Linear prediction and resolution enhancement of complex line shapes in two-dimensional electron-spin-echo spectroscopy[a)]

G. L. Millhauser and J. H. Freed
Baker Laboratory of Chemistry, Cornell University, Ithaca, New York 14853

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A new type of two-dimensional electron-spin-echo (2D-ESE) spectroscopy was recently shown to be useful for studying slow molecular motions in liquids. A recently developed method of spectral enhancement based upon linear prediction with singular value decomposition (LPSVD) is applied in the present work to dramatically improve the signal-to-noise ratio and to correct for finite dead time in the data from this 2D-ESE experiment. This permitted a more accurate comparison between theory and experiment. Good agreement is now obtained with a model of nearly isotropic Brownian motion for tempone in glycerol/water solvent.

I. INTRODUCTION

Recently it was shown by Millhauser and Freed[1] that two-dimensional electron-spin-echo spectroscopy (2D-ESE) is useful for studying slow molecular motions in liquids. As with most new forms of spectroscopy, certain difficulties arise that hinder a complete quantitative analysis of the results. We report here on the application of a technique of spectral analysis that is based on linear prediction. We show that not only is the signal-to-noise ratio (S/N) improved dramatically, but, in addition, certain spectral artifacts are removed. Furthermore, we show that it allows for more efficient data collection. Finally we show, that with this improvement in S/N and removal of artifacts, the comparison with theory becomes easier and more successful.

The 2D-ESE spectrum is obtained by monitoring the height of a spin echo obtained from a two-pulse sequence as the magnetic field is scanned.[1,2] Typically a family of 50 scans, each taken at an increased time, τ, between the pulses, is collected and Fourier transformed with respect to τ. Two difficulties arise from this approach. First, to avoid so-called fast-Fourier transform (FFT) window effects, it is necessary to collect data over a time range greater than five times the longest T_2. This means that a considerable amount of experimental time is spent collecting data in regions where the signal-to-noise ratio is low, and hence, the spectral resolution is low. (This loss of resolution is more pronounced in spectral regions with more rapidly relaxing components. Thus, this problem is not uniform across the spectrum when a common time range is used.) The second difficulty arises from the spectrometer dead time, τ_d, which is the shortest delay after a microwave pulse before a signal can accurately be detected. Since the T_2's are found to vary across the spectrum,[1] this dead time affects the different spectral regions to a different extent. In effect, the more rapidly relaxing spectral regions tend to be filtered out.[1]

To remedy these problems we have applied a linear prediction method developed by Kumaresan and Tufts.[3] The first application to magnetic resonance problems, both NMR and ESR, was demonstrated by van Ormondt *et al.*[4,5] In the latter work,[4] details of the technique were developed, and it was shown how dead-time artifacts could be removed giving rise to distortion-free frequency-domain representations of both one- and two-dimensional data. In that initial application, the emphasis was on obtaining accurate frequency information, whereas for our purposes it is the accuracy of the complete line shapes that is critical. We show here, that indeed the linear prediction method is useful for resolving line shapes, and furthermore, that the analysis can be applied in an automated fashion to two-dimensional spectra. We also find that by collecting the data in a new mode, different from that required by the FFT, we can maximize the advantages gained by the linear prediction treatment.

II. LINEAR PREDICTION WITH SINGULAR-VALUE DECOMPOSITION (LPSVD)

The basis for (autoregressive) linear prediction is that a discrete time series:

$$\{x_1, x_2, \ldots, x_N\} \tag{1}$$

can be modeled by the expression

$$x_n = \sum_{i=1}^{M} a_i x_{n-i}, \tag{2}$$

where the set $\{a_i\}$ are called the linear prediction (l.p.) coefficients, and the order M is less than N. The least squares solution for the set of l.p. coefficients, in terms of the entire N data points, is written as

$$\begin{vmatrix} x_1 & x_2 & \cdots & x_M \\ x_2 & x_3 & \cdots & x_{M+1} \\ \cdot & & & \cdot \\ \cdot & & & \cdot \\ \cdot & & & \cdot \\ \cdot & & & \cdot \\ x_{N-M} & & \cdots & x_{N-1} \end{vmatrix} \begin{vmatrix} a_M \\ a_{M-1} \\ \cdot \\ \cdot \\ \cdot \\ a_1 \\ \end{vmatrix} = \begin{vmatrix} x_{M+1} \\ x_{M+2} \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ x_N \end{vmatrix}. \tag{3}$$

