Theory of Nuclear Magnetic Relaxation by Spin-Rotational Interactions in Liquids*

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The contribution of spin-rotational interactions to the nuclear magnetic relaxation of identical spin-$\frac{1}{2}$ nuclei at equivalent positions in spherical liquid molecules is calculated by use of the semiclassical form of the density-operator theory of relaxation, and the result is compared with the contributions of intra- and intermolecular dipole-dipole interactions. The angular velocity of a molecule is treated classically by assuming that it obeys an equation analogous to the Langevin equation that is postulated in treatments of translational Brownian motion. The change in orientation of a molecule is assumed to be due to isotropic rotational Brownian motion. By use of this model the correlation functions of components of the angular velocity of a molecule are calculated, and are found to have an exponentially decaying time dependence with a time constant (correlation time) τ_1 that is quite different in its temperature dependence than the correlation time τ_2 of the dipole-dipole interactions. In typical situations τ_1 is much smaller than τ_2. Use is made of this fact to evaluate the correlation functions of the functions of the orientation and angular velocity that occur in the tensor spin-rotational interactions. The result that $\tau_1 \ll \tau_2$ explains the experimentally observed "quenching" of the relaxation effect of spin-rotational interactions in liquids, and the result that $\tau_1 T$ increases as the temperature increases explains the experimentally observed temperature dependence of the relaxation effect of spin-rotational interactions in liquids.

1. INTRODUCTION

THE interaction of a nuclear magnetic moment with the magnetic field produced at the position of the nucleus by the rotation of the molecule containing the nucleus is called a spin-rotational interaction. Evidence has recently been given that spin-rotational interactions contribute significantly to the nuclear magnetic relaxation of some liquids.

The temperature dependence of the proton and fluorine spin-lattice relaxation rates in several freons has been measured by Gutowsky, Lawrenson, and Shimomura.[1] The spin-lattice relaxation of the fluorine nuclei was found to be more rapid than that of the protons, and to have a different temperature dependence. This behavior was attributed to a greater spin-rotational interaction for the fluorine nuclei than for the protons, since both experience comparable dipole-dipole interactions. They give an expression for the spin-lattice relaxation time, T_1, of a nucleus in a linear molecule, derived on the assumptions that the spin-rotational interaction is scalar, and that the correlation times for the spin-rotational interactions and the dipole-dipole interaction are the same. However, they point out that the spin-rotational interactions are, in general, tensor in form, $\mathbf{I}_i \cdot \mathbf{C} \cdot \mathbf{J}$, and that the assumption that the nuclear relaxation is governed by a single correlation time for all processes is much too drastic.

Johnson, Waugh, and Pinkerton[2] have extrapolated their experimental results for relaxation in gaseous CHF_3 to densities and temperatures appropriate to a liquid. They conclude that spin-rotational interactions are an important relaxation mechanism for the fluorine nuclei in liquid CHF_3.

Johnson and Waugh[3] have estimated that spin-rotational interactions are a significant relaxation mechanism in liquid methane. However, Bloom and Sandhu[4] have interpreted their experimental results for the proton spin-lattice relaxation in liquid samples of deuterated methane as indicating that the relaxation is mainly due to intermolecular dipole-dipole interactions, and that the contribution of spin-rotational interactions is at least a factor of 2 smaller than estimated by Johnson and Waugh.

Brown, Gutowsky, and Shimomura[5] have recognized that the statistical properties of the spin-rotation Hamiltonian in a liquid may be quite different from those of the orientation-dependent interactions. They propose a transient rotation model in which molecules jump from one orientation to another at random times; the spin-rotational interaction is assumed to operate during these jumps when the molecule is actually rotating. The statistical properties of such a model lead to an expression for the contribution of spin-rotational interactions to $(1/T_1)$ which has a temperature dependence which agrees with what they observe for the fluorine relaxation in liquid $CHFCl_2$.

In the present paper, the semiclassical form of the density operator theory of relaxation is employed to calculate the contribution of spin-rotational interactions to the nuclear magnetic relaxation of identical spin-$\frac{1}{2}$ nuclei at equivalent positions in spherical molecules in a liquid. The angular velocity of a molecule is treated classically by assuming that it obeys an equation

[1] H. S. Gutowsky, I. J. Lawrenson, and K. Shimomura, Phys. Rev. Letters **6**, 349 (1961).

[2] C. S. Johnson, Jr., J. S. Waugh, and J. N. Pinkerton, J. Chem. Phys. **35**, 1128 (1961).

[3] C. S. Johnson, Jr., and J. S. Waugh, J. Chem. Phys. **35**, 2020 (1961).

[4] M. Bloom and H. S. Sandhu, Can. J. Phys. **40**, 289 (1962).

[5] R. J. C. Brown, H. S. Gutowsky, and K. Shimomura, J. Chem. Phys. **38**, 76 (1963).

analogous to the Langevin equation that is frequently postulated in treatments of translational Brownian motion. By use of this model, the correlation functions of components of the angular velocity of a molecule can be calculated, and are found to have an exponentially decaying time dependence with a time constant (correlation time) τ_1 that is quite different in its dependence on the temperature and the properties of the liquid than the correlation time τ_2 of the functions of the orientation of the molecule that occur in the dipole-dipole interactions. In typical situations, τ_1 is much smaller than τ_2. Use is made of this fact to evaluate the correlation functions of the functions of the orientation and angular velocity of the molecule that occur in the tensor spin-rotational interactions. The contribution of spin-rotational interactions to the longitudinal and transverse relaxation rates is compared with the contribution of intra- and intermolecular dipole-dipole interactions, which are calculated for spherical molecules containing identical spin-$\frac{1}{2}$ nuclei in equivalent positions, assuming that correlations of different dipole-dipole interactions produce negligible effect.

2. FORM OF THE HAMILTONIAN

Consider a system of N identical nuclei in equivalent positions in spherical molecules in a liquid, each nucleus having a spin of $\frac{1}{2}$ and a gyromagnetic ratio γ. The molecules are exposed to a constant magnetic field $H_0\mathbf{k}$. The Hamiltonian of the system can be written

$$\mathcal{3C}=\hbar[E+F+G],\qquad(2.1)$$

where $\hbar E$ is the Zeeman interaction energy of the nuclear magnetic moments with the externally applied field, $\hbar F$ is the part of the Hamiltonian that involves only the molecular coordinates but not the spins, and $\hbar G$ is the interaction energy of the spins and the molecular surroundings. For the case considered here, it is convenient to express $\hbar G$ as $\hbar G_1 + \hbar G_2$, where $\hbar G_1$ represents the spin-rotational interactions and $\hbar G_2$ the dipole-dipole interactions of all the spins in the liquid. If the spin operator for the ith nucleus is denoted by $\mathbf{I}_i$, and the following notation introduced,

$$I_i^{\pm 1}=I_{ix}\pm iI_{iy},\quad I_i^0=I_{iz},\qquad(2.2)$$

$$I^\mu=\sum_{i=1}^{N} I_i^\mu,\qquad \mu=-1,0,1,\qquad(2.3)$$

the Zeeman interaction divided by $\hbar$ is

$$E=-\omega_0 I^0,\qquad(2.4)$$

where $\omega_0\equiv\gamma H_0$.

The spin-rotational interaction Hamiltonian of the ith nucleus can be written

$$\hbar G_1^{(i)}=\hbar\mathbf{I}_i\cdot\mathbf{C}^{(i)}\cdot\mathbf{J}_i,\qquad(2.5)$$

where $\hbar\mathbf{J}_i$ is the angular momentum of the molecule containing the ith nucleus and $\mathbf{C}^{(i)}$ is a dyadic. Suppose that $S^{(i)}$ is a coordinate system fixed in the molecule, having its z axis directed from the center of the molecule to the ith nucleus. Because of the assumed symmetry of the molecules, $\mathbf{C}^{(i)}$ is diagonal in $S^{(i)}$ with elements $C_z^{(i)}\equiv C_{\text{II}}$, $C_x^{(i)}=C_y^{(i)}\equiv C_\perp$, so that

$$G_1^{(i)}=C_\perp(I_{ix}^{(i)}J_{ix}^{(i)}+I_{iy}^{(i)}J_{iy}^{(i)})+C_{\text{II}}I_{iz}^{(i)}J_{iz}^{(i)},\qquad(2.6)$$

in terms of the components of $\mathbf{I}_i$ and $\mathbf{J}_i$ in $S^{(i)}$. The spherical components of $\mathbf{I}_i$ and $\mathbf{J}_i$ are defined, respectively, by

$$V_i^0\equiv I_{iz},\quad V_i^{\pm 1}\equiv\mp 2^{-\frac{1}{2}}(I_{ix}\pm iI_{iy})=\mp 2^{-\frac{1}{2}}I_i^{\pm 1},\qquad(2.7)$$

and

$$J_i^0\equiv J_{iz},\quad J_i^{\pm 1}\equiv\mp 2^{-\frac{1}{2}}(J_{ix}\pm iJ_{iy}),\qquad(2.8)$$

in terms of which

$$G_1^{(i)}=\sum_{k'=-1}^{1} C_{k'}(V_i^{k'})^{(i)}(J_i^{-k'})^{(i)},\qquad(2.9)$$

