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Water Molecules in Single File: First-Principles Studies of One-Dimensional Water Chains in Zeolites

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The static and dynamical properties of one-dimensional water chains confined in zeolitic channels are studied by means of the Car Parrinello method. The properties of such an unusual water structure, present in zeolites Li-ABW and bikitaite, are reported and compared. Differences in the zeolitic frameworks are responsible for the different properties of the water chains. A more rigid chain structure is found in bikitaite, whereas our calculations predict that in Li-ABW water molecules are allowed some rotational degrees of freedom. We interpret such a finding on the basis of the different strengths of host-guest dipolar interactions. Weaker interactions in Li-ABW allow for rotation of water molecules.

Introduction

Bikitaite, $\text{Li}[\text{AlSi}_2\text{O}_6](\text{H}_2\text{O})$, and Li-ABW, $\text{Li}[\text{AlSiO}_4](\text{H}_2\text{O})$, are two zeolites, the former a rare mineral, the latter a synthetic phase, that share a set of features. They are high-density zeolites, ranking around the top of the known frameworks density scale, with 100% Li as extraframework cations. They have high Al/Si ratios (2/1 in bikitaite, 1/1 in Li-ABW). Their framework topology is characterized by sheets of tetrahedra forming a hexagonal tiling, but they differ in the way each tetrahedron (a TO_4 unit, where T stands for Si or Al) is connected to its neighbor in the sheet, see Figure 1, and in the way these sheets are arranged. While in bikitaite, parallel sheets are connected by chains of SiO_4 tetrahedra (pyroxene chains) to form a triclinic structure,¹ in Li-ABW, the hexagonal sheets are directly connected each other to form an orthorhombic frame.^{2,3} However both structures form eight-membered TO_4 rings, nearly perpendicular to the hexagonal tiling, developing non-crossing channels whose section is roughly $3 \times 4 \text{ \AA}^2$ (Figure 2). The main characteristic that renders such structures interesting is however the content of the channels system: the Li^+ cations are coordinated to three framework oxygens and one water molecule oxygen, respectively. The water molecules are hydrogen-bonded to each other and form a peculiar one-dimensional chain, parallel to the channel direction. Such water molecules are also weakly hydrogen-bonded to the framework oxygens in the case of Li-ABW, whereas no hydrogen bond has been found between water and framework in bikitaite.

It is such a one-dimensional water structure that has attracted our attention. Recently, we have reported studies on the bikitaite system,^{4,5} whose main results may be summarized here:

- (i) the water chain stability is independent of the (Si, Al) distribution in the framework;
- (ii) rotational motion of water molecules has been excluded, therefore justifying the name of one-dimensional ice given to the structure and indicating high rigidity and stability of the chains;

and (iii) the water chain system develops a permanent dipole parallel to that of the channel system, and such a dipole is antiparallel to the dipole moment calculated for the water-free framework.

The origin and the stability of such a peculiar water structure have been suggested to be due to a number of concomitant causes, namely, the ad hoc size of the non-crossing eight-membered-ring channel system, the fact that the channels do not cross each other, and the permanent polarization of the Li-bikitaite (water-free) system that stabilizes the entropically unfavored one-dimensional ice structure via dipolar host-guest interactions, without the need of direct water-frame hydrogen bonds. Such permanent and high polarization of the framework may be ascribed to the structure itself of bikitaite, characterized by ditrigonally distorted 6-ring sheets and pyroxene chains.⁵

In this view, a study of Li-ABW may help to give a better explanation about the origin and stability of the arrays of one-dimensional water molecules.

Li-ABW was synthesized in 1951 by Barrer and White.⁶ Structural studies on this zeolite were carried out by single-crystal X-ray² and powder neutron diffractions.³ The isomorphous $\text{Li}[\text{GaSiO}_4](\text{H}_2\text{O})$ ⁷ and $\text{Li}[\text{ZnAsO}_4](\text{H}_2\text{O})$ ⁸ have been synthesized as well. Moreover, a series of specimen with extraframework cations different from Li have been studied.^{9,10} Contrary to Li-ABW and its isomorphous Ga and Zn-As forms, in which the water/extraframework cation ratio is 1, in Na-ABW and Ag-ABW, such a ratio is lower than 1. This indicates that these ABW forms may have different water contents in their channels and therefore possibly a different geometrical arrangement of the extraframework species. This structural feature is at present not clarified since the structural refinements of Na-ABW and Ag-ABW are not reported in the literature.

