Theory of Saturation and Double Resonance Effects in Electron Spin

Resonance Spectra. II. Exchange *vs.* Dipolar Mechanisms[1]

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The theory of saturation and line widths in the electron spin resonance spectra of dilute solutions of free radicals has been extended to include incipient effects of chemical exchange and spin–spin or Heisenberg exchange processes as well as the effects of intramolecular terms such as the g-tensor, spin–rotational, and electron–nuclear dipolar (END) interactions. The development is based on an assumption of the statistical independence of the exchange and molecular rotational processes and involves combining the Bloch–Redfield density matrix treatment with the Kaplan–Alexander exchange formalism. It is shown that exchange effects act to average out the differences in widths of components of a composite hyperfine line, so that when the exchange frequency is significantly greater than any such differences, the composite line may be treated as a simple Lorentzian line with an averaged width. In such cases, the esr saturation behavior is again describable in terms of a simple Lorentzian and one may average over the degenerate states. This result is in contrast to the case when exchange effects are weak, while the END effects are important. In an electron–nuclear double resonance (endor) experiment, simple averaging over degenerate states and transitions is no longer adequate because of the specific selection rules of the radiofrequency-induced nmr transitions, and the appropriate modifications are discussed. It is found that a chemical exchange mechanism, in which the diamagnetic species are polarized by the radicals under esr saturation, has effects identical with Heisenberg exchange on any spectra with well-resolved hyperfine structure. They both affect esr saturation parameters as though they yield nuclear-spin transitions between all pairs of states for which $\Delta M_S = 0$. However, they do *not* lead to endor enhancements, but rather are found to diminish the enhancements resulting from other processes. If the diamagnetic species remain unpolarized by the radicals under esr saturation, a situation that does not appear likely, then the exchange would lead to endor enhancements, which, however, could in many cases be distinguished from those induced by an END mechanism. The endor experiments of Hyde are discussed and are found to agree well with the predictions that the END mechanism is the dominant nuclear spin flip process and that exchange effects act to reduce enhancements. Temperature-dependent effects on enhancements are also considered.

I. Introduction

In a previous paper,[3] a detailed theoretical analysis was presented of the saturation behavior of hyperfine lines in well-resolved electron spin resonance spectra of free radicals in liquids. The analysis was based on the general Boltzmann equation for the spin-density matrix given by Bloch[4] and modified by Redfield[5] and Abragam.[6] Since this theory is essentially an "independent molecule" theory, intermolecular effects such as chemical exchange[7] (CE), where an unpaired

electron exchanges from free radical to (electronically) diamagnetic parent molecule, and also spin–spin or Heisenberg exchange (HE)[8–10] between pairs of free radicals were not explicitly included. Such intramolecular spin effects as rotational averaging of the g tensor and the electron–nuclear dipolar (END) interactions were, however, considered in detail,[3] and effects such as spin–rotational interactions[11,12] may also be readily included.

The emphasis in I was on situations in which nuclear spin transitions occur at rates that are significant compared to electron spin transitions, so that the saturation effects of the hyperfine lines were interdependent. The rather specific selection rules of the END mechanism leads to predictions that are different from an earlier theory of saturation given by Stephen and Fraenkel,[13,14] who assumed that a multiple (or degenerate) hyperfine line behaves as a simple saturated Lorentzian, an assumption which is without fundamental justification.[15] Thus, for a set of completely equivalent nuclei, only states of the same total nuclear spin quantum number J can interact *via* the END mechanism, so that in general a multiple line is a superposition of components with different J values each of which saturates differently. Such considerations lead immediately to the conclusion that saturation can lead to deviations from the theoretically predicted intensity ratios of unsaturated hyperfine lines, a phenomenon that was investigated experimentally by Schreurs and Fraenkel[16] and which the Stephen–Fraenkel theory attempted to explain, but with an assumption of relatively weak nuclear spin transitions.

It was also shown in I that steady-state electron–nuclear double resonance experiments such as those of Hyde and Maki[17] are predicted to occur if the lattice-induced nuclear spin transitions are comparable to the electron spin transitions. Thus in this new technique, closely related to saturation effects, the importance of nuclear spin transitions in the experimental observations is greatly magnified. One can then ask the question about the importance of mechanisms other than the END one in inducing nuclear spin flips. It was suggested in I that the CE and HE processes might play such a role, and one of the purposes of the present work is to elucidate their saturation and endor effects in detail. While their effects on unsaturated line widths have received considerable theoretical and experimental attention,[7–10] little has been said about their saturation effects. We note, first of all, that exchange processes will not depend directly on the particular nuclear-spin configurations of the exchanging molecules, so that their "selection rules" will be entirely different from those of the END

mechanism. One may then expect that the exchange processes could be distinguishable by means of their detailed effects on esr saturation and endor enhancement. Such a possibility is suggested by more recent experiments of Hyde,[18] where unusual endor effects were observed. We attempt, here, to analyze some of these effects in terms of the relative contribution of the END and exchange mechanisms.

The general method adopted in this work is to augment the Bloch formulation by introducing a spin-exchange expression that was developed by Kaplan[19] and Alexander.[20]

II. Exchange Processes and Relaxation Theory

We describe a spin system in the absence of exchange by a spin Hamiltonian of the form

$$\hbar\mathfrak{H}(t) = \hbar\mathfrak{H}_0 + \hbar\mathfrak{H}_1(t) + \hbar\epsilon(t) \qquad (2.1)$$

where $\mathfrak{H}_0$ is the time-independent Hamiltonian given in the high-field approximation by

$$\hbar\mathfrak{H}_0 = \bar{g}_s\beta_e B_0 S_z - \hbar\sum_i \gamma_i I_{zi} B_0 - \hbar\gamma_e \sum_i \bar{a}_i S_z I_{zi} \qquad (2.2a)$$

where the three terms on the right are, respectively, the electron spin and nuclear spin Zeeman terms and the isotropic hyperfine interaction, and the notation is the same as in I. $\mathfrak{H}_1(t)$ includes the perturbations, which are randomly modulated by the lattice, leading to relaxation effects, while $\epsilon(t)$ gives the interaction of spins with the radiation field. Under the assump-

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(14) M. J. Stephen, *ibid.*, **34**, 484 (1961).

(15) J. H. Freed and G. K. Fraenkel, *ibid.*, **39**, 326 (1963).

(16) (a) J. W. H. Schreurs and G. K. Fraenkel, *ibid.*, **34**, 756 (1961); (b) J. W. H. Schreurs, G. E. Blomgren, and G. K. Fraenkel, *ibid.*, **32**, 1861 (1960).

(17) J. S. Hyde and A. H. Maki, *ibid.*, **40**, 3117 (1964).

(18) J. S. Hyde, *ibid.*, **43**, 1806 (1965).

(19) (a) J. I. Kaplan, *ibid.*, **28**, 278 (1958); (b) J. I. Kaplan, *ibid.*, **29**, 462 (1958).

(20) (a) S. Alexander, *ibid.*, **37**, 966 (1962); (b) S. Alexander, *ibid.*, **37**, 974 (1962).

tion that the hyperfine lines remain well separated even under saturation, one obtains the equation of motion for the spin-density matrix σ

$$\dot{\sigma} = -i[\mathfrak{H}_0 + \epsilon(t), \sigma] - \Gamma(\sigma - \sigma_0) \qquad (2.3)$$

where $\Gamma(\sigma - \sigma_0)$ is a relaxation matrix containing the effects of $\mathfrak{H}_1(t)$ and is discussed in detail in I. The validity of eq 2.3 for well-separated hyperfine lines requires that

$$\left|\gamma_e B_0\right|, \left|\gamma_i B_0\right|, \left|\gamma_e \bar{a}_i\right|, \tau_c^{-1} \gg \epsilon(t), \left|\Gamma(\sigma - \sigma_0)\right| \quad (2.4)$$

as well as a high-temperature approximation

$$\sigma_0 \equiv \frac{\exp(-\hbar\mathfrak{H}_0/kT)}{Tr[\exp(-\hbar\mathfrak{H}_0/kT)]} \cong N^{-1}(1 - q\mathfrak{H}_0) \quad (2.5)$$

where σ_0 is the equilibrium density matrix, N is equal to the number of eigenstates of $\mathfrak{H}_0$ and $q = \hbar/kT$. In eq 2.4, τ_c is a correlation time for the random motions modulating $\mathfrak{H}_1(t)$.

