

Dynamical Properties of Confined Water Nanoclusters: Simulation Study of Hydrated Zeolite NaA: Structural and Vibrational Properties

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The behavior of water in restricted geometries has recently received a renewed interest, from both an experimental and a theoretical viewpoint. The confining media may be of biological nature, like cellular membranes or enzyme channels, as well as inorganic, such as carbon nanotubes, porous silica glasses, and zeolites or molecular sieves, which are important for their industrial and environmental applications. There is much experimental and theoretical evidence indicating that the properties of water, when confined in nanopores, are different from those of common bulk water.¹ For instance, the behavior of water in nanotubes has been investigated extensively.^{1–4} For example, the experimental evidence of possible phase transitions in supercooled liquid water at low temperatures has been looked for in hydrated phyllosilicates,¹ where the confinement would prevent nucleation. The behavior of water in the nanopores of protein crystals has been investigated.⁵

In most of the previous studies, the nanopores accommodating water molecules were cylindrical channels or narrow slits, and less attention was devoted to cavities of approximately spherical shape. Among the materials characterized by these kinds of cavities, one of the best known for its widespread use as molecular sieve and cation exchanger, is the synthetic Linde 4A-type zeolite, also called zeolite NaA.^{6,7} Zeolites are natural or synthetic crystalline compounds usually containing silicon, aluminum, oxygen, and exchangeable cat-

ABSTRACT Water nanoclusters confined to zeolitic cavities have been extensively investigated by various experimental techniques. We report a series of molecular dynamics simulations at different temperatures and for water nanoclusters of different sizes in order to attempt an atomistic interpretation of the properties of these systems. The cavities of zeolite NaA are spherical in shape and about 1 nm in diameter and can host nanoclusters of water containing nearly up to 24 water molecules. A modified interaction potential, yielding a better reproduction of experimental hydration energy and water diffusivity across a number of different zeolites, is proposed. Molecular dynamics simulations reproduce the known experimental structural features obtained by X-ray diffraction. Variations of simulated vibrational IR and IINS spectra with temperature and size of nanoclusters are in good agreement with experiment. The simulated water nanoclusters in zeolite NaA are found to be too small to crystallize and, at low temperature, behave as amorphous ice, in agreement with recent experimental results for similar water nanoclusters in reverse micelles.

KEYWORDS: zeolites · molecular sieves · confined water · nanoclusters · molecular dynamics simulations

ions.⁸ The aluminosilicate framework is built up by corner sharing TO₄ tetrahedra (in which the T-sites are occupied by either silicon or aluminum), giving rise to a rather complex but precisely repetitive atomic network with regular nanometric cavities connected by channels or windows, where guest molecules of appropriate size can be adsorbed. These void interior spaces are studded with cations (usually metallic), which compensate for the charge deficit due to the substitution of silicon by aluminum and can admit water, many simple gases, and larger molecules. Zeolite NaA is of cubic symmetry and contains two kinds of approximately spherical cavities: the α -cages with free diameter of about 10 Å, which are connected through octagonal windows about 4.1 Å wide and form a simple cubic lattice, and β -cages with a

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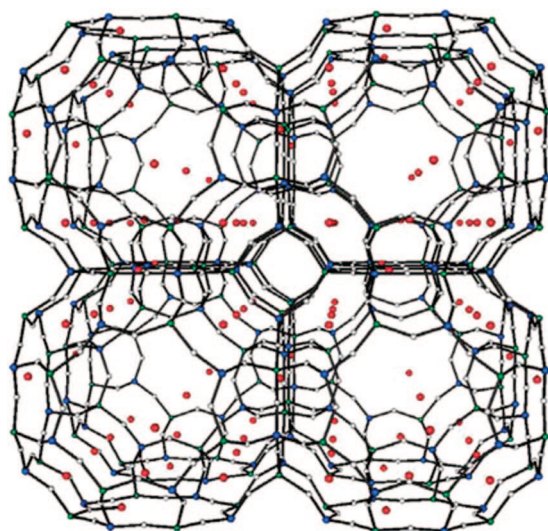


Figure 1. Pictorial view of the structure of hydrated zeolite NaA. Top: aluminosilicate framework (one crystallographic unit cell) containing eight α -cages. Si atoms are blue, Al atoms are green, O atoms are light gray, and Na cations are red. Bottom: snapshot of the forefront water molecule clusters contained in the unit cell. Four nanoclusters contained in the α -cages and, at the center of the figure, the four molecules contained in the β -cage are visible.

free diameter of about 6 Å, which are located in the interstitials between α -cages. The smaller β -cages are also called sodalite cages, as the natural zeolite sodalite is made of these kinds of cages arranged in a simple cubic lattice. As synthesized zeolite NaA contains water in both α - and β -cages, forming nanoclusters of 24 and 4 molecules, respectively (see Figures 1–3),⁶ so that one crystallographic unit cell contains 224 water molecules. Water can be removed by heating *in vacuo* or in inert gas flow, and the complete removal occurs at temperatures above 423 K.⁹

Water confined in zeolite NaA has been investigated experimentally by using various techniques: X-ray diffraction (XRD),⁶ Fourier-transform infrared (FT-IR),^{10–14} quasi-elastic neutron scattering

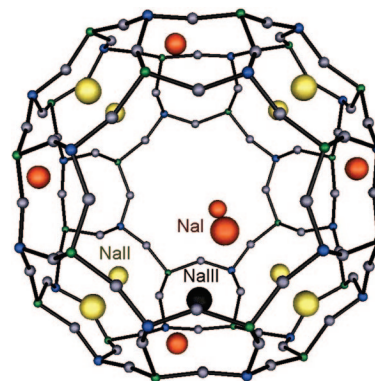


Figure 2. Pictorial view of the structure of one α -cage. Si, Al, and O atoms as in Figure 1, Na cations: Nal are yellow (light gray), Nail are red (medium gray), and NaIII are black.

(QENS),^{11,15,16} elastic neutron scattering (ENS),¹⁷ incoherent inelastic neutron scattering (IINS),¹⁸ and pulsed field gradient nuclear magnetic resonance (PFG-NMR).¹⁵ The information, which can be extracted from experimental techniques, suggest that the dynamical behavior of the water molecules adsorbed in zeolite NaA is not homogeneous, but it is possible to distinguish different kinds or classes of the molecules, depending on their location and on the interactions with the aluminosilicate framework, the Na cations, and the other water molecules. However, an atomistic interpretation of the different behaviors is still incomplete.

