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Mobility of water in Linde type A synthetic zeolites: an inelastic neutron scattering study

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Abstract

In the present work the effects produced by cation substitution on the dynamics of water in Linde type A (LTA) synthetic zeolites were investigated by means of inelastic neutron spectroscopy (INS). In particular, we performed measurements on fully hydrated Na-A and Mg-exchanged-A zeolites. The collected INS spectra showed two broad bands due to the vibrational (water–cation and hydrogen bond stretch) and librational (rock, twist and wag) modes of water. To quantitatively assign these various modes, the spectra were decomposed into Gaussian components and compared with the INS spectra of ice and of water in other zeolites. The observed shifts of the band positions for different temperatures were discussed. In particular, a slight shift of the three librational modes towards higher frequencies with increasing temperature was revealed for both samples. The hydrogen bond stretching and librational modes of water in Na-A and Mg50-A zeolites shift to lower frequencies with respect to ice. Furthermore, in the case of Mg50-A zeolite, we observed a shift upwards in frequency of librational bands with respect to Na-A zeolite. The obtained results were discussed in relation to our previous elastic and quasi-elastic neutron scattering (ENS and QENS respectively) measurements on the same samples.

1. Introduction

Water confined in various matrices offering nanometre pores or cavities has been involved in a wide range of industrial processes, attracting increasing interest in many research fields, such as chemistry, biology and soil science. Theoretical and experimental studies showed different structural and dynamical properties of confined water compared to the bulk state [1–11].

Recently, among the various micro-porous confining media, several efforts have been devoted to studying the behaviour of water in zeolites [12–14]. These systems are microporous crystalline aluminosilicates of natural or synthetic origin. Their framework can be regarded as consisting of the packing of units made up from SiO_4 and AlO_4 tetrahedra. Each apical oxygen atom of these units is shared with an adjacent tetrahedron.

In general the aluminosilicate zeolites can be represented by the following formula:

$$M^{m+}_{x/m}[Si_{1-x}Al_xO_2] \cdot nH_2O$$

where M^{m+} indicates an extraframework cation. In fact each aluminium atom present in the tetrahedral units induces a negative charge in the zeolitic framework; so a corresponding number of extraframework cations, usually metals, protons or organic cations, balances this negative charge.

A wide variety of different zeolites containing internal voids, channels and cavities, of well defined size in the nanometre range, able to adsorb water molecules and ions of different species, can be formed by the different connection of the tetrahedral units [15–18].

The increasing interest in zeolites is mainly due to the broad spectrum of their technological applications [19]. In particular, the very narrow distribution of pore sizes is the fundamental characteristic that distinguishes zeolites from other porous materials, such as alumina and silica gel. This intrinsic characteristic of their structure allows us to achieve high selectivities in both catalysis and sorption processes. In addition, the extraframework cations can be replaced by ionic exchange and as a consequence the pore size of the zeolite is modified.

Because water is encountered in almost all industrial processes, the influence of zeolite type, aluminium content and exchanged cation on the adsorption with respect to water have been the scope of numerous studies [20–26]. However, the understanding of the location of water molecules and their interactions with the zeolite framework and extraframework cations remains still an open question.

Recently, we studied the effect induced by the cation substitution on the properties of water in Linde type A (LTA) synthetic zeolites. Information on dynamics of water in Na-A and Mg-exchanged A zeolites was obtained by Fourier transform infrared (FTIR) spectroscopy in attenuated total reflection (ATR) geometry [27]. FTIR data revealed, in a wide range of temperature, the contribution linked to the ice-like tetrahedral environment, typical of bulk water. In this sense, we attributed a ‘structure maker’ role to the zeolitic surface on physisorbed water. We found that this role is enhanced by increasing the percentage of induced ion exchange. For more details the reader can refer to [27].

