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Spatial correlation of desorption events accelerates water exchange dynamics at Pt/water interfaces

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Table S1 The energy/force RMSE for Pt(100) and Pt(111)/water interface models between DFT calculation and MLP calculation.

	Pt(100)/water				Pt(111)/water	
	Γ		K		K	
	Training	Validation	Training	Validation	Training	Validation
E (meV/atom)	0.689	0.662	0.52	0.384	0.458	0.35
F _x (meV/)	54.7	49.8	49.7	45.7	57.1	51.80
F _y (meV/)	54.7	49.7	49.8	45.7	57.2	51.90
F _z (meV/)	81.8	77.9	63.3	58.5	76.1	63.80

Table S2 Definition for different types of water molecules for Pt(100) and Pt(111) interface models.

Water Type	Pt(100)/water			Pt(111)/water		
	z[Å]	cos θ	cos Ψ	z[Å]	cos θ	cos Ψ
A	1.8-2.65	0.0-0.5	0.25-1.0	1.8-2.65	0.0-0.5	0.25-1.0
B low	2.65-3.3	-1.0-0.75,0.0-0.75	-1.0-0.0	2.65-3.4	-1.0-1.0	-1.0-0.0
B high	3.3-4.5	-0.75-0.0,0.75-1.0	0.25-1.0	3.4-4.5	-1.0-1.0	0.25-1.0
C	4.5-6.8	-1.0-1.0	-1.0-1.0	4.5-6.8	-1.0-1.0	-1.0-1.0

Table S3 The time used to study the lifetime correlation function of hydrogen-bond dynamics, reorientation dynamics, residence and exchange dynamics. As in the main text, A and B denote the chemisorbed and physisorbed water. The exchange timescale of water molecule at 320 K extends beyond the present simulation. For example, we find that 4000 ps is still not enough to get converged residence time of water AB. So we will not include the related dynamics at 320K.

	HB	Reorientation	Residence		Exchange Time (ps)	
			A	AB	A	AB
317 (K)	200	200	-	-	-	-
352 (K)	60	60	600	2000	40	300
387 (K)	20	20	300	1000	20	200

Table S4 The exponential forms used to fit the correlation functions.

Single exponential form	$a \cdot e^{-t/\tau} + c$
Double exponential form	$a_1 \cdot e^{-t/\tau_1} + a_2 \cdot e^{-t/\tau_2} + c$

Table S5 The fitted lifetime of residence time correlation functions of water AB using two exponential forms,corresponding to a slow and a fast timescale.

	Pt(100)/water				Pt(111)/water			
	352K	NVE2	387K	NVE3	352K	NVE2	387K	NVE3
Slow(ps)	397(86)	397(87)	196(104)	208(69)	393(134)	394(112)	214(69)	217(83)
Fast(ps)	62(9)	66(10)	32(9)	36(7)	71(26)	71(23)	41(8)	40(11)

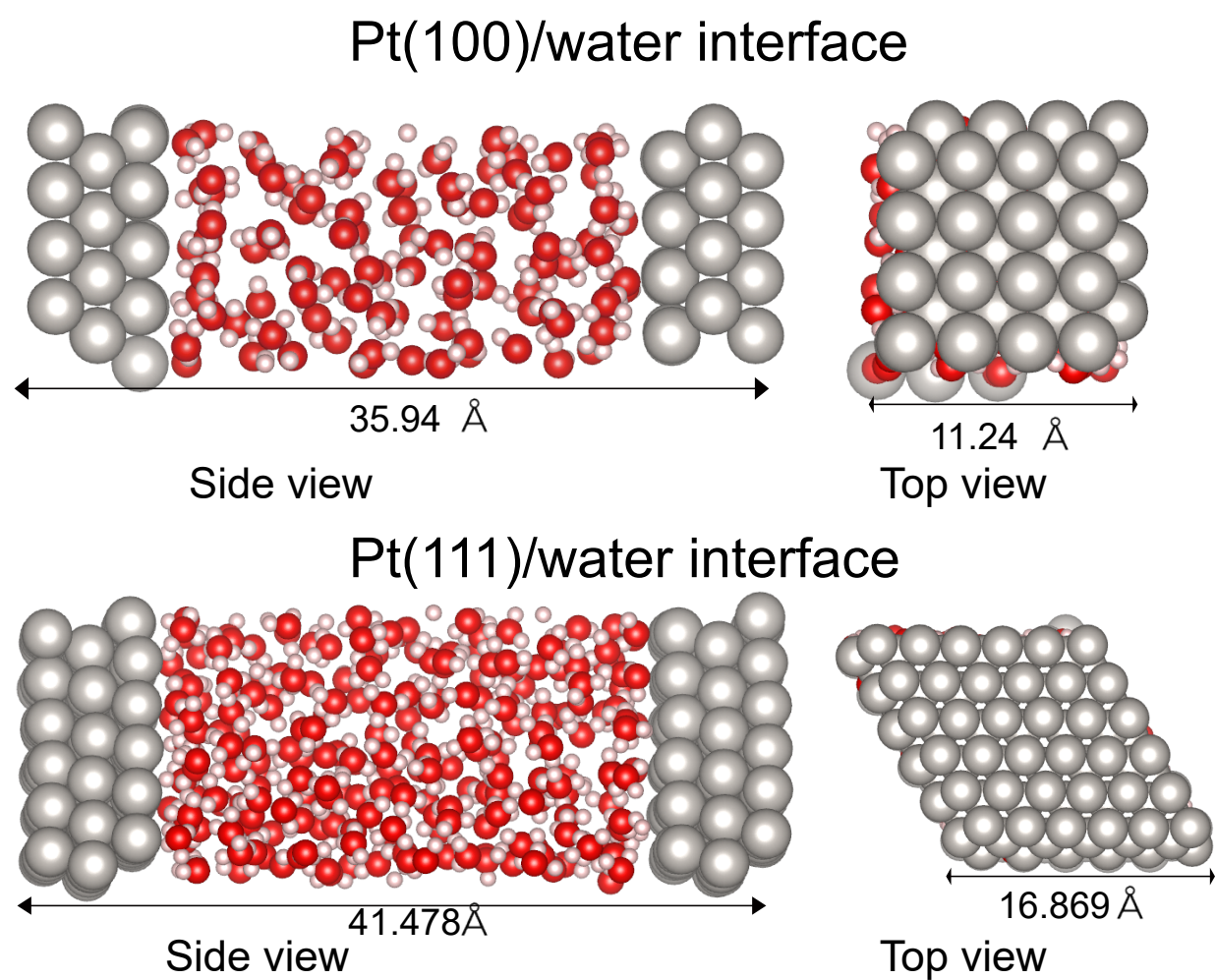


Fig. S1 Top, the side and top view Pt(100)/water models used for the potential training. Bottom, the Pt(111)/water model. Here, the water density has been determined to be 0.97 g cm^{-3} at the middle 10 Å for Pt(100)/water interface. The water density is around 1.00 g cm^{-3} at the middle 10 Å for Pt(111)/water interface.