Among the different approaches to get a microscopic insight of hydrated systems, the molecular dynamics (MD) simulation technique is very promising in order to complement the experimental information about structural and dynamical properties of zeolites,^{19–25} and we used this technique to evaluate the hydration energy, the position of the water molecules, the vibrational spectra, the relaxation time of the flip motion of the water molecules around their axes, and the diffusivity. Previous MD simulations in hydrated zeolite NaA were reported by Lee *et al.*,²⁶ who represented the hydrated zeolite Na by means of a rigid framework where rigid water molecules were hosted, and by Faux *et al.*,^{27–29} who considered a true unit cell

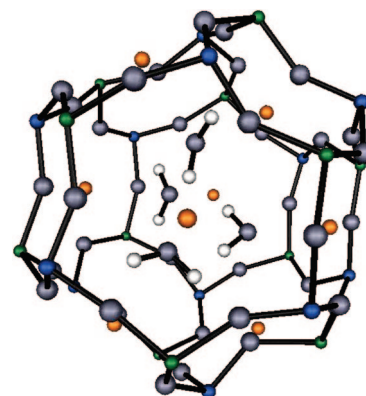


Figure 3. A pictorial view of the structure of one β -cage or sodalite cage. Symbols as in Figure 2.

with flexible framework but still adopted a rigid water molecule model.

This paper is devoted to the atomistic interpretation of the structure of water nanoclusters adsorbed in zeolite NaA as well as of the trend of vibrational spectra. Both framework and water molecules were considered as flexible. A companion paper in preparation will report on the diffusive properties of water. Indeed, water can diffuse in the pores of zeolite NaA, but the diffusion coefficient is small (about 10^{-10} m² s⁻¹ at room temperature; see ref 15), that is, 1 order of magnitude smaller than in liquid water (see Supporting Information) so that, in order to study diffusion, simulations much longer than those illustrated in this paper are required.

The potential model adopted in the simulations has been developed by our research group to be used for extended MD simulations of dynamical processes occurring in hydrated zeolites, including diffusion, cation exchange, and dynamical heterogeneities. It was recently refined in order to reproduce better the hydration energies and the diffusivities since some preliminary tests showed that it is unsatisfactory.

RESULTS AND DISCUSSION

Comparison with X-ray Structure of Fully Hydrated Zeolite A.

The symmetry of the simulated framework, which was not imposed, was conserved accurately, as evidenced by symmetric and unimodal distribution functions of the coordinates of the asymmetric unit atoms.^{19,42} The average coordinates of the fully hydrated zeolite NaA (224 molecules per u.c.) are compared with those resulting from X-ray diffraction⁶ in Table 1. For the framework atoms, the agreement with experiment is good, as the average standard error of the computed coordinates with respect to the experimental ones is 0.05 Å. In the XRD study reported in ref 6, the coordinates of Na cations are reported only for NaI, whereas for NaII and NaIII, these were not resolved. In Table 1, we compare the average coordinates of NaII and NaIII ions obtained from the simulation with the experimental ones for dehydrated zeolite,⁷ and indeed they are similar, as the average standard error of the computed coordinates with respect to the experimental ones is 0.05 Å for NaI and NaIII. On the contrary, for NaII, which in the dehydrated zeolite lies in the plane of the 8-ring windows connecting adjacent α -cages, the error becomes 0.22 Å, probably due to the influence of the water molecules. Moreover, the coordinates of NaI given in ref 6 are different from those reported for the dehydrated zeolite, as they are shifted perpendicularly to the plane of the six-membered ring into the interior of the sodalite cage by about 0.6 Å. A careful inspection of the computed distribution functions of the coordinates of NaI evidenced a small peak corresponding to the coordinates given in ref 6, but the small ratio of its area to that of the whole distribution function means that the probability

TABLE 1. Experimental (Ref 6) and Calculated Coordinates of Hydrated Zeolite NaA at Room Temperature and Mean Square Displacements in Å². Ows Are the Water Molecule Oxygens, the Other Oxygens Belonging to the Framework

atom		<i>x/a</i>	<i>y/a</i>	<i>z/a</i>
Si	exptl	0	0.0927	0.1840
	calcd	-0.0012	0.0903	0.1862
Al	exptl	0	0.1860	0.0900
	calcd	-0.0012	0.1850	0.0899
O1	exptl	0	0.1114	0.2467
	calcd	0.0021	0.1122	0.2464
O2	exptl	0	0.1460	0.1473
	calcd	-0.0010	0.1402	0.1438
O3	exptl	0.0537	0.0582	0.1700
	calcd	0.0526	0.0570	0.1742
NaI	exptl	0.064	0.064	0.064
	exptl ^b	0.0996	0.0996	0.0996
	calcd	0.0973	0.0987	0.0996
		(0.063) ^a	(0.061) ^a	(0.066) ^a
NaII ^b	exptl	0	0.2165	0.2111
	calcd	-0.0020	0.2077	0.2121
NaIII ^b	exptl	0.2500	0.1060	0.1060
	calcd	0.2490	0.1062	0.1045
OwI	exptl	0.02	0.03	0.064
	calcd	0.03	0.04	0.056
OwI'	exptl	0.03	0.02	0.064
	calcd	0.04	0.03	0.056
OwII	exptl	0.160	0.160	0.160
	calcd	0.169	0.169	0.169
OwIII	exptl	0.1155	0.167	0.262
	calcd	0.1144	0.162	0.259
OwIII'	exptl	0.167	0.1155	0.262
	calcd	0.162	0.1144	0.259
OwIV	exptl	0.041	0.210	0.235
	calcd	0.041	0.228	0.251
OwIV'	exptl	0.210	0.041	0.235
	calcd	0.228	0.041	0.251
OwV	exptl	0.250	0.250	0.250
	calcd	0.252	0.252	0.252

^aThis position corresponds to a small peak in the distribution function of the coordinate of NaI resulting from the simulation. ^bRef 30.

of finding the ions in that position (reported in Table 1 in parentheses) is a few percent only, so that it corresponds to a secondary minimum of the potential. The average positions of the oxygen atoms of the water molecules compare well with the experimental ones, but it must be noted that at room temperature the computed mean square displacement of water molecules is of the order of 1 Å² and that they undergo diffusive jumps, so that the average coordinates represent only the preferred positions. Indeed, while in bulk water the preferred positions exist but move continuously with respect to a fixed reference frame, in nanoconfined clusters they can be often localized, especially if regularly distributed ions are present. Finally, at room temperature, rotation and/or flip motion of the water molecules are present, which make the computed coordinates of the hydrogen atoms meaningless, so that they are not reported in Table 1.

