NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

*Can we actually "know" the universe?
My God, it's hard enough finding your way
around in Chinatown.*

**"My Philosophy"
W. Allen**

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

26

TABLE OF CONTENTS

ABSTRACT	v
I. INTRODUCTION	1
A. Historical Perspective	1
B. Coherence and Two-Level Systems	4
II. ESESC AS A PROBE OF INTRAMOLECULAR TUNNELING IN CYCLOPENTANONE 13	
A. Background	14
B. Energy Exchange Between Two-Level Systems	15
1. Slow Exchange: $\delta\omega \gg 1$	23
2. Fast Exchange: $\delta\omega \ll 1$	25
C. Spin Locking	26
D. Experimental Procedure	33
E. Results and Discussion	36
III. ROTARY ECHOES IN EXCITED TRIPLET STATES	42
A. The Rotary Echo	42
B. Average Hamiltonian Theory	46
C. Application to Triplet States	49
D. Coherent Averaging via Rotary Echoes	52
1. $\pi/2$ Pulse Method	52
2. Integral Method	55
E. Coherent Averaging in the Presence of Pulse Imperfections 62	
1. Phase Angle Errors	62
2. Off-Resonance Averaging	63
F. Rotary Echo Calculations	67
1. Phase Angle Errors	67
2. Off-Resonance Driving Fields	68
3. Population Feeding and Decay	71
4. Inhomogeneous Broadening	77
G. Experimental Results and Discussion	83
1. Experimental Details	83
2. Results and Conclusions	86
RETROSPECTIVE	95
APPENDIX	97
ACKNOWLEDGMENTS	100
REFERENCES	101

EXCITED STATE ELECTRON SPIN COHERENCE (EDESC)
STUDIES OF TRIPLET STATES IN MOLECULAR SOLIDS

Marc Edward Tarrasch

Materials and Molecular Research Division
Lawrence Berkeley Laboratory and Department of Chemistry
University of California
Berkeley, California 94720

ABSTRACT

The field of coherent spectroscopy of two-level systems is applied to the lowest triplet state of organic molecules. By neglecting the triplet sublevel not coupled by the field, it is possible to describe the remaining two levels with Feynman-Vernon-Hellwarth geometrical representation of a general two-level system. The equations of motion of the pseudomagnetization are derived after transformation to the rotating frame, as are Bloch-type equations which include phenomenological relaxation times.

The loss of coherence due to exchange between triplet states with different Larmor frequencies but identical zero-field dipolar tensor axes is then discussed. By writing two sets of coupled Bloch equations,

expressions for the effective decay rate and frequency shift of the experimentally monitored triplet system are derived and discussed in the limits of slow and rapid exchange. This analysis is applied to intramolecular tunneling between different configurations of cyclopentanone. It is shown by both spin locking and CW spectra that the tunneling rate is considerably slower than the phosphorescence decay rate of the lowest triplet state.

Rotary echoes are considered, both on- and off-resonance, with Average Hamiltonian theory. It is shown that relaxation fields perpendicular to the driving field are averaged while those parallel to it are not. The inhomogeneity in the broadening mechanism is completely removed by on-resonance rotary echoes but only partially eliminated by off-resonance rotary echoes. Calculations for off-resonance rotary echo intensities are presented and extended to include triplet sublevel population kinetics and inhomogeneous broadening. Finally, experimental observation of rotary echoes in several 1,2,4,5-Tetrachlorobenzene systems is reported and compared with the theoretical predictions made.

CHAPTER I
INTRODUCTION

A. Historical Perspective

The framework for excited state electron spin coherence (ESESC) has been established in various areas of physics and chemistry over the last thirty years. The initial experiments by Bloch in 1946¹ demonstrated the feasibility of observing a magnetic dipole transition on a nuclear spin system. Further work in NMR during the 1950's introduced a variety of pulsed coherence experiments²⁻⁹ designed to measure relaxation rates and mechanisms. This trend was extended by the development in the late 1960's of Average Hamiltonian theory,^{10,11} which permits far more elaborate and highly specific pulse techniques to be applied to spin systems.

At roughly the same time as the first NMR experiments, G. N. Lewis and co-workers associated phosphorescence from certain organic molecules with a supposedly forbidden triplet-singlet transition¹² and later proved this mechanism by measuring the magnetic susceptibility of the phosphorescing molecules.¹³ Optical detection of excited state magnetic resonance in gases¹⁴ and inorganic solids¹⁵ was subsequently observed, but it was not until 1967 that the first double resonance experiments on excited triplet states in zero-field were successfully carried out.¹⁶ The area of optically detected magnetic resonance (ODMR) in zero-field has since expanded greatly and has been used to measure zero-field splittings,¹⁷ hyperfine and nuclear quadrupole interactions,^{18,19} sublevel population kinetics,²⁰ and other relevant triplet state parameters.^{21,22} Finally,

the possibility of observing coherent phenomena in excited triplet states was proposed²³ and experimentally verified.²⁴

To optically detect the ESESC analogues to many pulsed NMR experiments, the probe pulse method²⁵ was introduced in 1973. Conventional detection methods can directly measure the degree of coherence in a triplet ensemble, but optical detection is sensitive to the time-dependent population difference between the triplet sublevels and thus requires the coherence to be displayed as a spin alignment. With the advent of the probe pulse, spin locking,²⁶⁻³⁰ free induction decays,²⁵ spin echoes,²⁵ and adiabatic demagnetization in the rotating frame (ADRF)^{31,32} have been reported and applied to both localized and delocalized states in molecular molecules.

All of these techniques are capable of monitoring the time evolution of coherence in the triplet ensemble established at a definite time $t = 0$. This is in contrast to the simpler time-resolved kinetic experiments²⁰ which are sensitive only to the population of the triplet sublevels. Because the decay of coherence is affected by energy transfer processes of interest, ESESC techniques can be used as a probe of these processes. The ultimate goal in this kind of coherent spectroscopy is therefore not so much to learn what the relaxation time is but to use that information to understand the mechanisms and decay channels which result in dephasing events.

The merging of the previously separate areas of multiple pulse NMR and ODMR of triplet states was made possible by the geometrical representation of the Schrödinger equation.³³ Known as the Feynman-Vernon-Hellwarth (FVH) representation, this geometrical picture rigorously

describes a two-level system by an equation of the same form as the torque equation describing the classical precession of a gyromagnet in a magnetic field. One great advantage of using the FVH representation is that any two-level system is formally equivalent to the well known nuclear spin- $\frac{1}{2}$ system and thus the pulsed techniques developed for NMR carry over directly to virtually all regions of the electromagnetic spectrum. Another important feature is that it becomes relatively simple to *visualize* the time evolution of a two-level system even when the mathematics describing the pulse sequence becomes very dense.

Because the geometrical representation is so fundamental to a description of ESESC, the remainder of this chapter will be devoted to the quantum mechanics of an isolated two-level system. The discussion will utilize a density matrix³⁴ approach rather than the more familiar Schrödinger equation solution, since the former lends itself more naturally to mathematical descriptions of exchange between two two-level systems³⁵ and between a two-level system and a population "reservoir."³⁶ Several assumptions will be made concerning the following treatment:

- i) The wavelength of the radiation is large compared to the sample size, i.e., $\lambda^3 \gg V_{\text{sample}}$. Thus, spatial effects can be ignored.
- ii) The strength of the applied field is much greater than any fields produced by the sample itself. This approximation, along with the first approximation, allows one to disregard Maxwell's equations and any pulse propagation effects.
- iii) Transverse (T_2) and longitudinal (T_1) relaxation will be neglected initially but discussed in later chapters.

Generally, it is valid to set $T_1 = \infty$ for the situation of a molecular solid at liquid helium temperatures. T_2 processes do not affect spin locking (Chapter II) but will play an important role in the rotary echo experiment (Chapter III).

B. Coherence and Two-Level Systems

We begin with an ensemble of non-interacting two-level systems with eigenstates $|a\rangle$ and $|b\rangle$ whose eigenvalues are $+\hbar\omega_0/2$ and $-\hbar\omega_0/2$ respectively. In the a-b basis, the wavefunction $|\psi\rangle$ at any time t for an individual system is given by

$$|\psi\rangle = a|a\rangle + b|b\rangle \quad (1)$$

where a and b are time-dependent. The density matrix for the system is

$$\rho(t) = |\psi\rangle\langle\psi| = \begin{bmatrix} aa^* & ab^* \\ ba^* & bb^* \end{bmatrix} \quad (2)$$

and the time evolution of the density matrix is written as

$$i\hbar\dot{\rho}(t) = [\mathcal{H}, \rho(t)] \quad (3)$$

where $\mathcal{H} = \mathcal{H}_0 + V(t)$. $\mathcal{H}_0$ represents the time-independent part of the Hamiltonian giving rise to the aforementioned eigenenergies $\pm\hbar\omega_0/2$ and $V(t)$ is a coherent perturbation without diagonal elements in the a-b basis. The form of $V(t)$ is usually expressed as

$$V(t) = \gamma H_1 S_z \cos(\omega t + \phi) \quad (4)$$

for triplet states in the x-y basis, where γ is the electron magnetogyric ratio, H_1 is the applied field strength, S_z is the triplet state spin operator for the $|x\rangle \leftrightarrow |y\rangle$ transition, and ω is the frequency of the

of the applied field of phase ϕ .

Because ρ is a 2×2 Hermitian matrix, we can always write

$$\rho = \frac{1}{2}[\hat{1} + \underline{r} \cdot \underline{\sigma}] \quad , \quad (5)$$

where the components of $\underline{g}$ are the Pauli spin matrices. Expanding Eq. (5), we have

$$\rho = \frac{1}{2} \begin{bmatrix} 1 + r_3 & r_1 - ir_2 \\ r_1 + ir_2 & 1 - r_3 \end{bmatrix} \quad . \quad (6)$$

We can thus equate the matrix elements in Eqs. (2) and (6) and construct the vector $\underline{r}$ from the time-dependent coefficients a and b :

$$r_1 = ab^* + ba^* \quad (7a)$$

$$r_2 = i(ab^* - ba^*) \quad (7b)$$

$$r_3 = aa^* - bb^* \quad . \quad (7c)$$

If the Hamiltonian $\mathcal{H}$ is represented by $\frac{\hbar}{2} \underline{\Omega} \cdot \underline{\sigma}$, where $\underline{\Omega}$ is given by

$$\Omega_1 = 1/\hbar (V_{ab} + V_{ba}) \quad (8a)$$

$$\Omega_2 = i/\hbar (V_{ab} - V_{ba}) \quad (8b)$$

$$\Omega_3 = \omega_0 \quad , \quad (8c)$$

Equation (3) can be written as

$$i\hbar \dot{\rho}(t) = \left[\frac{\hbar}{2} \underline{\Omega} \cdot \underline{\sigma}, \frac{1}{2}(\hat{1} + \underline{r} \cdot \underline{\sigma}) \right] = \frac{i\hbar}{2} (\underline{\Omega} \times \underline{r}) \cdot \underline{\sigma} \quad . \quad (9)$$

Since Eq. (5) yields $\dot{\rho} = \frac{1}{2}(\dot{\underline{r}} \cdot \underline{\sigma})$ upon differentiation, we can identify the time dependence of the $\underline{r}$ -vector by

$$\dot{\underline{r}} = \underline{\Omega} \times \underline{r} \quad . \quad (10)$$

This is the central result of the FVH paper. The physical meaning of the $\underline{r}$ -vector is most easily seen by comparing Eq. (10) with the more familiar NMR result for a spin- $\frac{1}{2}$ nucleus in a magnetic field:

$$\dot{\underline{\mu}} = \gamma \underline{\mu} \times \underline{H} . \quad (11)$$

The $\underline{r}$ -vector is thus analogous to the magnetization $\underline{\mu}$ produced by the alignment of nuclear magnetic moments in a static field $(\underline{H}_0)_z$. However, there are no real physical directions in r -space and there need not be a static field present to achieve a population difference in the FVH picture. It is therefore common to call $\underline{r}$ the *pseudomagnetization*. Similarly, the term $\underline{H}$ in Eq. (11) usually refers to a static field $\underline{H}_0$ along a true z axis and an oscillating rf field $\underline{H}_1$ along the x direction. The analogous FVH field $\underline{\Omega}$ is a mathematical construct based on linear combinations of matrix elements from a matrix representation of the Schrödinger equation.

It is simple to deduce some properties of $\underline{r}$ before making the standard transformation to the rotating frame.³⁷ First, in the absence of any perturbation, $\Omega_1 = \Omega_2 = 0 = r_1 = r_2$ and thus Eq. (10) shows that $\dot{\underline{r}} = 0$. The only component of $\underline{r}$ is aligned along the r_3 axis and is stationary. (This is not true if $\underline{r}$ is disturbed from its equilibrium position by a previously applied field.) The r_3 component represents a population difference term, as can be seen in Eq. (7c). Secondly, the length of $\underline{r}$ is constant if the number of spin systems is conserved. Evaluating the sum $(r_1^2 + r_2^2 + r_3^2)^{1/2}$ using Eqs. (7) shows that $|\underline{r}| = (aa^* + bb^*)$. This is a time-independent quantity since $(aa^* + bb^*)$ is the quantum mechanical probability of finding the system in either state $|a\rangle$ or state $|b\rangle$.

The solution to Eq. (10) is greatly facilitated by a transformation to a rotating coordinate system. This is accomplished by performing a unitary transformation on the density matrix

$$\rho^*(t) = U \rho(t) U^{-1} , \quad (12)$$

where U is given by

$$U = \exp(i\omega \mathcal{H}_0 t / \hbar \omega_0) . \quad (13)$$

The new matrix $\rho^*(t)$ is described by an equation similar to Eq. (3):

$$i\hbar \dot{\rho}^*(t) = [\mathcal{H}^*, \rho^*(t)] , \quad (14)$$

where $\mathcal{H}^*$ is now a time-independent Hamiltonian

$$\mathcal{H}^* = \mathcal{H}_0 \left[1 - \frac{\omega}{\omega_0} \right] + U V(t) U^{-1} . \quad (15)$$

This transformation reduces to the interaction representation for $\omega = \omega_0$. The effect of the transformation is to remove the motion in r -space due to the circular frequency of the applied field. The $\underline{r}^*$ -vector now precesses about a field $\underline{\Omega}^*$ in the rotating frame whose Ω_3^* component is $\Omega_3^* = \omega_0 - \omega = \Delta\omega$. The time dependence of $\underline{r}^*$ observed in the rotating frame is given by

$$\dot{\underline{r}}^* = (\underline{\Omega} - \underline{\omega}) \times \underline{r}^* \equiv \underline{\Omega}^* \times \underline{r}^* . \quad (16)$$

Because $\mathcal{H}^*$ is now time-independent, one can solve Eq. (14) and obtain

$$\rho^*(t) = S \rho^*(0) S^{-1} \quad (17)$$

where the time evolution operator S is

$$S = \exp(-i\mathcal{H}^* t / \hbar) . \quad (18)$$

Finally, using Eqs. (15) and (18), S can be expressed as

$$S = \begin{bmatrix} \cos \frac{\bar{\omega}t}{2} - \frac{i\Delta\omega}{\bar{\omega}} \sin \frac{\bar{\omega}t}{2} & \frac{\omega_1}{\bar{\omega}} e^{-i\phi} \sin \frac{\bar{\omega}t}{2} \\ -\frac{\omega_1}{\bar{\omega}} e^{i\phi} \sin \frac{\bar{\omega}t}{2} & \cos \frac{\bar{\omega}t}{2} + \frac{i\Delta\omega}{\bar{\omega}} \sin \frac{\bar{\omega}t}{2} \end{bmatrix} \quad (19)$$

We have used the definitions

$$\Delta\omega = \omega_0 - \omega \quad (20)$$

and

$$\bar{\omega} = \sqrt{\omega_1^2 + \Delta\omega^2} \quad (21)$$

Analytic expressions for the three components of $\underline{r}^*$ can be derived if ρ^* is written as the rotating frame equivalent to Eq. (6):

$$\rho^* = \frac{1}{2} \begin{bmatrix} 1 + r_3^* & r_1^* - ir_2^* \\ r_1^* + ir_2^* & 1 - r_3^* \end{bmatrix} \quad (22)$$

The operations indicated in Eq. (17) can be carried out to yield ρ^* for a given time t , or equivalently, the $\underline{r}^*$ components. Successive time-ordered unitary transformations can also be applied if more than one set of conditions is imposed on ρ^* .

The equations for r_1^* are lengthy, but they will be used in later chapters and are therefore presented here. For arbitrary initial values $r_i^*(0)$, we have

$$\begin{aligned} r_1^*(t) = & \frac{1}{\bar{\omega}^2} \left\{ r_1^*(0)\bar{\omega}^2 \cos \bar{\omega}t - [r_2^*(0)\Delta\omega\bar{\omega} + r_3^*(0)\omega_1\bar{\omega} \cos \phi] \sin \bar{\omega}t \right. \\ & + [r_1^*(0)\omega_1^2 \sin^2 \phi - r_2^*(0)\omega_1^2 \sin \phi \cos \phi + r_3^*(0)\omega_1\Delta\omega \sin \phi] \\ & \times (1 - \cos \bar{\omega}t) \left. \right\} \quad (23a) \end{aligned}$$

$$\begin{aligned}
 r_2^*(t) = & \frac{1}{\bar{\omega}^2} \left\{ r_2^*(0) \bar{\omega}^2 \cos \bar{\omega} t + [r_1^*(0) \Delta \omega \bar{\omega} - r_3^*(0) \omega_1 \bar{\omega} \sin \phi] \sin \bar{\omega} t \right. \\
 & + [r_2^*(0) \omega_1^2 \cos^2 \phi - r_1^*(0) \omega_1^2 \sin \phi \cos \phi - r_3^*(0) \omega_1 \Delta \omega \cos \phi] \\
 & \times (1 - \cos \bar{\omega} t) \left. \right\}
 \end{aligned} \tag{23b}$$

$$\begin{aligned}
 r_3^*(t) = & \frac{1}{\bar{\omega}^2} \left\{ r_3^*(0) \bar{\omega}^2 \cos \bar{\omega} t + [r_1^*(0) \omega_1 \bar{\omega} \cos \phi + r_2^*(0) \omega_1 \bar{\omega} \sin \phi] \sin \bar{\omega} t \right. \\
 & + [r_1^*(0) \omega_1 \Delta \omega \sin \phi - r_2^*(0) \omega_1 \Delta \omega \cos \phi + r_3^*(0) \Delta \omega^2] (1 - \cos \bar{\omega} t) \left. \right\}
 \end{aligned} \tag{23c}$$

Equations (23) are not as formidable as they appear, since there are usually many simplifying substitutions that can be made. For example, $\phi = 0^\circ$, 90° , or 180° , $\Delta \omega = 0$, and $r_1^*(0) = r_2^*(0) = 0$ describe conditions which apply to many coherence experiments. In particular, the above choice of $r_1^*(0)$ is not necessarily valid for an isolated two-level system. This discussion has used a quantum mechanical system and classical gyromagnet interchangeably for simplicity. A more rigorous treatment shows that the quantum mechanical and classical pictures are equivalent in the limit of a large number of isolated two-level systems so that the pseudomagnetization represents an ensemble average $\langle \underline{r}^* \rangle$. Then, before the application of the coherent perturbation $V(t)$, the off-diagonal elements of $\rho^*(t)$ are zero if one assumes the Random Phase Approximation, because the phase factors in the cross terms $\langle ab^* \rangle$ and $\langle ba^* \rangle$ in Eq. (2) are uncorrelated and average to zero over the ensemble. Recalling Eqs. (7a) and (7b), $\langle r_1^*(0) \rangle$ and $\langle r_2^*(0) \rangle$ are also zero in the absence of an applied field and thus the appropriate simplifications in Eqs. (23) are justified.

