

CHAPTER I.7  
LINEWIDTHS, LINESHAPES, AND SPIN RELAXATION IN THE ONE AND  
TWO-DIMENSIONAL ESR OF ORGANIC RADICALS AND SPIN-LABELS  
JACK H. FREED

**1. Continuous Wave ESR Theory And Methods**

When I was a graduate student with George Fraenkel at Columbia University from 1958-1962, his laboratory was teeming with interest and activity in the area of spin-relaxation, mainly of organic free radicals in liquid solution. In 1959 George, working with an excellent theoretical postdoc Mike Stephen, had developed a new theory (1) which could successfully account for the fact that the measured  $T_1$ 's from each hyperfine line of semiquinone spectra obtained by Jan Schreurs in George's lab were different in magnitude (2). Dan Kivelson, who had been stimulated by his visits to the Fraenkel Lab, was completing his theory of unsaturated linewidths (3) that he developed from the seminal Kubo and Tomita theory of lineshapes (4). The Stephen-Fraenkel theory deriving more from the Wangness-Bloch (5)-Redfield (6) theory (more commonly known as Redfield theory today) also incorporated components of Kubo and Tomita theory. In fact, the Stephen-Fraenkel theory of ESR saturation and the Kivelson theory of unsaturated linewidths were complementary in the insight and understanding they provided into spin-relaxation of organic radicals in solution.

My own interest in these matters became focused by the project I was undertaking of trying to extend to free radicals in the liquid state George Feher's great invention of ENDOR in solids. It seemed to me that I needed to understand steady-state saturation in these systems and how irradiating the NMR transitions affects the saturated ESR signal. Mike Stephen encouraged me to study Redfield's 1957 paper as well as his and George Fraenkel's saturation theory, and he was a major source of advice as I continued my efforts. The important concept here was that of coupled first-order rate equations that emerge from the spin-relaxation of coupled spin-eigenstates. This is an idea that was already made clear in the early Wangness-Bloch (WB) papers (1953-1956). Al Redfield showed (1957) how the concepts of spectral densities arising from random motions in liquids that are central to the pioneering paper of Bloembergen, Purcell, and Pound (7) could be incorporated into the WB theory. In addition, by irradiating the NMR transitions one could then "short out" the nuclear-spin transitions induced by the random motions and thereby enhance the coupled relaxation of a saturated ESR line.

Needless to say, when I inserted estimates of spin-relaxation terms from Schreurs and Fraenkel's saturation study on semiquinones I concluded that the

effects would be very small, of the order of or even less than a 1% modification of the existing ESR intensity. I convinced George of this and promptly terminated my efforts at constructing an ENDOR spectrometer. My new project was to be "a noise analysis of a superheterodyne spectrometer."

Fortunately, there was a great deal of other exciting activity going on in the Fraenkel lab at that time. Fellow graduate students Ivan Bernal and Phil Rieger, following in the footsteps of Maki and Geske at Harvard, had developed a very successful experiment to generate stable organic free radicals by electrochemical methods with the help of Willy Reinmuth (8). This provided a wealth of data for analysis in terms of the then current theories of spin density and molecular electronic structure. However, there were new surprises and discoveries that pertained to spin relaxation and molecular motions. Most intriguing of all was the "anomalous alternating linewidth" effect.

The electrochemically generated ESR spectrum of the *p*-dinitrotetramethylbenzene anion showed features that had not been seen before: well-resolved proton shfs appeared on the 1st, 3rd, and 5th lines of the hf splitting from the two equivalent  $^{14}\text{N}$  nuclei; but the 2nd and 4th lines were so broad that the proton shfs was completely masked (see Fig. 1). It was not hard to show that neither the Kivelson theory of linewidths nor the Stephen-Fraenkel theory of spin-relaxation could explain such a phenomenon. It was a problem that I struggled with for many months, fortunately with the encouragement of George Fraenkel and of Dan Kivelson when he visited the lab at Columbia. Finally, I found that the problem with the earlier theories rested in their treatment of multiple or degenerate hf lines which are commonplace for organic radicals. A simple extension of the Kubo-Tomita theory led to the viewpoint that such a multiple hf line must be

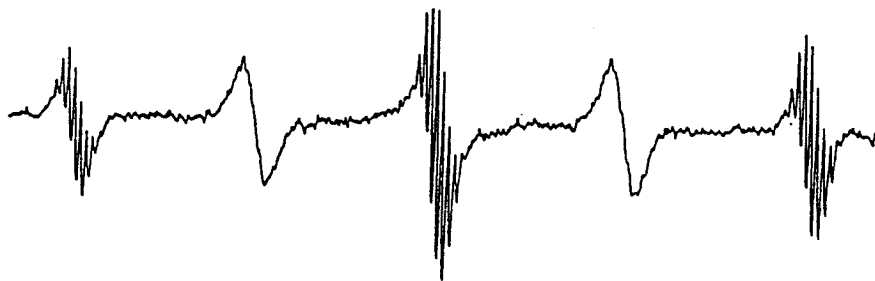


Figure 1 ESR spectrum of *p*-dinitrotetramethylbenzene radical at 20°C showing the alternating linewidth effect. (Magnetic field increases to the right). From ref.9.

an "average Lorentzian". I was able to show rigorously from the Redfield theory, with aid from Abragam's prepublication book notes, that such a multiple hf line must, in general, be a superposition of Lorentzians by solving the coupled relaxation problem. For the specific case of the alternating-linewidths of *p*-dinitrotetramethylbenzene, a particular molecular motional model was needed to complete the explanation. The new theory required out-of-phase correlation of the two  $^{14}\text{N}$  hfs, which are assumed to be fluctuating in time (9). One such model would be a rotation of one nitro-group into the benzene plane, thereby increasing its spin-density, while the other is forced to rotate out of the plane, thereby decreasing its spin density, possibly assisted by counterion motions. Such a process would broaden all the hf components except for those arising from nuclear spin configurations in which the two  $^{14}\text{N}$  nuclear spin quantum numbers were equal. Work by Jim Bolton and Alan Carrington at that time on alternating linewidths in durosemiquinone using modified Bloch equations was also consistent with this analysis (10).

As is often the case in science, the resolution of an "anomaly" led to the formulation of a more generally inclusive theory, in this case the theory of linewidths for organic free radicals. However, George Fraenkel and I had many friendly but challenging discussions before my conclusions could be accepted. George most certainly appreciated their importance, and he made a significant effort at codifying them in what became a formal exposition of ESR linewidth theory. It is, with pleasure, that I note this theory, published in 1963 (11), is still accepted today as valid for spectra in the motional narrowing regime. The important improvements to the Freed-Fraenkel theory since then have largely to do with the incorporation of more precise and detailed models of the molecular dynamics into the formulation. One important example of this, undertaken shortly after I came to Cornell University as an assistant professor in 1963, was the incorporation of Perrin's model (12) of anisotropic rotational diffusion into the linewidth theory, and its illustration by reinterpreting a linewidth study on *p*-dinitrobenzene that I had performed as a graduate student at Columbia (13a). George, at that time, extended the linewidth theory to include the complementary effects of dynamic frequency shifts (13b).

