

## The Inelastic Neutron Scattering Spectrum of Rotational Tunnelling in Phase III of $\text{NH}_4\text{PF}_6$

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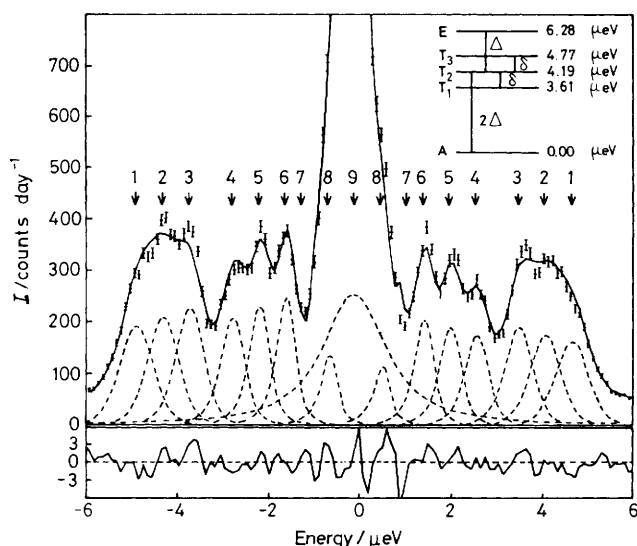
The first example of tunnelling of an ammonium ion under  $C_2$  rotational symmetry is described, i.r. spectroscopy having previously suggested higher symmetries; the inelastic neutron scattering (i.n.s.) spectrum shows extra intensity in the near-elastic region as well as unexpected peak broadening and two interpretations of the observed i.n.s. spectrum are discussed.

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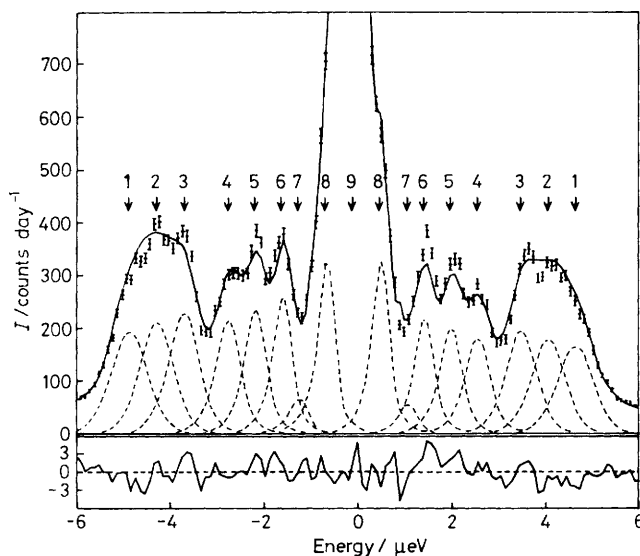
High-resolution inelastic neutron scattering (i.n.s.) spectroscopy provides a useful means of studying rotational tunnelling in molecular species.<sup>1</sup> Hüller and Press<sup>2</sup> have presented a

generalised method by which the tunnelling spectra of suitable tetrahedral species can be used to deduce rotational symmetry-elements when this species occupies a crystallographic site of reduced symmetry.<sup>3</sup> In practice however, environments of low symmetry frequently arise from an optimisation of hydrogen-bond interactions within the crystal, and although these interactions may be relatively slight,

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**Figure 1.** The tunnelling spectrum of  $\text{NH}_4\text{PF}_6$  (4 K). The solid line represents best fit to data using parameters  $\delta$  and  $\Delta$  (defined in inset), and intensities for  $T \leftrightarrow T$ ,  $T \leftrightarrow E$ , and  $A \leftrightarrow T$  in the ratio 1 : 4 : 5 respectively. A quasielastic component of Lorentzian peak-shape has been included. Natural peak-widths were constrained to be a linear function of the energy transfer. The components of the calculated spectrum are illustrated by the broken curves and weighted residual-differences ( $\Delta I/I$ ) between the observed and calculated spectra are shown below these. Assignments denoted by the numbers 1 to 9 are: A  $\leftrightarrow$  T<sub>3</sub>, A  $\leftrightarrow$  T<sub>2</sub>, A  $\leftrightarrow$  T<sub>1</sub>, T<sub>1</sub>  $\leftrightarrow$  E, T<sub>2</sub>  $\leftrightarrow$  E, T<sub>3</sub>  $\leftrightarrow$  E, T<sub>1</sub>  $\leftrightarrow$  T<sub>3</sub>, T<sub>1</sub>  $\leftrightarrow$  T<sub>2</sub> + T<sub>2</sub>  $\leftrightarrow$  T<sub>3</sub>, quasielastic, respectively.