Other structural characteristics will be discussed in connection with the comparison with experimental spectra.

Different Kinds of Adsorbed Water Molecules. In most of the experimental works^{10–14,16–18} about the dynamics of adsorbed water, it is assumed that the full hydration corresponds to 216 molecules per unit cell, and accordingly, this assumption was adopted when simulating the dynamics of guest molecules. In the same works, it is suggested that there are at least three “kinds” of water molecules adsorbed in zeolite A, and we tentatively propose to identify these kinds of water molecules as:

- (A) molecules adsorbed in β -cages. They are 4 per β -cage (32 per unit cell), and their hydration enthalpy is the highest as, starting from fully hydrated zeolite, they are desorbed at high temperature (>423 K).⁹ They will be referred to as molecules of kind A.
- (B) molecules adsorbed in α -cages and coordinated to the Na ions (first solvation shell). By considering the distance corresponding to the first minimum in the Na–O_w radial distribution functions (RDF), 3.0 Å, we found that they are 19 (152 per unit cell). Experimentally, one could obtain zeolite NaA containing only molecules of kind B by adsorbing water in a completely evacuated sample at low temperature. As the barrier to penetrate into the sodalite cage is relatively high (from our simulations of at least the order of 80 kJ/mol), at reasonably low temperature (below 423 K), the adsorbed molecules will remain in the α -cages for times sufficiently long to perform realistic simulations of zeolite A containing kind B molecules only. This problem could also affect experiments because, if after calcination at high temperature, water is admitted with low coverage at temperatures lower than 423 K or the sample is not equilibrated for a sufficiently long time (at least many hours or some days) before undertaking the experiment, it is most probable that the water molecules enter into the β -cage only in part or not at all. Therefore, the comparison between simulations and experiments will require some caution, and this problem was considered when appropriate. By adding the molecules adsorbed in sodalite cages, the molecules become 23 per α -cage (184 per unit cell), which are all coordinated to Na ions.
- (C) “bulk” water molecules (coordinated to other water molecules only), which are located around the center of the α -cages. If one assumes that fully hydrated zeolite NaA contains 216 water molecules per unit cell the number of “bulk” water molecules are only 4 per α -cage (32 per unit cell). We distinguish type B and C molecules because they are in different environments and show different coordination and spectroscopic properties.

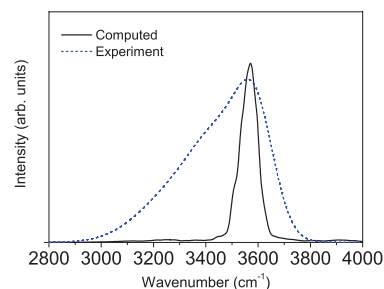


Figure 4. Computed and experimental^{10,12} O–H vibrational stretching band of IR spectra of water contained in sodalite cages of zeolite NaA at room temperature. The experimental spectrum was recorded for a sample containing also two water molecules per α -cage.

Accordingly, we performed separately the simulations in zeolite NaA containing the molecules of kind A, B, A + B, and A + B + C, in the temperature range chosen by the experimentalists (50–353 K).

Water Nanoclusters in Sodalite Cages. As reported in ref 6, sodalite or β -cages in zeolite NaA usually contain four water molecules. In order to study their specific features, we performed a series of simulations including only the 32 kind A molecules adsorbed in the sodalite cages. In the simulated structure of this partially dehydrated zeolite at room temperature, the framework as well as NaI and NaIII ions maintains practically the same coordinates as in the case of fully hydrated zeolite, the differences not exceeding 0.03 Å. In contrast, NaII ions, which are adsorbed on the surface of the sodalite cages, are shifted by 0.4 Å inward from the plane of the 6-rings because of the lack of coordination of the missing water molecules in the α -cage. The average coordinates of the water molecules fit well the experimental values (OwI and OwI' in Table 1) of the fully hydrated zeolite, indicating that they are scarcely influenced by the dehydration of the α -cage. A snapshot of the hydrated sodalite cage is shown in Figure 3. Another experimental result for zeolite NaA with similar water content, or loading, according to the use in zeolite field (48 molecules per u.c.) is the FT-IR spectrum in the O–H stretching band (2800–3800 cm⁻¹)^{10,12} at room temperature. It is compared in Figure 4 with the results of the simulation. The agreement is reasonable, taking in account the classical mechanics derivation of the simulated spectrum, where intensities are only approximate. The agreement with the available experimental data (spectrum and coordinates) would permit one to consider the atomic scale behavior at room temperature of kind A water molecules, which should be not too far from the real one.

From the computed average coordinates, it appears (as expected because there are four water molecules inside the cage and eight NaIII cations on its surface) that each water molecule is coordinated to two Na cations, at the realistic average distance of 2.4 Å. The computed water–Na⁺ interaction energy per water molecule is 84.5 kJ/mol. Water molecules form hydro-