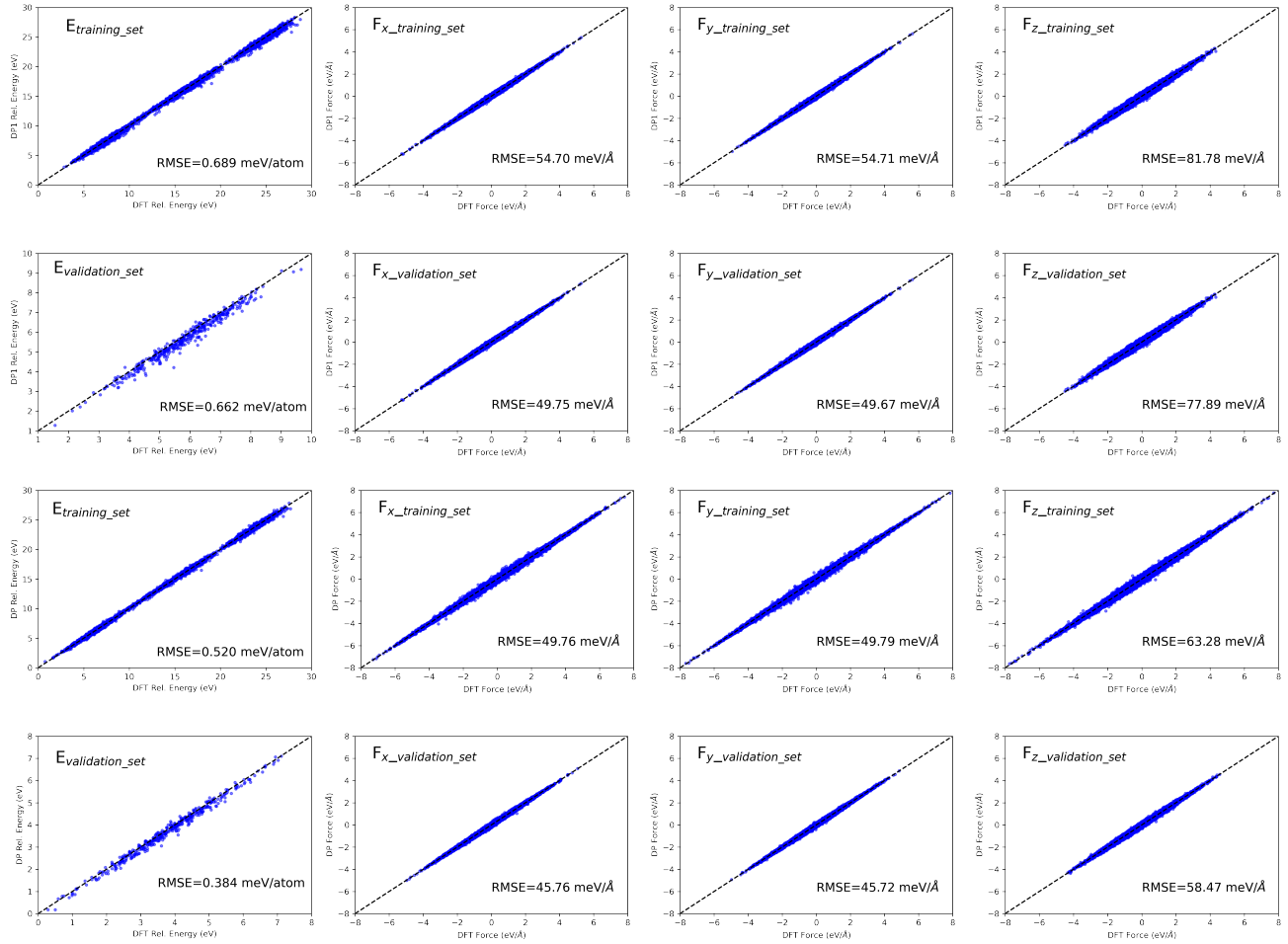


Fig. S2 The energy and force (in x/y/z direction) plot for Pt(100)/water interface model. The first row is the training set labelled by gamma point setup (denote as DP1). The second row is the validation set for this MLP. The third row is the training set adding the energy/force difference (denote as DP). The last row is the validation set result for DP. For clarity, we only display the DP result for Pt(111)/water as shown in the next figure.

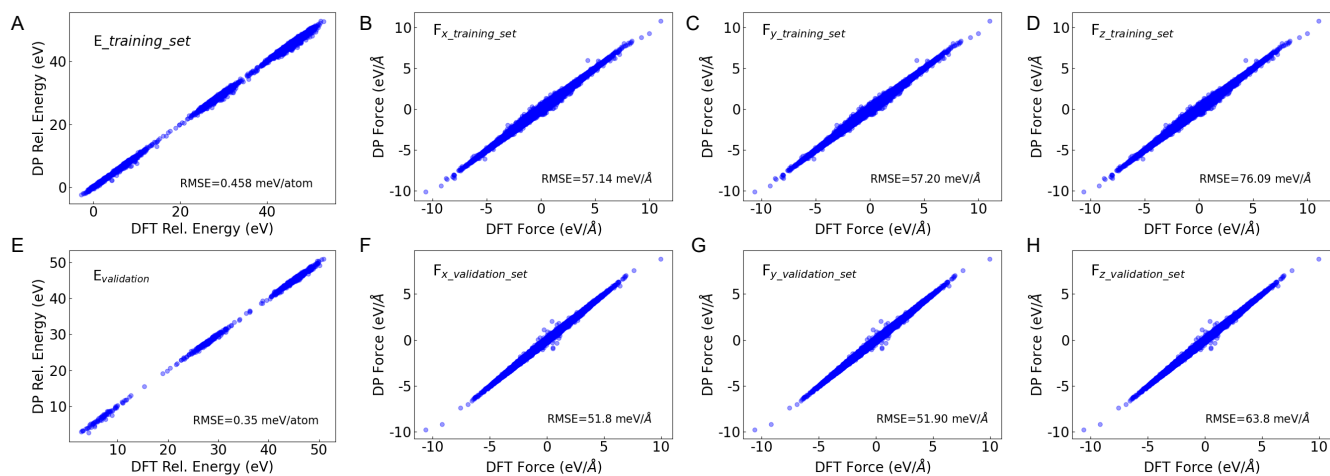


Fig. S3 The energy/force plot for the training (A-D)/validation (E-H) set of Pt(111)/water interface model. To validate the quality of our MLP over different temperatures, we tested the Pt(111)/water interface with three temperature setups.

