on the surface. In situations in which CO islands exist, even at low coverages, the band maxima at all coverages is at the high wavenumber end of the observed band position excursion.[7] While we observe an increase in the frequency of the band center as a decrease in coverage occurs due to CO oxidation to CO_2 it is not possible to determine whether the oxidation reaction in 1 N H_2SO_4 occurs at the edges of adsorbed CO islands at all CO coverages, or if the voltage dependence of the frequency shift obscures shifts due to intermolecular interactions.

Further, since the plot of band center position vs. electrode potential appears linear at constant coverage we infer that the force constant associated with the linear CO stretching vibration (and hence the bond order) is influenced predominantly by electron donation or withdrawal by the Pt electrode. However, we cannot ignore the possibility that coverage-dependent intermolecular interactions influence the linear CO band position since deviations from linearity in the band position vs. electrode potential plot cannot be ruled out (viz. Figure 3).

The Oscillatory Nature of Polarization Evolution in CIDEP

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An unusual and striking pattern of oscillations in the time evolution of the polarization has been observed in a time-resolved CIDEP study of photoelectrons generated in high concentration Rb/THF solutions. It is suggested that such oscillations may be characteristic of a (geminate) radical-pair mechanism when observed under sufficient time resolution.

The CIDEP phenomenon is of considerable interest because it often depends upon the early time history of interacting radical pairs.[1] Modern time-resolved ESR techniques permit one to study CIDEP in greater detail.[1,2] We have been engaged[3] in an extensive study of the Rb/THF system[4] by time-resolved ESE techniques. In THF (tetrahydrofuran) the Rb exists as Rb^+Rb^- ion pairs. The use of complexing agents can greatly enhance the concentration of these species. A short-lived photoelectron, e_p^-, can be produced with a laser pulse. In work we have done in concentrations of $Rb^- < 10^{-2}$ M we have been able to measure both the rate of evolution of the initial polarization with inverse rate constant $k^{-1} \sim 20$–70 ns and the final polarization P^∞ which is $\sim$50–200 times greater than the equilibrium polarization P_{eq}, and we have observed their temperature, wavelength, and concentration dependences.[3] These results appear to imply a geminate radical-pair mechanism for the generation of the CIDEP. A likely mechanism would involve geminate interaction between Rb· and e_p^-, but one does not observe the Rb·.

In this Letter we describe new and unusual observations we have made at higher concentration ($[Rb^-] = 10^{-2}$ M) which we believe to be of fundamental significance to the study of the radical-pair mechanism.

These experiments were performed on Rb metal dissolved in a solution of 2,2,2-cryptate (Cr) in THF at −107 °C. The concentration of the Cr was 10^{-2} M. At this high concentration a stable solvated electron e_s^- is present at all times independent of any laser irradiation. We determined from the fact that $P_{eq}(e_s^-) = 2P_{eq}(e_p^-)$ that the concentration of e_s^- is twice that of e_p^-. We estimate 10^{14} e_s^- spins. Since the concentration of e_s^- is a measure of the concentration of cryptate, we could use the e_s^- signal height to monitor the amount of cryptate during the course of the experiment. The e_s^- was not present in the lower concentration solutions. The experiments consist of irradiating the solution with 10–15-ns laser pulses of 2-mJ energy from a Lambda-Physik dye laser at wavelength $\lambda = 898$ nm corresponding nearly to the absorption maximum for Rb^- in THF. This is followed at time t by a 90°−τ−180°−τ microwave echo sequence in the case of echo experiments, or just by a 90° pulse at time t for an FID experiment. (The 90° pulses were of 25-ns duration.) Because of the presence of the e_s^- at all times, which interferes with the echo from the e_p^-, we modified the echo sequence in the following manner to suppress the echo from the e_s^-. We used the sequence 90°−τ'−laser−t−90°−τ−180°−τ, where $\tau' \approx 6T_{2,s}$ or 12 μs, while $\tau = 250$ ns. Here $T_{2,s}$ is the transverse relaxation time of e_s^-. The 90° pulse prior to the laser pulse just rotates the e_s^- signal into the rotating x–y plane where it dephases in the time $\sim\tau'$. Since $T_{1,s} \gg T_{2,s}$, we can set $(\tau' + t + 2\tau) < T_{1,s}$ so the e_s^- signal cannot recover significantly before the echo from the e_p^- is observed. In this manner the e_s^- echo was suppressed by an order of magnitude. The FID from e_p^- could be suppressed with a field gradient.

