A theoretical investigation on pressure-induced changes in the vibrational spectrum of zeolite bikitaite

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In this paper, the vibrational spectra of the natural zeolite bikitaite obtained from ab initio MD simulations are discussed. The calculated spectra, in line with experimental IR and Raman spectra of other zeolitic systems, predict that applied pressure significantly affects the O-H and T-O vibrational frequencies. The observed broadening of the OH stretching band is attributed to pressure induced changes in the host-guest and guest-guest hydrogen bond interactions.

1. INTRODUCTION

Confinement of materials in ordered matrices is currently of primary interest for applied research. It is known that a low-dimensional system shows chemical and electro-optical properties which are, in general, significantly different from the ones of the corresponding bulk material and can be of relevant technological interest for the tailoring of new kinds of materials [1]. Zeolitic frameworks hosting low-dimensional systems may be taken as useful models to study the factors governing at atomic level the stability and the properties of confined materials [2].

One of these interesting model structures has been found in the natural zeolite bikitaite (Li₂ [Al₂Si₄O₁₂]·2H₂O)[3,4]. This is a rare lithium zeolite characterized by a high framework density and by a monodimensional system of channels in which water molecules and Li cations are hosted. It is composed by sheets of 6-membered TO₄ rings laying in the ab plane and connected to each other by pyroxene-chains of tetrahedra. Non-crossing channels, whose section in the ac plane is an eight membered ring of tetrahedra, run parallel to the b direction (Figure 1a). Each extraframework Li⁺ cation is tetrahedrally coordinated to three framework oxygens and one water oxygen. Experimental and theoretical investigations on bikitaite at ambient conditions proved that water molecules form one
dimensional chains held together by hydrogen bonds (HB), whereas no water-framework HB exist [5,6]. Such a peculiar one-dimensional water chain, that runs parallel to the channel direction, has been found to date only in another high density lithium zeolite characterized by the same one-dimensional 8-ring channels, the synthetic Li-ABW [7,8].

Figure 1: Ball-and-stick representation of the bikitaite structure projected on the ac plane, at ambient pressure (a) and at 9.0 GPa (b). Black spheres represent H atoms, light grey spheres Si atoms, grey spheres O atoms and dark grey spheres Al and Li atoms.

Theoretical studies on bikitaite [6] allowed to explain the stability of the guest “floating” water chain on the basis of long-range electrostatic host-guest interactions. At difference from bikitaite, water molecules in Li-ABW are hydrogen bonded to each other as well as to framework oxygens, thus indicating as additional stabilization factor the presence of short-range interactions [9]. Both experimental and simulated vibrational spectra account for the different dynamical properties of water in these two related zeolites and have allowed to assess the leading role of weak interactions (such as hydrogen bonds) in influencing its vibrational behaviour [9,10].

In this respect, it would be of interest to study these water chains under different conditions with respect to the ambient ones. In particular, we are interested to investigate how the stretching and bending frequencies of water molecules in bikitaite are affected by high pressure (HP).

Little is known about the behaviour of zeolites under hydrostatic pressure. This is partly due to the difficulty in finding non-penetrating pressure transmitting media that behave hydrostatically over a wide range of pressure. Moreover, crystal structure refinements are often prevented by a number of factors that cope to decrease resolution, thus allowing only the experimental determination of cell parameters. This problem is particularly severe for X-ray powder diffraction experiments [11,12].

The usefulness of techniques that can integrate the experimental data with atomic-scale information is therefore clearly evident. In this context, the use of ab-initio methods
may lead to significant progress in this largely unexplored area, providing additional information not accessible through experiment. A combined theoretical-experimental approach has already been successfully applied to the study of zeolites scolecite [11] and bikitaite [12] under HP. As far as bikitaite is concerned, both experiment and calculations have proved that this zeolite is remarkably stable under HP, as no amorphization or pressure induced phase transition has been observed up to 10 GPa [12].

2. DETAILS OF THE CALCULATIONS

Simulations on bikitaite have been performed using the Car-Parrinello \textit{ab initio} molecular dynamics method (CPMD) [13], which has proved to provide a satisfactory description of many condensed-phase systems, including zeolites. The method allows one to obtain reliable information at microscopic level on both static and dynamical properties. In particular, simulated IR spectra satisfactorily reproduce shifts in the O-H stretching and bending frequencies resulting from changes in the chemical environment [6]. Moreover, they allow to single out the contributions of distinct modes or groups of atoms to the total spectra, leading to an increased resolution and providing additional information not accessible through experiment.

We report here only the technical details adopted in the simulation runs. For a more detailed description of this methodology, the reader is referred to Ref. [14].

Two constant volume CPMD [15] simulations of bikitaite were performed using the experimentally determined cell parameters at the pressures of 5.7 GPa and 9.0 GPa, reported in Ref. [12]. A periodically repeated triclinic supercell containing two crystallographic unit cells along the \textit{b} direction was adopted. We used the same plane-waves cutoff, density functional approximations, pseudopotentials and MD simulation parameters (i.e. integration time step, fictitious mass) adopted in previous theoretical studies on bikitaite at ambient conditions ([5,6]). After equilibration, the time evolution of the system was followed for 5.0 ps for both simulations.

