

### Molecular Hydrophobicity Signature in Charged Bidimensional Clay **Materials**

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ity molecular signature of nanometric bidimensional confined systems represents a challenging task with repercussions in environmental transport processes. Swelling clay minerals represent an ideal model system, as hydrophobicity can be modified during material synthesis by substituting hydroxyls by fluorine in the structure, without additional surface treatment. This following work presents a combined approach, integrating experimental inelastic neutron scattering spectroscopy and ab initio molecular dynamics simulations, with the objective of advancing our understanding of the role of surface hydroxylation/ fluorination and the extent of confinement on water properties. From computed structures, the analysis of molecular hydro-



phobicity/hydrophilicity signature was investigated in detail through water-cation-surface interactions. The results elucidate the influence of fluorination on interlayer species, thereby tracing the impact of the surface on the diminished number of water molecules in such a sample. It is notable that the strong cation-water interaction can overcome the disruptive influence of fluorine, thereby maintaining comparable water hydration shells around cations and resulting in an almost identical bidimensional confinement geometry for both hydroxylated and fluorinated specimens. The analysis of the hydrogen-bond network revealed a significant reorganization of the water molecules due to fluorination. Our results suggest that a quantitative molecular signature of hydrophobicity/hydrophilicity can be derived from the analysis of the formation of cavities in the confined fluid. This new finding represents a robust approach for generalizing the hydrophobicity/hydrophilicity character for a wide variety of bidimensional systems while proposing a framework for the design of new materials with controlled water properties.

#### 1. INTRODUCTION

Nanoscale hydrophilicity and hydrophobicity play an essential role in the mediation of many environmental processes. It controls the transport of contaminants in low-permeability systems, with water serving as the primary vector for element transport. From an applied perspective, nanofluidic devices of both 1D and 2D are currently the subject of intensive research effort. Fluid and ion transport in nanometric or subnanometric pores has been shown repeatedly to exhibit features that deviate significantly from continuum behavior,<sup>1-5</sup> paving the way to direct applications in membrane science.<sup>6,7</sup> Throughout the literature on nanofluidics, one key point emerges: the observed processes are linked to the fact that the structure and dynamics of water are significantly affected when water molecules are strongly confined in porous spaces, the dimensions of which are a few molecular diameters or less. This was identified decades ago, and a substantial body of literature, based on both experimental and simulation approaches, has then been produced on the influence of confinement in one or two dimensions on the properties of water.

The numerous studies addressing this question have repeatedly demonstrated that pore sizes and the hydrophilicity/hydrophobicity of the interfaces are crucial parameters controlling the structure and dynamics of confined water. For one-dimensional materials, this latter parameter has been the subject of particular attention since the first simulation study predicting fast water flow in carbon nanotubes<sup>8</sup> was subsequently confirmed experimentally.<sup>9–12</sup> The strong increase in the water flow in carbon nanotubes was attributed to the hydrophobic nature of the carbon surface. Consequently, intense research activity was devoted to tune the

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hydrophobicity in nanoporous structures both to assess the influence of this parameter on the structure and dynamics of water and to develop tailored materials for various applications. Recent reviews<sup>13-15</sup> list the numerous strategies employed for tailoring the hydrophobicity of carbon nanotubes through chemical or physical modifications. Similar approaches have been employed for other nanotubular structures including boron nitride,<sup>16,17</sup> silicon carbide,<sup>18</sup> or imogolite.<sup>19,20</sup> As far as bidimensional materials are concerned, recent developments of nanoconfining sheets have focused on graphene,<sup>21,22<sup>-</sup></sup>graphene oxide,<sup>23</sup> molybdenum sulfide, or MXenes.<sup>24,25</sup> In all of these instances, as with one-dimensional materials, efforts are being made to apply physical or chemical modifications with the objective of fine-tuning the hydrophilicity of the pore surface. Although often effective, such strategies are not without shortcomings, as the introduced modifications do not allow for probing the influence of hydrophilicity on the exact same material. In that regard, attaining precise control over the hydrophilicity of a surface could represent significant progress for analyzing in detail the influence of surface properties on materials that are almost unchanged.

Swelling clay minerals are natural charged bidimensional materials that are systematically present in the inorganic fraction of soil and sedimentary rocks in the first kilometers of Earth's crust. Swelling clays are lamellar minerals that are characterized by the stacking of layers, each of which is formed by an octahedral (oct.) sheet sandwiched between two tetrahedral (tet.) sheets. Due to their structure and their crystal chemistry, the interlayer space (inter.) is filled with cations and water molecules both displaying structural and dynamical properties affected by confinement (Figure 1).<sup>26–28</sup>



**Figure 1.** Snapshots of AIMD calculations showing the structure and interlayer configuration for fluorinated (F-Hect) and hydroxylated hectorite (OH-Hect) under monolayer (1W) and bilayer (2W) water confinement. In the interlayer space, sodium, oxygen, and hydrogen atoms are colored blue, red, and light gray, respectively. For atoms of the clay structure, silicon, magnesium or lithium, fluorine, oxygen, and hydrogen are shown in yellow, purple, cyan, red, and light gray, respectively. Each structure represents a  $3 \times 1 \times 1$  supercell along *a*, *b*, and *c* crystallographic directions.

These changes in properties are associated with both the nanometer-scale bidimensional confinement between clay layers and the polarization of water molecules on the clay surface, owing to the electrostatic field of the clay layers. In addition to their strong environmental and industrial relevance, swelling clay minerals serve as exemplary model systems for

investigating hydrophobicity/hydrophilicity in bidimensional confined systems, offering three key advantages: (i) The extent of confinement can be controlled by adjusting the relative humidity. Swelling clay minerals can thus exhibit both nanometric monolayer (1W) and bilayer (2W) water confinement. (ii) Their surface chemistry can be controlled and well defined crystallographically, and (iii) their hydrophobicity can be modified through synthesis by substituting structural OH groups by fluorine atoms without any additional surface modification. This is exemplified by the case of talc whose hydrophobicity is markedly altered by OH/F substitution<sup>29</sup> as well as by hectorites for which OH/F substitutions significantly affect water uptake in the interlayer space (Figure 1).<sup>3</sup> However, beyond the impact of fluorination on the water uptake, the origin and molecular signature of hydrophilicity/ hydrophobicity under strong bidimensional confinement remain elusive.

The present article focuses on a detailed investigation into the role played by OH-for-F substitution on the molecular hydrophobicity/hydrophilicity signature in bidimensional clay systems. This aforementioned research is made possible thanks to a detailed analysis of the various interactions (i.e., water/ water, water/cation, cation/surface, and water/surface) that occur within the system by combining spectroscopy experiments (inelastic neutron scattering and infrared spectroscopy) and ab initio molecular dynamics simulations for both hydroxylated and fluorinated hectorite samples. The computed structures are initially validated through a comparison with experimental spectroscopic data, taking into account the variations in orientation and confinement of water molecules. Once validated, a more detailed analysis of the computed structures and the underlying interactions that give rise to the observed differences in hydrophobicity and hydrophilicity between hydroxylated and fluorinated systems can be undertaken.