The echo experiment we report on here consists of stepping out the time t between the laser pulse and the subsequent 90° echo pulse. In this experiment it was important to achieve very short time resolution in order to study the polarization evolution in detail. We therefore employed BNC digital delay generators with a stepping time of 1 ns, and adjusted our bridge and our cavity-Q to maximize the resolution.

We display in Figure 1 the evolution of the polarization as a function of t. Three important facts immediately emerge. First of all, the final polarization P^∞ which develops is an order of magnitude smaller than for lower concentrations solutions. That is: $P^\infty/P_{eq} \approx 10$. Second, the rate of the evolution is about an order of magnitude slower, i.e., $k^{-1} \sim 500$ ns. Third, and most dramatic, the polarization evolution is a highly oscillatory process superimposed on the gradual rise of $P(t)$ to its asymptotic value P^∞. As the Rb^- concentration decreases over a period of several hours, the values of k and P are found to increase and the oscillations are suppressed.

One might at first suspect that, in the more concentrated solution, random encounters of f-pairs may be important in initiating the polarization process. But this is contradictory to our observations that, at the high concentration, k, the rate of polarization evolution, is an order of magnitude *slower* and P^∞/P_{eq} is an order of magnitude smaller. It therefore appears that geminate interactions are again responsible for the CIDEP.

The fact that both k and P^∞ are both significantly reduced is consistent with a radical-pair mechanism, if Q (defined as half the difference between the resonant frequencies of the two in-

(1) L. T. Muus, P. W. Atkins, K. A. McLauchlan, and J. B. Pedersen, "Chemically-Induced Magnetic Polarization", Reidel, Dordrecht, 1977.

(2) A. D. Trifunac and J. R. Norris, *Chem. Phys. Lett.,* **59,** 140 (1978); A. D. Trifunac, J. R. Norris, and R. G. Lawler, *J. Chem. Phys.,* **71,** 4380 (1979).

(3) U. Eliav and J. H. Freed, to be submitted for publication.

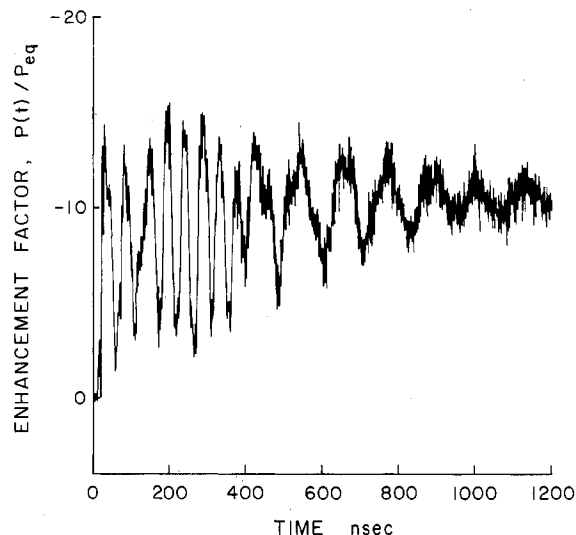(4) U. Eliav, H. Levanon, P. M. Carton, and R. W. Fessenden, *Chem. Phys. Lett.,* **82,** 365 (1981).

Figure 1. Evolution of polarization with time. The ordinate gives the enhancement factor, $V = P(t)/P_{eq}$. The time interval between the laser pulse and the 90° pulse was stepped in 1-ns intervals. (The signal was observed by a 90°–180° echo sequence with $\tau = 250$ ns.)

teracting radicals) has been reduced in the higher concentration solution. More precisely, the theory based upon radical reencounters predicts a monotonic dependence of both k and P^∞ upon Q.[5] Previous studies[6] have shown that Rb·, the likely candidate for the counterradical, exhibits a large variation in hfs and g factor with temperature and solvent (although its ESR spectrum cannot be seen in THF solvent), so concentration-dependent effects on Q are not unreasonable. We estimate that Q is positive since $g_{e_p^-} = 2.0023 > g_{Rb} \sim 1.998–2.001$.[7] Also, since the optical transition is highly allowed, the excited Rb⁻ should be singlet in character. Thus the emissive character of the CIDEP indicates that the exchange interaction J is negative;[1] i.e., the Rb· + e_p^- exchange interaction is such that the singlet lies lower in energy. This would be consistent with a model of simple bonding overlap of the Rb· 5s orbital with that of the e_p^- restricted for short times to a solvent cavity.

