

# Structure and Dynamics of Water-Smectite Interfaces: Hydrogen Bonding and the Origin of the Sharp O-Dw/O-Hw Infrared Band From Molecular Simulations

Marek Szczerba, Artur Kuligiewicz, Arkadiusz Derkowski, Vassilis Gionis,

Georgios D. Chryssikos, Andrey G. Kalinichev

# ▶ To cite this version:

Marek Szczerba, Artur Kuligiewicz, Arkadiusz Derkowski, Vassilis Gionis, Georgios D. Chryssikos, et al.. Structure and Dynamics of Water-Smectite Interfaces: Hydrogen Bonding and the Origin of the Sharp O-Dw/O-Hw Infrared Band From Molecular Simulations. Clays and Clay Minerals, 2016, 64 (4), pp.452-471. 10.1346/ccmn.2016.0640409 . in2p3-01577621

# HAL Id: in2p3-01577621 https://hal.in2p3.fr/in2p3-01577621

Submitted on 9 Oct 2018

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

1	
2	Structure and dynamics of water-smectite interfaces:
3	Hydrogen bonding and the origin of the sharp $O-D_w/O-H_w$ infrared band
4	from molecular simulations
5	
6	Marek Szczerba <sup>1,*</sup> , Artur Kuligiewicz <sup>1</sup> , Arkadiusz Derkowski <sup>1</sup> ,
7	Vassilis Gionis <sup>2</sup> , Georgios D. Chryssikos <sup>2</sup> ,
8	Andrey G. Kalinichev <sup>3</sup>
9	
10	<sup>1</sup> Institute of Geological Sciences, Polish Academy of Sciences, Krakow, Poland
11	
12	<sup>2</sup> Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation,
13	Athens, Greece
14	
15	<sup>3</sup> Laboratoire SUBATECH (UMR 6457), Ecole des Mines de Nantes, Nantes, France
16	
17	
18	*) Corresponding author: <u>ndszczer@cyf-kr.edu.pl</u>
19	
20	
21	KEY WORDS: clay-water interface, adsorbed water, smectite, molecular dynamics, infrared
22	spectroscopy
23	

#### ABSTRACT

Experimental studies have shown that a sharp high-frequency IR band at  $\sim$ 3615 cm<sup>-1</sup> 25 (in H<sub>2</sub>O form) and at ~2685 cm<sup>-1</sup> (in D<sub>2</sub>O form) is a common feature for all smectites, and its 26 position correlates with layer charge. In order to explain the molecular origin of this band in 27 terms of total layer charge, charge localization, as well as nature of interlayer cations 28 influencing the position and intensity of this peak, a series of classical MD simulations were 29 performed for several smectite models. The smectite layers were described using a modified 30 CLAYFF force field, where the intramolecular vibrations of H<sub>2</sub>O were more accurately 31 described by the Toukan-Rahman potential. The power spectra of molecular vibrations of 32 33 hydrogens were calculated for selected sub-sets of interlayer H<sub>2</sub>O to quantitatively analyze their contribution to the observed spectral features. The statistics of hydrogen bonds in the 34 smectite interlayers were also analyzed to support the spectral calculations. 35

The simulation results demonstrated clearly that only the H<sub>2</sub>O molecules in close 36 proximity with the smectite surface are responsible for the observed sharp vibrational band. 37 Other hypotheses on the possible origins of this band were carefully considered and 38 eventually rejected. Two orientations of H<sub>2</sub>O molecules donating one or two H-bonds to the 39 basal oxygens of the smectite surface (monodentate and bidentate orientations, respectively) 40 are observed. In both orientations these H-bonds are quite weak, pointing to a generally 41 hydrophobic character of the smectite surface. Both orientations were found to contribute to 42 the high-frequency band, but the monodentate orientation provides the predominant 43 contribution because surface H<sub>2</sub>O molecules in this orientation are much more abundant. In 44 good agreement with experiment, only a small difference in the peak position was observed 45 between smectites with different charge localization. The effect of the total layer charge, i.e. 46 the red-shift for higher charge smectites, was also confirmed. This shift arises from the 47 decrease of the H-bonding distances of H<sub>2</sub>O in monodentate and bidentate orientation. 48

#### **INTRODUCTION**

Fourier transform infrared spectroscopy (FTIR) is one of the most commonly used techniques for studying clay minerals. However, unambiguous assignment of the vibrational bands originating from the stretching modes of adsorbed molecular  $H_2O$  (O-H<sub>w</sub>) and structural OH (O-H<sub>s</sub>) in the clay materials is not always feasible. This is especially true for swelling clay minerals like smectites, which have large water sorption capacities (e.g., Cases *et al.*, 1997; Sato *et al.*, 1992) and may contain significant amounts of adsorbed water under air-dry conditions even upon prolonged drying (e.g., Środoń and McCarty, 2008).

Kuligiewicz *et al.* (2015a) have recently presented new evidence that the sharp highfrequency bands observed at ~3610-3640 cm<sup>-1</sup> involve a significant contribution from weakly hydrogen-bonded O-H<sub>w</sub> of adsorbed H<sub>2</sub>O molecules. These observations were in agreement with earlier spectroscopic measurements (Russell and Farmer, 1964; Farmer and Russell, 1971; Suquet *et al.*, 1977; Sposito and Prost, 1982; Cariati *et al.*, 1981, 1983; Sposito *et al.*, 1983), and opened the possibility for obtaining layer charge diagnostics based on the vibrational signature of H<sub>2</sub>O in smectite (Kuligiewicz *et al.*, 2015b).

Early computational molecular modeling studies of clays (Skipper *et al.*, 1991; Chang *et al.*, 1995; Boek *et al.*, 1995; Greathouse and Sposito, 1998; Sposito *et al.*, 1999) suggested the existence of H-bonds between water and siloxane surfaces. This H-bonding implies a specific spatial arrangement of the surface  $H_2O$  molecules with respect to oxygen atoms of the basal plane. These MD calculations confirmed the model of Prost (1975) with one O-H<sub>w</sub> bond of the H<sub>2</sub>O molecule directed towards the clay surface, donating an H-bond to the basal oxygen atom.

The existence of such interfacial H-bonding with one O-H<sub>w</sub> bond oriented towards the clay surface was later confirmed by simulations of smectites and muscovite (e.g. Wang *et al.*, 2005b, 2009; Marry *et al.*, 2008, 2013; Morrow *et al.*, 2013; Ngouana Wakou and Kalinichev,

2014; Greathouse et al., 2015; Teich-McGoldrick et al., 2015; Zaunbrecher et al., 2015, 75 Loganathan et al., 2016a, 2016b), using more sophisticated force fields, specifically 76 optimized for clay mineral studies, such as CLAYFF (Cygan et al., 2004). The existence of an 77 additional type of interfacial H<sub>2</sub>O located above the ditrigonal cavities of smecites and with 78 both O-H<sub>w</sub> bonds directed towards the basal surface was also reported for 2:1 sheet silicates of 79 high total layer charge (Wang et al., 2005b, 2009). Ab-initio calculations showed that these H-80 bonds are relatively short-lived and weaker than typical H<sub>2</sub>O···H<sub>2</sub>O in liquid water (Boek and 81 Sprik, 2003). 82

In addition, Suzuki and Kawamura (2004) calculated the theoretical FTIR spectra of water adsorbed on Na-beidellite with total layer charge of 0.33 per half unit cell (phuc). Based on their modeling, the O-H<sub>w</sub> bonds pointing towards the surface of beidellite contribute to a vibrational band at  $\sim$ 3500 cm<sup>-1</sup>, whereas the O-H<sub>w</sub> H-bonded to other H<sub>2</sub>O molecules produce a band at  $\sim$ 3365 cm<sup>-1</sup>. The relative intensity of the  $\sim$ 3365 to the  $\sim$ 3500 cm<sup>-1</sup> bands increased with increasing water content, and for 7 H<sub>2</sub>O molecules phuc the band at  $\sim$ 3500 cm<sup>-1</sup> was no longer detectable.

The experimental and theoretical evidence of the hydrophobic character of the 90 siloxane surface of uncharged clays has been broadly discussed in the literature (e.g., Michot 91 et al., 1994, Bridgeman and Skipper, 1997; Arab et al., 2003; Tunega et al., 2004; Wang et al., 92 2004; 2005a; Churakov, 2006; Rotenberg et al., 2011; Šolc et al., 2011). However, for the 93 siloxane surface of charged clays, like smectites, the picture is not as clear. Based on aromatic 94 hydrocarbon adsorption experiments, Jaynes and Boyd (1991) have classified this surface as 95 mostly hydrophobic. On the other hand, Sobolev et al. (2010) have used neutron scattering 96 technique to determine that the surfaces of smectite clays with tetrahedral substitutions are 97 hydrophilic. The importance of the specific structural charge location within a clay layer for 98 the existence of hydrophobic and hydrophilic patches on its surface has also been determined 99

in Monte Carlo computer simulations (Sposito et al., 1999). The relative weakness of the Hbonds donated by the interlayer water molecules to the clay basal surface, compared to the typical strength of the  $H_2O\cdots H_2O$  bonds in bulk liquid water can be considered as a molecular-scale indication of relative hydrophobicity of the smectite siloxane surface.

