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EXCITED STATE ENERGY TRANSFER STUDIES USING ELECTRON SPIN COHERENCE

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EXCITED STATE ENERGY TRANSFER STUDIES USING ELECTRON SPIN COHERENCE

John Conarroe Brock
(Ph. D. thesis)

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For Reference
Not to be taken from this room
This work is dedicated to my amazing family - to my parents for the constant love and support they have provided, and to my brothers for keeping me in touch with the important things in life.

Imi 'ike na 'opio
A me kokua o ka Haku
Ka malamalama no 'oukou
Mau loa e.

...from a song by Palani Vaughan
EXCITED STATE ENERGY TRANSFER STUDIES
USING ELECTRON SPIN COHERENCE

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EXCITED STATE ENERGY TRANSFER STUDIES
USING ELECTRON SPIN COHERENCE

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ABSTRACT

The use of electron spin coherence techniques for examining the dynamics of excited states subject to energy transfer processes is described. Equations detailing the time evolution of a coherently coupled two-level system are presented and developed to include the effects of feeding and decay processes on coherence induced in an excited state ensemble.

Various mechanisms responsible for a loss of phase coherence in an excited state ensemble are identified and discussed, including the effects of energy exchange between systems that are not translationally equivalent. Application of these considerations to several coherence experiments reveals that non-equivalent exchange processes produce a loss of coherence independent of any interactions between the excitation and its environment. One coherence experiment, spinlocking, is discussed in detail, along with a model describing the effect of multiple energy transfer routes on the decay of the spinlocked coherent component.

Also described is electron spin ordering, a new approach for examining electronically excited states. Induced by adiabatic demagnetization in the rotating frame (ADRF), electron spin ordering is capable
of monitoring certain features of the time evolution of environments surrounding an ensemble of excitations without the use of a coherent component subject to dephasing. A model incorporating kinetic features of excited state ensembles is developed to characterize the decay of the ordered state for both on and off resonance applications. Experimental considerations involved with electron spin ordering are also discussed.

To illustrate the above considerations, spinlocking and electron spin ordering are used to study exciton transport between localized isotopic impurity states via the one-dimensional triplet exciton band of 1,2,4,5 d$_2$-tetrachlorobenzene. Measurements of the rate constant for trap to trap migration as a function of both temperature and trap concentration are presented, along with a model for calculating the quantum yield of excitons that migrate to different trap sites upon thermal promotion.
Chapter I

I. INTRODUCTION

When this work was first started the major emphasis was directed towards the examination of the dynamics of various aspects of exciton transport in imperfect solids. This is still the case today, however during the course of the project it became increasingly clear to the author that the coherence techniques being developed and expanded upon for this work were remarkably powerful methods for examining properties of excited states in general and that a presentation of these techniques and their applications to a particular problem would be of considerable value.

As an experimental field, the application of magnetic resonance coherence experiments to excited states is still under development, both in experimental finesse and interpretation of results. Thus it is not the intention of this work to present a comprehensive "cook book" for the use of coherence in excited states; rather it is meant to provide a foundation of general considerations that can be expanded upon to meet the physical, experimental, and interpretive requirements of a particular problem. In addition, it is hoped that the use of a specific application as an illustration will serve to demonstrate the many pitfalls and blind alleys that have been encountered in the course of developing these experiments and aid future workers in identifying and avoiding them.

HISTORICAL CONTEXT

Although manifestations of coherent coupling in excited states were discovered many years ago, (1-5) it was not until relatively recently that magnetic resonance coherence techniques were applied to
ensembles of excited states. Harris (6) initiated the development by considering the ramifications of coherently coupling magnetic sublevels in triplet states. Shortly thereafter, optically detected transient nutations (7) were observed, marking the first experimental application of coherence techniques as a means for examining excited triplet states. Subsequently spin echoes (8) and Carr-Purcell-Meiboom-Gill multiple pulse echoes (9) were observed in excited triplet states using conventional detection methods.

In 1973, a new method for detection, the probe pulse, (10) was developed permitting coherent components of a triplet ensemble to be displayed as a time-dependent population difference between the coupled levels. Thus coherence information could be obtained in double resonance experiments, (11-12) frequently providing an increase of several orders of magnitude in sensitivity over conventional transverse coil methods. Since that time, a number of coherence experiments, including those described in this work, have been performed in triplet states using this method for optical detection. These include rotary precessions, (13) spinlocking, (14, 15) free-induction decay (10, 16) and electron spin ordering induced by adiabatic demagnetization in the rotating frame. (17)

DEVELOPMENT

In order to acquaint the reader with some concepts that will be drawn upon throughout the work, the presentation is begun with some general considerations. Chapter II presents some formalism associated with coherence in excited states, while Chapter III concentrates on
mechanisms that produce a loss of excited state coherence.

Using this material as background, a more detailed examination of particular techniques is presented in the subsequent chapters. Chapter IV focuses on spinlocking, (14,18-19) a technique of considerable importance for examining inhomogeneously broadened systems. Chapter V details a different and exciting approach to coherence. This technique, electron spin ordering by adiabatic demagnetization in the rotating frame (ADRF), provides unique information concerning the time development of the local environments around an excited state. A specific application of ADRF and spinlocking to the study of the dynamics of localized and delocalized states interacting in molecular solids is presented in Chapter IV, along with a discussion of interpretive problems encountered in the application of coherence techniques to systems with multiple decay channels. Experimental methods and equipment necessary to carry out these experiments in excited triplet states are also detailed in this last chapter.
Chapter II

Coherence in Excited States: General Considerations

In this chapter, the well-known mathematical formalism and a geometric representation of this formalism are presented to describe the time development of a coherently coupled two level system. Initially the presentation will deal with states that are not fed from or decay to an outside population reservoir, the case for example in nuclear magnetic resonance. Feeding and decay processes affecting the time dependent populations of the coupled levels are then considered to permit the extension of the formalism to excited states. Additional corrections due to spin-spin and spin-lattice relaxation are discussed briefly along with a presentation of the "probe pulse" method for explicitly displaying coherence information as a population difference between the coupled levels.

In the following discussion, the driving field coupling the levels is treated classically and it is assumed that the wavelength of the field is much larger than the dimensions of the ensemble of two level systems. Furthermore, it is assumed that the driving field is of sufficient strength that any intrinsic fields induced in the sample are negligible by comparison.

Basic Theory

Consider an ensemble of two level systems characterized by the intrinsic time-independent hamiltonian $\mathcal{H}_0$ and its associated eigenvector spectrum $|X>$ and $|Y>$. At any time, the state of a particular
system \( j \) may be represented by the superposition,

\[
\psi_j(t) = a_j(t)e^{-(i\hbar\alpha)E_x t}|x\rangle + b_j(t)e^{-(i\hbar\alpha)E_y t}|y\rangle.
\]

The equation of motion describing the system is

\[
i\hbar\dot{\psi}_j = \begin{pmatrix} \mathcal{H}_0 & \mathcal{V}(t) \end{pmatrix}\psi_j,
\]

where \( \mathcal{H} = \mathcal{H}_0 + \mathcal{V}(t) \), and \( \mathcal{V}(t) \), the perturbation associated with the oscillating driving field, is represented by

\[
\mathcal{V}(t) = \hbar\tilde{\omega}_1 \cdot \tilde{A} \cos(\omega t + \phi).
\]

\( \tilde{\omega}_1 \) represents the strength and orientation of the driving field, while \( \tilde{A} \) represents the appropriate quantum mechanical operator that couples \( |x\rangle \) and \( |y\rangle \). As long as \( \mathcal{V}(t) \) is large compared to interactions affecting individual members of the ensemble, Equations 1 and 2 are identical for all \( j \) and represent ensemble averages.

It has been demonstrated many times (20) that for perturbations of the form of Equation 3, a transformation to a representation rotating at the perturbation frequency, \( \omega \), is particularly useful. This is accomplished by applying the unitary operator

\[
U_j^{-1} = \exp(i\tilde{\omega}_1 t/h\omega_0),
\]
where \( \hbar \omega_0^j \) is the energy splitting \( (E_Y - E_X)^j \) between the two states of the \( j \)th system. The transformed wavefunction becomes

\[
\psi_j(t) = U^{-1} \psi_j(t) = a_j(t)e^{-i(\omega_0^j - \omega)E_X^j t/\hbar \omega_0^j} |X> - i(\omega_0^j - \omega)E_Y^j t/\hbar \omega_0^j + b_j(t)e^{i(\omega_0^j \omega)E_Y^j t/\hbar \omega_0^j} |Y>
\]

and the transformed Hamiltonian is given by

\[
\hat{\mathcal{H}}^* = \mathcal{H}_0^j [1 - (\omega/\omega_0^j)] + U^{-1} V(t) U.
\]

Replacing \( \psi_j(t) \) in Equation 2 by \( U_j \psi_j(t) \), performing the differentiation, collecting terms, and projecting out the \( |Y> \) component yields

\[
\dot{b}_j(t) = b(t)E_Y^j [1 - (\omega/\omega_0^j)] + (\hbar \omega_Y/2) a(t) \left( e^{-i\phi} e^{i(2\omega t + \phi)} \right) \times <Y|A|X>.
\]

Only the stationary terms corresponding to one circularly polarized component of \( V(t) \) are important; hence

\[
\dot{b}_j(t) = \frac{-i b(t)}{\hbar} E_Y^j [1 - (\omega/\omega_0^j)] + \frac{i \omega_Y}{2} a(t) e^{-i\phi} <Y|A|X>.
\]
Similarly,

\[ (8b) \quad \dot{a}_j(t) = -\frac{ia(t)}{h} E_X \left[ 1 - \left( \frac{\omega}{\omega_{o_j}} \right) \right] - \frac{i\omega_j}{2} b(t) e^{i\phi} <X|A|Y>. \]

Choosing the zero of energy to lie halfway between \( E_X \) and \( E_Y \) and defining \( \Delta \omega_j = \omega_{o_j} - \omega \), i.e., the difference between the resonant frequency of the jth system and the driving field frequency, one can integrate Equations 8 to get the rotating frame coefficients,

\[ (9a) \quad b(t) = b^0 \cos(\omega_j/2)t + \left( a^0 e^{-i\phi} - i\Delta \omega_j b^0 \right) \frac{\sin(\omega_j/2)t}{\omega}, \]

\[ (9b) \quad a_j(t) = a^0 \cos(\omega_j/2)t + \left( i\Delta \omega_j a^0 - b^0 e^{i\phi} \right) \frac{\sin(\omega_j/2)t}{\omega}, \]

where \( \omega_j = (\omega_1^2 + \Delta \omega_j^2)^{1/2} \) and the matrix elements have been chosen to correspond to magnetic dipole transitions. Returning to the laboratory frame by operating with \( U \) results in multiplying the above coefficients by the energy phase factors associated with their respective states, as in Equation 1.

The terms \( aa^* \) and \( bb^* \) are the same in both representations and are the occupation probabilities of the states \( |X> \) and \( |Y> \) respectively, while the cross terms \( ab^* \) and \( ba^* \) display information about coherence in the ensemble. Since \( ab^* \) and \( ba^* \) contain phase factors that depend on the energy difference of the two levels, it is apparent that random fluctuations of the energies of these states will cause the ensemble averages <\( ab^* \) > and <\( ba^* \) > to be zero, the
phases being randomized by the small fluctuations in the energies of each system. Thus even though each system \( j \) may have non-zero cross terms, the ensemble average of the phase factors is in general zero, and the ensemble displays no coherent component. If a perturbation that is strong relative to the interactions responsible for the energy fluctuations is applied, the energy difference is essentially constant throughout the ensemble, the ensemble average of the phase factors is non-zero, and the ensemble displays a coherent component. If the perturbation is removed, the phase factors again start to interfere or "dephase" in a characteristic time that reflects the range of energy differences between the levels in the ensemble, i.e., the linewidth of the transition between the states. This energy spread may result from interactions of the systems with their local environments or may be due to lifetime broadening of the energy levels. Only an ensemble of infinitely long-lived levels completely decoupled from their surroundings can display a non-decaying coherent component in the absence of a coherent perturbation.

A Geometric Picture

A particularly elegant geometrical interpretation of the above formalism was first developed by Feynman, Vernon and Hellwarth (FVH) (21), who constructed a vector \( \vec{r} \) whose components in the laboratory frame are given by
(10a) \[ r_1' = (ba e^{-i\omega_0 t} + ab e^{i\omega_0 t})/(aa^* + bb^*) \]

(10b) \[ r_2' = i(ba e^{-i\omega_0 t} - ab e^{i\omega_0 t})/(aa^* + bb^*) \]

(10c) \[ r_3' = r_Y' - r_X' \]

where \( r_Y' = bb^*(aa^* + bb^*) \) and \( r_X' = aa^*(aa^* + bb^*) \).

The time evolution of the system can then be represented by a vector torque equation of the form,

\[ \dot{\mathbf{r}}' = \mathbf{\Omega} \times \mathbf{r}' \]

where the components of \( \mathbf{\Omega} \) are given by

(12a) \[ \Omega_1' = (V_{XY} + V_{YX})/\hbar \]

(12b) \[ \Omega_2' = (V_{YX} - V_{XY})/\hbar \]

(12c) \[ \Omega_3' = \omega_0. \]

This geometric representation of the equation of motion permits the time evolution of an ensemble to be viewed as a vector precessing around an axis defined by the effective field \( \mathbf{\Omega}' \). Note that \( r_3' \) is just the population difference of the levels, while \( r_1' \) and \( r_2' \) are the coherent components. For a two level system, these components
correspond to a detectable "pseudo magnetization"; indeed it is just
\( r_1 \) and \( r_2 \), the "in-plane" components, that are sensed by the transverse
coils in conventionally detected magnetic resonance.

As mentioned before, it is convenient to view this vector in
a representation rotating at the perturbation frequency \( \omega \). In
this case, a rotating \( \mathbf{r} \) is defined as above using the rotating frame
coefficients (no phase factors) defined in Equations 9a and 9b, while the
effective field components are transformed to

\[
\Omega_1 = (e^{i\omega t} V_{yx} + e^{-i\omega t} V_{xy})/h
\]

(13) \[
\Omega_2 = (e^{i\omega t} V_{yx} - e^{-i\omega t} V_{xy})/h
\]

\[
\Omega_3 = \omega_0 - \omega = \Delta \omega.
\]

In this representation, the in-plane coherent components rotate at
the off-resonance frequency \( \Delta \omega \), while \( r_3 \) is left unaltered as before.\n\( \Omega_3 \) now corresponds to a driving field of magnitude \( \Delta \omega \) along \( r_3 \), and
is referred to as the local field.

Since the in-plane components \( r_1 \) and \( r_2 \) will precess with
frequency \( \Omega_3 \), the loss of coherence can be visualized as a dephasing
of the in-plane components of members of the ensemble due to the
different local fields \( \Delta \omega_j \) and hence precessional frequencies
experienced by the various systems. The vector sums \( \frac{1}{N} \sum_j r_1 \) or
\( \frac{1}{N} \sum_j r_2 \) representing the ensemble average of the coherent components
will decay to zero in a time governed by the frequency range of the $\Delta \omega_j$ terms. This is illustrated in Figure 1.

**Feeding and Decay**

The above presentation is well known and has been developed by many workers. However, it is not applicable to excited states which are subject to feeding and decay processes. In a comprehensive study of this case, Breiland, Fayer, and Harris (22,23) explicitly considered the effect of feeding and decay on coherence in excited states, as well as the effects of various relaxation mechanisms on the $r$ vector components. Although this work was couched in a density matrix formulation, it is easily treated in a Schrödinger representation as follows.

Decay processes are incorporated into the model by allowing the state amplitude terms $a(t)$ and $b(t)$ to decay exponentially, with the condition that $aa^*$ decay exponentially with a rate constant reflecting the lifetime of the state $|X>$ and a similar requirement for $bb^*$. This is accomplished by adding decay terms to Equations (8) such that

$\dot{a}(t) = a^0 \cos(\bar{\omega}/2)t + \left[ i\Delta \omega a^0 - b^0 e^{i\phi}/\bar{\omega} \right] \sin(\bar{\omega}/2)t - k_x/2
(14)$

$\dot{b}(t) = b^0 \cos(\bar{\omega}/2)t + \left[ a^0 e^{-i\phi} - i\Delta \omega b^0/\bar{\omega} \right] \sin(\bar{\omega}/2)t - k_y/2,$

where $k_x$ and $k_y$ are the decay rate constants for states $|X>$ and $|Y>$ respectively. It should be noted that $r_1$ and $r_2$ will also decay, displaying an average decay constant $k_A = (k_x + k_y)/2$, i.e. decay from the superposition state is accounted for.
A. The effective driving field in the rotating frame

B. Dephasing in the $r_1 - r_2$ plane caused by free precession about the local field

Fig. 1
Feeding, however, can only occur to the eigenstates $|X\rangle$ and $|Y\rangle$, (22) since entering population does not experience the perturbation until it enters one of these states. Let $r_z^0(0)(z=1,2,3,x,y)$ be the component at $t = 0$. Then at $t = \tau$,

$$r_z(\tau) = r_z^0(\tau) + C_y \int_0^\tau r_y(t)dt + C_x \int_0^\tau r_x(t)dt$$

where $C_y$ and $C_x$ are feeding rates to the states $|Y\rangle$ and $|X\rangle$, and $r_z^L(t)$ ($L = x,y$) is the time dependent contribution of $r_z^L$ to $r_z$. Since each $r$ component will explicitly depend on both $r_y$ and $r_x$, the term $r_z^L(t)$ is just the coefficient of $r_z^L$ in the decay expression for the $z^{th}$ $r$ vector component.

Integrating Equation (14), substituting into Equation (10) and calculating the feeding coefficients produces equations describing the full time evolution of $\mathbf{r}$ in the absence of spin-lattice or spin-spin relaxation. Defining

$$k_D = \frac{(k_x - k_y)}{2} \quad \alpha = Re\{\omega_1^2 + (\omega_\Delta + i k_D)^2\}^{1/2}$$

$$k_A = \frac{(k_x + k_y)}{2} \quad \beta = Im\{\omega_1^2 + (\omega_\Delta + i k_D)^2\}^{1/2}$$

$$A = \left[1/(k_A^2 + \alpha^2)\right] \left[k_A + e^{-k_A \tau}(\alpha \sin&\tau - k_A \cos&\tau)\right]$$

$$B = \left[1/(k_A^2 + \alpha^2)\right] \left[\alpha - e^{-k_A \tau}(k_A \sin&\tau + \alpha \cos&\tau)\right]$$

$$C = \left[1/(k_A^2 - \beta^2)\right] \left[k_A - e^{-k \tau}(\beta \sin&\beta \tau + k_A \cosh&\beta \tau)\right]$$

$$D = \left[1/(k_A^2 - \beta^2)\right] \left[\beta - e^{-k \tau}(k_A \sinh&\beta \tau + \beta \cosh&\beta \tau)\right]$$
results in these equations for the $r$ vector components:

$$\begin{align*}
\mathbf{r}_1(t) &= \frac{e^{-k_0 t}}{2(\alpha^2 + \beta^2)} \left\{ r_1^0 (\alpha^2 + \beta^2 + k_D^2 + \Delta \omega^2) \ight. \\
&\quad + \omega_1^2 (ba^* e^{2i\phi} + ab^* e^{-2i\phi}) \\
&\quad + 2\omega_1 (k_D (r_x^0 + r_y^0) \cos \phi + \Delta \omega (r_x^0 - r_y^0) \sin \phi) \cos \omega t \\
&\quad - \omega_1 (r_x^0 (\alpha^2 + \beta^2 - k_D^2 - \Delta \omega^2) - \omega_1^2 (ba^* e^{2i\phi} + ab^* e^{-2i\phi}) \\
&\quad - 2\omega_1 (r_x^0 + r_y^0) \cos \phi + \Delta \omega (r_x^0 - r_y^0) \sin \phi) \cosh \beta t \\
&\quad - 2(r_x^0 (\alpha^2 + \beta^2 - k_D^2 - \Delta \omega^2) - \omega_1 (r_x^0 - r_y^0) \cos \phi \\
&\quad + (r_x^0 + r_y^0) \sin \phi \} \} + \frac{\omega_1}{\alpha^2 + \beta^2} \left\{\begin{array}{l}
\mathbf{D}(\mathbf{C}_x + \mathbf{C}_y) \\
\mathbf{A} - \mathbf{C} + (\mathbf{C}_x - \mathbf{C}_y) (\mathbf{A} - \mathbf{C}) + (\mathbf{C}_x + \mathbf{C}_y) (\mathbf{A} + \mathbf{B}) \end{array}\right\} \\
&\quad \times \sin \omega t + 2\omega_1 (\alpha k_D - \Delta \omega) + \omega_1 ((r_x^0 - r_y^0) \cos \phi \\
&\quad + (r_x^0 + r_y^0) \sin \phi) \} \} \\
\mathbf{r}_2(t) &= \frac{e^{-k_0 t}}{2(\alpha^2 + \beta^2)} \left\{ r_2^0 (\alpha^2 + \beta^2 + k_D^2 + \Delta \omega^2) - i$}$}
$$

(16)
(16) continued

\[ \begin{align*}
&+ 2l r_{1y}(\Delta \omega + \beta k_D) + \omega_1((r_{xy}^0 - r_{xy}^0) \alpha \sin \phi + (r_{xy}^0 + r_{xy}^0) \beta \cos \phi) \sin \alpha t \\
&- 2l r_{1y}(k_D \alpha - \Delta \omega B) + \omega_1((r_{xy}^0 + r_{xy}^0) \alpha \cos \phi - (r_{xy}^0 - r_{xy}^0) \beta \sin \phi) \sinh \beta t \\
&+ \frac{\omega_1}{(\alpha^2 + \beta^2)} \{ \Delta \omega (C_y - C_x)(A - C) + (C_x + C_y)(\beta B - \alpha D) \} \cos \phi \\
&+ \{ k_D(C_x + C_y)(A - C) + (C_x - C_y)(\alpha B + \beta D) \} \sin \phi \}
\end{align*} \]

\[ r_{xy}(t) = \frac{e^{-k_A t}}{2(\alpha^2 + \beta^2)} \left\{ r_{xy}^0(\alpha^2 + \beta^2 - k_D^2 - \Delta \omega^2) - r_{xy}^0 \omega_1 \right. \\
- \omega_1(k_D(yx^* e^{i \phi} + xy^* e^{-i \phi}) - i \Delta \omega (yx^* e^{i \phi} - xy^* e^{-i \phi})) \cos \alpha t \\
+ [r_{xy}^0(\alpha^2 + \beta^2 k_D^2 + \Delta \omega^2) + r_{xy}^0 \omega_1^2 + \omega_1 r_{xy}^0 k_D(yx^* e^{i \phi} + xy^* e^{-i \phi}) \\
- i \Delta \omega (yx^* e^{i \phi} - xy^* e^{-i \phi})] \cosh \beta t \\
+ \{ 2r_{xy}^0(\alpha k_D - \Delta \omega B) + \omega_1(\beta(yx^* e^{i \phi} - xy^* e^{-i \phi}) + \alpha(yx^* e^{i \phi} + xy^* e^{-i \phi}) \} \sin \alpha t \}
\end{align*} \]

\[ + [2r_{xy}^0(\Delta \omega + \beta k_D) + \omega_1(\beta(yx^* e^{i \phi} + xy^* e^{-i \phi})) - i \alpha(yx^* e^{i \phi} - xy^* e^{-i \phi})] \sinh \beta t \\
\]

\[ + \frac{C_y}{2(\alpha^2 + \beta^2)} \left\{ (\alpha^2 + \beta^2 - k_D^2 - \Delta \omega^2) A + 2(\alpha k_D - \Delta \omega B) B + (\alpha^2 + \beta^2 + k_D^2 + \Delta \omega^2) C + 2(\alpha \Delta \omega + k_D \beta D) \right\} \\
+ \frac{C_x}{2(\alpha^2 + \beta^2)} \left\{ \omega_1^2 (C - A) \right\} \]
Continued

\[
r_x(t) = e^{-\frac{k_A t}{2(\alpha^2 + \beta^2)}} \left\{ \left[ r_x^0(\alpha^2 + \beta^2 - k_D^2 - \Delta \omega^2) - r_y^0 \omega_1^2 \right] - \omega_1 \left( k_D (yx e^{i\phi} + xy e^{-i\phi}) + i \Delta \omega (yx e^{i\phi} - xy e^{-i\phi}) \right) \right. \\
+ i \Delta \omega (yx e^{i\phi} - xy e^{-i\phi}) \right\} \cos \Phi + \{ r_x^0(\alpha^2 + \beta^2 + k_D^2 + \Delta \omega^2) + r_y^0 \omega_1^2 \left( k_D (yx e^{i\phi} + xy e^{-i\phi}) + i \Delta \omega (yx e^{i\phi} - xy e^{-i\phi}) \right) \} \cosh \beta t \\
- \{2r_x^0(\alpha k_D - \Delta \omega \beta) + \omega_1(\alpha (yx e^{i\phi} + xy e^{-i\phi}) - i \beta (yx e^{i\phi} - xy e^{-i\phi})) \} \sin \Phi \\
- \{2r_x^0(\Delta \omega \alpha + \beta k_D) + \omega_1(\beta (yx e^{i\phi} + xy e^{-i\phi}) + i \alpha (yx e^{i\phi} - xy e^{-i\phi})) \} \sin \beta t \} \\
+ \frac{C_x}{2(\alpha^2 + \beta^2)} \left\{ (\alpha^2 + \beta^2 - k_D^2 - \Delta \omega^2)A - 2(k_D \alpha - \Delta \omega \beta)B \\
+ (\alpha^2 + \beta^2 + k_D^2 + \Delta \omega^2)C - 2(\Delta \omega \alpha + k_D \beta)D \right\} \\
+ \frac{C_y}{2(\alpha^2 + \beta^2)} \left\{ \omega_1^2(C - A) \right\}
\]
(16) Continued

\[ r_3(t) = \frac{e^{-k \Delta t}}{2(\alpha^2 + \beta^2)} \left\{ r_3^0 (\alpha^2 + \beta^2 - k_D^2 - \Delta \omega^2 + \omega_1^2) + 2i\Delta \omega_1 (yx^* e^{i\phi} - xy^* e^{-i\phi}) \right\} \cos \alpha t \\
+ [r_3^0 (\alpha^2 + \beta^2 + k_D^2 + \Delta \omega^2 - \omega_1^2) - 2i\Delta \omega_1 (yx^* e^{i\phi} - xy^* e^{-i\phi})] \cosh \beta t \\
+ 2I (k_D \alpha - \Delta \omega \beta)(r_{x}^0 + r_{y}^0) + \omega_1 \alpha (yx^* e^{i\phi} + xy^* e^{-i\phi}) \sin \alpha t \\
+ 2I (\Delta \omega \alpha + \beta k_D)(r_{x}^0 + r_{y}^0) + \omega_1 \beta (yx^* e^{i\phi} + xy^* e^{-i\phi}) \sin \beta t \right\} \\
+ \frac{C_y}{2(\alpha^2 + \beta^2)} \left\{ \frac{\alpha^2 + \beta^2 - k_D^2}{2} + \frac{\Delta \omega^2 + \omega_1^2}{2} \right\} A + 2(\alpha k_D - \Delta \omega \beta)B \\
+ (\alpha^2 + \beta^2 + k_D^2 + \Delta \omega^2 - \omega_1^2) C + 2(\Delta \omega \alpha + k_D \beta)D \right\} \\
+ \frac{C_x}{2(\alpha^2 + \beta^2)} \left\{ \left( k_D^2 + \Delta \omega^2 - \alpha^2 + \beta^2 - \omega_1^2 \right) A + 2(k_D \alpha - \Delta \omega \beta)B \\
+ (\omega_1^2 - \alpha^2 - \beta^2 - k_D^2 - \Delta \omega^2) C + 2(\Delta \omega \alpha + k_D \beta)D \right\} \}
Relaxation

The above treatment ignores $T_1$ and $T_2$ relaxation processes, not only for simplicity and clarity, but also because these processes can be unimportant in certain applications of coherence techniques. To date, coherence experiments applied to ensembles of triplet states are limited to the solid state at low temperature where spin-lattice relaxation is relatively unimportant. $T_2$ processes will always produce a loss of coherence, even in homogeneous lines, and cannot in general be neglected unless the perturbation (assumed strong relative to the couplings responsible for the energy difference spread in the ensemble) is maintained throughout the experiment, effectively increasing the $T_2$ time to the point where it is an unimportant decay channel. The experiments discussed in this work fall under this classification or contain "coherent" information in a population difference component $r_3$, so that the formalism presented above is an adequate representation. Detailed considerations of the effects of relaxation are presented in Reference (23).