In this study we employed inelastic neutron scattering (INS) on fully hydrated Na-A and Mg50-A zeolites (in this last sample 50% of the Na^+ cations being exchanged with Mg^{2+} ions), attempting to characterize the various modes of water which are seen.

The INS method allows us to follow directly the motions of nuclei and, since the energy transfer is not limited by specific selection rules, the INS spectrum provides information about all vibrations of the system [28]. Furthermore, this technique turns out to be suited to analyse the spectral region below 1200 cm^{-1}, where it is often difficult to use infrared spectroscopy because of the strong absorption by the zeolite framework [25].

INS spectra, collected as a function of temperature in the 30–1200 cm^{-1} region, contain information on vibrational (water–cation and hydrogen bond stretch) and librational (rock, twist and wag) modes of confined water. From a deconvolution of the spectra and a comparison of the obtained sub-bands with the INS spectra of hexagonal ice [29] and of water in different zeolites [23, 25], we can unambiguously assign the various modes of water. The librational modes for water in Na-A and Mg50-A turned out to be shifted to lower frequencies with respect to ice. Moreover, librational bands of Mg50-A are shifted upwards in frequency with respect to Na-A zeolite. A comparison with previous QENS and ENS measurements [30] on the same samples reveals a full agreement of new and already collected data.

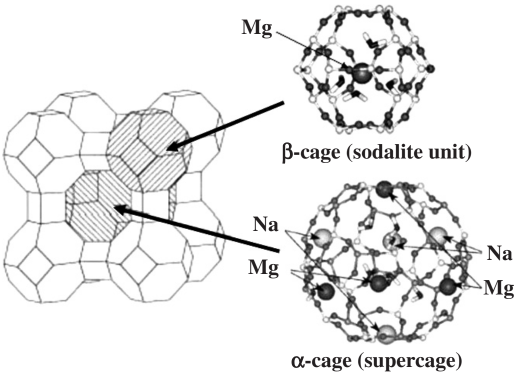

Figure 1. Illustration of the zeolite A framework.

2. Experimental details

INS measurements were performed on fully hydrated Linde type A (LTA) synthetic zeolites. In particular, the investigated samples were Na-A (abbreviation of the sodium form of the Linde type A zeolite) and Mg50-A zeolites, fully hydrated powders purchased from Nippon Chemical Industrial Co. As mentioned in the introduction, we denoted as Mg50-A the Na-A zeolite in which 50% of the Na^+ cations were exchanged with Mg^{2+} ions. The formula units of Na-A and Mg50-A zeolites can be written as $Na_{12}Al_{12}Si_{12}O_{48}\cdot 27H_2O$ and $Mg_3Na_6Al_{12}Si_{12}O_{48}\cdot 33H_2O$ (based on the oxygen number of 48), respectively.

In order to interpret the INS spectra, a brief description of the structure of both analysed systems is reported here. The zeolitic framework is the same for both samples, while different locations can be associated with the extraframework cations, Na^+ and Mg^{2+} ions.

In general, the framework of zeolite A can be regarded as consisting of two types of cages: β-cages and α-cages. The β-cages, also called sodalitic units, are cubo-octahedra, constituted of six and four-membered rings. The α-cages, also called supercages of zeolite A, are pentagonal dodecahedra. They are formed by β-cages interconnected by oxygen bridges at the double four-membered rings. Hence, the A framework consists of α-cages by sharing the eight-membered rings. The eight-membered ring is called the window of the α-cage and its effective size is about 5 Å. The α-cages are arranged in a simple cubic structure [15, 24, 31]. The zeolite A framework is shown in figure 1.

The presence of three crystallographically different oxygen sites can be observed, namely O(1), O(2) and O(3). The O(1) oxygens make up the bridges between the adjacent sodalite units. In the β-cages, both O(2) and O(3) oxygens form six-rings, while only O(3) oxygens make up the four-rings.