#### 2. MATERIALS AND METHODS

2.1. Samples. The two swelling clay samples used in this study are hectorite clay minerals obtained by hydrothermal synthesis, aiming at an ideal structural formula of  $[Na_{0.8}]^{inter}[Mg_{5.2}Li_{0.8}]^{oct}[Si_{8.0}]^{tet}O_{20}(F,OH)_4$ . The hydroxylated hectorite, hereafter referred to as OH-Hect, was matured at 400 °C and 1 kbar  $P(H_2O)$  during 4 weeks, from a gel precursor, in an externally heated Morey-type pressure vessel with an internal silver tubing.<sup>31,32</sup> The fluorinated hectorite, termed F-Hect, was obtained using similar conditions. The gel was prepared using a two-step procedure, and a sealed gold tube was utilized instead of silver tubing to prevent interactions with the metallic vessel.<sup>30</sup> Both hydroxylated and fluorinated hectorite samples were sodium-saturated by contact with a saline aqueous solution of NaCl (1 mol/L) for a period of 24 h prior to separation of the solid by centrifugation and addition of a freshly prepared saline solution. To ensure complete sodium saturation of the samples, four repetitions of these steps were carried out. Subsequently, the excess sodium chloride was removed through four washing steps of the solid by contact for 24 h with deionized water (Siemens UltraClear, 18.2 MW cm<sup>-1</sup>). The final structural formulas of the samples, previously verified by particle-induced gamma/X-ray emission,<sup>30</sup> are  $[Na_{0.72}]^{inter}[Mg_{5.27}Li_{0.73}]^{oct}[Si_{8.0}]^{tet}O_{20}(OH)_4$  and  $[Na_{0.69}]^{inter}[Mg_{5.31}Li_{0.69}]^{oct}[Si_{8.0}]^{tet}O_{20}(OH)_{0.76}F_{3.24}$ , for OH-Hect and F-Hect samples, respectively.

sample	confinement type	$\langle P_2 \rangle$	water confinement thickness (Å)	water content <sup>a</sup> / O <sub>20</sub> (OH,F) <sub>4</sub>	water content/Na	<i>n</i> H <sub>2</sub> O per 1st hydration shell	% of bonded/free water molecule
hydroxylated	1W	0.86	~2.8	4.0	5.5	3.3	60/40
hydroxylated	2W	0.86	~6.0	9.0	12.5	5.2	42/58
fluorinated	1W	0.85	~2.8	2.7	3.9	3.0	77/23
fluorinated	2W	0.85	~6.0	6.0	8.7	4.3	49/51
<sup>a</sup> Ref 30.							

Table 1. Structural and Interlayer Properties in OH-Hect and F-Hect Samples

2.2. Inelastic Neutron Scattering Experiments and Ab Initio Molecular Dynamics Simulations. 2.2.1. Inelastic Neutron Scattering Experiments. To conduct inelastic neutron scattering (INS) experiments, three oriented specimens were prepared for both OH-Hect and F-Hect samples by drying a sedimented dispersed suspension at 60 °C. The resulting films were then punched out to form a ring-shaped structure (11 mm outer and 4 mm inner diameters) and were stacked to reach a thickness of 7 mm. Subsequently, the samples experienced equilibration at a relative humidity (RH) of  $\approx$ 98%, which was ensured by using a saturated aqueous solution of CuSO<sub>4</sub>. For a second time, two specimens from each sample were subjected to 2 weeks of equilibration with either NaCl (RH  $\approx$  75%) or MgCl<sub>2</sub> (RH  $\approx$  33%) saturated salt solutions, with the objective of achieving homogeneous 2W and 1W water confinements, respectively. Finally, one specimen from each sample was subjected to drying at 110 °C under secondary vacuum conditions to expel the interlayer water and reach a dehydrated state. INS spectra were measured at 10 K in the range of energy transfers from 1 to 500 meV with an energy resolution of  $\Delta E/E \sim 2\%$  using the Lagrange neutron spectrometer installed at the hot source of the highflux reactor at the Institute Laue-Langevin in Grenoble (France).  $^{33,34}$  This energy range was obtained by combining the mosaic Cu(220) monochromator for the intermediate energy range with the elastically bent Si(111) and Si(311)monochromators for the lower energy range. The energy transfer was calculated by subtracting 4.5 meV, the constant final energy of the pyrolytic graphite analyzers, from the energy of the incoming neutrons selected with the different monochromators. Because the final wavevector,  $k_{tr}$  where k  $\equiv 2\pi/\lambda_i$  is much smaller than the incident wavevector  $k_i$  (and therefore high Q), the observed intensity can be considered as directly proportional to the generalized density of states (GDOS), which is the partial density of states,  $g_{\rm H}(E)$  in the case of hydrogenated materials. Oriented hectorite samples were placed in aluminum cells, and INS spectra were recorded using two different orientations of the sample holder to precisely analyze movements in the parallel and perpendicular directions to the clay layers. Data sets were then normalized for monitor counts and corrected for an empty cell.

2.2.2. Ab Initio Molecular Dynamics Simulations. For ab initio molecular dynamics (AIMD) simulations, a  $3 \times 1 \times 1$  supercell was considered to have an integer number of water molecules and Li-for-Mg substitution in the octahedral sheet (2 substitutions per supercell) that corresponds to the chemical composition and water content determined from water vapor desorption experiments and X-ray diffraction profile modeling.<sup>30</sup> For the F-Hect sample, the final composition was  $[Na_{0.66}]^{inter}[Mg_{5.27}Li_{0.66}]^{oct}[Si_{8.0}]^{tet}O_{20}(F)_4$  with 2.66 and 6 H<sub>2</sub>O in the 1W and 2W configurations, respectively (Table 1). For the OH-Hect sample, the composition was  $[Na_{0.66}]^{inter}[Mg_{5.27}Li_{0.66}]^{oct}[Si_{8.0}]^{tet}O_{20}(OH)_4$ 

with 4 and 9 H<sub>2</sub>O in the 1W and 2W configurations, respectively (Table 1). Note that, for the simulated F-Hect sample, the residual amounts of OH in the structure (see Section 2.1) were disregarded to better highlight the contrasted behavior of interlayer species between the two types of samples. For these systems, layer-to-layer distances of 12.56 and 15.7 Å were assigned to 1W and 2W interlayer configurations, respectively. To separate the H-bearing vibration modes of H<sub>2</sub>O from OH groups of the clay layer in the OH-Hect sample and to validate the simulated model, this sample was also simulated in the dried state with a layerto-layer distance of 9.75 Å.30 During AIMD simulations, the atoms are moved according to classical Newton's mechanics, whereas the interatomic forces acting between atoms are computed according to quantum mechanics, solving from first principles the electronic structure for a given set of atomic positions and then calculating the resulting forces on each atoms. In this case, the vibrational spectra can be extracted from MD trajectories, via the time Fourier transform of the velocity-velocity autocorrelation function:

$$g(\omega) = \sqrt{\frac{1}{2\pi}} \int_{-\infty}^{\infty} e^{i\omega t} \sum_{i} \frac{\langle \vec{v}_{i}(t) \cdot \vec{v}_{i}(0) \rangle}{\langle \vec{v}_{i}(0) \cdot \vec{v}_{i}(0) \rangle} dt$$
(1)