The equations of motion for r_i^* represent a very simple model system in which all the oscillators are of the same resonance frequency ω_0 and have a δ -function linewidth. No provisions are made for spin-lattice (T_1), homogeneous (T_2), inhomogeneous (T_2^*), and spin-diffusion relaxation processes. These latter two types of processes which disrupt the phase coherence are often treated by choosing a frequency distribution $g(\omega - \omega_0)$ for the spins and a statistical model for energy exchange within the inhomogeneous line;³⁸⁻⁴¹ the accumulated loss of phase memory during a coherence experiment (e.g., spin echoes) can then be calculated. Even in this situation of an inhomogeneously broadened interacting ensemble of spin systems, the basic model with which one starts is the isolated two-level system. The spin-diffusion problem is outside the scope of this thesis and will not be discussed further, but inhomogeneous broadening will be considered later in Chapter III.

Non-interacting two-level systems can experience T_1 and T_2 processes due to the presence of the lattice and surrounding spins, respectively. The effects of relaxation can be incorporated phenomenologically into the FWH representation by writing Bloch-type equations and including relaxation terms. This is accomplished by evaluating the components in the rotating frame torque equation [Eq. (16)]. Specifically, for triplet states, we have in the x-y basis,

$$v_{xy} = -v_{yx} = i\hbar \quad (24)$$

so that

$$\mathcal{H}^* = \frac{\hbar}{2} \begin{bmatrix} \Delta\omega & i\omega_1 e^{-i\phi} \\ -i\omega_1 e^{i\phi} & -\Delta\omega \end{bmatrix}. \quad (25)$$

The components of $\tilde{\Omega}^*$ with $\phi = 0^\circ$ are therefore

$$\Omega_1^* = 0 \quad (26a)$$

$$\Omega_2^* = -\omega_1 \quad (26b)$$

$$\Omega_3^* = \Delta\omega \quad (26c)$$

Substituting into Eq. (16) and adding the relaxation terms to each differential equation yields the desired result:

$$\dot{r}_1^* = -\Delta\omega r_2^* + \omega_1 r_3^* - r_1^*/T_2 \quad (27a)$$

$$\dot{r}_2^* = \Delta\omega r_1^* - r_2^*/T_{2e} \quad (27b)$$

$$\dot{r}_3^* = -\omega_1 r_1^* + [(r_3^0)^* - r_3^*]/T_1 \quad (27c)$$

The transverse relaxation times for the in-plane components are not equal since the applied field is along the r_2 direction; relaxation along the r_2 axis requires that work be done against the field, as first suggested by Redfield.⁴² The T_{2e} term reflects this and is assumed to be dependent upon the field strength ω_1 . In the limit of zero applied field, $T_{2e} = T_2$ and the standard Bloch equations emerge. This point will be discussed in more depth with respect to spin locking (Chapter II).

Solutions to Eqs. (27) have been considered in detail by Breiland⁴³ for some simple pulse sequences and for slow passage lineshapes. For the much more complicated situation which includes population kinetics for the individual states, it is more convenient to work with density matrix techniques. We will discuss the solutions to the Bloch-type equations for rotary echoes in Chapter III and show that the decay rate for the echo is the arithmetic average of the transverse and longitudinal decay rates. Equations (27) are also central to the discussion of exchange

between two-level systems. It is a straightforward procedure to write down two sets of Bloch-type equations and couple the two by including terms which transfer population and coherent components back and forth between the systems. The Bloch-type equations modified for exchange will be presented in Chapter II.

Generally, Bloch equation solutions, density matrix methods, and lineshape theories all entail considerably more effort than solutions in the absence of relaxation. Simplification of the problem by omitting one or more relaxation mechanisms is fortunately a reasonable approximation. Spin-lattice relaxation will be neglected in Chapters II and III as a cause of dephasing, since $T_2 \ll T_1$ for most molecular solids at liquid He temperatures. The principal dephasing mechanisms which will be considered are energy exchange and T_{2e} processes (Chapter II) and T_2 processes (Chapter III).

CHAPTER II

ESESC AS A PROBE OF INTRAMOLECULAR TUNNELING IN CYCLOPENTANONE

The ESESC techniques mentioned in Chapter I are very selective experiments, and if used properly, can separate the various dephasing channels available to a spin system. Clearly, the time scale of the experiment must be comparable to the time scale of the dephasing mechanism. Transverse relaxation processes are usually the most rapidly occurring dephasing processes in molecular crystals and are amenable to study by an experiment with appropriate temporal resolution. With optical detection methods, high power microwave fields, and TTL pulse generators, it is technically possible to measure T_2 times down to about 10^{-7} seconds. Since all triplet state systems studied to date have relaxation times at least an order of magnitude longer than this figure, relaxation studies do not present a technical problem.

"Classical NMR" relaxation processes — those which can affect a single two-level system associated with an isolated guest molecule in a host lattice, for example — represent one class of relaxation mechanisms which may be termed "static." Hyperfine interactions, inhomogeneous broadening, and spin-lattice relaxation all belong to this class. Relaxation processes which involve the exchange of energy between systems comprise another type of mechanism called "dynamic." The choice of terms "dynamic" and "static" may appear to be misleading because these energy exchange processes are generally several orders of magnitude slower than static processes in molecular solids. Measuring a dynamic mechanism therefore requires a pulse technique capable of suppressing the more rapid and interfering T_2 processes.

In this chapter, the spin locking experiment will be discussed and applied to a dynamic exchange mechanism in cyclopentanone, intramolecular tunneling. Inhomogeneous broadening and proton hyperfine interactions, which give rise to an ESR absorption FWHM of roughly 4 to 5 MHz in cyclopentanone, should yield T_2 times on the order of microseconds. Hahn spin echoes,² Carr-Purcell-Meiboom-Gill (CPMG) spin echoes,^{4,5} rotary echoes,⁶ and free induction decays can measure these relaxation times but would be insensitive to a possibly slower dephasing process such as tunneling. Spin locking, by the application of a strong ($\omega_1 > \text{FWHM}$) H_1 field, requires that a dephasing event change the local fields by an amount greater than ω_1 in order to cause a loss of coherence and is ideally suited to measuring tunneling rates in cyclopentanone.

We will first describe briefly the motivation for studying cyclopentanone. Exchange theory will then be discussed and applied to the spin locking experiment. The results for cyclopentanone, using both ESESC and conventional ODMR methods can then be analyzed with exchange theory to yield the tunneling rate.

A. Background

The cyclopentanone system is a fairly uncommon example of a triplet species to be studied by ODMR methods, since it is non-aromatic in character. Because of its lack of stabilizing conjugation, cyclopentanone undergoes a rearrangement (α -cleavage) upon photolysis in the liquid phase to form 4-pentenal.⁴⁴ The photochemistry of this reaction is known to involve the lowest triplet state.

Sharnoff and co-workers were the first to examine the triplet state properties of polycrystalline cyclopentanone at liquid He temperatures using ODMR.⁴⁵ Initially, three zero-field transitions at 1625 MHz, 3394 MHz, and 5019 MHz were observed, as expected.⁴⁶ However, more careful examination subsequently revealed two additional sets of three ESR resonances each (a "satellite" and a "weak" triad), separated from the "normal" triad by 9 to 214 MHz.⁴⁷ Their results are illustrated in Fig. 1, in which the intensities of the weak triad are drawn greatly enlarged for the sake of clarity. A double resonance experiment using two microwave fields to excite transitions in different triads simultaneously seemed to indicate an interaction between cyclopentanone molecules having resonance frequencies associated with different triads. An exchange mechanism was postulated by Shain and Sharnoff as a quantum mechanical tunneling between electronic configurations of the same cyclopentanone molecule, which can generally be classified as a dynamic intramolecular process. The exchange rate was placed between $5 \times 10^2 \text{ sec}^{-1}$ and $5 \times 10^7 \text{ sec}^{-1}$, which represent the limits placed by the triplet sublevel lifetimes and the resolution of the ESR lines respectively.

B. Energy Exchange Between Two-Level Systems

The basic problem of exchange has been treated by many authors since the initial work of Van Vleck and Gorter^{48,49} and Bloembergen, Purcell, and Pound⁵⁰ on exchange narrowing in paramagnetic salts and motional averaging in condensed phases, respectively. General theories based on line narrowing were subsequently put forth by Anderson⁵¹ and Kubo⁵² in

OPTICALLY DETECTED ESR OF CYCLOPENTANONE: NORMAL TRIAD AND TWO SATELLITES

REFERENCE: A. L. SHAIN AND M. SHARNOFF,
CHEM. PHYS. LETTERS 22 (1973) 56.

XBL 768 -7297

Fig. 1. ESR spectrum of the lowest triplet state of cyclopentanone from Shain and Sharnoff. Three sets of resonances are observed, one strong ("normal") and two less intense ("satellite" and "weak") triads. The weak triad is not drawn to scale but is enlarged.

the early 1950's. The exchange mechanism was modeled by a Markoffian modulation of the spins' frequency and the resulting correlation function of the frequency calculated by diagonalizing an $n \times n$ matrix, where n is the number of different frequencies experienced by the spins. The resonance lineshape is then found by Fourier transforming the correlation function. A major advantage of this theory over Van Vleck's earlier work is that the complete lineshape is obtained for any exchange rate, as opposed to the second and fourth moments of the line which become inaccurate as the exchange rate approaches the line-narrowing regime.

Anderson's result predicts the famous two-site NMR demonstration of exchange in which two resonance lines at frequencies $\omega_0 \pm \Delta\omega$ coalesce to a single peak at frequency ω_0 when the temperature is increased. One could, in principle, easily modify the theory to include the case of unequal populations at the two sites, so that in the limit of zero exchange, the separate resonances at $\omega_0 \pm \Delta\omega$ would have different intensities. Such a model system would describe the lowest triplet state of cyclopentanone quite well, since one of the weak triads is considerably more intense than the other. The two-site system would consist of site T with resonance lines at 1625 MHz, 3394 MHz, and 5019 MHz (normal) and site T' with resonance lines at 1616 MHz, 3189 MHz, and 4805 MHz (satellite), with the third triad's population neglected.

Unfortunately, Anderson-Kubo formalism assumes that the individual resonance lines at sites T and T' in the absence of exchange are homogeneous. While this may be true in liquids, this approximation does not hold for molecular solids and renders such a lineshape calculation invalid. In the limit of very strong H_1 fields, the inhomogeneity of the line can be

neglected, as is common in pulsed NMR; however, power broadening of the CW absorption spectrum would wash out any information on exchange based on a lineshape analysis.

One is therefore forced to attack the exchange problem in another manner. We follow the pioneering work of McConnell,⁵³ who treated exchange by modifying the Bloch equations directly. The coupled two-site system is illustrated in Fig. 2. Provision is made for an energy difference E_i between the two states, although this need not be the case. The exchange rate from T to T' is called W_+ and the reverse exchange rate from T' to T is called W_- . If $E_i = 0$, W_+ and W_- become equal and one can drop the subscripts; for $E_i \neq 0$, T' represents an excited state and W_- is inversely related to the lifetime τ of the excitation in T':

$$\tau = (W_-)^{-1} \quad (28)$$

We also assume that the magnetic axes of the triplet states are parallel so that spin is conserved during the transfer of excitation from T to T' and vice versa. The situation where the two sets of molecular spin axes are rotated with respect to each other by the Euler angles has been considered in depth by Brenner, Brock, and Harris using a density matrix approach.³⁵ Finally, we note that even though the zero-field dipolar tensors for T and T' have the same orientations, the zero-field splittings are different by an amount $\delta\omega$ for the relevant $|x\rangle \leftrightarrow |y\rangle$ transition.

Following McConnell, one can rewrite Eqs. (27) for T as

$$\left(\frac{dr_1}{dt}\right)_{\text{ex}} = \left(\frac{dr_1}{dt}\right) + \frac{r_1'}{\tau} - W_+ r_1 \quad (29a)$$

$$\left(\frac{dr_2}{dt}\right)_{\text{ex}} = \left(\frac{dr_2}{dt}\right) + \frac{r_2'}{\tau} - W_+ r_2 \quad (29b)$$

EXCHANGE BETWEEN EXCITED TRIPLET STATES

XBL 78I-4443

Fig. 2. Model system for treating exchange between triplet states. State T is observed experimentally and has a resonance frequency ω_0 and an average phosphorescence decay rate k_A . T' has a different Larmor frequency $\omega_0 + \delta\omega$ but the same molecular spin axes.

$$\left(\frac{dr_3}{dt}\right)_{\text{ex}} = \left(\frac{dr_3}{dt}\right) + \frac{r_3'}{\tau} - W_+ r_3 \quad (29c)$$

where (dr_1/dt) are given by Eqs. (27). Since we will be dealing exclusively in the rotating frame, all the asterisks used in Chapter I to denote "rotating frame" will be dropped. These equations account for the transfer of r_1 component to T' at the rate W_+ and the back-transfer of r_1' component from T' at the rate τ^{-1} . Equations similar to Eqs. (29) can be written for the components $(dr_1'/dt)_{\text{ex}}$ associated with T' ; one only has to change the signs of the terms r_1'/τ and $W_+ r_1$ to describe transfer into T at a rate τ^{-1} and depletion of T at a rate W_+ .

These two sets of coupled Bloch-type equations become much simpler to solve if we make the following assumptions:⁵⁴

- i) The frequency difference $\delta\omega$ between the two levels coupled by the applied field is much larger than the strength of the applied field H_1 :

$$\delta\omega \gg \omega_1.$$

- ii) The applied field is on-resonance with the $|x\rangle \leftrightarrow |y\rangle$ transition in state T . Thus, the field component Ω_3 [see Eq. (26c)] for T is zero, since $\Delta\omega = 0$, and the field component Ω_3' for T' is

$$\Omega_3' = (\Delta\omega)' = \Delta\omega + \delta\omega = \delta\omega.$$

The applied field does not perturb T' because of assumption i) and hence when a coherently driven excitation in T is transferred to T' , it loses phase coherence with respect to T at a rate determined by $\delta\omega$ and the strength of any relaxation processes perturbing T and T' .

In the absence of T_1 and T_2 processes, the simplified sets of Bloch equations are written as follows:

$$\left(\frac{dr_1}{dt}\right)_{\text{ex}} = \omega_1 r_3 + \frac{r_1'}{\tau} - W_+ r_1 \quad (31a)$$

$$\left(\frac{dr_2}{dt}\right)_{\text{ex}} = \frac{r_2'}{\tau} - W_+ r_2 \quad (31b)$$

$$\left(\frac{dr_3}{dt}\right)_{\text{ex}} = -\omega_1 r_1 + \frac{r_3'}{\tau} - W_+ r_3 \quad (31c)$$

$$\left(\frac{dr_1'}{dt}\right)_{\text{ex}} = -\delta\omega r_2' - \frac{r_1'}{\tau} + W_+ r_1 \quad (32a)$$

$$\left(\frac{dr_2'}{dt}\right)_{\text{ex}} = \delta\omega r_1' - \frac{r_2'}{\tau} + W_+ r_2 \quad (32b)$$

$$\left(\frac{dr_3'}{dt}\right)_{\text{ex}} = -\frac{r_3'}{\tau} + W_+ r_3 \quad (32c)$$

Because one monitors the lower state T in an experiment, it is desirable to eliminate the r_1' terms in Eqs. (31). This is best done by using Laplace transformations, and yields, for $t > \tau$:

$$r_1' = \left[\frac{W_+ \tau}{1 + (\delta\omega \tau)^2} \right] (r_1 - \delta\omega \tau r_2) \quad (33a)$$

$$r_2' = \left[\frac{W_+ \tau}{1 + (\delta\omega \tau)^2} \right] (r_2 + \delta\omega \tau r_1) \quad (33b)$$

$$r_3' = W_+ \tau r_3 \quad (33c)$$

The assumption that $t > \tau$ is physically equivalent to letting the lifetime in T' be shorter than $(\omega_1)^{-1}$, where $\omega_1 = \gamma H_1$, the applied field strength.

When an excitation is transferred from T to T', the time τ spent in T' is so short that the r_i components of T do not change appreciably. Because typical driving field strengths are on the order of MHz (angular frequency units), Eqs. (33) are valid only for $\tau \leq 10^{-7}$ seconds.

Substitution of Eqs. (33) into Eqs. (31) leads to the final result for the time dependence of $\underline{r}$ in state T:

$$\frac{dr_1}{dt} = \omega_1 r_3 - \left[\frac{W_+ \delta\omega\tau}{1 + (\delta\omega\tau)^2} \right] r_2 - \left[\frac{W_+ (\delta\omega\tau)^2}{1 + (\delta\omega\tau)^2} \right] r_1 \quad (34a)$$

$$\frac{dr_2}{dt} = \left[\frac{W_+ \delta\omega\tau}{1 + (\delta\omega\tau)^2} \right] r_1 - \left[\frac{W_+ (\delta\omega\tau)^2}{1 + (\delta\omega\tau)^2} \right] r_2 \quad (34b)$$

$$\frac{dr_3}{dt} = -\omega_1 r_1 \quad (34c)$$

Comparison of Eqs. (34) with the unmodified Bloch equations [Eqs. (27)] reveals that the presence of an exchanging state T' introduces effective relaxation and frequency shift terms for the state T. We identify terms with coefficients $W_+ (\delta\omega\tau)^2 / 1 + (\delta\omega\tau)^2$ as relaxation terms corresponding to a loss of phase coherence due to exchange. If one now includes T_2 processes and excited state lifetime effects (recalling that both T and T' are triplet states), one can write

$$k_{\text{eff}} = k_A + \frac{1}{T_2} + \frac{W_+ (\delta\omega\tau)^2}{1 + (\delta\omega\tau)^2} \quad (35)$$

where $k_A = \frac{1}{2}(k_x + k_y)$, the average decay rate of the two sublevels coupled in system T. As will be discussed later, k_{eff} is the decay rate one observes in a spin locking experiment on state T, representing the loss

of coherence due to all the above processes.