Detection of Coherence: The Probe Pulse

In classic magnetic resonance experiments, the "in-plane" coherent components are detected directly by the signal they induce in transverse coils. Several coherence experiments in excited states have also been monitored successfully with this technique, including the first observation of spin echoes in triplet states states by Schmidt (8). However, this method has several distinct drawbacks:

(1) The available sensitivity is somewhat limited, being comparable to ESR and NMR sensitivities of approximately $10^{13}$ systems/cc. This
frequently poses a problem when dealing with excited states because this excitation density may not be obtainable if the lifetimes of the levels involved are sufficiently short. In other cases it can often require extremely strong optical pumping sources.

(2) The time resolution is not adequate to monitor all features of some coherence experiments. Because of cavity overload and amplifier saturation induced by the on-resonance r.f. perturbation, the available time regime is limited to the microsecond region. Although this is adequate for nuclear systems, the much larger gyromagnetic ratio associated with electrons produces dynamic effects on the nanosecond time scale. As an example, free induction decays associated with zero-field transitions in organic molecules are typically on the order of a 100 nanoseconds, (10,16) much too fast to be measured conventionally.

In 1973 Breiland, Harris and Pines (10) demonstrated that the coherent information contained in \( r_1 \) and \( r_2 \) can be directly converted into an \( r_3 \) component, i.e. coherent information can be displayed as an explicit population difference between the two levels involved. Their technique requires the application of a "probe pulse" of duration \( \tau = \omega_1/2\pi \), which converts either the \( r_1 \) or \( r_2 \) component into an \( r_3 \) component depending on the phase of the perturbation as may be verified by substitution into Equations (16). In addition, any \( r_3 \) component existing previous to the probe pulse is converted into an in-plane component, so that the population difference after the pulse directly measures one of the coherent components. A pictorial representation of this is presented in Figure 2.
OPTICAL DETECTION OF COHERENT COMPONENTS
THE PROBE PULSE

Fig. 2. The effect of a probe $\pi/2$ pulse on the $r$-vector. Which component is converted to a population difference is dependent upon the phase of the r.f. field.
The probe pulse method has the distinct disadvantage of being a "point-by-point" probe in time, unlike the essentially continuous monitoring available with conventional techniques; however it presents several attractive features. These include:

(1) optical detection of coherence. By using the optical emission of the levels involved to monitor their populations, one has a particularly sensitive double resonance technique for monitoring the loss of coherence in an excited ensemble. Since optical frequency photons are detected, an increase of $10^4$ or $10^5$ in sensitivity over conventional methods can be achieved, permitting the use of coherence techniques on systems with very short lifetimes.

(2) The time domain is extended to the submicrosecond region, and is limited in principle only by the duration of the probe pulse.

(3) The technique can be used to monitor coherence in systems in zero external field, thereby providing information concerning the intrinsic nature and time evolution of the environment surrounding the excitation.

For these reasons the probe pulse technique is particularly well suited for detecting coherence in excited states, and has been the method employed in most of the experiments performed to date.
Chapter III
Decay of Coherence

In this chapter, a number of physical processes responsible for loss of coherence are identified and discussed. The presentation will focus briefly on general considerations and then center on a most important decay mechanism for coherence, energy transfer. Much of the formalism presented in describing the effect of energy exchange may be used unaltered to understand the effects of other decay processes.

For the following discussion, it will prove most illustrative to present the formalism of Chapter II in terms of a density matrix \( \rho'(t) \). In the \(|Y\rangle, |X\rangle\) basis of the two levels that are coupled by the perturbation \( V(t) \), \( \rho'(t) \) is given by

\[
\rho'(t) = \frac{(aa^* + bb^*)}{2} \begin{bmatrix}
1 + r_1' & r_1' - ir_2' \\
r_1' + ir_2' & 1 - r_1'
\end{bmatrix}
\]

and follows the equation of motion

\[
\text{ih}\dot{\rho}' = [\mathcal{H}_0 + V(t), \rho(t)].
\]
Applying the unitary transformation defined in Equation 4 yields the rotating frame density matrix ρ(t):

\[
\rho(t) = \frac{(aa^*bb)^*}{2} \begin{bmatrix}
1 + r_3 & r_1 - ir_2 \\
r_1 & ir_2 & 1 - r_3
\end{bmatrix}.
\]

In the rotating representation, the equation of motion becomes

\[
\rho(t) = S^{-1} \rho(0) S,
\]

where in the absence of feeding and decay

\[
S = \exp \left( -iX \frac{t}{\hbar} \right)
\]

and is the time-evolution operator associated with the transformed hamiltonian presented in Equation 6. It is easily verified that Equation 20 corresponds to Equations 16 with feeding and decay terms set to zero by considering the explicit form of \(S^{-1}\) in the two level rotating basis:

\[
S^{-1}(\omega, \phi) = \begin{bmatrix}
\frac{-i\Delta \omega}{\omega} \sin \frac{\omega}{2}t + \cos \frac{\omega}{2}t & \frac{\omega}{2} e^{-i\phi} \sin \frac{\omega}{2}t \\
\frac{\omega}{2} e^{i\phi} \sin \frac{\omega}{2}t & \frac{i\Delta \omega}{\omega} \sin \frac{\omega}{2}t + \cos \frac{\omega}{2}t
\end{bmatrix}.
\]

Decay terms can be easily incorporated into the expression for \(S^{-1}\), however feeding must be dealt with separately in the equation of motion, i.e.
One must use $S^\dagger$ instead of $S^{-1}$ in this situation because the time evolution operator incorporating decay processes is no longer simply a similarity transformation, and hence $S^\dagger$ is no longer equal to $S^{-1}$.

However, for the purposes of this discussion feeding and decay may be neglected so that the effect of various other physical processes are directly manifested in the time dependence of the elements of the density matrix.

Decay of Coherence: General Considerations.

As discussed previously, the loss of coherence in an ensemble is the direct result of energy fluctuations of the states comprising the ensemble since they in turn determine the phase factors governing the time evolution of the coherent terms. These fluctuations may be rapid with respect to the time scale of a coherence experiment, i.e., the ensemble gives rise to a single homogeneously broadened transition, or they may be slow or static (corresponding to differences in the time-averaged environments of the members of the ensemble) in which case the transition is inhomogeneously broadened. In this latter case, the transition is a sum of homogeneous lines distributed in frequency space according to the inhomogeneous lineshape.

Viewed in the rotating frame, the phase factors are of the form $e^{\pm i \Delta \omega t}$, where $\Delta \omega$ is the off-resonance or local field corresponding to
the $r_3$ direction (Figure 1). Strictly speaking

\begin{equation}
\Delta \omega = \frac{1}{h} \left( \langle Y | \mathcal{H}^{\text{INT}} | Y \rangle - \langle X | \mathcal{H}^{\text{INT}} | X \rangle \right),
\end{equation}

where $\mathcal{H}^{\text{INT}}$ are the terms in the interaction Hamiltonian of the excitation and its environment that commute with $\mathcal{H}_0$. An ensemble variation of $\Delta \omega$ (inhomogeneous) or a rapid fluctuation in $\Delta \omega$ (homogeneous) corresponds to a range of local fields, producing a dephasing of the in-plane coherent components in the ensemble.

The interaction Hamiltonian of the excitation and its environment is given by

\begin{equation}
\mathcal{H}^{\text{INT}} = \mathcal{H}_Q + \mathcal{H}_\text{HF} + \mathcal{H}_\text{P-E},
\end{equation}

where $\mathcal{H}_Q$ represents quadrupole coupling to the nuclei, $\mathcal{H}_\text{HF}$ is the hyperfine interaction, and $\mathcal{H}_\text{P-E}$ is interaction of the excitation with phonons.\((26-30)\) The first two terms may have essentially static or slowly varying components due to the set of quantum states of the nuclei with long $T_1$'s surrounding a particular excitation. These components give rise to an inhomogeneous spread in environments, each particular set of quantum numbers corresponding to a particular environment and hence to a particular local field value. There are also rapidly varying components resulting from small fluctuations in the set of nuclear quantum states associated with a particular
environment producing a homogeneous broadening of the transition energy.

The excitation-phonon coupling is capable of producing additional energy fluctuations by inducing transitions between isochromats (homogeneous lines) within an inhomogeneous line, or promoting transitions to states that are outside of the ensemble, thus contributing additionally to the homogeneous linewidth.

A number of coherence experiments have been developed to examine various aspects of $\mathcal{K}_{\text{INT}}$. Free induction decays (31) sample the full inhomogeneous broadening of the ensemble and provide a correlation time corresponding to the observed lineshape. Spin echoes (32) and multiple pulse echoes (33) sample only the homogeneous linewidth by employing "refocussing pulses" that effectively remove the inhomogeneous or slowly varying components of $\mathcal{K}_{\text{INT}}$. Spinlocking, a technique in which the perturbation (stronger than interactions coupling the members of the ensemble) is maintained throughout the experiment, can be used to measure the loss of coherence induced by transitions to states outside the ensemble and hence is a particularly valuable technique for examining energy exchange and decay processes of excited states. Its application to excited states is discussed in detail in Chapter IV.

Effect of Energy Exchange

Energy exchange resulting in transitions among members of the ensemble can also produce a loss of coherence independent of any energy fluctuations if the transition is between non-equivalent systems
sharing the same environment (Fig. 3). In most instances this corresponds to exchange between identical molecules that are not translationally equivalent, an easily realizable situation in gases, liquids and most solids.

Since non-equivalent exchange can mix any and all levels in a multi-level system of excited states, it is illustrative to include a third level \( |Z\rangle \) in our rotating-frame basis. The perturbation will still be taken as coupling only \( |X\rangle \) and \( |Y\rangle \) so that in the absence of exchange,

\[
\rho(t) = \frac{aa^* + bb^*}{2} \begin{bmatrix}
2zz^*(t) & 0 & 0 \\
0 & 1 + r_3(t) & r_1(t)ir_2(t) \\
0 & r_1(t) + ir_2(t) & 1 - r_3(t)
\end{bmatrix}
\]

(25)

and the time evolution operator becomes

\[
\left( -\frac{(i/h)E_z\Delta \omega t}{\omega_0} \right) e^\frac{\omega_0}{\omega} I_{\phi} e^{\omega_0 t}
\]

(26)

\[
S^{-1} = 
\begin{bmatrix}
0 & -\frac{i\Delta \omega}{\omega}\sin \frac{\omega_0}{2}t + \cos \frac{\omega_0}{2}t & \frac{\omega_1}{\omega}e^{-i\phi\sin \frac{\omega_0}{2}t} \\
0 & 0 & \frac{\omega_1}{\omega}e^{i\phi\sin \frac{\omega_0}{2}t} \\
0 & -\frac{i\Delta \omega}{\omega}\sin \frac{\omega_0}{2}t & \frac{\omega_1}{\omega}\sin \frac{\omega_0}{2}t + \cos \frac{\omega_0}{2}t
\end{bmatrix}
\]

Equation 20 again describes the time evolution of \( \rho \). However, if non-equivalent exchange occurs, both diagonal and non-diagonal elements of \( \rho \) in any basis will suffer discontinuous changes. The time evolution operator may also change depending on the environment and perturbation strength experienced at the second site.
Let $\rho_1$ be the laboratory frame density matrix describing the systems at site 1. Since the orientations of the systems at the two sites are related to each other by at most a translation ($\Delta \hat{a}$) and rotation ($\phi, \theta, \psi$), the effect of exchange may be written as

$$
\rho_2 = R \rho_1 R^{-1},
$$

where the exchange operator $R$ is given by

$$
R = e^{-(i/\hbar)\hat{p} \cdot \hat{a}} e^{-i\psi \hat{J}_z} e^{-i\theta \hat{J}_y} e^{-i\phi \hat{J}_z}
$$

and $\rho_2$ is the density matrix describing the system immediately after exchange from site 1 to site 2; $\hat{p}$ is the momentum of the coupled system, and $\hat{J}_z, \hat{J}_y,$ and $\hat{J}_z$ are the angular momentum operators associated with the various axes of rotation. In general, the rotations have no effect on the intrinsic Hamiltonian $\mathcal{H}_0$, and merely alter the strength of externally applied perturbations experienced at the different sites. If the unperturbed Hamiltonian is externally induced (e.g., by a D.C. Zeeman field), the local field $\Delta \omega$ at the second site will be different, and coherence will be lost both by mixing of the states and energy fluctuation.

The state of the system after exchange is merely a linear combination of the eigenstates of $\mathcal{H}_0$ expressed in the basis set of the original site, with coefficients that depend not only on the relative orientations of the sites, but also on the time of the exchange event.
RESONANT ENERGY EXCHANGE ROUTES BETWEEN COHERENTLY COUPLED MOLECULES

Fig. 3
if the system was initially in a coherent superposition state.

The energy exchange process may be represented by the density matrix transformation,

\[ \rho_1(t) \xrightarrow{UU^{-1}} \rho_1'(t) \xrightarrow{R'R'^{-1}} \rho_2'(t) \xrightarrow{U'^{-1}U} \rho_2(t), \]

where the primes ('') indicate the laboratory reference frame. This can be simplified to

\[ \rho_1(t) \xrightarrow{RR'^{-1}} \rho_2(t), \]

where we have defined a rotating frame exchange operator

\[ R = U^x \cdot R \cdot U. \]

\( U^x \) is equal to \( U \) if \( \mathcal{H}_0 \) is invariant under the rotations. In the rotating \(|Z>, |Y>, |X>\) basis, \( R \) is given explicitly by (35)

\[ R = e^{-(1/t)P \cdot \frac{\hbar}{\omega}} \begin{bmatrix} \cos \theta & -\sin \theta \cos \phi & \sin \phi e^{-(1/t \omega_0) t} \\ \cos \theta \sin \phi e^{-(1/t \omega_0) t} & -\sin \phi & -\cos \phi e^{-(1/t \omega_0) t} \\ \sin \theta & \cos \phi & e^{-(1/t \omega_0) t} \end{bmatrix} \]
where \( \omega \) is the rotating frame frequency,

\[
\omega_0 = (E_y - E_x)/\hbar
\]

(33)
\[
\omega_0 = (E_z - E_y)/\hbar
\]
\[
\omega_0 = (E_z - E_x)/\hbar
\]

and the angles are defined as

\( \phi \), a rotation about the Z axis of quantization (corresponding to \(|Z\rangle \) of site 1;

\( \theta \), a rotation about the new X axis;

\( \psi \), a rotation about the new Z axis.

The translation operator acts as a constant phase factor affecting all elements of \( \rho \), and will be ignored for the rest of the discussion.

The transformed density matrix \( \rho_2(T) \) is calculated using Equation 30, where \( T \) is the time of the exchange event and \( \rho_1(T) \) is given by Equation 19. In the transformed basis, \( \rho_2(T) \) is given by

\[
\rho_2(T) = \frac{(aa^* + bb^*)}{2} \begin{bmatrix}
\rho_2(ZZ) & \rho_2(ZY) & \rho_2(ZX) \\
\rho_2(YZ) & \rho_2(YY) & \rho_2(YX) \\
\rho_2(XZ) & \rho_2(XY) & \rho_2(XX)
\end{bmatrix}
\]

(34)

and represents the density matrix for a system that has undergone nonequivalent exchange. For equivalent exchange, all angles are zero and \( \rho_2(T) = \rho_1(T) \). The expressions for elements of \( \rho_2(T) \) are quite
lengthy and are presented in detail in Appendix I.

In general, all of the matrix elements are non-zero indicating that immediately after the exchange all three levels are involved in coherent superposition, i.e. the exchange has the effect of introducing coherence into superposition states that are not driven by a coherent perturbation. However, the ensemble average of all of the off diagonal elements will decay away in a time characterized by the inhomogeneous $T_2$ associated with the corresponding transitions, unless the perturbation is reapplied to maintain the coherent components of the driven transition.

The coherent components of a system that has undergone exchange now contribute to the total coherence in the subensemble of systems that are at the second site. Defining $\mathbf{R}$ to be the $r$-vector of the exchanging system in the transformed basis set, it is easily shown that

\begin{align}
R_3(T) &= \frac{\rho_2(YY)-\rho_2(XX)}{2} = \frac{1}{2} \left[ \rho_1(ZZ) \sin^2 \theta \cos 2\psi - 2 r_3(T) \sin \psi \sin 2\phi \cos \theta ight. \\
&\quad - \cos 2\psi (1-r_3(T) \cos 2\phi) + \cos 2\psi (1+r_3(T) \cos 2\phi) \cos^2 \theta \\
&\quad - \left. \left[ r_1(T) \cos \omega T - r_2(T) \sin \omega T \right] (2 \sin \psi \cos \phi \cos 2\phi + \cos 2\psi \sin 2\phi (1+\cos^2 \theta)) \right] \\
&\quad \text{(35)}
\end{align}
Continued

\[
R_1(T) = \frac{\rho_2(YX) + \rho_2(XY)}{2} = \left[ \rho_1(ZZ) \sin2\psi \sin^2\theta + \frac{1}{2} \sin2\psi (\cos^2\theta - 1 + r_3(T) \cos2\phi(1 + \cos^2\theta)) \right] \\
+ r_3(T) \cos\theta \sin2\phi \cos2\psi \cos\omega T + r_1(T) \cos\theta (\sin^2\phi \sin^2\psi + \cos^2\psi \cos^2\phi) \\
- \frac{1}{4} \sin2\psi \sin2\phi (1 + \cos^2\theta)] \\
- [r_1(r) \cos2\omega T - r_2(T) \sin2\omega T] \left[ \frac{1}{4} \sin2\psi \sin2\phi (1 + \cos^2\theta) + \cos\theta (\cos^2\phi \sin^2\psi \\
+ \cos^2\psi \sin^2\phi) \right]
\]

\[
R_2(T) = \frac{\rho_2(XY) - \rho_2(YX)}{2} = - \left[ \rho_1(ZZ) \sin2\psi \sin^2\theta \right] \\
+ \frac{1}{2} \sin2\psi (\cos^2\theta - 1 + r_3(T) \cos2\phi(1 + \cos^2\theta)) + r_3(T) \cos\theta \sin2\phi \cos2\psi \cos\omega T \\
+ r_2(T) [\cos\theta (\sin^2\phi \sin^2\psi + \cos^2\phi \cos^2\psi) - \frac{1}{4} \sin2\psi \sin2\phi (1 + \cos^2\theta)] \\
+ [r_1(T) \sin2\omega T + r_2(T) \cos2\omega T] \left[ \frac{1}{4} \sin2\psi \sin2\phi (1 + \cos^2\theta) \right. \\
\left. + \cos\theta (\cos^2\phi \sin^2\psi + \cos^2\psi \sin^2\phi) \right]
\]

\[
R_Y(T) = \rho(YY)/2
\]

\[
R_X(T) = \rho(XX)/2
\]
The time development of \( \mathbf{\hat{R}} \) for \( t > T \) is then obtained by applying the time-evolution operator to \( \rho_2(T) \) with appropriate changes in \( \Delta \omega \) and \( \omega_1 \) to reflect conditions at the second site.

Effect of Exchange on Some Coherence Experiments

To illustrate the considerations outlined above, the effect of non-equivalent energy exchange on three common coherence experiments will be presented. It is assumed that \( \mathcal{H}_0 \) is completely intrinsic to the systems, that there are only two distinct orientations experiencing identical environments, and that both sites are equally populated. Furthermore, assume that the sample size is such that the perturbation phase \( \phi \) is constant over this sample. Let

\[
\gamma_1 = \tilde{\omega}(1) = (\omega_1^2 + \Delta \omega^2)^{1/2}
\]

be the driving frequency at site 1 and

\[
\gamma_2 = \tilde{\omega}(2)
\]

at site 2, and consider first a free induction decay experiment (FID).

The relevant density matrix equation for a FID is

\[
\rho_1^{\text{FID}}(t) = S_\tau^{-1}S^{-1}(\pi/2,0^\circ)\rho_1(0)S(\pi/2,0^\circ)S_\tau,
\]

where \( S(\pi/2,0^\circ) \) is the evolution operator for the perturbation applied for a time \( t' = \pi/2\omega_1 \) with no phase shift, and \( S_\tau \) is a dephasing
transformation describing the evolution of the density matrix for a time $\tau$ when there is no perturbation. $S_\tau$ is obtained by setting $\omega_1 = 0$ in Equation 26. If

$$
\rho_1(0) = \begin{bmatrix}
z z^* & 0 & 0 \\
0 & b b^* & 0 \\
0 & 0 & a a^*
\end{bmatrix},
$$

then

$$
\rho_{1}^{\text{FID}}(t + \tau) = \frac{a a + b b^*}{2} \begin{bmatrix}
z z^* & 0 & 0 \\
0 & \left(1 + \cos \gamma_1 t'\right) + \frac{\Delta \omega}{\gamma_1} \left(1 - \cos \gamma_1 t'\right) \\
0 & \left(\omega_1 \gamma_1\right) \sin \gamma_1 t' e^{i \Delta \omega t}
\end{bmatrix}
$$

$$
\left(\begin{array}{c}
\left(\frac{a a^* - b b^*}{a a + b b^*}\right) \left(1 - \cos \gamma_1 t'\right) \\
\left(\frac{a a^* - b b^*}{a a + b b^*}\right) \left(\gamma_1\right) \sin \gamma_1 t' e^{i \Delta \omega t}
\end{array}\right)
$$

$$
\left(\begin{array}{c}
\left(\frac{a a^* - b b^*}{a a + b b^*}\right) \left(\omega_1 \gamma_1^2\right) \left(1 - \cos \gamma_1 t'\right) \\
\left(\frac{a a^* - b b^*}{a a + b b^*}\right) \left(\omega_1 \gamma_1^2\right) \left(1 - \cos \gamma_1 t'\right)
\end{array}\right)
$$
and the coherent component generated by the pulse \( S(t', 0°) \), \( r_1 \), is given by

\[
(40) r_1(t' + \tau) = \left( \frac{a a^* - b b^*}{a a^* + b b^*} \right) \left[ \frac{\omega_1}{\gamma_1} \sin y_1 t \cos \Delta \omega t - \frac{\Delta \omega}{\gamma_1^2} (1 - \cos y_1 t) \sin \Delta \omega t \right].
\]

Averaging over the lineshape gives the average \( r_1 \) component per system:

\[
(41) \quad \langle r_1 \rangle = \frac{1}{N} \int_{-\infty}^{\infty} g(\Delta \omega) r_1(\Delta \omega) d\Delta \omega.
\]

For a Lorentzian line,

\[
(42) \quad g(\Delta \omega) = \left( \frac{T_2^*}{\pi} \right) \left[ 1 + \frac{T_2^* 2 \Delta \omega^2}{1} \right]
\]

and

\[
(43a) \quad \langle r_{1(1)} \rangle \text{ Lorentzian} = \left( \frac{a a^* - b b^*}{N(a a^* + b b^*)} \right) \left[ \sin \omega_1(1)t' - \frac{1}{T_2^* \omega_1(1)} \right]

\times (1 - \cos \omega_1(1)t') e^{-(\tau/T_2^*)},
\]

where it has been assumed that \( \omega_1 >> \Delta \omega \).

Under the same conditions,

\[
(43b) \quad \langle r_{3(1)} \rangle \text{ Lorentzian} = \left( \frac{b b^* - a a^*}{N(a a^* + b b^*)} \right) \cos \omega_1(1)t'
\]

\[
(43c) \quad \langle r_{2(1)} \rangle \text{ Lorentzian} = 0.
\]
As seen from Equation 43a, the coherent component in a free induction decays exponentially in a time governed by the inhomogeneous linewidth term, $1/T_2^*$, if no non-equivalent exchange is occurring. The equations describing the $\mathbf{r}$ vector for systems at site 2 are identical to Equation 43 except that $\omega_1(2)$, the perturbation strength at the second site, must replace $\omega_1(1)$. Decay out of the ensemble can be accounted for by multiplying Equation 43a by $e^{-k_A t}$, where $k_A$ is the rate constant for decay to the ground state from the coherent superposition state.

The contribution of the $\mathbf{r}$ vector at site 1, $r(1,T)$, to the coherent component at site 2, $R_1(T)$, for a system undergoing non-equivalent exchange at time $T$ is

$$R_1(T) = \{\rho_1(zz^*)\sin 2\psi \sin^2 \theta + \frac{1}{2}\sin 2\phi \cos \theta - 1 + r_3(1,T)\cos 2\phi(1 + \cos^2 \theta)\} + r_3(1,T)\cos \theta \sin 2\phi \cos 2\psi$$

$$\times \cos \omega T + r_1(1,T)F_{xy} - r_1(1,T)\cos 2\omega T$$

$$\times [(1/4)\sin 2\psi \sin 2\phi(1 + \cos^2 \theta) + \cos \theta (\cos^2 \phi \sin^2 \psi + \cos \phi \sin^2 \phi)],$$

where $F_{xy} = \cos \theta (\sin 2\phi \sin^2 \psi + \cos^2 \phi \cos^2 \psi) - \frac{1}{4} \sin 2\psi \sin 2\phi(1 + \cos^2 \theta)$. Averaging this over the exchange time $T$ reduces this expression to

$$R_1(T) = r_1(1,T)F_{xy}$$

for the ensemble, i.e. the original coherent component times a
geometric factor relating the orientations of the two sites. It should be noted that $F$ will be different for the other transitions because of the manner in which the angles of rotation are defined.

For the $|Z> \leftrightarrow |Y>$ transition,

\begin{equation}
F_{zy} = \cos^2 \theta \cos \phi \cos \psi - \sin \psi \sin \phi \cos \theta
\end{equation}

while

\begin{equation}
F_{zx} = \cos \theta \cos \psi \cos \phi - \cos^2 \theta \sin \phi \sin \psi.
\end{equation}

All of these geometric factors reduce to 1 for the case of equivalent exchange.

The coherent component $\langle r_1(l,t) \rangle$ corresponding to the subensemble of systems occupying site $l$ may be written as

\begin{equation}
\langle r_1(l,t) \rangle = e^{-(t/T_2^*)} \left\{ \frac{aa^* - bb^*}{[aa^* + bb^*]} \left( \frac{\sin \omega_1(1)t'}{\omega_1(1)T_2^*} - \left[ 1 - \cos \omega_1(1)t' \right] \right) \right\}
\end{equation}

\begin{equation}
\times \sum_{L=0}^{\infty} \sum_{L=0}^{\infty} F_{xy}^L N_1(L,t) + \left[ \frac{aa^* - bb^*}{[aa^* + bb^*]} \right]^2 \left( \frac{\sin \omega_1(2)t'}{\omega_1(2)T_2^*} - \left[ 1 - \cos \omega_1(2)t' \right] \right)
\end{equation}

\begin{equation}
\times \sum_{L=1}^{\infty} F_{xy}^L N_2(L,t) \right\},
\end{equation}
where \( \frac{bb^* - aa^*}{aa^* + bb^*} \) \((z = 1,2)\) is the initial \( r_3 \) at the site \( z \), and \( N_z(L,t) \) is the number of systems originating at site \( z \) that have exchanged \( L \) times in time \( t \). The sum over an even number of exchanges represents systems that originated at site 1 and are at site 1 at time \( t \), while the odd exchange sum represents systems at site 1 that were at site 2 at \( t = 0 \). A similar equation describes \( r_1(2,t) \).

\( N_z(L,t) \) can change due to three processes; decay to states outside the ensemble, decay to \( N_z(L+1,t) \), or by feeding from \( N_z(L-1,t) \).

Thus

\[
\begin{align*}
\dot{N}(0,t) &= -(\lambda + \beta)N(L,t) \\
\dot{N}(L,t) &= -(\lambda + \beta)N(L,t) + \lambda N(L-1,t), \quad L \geq 1
\end{align*}
\]

where \( \lambda \) is the rate constant for exchange and \( \beta \) is the rate constant for decay out of the ensemble. Solving these differential equations (36) yields

\[
\begin{align*}
N_z(0,t) &= N_z e^{-(\lambda+\beta)t} \\
N_z(L,t) &= N_z \frac{(\lambda t)^L}{L!} e^{-(\lambda+\beta)t}
\end{align*}
\]

where \( N_z \) is the original number of systems at site \( z \). Substituting Equation 49 into Equation 47 and recognizing that the two series in \( \left( F \lambda t \right)^L \) \( L! \) can be expressed in terms of hyperbolic functions gives
which corresponds to Equation 43a. It is apparent that non-equivalent exchange ($F < 1$) is a new decay channel for coherence, shortening the free-induction decay time and producing an apparent linebroadening. This is to be expected since the exchange is between non-equivalent states, producing an additional lifetime broadening of the energy widths. Note that for equivalent exchange ($F = 1$), the energy transfer
has no effect on the decay time.