But whatever came of the prediction that ENDOR effects for organic radicals in liquids would be too small to see? Fortunately, Jim Hyde and Gus Maki had no idea of such a prediction when in 1964 they first observed such ENDOR effects (14)! Nobody seemed to understand these effects, least of all myself, or so I thought. It seemed appropriate at that time to undertake a reformulation and generalization of the theory of ESR saturation by analogy to what Fraenkel and I

had done with ESR linewidths, and to see if a complete theory would allow for a satisfactory explanation of the Hyde-Maki experiment. George had earlier recommended that I have a try at improving the theory of ESR saturation, even before Hyde and Maki's success. My efforts at looking into every "nook-and-cranny" to find where an observable ENDOR effect could be coming from, ultimately led to a very general theory of ESR saturation and double resonance which appeared in 1965 (15). Many detailed features were explored, and the theory was generalized to allow for the superpositions of Lorentzians of Freed-Fraenkel theory. Still, it was not possible for me to change my earlier prediction that any ENDOR effects must be small. Fortunately, my colleague, Dave Geske, invited Jim Hyde to give us a lecture on his ENDOR experiment. When Jim arrived at Cornell, I had a draft of my manuscript on my desk. I had been trying to get it typed properly, but that was proving to be almost as great a challenge for our chemistry department secretaries as the actual research work was for me. After all, as Larry Dalton would jokingly accuse me of, I did write it in Greek. I explained to Jim how I had looked everywhere in "spin-relaxation space", and I still couldn't find effects of more than about a percent. Jim promptly assured me that was about the magnitude of the effects he was seeing! Jim, the clever experimentalist that he is, had been chopping the NMR frequency, so that by detecting at the chopping frequency, he could get just the difference signal due to the ENDOR! It was a great relief to know this when I shortly thereafter submitted my paper on the theory of saturation and double resonance. Again, I am pleased that this formulation and its later extensions have served as the basis of interpreting ESR saturation and ENDOR experiments for motionally-narrowed spectra up to today, including the very extensive ENDOR studies of Klaus Möbius and his co-workers.

As a result of the efforts of my graduate students Henry Connor and Dan Leniart, it was possible to quantitatively test the ENDOR theory on several semiquinones (16). There we showed that aside from explaining the ENDOR enhancements in terms of the spin-relaxation processes, a very important feature was the observed linewidths for the NMR transitions of the free radicals. They very nicely complement the information obtained from the ESR linewidths. This is most important for the case of concentration-dependent linewidths. The sources are Heisenberg spin exchange and electron-electron dipolar interactions between colliding radicals. Their very similar effects on ESR linewidths make it very difficult to separate them out, but it is important to do so in order to utilize these interactions to study microscopic molecular diffusion in liquids. However, these two mechanisms have very different relative effects on NMR vs. the ESR linewidths. Thus Leniart, Connor, and I were able to successfully separate them

from our ENDOR studies. I believe that this is the only example of their separation based solely on spin selection rules, although modern time domain techniques I describe below also enable such a separation.

Jim Hyde and I were able to collaborate on aspects of ENDOR. However, our most important collaboration was undoubtedly the development of ELDOR in liquids (17). This came about during a 3-week visit to Varian in the spring of 1967, when Jim showed me the very exciting ELDOR spectra he and Jimmy Chien had obtained with a bimodal cavity that Jim had developed. It was perhaps a triumph of the thorough saturation and double resonance theory that I had developed, that within the 3-week period I could come up with the appropriate theory for the ELDOR experiment. ELDOR, today, has taken on many new configurations, but in all of them it serves as a powerful means of studying spin-relaxation for purposes of exploring both rotational and translational motions in liquids.

With the theory of ESR linewidths, spin relaxation, saturation, and double resonance well-established by the mid to late 1960's, it could have appeared that all that remained was to apply it to a wide variety of experiments. However, I personally was concerned with some of the theoretical foundations of Wangness-Bloch-Redfield and Kubo-Tomita theory. It appeared to work so well in the motional narrowing region, but it was essentially a perturbation theory, which was ill-defined in the sense that one kept the first non-trivial term in a perturbation expansion, and for which there was no way of generating the higher order terms in the expansion. Abragam's cogent summary of this theory illustrated how one "swept under the rug" higher order terms when they are unimportant (18). The question remained how to extend Redfield theory to all orders in a systematic fashion as motional rates slow. I was intrigued by this question, and I began to study papers by R. Kubo from the early 1960's in which he introduced the concept of generalized cumulant expansions into the methodology of statistical mechanics (19). Ordinary cumulant expansions arise in probability theory when one examines statistical averages of exponential functions. Spin relaxation, however, involves ensemble averages of exponentiated Hamiltonian super-operators, so one must generalize the conventional probability techniques. In fact, it proved possible to utilize Kubo's generalized cumulant method to develop general theorems about spin-relaxation. For example, one could in principle, calculate the relaxation matrix to all orders in perturbation theory, and I could show that the  $n^{\text{th}}$  order term involved a particular form of the  $n^{\text{th}}$  order time correlation function of the molecular motion treated as a random function. Relaxation theory is a long-time limiting theory, but the generalized cumulant method even allowed one to get the

finite time corrections. Thus I found that I had a general formulation of relaxation theory valid to all orders (20). Redfield theory provided the leading or 2<sup>nd</sup> order term. I even succeeded in calculating and using the 3<sup>rd</sup> and 4<sup>th</sup> order terms. But generalized cumulant expansions suffer very severely from the problems of perturbation expansions, viz. each higher order term is much harder to compute than the previous term.

When I was visiting Jim Hyde at Varian in 1967 I paid a visit to Stanford. Harden McConnell told me about the pioneering spin-labeling work going on in his lab, and he encouraged me to seriously consider the slow motional ESR problem, which becomes important when one studies spin-labeled macromolecules. I pointed out that I had a solution, at least in principal, by generalized cumulants. In my visit to Dan Kivelson's lab, I found that he and his postdoc, Hans Sillescu, were also working seriously on this problem in another way that also supplied perturbative corrections to Redfield theory (21). They pointed out to me the early work of Korst and Khazanovitch (22), who had solved the slow-motional problem for the simple case of only a secular perturbation, i.e. a perturbation term in the spin-Hamiltonian that commutes with the main term. With all its complexities, at least the generalized cumulant theory was appropriate for all types of perturbation and all types of motions.

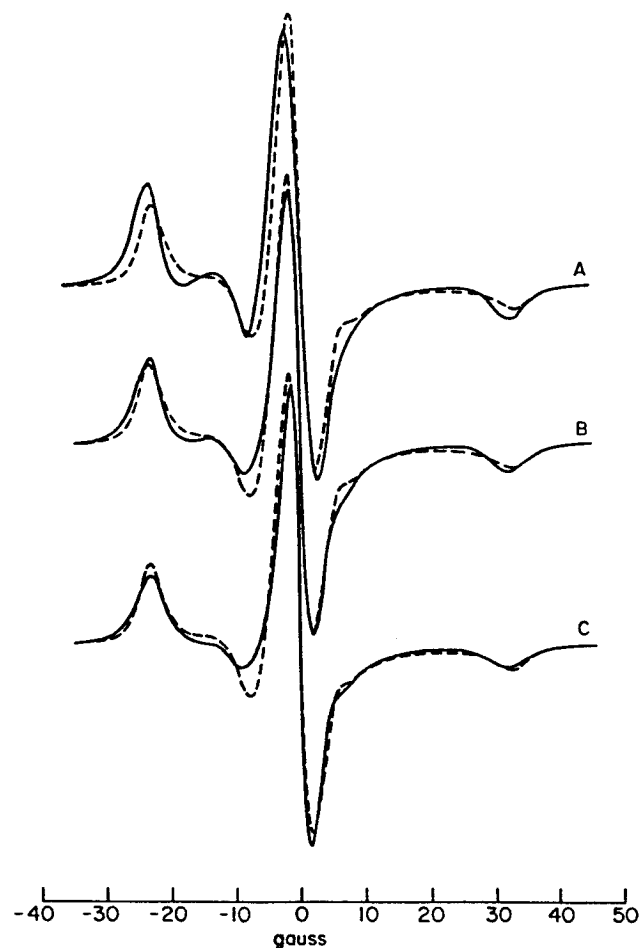
Because of all the complexities in generalized cumulant theory, in particular and in the statistical mechanics required for analyzing the slow-motional problem in general, I decided to visit Ryogo Kubo in Tokyo for the fall semester of 1969 during my first sabbatic. It was a relief to leave Cornell in the summer of '69 after a semester of student demonstrations, and the infamous "guns at Cornell". However, when I arrived at Tokyo University I found that it was engulfed in major student demonstrations. There were even warring factions of students. Some had occupied Humanities buildings and others were trying to extricate them with showers of stones and rocks. I could, however, find peace and quiet in the Physics building where I had an office. Kubo, it turned out, had been made Dean of the Science Faculty. He is not only a great theoretical physicist but also a very able administrator to whom his colleagues turned in their period of great campus strife. Needless to say, our scientific conversations were very limited, although he and his wife found time to be excellent hosts.

