

# Magnetic Proton Relaxation of Ammonia Adsorbed on Na-X Zeolite

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(Received January 16, 1989; accepted June 15, 1989)

## *Pulsed NMR / Na-X zeolite / Ammonia / Adsorption*

The microdynamical motion of the ammonia molecule adsorbed on Na-X zeolite ( $\theta = 0.2$ ) was studied by pulsed NMR between 225 K and 430 K. Measuring the longitudinal and transversal relaxation times and the second moment with the solid echo method, the dynamic behaviour of the ammonia molecule could be determined: A rigid lattice like state of the  $\text{NH}_3$  molecule in the sodalitic unit was found, and a nearly free reorientational motion for the ammonia placed in the supercage.

Die mikrodynamische Bewegung des an Na-X-Zeolithen adsorbierten Ammoniakmoleküls wurde zwischen 225 K und 430 K mit gepulster NMR untersucht. Durch Messung der longitudinalen und transversalen Relaxationszeiten und des zweiten Moments mit der Festkörper-Echomethode konnte das dynamische Verhalten des Ammoniaks bestimmt werden: In der Sodalitheinheit wurde ein Gitter-ähnlich starres Ammoniakmolekül gefunden und im großen Käfig ein Ammoniakmolekül mit fast freier Rotationsbewegung.

## Introduction

Faujasitic zeolites are crystalline aluminosilicates of high porosity, and of manifold applications in the industry. The basic geometrical element of the zeolitic lattice is a tetrahedron with oxygens in the vertex and silicon or aluminium in the center of the tetrahedron [1]. 24 tetrahedrons form the sodalitic unit with a diameter of 6.6 Å, and then sodalitic units construct the supercage with a diameter of 11.6 Å approximately. To compensate the charge defect of the aluminium, sodium ions are included normally in the commercial products. The sodium ions, oxygens of the zeolitic crystalline surface and OH groups are able to interact with adsorbed molecules and to cause catalytic effects.

In the supercage, the ammonia is adsorbed predominantly on cations placed in sites II [2] by means of an hybridized N- $\text{Na}^+$  bond [3, 4]. For coverages less than 70% no intermolecular interaction could be detected

and furthermore neither coupling to OH groups. By means of wide band techniques, the  $\text{NH}_3$  absorption band width was measured as a function of the sample temperature for several zeolites [5]. For Na-Y zeolite and a coverage of 0.5  $\text{NH}_3$  molecules per supercage, the band width was between 100 mG and 150 mG at room temperature. The ammonia in the sodalitic unit could not be measured because too low a signal to noise ratio. The diffusion of the  $\text{NH}_3$  molecule into the small cage is very slow and dependent of temperature, so it needs, for instance, 1 h at 463 K to obtain an equilibrium concentration among the small cages for an initial concentration of 0.5 molecules per supercage.

Although some relaxation time data at room temperature were reported [6], systematic studies of the microdynamical motion of the ammonia adsorbed in the supercage and in the sodalitic unit of faujasitic zeolites by pulsed NMR were not published before recently [7]. The present work continues the preliminary measurements of the  $\text{NH}_3$  adsorption on Na-X zeolite; in this case, however, a sample of very high purity was measured.

## Experimental setup

The used Na-X zeolite consists of a highly crystalline sample with a Si/Al ratio of 1.23, and it was supplied by the Physics Department of the University of Torun, Poland. To burn out its carbon compounds, the zeolite powder was heated at 673 K under air flow for 3 h. A subsequent washing of the zeolite powder with heavy water avoided unwanted proton signals. After evacuating to  $10^{-4}$  mbar at 533 K [8], 0.487 g of zeolite were charged with 0.01 g of purified and degassed ammonia. The sample was sealed off in a small glass tube and heated afterwards for 4 h at 468 K. An EPR analysis showed only a paramagnetic impurity concentration of the order of 1 ppm.

The used NMR equipment was a homemade pulsed NMR spectrometer of 89.5 MHz with an electromagnet bestowed by the Volkswagenwerkstiftung in FRG. The longitudinal and transversal relaxation times were measured by means of the pulse sequences  $\pi$ - $\tau$ - $\pi/2$ ,  $15\pi/2$ - $\tau$ - $\pi/2$  and  $\pi/2$ - $\tau$ - $\pi$ , respectively. The second moment was determined by the  $\pi/2$ - $\tau$ - $\pi/2$  pulse sequences. All experimental relaxation data could be well fitted by one exponential function, making use of a program for minimization of the quadratic deviation.

