exhibited by most samples, in both transient and steady-state measurements, sets iodine apart from any known nonmolecular insulator. The large value of θ ($\sim 10^{-2}$ at room temperature) is to be contrasted, e.g., with the 10^{-9} quoted[7] for CdS. Preliminary measurements on anthracene[8] suggest a similar behavior.[9] It is quite possible that such a behavior is typical for molecular crystals.

In conclusion, it is believed that measurements of transient SCLC, especially when combined with steady-state measurements, constitute a powerful tool for the study of electronic processes in solids. This is particularly the case for materials characterized by low mobilities. At the same time, transient measurements under space-charge-free conditions seem promising in yielding information on such processes as surface recombination and carrier photogeneration in these materials.

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[7] R. W. Smith, RCA Rev. **20**, 69 (1959).

[8] M. Silver, M. Swicord, R. C. Jarnigan, A. Many, S. Z. Weisz, and M. Simhony, J. Phys. Chem. Solids **24** (1962).

[9] *Note added in proof:* Studies of SCLC in anthracene have also been reported by P. Mark and W. Helfrich [J. Appl. Phys. **33**, 205 (1962)].

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Theory of Exchange Relaxation of Hyperfine Structure in Electron Spin Resonance*

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The electron spin exchange interaction between colliding molecules is examined as a possible relaxation mechanism for the hyperfine structure of free-radical molecules in solution. An expression is derived which, under suitable conditions, relates the frequency-dependent susceptibility to a single parameter q, which can be interpreted as the frequency of spin exchanges. For large values of q the absorption narrows to a single line of width σ^2/q, where σ is the mean square width of the unperturbed spectrum. For small values of q the widths of the individual hyperfine lines are found to depend upon their relative intensities. These results are compared with some recent experiments.

I. INTRODUCTION

ELECTRON paramagnetic resonance spectra of many free radicals exhibit hyperfine splittings due to magnetic dipole coupling between the unpaired electron and magnetic nuclei within the molecule. This coupling consists of two contributions; the ordinary dipole-dipole interaction which is dependent upon the molecular orientation, and the "contact" interaction, $a\mathbf{I}\cdot\mathbf{S}$, between the nuclear spin $\mathbf{I}$ and the electron spin $\mathbf{S}$, with the coupling constant a proportional to the electron charge density at the site of the magnetic nucleus. Typically, the hyperfine splittings are observed by dissolving the radical in a diamagnetic solvent, which reduces the intermolecular exchange and intermolecular dipole-dipole interactions to the point where the hyperfine structure is resolved. At sufficiently high temperatures, molecular tumbling averages the orientation-dependent part of the hyperfine coupling leaving only the contact interaction. If, in addition, the Larmor frequency due to the external magnetic field is much larger than the coupling constant a, then the electronic and nuclear spin can be separately space quantized and it is thus possible to treat the hyperfine coupling as a small increment to be added to the external magnetic field.

Our purpose in this paper is to examine in some detail a possibly important relaxation mechanism for these systems, namely, exchange interaction occurring during collisions between the free radical molecules. We will then attempt to apply our conclusions to some recent experimental results.

One method of attack on this problem would be to treat it as an application of a general theory of motional narrowing, as has been formulated, for example, by Kubo and Tomita.[1] One would then treat the hyperfine interaction as a perturbation which is modulated by the (time-dependent) exchange interaction. The "motional" Hamiltonian would then commute with the Zeeman Hamiltonian and also with the total electron magnetic moment and thus would obey the criteria for the applicability of motional narrowing theories. This approach would enable one to calculate the over-all second moment of the spectral intensity and in the case of strong motional narrowing ("fast motion") should represent the observed line shape quite well. It would not be of any use if one wished to study the various hyperfine lines individually. In this case the Zeeman and hyperfine interactions would have to be treated as a single unit which is perturbed by the exchange interaction. In the region intermediate between good hyperfine resolution and strong narrowing neither

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[1] R. Kubo and K. Tomita, J. Phys. Soc. Japan **9**, 888 (1954).

method holds much promise. This "pincer" approach to the problem has been carried out by Kivelson.[2]

Our method will have the advantage of resulting in a single analytic expression with which the entire range of situations, from good hyperfine resolution to extreme narrowing, can be described. We will use a Hamiltonian consisting of two parts; an unperturbed part which describes the interaction of each molecular electron with the external magnetic field and with the local field due to the hyperfine coupling, and a part which describes exchange interactions between pairs of molecules. By treating the hyperfine interaction as if the electron were interacting with a classical magnetic field, we will be assuming that the external field is much larger than the hyperfine coupling constant, and also that the relaxation times of the magnetic nuclei are long compared to electron relaxation times. The motion of the molecules will be treated classically by having the various exchange integrals be time dependent. We will use the correlation function method as described, for example, by Kubo.[3]

