ESR LINESHAPES AND SATURATION IN THE SLOW MOTIONAL REGION: ELDOR*

G.V. BRUNO† and J.H. FREED
Department of Chemistry, Cornell University, Ithaca, New York 14850, USA

Received 28 November 1973

It is shown how the stochastic Liouville approach of Freed, Bruno, and Polnaszek for describing ESR lineshapes in the slow motional region may be applied to the ELDOR experiment. It is possible, in the slow motional region, to pump with a saturating microwave field at one resonant frequency corresponding to a particular orientation and observe effects from the rotational motion in transmitting the saturation to another resonant position. Some effects are illustrated by simulation of ELDOR spectra for a simple ESR line in the slow motional region.

1. Introduction

Freed et al. [1] (I) have presented a detailed theoretical analysis of ESR lineshapes and saturation in the slow-motional region based upon the stochastic Liouville method. These analyses have been carefully tested in a series of experiments [2–4] and they were found to be very successful in predicting slow-tumbling spectra from nitroxide radicals. Analyses of unsaturated spectra were able not only to permit determinations of rotational correlation times, but also were found to shed light on the detailed molecular dynamics of the reorientational process [2, 4]. On the basis of this work, it has also been possible to develop simplified methods of spectral analysis in terms of the outer hyperfine extrema, for estimating τ_R [5, 6]. Analysis of slow tumbling saturated spectra has allowed the extraction of W_e, the lattice-induced electron-spin flip rate from such experiments [3].

Electron–electron double resonance (ELDOR) is a useful technique, which is an extension of the saturation method [7]. One saturates (or pumps) at one spectral position, and observes with a usually weak observing signal at another spectral position. In the past, the ELDOR method has usually been applied to pumping a single hyperfine line and observing its effect on a different line, and this provides information on W_n, the lattice-induced nuclear spin-flip rate. ELDOR in the slow tumbling region is of particular interest, because it should, under appropriate conditions, provide direct information on the reorientational rate. That is, for the simplest case of a single line (broadened by a symmetric g-tensor) the resonant frequency, for slow motion, is determined by its orientation; thus the effects that a saturating pump microwave field at a particular resonant frequency will have at another observing resonant position will be due to the rotational motion of the molecule. By analogy with the motional narrowing ELDOR where the ratio $b \equiv W_n/W_e$ or $b' \equiv \omega_{HE}/W_e$ (ω_{HE} is the Heisenberg exchange frequency) *and* the selection rules are important [7], we expect for slow-tumbling ELDOR the ratio τ_R^{-1}/W_e and the reorientational model to be important as well as aspects of the shape of the unsaturated spectrum.

We present here in the spirit of I, a theoretical analysis for this experiment, and we emphasize the simple single-line case for which the only source of an ELDOR signal would be the transfer of saturation from one portion of the spectrum to the other parts by the reorientation process. We avoid giving excessive computational detail as that may be found elsewhere [8], and we take advantage of the detailed discussions in I.

* Supported in part by the National Science Foundation (Grant No. GP-13780) and the Materials Science Center, Cornell University.

† Present address: Department of Chemistry, Stanford University, Palo Alto, California 94305, USA.

2. Analysis

As in I, we expand the absorption, $\mathrm{Im}Z_\lambda^{(1)}(\Omega,\omega)$, and the deviation of the population difference from its equilibrium value, $\Delta\chi^{(0)}(\Omega,\omega)$, in terms of eigenfunctions of the rotational-diffusion equation; i.e., the normalized Wigner rotation matrices, $[(8\pi^2)^{-1}(2L+1)]^{1/2}\mathcal{D}^L_{K,M}(\Omega)=G^L_{KM}(\Omega)$, as:

$$Z_\mathrm{o}(\Omega,\omega_\mathrm{o},\omega_\mathrm{p})=\sum_{L,K,M}C^L_{KM}(\mathrm{o})G^L_{KM}(\Omega), \tag{1a}$$

$$Z_\mathrm{p}(\Omega,\omega_\mathrm{o},\omega_\mathrm{p})=\sum_{L,K,M}C^L_{KM}(\mathrm{p})G^L_{KM}(\Omega), \tag{1b}$$