## Results

In Fig. 1, the measured relaxation times  $T_1$  and  $T_2$  are shown as a function of the reciprocal temperature. The error of measurement is of the order of 10%. The positive slope of the  $T_1$  curve is equal to the negative slope of the  $T_2$  behaviour in the upper temperature range between 450 K and 250 K. The observed free induction decay (FID) was composed of a long exponential decay superimposed to a fast solid state like decay. If a gaussian function for the last one was assumed, their amplitude ratio was of the value of 1 within the range of error of the measurement. At 360 K the second moment evaluated by the solid echo program was  $1.43 \cdot 10^{-2} G^2$ .

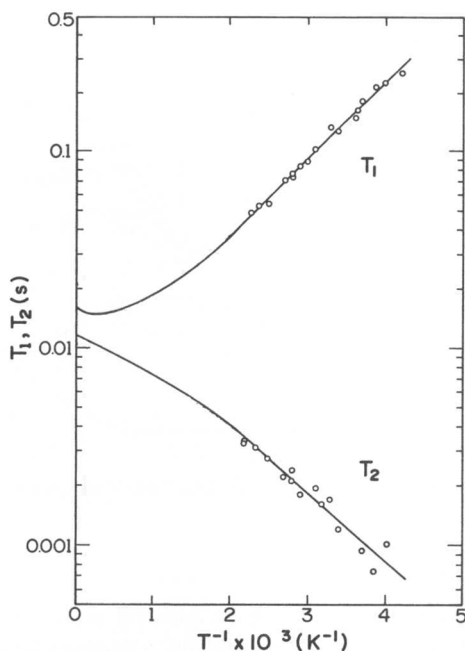


Fig. 1. The measured  $T_1$  and  $T_2$  relaxation times ( $\circ$ ).

## Discussion

An ammonia adsorption at room temperature allows to charge the supercages only of the Na-X zeolite [5]. However, during the thermal treatment at 468 K, the  $\text{NH}_3$  molecules diffuse also into the sodalitic unit producing finally a homogeneous  $\text{NH}_3$  distribution. From the amplitude relation of the two components of the FID, it can be estimated that always two supercages or sodalitic units are charged with one ammonia molecule. For this reason, two different relaxation systems should be expected.

The first hint of the two relaxation systems was obtained by comparing the second moments evaluated by the different NMR methods applied. The here determined value of  $(1.43 \pm 0.11) 10^{-2} G^2$ , obtained by the solid echo method in NaX, is of the same order of magnitude as the one calculated from the published band widths of ammonia adsorbed on Na-Y zeolite [2]. This calculation yields values of the second moments between  $(0.4 \text{ and } 0.9) 10^{-2} G^2$  at room temperature, if we assume a Lorentzian line shape for the absorption curve, in good agreement with the observed exponential FID. Because the sample was heated up to only 413 K for this wide band NMR study, the measured signal has to be attributed predominantly to ammonia in the supercage, adsorbed on sites II. As it can be proved easily that a

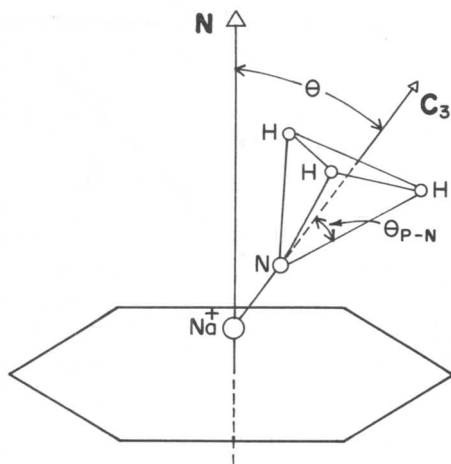


Fig. 2. Schematic representation of the dynamics of the ammonia molecule adsorbed in the supercage.

tumbling of the rotating  $C_3$  symmetry axis [9] is not able to reduce the second moment to the observed magnitude, a microdynamical motion has to be proposed which produces a nearly free reorientation of the molecule, almost like in the gaseous state. For this reason we suggest the following combined motion: an almost free rotation around the  $C_3$  symmetry axis of the  $\text{NH}_3$  molecule, which can be perturbed by a three-well or a six-well potential, together with a random diffusional reorientation of the ammonia molecule, coupled both by the nitrogen atom to the  $\text{Na}^+$  ion, and by the protons to the oxygens around the hexagonal ring in the site II in the supercage. In this case the second moment can be calculated by means of the simple expression:

$$\langle \Delta H^2 \rangle = \gamma_P^2 \hbar^2 \left[ \frac{9}{160 R_{P-P}^6} + \frac{5.2345 \times 10^{-3} [3 \cos^2(\theta_{P-N}) - 1]^2}{30 R_{P-N}^6} \right] [3 \cos^2(\theta) - 1]^2 \quad (1)$$