It was shown that by using Prony's method on a set of equations similar to Eq. (3) but written in the backwards sense, i.e.,

$$x_n = \sum_{i=1}^{M} a_i x_{n+i}, \tag{4}$$

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one can model the time series in terms of exponentially damped sinusoids and determine all of the relevant parameters: frequency, time constant, amplitude, and phase.[6] Hence the time series can be regenerated and extended both forward and backward in time.

If the series is corrupted by noise, the solution to Eq. (3) becomes unstable. The proven method for handling this is to apply a singular value decomposition on the matrix and then to subtract out the effects of the noisy singular values. Thus to model a particular time series there are two adjustable parameters to optimize the analysis: (1) the number of l.p. coefficients (i.e., the order M) and (2) the number of singular values attributable to signal, which is often referred to as the reduced order, K which is less than M.

The application of LPSVD to two-dimensional ESE is based upon the following approximate theoretical expressions which describe the experiment.[1] Let $S(2\tau,\omega')$ be the echo height at time 2τ from a $\pi/2$–τ–π sequence corresponding to the field position $\omega'/\gamma e$. Then

$$S(2\tau,\omega') \propto \sum_j c_j \exp\left[\frac{-2\tau}{T_{2,j}}\right]\exp\left[\frac{-(\omega'-\omega_j)^2}{\Delta^2}\right], \qquad (5)$$

where $T_{2,j}$ and ω_j/γ_e are, respectively, the T_2 and the resonant field position of the jth dynamic spin packet (DSP) with relative amplitude c_j, while Δ is the width of the Gaussian inhomogeneous broadening. LPSVD may be applied to Eq. (5) for each field position ω'/γ_e yielding, in general, a sum of simple exponential decays for which the S/N has been improved.

The final 2D representation is obtained by performing a Fourier transform with respect to 2τ. When there is finite dead time τ_d, then one obtains[1]

$$S(\omega,\omega') \propto \sum_j c_j \frac{T_{2,j}}{1+\omega^2 T_{2,j}^2} \times \exp\left[\frac{-2\tau_d}{T_{2,j}}\right]\exp\left[\frac{(\omega'-\omega_j)^2}{\Delta^2}\right]. \qquad (6)$$

In principle, LPSVD analysis of Eq. (5) would allow for the backextrapolation of the experimental data to correct for the dead time, provided sufficient relevant information is recovered during the time interval sampled by the experiment. This would remove the factor of $\exp[-2\tau_d/T_{2,j}]$ in Eq. (6), a factor which reduces the relative importance of the DSP with relatively shorter $T_{2,j}$, thereby distorting the 2D-ESE spectrum.[7]

III. RESULTS AND DISCUSSION

In our 2D-ESE experiment we measure 100 times series, each one a 50 point echo decay envelope taken at a different magnetic field location. We display the 5000 data points as normalized contour plots (such that each slice along the width direction is normalized to unity at 0 MHz), to reveal the linewidth variations across the spectrum.[1] The spectrum of tempone in 85% glycerol/water, at -75 °C, analyzed by our standard FFT method (zero filled to 128 points and then fast Fourier transformed) is shown in Fig. 1(a). The steps in τ were 40 ns so that τ ranged from 0.2 to 2.2 μs. The phase memory time, T_M in the center of the spectrum, where it is