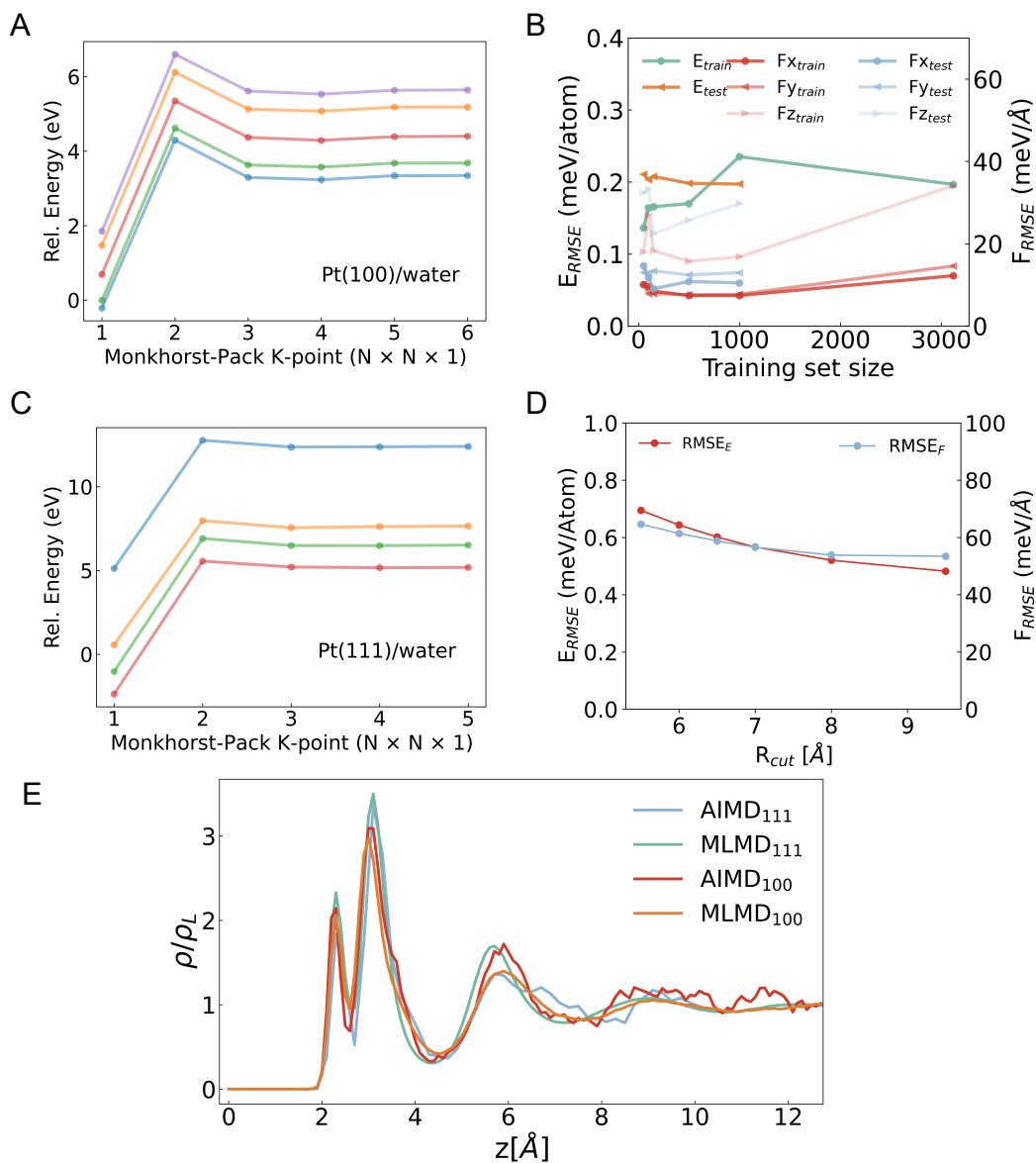


Fig. S4 A, The relative energy of test models over different K point density setup for Pt(100)/water model. B, The RMSE for energy/force difference (this MLP is denoted as DP2) of training and validation set over a series of dataset. It can be seen that a few hundred structures are enough to get reliable DP2 MLP. C, The k point density setup test for Pt(111)/water interface model. D, The test of R_{cut} used in MLP training. E, The oxygen density profile extracted from AIMD and machine learning molecular dynamics. The adsorbed water layers at Pt/water interfaces studied by classical molecular dynamics were determined to be a passivated layer¹. A hybrid molecular dynamics and first-principles study of the Pt/water interface found that the first adsorbed peak has a lower coverage². Le et al., conducted ab initio molecular dynamics simulations (AIMD) of the Pt/water interface and observed two adsorbed peaks³. These peaks are also reported in other reports^{4,5}. As shown in Figure S4E, the machine learning molecular dynamics simulations clearly distinguished the first peak and the second peak in the adsorbed water layer as AIMD did. The coverage for A is 0.15 ML and for AB is 0.58/0.71 ML for Pt(111)/Pt(100). In addition, the MLMD also reproduced the third peak at around 6 Å away from the Pt surface as AIMD showed. At ambient conditions, when metal interfaces are in contact with liquid water, the molecular structure of the interface is no longer directly accessible⁶ as it is at low coverage and ultrahigh vacuum conditions. To the best of the author's knowledge, there is no report directly identify the bound water molecules at Pt/water interfaces. A previous surface X-ray scattering study probed the distribution of water molecules at the Ag(111)/electrolyte interface⁷. Nevertheless, a significant compression of the first water layer on Ag(111) was reported and debated⁸. The experimental uncertainty makes it difficult to obtain the feature of the directly bound water molecules at metal/water interfaces with high accuracy.

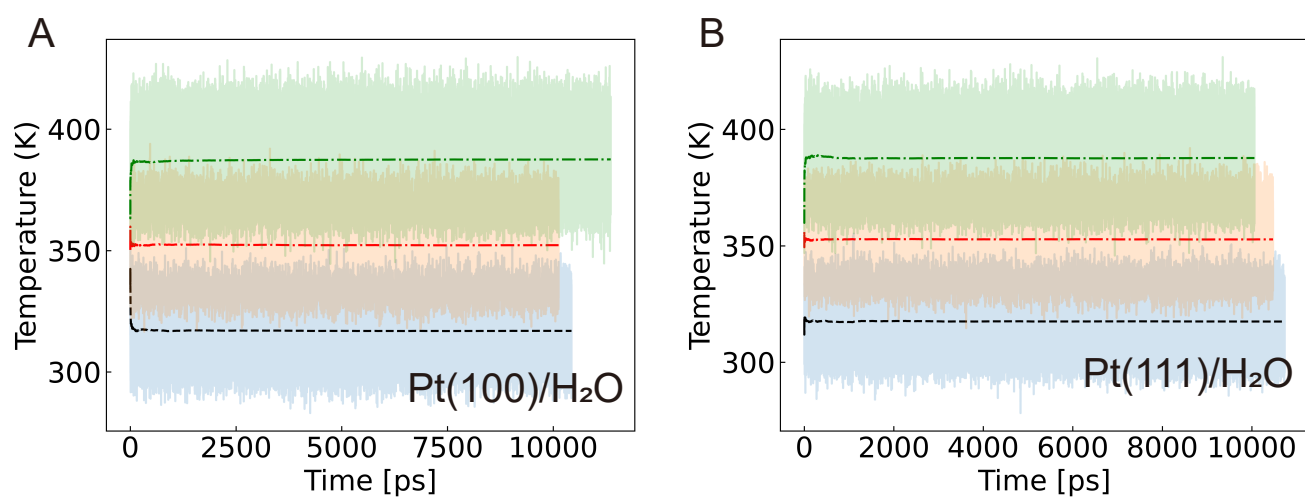


Fig. S5 A, the temperature evolution over 10 ns trajectories with cumulative values 320/352/387 K (the calibrated temperature is 270/302/337 K) for Pt(100)/water model. B, the same data for Pt(111)/water interface model. All these simulations are conducted in NVT ensemble.

