A Quasi-Elastic Neutron Scattering Study of the Ammonium Ions in CsNH4-Y Zeolite

Published in:
Journal of Physical Chemistry

DOI:
10.1021/j100059a035

Published: 01/01/1994

Document Version
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:
- A submitted manuscript is the author’s version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher’s website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

Citation for published version (APA):

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.
- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal?

Take down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Download date: 27. Dec. 2018
Quasi-elastic neutron scattering has been used to study the reorientation mechanism for ammonium ions in cesium-exchanged zeolite Y. This sample contains ammonium ions preferentially located in the sodalite cages at site I. These ions reorientate with 120\(^\circ\) or 180\(^\circ\) jumps around fixed axes through the nitrogen atom. This corresponds to a bonding geometry in which the ammonium ion interacts via three or two hydrogen atoms with the lattice oxygen atoms. Additionally, a reorientation around a fixed axis through two hydrogen atoms of the ammonium ion may occur. The ammonium ion then jumps between two equilibrium positions: one position involves a 2-fold bonding geometry and the other a 3-fold bonding geometry. At 300 K the effective time interval between two jumps is \(\tau = 1.2 \pm 0.5\) ps. Compared to zeolite Rho, the ammonium ions in the cesium-exchanged zeolite Y show a more restricted reorientational behavior, resulting in a larger elastic incoherent structure factor.

**Experimental Section**

The sample has been obtained by exchanging the ammonium form of zeolite Y (Linde LZ-Y62, Si/Al = 2.4, Na\(^+\)/NH\(_4\)\(^+\) = 0.2) four times at 353 K in 1 M solutions of NH\(_4\)NO\(_3\) and three times at room temperature in 0.3 M solutions of CsCl. According to elemental analyses on silicon, aluminum, sodium, and cesium and Kjeldahl analysis for the determination of the ammonium content, the composition of the sample was (NH\(_4\))\(_2\)Na\(_2\)Cs\(_{95}\)Y.

For the QENS measurement an anhydrous ammonium-containing sample was used. This sample was obtained by heating in an ampule 20 g of the hydrated zeolite at a rate of 0.2 \(^\circ\)C/min in vacuo up to 623 K in order to desorb water and ammonia. After 16-h evacuation at this temperature the zeolite was cooled to room temperature, and 0.01 mol of anhydrous ammonia (UCAR, 99.997% purity) was adsorbed. Then the sample was evacuated for 14 h at 353 K to desorb weakly bonded ammonia, and the ampule was sealed. Finally, in a glovebox filled with dry nitrogen, the sample was transferred to a flat aluminum sample chamber, shielded with cadmium, for the neutron measurements.

The neutron scattering experiments were performed on the rotating-crystal time-of-flight spectrometer at the Delft 2 MW reactor. A pulsed monochromatic neutron beam with a...
wavelength of $\lambda = 0.238$ nm ($E = 14.4$ meV) was produced by a rotating pyrolytic graphite crystal. Undesired reflections were suppressed by two Fermi choppers, rotating in phase with the crystal. Time-of-flight spectra were obtained simultaneously with 75 $^3$He detectors (20 cm long and 2.5 cm diameter) arranged at different angles from $3.95^\circ$ to $85^\circ$, covering a wavevector-transfer range of 1.8–36 nm$^{-1}$ at zero energy transfer. Experiments were carried out at 15 and 300 K for the zeolite sample and a vanadium sample. The latter measurement was used to determine the Bragg peak intensities of the sample (see below).

The procedures for data handling have been described in detail elsewhere (section 4.2 of ref 22). These procedures consist of the following steps:

**TINO:** A linear time-independent background was subtracted from the time-of-flight spectra for the sample, and vanadium measurements and the measured intensities were normalized with respect to the number of incident neutrons. The resolution was determined by the measurement of the sample at 15 K.

**DEFF:** The time-of-flight spectra are corrected for the detector efficiencies.

**INTPOL:** The double-differential cross section obtained at the experimental scattering angles is converted to the dynamic structure factor $S(k,\omega)$ at a constant angle and equidistant $\omega$ grid.

**TOP:** The relation between the time-of-flight scale and the wavelength scale is determined.

**DECO:** This step calculates the Fourier transform $F_i(k,t)$ of $S(k,\omega)$ and corrects for the instrumental resolution. A real (Re) and an imaginary (Im) part are obtained after the transformation. A nonzero Im $F_i(k,t)$ indicates asymmetries in $S(k,\omega)$ due to the neglect of imperfections such as multiple scattering, statistics, and the fact that $S(k,\omega)$ was taken at constant angle, rather than at constant $k$. We will use Re $F_i(k,t)$ only when Im $F_i(k,t)$ is small. In order to improve the statistics, the results for three to five neighboring detectors were summed after executing DECO.