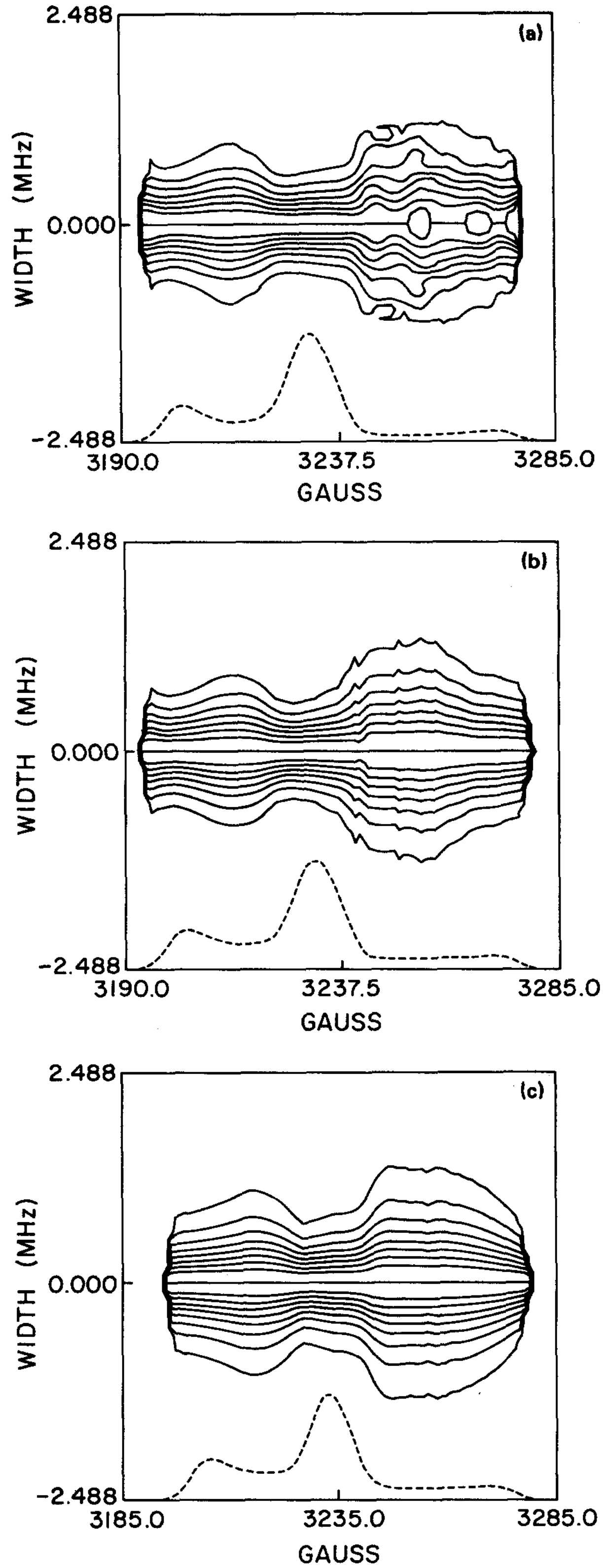

FIG. 1. Normalized contour 2D-ESE spectra of tempone in glycerol/water at -75 °C. (a) Experimental spectrum from Ref. 1, which was processed by standard FFT methods (without the apodization window, cf. Ref. 1); (b) spectrum after LPSVD is applied to the data set from which (a) is obtained; (c) spectrum obtained from an experiment (at -77 °C) where the data was collected to optimize the LPSVD analysis that was applied (cf. the text). The contours have been normalized to the 0 MHz slice, shown in each figure by dashed lines, as described in Ref. 1. Each successive contour line represents a 10% change relative to the normalized maximum. In (a) and (b) we have deleted the two contours because of the low S/N. In all other graphs only the lowest contour is deleted.

found to be the longest, is 450 ns. The dashed line across the bottom of the plot shows the 0 MHz spectrum, which is the slice from the unnormalized spectrum, taken in the field direction at 0 MHz, [i.e., set $\omega = 0$ in Eq. (6)].

