Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for:

Structure and Dynamics of Water at Water-Graphene and Water-Hexagonal Boron-Nitride Sheet Interfaces Revealed by *Ab initio* Sum-Frequency Generation Spectroscopy

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I. Density Profile of Water near Graphene and hexagonal Boron-Nitride (hBN)

Figure S1 shows the axial profiles of water density at the water-graphene and water-BN interfaces. Both profiles are similar and are characterized by two peaks; the first and second peaks are located at z = ~3 Å with the height of ~2.1 g/cm^3 and at z = ~6 Å with ~1.5 g/cm^3, respectively. Here, the z-axis forms the surface normal and the origin point of the z-axis is given by the position of the graphene/BN density maximum. The similar water density profiles at the graphene and hBN interfaces are consistent with the previous report,[1] while the peak height of the first peak of 3.7 g/cm^3 differs significantly from our results. This difference in the peak height can be attributed to the different exchange-correlation functional and the van der Waals correction method (optB88-vdW[2-3] in Ref. 1 and BLYP-D3 in our work). Here, we note that the optB88-vdW tends to overestimate the absorption energy of water on the graphene,[1] while the BLYP+D3 provides good agreement of the simulated SFG spectra with the experimental spectra[4] as well as the surface tension of water at the water-air interface.[5] It has been also reported that the BLYP+D3 reproduces the same stability of water near the hBN sheet to the optB88-vdW functional,[6] indicating that BLYP-D3 is appropriate to describe the weak interaction between the 2D sheets and water. Finally, the 6 × 10 orthorhombic cell used in our calculations is a sufficient size to reproduce the electronics structure of graphene and hBN only with the Gamma point.[1]

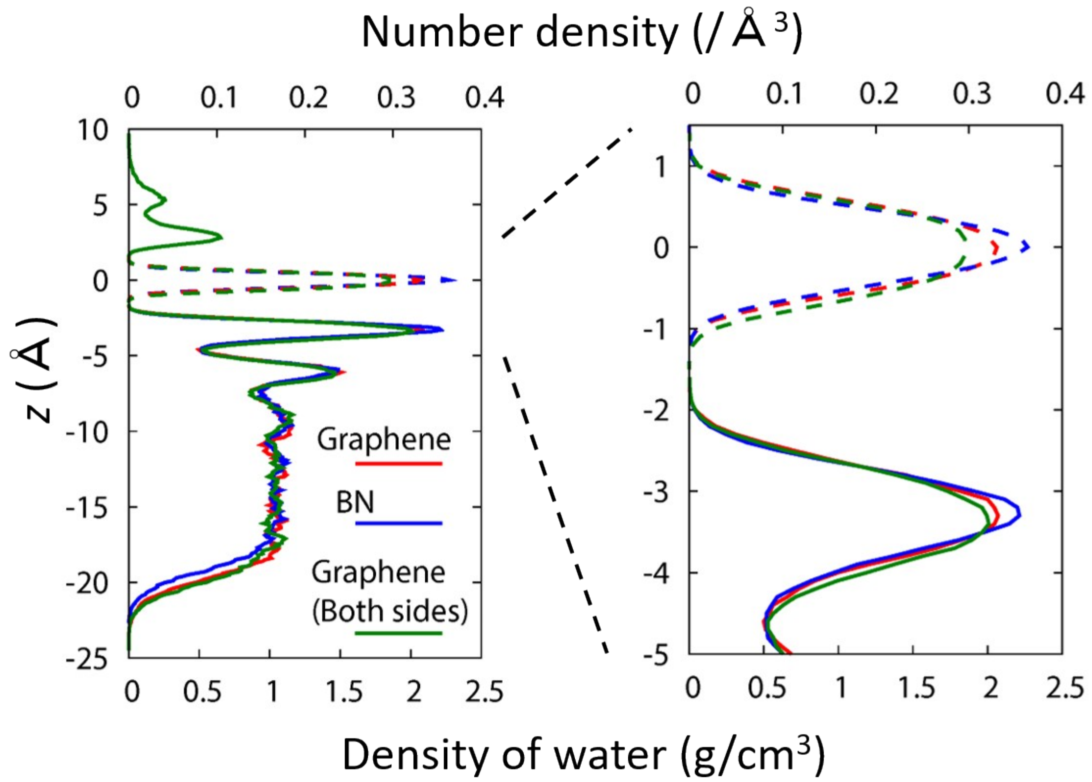

Figure S1. Axial profiles of the density of water (solid lines) as well as the number density of C and B/N and N atoms of graphene and hBN, respectively (dashed lines). In these profiles, the heavy water (D_2O) molecules used in the MD simulations were considered as the H_2O. The origin point is given by the graphene/BN sheet position.

