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Temperature and Pressure Dependence Studies of the *Motions of the* $^+NH_3$ *Radical* Trapped in γ Irradiated Ammonium Perchlorate Single Crystal

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The temperature and pressure dependences of the $^+NH_3$ coupling tensors have been investigated by ESR spectroscopy. The linear variation of the reduced correlation time of the "rotational diffusion" motion with the reciprocal of the temperature is shown to be unrelated to the dilatation of the matrix. Comparison with $^+ND_3$ results gives the contribution to the nitrogen isotropic coupling constant of the out of plane vibration of the nitrogen atom.

INTRODUCTION

Due to the theoretical importance of the $^{13}CH_3$ radical, many calculations[1] of the dipolar coupling tensor of the ^{13}C have been performed. Some experimental results[2] on that radical have been obtained too but, as no experiment has allowed the determination of the contribution of the motions to this tensor, no comparison between theoretical and experimental values can be done. $^+NH_3$ radical is isoelectronic with CH_3 and constitutes the simplest of the aminium radicals. In a previous paper[3] the motions the $^+NH_3$ radical undergoes have been determined and one can expect to obtain the intrinsic coupling tensors of this radical (i.e. those of the hypothetic motionless radical) which are those that can be calculated. These motions were determined through an analysis of values of the nitrogen and proton coupling tensors of the $^+NH_3$ radical trapped in NH_4 ClO_4 single crystal at 4.2 K and 81 K. These motions are:

1) Jumping reorientations of 120° around its C_{3v} axes.

2) Jumping reorientations between two equilibrium positions in the crystal.

3) "Rotational diffusion" of its C_{3v} axis.

As the three protons coupling tensors are equivalent at 81 K and above, the full averaging effect is obtained for the motion 1) and the proton coupling tensor is insensitive to this motion above 81 K.

From the symmetry of the crystal it can be shown there are only two equivalent crystallographic sites A and B in the matrix.[4] At 4.2 K for each of these sites, the radical has two equilibrium positions $(A_1 A_2)$ and $(B_1 B_2)$ so that there are four magnetically unequivalent sites at this temperature. As these four sites reduce to only two at 81 K and above, one can conclude that the motion 2) is also very fast and that the variation of the coupling tensors is no longer sensitive to this motion above 81 K. Therefore the only motion which affects the variation of the coupling tensors between 81 K and room temperature is the third one. This third motion has been previously studied by Janecka and Fujimoto[5] from the temperature dependence of the nitrogen coupling for a particular direction in the crystal. However, due to the lack of structural informations on the equilibrium positions of the radical in the NH_4ClO_4 matrix when the study of Janecka and Fujimoto was performed, the direction chosen does not correspond to a principal direction of the nitrogen coupling tensor in its equilibrium position. This is one of the reasons which incited us to reinvestigate the problem of the temperature dependence of the reduced correlation time for the third motion between 81 K and 293 K. Moreover, the temperature range in such a study is rather large and it is possible that the expansion of the matrix affects this motion. This is why we have also investigated the pressure dependence of the nitrogen coupling tensor between 1 and 8,000 bars for different temperatures. Finally, as it has been shown for AX_3 type radicals,[6,7] the out of plane vibrations of the central atom can seriously change the isotropic constant. We have evaluated this change from the comparison of the results obtained for $^+NH_3$ radical in NH_4 ClO_4 matrix and $^+ND_3$ radical trapped in a ND_4 ClO_4 single crystal.

EXPERIMENTAL

For the temperature dependence study at one atmosphere the experimental procedure has already been described in Ref. (3). The pressure dependence study for various temperatures was performed in the laboratory of Professor

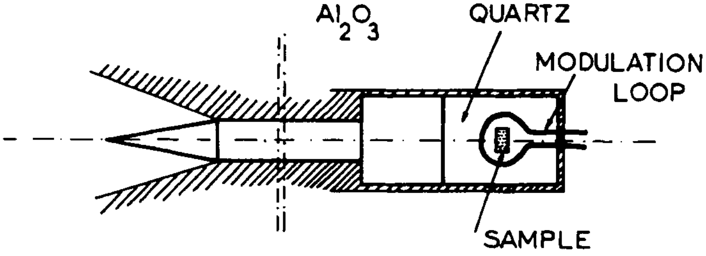

FIGURE 1 High Pressure ESR cavity.

