

Inelastic neutron scattering study of NH₄Y zeolites

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Inelastic Neutron Scattering Study of NH_4Y Zeolites

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An inelastic neutron scattering study of NH_4Y and CsNH_4Y zeolites is presented from 2 to 350 meV ($16\text{--}2800\text{ cm}^{-1}$). The spectra are interpreted in terms of translational and librational motions of ammonium ions, ammonia and water molecules. For the hydrated samples the translational modes of water species are observed at 12 meV and librational modes are found above ca. 50 meV. The translational and librational modes of the ammonium ions also depend on the location of the cations. Ammonium species give rise to (ion–lattice) translational modes at 10–15 meV and at 15–25 meV for species localised in sodalite cages and supercages, respectively. The corresponding librational modes are observed at ca. 8 meV and in the region 3–6 meV, respectively. Strongly hindered librations are observed at 50–70 meV and 30–50 meV, respectively, for the ions in the two different cages. Low-frequency as well as high-frequency librational modes of the ammonium species may occur caused by the presence of different ammonium species.

Differences in reorientational motions are observed for hydrated zeolites and for reammoniated zeolites. For the latter, a stronger interaction of the ammonium ions with the zeolitic lattice is present and the low-frequency librational modes are shifted to higher energy-transfer values.

When increasing the loading with ammonia, librational and translational motions of ammonia species could be observed. Again, a heterogeneity in the reorientational barriers is present, indicating the presence of different ammonia species.

Zeolites are frequently used as part of commercial catalysts.¹ Owing to the presence of channels and pores containing catalytically active sites, these materials are very efficient in obtaining high conversions and selectivities for various industrially important reactions. The active sites can consist of acidic protons, the Brønsted sites, Lewis acid sites or small metal clusters. In zeolite synthesis, generally the Brønsted sites are not created immediately. Depending on the type of zeolite synthesized, calcination procedures have to be used in order to remove templating molecules. Ion-exchange procedures are also used to produce zeolites containing ammonium ions. The ammonium form of the zeolite is converted to the acidic form by heating at elevated temperature in order to desorb ammonia, leaving a proton behind at a Brønsted site.²

Because of the importance for catalysis, ammonium-containing zeolites have been studied extensively in the past.^{3,4} Adsorption of ammonia on the hydrogen form of zeolites has been used to study quantitatively and qualitatively the acidic properties by, e.g. IR spectroscopy.^{5–7} The desorption of ammonia has been studied by temperature-programmed desorption and related methods, leading to reported energies of activation for the desorption process of 40–190 kJ mol^{-1} for various zeolites.^{8–13} These energies correspond to the rate-limiting step in the desorption process, the transfer of a proton from an ammonium ion to the zeolitic lattice. This step is energetically very unfavourable, causing diffusion effects to be of minor importance for zeolites with small crystallites.¹³ At present, an *ab initio* quantum chemical description of the proton-transfer process is being developed.^{14–24} In order to evaluate the rate constant for desorption or the rate constant for proton transfer theoretically, the thermodynamic partition functions of the ground and excited states in the rate-limiting step, as well as the translational and librational motions of the ammonium ions inside the zeolitic lattice, have to be known. From spectroscopic studies in the far-IR region, information about the translational modes of the ammonium ions in zeolites has been obtained.^{25–28} Quasi-elastic neutron scattering (QENS)

and inelastic neutron scattering (INS) can be used to study the librational motions of the ammonium ions and their translational modes with respect to the oxygen atoms of the zeolite walls.²⁹ INS is especially sensitive for hydrogen-containing compounds. The intensities in the neutron spectra are then proportional to the number of hydrogen atoms present in the sample.³⁰

In this paper we will present an inelastic neutron scattering study of Y zeolites containing ammonium ions. We will discuss the changes in the INS spectra during dehydration and deammoniation of the samples and after subsequent adsorption of ammonia.

