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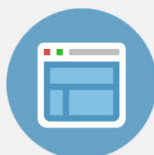
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cause the computed value of the property to depend on the origin taken for the vector potential. It also is clear that caution must be exercised in applying sum rules to estimate the excited state parts. With a single average excited state energy the excited state part of the magnetic susceptibility for a hydrogen atom can be estimated for any origin of the vector potential. However, no single average excited state energy can give a correct sum rule estimate of the excited state contribution to the nuclear magnetic shielding for all positions

of the test magnetic dipole. The presence of these difficulties in the perturbation method should encourage the continued investigation of variation or other methods<sup>13-17</sup> as the way to achieve quantitative computation of the magnetic properties of molecules.

<sup>13</sup> M. J. Stephen, Proc. Roy. Soc. (London) **A242**, 264 (1957).

<sup>14</sup> B. R. McGarvey, J. Chem. Phys. **27**, 68 (1957).

<sup>15</sup> J. A. Pople, Proc. Roy. Soc. (London) **A239**, 541 (1957).

<sup>16</sup> Y. Kurita and K. Ito, J. Am. Chem. Soc. **82**, 296 (1960).

<sup>17</sup> H. F. Hamerka, Z. Naturforsch. **14a**, 599 (1959).

## Proton Relaxation Times in Paramagnetic Solutions. Effects of Electron Spin Relaxation\*

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The proton relaxation time in solutions of paramagnetic ions depends, among other factors, on the relaxation time of the electron spins,  $\tau_s$ . It is shown that the latter, for ions of the iron group, is determined mostly by the distortion of the hydrated complex by collisions with other water molecules. The theory provides a quantitative explanation for the decrease in  $T_2$  in  $Mn^{++}$  (and other) solutions in very high magnetic fields. The experimentally observed field and temperature dependence of the proton relaxation times,  $T_1$  and  $T_2$ , for ions of the iron group is compared with theory and the features which depend on  $\tau_s$  are stressed.

### I. INTRODUCTION

RELAXATION of protons in aqueous solutions of paramagnetic ions is dominated by interactions between the electronic spin of the ions and the spins of neighboring protons. If exchange among proton types in the solution is rapid, all protons exhibit similar relaxation behavior as a result of the mixing. The over-all relaxation observed is then a weighted average of relaxation rates in each different local proton environment. In the specific case of hydrated paramagnetic ion solutions at moderate concentrations the principal contribution occurs when the proton is within the hydration sphere of the ion.

Results of a wide variety of measurements, including both temperature and frequency dependences of proton relaxation, have been summarized in the recent literature.<sup>1-3</sup> In general, the most successful correlation of experimental results has been achieved through consideration of proton-electron spin dipole-dipole inter-

action as formulated by Solomon<sup>4</sup> and of isotropic proton-electron spin exchange.<sup>5</sup> The combined equations are

$$(1/NT_1) = (4/30) S(S+1) g^2 \beta^2 \gamma_I^2 (n_h/N_p) r^{-6} \\ \times [3\tau_c + 7\tau_c(1 + \omega_s^2 \tau_c^2)^{-1}] \\ + (2/3) S(S+1) A^2 \hbar^{-2} (n_h/N_p) [\tau_e(1 + \omega_s^2 \tau_e^2)^{-1}] \quad (1)$$

and

$$(1/NT_2) = (4/60) S(S+1) g^2 \beta^2 \gamma_I^2 (n_h/N_p) r^{-6} \\ \times [7\tau_c + 13\tau_c(1 + \omega_s^2 \tau_c^2)^{-1}] \\ + (1/3) S(S+1) A^2 \hbar^{-2} (n_h/N_p) [\tau_e + \tau_e(1 + \omega_s^2 \tau_e^2)^{-1}] \quad (2)$$

for  $\omega_I \tau_c \ll 1$  and  $\omega_I \ll \omega_s$ . These conditions are not severe since  $\tau_c$  is expected to be of the order of  $10^{-11}$  sec, or shorter, and  $\omega_s = 650 \omega_I$ .

In Eqs. (1) and (2) indexes  $I$  and  $S$  refer to proton and electron spins, respectively;  $\omega$  is the Larmor precessional frequency;  $\gamma$ , the gyromagnetic ratio;  $r$ , the ion-proton internuclear distance;  $A$ , the spin exchange constant;  $\tau_c$  and  $\tau_e$ , the correlation times for dipolar and spin exchange interactions respectively;  $n_h$ , the number of protons in the hydration sphere of the ion;  $N_p$ , the molar concentration of H (in any form) in the

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<sup>1</sup> R. Hausser and G. Laukien, Z. Physik **153**, 394 (1959).

<sup>2</sup> R. A. Bernheim, T. H. Brown, H. S. Gutowsky, and D. E. Woessner, J. Chem. Phys. **30**, 950 (1959).

<sup>3</sup> L. O. Morgan and A. W. Nolle, J. Chem. Phys. **31**, 365 (1959).

<sup>4</sup> I. Solomon, Phys. Rev. **99**, 559 (1955).

<sup>5</sup> N. Bloembergen, J. Chem. Phys. **27**, 572, 595 (1957).

solution; and  $N$ , the molar concentration of paramagnetic ions. All other symbols have their usual meanings.

Temperature dependence of the dipolar part of  $T_1$  and  $T_2$  is attributable to variation of  $\tau_c$ , which for a number of paramagnetic ions, e.g.,  $Mn^{++}$ ,  $Cu^{++}$ ,  $Gd^{3+}$ ,<sup>2,3</sup> has been shown to be related to the ion tumbling time  $\tau_r$ . Thus,  $\tau_c$  should have an exponential temperature dependence<sup>2</sup>

$$\tau_c = \tau_c^0 \exp(V_c/RT). \quad (3)$$

This is well confirmed experimentally.<sup>1,2,6</sup> However, the exponential dependence does not necessarily follow for the spin exchange contribution, nor for the dipolar contribution when  $\tau_c$  is not primarily determined by tumbling of the complex, but also by the time dependence of the magnetization of the electron spin  $\tau_s$ . The time dependence of the scalar interaction is determined by the time  $\tau_h$  for chemical exchange of protons in the complex and also by  $\tau_s$ .<sup>5</sup> If the interaction between the  $i$ th proton and  $j$ th electron spin is written as

$$3\mathcal{C}_{ij} \exp(t) = A_{ij}(t) \mathbf{I}_i \cdot \mathbf{S}_j(t), \quad (4)$$

the correlation function may be written

$$\begin{aligned} \langle A_{ij}(t) S_{zj}(t) A_{ij}(t+\tau) S_{zj}(t+\tau) \rangle \\ = \langle A_{ij}(t) A_{ij}(t+\tau) \rangle \langle S_{zj}(t) S_{zj}(t+\tau) \rangle \\ = A^2 \exp(-\tau/\tau_H) \frac{1}{3} S(S+1) \exp(-\tau/\tau_s) \end{aligned} \quad (5)$$

because the motion of the protons in and out of the complex is not correlated with the motion of the electron spin. This is shown in more detail in the following section where the electron spin relaxation time is discussed. A similar relation holds for the transverse components of the electron spin, in the limit of rapid motion for electron spin relaxation. One has therefore