 $\frac{\langle \vec{v}_i(t) \cdot \vec{v}_i(0) \rangle}{\langle v_i(t) \cdot \vec{v}_i(0) \rangle}$  is the velocity-velocity where the function  $\langle \vec{v}_i(0) \cdot \vec{v}_i(0) \rangle$ autocorrelation function (VACF), calculated from a chosen initial time (t = 0) for the MD trajectory and for each atom of the system *i*, along all three components of the velocity  $\vec{v}_i$  with  $\omega$  being the angular frequency expressed in rad/s that is converted afterward to cm<sup>-1</sup> for the comparison with the INS results. The AIMD simulations were performed using the CASTEP code.<sup>35</sup> All calculations use optimized ultrasoft pseudopotentials generated with the Perdew-Burke-Ernzerhof (PBE)<sup>36</sup> functional within the generalized-gradient approximation with a van der Waals term. We used a planewave cutoff energy of 500 eV. Optimized structures were used as input to produce AIMD trajectories. They were first equilibrated at 300 K in the NVT ensemble over 4 ps with a 1.0 fs time step. The equilibration run was followed by a production run of 10 ps, performed also in the NVT ensemble at 300 K. The density of states (DOS) was then computed as the time Fourier transform of the velocity autocorrelation function (VACF) computed from the coordinates of each step of the trajectories, as implemented in the mDANSE program.<sup>3</sup>

**2.3.** Mid-Infrared Spectroscopy. Mid-infrared (MIR) spectra were obtained from Fourier transform attenuated total reflection spectroscopy for oriented F-Hect and OH-Hect samples. The spectra were collected using a Nicolet IS 50 (Thermo Scientific Co., Waltham, Massachusetts, USA) equipped with a VeeMax III (Pike Technologies, Fitchburg, Wisconsin, USA) consisting of a germanium crystal ( $n_1 = 4$ ) designed with a 45° angle of incidence ( $\theta$ ). For each sample, a droplet of suspension was deposited directly onto the crystal

were achieved by flushing the samples with dried nitrogen gas. The s (perpendicular)- and p(parallel)-polarized reflectance spectra,  $R_{\rm s}$  and  $R_{\rm p}$ , were measured by placing a ZnSe wire grid polarizer before the sample compartment. The measured  $R_{\rm s}$  and  $R_{\rm p}$  spectra were then analytically transformed into phase-shift spectra,  $\delta_{\rm s}$  and  $\delta_{\rm p}$ , using the Kramers–Kroning relation-ship with  $n_{\infty} = 1.5$  as follows:

humidity generator. Dehydrated conditions for both samples

$$\delta_{\rm s}(\nu_{\rm a}) = I_{\rm s} - \frac{2}{\pi} P \int_0^\infty \frac{\nu \cdot \ln(R_{\rm s})^{1/2}}{\nu^2 - \nu_{\rm a}^2} d\nu \text{ with } I_{\rm s}$$
$$= 2 \arctan \frac{\sqrt{n_1^2 \sin^2 \theta - n_{\infty}^2}}{n_1 \cos \theta} \tag{2}$$

$$\delta_{\rm p}(\nu_{\rm a}) = I_{\rm p} - \frac{2}{\pi} P \int_{0}^{\infty} \frac{\nu \cdot \ln(R_{\rm p})^{1/2}}{\nu^{2} - \nu_{\rm a}^{2}} d\nu \text{ with } I_{\rm p}$$
  
= 2 arctan  $\frac{n_{\rm l} \sqrt{n_{\rm l}^{2} \sin^{2} \theta - n_{\infty}^{2}}}{n_{\infty}^{2} \cos \theta}$  (3)

where *P* indicates the Cauchy principal value, and  $\nu$  corresponds to the wavenumbers. The integration was performed numerically using Mclaurin's formula.<sup>38</sup> The anisotropic extinction coefficients  $k_{para}$  and  $k_{perp}$ , along the parallel or perpendicular direction to the germanium crystal and, thus, of the clay layers, respectively, are then calculated by solving the complex reflection coefficient  $\hat{r}^{j} = R_{i}^{1/2} \exp(i\delta_{i})$  (i = s- or *p*-polarization) and by calculating the anisotropic complex dielectric function.<sup>39,40</sup>

**2.4. Wide-Angle X-ray Scattering Experiments.** The wide-angle X-ray scattering (WAXS) experiments were carried out at the Laboratoire de Physique des Solides (Orsay, France) using a methodology and experimental setup described in detail elsewhere.<sup>41-43</sup> The sample films retrieved after INS experiments were sliced into thin lamellas and mounted on a goniometer head so that the axis of the main stratigraphic direction was perpendicular to the incident X-ray beam and to the MAR345 bidimensional detector (marXperts GmbH, Germany, 150  $\mu$ m pixel size). Orientation distribution functions were deduced from the angular modulation of intensity along the 001 diffraction ring after background subtraction.<sup>41-43</sup>

#### 3. RESULTS AND DISCUSSION

The detailed analysis of the role played by the hydrophobic nature of clay surfaces on the cation-water-surface interactions in 2D confined systems is performed here by combining experiments, i.e., inelastic neutron scattering (INS) and middle-infrared spectroscopy (MIR), with ab initio molecular dynamics (AIMD) simulations. By preparing oriented clay samples and recording INS and MIR spectra following two different orientations of the sample holder (INS) or the electric field (MIR), the cation-water-surface interactions are then investigated by analyzing motions in directions both parallel and perpendicular to the clay layers. Furthermore, humidity conditions were controlled to analyze, in both orientations, two types of confinements in the interlayer space, corresponding to either a monolayer-hydrate (1W) or a bilayer-hydrate (2W) solution (Table 1). Given that the dehydrated (0W) clay layer thickness of both hydroxylated and fluorinated swelling clay minerals is estimated to be ~9.75 Å, it can be deduced that the 1D confinement, or interlayer space, of both OH/F samples is ~2.8 and ~6.0 Å for their 1W and 2W configurations, respectively.<sup>30</sup>

**3.1. Analysis of Particle Orientation in Hydroxylated and Fluorinated Samples.** Comparing the directional dependencies of vibrational modes between hydroxylated and fluorinated clays first requires ensuring that the particles are properly oriented in both samples. The degree of anisotropy in the orientation of clay particles was quantified based on the wide-angle X-ray scattering (WAXS) experiments performed by Dabat et al.<sup>41</sup> on these samples (Figure 2). The collected



**Figure 2.** Extraction of orientation distribution functions of particles in fluorinated (F-Hect) and hydroxylated hectorite (OH-Hect) samples from 2D WAXS measurements. Left: experimental 2D diffraction patterns. The arrow indicates the position of the 001 reflection diffraction ring. Right: corresponding orientation distribution functions from the angular scan of the 001 reflection over 180°.

