TWO-DIMENSIONAL ELECTRON SPIN ECHOES: MAGNETIZATION TRANSFER AND MOLECULAR DYNAMICS ☆

L.J. SCHWARTZ [1], G.L. MILLHAUSER and J.H. FREED

Baker Laboratory of Chemistry, Cornell University, Ithaca, NY 14853, USA

Received 5 February 1986; in final form 5 March 1986

The utility of inversion recovery and stimulated echoes in studying slow motional dynamics is analyzed. A comparison between theory and experiment is provided for a nitroxide radical in viscous solvent. A new two-dimensional stimulated echo technique, suggested by the theory, is applied to study NO_2 physisorbed on vycor.

1. Introduction

Modern electron-spin-echo techniques [1–4] are beginning to play a useful role in the study of electron-spin relaxation in fluids. Thus, for example, echo sequences may be used in the motional-narrowing regime for measurements of T_2 and T_1 [2]. In the slow-motional regime, the theory for T_2 (or phase memory time T_M) is now well understood [5,6], and this has led to a new two-dimensional electron-spin-echo (2D ESE) technique based upon the $\pi/2-\tau-\pi-\tau$ Hahn echo sequence [7–9]. From this technique, one obtains slow-motional spectra plotted as a function of both the swept magnetic field (as in a normal cw *absorption* ESR spectrum) and a frequency or "width". This latter width axis shows the natural (homogeneous) lineshapes at the different resonance positions of the ESR spectrum. The theory [6,10] shows that the slow-motional cw spectrum is a superposition of Lorentzian lines due to the "dynamic spin packets", which are the normal-mode solutions of the relevant stochastic Liouville equation. The slow-motional 2D ESE spectrum may then be thought of as a plot of the spectrum as a function of both the natural widths (T_2^{-1}) of these dynamic spin packets and their resonance positions. There is, in general, substantial variation of the homogeneous T_2s across the ESR spectrum, and this variation can be related to the nature of the motion [6–9].

One may ask whether analogous experiments may be performed in the context of T_1 measurements. (In fact, recent ELDOR-echo experiments properly fall into this class [10–12].) We have recently carried out a detailed theoretical analysis of such matters [10,13]. Specifically, we sought to answer the question: given an arbitrary sequence of pulses, what would the ESE response be in the presence of (slow) motional dynamics? The analysis of this matter would permit a comparison of various T_2-type and T_1-type pulse sequences and perhaps enable a wise choice of the sequence(s) most appropriate for studying motional dynamics. We have considered as model examples of our general approach, the inversion recovery (IR) sequence: $\pi-T-\pi/2-\tau-\pi-\tau$; the stimulated echo (SE) sequence: $\pi/2-\tau-\pi/2-T-\pi/2-\tau$, and the ELDOR sequence related to inversion recovery (e.g., a field or frequency jump just after the first π pulse). (In the NMR field a somewhat related point of view was adopted by Spiess [14].) For these sequences, τ is usually fixed, and T, the time interval during which the magnetization is along the z-axis, is varied. The theory is appropriate for the slow motional regime wherein there is a continuum distribution of dynamic spin packets, but

☆ Supported by NSF Grant No. CHE83-19826, by the Cornell Materials Science Center (NSF), and by NIH Grant No. GM25862.

[1] Present address: Department of Chemistry, St. John Fisher College, Rochester, NY 14618, USA.

we are nevertheless able to consider both non-selective pulses (i.e. full irradiation, hence "rotation" of the whole ESR spectrum by the pulse) and selective pulses (i.e. partial irradiation, hence "rotation" of only a small portion of the ESR spectrum by the pulse), as well as phase-shifted pulses. We consider explicitly T_2-type relaxation for the spin magnetization in the $x-y$ plane and T_1-type relaxation for the z-magnetization, M_z.

