

Electron paramagnetic resonance of NH_3^+ radical in potassium sulphate

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Abstract. Room temperature EPR spectra of $(\text{NH}_4)_2\text{SO}_4$ doped K_2SO_4 monocrystals irradiated with x-rays show the presence of NH_3^+ radicals. The EPR parameters are $g_{\parallel}=2.0037$ and $g_{\perp}=2.0068$; $^{14}\text{N } A_{XX}=13.75$; $A_{YY}=24.5$; $A_{ZZ}=25.5$ gauss; $^1\text{H } A_{XX}=A_{YY}=22$ and $A_{ZZ}=25$ gauss. From the ^{14}N and ^1H coupling constants it has been inferred that at room temperature the planar NH_3^+ radical undergoes rotation about the C_3 axis which corroborates with the equivalence of the protons, but the radical itself is in an asymmetric crystal field environment. The 77K spectra indicate a considerable reduction in the motion of the radical with the free motion almost completely stopped.

Keywords. g -tensor; proton hyperfine coupling constant; INDO calculations; nitrogen hyperfine coupling constant.

1. Introduction

The electron paramagnetic resonance studies of small open-shell molecules produced as a result of high energy radiation damage and stabilised in pure and doped single crystals or glassy matrices is by now a well traversed field (Atkins and Symons 1967). In this paper we present the EPR results for a stable NH_3^+ radical produced by x-ray damage of NH_3^+ doped K_2SO_4 , where it has a half-life of several months. Previous work on NH_3^+ has been reported by Cole (1961), Hyde and Freeman (1961), Janecka and Fujimoto (1971) and Fujimoto and Morton (1965). In all these studies the nitrogen hyperfine coupling constants are axially symmetric and the proton hyperfine coupling constants are nearly isotropic at room temperature. Following Cole (1961), Fujimoto and Morton (1965) reported results of NH_3^+ in NH_4ClO_4 lattice at 77K and 4K. As the temperature is lowered the nitrogen and proton hyperfine anisotropies increase. A complete analysis of the static NH_3^+ has however not been reported.

2. Experimental

Single crystals of K_2SO_4 containing $\sim 1\%$ by weight of $(\text{NH}_4)_2\text{SO}_4$ were grown by slow evaporation from aqueous solution and these were examined in a polarising

Part of Ph.D. work of the second author

microscope to avoid twinned crystals and to identify the crystallographic axes (Heartshorne and Stuart 1960) together with the crystal morphology. Selected crystals were irradiated with x-rays at room temperature using a copper x-ray tube operating at 50 kV and 20 mA for periods ranging from 3 to 6 hr. Irradiation imparted a light yellow colour to the crystals.

EPR spectra were measured using a Varian E-4 X-band spectrometer with 100 kHz field modulation and phase-sensitive detection. The crystals were mounted about the crystallographic axes using an adhesive at the end of the perspex rod attached to a large diameter protractor to enable rotations to be carried out with an accuracy of $\pm 1^\circ$. Low temperature measurements were performed by immersing the crystals in liquid nitrogen contained in a Dewar vessel whose quartz tail fitted inside the EPR cavity. Field calibrations were done using diphenyl picryl hydrazyl (DPPH) as internal field marker.

3. Results and discussion

Figure 1 shows typical EPR spectra of the irradiated crystals at the indicated orientations. It is evident that the unpaired electron interacts with many magnetic nuclei. The free radical, therefore, is not a product from the host lattice SO_4^{2-} which could undergo radiation damage to produce radicals such as SO_4^- , SO_4^{3-} , SO_3^- (Gromov and Morton 1966; Aiki and Hukunda 1967), all of which could give a single line per magnetically distinct site. The radiation damage product, therefore, must come from the NH_4^+ impurity which is expected to occupy a substitutional K^+ site in the lattice, size and charge being ideal for such a situation ($\gamma_{\text{K}^+} = 1.33 \text{ \AA}$; $\gamma_{\text{NH}_4^+} = 1.43 \text{ \AA}$). At an arbitrary orientation, a careful counting of the hyperfine features, accounting for overlaps, shows the presence of 24 lines which could be analysed in terms of two

