

Supporting Information for “Asymmetric Hydrogen-Bonding Structure at Water/Ice Interface”

Tatsuya Ishiyama* and Kazuya Kitanaka

*Department of Applied Chemistry, Graduate School of Science and Engineering, University
of Toyama, Toyama 930-8555, Japan*

E-mail: ishiyama@eng.u-toyama.ac.jp

S1. Development of flexible TIP4P/Ice model

A flexible version of the TIP4P/Ice water model was developed to calculate the VSFG spectra at the water/ice interface. The strategy for the development of the flexible model was same as the previous studies,^{1,2} in which the intramolecular potential parameters were empirically optimized to well reproduce the peak frequency and the width of the IR spectrum of liquid water and the VSFG spectrum of the liquid water/vapor interface.

All the water molecules were treated as HOD to remove possible intramolecular couplings. The intramolecular potential in the present flexible model includes the anharmonic term for O-H (O-D) bond potential described as

$$u_{\text{intra}}^{\text{HOD}} = \sum_{n=2}^6 [k_n(\Delta r_1)^n + k_n(\Delta r_2)^n] + \frac{1}{2}k_\theta(\Delta\theta)^2, \quad (\text{S1})$$

where Δr_1 and Δr_2 are the displacements of the O-H (O-D) bond lengths from its equilibrium distance, and $\Delta\theta$ is that of the HOD angle. In most flexible and non-polarizable water models, equilibrium HOH angle decreases while OH bond length increases.³ Thus in the present flexible TIP4P/Ice water model, the equilibrium O-H (O-D) distance is changed from the original value of TIP4P/Ice model $r_{\text{eq}} = 0.9572 \text{ \AA}$ to $r_{\text{eq}} = 0.9419 \text{ \AA}$ and $\theta_{\text{HOH,eq}} = 104.52^\circ$ to $\theta_{\text{HOH,eq}} = 107.4^\circ$, which are same as the values reported in Ref. 4, so that the average molecular geometry of the present model is almost consistent to the original rigid TIP4P/Ice model. The potential parameters were parametrized to reproduce the IR and SFG spectra of pure water, and we set to $k_2 = 0.2504$, $k_3 = -0.3$, $k_4 = 0.6$, $k_5 = -5.0$, $k_6 = 10.0$ in the atomic units. The parameter of k_θ in Eq. (S1) was also taken from Ref. 4.

S2. Estimation of the melting point of flexible TIP4P/Ice model

The melting temperature T_m of the original rigid TIP4P/Ice model was reported as 272.2 K.⁵ After that, some subsequent studies tried to estimate a correct value of T_m for the TIP4P/Ice model, as 268 ± 2 K in Ref. 6 and 269.8 ± 0.1 K in Ref. 7. The present flexible TIP4P/Ice model may change T_m for the original TIP4P/Ice model, because the molecular geometry of the flexible TIP4P/Ice model is not strictly same as that of the original one. So we estimate T_m for the present flexible TIP4P/Ice model by the direct coexistence method.^{6,7} In this method, water and ice phases contact with each other in NPT ($P = 1$ atm with the anisotropic pressure coupling in all three directions) ensemble MD simulation, and the total energy in the MD system is monitored as a function of time. If the total energy increases (decreases) at a constant temperature, then the ice in the system gradually melts (grows). The melting temperature can be estimated by finding a temperature at which the energy keeps a constant value in a long simulation time.

