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THEORY OF SPIN-LATTICE QUADRUPOLE RELAXATION IN LIQUID SOLUTIONS OF DIAMAGNETIC SALTS

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Quadrupole spin-lattice relaxation of nuclear spins in liquid solutions of diamagnetic salts is considered theoretically. The calculations are performed under the assumption that stable complexes are formed around ions, these complexes consisting of molecules of the solvent or of molecules of the solvent and anions (or cations) simultaneously. It is found that lattice relaxation of the nuclear spin of the central ion is due to normal vibrations of the complex if the addends of the complex are identical particles, and by diffuse rotation if the addends are different particles. The calculated magnetic resonance line widths agree with the experimental data for aqueous solutions of Al^{3+} and Ga^{3+} salts. The resonance line widths of weakly hydrated ions (Na^+, Br^-, I^-) are related to the times of stable existence of the corresponding complexes.

1. MECHANISM OF QUADRUPOLE SPIN-LATTICE RELAXATION IN DIAMAGNETIC IONIC SOLUTIONS

If the nucleus of a diamagnetic atom (or ion) possesses an electric quadrupole moment, energy is exchanged between the nuclear spin and the lattice (spin-lattice relaxation) as thermal motion causes changes in the quadrupole moment energy. Van Kranendonk[1] has calculated the quadrupole relaxation time of nuclear spins in crystals and Masuda[2] has performed a similar calculation for molecular liquids. In the present paper the quadrupole relaxation time is calculated for ionic liquid solutions of diamagnetic salts.

In ionic liquid solutions the immediate neighborhood of a positive (or negative) ion most frequently consists of six particles surrounding the ion in the form of an octahedron; these are molecules of the solvent or anions (or cations). We assume that a stable ionic complex endures longer than the spin-lattice relaxation time of the ionic nucleus. It is then evident that in studying the spin-lattice relaxation of the central ion we must first consider the thermal motions of members of the complex. The thermal motion of the complex consists of internal vibrations and diffuse rotation, both of which can result in relaxation of the nuclear spin. Diffuse rotation of the complex is found to play the principal part in quadrupole spin relaxation in mixed complexes consisting of different addends.* On the other hand, in complexes consisting of identical addends quadrupole relation results from the internal thermal vibrations of the complex.

Let us consider an ion located at the center of a mixed complex consisting of water molecules and anions. The strong inhomogeneous electric field at the center of the mixed complex will act on the nuclear quadrupole moment to induce quadrupole splitting of the ion's spin levels superposed on the Zeeman splitting. The magnitude of the quadrupole splitting depends on the orientation of the axes of the complex with respect to the external magnetic field; therefore Brownian rotation of the complex will change the splitting in a random fashion, which results in an energy exchange between the spin and thermal motion of the lattice.

When the addends of the complex are identical the electric field at the center of the octahedron will possess cubic symmetry and will not induce splitting of the nuclear spin levels. Therefore rotation of a complex with identical addends cannot result in spin relaxation. In this case we must consider the internal vibrations of the complex, as a result of which the symmetry of the electric field at the center of the octahedron is disturbed in a time-dependent manner. The splitting of the spin levels is consequently time-dependent, and

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*An addend is a diamagnetic particle in the first coordination sphere of the ion.

spin relaxation results.

In mixed complexes spin relaxation is obviously produced by both the rotation and internal vibrations of the complex, but we shall see below that the vibrations play a subordinate part.

In real solutions mixed and unmixed complexes exist simultaneously. Thus Connick and Poulson[3] have shown that aqueous solutions of NaF and $Al(NO_3)_3$ contain approximately identical numbers of the complexes $Al(H_2O)_6^{3+}$, $Al(H_2O)_5F^{2+}$ and $Al(H_2O)_4F_2^{+}$. It is noteworthy, however, that the intensity of magnetic resonance absorption in Al^{27} nuclei is proportional to the number of hydrated $Al(H_2O)_6^{3+}$ complexes. It is evident that Al^{27} quadrupole relaxation in mixed complexes is very rapid and that absorption by these nuclei is not observed because of the extremely large line width. This has been confirmed by our calculations for Al^{27} and a number of other ionic nuclei.

