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**Structure and dynamics of water-smectite interfaces:  
Hydrogen bonding and the origin of the sharp O-D<sub>w</sub>/O-H<sub>w</sub> infrared band  
from molecular simulations**

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KEY WORDS: clay-water interface, adsorbed water, smectite, molecular dynamics, infrared spectroscopy

## ABSTRACT

Experimental studies have shown that a sharp high-frequency IR band at  $\sim 3615\text{ cm}^{-1}$  (in  $\text{H}_2\text{O}$  form) and at  $\sim 2685\text{ cm}^{-1}$  (in  $\text{D}_2\text{O}$  form) is a common feature for all smectites, and its position correlates with layer charge. In order to explain the molecular origin of this band in terms of total layer charge, charge localization, as well as nature of interlayer cations influencing the position and intensity of this peak, a series of classical MD simulations were performed for several smectite models. The smectite layers were described using a modified CLAYFF force field, where the intramolecular vibrations of  $\text{H}_2\text{O}$  were more accurately described by the Toukan-Rahman potential. The power spectra of molecular vibrations of hydrogens were calculated for selected sub-sets of interlayer  $\text{H}_2\text{O}$  to quantitatively analyze their contribution to the observed spectral features. The statistics of hydrogen bonds in the smectite interlayers were also analyzed to support the spectral calculations.

The simulation results demonstrated clearly that only the  $\text{H}_2\text{O}$  molecules in close proximity with the smectite surface are responsible for the observed sharp vibrational band. Other hypotheses on the possible origins of this band were carefully considered and eventually rejected. Two orientations of  $\text{H}_2\text{O}$  molecules donating one or two H-bonds to the basal oxygens of the smectite surface (monodentate and bidentate orientations, respectively) are observed. In both orientations these H-bonds are quite weak, pointing to a generally hydrophobic character of the smectite surface. Both orientations were found to contribute to the high-frequency band, but the monodentate orientation provides the predominant contribution because surface  $\text{H}_2\text{O}$  molecules in this orientation are much more abundant. In good agreement with experiment, only a small difference in the peak position was observed between smectites with different charge localization. The effect of the total layer charge, i.e. the red-shift for higher charge smectites, was also confirmed. This shift arises from the decrease of the H-bonding distances of  $\text{H}_2\text{O}$  in monodentate and bidentate orientation.

## INTRODUCTION

50

51 Fourier transform infrared spectroscopy (FTIR) is one of the most commonly used  
52 techniques for studying clay minerals. However, unambiguous assignment of the vibrational  
53 bands originating from the stretching modes of adsorbed molecular H<sub>2</sub>O (O-H<sub>w</sub>) and  
54 structural OH (O-H<sub>s</sub>) in the clay materials is not always feasible. This is especially true for  
55 swelling clay minerals like smectites, which have large water sorption capacities (e.g., Cases  
56 *et al.*, 1997; Sato *et al.*, 1992) and may contain significant amounts of adsorbed water under  
57 air-dry conditions even upon prolonged drying (e.g., Środoń and McCarty, 2008).

58 Kuligiewicz *et al.* (2015a) have recently presented new evidence that the sharp high-  
59 frequency bands observed at ~3610-3640 cm<sup>-1</sup> involve a significant contribution from weakly  
60 hydrogen-bonded O-H<sub>w</sub> of adsorbed H<sub>2</sub>O molecules. These observations were in agreement  
61 with earlier spectroscopic measurements (Russell and Farmer, 1964; Farmer and Russell,  
62 1971; Suquet *et al.*, 1977; Sposito and Prost, 1982; Cariati *et al.*, 1981, 1983; Sposito *et al.*,  
63 1983), and opened the possibility for obtaining layer charge diagnostics based on the  
64 vibrational signature of H<sub>2</sub>O in smectite (Kuligiewicz *et al.*, 2015b).

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

72 The existence of such interfacial H-bonding with one O-H<sub>w</sub> bond oriented towards the  
73 clay surface was later confirmed by simulations of smectites and muscovite (e.g. Wang *et al.*,  
74 2005b, 2009; Marry *et al.*, 2008, 2013; Morrow *et al.*, 2013; Ngouana Wakou and Kalinichev,

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

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

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

100 in Monte Carlo computer simulations (Sposito et al., 1999). The relative weakness of the H-  
101 bonds donated by the interlayer water molecules to the clay basal surface, compared to the  
102 typical strength of the H<sub>2</sub>O···H<sub>2</sub>O bonds in bulk liquid water can be considered as a  
103 molecular-scale indication of relative hydrophobicity of the smectite siloxane surface.