2. Theoretical predictions

It is now appreciated [1,2,15] that the IR and SE sequences measure different forms of the spin–lattice relaxation time, T_1. For full irradiation, we find over the whole dynamic range of fast through slow motions that in the IR experiment, the signal decays exponentially with a decay constant T_1 equal to $(2W_e)^{-1}$, where W_e is the (orientation-independent) electron-spin-flip rate. In contrast, the SE sequence can yield a non-exponential decay, which, if forced to fit a single exponential function, will give an apparent T_1 that is less than $(2W_e)^{-1}$. For partial irradiation of the spectrum, both experiments give non-exponential decays showing decreased apparent T_1s relative to the full irradiation cases; the apparent T_1 from the SE is still smaller than the apparent T_1 from the IR. (We illustrate this latter predicted behavior by experimental results in fig. 1. These results are discussed further below.)

These predictions can be explained qualitatively as follows. For the case of full irradiation and the IR sequence, the first π-pulse inverts the M_zs from each of the dynamic spin packets equally. There is no phase coherence or other structure superimposed onto the different spin packets, and so during the long time interval T, M_{zT} (the total z-component of magnetization) decreases uniformly via electron-spin flips with exponential time constant $(2W_e)^{-1}$. The subsequent $\pi/2-\pi$ part of the sequence simply probes M_{zT} after the time T.

In contrast, the first pulse of the SE sequence nutates the dynamic spin packets first into the $x-y$ plane, where they precess at their individual Larmor frequencies for a time τ. During this time, the spin packets get out of phase, and the projection of each spin packet onto the rotating y'-axis at time τ, which will be nutated onto the z-axis by the second pulse, will depend on its Larmor frequency. Thus, the spin packets are "frequency labaled" during the first τ interval. During the second (i.e. T) interval, electron-spin flips reduce M_z

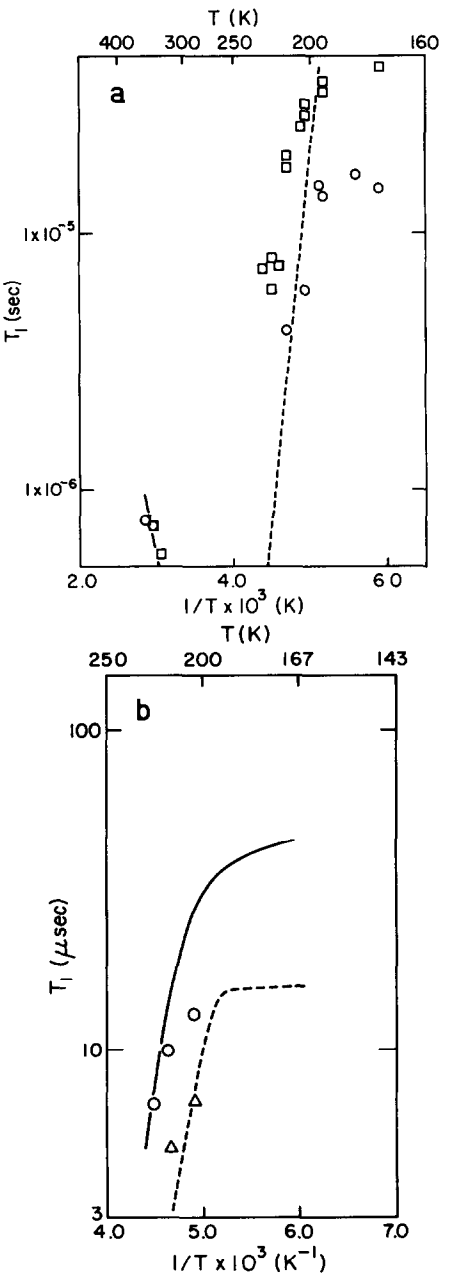

Fig. 1. Experimental results on inversion recovery (IR) and stimulated echo (SE) sequences for tempone (5×10^{-4} M) dissolved in 85% glycerol–15% H_2O: (a) Apparent T_1 versus inverse temperature for IR (□) and SE (○) sequences with central region of the spectrum irradiated. The solid line is the measured T_2 for the center line, while the dashed line is the extrapolated fast motional τ_R for reference. The experiments are performed with $\tau > T_2^*$, cf. text. (b) Comparison of experimental and calculated apparent T_1s: Solid line, experimental IR; dashed line, experimental SE; (○), calculated IR; (△), calculated SE. Calculations are with parameters as noted in text.

as in the IR sequence (in a way which is independent of the individual spin packet labeling). Motion and nuclear-spin flips will also have an effect during this interval, since as the molecules reorient or change their nuclear spin state, their spin packets' Larmor frequencies change, and the frequency labels become less accurate. An echo will be formed at a time τ after the third pulse only to the extent that the frequency labeling is still accurate at the end of the T interval. The more effective is the motion and/or the nuclear spin flips at destroying the frequency labeling set up during the first τ interval, the less the echo will be refocused during the third τ interval.