The simulation methodology is almost same as the one described in the main text (ice and water phases consist of 1680 water molecules, respectively), but the only difference is the contact plane between water and ice, where the secondary prismatic plane was employed for the interface between water and ice. This is because it is known that the secondary prismatic plane is the fastest growing face,⁸ and the computational efficiency to estimate T_m is relatively high.^{6,7}

Figure S1 shows a temporal evolution of the total energy for the MD system at various temperatures. At the temperature above 277 K, the total energy increases, and finally reaches a constant value, indicating that all the ice melts completely. On the other hand, below 276 K, the total energy decreases, and hence the ice phase gradually grows. T_m and

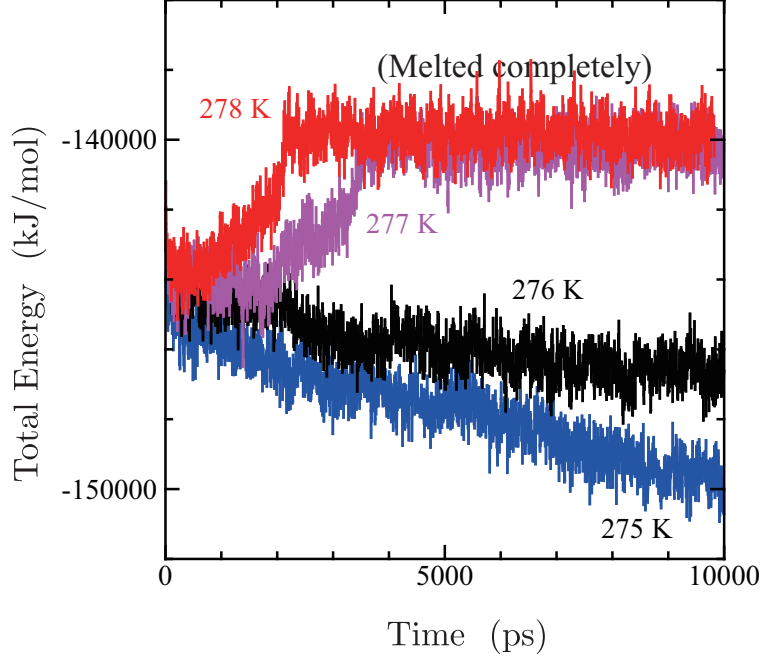


Figure S1: Total energy of the MD system at each temperature as a function of the simulation time, where water contacts with the secondary prismatic plane of ice.

its maximum error δ_{\max} are estimated to be⁷

$$T_m = \frac{T_1 + T_2}{2} \quad (\text{S2})$$

$$\delta_{\max} = \frac{(T_1 + \delta_1) - (T_2 - \delta_2)}{2} \quad (\text{S3})$$

where T_1 is the lowest temperature for which the solid phase melts, T_2 is the highest temperature for which the ice phase grows, δ is the error associated with each temperature, respectively. In the preset case, $T_1 = 276.998$ K, $T_2 = 275.997$ K, $\delta_1 = 0.004$ K and $\delta_2 = 0.001$ K. Thus the present simulation predicts that the melting temperature of the flexible TIP4P/Ice is 276.5 ± 0.5 K. Although the melting or the freezing behavior of the water/ice coexistence system somewhat depends on the initial velocity of each molecule and the system size, and hence the stochastic nature of the melting/freezing behaviors for several trajectories with different system size should be systematically examined to estimate T_m in a high precision.⁷ The results of the present simulation in the main text are however robust

even though a more precise T_m of the flexible TIP4P/Ice water model is slightly different from 276 K, because we confirmed that the total energy (or interfacial position) in the system where water contacts with the basal plane of ice at 276 K is little changed within the present simulation time (see Fig. S2).