II. Simulation Protocols for SFG Spectra

We used the surface-specific velocity-velocity correlation function (ssVVCF) algorithm,[4] where the resonant part of the SFG response function, $\chi^{(2),R}_{xxz}(\omega)$ can be written as:

$$\chi^{(2),R}_{xxz}(\omega) = \frac{Q(\omega)\mu^{'}(\omega)\alpha^{'}(\omega)}{i\omega^{2}}\chi^{ssVVAF}_{xxz}(\omega), \tag{S1}$$

$$\chi^{ssVVCF}_{xxz}(\omega) = \int_0^{\infty} dt e^{-i\omega t}\left\langle \sum_{i,j} g_{ds}(z_i(0))\dot{r}^{OD}_{z,i}(0)\frac{\dot{\vec{r}}^{OD}_{j}(t)\cdot\vec{r}^{OD}_{j}(t)}{\left|\vec{r}^{OD}_{j}(t)\right|}\right\rangle. \tag{S2}$$

$z_i(t)$ is the *z*-coordinate of the *i*th oxygen atom at time *t*, and $g_{ds}(z_i)$ is the function for the dividing surface to selectively extract the vibrational responses of D_2O molecules near the interface. For the D_2O-graphene interface and D_2O-BN interface, we used

$$g_{ds}(z_i) = \begin{cases} 1 & for \quad -9\ \text{Å} \le z_i \\ 0 & for \quad z_i < -9\ \text{Å} \end{cases}. \tag{S3}$$

where z_{ds} is the z-coordinate of the dividing surface and. For the D_2O-air interface, we used

$$g_{ds}(z_i) = \begin{cases} 1 & for \quad z_i < -13\ \text{Å} \\ 0 & for \quad -13\ \text{Å} \le z_i \end{cases}. \tag{S4}$$

For the penetrated water cases on the graphene interface, we used.

$$g_{ds}(z_i) = \begin{cases} 0 & for \quad z_i < 0\ \text{Å} \\ 1 & for \quad 0\ \text{Å} \le z_i < 4.5\ \text{Å} \\ 0 & for \quad 4.5\ \text{Å} \le z_i \end{cases}. \tag{S5}$$

Such z_{ds} are schematically depicted in Figure S2. The criterion of *z* = 4.5 Å for the penetrated water was selected to include the topmost water layer near the graphene (see Figure S1). This is rationalized by the fact the thickness for the corrugated graphene is sub-nm scale.[7-9]

In this study, we consider the case that the O-D stretch chromophores are decoupled from the other O-D chromophores. This corresponds to the situation of isotopically diluted water (H-O-D in D_2O). When the O-D stretch chromophores are isolated, the cross-correlation term in Equation (S2) is zero and thus Equation (S2) reduced to the surface-specific autocorrelation function (ssVVAF) as:

$$\chi_{xxz}^{ssVVAF}(\omega) = \int_0^{\infty} dt e^{-i\omega t} \left\langle \sum_i g_{ds}(z_i(0)) \dot{r}_{z,i}^{OD}(0) \frac{\vec{\dot{r}}_i^{OD}(t) \cdot \vec{r}_i^{OD}(t)}{\left|\vec{r}_i^{OD}(t)\right|} \right\rangle. \tag{S6}$$

The induced dipole moment due to the surrounding water molecules (solvation effects) are included through the frequency dependent transition dipole moment ($\mu'(\omega)$) and polarizability ($\alpha'(\omega)$):[10-11]

$$\mu'(\omega) \equiv \left(1.377 + \frac{53.03(2745.8 - \omega)}{4870.3}\right)\mu^0, \tag{S7}$$

$$\alpha'(\omega) \equiv \left(1.271 + \frac{5.287(2745.8 - \omega)}{4870.3}\right)\alpha^0, \tag{S8}$$

where ω is in cm^{-1}. $Q(\omega)$ is the quantum correction factor given by:[12]

$$Q(\omega) = \frac{\beta\hbar\omega}{1 - \exp(-\beta\hbar\omega)},$$

(S9)

where β = 1/*kT* is the inverse temperature.