Simulated vibrational spectra were calculated by Fourier transforming the velocity autocorrelation function obtained from the MD trajectory, and compared with the ambient pressure ones reported in Ref. [5].

3. RESULTS AND DISCUSSION

In zeolites, strong covalent T-O bonds with a partial ionic character are present, therefore long range electrostatic forces play a dominant role. On the other hand, the presence of short-range forces arising from HB can also be of significant relevance [16]. Hydrogen is incorporated in zeolites mainly in the form of guest water molecules, which are in most cases hydrogen bonded to framework oxygens and extra-framework cations. Information on the strength of these bonds are generally drawn from vibrational frequencies of O-H covalent bonds [17]. As far as HP conditions are concerned, studies on a series of minerals have evidenced a decrease in the OH stretching frequency, which is attributed to an
increase of hydrogen bonding character [16,17]. In fact, the presence of an HB results in a broadening of the potential energy curve of the covalent OH bond and a decrease of spacing between vibrational levels. As an effect, the stretching frequency decreases with the strengthening of the O...H interaction. However, this simplified picture is inadequate for three centered hydrogen bonds [16], which are often found in minerals at HP. Volume shrinking due to applied pressure can in fact bring two oxygens close enough to a guest water proton to allow formation of two weak HB’s. Presence of bifurcated hydrogen bonds may significantly affect O-H stretching frequencies.

Before discussing our simulated bikitaite spectra, let us briefly summarize the results of IR and Raman studies on zeolites under HP. Velde and Besson [18] found that the OH stretching band in analcime was splitted in two components with increasing pressure and attributed such change to a pressure-induced deformation of the framework, resulting in two different HB lengths. Huang [19] reported a red shift of the three O-H stretching peaks in zeolite Y for pressures lower than 1.9 GPa, while for higher pressure the three bands collapsed to a broad, unresolved profile. Also the water bending modes are influenced by pressure, and such changes are attributed to the increased strength of hydrogen bonds. Moreover, the three bands associated with T-O stretching modes are shifted to higher energy with increasing pressure, suggesting a shortening of the T-O bonds. Another study reports a slight pressure-induced blue shift of the T-O stretching modes for the zeolite LTA [20]. Belitsky et al. [21] found for the pressure-induced phase transition
natrolite I - natrolite II significant shifts in the T-O Raman bands, that point to a strong deformation of the primary structural units TO$_4$. Also the HP Raman spectra of Gillet et al. [22] indicate strong modifications in the O-T-O, T-O-T bands as well as in the O-H stretching bands of zeolites scolecite and mesolite.

On the whole, these experimental data on vibrational behaviour of zeolites under HP [19-22] seem to support the idea that tetrahedral units are indeed not rigid. Rather, the T-O bonds slightly contract as a response to external pressure, thus resulting in a decrease of the tetrahedral volume. The results of our calculations on bikitaite [12] are in agreement with such description, predicting a negative change in the SiO$_4$ and AlO$_4$ volumes of the order of 2% and 3% respectively at a pressure of 9.0 GPa.

The simulated bikitaite spectra at 9.0 and 5.7 GPa are compared with the ambient pressure one in Figure 2. It is to point out that the simulated bikitaite spectra at 1 atm were found to be in good qualitative agreement with the micro-IR one reported in Ref. [5]. Underestimation of the absolute values of the stretching frequencies is a well-known artifact due to the use of fictitious masses in CP simulations, and prevents quantitative agreement with the experiment. On the other hand, relative frequencies calculated with respect to a reference state (for instance, an isolated water molecule in the gas phase) have proved to well compare with the corresponding experimental frequency shifts.

We first examine the region typical of framework modes, i.e. between 200 and 1200 cm$^{-1}$, focusing our attention on the three bands at highest frequency (i.e. 980, 880 and 660 cm$^{-1}$ at ambient pressure) commonly attributed to the T-O stretching modes [19,20]. Remarkably, they undergo a significant blue shift at 5.6 GPa, passing to 1000, 920 and 740 cm$^{-1}$ respectively, while the frequency shift from 5.7 to 9.0 GPa is lower (1020, 920 and 740 cm$^{-1}$). On the whole, these data indicate that pressure-induced strengthening of the T-O bonds occur in bikitaite, in line with the findings of recent HP IR and Raman studies on other zeolites [19,20] and with the calculated shortening of T-O distances at HP in bikitaite [12].

