

# Direct determination of rotational correlation time by electron-spin echoes<sup>a)</sup>

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There is considerable interest in the determination of rotational correlation times  $\tau_R$  by ESR techniques especially in the case of nitroxide spin probes and spin labels which have a wide variety of applications.<sup>1</sup> It has been shown that by a careful analysis of ESR motional-narrowing line widths and both unsaturated and saturated ESR slow-motional lineshapes, it is possible to obtain  $\tau_R$  as well as additional information pertaining to the microscopic details of the motion.<sup>2-5</sup> A particular saturation technique, viz., saturation transfer, is especially useful for the slower motions.<sup>6</sup> All these methods may be characterized as indirect ones, especially those involving slow tumbling, in that detailed spectral simulations are required in order to obtain  $\tau_R$ . The sophistication of the analysis appears to increase with the sophistication of the technique.

Some time ago Mason and Freed<sup>7</sup> suggested that measurement of the widths of the outer ESR hyperfine extrema from slow-motional spectra could yield  $\tau_R$  as long as  $3 \times 10^{-6}$  sec, based upon rigorous spectral simulations. This approach has now been experimentally confirmed, although the analysis is complicated by inhomogeneous broadening as well as overlap effects.<sup>8</sup> These predictions were consistent with a homogeneous broadening contribution  $T_2 \propto \tau_R$  with a proportionality constant of order  $1-\frac{1}{5}$  depending upon the nature of the microscopic model for rotational diffusion as well as the extent of inhomogeneous broadening.<sup>7,8</sup>

This detailed prediction was rationalized in terms of the lifetime uncertainty principle, viz., the outer hyperfine extrema (corresponding to those nitroxides oriented such that their magnetic  $z$ -axes are parallel to the magnetic field) are broadened by the rate at which the nitroxides reorient and then contribute to another region of the spectrum.

In view of these observations, it would appear that a direct determination of the intrinsic or homogeneous part of  $T_2$  in the slow-motional region would directly yield an estimate of  $\tau_R$ . Such an experiment should be achievable by means of electron-spin echoes (ESE).<sup>9</sup> We have, therefore, undertaken such a study, and we wish to report on our positive results.

We do note that the rigorous theory of ESE in the slow-motional region<sup>10</sup> is no less sophisticated than that of the other experiments noted above. However, the simple two-jump motional model, which can be solved exactly for ESE is in exact agreement with the lifetime-uncertainty principle. We comment further below on the relevance to nitroxide slow-tumbling theory.

The ESE spectrometer is very similar to one used at Argonne Labs,<sup>11</sup> permitting two- and three-pulse se-

quences of minimum pulse width 10 nsec and maximum pulse power 1 kW. The  $T_2$ 's were determined by two pulse  $90^\circ$ - $180^\circ$  echoes. We studied most extensively a sample of Tempone in 85% glycerol-15% water by weight and prepared to be very similar to that studied in detail by cw ESR by HMHF<sup>4</sup> except that deuterated materials used by HMHF were deemed unnecessary for the present work especially since we wished to suppress any effects of nuclear modulation.<sup>9</sup> Most experiments in the slow motional region were performed on the central portion of the spectrum, where there is maximum absorption intensity, and good echoes could be obtained with pulses of 20-70 W peak power.

We show in Fig. 1 our results obtained in both the fast and slow motional regions. The dead time of about 200 nsec currently restricts us to phase memory times  $T_M \geq 0.5 \times 10^{-7}$  sec. Also shown on this figure are lines representing the cw results and analysis of HMHF. The fast motional  $T_M$  obtained here for the central ESR hf line are seen to be in excellent agreement with the intrinsic  $T_2$ 's of HMHF for that line as they should be,<sup>12</sup> thus confirming the equivalence of the samples. HMHF

