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The Crystal Structure of Deuteroammonia between 2 and 180 K by Neutron Powder Profile Refinement

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Abstract

The structure of ND₃ has been refined by neutron powder profile analysis at 2, 77 and 180 K to a resolution of $\sin \theta/\lambda = 0.85 \text{ \AA}^{-1}$. No orientational phase transition was found in this range. However, even at 2 K, a strong librational motion exists. The N–D bond length, after correction for libration, is constant with temperature (1.06 Å), as are the D–N–D angles ($107.5 \pm 0.2^\circ$). This bond length is 5% longer than that found in the free molecule, because of hydrogen bonding, but the bond angles are virtually identical.

Introduction

Solid ammonia has one of the simplest molecular structures. The molecules are bound together by rather weak hydrogen bonds involving the lone pair of electrons, which with the three H atoms make up an almost regular rigid tetrahedron around the N atom (Olovsson & Templeton, 1959; Reed & Harris, 1961).

NH₃ in its solid state is an ideal material for the study of the dynamics of simple molecular crystals. Righini & Klein (1978) have set up a lattice-dynamical model, which has been used by Dolling, Powell & Pawley (1978) to explain their inelastic neutron scattering results. Such model calculations require a precise knowledge of the structure, and this was one justification for the present study.

The structure of NH₃ and ND₃

Olovsson & Templeton (1959) studied single crystals of NH₃ and ND₃ by photographic X-ray techniques at 77 and 113 K. A neutron powder diffraction study of ND₃ was made by Reed & Harris (1961) at 77 K. Both

studies were limited by rather low resolution, *i.e.* $\sin \theta/\lambda = 0.58 \text{ \AA}^{-1}$ (Olovsson & Templeton) and 0.46 \AA^{-1} (Reed & Harris). However, both agreed on the space group *P2₁3* (*T⁴*) in which the atoms are placed as follows: 4 N at *u,u,u* with *u* $\simeq 0.21$; 12 H at *x,y,z* with *x* $\simeq 0.37$, *y* $\simeq 0.26$, *z* $\simeq 0.11$. The refined coordinates (Table 1) agree within the rather large experimental errors.

Experiment

The experiment was performed in two parts, both on the D1A high-resolution powder diffractometer (Hewat & Bailey, 1976) using a He gas flow cryostat. For the first part, data were collected at 77 K with a wavelength of 1.5 Å up to $\sin \theta/\lambda = 0.66 \text{ \AA}^{-1}$. Later, more precise results were collected at 2 and 180 K with a wavelength of 1.17 Å to extend the resolution to $\sin \theta/\lambda = 0.85 \text{ \AA}^{-1}$.

ND₃ (Saclay, 99% deuterated) was purified over Na and distilled. Some difficulties were experienced in preparing the powder sample. In the first attempt, ND₃ was sublimed from a solid-CO₂-cooled reservoir into a liquid-N₂-cooled vacuum-tight vanadium can. However, even at 77 K the intensities of some lines in the neutron diffraction pattern changed within a few hours, indicating the growth of crystallites in the sample. A similar effect was found when liquid ND₃ was snap frozen to 77 K. Finally, liquid ND₃ was frozen into a mortar immersed in a bath of liquid N₂ in a dry glove bag. It was then relatively easy to crush the solid ND₃ into a fine powder and to fill the vanadium can which was also cooled to liquid N₂ temperature. The can with about 6 g of ND₃ was transferred to the cryostat while still cold, and the temperature raised briefly to boil off any remaining N₂. Careful checks for preferred orientation during the experiments revealed

Table 1. Parameters for solid ND₃ at 2, 77 and 180 K together with those found by Reed & Harris (1961) at 77 K, and Olovsson & Templeton (1959)

The thermal ellipsoids B_{ij} defined by the temperature factor $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + kl\beta_{23})]$, where $\beta_{ij} = \frac{1}{2}a_i^*a_j^*B_{ij}$, are oriented with axes perpendicular to and along the (N-D) bonds (Fig. 2), and indicate strong libration even at 2 K. After correction for this libration, the N-D bond length increases by up to 0.069 Å, becoming (N-D)_o. Refinements of the occupation number n_D for D shows that, with the assumed scattering lengths $b_N = 0.940$ and $b_D = 0.667$, the sample was completely deuterated. The R percentage factors for integrated reflexions R_I and profile intensities R_p have their usual meanings and show that good agreement was obtained with the data, especially at 2 K. The R_p factor expected for purely statistical errors is R_E .