where

$$C_0\equiv C_{\text{II}},\quad C_{\pm 1}\equiv -C_\perp.\qquad(2.10)$$

Since the spherical components of a vector constitute a first-rank irreducible tensor,[6] the components $(V_i^{k'})^{(i)}$ in $S^{(i)}$ are related to the components V_i^k in the laboratory coordinate system, S, by

$$(V_i^{k'})^{(i)}=\sum_{k=-1}^{1} V_i^k \mathfrak{D}_{k'k}^{(1)*}(\alpha_i\beta_i\gamma_i),\qquad(2.11)$$

where $(\alpha_i\beta_i\gamma_i)\equiv\Omega_i$ are the Euler angles of $S^{(i)}$ with respect to S.[7] There is a similar relation between the components $(J_i^{k'})^{(i)}$ in $S^{(i)}$ and the components J_i^k in the laboratory coordinate system. Hence, the sum of all the spin-rotational interactions, $G_1\equiv\sum_i G^{(i)}$, can be written in terms of components of $\mathbf{I}_i$ and $\mathbf{J}_i$ in the laboratory coordinate system as

$$G_1=\sum_{i=1}^{N}\sum_{k=-1}^{1} U_i^k V_i^k,\qquad(2.12)$$

where

$$U_i^k\equiv\sum_{k',k''=-1}^{1} C_{k'}\mathfrak{D}_{k'k}^{(1)*}(\Omega_i)\mathfrak{D}_{-k'k''}^{(1)*}(\Omega_i)J_i^{k''}.\qquad(2.13a)$$

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[6] A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, New Jersey, 1957), Chap. 5.

[7] Equation (2.11) follows from Eq. (5.2.1) of Ref. 6, and the fact that

$$\sum_{m''}\mathfrak{D}_{m''m'}^{(i)*}(\alpha\beta\gamma)\mathfrak{D}_{m''m}^{(i)}(\alpha\beta\gamma)$$

$$=\sum_{m''}\mathfrak{D}_{m'm''}^{(i)*}(\alpha\beta\gamma)\mathfrak{D}_{mm''}^{(i)}(\alpha\beta\gamma)=\delta_{m'm}.$$

The properties of the coefficients $\mathfrak{D}_{mm'}^{(i)}(\alpha\beta\gamma)$ are discussed extensively in Chap. 4 of Ref. 6.

It is shown in Appendix A that $U_i{}^k$ can also be written

$$U_i{}^k = (1/3)(2C_\perp + C_{11})(-1)^k J_i^{-k} + (10/3)^{1/2}(C_{11} - C_\perp)$$

$$\times \sum_{k''=-1}^{1} J_i{}^{k''} \sum_{k'=-2}^{2} \begin{pmatrix} 2 & 1 & 1 \\ k' & k & k'' \end{pmatrix} \mathfrak{D}_{0k'}{}^{(2)}(\Omega_i), \quad (2.13b)$$

where $\begin{pmatrix} 2 & 1 & 1 \\ k' & k & k'' \end{pmatrix}$ is a 3-j symbol. Note that, in general, the spin-rotational interaction depends on the orientation of the molecule, since it involves the sets of Euler angles $\Omega_i \equiv (\alpha_i \beta_i \gamma_i)$ that specify the orientation with respect to the laboratory system of each body coordinate system $S^{(i)}$ in which the spin-rotational interaction of one of the spins is diagonal. However, if $C_\perp = C_{11}$, Eq. (2.13b) reduces to $C_\perp(-1)^k J_i^{-k}$, so that G_1 depends on the angular momentum of the molecule, but not its orientation. Note also that C_k is independent of i because of the assumption that the spins are in equivalent positions in the molecules.

The dipole-dipole interactions $\hbar G_2$ can be expressed in the form[8]

$$G_2 = \sum_{i,j=1}^{N} \sum_{k=-2}^{2} (1 - \delta_{ij}) U_{ij}{}^k V_{ij}{}^k, \quad (2.14)$$

where the $V_{ij}{}^k$ are second-rank irreducible tensor operators defined by

$$V_{ij}{}^0 \equiv -(8/3)^{1/2}[I_i{}^0 I_j{}^0 - \tfrac{1}{4}(I_i{}^1 I_j{}^{-1} + I_i{}^{-1} I_j{}^1)], \quad (2.15a)$$

$$V_{ij}{}^{\pm 1} \equiv \pm(I_i{}^0 I_j{}^{\pm 1} + I_i{}^{\pm 1} I_j{}^0), \quad (2.15b)$$

$$V_{ij}{}^{\pm 2} \equiv -I_i{}^{\pm 1} I_j{}^{\pm 1}, \quad (2.15c)$$

and the $U_{ij}{}^k$ are defined by

$$U_{ij}{}^k \equiv (3\pi/10)^{1/2} \gamma^2 \hbar r_{ij}^{-3} (-1)^k Y_2^{-k}(\theta_{ij}, \phi_{ij}), \quad (2.16)$$

where the $Y_2{}^k$ are normalized second-rank spherical harmonics. The length of the vector from the jth to the ith nucleus is denoted by r_{ij}, and the polar angles specifying the direction of $\mathbf{r}_{ij}$ in the laboratory coordinate system are denoted by θ_{ij} and ϕ_{ij}.

3. DENSITY OPERATOR RELAXATION THEORY

The nuclear magnetic relaxation can be calculated by considering an ensemble of systems each having a Hamiltonian of the form of Eq. (2.1). The spin part of the system is described by a reduced density operator σ, in the sense that the ensemble average of the expectation value of any spin operator, say, Q, is given by

$$\langle Q \rangle = \text{Tr}[\sigma Q]. \quad (3.1)$$

If it is assumed that the molecular degrees of freedom remain in thermal equilibrium at temperature T, independently of the state of the spin system, it can be

[8] Paul S. Hubbard, Rev. Mod. Phys. **33**, 249 (1961).

shown that the reduced density operator is a solution of the differential equation

$$(d\sigma/dt) + i[E + N, \sigma] = R(\sigma), \quad (3.2)$$

if certain conditions to be specified below are satisfied.[8] The relaxation operator $R(\sigma)$ and the operator N are second order in the interaction G. Since N is a small correction to E, it will be neglected in the present calculation. Also, since here E does not depend explicitly on the time, it is known that $R(\sigma) = R(\chi)$, where $\chi \equiv \sigma - \sigma^T$, and

$$\sigma^T \equiv e^{-\beta E} / \text{Tr}[e^{-\beta E}], \quad \beta \equiv \hbar/kT. \quad (3.3)$$

Since R is second order in G, and since for the present problem $G = G_1 + G_2$, it follows that R can be expressed as

$$R(\chi) = R_{11}(\chi) + R_{12}(\chi) + R_{21}(\chi) + R_{22}(\chi), \quad (3.4)$$

where R_{11} is the relaxation operator for the spin-rotational interactions G_1, R_{22} is the relaxation operator for the dipole-dipole interactions G_2, and R_{12} and R_{21} each involve both the spin-rotational and the dipole-dipole interactions. It is shown in Appendix B that

$$R_{11}(\chi) = \sum_{i,i'=1}^{N} \sum_{k,l=-1}^{1} J_{i'i}{}^{lk}(-l\omega_0)[[V_{i'}{}^l, \chi], V_i{}^k], \quad (3.5)$$

where

$$J_{i'i}{}^{lk}(\omega) \equiv \frac{1}{2} \int_0^\infty [C_{i'i}{}^{lk}(\tau)e^{i\omega\tau} + C_{ii'}{}^{kl}(\tau)e^{-i\omega\tau}] d\tau, \quad (3.6)$$

$$C_{i'i}{}^{lk}(\tau) \equiv \langle U_{i'}{}^l(t+\tau) U_i{}^k(t) \rangle, \quad (3.7)$$

and

$$R_{22}(\chi) = \sum_{i,j=1}^{N} \sum_{k=-2}^{2} \sum_{i',j'=1}^{N} \sum_{l=-2}^{2} (1 - \delta_{i'j'})(1 - \delta_{ij})$$

$$\times J_{(i'j')(ij)}{}^{lk}(-l\omega_0)[[V_{i'j'}{}^l, \chi], V_{ij}{}^k], \quad (3.8)$$

where

$$J_{(i'j')(ij)}{}^{lk}(\omega) \equiv \frac{1}{2} \int_0^\infty [C_{(i'j')(ij)}{}^{lk}(\tau)e^{i\omega\tau} + C_{(ij)(i'j')}{}^{kl}(\tau)e^{-i\omega\tau}] d\tau, \quad (3.9)$$

$$C_{(i'j')(ij)}{}^{lk}(\tau) \equiv \langle U_{i'j'}{}^l(t+\tau) U_{ij}{}^k(t) \rangle. \quad (3.10)$$

The operators $R_{12}(\chi)$ and $R_{21}(\chi)$ are similar in form to R_{11} and R_{22}; however they contain, respectively, the correlation functions

$$C_{i'(ij)}{}^{lk}(\tau) \equiv \langle U_{i'}{}^l(t+\tau) U_{ij}{}^k(t) \rangle \quad (3.11)$$

and

$$C_{(i'j')i}{}^{lk}(\tau) \equiv \langle U_{i'j'}{}^l(t+\tau) U_i{}^k(\tau) \rangle. \quad (3.12)$$

All of the classical correlation functions occurring in the semiclassical relaxation theory approach zero as τ approaches infinity, since $C_{lk}(\tau) \equiv \langle U^l(t+\tau) U^k(t) \rangle \to \langle U^l(t+\tau) \rangle \langle U^k(t) \rangle$ as $\tau \to \infty$, and the functions U^k are defined in such a manner that $\langle U^k(t) \rangle = 0$ for any time t. When a physical model is used to calculate the cor-

relation functions, it is usually found that if $C_{lk}(0)=0$, then $C_{lk}(\tau)=0$ for all values of τ. It will be assumed that this is the case for all correlation functions occurring in this calculation. It is easy to show that $C_{i'(ij)}{}^{lk}(0)=0$ and $C_{(i'j')i}{}^{lk}(0)=0$, since these correlation functions contain a single component, $J_i{}^{k''}$, of the angular momentum of a molecule, which at any instant is independent of the orientation of the spherical molecule and has zero average value, $\langle J_i{}^{k''}\rangle=0$, since all orientations of the angular momentum are equally probable. Hence, $C_{i'(ij)}{}^{lk}(\tau)$ and $C_{(i'j')i}{}^{lk}(\tau)$ are taken to be zero for all τ, with the result that $R_{12}(\chi)=R_{21}(\chi)=0$.