In the presence of exchange effects, we augment eq 2.3 following Kaplan[19] and Alexander[20] to obtain

$$\dot{\sigma} = -i[\mathfrak{H}_0 + \epsilon(t), \sigma] -$$
$$\Gamma(\sigma - \sigma_0) + \Phi(\sigma - \sigma_0) \quad (2.6)$$

where $\Phi(\sigma - \sigma_0)$ includes the effects of exchange. That is, we assume that the exchange effects and the $\mathfrak{H}_1(t)$ effects are statistically independent. This is reasonable provided that: (1) the duration of "collision" or rather of contact between the exchanging pair, τ_d obeys

$$\tau_d \ll \tau_{ex} \qquad (2.7a)$$

where τ_{ex} is an effective exchange time, so that the interaction pair is too short-lived to introduce observable effects other than the exchange; and also (2)

$$\tau_c \ll \tau_{ex} \qquad (2.7b)$$

so that rotational (and translational) relaxation occurs in times short compared to intervals between "exchange collisions." Finally, in order to preserve the resolution of the hyperfine lines, we must assume that

$$\gamma_e \bar{a}_i \gg \tau_{ex}^{-1} \qquad (2.7c)$$

These conditions together with eq 2.4 yield as the general conditions for validity of eq 2.6

$$\left|\gamma_e B_0\right|, \left|\gamma_i B_0\right|, \left|\gamma_e \bar{a}_i\right|, \tau_c^{-1}, \tau_d^{-1} \gg$$
$$\epsilon(t), \Gamma(\sigma - \sigma_0), \tau_{ex}^{-1} \quad (2.4a)$$

Now, although in dilute solutions the exchange process is bimolecular, it is possible to linearize the term $\Phi(\sigma - \sigma_0)$ by recognizing that a high-temperature

approximation equivalent to eq 2.5 will still be appropriate for a nonequilibrium value of σ. That is, we let

$$\chi \equiv \sigma - \sigma_0 \cong N^{-1}(1 - \rho) \qquad (2.8)$$

where ρ is of the order $q\mathfrak{H}_0$ or less. Here χ is the departure of σ from its thermal equilibrium value. Now the evaluation of $\Phi(\chi)$ involves the construction of the appropriate exchange operator P according to the prescription given by Alexander.[20] The exchange operator essentially permutes nonequivalent spins between the two exchanging molecules, so that a "strong exchange" approximation is inherent. For both CE and HE processes it is seen that the initial and final states differ at most by magnetic energies of the order of hyperfine frequencies (that is, the exchange commutes with the Zeeman terms in eq 2.2 but not with the Fermi term) which should be small compared to lattice energy available via the rapidly changing exchange interactions between collision pairs.[21] A further property of P is that it is invariant to the choice of spin representation of the exchanging parts of the molecules as well as of the nonexchanging parts, but it requires a representation utilizing a product of the exchanging part with the nonexchanging part. Thus the basis functions utilized in I are appropriate. They may be abbreviated by

$$\left|\gamma_j{}^m\right\rangle \equiv \left|m; \{J_{r_u}{}^{(k)}M_{r_u}\}\right\rangle$$
$$\equiv \left|m_s = \pm^1/_2\right\rangle \prod_{r_u} \left|J_{r_u}{}^{(k)}M_{r_u}\right\rangle \quad (2.9)$$

that is, the product of an electron spin wave function $\left|m_s\right\rangle$ with the products of nuclear spin functions $\left|J_{r_u}{}^{(k)}M_{r_u}\right\rangle$, where $\left|J_{r_u}{}^{(k)}M_{r_u}\right\rangle$ is the eigenfunction of $J_{r_u}{}^2$ with eigenvalues $J_{r_u}(J_{r_u} + 1)$ and M_{r_u}, respectively, and k orders the different degenerate states belonging to the same value of J_{r_u} and M_{r_u}. The subscript r_u refers to the uth completely equivalent subgroup of nuclei of the rth group of equivalent nuclei, so that

$$J_{r_u} = \sum_{i \text{ in } r_u} I_i \qquad (2.10)$$

(A) Heisenberg Exchange. It is assumed that when two paramagnetic species collide, they exchange their

(21) We note that there are other intermolecular magnetic interactions besides the exchange processes, such as the dipolar interaction between electron spins on different paramagnetic molecules. This mechanism can lead to exchange-type effects as well as electron spin flip relaxation processes. It is, of course, dependent on radical concentration, but it differs from HE in that it is weaker but more long-range (with a $1/r^3$ dependence) and must be treated in a somewhat different fashion theoretically (*cf.* ref 6, Chapter VIII for the related nmr case). Order-of-magnitude calculations (J. H. Freed, unpublished work) indicate that a "strong HE mechanism" should dominate over this intermolecular dipolar mechanism for normal liquids.

electron spin states with frequency $\omega_H = \tau_H^{-1}$. Then, utilizing eq 21 of Alexander,[20b] we obtain[22,23]

$$\langle \alpha^m | \Phi_H(\chi) | \alpha'^{m'} \rangle = \omega_H \left[\sum_{m''} \frac{\langle \alpha^{m''} | \chi | \alpha'^{m''} \rangle}{2} \delta_{m,m'} + \right.$$

$$\left. \sum_\gamma \frac{\langle \gamma^m | \chi | \gamma^{m'} \rangle}{N/2} \delta_{\alpha,\alpha'} - \langle \alpha^m | \chi | \alpha'^{m'} \rangle \right] \quad (2.11)$$

These terms supply further relaxation effects to be added to those contained in $\Gamma(\chi)$. We note that those terms off-diagonal in χ lead to line broadening while the diagonal ones give spin transitions.

(i) *Off-Diagonal Elements of* χ. There are three types of off-diagonal matrix elements. (a) Let $\alpha = \alpha'$ but $m \neq m'$

$$\langle \alpha^\pm | \Phi_H(\chi) | \alpha^\mp \rangle =$$

$$\omega_H \left[\sum_{\gamma \neq \alpha} \left(\frac{2}{N} \chi_{\gamma^\pm,\gamma^\mp} \right) - \frac{N-2}{N} \chi_{\alpha^\pm,\alpha^\mp} \right] \quad (2.12)$$

These terms are important in determining the line widths of esr spectra. The second term represents a simple line broadening, which is weighted to account for the fact that not all electron exchanges lead to changed molecular states.[10] The first term leads to a coupling of *all* the different esr transitions, *via* the exchange. As a result of eq 2.7c and 2.3, it follows that those $\chi_{\gamma^\pm,\gamma^\mp}$ may be neglected which do not contribute to the same (degenerate) transition that $\chi_{\alpha^\pm,\alpha^\mp} \equiv \chi_{\lambda_j}$ does. Thus eq 2.12 becomes

$$[\Phi_H(\chi)]_{\lambda_j} = \omega_H \left[\sum_{k \neq j} \frac{2}{N} \chi_{\lambda_k} - \frac{N-2}{N} \chi_{\lambda_j} \right] \quad (2.13)$$

for the λth degenerate esr transition.

(b) Let $m = m'$ but $\alpha \neq \alpha'$. This gives

$$[\Phi_H(\chi)]_{\eta_j^\pm} = \frac{\omega_H}{2} (\chi_{\eta_j^\mp} - \chi_{\eta_j^\pm}) \quad (2.14)$$

where $\eta_{j\pm}$ refers to the nuclear spin transition $| \alpha^\pm \rangle \rightarrow | \alpha'^\pm \rangle$. Again eq 2.7c and 2.3 lead to the neglect of the first term on the rhs of eq 2.14. The remaining term leads to a broadening of the nmr lines.

(c) Let $m \neq m'$ and $\alpha \neq \alpha'$. This gives

$$\langle \alpha^m | \Phi_H(\chi) | \alpha'^{m'} \rangle = -\omega_H \chi_{\alpha^m,\alpha'^{m'}} \quad (2.15)$$

or a simple line broadening. These terms will come into play when multiple quantum transitions are excited by endor.

(ii) *Diagonal Elements of* χ. For the diagonal elements we obtain from eq 2.11

$$[\Phi_H(\chi)]_{\alpha^\pm} = \omega_H \left[\frac{1}{2} \chi_{\alpha^\mp} + \frac{2}{N} \sum_{\gamma \neq \alpha} \chi_{\gamma^\pm} - \left(\frac{N-4}{2N} \right) \chi_{\alpha^\pm} \right]$$

$$(2.16)$$

It is seen from eq 2.16 that the linearized transition probabilities (actually derived from second-order rate equations), appear to involve transitions to state $\alpha^\pm$ from all other states where either an electron spin is flipped or the nuclear spin state changes. If we define

$$\chi_\pm = \frac{2}{N} \sum_\gamma \chi_{\gamma^\pm} \quad (2.17)$$

then eq 2.16 may be rewritten as

$$[\Phi(\chi)]_{\alpha^\pm} = \omega_H \left[\frac{1}{2} (\chi_{\alpha^\mp} - \chi_{\alpha^\pm}) + \chi_\pm \right] \quad (2.18)$$

The steady-state solution obtained by equating eq 2.18 to zero then gives

$$\chi_{\alpha^\pm} - \chi_{\alpha^\mp} = 2\chi_\pm \quad (2.19a)$$

which (upon neglect of hyperfine terms in $q\mathfrak{H}_0$) yields

$$\sigma_{\alpha^\pm} - \sigma_{\alpha^\mp} = 2\sigma_\pm \quad (2.19b)$$

with

$$\sigma_\pm = \frac{2}{N} \sum_\gamma (\chi_{\gamma^\pm} + \sigma_{0\gamma^\pm})$$

Now since α is arbitrary in eq 2.19, it follows that the effect of the HE mechanism is to cause the difference in population for all pairs of levels differing only in m_s to be equal. It may be found from the unlinearized rate equation that at steady state the *ratios* of the populations are equal, and when linearized, this yields the result above.

B. *Chemical Exchange.* We must now define sepa-

(22) Alexander actually defined a ρ such that linearizing σ gives $\sigma \cong N^{-1}(1 + \rho)$. It then follows that for nondiagonal elements, $\sigma_{non} = \chi_{non} \cong \rho/N$, while for diagonal elements, $\sigma_{diag} - \sigma_0 = \chi_{diag} \cong (\rho + q\mathfrak{H}_0)/N$. As long as only the Zeeman terms in eq 2.3 are included in $\mathfrak{H}_0$, it is easily shown that the equations Alexander develops for ρ are appropriate for $\rho \rightarrow N\chi$. The hyperfine term in eq 2.3 is always small compared to the electron-spin Zeeman term at high fields so that this assumption is certainly justified. If there is more than one exchanging species, as in chemical exchange, these remarks are still appropriate for both species.