$$\Delta\chi(\Omega,\omega_\mathrm{o},\omega_\mathrm{p})=\sum_{L,K,M}b^L_{KM}G^L_{KM}(\Omega), \tag{1c}$$

where the indices o and p refer to the observing and pump signals; and $C^L_{KM}(\mathrm{o})\equiv C^L_{KM}(\mathrm{o},\omega_\mathrm{o},\omega_\mathrm{p})$ refers to the observing signal expansion coefficient, etc., and ω_o and ω_p are the observing and pump modes, respectively. (We are also dropping indices not needed for the discussion.) One then solves the stochastic Liouville equation [1]:

$$\partial\rho/\partial t=-\mathrm{i}[\mathcal{H}(\Omega),\rho(\Omega,t)]-\Gamma_\Omega\rho(\Omega,t), \tag{2}$$

with Γ_Ω the rotational diffusion operator and the hamiltonian

$$\mathcal{H}(\Omega)=\mathcal{H}_0+\mathcal{H}_1(\Omega)+\epsilon(t), \tag{3}$$

with the orientation-dependent perturbation

$$\mathcal{H}_1(\Omega)=\mathcal{F}\mathcal{D}^2_{0,0}(\Omega)S_z \tag{4a}$$

and

$$\mathcal{F}=\tfrac{2}{3}(\beta_e B_0/\hbar)(g_\parallel-g_\perp). \tag{4b}$$

For ELDOR one has:

$$\epsilon(t)=d_\mathrm{p}[S_+\exp(-\mathrm{i}\omega_\mathrm{p}t)+S_-\exp(\mathrm{i}\omega_\mathrm{p}t)]$$
$$+d_\mathrm{o}[S_+\exp(-\mathrm{i}\omega_\mathrm{o}t)+S_-\exp(\mathrm{i}\omega_\mathrm{o}t)], \tag{5}$$

where $d_\mathrm{o}=\frac{1}{2}\gamma_e B_\mathrm{o}$ and $d_\mathrm{p}=\frac{1}{2}\gamma_e B_\mathrm{p}$ are the strengths of the observing and pump microwave fields respectively. Then, in a manner very similar to the solution for steady-state saturation [1], one has:

$$[(\omega_\alpha-\omega_\mathrm{e})-\mathrm{i}(T_{2,a}^{-1}+\tau_L^{-1})]C^L_{0,0}(\alpha)$$
$$-(\mathcal{F}+\mathrm{i}T_{2,b}^{-1})\sum N(L,L')\begin{pmatrix}L&2&L'\\0&0&0\end{pmatrix}^2C^{L'}_{0,0}(\alpha)$$
$$+2^{1/2}d_\mathrm{p}b^L_{0,0}=q\omega_\mathrm{e}d_\alpha\delta_{L,0}, \tag{6}$$

where $\alpha=$ o or p, and

$$-\mathrm{i}[T_{1,a}^{-1}+\tau_L^{-1}]b^L_{0,0}-\mathrm{i}T_{1,b}^{-1}\sum_{L'}N(L,L')\begin{pmatrix}L&2&L'\\0&0&0\end{pmatrix}^2b^{L'}_{0,0}$$
$$+2^{1/2}\sum_{\alpha=\mathrm{o,p}}d_\alpha\mathrm{Im}C^L_{0,0}(\alpha)=0. \tag{7}$$

Also, the observing absorption line shape is given by:

$$(1/8\pi^2)\int\mathrm{Im}Z_\mathrm{o}(\Omega,\omega)\mathrm{d}\omega=(1/8\pi^2)^{1/2}\mathrm{Im}C^0_{0,0}(\mathrm{o},\omega_\mathrm{o},\omega_\mathrm{p}). \tag{8}$$

In eqs. (6) and (7) we have ω_e, the Zeeman frequency [resulting from $\mathcal{H}_0$ in eq. (3)], $q=\hbar/4kT$, $N(L,L')=[(2L+1)(2L'+1)]^{1/2}$, and τ_L^{-1} is the Lth eigenvalue of Γ_Ω, which for isotropic brownian diffusion is given by

$$\tau_L^{-1}=RL(L+1), \tag{8a}$$

with R the rotational diffusion constant. In general, we may introduce model-dependent effects by letting

$$\tau_L^{-1}=B_L L(L+1)R, \tag{8b}$$

with the model parameter B_L discussed elsewhere for a variety of models [2, 8]. Also, we have introduced an orientation-independent width $T_{2,a}^{-1}$ and electron-spin flip rate $W_\mathrm{e}=\frac{1}{2}T_{1,a}^{-1}$ as well as orientation-dependent components $T_{2,b}^{-1}\mathcal{D}^2_{0,0}(\Omega)$ and $T_{1,b}^{-1}\mathcal{D}^2_{0,0}(\Omega)$. The nature of the 3j symbols: $\begin{pmatrix}L&2&L\\0&0&0\end{pmatrix}$ is such as to introduce only even values of L into the problem.

