a one-mass unit shift from 175 to 176 is observed in going from the proton to deuteron ion reagents, supporting a localized proton transfer ionization mechanism.

The case for localized proton or deuteron addition to the ester terminus is complicated by hydrogen atom rearrangements within the protonated molecule ion as evidenced by ions at masses 44, 104, 143, and 175 in proton transfer spectra. Internal hydrogen–deuterium exchange processes account for ions at mass 45, 87, 115, and 186 in the deuteron transfer spectra. However, if the "ionizing"deuteron were randomly attached, peaks corresponding to a + b + D at 116, and a + b + c + D at *m/e* 187 would be expected. Failure to observe these species supports the argument that proton transfer is indeed limited to the ester terminus of this molecule.

This technique utilizing protons in various states of solvation as the ionizing reagent permits controlled deposition of excess internal energy in the protonated parent molecule product. This single collision technique operates at very low pressures which may afford an advantage in treatment of relatively nonvolatile materials and which eliminates subsequent ion–molecule collisions that may perturb the final mass spectrum observed. It is clear that these secondary collisions are not required to stabilize protonated parent molecule ions when these ions are generated with very little excess energy.

The potential of this technique for sequence analysis of amino acids in peptides is demonstrated in these experiments. Experiments are in progress to test the value of the single ion impact technique on a variety of peptides including cases of polyfunctional amino acid systems.

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Transient Effects in Excitation of Triplet States

Sir:

A number of experiments designed to demonstrate selectivity in population and depopulation of individual sublevels of photoexcited triplet states have been performed at temperatures of a few degrees Kelvin. The observations include anomalous intensities in esr lines under steady illumination[1-3] and transient effects in both electron spin resonance intensities and in intensities and polarization of phosphorescence accompanying modulation of the exciting light.[2-5] Apparently it has been presumed that low temperatures are necessary for detection of the effects in order to retard sufficiently the rates of equilibration between states so as to make them slower than or comparable to the rates of dissipation of the states.

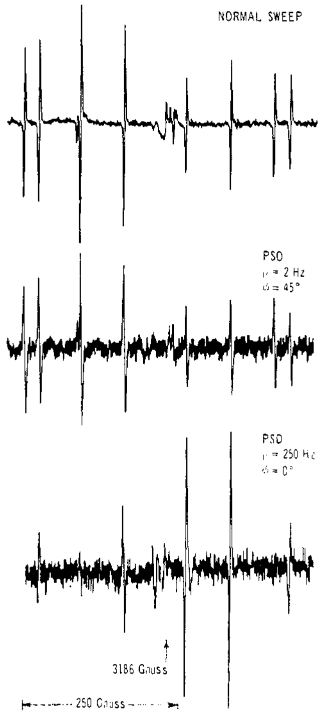

Figure 1. Esr recorded spectra of anthracene-d_{10} in crystalline benzophenone.

We report here observation of electron spin resonance carried out at 77°K which shows a variety of transient effects. The requirements for observation of the transients are simply that their amplitudes and duration, respectively, lie within the sensitivity and frequency response of the detecting instruments.

We describe as two examples among the several systems in which we have observed similar phenomena the behavior of anthracene-d_{10} dissolved in crystalline benzophenone and of phenazine dissolved in crystalline biphenyl. In each case the electron spin resonance is detected by a conventional electron spin resonance spectrometer (Varian E-3). The output of the spectrometer is recorded either in the usual way as derivative of susceptibility *vs.* field under steady illumination or with a modulated light source to yield the time variation of the signal. In the latter mode either the rise and decay of the signals at fixed fields are averaged over several thousand repetitions by means of a PAR wave form eductor or the signal is passed through a phase-sensitive detector which is referenced to the light pulse.[6] Low-frequency modulation is achieved by a rotating sector. Higher frequency modulation is produced by an electronically controlled high-pressure xenon arc (Eimac 150 XSR) which yields flat-topped pulses of variable duration and interval. The rise and decay times of the light pulses are 10–20 μsec. The resolution in time is limited to 150 μsec by the band width of the spectrometer.

The esr spectrum of anthracene-d_{10} in benzophenone excited to its triplet state by steady illumination is shown in Figure 1. Slow modulation of the light at 2 Hz and phase-sensitive detection of the esr, the light

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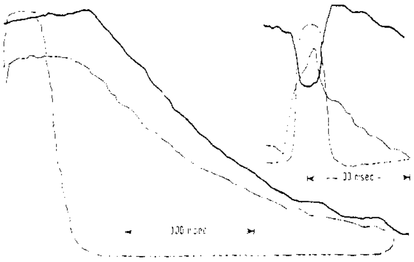

Figure 2. Kinetic curves for anthracene-d_{10} in benzophenone. The dashed curve is the time dependence of the light intensity and the heavy and light curves are the time dependence of a high- and low-field line, respectively.