We now note how the simple theory for the time evolution of polarization $P(t)$ would imply an oscillatory behavior. For example, in the case where the initial radical-pair encounter dominates and reencounters are unimportant, one may write[8,9]

$$P(t) = \frac{2}{\tau_c} \frac{QJ}{\omega^2} \int_0^t e^{-t'/\tau_c} \sin^2 \omega t' \, dt' =$$

$$P^\infty \left[(1 - e^{-t/\tau_c}) - (1 - \cos 2\omega t)\frac{e^{-t/\tau_c}}{4\omega^2\tau_c^2} - (\sin 2\omega t)\frac{e^{-t/\tau_c}}{2\omega\tau_c} \right]$$

$$(1)$$

where

$$P^\infty = QJ\frac{4\tau_c^2}{1 + 4\omega^2\tau_c^2}$$

and

$$\omega \equiv (Q^2 + J^2)^{1/2}$$

Here τ_c is the mean lifetime of the radical pair. This very simple model predicts an oscillatory behavior in $P(t)$ with frequency 2ω. The observation that there are many oscillations during the buildup of polarization would require $\omega\tau_c \gg 1$, but in this limit the

(5) J. H. Freed and J. B. Pedersen, *Adv. Magn. Reson.*, **8**, 1 (1976).
(6) (a) J. L. Dye in "Progress in Macrocyclic Chemistry", Vol. I, J. J. Christensen and R. M. Izatt, Eds., Wiley-Interscience, New York, 1979, and references therein; (b) R. Catterall and P. P. Edwards, *J. Phys. Chem.*, **84**, 1196 (1980); (c) C. A. Friedenberg and H. Levanon, *Chem. Phys. Lett.*, **41**, 84 (1976).
(7) R. Catterall and P. P. Edwards, *J. Phys. Chem.*, **79**, 3010 (1975); also ref 6c).
(8) F. J. Adrian, Ref 1, Chapter V.
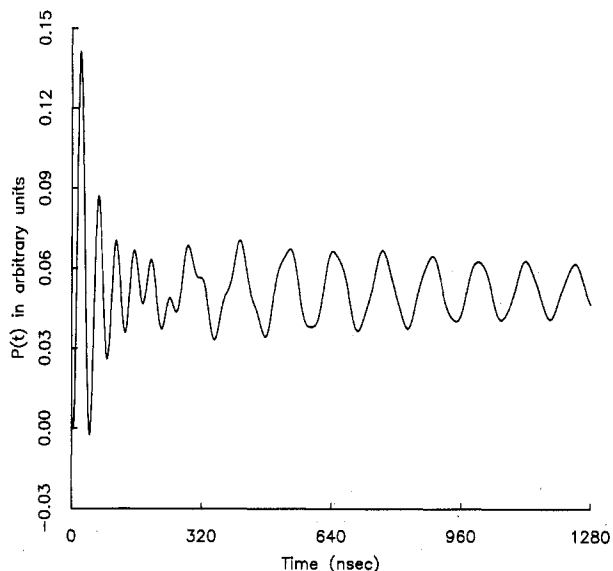(9) J. H. Freed, *Annu. Rev. Phys. Chem.*, **23**, 265 (1972).

