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A Phenomenological Description of Electron Paramagnetic Double-Resonance Relaxation of Organic Free Radicals in Solution. I. Theory of ENDOR Based on the Spin-Population Number Method

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ENDOR enhancement is phenomenologically described, applying the method of Lloyde and Pake. Emphasis is placed on the effect of incomplete hf separation. It is shown that fractional ENDOR enhancement can approximately be expressed as the product of that which Freed has formulated when the effect is absent, and an modified Allendoerfer-Maki type correlation, $T_{2e}{}^2\Delta\omega^2/(c+T_{2e}{}^2\Delta\omega^2)$, where c is a constant dependent on the microwave power. Also, a simplified method is proposed for calculating the fractional ENDOR enhancement for a multi-level system consisting of several sets of equivalent protons, when $W_n \ll W_e$, and it is proven that the week rf power irradiated leads to an ENDOR enhancement proportional to the number of equivalent protons, in the absence of the effect of incomplete hf separation.

The ENDOR measurements for an organic radical in solution give, in general, very simple spectra. The spacing among the ENDOR lines easily results in an accurate value of the hfs constant even for a proton having its hfs hidden within the ESR linewidth. On the other hand, the intensity of ENDOR lines (ENDOR enhancement) conspicuously varies with temperature (viscosity), concentration, microwave (mw) power and radiofrequency (rf) power. Thus, under the usual conditions of measurement, ENDOR enhancement does not directly reflect the number of equivalent protons which considerably helps in the assignment of the proton. Such a complicated behavior of ENDOR enhancement has stimulated some experimental and theoretical investigations for the purpose of extracting the relaxational characteristics of an observed proton. This paper covers the theoretical part of those investigations.

It has been established that the relaxation matrix theory developed by Freed and coworkers[1–5] describes ENDOR phenomena quite satisfactorily.[4–7] However, it is not easy to obtain an exact solution to the Freed equations for a simple system consisting of only a few sets of equivalent protons, even with the aid of a computer. Therefore, a simplification based on a phenomenological theory is still of value in spite of its lack of rigor, as long as it can explain, to some extent, the experimental results for complex molecules.

The Freed theory assumes that all the hfs are completely separated. However, one often encounters cases for which the hfs is of the order of the ESR linewidth (and for which ENDOR exhibits its full capability). In this situation, when one of the spin packets is saturated by mw irradiation, other packets are partially saturated because of the overlapping of the packets, which consequently reduces the ENDOR enhancement. This effect of incomplete hf separation, or the self-ELDOR effect, was first treated by Allendoerfer and Maki,[8] who have proposed the following formula,

$$I = I_{\max}\frac{T_{2e}{}^2\Delta\omega^2}{2.5+T_{2e}{}^2\Delta\omega^2}, \tag{1}$$

where $I_{\max}$ is the ENDOR enhancement in the absence of the effect, $\Delta\omega$ is a hfs constant and T_{2e} is the spin-spin relaxation time of an electron spin corresponding to the ESR linewidth. The applicability of the formula has been discussed by several authors.[9–14] The beauty of the formula is its simplicity, although it has inevitable defects. A difficult point is that it does not contain any relaxation term, except for T_{2e}, and therefore it is not clear under which conditions it is applicable. Indeed, it is known that the ratio of the ENDOR enhancement corresponding to each proton in a molecule also varies markedly with the measurement conditions mentioned above.

The present work is a direct extention of the idea of Allendoerfer and Maki. Here, the method for the spin population number of Lloyd and Pake[15] and Stephan[16] is applied. Introducing a coefficient of incomplete hf separation, we can express the ENDOR enhancement in terms of this coefficient and various kinds of transition probabilities, and thus we wish to examine the role of the effect of incomplete hf separation. In addition, a simplified method is proposed for calculating the ENDOR enhancement for a multi-level system consisting of several sets of equivalent protons, under the condition that $W_n \ll W_e$.

Theory

(a) Outline. We assume first-order formalism for the transition velocity of the spin population number in a stationary state, thus

$$\dot{\mathbf{N}} = \mathbf{CN} = 0. \tag{2}$$

$\mathbf{N}=\{N_i\}$ is the spin population number of each spin level, in which case the total spin population number should be conserved, thus

$$\sum_i N_i = N. \tag{3}$$

$\mathbf{C}$ is a conduction matrix composed of various kinds of transition probabilities. For the lattice-induced transition probabilities, we assume that

$$\frac{W_{\uparrow}{}^{(e)}}{W_{\downarrow}{}^{(e)}} = \varepsilon = \exp\left(\frac{-\gamma_e\hbar H_0}{kT}\right) \tag{4}$$

and

$$\frac{W_{\uparrow}{}^{(n)}}{W_{\downarrow}{}^{(n)}} = 1, \tag{5}$$

where $W^{(e)}$ and $W^{(n)}$ are the transition probabilities satisfying $\Delta M_S=\pm 1$, and $\Delta M_S=0$, $\Delta M_J=\pm 1$, respectively. The latter equation is assumed because the nuclear Zeeman and hf interactions are too small to bear a net population difference among electron spin levels. Also, we assume a Lorentzian shape function for the transition probabilities induced by the mw and rf fields. When the mw field, $2H_1\cos\omega_e t$, is applied, we have

$$P_e = \frac{1}{2}\gamma_e{}^2 H_1{}^2 T_{2e} |\langle\frac{1}{2}|S_+|-\frac{1}{2}\rangle|^2 \frac{1}{1+T_{2e}{}^2(\omega_e-\omega_{e0})^2}, \qquad (6)$$

and when the rf field, $2H_2\cos\omega_n t$, is applied,

$$P_n = \frac{1}{2}\gamma_n{}^2 H_2{}^2 T_{2n} |\langle M_J|J_+|M_J-1\rangle|^2 \frac{1}{1+T_{2n}{}^2(\omega_n-\omega_{n0})^2}. \qquad (7)$$

