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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 methods¹³⁻¹⁷ as the way to achieve quantitative computation of the magnetic properties of molecules.

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

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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, τ_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 τ_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.¹⁻³ 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 Solomon⁴ and of isotropic proton-electron spin exchange.⁵ 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 τ_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; ω is the Larmor precessional frequency; γ , the gyromagnetic ratio; r , the ion-proton internuclear distance; A , the spin exchange constant; τ_c and τ_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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¹ R. Hausser and G. Laukien, Z. Physik **153**, 394 (1959).

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

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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 τ_c , which for a number of paramagnetic ions, e.g., Mn^{++} , Cu^{++} , Gd^{3+} ,^{2,3} has been shown to be related to the ion tumbling time τ_r . Thus, τ_c should have an exponential temperature dependence²

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

This is well confirmed experimentally.^{1,2,6} However, the exponential dependence does not necessarily follow for the spin exchange contribution, nor for the dipolar contribution when τ_c is not primarily determined by tumbling of the complex, but also by the time dependence of the magnetization of the electron spin τ_s . The time dependence of the scalar interaction is determined by the time τ_h for chemical exchange of protons in the complex and also by τ_s .⁵ If the interaction between the i th proton and j th electron spin is written as

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

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, τ_s will be a function of the temperature and the magnetic field. In fact, τ_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 Woessner² and of Morgan and Nolle.³ 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 τ_s will then have to be considered.

Kivelson⁷ 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 Pake⁸ 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 Kip⁹ 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.¹⁰ Van Vleck¹¹ 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 workers¹²⁻¹⁶ 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

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

¹⁰ R. deL. Kronig, *Physica* **6**, 33 (1939).

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¹⁴ 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)].

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

⁶ 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 Ti^{3+} and Cu^{++} ions, with $S = \frac{1}{2}$ but an anisotropic g different from 2, modulation of the g tensor is probably dominant. McConnell,¹⁶ Kivelson⁷ and Rogers and Pake⁸ have discussed these effects. For ions with $S \geq 1$, such as Ni^{++} , Cr^{3+} , V^{++} , Fe^{3+} , and Mn^{++} , modulation of the crystalline field parameters will be the most important mechanism, as was first discussed by McGarvey.¹⁷ His equations are only qualitatively correct. Al'tshuler and Valiev¹² have given a very interesting discussion of electron spin relaxation in paramagnetic solutions. They arrive at the conclusion that for ions such as Cu^{++} and 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,¹⁸ 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 τ_r is the correlation time for the rotation of the complex with an orientation described by spherical angles θ and ϕ . 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 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 δ 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 σ

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 Redfield¹⁹ [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,¹⁹ 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 Pound²⁰ 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,¹⁸ 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 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 τ_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 times²¹ 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

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

¹⁶ H. McConnell, J. Chem. Phys. **25**, 709 (1956).

¹⁷ B. R. McGarvey, J. Phys. Chem. **61**, 1232 (1957).

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

¹⁹ A. G. Redfield, IBM J. Research Develop. **1**, 19 (1957).

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

²¹ 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.^{18,19}

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

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 τ_s and consequently six different times τ_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 τ_e . Therefore, T_2^{-1} increases with τ_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^{11,22}

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

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 τ_s as evaluated from Eq. (19) gives a fair indication of how T_2^{-1} , given by Eq. (2), increases with increasing ω_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 ω_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 complex¹²

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 τ_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