Experimental

The starting material was the sodium form of zeolite Y (Si : Al = 2.8 : 1) which was converted to NH_4Y by nine-fold ion-exchange with NH_4NO_3 at 353 K. Chemical analysis indicated that almost 100% of the sodium ions were replaced by ammonium ions. A zeolite with different composition was obtained from NH_4Y (LZ-Y62, Si : Al = 2.4 : 1) after four-fold ion-exchange with NH_4NO_3 at 353 K followed by a three-fold exchange with CsNO_3 at 295 K. The composition of this sample as obtained by chemical analysis was $\text{Cs}_{35}(\text{NH}_4)_{18}\text{Na}_3[(\text{SiO}_2)_{136}(\text{AlO}_2)_{56}]$.

For the pretreatment of the samples 13 g of hydrated zeolite were placed in a glass ampoule. Each sample was first evacuated at 323 K for several h. Then the temperature was increased at a rate of 0.2 K min^{-1} to the desired temperature level. After evacuation at this temperature for several h the sample was cooled to room temperature. For three of the samples at this stage anhydrous ammonia (99.98% purity) was adsorbed. Finally, the ampoule was sealed. A more detailed summary of the pretreatment conditions is given in Table 1. The ammonium content of the dehydrated samples was obtained from chemical analysis. The amount of ammonia adsorbed was determined volumetrically. These results are also listed in Table 1.

Table 1 Sample properties and measurement conditions

sample	treatment	adsorbed ammonia (NH ₃ per unit cell)	remaining ammonium (NH ₄ ⁺ per unit cell)
1	NH ₄ Y no	—	51
2	NH ₄ Y INS: 24 h at 373 K	—	51
3	NH ₄ Y INS: 24 h at 473 K	—	36
4	NH ₄ Y INS: 16 h at 623 K	24	—
5	NH ₄ Y INS: 16 h at 623 K	124	—
6	NH ₄ Y INS: 16 h at 623 K	180	—
7	NH ₄ Y FTIR: 1 h at 723 K	—	—
8	CsNH ₄ Y no	—	18
9	CsNH ₄ Y INS: 60 h at 323 K	—	15
10	CsNH ₄ Y FTIR: 1 h at 723 K	—	—

The crystallinity of the samples was checked by XRD experiments before the treatment in the glass ampoules and after the INS measurements. These experiments showed that there was no severe damage of the crystal structure by the pretreatment conditions.

IR spectra were recorded by a Bruker IFS 113v FTIR spectrometer. In these experiments self-supporting samples of 3–8 mg cm⁻² were evacuated for 1 h at 723 K. After cooling

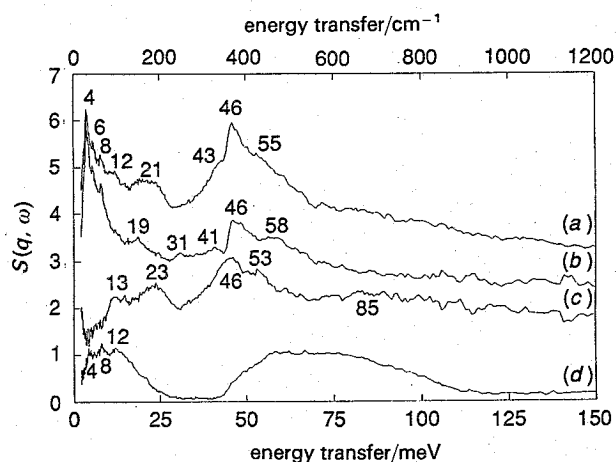


Fig. 1 Inelastic neutron scattering spectra from 2 to 150 meV for (a) NH₄Y desorbed at 373 K (sample 2), (b) 473 K (sample 3), (c) difference spectrum (sample 2 – sample 3), and (d) CsNH₄Y desorbed at 323 K (sample 9)

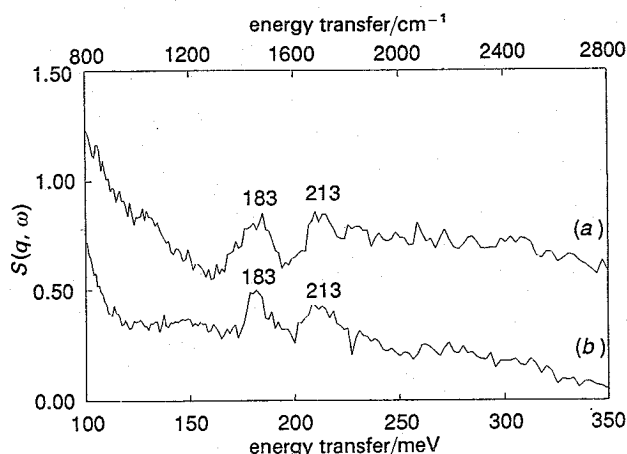


Fig. 2 Inelastic neutron scattering spectra from 100 to 350 meV for (a) NH₄Y desorbed at 373 K (sample 2) and (b) CsNH₄Y desorbed at 323 K (sample 9)