$$\tau_e^{-1} = \tau_h^{-1} + \tau_s^{-1}. \quad (6)$$

Similarly one has for the dipolar interaction

$$\tau_c^{-1} = \tau_r^{-1} + \tau_s^{-1} \quad (7)$$

because it will be shown that the electron spin motion is—to a good approximation—not correlated with the rotation of the complex. For the  $Mn^{++}$  ion one has at low temperature

$$\tau_h > \tau_a \gg \tau_r.$$

In general,  $\tau_s$  will be a function of the temperature and the magnetic field. In fact,  $\tau_s$  can be expected to increase if the precession period of the electron spin becomes comparable with the characteristic time for motions leading to electron spin relaxation in the solution. Accordingly, the transverse relaxation time for the protons should decrease. This is in qualitative agreement with the data of Bernheim, Brown, Gutow-

sky, and Woessner<sup>2</sup> and of Morgan and Nolle.<sup>3</sup> A quantitative discussion requires a more careful analysis of electron spin relaxation, when the motion in the liquid is not fast compared to the electronic Larmor precession. In general, several relaxation times  $\tau_s$  will then have to be considered.

Kivelson<sup>7</sup> has developed a theory of electron spin resonance linewidths for free radicals and paramagnetic ions in magnetically dilute crystals and in dilute liquid solutions which includes consideration of nuclear quadrupole moments, zero field splittings, anisotropic Zeeman terms and intramolecular electron-nuclear dipolar interactions, motional and exchange effects. The theory has been applied by Rogers and Pake<sup>8</sup> to explain the variation in linewidth with  $m_I$  in the hyperfine ESR spectrum of  $VO^{++}$  in aqueous solution. Spin-orbit coupling was specifically excluded in both considerations. It is shown in the following section that the latter is the principal mechanism leading to electron spin relaxation in dilute aqueous solutions of iron group ions. A comparison with experimental data in the last section of this paper shows that it is sufficient to explain satisfactorily the observed features of the contribution of electron spin relaxation to proton spin relaxation in many such solutions.

## II. THEORY OF THE ELECTRON SPIN RELAXATION TIME

The data of Tinkham, Weinstein, and Kip<sup>9</sup> show that the interaction between  $Mn^{++}$  ions plays a negligible role in the relaxation mechanism in dilute solutions ( $<0.05N$ ). In such solutions the dominant mechanism is undoubtedly via the spin-orbit coupling, first considered by Kronig.<sup>10</sup> Van Vleck<sup>11</sup> has made an elaborate model of this relaxation mechanism considering the coupling of the spins with the normal modes in a complex, which in turn are modulated by the Debye waves of the crystalline lattice. This model has been adopted by Russian workers<sup>12-16</sup> to discuss the relaxation time of ions in crystals and solutions.

In a liquid one considers the modulation of the crystalline field splitting, the  $g$ -tensor, and the hyperfine coupling by the Brownian motion. In a similar way the Kronig-Van Vleck mechanisms could be described in terms of a modulation of the coefficients in

<sup>7</sup> D. Kivelson, *J. Chem. Phys.* **33**, 1094 (1960).

<sup>8</sup> R. N. Rogers and G. E. Pake, *J. Chem. Phys.* **33**, 1107 (1960).

<sup>9</sup> M. Tinkham, R. Weinstein, and A. F. Kip, *Phys. Rev.* **84**, 848 (1951).

<sup>10</sup> R. deL. Kronig, *Physica* **6**, 33 (1939).

<sup>11</sup> J. H. Van Vleck, *Phys. Rev.* **57**, 426 (1940).

<sup>12</sup> S. A. Al'tshuler and K. A. Valiev, *J. Exptl. Theoret. Phys. (U.S.S.R.)* **35**, 947 (1958) [translation: *Soviet Phys. JETP* **8**, 661 (1959)].

<sup>13</sup> A. A. Kokin, *J. Exptl. Theoret. Phys. (U.S.S.R.)* **36**, 508 (1959) [translation: *Soviet Phys. JETP* **9**, 353 (1959)].

<sup>14</sup> G. V. Skrotskii and A. A. Kokin, *J. Exptl. Theoret. Phys. (U.S.S.R.)* **36**, 169, 481 (1959) [translation: *Soviet Phys. JETP* **9**, 116, 335 (1959)].

<sup>15</sup> Sh. Sh. Bashkirov, *Phys. Metals and Metals Research (U.S.S.R.)* **6**, 2 (1958).

<sup>6</sup> P. F. Cox and L. O. Morgan, *J. Am. Chem. Soc.* **81**, 6409 (1959).

a spin-Hamiltonian by the lattice vibrations. For free radicals with spin  $S = \frac{1}{2}$  and a  $g$  value close to the free electron value modulation of the isotropic and/or anisotropic hyperfine coupling is important. For  $\text{Ti}^{3+}$  and  $\text{Cu}^{++}$  ions, with  $S = \frac{1}{2}$  but an anisotropic  $g$  different from 2, modulation of the  $g$  tensor is probably dominant. McConnell,<sup>16</sup> Kivelson<sup>7</sup> and Rogers and Pake<sup>8</sup> have discussed these effects. For ions with  $S \geq 1$ , such as  $\text{Ni}^{++}$ ,  $\text{Cr}^{3+}$ ,  $\text{V}^{++}$ ,  $\text{Fe}^{3+}$ , and  $\text{Mn}^{++}$ , modulation of the crystalline field parameters will be the most important mechanism, as was first discussed by McGarvey.<sup>17</sup> His equations are only qualitatively correct. Al'tshuler and Valiev<sup>12</sup> have given a very interesting discussion of electron spin relaxation in paramagnetic solutions. They arrive at the conclusion that for ions such as  $\text{Cu}^{++}$  and  $\text{Co}^{++}$ , which have some closely spaced low orbital levels, the transverse electron spin relaxation time may be considerably shorter than the longitudinal one. For other ions they reach conclusions similar to those presented here. Our work considers in more detail the various motions in the liquid and the different relaxation times that may result when the motion in the liquid is not very fast compared to the splitting of the electron spin levels. It is also shown that the proton spin relaxation times provide a check on the details of the electron spin relaxation mechanism.