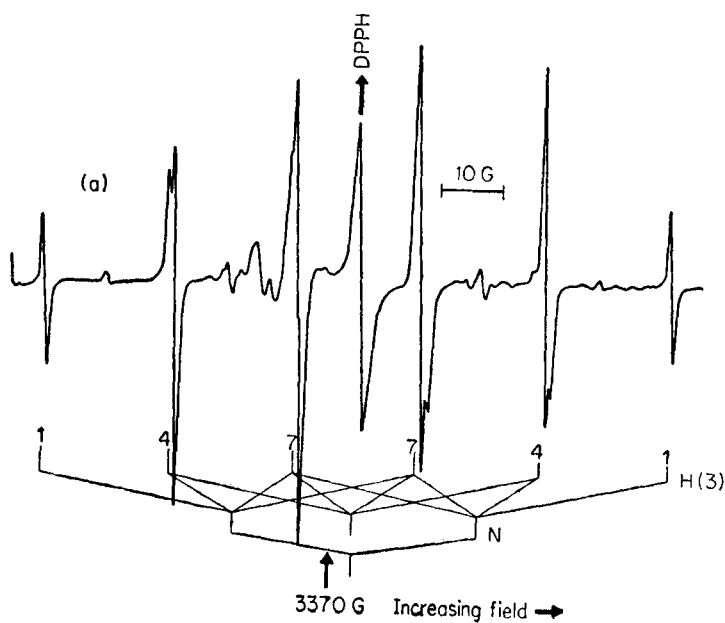


Figure 1a.

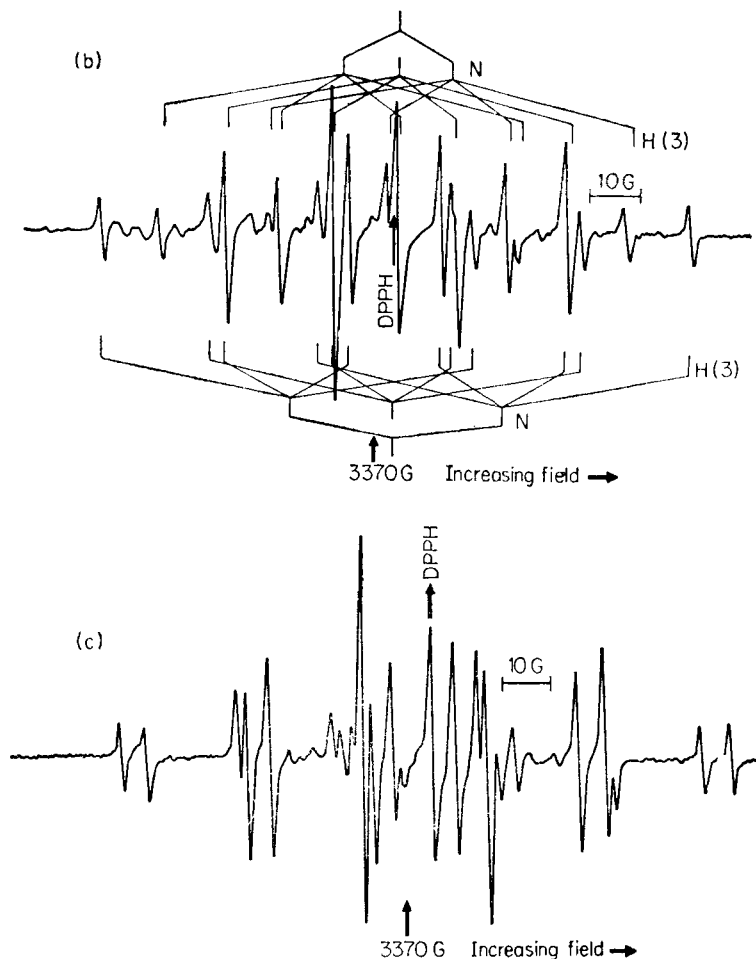


Figure 1. Typical x-band EPR spectra of the NH_3^+ radical in K_2SO_4 crystals at room temperature for (a) a -axis parallel to the magnetic field (b) b -axis parallel to the magnetic field, (c) arbitrary orientation. In (a) and (b) schematic stick pattern of the ^{14}N and 1H hyperfine features are indicated.

symmetric 12-line patterns. Each of these patterns is a triplet of quartets with the former having an intensity ratio 1:1:1 and the latter 1:3:3:1.

The crystal structure of K_2SO_4 shows that it belongs to the orthorhombic crystal class with space group $Pnam$ (Robinson 1958; Wyckoff 1931). There are four formula units per unit cell and the presence of mirror plane indicates the possibility of two types of SO_4^{--} and K^+ sites in the unit cell. If the radical produced is NH_3^+ then we expect two sites for an arbitrary orientation as long as the radical does not tumble freely.