2. SPIN-LATTICE INTERACTION ENERGY OF NUCLEI HAVING AN ELECTRIC QUADRUPOLE MOMENT

The quadrupole part of the energy of any charge system (such as an atomic nucleus) in an inhomogeneous electric field induced by external charges is the scalar product of two symmetric second-order tensors — the tensor of the nuclear quadrupole moment, D_{ik}, and the tensor of the electric field gradient at the nucleus, $(\nabla E)^{ik} = \partial^2\varphi/\partial x_i \partial x_k$:[4]

$$H = \sum_{i,k} \tfrac{1}{6} D_{ik}\partial^2\varphi / \partial x_i \partial x_k. \tag{1}$$

In the representation in which I^2 and I are diagonal the five independent components of the nuclear quadrupole moment tensor D_{ik} can be given in terms of the nuclear spin projection:

$$D_0 = \tfrac{1}{2} C\,(3I_z^2 - I\,(I+1)), \qquad D_{\pm 1} = \tfrac{3}{2} C\,\{I_z I_\pm\},$$
$$D_{\pm 2} = 3CI_\pm^2, \quad I_\pm = I_x \mp iI_y, \quad \{I_i I_k\} = I_i I_k + I_k I_i,$$
$$C = eQ / I\,(2I-1), \tag{2}$$

where Q is the nuclear quadrupole moment.

With the coordinate origin at the center of mass of the given nucleus, $\mathbf{r}_A(x_A, y_A, z_A)$ will denote the radius vector of an outside charge e_A. The independent components of the tensor $(\nabla \mathbf{E})^{ik}$ are then

$$(\nabla \mathbf{E})^0 = \sum_A 3e_A r_A^{-5}\,(3z_A^2 - r_A^2),$$
$$(\nabla \mathbf{E})^{\pm 1} = \sum_A 3e_A r_A^{-5} z_A (x_A \pm iy_A)$$
$$(\nabla \mathbf{E})^{\pm 2} = \sum_A \tfrac{3}{4} e_A r_A^{-5} (x_A \pm iy_A)^2. \tag{3}$$

We now denote by $\mathbf{s}_A(X_A, Y_A, Z_A)$ the change of distance between the given nucleus and the charge e_A which results from internal thermal vibrations of the complex. $\mathbf{s}_A$ will obviously be small compared with the equilibrium distance $\mathbf{r}_A^0$ between the nucleus and charge; the tensor components $(\nabla \mathbf{E})^{ik}$ may therefore be expanded in powers of the projections of the $\mathbf{s}_A$, and for our purposes the linear term is sufficient. The form of the expansion is simple when the cubic axes of symmetry of the complex are the coordinate axes x, y, z; the equilibrium separation $\mathbf{r}_A^0$ is then represented by

$$r_1^0(a, 0, 0), \quad r_2^0(0, a, 0), \quad r_3^0(0, 0, a),$$
$$r_4^0(-a, 0, 0), \quad r_5^0(0, -a, 0), \quad r_6^0(0, 0, -a).$$

Furthermore, in an unmixed complex all addends are identical and possess identical effective charges $e_A = e'$, in which case we also have the identities

$$(\nabla \mathbf{E})^0_{s_A=0} = (\nabla \mathbf{E})^{\pm 1}_{s_A=0} = (\nabla \mathbf{E})^{\pm 2}_{s_A=0} = 0.$$

It follows easily from the foregoing that

$$(\nabla \mathbf{E})^0 = 18\sqrt{3}\,(1+\gamma)\,e'a^{-4}Q_3,$$
$$(\nabla \mathbf{E})^{\pm 1} = 6\,(1+\gamma)\,e'a^{-4}\,(Q_5 \pm iQ_6),$$
$$(\nabla \mathbf{E})^{\pm 2} = \tfrac{3}{2}(1+\gamma)\,e'a^{-4}\,(-3Q_2 \pm 2iQ_4). \tag{4}$$