It is well known that only weak ENDOR enhancement is observed for a proton whose hfs is equal to or smaller than the ESR linewidth. In order to treat such cases, one must explicitly take into account the effect of incomplete hf separation. Now, mw excitation induces a transition between the observed spin levels at the ESR resonance, with probability,

$$P_e = \frac{1}{2}\gamma_e{}^2 H_1{}^2 T_{2e}. \qquad (8)$$

At the same time, another transition is induced between the neighboring spin levels (Fig. 1), with probability,

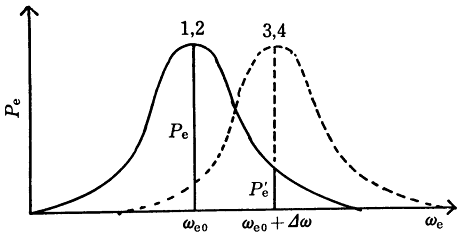

Fig. 1. Schematic diagram of the effect of the incomplete hf separation.

$$P_e' = \frac{1}{2}\gamma_e{}^2 H_1{}^2 T_{2e} \frac{1}{1+T_{2e}{}^2\Delta\omega^2}. \qquad (9)$$

Therefore, a coefficient of incomplete hf separation is introduced as follows:

$$\alpha = \frac{1}{1+T_{2e}{}^2\Delta\omega^2}. \qquad (10)$$

α takes any value between 0 and 1 which correspond to complete hf separation ($\Delta\omega=\infty$) and complete overlap ($\Delta\omega=0$), respectively. Then,

$$P_e' = \alpha P_e. \qquad (11)$$

The alternating field-induced transition probabilities have inherent reversibility in contrast to the lattice-induced transition probabilities. Therefore, the role of the field-induced probabilities is thought to be that of making a partial short-circuit over the relaxation pathways, which decreases the difference in the spin population numbers among the spin levels, whereas that of the lattice-induced probabilities is to be that of keeping the Boltzmann distribution. Thus, the presence of P_e' causes the ELDOR-like effect to decrease the ENDOR enhancement.

Equations 2 and 3 result in the difference in the spin population numbers, n, between the two spin levels at which ESR is observed. Then, using the mw energy absorbed per unit time, which is given by

$$A = 2\omega_e\chi'' H_1{}^2 = nP_e\hbar\omega_e, \qquad (12)$$

the integral intensity of the ESR absorption line (I), the peak intensity of the first derivative (I_{ESR}), the ENDOR enhancement (I_{ENDOR}) and the fractional ENDOR enhancement (E) are defined as follows:

$$I = \chi'' H_1, \qquad (13)$$

$$I_{\mathrm{ESR}} = \left(\frac{\partial I}{\partial\omega_e}\right)_{\max}, \qquad (14)$$

$$I_{\mathrm{ENDOR}} = I_{\mathrm{ESR}}(\mathrm{ON}) - I_{\mathrm{ESR}}(\mathrm{OFF}), \qquad (15)$$

$$E = \frac{I_{\mathrm{ENDOR}}}{I_{\mathrm{ESR}}(\mathrm{OFF})}, \qquad (16)$$

where ON denotes rf irradiation and OFF the absence of rf power. As a whole, the present approach to ENDOR enhancement may be regarded as a simplified version[17)] of the relaxation matrix formulation developed by Freed.

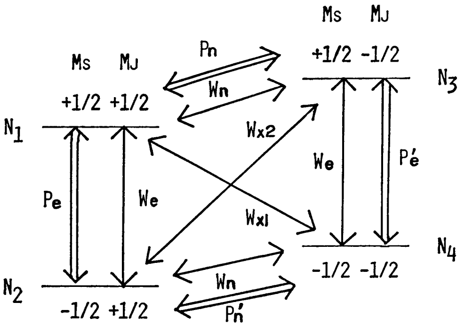

Fig. 2. Schematic diagram of the energy levels and the transition probabilities for a four-spin-level system.

(b) Four-level System (J=1/2). We first treat the four-level system shown in Fig. 2 in order to illustrate the main feature of double resonance relaxation. In the following treatment, we neglect the effects of exchange processes. It is convenient to represent transition probabilities in units of W_e, thus

$$b = \frac{W_n}{W_e},\quad b_{x1} = \frac{W_{x1}}{W_e},\quad b_{x2} = \frac{W_{x2}}{W_e},$$

$$p_e = \frac{P_e}{W_e},\quad p_n = \frac{P_n}{W_e}. \qquad (17)$$

TABLE 1. CONDUCTION MATRIX FOR A FOUR-LEVEL SYSTEM

For ENDOR enhancement, either p_n or p_n' is set to 0.