The present study is aimed at advancing the aforementioned discussion by adding new spectroscopic arguments. Vibrational spectra of interfacial water molecules in several smectites are calculated and carefully analyzed here on the basis of molecular dynamics simulations in order to identify, interpret and quantify the variability of the position of the sharp H<sub>2</sub>O vibrational band as a function of total clay layer charge, layer charge localization, and nature of the interlayer cations, as recently observed experimentally (Kuligiewicz *et al.,* 2015a).

111

112

#### **METHODOLOGY**

113

# 114 Smectite structures and MD simulations

In order to explore systematically the effects of smectite composition, type of the interlayer cations and water content on the structure of interlayer  $H_2O$ , a series of MD simulations were performed on four models of dioctahedral smectites with a total layer charge of 0.3 or 0.5 phuc and octahedral (montmorillonitic) or tetrahedral (beidellitic) charge localization:

120	Beid03: M <sup>+</sup> <sub>0.3</sub> (Al <sub>2.0</sub> )(Si <sub>3.7</sub> Al <sub>0.3</sub> )O <sub>10</sub> (OH) <sub>2</sub>

- 121 Beid05:  $M^+_{0.5}(Al_{2.0})(Si_{3.5}Al_{0.5})O_{10}(OH)_2;$
- 122  $Mtm03: M^+_{0.3}(Al_{1.7} Mg_{0.3})(Si_{4.0})O_{10}(OH)_2;$
- 123  $Mtm05: M^+_{0.5}(Al_{1.5} Mg_{0.5})(Si_{4.0})O_{10}(OH)_2$ .
- 124 The interlayer water content (2.5, 5.0 and 7.5 H<sub>2</sub>O phuc) and the type of the interlayer cation

125  $(Na^+, Cs^+, and Ca^{2+})$  for selected water contents were used as additional variables.

The structural models of the smectites were built on the basis of the pyrophyllite 126 crystal structure (Lee and Guggenheim, 1981), with isomorphic substitutions introduced at 127 specific atomic sites. The Mg/Al ordering in the octahedral sheets was set by maximizing the 128 distance between Mg atoms, following the work of Ortega-Castro et al. (2010). The Al/Si 129 ordering in the tetrahedral sheet was random but following the Löwenstein rule, *i.e.* excluding 130 Al-O-Al linkages (Löwenstein, 1954). The simulation supercell was  $8 \times 4 \times 2$  unit cells in the *a*, 131 b, and c crystallographic directions, respectively (~41.6 Å  $\times$  36.1 Å  $\times$  Z Å; the value of Z 132 varied in the ~12.5-19.0 Å range depending mainly on the amount of water in the interlayer 133 134 space). The edge surfaces were not considered.

The atoms of the smectite structure were not fixed -i.e. they were allowed to move 135 around their crystallographically determined positions according to the modeling force field 136 used. Only one cation in one octahedral sheet was kept frozen in its position in order to keep 137 2:1 layers in place during the entire simulation span. Partial atomic charges and other 138 interatomic interaction parameters of smectite layers were described using the CLAYFF force 139 field (Cygan et al., 2004) with structural OH groups modified by introducing a more accurate 140 Morse potential (Greathouse et al., 2009). Ewald summation was used to calculate the long 141 range corrections to the electrostatic interactions and the cutoff distance was set at 10.0 Å. 142 Non-electrostatic Lennard-Jones parameters of the interatomic interactions involving bridging 143 oxygen atoms were modified after Ferrage et al. (2011) in order to improve the description of 144 the interlayer water structure of hydrated smectites. The necessity of this modification was 145 justified based on comparisons of experimental and calculated XRD and neutron diffraction 146 data (Ferrage et al., 2011). However, unlike the original suggestion of Ferrage et al. (2011), 147 only the parameters of surface oxygen atoms were modified in our work, because initial test 148 simulations showed that the modification for all bridging oxygen atoms leads to a substantial 149

and unrealistic deformation of the clay octahedral sheet if the cell volume is not constrained in the simulations at constant pressure, i.e., in the *NPT* statistical ensemble (see Supplementary materials). Additionally, the Lennard-Jones parameters of tetrahedral Si and tetrahedral Al in the clay structure were also modified to compensate for the increased size of the surface bridging oxygen atoms by applying the usual arithmetic mixing rules for the parameters of interatomic interactions (Table 1).

156

# === Table 1 ===

For a more accurate description of the vibrational properties of water molecules, the parameters of intramolecular interactions for  $H_2O$  were taken from the work of Toukan and Rahman (1985) using the implementation proposed by Praprotnik *et al.* (2004). This allowed a more accurate description of the anharmonicity of the O<sub>w</sub>-H<sub>w</sub> stretching vibrations in the calculated IR spectra in comparison to the simple harmonic vibrational terms of the original CLAYFF parameterization (Cygan *et al.*, 2004).

NPT-ensemble MD simulations at constant pressure (P = 1 bar) and temperature (T = 300 K) were performed for 2.0 ns with the time step of 1 fs, preceded by one temperature annealing cycle from 400 K to 300 K of 0.1 ns. This long equilibration run was followed by a short 10 ps data analysis run when atomic positions and velocities were recorded every 2 fs. Standard periodic boundary conditions were applied (e.g., Allen and Tildesley, 1987) and all

simulations were performed using the LAMMPS molecular modeling program (Plimpton,1995).

170

## 171 Simulation analysis

The MD-simulated structural data were used to calculate the distributions of angles formed by the dipole axis of interfacial H<sub>2</sub>O molecules with respect to a vector normal to the 2:1 surfaces (angle  $\alpha$ ) as a function of the distance z of O<sub>w</sub> from the plane of the basal

bridging oxygens (O<sub>b</sub>). The direction of the H<sub>2</sub>O dipole was defined as a vector from the 175 176 oxygen atom O<sub>w</sub> to the central point between the two hydrogen atoms H<sub>w</sub> of the same molecule. As the HOH angle was allowed to vary in the flexible H<sub>2</sub>O molecular model used, 177 this methodology introduces some small additional spread of the calculated angles. 178 Additionally, the distributions of angles between a given OH bonds of H<sub>2</sub>O and a vector 179 normal to the 2:1 surfaces were calculated as a function of the distance z from the O<sub>b</sub> plane 180 (angle  $\beta$ ). The position of the plane of basal oxygen atoms was determined by the maximum 181 of the atomic density distribution for these atoms, similarly to the previous studies (Wang et 182 al., 2005b, 2009; Loganathan and Kalinichev, 2013; Szczerba et al., 2014, Ngouana Wakou 183 184 and Kalinichev, 2014; Greathouse et al., 2015; Teich-McGoldrick et al., 2015; Loganathan et al., 2016a, 2016b). All these properties were calculated by averaging over the last 1 ns of the 185 equilibrium MD simulation runs. 186

187

## 188 Calculation of power spectra

MD-simulated atomic trajectories can be used to calculate so-called power spectra 189 (PS) of atomic vibrations that contain an entire distribution of the power (density of states) of 190 all atomic motions in the simulated system in a function of vibrations frequency. With certain 191 restrictions, these power spectra can be compared to the experimental vibrational spectra (e.g., 192 Allen and Tildesley, 1987; Kleinhesselink and Wolfsberg 1992). The power spectra are 193 obtained as Fourier transformations of the so-called velocity autocorrelation function (VACF), 194 which, in turn, can be directly calculated from the MD-simulated dynamic trajectories of the 195 atoms in the modeled system. The frequency of H<sub>2</sub>O stretching vibration is usually well 196 197 captured by the VACF of the water hydrogen atoms (e.g., Kalinichev, 2001).

In the present work, normalized VACF based on the last 10 ps period of every MD simulation run were calculated for selected hydrogen atoms with a moving window of 1 ps from the equilibrium part of the MD trajectory recorded every 2 fs:

201

$$VACF(t) = \frac{\sum_{f=1, \text{ sel atoms}}^{n-n_{VACF}} \sum_{f=1, \text{ sel atoms}} \vec{v}_f \cdot \vec{v}_{f+t}}{\sum_{f=1}^{n-n_{VACF}} \sum_{sel atoms} \vec{v}_f \cdot \vec{v}_f};$$
(2)

where n - is the total number of windows,  $n_{VACF}$  - is the number of windows used in a 202 particular calculation of VACF. The first sum in nominator and denominator corresponds to 203 averaging over total number of windows minus the number of VACF windows. The second 204 sum is calculated over all hydrogen atoms of water molecules, or their selected subset based 205 on the distance of the respective H<sub>2</sub>O from the clay surface and the angle of H<sub>2</sub>O dipole 206 orientation (or angle between one of OH groups of H<sub>2</sub>O and a vector normal to the 2:1 207 surface). The scalar products of instantaneous atomic velocities and their subsequent Fourier 208 transformation into vibrational power spectra were calculated according to standard VACF 209 and PS definitions (e.g., Allen and Tildesley, 1987; Kleinhesselink and Wolfsberg, 1992). For 210 every VACF window, the determination of a H<sub>2</sub>O molecule as belonging to a selected 211 position/orientation population was checked at the beginning and at the end of the VACF 212 window. The chosen short duration of the analysis run (10 ps) is, nevertheless, long enough in 213 respect to a typical H-bonding lifetime (0.8-0.9 ps; Kumar et al., 2007), but still short enough 214 not to allow H<sub>2</sub>O to change significantly their positions in the interlayer with respect to the 215 clay surface. At the same time, the relatively short time of the individual VACF window (1 ps) 216 is comparable with a typical H-bonding lifetime, but still allows to probe the stretching 217 dynamics of the selected O-H<sub>w</sub> bonds (e.g., Kalinichev, 2001). The choice of both 218 characteristic calculation times ensured that the H-bonding situation of each H<sub>2</sub>O molecule 219 was included in a certain selected angle/position subset for VACF calculation. 220