**Results**

In Figure 2a the time-of-flight spectra at $44^\circ$ ($k = 19.6$ nm$^{-1}$) are given for the measurement of the sample at 300 and 15 K. The corresponding Fourier transform $F_i(k,t)$ of $S(k,\omega)$ is shown in Figure 2b. In Figure 3 the total number of neutrons counted for each detector is given for the sample and vanadium measurements. For a pure incoherent scattering sample the ratios of the intensities should be constant for each detector, apart from the effect of Debye–Waller factors. We see that strong Bragg reflections from the zeolite and the sample chamber are present. The first intense reflection corresponds to reflection of the (111) plane of the zeolitic lattice. The detectors at the positions of these strong Bragg reflections are not used for further analyses. Also, weak Bragg reflections are observed at various angles. For larger angles we see a decrease in intensity due to the increasing absorption in the sample.

We will use a simple model21 for fitting to the real part of the intermediate incoherent scattering function $F_i(k,t)$:

$$\text{Re } F_i(k,t) = C(k) [A(k) + (1 - A(k)) \exp(-t/\tau)] + B(k)$$

Here $A$ describes the contribution of the elastic scattering, $\tau$ is an effective relaxation time for rotational jump diffusion, and $C = \exp(-k^2u^2)$ is the Debye–Waller factor at 300 K of the zeolite with $u^2$ the mean-square translational amplitude of the hydrogen atoms and $k$ the wavevector transfer. In the preceding part, we already mentioned the presence of weak Bragg reflections of the zeolite, which contribute to the elastic scattering. This elastic contribution has to be measured and subtracted. One way to do this is to record the quasi-elastic spectra of the proton zeolite, before adsorption of ammonia. However, the structures of proton and ammonium zeolites differ, since protonation of the zeolite lattice results in structural deformations.22,24 Further, the locations of the acidic protons and the ammonium ions are different. The former are covalently bound to oxygen atoms of the lattice,5
Two examples of such a fit are shown in Figure 4. Experimental points are obtained after summation of the intensities of neighboring detectors. The curve is the result of the fit. (a) $\phi = 35^\circ$, $k = 15.8$ nm$^{-1}$ (detectors 28–31). Fit: $r = 1.3 \pm 0.2$ ps, $A = 0.67 \pm 0.02$, and $u^2 = 0.0058 \pm 0.0001$ nm$^2$. (b) $\phi = 75^\circ$, $k = 32.3$ nm$^{-1}$ (detectors 65–68). Fit: $r = 0.8 \pm 0.2$ ps, $A = 0.69 \pm 0.02$, and $u^2 = 0.0003 \pm 0.0001$ nm$^2$.

whereas the ammonium ions are located at the different cation positions (see Figure 1). As a result, the elastic contribution of the unloaded sample cannot be used to model the weak Bragg reflections of our sample. Using sodium ions, instead of the ammonium ions, eliminates the problem of lattice deformations caused by protonation of the lattice. Differences in the elastic contributions result now from the different coherent cross sections of the ammonium and sodium ions and from differences in the cation positions. Therefore, we use a different approach by introducing the term $B(k)$ to account for the small Bragg reflections of the zeolite (see also ref 25). This term is almost independent of the temperature in our case. The term $B(k)$ was determined by comparing the sample measurement at 15 K to the vanadium measurement at 15 K. The total scattering intensities for the sample $I_s(i)$ and for vanadium $I_v(i)$ are then given by

$$I(i) = I_s(i) + B(k) a_q(i)$$

$$I_s(i) = I_v(i) a_i(i)$$

where $i$ denotes the detector number, $k$, the wavevector transfer for detector $i$ at zero energy transfer, and $a_q(i)$ and $a_i(i)$ are the attenuation factors due to absorption of neutrons in the sample and the vanadium, respectively. The contribution of the weak Bragg reflections is then given by

$$B(k) = \frac{I_s(i) a_q(i)}{I_v(i) a_i(i)} - 1$$

The ratio $I_s/I_v$ was determined by comparing the coherent scattering cross section of the whole sample ($\sigma^{coh}$) to the incoherent scattering cross section of the hydrogen atoms in the sample ($\sigma^{inc}$), summed for all detectors ($n = 75$):

$$I_s = \frac{1}{n} \frac{\sigma^{inc}}{\sigma^{coh} + \sigma^{inc}} \sum I_v(i) a_i(i) = 1.08$$

Using this information, the obtained Re $F(k,t)$ have been fitted with respect to $A(k)$ and $r$ for the different groups of detectors. The region between 0.4 and 4.0 ps has been used for fitting, since for smaller times Re $F(k,t)$ contains contributions due to translational modes (10–25 meV, 80–200 cm$^{-1}$) of the ammonium ions. Two examples of such a fit are shown in Figure 4. From the results of all fits we obtain for the correlation time $r = 1.2$

$$A(k) = \frac{1}{4} [1 + 3j_0(kR_{HH})]$$

where $j_0(kR_{HH}) = \sin(kR_{HH})/(kR_{HH})$ is the zero-order spherical Bessel function and $R_{HH}$ is the proton–proton distance in the ammonium ion ($R_{HH} = 0.1689$ nm$^2$).

