ON THE THEORY OF SPIN-LATTICE RELAXATION IN LIQUID SOLUTIONS OF ELECTROLYTES

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Spin-lattice relaxation of hydrated metal ions in aqueous solutions due to the interaction between the ion spin and the internal vibrations of the complex ion is investigated by the method of the theory of random processes.

1. INTRODUCTION

THIS paper is devoted to the calculation of the lifetime of the spin of a paramagnetic ion in a liquid solution in a given energy level. We base our discussion on the generally accepted notion that in solution a paramagnetic ion M forms together with the nearest diamagnetic particles X_i a stable paramagnetic complex ion whose vibrations can be characterized by a set of normal coordinates Q_j. The oscillations of Q_j produce variations of the electric field due to the particles X_i at the position of the paramagnetic ion at the center of the complex ion and interact via the spin-orbit coupling of the ion ($\mathcal{K}_{S0} = \lambda \mathbf{L} \cdot \mathbf{S}$) with the spin $\mathbf{S}$ of particle M. On the other hand, the oscillations of Q_j interact with the Brownian motion of the particles of the liquid surrounding the complex ion, giving rise to a set $Q_j(t)$ of independent narrow-band random Gaussian processes; the properties of the latter have been studied in detail.[1-3] Although the energy $\hbar\omega_{MM'}$ released in the reorientation of the spin is small compared to the energy intervals $\hbar\omega_j$ between the sublevels of the oscillators Q_j, the random nature of the variation of the coordinates Q_j determines the possibility of the transfer of the spin energy of the ion M to the oscillations of Q_j describing the complex ion. We shall treat the coordinates Q_j semiclassically; a quantum mechanical treatment of the interaction of the oscillators Q_j with the medium yields results which are basically in agreement with the classical discussion.[3]

The energy of interaction of the spin $\mathbf{S}$ of the central ion of the complex with the oscillations of Q_j can be represented in the general case in the form of the series

$$\mathcal{K} = \mathcal{K}^{(1)} + \mathcal{K}^{(2)} + \ldots = \sum_i P_i(S)\, Q_i + \sum_{ij} P_{ij}(S)\, Q_i Q_j + \ldots, \tag{1}$$

where $P_j(S)$, $P_{ij}(S)$ are quadratic functions in the components of the vector $S\,(S_x,\ S_y,\ S_z)$. If x, y, z, define the laboratory system of coordinates, then the coefficients $P_{ij}(S_x,\ S_y,\ S_z)$ will, under rotation of the complex ion, turn out to be functions of randomly varying angles specifying the orientation of the complex ion with respect to the x, y, z system.

In the paper by one of the authors together with Al'tshuler[4] a calculation was given of the rate of relaxation of the spin $\mathbf{S}$ due to the terms linear in Q_j in the expansion of the spin energy. Analysis shows, however, that a more effective relaxation is induced by the terms in the expansion of $\mathcal{K}^{(2)}$ which are quadratic in the Q_j.* The same conclusion was obtained independently of us by Aleksandrov and Zhidomirov[5] who considered the relaxation of the spin of a free radical due to its interaction with intramolecular oscillations. Therefore, for the analysis of this problem we refer the reader to the paper by Aleksandrov and Zhidomirov.[5]

We shall evaluate the probability of relaxation transitions between the spin energy sublevels by means of the perturbation theory formula

$$w_{M,M'} = \hbar^{-2} \sum_{i,j} \overline{|\langle M|P_{ij}(S)|M'\rangle\, Q_i Q_j|^2}\, \rho_{ij}(\omega_{M,M'}), \tag{2}$$

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*Although the quadratic terms in the expansion give rise to a more rapid spin relaxation than the linear terms, a satisfactory description of the experimental results was achieved in[4] because the expression $\exp(-\lambda_j|\tau'|)$ describing the correlation of the amplitudes $A_j(t)$ of the processes $Q_j(t)$ = $A_j(t)\cos(\omega t + \varphi_j)$ was chosen for the correlation function of the random processes $Q_j(t)$.