Partial irradiation can be viewed as allowing a new pathway for decay of M_z during an experiment. By virtue of rotational reorientation, the resonance frequencies of spins initially irradiated can shift to frequencies outside the irradiated region. When this occurs, the spin is no longer detectable. Thus, the effect of partial irradiation is a lowering of the apparent T_1 for both sequences. The SE sequence will always give a faster decay, however, since it still has an extra relaxation pathway relative to the IR sequence: viz. the delabeling of the initially frequency-labeled spin packets.

We shall refer to the above class of experiments as magnetization transfer (MT) experiments.

Our general theoretical results [10,13] (for both $I = 0$ and $I = 1$, i.e. simple g-tensor and nitroxide spectra) predict that the relaxation of M_z in these slow-motional MT experiments may be expressed as the weighted sum over many exponential decays, whose time constants represent the normal modes of magnetization transfer and relaxation of M_z. (These normal modes are, in general, different from the normal modes which constitute the dynamic-spin packets, since the latter [6] relate to the T_2-type of spin relaxation, but our general theory accounts for their interrelationship.) However, as discussed above, the case of the IR sequence with full irradiation reduces to the well-known single exponential form:

$$S(T + 2\tau) = A\,[1 - 2\exp(-2W_e T)], \qquad (1)$$

where $S(T + 2\tau)$, the signal at time $T + 2\tau$, is that of the echo maximum. For SE with full irradiation, the result must be written as a sum of exponentials:

$$S(T + 2\tau) = \sum_r a_r(\tau)\exp(-\Lambda_{d,r} T), \qquad (2)$$

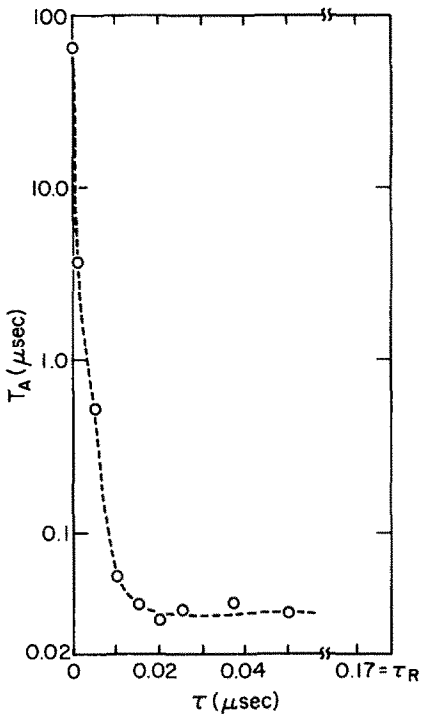

Fig. 2. Calculated T_A versus τ for the SE sequence with full irradiation for a nitroxide. Brownian motion is assumed, τ_R = 170 ns, $W_e = 0.02/\tau_R$, $W_n = 0$. The T_As are obtained from a fit to eq. (3). Also one obtains $T_M \approx 60$ ns, and $T_2^* \approx 10$ ns.

where $\Lambda_{d,r}$ is the decay rate for the rth normal mode. However, we find that in the limit of $W_e\tau_R \ll 1$, eq. (2) can be fit to a good approximation by a sum of only two exponential decays in the form:

$$S(T + 2\tau) = A + B\exp(-2W_e T) + C\exp[-T/T_A(\tau)], \qquad (3)$$

while for $W_e\tau_R \gg 1$, only a single exponential decay with $T_1 = (2W_e)^{-1}$ may be observed. One finds that $T_A \ll (2W_e)^{-1}$ in eq. (3) but it depends upon τ. This predicted τ dependence is illustrated in fig. 2. Actually, one finds that $T_A(\tau)$ decreases from a $\tau = 0$ limiting value of $(2W_e)^{-1}$ to an asymptotic value roughly equal to τ_R/b for Brownian motion where $b \approx 2$–5 (with the smaller (larger) values of b for $I = 0$ ($I = 1$)). This τ dependence may be rationalized in the following way. For $\tau < T_2^*$ (where T_2^* is the usual decay time of the FID), the spins will hardly get out of phase with one another after the first $\pi/2$ pulse, and so, the frequency labeling is not complete. Thus, in this limit, the role of