If Eq. (3.2) is multiplied on the right by the operator I^ν, and the trace taken, one obtains

$$d(\mathrm{Tr}[\sigma I^\nu])/dt + i\,\mathrm{Tr}[E,\sigma]I^\nu = \mathrm{Tr}R(\sigma)I^\nu, \quad (3.13)$$

if the operator N is neglected. Since $E=-\omega_0 I^0$, and since the trace of a product of operators is unchanged by a cyclic permutation of the operators, $i\,\mathrm{Tr}[E,\sigma]I^\nu = i\omega_0\,\mathrm{Tr}[\sigma,I^0]I^\nu = i\omega_0\,\mathrm{Tr}\sigma[I^0,I^\nu]$. Hence, using the commutation relation

$$[I^\mu,I^\nu]=(-1)^{\mu+\nu}(\mu-\nu)I^{\mu+\nu}, \quad (3.14)$$

which follows from the usual angular momentum commutation relations $\mathbf{I}\times\mathbf{I}=i\mathbf{I}$, one obtains $i\,\mathrm{Tr}[E,\sigma]I^\nu = -i\omega_0(-1)^\nu\nu\,\mathrm{Tr}[\sigma I^\nu]=i\omega_0\nu\,\mathrm{Tr}[\sigma I^\nu]$, since the expression is zero except for $\nu=\pm1$. Thus, Eq. (2.13) can be written

$$d\langle I^\nu\rangle/dt + i\omega_0\nu\langle I^\nu\rangle = \mathrm{Tr}[R_{11}(\chi)I^\nu]$$
$$+\mathrm{Tr}[R_{22}(\chi)I^\nu], \quad (3.15)$$

where use has been made of the relation $R(\sigma)=R_{11}(\chi)+R_{22}(\chi)$ discussed above, and $\langle I^\nu\rangle=\mathrm{Tr}[\sigma I^\nu]$.

4. RELAXATION BY SPIN-ROTATIONAL INTERACTIONS

By use of Eq. (3.5) for $R_{11}(\chi)$, one obtains

$$\mathrm{Tr}[R_{11}(\chi)I^\nu]=\sum_{i,i'=1}^{N}\sum_{k,l=-1}^{1} J_{i'i}{}^{lk}(-l\omega_0)$$
$$\times\mathrm{Tr}[[V_{i'}{}^l,\chi],V_i{}^k]I^\nu. \quad (4.1)$$

Since the operators $V_i{}^k$ are the elements of a first-rank irreducible tensor operator with respect to $\mathbf{I}$, they satisfy the commutation relations[9]

$$[I^\nu,V_i{}^k]=A^\nu(1,k)V_i{}^{k+\nu}, \quad (4.2)$$

where

$$A^0(K,k)=k, \quad (4.3a)$$

$$A^{\pm1}(K,k)=[(K\mp k)(K\pm k+1)]^{1/2}, \quad (4.3b)$$

If the order of the operators in the trace in Eq. (4.1) is cyclicly permuted, use made of Eq. (4.2), and the

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operators again cyclicly permuted, one obtains

$$\mathrm{Tr}[[V_{i'}{}^l,\chi],V_i{}^k]I^\nu = \mathrm{Tr}[V_{i'}{}^l,\chi][V_i{}^k,I^\nu]$$
$$= A^\nu(1,k)\,\mathrm{Tr}[\chi,V_{i'}{}^l]V_i{}^{k+\nu}$$
$$= A^\nu(1,k)\,\mathrm{Tr}\chi[V_{i'}{}^l,V_i{}^{k+\nu}]. \quad (4.4)$$

But $[V_{i'}{}^l,V_i{}^{k+\nu}]=\delta_{ii'}[V_i{}^l,V_i{}^{k+\nu}]$, so that substitution of (4.4) into (4.1) leads to

$$\mathrm{Tr}[R_{11}(\chi)I^\nu]=\sum_{i=1}^{N}\sum_{k,l=-1}^{1} J_{ii}{}^{lk}(-l\omega_0)A^\nu(1,k)$$
$$\times\mathrm{Tr}\chi[V_i{}^l,V_i{}^{k+\nu}]. \quad (4.5)$$

In order to evaluate the functions $J_{ii}{}^{lk}(-l\omega_0)$, one must know the correlation functions $C_{ii}{}^{lk}(\tau)$. From the expression (2.13b) for the $U_i{}^k$ and the definition (3.7) of $C_{i'i}{}^{lk}(\tau)$, it follows that

$$C_{ii}{}^{lk}(\tau)\equiv\langle U_i{}^l(t+\tau)U_i{}^k(\tau)\rangle$$

$$= (1/9)(2C_\perp+C_{11})^2(-1)^{l+k}\langle[J_i{}^{-l}]_{t+\tau}[J_i{}^{-k}]_t\rangle$$

$$+ (10/27)^{1/2}(2C_\perp+C_{11})(C_{11}-C_\perp)$$

$$\times\Bigg\{(-1)^l\sum_{k''=-1}^{1}\sum_{k'=-2}^{2}\begin{pmatrix}2&1&1\\k'&k&k''\end{pmatrix}$$

$$\times\langle[J_i{}^{-l}]_{t+\tau}[J_i{}^{k''}\mathfrak{D}_{0k'}{}^{(2)}(\Omega_i)]_t\rangle$$

$$+(-1)^k\sum_{l''=-1}^{1}\sum_{l'=-2}^{2}\begin{pmatrix}2&1&1\\l'&l&l''\end{pmatrix}$$

$$\times\langle[J_i{}^{l''}\mathfrak{D}_{0l'}{}^{(2)}(\Omega_i)]_{t+\tau}[J_i{}^{-k}]_t\rangle\Bigg\}$$

$$+ (10/3)(C_{11}-C_\perp)^2\sum_{l'',k''=-1}^{1}$$

$$\times\sum_{l',k'=-2}^{2}\begin{pmatrix}2&1&1\\l'&l&l''\end{pmatrix}\begin{pmatrix}2&1&1\\k'&k&k''\end{pmatrix}$$

$$\times\langle[J_i{}^{l''}\mathfrak{D}_{0l'}{}^{(2)}(\Omega_i)]_{t+\tau}[J_i{}^{k''}\mathfrak{D}_{0k'}{}^{(2)}(\Omega_i)]_t\rangle. \quad (4.6)$$

The second and third correlation functions on the right-hand side of Eq. (4.6) are zero at $\tau=0$ and, hence, will be taken to be zero for all values of τ. They are zero at $\tau=0$ as a consequence of the assumption that at any instant the orientation of a molecule is independent of its angular momentum, so that, for example,

$$\langle[J_i{}^{-l}J_i{}^{k''}\mathfrak{D}_{0k'}{}^{(2)}(\Omega_i)]_t\rangle=\langle[J_i{}^{-l}J_i{}^{k''}]_t\rangle\langle[\mathfrak{D}_{0k'}{}^{(2)}(\Omega_i)]_t\rangle.$$

The second factor is zero when the average is performed considering all orientations of the molecule to be equally probable at time t.[10]

The other two correlation functions on the right-hand

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[9] Equations (4.2) and (4.3) of the present paper follow from Eqs. (5.2.2) and (5.2.3) of Ref. 6.

[10] The average is given by Eq. (4.6.1) of Ref. 6, with
$$\mathfrak{D}_{m_1'm_1}{}^{(i_1)*}(\alpha\beta\gamma)=\mathfrak{D}_{00}{}^{(0)*}(\Omega_i)=1$$
and
$$\mathfrak{D}_{m_2'm_2}{}^{(i_2)}(\alpha\beta\gamma)=\mathfrak{D}_{0k'}{}^{(2)}(\Omega_i).$$

side of Eq. (4.6) are calculated in the following section. When the results given below in Eqs. (5.11) and (5.19) are used in the expression (4.6), and use made of the properties of the 3-j symbols, one obtains

$$C_{ii}{}^{lk}(\tau) = (IkT/9\hbar^2)(-1)^k \delta_{-l,k}[(2C_{\perp}+C_{11})^2$$
$$\times \exp(-\tau/\tau_1)+2(C_{11}-C_{\perp})^2 \exp(-\tau/\tau_{12})], \quad (4.7)$$

where the k multiplying T is the Boltzmann constant, and where τ_{12} is defined by

$$(1/\tau_{12}) \equiv (1/\tau_1)+(1/\tau_2), \quad (4.8)$$

in terms of the quantities τ_1 and τ_2 defined below in Eqs. (5.12) and (5.17), respectively. It is argued in the next section that the term involving τ_{12} in (4.7) is correct only if either $\tau_1 \ll \tau_2$ or $\tau_2 \ll \tau_1$.