In an early conversation he thanked me for utilizing his generalized cumulant theory to develop a general spin-relaxation theory. He realized how complicated it gets to actually utilize this theory. He then handed me two current papers of his, saying that their approach would be easier for computations. In these two 1969 papers, Kubo had congealed, in a largely heuristic sense, his ideas on stochastic

Liouville equations (23). It was not long before I realized how I could incorporate an approach based on the stochastic Liouville equation to develop a complete analysis of the ESR slow-motional problem. I had many quiet hours in my office, while others worried about problems of student riots. There was a price in using the stochastic-Liouville equation (SLE). One had to assume that the motional dynamics could be described statistically by a Markov process. More serious in practical terms was the need to take the matrix representations of the SLE and solve for the ESR spectrum on a computer. Not only did this conflict with my preference for analytic solutions, I had no real access to computers at Tokyo University. Thus, as I generated expressions for bigger and better spin Hamiltonians and rotational motions, I would mail them back to my students at Cornell. In particular, my graduate student Gerry Bruno undertook to program them.

By the time I left Tokyo the theory had been worked out for all relevant cases of  $g$ -tensor and hyperfine anisotropy, and it was extended to include saturation phenomena. However, given the limitations on communication then (no fax, certainly no e-mail) Gerry and I could not finalize the computations until my return to Cornell in the fall of 1970 (24). Prior to that time, while I was at the Weizmann Institute during the spring semester of 1970, I was able to show Ze'ev Luz and Shlomo Alexander and especially their graduate student Asher Baram this new approach, and we considered applications to the EPR of transition metal ions. Also, by that time, the instructive but approximate solutions to slow motional ESR by Korst and Lazarev became available (25).

Upon my return, we also successfully completed experiments using peroxyamine-disulfonate (PADS) in ice. These gave lovely slow-motional spectra with none of the inhomogeneous broadening of typical spin-labels (see Fig. 2). Steve Goldman carried these experiments out very effectively both for unsaturated and saturated lineshapes, and he was aided in fitting the theory to them by Gerry Bruno and Carl Polnaszek. An important discovery then was that we could fit these spectra significantly better if we assumed jump-type reorientations rather than simple Brownian motion (26). Thus, the slow motional spectra were proving to be more sensitive to the microscopic molecular dynamics than are the fast motional spectra. It was also possible to extend the SLE approach to a complete solution of slow-tumbling triplets (27), generalizing earlier work of Jim Norris and Sam Weissman (28). At a historic meeting on electron-spin-relaxation in the summer of 1971, in Norway, I was able to learn about work that Roy Gordon and Ruth Lynden-Bell had been doing on the slow motional problem (29).



**Figure 2** Slow motional ESR spectrum from peroxyamine disulfonate anion in frozen  $D_2O$  at  $T = -60^\circ C$ . The dashed line is the experimental spectrum, and the solid lines are calculated for a particular microscopic model of rotational reorientation but with differing anisotropy of the rotational diffusion tensor: A) isotropic; B) moderate anisotropy; C) larger anisotropy. From ref. 26.

Our group continued to work on slow-motional ESR through the 1970's utilizing the spectra to obtain new insights into molecular rotational motions in ordinary isotropic fluids and in liquid crystals as well. The work on isotropic liquids was taken up by Jimmy Hwang and Ron Mason with theoretical help from Lian-Pin Hwang (30). The applications to liquid crystals were extensively explored by Carl Polnaszek (31). Ron Mason, a postdoc in my group at the time, succeeded



in synthesizing a perdeuterated spin probe: PD-tempone. It proved particularly valuable for these studies, because of the greatly reduced inhomogeneous broadening. The great challenge was in carrying out the rather tedious slow-motional simulations. Unfortunately, at Cornell at that time we had to pay hard cash for our computer time, and we had very little of it. Ron and his fellow students had to show ingenuity in order that we could accomplish our work. They were able to exploit a flaw in the billing system of our computer center. It only checked to see that we still had funds (not how much) before a batch job would run, but it didn't stop the job if and when the money ran out. By using many mini-accounts, many thousands of dollars worth of computing were successfully completed at a fraction of the cost. When the computer center's accountants caught up with me, Ron and the others were already gone, and *of course* I didn't know what my subordinates had been up to!

When, during that period, Jim Hyde tried to interest me to apply our stochastic Liouville methods to his and Dalton's new saturation-transfer technique, I had to politely decline. I knew the problem would take much greater computer time than did our existing programs, and I already was deeply in debt from them. Fortunately Larry Dalton and Bruce Robinson managed to successfully carry out these computations. I am sure they didn't have to pay Cornell's rates.

During that period, (1970-1980) it was also possible to improve on the formulation of the SLE, to study more thoroughly its range of validity, and to extend its range of applicability. Nevertheless, these initial efforts have successfully withstood the tests of time. Clearly, the most important accomplishment in the later period (1980-1989) was a very efficient method of computing solutions to the SLE that drastically reduced the computation time and storage requirements and ultimately led to a version that could be made generally available on a PC diskette.

By the end of the 1970s we were learning how to program sophisticated slow motional and chemically-induced spin polarization algorithms on our own PDP 11/34 mini-computer with its 32 kbytes of memory. Giorgio Moro, a postdoc from the University of Padua, was particularly skilled at fitting a sophisticated version of the slow motional program onto this mini-computer. This was crucial for Eva Meirovitch's efforts on membrane biophysics and liquid crystals. One day I noticed on Giorgio's desk new reprints sent from Padua of work based on his Ph.D. thesis. They were mainly about solutions to the SLE in the strong-jump limit, but one of them had an additional section on the use of Padé Approximants to aid in carrying out the solution. The details were unclear to me so I asked Giorgio about them. His reply was that he knew nothing about that work; Segre and Nordio, his co-authors must have added that section since he had left for Cornell. I told him that it was

