BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 1939—1950 (1970)

A Deuteron and Proton Magnetic Resonance Study of Ammonium Oxalate Monohydrate

Takehiko CHIBA

Department of Chemistry, Nihon University, Sakurajosui, Setagaya-ku, Tokyo

(Received October 25, 1969)

The quadrupole spectra of deuteron magnetic resonance were observed on single crystals of $(ND_4)_2C_2O_4D_2O$. The quadrupole coupling tensors for stationary deuterons were determined at -110°C. eqQ/h and η are 163.7—172.8 kHz and 0.005—0.015 for the ammonium deuterons and 213.3 kHz and 0.090 for the water deuteron. The eqQ values and principal axis directions of EFG tensors are consistent with the structure deduced from the diffraction studies with the exception that the z principal axes of D in the ammonium ion deviate appreciably from the NH directions derived from neutron diffraction. From the change in the line-width with the temperature, the rate of the C_3 reorientation of ammonium ions and that of the 180° flip of water molecules were estimated at various temperatures. The ammonium-ion reorientation is found to be quite isotropic. The temperature dependence of the proton T_1 and $T_{1\rho}$ and the deuteron T_1 were measured on $(NH_4)_2C_2O_4H_2O$ and $(ND_4)_2C_2O_4D_2O$ powers. The T_1 values were then compared with the calculated values, assuming ammonium reorientation. The sharp drop of the proton $T_{1\rho}$ with the temperature above 50°C can be interpreted as being due to the 180° flip motion of water molecules through a relaxation mechanism of "slow motion." The rates of motion derived from the relaxation-time measurements are consistent with those estimated from the line-width change.

Deuteron magnetic resonance (DMR) has been successfully applied to problems of the structure and the motions of molecules in the crystals in which hydrogen atoms participate. DMR studies have often been made of O–H–bond systems, but studies of systems in which H is bonded to atoms other than O have been rather rare. The electric field gradient (EFG) at a deuteron is always nearly in the direction of the D–X bond. The DMR of an ND_4^+ ion gives, at a high temperature, a single line or a doublet of small separation due to the effect of the averaging of the EFG at each D by rapid reorientation. The doublet line may originate from the deviation from the regular tetrahedron of the ND_4^+ ion as well as from the effect due to external charge distribution. However, it is not clear what the relative importance of each contribution is. The motion of the NH_4^+ ion in ammonium salts has been studied by various techniques: IR, heat capacity, neutron diffraction, neutron inelastic scattering, proton magnetic resonance, *etc.* The mode of the NH_4^+ reorientational motion in the crystal has not been well known in most of the cases with the exception of some of the ammonium halides with a high crystal symmetry. Although reorientation about a single C_2 axis of NH_4^+ ions has been assumed in a particular case to explain the change in the second moment of the proton magnetic resonance (PMR),[1] the evidence is not fully decisive.

1) D. Pendred and R. E. Richards, *Trans. Faraday Soc.*, **51**, 468 (1955); J. B. Leane and R. E. Richards, *Spectrochim. Acta*, **10**, 154 (1957).

In DMR on single crystals, as compared to PMR, the line-width transition due to motion is often much more specific to the mode of the motion in the crystal, and if the line-width change is carefully followed it can provide more detailed information than does PMR. DMR study with single crystals, including the measurement for the stationary ND_4^+ ion, has thus far been made on ND_4Cl,[2,3] ND_4Br,[2] and $(ND_4)_2SO_4$.[4] In the cubic phase of ammonium halides, the D's are all equivalent, the bond directions are strictly fixed by the high symmetry of the crystal, and there is no preferred axes of rotational motion. Ammonium sulfate has a phase transition which complicates the DMR spectra so much that the accurate determination of quadrupole coupling for each deuteron is almost impossible. Ammonium oxalate monohydrate $(NH_4)_2C_2O_4H_2O$ provides a favorable system for a detailed study of the ND_4^+ ion—its structure and motion—because it has no phase transition in the temperature range of our interest, because each N–H bond is linked by a hydrogen bond of moderate strength, because the barrier to reorientation appears to be sufficiently high so that, for the observation of the spectra of the stationary ND_4^+ ion, one need not go down to very low temperatures, because its crystal structure is well established and is relatively simple, and because single crystals can be easily grown from the aqueous solution.

The four N–H···O hydrogen bond distances in this crystal are slightly different from each other; therefore, one might be able to detect an anisotropy in the reorientational motion. From the results of neutron diffraction study[5] the NH_4^+ ion in ammonium oxalate monohydrate can be said to assume fairly distorted tetrahedron; therefore, if one gets a quadrupole coupling tensor for each D of the four N–D bonds, one might be able to get information about the relation between the distortion of the ammonium ion and the quadrupole coupling averaged by rapid motion. These are the motivations of the present investigation.

In addition to steady-state DMR measurements of single crystals, the proton spin-lattice relaxation time in the laboratory frame, T_1, and that in the rotating frame, $T_{1\rho}$, were measured by pulse techniques on powdered samples at various temperatures. The temperature dependence of the T_1 of the deuteron in the deuterated crystal powder was also measured.

Experimental

The $(ND_4)_2C_2O_4D_2O$ was obtained by repeated exchange with D_2O of $(NH_4)_2C_2O_4$. The single crystals were grown from a saturated, heavy-water solution of deuterated ammonium oxalate by slow cooling. The single crystals used for the study were about $5\times5\times10$ mm^3. For proton resonance, a recrystallized powder sample of a reagent-grade product was used. The measurements of the steady-state DMR were made by sweeping frequency. The field was fixed at a value corresponding to the deuteron Larmor frequency of 10 MHz. The accuracy of the mounting of the crystal on the probe head was achieved by using a reflecting goniometer. In order to reduce complication in the rotation pattern as much as possible, the measurements were made with a static field (H_0) in the *ab*, *bc*, or *ac* plane. The T_1 for the proton and that for the deuteron were measured by the pulse technique at 10 MHz. The T_1 for the proton was measured at 30 MHz. The apparatus for the measurement of the steady-state type and those of the pulse type have been described previously.[6–8]

Results

According to X-ray and neutron structure analyses[9,5] the crystal is orthorhombic, belonging

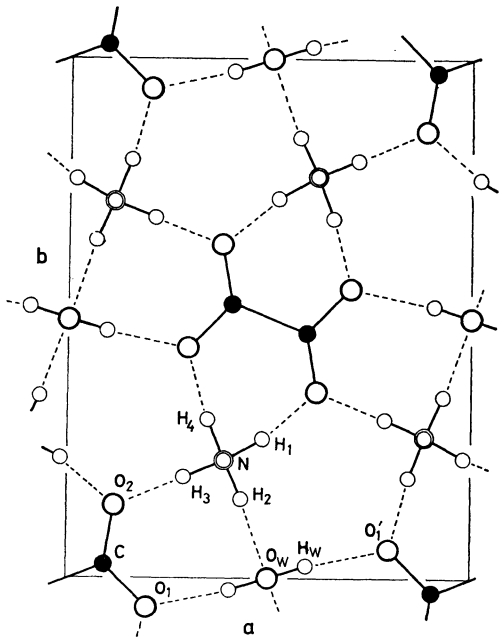

Fig 1. Crystal structure of $(NH_4)_2C_2O_4H_2O$. (001) projection.