Since the motion is random and isotropic, one has for tensor components in irreducible form,  $\mathbf{T}$  [compare, e.g., Rose,<sup>18</sup> Eq. (4.32)].

$$\langle \mathbf{T}_{lm}(\theta, \phi, t) \mathbf{T}_{l'm'}(\theta, \phi, t + \tau) \rangle = c_l^2 \delta_{ll'} \delta_{mm'} \exp(-\tau l(l+1)/\tau_r), \quad (8)$$

where  $\tau_r$  is the correlation time for the rotation of the complex with an orientation described by spherical angles  $\theta$  and  $\phi$ . For a sphere of radius  $a$  in a viscous medium,

$$\tau_r/2 = 4\pi\eta a^3/3kT. \quad (9)$$

The constants  $c_l$  should be determined from the trace relationship

$$T\tau \mathcal{H}_{cr,l^2} = \sum_{m_s} \mathcal{H}_{cr,l^2} = (2l+1)c_l^2, \quad (10)$$

where  $\mathcal{H}_{cr,l}$  is the  $l$ th power polynomial in the crystalline field potential with zero average. In the case of a cubic  $\text{Mn}^{++}$  complex, e.g., only  $c_4$  is nonvanishing. The left-hand side of (10) is then equal to  $\frac{4}{3}\delta^2$ , where  $\delta$  is the energy separation between the doublet and quartet state of the  $S = \frac{5}{2}$  ion in a cubic field. In terms of the constant  $a$  of the spin-Hamiltonian  $a(S_x^4 + S_y^4 + S_z^4)$  one has  $c_4 = 3^{-\frac{1}{2}} \times 48a$ . The relaxation times can now be determined in the usual way from the equation of motion for the spin density matrix  $\sigma$

in the rotating coordinate system in the Schrödinger representation.

$$\dot{\sigma}_{\alpha\alpha'} = \sum_{\beta, \beta'} R_{\alpha\alpha'\beta\beta'} (\sigma_{\beta\beta'} - \sigma_{\beta\beta'}^0 \delta_{\beta\beta'}), \quad (11)$$

where the notation of Redfield<sup>19</sup> [his Eq. (2.19)] has been adopted and where the indexes refer to the  $m_s$ -states with values from  $-\frac{5}{2}$  to  $+\frac{5}{2}$ . The relaxation coefficients can readily be expressed in terms of spectral densities which are Fourier transforms of Eq. (8). For the longitudinal relaxation times one is interested in the diagonal terms  $R_{\alpha\alpha\beta\beta}$ . For the transverse relaxation time one needs terms with  $\alpha - \alpha' = \beta - \beta' = \pm 1$ . One finds [Redfield,<sup>19</sup> Eqs. (2.16) and (2.24)]

$$R_{m_s m_s' m_s' m_s} = \hbar^{-2} \sum_l 2\tau_r l^{-1} (l+1)^{-1} c_l^2 C^2(SlS; m_s m_s') \times [1 + \omega_s^2 (m_s - m_s')^2 \tau_r^2 l^{-2} (l+1)^{-2}]^{-1}. \quad (12)$$

In the limit of extreme narrowing the last factor may be put equal to unity. One then has a single relaxation time. Following the method of Abragam and Pound<sup>20</sup> for the solution of the rate equations in this case, one obtains for the relaxation time of the longitudinal component

$$\tau_s^{-1} = 4\tau_r \hbar^{-2} \sum_l [c_l^2/l(l+1)] \times [1 - (2S+1)W(Sl1, S, S, S)], \quad (13)$$

where  $W$  is a Racah coefficient, tabulated by Rose,<sup>18</sup> in his Appendix I. On substituting its value into Eq. (13), one finds

$$\tau_s^{-1} = 2\tau_r \hbar^{-2} \sum_l c_l^2/S(S+1). \quad (14)$$

For the cubic  $\text{Mn}^{++}$  complex  $\sum_l c_l^2 = 16 \times 48a^2$ . It is easy to show that the same relaxation time also applies to a transverse component in this limit.

To explain the field variation of  $\tau_s$  one has of course to go back to the set of rate equations (11), because one is then interested in the deviations from the extreme narrowing case. In general, there are  $2S = 5$  characteristic longitudinal relaxation times. Because of the symmetry property of the matrix elements, the relaxation coefficients in (11) satisfy the relation  $R_{mm, m'm'} = R_{-m, -m', -m'}$ . The magnetic moment operator decays with only  $S + \frac{1}{2} = 3$  characteristic times<sup>21</sup> which may be obtained by solving the three simultaneous equations for  $\dot{\sigma}_{5/2, 5/2} - \dot{\sigma}_{-5/2, -5/2}$ ,  $\dot{\sigma}_{3/2, 3/2} - \dot{\sigma}_{-3/2, -3/2}$ , and  $\dot{\sigma}_{1/2, 1/2} - \dot{\sigma}_{-1/2, -1/2}$ . The eigenvectors  $v_{m, \lambda}$  ( $m = \frac{5}{2}, \frac{3}{2}, \frac{1}{2}$ ) corresponding to the three relaxation times  $\tau_{l, \lambda}$  ( $\lambda = 1, 2, 3$ ) are then found. The correlation function for the  $z$  component of magnetization is then

$$\langle S_z(t) S_z(t + \tau) \rangle = \sum_m \sum_{\lambda=1,2,3} m v_{m, \lambda} \times \exp\{-\tau/\tau_{l, \lambda}\} \frac{1}{3} S(S+1) / \sum_m \sum_{\lambda} m v_{m, \lambda}. \quad (15)$$

<sup>16</sup> H. McConnell, *J. Chem. Phys.* **25**, 709 (1956).

<sup>17</sup> B. R. McGarvey, *J. Phys. Chem.* **61**, 1232 (1957).

<sup>18</sup> M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, Inc., New York, 1957).

<sup>19</sup> A. G. Redfield, *IBM J. Research Develop.* **1**, 19 (1957).

<sup>20</sup> A. Abragam and R. V. Pound, *Phys. Rev.* **92**, 943 (1953).

<sup>21</sup> F. Lurcat, *Compt. rend.* **240**, 2402, 2517 (1955).

A similar program could be carried through for the transverse components of the magnetization, starting from the rate equations for the off-diagonal elements of the density matrix.<sup>18,19</sup>

$$\dot{\sigma}_{m,m+1} = \sum_{m'} R_{m,m+1,m',m'+1} \sigma_{m',m'+1} \quad (16)$$

with

$$R_{m,m+1,m',m'+1} = 2(-1)^{m'-m} C(SlS; m, m'-m) \\ C(SlS; m+1, m'-m) \frac{2\hbar^{-2}\tau_r l^{-1}(l+1)^{-1}c_i^2}{1+\omega_s^2(m-m')^2\tau_r^2 l^{-2}(l+1)^{-2}} \\ - 2\delta_{mm'} \sum_q C^2(SlS; mq) \\ \times \{2\hbar^{-2}\tau_r l^{-1}(l+1)^{-1}c_i^2/[1+\omega_s^2q^2\tau_r^2 l^{-2}(l+1)^{-2}]\}. \quad (17)$$

This will lead to three transverse relaxation times, which are in general not equal to the longitudinal times.

Thus one will have six different times  $\tau_s$  and consequently six different times  $\tau_e$  to substitute in Eq. (2), three in the first term, and three others in the second term. The experimental data do not warrant such a computational effort. When  $T_2$  is much shorter than  $T_1$  the difference is due primarily to the term in Eq. (2) which is linear in  $\tau_e$ . Therefore,  $T_2^{-1}$  increases with  $\tau_e$  for large values of  $\omega_s\tau_r$ .