Here, we present computer simulation studies of Li-ABW with the main target of investigating the one-dimensional water system. Also, the aim of this work is to compare the results with those obtained for bikitaite to extend our knowledge of such an unusual water arrangement, as well as to study the effect of the confining structure on the stability of the water chains.

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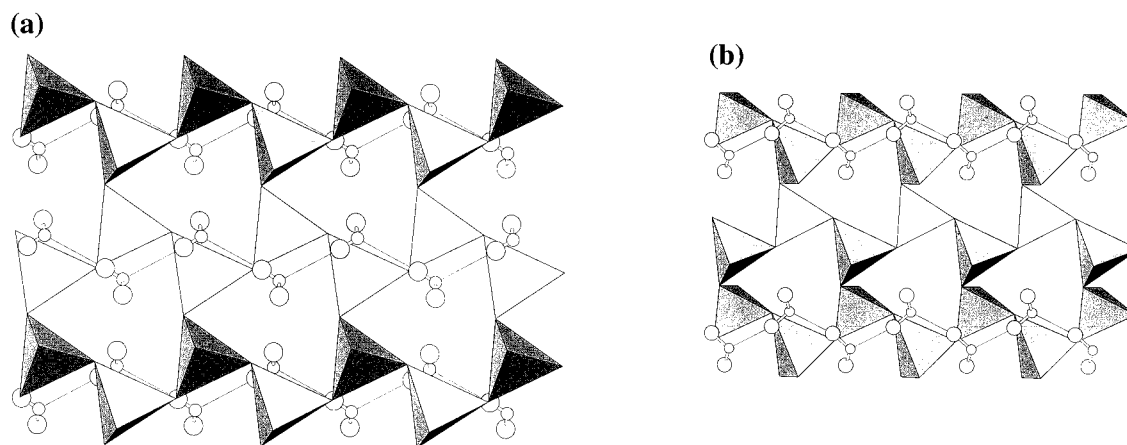


Figure 1. Representation of the six-ring sheet structures: (a) Li-ABW and (b) bikitaite. Ball-and-stick representations of the hydrogen bonded one-dimensional water chains are superimposed on the tetrahedra-formed six-ring sheets.

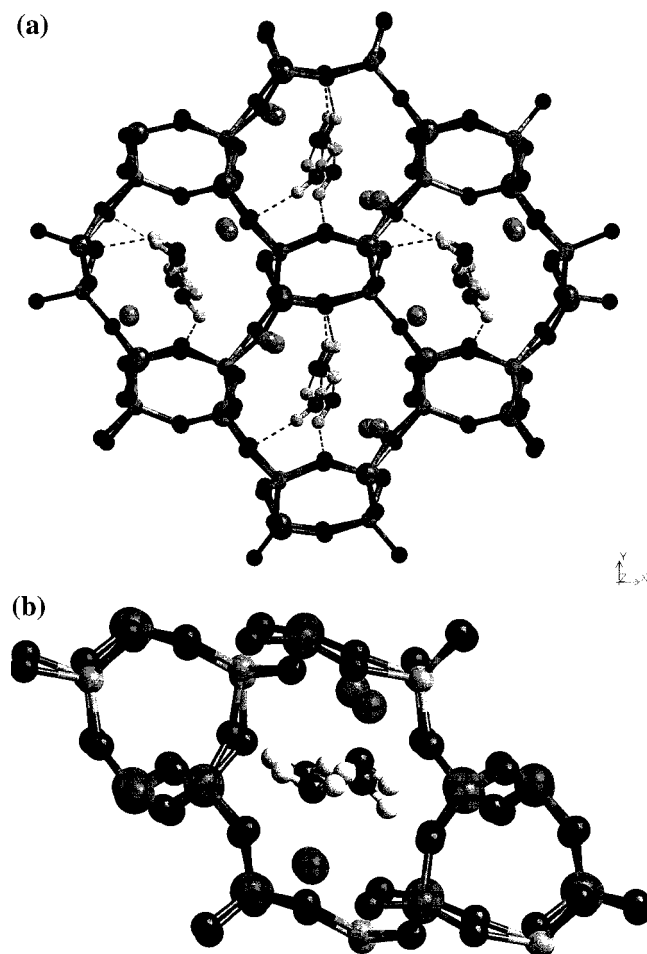


Figure 2. Ball-and-stick representations of Li-ABW (a) and bikitaite (b). They are snapshots extracted from the calculated trajectories. One eight-membered ring is pictured in the bikitaite representation, whereas four eight-membered rings are shown for Li-ABW. The spheres represent, respectively, black, oxygen; small pale gray, hydrogen; large dark gray, silicon; small gray, aluminum; medium gray lithium. Water-framework oxygen hydrogen bonds are represented by dashed lines.