MT will be suppressed, so that those modes in eq. (2) representing significant MT are relatively less important in the sum. However, if $\tau > T_2^*$, while also $\tau < T_2$, there is sufficient time, τ for the magnetization to distribute itself uniformly in the x, y plane before the second $\pi/2$ pulse. (The reason why $b > 1$ for Brownian motion is most likely the result of the greater influence of spherical-harmonic components with $L > 2$ in eq. (2) and of (orientation-dependent) nuclear spin relaxation for $I > 0$ [16].)

In the case of partial irradiation, both IR and SE sequences yield signals that are of the form eq. (2) for which a fit to the sum of two exponentials as given by eq. (3) proves adequate. But now T_A is also dependent on $\delta\omega$, the partial irradiation window, i.e. $T_A = T_A(\tau, \delta\omega)$. This dependence is such that T_A decreases from the full irradiation value as $\delta\omega$ decreases, due to the extra MT out of the irradiation window as explained above. This effect is more dramatic for the IR sequence bringing its T_A into closer correspondence with that of the SE sequence, which is less affected. We shall regard this T_A as the primary parameter to be measured in an MT experiment.

A further general result of our theoretical analysis is that the T_A usually varies across the spectrum in a partial irradiation experiment. The reason why the different spin packets can differ in their efficiency at transferring and relaxing the initial M_z is that such efficiency depends on molecular orientation. For example, if a molecule, whose principal magnetic axis is parallel to the applied field ($\theta = 0$) makes a small Brownian jump by $\Delta\theta$, its new spectral frequency will hardly change, because the orientation-dependent part of the resonance frequency mainly goes as $3\cos^2\theta - 1$, which for $\theta \approx 0$ or $\pi/2$ gives a change of $\Delta\omega \propto (\Delta\theta)^2$. However for a molecule oriented at $\theta \approx 45°$, that same Brownian jump, will cause a corresponding spectral frequency change given by $\Delta\omega \propto \Delta\theta$. Thus, the spin packet at the $\theta = 45°$ orientation will experience more effective MT out of an irradiated region than will the spin packet at $\theta = 0°$ or $\pi/2$.

We show in fig. 3 the predicted effect of partial irradiation for nitroxides in the slow motional regime as a function of irradiation frequency. Fig. 3 shows plots of T_A (and T_M) calculated as the irradiation frequency is swept with constant window width.

The main result to notice from fig. 3 is the very different variation in T_A obtained for the Brownian versus jump models across the spectrum. The Brownian motion result has maxima located at the extrema of the spectrum (the extrema represent molecular orientations such that $\theta = 0$ or $\pi/2$), while jump diffusion gives an essentially flat result across the spectrum. Analogous results have been calculated and seen experimentally [7,8] for nitroxides studied by the basic Hahn sequence. The predicted (cf. fig. 3) greater model discrimination