	2 K	77 K	180 K	Reed & Harris (77 K)	Olovsson & Templeton (113 K)
λ (Å)	1.1655	1.4951	1.1655		
a_o (Å)	5.048	5.073*	5.125		
x_N	0.2109 (3)	0.2108 (11)	0.2107 (7)	0.2127 (21)	0.2099 (5)
x_D	0.3750 (3)	0.3694 (13)	0.3689 (6)	0.3740 (19)	0.40
y_D	0.2712 (4)	0.2694 (10)	0.2671 (6)	0.2632 (37)	0.26
z_D	0.1129 (3)	0.1141 (11)	0.1159 (7)	0.1094 (16)	0.11
N-D (Å)	1.012 (2)	0.988 (9)	0.989 (5)	1.005 (23)	1.12
(N-D) _o (Å)	1.061 (5)	1.039 (20)	1.058 (8)		
\angle D-N-D (°)	107.5 (2)	108.0 (7)	107.8 (4)	110.4 (2.0)	107
D...N (Å)	2.357 (2)	2.393 (9)	2.425 (5)	2.374 (28)	
N-N (Å)	3.325 (2)	3.342 (8)	3.375 (5)	3.352 (11)	
\angle ND...N (°)	160.0 (2)	160.7 (6)	160.3 (4)		

* This lattice dimension (Olovsson & Templeton) was used to determine the neutron wavelength.

Table 1 (cont.)

	2 K	77 K	180 K
B_{ii} (N) (Å ²)	0.80 (3)	2.29 (18)	3.03 (6)
B_{ij} (N) (Å ²)	-0.04 (3)	-0.12 (12)	-0.11 (4)
B_{11} (D) (Å ²)	1.76 (7)	3.69 (29)	4.54 (13)
B_{22} (D) (Å ²)	2.13 (9)	3.22 (30)	5.60 (16)
B_{33} (D) (Å ²)	2.14 (7)	4.36 (24)	5.34 (17)
B_{12} (D) (Å ²)	-0.28 (5)	-0.76 (17)	-1.47 (9)
B_{13} (D) (Å ²)	0.56 (6)	0.72 (27)	0.74 (11)
B_{23} (D) (Å ²)	0.18 (6)	-0.22 (19)	-0.23 (11)
u (N) (Å)	0.096	0.161	0.189
	0.103	0.175	0.199
	0.103	0.175	0.199
u (D) (Å)	0.125	0.182	0.207
	0.169	0.214	0.257
	0.179	0.252	0.295
n_D	1.013 (13)	1.007 (55)	1.003 (22)
R_I (%)	2.24	3.28	6.17
R_p/R_E	9.56/3.41	13.16/4.71	17.53/12.42

Refinement and results

The profile-refinement program (Rietveld, 1967), modified for anisotropic vibrations (Hewat, 1973), was used for all three scans. No correction for preferred orientation or absorption was deemed necessary. Each point in the diffraction pattern was weighted according to the number of counters contributing and the average count. For such a simple structure on a high-resolution machine, it was easy to measure precisely the background between the peaks, even at the highest scattering angles: this was important for the refinement of the Debye-Waller factors.

As expected, the best fit to the observed profile was obtained at the lowest temperature (Fig. 1); at higher temperatures, the large ND₃ librations are not so well described by the usual second-order tensor of B_{ij} . The fit at 2 K is really very good, corresponding to a value

none, and this was confirmed on refinement to low R values without preferred-orientation corrections.