where $\rho_{ij}(\omega_{M,M'})$ is the spectral density of the perturbing energy $\mathcal{3C}^{(2)}$ at the transition frequency $\omega_{M,M'}$; the bar above the expression denotes averaging over the arguments of $\mathcal{3C}^{(2)}_{MM'}$. By treating $\mathcal{3C}^{(2)}$ as a product of independent random processes $<M|P_{ij}(S)|M'>$ and Q_iQ_j we evaluate the density $\rho(\omega_{M,M'})$ by means of the formula[1,2]

$$\rho(\omega) = \int_{-\infty}^{+\infty} \exp(i\omega\tau) g(\tau) d\tau, \qquad (3)$$

where $g(\tau)$ is the product of the correlation functions of the corresponding independent processes normalized to $g(0) = 1$. On assuming for the correlation functions the expressions [1,2]

$$g_{Q_iQ_j}(\tau) = \exp(-(\lambda_j + \lambda_i)|\tau|)\cos\omega_i\tau\cos\omega_j\tau,$$

$$g_{Q_j^2}(\tau) = \tfrac{1}{3} + \tfrac{1}{3}\exp(-2\lambda_j|\tau|) + \tfrac{1}{3}\exp(-2\lambda_j|\tau|)\cos 2\omega_j\tau,$$

$$g_{P(S)}(\tau) = \exp(-|\tau|\tau_r^{-1}), \qquad \tau_r = \tfrac{4}{3}\pi\eta a^3/kT, \quad (4)$$

we obtain for the densities $\rho_{ij}(\omega)$ and $\rho_{jj}(\omega)$

$$\rho_{ij}(\omega) = \frac{1}{2}\frac{\lambda_i + \lambda_j + \tau_r^{-1}}{(\omega_i + \omega_j - \omega)^2 + (\lambda_i + \lambda_j + \tau_r^{-1})^2}$$
$$+ \frac{1}{2}\frac{\lambda_i + \lambda_j + \tau_r^{-1}}{(\omega_i + \omega_j + \omega)^2 + (\lambda_i + \lambda_j + \tau_r^{-1})^2}$$
$$+ \frac{1}{2}\frac{\lambda_i + \lambda_j + \tau_r^{-1}}{(\omega_i - \omega_j - \omega)^2 + (\lambda_i + \lambda_j + \tau_r^{-1})^2}$$
$$+ \frac{1}{2}\frac{\lambda_i + \lambda_j + \tau_r^{-1}}{(\omega_i - \omega_j + \omega)^2 + (\lambda_i + \lambda_j + \tau_r^{-1})^2},$$

$$\rho_{jj}(\omega) = \frac{2}{3}\frac{\tau_r^{-1}}{\tau_r^{-2} + \omega^2} + \frac{2}{3}\frac{2\lambda_j + \tau_r^{-1}}{\omega^2 + (2\lambda_j + \tau_r^{-1})^2}$$
$$+ \frac{2\lambda_j + \tau_r^{-1}}{(2\lambda_j + \tau_r^{-1})^2 + (2\omega_j + \omega)^2} + \frac{2\lambda_j + \tau_r^{-1}}{(2\lambda_j + \tau_r^{-1})^2 + (2\omega_j + \omega)^2}. \quad (5)$$

The parameters λ_j appearing in (4) and (5) can be interpreted as the probability for the dissipation of the vibrational energy of the complex ion. In accordance with[6], $\lambda_j \sim \tau_c^{-1}$ for $\omega_j\tau_c \gg 1$, while the value of λ_j is $\lambda_j \sim 10^{12}$ sec^{-1}. The frequencies ω_j are of the order $\sim 10^2$ cm^{-1}. Therefore, for $\omega_{M,M'} \ll \lambda_j$ we obtain $\rho_{jj}(\omega) \approx 10^{-11}$ sec, $\rho_{ij}(\omega) \approx 10^{-13}$ sec. In the case when the coordinates Q_i and Q_j are degenerate ($\omega_i = \omega_j$), we have $\rho_{ij} \approx \rho_{jj}$.