104 The present study is aimed at advancing the aforementioned discussion by adding new  
105 spectroscopic arguments. Vibrational spectra of interfacial water molecules in several  
106 smectites are calculated and carefully analyzed here on the basis of molecular dynamics  
107 simulations in order to identify, interpret and quantify the variability of the position of the  
108 sharp H<sub>2</sub>O vibrational band as a function of total clay layer charge, layer charge localization,  
109 and nature of the interlayer cations, as recently observed experimentally (Kuligiewicz *et al.*,  
110 2015a).

111

## 112 **METHODOLOGY**

113

### 114 ***Smectite structures and MD simulations***

115 In order to explore systematically the effects of smectite composition, type of the  
116 interlayer cations and water content on the structure of interlayer H<sub>2</sub>O, a series of MD  
117 simulations were performed on four models of dioctahedral smectites with a total layer charge  
118 of 0.3 or 0.5 phuc and octahedral (montmorillonitic) or tetrahedral (beidellitic) charge  
119 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<sup>+</sup><sub>0.5</sub>(Al<sub>2.0</sub>)(Si<sub>3.5</sub>Al<sub>0.5</sub>)O<sub>10</sub>(OH)<sub>2</sub>;

122 Mtm03: M<sup>+</sup><sub>0.3</sub>(Al<sub>1.7</sub> Mg<sub>0.3</sub>)(Si<sub>4.0</sub>)O<sub>10</sub>(OH)<sub>2</sub>;

123 Mtm05: M<sup>+</sup><sub>0.5</sub>(Al<sub>1.5</sub> Mg<sub>0.5</sub>)(Si<sub>4.0</sub>)O<sub>10</sub>(OH)<sub>2</sub> .

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<sup>+</sup>, Cs<sup>+</sup>, and Ca<sup>2+</sup>) for selected water contents were used as additional variables.

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

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

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

156 === Table 1 ===

157 For a more accurate description of the vibrational properties of water molecules, the  
158 parameters of intramolecular interactions for H<sub>2</sub>O were taken from the work of Toukan and  
159 Rahman (1985) using the implementation proposed by Praprotnik *et al.* (2004). This allowed  
160 a more accurate description of the anharmonicity of the O<sub>w</sub>-H<sub>w</sub> stretching vibrations in the  
161 calculated IR spectra in comparison to the simple harmonic vibrational terms of the original  
162 CLAYFF parameterization (Cygan *et al.*, 2004).

163 *NPT*-ensemble MD simulations at constant pressure ( $P = 1$  bar) and temperature  
164 ( $T = 300$  K) were performed for 2.0 ns with the time step of 1 fs, preceded by one temperature  
165 annealing cycle from 400 K to 300 K of 0.1 ns. This long equilibration run was followed by a  
166 short 10 ps data analysis run when atomic positions and velocities were recorded every 2 fs.  
167 Standard periodic boundary conditions were applied (e.g., Allen and Tildesley, 1987) and all  
168 simulations were performed using the LAMMPS molecular modeling program (Plimpton,  
169 1995).

170

### 171 ***Simulation analysis***

172 The MD-simulated structural data were used to calculate the distributions of angles  
173 formed by the dipole axis of interfacial H<sub>2</sub>O molecules with respect to a vector normal to the  
174 2:1 surfaces (angle  $\alpha$ ) as a function of the distance  $z$  of O<sub>w</sub> from the plane of the basal



175 bridging oxygens ( $O_b$ ). The direction of the  $H_2O$  dipole was defined as a vector from the  
176 oxygen atom  $O_w$  to the central point between the two hydrogen atoms  $H_w$  of the same  
177 molecule. As the HOH angle was allowed to vary in the flexible  $H_2O$  molecular model used,  
178 this methodology introduces some small additional spread of the calculated angles.  
179 Additionally, the distributions of angles between a given OH bonds of  $H_2O$  and a vector  
180 normal to the 2:1 surfaces were calculated as a function of the distance  $z$  from the  $O_b$  plane  
181 (angle  $\beta$ ). The position of the plane of basal oxygen atoms was determined by the maximum  
182 of the atomic density distribution for these atoms, similarly to the previous studies (Wang *et*  
183 *al.*, 2005b, 2009; Loganathan and Kalinichev, 2013; Szczerba *et al.*, 2014, Ngouana Wakou  
184 and Kalinichev, 2014; Greathouse *et al.*, 2015; Teich-McGoldrick *et al.*, 2015 ; Loganathan *et*  
185 *al.*, 2016a, 2016b). All these properties were calculated by averaging over the last 1 ns of the  
186 equilibrium MD simulation runs.