In order to extract the principal values of the g , 1H and ^{14}N hyperfine tensors, EPR spectra were recorded for rotations of the crystal about the a , b and c axes. In all these planes there were two sites which became magnetically equivalent for the magnetic field parallel to a axis. The isofrequency plot of the EPR spectra in the ab plane is given in figure 2. From these, the principal values and the direction cosines of the g and hyperfine tensor were extracted using the method of Schonland (1959) and are presented in table 1. Their direction cosines were verified by recalculating the line

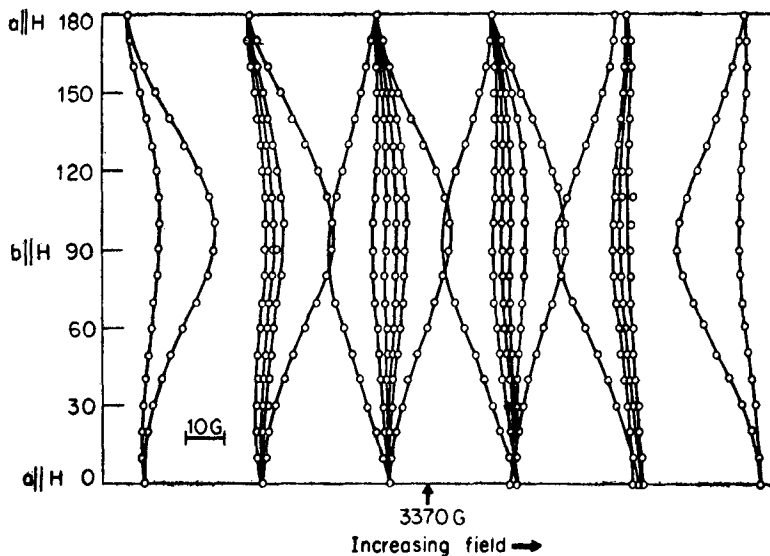
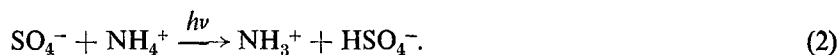


Figure 2. Experimental angular variation of the hyperfine lines for NH_3^+ (two inequivalent sites) for a rotation about the crystal c -axis. The sites become equivalent when a axis is parallel to the magnetic field.

positions for the two sites and the agreement between calculated and experimental spectra was good. For the room temperature g , ^1H and ^{14}N hyperfine tensors have their axes coincident. In table 2 we have listed the EPR parameters for NH_3^+ derived by previous authors for comparison.

A simple mechanism as given below presumably happens during the radiation damage,



Process (1) happens in the pure host lattice and will undoubtedly happen here also because the concentration of SO_4^{2-} is $>99\%$. In the presence of NH_4^+ , process (2) is apparently thermodynamically favourable.

3.1. ^{14}N hyperfine coupling constant

For a planar NH_3^+ radical, whether it undergoes rotation about C_3 axis or not, we expect an axially symmetric nitrogen hyperfine tensor by analogy with systems such as NO_3^- , CO_3^- and ClO_3 , etc (Atkins and Symons 1967). Deviation from axial symmetry is expected only when the system experiences an asymmetrical crystal field or when it undergoes restricted rotation or limited librations about an axis other than C_3 axis.

We have performed INDO calculations (Pople and Beveridge 1970) on NH_3^+ using the force method (Pulay and Torok 1973). The minimum energy configuration cor-

Table 1. EPR parameters for NH_3^+ in K_2SO_4 .†

		Direction cosines		
		<i>a</i>	<i>b</i>	<i>c</i>
Room temp.	$g_{\parallel} = 2.0037 \pm 0.0005$	1.0	0.0	0.0
	$g_{\perp} = 2.0068 \pm 0.0005$	<i>b</i>	*	*
¹⁴ N (site 1)	$A_{XX} = 13.75$	0.0	1.0	0.0
	$A_{YY} = 24.50$	0.0	0.0	1.0
	$A_{ZZ} = 25.50$	1.0	0.0	0.0
(site 2)	$A_{XX} = 13.75$	0.0	0.0	1.0
	$A_{YY} = 24.50$	0.0	1.0	0.0
	$A_{ZZ} = 25.50$	1.0	0.0	0.0
¹ H (site 1 and 2)	$A_{XX} = 22.0$			
	$A_{YY} = 22.0$		**	
	$A_{ZZ} = 25.0$			
77K (a H)	¹⁴ N A = 31.00	} Sites coincident and protons inequivalent		
	¹ H ⁽¹⁾ A = 33.50			
	¹ H ^(2,3) A = 22.75			
	Site 1	Site 2		
	¹⁴ N A = 20.5	24.5		
(c H)	¹ H ⁽¹⁾ A = 35.25	7.0		
	¹ H ^(2,3) A = 20.5	14.0		

†All hyperfine coupling constants are in gauss. The error involved is ± 0.2 gauss.