One can also identify the terms with coefficients $W_+ \delta\omega\tau / 1 + (\delta\omega\tau)^2$ with frequency shift terms. For the more general case where H_1 is not necessarily on-resonance with the $|x\rangle \leftrightarrow |y\rangle$ transition in T, one can write

$$\Delta\omega_{\text{eff}} = \Delta\omega + \frac{W_+ \delta\omega\tau}{1 + (\delta\omega\tau)^2} \quad (36)$$

The frequency shift arises from the time-weighted average frequency that the spins experience in state T with frequency ω_0 and in state T' with frequency $\omega_0 + \delta\omega$. When a spin is promoted to T', it is off-resonance from the driving field by $\delta\omega$ and is dephased by the amount $\delta\omega\tau$. Since the approximation $\tau < (\omega_1)^{-1}$ has been made, the spin returns to T in a time short compared with the nutation of $\underline{r}$ about H_1 and the loss of coherence $\delta\omega\tau$ contributes directly to the coherent components of $\underline{r}$. The relative size of $\delta\omega\tau$ is directly related to what is known as spin memory, or the ability of the spins to retain the coherent information (off-diagonal density matrix elements) during the time spent out of state T.

It is very useful to examine the limiting cases for $\Delta\omega_{\text{eff}}$ and k_{eff} :

1. Slow Exchange: $\delta\omega\tau \gg 1$

The condition $\delta\omega\tau \gg 1$ is termed the slow exchange limit in which essentially all spin memory is lost during an exchange event from T to T'. Clearly, $\delta\omega$ and/or τ have to be large for this limiting case. Examining the effective decay rate and frequency shift shows that

$$\lim_{\delta\omega\tau \rightarrow \infty} k_{\text{eff}} = k_A + \frac{1}{T_2} + W_+ \quad (37a)$$

$$\lim_{\delta\omega\tau \rightarrow \infty} \Delta\omega_{\text{eff}} = \Delta\omega \quad (37b)$$

No frequency shift is observed in this limit and therefore the resonance frequency of T' is never "mixed" with the resonance frequency of T. Physically, $\delta\omega$ is so large that the spins dephase completely and return to T with no coherent information whatsoever. In the case that $\Delta\omega = 0$, $\Delta\omega_{\text{eff}} = 0$ in the slow exchange limit and one observes the same resonance frequency ω_0 in a CW absorption experiment regardless of the presence of state T'.

However, since the coherence is not back-transferred to T, k_{eff} is affected considerably and becomes the direct sum of k_A and the exchange rate from T to T', W_+ , in the limit that T_2 approaches ∞ . Even though CW spectra cannot be used to measure exchange processes if $\delta\omega\tau \gg 1$, a time-resolved coherence experiment such as spin locking can extract W_+ directly, provided that k_A is known from a separate measurement. The exchange process looks like an irreversible decay channel no different from radiative or non-radiative decay since no spin memory is involved.

A particularly noteworthy feature of the above development occurs when T and T' are in Boltzmann equilibrium. In this case, it is valid to write

$$W_+\tau = \exp(-E_1/k_B T) \quad (38)$$

where k_B is Boltzmann's constant. Assuming that k_A is obtained by measuring the phosphorescence lifetimes²⁰ and W_+ is known from a coherence experiment, the lifetime of the excitation in T' can be found. This is a quantity difficult to measure by other methods, since conventional monitoring of the phosphorescence decay of T' yields a combination of decay to both T and the ground singlet state.

2. Fast Exchange: $\delta\omega\tau \ll 1$

In the limit that $\delta\omega\tau \ll 1$, the spin system conserves spin memory upon exchange from T to T' and back again to T. This condition is termed fast exchange, because small values for τ (and/or $\delta\omega$) lead to $\delta\omega\tau \ll 1$. Again, we evaluate k_{eff} and $\Delta\omega_{\text{eff}}$ to obtain

$$\lim_{\delta\omega\tau \rightarrow 0} k_{\text{eff}} = k_A + \frac{1}{T_2} + W_+(\delta\omega\tau)^2 \quad (39a)$$

$$\lim_{\delta\omega\tau \rightarrow 0} \Delta\omega_{\text{eff}} = \Delta\omega + W_+\delta\omega\tau. \quad (39b)$$

The frequency shift is observable in the fast exchange limit and is proportional to the difference in resonance frequencies of the two states times the factor $W_+\tau$ which is related to the fraction of time the excitation is off-resonance from the driving field H_1 while in state T'. The resonance frequency of T one would observe in a CW absorption spectrum would be shifted towards the resonance frequency of T' by the amount $W_+\delta\omega\tau$. Because little spin memory is lost during the exchange, it takes many exchange events to lose coherence. The spins therefore spend a considerable amount of time in T' and this causes an averaging of the two resonance frequencies.

It is more difficult to detect the change in k_{eff} for rapid exchange, especially as $\delta\omega\tau$ becomes vanishingly small. Neglecting T_2 processes, the decay rate is increased over the excited state-ground state decay rate by the factor $W_+(\delta\omega\tau)^2$ which approaches zero rapidly due to the quadratic dependence on $\delta\omega\tau$. When the spin is transferred from T to T', the coherent components do not dephase appreciably since T and T' have nearly the same resonance frequency or because τ is very short compared to $(\omega_1)^{-1}$.

The spin returns to T in phase, preserving the coherent components, and does not contribute to k_{eff} .

C. Spin Locking

The spin locking technique provides a useful way to measure W_+ [Eq. (37a)] without being affected by any T_2 processes which could possibly dephase the spins before an exchange event. The theoretical foundation for spin locking was proposed in 1955 by Redfield,⁴² who recognized that in the presence of strong H_1 fields, the nuclear T_2 time was increased by orders of magnitude. Redfield explained the anomalously long T_2 times (not predicted by the Bloch equations with relaxation to static fields only) by invoking the second law of thermodynamics. If $H_1 > \delta H$, the local fields of the spins responsible for dephasing, then an irreversible T_2 process corresponds to a decrease in the spin entropy, a violation of the second law. The spin system is incapable of accepting the entire energy of the spin alignment and thus the transverse decay is partially forbidden. Redfield replaced T_2 by T_{2e} in the equation of motion describing the component of the magnetization parallel to the applied field, as in Eq. (27b). Transformation from the single rotating coordinate system to a double rotating reference frame aligns the effective driving field H_{eff} with the z axis (r_3 axis in the FVH picture) of the new coordinate system. Relaxation along z (T_{2e} in the single rotating frame) looks like a longitudinal relaxation process and is called $T_{1\rho}$ in the double rotating frame. If the H_{eff} field is along the y axis in the single rotating frame (r_2), then T_{2e} in Eq. (27b) and $T_{1\rho}$

are equivalent. Because the spins are oriented along H_{eff} and decay in a time $T_{1\rho} > T_2$, Redfield termed this condition rotary saturation (subsequently amended to spin locking).

The transition from Redfield's work in NMR to ESESC involves replacing the real coordinate system with the FVH picture, a straightforward procedure. The only other modification, not previously discussed, concerns the spin temperature⁵⁵ θ_s of the two level system prior to the application of H_1 . In NMR, the spin temperature is either equal to the lattice temperature θ_L (including T_1 processes which equilibrate the two temperatures) or is infinite (the two levels are saturated if no T_1 processes are present). However, in zero-field ODMR, the steady-state triplet sublevel populations are determined by intersystem crossing matrix elements and are generally *not* describable by a spin temperature. Neglecting the third sublevel not coupled by the applied field, one can always describe the remaining two levels by a spin temperature and associate a "pseudo-dc" field $(H_0)_{\text{eff}}$ with the populations. Following Redfield's argument, the spin temperature at rotary saturation is initially

$$\theta_s(0) = \theta_L \frac{H_1}{(H_0)_{\text{eff}}} \quad (40)$$

and warms up to a temperature

$$\theta_s(t) = \theta_s(0) e^{t/T_{1\rho}} \quad (41)$$

Because the spins change temperature via spin-lattice relaxation, the time constant for this process is analogous to a T_1 process in the rotating frame and is called $T_{1\rho}$. We can incorporate $T_{1\rho}$ processes into the effective decay rate equations by substituting $T_{1\rho}^{-1}$ in Eqs. (35),

(37a), and (39a) for T_2^{-1} .

Rotary saturation decouples the spins from the surrounding spins (local fields) to a high degree, provided that $H_1 > \delta H$. The only processes which do *not* involve relaxation against H_{eff} and which *do* contribute to k_{eff} are those for which $H_1 < \delta H$; exchange processes and phosphorescence decay constitute such processes. The change in local field must be large compared to the applied field strength; the spin must change its environment by an amount larger than the inhomogeneous linewidth (comparable to $\gamma H_1 = \omega_1$) in order to cause a loss of coherence. Referring back to Section B of this chapter, the assumption that $\delta\omega \gg \omega_1$ [Eq. (30)] is the same as the requirement for the loss of coherence in spin locking. Exchange to T' will affect the spin locked decay of T if T' has a substantially different resonance frequency. This is easily satisfied by the |D-E| transition in cyclopentanone, for which $\omega_1 \sim 5$ MHz, FWHM ~ 4.5 MHz, and $\delta\omega = (3394 - 3189)$ MHz = 205 MHz.

The spin locking experiment is the same as originally proposed by Solomon⁷ and is presented schematically in Fig. 3. The preparation of the spin locked state consists of an initial $\pi/2$ pulse which coherently saturates the two levels. Because the time scale of the experiment is much longer than $(\omega_1)^{-1}$, it is assumed that the $\pi/2$ pulse is a δ -function. Spin locking is accomplished by phase shifting the applied field by 90° so that the coherent component is parallel to $H_{\text{eff}} = H_1$ (on-resonance). The spin locking field is maintained for a time τ_{SL} after which a second $\pi/2$ pulse of 0° phase is applied to rotate the remaining coherent component into a population difference. The final $\pi/2$ pulse, or probe pulse, is required for optical detection and is again assumed to be a δ -function.

Fig. 3. A) Schematic of spin locking in the FVH representation with incoherent feeding to only one sublevel. (a) $r_1(0) = r_2(0) = 0$ before H_1 is turned "on"; (b) H_1 along the r_2 axis rotates $\underline{r}$ by $\pi/2$ onto the r_1 axis; (b') 90° phase shifted H_1 locks $\underline{r}$ along the r_1 axis; the partial disk in the r_2 - r_3 plane represents population entering the triplet state after the initial $\pi/2$ pulse; (c) k_{eff}^{-1} decay events result in a shrinking $\underline{r}$ -vector; the double-headed arrow indicates relaxation against the applied field ($T_{1\rho}$ processes); (d) final $\pi/2$ probe pulse rotates $\underline{r}$ onto the $-r_3$ axis and the complete disk into the r_1 - r_2 plane.

B) Laboratory frame diagram of population in the triplet sublevels at each stage of the spin locking experiment. The black balls represent population present at time $t = 0$ which contribute to the size of $\underline{r}$; the white balls represent population entering after $t = 0$ and appear as the incoherent disk in part A.

C) Microwave pulse sequence for spin locking.

D) Hypothetical change in phosphorescence intensity observed experimentally at each point of the pulse sequence. The change in signal at point d (final $\pi/2$ pulse) represents the coherence remaining after τ_{SL} . ΔI as a function of τ_{SL} yields the total relaxation rate k_{eff}^{-1} .

OPTICALLY DETECTED SPIN LOCKING IN THE PRESENCE OF FLUCTUATING SPIN SUBLEVEL POPULATIONS

(The Relationship between the Laboratory Frame and the Interaction Representation)

XBL 7311-5594B

Figure 3

Conventional cavity detection would instead monitor the strength of the free induction decay signal which starts when the spin locking field is non-adiabatically⁸ turned off.

An additional feature of spin locking which makes it especially suited to study excited states is that the population which enters into the state during the pulse sequence has no effect on the decay time k_{eff}^{-1} . The entering population appears as new vectors along the r_3 axis and is driven in a plane perpendicular to the spin locking field. After a time greater than the inverses of the "feeding" rates of the sublevels, the incoherently distributed population has formed a disk in the r_1 - r_3 plane whose net vector sum is zero. The final $\pi/2$ probe pulse rotates the disk into the r_1 - r_2 plane where it cannot contribute to the optically detected signal. This is also shown in Fig. 3, parts A and B.

Finally, we can use the formalism of Chapter I to show that the spins are indeed locked along H_1 during the 90° phase shifted part of the pulse sequence. Starting with a density matrix $\rho(0)$, the final value for $\rho(\tau_{\text{SL}})$ is given by

$$\begin{aligned} \rho(\tau_{\text{SL}}) &= [S(\pi/2, 0^\circ) S(\omega_1 \tau_{\text{SL}}, 90^\circ) S(\pi/2, 0^\circ)] \times \rho(0) \\ &\times [S^{-1}(\pi/2, 0^\circ) S^{-1}(\omega_1 \tau_{\text{SL}}, 90^\circ) S^{-1}(\pi/2, 0^\circ)] \end{aligned} \quad (42)$$

in the absence of relaxation. We will now calculate ρ at each stage of the pulse sequence and decompose it to yield the components of $\underline{r}$.

Assuming $r_1(0) = r_2(0) = 0$, $\rho(0)$ is given by

$$\rho(0) = \frac{1}{2} \begin{bmatrix} 1 + r_3 & 0 \\ 0 & 1 - r_3 \end{bmatrix}. \quad (43)$$

The initial $\pi/2$ pulse rotates $\underline{r}$ from the r_3 axis to the r_1 axis if $\Delta\omega = 0$:

$$\rho(0^+) = \frac{1}{2} \begin{bmatrix} 1 & -r_3 \\ -r_3 & 1 \end{bmatrix}. \quad (44)$$

The + superscript in Eq. (44) refers to the δ -function width of the $\pi/2$ pulse. Comparing Eq. (44) with Eq. (6) clearly shows that the spin system is saturated since $r_3(0^+) = 0$ and $r_1(0^+) = -r_3(0)$. The spin locking pulse operators applied to $\rho(0^+)$ do not alter the form of Eq. (44).

Thus, in the absence of relaxation, the components of $\underline{r}$ do not change for as long as H_1 ($\phi = 90^\circ$) is turned on. We can heuristically account for relaxation during the spin locking pulse by damping the r_1 component at a rate k_{eff} as given by Eq. (35) with $T_{1\rho}^{-1}$ replacing T_2^{-1} :

$$\rho(\tau_{\text{SL}}^-) = \frac{1}{2} \begin{bmatrix} 1 & -r_3 \exp(-k_{\text{eff}} \tau_{\text{SL}}^-) \\ -r_3 \exp(-k_{\text{eff}} \tau_{\text{SL}}^-) & 1 \end{bmatrix}. \quad (45)$$

Again, the - superscript indicates that Eq. (45) describes the system just prior to the probe pulse. Applying the final 0° -phase $\pi/2$ pulse operators to $\rho(\tau_{\text{SL}}^-)$ rotates $\underline{r}$ from the r_1 axis down to the negative r_3 axis:

$$\rho(\tau_{\text{SL}}) = \frac{1}{2} \begin{bmatrix} 1 - r_3 \exp(-k_{\text{eff}} \tau_{\text{SL}}) & 0 \\ 0 & 1 + r_3 \exp(-k_{\text{eff}} \tau_{\text{SL}}) \end{bmatrix}. \quad (46)$$

The final change in phosphorescence (ΔI in Fig. 3D) is proportional to

the difference in the diagonal terms in Eq. (46), $r_3 \exp(-k_{\text{eff}} \tau_{\text{SL}})$, and yields k_{eff} when ΔI is measured for increasing values of τ_{SL} .

D. Experimental Procedure

MC & B reagent grade cyclopentanone (m.p. $\sim 222\text{K}$) was washed with reagent grade H_2SO_4 , rinsed with H_2O , and dried over Na_2SO_4 . After repeated vacuum distillations, a small amount was sealed under vacuum in a quartz ampoule designed to fit into a slow-wave helix.⁵⁶ Sample purity was confirmed by low resolution mass spectroscopy. The ampoules were cooled fairly quickly to cryogenic temperatures, resulting in polycrystalline cyclopentanone.

Phosphorescence spectra were recorded with a 3/4-meter medium-resolution Jarrell-Ash Czerny-Turner monochromator, the emission detected at a right angle to the exciting light (100 watt high-pressure Osram Hg arc lamp). Cyclopentanone exhibits a very broad emission extending from roughly $3600 \text{ \AA}$ to well into the visible region ($5500 \text{ \AA}$) and peaked at approximately $4300 \text{ \AA}$. All experiments were therefore conducted with the monochromator set at $4300 \text{ \AA}$ and with the slits open wide enough to get maximum phosphorescence intensity without saturating the cooled photomultiplier (EMI 6256S).

Microwave experiments were done using the apparatus illustrated in Fig. 4. For CW experiments, the microwaves (15 - 30 mW) were amplitude modulated either by the sweeper itself (HP 8690B with HP plug-ins) or by high-speed PIN diodes (HP 33124A) capable of providing at least 60 dB isolation. Sweep linearity was ensured by externally driving the sweeper

OPTICALLY DETECTED MAGNETIC RESONANCE PULSE SPECTROMETER

XBL743-5724

Fig. 4. Block diagram of pulsed ODMR spectrometer used for spin locking (Chapter II) and rotary echoes (Chapter III). A four-channel arrangement is shown, although only two channels, one for $\phi = 0^\circ$ and the other for $\phi = 90^\circ$ or 180° , were used in this work.

with a digitally stepped voltage ramp. The output of the photomultiplier was phase-sensitive detected with a PAR HR-8 lock-in amplifier and fed into an X-Y recorder (HP 7004B).

ESESC experiments demand considerably higher power than CW experiments; large field strengths were obtained by amplifying the microwaves with a 20 watt Varian TWT inserted in the microwave line after the two channels are recombined.

The experimental procedure for spin locking requires a measurement of γH_1 and adjustment of a delay line to set $\phi = 90^\circ$. The field strength was found by a transient nutation experiment in which a single pulse is stroboscopically applied to the crystal and slowly lengthened in time. The resulting signal was fed into a lock-in amplifier referenced to the strobe frequency. The maximum change in emission corresponds to a π pulse and hence determines the pulse time needed for a $\pi/2$ pulse. The length of the $\pi/2$ pulse ($\sim 50 - 75$ nsec) was minimized by adjusting a "trombone" impedance matching device, helping to ensure that γH_1 was as large as possible. The phases were set by adjusting the pathlengths of two microwave channels with 10 cm General Radio 874-LK10L constant impedance adjustable lines. Maximum spin locking signals occur when $\phi = 90^\circ$ and this criterion was used to fix ϕ .

Optical detection of spin locking was accomplished by feeding the photomultiplier output into a Tracor Northern 575 transient averaging computer, pretriggered by the strobe pulse (~ 12 Hz) to provide a steady-state phosphorescence baseline.