In order to calculate the power spectra of H<sub>2</sub>O vibrations, a cosine Fourier transform of VACF for the water hydrogen atoms was performed as:

223	$PS(\omega) = \sum_{t=1}^{n_{VACF}} VACF(t) \cdot \cos(\frac{\pi}{n_{VACF}} \cdot t \cdot \omega) $ (3)
224	The statistical noise was preliminarily reduced by applying a filtering function:
225	$VACF(t) = VACF(t) \cdot \exp(-t/\tau) $ (4)
226	where $\tau$ was set to 0.25 ps.
227	Due to the normalization of VACF, the intensity of the calculated power spectra can,
228	therefore, be considered as proportional to the total number of H <sub>2</sub> O molecules selected for
229	each calculation.
230	
231	<b>RESULTS AND DISCUSSION</b>
232	
233	Characteristic features of MD simulations
234	The composition and adsorbed water content of all simulated clay models are
235	presented in Table 2 along with the resulting basal spacings. The 2W model for Cs-smectite is
236	purely hypothetical and does not correspond to any experimental or natural conditions (e.g.,
237	Ngouana Wakou and Kalinichev, 2014).
238	=== Table 2 ===
239	The values of the calculated basal spacings closely match those obtained by modelling
240	the experimental diffractograms: $d_{001_1W} = 11.6-12.9$ Å, $d_{001_2W} = 14.9-15.7$ Å and $d_{001_3W} = 18-19$
241	Å (e.g., Dazas et al., 2015). The data show clearly that for the same water content and
242	interlayer cation (Na <sup>+</sup> ) the basal spacing $d_{001}$ decreases with increasing layer charge (e.g.
243	15.95 Å for Mtm03Na_2W and 15.37 Å for Mtm05Na_2W). This trend is in agreement with
244	literature data (e.g., Sato et al., 1992, Ferrage et al., 2005, 2007), whereas some variation is
245	related also to the layer charge location. Substantial differences in basal spacings were also
246	observed as a result of the replacement of interlayer cations from $Na^+$ or $Ca^{2+}$ to $Cs^+$ (e.g.,

15.37 Å for Mtm05Na\_2W, 15.38 Å for Mtm05Ca\_2W and 16.14 Å for Mtm05Cs\_2W).
These differences were caused mainly by the increased size of the cation and by differences in
hydration energies.

In agreement with other recent simulations (e.g. Wang et al., 2005b, 2009; Morrow et 250 al., 2013; Ngouana Wakou and Kalinichev, 2014; Greathouse et al., 2015; Teich-McGoldrick 251 et al., 2015; Zaunbrecher et al., 2015; Loganathan et al., 2016a, 2016b), a typical snapshot of 252 the interlayer structure (Figure 1) illustrated that H<sub>2</sub>O molecules close to the siloxane surface 253 tend to be specifically oriented. Within a distance of < 3.5 Å between O<sub>w</sub> and the siloxane 254 surface two such preferred orientations could be distinguished. The population closer to the 255 surface corresponds to H<sub>2</sub>O with both O-H<sub>w</sub> bonds pointing towards the surface (bidentate), 256 whereas a more distant and more pronounced population is due to the H<sub>2</sub>O pointing only one 257 of their O-H<sub>w</sub> bonds towards the surface and the second one towards the bulk of the interlayer 258 (monodentate). In order to quantify these differences, these two populations were investigated 259 as a function of smectite charge, type of the interlayer cations, and degree of hydration. 260

261

==== Figure 1 ====

#### *Position of the cations in the interlayer space* 263

The distribution of interlayer cations for different smectites (blue solid lines in Figures 264 2 and 3) exhibited a clear dependence on the amount and location of layer charge, as well as 265 on the type of the cation. In the case of 1W sodium smectites, two separate maxima were 266 visible, each corresponding to inner-sphere coordination of H<sub>2</sub>O to the surface. For 2W 267 sodium structures, a strong tendency to form a third maximum corresponding to fully 268 hydrated cations (outer sphere) in the middle of the interlayer was observed. The ratio 269 between the central and wing (inner sphere) cation distributions depended on the charge 270 location, whereas changes in total charge had similar effect on both of these maxima. This 271 result is in agreement with other recent simulations and is supported by calculated XRD data 272 (Dazas et al., 2015; Teich-McGoldrick et al., 2015). In the case of 3W structures, outer-sphere 273 sodium ions formed two maxima close to the interlayer center instead of one as in 2W. The 274 data for the Mtm03Na 3W structure were very similar to the results presented by Dazas et al. 275 (2014). With increasing tetrahedral charge a tendency to form higher amount of inner-sphere 276 complexes with the siloxane surface was observed. 277

The effect of changing interlayer cation from Na<sup>+</sup> to Ca<sup>2+</sup> was investigated for the 278 models with 2W hydration. Comparison of smectites in  $Ca^{2+}$  form (Figure 3) with those in 279 Na<sup>+</sup> form (Figure 2) indicated that, despite the two-fold increase in the cation hydration 280 enthalpy, the only effect was the vanishing of the (already weak) population of cations in the 281 vicinity of the surface. The only exception was Beid05Ca 2W, for which some remaining 282 contribution of ions forming inner-sphere complexes was observed. 283

284

==== Figure 2 ====

285

Oppositely, the lowest hydration enthalpy Cs<sup>+</sup> ions had a tendency to remain close to 286 the surface (Figure 3), which is in excellent agreement with other recent Cs<sup>+</sup>-smectite 287

==== Figure 3 ====

simulations (Ngouana Wakou and Kalinichev, 2014; Teich-McGoldrich *et al.*, 2015; Zaunbrecher *et al.*, 2015; Loganathan *et al.*, 2016a). The distribution of  $Cs^+$  in the interlayer was substantially different from those of Na<sup>+</sup> and Ca<sup>2+</sup>, which were generally quite similar to each other (compare Figures 2 and 3).

292

#### 293 *H*<sub>2</sub>*O* orientation

The contour maps of the angular distributions of the interlayer H<sub>2</sub>O dipole vectors 294 with respect to the direction normal to the surface ( $\alpha$  angle) plotted in a function of the 295 distance z from the surface (Figure 2) enabled the distinction of the two preferred surface-296 oriented types of water molecules marked in Figure 1. The predominantly bidentate 297 population was located closer to the surface at  $z \sim 2.0$  Å and  $\alpha \sim 0.30^{\circ}$ , similarly to ideal 298 theoretical values (observed in smectites with charge 0.5). A more distant and more 299 300 pronounced monodentate population was at distances  $z \sim 2.8$  Å and oriented in a broad range of angles between 30° and 80° with a maximum at  $\alpha \sim 55^\circ$ , which matches the ideal 301 theoretical value for one OH vector pointing perpendicularly to the smectite surface (half of 302 the 105° angle of H<sub>2</sub>O). For higher hydration levels, a third population of water molecules 303 was observed closer to the middle of the interlayer. The orientational distribution of this 304 population depended significantly on both, the hydration level of the specific smectite and the 305 type of the interlayer cation. The latter dependence is observed clearly when comparing the 306 distribution in Mtm05 for the same hydration levels but different interlayer cations (Figures 2 307 and 3). 308

The presence of monodentate  $H_2O$  was ubiquitous. This sub-population was abundantly visible for all smectites, all cations and all hydration levels. A noticeable dependence of the location of the distribution maxima was however observed: higher average  $H_2O$  dipole vector angles were observed for low charge smectites, lower hydration levels, and 313 for  $Cs^+$  as interlayer cation.

314 The bidentate H<sub>2</sub>O population was far less abundant. It could be detected only in high charge smectites and was practically absent in their low charge analogs. Layer charge 315 increasing beyond 0.5 phuc is therefore expected increase further the amount of bidentate 316 molecules, predicting its high contribution at charges approaching 1 phuc (mica, vermiculite), 317 which was indeed reported by Wang et al. (2005b, 2009) and Loganathan and Kalinichev 318 (2013) on muscovite. Further, in all smectites studied, a dependence of the bidentate H<sub>2</sub>O 319 population on hydration level was observed: for a given smectite, the relative number of 320 bidentate H<sub>2</sub>O decreases upon drying. 321

The H<sub>2</sub>O orientation also depends on the type of the interlayer cation. As the majority of Cs<sup>+</sup> cations are located close to smectite surface, a noticeable decrease of bidentate H<sub>2</sub>O population in Cs<sup>+</sup>-smectites in comparison to their Na<sup>+</sup>- and Ca<sup>2+</sup>-analogs was observed. This effect was, however, small compared to the dependence of the bidentate population on layer charge. A noticeable decrease of the maximum amplitude corresponding to monodentate population was additionally observed for the Cs<sup>+</sup> form. This decrease was accompanied by the transfer of H<sub>2</sub>O to the middle of the interlayer.