If one detected the coherent component directly with induction coils, the observed signal would be

\[ I(t) = I(0) e^{-[(1/T_2^*) + \beta + \lambda(1 - F)]t} \]

However, if the signal is optically detected by applying a probe pulse,

\[ I(t) = r_1(1,t) \left[ \sin \omega_1(1)t' - \frac{1 - \cos \omega_1(1)t'}{T_2^*(1)} \right] \]
\[ + r_1(2,t) \left[ \sin \omega_1(2)t' - \frac{1 - \cos \omega_1(2)t'}{T_2^*(2)} \right], \]

where again \( t' \) is the duration of the pulse nominally taken to be equal to the original \( \pi/2 \) pulse. Thus

\[ I(t) = (P_1 \Phi_1^2 + P_2 \Phi_2^2) [\cosh(\kappa t) + \epsilon \sinh(\kappa t)] e^{-[(1/T_2^*) + \lambda t + \beta]t}, \]

where

\[ \Phi_1 = \sin \omega_1(1)t' - \frac{1 - \cos \omega_1(1)t'}{T_2^*(1)} \]
\[ \Phi_2 = \sin \omega_1(2)t' - \frac{1 - \cos \omega_1(2)t'}{T_2^*(2)} \]

and

\[ \epsilon = (P_1 + P_2) \Phi_1 \Phi_2 / (P_1 \Phi_1^2 + P_2 \Phi_2^2). \]
or

$$I(t) = I_0 \left[ \cosh(F\lambda t) + \epsilon \sinh(F\lambda t) \right] e^{-[(1/T_2^*) + \lambda + \beta]t}.$$  

Thus the optically-detected signal displays a biexponential decay, whereas the induction signal exhibits a single exponential decay. Only for geometries such that $\omega_1(1) = \omega_1(2)$ will the optically detected signal decay in the same fashion as the induction signal. The above solutions are valid only if both $\omega_1(1)$ and $\omega_1(2)$ are non-zero. If one site does not experience the perturbation, then any exchange to that site results in a loss of phase coherence if the exchange frequency $\lambda$ is much smaller than $1/T_2^*$. This will be the case in general for excited states since there are other decay processes contributing to the linewidth. If any exchange event produces a loss in the coherent component, then

$$\rho_1(t) = r_1(1,t) = r_1(1,0)e^{-[(1/T_2^*) + \lambda + \beta]t},$$

that is, all exchange events result in a loss regardless of the geometric factor $F$.

The above treatment can be directly applied to the spin echo experiment. The relevant density matrix equation becomes

$$\rho_{ECHO}^{1}(t) = S_{\pi}^{-1} S_{\tau}^{-1}(Y_1 t', 0^o) S_{\pi}^{-1} S_{\tau}^{-1}(Y_1 t, 0^o) \rho(0) S(Y_1 t', 0^o) \times S_{\pi} S(Y_1 t, 0^o) S_{\tau}$$

and results in equations identical to Equations 52 and 53 except that the
inhomogeneous $T_2^*$ time is replaced by a homogeneous term $T_2^H$. The effect of non-equivalent exchange on the decay of spinlocking is discussed in detail in the next chapter.
Chapter IV

Spinlocking

A particularly useful coherence experiment for examining energy transfer in excited states is spinlocking, a technique that is insensitive to energy fluctuations within an inhomogeneously-broadened ensemble if the applied perturbation is of sufficient strength. Developed in the 1950's (18) and first applied to excited states in 1974 (14), spinlocking is well-suited for measuring the frequency of energy fluctuations that are large compared to the linewidth characterizing a particular transition in an ensemble and hence is applicable to a number of problems dealing with excitation transfer. (37)

Viewed in the rotating basis discussed in Chapter II and presented schematically in Figure 4, the spinlocking experiment consists of a $\pi/2$ pulse that converts the initial population difference between the two coupled levels ($r_0$) into a coherent component ($r_1$). Spinlocking is accomplished by phase-shifting the applied r.f. perturbation by 90° immediately after the initial pulse so that the coherent component is aligned along the applied field. This prevents the loss of spin coherence if the spinlocking field $\omega_1$ is large compared to the interactions producing the local fields in the ensemble because the direction and magnitude of the effective driving field in Equations 16

$$\bar{\omega} = (\omega_1^2 + \Delta \omega^2)^{1/2}$$
OPTICALLY DETECTED SPIN LOCKING IN THE PRESENCE OF FLUCTUATING SPIN SubLEVEL POPULATIONS
(The Relationship between the Laboratory Frame and the Interaction Representation)

A

B

T

C

D

Fig. 4
Fig. 4:

(A) A diagrammatical representation of the rotating frame $r$ vector for a system in which intersystem crossing occurs only to one level: (a) $r$ vector before the application of microwaves; (b) after initial $\pi/2$ pulse applied along the rotating frame x-axis; (b') the field is shifted $90^\circ$ to the y-axis spin locking the initial in-plane coherent component. The partial disk indicates incoming population being driven in a plane perpendicular to the spin-locked population; (c) an $r$ vector component developing along the negative y-axis ($r_1$) due to longitudinal relaxation along the spin locking field is indicated by the double headed arrow. (d) after the application of the final $\pi/2$ pulse along the x ($r_2$) direction, the remaining spin lock population is restored to the z-axis ($r_3$).

(B) An illustration of the spin sublevel population change in the laboratory frame under the application of the spin locking pulse sequence.

(C) A representation of microwave pulse sequence.

(D) Illustration of the change in the phosphorescence intensity as observed in an actual experiment due to the spin locking pulse sequence. The change in intensity labeled $\Delta I$ is caused by the application of the final $\pi/2$ pulse and is proportional to the spin locked pseudomagnetization remaining at time $\tau$. 
is essentially constant for the entire ensemble. Of course, the coherent component decays due to other processes, but fluctuations of the local fields that are small relative to \( \omega_1 \) no longer cause dephasing. If \( \omega_1 \) is large compared to the linewidth defined by the ensemble, only states outside of the ensemble can have associated local fields large enough to produce dephasing. Thus the loss of coherence in the spinlocked state is due to decay out of the ensemble. This loss can be monitored directly and continuously by means of induction coils; however, optical detection requires that the spin-lock field be interrupted and a probe \( \pi/2 \) pulse with the same phase as the initial pulse be applied to reconvert the coherent component to a population difference. The resulting change in signal as a function of the spinlocking time measures the coherence decay. Figure 5 shows a typical optically-detected decay.

The requirement that \( \omega_1 \gg \Delta \omega \) is not particularly stringent in the absence of feeding as is illustrated in Figure 6A. For \( \omega_1 \approx 1/2T_2^* \), the maximum local field in the ensemble, the effective field is at a 45° angle in the \( r_2-r_3 \) plane and systems experiencing this field will precess about it eventually forming a cone due to homogeneous broadening of the environment. The result is a diminished coherent component which is nonetheless spinlocked since energy fluctuations within the ensemble can only reduce the magnitude of the local field. If feeding is present, however, and the two levels are fed at different rates, a non-decaying coherent component is maintained that produces a baseline shift distorting
T₁ρ FOR h₂-1, 2, 4, 5 TETRACHLOROBENZENE IN d₂-1, 2, 4, 5 TETRACHLOROBENZENE

Δ = 23.5 cm⁻¹, τₓ→τᵧ TRANSITION (3.5780 GHz)

Fig. 5. Decay of the Spinlocked State.
A. OFF-RESONANCE EFFECTS
NO FEEDING

B. OFF-RESONANCE EFFECTS
WITH FEEDING

Fig. 6
Fig. 6.

(A) Effect of off-resonance driving field in the absence of feeding; (a) the initial r-vector for the set of systems experiencing a given $\Delta \omega$; (b) production of cone due to homogeneous broadening of environment; (c) resulting projections after cone is formed; (d) decay of coherent component due to lifetime of sublevels.

(B) Effect of off-resonance driving field in presence of feeding. The effects are the same as in 6(A), however (e,f) incoming population feeding into the sublevel is also driven in the cone giving a contribution to the in-plane coherent component; (g) feeding balances decay yielding a non-decaying coherent component.
the observed decay. This is discussed in more detail further on.

Loss of Spinlocking

As mentioned before, transitions to states outside of the ensemble will result in a loss of spinlocking. These transitions may be of the form of radiative and/or non-radiative decay to the groundstate or "promotion" to excited states that are not in the ensemble. This latter process usually involves energy transfer to a distinct molecular species or to another system in a radically different environment. Photochemical dissociation and polymerization also are pathways for decay out of the ensemble.

There are also two processes which produce a loss of spin-locking independent of decay out of the ensemble. One is non-equi- valent energy exchange between members of the ensemble and the other is spin lattice relaxation of the coherent component against the applied r.f. field. Completely analogous to spin-lattice relaxation in spin-1/2 system, this latter process corresponds to the coherently coupled system making a transition between the Zeeman states quantized by the applied field and results in a change in sign of the coherent component. The work required for such a process is just

$$\Delta E = \hbar \tilde{\omega},$$

i.e. the energy difference between the states quantized by \( \tilde{\omega} \), and is either given up to or provided by phonons in the medium surrounding the system. The efficiency is dependent upon the nature of the coupling between the system and its surroundings.

Examination of Equations 16 indicates that the coherent components \( r_1 \) and \( r_2 \) decay to the ground state with a rate constant,
Fig. 7. Steady-state r-vector components generated because of feeding during off-resonance driving. No coherent components are generated unless the cones produced by incoming population are unequal (b') requiring that the two sublevels experience different feeding rates.
\( k_A \), the average of the decay rate constants of the two levels that are spin locked. Thus in the absence of non-equivalent transfer, the loss of spinlock signal is given by

\[
I(t) = I_0 \exp(k_A + k_{T_{\text{pm}}} + \sum_f k_{pf})t = I_0 \exp(-k_Tt),
\]

where \( k_{T_{\text{pm}}} \) is the rate constant for relaxation against the spin locking field and \( k_{pf} \) is the rate constant for promotion to state \(|f\rangle\).

Both \( k_A \) and \( k_{pf} \) will be temperature dependent in general since they usually involve coupling to phonons, however \( k_{T_{\text{pm}}} \) is not expected to exhibit any strong temperature dependence since the energy difference \( \Delta E = \hbar \omega \) usually corresponds to only a few tenths of a degree kelvin. The phonon occupation number for the mode corresponding to this energy will be

\[
<n> = \frac{1}{\exp(\Delta E/k_B T) - 1},
\]

a large number at all but the lowest temperatures, so that \( k_{T_{\text{pm}}} \) will depend on two essentially temperature independent parameters: the phonon density of states and the nature of the coupling between the phonons and the system. In Figure 8, a plot of \( k_T \) versus reciprocal temperature clearly indicates the presence of a temperature independent component. For this experiment both \( k_A \) and \( k_{T_{\text{pm}}} \) can be taken as temperature independent so that the temperature dependence reflects thermal promotion of systems out of the ensemble. The activation energy calculated from such a plot should correspond to the energy
TEMPERATURE DEPENDENCE OF SPINLOCKING DECAY CONSTANT $k_T$

0.06% $h_2$-1, 2, 4, 5 tetrachlorobenzene in $d_2$-1, 2, 4, 5 tetrachlorobenzene

D-IEI transition: 35778 MHz

Fig. 8
One must employ caution in interpreting the meaning of the activation energy since the promotion process is actually the sum of processes to various final states \(|f>| \) at various energies \(E_f\). Thus the observed activation energy is actually a weighted average that depends on the nature of the matrix elements coupling the ensemble to states \(|f>| \) and on the density of final states \(\rho(E_f)\).

Formulating the promotion process in terms of a Golden Rule rate yields\(^{(14)}\)

\[
\sum_{f} k_{pf} = \frac{2\pi}{\hbar} \sum_{f} |<g,i|g',f>|^2 \rho(E_f),
\]

where the product states \(<g,i>| \) and \(|g',f>| \) are such that the total energy of the system is conserved. The nature of the states \(|g>| \) and \(|g'>\) depends on the manner in which the transition is induced (either direct or by Raman \((38)\) or Orbach processes \((39)\) ) but corresponds to occupation numbers of modes in the perturbing photon or phonon field.

The rate of transition to a particular state \(k_{pf}\) may be calculated from first principles if the mechanism and appropriate matrix elements are known. This is usually not the case, so one is forced to partition Equation 58 and use the experimentally observed value \(k_{p}^{obs}\), i.e.
This approach has the advantage that the matrix elements may be known relative to one another, resulting in considerable simplification and removing some of the dependence on the model for the mechanism involved.

In the above discussion, it has been implied that transitions to states \(|f\rangle\) outside of the ensemble produce an irreversible and total loss of spin coherence. This is only true if there is no recurrence back to the ensemble before dephasing is complete. Viewed in the rotating frame (and assuming equivalent transfer) it is easily seen that a particular coherent component \(r_x\) will dephase according to

\[
(60) \quad r_x(\tau) = r_x^0 \cos(\Delta \omega' - \Delta \omega) \tau,
\]

where \(\Delta \omega'\) is the large local field experienced after the transfer and \(\tau\) is the residence time outside of the ensemble. To see any dephasing requires that \(\Delta \omega' > \omega_i > \Delta \omega\), consequently \((\Delta \omega' - \Delta \omega) \approx \Delta \omega'\). If recurrence occurs in a time \(\tau^* \approx 2\pi/\Delta \omega'\), then some spin coherence is maintained. However, for times longer than \(\tau^*\), an average over the residence time \(\tau\) indicates that the ensemble averaged coherent component of a recurring system is zero. Experi-
mentally, efficient recurrence would cause the measured promotion rate to be smaller than the actual rate.

Non-equivalent exchange within the ensemble also produces a loss in the spinlocking signal. The equation of motion for the spinlocked density matrix is

\[
\rho_{S.L.}^{\text{S.L.}}(t) = S^{-1}(\gamma_1 t, 90^\circ)S^{-1}(\pi/2, 0^\circ)\rho_1(0)S(\pi/2, 0^\circ)S(\gamma_1 t, 90^\circ).
\]

If \(\rho_1(0)\) is given by Equation 38, and \(\omega_1\) is large compared to \(\Delta\omega\), then

\[
\rho_{S.L.}^{\text{S.L.}}(t) = \begin{bmatrix}
\frac{2\pi z^*}{a^* + b^*} & 0 & 0 \\
0 & 1 - \frac{(a^* - b^*) \cos\gamma_1 t' \cos\gamma_1 (t - t')}{(a^* + b^*)} & \frac{a^* - b^*}{a^* + b^*} [\sin\gamma_1 t' - i \cos\gamma_1 t' \cos\gamma_1 (t - t')] \\
0 & \frac{a^* - b^*}{a^* + b^*} [\sin\gamma_1 t' + i \cos\gamma_1 t' \cos\gamma_1 (t - t')] & 1 + \frac{(a^* - b^*)}{(a^* + b^*)} \cos\gamma_1 t' \cos\gamma_1 (t - t')
\end{bmatrix}
\]

(62)

where \(t'\) is the length of the \(\pi/2\) pulse.

Rewriting in terms of Equation 43 gives

\[
(63a) \quad r_3(t) = -\frac{[a^* - b^*]}{[a^* + b^*]} \cos\gamma_1 t' \cos\gamma_1 (t - t')
\]

\[
(63b) \quad r_2(t) = \frac{[a^* - b^*]}{[a^* + b^*]} \cos\gamma_1 t' \sin\gamma_1 (t - t')
\]
i.e. spinlocking appears as a stationary component along $r_1$.
If one considers an ensemble of systems with a range of values for
$\Delta \omega$, both $r_2$ and $r_3$ will average to zero in a time on the order of
$2\pi/\Delta \omega_{\text{max}}$.

The effect of non-equivalent energy exchange is calculated as before. The explicit forms of the matrix elements of the transformed
density matrix $\rho_2(T)$ are not presented here but may be generated
using the equations for the elements presented in Appendix I. After
the exchange, the system again experiences the r.f. driving field,
i.e.

$\rho_2(t) = S^{-1}(\gamma_2 t^*, 90^\circ)\rho_2(T)S(\gamma_2 t^*, 90^\circ),$

where $t^* = t - T$. The elements of $\rho_2(t)$ are quite complex and
lengthy, but fortunately may be simplified since $\rho_2(t)$ represents a
system that has experienced particular driving fields $\gamma_1$ and $\gamma_2$,
so that one must average over all three quantities: the frequency
terms because of the $\Delta \omega$ contribution to the driving field (and in
practice because of field inhomogeneities in $\omega_1$) and the exchange
time $T$. Under these conditions, the $r_3(1,t)$ and $r_2(1,t)$ components
average to zero before exchange, leaving only the $r_1(1,t)$ spinlocked
component. After exchange the inhomogeneous effective field $\gamma_2$
averages the $R_3$ and $R_2$ components to zero, while an average over $T$
in general reduces the magnitude of the resulting $R_1$ component. The density matrix describing the exchanged systems then becomes

$$\rho_2(t) = \frac{aa^* + bb^*}{2} \begin{bmatrix} 0 & 0 & 0 \\ 0 & \frac{zz^*}{aa^* + bb^*} \cos^2\theta + \sin^2\theta & \frac{zz^*}{aa^* + bb^*} \sin^2\theta + \frac{1}{2} (1 + \cos^2\theta) \\ 0 & \frac{zz^*}{aa^* + bb^*} \sin^2\theta + \frac{1}{2} (1 + \cos^2\theta) & R_1 \end{bmatrix}$$

(65)

where

$$R_1 = \frac{aa^* - bb^*}{aa^* + bb^*} \sin \gamma_1 t' F_{xy} = r_1(1,T)F_{xy}$$

(66)

and $F_{yx}$ is the geometric factor discussed in Chapter III.

The decay of the spinlocked signal due to non-equivalent exchange is derived in a manner analogous to that presented in Equations 47.

The spinlocked components are just

$$r_1(1,t) = \left(\frac{aa^* - bb^*}{aa^* + bb^*}\right) \sin \gamma_1 t' \sum_{L=0}^{\infty} F_{xy}^L N_1(L,t)$$

(67a)

$$+ \left(\frac{aa^* - bb^*}{aa^* + bb^*}\right) \sin \gamma_2 t' \sum_{L=1}^{\infty} F_{xy}^L N_2(L,t)$$

odd
Substituting for $N(L,t)$ (cf. Equation 49) and setting $\beta = 0$ since we want only the contribution due to exchange yields

$$r_1(1,t) = e^{-\lambda t} [P_1 \sin \gamma_1 \cosh(F \lambda t) + P_2 \sin \gamma_2 \sinh(F \lambda t)]$$

(70)

$$r_1(2,t) = e^{-\lambda t} [P_2 \sin \gamma_2 \cosh(F \lambda t) + P_1 \sin \gamma_1 \sinh(F \lambda t)].$$

If one detected the signal conventionally, then the decay due to non-equivalent exchange would be

(71a) \hspace{1cm} I(t) \propto r_1(1,t) + r_1(2,t) = (P_1 \sin \gamma_1 + P_2 \sin \gamma_2)e^{-[\lambda(1-F)]t}

and the total decay of the spinlock signal would be given by

(71b) \hspace{1cm} I(t) = I_0 \exp[-kA + kT_{\rho m} + \sum_f k_p f + \lambda(1 - F)]t.

Optical detection requires application of a probe "\(\pi/2\)" pulse. The decay due to exchange can then be represented as

(72a) \hspace{1cm} I(t) \propto r_1(1,t)\sin \gamma_1 t' + r_1(2,t)\sin \gamma_2 t'

\[= (P_1 \sin^2 \gamma_1 t' + P_2 \sin^2 \gamma_2 t')[\cosh(F \lambda t) + e' \sinh(F \lambda t)]e^{-\lambda t}.\]
where

\[
\varepsilon' = \frac{(P_1 + P_2) \sin \gamma_1 t' \sin \gamma_2 t'}{P_1 \sin^2 \gamma_1 t' + P_2 \sin^2 \gamma_2 t'}
\]

and the total decay becomes

\[
(72c) \quad I(t) = I_0 \left[ \cosh(\gamma 1 t') + \varepsilon' \sinh(\gamma 2 t') \right] \\
\times \exp\left( \frac{-k_A + k_{\text{pm}} + \sum_{f} k_{pf} + \lambda}{} \right) t.
\]

As before, non-equivalent exchange produces a biexponential decay if the signal is detected by means of a probe pulse. Only when \( \gamma_1 = \gamma_2 \) will a single exponential be observed.

If either \( \gamma_1 \) or \( \gamma_2 \) is equal to zero, Equations 67 are no longer valid. However, in this case, any non-equivalent exchange results in a total loss of coherence if recurrence is unimportant, and

\[
(73) \quad I(t) = I_0 \exp\left( \frac{-k_A + k_{\text{pm}} + \sum_{f} k_{pf} + \lambda}{} \right) t
\]

for either method of detection.

**Experimental Considerations**

There are two important experimental factors that must be considered in performing a spinlock experiment. The first is that the applied field \( \omega_1 \) be sufficiently strong so that energy fluctuations within the linewidth of the transition do not produce a loss of coherence. The second is choosing the frequency of the applied field so as to minimize off-resonance effects such as the non-decaying
"feeding" component previously mentioned. This is not always a trivial task because the lineshapes associated with transitions in excited states are frequently asymmetric and contain components with different transition probabilities. For example, the zero-field ESR transitions between triplet state sublevels in organic molecules are usually asymmetric and contain both hyperfine and quadrupole "wings" within the lineshape.

One way of determining the spinlock resonance frequency is to perform a rotary precession followed by a $\pi/2$ probe pulse phase-shifted by $90^\circ$ if one is employing optical detection. This experiment is illustrated in Figure 6B where the phase of the driving field during the rotary precession has been taken to be $90^\circ$ to facilitate comparison to the spinlock experiment. For systems that are resonant with the applied field ($\Delta \omega = 0$) the rotary precession produces a fan in the $r_2$-$r_3$ plane due to feeding to the two levels and homogeneous broadening. There are no net $r$-vector components and the on-resonance subensemble is saturated. There are no in-plane components to be detected conventionally, and there is no change in observables upon application of the $\pi/2$ probe pulse. For systems that are off-resonance by a particular $\Delta \omega$, the effective field $\tilde{\omega}$ is in the $r_1$-$r_3$ plane and the rotary precession results in a cone instead of a fan. The vector sum of the components of this cone has both an $r_1$ and $r_3$ component. Systems experiencing a local field $-\Delta \omega$ produce an equivalent $r_1$ component but an opposing $r_3$ component resulting in a net $r_1$ component and apparent saturation of the sublevel populations.
Thus the off-resonance condition can be determined by detecting the resulting $r_1$ component, either directly or by observing a change from saturation upon application of the phase-shifted probe pulse.

A most important feature is that in the off-resonance case, incoming population entering either sublevel is also driven in the cone producing a steady-state in-plane coherent component along $r_1$, in turn producing a non-decaying contribution to the spinlock signal. This is only true, however, if the feeding rates to the two sublevels are unequal as is shown in Figure 7.

The driving field frequency at which the $r_1$ component produced by the rotary precession is a minimum corresponds to the frequency where the maximum number of systems are "on-resonance." This experiment also provides a measure of how well $\omega_1$ "spans" the line since the sensitivity to changes in frequency depends on the effective field $\bar{\omega}$ and hence on the relative magnitude of $\omega_1$ and $\Delta\omega$. In experiments performed on the D - |E| zero-field transition of the lowest excited triplet state of 1,2,4,5-tetrachlorobenzene, frequency shifts equivalent to 15% of the linewidth about the center of the line produced no detectable $r_1$ component indicating that $\omega_1$ was more than sufficient to spinlock the transition.
Chapter V

Electron Spin Ordering

A different approach for examining the dynamics of excited states is the use of an "ordered" electron spin state produced by adiabatic demagnetization in the rotating frame (ADRF) (40-41). This technique effectively converts the spin coherence of an excited ensemble into a highly ordered sublevel population distribution in which the $r_3$ component for a particular system depends explicitly on the local field it experiences. A unique feature of this ordered state is that energy fluctuations, no matter how large, do not necessarily produce a decay of the state because the "coherent" information is not contained in an in-plane component subject to dephasing. Only fluctuations that have resulted in a change in sign of the local field $\Delta \omega$ at the time of detection are effective in producing a loss of order. Two other processes can destroy order; transitions between the two sublevels themselves and the decay of the ensemble to the ground state.

Description and Preparation of the Ordered State

The ordered state is very easy to conceptualize; it corresponds to inverting the initial $r_3$ component for all of the systems whose transition frequencies $\omega_0$ lie to one side of the applied r.f. field frequency $\omega$. If $\omega$ is applied "on-resonance," half of the line corresponding to systems with negative values for $\Delta \omega$ is inverted. This is illustrated in Figures 9 and 10, which show the preparation
PREPARATION OF AN "ORDERED" TRIPLET STATE BY ADIABATIC DEMAGNETIZATION

(relationship between the laboratory frame and the interaction representation)

Fig. 9
Fig. 9. Schematic representation of r-vector during adiabatic demagnetization. (a) r-vector before application of microwaves is along r₃ (z) axis; (b) initial π/2 pulse produces r₁ component (y axis); (b') the microwave field H₁ is phase shifted to spinlock the ensemble; (c) H₁ is adiabatically reduced causing the effective field to swing to the +r₃ axis for Δω > 0 and to the -r₃ axis for Δω < 0. If the reduction is adiabatic, each system remains aligned along its effective field until (c') it is aligned in its local field (H₁ = 0). Also shown is the laboratory frame population difference as well as the microwave pulse sequence. The lowest part of the figure illustrates the phosphorescence response observed during optical detection. The dashed line represents the phosphorescence response in the presence of feeding to and decay from the sublevels.
Preparation of an "Ordered" State by Adiabatic Demagnetization

Fig. 10. Preparation of an ordered state for a case where the nuclear state experienced by the electrons via a quadrupole coupling determines which systems have $\Delta \omega < 0$ and which systems have $\Delta \omega > 0$. Adiabatically demagnetizing this system results in inverting the electronic spin polarization for systems experiencing a nuclear quadrupole state equal to $\pm 3/2$.
of an ordered electron spin state by adiabatic demagnetization. The procedure is as follows: (1) A "\(\pi/2\)" pulse applied at \(\phi = 0^\circ\) converts the initial \(r_3^0\) component into an \(r_1\) component as has been shown previously. Letting \(t'\) be the length of the pulse gives

\[
(74) \quad r_1(\Delta \omega) = -r_3^0(\Delta \omega) \sin \omega t'
\]

(2) A spinlocking field at \(\phi = 90^\circ\) is applied, averaging out all \(r_2\) and \(r_3\) components as discussed in Chapter IV. (If the field is applied at \(\phi = 270^\circ\), ADRF will invert all systems with positive values for \(\Delta \omega\).) The spinlocked component is given by Equation 63c.

(3) The strength of the applied field \(\omega_1\) is reduced adiabatically to zero. Since the effective field \(\omega_{\text{eff}}\) experienced by a system is the vector sum of \(\omega_1\) and \(\Delta \omega\), and since \(\Delta \omega\) corresponds to the \(r_3\) direction (see Figure 1), \(\omega_{\text{eff}}\) slowly swings to the \(\omega_1^+\) direction; specifically \(\omega_{\text{eff}}\) swings to the \(+r_3\) direction for systems with \(\Delta \omega > 0\) (henceforth called "fast" systems) and to the \(-r_3\) direction for systems with \(\Delta \omega < 0\) ("slow" systems). Under the assumption that the reduction of \(\omega_1\) is adiabatic, each system will remain parallel to its effective field, and have an \(r_3\) component given by

\[
(75) \quad r_3(\Delta \omega, \omega_1) = \frac{r_3^0(\Delta \omega) \sin \omega t' \Delta \omega}{|\omega_1^2 + \Delta \omega^2|^{1/2}}.
\]

The ensemble average for \(r_3\) is just

\[
(76) \quad <r_3> = \frac{1}{N} \int_{-\infty}^{\infty} g(\Delta \omega) \frac{r_3^0(\Delta \omega) \sin \omega t' \Delta \omega \Delta \omega}{|\omega_1^2 + \Delta \omega^2|^{1/2}},
\]
where $g(\Delta \omega)$ is the lineshape function. If the line is symmetric about
$\Delta \omega = 0$, the integral is zero for any value of $\omega_1$ and the ensemble
appears saturated throughout the demagnetization. For total
demagnetization ($\omega_1 = 0$), the resulting $r$-vector components are

$$r_3 = r^0_3 \sin \omega t' \quad (\Delta \omega > 0)$$

(77) $$r_3 = -r^0_3 \sin \omega t' \quad (\Delta \omega < 0)$$

$$r_1 = r_2 = 0.$$  

The total ensemble still appears saturated ($<r_3> = 0$) but is ordered
since the slow and fast system ensembles have opposite population
polarizations.