By use of (4.7) in expression (3.6), one obtains

$$J_{ii}{}^{lk}(\omega) = (-1)^k \delta_{-l,k} J_1(\omega), \quad (4.9)$$

where $J_1(\omega)$ is an even function of ω defined by

$$J_1(\omega) \equiv (IkT/9\hbar^2)\{(2C_{\perp}+C_{11})^2 \tau_1[1+(\omega\tau_1)^2]^{-1}$$
$$+2(C_{11}-C_{\perp})^2 \tau_{12}[1+(\omega\tau_{12})^2]^{-1}\}. \quad (4.10)$$

Note that the expressions for $C_{ii}{}^{lk}(\tau)$ and $J_{ii}{}^{lk}(\omega)$ are independent of i, which has resulted from the assumption that all the nuclei are in equivalent positions in spherical molecules.

After substitution of expression (4.9) into (4.5), the sum over l can be immediately performed due to the presence of the factor $\delta_{-l,k}$. If the sum over k is then written out, use made of the commutation relations

$$[V_i{}^{\pm 1}, V_i{}^0] = 2^{-\frac{1}{2}} I_i{}^{\pm 1}, \quad [V_i{}^{\pm 1}, V_i{}^{\mp 1}] = \mp I_i{}^0, \quad (4.11)$$

and the definition (4.3) of $A^\mu(K,k)$, one obtains, in the case $\nu = 0$, the result

$$\mathrm{Tr}[R_{11}(\chi)I^0] = -(1/T_1)_1(\langle I^0 \rangle - \langle I^0 \rangle^T), \quad (4.12)$$

where

$$(1/T_1)_1 \equiv 2J_1(\omega_0) \quad (4.13)$$

and

$$\langle I^0 \rangle^T = N\beta\omega_0/4. \quad (4.14)$$

The expression (4.14) for $\langle I^0 \rangle^T \equiv \mathrm{Tr}[\sigma^T I^0]$ is correct to first order in $\beta\omega_0$, which is consistent with the approximation made in obtaining the form of the relaxation operator R used in the calculation.

In a similar manner, one obtains from (4.5) with $\nu = \pm 1$ the result

$$\mathrm{Tr}[R_{11}(\chi)I^{\pm 1}] = -(1/T_2)_1 \langle I^{\pm 1} \rangle, \quad (4.15)$$

where

$$(1/T_2)_1 \equiv [J_1(0)+J_1(\omega_0)]. \quad (4.16)$$

5. CORRELATION FUNCTIONS

The theory of the translational Brownian motion of a spherical particle is frequently based upon the Langevin equation

$$d\mathbf{u}/dt = -B\mathbf{u}+\mathbf{A}(t), \quad (5.1)$$

where $\mathbf{u}$ denotes the velocity of the particle.[11] Equation (5.1) results from the assumption that the force acting on a particle consists of two parts: (1) a frictional force $-f\mathbf{u}$, where $f \equiv mB$ and m is the mass of the particle, and (2) a fluctuating force $m\mathbf{A}(t)$ which is characteristic of the Brownian motion. The quantity $\mathbf{A}(t)$ has statistically defined properties such that the conditional probability density that a particle has a velocity $\mathbf{u}$ at time $t+\tau$ if it has velocity $\mathbf{u}_0$ at time t approaches a Maxwellian distribution as τ approaches infinity:

$$W(\mathbf{u},\tau;\mathbf{u}_0) \rightarrow (m/2\pi kT)^{3/2} \exp(-m\mathbf{u}^2/2kT),$$
$$(\tau \rightarrow \infty). \quad (5.2)$$

The condition (5.2) and the Langevin equation (5.1) are sufficient to determine the conditional probability density for the velocity of a molecule. The result is

$$W(\mathbf{u},t;\mathbf{u}_0) = [m/2\pi kT(1-e^{-2B\tau})]^{3/2}$$
$$\times \exp[-m|\mathbf{u}-\mathbf{u}_0 e^{-B\tau}|^2/2kT(1-e^{-2B\tau})]. \quad (5.3)$$

In terms of f, the viscous retarding force per unit velocity, the diffusion coefficient of the particles is[11]

$$D = kT/f, \quad (5.4)$$

where k is the Boltzmann constant and T is the absolute temperature.

The conditional probability density for the angular velocity of a spherical particle can be calculated in a manner analogous to the treatment of translational velocity described in the previous paragraphs. It is assumed that the torque acting on a spherical particle is the sum of a frictional part $-f'\boldsymbol{\omega}$ and a fluctuating part $I\mathbf{A}'(t)$, where I is the moment of inertia of the spherical particle. The equation describing the rotational motion is, thus, of the Langevin form

$$d\boldsymbol{\omega}/dt = -B'\boldsymbol{\omega}+\mathbf{A}'(t), \quad (5.5)$$

if one defines B' by $f' \equiv IB'$. Also it is assumed that the conditional probability density approaches a Maxwellian form as τ approaches infinity:

$$W'(\boldsymbol{\omega},\tau;\boldsymbol{\omega}_0) \rightarrow (I/2\pi kT)^{3/2} \exp(-I\omega^2/2kT),$$
$$(\tau \rightarrow \infty). \quad (5.6)$$

With these assumptions, the calculation of $W'(\boldsymbol{\omega},\tau;\boldsymbol{\omega}_0)$ is formally the same as the calculation of $W(\mathbf{u},\tau;\mathbf{u}_0)$, so that $W'(\boldsymbol{\omega},\tau;\boldsymbol{\omega}_0)$ can be obtained from (5.4) by replacing m by I and B by B':

$$W'(\boldsymbol{\omega},\tau;\boldsymbol{\omega}_0) = [I/2\pi kT(1-e^{-2B'\tau})]^{3/2}$$
$$\times \exp[-I|\boldsymbol{\omega}-\boldsymbol{\omega}_0 e^{-B'\tau}|^2/2kT(1-e^{-2B'\tau})]. \quad (5.7)$$

The correlation function of two Cartesian components of the angular velocity of a molecule can be expressed as

$$\langle \omega_i(t+\tau)\omega_j(t) \rangle$$
$$= \int \left\{ \int \omega_i W'(\boldsymbol{\omega},\tau;\boldsymbol{\omega}_0)d\boldsymbol{\omega} \right\} \omega_{0j} P(\boldsymbol{\omega}_0)d\boldsymbol{\omega}_0, \quad (5.8)$$

[11] S. Chandrasekhar, Rev. Mod. Phys. 15, 1 (1943), Chap. II.

where for spherical molecules $W'(\omega,\tau;\omega_0)$ is given by (5.7), and $P(\omega_0)$ is the probability density that at any time t the molecule has angular velocity ω_0, which is the Maxwellian distribution

$$P(\omega_0) = (I/2\pi kT)^{3/2}\exp(-I\omega_0^2/2kT). \quad (5.9)$$

After substitution of (5.7) and (5.9) into (5.8), the integrals can be easily performed; the result is

$$\langle\omega_i(t+\tau)\omega_j(t)\rangle = \delta_{ij}(kT/I)e^{-B'\tau}. \quad (5.10)$$

The angular momentum of a spherical molecule, in units of $\hbar$, is related to the angular velocity of the molecule by $\hbar\mathbf{J}=I\boldsymbol{\omega}$. Hence, from the definition of the spherical components of $\mathbf{J}$, Eqs. (2.8), and from Eq. (5.10), it follows that

$$\langle J_i^{l''}(t+\tau)J_i^{k''}(t)\rangle = (-1)^{l''}\delta_{l'',-k''}(IkT/\hbar^2)$$
$$\times\exp(-\tau/\tau_1), \quad (5.11)$$

where

$$\tau_1\equiv(1/B'). \quad (5.12)$$

In order to calculate the other nonzero correlation function in (4.6),

$$\langle[J_i^{l''}\mathfrak{D}_{0l'}^{(2)}(\Omega_i)]_{t+\tau}[J_i^{k''}\mathfrak{D}_{0k'}^{(2)}(\Omega_i)]_t\rangle, \quad (5.13)$$

one needs to know the conditional probability density, $W'(\omega_i,\Omega_i,\tau;\omega_{i0},\Omega_{i0})$, that the ith molecule has angular velocity ω_i and orientation Ω_i at time $t+\tau$ if it has angular velocity ω_{i0} and orientation Ω_{i0} at an earlier time t. It should be recalled that Ω_i is an abbreviation for the Euler angles $(\alpha_i,\beta_i,\gamma_i)$ which specify the orientation of the body coordinate axes $S^{(i)}$ with respect to the laboratory coordinate system S. The analogous conditional probability density for translational Brownian motion, $W(\mathbf{u},\mathbf{r},\tau;\mathbf{u}_0,\mathbf{r}_0)$, can be calculated from the Langevin equation, Eq. (5.1), by use of the fact that the velocity $\mathbf{u}$ of a particle is the derivative with respect to time of its position $\mathbf{r}$.[11] However, the angular velocity of a molecule, $\boldsymbol{\omega}$, is not the derivative of a vector that can be used to specify the orientation of the molecule, as is well known. Hence, $W'(\omega_i,\Omega_i,\tau;\omega_{i0},\Omega_{i0})$ cannot be obtained by analogy with the result for translational motion; nor has it previously been calculated by any other method, as far as the author knows.