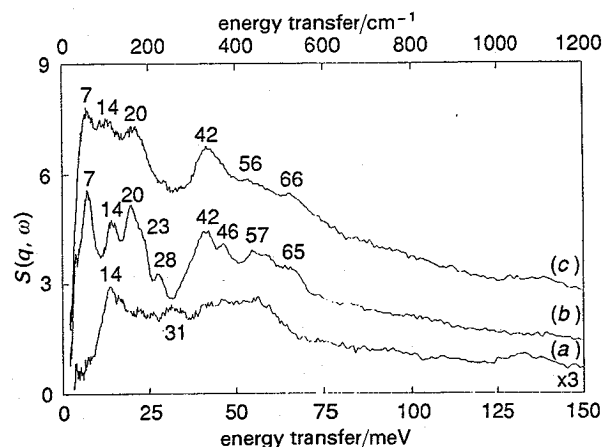


Fig. 3 Inelastic neutron scattering spectra from 2 to 150 meV for NH₄Y readsorbed with increasing amounts of ammonia: (a) sample 4, (b) sample 5 and (c) sample 6. The spectrum for sample 4 has been multiplied by a factor of 3.

to room temperature, spectra were recorded at a resolution of 1 cm⁻¹.

The INS measurements in the region from 2 to 350 meV were performed on the time-of-flight spectrometer TFXA (ISIS, Chilton, UK). This spectrometer has an energy-transfer range from 2 meV to 1 eV with a resolution of $\Delta E/E \leq 2\%$.³¹ The partly dehydrated and deammoniated samples were transferred from the glass ampoules to aluminium sachets for the measurements, while keeping them in an inert atmosphere. The advantage of this procedure is a reduction of the background scattering, but the disadvantage is that the amount of sample in the neutron beam can vary slightly. For the reammoniated samples an aluminium vacuum-tight cell was used instead of the sachets in order to enable adsorption of ammonia. The measurements were carried out at 20 K and the spectra obtained are corrected for the background of the empty cryostat or the empty aluminium container.

Results

Dehydrated Ammonium Zeolites

In Fig. 1 the INS spectra for the region below 150 meV are presented for the samples evacuated at different temperatures (samples 2, 3 and 9 of Table 1). The spectrum of sample 2 [Fig. 1(a)] contains sharp peaks near 4, 6 and 8 meV which

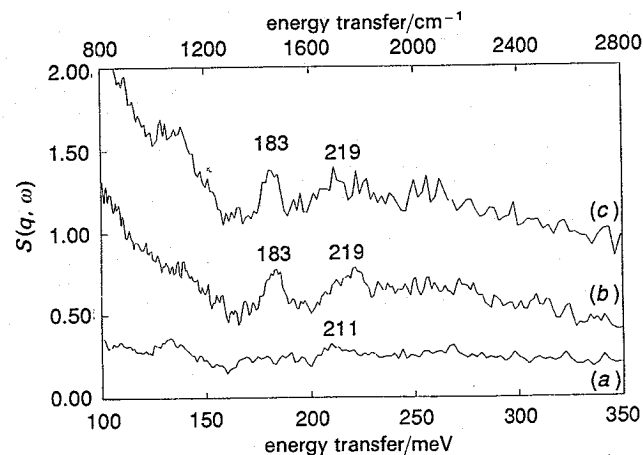


Fig. 4 Inelastic neutron scattering spectra from 100 to 350 meV for NH₄Y readsorbed with increasing amounts of ammonia: (a) sample 4, (b) sample 5 and (c) sample 6