2. RELAXATION IN AQUEOUS SOLUTIONS OF Cr^{+3} SALTS

The energy of interaction $\mathcal{3C}^{(2)}$ of the magnetic electrons of the ion with the vibrations of Q_j has the form*

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*The evaluation of $\mathcal{H}^{(2)}$ has been carried out for us by A. M. Leushin, to whom the authors express their sincere gratitude.

$$\mathcal{H}^{(2)} = W_1(2Q_1^2 + 2Q_2^2 + 2Q_3^2 - Q_4^2 - Q_5^2 - Q_6^2)$$
$$+ W_2'(2\sqrt{2}Q_1Q_2 + 2Q_2Q_3) + W_2''(2\sqrt{2}Q_1Q_3 + Q_2^2 - Q_3^2)$$
$$+ W_3'(\sqrt{3}Q_5^2 - Q_6^2\sqrt{3}) + W_3''(2Q_4^2 - Q_5^2 - Q_6^2)$$
$$+ 2W_4'Q_2Q_4 + W_4''(Q_2Q_5 + \sqrt{3}Q_3Q_5) + W_4'''(Q_2Q_6$$
$$- \sqrt{3}Q_3Q_6) + W_5'(2\sqrt{2}Q_1Q_4 + 2Q_3Q_4) + W_5''(2\sqrt{2}Q_1Q_5$$
$$+ \sqrt{3}Q_2Q_5 - Q_3Q_5) + W_5'''(2\sqrt{2}Q_1Q_6 - \sqrt{3}Q_2Q_6$$
$$- Q_3Q_6) + W_6'Q_4Q_5 + W_6''Q_4Q_6 + W_6'''Q_5Q_6, \qquad (6)$$

where

$$W_1 = A - 20F(x^4 + y^4 + z^4 - 3r^4/5),$$
$$W_2' = B\sqrt{3}(x^2 - y^2) - 20F\sqrt{3}(x^4 - y^4),$$
$$W_2'' = B(r^2 - 3z^2) - 20F(x^4 + y^4 - 2z^4),$$
$$W_3' = C\sqrt{3}(x^2 - y^2) + 11\sqrt{3}(x^4 - y^4),$$
$$W_3'' = C(r^2 - 3z^2) + 11F(x^4 + y^4 - 2z^4),$$
$$W_4' = 48F(x^3y - xy^3),$$
$$W_4'' = 48F(x^3z - xz^3),$$
$$W_4''' = 48F(yz^3 - zy^3), \qquad (7)$$
$$W_5' = \sqrt{3}Dxy + 16\sqrt{3}F(x^3y + xy^3),$$
$$W_5'' = \sqrt{3}Dxz + 16\sqrt{3}F(x^3z + xz^3),$$
$$W_5''' = \sqrt{3}Dyz + 16\sqrt{3}F(y^3z + yz^3),$$
$$W_6' = Exy + 48F(x^3y + xy^3),$$
$$W_6'' = Exz + 48F(x^3z + xz^3),$$
$$W_6''' = Exz + 48F(y^3z + yz^3);$$
$$A = -\tfrac{1}{2}ee'R^{-3}, \qquad B = -\tfrac{3}{8}ee'R^{-5}(4 - 25r^2R^{-2}),$$
$$C = \tfrac{3}{32}ee'R^{-5}(2 - 55r^2R^{-2}), \qquad D = \tfrac{1}{2}ee'R^{-5}(4 - 15r^2R^{-2}),$$
$$E = -\tfrac{3}{2}ee'R^{-5}(1 + 15r^2R^{-2}), \qquad F = \tfrac{35}{64}ee'R^{-7}. \qquad (8)$$

Here $\mathbf{r}(x, y, z)$ are the coordinates of the magnetic electron of the ion; R is the equilibrium distance between the nucleus of the ion and the center of charge e' of the diamagnetic particle appearing in the complex ion.