We applied the linear prediction analysis to this same data set by using up to 16 l.p. coefficients (i.e., $M \leqslant 16$), attributing up to 12 of the singular values to signal (i.e., $K \leqslant 12$) and repeating the treatment for all of the 100 decay envelopes. The required cpu time was approximately 4 min on a Prime 9950 computer. In regions where there was resolvable signal, the linear prediction routines typically recovered between one and four decay components. However, upon examination we found that there was rarely more than one component of significant amplitude, and this dominant component is a simple (nonoscillating) decay consistent with the form of Eq. (5). [The amplitudes of the remaining components were approximately a factor of 300–1000 less than the dominant component and they were oscillatory at nonzero frequency with generally slower time constants than the dominant component. Given that this is inconsistent with Eq. (5), we attribute these extremely weak components to spurious origin or else to beats between DSP's not included in Eq. (5) since they should be very weak.[1]] The decay envelopes were then corrected for dead time and extended to 256 points to eliminate any FFT window problems. The curves were then Fourier transformed. This spectrum, shown in Fig. 1(b), has a substantially improved signal-to-noise ratio such that now all regions are well resolved. The results of suppressing noise can be seen, for example, in the greater curvature of the contours near the center field maximum. The dead-time correction is expressed by the buildup of intensity in the 0 MHz spectrum in the regions between 3240 and 3260 G and between 3210 and 3220 G.

We now wish to consider why it is that LPSVD recovers only a single dominant exponential at each field position, given that the theory expressed by Eq. (5), predicts, in general, a sum of exponential decays. The answer, we believe, lies in the nature of the DSP's which contribute significantly to the 2D-ESE spectrum in the very slow motional regime that is being studied. One finds, from the theoretical predictions discussed below, that all these DSP's have $T_{2,j}$'s of comparable magnitude, i.e., they vary only by about a factor of 2 across the spectrum. The differences in $T_{2,j}^{-1}$ among the DSP's, which contribute to each spectral region, are typically even smaller. Thus, the LPSVD method, applied to our data with finite noise, tends to recover a single average decay, which varies smoothly across the 2D spectrum. It seems reasonable that given such *average* exponential decays adequately represent the finite time region studied (and there are no important very fast decaying exponentials predicted theoretically for these experiments), then they can be used to backextrapolate in order to correct for finite dead time. Certainly the comparisons between experiment treated by LPSVD and theory as discussed below are supportive of this. Finally, it should be emphasized that it is the LPSVD method which tells us that the data are adequately represented by *average* exponentials; it is not forced on the method, nor was it necessarily anticipated from the theory.

Because the linear prediction analysis allows the extension of a time series, it is no longer necessary to collect data in a region where τ is large and the corresponding signal is small. This suggests that by collecting the echo decays in smaller time steps and thus concentrating the data gathering to a region where the signal is strong, the spectral resolution can be further enhanced. We tested this hypothesis by generating a new data set from the sample under approximately the same conditions (the temperature was 2 or 3 °C lower), but with 50 steps in τ of 20 ns each, so τ ranged from 0.2 to 1.2 μs. The linear prediction analysis was applied in the manner described above. The new spectrum, displayed in Fig. 1(c), shows yet a further improvement. The sharp contour changes seen as one traces the lines toward the center of the spectrum had not previously been observed.

Van Ormondt and co-workers mention in their concluding remarks[4] that there was a need to study the usefulness of the linear prediction method on solid disordered systems. For our spectra, the only reasonable way that the l.p. technique applied independently to 100 different field positions (of a complicated inhomogeneously broadened spectrum) could yield smooth 2D contours would be to reconstruct these line shapes with a very high degree of accuracy. Thus, our results (and related experiments[2]) suggest considerable future utility for this method in the analysis of spectra with complicated structure, and in particular for time domain experiments with, in general several, superposed exponential decays.

