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Coherence in multilevel systems. I. Coherence in excited states and its application to optically detected magnetic resonance in phosphorescent triplet states

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A method for monitoring the time development of the coherent components in a multilevel system using an observable which can measure only the relative populations in the levels is presented. Using standard density matrix formulation, expressions are obtained for the conventional and this new "probe" pulse method. For several of the more common coherence experiments, optically detected magnetic resonance of molecular excited triplet states is used to illustrate the principles. The effect of coherent averaging of relaxation terms in the spin Hamiltonian is discussed and specifically applied to excited triplet states in zero field. Finally, experimental results of coherence measurements are presented along with a detailed description of the apparatus and methods used.

I. INTRODUCTION

The observation of coherent phenomena in an ensemble of two-level systems has been well established in the field of magnetic resonance.¹⁻⁶ Analogous experiments have also been performed on optical systems by monitoring superradiance in emission from crystals and gases.⁷ In both cases, a macroscopic oscillating magnetic or electric dipole moment is observed and is used to measure the coherence in the ensemble. Recently, conventional methods of spectroscopy have been supplemented by a rapidly increasing number of double-resonance techniques^{8,9} that provide an enormous increase in sensitivity for the experimenter. However, the major important difference between the conventional and double-resonance methods lies in the fact that the double-resonance technique effectively monitors changes in the populations of the energy levels coupled by the oscillating field and does not measure the oscillating dipole moment. As a result, coherent information contained in the time dependent density matrix describing the ensemble cannot in general be observed directly. Thus, one is apparently faced with the dilemma that in order to increase sensitivity, one must relinquish those measurements of relaxation phenomena that are based on coherence effects. In the following discussion we wish to point out that this difficulty is circumvented by the proper application of a probe pulse which effectively samples the "degree" of coherence at any time. From this it becomes obvious that *coherence phenomena may be observed in any multilevel system using any observable that can monitor the population of one of the levels associated with the coherence*, provided, of course, that the observable used can follow the ensemble on a time scale compatible with the relaxation effects that one wishes to measure. Using time-dependent density matrix formalism in combination with the Feynman, Vernon, and Hellwarth (FVH) geometrical model,¹⁰ we shall derive analytical expressions for the method for several of the more common experiments, and demonstrate that, except in the case of the low-power cw spectrum, the expressions obtained by monitoring energy level populations are identical in form to those obtained by measuring "in-phase" or "out-of-phase" components of the oscillating magnetic or electric dipole

as is done in conventional microwave and laser spectroscopy. We shall use optically detected magnetic resonance of phosphorescent triplet states in zero field⁹ as a specific example of the situation in which a probe pulse is required, but would like to stress that this method is applicable to a wide variety of additional phenomena, including light pulse experiments. We shall also present experimental results using the method and a detailed description of the apparatus used to perform double-resonance pulse experiments.

Since the triplet state coherence experiments which we describe are performed at liquid helium temperatures, we make the usual low temperature assumption that thermalization of the triplet sublevels, i.e., spin-lattice relaxation, is very slow compared to the triplet state lifetimes. Hence, these T_1 processes can be neglected in the theoretical development.

In an attempt to provide continuity to the historical development of coherence in a two-level system and to cast this particular method as an extension of this development, we begin with the use of standard methods of density matrix formulation¹¹ and apologize in advance for the initial repetition of what is well known to many workers in a wide variety of fields.

II. DISCUSSION

A. Preliminaries

Consider an ensemble of two-level systems characterized by the nondegenerate states $|a\rangle$ and $|b\rangle$, with eigenvalues $\hbar\omega_0/2$ and $-\hbar\omega_0/2$, respectively, that result from a time independent Hamiltonian $\mathcal{H}_0$. The ensemble is subjected to a perturbation $V(t)$ that has no diagonal elements in the a - b basis. The equation of motion for the density matrix describing the ensemble is

$$i\hbar\dot{\rho}(t) = [\mathcal{H}, \rho(t)], \quad (1)$$

where

$$\mathcal{H} = \mathcal{H}_0 + V(t); \quad (2)$$

Equation (1) can be rewritten as¹¹

$$\dot{\mathbf{r}} = \boldsymbol{\Omega} \times \mathbf{r}. \quad (3)$$

This describes the precession of a three-component vector $\mathbf{r}$ about a field Ω in the abstract vector space introduced by Feynman, Vernon, and Hellwarth (FVH).¹⁰ The components of the $\mathbf{r}$ vector are related to the density matrix by

$$\rho(t) = \frac{1}{2} \begin{bmatrix} 1+r_3 & r_1-ir_2 \\ r_1+ir_2 & 1-r_3 \end{bmatrix} \quad (4)$$

and the "field" is given by

$$\Omega_1 = \frac{V_{ab} + V_{ba}}{\hbar}, \quad (5a)$$

$$\Omega_2 = \frac{i(V_{ab} - V_{ba})}{\hbar}, \quad (5b)$$

$$\Omega_3 = \omega_0. \quad (5c)$$

B. The triplet state and the rotating frame transformation in zero field

$\mathcal{H}_0$ for a zero-field triplet state is given by

$$\mathcal{H}_0 = -XS_x^2 - YS_y^2 - ZS_z^2 \quad (6)$$

and has three spin sublevel eigenfunctions τ_x , τ_y , and τ_z . If we connect any two of these sublevels with a coherent microwave field, the third sublevel, in the absence of spin-lattice relaxation, is not affected and we may neglect it if we wish to observe only changes in the total phosphorescence intensity. This will be demonstrated explicitly in Sec. II, D. We consider specifically the τ_y and τ_x sublevels where we assume $E_y > E_x$. $V(t)$ then has the form

$$V(t) = \gamma H_1 S_z \cos(\omega t + \phi), \quad (7)$$

where γ is the magnetogyric ratio of the electron; H_1 is the strength of the microwave field in the z direction, S_z is the triplet state spin operator; and ω is the circular frequency of the microwaves applied with a given phase ϕ . S_z has the following nonzero matrix elements in the τ_y , τ_x basis:

$$\langle \tau_y | S_z | \tau_x \rangle = i\hbar = -\langle \tau_x | S_z | \tau_y \rangle. \quad (8)$$

It is convenient to transform to a rotating frame¹² where the density matrix is defined as

$$\rho^*(t) = U^{-1} \rho(t) U \quad (9)$$

and the unitary operator U is given by

$$U = \exp(-i\omega \mathcal{H}_0 t / \hbar \omega_0). \quad (10)$$

ω_0 is taken to be the Larmor frequency associated with the τ_x to τ_y transition. It is important to note that this is a generalized interaction representation that is valid at any frequency, ω , of the applied field including "off" resonance experiments, and reduces to the interaction representation when the applied field is on resonance. $\rho^*(t)$ satisfies the equation of motion

$$i\hbar \frac{d\rho^*(t)}{dt} = [\mathcal{H}^*, \rho^*] \quad (11)$$

where the Hamiltonian $\mathcal{H}^*$ is given by

$$\mathcal{H}^* = \mathcal{H}_0(1 - \omega/\omega_0) + U^{-1} V(t) U \quad (12)$$

and is given explicitly in the τ_y , τ_x basis by

$$\mathcal{H}^* = \frac{\hbar}{2} \begin{bmatrix} \Delta\omega & i\omega_1 \exp(-i\phi) \\ -i\omega_1 \exp(i\phi) & -\Delta\omega \end{bmatrix}, \quad (13)$$

where

$$\Delta\omega \equiv \omega_0 - \omega \quad (14)$$

and

$$\omega_1 \equiv \gamma H_1. \quad (15)$$

As is customary, only one circularly polarized component of $V(t)$ has been considered.¹³ The useful feature of this transformation is that $\mathcal{H}^*$, which includes the microwave perturbation, is time independent. The density matrix evolves as

$$\rho^*(t) = S^{-1} \rho^*(0) S, \quad (16)$$

where $\rho^*(0)$ is the initial value of the density matrix in the rotating frame. The time evolution operator,

$$S^{-1} = \exp(-i\mathcal{H}^* t / \hbar) \quad (17)$$

is given explicitly by

$$S^{-1} = \begin{bmatrix} -\frac{i\Delta\omega}{\omega} \sin \frac{\bar{\omega}t}{2} + \cos \frac{\bar{\omega}t}{2} & \frac{\omega_1}{\omega} e^{-i\phi} \sin \frac{\bar{\omega}t}{2} \\ -\frac{\omega_1}{\omega} e^{+i\phi} \sin \frac{\bar{\omega}t}{2} & \frac{i\Delta\omega}{\omega} \sin \frac{\bar{\omega}t}{2} + \cos \frac{\bar{\omega}t}{2} \end{bmatrix}, \quad (18a)$$

where

$$\bar{\omega} = (\Delta\omega^2 + \omega_1^2)^{1/2}. \quad (18b)$$

The dynamical behavior of the coherence in the ensemble and its quantitative relationship to the phosphorescence intensity (or fluorescence) can be generalized for any sequence of microwave (or light) pulses in any phase relation to one another by constructing "S" matrices, one for each experimental condition (1, 2, 3, ..., n) imposed on the system.¹⁴ The time dependent density matrix $\rho^*(t)$ is given by a series of unitary transformations of $\rho^*(0)$:

$$\rho^*(t) = S^{-1}(n) \dots S^{-1}(2) S^{-1}(1) \times \rho^*(0) S(1) S(2) \dots S(n). \quad (19)$$

