NMR INVESTIGATION OF REORIENTATION OF NH_4 GROUPS IN AMMONIUM PERCHLORATE AT HELIUM TEMPERATURES

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Measurements of broad proton resonance lines in polycrystalline NH_4ClO_4 have been made at temperatures of 4.2°K and 1.2°K. Second moments of 8.9 gauss² and 13.5 gauss², respectively, were obtained. The complex shape of the lines is interpreted as due to the appearance of two groups of molecules: those undergoing isotropic reorientation and those undergoing reorientation about their own C_3 axis. The extent of the latter increases at lower temperatures in accord with Arrhenius' law with a potential barrier of about 0.002 kcal/mol.

Introduction

The ammonium ion NH_4^+ in a crystal of ammonium perchlorate features a large freedom of reorientation. This is proved by analyses of near infrared spectra (Waddington 1958), elastic and inelastic neutron scattering spectra (Smith, Levy 1962, Janik *et al.* 1965), and Raman spectra (Trefler, Wilkinson 1969). Smith and Levy (1962) determined the crystal structure of NH_4ClO_4 and associated the ease of reorientation of the ammonium ion with the symmetry of its localization in the crystal lattice. The NH_4ClO_4 crystal has $BaSO_4$ type structure of D_{2h}^{16} symmetry. The orthorhombic elementary cell is characterized by its large lattice constants, $a = 9.202$ Å, $b = 5.816$ Å, $c = 7.449$ Å (Wyckoff 1951). The ammonium ion is surrounded by eight closest oxygen atoms from 2.94 to 3.08 Å away, in a configuration void of any elements with tetrahedral symmetry. Therefore, structural conditions do not permit the simultaneous formation of four strong linear hydrogen bonds N—H...O, and this makes easy reorientation possible.

It appears that this structure of the crystal is sustained even at the lowest temperatures, for no change in specific heat has been found in the range from 5°K to 350°K (Justice, Westrum 1969).

Analyses of nuclear magnetic resonance lines in polycrystalline NH_4ClO_4 also corroborate the appearance of NH_4 ion reorientation. For, as seen in Table I, the values of the second Van Vleck moment obtained by various authors are much smaller in the entire range of

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temperatures from 298°K to 20°K examined hitherto than the value of 43 gauss[2] calculated theoretically for an immobile NH_4^+ ion having the shape of a tetrahedron with an N—H distance equal to 1.035 ± 0.01 Å (Pendred, Richards 1955).

On the other hand, these values are in accord with the value of $M_2 = 1.34$ gauss[2] (Ibers 1960) calculated for intermolecular interactions themselves. This is proof that dipole interactions within the ion have been averaged out to zero by isotropic reorientation.

TABLE I

Values of second moment for NH_4ClO_4 at various temperatures

Temperature (°K)	M_2 (gauss[2])	References
298	1.18 ± 0.01	Ibers (1960)
77	1.20 ± 0.05	this study
70	1.27 ± 0.02	Ibers (1960)
63.5	1.73 ± 0.05	this study
20	2.42 ± 0.8	Richards, Schaefer (1961)

Ibers (1960) performed measurements of the longitudinal relaxation time of protons by the gradual saturation technique and on this basis calculated that the height of the barrier hindering the rotation of the NH_4^+ is 2.0 ± 0.6 kcal/mol. Using the relation $E = AT_t (A = \text{constant} = 0.037$ kcal/mol degree) between the barrier height E and temperature T_t at which line broadening occurs, given by Wert and Max (1953), line broadening should have been expected at a temperature of about 50°K. This is not corroborated by experiment, for Richards and Schaefer (1961) revealed only a slightly broadened line at 20°K (Table I) and, thus, a barrier lower than 1 kcal/mol.

Measurements of total scattering cross-sections for cold neutrons show that the barrier for the reorientation of an NH_4 ion equals 0.15 ± 0.5 kcal/mol (Rush et al. 1962).

The aim of this study was to obtain data on the reorientation of the NH_4 group at temperatures below 20°K.

Experiment

The measurements of the proton resonance lines in polycrystalline NH_4ClO_4 were performed with a broad line spectrometer possessing an autodyne generator in a magnetic field of 0.4070 tesla, using modulation of a frequency of 71 Hz and amplitude 0.8×10^{-4} tesla.

The sample was in the form of a phial of an approximate volume of 3 cm³ filled with the carefully dried substance, then pumped off and sealed after being filled with helium.

The measurements were made with a cryostat enabling variation of temperature within the range from 4.2°K to 1.2°K by pumping off the vapours from above the surface of liquid helium. The temperature was determined on the basis of the helium vapour pressure.

By changing the strength of the high frequency field H_1 within a wide range it was ascertained that saturation effects do not give rise to any substantial perturbations.