K. Leibler at the Institut Fiziki Polskiej Adademi Nauk (Warszawa). The sample was submitted to an hydrostatic pressure in a special high pressure cavity constructed in the laboratory.[8] The main features of this cavity, shown schematically in Figure 1, are: —pressure range from 1 bar to 8,000 bars —temperature range from 81 K to 293 K. The pressure is transmitted by compressed helium gas through a copper capillary tube of 0.3 mm internal diameter. Spectra were recorded on a Brucker spectrometer.

RESULTS

Table I gives the proton and nitrogen coupling tensors of the $^+NH_3$ radical for five different temperatures between 81 K and 293 K. In this table we also report the values of the nitrogen coupling tensors for $^+ND_3$ trapped in a ND_4 ClO_4 matrix at 186 K and 293 K. Since the nitrogen dipolar coupling tensor of the motionless $^+NH_3$ radical must be cylindrical for symmetry reasons, the jumping reorientations of 120° around its C_{3v} axes (motion 1) do not affect the magnitude of the principal value of the nitrogen dipolar coupling tensor. Motion 2 (jumping reorientations between two equilibrium positions of $^+NH_3$) does not affect the principal value corresponding to the principal direction of the dipolar nitrogen coupling tensor around which the motion takes place. So, the variation of this principal value reflects exclusively the effects of the third motion ("rotational diffusion" of the C_{3v} axis). This direction is that of the medium principal value of the dipolar nitrogen coupling tensors reported in Table I. Figure 2 shows the temperature dependence of this coupling. Table II gives the proton and nitrogen coupling tensors for the $^+NH_3$ radical measured at 81 K for five different pressures between 60 and 5400 bars. Figure 3 shows the variations with pressure of the medium principal value of the nitrogen dipolar coupling tensor at five different temperatures. Figure 4 illustrates the correspondence between temperature and pressure for a constant density i.e. for a constant dimension of the unit crystallographic cell. (The reference density for NH_4ClO_4 is taken at $T = 10$ K and $P = 1$ bar.)

TABLE I

Variations with temperature of the nitrogen and proton couplings of the $^+NH_3$ radical trapped in NH_4ClO_4. Values in brackets are obtained from $^+ND_3$ in ND_4ClO_4 single crystal.

T	2α	aN (Gauss)		aH (Gauss)	
			-2.1		
293K	48.5°	19.7	(-2.3)		+0.1
		(19.1)	-0.6		+0.2
			(-0.4)	-26.1	
			2.7		
			(2.7)		-0.3
			-3.0		+0.3
243K	47.8°	19.6	-0.8	-26.0	+0.1
			3.8		-0.4
			-4.0		+0.3
186K	45.6°	19.5	(-4.2)	-26.0	+0.2
		(18.9)	-1.5		-0.5
			(-1.5)		
			5.5		
			(5.7)		
			-5.9		+0.6
136K	41.3°	19.5	-3.2	-26.0	+0.3
			9.1		-0.9
			-10.0		+1.0
81K	31.6°	19.6	-6.0	-26.2	+0.8
			16.0		-1.8

This curve is calculated from the NH_4 ClO_4 crystal structure obtained by neutron diffraction at 298, 78 and 10 K[4] and from compressibility data on NH_4 ClO_4.[9]