329

# 330 Vibrational spectra of H<sub>2</sub>O in the smectite interlayer

Kuligiewicz *et al.* (2015a, 2015b) found that the sharp high-frequency IR band originating from adsorbed water at ~3615 cm<sup>-1</sup> (in H<sub>2</sub>O form) and ~2685 cm<sup>-1</sup> (in D<sub>2</sub>O form) is a common feature for all hydrated smectites. Its intensity depended very little on the degree of clay hydration over a broad range of relative humidity, and its frequency exhibited a weak but systematic decrease (red-shift) upon increasing the total layer charge, with no measurable dependence on charge location. For a given layer charge, the dependence of the peak position on the field strength of the interlayer cation for high hydration enthalpy cations (Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>) was negligible and only low hydration cations (Cs<sup>+</sup>, K<sup>+</sup>) could be distinguished. These trends were opposite to what was observed for the main O-H<sub>w</sub> (O-D<sub>w</sub>) stretching envelopes, located at ~3400 cm<sup>-1</sup> (~2500 cm<sup>-1</sup>). The latter envelopes were known to exhibit a strong dependence of their intensity on hydration level and their position on interlayer cation, but were relatively unaffected by the smectite layer charge or charge localization (e.g., Xu *et al.*, 2000, Madejová *et al.*, 2002, Kuligiewicz *et al.*, 2015a, 2015b).

Thus, the sharp high-frequency IR band observed in water vapor-saturated smectites was attributed to a mechanism that must be common to all smectites at high hydration levels, regardless of interlayer cation. In addition, the high-frequency band must account for Hbonding interactions that are considerably weaker than those encountered in bulk H<sub>2</sub>O or aqueous solutions of common salts, and its exact position ought to show a measurable dependence on the total charge of the 2:1 layer (Kuligiewicz *et al.*, 2015a, 2015b).

In order to provide a quantitative explanation for the aforementioned experimental phenomenology, the power spectra for hydrogen atoms of interlayer  $H_2O$  molecules were calculated for different smectites and compared to the spectrum of pure bulk water, the latter calculated with the same molecular model (Figure 4).

354

#### === Figure 4 ===

The results showed that water in smectites exhibits a considerable increase of its 355 spectral density at higher frequencies (~3600-3800 cm<sup>-1</sup>) in respect to bulk water spectrum. 356 The simulated spectrum of bulk water, however, shows some excessive high-frequency 357 spectral density around 3730 cm<sup>-1</sup>, which is not observed experimentally, and indicates some 358 limitations of the present model. Nevertheless, the shape of the power spectrum of bulk water 359 agrees perfectly well with the spectrum obtained earlier by the same methodology (Tay and 360 Bresme, 2006) and still represents one of the most accurate models describing the dynamics 361 of O<sub>w</sub>-H<sub>w</sub> stretching vibrations in water (e.g., Kalinichev, 2001; Guillot, 2002). Additionally, 362

the calculated results do not show the low-frequency band at  $\sim$ 3250 cm<sup>-1</sup>, which has been found in experimental data thus is consistent with an assignment of this band to Fermi resonance (Efimov and Naberukhin, 2002; Sovago *et al.*, 2009).

Power spectra were also calculated for four different smectites with varying content of 366 adsorbed water: Beid03Na, Beid05Na, Mtm03Na and Mtm05Na (Figure 5). The results 367 showed that with increasing number of H<sub>2</sub>O molecules in the smectite interlayer the relative 368 intensity of the lower-frequency peak at ~3500 cm<sup>-1</sup> increased. This was in qualitative 369 agreement with the experimental observations of Kuligiewicz et al. (2015a), who reported 370 that the higher-frequency peak is nearly fixed and the intensity of the lower-frequency peak is 371 greatly varying with water content. In the present study, the peak intensity at ~3750 cm<sup>-1</sup> was 372 found to depend on hydration, but this can be to some extent related to the limitations of the 373 specific H<sub>2</sub>O molecular models used. 374

375

# ==== Figure 5 ====

In order to further analyze the influence of different factors on the higher-frequency band, its positions was determined by fitting procedures. The low-frequency band was fitted with a mixed Gauss-Lorentz function (percentage of Lorentz function was optimized), while the higher-frequency one with a simple Gauss function. Additionally, a small combination band at ~ 4000 cm<sup>-1</sup> was fitted with another Gaussian (Figure 6).

== Figure 6 ===

Increasing smectite total layer charge was found to induce a noticeable red-shift of the high-frequency peak, in remarkable agreement with experiment data (Kuligiewicz et al., 2015b). This shift was observed in Na<sup>+</sup> montmorillonites and beidellites at any hydration level (Figure 7a) and also in the 2W forms for any cation (Figure 7b). Only one exception was found: Mtm05Na\_3W exhibited higher frequency of the sharp peak than Mtm03Na\_3W. In contrary to the experimental observations (Kuligiewicz *et al.*, 2015a), the position of the high-frequency peak was found to depend on charge location and water content.

389

==== Figure 7 ====

In addition, the MD results showed a substantial difference in peak position between the Na<sup>+</sup> and Ca<sup>2+</sup> forms of smectites (Figure 7b), which are not visible experimentally (Figure 7c, Kuligiewicz *et al.*, 2015a). Also the peak positions of the Cs<sup>+</sup> forms exhibited trends in relation to Na<sup>+</sup> and Ca<sup>2+</sup> forms that are different in MD than in experiment.

These discrepancies between the experimental trends and the outcome of MD 394 simulations can be related to the approximations involved in the latter, primarily in certain 395 features of the CLAYFF model (Cygan et al., 2004). The Lennard-Jones parameters of 396 Ferrage et al. (2011) should be more accurately optimized, the hexagonal cavity in the 397 tetrahedral sheet ought to have lower ditrigonal symmetry. A better description of the structure 398 would affect the distribution and orientation of H<sub>2</sub>O. The model for H<sub>2</sub>O may also have 399 400 limitations and the power spectra have excessive high-frequency spectral density at 3728 cm<sup>-1</sup>. Finally, uncertainties introduced by the fitting procedure can be observed (Figure 401 6). In spite of all these limitations, the overall picture is relatively consistent: All the studied 402 smectites exhibit a stretching band at lower frequencies and this band shift to lower energy 403 upon increasing layer charge (Figure 7ab). 404

405

#### 406

# Molecular origin of the sharp O-D<sub>w</sub>/O-H<sub>w</sub> band

Calculations of the power spectra of specific sub-sets of interlayer water hydrogen atoms were performed in order to explain in more detail which part of the surface H<sub>2</sub>O population is responsible for the sharp high-frequency vibrational band observed in the experimental spectra (Kuligiewicz *et al.*, 2015a). Each subset was defined by a common range of distances from the surface, *z*, and H<sub>2</sub>O dipole orientation angle,  $\alpha$  (Figure 1). A H<sub>2</sub>O molecule belongs to a certain sub-set if it is found within the same (*z*,  $\alpha$ ) range in both the first and the last time-window of the VACF calculation. The results for three representative
smectites (Mtm03Na\_2W, Beid03Na\_2W and Mtm05Ca\_2W) are presented in Figure 8.
Spectral intensities were scaled by the number of H<sub>2</sub>O molecules identified in each subset in
order to compare the contribution of each subset to the total spectrum.

417

### ==== Figure 8 ====

This analysis demonstrates that  $H_2O$  molecules at the center of the interlayer are not responsible for producing the sharp spectral feature. The latter originates instead from the overlapping contributions of both monodentate and bidentate orientations of surface  $H_2O$ . The contribution of the monodentate orientation is, however, much stronger because of the higher number of  $H_2O$  molecules populating this sub-set. If present, bidentate  $H_2O$  gives a very small, although non-negligible, contribution to the power spectrum at frequencies that are on average higher than those of the monodentate population.

Based on the correlation of IR frequency of the O-H stretching band and the length of 425 the H-bond, O-H<sub>w</sub>...O, (Libovitzky, 1999), a peak at ~ 3600 cm<sup>-1</sup> may correspond to a O-426  $H_w$ ...O distance > 2.2 Å (i.e. an O<sub>w</sub>...O distance >3.2 Å), and indicates a relatively weak H-427 bond donated to the surface (e.g., Kalinichev, 2001; Kumar et al., 2007). Therefore, in order 428 to obtain deeper insight into the studied problem, the distribution of the shortest Ow-Hw...Ob 429 430 distances in the monodentate and bidentate sub-sets were calculated (Figure 8, right column). The results showed a relatively broad distribution of the distances, with the maximum for 431 monodentate H<sub>2</sub>O at ~1.9 Å for Beid03 Na and Mtm05Ca 2W, and ~2.0 Å for 432 Mtm03Na 2W. For comparison, in bulk liquid water the maximum of the shortest Ow-433 H<sub>w</sub>···O<sub>w</sub> distance is at ~1.8 Å (e.g., Kalinichev, 2001; Kumar et al., 2007). The weighted 434 average of the calculated O<sub>w</sub>-H<sub>w</sub>...O<sub>b</sub> distributions is, however, a little bit greater than the 435 maxima: 2.24 Å for Beid03 Na, 2.16 Å for Mtm05Ca 2W, and 2.27 Å for Mtm03Na 2W, 436 comparing to 1.95 Å in bulk water. In bulk water a contribution of H-bond distances > 2.2 Å 437

was observed, but this is much smaller than for smectites. Low charge smectites exhibited a 438 significantly larger contribution of weak H-bonds. For the high charge smectite 439 Mtm05Ca 2W the contribution of weak H-bonds due to H<sub>2</sub>O molecules in monodentate 440 orientation was noticeably smaller. This explains the higher frequency and intensity of the 441 high-frequency monodentate peak in the vibrational spectrum of this smectite. In the case of 442 bidentate population, one of the O-H<sub>w</sub> $\cdots$ O<sub>b</sub> distances had a maximum also at ~1.9-2.0 Å, 443 resulting in an H-bond of a comparable strength, while the second one was significantly 444 longer and, respectively, weaker. This analysis suggests that upon increasing total layer 445 charge the H-bond distances of the bidentate sub-set are decreasing and causing the red-shift 446 of the calculated power spectrum. 447

