ELDOR SPIN ECHOES AND SLOW MOTIONS

Joseph P. HORNAK and Jack H. FREED
Baker Laboratory of Chemistry, Cornell University, Ithaca, New York 14853, USA

Received 25 July 1983

It is shown how an ELDOR technique based upon spin echoes and rapid stepping of the magnetic field may be employed to measure rotational correlation times, τ_R for very slow motions. Experiments on PD-Tempone in 85% glycerol/D_2O at low temperatures led to τ_R values of 10^{-4} to 10^{-5} s obtained with a simple analysis of the data.

Electron–electron double resonance (ELDOR) is a useful technique for studying cross-relaxation phenomena [1,2]. While it has typically been applied in the past as a cw technique [2], pulsed ELDOR is relatively unexplored [3,4]. We wish to describe here an ELDOR technique based upon spin echoes which may effectively be used in the study of slow motions.

The use of cw ELDOR for the study of slow motions was suggested some time ago by Bruno and Freed [5], and detailed cw studies and analysis have been performed by Hyde and Dalton [6–8]. The use of spin echoes in such studies has also been suggested previously [9]. The advantages of an echo technique are (1) the absence of the radiation fields (as well as any dc field modulation) during the evolution time of the spins and the (rotational) diffusion of the molecules, (2) the cancellation of effects of inhomogeneous broadening, and (3) the direct measurement of relaxation rates rather than just their ratios are obtained by cw ELDOR. Thus (1) permits a much simpler theoretical analysis (in terms of the stochastic Liouville equation [9–14]), while (2) suggests greater accuracy in data analysis (without having to resort to deuteration of spin labels) [12,15] and (3) removes the need for additional techniques.

The precise technique that we have employed is a stepped-field method [16] in conjunction with a conventional three-pulse $180°-\tau_1-90°-\tau_2-180°-\tau_2$ sequence (spin-echo STELDOR). The first 180° pulse inverts the magnetization at one resonant field H_0, in the spectrum. Then H_0 is rapidly stepped by ΔH_0 to a new region of the spectrum, and the 90°–180° pulses are applied to yield the usual echo at time τ_2 after the last 180° pulse. The timing of the various pulses is shown in fig. 1a. In this experiment τ_1 is varied, while τ_2 is maintained at a fixed value. The echo amplitude, as a function of τ_1 gives the variation of the spin magnetization at the spectral region $H_0 + \Delta H_0$ due to initial inversion of the spins at H_0 (Salikhov [17] and coworkers are using a similar technique). It is thus a direct measure of transfer of spin polarization.

Our electron-spin-echo (ESE) spectrometer is described elsewhere [15,18]. Stepped magnetic fields in the local region of the ESR sample were produced by a coil wound on the inside tube of a variable temperature dewar cavity insert. The geometry of this coil was chosen to keep its capacitance low, and it was epoxied firmly to the dewar to eliminate mechanical vibration during the application of current. A specially constructed pulsed current supply provided the current for driving the coil. It was driven by a variable width and amplitude pulse from a pulse generator triggered by the ESE spectrometer. Several precautions were taken to reduce the rise time of the pulse to a minimum. They include (i) adjusting the rise and fall times of the pulse generator to match the characteristics of the pulsed current supply; (ii) selecting a suitable *RC* combination on the input of the supply to initially overdrive its transistors; (iii) powering the circuit with two 12 V storage batteries; (iv) locating the current pulsing circuit close (≈10 cm) to the coil. A typical STELDOR field pulse is shown in fig. 1b. Current pulses with a risetime of