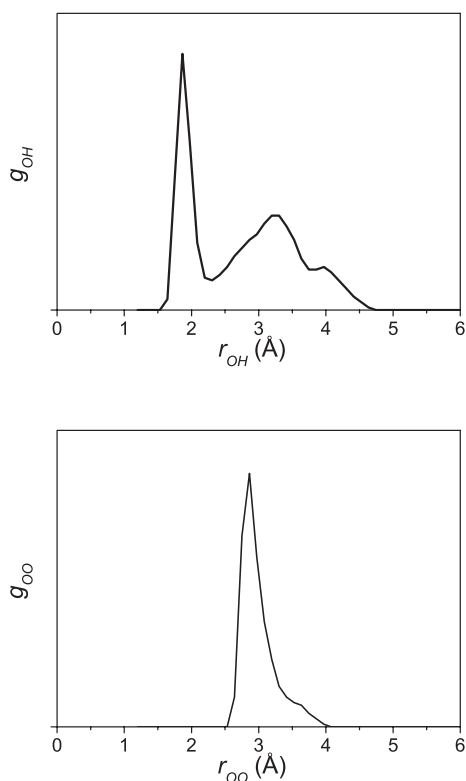


Figure 5. Computed water–water radial distribution functions (RDFs) for water contained in sodalite cages of zeolite NaA. Top: Oxygen–hydrogen RDF; bottom: oxygen–oxygen RDF.

gen bonds (HBs) with each other and with the oxygen atoms of the framework. A more detailed inspection of a series of snapshots and the average water–water interaction energy suggests that for most of the time there are only three HBs between the four molecules contained in a β -cage, and the fourth molecule is hydrogen bonded to two oxygen atoms of the framework and not to the other molecules. This is confirmed by the O–O radial distribution function (RDF), which is reported in Figure 5, showing a shoulder at 3.6 Å, besides a maximum at 2.9 Å, characteristic of HBs. No bifurcated configuration was observed. These findings are consistent with those reported in previous MD simulations in hydrated zeolite NaA.^{26,29} The computed hydration energy is 127.4 kJ/mol, close to that computed for natrolite (135 kJ/mol), which shows a similar environment of water molecules, sharing two Na cations each, and is to be compared with the experimental one (100 kJ/mol).³⁹

As the Na cations are located at the center of the six-membered ring windows connecting the sodalite cage with the adjacent α -cages and must be displaced to let a water molecule cross the window, the molecule must overcome an energy barrier, which was evaluated by umbrella sampling method.⁴⁵ The details will be reported (in detail) in a forthcoming paper. A resulting estimate of the energy barrier is 88 ± 25 kJ/mol, and probably it is overestimated by at least 10%, by consid-

ering the performances of our potential with respect to the experimental values, but it is sufficiently high to prevent the observation of the six-membered ring window crossing in MD simulations lasting some nanoseconds even at temperatures as high as 750 K.

From a dynamical point of view, around room temperature, the oxygen atoms vibrate with a MSD of about 0.25 \AA^2 , without diffusing, while a flip motion of the molecules around their bisectors occurs, with a relaxation time (evaluated from the autocorrelation function of the rotation around the molecule bisector) $\tau_2 = 3.8$ ps and an activation energy of 7.5 ± 1.5 kJ/mol, in the temperature range of 278–353 K, where the Arrhenius law applies. In order to compare these values with the corresponding one for bulk water with the same potential model, one can recall that at room temperature the experimental relaxation time for flip motion in bulk water was reported as 2.2 ps in ref 46, but a more recent work⁴⁷ gives a value of 1.07 ± 0.08 ps. Although τ_2 does not follow an Arrhenius behavior, around room temperature, the activation energy can be estimated from the data of ref 46 as about 9 kJ/mol. Using our model, for bulk water (classical MD simulations for 343 water molecules at the experimental density), the same quantities are 0.6 ps and 12.5 ± 1.6 kJ/mol, respectively. The agreement is only fair, but it is in line with the results obtained from classical MD of water modeled by empirical potentials.⁴⁸ In ref 23, the reasons for the discrepancy between experimental and calculated values related to flip motion of water were discussed, and it was suggested that it was due essentially to the classical mechanics approximation, which does not include zero point contributions to the vibration amplitude of the framework and water atoms, thus overestimating the dimensions of the volume accessible by the guest molecules. In any case, our result suggests that at room temperature for water in sodalite cage the relaxation time for flip motion of water molecules is longer than that in bulk water.

In conclusion, according to our potential model, water in the sodalite cage at room temperature behaves as a rotationally disordered solid because translational motion is oscillatory and librations (rotational oscillations) are so large that they allow for frequent flips of the molecules. This kind of dynamics permits frequent shifts of the three HBs linking the water molecules from a group to another one.

Nanoclusters of Water Coordinated to Na Cations. We consider first the molecules coordinated to Na cations, which are contained in α -cages (type B molecules). The average number of molecules coordinated to a cation is 1.58. The RDFs shown in Figure 6 are similar to the RDFs of bulk water that are reported in Figures S1–S3 of Supporting Information. In particular, there is no evidence of bifurcate configurations, which would entail a peak or a shoulder around $r = 3.2 \text{ \AA}$ in the g_{HH} RDF, where instead a minimum appears. Some water

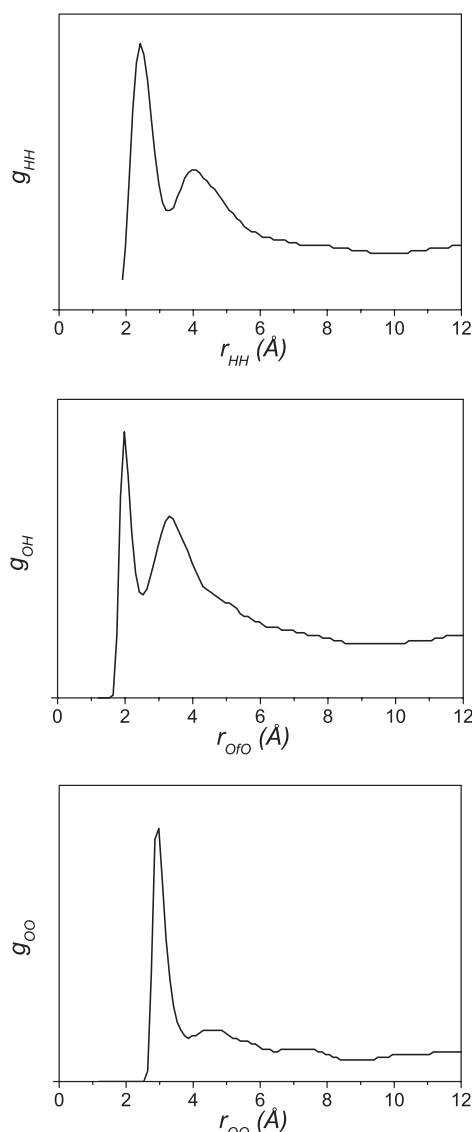


Figure 6. Computed water–water radial distribution functions (RDFs) for water of kind B contained in α -cages of zeolite NaA (19 molecules per cage or 152 per u.c.). Top: Hydrogen–hydrogen RDF; center: oxygen–hydrogen RDF; bottom: oxygen–oxygen RDF.