(23) In the case of HE, one may alternatively describe the exchange as due to the random turning on and off of the exchange interaction $J\mathbf{S}_1 \cdot \mathbf{S}_2$ between pairs of electron spins with mean frequency ω_H. In the limit of strong exchange, $J\tau_d \gg 1$ (while still requiring $a_i\tau_d \ll 1$), we have $\omega_H = \omega_M$. The exchange operator in this case can actually be defined[19b] as $P = \frac{1}{2}1 + 2\mathbf{S}_1 \cdot \mathbf{S}_2$. It is possible in the case of HE, where the intermolecular interaction term $J\mathbf{S}_1 \cdot \mathbf{S}_2$ is specified, to consider weak, as well as strong, exchange.[8,10] This was done by Kivelson[8] and by Currin,[10] but we note that their results are, in fact, mutually incompatible. The detailed effects of the exchange process were recently reexamined by the present author by utilizing the Kaplan–Alexander method, and explicitly including a density matrix expression for the collision pair, whose lifetime is τ_d, in a manner similar to that utilized by R. M. Lynden-Bell (*Mol. Phys.*, **8**, 71 (1964)) for a somewhat different problem. Results substantially in agreement with Currin[10] were obtained. However, this recent treatment (unlike Currin's or Kivelson's) readily allows for an analysis of saturation effects. The result is that the effective exchange frequency $\omega_H = \omega_M(J\tau_d)^2(1 + J^2\tau_d^2)^{-1}$ provided that $a_i\tau_d \ll 1$. For further details see J. H. Freed, *J. Chem. Phys.*, **45**, 3452 (1966).

rate spin-density matrices σ_R and σ_D for the radical and diamagnetic species, and they are separately normalized, although they are coupled by the exchange. They will, in general, have different lifetimes given, respectively, by τ_R and τ_D. If the rate constant for the exchange is k_{CE}, then we have

$$\omega_R \equiv \tau_R^{-1} = k_{CE}[D] \qquad (2.20a)$$

$$\omega_D \equiv \tau_D^{-1} = k_{CE}[R] \qquad (2.20b)$$

where [R] and [D] are the equilibrium concentrations of the radical and diamagnetic species. Since the exchange operator technique requires that the exchanging part of the molecules have the same representation, one must adopt the convention that the nuclei (not the electrons) exchange. This leads (in our notation) to the equation for χ_R[22]

$$\langle \alpha^m | \Phi_R(\chi_R) | \alpha'^{m'} \rangle = \omega_R \Bigg[\sum_\gamma \frac{[\langle \gamma^m | \chi_R | \gamma^{m'} \rangle}{N/2} \delta_{\alpha,\alpha'} + \frac{\langle \alpha | \chi_D | \alpha' \rangle}{2} \delta_{mm'} - \langle \alpha^m | \chi_R | \alpha'^{m'} \rangle \Bigg] \qquad (2.21)$$

Again we may distinguish the different types of terms.

(i) *Off-diagonal Elements of* χ. (a) Let $\alpha = \alpha'$ but $m \neq m'$; then

$$\langle \alpha^\pm | \Phi_R(\chi_R) | \alpha^\mp \rangle = \omega_R \Bigg[\sum_{\gamma \neq \alpha} \frac{2}{N} \chi_{R\gamma^\pm, \gamma^\mp} - \frac{N-2}{N} \chi_{R\alpha^\pm, \alpha^\mp} \Bigg] \qquad (2.22)$$

Equation 2.22 contributes to the esr line widths, and, except for the replacement of ω_H by ω_R, is identical with eq 2.12, so the same remarks apply. Thus, utilizing eq 2.7c we obtain

$$[\Phi_R(\chi_R)]_{\lambda_j} = \omega_R \Bigg[\sum_{k \neq j} \frac{2}{N} \chi_{R\lambda_k} - \frac{N-2}{N} \chi_{R\lambda_j} \Bigg] \qquad (2.23)$$

(b) Let $m = m'$ but $\alpha \neq \alpha'$. This gives

$$\langle \alpha^\pm | \Phi_R(\chi_R) | \alpha'^\pm \rangle = \omega_R \Bigg[\frac{1}{2} \chi_{D,\alpha,\alpha'} - \chi_{R,\alpha^\pm,\alpha'^\pm} \Bigg] \qquad (2.24)$$

which, in general, couples the nmr transitions of the radical and diamagnetic species. However, since their transition frequencies [for the same configuration of nuclear spins] differ by a hyperfine splitting, we may drop the first term on the right-hand side of eq 2.24 and obtain

$$[\Phi_R(\chi_R)]_{\eta_j \pm} = -\omega_R \chi_{R\eta_j \pm} \qquad (2.25)$$

(c) Let $m \neq m'$ and $\alpha \neq \alpha'$. Then

$$\langle \alpha^m | \Phi_R(\chi_R) | \alpha'^{m'} \rangle = -\omega_R \chi_{R\alpha^m, \alpha'^{m'}} \qquad (2.26)$$

(ii) *Diagonal Elements of* χ_R. The equation for the diagonal elements becomes

$$[\Phi_R(\chi_R)]_{\alpha \pm} = \omega_R \Bigg[\frac{1}{2} \chi_{D,\alpha} + \frac{2}{N} \sum_{\gamma \neq \alpha} \chi_{R,\gamma \pm} - \left(\frac{N-2}{N} \right) \chi_{R,\alpha \pm} \Bigg] \qquad (2.27)$$

It follows from eq 2.27 that, in general, there is a coupling of the diagonal density matrix elements of the paramagnetic with the diamagnetic species. It is thus necessary to consider the equation for the diagonal elements of χ_D equivalent to eq 2.27 or

$$[\Phi_D(\chi_D)]_\alpha = [(\dot\chi_D)_\alpha]_{CE} = \omega_D(\chi_{R,\alpha^+} + \chi_{R,\alpha^-} - \chi_{D,\alpha}) \qquad (2.28)$$

Now, if no other processes significantly affect the diamagnetic spin populations (*viz.*, there is no radiofrequency radiation exciting the nmr resonance of diamagnetic species and there are no rapid relaxation processes), then $(\dot\chi_D)_\alpha$ is completely determined by the chemical exchange process. Thus, if we assume a steady state with $\dot\chi_D = 0$, then eq 2.28 yields

$$\chi_{D,\alpha} = \chi_{R,\alpha^+} + \chi_{R,\alpha^-} \qquad (2.29)$$

Substitution of eq 2.29 into 2.27 then yields

$$[\Phi_R(\chi_R)]_{\alpha \pm} = \omega_R \Bigg[\frac{1}{2} (\chi_{R\alpha^\mp} - \chi_{R\alpha \pm}) + \chi_{R \pm} \Bigg] \qquad (2.30)$$

which is *identical* with eq 2.18 for HE, except that ω_R replaces ω_H. Thus, any further comments on HE will apply equally to this case of CE, which we designate as *polarized* CE.

If CE is to be a veritable relaxation mechanism, it must be possible to treat it in the sense of interaction of the paramagnetic species with a "thermal bath." That is, the polarization effects on the diamagnetic species must be negligible. This can in principle be achieved in two ways: (1) [D] ≫ [R] so that there is essentially an infinite amount of diamagnetic species; and/or (2) if the nuclear spin lattice relaxation time $T_{1,D}$ of the diamagnetic species is short enough that $T_{1,D} \ll \tau_D$, so that the diamagnetic species relax more rapidly than they are perturbed by the CE process. Perhaps the most obvious way of achieving case 1 would involve pulse-type "steady-state" experiments such that the duration of resonance t_d obeys

$$\omega_D t_d \ll 1 \ll \omega_R t_d$$

[The endor experiments to be discussed in sections IV and V are only partially of the pulse type, since the esr field is maintained while the nmr field is pulsed, so a mixed situation could ensue.] In examining the like-

lihood of case 2, we first note that in the presence of paramagnetic species, the dominant mechanism contributing toward $T_{1,D}$ should be the intermolecular dipolar interaction with the unpaired electrons.[6] Since both $T_{1,D}^{-1}$ and ω_D are proportional to [R], their ratio $T_{1,D}^{-1}/\omega_D$ is independent of [R]. Typical values of $T_{1,D}^{-1}$ in ordinary solvents tend to range ~ 0.1 to 10 sec^{-1} when [R] $= 10^{-3} M$.[24] Thus for case 2 to be applicable, $\omega_D \ll \sim 1$ sec^{-1}, which is unreasonably low if $\omega_R = \omega_D[D]/[R] \sim 10^3$ to 10^6 sec^{-1}, so that CE may have non-negligible effects on the esr spectrum. It therefore appears that an *unpolarized* CE mechanism is not important in steady-state esr experiments in normal liquids. However, we shall consider it further, since it will be found to give interesting comparisons with the other mechanisms. An unpolarized CE mechanism amounts to setting $\chi_D = 0$, so the rate equation 2.27 takes the simple form of first-order transitions among *all* states with the same m_s; *i.e.*, it tries to equalize the populations of *all* spin states having the same m_s. In this limit we have a situation similar to the END mechanism, but with different selection rules.