Results of measurements and discussion

Examples of the obtained derivative proton resonance absorption lines are presented in Fig. 1, and the results of second moment calculations are given in Table II and Fig. 3. The given values are average ones calculated on the basis of at least three lines.
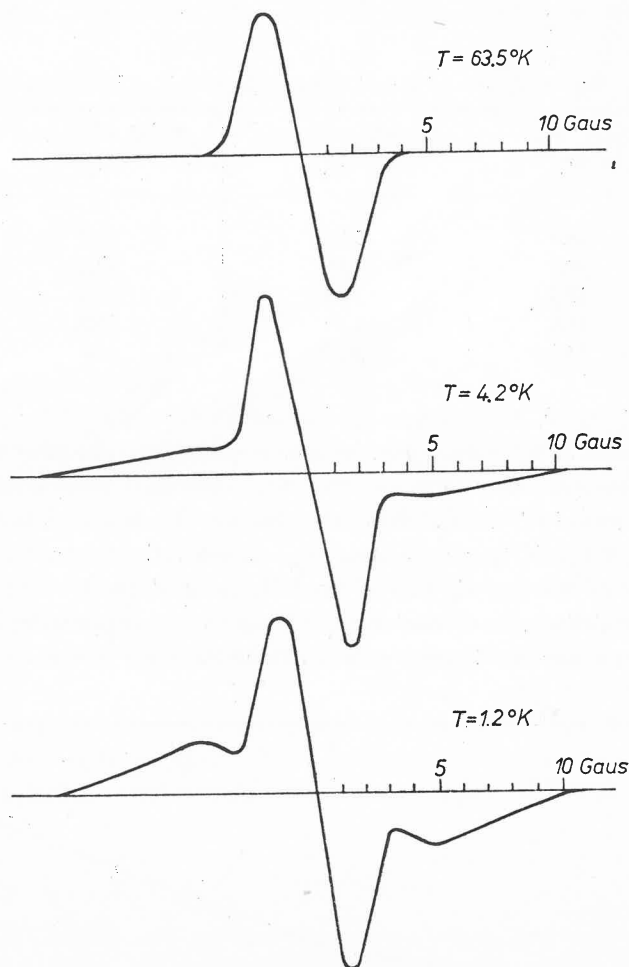

Fig. 1. Derivative NMR absorption lines in polycrystalline NH_4ClO_4 at different temperatures

The shape of the obtained spectra implies that in the 4.2°K to 1.2°K temperature range they are composed of two component lines, a broad one and a narrow one. The second moments of the component lines are approximately independent of temperature (Table II), whereas a change in temperature bears a strong effect on the intensity of these lines. Lowering temperature increases the relative proportion of the broad line.

The value of the narrow line's second moment is near that of the second moment obtained at higher temperatures (cf. Table I). Hence, it corresponds to the intermolecular

interaction alone. It follows thus that at temperatures between 4.2 to 1.2°K some of the NH_4 ions still undergo isotropic reorientation.

The value of the second moment of the broad component can be linked up with the reorientation of the ammonium ion about a preferred axis. Pendred and Richards (1955) calculated the second moment for the NH_4 groups assuming rotation about the C_3 axis,

TABLE II

Results of measurements of second moment (in gauss²) at helium temperatures

Temp. (°K)	Total M_2^{tot}	Narrow component M_2^s	Broad component M_2^b	p
4.2	8.9	1.30	13.7	0.6
1.9	9.3	1.31	13.1	0.7
1.4	12.3	1.33	15.8	0.75
1.3	12.6	1.50	15.9	0.77
1.2	13.5	1.67	16.9	0.79

getting $M_2 = 12.5$ gauss². Adding the contribution from intermolecular interactions equal to the second moment of the narrow line, we get the values of 13.8 gauss² at 4.2°K and 14.17 gauss² at 1.2°K. These are close to the experimental values for the broad component, being equal 13.7 to 16.9 gauss² (Table II). This enables the broad component to be associated with the reorientation of the NH_4 groups about the C_3 axis. Consequently, this proves that rotation about one of the four C_3 axes of the NH_4 group is linked with a lower potential barrier. The slight differences of the compared values are presumably due to the effect of the reorientation about the C_3 axis on the contribution from intermolecular interactions.
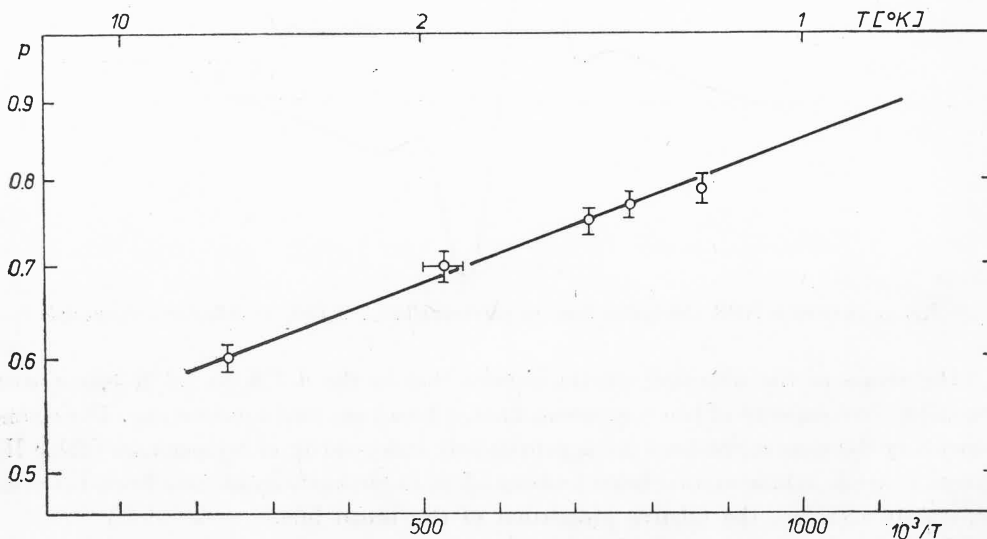