Now that we have considerably improved the S/N, and have corrected for the dead time, we are encouraged to reexamine the theoretical simulations of Ref. 1, which we can now calculate for zero dead time. Relevant simulations are shown in Fig. 2. They correspond to slow Brownian motion with (mean) rotational diffusion coefficient in the range of 5×10^3–10^4 s^{-1}. We consider the effects of introducing a small anisotropy of reorientation, $N \equiv R_{\parallel}/R_{\perp}$ (where $R_{\parallel}$ and $R_{\perp}$ are, respectively, the components of a rotational diffusion tensor for reorientation parallel and perpendicular to the molecular principal y axis).[8] We also consider the effects of small variations of the magnetic tensor components, but within the experimental uncertainty of the measured values.[8,9] The simulations in Fig. 2 corresponding to $N = 1,2$, and 3 show a considerable change in contour shapes with N, indicating their sensitivity to relatively small rotational asymmetry. When we compare these contours and 0 MHz spectra with that of Fig. 1(c), we can observe a rather good similarity in shape such that the experimental result appears to lie somewhere between the simulations in Figs. 2(a) and 2(b). This agreement is significantly improved over that in Ref. 1.

Principally, the experimental spectrum shows contour narrowing through the middle region, and this is reproduced by our simulations. This contour variation was previously[1] found to be characteristic of Brownian motion as distinct from a jump motion. The latter is predicted to yield parallel horizontal, featureless contours.

Our 2D-ESE simulations produced to study the effect of small variations in the magnetic tensors showed a remarkable sensitivity to these small variations as long as $1 < N < 1.5$, i.e., isotropic reorientation. This is illustrated in

Fig. 3. We attribute this to certain accidential near degeneracies of the parallel edges in the central region of the spectrum. This effect is found in one case to cause a more pronounced contour narrowing but in a more limited region just downfield of the center maximum as well as significant changes in the 0 MHz spectrum [cf. Fig. 3(a)]; while in another case the contour narrowing is suppressed [cf. Fig. 3(b)]. Such small variations (i.e., spectral shifts of less than 1 G), can be effective because of an inherent degeneracy in the eigenvalues of the rotational diffusion operator of the stochastic Liouville equation (SLE) when $N = 1$, which is lifted when $N > 1$.[10] Thus, while such effects could complicate the analysis, we expect that the combination of $N = 1$ and accidential spectral resonances is rare (and easily lifted). Nevertheless, it would be desirable to perform 2D-ESE studies over a range of microwave frequencies and/or stud-