are also present with approximately equal intensity in the spectrum for sample 3 [Fig. 1(b)]. A feature found at 12 meV is almost absent in the spectrum for sample 3 and a broad band can be observed at 21 meV for sample 2 which is converted into a band with a reduced intensity at 19 meV for sample 3. Finally, the spectrum of sample 2 is characterised by a broad band from 30 to 70 meV, with a maximum at 46 meV and shoulders near 43 and 55 meV. The intensity above 70 meV is mainly due to multiphonon excitations. After evacuation at 473 K (sample 3) the intensity of the broad band has decreased and peaks at 31, 41, 46 and 58 meV can be observed. Fig. 1(c) is the difference spectrum: sample 2 - sample 3. This spectrum is characterized by a band from ca. 10 to 30 meV, with maxima near 13 and 23 meV. A strong band is observed between 30 and 70 meV, with a maximum at 46 meV and a shoulder near 53 meV. Furthermore, we can observe a very weak band from 70 to 150 meV, with a broad maximum near 85 meV.

The spectrum of sample 9 [Fig. 1(d)] contains sharp bands at 4 and 8 meV and a broader band at 12 meV. The band at 4 meV has a reduced intensity when compared with the spectra for samples 2 and 3. The feature near 6 meV is missing for sample 9. At 21 meV, a small shoulder can be observed and a broad band is located between 40 and 120 meV.

Furthermore, the spectra are characterised by a peak at 183 meV and a peak at 213 meV with a shoulder extending to 350 meV (Fig. 2).

Reammoniated Zeolites

The results for the reammoniation experiments are presented in Fig. 3 for the region 2-150 meV. Sample 4 is characterised by a broad band extending between 10 and 70 meV with maxima at 14, 31 and ca. 43 and 53 meV. A peak near 133 meV is also clearly visible and a very weak, broad feature may be observed at 211 meV (Fig. 4).

After adding more ammonia (sample 5 and 6) peaks at 7, 14, 20 and 42 meV develop. For sample 5 additional peaks can be found at 28, 46 and 57 meV and also shoulders at 23 and 65 meV can be found here. For sample 6 shoulders can be distinguished at 56 and 66 meV. The spectra for samples 5 and 6 contain peaks at both 183 and 219 meV.

Discussion

From the results presented in Table 1 it can be concluded that during evacuation of NH_4Y at 373 K desorption of ammonia is negligible. After evacuation at 473 K, 71% of the original amount of ammonium ions are still present. In the INS spectra a decrease of approximately a factor of two in the intensity is observed subsequently for the samples evacuated at 373 and 473 K. This decrease can be explained partially by the presence of adsorbed water in the samples. After evacuation at 473 K the amount of water present in the zeolitic cavities is negligible. Hence, the features in the difference spectrum [Fig. 1(c)] correspond to adsorbed water, with contributions from ammonium species.

For the CsNH_4Y zeolite similar arguments can be used. A negligible amount of ammonia is desorbed during the heat treatment at 323 K. The INS spectrum contains contributions due to adsorbed water because of the low desorption temperature used. This sample contains caesium ions located in the supercages and ammonium ions located in the sodalite cages.^{28,32} The caesium ions are too large to penetrate into the sodalite cages, whereas the ammonium ions can enter these cages. Consequently, the IR spectrum of the caesium-

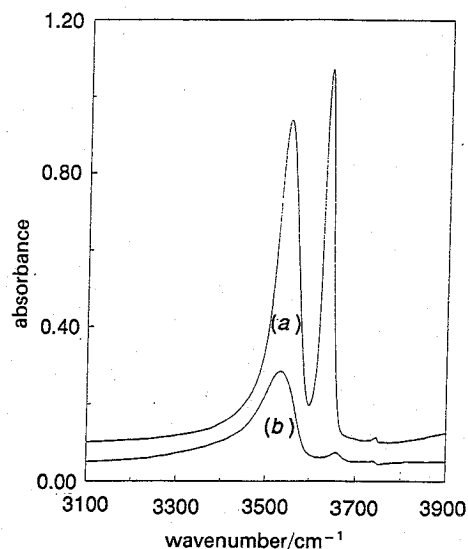


Fig. 5 Room-temperature IR spectra for the samples NH_4Y (a) and CsNH_4Y (b) after evacuation at 723 K