Method of Calculation

The Car Parrinello *ab initio* Molecular Dynamics (MD) method^{1,12} has been used to investigate the structure and the dynamical behavior of Li-ABW. We used an *ab initio* approach for a series of reasons. First of all, the results' accuracy is highly enhanced by adopting an *ab initio* scheme for force calculations. This is especially relevant when, as in the present case, host-

guest interactions may influence the polarization of guest species. The crystals have small unit cells and therefore a relatively small number of atoms and electrons to be accounted for. This makes such calculations also affordable on relatively small computers. Last but not least, within this scheme, the transferability problem of empirical potentials is completely bypassed.

The adopted MD supercell contains two crystallographic cells in the direction along which the water chains develop (the *z* axis, in this case); hence, the formula of the simulated system is $\text{Li}_8[\text{Al}_8\text{Si}_8\text{O}_{32}]\cdot 8\text{H}_2\text{O}$. The parameters of the periodically repeated orthorhombic MD supercell are $a = 10.313 \text{ \AA}$; $b = 8.194 \text{ \AA}$; and $c = 9.986 \text{ \AA}$. The initial positions of all atoms, except H, were taken from an earlier single-crystal X-ray diffraction study,² whereas the H coordinates (not reported earlier²) are those determined by Norby et al.³ by neutron powder diffraction.

The ion-electron interactions were described by norm-conserving pseudopotentials:¹³⁻¹⁵ d-nonlocality was adopted for Al, Si and O atoms, p-nonlocality was adopted for Li atoms, and a local norm-conserving pseudopotential was used for H. Electron-electron interactions were calculated with gradient-corrected density functional approximations.^{16,17} As in the bikitaite simulations, the Becke functional was used for the exchange interaction,¹⁸ whereas the functional of Perdew was adopted for the correlation.¹⁹

The simulation system contains 320 valence electrons; the electronic states²⁰ were expanded in plane waves (only the Γ point of the Brillouin zone was considered) up to a cutoff energy of 60 Ry, as in the case of bikitaite.^{4,5} The equations of motion were integrated¹² using a time step of 0.121 fs, and a fictitious mass of 500 au was used for the wave function coefficients. A molecular dynamics step for this system costs ≈ 150 CPU seconds on a medium-sized workstation. On a parallel CRAY T3E with 32 processors, the same calculation costs ≈ 5 s. The dynamics of Li-ABW was performed at room temperature and followed for 4.1 ps after equilibration.

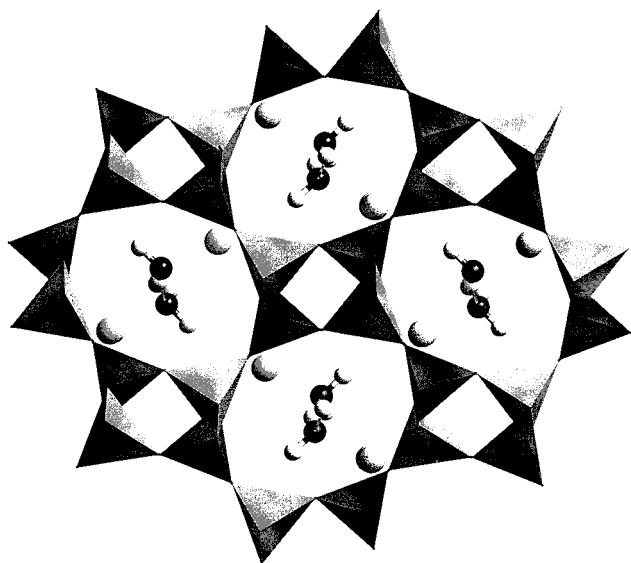
Results

We obtained the crystallographic atomic coordinates from the calculated trajectory by folding each Cartesian coordinate to the asymmetric unit using the symmetry operations of the experimentally found space group, and then averaging over the trajectory. The calculated crystallographic coordinates are reported in Table 1 where, for comparison the experimental results are reported as well. The overall agreement between