The positions of sodium and water molecules in Na-A zeolite have been identified by Gramlich and Meier [31] by means of a detailed x-ray diffraction study. Na(1) is located on the threefold axis near the centre of the six-membered ring. At this site, Na^+ turns out to be tetrahedrally coordinated by three framework oxygen atoms O(3) and one molecule. The further sodium ions and water molecules are discovered in five different sites. Site I appears to be occupied by four molecules, giving rise to a distorted tetrahedron, and is located in the small β-cage. About 20 water molecules, making up a pentagonal dodecahedron, are found in sites II and III inside the α-cage. The linkages between the water polyhedra are furnished by the contents of site IV, inside the eight-membered ring. Finally, site V is indicated as a broad peak, discovered at the centre of the dodecahedron, probably originated by a less symmetrical arrangement, including one water molecule and one sodium ion. Recently, Higgins *et al* [24], employing atomistic simulation techniques, investigated the location of water and of a set of extraframework cations in the framework of zeolite A. According to this study, the energetically preferred location for water molecules is situated in a six-membered ring inside the β-cage. The energetically most favourable adsorption site for Na^+ ions was identified as the α-cage, in the six-ring window adsorption. The Na^+ ion is calculated to be coordinated at three water molecules in the α-cage and at one water molecule in the β-cage. Finally, bivalent ions occupy the six-membered ring inside the β-cage. In this position they are calculated to be fourfold coordinated at four water molecules. As a consequence of the different locations of monovalent and bivalent ions, the pore dimensions are modified passing from Na-A to Mg-exchanged-A zeolites. In particular, the pore dimension is ~4 Å in Na-A, while after ionic substitution it turns out to be ~5 Å.

INS measurements on Na-A and Mg50-A zeolites were performed using the TOSCA spectrometer at the ISIS Facility, Rutherford–Appleton Laboratory, UK. INS spectra were recorded at temperatures of 50, 180 and 220 K. The used instrument, TOSCA, is an indirect geometry t.o.f. spectrometer with an optimal energy range of 0–4000 cm^{-1}. The best results are normally obtained below 2000 cm^{-1}. In particular, we observed that signals from the backscattering detectors showed lower noise level than the forward-scattering bank. Hence, INS spectra obtained from the backscattering detectors are reported and analysed. The contribution from the empty can, resulting in a flat background, was subtracted from all INS spectra. The time of flight spectra were converted to dynamic structure factor $S(Q, \omega)$ versus energy transfer $\hbar\omega$ by using the standard programs at ISIS.

3. Results and discussion

First of all, we evaluated the contributions to the total intensity coming from the zeolitic framework by considering the coherent and incoherent cross sections of our samples. We found that the contributions of the two frameworks are mainly coherent and amount to 6% for Na-A, 5% for Mg50-A. Therefore, since the incoherent scattering coming from hydrogen dominates the INS spectrum, this technique is an ideal tool for the study of water adsorbed in porous solids, with only a negligible contribution coming from the inorganic framework.

The INS spectra of water in Na-A and in Mg50-A zeolites, in the region 30–1200 cm^{-1} (3.7-148.8 meV), at the examined temperatures, are shown in figures 2(A) and (B) respectively. Two broad bands associated with vibrational and librational modes occur in all INS spectra. The fact that these bands are broad could be indicative of the existence of different species of adsorbed water molecules [25]. In order to obtain information on the modes of water, all spectra were decomposed by the minimum number of Gaussian profiles. The INS spectra, together with the best fit and the deconvolution components, for Na-A and Mg50-A zeolites are shown in figures 3 and 4 respectively. As can be seen from an inspection of figures 3 and 4, the spectra are composite and a satisfactory reproduction of the experimental data can be achieved by the superposition of four and three components in the lower (30–355 cm^{-1}) and higher (355–1200 cm^{-1}) frequency regions respectively. Table 1 reports the relevant parameters of each sub-band, i.e. the frequency peaks and relative intensities, obtained from the fitting procedure for all the analysed samples.

