Electronic Supplementary Material (ESI) for Faraday Discussions.

Supporting Information for "Raman and IR spectra of water under graphene nanoconfinement at ambient and extreme pressure-temperature conditions: a first-principles study"

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SUPPLEMENTARY METHODS

We performed the simulations with a time step of 0.24 fs using the SG15 optimized norm-conserving Vanderbilt (ONCV) pseudopotentials [1, 2]. We used a plane-wave kinetic energy cutoff of 65 Ry in the AIMD simulations, and increased the cutoff to 85 Ry when calculating pressure. We controlled the temperature with the Bussi-Donadio-Parrinello thermostat [3], which had a damping factor (τ) of 24.2 fs. Each simulation cell contains 48 water molecules with periodic boundary conditions (see Tab. SI).

We calculated the lateral pressure in the simulation cell using the formula $P_{\parallel} = \left(\sigma'_{xx} + \sigma'_{yy}\right)/2$. To account for the vacuum in the unit cell, we modified the diagonal elements of the computed stress tensor, σ_{xx} and σ_{yy}, with the expression $\sigma'_{xx/yy} = \sigma_{xx/yy}\,(L_z/h_z)$, where L_z represents the z-dimension of the unit cell, and h_z denotes the distance between graphene sheets. Previous studies have utilized this method [4, 5].

We fitted the graphene-oxygen interaction to the diffusion Monte Carlo calculations for water molecules in the two-legged configuration adsorbed on the graphene sheet [6]. The molecular force was applied to the oxygen atoms, and the interaction was modeled using the Morse potential shape:

$$E_b^{\mathrm{O}}(d) = D_e^{\mathrm{O}}\left[\left(1 - e^{-a^{\mathrm{O}}(d-d_0^{\mathrm{O}})}\right)^2 - 1\right], \tag{S1}$$

where $D_e^{\mathrm{O}} = 9.55185$ kJ mol^{-1}, $a^{\mathrm{O}} = 1.34725$ Å^{-1}, and $d_0^{\mathrm{O}} = 3.37265$ Å [6].

TABLE SI. P-T data of graphene-confined water in the AIMD simulations in Fig. 1. The z dimension of simulation cells (L_z) is fixed at 1.470 nm.

Confinement	P (GPa)	T (K)	x(y) dimension (nm)
(a)	0.52 ± 0.39	400	1.950
(b)	9.72 ± 0.59	1000	1.288
(c)	20.15 ± 1.13	1000	1.190

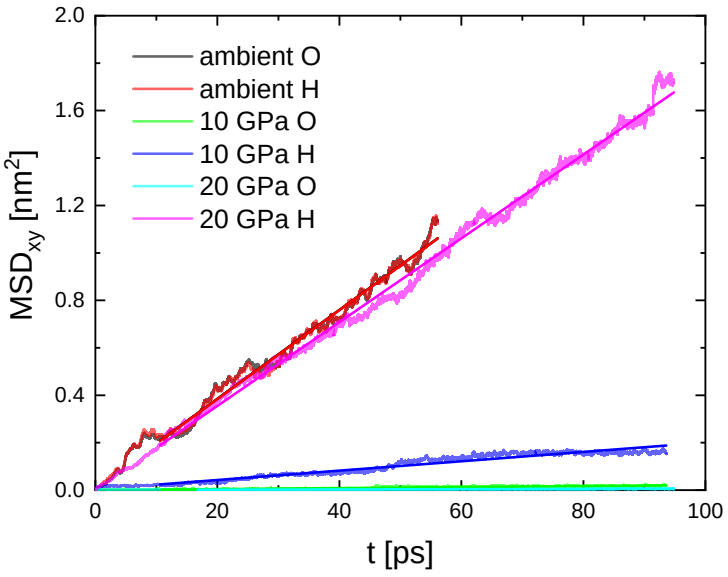

FIG. S1. Mean-squred displacement of oxygen and hydrogen atoms in graphene-confined water at ambient and extreme P-T conditions. The temperature is 1000 K when the pressure is ∼10 or ∼20 GPa (see Tab. SI).