where  $R_{P-P}$  and  $R_{P-N}$  represent the proton-proton and proton-nitrogen distances, respectively, and  $\theta_{P-N}$  is the angle between the  $C_3$  symmetry axis of the ammonia molecule and the vector connecting the nitrogen and proton.  $\theta$  is the angle between the  $C_3$  symmetry axis and the normal line to the hexagonal ring of the adsorption site, as can be seen in Fig. 2. Equation (1) was obtained under the assumptions: i) that the nearly free reorientation around the  $C_3$  symmetry axis is independent of the motion around the axis perpendicular to the adsorption site plane, and ii) that

these two motions are performed in time scales shorter than the Larmor period. Thus, only the dynamical average of the dipole-dipole interaction has to be considered. Finally a powder average is performed. The numerical factor in (1) comes from the relation between the nitrogen gyromagnetic ratio compared to the proton gyromagnetic ratio. From this equation it can be seen that the second moment depends strongly on the value of the angle  $\theta$ . A concordance between the experimentally determined second moments and the results of expression (1) can be obtained by choosing a mean value of  $\theta = 54.766 \pm 0.003$  for the second moment computed from  $T_2$  data, and of  $\theta = 54.770 \pm 0.002$  for the second moment measured by means of the solid echo sequence. These  $\theta$  values are in close correspondence with the magic angle value of  $54.735^\circ$ . The geometrical parameters used for the calculation were:

$$\begin{aligned} R_{P-P} &= 1.628 \cdot 10^{-8} \text{ cm} \\ R_{P-N} &= 1.014 \cdot 10^{-8} \text{ cm} \\ \theta_{P-N} &= 67.96^\circ. \end{aligned} \quad (2)$$

The agreement of the second moments evaluated by the wide band and the solid echo method allows us to estimate the minimum value of the  $T_1$  relaxation curve, using the BPP theory [10]:

$$T_{1 \text{ min}} = \frac{1.05 \omega_0}{\gamma^2 \langle \Delta H^2 \rangle} \simeq 60 \text{ s}. \quad (3)$$

According to our hypothesis, concerning two different adsorption systems in the studied sample, and taking into account the distribution of the ammonia in the zeolitic structure, the  $T_2$  values in the measured temperature range have to be assigned to ammonia molecules in the sodalitic unit. Supposing again a BPP like behaviour of the relaxation mechanism, the experimental data allow us to calculate an activation energy of 0.078 eV, and by means of the  $T_1/T_2$  quotient, the correlation time as a function of temperature, whose extrapolation to infinite temperatures yields  $\tau_\infty = 9.14 \cdot 10^{-10}$  s. A fit of the theoretically expected  $T_1$  relaxation curve to the measured points permits to extrapolate to higher temperatures and to estimate a value of the  $T_1$  minimum of 16 ms at about 5000 K, see Fig. 1. Applying again Eq. (3) to calculate the second moment, we found  $\langle \Delta H^2 \rangle \simeq 50G^2$ . This value is unquestionably a rough estimation: firstly there is no evidence for the strict validity of the used formula (BPP theory), and furthermore, the extrapolation to higher temperatures increases the uncertainty appreciably. Finally, the very low but still present paramagnetic impurities can swell slightly the second moment.

The value  $\langle \Delta H^2 \rangle \approx 50G^2$  can therefore be taken only as an order of magnitude, and its interpretation can be only tentative and preliminary at present. For such a provisional interpretation we refer to a list of values of second moments of ammonia, calculated for the more suitable relaxation

**Table 1.** The second moments of the most suitable relaxation mechanisms.

Relaxation mechanism	Second moment ( $G^2$ )
Rigid $\text{NH}_3$ molecule [11] <sup>a</sup>	40.54
Anisotropic rotation around the $C_3$ symmetry axis (small jumps) [9, 11]*	9.80
Tumbling of the $C_3$ symmetry axis [9]	29.40
Anisotropic rotation of the $C_3$ symmetry axis (large jumps) [12]	28.90
Experimental value	≈ 50

<sup>a</sup> Magnetic N–H interaction included.

mechanisms, see Table 1. Here the rigid  $\text{NH}_3$  molecule has the highest value of  $40.54 G^2$ , where the magnetic proton-proton and the nitrogen-proton interactions are included. All other second moments are smaller because of the averaging due to microdynamical motions. It seems to be obvious, therefore, to attribute the high value found to rigid  $\text{NH}_3$  molecules, fixed in sodalitic units of the zeolite. The difference of  $10 G^2$  is within the range of uncertainties of the experimental value, and will therefore not be discussed further. There can be made also no suggestion of the spatial arrangement of the  $\text{NH}_3$  molecule in the sodalitic unit; this must be left to further, more detailed investigations.

### Acknowledgement

This work was supported by the Consejo de Desarrollo Científico y Humanístico of the Universidad Central de Venezuela, and the Volkswagenwerk-stiftung of the Federal Republic of Germany.

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