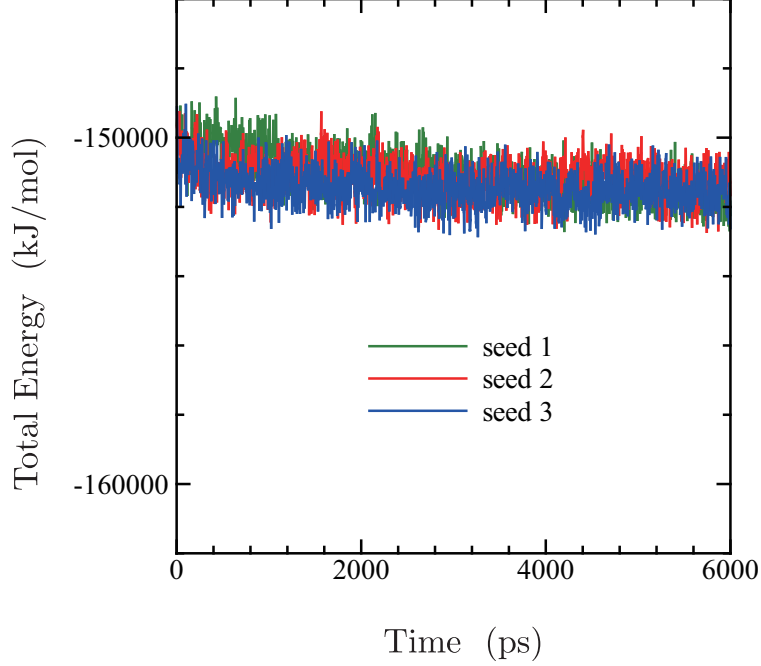


Figure S2: Total energy of the MD system at 276 K for three representative trajectories starting with different seeds as a function of the simulation time, where water contacts with the basal plane of ice.

S3. Calculation of VSFG spectrum

χ_{pqr} is calculated by the following time correlation function of the system polarizability tensor A_{pq} and the dipole vector M_r ^{9,10}

$$\chi_{pqr} = \frac{i\omega_{\text{IR}}}{k_B T} \int_0^\infty dt \exp(i\omega_{\text{IR}} t) \langle A_{pq}(t) M_r(0) \rangle, \quad (\text{S4})$$

where k_B and T are the Boltzmann constant and temperature, and $\langle \rangle$ is the statistical average. \mathbf{A} and \mathbf{M} consist of the sum of the molecular polarizability α_i and dipole moment

$\boldsymbol{\mu}_i$ of the i th molecule, $\mathbf{A} = \sum_i \boldsymbol{\alpha}_i$, $\mathbf{M} = \sum_i \boldsymbol{\mu}_i$. Thus $A_{pq}(t)M_r(0)$ in eq S4 can be decomposed into the following two parts,

$$A_{pq}(t)M_r(0) = \sum_i \boldsymbol{\alpha}_i(t)\boldsymbol{\mu}_i(0) + \sum_i \sum_{j(\neq i)} \boldsymbol{\alpha}_i(t)\boldsymbol{\mu}_j(0), \quad (\text{S5})$$

where the first and the second terms of r . h . s correspond to the self correlation and the cross correlation terms, respectively. For each snapshot in MD simulation, $\boldsymbol{\mu}_i$ and $\boldsymbol{\alpha}_i$ were calculated according to the charge response kernel (CRK) model developed in Ref. 1. In the CRK formalism, $\boldsymbol{\mu}_i$ and $\boldsymbol{\alpha}_i$ are calculated by¹

$$\boldsymbol{\mu}_i = \sum_a^{\text{site}} Q_{ai}^0 \left[\sum_j^{\text{site}} \sum_c^{\text{site}} [G^{-1}]_{ai,cj} \mathbf{r}_{cj} \right] \quad (\text{S6a})$$

$$\boldsymbol{\alpha}_i = - \sum_a^{\text{site}} \sum_b^{\text{site}} K_{abi} \left[\sum_{j'}^{\text{site}} \sum_{c'}^{\text{site}} [G^{-1}]_{ai,c'j'} \mathbf{r}_{c'j'} \right] \otimes \left[\sum_j^{\text{site}} \sum_c^{\text{site}} [G^{-1}]_{bi,cj} \mathbf{r}_{cj} \right] \quad (\text{S6b})$$

where Q_{ai}^0 is the a th site charge in an isolated molecule i , K_{abi} is the charge response kernel, \mathbf{r}_{ai} represents the (nuclear) coordinates of the site a of the i th molecule, where the flexible TIP4P/Ice trajectories were employed for \mathbf{r}_{ai} in the present case. $G_{ai,cj}$ is the local field correction defined by¹

$$[G]_{ai,cj} = \delta_{ac}\delta_{ij} - \sum_b^{\text{site}} \frac{f(\xi_{ai,bj})K_{bcj}}{r_{ai,bj}}. \quad (\text{S7})$$