Temperatures below 4.2K were achieved by pumping on the liquid He bath and were stabilized to within ± 0.05 K by a Computer Optimized Non-

Digital Overdrive Mechanism (PNT 223/4). Precise temperature readings were measured by monitoring the resistance of a calibrated resistor with a Keithley nanowatt dissipation resistance bridge (Model 520).

E. Results and Discussion

The results of the spin locking of the lowest triplet state of cyclopentanone can be understood as follows. Within experimental error, the observed k_{eff}^{-1} appears to be temperature independent from 1.4K to 4.2K. This is what one would expect from the simple quantum mechanical treatment of tunneling between configurations of the same energy. If there were an energy separation E_i between two of the configurations however, a phonon would either be emitted or absorbed in the exchange process to conserve energy and the tunneling would show an exponential temperature dependence since the number of phonons present with energy E_i is proportional to $\exp(-E_i/k_B T)$ at low temperatures.

Figure 5 shows the data for one temperature (1.85K); the lifetime of the coherently coupled $|z\rangle \leftrightarrow |y\rangle$ transition was measured to be ~ 3.03 msec. Figure 6 presents k_{eff}^{-1} as a function of temperature; a least squares fit of the spin locking data to an exponential does not yield any reliable temperature effect or dependence. Equation (35) shows that k_A represents a lower limit for k_{eff} and that any exchange or relaxation processes are reflected in a value for k_{eff} greater than the lifetime limit k_A . Shain and Sharnoff have measured k_A for the $|z\rangle \leftrightarrow |y\rangle$ ($|D-E\rangle$) transition to be 402 sec^{-1} , which sets an upper limit of 2.5 msec for the value of k_{eff}^{-1} . We see from Fig. 6 that all values of k_{eff}^{-1} were found to lie between 2.5 msec and 3.5 msec (3.02 ± 0.28 msec). Since the observed k_{eff}^{-1} is

Fig. 5. Decay of the spin locked $|D-E|$ ($|z\rangle \leftrightarrow |y\rangle$) transition of cyclopentanone. The vertical axis is in arbitrary units, normalized to the initial change in phosphorescence due to the first $\pi/2$ pulse, ΔI_0 .

Fig. 6. Temperature dependence of k_{eff}^{-1} for the $|D-E|$ transition in cyclopentanone. The shaded region represents the upper limit for the lifetime of the spin locked state, based on previously determined sublevel phosphorescence lifetimes. The average k_{eff}^{-1} was found to be 3.02 ± 0.28 msec.

essentially the average phosphorescence lifetime of the triplet sublevels, $k_{\text{eff}} \approx k_A$. This eliminates slow exchange as a mechanism unless $W_+ \ll k_A$.

One cannot yet rule out rapid tunneling between configurations of the same energy on the basis of the spin locking results alone. Because k_{eff} approaches $k_A + (T_{1\rho})^{-1} + W_+(\delta\omega\tau)^2$ in the limit that $\delta\omega\tau \ll 1$, it becomes increasingly difficult to detect a difference between k_{eff} and k_A the smaller $\delta\omega\tau$ becomes. For example, if $W_+(\delta\omega\tau)^2$ is less than 10% of k_A , the spin locking technique cannot extract a reliable value for the exchange rate. One can estimate a value for τ such that this condition is met by noting that for tunneling between isoenergetic states ($E_i = 0$), $W_+\tau = 1$. Equation (39a) in the rapid exchange limit then reduces to

$$k_{\text{eff}} = k_A + (T_{1\rho})^{-1} + \tau(\delta\omega)^2 \quad (47)$$

Substituting in 402 sec^{-1} for k_A , $2.05 \times 10^8 \text{ sec}^{-1}$ for $\delta\omega$, and 0 for $(T_{1\rho})^{-1}$, we see that τ would have to be 10^{-15} sec for rapid exchange to be unobservable. The fact that one can resolve the various ESR resonances in the MHz region is completely inconsistent with a lifetime τ being shorter than $10^{-7} - 10^{-8} \text{ sec}$.

As further evidence that tunneling does not occur on a rapid time scale with any temperature dependence between 1.4K and 4.2K, the results of CW spectra of the $|D-E|$ transition are shown in Fig. 7. Within the limits of the frequency stability of the microwave sweeper (roughly 0.01% of the frequency), no frequency shift is present. Rewriting Eq. (36) for the equienergetic case ($W_+\tau = 1$) and expanding, we obtain

$$\Delta\omega_{\text{eff}} \approx \delta\omega - (\delta\omega)^2\tau + \dots \quad (48)$$

If τ were 10^{-15} sec , as required by the rapid exchange case for which

Fig. 7. Temperature dependence of the |D-E| transition in cyclopentanone. The average resonance frequency is 3394.44 ± 0.36 MHz.

frequency shifts are observable, $\Delta\omega_{\text{eff}} \sim \delta\omega \sim 205 \text{ MHz}$ and the ESR lines would coalesce. For $\tau > 10^{-9} \text{ sec}$, the frequency shift would be too small to be observed with the spectrometer used in these experiments.

The CW experiments in this case set an upper limit on the rate W_+ which is essentially that obtained from experimentally resolving the triads, approximately 10^7 sec^{-1} . Spin locking rules out fast exchange as a mechanism, since τ would have to be shorter than 10^{-15} sec to explain the lifetime limit found for the spin locked state. For $\tau > 10^{-7} \text{ sec}$, the slow exchange limit applies and W_+ must be less than 10% of k_A so that $k_{\text{eff}} \sim k_A$. Therefore, $W_+^{-1} = \tau \geq 25 \text{ msec}$, an order of magnitude longer than the triplet state lifetime of cyclopentanone. This value of W_+ is the only one which is consistent with all of the above data and the predictions of exchange theory. We conclude that if tunneling does occur in cyclopentanone as claimed by Sharnoff et al., the tunneling rate is so slow that, on the average, an excited cyclopentanone molecule decays to the ground state before it can tunnel to a different configuration.

CHAPTER III

ROTARY ECHOES IN EXCITED TRIPLET STATES

In this chapter we will examine another ESESC technique designed to measure T_2 processes, the rotary echo. Average Hamiltonian theory, developed by Waugh and co-workers, will be applied to the rotary echo, both on- and off-resonance. The results allow for a quantitative description of the echo phenomenon and also clearly differentiate the rotary echo from several other ESESC experiments. The next section of the chapter will present expressions for the off-resonance echo intensity, including population feeding and decay and inhomogeneous line broadening. Finally, experimental details are described in the last part of Chapter III.

A. The Rotary Echo

With the exception of the transient nutation, the rotary echo is the simplest of the cyclic pulse techniques. Designed by Solomon⁶ to eliminate applied field (H_1) inhomogeneities, the pulse sequence consists of two equally long pulses phase shifted with respect to each other by 180° . No probe pulse is required, in contrast to other ESESC experiments, because the echo itself is a constructive interference of the spin alignments of an ensemble of two-level spin systems. In FVH representation, the H_1 field is applied along the r_2 axis so that for the on-resonance case, the pseudo-magnetization $\underline{r}$ is confined to the r_1 - r_3 plane and the echo rephases along the r_3 axis. Schematic representations of the rotary echo in both the rotating and laboratory frames are shown in Fig. 8. The inhomogeneous

ON-RESONANCE ROTARY ECHO ROTATING AND LABORATORY FRAME REPRESENTATIONS

XBL 7711-6491

Fig. 8. Schematic representation of a rotary echo in the rotating (FVH) frame and laboratory frame. No relaxation processes are included, but inhomogeneities in H_1 cause a loss of coherence, as indicated by the "fanning out" of $\underline{r}$. The 180° pulse reverses the dephasing and collapses the fan at time 2τ . T_{2p} processes would manifest themselves as a three-dimensional solid in r -space whose r_3 component at 2τ is smaller than $r_3(0)$.

H_1 field causes the $\underline{r}$ -vectors associated with a *single* resonance frequency (δ -function line) to fan out in the r_1 - r_2 plane, since different $\underline{r}$ -vectors in the sample experience varying applied field strengths and nutate through a range of angles $\theta = \omega_1 t$ determined by the maximum and minimum values of H_1 . The maximum angular spread of the fan is reached at time $t = \tau$, when the phases are shifted. The 180° phase field reverses the direction of the $\underline{r}$ -vectors, causing the fan to shrink and the echo to form at $t = 2\tau$. The rotary echo is basically a pair of back-to-back transient nutations, much the same as a spin echo consists of back-to-back free induction decays. However, the spin echo requires a $\pi/2$ preparation pulse to coherently saturate the system and to allow the $\underline{r}$ -vectors to dephase in the absence of an H_1 field; the rotary echo uses neither a preparation nor a probe pulse since the r -vector is continuously sampling the r_1 - r_2 plane and the r_3 axis.

The decay time which characterizes both the transient nutation and rotary echo is known as T_{2p} in the literature, although it would be more suitable to characterize a transient nutation by T_{2p}^* and a rotary echo by T_{2p} . This distinction, in analogy to T_2^* and T_2 associated with free induction decays and spin echoes respectively, refers to the increase in the decay time obtained by removing applied field inhomogeneities. An analytical expression for T_{2p}^* would depend explicitly on knowledge of field distributions in the slow-wave helix, f -values of the transition, orientation of the molecules with respect to the field, and other parameters, and is generally incalculable. However, it is fairly simple to relate T_{2p} to the phenomenological Bloch relaxation times of Eqs. (27). This is done by applying the Laplace transform technique to the Bloch-type equations,

as initially carried out by Torrey.³ With initial values $r_1(0) = r_2(0) = 0$ and $r_3(0) = r_3^0$ and for the on-resonance case

$$r_1(t) = r_3^0 \omega_1 \left(1 + \frac{1}{T_1}\right) e^{-\frac{1}{2}\left(\frac{1}{T_1} + \frac{1}{T_2}\right)t} \frac{\sin \alpha t}{\alpha} \quad (49a)$$

$$r_2(t) = 0 \quad (49b)$$

$$r_3(t) = r_3^0 \left(1 + \frac{1}{T_1}\right) e^{-\frac{1}{2}\left(\frac{1}{T_1} + \frac{1}{T_2}\right)t} \left\{ \left[\frac{1}{T_2} + \frac{1}{2} \left(\frac{1}{T_1} + \frac{1}{T_2} \right) \right] \frac{\sin \alpha t}{\alpha} - \cos \alpha t \right\} \quad (49c)$$

where

$$\alpha = \sqrt{\omega_1^2 - \frac{1}{4} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)^2}.$$

These equations describe the damped oscillatory motion of the r_1 and r_3 components. One can effectively remove the oscillations by observing the nutation at the oscillation frequency α , in which case the value of r_3 (the observable) is seen to decay at a rate

$$T_{2\rho}^{-1} \equiv \frac{1}{2} \left(\frac{1}{T_1} + \frac{1}{T_2} \right). \quad (50)$$

The average relaxation rate in Eq. (50) reflects the fact that $\underline{r}$ spends an equal amount of time along both the r_3 and r_1 axes and is affected by T_1 and T_2 processes alternately as it describes a disk in r -space.

If as before, we neglect T_1 processes at low temperatures, Eqs. (49) reduce to

$$r_1(t) = r_3^0 \omega_1 e^{-t/2T_2} \frac{\sin \beta t}{\beta} \quad (51a)$$

$$r_2(t) = 0 \quad (51b)$$

$$r_3(t) = r_3^0 e^{-t/2T_2} \left\{ \frac{3}{2T_2} \frac{\sin \beta t}{\beta} - \cos \beta t \right\} \quad (51c)$$

where
$$\beta = \sqrt{\omega_1^2 - \frac{1}{4T_2^2}}$$

In this limit, the transient nutation/rotary echo decays with relaxation time $2T_2 = T_{20}$, where T_2 is the relaxation time measured by a spin echo in the absence of spin diffusion. It will be shown later in this chapter that inhomogeneous broadening affects rotary echo decays very strongly so that T_{20} depends on T_2^* as well as T_2 .

B. Average Hamiltonian Theory

A detailed account of Average Hamiltonian theory is beyond the scope of this thesis. The original papers are listed as Refs. 10 and 11 and a very complete discussion is given by Haeberlen in Advances in Magnetic Resonance.⁵⁷ What follows is a brief derivation of the main result of the theory, which serves as the starting point for the work on rotary echoes.

We consider a spin system characterized by a static internal Hamiltonian $\mathcal{H}$ whose "size" in angular frequency units $|\mathcal{H}|$ determines the resonance line-width T_2^{-1} . A time dependence can be introduced to the system by applying an ideal δ -function pulse which is represented by a rotation operator S_1 . The system can then evolve for a time t_1 , after which another pulse S_2 is applied, followed by a second field-free interval t_2 and so on. After n

such pulses and waiting periods, the system is in a state

$$|t_0 + \sum_{k=1}^n t_k\rangle = \left\{ \prod_{k=1}^n [\exp(-i\mathcal{H}t_k)S_k] \right\} |t_0\rangle, \quad (52)$$

where $|t_0\rangle$ is the initial state and the product is time-ordered so that the indices increase towards the left. One can now rewrite Eq. (52) to give

$$|t_0 + \sum_{k=1}^n t_k\rangle = \left\{ \prod_{k=1}^n \exp(-i\mathcal{H}_k^c t_k) \right\} \left\{ \prod_{m=1}^n S_m \right\} |t_0\rangle, \quad (53)$$

where

$$\mathcal{H}_k^c = \left(\prod_{\ell=1}^k S_{\ell} \right) \mathcal{H} \left(\prod_{\ell=1}^k S_{\ell} \right)^{-1}. \quad (54)$$

We now impose the requirement that the pulse sequence be cyclic and periodic with period less than or equal to the cycle time t_c :

$$\prod_{m=1}^n S_m = \mathbf{1} \quad (55)$$

where $\mathbf{1}$ is the unit matrix. The cycle duration time t_c is defined by

$$\sum_{k=1}^n t_k \equiv t_c. \quad (56)$$

Thus, Eq. (53) can now be written as

$$|t_0 + t_c\rangle = \left\{ \prod_{k=1}^n \exp(-i\mathcal{H}_k^c t_k) \right\} |t_0\rangle. \quad (57)$$

If we apply the periodic sequence N times so that

$$|t_0 + Nt_c\rangle = \left\{ \prod_{k=1}^n \exp(-i\mathcal{H}_k^c t_k) \right\}^N |t_0\rangle, \quad (58)$$

the term in the curly brackets in Eq. (58) can be rewritten using the Magnus expansion and one can show that

$$\lim_{\substack{t_c/T_2 \rightarrow 0 \\ N \rightarrow \infty \\ Nt_c \rightarrow t}} \left\{ \prod_{k=1}^n \exp(-i\mathcal{H}_k t_k) \right\}^N \cong \exp(-i\bar{\mathcal{H}} N t_c) \quad , \quad (59)$$

where

$$\bar{\mathcal{H}} = \sum_{k=1}^n \mathcal{H}_k \left(\frac{t_k}{t_c} \right) \quad . \quad (60)$$

Under these conditions, particularly $t_c \ll T_2$, the system behaves as though it were under the influence of a time-independent Hamiltonian $\bar{\mathcal{H}}$. Equation (59) is the central result of the theory and defines what Waugh's group named the Average Hamiltonian. To the lowest order approximation, Eqs. (59) and (60) are valid; however, $\bar{\mathcal{H}}$ must be supplemented with higher order correction terms given by the Magnus expansion to accurately describe finite pulse widths, pulse imperfections, and different kinds of internal spin Hamiltonians.

The time evolution of the system is now conveniently written as

$$|t_0 + t\rangle \cong \exp(-i\bar{\mathcal{H}}t) |t_0\rangle \quad (61)$$

where it is implicitly understood that t is an integral multiple of t_c . The periodic nature of the pulse sequence produces periodicities in the signal, which show up as sidebands in the Fourier transformed spectrum, exactly analogous to the sidebands caused by sample spinning in NMR. If observations are made stroboscopically at the frequency determined by t_c , these periodicities are removed. This may be easily seen by the

analogy suggested by M. T. Lewellyn, in which periodic observation of averaging in spin space and pushing an elastic ball off a ledge are compared.⁵⁸ Measurement of drag forces induced by air friction are difficult to make on an inelastic ball, since they are obscured by gravity. Imposing periodicity by making the ball elastic and observing the height of the ball at the apex of each bounce effectively removes gravitational forces and makes the measurement of drag forces simpler.

Similar spatial averaging effects in NMR can be achieved by sample spinning, particularly when the sample is oriented at the "magic angle" $\theta = \arccos(1/\sqrt{3}) = 55^\circ 44'$ with respect to the static H_0 field to remove dipolar spin-spin coupling. The great advantage of spin averaging is that the form of $\bar{\mathcal{H}}$ can be controlled through the choice of pulse sequence and different interactions may be suppressed to study processes of interest.

C. Application to Triplet States

Average Hamiltonian theory was first used to examine ESESC techniques by Breiland, Brenner, and Harris (BBH),⁵⁹ and we will use their notation and conventions in what follows. The internal Hamiltonian $\mathcal{H}_i$ responsible for line broadening and used in all calculations of $\bar{\mathcal{H}}_R$ is written as a general 3x3 Hermitian matrix in the z-y-x basis for triplet states:

$$\mathcal{H}_R = \begin{bmatrix} H_{zz} & H_{zy} & H_{zx} \\ H_{yz} & H_{yy} & H_{yx} \\ H_{xz} & H_{xy} & H_{xx} \end{bmatrix} \quad (62)$$

where the subscript R indicates a relaxation Hamiltonian. $\mathcal{H}_R$ is assumed

to vary over different sites in the sample, resulting in a range of different resonance frequencies for the ESR transition of interest. We have written $\mathcal{H}_R$ as a time-independent quantity, though this is not strictly the case; however, Average Hamiltonian theory is applicable if $\mathcal{H}_R$ is static on the same time scale as the experiment. Variation of $\mathcal{H}_R$ during the cycle time is known as spin diffusion and corresponds physically to a particular spin ensemble "moving" within the broadened line by changing its resonance frequency. Spin diffusion gives rise to much shorter relaxation times than predicted for a static internal Hamiltonian and can be suppressed by spin locking, as mentioned in Chapter II.