**Loss of Order**

Another way to view the ordered state is in terms of the highly
asymmetric distribution of local fields associated with the populations
of each sublevel. One sublevel is populated predominantly by slow
systems, the other by fast systems, a situation that can be altered
by two types of processes. The first are "vertical" processes
involving transitions between the two sublevels without changes in
the local field. As can be seen in Figure 9, these processes can
very quickly return the distribution of local fields in each sublevel
to its steady-state value, corresponding to a total loss of order.
Such processes include spin-lattice relaxation, $T_1$, and transitions
induced by a resonant r.f. perturbation. The other class of processes
are "horizontal" and must induce a change in the local field
experienced by a particular member of the ensemble large enough to
have changed the sign of $\Delta \omega$ at the time the order remaining in the ensemble is probed. Horizontal processes include spectral diffusion, in which the local environment about a stationary system evolves in time, as well as energy transfer processes, in which the system is physically transported to a site with a different local field.

The requirement that a horizontal process induce a change in sign of $\Delta \omega$ before a loss of order occurs is a consequence of the manner in which the ordered state is monitored. To date, two methods for probing the order in excited states have been developed, each with distinct advantages and disadvantages. Both techniques determine the order remaining in the ensemble by measuring the difference of the $r_3$ components of the two subensembles, fast and slow, i.e.

$$I(\text{order}) = \int_0^\infty r_3(\Delta \omega) d\Delta \omega - \int_{-\infty}^0 r_3(\Delta \omega) d\Delta \omega.$$  

If no order has been lost,

$$\int_0^\infty r_3(\Delta \omega) d\Delta \omega = -\int_{-\infty}^0 r_3(\Delta \omega) d\Delta \omega = \frac{1}{2} \int_{-\infty}^\infty r_3(\Delta \omega) d\Delta \omega$$

and

$$I(\text{ordered}) = \int_{-\infty}^\infty r_3(\Delta \omega) d\Delta \omega = N<r_3^0>,$$

where $N$ is the number of excited systems. It is apparent that a
particular system must have its $r_3$ component either inverted (vertical process) or exchanged between the integrals in Equation 78 before order is lost. This exchange requires a change in the sign of $\Delta \omega$.

One method for determining $I(\text{order})$ is to apply a spin echo pulse sequence to the ensemble. The effect of this sequence is shown in Figure 11. After the first pulse in the sequence $(\pi/2(0^\circ))$, the $r_1$ components for the subensemble

$$r_1(+\Delta \omega) = -r_3(+\Delta \omega) \sin \omega t' = - r_3^0 \sin^2 \omega t'$$

(80)

$$r_1(-\Delta \omega) = -r_3(-\Delta \omega) \sin \omega t' = - r_3^0 \sin^2 \omega t'.$$

Dephasing occurs so that at time $\tau$ each component has precessed $\Delta \omega \tau$ radians relative to the rotating reference frame. Since the direction of rotation is opposite for fast (+$\Delta \omega$) and slow (-$\Delta \omega$) systems, a net projection along $r_2$ is generated. For a particular system $j$,

$$r_2^j(\tau) = r_1^j(t - \tau) \sin \omega_j \tau = -r_3^j(\omega_j) \sin \omega t' \sin \omega_j \tau,$$

so that the ensemble total is given by

$$r_2(\tau)_{\text{TOT}} = \int_{-\infty}^{\infty} -r_3(\Delta \omega) \sin \omega t' \sin \Delta \omega \tau d\Delta \omega$$

(81a)

which may be rewritten as
OPTICAL DETECTION OF THE ORDERED STATE
BY SPIN ECHO

Fig. 11
Fig. 11. Spin echo method for probing ordered state. (a) Initial r vectors for fast and slow ensembles. The downward pointing component of the $+\Delta \omega$ ensemble represents fast systems that have undergone order destroying processes as does the upward pointing component for the $-\Delta \omega$ ensemble. (b) Effect of first $\pi/2$ pulse in echo sequence (c) The first dephasing period. Systems that have not undergone order destroying processes develop a projection along the $+r_2$ direction, the systems that have experienced order destroying processes have a projection along $-r_2$. (d) effect of $\pi$ pulse and rephasing (e,g). If order remains in the ensemble, a net $r_2$ component will exist for all times except $\tau = \tau'$. This component can be detected by a probe pulse (f,h) that converts $r_2$ to a population difference.
\[ r_2(\tau)_{\text{TOT}} = -\int_0^\infty [r_3(+\Delta \omega) - r_3(-\Delta \omega)] \sin \omega t' \sin \Delta \omega \tau d\Delta \omega. \]

To negate field and sample inhomogeneities, a \( \pi \) pulse is applied to the system. This rotates every component 180° about the \( r_2 \) axis so that the \( r_2 \) projection is unchanged. However, the \( r \)-vector for each system has experienced a rotation of \( (\pi - 2\Delta \tau t) \) radians in the \( r_1-r_2 \) plane, resulting in a change of sign of the \( r_1 \) component. Subsequent free precession results in a rephasing of the \( r_1 \) components, as is illustrated in Figure 12. If \( \tau' \) is the rephasing period,

\[ r_2(\tau,\tau')_{\text{TOT}} = -\int_0^\infty [r_3(+\Delta \omega) - r_3(-\Delta \omega)] \sin \omega t' \sin \Delta \omega (\tau - \tau') d\Delta \omega. \]

The \( r_2 \) component can be detected conventionally or monitored by applying a probe \( \pi/2(0°) \) pulse.

Figure 12 presents a typical optically detected spin echo performed on an ordered state. It is antisymmetric about the echo time \( (\tau' = \tau) \) as predicted by Equation 83, and displays an amplitude proportional to the difference in the \( r_3 \) components of the two ensembles, i.e. the order remaining in the ensemble. The decay of an ordered state induced in a triplet ensemble is shown in Figure 13 which presents a plot of echo amplitude versus time in the ordered state, \( \tau_0 \).

The ordered state may also be probed by adiabatic remagnetization as illustrated in Figure 14. After time \( \tau_0 \) in the ordered
OPTICALLY DETECTED ELECTRON SPIN ECHO IN THE ORDERED STATE

Fig. 12. Optically detected electron spin echo in an ordered $3\pi^*$ state of $d_2$-1, 2, 4, 5-tetrachlorobenzene in $h_{14}$-durene.
LIFETIME OF THE "ORDER" IN THE $^3\pi\pi^*$ STATE OF 1,2,4,5 TETRACHLOROBENZENE

**Fig. 13.** Ordered state echo amplitude versus time in ordered state.
DETECTION OF THE ORDERED STATE
BY ADIABATIC REMAGNETIZATION

(a) "ordered" state
(b) adiabatic remagnetization
(c) spinlocking
(d) probe pulse

(a) \( r_1 \)
(b) \( +\Delta \omega \)
(c) \( +\Delta \omega \)
(d) \( +\Delta \omega \)

\( \omega_0 < \omega \omega_0 > \omega \)

\( \omega \)

\( \pi/2 \) pulse

Phosphorescence Intensity

Fig. 14
Fig. 14. Detection of Ordered State by Adiabatic Remagnetization.

(b) The microwave field is adiabatically increased to its original value causing the effective fields for all systems to swing to the $-r_1$ direction (c) The ensemble is spinlocked, but now an oppositely directed component comprised of systems that underwent order-destroying processes reduces the net coherent component (d) The net coherent component, which is directly proportional to the remaining order, is detected by a probe pulse. Also shown are the sublevel populations in the laboratory representation, the microwave sequence, and the observed phosphorescence response during the sequence.
state, $\omega_1$ is adiabatically increased. The effective fields for members in each of the two ensembles swing to the $-r_1$ direction and the ensemble is again spinlocked. If no order has been lost, the original spinlocked component is regenerated save for losses due to the decay of the level to the ground state. However, if order has been lost, the spinlock component is attenuated by an oppositely directed component composed of systems that have undergone order-destroying processes. Letting $r_3(+\Delta\omega, \tau_D)$ and $r_3(-\Delta\omega, \tau_D)$ be the $r_3$ components at the time of detection, and noting that during the remagnetization

$$r_1(\omega_1, \Delta\omega, \tau_D) = \frac{-r_3(\Delta\omega, \tau_D)\omega_1}{|\omega_1^2 + \Delta\omega^2|^{1/2}}$$

results in a total component given by

$$r_1(\omega_1, \tau_D)_{TOT} = -\int_{-\infty}^{\infty} \frac{r_3(\Delta\omega, \tau_D)\omega_1}{|\omega_1^2 + \Delta\omega^2|^{1/2}} d\Delta\omega .$$

This may be rewritten as

$$r_1(\omega_1, \tau_D)_{TOT} = -\int_{-\infty}^{0} \frac{r_3(-\Delta\omega, \tau_D)\omega_1}{|\omega_1^2 + \Delta\omega^2|^{1/2}} d\Delta\omega ,$$

$$+ \int_{0}^{\infty} \frac{r_3(+\Delta\omega, \tau_D)\omega_1}{|\omega_1^2 + \Delta\omega^2|^{1/2}} d\Delta\omega$$

or more simply
The magnitude of the spinlocked component is directly proportional to the difference in the $r_3$ components of the two ensembles and hence directly measures the order in the ensemble at time $\tau_D$. As long as the final spinlocking time (cf. Figure 14) is constant for each determination, the decay of spinlocking directly measures the loss of order. As discussed in Chapter IV, the spinlocked component may be detected conventionally or by means of a probe pulse (Part (d), Figure 3). Figure 14 also presents the optically detected waveform obtained when using the remagnetization method in an electron-spin ordering experiment.

Table 1 presents a comparison of the results obtained using the two different techniques to monitor the loss of order in a triplet ensemble subject to slow vertical and horizontal processes. Although the agreement is excellent, certain features of each detection method dictate which is appropriate for a given situation. The spin echo method is advantageous in that it avoids problems associated with non-adiabatic effects encountered during remagnetization. However, optically detected echoes require that the probe pulse be swept in time complicating the time-averaging required to surmount signal-to-noise problems associated with these experiments. In addition, it is difficult to normalize the echo amplitude to account for fluctuations in experimental conditions. On the other hand, the remagnetization
Table 1: Comparison of Detection Methods for the Ordered State

<table>
<thead>
<tr>
<th>TEMPERATURE (K)</th>
<th>OBSERVED ORDERED STATE LIFETIME (MSEC)</th>
<th>REMAGNETIZATION</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ECHO</td>
<td></td>
</tr>
<tr>
<td>1.48</td>
<td>32.2 ± 2</td>
<td>32.0 ± 2</td>
</tr>
<tr>
<td>1.65</td>
<td>33.5 ± 2</td>
<td>--</td>
</tr>
<tr>
<td>1.95</td>
<td>32.6 ± 2</td>
<td>--</td>
</tr>
<tr>
<td>4.20</td>
<td>34.0 ± 2</td>
<td>34.0 ± 2</td>
</tr>
</tbody>
</table>

§ Sample: 1% $\text{H}_2$, 1,2,4,5 tetrachlorobenzene in $\text{h}_{14}$-durene.
method is easily averaged and has the distinct advantage of displaying the entire waveform for normalizing the ordered signal. Thus, the spin echo method is the technique of choice only for the case of conventionally detected experiments with conditions stable enough to insure reproducible excited state ensembles.

Adiabatic Conditions

The ability of a system's r-vector to remain aligned along its effective field \( \hat{\omega} \) depends on the angular rate-of-change of the field. If this change is not adiabatic, the r-vector can no longer remain parallel and starts to precess about \( \hat{\omega} \) according to the torque equation,

\[
\dot{r} = r \times \frac{\hat{\omega}}{\omega}.
\]

What constitutes an adiabatic change?

Defining \( \theta \) to be the angle between \( \hat{\omega}_{\text{eff}} \) and \( -\hat{\omega} \) (see Figure 1), it is easily shown that

\[
\theta = \cot^{-1}[-\omega_1(t)/\Delta\omega].
\]

The rate of change of \( \theta \) during demagnetization is given by

\[
\dot{\theta} = \frac{\omega_1}{\Delta\omega + (\omega_1^2/\Delta\omega)}.
\]

For the rate of change to be adiabatic, the angular velocity of the effective field must be much less than the precession frequency of a system experiencing that field, i.e.

\[
\dot{\theta} \ll \omega_{\text{eff}}.
\]
Thus

\[(89a)\quad \omega_1 \ll \omega_{\text{eff}}[\Delta\omega + (\omega_1^2/\Delta\omega)].\]

Substituting in for $\omega_{\text{eff}}$ yields the general condition for the time rate of change in the applied r.f. field,

\[(89b)\quad \omega_1 \ll [\omega_1/\Delta\omega]^2 + 1]^{1/2} (\Delta\omega + \omega_1^2).\]

As $\omega_1$ is reduced to zero, the condition becomes more stringent. The maximum rate that will be adiabatic for all values of $\Delta\omega$ is determined by taking the limit of Equation 89 as $\omega_1$ goes to zero, yielding

\[(90)\quad \omega_{\text{max}}^2 \ll \Delta\omega^2.\]

One immediately sees that systems close to resonance are the most difficult to demagnetize adiabatically. (On-resonance systems are a pathological case. Because $\omega_{\text{eff}} = \omega_1$, $\theta$ is zero for any value of $\omega_1$ and demagnetization has no effect.) However, all systems that are off-resonance are at least partially adiabatically demagnetized before $\omega_1$ is reduced to the point where the more stringent condition (cf. Equation 90) is in effect, and hence contribute to the ordered state. Figure 15 presents a plot of the amount of order induced in two different triplet state ensembles as a function of the rate at which the applied field is reduced.

A decrease in the induced order is observed for both systems if the rate of demagnetization is too rapid, suggesting that the adiabatic condition is not being met for a significant portion of the line at
Fig. 15. Effect of rate of demagnetization on the amount of order induced in a triplet state ensemble. The dashed line in the figure on the left are the results of a second determination in a different sample.
the faster rates. Both systems exhibit the same maximum "adiabatic" rate as would be expected from Equation 90 since the linewidths are comparable. A faster demagnetization rate would be anticipated for a broader line since a larger portion of the line is well off-resonance. For the system of 1,2,4,5-tetrachlorobenzene in h_{14} durene, a decrease in induced order is observed for slower rates of demagnetization also. This effect may be due to cross-polarization between the ordered electron state and another spin reservoir. This effect is discussed in a later section.

Mathematical Treatment of Loss of Order

For the purposes of describing the loss of order in an ensemble of excited states, it is convenient to identify four subensembles:

- $Y(\pm \Delta \omega)$...the number of fast systems in the $Y$ sublevel
- $Y(\mp \Delta \omega)$...the number of slow systems in the $Y$ sublevel

These populations change due to decay to the ground state, horizontal processes that exchange populations between the fast and slow ensembles in a particular level, and vertical processes that exchange population between the sublevels. Defining

- $k_x, k_y =$ rate constants for decay to the ground state for sublevels $X$ and $Y$ respectively
- $c_x, c_y =$ feeding rates to sublevels $X$ and $Y$
- $k_{fs} =$ rate constant for transfer from the fast to slow ensemble
- $k_{sf} =$ rate constant for transfer from the slow to fast ensemble
\[ k_{VD} = \text{rate constant for transitions from } |Y\rangle \text{ to } |X\rangle \]
\[ k_{VU} = \text{rate constant for transitions from } |X\rangle \text{ to } |Y\rangle \]
\[ k_{VU} \text{ where } \gamma \text{ is a proportionality constant. For thermally induced vertical processes, } \gamma \text{ is just the Boltzmann factor } e^{-\frac{\hbar \omega}{k_B}} \]

one can write the following differential equations describing the subensembles:

\[ \dot{Y}(+\Delta \omega) = -\gamma(+\Delta \omega) (k_y + k_{fs} + k_{VD}) + \gamma(-\Delta \omega) k_{sf} + C_y + X(+\Delta \omega) k_{VU} \]
\[ \dot{Y}(-\Delta \omega) = -\gamma(-\Delta \omega) (k_y + k_{sf} + k_{VD}) + \gamma(+\Delta \omega) k_{fs} + C_y + X(-\Delta \omega) k_{VU} \]
\[ \dot{X}(+\Delta \omega) = -\gamma(+\Delta \omega) (k_x + k_{fs} + k_{VD}) + X(-\Delta \omega) k_{sf} + C_x + X(+\Delta \omega) k_{VU} \]
\[ \dot{X}(-\Delta \omega) = -\gamma(-\Delta \omega) (k_x + k_{sf} + k_{VD}) + X(+\Delta \omega) k_{fs} + C_x + X(-\Delta \omega) k_{VU} \]

In general, these four coupled equations cannot be solved in closed form. For special conditions, however, Equations 92 can be decoupled and simplified.

Of particular interest is the "on-resonance" case, in which the fast and slow ensembles are equal in size. Since ordering results in inverting the slow system ensemble,

\[ X^0(+\Delta \omega) = Y^0(-\Delta \omega) \]
\[ X^0(-\Delta \omega) = Y^0(+\Delta \omega) \]

Further simplification results by noting that in this situation \( k_{fs} \) is equal to \( k_{sf} \), resulting in two sets of coupled equations:

\[ \dot{Y}(+\Delta \omega) = -\gamma(+\Delta \omega) (k_y + k_{fs} + k_{VD}) + \gamma(-\Delta \omega) (k_{fs} + \gamma k_{VD}) + C_y \]
\[ \dot{Y}(-\Delta \omega) = -\gamma(-\Delta \omega) (k_y + k_{fs} + k_{VD}) + \gamma(+\Delta \omega) (k_{fs} + \gamma k_{VD}) + C_y \]

and
\( \dot{X}(\Delta \omega) = -X(\Delta \omega)(k_x + k_{fs} + \gamma k_{VD}) + X(-\Delta \omega)(k_{fs} + k_{VD}) + c_X \)

\( \dot{X}(-\Delta \omega) = -X(\Delta \omega)(k_x + k_{fs} + \gamma k_{VD}) + X(-\Delta \omega)(k_{fs} + k_{VD}) + c_X \).

These coupled equations are readily solved by means of LaPlace transforms yielding

\[
Y(\Delta \omega, t) = \frac{Y^0(\Delta \omega) - Y^0(-\Delta \omega)}{2} e^{[k_y + 2k_{fs} + (1 + \gamma)k_{VD}]t}
\]

\[
+ \left[ \frac{Y^0(\Delta \omega) + Y^0(-\Delta \omega)}{2} - \frac{c_y}{2[k_y + (1 - \gamma)k_{VD}]} \right] \times e^{-[k_y + (1 - \gamma)k_{VD}]t} + \frac{c_y}{k_y + (1 - \gamma)k_{VD}}
\]

\[
Y(-\Delta \omega, t) = \frac{Y^0(-\Delta \omega) - Y^0(\Delta \omega)}{2} e^{[k_y + 2k_{fs} + (1 + \gamma)k_{VD}]t}
\]

\[
+ \left[ \frac{Y^0(-\Delta \omega) + Y^0(\Delta \omega)}{2} - \frac{c_y}{2[k_y + (1 - \gamma)k_{VD}]} \right] \times e^{-[k_y + (1 - \gamma)k_{VD}]t} + \frac{c_y}{k_y + (1 - \gamma)k_{VD}}
\]

\[
X(\Delta \omega, t) = \frac{X^0(\Delta \omega) - X^0(-\Delta \omega)}{2} e^{[k_x + 2k_{fs} + (1 + \gamma)k_{VD}]t}
\]

\[
+ \left[ \frac{X^0(\Delta \omega) + X^0(-\Delta \omega)}{2} - \frac{c_x}{2[k_x + (\gamma - 1)k_{VD}]} \right] \times e^{-[k_x + (\gamma - 1)k_{VD}]t} + \frac{c_x}{k_x + (\gamma - 1)k_{VD}}
\]
\[ x(-\omega, t) = \frac{x^0(-\omega) - x^0(+\omega)}{2} e^{-(k_x + 2k_{fs} + (1 + \gamma)k_{vD})t} + \left[ \frac{x^0(+\omega) + x^0(-\omega)}{2} - \frac{C_x}{2(k_x + (\gamma - 1)k_{vD})} \right] \nonumber \\
\times e^{-(k_x + (\gamma - 1)k_{vD})t} + \frac{C_x}{k_x + (\gamma - 1)k_{vD}}. \]

If it is assumed that local environments are randomly distributed \((45)\) a particular system is equally likely to exchange to a fast or slow environment and hence

\[ 2k_{fs} = k_m, \]

where \( k_m \) is the rate constant for exchange between any environment. Noting that

\[ Y(+\omega, t) - X(+\omega, t) = \int_0^\infty r_3(\omega, t) d\omega \] (97a)

and

\[ Y(-\omega, t) - X(-\omega, t) = \int_{-\infty}^0 r_3(\omega, t) d\omega, \] (97b)

it is easily shown that the ordered component is given by
Using Equation 93 this may be rewritten as

\[ I_{\text{ordered}}(t) = \frac{1}{2}(N^0_y - N^0_x)(e^{-(k_y + k_m + (1 + \gamma)k_{VD})t} \right. \\
+ e^{-(k_x + k_m + (1 + \gamma)k_{VD})t} \left. \right) \]

Thus the ordered state is expected to decay biexponentially. Furthermore, feeding has no effect on the ordered state if one is on-resonance since the incoming population is unordered and evenly distributed to the fast and slow ensembles.

This is not the case if the experiment is performed off-resonance. For this case, one must ignore vertical processes to uncouple the two sets of equations since Equation 93 is no longer valid. This is not an unreasonable assumption for systems at low temperatures. Using this approximation and defining the ensemble exchange constants as

\[ k_{fs} = \left( \int_{-\infty}^{0} g(\Delta \omega) d\Delta \omega / \int_{-\infty}^{\infty} g(\Delta \omega) d\Delta \omega \right) k_m = \lambda k_m \]

\[ k_{sf} = \left( \int_{0}^{\infty} g(\Delta \omega) d\Delta \omega / \int_{-\infty}^{\infty} g(\Delta \omega) d\Delta \omega \right) = (1 - \lambda)k_m \]

one may proceed as before. The parameter \( \lambda \) is just the fraction of systems that are "slow", and hence is the fraction of exchange events
that terminate in a slow environment. Solving for the time evolution of the subensemble populations and calculating the ordered component as before gives

\[
I_{\text{order}} = 2[\lambda y^0(+\Delta\omega) - (1-\lambda)y^0(-\Delta\omega) + \frac{C_y}{k_m+k_y}(1-2\lambda)] 
\times e^{-(k_y+k_m)t} + (1-2\lambda)[y^0(+\Delta\omega) + y^0(-\Delta\omega)] - \frac{2C_y}{k_y} e^{-(k_y)t}
\]

\[
+ 2[(1-\lambda)x^0(-\Delta\omega) - \lambda x^0(+\Delta\omega)] + \frac{C_x}{k_m+k_x}(2\lambda-1)e^{-(k_x+k_m)t} + (2\lambda-1)
\times ((x^0(+\Delta\omega) + x^0(-\Delta\omega)] - \frac{2C_x}{k_x} e^{-(k_x)t}
\]

\[
+ 2k_m(1-2\lambda)\left[\frac{C_y}{k_y(k_y+k_m)} - \frac{C_x}{k_x(k_x+k_m)}\right].
\]

This equation reduces to Equation 98 for \(\lambda = 0.5\) and \(k_{VD} = 0\), i.e. on-resonance with no vertical decay processes. The feeding terms are non-zero for experiments that are performed off-resonance because the two subensembles, fast and slow, are populated unequally. It is important to note that a non-decaying component is present to distort the pure bi-exponential decay of the ordered state that one would observe if on-resonance. This distortion is quite apparent in Figure 16, which presents the decay of the ordered state as a function of \(\lambda\). Figure 17 compares some calculated and experimental decay curves for 1,2,4,5-h_2-tetrachlorobenzene and
CALCULATED DECAY OF ORDERED STATE IN THE ABSENCE OF VERTICAL PROCESSES

\begin{align*}
\lambda &= 0.7 \\
\lambda &= 0.3 \\
\lambda &= 0.6 \\
\lambda &= 0.4 \\
\lambda &= 0.5 \\
\end{align*}

\begin{align*}
k_x &= 1.45 \text{ sec}^{-1} \\
k_y &= 27.5 \text{ sec}^{-1} \\
C_x &= 1.3 \text{ sec}^{-1} \\
C_y &= 26.0 \text{ sec}^{-1} \\
k_m &= 50 \text{ sec}^{-1} \\
\end{align*}

Fig. 16. Decay of Ordered State calculated for different fractions of slow systems, $\lambda$. 
CALCULATED AND EXPERIMENTAL DECAY CURVES FOR
h$_2$-1, 2, 4, 5 TETRACHLOROBENZENE
\( \lambda = 0.3 \) \( T = 1.7 \, ^\circ\text{K} \)

**Fig. 17**
demonstrates the strong dependence of the order decay on the experimental frequency. The experimental and calculated decay curves for 1,2,4,5-h₂-tetrachlorobenzene in 1,2,4,5-d₂-tetrachlorobenzene display the same gross features, but cannot be compared too closely because absolute values for the feeding rates $C_x$ and $C_y$ are not known and vary according to the strength of the optical pumping source. Relative values have been published (46) and were used to approximate the feeding effects in the calculated curve. The fraction of slow systems $\lambda$ was calculated by assuming a Lorentzian distribution of local fields around $\Delta \omega = 0$.

If vertical processes are important, Equations 92 must be integrated numerically to determine the decay of the ordered state for off-resonance conditions. However, if one is forced to use numerical methods, there is an alternate description for the loss of order that permits one to examine the time evolution of the populations of the two sublevels in each homogeneous environment $\Delta \omega_j$. This is advantageous if the inhomogeneous line is quite asymmetric since it allows one to follow the redistribution of population between many homogeneous ensembles instead of just the four ensembles of Equation 91. Defining $P^Y_i$ to be the number of systems experiencing a local field $\Delta \omega_i$ and populating the upper sublevel, one may write

$$
\dot{P}_i^Y = -P_i^Y [k_y + k_{VD} + k_m (1 - g_i)] + P_i^X k_{VD} \\
+ g_i (k_m \sum_{j \neq i} P_j^Y + C_y),
$$

(102)

where $P_i^X$ is the population of the lower sublevel in the same
local environment and $g_i$ is a weighting factor equal to the fraction of environments with local fields equal to $\Delta \omega_i$. The first term reflects losses due to decay to the ground state, vertical transitions to the lower sublevel, and exchange to other environments. The second and third terms reflect feeding from transitions from the lower state, feeding to the sublevel, and exchange from other environments. Equation 102 can be rewritten as

$$\dot{p}^y_i = -p^y_i(k + k_{VD} + k_m) + p^x_i k_{VD} + g_i(k_m \sum_j p^y_j + C_y).$$

Similarly

$$\dot{p}^x_i = -p^x_i(k + \gamma k_{VD} + k_m) + p^y_i k_{VD} + g_i(k_m \sum_j p^x_j + C_x).$$

The result of this treatment is 2L coupled equations where L is the number of homogeneous environments necessary to describe the inhomogeneous line. As before, the loss of order is given by

$$I_{\text{order}} = \frac{1}{N} \left[ \sum_{\Delta \omega_i > 0} (p^y - p^x) - \sum_{\Delta \omega_i < 0} (p^y - p^x) \right].$$

Figure 18 presents the results of such a calculation for a Lorentzian distribution of 251 environments. $k_{VD}$ was chosen to be small to facilitate comparison with the results of Equation 101. The basic features are identical, but there are differences that result from the averaging effect of vertical processes on the feeding and decay rates of the two sublevels.
Fig. 18. Calculated decay curves for the ordered state obtained by integrating Eq. 103 for a Lorentzian line comprised of 251 isochromats. Rate constants for vertical processes were minimized to facilitate comparison to Fig. 16. $\lambda$ represents amount off-resonance in MHz.
Effect of Non-Equivalent Exchange

Although there is no in-plane coherent component that can be altered, non-equivalent exchange does produce a loss of order, even if the exchange is between systems experiencing exactly the same local environment. The loss of order results from the mixing of sublevels during the exchange, and hence appears to result both from vertical processes between the two sublevels involved in the ordered state and additional decay out of the ensemble.