II. CALCULATION OF THE CORRELATION FUNCTION AND FREQUENCY SPECTRUM

We write the Hamiltonian for N molecules as

$$\mathcal{H}(t)=\sum_{i=1}^{N}\omega_i S_{iz}+\sum_{i>j}J_{ij}(t)\mathbf{S}_i\cdot\mathbf{S}_j, \tag{2.1}$$

where $J_{ij}(t)$ is the time-dependent exchange interaction between the ith and jth molecules, ω_i is the Larmor frequency of the ith molecule, including the contribution of its hyperfine coupling, and $\mathbf{S}_i$ is electronic spin angular momentum operator of the ith molecule. The quantity which we will calculate is the correlation function, which we will define as[4]

$$\begin{aligned}G(t)&\equiv\gamma^2/4\mathrm{Re}\{\psi(t)\},\\ \psi(t)&=\mathrm{Tr}\{\rho_0[S^+(t)S^-(0)+S^-(0)S^+(t)]\},\end{aligned} \tag{2.2}$$

where γ is the electron magnetic moment. Here $S^{\pm}(t)$ obeys the Heisenberg equation of motion (with $\hbar=1$):

$$dS^{\pm}/dt=\pm i[\mathcal{H}(t),S^{\pm}(t)], \tag{2.3}$$

with

$$S^{\pm}(0)=\sum_i S_i^{\pm},\quad S_i^{\pm}=S_{ix}\pm iS_{iy}.$$

We shall assume that the temperature is high enough that the density matrix ρ_0 may be taken simply as

$$\rho_0=1/\mathrm{Tr}\{1\},$$

so that we may write

$$\psi(t)=2\,\mathrm{Tr}\{S^+(t)S^-(0)\}/\mathrm{Tr}\{1\}. \tag{2.4}$$

The solution of Eq. (2.3) can be expressed formally as a linear superposition of basis operators for the system.[5] Thus we write

$$S^+(t)=\sum_i\sum_\mu a_i^\mu S_i^\mu+\sum_{i<j}\sum_{\mu,\nu}b_{ij}^{\mu\nu}S_i^\mu S_j^\nu+\sum_{i<j<k}\sum_{\mu,\nu,\lambda}c_{ijk}^{\mu\nu\lambda}S_i^\mu S_j^\nu S_k^\lambda+\cdots, \tag{2.5}$$

where the Greek superscripts can assume values which correspond to the spin operators S_i^+, S_i^-, $S_i^0\equiv S_{iz}$. Now the trace operation can be factored into a product of traces over the spin coordinates of the individual molecules. Therefore if we substitute Eq. (2.5) into Eq. (2.4) and remember that the trace of any single spin operator S_i^μ vanishes, and that the trace of $S_i^\mu S_i^\nu$ vanishes unless $\mu=-\nu$, we get

$$\psi(t)=2\sum_i a_i^+(t)\,\mathrm{Tr}\{S_i^+S_i^-\}/\mathrm{Tr}\{1\}=\sum_i a_i^+(t). \tag{2.6}$$

Thus the only coefficients in the expansion (2.5) that we shall need to calculate are the $a_i^+(t)$. If we now substitute Eq. (2.5) into Eq. (2.3), multiply both sides of the resulting equation by S_l^- and take the trace of both sides, we obtain

$$(d/dt)a_l^+(t)=i\omega_l a_l^+(t)+\sum_{\substack{m\\ m\neq l}}\tfrac{1}{4}J_{lm}(t)[b_{lm}^{+0}(t)-b_{ml}^{+0}(t)]. \tag{2.7a}$$

By the same method except that we multiply by $S_l^-S_m^0$, we get

$$\begin{aligned}(d/dt)b_{lm}^{+0}(t)&\\ =i\omega_l b_{lm}^{+0}(t)&+iJ_{lm}(t)[a_l^+(t)-a_m^+(t)]\\ &+i\sum_n\tfrac{1}{4}J_{ln}(t)[C_{lmn}^{+00}(t)-C_{nlm}^{+00}(t)]\\ &+i\sum_n\tfrac{1}{4}J_{mn}(t)[C_{lmn}^{+-+}(t)-C_{lnm}^{+-+}(t)].\end{aligned} \tag{2.7b}$$

It is clear that by continuing this process one would obtain a coupled system of equations that could in principle be solved for all the coefficients in the expansion (2.5). What will be done here is to assume the conditions of a dilute solution, i.e., that the spins interact only in pairs, at any given time. Under these conditions Eqs. (2.7) can be solved independently for each pair of interacting spins, by assuming initial conditions which apply at a time just before the interaction takes place. To illustrate, we suppose that the lth and mth molecules interact during an interval $t_1<t<t_2$. Equations (2.7) will then involve only the lth and mth molecules and will then read

$$\begin{aligned}(d/dt)a_l^+(t)&=i\omega_l a_l^+(t)+(i/4)J_{lm}(t)[b_{lm}^{+0}(t)-b_{ml}^{+0}(t)],\\ (d/dt)a_m^+(t)&=i\omega_m a_m^+(t)-(i/4)J_{lm}(t)[b_{lm}^{+0}(t)-b_{ml}^{+0}(t)],\\ (d/dt)b_{lm}^{+0}(t)&=i\omega_l b_{lm}^{+0}(t)+iJ_{lm}(t)[a_l^+(t)-a_m^+(t)],\\ (d/dt)b_{ml}^{+0}(t)&=i\omega_m b_{ml}^{+0}(t)-iJ_{lm}(t)[a_l^+(t)-a_m^+(t)].\end{aligned} \tag{2.7'}$$

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[2] D. Kivelson, J. Chem. Phys. **33**, 1094 (1960).