WAXS images present well-oriented patterns on the 001 reflection rings for both samples, without any contribution of accessory mineral.<sup>30</sup> The obtained average values of the second-order Legendre polynomial parameter (i.e.,  $\langle P_2 \rangle$ ) are calculated from the angular distribution of the intensity corresponding to the 001 reflection for both samples. This parameter evolves from 1 for perfectly oriented particles to 0 for an isotropic organization. The derived  $\langle P_2 \rangle$  values of 0.86 and 0.85 for hydroxylated and fluorinated samples, respectively (Table 1), are consistent with well-oriented samples and thus fully justify that the analysis of the directional dependence of vibrational modes can be directly assigned to specific confinement-related features of cation–water–surface interactions.



**Figure 3.** Experimental (GDOS(*E*)) and calculated ( $g_H$ ) directional dependence of vibrational modes in fluorinated (F-Hect) and hydroxylated hectorite (OH-Hect) samples (a.u.). From top to bottom: dehydrated state (0W), monolayer water configuration (1W), and bilayer water configuration (2W). The spectra obtained along the direction parallel (//) and perpendicular ( $\perp$ ) to the clay layer are shown in green and brown for F-Hect and in blue and red for OH-Hect, respectively. (a) Experimental INS spectra. (b) AIMD calculated the partial density of state of H atoms ( $g_H$ ). The *y*-axis scaled was adapted to enhanced readability. Contributions from structural OH groups of the clay layer and water are highlighted in Figures SI 2 and SI 3.

**3.2. Experimental Validation of Computed INS Spectra.** Inelastic neutron scattering (INS) is a highly powerful molecular probe, offering high sensitivity to vibrations involving hydrogen atoms over a broad energetic spectrum (i.e.,  $5-4000 \text{ cm}^{-1}$ ). It also has the advantage of not being subject to selection rules, in contrast with other common vibrational techniques (e.g., infrared or Raman spectroscopies). As illustrated in Figure 3a, the observed INS intensity is thus directly proportional to the generalized density of states (GDOS(*E*)) as it depends upon the number of vibrating species and on the amplitude of the vibrations of each atom involved in a particular mode weighted by their scattering power  $\sigma_i/M_i$  (with  $\sigma_i$  and  $M_i$  the scattering cross section and mass of atom *i*, respectively) as GDOS( $\omega$ ) ~  $\sum_i \frac{\sigma_i}{M_i} g_i$ , with  $g_i$ being the partial density of state of atom *i*. In contrast to infrared and Raman spectroscopies, where the correctness of the calculated intensities and frequencies requires accurate calculation of the entire potential energy surface and electron density, the ab initio prediction of INS intensity and frequencies by AIMD is more readily achieved since it solely depends on the nucleus amplitude of motion (Figure 3b). It is



**Figure 4.** (a) Experimental MIR spectra in the OH stretching region and (b) calculated  $(g_{H})$  directional dependence of the stretching region for both fluorinated (F-Hect) and hydroxylated hectorite (OH-Hect) samples (a.u.). From top to bottom: dehydrated state (0W), monolayer water configuration (1W), and bilayer water configuration (2W). The spectra obtained along the direction parallel (//) and perpendicular ( $\perp$ ) to the clay layer are shown in green and brown for F-Hect and in blue and red for OH-Hect, respectively.

anticipated that this approach will facilitate a more precise alignment between the calculated and experimental INS spectra, thereby enhancing the precision of the molecular description of the investigated sample. At high energies (>3000 cm<sup>-1</sup>), the definition of INS spectra diminishes due to the Debye–Waller factor, which overdamps the signal, along with degraded energy resolution. Additionally, the presence of overtones and combinations of fundamental bands becomes the dominant factor contributing to signal degradation. In this spectral window, which corresponds to the stretching region of

OH bonds, it is therefore of particular relevance to complement INS experiments with MIR spectroscopy measurements (Figure 4a). The experimental INS spectra of hydroxylated and fluorinated specimens are shown in Figure 3 for the 0W, 1W, and 2W interlayer configurations in both directions parallel and perpendicular to the clay layers. The obtained INS (Figure 3a) and MIR (Figure 4a) spectra are compared to the computed partial hydrogen density of state  $g_{\rm H}$  derived from AIMD shown in Figures 3b and 4b, respectively.

The 0W state is also investigated for validating our model and for assigning the  $GDOS(\omega)$  contribution to the clay layer only.

3.2.1. Validation of AIMD Description of the Clay Layer. In the 0W configuration, which corresponds to the dehydrated state, the calculated  $g_{\rm H}$  for the hydroxylated specimen (Figure 3b) is in reasonable agreement with the experimental INS data (Figure 3a). The data set displays signals attributable to the presence of structural OH groups from the clay layer. These hydroxyls can be evidenced by (i) the sharp peak at ~650 cm<sup>-1</sup>, corresponding to (Mg,Li)<sub>3</sub>OH libration modes, that is only visible in the parallel direction in the simulated spectrum and (ii) as a doublet around 3790 cm<sup>-1</sup> that is only observed in the perpendicular direction for the calculated spectra (Figure 4b). The latter band is discernible but poorly defined in experimental INS spectra due to the increased influence of the Debye-Waller factor with increasing energy transfer (Figure SI 1). It is therefore pertinent to validate experimentally the computed  $g_{\rm H}$  in the stretching region through a comparison with the MIR spectra obtained on the similar oriented specimens (Figure 4a). In this regard, the MIR spectra exhibit relatively close agreement with the computed  $g_{\rm H}$ . However, it should be noted that stretching OH vibrations are also observed for the fluorinated sample in both INS and MIR spectra (Figure SI 1 and Figure 4a), which is consistent with the residual hydroxylation of the structure ( $\sim$ 20% of structural OH groups; see Section 2.1). The INS spectra (Figure 3a) for both hydroxylated and fluorinated dehydrated clays display the presence of additional peaks belonging to vibrational modes that do not involve OH groups, i.e., Si-O-Si bending or Si-O stretching vibrational modes and their associated overtones.<sup>44</sup> The agreement between computed  $g_{\rm H}$  and experimental spectra for the dehydrated specimen demonstrates that the clay layer is correctly described in the AIMD simulations. Accordingly, the additional experimental signals that are observed in the hydrated 1W and 2W samples can be directly assigned to H-bearing vibrations of confined water molecules (Figures 3 and 4) and can be compared to computed  $g_{\rm H}$ .