For ELDOR reduction, both p_n and p_n' are set to 0.

$$\begin{pmatrix} -(1+b+b_{x1}+p_e+p_n) & (\varepsilon+p_e) & (b+p_n) & b_{x1}\varepsilon \\ (1+p_e) & -(\varepsilon+b+b_{x2}+p_e+p_n') & b_{x2} & (b+p_n') \\ (b+p_n) & b_{x2} & -(1+b+b_{x2}+p_n+p_e') & (\varepsilon+p_e') \end{pmatrix}$$

TABLE 2. COEFFICIENTS IN Eq. 19

A_0, E_0: $1+2b+(1+b)(b_{x1}+b_{x2})+b_{x1}b_{x2}+(2+b_{x1}+b_{x2})p_n'$;
A_1: $1+b_{x2}$; B_0, F_0: $(1+b)\{2b+(1+b)(b_{x1}+b_{x2})+2b_{x1}b_{x2}\}+\{1+2b+(1+b)(b_{x1}+b_{x2})+b_{x1}b_{x2}\}p_n'$;
B_1: $2b+(1+b)(b_{x1}+b_{x2})+2b_{x1}b_{x2}+(1+b_{x1})p_n'$;
C_0: $1+b+b_{x1}+p_n$;
C_1: 1;
D_0: $b(2+b)+(1+b)(b_{x1}+b_{x2})+b_{x1}b_{x2}+(1+b+b_{x2})p_n'$;
D_1: $2b+b_{x1}+b_{x2}+p_n'$;
E_1: $1+b+b_{x2}+p_n'$;
F_1: $b(2+b)+(1+b)(b_{x1}+b_{x2})+b_{x1}b_{x2}+(1+b+b_{x1})p_n'$.

Note that $p_e=\gamma_e^2H_1^2T_{2e}/2W_e \approx \gamma_e^2H_1^2T_{1e}T_{2e}$ at the ESR resonance. Then, using the conduction matrix listed in Table 1, we obtain the difference in the spin population numbers between the 1 and 2 spin levels in the form

$$n = n_0\frac{Ap_n+B}{(Cp_n+D)p_e+Ep_n+F}\frac{F}{B}, \tag{18}$$

with

$$A = A_0+A_1p_e',\ B = B_0+B_1p_e', \cdots, F = F_0+E_1p_e', \tag{19}$$

$A_0, A_1, \cdots\cdots, F_0, F_1$ being listed in Table 2. n_0, the difference in the spin population numbers in the absence of alternating fields, is related by $n_0=(1-\varepsilon)N/4$ and by

$$M_0 = \chi_0H_0 = \frac{1}{2}\gamma_e\hbar n_0 = \frac{N'\gamma_e^2\hbar^2}{4kT} \qquad \left(N' = \frac{N}{2}\right). \tag{20}$$

Complete hf Separation ($P_e'=0$ or $\Delta\omega=\infty$). Using Eqs. 6 and 18, Eq. 13 can be expressed as a saturated Lorentzian, thus

$$I = \frac{1}{2}\chi_0H_0\frac{\gamma_eH_1T_{2e}}{1+T_{2e}^2(\omega_e-\omega_{e0})^2+\gamma_e^2H_1^2T_{1e}(\mathrm{ON})T_{2e}}, \tag{21}$$

where $T_{1e}(\mathrm{ON})$ is the effective longitudinal relaxation time of an electron spin under NMR excitation:

$$T_{1e}(\mathrm{ON}) = \frac{1}{2W_e}\frac{C_0p_n+D_0}{A_0p_n+B_0}. \tag{22}$$

Note that when $W_n=W_{x1}=W_{x2}=0$, $T_{1e}(\mathrm{ON})=1/2W_e$. Then,

$$I_{\mathrm{ESR}} = \frac{3\sqrt{3}}{16}\chi_0H_0\frac{\gamma_eH_1T_{2e}^2}{\{1+\gamma_e^2H_1^2T_{1e}(\mathrm{ON})T_{2e}\}^{3/2}}, \tag{23}$$

$$I_{\mathrm{ENDOR}} = \frac{9\sqrt{3}}{32}\chi_0H_0\frac{\gamma_e^3H_1^3T_{2e}^3\Delta T_{1e}}{\{1+\gamma_e^2H_1^2T_{1e}(\mathrm{ON})T_{2e}\}^{5/2}}, \tag{24}$$

and

$$E = \frac{3}{2}\frac{\gamma_e^2H_1^2\Delta T_{1e}T_{2e}}{1+\gamma_e^2H_1^2T_{1e}(\mathrm{ON})T_{2e}}, \tag{25}$$

where $\Delta T_{1e}=T_{1e}(\mathrm{OFF})-T_{1e}(\mathrm{ON})$ and Eq. 23 is expanded to the first order in ΔT_{1e} to give Eq. 24. If $\gamma_e^2H_1^2T_{1e}T_{2e}\gg 1$, then

$$E_\infty = \frac{3}{2}\frac{\Delta T_{1e}}{T_{1e}} = E_{\infty\infty}\frac{p_n}{p_n+D_0/C_0}, \tag{26}$$

where

$$E_{\infty\infty} = \frac{3}{2}\frac{\{b(1+b_{x2})+b_{x2}(1+b_{x1})\}^2}{(1+b)(1+b+b_{x1})\{2b+(1+b)(b_{x1}+b_{x2})+2b_{x1}b_{x2}\}}. \tag{27}$$

