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**Structure and dynamics of water-smectite interfaces:
Hydrogen bonding and the origin of the sharp O-D_w/O-H_w 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 H_2O form) and at $\sim 2685\text{ cm}^{-1}$ (in D_2O 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 H_2O 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 H_2O 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 H_2O 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 H_2O 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 H_2O 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 H_2O in monodentate and bidentate orientation.

INTRODUCTION

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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 H₂O (O-H_w) and structural OH (O-H_s) 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 high-frequency bands observed at ~3610-3640 cm⁻¹ involve a significant contribution from weakly hydrogen-bonded O-H_w of adsorbed H₂O 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 H₂O 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 H₂O molecules with respect to oxygen atoms of the basal plane. These MD calculations confirmed the model of Prost (1975) with one O-H_w bond of the H₂O 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_w 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,

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 H₂O located above the ditrigonal cavities of smectites and with
79 both O-H_w 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 H₂O···H₂O 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_w bonds pointing towards the surface of beidellite contribute to a
86 vibrational band at ~3500 cm⁻¹, whereas the O-H_w H-bonded to other H₂O molecules produce
87 a band at ~3365 cm⁻¹. The relative intensity of the ~3365 to the ~3500 cm⁻¹ bands increased
88 with increasing water content, and for 7 H₂O molecules phuc the band at ~3500 cm⁻¹ 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 H₂O···H₂O 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 H₂O 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 H₂O, 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⁺_{0.3}(Al_{2.0})(Si_{3.7}Al_{0.3})O₁₀(OH)₂;

121 Beid05: M⁺_{0.5}(Al_{2.0})(Si_{3.5}Al_{0.5})O₁₀(OH)₂;

122 Mtm03: M⁺_{0.3}(Al_{1.7} Mg_{0.3})(Si_{4.0})O₁₀(OH)₂;

123 Mtm05: M⁺_{0.5}(Al_{1.5} Mg_{0.5})(Si_{4.0})O₁₀(OH)₂ .

124 The interlayer water content (2.5, 5.0 and 7.5 H₂O phuc) and the type of the interlayer cation

125 (Na⁺, Cs⁺, and Ca²⁺) 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 H₂O 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_w-H_w 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 H₂O molecules with respect to a vector normal to the
174 2:1 surfaces (angle α) as a function of the distance z of O_w 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 β). 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_{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 H₂O from the clay surface and the angle of H₂O dipole
207 orientation (or angle between one of OH groups of H₂O 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 H₂O 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 H₂O 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_w bonds (e.g., Kalinichev, 2001). The choice of both
219 characteristic calculation times ensured that the H-bonding situation of each H₂O molecule
220 was included in a certain selected angle/position subset for VACF calculation.

221 In order to calculate the power spectra of H₂O vibrations, a cosine Fourier transform
222 of VACF for the water hydrogen atoms was performed as:

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

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

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

226 where τ 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 H₂O 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 \AA (e.g., Dzas *et al.*, 2015). The data show clearly that for the same water content and
 242 interlayer cation (Na⁺) the basal spacing d_{001} decreases with increasing layer charge (e.g.
 243 15.95 \AA for Mtm03Na_2W and 15.37 \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⁺ or Ca²⁺ to Cs⁺ (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 H₂O molecules close to the siloxane surface
254 tend to be specifically oriented. Within a distance of < 3.5 Å between O_w and the siloxane
255 surface two such preferred orientations could be distinguished. The population closer to the
256 surface corresponds to H₂O with both O-H_w bonds pointing towards the surface (bidentate),
257 whereas a more distant and more pronounced population is due to the H₂O pointing only one
258 of their O-H_w 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 H₂O 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⁺ to Ca²⁺ was investigated for the
279 models with 2W hydration. Comparison of smectites in Ca²⁺ form (Figure 3) with those in
280 Na⁺ 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⁺ ions had a tendency to remain close to
287 the surface (Figure 3), which is in excellent agreement with other recent Cs⁺-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⁺ in the interlayer
290 was substantially different from those of Na⁺ and Ca²⁺, which were generally quite similar to
291 each other (compare Figures 2 and 3).