If we define a density matrix in terms of a FVH-type vector in the rotating frame as

$$\mathbf{r}^* \equiv \frac{1}{2} \begin{bmatrix} 1+r_3^* & r_1^*-ir_2^* \\ r_1^*+ir_2^* & 1-r_3^* \end{bmatrix}, \quad (20)$$

we can obtain expressions for the components of $\mathbf{r}^*$ by straightforward matrix multiplication indicated in Eq. (16). In terms of their initial values, $r_1^*(0)$, $r_2^*(0)$, and $r_3^*(0)$, the time dependent values are given by

$$\begin{aligned} r_1^*(t) = & \frac{1}{\omega^2} \{ r_1^*(0) \bar{\omega}^2 \cos \bar{\omega}t - [r_2^*(0) \Delta\omega \bar{\omega} + r_3^*(0) \omega_1 \bar{\omega} \cos \phi] \sin \bar{\omega}t \\ & + [r_1^*(0) \omega_1^2 \sin^2 \phi - r_2^*(0) \omega_1^2 \sin \phi \cos \phi + r_3^*(0) \omega_1 \Delta\omega \sin \phi] (1 - \cos \bar{\omega}t) \}, \end{aligned} \quad (21a)$$

$$r_2^*(t) = \frac{1}{\omega^2} \{ r_2^*(0) \omega^2 \cos \bar{\omega} t + [r_1^*(0) \Delta \omega \bar{\omega} - r_3^*(0) \omega_1 \bar{\omega} \sin \phi] \sin \bar{\omega} t \\ + [r_2^*(0) \omega_1^2 \cos^2 \phi - r_1^*(0) \omega_1^2 \sin \phi \cos \phi - r_3^*(0) \omega_1 \Delta \omega \cos \phi] (1 - \cos \bar{\omega} t) \}, \quad (21b)$$

$$r_3^*(t) = \frac{1}{\omega^2} \{ r_3^*(0) \omega^2 \cos \bar{\omega} t + [r_1^*(0) \omega_1 \bar{\omega} \cos \phi + r_2^*(0) \omega_1 \bar{\omega} \sin \phi] \sin \bar{\omega} t \\ + [r_1^*(0) \omega_1 \Delta \omega \sin \phi - r_2^*(0) \omega_1 \Delta \omega \cos \phi + r_3^*(0) \Delta \omega^2] (1 - \cos \bar{\omega} t) \}. \quad (21c)$$

An important special case of Eqs. (21a)–(21c) is the following. Before the application of the perturbation $V(t)$, the ensemble is assumed to be incoherent, and therefore $r_1(0) = r_2(0) = 0$. $r_3(0)$ corresponds to the initial population difference or spin alignment between the τ_y and τ_x spin sublevels, produced by selective intersystem crossing. Equations (21a)–(21c) reduce to

$$r_1^*(t) = -r_3(0) \frac{\omega_1}{\omega} (\sin \bar{\omega} t), \quad (22a)$$

$$r_2^*(t) = -r_3(0) \frac{\Delta \omega \omega_1}{\omega^2} (1 - \cos \bar{\omega} t), \quad (22b)$$

$$r_3^*(t) = r_3(0) \frac{1}{\omega^2} (\Delta \omega^2 + \omega_1^2 \cos \bar{\omega} t). \quad (22c)$$

C. The relationship between the geometrical representation and phosphorescence

It can be seen from Eq. (4) that *any observable which monitors only the relative energy level populations, represented by r_3 , cannot directly depict the coherence information of the ensemble, which is contained in the off-diagonal terms, r_1 and r_2* . The phosphorescent emission from a triplet state is an example of an observable which usually only monitors populations. To see this, we construct a "phosphorescence operator,"¹⁵ P , in terms of the three optical polarizations, $J = x, y$, or z :

$$P^J = |\mu_J| S_0 \langle S_0 | \mu_J |, \quad P = P^x + P^y + P^z, \quad (23)$$

where μ_J is the electric dipole moment operator for emission to the ground state, S_0 , with J polarization. The experimentally observable phosphorescence intensity is then given by

$$I^J \propto \langle P^J \rangle = \text{Tr} [\rho(t) P^J]. \quad (24)$$

In general, the triplet state zero-field spin sublevels are admixtures of triplet and singlet states of different symmetry due to spin-orbit coupling.¹⁶ The triplet terms will vanish when P^J operates on τ_α , but the singlet admixture will give a nonzero amplitude which we define as

$$\langle S_0 | \mu_J | \tau_\alpha \rangle = C_\alpha^J. \quad (25)$$

From Eqs. (24) and (4), the observed phosphorescence is simply

$$I^J \propto \frac{1}{2} |C_y^J|^2 (1 + r_3) + \frac{1}{2} |C_x^J|^2 (1 - r_3) + \text{Re}(C_y^{J*} C_x^J) (r_1 - i r_2), \quad (26)$$

where $|C_y^J|^2$ and $|C_x^J|^2$ may be identified with the radiative rate constants k_y^J and k_x^J , respectively. For "on resonance" experiments, Eq. (26) reduces to the expression arrived at earlier by Harris from a slightly different point of view.¹⁷

Equation (26) expresses a result which is *generally* applicable to a three-level system as illustrated in Fig. 1a. *If the two levels, $|\tau_y\rangle$ and $|\tau_x\rangle$, are coupled by an oscillating electric or magnetic field and radiation to a third level S_0 is observed, no coherence information can be observed in the emission to the third level unless both $|\tau_y\rangle$ and $|\tau_x\rangle$ have nonzero emission probabilities with the same polarization.* In the present case, this means that both C_x^J and C_y^J must be nonzero in order to allow the coherence information contained in r_1 and r_2 to be observed in the phosphorescence emission. In most zero-field triplet systems, symmetry considerations do not allow both C_x^J and C_y^J to be simultaneously nonzero, and hence no electron spin coherence is manifest in the phosphorescence.

A similar but more restrictive situation exists for fluorescence in a three-level system, illustrated in Fig. 1(b). If molecules in the ground state S_0 are pumped coherently by an oscillating electric field to an excited state S_1 and fluorescence to vibronic levels V_1, V_2 is observed, there will be no modulation of the fluorescence intensity by the in-plane components because only the population in the upper level S_1 is being monitored, the fluorescence being proportional to $1 + r_3$. As we will show, however, this problem could be circumvented in both the phosphorescence or fluorescence cases by rotating either in-plane component r_1 or r_2 to the r_3 direction with a "probe pulse" where it can be observed point by point in time via the optical emission. Thus, the extension to light pulse coherence experiments is in principle simple and straightforward. (Naturally, one must introduce the wavevector k , because in the optical case the wavelength of the radiation field is small relative to the sample size.)

For clarity and simplicity, consider the case where only one of the two spin sublevels (e.g., τ_x), emits to the ground singlet manifold with J polarization. This represents the usual case for phosphorescence in triplet states.¹⁸ It might be noted that this is the analogue of the optical case discussed in connection with Fig. 1(b). Setting $k_y^J = 0 = C_y^J$, the phosphorescence intensity is given by

$$I^J \propto [(k_x^J)(1 - r_3)]/2. \quad (27)$$

or

$$I^J \propto r_3 + \text{constant}. \quad (28)$$

Hence, any change in r_3 will produce a proportional change in the total phosphorescence intensity, and we may thus directly relate the dynamical behavior of r_3 with an experimental observable, which in general will be some property that monitors the relative populations

FIG. 1. Optically detected coherence in multilevel systems. (a) When a strong oscillating magnetic field coherently couples two sublevels of the triplet state, no coherence information can be observed in the phosphorescence intensity unless both sublevels have nonzero emission probabilities with the same polarization. (b) When the ground state is coherently coupled with the first excited singlet state by a strong oscillating electric field, coherence information is not observable in the fluorescence intensity to the ground vibrational levels, V_1 , V_2 , ..., since these intensities depend only on the population of S_1 . As shown in the text, the coherence can nevertheless be sampled in both these types of systems by using a probe pulse to produce changes in the populations of emissive levels proportional to the coherent components.

of the two levels. The fact that $r_3^*(t) = r_3(t)$ allows us to always work in the more convenient rotating frame, and one thus needs only to calculate the time dependence of $r_3^*(t)$ in order to determine how the optical emission will be modulated.

D. Optical detection of the coherent terms

Close inspection of Eqs. (21) and (22) illuminates two obvious but important facts. First, as in all resonance experiments, coherence can be introduced into the ensemble by the application of a $\pi/2$ pulse ($\bar{\omega}t = \pi/2$). For an on-resonance experiment, $r_1^*(\pi/2)$ takes on a value equal to $r_3(0)$, which for excited triplet states is the electron spin alignment created in this case by selective intersystem crossing from excited singlet states. Even though the coherence dephases, this decay is not manifest in the populations of the states, and hence no corresponding change in phosphorescence emission could be observed. The phosphorescence intensity simply corresponds to saturated spin sublevel populations, $r_3(\pi/2) = 0$.

Second, because of the interrelationship between r_1^* , r_2^* , and r_3^* as given by Eqs. (21a)–(21c), the ability to change the value of r_3 with an additional $\pi/2$ pulse at some later time t depends explicitly on the value of coherence $r_1^*(t)$ remaining in the ensemble at time t . If, for example, the electron spins are completely dephased, no further change in r_3 can be brought about by an additional $\pm \pi/2$ pulse, and hence, the spin sublevel populations in the laboratory frame remain constant. Alternatively, when some spin coherence remains in the ensemble, a change in r_3 can be effected by a microwave pulse and hence the spin sublevel populations in the laboratory frame and the phosphorescence intensity take on new values that depend upon the extent to which the ensemble has dephased.

