

Two-dimensional FTESR and Solute Dynamics in Smectics

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Two-dimensional spectroscopies based on the Fourier transform technique may now be applied to the ESR of nitroxides [1]. To achieve uniform coherent excitation of spectral bandwidths in excess of 90 MHz we have developed a TWT anode modulator with switching times of 3-4 ns. [2,3] which is used in conjunction with two emitter coupled logic PIN switches connected in series. Simultaneous detection of in-phase and out-of-phase components of the time-domain response (free induction decay or FID) is achieved with a monolithic quadrature mixer and a two-channel digital storage oscilloscope. In order to correct for any phase or amplitude inaccuracy in the two detector channels, a four step phase alternation sequence is employed (CYCLOPS [4]) using a 2-bit digital phase shifter capable of 7 ns. MW switching speeds for phase shifts of 0°, 90°, 180°, and 270°. To date we have obtained 15 Gauss of H_1 in a bridged loop-gap resonator [5] with a loaded Q of ~ 35 , enabling uniform excitation exceeding 90MHz bandwidths in single pulse (cf. Fig. 1) and multiple pulse (two-dimensional) FTESR experiments.

A two-dimensional correlation spectrum is obtained utilizing the three pulse sequence: $\pi/2 - t_1 - \pi/2 - t_m - \pi/2 - t_2$ by collecting the FID in the t_2 domain with systematic variation of t_1 . The two-dimensional spectrum, obtained upon 2D FT of the motionally-narrowed nitroxide data, consists of cross-peaks connecting the auto-correlation lines appearing along the diagonal $\omega_1 = \omega_2$. A typical spectrum of this nature is shown in Fig. 2. The appearance of cross-peaks in these spectra indicates magnetization transfer (MT) induced by Heisenberg exchange (HE) and/or ^{14}N spin relaxation during the mixing time t_m . The rates of

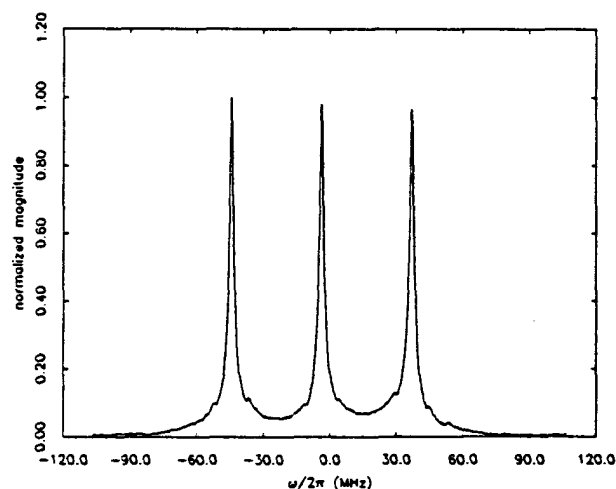


Figure 1: FT spectrum of 5.0×10^{-4} M tempone- d_{16} in toluene- d_8 at 22°C obtained with a 6.7 ns. $\pi/2$ pulse and a sampling resolution of 4.7 ns. (from Ref. 2).

MT may be determined by measurement of cross-peak and auto-peak volume integrals, whereas the mechanism of MT may be deduced from the geometrical pattern of the spectral contours. These two mechanisms of MT may be distinguished due to the selection rule $\Delta m_I = \pm 1$ for ^{14}N spin relaxation which restricts the cross-peaks to predominantly those connecting adjacent hyperfine (hf) lines. No such selection rule exists for the HE mechanism and thus HE contributes equally to all six cross-peaks. The quantitative accuracy of this method of determination of mechanisms and rates of MT has been confirmed by electron spin echo (ESE) experiments. We call this experiment 2D ELDOR because of its close similarity to that double resonance technique.

