Molecular Dynamics Simulation Study of Superhydrated Perdeuterated Natrolite Using a New Interaction Potential Model

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To test a new interaction potential, molecular dynamics simulations of zeolite natrolite were performed for the structures under ambient conditions hydrated by perdeuterated water and at high pressure (1.87 GPa) in the superhydrated phase, which were recently studied by neutron diffraction. The experimental structures were reproduced with reasonable accuracy, and the hydrogen bond features are discussed. As in ordinary natrolite, a flip motion of water molecules around the HOH bisector is found, which, together with translational oscillations, gives rise to transient hydrogen bonds between water molecules, which do not appear from experimental equilibrium coordinates. The dynamics of water molecules can explain some problems encountered in refining the experimental structure. Vibrational spectra of natrolite containing perdeuterated water, which are not yet measured, were simulated, and their qualitative trend is discussed.

1. Introduction

The stability of zeolites is essential to their wide range of applications. Many experimental and theoretical studies have been focused on the thermal stability of zeolites,[1−3] but the behavior of zeolites under external pressure has received less attention, although some experimental[4−10] and theoretical[11] work has been carried out. Natrolite ($Na_{16}Al_{16}Si_{24}O_{80} \cdot 16H_2O$) is a natural zeolite belonging to the group of fibrous, small pore zeolites.[12] It shows helical channels of elliptical sections running along the *c* axis, containing sodium cations and water molecules in a 1:1 ratio. The water molecules form weak hydrogen bonds with the oxygens of the aluminosilicate framework *but not with each other*. The structure belongs to the orthorhombic symmetry group *Fdd*2. Recent X-ray diffraction studies of natrolite under hydrostatic conditions at high pressure (up to 5 GPa)[13,14] found an abrupt volume expansion that occured between 0.8 and 1.5 GPa without altering the framework topology. This anomalous swelling is due to the selective sorption of water molecules, which expands the channels along *a* and *b* unit cell axes and gives rise to a "superhydrated" ordered phase of natrolite, maintaining the *Fdd*2 symmetry, which contains two water molecules per sodium ion, with the chemical formula $Na_{16}Al_{16}Si_{24}O_{80} \cdot 32H_2O$. However, the experimental results did not include the position of hydrogens or any dynamical information concerning this new phase of natrolite. Recently, a neutron diffraction study of natrolite under ambient conditions hydrated with perdeuteured water and in a superhydrated phase at a pressure of 1.87 GPa was reported[15] and molecular dynamics (MD) simulations were performed in order to verify previous predictions about the positions of the hydrogens[16] and to validate

the performance of the adopted model, which is currently used for extensive MD simulations of different hydrated zeolites.

Among the different approaches, the molecular dynamics (MD) simulation technique is very promising in order to complement the experimental information about structural and dynamical properties of zeolites,[17] and we used this technique to evaluate the position of the hydrogens, the vibrational spectrum, and the relaxation time of the flip motion of the water molecules around their axes.[16]

The purposes of this paper are to verify the reliability of an interaction empirical potential, which was refined by fitting a series of experimental and quantum chemical data including the structure of ordinary natrolite,[16,18] as well as to clarify uncertainties remaining from experimental analysis and to predict the trend of vibrational spectra.

We stress that, because of the relatively large available space for water molecules in ordinary natrolite, the results of the simulations are very sensitive to small differences in the framework structures, such as those caused by changes of the temperature (see, for instance, Table 2). Moreover, the recent the neutron diffraction study of the structure of the perdeuterated natrolite[15] includes the coordinates of deuteriums, which can be compared with the simulated results, while in the previous X-ray structures of the high pressure phase the hydrogen coordinates were not evaluated. Therefore, the results obtained in this work are independent of those reported in ref 16 and are a further test of the reliability of the interaction potential. This potential model has been developed to be used for extended MD simulations of dynamical processes occurring in hydrated zeolites, including diffusion, cation exchanges, and dynamical heterogeneities, and, indeed, is being applied for some calculations in progress, which are encouraging.