For the triplet state in zero field, the proper representation of the magnetic spin sublevels, τ_x , τ_y , and τ_z , is a three-by-three density matrix whose off-diagonal elements are related to coherence in the triplet ensemble and are affected by T_2 relaxation processes. The S matrix for the applied field given by Eqs. (17), (18a), and (18b) becomes in the z , y , x basis:

$$S_{xy} = \begin{bmatrix} \exp\left(\frac{iE_x\Delta\omega t}{\hbar\omega_0}\right) & 0 & 0 \\ 0 & \frac{i\Delta\omega}{\bar{\omega}} \sin \frac{\bar{\omega}t}{2} + \cos \frac{\bar{\omega}t}{2} & -\frac{\omega_1}{\bar{\omega}} e^{-i\phi} \sin \frac{\bar{\omega}t}{2} \\ 0 & +\frac{\omega_1}{\bar{\omega}} e^{+i\phi} \sin \frac{\bar{\omega}t}{2} & -\frac{i\Delta\omega}{\bar{\omega}} \sin \frac{\bar{\omega}t}{2} + \cos \frac{\bar{\omega}t}{2} \end{bmatrix}, \quad (29)$$

where $\omega_0 = (Y - X)/\hbar$ and $E_x = Z - (X + Y)/2$ for the τ_x, τ_y transition. Also

$$S_{yz} = \begin{bmatrix} \frac{i\Delta\omega}{\bar{\omega}} \sin \frac{\bar{\omega}t}{2} + \cos \frac{\bar{\omega}t}{2} & -\frac{\omega_1}{\bar{\omega}} e^{-i\phi} \sin \frac{\bar{\omega}t}{2} & 0 \\ \frac{\omega_1}{\bar{\omega}} e^{+i\phi} \sin \frac{\bar{\omega}t}{2} & -\frac{i\Delta\omega}{\bar{\omega}} \sin \frac{\bar{\omega}t}{2} + \cos \frac{\bar{\omega}t}{2} & 0 \\ 0 & 0 & \exp\left(\frac{iE_x\Delta\omega t}{\hbar\omega_0}\right) \end{bmatrix}, \quad (30)$$

where $\omega_0 = (Z - Y)/\hbar$ and $E_x = X - (Y + Z)/2$ for the τ_y, τ_z transition, and

$$S_{xz} = \begin{bmatrix} \frac{i\Delta\omega}{\omega} \sin \frac{\bar{\omega}t}{2} + \cos \frac{\bar{\omega}t}{2} & 0 & \frac{\omega_1}{\omega} e^{-i\phi} \sin \frac{\bar{\omega}t}{2} \\ 0 & \exp\left(\frac{iE_y \Delta\omega t}{\hbar\omega_0}\right) & 0 \\ -\frac{\omega_1}{\omega} e^{i\phi} \sin \frac{\bar{\omega}t}{2} & 0 & -\frac{i\Delta\omega}{\omega} \sin \frac{\bar{\omega}t}{2} + \cos \frac{\bar{\omega}t}{2} \end{bmatrix}, \quad (31)$$

where $\omega_0 = (Z - X)/\hbar$ and $E_y = Y - (X + Z)/2$ for the τ_x, τ_z transition. The terms E_z, E_y , and E_x account for the different energy zeroes in the three expressions.

For "on-resonance" transformations ($\Delta\omega = 0, \bar{\omega} = \omega_1$), the above matrices are designated $S_{ij}(\theta, \phi)$, where i and j correspond to the spin sublevels being coupled by the field, θ is defined in terms of how long the field is left on, $\theta = \bar{\omega}t = \omega_1 t$, and ϕ denotes the phase of the applied field.

The relationship between the phosphorescence intensity and the degree of coherence in the density matrix can now be quantitatively expressed. In order to demonstrate the relationship between the interaction representation form of the density matrix and the laboratory frame sublevel populations, we shall first express the triplet state density matrix in terms of these initial populations and observe how the microwave pulses affect the diagonal terms.

Under steady-state illumination and before the application of microwaves, the density matrix describing the triplet ensemble is diagonal, as mentioned above, with diagonal elements proportional to the spin sublevel populations, i.e.,

$$\rho^*(0) = \begin{bmatrix} N_z/N_t & 0 & 0 \\ 0 & N_y/N_t & 0 \\ 0 & 0 & N_x/N_t \end{bmatrix}, \quad (32)$$

where N_x, N_y , and N_z are the spin sublevel populations in τ_x, τ_y , and τ_z , respectively, and N_t is the total number of triplet systems in the ensemble. The effect of an on-resonance $\pi/2$ pulse connecting the τ_y and τ_x spin sublevels applied at 0° phase is seen from Eqs. (16) and (29):

$$\begin{aligned} \rho^*(\pi/2, 0^\circ) &\equiv S_{xy}^{-1}(\pi/2, 0^\circ) \rho^*(0) S_{xy}(\pi/2, 0^\circ) \\ &= \frac{1}{2N_t} \begin{bmatrix} 2N_z & 0 & 0 \\ 0 & N_x + N_y & N_x - N_y \\ 0 & N_x - N_y & N_x + N_y \end{bmatrix}, \end{aligned} \quad (33)$$

and we note that all elements in the z th row and z th column are left unchanged; the population of the z level remains the same. It is generally true that if ρ is initially diagonal, then pulses of frequency resonant with the xy transition will not affect elements of ρ in the z th row and column; this means that it is entirely adequate to deal only with the 2×2 submatrix in the xy basis, as long as only pulses close to resonance with the xy transition are

applied. This illustrates a remark made earlier, namely that the third level may be neglected if only one of the zero-field transitions is pumped. Hence for our purposes, ρ^* can be reduced and renormalized to

$$\rho^*(0) = \frac{1}{N_x + N_y} \begin{bmatrix} N_y & 0 \\ 0 & N_x \end{bmatrix} \quad (34)$$

and

$$\rho^*(\pi/2, 0^\circ) = \frac{1}{2(N_x + N_y)} \begin{bmatrix} N_x + N_y & N_x - N_y \\ N_x - N_y & N_x + N_y \end{bmatrix}. \quad (35)$$

In the r^* representation defined by Eq. (20), the components take on values

$$r_1^*(0) = r_2^*(0) = 0, \quad (36a)$$

$$r_3^*(0) = \frac{N_y - N_x}{N_x + N_y}, \quad (36b)$$

and, at $t = \pi/2$,

$$r_1^*(\pi/2, 0^\circ) = (N_x - N_y)/(N_x + N_y) = -r_3^*(0), \quad (37a)$$

$$r_2^*(\pi/2, 0^\circ) = 0, \quad (37b)$$

$$r_3^*(\pi/2, 0^\circ) = 0. \quad (37c)$$

These of course agree with what could be obtained from Eqs. (22a)–(22c). The nonzero value of $r_1^*(\pi/2, 0^\circ)$ represents the coherence introduced into the ensemble and is equal in magnitude to the initial steady state spin alignment of the triplet spin sublevels. The diagonal terms, however, result in what appears to be a saturated transition as far as the phosphorescence intensity is concerned.

In the absence of the applied field and of optical pumping of the triplet state, the elements of $\rho^*(\pi/2, 0^\circ)$ decay via the radiative and radiationless channels associated with the individual spin sublevels. The diagonal elements are also influenced by communication between the levels (T_1 processes), while the off-diagonal elements decay according to spin-spin relaxation interactions (T_2 processes). We assume T_1 is very long and therefore can be neglected at sufficiently low temperatures, and represent the spin-spin interactions phenomenologically via the Bloch equations.¹⁹

Generally speaking, coherence introduced into the spin sublevels will decay at a much greater rate than the decay of the excited triplet state. The density matrix to a very good approximation for times short compared to the excited state lifetimes is given by

$$\rho^*(\pi/2, 0^\circ; t) = \frac{1}{2} \begin{bmatrix} 1 & \left(\frac{N_x - N_y}{N_x + N_y}\right) \exp(-t/T_2) \\ \left(\frac{N_x - N_y}{N_x + N_y}\right) \exp(-t/T_2) & 1 \end{bmatrix} \quad (38)$$

In order to observe the decaying coherence given by the off-diagonal term as a modulation of the phosphorescence intensity, it is necessary to cause a change in r_3 proportional to $r_1^*(\pi/2, t)$. This is accomplished by an additional $\pi/2$ pulse applied at a time t after the initial preparatory pulse,

$$\rho^*(\pi/2, 0^\circ; t; \pi/2, 0^\circ) = \frac{1}{2(N_x + N_y)} \begin{bmatrix} N_x[1 + \exp(-t/T_2)] + N_y[1 - \exp(-t/T_2)] & 0 \\ 0 & N_y[1 + \exp(-t/T_2)] + N_x[1 - \exp(-t/T_2)] \end{bmatrix} \quad (39)$$

and in terms of the vector representation,

$$r_1^*(\pi/2, 0^\circ; t; \pi/2, 0^\circ) = 0, \quad (40a)$$

$$r_2^*(\pi/2, 0^\circ; t; \pi/2, 0^\circ) = 0, \quad (40b)$$

$$\begin{aligned} r_3^*(\pi/2, 0^\circ; t; \pi/2, 0^\circ) &= \frac{N_x - N_y}{N_x + N_y} \exp(-t/T_2) \\ &= r_1^*(\pi/2, 0^\circ; t) \\ &= -r_3(0) \exp(-t/T_2). \end{aligned} \quad (40c)$$

It is apparent from the above that if no decay in the coherence has occurred in the time t , then the second $\pi/2$ pulse results in an inversion of the population between τ_x and τ_y . The phosphorescence intensity would exhibit a corresponding change. On the other hand, if all the coherence in the ensemble has decayed at time t , the $r_1^*(\pi/2, 0^\circ; t)$ would be zero and no further change in the spin sublevel populations, which were initially saturated by the first $\pi/2$ pulse, could be effected, and no further change would be manifest in the phosphorescence.

Hence the final phosphorescence intensity would range from that resulting from an inversion for $t=0$ to the saturation level after the coherence has decayed completely. *The final probe pulse thus samples the coherence remaining in the ensemble in a well-defined quantitative fashion.* Figure 2 demonstrates schematically the relationship between the laboratory frame populations and the interaction representation r vector developed above.