DISCUSSION

1 Out of plane vibrations of the N atom in the $^+NH_3$ Radical

In Table I we notice that the isotropic nitrogen coupling constant decreases by 0.6 Gauss when passing from $^+NH_3$ to $^+ND_3$. This result which is in perfect agreement with that obtained by Cole[10] at room temperature has the same origin as the decrease of the ^{13}C coupling from 38 to 36 Gauss observed as one passes from $^{13}CH_3$ to $^{13}CD_3$[6] i.e. the out of plane vibrations of the nitrogen central atom. These vibrations produce a mixing of some *s* character to the free electron orbital. From the variations of the ^{14}N isotropic coupling

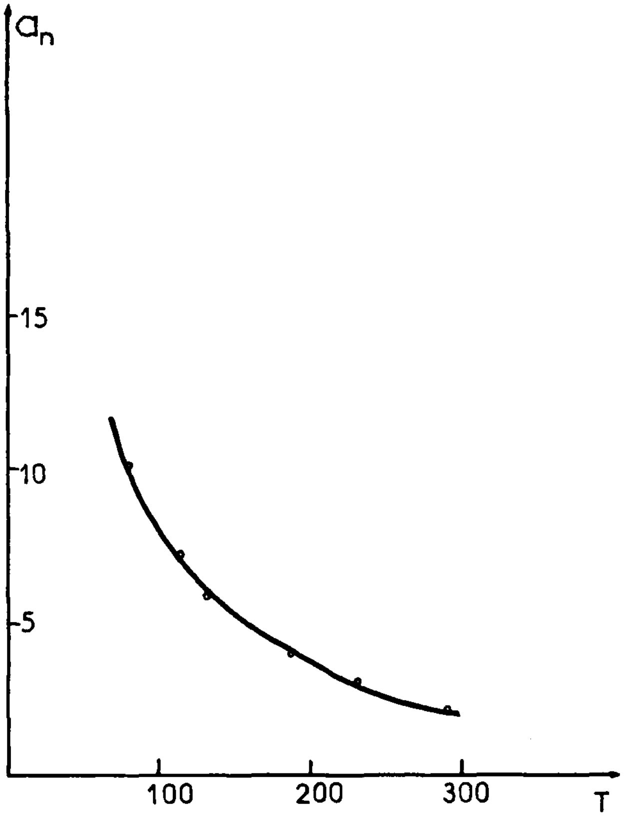

FIGURE 2 Variations with temperature of the nitrogen medium principal value.

constant we may calculate[7–11] the contribution of this out of plane vibration to the total isotropic nitrogen coupling constant of $^{+}NH_3$. The value obtained is 2.6 Gauss. We deduce the contribution of the inner shell polarisation to the coupling to be 19.6 − 2.6 = 17 Gauss. We may notice that the frequency so derived for this motion ($\nu = 8{,}000\ \text{cm}^{-1}$ for $^{+}NH_3$) is too high. This indicates an important incomplete orbital following as it is also the case for CH_3 radical.[6]

2 Rotational diffusion motion of the $^{+}NH_3$ radical

In contrast to what we have seen for the isotropic coupling, the nitrogen dipolar coupling is, within the limits of experimental errors, insensitive to isotropic substitution (see Table I). This is rather surprising if we consider that the "rotational diffusion" motion may arise from additive effects of the

TABLE II

Variations with pressure of the nitrogen and proton couplings of $^+NH_3$ radical trapped in NH_4ClO_4 at 81K.

P	2α	aN (Gauss)		aH (Gauss)	
60	31.1°	19.1	−10.2	−25.8	+1.1
			−6.0		+0.7
			+16.2		−1.8
2500	28.7°	19.4	−11.1	−25.8	+1.4
			−6.7		+0.7
			+16.8		−2.1
3600	25.1°	19.6	−12.2	−25.9	+1.3
			−7.1		+1.0
			+19.4		−2.3
4100	25.1°	19.4	−12.4	−26.0	+1.5
			−7.7		+1.0
			+20.0		−2.5
5400	24.0°	19.4	−12.8	−26.1	+1.7
			−8.0		+0.2
			+20.8		−2.6