A qualitative idea about this increase may be obtained in the following way. There is a situation in which there is only one longitudinal relaxation time even for slow motion  $\omega_s\tau_r \geq 1$ . If thermodynamic equilibrium is assumed at all times within the spin system one has the single relaxation time<sup>11,22</sup>

$$\tau^{-1}_s = 2 \sum_m \sum_{m'} R_{mm'm'} (E_m - E_{m'})^2 / \sum_m \sum_{m'} (E_m - E_{m'})^2. \quad (18)$$

This assumption is clearly not valid in our case. It supposes an infinitely short transverse relaxation time. In a solid with rapid dipole-dipole flip-flops between the various  $m$ -states it is applicable. Let us nevertheless evaluate Eq. (18) for our case

$$\frac{1}{\tau_s} = \frac{2 \sum_{m=-s}^{+s} \sum_{m'=-s}^{+s} C^2(SlS; mm') (m-m')^2 [1+\omega_s^2(m-m')^2\tau_r^2 l^{-2}(l+1)^{-2}]^{-1} \hbar^{-2} c_i^2 2\tau_r}{\frac{2}{3}(2S+1)S(S+1)}. \quad (19)$$

The numerator may be evaluated as follows

$$\sum_m \sum_{m'} C^2(SlS, mm'-m) (m-m')^2 = \sum_\mu \sum_m \sum_{m'} C^2(SlS; m\mu m') \mu^2 \\ = [(2S+1)/(2l+1) \sum_\mu \sum_m \sum_{m'} C^2(SlS, mm'\mu) \mu^2] = [(2S+1)/(2l+1)] \sum_{m'} \sum_\mu \mu^2 = (2S+1)^2 \frac{1}{3} l(l+1).$$

In the extreme narrowing limit this expression reduces properly to the previous result Eq. (14). There it was shown that magnetization decays with a single exponential, regardless of the initial distribution over the various spin states. In particular, the same value should be obtained for an initial Boltzmann distribution. It is believed that  $\tau_s$  as evaluated from Eq. (19) gives a fair indication of how  $T_2^{-1}$ , given by Eq. (2), increases with increasing  $\omega_s$ . Note that the decrease in  $T_2$  should begin for  $\omega_s(4/20)\tau_r \sim 1$ , with  $m-m'=4$  and  $l=4$ , whereas the increase in  $T_1$  due to reduced dipole-dipole relaxation should begin for  $\omega_s(2/6)\tau_r \sim 1$ , with  $m-m'=2$  and  $l=2$ .

The experimental data for  $Mn^{++}$  solutions indicate that the important decrease in  $T_2$  occurs for much higher values of  $\omega_s$  than the increase in  $T_1$ . The probable reason is that the main relaxation mechanism of the  $Mn^{++}$  ion is not the modulation of the 16-pole interaction by rotation of the cubic complex [term with  $l=4$  in Eq. (19)], but rather the distortion from cubic symmetry by the water molecules outside the complex which dart rapidly in and out and deform the complex<sup>12</sup>

with a characteristic time,  $\tau_v < \tau_r/l(l+1)$ . Although this motion is much more complex and cannot be treated rigorously, one may add, in analogy with the case of rotational motion a term with  $l=2$  in the various Eqs. (11)-(18) with  $\tau_r/6$  replaced by  $\tau_v$ , and the constant  $c_2$  determined by

$$5c_2^2 = Tr\{D[S_z^2 - \frac{1}{3}S(S+1)] + E[S_x^2 - S_y^2]\}^2. \quad (20)$$

This is the only term in Eq. (14) present for  $Ni^{++}$  and  $Cr^{3+}$  with  $S < 2$ . It should be emphasized once more that the correct way to calculate the decrease in  $T_2$  is by using the solutions of the rate Eqs. (11), rather than (18) which is strictly valid only in a solid with strong interaction between neighboring ions.

Finally the possibility of interference with other electron spin relaxation mechanisms should be considered. In the following enumeration **I** will denote the nuclear spin of the paramagnetic ion, not as heretofore the spin of the protons. The interaction of the latter with the electron spin determines their relaxation time

<sup>22</sup> I. C. Hebel and C. P. Slichter, Phys. Rev. **113**, 1504 (1959).

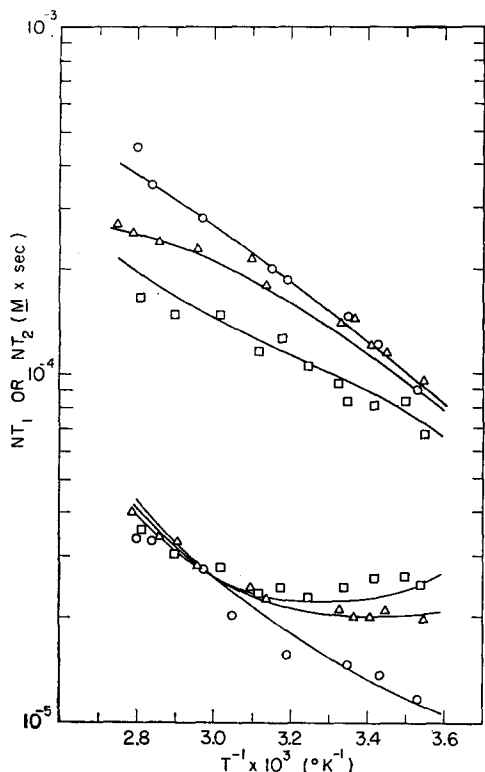


FIG. 1. Proton  $NT_1$  and  $NT_2$  for  $Mn^{++}$  solutions as functions of  $1/T$ .  $\square$ —14 Mc,  $\Delta$ —30 Mc,  $\circ$ —60 Mc. Upper curves— $NT_1$ , lower curves— $NT_2$ . Solid lines were calculated using the constants given in the text.

according to Eqs. (1) and (2), but it can be ignored in the calculation of  $\tau_s$ . The following processes can be distinguished:

- Relaxation by modulation of the isotropic hyperfine interaction  $A(t) \mathbf{I} \cdot \mathbf{S}$ ;
- Relaxation by modulation of the anisotropic hyperfine interaction  $\mathbf{I} \cdot \mathbf{B}(t) \cdot \mathbf{S}$ ;
- Relaxation by modulation of the anisotropic  $g$ -factor  $\mathbf{H}_0 \cdot \Delta \mathbf{g}(t) \cdot \mathbf{S}$ ;
- Relaxation by modulation of the quadratic crystalline field splitting  $\mathbf{S} \cdot \mathbf{D}(t) \cdot \mathbf{S}$ ;
- Relaxation by modulation of crystalline 16-pole interaction, etc.

The modulation of the scalar  $A(t)$  is caused only by impinging of molecules outside the complex. The wave function at the nucleus is thus distorted with a correlation time  $\tau_v$ . The modulation of the second-order traceless tensors  $\mathbf{B}(t)$ ,  $\Delta \mathbf{g}(t)$ , and  $\mathbf{D}(t)$ , has two causes. The rotation of the complex as a whole modulates the angular factors with correlation time  $\tau_r$ , describing the orientation of the tensor axes with respect to the laboratory coordinate system. If the complex had perfect cubic symmetry and this were the only motion, the interactions would vanish and no relaxation would result. The ratio of the axes of these tensors may, however, be modulated by molecular distortions of the

complex with correlation time  $\tau_v$ . This was shown to be the most important mechanism for the tensor  $\mathbf{D}(t)$ . Although the modulation of the dipolar hyperfine structure and anisotropic  $g$ -value is usually considered to arise from a rotating rigid complex, it should be emphasized that this model is adopted mainly for mathematical elegance. The dipolar interaction has only three independent elements rather than five for a general traceless second order tensor, but one is the radial factor, which may be modulated by distortion of the complex from outside. The same motion can also modulate  $\Delta \mathbf{g}$  in the same way as it modulates  $D$ ,  $E$  and the Eulerian angles of the tensor  $\mathbf{D}(t)$ .