2. Model and Calculations

The natrolite structure under ambient conditions and high pressure ordered phases[13,14] belongs to the orthorhombic sym-

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TABLE 1: Values of the Parameters Included in Equations 1−3^a

interaction	A	B	C	D	σ
Na$^+$−O	1.004×10^6	4.526	62.76	3138	0.5
Na$^+$−H	4.895×10^5	7.07	460.24		0.5
Na$^+$−O$_f$	1.5417×10^8	6.0	2.3656×10^4		

charge	q_{Na^+}/e	q_O/e	q_H/e	q_{O_f}/e	q_{Si}/e	q_{Al}/e
this work	1.0	−0.65966	0.32983	−1.0	1.8	1.3
ref 21	1.0	−0.59 ± .03	0.24 ÷ 0.36	−0.87 ÷ −1.21	1.65 ÷ 1.84	1.51

^{a} The energies are obtained in kJ/mol if the distances are in units of Å.

TABLE 2: Experimental (Ref 15) and Calculated Coordinates of Natrolite under Ambient Conditions and in the Superhydrated Phase at High Pressure ($\times 10^4$)^a

atom		0.0001 GPa			1.87 GPa		
		x/a	y/b	z/c	x/a	y/b	z/c
Si1	exp	0	0	0	0	0	0
	cal 300 K	−15	0	62	−15	0	−18
	cal 50 K	−15	0	76	−15	0	61
Si2	exp	1494	2104	6182	1529	1998	6180
	cal 300 K	1508	2139	6125	1513	2086	5908
	cal 50 K	1505	2141	6132	1519	2082	6139
Al	exp	348	929	6130	4150	875	6360
	cal 300 K	314	889	6156	3686	859	5947
	cal 50 K	312	889	6161	3574	875	6169
O1	exp	212	700	8660	410	663	8910
	cal 300 K	−15	706	8573	528	467	8275
	cal 50 K	−19	707	8582	475	518	8551
O2	exp	681	1801	6033	705	1698	5980
	cal 300 K	687	1797	6179	682	1776	5978
	cal 50 K	683	1799	6187	680	1796	6160
O3	exp	974	353	4998	952	304	4680
	cal 300 K	982	293	5349	955	390	4383
	cal 50 K	982	293	5365	941	371	4704
O4	exp	2053	1527	7228	2097	1524	7690
	cal 300 K	2107	1547	6838	1978	1614	7625
	cal 50 K	2107	1549	6837	1978	1557	7729
O5	exp	1801	2257	3881	1951	2037	3930
	cal 300 K	1756	2493	3967	1959	2026	3775
	cal 50 K	1753	2494	3970	1949	2029	3989
Na	exp	2220	325	6100	2181	226	5630
	cal 300 K	2310	243	6083	1897	295	7143
	cal 50 K	2312	250	6068	2233	356	6003
Ow1	exp	536	1881	1075	555	1862	1200
	cal 300 K	590	1932	1034	478	1755	1433
	cal 50 K	588	1943	1005	657	1955	949
D11	exp	525	1430	333	452	144	400
	cal 300 K						
	cal 50 K	500	1476	414	444	165	−73
D12	exp	1020	1908	1679	1035	1869	1760
	cal 300 K						
	cal 50 K	1110	2013	1108	1166	1998	632
Ow2	exp				1871	760	1000
	cal 300 K				1888	574	882
	cal 50 K				1851	657	1300
D21	exp				1584	787	2170
	cal 300 K						
	cal 50 K				1584	956	2243
D22	exp				1490	712	−110
	cal 300 K						
	cal 50 K				1626	719	−14

^{a} OW1 and OW2 are the water molecule oxygens; the other oxygens belonging to the framework.

metry group *Fdd*2. For the simulations, we started from the novel neutron diffraction structures reported in ref 15 as supporting information. The MD simulation box corresponds to three crystallographic cells superimposed along the *c* axis in order to obtain an approximately cubic box of about $20 \times 20 \times 20$ Å^3, including 552 atoms for the ambient pressure natrolite and 696 atoms for the high-pressure phase. This choice is a compromise to satisfy the requirement of simulating a system as large as possible to study the dynamics of the water molecules within a reasonable computer time. The full hydration of the crystal corresponds to 48 perdeuterated water molecules per simulation box for natrolite at ambient pressure and temperature and to 96 for the superhydrated natrolite.