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

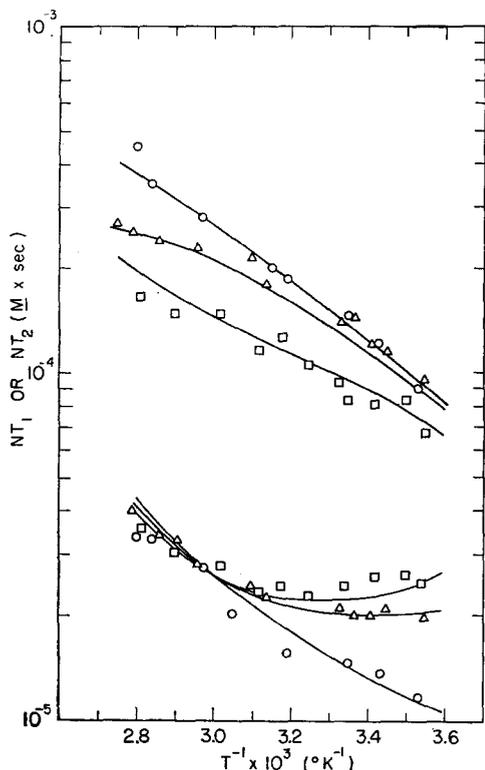


FIG. 1. Proton NT_1 and NT_2 for Mn^{++} solutions as functions of $1/T$. \square —14 Mc, Δ —30 Mc, \circ —60 Mc. Upper curves— NT_1 , lower curves— NT_2 . Solid lines were calculated using the constants given in the text.

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

- (a) Relaxation by modulation of the isotropic hyperfine interaction $A(t) \mathbf{I} \cdot \mathbf{S}$;
- (b) Relaxation by modulation of the anisotropic hyperfine interaction $\mathbf{I} \cdot \mathbf{B}(t) \cdot \mathbf{S}$;
- (c) Relaxation by modulation of the anisotropic g -factor $\mathbf{H}_0 \cdot \Delta \mathbf{g}(t) \cdot \mathbf{S}$;
- (d) Relaxation by modulation of the quadratic crystalline field splitting $\mathbf{S} \cdot \mathbf{D}(t) \cdot \mathbf{S}$;
- (e) 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 τ_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 τ_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 τ_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). McConnell¹⁶ and Kivelson⁷ 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 previously¹⁻³ 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° to $80^\circ C$,²³ 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,² we assume that τ_s at high temperatures is essentially τ_h , and that

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

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

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

²³ 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 $\tau_e \approx \tau_s$, τ_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 τ_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 τ_v gives $V_v = 3.9$ kcal/mole.

Bleaney and Ingram²⁴ found $D = 0.018$ cm⁻¹ and $E = 0$ for MnSiF₆·6H₂O crystals and $D = 0.024$ cm⁻¹ and $E = 0.01$ cm⁻¹ for the Tutton salt, (NH₄)₂Mn(SO₄)₂·6H₂O, from the ESR spectrum at room temperature. In these substances the Mn²⁺ 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⁻¹ in Eq. (22). Then, taking $\tau_v = 2.4 \times 10^{-12}$ sec, τ_s at 300°K and 30 Mc is found to be 4.5×10^{-9} sec. This corresponds to a low-field value of 3.5×10^{-9} sec, which is in good agreement with $\tau_s = 3 \times 10^{-9}$ sec estimated⁵ from the ESR linewidth data of Tinkham, Weinstein, and Kip.⁹ The values of D and τ_s used here are considerably smaller than those obtained by Kokin,¹³ whose value for D (0.08 cm⁻¹) 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 τ_v in Mn²⁺ solutions.

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

^a Frequency at which $\omega_e \tau_v = 1$.