There is no interference term between process (a) and any other mechanism. When the statistical average over all orientations in space of the tensors is taken in the isotropic liquid, a vanishing result for the cross term is obtained as  $A$  itself does not depend on the angle.

In the same way the cross term between mechanism (e) and any other mechanism vanishes, since the orders of the spherical harmonics involved are different.

It remains to investigate the cross-effects between (b), (c), and (d). McConnell<sup>16</sup> and Kivelson<sup>7</sup> have shown the existence of cross terms between (b) and (c), and in principle similar cross terms should arise with (d). The interest is here, however, centered on paramagnetic ions which have no resolved fine or hyperfine splittings in aqueous solution. Therefore, averages over all  $m_I$  and  $m_S$  states should be taken. Then all interference terms between (b), (c), and (d) vanish, because  $\langle \mathbf{I} \rangle = \langle \mathbf{S} \rangle = \langle I_k S_l \rangle = 0$ , etc.

### III. COMPARISON WITH EXPERIMENTAL RESULTS

#### $Mn^{++}$ Solutions: ( $S = \frac{5}{2}$ ; $3d^5 \ ^6S$ )

In addition to data reported previously<sup>1-3</sup> for proton relaxation in aqueous  $Mn^{++}$  solutions, results have been obtained at proton resonance frequencies of 14, 30, and 60 Mc over the temperature range  $5^\circ$  to  $80^\circ C$ ,<sup>23</sup> and are shown graphically in Fig. 1 as a function of  $T^{-1}$ . The solid curves indicated for  $NT_1$  are those expected for  $\tau_c(300^\circ K) = 3.0 \times 10^{-11}$  sec and  $V_c = 4.5$  kcal/mole, using the first term (dipolar) of Eq. (1) and Eq. (3); with  $r = 2.8$  A,  $\mu = 5.9\beta$ , and  $n_h = 12$ .

Following the suggestion of Bernheim, Brown, Gutowsky, and Woessner,<sup>2</sup> we assume that  $\tau_s$  at high temperatures is essentially  $\tau_h$ , and that

$$\tau_h = \tau_h^0 \exp(V_h/RT), \quad (21)$$

while at low temperatures  $\tau_s$  contributes heavily to  $\tau_s$ [Eq. (6)]. According to Eq. (19), for  $l=2$

$$\frac{1}{\tau_s} = \frac{12c_2^2 \hbar^{-2}}{5S(S+1)} \left[ \frac{\tau_v}{1 + \omega_s^2 \tau_v^2} + \frac{4\tau_v}{1 + 4\omega_s^2 \tau_v^2} \right] \quad (22)$$

<sup>23</sup> Experimental methods used were those given in detail in footnote 3. Temperature control was obtained using a flowing gas thermostat. Reported temperatures are probably accurate to within  $\pm 1^\circ C$ .

and according to Eq. (20)

$$c_2^2 = 2/225(2S+1)S^2(S+1)^2 \times \{1 - [3/4S(S+1)]\} [2\langle D^2 \rangle_{Av} + 3\langle E^2 \rangle_{Av}]. \quad (23)$$

From the experimental data shown in Fig. 1 the spin exchange contribution to  $(NT_2)^{-1}$  may be calculated as a function of temperature and frequency. At low temperatures, where  $\tau_e \approx \tau_s$ ,  $\tau_v$  may then be evaluated from the frequency dependence of  $(NT_2)_{ex}$  predicted by Eqs. (2) and (22). The results of this calculation are given in Table I. Noting that  $\tau_v$  is the correlation time for the impact of water molecules of the solvent upon the hydrated ion, we expect that

$$\tau_v = \tau_v^0 \exp(V_v/RT). \quad (24)$$

The observed exponential temperature dependence of  $\tau_v$  gives  $V_v = 3.9$  kcal/mole.

Bleaney and Ingram<sup>24</sup> found  $D = 0.018$  cm<sup>-1</sup> and  $E = 0$  for MnSiF<sub>6</sub>·6H<sub>2</sub>O crystals and  $D = 0.024$  cm<sup>-1</sup> and  $E = 0.01$  cm<sup>-1</sup> for the Tutton salt, (NH<sub>4</sub>)<sub>2</sub>Mn(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O, from the ESR spectrum at room temperature. In these substances the Mn<sup>2+</sup> ion is surrounded by an octahedron of water molecules in a manner similar to that proposed for the hydrated ion in solution. Assuming that the effect on  $D$  of fields external to the hydrated ion in the crystal is small, we use the value  $D = 0.018$  cm<sup>-1</sup> in Eq. (22). Then, taking  $\tau_v = 2.4 \times 10^{-12}$  sec,  $\tau_s$  at 300°K and 30 Mc is found to be  $4.5 \times 10^{-9}$  sec. This corresponds to a low-field value of  $3.5 \times 10^{-9}$  sec, which is in good agreement with  $\tau_s = 3 \times 10^{-9}$  sec estimated<sup>5</sup> from the ESR linewidth data of Tinkham, Weinstein, and Kip.<sup>9</sup> The values of  $D$  and  $\tau_s$  used here are considerably smaller than those obtained by Kokin,<sup>13</sup> whose value for  $D$  (0.08 cm<sup>-1</sup>) is much larger than that expected on the basis of results for hydrated ions in crystals. Since the pertinent motion is not rotation of the complex, our shorter value for the correlation time appears to be more reasonable and is consistent with the high field behavior of the proton  $T_2$ .

At high temperatures ( $\tau_e \approx \tau_h$ ) the best fit of Eq. (2) to experimental data is obtained with  $\tau_h(300^\circ\text{K}) = 2.3 \times 10^{-8}$  sec and  $V_h = 8.1$  kcal/mole, which are com-

TABLE I. Temperature dependence of  $\tau_v$  in Mn<sup>2+</sup> solutions.

$T(^{\circ}\text{C})$	$T^{-1}(^{\circ}\text{K}^{-1})$	$(\omega_e)_c^a$ (Mc)	$\tau_v$ (sec)
12	3.5	72	$3.4 \times 10^{-12}$
21	3.4	89	$2.8 \times 10^{-12}$
30	3.3	105	$2.3 \times 10^{-12}$
40	3.2	127	$1.9 \times 10^{-12}$

<sup>a</sup> Frequency at which  $\omega_e \tau_v = 1$ .

<sup>24</sup> B. Bleaney and D. J. E. Ingram, Proc. Roy. Soc. (London) **A205**, 336 (1951).