A full density matrix formulation of the theory for 2D FTESR yields the expression for 2D

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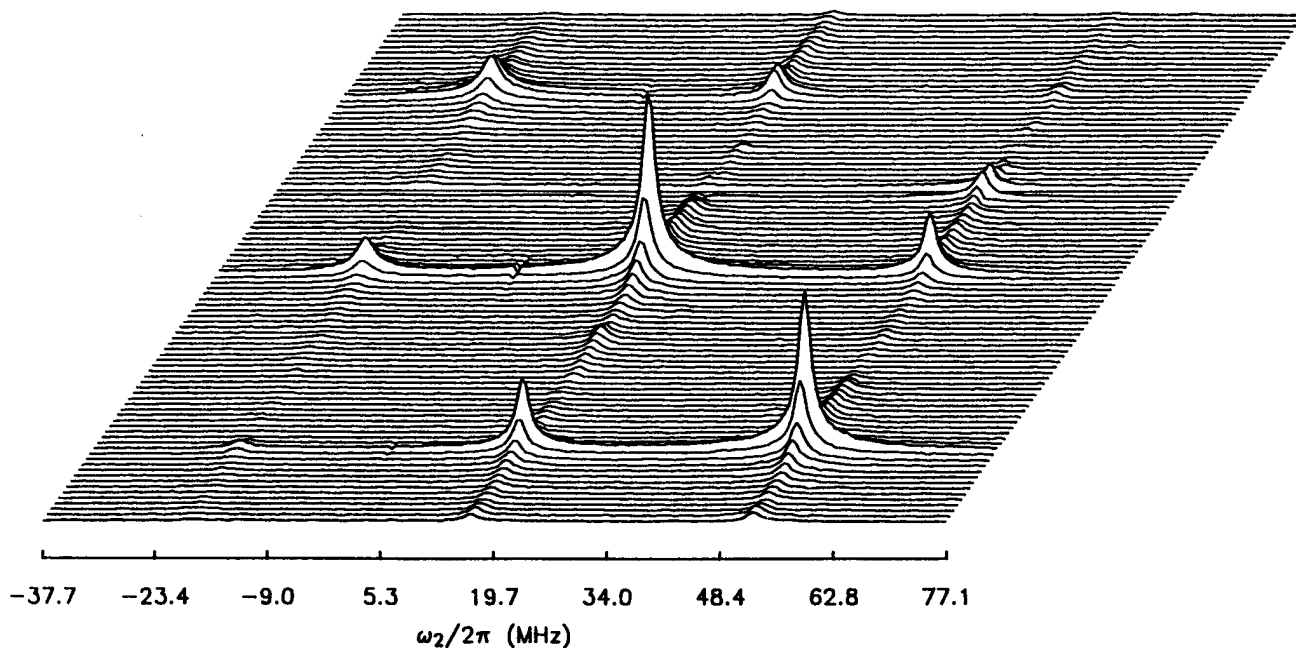


Figure 2: Absolute value 2D ELDOR spectrum of 5.0×10^{-4} M PD-tempone in phase V at 24°C ; pulse length 9.5 ns.; $t_m = 6.0 \times 10^{-7}$ s.; $\Delta t_1 = 7$ ns.; $\Delta t_2 = 3.9$ ns.; 128 samplings in t_1 ; 256 complex data points per FID extending to 1 $\mu\text{sec.}$; acquisition time 49 min.

ELDOR [6]

$$S(t, \omega_1, \omega_2) = \sum_{nmj} c_{nmj} \text{Re} \left(\frac{1}{i\omega_2 - \Lambda_n} \right) \times \text{Re} \left(\frac{1}{i\omega_1 - \Lambda_j} \right) \exp(-t/\tau_m), \quad (1)$$

where the τ_m and Λ_i are the normal modes of spin relaxation for longitudinal and transverse magnetization, and the c_{nmj} are the real coefficients. Eq. 1 leads to the particularly simple expression applicable in the motional narrowing regime [7]

$$\mathbf{Q}(t_m) = \epsilon[\exp(-\mathbf{W}t_m)], \quad (2)$$

relating the matrix \mathbf{Q} of 2D ELDOR volume integrals to the 3×3 transition probability matrix \mathbf{W} . Eq. 2 may be utilized to obtain Heisenberg spin exchange rates and ^{14}N spin relaxation rates *directly* from the 2D ELDOR volume integrals [7]. In the case of ^{14}N spin relaxation and negligible Heisenberg spin exchange (i.e., when only $\Delta m_I = \pm 1$ cross-peaks appear in the 2D ELDOR spectrum), Eq. 2 yields the expression for W_n