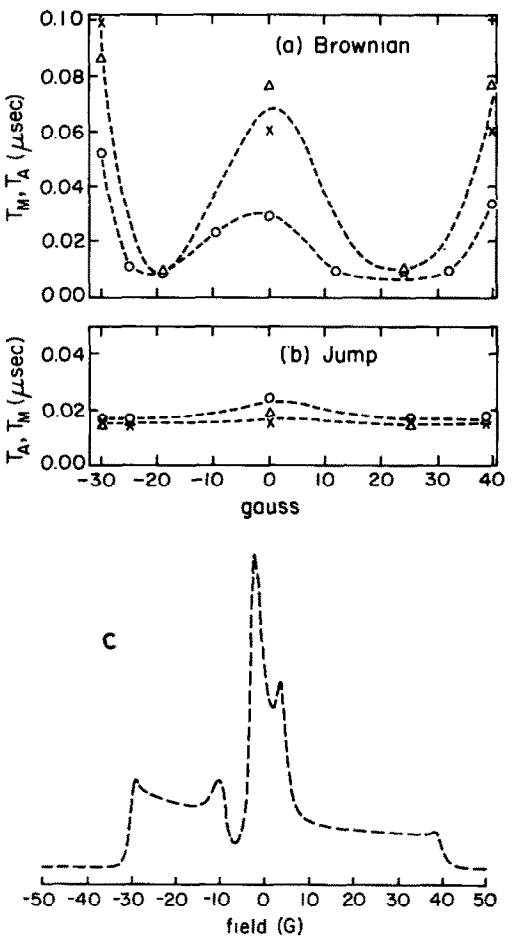

Fig. 3. Calculated time constants T_A and T_M versus dc field across the nitroxide spectrum for partial irradiation. The irradiation window is $\delta\omega/\gamma_e = 4$ G. The T_A are obtained from fits to eq. (3) (with $\tau > T_2^*$). The T_A from the IR sequence are (×), those from the SE sequence are (△), while the T_M from a Hahn sequence are (○). (a) Brownian motion and $\tau_R = 170$ ns, $W_e = 0.05/\tau_R$, $W_n = 0$; (b) Moderate jump model ($Rt = 1.0$), $\tau_R = 17$ ns, $W_e = 0.05/\tau_R$, $W_n = 0$. (c) The predicted nitroxide absorption ESR spectrum for Brownian motion associated with (A).

resulting from the two MT sequences (i.e. IR and SE) could prove to be useful.

The model dependence for the MT sequences seen in fig. 3 is easily explained. For Brownian motion, which implies infinitesimal jumps, the description given above applies, i.e. the effectiveness of MT depends on the orientation of the molecule, and the orientation varies across the spectrum. The jump model, in contrast, causes reorientation via large jumps. One or two large jumps can cause MT from any initial resonance frequency to almost any other, and so all the orientations redistribute M_z equally effectively.

Another source of model dependence will be anisotropy of the diffusion tensor. Thus, for example, if rotation is relatively rapid about the molecular z axis, the x and y magnetic tensor components are more rapidly interchanged, so that those dynamic spin packets associated with molecules oriented with their z axes at $\theta = \pi/2$ (i.e. perpendicular to the field) will experience more rapid MT, thus yielding a shorter T_A.

3. Experimental results

We first consider the experimentally observed differences between apparent T_1s obtained from the IR and SE sequences in the case of the slow motion of a nitroxide (5×10^{-4} M tempone), dissolved in 85% glycerol–15% H_2O, which has been studied previously by other methods [5–7,11].

We see from fig. 1a that in the fast motional regime, the apparent T_1s measured by the two types of pulse sequences are equal to each other and to the phase memory time, T_M. In the slow motional regime, however, the apparent T_1 measured by the IR method is consistently longer than that measured by the SE sequence, reflecting the additional processes that can contribute to the apparent T_1 from SE over and above those which contribute to the apparent T_1 from IR.

We have calculated $S(T + 2\tau)$ for both the IR and SE sequences and fit them to the best single exponential in order to compare theory with the experimental apparent T_1s. This comparison is shown in fig. 1b. The theoretical calculations were performed with a single set of parameters: a Brownian motion model supported by the recent 2D ESE study [7,9], τ_Rs according to extrapolated fast motional values [17] and the recent 2D ESE study [7,9], axially symmetric g and A tensors for simplicity [18], τ and T equal to the experimental values, $\delta\omega/\gamma_e \approx 10$ G, and W_e and W_n extrapolated from newer fits [10] to the ELDOR experiments of Hornak and Freed [11] ‡. Given the considerable uncertainties, at this stage, in the data and the various analyses, we regard the comparison as quite good.

Next we consider a 2D experiment based on the SE sequence. It is designed to observe how the relaxation time, T_A varies across the spectrum, and it is suggested by our above theoretical predictions, that, in general, T_A will vary over the spectrum in a manner that is dependent upon the motional model.

