

CONCERNING THE THEORY OF SPIN-LATTICE RELAXATION IN RADICALS IN LIQUIDS

I. V. ALEKSANDROV and G. M. ZHIDOMIROV

Institute of Chemical Physics, Academy of Sciences, U.S.S.R.

Submitted to JETP editor December 19, 1960

J. Exptl. Theoret. Phys. (U.S.S.R.) 40, 1720-1724 (June, 1961)

Spin-lattice relaxation times due to the interaction between the spin and the vibrations of individual atoms of a radical are calculated for radicals in a liquid. It is demonstrated that the direct, as well as the combinational ("two-phonon") relaxation transitions yield, as a rule, larger relaxation times than the Brownian rotational motion of the radical.

McCONNELL¹ has considered the mechanism of spin-lattice relaxation associated with the Brownian rotational motion of a radical as a whole in a liquid. In this case the relaxation transitions are due to the anisotropy of the spin-orbit and the hyperfine interactions and to the rotation of the radical. Al'tshuler and Valiev² have proposed a different mechanism for the spin-lattice relaxation associated with the interaction of the spin with the orbital motion of the electron and with the normal vibrations of the complex ion in solution; however, as will be shown here, the method of calculation proposed by Al'tshuler and Valiev² is incorrect. In this paper we shall examine in greater detail this mechanism for spin-lattice relaxation as applied to radicals in liquids.

We shall discuss relaxation processes associated with the intramolecular vibrations due to the Fermi interaction of the electron spin **S** with the nuclear spin **I** (the contribution of the spin-orbit (**S**·**L**) and of the dipole-dipole (**S**·**I**) interactions usually turns out to be smaller in the case of radicals; we also note that, if necessary, these interactions can be easily taken into account within the framework of the calculation proposed below). The spin-Hamiltonian of the unpaired electron interacting with one of the nuclei of the radical has the form

$$\mathcal{H} = g\beta\mathbf{SH} + A\mathbf{SI}, \tag{1}$$

where the constant describing the Fermi interaction is $A = A(Q)$, Q is the displacements of the nucleus of spin **I** from its equilibrium position **R**, and the remaining notation is the usual one. Following Al'tshuler and Valiev,² we shall assume that the vibrations take place classically, i.e., $Q = Q(t)$. By expanding the quantity A in a power series in terms of the small displacements from the equilibrium position, and by restricting our-

selves to the linear and the quadratic terms, we obtain

$$\begin{aligned} \mathcal{H} &= \mathcal{H}_0 + V_1(t) + V_2(t), & \mathcal{H}_0 &= g\beta\mathbf{SH} + A_0\mathbf{SI}, \tag{2} \\ \text{where} & & & \\ V_1(t) &= A_1 \frac{Q(t)}{R} \mathbf{SI}, & V_2(t) &= A_2 \frac{Q^2(t)}{2R^2} \mathbf{SI}, \\ A &= A_0 + A_1 Q(t)/R + A_2 Q^2(t)/R^2. \end{aligned} \tag{3}$$

In formulas (2) and (3), $Q(t)$ is a random function describing the vibration of the nucleus under consideration, modulated by the random interactions with the surrounding medium.

We first evaluate the probability of relaxation transition per unit time due to the term $V_1(t)$. By regarding the quantity V_1 as a perturbation we obtain for the transition probability between the magnetic levels k and k' ³

$$\omega_{kk'} = \frac{A_1^2}{\hbar^2} \frac{\overline{Q^2(t)}}{R^2} |(k|\mathbf{SI}|k')|^2 \int_{-\infty}^{\infty} \varphi(\tau) e^{i\omega_{kk'}\tau} d\tau, \tag{4}$$

where $\hbar\omega_{kk'}$ is the spacing between the levels k and k' , and $\varphi(\tau) = \overline{Q(t)Q(t+\tau)}/\overline{Q^2}$ is the correlation function for the random variable Q .

In the case when the interaction of the vibrations with the medium is large (much larger than the energy of the natural vibrations of the nucleus) it is reasonable to assume for the correlation function

$$\varphi(\tau) = \exp\{-|\tau|/\tau_c\}, \tag{5}$$

where τ_c is some characteristic correlation time. Then we immediately obtain from (4)

$$\omega_{kk'} = \frac{A_1^2}{\hbar^2} \frac{\overline{Q^2}}{R^2} |(k|\mathbf{SI}|k')|^2 \frac{2\tau_c}{1 + \omega_{kk'}^2 \tau_c^2}, \tag{6}$$

i.e., an expression analogous to formula (9) of the paper of Al'tshuler and Valiev.² However, in the case under consideration of strong interaction it is not possible to relate the quantity τ_c to the op-

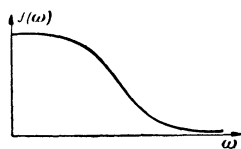


FIG. 1.

tical characteristics of an individual intramolecular vibration (as is done in reference 2). Indeed, the correlation function (5) yields for the spectral density of the nuclear vibrations $J(\omega)$ the curve shown in Fig. 1, and this corresponds to a continuous optical spectrum and to the absence of any spectral lines due to the natural vibrations of the nucleus.