The ^4F term of the free Cr^{+3} ion in the cubic field due to six particles X_i is split in such a way that the lowest orbital level turns out to be single; the remaining orbital levels are separated from the lower one by $\sim 10^{-4}$ cm^{-1}. The matrix element of the perturbation $\mathcal{3C}^{(2)} + \lambda\,\mathbf{LS}$ connecting the two spin levels M and M' appears in the third order approximation and is equal to

$$\mathcal{H}'_{M,M'} = \varepsilon_1[(-\sqrt{3}Q_2Q_3 + \tfrac{33}{40}(Q_5^2 - Q_6^2))(S_{y'}^2 - S_{x'}^2)$$
$$+ (3S_{z'}^2 - S^2)(-\tfrac{1}{2}(Q_2^2 - Q_3^2) + \tfrac{11}{40}(2Q_4^2 - Q_5^2 - Q_6^2))]$$
$$+ \varepsilon_2[Q_5Q_6\{S_{x'}S_{y'}\} + Q_4Q_5\{S_{x'}S_{z'}\} + Q_4Q_6\{S_{y'}S_{z'}\}],$$

$$\varepsilon_1 = -\frac{27}{R^2}\left(\frac{\lambda}{\Delta}\right)^2\left(\frac{ee'}{R}\right)\overline{\frac{r^4}{R^4}}, \quad \varepsilon_2 = \frac{18\cdot38\sqrt{3}}{175R^2}\left(\frac{\lambda}{\Delta}\right)^2\left(\frac{ee'}{R}\right)\left(\overline{\frac{r^2}{R^2}} - \frac{5}{38}\overline{\frac{r^4}{R^4}}\right).$$
$$(9)$$

Here Δ is the total splitting of the ^4F term in the cubic field; figure brackets denote the symmetrized product: $\{ab\} = ab + ba$. The data of Van Vleck[7] have been utilized to simplify the expressions for ε_1 and ε_2. We also note that in (9) we have omitted products of the coordinates Q_j with different frequencies which, in accordance with Sec. 1, give no essential contribution to spin relaxation. Before evaluating the matrix element between the spin states M and M' the spin variables in (9) must be transformed to the laboratory system of coordinates with the z axis parallel to the constant field H_0:

$$S_{x'} = \alpha_\mu S_\mu, \qquad S_{y'} = \beta_\nu S_\nu,$$

$$S_{z'} = \gamma_\varkappa S_\varkappa; \qquad \mu, \ \nu, \ \varkappa = x, \ y, \ z. \tag{10}$$

Here α_μ, β_ν, $\gamma_\varkappa$ are the direction cosines between the axes of the moving system of coordinates (corotating with the complex ion) and the laboratory system. In averaging $|\, \mathcal{H}\, |^2$ over the sphere it is convenient to express α_μ, β_ν, and $\gamma_\varkappa$ in terms of the Eulerian angles; in this way we can easily obtain

$$\overline{|(S_{z'})_{M,M'}|^2} = \tfrac{2}{15}\{S_x S_z\}^2_{M,M+1}; \qquad \tfrac{8}{15}(S_x^2)^2_{M,M+2},$$

$$\overline{|(S_{x'}^2 - S_{y'}^2)_{M,M'}|^2} = \tfrac{2}{15}\{S_x S_z\}^2_{M,M+1}; \qquad \tfrac{16}{15}(S_x^2)^2_{M,M+2},$$

$$\overline{|\{S_{\mu'} S_{\nu'}\}|^2} = \tfrac{2}{15}\{S_x S_z\}^2_{M,M+1}; \qquad \tfrac{16}{15}(S_x^2)^2_{M,M+2}. \tag{11}$$

By combining (2), (9), and (11) we obtain for the probability of the transition M, M + 2

$$w_{M,M+2} = (S_x^2)^2_{M,M+2}\hbar^{-2}\{\varepsilon_1\,[\tfrac{6}{5}\,(\overline{Q_1^4}\rho_{22} + \overline{Q_3^4}\rho_{33}) + \tfrac{48}{5}\overline{Q_2^2}\,\overline{Q_3^2}\rho_{23}$$

$$+ \tfrac{263}{250}\overline{Q_2^4}\,\rho_{22} + \tfrac{19}{5}(\tfrac{23}{40})^2\,(\overline{Q_5^4}\rho_{55} + \overline{Q_6^4}\rho_{66})] + \tfrac{16}{5}\,\varepsilon_2^2\,[\overline{Q_4^2}\,\overline{Q_5^2}\rho_{45}$$

$$+ \overline{Q_5^2}\,\overline{Q_6^2}\rho_{56} + \overline{Q_4^2}\,\overline{Q_6^2}\rho_{46}]\}. \tag{12}$$