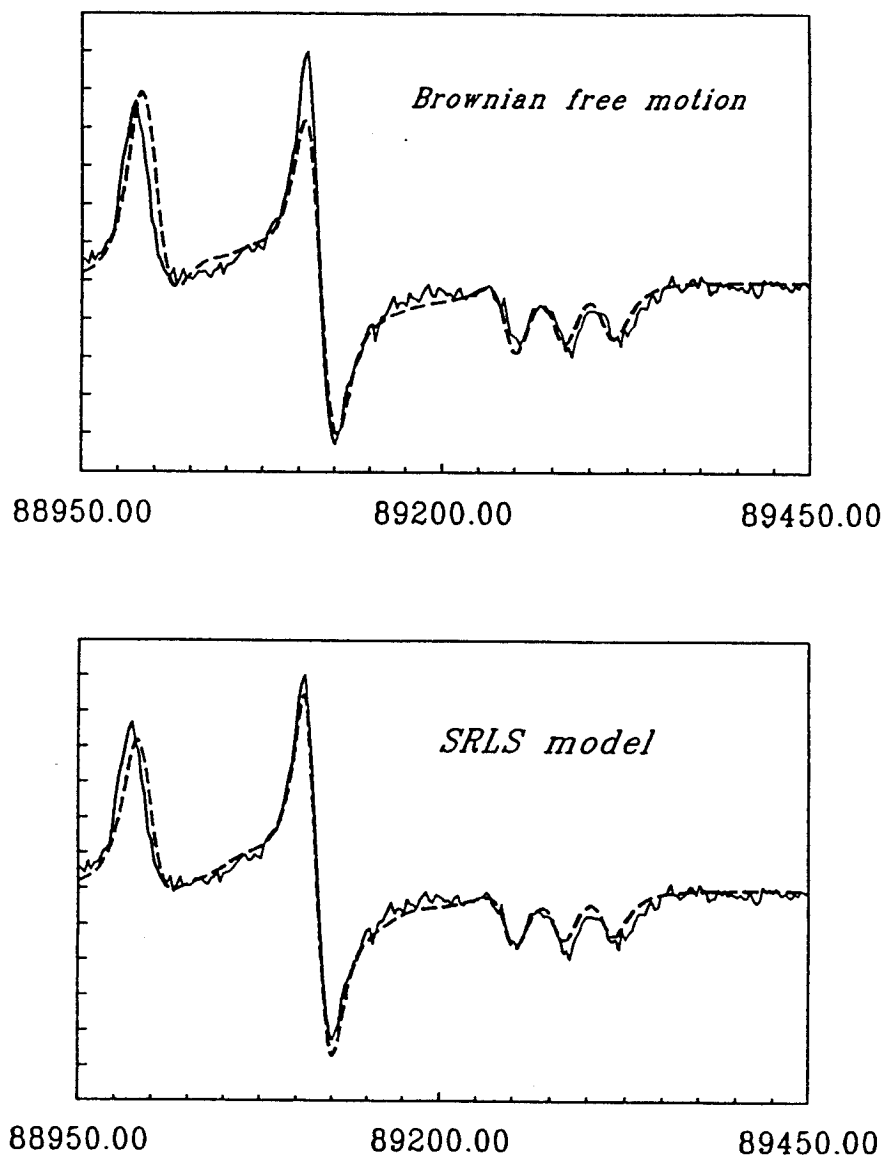
still his responsibility to understand the material in a paper of which he was the first author. Furthermore, it could prove useful for us in our efforts to squeeze huge programs onto mini-computers.

Giorgio undertook this task with thoroughness. The Padé Approximant route did not prove particularly useful, but in the process he uncovered material about the Method of Moments, primarily in the Russian mathematics literature. This is a formal procedure for projecting out a sub-space, known as a Krylov space, starting from a real symmetric or Hermitian matrix and an initial vector, each of dimension  $n$ . This sub-space will, in general, be of dimension lower than  $n$  (i.e.  $m < n$ ), and in the representation of the basis vectors obtained, the  $m$ -dimensional approximation to the original matrix will be in tridiagonal form. Giorgio found what were then recent examples in the solid-state physics literature of its use to calculate the low-lying electronic energy states of solids. However, the practical implementation for computation involved a specific algorithm, known, especially in the Western literature, as the Lanczos Algorithm (LA). We were impressed by the efficiency of this algorithm for a classic solid-state problem, especially since the classic reference on numerical algebra by Wilkinson had long ago warned that the LA was an inherently unstable algorithm, because it suffers badly from computer round-off error. Actually S. Alexander provided an early example of the analytic use of what is equivalent to the method of moments for a simple ESR case involving a real symmetric matrix, but its computational value was not explored (32). The "magic" whereby the LA worked for practical computations was not entirely clear. Another problem confronted us in that the LA had been developed for real-symmetric or Hermitian matrices, but not for the complex symmetric matrices (which are non-Hermitian) that one generates with the SLE. The available theorems no longer necessarily applied, including a guarantee that the matrix is diagonalizable. We were not especially troubled by the latter fact, since we could diagonalize SLE matrices by standard, but slow, methods. However, the complex symmetric arithmetic could (and does) increase the problem of computer round-off error.

When we did try out the LA for solving the SLE, we found it succeeded admirably (33). It reduced computation time by at least an order of magnitude, and it also greatly reduced storage requirements. Why does the LA work so well? First of all, it takes full advantage of the sparsity of the SLE matrix. Secondly, after just a few Lanczos projections it produces a sub-space that very effectively includes what is important for the ESR experiments. This is partly because the initial vector is a kind of statement of the physics of the ESR experiment. It essentially represents the ESR transition moments. Thirdly, the ESR experiment is dominated by the slowly decaying eigenvalues of the SLE, and these are accurately obtained

from the small sub-space approximation. But what about the eigenvalues that are poorly represented? They are automatically projected out of the solution when one calculates the specific ESR observable, viz. the lineshape! And what about the round-off error? Since we only need a small sub-space generated by a relatively small number of Lanczos projections, the calculation is terminated before the round-off error becomes serious! The original PDP 11/34 programs written by Giorgio Moro were so inclusive that they served as the basis for current programs adapted to modern computer architecture largely through the work of Dave Schneider while a graduate student (34). Important for these programs are very powerful methods we developed for selecting the minimum possible basis set to represent the SLE, and for reliably determining when sufficient Lanczos projections have been utilized.

Thus the Lanczos algorithm provided us with both a conceptually insightful approach as well as an extremely powerful computational algorithm for the SLE. It has since been possible to show the connection of the LA with other mathematical methodologies, but none other lends itself so effectively to a computational algorithm. The most instructive connection for us is that to the Mori method, well-known in statistical mechanics, and discussed by Dan Kivelson in the ESR context. We were able to show that the Mori projection operator is virtually identical to that of the Method of Moments, hence to the LA. In formal Mori theory, however, one performs projections on the many-body Hamiltonian, whereas in SLE theory one starts with an approximate, usually diffusion-like, model representing one's best understanding of the molecular dynamics (35). In fact, in just the last few years, with the advent of high field far-infrared (250 GHz) ESR, with its enhanced resolution to motional dynamics, as shown in work of Keith Earle and Dave Budil in my lab (36), we have found it desirable to use enhanced models for molecular reorientation to fit these spectra. We can now dispense with the old and worn jump models of diffusion. Instead we approximate the many-body problem of dealing with the microscopic details of the fluid by a set of collective degrees of freedom that represent the main effects of the solvent on a rotating solute. These collective variables are taken as a loose solvent "cage" that is slowly relaxing. Since we approximate the combined system of solute plus cage by Markovian equations, the SLE remains valid in its augmented form. Then the Lanczos projections effectively determine the extent to which the cage variables are needed to interpret the ESR spectrum. These formulations have been beautifully executed by my co-worker Nino Polimeno, from the University of Padua (37a). Current studies on ordinary liquids, liquid crystals, and model membranes appear to be yielding new insights into the cage potential and its relaxation (see Fig. 3 and ref. 37b).