Due to its ubiquitous presence and relative abundance, the population of monodentate 448 surface H<sub>2</sub>O is mainly responsible for the presence of the sharp high-frequency OH stretching 449 450 feature observed in the experiments (Kuligiewicz et al., 2015a). This is in very good agreement with earlier experimental data (e.g., Russell and Farmer 1964; Farmer and Russell 451 1971; Prost 1975; Suquet et al., 1977; Sposito and Prost 1982; Sposito et al., 1983) which 452 linked the high frequency band to H<sub>2</sub>O at the surface of the interlayer, pointing one of their O-453 H<sub>w</sub> bonds towards the siloxane surface. In certain cases the bidentate sub-population may 454 provide a non-negligible contribution as observed for higher charged smectites, e.g., for 455 Mtm05 Ca 2W. 456

457

# 458 Possible alternative molecular mechanisms responsible for the sharp O-Dw/O-Hw band

Evidence from MD simulations in support of the experimental data, suggested that the sharp high-frequency band in the IR spectra of hydrated smectite is clearly originating from  $H_2O$  molecules oriented towards the clay surface. Can there be any other contribution to this sharp IR band? One possibility that would also be linked to surface  $H_2O$ , could, for example,

involve the second O-H<sub>w</sub> bond of monodentate H<sub>2</sub>O, i.e. the one oriented towards the middle 463 of the interlayer, away from the siloxane surface. As the surface H<sub>2</sub>O molecules have 464 relatively fixed orientations, their O-H<sub>w</sub> bonds that are pointing away from the surface might 465 have a decreased number of available H-bond acceptors within a suitable range and 466 orientation around them. Such a lower coordination could, in principle, contribute in part to 467 the observed sharp high-frequency infrared band. To examine this possibility, the subsets 468 representing two separate hydroxyls of the monodentate population in Mtm05Ca 2W and 469 Mtm05Na 2W were investigated (Figure 9). 470

471

# === Figure 9 ===

472 In the case of monodentate H<sub>2</sub>O, one H-bond is donated to the surface (thick blue rectangle in Figure 9), while the second one is donated to another H<sub>2</sub>O (dashed orange 473 rectangle in Figure 9). The corresponding power spectra show that only the hydrogens 474 oriented towards the surface contribute to the high-frequency band. The power spectrum of 475 the second hydrogen resembles that of bulk water, with even a slightly higher intensity of the 476 vibrational band at lower frequency ~3500 cm<sup>-1</sup>, indicating a relatively strong H-bonding to 477 other interlayer H<sub>2</sub>O molecules. This is additionally confirmed by comparison of the shortest 478 Ow-Hw...Ow distances of this sub-population and the corresponding distances in pure water 479 (right column in Figure 9). The two distributions are practically identical. 480

A second mechanism potentially responsible for the emergence of the high-frequency H<sub>2</sub>O stretching band could be related to the influence of interlayer cations. The latter could deform the H-bonding structure of H<sub>2</sub>O molecules around them and possibly induce some Hbond breaking. A clear evidence against this possibility has been provided already in Figure 8: H<sub>2</sub>O molecules in the middle of the interlayer (red rectangle) were found not to contribute to the high-frequency band of interest. This is especially obvious in the case of Mtm05Ca\_2W, where H<sub>2</sub>O molecules in the hydration shell of Ca<sup>2+</sup> are oriented around the ions exactly in the 488 center of the interlayer.

- 489
- 490 Hydrogen bonding in the interlayer space of smectite

The question regarding other possible molecular mechanisms responsible for the sharp high-frequency  $O-D_w/O-H_w$  band can be alternatively expressed as follows: Does interlayer water contain a sub-population of H<sub>2</sub>O molecules for which the  $O-H_w\cdots O$  distance of donated H-bonds is longer than ~2.2 Å (Libovitzky, 1999)? Obviously, the results of this analysis are only valid in comparison to those on pure bulk liquid water, due to the method-artificial nonnegligible contribution of weak H-bonds in the latter (see Figure 8 and 9).

497 To address this question, the numbers of accepted and donated H-bonds were calculated depending on the distance z of the involved H<sub>2</sub>O molecules from the smectite 498 siloxane surface. In the ordered ice structure, each H<sub>2</sub>O donates two strong H-bonds to other 499 H<sub>2</sub>O and also accepts two strong H-bonds from two other H<sub>2</sub>O molecules. In liquid water, the 500 number of donating and accepting H-bonds formed by each H<sub>2</sub>O molecule is somewhat lower 501 than in ice due to the molecular disorder, and depends on temperature, density, and other 502 thermodynamic factors. The exact number of H-bonds experienced by a H<sub>2</sub>O molecule in 503 each situation also depends to some extent on the assumed criterion used in H-bonding 504 calculation (see., e.g., Kalinichev, 2001; Kumar et al., 2007). 505

A geometric definition for counting H-bonds (HB) was adopted from the literature (Wang *et al.*, 2009; Loganathan and Kalinichev, 2013). According to this definition, an Hbond is assumed to exist if the H···O distance between the donor and acceptor is below 2.45 Å and the angle between the O–H and O···O vectors is below 30°. A systematic application of this criterion enabled the quantitative visualization of the general H-bonding trends of interlayer H<sub>2</sub>O molecules for several model smectites (Figure 10). As expected, Hbonds donated to surface O<sub>b</sub> atoms from both bidentate and monodentate H<sub>2</sub>O populations

were identified in all cases (thick solid lines in Figure 10). The maximum of their distribution 513 514 corresponded to the monodentate population, whereas the small shoulder closer to the surface originated from bidentate H<sub>2</sub>O. Besides donating to the basal surface, both bidentate and 515 monodentate H<sub>2</sub>O accepted H-bonds from and donated to other H<sub>2</sub>O in the interlayer (dashed 516 and thin solid lines, respectively in Figure 10). The maxima of the accepted and donated H-517 bonding distributions corresponded clearly to the expected (e.g., Ferrage et al., 2011; 518 Ngouana Wakou and Kalinichev, 2014) twin maxima of the Ow distribution along z, shown 519 previously for all 2W structures (Figures 2 and 3). Subtler differences in the fractions of 520 accepting and donating H-bonds depended on the charge and the type of the interlayer cation 521 (Figure 10). 522

523

#### === Figure 10 ===

The distributions of H-bonds along z (Figure 10) provide a general picture of the H-524 bonding structure in smectite interlayers, but they do not directly indicate the location of 525 particularly weak hydrogen bonds. To address this issue, the distributions of H-bonds on the 526 basis of their strength was also calculated (Figure 11). This was achieved by modifying the 527 aforementioned geometric definition of H-bond to probe only the relatively weak interactions 528 having O<sub>w</sub>-H···O distances in the range 2.2-2.7 Å and compare such a subset of the H-bonds 529 distribution to the original definition (Ow-H···O distance <2.45 Å). In both cases the H-530  $O_w$ ...O angle was kept < 30°. The plots in Figure 11 show only the average distributions of H-531 bonds experienced by each H<sub>2</sub>O molecule, and therefore do not inform on the absolute 532 contribution of each molecular orientation to the final spectra. 533

534

# ==== Figure 11 ====

For the general case considering all possible H-bonds in the system (Figure 11a), the number of accepted H-bonds per  $H_2O$  molecule was found relatively constant with small dependence on the smectite charge and the type of the interlayer cation (dashed lines in Figure 538 11a). The number of H-bonds donated to basal oxygen atoms was around 2.0 per  $H_2O$ 539 molecule for the bidentate orientation and slightly below 1.0 for the monodentate orientation 540 for all types of simulated smectite systems (thick solid lines in Figure 11a). The number of H-541 bonds per  $H_2O$  donated to other  $H_2O$  was independent of charge and interlayer cation (thin 542 solid line in Figure 11a).

The average number of weak H-bonds calculated according to the modified geometric 543 criterion also did not show substantial dependence on the type of smectite (Figure 11). The 544 weakest H-bonds (0.8-1.0 of donated H-bonds per H<sub>2</sub>O; thick solid line in Figure 11b) was 545 clearly attributed to the bidentate orientation, but some contribution from the monodentate 546 547 population, amounting to ~0.3 donated H-bonds per H<sub>2</sub>O was also observed. For comparison, the average number of weak H-bonds in bulk liquid water, calculated using the same criteria 548 was  $\sim 0.17$  per molecule. Therefore, only the fraction of weak H-bonds that is in excess of the 549 550 value of  $\sim 0.17$  per molecule can be considered as contributing to the sharp high-frequency vibrational band. In agreement with the calculated power spectra, these H-bonds are solely 551 due to the bidentate and monodentate populations in the vicinity of the surface and no 552 contribution from the central part of the interlayer was found. 553

- 554
- 555

#### CONCLUSIONS

556

(1) Interfacial water molecules in bidentate and monodentate orientation with respect to the siloxane surface are the only species contributing to the experimentally observed sharp high-frequency O-H<sub>w</sub> stretching band of smectites (Kuligiewicz *et al.*, 2015a, Kuligiewicz *et al.*, 2015b). The number of interlayer H<sub>2</sub>O molecules in the monodentate orientation greatly exceeds that in the bidentate orientation and is, thus, the predominant contributor to the highfrequency vibrational band. (2) In the bidentate orientation each H<sub>2</sub>O molecule donates two hydrogen bonds to the surface: one relatively strong, and another much weaker, while in the monodentate orientation it donates only one relatively weak H-bond to the surface.