Equation 26 also justifies the conventional interpretation that ENDOR measures the variation in the longitudinal electron spin relaxation time by NMR excitation. Substitution of Eq. 7 into Eq. 26 again gives a saturated Lorentzian for the NMR transition, thus

$$E_\infty = E_{\infty\infty}\frac{\gamma_n^2H_2^2T_{1n}T_{2n}}{1+T_{2n}^2(\omega_n-\omega_{n0})^2+\gamma_n^2H_2^2T_{1n}T_{2n}}, \tag{28}$$

with the effective nuclear spin longitudinal relaxation time

$$T_{1n} = \frac{1}{2W_n}\frac{C_0}{D_0}. \tag{29}$$

Note that if $W_e=W_{x1}=W_{x2}=0$, then $T_{1n}=1/2W_n$.

Incomplete hf Separation. In this case, the ESR absorption line is neither expressed by a simple Lorentzian curve nor by superposition of such curves. Therefore, it is more convenient to define the fractional ENDOR enhancement by the following equation, using Eq. 12 at the ESR resonance:

$$E = \frac{n(\mathrm{ON})-n(\mathrm{OFF})}{n(\mathrm{OFF})}. \tag{30}$$

In addition, we restrict our discussion to the case of an electron-nuclear dipolar (END) mechanism and we neglect the cross relaxations to avoid complexity. Such an approximation may well be satisfied for protons in most of the organic radicals in solution except for some cases in which isotopic hf modulation may be effective.[9,13] A straight forward calculation of Eq. 30 gives

$$\begin{aligned}E=&(1-\alpha)b(1+\alpha p_e)p_np_e[2(1+b+\alpha p_e)[\{2(1+b)\\&+(1+\alpha)(2+b)p_e+2\alpha p_e^2\}b+\{1+2b\\&+(1+\alpha)(1+b)p_e+\alpha p_e^2\}p_n]]^{-1}.\end{aligned} \tag{31}$$

For further analysis, the reciprocal of the above equation is expanded to the first order in p_e, thus

$$\begin{aligned}\frac{1}{E} =& \frac{2}{(1-\alpha)bp_np_e}[(1+b)\{2b(1+b)+p_n(1+2b)\}\\&+(b\{(1+b)(2+b)+\alpha(2+b-b^2)\}\\&+p_n\{(1+b)^2+\alpha(1+b-b^2)\})p_e+\alpha\mathrm{O}(p_e^2)].\end{aligned} \tag{32}$$

Hence, we obtain a straight line in plotting E^{-1} *vs.* p_e^{-1}, in the region where we can neglect the quadratic terms for p_e which can be proven to be proportional to α. The reciprocal of the intercept in this plot is thus expressed as

$$\begin{aligned}E_\infty=&(1-\alpha)bp_n/2[\{(1+b)(2+b)+\alpha(2+b-b^2)\}b\\&+\{(1+b)^2+\alpha(1+b-b^2)\}p_n]^{-1}.\end{aligned} \tag{33}$$

Also, the intercept divided the slope become proportional to the product of T_{2e} and T_{1e}, the latter being expressed, in this case, as

$$\begin{aligned}T_{1e} =& \left(\frac{1}{2W_e}\right)b\{(1+b)(2+b)+\alpha(2+b-b^2)\}\\&+p_n\{(1+b)^2+\alpha(1+b-b^2)\}\\&[(1+b)\{2b(1+b)+p_n(1+2b)\}]^{-1}.\end{aligned} \tag{34}$$

Substitution of Eq. 7 into Eq. 33 again gives a saturated Lorentzian for the NMR transition, with

$$T_{1n} = \frac{1}{2W_n}\frac{(1+b)^2+\alpha(2+b-b^2)}{(1+b)(2+b)+\alpha(2+b-b^2)}. \tag{35}$$

Then, we obtain a straight line in plotting E^{-1} *vs.* p_n^{-1}.

Equation 31, as well as Eq. 33, is still of too complicated a form for practical use. One may generally consider that a proton with a small hfs (or large α) has a small END term (or small b) and *vice versa*, as deduced from the McConnell-Strathdee formula.[18] If $b\ll 1$, the linear part of Eq. 32 can be written as

$$E = \frac{(1-\alpha)p_e}{1+(1+\alpha)p_e}\,\frac{bp_n}{2(2b+p_n)}. \tag{36}$$

Hence, the effect of incomplete hf separation reduces the fractional ENDOR enhancement by the following factors, depending on p_e:

(i) for small p_e by $T_{2e}^2\Delta\omega^2/(1+T_{2e}^2\Delta\omega^2)$

(ii) at the ESR maximum ($p_e=1/2$) by $T_{2e}^2\Delta\omega^2/\{(4/3)+T_{2e}^2\Delta\omega^2\}$

(iii) at the ENDOR maximum ($p_e=3/2$) by $T_{2e}^2\Delta\omega^2/\{(8/5)+T_{2e}^2\Delta\omega^2\}$

(iv) and at infinite p_e by $T_{2e}^2\Delta\omega^2/(2+T_{2e}^2\Delta\omega^2)$.