2) V. Hovi and P. Pyykkö, *Phys. Kondens. Materie*, **5**, 1 (1966).
3) M. Linzer and R. A. Forman, *J. Chem. Phys.*, **46**, 4690 (1967).
4) D. E. O'Reilly and T. Tsang, *ibid.*, **46**, 1291 (1967).
5) V. M. Padmanabhan, S. Srikantha and S. Medhi Ali, *Acta Crystallogr.*, **18**, 567 (1965).
6) G. Soda and T. Chiba, *J. Chem. Phys.*, **50**, 439 (1969).
7) T. Chiba and Y. Kakiuchi, This Bulletin, **41**, 828 (1968).
8) T. Chiba and T. Ito, *Proceedings of the Institute of Natural Sciences, Nihon University* No. 4, Chemistry Section, (1968), pp. 15—34.
9) J. H. Robertson, *Acta Crystallogr.*, **18**, 410 (1965).

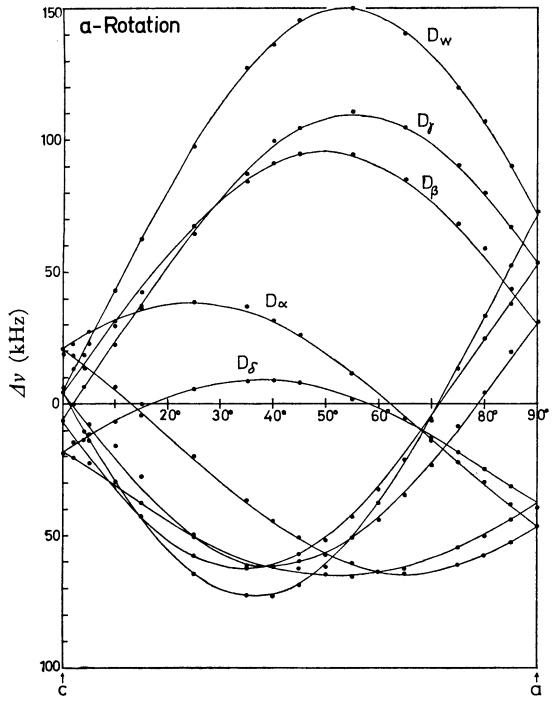

Fig. 2—1.

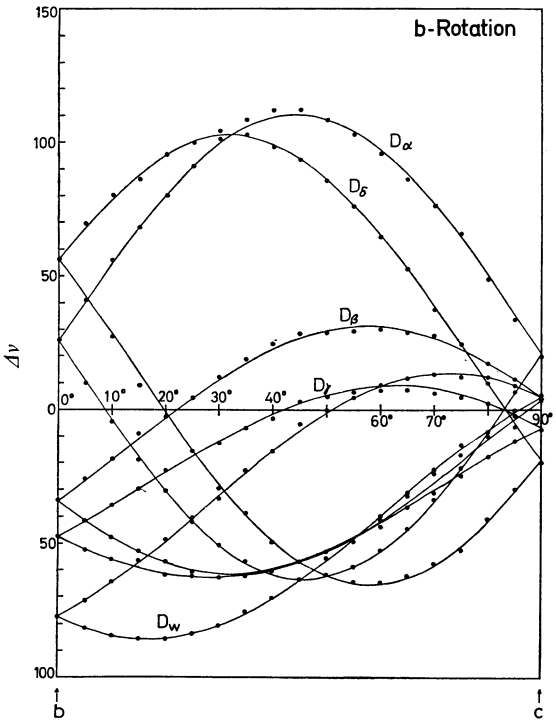

Fig. 2—2.

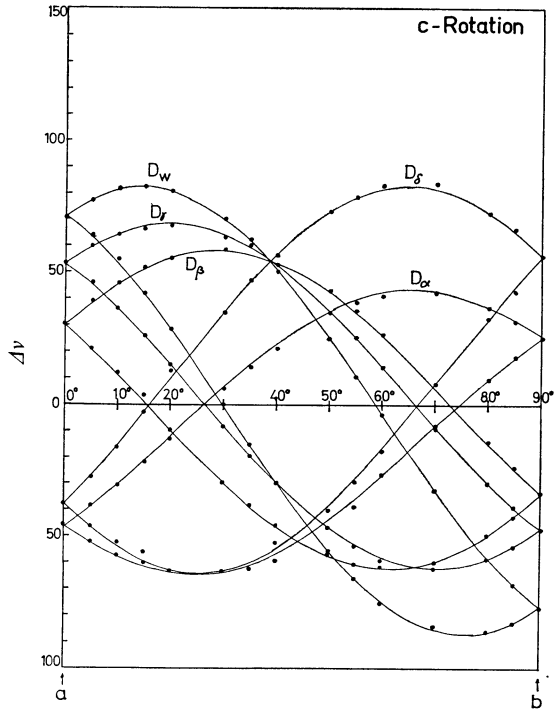

Fig. 2—3.

Fig. 2. Rotation patterns of deuteron magnetic resonance lines of $(ND_4)_2C_2O_4D_2O$ single crystal when the magnetic field is rotated about the crystalline axes *a*, *b* and *c*.

Solid lines represent calculated rotation patterns from the quadrupole coupling tensors given in Table 1.

to the $P2_12_12$ space group. A unit cell contains two formula units (Fig. 1). The ammonium ions are all crystallographically equivalent, and so are all the water molecules. Four hydrogen atoms of the ammonium ions are nonequivalent. The water oxygen atom is placed on the two-fold axis and therefore the water hydrogen atoms are equivalent. There are, thus, a total of 5 nonequivalent deuterons in the crystal of $(ND_4)_2C_2O_4D_2O$. Because a quadrupole interaction splits a deuteron resonance line into two components, from the symmetry of the crystal the maximum number of resonance-line-pairs is expected to be 10 when the static field is applied in the *ab*, *bc*, or *ac* plane, and 20 when H_0 is applied in an arbitrary direction. Spectra in accordance with the expectation are observed below -106°C. Above about -30°C a single line or a pair of lines with a small separation depending on the direction of H_0 characteristic of rapidly-reorienting ammonium ions were observed, together with the lines from the water deuterons. The water lines did not change their shape and position appreciably up to 50°C, where they started to broaden. The angular dependence of the quadrupole splitting for the stationary deuterons was measured at -110°C with H_0 in the *bc* plane (*a*-axis rotation), in the *ac* plane (*b*-axis rotation), and in the *ab* plane (*c*-axis rotation). Since the rotation patterns are symmetric about the crystalline axis direction, it is necessary only to measure the spectra for the angles between the two axes (for instance, between *b* and *c* axes in the *a*-axis rotation pattern). The rotation patterns are shown in Fig. 2.