(3) Increasing total layer charge leads to increasing number of bidentate molecules, but also to decreasing of  $O_w$ -H···O<sub>b</sub> distances for both monodentate and bidentate populations. Both factors are responsible for the red-shift of the sharp high-frequency band in smectites upon increasing the layer charge.

(4) The experimentally observed low sensitivity of the position of the high-frequency vibrational band on the type of the (Na<sup>+</sup> or Ca<sup>2+</sup>) high hydration enthalpy interlayer cation remains unexplained. The differentiation of Cs<sup>+</sup> from Na<sup>+</sup> or Ca<sup>2+</sup> may be due to its tendency to displace surface H<sub>2</sub>O and form inner-sphere complexes with the siloxane surface as suggested by Kuligiewicz *et al.* (2015a), but further simulation work is needed to account for the experimental data on Cs<sup>+</sup> smectites.

576 (5) The presence of the sharp high-frequency vibrational band in experimental and 577 simulated spectra can be considered as a strong evidence of intrinsic hydrophobicity of the 578 smectite siloxane surface within the studied range of layer charge (0.3-0.5 phuc), independent 579 on the specific charge localization in the clay structure.

580

# 581 ACKNOWLEDGMENTS

This work was supported by the project ATLAB (FP7-REGPOT-2011-1 No. 285989) funded by the European Union. MS also acknowledges NCN (grant 2012/05/B/ST10/01948), which provided IGS PAS with a high-performance computing server and also PLGRID infrastructure. AGK acknowledges the support of the industrial chair "Storage and Disposal of Radioactive Waste" at the Ecole des Mines de Nantes, funded by ANDRA, Areva, and

587 EDF. VG and GDC acknowledge partial support from project KRHPIS 447963 -Polynano 588 (GSRT, TPCI-NHRF).

590	REFERENCES
591	Allen, M.P. and Tildesley, D.J. (1987) Computer Simulation of Liquids. Oxford University
592	Press, New York, 385pp.
593	Arab, M., Bougeard, D., and Smirnov, K.S. (2003) Structure and dynamics of the interlayer
594	water in an uncharged 2 : 1 clay. Physical Chemistry Chemical Physics, 5, 4699-4707.
595	Boek, E.S., Coveney, P.V., and Skipper, N.T. (1995) Monte Carlo molecular modeling stud-
596	ies of hydrated Li-, Na-, and K-smectites: Understanding the role of potassium as a
597	clay swelling inhibitor. Journal of the American Chemical Society, 117, 12608-12617.
598	Boek, E.S. and Sprik, M. (2003) Ab initio molecular dynamics study of the hydration of a
599	sodium smectite clay. Journal of Physical Chemistry B, 107, 3251-3256.
600	Bridgeman, C.H. and Skipper, N.T. (1997) A Monte Carlo study of water at an uncharged clay
601	surface. Journal of Physics-Condensed Matter, 9, 4081-4087.
602	Cariati, F., Erre, L., Micera, G., Piu, P., and Gessa, C. (1981) Water molecules and hydroxyl
603	groups in montmorillonites as studied by near infrared spectroscopy. Clays and Clay
604	Minerals, <b>29</b> , 157-159.
605	Cariati, F., Erre, L., Micera, G., Piu, P., and Gessa, C. (1983) Polarization of water molecules
606	in phyllosilicates in relation to exchange cations as studied by near infrared
607	spectroscopy. Clays and Clay Minerals, 31, 155-157.
608	Cases, J.M., Berend, I., Francois, M., Uriot, J.P., Michot, L.J., and Thomas, F. (1997)
609	Mechanism of adsorption and desorption of water vapor by homoionic
610	montmorillonite. 3. The Mg <sup>2+</sup> , Ca <sup>2+</sup> , Sr <sup>2+</sup> and Ba <sup>2+</sup> exchanged forms. <i>Clays and Clay</i>
611	Minerals, 45, 8-22.
612	Chang, F.R.C., Skipper, N.T., and Sposito, G. (1995) Computer simulation of interlayer
613	molecular structure in sodium montmorillonite hydrates. Langmuir, 11, 2734-2741.
614	Churakov, S.V. (2006) Ab initio study of sorption on pyrophyllite: Structure and acidity of the

- edge sites. *Journal of Physical Chemistry B*, **110**, 4135-4146.
- Cygan, R.T., Liang, J.J., and Kalinichev, A.G. (2004) Molecular models of hydroxide,
   oxyhydroxide, and clay phases and the development of a general force field. *Journal of Physical Chemistry B*, **108**, 1255-1266.
- Dazas, B., Ferrage, E., Delville, A., and Lanson, B. (2014) Interlayer structure model of tri hydrated low-charge smectite by X-ray diffraction and Monte Carlo modeling in the
   Grand Canonical ensemble. *American Mineralogist*, **99**, 1724-1735.
- Dazas, B., Lanson, B., Delville, A., Robert, J.L., Komarneni, S., Michot, L.J., and Ferrage, E.
- (2015) Influence of tetrahedral layer charge on the organization of interlayer water and
  ions in synthetic Na-saturated smectites. *Journal of Physical Chemistry C*, **119**, 4158-
- 625 **4172**.
- Efimov, Y.Y. and Naberhukhin, Y.I. (2002) On the interrelation between frequencies of
  stretching and bending vibrations in liquid water. Spectrochimica Acta A, 58, 519 524.
- Farmer, V.C. and Russell, J.D. (1971) Interlayer complexes in layer silicates: The structure of
   water in lamellar ionic solutions. *Transactions of the Faraday Society*, 67, 2737-2749.
- Ferrage, E., Lanson, B., Sakharov, B.A., and Drits, V.A. (2005) Investigation of smectite hy-
- dration properties by modeling experimental X-ray diffraction patterns: Part I. Mont morillonite hydration properties. *American Mineralogist*, **90**, 1358-1374.
- Ferrage, E., Lanson, B., Sakharov, B.A., Geoffroy, N., Jacquot, E., and Drits, V.A. (2007)
- 635 Investigation of dioctahedral smectite hydration properties by modeling of X-ray dif-
- 636 fraction profiles: Influence of layer charge and charge location. *American Mineralo-*637 gist, 92, 1731-1743.
- Ferrage, E., Sakharov, B.A., Michot, L.J., Delville, A., Bauer, A., Lanson, B., Grangeon, S.,
  Frapper, G., Jiménez-Ruiz, M., and Cuello, G.J. (2011) Hydration properties and inter-

layer organization of water and ions in synthetic Na-smectite with tetrahedral layer
 charge. Part 2. Toward a precise coupling between molecular simulations and diffrac-

tion data. *Journal of Physical Chemistry C*, **115**, 1867-1881.

- Greathouse, J.A. and Sposito, G. (1998) Monte Carlo and molecular dynamics studies of interlayer structure in Li(H<sub>2</sub>O)<sub>3</sub>–smectites. *Journal of Physical Chemistry B*, **102**, 24062414.
- Greathouse, J.A., Durkin, J.S., Larentzos, J.P., and Cygan, R.T. (2009) Implementation of a
  Morse potential to model hydroxyl behavior in phyllosilicates. *Journal of Chemical Physics*, 130, 134713.
- Greathouse, J.A., Hart, D.B., Bowers, G.M., Kirkpatrick, R.J., and Cygan, R.T. (2015)
  Molecular simulation of structure and diffusion at smectite-water interfaces: Using
  expanded clay interlayers as model nanopores. *Journal of Physical Chemistry C*, **119**,
  17126-17136.
- Guillot, B. (2002) A reappraisal of what we have learnt during three decades of computer
   simulations on water. *Journal of Molecular Liquids*, **101**, 219-260.
- Jaynes, W.F. and Boyd, S.A. (1991) Hydrophobicity of siloxane surfaces in smectites as
  revealed by aromatic hydrocarbon adsorption from water. *Clays and Clay Minerals*, **39**, 428-436.
- Kalinichev, A.G. (2001) Molecular simulations of liquid and supercritical water:
   Thermodynamics, structure, and hydrogen bonding. *Reviews in Mineralogy and Geochemistry*, 42, 83-129.
- Kleinhesselink, D. and Wolfsberg, M. (1992) The evaluation of power spectra in molecular
   dynamics simulations of anharmonic solids and surfaces. *Surface Science*, 262, 189 207.
- 664 Kuligiewicz, A., Derkowski, A., Szczerba, M., Gionis, V., and Chryssikos, G.D. (2015a)