We use as our radical NO_2 physisorbed on a crushed vycor surface [9,19]. This system has been studied in the past by cw ESR [19] and very recently by 2D ESE using the Hahn echo sequence [9,20]. That study demonstrated two types of NO_2: a strongly bound component that is predominant at the lowest temperatures and a rotating component, predominant at higher temperatures. The rotation is anisotropic, being an order of magnitude faster about the molecular y axis (the axis parallel to the line passing through the two oxygen atoms) than the other two molecular axes.

In the present experiment, our strategy was to collect the data and then to use the methods of linear prediction [9,20–22] to remove the contribution from the exponential decay term with time constant $(2W_e)^{-1}$ (cf. eq. (3)). After Fourier transformation with respect to the time T, one has a map of "T_A^{-1}".

Data were collected at 5, 20 and 35 K in a manner analogous to that employed previously for the Hahn echo 2D experiment [7–9]. Fifty data points were collected as T was stepped, and the maximum value of T was about equal to $T_1 \equiv (2W_e)^{-1}$. This resulted in a high density of data points collected in the region of the decay sensitive to T_A (since $T_A \ll T_1$). The resulting decay was examined after the use of linear prediction, and a cut-off filter was chosen such that the amplitude of all components with decay times longer than

‡ The original analysis of these ELDOR experiments [11] was based on a strong-jump model of MT, but we have found that an orientation-independent nuclear-spin-flip process, W_n can explain those results just as well. In fact, we find (i) such a $W_n \approx W_e$ is expected from high-field corrections to the analysis of W_e [16], and (ii) it offers a more realistic explanation instead of the apparent low activation energy [11] at low temperatures for τ_R in this viscous medium.