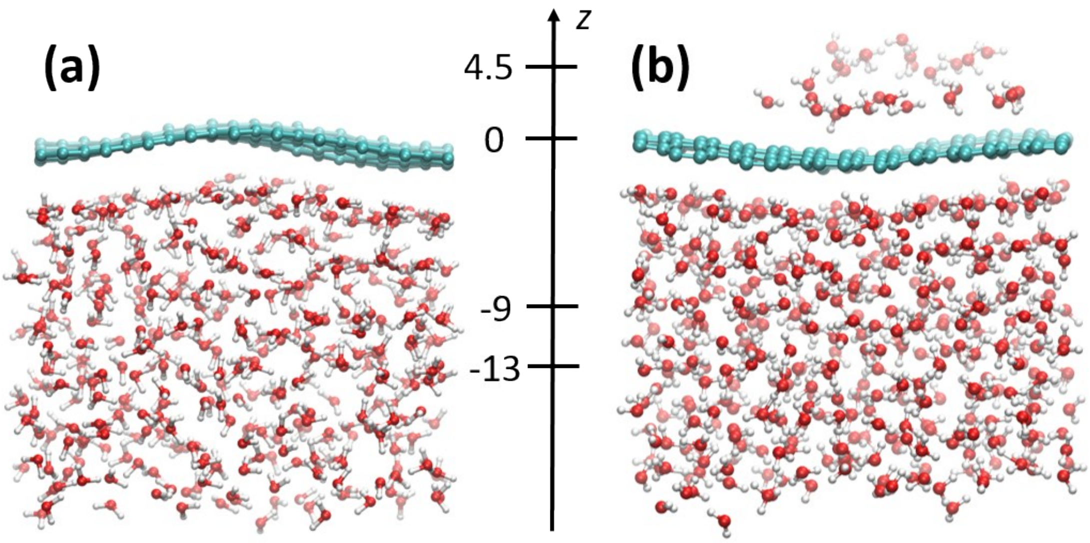

Figure S2. Snapshots of water-graphene interfaces. Water molecules exist (a) down side only and (b) both sides of graphene. The water-molecules

III. Dangling O-D Group Definition

The H-bond of water is defined based on the water dimer conformation shown in Fig. S4(d). Here, R and r are the intermolecular O…O and O…D distances of water dimer, respectively. β and θ denote the angles of D-O…O and O-D…O, respectively, while ψ is the angle formed by the O…D vector and the plane formed by H-O-D atoms. It has been already shown using the POLI2VS water model[13] that the R-θ definition is the most appropriate to define the free O-H groups at the water-air surface.[14] We calculated the SFG spectra with the criteria of (R_c, θ_c) = (3.5 Å, 110^0), where R_c and θ_c are the critical distance and angle, respectively. Figs S3(a)-(c) show that the free OD groups are captured well with the R-θ definition, even at the water-graphene and water-hBN interfaces based on AIMD simulations.