III. SPECIFIC COHERENCE EXPERIMENTS

In the following sections we shall discuss several of the more common coherence experiments in terms of the previous development. However, because the equations in the earlier sections apply only to an ensemble of identical, noninteracting systems, each system having the same Hamiltonian, we will need to introduce subensembles of identical systems in order to explain the behavior of a real system. We wish for clarity to keep these additions as simple as possible, reserving more detailed treatments of orientational effects and relaxation for future publications.

We shall develop parallel equations for conventional and optical detection methods. The solutions for r_2 and r_1 correspond to the expectation values $\langle S_i \rangle$ and $\langle S_i S_j + S_j S_i \rangle$, respectively, where the microwave perturbation is $\gamma H_1 S_i \cos \omega t$. These quantities could be monitored by a pickup coil. The solutions to r_1^* and r_2^* in the rotating

frame will give the *amplitudes* of the signal received in the fixed frame.

FIG. 2. Optically detected free precession in excited triplet states: A diagrammatical representation of the time development of the interaction representation r^* vector and the laboratory frame spin sublevel populations. (a) For simplicity, consider a case where intersystem crossing occurs only to the middle sublevel, and only emission from the lower sublevel is monitored. Before the application of microwaves coupling the lower two sublevels, the r^* vector points along the positive z axis. (b) A $\pi/2$ pulse applied along the rotating frame x axis tips the r^* vector along y and the populations of the lower two sublevels are equalized. The phosphorescence intensity now corresponds to saturation. (c), (d) With the microwaves off, the in-plane y component decays to zero due to variations in local fields within the sample and homogeneous dephasing processes. The laboratory frame sublevel populations remain constant, however, so that the decay of the coherence is not directly manifested as a change in phosphorescence. (e⁰), (e¹), (e²) The decay of the coherence can be detected optically, however, by the application of an additional $\pi/2$ pulse. This probe pulse, applied along x , tips the coherent component down along z , producing an additional change in the sublevel populations and consequently in the phosphorescence intensity. The phosphorescence change induced by the probe pulse is proportional to the coherence remaining in the ensemble at the time the probe pulse is applied. This is shown in (e⁰), (e¹), (e²), which demonstrate the behavior of the r^* vectors and the laboratory frame sublevel populations when the probe pulse is applied at times corresponding to (b), (c), and (d), respectively. The probe at $t=0$ results in population inversion [relative to (a)] but the probe at $t=\tau$, after complete decay of the coherence, produces no further change in population.

A. Optically detected transient nutation

Equation (22c) represents a general expression for the modulation of the phosphorescence intensity by the coherent coupling of the spin system to a microwave field on or off resonance in the absence of relaxation. It should be noted that this form of coupling represents the "transient nutation"²⁰ of the population under the influence of the microwave field and is not related to the coherence terms r_1 or r_2 , which are oscillatory modulations at the Larmor frequencies. For on-resonance experiments, the expressions reduce to a form identical to that predicted by Harris¹⁷ and subsequently observed by Schmidt and co-workers.²¹ In particular, when the applied frequency ω is equal to the Larmor frequency, ω_0 , then $\bar{\omega} = \omega_1$, and

$$r_3^*(t) = r_3(0) \cos \omega_1 t. \quad (41)$$

If the pulse remains on for a time comparable to the homogeneous relaxation time T_2 , dephasing of the coherent ensemble will occur owing to interactions between the systems. This relaxation is most easily incorporated into the dynamics of the r vector by adding phenomenological decay terms to the r_1 and r_2 components of Eq. (3) after transforming to the rotating frame. This results in Bloch-type equations¹⁹ given by

$$dr_1^*/dt = -\omega_1 r_3^* - \Delta\omega r_2^* - r_1^*/T_2, \quad (42a)$$

$$dr_2^*/dt = \Delta\omega r_1^* - r_2^*/T_2, \quad (42b)$$

$$dr_3^*/dt = \omega_1 r_1^*. \quad (42c)$$

We have neglected the T_1 term since T_1 is very much longer than the dephasing time T_2 for these systems.

The solution to Eqs. (42a)–(42c) can be obtained for two special cases of interest using the Laplace transform method used by Torrey²⁰ for transient nutation in nuclear magnetic resonance. The on-resonance case, $\Delta\omega = 0$, gives, using the initial conditions, $r_1^* = r_2^* = 0$ and $r_3^*(0) = r_3(0)$:

$$r_3^* = r_3^*(0) \exp(-t/2T_2) \left(\cos \alpha t + \frac{1}{2\omega_1 T_2 \alpha} \sin \alpha t \right), \quad (43)$$

where

$$\alpha = [\omega_1^2 - 1/(4T_2^2)]^{1/2}. \quad (44)$$

Note that for sufficiently high power, $\omega_1^2 \gg 1/(4T_2^2)$, and Eq. (43) becomes

$$r_3^* = r_3^*(0) \exp(-t/2T_2) \cos \omega_1 t. \quad (45)$$

For short times, Eq. (45) reduces to Eq. (41). The off-resonance solution to Eqs. (42a)–(42c) may be obtained in the special high power case, $1/\omega_1 T_2 \ll 1$. Neglecting terms of order $1/\omega_1^2 T_2^2$ and higher, we obtain

$$r_3 = (r_3(0)/\bar{\omega}^2) \{ \Delta\omega^2 \exp[-(\omega_1^2 t)/(\bar{\omega}^2 T_2)] + \omega_1^2 \exp[-(t/2T_2)(1 + \Delta\omega^2/\bar{\omega}^2) \cos \bar{\omega} t] + (\omega_1^2/2T_2 \bar{\omega})(1 + 3\Delta\omega^2/\bar{\omega}^2) \exp[-(t/2T_2)(1 + \Delta\omega^2/\bar{\omega}^2)] \sin \bar{\omega} t \}, \quad (46)$$

where

$$\bar{\omega} = \sqrt{\omega_1^2 + \Delta\omega^2}. \quad (47)$$

If the applied microwave field is inhomogeneous, we must partition the sample into subensembles, each subensemble having a single driving term, ω_1^i . The observed signal is then given by a sum over the distribution of H_1 field strengths, $g(\omega_1)$. For large numbers of subensembles, the sum becomes an integral:

$$\langle r_3 \rangle = \int_{-\infty}^{\infty} g(\omega_1) r_3(\omega_1) d\omega_1. \quad (48)$$

$r_3(\omega_1)$ is the solution of Eqs. (43) or (46) for a particular value ω_1 . Figure 3 gives experimental transient nutation curves for high power on- and off-resonance pulses. The decay of the signal is due mainly to inhomogeneities in H_1 , since spin echo experiments give a homogeneous relaxation time of $4 \mu\text{sec}$ for this sample, which is too long to account for the rapid decay. For times short compared to T_2 , Eq. (48) reduces to

$$\langle r_3 \rangle = \int_{-\infty}^{\infty} (r_3(0)/\bar{\omega}^2) (\Delta\omega^2 + \omega_1^2 \cos \bar{\omega} t) g(\omega_1) d\omega_1. \quad (49)$$

Notice that in the off-resonance case, Eq. (49), r_3 contains a constant term which will not decay due to inhomogeneous field considerations. This is reflected in the experimental data as a progressively lower steady-state value after the oscillations have decayed as one gets

further from resonance. Notice also that the increase in frequency associated with off-resonance effects agrees with predictions. The apparent "beating" seen on the tail of the on-resonance transient nutation is not noise and most likely is a result of orientational effects due to the polarized nature of the slow-wave helix used to apply the microwaves and the two inequivalent molecules in the durene unit cell.

B. Optically detected free induction decay

If the sample is allowed to evolve freely without the high power microwave field, it becomes necessary to integrate over the inhomogeneous lineshape function $g(\omega_0 - \bar{\omega}_0)$, which is generally taken to be a symmetric distribution of Larmor frequencies centered about some average Larmor frequency $\bar{\omega}_0$. The conventional sequence for a free induction decay consists of a single high-power $\pi/2$ pulse. Following the pulse, the r_1^* and r_2^* components will decay as the individual isochromats in the distribution $g(\omega_0 - \bar{\omega}_0)$ fan out in the rotating frame plane. (See Fig. 2.) The behavior of the system is obtained from the time evolution operator $S = S(\pi/2, 0^\circ) S_\tau$, where S_τ denotes free precession for a time period τ . From Eq. (19), we obtain

$$r_1^* \propto \langle S_x S_x + S_y S_y \rangle \propto \int_{-\infty}^{\infty} g(\omega_0 - \bar{\omega}_0) \cos(\omega_0 - \omega) \tau d\omega_0, \quad (50a)$$

FIG. 3. Optically detected transient nutation for the $\tau_x \rightarrow \tau_y$ transition of $h_2-1, 2, 4, 5$ -tetrachlorobenzene in h_{14} -durene. The observed microwave induced change in phosphorescence is plotted vs duration of the microwave pulse (zero denotes zero change in phosphorescence).

$$r_2^* \propto \langle S_x \rangle \propto \int_{-\infty}^{\infty} g(\omega_0 - \bar{\omega}_0) \sin(\omega_0 - \omega) \tau d\omega_0. \quad (50b)$$

The double resonance experiment uses an additional $\pi/2$ pulse giving $S = S(\pi/2, 0^\circ) S_\tau S(\pi/2, 0^\circ)$ and

$$r_3^* \propto \int_{-\infty}^{\infty} g(\omega_0 - \bar{\omega}_0) \cos(\omega_0 - \omega) \tau d\omega_0. \quad (50c)$$