[3] R. Kubo, J. Phys. Soc. Japan **12**, 570 (1957).

[4] One can easily show that this is equivalent to the more usual definition $G(t)=(\gamma^2/2)\,\mathrm{Tr}\rho_0[S_i(t)S_i+S_iS_i(t)]$, where $i=x$ or y, by substituting for S^+ and S^- their definition in terms of S_x and S_y.

[5] U. Fano, Revs. Modern Phys. **29**, 74 (1957), Sec. 6.

By assuming some time dependence for the interaction and specifying initial conditions at $t=t_1$ we can solve this system of equations. We shall take J_{lm} to be constant inside the interval $t_1 \leq t \leq t_2$ and zero outside it. That is

$$\begin{aligned} J_{lm}(t) &= 0,\ t<t_1 \\ &= J,\ t_1<t<t_2 \\ &= 0,\ t_2<t. \end{aligned}$$

At $t=t_2$, Eqs. (2.7′) give for $a_l^+(t_2)$

$$\begin{aligned} a_l^+(t) = e^{i(\omega_l+\omega_m)\Delta/2}\{ & f(\beta,\phi_{lm})a_l^+(t_1)+g(\beta,\phi_{lm})a_m^+(t_1) \\ & +f'(\beta,\phi_{lm})b_{lm}^{+0}(t_1)+g'(\beta,\phi_{lm})b_{ml}^{+0}(t_1)\}, \end{aligned} \tag{2.8}$$

where

$$\begin{aligned} f(\beta,\phi_{lm}) &= \cos\beta[\cos(\beta^2+\phi_{lm}^2)^{\frac{1}{2}} \\ &\qquad +i\phi_{lm}(\beta^2+\phi_{lm}^2)^{-\frac{1}{2}}\sin(\beta^2+\phi_{lm}^2)^{\frac{1}{2}}], \\ g(\beta,\phi_{lm}) &= \beta(\beta^2+\phi_{lm}^2)^{-\frac{1}{2}}\sin\beta\,\sin(\beta^2+\phi_{lm}^2)^{\frac{1}{2}}, \\ f'(\beta,\phi_{lm}) &= (i/2)\sin\beta[\cos(\beta^2+\phi_{lm}^2)^{\frac{1}{2}} \\ &\qquad +i\phi_{lm}(\beta^2+\phi_{lm}^2)^{-\frac{1}{2}}\sin(\beta^2+\phi_{lm}^2)^{\frac{1}{2}}], \\ g'(\beta,\phi_{lm}) &= (-i/2)\beta(\beta^2+\phi_{lm}^2)^{-\frac{1}{2}}\cos\beta\,\sin(\beta^2+\phi_{lm}^2)^{\frac{1}{2}}, \\ \beta &= J\Delta/2, \\ \phi_{lm} &= (\omega_l-\omega_m)\Delta/2, \\ \Delta &= t_2-t_1. \end{aligned}$$

In Eq. (2.8) $b_{lm}^{+0}(t_1)$ and $b_{ml}^{+0}(t_1)$ take into account possible correlations of the lth and mth molecules prior to the interaction at t_1. Equation (2.7b) shows how these terms arise in lowest order from previous collisions between l and m and in next lowest order from a previous collision of both l and m with a third molecule n. We shall neglect these effects and take $b_{lm}^{+0}(t_1)$ and $b_{ml}^{+0}(t_1)$ to be zero.

We next wish to modify Eq. (2.8) by introducing the artificial quantities

$$a_l^+(\bar{t}_-)=\exp[i\omega_l(\bar{t}-t_1)]a_l^+(t_1), \tag{2.9a}$$

$$a_l^+(\bar{t}_+)=\exp[i\omega_l(t_2-\bar{t})]a_l^+(t_2), \tag{2.9b}$$

where $\bar{t}=(t_1+t_2)/2$. In terms of these quantities Eq. (2.8) is

$$a_l^+(\bar{t}_+)=f(\beta,\phi_{lm})e^{-i\phi_{lm}}a_l^+(\bar{t}_-)+g(\beta,\phi_{lm})a_m^+(\bar{t}_-). \tag{2.8′}$$

By means of these quantities we shall be able to express the change in $a_l^+(t)$ caused by the collision as a discontinuous change occurring at $t=\bar{t}$ instead of being spread over a short interval Δ, while not neglecting effects proportional to Δ. If Δ is small in comparison with all other periods of interest this should be an excellent approximation to the actual behavior of $a_l^+(t)$. At any rate an idealization of this kind will be necessary for any simple statistical treatment of the collisions, since we shall wish to speak of probabilities of collisions occurring during differential time intervals.

It will be convenient to redefine f and g as explicit functions of the interaction strength J and the duration of the interaction Δ, so we let

$$e^{-i\phi_{lm}}f(\beta,\phi_{lm})\equiv F(\omega_l-\omega_m;\,J,\Delta), \tag{2.10a}$$

$$g(\beta,\phi_{lm})\equiv G(\omega_l-\omega_m;\,J,\Delta). \tag{2.10b}$$

We also define the joint probability distribution function $\Phi(J,\Delta)$ to have the property that $\Phi(J,\Delta)dJd\Delta dt$ is the probability that any particular pair of molecules, say l and m, should have an interaction of strength J, duration Δ, and a midpoint falling inside the interval dt.