It will now be shown that, even though $W'(\omega_i,\Omega_i,\tau;\omega_{i0},\Omega_{i0})$ is not known, the correlation function (5.13) can be evaluated to a certain approximation that should be quite good in many actual liquids. A diffusion equation governing the orientation of a spherical particle has been derived and solved by Furry.[12] From his calculation, the expression for the probability that, in a time t, a particle undergoes a rotation through an angle between χ and $\chi+d\chi$, $0\leq\chi\leq\pi$, about an axis pointing into the element of solid angle $\sin\theta d\theta d\phi$ is

[12] W. H. Furry, Phys. Rev. **107**, 7 (1957).

$F(\chi)d\chi\sin\theta d\theta d\phi$, where

$$F(\chi) = (1/4\pi^2)\sum_{n=0}^{\infty}(2n+1)[\cos n\chi-\cos(n+1)\chi]$$
$$\times\exp[-n(n+1)D't]. \quad (5.14)$$

The diffusion coefficient, D', occurring in Furry's theory can be related to the viscous retarding torque per unit angular velocity, $f'\equiv IB'$, by the expression[13]

$$D' = kT/f'. \quad (5.15)$$

It is shown in Appendix C, by use of (5.14), that

$$\langle[\mathfrak{D}_{0l'}^{(2)}(\Omega_i)]_{t+\tau}[\mathfrak{D}_{0k'}^{(2)}(\Omega_i)]_t\rangle = (1/5)\delta_{-l',k'}(-1)^{k'}$$
$$\times\exp(-\tau/\tau_2), \quad (5.16)$$

where

$$\tau_2\equiv(6D')^{-1}. \quad (5.17)$$

Since $f'\equiv IB'$, it follows from Eqs. (5.12), (5.15), and (5.17) that

$$\tau_1\tau_2 = (I/6kT). \quad (5.18)$$

The functions that occur in the two correlation functions (5.11) and (5.16) are the same functions present in the more complicated correlation function (5.13). If the orientation of a molecule at any time were independent of its angular momentum at any time, the correlation function (5.13) would be the product of the correlation functions (5.11) and (5.16), which would give

$$\langle[J_i^{l''}\mathfrak{D}_{0l'}^{(2)}(\Omega_i)]_{t+\tau}[J_i^{k''}\mathfrak{D}_{0k'}^{(2)}(\Omega_i)]_t\rangle$$
$$= \langle J_i^{l''}(t+\tau)J_i^{k''}(t)\rangle\langle[\mathfrak{D}_{0l'}^{(2)}(\Omega_i)]_{t+\tau}[\mathfrak{D}_{0k'}^{(2)}(\Omega_i)]_t\rangle$$
$$= \{(-1)^{l''}\delta_{l'',-k''}(IkT/\hbar^2)\exp(-\tau/\tau_1)\}$$
$$\times\{(1/5)\delta_{-l',k'}(-1)^{k'}\exp(-\tau/\tau_2)\}. \quad (5.19)$$

Even though the angular momentum and the orientation of a molecule are not independent, if the motion of the molecules is such that the components of angular momentum change much more rapidly than the functions $\mathfrak{D}_{0k}^{(2)}(\Omega_i)$ of the orientation, or vice versa, one would expect the time dependence of the correlation function (5.13) to be determined by the more rapidly fluctuating functions. This reasoning suggests that expression (5.19) for the correlation function should be approximately correct if either $\tau_1\ll\tau_2$ or $\tau_2\ll\tau_1$, since $(1/\tau_1)$ and $(1/\tau_2)$ are measures, respectively, of the rates of fluctuation of the components of the angular momentum and the functions $\mathfrak{D}_{0k}^{(2)}(\Omega_i)$. Since we are unable to calculate the correlation function rigorously, the expression (5.19) was used in the previous section to obtain Eq. (4.7), which, it was noted, can be expected to be a good approximation only if $\tau_1\ll\tau_2$ or $\tau_2\ll\tau_1$.

6. RELAXATION BY DIPOLE-DIPOLE INTERACTIONS

The relaxation effect of dipole-dipole interactions between nuclei has previously been calculated for

[13] P. S. Hubbard, Phys. Rev. **109**, 1153 (1958); **111**, 1746(E) (1958).

various physical situations. For an arbitrary number of identical spin-$\frac{1}{2}$ nuclei in equivalent positions, a simple result is obtained only if

$$J_{(ij')(ij)}{}^{lk}(\omega)=\delta_{jj'}J_{(ij)(ij)}{}^{lk}(\omega),\qquad(6.1)$$

where $J_{(ij')(ij)}{}^{lk}(\omega)$ is given by (3.9). If (6.1) is satisfied, it has been shown that,[14] in terms of the present notation, the quantity $\mathrm{Tr}[R_{22}(\chi)I^\nu]$ in Eq. (3.15) is given by, for $\nu=0$ and $\nu=\pm1$, respectively,

$$\mathrm{Tr}[R_{22}(\chi)I^0]=-(1/T_1)_2(\langle I^0\rangle-\langle I^0\rangle^T),\qquad(6.2)$$

where

$$(1/T_1)_2\equiv2\sum_{l=-2}^{2}(-1)^l l^2 J_{l,-l}(-l\omega_0),\qquad(6.3)$$

and

$$\mathrm{Tr}[R_{22}(\chi)I^{\pm1}]=-(1/T_2)_2\langle I^{\pm1}\rangle,\qquad(6.4)$$

where

$$(1/T_2)_2=\sum_{l=-2}^{2}(-1)^l(6-l^2)J_{l,-l}(-l\omega_0).\qquad(6.5)$$

The quantity $J_{l,-l}(\omega)$ in the above expressions is defined by

$$J_{l,-l}(\omega)\equiv\sum_i(1-\delta_{ij})J_{(ij)(ij)}{}^{l,-l}(\omega),\qquad(6.6)$$

which is independent of j since the nuclei are assumed to be in equivalent positions.

The condition (6.1) is satisfied only if the correlation functions $C_{(ij')(ij)}{}^{lk}(\tau)$ are zero when $j'\neq j$, which is not in general found to be the case. If (6.1) is not satisfied, $\mathrm{Tr}[R_{22}(\chi)I^0]$ does not reduce to a term proportional to $\mathrm{Tr}[\chi I^\nu]$, so that expressions of the form of (6.2) and (6.4) are not obtained. Hence Eq. (3.15) does not lead directly to an expression for $\langle I^\nu\rangle$. One must instead calculate by use of Eq. (3.2) the matrix elements of the reduced density operator σ in some convenient representation, and then evaluate $\langle I^\nu\rangle=\mathrm{Tr}[\sigma I^\nu]$ by working out the trace. This procedure has been carried out only for the cases of relaxation by intramolecular dipole-dipole interactions of spherical liquid molecules containing three or four identical spin $\frac{1}{2}$ nuclei.[13,15,16] It was found in these investigations that the relaxation is the sum of several exponentially decaying terms, but the time constants and the magnitudes of the terms are such that the relaxation differs very little from the simple exponential decay that results from the assumption (6.1). These results do not prove that the assumption (6.1) is justified for any possible structure or motion of the molecules. However, in order to easily compare the relaxation effect of the spin-rotational and the dipole-dipole interactions, even though only approximately, we will in this paper employ the frequently used expressions (6.2), (6.3), (6.4), and (6.5).

The quantities $(1/T_1)_2$ and $(1/T_2)_2$ can each be written as the sum of two terms which contain, respectively, the effects of intramolecular and intermolecular dipole-dipole interactions:

$$(1/T_1)_2=(1/T_1)_2'+(1/T_1)_2'',\qquad(6.7)$$

$$(1/T_2)_2=(1/T_2)_2'+(1/T_2)_2''.\qquad(6.8)$$

If it is assumed that the molecules undergo isotropic rotational Brownian motion, it can be shown that the intramolecular contributions are[17]

$$(1/T_1)_2'=(3/10)\gamma^4\hbar^2\tau_2\sum_i' r_{ij}{}^{-6}\{[1+(\omega_0\tau_2)^2]^{-1}+4[1+(2\omega_0\tau_2)^2]^{-1}\},\qquad(6.9)$$

$$(1/T_2)_2'=(3/20)\gamma^4\hbar^2\tau_2\sum_i' r_{ij}{}^{-6}\{3+5[1+(\omega_0\tau_2)^2]^{-1}+2[1+(2\omega_0\tau_2)^2]^{-1}\}.\qquad(6.10)$$

The symbol $\sum_i'$ represents a sum over all other spins in the same molecule as the jth. The sum is independent of j because all the nuclei are in equivalent positions. The correlation time τ_2 is given by Eq. (5.17). The distance between the ith and jth spins is r_{ij}.