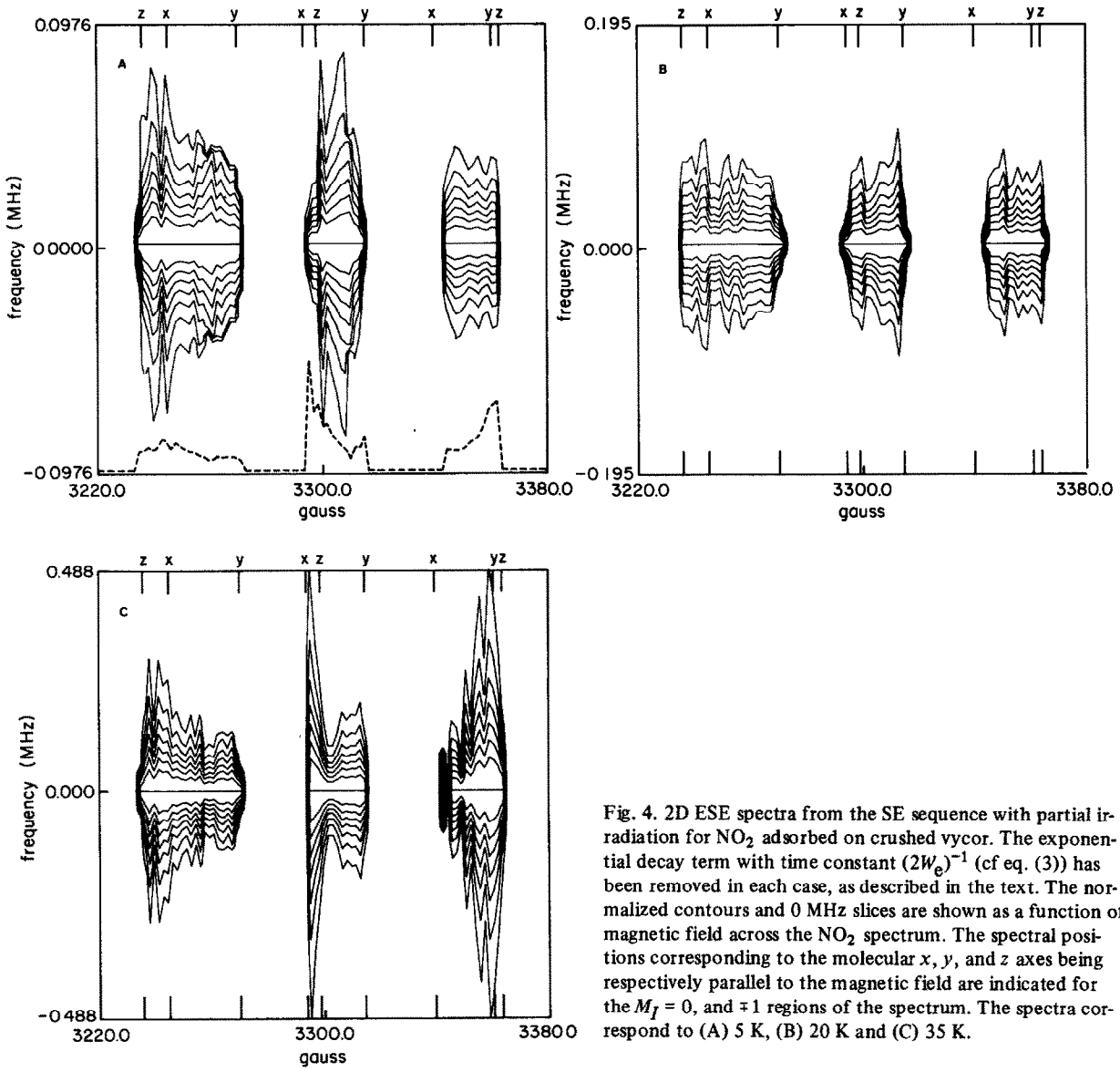

Fig. 4. 2D ESE spectra from the SE sequence with partial irradiation for NO_2 adsorbed on crushed vycor. The exponential decay term with time constant $(2W_e)^{-1}$ (cf eq. (3)) has been removed in each case, as described in the text. The normalized contours and 0 MHz slices are shown as a function of magnetic field across the NO_2 spectrum. The spectral positions corresponding to the molecular x, y, and z axes being respectively parallel to the magnetic field are indicated for the $M_I = 0$, and ∓ 1 regions of the spectrum. The spectra correspond to (A) 5 K, (B) 20 K and (C) 35 K.

the cut-off were set equal to zero. The final Fourier-transformed results are shown in fig. 4 in the form of normalized contours, i.e. the signal at each field position, which is still a function of the T_A^{-1} or MHz axis, is normalized by dividing it by its respective value at 0 MHz (cf. refs. [7–9] for an analogous normalization). The lineshapes of the 2D signal along the MHz axis are Lorentzians of width T_A^{-1}. The resulting contours will thus fall off more rapidly (slowly) if T_A^{-1} is small (large). We also show the 0 MHz slices in fig. 4, and they are seen to resemble the ESR absorption spectrum (but weighted by the value of T_A at each point in the spectrum, cf. refs. [7–9]).

At all temperatures we see a definite variation of T_A across the spectrum. In the 5 K spectrum for $M_I = 0$ (the central peak) the contours are closely spaced at the low and high field extremes. This could correspond to the long T_As predicted in fig. 3 (with typical nitroxide parameters) at the spectral extremes from a Brownian model. (The $M_I = 0$ line for NO_2 is essential-

ly just that of a simple g tensor, which is also predicted to yield longer T_As at the spectral extremes [10].) However, the analysis of both the 5 and 20 K spectra is probably obscured by appreciable amounts of the two types of adsorbed NO_2, so we emphasize the 35 K spectrum, which is mainly due to the more rapidly rotating species. We again focus on the $M_I = 0$ region. Here the broadening of the spectral regions which correspond to the x and z molecular axes being parallel to the field is quite dramatic, strongly suggesting more rapid rotation about the y axis, an observation which is consistent with the results from 2D ESE experiments based upon the Hahn echo sequence [9,19].

The contours in the $M_I = \mp 1$ lines indicate less clear trends. We believe that the cause of this is added inhomogeneous broadening due to site variation in the A tensor from different surface sites [19].

At present, we can only interpret the data from this 2D ESE experiment in a semi-quantitative way. The quality of the spectra in fig. 4 is somewhat less than that of the 2D ESE spectra obtained from the Hahn echo sequence [9,20]. There are two reasons for the presence of extra noise. First, the stimulated echo is composed of only half of the magnetization that is present in a T_M echo [1,10]. Second, we have subtracted out the component decaying as $\exp(-2W_e T)$ (cf. eq. (3)) which introduces further uncertainty. (Also, in the future one should collect sufficient data for accurately resolving the T_1 as well as the T_A time scales.)