292

293 ***H₂O orientation***

294 The contour maps of the angular distributions of the interlayer H₂O dipole vectors
295 with respect to the direction normal to the surface (α 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° and 80° 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° angle of H₂O). 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 H₂O 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 H₂O dipole vector angles were observed for low charge smectites, lower hydration levels, and

313 for Cs⁺ as interlayer cation.

314 The bidentate H₂O 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 H₂O
320 population on hydration level was observed: for a given smectite, the relative number of
321 bidentate H₂O decreases upon drying.

322 The H₂O orientation also depends on the type of the interlayer cation. As the majority
323 of Cs⁺ cations are located close to smectite surface, a noticeable decrease of bidentate H₂O
324 population in Cs⁺-smectites in comparison to their Na⁺- and Ca²⁺-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⁺ form. This decrease was accompanied by the
328 transfer of H₂O to the middle of the interlayer.

329

330 ***Vibrational spectra of H₂O 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⁻¹ (in H₂O form) and ~2685 cm⁻¹ (in D₂O 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⁺, Ca²⁺,

338 Mg^{2+}) was negligible and only low hydration cations (Cs^+ , K^+) could be distinguished. These
339 trends were opposite to what was observed for the main O-H_w (O-D_w) 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 H₂O 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 H₂O 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 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_w-H_w 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 H₂O 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 H₂O 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⁺ 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⁺ and Ca²⁺ forms of smectites (Figure 7b), which are not visible experimentally (Figure
392 7c, Kuligiewicz *et al.*, 2015a). Also the peak positions of the Cs⁺ forms exhibited trends in
393 relation to Na⁺ and Ca²⁺ 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 H₂O. The model for H₂O may also have
400 limitations and the power spectra have excessive high-frequency spectral density at
401 3728 cm⁻¹. 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_w/O-H_w 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 H₂O
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 H₂O dipole orientation angle, α (Figure 1). A H₂O
412 molecule belongs to a certain sub-set if it is found within the same (z , α) 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 H₂O 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 H₂O 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 H₂O. The
421 contribution of the monodentate orientation is, however, much stronger because of the higher
422 number of H₂O molecules populating this sub-set. If present, bidentate H₂O 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_w···O, (Libovitzky, 1999), a peak at ~ 3600 cm⁻¹ may correspond to a O-
427 H_w···O distance > 2.2 Å (i.e. an O_w...O distance >3.2 Å), 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_w-H_w···O_b
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 H₂O at ~1.9 Å for Beid03_Na and Mtm05Ca_2W, and ~2.0 Å for
433 Mtm03Na_2W. For comparison, in bulk liquid water the maximum of the shortest O_w-
434 H_w···O_w distance is at ~1.8 Å (e.g., Kalinichev, 2001; Kumar *et al.*, 2007). The weighted
435 average of the calculated O_w-H_w···O_b distributions is, however, a little bit greater than the
436 maxima: 2.24 Å for Beid03_Na, 2.16 Å for Mtm05Ca_2W, and 2.27 Å for Mtm03Na_2W,
437 comparing to 1.95 Å in bulk water. In bulk water a contribution of H-bond distances > 2.2 Å

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 H₂O 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_w···O_b 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 H₂O 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 H₂O at the surface of the interlayer, pointing one of their O-
454 H_w 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 H₂O 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 H₂O, could, for example,