Figure 2. A predicted oscillatory polarization evolution curve for the jump reencounter mechanism. There are two species, each obeying eq 2. Species 1 and 2 have $2\omega_s/(2\pi) = 23$ and 8.5 MHz, respectively. Also, the effective reencounter time $\hat{\tau}_{d,i} \equiv \frac{3}{4}[(r_{0,i} - d_i)/r_{0,i}]^2 \tau_{d,i}$ is 24 and 720 ns for $i = 1$ and 2, respectively. The ordinate is $P(t)/Y$ where $Y = (3/\pi)^{1/2}(Q_1/\omega_{s1})J_1\tau_{c,1}(\hat{\tau}_{d,1}/16 \text{ ns})$ and $P(t)$ is for a single e_p^- of species 1 (plus the appropriate amount of species 2). The ratio of concentrations of species 2 to species 1 equals $\frac{2}{3}(J_1/J_2)(Q_1/Q_2)/(\tau_{c,1}/\tau_{c,2})$. The limit $4\omega_{c,i}^2\tau_{c,i}^2 \ll 1$ was used.
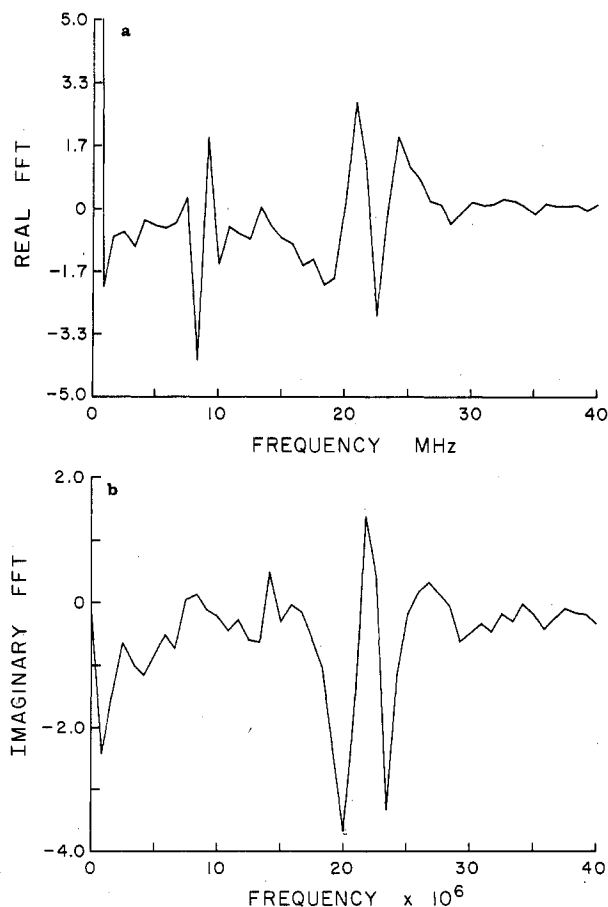

Figure 3. Fourier transform of Figure 1: (a) the cosine or real part; (b) the sine or imaginary part.