Here Q_i are the orthogonal normal vibrational coordinates of the complex which were first introduced by Yost et al:[5]

$$Q_2 = (X_1 - X_4 - Y_2 + Y_5)/2,$$
$$Q_3 = \left[\tfrac{1}{2}(X_1 - X_4 + Y_2 - Y_5) + (Z_6 - Z_3)\right]/\sqrt{3},$$
$$Q_4 = (X_2 - X_5 + Y_1 - Y_4)/2,$$
$$Q_5 = (Z_1 - Z_4 + X_3 - X_6)/2,$$
$$Q_6 = (Y_3 - Y_6 + Z_2 - Z_5)/2. \tag{5}$$

The factor $(1+\gamma)$ in (4) takes antishielding into account; the inhomogeneous field of the outer particles distorts the electron shell of the central ion, creating an additional inhomogeneous field at the nucleus which is similar to the field of the outer particles. This effect must obviously be taken into account in calculating the relaxation time of nuclear spins. Antishielding factors γ have been calculated theoretically for a majority of ions possessing a nuclear quadrupole moment.[6]

The part of the energy of the quadrupole moment which is dependent on the lattice coordinates and on time may therefore be represented by the sum $\mathcal{H}' = \sum_{i=-2}^{2} \mathcal{H}'_i$, where

$$\mathcal{H}'_0 = 3\sqrt{3}\,\Lambda\,(3I_z^2 - I(I+1))\,Q_3,$$

$$\mathcal{H}'_{\pm} = \tfrac{3}{2}\Lambda\,\{I_zI_{\pm}\}\,(Q_5 \pm iQ_6),$$

$$\mathcal{H}'_{\pm 2} = \tfrac{3}{4}\Lambda I_{\pm}^2\,(-3Q_2 \pm 2iQ_4),$$

$$\Lambda = ee'(1+\gamma)\,Qa^{-4}/I(2I-1). \tag{6}$$

In liquids only nuclear magnetic resonance can be observed since the quadrupole interaction of the nucleus varies randomly because of thermal motion and cannot induce constant splitting of the nuclear spin levels. The integrals of motion of a spin in a strong magnetic field are the values of I^2 and of the projection $I_{z'}$ in the external field direction. Therefore the spin variables in the right member of (6) must be transformed to the laboratory coordinate system $x'y'z'$ with z' in the external magnetic field direction. If θ and φ are the polar angles of the z' laboratory axis in the xyz coordinate system of the ionic complex, after a simple transformation of the components of I we obtain

$$I_{\pm}^2 = e^{\mp 2i\varphi}\,[I_{x'}^2\cos^2\theta - I_{y'}^2 + \{I_{x'}I_{z'}\}\sin\theta\cos\theta \mp i\,\{I_{x'}I_{y'}\}\cos\theta$$
$$\mp i\,\{I_{z'}I_{y'}\}\sin\theta + I_{z'}^2\sin^2\theta],$$

$$\{I_zI_{\pm}\} = e^{\mp i\varphi}\,[(I_{z'}^2 - I_{x'}^2)\sin 2\theta \mp i\,\{I_{x'}I_{y'}\}\sin\theta$$
$$+ \{I_{x'}I_{z'}\}\cos 2\theta \mp i\,\{I_{z'}I_{y'}\}\cos\theta],$$

$$I_z^2 = I_{x'}^2\sin^2\theta + I_{z'}^2\cos^2\theta - \{I_{x'}I_{y'}\}\sin\theta\cos\theta. \tag{7}$$

The primes in (7) will hereinafter be omitted

3. RELAXATION TRANSITION PROBABILITIES

The perturbation (6) contains both spin variables and lattice variables of the system; the latter are the normal internal vibrational coordinates Q_i of the complex. The remaining lattice coordinates, which do not interact directly with the spin variables, interact with the Q_i coordinates and ultimately determine the character of their time dependence. Thus in liquids the Q_i interact with the random Brownian motion of particles surrounding the complex; this determines the random, fluctuating temporal variation of Q_i.[7]