exchanged sample recorded after deammoniation at 723 K *in vacuo* [Fig. 5(b)] shows only the low-frequency (LF) hydroxy-group stretching band (3550 cm^{-1}), which is assigned to protons pointing into the sodalite cage.^{33,34} The high-frequency (HF) hydroxy-group stretching band (3650 cm^{-1}), which is due to protons pointing into the supercage, is almost completely absent. (According to ^1H NMR experiments, these protons are rather immobile. In the absence of residual ammonium ions or water molecules their residence time at the lattice oxygen atoms is at least 10^{-4} s .³⁵ This is very large compared with the hydroxy-group stretching vibration. Therefore, the IR signal corresponds to the energetically most favourable distribution of protons among the different sites.) The NH_4Y sample, on the other hand, possesses both the LF and HF hydroxy-group bands after deammoniation [Fig. 5(a)]. A comparison of the INS spectra of these two zeolites can be used to differentiate between ammonium species in supercages and those localised in sodalite cages.

Finally, we note, from the composition of the samples in Table 1, that only the INS spectra for samples 3, 4, and 9 may contain very weak contributions due to the presence of acidic protons. In a previous INS study, acidic Y zeolites have been investigated.^{36,37} The main features in the INS spectra for acidic Y zeolites are due to the in-plane (135 meV) and out-of-plane (52 meV) bending modes of the acidic hydroxy groups.

Dehydrated Ammonium Zeolites

When comparing the INS spectra of NH_4Y after desorption at 373 and 473 K, one observes a decrease in intensity for the peak at 21 meV and for a band extending from 30 to 70 meV, which is related to the shoulders at 43 and 55 meV [Fig. 1(a)]. Furthermore, the peak at 12 meV has almost completely disappeared after evacuation at 473 K. Some of these features may be assigned to water species present inside the zeolite. Increasing the desorption temperature from 373 to 473 K results in the desorption of water species that are responsible for part of the features in the difference spectrum [Fig. 1(c)]. The other part in this spectrum is due to ammonium ions which are desorbed as ammonia, leaving behind an acidic Brønsted site.

Several authors have studied water adsorbed in zeolites and other porous materials using INS.³⁸⁻⁴² Their results

indicate that the translational modes of water species are located below 50 meV. The librational modes are found at higher energy-transfer values, typically in the region from 50 to 150 meV. Furthermore, owing to the inverse dependence of the intensity on the effective mass for the translations and librations, the former are expected to have the lower intensity.⁴³ Using these considerations and the observed behaviour upon evacuation at elevated temperatures, the features at 13 and 23 meV [Fig. 1(c)] could both originate from translational motions of water species. After evacuation at 473 K, a peak at 19 meV remains, together with a weak shoulder at 12 meV [Fig. 1(b)]. These remaining features can be assigned to the translational modes of ammonium ions, which is in agreement with results obtained from far-IR measurements,^{25–28} where the IR-active translational modes are observed in the range 10–25 meV. So it is not possible to discriminate between the translational modes of the water and ammonium ions.

Apart from the IR-active translational modes of the ammonium ions, translational modes may also be present that are not observable in the far-IR spectrum. These modes are due to the parallel motion of the ammonium ions to the zeolite walls. The corresponding vibrational frequencies are not known, but may be very low. Furthermore, translational modes of cations can have a weak intensity in the far-IR spectrum, whereas these modes are more pronounced in the INS spectra. So, compared with results from far-IR spectroscopy, the translational modes for the ammonium ions need not be restricted within the region 10–25 meV. However, since the intensities of the features observed below 10 meV and above 25 meV are relatively high, the main contribution here comes from librational modes.

Peaks near 4, 6 and 8 meV are found for samples 2 and 3 with comparable intensities. From the composition of these samples it has to be concluded that these features are due to ammonium ions. Furthermore, since these bands are much more intense than the translational modes of the ammonium ions (12 and 19 meV), they have to be assigned mainly to librational modes.