4. Concluding comments

2D ESE based upon the SE sequence (and MT in general) is a new technique that still requires considerable improvement. However, we are very encouraged by two observations. First, the spectra at 20 and 35 K have contour shapes that are consistent with the 2D ESE T_M spectra supporting the notion of anisotropic rotational diffusion. Second, it appears that rotational motion is detectable at lower temperatures with this new approach. Thus, this 2D ESE SE experiment may be useful for examining molecular motion with very long correlation times.

Finally, we note that our theoretical analysis suggests a variety of 2D experiments related to the SE and IR sequences. For example, the present experiment could be augmented by including the effects of varying τ and $\delta\omega$. Even more possibilities are opened up with the use of non-selective pulses which can irradiate the whole spectrum. Such pulses are becoming more feasible [23], and they permit 2D experiments in which Fourier transform techniques replace the need to sweep through the spectrum [24].

References

[1] L. Kevan and R.N. Schwartz, eds., Time domain electron spin resonance (Wiley–Interscience, New York, 1979).
[2] A.E. Stillman and R.N. Schwartz, J. Phys. Chem. 85 (1981) 3031.
[3] K.M. Salikhov, A.G. Sevenov and Yu.D. Tsvetkov, Electron spin echoes and their applications (Nauka, Novosibirsk, 1976).
[4] J.F. Norris, M.D. Thurnauer and M.K. Bowman, Advan. Biol. Med. Phys. 17 (1980) 365.
[5] A.E. Stillman, L.J. Schwartz and J.H. Freed, J. Chem. Phys. 73 (1980) 3502.
[6] L.J. Schwartz, A.E. Stillman and J.H. Freed, J. Chem. Phys. 77 (1982) 5410.
[7] G.L. Millhauser and J.H. Freed, J. Chem. Phys. 81 (1984) 37.
[8] L.J. Kar, G.L. Millhauser and J.H. Freed, J. Phys. Chem. 88 (1984) 3951.
[9] G.L. Millhauser, Ph.D. Thesis, Cornell University (1986).
[10] L.J. Schartz, Ph.D. Thesis, Cornell University (1984).
[11] J.P. Hornak and J.H. Freed, Chem. Phys. Letters 101 (1983) 115.
[12] S.A. Dzuba, A.G. Maryasov, K.M. Salikhov and Yu.D. Tsvetkov, J. Magn. Reson. 58 (1984) 95.
[13] L.J. Schwartz and J.H. Freed, to be published.
[14] H.W. Spiess, J. Chem. Phys. 72 (1980) 6755.
[15] R.N. Schwartz, L.L. Jones and M.K. Bowman, J. Phys. Chem. 83 (1979) 3429.
[16] J.H. Freed, in: Multiple electron resonance, eds. M. Dorio and J.H. Freed (Plenum Press, New York, 1979) ch. 3; in: Time domain electron spin resonance, eds. L. Kevan and R.N. Schwartz (Wiley–Interscience, New York, 1979) ch. 2.
[17] J.S. Hwang, R.P. Mason, L.P. Hwang and J.H. Freed, J. Phys. Chem. 79 (1975) 489.
[18] S.A. Goldman, G.V. Bruno and J.H. Freed, J. Chem. Phys. 59 (1973) 3071.
[19] M. Shiotani and J.H. Freed, J. Phys. Chem. 85 (1981) 3873.
[20] G.L. Millhauser and J.H. Freed, to be published.
[21] R. Kumaresan and D.W. Tufts, IEEE Trans. ASSP-30 (1982) 833.
[22] H. Barkhuijsen, R. de Beer, W.M.M.J. Bovee and D. van Ormondt, J. Magn. Reson. 61 (1985) 465.
[23] J. Hornak and J.H. Freed, J. Magn. Reson. (May 1986), to be published;
J.F. Norris and M.K. Bowman, private communication.
[24] J. Gorcester and J.H. Freed, unpublished results.