The apparatus necessary for deriving a kinetic equation for $a_l^+(t)$ is thus at hand. To this end, let us consider the change induced in $a_l^+(t)$ during a small interval δt. We have, using Eqs. (2.8′) and (2.10) for the effect of a collision during δt,

$$\begin{aligned} & a_l^+(t+\delta t) \\ &= \left\{1-(N-1)\left[\int\!\!\int\Phi(J,\Delta)dJd\Delta\right]\delta t\right\}(1+i\omega_l\delta t)a_l^+(t) \\ &\quad +\sum_{m\neq l}\left\{\int\!\!\int\Phi(J,\Delta)F(\omega_l-\omega_m;\,J,\Delta)dJd\Delta\right\}a_l^+(t)\delta t \\ &\quad +\sum_{m\neq l}\left\{\int\!\!\int\Phi(J,\Delta)G(\omega_l-\omega_m;\,J,\Delta)dJd\Delta\right\}a_m^+(t)\delta t \\ &\quad +O(\delta t^2); \end{aligned}$$

or, taking the limit as $\delta t \to 0$,

$$\begin{aligned} & \lim_{\delta t\to 0}\frac{a_l^+(t+\delta t)-a_l^+(t)}{\delta t}\left(\equiv\frac{d}{dt}a_l^+(t)\right) \\ &= i\omega_l a_l^+(t)-(N-1)\lambda a_l^+(t)+\lambda\sum_{m\neq l}F(\omega_l-\omega_m)a_l^+(t) \\ &\quad +\lambda\sum_{m\neq l}G(\omega_l-\omega_m)a_m^+(t), \end{aligned} \tag{2.11}$$

where

$$\lambda=\int\!\!\int\Phi(J,\Delta)dJd\Delta,$$

$$\lambda F(\omega_l-\omega_m)=\int\!\!\int\Phi(J,\Delta)F(\omega_l-\omega_m;\,J,\Delta)dJd\Delta,$$

$$\lambda G(\omega_l-\omega_m)=\int\!\!\int\Phi(J,\Delta)G(\omega_l-\omega_m;\,J,\Delta)dJd\Delta.$$

From Eqs. (2.8) and (2.10) it is easily established that

$$\begin{aligned} & \lambda F(0)+\lambda G(0) \\ &= \int\!\!\int\Phi(J,\Delta)[F(0;\,J,\Delta)+G(0;\,J,\Delta)]dJd\Delta=\lambda. \end{aligned}$$

Using this we will rewrite Eq. (2.11) letting the summations over the index m include a term for $m=l$. We then have

$$\frac{d}{dt}a_l^+(t)=i\omega_l a_l^+(t)-\lambda\Big[N-\sum_{m=1}^{N}F(\omega_l-\omega_m)\Big]a_l^+(t)$$
$$+\lambda\sum_{m=1}^{N}G(\omega_l-\omega_m)a_m^+(t).\quad(2.11')$$

We can greatly reduce the complexity of the system of coupled equations by grouping all molecules which have the same particular Larmor frequency, ω_α. In order to do this we define the partial sums,

$$\psi_\alpha=\textstyle\sum_l a_l^+(t)\delta(\omega_l,\omega_\alpha),$$

and by multiplying Eq. (2.11′) by $\delta(\omega_l,\omega_\alpha)$ and summing over l we get

$$(d/dt)\psi_\alpha(t)=i\omega_\alpha\psi_\alpha(t)-\lambda N[1-\textstyle\sum_\beta\rho_\beta F(\omega_\alpha-\omega_\beta)]\psi_\alpha(t)$$
$$+\lambda N\rho_\alpha\textstyle\sum_\beta G(\omega_\alpha-\omega_\beta)\psi_\beta(t),\quad(2.12)$$

where $\rho_\alpha=N_\alpha/N$ and where the N_α are the populations of the various hyperfine structure levels. We now have a system of coupled equations with the same multiplicity as the hyperfine structure of the molecule.

In terms of the real quantities

$$\delta\omega_\alpha\equiv\mathrm{Im}\{\lambda N\textstyle\sum_{\beta\neq\alpha}\rho_\beta F(\omega_\alpha-\omega_\beta)\},$$
$$Q_\alpha\equiv\lambda N(1-\rho_\alpha)-\mathrm{Re}\{\lambda N\textstyle\sum_{\beta\neq\alpha}\rho_\beta F(\omega_\alpha-\omega_\beta)\},$$
$$Q_{\alpha\beta}=\lambda N\rho_\alpha G(\omega_\alpha-\omega_\beta),$$

Eq. (2.12) can be written in the simple form

$$\frac{d}{dt}\psi_\alpha(t)=i(\omega_\alpha+\delta\omega_\alpha)\psi_\alpha(t)-Q_\alpha\psi_\alpha(t)+\textstyle\sum_{\beta\neq\alpha}Q_{\alpha\beta}\psi_\beta(t).\quad(2.13)$$

The correlation function is, by (2.6) and (2.2),

$$G(t)=(\gamma^2/4)\,\mathrm{Re}\textstyle\sum_\alpha\psi_\alpha(t).\quad(2.14)$$