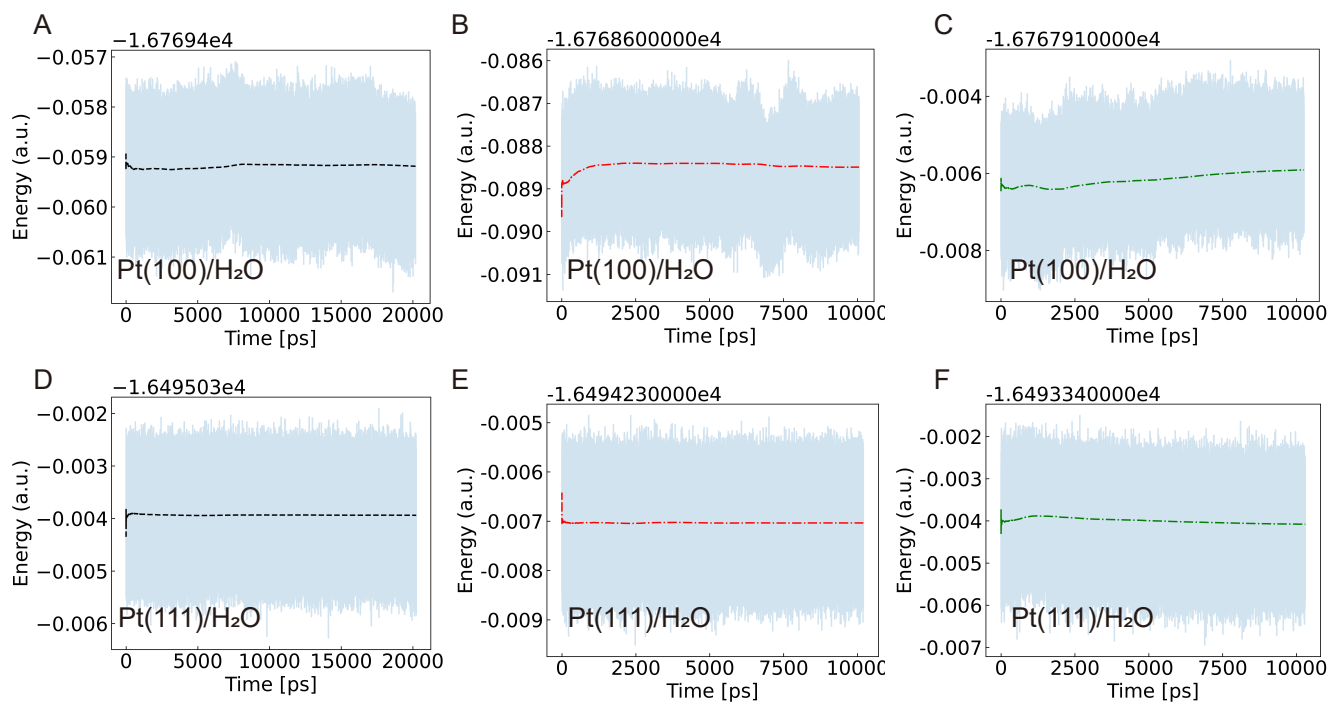


Fig. S6 A-C The total energy evolution over 10 ns trajectories starting from the NVT trajectories for Pt(100)/water model (at the calibrated temperature 270/302/337 K). D-F, the same data for Pt(111)/water interface model. All these simulations are conducted in NVE ensemble. To better converge the dynamics, we run 20 ns at 270 K.

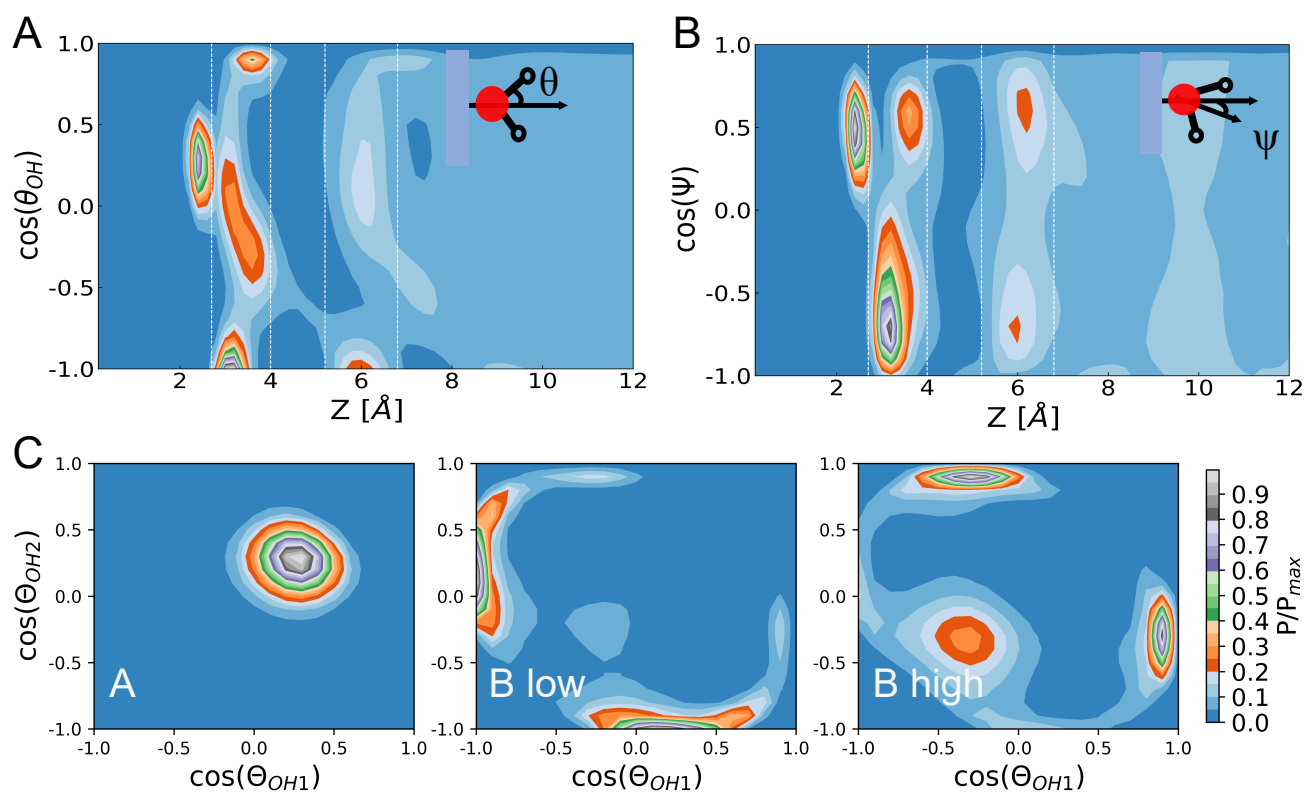


Fig. S7 A-B, The distribution of the OH vector and water bisector angle vs. the surface normal of Pt(100)/water interface. C, The joint probability distribution for both OH vector of a water molecule vs. the surface normal of Pt(100)/water interface.

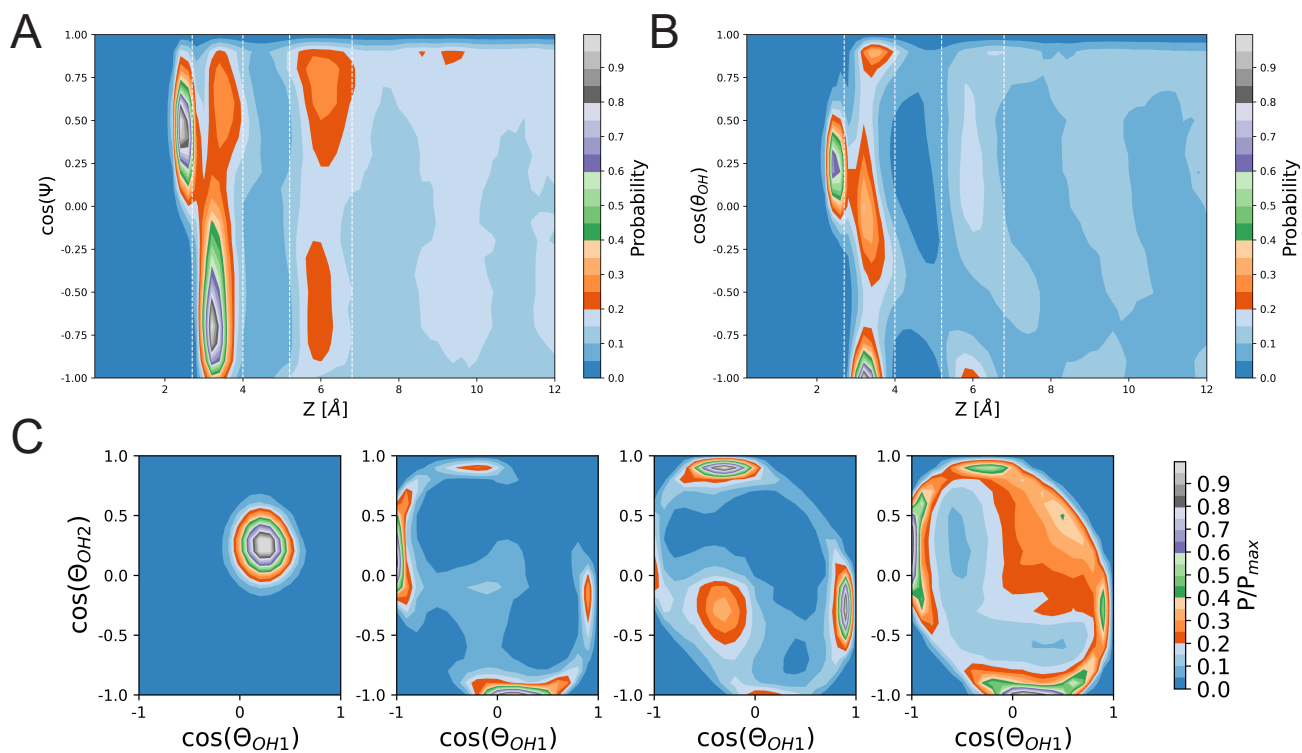


Fig. S8 A-B, The distribution of the OH vector and water bisector angle vs. the surface normal of Pt(111)/water interface. C, The joint probability distribution for both OH vector of a water molecule vs. the surface normal of Pt(111)/water interface.

