

with our data analysis shifts the problem of measuring accurate beam velocities to the problem of determining accurate field strengths, which is a common difficulty to all other methods also.

In conclusion, we are convinced that by employing our data-analysis technique, the quantum-beat method extended to long delay times will become competitive with other methods and even superior as soon as ionic states can be studied.

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Optically Detected Electron Spin Echoes and Free Precession in Molecular Excited States

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Electron free precession and electron spin echoes have been detected for molecules in their excited triplet states in zero field by monitoring the microwave-induced modulation of the phosphorescence. The technique is capable of measuring as few as 10^4 excited-state spins and should be applicable to a wide variety of problems.

While it is generally recognized¹ that an ensemble of two-level systems coupled to a resonant oscillating electric or magnetic field is, in principle, capable of exhibiting free precession and echoes, it is not always apparent precisely how the coherence of the phenomena is manifested in the experimental observables. In magnetic resonance and more recently in optical spectroscopy, spin echoes² and their optical analogs, photon echoes,³ have been observed and explained in terms of dephasing and rephasing of the magnetization of the spins or of the phase of the oscillating electric dipole associated with the electronic transition moment connecting the ground and excited states. On the other hand, when optical properties such as emission or absorption of light are used to monitor magnetic properties

such as in optically detected magnetic resonance,⁴ the coherent phenomena in many cases are not directly observable via a modulation of the emission or absorption of light at the Larmor frequency of the spins. In phosphorescent triplet states, or, for that matter, in any state where the emission from the individual spin states is unresolved optically, it has been shown⁵ that modulation of the light at the Larmor frequency is unobservable unless the electric dipole transition from each of the individual spin levels is of the same polarization. In many excited triplet states, however, the spin sublevels of molecules have different spin-orbit symmetries⁶ and, thus, direct detection of the Larmor term is usually forbidden. The result is that only rotary precession has been observed⁷ optically, while coherent phenom-

ena such as electron free-induction decays and, more importantly, electron spin echoes in excited states, have only been observed in a few cases thus far utilizing conventional techniques.⁸

In this communication we would like to report the first observation of optically detected free precession and spin echoes in molecular-excited triplet states utilizing a technique that is capable of measuring any state of the coherence of the spin ensemble, regardless of the optical polarization of emission from the spin sublevels. The method is limited only by the sensitivity of photon detection, and thus should permit observation of as few as 10^4 spins in the sample, depending upon the specifics of the radiative processes being monitored.

Zero-field optically detected magnetic resonance in phosphorescent triplet states can be viewed⁵ as a Zeeman spin system in its rotating frame in an interaction representation which removes the zero-field Hamiltonian. In this sense it is analogous to an integral-spin nuclear quadrupole system in zero field.⁹ In the interaction representation, magnetization along the z axis (M_z) is related to the populations of the individual spin sublevels in the laboratory frame.¹⁰ Unlike conventional magnetic resonance where components along x or y may be observed, optically detected magnetic resonance requires that the time-dependent density matrix describing the spin ensemble be displayed through the electric dipole transition moment.⁵ The result is that only components along z in the interaction representation are directly observable via a change in the rf-induced modulation of phosphorescence intensity. Since the coherence of the spin ensemble in the interaction representation is confined to the xy plane, phasing or dephasing phenomena do not normally⁵ affect the phosphorescence polarization or intensity. Components of the spin in the xy plane correspond simply to unchanging saturated populations of the two spin sublevels in the laboratory frame, i.e., M_z remains constant in the interaction representation. After an initial $\pi/2$ pulse, however, the ability to restore magnetization from the xy plane to the $+z$ axis with an additional $-\pi/2$ pulse or to invert the magnetization to the $-z$ axis with the addition of a $+\pi/2$ pulse is related to the extent of dephasing. If the spins are completely dephased in the xy plane, no further change in M_z can be brought about by an additional $\pm\pi/2$ pulse, and hence the population of the spin sublevels in the lab frame remains constant. On the other hand, if the spins are only

partially dephased in the xy plane, some magnetization can be either restored from the xy plane, or inverted to the $-z$ axis, and the spin sublevel populations in the lab frame can be taken to a new value that depends upon the extent to which the spin ensemble has dephased. The net result is that a further change in the phosphorescence intensity can be affected by an additional $\pm\pi/2$ pulse. It is expected therefore that free precession can be followed point by point by observing the phosphorescence intensity after two $\pi/2$ pulses, the first to prepare the coherent state and a second to probe the instantaneous value of the coherence in the xy plane by returning the spins at various times to the z axis. Likewise, spin echoes in excited states can be optically detected by a three-pulse sequence: $\pi/2$, π , and $\pi/2$. The first two pulses are used to prepare the echo, while the last pulse is applied at the time when the spins are rephasing and is used to monitor point by point the formation of the echo in the xy plane by monitoring the effective population restored to z and the resulting change in the phosphorescence intensity at the end of the sequence.