As an example of a specific type of relaxation Hamiltonian, we consider the hyperfine interactions between the triplet electron spins and the adjacent paramagnetic nuclei, both on the same molecule as the electrons (internal) and in the bulk lattice (external). The Hamiltonian for hyperfine interactions is given by⁵⁵

$$\mathcal{H}_{HF} = \sum_i \mathbf{S} \cdot \mathbf{A}_i \cdot \mathbf{I}_i \quad (63)$$

where $\mathbf{S}$ and $\mathbf{I}_i$ are electron and nuclear operators, $\mathbf{A}_i$ is a symmetric second rank tensor, and the sum is over all nuclear spins. The internal hyperfine interaction is stronger than the external hyperfine and tends to split the resonance lines; it also does not vary from site to site, since the nuclear and electron spins are confined to the same molecule. Therefore, we do not consider the internal hyperfine interaction as a source of inhomogeneous broadening, but rather as a means of mixing the pure zero-field states of the triplet electrons. More quantitatively, if the internal hyperfine field has only a z-component, then the $|x\rangle$ and $|y\rangle$

spin states are mixed, since

$$\langle x | \mathcal{H}_{\text{HF}}^{\text{int}} | y \rangle = -iA_z^{\text{int}} \quad (64a)$$

$$\langle y | \mathcal{H}_{\text{HF}}^{\text{int}} | x \rangle = iA_z^{\text{int}} \quad (64b)$$

The new energies of the $|x\rangle$ and $|y\rangle$ levels are given by first order perturbation theory to be $X + (A_z^{\text{int}})^2 / X - Y$ and $Y - (A_z^{\text{int}})^2 / X - Y$, where X and Y are the energies of $|x\rangle$ and $|y\rangle$ in the absence of internal hyperfine interactions. The weaker external hyperfine interaction now has first-order non-zero diagonal elements in the new basis set determined by the mixing of $|x\rangle$ and $|y\rangle$. As will be shown later, non-zero diagonal elements of $\mathcal{H}_R$ are required for T_2 processes and line broadening if T_1 processes are neglected. Returning now to Eq. (62), BBH have shown that the form of $\mathcal{H}_R$ in the rotating frame is

$$\mathcal{H}_R = \begin{bmatrix} 0 & 0 & 0 \\ 0 & -\frac{2A_z^{\text{int}}}{X-Y} A_z^{\text{ext}} & 0 \\ 0 & 0 & \frac{2A_z^{\text{int}}}{X-Y} A_z^{\text{ext}} \end{bmatrix} \quad (65)$$

where non-secular terms have been neglected.

Finally, we note that the formalism of Chapter I can easily be extended to a three-level system in which only two of the levels are coupled by the field. The time evolution operator in Eq. (19) now becomes

$$S = \begin{bmatrix} \exp(-iE_z \Delta\omega t / \hbar\omega_0) & 0 & 0 \\ 0 & \cos \frac{\bar{\omega}t}{2} - \frac{i\Delta\omega}{\bar{\omega}} \sin \frac{\bar{\omega}t}{2} & \frac{\omega_1}{\bar{\omega}} e^{-i\phi} \sin \frac{\bar{\omega}t}{2} \\ 0 & -\frac{\omega_1}{\bar{\omega}} e^{i\phi} \sin \frac{\bar{\omega}t}{2} & \cos \frac{\bar{\omega}t}{2} + \frac{i\Delta\omega}{\bar{\omega}} \sin \frac{\bar{\omega}t}{2} \end{bmatrix} \quad (66)$$

where $\hbar\omega_0 = Y - X$ and $E_z = Z - \frac{1}{2}(X + Y)$. We will work with the 3×3 representation initially for the sake of completeness. However, the inclusion of the $|z\rangle$ sublevel does not affect the results and it is more convenient to work with the reduced two-level system.

D. Coherent Averaging via Rotary Echoes

It is instructive to follow through the calculation in detail for the simple on-resonance case, using the equations presented in Sections B and C of this chapter. Two methods of calculation will be worked out, one using a sequence of $\pi/2$ pulses and the other, an integral method.

1. $\pi/2$ Pulse Method

We imagine the rotary echo to be a series of $\pi/2$ pulses with zero temporal width:

$$\lim_{\substack{YH_1 \rightarrow \infty \\ t \rightarrow 0}} YH_1 t = \pi/2. \quad (67)$$

Figure 9 illustrates the entire sequence in the same manner as Waugh's school. There are $4N$ 0° -phase $\pi/2$ pulses applied along $-r_2$ and a single 0° pulse of angle θ along $-r_2$ to account for the arbitrary orientation of

XBL 781-4430

Fig. 9. $\pi/2$ pulse method of calculating $\bar{\varphi}_R$ for a rotary echo. There are $4N+1$ 0° pulses along the $-r_2$ axis followed by $4N+1$ 180° pulses along the $+r_2$ axis. The final form of $\bar{\varphi}_R$ depends only on the first eight 0° pulses, as discussed in the text.

$\underline{r}$ after a single long 0° -phase pulse. The phases are then reversed and a single 180° -phase pulse of angle θ and $4N$ 180° -phase $\pi/2$ pulses are applied along the r_2 direction. Each pulse has the same waiting period t associated with it so that the total time of the experiment is $(8N+2)t$.

The actual calculation is trivial, since Eq. (66) takes a very simple form for $\Delta\omega = 0$, $\phi = 0^\circ$ or 180° , and $\bar{\omega}t = \omega_1 t = \pi/2$. Three features emerge from the mathematics:

- i) The final θ -pulse has no effect on the form of $\bar{\mathcal{K}}_R$ and can be omitted from the sequence;
- ii) The entire 180° -phase series of pulses gives the same result as the 0° -phase series, and therefore does not contribute to the averaging;
- iii) There are eight distinct forms of $\mathcal{K}_R$, corresponding to the eight $\pi/2$ rotations needed to effect a 4π pulse. Thus, a rotation by 2π does *not* return $\mathcal{K}_R$ to its initial form.

This is a property typically associated with crystal double groups and spinors.⁶⁰

The form of $\bar{\mathcal{K}}_R$ is thus determined by a rotation of only 4π and is easily written down by directly averaging the eight relaxation matrices:

$$\bar{\mathcal{K}}_R = \frac{1}{8t} \sum_{i=1}^8 t \mathcal{K}_R \left(\frac{i\pi}{2} \right) = \begin{bmatrix} H_{zz} & 0 & 0 \\ 0 & \frac{1}{2}(H_{yy} + H_{xx}) & \frac{1}{2}(H_{yx} - H_{xy}) \\ 0 & \frac{1}{2}(H_{xy} - H_{yx}) & \frac{1}{2}(H_{yy} + H_{xx}) \end{bmatrix} \quad (68)$$

We will delay discussing the features of Eq. (68) until after the integral method is worked out.

2. Integral Method

The integral method models the true rotary echo more closely than the previous $\pi/2$ pulse method, since the field is "on" continuously and there are no waiting periods t at the end of each pulse. As opposed to calculating $\mathcal{K}_R$ after a rotation of $i\pi/2$, $\mathcal{K}_R$ is found for a general angle θ . For $\phi = \Delta\omega = 0$, we have

$$\mathcal{K}_R^{0*}(\theta) = \begin{bmatrix} H_{zz} & (H_{zy} \cos \frac{\theta}{2} + H_{zx} \sin \frac{\theta}{2}) & (H_{zx} \cos \frac{\theta}{2} - H_{zy} \sin \frac{\theta}{2}) \\ (H_{yz} \cos \frac{\theta}{2} + H_{xz} \sin \frac{\theta}{2}) & \begin{bmatrix} H_{xx} \sin^2 \frac{\theta}{2} + H_{yy} \cos^2 \frac{\theta}{2} \\ + (H_{xy} + H_{yx}) \sin \frac{\theta}{2} \cos \frac{\theta}{2} \end{bmatrix} & \begin{bmatrix} H_{yx} \cos^2 \frac{\theta}{2} - H_{xy} \sin^2 \frac{\theta}{2} \\ - (H_{yy} - H_{xx}) \sin \frac{\theta}{2} \cos \frac{\theta}{2} \end{bmatrix} \\ (H_{xz} \cos \frac{\theta}{2} - H_{yz} \sin \frac{\theta}{2}) & \begin{bmatrix} H_{xy} \cos^2 \frac{\theta}{2} - H_{yx} \sin^2 \frac{\theta}{2} \\ - (H_{yy} - H_{xx}) \sin \frac{\theta}{2} \cos \frac{\theta}{2} \end{bmatrix} & \begin{bmatrix} H_{yy} \sin^2 \frac{\theta}{2} + H_{xx} \cos^2 \frac{\theta}{2} \\ - (H_{xy} + H_{yx}) \sin \frac{\theta}{2} \cos \frac{\theta}{2} \end{bmatrix} \end{bmatrix} \quad (69)$$

Consider now that the applied field H_1 is on for a time τ long enough to rotate the $\underline{r}$ -vector through an angle θ , where

$$\theta \gg 2\pi \quad (70)$$

We can then find $\overline{\mathcal{K}}_R$ by incrementing the rotation angle by $d\theta$ and assigning a waiting time of $\tau d\theta/\theta$ to each value of $\mathcal{K}_R(\theta)$. Thus, we have

$$\overline{\mathcal{K}}_R^{0*} = \frac{\sum_{i=1}^{\theta/d\theta} \mathcal{K}_R(i d\theta) \frac{\tau d\theta}{\theta}}{\tau} \rightarrow \frac{1}{\theta} \int_0^{\theta} \mathcal{K}_R(\theta) d\theta \quad (71)$$

in the limit that $d\theta$ approaches zero. Using the inequality (70) to

neglect terms of order $(\sin\theta)/\theta$, $(\sin^2\theta)/\theta$, etc., we obtain

$$\bar{\mathcal{H}}_R^{0^\circ} = \frac{1}{2} \begin{bmatrix} 2H_{zz} & 0 & 0 \\ 0 & (H_{yy} + H_{xx}) & (H_{yx} - H_{xy}) \\ 0 & (H_{xy} - H_{yx}) & (H_{yy} + H_{xx}) \end{bmatrix} \quad (72)$$

exactly as in Eq. (68). One can then take the matrix $\mathcal{H}_R(\theta)$ as a zero-time matrix for the 180° -phase pulse and operate on it in the same manner with S and S^{-1} , choosing $\phi = 180^\circ$. $\bar{\mathcal{H}}_R^{180^\circ}$ is found to be identical to $\bar{\mathcal{H}}_R^{0^\circ}$ and therefore $\bar{\mathcal{H}}_R = \frac{1}{2}(\bar{\mathcal{H}}_R^{0^\circ} + \bar{\mathcal{H}}_R^{180^\circ}) = \bar{\mathcal{H}}_R^{0^\circ}$. It is clear that the second half of the pulse sequence is unnecessary with respect to the averaging of $\mathcal{H}_R$. A transient nutation performs the same averaging as the rotary echo, but cannot eliminate H_1 inhomogeneities and therefore is of little value for measuring relaxation times relative to the rotary echo decay. One can also obtain $\bar{\mathcal{H}}_R$ by letting $\Theta = 4\pi$ in Eq. (71), as in the $\pi/2$ pulse calculation. The true cycle time is $t_c = 4\pi/\omega_1$, even though one loosely speaks of the cycle time as being 2τ , the time it takes for the echo to form.

Looking at Eq. (72), we see that all off-diagonal terms involving the $|z\rangle$ sublevel are averaged to zero, as expected, and that the zz term is unaffected. Since this will always be the case when only two of the three sublevels are connected, we will drop the $|z\rangle$ sublevel column and row from $\bar{\mathcal{H}}_R$ and work only with 2×2 matrices.

The most important thing to note about the 2×2 submatrix in Eq. (72) is that the diagonal terms are equal. Physically, this corresponds to adding the same energy term $\frac{1}{2}(H_{yy} + H_{xx})$ to the energy of each sublevel coupled by the field. Recalling that H_{yy} and H_{xx} vary over different

sample sites, the rotary echo eliminates the effects of an inhomogeneous distribution of relaxation fields. Figure 10 illustrates this: before the application of the echo, the $|x\rangle \leftrightarrow |y\rangle$ transition would appear at the energy $Y - X + H_{yy} - H_{xx}$, where the quantity $(H_{yy} - H_{xx})$ contributes to the linewidth of the absorption. After applying the echo sequence, the absorption now occurs at $Y - X$ and the inhomogeneous contribution of the relaxation term to the linewidth is removed.

This can be seen more quantitatively by evaluation of the commutator in Eq. (14), where $\mathcal{K}^*$ includes the relaxation matrix $\mathcal{K}_R$. Dropping the asterisks (all equations are in the rotating frame), the effect of the relaxation field on the components of $\underline{r}$ is given by

$$\frac{dr_1}{dt} = -(H_{yy} - H_{xx}) \frac{r_2}{\hbar} - \left(\frac{2}{\hbar}\right) (\text{Im } H_{yx}) r_3 \quad (73a)$$

$$\frac{dr_2}{dt} = -\left(\frac{2}{\hbar}\right) (\text{Re } H_{yx}) r_3 + (H_{yy} - H_{xx}) \frac{r_1}{\hbar} \quad (73b)$$

$$\frac{dr_3}{dt} = \left(\frac{2}{\hbar}\right) (\text{Re } H_{yx}) r_2 + \left(\frac{2}{\hbar}\right) (\text{Im } H_{yx}) r_1 \quad (73c)$$

The time dependence of the spin polarization r_3 requires that the off-diagonal matrix elements be non-zero in the rotating frame. Because one usually assumes $T_1 = \infty$, $H_{yx} = H_{xy}^*$ are set equal to zero, eliminating T_1 processes. T_2 processes then depend solely on the difference of the diagonal terms $(H_{yy} - H_{xx})$ and Eqs. (72) and (73) clearly show that r_1 and r_2 are made time-independent by the averaging of $\mathcal{K}_R$.

The directional dependence of the averaging process in the rotating frame can be elucidated by representing the relaxation field prior to

COHERENT AVERAGING VIA ROTARY ECHOES

XBL 7711-6492

Figure 10

averaging as a field $\tilde{\Omega}_R$ which exerts a torque on $\underline{r}$. The components of $\tilde{\Omega}_R$ are

$$\Omega_{1R} = \frac{(H_{xy} + H_{yx})}{\hbar} \quad (74a)$$

$$\Omega_{2R} = \frac{i(H_{yx} - H_{xy})}{\hbar} \quad (74b)$$

$$\Omega_{3R} = \frac{(H_{yy} - H_{xx})}{\hbar} \quad (74c)$$

For the general driving field Hamiltonian given by Eq. (25), the components of $\tilde{\Omega}$ (on-resonance) are

$$\Omega_1 = 0 \quad (75a)$$

$$\Omega_2 = -\omega_1 \quad (75b)$$

$$\Omega_3 = 0 \quad (75c)$$

Using the 2x2 submatrix of Eq. (72) and Eqs. (74), the relaxation fields *after* averaging are

$$\bar{\Omega}_{1R} = 0 \quad (76a)$$

$$\bar{\Omega}_{2R} = \frac{i}{\hbar} (H_{yx} - H_{xy}) = -\frac{2}{\hbar} \text{Im } H_{yx} \quad (76b)$$

$$\bar{\Omega}_{3R} = 0 \quad (76c)$$

It is clear, comparing Eqs. (75) and (76), that $\bar{\Omega}_R$ is parallel to $\tilde{\Omega}$ and that the only component of $\tilde{\Omega}_R$ that is not averaged to zero lies along the driving field. Any relaxation field $\tilde{\Omega}_R$ that is diagonal (no T_1 processes) is perpendicular to $\tilde{\Omega}$ and after averaging has all zero components.

One can easily demonstrate that for an arbitrary phase ϕ for the applied field, the argument is identical and no additional insight is gained. The off-resonance case is more important and will be discussed later in this chapter (Section E).

This analysis allows one to make an interesting comparison between rotary echoes and two other ESESC experiments. $\bar{\mathcal{H}}_R$ has been calculated by BBH for spin locking and CPMG echo sequences. In both cases, the form of $\bar{\mathcal{H}}_R$ is identical to Eq. (72). How these experiments must differ therefore lies in the geometric relations between $\bar{\Omega}$, $\bar{\Omega}_R$, and $\underline{r}$ itself. (One cannot discuss free induction decays and Hahn spin echoes in this manner, since they do not satisfy the cyclic criteria for coherent averaging.)

Spin locking is very similar to a rotary echo because the H_1 field is "on" continuously during the course of the experiment. Despite this, k_{eff}^{-1} decay times from spin locking have been shown to approach the lifetimes of the excited triplet state, whereas $T_{2\rho}$ decays for rotary echoes are several orders of magnitude shorter. The difference arises because $\underline{r}$ lies *along* $\bar{\Omega}$ in spin locking but is *perpendicular* to it in a rotary echo. If a relaxation field $\bar{\Omega}_R$ is present, the only non-zero component of $\bar{\Omega}_R$ lies along $\bar{\Omega}$; $\underline{r}$ will then precess about the combined field $(\bar{\Omega}_R + \bar{\Omega})$. The presence of the additional field $\bar{\Omega}_R$ does not affect spin locking, since $\underline{r}$ is locked along $(\bar{\Omega}_R + \bar{\Omega})$; the only difference to be expected is that the rate of relaxation against the fields $(T_{1\rho})^{-1}$ would change, depending on the magnitude of $\bar{\Omega}_R$. Experiments show that $T_{1\rho}$ processes are slower than most other processes (lifetime decay and dynamic processes in Chapter II) and do not affect the value of k_{eff}^{-1} very strongly; any

small change in the $T_{1\rho}$ value is therefore not reflected in the spin locking decay. The experimentally verified fact that $k_{\text{eff}}^{-1} \gg T_{2\rho}$ even though $\bar{H}_R$ is the same for spin locking and rotary echoes is in direct support for Redfield's argument that the T_2 constant in the Bloch equations must be replaced by a $T_{1\rho}$ (or T_{2e}) decay time.

A rotary echo is much more sensitive to the addition of a relaxation field $\bar{\Omega}_R$ along $\bar{\Omega}$ since $\bar{r}$ and $\bar{\Omega}$ are perpendicular to each other. The rate of precession about $(\bar{\Omega}_R + \bar{\Omega})$ will depend on $|\bar{\Omega}_R|$. For a 0° -phase field, the effective field looks like $(\bar{\Omega}_R + \bar{\Omega})$ and for a 180° -phase field, it is $(\bar{\Omega}_R - \bar{\Omega})$; thus, instead of experiencing equal but opposite fields during the two halves of the sequence, there is a refocusing error of $\theta = 4\tau|\bar{\Omega}_R|$ radians accumulated during the experiment. The echo intensity will decrease by $\cos\theta$, the projection of $\bar{r}$ along the r_3 axis at the echo time 2τ .

The CPMG experiment yields a relaxation time intermediate to the decay times for rotary echoes and spin locking. Again, the reason is geometrical: the only field $\bar{r}$ experiences during dephasing is $\bar{\Omega}_R$, since $\bar{\Omega}$ is "off" in between π pulses in the CPMG sequence. Thus, the magnitude $\bar{\Omega}_R$ is important, since it alone determines the dephasing time measured. CPMG decays are shorter than spin locking decays since T_2 is the appropriate decay time in the Bloch equations; the spins are not locked along $\bar{\Omega}$ during the intervals between π pulses and Redfield's work does not pertain to CPMG echoes. CPMG decays are longer than those for rotary echoes, since the π pulses eliminate inhomogeneous broadening and spin diffusion, a geometrical consequence not related to coherent averaging.