C. Optically detected electron spin echo

The conventional echo^{1,2} has $S = S(\pi/2, 0^\circ) S_\tau S(\pi, 0^\circ) S_\tau$;

$$r_1^* \propto \langle S_x S_y + S_y S_x \rangle \propto \int_{-\infty}^{\infty} g(\omega_0 - \bar{\omega}_0) \cos(\omega_0 - \omega) (\tau - \tau') d\omega_0, \quad (51a)$$

$$r_2^* \propto \langle S_x \rangle \propto \int_{-\infty}^{\infty} g(\omega_0 - \bar{\omega}_0) \sin(\omega_0 - \omega) (\tau - \tau') d\omega_0, \quad (51b)$$

and $S = S(\pi/2, 0^\circ) S_\tau S(\pi, 0^\circ) S_\tau S(\pi/2, 0^\circ)$ for the double resonance case;

$$r_3^* \propto \int_{-\infty}^{\infty} g(\omega_0 - \bar{\omega}_0) \cos(\omega_0 - \omega) (\tau - \tau') d\omega_0. \quad (51c)$$

If $g(\omega_0 - \bar{\omega}_0)$ is Lorentzian,²² characterized by the inhomogeneous relaxation time T_2^* , the optically detected free induction decay and echo are given by

$$\text{FID} \propto \exp(-\tau/T_2^*) \cos \Delta\bar{\omega} \tau, \quad (52)$$

$$\text{echo} \propto \exp[-(\tau - \tau')/T_2^*] \cos \Delta\bar{\omega} (\tau - \tau'), \quad (53)$$

where $\Delta\bar{\omega} = \bar{\omega}_0 - \omega$. These are identical to the familiar expressions obtained from conventional measurements of the in-plane components in the absence of the probe pulse.

Experimental results of an optically detected spin echo²³ are given in Fig. 4. The "inverted" appearance of the echo arises from the instrumental method used to record it. The three pulse sequence $\pi/2, \pi, \pi/2$ results in a complete 2π rotation of the population difference vector, and the phosphorescence intensity would therefore not change if complete rephasing results at the echo maximum. Owing to the fact that a lock-in amplifier is used to monitor the echo, a minimum signal is obtained. When very little rephasing occurs, far from the echo maximum, the phosphorescence intensity changes to a value that could be obtained by saturating the transition. This is illustrated in Fig. 5, which is an oscilloscope trace of the photomultiplier output for "on" and

FIG. 4. Optically detected zero-field electron spin echo. The π refocusing pulse is applied 2 μ sec after the initial $\pi/2$ pulse and the final $\pi/2$ probe pulse is swept in time. The echoes at the right are traced out point by point as the probe pulse is applied at the time given on the abscissa. The vertical lines are noise at each point in time. The off-resonance oscillations in the lower echo are described by Eq. (53).

FIG. 5. Photomultiplier output observed in an optically detected spin echo experiment. The first spike is observed when the three pulses are equally spaced, so that the probe pulse occurs at the rephasing time, τ , after the π refocussing pulse, i. e., on the echo maximum. The second spike is seen when the probe pulse is applied off maximum at $\tau + 2 \mu\text{sec}$. The two spikes result from separate three pulse sequences, applied several hundred milliseconds apart.

"off" echo maximum sequences. The height of the on-maximum spike is proportional to the signal produced by a 2π pulse (first minimum in Fig. 3). The height of the off-maximum spike is proportional to the difference between the steady-state phosphorescence intensity and the phosphorescence intensity when the two spin sub-levels are saturated (steady-state value in Fig. 3).

D. Continuous wave spectrum

If we include a T_1 term in Eqs. (42a)–(42c), the Laplace transform method yields a steady-state solution which is the cw spectrum, i. e., the spectrum obtained by low power, conventional optical detection:

$$r_1^* = [r_3^*(0)\omega_1 T_2] / (1 + \Delta\omega^2 T_2^2 + \omega_1^2 T_1 T_2), \quad (54a)$$

$$r_3^* = [r_3^*(0)] / [1 + (T_1 T_2 \omega_1^2) / (1 + \Delta\omega^2 T_2^2)]. \quad (54b)$$

In the low-power limit, we obtain

$$r_1^* = \omega_1 T_2 r_3^*(0) / (1 + \Delta\omega^2 T_2^2), \quad (55a)$$

$$r_3^* = [r_3(0)] [1 - (\omega_1^2 T_1 T_2) / (1 + \Delta\omega^2 T_2^2)]. \quad (55b)$$

Thus, the optically detected cw spectrum differs from the conventional spectrum in the same fashion that nuclear absorption and induction spectra differ. The intensity of phosphorescence will vary as the square of the H_1 field (linear in power).

E. Optically detected Fourier transform spectroscopy

The free induction decay, or equivalently, the echo shape is the cosine Fourier transform of the frequency distribution function, $g(\omega_0 - \bar{\omega}_0)$, Eqs. (50c) and (51c). One would therefore expect that Fourier transform spec-

troscopy (FTS)²⁴ would be feasible in optically detected magnetic resonance. In conventional NMR, FTS has many advantages over the spectral sweep technique. The only major difficulty with the method lies in the additional instrumentation, including computer data reduction. Since optically detected magnetic resonance does not suffer from the problems of cavity and detector overload and recovery time, it is relatively simple to convert a standard optically detected magnetic resonance cw spectrometer to a pulse spectrometer. There are, however, several fundamental problems which prevent optically detected FTS from being as useful as it is in NMR.

First, the necessary final probe pulse prevents one from collecting an entire spectrum with a single series of pulses. One is forced to slowly sweep the FID or echo in the same time it would take to sweep the cw spectrum. Because of the sensitivity of photon detection, this is not a severe limitation, and spectra can be obtained in a reasonable amount of time. The second problem is a result of the systems studied. Typical linewidths are on the order of 1 MHz,²⁵ requiring very large H_1 fields in order to meet the condition $\omega_1 \gg \Delta\omega$. Since fields on the order of 3 G can be obtained experimentally, only closely-spaced narrow multiplets could be studied. This condition is further complicated, however, by the fact that the transition probabilities in a triplet-state multiplet can vary from values of 1 for completely allowed transitions to 10^{-4} for forbidden transitions.²⁶ The result of this is that the condition $\omega_1 \gg \Delta\omega$, where now $\omega_1 = \gamma H_1 f$, may be satisfied marginally for a strong transition, $f = 1$, but not at all for a weaker transition which is only slightly removed in frequency from the applied microwave frequency. These conditions lead to the situation in which the various r vectors in a multiplet are precessing about widely differing Ω_{eff} directions, resulting in large intensity errors for the Fourier transform. This problem is exemplified in Fig. 6, which is the Fourier transform of a $\tau = 1.5 \mu\text{sec}$ echo in 2,3-dichloroquinoline.²⁶ Since even under the most ideal conditions FTS gives only the same information as the cw spectrum, we have concluded that there is no overriding advantage in doing FTS by using a double-resonance method.

F. Coherent averaging of relaxation effects

We conclude this section with a general discussion of interactions which can lead to electron spin relaxation processes in excited triplet states in zero field and show how relaxation may be suppressed, and coherence preserved, by multiple pulse experiments, such as the Carr-Purcell echo train,² and by spin locking.^{27,3} Many of the pulse experiments are both periodic and cyclic insofar as they consist of a repetition of a fixed series of pulses and waiting periods that have the property that for some value of n , the product of n successive pulse operators in the sequence is the identity operator. When the cycle time for the experiment is short compared to the dephasing time of the r_1 and r_2 components, we can apply the average Hamiltonian theory first devised and pioneered by Waugh and co-workers.^{5,28}

The standard approach to the problem is to partition the total Hamiltonian into three parts:

FIG. 6. Top: Optically detected spin echo of the 1.054 GHz transition of 2,3-dichloroquinoxaline in 1,2,4,5-tetrachlorobenzene. The interval τ between the initial $\pi/2$ pulse and the π pulse is 1.5 μ sec. The probe pulse is applied at time t after the initial $\pi/2$ pulse and is swept in time. Bottom: Fourier transform of the echo superimposed on the low power conventional ODMR spectrum.

$$\mathcal{H}(t) = \mathcal{H}_0 + V(t) + \mathcal{H}_R(t), \quad (56)$$

where $\mathcal{H}_0$ is the static zero-field splitting; $V(t)$ is the microwave perturbation; and $\mathcal{H}_R(t)$ a time dependent relaxation Hamiltonian which produces line broadening. $\mathcal{H}_R(t)$ takes on different values for different subensembles comprising the triplet sample, producing a spread of resonance frequencies at any one instant. The range of values of $\mathcal{H}_R(t)$ and their time dependence determine the observed times for free induction decay and spin echo decay.

Incorporating relaxation into the density matrix is straightforward provided the resonant microwave field $H_1(t)$ dominates the relaxation process during the application of a microwave pulse. As before, one can transform in zero field to an interaction representation, i.e., an on-resonance rotating frame, generated according to Eq. (9). In multiple pulse experiments, the ensemble is subjected to a series of pulses $S_1, S_2, \dots$ interspersed with a series of waiting periods of length $\tau_1, \tau_2, \dots$. When the product of n successive pulses in the sequence

equals the unit matrix

$$S_i S_{i+1} \cdots S_{i+n} = I, \quad (57)$$

the cycle time t_c is given by

$$t_c = \tau(S_i) + \tau_i + \tau(S_{i+1}) + \tau_{i+1} + \cdots + \tau(S_{i+n}) + \tau_{i+n}. \quad (58)$$

It has been shown^{5,28} that if t_c is short compared to the effective time required for irreversible dephasing, then the ensemble can be pictured as being subjected during the cycle to a series of Hamiltonians $\mathcal{H}_{RI}(1), \mathcal{H}_{RI}(2), \dots$ in the interaction representation, each of which acts for a period of time $\tau_1, \tau_2, \dots$, respectively. Under these conditions, the long time behavior of the density matrix, when sampled periodically at the same point in each cycle, is governed by an average Hamiltonian $\bar{\mathcal{H}}$:

$$i\hbar \frac{\partial \rho_I}{\partial t} = [\bar{\mathcal{H}}, \rho_I], \quad (59)$$

where

$$\bar{\mathcal{H}} = \sum_{k=1}^n \mathcal{H}_{RI}(k) (\tau_k / t_c) \quad (60)$$

and the sum is taken over the cycle. $\bar{\mathcal{H}}$ is the weighted average (weighted by waiting periods) of the several $\mathcal{H}_{RI}(k)$ defined by

$$\mathcal{H}_{RI}(k) = \left(\prod_{i=1}^k S_i \right) \mathcal{H}_{RI} \left(\prod_{i=1}^k S_i \right)^{-1} \quad (61)$$

and acting for a period τ_k .