*The direction cosines have no significance.

**The proton hyperfine tensor at room temperature are coincident with those of the nitrogen tensor.

responds to a planar NH_3^+ with an N–H bond length 1.0 Å and having D_{3h} symmetry. INDO calculations predict a ¹⁴N isotropic hyperfine constant of -26.3 gauss. Cole (1961) suggested a simple way of calculating the dihedral angle in NH_3^+ using the language of hybridisation. For a planar NH_3^+ we expect a ¹⁴N isotropic coupling constant of 27.5 gauss and for a pyramidal molecule with H–N–H angle of $109^\circ 28'$, the corresponding value is 157.5 gauss. The observed isotropic coupling of $+21.25$ gauss certainly indicates a planar structure as predicted by the INDO calculations. The hybridisation procedure ignores the core (1s) polarisation and when this is included (Cole 1961) we arrive at a value of $+22$ gauss for the ¹⁴N isotropic hyperfine coupling constant as experimentally observed.

Regarding the dipolar hyperfine coupling to ¹⁴N, the major term arises via an interaction between N $2p_z$ electron and ¹⁴N nucleus. This will have a cylindrical symmetry about the C_3 axis. However, a minor term which also has the same symmetry has to be included due to the spin-polarisation of the in-plane p_x and p_y electrons. This mechanism is also responsible for any isotropic hyperfine coupling to the protons. INDO calculations as well as observed ¹⁴N isotropic hyperfine coupling constants indicate that almost all the unpaired spin-density is present in non-bonding

Table 2. EPR parameters for NH_3^+ in various systems

System	Temperature	g tensor	^{14}N hyperfine coupling tensor in gauss	^1H hyperfine coupling tensor in gauss	Direction cosines for nitrogen hyperfine tensor	Reference							
1	2	3	4	5	6	7							
NH_4ClO_4	300K	2.0039 ± 0.0003 2.0034 ± 0.0003 2.0032 ± 0.0003	26.30 ± 0.15 25.80 ± 0.15 25.57 ± 0.14	22.07 ± 0.15 19.07 ± 0.14 17.39 ± 0.14	0.000 0.000 0.000	<i>a</i>							
							NH_4ClO_4	300K	2.0034 ± 0.0001	18.1	25.0	0.994 0.000 0.000	<i>b</i>
$^{10}\text{NH}_3^+$ in NH_4ClO_4	300K	^{10}N 30.60 26.14 24.85	26.17 25.14 24.68	0.000 0.000 1.000	<i>d</i>								
						$^{10}\text{NH}_3^+$ in NH_4ClO_4	77K	^{10}N 50.35 17.14 14.00	28.00 25.14 24.68	± 0.995 0.000 ± 0.099			
$^{10}\text{NH}_3^+$ in NH_4ClO_4	4K	^{10}N 62.50 5.35 14.64	H_1 29.10 \pm 0.20 42.85 \pm 2.00 8.93 \pm 0.40 H_2 29.10 \pm 0.20 25.00 \pm 2.00 25.40 \pm 0.20 H_3 29.10 \pm 0.20 7.14 \pm 2.00 44.64 \pm 0.40	0.000 0.000 0.000									

Table 2—(Contd.)