In the first-order perturbation the frequency difference between the quadrupole-split doublet, $2\Delta\nu=\nu_+(m=1\leftrightarrow0)-\nu_-(m=0\leftrightarrow-1)$, is given by:[10]

$$2\Delta\nu = (3eQ/4h)\{-q_{ZZ}+(q_{XX}-q_{YY})\cos 2\theta + 2q_{XY}\sin 2\theta\}, \quad (1)$$

where q_{ij} is the ij element of the EFG tensor in the XYZ coordinate system and where θ is the angle of rotation of H_0 about the Z-axis in the XY plane, measured from the X-axis. The estimated angular dependence of the quadrupole splitting or the "rotation pattern" was drawn with the following assumptions for the EFG. For ammonium deuterons, the EFG is axially symmetric about the direction of the N–H bond, as determined by the neutron diffraction. For water deuterons, the z principal component of EFG, q_{zz}, is along the OH bond, as determined by the neutron diffraction; the y component, q_{yy}, is perpendicular to the H_2O plane, and the asymmetry parameter $\eta=0.1$ ($|q_{zz}|\geq|q_{yy}|\geq|q_{xx}|$). Each curve of the rotation pattern is assigned to a particular deuteron with the help of this estimated pattern. The lines of the water deuterons are generally sharp and strong and can easily be discriminated from those of the ammonium deuterons, which are relatively weak, broad, and structureless. The rotation patterns of five nonequivalent deuterons are designated as D_α, D_β, D_γ, D_δ (ammonium), and D_w (water). For ammonium deuterons, due to the complexity of the rotation patterns, the assignment of each line is not as simple as for water deuterons. However, the following fact was useful for this purpose. It is seen that each rotation pattern always has one extremum about 60 kHz from the center. We expect this to occur when H_0 is perpendicular to the z axis, and $\Delta\nu$ in this case must be negative (assuming $q_{zz}>0$). Thus, in the *c* rotation pattern, the $\Delta\nu$'s of D_α and D_δ at the *b* axis are positive and those of D_β and D_γ are negative, and the sum of the four $\Delta\nu$'s is nearly zero. The sign of $\Delta\nu$ for the *a* or *b* rotation could, then, be determined referred to the above sign by comparing the $\Delta\nu$ values in the crystalline axis directions. D_α, D_β, D_γ, and D_δ are assigned to H_4, H_1, H_3, and H_2 respectively.*1 In order to determine the eqQ tensor from the rotation patterns about the *a*, *b*, and *c* axes by the method described previously,[6] we must combine the rotation patterns of the right phase, for there are two alternative rotation patterns 90° out-of-phase to each other. The four orientations for the NH_4^+ ion and the H_2O molecule will be denoted by A, B, C, and D, for which the equivalent interatomic vectors have the (xyz), $(x\bar{y}\bar{x})$, $(\bar{x}y\bar{z})$, and $(\bar{x}\bar{y}z)$ components respectively. In the *a* axis rotation, the pattern of A overlaps that of B, and the pattern of C, that of D. In the *b* rotation, the patterns of A and C, and of B and D, overlap. In the *c* rotation, the patterns of A and D, and of B and C, overlap. The rotation patterns of $\Delta\nu$ corresponding to the site-A deuterons were chosen and were combined to determine the quadrupole coupling tensor.*2 The values of eqQ, η and the direction cosines of the principal axes are given in Table 1.

The rotation patterns for the reorienting NH_4^+ deuteron were measured at room temperature. The separations are so small that it is not possible to determine the eqQ tensor. From the observed maximum separation frequency, the value of quadrupole coupling is estimated to be about 1.5 kHz.

To estimate the rate of the reorientation of the ND_4^+ ion and to get information about the mode of

10) M. H. Cohen and F. Reif, "Solid State Physics," Vol. 5, ed by F. Seitz and D. Turnbull, Academic Press Inc., New York, (1957) p. 435.

*1 The numbering of ammonium H atoms differs between Refs. 9 and 5. In this article we use Padmanabhan's (Ref. 5).

*2 All the observed points on the two sets of rotation patterns 90° out-of-phase are included in the least-square process used to determine the quadrupole coupling tensor.

Table 1. Deuteron quadrupole couplings, asymmetry parameters, and direction cosines of principal axes (x, y, z) of field gradient tensors in the coordinate system of crystalline axes (a, b, c) in $(ND_4)_2C_2O_4D_2O$, at $-110°C$

			a	b	c
Water					
$D_w(H_w)$	eqQ/h: 213.3±0.4 kHz	x	0.569 ±0.004	0.106 ±0.016	0.816 ±0.001
	η: 0.090±0.002	y	−0.229 ±0.009	0.973 ±0.002	0.033 ±0.013
		z	0.7900±0.0005	0.2051±0.0009	−0.5778±0.0007
Ammonium					
$D_\alpha(H_4)$*	eqQ/h: 170.5±0.4 kHz	x	0.34 ±0.20	−0.57 ±0.10	0.75 ±0.01
	η: 0.009±0.003	y	−0.89 ±0.08	−0.45 ±0.13	0.06 ±0.17
		z	0.3056±0.0013	−0.6831±0.0009	−0.6633±0.0010
$D_\beta(H_1)$	eqQ/h: 163.7±0.6 kHz	x	0.45 ±0.09	0.40 ±0.14	0.80 ±0.02
	η: 0.015±0.005	y	−0.55 ±0.07	0.83 ±0.07	−0.11 ±0.13
		z	−0.7054±0.0010	−0.3860±0.0016	0.5945±0.0014
$D_\gamma(H_3)$	eqQ/h: 166.1±0.5 kHz	x	−0.61 ±0.05	0.50 ±0.40	0.62 ±0.28
	η: 0.005±0.004	y	−0.10 ±0.30	−0.82 ±0.25	0.57 ±0.30
		z	0.7865±0.0008	0.2850±0.0015	0.5479±0.0012
$D_\delta(H_2)$	eqQ/h: 172.8±0.5 kHz	x	0.86 ±0.10	0.49 ±0.10	0.14 ±0.24
	η: 0.008±0.004	y	0.35 ±0.24	−0.37 ±0.14	−0.86 ±0.04
		z	−0.3738±0.0014	0.7870±0.0008	−0.4909±0.0013

* (H_4) *etc.* are H atom sites by Padmanabhan (Ref. 5).

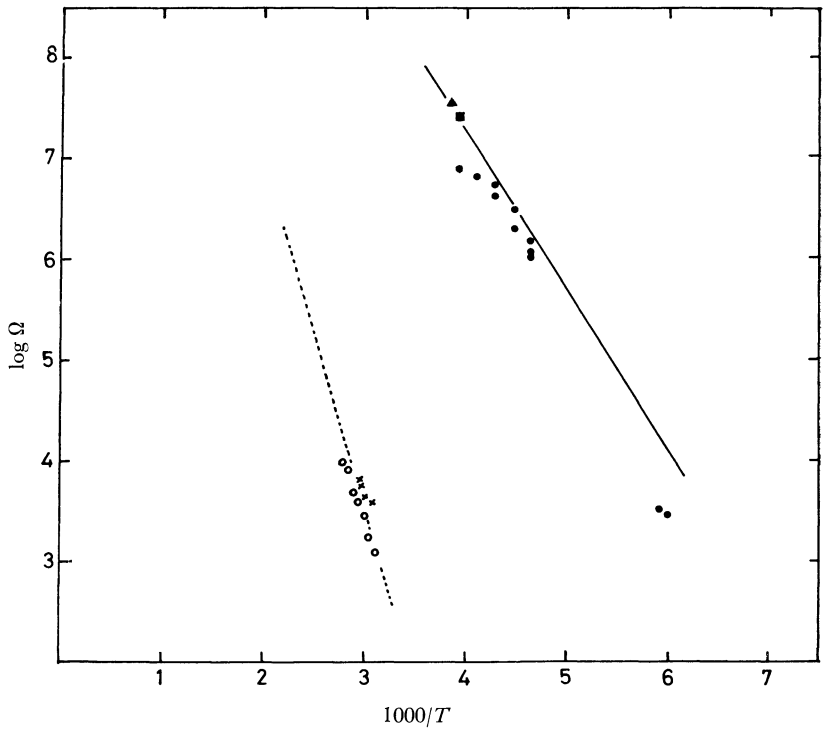

Fig. 3. Reorientation rates of water molecule and ammonium ion in $(NH_4)_2C_2O_4H_2O$. Ammonium ion (C_3) reorientation rate: ● from DMR line width change: ■ from proton T_1 minimum: ▲ from deuteron T_1 minimum. Relation of Eq. (8) is shown by a solid line. Water molecule reorientation rate: × from DMR line width change: ○ from proton $T_{1\rho}$. Dotted line corresponds to ΔE of 15.5 kcal/mol.