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

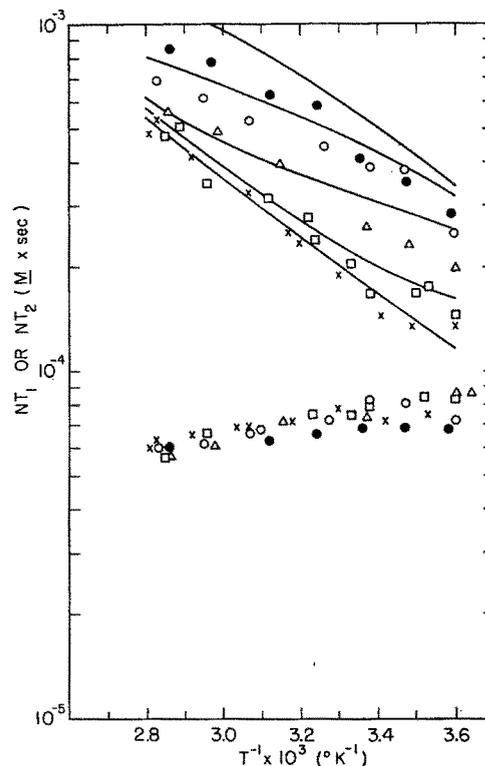


Fig. 2. Proton NT_1 and NT_2 for V^{++} solutions as functions of $1/T$. \times —2.7 Mc, \square —6 Mc, Δ —14 Mc, \circ —30 Mc, \bullet —60 Mc. Upper curves— NT_1 , lower curves— NT_2 . Solid lines were calculated for NT_1 using the constants given in the text. To avoid confusion the calculated curves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

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

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 τ_r and τ_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 VSO₄ in dilute H₂SO₄ 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.³ It was verified that both T_1 and T_2 are independent of concentration to at least 0.01 M VSO₄ and 0.1 M H₂SO₄. The predominant ionic species in such solutions is usually assumed to be the hydrated

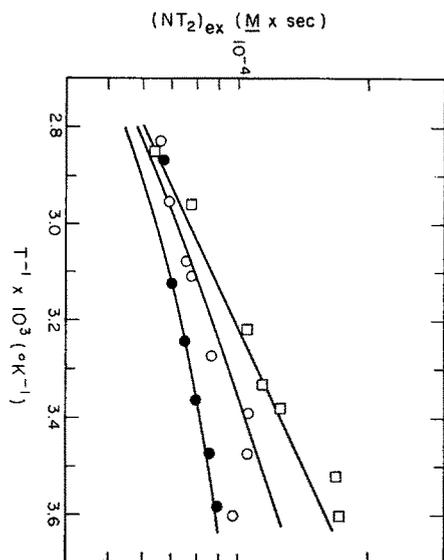


FIG. 3. Spin exchange contribution to proton NT_2 for V^{++} solutions as a function of $1/T$. \square —6 Mc, \circ —30 Mc, \bullet —60 Mc. Solid lines were calculated using the constants given in the text.

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.³ 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 τ_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 τ_s [and $(NT_2)_{ex}$] is an explicit function of τ_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 Scovil²⁵ for which $D=0.158 \pm 0.01$ cm^{-1} and $E=0.049 \pm 0.005$ cm^{-1} . 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 6×10^{-10} sec at 30 Mc. On that basis Eq. (2) yields $(A/h)=2 \times 10^6$ sec^{-1} . In the temperature range $0^\circ - 100^\circ C$ $\tau_s^{-1} \ll \tau_r^{-1}$ and $\tau_c = \tau_r$.

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

Among hydrated ions of the iron group Cr^{3+} is unique in that the mean lifetime τ_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.²⁶

A similar case of slow proton exchange has been examined in detail for solutions of the bisethylenediaminecopper(II) ion⁶ and general relaxation rate equations were used in connection with that work of the type introduced by McConnell.²⁷ Pearson, Palmer, Anderson, and Allred²⁸ 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 τ_v in V^{++} solutions.

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

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

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

²⁷ H. McConnell, J. Chem. Phys. **28**, 430 (1958).

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

detail by Broersma.²⁹ 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 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, τ_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. τ_h is found to be 4×10^{-6} sec at 300°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 Cr^{3+} solutions reported previously.³ With the value of τ_h in the foregoing, the revised τ_c for dipolar interaction in such solutions is then 8×10^{-11} sec at 300°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°K T_2 continues to decrease with increasing temperature, but with somewhat smaller slope. Assuming that this is attributable to the increase in τ_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°K .