0 009-2614/83/0000–0000/S 03.00

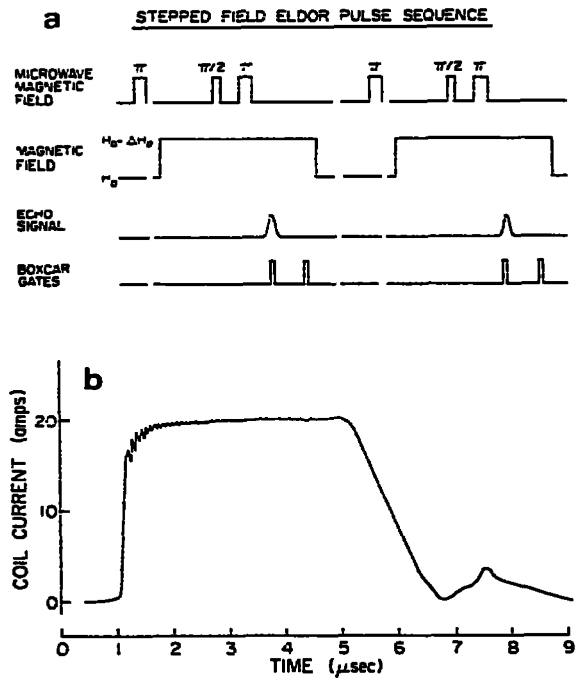

Fig. 1. (a) Pulse sequences for the stepped field ELDOR electron spin echo experiment. The first π pulse is applied at H_0 and the $\pi/2$, π pulses at $H_0 + \Delta H$. The observed echo is recorded as a function of the time between the end of the first π pulse and $\pi/2$ pulse using the boxcar signal gate set at the maximum echo intensity and the baseline gate at a point later on the step. (b) The stepped magnetic field as represented by the current through the STELDOR coil and measured across a 22 mΩ resistor in series with the coil. The risetime (to 90% of the peak value) is ≈100 ns and the falltime ≈4μs. High-frequency oscillations in ΔH_0 during the first 2 μs impeded the observation of an echo at times <2 μs onto the step.

100 ns could be produced, but the characteristics of the turn-off are much poorer. This dictated that the field-step be turned on after the first 180° pulse and be maintained during the 90°–τ_2–180°–τ_2 sequence.

We show in fig. 2 the echo-induced ESR spectrum from a 5 × 10^{-4} M sample of PD Tempone in 85% glycerol-d_8–D_2O at –86°C. (A simple two-pulse 90°–180° sequence was used with τ = 250 ns). This has the appearance of a rigid-limit cw ESR absorption spectrum [11], which is insensitive to residual rotational motion of the probe. Typical spin-echo STELDOR results are shown in fig. 3 for various temperatures. For these

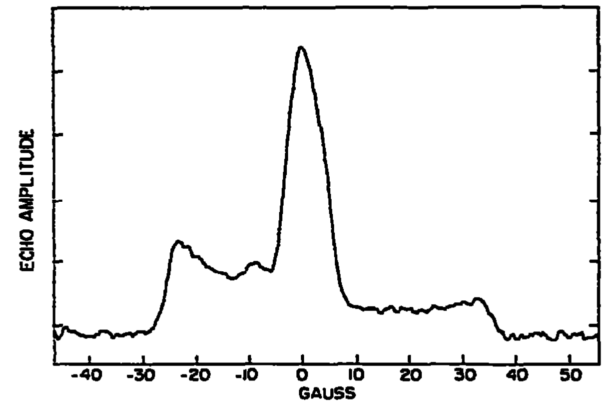

Fig. 2. Echo amplitude spectrum from a fixed 90°–τ–180° pulse sequence of 0.5 mM PD tempone in glycerol-d_8–D_2O at –86°C as a function of the externally applied H_0 magnetic field strength (relative to the point of maximum echo intensity taken as H_0 = 0).

cases H_0 = –22.5 G (cf. fig. 2) while ΔH_0 = 22.5 G. The 180° inverting pulse width is 60 ns (corresponding to an *average* rotating H_1 = 3 G). A variety of tests were conducted to assure that these signals were not instrumental artifacts. Data are shown in fig. 3 only for $\tau_1 \geqslant 4$ μs, because, even though the rise of the field step is ≈100 ns, there is a severe attenuation of the echo intensity when the 90° pulse is started earlier than 2 μs after the step. This could be due to high-frequency transients in the field during the initial "ring-time" (cf. fig. 1b).

The characteristic feature of all the curves in fig. 3 is the initial decrease in signal to a minimum followed by a slower return to an equilibrium value. This shape is consistent with a model in which a portion of the spin inversion at H_0 = –22.5 G is transferred to the $H_0 + \Delta H_0$ = 0 G region, and then it relaxes back to equilibrium. The transfer of spin polarization would be due to rotational reorientation, while electron-spin T_1 processes would then restore the spins to equilibrium. A thorough theoretical analysis of this experiment can be provided by the methods given elsewhere [14,19]. Instead of this time-consuming and arduous analysis, we present here a simplified approach, which may be expected to give correct order-of-magnitude estimates of τ_R, the rotational correlation time.