On the other hand, if $\alpha=0$, Eq. 33 becomes

$$E_\infty^{(0)} = \frac{1}{2}\,\frac{bp_n}{b(1+b)(1+2b)+p_n(1+b)^2}, \tag{37}$$

which coincides with the Freed equation. Note that Eq. 37 also coincides with Eq. 27, except for a trival numerical factor, if p_n is set to infinity. Therefore, an inspection of the above two equations allows us to express approximately the fractional ENDOR enhancement as a formula including correlation of the modified Allendoerfer-Maki type and the Freed formula for $b\lesssim 1$, thus

$$E = \frac{(1-\alpha)p_e}{1+(1+\alpha)p_e}E_\infty^{(0)}. \tag{38}$$

From an experimental point of view, it is desirable to use the mw power at the ESR maximum for ENDOR signals with good S/N ratios. The maximum deviation of Eq. 38 from the linear part of Eq. 32 under these conditions is 6%, for $\alpha=1$ and $b=1$.

(c) Multi-level System—a Simplified Method. The ESR absorption line of an actual molecule is formed by the superposition of its component lines, designated by the various quantum numbers of the total nuclear spin angular momentum.[19] Therefore, for quantitative discussions of the ENDOR relaxation, we must proceed to a multi-level system consisting of several sets of equivalent protons. Treatment of this system along same lines as the scheme in (*b*) may be possible, in principle, but is too complicated and deviates from the purpose of the present work. Instead, a simplified method for calculating the fractional ENDOR enhancement for such a system is proposed with the following approximations and derivations.

In this system, the spin state is represented by

$$|\gamma\pm\rangle = |\pm\tfrac{1}{2}\rangle\prod_{u}|J_u^{(\kappa)}M_u\rangle, \tag{39}$$

where J_u and M_u are the quantum numbers of the total nuclear angular momentum for the u'th set of equivalent protons and κ denotes the different degenerate states with the same value of J_u. Now, we assume that T_{2e} is independent of J_u and M_u, so that the ESR absorption is expressed as a superposition of component lines with the same linewidth, corresponding to the transitions from $|\gamma-\rangle$ to $|\gamma+\rangle$. On the other hand the nuclear spin transition probabilities are dependent on the nuclear spin quantum numbers, as follows:[5]

$$1/T_{2n}(J_n, M_u \leftrightarrow J_u, M_u-1) = W_e\left[1+\left\{2f(J_u, M_u)+\frac{1}{3}\right\}b_u\right], \tag{40}$$

$$W_n(J_u, M_u \leftrightarrow J_u, M_u-1) = f(J_u, M_u)W_n^{(u)}, \tag{41}$$

and

$$P_n(J_u, M_u \leftrightarrow J_u, M_u-1) = f(J_u, M_u)P_n^{(u)}, \tag{42}$$

where $W_n^{(u)}$ and $P_n^{(u)}$ are the nuclear spin transition probabilities for a four-level system consisting of a single u'th proton, and with

$$f(J_u, M_u) = J_u(J_u+1) - M_u(M_u-1), \tag{43a}$$

and

$$f\left(J_u, 0 \text{ or } \frac{1}{2}\right) \equiv f_{J_u}. \tag{43b}$$

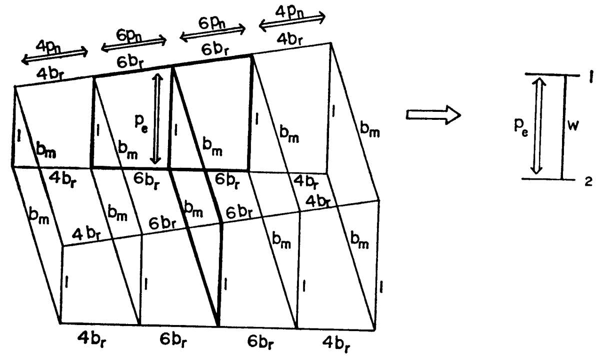

Fig. 3. Schematic diagram of the energy levels and the transition probabilities for a system with $J_m=1/2$ and $J_r=2$. The cetral line of the each quintet of the ESR absorption is observed, and the rf power corresponding to the hfs of the r'th equivalent protons is irradiated. Left side diagram draws an equivalent two-spin-level system corresponding to the relaxation pathways with thick line.