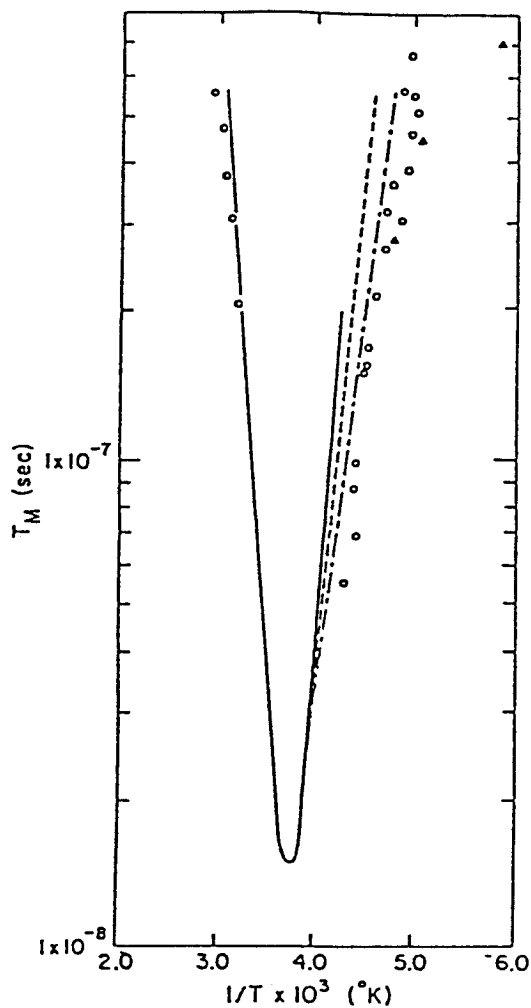


**Figure 3** The 250 GHz. ESR spectrum of perdeuterated tempone in toluene at  $-128^{\circ}\text{C}$  (solid line) compared to simulated best fit spectra (dashed lines) for models of a) free Brownian reorientation; b) a slowly-relaxing cage model. From ref. 37.

## 2. Time Domain ESR Theory And Methods

In late 1978 Art Stillman joined my lab as a postdoctoral fellow. He had worked as a graduate student with Bob Schwartz on theoretical aspects of electron spin echoes (ESE) in liquids (38). I had succeeded in getting some funds from the NSF to initiate construction of a spin-echo bridge. I was principally motivated by the problems of extracting reliable homogeneous  $T_2$ 's from inhomogeneously broadened ESR spectra such as from nitroxide spin labels. This was a particular problem for our work on macroscopically aligned samples of liquid crystals, because small amounts of misalignment could appear as extra broadening which varies for the different  $^{14}\text{N}$  hf lines, thereby being easily mistaken for the homogeneous broadening with its well-known variation with hf line. Art Stillman, though he had primarily worked on theory as a graduate student, was so anxious to test out the theoretical ideas on ESE, that he undertook the ambitious project of constructing our first ESE bridge. During the early months of design, Art was in close communication with Mike Bowman, who was then at Argonne Labs where he was conducting a very active program on electron-spin-echoes, and he provided us with useful advice. After some setbacks, partly due to our trying out some of the latest products (e.g. a microwave limiter with outstanding specs that in actual fact didn't even limit) and to a lightning surge during a powerful electrical storm, we succeeded in assembling an effective ESE spectrometer.

We conducted initial ESE experiments on fluids. In particular, we were able to explore  $T_2$ 's for fast through slow motions for the system of PD-Tempone in glycerol-water solvent (see Fig. 4) (39). For fast motion,  $T_2$  has the well-known inverse dependence on correlation time, but for slow motion the homogeneous  $T_2$  depends on the correlation time to a positive, usually fractional, power. Thus there is a  $T_2$  minimum not generally appreciated. Our results in this respect were similar to earlier observations of Ian Brown (40), but we were able to offer a coherent explanation in terms of the SLE. Leslie Schwartz took over the theoretical aspects from Art Stillman, and we established a comprehensive theory for spin-relaxation and ESE (41). What then is the interpretation for  $T_2$  in the slow-motional regime? In the limit of strong jump reorientation each jump leads to a large change in resonant frequency, hence an uncertainty in lifetime broadening, a point-of-view that Ron Mason and I had suggested some time earlier. Thus, in this limit,  $T_2$  equals the correlation time. In the limit of simple Brownian motion,  $T_2$  is roughly proportional to the half power of the correlation time. A heuristic interpretation is due to Dan Kivelson and Sook Lee (42). For slow motions there is incomplete averaging in the sense that the molecule experiences a limited range of orientations in the time scale of the experiment, which is just  $T_2$ . When a standard fast



**Figure 4** A graph of  $T_2$  (or  $T_M$ ) vs. inverse temperature for the spin probe tempone in 85% glycerol/ $\text{H}_2\text{O}$ . Experimental data are shown as circles (from ref 39) and triangles (from ref. 48). The different lines show predictions for  $T_2$  for Brownian and Jump models.

motional  $T_2$  calculation is performed, but with this finite time restriction, the  $1/2$  power law emerges.

We also explored longitudinal and cross-relaxation in liquids with our ESE spectrometer, and Leslie Schwartz incorporated these matters into her Ph.D. thesis, which became a comprehensive theory of spin relaxation in ESE for fast and slow

motions (43,44). A major motivation for the analysis of cross-relaxation was the successful spin-echo ELDOR experiment that Joe Hornak and I had performed in the very viscous regime for PD-Tempone in glycerol/water (45). Instead of using two microwave frequencies, we stepped the magnetic field during the time between the first inverting  $\pi$  pulse and the detecting  $\pi/2 - \pi$  spin echo sequence. [This clever technique had been independently developed by Tsvetkov and co-workers (46) as I learned from Kev Salikhov at a chance meeting in Oxford in 1983]. Our preliminary interpretation had indicated a reduced activation energy for reorientation in the very slow motional regime. However, using Leslie Schwartz's more complete analysis we showed that a substantial orientation-independent nuclear-spin-flip rate, likely induced by solid-state mechanisms, could equally well explain the ELDOR experiment without having to invoke a dramatic change in the activation energy for reorientation (43,44). Our more recent 2D-ESR experiments have confirmed this (cf. below), and very recently Bruce Robinson has studied this matter in detail by very nice saturation recovery experiments (47). Although it may not be clear in Robinson's work, it is in essential agreement with our work of 1984-1990 on the subject of spin relaxation studied by ESE methods.