molecules are hydrogen bonded also to the framework oxygen atoms, as evidenced by the related RDFs (Figure 7). The computed water– Na^+ interaction energy per water molecule of kind B at room temperature is 44 kJ/mol, about one-half of the corresponding one for water molecules in sodalite cage (84.5 kJ/mol), which are coordinated to two cations. Indeed, snapshots of the water configurations show that the Na cations are coordinated to only one molecule of kind B, and the remaining molecules form hydrogen bonded bridges between the other ones. This finding is consistent with the RDFs shown in Figure 6.

The relatively high water– Na^+ interactions force the water molecules of the coordination shell contained in the α -cages to stay for long times at a given distance from the cation, although without strong directional constraints, so that the cations are important

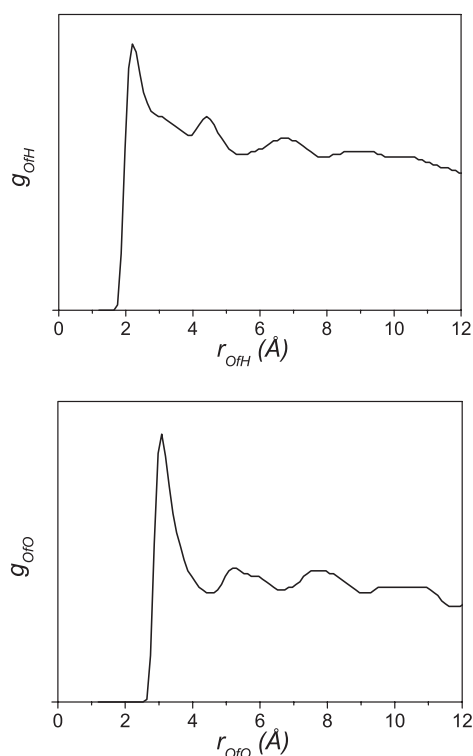


Figure 7. Computed framework oxygen (O_f)–water RDFs for water of kind B. Top: O_f –water hydrogen RDF; bottom: O_f –water oxygen RDF.

to determine the structure of water molecules and to diminish their mobility. In conclusion, energetic and structural results converge to indicate the importance of the Na cations, in determining the structure of the water molecules cluster adsorbed in α -cages.

It is worth it to recall that, as the form of the cluster of the molecule of kind B is a spherical crust about 3 Å thick, in the center of the α -cage there is a void sphere 4 Å in diameter, letting the molecules “evaporate” or move more freely than in a bulk cluster. Indeed, the computed average mobility of the molecules at room temperature ($\text{MSD} = 0.93 \text{ \AA}^2$) is larger not only than the one of kind A molecules adsorbed in the sodalite cages ($\text{MSD} = 0.25 \text{ \AA}^2$), as obvious, but also than the one of the fully hydrated system ($\text{MSD} = 0.76 \text{ \AA}^2$). This point will be discussed in more detail in the following.

As expected, the inclusion of the water molecules of kind A in the simulated system (184 molecules per u.c. in total) leads to results that are close to weighted averages of the values obtained for the two separate systems because the two kinds of water clusters, A and B, connected through six-membered windows hosting NaII ions do not interact significantly.

Nanoclusters of Water in Fully Hydrated Zeolite NaA. Most experimental data about vibrational properties and local mobility of water clusters in zeolite NaA have been reported for the fully hydrated system or, better, for a water loading of 216 molecules per u.c. Therefore, we performed a series of MD simulations in order to evaluate

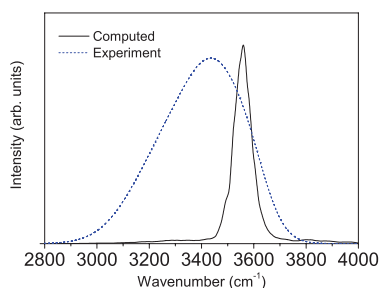


Figure 8. Computed and experimental^{10–14} O–H vibrational stretching band of IR spectra of fully hydrated zeolite NaA at room temperature.

the measured quantities at the different experimental temperatures.

Structural features derived from the simulations, such as RDFs, resulted to be almost indistinguishable from the ones reported in Figures 6 and 7. The g_{OO} , $g_{\text{O}_f\text{O}}$, and $g_{\text{O}_f\text{H}}$ RDFs (O_f stands for the framework oxygens) were evaluated also by Faux *et al.*,²⁷ who report a g_{OO} less structured than the ones obtained in the present work, probably due to a different water–water potential. The others RDFs, instead, are similar.

The stretching O–H vibrational band of the IR spectrum of fully hydrated zeolite NaA at room temperature is reported in refs 10–14 and is compared with the simulated one in Figure 8. The reproduction is slightly less satisfactory than in the case of low hydration (see Figure 4); however, the reported stretching band is red-shifted with respect to the corresponding one at low hydration, qualitatively as in experiment. Also the trend *versus* temperature is in qualitative agreement with experimental spectra¹² (see Figure 9), taking into account the limits of the simulated spectra derived from classical dynamics simulation of limited duration, as a slight overall blue shift appears for increasing temperature.

The vibrational properties of water, in the fully hydrated zeolite, were investigated also by IINS (incoherent inelastic neutron scattering) experiments by Corsaro *et al.*,¹⁸ who measured the vibrational spectra in the range of 0–1200 cm^{-1} at three different temperatures (50, 180, and 220 K). In this temperature range, water is most probably in the state of amorphous solid (see General Discussion below). The spectra show only two broad bands but were decomposed by the mini-

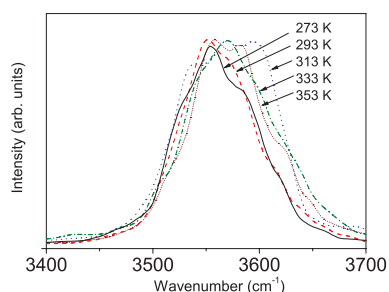


Figure 9. Computed O–H vibrational stretching band of IR spectra of fully hydrated zeolite NaA at different temperatures in the range of 273–353 K.