TABLE 1: Calculated Fraction Crystallographic Coordinates (*x*, *y*, *z*) for Li-ABW^a

atom	<i>x</i> (calc)	<i>x</i> (exp)	<i>y</i> (calc)	<i>y</i> (exp)	<i>z</i> (calc)	<i>z</i> (exp)
Li	0.1687	0.1862	0.6618	0.6849	0.2508	0.2520
Al	0.1615	0.1593	0.0692	0.0810	0.2509	0.2500
Si	0.3606	0.3544	0.3607	0.3575	0.2496	0.2492
O1	0.0132	0.0061	0.1671	0.1584	0.1893	0.1970
O2	0.2863	0.2736	0.1995	0.2198	0.1340	0.1391
O3	0.1913	0.1912	0.0256	0.0399	0.5956	0.5907
O4	0.1726	0.1804	-0.1191	-0.1008	0.0691	0.0689
Ow	0.5125	0.4891	0.0861	0.0903	-0.2402	-0.2395
H1	0.5555	0.5749	0.1495	0.1498	0.8258	0.7306
H2	0.5453	0.4965	0.0487	0.0415	0.6345	0.6236

^a In the table are also reported the corresponding experimental values from diffraction studies (for Li, Al, Si, and O, see Krogh Andersen and Plough-Sørensen;² for H: see Norby et al.³).

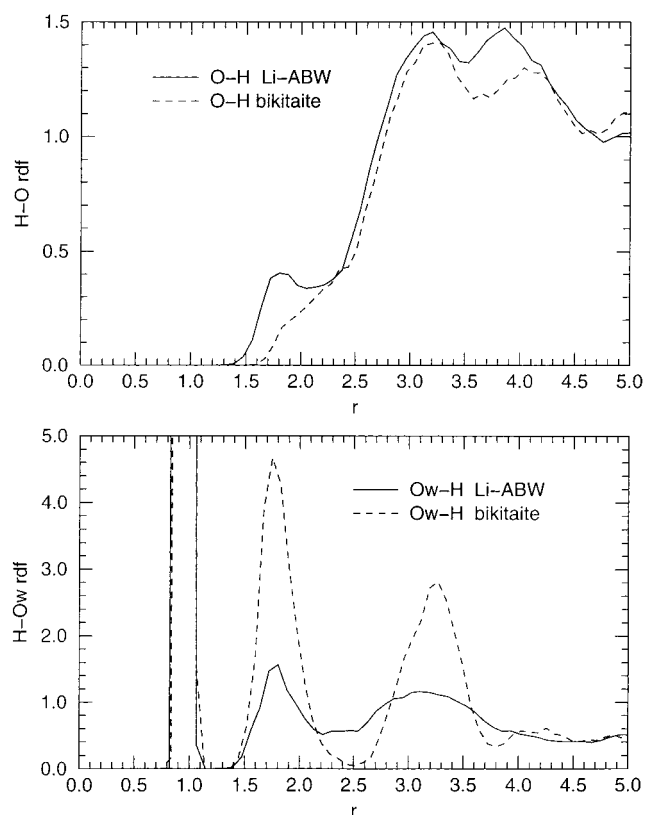
**Figure 3.** Average Li-ABW structure projected on the *xy* plane. AlO_4 and SiO_4 units are represented by tetrahedra. Water oxygens are represented by black spheres, water hydrogens by small light gray spheres, and extraframework lithium cations by large light gray spheres.**TABLE 2: Calculated Average Geometrical Parameters for H_2O in Li-ABW and in Bikitaite^a**

	Li-ABW	bikitaite
Ow-H	0.989	0.993
HOw-H	106.8	103.5
Ow...H	2.319	1.866
O*...H	2.162	2.265
Ow...Ow	2.916	2.831

^a Ow represents the water oxygen atoms, and O* represents the nearest framework oxygen atom.

calculated and experimental data is satisfactory, and we are confident that other quantities obtained from the same set of data, namely, the calculated trajectory, can have the same level of reliability.