III. Esr Spectra and Saturation Effects

A. Absorption. Following I, we note that when the λth degenerate transition of resonant frequency ω_λ is excited by an oscillatory radiofrequency field at frequency ω there will be a steady-state solution

$$\chi_{\lambda_j} = Z_{\lambda_j} \exp(i\omega t) \qquad (3.1)$$

where Z_{λ_j} is time independent. From eq 2.6, we find

$$\Delta\omega_\lambda Z_{\lambda_j} = \exp(-i\omega t)\{[\Gamma(\chi)]_{\lambda_j} - [\Phi(\chi)]_{\lambda_j}\} + $$
$$d_\lambda(\chi_{\lambda_j^+} - \chi_{\lambda_j^-}) = q\omega_\lambda d_\lambda \quad (3.2)$$

where $\Delta\omega = \omega - \omega_{\lambda'}$ and $\chi_{\lambda_j^+}$ and $\chi_{\lambda_j^-}$ correspond to the diagonal density matrix elements for the states between which the λ_jth degenerate transition occurs and d_λ is its transition moment multiplied by the radiofrequency magnetic field strength. We note that the relaxation terms in eq 3.2 may be written as

$$-\{[\Gamma(\chi)] - [\Phi(\chi)]\}_{\alpha\alpha'} = \sum_{\beta\beta'}{}' R^T{}_{\alpha\alpha'\beta\beta'}\chi_{\beta\beta'} \quad (3.3a)$$

where

$$R^T{}_{\alpha\alpha'\beta\beta'} = (R^\Gamma{}_{\alpha\alpha'\beta\beta'} + R^{EX}{}_{\alpha\alpha'\beta\beta'}) \quad (3.3b)$$

$R_{\alpha\alpha'\beta\beta'}$ arises from $\Gamma(\chi)$ and is discussed in I. $R^{EX}{}_{\alpha\alpha'\beta\beta'}$, which arises from $\Phi(\chi)$, includes all the terms arising from exchange mechanisms that are still important under the weak exchange condition eq 2.7c and include eq 2.12-2.15 and 2.18 for HE and eq 2.23-2.27 for CE. From the nature of these terms it readily follows that

$$\exp(-i\omega t)[\Gamma(\chi)]_{\lambda_j} = \sum_{kl}(R^\Gamma{}_{\lambda_j,\lambda_{kl}} + R^{EX}{}_{\lambda_j,\lambda_k}\delta_{kl})Z_{\lambda_{kl}}$$

$$(3.4)$$

Thus R^{EX} can couple degenerate transitions as a result of the terms which appear in eq 2.13 and 2.23. R^Γ can lead to more complex effects involving mixed transitions λ_{kl} involving different degenerate nuclear spin configurations (see I), but for simplicity we shall neglect any such effects and in fact set $R^\Gamma{}_{\lambda_j\lambda_{kl}} = R^\Gamma{}_{\lambda_j,\lambda_j} \cdot \delta_{jk}\delta_{jl}$ which is valid if each equivalent set of nuclei is completely equivalent.

We note that when the λth esr hyperfine line is being observed, one sees an absorption proportional to the imaginary part of[25]

$$\bar{Z}_\lambda = \sum_j Z_{\lambda_j} \qquad (3.5)$$

with

$$Z_{\lambda_j} = Z_{\lambda_j}' + iZ_{\lambda_j}'' \qquad (3.5a)$$

Thus, from (3.2) to (3.5) we obtain

$$\Delta\omega_\lambda \bar{Z} - i\sum_{j,k}R_{\lambda_j,\lambda_k}Z_{\lambda_k} + (d_\lambda\bar{\chi}_{\lambda^+} - d_\lambda\bar{\chi}_{\lambda^-}) = D_\lambda q\omega_\lambda d_\lambda$$

$$(3.6)$$

where

$$\bar{\chi}_{\lambda^\pm} = D_\lambda\chi_{\lambda^\pm} = \sum_j \chi_{\lambda_j^\pm} \qquad (3.7)$$

and D_λ is the degeneracy of the λth transition. Here the subscript $\lambda_{j\pm}$ refers to the $m_s = \pm$ states between which the λ_jth transition occurs. Now from eq 2.13 and 2.23

$$\sum_{j,k}R^{EX}{}_{\lambda_j,\lambda_k}Z_{\lambda_k} = -\frac{(N - 2D_\lambda)}{N}\omega_{EX}\bar{Z}_\lambda \qquad (3.8)$$

with $\omega_{EX} = \omega_H + \omega_R$. Thus, by studying $\bar{Z}_\lambda$, the line width coupling between the Z_{λ_j} due to the exchange may be circumvented. However, because in general $R^\Gamma{}_{\lambda_j} \neq R^\Gamma{}_{\lambda_k}$, this averaging procedure is unsatisfactory unless

$$|R_\lambda^{EX}| \gg |R_{\lambda_j}{}^\Gamma - R_{\lambda_k}{}^\Gamma| \quad \text{(for all } j \neq k) \quad (3.8a)$$

That is, the exchange effects dominate over END effects. When eq 3.8a is not valid because both effects are comparable, it is then necessary to diagonalize the R matrix obtained from eq 3.4 for the λth transition

(24) Reference 6, p 328.

(25) In I, the power absorbed was calculated and it is proportional to $\sum_j d\lambda_j Z''_{\lambda_j} = d_\lambda Z''_\lambda$ since $d\lambda_j = d_\lambda$. However, as is well known, it is the magnetization, proportional to $\bar{Z}''_\lambda$, which is actually observed in a magnetic resonance experiment, *cf.* ref 6, p 48.

in order to find the "normal modes" of the Z_{λ_j}.[3] For simplicity in analyzing exchange effects, we shall assume eq 3.8a to be valid. Then by defining

$$R_\lambda{}^\Gamma = D_\lambda{}^{-1}\sum_j R^\Gamma{}_{\lambda_j}$$

and

$$R_\lambda = R_\lambda{}^\Gamma + R_\lambda{}^{EX}$$

eq 3.6 becomes

$$(\Delta\omega_\lambda - iR_\lambda)\bar{Z}_\lambda + D_\lambda d_\lambda(\chi_{\lambda^+} - \chi_{\lambda^-}) = D_\lambda d_\lambda q\omega_\lambda \quad (3.9)$$

In the absence of saturation, $\chi_{\lambda^+} \approx \chi_{\lambda^-} \approx 0$, so eq 3.9 gives

$$\bar{Z}_\lambda = D_\lambda d_\lambda q\omega_\lambda T_\lambda[\Delta\omega_\lambda T_\lambda + i]/[1 + \Delta\omega_\lambda{}^2 T_\lambda{}^2] \quad (3.10)$$

with $T_\lambda{}^{-1} = -(R_\lambda)$ and is the width of a Lorentzian line. The statistical factor of $(N - 2D_\lambda/N)$ in eq 3.8 is the result of Zandstra and Weissman[7a] for CE and Currin[10] for HE and indicates that exchange processes involving degenerate nuclear spin states lead to no observable line broadening effects as long as eq 3.8a applies.

B. Transition Probability Matrix. Now eq 3.9 in the presence of saturation includes the diagonal matrix elements $\chi_{\lambda^\pm}$ whose relaxation is found from eq 2.6 to be[3]

$$[\Gamma(\chi)]_{\lambda_j^\pm} - [\Phi(\chi)]_{\lambda_j^\pm} = \pm 2d_{\lambda_j}Z_{\lambda_j}{}'' \quad (3.11)$$

Also

$$[\Gamma(\chi)]_{\beta\beta} - [\Phi(\chi)]_{\beta\beta} = 0 \quad (3.12)$$

where β refers to all eigenstates except $|\lambda_j^\pm\rangle$, and there are $N - 2D_\lambda$ such states. For completely equivalent nuclei, we find

$$[\Gamma(\chi)]_{\alpha_j\alpha_j} = \sum_{\gamma_k}W^\Gamma{}_{\alpha_j\gamma_k}(\chi_{\alpha_j} - \chi_{\gamma_k}) \quad (3.13)$$

where $W^\Gamma{}_{\alpha_j\gamma_k}$ is the transition probability between the α_jth and γ_kth states and is discussed in detail in I. [In this notation, j represents the jth degenerate state of the αth manifold of degenerate states.] The transition probabilities arising from eq 2.18 for HE (or 2.30 for polarized CE) and eq 2.27 for unpolarized CE are different, so we treat them separately.

(i) Unpolarized Chemical Exchange. Assuming that χ_D may be neglected in eq 2.27, we obtain

$$W^{CE}{}_{\alpha_j\gamma_k} = W^{CE} = \frac{2}{N}\omega_R \quad (3.14)$$

for all α_j *and* γ_k including $\alpha = \gamma$, so that

$$-[\Phi(\chi)]_{\alpha_j\alpha_j} = W^{CE}\sum_{\gamma_k}(\chi_{\alpha_j} - \chi_{\gamma_k}) \quad (3.14a)$$

If we now assume that

$$|W^\Gamma{}_{\alpha_j\gamma_k} - W^\Gamma{}_{\alpha_i\gamma_m}| \ll W^{CE}{}_{\alpha\gamma} \quad \text{(for all } j, k, l, m)$$

$$(3.15)$$

which is similar to eq 3.8a for the line widths, then we may combine eq 3.13 and 3.14 and sum over j to obtain

$$\sum_j\{[\Gamma(\chi)]_{\alpha_j\alpha_j} - [\Phi(\chi)]_{\alpha_j\alpha_j}\} = \sum_\gamma{}'W'_{\alpha\gamma}(\chi_\alpha - \chi_\gamma)$$

$$(3.16)$$

where

$$W'_{\alpha\gamma} = (D_\alpha D_\gamma)W_{\alpha\gamma} \quad (3.17)$$

$$W_{\alpha\gamma} = W^{CE} + W^\Gamma{}_{\alpha\gamma} \quad (3.17a)$$

with

$$W^\Gamma{}_{\alpha\gamma} = (D_\alpha D_\gamma)^{-1}\sum_{j,k}W^\Gamma{}_{\alpha_j\gamma_k} \quad (3.17b)$$

the χ_α and χ_γ are average values (*e.g.*, $\chi_\alpha = D_\alpha{}^{-1}\bar{\chi}_\alpha$ with D_α the degeneracy of the αth set of states). Utilization of eq 3.16 in place of eq 3.12 requires then that the right-hand side of (3.12a) becomes $\pm D_\lambda d_\lambda Z''_\lambda$. This formulation, in which the dimension of $\mathbf{W}'$ is considerably reduced over that of $\mathbf{W}$, is a consequence of the fact that $\chi_{\alpha_j} = \chi_\alpha$, independent of j and results from eq 3.15 as well as $d_{\lambda_j} = d_\lambda$. If eq 3.15 does not hold, it will no longer be valid.