To simulate flexible water molecules, a sophisticated electric field dependent empirical model[18] developed in this laboratory was adopted, by assuming the same potentials for deuterium and hydrogen. The flexibility of water molecules was needed in order to reproduce the deformation of the water molecule geometry in zeolites and the corresponding changes of the vibrational spectra. To include lattice deformations and vibrations in the simulated system, a flexible zeolite framework model developed in this laboratory as well[19,20] has been used. Moreover, new empirical potential functions had been elaborated for representing Na$^+$−water interactions, as the ones previously proposed for simulating aqueous solutions containing sodium ions did not reproduce satisfactorily the structure of water in natrolite. They were used for the simulations described in ref 16, where they were not reported for reasons of space, and in the present work, they were left unchanged. The final form of the Na$^+$−water potential function reads

$$V_{NaO,H}(r) = \frac{1}{4\pi\epsilon_0} \frac{q_{Na}q_{O,H}}{r} + A_{NaO,H} \exp(-b_{NaO,H}r) - \frac{C_{NaO,H}}{r^4}S(\sigma,r) - \frac{D_{NaO,H}}{r^6} \quad (1)$$

where $S(\sigma,r)$ is a switching function given by

$$S(\sigma,r) = \begin{cases} 1 & \text{if } r < r_0 = 0.4 \text{ nm} \\ \exp(-\sigma(r-r_0)^2) & \text{if } r \geq r_0 = 0.4 \text{ nm} \end{cases} \quad (2)$$

which is necessary because the r^{-4} term does not become negligibly small at the cell boundaries. The form of the switching function ensures that in r_0 both the potential and its first derivative are continuous. For perdeuterated water, the same potential functions were used.

The values of the parameters are reported in Table 1. The charges assigned to the atoms were similar to those corresponding to the Mulliken populations reported in many quantum calculations on clusters and zeolites, approximately one-half of the formal ionic charges, except for the exchangeable cations, which retained a full charge. It is gratifying that the charges used in our model are close the experimental ones[21] (see Table 1). As in our previous simulations,[16,20,22,23] water was assumed to interact with Si and Al atoms via a Coulomb potential only, because the interaction is repulsive and the oxygens of the framework are interposed between, so that they should screen the short range interactions. The potentials for interactions between an oxygen atom of the zeolite framework (O$_f$) and an oxygen (O) or a deuterium (D) atom of the water molecule were the same adopted for the simulation of water in silicalite,[20] by

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assuming the same potentials for deuterium and hydrogen. On the basis of the same reasons reported above about water, for the interactions between Na^+ and Si and Al atoms, a simple Coulomb potential was considered. Finally, the potential functions between Na^+ and the oxygens of the framework were represented by

$$V_{NaO_f}(r) = \frac{1}{4\pi\epsilon_0}\frac{q_{Na}q_{O_f}}{r} + A_{NaO_f}\exp(-b_{NaO_f}r) - \frac{C_{NaO_f}}{r^6} \quad (3)$$

The values of the parameters are reported in Table 1. More details of the model potentials and the computed main characteristics of the isolated Na^+-H_2O system are reported in the Supporting Information.

The evaluation of the Coulomb energy was performed using the efficient method proposed by Wolf et al.[24] and extended in our laboratory to complex systems.[25] For ambient conditions with natrolite, the cutoff radius was $R_c = 16.37$ Å, equal to one-half of the largest diagonal of the simulation box, and, correspondingly, the damping parameter was $\alpha = 2/R_c = 0.1221$ Å^{-1}. The corresponding values for superhydrated natrolite were $R_c = 16.42$ Å and $\alpha = 0.1218$ Å^{-1}. The simulations, in NVE ensemble, lasted 1 ns, after 0.5 ns of equilibration runs. Conservation of energy was smaller than 0.1%, and the temperature remained constant within a few percent. To compare the results of the simulations with the experimental structures, the simulations at different pressures were carried out using the experimental cell dimensions without any constraint on the coordinates. Besides structural properties (average coordinates, symmetry, and radial distribution functions), the vibrational spectra and the time autocorrelation functions of water molecule rotations were evaluated using standard methods.[16,17,22,23] In particular, the vibrational spectra were obtained by Fourier transforming the autocorrelation function of the total dipole moment of the system (see ref 17 and references therein).