$$W_n = \frac{1}{6t_m} \ln \left(\frac{2\hat{Q}_{ij}A_j + A_i}{A_i - \hat{Q}_{ij}A_j} \right); \quad i, j = -1, 0, +1, \quad (3)$$

where \hat{Q}_{ij} is the volume of cross-peak ij normalized to the central ($m_I = 0$) auto-peak [i.e., $\hat{Q} = \mathbf{Q}/Q_{00}$] and A_i is the area of the i -th hyperfine line obtained in a single pulse FTESR experiment.

Eq. 3 is applicable in the absence of cross-relaxation associated with nuclear-spin dependent nonsecular terms in the spin Hamiltonian [2,7]. A similar expression is obtained from Eq. 2 in the case of significant Heisenberg exchange and $W_n = 0$. When both Heisenberg exchange and W_n are significant, an overdetermined system of six linear equations in the two unknowns W_n and ω_{HE} is obtained, which may be solved conveniently by the linear least squares method [7]. A complete treatment of 2D ELDOR in the motional narrowing regime, incorporating cross-relaxation and other nonsecular contributions, may be found in Refs. [2] and [7].

Additional contributions to the 2D FTESR spectrum, not represented in Eq. 1, arise from electron spin-flips during the mixing time t_m (giving rise to axial-peaks) and transverse interference arising from e.g., coherence transfer. These contributions, if not eliminated, complicate the interpretation and threaten the quantitative accuracy of the technique. Guided by the theory, we have developed an eight-step phase alternation sequence for the cancellation of transverse interference and axial-peaks (cf. Ref. [6]); this sequence also provides the necessary CYCLOPS image rejection for improved quadrature detection in both the t_1 and t_2 time domains.

In order to obtain accurate MT rates from general 2D ELDOR spectra it is imperative that one obtain volume integrals of the pure absorption phase 2D Lorentzian lineshapes, i.e. not simply the amplitudes of absolute value 2D lineshapes, which are more easily obtained. The projection of 2D absorption lineshapes from the arbitrarily phased

lineshapes is usually accomplished by the application of frequency-dependent phase corrections in both ω_1 and ω_2 frequency domains. Because of the very large phase variation across the spectrum, such interactive phase corrections are extremely difficult, especially when applied in two dimensions. To resolve this difficulty we have employed linear predictive methods [8], which we have generalized to enable projection of pure absorption lineshapes as well as to analyze 2D correlation spectra. In order to make such calculations more feasible, we have developed a method of 2D linear prediction which exploits the many symmetries of 2D correlation spectra and at the same time determines volume integrals directly in the time-domain (i.e. without the need for Fourier transformation) [2,9]. With our vectorized 2D linear prediction algorithm we can compute all of the relevant spectral information in 63 sec. for a data matrix of size 256×512 using a Convex C1 superminicomputer.

NMR and ESR have been extensively utilized to study solute dynamics in liquid crystalline media. The solute spin probe molecule experiences a potential associated with the anisotropic solvent-solute interaction. Rotational motion of the spin probe is strongly influenced by this potential, and this in turn significantly influences spin relaxation. In the simplest model the probe experiences a static orienting potential due to the equilibrium potential of mean torque [10] in the liquid crystal. Spin relaxation induced by the restricted rotational diffusion of the probe molecule in the presence of this orienting potential may be used to probe the dynamic structure in the anisotropic medium. More detailed models of solute dynamics also consider the translational diffusion of the spin probe in the medium [11]. In particular, if there is positional ordering of the liquid crystalline molecules, as in smectic phases, there will be a coupling of translation and rotation as the probe experiences different regions of the smectic layers. In other words, the probe experiences a continuously variable local orienting potential, as it translates through the medium.