the motion, the line broadening of the spectra in the limits of rapid motion and of slow motion were observed. As will be mentioned in the next section, we assume only C_3 reorientations for the motion of the NH_4^+ ion in this crystal. In the case of isotropic reorientation, the average rate, Ω, of C_3 reorientation about one of the four axes is related to the average lifetime, τ, for a hydrogen atom to be in one of the four equilibrium positions by:

$$3\Omega = 1/\tau . \quad (2)$$

From the theory of the motional broadening of the spectral line,[11] we have, for the rapid limit spectra:

$$\Delta\nu_M = \frac{\pi}{8\Omega}\sum(\Delta\nu_i)^2 , \quad (3)$$

and, for the slow limit spectra:

$$\Delta\nu_M = \frac{3}{2\pi}\Omega , \quad (4)$$

where $\Delta\nu_M$ is the line width due to the motion and where $\Delta\nu_i$ is the separation from the average frequency (here, the Larmor frequency) of the line of the stationary i-th deuteron. The broadening process is observed with H_0 in the a- and b-axisdirections. (The rapid-limit spectra, except when H_0 is in the crystalline axis directions, consist of two-line components with different degrees of broadening.) The values of $\Delta\nu_M$ at the two limiting cases were estimated by an approximate procedure from the observed line width, which includes the dipolar width.[7] These values were then used to derive the reorientation rate, Ω, of the ND_4^+ ion. The results are shown in Fig. 3. From the slope of this plot, the activation energy of reorientation, ΔE, is estimated to be 8.8 kcal/mol. The effect of the possible anisotropy of the motion will be discussed in the next section.

The lines of water deuterons start to broaden at about 50°C. The line-broadening process of water deuterons was observed, and the rate of reorientation was estimated in the same way as was done in the case of other hydrates. The reorientation rates thus derived are shown in Fig. 3.

The results of pulse measurements are shown in Fig. 4. It can be seen in this figure that the temperature dependence of the T_1 of both the proton and the deuteron is adequately explained by the reorientational motion, whose correlation frequency is expressed by the Arrhenius equation. The relevant motion is that of the NH_4^+ ion. The T_1 values will be analyzed in the next section. As is to be exprected from the theory, the log $T_{1\rho}$ *vs.* $1/T$ plot is roughly a straight line, coinciding with the log T_1 curve at the high-temperature side of the minimum and then extending further to low temperatures. The $T_{1\rho}$ could not be measured down to its minimum because of the instrumental difficulty. Above 50°C $T_{1\rho}$ starts to drop again.

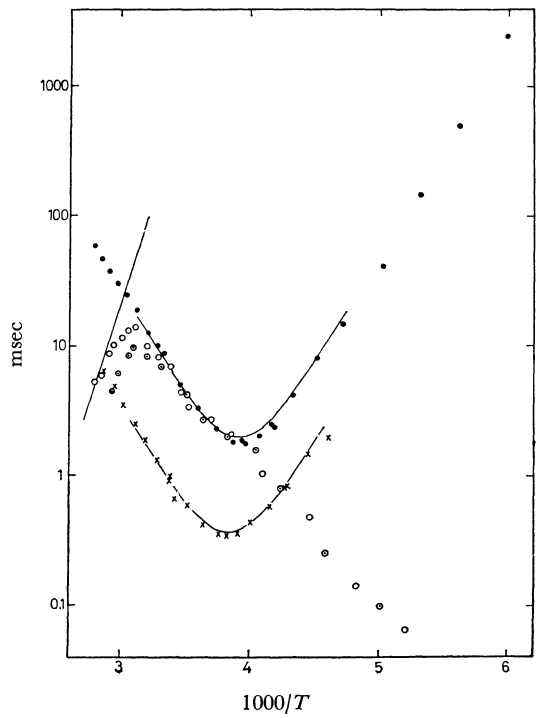

Fig. 4. Temperature dependence of the relaxation times of ammonium oxalate monohydrate powder samples.
● Proton T_1 ○ Proton $T_{1\rho}(H_1=6G)$
⊙ Proton $T_{1\rho}(H_1=4G)$ × Deuteron T_1
The straight line at the left represents $T_{1\rho}$ due to 180° flip of H_2O. Curves through T_1 minima are from Eqs. (5), (7) and (8).

This is considered to be due to the effect of the reorientation of the water molecule and will be discussed in the next section.

Discussion

In 1965, almost concurrently two independent works on the structure analysis of ammonium oxalate monohydrate were published; one was a refinement of the X-ray analysis at 30°K by Robertson,[9] and the other was a neutron diffraction study by Padmanabhan *et al.*[5] In view of the practical limits of precision of the two techniques, we will quote, in comparing the structure and EFG tensors, the heavy-atom coordinates from the X-ray study and the NH and OH bond directions from the neutron study.

Quadrupole Coupling Values. As has been discussed previously, the correlation between the O–D···O hydrogen bond length and the eqQ/h of D is fairly well represented by an empirical curve[12] or by empirical formulas.[6] The value of eqQ/h 213.3±0.4 kHz for the water deuteron is a reasonable value for a "fairly strong" hydrogen

11) P. W. Anderson, *J. Phys. Soc. Jap.*, **9**, 316 (1954).

12) T. Chiba, *J. Chem. Phys.*, **41**, 1352 (1964).

Table 2. Deuteron quadrupole coupling values, N-H bond distances and N···O hydrogen bond distances

	eqQ/h (kHz)	N-H[a] (Å)	N···O[b] (Å)
H_1	163.7	1.02	2.803
H_2	172.8	1.03	2.879
H_3	166.1	1.01	2.830
H_4	170.5	1.03	2.833

a) Ref. 5, mean standard deviations for bond lengths: 0.023 Å.
b) Ref. 9, estimated standard deviation of N···O lengths: 0.006 Å.

bond with an O-O length of 2.743 Å, and it falls on the empirical curve. This value is close to that of 209.7±2.5 kHz for D in $K_2C_2O_4D_2O$,[13] which has nearly the same hydrogen bond length, 2.744± 0.017 Å.[14] In Table 2 the eqQ values of ammonium deuterons are listed, along with the corresponding N—O hydrogen bond distances and N-H bond distances. The values of eqQ/h decrease as the N—O distance decreases and as the N-H distance increases. The correlation between eqQ and the N-D···O hydrogen bond length, similar to that in the O-D···O hydrogen bond system, is quite apparent. Table 3 lists some of the deuteron quadrupole coupling constants in the N-D bonds. It seems that it would be very interesting to know whether a curve similar to the one for the O-O system can be drawn of eqQ *vs.* the N-O distance, with $eqQ/h=282$ kHz as the limit of the weakest hydrogen bond. However, a few more experimental data must be added before this can be done.