However, if the interaction of the natural vibrations with the medium is small and may be treated as a perturbation of the characteristic vibrations, then a different expression is obtained for the correlation function. Representing the quantity $Q(t)$ in the form

$$Q(t) = q(t) \cos(\omega_0 t + \eta(t)), \quad (7)$$

where ω_0 is the natural frequency of the vibrations, while q and η are respectively the random amplitude and phase of the oscillator, and assuming that $q(t)$ and $\eta(t)$ are not correlated with one another, we obtain the correlation function for the quantity $Q(t)$ in the form

$$\varphi(\tau) = \exp\{-|\tau|/\tau_c\} \cos \omega_0 \tau. \quad (8)$$

In this case we obtain from (4)

$$\omega_{kk'} = \frac{A_0^2}{\hbar^2} \frac{\bar{q}^2}{R^2} |(k|S|k')|^2 \frac{2\tau_c}{1 + (\omega_0 - \omega_{kk'})^2 \tau_c^2}. \quad (9)$$

For $\omega_0 \tau_c \gg 1$ the spectral density $J(\omega)$ has the form shown in Fig. 2; the maximum at $\omega = \omega_0$ corresponds in the optical spectrum to a line due to the natural vibration of the nucleus, the breadth of this maximum being of the order of $1/\tau_c$.

We note that formulas (6) and (9) lead to essentially different results, for in all the cases of interest to us we have $\omega_0 \gg \omega_{kk'}$.

As an example we evaluate the probability of the relaxation transition for an unpaired electron in the C atom of the CH fragment caused by the vibrations of the C-H bond (modulated by the motion of the medium). The constant A for the CH fragment has been evaluated by McConnell:⁴

$$A = \frac{8\pi}{3} g\beta_H \beta_H \frac{I(C\pi) - I(\pi H)}{2I(CH)} |\Psi(0)|^2, \quad (10)$$

where g_H is the g -factor for the proton, β_H is the nuclear magneton, $\Psi(0)$ is the value of the 1s-wave function for the H atom at the origin;

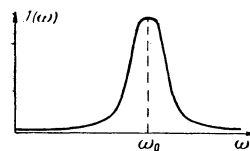


FIG. 2.

$I(C\pi)$ is the exchange integral between the 2p-orbit for the unpaired electron of the C atom and the hybridized orbit of the C atom responsible for the C-H bond; $I(\pi H)$ is the exchange integral between the 2p-orbit of the C atom and the 1s-orbit of the H atom; $I(CH)$ is the exchange integral between the hybridized orbit of the C atom and the 1s-orbit of the H atom. Keeping in mind that $I(\pi H) \ll I(C\pi)$, we note that the dependence of A on Q is essentially determined by the dependence on Q of the exchange integral $I(CH)$. The latter can be approximated by the formula⁵

$$I(CH) = I_0 \exp\{-Q/R\}. \quad (11)$$

Thus, in formula (3) $A_1 = A_0$, and for the transition probability we have

$$\omega_{kk'} = \frac{A_0^2}{\hbar^2} \frac{\bar{q}^2}{R^2} |(k|S|k')|^2 \frac{2\tau_c}{1 + (\omega_0 - \omega_{kk'})^2 \tau_c^2}. \quad (12)$$

The quantity A_0 can be estimated from the hyperfine structure of the electron paramagnetic resonance (e.p.r.) spectra of the aromatic radicals, while \bar{q}^2 and τ_c can be estimated as in the paper by Al'tshuler and Valiev;² finally, on assuming for the natural frequency of the vibrations of the C-H bond a magnitude of the order of $10^{14} - 10^{15} \text{ sec}^{-1}$, we obtain

$$\omega_{kk'} \sim 1 - 10^{-3} \text{ sec}^{-1}$$

and this corresponds to a spin-lattice relaxation time of the order of $10^3 - 1$ sec. Taking the relaxation mechanism associated with deformational vibrations into account does not lead to any essential increase in the quantity $\omega_{kk'}$ which would be sufficient to explain the experimental data.

The direct process considered above, that of transfer of energy from the spin system to thermal motion, is a process involving the transfer to the oscillator of a quantum of energy $\hbar\omega_{kk'}$, which is considerably smaller than the mean self energy of the oscillator. As can be seen from formula (9), the probability of this process is proportional to the spectral density of the coordinate of the oscillator far from the maximum ($\omega_{kk'} \sim J(\omega_{kk'})$, $\omega_{kk'} \ll \omega_0$; cf. Fig. 2), and this is responsible for the low probability of relaxation transitions. From this point of view one might expect that those second order processes will turn out to be more ef-

fective which are associated with changes (actual or virtual) in the vibrational energy of the oscillator by a quantity of the order of $\hbar\omega_0$, which evidently occur with a probability proportional to the value of $J(\omega)$ at the maximum.