In an extensive study of solute dynamics in the smectic liquid crystalline phase S2, we have utilized 2D ELDOR and electron spin echo (ESE) techniques for the measurement of angular dependent spin relaxation rates of the nitroxide tempone- d_{16} [7]. The 2D ELDOR cross-peak patterns revealed significant ^{14}N spin relaxation and negligible Heisenberg spin exchange over the entire temperature range studied. From the ^{14}N spin relaxation rates (W_n 's) we obtained the dipolar spectral densities at the hyperfine frequency [$J(\omega_{hf})$], whereas from a combination of ESE and 2D ELDOR we obtained the dipolar and Zeeman-dipolar spectral densities at zero frequency. The angular dependence of W_n was measured for seven different temperatures between 15°C and 43°C . Characteristic of these measurements is a substantial

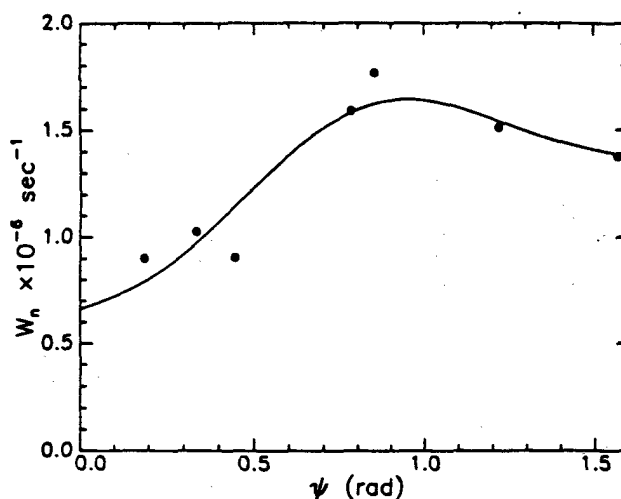


Figure 3: Angular dependence of W_n for tempone- d_{16} in S2 at 20°C .

angular dependence, exceeding a factor of three at room temperature (cf. Fig. 3). The dipolar spectral densities obtained from these measurements are not in agreement with a model of restricted anisotropic rotational diffusion, irrespective of the assumed orienting potential and rotational correlation time. Furthermore, agreement between theory and experiment could not be obtained with a variety of other models of the reorientational dynamics, including those of anisotropic viscosity, slowly relaxing local structure, and order director fluctuations (cf. Ref. [7]). However, excellent agreement between theory and experiment could be obtained with a model of rototranslational diffusion due to Moro and Nordio [11], which accounts for the positional arrangement of the solvent molecules in the smectic bilayers as well as solute translational diffusion through the bilayers.

In the Moro and Nordio description of solute diffusion in smectics, the solute is subjected to a McMillan-type potential [12] of the form

$$U(\beta, z/d)/kT = \{A + B \cos(2\pi z/d)\} D_{00}^2(\beta) + C \cos(2\pi z/d), \quad (4)$$

where d is the bilayer thickness (i.e., the lattice constant), β is the orientation of the nitroxide with respect to the smectic director, and z is associated with translation along the smectic director. The potential of Eq. 4 is of the same symmetry as that obtained by McMillan [12] and Kobayashi [13] in mean-field theoretical treatments of the smectic phase. In the present case of probe ordering Eq. 4 may be interpreted as a potential of mean force and torque. The parameters A , B , and C in Eq. 4 were estimated by simulation, requiring agreement between calculated and observed dipolar spectral densities. For each of these potential terms is an