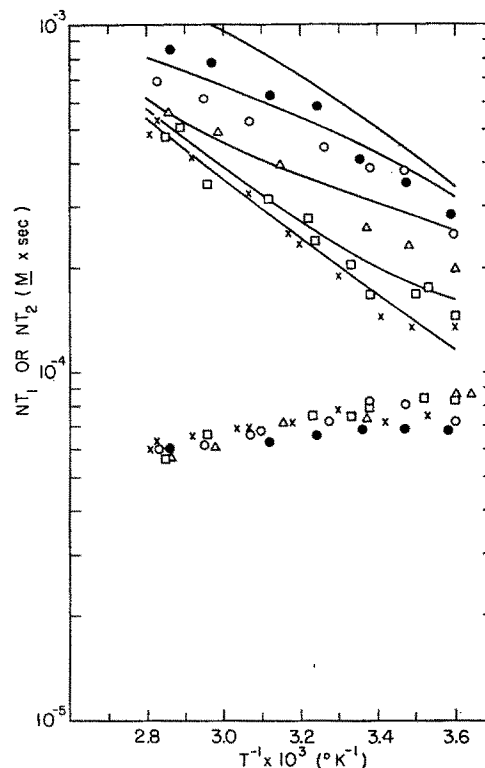


Fig. 2. Proton  $NT_1$  and  $NT_2$  for  $V^{++}$  solutions as functions of  $1/T$ .  $\times$ —2.7 Mc,  $\square$ —6 Mc,  $\Delta$ —14 Mc,  $\circ$ —30 Mc,  $\bullet$ —60 Mc. Upper curves— $NT_1$ , lower curves— $NT_2$ . Solid lines were calculated for  $NT_1$  using the constants given in the text. To avoid confusion the calculated curves for  $NT_2$  are shown in Fig. 3 for the spin exchange contribution.

parable to the values reported by Bernheim, *et al.*<sup>3</sup> Thus,  $\tau_s(300^\circ\text{K}) \approx 3.8 \times 10^{-9}$  sec and  $(A/h) = 1.0 \times 10^6$  sec<sup>-1</sup>.

The solid curves drawn in for  $NT_2$  in Fig. 1 represent Eq. (2), taking all contributions into account according to the preceding discussion. The agreement is well within the expected experimental error and must be considered satisfactory. The behavior of  $T_1$  and  $T_2$  clearly indicates that two distinct motions in the solutions, described by  $\tau_r$  and  $\tau_v$ , are important in the relaxation mechanism, and corroborate the assumption that proton chemical exchange becomes important if electron spin relaxation times are sufficiently long.

#### $V^{++}$ Solutions: ( $S = \frac{3}{2}$ ; $3d^3$ $^4F$ ; Orbital Singlet Lowest in a Cubic Field)

Proton relaxation times for solutions of VSO<sub>4</sub> in dilute H<sub>2</sub>SO<sub>4</sub> are presented in Fig. 2. These data were obtained using samples maintained in a reducing atmosphere and containing an excess of solid zinc amalgam. Other experimental details have been given previously.<sup>3</sup> It was verified that both  $T_1$  and  $T_2$  are independent of concentration to at least 0.01  $M$  VSO<sub>4</sub> and 0.1  $M$  H<sub>2</sub>SO<sub>4</sub>. The predominant ionic species in such solutions is usually assumed to be the hydrated

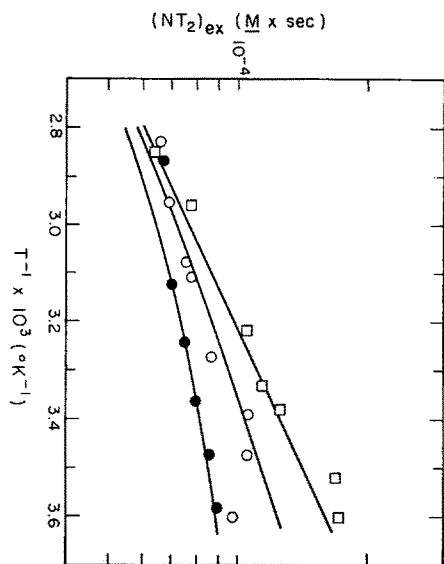


FIG. 3. Spin exchange contribution to proton  $NT_2$  for  $V^{++}$  solutions as a function of  $1/T$ .  $\square$ —6 Mc,  $\circ$ —30 Mc,  $\bullet$ —60 Mc. Solid lines were calculated using the constants given in the text.

vanadium(II) ion and no evidence was obtained in this work to the contrary.

The solid curves representing  $T_1$  in Fig. 2 are those expected for the several proton resonance frequencies employed according to the first term (dipole-dipole) of Eq. (1). The constants used were the same as those for  $Mn^{++}$  solutions except  $\mu_s=3.83$ ,  $V_c=4.3$  kcal/mole, and  $\tau_c(300^\circ K)=2.0 \times 10^{-11}$  sec. It should be noted that in each case the curves give essentially the correct temperature dependence. However, the expected 10/3 increase in  $T_1$  at high fields relative to the low-field values is not entirely realized. A similar situation in  $Cu^{++}$  and  $Gd^{3+}$  solutions has been previously noted.<sup>3</sup> The cause of the discrepancy is not known, but may be the contribution of relaxation occurring in the second and more remote layers of water molecules around the paramagnetic ions. There the effective correlation time may be considerably shorter than for protons in the primary hydration sphere so that the important increase in that part of  $T_1$  occurs at higher frequency.

Certain features of the transverse proton relaxation behavior are apparent even in the unresolved data shown in Fig. 2: (1)  $T_2$  is considerably less than  $T_1$  at all frequencies, (2) there is no gross frequency dependence, and (3) in general,  $T_2$  decreases with increasing temperature. These observations suggest that  $\tau_s < \tau_h$  and  $\tau_s > \tau_c$ , so that  $\tau_e = \tau_s$  and  $\omega_s \tau_e \gg 1$ . The spin exchange contributions to  $NT_2$  are shown in Fig. 3. Application of Eqs. (2) and (22) to the observed frequency dependence of  $(NT_2)_{ex}$  gives the values of  $\tau_v$  listed in Table II, from which  $V_v=2.8$  kcal/mole. The value of  $V_v$  calculated from the temperature variation of  $(NT_2)_{ex}$  at 2.7 Mc is 2.6 kcal/mole, assuming that  $\tau_s$  [and  $(NT_2)_{ex}$ ] is an explicit function of  $\tau_v$

and is essentially equal to its zero field value at that frequency.

A value of  $D$  for the hydrated  $V^{++}$  ion in solution may be estimated from data reported for the vanadium(II) Tutton salt,  $(NH_4)_2V(SO_4)_2 \cdot 6H_2O$ , by Bleaney, Ingram, and Scovil<sup>25</sup> for which  $D=0.158 \pm 0.01$  cm<sup>-1</sup> and  $E=0.049 \pm 0.005$  cm<sup>-1</sup>. Assuming that  $D$  for the ion in solution is approximately  $\frac{2}{3}$  of that for the solid Tutton salt and  $E=0$  as in the case of  $Mn^{++}$ , we obtain  $\tau_s(300^\circ K)=5 \times 10^{-10}$  sec at low fields and  $6 \times 10^{-10}$  sec at 30 Mc. On that basis Eq. (2) yields  $(A/h)=2 \times 10^6$  sec<sup>-1</sup>. In the temperature range  $0^\circ$ – $100^\circ C$   $\tau_s^{-1} \ll \tau_r^{-1}$  and  $\tau_c = \tau_r$ .