The absorptive part of the linear susceptibility has, at high temperature, been shown by Kubo and Tomita[1] to be

$$\chi''(\omega)=\left(\frac{\omega}{kT}\right)\int_0^\infty G(t)\cos\omega t dt$$
$$=\left(\frac{\gamma^2\omega}{8kT}\right)\mathrm{Re}\left\{\textstyle\sum_\alpha\displaystyle\int_0^\infty\psi_\alpha(t)e^{-i\omega t}dt\right\}$$
$$+\left(\frac{\gamma^2\omega}{8kT}\right)\mathrm{Re}\left\{\textstyle\sum_\alpha\displaystyle\int_0^\infty\psi_\alpha(t)e^{i\omega_\alpha t}dt\right\}.\quad(2.15)$$

The second term in Eq. (2.15) will always be small and slowly varying in the resonance region and will be dropped. Thus we write

$$\chi''(\omega)=(\gamma^2\omega/8kT)\,\mathrm{Re}\{\textstyle\sum_\alpha\bar{\psi}_\alpha(i\omega)\},\quad(2.16)$$

where

$$\bar{\psi}_\alpha(S)=\int_0^\infty\psi_\alpha(t)e^{-St}dt.$$

From (2.13) we find that $\bar{\psi}_\alpha(S)$ is a solution of the system of linear equations

$$\bar{\psi}_\alpha(S)=\frac{N\rho_\alpha+\sum_{\beta\neq\alpha}Q_{\alpha\beta}\psi_\beta(S)}{S+Q_\alpha-i(\omega_\alpha+\delta\omega_\alpha)}.\quad(2.17)$$

Thus, assuming knowledge of the parameters Q_α, $Q_{\alpha\beta}$, and $\delta\omega_\alpha$, one may compute the spectral absorption in a straightforward manner. In order to get an indication of how these parameters enter into the results we shall solve a simple system consisting of just two hyperfine levels with equal populations. In this case one can easily verify that

$$Q_1=Q_2\equiv Q,$$
$$Q_{12}=Q_{21}\equiv Q',$$
$$\delta\omega_1=\delta\omega_2\equiv\delta\omega.$$

Putting

$$\omega_1=\omega_0+\delta\Omega-\delta\omega,$$
$$\omega_2=\omega_0-\delta\Omega+\delta\omega,$$

we find that

$$\bar{\psi}_1(\omega)+\bar{\psi}_2(\omega)=\frac{N[i(\omega-\omega_0)+Q+Q']}{[i(\omega-\omega_0)+Q+i(\delta\Omega^2-Q'^2)^{\frac{1}{2}}][i(\omega-\omega_0)+Q-i(\delta\Omega^2-Q'^2)^{\frac{1}{2}}]},\quad(2.18)$$

$$\psi_1(t)+\psi_2(t)=(N/2)\{[1-iQ'(\delta\Omega^2-Q'^2)^{-\frac{1}{2}}]\exp[i\omega_0-Q+i(\delta\Omega^2-Q'^2)^{\frac{1}{2}}]t$$
$$+[1+iQ'(\delta\Omega^2-Q'^2)^{-\frac{1}{2}}]\exp[i\omega_0-Q-i(\delta\Omega^2-Q'^2)^{\frac{1}{2}}]t\}.\quad(2.19)$$

For positive values of $(\delta\Omega^2-Q'^2)$, Eq. (2.19) represents the sum of two exponential decays, each with a decay constant Q and of frequencies $\omega_0+(\delta\Omega^2-Q'^2)^{\frac{1}{2}}$ and $\omega_0-(\delta\Omega^2-Q'^2)^{\frac{1}{2}}$, respectively. For $(\delta\Omega^2-Q'^2)$ negative the decay constants are $Q-(Q'^2-\delta\Omega^2)^{\frac{1}{2}}$ and $Q+(Q'^2-\delta\Omega^2)^{\frac{1}{2}}$ and the frequency ω_0. It is quite similar to an expression derived by Anderson[6] and others to describe an oscillator which switches randomly between two distinct frequencies. In fact if we take $Q=Q'$ the expressions are identical in form. We now proceed to specify the conditions under which it is permissible to take $Q=Q'$.

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[6] P. W. Anderson, J. Phys. Soc. Japan **9**, 316 (1954).

Let us suppose that the magnitude of the exchange interaction J is the same for all collisions and further that

$$J \gg (\omega_\alpha - \omega_\beta)$$

for all values of the hyperfine structure frequencies ω_α and ω_β. Next we rewrite Eq. (2.8) for $f(\beta,\phi_{lm})$ and $g(\beta,\phi_{lm})$ correct to first order in ϕ_{lm}/β as

$$\begin{aligned} f(\beta,\phi_{lm}) &= \cos^2\beta + i(\phi_{lm}/\beta)\sin\beta\cos\beta, \\ g(\beta,\phi_{lm}) &= \sin\beta. \end{aligned} \tag{2.8$'$}$$