3. Results and Discussion

The symmetry of the simulated structure, which is not imposed, is conserved accurately, as evidenced by narrow, symmetric, and unimodal distribution functions of the coordinates of the asymmetric unit atoms.[16,26] However, at room temperature and at any pressure, water molecules undergo a flip motion, which makes the computed distribution of the coordinates of the hydrogens bimodal or larger than expected and practically the same for both deuteriums of the same molecule, so that the average coordinates are meaningless. Fortunately, as the influence of temperature on the cell parameters of natrolite, at least in the range 21−471 K, is very small,[27−29] simulations at different temperatures can be performed using the same cell parameters and the resulting crystallographic coordinates can be compared without rescaling. Therefore, as for bikitaite[22] and Li-ABW,[23] where the same problem was present, the equilibrium coordinates of deuteriums were evaluated from simulations at 50 K, at which no flip motion of the water molecules occurs. On the other hand, since the potential functions are anharmonic, the computed average coordinates of all atoms are slightly different from those evaluated at room temperature, and in Table 3, the results for both 50 and 300 K are reported. The agreement with experimental values appears reasonable, as the average standard error of the computed coordinates with respect to the experimental ones is 0.14 Å for the ambient condition natrolite and 0.30 Å for superhydrated natrolite at room temperature, excluding deuteriums. We verified that this error is mainly due to the

TABLE 3: Geometrical Parameters of the Water Molecules Adsorbed in Hydrated Perdeuterated Natrolite (top) and Ordinary Natrolite (bottom) at Different Pressures and Temperatures[h]

pressures (GPa)	0.0001				1.87	
	low temp		room temp		room temp	
	cal	exp	cal	exp	cal	exp
OW1−D11	0.977[a]		0.980[d]	0.973(7)[f]	0.978[d]	0.974(24)[f]
OW1−D21	0.978[a]		0.980[d]	0.971(7)[f]	0.978[d]	0.955(25)[f]
D11−OW1−D12	108.2[a]		107.6[d]	105.6(13)[f]	106.1[d]	113.5(34)[f]
OW2−D21					0.979[d]	0.933(25)[f]
OW2−D22					0.979[d]	1.016(26)[f]
D21−OW2−D22					105.9[d]	101.9(32)[f]
OW1−H11	0.977[b]	0.995[c]	0.980[e]	0.98[g]	0.978[e]	
OW1−H21	0.977[b]	0.991[c]	0.980[e]	0.98[g]	0.978[e]	
H11−OW1−H12	108.2[b]	107.9[c]	107.6[e]	108[g]	106.2[e]	
OW2−H21					0.979[e]	
OW2−H22					0.979[e]	
H21−OW2−H22					106.6[e]	

[a] This work, 50 K. [b] Reference 16, 50 K. [c] Reference 27, 21 K. [d] This work, 300 K. [e] Reference 16, 300K. [f] Reference 15. [g] Reference 29. [h] Distances are in units of angstroms, angles are in degrees, pressures are in gigapascals. The errors of experimental values (last one or two figures) are reported in brackets.

orientation of $(Al,Si)O_4$ tetrahedra and negligible to an uncertainty of mean interatomic distances, for which the error is 1 order of magnitude smaller. The quantitative comparison between experimental and computed deuterium coordinates is made difficult by the relatively large uncertainty of the diffraction data, yielding an unrealistic geometry of perdeuterated water molecules in the superhydrated phase.[15] The largest difference between experimental and calculated coordinates in ordinary natrolite is the z coordinate of D12, but as c is the smallest cell parameter, the absolute value of this difference is 0.36 Å; more importantly, it does not affect the water−framework hydrogen bond. Slightly worse is the reproduction of the same coordinate in the high pressure structure. However, in this case, also the z coordinate of OW1, to which D12 is bonded, is only in fair agreement with the experiment and depends on temperature.