187

### 188 ***Calculation of power spectra***

189 MD-simulated atomic trajectories can be used to calculate so-called power spectra  
190 (PS) of atomic vibrations that contain an entire distribution of the power (density of states) of  
191 all atomic motions in the simulated system in a function of vibrations frequency. With certain  
192 restrictions, these power spectra can be compared to the experimental vibrational spectra (e.g.,  
193 Allen and Tildesley, 1987; Kleinhesselink and Wolfsberg 1992). The power spectra are  
194 obtained as Fourier transformations of the so-called velocity autocorrelation function (VACF),  
195 which, in turn, can be directly calculated from the MD-simulated dynamic trajectories of the  
196 atoms in the modeled system. The frequency of  $H_2O$  stretching vibration is usually well  
197 captured by the VACF of the water hydrogen atoms (e.g., Kalinichev, 2001).

198 In the present work, normalized VACF based on the last 10 ps period of every MD  
199 simulation run were calculated for selected hydrogen atoms with a moving window of 1 ps

200 from the equilibrium part of the MD trajectory recorded every 2 fs:

$$201 \quad \text{VACF}(t) = \frac{\sum_{f=1, \text{sel.atoms}}^{n-n_{\text{VACF}}} \sum \vec{v}_f \cdot \vec{v}_{f+t}}{\sum_{f=1, \text{sel.atoms}}^{n-n_{\text{VACF}}} \sum \vec{v}_f \cdot \vec{v}_f}; \quad (2)$$

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

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

223 
$$PS(\omega) = \sum_{t=1}^{n_{VACF}} VACF(t) \cdot \cos\left(\frac{\pi}{n_{VACF}} \cdot t \cdot \omega\right) \quad (3)$$

224 The statistical noise was preliminarily reduced by applying a filtering function:

225 
$$VACF(t) = VACF(t) \cdot \exp(-t / \tau) \quad (4)$$

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 **RESULTS AND DISCUSSION**

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 
$$\text{=== Table 2 ===}$$

239 The values of the calculated basal spacings closely match those obtained by modelling  
240 the experimental diffractograms:  $d_{001\_1W} = 11.6\text{--}12.9 \text{ \AA}$ ,  $d_{001\_2W} = 14.9\text{--}15.7 \text{ \AA}$  and  $d_{001\_3W} = 18\text{--}19$   
241  $\text{ \AA}$  (e.g., Dzas *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  $15.95 \text{ \AA}$  for Mtm03Na\_2W and  $15.37 \text{ \AA}$  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<sup>+</sup> or Ca<sup>2+</sup> to Cs<sup>+</sup> (e.g.,

247 15.37 Å for Mtm05Na\_2W, 15.38 Å for Mtm05Ca\_2W and 16.14 Å for Mtm05Cs\_2W).  
248 These differences were caused mainly by the increased size of the cation and by differences in  
249 hydration energies.

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

261 === Figure 1 ===

262

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

264 The distribution of interlayer cations for different smectites (blue solid lines in Figures  
265 2 and 3) exhibited a clear dependence on the amount and location of layer charge, as well as  
266 on the type of the cation. In the case of 1W sodium smectites, two separate maxima were  
267 visible, each corresponding to inner-sphere coordination of H<sub>2</sub>O to the surface. For 2W  
268 sodium structures, a strong tendency to form a third maximum corresponding to fully  
269 hydrated cations (outer sphere) in the middle of the interlayer was observed. The ratio  
270 between the central and wing (inner sphere) cation distributions depended on the charge  
271 location, whereas changes in total charge had similar effect on both of these maxima. This  
272 result is in agreement with other recent simulations and is supported by calculated XRD data  
273 (Dazas *et al.*, 2015; Teich-McGoldrick *et al.*, 2015). In the case of 3W structures, outer-sphere  
274 sodium ions formed two maxima close to the interlayer center instead of one as in 2W. The  
275 data for the Mtm03Na\_3W structure were very similar to the results presented by Dazas *et al.*  
276 (2014). With increasing tetrahedral charge a tendency to form higher amount of inner-sphere  
277 complexes with the siloxane surface was observed.