Next, we neglect the relaxation pathways passing more than twice through the W_n's, under the assumption that $b\ll 1$. For example, for the system with $J_m=1/2$ and $J_r=2$ illustrated in Fig. 3, only the relaxation pathways with thick lines are considered. Then, all of the multi-level systems are reduced to a superposition of the maximum six-level systems. This can further be reduced to the two-level system illustrated in the right side of Fig. 3, using a summing method for the electric conduction. The energy of the ESR absorption for this system is easily obtained as

$$A = \frac{n_0\hbar\omega_e WP_e}{2(W+P_e)}, \tag{44}$$

so that the spin lattice relaxation becomes the rate-determining step of the energy absorption, if P_e is set to infinity. Therefore, the fractional ENDOR enhancement, corresponding to Eq. 37, is expressed as

$$E^{(0)} = \frac{w(\text{ON})-w(\text{OFF})}{w(\text{OFF})}, \quad \left(w=\frac{W}{W_e}\right). \tag{45}$$

For actual application it is sufficient only to treat the central line of the ESR absorption. In this case, the summing method leads to the following resultant transition probability for an electron spin:

$$w = 1 + \sum_{u}\sum_{J_u}\frac{D_{J_u}}{D_u}\,\frac{2f_{J_u}(b_u+p_n^{(u)})}{(f_{J_u}+2)b_u+(f_{J_u}+1)p_n^{(u)}}$$

$$+\sum_{\mathrm{u}'}\sum_{J_{\mathrm{u}'}}\frac{D_{J_{\mathrm{u}'}}}{D_{\mathrm{u}'}}\left[\frac{(f_{J_{\mathrm{u}'}}-1)b_{\mathrm{u}'}(b_{\mathrm{u}'}+p_{\mathrm{n}}^{(\mathrm{u}')})}{\{2+(f_{J_{\mathrm{u}'}}-1)b_{\mathrm{u}'}\}b_{\mathrm{u}'}+\{1+(f_{J_{\mathrm{u}'}}-1)b_{\mathrm{u}'}\}p_{\mathrm{n}}^{(\mathrm{u}')}}\right.$$
$$\left.+\frac{f_{J_{\mathrm{u}'}}b_{\mathrm{u}'}(b_{\mathrm{u}'}+p_{\mathrm{n}}^{(\mathrm{u}')})}{(2+f_{J_{\mathrm{u}'}}b_{\mathrm{u}'})b_{\mathrm{u}'}+(1+f_{J_{\mathrm{u}'}}b_{\mathrm{u}'})p_{\mathrm{n}}^{(\mathrm{u}')}}\right], \qquad (46)^{*}$$

where u and u′ denote even and odd numbers equivalent protons, respectively, D_{u} is the total degeneracy of the central absorption line of the u'th set of equivalent protons, and $D_{J_{\mathrm{u}}}$ is the degeneracy of the state with the same value of J_{u}. These are given by

$$D_{J_{\mathrm{u}}}=\frac{n_{\mathrm{u}}(n_{\mathrm{u}}-1)\cdots\{(n_{\mathrm{u}}/2)-J_{\mathrm{u}}+1\}(2J_{\mathrm{u}}+1)}{\{(n_{\mathrm{u}}/2)+J_{\mathrm{u}}+1\}!}, \qquad (47)$$

$$D_{\mathrm{u}}=\sum_{J_{\mathrm{u}}}D_{J_{\mathrm{u}}}=\binom{n_{\mathrm{u}}}{[n_{\mathrm{u}}/2]}, \qquad (48)$$

where n_{u} is the number of u'th equivalent protons.

It can also be proven that for a six-level system for which the hfs is incompletely separated, a calculation similar to Eq. 30 leads to the same form of the fractional ENDOR enhancement as Eq. 38. Therefore, it is considered that Eq. 38 is still valid for general multi-level systems, as long as the above approximation of treating them as the superposition of maximum six-level systems is valid. Hence, we obtain the following limiting expressions for the fractional ENDOR enhancement of the u'th proton, corresponding to Eq. 38. If p_{n} is set to infinity, then

$$E_{,\infty}^{(\mathrm{u})}=\frac{(1-\alpha)p_{\mathrm{e}}}{1+(1+\alpha)p_{\mathrm{e}}}\sum_{J_{\mathrm{u}}}\frac{D_{J_{\mathrm{u}}}}{D_{\mathrm{u}}}\frac{2f_{J_{\mathrm{u}}}b_{\mathrm{u}}}{(1+f_{J_{\mathrm{u}}}b_{\mathrm{u}})(2+f_{J_{\mathrm{u}}}b_{\mathrm{u}})}/w(\mathrm{OFF}) \qquad (49)$$

for an even number of equivalent protons. Also, if p_{n} approaches 0, then

$$E_{,0}^{(\mathrm{u})}=\frac{(1-\alpha)p_{\mathrm{e}}}{1+(1+\alpha)p_{\mathrm{e}}}\sum_{J_{\mathrm{u}}}\frac{D_{J_{\mathrm{u}}}}{D_{\mathrm{u}}}\frac{2f_{J_{\mathrm{u}}}p_{\mathrm{n}}^{(\mathrm{u})}}{(2+f_{J_{\mathrm{u}}}b_{\mathrm{u}})^{2}}/w(\mathrm{OFF}). \qquad (50)$$