As was done in I, we can define cofactors C_{ij} and double cofactors $C_{ij,kl}$ of the transition probability matrix $\mathbf{W}'$. However, the matrix $\mathbf{W}'^j$ with cofactors $C^j{}_{ik}$ is now defined by replacing each of the $W'_{j\alpha}$ of the jth row by D_α. This is necessary in order to remove the singularity of $\mathbf{W}'$ and amounts to utilizing the normalization condition in terms of χ or

$$\sum_\gamma D_\gamma\chi_\gamma = 0 \quad (3.18)$$

The relationships expressed by eq 2.41 of I for the C_{ij}, $C_{ij,kl}$, and $C^i{}_{jk}$ are again found to hold true with $A = N$ so that the method of solution is identical. Letting

$$\Omega_\lambda = \frac{2C_{\lambda,\lambda}}{C} \quad (3.19)$$

we find that

$$\bar{Z}_\lambda = D_\lambda d_\lambda T_\lambda q\omega_\lambda(\Delta\omega_\lambda T_\lambda + i)/$$
$$[1 + (\Delta\omega_\lambda T_\lambda)^2 + D_\lambda d_\lambda{}^2 T_\lambda\Omega_\lambda] \quad (3.20)$$

This is, in fact, formally identical with the Stephen-Fraenkel result, but is valid *only* because END effects have been assumed to be small. Furthermore, the details of Ω_λ are different for CE effects. In Table I, we give the results of Ω_λ for one and two equivalent spins of $I = \frac{1}{2}$ assuming that W^Γ contributes the im-

Table I: Esr Saturation Parameters for END and Exchange Effects

$$I = \tfrac{1}{2},\, n = 1^a$$

$$\Omega_e = W_e^{-1}\frac{[2W_e + W_n + \tfrac{1}{2}(\omega_H + \omega_R)]}{[W_e + W_n + \tfrac{1}{2}(\omega_H + \omega_R)]}$$

$$I = \tfrac{1}{2},\, n = 2$$

(A) END Mechanism[b]

$$\Omega_e(1,\pm1) = 2W_e^{-1}\frac{(1 + 3b + b^2)}{(1 + 3b)(1 + b)}$$

$$\Omega_e(1,0) = 2W_e^{-1}\frac{(1 + b)}{(1 + 3b)}$$

$$\Omega_e(0,0) = 2W_e^{-1}$$

(B) (i) CE-Unpolarized[c]
or (ii) HE (and Polarized CE)[d]

$$\Omega_e(1,\pm1) = (2W_e)^{-1}\left(\frac{8 + b'}{2 + b'}\right)$$

$$\Omega_e(0) = (2W_e)^{-1}\left(\frac{4 + b'}{2 + b'}\right)$$

[a] n is number of equivalent nuclei of spin I. [b] $b = W_n/W_e$. [c] $b' = \omega_R/W_e$. [d] $b' = (\omega_R + \omega_H)/W_e$.

portant terms to W_e, the lattice-induced electron spin transitions (which are taken to be equal for all hyperfine lines),[26] while W^{CE} yields the lattice-induced nuclear spin transitions.

(ii) Heisenberg Exchange (or Polarized CE). We rewrite eq 2.18 as

$$[\Phi(\chi)]_{\alpha_j \pm \alpha_j^\mp} = W^{HE}_{\alpha_j \pm \alpha_j^\mp}(\chi_{\alpha_j^\mp} - \chi_{\alpha_j^\pm}) + \sum_{\gamma k} W^{HE}_{\alpha_j \gamma_k \rightarrow} \chi_{\gamma_k} \quad (3.21)$$

where

$$W^{HE}_{\alpha_j \pm \alpha_j^\mp} = \frac{\omega_H}{2} \quad (3.22a)$$

$$W^{HE}_{\alpha_j^+ \gamma_k^+ \rightarrow} = -W^{HE}_{\alpha_j^- \gamma_k^+ \rightarrow} = \frac{2\omega_H}{N} \quad \text{(all } \gamma_k^+) \quad (3.22b)$$

and

$$W^{HE}_{\alpha_j \pm \gamma_k^- \rightarrow} = 0 \quad \text{(all } \gamma_k^-) \quad (3.22c)$$

We note that the matrix $\mathbf{W}^{HE}$ is *not* symmetric due to the presence of the "one-way" transition probabilities $W^{HE}_{\alpha_j \gamma_k \rightarrow}$. When eq 3.13 and 3.21 are combined (assuming eq 3.15 holds) and summed over j, one obtains

$$\sum_j \{[\Gamma(\chi)]_{\alpha_j \alpha_j} - [\Phi(\chi)]_{\alpha_j \alpha_j}\} = \sum_\gamma{}' W'_{\alpha\gamma}(\chi_\alpha - \chi_\gamma) - \sum_\gamma W'_{\alpha\gamma \rightarrow} \chi_\gamma \quad (3.23)$$

where $W'_{\alpha\gamma}$ is given by eq 3.17 with the superscript HE replacing CE, and

$$W'_{\alpha \pm \gamma^+ \rightarrow} = (\pm)\frac{D_\alpha D_\gamma}{N}\omega_H \quad \text{(for all } \gamma) \quad (3.23a)$$

One may again define the cofactors C_{ij} and $C_{ij}{}^k$ where eq 3.18 is again employed in the latter, but the non-symmetric matrix $\mathbf{W}'$ no longer has the property that the sum of all elements in a row yields zero, although the sum of all elements in a column still does. Thus we obtain the following restricted relations

$$(1) \quad C_{ij} = C_{kj} \quad \text{(all } i, j, k)$$

$$(2) \quad C_{ji}{}^i = -C_{ii}{}^j = C_{ji}{}^k - C_{ii}{}^k \quad (i \neq j \neq k)$$

$$(3.24)$$

Now *define*

$$(3) \quad C_{ki}{}^l - C_{kj}{}^l \equiv N\tilde{C}_{kl,ij} \quad (l \neq k;\ i \neq j)$$

Then

$$(4) \quad \tilde{C}_{kl,ij} - \tilde{C}_{ll,ij} = \tilde{C}_{lk,ij} \quad (l \neq k;\ i \neq j, k)$$

$$(5) \quad \tilde{C}_{kl,ij} = -\tilde{C}_{lk,ij} = \tilde{C}_{lk,ji} \quad (l \neq k;\ i \neq j)$$

where the $\tilde{C}_{ij,kl}$ are *not* simply the double cofactors $C_{ij,kl}$.[27]

It is also noted that

$$\det|\mathbf{W}^j| = \sum_k C_{jk} = \sum_k C_{lk} \equiv N\tilde{C} \quad (3.25)$$

independent of j. With the relations given by eq 3.24 and 3.25, the procedure follows that for CE. One again obtains eq 3.20, but now

$$\Omega_\lambda = \frac{2\tilde{C}_{\lambda,\lambda}}{\tilde{C}} \quad (3.26)$$

The matrix $\mathbf{W}^{HE}$, which is an $N \times N$ matrix, is of rank $N/2$. This is seen by noting from eq 3.22 that the sums

$$W^{HE}_{\alpha^+\gamma} + W^{HE}_{\alpha^-\gamma} = 0 \quad \text{(for all } \alpha \text{ and } \gamma) \quad (3.27)$$

so that each pair of rows labeled α^+ and α^- according to their spin states are linearly dependent. This is a simple consequence of the fact that HE does not act

(26) We are assuming that nuclear-spin independent processes such as the g tensor and spin-rotational mechanisms dominate the W_e, while the END mechanisms does not make a significant contribution to it (*cf.* section V and ref 3).

(27) In fact, one finds that

$$N\tilde{C}_{kl,ij} \equiv C_{ki}{}^l - C_{kj}{}^l = NC_{kl,ij} + (D_\alpha D_\gamma \omega_H)\sum_{a \neq k,l}^N (-1)^{a+l} C_{ka,ij}{}^l$$

where a will be even (odd) if it corresponds to a state with $m_s = -(+)$.

to change $(\chi_{\alpha^+} + \chi_{\alpha^-})$, but rather to equate all $(\chi_{\alpha^+} - \chi_{\alpha^-})$ independent of α (cf. eq 2.19a). However, a singularity of order $N/2$ prevents one from obtaining eq 3.26 (that is, one is attempting to invert the highly singular matrix $\mathbf{W}^{CE}$). We note that addition of $\mathbf{W}^{\Gamma}$ does not reduce this high order singularity if it contains only $\mathbf{W}_e{}^{\Gamma}$ electron spin transitions, but it will if it contains nuclear spin transitions $W_n{}^{\Gamma}$ connecting the states of different nuclear spin configuration. In examining the effects of $\mathbf{W}^{HE}$, it will therefore be useful to introduce a fictitious $W_n{}^{\Gamma}$ with selection rules similar to the exchange processes, so that eq 3.9 and 3.23 may be employed.[28] Once the $\Omega_{\lambda,\lambda}$ are obtained, the "fictitious" transition probabilities can be set equal to zero and any finite $\Omega_{\lambda,\lambda}$ (for which the singularities of $C_{\lambda,\lambda}$ and C cancel) will be retained. This procedure has been carried out for one and two equivalent spins of $^1/_2$ and the results are given in Table I.[26] It is noted that the results for the unpolarized and polarized CE mechanisms are identical.