We also will assume that the distribution function for Δ is appreciable only for times Δ such that

$$(\omega_l - \omega_m)\Delta/2 (\equiv \phi_{lm}) \ll 1.$$

Working then to first order in ϕ_{lm}, we find that the functions $F(\omega_l-\omega_m)$ and $G(\omega_l-\omega_m)$ used in Eq. (2.11) are

$$\begin{aligned} F(\omega_l - \omega_m) &= \int \Phi(\Delta)\cos^2(J\Delta/2)d\Delta + (i/2)(\omega_l - \omega_m) \\ &\times \int \Phi(\Delta)\Delta\left[\frac{\sin(J\Delta/2)}{J\Delta/2} - \cos(J\Delta/2)\right]\cos(J\Delta/2)d\Delta, \end{aligned}$$

$$G(\omega_l - \omega_m) = \int \Phi(\Delta)\sin^2(J\Delta/2)d\Delta,$$

where we have also put

$$\Phi(J',\Delta) = \lambda\delta(J'-J)\Phi(\Delta).$$

It is then clear that Q_α and $Q_{\alpha\beta}$ are related by

$$\begin{aligned} Q_\alpha &= (1-\rho_\alpha)Q_{\alpha\beta}/\rho_\alpha \\ &= (1-\rho_\alpha)q, \end{aligned} \tag{2.20a}$$

where

$$q = Q_{\alpha\beta}/\rho_\alpha = \lambda N \int \Phi(\Delta)\sin^2(J\Delta/2)d\Delta. \tag{2.20b}$$

Also $\delta\omega_\alpha$ may be written

$$\begin{aligned} \delta\omega_\alpha &= \lambda N \textstyle\sum_\beta (\omega_\alpha - \omega_\beta)\rho_\beta\tau_c \\ &= \lambda N(\omega_\alpha - \langle\omega\rangle)\tau_c, \end{aligned} \tag{2.21}$$

where

$$\langle\omega\rangle = \textstyle\sum_\beta \rho_\beta\omega_\beta$$

and

$$\tau_c = \frac{1}{2}\int \Phi(\Delta)\Delta\left[\frac{\sin(J\Delta/2)}{J\Delta/2} - \cos(J\Delta/2)\right]\cos(J\Delta/2)d\Delta.$$

Thus $\delta\omega_\alpha$ is proportional to the separation of ω_α from the "center" of the pattern and to a quantity $\lambda N\tau_c$ which is of the order of magnitude of the fraction of time that each molecule spends in collision with its neighbors. We therefore expect it to cause a very small proportional "stretching" of the spectrum about the mean. From now on we will absorb it into ω_α by writing

$$\Omega_\alpha \equiv \omega_\alpha + \delta\omega_\alpha.$$

We can now write Eq. (2.13) as

$$(d/dt)\psi_\alpha(t) = i\Omega_\alpha\psi_\alpha(t) - q\psi_\alpha(t) + q\rho_\alpha \textstyle\sum_\beta \psi_\beta(t); \tag{2.13$'$}$$

or, integrating and summing over α,

$$\begin{aligned} \psi(t)[\equiv \textstyle\sum_\alpha \psi_\alpha(t)] &= N \textstyle\sum_\alpha \rho_\alpha e^{i\Omega_\alpha t - qt} \\ &+ q\int_0^t \textstyle\sum_\alpha \rho_\alpha e^{(i\Omega_\alpha - q)(t-\tau)}\psi(\tau)d\tau. \end{aligned} \tag{2.22}$$

Thus we have succeeded in obtaining an equation which depends upon just one parameter, q. For our two-frequency example, Eq. (2.19) becomes

$$\begin{aligned} \psi(t) = (N/2)\{&[1 - i(q/2)(\delta\Omega^2 - q^2/4)^{-\frac{1}{2}}] \\ &\times \exp[i\omega_0 - q/2 + i(\delta\Omega^2 - q^2/4)^{\frac{1}{2}}]t \\ &+ [1 + i(q/2)(\delta\Omega^2 - q^2/4)^{-\frac{1}{2}}] \\ &\times \exp[i\omega_0 - q/2 - i(\delta\Omega^2 - q^2/4)^{\frac{1}{2}}]t\}. \end{aligned} \tag{2.19$'$}$$

This is identical with the result of Anderson with $q/2$ playing the role of the frequency-switching rate. The spectral intensity corresponding to Eq. (2.19) is plotted in Anderson's paper[6] and shows that the two sharp lines at $\omega_0 \pm \delta\Omega$ merge together as q is increased, until for large values of q there is just one sharp line at ω_0. We now proceed to show that this behavior is characteristic of the general case by examining our results in the limits of large q and small q.