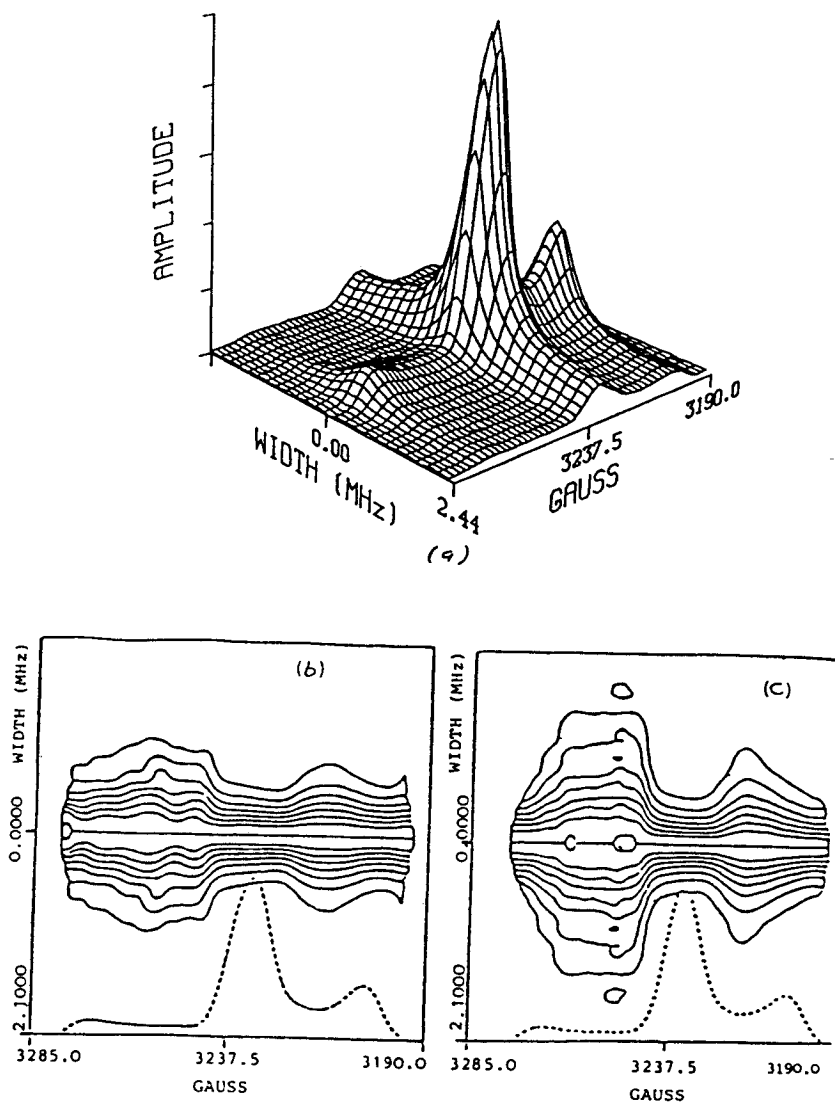
One disturbing limitation of ESE measurements of  $T_2$  is that one just obtains a single parameter from which to extract information on motional dynamics. Of course, in the fast motional regime one may study the variation of  $T_2$  with hf line. For the slow motional regime, initial theory and experiment did show that the measured  $T_2$  displays some variation across the spectrum. It seemed reasonable to suppose that by studying this variation, sufficient information could be obtained from which to infer details of motional models. This would be analogous to studying the full lineshape of a slow-motional ESR experiment, but it would have the big advantage that the homogeneous  $T_2$  relates solely to the dynamical processes. This advantage is, however, limited by the fact that when molecular motions are slow enough, then solid-state relaxation processes, such as spin diffusion, take over. However, one should be able to explore slower processes by studying the homogeneous  $T_2$  rather than the near-rigid-limit cw-ESR spectra.

Glenn Millhauser undertook, as a graduate student, to realize what proved to be our first two-dimensional (2D) ESE experiments (48). Given the ESE technology in the early 1980's these experiments were performed by sweeping the magnetic field and collecting the spin echo from weak, or highly selective, microwave pulses. When Fourier-Transformed in the echo delay time,  $\tau$  this led to a 2D-ESR spectrum in which the homogeneous lineshape is plotted along the frequency axis, and essentially the ESR lineshape appears along the field axis (see Fig. 5). This 2D spectrum thus effectively supplies the homogeneous  $T_2$  variation

across the ESR spectrum. For the case of Tempone in glycerol-water, we found a substantial variation in the  $T_2$ . Our theoretical analysis showed that a Brownian reorientational model could quite successfully explain this variation. This is because, given the  $\cos^2\theta$  type of angular dependence of the hf and g-tensor interaction terms, the variation in these terms with a small change in angle,  $\theta$  depends significantly on the value of  $\theta$ , hence on the position in the very slow-motional spectrum. On the other hand, a strong jump diffusion model leads to a uniform  $T_2$  across the spectrum, since for this case  $T_2 = \tau_R$ , the mean rotational jump time, as already mentioned. In fact, we found that the patterns of  $T_2$  variation across the spectrum, plotted in a normalized contour fashion could themselves be utilized to distinguish the model of motion, and the degree of rotational anisotropy (see Fig. 5). Shortly thereafter, Glenn and Leela Kar successfully applied this method to spin labels in oriented model membranes and to labelled proteins, showing their potential for biophysical studies, and their application to slow motions on surfaces was also demonstrated by us.

Given Leslie Schwartz's theoretical work on  $T_1$ 's and magnetization transfer (i.e. cross-relaxation) in the slow motional regime, a field-swept 2D-ESE experiment, from which one obtains the magnetization transfer rates across the ESR spectrum, occurred to us (44). It is performed in a manner analogous to the  $T_2$ -type 2D-ESE experiment, except that a stimulated echo sequence:  $\pi/2 - \pi/2 - \pi/2$ , replaces the spin-echo sequence:  $\pi/2 - \pi$ , and one steps out the time  $T$  between the second and third pulses. Here theory showed that as a function of  $T$  there are at least two exponential decays: one is in  $T_1$  and the second (to a reasonable approximation) is in  $T_A$ , an effective magnetization transfer time (for the relevant case of  $T_A \ll T_1$ ). The slow rotational reorientations shift spin-bearing molecules irradiated by the first two  $\pi/2$  pulses to frequencies outside the irradiated region. Thus they are not detected after the third  $\pi/2$  pulse. This magnetization transfer process, thus leads to a more rapid decay of the stimulated echo as a function of  $T$ . A Brownian rotation model will also give a  $T_A$  variation across the spectrum, because the effectiveness of a rotation taking the spins out of the irradiated region depends upon angle,  $\theta$  through the  $\cos^2\theta$  dependence of the magnetic tensor terms. In experiments Glenn Millhauser performed, we obtained dramatic variation of  $T_A$  across the spectrum for  $\text{NO}_2$  adsorbed on crushed vycor, which could be attributed to very anisotropic rotational motion on the surface. For this case there is an enhanced  $T_A$  for the spectral regimes corresponding to the x and z molecular axes being parallel to the magnetic field, which clearly implies more rapid rotation about the y-axis (which is parallel to the line connecting the two oxygen atoms).

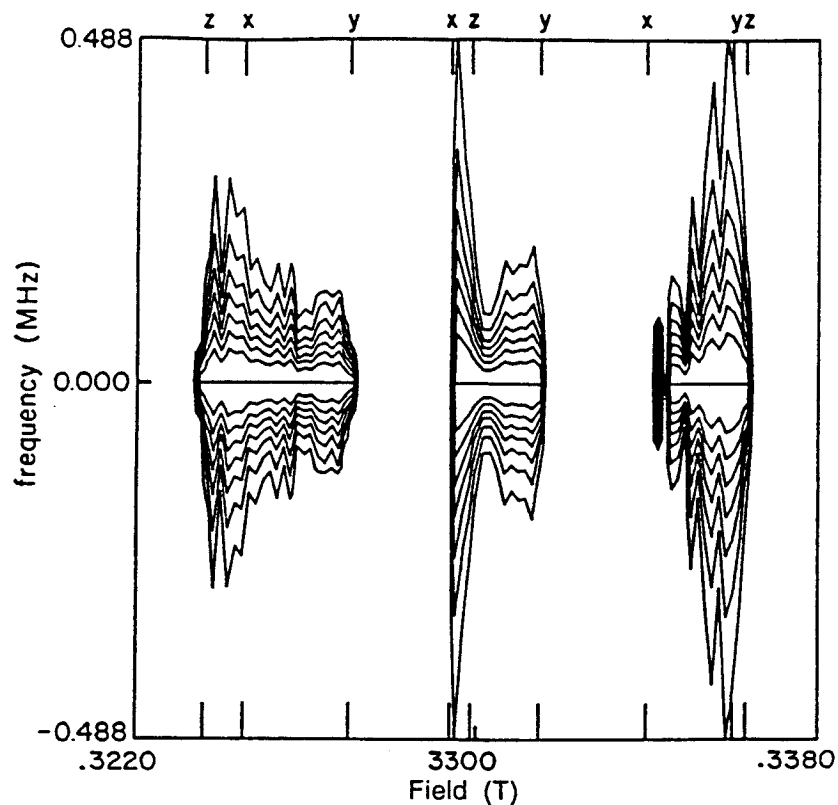




**Figure 5** Fig. 4a shows the 2D-ESE spectrum of tempone in 85% glycerol/H<sub>2</sub>O at -75°C. Slices along the width axis provide the homogeneous lineshape for the different magnetic field positions of the ESR spectrum. Fig. 4b shows the normalized contours for Fig. 4a as well as the spectral slice from Fig. 4a taken along the width = 0 MHz axis. Fig. 4c provides the analogous contours for cholestane in n-butylbenzene at -135°C. These show the different contour patterns from the nearly spherical tempone vs. that from the cigar-shaped cholestane. From ref. 48.