librational motions around each of the NH bonds.[3] The substitution of the protons by deuterons should change the frequency of these motions and therefore affect the dipolar part of the nitrogen coupling tensors. A possible explanation is that the inertial effect may almost be cancelled out by the lowering of the hydrogen bond strength when hydrogen is replaced by denterium. Motion 3 was first termed "rotational diffusion" by Janecka and Fujimoto[5] for their observation of the linear dependence of the coupling versus the inverse of the temperature. Such a variation does not allow the calculation of the coupling of the motionless radical. As noted above this behaviour could be due: 1 to the fact that at this time it was impossible to be sure that the sample was in the right orientation. 2 the thermal expansion of the matrix. In order to try to solve this problem we have performed new experimental data: the study of the variation with pressure of the correct medium principal value of the nitrogen dipolar coupling tensor. We have reported on Figure 5 (curve A) the reduced correlation time of motion 3 versus the reciprocal of the temperature calculated as in Ref. (3) from the data of Table I. On Figure 5 the B curve which represents the same reduced correlation time versus $1/T$ has been calculated as follows:

From the data of Figure 4 which gives the correspondence between temperature and pressure at constant density, we have calculated and plotted

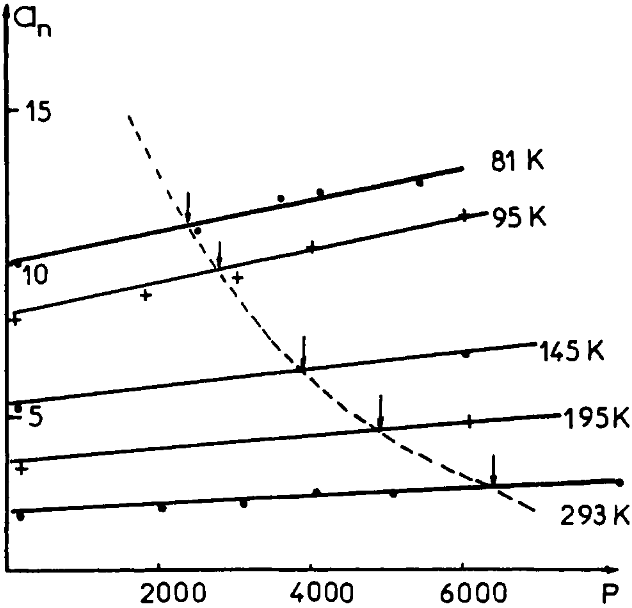

FIGURE 3 Variations with pressure of the nitrogen medium principal value for various temperatures. Dotted line gives the points of constant density (reference density is taken at $T = 10$ K, P = 1 bar).

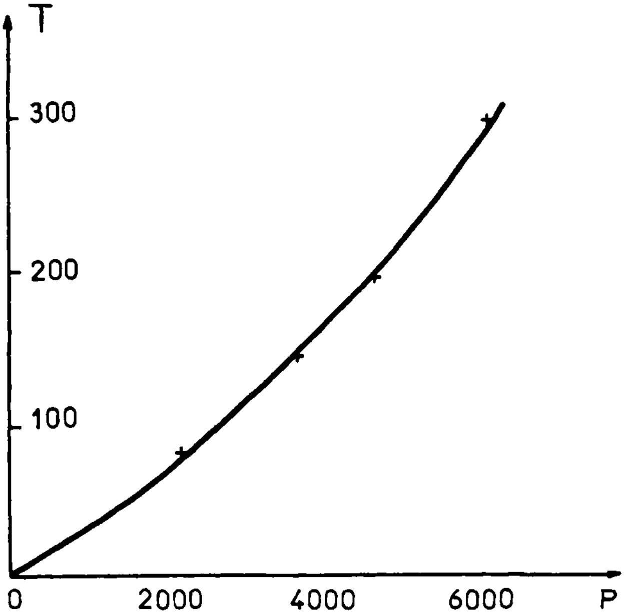

FIGURE 4 Correspondence between temperature and pressure at constant density.