The probability that the perturbation $\mathcal{H}'(t)$ induces a transition of the system from the state l to the state k in one second will be calculated by means of the familiar perturbation formula

$$w_{lk} = \frac{1}{t\hbar^2}\left|\int_0^t \mathcal{H}'_{lk}(t')\exp(-i\omega_{lk}t')\,dt'\right|^2, \tag{8}$$

where $\omega_{lk} = (E_l - E_k)/\hbar$. When, as occurs in our problem, the matrix element $\mathcal{H}'_{lk}(t)$ is a random function of time, (8) can be transformed by introducing the correlation function[8]

$$G(\tau) = \overline{\mathcal{H}'_{lk}(t')\,\mathcal{H}'_{lk}(t'-\tau)}.$$

Then

$$w_{lk} = \hbar^{-2}\int_{-\infty}^{+\infty} G(\tau)\exp(-i\omega_{lk}\tau)\,d\tau. \tag{9}$$

Denoting the characteristic correlation time by τ_c as usual, we represent the correlation function as decreasing exponentially:

$$G(\tau) = G(0)\exp(-|\tau|/\tau_c). \tag{10}$$

The transition probability is then given by

$$w_{lk} = \hbar^{-2}\,\overline{|\mathcal{H}'_{lk}|^2}\,2\tau_c/(1+\omega_{lk}^2\tau_c^2). \tag{11}$$

The bar denotes averaging over all possible values of the coordinates Q_i, θ, and φ. The time τ_c in (10) and (11) characterizes the damping of vibrations of Q_i. Al'tshuler and the present author[7] have shown that $\tau_c \sim 1/\gamma$, where γ is the vibrational line width in the optical spectra of liquid ions; τ_c is of the order 10^{-12} sec. The temperature variation of τ_c obeys a $T^{-1/2}$ law approximately; this reflects an increase in oscillator damping resulting from a temperature-associated increase in the number of collisions between the complex and neighboring Brownian particles.

We shall now calculate the coefficients in (11). The matrix element $\mathcal{H}'_{m,m-1}$ corresponding to the relaxation transition $m \to m-1$ is

$$\mathcal{H}'_{m,\,m-1} = \Lambda\,\{I_xI_z\}_{m,\,m-1}\,[Q_3(-9\sqrt{3}\sin\theta\cos\theta)$$
$$+ \tfrac{3}{2}(Q_5 + iQ_6)\,e^{-i\varphi}(\cos 2\theta - \cos\theta)$$
$$+ \tfrac{3}{2}(Q_5 - iQ_6)\,e^{i\varphi}(\cos 2\theta + \cos\theta)$$
$$+ \tfrac{3}{4}(-3Q_2 - 2iQ_4)\,e^{-2i\varphi}\sin\theta(\cos\theta - 1)$$
$$+ \tfrac{3}{4}(-3Q_2 + 2iQ_4)\,e^{2i\varphi}\sin\theta(1 + \cos\theta)]. \tag{12}$$

In averaging the square of this quantity the orthogonality of the Q_i coordinates must be taken into account. It is not actually possible to establish the differences between the normal frequencies ω_{0i} and masses m_i of individual Q_i oscillators; we therefore assume the following identical statistical mean square amplitude for all Q_i oscillators:[9]

$$\overline{Q_i^2} = \overline{Q^2} = (\hbar/2m\omega_0)\coth(\hbar\omega_0/2kT), \tag{13}$$

where m and ω_0 are mean values, with m close to the mass of the entire complex. The normal vibrational frequencies ω_0 of octahedral complexes of transition group ions in liquids lie in the range[10] $(4-16)\times 10^{13}$ sec^{-1}.

The result obtained by averaging is

$$\overline{|H'_{m,\,m-1}|^2} = (103\,/\,2)\,|\{I_xI_z\}_{m,\,m-1}|^2\,\Lambda^2\overline{Q^2}. \tag{14}$$