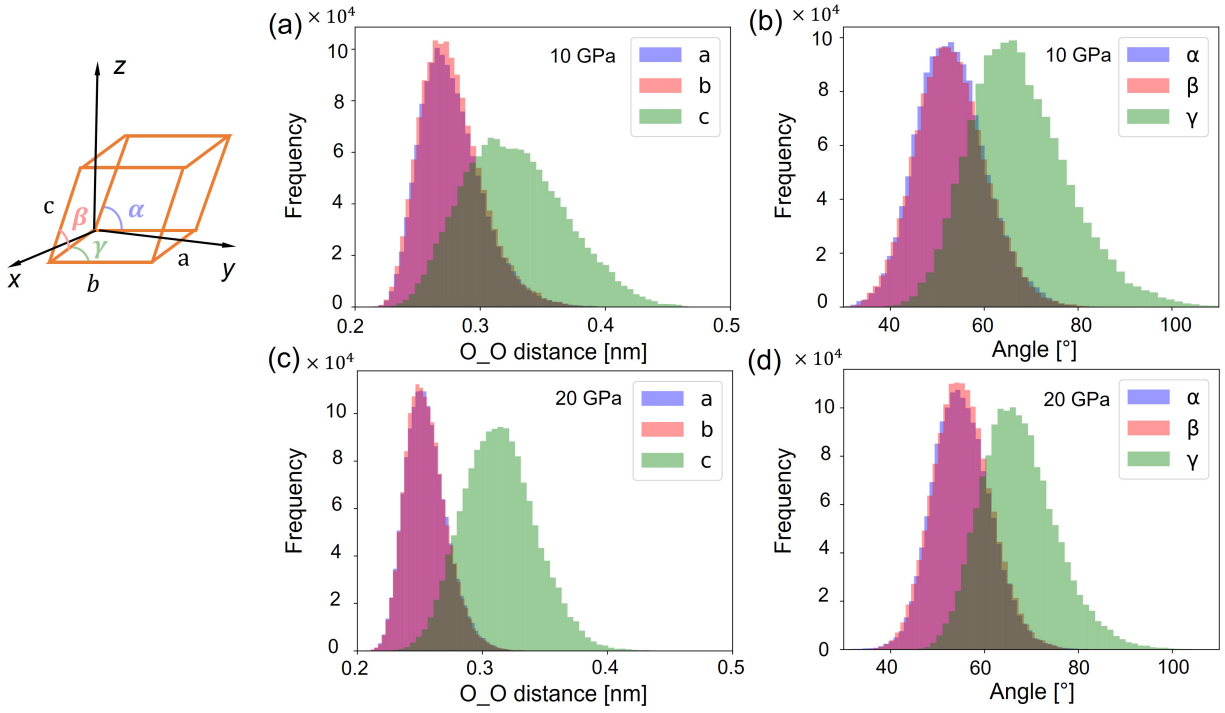

FIG. S2. The oxygen lattices at extreme P-T conditions. The left panels (a and c) show the distribution of the lattice constants. The right panels (b and d) show that distribution of the lattice angles. The temperature is 1000 K (see the main text).

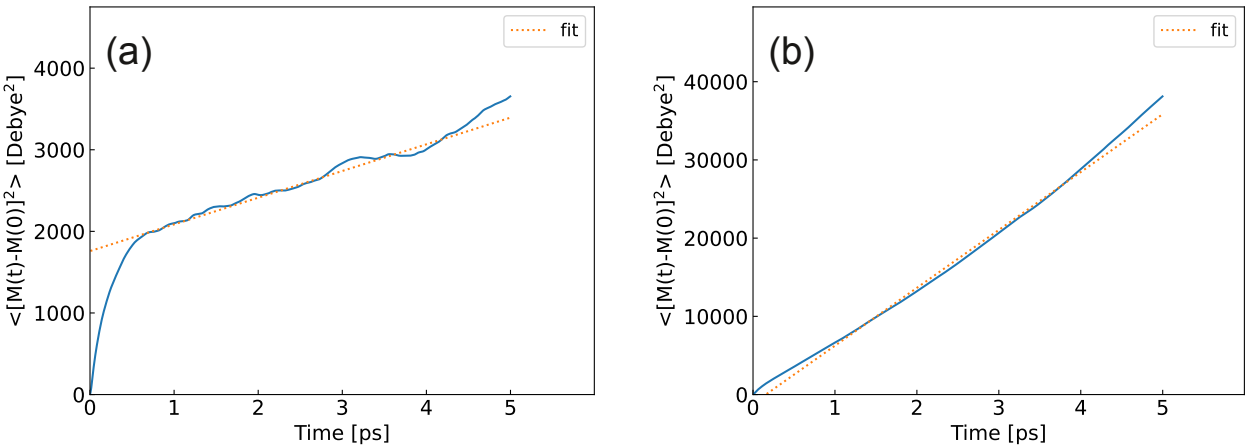

FIG. S3. Time-averaged mean squared displacement of the total dipole moment **M** as a function of separation time at (a) $\sim$ 10 GPa and 1000 K, and (b) $\sim$ 20 GPa and 1000 K.

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