oscillatory terms are greatly suppressed in eq 1. [We would have to associate τ_c with k^{-1} leading to $2\omega\tau_c \sim 60–150$.] Thus, we find that eq 1 *cannot* predict substantial oscillations in $P(t)$ such as are observed in Figure 1. However, we note that eq 1 is just for
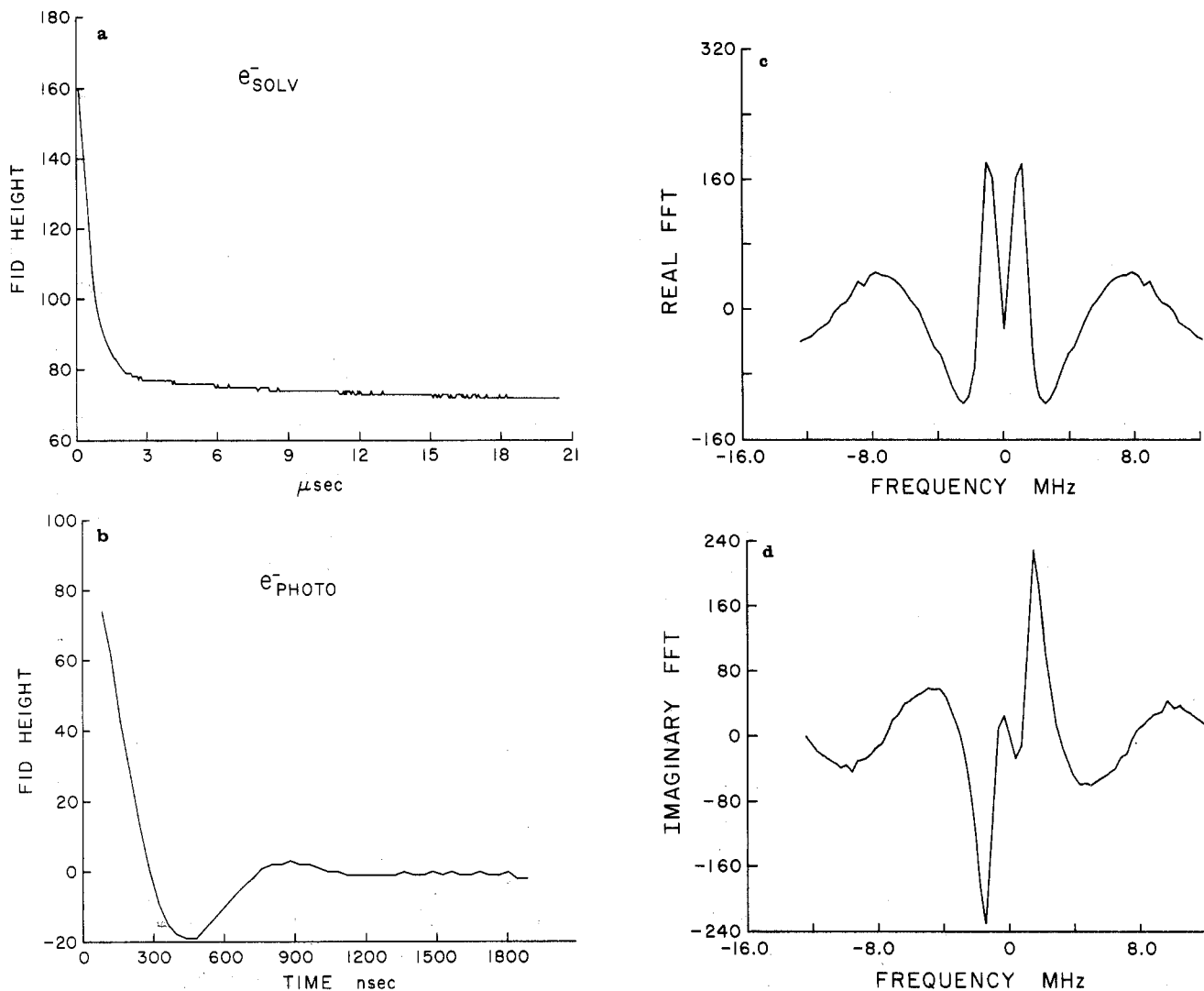
Figure 4. (a) FID of e_s^-; (b) FID of e_p^- obtained with a 400-ns time interval between the laser pulse and the 90° pulse; (c) cosine FT of (b); (d) sine FT of (b). (The FT was performed by taking the first data point after the dead time as $t = 0$.)

those e_p^- after they have separated. Those e_p^- still in contact with the counterradical would experience oscillatory polarization given by $P(t) = 2QJ\omega^{-2}e^{-t/\tau_c}\sin^2 \omega t$. This would require radical pairs with a substantial lifetime of the order of 500 ns. While this might be reasonable for the diamagnetic ion pair Rb^+Rb^- held together by Coulombic forces in a nonpolar solvent, we do not believe it is likely for an $Rb\cdot + e_p^-$ radical pair in a nonviscous liquid solvent. Furthermore, if J were appreciable, then the radical-pair resonances could be sufficiently shifted, relative to e_s^-, and broadened (i.e., a likely reason why $Rb\cdot$ is not seen in our experiments would be its short T_2) so that the 90° –180° echo sequence would not even detect it. We will point out below other reasons why we do not, at present, favor this "long-lived" radical-pair mechanism.

If we now invoke the radical-pair mechanism with reencounters,[1] then it becomes possible to rationalize the prominent oscillatory character without requiring long-lived radical pairs. We first consider the reencounter mechanism in its simplest form. We take, for example, an $Rb\cdot + e_p^-$ pair that have formed at $t = 0$ in the singlet state and have separated to a distance of r_0. This temporary structure persists for a short time, whereupon the e_p^- has a finite probability for reencountering the $Rb\cdot$. During the short reencounter, the exchange interaction is again "turned on". The time evolution for this simple model[8] may be written as

$$P(t) = \frac{JQ}{\omega_s\omega_c} \int_0^t dt'' \int_{t''}^t dt' \sin (2\omega_s t'') \sin 2\omega_c(t' - t'') \times$$