E. Coherent Averaging in the Presence of Pulse Imperfections

In this section, an elementary discussion of two types of pulse errors and their detrimental effects on coherent averaging will be presented. It should be clear from the previous section that coherent averaging is by no means the most important feature of rotary echoes. One can expect that the reduced averaging efficiency caused by pulse errors is less significant than the geometrical consequences. The problems of echo formation and refocusing will be discussed in detail in Section F.

1. Phase Angle Errors

Probably the simplest error to treat is improper phase shifting: the refocusing pulse is applied with phase $180^\circ + d\phi$. We need only to calculate $\bar{\kappa}_R^{180^\circ + d\phi}$, since the first pulse is of the proper phase. The result is

$$\bar{\kappa}_R = \frac{1}{2}(\bar{\kappa}_R^{0^\circ} + \bar{\kappa}_R^{180^\circ + d\phi}) = \frac{1}{2} \begin{bmatrix} H_{yy} + H_{xx} & H_{yx} - H_{xy}(1 - id\phi) \\ H_{xy} - H_{yx}(1 + id\phi) & H_{yy} + H_{xx} \end{bmatrix}. \quad (77)$$

It is only the off-diagonal terms that are affected to first order in the phase error $d\phi$. Assuming that $H_{xy} = H_{yx} = 0$ (no T_1 processes), then Eq. (77) reduces to Eq. (72), the result without phase error. This is reasonable, since all the averaging takes place during the first two revolutions of the $\underline{r}$ -vector. The refocusing pulse by itself would average as efficiently as the 0° pulse, since the averaging is not dependent on ϕ

in Eq. (66): one can set the phase arbitrarily to $\phi = 0^\circ$ for any single pulse. It is only when the two pulses are applied relative to each other that the phase $180^\circ + d\phi$ has any meaning, because $\underline{r}$ is no longer perpendicular to $\underline{H}_1(180^\circ + d\phi)$ at the beginning of the refocusing pulse. Fields perpendicular to $\underline{H}_1(180^\circ + d\phi)$ are still averaged, including all fields along the r_3 axis; however, those fields which were perpendicular to $\underline{H}_1(0^\circ)$ in the r_1 - r_2 plane are no longer perpendicular to $\underline{H}_1(180^\circ + d\phi)$, which is the reason the off-diagonal terms are slightly different.

2. Off-Resonance Averaging

Off-resonance coherent averaging^{61,62} is considerably more cumbersome to calculate; we will discuss only the 0° -phase field equation for the $|x\rangle \leftrightarrow |y\rangle$ 2×2 submatrix. The average Hamiltonian for the 180° -phase field would contain many terms and obscures the physical interpretation.

Neglecting H_{xy} and H_{yx} in $\mathcal{H}_R$, the average Hamiltonian for the 0° -phase field is:

$$\bar{\mathcal{H}}_R^{0^\circ} = \frac{1}{2} \begin{bmatrix} H_{yy} \left[1 + \left(\frac{\Delta\omega}{\omega} \right)^2 \right] + H_{xx} \left(\frac{\omega_1}{\omega} \right)^2 & \frac{i\Delta\omega\omega_1}{\omega^2} (H_{yy} - H_{xx}) \\ \frac{i\Delta\omega\omega_1}{\omega^2} (H_{xx} - H_{yy}) & H_{yy} \left(\frac{\omega_1}{\omega} \right)^2 + H_{xx} \left[1 + \left(\frac{\Delta\omega}{\omega} \right)^2 \right] \end{bmatrix} \quad (78)$$

There are two important differences between this equation and Eq. (72):

- i) Even though $\mathcal{H}_R$ was assumed to be diagonal, $\bar{\mathcal{H}}_R$ develops non-zero off-diagonal terms corresponding to field-induced T_1 processes. Since no spin-lattice relaxation processes were allowed for prior to the averaging, we interpret this off-resonance effect

as follows: the effective field $\underline{H}_{\text{eff}}$ that $\underline{r}$ precesses about lies in the r_2 - r_3 plane and $\underline{r}$ therefore is not constrained to the r_1 - r_3 plane as it would be on-resonance. The cone that $\underline{r}$ describes about $\underline{H}_{\text{eff}}$ leaves $\underline{r}$ with a different average projection along the r_3 axis. This represents a different spin-aligned triplet state and translates mathematically into a non-zero off-diagonal element in $\bar{\mathcal{H}}_R$. Since the number of spins in the system is conserved, this "effective T_1 " process must occur simultaneously with an "inverse T_2 " process. Indeed, the change in the average r_3 component is accompanied by the creation of a net averaged coherent component along the $\underline{H}_1$ direction.

- ii) The diagonal elements of $\bar{\mathcal{H}}_R$ are no longer equal for the off-resonance case. This means that dr_1/dt and dr_2/dt will both depend on the difference of the diagonal terms, which is $(H_{yy} - H_{xx})(\Delta\omega/\omega)^2$, as well as the real and imaginary parts of the off-diagonal elements. The former correspond to "true" energy-conserving T_2 processes, while the latter reflect the fact that a T_1 process also causes a dephasing event. Rewriting Eqs. (73) for off-resonance effects,

$$\frac{dr_1}{dt} = (H_{yy} - H_{xx}) \left[- \left(\frac{\Delta\omega}{\omega} \right)^2 \frac{r_2}{\hbar} - \left(\frac{\Delta\omega\omega_1}{\omega^2} \right) \frac{r_3}{\hbar} \right] \quad (79a)$$

$$\frac{dr_2}{dt} = (H_{yy} - H_{xx}) \left[\left(\frac{\Delta\omega}{\omega} \right)^2 \frac{r_1}{\hbar} \right] \quad (79b)$$

$$\frac{dr_3}{dt} = (H_{yy} - H_{xx}) \left[\left(\frac{\Delta\omega\omega_1}{\omega^2} \right) \frac{r_1}{\hbar} \right] \quad (79c)$$

We find for small $\Delta\omega$, terms with the coefficient $\Delta\omega\omega_1/\bar{\omega}^2$ dominate, since $\omega_1 \approx \bar{\omega}$. For large $\Delta\omega$, terms with $(\Delta\omega/\bar{\omega})^2$ are more important, since $\Delta\omega \approx \bar{\omega}$. Typical driving field strengths, as determined by the time required to effect a $\pi/2$ pulse, are roughly 5 MHz. Therefore, a $\Delta\omega$ of less than about 1 MHz would be classified as "small" while a "large" value for $\Delta\omega$ would be about 10 MHz. Although it is difficult to estimate the magnitudes of H_{yy} and H_{xx} , a general idea of the effects of off-resonance fields can be obtained if we let $(H_{yy} - H_{xx}) = \Delta\omega = 1$ MHz and $\omega_1 = 5$ MHz. In this instance, $(H_{yy} - H_{xx})$ is reduced by the factor $\Delta\omega/\bar{\omega}$; that is, the off-resonance averaging increases the dephasing time by about a factor of five. For large $\Delta\omega$, the term $(\Delta\omega/\bar{\omega})^2 \approx 1$ and the averaging is minimal.

One can perhaps gain a clearer physical picture of off-resonance averaging by considering the geometrical components of $\bar{\Omega}_R$ and $\underline{\Omega}$ as in Section D. Again, one finds that any vector perpendicular to $\underline{\Omega}$ is also perpendicular to $\bar{\Omega}_R$ and, as before, fields parallel to the effective field are not averaged while those perpendicular to it are. However, those fields perpendicular to $\underline{\Omega}$ now lie in a plane, specified by ω_1 and $\Delta\omega$, which does not contain the r_3 axis. A relaxation field solely along the r_3 axis which would be totally averaged were $\Delta\omega = 0$, is now only partially averaged. Referring to Fig. 11, the angle H_{eff} makes with the r_2 axis is

$$\alpha = \arctan\left(\frac{\Delta\omega}{\omega_1}\right) \quad (80)$$

Therefore, any field $\bar{\Omega}_R$ along the r_3 axis has a projection along H_{eff} of $\bar{\Omega}_R \sin \alpha = \bar{\Omega}_R (\Delta\omega/\bar{\omega})$. The term $(\Delta\omega/\bar{\omega})$ acts as a reduction factor for the relaxation field strength and physically corresponds to the component of $\bar{\Omega}_R$ not averaged (parallel to H_{eff}). This simple trigonometric argument

EFFECTIVE FIELD ORIENTATION
FOR OFF-RESONANCE APPLIED FIELD
IN ROTATING FRAME

XBL 7711-6490

Fig. 11. Definition of the angle α between H_{eff} and the r_2 axis in the rotating frame.

gives a result very similar to the more rigorous averaging treatment, if one assumes that the component of Ω_R parallel to H_{eff} is responsible for relaxation after application of the rotary echo.

F. Rotary Echo Calculations

ESESC experiments which depend on the measurement of the intensity of an echo will be very sensitive to the mechanics of the echo formation. As an example, if the 180° -phase pulse is 15 nsec too short (a 0.1% error in pulse length), $\omega_1 = 5$ MHz, and $\tau = 15$ μ sec, the echo intensity drops by roughly 10%. It is trivial to circumvent a pulse error such as this one (make the 180° pulse longer than the 0° pulse), but this simple case illustrates the strong dependence of the echo signal on the pulse characteristics.

1. Phase Angle Errors

The method used to calculate echo intensities is very straightforward and is based on the equations of motion for the $\underline{r}$ -vector [Eqs. (23)] without relaxation of any kind. We will first treat the case of a phase shift error, because it complements the discussion in Section E.1 and because the succeeding calculations are made following the same steps. The first half of the pulse sequence is accounted for by setting $r_1(0) = r_2(0) = \Delta\omega = \phi = 0$. The $\underline{r}$ -vector nutates through an angle $\theta = \omega_1\tau$ so that

$$r_1(\tau) = -r_3(0)\sin\theta \quad (81a)$$

$$r_2(\tau) = 0 \quad (81b)$$

$$r_3(\tau) = r_3(0)\cos\theta \quad (81c)$$

Clearly, $\underline{r}$ now lies in the r_1 - r_3 plane with components determined by the time $\tau - 2n\pi/\omega_1$ (i.e., $0 \leq \theta \leq 2\pi$). The refocusing pulse is now applied with $\phi = 180^\circ + d\phi$, $r_1'(0) = -r_3(0)\sin\theta$, $r_2'(0) = 0$, and $r_3'(0) = r_3(0)\cos\theta$; the equations are referenced to a starting time $t = \tau$. Since the experimental observable is $r_3(2\tau)$, this is the only component of interest, and is given by

$$r_3(2\tau) = r_3(0) \left[\cos^2\theta - \sin^2\theta \cdot \cos(180^\circ + d\phi) \right] \cong r_3(0) \left[1 - \frac{(d\phi)^2}{2} \sin^2\theta \right]. \quad (82)$$

Thus, errors in ϕ are a second order effect for small $d\phi$ and cause the echo height to oscillate as $\sin^2(\omega_1\tau)$ for increasing τ . Equation (82) shares a general feature with the more complicated expressions for $r_3(2\tau)$, due to the trigonometric terms in the expression: certain values of τ allow the echo to reform as though no errors were present. For improper phase shifting, $\omega_1\tau = n\pi$ is the condition for $r_3(2\tau) = r_3(0)$, while for off-resonance cases, the mixture of trigonometric functions makes these special values of τ very difficult to solve for.

2. Off-Resonance Driving Fields

The result for $\Delta\omega \neq 0$, again for a single isochromat without relaxation, is

$$r_3(2\tau) = r_3(0) \left(\frac{1}{\omega^4} \right) \left[\Delta\omega^2 (\Delta\omega^2 - \omega_1^2) + 4\Delta\omega^2 \omega_1^2 \cos\theta + \omega_1^2 \omega^2 \sin^2\theta + (\omega^4 - \Delta\omega^2 \omega_1^2) \cos^2\theta \right]. \quad (83)$$

The physical significance of this equation is as follows: a rotary echo is performed off-resonance by $\Delta\omega$ on a δ -function line by increasing τ and measuring the echo intensity. Equation (83) describes the oscillation of

the echo maxima; it does *not* correspond to the echo waveform detected experimentally ("raw" data) but rather to the reduced data after signal intensities have been measured.

Figure 12 shows Eq. (83) plotted out for three values of $\Delta\omega$: 1 MHz, 5 MHz, and 25 MHz. The vertical axis is unitless and has been scaled by the arbitrary choice of $r_3(0) = +1.0$. Three interesting features can be pointed out:

- i) Off-resonance effects become noticeable for $\Delta\omega \gtrsim 0.5$ MHz. At $\Delta\omega = 1$ MHz, the amplitude of the oscillations is roughly 30% of the initial r_3 value, an experimentally observable quantity.
- ii) The oscillation amplitude is small for both large and small values of $\Delta\omega$, reaching a maximum at $\Delta\omega = \omega_1$ (5 MHz in these and all succeeding calculations). For $\Delta\omega < \omega_1$, the low amplitude reflects the fact that the applied field is nearly on-resonance. If $\Delta\omega = 0$, the r_3 versus 2τ curve would be a horizontal line with $r_3 = +1.0$. At relatively small $\Delta\omega$, therefore, the effects of being off-resonance are not especially pronounced and the amplitude is low. On the other hand, for $\Delta\omega > \omega_1$, the small amplitude is a consequence of the weak coupling of the radiation field with the two-level system. The $\underline{r}$ -vector precesses about $\underline{H}_{\text{eff}}$, which is nearly parallel to the r_3 axis; the r_3 component of $\underline{r}$ never dips very far below +1.0. Generally, the value for the minimum in the curves in Fig. 12 is given by the expression

$$r_3(\text{min}) = 8\cos^4\alpha - 8\cos^2\alpha + 1 \quad (84)$$

where $\alpha = \arctan(\Delta\omega/\omega_1)$ as in Fig. 11.

r_3 VS. 2τ FOR OFF-RESONANCE ROTARY ECHO

XBL 7711-6493

Figure 12

iii) It is possible to achieve complete inversion of the echo signal when $\Delta\omega = \omega_1$ or $\alpha = \pi/4$. In this case, $\underline{H}_{\text{eff}}$ lies at a 45° angle from both the r_2 and r_3 axes; the cone that $\underline{r}$ describes is tangential to both the axes. If τ is such that $\underline{r}$ lies along the r_2 axis at $t = \tau$, then $\underline{r}$ will be along the $-r_3$ axis at $t = 2\tau$. In practice, total inversion cannot be achieved unless the ESR line is homogeneously broadened with a T_2 time long enough to observe several oscillations of the echo intensity.

3. Population Feeding and Decay

A general treatment of an ESESC experiment should include the time evolution of the population of the two levels coupled by the field. Specifically, the lowest triplet state is usually populated ("fed") indirectly via the first excited singlet state and decays to the ground state in the absence of dynamic processes. Figure 13 illustrates the relevant states with the feeding and decay rate-parameters F_i and k_i . In molecular crystals with isotropic, structural, or impurity traps (see Section III.G), the redistribution of population between trap and exciton band states constitutes another class of feeding and decay processes which affect ESESC experiments. One would intuitively expect that feeding events would have no effect on a coherence experiment, since they are incoherent processes. This is true for on-resonance probe pulse experiments because the entering population is rotated into the r_1 - r_2 plane at the final $\pi/2$ pulse and does not contribute to the signal; spin locking is an excellent example of an ESESC technique which illustrates this point (Section II.C). However, rotary echoes do not use a probe pulse and one should in principle modify Eqs. (23) to include feeding and decay.

TRIPLET SPIN SUBLEVELS

XBL 7611-7718

Fig. 13. Schematic of the model used to treat population feeding and decay processes for an excited triplet state. Population enters sublevels $|y\rangle$ and $|x\rangle$ by intersystem crossing from the lowest excited singlet state at rates F_y and F_x and decay to the ground singlet state occurs at rates k_y and k_x . Dynamic energy exchange processes can also be included in these rate parameters so that F_i and k_i would account for population entering and leaving T_1 by more than one route.

One can immediately make two predictions concerning a set of r_3 versus 2π curves (as in Figs. 14 and 15) which account for feeding and decay processes:

- i) The decay processes will dominate the feeding processes.

Every decay event appears as a unit loss in the magnitude of the $\underline{r}$ -vector and its effect on the echo is independent of the time during the experiment when the decay took place. However, feeding events manifest themselves as unit increases in the r_3 component *only* and therefore their effect on the echo is dependent on the orientation of the $\underline{r}$ -vector at the time the population enters. The contribution can actually be a negative one if feeding occurs when $\underline{r}$ has a negative r_3 component. If the inverses of the feeding rates are small compared to τ , then the net feeding contribution is zero for the on-resonance case, since the vector sum of the r_3 components of the population entering after time $t \approx 0$ vanishes. This is not true for the off-resonance situation for which rapid feeding generates a net r_3 component and alters the echo intensity.

- ii) Feeding and decay rates which are significantly different from the time scale of the rotary echo should be ineffective. Thus, even though a feeding or decay event might contribute to the net r_3 component, very few or none of these processes occur before the echo forms. This essentially rules out triplet state phosphorescence lifetimes as processes which affect the rotary echo, since most values for the triplet sublevel decay rates (k_x and k_y for sublevels $|x\rangle$ and $|y\rangle$ respectively) are smaller than $10^3 - 10^4 \text{ sec}^{-1}$.

The modifications of Eqs. (23) to account for feeding and decay are based on the treatment by Breiland, Fayer, and Harris.³⁶ Basically, the equation for the time evolution of the density matrix now includes terms which cause the diagonal elements to be populated at the rates F_y and F_x and depleted at the rates k_y and k_x , and the off-diagonal elements to be depleted at an average rate $k_A = \frac{1}{2}(k_y + k_x)$. Solutions which describe the motion of the $\underline{r}$ -vector components similar to Eqs. (23) are then obtained and used to generate an expression for $r_3(2\tau)$ analogous to Eq. (83). This equation is quite lengthy and is derived in the Appendix. The feeding rates are not a variable in Eq. (A.6), but appear indirectly by the choice of the spin polarization $r_3(0)$ without the applied field. In our calculations, we have set $r_3(0) = +1.0$ to provide comparison with the calculations without kinetic processes. Since the population of sublevel i is given by F_i/k_i , this choice of $r_3(0)$ corresponds to

$$F_y/k_y - F_x/k_x = 1.0 \quad (85)$$

Once k_y and k_x are fixed, F_y and F_x are constrained to lie on the line described by Eq. (85).

Figures 14 and 15 represent $r_3(2\tau)$ as a function of τ with various assigned values for k_A and $\Delta\omega$. As in Fig. 12, these curves show the oscillations in the echo intensity as the pulse width τ is increased. Decay rates range from $k_A = 10^2 \text{ sec}^{-1}$ to $k_A = 10^6 \text{ sec}^{-1}$, which are values commonly found in excited triplet states.