For an odd number of equivalent protons,

$$E_{,\infty}^{(\mathrm{u}')}=\frac{(1-\alpha)p_{\mathrm{e}}}{1+(1+\alpha)p_{\mathrm{e}}}\sum_{J_{\mathrm{u}'}}\frac{D_{J_{\mathrm{u}'}}}{D_{\mathrm{u}'}}\left[\frac{f_{J_{\mathrm{u}'}}}{(1+f_{J_{\mathrm{u}'}}b_{\mathrm{u}'})(2+f_{J_{\mathrm{u}'}}b_{\mathrm{u}'})}\right.$$
$$\left.+\frac{f_{J_{\mathrm{u}'}}-1}{\{1+(f_{J_{\mathrm{u}'}}-1)b_{\mathrm{u}'}\}\{2+(f_{J_{\mathrm{u}'}}-1)b_{\mathrm{u}'}\}}\right]b_{\mathrm{u}'}/w(\mathrm{OFF}). \qquad (51)$$

$$E_{,0}^{(\mathrm{u}')}=\frac{(1-\alpha)p_{\mathrm{e}}}{1+(1+\alpha)p_{\mathrm{e}}}\sum_{J_{\mathrm{u}'}}\frac{D_{J_{\mathrm{u}'}}}{D_{\mathrm{u}'}}\left[\frac{f_{J_{\mathrm{u}'}}}{(2+f_{J_{\mathrm{u}'}}b_{\mathrm{u}'})^{2}}\right.$$
$$\left.+\frac{f_{J_{\mathrm{u}'}}-1}{\{2+(f_{J_{\mathrm{u}'}}-1)b_{\mathrm{u}'}\}^{2}}\right]p_{\mathrm{n}}^{(\mathrm{u}')}/w(\mathrm{OFF}). \qquad (52)$$

Equations 49 and 51 and Eqs. 50 and 52 correspond approximately to the reciprocal of the intercept and that of the slope of the plot of E^{-1} *vs*. p_{n}^{-1}, respectively. The linearity of this plot is approximately assured, because, in general, if $x \ll r_i/q_i$,

$$y=\sum_{i}\frac{p_i x}{q_i x+r_i}\simeq\frac{\sum_{i}(p_i/q_i)^2 x}{\sum_{i}(p_i/q_i)x+\sum_{i}(p_i r_i/q_i^2)}. \qquad (53)$$

Application of Eqs. 47 and 48 to a four-level system leads, of cource, to the same result as Eq. 38 with Eq. 37. Because $\sum_{J_{\mathrm{u}}} f_{J_{\mathrm{u}}}D_{J_{\mathrm{u}}}/D_{\mathrm{u}}=n_{\mathrm{u}}/2$, the above equations can further be reduced to more simplified forms, if we can neglect the quadratic terms for b_{u}, thus

$$E_{,\infty}^{(\mathrm{u})}\simeq\frac{(1-\alpha)p_{\mathrm{e}}}{1+(1+\alpha)p_{\mathrm{e}}}\frac{n_{\mathrm{u}}b_{\mathrm{u}}}{2}, \qquad (54)^{**}$$

$$E_{,0}^{(\mathrm{u})}\simeq\frac{(1-\alpha)p_{\mathrm{e}}}{1+(1+\alpha)p_{\mathrm{e}}}\frac{n_{\mathrm{u}}p_{\mathrm{n}}^{(\mathrm{u})}}{4}. \qquad (55)^{**}$$

Considering that from Eq. 36, $p_{\mathrm{n}}^{(\mathrm{u})}$ is independent of u under this condition, Eq. 55 indicates that the fractional ENDOR enhancement is proportional to the number of equivalent protons, if $\alpha=0$ and enough weak rf power is irradiated. This conclusion is the same as the result of the "average ENDOR" proposed by Freed *et al.*[3]

Although ENDOR experiments have been reported in the literature for many radicals in solution since the first successful observation by Hyde and Maki,[20] ENDOR detection for many radicals remains impossible or at least difficult, in spite of the ease of ESR observation. Perhaps, Heisenberg and chemical exchange may be the reason. However, Eqs. 49—52 may offer an additional reason. In these equations, all the END terms of atoms with nuclear spins make contributions to the denominator, w(OFF), whereas only that of the observed proton makes a contribution to the numerator. Therefore, if a radical contains atoms with nuclear spins on which the electron spin density is moderately localized resulting in a large END term, one may observe only weak ENDOR enhancement. This may be a possible reason why ENDOR enhancement for hydrocarbon radicals is, in general, more easily observed than that for nitroxide radicals.

Summary

A simple theory has been formulated to calculate the fractional ENDOR enhancement (E) in the presence of the effect of incomplete hf separation, using the conduction matrix composed of the lattice-induced transtition probabilities and the alternating field-induced transition probabilities, the latter being assumed to be a Lorentzian. The coefficient of incomplete hf separation, α, has been introduced and it is shown that a plot of E^{-1} *vs*. H_1^2 results in a straight line even in the presence of this effect, if $\alpha p_{\mathrm{e}} \ll 1$, where p_{e} is the mw-induced transition probability in units of W_{e}. Also, it is shown that the effect of incomplete hf separation reduces the fractional ENDOR enhancement formulated by Freed, by an Allendoerfer-Maki type factor. However, this factor should be modified to $T_{2\mathrm{e}}^2\Delta\omega^2/\{(4/3)+T_{2\mathrm{e}}^2\Delta\omega^2\}$ at the mw power corresponding to the ESR maximum.