To determine the magnitude of the effect, consider a three-level system characterized by the states \(|j>, |k>, \text{ and } |m>\). In the laboratory frame, the rotated states are given by

\[
\begin{pmatrix}
  j' \\
  k' \\
  m'
\end{pmatrix} =
\begin{pmatrix}
  j \\
  k \\
  m
\end{pmatrix}
\]

where \(R\), the rotation operator, is obtained from Equation 32 by setting the rotating-frame frequency to zero. Carrying through the calculation yields

\[
|j'> = \cos \theta |j> - \sin \theta \cos \phi |k> + \sin \theta \sin \phi |m>
\]

\[
|k'> = \cos \psi \sin \theta |j> + (\cos \theta \cos \phi \cos \psi - \sin \theta \sin \phi) |k> - (\sin \psi \cos \phi + \cos \theta \sin \phi \cos \psi) |m>
\]

\[
|m'> = \sin \psi \sin \theta |j> + (\cos \psi \sin \phi + \cos \theta \cos \phi \sin \psi) |k> + (\cos \psi \cos \phi - \cos \theta \sin \phi \sin \psi) |m>
\]

where the angles are as defined in Chapter III. If \(k_{CCH}\) is the rate constant for non-equivalent exchange, the rate constant for transitions from \(|j>\) to \(|k>\) induced by the transfer is just
\begin{equation}
K(j \rightarrow k) = (\sin \theta \cos \phi)^2 \ k_{\text{CH}}.
\end{equation}

Similar rate constants are defined for the other transitions. For an ordered state that involves \(|j\rangle\) and \(|k\rangle\), \(K(j \rightarrow k)\) and \(K(k \rightarrow j)\) correspond to vertical processes, \(K(j \rightarrow m)\) and \(K(k \rightarrow m)\) are additional decay routes out of the ordered state, and \(K(m \rightarrow j)\) and \(K(m \rightarrow k)\) are new feeding channels to the ordered state. Thus the ordered state is also sensitive to non-equivalent energy exchange independent of the local environments at the two sites.

**Effect of Non-Random Exchange**

Up to this point, it has been assumed that a system undergoing an exchange event can sample all possible environments, i.e. the probability of exchanging between the fast and slow ensembles is given by their relative sizes. This is not true if exchange events are between neighboring environments, where there is an excellent chance of exchanging back to the original environment.

If exchange events are between environments that are spatially adjacent, a system undergoing exchange events with a rate constant \(k_m\) appears to "random walk" away from its original environment. However, its most probable environment at any time will still be its original one, and hence \(k_m\) can no longer be taken as simply the ensemble exchange rate constant times some factor determined by the two ensemble sizes. In fact, \(k_m\) can be substantially larger than the observed ensemble exchange rate constants that are responsible for a loss of order.
The probability distribution for a random walk is given by the binomial distribution, so that the probability of a system being in its original site after \(L\) hops is just

\[
P(0,L) = \frac{L!}{[(\frac{L}{2})!]^2} \left(\frac{1}{2}\right)^L, \quad L = \text{even}
\]

Note that if the exchange is between adjacent environments, \(P(0,L) = 0\) for all odd \(L\). Of the systems making \(L\) exchanges, only \((1 - P(0,L))\) can possibly experience different environments so that

\[
k_{EE}(L) = \phi k_m (1 - P(0,L)),
\]

where \(k_{EE}\) is the ensemble exchange rate constant (\(k_{fs}\) or \(k_{sf}\)) and \(\phi\) is the relative size of the sub ensemble into which the exchange occurs. The total exchange rate constant is given by

\[
k_{EE}(t) = \phi k_m \sum_{L=0}^{\infty} f(L,t)(1 - P(0,L)), \quad L = \text{even}
\]

where \(f(L,t)\) is the fraction of systems that undergo \(L\) exchanges in time \(t\). From Chapter III,

\[
f(L,t) = \frac{(k_m t)^2}{L!} e^{-k_m t},
\]

so that
This exchange rate constant can then be introduced into the differential equations (Equations 92).

An illustrative example proposed by H. C. Brenner (47) is to consider random walk exchange in the "on-resonance" case. In this situation, exchange to any environment except the original populates either the fast or slow ensemble with equal probability so that the ADRF signal is due only to those systems that are in their original environment, i.e. is proportional to

\( I(t) = I(0)(e^{-(k_x \pm k_y + (1+\gamma)k_{VD})t} + e^{-(k_x \pm k_y + (1+\gamma)k_{VD})t})R, \)

where

\[ R = \sum_{L=0}^{\infty} \frac{(k_m)^L}{(1/2L)!^2} = 1 + \frac{(k_m)^2}{4} + \frac{(k_m)^4}{64} + \frac{(k_m)^6}{2304} + \ldots \]
It is apparent that only the first few terms will be important, and then only for large exchange rate constants where the probability for a system undergoing multiple exchanges within the time range of the experiment is non-negligible.

Experimental Considerations

From an experimental viewpoint, one must be concerned about whether or not an ordered state is actually being produced, and if so, what is the appropriate frequency to use for a particular transition.

There are several different procedures that can provide experimental evidence of ordering. The easiest method is to observe the populations of the two sublevels as one demagnetizes the in-plane spinlocked component. If the resulting state is ordered, an $r_3$ component is created only if the experiment is performed off-resonance, when the two ensembles are unequal in size. This provides the best means for determining the resonance frequency if electron ordering is actually occurring. If the state is not ordered there are two distinct situations. The first is if the demagnetization has no effect on the spinlocked component. In this case, even if the experimental frequency is off-resonance, no additional $r_3$ component will be generated during the demagnetization if the process is rapid compared to $T_1$ and feeding processes. If adiabatic demagnetization does affect the spinlocked component but does not create an ordered state, a large $r_3$ component will be generated even if the frequency is on-resonance.
A more conclusive experiment for establishing that demagnetization is resulting in an ordered state is the "ordered" spin echo previously discussed. Since the amplitude of the echo depends on the order induced in the ensemble (on-resonance), one can readily establish if an ordered state is being produced. Equally conclusive and somewhat simpler is to adiabatically remagnetize the ensemble after a time corresponding to several $T_2$ times. If demagnetization had no effect on the in-plane components, they will undergo free precession ($\omega_1 = 0$) and dephase completely. Remagnetization and application of a probe pulse can produce no additional changes in observables since there are no net $r$-vector components. If the demagnetization did affect the in-plane components but did not result in order, a large change in the $r_3$ component will be observed as mentioned previously.

**Cross Polarization**

In addition to gaining information about the dynamics of local environments, one can use an ordered electron spin state to induce large spin-polarizations in other electronic and nuclear spin systems by means of cross-relaxation. (48) This phenomenon can be employed to examine specific features of the coupling between excited states and their environments. For example, by observing the loss of order resulting from energy conserving simultaneous transitions in the two spin reservoirs, one can determine the relative contribution of particular nuclear species to the total hyperfine and quadrupole interaction experienced by the ordered electron spin ensemble. Schuch and Harris (44) have observed cross-relaxation
between coupled triplet spin sublevels and H and D spin reservoirs, and qualitatively measured the distribution of nuclear splittings around an electronic excitation. In addition, one can take advantage of the high spin-polarization frequently found in triplet spin systems to pump nuclear spin reservoirs to high spin temperatures by means of cross-relaxation from an ordered state. This permits magnetic resonance experiments to be performed on rare nuclear spins by a double resonance technique that uses the electronic spin reservoir for both pumping and detecting the nuclear transitions. (43) Cross-relaxation experiments also provide a means for optically detecting resonances in non-radiative spin systems.

Cross-relaxation occurs during demagnetization when the field strength $\omega_1$ is reduced to the point where

$$ (\omega_1^2 + \Delta \omega^2)^{1/2} = \omega_N , $$

i.e. where the energy splitting of the Zeeman states quantized by the effective field just matches the energy splitting of species in another spin ensemble, N. Figure 19 presents the expected electronic spin-polarization as a function of the amount of resonance for several different final values of $\omega_1$. When the condition in Eq. 112 is met, simultaneous transitions in the two spin ensembles are energy-conserving and the ensembles evolve to a common spin temperature if they are coupled together by an appropriate hamiltonian, $\mathcal{H}_{\text{INT}}$. For the case of cross-relaxation from an ordered electron spin state to a nuclear spin reservoir, $\mathcal{H}_{\text{INT}}$ consists
Fig. 19. Spin polarization induced by partial demagnetization as a function of the local field $\Delta \omega$. 
primarily of the components of the hyperfine interaction oscillating at $\omega_N$ that do not commute with the intrinsic hamiltonians of either spin reservoir. Use of this technique to study ground state nuclear spin systems is described in detail by Hartmann and Hahn (42) and Schwab (43).
Chapter VI

Excited State Energy Migration in Solids:
An Application of Coherence Techniques

The transport of electronic energy in crystalline solids depends strongly on the nature of the chemical impurities and crystal defects that interrupt the translational symmetry of the host lattice. (14,49,50,51) These imperfections give rise to localized impurity states that interact with the delocalized band states of the host lattice to limit the coherent nature of the excitation transfer process, (52) not only by scattering excitations between different band states, but also by providing a localized energy "trap" if the impurity state is of lower energy than the exciton band (Figure 20). This phenomenon of excitation localization in impurity states is most important in governing the efficiency of energy transport in solids because it corresponds to excitations becoming stationary at particular sites in the lattice. Thus long-range energy transport in real solids consists of energy migration events between localized states via the host exciton band. Central to the dynamics of this process is the manner in which an excitation localized around an impurity site is thermally promoted to the host band and the "quantum yield" for subsequent evolution to a mobile excitation. Of particular interest is the role of the density of states in the exciton band in determining the efficiency with which an excitation migrates away from its initial trap site. The role is two-fold since the nature of the migration
BAND AND ISOTOPIC TRAP STRUCTURE OF PERDEUTERATED 1,2,4,5 TETRACHLOROBENZENE

\[ \Delta = 11.2 \text{ cm}^{-1} \]

\[ \Delta = 22.3 \text{ cm}^{-1} \]

\( \tau_s \)

\( \tau_d \)

XBL766-7096

Fig. 20
process and the quantum yield for the decay of localized states into the band upon promotion depend on the density of states as well as the lattice temperature. These features will be reflected in the temperature and concentration dependence of the rate constant for trap-to-trap migration.

The System

To examine some of the features outlined above, triplet state energy migration between isotopic traps in 1,2,4,5-d$_2$-tetrachlorobenzene (d$_2$-TCB) was investigated using spinlocking and electron spin ordering techniques. Although triplet exciton bandwidths are small compared to singlet bandwidths, the relatively long life of the triplet state permits excitation transfer over long distances. (53) In addition, the triplet sublevels of most molecules are non-degenerate in zero external field as a result of the anisotropic dipolar interaction of the two unpaired electrons. Their interaction is commonly expressed in terms of the Hamiltonian (54)

\[ H_0 = -X S_x^2 - Y S_y^2 - Z S_z^2. \]

The three zero-field eigenfunctions of this Hamiltonian, $\tau_x$, $\tau_y$, and $\tau_z$, are quantized along the molecular axes of symmetry in tetrachlorobenzene, and are mixed by the triplet state angular momentum operators $S_x$, $S_y$, and $S_z$ providing convenient transitions for coherence experiments. By spinlocking and ordering these transitions in a triplet state ensemble populating a particular type of trap, one can examine the dynamics of energy transfer into and out of localized impurity states.
Several features of 1,2,4,5-d$_2$-tetrachlorobenzene are particularly advantageous for such studies. There are two distinct isotopic traps below the exciton band, h$_2$-TCB with a trap depth $\Delta$ of 22.3 cm$^{-1}$ below the $k = 0$ state and hd-TCB with $\Delta = 11.2$ cm$^{-1}$, as is illustrated schematically in Figure 20. Both are sufficiently shallow so that thermal promotion (14) of excitations to states isoenergetic with the band is observed even at liquid helium temperatures. Several workers (46,55) have examined the triplet state parameters of these species. A summary of the results is presented in Table 2. Perhaps the most important feature is that the exciton interaction in tetrachlorobenzene is essentially one-dimensional and along chains of translationally equivalent molecules. (56) Since isotopic substitution is not expected to affect the crystal symmetry, non-equivalent exchange is absent. This is confirmed by the single exponential decays observed when one optically-detects spinlocking in this system.

Promotion of Excitations out of Localized States

To measure the rate constant for thermal promotion out of the deep trap, the D - |E| transition ($\tau_y \leftrightarrow \tau_x$) of h$_2$-TCB was spinlocked. This transition is easily spinlocked since the linewidth at half-height (3.4 MHz) is smaller than the available r.f. field strength $\omega_1$ (~ 5 MHz) so that aside from decay to the ground state and $T_{1\text{mol}}$ processes, phase coherence can be lost only by promotion to states where the transition frequency D - |E| has changed by more than 5 MHz. Since an excitation localized at an impurity site is in general...
Table 2: Triplet State Kinetic Parameters of 1,2,4,5 tetrachlorobenzene

<table>
<thead>
<tr>
<th>PARAMETER</th>
<th>$h_2$-TCB</th>
<th>$d_2$-TCB</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ref.</td>
<td>ref.</td>
</tr>
<tr>
<td>zero field transitions (GHz)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$2</td>
<td>E</td>
<td>$</td>
</tr>
<tr>
<td></td>
<td>1.7450 (46)</td>
<td></td>
</tr>
<tr>
<td>$D-</td>
<td>E</td>
<td>$</td>
</tr>
<tr>
<td></td>
<td>3.6814 (46)</td>
<td></td>
</tr>
<tr>
<td>$D+</td>
<td>E</td>
<td>$</td>
</tr>
<tr>
<td></td>
<td>5.4264 (46)</td>
<td></td>
</tr>
<tr>
<td>$\tau_x$</td>
<td>790±40</td>
<td>750±40</td>
</tr>
<tr>
<td></td>
<td>700±30 (46)</td>
<td></td>
</tr>
<tr>
<td>$\tau_y$</td>
<td>36±1</td>
<td>36±1</td>
</tr>
<tr>
<td></td>
<td>34±1 (46)</td>
<td></td>
</tr>
<tr>
<td>$\tau_z$</td>
<td>38±1</td>
<td>38±1</td>
</tr>
<tr>
<td></td>
<td>36±1 (46)</td>
<td></td>
</tr>
</tbody>
</table>

Relative feeding rates ($h_2$-TCB) $\tau_x:\tau_y:\tau_z = 1:10:20$

† in a host of $h_{14}$-durene. Reference is Ref. 55 unless otherwise specified.
surrounded by host molecules, the promotion process is likely to be to the delocalized exciton k states. The question then becomes whether or not the band transition frequency is sufficiently different to affect a loss of coherence. Extrapolation of the D - |E| values of h$_2$-TCB and hd-TCB would suggest that the band transition frequency is approximately 3458 MHz, more than sufficient to produce a loss of spinlocking. Recent experimental evidence supports this assignment of the band frequency. (57)

A theoretical treatment of the promotion of localized states to exciton bands is contained in the model of Fayer and Harris. (14) In this model, the promotion is viewed as a two-step process involving an intermediate state |$\phi$> that is isoenergetic with one or more of the delocalized k states of the band. In the first step, a phonon scatters with the impurity state |$\tau$>, promoting the excitation to the localized intermediate |$\phi$>. In the second step, |$\phi$> decays radiationlessly into the exciton band, a process that is facilitated by the density of k states.

The probability per unit time of a phonon mode |$P(\epsilon)$> interacting with the impurity state |$\tau$> and decaying into a particular k state via the intermediate state |$\phi$> is given by the golden rule rate

$$K_{k\epsilon} = (2\pi/\hbar)|N(\epsilon)|_{\tau}|\langle P(\epsilon)|J_{\tau P}|\phi( P(\epsilon)-E_\phi)\rangle|^2 |\phi( P(\epsilon)-E_\phi)|H_{k\phi} |k( P(\epsilon)-E_\phi) >|^2 \rho(E_\phi),$$

(114)

where $E_\phi$ is the energy of the intermediate state, $\epsilon$ is the energy of phonons in mode |$P(\epsilon)$> and $\rho(E_\phi)$ is the density of k states at the
energy of the intermediate. The term \((P(\varepsilon) - E_\phi)\) represents the phonon state after the extraction of energy \(E_\phi\). Both steps conserve the total energy of the system. In the first step, the energy required to promote the localized state is extracted from the phonon field and hence the transition probability to \(|\phi\rangle\) depends not only on the matrix element between the phonon-excitation product states

\[ <\!\!\langle \!\!\langle P(\varepsilon)|H_{TP}\!\!\rangle\!\!\rangle |P(\varepsilon)E_\phi\!\!\rangle \!\!\rangle, \]

but also on the average number of phonons \(<N(\varepsilon)>_T\) occupying \(|P(\varepsilon)\rangle\) at temperature \(T\). \(<N(t)>_T\) is given by the Planck distribution function times \(\rho(\varepsilon)\), the density of states characterizing the phonon dispersion at energy \(\varepsilon\). The radiationless decay into the exciton \(k\) state conserves energy and is characterized by

\[ <\!\!\langle \!\!\langle \phi(\varepsilon) - E_\phi \!\!\rangle\!\!\rangle |H_{\phi k}\!\!\rangle |k(P(\varepsilon) - E_\phi)\!\!\rangle \!\!\rangle. \]

The total rate constant \(k_p\) is then obtained by summing Equation 114 over phonon energies \(\varepsilon \geq E_\phi\) and then summing over all possible intermediate states corresponding in energy to various \(k\) states in the band.

Since these experiments are performed at liquid helium temperatures, \(<N(\varepsilon)>_T\) can be approximated by \(\rho(\varepsilon) \exp(-\varepsilon/k_BT)\) because \(k_BT\) is much less than \(\Delta\). Furthermore, only linear regions of the acoustic phonon branches are likely to be populated at these temperatures so that \(\rho(\varepsilon)\) will be constant over the energies under consideration. If the exciton bandwidth is narrow, the small range of effective phonon energies \(\varepsilon\) that can result in promotion may be approximated by the trap depth \(\Delta\), so one would expect the promotion rate constant to increase exponentially with temperature with a characteristic
activation energy equal to the trap depth.

The results from a spinlocking experiment on the deep trap have already been presented in Figure 8. As discussed in Chapter IV, it shows both temperature dependent and independent components. In this particular system, contributions to the loss of spinlocking from both $T_{1\text{pm}}$ processes and decay to the ground state are expected to be essentially temperature independent, and so their contribution can be easily subtracted out to obtain the temperature dependence of the promotion rate constant $k_p$. This temperature dependence is presented in Figure 21 and was obtained by fitting the experimental data to an exponential plus a constant and then subtracting the constant value from each of the observed total decay constants for spinlocking. Since the contribution of the lifetimes $k_A$ is known, the value of the constant determines $k_{T_{1\text{pm}}}$, the rate constant for $T_{1\text{pm}}$ processes. Table 3 presents the results for several samples with different deep trap concentrations.

A disturbing feature is that the activation energy characteristic of the promotion process is considerably less than the spectroscopic trap depth for each of the crystals. Even though the trap depth is measured from the top of the band in TCB, the bandwidth of 1-2 cm$^{-1}$ (36,58) is not large enough to account for this discrepancy. Two possible explanations for the spinlocking activation energy are:

(i) the existence of an intermediate trap with $\Delta \approx 6$ cm$^{-1}$. This trap would most likely be a host $d_2$-TCB molecule whose energy is strongly perturbed by a nearest neighbor deep trap.

(ii) The observed activation energy is a weighted average of thermal promotion to the band and thermally-activated tunnelling to shallow
PROMOTION RATE CONSTANT $k_p$ VERSUS RECIPROCAL TEMPERATURE

0.06% $\text{h}_2\text{-tetrachlorobenzene}$ in $\text{d}_2\text{-tetrachlorobenzene}$

$D-\text{E}$ transition: 3577.8 MHz

$\Delta_{\text{activation}} = 16.1 \text{ cm}^{-1}$
Table 3: Temperature Dependence of Promotion Rate Constant

<table>
<thead>
<tr>
<th>DEEP TRAP CONCENTRATION (% h₂-TCB)</th>
<th>OBSERVED ACTIVATION ENERGY, Δ (cm⁻¹)</th>
<th>OBSERVED Kₚ₁₅₀m (sec⁻¹)</th>
<th>FITTING PARAMETER η A x 10⁻⁷</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.003</td>
<td>16.9</td>
<td>13.6</td>
<td>7.10478</td>
</tr>
<tr>
<td>0.06</td>
<td>16.1</td>
<td>15.3</td>
<td>4.65692</td>
</tr>
<tr>
<td>0.7</td>
<td>14.7</td>
<td>4.0</td>
<td>1.69493</td>
</tr>
<tr>
<td>6.0</td>
<td>17.0</td>
<td>26.6</td>
<td>9.56820</td>
</tr>
</tbody>
</table>

η Parameter obtained by fitting experimental data to \( k_p(T) = A \exp(-\Delta/k_B T) \).
† For the D-|E| transition, \( k_A \approx 14.5 \) sec⁻¹.
traps (hd-TCB).

Although an intermediate trap has never been observed spectroscopically in emission, this does not necessarily rule out its existence. Excitation entering this intermediate trap may be promoted immediately to the band or trap on the neighboring $h_2^{-}$-TCB molecule that is 16 cm$^{-1}$ lower in energy. If either or both of these processes are rapid, the intermediate trap population will be negligible and no emission will be observed. Even though the residence time is negligible, spinlocking can still be lost by promotion to this state if subsequent detrapping to the band is efficient. However, since it is associated with a deep trap, the intermediate trap should be observed in absorption whenever the deep trap is present in sufficient concentration to be observed also. Narrow band laser excitation spectra which display absorption due to the deep trap do not show any absorption at the energy corresponding to the spinlocking activation energy, suggesting that there is no intermediate trap. This conclusion is further supported by calculating the effect of the $h_2^{-}$-TCB impurity state on the host band energies. (57) For this calculation, the nearest neighbor interaction energy, $\beta$, was chosen to be 1 cm$^{-1}$ (larger than estimated value of 0.2-0.5 cm$^{-1}$ for TCB), and the impurity $h_2^{-}$-TCB was surrounded by 80 $d_2^{-}$-TCB molecules on both sides to insure that end effects in the band would be minimized. Diagonalization of the resulting matrix showed that the nearest neighbors to the trap are perturbed only slightly, and that no states corresponding to a trap depth of 6 cm$^{-1}$ are generated.
With these considerations in mind, it is difficult to explain the spinlocking activation energy in terms of an intermediate trap state.

Up to this point it has been assumed that there is only one pathway for promotion since the probability of shallow traps adjacent to deep traps is quite small. However, this assumption ignores thermally induced tunnelling to shallow traps several lattice sites away that are virtually coupled to the deep trap by means of the band states on the intervening host molecules. Although this coupling is expected to be much weaker than the trap-band interaction, the transition probabilities for the two paths can be comparable because the associated phonon term for promotion to the shallow trap is much larger than that for promotion to the band.

Rewriting Equation 114 to reflect both pathways yields

\[
\kappa = \frac{2\pi}{\hbar} \left[ \rho(E_s) e^{-E_s/k_BT} |\langle \tau_D | \phi_{D_s} | \tau_s \rangle|^2 \rho(E_s) \right] \\
+ \sum_k \rho(E_k) e^{-E(k)/k_BT} |\langle \tau_D | \phi_{D_k} | k \rangle|^2 \rho(E(k))],
\]

(115)

where \(E_s\) is the energy of the shallow trap relative to the deep trap, \(\epsilon(k)\) is the energy difference between the deep trap and the \(k^{th}\) band state, \(\rho(E_s)\) and \(\rho(E(k))\) are the respective densities of electronic states, and the two matrix elements involved for each path have been represented as one connecting the deep trap \(\tau_D\) to
either the shallow trap $\tau_s$ or a band state $k$. If it is assumed that both phonon energies $\varepsilon_s$ and $\varepsilon(k)$ are in the linear portion of the acoustic phonon dispersion, $\rho(\varepsilon_s) = \rho(\varepsilon(k))$ and Equation 115 can be further simplified to

\begin{align}
K_p = \frac{2\pi\rho(e)}{h} & \left[ e^{-\varepsilon_s/k_B T} |\langle \tau_D | H_{DS} | \tau_s \rangle |^2 \rho(\varepsilon_s) \\
& + \sum_k e^{-\varepsilon(k)/k_B T} |\langle \tau_D | H_{Dk} | k \rangle |^2 \rho(\varepsilon(k)) \right].
\end{align}

This expression must be averaged over the number of band molecules separating the deep and shallow traps. This separation not only affects the coupling between the two traps, but also determines the number of states in the band, and hence changes the efficiency of both pathways.

In order to perform the averaging, the functional dependence of the matrix elements on the number of intervening band molecules, $N$, must be determined. First consider the coupling between the two traps and let $\langle \tau_D | H_{DS} | \tau_s \rangle = \beta'$. Following the derivation of McConnell, (59) it is readily shown that the coupling between two states of energies $-\Delta$ and $-\Delta_2$ through a band of $N$ virtual states, $\phi_j$, is given by

\begin{equation}
(117a) \quad \beta' = \frac{\beta_1 \beta_2 \beta^{N-1}}{\Delta N},
\end{equation}

where $\beta = \langle \phi_j | H | \phi_{j+1} \rangle$, the exciton interaction; $\beta_1 = \langle \phi_1 | H | \tau_D \rangle$;
\[ \beta_2 = \langle \psi_N | \tau_s \rangle \] and \[ \Delta = (1/2)(\Delta_1 + \Delta_2), \] the average trap depth.

For the case of isotopic impurities, \( \beta_1 \) and \( \beta_2 \) are expected to be the same as \( \beta \) except for a factor \( \chi \) determined by the change in the Franck-Condon factors describing the overlap of vibrations involving the isotope in question. For the case of proton substitution on the ring in \( d_2 \)-TCB, these changes are expected to be small so that \( \chi \approx 1 \) and \( \beta' \) may be approximated by

\[ \beta' = \beta (\beta/\Delta)^N. \]

In the case of the band, the number of \( k \) states to sum over is \( N \), the number of band molecules between the two traps. Each \( k \) state can be represented as a linear combination of the localized states \( \phi_j \).

\[ |k\rangle_i = \sum_{j=1}^{N} (1/\sqrt{N}) \phi_j e^{i(j \cdot \vec{r})}, \]

and since the overlap of the trap with its neighbor \( \phi_1 \) is approximated by \( \beta \), then

\[ \langle \tau_D | \chi_{DK} | k \rangle = (1/\sqrt{N}) \beta, \]

which satisfies the requirement that

\[ \sum_k |\langle k | \phi_1 \rangle|^2 = 1. \]

\[ \langle \tau_D | \chi_{DK} | k \rangle = 0 \] if there are no band molecules adjacent to the deep trap. One can now rewrite Equation 116 to reflect the dependence on \( N \), i.e.
\[
kp(N) = \frac{\beta^2 2\pi \rho(e)}{h} \left[ e^{-\frac{e_s}{k_BT}} (\beta/\Delta)^{2N} \rho(e_s) \right. \\
\left. + \frac{1}{N} \sum_{k=1}^{N} e^{-\varepsilon(k)/k} \rho(E(k)) \right].
\] (119)

To average this expression, let \( P \) be the fraction of shallow traps and assume that the deep trap concentration is negligible by comparison. Then

\[
<kp> = P \sum_{N=0}^{(1/P)-1} kp(N)
\]

\[
= \frac{2\pi \beta^2 \rho(e)}{h} \left[ e^{-\frac{e_s}{k_BT}} \rho(e_s) \sum_{N=0}^{(1/P)-1} (\beta/\Delta)^{2N} \right. \\
\left. + \sum_{N=1}^{(1/P)-1} \frac{1}{N} \sum_{k=1}^{N} e^{-\varepsilon(k)/k} \rho(E(k)) \right].
\] (120)

Since this equation contains an explicit summation over \( k \) states, \( \rho(E(k)) = \rho(E_s) \), which in turn is determined by the number of equivalent directions surrounding a deep trap.

A branching ratio \( \psi(T,P,B) \) describing the fraction of promotion events that are to the band can now defined by

\[
\psi(T,P,B) = \frac{\sum_{N=1}^{1/P-1} \frac{1}{N} \sum_{k=1}^{N} e^{-\varepsilon(k)/kBT} \rho(E(k))}{e^{-\varepsilon_s/k_BT} \rho(E_s) \sum_{N=0}^{1/P-1} \left( \frac{\beta}{\Delta} \right)^{2N} \rho(e_s) + \sum_{N=0}^{1/P-1} \frac{1}{N} \sum_{k=1}^{N} e^{-\varepsilon(k)/k_BT} \rho(E(k))}
\]

(121)
and used to estimate a correction for experimentally obtained values of
the promotion rate constant to obtain a promotion rate to the band $k_p^B$.