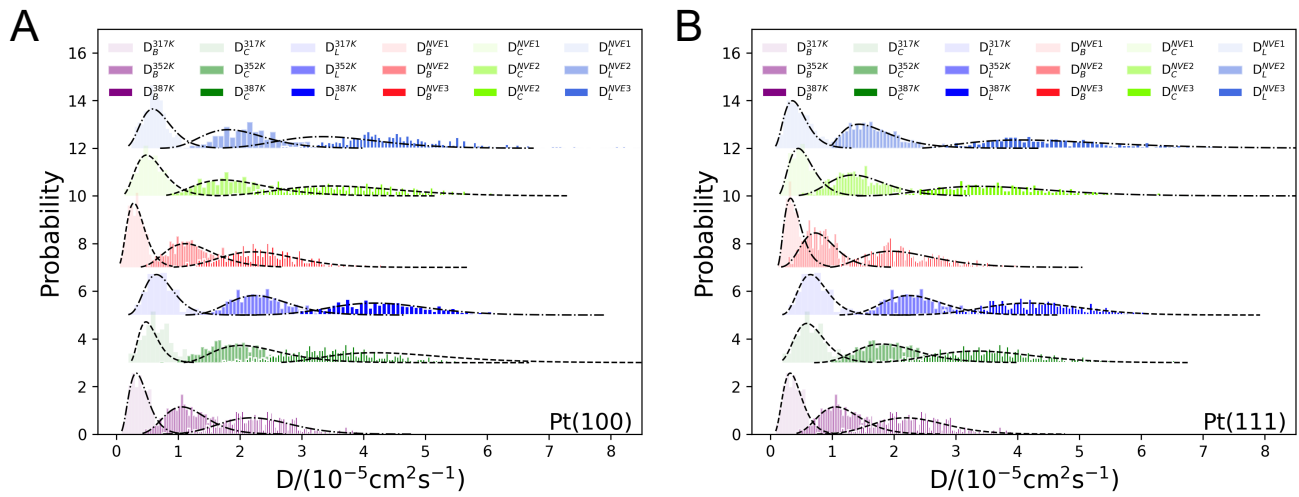


Fig. S9 A, The diffusion coefficients distribution of water molecules in different regions from NVT/NVE simulations. Here, D represents diffusion coefficients in units of $10^{-5} \text{ cm}^2 \text{ s}^{-1}$. The superscript denotes the temperature. When the results are from NVE ensemble, it means that the simulation starts from the NVT simulation restart files. The subscript stands for the type of water molecules as defined in the main text.

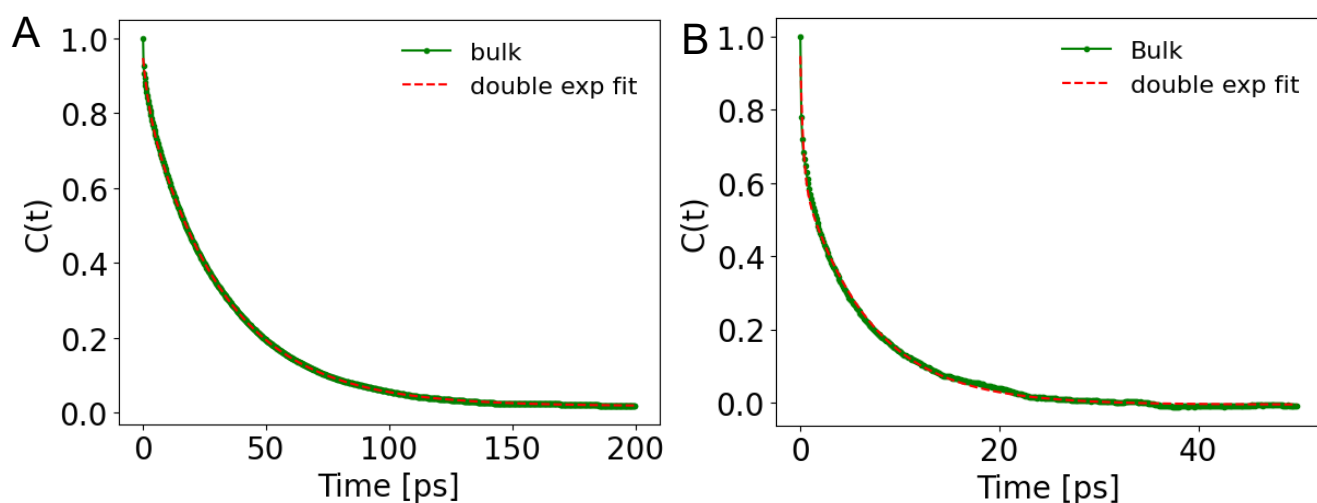


Fig. S10 A, The hydrogen bond correlation function. B, the reorientation correlation function. The fits of the correlation functions are also shown. Here, we used two exponential forms (as shown in Table S4) to fit the hydrogen bond correlations and reorientation correlation functions. The fitted results correspond to two characterized timescales: one for the slow and the other for the fast processes. We only take the fitted results with R larger than 0.9 and drop those with large fitting errors. For clarity, we only present a schematic representation of the hydrogen bond correlation function and the orientation correlation function.

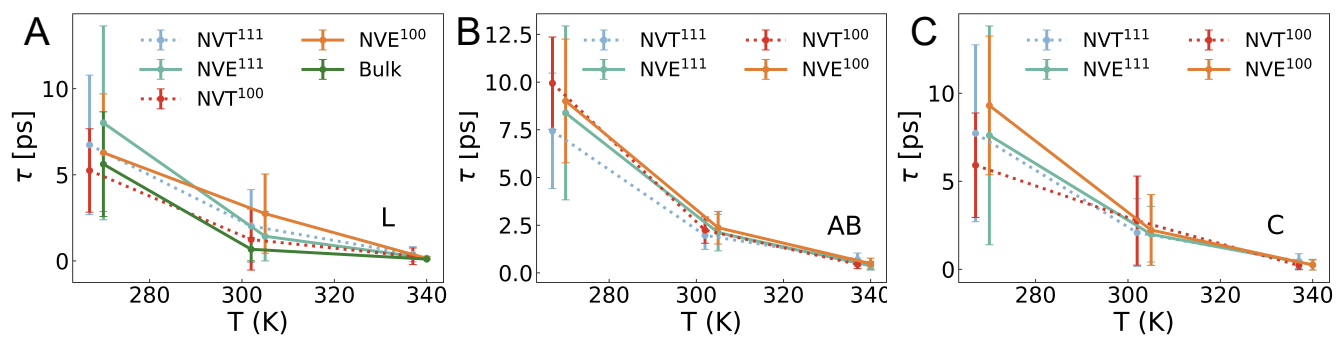


Fig. S11 The lifetime of hydrogen bond dynamics for the faster process at different temperatures in NVT/NVE ensembles.