278 The effect of changing interlayer cation from Na<sup>+</sup> to Ca<sup>2+</sup> was investigated for the  
279 models with 2W hydration. Comparison of smectites in Ca<sup>2+</sup> form (Figure 3) with those in  
280 Na<sup>+</sup> form (Figure 2) indicated that, despite the two-fold increase in the cation hydration  
281 enthalpy, the only effect was the vanishing of the (already weak) population of cations in the  
282 vicinity of the surface. The only exception was Beid05Ca\_2W, for which some remaining  
283 contribution of ions forming inner-sphere complexes was observed.

284 === Figure 2 ===

285 === Figure 3 ===

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

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

292

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

294 The contour maps of the angular distributions of the interlayer H<sub>2</sub>O dipole vectors  
295 with respect to the direction normal to the surface ( $\alpha$  angle) plotted in a function of the  
296 distance  $z$  from the surface (Figure 2) enabled the distinction of the two preferred surface-  
297 oriented types of water molecules marked in Figure 1. The predominantly bidentate  
298 population was located closer to the surface at  $z \sim 2.0$  Å and  $\alpha \sim 0-30^\circ$ , similarly to ideal  
299 theoretical values (observed in smectites with charge 0.5). A more distant and more  
300 pronounced monodentate population was at distances  $z \sim 2.8$  Å and oriented in a broad range  
301 of angles between  $30^\circ$  and  $80^\circ$  with a maximum at  $\alpha \sim 55^\circ$ , which matches the ideal  
302 theoretical value for one OH vector pointing perpendicularly to the smectite surface (half of  
303 the  $105^\circ$  angle of H<sub>2</sub>O). For higher hydration levels, a third population of water molecules  
304 was observed closer to the middle of the interlayer. The orientational distribution of this  
305 population depended significantly on both, the hydration level of the specific smectite and the  
306 type of the interlayer cation. The latter dependence is observed clearly when comparing the  
307 distribution in Mtm05 for the same hydration levels but different interlayer cations (Figures 2  
308 and 3).

309 The presence of monodentate H<sub>2</sub>O was ubiquitous. This sub-population was  
310 abundantly visible for all smectites, all cations and all hydration levels. A noticeable  
311 dependence of the location of the distribution maxima was however observed: higher average  
312 H<sub>2</sub>O dipole vector angles were observed for low charge smectites, lower hydration levels, and

313 for Cs<sup>+</sup> as interlayer cation.

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

322 The H<sub>2</sub>O orientation also depends on the type of the interlayer cation. As the majority  
323 of Cs<sup>+</sup> cations are located close to smectite surface, a noticeable decrease of bidentate H<sub>2</sub>O  
324 population in Cs<sup>+</sup>-smectites in comparison to their Na<sup>+</sup>- and Ca<sup>2+</sup>-analogs was observed. This  
325 effect was, however, small compared to the dependence of the bidentate population on layer  
326 charge. A noticeable decrease of the maximum amplitude corresponding to monodentate  
327 population was additionally observed for the Cs<sup>+</sup> form. This decrease was accompanied by the  
328 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***

331 Kuligiewicz *et al.* (2015a, 2015b) found that the sharp high-frequency IR band  
332 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)  
333 is a common feature for all hydrated smectites. Its intensity depended very little on the degree  
334 of clay hydration over a broad range of relative humidity, and its frequency exhibited a weak  
335 but systematic decrease (red-shift) upon increasing the total layer charge, with no measurable  
336 dependence on charge location. For a given layer charge, the dependence of the peak position  
337 on the field strength of the interlayer cation for high hydration enthalpy cations (Na<sup>+</sup>, Ca<sup>2+</sup>,

338  $\text{Mg}^{2+}$ ) was negligible and only low hydration cations ( $\text{Cs}^+$ ,  $\text{K}^+$ ) could be distinguished. These  
339 trends were opposite to what was observed for the main O-H<sub>w</sub> (O-D<sub>w</sub>) stretching envelopes,  
340 located at  $\sim 3400 \text{ cm}^{-1}$  ( $\sim 2500 \text{ cm}^{-1}$ ). The latter envelopes were known to exhibit a strong  
341 dependence of their intensity on hydration level and their position on interlayer cation, but  
342 were relatively unaffected by the smectite layer charge or charge localization (e.g., Xu *et al.*,  
343 2000, Madejová *et al.*, 2002, Kuligiewicz *et al.*, 2015a, 2015b).

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

350 In order to provide a quantitative explanation for the aforementioned experimental  
351 phenomenology, the power spectra for hydrogen atoms of interlayer H<sub>2</sub>O molecules were  
352 calculated for different smectites and compared to the spectrum of pure bulk water, the latter  
353 calculated with the same molecular model (Figure 4).