First of all, the structure of the one-dimensional water chain is confirmed by our calculations. The average calculated structure at 298 K is reported in Figure 3, where the presence of one water chain per channel is evident. Some geometrical parameters characterizing the H_2O arrangement have been calculated for both Li-ABW and bikitaite and are reported in Table 2. These data indicate that the average water chain geometry in Li-ABW is quite similar to that found in bikitaite. The only significant differences in the two zeolites are the distance between the water molecules and the hydrogen-bond distance, which is larger in Li-ABW with respect to bikitaite,

**Figure 4.** Radial distribution functions (rdfs). Top panel: framework oxygen with water hydrogen rdfs. Bottom panel: water oxygen with water hydrogen rdfs. Continuous lines refer to Li-ABW; dashed lines refer to bikitaite. Distances in angstroms.

and the distance between H and the closest framework oxygen atom, which is significantly shorter in Li-ABW.

The radial distribution functions (rdf) for protons with the water oxygens and with the framework oxygens are reported in Figure 4 for the two zeolites. Clearly, it emerges that the hydrogen-framework oxygen rdf presents a peak in the region typical of hydrogen bonds, a feature that is missing in the bikitaite case. Also, the hydrogen-water oxygen rdfs, beyond the first (intramolecular) peak at around 1 Å, are different in the two cases: they are broader and lower in the case of Li-ABW, indicating a more “disordered” situation than that in bikitaite. In Figure 5 the variations versus time of some intermolecular $\text{O}\cdots\text{H}$ distances are reported: the picture shows the time evolution of the distance between a hydrogen and the oxygen of two neighbor water molecules and with its nearest framework oxygen. By inspecting Figure 5, it is possible to see that the nearest oxygen to the hydrogen changes during the simulation. This indicates that the hydrogen-bond partner has changed along the trajectory, suggesting that the water molecule to whom the hydrogen belongs has performed some rotational motion. This finding may be of relevance in unraveling the very cause of the stability of the one-dimensional water system. Indeed, the simulations, as well as the diffraction studies, indicate that in bikitaite the water system is more stable, and therefore, water molecules are more constrained in the chain geometry than in Li-ABW. As in the case of bikitaite,⁵ we have calculated the Li-ABW polarization P and dipole moment μ by means of the single-point Berry phase approach.^{21,26} It should be pointed out that with our *ab initio* approach, dipole moments and polarization are “results” of the calculations, and their accuracy rest only on the adopted DFT approximations. In standard classical molecular dynamics simulations (e.g., Fois et al.²⁸), on the other hand, such quantities are in a sense

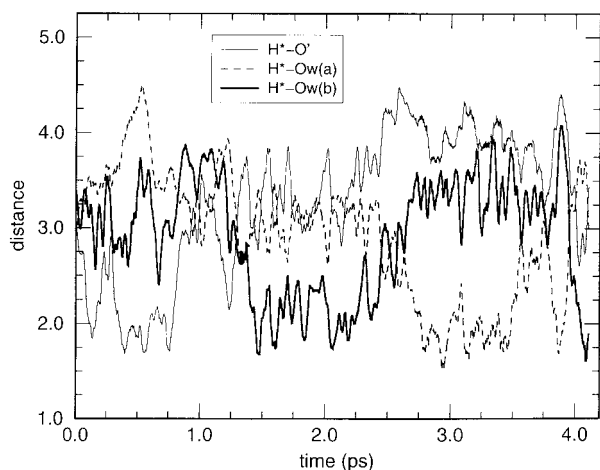


Figure 5. Time variation of the distances of one water hydrogen with three different oxygens in Li-ABW. Thin continuous line: hydrogen-nearest framework oxygen distance. Dashed and thick continuous lines: hydrogen with the two nearest water oxygens. Distances in angstroms, time in picoseconds.

TABLE 3: Dipole Moments Per Unit Cell $|\mu|$, Their Components and Polarization $|P|$ for Li-ABW and Bikitaite^a

structure	$ \mu $	μ_x	μ_y	μ_z	$ P $
bikitaite	48.32	28.48	37.13	11.95	0.273
Li-ABW	11.40	0.97	0.77	9.38	0.045
Li ₈ [Al ₈ Si ₈ O ₃₂] [*]	3.68	0.04	0.87	3.57	0.015
(H ₂ O) ₈ [*]	12.38	0.98	0.04	12.34	0.049
Li-ABW [*]	8.49	2.01	0.33	8.25	0.033
Li ₄ [Al ₄ Si ₈ O ₂₄] [*]	56.06	27.92	47.34	11.06	0.317
(H ₂ O) ₄ [*]	9.35	0.25	9.35	0.06	0.053
bikitaite [*]	47.63	27.75	37.01	11.34	0.269