Table 3. Deuteron quadrupole couplings, asymmetry parameter and N···O hydrogen bond distances in some N-H systems*

	eqQ/h (kHz)	η	N···O distance (Å)
$CO(NH_2)_2$	211[a]	0.14	3.00[b]
$(NH_4)_2SO_4$	174[c]	(0)	2.92[d]**
NH_4Cl	180.1±1.0[e,f]	0±0.01	
NH_4Br	180[e]	0	
NH_3(Solid, 75°K)	156±7[g]	0—0.3	
(Free molecule)	282±12[h]	0.05±0.06	
$(NH_4)_2C_2O_4H_2O$	168.3	0.01	2.84

* Average value is listed when more than one value are involved.
** Bifurcated or trifurcated long hydrogen bonds are not included.
a) T. Chiba, This Bulletin, **38**, 259 (1965).
b) A. Caron and J. Donohue, *Acta Crystallogr.* **17**, 544 (1964).
c) Ref. 4.
d) E. O. Schlemper and W. C. Hamilton, *J. Chem. Phys.* **44**, 4498 (1966).
e) Ref. 2.
f) Ref. 3.
g) S. W. Rabideau and P. Waldstein, *J. Chem. Phys.*, **45**, 4600 (1966).
h) P. Thaddeus, L. C. Krisher and P. Cahill, *ibid.*, **41**, 1542 (1964).

Structure of Water Molecules. The direction of the z principal axis of the water deuteron is in good agreement with the O-H bond direction obtained from the neutron diffraction, the deviation being only 3.0°. The angle between the z axes of the two water deuterons in the water molecule is 109.4°. It should be noted that the plane containing two z principal axes makes an angle of 14.6° with the crystalline a axis; this angle is in excellent agreement with 15.2°, the angle between the O_1–O_w–O_1' plane and the a axis, in contrast to a fairly large twisting of the water molecule in the hydrogen bond system (4.6° between O_1–O_1' and H_w–H_w' directions) reported in the neutron diffraction study. The principal y axis of EFG of the water deuteron is nearly perpendicular (within 2.3°) to the plane formed by the two z axes, which is in accord with the empirical relation about the y axis.[12,15]

Structure of Ammonium Ions. The directions of the z principal axes of the EFG tensors in the ND_4^+ ions are approximately in the N-H directions, as determined by the neutron diffraction, but the deviation angles, 5.2°, 2.3°, 4.6°, and 7.3° for NH_1, NH_2, NH_3, and NH_4 respectively, are somewhat larger than those usually found. The mean standard deviations in bond angles from the neutron diffraction study are estimated to be 1.9°, and the standard deviation of the z direction in this study is well below 1°. Therefore, these deviation angles exceed the limits of experimental error. The angles between the z principal axes in the ND_4^+ ion are quite close to the tetrahedral angle, as is shown in Table 4. A comparison of these with the HNH angles from the neutron diffraction study indicates a rather large distortion of the NH_4^+ tetrahedron. The small deviation angles from perfect parallelism of the z axis of the deuteron EFG with the bond direction determined from the diffraction study may be attributed to the effect of charges from the atoms which are not directly bonded to the hydrogen atom in question. In the present case of the ND_4^+ ion, however, it seems rather unrealistic that a nearly tetrahedral arrangement of the EFG tensors is due to the effect of nearby atoms on an otherwise considerably dis-

13) J. W. McGrath and G. W. Ossman, *J. Chem. Phys.*, **46**, 1824 (1967).
14) R. Chidambaram, A. Sequeira and S. K. Sikka, *ibid.*, **41**, 3616 (1964).
15) T. Chiba and G. Soda, "Magnetic Resonance and Relaxation," Proc. 14th Colloque Ampère, Ljubljana, North-Holland Publ. Co., Amsterdam (1966), p. 722.

TABLE. 4. DEVIATION FROM 109.5° OF HNH ANGLES DETERMINED BY DMR, AND BY NEUTRON DIFFRACTION STUDY (in the parentheses)

	H_1	H_2	H_3
H_2	−0.1 (−0.6)		
H_3	+0.3 (+7.6)	+0.3 (−4.4)	
H_4	+0.8 (−5.2)	−0.5 (+1.9)	−1.0 (+0.1)

torted arrangement of the z principal axes along the N-D bonds. The parallelism between the N–O directions and the z axis is to be compared with that between the N-O and N–H directions. The average angle of deviation of the N–H···O hydrogen bond from perfect linearity, assuming that the N–H bond is in the direction of the z axis, is 7.5°, while that determined by the neutron diffraction is 6.0°. Therefore, in this respect at least, the N–D bonds directed in the z axes can be almost as reasonable as the directions given by the neutron diffraction.

Let us now consider a few possible causes of these rather large discrepancies between the bond directions derived from the two methods:

a) The isotope effect as the cause of discrepancies—that is, the NH_4^+ ions in this compound are distorted, while the ND_4^+ ions are not. The changes in the bond angles seem to be too large to be ascribed to an isotope effect, however, and it is difficult to find any particular reason for such a large effect to be operative in this case.

b) The z principal direction not in the true bond direction—(1) crystalline field effect. External charges in the crystal to the EFG, the type of effect considered previously,[16,17] would cause a deviation of the z axis from the bond direction. However, it seems too artificial to say that such an effect results in the regular tetrahedral arrangement of the z directions. (2) Bent orbital effect. Assume that the bond orbitals of N are tetrahedrally directed, but the the H–N–H angle, for instance, is larger than the tetrahedral angle because of a force in intermolecular nature. In such a bent orbital or incomplete orbital-following case, the center of the overlap charge of the bond orbitals of N and H are located slightly inside the HNH triangle. A negative contribution to the EFG from this charge will have the effect of tipping the z principal axis of the total EFG at H (which is positive) in such a way that the angles between the two z directions of EFG will be closer to the tetrahedral angle than the actual HNH angle. When the HNH angle is smaller than the tetrahedral angle, the situation is reversed and again the HNH angle becomes closer to the tetrahedral angle. At least qualitatively, this seems to be a plausible explanation; it could also favorably account for the smaller net distortion of eqQ from a regularly tetrahedral arrangement in ammonium sulfate than that expected from structure analysis.[4] We have, however, no estimate of the magnitude of this effect at present. Moreover, in the case of ammonium dihydrogen phosphate (ADP), distortion from the tetrahedral symmetry determined by neutron diffraction is consistent with that estimated from the quadrupole interaction[17] despite the fact that, from the symmetry at the site of ND_4^+, a pronounced effect of deviation from the orbital following is to be expected.*3 Another experimental evidence against the above view is to be found in the deuteron-quadrupole coupling in some C–ND_3 systems where there is a rapid reorientation of the ND_3 group about the C–N bond. In triglycine sulfate, eqQ values ranging from 37.3 to 54.8 kHz have been reported from various ND_3 sites of para- and ferro-electric phases.[18,19] For CH_3ND_3Cl we obtained an eqQ value of 45 kHz from the room-temperature powder spectrum. In these cases the quadrupole coupling is given approximately by $eq_0Q(1-3\cos\theta)2$, where θ is the angle between the z axis of EFG of D at rest and the C–N bond and where q_0 is the magnitude of this EFG. Though q_0 should vary from one compound to another, the wide distribution of the observed eqQ values can be attributed to a wide distribution in θ. A definite conclusion as to the validity of the above effect must, however, be deferred until a quantitative calculation is made for this effect and until the measurements of the DMR as well as of the neutron diffraction are made on various ammonium salt crystals. Such studies seem to be of great importance because, in view of the usefulness of DMR as a means of determining the bond direction of H–(X), the limitations of this technique should be well established.