This motional anisotropy is clearly visible from the 2D-contours without the need for detailed spectral analysis (see Fig. 6).

Clearly the most informative method of studying magnetization transfer is by ELDOR. One observes not only the transitions out of a certain spectral region but also the spectral region to which the transition is made. This was the basic idea of the stepped field spin-echo ELDOR experiment of Tsvetkov's group and my group. One could attempt, by a combination of sweeping one or both frequencies of an ELDOR experiment and/or sweeping the field and the field jump, to perform a 2D experiment as a function of the pumping and observing frequencies. Tsvetkov and his co-workers did, in fact, develop the use of two microwave sources, wherein they swept one of them (49). This requires a resonator with a low enough  $Q$  that it could



**Figure 6** 2D-ESE contours from the stimulated echo sequence for  $\text{NO}_2$  adsorbed on vycor at 35°K showing rates of magnetization transfer. It shows relatively rapid rotation about the molecular  $y$  axis (i.e. the axis parallel to the oxygen-oxygen internuclear vector). From ref. 44.

sustain two separated frequencies. But once this is the case, another more general and more elegant method suggests itself, which removes the need for field sweeping and stepping, and it only requires one microwave source. It does require collection of the free-induction decay or the echo decay after the last pulse, but it could be obtained very rapidly. I describe it next.

1971 was an important year for the development of 2D-NMR. Jean Jeener in a summer-school meeting first introduced the concept (50), and in 1976 Richard Ernst and co-workers published the first such experiments (51). In 1971, in my lab, Gunther Rist, who was a postdoc, and I seriously considered a step-by-step mapping out of cw-ELDOR as a function of magnetic field and of frequency separation of the pump and observing fields. But in terms of the lack of sophistication of ESR experiments at that time, and the lack of modern computers for data processing, we convinced ourselves that each such experiment would require a few months of intensive work, which did not seem practical. What made analogous experiments practical in 1979 for Jeener and Ernst was, first of all, the use of Fourier Transform methods with their multiplex advantage for collecting the whole spectrum simultaneously (52). This also means the successful irradiation of the whole spectrum with a single non-selective rf pulse, and the ability to collect data shortly after such a pulse. Secondly, and more interesting, was the basic idea of Jeener that the non-selective pulse from a single rf source introduces coherence simultaneously to all spectral components enabling the observation of coherence transfer between these components. The 1979 work showed how magnetization transfer could also be studied in this manner.

Why were these ideas not incorporated into ESR until 1986? Clearly the ESR experiment is much more difficult than the comparable NMR one. In ESR we use microwave rather than rf technology. Relaxation times are orders of magnitude faster, pulse widths need to be orders of magnitude shorter, and spectral bandwidths are orders of magnitude wider.

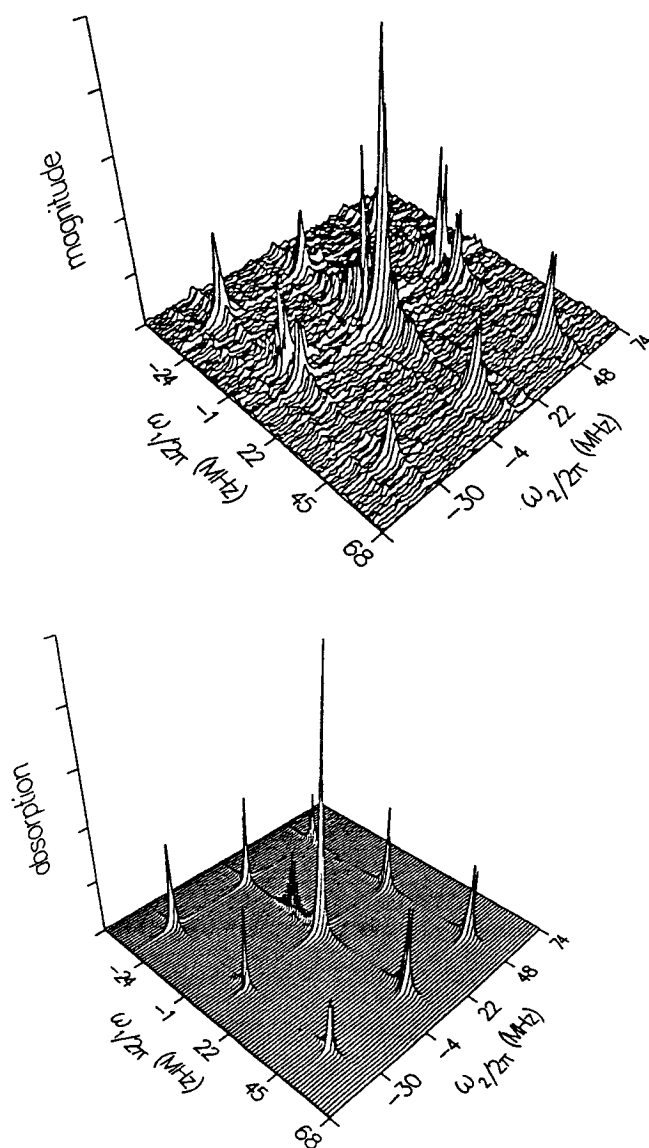
Clearly, it was necessary to develop modern FT techniques in ESR as a prerequisite to developing the ESR analogues to 2D-NMR. Modern FT techniques appeared almost the same time in Mike Bowman's lab in Argonne (53), Peter Dinse's lab in Dortmund, Germany (54), and my own lab in the 1984-1986 period. My motivation was partly the hope of performing modern 2D-FT-ESR experiments and partly the hope of studying the spectra from transient radicals. In fact, in 1984, Uzi Eliav working as a postdoc with me, succeeded in obtaining the FID of a transient photogenerated electron from Rb/THF solutions, thereby distinguishing its spectrum from the stable solvated electron (55). However, we had to step out the boxcar averager to map out the full FID. In another experiment, Joe Hornak and I

in the summer of 1985 showed that the  $B_1$  microwave fields in the rotating frame need not be much larger than the spectral bandwidth to obtain reasonable coverage in an FT-ESR experiment (56). One merely has to accept a rotation of the spins into the rotating  $x'$ - $y'$  plane instead of precisely along the  $x'$  axis (for a  $B_1$ , along the  $y'$  axis). Then quadrature detection plus standard phase corrections yielded the pure absorption from the FID. Also we showed the advantages of utilizing a loop-gap resonator which can supply large  $B_1$  fields, but with low  $Q$ 's to reduce resonator ringing and thereby spectrometer dead time after the pulse. However, we still stepped out the boxcar averager to collect the full FID.