First we note that cw ESR spectra of PD Tempone in 85% glycerol have been previously fit to a model of

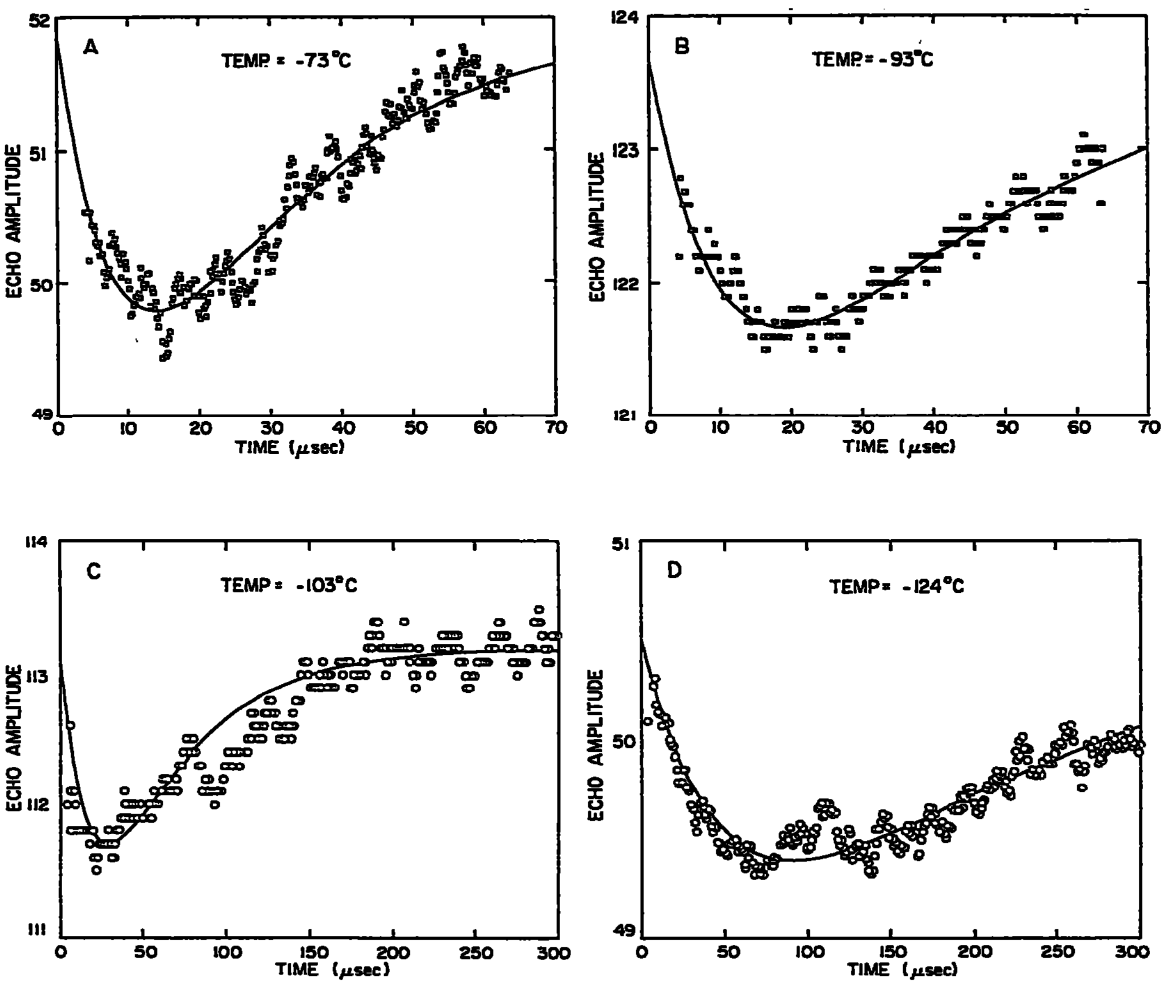

Fig. 3. Stepped field ELDOR echo amplitude versus time in μs between the first 180° pulse and the 90° pulse for a 0.5 mM PD tempone in 85% glycerol-d_8–D_2O at (a) −73, (b) −93, (c) −103, and (d) −124°C. The circles represent a seven point smoothing of the data obtained by averaging of (45–180) × 10^3 pulse sequences. The solid line is the best non-linear least-squares fit to the data.