Based on the work of other authors and by a comparison with the INS spectra of hexagonal ice Ih [29] and of water in other zeolites [23, 25], an overall assignment of the observed peaks was performed and the main results are reported in table 2. In particular, ice Ih was chosen because it is produced by nucleation of liquid water in the bulk state at ambient pressure.

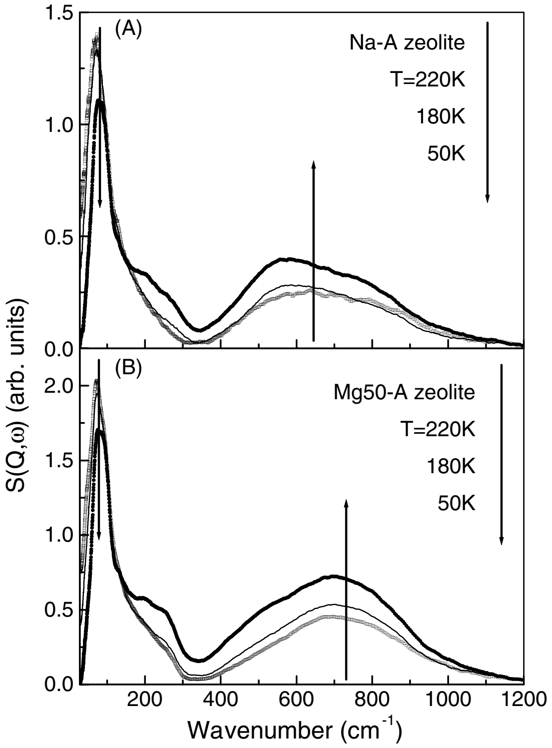

Figure 2. INS spectra of water in Na-A and in Mg50-A zeolites at temperatures of 50 K (filled circles), 180 K (continuous line) and 220 K (open squares).

Table 1. Centre frequencies and relative intensities of each sub-band, obtained by the best fit of INS spectra for Na-A and Mg50-A zeolites at all the investigated temperatures.

T (K)	ω_1 (cm^{-1})	I_1 (%)	ω_2 (cm^{-1})	I_2 (%)	ω_3 (cm^{-1})	I_3 (%)	ω_4 (cm^{-1})	I_4 (%)	ω_5 (cm^{-1})	I_5 (%)	ω_6 (cm^{-1})	I_6 (%)	ω_7 (cm^{-1})	I_7 (%)
Na-A zeolite														
50	77.25	15.64	113.06	9.15	189.43	13.53	274.05	3.39	420.04	7.27	560.03	22.69	764.91	28.33
180	70.22	31.55	126.51	14.82	194.77	5.13	257.69	3.07	473.89	2.74	574.49	19.21	766.13	23.48
220	69.70	40.17	140.70	10.13	195.87	4.44	245.72	1.68	485.28	4.36	590.43	11.38	770.92	27.84
Mg50-A zeolite														
50	79.09	14.11	119.20	6.24	201.24	17.63	265.47	0.72	448.67	4.92	598.00	27.61	775.29	28.77
180	74.63	22.70	120.89	19.95	206.73	3.26	257.54	3.17	478.65	3.80	620.23	17.16	777.50	29.96
220	73.75	20.63	110.34	29.04	218.44	0.36	257.58	0.83	479.49	1.43	683.05	23.14	785.99	24.57

As far as the low frequency region is concerned, the peak $\omega_1 \sim 74$ cm^{-1} is identifiable as a translational mode of water according to INS study of ice Ih.

The peak ω_2, centred at ~120 cm^{-1}, could be assigned to water–cation stretch in agreement with other studies, where it is revealed every time the water molecules are attached to one or more cations [23].