Eq. (6) for the signals with $\alpha=$ o or p is seen (by comparison with I) to be identical to the case of simple saturation, while eq. (7) differs only in that the b^L_{KM} representing the "components" of the population differences are coupled to both observing and pump signals.

Note from eq. (7) that $b^0_{0,0}$ representing the average saturation is essentially just relaxed by W_e and not the rotational motion. It is only the non-spherically-

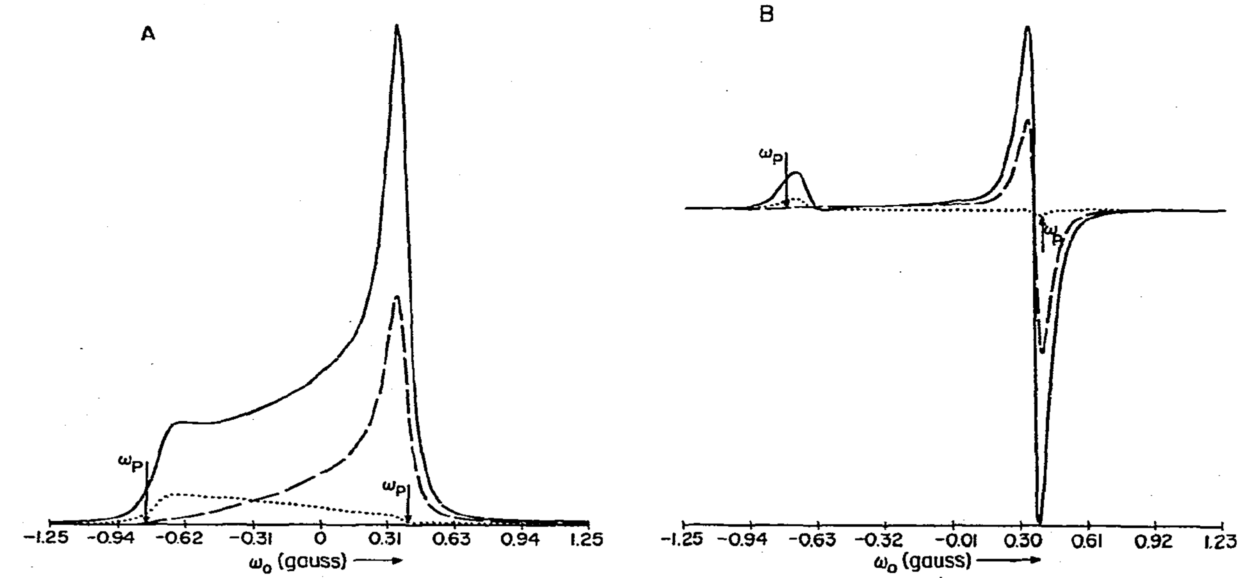

Fig. 1. Observing frequency-sweep ELDOR lineshapes for an axially symmetric g-tensor undergoing isotropic brownian rotational diffusion with $\tau_R = 2.3 \times 10^{-6}$ sec. A – absorption, B – first derivative lineshapes. —— pure ESR; ··· pump on and $\omega_p|\gamma_e| = 0.4$ G; – – –, pump on and $\omega_p|\gamma_e| = -0.8$ G. All have $g_\parallel = 2.00235$, $g_\perp = 2.00310$, $H_0 = 3\,300$ G, $T_{1,a}^{-1} = 1.76 \times 10^5$ sec^{-1}, $(2/\sqrt{3})\,T_{2,a}^{-1}/|\gamma_e| = 0.02$ G, $T_{1,b}^{-1} = T_{2,b}^{-1} = 0$.

symmetric components $b_{0,0}^L$, $L > 0$ which are directly relaxed by the rotational motion, and their relative importance goes as $B_L L(L+1)R/2W_e$.