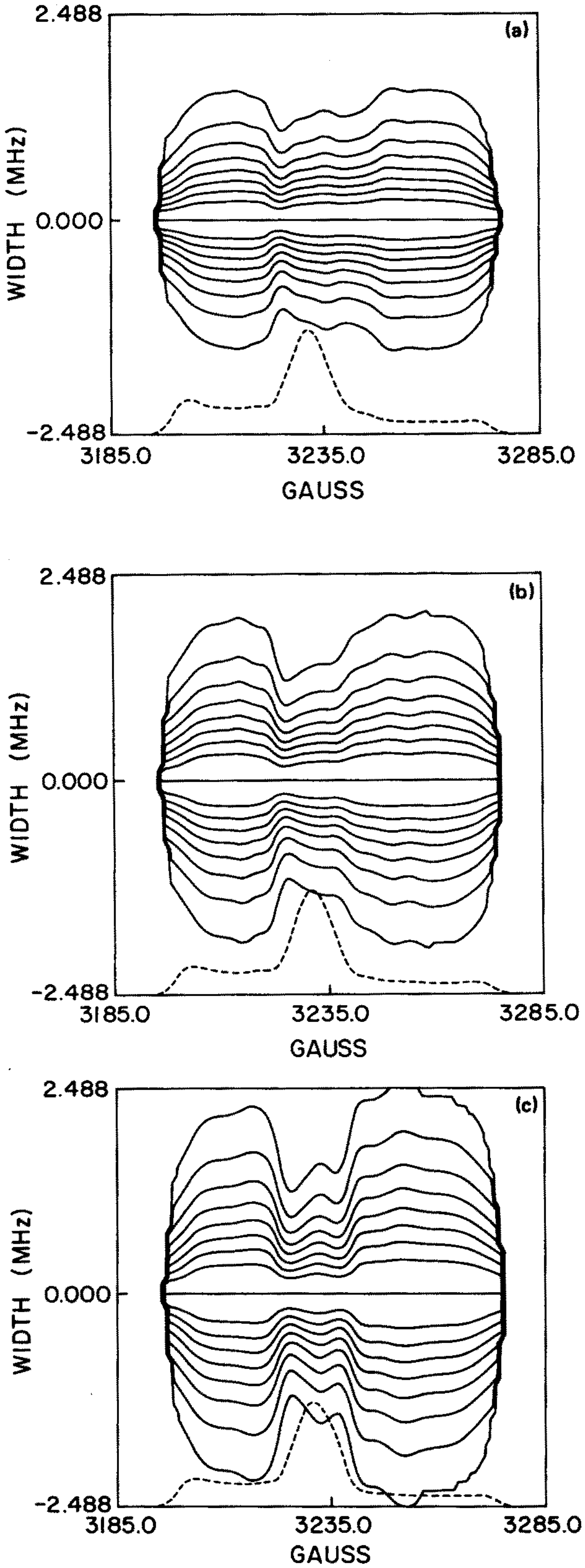

FIG. 2. Theoretical simulations of 2D-ESE spectra for a model of Brownian motion for comparison with Fig. 1(c): (a) $N \equiv R_{\parallel}/R_{\perp} = 1$; (b) $N = 2$; (c) $N = 3$. $R_{\perp} = 6\times10^3$ s^{-1} in all cases, and $R_{\parallel}$ refers to rotation about the molecular y axis. The magnetic parameters utilized were: $g_x = 2.0089$, $g_y = 2.0058$, $g_z = 2.0022$ [except for (a) where $g_z = 2.0021$]; $A_x = A_y = 5.27$ G, $A_z = 36.0$ G. The Lanczos convergence parameters [cf. G. Moro and J. H. Freed, J. Chem. Phys. **74**, 3757 (1981)], were $L_{max} = 44$, $K_{max} = 26$, $M_{max} = 2$, $n_L = 300$. The inhomogeneous broadening is 3 G and $\tau_d = 0$.