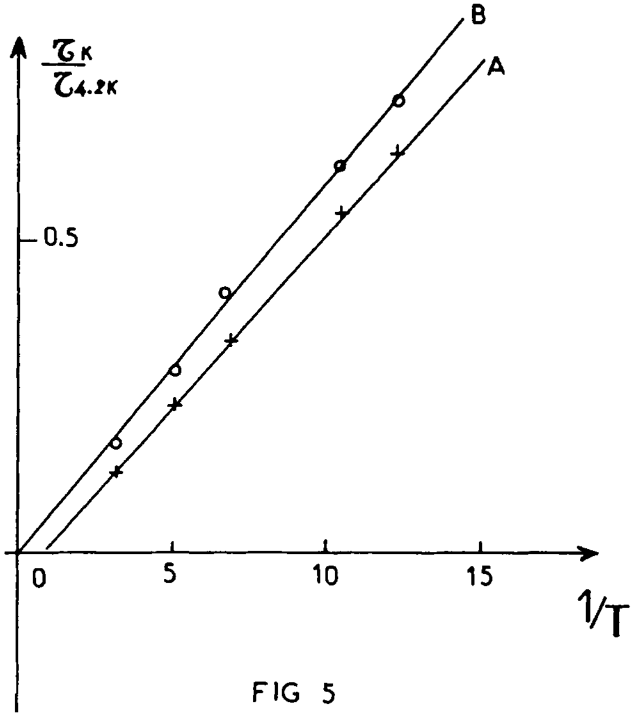

FIGURE 5 Variations with the reciprocal of temperature of the reduced correlation time of the rotational diffusion motion. Curve A: without correction related to the matrix expansion; curve B: with this correction.

on Figure 3 the variations of the medium principal value of the nitrogen dipolar coupling tensor at constant density (The density of NH_4ClO_4 at 10 K is taken as reference density). It can be seen on Figure 5 that curves A and B give both a linear dependence of the correlation time versus $1/T$, the only effect of the thermal expansion of the matrix being to change slightly the slope of the curve and the intersection point with the axis $\tau = 0$ (the equation representating curve A is: $\tau_T/\tau_{4.2\,K} = 56.6/T - 0.045$ and for curve B $\tau_T/\tau_{4.2\,K} = 60.5/T - 0.005$). So it is definitively established that it is not possible to calculate *Bo*, the value of the dipolar nitrogen coupling constant for the radical $^+NH_3$ from the study of the third motion. Nevertheless, as it has been noted in a previous paper,[12] if we take $Bo = 34$ Gauss as it has been suggested from the study of the motions of the $SO_3^-N^+H_2$ radical, one can calculate the values of the angle α($3\cos^2\alpha = 2B/Bo + 1$ where B is that principal value of the nitrogen coupling tensor which is not affected by the first and the second motion) which characterize the third motion. Here α represents the mean value of the angle between the C_{3v} axis of the radical

N^+H_3 and the same axis for the equilibrium position of the motionless radical in the crystal. The good correlation between the values of α and the RMS libration angles of the NH_4 groups in NH_4ClO_4[4] gives some confidence in the value $Bo = 34$ Gauss.

CONCLUSION

In this paper, using the variation of the coupling constant of the nitrogen atom when N^+H_3 is replaced by $^+ND_3$ radical, we have calculated the contribution of the out of plane vibration to this coupling constant. Although the effect of the thermal expansion of the matrix on the variation of the nitrogen coupling of the $^+NH_3$ radical with the temperature is notable, it does not change significantly the relation between the temperature and the correlation time of the motion. Nevertheless this work suggests as the variations with pressure of the coupling constant are quite important that for activated motions the potential barrier may be strongly affected by thermal expansion of the matrix.

Acknowledgements

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