354 === Figure 4 ===

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



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

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

375 === Figure 5 ===

376 In order to further analyze the influence of different factors on the higher-frequency  
377 band, its positions was determined by fitting procedures. The low-frequency band was fitted  
378 with a mixed Gauss-Lorentz function (percentage of Lorentz function was optimized), while  
379 the higher-frequency one with a simple Gauss function. Additionally, a small combination  
380 band at  $\sim 4000\text{ cm}^{-1}$  was fitted with another Gaussian (Figure 6).

381 === Figure 6 ===

382 Increasing smectite total layer charge was found to induce a noticeable red-shift of the  
383 high-frequency peak, in remarkable agreement with experiment data (Kuligiewicz *et al.*,  
384 2015b). This shift was observed in Na<sup>+</sup> montmorillonites and beidellites at any hydration level  
385 (Figure 7a) and also in the 2W forms for any cation (Figure 7b). Only one exception was  
386 found: Mtm05Na\_3W exhibited higher frequency of the sharp peak than Mtm03Na\_3W. In  
387 contrary to the experimental observations (Kuligiewicz *et al.*, 2015a), the position of the

388 high-frequency peak was found to depend on charge location and water content.

389 === Figure 7 ===

390 In addition, the MD results showed a substantial difference in peak position between  
391 the Na<sup>+</sup> and Ca<sup>2+</sup> forms of smectites (Figure 7b), which are not visible experimentally (Figure  
392 7c, Kuligiewicz *et al.*, 2015a). Also the peak positions of the Cs<sup>+</sup> forms exhibited trends in  
393 relation to Na<sup>+</sup> and Ca<sup>2+</sup> forms that are different in MD than in experiment.

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

405

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

407 Calculations of the power spectra of specific sub-sets of interlayer water hydrogen  
408 atoms were performed in order to explain in more detail which part of the surface H<sub>2</sub>O  
409 population is responsible for the sharp high-frequency vibrational band observed in the  
410 experimental spectra (Kuligiewicz *et al.*, 2015a). Each subset was defined by a common range  
411 of distances from the surface,  $z$ , and H<sub>2</sub>O dipole orientation angle,  $\alpha$  (Figure 1). A H<sub>2</sub>O  
412 molecule belongs to a certain sub-set if it is found within the same ( $z$ ,  $\alpha$ ) range in both the first

413 and the last time-window of the VACF calculation. The results for three representative  
414 smectites (Mtm03Na\_2W, Beid03Na\_2W and Mtm05Ca\_2W) are presented in Figure 8.  
415 Spectral intensities were scaled by the number of H<sub>2</sub>O molecules identified in each subset in  
416 order to compare the contribution of each subset to the total spectrum.

417 === Figure 8 ===

418 This analysis demonstrates that H<sub>2</sub>O molecules at the center of the interlayer are not  
419 responsible for producing the sharp spectral feature. The latter originates instead from the  
420 overlapping contributions of both monodentate and bidentate orientations of surface H<sub>2</sub>O. The  
421 contribution of the monodentate orientation is, however, much stronger because of the higher  
422 number of H<sub>2</sub>O molecules populating this sub-set. If present, bidentate H<sub>2</sub>O gives a very  
423 small, although non-negligible, contribution to the power spectrum at frequencies that are on  
424 average higher than those of the monodentate population.

425 Based on the correlation of IR frequency of the O-H stretching band and the length of  
426 the H-bond, O-H<sub>w</sub>···O, (Libovitzky, 1999), a peak at  $\sim 3600\text{ cm}^{-1}$  may correspond to a O-  
427 H<sub>w</sub>···O distance  $> 2.2\text{ \AA}$  (i.e. an O<sub>w</sub>···O distance  $> 3.2\text{ \AA}$ ), and indicates a relatively weak H-  
428 bond donated to the surface (e.g., Kalinichev, 2001; Kumar *et al.*, 2007). Therefore, in order  
429 to obtain deeper insight into the studied problem, the distribution of the shortest O<sub>w</sub>-H<sub>w</sub>···O<sub>b</sub>  
430 distances in the monodentate and bidentate sub-sets were calculated (Figure 8, right column).  
431 The results showed a relatively broad distribution of the distances, with the maximum for  
432 monodentate H<sub>2</sub>O at  $\sim 1.9\text{ \AA}$  for Beid03\_Na and Mtm05Ca\_2W, and  $\sim 2.0\text{ \AA}$  for  
433 Mtm03Na\_2W. For comparison, in bulk liquid water the maximum of the shortest O<sub>w</sub>-  
434 H<sub>w</sub>···O<sub>w</sub> distance is at  $\sim 1.8\text{ \AA}$  (e.g., Kalinichev, 2001; Kumar *et al.*, 2007). The weighted  
435 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  
436 maxima:  $2.24\text{ \AA}$  for Beid03\_Na,  $2.16\text{ \AA}$  for Mtm05Ca\_2W, and  $2.27\text{ \AA}$  for Mtm03Na\_2W,  
437 comparing to  $1.95\text{ \AA}$  in bulk water. In bulk water a contribution of H-bond distances  $> 2.2\text{ \AA}$