In the remainder of this section we will use average Hamiltonian theory to show how relaxation can be suppressed in multiple pulse experiments in excited triplet states in zero field. The general form of the average Hamiltonian will be computed for the simplest cyclic pulse sequence, the zero-field Carr-Purcell (CP) train, which is given by

$$[S(\pi/2), \tau, S(\pi), 2\tau, S(\pi), 2\tau, \dots]. \quad (62)$$

The average Hamiltonian for the hyperfine interaction of triplet spins with host nuclear spins will be calculated as an illustrative example. Finally we will discuss the spin locking technique as a limiting case when 2τ in the CP train becomes short. Representative experimental coherence lifetimes are presented for the free induction decay, the simple Hahn spin echo, the CP train, and spin locking.

1. Spin relaxation in the triplet state in zero field

General considerations. Several interactions can contribute to $\mathcal{H}_R(t)$ for excited triplets to varying degrees. One is the hyperfine interaction between the triplet spins on excited molecules and nuclear spins in the host lattice. The time variation of $\mathcal{H}_R(t)$ is then largely determined by nuclear spin diffusion. Another contribution arises from small motions of the triplet molecules in the host crystal field due to lattice phonons. A third possibility is vibrations of the triplet molecule itself which alter the spin distribution, thereby modulating the zero-field splitting.

The time dependence of $\mathcal{H}_R(t)$ determines the nature of its effect on spin relaxation.²⁹ Frequency components

of $\mathcal{H}_R(t)$ which are very fast relative to Larmor frequencies make only a constant time-averaged contribution to the zero-field splitting measured in an ESR experiment and have little effect on T_1 and T_2 processes. For example, most molecular vibrational frequencies are at least 10^3 times the zero-field splitting frequencies and the resulting $\mathcal{H}_R(t)$ would be manifest only as a time average for a particular vibrational level. On the other hand, if there were fluctuations in the vibrational level populations at rates comparable to Larmor frequencies, then spin relaxation could result.

In general, if $\mathcal{H}_R(t)$ has off-diagonal elements in the τ_z, τ_y, τ_x basis with frequency components near the Larmor frequencies, then, in the interaction representation, $\mathcal{H}_{RI}$ has nearly stationary off-diagonal elements. These elements appear as resonant fields and both T_1 and T_2 processes can occur. By contrast, if $\mathcal{H}_R(t)$ is only slowly varying, it produces only spin-spin relaxation. These considerations are made very clear from the equations of motion of the r vector in the interaction representation, under the influence of $\mathcal{H}_{RI}$. We confine our attention for simplicity to only two spin sublevels, τ_x and τ_y , and drop subscripts RI . In the r basis,

$$dr_1/dt = -(\mathcal{H}_{yy} - \mathcal{H}_{xx})r_2/\hbar - (2/\hbar)(\text{Im}\mathcal{H}_{yx})r_3, \quad (63a)$$

$$dr_2/dt = -(2/\hbar)(\text{Re}\mathcal{H}_{yx})r_3 + (\mathcal{H}_{yy} - \mathcal{H}_{xx})r_1/\hbar, \quad (63b)$$

$$dr_3/dt = (2/\hbar)(\text{Re}\mathcal{H}_{xx})r_2 + (2/\hbar)(\text{Im}\mathcal{H}_{yx})r_1. \quad (63c)$$

If $\mathcal{H}_R$, the relaxation Hamiltonian in the Schroedinger representation, were only slowly varying, then $\mathcal{H}_{yx}$ would fluctuate at the Larmor frequency in the interaction representation and would have a negligible effect on r . If, on the other hand $\mathcal{H}_R(t)$ had a frequency component at the Larmor frequency, then $\mathcal{H}_{yx}$ would have a static term which would give rise to nonzero dr_3/dt , i.e., spin-lattice relaxation. Although phonon modulation of the zero-field tensor has been cited by some authors as a source of T_1 processes in the triplet state,³⁰ we neglect spin-lattice relaxation for the present discussion since it is much slower than spin-spin relaxation for the systems of interest. This means $\mathcal{H}_{yx}$ and $\mathcal{H}_{xy}$ can be set to zero in Eqs. (63a)–(63c).

$\mathcal{H}_R(t)$ is assumed to have different diagonal values for different subensembles in the sample, producing a spread in Larmor frequencies which are manifest as different precession frequencies about z in the rotating frame. If $\mathcal{H}_R(t)$ is constant with time, then all the subensemble isochromats will refocus perfectly in a spin echo experiment, and the echo will not decay as the interval between pulses is lengthened. If, however, the values of $\mathcal{H}_R(t)$ associated with particular subensembles change during the waiting periods, the isochromats will not refocus completely. Now if a Carr–Purcell experiment is performed with 2τ much shorter than the apparent decay time of the single spin echo, the lifetime of the echo train will be prolonged owing to coherent averaging. Qualitatively, this results from the fact that the subensemble r vectors are defocussed and refocussed before the $\mathcal{H}_R$ pertaining to each one can change its value. This can be demonstrated in a more quantitative way using the average Hamiltonian for the Carr–Purcell train.

Because a triplet state has three spin sublevels, the most general CP cycle would require four identical π pulses and a t_c of 8τ (neglecting pulse durations). However, under conditions where the ensemble is totally incoherent before the application of the first $\pi/2$ pulse and also when relaxation effects between the two spin sublevels being coupled by the microwave field and the third sublevel are unimportant, the third sublevel may be ignored, and a treatment based on 2×2 submatrices is adequate. In such cases, $S(\pi) \cdot S(\pi) = 1$, so that, neglecting pulse durations, the cycle time is 4τ . Accordingly, the average Hamiltonian for the Carr–Purcell train for triplet spins in zero field becomes

$$\bar{\mathcal{H}} = \frac{2\tau}{t_c} [\mathcal{H}_{RI} + S^{-1}(\pi)\mathcal{H}_{RI}S(\pi)]. \quad (64)$$

The average Hamiltonian can now be computed. Ignoring nonsecular terms, the matrix of $\mathcal{H}_{RI}$ in the τ_y, τ_x basis is diagonal:

$$\mathcal{H}_{RI} = \begin{bmatrix} \mathcal{H}_{yy} & 0 \\ 0 & \mathcal{H}_{xx} \end{bmatrix}. \quad (65)$$

A π pulse of any phase yields

$$S_{xy}(\pi, \phi)\mathcal{H}_{RI}S_{xy}^{-1}(\pi, \phi) = \begin{bmatrix} \mathcal{H}_{xx} & 0 \\ 0 & \mathcal{H}_{yy} \end{bmatrix}. \quad (66)$$

[Note that $S^{-1}(\pi, \phi) = S(\pi, -\phi)$.] A second π pulse restores $\mathcal{H}_{RI}$ to its original value. Thus the general average Hamiltonian is

$$\bar{\mathcal{H}} = \begin{bmatrix} \frac{1}{2}(\mathcal{H}_{xx} + \mathcal{H}_{yy}) & 0 \\ 0 & \frac{1}{2}(\mathcal{H}_{xx} + \mathcal{H}_{yy}) \end{bmatrix} = \frac{1}{2}(\mathcal{H}_{xx} + \mathcal{H}_{yy})I. \quad (67)$$

Since this is a scalar matrix, it commutes with ρ_I and therefore $\partial\rho_I/\partial t = 0$. Thus the r vector for each subensemble appears constant in time in the interaction representation; under the influence of $\bar{\mathcal{H}}$, the coherence would be completely preserved.

2. Coherent averaging of hyperfine interactions

To illustrate the above considerations, we now compute the average Hamiltonian for the general form of the hyperfine interaction between excited triplet electrons and paramagnetic nuclei in the bulk lattice adjacent to the excited molecule. This interaction can lead to line broadening and to a dephasing of the r vectors of the spin ensembles when nuclear spin flips in the lattice modulate the local field as seen by the electrons at a sufficiently rapid rate. Such a process has been cited as the cause of decay of electron spin echoes from free radicals dissolved in rigid glass matrices,³¹ and is a likely source of relaxation in ODMR experiments in excited triplet states.³²

The results of coherently averaging the hyperfine fields can be seen as follows. The hyperfine interaction is represented in general by $\sum_i \mathcal{A}_i \cdot \mathcal{A}_i \cdot \mathcal{S}$, where $\mathcal{A}_i$ and $\mathcal{S}$ are nuclear and electronic spin operators, $\mathcal{A}_i$ being a second rank tensor. We sum over nuclei in the host

lattice surrounding the triplet molecule and represent the combined effective fluctuating hyperfine field as $\mathcal{F}(t)$.

At this point one must distinguish between the effects of hyperfine interactions between triplet spins and nuclei within the excited molecule (internal hyperfine interactions), and the external hyperfine interaction discussed so far. The internal interaction yields a discrete number of resonance lines, commonly unresolved or only partly resolved in zero field.²⁵ The external interaction produces a broadening of each of these lines which can be removed by coherent averaging as shown in the following.