As it appears in Table 3, the structural properties of the perdeuterated water molecule for the ambient pressure natrolite obtained by the simulations were well reproduced, as well as for ordinary water at different temperatures as reported in ref 16. Therefore, we expect that the structure of the two water molecules predicted for the high pressure natrolite should be reliable. It is interesting to remark that the computed DOD (or HOH) angles are smaller at high pressure than at ambient pressure, as the water molecules interact with each other (see below) and are less influenced by the sodium cations. From an overall consideration of the calculated and experimental values reported in Table 3, it appears that probably the experimental geometry of perdeuterated water in the high pressure phase is affected by errors larger than those reported in ref 15, so that a detailed discussion of its features is not possible.

The discussion of the pattern of the hydrogen bonds (HBs) of the water molecules with the framework and with other molecules needs special attention. In ordinary natrolite at any temperature, the minimum distance between the oxygens of water is larger than 4 Å and no HBs between water molecules can be present, as is also remarked in refs 13 and 15, even if the molecules flip around their axes or rotate. On the other hand, two HBs of different length are formed between each water molecule and the framework, as clearly shown in experimental neutron diffraction studies[15,27,29] and confirmed by the simulations. Indeed, the distance between the oxygen of water and the closest two oxygens of the framework resulting from the

Figure 1. Snapshot of the simulated structure of perdeuterated water molecules and sodium cations (dark gray spheres) contained in superhydrated natrolite in the high pressure form at 50 K, as seen from the *c* axis.

simulations is about 3.1 Å and ODO$_f$ angles are about 150° (O$_f$ stands for the framework oxygen atom). Accordingly, the water−framework interaction energy is −18.5 kJ/mol, a value larger than twice the HB interaction energy of one water−water HB, about 8 kJ/mol according to our model.[18,20,22,23] The high pressure structure is different, as the minimum distance between the oxygens of water molecules adsorbed in the same channel along *c* is about 2.7 Å, both in experimental and in simulated structures, a value close to the corresponding average distance in bulk water and typical of a HB. However, in the experimental structure of superhydrated perdeuterated natrolite, the deuteriums in their average positions point out of the sodium cations and toward some oxygens of the framework, with which they form HBs, as in ordinary natrolite. As shown in Figure 1, where the computed structure of water molecules and sodium cations is pictorially represented, this is substantially true also for the structure resulting from the simulations at low temperature, at which no flip motion is present. At room temperature, the water molecules begin to flip and their translational oscillations are relatively large, so that the deuteriums can approach the oxygens of the closest water molecules and *transient* HBs are formed between the water molecules. Other transient HBs connect water molecules belonging to two adjacent channels, resulting in the general pattern, which was discussed in ref 16.

The appearance of transient HBs in superhydrated natrolite for increasing temperature can be discussed in more detail by considering the radial distribution functions (RDFs) displayed in Figure 2. From Figure 2b, it appears that at low temperature the first peak of g_{OD} corresponds to an O−D distance larger than 2 Å, while at 300 K it is higher and located at a distance from the closest oxygen smaller than 2 Å, due to the formation of transient HBs. Indeed, the g_{OO} first peak (see Figure 2a) does not changes appreciably but is only smoothed because of thermal motion. Accordingly, by considering the g_{O_fO} and g_{O_fD} RDFs, which are reported in Figure 3, it appears that the first peak of g_{O_fD} at room temperature falls at a distance larger than at 50 K, besides the smoothing due to thermal motion, while the first peak of g_{O_fO} remains substantially unchanged.