If it is assumed that the translational motion of the molecules is classical diffusion with translational diffusion coefficient D, and if the correlation time τ_0 defined by

$$\tau_0\equiv(2a^2/D)\qquad(6.11)$$

is sufficiently short that $(\omega_0\tau_0)^2\ll1$, it can be shown[18] that the intermolecular contributions $(1/T_1)_2''$ and $(1/T_2)_2''$ are equal, and can be expressed as an infinite series, the first three terms of which are

$$(1/T_1)_2''=(n\pi\gamma^4\hbar^2/5aD)\times[1+0.233(b/a)^2+0.15(b/a)^4+\cdots],\qquad(6.12)$$

where n is the number of spins per unit volume in the liquid, a is the radius of each molecule, and b is the distance of each nuclear spin from the center of the spherical molecule in which it is contained. In obtaining the second and third terms in Eq. (6.12), it is assumed that

$$(D/D')=(4a^2/3),\qquad(6.13)$$

which is the relation between D and D' that is obtained if one assumes the Stokes expression for the viscous retarding force per unit velocity,[11]

$$f=6\pi a\eta,\qquad(6.14)$$

and the analogous expression for the viscous retarding torque per unit angular velocity,[19]

$$f'=8\pi a^3\eta.\qquad(6.15)$$

The coefficient of viscosity of the fluid is denoted by η. Equation (6.13) follows from Eqs. (5.4), (5.15), (6.14), and (6.15). The result depends only on the ratio (f'/f).

[14] See Ref. 8, Sec. 5, especially part A.
[15] G. W. Kattawar and M. Eisner, Phys. Rev. 126, 1054 (1962).
[16] Paul S. Hubbard, Phys. Rev. 128, 650 (1962).
[17] Paul S. Hubbard, Phys. Rev. 131, 275 (1963), Eqs. (4.3) and (4.4).
[18] See Refs. 17, Eq. (3.34).
[19] H. Lamb, Hydrodynamics (Cambridge University Press, London, 1930), 5th ed., p. 558.

7. SUMMARY AND DISCUSSION

The longitudinal relaxation is calculated by substituting expressions (4.12) and (6.2) into Eq. (3.15) written for $\nu=0$, and solving the resulting equation, which gives

$$\langle I^0 \rangle_t - \langle I^0 \rangle^T = (\langle I^0 \rangle_0 - \langle I^0 \rangle^T) \exp(-t/T_1), \quad (7.1)$$

where the longitudinal relaxation time T_1 is defined by

$$(1/T_1) \equiv (1/T_1)_1 + (1/T_1)_2' + (1/T_1)_2''. \quad (7.2)$$

$(1/T_1)_1$, the contribution of the spin-rotational interactions, is given by Eq. (4.13); $(1/T_1)_2'$, the contribution of the intramolecular dipole-dipole interactions, is given by Eq. (6.9); and $(1/T_1)_2''$, the contribution of the intermolecular dipole-dipole interactions, is given by Eq. (6.12) if $(\omega_0\tau_0)^2 \ll 1$.

The transverse relaxation is calculated in a similar manner by use of expressions (4.15) and (6.4) in Eq. (3.15) written for $\nu=\pm1$. The result is

$$\langle I^{\pm1} \rangle_t = \langle I^{\pm1} \rangle_0 \exp(-t/T_2) \exp(\mp i\omega_0 t), \quad (7.3)$$

where the transverse relaxation time T_2 is defined by

$$(1/T_2) \equiv (1/T_2)_1 + (1/T_2)_2' + (1/T_2)_2''. \quad (7.4)$$

The contribution of the spin-rotational interactions, $(1/T_2)_1$, is given by Eq. (4.16); the contribution of the intramolecular dipole-dipole interactions, $(1/T_2)_2'$, is given by Eq. (6.10); and the contribution of the intermolecular dipole-dipole interactions, $(1/T_2)_2''$, is given by Eq. (6.12) if $(\omega_0\tau_0)^2 \ll 1$.

The correlation time τ_0 is defined as $\tau_0 \equiv (2a^2/D)$, Eq. (6.11), and the correlation time τ_2 is defined as $\tau_2 \equiv (6D')^{-1}$, Eq. (5.18). If the ratio of the translational diffusion coefficient D to the rotational diffusion coefficient D' has the value obtained by using the ratio of the Stokes expressions for the viscous retarding force, f, and viscous retarding torque f' on a spherical particle, $(D/D') = (4a^2/3)$, Eq. (6.13), it follows that

$$\tau_2 = \tau_0/9 = (2a^2/9D). \quad (7.5)$$

Hence, since $\tau_1\tau_2 = (I/6kT)$, Eq. (5.18), it follows that

$$\tau_1 = (3ID/4a^2kT). \quad (7.6)$$

Since the temperature dependence of the diffusion coefficient in many liquids can be expressed as $D = D_0 \exp(-E_D/RT)$, where D_0 and the activation energy E_D are approximately independent of the temperature, it is apparent that the correlation times τ_0 and τ_2 decrease as the temperature increases, while the product of the temperature and the correlation time τ_1 increases as the temperature increases.

If the Stokes expression $f = 6\pi a\eta$ is valid, it follows from Eq. (5.4) that $D = (kT/6\pi a\eta)$, so that the correlation times τ_0, τ_1, and τ_2 can also be expressed in terms of the viscosity rather than the diffusion coefficient.

In many experimental situations the conditions

$$\tau_1 \ll \tau_2, \quad (\omega_0\tau_0)^2 \ll 1 \quad (7.7)$$

are satisfied. For example, consider liquid methane. At a temperature of 100°K, the translation diffusion coefficient is $D \approx 3.1 \times 10^{-5}$ cm²/sec.[20] The moment of inertia of the methane molecule is 5.33×10^{-40} gm cm².[21] The radius of a molecule is taken to be the Van der Waals radius of the methyl group, which is 2.0 A^0.[22] The expression (7.5) for τ_2 thus has the value $\tau_2 = 2.9 \times 10^{-12}$ sec. Hence, from Eq. (5.18), $\tau_1 = (I/6kT\tau_2) = 2.2 \times 10^{-15}$ sec, which is smaller than τ_2 by more than three orders of magnitude. If the applied magnetic field is 10 kG, then $\omega_0 = 2.67 \times 10^8$ sec⁻¹, so that $(\omega_0\tau_0)^2 = (9\omega_0\tau_2)^2 = 7.1 \times 10^{-5} \ll 1$. Hence, for the case considered, the conditions (7.7) are satisfied.

If the conditions (7.7) are satisfied, it follows from Eqs. (4.13), (4.16), (4.10), and (4.8) that the spin-rotational contributions are

$$(1/T_1)_1 = (1/T_2)_1 = (2IkT\tau_1/3\hbar^2)(2C_\perp^2 + C_{||}^2). \quad (7.8)$$

Also, from Eqs. (6.9) and (6.10), the contributions of the intramolecular dipole-dipole interactions reduce to

$$(1/T_1)_2' = (1/T_2)_2' = \tfrac{3}{2}\gamma^4\hbar^2\tau_2 \sum_i' r_{ij}^{-6}. \quad (7.9)$$

The contributions of the intermolecular dipole-dipole interactions are given by Eq. (6.12). By using the relation (7.5) in Eq. (6.12), and adding the result to the sum of Eqs. (7.8) and (7.9), one obtains

$$(1/T_1) = (1/T_2) = (2IkT\tau_1/3\hbar^2)(2C_\perp^2 + C_{||}^2)$$
$$+ \tfrac{3}{2}\gamma^4\hbar^2\tau_2 \sum_i' r_{ij}^{-6} + (9n\pi\gamma^4\hbar^2\tau_2/10a^3)$$
$$\times [1 + 0.233(b/a)^2 + 0.15(b/a)^4 + \cdots], \quad (7.10)$$

the validity of which depends upon the satisfaction of the conditions (7.7).

If it had been assumed that the correlation functions (3.7) that occur in the spin-rotational relaxation term had a decaying exponential time dependence with time constant τ_1, the expressions obtained for $\mathrm{Tr}[R_{11}(\chi)I^\nu]$ would be the same as those given in Sec. 4 if one put $\tau_{12} = \tau_1$. However, τ_1 would be unspecified. By use of the physical model assumed in this paper, it has been possible to calculate τ_1 and τ_2 in terms of the properties of the molecules and the liquid. The fact that the expressions for τ_1 and τ_2 have a different temperature dependence and, in general, a different magnitude is of considerable interest.

The fact that τ_2 decreases with temperature and $T\tau_1$ increases with temperature is in agreement with the experimental results of Brown et al.,[5] which they

[20] J. V. Gaven, Jr., J. S. Waugh, and W. H. Stockmayer, J. Chem. Phys. 38, 287 (1963).

[21] G. Herzberg, Infrared and Raman Spectra of Polyatomic Molecules (D. Van Nostrand Company, Inc., New York, 1945), p. 455.

[22] L. Pauling, The Nature of the Chemical Bond (Cornell University Press, Ithaca, New York, 1960), 3rd ed., p. 261.

explain by using a quite different random jump model. Also, the result of the present calculation that τ_1 is usually smaller than τ_2 explains the experimentally observed "quenching" of the relaxation effect of the spin-rotational interactions in liquids.

The model used in this paper to describe the motion of liquid molecules is undoubtedly crude. However, the classical description of the change in angular velocity used here would appear *a priori* to be as plausible as the description of changes in orientation which has been used with some success since the original work of Bloembergen, Purcell, and Pound.