Model 2 describes 90° jumps at random around three $C_3$ axes:

$$A(k) = \frac{1}{8} [1 + 3j_0(kR_{HH}) + 3j_0(kR_{HH}\sqrt{\frac{1}{2}}) + j_0(kR_{HH}\sqrt{\frac{3}{2}})]$$

Model 3 describes 90° jumps around a fixed $C_2$ axis:

$$A(k) = \frac{1}{4} [1 + 2j_0(kR_{HH}\sqrt{\frac{1}{2}}) + j_0(kR_{HH})]$$

Model 4 describes reorientations of 120° around one fixed $C_3$ axis or of 180° around one fixed $C_2$ axis (see Figure 6):

$$A(k) = \frac{1}{2} [1 + j_0(kR_{HH})]$$

Model 5 describes jumps around a fixed axis through two
Ammonium Ions in CsNH4-Y Zeolite

Figure 6. Geometries of the ammonium ions bound to the oxygen atoms of the zeolite lattice. (a) Singly bound. Reorientation can occur around the 3-fold axis (model 4). (b) Doubly bound. Reorientation can occur around the 2-fold axis (model 4) or around the axis through the two hydrogen atoms near the oxygen atoms (model 5). (c) Triply bound. Reorientation can occur around the 3-fold axis (model 4) or around an axis through two hydrogen atoms near the oxygen atoms (model 5).

hydrogen atoms:

\[ A(k) = \frac{1}{4}[3 + j_0(kR_D)] \]  
\( (5) \)

In this model the nitrogen atom and two hydrogen atoms jump between two equilibrium positions, while the other two hydrogen atoms remain at fixed positions, bonded to the lattice oxygen atoms. Quantum chemical calculations have shown that the ammonium ions are preferentially bonded via two or three hydrogen atoms. Model 5 corresponds with jumps between a 2-fold bonding geometry (Figure 6b) and a 3-fold bonding geometry (Figure 6c). Assuming tetrahedral symmetry for the ammonium ion, we calculate for the jump distance \( R_D \) a value of 0.1344 nm.\(^\text{28} \) This distance corresponds to the movement of one nonbonded hydrogen atom of Figure 6b into the plane through the two bonding hydrogen atoms, which is perpendicular to the \( C_3 \) axis, resulting in the geometry of Figure 6c.

For isotropic rotational diffusion, model 6, the following relation is obtained:

\[ A(k) = j_0\left( kR_{HH} \sqrt{\frac{3}{8}} \right) \]  
\( (6) \)

In Figure 5 the results of these models are compared with the experimentally obtained values for \( A(k) \). From this figure we see that the experimental points are in between the curves for models 4 and 5. We conclude that reorientation of the ammonium ions, as measured by QENS, occurs around a fixed axis. However, we cannot discriminate whether this is a reorientation of 120° around a \( C_3 \) axis or a reorientation of 180° around a \( C_2 \) axis (model 4) or a reorientation around an axis through two protons (model 5). Probably these reorientational mechanisms are all operative. This may be indicative for differences in ordering of the silicon and aluminum of the zeolite framework at the cation sites.

Udovic and co-workers\(^\text{29,30} \) investigated the reorientation mechanism of ammonium ions in zeolite Rho. The locations of these ammonium ions depend on the pretreatment conditions used. In an anhydrous sample of ammonium-exchanged zeolite Rho, as used by Udovic, the ammonium ions are located on the faces of distorted 8-rings.\(^\text{31} \) However, when the sample is obtained after readsoption of ammonia onto the proton form of zeolite Rho, one ammonium position is found in the center of the double 8-ring and the other position is outside the double 8-ring in the truncated cuboctahedron.\(^\text{32} \) Udovic and co-workers concluded that model 4 gives the best description for the reorientation mechanism. However, they ignored that reorientation about a fixed \( C_2 \) axis by 180° is also described by model 4. For the reorientation relaxation time at 300 K they obtained a slightly higher value for zeolite Rho (\( \tau = 4 \) ps). This may be indicative of a slightly higher reorientation barrier for the ammonium ions in zeolite Rho, for which a value of approximately 35 meV was obtained.