The region from 30 to *ca.* 70 meV contains contributions from the librational motions of ammonium species with a possible contribution from water for the sample evacuated at 373 K. For the sample evacuated at 473 K the contribution due to water species is negligible. Hence, we assign the features at 31, 41, 46 and 58 meV to restricted librational modes of ammonium ions. This assignment is supported by the observation of similar features for the reammoniated sample (4) [Fig. 3(a)], though less well resolved. The differences in the region 30–150 meV for samples 2 and 3 are caused by the different water and ammonium contents. The librational modes of water are present above *ca.* 50 meV. Hence, part of the shoulder at 53 meV and the weak, broad band at 85 meV in the difference spectrum [Fig. 1(c)] may be assigned to librational modes of water species. The broad band from 30 to 70 meV and centred at 46 meV in the difference spectrum [Fig. 1(c)] is observed at an energy-transfer value that is too low to allow assignment of this band to water librations exclusively. Therefore, we assign part of this band to librations of weakly bound ammonium ions. The maxima at 46 and 58 meV may be related to more strongly bound ammonium ions, since they are still observed after evacuation at 473 K. So, owing to the overlap of the librational modes of ammonium and water species, the modes are not resolved and the shoulders at 43 and 55 meV result, as observed in Fig. 1(a). Except for the weaker modes at 31 and 41 meV, the librational modes of the ammonium ions observed for sample 3 [Fig. 1(b)] are much more intense than the corresponding translational modes, which is to be expected.⁴³

Different research groups have studied ammonium-containing compounds using INS.^{43–48} Values ranging from 6 to 48 meV were found for the librational modes of ammonium ions in inorganic salts, which is in the range of our results, except for the feature near 58 meV. These values correspond to activation energies for reorientation ranging from 1 to 200 kJ mol⁻¹.⁴³ For ammonium ions in zeolite rho, a librational energy of 10–14 meV was found, corresponding to a very low reorientational barrier of *ca.* 3.4 kJ mol⁻¹.²⁹ So we will assign the features between 3 and 8 meV in our spectra to librations of ammonium ions, having a weak reorientational barrier. However, librations of ammonium ions with a high reorientational barrier are also present.

From the influence of desorption temperature on the intensities of the various bands we can conclude that the modes at 4, 6 and 8 meV, the relatively narrow band at 46 meV and probably also the shoulder at 58 meV are related to ammonium ions which are relatively firmly bonded to the zeolitic lattice. The broad band from 30 to 70 meV, also centred near 46 meV [Fig. 1(c)], contains contributions due to weakly bound ammonium species.

According to Ozin *et al.*²⁸ the ammonium ions in Y zeolites are located at the exchangeable cation positions S_I, S_{II} and S_{III} (Fig. 6). In zeolites, the ammonium ions depart from tetrahedral symmetry,⁵ because electrostatic interactions with the negatively charged zeolite lattice deform the ammonium ions. *Ab initio* quantum chemical calculations indicate that these interactions occur by bonding of two or three protons to the zeolite oxygen atoms.^{14,15} We can therefore conclude that two types of reorientational modes can be discriminated for the different ammonium species present. Slightly hindered librations are found from 3 to 8 meV. For freely rotating ammonium ions a value of 1.5 meV can be calculated.⁴⁵ Librational modes of ammonium ions reorientating in a stronger potential field are located in the region from 30 to

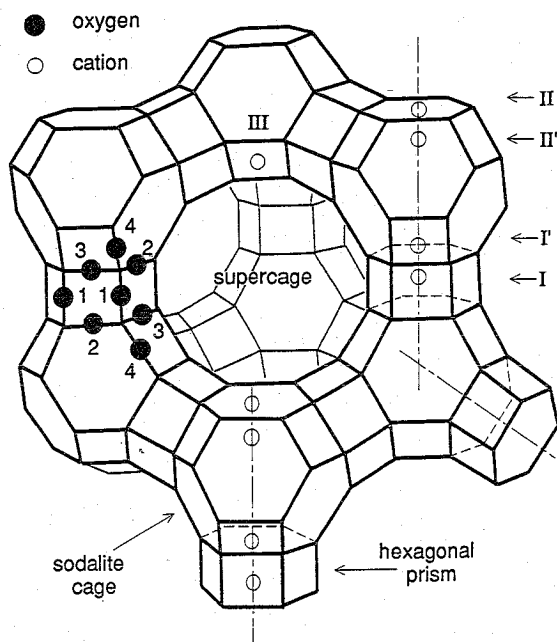


Fig. 6 Faujasite structure: different oxygen atoms are numbered 1 to 4. Cation positions are indicated by roman numerals. For position III two slightly different positions III' and III'' can be discriminated which differ in location with respect to the adjacent four-rings: for position III' the cation interacts with four oxygen atoms [O(1) and O(4)]; for position III'' the main interaction is *via* one O(4) oxygen atom and weaker interactions are *via* two O(2) oxygen atoms.