All these results are consistent with the trend of interaction energies, keeping in mind that, according to our potential model, for one water−water HB, the bonding energy is about 8 kJ/mol.[18,20,22,23] For the high pressure structure, the computed water−water interaction energy is only −3.8 kJ/mol at 50 K, showing that no HB is present, while at 300 K it becomes −17.7 kJ/mol. Correspondingly, at low temperature, the computed framework−water interaction energy (not including Na−water
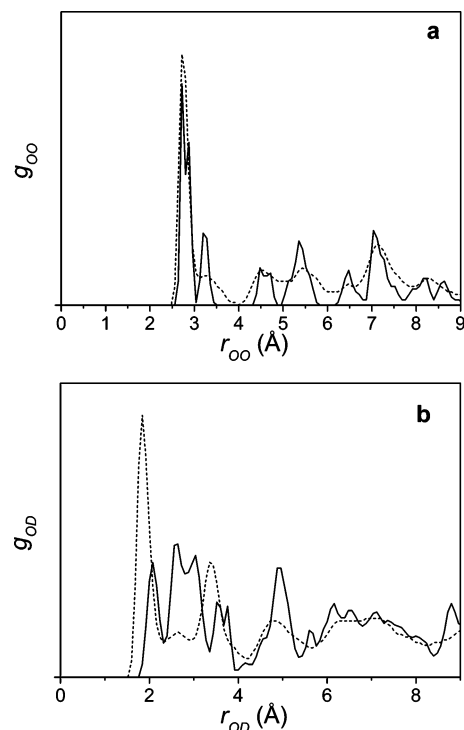

Figure 2. Computed water−water radial distribution functions (RDFs) at different temperatures for superhydrated perdeuterated natrolite: (solid line) structure at 50 K; (dashed line) ambient temperature structure. (a) Oxygen−oxygen RDF. (b) Oxygen−deuterium RDF.
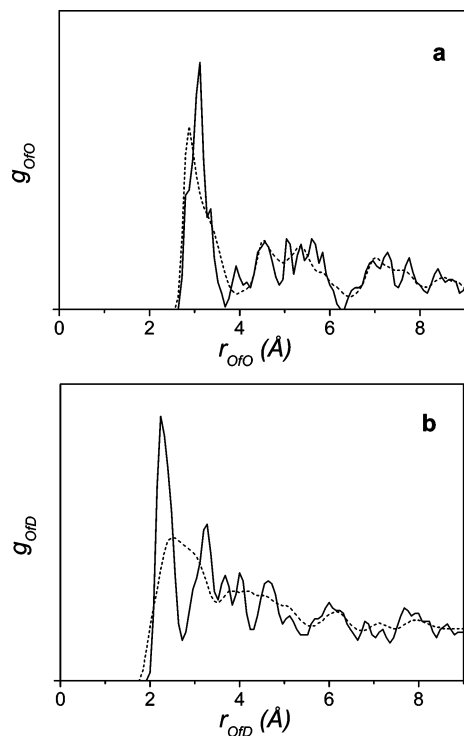

Figure 3. Computed framework oxygen O$_f$−water RDFs at different temperatures for superhydrated perdeuterated natrolite. The lines represent the same conditions as in Figure 2. (a) O$_f$−water oxygen RDF. (b) −O$_f$−water deuterium RDF.

interactions) is −28.5 kJ/mol per molecule, and at room temperature, it becomes −14.0 kJ/mol. The first framework−water interaction energy includes two strong HBs with the two closest oxygens of the framework (we are reminded that these oxygens bear a charge of −*e*, while the charge of those of water is about −0.66*e*, see Table 1) and the interactions with all the

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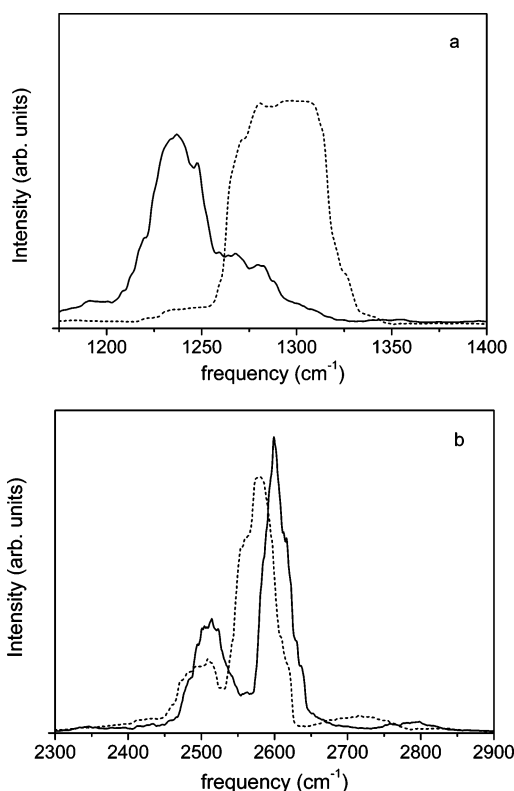*J. Phys. Chem. B, Vol. 110, No. 14, 2006* **7517**