Equation (2.22) can be solved by taking its Laplace transform, which gives

$$\bar{\psi}(S) = \frac{N\sum_\alpha \rho_\alpha/(S - i\Omega_\alpha + q)}{1 - q\sum_\alpha \rho_\alpha/(S - i\Omega_\alpha + q)}. \tag{2.23}$$

For large q we expand numerator and denominator

$$\bar{\psi}(S) = (N/q)\frac{\sum_\alpha \rho_\alpha\{1 - (S - i\Omega_\alpha)/q + (S - i\Omega_\alpha)^2/q^2 + \cdots\}}{1 - \sum_a \rho_a\{1 - (S - i\Omega_a)/q + (S - i\Omega_a)^2/q^2 + \cdots\}}.$$

The expansions are convergent for $|S - i\Omega_\alpha| < q$. Working consistently to order $(S - i\Omega_\alpha)/q$ and using

$$\textstyle\sum_\alpha \rho_\alpha = 1, \quad \sum_\alpha \rho_\alpha\Omega_\alpha = \langle\Omega\rangle, \quad \sum_\alpha \rho_\alpha(\Omega_\alpha - \langle\Omega\rangle)^2 = \sigma^2,$$

we obtain after considerable manipulation

$$\bar{\psi}(S) = \frac{N}{S - i\langle\Omega\rangle + \sigma^2/q}. \tag{2.24}$$

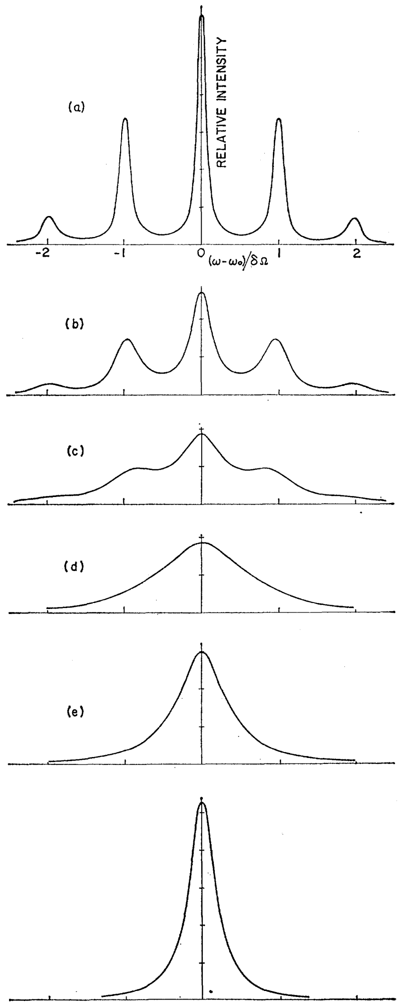

FIG. 1. Absorption vs frequency for a system of five lines whose intensity ratios are 1:4:6:4:1. (a) $q/\delta\Omega=0.1$; (b) $q/\delta\Omega=0.25$; (c) $q/\delta\Omega=0.5$; (d) $q/\delta\Omega=1$; (e) $q/\delta\Omega=2.5$; (f) $q/\delta\Omega=5$. Note that in (a) and (b) the less intense lines are the broadest, as was predicted by Eq. (2.28).

The absorption then is proportional to

$$\chi''(\omega)\sim\frac{N\sigma^2/q}{\sigma^4/q^2+(\omega-\langle\Omega\rangle)^2}. \qquad (2.25)$$

Thus we have shown that, for large q, the absorption narrows into a single Lorentzian line centered at the mean of the unperturbed spectrum and whose width is narrowed by a factor σ/q times the unperturbed second moment, σ, about the mean. This result is, of course, to be expected in general for motionally narrowed systems where the correlation time for the perturbation is short compared with the periods associated with the perturbation.

We next investigate the line shape for small q. Writing Eq. (2.23) in the form

$$\bar{\psi}(S)=[\textstyle\sum_\alpha \rho_\alpha/(S-i\Omega_\alpha+q)][1+q\bar{\psi}(S)],$$

and solving by successive substitution, we get

$$\bar{\psi}^0(S)=\textstyle\sum_\alpha \rho_\alpha/(S-i\Omega_\alpha+q)$$

and

$$\begin{aligned}\bar{\psi}^{(1)}(S)=&\textstyle\sum_\alpha \{[1+q\rho_\alpha/(S-i\Omega_\alpha+q)]\rho_\alpha/(S-i\Omega_\alpha+q)\}\\ &+2q\textstyle\sum_\alpha \{\rho_\alpha/(S-i\Omega_\alpha+q)\}\\ &\times\sum_{\beta\neq\alpha} \{\rho_\beta/i(\omega_\alpha-\omega_\beta)\}. \qquad (2.26)\end{aligned}$$

The second term in Eq. (2.26) leads to an antisymmetric contribution of order q to each hyperfine component and will be of no further interest to us. The first term can be written to order q as

$$\bar{\psi}^{(1)}(S)=N\textstyle\sum_\alpha \rho_\alpha/[S-i\Omega_\alpha+q(1-\rho_\alpha)]. \qquad (2.27)$$

The absorption is then

$$\begin{aligned}\chi''(\omega)\sim N\textstyle\sum_\alpha\{&\rho_\alpha q(1-\rho_\alpha)/\\ &[q^2(1-\rho_\alpha)^2+(\omega-\Omega_\alpha)^2]\}, \qquad (2.28)\end{aligned}$$

i.e., a sum of Lorentzian lines whose intensities are their statistical weights ρ_α, and whose widths are $q(1-\rho_\alpha)$. This is just as we should expect since the width of each hyperfine component is caused by collisions of molecules of that species with molecules having different Larmor frequencies (an exchange interaction between molecules of the same Larmor frequency commutes with their magnetic moment), and the fraction of the molecules of a species other than α is just $(1-\rho_\alpha)$.