A plot of $\Psi$ versus $T$ for a 1% concentration of hd-TCB and $B = 0.25$
cm$^{-1}$ is presented in Figure 22, while Table 4 gives the results of applying
this model to spinlocking data obtained for the various crystals.
The activation energies now lie slightly above the band suggesting that
promotion may be a multiphonon Raman phonon process. For example, a pho-
non of energy slightly greater than the trap depth can be absorbed with
simultaneous emission of a low energy phonon, resulting in promotion to
the band. This is a reasonable mechanism if the phonon density of states
function is peaked for phonon energies slightly greater than the trap
depth. However, there is no requirement that phonon absorption be limited
to a single phonon process, i.e., promotion may involve absorption of several
low energy phonons followed by emission if energy matching with the band
is required. The activation energy for the 6% crystal must be interpreted
cautiously because the assumption that the deep trap concentration is un-
important is no longer valid.

The spinlocking activation energy appears to decrease with increasing
deep trap concentration, which may reflect a change in the relative impor-
tance of one (direct) and multi (Raman) phonon processes. At high trap
concentrations, the cross section for multi-phonon processes can be re-
duced because the increasingly localized nature of the modes results in a
decrease in the density of states at appropriate energies in the phonon
dispersion.

Decay of Localized States into Mobile Excitations

Having measured the rate constant for thermal promotion, the question
FRACTION OF PROMOTION EVENTS THAT OCCUR TO EXCITON BAND

hd-tetrachlorobenzene: 1%
\( \beta = 0.25 \text{ cm}^{-1} \)
\( \chi = 1 \)

Fig. 22. Band branching ratio \( \psi \) as a function of temperature.
Table 4: Temperature Dependence of Promotion Rate Constant to Exciton Band \((k_{p}^{B})\)

<table>
<thead>
<tr>
<th>DEEP TRAP CONCENTRATION (% (h_2)-TCB)</th>
<th>ACTIVATION ENERGY ((\Delta'), (\text{cm}^{-1}))</th>
<th>FITTING PARAMETER (\text{A}^\dagger)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.003</td>
<td>25.9</td>
<td>(2.29432 \times 10^9)</td>
</tr>
<tr>
<td>0.06</td>
<td>24.8</td>
<td>(1.23977 \times 10^9)</td>
</tr>
<tr>
<td>0.7</td>
<td>23.8</td>
<td>(6.13676 \times 10^8)</td>
</tr>
<tr>
<td>6.0</td>
<td>28.0</td>
<td>(1.33970 \times 10^{10})</td>
</tr>
</tbody>
</table>

\(\dagger\) Parameter obtained by fitting corrected values of \(k_p\) to the equation \(k_{p}^{B} = A \exp(-\Delta'/k_BT)\)
becomes whether or not upon promotion an excitation remains localized and eventually retraps at the same site or becomes a mobile exciton and migrates to another impurity site before retrapping occurs. Defining $\alpha$ as the fraction of promoted excitations that migrate to other traps, one may define a migration rate constant,

$$k_{m}^T = \alpha k_p$$

where $k_{m}^T$ is the rate constant for thermally induced excitation exchange between impurity sites. Similarly $\beta k_p$ is the rate constant for localized retrapping, and can be distinguished from $k_{m}^T$ by means of electron spin ordering since order will only be destroyed by events resulting in trap-to-trap exchange. In the absence of vertical processes and direct exchange between trap sites, the total exchange rate, $k_{m}$, characterizing the decay of the ordered state will be equal to $k_{m}^T$.

To determine $k_{m}^T$, the same transition as used in the spinlocking measurements (deep trap D - |E|) was ordered and monitored optically by adiabatic remagnetization. The value of $k_{m}$ was then extracted by fitting the observed decay to Equation 99 with the assumption that vertical processes, $k_{VD}$, were negligible. The result of this treatment as a function of temperature for one of the crystals is presented in Figure 23. The temperature dependence of $k_{m}$ bears a striking resemblance to that of the loss of spinlocking (Figure 8), i.e. appears to have a temperature independent component. Extensive curve fitting confirmed that this component, corresponding to a "bottoming-out" value in $k_{m}$, has an activation energy that is essentially zero. The origin of the "bottoming-out" effect is
TEMPERATURE DEPENDENCE OF DECAY OF ORDERED STATE

0.003\% h_2-tetrachlorobenzene in d_2-tetrachlorobenzene

D-IEI transition: 3577.8 MHz

Fig. 23. Temperature dependence of $k_m$. 
not well understood. There are several different processes that can contribute to a temperature-independent loss of order, including vertical processes, direct exchange between trap sites, and large changes in the local environment of a particular site that would cause a loss of order even in the absence of exchange events. However, there is considerable evidence that vertical processes in this system (46,55,60) are slow at liquid helium temperatures. Furthermore, the evolution of a particular site's environment requires nuclear transitions which are also too slow at low temperatures to account for all of the "bottoming-out" value. The third mechanism, direct coupling of deep traps by means of virtual coupling through the band is plausible; however the "bottoming-out" value decreases with increasing \( h_2 \)-TCB concentration, contrary to what one would anticipate if this mechanism were primarily responsible for the observed value.

In any case, the temperature-independent component represents a loss of order due to processes other than promotion with subsequent migration, and must be subtracted out to obtain \( k_m^T \). This was accomplished by fitting the data to an exponential plus a constant, the constant corresponding to the "bottoming-out" value. The results of this treatment for the different crystals are presented in Table 5. Along with the "bottoming-out" value for \( k_m \), the apparent activation energy also decreases with increasing \( h_2 \)-TCB concentration suggesting that the decreasing distance between traps facilitates the energy exchange process. The effect of trap separation is twofold; not only does it determine in part the
Table 5: Temperature Dependence of Rate Constant $k_m^T$

<table>
<thead>
<tr>
<th>DEEP TRAP CONCENTRATION (% $h_2$-TCB)</th>
<th>OBSERVED ACTIVATION ENERGY, $\Delta''$ (cm(^{-1}))</th>
<th>&quot;BOTTOM OUT&quot; VALUE (sec(^{-1}))</th>
<th>FITTING PARAMETER(^*$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.003</td>
<td>21.4</td>
<td>27.9</td>
<td>$1.14816 \times 10^8$</td>
</tr>
<tr>
<td>0.06</td>
<td>20.1</td>
<td>24.8</td>
<td>$5.72475 \times 10^7$</td>
</tr>
<tr>
<td>0.7</td>
<td>$\n$</td>
<td>14.4</td>
<td>$\n$</td>
</tr>
<tr>
<td>6.0</td>
<td>9.8</td>
<td>4.0</td>
<td>$1.96816 \times 10^5$</td>
</tr>
</tbody>
</table>

\(^*$ Parameter obtained by fitting experimental data to $k_m^T = A \exp(-\Delta''/k_BT) + \text{bottom out value.}$

$\n$ Poor fit to exponential.
fraction of mobile excitons that migrate sufficiently far enough to trap at another site, it also determines the relative importance of trap-trap exchange events that involve promotion to the band via a shallow trap. As was demonstrated in an earlier section, tunnelling to the shallow trap is an important pathway out of the deep trap at low temperatures and if followed by detrapping to the band can provide an alternate route for promotion and subsequent migration.

The effect of decreasing trap separation is illustrated by the change in the observed $k_T^m$ values for the different crystals at a particular temperature:

<table>
<thead>
<tr>
<th>$h_2$-TCB concentration</th>
<th>observed $k_T^m$ ($\sim 2.0^\circ K$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.003 %</td>
<td>6.9 sec$^{-1}$</td>
</tr>
<tr>
<td>0.06 %</td>
<td>50.23 sec$^{-1}$</td>
</tr>
<tr>
<td>0.7 %</td>
<td>35.70 sec$^{-1}$</td>
</tr>
<tr>
<td>6.0 %</td>
<td>173.1 sec$^{-1}$</td>
</tr>
</tbody>
</table>

Because of the shallow trap concentration ($\sim 1\%$), the density of band states does not change appreciably in the crystals with low $h_2$-TCB concentration, so that the observed change in $k_T^m$ is primarily due to the decrease in trap separation rather than the

The electron ordering data for this concentration displayed considerable scatter and anomalous trends. Because of this, interpretations relying on ADRF data will not consider this sample, however calculations and tables will continue to include entries for the crystal.
effect of the density of states on the fraction of localized excitations that become mobile excitons. Thus one can consider \( \alpha \) as a product of two quantum yields:

\[
\alpha = (\alpha_{me})(\alpha_{mig})
\]

where \( \alpha_{me} \) is the quantum yield for evolution of localized states to mobile excitons and \( \alpha_{mig} \) is the fraction of mobile excitons that migrate far enough to trap at a different site. Consequently the dependence of \( \alpha \) on temperature and the density of states in the exciton band reflect the effects of these same parameters on mechanisms for energy transfer as well as the manner in which localized states evolve into excitons.

From Equation 122 it is seen that \( \alpha \), the quantum yield for trap-to-trap migration upon promotion, is determined by the ratio \( k_{T}^{m} / k_{B}^{p} \). Using the fitting parameters presented in Tables 4 and 5, \( \alpha \) as a function of temperature was calculated. The results for the various crystals are represented as solid lines in Figure 24, while the circles and associated error bars are values of \( \alpha \) determined directly from experimental values.

Several features of the temperature dependence should be noted. In all crystals, \( \alpha \) decreases inversely with increasing temperature, in accordance with qualitative considerations of exciton-phonon scattering. (26-30) As the temperature is increased, both \( \alpha_{me} \) and \( \alpha_{mig} \) are expected to decrease due to rapid scattering between the delocalized k states of the band. In the case of \( \alpha_{me} \),
Dependence of the Exciton Quantum Yield on the Host Density of States

$h_2$-1,2,4,5 tetrachlorobenzene in $d_2$-1,2,4,5 tetrachlorobenzene

Fig. 24
Fig. 24. The quantum yield for trap-trap migration as a function of deep trap concentration. Solid lines represent values calculated from the best fit parameters in Tables 4 and 5 while circles with associated error bars represent values calculated from actual data points. The slopes for the 0.003% and 0.06% crystals are essentially the same. Note the change of scale for the 6.0% crystal.
at higher temperatures the localized state $|\phi\rangle$ decays into a band state composed of a superposition of $k$ states that is rapidly fluctuating. This state tends to be localized around the impurity site and hence corresponds to a localized rather than mobile exciton. Increased exciton-phonon scattering also limits the coherent nature of energy migration in the band, \(^{(61)}\) resulting in a change from wavepacket propagation \(^{(62)}\) to random-walk hopping as the dominant mechanism for energy transfer and resulting in a reduction in $\alpha_{\text{mig}}$. The slopes of $\alpha$ versus $1/T$ for the various crystals appear to correlate with the density of exciton states; the .003\% and .06\% samples have essentially the same density of states (because of the high hd-TCB concentration) and exhibit similar slopes, \(^{(63)}\) while the 6.0\% crystal with a substantially lower density of states shows a much steeper dependence of $\alpha$ on temperature. A possible explanation for this is that the larger energy separation between $k$ states when the state density is low results in a more rapid loss of phase coherence in a mobile wavepacket for a given exciton-phonon scattering rate.

Although the temperature dependence of $\alpha$ is in accord with that predicted from these simple considerations, it is disturbing that the magnitude of $\alpha$ corresponds to a physically unrealizable situation, i.e. it appears that more excitations migrate than are promoted. Several different factors can account for this error including:

(i) problems of taking ratios of numbers whose magnitudes are
much less than the certainty with which they are known. The errors in experimental values of $k_T$ are estimated at about 5%, while those for $k_m$ are estimated at 10-15%. After treatment of the data, these errors can be large compared to the values obtained for $k_p^B$ and $k_m^T$, particularly at the lower temperatures.

(ii) $\chi$, describing the change in the Franck-Condon factors upon isotopic substitution, is not exactly unity. The effect of decreasing $\chi$ is to decrease the weight of the shallow trap, increasing the apparent promotion rate constants to the band and reducing the ratio $k_m^T/k_p^P$. However, this effect alone cannot account for the large values of $\alpha$. Calculations with $\chi = 0.5$ still result in quantum yields greater than unity at low temperatures.

(iii) The values for $k_m^T$ include a contribution from excitations that are promoted to the band via the shallow trap whereas $k_p^B$ measures only promotion events directly to the band.

The fact that the 6.0% crystal shows the most anomalous values for $\alpha$ would indicate that the third source of error is the most significant. Also, the decrease in the observed activation energy associated with $k_m^T$ for this concentrated crystal suggests that detrapping via the shallow trap is an important route to the band.

Although the fraction of excitations detrapping to the shallow trap can be determined from the model presented in Equation 120, it is difficult to determine an appropriate
correction function for the values of $k_{m}^{T}$ because there are two processes: promotion to the band and decay to the ground state affecting population entering the shallow trap. Attempts to spinlock the shallow trap in order to determine promotion rate constants have proven unsuccessful. An additional problem is that the measured level lifetimes (60) for the shallow trap contain a significant contribution due to promotion making it difficult to determine the rate constants for decay to the ground state. A third aspect is that excitations originating in a deep trap that end up in a shallow trap at the time of detection appear to have left the ensemble, producing a loss of order regardless of whether or not the excitation ever migrated in the band. To correct for these features would require that the decay rate constants from the deep trap, $k_{x}$ and $k_{y}$, be adjusted to reflect the percentage of excitations that are thermally promoted to the shallow trap but do not undergo subsequent promotion to the band. The increase in these rate constants would result in reduced values for $k_{m}^{T}$ as determined by Equation 99, which in turn would decrease values for $\alpha$. In addition, one would have to correct $k_{p}^{B}$ to reflect the additional contribution of promotion to the band via the shallow trap. Unfortunately, these corrections require knowledge of the promotion rate constant for detrapping from the shallow trap, information that can presently be obtained in a straightforward manner only by spinlocking.

Thus the magnitude of $\alpha$, which would permit the calculation of certain features of the migration process such as the coherence
length, remains undetermined.

Experimental Procedure

In this section, a short description of equipment and procedures employed for the experimental work is presented along with references to more complete discussions of pulse spectrometers and experimental techniques for obtaining coherence information.

(1) Sample Preparation. All samples consisted of single crystals that had been cut and cleaved to a size that could be inserted inside of a slow-wave helix. (64) A typical sample size was 2 x 2 x 6 mm. Single crystals were grown from the melt under vacuum in a Bridgman furnace and then annealed in a temperature-controlled oil-bath for approximately one week. All samples were characterized by their phosphorescence emission spectra.

Perprotonated 1,2,4,5-tetrachlorobenzene (h$_2$-TCB) and 1,2,4,5-tetramethyl benzene(durene) were obtained commercially. Perdeuterated TCB (d$_2$-TCB) was synthesized by the Fooladi method (65) from d$_6$-benzene (99.5% deuterated) and recrystallized from methanol and ethanol to remove the other chlorobenzenes. The resulting product consisted of .003% h$_2$-TCB, 1% hd-TCB and very small traces of 1,3,5-d$_3$-trichlorobenzene. Low resolution mass spectroscopy confirmed that d$_2$-TCB and hd-TCB were present in a statistical ratio. All compounds were purified by vacuum sublimation and extensive zone-refining (~ 300 passes for the host d$_2$-TCB and ~ 1800 passes for the doping materials).

Deep trap concentrations were determined by careful addition
of extensively purified $h_2$-TCB and checked by means of low resolution mass spectroscopy.

(2) Apparatus. Both cw and pulsed magnetic resonance spectrometers designed for optical detection have been described in detail elsewhere. (66) A block diagram for a pulsed spectrometer set up for coherence measurements (23) is shown in Figure 25. The microwave pulse sequence is delivered to the sample through a four channel phase shifter (Figure 26) that is driven by a transistor-transistor logic (TTL) pulse generator. The pulse sequence from the generator triggers the four PIN-driver circuits, each one of which operates a PIN diode microwave switch in one of the channels of the phase shifts. The PIN-driver circuit is presented on the data sheet of a National Semiconductor Corporation DH0035C PIN diode switch driver.

For electron spin ordering, an additional PIN diode was introduced into the spinlocking ($90^\circ$) channel and driven by the circuit presented in Figure 27. This circuit is a high current voltage follower and is not recommended for this application since the PIN diode requires a current ramp for attenuation. Several manufacturers now produce diode-driver packages with attenuation that is linear in the applied voltage for about the same cost as a high-speed PIN diode. A voltage ramp, properly timed and biased, was generated by a General Radio 1395-A pulse generator equipped with a 1395-P3 pulse shaping unit, and applied to the biased input of the voltage follower to produce the microwave ramps.
FOUR-CHANNEL PHASE SHIFTER

MICROWAVE SIGNAL OUT
TO 20W MICROWAVE GENERATOR

HYBRID TEES
USED AS SIGNAL ADDERS

ISOLATORS

PIN DIODE INPUTS (1–4)
FROM TTL PULSE GENERATOR
AND PIN DRIVER CIRCUITS

ISOLATORS

VARIABLE ATTENUATORS

10 CM CONSTANT-IMPEDANCE
ADJUSTABLE LINES
USED AS PHASE SHIFTERS

HYBRID TEES
USED AS SIGNAL DIVIDERS

MICROWAVE SIGNAL IN
FROM 1W MICROWAVE GENERATOR

Fig. 26
Fig. 26. Network for producing four separate microwave phases. The input signal is split by a 180° hybrid tee and then run through two 90° tees all manufactured by Anaren Corporation. The four resulting signals are then phase shifted relative to one-another by means of variable path length lines, attenuated to a common amplitude with Narda 792FF attenuators and passed through Hewlett-Packard HP 33124A high isolation, high speed PIN diodes. The four signals are then recombined through three 180° hybrid tees.
HIGH CURRENT VOLTAGE FOLLOWER

Fig. 27

XBL 767-8612
Two different TTL pulse sequence generators were designed and constructed for these experiments, one for spin echo detection and the other for detection by remagnetization. Figure 28 shows the logic diagram for the "echo" box, ODAD II. The output pulse sequence is initiated by application of a TTL strobe pulse to input Z, which triggers the first π/2 pulse (OUTPUT 1) followed immediately by a spinlocking pulse (OUTPUT 3). In addition, a +15 V 100 µsec pulse for triggering the General Radio voltage ramp is delivered to the "+15 out" port after a variable delay. This part of the sequence produces the ordered state. The spin echo probe sequence is then triggered by a TTL pulse to input µ. This may be either another external pulse or delivered internally by delaying the Z input pulse the desired amount of time. The first two pulses of the echo sequence are delivered at OUTPUT 1, while the final probe pulse is delivered at OUTPUT 2. The probe pulse is swept linearly in time by means of a 10-turn variable resistor and positioned in time near the echo maximum by means of a trimming delay. Internal switching permits one to suppress the π pulse in the echo sequence and/or the initial π/2 pulse in the demagnetization sequence.

The logic diagram of a generator designed for detection by adiabatic remagnetization, "ODADASL", is presented in Figure 29, along with the output pulse program. Based on the spinlocking pulse sequence [π/2(0°), SPINLOCK(90°), π/2(0°)], this generator has several operating modes providing considerable flexibility to the experimenter.
Fig. 28. Logic diagram for circuit designed for optical detection of ordered state echoes.
Fig. 29. Logic diagram for circuit designed for monitoring ordered state by optically-detected adiabatic remagnetization.
Not only is it capable of delivering spinlocking and ADRF pulse sequences, but it is also capable of alternating the two experiments and routing the separate signals to different memories in a signal averager. Options are also provided for (i) a +15 V spike that is generated either every time or only during ADRF experiments; (ii) a logic output for controlling external equipment during alternate experiments; and (iii) an option for interrupting the spinlock pulse (ADRF hole) during ADRF experiments to minimize microwave leakage through the ramp PIN diodes after demagnetization. All pulses, gaps and the ADRF hole are continuously variable in length, and provision has been made for deleting the detection sequence (i.e. adiabatic remagnetization) as well as overlapping the first $\pi/2$ pulse with the spinlock pulse for the purpose of setting phases.

Microwaves were generated by a Hewlett-Packard (HP) 8690B sweep oscillator with plug-ins and amplified by a 1 watt Servo Corporation Model 3003 travelling wavetube amplifier. This signal was then split, phase-shifted and recombined as shown in Figure 26 before final amplification by a 20 watt Varian TWT. The signal output of the TWT was then delivered to the sample through a slow-wave helix terminating a 50 $\Omega$ rigid coaxial line manufactured by the Micro Delay Division of Uniform Tubes, Inc. The microwave frequency was monitored with an HP 5245 L frequency counter equipped with extended range plug-ins.

Samples were placed in a liquid helium cryostat and illuminated by a 100 watt high pressure Hg arc lamp (Ortek or PEK) filtered
through H₂O and a 3100 Å Schott interference filter. Resulting luminescence was detected at 90° to the excitation optical path by means of a Jarrell-Ash 3/4 meter Czerny-Turner monochromater coupled to a cooled EMI 6256S photomultiplier.

(3) Procedure. Samples were cleaved just prior to introduction to the warm cryostat and positioned so that both excitation and detection optical paths passed through visibly clear faces of the crystal. The dewar and sample were than purged with gaseous He and cooled to liquid N₂ temperature before introduction of liquid He.

Upon filling, a phosphorescence spectrum was taken, not only to determine the monitoring wavelength for the experiments (0,0) but also to characterize the sample and detect any anomalous emissions. For these experiments, the (0,0) emission from the deep trap (h₂-TCB) at 3751 Å was monitored to observe changes in phosphorescence intensity induced by pumping the D - |E| transition at 3577.8 MHz.

Pulse lengths used for the microwave sequence were determined by the response of the sample to a rotary precession experiment (13) phase-sensitive detected by means of a PAR HR-8 lock-in amplifier. In this experiment, a single pulse was delivered to the sample and the phosphorescence change observed. The shortest pulse resulting in a maximum change in intensity corresponds to an "inverting" or π pulse and was typically between 80-150 nsec for the transition of interest.

The relative phases of the four channels in the phase shifter
were adjusted by altering the pathlengths with General Radio 874-LK102 constant impedance adjustable lines. The phases were set either by maximizing the spinlock signal since its amplitude is sensitive to the phase difference between two channels or by overlapping the outputs of the various channels if more than two channels were required (echo detection). Using the overlap method, the phases of the four channels may be set as follows:

(i) Adjust the pathlength of channel 3 so that the combined output of channels 1+3 is zero. This results in a phase difference of 180° between these channels.

(ii) Adjust the pathlength of channel 2 so that the combined output of channels 1+2 and 2+3 are equal. This produces a channel with a relative phase of 90° to either channels 1 or 3.

(iii) Adjust the pathlength of channel 4 so that the overlap of channels 2+4 is also zero.

As long as the amplitudes of the channels are equal, the relative phase shift between adjacent channels will be 90°.

For experiments employing echo detection, the signal from the photomultiplier was directed to the lock-in amplifier referenced to the strobe frequency that triggered the pulse sequence. The final probe pulse in the echo was moved in time by a mechanical motor connected to a 10-turn variable resistor so that the lock-in output signal versus time traces out the echo directly. Maximum experimental repetition rates (strobe frequency) were determined by the time required for the system to relax to steady state after a pulse sequence; for TCB it is on the order 5 Hz. At rates above this
value, the signal-to-noise ratio was reduced.

A different method for signal processing was used for detection by adiabatic remagnetization. The strobe pulse used to trigger the experimental sequence also started the data acquisition sweep on a Tracor Northern 575 transient averaging computer, thus storing the time-resolved phosphorescence intensity changes during the experiment. A baseline for normalization purposes could be added to the sampled waveform by pre-triggering the CAT.

Temperature dependent data below 4.2°K was obtained by pumping on the liquid He bath. Temperatures were determined either by measuring the vapor pressure of helium gas in the cryostat with an NRC Equipment Model 530 Alphatron gauge, or by monitoring the resistance of a calibrated resistor with a Keithley Model 520 Resistance Bridge. Temperature regulation was accomplished with a pressure sensor capable of varying the pumping speed on the cryostat.
Appendix I

In this appendix, expressions for the transformed density matrix elements after a non-equivalent site exchange are presented in terms of the $r$-vector components $r(l,T)$ at the original site at the time of the exchange. The result is general and can be applied to any transition; however, one must redefine the rotation angles $(\theta, \phi, \psi)$ if indices in the basis set are exchanged. The elements as presented below are consistent with the formulation in Chapter III, i.e. they are written for the $|Y\rangle \leftrightarrow |X\rangle$ transition with angles defined by Equation 32. Starting from a generalized density matrix in the $|Z\rangle$, $|Y\rangle$, $|X\rangle$ basis in the rotating representation

\[
\rho_1(T) = \frac{aa^*+bb^*}{2} \begin{bmatrix}
2zz^* & 0 & 0 \\
0 & 1+r_3(l,T) & r_1(l,T)-ir_2(l,T) \\
0 & r_1(l,T)+ir_2(l,T) & 1-r_3(l,T)
\end{bmatrix}
\]

the transformed density matrix is calculated from Equation 30, yielding
\[ \rho_2(0) = R \rho_1(T) R^{-1} \]

\[
\begin{pmatrix}
\rho_{zz} & \rho_{zy} & \rho_{z}\rho_{x}
\end{pmatrix}
\begin{pmatrix}
\rho_{zz} & \rho_{zy} & \rho_{zx}
\end{pmatrix}
\]

\[
\rho_{zz} = \frac{2zz \cos^2 \theta}{aa^* + bb^*} + \sin^2 \theta(1 + r_3(1,T) \cos 2\phi) - \sin^2 \theta \sin 2\phi [r_1(1,T) \cos \omega T - r_2(1,T) \sin \omega T]
\]

\[
\rho_{zy} = e^{\frac{i \omega T}{2}} \left( \frac{zz \cos \phi \sin 2\theta}{aa^* + bb^*} - \frac{\sin 2\theta \cos \phi}{1 + r_3(1,T) \cos 2\phi} + r_3(1,T) \sin \phi \sin 2\phi \sin \psi + [r_1(1,T) - ir_2(1,T)] \right)
\]

\[
\times e^{-i \omega T} (\sin \phi \sin \phi \cos 2\phi + \frac{1}{2} \sin \phi \cos \phi \cos 2\phi) + [r_1(1,T) + ir_2(1,T)]
\]

\[
\times e^{i \omega T} \left( \frac{\sin 2\theta \sin 2\phi \sin \psi + \sin \phi \cos \phi \sin 2\phi}{r_3(1,T) \sin \phi \sin 2\phi \cos \phi} \right)
\]

\[
\rho_{zx} = e^{\frac{i \omega T}{2}} \left( \frac{zz \sin \phi \sin 2\theta}{aa^* + bb^*} - \frac{\sin 2\theta \sin \phi}{1 + r_3(1,T) \cos 2\phi} + r_3(1,T) \sin \phi \sin 2\phi \cos \phi
\]

\[
- r_3(1,T) \sin \phi \sin 2\phi \cos \phi + [r_1(1,T) - ir_2(1,T)]
\]

\[
\times e^{-i \omega T} (\sin 2\theta \sin 2\phi \sin \psi + \sin \phi \cos \phi \sin 2\phi) + [r_1(1,T) + ir_2(1,T)]
\]

\[
\times e^{i \omega T} \left( \frac{\sin 2\theta \sin 2\phi \sin \psi + \sin \phi \cos \phi \sin 2\phi}{r_3(1,T) \sin \phi \sin 2\phi \cos \phi} \right)
\]
\[\rho_{yz} = \rho_{zy}\]

\[\rho_{yx} = e^{i\omega T} \left( \frac{2zz* \cos^2 \psi \sin^2 \theta}{aa* + bb*} - r_3(1,T) \sin 2\psi \sin 2\phi \cos \theta + \sin^2 \psi [1 - r_3(1,T) \cos 2\phi] \right.\]

\[\left. + \cos^2 \psi [1 + r_3(1,T) \cos 2\phi] - [r_1(1,T) \cos \omega T - r_2(1,T) \sin \omega T]\right) \times [\sin 2\psi \cos \theta \cos 2\phi + \sin 2\phi (\cos^2 \psi \sin^2 \psi - \sin^2 \psi)]\]

\[\rho_{xy} = \rho_{yx}\]

\[\rho_{xz} = \rho_{zx}\]

\[\rho_{xx} = \frac{2zz* \sin^2 \psi \sin^2 \theta}{aa* + bb*} + r_3(1,T) \sin 2\psi \sin 2\phi \cos \theta \]

\[+ \cos^2 \psi [1 - r_3(1,T) \cos 2\phi] + \cos^2 \theta \sin^2 \psi [1 + r_3(1,T) \cos 2\phi] \]

\[+ [r_1(1,T) \cos \omega T - r_2(1,T) \sin \omega T] [\sin 2\psi \cos \theta \cos 2\phi + \sin 2\phi (\cos^2 \psi - \cos^2 \theta \sin^2 \psi)]\]
T is the time of the exchange event and $\omega$ is the driving field frequency applied to the $|Y\rangle \leftrightarrow |X\rangle$ transition.
Appendix II: Computer Programs

This appendix presents listings for the various computer programs written for this work. All codes except the first program and its associated subroutines are single precision and compatible with CDC systems programming. The first program is designed to run on IBM 360/370 systems and is written in double precision. Several of the subroutines it calls are not listed here but are fully explained and documented in the text, Computer Solution of Ordinary Differential Equations--The Initial Value Problem, by L. F. Shampine and M. K. Gotdon.
IMPLICIT REAL*8 (A-H,O-Z)

THIS PROGRAM CALCULATES EITHER THE SIGNAL WAVEFORM OR THE DECAY OF SPINLOCKING OR ELECTRON SPIN ORDERING. VERTICAL PROCESSES (T1) ARE INCORPORATED. THE PROGRAM IS BASED ON THE SEPARATE ISOCHROMAT

METHD DICSUSSED IN THE MATHEMATICAL DESCRIPTION SECTION OF CHAPTER V. THE PROGRAM AS SET UP INTEGRATES OVER A LINE OF 251 ISOCHROMATS WHICH ARE DISTRIBUTED ACCORDING TO A LINESHAPE CHOSEN BY THE USER. THE PROGRAM IS WRITTEN IN DOUBLE PRECISION AND IS COMAT-

IBLE WITH IBM SYSTEMS PROGRAMMING. THE STRUCTURE OF THE PROGRAM IS A MAIN BODY CALLING VARIOUS SUBROUTINES THAT PERFORM SPECIFIC CALCULATIONS. SUBROUTINES DE, STEP, AND INTERP ARE NOT PRESENT-

HERE BUT ARE COMPLETELY EXPLAINED AND DOCUMENTED IN THE TEXT ...