moderate-to-large angle jumps [20]. The limiting case of large angle jumps would imply that a rotational jump at rate τ_R^{-1} would occur to all angles on the unit sphere with equal probability, independent of initial angle. We find that to within a factor of ≈2, the same ELDOR effect is observed as ΔH_0 is varied from ±28 to ±10 G (keeping $H_0 + \Delta H_0 = 0$ G), and this is consistent with large angle jumps. (For $|\Delta H_0| < 10$ G one begins to observe the direct spin inversion effect in the region $H_0 \approx 0$ G that is initially produced by the first 180° pulse. It is distinguished by the minimum signal occuring at $\tau_1 \approx 0$.) We therefore invoke the theory previously given for time-dependent slow-motional ELDOR [9, 10] in the strong-jump and very slow motional limit. In this limit, we find that the orientation-dependent echo-signal, $\Delta S(\Omega_i, t)$ at Euler angles specified by Ω_i

due to initially irradiating at Ω_j is given by:

$$\Delta S(\Omega_j, t) \propto (-1/8\pi^2)\{\exp(-w_{00}t) + \exp(-w't)[8\pi^2\delta(\Omega_i - \Omega_j) - 1]\} , \quad (1)$$

where $w_{00} = T_1^{-1}$, $w' = T_1^{-1} + \tau_R^{-1}$, and $\delta(\Omega_i - \Omega_j)$ is the Dirac delta function †. Here T_1 is the electron-spin T_1 which is largely independent of orientation. Thus, if $\Omega_j \neq \Omega_i$ one has:

$$\Delta S(\Omega_j, t) \propto (-1/8\pi^2)[\exp(-w_{00}t) - \exp(-w't)] , \quad \Omega_i \neq \Omega_j . \quad (2)$$

Eq. (2) clearly shows that there will be a non-negligible effect only if τ_R is not much longer than T_1. In actual fact, a range of Ω_j are affected by the first 180° pulse, while the detecting pulses "observe" a range of Ω_i. Thus we may write:

$$S(\tilde{\Omega}_i, \tau_1, \tau_2) = S_0(\tilde{\Omega}_i, \tau_2)\{1 - C(\tilde{\Omega}_i, \tilde{\Omega}_j) \times [\exp(-w_{00}\tau_1) - \exp(-w'\tau_1)]\} , \quad \tilde{\Omega}_i \neq \tilde{\Omega}_j , \quad (3)$$

where $S_0(\tilde{\Omega}_i, \tau_2)$ measures the echo signal from a conventional 90°$-\tau_2-$180°$-\tau_2$ sequence that arises from the appropriate range of orientations centered about Ω_i. Also, $C(\tilde{\Omega}_i, \tilde{\Omega}_j)$ is a factor determined by the range of orientations centered about Ω_j whose spins are initially inverted and the range about Ω_j whose spins are "observed". It is both an instrumental factor via H_1 (and its inhomogeneity over the sample) and a function of the spectral lineshape of fig. 2. This factor can be removed from the analysis by solving for $\tau_{1,\mathrm{min}}$ such that $S(\tilde{\Omega}_i, \tau_1, \tau_2)$ is a minimum. One easily obtains:

$$\ln(1 + T_1/\tau_R) = \tau_{1,\mathrm{min}}/\tau_R . \quad (4)$$

Also, one finds that $\tau_{1,\mathrm{min}}$ is accurately determined from the experimental data. Eq. (4) plus independent measurements of T_1, utilizing strong irradiating pulses of conventional 180°–90°–180° sequences (without field stepping) [9,10,15,19] can then be employed to obtain τ_R. These results can be independently verified by means of a non-linear least-squares fit of the data to eq. (3) to obtain the rate constants directly.