We obtain similarly:

$$\begin{aligned}\mathscr{H}'_{m,m-2} = \Lambda\,(I_x^2)_{m,\,m-2}\,[Q_3\cdot 9\sqrt{3}\sin^2\theta \\ -3\,(Q_5+iQ_6)\,e^{-i\varphi}\sin\theta\,(1+\cos\theta) \\ +3\,(Q_5-iQ_6)\,e^{i\varphi}\sin\theta\,(1-\cos\theta) \\ +{}^3/_4\,(-3Q_2+2iQ_4)\,e^{-2i\varphi}\,(1-\cos\theta)^2 \\ -{}^3/_4\,(3Q_2+2iQ_4)\,e^{2i\varphi}\,(1+\cos\theta)^2].\end{aligned} \tag{15}$$

$$\overline{|\mathscr{H}'_{m,\,m-2}|^2} = (1023\,/\,5)\,|\,(I_x^2)_{m,\,m-2}|^2\,\Lambda^2\overline{Q^2}. \tag{16}$$

Nonvanishing transition probabilities subject to the condition $\omega_{lk}^2\tau_c^2 \ll 1$ are

$$\begin{aligned} I={}^3/_2: \quad & w\,({}^3/_2,{}^1/_2) = w\,(-{}^1/_2,-{}^3/_2) = 309U, \\ & w\,({}^3/_2,-{}^1/_2) = w\,({}^1/_2,-{}^3/_2) = (3069\,/\,10)\,U. \end{aligned} \tag{17}$$

$$\begin{aligned} I={}^5/_2: \quad & w\,({}^5/_2,{}^3/_2) = w\,(-{}^3/_2,-{}^5/_2) = 2060U, \\ & w\,({}^3/_2,{}^1/_2) = w\,(-{}^1/_2,-{}^3/_2) = 824U, \\ & w\,({}^5/_2,{}^1/_2) = w\,(-{}^1/_2,-{}^5/_2) = 1023U, \\ & w\,({}^3/_2,-{}^1/_2) = w\,({}^1/_2,-{}^3/_2) = 4.5\cdot 1023U, \end{aligned} \tag{18}$$

where $U = \hbar^{-2}\Lambda^2\overline{Q}^2\tau_c$.

4. CALCULATION OF THE TIME T_1 AND OF THE LINE WIDTH

The table contains experimental data on relaxation times or magnetic resonance line widths for nuclei with quadrupole moments in aqueous ionic solutions. A resonance line whose width is determined by the spin-lattice interaction possesses Lorentz shape and width $\Delta\nu = 1/\pi T_1$.[11] In order to estimate the line width we calculate the time T_1, using the transition probabilities (17) and (18).

The spin-lattice relaxation time T_1 is obtained from the relation $T_1^{-1} = \alpha/C$, where α is the coefficient of thermal conductivity between the spin-system and the lattice, and C is the specific heat of the spin-system. Substituting the known formulas for α and C, we obtain[12]

$$T_1^{-1} = (2I+1)\sum_{l>k} w_{lk}\,(E_l-E_k)^2 \Big/ \sum_{l>k}(E_l-E_k)^2. \tag{19}$$

This equation is valid when $E_l - E_k \ll kT$, which is always fulfilled in our problem. By means of (17), (18), and (19) we obtain for spins $^5/_2$ and $^3/_2$, respectively:

$$T_1^{-1} = \frac{20312}{7}\left[\frac{ee'\,(1+\gamma)\,Q}{I\,(2I-1)\,a^4}\right]^2\overline{Q^2}\hbar^{-2}\tau_c, \tag{20}$$

$$T_1^{-1} = \frac{15336}{25}\left[\frac{ee'\,(1+\gamma)\,Q}{I\,(2I-1)\,a^4}\right]^2\overline{Q^2}\hbar^{-2}\tau_c. \tag{21}$$

We now proceed to evaluate the parameters in (20) and (21). These formulas were derived on the basis of a model in which the water molecule was regarded as a point charge; e′ and a are the effective charge of a dipolar water molecule and the effective distance between e′ and the nucleus of the central ion. The effective negative charge of the oxygen atom by which a water molecule is joined to the positive ion at the center of the complex is 0.66 e, judging from the dipole moment of water. The influence of the positive charges borne by the two hydrogen atoms may be neglected because the relaxation time is very strongly dependent on distance: $T_1 \backsim a^8$. It is clear from this relation that relaxation depends principally on the charge in the part of the oxygen atom electron shell which is closest to the central ion. The effective charge of the oxygen ion is displaced to the part of the electron shell closest to the central ion because of electric polarization induced by this positively charged central ion. Such polarization is of considerable magnitude because oxygen ions are highly polarizable ($\alpha = 3.88 \times 10^{-24}$ cm^3).[13] We therefore assume that the effective charge of the oxygen ion is not located on the oxygen nucleus but at a point where the field gradient falls off doubly compared with the gradient of the charges in the immediate vicinity of the central ion. Under this condition the distance a becomes $2^{1/3}r_u = 1.26\,r_u$ where r_u is the crystalline radius of the central ion.