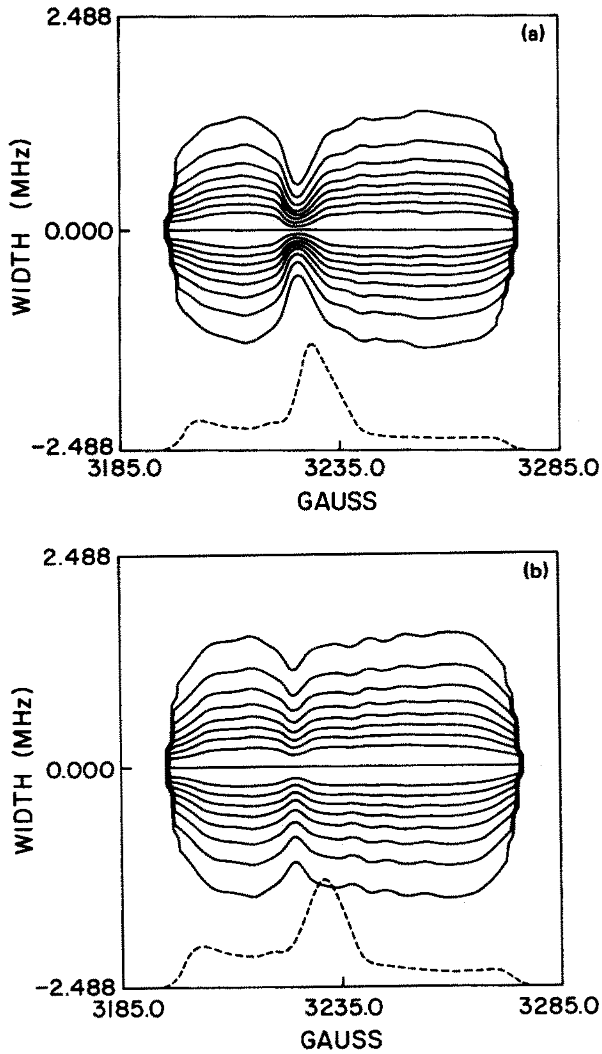

FIG. 3. Theoretical simulations of 2D-ESE spectra showing sensitivity to magnetic parameters for a model of isotropic Brownian motion (i.e, $N = 1$). (a) $R_{\parallel} = R_{\perp} = 5\times10^3$ s^{-1} and the magnetic parameters are: $g_x = 2.0084$, $g_y = 2.0060$, $g_z = 2.0022$, $A_x = 5.5$ G, $A_y = 5.7$ G, $A_z = 35.8$ G. (b) The magnetic parameters and diffusion tensor are identical to those of Fig. 2(a) but $g_z = 2.0022$ is utilized instead of 2.0021.

ies with ^{15}N labeled nitroxides to be fully confident of avoiding such accidental near degeneracies (in addition to the other sensible reasons for such experiments).

IV. CONCLUSIONS

We have demonstrated the considerable value of linear prediction methods in enhancing the spectral resolution in two-dimensional electron-spin-echo spectroscopy. The improved S/N and the removal of a dead-time artifact enabled a much better comparison between theory and experiment. The resulting 2D contours obtained for tempone in glycerol/H_2O solvent are found to clearly show the variations across the spectrum that are predicted for a model of Brownian motion. Also, the predicted sensitivity of 2D spectra to subtle variations of magnetic tensor components in special cases (i.e., isotropic diffusion) provides further evidence for the potential sensitivity and power of the 2D method, although care must be exercised to accurately produce the theoretical predictions. Further improvements in data gathering, processing, and S/N may be anticipated as a result of new developments, such as the use of nonselective pulses to irradiate the whole spectrum,[11] thereby permitting Fourier transform techniques to replace the need to sweep through the spectrum.[12] Such improvements in spectral enhancement should enable 2D-ESE techniques to provide more detailed information on molecular motions and dynamics.

ACKNOWLEDGMENTS

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[7]A dramatic demonstration of this is given for theoretical simulations in Ref. 1; cf. Fig. 5(a) vs Fig. 8 in that reference.

[8]J. H. Freed, in *Spin-Labeling: Theory and Applications*, edited by L. J. Berliner (Academic, New York, 1976), Chap. 3.

[9]J. S Hwang, R. Mason, L. P. Hwang, and J. H. Freed, J. Phys. Chem. **79**, 489 (1975).

[10]The eigenvalues of the Brownian rotational diffusion operator are $E_{L,K,M} = R_\perp L(L+1) + (R_\parallel - R_\perp)K^2$ (Ref. 8). When $R_\parallel = R_\perp$, corresponding to isotropic rotation, there is a "K degeneracy." Thus small "resonant-like" effects of matrix elements of the SLE between basis states of different K but the same L (due to the spin-Hamiltonian) could be expected to significantly alter the results. But such effects would be suppressed when the K degeneracy of $E_{L,K,M}$ is lifted as $(R_\parallel - R_\perp)$ deviates from zero. In simulations for another spin-label (CSL) no such problems were encountered (Ref. 2) even when $N = 1$.

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