438 was observed, but this is much smaller than for smectites. Low charge smectites exhibited a  
439 significantly larger contribution of weak H-bonds. For the high charge smectite  
440 Mtm05Ca\_2W the contribution of weak H-bonds due to H<sub>2</sub>O molecules in monodentate  
441 orientation was noticeably smaller. This explains the higher frequency and intensity of the  
442 high-frequency monodentate peak in the vibrational spectrum of this smectite. In the case of  
443 bidentate population, one of the O-H<sub>w</sub>···O<sub>b</sub> distances had a maximum also at ~1.9-2.0 Å,  
444 resulting in an H-bond of a comparable strength, while the second one was significantly  
445 longer and, respectively, weaker. This analysis suggests that upon increasing total layer  
446 charge the H-bond distances of the bidentate sub-set are decreasing and causing the red-shift  
447 of the calculated power spectrum.

448         Due to its ubiquitous presence and relative abundance, the population of monodentate  
449 surface H<sub>2</sub>O is mainly responsible for the presence of the sharp high-frequency OH stretching  
450 feature observed in the experiments (Kuligiewicz *et al.*, 2015a). This is in very good  
451 agreement with earlier experimental data (e.g., Russell and Farmer 1964; Farmer and Russell  
452 1971; Prost 1975; Suquet *et al.*, 1977; Sposito and Prost 1982; Sposito *et al.*, 1983) which  
453 linked the high frequency band to H<sub>2</sub>O at the surface of the interlayer, pointing one of their O-  
454 H<sub>w</sub> bonds towards the siloxane surface. In certain cases the bidentate sub-population may  
455 provide a non-negligible contribution as observed for higher charged smectites, e.g., for  
456 Mtm05\_Ca\_2W.

457

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

459         Evidence from MD simulations in support of the experimental data, suggested that the  
460 sharp high-frequency band in the IR spectra of hydrated smectite is clearly originating from  
461 H<sub>2</sub>O molecules oriented towards the clay surface. Can there be any other contribution to this  
462 sharp IR band? One possibility that would also be linked to surface H<sub>2</sub>O, could, for example,

463 involve the second O-H<sub>w</sub> bond of monodentate H<sub>2</sub>O, i.e. the one oriented towards the middle  
464 of the interlayer, away from the siloxane surface. As the surface H<sub>2</sub>O molecules have  
465 relatively fixed orientations, their O-H<sub>w</sub> bonds that are pointing away from the surface might  
466 have a decreased number of available H-bond acceptors within a suitable range and  
467 orientation around them. Such a lower coordination could, in principle, contribute in part to  
468 the observed sharp high-frequency infrared band. To examine this possibility, the subsets  
469 representing two separate hydroxyls of the monodentate population in Mtm05Ca\_2W and  
470 Mtm05Na\_2W were investigated (Figure 9).

471 === Figure 9 ===

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

481 A second mechanism potentially responsible for the emergence of the high-frequency  
482 H<sub>2</sub>O stretching band could be related to the influence of interlayer cations. The latter could  
483 deform the H-bonding structure of H<sub>2</sub>O molecules around them and possibly induce some H-  
484 bond breaking. A clear evidence against this possibility has been provided already in Figure 8:  
485 H<sub>2</sub>O molecules in the middle of the interlayer (red rectangle) were found not to contribute to  
486 the high-frequency band of interest. This is especially obvious in the case of Mtm05Ca\_2W,  
487 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***