- 665 Water-smectite interface by infrared spectroscopy, *Clays and Clay Minerals*, **63**, 15-666 29.
- Kuligiewicz, A., Derkowski, A., Emmerich, K., Christidis, G. E., Tsiantos, C., Gionis, V., and 667 Chryssikos, G. D. (2015b) Measuring the Layer Charge of Dioctahedral Smectite by 668 O-D Vibrational Spectroscopy. Clays and Clay Minerals, 63, 443-456. 669 Kumar, R., Schmidt, J.R., and Skinner, J.L. (2007) Hydrogen bonding definitions and 670 dynamics in liquid water. Journal of Chemical Physics, 126, 204107-12. 671 Lee, J.H. and Guggenheim, S., (1981) Single crystal X-ray refinement of pyrophyllite-1Tc. 672 American Mineralogist, 66, 350–357. 673 Libowitzky, E. (1999) Correlation of O-H stretching frequencies and O-H…O bond lengths in 674 minerals. Monatshefte für Chemie, 130, 1047-1059. 675 Loganathan, N. and Kalinichev, A.G. (2013) On the hydrogen bonding structure at the 676 aqueous interface of ammonium-substituted mica: A molecular dynamics simulation. 677 *Zeitschrift für Naturforschung A*, **68**, 91-100. 678 Loganathan, N., Yazaydin, A.O., Bowers, G.M., Kalinichev, A.G., and Kirkpatrick, R.J. 679 (2016a) Structure, energetics, and dynamics of Cs<sup>+</sup> and H<sub>2</sub>O in hectorite: Molecular 680 dynamics simulations with an unconstrained substrate surface. Journal of Physical 681 *Chemistry C*, **120**, 10298-10310. 682 Loganathan, N., Yazaydin, A.O., Bowers, G.M., Kalinichev, A.G., and Kirkpatrick, R.J. 683 (2016b) Cation and water structure, dynamics, and energetics in smectite clays: A 684 molecular dynamics study of Ca-hectorite. Journal of Physical Chemistry C, 120, 685 12429-12439.Löwenstein, W. (1954) The distribution of aluminum in the tetrahedral 686 of silicates and aluminates, American Mineralogist, 39, 92-96. 687 Madejová, J., Janek, M., Komadel, P., Herbert, H.-J., and Moog, H.C. (2002) FTIR analyses 688
  - of water in MX-80 bentonite compacted from high salinary salt solution systems.

*Applied Clay Science*, **20**, 255-271.

- Marry, V., Rotenberg, B., and Turq, P. (2008) Structure and dynamics of water at a clay
  surface from molecular dynamics simulation. *Physical Chemistry Chemical Physics*,
  10, 4802-4813.
- Marry, V., Dubois, E., Malikova, N., Breu, J., and Haussler, W. (2013) Anisotropy of water
   dynamics in clays: Insights from molecular simulations for experimental QENS analy sis. *Journal of Physical Chemistry C*, **117**, 15106–15115.
- Michot, L.J., Villieras, F., Francois, M., Yvon, J., Le Dred, R., and Cases, J.M. (1994) The
  structural microscopic hydrophilicity of talc. *Langmuir*, **10**, 3765-3773.
- Morrow, C.P., Yazaydin, A.O., Krishnan, M., Bowers, G.M., Kalinichev, A.G., and Kirkpat-

rick, R.J. (2013) Structure, energetics, and dynamics of smectite clay interlayer hydra-

- tion: molecular dynamics and metadynamics investigation of Na-hectorite. *Journal of Physical Chemistry C*, **117**, 5172-5187.
- Ngouana Wakou, B.F. and Kalinichev, A.G. (2014) Structural arrangements of isomorphic
- substitutions in smectites: Molecular simulation of the swelling properties, interlayer
- structure, and dynamics of hydrated Cs–montmorillonite revisited with new clay models. *Journal of Physical Chemistry C*, **118**, 12758-12773
- 707 Ortega-Castro, J., Hernández-Haro, N., Dove, M.T., Hernández-Laguna, A., and Saínz-
- 708 Diaz, C.I. (2010) Density functional theory and Monte Carlo study of octahedral cati-
- on ordering of Al/Fe/Mg cations in dioctahedral 2:1 phyllosilicates. American Miner-
- 710 *alogist*, **95**, 209–220.
- Plimpton, S. (1995) Fast parallel algorithms for short-range molecular dynamics. *Journal of Computational Physics*, **117**, 1–19.
- 713 Praprotnik, M., Janezic, D., and Mavri, J. (2004) Temperature dependence of water
- 714 vibrational spectrum: A molecular dynamics simulation study. *Journal of Physical*

*Chemistry A*, **108**, 11056–11062.

- Prost, R. (1975) Interactions between adsorbed water molecules and the structure of clay
   minerals: Hydration mechanism of smectites. *Proceedings of International Clay Conference of The Clay Minerals Society, Mexico City*, 351-359.
- Rotenberg, B., Patel, A.J., and Chandler, D. (2011) Molecular explanation for why talc
  surfaces can be both hydrophilic and hydrophobic. *Journal of the American Chemical Society*, 133, 20521-20527.
- Russell, J.D. and Farmer, V.C. (1964) Infrared spectroscopic study of the dehydration of
   montmorillonite and saponite. *Clay Minerals Bulletin*, 5, 443-464.
- Sato, T., Watanabe, T., and Otsuka, R. (1992) Effects of layer charge, charge location, and
   energy change on expansion properties of dioctahedral smectites. *Clays and Clay Minerals*, 40, 103-113.
- Skipper, N.T., Soper, A.K., and McConnell, J.D.C. (1991) The structure of interlayer water in
   vermiculite. *Journal of Chemical Physics*, 94, 5751-5760.
- Sobolev, O., Favre Buivin, F., Kemner, E., Russina, M., Beuneu, B., Cuello, G.J., and Charlet,
- L. (2010) Water-clay surface interaction: A neutron scattering study. *Chemical Physics*, **374**, 55-61.
- Šolc, R., Gerzabek, M.H., Lischka, H., and Tunega, D. (2011) Wettability of kaolinite (001)
   surfaces Molecular dynamic study. *Geoderma*, 169, 47-54.
- Sovago, M., Kramer Campen, R.K., Bakker H.J., and Bonn, M. (2009) Hydrogen bonding
- strength of interfacial water determined with surface sum-frequency generation.
- 736 *Chemical Physics Letters*, **470**, 7 12.
- Sposito, G. and Prost, R. (1982) Structure of water adsorbed on smectites. *Chemical Reviews*,
  82, 554-573.
- 739 Sposito, G., Prost, R., and Gaultier, J.-P. (1983) Infrared spectroscopic study of adsorbed

740	water on reduced-charge Na/Li-montmorillonites. Clays and Clay Minerals, 31, 9-16.
741	Sposito, G., Skipper, N.T., Sutton, R., Park, S-H., Soper, A.K., and Greathouse, J.A. (1999)
742	Surface geochemistry of clay minerals. Proceedings of National Academy of Science
743	<i>USA</i> , <b>96</b> , 3358-3364.
744	Suquet, H., Prost, R., and Pezerat, H. (1977). Etude par la spectroscopie infrarouge de l' eau
745	adsorbée par la saponite-calcium. Clay Minerals, 12, 113-125.
746	Suzuki, S. and Kawamura, K. (2004) Study of vibrational spectra of interlayer water in
747	sodium beidellite by molecular dynamics simulations. Journal of Physical Chemistry
748	<i>B</i> , <b>108</b> , 13468-13474.
749	Środoń, J. and McCarty, D.K. (2008) Surface area and layer charge of smectite from CEC and
750	EGME/H <sub>2</sub> O retention measurements. <i>Clays and Clay Minerals</i> , <b>56</b> , 155-174.
751	Szczerba, M., Kłapyta, Z., and Kalinichev, A.G. (2014) Ethylene glycol intercalation in
752	smectites. Molecular dynamics simulation studies. Applied Clay Science, 91, 87-97.
753	Tay, K. and Bresme, F. (2006) Hydrogen bond structure and vibrational spectrum of water at a
754	passivated metal nanoparticle. Journal of Materials Chemistry, 16, 1956–1962.
755	Teich-McGoldrick, S.L., Greathouse, J.A., Jové-Colón, C.F., and Cygan, R.T. (2015) Swell-
756	ing properties of montmorillonite and beidellite clay minerals from molecular simula-
757	tion: Comparison of temperature, interlayer cation, and charge location effects. Jour-
758	nal of Physical Chemistry C, <b>119</b> , 20880-20891.
759	Toukan, K. and Rahman, A. (1985) Molecular-dynamics study of atomic motions in water.
760	<i>Physical Review B</i> , <b>31</b> , 2643–2648.
761	Tunega, D., Gerzabek, M.H. and Lischka, H. (2004) Ab initio molecular dynamics study of a
762	monomolecular water layer on octahedral and tetrahedral kaolinite surfaces. Journal of
763	<i>Physical Chemistry B</i> , <b>108</b> , 5930-5936.

- Wang, J.W., Kalinichev, A.G., and Kirkpatrick, R.J. (2004) Molecular modeling of the 10angstrom phase at subduction zone conditions. *Earth and Planetary Science Letters*,
  222, 517-527.
- Wang, J.W., Kalinichev, A.G., and Kirkpatrick, R.J. (2005a) Structure and decompression
   melting of a novel, high-pressure nanoconfined 2-D ice. *Journal of Physical Chemis- try B*, 109, 14308-14313.
- Wang, J., Kalinichev, A.G., Kirkpatrick, R.J., and Cygan, R.T. (2005b) Structure, energetics,
  and dynamics of water adsorbed on the muscovite (001) surface: a molecular
  dynamics simulation. *The Journal of Physical Chemistry B*, **109**, 15893-15905.
- Wang, J., Kalinichev, A.G., and Kirkpatrick, R.J. (2009) Asymmetric hydrogen bonding and
  orientational ordering of water at hydrophobic and hydrophilic surfaces: A comparison
  of water/vapor, water/talc, and water/mica interfaces. *Journal of Physical Chemistry C*, **113**, 11077-11085.
- Xu, W., Johnston, C.T., Parker, P., and Agnew, S.F. (2000) Infrared study of water sorption on
   Na-, Li-, Ca- and Mg-exchanged (SWy-1 and SAz-1) montmorillonite. *Clays and Clay*
- 779 *Minerals*, **48**, 120-131.
- Zaunbrecher, L.K., Cygan, R.T., and Elliott, W.C. (2015) Molecular models of cesium and
- rubidium adsorption on weathered micaceous minerals. *Journal of Physical Chemistry*
- 782 *A*, **119**, 5691-5700.