3.2.2. Influence of Confinement on Water Vibrational Properties. The H-related vibration modes of water in 1W and 2W confinements can be separated into four distinct regions (the three first are highlighted in Figure 3), namely, lattice translational modes  $(0-300 \text{ cm}^{-1})$ , molecular libration (300-1500 cm<sup>-1</sup>) modes, bending  $(1500-2000 \text{ cm}^{-1})$ , and stretching modes (>3000 cm<sup>-1</sup>). Simulated spectra reveal significant differences between the parallel and perpendicular orientations for all vibrational modes in both 1W and 2W confinements (Figure 3b). Such a feature can also be evident in the experimental spectra (Figures 3a and 4a), which corroborate the well-oriented nature of the samples (Figure 2). In the very low-energy region associated with lattice translational modes, some misfits in peak position between experimental and calculated spectra can be noticed. Such discrepancies can be attributed to the limited size of the simulation box, which does not capture the full range of water network configurations necessary for accurately describing the intermolecular modes. In both experimental and calculated spectra, the libration modes (including rocking, twisting, and wagging of the rigid water molecule) exhibit a shift toward higher energy transfers when the confinement is reduced (i.e., between 1W and 2W interlayer configurations). Such evolution, also visible in the lattice modes as well as the molecular libration regions  $(0-1500 \text{ cm}^{-1}; \text{ Figure 3b})$ , is fully consistent with increased water content and improved

development of the hydrogen-bond network.44-47 The strengthening of hydrogen-bond networks is also evidenced by a shift toward higher energy transfer of the bending modes of water between 1W and 2W confinements (Figure 3a,b). Indeed, in the absence of intermolecular couplings, the bending vibrational mode serves as a direct indicator of the net water intramolecular structure. The significant change in bending mode frequency between the 1W and 2W configurations, accompanied by a change in band profile with orientation (Figure 3a,b), confirms the more extensive development of the hydrogen-bond network in the 2W confinement. The stretching vibration is also sensitive to the hydrogen-bond network. However, as it involves a very complex interplay between intermolecular and intramolecular couplings as well as the presence of multiphonons, a straightforward interpretation of this spectral region is rather challenging. Nevertheless, an examination of the parallel direction in which structural hydroxyl vibrations do not interfere reveals a shift toward lower energies for 2W specimens, which also points toward an enhanced development of the hydrogen-bond network.<sup>48</sup> A similar conclusion can be drawn from the MIR spectra, which also reveals a more developed hydrogen-bond network in the 2W confinement.

3.2.3. Influence of Hydrophobic/Hydrophilic Nature of the Clay Surface on Water Vibrational Properties. The role played by the hydrophobic/hydrophilic nature of the clay surface can be assessed by comparing hydroxylated and fluorinated INS spectra for a given type of confinement and orientation, respectively, to clay layers. As far as libration modes are concerned, in 1W confinement, replacing OH by F induces a small apparent shift of the main band toward lower energy transfers, visible in both experimental and calculated spectra (Figure 3a,b). This shift may indicate an alteration of the hydrogen-bond network in the fluorinated specimen. Such an effect appears to be attenuated for the 2W configuration due to the limited influence of the surface on the water network when decreasing the confinement (Figure 3b). The bending mode spectral profile in 1W confinement reveals two components located at 1610 and 1650 cm<sup>-1</sup>. Given that water molecules exhibit a single bending mode, these two components may be interpreted as originating from two distinct water populations coexisting in the sample, which may be assigned to water coordinated to interlayer cations or to surface water. The existence of two water populations deduced from the analysis of the bending region is further confirmed by the MIR spectra (Figure 4a), which exhibit a systematic blueshift of the high-frequency stretching band at 3630 cm<sup>-1</sup>, especially visible in F-Hect (Figure 4b, 1W) that can be assigned to the presence of free water, most likely hydrating clay surfaces. The F-for-OH replacement in the clay structure and the associated modulation of the hydrophobic/hydrophilic nature of the surface result in a clear modification of spectral vibration modes. The reported changes are likely associated with a lower water content in the fluorinated specimen, indicating the existence of a contrasted water population as well as an altered hydrogen-bond network in the F-Hect sample.

**3.3. Exploiting AIMD for Revealing the Influence of Hydrophobic 2D Charged Surfaces.** In agreement with experimental INS and MIR data, the calculated  $g_H$  spectra show a clear dependence of the water hydrogen-bond network on the orientation, confinement, and hydrophobic/hydrophilic nature of the clay surface. These computed results can now be



**Figure 5.** Interlayer atomic density profiles along the *z*-axis of unit cells for oxygen (red) and hydrogen (light gray) atoms of water molecules and (blue) sodium atoms associated with fluorinated and hydroxylated hectorite samples (F-Hect and OH-Hect, respectively). Atomic *z*-coordinates are given in Angstroms relative to the interlayer midplane. Right: bilayer water configuration (2W). Left: monolayer water configuration (1W). The green vertical dotted lines represent the surface of clay layers. For OH-Hect 2W, the vertical gray bars highlight the difference in main O plane positions between fluorinated and hydroxylated 2W water configurations.

employed to analyze in-depth the intimate cation—water surface interactions at a molecular level and the influence of surface hydrophobicity on confined fluids in clay bidimensional charged systems.

3.3.1. Stability of the Structure Induced by Cationic Hydration. For natural 2D clay materials, the type of confinement (i.e., 1W or 2W) is known to be linked to the nature and hydration of the cation.<sup>49</sup> At the RH value considered here and for both interlayer configurations, the water confinement thicknesses are found to be similar, irrespective of the OH vs F substitution. This is evidenced by the values of 2.8 and 6 Å for 1W and 2W configurations,<sup>30</sup> respectively (Table 1). To better understand this feature, AIMD simulations can be employed to derive the atomic density profiles along the z-axis of the simulation box (Figure 5). These profiles demonstrate a comparable overall cationic organization for both the hydroxylated and fluorinated samples. In both cases, cations are situated in the middle of the interlayer for the 1W configuration and distributed more widely along the z-axis in the 2W configuration. Furthermore, the specific cation-water interaction for these two types of samples is most effectively represented by the computed radial distribution functions (RDFs)  $gNa - O_{water}(r)$ , which indicate the probability of finding an O atom from a water molecule at a distance r from an interlayer Na cation (Figure 6a). The associated coordination number function (i.e.,  $CN_{H_2O}(r)$ function; Figure 6a) allows extracting the average number of water molecules surrounding the interlayer Na cations from the values of the first plateau (at r = 3.25 Å). This results in the

formation of hydration shells containing  $\sim$ 3.3 and  $\sim$ 3.0 H<sub>2</sub>O/ cation in 1W and  $\sim$ 5.2 and  $\sim$ 4.3 H<sub>2</sub>O/cation in 2W interlayer configuration for the OH-Hect and F-Hect specimens, respectively (Table 1). Furthermore, by normalizing the water content of each cell to its number of cations, one can estimate the total quantity of water per cation (Table 1). The extraction of water in the first hydration sphere allows for the estimation that, within this hydration shell, approximately 77% of water is bound to the cation for 1W F-Hect and 60% for the OH counterpart. This value decreases to 49% for 2W F-Hect and 42% for 2W OH-Hect. The influence of fluorine on the interlayer marginally affects the quantity of water per cation, resulting in reductions of 10 and 18% in the 1W and 2W samples, respectively. It should be noted, however, that the order of magnitude of this decrease is less important than the overall reduction in water content (i.e., a 30% decrease in F-Hect compared to OH-Hect). Finally, the quantification of bound water vs free water revealed that the diminished water content in F-Hect is predominantly attributable to water molecules that are not coordinated within the first hydration shell of cations. The cation/water cluster thus remains relatively constant for OH-Hect and F-Hect, which may also explain why both samples exhibit analogous layer-to-layer distances or interlayer space thickness, as evidenced experimentally from X-ray diffraction.<sup>30</sup> It thus can be reasonably deduced that the primary impact of a more hydrophobic surface on confined water will be observed in changes in the interactions between water-clay surfaces and water-water. These changes are examined in further detail below.