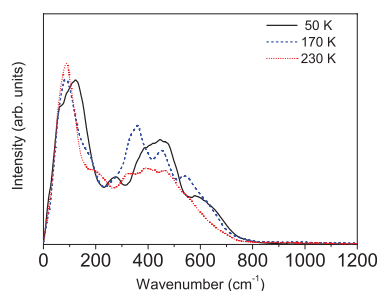


Figure 10. Computed IINS spectra of fully hydrated zeolite NaA in the wavenumber range of 0–1200 cm^{-1} at three different temperatures.

mum number of Gaussian profiles in order to obtain information on the vibrational modes of water. The simulated spectra are reported in Figure 10. They are similar to the experimental ones, although slightly more structured and, if the secondary peaks are taken into account and the decomposition by the minimum number of Gaussian profiles is applied, one can obtain the deconvolution components, whose maxima can be compared with those derived from the experiments. The comparison is reported in Table 2, and the agreement is satisfactory, except for the highest frequency components, which correspond to a low intensity frequency range in the simulated spectra. It is not straightforward to derive the interpretation of vibrational spectra from MD simulations, but in this case, it can be confirmed that the band around 120 cm^{-1} is connected with the Na–water stretch because the same band appears in the power spectrum of the Na ions, which was evaluated independently.

The dynamics of water in zeolite NaA and in particular the MSD of H atoms was studied by ENS (elastic neutron scattering) by Corsaro *et al.*¹⁷ The experimental time window, $\tau \leq 150$ ps, corresponds to the duration of the simulations, so that a direct comparison of experimental and calculated values, which is reported in Figure 11, is possible. It is to be remarked, as discussed in ref 17, that the quantity monitored by the experiment is the flip or rotational motion of the water molecules superimposed to their vibrations about equilibrium positions. It appears that the general trend is similar, although the calculated values are larger than

TABLE 2. Experimental (exptl¹⁸) and Calculated (calcd) Average Values of Frequencies of Sub-bands Obtained from the Best Fit at the Investigated Temperatures. Frequencies are in cm^{-1} (wavenumbers)

temperatures (K)	exptl	calcd	exptl	calcd	exptl	calcd
	50	50	180	170	220	230
	77	73 ± 1	70	75 ± 2	70	81 ± 2
	113	126 ± 3	127	116 ± 3	141	132 ± 5
	189	196 ± 13	195	164 ± 5	196	199 ± 4
	274	260 ± 5	258	261 ± 5	246	261 ± 55
	420	446 ± 1	473	450 ± 2	485	451 ± 3
	560	609 ± 3	574	526 ± 6	590	534 ± 8
	765	666 ± 18	766	593 ± 48	771	1109 ± 50

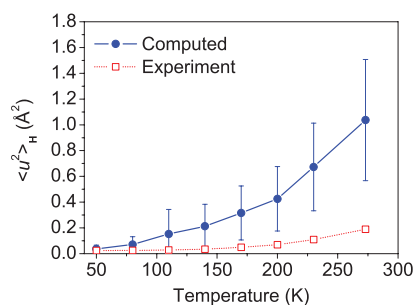


Figure 11. Computed and experimental¹⁷ average mean square displacements (MSDs) in \AA^2 of hydrogen atoms in fully hydrated zeolite NaA in the temperature range of 50–263 K. The lines are to help guide the eye.

experimental ones, except at very low temperature. This result should be expected in view of the use of the classical mechanics approximation in the simulations, as discussed in ref 23 and recalled above. However, it is to be added that, at very low temperature, classical mechanics yields MSDs smaller than the corresponding quantum (and real) ones because it neglects zero point oscillation amplitudes (see also ref 19). In ref 17, the MSDs are reported also for zeolite NaA containing 144 water molecules per u.c. and, at least above 220 K, they are larger than the corresponding values for the fully hydrated zeolite. A water mobility higher for partially hydrated than for fully hydrated zeolite is what was found in simulations (see above), due to the larger volume available to the molecules. Corsaro *et al.*¹⁷ evaluated also the activation energies for the flip motion at full hydration and for 144 water molecules per u.c., and in Figure 12, they are compared with the values derived from the simulations, and the agreement seems reasonable.

General Discussion. The comparison between the results of the simulations and the experimental data derived by using different techniques is encouraging and suggests that the behavior of the simulated systems is substantially similar to that of the real ones. Therefore, one could discuss some more detailed microscopic features of the water nanoclusters confined in the cages of zeolite NaA. The role of Na cations in determining the structure of water contained in sodalite cages was already evidenced, obviously because there four water molecules are coordinated to eight Na cations, but also

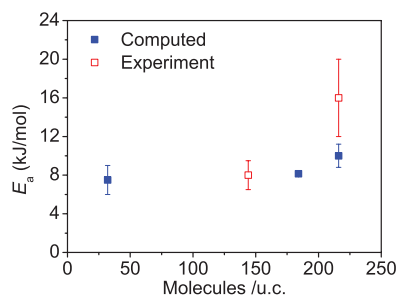


Figure 12. Computed and experimental¹⁷ activation energies (in kJ/mol) for flip motion of water molecules adsorbed in zeolite NaA for different water loading.

in the α -cages, as a large fraction of water molecules contained is coordinated to the cations.