463 involve the second O-H_w bond of monodentate H₂O, i.e. the one oriented towards the middle
464 of the interlayer, away from the siloxane surface. As the surface H₂O molecules have
465 relatively fixed orientations, their O-H_w 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 H₂O, one H-bond is donated to the surface (thick blue
473 rectangle in Figure 9), while the second one is donated to another H₂O (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 H₂O molecules. This is additionally confirmed by comparison of the shortest
479 O_w-H_w···O_w 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 H₂O stretching band could be related to the influence of interlayer cations. The latter could
483 deform the H-bonding structure of H₂O 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 H₂O 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 H₂O molecules in the hydration shell of Ca²⁺ 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_w/O-H_w band can be alternatively expressed as follows: Does interlayer
493 water contain a sub-population of H₂O molecules for which the O-H_w···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 H₂O molecules from the smectite
499 siloxane surface. In the ordered ice structure, each H₂O donates two strong H-bonds to other
500 H₂O and also accepts two strong H-bonds from two other H₂O molecules. In liquid water, the
501 number of donating and accepting H-bonds formed by each H₂O 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 H₂O 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 H₂O molecules for several model smectites (Figure 10). As expected, H-
512 bonds donated to surface O_b atoms from both bidentate and monodentate H₂O 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 H₂O. Besides donating to the basal surface, both bidentate and
516 monodentate H₂O accepted H-bonds from and donated to other H₂O 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_w 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_w-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_w-H···O distance <2.45 Å). In both cases the H-
531 O_w···O angle was kept < 30°. The plots in Figure 11 show only the average distributions of H-
532 bonds experienced by each H₂O 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 H₂O 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 H₂O
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 H₂O donated to other H₂O 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 H₂O; 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 H₂O 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_w stretching band of smectites (Kuligiewicz *et al.*, 2015a, Kuligiewicz *et*
560 *al.*, 2015b). The number of interlayer H₂O 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 H₂O 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_w-H···O_b 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⁺ or Ca²⁺) high hydration enthalpy interlayer cation
572 remains unexplained. The differentiation of Cs⁺ from Na⁺ or Ca²⁺ may be due to its tendency
573 to displace surface H₂O 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⁺ 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	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	$9.0298 \cdot 10^{-7}$	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	$n(\text{H}_2\text{O})/n(\text{M}^+)$	H ₂ O wt%	H ₂ O wt%	calculated d_{001} (Å)*
			normalized to the total mass (smectite + H ₂ 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. H₂O closer to the layer surface is
837 oriented with two O-H_w bonds pointing to the surface (thin green circle), whereas H₂O farther from the
838 surface - with one O-H_w bond oriented towards the surface (thick blue circle). The inset shows the
839 definition of the angle α formed by the H₂O 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 H₂O dipole vector orientation contours (see Figure 1 for the definition of α) on the
843 distance from the basal surface, z , for various hydration levels of different Na⁺-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 H₂O dipole orientation contours on the distance from the basal surface, z , for 2W
848 hydration level of Ca²⁺ and Cs⁺-smectites.
849
- 850 Figure 4. Power spectra for hydrogens of interlayer H₂O in smectites with two hydration layers (2W) in the O-
851 H_w stretching range showing the effect of the total layer charge and the cation-dependence: a) Na⁺ form,
852 b) Ca²⁺ form, c) Cs⁺ 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 H₂O in the O-H_w stretching range for Na⁺-beidellites (top)
856 and Na⁺-montmorillonites (bottom) with different total layer charge and different water contents. The
857 spectra were scaled by their H₂O 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⁺-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 H₂O, the experimental values for D₂O were scaled by factor of x
865 1.36.
866
- 867 Figure 8. H₂O dipole orientation with respect to the surface normal for selected sub-sets of water molecules
868 having their z and α values within the marked ranges (left) and power spectra of O-H_w 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 H₂O molecules with basal oxygens (O_w-H_w···O_b) in
872 the bidentate and monodentate orientations, compared to distribution of O_w-H_w···O_w distances in pure
873 water.
874
- 875 Figure 9. Orientation of the O-H_w vector of interfacial H₂O with respect to the surface normal (β) 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 H₂O molecules (color marked for the selected β and z ranges) are
878 shown in the center. Right: the distributions of the shortest H-bonding distances of monodentate H₂O
879 with the basal oxygens (O_w-H_w···O_b) and/or other oxygen of H₂O (O_w-H_w···O_w), compared to
880 distribution of O_w-H_w···O_w distances in pure water. Thin green – bidentate population, thick blue –
881 water O-H_w bond oriented towards the surface, dashed orange – O-H_w bond oriented towards the
882 interlayer. Power spectra were scaled by the number of H₂O molecules. A bulk water spectrum is also
883 shown for comparison.
884
- 885 Figure 10. Distributions of O_w atoms with H-bonds donated and accepted and donated by the interlayer H₂O and
886 O_b in the 2W smectite structures studied.
887
- 888 Figure 11. Distributions of O_w atoms with H-bonds of various types (normalized per one H₂O) for the 2W
889 smectite structures studied. (a) - all H-bonds with O_w-H···O distances below 2.45 Å. (b) - weak (long)
890 H-bonds with O_w-H···O distances in the range of 2.2-2.7 Å. In both cases the H-O_w···O angle is < 30°.
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