### Cr<sup>3+</sup> Solutions: ( $S=\frac{3}{2}$ ; $3d^3$ $^4F$ )

Among hydrated ions of the iron group  $Cr^{3+}$  is unique in that the mean lifetime  $\tau_h$  for protons in the hydration sphere of the ion is sufficiently long that the rate of proton exchange with those of bulk solvent determines the overall proton relaxation time in the solution. Although this has not been recognized previously, it is perhaps not surprising in view of the very long (of the order of hours) characteristic lifetime for water molecules in the hydration sphere.<sup>26</sup>

A similar case of slow proton exchange has been examined in detail for solutions of the bisethylenediaminecopper(II) ion<sup>6</sup> and general relaxation rate equations were used in connection with that work of the type introduced by McConnell.<sup>27</sup> Pearson, Palmer, Anderson, and Allred<sup>28</sup> have made essentially the same application in a recent publication. The pertinent relation for this case is

$$(T_1)^{-1} = (T_{1w})^{-1} + Nn_h N_p^{-1} (T_{1c} + \tau_h)^{-1}, \quad (25)$$

in which  $T_{1w}$  is the relaxation time in pure water and  $T_{1c}$  is the relaxation time in the hydration sphere of the paramagnetic ion. This relation applies for  $Nn_h N_p^{-1} \ll 1$  and  $T_1 > \tau_h$ . The latter condition is valid in our experiments. It is necessary in order to have a homogeneous system, and not two distinct groups of protons with different relaxation times as discussed in

TABLE II. Temperature dependence of  $\tau_v$  in  $V^{++}$  solutions.

$T(^\circ C)$	$T^{-1}(^\circ K^{-1})$	$(\omega_s)_c$	$\tau_v(\text{sec})$
5	$3.6 \times 10^{-3}$	112	$2.17 \times 10^{-12}$
12	$3.5 \times 10^{-3}$	130	$1.87 \times 10^{-12}$
21	$3.4 \times 10^{-3}$	152	$1.60 \times 10^{-12}$
30	$3.3 \times 10^{-3}$	170	$1.43 \times 10^{-12}$

<sup>25</sup> B. Bleaney, D. J. E. Ingram, and H. E. D. Scovil, Proc. Phys. Soc. (London) **A64**, 601 (1951).

<sup>26</sup> J. P. Hunt and H. Taube, J. Chem. Phys. **18**, 757 (1950).

<sup>27</sup> H. McConnell, J. Chem. Phys. **28**, 430 (1958).

<sup>28</sup> R. G. Pearson, J. Palmer, M. M. Anderson, and A. L. Allred, Z. Elektrochem. **64**, 110 (1960).



detail by Broersma.<sup>29</sup> A similar equation applies to  $T_2$  in this case.

Proton  $T_1$  and  $T_2$  as functions of temperature are shown in Fig. 9 of footnote 1 for  $\text{Cr}^{3+}$  solutions. At low temperatures  $T_1$  and  $T_2$  decrease with increasing temperature because the rate of proton exchange increases and a proton remains in the hydration sphere of an ion for a time,  $\tau_h$ , long compared to its relaxation time in that environment. At higher temperatures just the reverse is true so that  $(T_1)^{-1} \cong (T_{1w})^{-1} + Nn_h N_p^{-1} (T_{1c})^{-1}$  and Eqs. (1) and (2) apply. Eq. (25) provides a natural explanation for these observations.  $\tau_h$  is found to be  $4 \times 10^{-6}$  sec at  $300^\circ\text{K}$  and  $V_h = 10$  kcal/mole. Results are the same for resolution of both  $T_1$  and  $T_2$  data.

Equation (25) can also explain quantitatively the frequency dependence of  $T_1$  and  $T_2$  for  $\text{Cr}^{3+}$  solutions reported previously.<sup>3</sup> With the value of  $\tau_h$  in the foregoing, the revised  $\tau_c$  for dipolar interaction in such solutions is then  $8 \times 10^{-11}$  sec at  $300^\circ\text{K}$ . The same value is obtained from both the low frequency  $T_1$  and the break in the  $T_1$  vs frequency curve.

At temperatures well above  $300^\circ\text{K}$   $T_2$  continues to decrease with increasing temperature, but with somewhat smaller slope. Assuming that this is attributable to the increase in  $\tau_s$  in the second term of Eq. (2),  $V_v \approx 2.5$  kcal/mole and  $(NT_2)_{\text{ex}} \approx 8 \times 10^{-5}$  at  $300^\circ\text{K}$ .

The ESR linewidth at  $x$  band for hydrated  $\text{Cr}^{3+}$  in solutions of violet  $\text{Cr}(\text{NO}_3)_3$  is about 150 gauss at  $300^\circ\text{K}$ , so that  $\tau_s \approx 5 \times 10^{-10}$  sec at low fields. Eqs. (22) and (23) then give  $D = 0.08\text{--}0.11$   $\text{cm}^{-1}$  depending upon the choice of  $\tau_v$  in the range  $2 \times 10^{-12}$  to  $2.5 \times 10^{-11}$  sec.  $(A/h)$  may then be evaluated from Eq. (2) and is found to be  $2 \times 10^6$   $\text{sec}^{-1}$ .

#### $\text{Cu}^{++}(S = \frac{1}{2}; 3d^9 2D)$ and $\text{Gd}^{3+}(S = \frac{7}{2}; 4f^7 8S)$ Solutions

The dipole-dipole mechanism appears to account satisfactorily for observed  $T_1$  and  $T_2$  for protons in  $\text{Cu}^{++}$  and  $\text{Gd}^{3+}$  solutions.<sup>1-3,6</sup> The calculated  $\tau_c$ 's are consistent with the ion tumbling process ( $2 \times 10^{-11}$  sec) although that value may be somewhat lower than expected for hydrated  $\text{Gd}^{3+}$ , around which the solvent stiffening would be expected to be greater than in the case of hydrated  $\text{Cu}^{++}$ .

On that basis, it is expected that  $\tau_s$  for both ions is of the order of  $10^{-9}$ – $10^{-10}$  sec. If it were shorter, so that  $\tau_s \leq \tau_r$ ,  $T_1$  and  $T_2$  would decrease with increasing temperature, at least at low temperatures. That does not seem to be the case.<sup>1,2,6</sup> If  $\tau_s$  were much longer than  $10^{-9}$  sec, it is probable that there would be some spin exchange contribution to  $T_2^{-1}$ , although that also depends upon the magnitude of  $A$ , which could be very small.