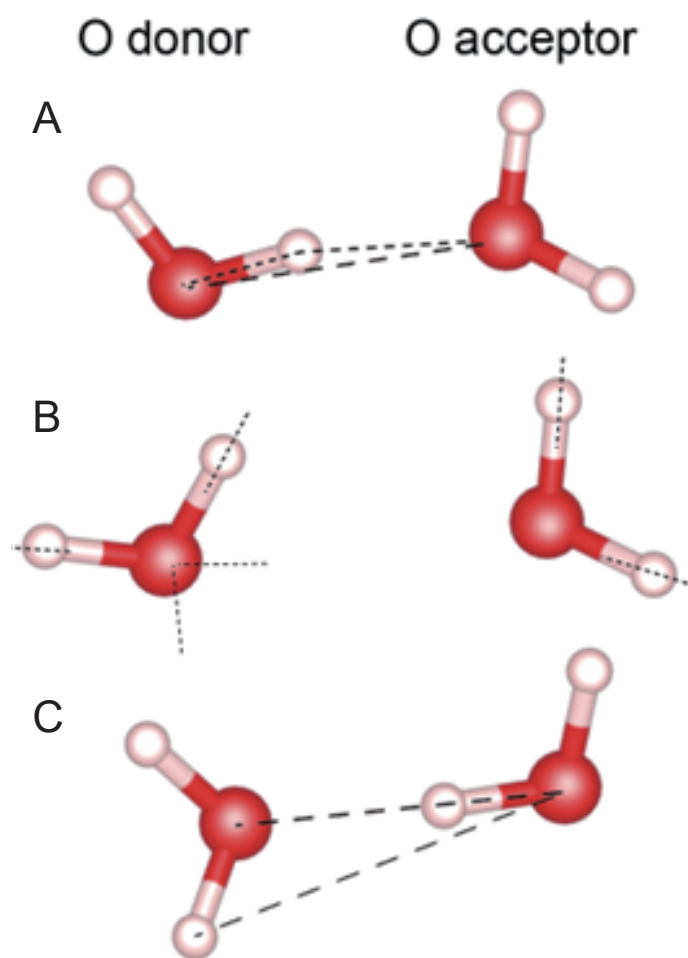


Fig. S12 The representative O-H-O' geometry for a,b, and c in Figure 3E in the main text. A, Stable hydrogen bond geometry. B, the O-H-O' geometry with more negative v . The hydrogen donor water molecules may not form stable hydrogen bonds with the observed acceptor water molecules, but these donor water molecules may form hydrogen bonds with other water molecules. C, This geometry corresponds to structures where donor water molecules accept hydrogen from acceptor water molecules, but do not donate hydrogen.

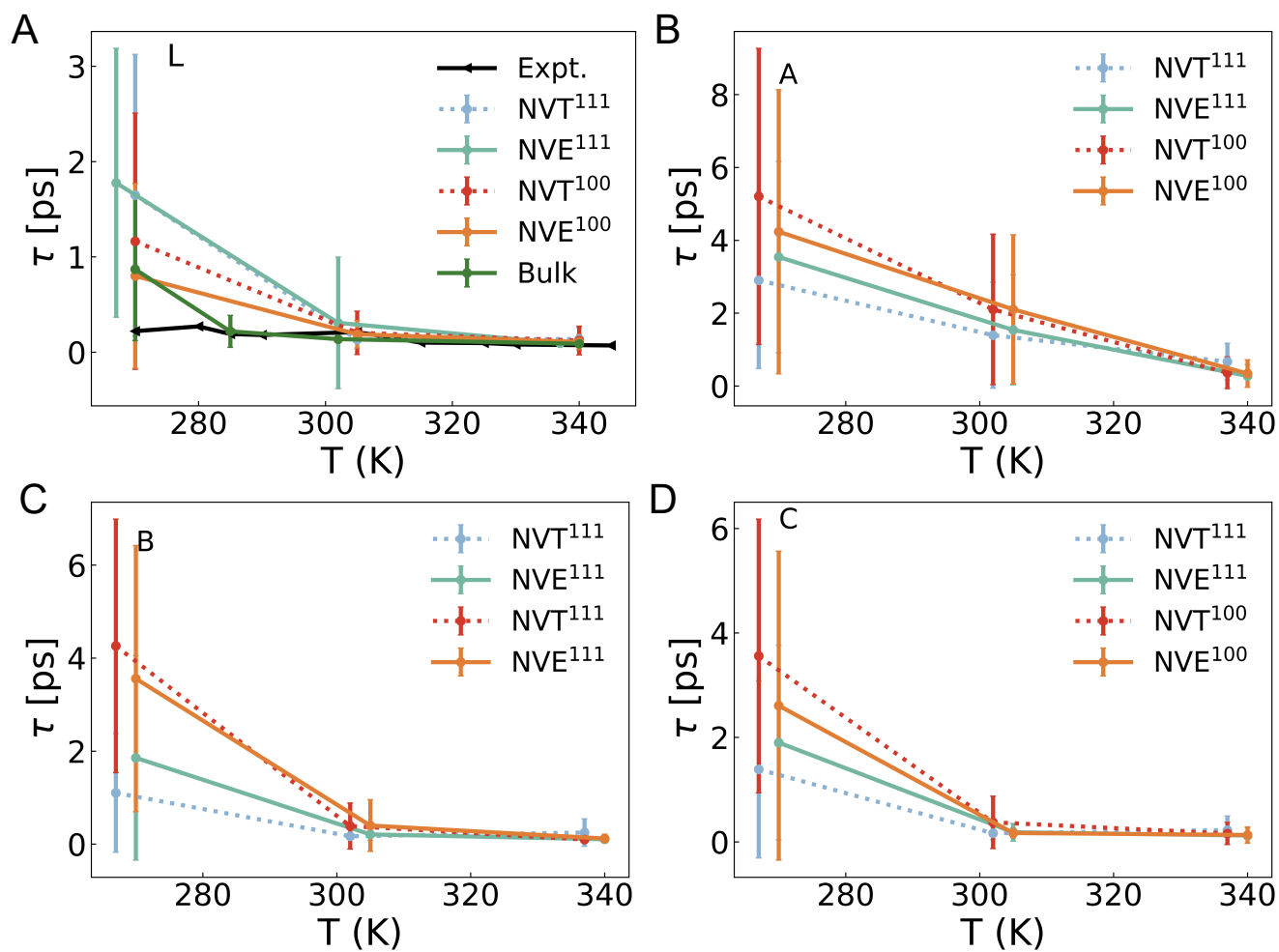


Fig. S13 A, The fast lifetime of water bisector orientation dynamics of bulk water (green) and water L. B-D, The fast lifetime of water bisector orientation dynamics of water A,B, and C. The experimental data is reproduced with permission from the reference⁹

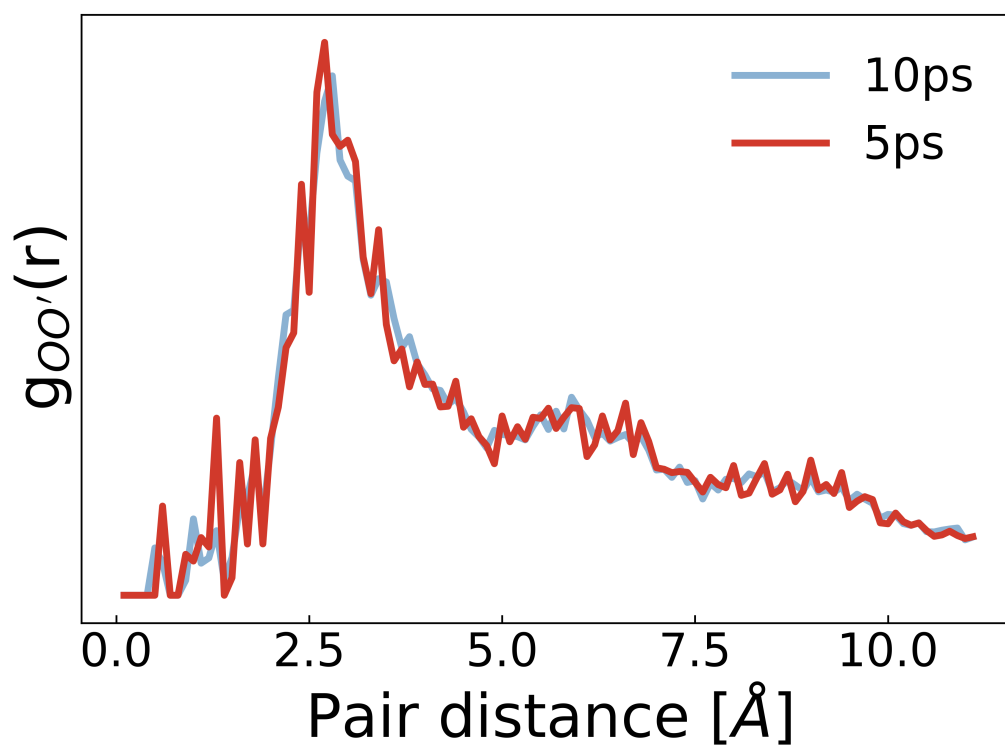


Fig. S14 The radial distribution function of O-O for the first desorption event and the following desorption events within 5/10 ps.