The cations are relevant also for explaining, at least in part, some features of the vibrational spectra of water. The influence of the Na cations on the stretching frequencies of the coordinated water molecules can be inferred from the experimental IR spectrum of natrolite⁴⁹ (where no water–water HBs are present and each water molecule is coordinated to two Na cations), which shows three bands peaked at 3256, 3341, and 3521 cm^{-1} , the first two corresponding to “symmetric” stretching vibration modes of water (the band is split because the two hydrogens are not equivalent in the crystal symmetry group) and to the asymmetric vibration mode (less influenced by the crystal symmetry). The frequencies of these bands are close to those of the three “sub-bands”, which were used by the experimentalists^{10–12} to fit the measured spectrum of fully hydrated zeolite NaA (3290, 3470, and 3590 cm^{-1}) and were related to three different substructures of adsorbed water. The lowest frequency band was attributed to “connective water” or water molecules involved in a tetrahedral ice-like local geometry, the middle one was related to the “intermediate water”, due to the partial formation of bifurcated HBs, and the highest frequency referred to the linear HBs. As the dimensions of the water molecule nanoclusters and the structural constraints due to the cations should not let the water free to assume many of these configurations, the interpretation of the spectra should include also the influence of the cations. The general trend of a slight red shift of the stretching vibration band of water as the water loading is diminished, which already had been reported²⁰ and was confirmed in refs 10 and 12, was reproduced qualitatively by the simulations and can be interpreted also as an average stronger and stronger influence of the Na cations on the water molecules as far as the interactions with other water molecules are weakened.

One of the most interesting questions about the characteristics of water nanoclusters is their behavior at low temperature, in particular whether freezing causes the water nanoclusters contained in zeolite NaA to assume an ordered (crystalline) or amorphous form. To the best of our knowledge, there is no direct experimental evidence of either form, so one can consider the simulation results. In Figure 13, the MSDs of the oxygen atoms of the water molecules are reported for the different kinds of clusters. It was remarked above that the four molecule cluster confined in β -cages behaves as a rotationally disordered solid at room temperature. Indeed, it appears that even at 350 K the MSDs of the water contained in the β -cages is very small, with mean linear displacements (MLDs), the square root of MSDs, hardly reaching 0.5 \AA , less than 18% of the average intermolecular distances. However, when the water molecules adsorbed in the α -cages are considered, the

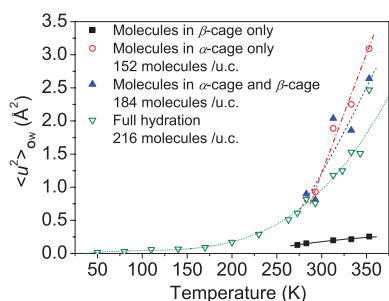


Figure 13. Computed average mean square displacements (MSDs) in \AA^2 of water oxygen atoms in fully hydrated zeolite NaA in the temperature range of 50–353 K. The lines are to help guide the eye.

MSDs become much larger. It is interesting to observe that the MSDs do not show any sudden change or discontinuity in their trend *versus* the temperature, which could be a signature of a crystallization. Using the commonly accepted rule that a molecular assembly can be considered as a liquid if the MLD of the molecules is larger than about 18% of the intermolecular distance when electrostatic intermolecular forces are present,⁵⁰ the “freezing point” of water in fully hydrated zeolite should be about 220 K. Indeed, assuming an intermolecular distance of 2.8 \AA , the critical MLD should be about 0.5 \AA , corresponding to a MSD of 0.25 \AA^2 , which indeed is reached at about 220 K. This temperature is slightly smaller the supercooling limit of bulk liquid water (236 K)¹ and close to upper bound of the estimated range (200–230 K) of the “fictive” temperature T_f at which water becomes “frozen in” during the hyperquench,^{1,51} although Angell¹ deduced a value $T_f = 200$ K from a detailed analysis of calorimetric experiments by Oguni *et al.*⁵² of water confined in silica gel nanopores. The finding that in our system water cannot reach a crystalline form can be related to recent experimental results in nanoclusters of water confined in reverse micelles.⁵³ In this investigation, the IR spectra of approximately spherical nanoclusters of water, containing up to 650 water molecules, were recorded at room temperature and at 180 K, and it was found that at 180 K nanoclusters containing less than 150 molecules do not show the stretching band characteristic of ice Ih (about 3290 cm^{-1}), but the stretching band is only slightly red-shifted with respect to the one at room temperature, so it can be concluded that the aqueous core of the micelles is stabilized in an amorphous form of ice. This trend is well reproduced by simulations for the nanoclusters confined in the α -cages, containing 23 water molecules (see Figure 14). However, the simulations permit a deeper insight of the freezing process through the consideration of the structural properties at different temperatures such as described by RDFs, which are reported in Figure 15. By decreasing the temperature from 353 to 50 K, the RDFs change smoothly, without evidencing any signature of crystal-like structure that would result in a series of narrow peaks (or at

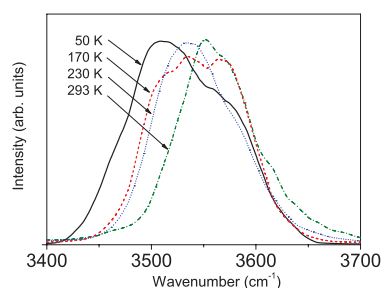


Figure 14. Computed O–H vibrational stretching band of IR spectra of fully hydrated zeolite NaA at different temperatures in the range of 50–293 K.

least in a first and second neighbors peak) of comparable height. On the contrary, they remain amorphous-like even at very low temperature, in agreement with the experimental results. This finding can be explained tentatively by considering that, for a molecule to be surrounded by at least four nearest neighbors located in the bulk of a spherical nanocluster and not on its surface, the nanocluster diameter (measured as distance between oxygen atoms) should be larger than 14–15 \AA , and the nanoclusters should contain about 150 molecules. In smaller clusters, surface effects would prevent crystallization. Finally, the use of a water–water potential different from that optimized for bulk water to simulate water nanoclusters is further supported by the experimental study of the vibrational dynamics of micelle-confined amorphous ice reported ref 53, where it is concluded that “the OH...O potential for amorphous

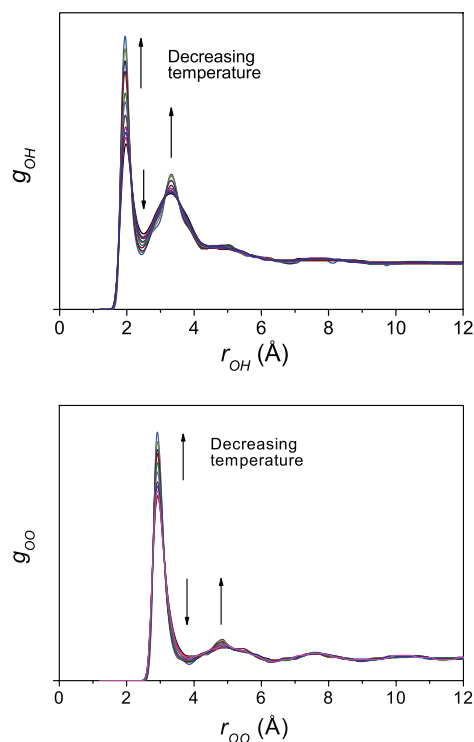


Figure 15. Computed water–water radial distribution functions (RDFs) for fully hydrated zeolite NaA at different temperatures in the range of 50–300 K. Top: Oxygen–hydrogen RDF; bottom: oxygen–oxygen RDF.

ice contained in the micelles differs from that of liquid water".