**Figure 2.** The best fit obtained with intensities constrained in the ratio 4 : 5 : 1 for  $T \leftrightarrow E$ ,  $A \leftrightarrow T$ , and  $T_1 \leftrightarrow T_3$  transitions respectively, but with the  $T_1 \leftrightarrow T_2$  and  $T_2 \leftrightarrow T_3$  unconstrained. Definitions are the same as for Figure 1.

tunnel-splittings are often too small to be accessible to the neutron technique, and only classical reorientations are observed at higher temperatures. Even when the tunnelling spectra of such salts fall within the i.n.s. window, the spectra are difficult to collect since the small splittings require very high resolution if they are to be detected, and the inelastic intensity is shared between many spectral features.

**Table 1.** Peak positions and intensities derived from the i.n.s. spectrum of  $\text{NH}_4\text{PF}_6$  for model 1 (with quasielastic scattering) and model 2 (with unconstrained  $T_1 \leftrightarrow T_2 + T_2 \leftrightarrow T_3$  intensities).<sup>a</sup>

Energy transfer/ $\mu\text{eV}$	Relative intensity		FWHM <sup>b</sup> / $\mu\text{eV}$	Assignment
	Model 1	Model 2		
0.00	52.59	54.35	1.41	Elastic peak
0.00	17.32	0.00*		Quasielastic
0.58	2.00*	4.83	0.138 $\times$ E	T <sub>1</sub> $\leftrightarrow$ T <sub>2</sub> + T <sub>2</sub> $\leftrightarrow$ T <sub>3</sub>
1.16	0.00*	1.00*		T <sub>1</sub> $\leftrightarrow$ T <sub>3</sub>
1.51	4.00*			E $\leftrightarrow$ T <sub>3</sub>
2.09	4.00*			E $\leftrightarrow$ T <sub>2</sub>
2.67	4.00*			E $\leftrightarrow$ T <sub>1</sub>
3.61	5.00*			T <sub>1</sub> $\leftrightarrow$ A
4.19	5.00*			T <sub>2</sub> $\leftrightarrow$ A
4.77	5.00*			T <sub>3</sub> $\leftrightarrow$ A

<sup>a</sup> The intensities marked with an asterisk were constrained to these relative values, and the E in the FWHM<sup>b</sup> column denotes energy transfer. These data required 3 days continuous collection using the IN10 spectrometer with polished Si<111> monochromator giving an incident energy of 2.08 meV. Si<111> analysers were placed at 107° and 154° giving an average momentum transfer of 1.78 Å<sup>-1</sup> and a measured resolution of 0.47  $\mu\text{eV}$ . <sup>b</sup> Full width at half maximum.

In the present communication we examine the tunnelling spectrum of  $\text{NH}_4\text{PF}_6$  in its lowest-temperature phase (below 130 K), i.r. spectroscopy having suggested that the ammonium ion occupies a site of  $C_3$  symmetry,<sup>4</sup> whilst isotopic dilution techniques give evidence of  $O_h$ .<sup>5</sup> Figures 1 and 2 illustrate the tunnelling spectrum obtained with a sample temperature of 4 K using the IN10 backscattering spectrometer at the Institut Laue-Langevin, Grenoble, France.

Inspection of Figures 1 and 2 reveals the presence of six features on either side of the central elastic peak, with considerable broadening at the base of the elastic peak. The six features fall into two triplets centred at energy-transfers of ca. 2.1 and 4.2  $\mu\text{eV}$ . On the basis of these energies, the two triplets are assigned to transitions between the T and E states and transitions between the A and T states,<sup>2</sup> respectively. The three peaks in each triplet are symmetrically split, with a constant separation of ca. 0.6  $\mu\text{eV}$  arising from the relaxation of the degeneracy of the three T states.

The arrangement of energy levels deduced from these peak positions is illustrated in the inset of Figure 1. The constraint for peak positions implied by  $\Delta$  (defined on the energy-level diagram) holds for all rotational symmetries but the equal separation of the T levels inferred by  $\delta$  dictates  $C_2$  or  $C_1$  symmetry. According to reference 2, the peak intensities should be in the ratio of 1 unit for each  $T \leftrightarrow T$  transition, 4 units for each  $T \leftrightarrow E$  transition, and 5 units for each  $A \leftrightarrow T$  transition. The observed symmetric peak-splittings strongly suggest  $C_2$  rotational symmetry, but a confirmation of this demands that the transitions between the highest and lowest T states ( $T_1 \leftrightarrow T_3$ ) are not observed.