Figure 1 illustrates the results of the free-precession experiment obtained while monitoring the phosphorescence at 1.7°K from the lowest excited triplet state of 2, 3 dichloroquinoxaline doped (10^{-3} mole/mole) in a 1, 2, 4, 5 tetrachlorobenzene host crystal. The extent to which the intensity of the phosphorescence changes depends in detail on both the amount of spin alignment¹¹ in the magnetic sublevels produced by selective intersystem crossing from the excited singlet state and the radiative rate constant ratios from the individual spin sublevels in the particular vibronic transition being monitored. Using the rates and populations reported¹² earlier for the lowest triplet state in 2, 3 dichloroquinoxaline, we expect that the phosphorescence intensity to the electronic origin can change by a factor ~ 7 when the spin sublevels are adiabatically inverted, and by a factor of ~ 3.5 when the spin sublevels are saturated. As a consequence, high signal-to-noise ratios are easily obtainable for both the envelopes of the free-induction decay and spin echo. Similar results have been obtained for other systems including d_{10} -benzophenone in its ${}^3n\pi^*$ state and 1, 2, 4, 5 tetrachlorobenzene in its ${}^3\pi\pi^*$ state. Details of the experimental setup are similar to those reported earlier.¹² Several features of the free-induction decay are noteworthy. First, it shows pronounced multiple interference patterns.

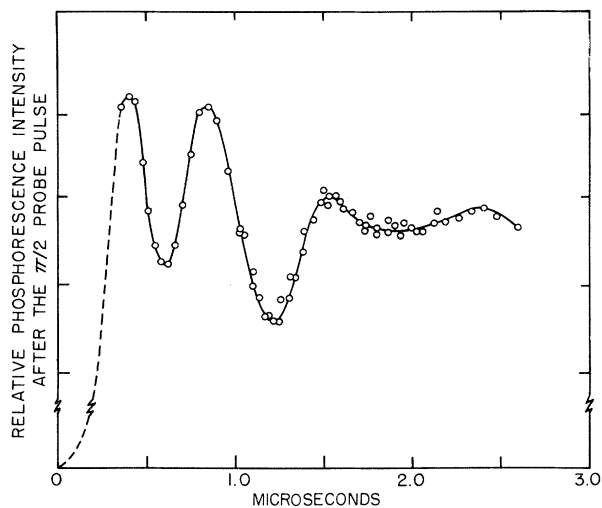


FIG. 1. Optically detected free-induction decay for the 2,3 dichloroquinoxaline $\tau_z \rightarrow \tau_y$ zero-field electron-spin transition at 1055.2 MHz. An initial $\pi/2$ pulse of ~ 100 nsec duration is applied along the x axis at $t=0$, and later the effective magnetization in the xy plane of the rotating frame is converted to the $-z$ axis with an additional $\pi/2$ pulse. The resulting phosphorescence intensity is measured as a function of the time between the two $\pi/2$ pulses.

The zero-field optically detected electron spin-resonance spectra have been explained¹³ in terms of zeroth-order N^{14} quadrupole interactions and

first-order N^{14} nuclear-electron hyperfine splittings. The beat pattern in the free-induction decay can be analyzed in terms of interferences between the individual zero-field hyperfine transitions. When different hyperfine components are subjected to $\pi/2$ pulses at their respective Larmor-center frequencies, the measured free precession shows different beat frequencies, as would be expected. Indeed, these data illustrate that the method can be used to obtain *optically detected Fourier-transform spectra in excited states*. Naturally, the spectrum would be folded back because of the "on" resonance nature of the experiment.¹⁴