The averaging of the four quadrupole coupling tensors of the ND_4^+ ion gives $eqQ/\hbar = -1.67$ kHz and $\eta = 0.92$, values consistent with the small quadrupole coupling value of ~1.5 kHz observed at room temperature. Since the principal z directions of EFG did not agree with the bond directions by neutron diffraction, no general conclusion can be drawn concerning the relation between the averaged quadrupole coupling in the rapidly reorienting ND_4^+ ion and the distortion of the ion. However, judging from the close correlation of eqQ values with the N···O distances,

16) T. Chiba, *J. Chem. Phys.*, **36**, 1122 (1962).
17) T. Chiba, This Bulletin, **38**, 490 (1965).

*3 In the tetragonal phase of ADP, NH_4^+ forms a slightly "flat" tetrahedron (site symmetry: D_{2d}) In this structure it is not possible to form 4 equivalent orthogonal orbitals of N directed in the N–H directions from s and p orbital hybridization.

18) J. L. Bjorkstam, *Phys. Rev.*, **153**, 599 (1967).
19) R. Blinc, M. Pintar and J. Zupančič, *J. Phys. Chem. Solids*, **28**, 405 (1967).

it appears that the average eqQ is determined mainly by the local structure of the ion and that the crystalline field effect is relatively unimportant.

Motion of Ammonium Ions. For an NH_4^+ tetrahedron, reorientational motions can either by about its C_2 axes or about its C_3 axes. In ammonium halides where the crystal structure is such that a rotation about the C_2 axis is subject to a four-fold potential, 90° reorientations about the C_2 axes are considered to be the substantial ones. When the NH_4^+ ion is held by four hydrogen-bond-acceptor oxygen atoms in a nearly tetrahedral arrangement, the potential barrier to the C_3 reorientation is considered to be less than that to the C_2 reorientation, for the former requires 3 hydrogen bonds to be broken in the course of the rotation, while the latter requires 4 bonds to be broken. Therefore, we assume only C_3 reorientations in the present case.

Suppose the rate of reorientation about the N–H_1 axis, Ω_1, is different from that about the other 3 axes (N–H_2, N–H_3, and N–H_4), Ω_2. Then the probability for a given hydrogen atom in site 1 to be transferred to other sites is $3\Omega_2$, while the corresponding probability for Sites 2, 3 and 4 is $2\Omega_2+\Omega_1$. The width due to motion at the slow exchange limit (measured in angular frequency units) of a line corresponding to a particular site is just the probability of a jump from that site to others. For instance, if $\Omega_1=2\Omega_2$ the width due to the motion of the Site-1 line relative to that of the Site-2 line at the slow exchange limit will be 0.75, and if $\Omega_1=1/2\Omega_2$ it will be 1.20. The spectra near the limit of the slow exchange rate when H_0 is in the b axis direction are shown in Fig. 5. At −110°C where deuterons are practically stationary, the lines corresponding to the four sites (D_1, D_2, D_3, and D_4) are separately observed with approximately the same intensity.

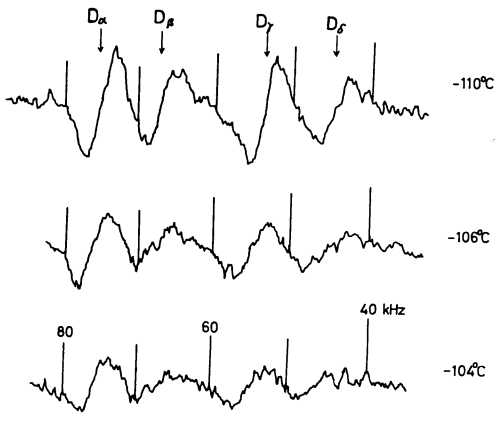

Fig. 5. Ammonium deuteron lines at the slow exchange limit recorded with H_0 in the b axis direction.

The broadened spectra at −106°C and at −104°C show no appreciable difference in the extent of broadening among the four lines. In view of the high sensitivity of the signal height as recorded as a derivative curve to the line-broadening effect, it can safely be said that the ratio of the motional line-width between any two of the four lines is well within the 0.75—1.20 range. Therefore, the reorientation of the NH_4^+ ion is considered to be quite isotropic.*4 If it is further assumed that Ω_1 and Ω_2 are governed by Arrhenius equations with the same pre-exponential factor, $\Omega_1=\Omega_0\exp(-\Delta E_1/RT)$ and $\Omega_2=\Omega_0\exp(-\Delta E_2/RT)$, $\Omega_1/\Omega_2=2$ or 0.5 gives, at −105°C, $\Delta\varepsilon=\Delta E_1-\Delta E_2=\pm 233$ cal/mol. From the rough estimate given above, it appears that the difference in the activation energy is quite small. This conclusion is unaltered when more than two different Ω values are involved. If one considers the hydrogen-bond energy to be a main factor in determining ΔE, one may conclude that the difference in hydrogen-bond energy in the four bonds is rather small, although a fairly large difference in hydrogen-bond lengths has been reported from the X-ray study. This is in contrast to the case of the H_2O flip motion, where a marked dependence of ΔE on the hydrogen-bond distance is seen.[6]

The average proton relaxation time for reorienting NH_4^+ ions (the intraionic effect only) in a powdered sample is given by O'Reilly and Tsang[4] as:

$$\frac{1}{T_1}=(1.91\times10^{10})\left(\frac{\tau_c}{1+\omega^2\tau_c^2}+\frac{4\tau_c}{1+4\omega^2\tau_c^2}\right) \qquad (5)$$

where τ_c is related to the τ in Eq. (2) as:

$$\tau_c=3\tau/4\,. \qquad (6)$$

with $\omega=2\pi\times10^7$ sec^{-1}, Eq. (5) gives a T_1 minimum of 2.27 msec at $\omega\tau=0.62$, or $\tau=1.31\times10^{-8}$ sec^{-1}. Since the cross-relaxation time between protons in the NH_4^+ ion and the H_2O molecule in the crystal must be much shorter than this T_1 value, the 10 protons in $(NH_4)_2C_2O_4H_2O$ are to be relaxed by this mechanism instead of the 8 protons in $2(NH_4)$. Therefore, the actual T_1 minimum will be $(10/8)\times$ 2.27 msec=2.84 msec. The observed T_1 minimum is 2.6 msec at T=254°K. Since the interionic contribution to relaxation is not included in Eq. (5), the agreement is quite satisfactory.

In the deuteron resonance, T_1 is determined almost entirely by the quadrupole interaction. The pulse experiment is made on the deuteron line of the reorienting ND_4^+ ion, which has a nearly zero spliting. Therefore, water deuterons which

*4 After this work had been completed we learned that, in a suitable temperature range, the $NaND_4SO_4$-$2D_2O$ crystal exhibits the DMR spectra of the ND_4^+ ion under rapid reorientation about a single C_3 axis (D. J. Genin and D. E. O'Reilly, *J. Chem. Phys.*, **50**, 2842 (1969)).

have a large splitting are not involved in the observed T_1 practically. The theoretical expression for the quadrupole relaxation in the present case is given in the Appendix. When numerical values $(eqQ/\hbar)=168$ kHz and $\omega=6.28\times10^7$ sec^{-1} are substituted in Eq. (A9), the T_1 for a powdered sample will be given by:

$$\frac{1}{T_1}=(8.36\times10^{10})\left(\frac{\tau}{1+\omega^2\tau^2}+\frac{4\tau}{1+4\omega^2\tau^2}\right). \quad (7)$$

The T_1 minimum is attained when $\omega\tau=0.62$ or $\tau=0.98\times10^{-8}$ sec. The calculated T_1 minimum= 0.53 msec is in good agreement with the experimental value, 0.52 msec, observed at 262°K.