Species	charge (e)	D <sub>0</sub> (kcal/mol)	$R_0({ m \AA})$
surface bridging O	-1.05000	0.1554	3.8000
surface bridging O near tetrahedral substitution	-1.16875	0.1554	3.8000
ordinary bridging O	-1.05000	0.1554	3.5532
ordinary bridging O near tetrahedral substitution	-1.16875	0.1554	3.5532
ordinary bridging O near octahedral substitution	-1.18085	0.1554	3.5532
tetrahedral aluminum	1.57500	$1.8405 \cdot 10^{-6}$	3.4596
tetrahedral silicon	2.10000	$1.8405 \cdot 10^{-6}$	3.4596
octahedral aluminum	1.05000	$1.3298 \cdot 10^{-6}$	4.7943
octahedral magnesium	1.05000	9.0298.10-7	5.9090
hydroxyl oxygen	-0.95000	0.1554	3.5532
hydroxyl hydrogen	0.42500	0.0	0.0
aqueous sodium ion	1.00000	0.1301	2.6378
aqueous calcium ion	2.00000	0.1000	3.2237
aqueous cesium ion	1.00000	0.1000	4.3002

Table 1. Parameters of interatomic interactions used in present MD simulations. The modifications compared to
 the original CLAYFF parameters (Table 1 in Cygan *et al.*, 2004) are highlighted in bold.

	lodel $n(H_2O)$ phuc $n$		H <sub>2</sub> O wt%	H <sub>2</sub> O wt%	calculated
Model		$n(H_2O)/n(M^+)$	normalized to the total	normalized to dry	
			mass (smectite + H <sub>2</sub> O)	mass (smectite)	$u_{001}(A)$
Beid03Na_1W	2.5	8.333	10.93	12.28	12.99
Beid03Na_2W	5	16.667	19.71	24.55	15.94
Beid03Na_3W	7.5	25.0	26.92	36.83	18.88
Beid05Na_1W	2.5	5.0	10.82	12.13	12.76
Beid05Na_2W	5.0	10.0	19.53	24.26	15.38
Beid05Na_3W	7.5	15.0	26.68	36.39	18.34
Mtm03Na_1W	2.5	8.333	10.95	12.29	12.86
Mtm03Na_2W	5.0	16.667	19.73	24.58	15.95
Mtm03Na_3W	7.5	25.0	26.94	36.88	18.95
Mtm05Na_1W	2.5	5.0	10.84	12.16	12.58
Mtm05Na_2W	5.0	10.0	19.56	24.31	15.37
Mtm05Na_3W	7.5	15.0	26.72	36.47	18.14
Beid03Ca_2W	5.0	33.334	19.75	24.61	15.82
Beid05Ca_2W	5.0	20.0	19.59	24.36	15.38
Mtm03Ca_2W	5.0	33.334	19.77	24.64	15.95
Mtm05Ca_2W	5.0	20.0	19.62	24.41	15.38
Beid03Cs_2W	5.0	16.667	18.39	22.53	16.34
Beid05Cs_2W	5.0	10.0	17.45	21.13	16.13
Mtm03Cs_2W	5.0	16.667	18.40	22.55	16.41
Mtm05Cs_2W	5.0	10.0	17.47	21.17	16.14

788 Table 2. Interlayer cation and water content of the simulated clay models and the resulting basal spacing.

789 <sup>\*)</sup>Standard deviation is  $\sim \pm 0.05$  Å.

790

834	FIGURE CAPTIONS
835 836 837 838 839 840 841	Figure 1. A snapshot of part of the MD simulation cell for Mtm05Na_3W. H <sub>2</sub> O closer to the layer surface is oriented with two O-H <sub>w</sub> bonds pointing to the surface (thin green circle), whereas H <sub>2</sub> O farther from the surface - with one O-H <sub>w</sub> bond oriented towards the surface (thick blue circle). The inset shows the definition of the angle $\alpha$ formed by the H <sub>2</sub> O dipole vector and the surface normal. Vertical scale showing average distance in z direction relative to the oxygens of the basal plane is shown in angstroms.
842 843 844 845 846	Figure 2. Dependence of the H <sub>2</sub> O dipole vector orientation contours (see Figure 1 for the definition of $\alpha$ ) on the distance from the basal surface, <i>z</i> , for various hydration levels of different Na <sup>+</sup> -smectites. The interlayer distribution of the cations is shown by solid lines (blue in the color copy). Dashed lines mark the location of the surface (basal oxygen positions).
840 847 848 849	Figure 3. Dependence of the H <sub>2</sub> O dipole orientation contours on the distance from the basal surface, $z$ , for 2W hydration level of Ca <sup>2+</sup> and Cs <sup>+</sup> -smectites.
850 851 852 853 854	<ul> <li>Figure 4. Power spectra for hydrogens of interlayer H<sub>2</sub>O in smectites with two hydration layers (2W) in the O-H<sub>w</sub> stretching range showing the effect of the total layer charge and the cation-dependence: a) Na<sup>+</sup> form, b) Ca<sup>2+</sup> form, c) Cs<sup>+</sup> form. Increase of the spectral density at higher frequency is clearly visible in comparison with the spectrum of bulk water.</li> </ul>
855 856 857 858	Figure 5. Power spectra for hydrogens of interlayer H <sub>2</sub> O in the O-H <sub>w</sub> stretching range for Na <sup>+</sup> -beidellites (top) and Na <sup>+</sup> -montmorillonites (bottom) with different total layer charge and different water contents. The spectra were scaled by their H <sub>2</sub> O content.
859 860	Figure 6. Examples of received fits <u>Deconvolution of power spectra</u> for <u>of</u> pure water and two representative smectites.
861 862 863 864 865	Figure 7. Comparison of fitted-frequencies: a) dependence on water content for Na <sup>+</sup> -smectites in MD; b) dependence on interlayer cation for 2W forms in MD-; e)-in comparison to c) results from Kuligiewicz et al. (2015a). To obtain frequencies for H <sub>2</sub> O, the experimental values for D <sub>2</sub> O were scaled by factor of x 1.36.
866 867 868 869 870 871 872 873	Figure 8. H <sub>2</sub> O dipole orientation with respect to the surface normal for selected sub-sets of water molecules having their z and $\alpha$ values within the marked ranges (left) and power spectra of O-H <sub>w</sub> stretching vibrations calculated for each individual sub-set (center): thin green – bidentate population, thick blue – monodentate population, dashed red – water in the center of interlayer. Right column – the distributions of the shortest H-bonding distances of interfacial H <sub>2</sub> O molecules with basal oxygens (O <sub>w</sub> -H <sub>w</sub> O <sub>b</sub> ) in the bidentate and monodentate orientations, compared to distribution of O <sub>w</sub> -H <sub>w</sub> O <sub>w</sub> distances in pure water.
874 875 876 877 878 879 880 881 882 883 884	Figure 9. Orientation of the O-H <sub>w</sub> vector of interfacial H <sub>2</sub> O with respect to the surface normal ( $\beta$ ) at various distances, <i>z</i> , from the basal surface of Mtm05Ca_2W and Mtm05Na_2W smectites (left). Calculated power spectra for the sub-sets of H <sub>2</sub> O molecules (color marked for the selected $\beta$ and <i>z</i> ranges) are shown in the center. Right: the distributions of the shortest H-bonding distances of monodentate H <sub>2</sub> O with the basal oxygens (O <sub>w</sub> -H <sub>w</sub> O <sub>b</sub> ) and/or other oxygen of H <sub>2</sub> O (O <sub>w</sub> -H <sub>w</sub> O <sub>w</sub> ), compared to distribution of O <sub>w</sub> -H <sub>w</sub> O <sub>w</sub> distances in pure water. Thin green – bidentate population, thick blue – water O-H <sub>w</sub> bond oriented towards the surface, dashed orange – O-H <sub>w</sub> bond oriented towards the interlayer. Power spectra were scaled by the number of H <sub>2</sub> O molecules. A bulk water spectrum is also shown for comparison.
885 886	Figure 10. Distributions of $\underline{O}_w$ atoms with H-bonds donated and accepted and donated by the interlayer H <sub>2</sub> O and $\underline{O}_b$ in the 2W smectite structures studied.
887 888 889 890	Figure 11. Distributions of $\underline{O}_w$ atoms with H-bonds of various types (normalized per one H <sub>2</sub> O) for the 2W smectite structures studied. (a) - all H-bonds with $O_w$ -H $\cdots$ O distances below 2.45 Å. (b) - weak (long) H-bonds with $O_w$ -H $\cdots$ O distances in the range of 2.2-2.7 Å. In both cases the H- $O_w$ $\cdots$ O angle is < 30°.
891	