IV. Endor Effects

In an endor experiment, nuclear (nmr) as well as electron spin resonances are excited. As was shown in I, the steady-state equations may be written in matrix notation as

$$(\mathbf{K} + i\mathbf{R})\mathbf{Z} = \mathbf{D}\chi + \mathbf{Q} \qquad (4.1)$$

and

$$(\mathbf{W}^j)\chi = -2\mathbf{D}^{\mathrm{tr}\,j}\mathbf{Z}'' \qquad (4.2)$$

$\mathbf{Z}$ and χ are vectors whose elements are all the nonvanishing transitions and nonequilibrium population deviations, respectively. The K matrix contains the frequency differences (e.g., $\Delta\omega_\lambda$) and would be diagonal except for the introduction of coherence effects, which amount to multiple quantum transitions. For simplicity, we shall neglect such effects, although they are not always negligible.[29] $\mathbf{Q}$ is a vector in "transition" space whose components are $q\omega_\lambda d_{\lambda j}$ for each of the λ_jth transitions which are excited. $\mathbf{D}$ is a matrix of transition moments $d_{\lambda j}$ whose nonzero values indicate a dependence of the $Z_{\lambda j}$ on the $\chi_{\alpha j^\pm}$ such as in eq 3.2, and $\mathbf{D}^{\mathrm{tr}\,j}$ is the transpose of $\mathbf{D}$ with the jth row replaced by zeros. When a summation over degenerate transitions and states is performed, as discussed in section III, and eq 3.8a and 3.15 hold, these equations are modified to

$$(\mathbf{K} + i\mathbf{R})\bar{\mathbf{Z}} = \mathbf{D}'\chi + \mathbf{Q}' \qquad (4.3)$$

and

$$(\mathbf{W}^j)\chi = -2\mathbf{D}^{\mathrm{tr}\,j}\bar{\mathbf{Z}}'' \qquad (4.4)$$

where $\mathbf{Z}$ involves sums over degenerate esr (but not nmr) transitions, and χ involves averages over degenerate spin states. $\mathbf{R}$ and $\mathbf{W}^j$ matrices are altered accordingly, so $\mathbf{R}$ becomes diagonal (cf. section III). The $\mathbf{D}'$ and $\mathbf{Q}'$ are obtained from the $\mathbf{D}$ and $\mathbf{Q}$ by replacing d_λ in any elements of the latter pair (where d_λ now refers only to the λth degenerate esr transition) by $D_\lambda d_\lambda$. For more than one equivalent nucleus, this treatment is not sufficient, since it is no longer necessarily true that $\chi_{\alpha\pm j} = \chi_{\alpha\pm k}$ or that $Z_{\lambda j} = Z_{\lambda k}$ (where λ_j is the $\alpha^+{}_j \leftrightarrow \alpha^-{}_j$ transition). This is because the $d_{\eta l}$ for the η set of degenerate nmr transitions obey selection rules governed by $J_{r\pm}$ (just as the END mechanism) so degenerate states of different J value are differently affected. It is then necessary to introduce appropriate difference terms such as $Z_{\lambda j} - Z_{\lambda k}$ and $\chi_{\alpha j} - \chi_{\alpha k}$ into the $\bar{\mathbf{Z}}$ and χ vectors. Nevertheless, the summations (cf. eq 3.5–3.9), which are initially called for to render $\mathbf{R}$ diagonal, still lead to considerable simplifications. We illustrate with the two equivalent spins of the $I = {}^1/_2$ case for which there are triplet $J = 1$ and singlet $J = 0$ nuclear spin states. The labeling of states is given in Figure 1. We use a new notation

$$\chi_{c\pm} = \frac{1}{2}(\chi_c + \chi_{c'}) \qquad (4.5a)$$

$$\chi_{d\pm} = \frac{1}{2}(\chi_d \pm \chi_{d'}) \qquad (4.5b)$$
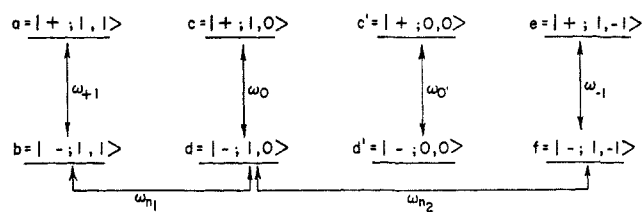
$$Z_{0\pm} = (Z_0 \pm Z_{0'}) \qquad (4.5c)$$

Figure 1. Transitions and eigenstates for double resonance in a radical with $S = {}^1/_2$ and two equivalent nuclear spins of $I = {}^1/_2$.

(28) Of course, the effects of an END mechanism may be included but this leads to complications including the necessity of diagonalizing the R matrix and of treating separately the matrix elements $\chi_{\alpha j}$ and $\chi_{\alpha k}$ of degenerate states.

(29) Their effect is probably most important in coupling the different degenerate nmr transitions which may be excited; cf. ref 3. A sufficient condition for their neglect on the esr transitions when $d_e \sim d_n$ may be simply stated as requiring that the dominant contribution to the esr line widths be secular and nuclear-spin independent.[3] This is realized if the secular g tensor effects dominate the width, while $\omega_e \tau_R \gg 1$, so the nonsecular effects are small. Then the exchange processes do not make an appreciable contribution to the width when ω_{ex} is comparable to the W_e resulting from nonsecular terms in the g tensor.

and assume that the excited esr transitions are ω_0, $\omega_{0'}$, and the excited nmr transitions are ω_{n_1} and ω_{n_2}. Then for an unpolarized CE mechanism, one has

$$
\mathbf{W} = \begin{array}{c} \\ a \\ b \\ c_+ \\ d_+ \\ e \\ f \\ c_- \\ d_- \end{array}
\begin{array}{cccccccc}
a & b & c^+ & d^+ & e & f & c^- & d^- \\
1 + \tfrac{3}{4}b' & -1 & -b'/2 & 0 & -b'/4 & 0 & & \\
-1 & 1 + \tfrac{3}{4}b' & 0 & -b'/2 & 0 & -b'/4 & & \\
-b'/2 & 0 & 2 + b' & -2 & 0 & -b'/2 & & \\
0 & -b'/2 & -2 & 2 + b' & -b'/2 & 0 & & \\
-b'/4 & 0 & -b'/2 & 0 & 1 + \tfrac{3}{4}b' & -b'/2 & & \\
0 & -b'/4 & 0 & -b'/2 & -1 & 1 + \tfrac{3}{4}b' & & \\
& & & & & & 1 + \tfrac{3}{4}b' & -1 \\
& & & & & & -1 & 1 + \tfrac{3}{4}b'
\end{array}
\quad (4.6)
$$

$$
\mathbf{D} = \begin{array}{c} \\ 0_+ \\ n_1 \\ n_2 \\ 0_- \end{array}
\begin{array}{cccccccc}
a & b & c^+ & d^+ & e & f & c^- & d^- \\
0 & 0 & -d_e & +d_e & 0 & 0 & 0 & 0 \\
0 & -d_n & 0 & d_n & 0 & 0 & 0 & d_n \\
0 & 0 & 0 & -d_n & 0 & +d_n & 0 & -d_n \\
0 & 0 & 0 & 0 & 0 & 0 & -d_e & d_e
\end{array}
\quad (4.7)
$$

$$
\mathbf{Q}' = q \begin{bmatrix} 2\omega_0 d_e \\ \omega_n d_n \\ \omega_n d_n \\ 0 \end{bmatrix} \approx q \begin{bmatrix} 2\omega_0 d_e \\ 0 \\ 0 \\ 0 \end{bmatrix} \quad (4.8)
$$

Equation 4.6 for $\mathbf{W}$ is written in units of W_e and $b' = \omega_R/W_e$. The separation of $\mathbf{W}$ into two blocks results from the form of the $W_{\alpha\gamma}$ given by eq 3.17 as well as eq 3.22 for HE. It is always possible to choose linear combinations of the degenerate $\chi_{\alpha j}$, for any value of D_α, such that they will be "orthogonal" to $\chi_\alpha = D_\alpha^{-1} \sum_j \chi_{\alpha j}$. The matrix $\mathbf{R}$ is diagonal with $R_{0+,0+}$ given by eq 3.8, $R_{n_1,n_1} = R_{n_2,n_2}$ given by eq 2.25 and $R_{0-,0-} = R_\lambda^\Gamma - \omega_R$. The diagonal elements of $\mathbf{K}$ are $K_{0\pm} = \Delta\omega_e$ and $K_{n_1} = K_{n_2} = \Delta\omega_n$.

The solution to eq 4.3 and 4.4 is

$$[\mathbf{K}(-\mathbf{R})^{-1}\mathbf{K} - \mathbf{R} + \mathbf{S}']\bar{\mathbf{Z}}'' = \mathbf{Q}' \quad (4.9)$$

with

$$S'_{\lambda_l,\eta_k} = [2\mathbf{D}'(W^j)^{-1}D^{\mathrm{tr}\,j}]_{\lambda_l,\eta_k} \quad (4.10)$$

Now, from the form of $\mathbf{W}^j$

$$\mathbf{W}^j \equiv \begin{bmatrix} \mathbf{W}^{j+} & 0 \\ 0 & \mathbf{W}^- \end{bmatrix} \quad (4.11)$$

it follows that

$$[W^j]^{-1} = \begin{bmatrix} [W^{j+}]^{-1} & 0 \\ 0 & [\mathbf{W}^-]^{-1} \end{bmatrix} \quad (4.12)$$