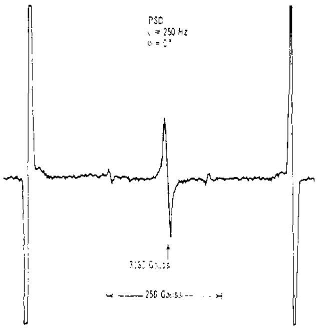

Figure 3. Phase-detected spectrum of phenazine. The central line at $g = 2$ is not identified. A similar light-modulated line appears in many systems.

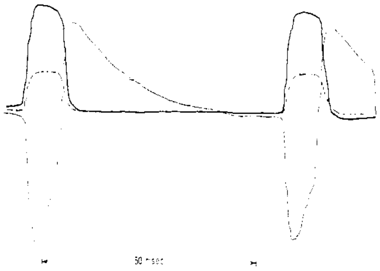

Figure 4. Kinetic curves of esr intensities of phenazine in biphenyl. The dashed curve is the light intensity *vs.* time and the heavy and light ones are the esr intensities of the high- and low-field lines, respectively.

modulation furnishing the reference, yield an almost identical spectrum (Figure 1). More rapid modulation at 250 Hz, again with phase-sensitive detection referenced to the light, yields the bottom spectrum of Figure 1. Some of the lines have disappeared and the surviving ones at low and high fields are inverted relative to each other. Direct observation of the associated kinetic behavior is shown in Figure 2. Under repeated pulses of light of about 10-msec duration, the low-field line is seen to be created with enhanced absorption, the high-field line with decreased absorption.[7]

The phenomena in phenazine in biphenyl host are similar but more pronounced. The spectra observed either under steady illumination or with low modulation are normal. At rapid modulation the phase-detected low- and high-field lines are inverted with respect to each other (Figure 3). The underlying kinetics as observed with pulsed excitation reveal the nature of the inversion. One line is born as an enhanced absorption, the other as an emission (Figure 4). We should note that phenazine in rigid glass does not exhibit the same phenomena. We believe that they exist but occur too rapidly for detection by our present equipment. We shall present detailed kinetic analyses of the phenomena in subsequent publications. We hope that with equipment presently under development the time resolution will be enhanced to permit observation of more rapid transients.

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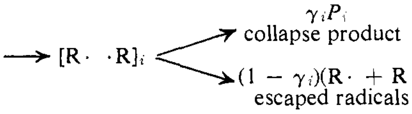
Suppression of High-Field (T_0–S) Chemically Induced Nuclear Spin Polarization (CIDNP) by Successive Trapping of Radicals. Persistence of Low-Field (T_1–S) CIDNP

Sir:

Current theory of CIDNP[1] holds the dynamic behavior of associated radical pairs responsible for the preferential formation of products in particular nuclear spin states.[3] Applied to reactions run in high magnetic fields (thousands of gauss), this is a spin selection theory. Each radical pair maintains its original nuclear spin state i as it collapses to products or separates to escaped radicals,[4] but the probability of collapse γ_i varies with i, so that nuclear spin states with larger γ_i are selected for preferential product formation.



$$\longrightarrow [\mathrm{R}\cdot\ \cdot\mathrm{R}]_i \begin{cases} \xrightarrow{\gamma_i P_i} \text{collapse product} \\ \longrightarrow (1-\gamma_i)(\mathrm{R}\cdot + \mathrm{R}\cdot)_i \ \text{escaped radicals} \end{cases}$$

According to this theory, there would be no CIDNP if all escaped radicals were somehow converted, with their original nuclear spin states, to P. This would be so even though the behavior of the individual radical pairs would normally give rise to CIDNP.

We report an example of this effect, the reaction of isopropyl chloride with sodium naphthalene. If the propane formed in this reaction resulted only from the *initial engagements* of intermediate alkyl radicals with naphthalene radical anion (:Naph·$^-$),[5] it would be

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[1] Accepting popular usage, we adopt the acronym CIDNP for the phenomenon more reasonably termed "chemically induced nuclear spin polarization," in spite of the fact that CIDNP was originally proposed as the name of a *theory* of this phenomenon,[2] not the phenomenon itself, and the fact that this theory no longer seems viable.[3]

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[4] *Escaped* radicals have been members of an associated radical pair, but they have a vanishing probability of a future mutual collision.

[5] In view of the fact that Noyes' treatment of the diffusion behavior of radical pairs has been made the basis of a promising new formula-