491 The question regarding other possible molecular mechanisms responsible for the sharp  
492 high-frequency O-D<sub>w</sub>/O-H<sub>w</sub> band can be alternatively expressed as follows: Does interlayer  
493 water contain a sub-population of H<sub>2</sub>O molecules for which the O-H<sub>w</sub>···O distance of donated  
494 H-bonds is longer than ~2.2 Å (Libovitzky, 1999)? Obviously, the results of this analysis are  
495 only valid in comparison to those on pure bulk liquid water, due to the method-artificial non-  
496 negligible 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  
498 calculated depending on the distance  $z$  of the involved H<sub>2</sub>O molecules from the smectite  
499 siloxane surface. In the ordered ice structure, each H<sub>2</sub>O donates two strong H-bonds to other  
500 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  
501 number of donating and accepting H-bonds formed by each H<sub>2</sub>O molecule is somewhat lower  
502 than in ice due to the molecular disorder, and depends on temperature, density, and other  
503 thermodynamic factors. The exact number of H-bonds experienced by a H<sub>2</sub>O molecule in  
504 each situation also depends to some extent on the assumed criterion used in H-bonding  
505 calculation (see., e.g., Kalinichev, 2001; Kumar *et al.*, 2007).

506 A geometric definition for counting H-bonds (HB) was adopted from the literature  
507 (Wang *et al.*, 2009; Loganathan and Kalinichev, 2013). According to this definition, an H-  
508 bond is assumed to exist if the H···O distance between the donor and acceptor is below  
509 2.45 Å and the angle between the O–H and O···O vectors is below 30°. A systematic  
510 application of this criterion enabled the quantitative visualization of the general H-bonding  
511 trends of interlayer H<sub>2</sub>O molecules for several model smectites (Figure 10). As expected, H-  
512 bonds donated to surface O<sub>b</sub> atoms from both bidentate and monodentate H<sub>2</sub>O populations

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

523 === Figure 10 ===

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

534 === Figure 11 ===

535 For the general case considering all possible H-bonds in the system (Figure 11a), the  
536 number of accepted H-bonds per H<sub>2</sub>O molecule was found relatively constant with small  
537 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<sub>2</sub>O  
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<sub>2</sub>O donated to other H<sub>2</sub>O was independent of charge and interlayer cation (thin  
542 solid line in Figure 11a).

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

554

## 555 CONCLUSIONS

556

557 (1) Interfacial water molecules in bidentate and monodentate orientation with respect  
558 to the siloxane surface are the only species contributing to the experimentally observed sharp  
559 high-frequency O-H<sub>w</sub> stretching band of smectites (Kuligiewicz *et al.*, 2015a, Kuligiewicz *et*  
560 *al.*, 2015b). The number of interlayer H<sub>2</sub>O molecules in the monodentate orientation greatly  
561 exceeds that in the bidentate orientation and is, thus, the predominant contributor to the high-  
562 frequency vibrational band.



563 (2) In the bidentate orientation each H<sub>2</sub>O molecule donates two hydrogen bonds to the  
564 surface: one relatively strong, and another much weaker, while in the monodentate orientation  
565 it donates only one relatively weak H-bond to the surface.

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

570 (4) The experimentally observed low sensitivity of the position of the high-frequency  
571 vibrational band on the type of the (Na<sup>+</sup> or Ca<sup>2+</sup>) high hydration enthalpy interlayer cation  
572 remains unexplained. The differentiation of Cs<sup>+</sup> from Na<sup>+</sup> or Ca<sup>2+</sup> may be due to its tendency  
573 to displace surface H<sub>2</sub>O and form inner-sphere complexes with the siloxane surface as  
574 suggested by Kuligiewicz *et al.* (2015a), but further simulation work is needed to account for  
575 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

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589

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783

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

| Species   | charge ( <i>e</i> ) | $D_0$ (kcal/mol)       | $R_0$ (Å)     |
|---|---------------------|------------------------|---------------|
| surface bridging O                                | -1.05000            | 0.1554                 | <b>3.8000</b> |
| surface bridging O near tetrahedral substitution  | -1.16875            | 0.1554                 | <b>3.8000</b> |
| 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             | $1.8405 \cdot 10^{-6}$ | <b>3.4596</b> |
| tetrahedral silicon                               | 2.10000             | $1.8405 \cdot 10^{-6}$ | <b>3.4596</b> |
| octahedral aluminum                               | 1.05000             | $1.3298 \cdot 10^{-6}$ | 4.7943        |
| octahedral magnesium                              | 1.05000             | $9.0298 \cdot 10^{-7}$ | 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        |

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787

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

| Model       | $n(\text{H}_2\text{O})$ phuc | $n(\text{H}_2\text{O})/n(\text{M}^+)$ | $\text{H}_2\text{O}$ wt%  |                                   | calculated $d_{001}$ (Å)* |
|-------------|------------------------------|---------------------------------------|---|-----------------------------------|---------------------------|
|             |                              |                                       | normalized to the total mass (smectite + $\text{H}_2\text{O}$ ) | normalized to dry mass (smectite) |                           |
| 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                     |

\*)Standard deviation is  $\sim \pm 0.05$  Å.