This experiment was then taken over by my graduate student Jeff Gorcester. With the purchase of a two-channel HP54100A digitizing oscilloscope and a home-built quadrature detector (later replaced by a commercial one), we were able to obtain good FID's and FT spectra from fast motional nitroxides with a total spectral width of 90 MHz. At the APS meeting in March 1986, Mike Bowman and I were able to report on our respective efforts at FT-ESR. By the time of the EPR symposium in early June at the University of Saskatchewan, I could report on our first two-dimensional FT-ESR experiments on the fast motional nitroxide system. Jeff Gorcester had successfully performed a 2D-ESE experiment, appropriately called a SECSY (spin-echo correlated spectroscopy) experiment and an FID-based 2D-exchange experiment, which we now call 2D-ELDOR (57). This first FT-based 2D-ELDOR experiment showed cross-peak development resulting from Heisenberg spin-exchange (see Fig. 7). The SECSY experiment showed how the homogeneous  $T_2$  values from all the hf lines could be obtained simultaneously from an inhomogeneously broadened ESR signal. Thus 2D-FT-ESR became a reality.

There were still a number of major challenges to make 2D-FT-ESR generally applicable. Jeff Gorcester and I improved the spectrometer, added sophisticated phase cycling, and completed a full theoretical analysis for the fast motional 2D spectra in terms of how Heisenberg exchange (HE) and electron-nuclear dipolar (END) terms generate the cross peaks. We showed how their respective contributions could be readily distinguished. This led to quantitative measurements of HE in an isotropic fluid (58) and of END terms in a liquid crystal (59). This latter study could be utilized to provide sophisticated insights on molecular dynamics in ordered fluids in a way that cw-ESR linewidths could not. Also, Mike Bowman showed how 2D-ELDOR could be used to measure rates of chemical exchange in a semi-quinone system (60).

With additional improvements to our 2D-FT-ESR spectrometer, largely due to my co-worker Dick Crepeau, which a) increased our spectral coverage to about 250 MHz, b) greatly increased our data acquisition rates (by a factor of 150), and c)



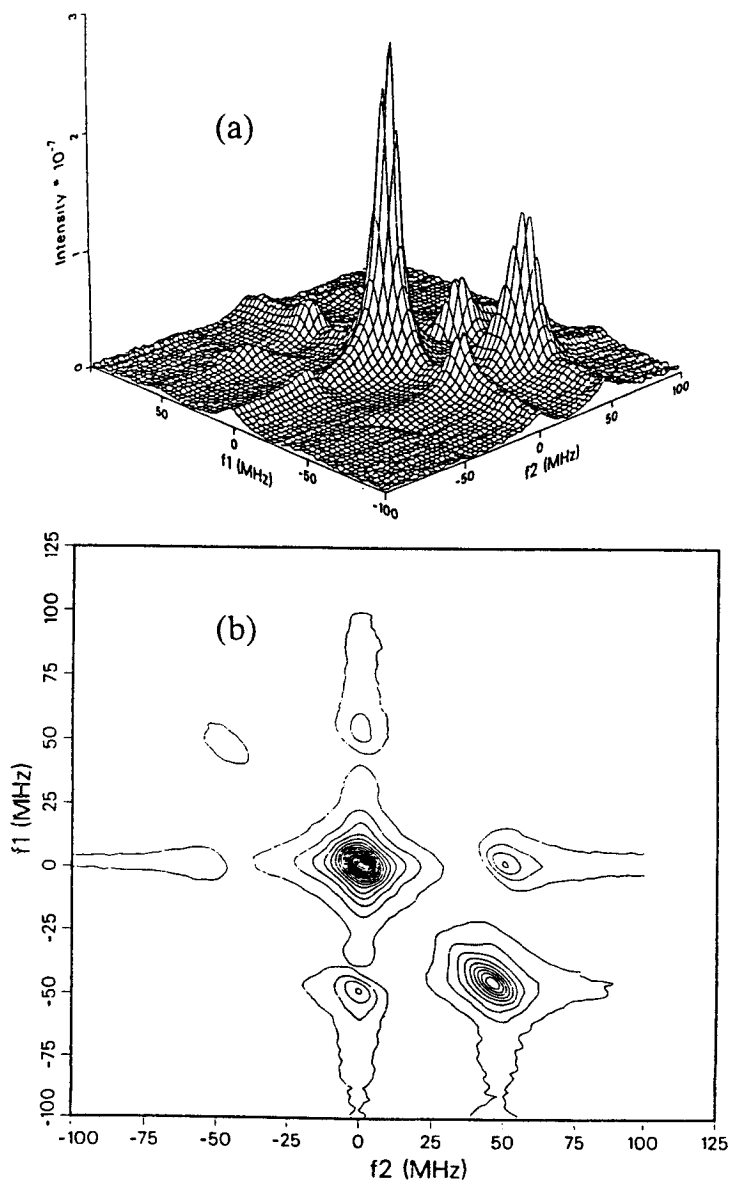
**Figure 7** 2D-FT-ELDOR spectrum of a mM. solution of PD-Tempone in toluene-d<sub>6</sub> at 21°C, a) raw data; b) after analysis by linear predictive methods. The cross-peaks are due to Heisenberg spin exchange. From ref 58.

significantly reduced our spectrometer dead-times, it became possible to extend 2D-FT-ESR to the slow motional regime (61). These developments necessitated more subtle instrumental and filtering improvements before we could fully benefit from the increased signal-to-noise we had realized. Also, a general theory for these experiments was needed for their interpretation. Sanghyuk Lee, a graduate student, with help from Dave Budil, carried this out admirably using as a starting-point Leslie Schwartz's Ph.D. thesis plus the work of Dave Schneider on his convenient cw-slow-motional program (62). Lee's work has enabled us to demonstrate the good agreement between theory and experiment for studying a range of spin labels in membrane vesicles (see Fig. 8) and for the study of very slow motions (with  $\tau_R \sim 10^{-6} - 10^{-3}$  sec.). Recently, the dynamic (solvent) cage model has been introduced into the theory and applied to liquid crystals (65) and to polymers (66).

It is my current hope that 2D-FT-ESR will become a general method for ESR spectroscopists just as 2D-NMR has for our NMR colleagues. With present technology, we can irradiate the full ESR spectrum for nearly all organic radicals and nitroxide spin labels! We can obtain 2D spectra from samples with total  $T_2^*$  as short as 15-20 nsec. By means of a two pulse SECSY (or closely related COSY) experiment one can simultaneously obtain the individual homogeneous  $T_2$ 's for each hf across the whole experiment. By means of 2D-ELDOR experiments performed as a function of mixing time, one can simultaneously study cross-relaxation,  $T_1$  and  $T_2$  processes, and one can distinguish different types of inhomogeneous broadening from each other and from the homogeneous broadening. This capability is, I believe, a major boon to the study of spectroscopically complex systems such as membrane vesicles, enabling one to accurately infer the microscopic details of ordering and dynamics. It is also a boon to the study of viscous systems and of macromolecules such as polymers and proteins, where the slow motional contributions to  $T_2$  and to magnetization transfer can be studied in great detail from a single set of 2D-ESR spectra. 2D-FT-ESR also has potential for structural studies by nuclear modulation, and by double quantum coherence, as we have recently shown (63) and Peter Dinse has recently found it useful for correlating the sequence of reaction steps of transient radicals (64). In the future one will also want to develop 2D-ESR techniques to cover a substantial range of frequencies to further enhance their applicability.

### 3. Acknowledgments

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**Figure 8** The 2D-FT-ELDOR spectrum from cholestane spin label in phospholipid membrane vesicles at 50°C. a) surface plot; b) contour plot. The cross-peaks are due to the electron-nuclear dipolar interaction. Simulations of this 2D spectrum yielded the rotational diffusion tensor, the microscopic orienting potential, and the Gaussian inhomogeneous broadening. From ref. 62.

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