The correlation time τ_c is taken to be 10^{-12} sec; T = 300°K. The values of I and Q given below were taken from reference 14, those of γ from reference 6 and those of r_u from reference 15. The following results were calculated:

Al^{27}: $I = {}^5/_2$, Q = 0.156 barn, $1+\gamma = 3.59$, r_u = 0.5 A. The complex $Al(H_2O)_6^{3+}$, because of the large charge of its central ion, is highly stable with a high natural frequency. Assuming $\omega_0 = 8 \times 10^{13}$ sec^{-1}, we have $T_1 = 1.22 \times 10^{-4}$ sec, $\Delta\nu$ = 2.6 kcs.

Ga^{69}: $I = {}^3/_2$, Q = 0.2318 barn, r_u = 0.62 A, $1+\gamma = 9.75$. Assuming $\omega_0 = 8 \times 10^{13}$ sec^{-1}, we

Salts in aqueous solution	Ions	Experimental line width, kcs	Salts in aqueous solution	Ions	Experimental line width, kcs
$AlCl_3$ $Al_2(SO_4)_3$	$(Al^{27})^{3+}$	5 [16]	NaCl	$(Na^{23})^+$	⩽1 [18]
$GaCl_3$	$(Ga^{69})^{3+}$	7 [17]	LiBr NaBr	Br^-	10 [19]
$GaCl_3$	$(Ga^{71})^{3+}$	3 [17]	NaI	$(I^{127})^-$	14 [17]

have $T_1 = 10^{-4}$ sec, $\Delta\nu = 3$ kcs.

Ga^{71}: $I = 3/2$, $Q = 0.1461$ barn, $T_1 = 2.6 \times 10^{-4}$ sec, $\Delta\nu = 1.2$ kcs.

Na^{23}: $I = 3/2$, $Q = 0.1$ barn, $r_u = 0.95$ A, $1 + \gamma = 5.1$. The ion Na^+ is known to form a very weak solvate. The stability of a solvate complex determines its bond energies and its normal vibrational frequency. Assuming $\omega_0 = 4 \times 10^{13}$ sec^{-1}, we have $T_1 = 0.01$ sec, $\Delta\nu = 30$ kcs.

Spin relaxation of negative ions will now be calculated using the same model that gave T_1 for positive ions. The following results are obtained for I^- and Br^-:

I^{127}: $I = 5/2$, $Q = 0.7$ barn, $r_u = 2.16$ A, $1 + \gamma = 179.75$. Assuming $\omega_0 = 4 \times 10^{13}$ sec^{-1}, we have $T_1^{-1} = 2.6 \times 10^3$ sec^{-1}, $\Delta\nu \approx 1$ kcs.

Br^{79}: $I = 3/2$, $Q = 0.335$ barn, $r_u = 1.95$ A, $1 + \gamma = 100.0$. Assuming $\omega_0 = 4 \times 10^{13}$ sec^{-1}, we have $T_1^{-1} = 1300$ sec^{-1}, $\Delta\nu \approx 400$ cps.