The values of the reorientation rate $\Omega(=1/3\tau)$ at the temperature of the T_1 minima derived above for the proton and the deuteron are found to be in satisfactory agreement with the results from the line-width transition, as may be seen in Fig. 3. The values of the activation energy, ΔE, derived from the high- and low-temperature-side slopes of the T_1 minima of log T_1 *vs.* $1/T$ curves are:

	From the high-temp. slope	From the low-temp. slope
Proton	7.07 kcal/mol	7.46 kcal/mol
Deuteron	7.27 kcal/mol	

Averaged: 7.27 kcal/mol.

With this average value of ΔE, the best fits of τ at the T_1 minimum for both the proton and the deuteron are obtained by:*5

$$\tau=10^{-14.1}\exp(7.27/RT). \quad (8)$$

log T_1 *vs.* $1/T$ curve near the T_1 minimum, calculated from Eqs. (5) and (8) for the proton and from Eqs. (7) and (8) for the deuteron, are drawn in Fig. 4. The agreement with the observed data is satisfactory.

The ΔE value of 7.27 kcal/mol obtained from the proton and deuteron relaxation times is probably more reliable than that obtained from the line-width transition. This value is higher than those for most of the ammonium salts, indicating fairly strong hydrogen bonds holding the ammonium ion.

In Fig. 3 a serious disagreement is found between the Ω derived from the line broadening at the slow exchange limit and that derived from Eq. (8) (shown by the solid line). This might seem to indicate a variation in activation energy at low temperatures. However, in the temperature dependence of T_1 in Fig. 4 no such effect is indicated. The reason for this disagreement is not clear.

Motion of Water Molecules. As has been stated before, the broadening of the water-deuteron line at about 50°C is considered to be due to the 180° flip motion about the bisector axis of the water molecule. The line broadening takes place at a considerably higher temperature than in most of the hydrates studied thus far. The water of hydration is lost before the temperature reaches the point where the motion is rapid enough to allow observation of the averaged spectrum. We estimate the value of activation energy from the reorientation rate derived from the line broadening at the slow exchange limit, assuming a pre-exponential factor of the reorientation rate to be 10^{14} sec^{-1}, a value often found for water of hydration.[6] The value of $\Delta E=15.5$ kcal/mol thus derived is the highest value obtained thus far for the 180° flip motion of water molecules. It is interesting that, in a crystal with a similar composition, $K_2C_2O_4H_2O$, a high activation energy of 14 kcal/mol has been reported.[20] In this latter compound, DMR line broadening begins just above room temperature.[13] The high activation energies in these crystals are parallel with the short hydrogen-bond distances and the small deuteron-quadrupole coupling values.

A short drop of the $T_{1\rho}$ of the proton at the high temperature in Fig. 4 can also be understood as associated with the 180° flip motion of water molecules. Since the *rf* field strength, H_1, used in the measurement of $T_{1\rho}$ is comparable to the local field, and since $T_{1\rho}$ decreases with an increase in the temperature, that is, with an increase in the assumed reorientation rate of the H_2O motion, the $T_{1\rho}$ in this range must be determined by the mechanism of "slow motion." Such cases have been dealt with by Slichter and Ailion.[21] $T_{1\rho}$ is given by the formula:

$$\frac{1}{T_{1\rho}}=\frac{2}{\tau}(1-p)\frac{H_L'^2}{H_L'^2+H_1^2}, \quad (9)$$

where $1/\tau$ is the rate of the motion and H_L' is the local field in the rotating frame and is related to the second moment, $\langle\Delta H^2\rangle$, by $H_L'^2=(1/3)\langle\Delta H^2\rangle$. The $1-p$ factor gives a measure of the effectiveness of the motion to the relaxation, and when the nuclei exchange positions between two sites, r and q, it is given by:

$$1-p=\sum_i(A_{ir}-A_{iq})^2/\{\sum_i(A_{ir}^2+A_{iq}^2)+\sum{}'A^2\} \quad (10)$$

where $A_{ab}=(3\cos^2\theta_{ab}-1)/r_{ab}^3$. r_{ab} is the length of the internuclear vector, $\boldsymbol{r}_{ab}$, joining a spin at Site a to that at Site b, and θ_{ab} is the angle between H_0 and $\boldsymbol{r}_{ab}$. The suffix i refers to all the stationary spins which interact with the spins, r and q, in

*5 The pre-exponential factor is dependent on the mass difference of H and D by a factor $1/\sqrt{2}$ (see Ref. 4, Appendix). In the present case, however, since unknown isotope effects of various origin may also be involved, the small correction of $1/\sqrt{2}$ is ignored.

20) J. W. McGrath and A. A. Paine, *J. Chem. Phys.*, **41**, 3551 (1964).

21) C. P. Slichter and D. Ailion, *Phys. Rev.*, **135**, A1099 (1964).

motion. The last term in the denominator represents a sum over all the spin-pairs which are motion-independent (including A_{rq}^2). To apply Eq. (9) to the present measurements, which are made on powdered samples, $1-p$ must be averaged over the direction of H_0. The denominator of Eq. (10) is just the lattice part of the second moment. The evaluation of the angular average of Eq. (10), $(1-p)_{AV}$, can be done by numerical integration, but would be quite laborious to perform. For the present discussion it may be sufficient to estimate $(1-p)_{AV}$. For this purpose it may be permitted to approximate it by taking the angular averages of the numerator and denominator separately. A second moment of about 7.5 G^2 is obtained from the powder spectrum of proton resonance at room temperature. Thus, the denominator averaged over the H_0 direction will be:

$$\langle \text{denom.} \rangle_{AV} = \langle \Delta H^2 \rangle / (4/5) \cdot (3/4) \hbar^2 I(I+1) = 0.021 \text{ Å}^{-6} .$$

For the evaluation of the numerator, a sum is taken over all the inter-proton pairs between a given H_2O molecule and the nearest 8 NH_4^+ ions. A can be expressed in terms of the inter-proton vectors and the H_0 directions in the coordinate system of the crystalline axes. The angular average is readily made, and

$$\langle \text{num.} \rangle_{AV} \simeq 0.0022 \text{ Å}^{-6} .$$

We get $(1-p)_{AV} \sim \langle \text{num.} \rangle_{AV} / \langle \text{denom.} \rangle_{AV} = 0.1$.