^a Bold values (first two lines of the table) are averages along MD trajectories. In the table are also reported the contributions of the water chains (line 3) and of the crystal without H₂O (line 4) to the dipole moment of the whole structure (line 5) for a selected configuration of Li-ABW, labeled by (*). Such contributions were also calculated for a selected configuration of bikitaite (lines 6–8). Dipole moments are measured in Debye, and polarization in C/m².

predetermined by the adopted intermolecular potential functions. Such functions are generally built to work at certain external conditions, and their transferability to different conditions is one of the major problems in classical simulations.

In Table 3, the dipole moment and its components are shown along with the corresponding data calculated for bikitaite.

Our results suggest that the Li-ABW structure has permanent polarization. However, its value is significantly lower with respect to bikitaite. This finding can be rationalized by inspecting lines 3–8 of Table 3, where the dipole moment of a single configuration sampled from the MD trajectory has been calculated for the whole crystal, for the (Li + framework) arrangement without water molecules, and for the water chains system separately. It emerges that in both zeolites, the framework contribution to the dipole moment has opposite sign with respect to that of the water chains. However, unlike bikitaite, in Li-ABW the total polarization arises mainly from the water chains. This explains the reason why the dipole moment of the crystal along the direction of the water chains (z for Li-ABW and y for bikitaite) changes sign on passing from bikitaite to Li-ABW.

Moreover, on the basis of these results, the existence of such an high framework dipole in bikitaite could be probably ascribed to pyroxene chains. How the pyroxene-chain system may contribute to increasing the total dipole can be deduced by

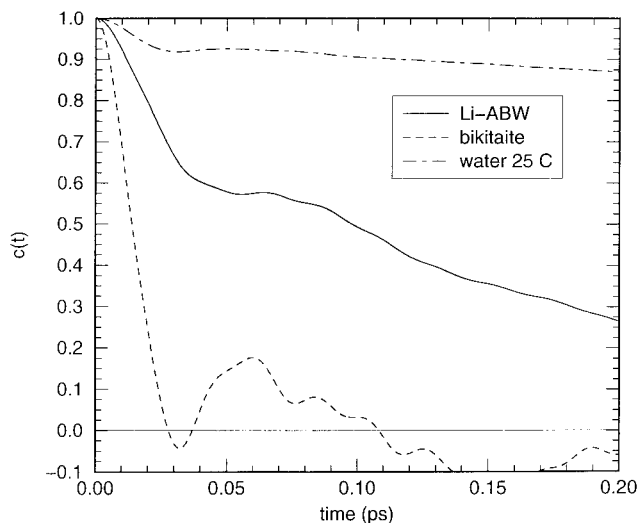


Figure 6. Orientational correlation functions $c(t)$'s for water molecules. Continuous line: Li-ABW. Dashed line: bikitaite. Dot-dashed line: liquid water at 25 °C.

remembering that the highest framework dipole in bikitaite⁵ arises when the pyroxene chains contain aluminum, also as the presence of Al renders the pyroxene chain more asymmetric with respect to the other structures where such a chain contains only a Si tetrahedra.

Another interesting point that emerges from Table 3 is the lower dipole moment per water molecule calculated for Li-ABW. This may indicate a more disordered arrangement of water in the Li-ABW channels, as suggested by the rdfs. This higher disorder and lower dipole per water molecule in the Li-ABW channels may be due to the lower dipole moment of the ABW framework with respect to bikitaite that causes a lower rigidity of the one-dimensional water structure in its channels. The different degree of stability of the water chain structure in the two zeolites may also affect water's dynamical behavior. On this respect, it should be noticed that while in bikitaite it was possible to refine quite accurately the H positions even by single-crystal X-ray diffraction,⁴ this was not possible in the case in Li-ABW, where the H positions have been refined only by powder neutron diffraction.