$$p_r(d,t''|r_0,0)\ p_e(t' - t'')$$

where $p_r(d,t''|r_0,0)$ is the probability density that the radical pair

initially at r_0 will first reencounter at separation d at time t'', while $p_e(\tau)$ is the probability density that the radical pair encountering at $r = d$ will first separate at time τ. Also ω_s and ω_c are the values of ω during separation and reencounter, respectively. If we substitute the usual expression for these probabilities, we can integrate over t' to obtain

$$P(t) = \frac{JQ}{\omega_s} \frac{2\tau_c}{1 + 4\omega_c^2\tau_c^2} \int_0^t dt''\, p_r(d,t''|r_0,0) \sin (2\omega_s t'') \times$$

$$\left[1 - e^{-(t-t'')/\tau_c} \cos 2\omega_c(t - t'') - \frac{e^{(t-t'')/\tau_c}}{2\omega_c\tau_c} \sin 2\omega_c(t - t'') \right] \quad (2)$$

with[10]

$$p_r(d,t''|r_0,0) =$$

$$\left(\frac{3}{4\pi}\right)^{1/2}\left(\frac{r_0 - d}{r_0}\right)\left(\frac{\tau_d}{t''}\right)^{3/2} \tau_d^{-1} \exp[-3(r_0 - d)^2\tau_d/4d^2t'']$$

Here τ_d is the time between diffusive jumps, while τ_c is again the mean lifetime of the radical pair. There is the possibility for two primary oscillatory frequencies, $2\omega_s$ and $2\omega_c$ (as well as their sum and difference), which could appear at different times.

We have numerically integrated eq 2 for a large range of values of the parameters. We found that it is quite possible to obtain

(10) This jump form of the first reencounter probability is given by F. J. Adrian (cf. ref 8). The diffusive form is given by J. B. Pedersen (cf. ref 1, Chapter XVII).

a $P(t)$ exhibiting strong oscillations with period $2\pi/(2\omega_s)$.

We now consider the fact that Figure 1 shows an increased period of oscillation as time progresses. That is, at short times the period is ca. 44 ns but later becomes ca. 120 ns (cf. Figure 1). One might have expected that the terms in $2\omega_c$ in eq 2 would lead to additional oscillations with period $2\pi/(2\omega_c)$. We find, from detailed calculations of eq 2, that is is not possible to obtain prominent oscillations at this frequency [for reasons analogous to the lack of any prominent oscillations from eq 1]. Instead, we suspect that there may be two species present with distinct values of ω_s, a possibility also suggested by the FID results discussed below. Simulations based upon this two species model (in the limit $2\omega_c\tau_c \ll 1$) do show characteristics of Figure 1, as illustrated in Figure 2. (The long-lived radical-pair model would also require two species with distinct values of ω or else a long lived plus a separated pair could be invoked.)

Equation 2 is, of course, a primitive model for the radical-pair mechanism, but it does emphasize a jump-type of motional process which we suspect is characteristic of e_p^- possibly involving nearby counterion traps. Preliminary calculations[3] based upon the rigorous Brownian diffusion model[5] do indicate an oscillatory component to $P(t)$ which becomes more prominent as Qd^2/D increases (with D the relative translational diffusion coefficient).

While we regard these simple attempts at modeling $P(t)$ to be very preliminary, they do serve to emphasize the fact that $P(t)$ in CIDEP should be oscillatory under reasonable conditions, and the details of this oscillatory behavior could be expected to be associated with the microscopic details of the radical-pair mechanism.

We have Fourier-transformed $P(t)$ vs. t of Figure 1. The cosine (real) and sine (imaginary) transforms are shown in Figure 3. The microwave reference phase in this experiment had been adjusted to give good in-phase echo signals from the e_s^-, which could therefore serve as a reference. We note that the peak (or peaks) at ca. 9 MHz appear to be in-phase (i.e., predominantly in the real transform) while the peak (or peaks) at ca. 22 MHz appears to be significantly phase shifted. These are just the inverse of the two characteristic periods of oscillation observed in Figure 1. We note also the unusual appearance of these peaks. The FT of the example of Figure 2 does show somewhat similar features for the lower frequency peak(s), and we believe this is supportive of the model. (The long-lived radical-pair model however, is predicted to show just simple Lorentzian absorption and dispersion, contrary to observation. Cf. Figure 3.) The predicted higher frequency peak(s) from the FT of Figure 2 is overly broad, possibly indicating that details of the model need to be improved.[11a] [One possibility might be that only species 1 is present initially, but it could in time complex (cf. below) with a counterion to form species 2 which could also reencounter. A similar complex formation could also be postulated for the long-lived radical-pair model.]