We have mainly studied prototype cases where $|\mathcal{F}|T_{1,a} \ll 1$ as is normally expected [3] (although cases where $|\mathcal{F}|T_1 \approx 1$ are given in ref. [8]). In general, whenever $T_{1,a} \gg \tau_R$, the resulting ELDOR spectrum had the same line shape as the ESR spectrum except at reduced intensity. In these cases, the pump field develops a steady-state saturation at a particular resonant frequency, which is then transferred by the rotational motion to the other resonant frequencies before any appreciable relaxation to a Boltzmann distribution can occur. This is equivalent to only saturating the $L = 0$ modes in eqs. (6) and (7). However, for $T_{1,a} \lesssim \tau_R$ one observes interesting effects which demonstrate that the saturation is no longer evenly spread over the spectrum.

Some typical results for strong pump saturation are shown in figs. 1–3. We have chosen to display our sample results in terms of simulations performed at constant dc field and fixed ω_p with ω_o swept‡. In these cases, the effects are reminiscent of "hole-burning", due to an incomplete spread of the saturation‡‡. As a result, one observes marked differences in the shapes of the saturated spectra for the different fixed values of ω_p (but with d_p the same). A comparison of figs. 1 and 2 indicates how the ELDOR experiment could aid in evaluating τ_R. These figures correspond to a change in τ_R by a factor of 2. While the unsaturated main peaks of the absorption and derivative spectra are each normalized to the same height in both cases, one has differences in their relative heights with the pump on (for $\omega_p = -0.8$ G). That is, the ELDOR signals are 46% and 54% of the respective heights for τ_R of 2.3 μsec and 5.75 μsec, respectively, representing the fact, that as the rotational motion slows it is

‡ It is shown in ref. [7] that this would tend to be the theoretically most sensitive mode of performing ELDOR. Typical experimental equipment [9] involves sweeping the pump, but by analysis of a sequence of field-swept experiments one may obtain the equivalent of frequency swept (either ω_o or ω_p) results [10]. Our results assume, for simplicity, perfect isolation between observing and pump modes.

‡‡ There is, of course, some off-resonance direct saturation resulting from the strong saturating fields utilized.

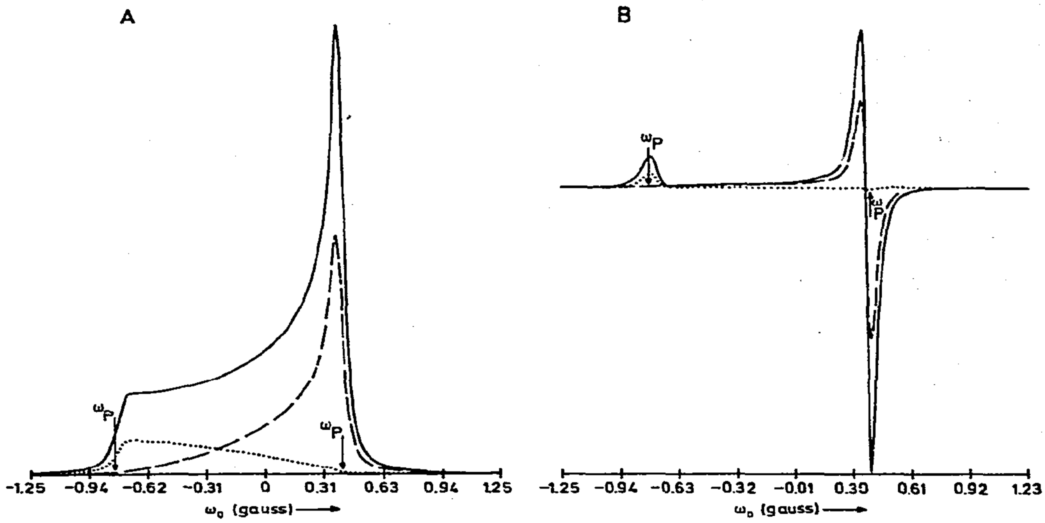

Fig. 2. Observing frequency-sweep ELDOR. All conditions as in fig. 1 except $\tau_R = 5.75 \times 10^{-6}$ sec.

less effective in transmitting the saturation.