III. COMPARISON WITH EXPERIMENT

The narrowing of the entire resonance pattern in the limit of rapid motion has been observed by Pake and Tuttle[7] for a system of diphenyl picryl hydrazyl in toluene, and by Powles and Mosley[8] for the biphenyl negative ion in tetrahydrofuran and also in diethylene glycol dimethyl ether. In order to compare our results with the brief analysis given by Pake and Tuttle, let us again consider the quantity q defined in Eq. (2.20b) as

$$q=\lambda N\int\Phi(\Delta)\sin^2(J\Delta/2)d\Delta. \qquad (2.20\text{b})$$

Now λN is the collision rate for a single molecule and, following Pake and Tuttle, we express it in terms of the diffusion coefficient D as[9]

$$\lambda N=4\pi D a_e N_v, \qquad (3.1)$$

where a_e is some effective range of the exchange interaction and N_v is the volume concentration of the free radical. Taking the diffusion coefficient as

$$D=kT/6\pi a_s\eta, \qquad (3.2)$$

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[7] G. E. Pake and T. R. Tuttle, Phys. Rev. Letters **3**, 423 (1959).

[8] J. G. Powles and M. H. Mosley, Proc. Phys. Soc. (London) **78**, 370 (1961).

[9] S. Chandrasekhar, Revs. Modern Phys. **15**, 1 (1943), Chap. III.

where a_s is the equivalent Stokes' law radius of the molecule and η is the viscosity, we can write q as

$$q=\left(\frac{N_v kT}{\eta}\right)\left[\frac{2}{3}\left(\frac{a_e}{a_s}\right)\int \Phi(\Delta)\sin^2(J\Delta/2)d\Delta\right]. \tag{3.3}$$

The quantity in square brackets is dimensionless and is of the order of magnitude unity. Pake and Tuttle estimated q from the measured width of the narrowed line and using the known values of N_v, T, and η, obtained an estimate for the bracket of about 10^{-1}. By similar methods Powles and Mosley found values of the bracket in the neighborhood of unity and decreasing with increasing T and decreasing η. In order to obtain a rough theoretical estimate of the size of the bracket, let us put (somewhat arbitrarily)

$$\Phi(\Delta)=(1/\tau_e)e^{-\Delta/\tau_e}, \tag{3.4}$$

where τ_e is some average correlation time for the exchange interaction during a collision. We will then have

$$\begin{aligned} q&=\left(\frac{N_v kT}{\eta}\right)\left[\frac{2}{3}\left(\frac{a_e}{a_s}\right)\int_0^\infty e^{-x}\sin^2(J\tau_e x/2)dx\right. \\ &=\left(\frac{N_v kT}{\eta}\right)\left[\frac{1}{3}\left(\frac{a_e}{a_s}\right)\left(\frac{J^2\tau_e^2}{1+J^2\tau_e^2}\right)\right]. \end{aligned} \tag{3.5}$$

Here the bracket decreases monotonically with decreasing τ_e, and has a maximum value of $\frac{1}{3}a_e/a_s$. If we make use of

$$\tau_e=6\pi\eta a_e^3/kT$$

for an estimate of τ_e, we find that the bracket indeed decreases with increasing T and decreasing η.

Finally, we wish to discuss briefly the behavior for small q predicted by Eq. (2.28). Schreurs, Blomgren, and Fraenkel[10] have studied the saturation of the resonance of *p*-benzohydroquinone ion and have found that the various hyperfine components, which arise from couplings with four equivalent protons, saturate at different rates. From this they infer that the hyperfine components must have different unsaturated linewidths with the widths increasing symmetrically as one moves outward from the central component. In the apparent absence of any intermolecular relaxation mechanism to account for this effect, they ascribe it to an intramolecular one, namely, anisotropic dipole-dipole coupling between the unpaired electron and the magnetic nuclei. Equation (2.8) shows, however, that the intermolecular exchange interaction does provide, in general, different linewidths for the various hyperfine components, and that for a symmetrical pattern the variation of the linewidths is symmetrical. In fact, for hyperfine coupling with four equivalent protons the statistical weights of the hyperfine components have the ratios 1:4:6:4:1. Equation (2.8) then gives their widths as $15q/16$: $12q/16$:$10q/16$:$12q/16$:$15q/16$. In Fig. 1 we have plotted the spectral intensity for this case, using Eq. (2.23) to calculate the intensity, for several values of q. Of course, for well-resolved hyperfine structure other sources of line broadening may be present in equal or greater amounts than this incipient exchange, so that in practice we might not expect such pronounced variations in the linewidths as the values above would indicate. Nevertheless, if care is taken to eliminate extraneous broadening effects, especially those effects caused by dissolved oxygen, the variations in linewidths should be observable under favorable conditions of concentration, viscosity, and temperature.

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[10] J. W. H. Schreurs, G. E. Blomgren, and G. K. Fraenkel, J. Chem. Phys. **32**, 1861 (1960); J. W. H. Schreurs and G. K. Fraenkel, *ibid.* **34**, 756 (1961). These authors have also examined linewidths of the peroxylamine disulfonate ion, which has three hyperfine components of equal intensities, and have found no variations in the linewidths of the three components. This is in agreement with our theory, which predicts linewidth variations only among hyperfine components of different intensities.