If, as before, we treat the nuclear vibrations classically, then the effect just mentioned can be evaluated by taking into account the term $V_2(t)$ in the spin Hamiltonian (2). Let the two-dimensional distribution function for the random variable q be given by the normal distribution function

$$F(q_1, q_2, \tau) = \frac{1}{2\pi\sigma^2(1-\rho^2)^{1/2}} \exp\left\{-\frac{q_1^2 + q_2^2 - 2\rho q_1 q_2}{2\sigma^2(1-\rho^2)}\right\}, \quad (13)$$

where $\sigma^2 = \overline{q^2}$ is the mean square amplitude of the oscillator, while $\rho = \rho(\tau)$ is the correlation function for the random changes of the amplitude. For the random phase η we can choose a distribution function of the form

$$P(\eta_1, \eta_2, \tau) = (2\pi)^{-1} \delta(\eta_1 - \eta_2) \exp\{-|\tau|/\tau_c\} + (2\pi)^{-2} (1 - \exp\{-|\tau|/\tau_c'\}), \quad (14)$$

where τ_c' is a time of the order of magnitude of the time between collisions. The distribution function (14) describes a process in which the phase of the oscillator does not change in the intervals between collisions, while the phase after a collision is not correlated with the value of the phase before the collision. We note that the function $P(\eta_1, \eta_2, \tau)$ could also have been chosen of a different form; for what follows it is essential only that all the values of the phase should be equally probable, and that the correlation of $\eta(t)$ and $\eta(t + \tau)$ should decrease with increasing time τ .

Further, we represent $V_2(t)$ in the form

$$V_2(t) = V_2'(t) + \overline{V_2(t)} = V_2'(t) + BSI \quad (15)$$

and include the constant quantity $B = A_2 \overline{Q^2(t)}/2R^2$ in A_0 . Then for the evaluation of the probability of a transition under the influence of $V_2(t)$ we can apply a formula analogous to (4), where $\varphi(\tau)$ now denotes

$$\varphi(\tau) = \overline{Q^2(t) Q^2(t + \tau) / Q^4(t)} \quad (16)$$

[formula (4) is inapplicable to $V_2(t)$, since the quantity $\overline{V_2(t) V_2(t + \tau)}$ does not tend to zero as $\tau \rightarrow \infty$].

By using (13) and (14) we easily obtain

$$\varphi(\tau) = \frac{1}{2} \rho^2 \sigma^4 + \frac{1}{8} \sigma^4 \exp\{-|\tau|/\tau_c'\} \cos 2\omega_0 \tau (1 + 2\rho^2). \quad (17)$$

Finally, by choosing $\rho(\tau)$ in the form $\rho(\tau) = \exp(-|\tau|/\tau_c)$, we obtain for the transition probability

$$\omega_{hk'} = \frac{A_2^2}{8\hbar^2 R^4} |(k|SI|k')|^2 (\overline{q^2})^2 \frac{4\tau_c}{1 + 4\omega_{hk'}^2 \tau_c^2}. \quad (18)$$

In expression (18) we have omitted the terms corresponding to the last term in (17), which leads in the expression for the spectral density of the quantity $Q^2(t)$ to a maximum at the frequency $\omega = 2\omega_0$.

Estimating the quantity $w_{kk'}$ by means of formula (18) in exactly the same manner in which we made an estimate of formula (12) we find that for $\omega_0 \sim 10^{14} - 10^{15} \text{ sec}^{-1}$ we have $w_{kk'} \sim 10^3 - 1 \text{ sec}^{-1}$. Thus, the combined transition indeed turns out to be more effective than the direct transition discussed by Al'tshuler and Valiev.²

Formulas (9) and (18) show that the mechanism of spin-lattice relaxation in radicals in liquids associated with the vibrational motion turns out to be, as a rule, less important ($T_1 \gtrsim 10^{-3} \text{ sec}$) than the mechanism proposed by McConnell¹ ($T_1 \sim 10^{-5} \text{ sec}$). The predominance of the "vibrational" mechanism can apparently be expected in cases when: 1) the anisotropy Δg of the g-factor and the anisotropy ΔA of the hyperfine interaction are both very small ($Aq^2/R^2 > \Delta A$ and $Aq^2/R^2 > \Delta g\beta H_0$; H_0 is the constant external magnetic field), or 2) the hyperfine splitting is large, and the constant A is determined by exchange integrals which depend on the coordinates corresponding to low frequency vibrations.

The authors wish to thank Professor N. D. Sokolov for discussions.

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