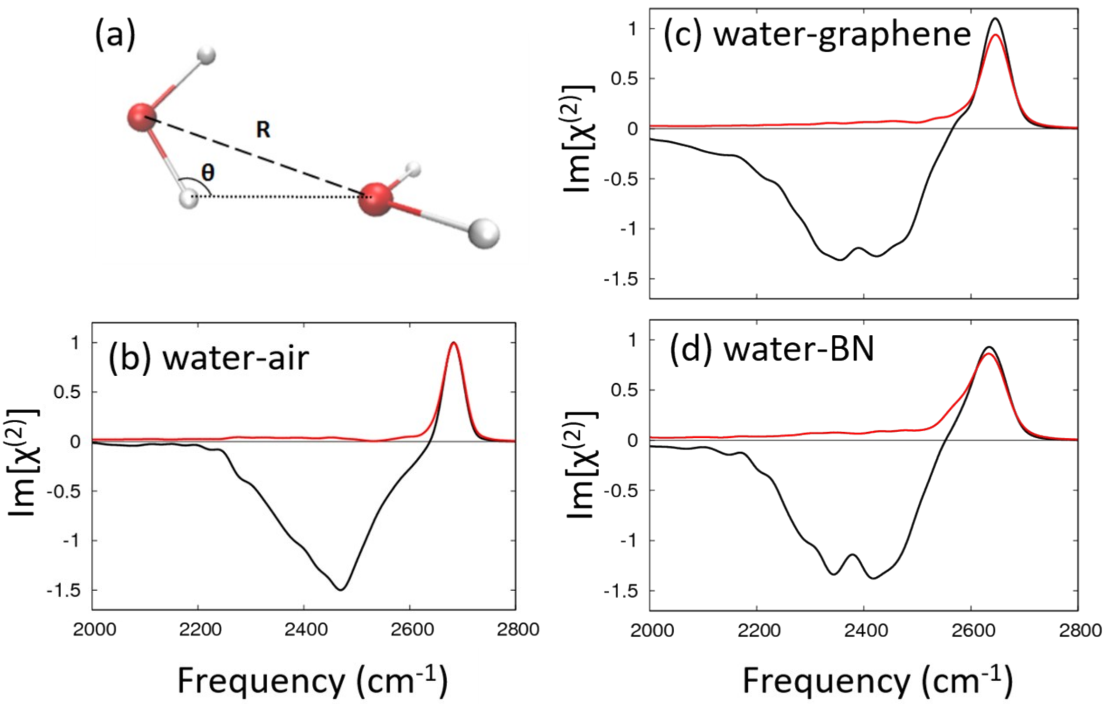

Figure S3. (a) Schematic of the heavy water dimmer conformation, the O…D distances *R* the O…O-D angles β for defining the free O-D group. A red (white) sphere represents a D atom. SFG spectra of the isotopically diluted O-D stretch mode at the (b) water-air, (c) water-graphene, and (d) water-BN interfaces. The black lines represent the total spectra and the red lines represent the contributions from the dangling O-D group defined using (R_c, θ_c) = (3.5 Å, 110^0).

IV. Structural Order of the First Layer Water

Figure S4 shows the two-dimensional position probability of D atom in the first layer of water molecules (-5 Å < z < 0 Å in Figure S1). D atoms distribute slightly localized on the ring at the graphene, while they are localized on the N atoms of hBN in the first layer of water ranging over 5 Å. Our data support the large friction of water molecules at the water-BN sheet interface.[1]

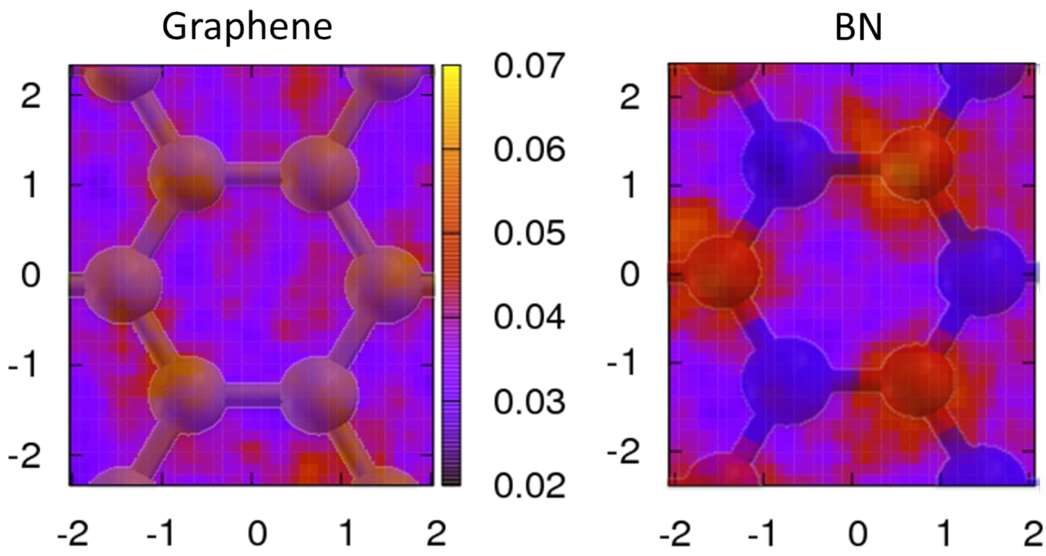

Figure S4. Position probability of D atoms of D_2O molecules near the graphene and hBN interface. We used the D_2O atom within the first layer of water.

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