The data were collected by sweeping the bank of six counters from 6 to 160° in steps of 0.05° (2θ), taking about 22 h for the entire experiment. The results were corrected for small differences in the relative efficiencies, and the different counters added together to give a single pattern covering the entire angular range of measurements. Some weeks later, the experiment was repeated at 2 and 180 K with a new sample and the shorter wavelength. By this time all ten counters were operational, and the extra efficiency compensated for the lower intensity with the shorter wavelength.

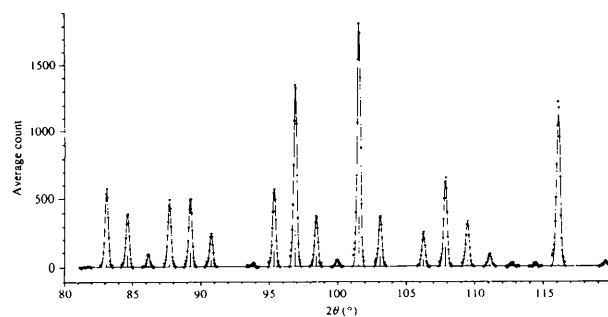


Fig. 1. The observed and calculated diffraction profiles for solid deuterioammonia at 2 K. The full pattern extends from 0 to 160°.

of about 1.1% for the R factor for structure factors usually quoted by crystallographers. The calculated errors for the parameters are also smallest at 2 K and largest at 77 K, where the data do not extend so far in $\sin \theta/\lambda$. No constraints were applied to any of the parameters, so that, for example, six independent B_{ij} factors were refined for the D atom. Nevertheless, the calculated thermal ellipsoids are physically reasonable, with their axes aligned almost along and perpendicular to the N–D bond.

The librational motion of the molecule is evident in Fig. 2. The magnitude of this libration is large even at 2 K, but none of the vibrational amplitudes increases as quickly with temperature as would be required for purely harmonic oscillators. We note that the barrier to C_3 rotation has been estimated to be as low as 7.32 kJ mol^{-1} (Rabideau & Waldstein, 1966) which would allow relatively rapid ($\sim 10^6 \text{ Hz}$) quantum-mechanical tunneling of the protons even at 2 K (Stejskal & Gutowsky, 1958). This might explain the observed deviation from a purely harmonic oscillator. Note also that the N–D...N bond is a little longer than that expected for a static hydrogen bond between N atoms.

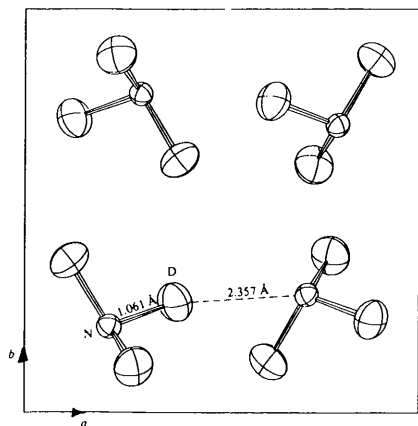


Fig. 2. ORTEP plots (Johnson, 1965) of the thermal ellipsoids of ND_3 , showing strong well defined librations, even at 2 K. These relatively large ellipsoids, and the fact that the amplitudes increase less quickly with temperature than expected for a simple harmonic oscillator, may indicate quantum-mechanical tunneling of the protons.

A correction to the N–D bond length is necessary owing to the strong librational motion (Bacon, 1963). Table 1 shows the r.m.s. amplitudes of displacement in the directions of the axes of the ellipsoids; for the deuterons, the axes of strongest vibration are approximately perpendicular to the N–D bond, so that after subtraction of the translational vibration of the complete molecule, these displacements give the librational amplitudes needed for the bond-length correction. Since these corrections are relatively large (between 0.05 and 0.07 Å) the N–D bond is lengthened by about 5% in the solid from the value of 1.012 Å found for ND_3 gas (Herzberg, 1966). This is a consequence of hydrogen bonding in the solid.

The uncorrected bond length is in good agreement with that found by Reed & Harris, but our D–N–D bond angle of $107.5 \pm 0.2^\circ$ is much closer to that found for the gas than is their less precise value of $110.4 \pm 2.0^\circ$.

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