Here[8]

$$\overline{Q_j^2} = \frac{\hbar}{2\omega_j\mu_j}\,\mathrm{cth}\,\frac{\hbar\omega_j}{2kT}, \qquad \overline{Q_j^4} = \frac{3}{4}\,\frac{\hbar^2}{\omega_j^2\,\mu_j^2}\mathrm{cth}^2\,\frac{\hbar\omega_j}{2kT}. \tag{13}*$$

Similarly we can obtain the probability of the transition M, M + 1; it is of the same order of magnitude.

In Eq. (12) we have, in accordance with (5), $\rho_{ij} \approx \rho_{jj} \approx 10^{-11}$ sec. We set $\overline{Q^4} = 1.5 \times 10^{-37}$ cm^4; by utilizing the values for the other constants quoted in[7] we have obtained $\varepsilon_1 = 1$, $\varepsilon_2 = 0.1$ and $W_{M,M+2} \approx 5 \times 10^7$ sec^{-1}, which is lower than the experimentally observed width ($\sim 5 \times 10^8$ sec^{-1},[9]) by an order of magnitude. It should be noted in this connection that we have not taken into account the contributions to the line width due to the parts of $\mathcal{H}^{(2)}$ diagonal with respect to the spin which describe the shifts of the spin levels due to the oscillations of Q_j. Moreover, in the perturbation

*cth = coth.

term $\mathcal{H}^{(2)}$ we have not retained the coordinates of the vibrations of $Q_7 \ldots, Q_{15}$ which are not symmetric under an inversion. We also note that the values of many of the parameters are known only up to an order of magnitude, and, therefore, the agreement between the calculated and the observed widths can be regarded as satisfactory.

Formula (12) gives a reasonably good representation of the temperature dependence of the width of the resonance line of the Cr^{+3} ions in an aqueous solution of $Cr(NO_3)_3$ where ΔH_{exp} is equal to 245, 190, 125, 107, and 105 oe respectively at temperatures[9] of 303, 323, 373, 423, and 473° K. On taking ΔH_{theor} (303° K) = 245 oe we have obtained values of ΔH_{theor} equal to 200, 137, 106, and 89 oe corresponding to temperatures of 323, 373, 423, and 473° K for $W_j = 560$ cm^{-1} and $E/k = 1250°$ K.

In the case of an anisotropic g-factor or of a Stark splitting of the spin sublevels of the ion $(S > \tfrac{1}{2})$ a different relaxation mechanism is possible which leads to the relation[10,11]

$$T_1^{-1} \sim \tau_r / (1 + \omega_{M,M'}^2 \tau_r^2). \tag{14}$$

In accordance with our calculation

$$T_1^{-1} \sim \mathrm{cth}^2\,(\hbar\omega_j/2kT)\,\tau_r/(1 + \omega_{M,M'}^2 \tau_r^2). \tag{15}$$
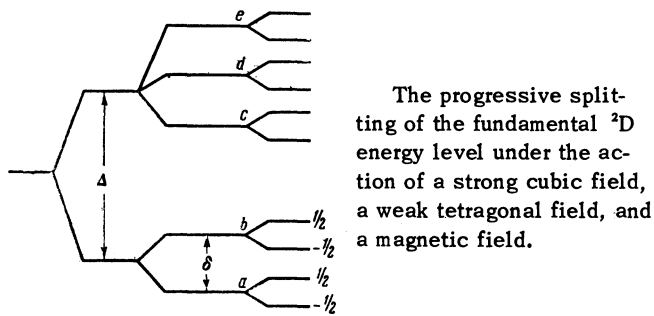
As can be seen from (14) and (15), up to temperatures $T \sim \hbar\omega_j/2K$ the dependence of T_1^{-1} on T in the theories of McConnell[10] and McGarvey,[11] and in the theory under discussion here, is practically identical. As the liquid is heated further the decrease in T_1^{-1} predicted by formula (15) will be slower than in the theories of McConnell and of McGarvey, and one can even expect an increase in T_1^{-1} at temperatures $T \gg \hbar\omega_j/2k$. Apparently, this case is in fact realized in aqueous solutions of Cr^{+3} salts.