ca. 70 meV. For zeolite rho the features in the region 38–45 meV were attributed to ammonium-coupled pore-opening modes of the zeolite framework,²⁹ but this work shows that we also have to assign these features to librational modes of ammonium ions.

Finally, the spectrum for sample 2 contains peaks at 183 and 213 meV which are due to the two N–H bending modes of the ammonium ion. The shoulder extending to 350 meV can be assigned to recoil scattering of weakly bonded ammonium ions or water molecules.

From the spectrum for CsNH₄Y [Fig. 1(d)] it is immediately obvious that the librational modes of the ammonium species at 4, 6 and in the region of 30–46 meV are missing. Hence, we assign these modes to reorientation of ammonium species located in the supercage. The mode near 8 meV can be assigned to ammonium species located in the sodalite cage. The region above ca. 45 meV is partly masked by the librational modes of water.

The translational mode at 21 meV is almost completely absent for this sample, but the mode at 12 meV still remains. Using results from far-IR spectroscopy, Ozin *et al.*²⁸ have assigned bands found at 24 and 19 meV to translational modes of ammonium ions located in the supercages (S_{II} or S_{III}). However, for a translational mode of ammonium ions observed at 11 meV a definite assignment could not be given: the ions responsible for this mode are located at site S_V, but there may also exist a contribution due to ions at site S_{III}. When comparing these assignments with our results for the hydrated samples we can conclude that ammonium ions localised in supercages give rise to translational modes in the region between 15 and 25 meV, because these modes are absent for the CsNH₄Y zeolite. The modes observed in the region 10–15 meV have then to be assigned to the translational motions of ammonium ions in the sodalite cages. The lower values are probably due to the more symmetric environment of the sodalite cages. In this region translational modes of water species are also observed, *e.g.* in an INS study of water adsorption on H-mordenite features at 7.5 and 13 meV are attributed to translations of water and hydronium species.⁴² Therefore, we cannot uniquely assign the translational mode near 12 meV to either water or ammonium ions in the sodalite cages. The modes found at 4 and 8 meV are not much affected by increasing the desorption temperature, so these modes are not assigned to water. Therefore, these modes represent exclusively the librational motion of ammonium ions. The decrease in intensity for these modes upon increasing the desorption temperature is due to a reduced population of ammonium ions. It is also not likely that the mode observed in the region between 15 and 25 meV contains contributions from water molecules because it is missing in the spectrum for CsNH₄Y.

Reammoniated Zeolites

From the spectrum of the partly reammoniated sample 4 it is clear that the slightly hindered librations of the ammonium ions (4, 6 and 8 meV), which were present in the water-containing samples, are now missing. A broad band is left between ca. 10 and 70 meV containing contributions due to translational and librational motions. A clear distinction between translational and librational motion is not observed, but from the preceding part it is known that the translational motions of ammonium ions in zeolites are located between 10 and 25 meV. Furthermore, we expect the intensity for the translational motions to be much less than that for the librational motions. So we attribute the peaks at 14, 31 and the broad band around 50 meV to librations of ammonium ions, while masking the less intense features due to translational

motions. Therefore, this region contains librational and translational modes belonging to different ammonium species; however, these modes are not resolved. Compared with the dehydrated samples the reammoniated zeolite has higher barriers for reorientation of the ammonium ions, since the librational modes below 10 meV are apparently shifted to higher energy-transfer values. These findings are in agreement with ¹H, ²⁹Si, ²⁷Al and ¹⁴N NMR experiments on hydrated and dehydrated ammonium-containing zeolites.^{35,49} These experiments indicate a stronger interaction of the ammonium ions with the zeolitic lattice for the water-free reammoniated zeolites compared with the dehydrated ammonium zeolites. QENS²⁹ and ¹H NMR relaxation measurements⁵⁰ on ammonium zeolites obtained after desorption at elevated temperatures indicated a low barrier for the reorientational motion of the ammonium ions. This is probably due to the fact that only the librations with the lowest barrier for reorientation are observed. When comparing our results for the librational modes with literature values for the librational modes of ammonium ions in inorganic salts and their corresponding reorientational barriers,⁵¹ we expect values from 2 to 65 kJ mol⁻¹ for the reorientational barriers for the different ammonium species in water-free reammoniated zeolites.