So partitioning $\mathbf{D}$ similarly, $\mathbf{D} = (\mathbf{D}^+; \mathbf{D}^-)$ we obtain

$$S'_{\lambda_l\eta_k} = d_{\lambda_l}d_{\eta_k}\Omega_{\lambda_j,\eta_k} + [2\mathbf{D}'-(\mathbf{W}^-)^{-1}\mathbf{D}^{\mathrm{tr}\,-}] \quad (4.13)$$

with $\Omega_{\lambda_j,\eta_k}$ determined solely by the $\mathbf{W}^{j+}$ matrix according to eq 3.19 (or 3.26). It is found that there are no terms of type S'_{e^+,e^-} in eq 4.13, and the only nonvanishing contributions from the second term are of type S'_{e^-,e^-}, $S'_{e^-,n}$, and their transposes. In this notation e^+ refers to the sum over the eth set of degenerate esr transitions and e^- to an appropriate difference combination of the eth set of transitions. It is because terms of type $S_{e^-,n}$ and Z_{e^-} vanish for $d_\eta = 0$, that the saturation treatment in section III is not affected by these considerations. The solution for $\bar{Z}''_{e^+}$ then becomes

$$
\bar{Z}''_{e^+} = D_e q \omega_e d_e T_e / [1 + (\Delta_e T_e)^2 + \\
D_e(\Omega_e - \xi_e)T_e d_e^2] \quad (4.14)
$$

with

$$D_e d_e^2 \xi_e = \sum_{i,j}^m S'_{i,e^+} S'_{e^+,j} \frac{F_{ij}}{F} \quad (4.15)$$

where F is the $m \times m$ determinant with elements

$$(f_{ii})^{-1} = T_i/(1 + \Delta_i^2 T_i^2 + T_i S'_i) \quad (4.16a)$$

$$f_{ij} = S'_{i,j} \quad (i \neq j) \quad (4.16b)$$

and m includes all the nuclear transitions as well as the transitions of type e^-. For $m > 1$, the nuclear line shapes given by eq 4.16a will be mixed in eq 4.15 so that, in general, ξ_e will not exhibit simple Lorentzian behavior as the nmr frequency is swept. Perhaps the simplest but still meaningful parameter to study is the value of $\bar{Z}''_{e^+}$ for $d_e \approx d_n \to \infty$ and $\Delta e = \Delta_n = 0$ for which eq. 4.17 hold.

$$\bar{Z}''_{e^+}{}^r(d_e, d_n \longrightarrow \infty) = \frac{q\omega_e}{d_e}\left[\frac{1}{\Omega_e - \xi_e}\right] \quad (4.17)$$

Then the difference signal[30]

$$[\bar{Z}''_{e^+}{}^r(d_e, d_n \longrightarrow \infty)(\text{endor}) -$$

$$\bar{Z}''_{e^+}{}^r(d_e \longrightarrow \infty)(\text{esr})] = \frac{q\omega_e}{d_e}\left[\frac{\xi_e}{\Omega_e}(\Omega_e - \xi_e)^{-1}\right] \quad (4.18)$$

The values of ξ_e are given for both HE and CE for one and two spins of $I = {}^1/_2$ in Table II. From the $n = 1$ case, it is clear that HE and a polarized CE mechanism *cannot* yield an endor signal. It is necessary

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Table II: Resonant Endor Enhancement Parameters for END and Exchange Effects under Very Strong Fields

$$I = {}^1/_2, \, n = 1^a$$

(A) Unpolarized CE

$$\xi_e{}^r = \frac{W_n + \omega_R/2}{\left[2W_n + W_e + \omega_R + \dfrac{\omega_H}{2}\right]\left[W_n + W_e + \dfrac{1}{2}(\omega_R + \omega_H)\right]}$$

(B) Polarized CE

$$\xi_e{}^r = \frac{W_n}{\left[2W_n + W_e + \dfrac{1}{2}(\omega_R + \omega_H)\right]\left[W_n + W_e + \dfrac{1}{2}(\omega_R + \omega_H)\right]}$$

$$I = {}^1/_2, \, n = 2^b$$

(A) END Mechanism[c]

$$\xi_e{}^r(1, \pm 1) = \frac{2b(1 + 6b + 10b^2)}{(1 + b)(1 + 2b)(1 + 3b)(1 + 6b)}(W_e)^{-1}$$

$$\xi_e{}^r(1, 0) = \frac{4b}{(1 + 6b)(1 + 3b)}W_e{}^{-1}$$

$$\xi_e{}^r(0, 0) = 0$$

(B) CE-Unpolarized[d] ($W_n = 0$)

$$\xi_e{}^r(\pm 1) = W_e{}^{-1}\frac{b'}{(2 + b')(3 + 2b')}$$

$$\xi_e{}^r(0) = W_e{}^{-1}\frac{4b'(1 + b')}{3(2 + b')^3}$$

(C) HE Mechanism (and CE-Polarized); ($W_n = 0$)

$$\xi_e{}^r(1, \pm 1) = \xi_e{}^r(0) = 0$$

[a] n is number of equivalent nuclei of spin I. [b] The notation here is (J, M_J) for END mechanism and (M_J) for exchange mechanisms. [c] $b = W_n/W_e$. [d] $b' = \omega_R/W_e$.

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to have a nonvanishing W_n such as is induced by the END mechanism. In the presence of a W_n, these exchange processes actually *diminish* the magnitude of ξ_e. An unpolarized CE mechanism is found, as expected, to yield precisely the same endor enhancement as an END mechanism, since in the $n = {}^1/_2$ case

there is no distinction in the "selection rules" of the two. These remarks carry over into the $n = 2$ case except that now the difference in "selection rules" of the unpolarized CE *vs.* the END mechanisms yield different enhancements. It is expected that for $n > 2$ these remarks are again appropriate.

V. Comparison with Experiment

The most detailed experiments appropriate for comparison are those of Hyde.[18] Perhaps their most interesting aspects are the observations of relative signal heights of the saturated esr hyperfine lines and of the endor signals obtained from each hyperfine line when a particular nmr transition is excited (*i.e.*, endor-induced epr[18]). These were found to be strongly temperature dependent. (Changes in absolute signals which are dependent on instrumental factors as well as radical concentrations are probably more difficult to analyze.)

The simplest case is for the two spins of $I = {}^1/_2$, for which we may define the ratios $(Z_0/Z_\pm)_{\text{esr}} = r$ and $(Z_0/Z_\pm)_{\text{endor}} = R$ as the ratio of center- to end-line signal intensity for esr and for endor-induced epr (*cf.* eq 4.18), respectively. They are plotted in Figures 2 and 3, respectively, for the END mechanism (as a function of $b = W_n/W_e$) and for the unpolarized CE mechanism (as a function of $b' = \omega_R/W_e$). The magnitude of the endor-induced epr signals for each hyperfine line relative to its own saturated value is given from eq 4.18 as

$$\xi_e(\Omega_e - \xi_e)^{-1}$$

and is given in Figures 4 and 5 for the two different mechanisms. Strong saturation and resonance conditions have been assumed for all induced transitions. It is seen that there is a significant variation of all these observables as a function of b and b'. This variation is more pronounced for the unpolarized CE mechanism. Now for a given value of b (or b') one obtains an associated pair of values for r and R and this may readily be compared to experiment. In Table III, such a comparison is given with Hyde's experimental results on 2,5-di-t-butyl semiquinone. The agreement of experiment with that predicted from an END mechanism is seen to be quite good (while that from the unpolarized CE mechanism is not nearly so good) at the various temperatures studied. There is a discrepancy, however, in that the prediction from Figure 2 (or 3) is that large (absolute) enhancements are expected at 10°, while experimentally they were actually found to be rather weak. This might possibly

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(30) This is observed by means of a differential-pulse technique; *cf.* ref 18.
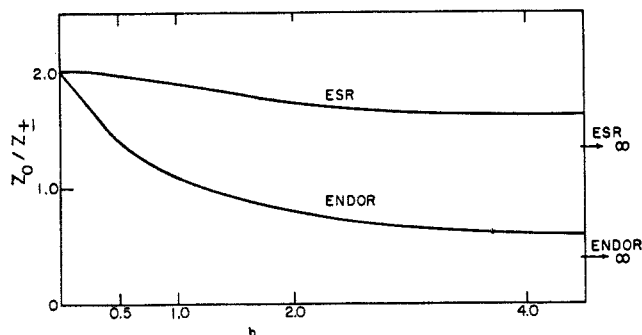
Figure 2. Relative saturated on-resonance signals of center to outside lines for esr and endor-induced epr as a function of $b = W_n/W_e$ for an END mechanism. There are two equivalent nuclear spins of $I = {}^1/_2$.
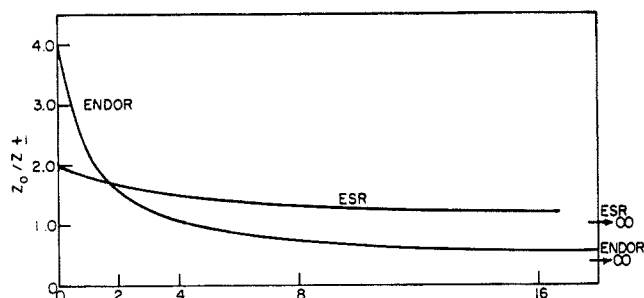

Figure 3. Relative saturated on-resonance signals of center to outside lines for esr and endor-induced epr as a function of $b' = \omega_R/W_e$ for an unpolarized CE mechanism. There are two equivalent nuclear spins of $I = {}^1/_2$.
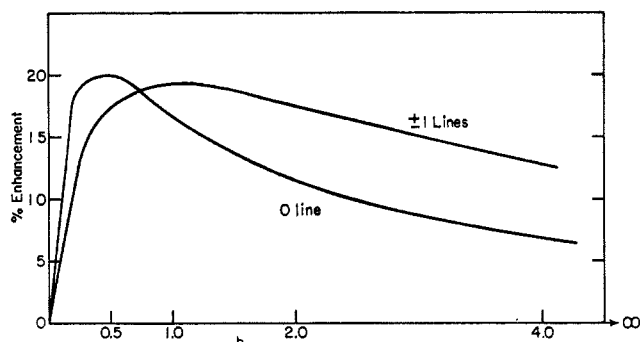

Figure 4. Per cent enhancement of saturated esr signal due to endor given as a function of $b = W_n/W_e$ for an END mechanism. It is given for the center and outside lines relative to their own saturated esr signal. There are two equivalent nuclear spins of $I = {}^1/_2$.
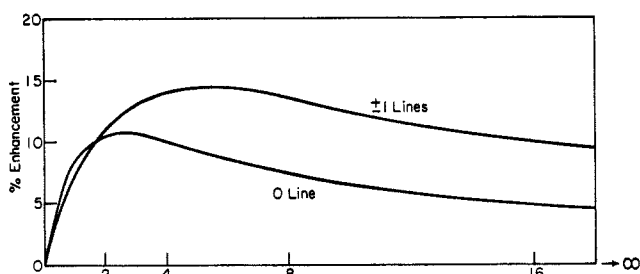

Figure 5. Per cent enhancement of saturated esr signal due to endor given as a function of $b' = \omega_R/W_e$ for an unpolarized CE mechanism. It is given for the center and outside lines relative to their own saturated esr signal. There are two equivalent nuclear spins of $I = {}^1/_2$.

be due to the presence of either a significant HE or polarized CE mechanism at the high temperature, the effect of which would be to reduce the observed enhancement (cf. Table II).[31] Concentration-dependent studies of Hyde's on the tetracene cation are also consistent with the idea that exchange mechanisms act to reduce the intensity of the endor signal.