The results of an optically detected spin-echo experiment are presented in Fig. 2. As in the free-induction decay, the beats on the echo also result from the interference of the nuclear-electron hyperfine interactions. A plot (cf. Fig. 2) of the echo amplitude versus $\tau(\pi/2-\pi)$ yields an exponential decay with an effective T_2 of 5 μsec . The echo decay also shows beats when $\tau < 1$ μsec , consistent with the interference observed in the free-induction decay and the echo itself. These results are similar to those reported for electron-spin echoes in high field.^{15,16}

A wide variety of additional experiments designed to exploit the analogy between optically detected magnetic resonance and the concepts of

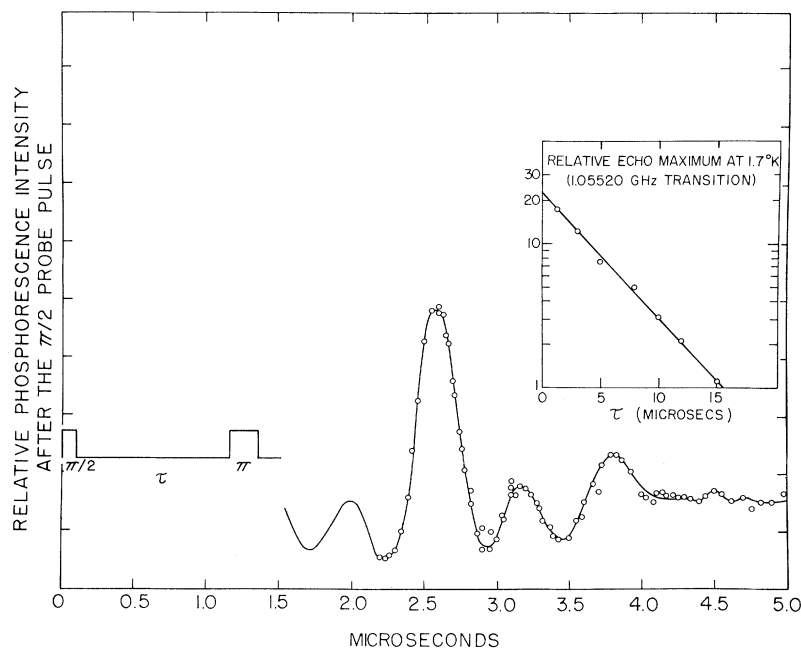


FIG. 2. Optically detected zero-field electron spin echo in 2,3 dichloroquinoxaline. The $\pi/2$ - π pulse separation τ is 1250 nsec. The data points are the resulting phosphorescence intensity at various times after the π pulse at which point a "restoring" $\pi/2$ pulse is applied.

conventional nuclear magnetic resonance are in progress. These include stimulated echoes, rotary echoes, spin locking, and multiple-pulse trains and their applications to molecular solids.

Finally, although the experiments were performed in triplet states by monitoring phosphorescence, in principle the optical absorption or fluorescence from a multiple-level system, in gases for example, could be monitored and the same pulse sequence adopted in the above experiments could be applied to many other radiative and nonradiative molecular states.

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Tunneling Resonances in Proton Spin-Lattice Relaxation

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Two sharp peaks have been observed in the magnetic field dependence of the proton spin-lattice relaxation rate of γ -irradiated 4-methyl 2, 6-ditertiarybutylphenol at liquid-helium temperatures. The peaks are attributed to resonances between the frequencies of tunneling rotation of the 4-methyl groups and the Larmor frequency of the unpaired electron spins associated with free radicals. One peak is assigned to the tunneling resonance of the methyl groups of the free radicals and the other to undamaged molecules.

At low temperatures proton spin-lattice relaxation is commonly dominated by the effects of rapidly relaxing paramagnetic impurities assisted by the process of proton spin diffusion which permits protons far from any impurity to relax via the protons located near paramagnetic centers. For solids which contain methyl groups undergoing tunneling rotation, an interesting possibility arises of a resonance between the frequency of tunneling rotation and the Larmor frequency of the paramagnetic center. In this case, energy-

conserving processes become possible which involve simultaneous flips of electron and nuclear spins combined with a change in the rotational motion of the methyl group. They are expected to give rise to resonant features in the field dependence of proton relaxation rate, especially at low temperatures where there is little competition from other processes. Recently, Glättli, Sentz, and Eisenkremer have observed similar resonances in the conversion rate of spin isomers of irradiated methane.¹ Combined proton