**Figure 6.** (a) Radial distribution functions  $gNa - O_{water}(r)$  (solid lines) and the associated number of water molecules  $NH_2O(r)$  (dotted lines) surrounding the interlayer cations (b) Radial distribution functions of  $gO_{surface} - H_{water}(r)$  and (c)  $gO_{water} - H_{water}(r)$ . Each function is derived from AIMD simulations for fluorinated and hydroxylated hectorite (F-Hect and OH-Hect, respectively). Top: monolayer water configuration (1W). Bottom: bilayer water configuration (2W).

3.3.2. Evidence of Enhanced Surface Water Repulsion in Hydrophobic Samples. One of the most significant effects associated with the hydrophobicity of fluorinated clay surfaces is illustrated by the RDF between the O atoms from the clay layer surface and the H atoms from water (i.e., gO<sub>surface</sub> - $H_{water}(r)$ ; Figure 6b). For a comparison of the F-Hect and OH-Hect samples in both 1W and 2W water confinements, the computed  $gO_{surface} - H_{water}(r)$  reveals a significant and systematic positional shift of ~0.15 Å of the first neighboring H from water at  $r \sim 2$  Å. This suggests that the fluorine atoms in the structure exert a systematic repulsion on the water molecules, causing them to move away from the surface. This effect of fluorine on the water molecules can also be observed in the atomic density profiles, where the main O planes are shifted outward from the surface in the F specimens in the 2W water configuration (Figure 5). Additionally, the hydrogen atoms are also displaced from the surface, becoming more polarized with respect to the positions of the oxygen atoms. This results in the emergence of dangling modes pointing out the surface. The presence of these modes is evident in Figure 3, wherein stretching bands shift to higher energies, indicating the presence of nearly free hydrogen bonds. This difference represents direct evidence of the role played by fluorinated surfaces in the properties of confined water in clay bidimensional systems and is likely at the origin of the reduced amount of water molecules in the F-Hect samples.

3.3.3. On the Deep Modification of the Water Hydrogen-Bond Network. Our findings demonstrate that the incorporation of fluorine into the clay structure exerts a direct influence on the distance at which water molecules approach clay surfaces, as well as on the overall water content. Further analysis is required to determine whether the influence of fluorine extends to larger distances within the interlayer bidimensional pores. Such an assessment can be done based on the  $gO_{water} - H_{water}(r)$  RDF (Figure 6c). In the case of liquid water, a shift of the first neighbor on the  $gO_{water} - H_{water}(r)$ curve, corresponding to the intramolecular O-H distance, implies a modification of the hydrogen-bond network. Although subtle, water molecules in the fluorinated sample F-Hect present a mean O-H distance systematically shorter by ~0.005 Å compared to the hydroxylated sample displaying intramolecular O-H distance values of 0.975 and 0.980 Å in 1W and 2W, respectively (insets in Figure 6c). While acknowledging the possibility of a statistical error in such small discrepancy, one may also tentatively assign this observed reduction in intramolecular O-H distance to the hypothesis of an altered water hydrogen-bond network in the F-Hect sample. This is due to the reduction in water amount, which results in O-H distance values that are closer to those of individual water molecules in a vacuum.<sup>50</sup> Beyond the intramolecular O-H distances (i.e., > 1 Å) the  $gO_{water} - H_{water}(r)$  RDF reveals the intermolecular organization of the hydrogen-bond network (Figure 6c). Bulk water typically exhibits first- and secondneighbor peak positions at 1.90 and 3.40 Å, respectively.<sup>51,52</sup> On  $gO_{water} - H_{water}(r)$  RDFs, these peaks are located at comparable positions in both 1W and 2W water confinements.



Figure 7. Molecular hydrophobic signature. (a) Evolution of free energy  $\cot \Delta \mu_v(z)$  of spherical probe insertion with different radii *r* along the *z*-direction. (b) Similar to panel (a) along the *z*-direction after correction from the probe radius *r* for the F-Hect sample under 2W water confinement. Panels (a) and (b) share the same color legend standing for the different radii in Å. The location of the interlayer equilibrium position  $z_{eq}$  (for which  $z_{eq} - r = 0$ ) is represented with gray crosses, while the position of the interlayer midplane  $z_{mid}$  is marked by black crosses. (c) Evolution of  $\Delta \mu_v(z^*)$  at position  $z^* = z_{eq}$  and/or  $z_{mid}$  of the different Hectorite specimens and comparison with the SPC water model for bulk water. (d) Same legend as panel (c) but by normalizing the free energy cost by the surface of the spherical probes.

The third-neighbor position, typically situated at 5.4 Å in bulk water,<sup>52</sup> is located in a region where the simulation is not significant as, beyond r = 4.55 Å (i.e., half of the AIMD simulation box), the statistics of the RDF begin to collapse. Comparison of the maxima positions for F-Hect and OH-Hect on  $gO_{water} - H_{water}(r)$  RDFs reveals contrasted behaviors depending on the degree of confinement. In the 1W confinement, the presence of fluorine induces a shift of the two water-water neighbors toward shorter distances, whereas the situation is reverse for the 2W configuration (red arrows on Figure 6c). This suggests that the reduction in water quantity, regulated by the hydrophobic fluorinated surfaces, results in a profound alteration of the intermolecular organization of water molecules. Although the observed shifts are similar to those found in liquid water, they are likely dependent on the orientation of water molecules. As seen in the atomic density profiles (Figure 5), for OH-Hect samples in both 1W and 2W configurations, the hydrogen distribution displays a dominating

contribution roughly at z-positions similar to those of the oxygen atoms. However, for F-Hect, the orientation of water molecules differs significantly with a shift of the hydrogen principal contribution out of the main z-altitude of oxygens. This results in a complete modification of water orientation in fluorinated specimens, which makes comparison with liquid water networks challenging. Consequently, using intermolecular O–H distances derived from RDFs is not an optimal approach for characterizing molecular hydrophobicity.<sup>53</sup> As demonstrated in the following sections, investigating density fluctuations is a more relevant avenue of inquiry.