3. WIDTH OF THE RESONANCE LINE OF Cu^{+2} IONS IN AQUEOUS SOLUTION

The problem of the nature of the width of the resonance line of the Cu^{+2} ion in an aqueous solution deserves special consideration. The energy level diagram for a doubly ionized copper ion surrounded by six particles forming a slightly distorted octahedron is shown in the figure. The orbital levels are characterized by the following wave functions:[12]

$$\psi_a = (\psi_2 + \psi_{-2})/\sqrt{2}, \qquad \psi_b = \psi_0, \qquad \psi_c = (\psi_2 - \psi_{-2})/\sqrt{2},$$

$$\psi_d = (\psi_1 + \psi_{-1})/\sqrt{2}, \qquad \psi_e = (\psi_1 - \psi_{-1})/\sqrt{2}. \tag{16}$$

The intervals Δ and δ respectively amount to $\sim 10^4$ and $\sim 10^3$ cm^{-1}. The spin sublevels arising

The progressive splitting of the fundamental ^2D energy level under the action of a strong cubic field, a weak tetragonal field, and a magnetic field.

when a constant magnetic field is applied are characterized by the quantum numbers $M = \pm\frac{1}{2}$.

We have found that the width $\Delta\nu$ of the resonance line observed as a result of transitions a, $M = -\frac{1}{2} \rightarrow$ a, $M = +\frac{1}{2}$ is determined not by the spin-relaxation transitions a, $M = \frac{1}{2} \rightarrow$ a, $M = -\frac{1}{2}$, excited by the combined action of $\mathfrak{K}^{(2)}$, the Zeeman and the spin-orbit interactions of the ion, but by the relaxation transitions between the orbital sublevels a and b excited under the action of $\mathfrak{K}^{(2)}$ alone with the interaction $\lambda \mathbf{L} \cdot \mathbf{S}$ taking no part.

Indeed, in accordance with the general principles of quantum mechanics the width $\Delta\nu$ of the resonance line of the transition a, $M = -\frac{1}{2} \rightarrow$ a, $M = +\frac{1}{2}$, is equal to the sum of the probabilities of relaxation transitions from each of the sublevels a, $M = \pm\frac{1}{2}$ to all the other sublevels. The relaxation transitions between the orbital sublevels a, $M = \frac{1}{2} \rightarrow$ b, $M = \frac{1}{2}$ and a, $M = -\frac{1}{2} \rightarrow$ b, $M = -\frac{1}{2}$ broaden the levels a, $M = \pm\frac{1}{2}$ in the same way as do the transitions a, $M = +\frac{1}{2} \rightleftarrows$ a, $M = -\frac{1}{2}$. However, the direct transitions a $\rightarrow$ b are considerably more probable than transitions accompanied by a reorientation of spin. The matrix element of the direct transitions calculated with the aid of (6) and (16) is in the first approximation:

$$\mathfrak{K}^{(2)}_{a \rightarrow b} = a(Q_5^2 - Q_6^2) + bQ_2Q_3 + cQ_5Q_6;$$

$$a = \frac{9\sqrt{3}}{8}\left(\Lambda_1 - \frac{825}{8}\Lambda_2\right), \qquad b = -18\left(\Lambda_1 - \frac{375}{16}\Lambda_2\right),$$

$$c = i\frac{45\sqrt{3}}{8}\Lambda_2; \qquad \Lambda_1 = ee'\alpha\,\overline{r^2}R^{-5}, \qquad \Lambda_2 = ee'_\rho\overline{r^4}R^{-7},$$