Experiments are in progress in the author's laboratory to measure the relaxation rates and diffusion coefficients of several different kinds of spherical molecules in liquids. The results of the experiments, and how well they agree with the theory presented in this paper, will be reported soon.

ACKNOWLEDGMENT

APPENDIX A

Since from (2.10) $C_0 \equiv C_{11}$ and $C_{\pm 1} \equiv -C_{\perp}$, Eq. (2.13a) can be written

$$U_i{}^k = \sum_{k',k''=-1}^{1} C_{\perp}(-1)^{k'} \mathfrak{D}_{k'k}{}^{(1)*}(\Omega_i)\mathfrak{D}_{-k'k''}{}^{(1)*}(\Omega_i)J_i{}^{k''}$$

$$+ (C_{11}-C_{\perp})\sum_{k''=-1}^{1} \mathfrak{D}_{0k}{}^{(1)*}(\Omega_i)\mathfrak{D}_{0k''}{}^{(1)*}(\Omega_i)J_i{}^{k''}. \quad (A1)$$

From Ref. 6, Eq. (4.27),

$$\mathfrak{D}_{-k'k''}{}^{(1)*}(\Omega_i) = (-1)^{k'-k''}\mathfrak{D}_{k',-k''}{}^{(1)}(\Omega_i).$$

Also, from the definition of the $\mathfrak{D}_{kk'}{}^{(j)}(\Omega)$ it follows that

$$\sum_{k'} \mathfrak{D}_{k'k}{}^{(1)*}(\Omega_i)\mathfrak{D}_{k',-k''}{}^{(1)}(\Omega_i) = \delta_{k,-k''}. \quad (A2)$$

The use of the above two relations permits the first sums over k' and k'' in (A1) to be carried out. If the second term is rewritten by use of Eq. (4.3.2) of Ref. 6, one obtains

$$U_i{}^k = C_{\perp}(-1)^k J_i{}^{-k}$$

$$+ (C_{11}-C_{\perp})\sum_{k''=-1}^{1} J_i{}^{k''} \sum_{j=0}^{2} \sum_{k'=-j}^{j} (2j+1)$$

$$\times \begin{pmatrix} 1 & 1 & j \\ 0 & 0 & 0 \end{pmatrix}\mathfrak{D}_{0k'}{}^{(j)}(\Omega_i)\begin{pmatrix} 1 & 1 & j \\ k & k'' & k' \end{pmatrix}. \quad (A3)$$

If in (A3) the sum over j is written out, and the values of the 3-j symbols[23] and $\mathfrak{D}_{00}{}^{(0)}(\Omega)=1$ substituted, Eq. (2.13b) is obtained.

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[23] The values of the 3-j symbols are given by M. Rotenberg *et al.*, *The 3-j and 6-j Symbols* (Technology Press, Cambridge, Massachusetts, 1959).

APPENDIX B

In Ref. 8 the density operator theory of relaxation is developed on the assumption that the interaction G can be expressed as a sum of products of spin operators V^k and operators U^k involving just the molecular coordinates[24]:

$$G = \sum_k U^k V^k. \quad (16')$$

For the case that E does not depend explicitly on the time, spin operators $V_s{}^l$ and frequencies $\omega_s{}^l$ are defined by the condition

$$e^{iEt}V^l e^{-iEt} = \sum_s V_s{}^l \exp(i\omega_s{}^l t). \quad (90')$$

It is shown in Ref. 8 that the relaxation operator can be written

$$R(\sigma) = R(\sigma-\sigma^T) = \sum_{kls} J_{lk}(\omega_s{}^l)[[V_s{}^l, \sigma-\sigma^T],V^k], \quad (106')$$

if $|\omega_s{}^l|\beta \ll 1$ for all the frequencies $\omega_s{}^l$ occurring in (90'). The functions $J_{kl}(\omega)$ are defined by

$$J_{kl}(\omega) = \frac{1}{2}\int_{-\infty}^{\infty} C_{kl}(\tau)e^{i\omega\tau}d\tau, \quad (86')$$

in terms of correlation functions $C_{kl}(\tau)$ defined by

$$C_{kl}(\tau) = \langle\{U^k(t+\tau)U^l(t)\}\rangle_q. \quad (81')$$

In the semiclassical form of the theory, a classical model of the motion of the molecular surroundings is assumed, which permits the calculation of the average in Eq. (81'). As a consequence of the assumption that $\langle U^k\rangle=0$, the correlation functions approach zero as τ approaches infinity. The correlation time τ_c is defined by the condition

$$C_{kl}(\tau) \approx 0 \quad \text{if} \quad |\tau| \gg \tau_c, \quad (87')$$

for all the $C_{kl}(\tau)$. The condition of validity of Eq. (3.2) is $\tau_c \ll |R|^{-1}$, $|N|^{-1}$. The correlation functions also satisfy the relation

$$C_{kl}(\tau) = C_{lk}(-\tau). \quad (84')$$

From (84') and (86') it follows that

$$J_{kl}(\omega) = \frac{1}{2}\int_{0}^{\infty} [C_{kl}(\tau)e^{i\omega\tau}+C_{lk}(\tau)e^{-i\omega\tau}]d\tau. \quad (B1)$$

In the present problem the interaction $G=G_1+G_2$ is, from (2.12) and (2.14),

$$G = \sum_{i=1}^{N}\sum_{k=-1}^{1} U_i{}^k V_i{}^k + \sum_{i,j=1}^{N}\sum_{k=-2}^{2} (1-\delta_{ij})U_{ij}{}^k V_{ij}{}^k, \quad (B2)$$

which can be written

$$G = \sum_{i,j=1}^{N}\sum_{k=-2}^{2} \bar{U}_{ij}{}^k \bar{V}_{ij}{}^k, \quad (B3)$$

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[24] The primed equation numbers in this Appendix are the numbers of the same equations in Ref. 8.

where

$$\bar{U}_{ij}{}^k \equiv \delta_{ij} U_i{}^k + (1-\delta_{ij}) U_{ij}{}^k, \tag{B4}$$

$$\bar{V}_{ij}{}^k \equiv \delta_{ij} V_i{}^k + (1-\delta_{ij}) V_{ij}{}^k, \tag{B5}$$

where the $U_{ij}{}^k$ are given by (2.16) and the $V_{ij}{}^k$ by (2.15). The $U_i{}^k$ are defined by (2.13) and the $V_i{}^k$ by (2.7) for $k = -1$, 0, 1, and are considered to be zero for $k = \pm 2$. Since G can be written as a sum of products of spin operators $\bar{V}_{ij}{}^k$ and molecular operators $\bar{U}_{ij}{}^k$, it is equivalent to (16') with the changes in notation

$$U^k \rightarrow \bar{U}_{ij}{}^k, \quad V^k \rightarrow \bar{V}_{ij}{}^k, \quad \sum_k \rightarrow \sum_{i,j=1}^{N} \sum_{k=-2}^{2}. \tag{B6}$$

Hence with corresponding changes in notation, Eq. (106') can be applied in the present calculation. But first the operators corresponding to $V_s{}^l$ must be calculated. Since $E = -\omega_0 I^0$, the equation corresponding to (90') is

$$e^{-i\omega_0 I^0 t} \bar{V}_{i'j'}{}^l e^{i\omega_0 I^0 t}$$

$$= e^{-i\omega_0 I^0 t} [(1-\delta_{i'j'}) V_{i'j'}{}^l + \delta_{i'j'} V_{i'}{}^l] e^{i\omega_0 I^0 t}$$

$$= [(1-\delta_{i'j'}) V_{i'j'}{}^l + \delta_{i'j'} V_{i'}{}^l] e^{-il\omega_0 t} = \bar{V}_{i'j'}{}^l e^{-il\omega_0 t}, \tag{B7}$$

so that

$$V_s{}^l \rightarrow (\bar{V}_{i'j'}{}^l)_s = \delta_{s0} \bar{V}_{i'j'}{}^l, \tag{B8}$$

$$\omega_s{}^l = -l\omega_0. \tag{B9}$$

Thus, with the notational changes (B6), (B8), (B9), and

$$\sum_l \rightarrow \sum_{i',j'=1}^{N} \sum_{l=-2}^{2},$$

Eq. (106') becomes

$$R(\sigma) = R(\chi)$$

$$= \sum_{i,j=1}^{N} \sum_{k=-2}^{2} \sum_{i',j'=1}^{N} \sum_{l=-2}^{2} \bar{J}_{(i'j')(ij)}{}^{lk}(-l\omega_0)$$

$$\times [[\bar{V}_{i'j'}{}^l, \chi], \bar{V}_{ij}{}^k], \tag{B10}$$

where $\chi \equiv \sigma - \sigma^T$, and

$$\bar{J}_{(i'j')(ij)}{}^{lk}(\omega) = \frac{1}{2} \int_0^{\infty} [\bar{C}_{(i'j')(ij)}{}^{lk}(\tau) e^{i\omega\tau}$$

$$+ \bar{C}_{(ij)(i'j')}{}^{kl}(\tau) e^{-i\omega\tau}] d\tau, \tag{B11}$$

$$\bar{C}_{(i'j')(ij)}{}^{lk}(\tau) = \langle \bar{U}_{i'j'}{}^l(t+\tau) \bar{U}_{ij}{}^k(t) \rangle. \tag{B12}$$

Equation (B10) is correct to first order in $\beta\omega_0$. Use of (B4), (B5), (B11), and (B12) gives Eq. (3.4).