Figure 4. Computed vibrational spectra of perdeuterated water in natrolite at room temperature and different pressures: (solid line) ambient pressure; (dashed line) superhydrated natrolite at 1.87 GPa. (a) Water bending frequency range. (b) Water stretching frequency range.

other atoms of the framework, but the value computed at the room temperature is still sufficiently strong to allow the survival of two weakened HBs. It is interesting to remark that the sums of water−water and water−framework energies for low and room temperature (32.8 and 31.7 kJ/mol, respectively) are essentially the same, as the difference can be attributed to thermal energy difference. Therefore, raising the temperature causes a partial exchange of energy between the two kinds of HBs.

In conclusion, according to our potential model, the experimental structure of hydrated and superhydrated perdeuterated natrolite corresponds to an energy minimum but the thermal motion of the water molecules about this minimum appears complex and of large amplitude, so as to permit the formation of transient HBs between water molecules, which from the equilibrium coordinates are not evident.

To the best of our knowledge, experimental vibrational spectra of natrolite under ambient conditions or in the superhydrated phase containing perdeuterated water are not yet available. It is to be expected,[12] and indeed it is verified (see the Supporting Information), that the vibrations of the framework, which fall in the frequency range 200−1200 cm^{-1}, do not change appreciably when H_2O is replaced by D_2O, so that the comparison with experimental data will not be discussed in detail, except by remarking that in the simulated spectra the maximum shift of the vibrational bands with respect to the experiments does not exceed 100 cm^{-1}.

Rather, the expected qualitative trend of vibrational spectra of D_2O stretchings and bendings in passing from the ambient natrolite to the high pressure structure will be shown. They are reported in Figure 4 and follow the same trend as that in natrolite hydrated with ordinary water. In the frequency range of the

bendings of water (Figure 4a), the formation of transient HBs between water molecules and, more importantly, the larger Na− water distances in the superhydrated phase cause a red shift of the bending frequencies (in the frequency range 1200−1350 cm^{-1}), while the different environment of the two kinds of water molecules causes the splitting of the bending band. The O−D stretching band, which is visible around 2500−2600 cm^{-1} in Figure 4b, is slightly blue-shifted in the superhydrated phase, probably due to a weaker influence of the Na ions.

4. Conclusions

A classical MD simulation technique was used to reproduce structural and dynamical properties of the recently discovered superhydrated phase of natrolite and, in particular, its perdeuterated form, some of which are still unknown. It was verified that a potential model for the interatomic interaction, which was *not* fitted to the experimental data of perdeuterated natrolite, but to a series of experimental and quantum chemical data including the ordinary form of natrolite (at room pressure), was able to reproduce reasonably the properties of the perdeuterated hydrated natrolite at ambient pressure as well as those of the corresponding superhydrated phase of natrolite at high pressure. A direct comparison with the experimental deuterium positions in the superhydrated phase was now possible, while in the previous X-ray structural studies of the high pressure phase the hydrogen coordinates were not reported.

In more detail, according to our potential model, the experimental structure of superhydrated perdeuterated natrolite corresponds to a minimum of the potential energy but the thermal motion of the water molecules about this minimum appears complex and of large amplitude, so as to permit the formation of transient HBs between water molecules, which from the equilibrium coordinates are not evident.

From the simulation results, it is expected that the vibrational spectra should not be deeply influenced by the deformation of the zeolite framework caused by the phase transition but more evident qualitative changes are predicted for the vibrational modes involving adsorbed perdeuterated water molecules.

Supporting Information Available: Details of the interaction potential model, computed main characteristics of the isolated Na$^+$−H_2O system, and simulated IR spectra of natrolite in the frequency range 0−1200 cm^{-1}. This material is available free of charge via the Internet at http://pubs.acs.org.

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