecule from 2 ps to 20 ps. The calculated self-diffusion constants with the finite size simulation cell with the box size of *L*,  $D_{PBC}(L)$ , were corrected via<sup>17,18</sup>

$$D_{PBC}(L) = D_{\infty} - \frac{kT\varsigma}{6\pi\eta L},$$
(S8)

where  $D_{\infty}$  denotes the self-diffusion coefficient in the limit of an large simulation cell,  $\zeta = 2.837$ , and  $\eta$  is the translational shear viscosity. The temperature dependent translational shear viscosity was obtained from Ref. 19. The simulated self-diffusion constants are summarized in Table S3, showing excellent agreement with the experimental data.<sup>20</sup>

**Table S3.** Simulated self-diffusion constant of the bulk water with different temperatures.Experimental data for the self-diffusion constants are given by Ref. 20.

temperature [K]	Simulation [Å <sup>2</sup> /ps]	Experiment [Å <sup>2</sup> /ps]
300	$2.22\pm0.02$	2.30
333	$4.73\pm0.08$	4.74
363	$7.65\pm0.06$	7.56

## 2.5 Temperature Dependence of Surface Tension

To explore the temperature dependence of the surface tension for this force field model, we prepared seven  $31.82 \text{ Å} \times 31.82 \text{ Å} \times 80.0 \text{ Å}$  cells containing 1200 water molecules. For each cell, the molecular configurations were different. After 1.8 ns NVT MD runs, we ran 0.5 ns  $\times$  3 NVT MD simulations for the temperatures of 280, 300, 325, and 350 K and recorded the configuration of the water molecules every 100 fs. From total over 1.6 ns MD trajectories (over 16000 snapshots), we calculated the perturbed configuration energies for the surface tension calculation.

For the surface tension calculation, we used the test-area method<sup>21-23</sup>. When the area of the interfaces  $S = 2 \times 31.82$  Å  $\times 31.82$  Å is increased to  $S + \Delta S$  under the condition that the system volume is constant, we can calculate the variation of the total energies of the system  $\Delta U^{\pm}(S) = U(S \pm \Delta S) - U(S)$ . The surface tension  $\gamma$  can be connected with these variations of the total energy due to the surface area change as

$$\gamma = -\frac{kT}{2\,\Delta\,S} \left( \ln\left\langle \exp\left(-\frac{\Delta\,U^+}{kT}\right) \right\rangle - \ln\left\langle \exp\left(-\frac{\Delta\,U^-}{kT}\right) \right\rangle \right). \tag{S9}$$

We scaled the simulation cell and the coordinates of the atoms in the *x* and *y* directions to satisfy  $\Delta S = 0.00005 S$  and the simulation cell was scaled in the *z* direction to keep the cell volume constant. Note that  $\Delta S$  used in this study is 10 times smaller than that used in the previous study<sup>21-23</sup>. Since we are using the flexible water model rather than the rigid water model such as SPC/E and TIP4P,  $\Delta S = 0.0005 S$  was too big to include huge nonlinear contribution, which mainly arises from the intramolecular interactions. The simulated surface tensions are listed in Table 4. The POLI2VS model reproduces the experimentally measured surface tension fairly accurately, although it systematically underestimates the surface tension. This can be understood by noting that we are using the cutoff for the Lennard-Jones potential (because of the finite size of the simulation box). This cutoff does not affect the molecular dynamics of the water, but it does affect the surface tension. Including long-range Lennard-Jones correction terms would increase the calculated surface tension by  $3 - 4 \text{ mN/m}^{22}$ , approaching the experimentally observed values. Note that  $\pm 12$ -15 mN/m difference between the experiment and simulation has been reported with the well-known SPC and TIP4P models.<sup>22</sup>

**Table S4.** Simulated surface tensions at temperatures of 300, 325, and 350 K. Note that the longrange corrections for Lennard-Jones potential are not used. The experimental values are obtained from Ref 24.

temperature [K]	Simulation [mN/m]	Experiment [mN/m]
300	60.3	71.69
325	56.2	67.63
350	50.4	63.25

## **3 EXPERIMENTALS**

## **3.1 Additional Experimental Data**

An additional set of experimentally measured  $\text{Im}[\chi^{(2)}]$  spectra of the water-air interface at three different temperatures are plotted in Figure S5. This figure shows the same trend as in Fig 1 in the main text. These spectra were recorded over a limited frequency range, and do not include the free O-H region. It is clear, however, that the trend of the data of the main text (shown in the middle panel of figure S5) is nicely reproduced.



**Figure S5**. Another set of experimental data (Exp 1) for  $\text{Im}[\chi^{(2)}]$  spectra of the water-air interface at three different temperatures. For comparison, we also plotted the experimental data (Exp 2) together with simulation data which are the same data in the main text.

## **3.2 Fresnel Factor Correction**

The measured experimental spectra,  $\chi_{eff,ssp}(\omega)$ , contain the contribution of the Fresnel factor as

$$\chi_{\text{eff},ssp}(\omega) \propto L_{YY}(\omega_{SFG})L_{YY}(\omega_{VIS})L_{ZZ}(\omega_{IR})\chi_{ssp}(\omega), \tag{S10}$$

where  $L_{\xi\xi}(\omega)$  is the frequency-dependent Fresnel factor.<sup>25</sup> To extract the pure contribution of the imaginary part of the susceptibility, we need to calculate the temperature-dependent Fresnel factor by using the equation given in Ref 25. We use the refractive index of water for the refractive index of the interface.<sup>26</sup> The temperature-dependent refractive index data are obtained from Ref. 27. The refractive index at 800 (visible) and 640 (SFG) nm are assumed to be frequency independent and constant upon varying the temperature. Therefore we divide the measured spectra  $\chi_{eff,ssp}(\omega)$  only by the Fresnel factor for the IR beam  $L_{ZZ}(\omega_{IR})$ . The in this

way obtained  $\chi_{ssp}(\omega)$  for the different temperatures are depicted in Fig. S6. Clearly, the Fresnel factors have only a small influence on the spectral shape. Moreover, the temperature dependent spectral variation is still present in the pure contribution of the imaginary part of the spectrum and can thus not traced back to variations in the Fresnel factor.



Figure S6. Fresnel factor corrected SFG spectra for Exp 1 and 2.

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