The ESR linewidth at x band for hydrated Cr^{3+} in solutions of violet $\text{Cr}(\text{NO}_3)_3$ is about 150 gauss at 300°K , so that $\tau_s \approx 5 \times 10^{-10}$ sec at low fields. Eqs. (22) and (23) then give $D = 0.08\text{--}0.11$ cm^{-1} depending upon the choice of τ_v in the range 2×10^{-12} to 2.5×10^{-11} sec. (A/h) may then be evaluated from Eq. (2) and is found to be 2×10^6 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 Cu^{++} and Gd^{3+} solutions.^{1-3,6} The calculated τ_c 's are consistent with the ion tumbling process (2×10^{-11} sec) although that value may be somewhat lower than expected for hydrated Gd^{3+} , around which the solvent stiffening would be expected to be greater than in the case of hydrated Cu^{++} .

On that basis, it is expected that τ_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.^{1,2,6} If τ_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.

McConnell¹⁶ has estimated $\tau_{s,1}$ and $\tau_{s,2}$ for the various hyperfine components of the 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 3×10^{-8} to 2×10^{-9} sec for $\tau_r \sim 3 \times 10^{-11}$ sec. The actual relaxation time is probably an order of magnitude shorter, because Cu^{++} solutions do not exhibit a resolved hyperfine structure in microwave spectra.

For Gd^{3+} , Weger and Low³⁰ report $D = 0.04$ 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 τ_s is found to be $4\text{--}7 \times 10^{-10}$ sec at 30 Mc, depending upon the choice of τ_v in the range 2×10^{-12} to 2.5×10^{-11} sec. The minimum calculated τ_s is found at $\tau_v = 8 \times 10^{-12}$ sec. A complete calculation of τ_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 τ_s given above is probably satisfactory.

$\text{Ni}^{++}(S = 1; 3d^8 3F)$, $\text{Co}^{++}(S = \frac{5}{2}; 3d^6 4F)$, 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 Ni^{++} , and Co^{++} , and Fe^{++} one finds $T_1 \cong T_2$ with no frequency dependence up to 60 Mc, and with a very slight increase or decrease (Ni^{++}) with increasing temperature.^{1,2}

If one determines, without justification, τ_c from the observed T_1 with Eq. (1), very short times $\tau_c = 3 \times 10^{-12}$ sec for Ni^{++} , 5×10^{-13} sec for Co^{++} , and 10^{-12} sec for Fe^{++} would be obtained. It should be emphasized that the theory of Sec. II breaks down, if it leads to values of τ_s shorter than the correlation time of the motion in the liquid τ_v [compare Eq. (2.20) of Redfield¹⁹]. This implies that the instantaneous values of the crystalline field interactions D and E are larger than $\hbar\tau_v^{-1}$. For Ni^{++} and Fe^{++} this is quite reasonable. One has nearly complete quenching of the electron spin angular momentum at each instant. The true relaxation time of Fe^{++} solution may even be longer than the experimental value quoted in the foregoing, if a few percent of Fe^{3+} had been present in the experiment.¹

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 ω_{cr} is very large compared to the circular Zeeman frequency ω_s .

In the case of the 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.¹² The argu-

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

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

ment for Fe^{++} and Ni^{++} may therefore also be applied to 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 Ramsey³¹ found $\hbar^{-1}c_p = 71$ kc for the proton and $\hbar^{-1}c_F = 320$ kc for F^{19} in HF. If the spin-rotational coupling were a dominant factor the relaxation time of 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.³²

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

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

³² 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 τ_v cannot be obtained with any precision from Eqs. (22) and (23) on the basis of the temperature dependence of τ_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 τ_v centering about $\tau_v = 8 \times 10^{-12}$ sec for $\omega_s = 1.2 \times 10^{11}$ sec⁻¹. On the other hand, variation of ω_s at a given temperature (and τ_v) provides the necessary sensitivity. Values of τ_v (300°K) calculated for Mn^{++} and V^{++} solutions, 2.4×10^{-12} and 1.5×10^{-12} sec, respectively, from the frequency dependence of τ_s are entirely consistent with the proposed molecular impact process.

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