The theory has been extended to a multi-level system consisting of several sets of equivalent protons and it is shown that the plot of E^{-1} *vs*. H_2^{-2} also results in a straight line and that the reciprocal of the slope in this plot is proportional to the number of equivalent protons, if $\alpha=0$ and $b \ll 1$. Thus, the effect of incomplete hf separation should be examined by the following procedure. The H_2 dependence of the ENDOR enhance-

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* $\sum_{J_{\mathrm{u}}}$ denotes the single summation over the u'th set of equivalent protons.

** In this case, u denotes odd and even numbers of equivalent protons.

ment is measured at high temperatures of which $b \ll 1$ is satisfied for all protons. E^{-1} is plotted against H_2^{-2}, and the reciprocal of the slope divided by the number of equivalent protons is compared with the proton species.

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Appendix

TRIPLE Enhancement. Recently, Möbius and coworkers were the first to succeed in observing electron-nuclear triple resonance (TRIPLE) in solution.[12] The most attractive results of their experiments are that TRIPLE enhancement has a better S/N ratio than does ENDOR enhancement and that TRIPLE enhancement is proportional to the number of equivalent protons.

It is worthwhile to interpret TRIPLE enhancement from the standpoint of the present theory. The fractional TRIPLE enhancement is defined by Eq. 30, where OFF means, in this case, that P_e is present but P_n and P_n' are absent, and ON means that P_e, P_n and P_n' are all present. Straightforward calculation gives the following expression for the fractional TRIPLE enhancement for a four-level system, where hf is incompletely separated and $P_n = P_n'$, thus

$$\begin{aligned} E_t = (1-\alpha)p_e p_n (1+\alpha p_e)(b+p_n)[(1+b+\alpha p_e)[\{p_n^2 \\ +2(1+b+\alpha p_e)p_n + b(2+b+2\alpha p_e)\}p_e \\ +(2+\alpha p_e)p_n^2 + 2\{1+2b+(1+b)\alpha p_e\}p_n \\ +b\{2+2b+(2+b)\alpha p_e\}]]^{-1}. \end{aligned} \tag{A1}$$

The above equation indicates that the effect of incomplete hf separation also reduces TRIPLE enhancement and that if $\alpha = 0$, TRIPLE enhancement has a S/N ratio eight times larger than does ENDOR enhancement, when Eq. A1 is compared with Eq. 37 at their optimum conditions. Indeed, the TRIPLE enhancement for 2,6-*di*-*t*-butyl protons in the 2,4,6-*tri*-*t*-butylphenoxyl radical[12] appears to support the presence of this effect.

For a multi-level system, we start with Eq. 45 as the basis of discussion. However, because P_n and P_n' are simultaneously excited, even the previous approximation to reduce a multi-level system to a superposition of the maximum six-level system is not valid. Instead, we consider the entire system in the extreme cases that $P_n = P_n' = 0$ (OFF) and that $P_n = P_n' = \infty$ (ON), under the condition that $b \ll 1$. In the former case, all the relaxation pathways are cut off except for the original two-level system (W_e). In the latter case, all the W_n pathways are completely short-circuited by P_n and P_n', so that all the W_e pathways are gathered to form a net twe-level system. Thus,

$$w(\mathrm{ON}) = \sum_{J_u} \frac{D_{J_u}}{D_u}(2J_u+1), \tag{A2}$$

with $w(\mathrm{OFF}) = 1$. Hence, the fractional TRIPLE enhancement is given by

$$E_t^{(u)} = \sum_{J_u} \frac{D_{J_u}}{D_u} 2J_u. \tag{A3}$$

Such a simple formula appears to explain fairly well the experimental results demonstrated by Möbius *et al.* For example, the ratio of the TRIPLE enhancement for 4,5,9,10-protons to that for 1,7-protons in the pyrene negative ion is obtained from Eq. A3 as 1.67, whereas the experimental ratio is 1.3 and the ratio of the number of equivalent protons is 2.

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17) According to the Freed theory presented in Ref. 3, $Z''_{a'a}$, which determines the energy of the ESR absorption and the line shape, is obtained by solving the system of simultaneous equations 4.5a—4.6e of that paper. Then, the fractional ENDOR enhancement is given by $E = \{Z''_{a'a}(\mathrm{ON}) - Z''_{a'a}(\mathrm{OFF})\}/Z''_{a'a}(\mathrm{OFF})$. It is possible to calculate $Z''_{a'a}$ using an approximate method instead of the exact solution of the complicated equations. First, the coherence effect is neglected, so that Eq. 4.5c and the third term on the left-hand side of Eq. 4.5a and b are neglected. Next, the second terms on the left-hand sides of both equations are tentatively neglected. Then, both $Z''_{a'a}$ and $Z''_{a'b'}$ become Lorentzian, and both are substituted into Eq. 4.6. $\chi_a - \chi_{a'}$, thus obtained, is again substituted into Eq. 4.5a in exact form, and finally $Z''_{a'a}$ is calculated. This procedure certainly corresponds to the present approach.

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