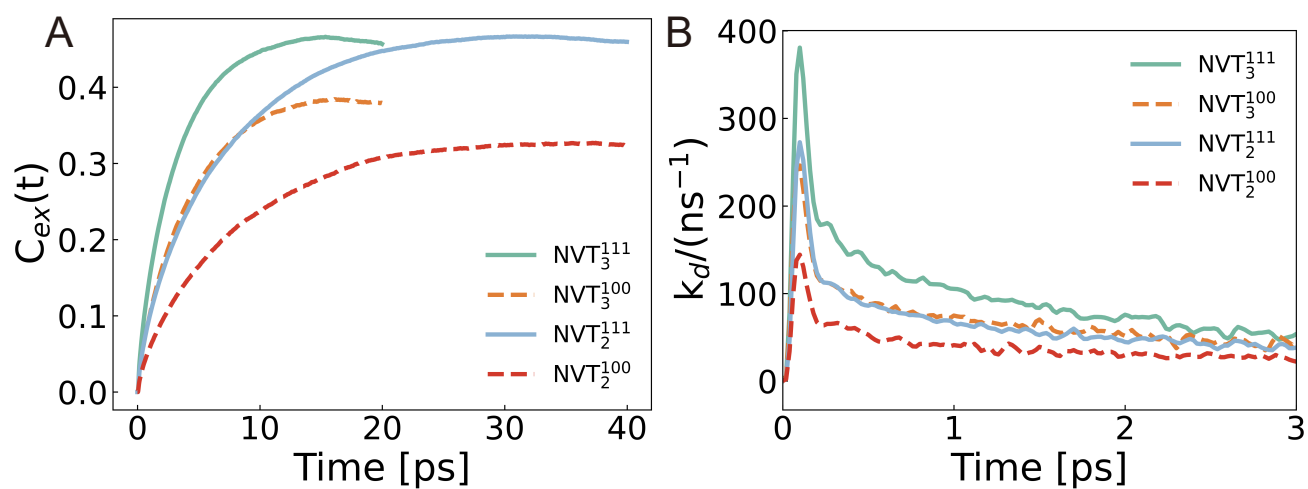


Fig. S15 A, the exchange between water A and water B at two different temperatures for Pt(100) and Pt(111). B, The slope of the flux correlation functions over time. Here, 2 and 3 denotes the temperature 352/387 K, which are 302/337 K after the theoretical calibration.

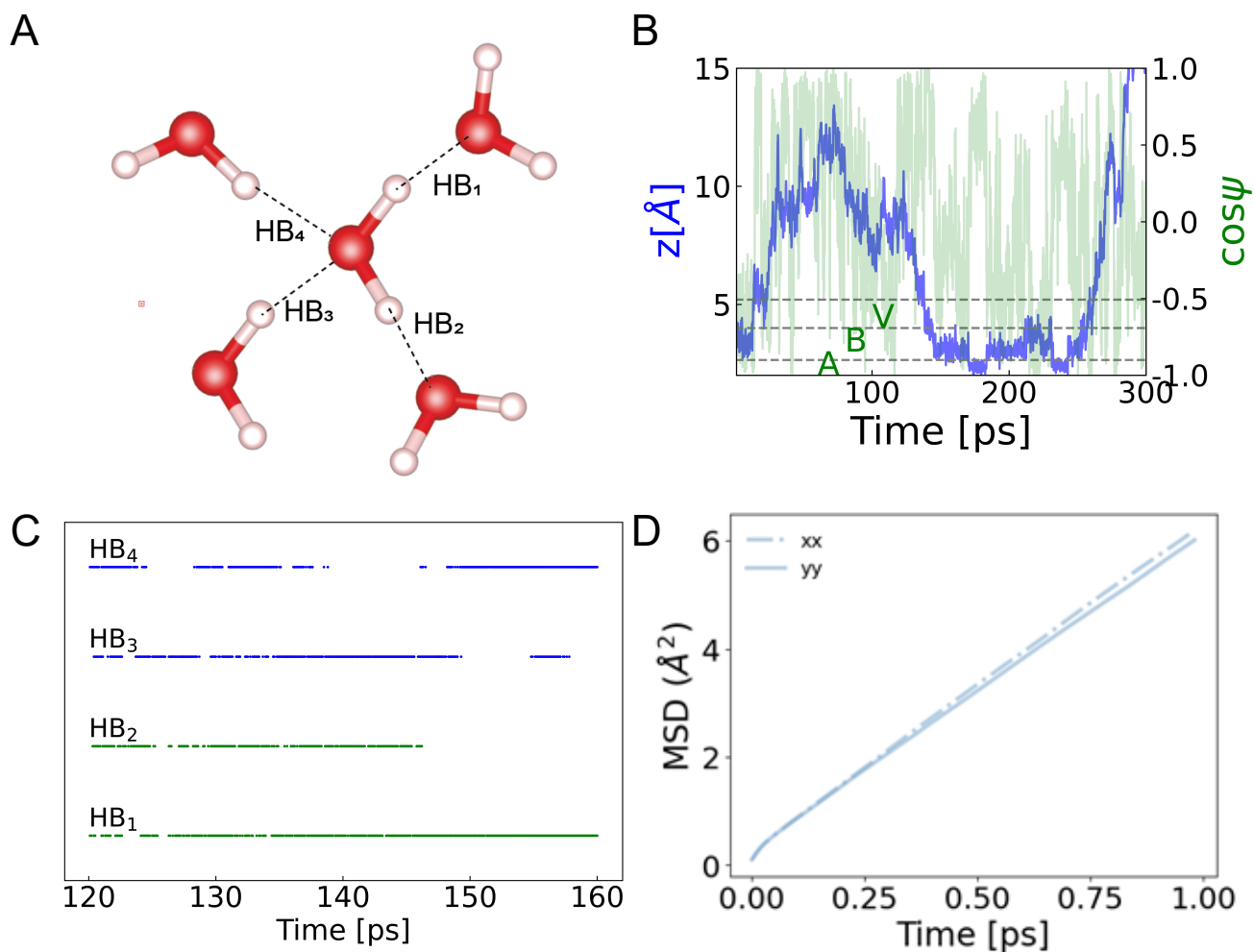


Fig. S16 A, the hydrogen bond of one center water molecule. HB1 and HB2 represent two donor H and HB3 and HB4 denote two acceptor H. B, the z coordinate and $\cos\psi$ value of one observed water molecule. C, The evolution of these four hydrogen bonds over time. When the dot is absent, it means the non existence of the related type of hydrogen bond. D, The MSD of water molecules in the V region analyzed from 120 ps to 160 ps (Figure S14C) of 1 ps, which corresponds to an instantaneous diffusion coefficient of approximately $30 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. This value is about six times faster than that of water L.