We have also performed an FID experiment with a 90° microwave pulse coming shortly after (400 ns) the laser pulse. In order to obtain the FID from the e_p^-, it was necessary to subtract out the FID from just the e_s^-, which could be generated in the absence of a laser pulse. These FID's are shown in parts a and b of Figure 4. The FID for the e_s^- is a simple exponential decay, while that for the e_p^- has a more unusual appearance. We also show in Figure 4 the cosine (real) and sine (imaginary) FFT results for e_p^-. [Again the FID's were performed with the microwave reference phased properly for the e_s^- signal (which shows a simple

resonance line in the FFT).] First and foremost, these results clearly demonstrate that there must be intrinsic differences between e_s^- and e_p^-. The results in Figure 4 appear to look like two frequency shifted lines (relative to e_s^-) appearing at about ± 1 and ± 7 MHz with the latter much broader. However, if this is a correct interpretation, then these results suggest the possibility of two species with the one at ± 7 MHz having the shorter lifetime. If we assume $\omega_s \approx Q$, then we would expect the frequency difference (or sum) between the two peaks in parts c and d of Figure 4 to match the difference for the main peak regions in Figure 3. However, this is not so. One possibility that occurs to us is that, on the basis of previous work,[4] there may be present a simple e_p^- and an ion pair: $(RbCr^+)$, e_p^-, and while $\omega_s \approx Q$, any differences in the g values, etc. of the respective Rb· counterradicals could modify the respective values of Q for the two species. We do wish to note that such a modest frequency shift of ± 1 MHz from the e_s^- is more in keeping with the existence of an e_p^- rather than a long-lived radical pair for which J could be substantially different from zero. We do not rule out a separated radical pair with a weak residual J[11b] (which then could contribute to the polarization). Lastly, we note the absence of oscillations in the FID, of the sort in Figure 1, appears to rule out oscillations in the radical concentration.

The reason why the oscillatory behavior was not seen in our previous studies on low concentration samples might have two sources: (1) for higher Q values, the oscillations would be of shorter period and therefore could be filtered out because of the finite spectrometer bandwidth and resolution; or (2) at lower concentrations, even though Q might be larger, if the product $Q\tau_d$ in eq 2 (or else $\omega\tau_c$ for the case of a long-lived radical pair) were decreased, then this would suppress the oscillatory character of the CIDEP.

In summary, we believe the striking oscillatory character we observe for Rb/THF in high concentration is consistent with the radical-pair mechanism. In this mechanism, the radical pairs continue to retain memory of their coupled spin state even if they should separate. Their difference in resonant frequency, or Q, continues to admix singlet and triplet in a coherent (and oscillatory) quantum-mechanical fashion, so that, when electron-spin polarization is produced upon their reencounter, this oscillation can manifest itself in the polarization evolution.[12]

Such observations of oscillatory CIDEP should permit a more detailed analysis and interpretation of the microscopic mechanism of interaction and encounter of radicals in solution.

(11) (a) Added in Proof: A Fourier inversion of Figure 1 by the maximum entropy method shows that the higher-frequency region is resovable into two peaks at 19.3 and 22.8 MHz, while the single low-frequency line is at 8.5 MHz. (b) A finite J might be expected to show phase shifts in the signals: cf. M. C. Thurnauer and J. R. Norris, *Chem. Phys. Lett.*, **76**, 557 (1980).

(12) Anisimov et al. [O. A. Anisimov, V. L. Bizyaev, N. N. Lukzen, V. M. Girgoryants, and Yu. N. Molin, *Chem. Phys. Lett.*, **101**, 131 (1983)] have just recently reported on oscillations in the time-dependent fluorescence intensity (corrected for the decreasing ion-pair concentration) from the singlet geminate recombination product formed from hydrocarbon radical ion pairs. They attribute this to the radical-pair mechanism for a long-lived ion pair.