associated order parameter, obtained upon appropriate ensemble averaging of $U(\beta, z/d)$. These order parameters describe the mean orientational, translational, and orientational-translational ordering of the probe molecule by the anisotropic solvent. In general, the orientational order parameter is z -dependent, implying a variation in the extent of probe ordering as the probe diffuses through the bilayer. The results of our simulations based on the rototranslational diffusion model may be briefly summarized as follows: (1) the probe molecule is distributed non-uniformly in the bilayer, strongly favoring the lipophilic environment of the aliphatic tails; (2) the local orientational ordering of the probe is non-uniform in z , falling off rapidly to nearly zero in the aliphatic region, consistent with observed segmental order parameters in related smectics [14]; and (3) the parallel translational diffusion coefficients, obtained in the rototranslational diffusion model, fall in the range $1 \times 10^{-6} \text{ cm}^2\text{s}^{-1}$ to $5 \times 10^{-6} \text{ cm}^2\text{s}^{-1}$ with an Arrhenius temperature behavior. The data also suggests that smectic order director fluctuations are not significant at frequencies on the order of 10MHz. For a more detailed discussion of these results, the interested reader is referred to Ref. [7].

In ESE experiments on this liquid-crystalline phase, the transverse relaxation time T_2 was measured as a function of temperature, director tilt, and hyperfine line. Unlike the W_n 's, the T_2 's are found to be only very weakly angular dependent. This very weak angular dependence of the T_2 's (and hence the linewidth parameters) is surprising considering that: (1) inhomogeneous linewidths obtained from the FID's for the same sample are orientation dependent; and (2) most models (rotational diffusion as well as the rototranslational diffusion model) predict substantial angular variation for $\text{tempone-}d_{16}$. Furthermore, the homogeneous linewidths obtained in our ESE measurements are consistently smaller than those obtained by CW spectroscopy upon numerical deconvolution of the presumed source of inhomogeneous broadening: unresolved hyperfine structure associated with the $\text{tempone-}d_{16}$ ring deuterons. The cause of these discrepancies between ESE and CW linewidth measurements is most likely an additional inhomogeneous broadening in smectic phases arising from a static distribution in orientation of the smectic director with respect to the magnetic field. The numerical deconvolution procedure assumes the only source of inhomogeneous broadening to be deuteron hyperfine structure, and thus attributes the extra broadening from incomplete sample alignment to a homogeneous broadening. The inherent angular dependence of this extra inhomogeneous broadening is therefore apparently misconstrued as an angular dependence of the homogeneous linewidths. Considering the experimental limitations in sample alignment, it would appear that ESE methods are essential for an accurate determination of homogeneous linewidths in smectics and other liquid crystalline phases.

As stated above, the very weak angular dependence of the observed T_2 's is not in agreement with predictions of the rototranslational diffusion model based on the 2D ELDOR results. This is suggestive of a second dynamical mechanism which selectively enhances the spectral densities at zero frequency [the rototranslational diffusion simulations give $J(0) \simeq J(\omega_{hf})$, whereas our measurements indicate $J(0) > J(\omega_{hf})$]. Such a mechanism would have to be relatively slow in order to affect predominantly $J(0)$, and might be associated with a slowly relaxing local structure [10] associated with slow collective motions in the aliphatic chains [7].

In summary, we have found that these new techniques of 2D ESR correlation spectroscopy enable efficient and accurate determination of ELDOR information associated with a motionally narrowed spectrum. The 2D ELDOR technique, in combination with ESE measurements of T_2 's, has enabled investigation of the temperature and angular dependences of the fundamental spectral densities of the reorientational motion. Earlier attempts at angular dependent relaxation measurements failed due to the presence of angular dependent inhomogeneous line broadening. 2D ELDOR and ESE methods, however, yield relaxation rates derived from the homogeneous resonance lines, and therefore yield the correct angular dependences. We have demonstrated that the determination of these angular dependent relaxation rates allows for a close comparison of model with experiment, and thereby provides very detailed information on the microscopic mechanisms of spin relaxation and molecular dynamics. In the case of the smectic liquid crystalline phase discussed above, these experiments have revealed a coupling of the reorientational dynamics to positional ordering of the solvent and translational diffusion of the probe molecule. These observations have important implications in spin relaxation studies of all smectic phases as well as the very similar lamellar phases of phospholipids. Further developments in instrumentation, now underway in our lab, should increase the speed and accuracy of 2D ELDOR and similar 2D ESR experiments, and will hopefully also extend the applicability of these techniques into the slow-tumbling regime of nitroxides.

Acknowledgements

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