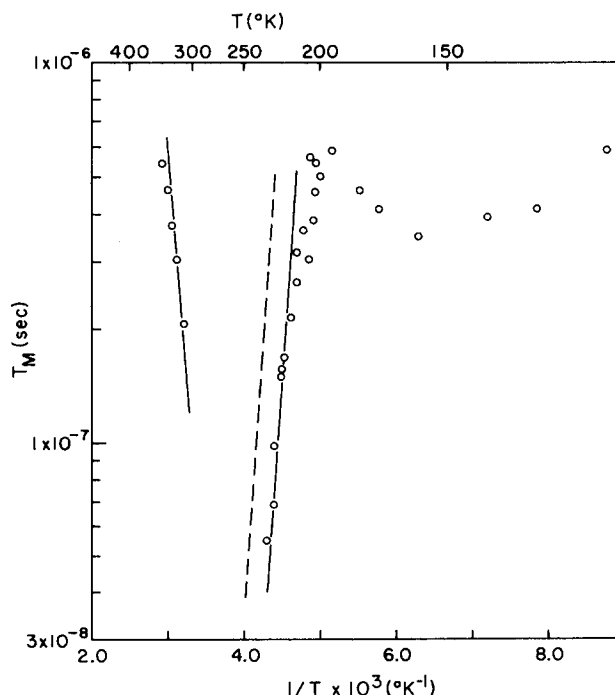


FIG. 1. Phase memory time,  $T_M$ , vs  $1/T$  for tempone in 85%/15% by weight glycerol-water solvent. Experimental points shown. Solid and dashed lines from cw results of HMHF.<sup>5</sup> Dashed line is  $\tau_R$  vs  $1/T$  while lower  $T$  solid line is  $\tau_R/6$  vs  $1/T$ .

showed that the isotropic  $\tau_R$  over several orders of magnitude spanning the fast motional and slow motional region could be linearly fit to  $\ln\tau_R/\tau_{R0} = E_A/RT$  where  $E_A = 15$  kcal/mole and  $\tau_{R0} = 2.3 \times 10^{-21}$  sec. This function is plotted as the dashed line in Fig. 1. One sees that, within experimental error, our results for  $T_M$  in the slow motional region:  $0.5 \times 10^{-7}$  sec  $\leq T_M \leq 5 \times 10^{-7}$  sec are parallel to this line such that  $T_M \approx \tau_R/6$ . Thus, at least for this decade of  $\tau_R$ ,  $T_M$  is a direct measure of  $\tau_R$ .

For lower temperatures it appears that a lower activation process(es), possibly a "solidlike" mechanism, dominates  $T_M$ .<sup>9</sup> Brown<sup>13</sup> has studied  $T_M$  in this region for the radical PADS<sup>2,3</sup> and has also observed more complicated behavior. In this very slow motional region one may observe nuclear modulation patterns from incomplete averaging of intramolecular anisotropic proton (or deuteron) hf structure.<sup>9,12</sup> A careful theoretical analysis of how these patterns are affected by  $\tau_R$  could enable such effects to be used as an indirect measure of  $\tau_R$ .

In the limit that pulse widths  $\bar{\tau} \ll T_1, T_2$ , and in the approximation that the finite radiation field rotates by  $\pi/2$  (or  $\pi$ ) only a particular region of the spectrum, one may readily show that the eigensolutions<sup>5</sup> of the unsaturated slow-tumbling cw solution may be used to predict the related FID or ESE spectrum.<sup>14</sup> Each Lorentzian-type eigenmode that contributes appreciably to the cw spectrum, and is close enough to the resonant field, yields an ESE contribution with its  $T_{M,n}^{-1} = \text{Re}E_n$ , i.e., the real part of its eigenvalue. Given the available time resolution, typically the slower decay constant(s) are measured in the experiment. We have studied theoretical predictions and we do indeed find that these slower modes are characterized by  $\text{Re}E_n \approx 6/\tau_R$ , in the case of a Brownian motion model but values of  $\sim 3/\tau_R$  and  $1/\tau_R$  are found for approximate free diffusion<sup>2,5</sup> and jump models,<sup>2,5</sup> respectively. In this latter case *all*  $\text{Re}E_n$  become nearly equal for slow motion.

It is expected that a direct determination of  $\tau_R^{-1}$  (or more precisely  $\text{Re}E_n$ ) by ESE would assist in the accurate analysis of slow-tumbling spectra obtained by the other ESR techniques.

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<sup>14</sup>In this context, we note that in Ref. 4 it was conjectured that a "fluctuating torque" model might just as successfully explain the anomalies in the cw slow-motional spectrum as a moderate jump model. Our ESE result would then favor the former because its non-Markovian features would not be present at the longer times we measure, but further analysis is called for.

## Photoelectron energy distribution following UV laser ionization of gas phase benzene

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One of the striking features commonly observed in recent molecular multiphoton ionization (MPI) mass spectrometry studies has been the appearance of small ion fragments.<sup>1-8</sup> Considerable speculation as to their origin has arisen. Molecules may absorb several photons and subsequently undergo violent explosions yielding the ionic fragments. Alternatively, it is possible that molecular ions are produced in a two or three photon process and fragments then derive from successive single

photon dissociation steps. In the case of KrF laser induced ionization of singly deuterated benzene we have previously found that certain ionic species such as  $C_6H_5D^{2+}$  are not produced and have suggested that this indirectly favors the latter mechanism.<sup>8</sup> The present experiments represent a more direct probe of the phenomenon. The photoelectrons generated in coincidence with the ions are monitored in an attempt to measure the molecular energy content at the instant of ionization. In