Going to higher energy, the two peaks ω_3 and ω_4, at ~200 and 260 cm^{-1}, can be associated with the hydrogen-bond stretch mode. In fact, their frequencies are comparable with the

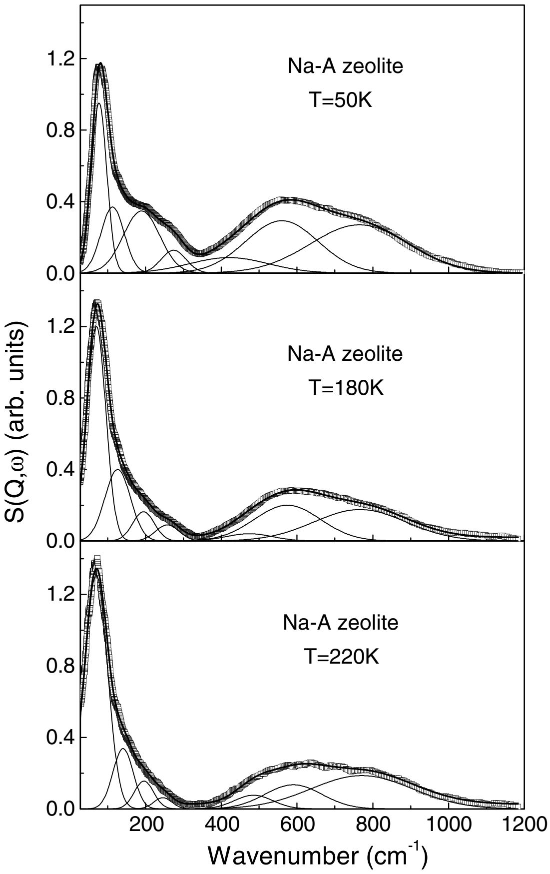

Figure 3. INS spectra (open squares) of water in Na-A, at all investigated temperatures, together with the theoretical best fit and the deconvolution components.

Table 2. Average values of frequencies of sub-bands, obtained by the best fit of INS spectra at the investigated temperatures, with tentative assignments. The band positions are compared with values of ice Ih [27].

	Na-A (cm^{-1})	Mg50-A (cm^{-1})	Ice Ih (cm^{-1})
Translational mode	72.39	75.82	57.26
Cation–water stretch	126.76	116.81	
H-bond stretch	193.6	208.80	229.05
	259.15	260.20	305.66
Librational edge			540.35
			975.86
Rock mode	459.74	468.94	
Twist mode	574.98	633.76	
Wag mode	767.32	779.59	

hydrogen-bond peaks at ~229 and ~305 cm^{-1} observed in the INS spectra of ice Ih [29]. In particular, for Na-A zeolite, the peak ω_3 is centred at ~189 cm^{-1} at the lowest analysed temperature and shifted to higher frequency ($\omega_3 \sim 196$ cm^{-1}) as the temperature increases.