McConnell<sup>16</sup> has estimated  $\tau_{s,1}$  and  $\tau_{s,2}$  for the various hyperfine components of the  $\text{Cu}^{++}$  spectrum in aqueous solution on the basis of anisotropy of the  $g$ - and hyper-

fine interaction tensors modulated by rotation of the hydrated ion. The calculated values fall within the range  $3 \times 10^{-8}$  to  $2 \times 10^{-9}$  sec for  $\tau_r \sim 3 \times 10^{-11}$  sec. The actual relaxation time is probably an order of magnitude shorter, because  $\text{Cu}^{++}$  solutions do not exhibit a resolved hyperfine structure in microwave spectra.

For  $\text{Gd}^{3+}$ , Weger and Low<sup>30</sup> report  $D = 0.04$   $\text{cm}^{-1}$  and  $E = 0.004$  in  $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ . Using that value of  $D$  in Eqs. (22) and (23), the value of  $\tau_s$  is found to be  $4\text{--}7 \times 10^{-10}$  sec at 30 Mc, depending upon the choice of  $\tau_v$  in the range  $2 \times 10^{-12}$  to  $2.5 \times 10^{-11}$  sec. The minimum calculated  $\tau_s$  is found at  $\tau_v = 8 \times 10^{-12}$  sec. A complete calculation of  $\tau_s$  would require consideration of the 16-pole and 64-pole interactions, as well as those of lower order. However, since we expect that terms in  $D$  are the most important, the estimate of  $\tau_s$  given above is probably satisfactory.

#### $\text{Ni}^{++}(S = 1; 3d^8 3F)$ , $\text{Co}^{++}(S = \frac{5}{2}; 3d^5 4F)$ , and $\text{Fe}^{++}(S = 2; 3d^6 5D)$ Solutions

Proton relaxation times in solutions of these ions are much longer than in solutions of comparable concentration of the ions discussed before. In each case for  $\text{Ni}^{++}$ , and  $\text{Co}^{++}$ , and  $\text{Fe}^{++}$  one finds  $T_1 \cong T_2$  with no frequency dependence up to 60 Mc, and with a very slight increase or decrease ( $\text{Ni}^{++}$ ) with increasing temperature.<sup>1,2</sup>

If one determines, without justification,  $\tau_c$  from the observed  $T_1$  with Eq. (1), very short times  $\tau_c = 3 \times 10^{-12}$  sec for  $\text{Ni}^{++}$ ,  $5 \times 10^{-13}$  sec for  $\text{Co}^{++}$ , and  $10^{-12}$  sec for  $\text{Fe}^{++}$  would be obtained. It should be emphasized that the theory of Sec. II breaks down, if it leads to values of  $\tau_s$  shorter than the correlation time of the motion in the liquid  $\tau_v$  [compare Eq. (2.20) of Redfield<sup>19</sup>]. This implies that the instantaneous values of the crystalline field interactions  $D$  and  $E$  are larger than  $\hbar\tau_v^{-1}$ . For  $\text{Ni}^{++}$  and  $\text{Fe}^{++}$  this is quite reasonable. One has nearly complete quenching of the electron spin angular momentum at each instant. The true relaxation time of  $\text{Fe}^{++}$  solution may even be longer than the experimental value quoted in the foregoing, if a few percent of  $\text{Fe}^{3+}$  had been present in the experiment.<sup>1</sup>

A simple theoretical argument shows that the factor between square brackets in Eqs. (1) and (2) should be replaced by  $10\tau_v(1 + \omega_{cr}^2\tau_v^2)^{-1}$  when quenching occurs because  $\hbar^{-1}D\tau_v = \omega_{cr}\tau_v \gg 1$ . The nuclear spin relaxation time is increased by a factor  $(\omega_{cr}\tau_v)^2$  and is independent of the external field because  $\omega_{cr}$  is very large compared to the circular Zeeman frequency  $\omega_s$ .

In the case of the  $\text{Co}^{++}$  ion with an odd number of electrons, the quenching will never be complete since the Kramers degeneracy remains. The dominant relaxation mechanism, however, will be that resulting from transitions between different Kramers doublets connected by the modulated crystalline potential of the kind introduced by Al'tshuler and Valiev.<sup>12</sup> The argu-

<sup>29</sup> S. Broersma, J. Chem. Phys. **24**, 153 (1956); **27**, 484 (1957).

<sup>30</sup> M. Weger and W. Low, Phys. Rev. **111**, 1526 (1958).

ment for  $\text{Fe}^{++}$  and  $\text{Ni}^{++}$  may therefore also be applied to  $\text{Co}^{++}$ .

A problem related to the quenching of the electron-spin angular momentum, is the quenching of rotational angular momentum  $J$  of a molecule in a liquid. In most discussions of nuclear spin relaxation, the spin-orbit coupling  $c\mathbf{I}\cdot\mathbf{J}$  has been ignored. This is justifiable in the case of liquid HF because of quenching of  $J$ , although the coupling constant  $c$  is actually quite large. Baker and Ramsey<sup>31</sup> found  $\hbar^{-1}c_p = 71$  kc for the proton and  $\hbar^{-1}c_F = 320$  kc for  $\text{F}^{19}$  in HF. If the spin-rotational coupling were a dominant factor the relaxation time of  $\text{F}^{19}$  in pure liquid HF should be 25 times shorter than that of hydrogen. Actually the two relaxation times are found to be about equal.<sup>32</sup>

In other molecules, however, the spin-rotational coupling may not be quenched as completely and may contribute significantly to the relaxation mechanism. It would be of considerable interest to extend the theories of relaxation to include the cases in which the interactions with electron spin or molecular rotation have a magnitude comparable to  $\hbar\tau_r^{-1}$ .

#### IV. DISCUSSION

In those cases in which data are available for the estimation of  $D$  according to Eq. (23) the values obtained are comparable to those reported for crystals

<sup>31</sup> M. R. Baker and N. F. Ramsey, *Bull. Am. Phys. Soc. Ser. II* **5**, 344 (1960).

<sup>32</sup> I. Solomon and N. Bloembergen, *J. Chem. Phys.* **25**, 261 (1956).

containing the appropriate hydrated ions. This indicates that the instantaneous values of the distortion of the water octahedron about the ion have the same order of magnitude as in crystals.

Values of  $\tau_v$  cannot be obtained with any precision from Eqs. (22) and (23) on the basis of the temperature dependence of  $\tau_s$  alone in the range of magnetic field strengths utilized in the experimental work considered here. A broad maximum is observed for  $[\tau_v(1+\omega_s^2\tau_v^2)^{-1}+4\tau_v(1+4\omega_s^2\tau_v^2)^{-1}]$  as a function of  $\tau_v$  centering about  $\tau_v = 8 \times 10^{-12}$  sec for  $\omega_s = 1.2 \times 10^{11}$  sec<sup>-1</sup>. On the other hand, variation of  $\omega_s$  at a given temperature (and  $\tau_v$ ) provides the necessary sensitivity. Values of  $\tau_v$  (300°K) calculated for  $\text{Mn}^{++}$  and  $\text{V}^{++}$  solutions,  $2.4 \times 10^{-12}$  and  $1.5 \times 10^{-12}$  sec, respectively, from the frequency dependence of  $\tau_s$  are entirely consistent with the proposed molecular impact process.

#### ACKNOWLEDGMENTS

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