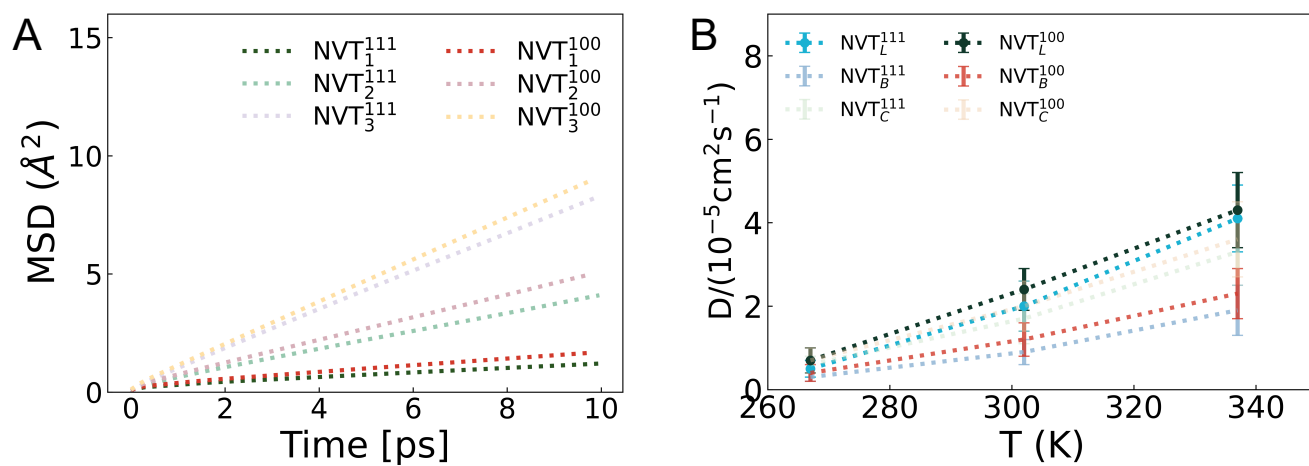


Fig. S17 A, Mean squared displacements (MSD) of the oxygen atom of water L parallel to the Pt surfaces. For all the NVT ensembles, the superscript 1/2/3 stands for the three temperatures. B, The diffusion coefficients for water B, C, and L of Pt(100) and Pt(111).

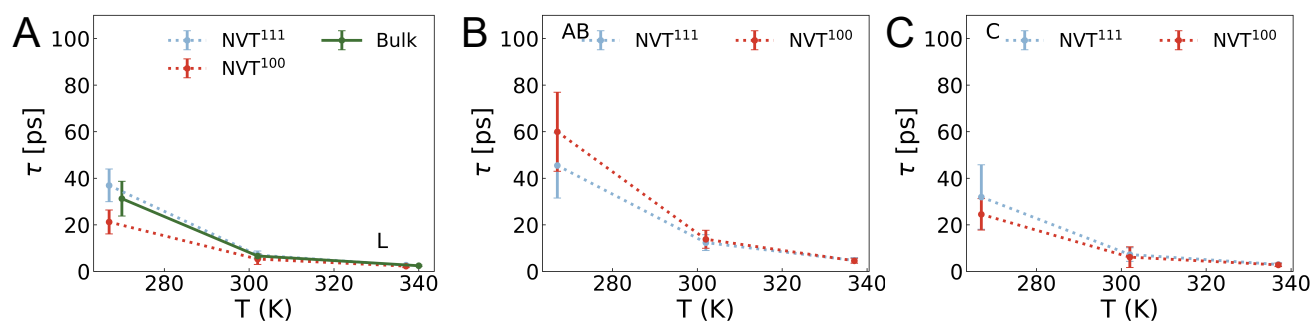


Fig. S18 A-C, The fitted (two exponential functions) lifetime of the slow hydrogen bond dynamics of water L, AB, and C based on NVT ensemble simulations.

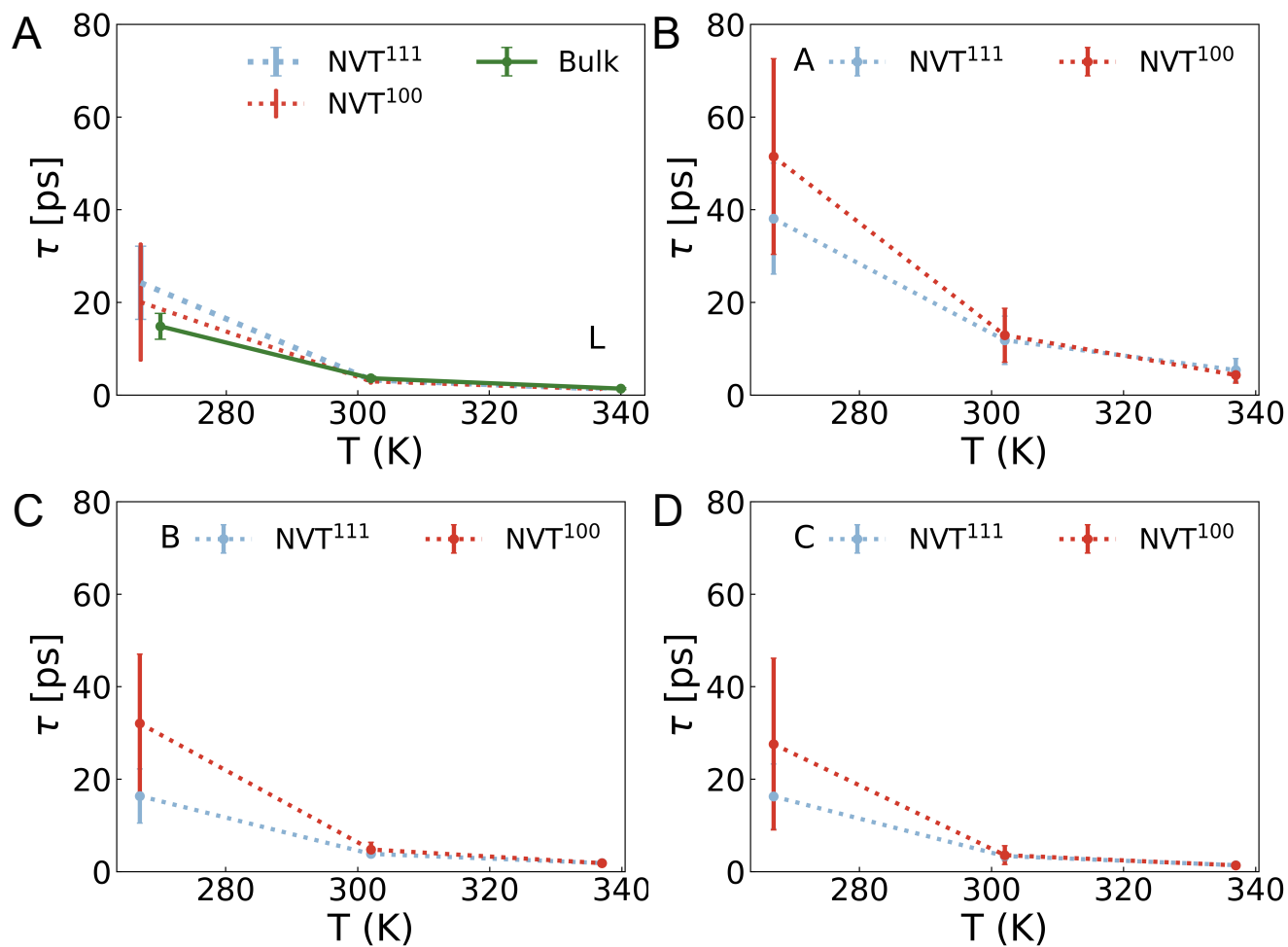


Fig. S19 A-D, The fitted lifetime for water bisector reorientation dynamics for water L, A, B, and C based on NVT ensemble simulations.

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