In eq S7, $r_{ai,bj}$ is the distance between ai site and bj site, and f denotes a damping function to avoid the so-called “polarization catastrophe” occurred in a short internuclear distance by assuming a site charge to be a Gaussian distribution with its width ξ (see Ref. 1 for the functional form of f). In the limit of $\xi \rightarrow 0$, the charge distribution approaches to a point charge. It was found in our preliminary simulation that the value lower than $\xi = 0.4 \text{ \AA}$ cause the polarization catastrophe in the present χ calculation. Since our previous study¹ elucidated that the value of ξ to calculate χ was best as small as possible to account for charge transfer effectively, we set the above-mentioned ξ values in the χ calculation. Since most

part of χ comes from the self correlation part,¹¹ we discuss the self part and its decomposed spectra. The spectral decomposition into the bonded and the weakly interacting species was performed by the same manner with our previous study.²

S4. Temperature dependence of the VSFG spectrum at the water/air interface

Here we check the consistency of the experimentally reported and the calculated $\text{Im}[\chi_{xxz}]$ spectra at the water/air interface near the melting temperature and the room temperature. Figure S3 shows $\text{Im}[\chi_{xxz}]$ spectra reported in the experiment¹² (panel(a)) and the present MD simulation with the flexible TIP4P/Ice model (panel(b)). In panel(a), one can see that the experimental spectrum shows slight positive enhancement at the shoulder of the free OH peak near 3550 cm^{-1} and is negatively enhanced at the lower frequency side of the H-bonding region below 3400 cm^{-1} with decreasing the temperature. These tendencies are qualitatively reproduced in the present MD simulation. The former shoulder band was recently assigned to the weakly interacting (WI) OH vibration coupled with the combination band between a neighboring hydrogen-bonded OH vibration and its bonding intermolecular oxygen-oxygen vibration.¹³ The positive enhancement of the shoulder band with decreasing temperature can

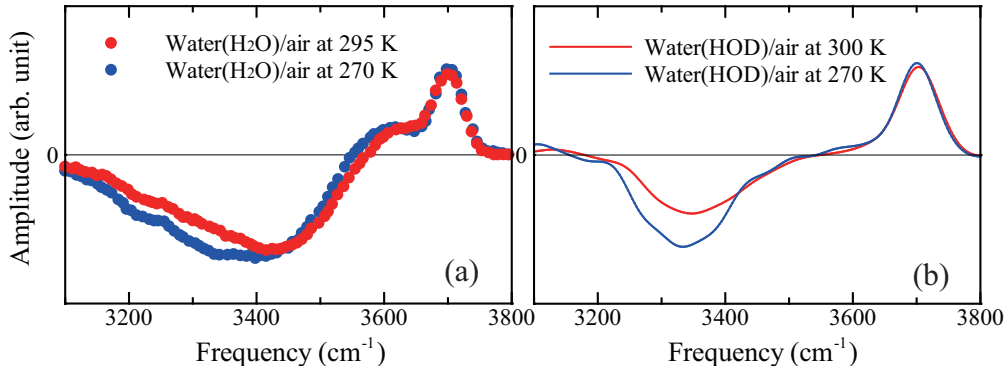


Figure S3: (a) The experimentally reported $\text{Im}[\chi_{xxz}]$ spectra at the water(H_2O)/air interface at 270 K and 295 K.¹² (b) The calculated $\text{Im}[\chi_{xxz}]$ spectra at the water(HOD)/air interface at 270 K and 300 K.

therefore be assigned to the positively directing WI OH bond with the enhanced coupling. The latter negatively enhanced band can also be understood by the enhanced H-bonding network of water directing their protons toward the liquid side.

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