At $H_1 = 6$ G, from Eq. (9) the $T_{1\rho}$ due to the H_2O motion is given by:

$$\frac{1}{(T_{1\rho})_{H_2O}} = \frac{2}{\tau} \times 0.1 \times \frac{(7.5/3)}{(7.5/3)+6^2} = \frac{1}{\tau} \times \frac{1}{77} \quad (11)$$

Near the $T_{1\rho}$ maximum, $1/T_{1\rho}$ consists of contributions from the H_2O motion and the NH_4^+ motion; that is, $(T_{1\rho})_{obs}^{-1} = (T_{1\rho})_{H_2O}^{-1} + (T_{1\rho})_{NH_4}^{-1}$. Since, in this case $\omega\tau \ll 1$ for the NH_4^+ motion, $(T_{1\rho})_{NH_4} \approx (T_1)_{NH_4}$ (see Eqs. (10) and (16) of Ref. 4). $(T_{1\rho})_{H_2O}$ is obtained from $(T_{1\rho})_{obs}$ by assuming $(T_{1\rho})_{NH_4}$ to be equal to the observed proton T_1. The values of $1/\tau (= \Omega)$ calculated from Eq. (11) at temperatures above 48°C are plotted in Fig. 3. The agreement of this result with that from the line-width change is satisfactory, considering the approximations in the analysis.*6 From the slope of $\log (T_{1\rho})_{H_2O}$ *vs.* $1/T$ curve in Fig. 4, an activation energy for the H_2O motion of about 14 kcal/mol is obtained; in view of the limited temperature range observed, this value is in good agreement with the 15.5 kcal/mol estimated in the previous section. Thus, the sharp drop of $T_{1\rho}$ at the high temperatures can be reasonably accounted for by the motion of the H_2O molecule in consistency with the line-width change of the D_2O spectra at these temperatures. It should be noted, however, that similar sharp drops of $T_{1\rho}$ are often observed in some ammonium salts at high temperatures; these drops may be considered to be due to the diffusional motion of the NH_4^+ ion or its fragments. We cannot exclude the possibility that, in the case of ammonium oxalate monohydrate, such effect is involved.

*6 Actually, in the present case H_1 (=6 G) is considerably larger than H_L'. Therefore, the application of the low-field relaxation formula of Eq. (9) may not be appropriate. However, since the difference between the high-field relaxation formula and the low-field one is small (Ref. 21, pp. 1103A—1104A), this does not have serious effect on the conclusion.

The author would like to thank Mr. Masaki Funakoshi for his great assistance in the preparation of the crystal and in the NMR measurements. Most of the measurements and the computor processing of the data were made at the Institute for Solid State Physics, the University of Tokyo. The author wishes also to thank the Institute for the use of its facilities.

Appendix

The expression for the T_1 of the deuteron is obtained from the standard treatment of the spin-lattice relaxation by a random modulation of a quadrupole interaction due to ND_4^+ reorientations. Assume an isotropic C_3 reorientation of a regularly-tetrahedral ND_4^+ ion. Let τ_c be the correlation time for this motion. The mean residence time of a spin in one site, τ, is then given by:

$$1/\tau = 3/4\tau_c \quad (A1)$$

The probability that a spin at Site 1 at $t=0$ remains in that site at $t=t$ is given by $\{1+3\exp(-t/\tau)\}/4$, and the probability that it is transferred to one of the other sites, by $\{1-\exp(-t/\tau)\}/4$. Therefore, the autocorrelation function of a given component of the EFG tensor, F, for a spin at Site 1 at $t=0$ will be:

$$F(0)F^*(t) = 1/4\{|F_1|^2(1+3x) + (F_1F_2^* + F_1F_3^* + F_1F_4^*)(1-x)\} , \quad (A2)$$

where $F_i(t)$ denotes that EFG component for a given spin at Site i at time t and $x \equiv \exp(-t/\tau)$. Since, at $t=0$, the probability of a spin in a particular site is 1/4, it follows that:

$$\langle F(0)F^*(t) \rangle_{AV} = \frac{1}{16}\{(1+3x)\Sigma_i |F_i|^2 + 2(1-x) \Sigma_{i>j} |F_iF_j|\} . \quad (A3)$$

The power spectrum of F at an angular frequency, ω, $I(\omega)$, is given by:

$$I(\omega) = \int_{-\infty}^{\infty} \langle F(0)F^*(t) \rangle e^{i\omega t} dt = \left\{\frac{3}{16}\Sigma_i |F_i|^2 + \frac{1}{8}\Sigma_{i>j} |F_iF_j|\right\} j(\omega) = \left\{\sum_{i>j} \frac{1}{16} |F_i - F_j|^2\right\} j(\omega) , \quad (A4)$$

with:

$$j(\omega) = 2\tau/(1+\omega^2\tau^2) . \quad (A5)$$

For deuterons ($I=1$), T_1 is given by:

$$1/T_1 = P_1 + 2P_2\,, \tag{A6}$$

where:

$$P_1 = (e^2Q^2/8\hbar^2)I^{(1)}(\omega) \text{ and } P_2 = (eQ^2/8\hbar^2)I^{(2)}(2\omega)\,. \tag{A7}$$

In $I^{(1)}(\omega)$ and $I^{(2)}(2\omega)$, the components of the EFG tensor relevant to $\Delta m=\pm 1$ and ± 2 transitions respectively are to be used for F's of Eq. (A4). Thus, for $I^{(1)}(\omega)$, $|F_i-F_j|^2$ in Eq. (A4) will be $\{(\varphi_{xz})_i-(\varphi_{xz})_j\}^2 + \{(\varphi_{yz})_i-(\varphi_{yz})_j\}^2$, and for $I^{(2)}(2\omega)$, it will be $[\{(\varphi_{xx})_i - (\varphi_{xx})_j\} - \{(\varphi_{yy})_i - (\varphi_{yy})_j\}]^2 + 4\{(\varphi_{xy})_i - (\varphi_{xy})_j\}^2$, where $(\varphi_{ab})_i$ denotes the ab element of the EFG tensor at Site i. We take, for convenience, a coordinate system of an ND_4^+ ion such that the x, y, and z axes coincide with their C_2 axes. φ's are expressed in terms of the EFG component along the D-N bond direction, q, and the direction cosines (l, m, n) of H_0 in the assumed coordinate system.

The expression of T_1 for an arbitrary direction of H_0 are computed following the procedure of O'Reilly and Tsang.[4] The symmetry consideration leads to the expression for P in Eq. (A7) of the form:

$$P = C_1 + C_2(l^4+m^4+n^4)\,.$$

where C_1 and C_2 are the factors to be determined. To do this it is only necessary to calculate P for two independent cases of H_0 direction, where such calculations are most conveniently made, and to solve the simultaneous equations thus obtained for C_1 and C_2. The expression for T_1 thus obtained is:

$$\frac{1}{T_1} = \frac{(eqQ)^2}{8\hbar^2}\left[(l^4+m^4+n^4)\frac{\tau}{1+\omega^2\tau^2} + \{3-(l^4+m^4+n^4)\}\frac{\tau}{1+4\omega^2\tau^2}\right] \tag{A8}$$

with a powdered sample, T_1 varies from one microcrystallite to another as $(l^4+m^4+n^4)$ takes values between 1 and 1/3, but since the orientation dependence of T_1 seen from Eq. (A8) is mild, the average T_1 measured for powdered sample may be compared with the theoretical expression, Eq. (A8), averaged over H_0 directions, as is done in the discussion of the proton T_1. Thus $\langle l^4+m^4+n^4\rangle_{AV}=3/5$ gives:

$$\frac{1}{(T_1)_{\text{powder}}} = \frac{3\pi^2}{10}\left(\frac{eqQ}{h}\right)^2\left(\frac{\tau}{1+\omega^2\tau^2}+\frac{4\tau}{1+4\omega^2\tau^2}\right) \tag{A9}$$

which is just the expression for quadrupole relaxation by the isotropic random rotation of the molecule.[22]

22) A. Abragam, "The Principles of Nuclear Magnetism," Oxford University Press (1961), p. 314.