COMPUTER SOLUTION OF ORDINARY DIFFERENTIAL EQUATIONS—THE INITIAL VALUE PROBLEM... BY L.F. SHAMPINE AND M.K. GOTO

INPUT PARAMETERS--

CARD 1 (15)

NODAT--NUMBER OF DATA SETS

CARD 2 (4(5,6,10,0))

1D--USER SUPPLIED IDENTIFICATION NUMBER

IMOD--PROGRAM MODE. IMOD=0 OR NEGATIVE GENERATES ADRF SIGNAL OR DECAY, IMOD=1 GENERATES SPINLOCK SIGNAL OR DECAY.

MODE--DETERMINES WHETHER SIGNAL WAVEFORM OR DECAY IS CALCULATED. MOD=0 GIVES DECAY, MOD NOT =0 GIVES SIGNAL

LSP--LINESHAPE PARAMETER. LSP=1 PRODUCES GAUSSIAN, LSP=2 PRODUCES LORENTZIAN, LSP=0 ALLOWS ARBITRARY LINESHAPE TO BE ENTERED.

T2--LINEWIDTH PARAMETER IN SECONDS.

CARD 3 (6(10,0))

KX--DECAY CONSTANT FOR LOWER LEVEL

KY--DECAY CONSTANT FOR UPPER LEVEL

CY--FEEDING RATE TO LOWER SUBLEVEL

CM--MIGRATION RATE CONSTANT

KSL--RATE CONSTANT FOR VERTICAL PROCESSES. ASSUMED TO BE SAME FOR UP AND DOWN TRANSITIONS.

CARD 4 (6(10,0))

W1--DRIVING FIELD STRENGTH IN HZ

VOF--AMOUNT APPLIED FIELD IS OFF RESONANCE IN HZ. CAN BE + OR -

RELERR--ERROR TOLERANCE FOR CODE DE. SEE TEXT BY SHAMPINE.

ABSERR--ANOTHER ERROR TOLERANCE FOR CODE DE.

CARD 5 (6(10,0))

TINC--EXPERIMENTAL TIME INCREMENT. SIGNAL IS CALCULATED AT THIS INTERVAL. PROGRAM IS FINALLY SET UP FOR TINC =100 NSEC.

THOLE--TIME SPINLOCK TIME, OR TOTAL SPINLOCK BEFORE DEMAGNET-

IZATION. CURRENTLY LIMITED TO 4 MILLISEC. (SEE ROUTINE SPNLCK)

THOLE--TIME IN ORDERED STATE. NOT USED IN DECAY MODE.

CARD 6 (6(10,0))

RPC,SR0,R10,R20--THE INITIAL R-VECTOR COMPONENTS.

OUTPUTS -- TIMES IN SECONDS, FREQUENCIES IN RADIANS/SEC, RATE

CONSTANTS IN SEC-1

FROM SUBROUTINE LINESHAPL--

WINC--FREQUENCY SPACING OF THE 251 ISOCHROMATS

FAST--FRACTION OF FAST ISOCHROMATS

SLOW--FRACTION OF SLOW ISOCHROMATS

RTHREE INITIAL--INITIAL Ensemble RTHREE

FROM MAIN PROGRAM--

TOTT--PI/2 PULSE LENGTH

TOTAL THOLE--VALUES USED IN PROGRAM. THESE MAY DIFFER BY TINC

FROM INPUT VALUES

DECAY OR SIGNAL VERSUS TIME

*** ANY OTHER OUTPUT CONSISTS OF WARNING MESSAGES ***
*************** PROGRAM NOTES ***************

RTTHREE IS THE MATRIX FOR STORING CALCULATED SIGNALS. IT IS CURRENTLY DIMENSIONED AT (1500) BY THE VARIABLE NLG. THIS IS THE MINIMUM SIZE FOR THE PROGRAM TO WORK CORRECTLY IN ANY MODE. SIGNAL CALCULATIONS REQUIRE MUCH LARGER STORAGE SINCEx THE RUNNING INDEX CORRESPONDS TO INTERVALS IN TIME DETERMINED BY TINC.

THE MATRIX ALSO CONTAINS THE LINE-SHAPE INFORMATION, WHICH IS CHANGED BY SUBSTITUTION IN VARIOUS SUBROUTINES. INTERMEDIATE RESULTS MUST BE TRANSFERRED OUT OF THIS MATRIX BEFORE CALLING A SUBROUTINE THAT ALTERS ALS.

THE SIGNAL GENERATING SECTIONS OF THIS PROGRAM ARE UNTESTED-GOOD LUCK.

REAL*4 XT9
REAL*8 XX,KY,KD,KA,KM,KSL
EXTERNAL F
COMMON ALS(251,6),TINC,PI,KD,KA,CX,CY,TEL,MOD0
COMMON/SET2/TOTT
COMMON/SET3/KX,KY,KSL,KM
DIMENSION ADRF1(100),ADRFR1(100),ADRFR3(100),SPLCK1(80),SPLCK2(80)
DIMENSION SPLCK3(80),Y(502)

*************** DIMENSION INFORMATION FOR RTTHREE-50TH STATEMENTS MUST BE CHANGED ***************

DIMENSION RTTHREE(1500)
NLG=1500

NEQN=502
RFST=0.00
RSL0W=0.00
PI=4.0D0*DATAN(1.00)

READ INPUT PARAMETERS
READ(5,5)MODAT
DO 1111 IK=1,MODAT
READ(5,5)ID,IMOD,MOD0,LSP,T2
5 FORMAT(4F5,0,0)
READ(5,55)XX,CX,KY,CY,KM,KSL
55 FORMAT(5F5,0,0)
READ(5,55)W1,VDF,FELEK,ASERR
READ(5,55)TINC,TOTSL,T0LE
READ(5,55)RPE,RMO,R10,R20
W1=W1*2.00*PI
W1?W1*2.00*PI
CONTINUE.

DO (KK=XX,KY)/2.00
KA=(KK*KY)/2.00
WRITE(6,199)
199 FORMAT(1X,6,F9,0)
WRITE(6,99)ID,LSP,T2,W1,TINC,VDF,KM,KSL
9 FORMAT(1X,6,13,6,2X,D10.3)
WRITE(6,9)
19 FORMAT(1X,KX,CX,KY,RP0
1
WRITE(6,99)KK,CX,KY,RP0,RMO,R10,R20
99 FORMAT(1X,8(D10.3,2X))
AF=0.00
AS=0.00
ATOT=0.00
RTHRO=0.00
CALCULATE INITIAL LINESHAPE MATRIX ALS
CALL LNSP(LSP,T2,VOF,RP0,RM0,R10,R20,AF,AS,ATOT,RTHRO)
ENTER STEADY STATE SIGNAL INTO RTHREE
DO 3 M=1,1000
     ITEL=M
     RTHREE(TEL)=RTHRO
3 CONTINUE
 INITIAL PI/2 PULSE
CALL HALFP(L1,0.0,E,RTHREE,VLG)
WRITE(6,777)
777 FORMAT(1H0,< PI OVER TWO PULSE?
WRITE(6,877)TITI
877 FORMAT(1H'~+20X,010.3)

C ADRF-SPINLOCK AND DEMAGNETIZE
1 CALL SPNLCK(L1,90.0,T,0,TIII,RTHREE,NLGL)
2 CALL MAG(L1,90.0,RP0,RP0+1,RTHREE,NLGL)
IFLAG=1

C INITIALIZE ISOCHROMAT POPULATIONS FOR INTEGRATION
DO 37 L=1,251
     Y(L)=-ALS*L2*ALS(L,3)
     Y(L+251)=ALS(L,2)*ALS(L,4)
     IF(ALS(L,1))=.376
4 RSLW=RSLION+Y(L)-Y(L+251)
GOTO 37
5 RFAST=RFAST+Y(L)-Y(L+251)
37 CONTINUE

C INITIAL ORDERED STATE SIGNAL
ADRF(1)=RFAST-RSLW
ADRF(1)=0.600
ADRF(1)=DLOG(ABS(ADRF(1)))
RFAST=0.00
RSLW=0.00
T=0.00
IF(MOD)40,23,40
C ADRF DECAY-DECAY CALCULATED EVERY MILLISEC OUT TO LAST NUMBER IN
C STATEMENT 23
23 DO 7 N=1,99
     TOUT=DFLOAT(N)*0.01DG
22 CALL DF(F,NEON,Y,T,TOUT,PEERR,ABSERR,IFLAG)
     IF(IFLAG.EQ.6)GOTO 66
21 IF(IFLAG.EQ.EQ.2)GOTO 15
     WRITE(6,777)IFLAG,1,RELLERR,ABSERR
47 FORMAT(1H3X,3X,5X,IFLAG IS $12,SERRCR TOLAT T5,3013.6)
     IF(TLT-TOUT)GOTO 22
15 DO 36 L=1,251
     IF(ALS(L,1))=.376,35
34 RSLW=RSLW+Y(L)-Y(L+251)
GOTO 35
35 RFAST=RFAST+Y(L)-Y(L+251)
36 CONTINUE
ADRF(N+1)=RFAST-RSLW
ADRF(N+1)=TOUT
ADRF(N+1)=DLOG(ABS(ADRF(N+1)))
RFAST=0.00
RSLW=0.00
7 CONTINUE
WRITE(6,29)
29 FORMAT(1HO,STOTT? TOTSL? THOLE? 5)
WRITE(6,39) TOTT,TOTSL THOLE
39 FORMAT(1H*5X,D10.3*3X,D10.3*3X,D10.3)
WRITE(6,1999)
1999 FORMAT(1HC,3X,SGRF SIGNAL DECAY5)
WRITE(6,2999)
2999 FORMAT(3X,TIME 5,5X,SIGNAL INTENSITY5,3X,LN SIGNAL INTENSITY5)
WRITE(6,999)(ADRF(K),A3RF1(K),ADRF3(K),K=1,100)
999 FORMAT(3X,D12.5,4X)
C PLOTTING SUBROUTINE GOES HERE
GO TO 111
C CALCULATE ADRF SIGNAL ANJ STORE IN RTHREE
40 TOUT=T+1000.00*TINC
41 CALL DEF,NENV,Y,T,TOUT,RELERR,AE3ERR,IFLAG)
IF(FLAG.EQ.6) GO TO 65
IF(FLAG.EQ.2) GO TO 16
WRITE(6,47)IFLAG,T,RELERR,ABSERR
IF(T.LT.TOUT) GO TO 41
16 CONT=0.00
DO 33 L=1,251
CONT=CONT+Y(L)-Y(L+251)
33 CONTINUE
42 CONTINUE
IF(T.LT.THOLE) GO TO 40
C REMAGNETIZE SPINLOCK,PROBE PULSE
CALL MAG(W1,90.000,RNF,RHQ,Q,PTHREE,NLG)
CALL SPNLCK(W1,90.000,1.00-03,RTHREE,NLG)
CALL HALFPI(W1,6.000,RTHREE,NLG)
C FINAL DECAY TO STEADY STATE AFTER PROBE PULSE
DO 8 M=1,20000
CONT=0.00
DO 10 N=1,251
CALL RFVCO0.000,TINC,0.00,N)
CONT=CONT+(ALS(N,3)-ALS(N,4))*ALS(N,2)
10 CONTINUE
ITEL=ITEL+1
RTHREE(IETEL)=CONT
8 CONTINUE
WRITE(6,29)
WRITE(6,39) TOTT,TOTSL,THOLE
WRITE(6,43)
49 FORMAT(1H0,RTHREE VERSUS TIME 5)
WRITE(6,55) (RTHREE(K),K=1,80000,100)
59 FORMAT(3X,D10.3,4X)
C PLOTTING SUBROUTINE GOES HERE
GO TO 111
66 WRITE(6,28)
38 FORMAT(1H0,1X,SOMETHING WRONG WITH INPUT PARAMETERS TO ROUTINE DE-
C PLEASE CORRECT#)
STOP
C SPINLOCK SECTION
2 IF(MOD0131,32,31)
C SPINLOCKING DECAY-CALCULATED EVERY .5 MSEC OUT TO 40 MSEC
32 RH1=0.00
RH2=0.00
DO 11 I=1.80
TOTSL1=DOTSL1=DOTSL1,1.0000
CALL SPNLCK(W1,90.000,TOTSL1,RTHREE,NLG)
C CALCULATE ENSEMBLE RTHREE BEFORE/AFTER PROBE PULSE
DO 12 I=1,251
   RH1=RH1+(ALS(I,3)-ALS(I,4))*ALS(I,2)
12 CONTINUE
C CALL HALFP1(W1,0.0,0.0,RTHREE,NLGI)
DO 13 J=1,251
   RH2=RH2+(ALS(J,3)-ALS(J,4))*ALS(J,2)
13 CONTINUE
C SPLCK1(M)=RH2-RH1
C SPLCK2(M)=TOTAL1
C SPLCK3(M)=DLOG(OABS(SPLCK1(M)))
11 CONTINUE
WRITE(6,129)
129 FORMAT(1H10,3X,5I5,6E12.5,10X,3X)
WRITE(6,2999)
WRITE(6,119)(SPLCK2(M),SPLCK1(M),SPLCK3(M),M=1,80)
119 FORMAT(3(I4,12.5,4X))
C PLOTTING SUBROUTINE GOES HERE
GO TO 1111
C CALCULATE SPINLOCK SIGNAL AND STORE IN RTHREE
31 CALL SPNLCK(W1,0.00,TOTSL,RTHREE,NLGI)
   CALL HALFP1(W1,0.00,RTHREE,NLGI)
DO 18 K=1,10000
   CONT=0.00
   DO 17 L=1,251
      CALL RVEC(0.00,TINC,0.00,L)
      CONT=CONT+(ALS(L,3)-ALS(L,4))*ALS(L,2)
17 CONTINUE
   ITEL=ITEL+1
C RTHREE(ITEL)=CONT
18 CONTINUE
WRITE(6,69)
69 FORMAT(1H10,3X,TOTSL?,TCTSL?,5I5,6E12.5,10X,3X)
WRITE(6,79)(TOTSL,K=1,80000,10D)
C PLOTTING SUBROUTINE GOES HERE
C CONTINUE
STOP
END
SUBROUTINE F(T,Y,YP)
C THIS SUBROUTINE CONTAINS THE DIFFERENTIAL EQUATIONS THAT ARE
C TO BE INTEGRATED BY SUBROUTINE DE. IT IS CALLED BY SUBROUTINE
C STEP, WHICH IN TURN IS CALLED BY CE. DETAILS OF DE AND STEP
C CAN BE FOUND IN THE TEXT LISTED IN THE COMMENT CARDS OF THE
C MAIN PROGRAM.
C IMPLICIT REAL*8(A-Z)
INTEGER J,K,ITEL,MOD0
COMMON ALS(251,6),TINC,PI,KD,KA,CX,CY,ITEL,MOD0
COMMON/SET3/KX,KY,KSL,KM
DIMENSION Y(502),YP(502)
YTP=0.00
YTH=0.00
DO 1 J=1,251
YTP = YTP + Y(J)
YTH = YTH + Y(J + 251)

1 CONTINUE
DO 2 K = 1, 251
YP(K) = Y(K) * (KM + KSL + KY) + Y(K + 251) * KSL + ALS(K, 2) * (KM * YTP + CY)
YP(K + 251) = -YP(K + 251) * (KM + KSL + KY) + Y(K) * KSL + ALS(K, 2) * (KM * YTH + CX)
2 CONTINUE
RETURN
END

SUBROUTINE HALFPICW(TTOT, PHASE, RTHREE, NLG)
C THIS SUBROUTINE PERFORMS A PI/2 PULSE ON THE LINE STORED IN THE
C MATRIX ALS. THE PULSE LENGTH IS PI/(2*W1) AND IS APPLIED AT PHASE
C IN ARGUMENT LIST. THE CODE CALLS SUBROUTINE RVEC.

IMPLICIT REAL*8 (A-H, O-Z)
REAL*8 KO, KA
COMMON ALSC251, OTINC, PI, KD, KA, CX, CY, ITEL, MOD0
COMMON /SETZIT/ TOTT = PI / (2.0 * W1)
IF THE EXPERIMENTAL INCREMENT TIME IS LONGER THAN PI/2 PULSE,
ONLY GO THROUGH LOOP ONCE

IF (TINC - TTOT) > 6.4 + 4
4 ITEL = ITEL + 1
5 CONT = 0.0
DO 1 I = 1, 251
CALL RVEC(W, TTOT, PH, I)
CONT = CONT + (ALS(I, 3) - ALS(I, 4)) * ALS(I, 2)
1 CONTINUE
RTHREE(ITEL) = CONT
GO TO 17
C TINC LESS THAN TTOT--CALCULATE INTERMEDIATE SIGNAL

6 DO 7 J = 1 + 20
CONT = 0.0
T = FLOAT(J) * TINC
DO 3 K = 1, 251
CALL RVEC(W, T, PH, K)
CONT = CONT + (ALS(K, 3) - ALS(K, 4)) * ALS(K, 2)
3 CONTINUE
IF (T - TTOT) > 2.9 + 5
2 ITEL = ITEL + 1
RTHREE(ITEL) = CONT
7 CONTINUE
17 RETURN
END
SUBROUTINE LNSPCLSP(Tz,VOF,RPO,RMO,R10,R20,AF,AS,ATOT,RTHRO)

THIS SUBROUTINE GENERATES A LINESHAPE MATRIX OF 251 ISOCHROMATS. FOR EACH ISOCHROMAT, THE STORAGE ORDER IN THE (251,6) MATRIX IS DELTA OMEGA, WEIGHT OF ISOCHROMAT, RX, RY, R1 And R2. IF LSP=1, THE LINE IS GAUSSIAN. IF LSP=2, THE LINE IS LORENTZIAN. IF LSP=0, AN ARBITRARY LINESHAPE MAY BE ENTERED. THIS LAST OPTION REQUIRES ADDING AN INPUT SECTION TO THE END OF THIS CODE TO ENTER THE ELEMENTS OF ALS.

IMPLICIT REAL*8(A-H,O-Z)
REAL*8 KD,KA
COMMON ALS(251,6),TINC,PI,KD,KA,CX,CY,ITEL,MODO
T2W=T2/(2*2.00*PI)

THE CARD THAT FOLLOWS DETERMINES HOW FAR THE ISOCHROMATS ARE APART.
WINC=3.00/(T2W*100.00)
WOF=2.00*PI*VOF
RTHRO=0.00
ATOT=0.00
AMIN=0.00
APLUS=0.00
IF(LSP-1)1,2,2
2 DO 4 J=1,251
DELM=(IF(LSP-1)1.00+(126.00*WINC)
F(LSP-1)1.00*1.00
3 ALS(J,2)=(T2W/2)+DELW*PII*IF(1.00+F(LSP-1))**2)
GO TO 11
10 ALS(J,2)=(T2W/PII)/(1.00+(T2W*DELW)**2)

CALCULATE FRACTION OF FAST AND SLOW SPINS

CALCULATE FRACTION OF FAST AND SLOW SPINS

11 ALS(J,1)=DELW-WOF
ATOT=ATOT+ALS(J,2)
IF(ALS(J,1))12,11,13
12 AMIN=AMIN+ALS(J,2)
GO TO 14
13 APLUS=APLUS+ALS(J,2)
14 ALS(J,3)=RPO
ALS(J,4)=RMO
ALS(J,5)=R10
ALS(J,6)=R20
4 CONTINUE
5 DO 5 L=1,251

NORMALIZE WEIGHTING FACTORS

5 CONTINUE
AF=APLUS/ATOT
AS=AMIN/ATOT
WRITE(6,19)
WRITE(6,9)WINC,AF,AS,RTHRO
RETURN
1 WRITE(6,19)
19 FORMAT(1X,5ARBITRARY LINESHAPE NOT OPERATIVE. SET LSP=1 OR 2 )
9 FORMAT(1X,4(U10,3X))
SUBROUTINE SPNLCK(W, PHASE, TOTSL, RTHREE, NLG)

C THIS SUBROUTINE APPLIES W TO THE LINESHAPE IN MATRIX ALS AT
C THE PHASE IN ARGUMENT LIST. THE CODE CALLS ROUTINE RVEC. AT
C PRESENT, THE LONGEST SPINLOCK TIME, TOTSL, IS 4 MILLISEC. IF
C LONGER TIMES ARE REQUIRED, CHANGE DO-LOOP PARAMETERS IN STATE-
C MENT 6.

C IMPLICIT REAL*8(A-H,O-Z)
C REAL*8 KD,KA
COMMON ALS(251,6), TINC, PI, KD, KA, GX, CY, ITEL, MODD
DIMENSION RTHREE(NLG)
W=W1
PH=PHASE
IF (MODD) 8, 10, 8

CALCULATE R-VECTOR AFTER SPINLOCKING

10 T=TOTSL
DO 1 I=1, 251
CALL RVEC(W, T, PH, I)
1 CONTINUE
GO TO 17

CALCULATE SIGNAL DURING SPINLOCKING AND STORE IN RTHREE

8 IF (TINC-TOTSL) 6, 4, 4
4 ITEL=ITEL+1
T=TINC
7 CONT=0.30
DO 2 J=1, 251
CALL RVEC(W, T, PH, J)
CONT=CONT+(ALS(J, 3)-ALS(J, 4))*ALS(J, 2)
2 CONTINUE
RTHREE(ITEL)=CONT
TOTSL=T
GO TO 17

6 DO 11 K=1, 100000
CONT=0.30
T=DFLOAT(K)*TINC
DO 3 L=1, 251
CALL RVEC(W, T, PH, L)
CONT=CONT+(ALS(L, 3)-ALS(L, 4))*ALS(L, 2)
3 CONTINUE
IF (T-TOTSL) 5, 7, 7
5 ITEL=ITEL+1
RTHREE(ITEL)=CONT
11 CONTINUE
17 RETURN
END
SUBROUTINE RVEC(W1,T,PHASE,I)

THIS SUBROUTINE CALCULATES THE R-VECTOR COMPONENTS RP,RM,R1,R2
FOR A PARTICULAR ISOCHROMAT (DELTAOMEGA, HEIGHT) AFTER AN INTER-
VAL T. THE PHASE MUST BE EQUAL TO EITHER 0.00 OR 90.00. THE
INITIAL COMPONENTS ARE ENTERED THROUGH THE COMMON STATEMENT
CONTAINING THE LINESHAPE MATRIX ALS, THE RESULTING COMPONENTS
TAKING THE LINESHAPE MATRIX ALS. THE RESULTING COMPONENTS ARE
THEN STORED IN THIS MATRIX FOR OTHER ROUTINES TO USE. THESE EQUA-
TIONS ACCOUNT FOR FEEDING AND DECAY, BUT DO NOT ACCOUNT FOR RELAX-
ATION PROCESSES.