We note also that the variation of b (or b') with temperature (as given in Table III) is again consistent with an END mechanism. That is, as long as $\omega_e\tau_R \gg 1$, where τ_R is an (isotropic) rotational correlation time,

we find for such terms as the g tensor and END mechanisms[3]

$$W_e \propto \tau_R^{-1} \qquad (5.1a)$$

while

$$W_n^{END} \propto \tau_R \qquad (5.1b)$$

since $\omega_n\tau_R \ll 1$ is usually obeyed.[3] Utilizing a Stokes–Einstein model, one has

$$\tau_R = 4\pi\eta a^3/3kT \qquad (5.2)$$

where η is the viscosity and a is a molecular radius. Thus we may define[32]

$$W_e \equiv A\frac{T}{\eta} \qquad (5.3a)$$

$$W_n \equiv B\frac{\eta}{T} \qquad (5.3b)$$

Table III: Comparison of Experimental[a] and Predicted Relative Saturated Esr and Endor Signals from 2,5-Di-t-butyl Semiquinone

R	Temp, °C	r (exptl)	r (END)	b	r (CE)	b'
1.5	10	2	1.97	0.40	1.65	2.25
1.0	−20	2	1.83	1.18	1.45	4.4
0.6	−40	1.4	1.60	4.0	1.25	14.0

[a] See ref 18.

(31) This is borne out by calculations including effects of both W_n^Γ and ω_H. When END and HE terms are comparable, the calculations are more difficult than those presented here; cf. section III.

where A and B are temperature independent and may be written in terms of the spectral densities given in I and ref 15. Then

$$b = \left(\frac{B}{A}\right)\left(\frac{\eta}{T}\right)^2 \qquad (5.4)$$

Now for most liquids, $\eta \propto Te^{W/kT}$, $W > 0$.[33] Thus b should increase significantly with decreasing T as observed.

The effects of viscosity and temperature on exchange processes are not so easy to analyze. Experimental line-width studies on HE[9] are consistent with a strong exchange, for which we may write[8b,10]

$$\omega_{HE} = 4\pi Da[R] \qquad (5.5)$$

where D is the translational diffusion coefficient given in a Stokes–Einstein model by

$$D = kT/6\pi a\eta \qquad (5.6)$$

Thus, the effect of HE should decrease with decreasing temperature. For weaker exchange, eq 5.5 should be multiplied by p, the probability of exchange per encounter which will, in general, be temperature and viscosity dependent.[8b,10] Similar remarks should apply to CE exchange processes.[7]

Assuming that it is the END mechanism which is the dominant nuclear-spin flip process that is "endor-active," then it is easy to understand another result of Hyde's experiments, namely that for a given sample, the best endor signal is obtained at a different temperature for the different nmr transitions, and that furthermore the optimum temperature is greater for those nmr transitions involving the nuclear spins with greater coupling constants. This observation was studied specifically for the tetracene cation.[18] While there is no simple relationship between the magnitude of the isotropic coupling constant of a proton and its END term, since the latter depends on unpaired electron density distributed *throughout* the molecule (*i.e.*, on $1/r^3$ averaged over a delocalized orbit) while the former depends only on the localized density at the particular nucleus, nevertheless we may expect that in many cases the larger END terms will be associated with the larger splittings. This is borne out for the case of tetracene by means of McConnell–Strathdee[34] type calculations.[35]

We again utilize eq 5.3 and 5.4 where eq 5.3b is written separately for each equivalent set of nuclei. These equations are quite appropriate here since Hyde and Brown[36] have found that $\omega_e\tau_R \ll 1$ over the relevant temperature range in the sulfuric acid solvent.[32,37] Now the endor enhancement is a maximum for $b \sim 1$, so from eq 5.4 we get

$$\left.\frac{B_i}{A}\right] \sim \left(\frac{T}{\eta}\right)^2$$

Thus the larger B_i (or END terms) require the higher temperatures. On the other hand, exchange processes will have effects independent of splitting a_i provided that $\omega_{ex} \ll a_i$, so they cannot yield the observed effect.

VI. Summary

For the case of esr spectra with well-separated hyperfine lines, the theoretical analysis given has shown that all the observable effects of *polarized* CE and HE (including line widths, saturation, and endor behavior) are identical. It is further shown that these exchange processes effectively act as nuclear spin transitions when studied by esr saturation techniques, but are "endor-inactive" and merely diminish the endor signals resulting from other mechanisms (*e.g.*, the END mechanism). While an *unpolarized* CE mechanism is not expected to be important (except, perhaps, as a result of the short duration of endor pulses), it was found in all cases analyzed that the effects of this mechanism on esr saturation are *identical* with those of the polarized CE mechanism, but in the case of endor it is an "endor-active" mechanism. Its endor effects are quantitatively distinguishable from those of an END mechanism as a result of their different spin-transition selection rules. This emphasizes the

(32) The dependence of W_e on T/η also results if a spin-rotational mechanism contributes to W_e.[11,12] That is, in a semiclassical treatment following Hubbard,[11] one finds that

$$W_e\text{spin-rot.} = \frac{IkTC^2}{\hbar^2}\left(\frac{\tau_J}{1 + \omega_e^2\tau_J^2}\right)$$

where I is the moment of inertia and C is the spin-rotational constant of the radical (and both are being assumed isotropic), and τ_J is the correlation time for the angular momentum. We note that this mechanism is nuclear-spin independent. Now in liquids, $\tau_J \ll \tau_R$ and usually $\tau_J \ll \omega_e^{-1}$. Utilizing a Stokes–Einstein model one has

$$\tau_J = I/8\pi a^3\eta$$

so that $W_e\text{spin-rot.} \propto T/\eta$.

(33) J. Frenkel, "Kinetic Theory of Liquids," Dover Publications, Inc., New York, N. Y., 1955, p 193.

(34) H. M. McConnell and J. Strathdee, *Mol. Phys.*, 2, 129 (1959).

(35) J. H. Freed, unpublished results.

(36) J. S. Hyde and H. W. Brown, *J. Chem. Phys.*, 37, 2053 (1962).

(37) We note that the apparent anomaly observed by Hyde and Brown[36] that at high temperatures, $T_1 \sim T_2$, although $\omega_e^2\tau_R^2 \gg 1$, can be resolved if the spin-rotational mechanism is dominant at the high temperatures. Their T_1 actually corresponds to $\Omega_e/4$ which obeys $\Omega_e \leq 2/W_e$, where the equality is appropriate in the absence of nuclear spin-dependent relaxation transitions.[3] The width contribution from the spin-rotational mechanism (since $\tau_J \ll \omega_e^{-1}$) is found to be[11]

$$[T_2\text{spin-rot.}]^{-1} = 2W_e = [T_1\text{spin-rot.}]^{-1}$$

At reduced temperatures, the line-broadening effects of the spin-rotational mechanism are reduced, while those of the g-tensor and END mechanisms are enhanced.

possibility of using endor to analyze for different nuclear spin transition selection rules.

An analysis of the relevant experimental results showed that they are consistent with both the END mechanism as the dominant "endor-active" process

and with exchange processes acting to reduce the endor signals.

The Isotropic Hyperfine Interaction[1]

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The isotropic contribution to the hyperfine interaction resulting from exchange polarization of inner s electrons has been computed for first-, second-, and third-transition metal ions from electron spin resonance data. Various trends with respect to bonding and the periodic table are noted. A perturbation approach to the calculation of the isotropic hyperfine term is developed and used to explain some of the observed trends.

Introduction

The isotropic contact term in the hyperfine interaction of paramagnetic ions has been the subject of many studies.[2] Abragam, Horowitz, and Pryce[3] have observed that the quantity χ, defined as

$$\chi = \frac{4\pi}{S}(\psi|\sum_i \delta(r_i)s_{zi}|\psi) \qquad (1)$$

is negative and of nearly constant magnitude for ions in the first transition series. Since unpaired electrons in d orbitals cannot contribute to χ, they proposed that the finite value of χ results from a polarization of the inner filled s orbitals by the unpaired d electrons. Their attempt to calculate χ by using configuration interaction with the excited state resulting from the promotion of a 3s electron to a 4s orbital was, however, unsuccessful. More successful calculations[4] of χ have been made using unrestricted Hartree–Fock methods. These calculations revealed that the polarization of both 2s and 3s orbitals is important and that the negative contribution of the 2s shell dominated the positive contribution of the 3s shell.

Matamura[5] and Title[6] have noted that χ for d^5 ions decreases as the electronegativity difference between the anion and cation of the host lattice decreases. A similar behavior has been assumed for χ in copper complexes by several investigators[7] when calculating molecular orbital coefficients from spin-Hamiltonian parameters, but Kuska and Rogers[8] have recently reported some measurements on substituted copper(II) acetylacetonates which contradict such an assumption.

(1) Work supported by NSF Grant GP-4215.

(2) For a complete review see A. J. Freeman and R. E. Watson, "Magnetism," Vol. IIA, G. T. Rado and H. Suhl, Ed., Academic Press, Inc., New York, N. Y., 1965, p 167.

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