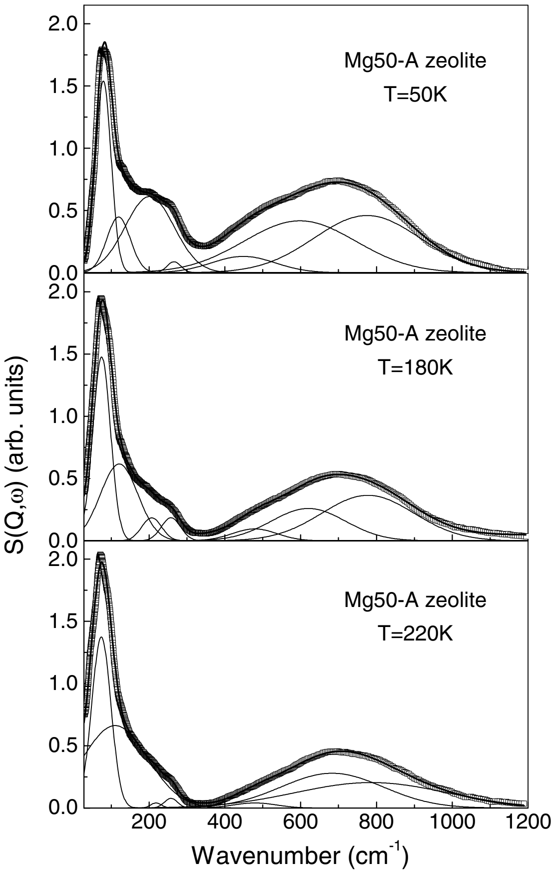

Figure 4. INS spectra (open squares) of water in Mg50-A, at all investigated temperatures, together with the theoretical best fit and the deconvolution components.

The same trend is observed in Mg50-A, where it is shifted from ~201 cm^{-1} (at $T = 50$ K) to higher frequency ($\omega_3 \sim 218$ cm^{-1}) going up in temperature. Furthermore, the relative intensity of this sub-band is higher in the spectra at the lowest temperature ($T = 50$ K) for both samples and diminishes as the temperature increases.

In the high energy region (355–1200 cm^{-1}) of INS spectra, the hindered rotations of the water molecule around its three principal axes of inertia, i.e. rock, twist and wag librational modes, are accessible and centred respectively at $\omega_5 \sim 464$ cm^{-1}, $\omega_6 \sim 604$ cm^{-1}, and $\omega_7 \sim 773$ cm^{-1}. The observed peak wavenumbers are in agreement with the frequencies of librational bands revealed for water in natrolite and in apophyllite [23].

As is well known, librational modes will only have observable intensity if a restoring force exists. Therefore, they are not observed in gaseous water, but always occur in the condensed phase, and their position and intensity are very sensitive to hydrogen bonding [25]. In the case of ice Ih, librational modes are shown to spread from ~548 to ~1008 cm^{-1} (left and right edges of the band, respectively) [29].

As can be seen by an inspection of table 1, the rock mode ω_5 shifts from ~420 to ~485 cm^{-1} for Na-A and from ~448 to ~479 cm^{-1} for Mg50-A, with increasing temperature. For both samples the corresponding relative intensity I_5 diminishes as the temperature increases.

The twist mode ω_6 also moves towards higher frequency with increasing temperature for both samples. This peak shifts from $\sim$560 to $\sim$590 cm^{-1} for Na-A and from $\sim$598 to $\sim$683 cm^{-1} for Mg50-A passing from $T = 50$ to 220 K.

Finally the position of wag mode ω_7 shows the same trend as the previous librational bands. So when temperature increases this peak shifts from $\sim$764 to $\sim$770 cm^{-1} and from $\sim$775 to $\sim$786 cm^{-1} for Na-A and Mg50-A, respectively. Its relative intensity I_7 remains the most relevant with respect to the other two librational modes for both samples at all the investigated temperatures.

A slight overall shift of the three librational modes towards the higher frequencies as the temperature increases can be observed for both samples. It is enhanced by increasing the percentage of induced ion-exchange.

Furthermore, a comparison of the obtained centre-frequencies of hydrogen-bond stretch and librational bands with those of ice Ih reveals a low-energy shift in the case of water confined in Mg50-A and Na-A zeolites. This evidence indicates that the positions of both hydrogen-bond stretch and librational modes are very sensitive to the local environment of water.

In fact, according to recent INS studies on water in various zeolites [23, 25], the positions of the librational bands could be correlated with the restoring force produced by the hydrogen bonding. In particular, stronger restoring forces for librations are indicated by bands with higher frequencies. Therefore, the always increasing low-frequency shift of the librational peaks observed, in order, in Mg50-A and Na-A zeolites compared to ice Ih indicates a stronger restoring force for librations in ice than in water upon confinement and in particular a maximum enhancement in Na-A zeolite with respect to Mg50-A. Hence, as a general result we can say that, first of all, the water transient H-bond network is less extended in zeolites than in ice Ih. This is in agreement with other INS studies of water confined in GelSil [4] and in various zeolites [23, 25], where the observed librational bands are shifted downward in frequency compared to the librational band of ice Ih.