Fig. 2. Temperature dependence of logarithm of relative proportion p of NH_4 groups undergoing reorientation about a C_3 axis

Considering the proportionality between the area under the absorption line and the number of protons, it is possible to calculate the relative proportion p of ions subject to reorientation about a preferred C_3 axis according to the formula

$$M_2^{tot} = pM_2^b + (1-p)M_2^s.$$

Here, M_2^{tot}, M_2^b and M_2^s are the respective values of second moments of the entire spectrum, the broad component and the narrow component.

The values of p in logarithmic scale lie on a straight line (Fig. 2), what proves the activation character of the transition from the state of isotropic reorientation to reorientation about
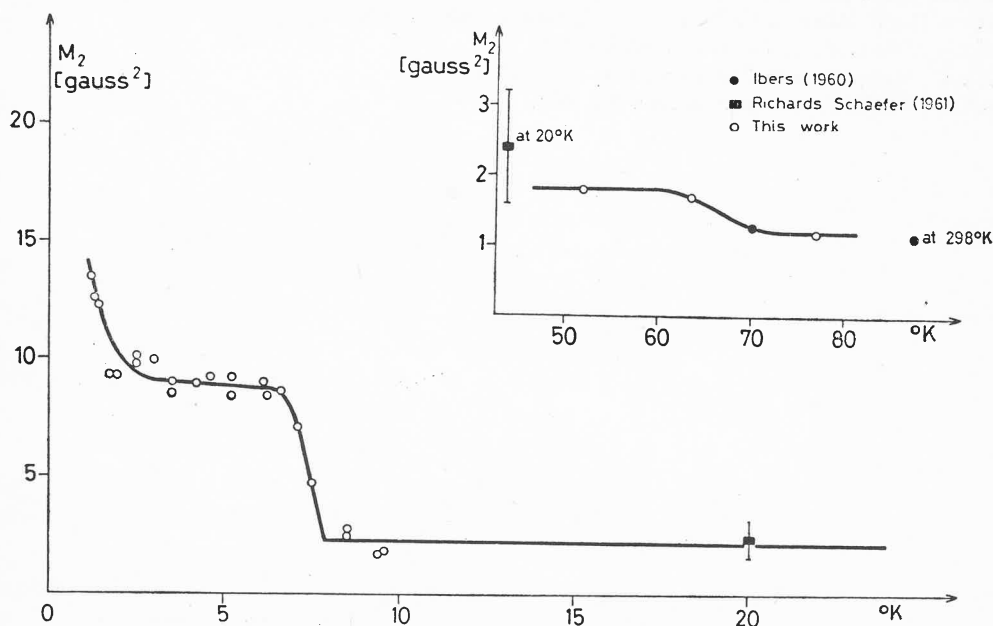

Fig. 3. Temperature dependence of the proton second moment in polycrystalline $NH_4 ClO_4$

a C_3 axis. The activation energy corresponding to this process is about 0.002 kcal/mol. By extrapolating the values of p to lower temperatures it may be expected that at a temperature of $0.8 \pm 0.1°K$ the narrow component will decay, and $M_2^{tot} \cong 17$ gauss^2. Freezing of the reorientational motion about the C_3 axis, associated with a lower potential barrier or tunneling, should be expected at even lower temperatures. Broader compound disappears at 7.8°K (Fig. 3).

An interesting phenomenon visible in Table I and Fig. 3 is the broadening of the narrow line between 70 and 63.5°K. Perhaps this broadening of the narrow line between 70 and 63.5°K is due to lattice contraction and is correlated with some changes in X-ray diffractograms observed near 83°K by Stammler et al. (1962, 1966).

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