† The opposite limit of brownian reorientation is characterized by a sum over many exponential decays with rate constants $w_{LL} = T_1^{-1} + L(L+1)/6\tau_R$ for integer L ranging from zero to infinity [9,10].

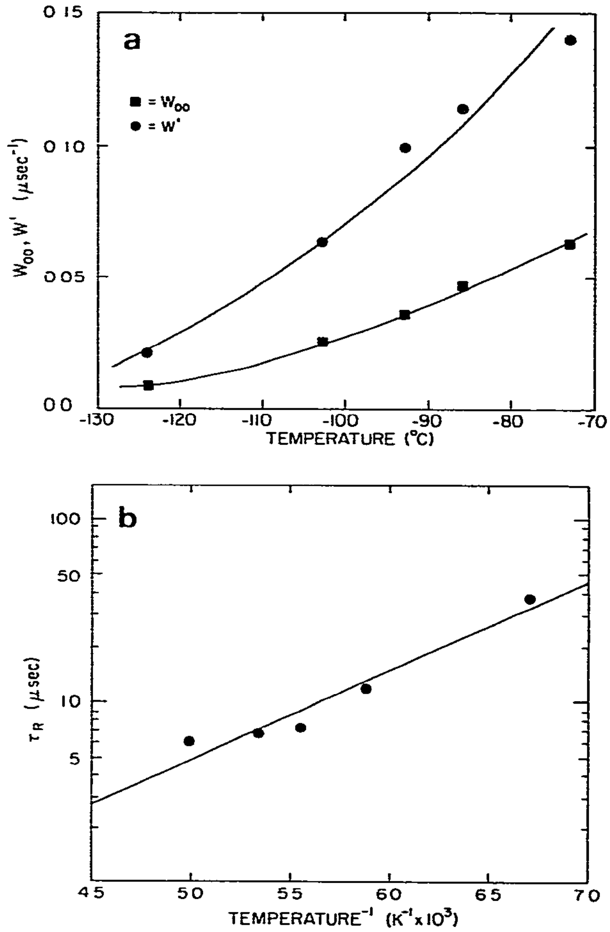

Fig. 4. (a) Mean values of w_{00}(■) and w'(●) in μs^{-1}. The solid lines are drawn to guide the eye. (b) Arrhenius plot of τ_R in μs versus inverse temperature in $10^3\,K^{-1}$.

Results covering the temperature range of −73°C to −124°C are shown in fig. 4 for w_{00}, w', and τ_R. We found that $C(\tilde{\Omega}_i, \Omega_j) \approx 0.06$ consistent with the fact that only a weak region of the low-field transition was observed (neglecting any effects of nuclear-spin flips). The estimates of τ_R range from 10^{-5} to 10^{-4} s, a time regime previously accessible only by cw saturation transfer techniques [6,21]. Below −124°C the echo signals become weak, so it becomes difficult to measure the ELDOR effect. We expect that, as the techniques are perfected, $\tau_R \approx 10^{-3}$ s should be accessible to study. In order to measure τ_R values significantly faster than 10^{-5} s it will be necessary to "stabilize" the stepped field in times much shorter than 2μs, so that shorter τ_1 values may be used. This latter requirement would also be necessary to extend the method to motionally narrowed spectra, wherein one would study cross-relaxation and nuclear spin relaxation rates rather than τ_R^{-1} [1–4].

The results on τ_R in fig. 4b are significantly faster than those obtained from a simple extrapolation of the motionally-narrowed results [20] utilizing an Arrhenius plot with activation energy E_a = 15.2 kcal/mole (or with a temperature dependent E_a that increases with $1/T$) [22]. Instead, we obtain from fig. 4: E_a = 2.2 kcal/mole (and $\tau_R = 5 \times 10^{-8}$ s) in the very slow motional regime studied here. Recent hydrodynamic theories [23,24] predict a saturation effect on the increase in τ_R with $1/T$ in the very viscous limit (i.e. τ_R is approaching an asymptotic value independent of temperature) with some supporting observations reported on other systems [23], and this could be compatible with an apparently small E_a, but further work of this type would be required to adequately explore this possibility ††.