APPENDIX C

The reference frame $S^{(i)}$ is fixed in the molecule containing the ith nucleus. Suppose that at time t the orientation of $S^{(i)}$ with respect to the laboratory coordinate system S is specified by the Euler angles $\alpha_i \beta_i \gamma_i \equiv \Omega_i$. The orientation of $S^{(i)}$ with respect to S at

a later time $t+\tau$ is specified by Euler angles $\alpha_i'' \beta_i'' \gamma_i'' \equiv \Omega_i''$. The Euler angles specifying $S^{(i)}$ at time $t+\tau$ with respect to $S^{(i)}$ at t are $\alpha_i' \beta_i' \gamma_i' \equiv \Omega_i'$. From page 63 of Ref. 6, it follows that

$$\mathfrak{D}_{m'm}{}^{(i)}(\Omega_i'') = \sum_{m''} \mathfrak{D}_{m'm''}{}^{(i)}(\Omega_i') \mathfrak{D}_{m''m}{}^{(i)}(\Omega_i), \tag{C1}$$

so that

$$\langle [\mathfrak{D}_{0l'}{}^{(2)}(\Omega_i)]_{t+\tau} [\mathfrak{D}_{0k'}{}^{(2)}(\Omega_i)]_t \rangle$$

$$= \sum_{m''} \left\{ \int \mathfrak{D}_{0m''}{}^{(2)}(\Omega_i') P(\Omega_i', \tau) d^3\Omega_i' \right\}$$

$$\times \left\{ \int \mathfrak{D}_{m''l'}{}^{(2)}(\Omega_i) \mathfrak{D}_{0k'}{}^{(2)}(\Omega_i) \rho(\Omega_i) d^3\Omega_i \right\}, \tag{C2}$$

where $P(\Omega_i', \tau)$ is the probability density that there is a rotation through Euler angles Ω_i' in time τ, and $\rho(\Omega_i)$ is the probability density that $S^{(i)}$ has orientation Ω_i at time t. Since all orientations are equally probable at time t,

$$\rho(\Omega_i) d^3\Omega_i = (1/8\pi^2) d\alpha_i \sin\beta_i d\beta_i d\gamma_i. \tag{C3}$$

After substitution of (C3), and use of the relation

$$\mathfrak{D}_{m''l'}{}^{(2)}(\Omega_i) = (-1)^{m''-l'} \mathfrak{D}_{-m'',-l'}{}^{(2)*}(\Omega_i),$$

the integral over $d^3\Omega_i$ in (C2) can be calculated from Eq. (4.6.1) of Ref. 6, with the result $(-1)^{m''-l'} \delta_{-m''0} \times \delta_{-l',k'}(1/5)$. Hence, (C2) can be written

$$\langle [\mathfrak{D}_{0l'}{}^{(2)}(\Omega_i)]_{t+\tau} [\mathfrak{D}_{0k'}{}^{(2)}(\Omega_i)]_t \rangle$$

$$= (\tfrac{1}{5}) \delta_{-l',k'} (-1)^{k'} \int \mathfrak{D}_{00}{}^{(2)}(\Omega_i') P(\Omega_i', \tau) d^3\Omega_i'. \tag{C4}$$

From Eq. (4.1.26) of Ref. 6,

$$\mathfrak{D}_{00}{}^{(2)}(\Omega_i') = P_2(\cos\beta_i') = \tfrac{1}{2}(3\cos^2\beta_i' - 1). \tag{C5}$$

The integral in (C4) is the average of the function $\mathfrak{D}_{00}{}^{(2)}(\Omega_i')$ over all possible rotations Ω_i' weighted by the probability $P(\Omega_i', \tau) d\Omega_i'$ that a rotation Ω_i' takes place in time, τ. Instead of specifying the rotation by the Euler angles $\alpha_i' \beta_i' \gamma_i' \equiv \Omega_i'$, it is more convenient to use the magnitude χ of the rotation about an axis having polar angles θ, ϕ. It can be shown by the use of the quaternion or Cayley-Klein descriptions of rotations and the definition of the Euler angles as three successive rotations, that

$$\sin\frac{\chi}{2} \sin\theta \cos\phi = \sin\frac{\beta_i'}{2} \sin\left(\frac{\gamma_i' - \alpha_i'}{2}\right), \tag{C6-a}$$

$$\sin\frac{\chi}{2} \sin\theta \sin\phi = \sin\frac{\beta_i'}{2} \cos\left(\frac{\gamma_i' - \alpha_i'}{2}\right), \tag{C6-b}$$

$$\sin\frac{\chi}{2} \cos\theta = \cos\frac{\beta_i'}{2} \sin\left(\frac{\alpha_i' + \gamma_i'}{2}\right). \tag{C6-c}$$

From (C5) and (C6) it follows that

$$\mathfrak{D}_{00}{}^{(2)}(\Omega_i') \equiv f(\chi,\theta,\phi)$$
$$= (1 - 3\sin^2\theta + (9/4)\sin^4\theta)$$
$$+ 3\sin^2\theta\cos^2\theta\cos\chi + \tfrac{3}{4}\sin^4\theta\cos2\chi. \quad (C7)$$

Hence, if the average in (C4) is expressed in terms of

the angles (χ,θ,ϕ), one obtains

$$\langle[\mathfrak{D}_{0l'}{}^{(2)}(\Omega_i)]_{t+\tau}[\mathfrak{D}_{0k'}{}^{(2)}(\Omega_i)]_t\rangle$$
$$= (\tfrac{1}{5})\delta_{-l',k'}(-1)^{k'}\int_0^{2\pi}\int_0^{\pi}\int_0^{\pi} f(\chi,\theta,\phi)F(\chi)$$
$$\times \sin\theta\,d\chi\,d\theta\,d\phi, \quad (C8)$$

where $F(\chi)$ is given by (5.14). The integrals in (C8) can be easily performed to obtain the result given by Eq. (5.16).

L-Shell Fluorescence Yields in Heavy Elements*

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Partial L-shell fluorescence yields of 23 heavy elements have been measured using an x-ray coincidence counting method. Vacancies in the K shell of the target atoms are created by photoelectric absorption of 122- and 136-keV gamma rays emitted by a Co^{57} source. A known fraction of these K-shell vacancies are filled by L electrons. The L-shell vacancies created in this way are then occupied by electrons from higher shells, causing emission of L x rays and Auger electrons. The coincidence rate between the L and K x rays determines the fluorescence yield ω_{KL}, which is defined as the partial L-shell fluorescence yield following the emission of K_α x rays. ω_{KL} is a linear combination of the fluorescence yields of the L_{II} and L_{III} subshells. A comprehensive comparison with previous measurements is given.

INTRODUCTION

IN a previous article,[1] a method of measuring fluorescence yields of the L shell of heavy elements was described. Vacancies are created in the K shell of an atom and the coincidence rate between the K and L x rays emitted subsequent to the ionization event is determined. This coincidence rate depends upon the partial L-shell fluorescence yield ω_{KL}, defined in Ref. 1 in the following way:

$$\omega_{KL} = \frac{N_c}{N_K}\frac{1}{aE_L A_L \Omega_L}. \quad (1)$$

In Eq. (1), N_c is the L to K x-ray coincidence rate, N_K the K x-ray counting rate, Ω_L the geometry of the L x-ray counter, and E_L the efficiency of the L x ray counter. The quantity A_L is the transmission of L x rays to the L x-ray counter, and a is the fraction of counts in K x-ray peak due to K_{α_2} and K_{α_1} x rays. The last the factor a must be included since the K x-ray counter cannot resolve those K x rays (K_α lines) which leave a vacancy in the L shell from those which do not (K_β lines). In the previous work, K-electron capture or K-shell internal conversion processes were used to create the K-shell vacancies. This method cannot be

applied to a large number of elements because most decay schemes are so complex that a unique interpretation of the results is not possible. In the present experiments, the K shells of the target atoms were ionized by photoelectric absorption. Thin foils of the target material are exposed to gamma rays with a sufficiently high energy to cause K-shell ionization, and the coincidence rate between the K and L x rays emitted by the foil is measured. Therefore, the methods described in Ref. 1 can be extended to a large number of elements.

EXPERIMENTAL PROCEDURE

The experimental geometry is shown in Fig. 1. A 20-mCi Co^{57} source was placed in a carefully shielded source holder. The gamma rays[2] emitted by the source were collimated and directed at the thin target foil ($\tfrac{5}{8}$ in. $\times \tfrac{5}{8}$ in.) placed between the two counters. The target foil was mounted on the aluminum target holder with very thin (less than 0.001-in. diam) nylon fibers. This was done to minimize the amount of material in the path of the gamma-ray beam in order to reduce the background from Compton scattering. The K and L x-ray counters were both similar to those used in the previous experiment. Thin (approximately 0.030 in.) NaI(Tl) crystals were used to detect both the L and

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[1] R. C. Jopson, Hans Mark, and C. D. Swift, Phys. Rev. 128, 2671 (1962).

[2] D. Strominger, J. M. Hollander, and G. T. Seaborg, Rev. Mod. Phys. 30, 585 (1958).