1	2	3	4	5	6	7	
$(NH_3^+) I$ in $(NH_4)_2SO_4$	225K		29.10 ± 0.20		±0.362	0.932	0.000
			18.30 ± 0.20		0.932	±0.362	0.000
			7.80 ± 0.20		0.000	0.000	1.000
$(NH_3^+) II$ in $(NH_4)_2SO_4$	225K		22.50 ± 0.20		0.929	±0.369	0.000
			13.30 ± 0.20		±0.369	0.939	0.000
			20.50 ± 0.20		0.000	0.000	1.000
$(NH_3^+) I$ in $(NH_4)_2SO_4$	222K		31.70 ± 0.20		0.800	0.557	±0.222
			10.60 ± 0.20		-0.344	0.729	±0.592
			15.20 ± 0.20		±0.492	±0.397	0.775
$(NH_3^+) II$ in $(NH_4)_2SO_4$	222K		30.40 ± 0.20		0.659	0.734	±0.167
			15.50 ± 0.20		0.641	-0.430	±0.636
			12.40 ± 0.20		±0.394	±0.526	0.754
$(NH_3^+) I$ in $(NH_4)_2SO_4$	156.5K		48.80 ± 0.20		0.731	0.635	±0.250
			12.00 ± 0.20		-0.660	0.750	±0.181
			6.70 ± 0.20		±0.173	±0.181	0.968
$(NH_3^+) II$ in $(NH_4)_2SO_4$	156.5K		39.70 ± 0.20		0.772	0.508	±0.382
			15.20 ± 0.20		-0.452	0.861	±0.232
			5.50 ± 0.20		±0.447	±0.006	0.895
ADP/KDA	300K		2.0037 ± 0.0005	25.10			
			2.0037 ± 0.0005	20.10			
			2.0041 ± 0.0005	14.70			
NH_4ClO_4	300K, 77K, 300K		19.30 ± 0.10	25.80 ± 0.10			
			19.30 ± 0.10	25.80 ± 0.20			
			17.30 ± 0.20	² H 3.60 ± 0.10			

a, Cole (1961); *b*, Hyde and Freeman (1961); *c*, Janecka and Fujimoto (1971); *d*, Fujimoto and Morton (1965); *e*, Fujimoto *et al* (1977); *f*, Suzuki and Ryuji (1971); *g*, Rao and Symons (1971)

$2p_z$ orbital. Assuming that one unpaired electron $2p_z$ on ^{14}N leads to 34 gauss (Watson and Freeman 1961) the net dipolar hyperfine tensor is

$$\begin{array}{c} X \\ Y \\ Z \end{array} \begin{pmatrix} -17 & & \\ & -17 & \\ & & +34 \end{pmatrix} + \begin{pmatrix} +0.7 & & \\ & +0.7 & \\ & & -1.4 \end{pmatrix} = \begin{pmatrix} -16.3 & & \\ & -16.3 & \\ & & +32.6 \end{pmatrix}. \quad (3)$$

due to p_z
due to polarisation
Net
electron
of p_x and p_y electrons

The minor dipolar tensor on the left hand side is calculated assuming an unpaired spin-density of 0.05 in the in-plane N $2p_x$, $2p_y$ orbitals. This value is to be compared with the value of 34 gauss obtained for the $^{15}\text{NH}_3^+/\text{NH}_4\text{ClO}_4$ system by Fujimoto and Morton (1965) which corresponds to a ^{14}N value of only 20.0 gauss. Therefore, even at 4K, there is some residual motion in the radical which wipes out 50% of the anisotropy.

We have measured the spectrum of NH_3^+ in K_2SO_4 at 77K. Typical EPR spectra are given in figure 3 for the magnetic field along a and c axis. The spectra show that the ^{14}N and ^1H anisotropic hyperfine couplings are increased and three protons are no longer equivalent. The spectra indicate however, that two of the protons are always almost equivalent. The same observation was also made by Fujimoto and Morton (1965). This means there are librations about a C_2 axis of NH_3^+ at low temperatures.

A complete analysis of the 77K spectrum, however could not be achieved in view of the complexity of the spectrum.

3.2. The proton hyperfine coupling constants

The INDO calculations as well as simple chemical intuition suggests that the unpaired electron spends almost all its time in the non-bonding p_z orbital in the central nitrogen. Therefore, isotropic hyperfine coupling to protons must arise via spin polarisation of N-H $-\sigma$ electrons and should be negative in sign. Such $-\alpha$ hydrogen isotropic coupling constants are fairly accurately predicted by INDO level of approximation and the calculated value is -26.3 gauss; this corresponds to an unpaired s density of 0.05 and agrees well with the experimental value of -23 gauss. However, anisotropic hyperfine interaction could arise via direct dipolar coupling between the unpaired electron in the N- p_z orbital and proton through space. This can be easily estimated from $\langle \gamma \rangle$ of the p_z orbital electron and the N-H bond distance. For a bond distance of 1.0 \AA and a value of $\langle \gamma \rangle = 1.113 \text{ \AA}$ this leads to a cylindrically symmetric dipolar tensor of the form $(+15.2, -7.6, -7.6)$ on each proton. With the unique axis parallel to the C_3 axis of NH_3^+ , we expect the following experimental hyperfine tensor:

$$\begin{pmatrix} -26.3 & & \\ & -26.3 & \\ & & -26.3 \end{pmatrix} + \begin{pmatrix} -7.6 & & \\ & -7.6 & \\ & & +15.2 \end{pmatrix} = \begin{pmatrix} -33.9 & & \\ & -33.9 & \\ & & -11.1 \end{pmatrix}. \quad (4)$$

isotropic
dipolar
total

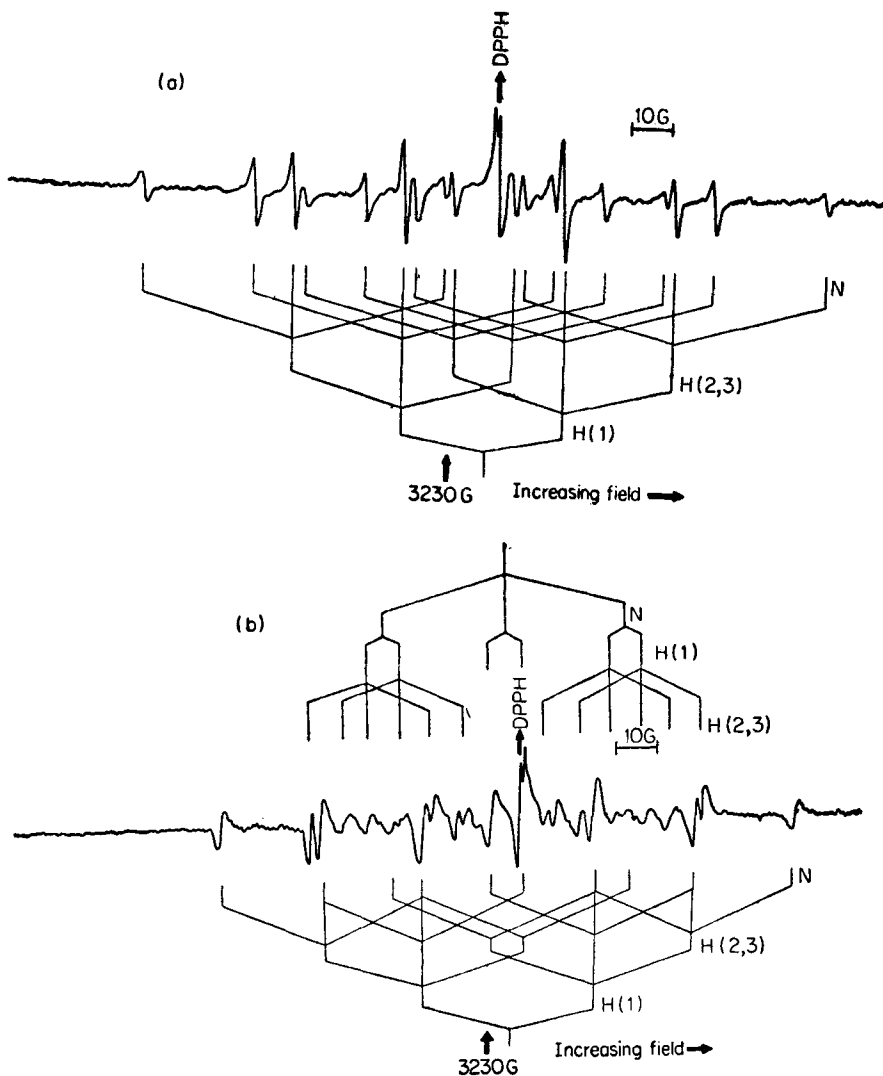


Figure 3. Typical x -band EPR spectra of NH_3^+ radicals in K_2SO_4 crystals at 77K for (a) a -axis parallel to the magnetic field and (b) for c -axis parallel to the magnetic field. Schematic stick diagrams of the hyperfine patterns are indicated. In (a) the sites become equivalent.