3.3.4. Energetics of Molecular Hydrophobicity. At the molecular scale, the primary consequence of hydrophobicity on water molecules is an increased density fluctuation, which promotes the formation of cavities or voids in regions of space where hydrogen bonding is impeded.<sup>53–58</sup> A quantitative assessment of molecular hydrophobicity can thus be achieved by evaluating the probability of cavity formation in a solvent.<sup>56</sup>

Based on the work of Serva et al.,<sup>58</sup> which demonstrated the adaptability of this approach to confined water near metal surfaces, the same methodology is adapted here for the characterization and quantification of the molecular hydrophobicity properties of confined interlayer water in charged bidimensional systems. In essence, an increase in the hydrophobicity is anticipated to disrupt the hydrogen-bond network, thereby elevating the probability of void formation in the interlayer space. The method thus relies on extracting the probability  $(Pv_{(0)})$  of finding zero water oxygen and/or cation within a spherical volume (v) of given radius (r) within the simulation cells. A total of 100 AIMD simulation frames (of 100 fs intervals), with 10000 insertions attempted per frame with spherical probes of varying radii (i.e., r = 1.25, 1.50, 1.75,2.00, 2.25, 3.00, 3.25, and 3.50 Å), were performed at random positions along the *x*-, *y*-, and *z*-axes of the simulation cell. The probability  $Pv_{(0)}$  was then extracted along the z-direction  $(Pv_{(0,z)})$  by discretization into 125 equally spaced bins. This probability is directly related to the free energy cost  $\Delta \mu_{\rm v}(z)$  of cavity formation 53-58 as

$$\Delta \mu_{\nu}(z) = -k_{\rm B} T \ln(P \nu_{(0,z)}) \tag{4}$$

with  $k_{\rm B}$  the Boltzmann constant, and T is the temperature.

The obtained  $\Delta \mu_{\rm v}(z)$  profiles, symmetrized along the zdirection relative to the interlayer midplane, are illustrated in Figure 7a,b in the case of the F-Hect sample under 2W water confinement. Near the clay surface, the free energy cost  $\Delta \mu_{\rm v}(z)$ increases drastically, highlighting the unfavorable formation of cavities in the clay layer due to the elevated density of atoms (left in Figure 7a). As the distance from the surface increases, a minimum that is shifted as a function of the probe radius is systematically observed. This equilibrium point  $(z_{eq})$  is equivalent to the position of the clay surfaces that have been added to the spherical probe radius and reveal the typical position occupied by hydrophobic molecules in outer-sphere adsorption complexes.<sup>58</sup> This apparent shift can be corrected<sup>58</sup> by accounting for the sphere radius through the entity  $z_{eq} - r$ (Figure 7b). The free energy cost  $\Delta \mu_{\rm v}(z)$  required to form a cavity in this most stable position can then be evaluated for the 4 specimens at the position  $z_{eq} - r = 0$  as shown in Figure 7c. Similarly, in the case of bidimensional materials, an additional equilibrium point may be identified, namely, the z-position of the interlayer midplane,  $z_{mid}$ , represented by crosses in Figure 7b. In contrast with  $z_{eq}$ , the  $\Delta \mu_v(z = z_{mid})$  evolution provides further insight into the accommodation of hydrophobic molecules within the water layer hydrate. It should be noted that position z will be referenced in Figure 7 as  $z^*$  when the latter refers to either position  $z_{\rm eq}$  or  $z_{\rm mid}$ .

It can be observed that, with the exception of OH-Hect 2W, at  $z_{mid}$ , the free energy costs are consistently lower in the clay water confined systems, regardless of probe radius, than in bulk water (Figure 7c). This indicates that, irrespective of the *z*-altitude considered (i.e.,  $z_{eq}$  or  $z_{mid}$ ), the formation and accommodation of hydrophobic solutes with radii up to r = 3.25 Å are consistently more favorable than in bulk water. This is primarily attributable to the substantial proportion of the interlayer space that remains vacant due to the van der Waals repulsion of oxygen atoms from the clay surface. This results in amplified density fluctuations under confinement, increasing the probability of empty sphere formation, which consequently reduces the  $\Delta \mu_v$  values (Figure 7c). Note however that, for the most hydrated system, i.e., OH-Hect 2W, at  $z_{eq}$  an isoenergetic point is reached with the water model for a cavity with a radius

of 3.25 Å. Furthermore, the free energy cost for sample OH-Hect 2W at  $z_{mid}$  even goes beyond the bulk water model for a cavity radius above 2.25 Å. For this specific case, the results thus indicate that the accumulation of larger hydrophobic solutes is no longer favorable in comparison with bulk water. All data gathered (Figure 7c) also demonstrate that, irrespective of the hydration state and z position, the F-Hect samples consistently exhibit lower  $\Delta \mu_{v}(z)$  values when compared to OH-Hect. This phenomenon is attributed to the increased water density fluctuations, which, as previously detailed, facilitate the accommodation of cavities. This new finding is highlighted for the first time in the case of confined systems and can be seen as the signature of the role played by the fluorination of the clay surfaces in the hydrogen-bond network disturbance. It can be argued that, despite exhibiting comparable patterns, the free energy costs are consistently higher in the middle of the interlayer region than at the surface equilibrium point. In more precise terms, the effect of the fluorine is therefore even more significant in the vicinity of the surface.

Nevertheless, a more detailed comparison of the OH-Hect and F-Hect systems (Figure 7d) reveals further insights when the free energy costs are normalized with respect to the surface area of the spherical probes.<sup>58</sup> It is important to note that the free energy cost  $\Delta \mu_{\rm v}$  is directly related to the size of the hydrophobic cavity introduced into the fluid.<sup>54</sup> By normalizing the free energy cost to the cavity surface area, the  $\frac{\Delta \mu_v}{4\pi r^2}$  relation evolves as a function of r following two typical regimes. For small cavities, hence, small *r* values,  $\frac{\Delta \mu_v}{4\pi r^2}$  is directly proportional to the volume of the cavities, i.e, dimensional analysis reveals that  $\frac{\Delta \mu_v}{4\pi r^2} \rightarrow \frac{r^3}{r^2} = r$ . In other words, in such a regime, a linear relationship is observed between the normalized free energy cost and the cavity radius. This reflects the molecular reorganization occurring locally around the cavity surface without disturbing global interactions. In this volumedominated regime, the molecules are able to readily reorganize themselves around the cavities, which has been attributed to a predominantly entropy-dominated state.<sup>54</sup> For higher cavity radii, a change is observed and the previously linear relationship between the variables ceases to exist and instead becomes a constant relation with increasing r, thus denoting a surface-driven regime, i.e.,  $\frac{\Delta \mu_c}{4\pi r^2} \rightarrow \frac{r^2}{r^2} = \text{cst.}$  In this regime, the free energy cost of a hydrophobic cavity is predominantly influenced by interactions between water molecules and the hydrophobic/cavity surface. This regime is distinguished by the reorganization of water molecules in the vicinity of the cavity with the objective of minimizing contact between water and the hydrophobic surface. In this context, the impact on water molecules is at a greater scale, implying the disruption of hydrogen bonds and a more energy-intensive reorganization of water molecules around the cavity. For this reason, this regime is often referred to as an enthalpic-driven state.<sup>54</sup>