Attempts to fit the spectrum within these intensity constraints, and with peak widths from instrumental effects only, resulted in very poor agreement between observed and calculated spectra. Two problems were evident. Firstly, the calculated  $T \leftrightarrow T$  transitions were much weaker than the observed intensity in the wings of the elastic peak, and secondly, the peaks within a triplet were not well represented by three peaks of equal intensity and 'zero' natural width.

Although inspection of Figure 1 might seem to suggest that peak intensities vary in a systematic way, it transpired that the equal-intensity constraint (within each triplet) could be

retained, by allowing each peak to have a Gaussian peak-shape of refinable width, convoluted with the instrumental resolution function. Finite peak-widths at low temperatures have previously been attributed to unresolved structure,<sup>3a</sup> differing spin symmetry-species of neighbouring molecules,<sup>6</sup> inhomogeneity within the crystallites,<sup>7</sup> or left unexplained.<sup>8</sup> In the present example it was found that the peak widths increase almost linearly with energy transfer indicating inhomogeneous broadening from stress and imperfections in the crystallites, presumably arising from cooling through the phase transitions.

By using the predicted relative intensities and a single refinable width-parameter it was found that the peaks arising from  $T \leftrightarrow E$  and  $A \leftrightarrow T$  transitions could be fitted rather well by the calculated spectrum. However, there continued to be significant errors in the calculated spectrum within the  $-1.5$  to  $1.5 \mu\text{eV}$  region, and various attempts were made to improve agreement in this near-elastic region. Two equally good descriptions were found.

Firstly, our preferred model considers the intensity at the base of the elastic peak to be composed of the  $T_1 \leftrightarrow T_2 + T_2 \leftrightarrow T_3$  transitions with the predicted relative intensity of  $1 + 1$  units, and a quasielastic component of refinable intensity and width. Results from a refinement using this model are collected in Table 1 with the observed and calculated spectra being illustrated in Figure 1. The peak intensities and positions deduced from this model are in complete agreement with the predictions of reference 2.

The second model considers the rotational symmetry of the ammonium to be lower than  $C_2$ , and thus allows the observation of the  $T_1 \leftrightarrow T_3$  transition. The presence of a symmetric splitting of the T levels implies  $C_2$  symmetry, but within the limits of our resolution a small distortion towards  $C_1$  symmetry would not be distinguished in the observed splittings. The presence of  $T_1 \leftrightarrow T_3$  transitions, however, definitely implies  $C_1$  symmetry. With this model however, a satisfactory fit could only be obtained by allowing the intensities of the  $T_1 \leftrightarrow T_2 + T_2 \leftrightarrow T_3$  transitions to refine unconstrained. The resulting fit is illustrated in Figure 2, and it is clear that in this model the calculated intensities of the  $T_1 \leftrightarrow T_2 + T_2 \leftrightarrow T_3$  are similar to those of  $T \leftrightarrow E$  transitions, that is about twice the value predicted by reference 2 (Table 1).

Although the second model is less attractive, it cannot be excluded, and even though we have recently determined the crystal structure of  $\text{ND}_4\text{PF}_6$  at 4 K by powder neutron diffraction,<sup>9</sup> which demonstrates that the ammonium ion occupies a site with twofold symmetry, it could be argued that differences might exist between the protiated and deuteriated analogues at 4 K.<sup>10</sup> Further, tunnelling spectroscopy is more sensitive to actual site symmetries than our diffraction measurements, which indicate only the average site symmetry.

On balance, in our opinion, the first model involving  $C_2$  symmetry for the ammonium ion with some quasielastic scattering arising from classical rotational motion is more reasonable. The alternative model not only requires a symmetry lower than that found from the diffraction data, but it is also difficult to reconcile the intensity of the  $T_1 \leftrightarrow T_2 + T_2 \leftrightarrow T_3$  transitions with existing theory.<sup>2</sup> A study of the quasielastic scattering from  $\text{NH}_4\text{PF}_6$  at temperatures between the limit of tunnelling and the  $\text{III} \rightarrow \text{II}$  phase transition, is planned. A confirmation of the width of the quasielastic component at 4 K would then be straightforward.

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