IMPLICIT REAL*8 (A-H,O-Z)
REAL*8 KD,KA
COMMON ALS(251,1),TINC,PI,KD,KA,CX,CY,ITEL,MGOO
COMPLEX*16 WBAR,DEC,CSW1,COELW

DEFINE QUANTITIES TO SIMPLIFY EQUATIONS

SW1=W1**2
DEC=DCMPLX(0.000,0D0)
CSW1=DCMPLX(SW1,0.000)
COELW=DCMPLX(ALS(I,1)+0.000)
WBAR=DCSRT(CSW1+(COELW+DEC)**2)
ALPH=REAL(WBAR)

GET RID OF PATHLOGICAL CASES

IF(KA)**2 .LT. 1.00
8 IF(ALPH)*2 .LT. 1.00
10 PRE1=0.00
GO TO 13
7 PRE1=1.00/(KA)**2+ALPH**2
13 IF(KA)**2 .LT. 0.00
16 PRE2=0.00
GO TO 9
15 PRE2=1.00/(KA)**2-ALPH**2
9 S=DSIN(ALPH*T)
C=DCOS(ALPH*T)
CH=0.500*(DEXP(ALPH*T)+DEXP(-ALPH*T)) SM=5.000*(DEXP(ALPH*T)-DEXP(-ALPH*T)) F1=PRE1*(KA*DEXP(-KA*T)*(ALPH*S-KA)) F2=PRE1*(ALPH*DEXP(-KA*T)*(KA+ALPH*C)) F3=PRE2*(KA*DEXP(-KA*T)*(BETA*SH+KA*CH)) F4=PRE2*(BETA*DEXP(-KA*T)*(KA*SH+BETA*CH)) RP=ALS(I,1)
RM=ALS(I,4)
R1=ALS(I,9)
R2=ALS(I,6)
IF(PHASE=-90.,00)1,2,100
1 RT1=R1
RT2=R2
GO TO 3
2 RT1=R2
RT2=-R1

CALCULATE Rp AND RM

3 ALS(I,3)=PRE*(((CM*RP-SW1*RM-W1*(KD*RT1-ALS(I,1)*RT2))*C+2.00*RM*R
1P+H1*(ALPH*RT1+ETA*RT2))*S+(CP*FP+SH1*RM-W1*(KD*RT1-ALS(I,1)*RT2)
2P+H1*(ALPH*RT1+ETA*RT2)))*SH+(CY/(2.00*AGAM)))*(CM
3*F1+2.00*DM*F2+CP*3.00*DP*F4)+(CY/(2.00*AGAM)))*(-SH1*F1+SH1*F3)
ALS(I,4)=PRE*(((CM*SH1*RM-W1*(KD*RT1-ALS(I,1)*RT2))*C-2.00*RM*R
1M+H1*(ALPH*RT1-ETA*RT2))*S+(CP*FP+SH1*RM-W1*(KD*RT1-ALS(I,1)*RT2)
2M+H1*(ALPH*RT1-ETA*RT2)))*SH+(CY/(2.00*AGAM)))*(-SH1*F1-SH1*F3)
IF(PHASE=-90.,00)4,5,100

CALCULATE R1 AND R2 FOR PHASE = 0

4 ALS(I,5)=PRE*(((CMPW*R1+2.00*RM-W1)*C-2.00*(R2*DP*(RP-RM)*W
1P+H1*(ALPH*RT1+ETA*RT2)))*S+(CMPW*R1+2.00*RM-W1)*(R2*DP*(RP-RM)*W
2P+H1*(ALPH*RT1+ETA*RT2)))*SH+(W1/AGAM))*(ALS(I,1)*F1*(CY-CX)+ALPH*F2*(CX-CY)
3*F3*(CX-CY))
ALS(I,6)=PRE*(((CM*W1*R1+2.00*RM-W1)*W1)+(CM*W1*R1+2.00*RM-W1)*W1)
3*F3*(CX-CY))
GO TO 6

CALCULATE R1 AND R2 FOR PHASE = 90

5 ALS(I,5)=PRE*(((CM*W1*R1+2.00*RM-RF)*ALS(I,1)*W1)*C-2.00*(R2*DP*(RP-RM)*W
1P+H1*(ALPH*RT1+ETA*RT2)))*S+(CM*W1*R1+2.00*RM-RF)*ALS(I,1)*W1)
3*F3*(CX-CY))
ALS(I,6)=PRE*(((CM*W1*R1+2.00*RM-RF)*ALS(I,1)*W1)+CM*W1*R1+2.00*RM-RF)*W1)
3*F3*(CX-CY))
3*F3*(CX-CY))
6 RETURN

100 WRITE(6,19)
19 FORMAT(99,6,99)
END

SUBROUTINE MAG(W1,PHASE,RP0,AMO,LMOD,THREE,NLG)

THIS SUBROUTINE PRODUCES AN ADIABATIC DEMAGNETIZATION OR REMAG-~
NETIZATION. ANY RESULTING IN-PLANE COMPONENTS ARE SET TO ZERO.
THE RAMP TIME IS SET AT 200*TINC. THE MODE IS DETERMINED BY THE
CALLING PARAMETER LMOD=-LMOD=0 GIVES REMAGNETIZATION TO A FINAL
FIELD VALUE W1. LMOD NOT =0 DEMAGNETIZES FROM AN INITIAL VALUE W1.
IMPLICIT REAL*8 (A-H,O-Z)
REAL*8 KD,KA
COMMON ALS(251,6),TINC,PI,KD,KA,CX,CY,ITEL,MODE
DIMENSION RTHREE(NLG)
PH: PHASE
CONT=0.00
ALO=0.00
IF(MODD)1,2,1
C
CALCULATE SIGNAL AND STORE IN RTHREE
1  DO 3 K=1,251
   IF(ALS(K,1))4,5,4
   4 IF(LMOD)6,7,6
   C
   DEMAGNETIZATION
   6 CONT=CONT-ALS(K,5)*ALS(K,2)
      ST=0.00
      GO TO 3
   C
   REMAGNETIZATION
   7 CONT=CONT+(ALS(K,3)-ALS(K,4))*ALS(K,2)
      ST=1.00
      GO TO 3
   5 ALO=(ALS(K,3)-ALS(K,4))*ALS(K,2)
   3 CONTINUE
   DO 8 J=1,200
      ITEL=ITEL+1
      W=ABS((DFLOAT(LMODO)-DFLOAT(J)/200.00)
      RTHREE(ITEM)=CONT*(ALS(J,1)/DSQRT(W**2+ALS(J,1)**2))+ST*ALO
   8 CONTINUE
C
DECAY ONLY-CALCULATE FINAL R-VECTCR COMPONENTS
2 IF(LMOD)9,10,9
C
DEMAGNETIZATION
9  DO 11 K=1,251
     IF(ALS(K,1))12,14,13
12 ALS(K,4)=(-ALS(K,5)/(RPO-RMO))*RPO
     ALS(K,3)=(-ALS(K,5)/(RPO-RMO))*RPO
     ALS(K,5)=0.00
     ALS(K,6)=0.00
     GO TO 15
13 ALS(K,3)=(-ALS(K,5)/(RPO-RMO))*RPO
     ALS(K,4)=(-ALS(K,5)/(RPO-RMO))*RMI
     ALS(K,5)=0.00
     ALS(K,6)=0.00
     GO TO 15
14 ALS(K,3)=500
     ALS(K,4)=500
     ALS(K,5)=0.00
     ALS(K,6)=0.00
15 CONT1=CONT1+(ALS(K,3)-ALS(K,4))*ALS(K,2)
11 CONTINUE
RTHREE(ITEM)=CONT1
GO TO 17
C
C REMAGNETIZATION

10 DO 16 K=1,251
11 IF (ALS(K,1)) 18,20,13
18 ALS(K,5)=ALS(K,3)-ALS(K,4)
19 ALS(K,3)=0.00
20 ALS(K,4)=0.00
21 GO TO 21
19 ALS(K,5)=ALS(K,4)-ALS(K,3)
20 ALS(K,3)=0.00
21 ALS(K,4)=0.00
20 GO TO 21
20 WAV=+.500*H1
21 T=200.00*TINC
22 CALL RVEC(WAV,T,96.00,K)
23 CONT1=CONT1+(ALS(K,3)-ALS(K,4))*ALS(K,2)
16 CONTINUE
17 RETURN
END
PROGRAM ALPHINF, OUTPUT, TAPE2=INPUT, TAPE3=OUTPUT

THIS PROGRAM CALCULATES THE QUANTUM YIELD FOR MIGRATION BETWEEN TRAP SITE, ALPHA, AS A FUNCTION OF TEMPERATURE

INPUT PARAMETERS ARE---
AX--THE PREEXPONENTIAL FACTOR FCF THE EXPONENTIAL DESCRIBING THE ADRF DECAY
AY--THE THE APPARENT ACTIVATION ENERGY IN CM-1 FOR THE ADRF DECAY
SX-- THE PREEXPONENTIAL FOR THE SPINLOCK DECAY
SY-- THE ACTIVATION ENERGY FOR SPINLOCKING IN CM-1
N-- THE NUMBER OF DATA SETS
THE OUTPUT GIVES THE RECIPROCAL TEMPERATURE, THE CALCULATED VALUES (FROM THE BEST FIT EXPONENTIAL PARAMETERS) FOR KM AND KP, AND THE QUANTUM YIELD AT THAT TEMPERATURE, ALPHA.

DIMENSION AJ(100), ALPHA(100), ZADRF(100), ZSL(100)
READ(2, 5) N
DO 1 I=1, N
READ(7, 5) AX, AY, SX, SY
WRITE(3, 9)
WRITE(3, 999)
DO 3 J=33, 6
AJ(J)=FLOAT(J)*.01
ZADRF(J)=AX*EXP(-AY*AJ(J)/.695)
ZSL(J)=SX*EXP(-SY*AJ(J)/.695)
ALPHA(J)=ZADRF(J)/ZSL(J)
WRITE(3, 999) AJ(J), ZADRF(J), ZSL(J), ALPHA(J)
3 CONTINUE
1 CONTINUE
5 FORMAT(15)
95 FORMAT(3E10.0)
99 FORMAT(1X, 'ADRIF INTERCEPT ADRF SLOPE SL INTERCEPT SL SLOPE')
999 FORMAT(1X, 1/7, 'KM
KP
ALPHA')
STOP
END
PROGRAM KRYST(INPNT,OUTPUT,TAPE2=INPUT,TAPE3=OUTPUT)

C THIS PROGRAM CALCULATES THE ENERGIES OF MOLECULES IN A ONE-
C DIMENSIONAL CHAIN WHERE THE NEAREST-NEIGHBOR INTERACTION IS
C BETA. PROVISION IS MADE TO LOCATE TWO IMPURITY MOLECULES WITH
C TRAP DEPTHS TRAP1 AND TRAP2. THE TRAPS ARE LOCATED IN THE
C CHAIN BY SPECIFYING LOCATIONS IT1 AND IT2. DIMENSION A IS
C THE CHARACTERISTIC MATRIX AND IS DIMENSIONED FOR THE TOTAL
C NUMBER OF MOLECULES IN THE CHAIN. SUBROUTINE JACVAT IS A
C USER SUPPLIED SUB ROUTINE FOR DIAGONALIZING A. N IS THE NUMBER OF
C DATA SETS TO BE RUN.

DIMENSION A(160,160),EIGVAL(160)
READ(2,55)N
DO 1 L=1,N
READ(2,5) BETA,TRAP1,IT1,TRAP2,IT2
WRITE(3,999)
WRITE(3,99) BETA,TRAP1,IT1,TRAP2,IT2
DO 3 I=1,160
DO 4 J=1,160
IF(FLOAT(I)-FLOAT(J))6,7,8
6 IF(FLOAT(J)-FLOAT(I)-1.)7,2,7
7 A(I,J)=BETA
GO TO 4
8 A(I,J)=0.
4 CONTINUE
3 CONTINUE
A(IT1,IT1)=TRAP1
A(IT2,IT2)=TRAP2
CALL JACVAT(A,160,160,0,EIGVAL,DLPMY)
WRITE(3,9999)
WRITE(3,999)((K,EIGVAL(K)),K=1,160)
WRITE(3,9999)
1 CONTINUE
5 FORMAT(2F10.3,F15,F10.3,I5)
55 FORMAT(10D)
9 FORMAT(6(2X,I3,F12.8))
99 FORMAT(1X,F8.5,F10.3,F10.3,3,F14X,I3)999 FORMAT(* BETA*,5X,*TRAP 1*,5X,*IT LOC*,5X,*TRAP 2*,5X,*IT LOC*)
9999 FORMAT(1H0)
STOP
END
PROGRAM PROMIT(INPUT,OUTPUT,TAPES=INPUT,TAPE=OUTPUT)

THIS PROGRAM CALCULATES KPO, THE PROMOTION RATE CONSTANT TO THE
EXCITON BAND FROM THE DEEP TRAP IN THE PRESENCE OF SHALLOW TRAPS.
THE INPUT PARAMETERS ARE --
CARD 1 -- NUMBER OF DATA SETS
CARD 2 --
N=THE NUMBER OF TEMPERATURES (EXPERIMENTAL DATA)
PERCENT SHALLOW TRAP CONCENTRATION
STE=SHALLOW TRAP ENERGY WRT DEEP TRAP
BCE=BAND CENTER ENERGY WRT DEEP TRAP
BETA=NEAREST NEIGHBOR INTERACTION
AVDEP=AVERAGE TRAP DEPTH EELCK BAND
FC=FRANK-CONDON FACTOR DESCRIBING OVERLAP OF TRAP/BAND MCLECULE
WAVEFUNCTIONS
THE NEXT N CARDS CONTAIN EXPERIMENTAL DATA--KP OBSERVED, TEMP
THE MODEL FOR THIS PROGRAM IS PRESENTED IN CHAPTER VI IN THE SEC-
TION ON INTERPRETATION OF SPINLOCKING RESULTS

REAL KPM,KPB,FC
PI=4.0*ATAN(1.0)
READ(5,51) NUM
      51 FORMAT(I5)
      DO 7 IK=1,NUM
      READ(5,55)N,FCT,STE,BCE,BETA,AVGEF,FC
      7 FORMAT(I5,6E10.0)
      WRITE(6,19)
      19 FORMAT(//,1X,*FCT SHALLOW TRAP S TRAP EN BAND C EN BE
CTA AVDEFTH FRANCK-CONDON*)
      WRITE(6,9)PCT,STE,BCE,BETA,AVGEF,FC
      9 FORMAT(6X,E10.3,5X,E10.3,4X,E10.3,4X,E10.3,4X,E10.3)
      WRITE(6,29)
      29 FORMAT(1X,*TEMP KP MEASURE [ KP TO BAND ATTEN]*)
      P=PCT/100.
      SME=1.0
      LP=FIX(1.0/P-1.)
      DO 6 M=1,LP
      SME=SME+J(BETA/AVDEP)**(2*M)
      6 CONTINUE
      DO 2 J=1,N
      BT=0.
      READ(5,55)KPM,T1
      T=T+T1
      2 CONTINUE
      55 FORMAT(2E10.0)
      DO 3 I=1,LP
      BF=0.
      RI=FLOAT(I)
      DO 4 K=1,I
      RK=FLOAT(K)
      EB=BCE+2.0*BETA*CSS((RK*PI)/(RI+1.))
      BF=BF+EXP(-EE/(1.695*T))
      4 CONTINUE
      3 CONTINUE
      WRITE(6,99)T,KPM,KPB,ATTEN
      WRITE(6,99)T,KPM,KPB,ATTEN
      99 FORMAT(5(2X,E10.3))
      2 CONTINUE
      7 CONTINUE
STOP
END
PROGRAM OFFRES(INPUT,OUTPUT,TAPE2=INPUT,TAPE3=OUTPUT)

C THIS PROGRAM CALCULATES THE ELECTRON ORDERING DECAY IN THE AB-
CSENSE OF VERTICAL (T1) PROCESSES. THE INPUT PARAMETERS ARE-
C
C KX,KY-- THE DECAY RATE CONSTANTS FOR THE TWO LEVELS
C KM-- THE MIGRATION RATE CONSTANT
C XX,YY-- THE NORMALIZED POPULATIONS OF THE LOWER AND UPPER STATES
C A-- THE FRACTION OF SLOW SYSTEMS
C
C THE MAXIMUM TIME PROGRAMMED IS 100 MSEC IN 1 MSEC STEPS.
C
C THIS MAY BE LENGTHENED BY INCREASING THE LOOP INDEX IN
C THE SECOND LOOP.
C
REAL KX,KY,KM,KYM,KXM,KYO
C
READ(2,5) KX,KY,KM
READ(2,5) KY,XX,A
5 FORMAT(5E10.0)
WRITE(1,19) A

19 FORMAT(7,F5.4,*THE FRACTION OF SLOW SPINS IS=*,F4.3)
WRITE(3,29) KX,KY,CX,CY,KM
29 FORMAT(1X,*KX=*,E10.3,*KY=*,E10.3,*CX=*,E10.3,*CY=*,E10.3,*KM=*
1,E10.3)
WRITE(3,39) YY,XX

39 FORMAT(4X,*TIME=,6X,*SIGNAL*,4X,*LN SIGNAL*)

TF=(1.,-A)
YF=TF*YY
YS=A*XX
XS=A*YY
XF=TF*XX

TPY=YF+YS
TPX=XF+XS

RPARM=1.-2.*A
KYM=KY+KM
KXM=KX+KM
KYO=KYM+KY

CO 2 J=1,100
T=FLOAT(J-1)*.001

EXPY1=EXP(-KYM*T)
EXPY2=EXP(-KY*T)
EXPX1=EXP(-KXM*T)
EXPX2=EXP(-XX*T)

T1=2.*EXPY1*(A*YF-TPY+YS)/(CY*RPARM)/KYM
T2=RPAR*M*EXPY2*(TPY-2.*CY/KY)
T3=2.*KMX*RPARM*(CY/KYO-CX/KXD)
T4=2.*EXPX1*(XF-XS-A*XF-(CX*RPARM)/KXM)
T5=-RPAR*M*EXPX2*(TPX-2.*CX/KX)

ORDLOS=T1*T2*T3*T4*T5
ALORD=ALCGADS(CALCLS)
WRITE(3,49) T,ORDLOS,ALORD

49 FORMAT(1X,E10.3,2X,E10.3,4X,E10.3)
CONTINUE
STOP
END
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References

36. The author gratefully acknowledges the assistance of Professor Paul Gans of New York University.
45. Assuming a Boltzmann nuclear spin equilibrium and uniform spin temperature, all nuclear spin states will be equally occupied even at liquid helium temperatures, so that the hyperfine fields which broaden the line should vary randomly from site to site.
47. H. Brenner, private communication.
57. A. Zewail, private communication.
63. The large change in trap-trap separation between the 0.06\% and 0.003\% crystals would suggest that exchange is more probable in the 0.06\% sample regardless of mechanism of transfer. This, coupled with the large experimental errors associated with these experiments, accounts for differences in the temperature dependence of $\alpha$.


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ABSOLUTE STRUCTURE DETERMINATION USING ELECTRON MICROSCOPY

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ABSTRACT

A dynamical theory of electron diffraction, based on the Howie-Whelan equations and generalised to the non-centrosymmetric case, has been used successfully to determine the absolute configuration of the structure in ordered lithium ferrite (LiFe$_5$O$_8$) crystals. The ability to distinguish between the P4$_1$32 and P4$_3$32 spacegroups on a very fine scale has been demonstrated.

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When the symmetry operations, which constitute the space group of a structure, includes neither an inversion nor a reflection operation, then the structure can exist in two enantiomorphous forms, a right-handed and a left-handed one. The presence of the two enantiomorphs co-existing within a sample can be verified in the electron microscope by imaging in dark-field in a multi-beam orientation, with the electron beam parallel with a zone axis, along which the crystal does not show a centre of symmetry in projection (Van der Biest and Thomas, 1975). One takes advantage here of violation in Friedel's law (Serneels et al., 1973) which may cause a difference in background intensity of the two structures. In this paper it will be shown that it is possible to determine uniquely the configuration of the structure i.e. whether it is left or right-handed using the results of a dynamical theory.

The material studied is lithium ferrite (LiFe$_{5}$O$_{8}$). All experimental observations in this paper were made on a Hitachi Hu-650 microscope operating at 650 kV. The samples were discs of ordered lithium ferrite, chemically polished in hot phosphoric acid. This preparation technique does cause some etching along the boundaries between the enantiomorphs, but it yields otherwise smooth surfaces.

Thickness fringe profiles were calculated for both structures using the Howie-Whelan equations (Howie and Whelan, 1961) generalised for the n beam case:

\[
\frac{d\psi_h}{dz} = \pi i \sum_{g \neq h} e^{2\pi i (s_h - s_g) z} \left( \frac{U_{h-g}}{k_z} + i \frac{U'_{h-g}}{k_z} \right) \psi_{h-g}
\]
These equations are of the same form as those for centro-symmetric crystals. In the present case however $U_{h-g}$ and $U'_{h-g}$ are complex quantities with the provision that $U_{h-g} = U^*_{g-h}$, $U'_{h-g} = U'^*_{g-h}$. It was assumed that the phase factors of $U_{h-g} = |U_{h-g}|e^{i\theta_{h-g}}$ and $U'_{h-g} = |U'_{h-g}|e^{i\phi_{h-g}}$ are the same i.e. $\theta_{h-g} = \phi_{h-g}$. $\Psi_h$ is the amplitude of beam $h$, $z$ is the depth in the crystal; $s_h$ is the deviation parameter of beam $h$. $k_z$ is the component normal to the foil surface of the wavevector representing the incident wave, after correction for refraction by the mean potential in the crystal. $U_h$ and $U'_h$ are the Fourier components of the real and complex parts of the crystal potential $V(r) + iW(r)$. The complex part is introduced to represent absorption processes in the crystal (Hashimoto, Howie and Whelan, 1960). The differential equations were integrated using a fourth order modified Runge-Kutta method. Up to 61 beams were included in the calculations. The 440 reflection has the shortest two beam extinction distance of the beams considered and this length was used to normalise the depth $z$.

Lithium ferrite has the spinel structure with a 3:1 mixture of ion and lithium ions on the octahedral sites. Below 750°C, these ions take on an ordered arrangement. The structure of ordered lithium ferrite was determined by Braun (1952). It can occur in two enantiomorphic forms, $P4_132$ (right-handed screw axis) and $P4_{3}32$ (left-handed screw axis). It has been shown that both forms coexist on a fine scale in an ordered sample (Van der Biest and Thomas, 1975). Figure 1 shows an example. The orientation in the figure was near [332]. The black and white contrast in the dark field is due to the change in spacegroup. In bright field no contrast is observed between the two enantiomorphic
forms. Figure 2a shows a crystal with a larger domain size. A boundary runs through the thick wedge-shaped crystal. It is clear from Fig. 2a that the black-white contrast observed in dark-field in figure 1 will be strongly dependent on the thickness of the crystal.

The orientation of figure 2 is very close to a symmetrical [332] orientation. Figure 3 shows a number of relevant thickness fringe profiles calculated for this orientation. When performing these calculations, a choice has to be made for the values of the absorption parameters. No attempt was made in this study to either calculate or experimentally determine these values. Instead, it was assumed throughout this study that the anomalous absorption parameters \( 1/\xi_{g-h} = |U_{g-h}|/k \) are the same for all beams. The thickness fringe profiles were calculated for a range of values with the ratios \( \xi_{g}/\xi_{\text{g-o}} \) and \( \xi_{g}/\xi_{\text{g-o}} \) between 0. and 0.1.

The orientation of the crystal in figure 1 could be deduced from the position of the Kikuchi lines on the plate. It was found that the projection of the incident wave vector \( k \) on the reciprocal lattice plane (332) is very close to \( k_x = (-.75, 1.25, -.75) \). Thickness fringe profiles for this orientation and \( g = \overline{1}10 \) are shown in figure 4. The thickness fringe profiles for the bright field are not shown in figures 3 and 4 but were found to be identical for both the \( P4_{1}32 \) and \( P4_{3}32 \) variant, as required by the reciprocity theorem (Pogány and Turner, 1968). This provided a useful check on the performance of the computer programs. It is evident from the results in figures 3 and 4 that especially in the thicker portions of the crystal, the fringe pattern is quite sensitive to the orientation and the values of the absorption parameters. However, it is noted (figure 3) that the first bright fringe will be closer to the edge of the foil in the \( P4_{3}32 \) variant than in the \( P4_{1}32 \) variant for \( g = \overline{1}10 \). This result is reversed when the sign of \( g \) is changed (figure 4). This result proved to be valid for a wide range of orientations and values of the absorption
parameter. The latter is understandable because near the edge of the foil absorption can be neglected. Using this result, it is clear that in figure 2 domain 1 has the $P4_332$ structures and domain 2 the $P4_132$ structure. When performing this analysis, care has to be taken to correctly index the diffraction pattern. The calculations were performed with atomic coordinates referred to right-handed axis, standard in crystallography. In the printed diffraction pattern, however, a left-handed reference system has to be used for indexing. In the general case of a non-centrosymmetric crystal, one would also need to distinguish between a $[Uvw]$ orientation and $[Uvw]$ In the present case, this is not necessary because $[332]$ and $[332]$ are related by a 180° rotation around the $[\bar{1}10]$ direction, which is a two-fold rotation axis in both space groups. Hence, these two orientations are equivalent here. This retardation in the formation of the first bright fringe occurs only for $110$ type reflections in lithium ferrite. For other reflections this does not occur (figure 3d).

An attempt was made to simulate the micrograph of figure 2a, using the overprinting technique on the line printer of the computer. The subroutine HALFTN, described by Head et al (1973), was used for this purpose in an adapted form. A grey scale of eight steps was used by overprinting up to three different symbols. An example is shown in figure 2b, which may be compared to figure 2a. The boundary between the domains has not been simulated. When making this comparison, one should disregard the relative widths of the fringes as these depend only on the local slope of the crystal wedge. What is important is the way the
thickness fringes meet at the boundary. Recognising the limitations of the grey scale used, which is inadequate to represent the differences in contrast in the micrograph, one may conclude that the agreement between the experimental and calculated micrographs is good.

Comparison of the simulated micrographs, calculated for a range of absorption parameters, showed that best agreement was obtained for the following values of the absorption parameters:

$$\frac{\xi_0}{\xi_0} = 0.07, \quad \frac{\xi_g}{\xi_g} = 0.05.$$  This choice of absorption parameters is somewhat subjective, as it was found that variations in absorption parameters could be compensated for, to a limited extent, by adjusting the grey scale used. No claim is made here that these values represent an accurate determination of the absorption parameters. Still, they represent a rough guide for the values that need to be used.

The method used to determine the spacegroup of the domains in figure 2, i.e. from the relative position of the first bright fringe, can only be used for domains ending at the edge of the crystal. In the general case, one needs to determine the thickness of the foil as accurately as possible and then deduce from the thickness fringe profiles which variant is the brightest. The thickness of the foil in figure 1 has been determined accurately using a method designed by von Heimendahl (1973), who determined that the accuracy of the method is around 4% for routine work. The result for the area in figure 1 is 3905Å or 4.31 Å440. Assuming an error of 5%, this yields a thickness range of 3710Å to 4100Å or 4.09 Å440 to 4.53 Å440. From figure 4b it can be deduced that within this thickness range P4132 is the brightest variant and that the largest difference occurs at 4.3 Å440. It is likely that in figure 1 the thickness is very close to this value, because the contrast is
very pronounced.

This conclusion is not altered if other values of the absorption parameters are considered (figs. 4a, c, d). A study of the points of intersection of the two thickness fringe profiles as a function of the absorption parameters shows that these points do not depend very much on the value of the absorption parameters, although small shifts do occur. For those thicknesses where strong contrast between enantiomorphs is predicted, the value of the absorption parameter will not determine which one has the stronger intensity.

The calculations yielded the following results regarding the contrast between enantiomorphic domains: (i) When only a systematic 110 row is operating, the thickness fringe profiles of both enantiomorphs are identical. This has been experimentally observed (see figure 3c in Van der Biest and Thomas, 1975). However, a moderately strong non-systematic reflection can be sufficient to introduce contrast (fig. 6c, op. cit.) (ii) No significant difference in intensity between left and right-handed variants has been calculated for spinel type reflections. No contrast is observed experimentally. This is understandable as the non-centrosymmetry is a direct result of the ordering process, hence the accompanying contrast phenomena such as anti-phase boundaries and contrast between enantiomorphs, will be associated with the superlattice reflections. (iii) The contrast between domains was not found for some superlattice reflections. No difference in thickness fringe profiles were found for 112 type reflections with $[UUU] = 345$ or $[UWW] = 342$. This was also confirmed experimentally.
It has been shown in this paper that the dynamical theory of electron diffraction, adapted to the non-centrosymmetric case can be used successfully to determine the absolute configuration of a structure. In the general case this will require an accurate determination of the thickness of the foil as the contrast between enantiomorphs is strongly thickness dependent. It was found that if the assumption can be made that the anomalous absorption parameter is the same for all beams, an accurate knowledge of this parameter is not necessary to make the analysis. In the particular case of lithium ferrite, the structure determination can be accomplished quickly by observing the relative location of the first fringe in domains which are terminated by the edge of the foil. This method may not be available in other structures and is in any case limited to 110 type reflections in lithium ferrite.

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Figure 1. Bright field and dark field (g = 110). Symmetrical orientation [UVW] = 332. Domains are separated by cation stacking faults. In the dark field, bright areas have the P4_32 structure. Dark areas have the P4_132 structure (for analysis, see text).

Figure 2. (a) Dark field (g = 110) with corresponding diffraction pattern of a wedge shaped crystal of lithium ferrite. The domain labelled 1 has the P4_32 structure. The domain labelled 2 has the P4_132 structure (for an analysis see text).

(b) Simulated micrograph of (a). The boundary has not been simulated. \( \xi_o / \xi'_o = 0.07 \) \( \xi_g / \xi'_g = 0.05 \) for all g. Symmetric [332] orientation. The corresponding thickness fringe profile is shown in figure 3b.

Figure 3. Calculated thickness fringe profiles. Voltage: 650 kV.
Symmetric orientation [UVW] = 332. 61 beam calculation \( t_{440} = 650 \text{ kV} = 906A. \)
(a) \( \xi_o / \xi'_o = \xi_g / \xi'_g = 0 \) for all g; \( g = \{110 \) (b) \( \xi_o / \xi'_o = 0.07 \) \( \xi_g / \xi'_g = 0.05 \) for all g; \( g = \{110 \) (c) \( \xi_o / \xi'_o = \xi_g / \xi'_g = 0.1 \) for all g; \( g = \{110 \)
(d) \( \xi_o / \xi'_o = 0.07 \) \( \xi_g / \xi'_g = 0.05 \) for all g; \( g = \{103 \)

Figure 4. Calculated thickness fringe profiles. Orientation corresponds to the one in figure 1, \( k_x = (-175, .125, - .75) \) 61 beam calculation.
Dark field g = 110. \( t_{440} = \xi_{440} = 906A. \)
(a) \( \xi_o / \xi'_o = \xi_g / \xi'_g = 0 \) for all g.
(b) \( \xi_o / \xi'_o = 0.07 \) \( \xi_g / \xi'_g = 0.05 \) for all g (c) \( \xi_o / \xi'_o = 0.05 \) \( \xi_g / \xi'_g = 0.03 \) for all g (d) \( \xi_o / \xi'_o = \xi_g / \xi'_g = 0.1 \) for all g.
Fig. 3a
Fig. 3d

- $P_{4132}$
- $P_{4332}$

$g = 203$
Fig. 4a

I/I₀

- P₄₁₃₂
- P₄₃₃₂

g = 110

z/t₄₄₀

XBL 766-8421
Fig. 4b

\[ \frac{I}{I_0} \]

- \( P_{4132} \)
- \( P_{4332} \)

\( g = 110 \)
Fig. 4c
Fig. 4d
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