We note first that the curve for $\Delta\omega = 1 \text{ MHz}$, $k_A = 10^2 \text{ sec}^{-1}$ is virtually identical to the curve in Fig. 12 for $\Delta\omega = 1 \text{ MHz}$. This value for k_A was chosen to represent an average triplet state phosphorescence decay rate. Rotary echoes have been carried out in several 1,2,4,5-Tetrachlorobenzene

.BL 7711-6498

Figure 14

XBL 77U-6496

Figure 15

(TCB) systems (see Section III.G); a representative value is $k_A \sim 30 \text{ sec}^{-1}$ for the $2|E| (|y\rangle \leftrightarrow |z\rangle)$ transition of TCB in Durene. Another more interesting system on which rotary echoes have been done is Parabenzo-quinone- h_4 (PBQ- h_4) in PBQ- d_4 . Here, the phosphorescence decay rate (but not k_A) is about $5 \times 10^3 \text{ sec}^{-1}$ for the $|y\rangle \leftrightarrow |z\rangle$ transition.⁶³ The curves for both the TCB and PBQ systems are indistinguishable, and could certainly never be differentiated experimentally from the simple situation without feeding and decay.

There are dynamic processes which do affect the echo decay in the same isotopically mixed PBQ system; specifically, promotion events from the PBQ- h_4 trap to a vibronic level 21 cm^{-1} above the trap energy proceed at rates greater than 10^5 sec^{-1} near 4.2K .⁶⁴ The other two curves in Fig. 14 and all the curves in Fig. 15 are clearly different from the curves in Fig. 12 and show pronounced damping effects. It is interesting that the curves do not damp to $r_3 = 0$, which is what one would observe if Eq. (83) were convoluted with an exponential. The feeding processes replenish the cone that $\underline{r}$ describes about $\underline{H}_{\text{eff}}$ and cause the oscillations to damp to a value related to the amount off-resonance. A situation in which the curves would decay to $r_3 = 0$ is *homogeneous* broadening, purely a lifetime effect without feeding. Inhomogeneous crystal site broadening would obscure such a situation in molecular solids.

4. Inhomogeneous Broadening

We now consider off-resonance rotary echoes in the presence of inhomogeneous broadening. In the absence of spin diffusion, this n -site problem can be set up using a $2n \times 2n$ block diagonal density matrix for the $\underline{r}$ -vector components, or equivalently as $3n$ Bloch-type equations.

It is much simpler to begin with Eq. (83) and numerically integrate across the resonance line, changing $\Delta\omega$ and $r_3(0)$ for each isochromat in the line. The values for $r_3(0)$ are weighted appropriately for the chosen lineshape and normalized to provide comparison with the curves in Fig. 12.

Figures 16 and 17 show the results of such a calculation for both Gaussian and Lorentzian inhomogeneously broadened lines. For all these curves, the resonance line was divided into 251 isochromats extending 5 FWHM's on either side of the center frequency. This rather limited integration range is satisfactory for a Gaussian line, but only gives qualitative results for a Lorentzian. Between five and ten percent of the area under a Lorentzian lineshape is contained in the wings cut off by the integration limits, leading to noticeably incorrect normalization for all curves in Fig. 17.

Inhomogeneous broadening shows up as a damping of the echo intensity dependent on the parameters $\Delta\omega$ and $(T_2^*)^{-1} \propto \text{FWHM}$. For a given value of the FWHM, the damping rate increases as $\Delta\omega$ increases; the destructive interference of the various $\underline{r}$ -vectors associated with the isochromats is more efficient as more of the isochromats are off-resonance by a greater amount. The steady-state value of $r_3(2\tau)$ is a function of $\Delta\omega$ and reflects the inability of the field to couple the two levels as $\Delta\omega$ is increased.

The most interesting, and in fact surprising, result of these calculations is demonstrated by Fig. 18, for which the FWHM is varied and the field is *on-resonance*: the oscillations in $r_3(2\tau)$ persist for $\Delta\omega = 0$ and are related in frequency and amplitude to the inhomogeneous linewidth $(T_2^*)^{-1}$. As $(T_2^*)^{-1}$ approaches zero (δ -function line), $r_3(2\tau)$ becomes a flat curve with value +1.0; however, for a typical linewidth

XBL 7711-6495

Figure 16

r_3 VS. 2τ FOR OFF-RESONANCE ROTARY ECHO
INHOMOGENEOUSLY BROADENED LORENTZIAN LINE

XBL7711-6494

Figure 17

XBL 7711-6497

Figure 18

observed in molecular solids ($\text{FWHM} \approx 1$ to 10 MHz), pronounced oscillations in the echo maxima appear. This situation has serious consequences, since these beats are not the result of an experimentally determined parameter (i.e., going off-resonance) and are thus unavoidable.

Visualizing the echo formation in r -space for an inhomogeneous distribution is extremely complicated. Because the field is on-resonance, exactly half the spins experience an effective field with a positive r_z component and half experience an effective field with a negative r_z component. The size of the r_z component varies with the position of the isochromat in the line (as does the weighting factor for the isochromat), implying that α (see Fig. 11) ranges from 0 to $\pm\pi/2$ as $\bar{\omega}$ ranges from ω_1 to $\pm\infty$ ($\pm\sqrt{25(\text{FWHM})^2 + \omega_1^2}$ in these calculations). The 0° pulse causes a large number of cones to form in r -space, one for each isochromat; the individual $\underline{r}$ -vectors lie on their cones in a position determined by the length of the pulse. The refocusing pulse takes these $\underline{r}$ -vectors and causes them to precess about a new $\underline{H}_{\text{eff}}$, forming a second set of cones whose net r_z projection determines the echo height. Some values of τ tend to align the $\underline{r}$ -vectors in a position with a larger $r_z(2\tau)$ component than other values of τ , resulting in the beats in Fig. 18.

The unique feature of the rotary echo responsible for the beats is that the applied field is always "on." One cannot make the approximation used for short pulses ($\theta = \pi/2, \pi$) that all the isochromats nutate through the same angle θ about a common $\underline{H}_{\text{eff}}$. The wide variation of $\underline{H}_{\text{eff}}$ and θ across the resonance line produces the beats even when $\Delta\omega = 0$. The rotary echo is the only cyclic coherence experiment which exhibits these beats for on-resonance driving fields.

The observation of the beats would be obscured by experimental error for narrow ($\text{FWHM} \lesssim 1 \text{ MHz}$) lines; wide lines could also be free of beats if τ were long enough for the oscillations to be damped. For example, in Fig. 18, beats in the decay of the 15 MHz-wide line have nearly disappeared by $2\tau = 8 \mu\text{sec}$. Successful exponential rotary echo decays in molecular crystals have been carried out by van't Hof and Schmidt on various PBQ systems.^{64,68} The $|z\rangle \leftrightarrow |y\rangle$ transition used to produce the echoes is roughly 15 - 20 MHz wide in PBQ; thus, it is conceivable that the beats were not observed because τ was then long enough to measure the detrapping rates ($10^4 - 10^5 \text{ sec}^{-1}$ in PBQ). Most TCB systems have ESR linewidths of only 2 - 4 MHz, however. Because T_2 times in TCB are generally quite short, these oscillations should be superimposed on the decay due to transverse relaxation processes and other processes (i.e., spin diffusion and trap-exciton band interactions).

G. Experimental Results and Discussion

1. Experimental Details

Three different TCB systems were studied using rotary echoes: TCB in Durene (1,2,4,5-tetramethylbenzene), neat TCB with impurity-induced trap centers (Y-traps), and isotopically mixed TCB- h_2 in TCB- d_2 samples of two different concentrations. All samples were made from recrystallized and extensively zone-refined materials whose purity was checked by mass spectral analysis and proton NMR (for the deuterated TCB). Single crystals were grown from the melt by standard Bridgman techniques and cleaved just prior to use in an experiment.

The concentrations of the various samples were as follows:

- i) 1% TCB in Durene, prepared by doping roughly 0.016 g TCB into 1 g Durene (molar ratios);
- ii) 1% Y-trap, prepared by doping roughly 0.0068 g para-Dichlorobenzene into 1 g TCB;
- iii) Concentrated (5% TCB- h_2) and dilute (0.06% TCB- h_2) isotopically mixed crystals, prepared by M. T. Lewellyn. The dilute sample was 97.5% deuterated and consisted of 95.31% TCB- d_2 , 4.63% TCB-hd, and 0.06% TCB- h_2 . The concentrated sample was prepared by doping TCB- h_2 into the dilute sample so that the final concentrations were 90.5% TCB- d_2 , 4.6% TCB-hd, and 4.8% TCB- h_2 .

All the above systems can be described by a guest-host model for the electronic states of the various components.⁶⁵ Guests, the much more dilute component of the system, have a triplet state energy (referenced to the ground singlet state) lower than the host triplet state energy and thus forms what is known as a trap. At low temperatures, Boltzmann equilibrium heavily favors the trap over the host band states and causes an excitation delocalized throughout the host species to become localized at a low energy trap site. It is these traps which are monitored in the following rotary echo experiments by observing their phosphorescence selectively with the monochromator. The relevant trap depths are:

<i>System</i>	<i>Trap depth (cm^{-1})</i>	<i>Reference</i>
TCB/Durene	1456	66
TCB Y-trap	48	22
TCB- h_2 /TCB- d_2	22	28

The experimental apparatus used in the rotary echo experiments is identical to that used for spin locking and is discussed in detail in

Section II.D. Different TTL pulse circuitry was used to produce the rotary echo pulse sequence and consisted of a variable delay device capable of putting out two pulses with reproducible pulse separation⁴³ and another "rotary echo box" which produced the actual pulses which drove the PIN diodes open and closed at the correct times.²⁶ The two pulses from the delay device served to begin and terminate the echo sequence and were linearly swept in time by a synchronous clock motor attached to a precision 10-turn variable resistor. The time period in between the two pulses acted as a microwave "window" to the sample, during which time the two outputs from the rotary echo box controlled the two microwave channels corresponding to $\phi = 0^\circ$ and $\phi = 180^\circ$. The pulse sequence was triggered by a strobe pulse (5 Hz) also referenced to the lock-in amplifier used to detect the signal.

The procedure for doing the rotary echo is again similar to spin locking. Initially, a transient nutation is performed, using only one of the microwave channels. It is important that efficient coupling of the sample and microwaves be achieved so that the criterion for coherent averaging, $t_c \ll T_2$, is met. Even though $\pi/2$ or π pulses are not used in rotary echoes, knowledge of ω_1 is needed in the calculations of the preceding section of this chapter. In addition, the quality of the transient nutation directly determines the quality of the rotary echo observed, since the latter consists of back-to-back transient nutations. Phases were set by combining the two microwave channels and feeding the sum into a power meter (HP 432A) with a thermistor mount (HP 478A). When $\phi = 180^\circ$, the net power reaching the meter was zero. The amplitudes of the separate channels were controlled by variable attenuators (Narda

792FF) and equalized using the power meter. Once ϕ is set and ω_i for each channel is known and matched, the rotary echo is produced by starting the motor which increases the pulse separation from the output of the delay device. As the microwave window grows larger, the sample receives more of the pulse sequence and the echo waveform itself is traced out on a strip-chart recorder (HP 7100B).

2. Results and Conclusions

Two types of rotary echo data can be taken in a single experiment. The first kind consists of just the initial transient nutation and the first rotary echo; all the calculations in Section III.F are for this initial echo only, since calculations of higher order echoes are very tedious. Different values for the first echo height are obtained as τ , the length of each pulse, is increased and a plot of echo intensity versus 2τ yields T_{2p} .

A second method for obtaining T_{2p} consists of keeping τ fixed and producing a train of echoes. Rotary echo trains require a string of phase shifted pulses as follows:

<i>Pulse phase</i>	<i>Time</i>
0°	$0, 3\tau, 7\tau, \dots (4n-1)\tau$
180°	$\tau, 5\tau, 9\tau, \dots (4n+1)\tau$
echo	$2\tau, 4\tau, 6\tau, \dots 2(n+1)\tau$

Because echoes form during a pulse (not a phase shift), field strength mismatches in trains is not an important consideration; phase shift errors could produce oscillations in the echo decays, however. The primary advantage of echo trains is that if a time-dependent nuclear process is present, τ can be made short enough so that the process appears to be

static. The relaxation time measured would be longer than that obtained from first echo measurements, which are sensitive to local field fluctuations at sufficiently long values for τ . There is one disadvantage to the train method, however: if $T_{2\rho}$ is very short, it may be difficult to observe a sufficient number of echoes to provide a complete decay.

An example of a rotary echo train on the $2|E|$ transition ($|y\rangle \leftrightarrow |z\rangle$) of TCB in Durene is shown in Fig. 19, for which $\tau = 1.5 \mu\text{sec}$. The bottom part of the figure shows the timing of the microwave pulses with respect to the echo waveform displayed in the top half of the figure. This particular choice of τ illustrates the disadvantage of using echo trains, since only four echoes are discernible (the higher number echoes are indistinguishable from noise). If τ is shortened, finding the echoes becomes difficult since all the oscillations from the transient nutations blend together.

One currently unresolved source of experimental difficulties is the change in phosphorescence level corresponding to the saturation of the two sublevels at each point when the phases of $\tilde{u}_1$ are shifted. This is also shown in Fig. 19 at the points where the dashed lines intersect the echo waveform. It was thought that off-resonance conditions might possibly cause such an effect, but changing ω_0 over the entire linewidth (roughly from 1743 MHz to 1746 MHz) did not remove the discontinuity. In addition, it is possible to use Eq. (23c) to calculate $r_3(\tau^-)$, $r_3(\tau^+)$, $\partial r_3/\partial t|_{\tau^-}$ and $\partial r_3/\partial t|_{\tau^+}$. The values of r_3 just before and after phase shifting at τ are equal, as are the first derivatives of r_3 , indicating that the waveform for the echo and its first derivative are continuous functions at the phase shift. We conclude that off-resonance effects do not result

Fig. 19. Optically detected on-resonance rotary echo train of 1% TCB-h₂ in Durene at 4.2K. Echoes form at $t = 2\tau, 4\tau, 6\tau, \dots$, where $\tau = 1.5 \mu\text{sec}$ in this experiment; phases are shifted at odd multiples of τ . The microwave pulse sequence on the bottom half of the drawing is aligned with the phosphorescence response to indicate where phase shifting occurs. The unresolved origin of the discontinuities at phase shifts is discussed in the text. The decay time T_{2p} for this particular train was roughly $17 \mu\text{sec}$.

Figure 19

XBL 781-4431

in the discontinuity.

Another explanation might lie in imperfections in the pulse sequence. If the two pulses corresponding to $\phi = 0^\circ$ and 180° are not well overlapped, then the sample experiences a "hole" in the microwave power and undergoes free induction decay in the absence of any driving field. T_2^* , as measured by the C absorption linewidth, is roughly 3×10^{-7} sec and determines the extent of dephasing during the microwave hole. For $0.5 \mu\text{sec} \leq \tau \leq 20 \mu\text{sec}$, a reasonable estimate for the hole width would be about 10 - 100 nsec or $0.1 (T_2^*)$. It is doubtful that enough dephasing could accumulate in such a short time relative to T_2^* to cause a discontinuity of the observed magnitude. Also, the discontinuity appears to alternate in sign, depending on whether the phase is 0° or 180° before the phase shift. If the discontinuity were caused by dephasing, it would have the same sign at each phase shift.

The quality of most of the rotary echo data is quite poor in the opinion of the author, and cannot be used to assign quantitative values to T_{2p} for various systems. Table 1 presents a general compilation of T_2 times measured by various ESESC experiments (both optically and cavity detected) and includes very rough estimates for T_{2p} obtained in these experiments. Without commenting on the details of the other experiments, we can make several positive remarks on the rotary echo data:

- i) T_{2p} measured by rotary echoes is at least an order of magnitude longer than T_{2p}^* measured by transient nutations for the same system. Thus, driving field inhomogeneities are being cancelled out by the rotary echo, at least in part.
- ii) Recalling that $T_{2p} = 2T_2$ if $T_1 = \infty$ [Eq. (50)], T_{2p} decays for

Table 1. T_2 relaxation times in molecular crystals.

System	ESESC Technique	T_2 time	Reference
C_9ND_7 /Durene	Transient nutation	2.5 μ sec	67
TCB/Durene		<1 μ sec	43,71
PBQ- h_4 /PBQ- d_4	Rotary echo	40 μ sec	64
TQ- h_3 /TQ- d_3 (*)		23 μ sec	64
PBQ/p-DBB (**)		18 μ sec	68
TCB- h_2 /TCB- d_2 (0.06%)		~10-17 μ sec	70
TCB- h_2 /TCB- d_2 (5%)		~5-9 μ sec	70
TCB Y-trap		~600 μ sec	26
TCB Y-trap		~40 μ sec	71
TCB/Durene (2 E)		~2-10 μ sec	71
TCB/Durene (D-E)		~20 μ sec	71
C_9ND_7 /Durene- d_{14}	Hahn echo	38 μ sec	69
C_9ND_7 /Durene- h_{14}		12, 18.5 μ sec	69, 67
C_9NH_7 /Durene- h_{14}		2.5 μ sec	69
TCB Y-trap		8 μ sec	25
TCB/Durene		4 μ sec	59
C_9ND_7 /Durene	CPMG echo train	≥ 500 μ sec	67
TCB/Durene		0.5 - 1 msec	59

(*) TQ = Toluquinone
 (**) p-DBB = para-Dibromobenzene

TCB in Durene ($2|E|$ transition) have been measured to be about 9 μ sec, twice the value obtained by the Hahn spin echo.

- iii) T_{2p} values were temperature independent over the range 1.4K to 4.2K, indicative that dephasing is caused by nuclear spin interactions.
- iv) T_{2p} for the concentrated isotopically mixed sample is about a factor of two shorter than T_{2p} for the dilute sample. Since T_{2p} was temperature independent for both crystals, this difference cannot be ascribed to any trap-to-exciton band or trap-to-trap communication, both of which show a strong temperature dependence and occur on a much slower time scale (20 - 900 sec^{-1}).²⁸ We interpret the shorter T_{2p} time observed in the 5% sample as being due to additional proton hyperfine interactions from the increased concentration of TCB- h_2 molecules. By removing the inhomogeneous contribution of the hyperfine interaction, the rotary echo is capable of demonstrating different relaxation times for these two systems, not evident from their CW spectra.

However, there are unfortunately many inconsistencies in the rotary echo results not well understood at this time:

- i) One would generally expect that T_{2p} as measured by an echo train with short enough τ would be longer than T_{2p} measured by first echoes only with increasing τ values. This was indeed observed in the dilute (0.06%) isotopic crystal, in which T_{2p} (train) was about 20 μ sec while T_{2p} (first echo) was about 13 μ sec. For TCB in Durene, just the opposite effect was found. Using echo trains

($\tau = 0.5 - 1.0 \text{ } \mu\text{sec}$), T_{2p} was measured to be roughly 2 - 3 μsec , while for first echoes, T_{2p} was found to be about 11 μsec .