An example of the effects of model dependence is given by comparing figs. 1 and 3 for brownian and free diffusion respectively [2] where all other parameters, including τ_R [defined by eq. (8b)] are set equal. Normal brownian diffusion (or reorientation by infinitesimal steps) is characterized by $B_L = 1$ [cf. eq. (8b)] while free diffusion (a crude model including inertial effects and found to yield spectral results equivalent to moderate jump diffusion in previous work [2, 3, 8]) has $B_L = [L(L+1)]^{-1/2}$. One finds here that the ELDOR signals, for the main absorption and derivative peaks, have the *same* heights relative to their unsaturated values, but, in particular, the asymmetries of

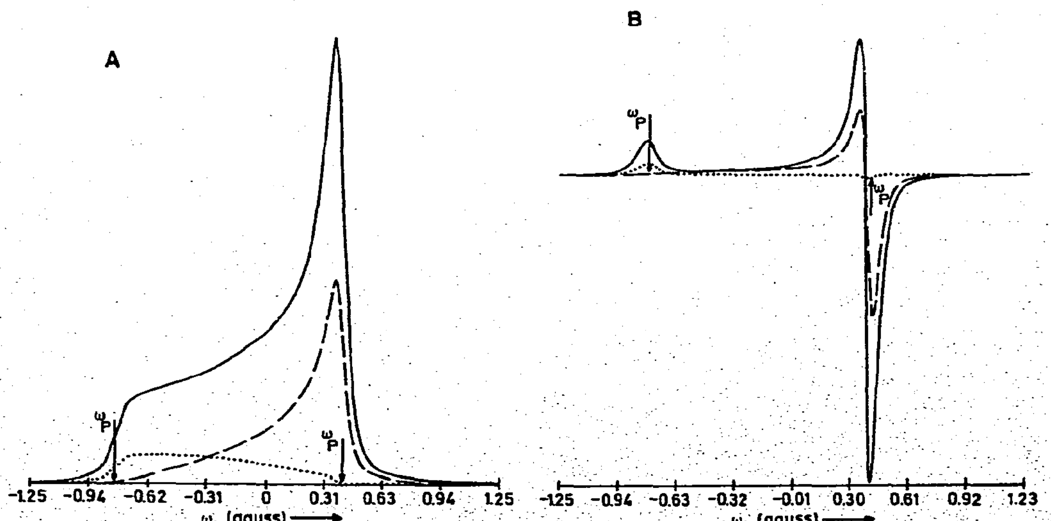

Fig. 3. Observing frequency-sweep ELDOR. All conditions as in fig. 1 except motional model is free diffusion (see text).

the main derivative extrema are different with ratios of high to low field extrema of 1.64 and 2.08 for brownian and free, respectively.

There are of course many other combinations of experimental conditions including pump sweep, pump power effects, etc., and application to other-type spectra†, but in conclusion the main point to be stressed is that ELDOR should prove to be a valuable adjunct to conventional ESR in the slow tumbling region especially where $\tau_R \gtrsim T_I$.

† Ref. [8] gives a discussion of the applications of this method for nitroxides.

References

[1] J.H. Freed, G.V. Bruno and C.F. Polnaszek, J. Phys. Chem. 75 (1971) 3358.
[2] S.A. Goldman, G.V. Bruno, C.F. Polnaszek and J.H. Freed, J. Chem. Phys. 56 (1972) 716.
[3] S.A. Goldman, G.V. Bruno and J.H. Freed, J. Chem. Phys. 59 (1973) 3071.
[4] J.S. Hwang, R.P. Mason and J.H. Freed, to be published.
[5] S.A. Goldman, G.V. Bruno and J.H. Freed, J. Phys. Chem. 76 (1972) 1858.
[6] R.P. Mason and J.H. Freed, J. Phys. Chem., submitted for publication.
[7] J.S. Hyde, J.C.W. Chien and J.H. Freed, J. Chem. Phys. 48 (1968) 4211.
[8] G.V. Bruno, Ph.D. Thesis, Cornell University, Ithaca, New York (1973).
[9] J.S. Hyde, R.C. Sneed Jr. and G.H. Rist, J. Chem. Phys. 51 (1969) 1404.
[10] G.H. Rist and J.H. Freed, to be published.