5. QUADRUPOLE RELAXATION OF NUCLEAR SPIN INDUCED BY DIFFUSE ROTATION OF A MIXED COMPLEX

We shall limit our consideration to a mixed complex of the form $M(H_2O)_5Y$, where M is the central ion and Y is an ion that replaces one of the water molecules in the octahedron. With the z axis in the M-Y direction, Eq. (3) gives $(\nabla E)^{\pm 1} = (\nabla E)^{\pm 2} = 0$ and

$$(\nabla \mathbf{E})^0 = 6\,(e_B / b^3 - e_A / a^3), \tag{22}$$

where e_A and e_B are the effective charges of a water molecule and of the ion Y respectively. If Y is a singly charged ion, $e_B = e$ and $e_A = 0.66\,e$. In our model the separations a and b are both equal to $1.26\,r_u$. Taking the antishielding effect into account, we therefore obtain

$$(\nabla \mathbf{E})^0 = 1.02\,(1 + \gamma)\, e r_u^{-3}. \tag{23}$$

The nonvanishing matrix elements are easily calculated:

$$\mathcal{H}'_{m,\,m-1} = 3\,(\nabla \mathbf{E})^0 (1 + \gamma)\, eQ\, \{I_z I_x\}_{m,\,m-1} \sin^2\theta(t),$$

$$\mathcal{H}'_{m,\,m-2} = -\,(\nabla \mathbf{E})^0 (1 + \gamma)\, eQ\, (I_x^2)_{m,\,m-2} \sin\theta(t)\cos\theta(t). \tag{24}$$

Transition probabilities are calculated by means of (11); for spin 3/2 we obtain

$$w\,(3/2,\ 1/2) = w\,(-1/2,\ -3/2) = (144/5)\,|\,eQ\,(1 + \gamma)\,(\nabla \mathbf{E})^0\,|^2\, \hbar^{-2}\, \tau_r,$$

$$w\,(3/2,\ -1/2) = w\,(1/2,\ -3/2) = (1/5)\,|\,eQ\,(1 + \gamma)\,(\nabla \mathbf{E})^0\,|^2\, \hbar^{-2}\, \tau_r. \tag{25}$$

Here τ_r is the correlation time of diffuse rotation of the complex. From the theory of Brownian motion we know that

$$\tau_r = 4\pi\eta l^3 / 3kT, \tag{26}$$

where η is the viscosity of the liquid and l is the radius of the complex. By means of (19) and (25) we calculate the relaxation time:

$$(T_1^{-1})_r = (58/5)\, e^2 Q^2 \hbar^{-2} (1 + \gamma)^2\, |(\nabla \mathbf{E})^0|^2\, \tau_r. \tag{27}$$

The radius of the complex $Al(H_2O)_5Y^{++}$ is taken to be 2.85 A; then $\tau_r = 2.3 \times 10^{-11}$ sec. With the above-mentioned values of the other parameters we obtain $(T_1^{-1})_r = 7.7 \times 10^6$ sec^{-1}. A similar calculation for the ion Na^+ in the complex $Na(H_2O)_5Y$ gives $(T_1^{-1})_r = 7.8 \times 10^6$ sec^{-1}.

The spin relaxation time of the central ion will be even shorter if the complex contains two or more anions (located nonsymmetrically in the complex) because all components of the gradient tensor $(\nabla E)^{ik}$ are then nonvanishing and of greater magnitude.

6. CONCLUSION

1. The spin-lattice relaxation time of nuclei with a large electric quadrupole moment is of the order $10^{-6} - 10^{-7}$ sec in mixed complexes, corresponding to $\sim 10^6$ kc for the line width. Lines with this width can obviously not be observed experimentally. It follows that the observed magnetic resonance line intensity for a nucleus with large quadrupole moment is proportional to the number of purely aqueous complexes. This suggests that measurements of magnetic resonance intensities provide a convenient method for investigating complexing in liquid solutions of diamagnetic salts.

2. For aqueous complexes of the ions Al^{3+} and Ga^{3+} good agreement is obtained between the calculated and measured resonance line widths. It is known from chemical investigations that hydrated complexes of Al^{3+} and Ga^{3+} are very stable. This confirms the correctness of our model if the lifetime of the complexes exceeds the spin-lattice relaxation time.

3. For the ions Na^+, Br^-, and I^- the calculated and observed resonance line widths do not agree. This evidently results from the weak stability of the complexes that these ions form with water. The experimentally observed line widths for the nuclei Na^{23}, Br^{79}, Br^{81}, and I^{127} are related to the lifetime of the complex rather than to the spin-lattice relaxation time.

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