In general, the HP-induced volume contraction in silicates is attributed to three mechanisms. The first one involves the rotation of rigid TO$_4$, the second one the distortion of intra-tetrahedral O-T-O angles, while the third and less significant one, implies a decrease of the T-O bond length [23]. Since the less energetically costly mechanism is the rotation of rigid structural units [24], current models describing the HP behaviour of silicates normally treat the effects of the third mechanism as negligible. Our calculations, together with the above quoted experimental data [19-22], indicate that shortening of TO bonds in zeolites under HP seems to be more effective than what predicted by such models.

At ambient pressure, the OH stretching band is broadened in the region between 2900 and 3400 cm$^{-1}$. The band profile is structured, in agreement with the experimental one, owing to the presence of four crystallographically different protons experiencing different interactions with their environment. At HP, the band still shows distinct peaks but is significantly broader than at 1 atm. The full width at half maximum, 300 cm$^{-1}$ at 1 atm, increases to 410 cm$^{-1}$ at 5.7 GPa and to 560 cm$^{-1}$ at 9.0 GPa. Moreover, the band is broadened in the low frequency region, indicating that the compression leads to stronger perturbing effects of HB to the H$_2$O vibrational modes. This may be due to different
Figure 3: Contributions of the four crystallographically different OH bonds to the vibrational spectra at 1 atm, 5.7 GPa and 9.0 GPa.

mechanisms, as at HP both a strengthening and an increase in the number of HB are observed.

In bikitaite, the \( a \) and \( c \) cell parameters decrease under compression and two framework oxygens come close enough to a water hydrogen to form bifurcated hydrogen bonds. In addition, the decrease of the \( b \) parameter is accompanied by a shortening of the O-O separation between water molecules and by a consequent strengthening of the inter-water hydrogen bonds already present at ambient pressure.

In order to have a better understanding of the role played by these mechanisms, we calculated the distinct contributions of the four hydrogens to the total spectra (Figure
3). W1 and W2 represent the two water molecules in the unit cell. In each molecule, a proton (H_a) is hydrogen bonded to the adjacent molecule in the chain, while the other one (H_b) points towards framework oxygens and at ambient pressure is not involved in HB. At ambient pressure, the four stretching bands are centered at distinct frequencies. OH bonds involving an hydrogen-bonded proton have lower stretching frequencies, in line with the previous discussion. The O-H_a bands are also broader, as both O and H_a are involved in strong HB with two adjacent water molecules. We also notice that the stretching frequencies of the two O-H bonds in the same molecule are rather close to each other in W1, and much more separated in W2. This strikingly different behaviour of the two water molecules could be rationalized by considering the difference between the two O-H bond distances in each molecule, that in W2 is three times larger than in W1 (i.e. 0.018 Å vs. 0.006 Å) [12].

At 5.7 GPa, the H_b atoms come at distances from O_frame short enough to form host-guest HB. As an effect, both the O-H_b peaks are red-shifted. The frequency shift is slightly more pronounced for W1, which at 5.7 GPa forms a significantly stronger water-framework HB (the calculated H_b-O_frame distances are 1.885 and 2.081 Å for W1 and W2 respectively) [12]. Moreover, hydrogen bonds between water molecules, already present at 1 atm, are significantly shorter at 5.7 GPa (from 1.886 to 1.714 Å) [12]. This leads to a red-shift of the O-H_b stretching frequencies as well. The global result is a broadening of the O-H stretching band with respect to 1 atm (Figure 2).

Remarkably, a further increase of the pressure, from 5.7 to 9.0 GPa, brings about a rather unexpected blue-shift of both the O-H_b stretching frequencies. We justify this result by considering that, even though at 9.0 GPa the H_b atoms form a higher number of HB they are indeed weaker than those at 5.7 GPa. In fact, the MD simulation showed that at 9.0 GPa two and sometimes three framework oxygens are in competition to form HB’s with H_b. As a consequence, water-framework HB’s involving different framework oxygens are continuously broken and formed, resulting on average, in a decrease of the hydrogen bonding strength [12]. In particular, W1, that at 5.7 GPa was involved in a single and rather strong water-framework HB, at 9.0 GPa forms a three centered bond, characterized by significantly larger O_frame-H_b distances (2.163 and 2.079 Å), therefore suggesting weaker HB interactions. The inter-water average HB distance is 1.719 Å at 9.0 GPa, therefore the average H_a-O stretching frequency undergoes no significant shift with respect to 5.7 GPa. On the whole, the above mentioned effects result in a further broadening of the total stretching band at 9.0 GPa (Figure 2).

Applied pressure also affects OH bending frequencies. Figure 2 shows that at 5.7 GPa the bending band is shifted towards higher frequencies with respect to 1 atm, and it is also significantly broader. The opposite trend is observed in passing from 5.7 to 9.0 GPa: the bending peak is red-shifted and the band becomes narrower. Again, these effects find a microscopic explanation in the pressure-induced formation of new HB. As discussed above, the perturbing effect of water-framework HB on the vibrational modes of water molecules is larger at 5.7 GPa, when a lower number of stronger hydrogen bonds are formed.

Work is in progress in order to perform experimental micro-IR spectra of bikitaite
under HP.

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