The above discussion has suggested that water molecules in Li-ABW may rotate around their equilibrium positions. It would be of interest to analyze such a motion. The orientational correlation functions²⁷ of water in Li-ABW and in bikitaite are shown in Figure 6 and compared to the same function for liquid water at room temperature calculated by an empirical pair potential.²⁸ The orientational correlation function of H₂O is calculated from the autocorrelation of the bisector of the HOH angle, and this function should give information on the librational and rotational motion undergone by H₂O. The slower the decay of such a function, the more the motion is hindered. In liquid water, each H₂O is surrounded by an approximately tetrahedral coordination environment of hydrogen-bonded water molecules. Therefore, the breaking of a number of hydrogen bonds is needed in order to allow a water molecule to rotate. Since such breaking has some energetic cost, the more numerous and stronger the hydrogen bonds surrounding a water molecule are, the slower is its rotational motion and decay of the correlation function. On the other hand, when a molecule is bound in its crystallographic position and no rotation is allowed, as with H₂O in bikitaite, only the librations are present (beyond the internal vibrational modes). Such a librational mode is very fast, compared to rotations; therefore its correlation function

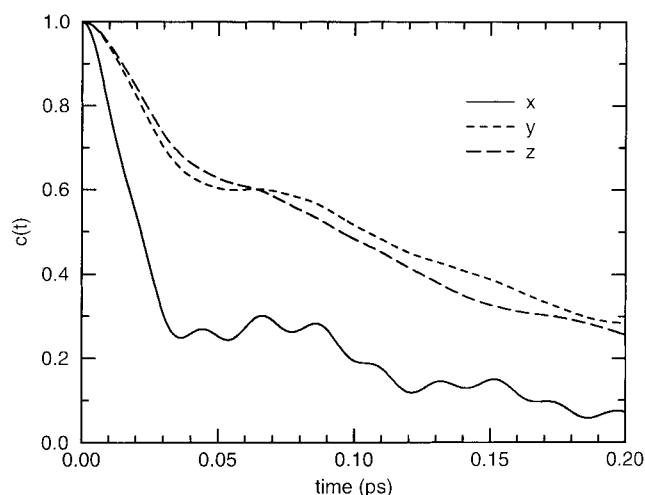


Figure 7. Cartesian components of water orientational correlation function in Li-ABW. Continuous line: x component. Dashed line: y component. Long dashed line: z component.

should decay consequently faster, because this motion is not hindered by the breaking and forming of hydrogen bonds. In Li-ABW, the situation is midway between that in bikitaite and in liquid water, because some degree of rotation is allowed, as can be deduced from Figure 5. However, the decay is faster than that in liquid water: in Li-ABW the number of hydrogen bonds per water molecule is lower than that in bulk water (~ 4 per molecule). We have decomposed the orientational correlation function of water in Li-ABW in its Cartesian components, as shown in Figure 7. The x component decays faster than the other two, and its behavior is comparable to that shown by the orientational correlation function in bikitaite. All of these findings may be rationalized by taking into account the fact that in Li-ABW hydrogen bonds lie mainly in the yz plane. Therefore, only the y and z components of the orientational correlation function should reflect the slower motions arising from the breaking and forming of hydrogen bonds involved in the rotation of water molecules. As a check, the autocorrelation of the normal to the plane defined by the three atoms in each water molecules also was calculated. The two approaches however lead exactly to the same conclusions.

Conclusions

We have presented a first-principles MD study of the zeolite Li-ABW. Our results, in agreement with experimental findings, show that the one-dimensional hydrogen-bonded chains are stable in the eight-membered ring channels of Li-ABW, as was found in bikitaite. However, unlike bikitaite, water molecules are also involved in hydrogen bonds with framework oxygens.

The calculations of the zeolite's dipole moment show that Li-ABW should also have permanent polarization, polarization arising mainly from the water chains. This suggests that, as in

bikitaite, dipolar host-guest interactions influence the stability of these one-dimensional hydrogen-bonded chains.

In Li-ABW, the fact that the framework contribution to the dipole moment is considerably lower than that in bikitaite allows the water molecules in the channels to arrange themselves in a slightly more disordered way. Apart from the formation of hydrogen bonds with framework oxygens, such a more "disordered" situation of the water chain is reflected by the rotational motion undergone by H_2O molecules in the yz plane. The considerably higher value of the framework polarization of bikitaite with respect to Li-ABW may reasonably be attributed to the presence of pyroxene chains of tetrahedra in the former structure.

It can be concluded that the water chains in Li-ABW are less stable than those in bikitaite and that the stability of such peculiar one-dimensional arrangement is strongly influenced by the zeolite's framework structure.

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