With regard to the 2W water confinement at position  $z_{eq}$  (Figure 7d, left), this representation demonstrates a proportional increase in the quantity  $\left(\frac{\Delta\mu_{\rm v}(z^*)}{4\pi r^2}\right)$ , which is consistent with a volume-dominated regime of cavity formation.<sup>58</sup> In contrast, the 2W water confinement at position  $z_{\rm mid}$  (Figure 7d, right) exhibits both trends, with the volume-dominated regime valid up to r = 2.25 and 3 Å for F-Hect and OH-Hect,

respectively. This trend in evolution has been repeatedly reported in the case of solute at the solid-solute interface and corresponds to the aforementioned transition from volumedominated to surface-dominated regime.<sup>54,56,58</sup> Once a clear plateau has been reached, the surface-dominated regime is established for both samples. Hence, in 2W states, close to the clay surface, the accumulation of hydrophobic solutes remains a possibility, with F-Hect exhibiting a difference of 12 kJ mol<sup>-1</sup> relative to OH-Hect for the r = 3.25 Å cavity. This discrepancy increases in the interlayer midplane (i.e.,  $z_{\rm mid}$  for similar rradius), with a 15 kJ mol<sup>-1</sup> difference between OH-Hect and F-Hect. Consequently, the incorporation of hydrophobic solutes becomes even more challenging in the OH-Hect interlayer midplane compared to the F-Hect one due to the important amount of interlayer water and cation. Furthermore, the early change in regime (i.e., cavity of r = 2.25 Å) in F-Hect indicates a saturation of the system, thereby exposing the challenging reorganization of water with greater probe radius, thus highlighting the rigid hydrogen-bond network in fluorinated systems.

The situation becomes even more contrasted in the case of 1W confinement where the change in slope of the  $\left(\frac{\Delta\mu_{\rm v}(z^*)}{4\pi r^2}\right)$ quantity evolution with cavity volume is also observed for r >2.25 Å at position  $z_{eq}$  (left on Figure 7d). The reduced number of water molecules and the limited space available force the previous 2W trends to shift to the surface in the outer-sphere complex region. The difference between OH-Hect and F-Hect increases to reach a maximum of 6 kJ mol<sup>-1</sup> for the r = 2.75 Å cavity. At the  $z_{\rm mid}$  position, the volume regime is completely absent for F-Hect. In contrast, the OH-Hect sample remains in the volume regime with a clear linear trend. Note that, at this position, the difference between OH-Hect and F-Hect also increases, reaching also a maximum of 6 kJ mol<sup>-1</sup> for the r =2.75 Å cavity. The limited confinement of 1W prevents the widening of the energetic variations between  $z_{\rm mid}$  and  $z_{\rm eq}$ positions, thus reflecting a less contrasted density between OH-Hect and F-Hect, compared to the 2W configuration. Nevertheless, the 1W interlayer appears globally in a surfaceoriented regime, which testifies to the important structuring of the water network, i.e., again even larger for the F-Hect sample.

#### 4. CONCLUSIONS

The present study reports extensive spectroscopic and simulation data on the influence of hydrophobicity of charged clay surfaces on water-cation-surface interactions under bidimensional confinement. The INS and MIR data obtained along the parallel or perpendicular direction of the lamellar surface demonstrate the role played by confinement, orientation, and fluorination of the clay surface in the water properties. The comparison between AIMD and experimental data is consistent and allows carrying out of a detailed analysis of the properties of confined water.

The cation—water interactions appear to be only minimally affected by the surface hydrophobicity. The presence of a comparable water hydration shell for both F-Hect and OH-Hect samples likely explains the similar layer-to-layer distances observed for both samples. This reveals that the strong cation water coupling governs the layer-to-layer distances, thus overriding the surface water interactions in these samples. The observed reduction in water content and the resulting increase in molecular hydrophobicity are therefore primarily attributable to the behavior of water molecules that are weakly bonded to cations and just hydrating the surfaces. This effect is revealed by the fact that water molecules are more repelled from the fluorinated clay surface than from the hydroxylated one. Such a modification is accompanied by a profound reorganization of the intramolecular and intermolecular water distances.

The quantitative description of nanoscale hydrophilicity/ hydrophobicity in charged bidimensional materials is a complex task. Our results likely plead for a complex interplay between different interactions (surface water, surface-cation, and cation-water). These individual interactions need to be individually analyzed to reach a full picture of the systems and to understand the development of different hydrogen-bond networks. By analyzing density fluctuation and cavity formation, we were able to quantitatively compare the free energy costs associated with both the hydroxylated/fluorinated nature and extent of bidimensional confinement. Although the interpretation given regarding the surface-driven vs volumedriven regimes described here could benefit from additional spectroscopy techniques such as terahertz spectroscopy<sup>59,60</sup> on the same samples, it was shown that the free energy cost can be related to macroscopic wettability properties.<sup>53</sup> This finding is likely of interest in the condensed-matter community as it could, on the one hand, help in the understanding of the macroscopic wetting properties of a large class of existing 1D and 2D materials and, on the other hand, help in the rational design of synthetic nanomaterials with controlled properties.

In that regard, a logical perspective of this work would be to further investigate the role played by charge density and the OH/F partially exchanged specimen in such a molecular hydrophobicity signature in an effort to refine the potential control on the obtained materials.

#### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpca.4c04922.

Experimental GDOS(E) spectra of F-Hect and OH-Hect in dehydrated/monolayer/bilayer states with ice Ih reference, calculated GDOS(E) spectra for OH-Hect, and calculated GDOS(E) spectra for F-Hect (PDF)

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#### Notes

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## Supporting Information for:

# Molecular hydrophobicity signature in charged bidimensional clay materials

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S1: Experimental (GDOS(E)) directional dependence of vibrational modes in fluorinated (F-Hect) and hydroxylated hectorite (OH-Hect) samples (a.u.). From top to bottom: dehydrated state (0W), monolayer water configuration (1W) and bilayer water configuration (2W). The spectra obtained along the direction parallel (//) and perpendicular ( $\perp$ ) to the clay layer are shown in green and brown for F-Hect, and in blue and red for OH-Hect, respectively. Experimental GDOS(E)) for ice Ih is also provided.



SI 2: Calculated (GDOS(E)) directional dependence of vibrational modes in hydroxylated hectorite (OH-Hect) samples (a.u.). From top to bottom: dehydrated state (0W), monolayer water configuration (1W) and bilayer water configuration (2W). The spectra obtained along the direction perpendicular ( $\perp$ ) and parallel (//) to the clay layer are on the left and the right side of the figure, respectively. Calculated partial density of state of H atoms ( $g_H$ ) is shown in black. Contributions from structural OH groups of the clay layer and from the water are highlighted in red and blue, respectively.



S2

SI 3: Calculated (GDOS(E)) directional dependence of vibrational modes from the interlayer water in fluorinated hectorite (F-Hect) sample (a.u.). From top to bottom: dehydrated state (0W), monolayer water configuration (1W) and bilayer water configuration (2W). The spectra obtained along the direction perpendicular ( $\perp$ ) and parallel (//) to the clay layer are on the left and the right side of the figure, respectively.