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## FIGURE CAPTIONS

834  
835  
836 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  
837 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  
838 surface - with one O-H<sub>w</sub> bond oriented towards the surface (thick blue circle). The inset shows the  
839 definition of the angle  $\alpha$  formed by the H<sub>2</sub>O dipole vector and the surface normal. Vertical scale  
840 showing average distance in  $z$  direction relative to the oxygens of the basal plane is shown in angstroms.

841  
842 Figure 2. Dependence of the H<sub>2</sub>O dipole vector orientation contours (see Figure 1 for the definition of  $\alpha$ ) on the  
843 distance from the basal surface,  $z$ , for various hydration levels of different Na<sup>+</sup>-smectites. The interlayer  
844 distribution of the cations is shown by solid lines (blue in the color copy). Dashed lines mark the  
845 location of the surface (basal oxygen positions).

846  
847 Figure 3. Dependence of the H<sub>2</sub>O dipole orientation contours on the distance from the basal surface,  $z$ , for 2W  
848 hydration level of Ca<sup>2+</sup> and Cs<sup>+</sup>-smectites.

849  
850 Figure 4. Power spectra for hydrogens of interlayer H<sub>2</sub>O in smectites with two hydration layers (2W) in the O-  
851 H<sub>w</sub> stretching range showing the effect of the total layer charge and the cation-dependence: a) Na<sup>+</sup> form,  
852 b) Ca<sup>2+</sup> form, c) Cs<sup>+</sup> form. Increase of the spectral density at higher frequency is clearly visible in  
853 comparison with the spectrum of bulk water.

854  
855 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)  
856 and Na<sup>+</sup>-montmorillonites (bottom) with different total layer charge and different water contents. The  
857 spectra were scaled by their H<sub>2</sub>O content.

858  
859 Figure 6. ~~Examples of received fits~~Deconvolution of power spectra ~~for~~ of pure water and two representative  
860 smectites.

861  
862 Figure 7. Comparison of ~~fitted~~ frequencies: a) dependence on water content for Na<sup>+</sup>-smectites ~~in MD~~; b)  
863 dependence on interlayer cation for 2W forms ~~in MD~~; ~~e)~~ in comparison to c) results from Kuligiewicz  
864 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~~  
865 1.36.

866  
867 Figure 8. H<sub>2</sub>O dipole orientation with respect to the surface normal for selected sub-sets of water molecules  
868 having their  $z$  and  $\alpha$  values within the marked ranges (left) and power spectra of O-H<sub>w</sub> stretching  
869 vibrations calculated for each individual sub-set (center): thin green – bidentate population, thick blue –  
870 monodentate population, dashed red – water in the center of interlayer. Right column – the distributions  
871 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  
872 the bidentate and monodentate orientations, compared to distribution of O<sub>w</sub>-H<sub>w</sub>···O<sub>w</sub> distances in pure  
873 water.

874  
875 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  
876 distances,  $z$ , from the basal surface of Mtm05Ca\_2W and Mtm05Na\_2W smectites (left). Calculated  
877 power spectra for the sub-sets of H<sub>2</sub>O molecules (color marked for the selected  $\beta$  and  $z$  ranges) are  
878 shown in the center. Right: the distributions of the shortest H-bonding distances of monodentate H<sub>2</sub>O  
879 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  
880 distribution of O<sub>w</sub>-H<sub>w</sub>···O<sub>w</sub> distances in pure water. Thin green – bidentate population, thick blue –  
881 water O-H<sub>w</sub> bond oriented towards the surface, dashed orange – O-H<sub>w</sub> bond oriented towards the  
882 interlayer. Power spectra were scaled by the number of H<sub>2</sub>O molecules. A bulk water spectrum is also  
883 shown for comparison.

884  
885 Figure 10. Distributions of O<sub>w</sub> atoms with H-bonds donated and accepted and donated by the interlayer H<sub>2</sub>O and  
886 O<sub>b</sub> in the 2W smectite structures studied.

887  
888 Figure 11. Distributions of O<sub>w</sub> atoms with H-bonds of various types (normalized per one H<sub>2</sub>O) for the 2W  
889 smectite structures studied. (a) - all H-bonds with O<sub>w</sub>-H···O distances below 2.45 Å. (b) - weak (long)  
890 H-bonds with O<sub>w</sub>-H···O distances in the range of 2.2-2.7 Å. In both cases the H-O<sub>w</sub>···O angle is < 30°.

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