The peaks observed at 180 and 211 meV are present both in the dehydrated and reammoniated samples. These features are assigned to the two N–H bending modes of the ammonium ion. Superimposed on these modes we observe a weak broad band which is due to recoil scattering of weakly bonded ammonium ions or ammonia molecules. For both the dehydrated and reammoniated zeolites weak features can be found in the region from 120 to 170 meV. For the samples containing no acidic sites (samples 5 and 6), these bands are due to multiphonon excitations. However, for partly dehydrated or partly reammoniated samples a small contribution due to the in-plane bending modes of the acidic hydroxy groups may be present.^{36,37}

When adding extra ammonia, new features develop in the region below 100 meV and the total intensity increases. Most of the features observed for sample 4 remain visible, although weakly. These features are superimposed on a spectrum which looks quite similar to that of solid ammonia,⁵² where energy-transfer values below 24 meV were assigned to translational motions and values between 24 and 70 meV to librational motions of ammonia molecules. We can adopt a similar assignment for the region above 30 meV for our spectra. The intensity observed below 30 meV is too high to be of purely translational character. We think that a librational contribution of ammonia molecules must be present here, indicating a larger heterogeneity in reorientational barriers compared with solid ammonia. This is probably due to librational modes of different ammonia species, resulting in low-frequency (below 30 meV) and high-frequency (above 30 meV) librational modes. This situation is very similar to that for samples 2 and 3. It is likely that differences in location and hydrogen-bonding interactions between the ammonium and ammonia species are now responsible for the presence of the different librational modes.

Conclusion

An INS study of hydrated CsNH₄Y and of NH₄Y after various dehydration, deammoniation and reammoniation treatments is presented. Together with the literature results, the spectra can be analysed in terms of translational and librational motions of ammonium, water and ammonia species. Water and ammonium species localised in the supercages and the sodalite cages give rise to different translational and librational motions. For the hydrated samples, water

species give rise to a translational mode at 12 meV and librational modes above ca. 50 meV. The ammonium species in the dehydrated zeolites give rise to translational modes observed between 10 and 15 meV for species localised in the sodalite cages and between 15 and 25 meV for species localised in the supercages. The librational modes of the ammonium ions are found in the regions between 3 and 8 meV and between 30 and 70 meV.

Our results indicate a large heterogeneity in reorientational barriers for the ammonium ions, which is caused by the different positions of the ammonium ions in the zeolite resulting in different interactions with the zeolite walls. The slightly hindered librations (near 4 and 6 meV) are due to species located in the supercage, while the librations at 8 meV are assigned to species located in the sodalite cage. The features at 30–50 meV are ascribed to librations of ammonium species in the supercages. The ammonium ions located in the sodalite cages give rise to librations which can be observed between 50 and 70 meV. Therefore, in general, the librations of the ammonium ions in the sodalite cages (CsNH_4Y) are observed at higher energy-transfer values than those localised in the supercages (NH_4Y). This implies a more strongly hindered rotation for the ammonium ions in the small sodalite cages.

When the ammonium form is obtained by reammoniation of the proton form of the zeolite, generally higher barriers for the reorientational motions of the ammonium ions are observed. These librations give rise to peaks at 14 and 31 meV and a broad band around 50 meV. The low-frequency librations are not found and the weaker translational modes are masked by librational modes. When increasing the loading of ammonia, features due to ammonia clusters become visible in the spectra. The translational motions of these species are observed below 30 meV and the librational motions can be found in the region 5–70 meV, again indicating high and low barriers for reorientation. This heterogeneity in reorientational barriers is due to differences in ammonia location resulting in different interactions with the zeolite walls and with neighbouring ammonia or ammonium species.

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