In summary, spin-echo ELDOR shows considerable potential for the direct measurement of rotational correlation times for very slowly rotating spin labels and probes. Simple analysis of the data allows approximate estimates, while the more complete theory [14,19], including full description of the microscopic model and the inclusion of effects of nuclear spin flips, can be performed to obtain accurate microscopic data. Improvements in experimental techniques to allow rapid "jumps" between pumping and observing spectral regions, to provide a more homogeneous microwave field over the sample, and general improvements in ESE methods can be expected to extend this potential.

We wish to thank Drs. V.S.S. Sastry and Uzi Eliav as well as G. Millhauser and L.J. Schwartz for their considerable help with this project. This research was supported by NSF Grant No. CHE 8024124 and NIH Grant No. GM-25862.

†† One can estimate, for our viscous and dilute samples, the role of intermolecular spin-relaxation processes such as electron-spin exchange and electron spin dipole–dipole interactions in the transfer of spin polarization. One finds they are of negligible importance [utilizing a Stokes–Einstein (SE) model] compared to the direct effect of the molecular rotation. However, this is best checked experimentally by performing concentration-dependent studies.

References

[1] J.S. Hyde, J.C.W. Chien and J.H. Freed, J. Chem. Phys. 48 (1968) 4211.
[2] M. Dorio and J.H. Freed, eds., Multiple electron-spin resonance (Plenum Press, New York, 1979).
[3] M. Nechtschein and J.S. Hyde, Phys. Rev. Letters 24 (1970) 672.
[4] L. Kevan and R.N. Schwartz, eds., Time domain electron spin resonance (Wiley, New York, 1979).
[5] G.V. Bruno and J.H. Freed, Chem. Phys. Letters 25 (1974) 328.
[6] J.S. Hyde, M.D. Smigel, L.R. Dalton and L.A. Dalton, J. Chem. Phys. 62 (1975) 1655.
[7] L.R. Dalton, B.H. Robinson, L.A. Dalton and P. Coffey, Advan. Magn. Reson. 8 (1976) 149.
[8] L.A. Dalton and L.R. Dalton, in: Multiple electron-spin resonance, eds. M. Dorio and J.H. Freed (Plenum Press, New York, 1979) ch. 5.
[9] J.H. Freed, in: Time domain electron spin resonance, eds. L.N. Kevan and R.N. Schwartz (Wiley, New York, 1979) ch. 2.
[10] J.H. Freed, J. Phys. Chem. 78 (1974) 1155.
[11] J.H. Freed, G.V. Bruno and C.F. Polnaszek, J. Phys. Chem. 75 (1971) 3385.
[12] J.H. Freed, in: Spin labeling: theory and applications, ed. L.J. Berliner (Academic, Press, New York, 1976) ch. 3.
[13] A.E. Stillman and R.N. Schwartz, in: Time domain electron spin resonance, eds. L.N. Kevan and R.N. Schwartz (Wiley, New York, 1979) ch. 5.
[14] L.J. Schwartz, A.E. Stillman and J.H. Freed, J. Chem. Phys. 77 (1982) 5410.
[15] A.E. Stillman and R.N. Schwartz, J. Phys. Chem. 85 (1981) 3031.
[16] S.K. Rengan, V.R. Bhagat, V.S.S. Sastry and B. Venkataraman, J. Magn. Reson. 33 (1979) 227.
[17] K.M. Salikhov, private communication.
[18] J.R. Norris, M.D. Thurnauer and M.K. Bowman, Advan. Biol. Med. Phys. 17 (1980) 365.
[19] L.J. Schwartz and J.H. Freed, unpublished.
[20] J.S. Hwang, R.P. Mason, L.P. Hwang and J.H. Freed, J. Phys. Chem. 79 (1975) 489.
[21] J.S. Hyde and L.R. Dalton, in: Spin labeling: theory and applications, Vol. 2, eds. L.J. Berliner (Academic Press, New York, 1979).
[22] S.A. Zager and J.H. Freed, J. Chem. Phys. 77 (1982) 3344.
[23] D. Kivelson and P.A. Madden, Ann. Rev. Phys. Chem. 31 (1980) 523;
J.L. Dote, D. Kivelson and R.N. Schwartz, J. Phys. Chem. 85 (1981) 2169.
[24] S.A. Zager and J.H. Freed, J. Chem. Phys. 77 (1982) 3360.