$$\alpha = -3\beta = 2/21. \tag{17}$$

[The probabilities of the transitions a $\rightarrow$ c, d, e, which are proportional to the Boltzmann factors $\exp(-\Delta/2kT)$, are small and are therefore not considered.] At the same time the matrix element for the transitions accompanied by a reorientation of spin a, $M = \frac{1}{2} \rightleftarrows$ a, $M = -\frac{1}{2}$ arises only in the third approximation taking into account the energies of the Zeeman and the spin-orbit interactions of the ion:

$$\mathfrak{K}_{a,\frac{1}{2} \rightleftarrows a,-\frac{1}{2}} \approx (\lambda g\beta H_0/\Delta^2)\,\mathfrak{K}^{(2)}_{ab} \approx 10^{-5}\mathfrak{K}^{(2)}_{ab}. \tag{18}$$

We also note that the contribution to the width made by spin-relaxation transitions will be proportional to the square of the field H_0, while the contribution of the direct transition a $\rightarrow$ b is independent of the field; experiments also did not show any apparent dependence of the width on the field.[19]

We now evaluate the probability of the transition a $\rightarrow$ b. The matrix element (17) is invariant under rotations of the complex ion; therefore, in writing down the probability of the transition a $\rightarrow$ b we should set $\tau_r = \infty$ in formulas (5). Moreover, the transition frequency $\omega_{ab} \approx 10^3$ cm^{-1} is large compared to λ_j, so that

$$\rho_{ij} = 4\lambda_j/3\omega_{ab}^2 + 2\lambda_j/(\omega_{ab} - 2\omega_j)^2 + 2\lambda_j/(\omega_{ab} + 2\omega_j)^2,$$

$$\rho_{ij} = \lambda_j\left(2/\omega_{ab}^2 + (\omega_{ab} - 2\omega_j)^{-2} + (\omega_{ab} + 2\omega_j)^{-2}\right). \tag{19}$$

By utilizing (2) and (17) we obtain for the probability of transitions a $\rightarrow$ b

$$w_{a,b} = \hbar^{-2}\left[a^2\left(\overline{Q_5^4}\rho_{55} + \overline{Q_6^4}\rho_{66}\right) + b^2\overline{Q_2^2}\,\overline{Q_3^2}\rho_{23}\right. \tag{20}$$

$$\left. + c^2\overline{Q_4^2}\,\overline{Q_5^2}\rho_{45}\right]e^{-\delta/2kT}.$$

The temperature dependence of (20) is given by the relation

$$w_{a,b} \sim \exp\left(-\delta/2kT\right)\text{cth}^2\left(\hbar\omega_j/2kT\right)\lambda_j, \tag{21}$$

with $\lambda_j \sim \exp(-E/RT)$ where E is a parameter which has the significance (and the order of magnitude) of the viscous barrier for the liquid.[6] We set $\delta = 10^3$ cm^{-1}, $\hbar\omega_j = 500$ cm^{-1}, $E = 2$ kcal/mole $= 700$ cm^{-1}, then in accordance with (21) the probability $w_{a,b}$ increases by approximately a factor of 4.2 as the temperature of the liquid varies from 300 to 400° K. In accordance with Kozyrev's experiment,[8] an increase in the line width by a factor of 1.8 is observed within the same temperature interval, and this is close to the calculated increase in width. The order of magnitude of (20) also agrees with the width observed in an aqueous solution. By setting, in agreement with Van Vleck,[7] $R = 2A$, $\overline{r^2} = 4.4\ a_0^2$, $\overline{r^4} = 31.2\ a_0^4$, $e' = e$, we obtain $|a| = 2.4 \times 10^4$, $|b| = 6 \times 10^4$, $|c| = 10^3$; further, at $T = 350°$ K we have $\mu_f = 3 \times 10^{-23}$ g (the mass of a molecule of water), $\omega_j = 500$ cm$^{-1} = 10^{14}$ sec^{-1} and $\overline{Q^4} = 1.5 \times 10^{-37}$ cm^4; finally, on taking $\rho_{ij} \approx 2\rho_{ij} \approx 10^{-16}$ and $\exp(-\delta/2kT) \approx 0.1$, we obtain $w_{a,b} \approx 5 \times 10^9$ sec^{-1}.

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