- ii) One would also expect that as τ is increased, T_{2p} measured by echo trains should decrease, since time-dependent nuclear interactions would dephase the echo if $\omega^{-1} < \tau$, where ω is the frequency of the time-dependent phenomena. In fact, just the opposite is observed for TCB in Durene. Rotary echo trains for $\tau = 0.5 \text{ } \mu\text{sec}$ and $1.0 \text{ } \mu\text{sec}$ gave $T_{2p} \approx 2 - 3 \text{ } \mu\text{sec}$, but trains with $\tau = 1.5 \text{ } \mu\text{sec}$ and $2.0 \text{ } \mu\text{sec}$ gave $T_{2p} \approx 9 \text{ } \mu\text{sec}$, almost the same value as the first echo decay time of 11 μsec .
- iii) Finally, we comment on the large amount of scatter in the rotary echo decay curves themselves. The values for T_{2p} given in Table 1 were obtained by least-squares fitting the decays to an exponential with time constant $(T_{2p})^{-1}$. Whether or not the true decay is exponential is not known with certainty. For example, with the first echo method, it is conceivable that the echo decay could exhibit a discontinuity at the point where $\tau > \omega^{-1}$ where ω is the frequency of a time-dependent nuclear interaction; no such obvious discontinuity was observed.

More significantly, the calculations of Section III.F.4 on inhomogeneous lines indicate that strong oscillations should be observable in the first echo decays even when the applied field is on-resonance. Because most first echo data was taken by increasing τ in units of $0.5 \text{ } \mu\text{sec}$, the scatter in the decays should be due in part to these oscillations. More simply, if one picks values of $r_3(2\tau)$ from Fig. 18 at points $2\tau = 1, 2, 3, \dots$ 10 μsec , then the theoretical decay curves appear to duplicate the scatter

found in the experimental data.

In an attempt to fit the data to a curve generated by the program which drew Fig. 18, the $2|E|$ transition of TCB in Durene was characterized carefully. The ESR line is slightly asymmetric, with a FWHM of 3.14 ± 0.55 MHz, and can be fit quite well to a Gaussian. For a driving field strength of $\omega_1 = 4.75$ MHz, first echo data were taken incrementing τ in 0.1 μ sec jumps so that the beats in Fig. 18 could be reproduced. The theoretical decay curve characterized by the above parameters unfortunately bears little or no resemblance to the data, which again show large amounts of scatter.

We have been as yet unable to cleanly demonstrate the predicted oscillations in the rotary echo decays. Any future work on rotary echoes using inhomogeneously broadened systems should concentrate initially on observing beats in the echo decay before any conclusions about T_{20} processes are made. If necessary, Eq. (83) can be convoluted with an exponential decay term simulating homogeneous relaxation processes and then fit to the experimental data to yield T_{20} values.

RETROSPECTIVE

Two different ESESC techniques, spin locking and rotary echoes, have been discussed in detail in this thesis. Both are characterized by the applied field being "on" continuously (no field-free intervals) and by identical average relaxation Hamiltonians. Spin locking, because of geometrical considerations in r -space, is a much more selective technique in that only large changes in the local fields result in a loss of coherence. This makes it an ideal choice for studying processes in which the excitation is transferred between triplet states with environments different enough to cause dephasing. Intramolecular tunneling in cyclopentanone represents a particularly clean example of a model system. Analysis of spin locking results with exchange theory showed that Sharnoff's assumption that $5 \times 10^2 \text{ sec}^{-1} \leq W_{\pm} \leq 5 \times 10^7 \text{ sec}^{-1}$ is incorrect by at least an order of magnitude: essentially no tunneling occurs. Of course, it is more interesting to observe an exchange process directly than to imply that exchange is not occurring to any significant extent. Other triplet systems which do exhibit exchange, such as the guest-host models discussed in Section III.G.1, can be and have been studied using the same approach as in Chapter II.

Rotary echoes have not often been used to study T_2 processes. It was therefore decided to analyze the experiment itself in conjunction with laboratory investigations on several TCB systems. We conclude that rotary echoes are fairly simple to obtain experimentally, but more difficult to interpret. Even in view of the calculations of Section III.F and the framework of coherent averaging, the significance of the T_{2p} relaxation

times for the various TCB systems is not clear. The choice of the TCB systems exhibits no correlations between T_{2p} and the host lattice; the data for the first echo method versus the echo train seem to be inconsistent; and the individual decays themselves are difficult to analyze, due to inhomogeneous broadening, pulse imperfections, and large amounts of "experimental error." The T_{2p} values in Table 1 are at best qualitative, but they do demonstrate the expected increase in line narrowing over transient nutations. The problems of inhomogeneous broadening, which convolute the echo decays regardless of any experimental conditions, make the rotary echo much less useful than other ESESC techniques which suppress T_2^* , such as spin echoes and spin locking.

APPENDIX

In this Appendix, an expression for the off-resonance rotary echo intensity in the presence of feeding and decay processes will be derived.

The equations of motion for the r_i components with all non-zero initial values are

$$r_1(t) = \frac{e^{-k_A t}}{\Gamma^2} \left\{ \begin{aligned} & (r_1^0 - r_1^S) \left[\Gamma^2 \cos^2 \frac{\Gamma t}{2} + (\Gamma^2 - 2\Delta\omega^2) \sin^2 \frac{\Gamma t}{2} \right] \\ & - (r_2^0 - r_2^S) [\Gamma \Delta\omega \sin \Gamma t] \\ & + (r_3^0 - r_3^S) [2\omega_1 \Delta\omega \sin^2 \frac{\Gamma t}{2}] \end{aligned} \right\} + r_1^S \quad (\text{A.1a})$$

$$r_2(t) = \frac{e^{-k_A t}}{\Gamma^2} \left\{ \begin{aligned} & (r_1^0 - r_1^S) [\Delta\omega \Gamma \sin \Gamma t] \\ & + (r_2^0 - r_2^S) [\Gamma^2 \cos \Gamma t] \\ & - (r_3^0 - r_3^S) [\omega_1 \Gamma \sin \Gamma t] \end{aligned} \right\} + r_2^S \quad (\text{A.1b})$$

$$r_3(t) = \frac{e^{-k_A t}}{\Gamma^2} \left\{ \begin{aligned} & (r_1^0 - r_1^S) [2\omega_1 \Delta\omega \sin^2 \frac{\Gamma t}{2}] \\ & + (r_2^0 - r_2^S) [\omega_1 \Gamma \sin \Gamma t] \\ & + (r_3^0 - r_3^S) \left[\Gamma^2 \cos^2 \frac{\Gamma t}{2} + (\Delta\omega^2 - \omega_1^2) \sin^2 \frac{\Gamma t}{2} \right] \end{aligned} \right\} + r_3^S \quad (\text{A.1c})$$

where

$$k_A = \frac{1}{2}(k_x + k_y) \quad (\text{A.2a})$$

$$k_D = \frac{1}{2}(k_x - k_y) \quad (\text{A.2b})$$

are average and difference decay rates for the two sublevels, and

$$\Gamma = \sqrt{\omega_1^2 + (\Delta\omega - ik_D)^2} \quad (A.3)$$

In Eqs. (A.1), the r_i^0 are the steady-state components of $\underline{r}$ in the absence of a driving field, and the r_i^s are the steady-state components of $\underline{r}$ with a driving field. In particular,

$$r_3^0 = \frac{F_y}{k_y} - \frac{F_x}{k_x} \quad (A.4)$$

is the spin alignment determined by intersystem crossing and phosphorescence rates (neglecting any dynamic processes). In terms of r_i^0 , the values of r_i^s are

$$r_1^s = \frac{r_3^0 \Delta\omega \omega_1 k_x k_y}{\Delta\omega^2 k_x k_y + k_A^2 \omega_1^2} \quad (A.5a)$$

$$r_2^s = \frac{-r_3^0 \omega_1 k_x k_y k_A}{\Delta\omega^2 k_x k_y + k_A^2 \omega_1^2} \quad (A.5b)$$

$$r_3^s = \frac{r_3^0 \Delta\omega^2 k_x k_y}{\Delta\omega^2 k_x k_y + k_A^2 \omega_1^2} \quad (A.5c)$$

Equations (A.1) and (A.5) have been simplified by assuming that $\omega_1^2/k_x k_y \gg 1$, $\Delta\omega \gg k_A$, and $\Gamma \gg k_D$.

Following through the same procedure as in Section III.F.1, we obtain

$$\begin{aligned}
 r_3(2\tau) = & \frac{e^{-2k_A\tau}}{\Gamma^4} \left\{ \begin{aligned} & r_1^S \left[\Delta\omega\omega_1\Gamma^2\sin^2\theta + 4\omega_1\Delta\omega(\omega_1^2 - \Delta\omega^2)\sin^4\frac{\theta}{2} \right] \\ & + r_2^S \left[\Gamma^3\omega_1\sin\theta\cos\theta - 2(\omega_1\Delta\omega^2\Gamma - \Gamma\omega_1^3)\sin^3\frac{\theta}{2}\cos\frac{\theta}{2} \right. \\ & \quad \left. - 2\Gamma^3\omega_1\sin\frac{\theta}{2}\cos^3\frac{\theta}{2} \right] \\ & + (r_3^0 - r_3^S) \left[(\Delta\omega^4 - 6\omega_1^2\Delta\omega^2 + \omega_1^4)\sin^4\frac{\theta}{2} + \omega_1^2\Gamma^2\sin^2\theta \right. \\ & \quad \left. + \Gamma^4\cos^4\frac{\theta}{2} + 2(\Delta\omega^2\Gamma^2 - \Gamma^2\omega_1^2)\sin^2\frac{\theta}{2}\cos\frac{\theta}{2} \right] \end{aligned} \right\} \\
 & + \frac{e^{-k_A\tau}}{\Gamma^2} \left\{ \begin{aligned} & -2(r_1^S + r_1^S(\tau))\omega_1\Delta\omega\sin^2\frac{\theta}{2} \\ & - (r_2^S + r_2^S(\tau))\Gamma\omega_1\sin\theta \\ & + (r_3^S - r_3^S(\tau))[\Gamma^2\cos^2\frac{\theta}{2} + (\Delta\omega^2 - \omega_1^2)\sin^2\frac{\theta}{2}] \end{aligned} \right\} + r_3^S(\tau) \quad .
 \end{aligned}
 \tag{A.6}$$

where $r_i^S(\tau)$ are the steady state values of r_i with the field "on" and initial values of $r_1(\tau)$, $r_2(\tau)$, and $r_3(\tau)$.

ACKNOWLEDGMENTS

I would like to express my deep appreciation and gratitude to all of my friends, scientific and otherwise, who gave me understanding and support during the course of this work. Without you, this thesis would never have been completed.

I wish to thank Henry Brenner for illuminating discussions on the material in Chapter III. I also acknowledge my two fellow classmates -- Mark Lewellyn, for shooting the bovine fecal material with me when science was tedious (but straightforward), and Alan Burns, for acclimating me to West Coast living and sitting next to me for 4½ years.

In particular, I want to express my love for all the Brocks. You have indeed provided a "home away from home" and I am very proud to be considered as a part of the family. Living for two years with John (Frank, Boyd Granger, Bojimbo, Buck Microwave, Broccoli) Brock was a uniquely high experience I will always remember.

Finally, I am indebted to Professor Charles B. Harris for suggesting these areas of research to me and for providing scientific and financial support.

This work was supported in part by the Materials and Molecular Research Division of the Lawrence Berkeley Laboratory under the auspices of the U.S. Department of Energy, and in part by a grant from the National Science Foundation.

REFERENCES

1. F. Bloch, Phys. Rev. 70, 460 (1946).
2. E. L. Hahn, Phys. Rev. 80, 580 (1950).
3. H. C. Torrey, Phys. Rev. 76, 1059 (1949).
4. H. Y. Carr and E. M. Purcell, Phys. Rev. 94, 630 (1954).
5. S. Meiboom and D. Gill, Rev. Sci. Instr. 29, 688 (1958).
6. I. Solomon, Phys. Rev. Lett. 2, 301 (1959).
7. I. Solomon, C. R. Acad. Sci. Paris 248, 92 (1959).
8. C. Slichter and W. Holton, Phys. Rev. 122, 1701 (1961).
9. A. Anderson and S. Hartmann, Phys. Rev. 128, 2023 (1962).
10. J. S. Waugh, C. H. Wang, L. M. Huber, and R. L. Vold, J. Chem. Phys. 48, 662 (1968).
11. U. Haeberlen and J. S. Waugh, Phys. Rev. 175, 453 (1968).
12. G. N. Lewis and M. Kasha, J. Am. Chem. Soc. 66, 2100 (1944).
13. G. N. Lewis and M. Calvin, J. Am. Chem. Soc. 67, 1232 (1945).
14. J. Brossel and F. Bitter, Phys. Rev. 86, 308 (1952).
15. S. Geschwind, G. Devlin, R. Cohen, and S. Chinn, Phys. Rev. 137, A1087 (1965).
16. J. Schmidt, I. Hesselman, M. DeGroot, and J. van der Waals, Chem. Phys. Lett. 1, 434 (1967).
17. S. McGlynn, T. Azumi, and M. Kinoshita, Molecular Spectroscopy of the Triplet State (Prentice Hall, New Jersey, 1969).
18. C. A. Hutchison, Jr., J. V. Nicholas, and G. W. Scott, J. Chem. Phys. 53, 1906 (1970).
19. M. J. Buckley and C. B. Harris, J. Chem. Phys. 56, 137 (1972).

20. J. Schmidt, D. A. Anthéunis, and J. H. van der Waals, Mol. Phys. 22, 1 (1971).
21. D. S. Tinti, M. A. El-Sayed, A. H. Maki, and C. B. Harris, Chem. Phys. Lett. 3, 343 (1969).
22. A. H. Francis and C. B. Harris, J. Chem. Phys. 57, 1050 (1972).
23. C. B. Harris, J. Chem. Phys. 54, 972 (1971).
24. J. Schmidt, W. G. van Dorp, and J. H. van der Waals, Chem. Phys. Lett. 8, 345 (1971).
25. W. G. Breiland, A. Pines, and C. B. Harris, Phys. Rev. Lett. 30, 158 (1973).
26. C. B. Harris, R. L. Schlupp, and H. Schuch, Phys. Rev. Lett. 30, 1019 (1973).
27. M. D. Fayer and C. B. Harris, Chem. Phys. Lett. 25, 149 (1974).
28. M. T. Lewellyn, A. H. Zewail, and C. B. Harris, J. Chem. Phys. 63, 3687 (1975).
29. M. E. Tarrasch, C. R. Chen, and C. B. Harris, Chem. Phys. Lett. 48, 579 (1977).
30. D. A. Zwemer, H. C. Brenner, and C. B. Harris, in press.
31. H. C. Brenner, J. C. Brock, and C. B. Harris, J. Chem. Phys. 60, 4448 (1974).
32. H. C. Brenner, J. C. Brock, M. D. Fayer, and C. B. Harris, Chem. Phys. Lett. 33, 471 (1975).
33. R. P. Feynman, F. L. Vernon, Jr., and R. W. Hellwarth, J. Appl. Phys. 28, 49 (1957).
34. U. Fano, Rev. Mod. Phys. 29, 74 (1957).
35. H. C. Brenner, J. C. Brock, and C. B. Harris, Chem. Phys. xx, xxxx (1978).

36. W. G. Breiland, M. D. Fayer, and C. B. Harris, Phys. Rev. A13, 383 (1976).
37. I. I. Rabi, N. F. Ramsey, and J. Schwinger, Rev. Mod. Phys. 26, 167 (1954).
38. B. Herzog and E. L. Hahn, Phys. Rev. 103, 148 (1956).
39. W. B. Mims, K. Nassau, and J. D. McGee, Phys. Rev. 123, 2059 (1961).
40. J. R. Klauder and P. W. Anderson, Phys. Rev. 125, 912 (1962).
41. P. Hu and S. R. Hartmann, Phys. Rev. B9, 1 (1974).
42. A. G. Redfield, Phys. Rev. 98, 1767 (1955).
43. W. G. Breiland, Ph.D. Thesis, University of California, Berkeley (1975).
44. P. Dunnion and C. N. Trumbore, J. Am. Chem. Soc. 87, 4211 (1965).
45. A. L. Shain, W. T. Chiang, and M. Sharnoff, Chem. Phys. Lett. 16, 206 (1972).
46. A. L. Shain and M. Sharnoff, Chem. Phys. Lett. 16, 503 (1972).
47. A. L. Shain and M. Sharnoff, Chem. Phys. Lett. 22, 56 (1973).
48. C. J. Gorter and J. H. Van Vleck, Phys. Rev. 72, 1128 (1947).
49. J. H. Van Vleck, Phys. Rev. 74, 1168 (1948).
50. N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. 73, 679 (1948).
51. P. W. Anderson, J. Phys. Soc. Jap. 9, 316 (1954).
52. R. Kubo and K. Tomita, J. Phys. Soc. Jap. 9, 888 (1954).
53. H. M. McConnell, J. Chem. Phys. 28, 430 (1958).
54. C. A. van't Hof and J. Schmidt, Chem. Phys. Lett. 36, 460 (1975).
55. A. Abragam, The Principles of Nuclear Magnetism (Oxford University Press, London, 1961).

56. R. H. Webb, Rev. Sci. Instr. 33, 732 (1962).
57. U. Haeblerlen, High Resolution NMR in Solids: Selective Averaging, Advances in Magnetic Resonance, Supplement 1 (Academic Press, New York, 1976).
58. M. T. Lewellyn, private communication.
59. W. G. Breiland, H. C. Brenner, and C. B. Harris, J. Chem. Phys. 62, 3458 (1975).
60. M. Tinkham, Group Theory and Quantum Mechanics (McGraw-Hill, Inc., New York, 1964).
61. U. Haeblerlen, J. D. Ellet, Jr., and J. S. Waugh, J. Chem. Phys. 55, 53 (1971).
62. A. Pires and J. S. Waugh, J. Mag. Res. 8, 354 (1972).
63. H. Veenvliet and D. A. Wiersma, Chem. Phys. 8, 432 (1975).
64. C. A. van't Hof and J. Schmidt, Chem. Phys. Lett. 36, 457 (1975).
65. M. D. Fayer and C. B. Harris, Phys. Rev. B9, 748 (1974).
66. R. V. Nazumann, Ph D. Thesis, University of California, Berkeley (1947).
67. C. A. van't Hof, J. Schmidt, P. J. F. Verbeek, and J. H. van der Waals, Chem. Phys. Lett. 21, 437 (1973).
68. C. A. van't Hof and J. Schmidt, Chem. Phys. Lett. 42, 73 (1976).
69. J. Schmidt, Chem. Phys. Lett. 14, 411 (1972).
70. M. T. Lewellyn, unpublished results.
71. M. E. Tarrasch, unpublished results.