In an electron spin basis that is diagonal in the zero-field spin dipolar Hamiltonian, the diagonal elements of $\mathcal{F} \cdot \mathbf{S}$ are zero. This means that *in first order* there will be no line broadening from this source and hence no T_2 processes. If, however, the pure electronic triplet levels are mixed by the internal hyperfine interaction, there is a first order shift in triplet energies due to $\mathcal{F}$. This shift is larger than the second order shift which would be calculated from $\mathcal{F}$ alone in the zero-field basis. The net result is that when the spin Hamiltonian is diagonal in both the zero-field Hamiltonian and the internal hyperfine interaction, T_2 processes can result from the external hyperfine interaction.

To illustrate this, consider an internal hyperfine field $\mathcal{G}$ in an excited triplet state with $\mathcal{G}_x = \mathcal{G}_y = 0$, $\mathcal{G}_z \neq 0$. This field mixes the τ_x and τ_y spin states, such that new states and energies are approximately given by

State	Energy
$ x\rangle - i\beta y\rangle$	$X - \mathcal{G}_z\beta$
$ y\rangle - i\beta x\rangle$	$Y + \mathcal{G}_z\beta$
$ z\rangle$	Z

(68)

$$\mathcal{H}_{RI} = \begin{bmatrix} -2\beta_{ex}\mathcal{F}_y + 2\beta_{ye}\mathcal{F}_x & 0 & 0 \\ 0 & -2\beta_{ye}\mathcal{F}_x + 2\beta_{xy}\mathcal{F}_z & 0 \\ 0 & 0 & -2\beta_{xy}\mathcal{F}_z + 2\beta_{ex}\mathcal{F}_y \end{bmatrix}, \quad (71)$$

neglecting nonsecular terms. A Carr-Purcell sequence between τ_u and τ_v yields

$$\bar{\mathcal{H}} = \begin{bmatrix} -2\beta_{ex}\mathcal{F}_y + 2\beta_{ye}\mathcal{F}_x & 0 & 0 \\ 0 & \beta_{ex}\mathcal{F}_y - \beta_{ye}\mathcal{F}_x & 0 \\ 0 & 0 & \beta_{ex}\mathcal{F}_y - \beta_{ye}\mathcal{F}_x \end{bmatrix}. \quad (72)$$

It is important to note that the uu and vv elements of $\bar{\mathcal{H}}$ are now equal. Analogous results apply for the wu and wv Carr-Purcell experiments. This effectively adds the same energy increment to both levels involved in the transition, so that the broadening effect of the external hyperfine interaction is eliminated. As we have shown above, this means that the decay of the induced coherence is effectively nullified in each case if the pulses are applied often enough. Hence when the time between refocussing π pulses in the CP train is short

with $\beta \equiv \mathcal{G}_z/(Y-X) \ll 1$. It should be clear that the *external* hyperfine interaction, $\mathcal{F} \cdot \mathbf{S}$, has nonzero diagonal elements in this new basis.

We now transform to an interaction representation generated from the combined zero-field splitting and internal hyperfine Hamiltonians. If we assume that $\mathcal{F}$ is static or only slowly varying, then the matrix of $\mathcal{F} \cdot \mathbf{S}$ in the interaction representation is

$$\mathcal{H}_{RI} = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 2\beta\mathcal{F}_z & 0 \\ 0 & 0 & -2\beta\mathcal{F}_z \end{bmatrix}, \quad (69)$$

where we have neglected the nonsecular high frequency terms. Since $S_{xy}(\pi)\mathcal{H}_{RI}S_{xy}^{-1}(\pi) = -\mathcal{H}_{RI}$, it is obvious from Eq. (64) that $\bar{\mathcal{H}} = 0$ when the experiment is done on the $\tau_x - \tau_y$ transition. The general result is that a Carr-Purcell train removes from the average Hamiltonian expression the external hyperfine field along the same direction as the magnetic dipole transition moment in the zero-field basis. If all three zero-field states are mixed, then the spin sublevels can be rediagonalized to a new basis, w, v, u , where

$$|w\rangle = |z\rangle - i\beta_{zx}|x\rangle - i\beta_{yz}|y\rangle, \quad (70a)$$

$$|v\rangle = |y\rangle - i\beta_{xy}|x\rangle - i\beta_{yz}|z\rangle, \quad (70b)$$

$$|u\rangle = |x\rangle - i\beta_{xy}|y\rangle - i\beta_{zx}|z\rangle, \quad (70c)$$

with $\beta_{ij} \ll 1$. The matrix of $(\mathcal{F} \cdot \mathbf{S})_I$ in the interaction representation in the w, v, u basis is

compared to the typical time required for the hyperfine fields to change (usually via nuclear spin diffusion), then the echoes will decay much more slowly than the apparent time for decay of a single Hahn echo. Moreover, the decay time of the train should vary from one zero-field transition to another. Adopting another viewpoint, we can investigate the time dependence of the hyperfine fields, manifested macroscopically as spin diffusion by measuring the decay rate of echoes in the Carr-Purcell train as a function of 2τ .

3. Spin locking

In some experiments it is desirable to make the triplet spin coherence insensitive to relaxation due to fluctuations in hyperfine or crystal fields so that it can be used purely as a probe of kinetic phenomena associated with excited states, such as energy migration. One way

to achieve this situation is to "average out" the relaxation by applying the microwave field continuously and then sample the coherence at later and later times. The decay of coherence then becomes due not to fluctuating local fields but rather to kinetic processes, such as decay of the triplet state to the ground state or promotion of a trap state to a band state.³³ Hence, in principle one is able to measure linewidths which are only lifetime broadened. Optically detected spin locking is an example of such a technique.³⁴ Simply stated, $T_{1\rho}$ measured from a spin locking experiment is in essence related to the Fourier transform of the lifetime limited linewidth when kinetic processes result in a new state whose Larmor frequency, ω'_0 , differs from that of the spin locked state's Larmor frequency, ω_0 , by an amount large compared to γH_1 ; i. e.,

$$|(\omega_0 - \omega'_0)| > \gamma H_1. \quad (73)$$

Spin locking is a limiting case of the Carr-Purcell method when $2\tau \rightarrow 0$. The common procedure for performing Carr-Purcell trains is to phase shift the π pulses by 90° relative to the $\pi/2$ pulses. This modification, introduced by Meiboom and Gill,³⁵ effectively cancels out cumulative errors due to incorrect π pulse length. If one now reduces 2τ in the Carr-Purcell Meiboom-Gill method to zero, the ensemble r vector is now spin locked along H_1 in the rotating frame. We have assumed that H_1 is so strong that it completely determines the evolution of the spin system during a pulse; this implies that $\mathcal{H}_R(t)$ would be completely dominated by H_1 in spin locking. Since the cycle time is now simply the length of two π pulses (or four, in the general case where communication among all three sublevels may be important), the average Hamiltonian $\bar{\mathcal{H}}$ [Eq. (64)] for zero waiting time is zero. Coherence should be very long lived.

Since in practice the fields available to the experiment are not infinite, the average Hamiltonian for spin locking may be more closely approximated by the following development. Consider a generalized Carr-Purcell experiment in which a series of δ -function pulses each rotate the magnetization an infinitesimal angle, $d\theta$. Each pulse is followed by a waiting period of duration $(d\theta/4\pi) \times t_c$. The average Hamiltonian $\bar{\mathcal{H}}$ is calculated by taking the average of $\mathcal{H}_{RI}(\theta, \phi)$ over the cycle, where

$$\mathcal{H}_{RI}(\theta, \phi) = S(\theta, \phi) \mathcal{H}_{RI} S^{-1}(\theta, \phi). \quad (74)$$

The result for the xy transition, with a general $\mathcal{H}_{RI}$ with all nonzero elements $\mathcal{H}_{ij}$ is

$$\bar{\mathcal{H}} = \frac{1}{t_c} \int_0^{4\pi} \mathcal{H}_{RI}(\theta, \phi) d\theta t_c / 4\pi$$

$$= \begin{bmatrix} \mathcal{H}_{xx} & 0 & 0 \\ 0 & \frac{\mathcal{H}_{xx} + \mathcal{H}_{yy}}{2} & \frac{\mathcal{H}_{yx} - \mathcal{H}_{xy} \exp(-2i\phi)}{2} \\ 0 & \frac{\mathcal{H}_{xy} - \mathcal{H}_{yx} \exp(+2i\phi)}{2} & \frac{\mathcal{H}_{xx} + \mathcal{H}_{yy}}{2} \end{bmatrix}. \quad (75)$$

This is exactly the same expression that would be obtained for four π pulses interspersed with four equal waiting periods.

The physical significance of this expression is as follows: For the systems of interest here, spin-lattice relaxation is negligible at low temperatures, and the elements $\mathcal{H}_{xy}$ and $\mathcal{H}_{yx}$ can be set to zero, as explained earlier in this section. The 2×2 yx submatrix in Eq. (75) then becomes identical to the matrix of Eq. (67) and the r vector appropriate to the xy submanifold will be stationary under the influence of $\bar{\mathcal{H}}$. The coherence then becomes immune to any decay due to $\mathcal{H}_R$.

4. Results of coherent averaging experiments

In Figs. 7 and 8 we show results of Carr-Purcell echo trains performed on the $^3\pi\pi^*$ state of tetrachlorobenzene (TCB). The Meiboom-Gill modification³⁵ was employed, in which the π refocussing pulses were shifted in microwave phase by 90° to cancel out errors in pulse length. As in other optically detected coherence experiments, a probe pulse terminates the pulse train and is slowly swept in time, establishing a final phosphorescence intensity which is proportional to the coherence remaining in the ensemble at that time. As expected, the echo maxima occur midway between refocussing pulses.