The presence of the ammonium ions in the 8-rings of zeolite Rho may result in a stronger interaction with the zeolite lattice and a more restricted reorientational behavior as compared to the zeolite Y sample, where the ammonium ions occupy positions in the sodalite cages near the 6-rings.

The librational modes of ammonium ions in zeolite Y and Rho are observed with inelastic neutron scattering.\(^\text{17,20} \) For zeolite Rho these modes are observed at 10–14 meV (80–120 cm\(^{-1} \)). However, it must be noted that in this region part of the features may also be due to translational modes of the ammonium ions.\(^\text{31,35} \) For ammonium ions in the sodalite cages of zeolite Y the librational modes are located near 8 meV (65 cm\(^{-1} \)). This value is somewhat lower than found for zeolite Rho. This is in agreement with the shorter reorientation time found in this work. The librational modes for ammonium ions in the supercages are observed at 3–6 meV (24–50 cm\(^{-1} \)).\(^\text{17} \) So we expect for ions in these cages even a lower barrier for reorientation.

Apart from these slightly hindered librations, more strongly hindered librations are observed at 30–70 meV (240–565 cm\(^{-1} \)) for zeolite Y.\(^\text{17} \) The ammonium ions in the supercages give again rise to the lower values in this region. These librations correspond to reorientation mechanism with a higher-energy barrier. The corresponding reorientation time \( \tau \) is longer. However, the resolution of our measurements enables only to resolve the fastest process.

Using results from far-infrared spectroscopy, information about the positions of cations in the zeolitic lattice has been obtained.\(^\text{36–8} \) The sodalite cage ammonium ions are located at site I', where three protons of the ion can interact with three oxygen atoms of one of the six rings of the hexagonal prisms. For such a bonding geometry a reorientation model with reorientations of 120° around a fixed \( C_3 \) axis is most likely to occur. The interaction of the ammonium ions with the lattice here occurs via three bonds. This is different from the mechanism adopted by Udovic and co-workers, where the ammonium ions interact only with one bond with the lattice.\(^\text{29,30} \) However, quantum-chemical ab-initio cluster calculations showed that two or three bonds are needed to transfer the proton from the zeolite lattice to the ammonia molecule, forming an ammonium ion.\(^\text{39,40} \) The 2-fold bonding geometry may then be obtained from the 3-fold bonding geometry after rotating the ammonium ion around an axis through two hydrogen atoms.

Conclusions

A QENS study of cesium-exchanged zeolite Y with ammonium ions almost exclusively located at site I' shows that these ions reorientate either with 120° jumps around a fixed \( C_3 \) axis or with 180° jumps around a fixed \( C_2 \) axis or that these ions jump from a 2-fold bonding geometry to a 3-fold bonding geometry. Except for the model with 180° jumps around the fixed \( C_2 \) axis, one or two protons remain at their positions during the reorientation. When the geometry of site I' is taken into consideration, a mechanism with 120° jumps around a \( C_3 \) axis seems to be most likely. Additionally, tumbling of ammonium ions between two equilibrium positions may occur, leaving two hydrogen atoms at fixed positions. The equilibrium positions correspond with a 2-fold and a 3-fold bonding geometry of the ammonium ion. At 300 K the time interval in between two jumps is \( \tau = 1.2 \pm 0.5 \) ps. For ammonium ions in zeolite Rho a slightly longer time was observed, while for ammonium ions in supercages of zeolite Y a slightly shorter time is expected. These differences are due to differences in the reorientation barriers, caused by differences in bonding interactions of the ammonium ions with the lattice.
to zeolite Rho, the ammonium ions in the cesium-exchanged zeolite Y studied are more rigidly bound to the lattice. This results in a larger EISF, since on an average the hydrogen atoms in the ammonium ions are less mobile. Apart from the reorientational motions observed here, other reorientations are present which could not be resolved. These reorientations have a much higher barrier for reorientation, and the corresponding residence time between two jumps is longer. For a more detailed analysis, including studies of the energy barriers for reorientation, temperature-dependent experiments on spectrometers with a range of resolutions (i.e., observation times) are necessary.

Acknowledgment. We thank Dr. A. A. van Well for the helpful discussions and advice during this work, and further we are grateful to Mr. J. H. M. C. van Wolput for assistance with the infrared measurements.

References and Notes

(28) Handbook of Chemistry and Physics, 62nd ed.; Weast, Ed.; The Chemical Rubber Co.: Cleveland, OH, 1981–82. Assuming tetrahedral symmetry of the ammonium ion, the proton–proton distance $R_{HH}$ is calculated from the proton–nitrogen distance $R_{HN} = 0.1034$ nm.