CONCLUSIONS

Classical MD simulation technique was used to reproduce structural and vibrational properties of water nanoclusters contained in the cages of zeolite NaA. The known experimental structural features obtained by X-ray diffraction were reproduced satisfactorily. Simu-

lated vibrational IR and IINS spectra followed the experimental trends against temperature and dimension of nanoclusters. In particular, the role of the Na cations located on the surface of the cavities in influencing the structure and the vibrational behavior of the nanoclusters was evidenced. In agreement with recent experimental results for water nanoclusters confined in reverse micelles,⁵³ the simulated ones in zeolite NaA are too small to crystallize and at low temperature behave as amorphous ice.

MODEL AND CALCULATIONS

The structure of hydrated zeolite NaA, $\text{Na}_{96}[\text{Al}_{96}\text{Si}_{96}\text{O}_{384}] \cdot 224\text{H}_2\text{O}$, belongs to the cubic symmetry group $Fm\bar{3}c$ ^{6,7} and is illustrated in Figure 1. For the simulations, we started from the XRD structure reported in ref 6, but the NaII and NaIII cations were added, assuming as their initial positions those found in dehydrated zeolite NaA,⁷ as in the XRD study reported in ref 6 they were not resolved. As shown in Figures 1 and 2, NaI cations are in the center of the six-membered rings, and all sites are occupied. The sites of NaII cations lie in the plane of the eight-membered rings slightly off-center forming a square 1.8 Å inside, and only one site per ring is occupied. Finally, NaIII cations are located opposite to the four-membered rings, and the NaIII ions lie inside the α -cage about 1.7 Å from the plane of the ring, but only one NaIII ion per α -cage is present. The experimental positions of water molecules are less precisely defined, with the exception of those contained in β -cages. In ref 6, it is suggested that about 20 of the remaining water molecules might form a cluster approximately 3.85 Å in radius, whose oxygen atoms lie ideally at the vertices of a pentagonal dodecahedron, while the other water molecules are located near the center of the α -cages. The initial positions of these molecules were found following these suggestions.

The MD simulation box corresponds to one cubic crystallographic cell with cell side $a = 24.555$ Å, including 576 framework atoms, 96 Na cations, and a different number of water molecules. As the thermal expansion of zeolite A in the simulated temperature range is very small,³¹ in the simulations, the cell side was left unchanged. According to ref 6, full hydration of the crystal would correspond to 224 water molecules per crystallographic unit cell, and indeed, we succeeded in inserting that number of molecules in the cell and in performing test simulations without any problem, and the corresponding simulation at room temperature was used for the comparison with the experimental diffraction data discussed in ref 6. However, the maximum number of water molecules reported in the experimental works on the water dynamics^{10–14,16–18} is 216, so we adopted this maximum content in the discussion about water dynamics.

Therefore, we performed separately the simulations in zeolite NaA containing the molecules of kind A, B, A + B, and A + B + C (see above) in the temperature range chosen by the experimentalists (50–353 K).

To simulate flexible water molecules, a sophisticated electric field dependent empirical model²¹ developed in this laboratory was adopted. 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^{20,25} has been used. However, preliminary test simulations performed to evaluate the diffusion coefficient of water in zeolite NaA at low water loading, using the previous potential model, which is reported as Supporting Information in ref 25, showed a poor agreement with experimental data. Therefore, the interactions between water molecules and between water and cations must be modified.

Moreover, the Na^+ –water potential previously used for natrolite and for preliminary simulations of NaA was able to reproduce the structure and the spectra reasonably well, but we had to check the hydration enthalpies. Although recent experimental hydration enthalpy of zeolite NaA was reported,^{9,31,32} it was not easy to obtain its value from simulations, by considering that it is not clear whether in the experimental conditions the adsorbed molecules include or not those of kind A. On the other hand, in ref 33, the structures of hydrated zeolite X at different water loading are reported along with the corresponding desorption energy distribution function of water, so that more realistic comparison with simulations was possible. Therefore, the Na–water was changed, until the best fit of the experimental data was obtained.

The modified potentials were checked against the experimental data of natrolite (low and room temperatures, ambient and high pressures, hydrated with normal water and perdeuterated water^{34–38}), and the results using the potentials optimized for zeolite X were found to be all better than the old ones for the structures, the spectra, and the hydration energies. More details of the procedure used to refine model potentials for the Na^+ – H_2O interactions are reported in the Supporting Information.

The evaluation of the Coulomb energy was performed using the efficient method proposed by Wolf *et al.*⁴⁰ and extended in our laboratory to complex systems.⁴¹ Under ambient conditions for natrolite, the cutoff radius was $R_c = 12.2775$ Å, equal to one-half of the side of the simulation box, and correspondingly, the damping parameter was $\alpha = 2/R_c = 0.1629 \text{ \AA}^{-1}$. The simulations in the *NVE* ensemble lasted 100 ps (150 ps at temperatures below 273 K), after 50 ps equilibration runs. In order to compare the results of the simulations with the experimental structures, the simulations 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.^{19,23,42} In particular, the vibrational spectra were obtained by Fourier transforming the autocorrelation functions of the total dipole moment of the system (see ref 19 and references therein), and to evaluate IINS spectra, the treatment proposed in refs 43 and 44 was adopted.

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Supporting Information Available: Details of the interaction potential model. Computed main characteristics of bulk water, including RDFs and simulated IR spectra, and structure of water dimer. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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