In addition, the partial exchange of Na^{+} with Mg^{2+} ions seems to influence the water dynamics in zeolites and in particular the librational band positions. As specified above, the observed slight shift of librations upwards in frequency in Mg50-A compared to Na-A is a consequence of the different locations of Na^{+} and Mg^{2+} ions in the zeolitic framework. In fact, while the preferential location for Na^{+} ions in hydrated zeolite A was calculated to be in six-ring window adsorption sites in the α-cage, the most favourable adsorption sites for Mg^{2+} ions were found to be in the six-membered ring in the β-cage. Furthermore, the partial substitution of Na^{+} ions with Mg^{2+} causes a reduction of the number of ions in the zeolite, leaving free the entrance channels to the zeolitic cavities. As a consequence, a more regular formation of the tetrahedral H-bonded network in Mg50-A zeolite can be favoured. This interpretation is in agreement with our previous ENS and QENS measurements [30] on the same samples. From the QENS data it turned out, on one hand, that the partial exchange of Na^{+} with Mg^{2+} ions involves an increase of the available volume for diffusion, as expected by the different spatial distribution of monovalent and bivalent ions in the zeolitic framework. In spite of this, on the other hand, a higher immobile fraction of water in Mg50-A than in Na-A zeolite was revealed. This occurrence was connected with the higher electronegativity and the smaller ionic radius of the Mg^{2+} than the Na^{+} ion. We concluded that, in the case of Na-A zeolite, the difficulty of water molecules to rearrange in a stable network, due to the presence of Na^{+} ions, leads to a higher number of mobile water molecules moving in the available space. In the case of the Mg50-A sample the Mg^{2+} ions, smaller than Na^{+} and located at the edges of the supercage leave the access channels to the cavities free and can favour a more regular formation of tetrahedral H-bonded network. This gives rise to a lower fraction of diffusing water molecules.

In addition, the existence of a transient structure network that is more extended in Mg50-A than in Na-A zeolite, indicated by INS spectra, is also confirmed by our previous ENS measurements on the same samples. In that case, in fact, the found values of the oscillator energies of the harmonic contribution to the total mean-square atomic displacements allowed us to attribute a stiffer hydrogen bonding network in the case of Mg50-A with respect to Na-A zeolite.

In order to shed more light on the influence of ion substitution on dynamics of water in zeolites, new measurements on fully and partially hydrated A zeolites are in progress, as a function of the percentage of the induced ion-exchange.

4. Conclusions

The dynamics of water in Na-A and Mg50-A zeolites was studied by means of inelastic neutron spectroscopy (INS). The two broad bands, observed in all INS spectra, were decomposed into Gaussian sub-bands. The obtained components were assigned to the various modes of water, by means of a comparison with the INS spectra of ice Ih [29] and of water in other zeolites [23, 25]. In particular, for both samples we identified the vibrational (water–cation and hydrogen bond stretch) and librational (rock, twist and wag) modes of water. An analysis in temperature allowed us to reveal, for both samples, a slight shift of the three librational modes towards the higher frequencies as the temperature increases. Furthermore, a shift upwards in frequency of the librational bands in Mg50-A compared to Na-A zeolite was observed. Again, both hydrogen bond stretching and librational modes turned out to be shifted downward in frequency with respect to ice Ih.

The observed shifts indicated that the positions of both hydrogen bond stretching and librational modes are influenced by the local environment of the water. In particular, stronger restoring forces for librations give rise to bands with higher frequencies. Our results indicated a stronger restoring force for libration in Mg50-A with respect to Na-A and hence the existence of a more extended transient structure network of water for Mg50-A zeolite. The data confirm our previous ENS and QENS results [30] on dynamics of water in the same zeolites.

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