The decay of echo maxima is markedly nonexponential and is not yet understood in detail. Qualitatively similar results have been obtained for the triplet state of d_7 -quinoline in a durene host using conventional techniques.³² It is nevertheless very clear that (1) the echo

FIG. 7. Optically detected Carr-Purcell Meiboom-Gill spin echo train in the $\tau_x \rightarrow \tau_y$ transition of the $^3\pi\pi^*$ state of 1,2,4,5-tetrachlorobenzene (Y trap). The probe pulse terminates the pulse train and is swept continuously in time. Irregular echo spacing is due to nonconstant sweep rate. Only the first few echoes are shown; echoes were detectable out to 1 msec. Other details are given in the text, Secs. III and IV.

FIG. 8. The decay of the echo maxima in the optically detected Carr-Purcell Meiboom-Gill spin echo train in the $\tau_y \rightarrow \tau_z$ transition of the $^3\pi\pi^*$ state of 1,2,4,5-tetrachlorobenzene in durene. The decay becomes slower as the pulse spacing 2τ is reduced.

maxima decay much more slowly than the single three pulse echo decay, and (2) when 2τ is shortened, the decay of echoes is greatly retarded. The single Hahn echo for the $2E$ transition of TCB in durene decays with a $1/e$ time of $4 \mu\text{sec}$, and the echo train lifetimes shown here are several hundred microseconds.

Reducing 2τ to zero converts the Carr-Purcell Meiboom-Gill train into a spin locking train. In this experiment, the probe pulse causes a jump in phosphorescence intensity proportional to the coherence remaining at the end of the long spin lock pulse. As discussed above, the coherence lifetime should be very long. In fact, the spin lock lifetimes of excited triplet ensembles reported in recent work³⁴ approached the triplet state lifetimes. For example, the spin lock signal for the $2E(\tau_y \rightarrow \tau_z)$ transition of h_2 -TCB in h_{14} -durene decays exponentially with a $1/e$ time of 24 msec.³³ The τ_y and τ_z sublevel lifetimes are 36.0 msec and 38.0 msec, respectively.³⁶ The slight difference between spin lock decay and triplet decay times is due to slow spin-lattice relaxation in the rotating frame ($T_{1\rho}$ processes).^{27,3} Figure 9 compares the coherence lifetimes measured in various types of experiments for the $2E$ transition of TCB in durene.

In summary, the Carr-Purcell Meiboom-Gill method and spin locking represent two experimental approaches, each of which is suited for a different class of investigations. The dependence of coherence lifetime on 2τ in the Carr-Purcell train potentially gives valuable information about molecular motions in the crystal field, the interaction of triplet electronic spins and nuclear spins in the host, and host nuclear spin diffusion. Spin locking is useful when one wishes to nullify the effects of the

above interactions on triplet spin relaxation in order to make the coherence lifetime sensitive to kinetic phenomena in the excited state, as in a recent measurement of the rate of detrapping of triplet excitation in a molecular crystal.³³

IV. EXPERIMENTAL

In the following section, details of the experimental apparatus used to measure coherence in excited states by optical detection are presented, and the general set-up for a pulse spectrometer and the methods used to obtain coherence information are discussed.

The conversion of a cw optically detected magnetic resonance spectrometer to a pulse spectrometer is quite simple because the optical detection feature of the instrument avoids cavity and detection system overload problems encountered in conventional ESR pulse spectrometers. Only a pulse generator, a fast microwave switch device, and a high power amplifier are required in addition to the normal cw setup. The experimental details of cw optically detected ESR have been described elsewhere.³⁷ A block diagram of the pulse spectrometer is given in Fig. 10.

Optical detection of electron spin coherence proceeds as follows: A strobe pulse generator is used to initiate a pulse sequence. The sequence is applied to the sample at a repetition rate compatible with the rate of phosphorescence decay. Measurement of relaxation times requires the pulse sequence to last on the order of microseconds, whereas the triplet lifetimes are commonly on the order of milliseconds. Thus, it is reasonable to neglect changes in phosphorescence during the pulse sequence. Experiments that involve pulse sequences which

FIG. 9. Optically detected coherence lifetime measured in different experiments performed on the $\tau_y \rightarrow \tau_z$ transition of h_2 -tetrachlorobenzene in durene. The free precession signal and the spin echo maxima, measured as described in Sec. III above, both decay exponentially as the pulse separation is increased. The $1/e$ time given for the Carr-Purcell experiment is estimated for the last part of the train (see Fig. 8). Spin locking time is taken from Ref. 33.

FIG. 10. Block diagram of optically detected magnetic resonance pulse spectrometer. Additional details are given in the text, Table I, and Figs. 11 and 12.

last for times on the same order as the triplet state decay, such as extended spin locking, have interesting ramifications due to the feeding and decay processes that are occurring while the microwave field is on and will be treated in a more general description in a later publication. In the present situation, the final probe establishes a phosphorescence intensity which is proportional to the coherence remaining in the triplet ensemble at that time. After the pulse sequence, this intensity decays towards the steady state value obtained in the absence of microwaves. The resulting waveform can be time averaged using a lock-in amplifier whose reference frequency is provided by the strobe pulse generator. The lock-in output signal, when measured relative to an appropriate baseline (e.g., complete echo decay), is then proportional to the coherence at the probe time. If the probe pulse is then swept in time at a rate compatible with the lock-in time constant, the echo formation may be recorded directly on a stripchart recorder and also stored on paper tape utilizing a suitable interface. The echo in Fig. 6 for 2, 3-dichloroquinoxaline was recorded with a lock-in reference frequency of 1.5 Hz, and a point was recorded every 2 sec.

In order to establish the microwave pulse times for

$\pi/2$, π , etc., pulses, a transient nutation is recorded by slowly lengthening a single pulse while monitoring the light as described above. The observed signal oscillations decay much faster than the homogeneous T_2 would predict because of inhomogeneities in the H_1 field, but as long as there are several maxima and minima, as in the curves illustrated in Fig. 3, the pulse widths can be set easily.

It is important to use high isolation PIN diodes such as a Hewlett Packard 33124A. Often, two or more of these diodes are placed in series in order to prevent feedthrough which would cause partial or total saturation of the microwave transition when the switch is in the off position. The PIN diodes are controlled by the pulse generator output into a DM 8830N buffer in conjunction with a National Semiconductor Corporation DH 0035C PIN diode switch driver using the circuit given in the driver data sheet. A summary of other equipment used in the pulse spectrometer is given in Table I.

The heart of the pulse spectrometer lies in the pulse sequence unit. We have built several devices designed for specific pulse sequences from transistor-transistor logic integrated circuit chips. The circuits are

Figure 10 equipment

Figure 12' equipment

straightforward combinations of NAND gates (SN 7400, 7420, etc), monostable multivibrators (SN 74121, 74123), and edge-triggered flip flops (SN 7479N). Fifty ohm transmission lines are used and care is taken to match impedance between devices.

For experiments such as the Carr-Purcell train, it

Flexibility in the pulse sequences used is made possible by the four-channel phase shifter illustrated in Fig. 12. Each of the PIN diode switches is controlled by a separate driver. Thus, any part of the pulse sequence may be phase shifted by 0° , 90° , 180° , or 270° . This is essential for experiments such as the Carr-Purcell echo train with the Meiboom-Gill modification, in which the π refocussing pulses are phase shifted by 90° from the initial $\pi/2$ pulse. Multiple phases are also required for spin locking and optically detected ad-

FIG. 11. Schematic diagram of a digital plus variable delay device capable of producing two pulses with highly reproducible pulse separation. See text for details.

FIG. 12. Block diagram of the four-channel phase shifter in Fig. 10.

abatic demagnetization in the rotating frame.³⁸ Phase adjustments are made by observing the response of a crystal diode detector to the output of the network when separate channels are switched on individually and to the resultant signal when two channels are opened concurrently and added together.

The procedure is as follows: The individual signals from two channels being compared are equalized by adjusting the variable attenuators in the lines. Combining two signals phase shifted by 180° produces zero detector output, and 0° phase shift produces the maximum combined output which varies from 2–4 times the output due to individual channels, depending on the total incident power and the response characteristics of the crystal. A 90° phase shift produces an intermediate signal. In three-channel experiments, an accurate 90° phase shift can be obtained by adjusting the phase of the signal in question, *A*, relative to two other signals, *B* and *C*, which are set to be 180° out of phase. One merely adjusts the phase of *A* until the crystal detector responds equally to $A + B$ and $A + C$. In two-channel experiments, the 90° phase shift can be achieved by setting the length of the adjustable line halfway between 0° and 180° positions. Alternatively, the ODMR echo or

spin lock signal itself, whose amplitude will be phase sensitive, can be used to set the phases.

V. CONCLUSION

Using optically detected magnetic resonance of excited triplet states in zero field as an example of an observable which monitors relative energy level populations, we have demonstrated that it is possible to perform any of the vast number of experiments that involve coherence effects in two-level systems. Equations (50)–(53) show that the results obtained from pulse experiments requiring the final “probe pulse” are identical in form to the standard methods which utilize an observable that measures coherent effects directly. Highly sensitive double-resonance methods may thus be used to extend further the study of energy transport and relaxation phenomena in both the ground and excited states of molecules and atoms.

The form of the zero-field spin Hamiltonian makes it particularly simple to extend these results to coherent optical excitation experiments. In both cases, an induced oscillating dipole is produced, the only difference being that the zero-field case is an induced magnetic dipole, whereas the optical case involves an induced electric dipole transition. By properly including the effects of spontaneous emission and the wavevector *k* in the treatment for the optical case, the probe pulse method should provide an equally valuable investigative tool for optical coherence experiments in multilevel systems.

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