When the molecule rapidly tumbles we expect an isotropic 1H coupling of -26.3 gauss and when frozen to static state at low temperatures the tensor should be of the form given on the right hand side of equation (4). However, when the rotation about the axis other than C_3 axis is considered then protons are no longer equivalent and there will be a partial loss of anisotropy; our 77K spectra in a majority of orientation (see figure 3) show that one proton is different from that of the remaining two which are equivalent. This general trend in the increase of the 1H anisotropy in the h.f.c. constants was also noticed by Fujimoto and Morton (1965). From our 77K spectra we estimate an isotropic coupling constant of 25.7 gauss and a maximum dipolar coupling constant of +10 gauss which should be compared with the predicted value of +15.2 gauss for a static NH_3^+ . However, only a complete analysis of 77K

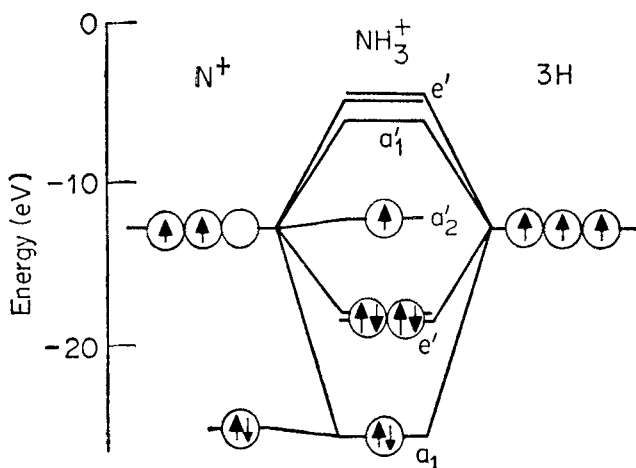


Figure 4. Molecular orbital correlation diagram for NH_3^+ radical based on INDO calculations.

spectrum can give us detailed information. The very low anisotropy in the ^1H dipolar coupling at room temperature indicates restricted rotations. Figure 4 is a qualitative molecular orbital correlation diagram for NH_3^+ with D_{3h} symmetry.

4. Conclusions

The radical NH_3^+ is very stable in K_2SO_4 lattice where charge compensation is not needed. The anisotropic proton hyperfine coupling constants derived experimentally are much less than those predicted for a static system, this together with the non-axial symmetry for the ^{14}N hyperfine tensor indicates restricted rotation at room temperature or a libration about the C_3 axis. At 77K, this seems to have stopped, although the non-equivalence of protons indicates the presence of either asymmetrical crystal field environment or limited librations about a C_2 axis or both. The results of Fujimoto and Morton (1965) at 4K indicates that two of the protons are equivalent and the third one is different, similar to our present results at 77K. The isotropic part of ^{14}N hyperfine coupling constant at all temperatures indicates a planar structure for the NH_3^+ moiety on a time average. It has however not been possible to establish with the present data whether the NH_3^+ occupies a K_α or K_β sites in K_2SO_4 .

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References

- Atkins P W and Symons M C R 1967 *The structure of inorganic radicals* (Amsterdam: Elsevier)
- Aiki K and Hukunda K 1967 *J. Phys. Soc. Jpn.* **22** 663
- Cole T 1961 *J. Chem. Phys.* **35** 1169
- Fujimoto M, Dressel L A and Yu T J 1977 *J. Phys. Chem. Solids* **38** 97
- Fujimoto M and Morton J R 1965 *Can J. Chem.* **43** 1012
- Gromov and Morton J R 1966 *Can. J. Chem.* **44** 527
- Hyde J S and Freeman E S 1961 *J. Phys. Chem.* **65** 1636
- Heartshorne N H and Stuart A 1960 *Crystals and the polarising microscope* (Edward Arnold Publications)
- Janecka J and Fujimoto M 1971 *J. Mag. Reson.* **4** 47
- Pople J A and Beveridge D L 1970 *Approximate molecular orbital theory* (New York: McGraw Hill)
- Pulay P and Torok 1973 *Mol. Phys.* **25** 1153
- Robinson M T 1958 *J. Phys. Chem.* **62** 925
- Rao K V S and Symons M C R 1971 *J. Chem. Soc. (A)* 2163
- Schonland D S 1959 *Proc. Phys. Soc. (London)* **73** 788
- Suzuki I and Ryuji A 1971 *J. Phys. Soc. Jpn.* **31** 951
- Watson R E and Freeman A J 1961a *Phys. Rev.* **123** 524
- Watson R E and Freeman A J 1961b *Phys. Rev.* **124** 1117
- Wyckoff R W G 1931 *The structure of crystals* (New York: Chemical Catalogue Co.) 2nd ed. p. 291