THE DECAY OF LOCALIZED STATES INTO DELOCALIZED BAND STATES.
THEORY AND PRELIMINARY EXPERIMENTAL INVESTIGATIONS
USING OPTICALLY DETECTED ELECTRON SPIN COHERENCE

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A technique for measuring the decay of localized excited triplet states into the delocalized band states of a solid utilizing the optical detection of electron spin coherence is described. Specifically, the use of optically detected electron spin locking for measuring kinetic phenomena in the presence of fluctuating triplet spin sublevel populations is presented and illustrated. In addition, preliminary experimental data is reported which yields the temperature dependence of the phonon assisted promotion of a localized isotopic site to an energy equal to that associated with the energies of the host exciton band. Finally, the data is analyzed in terms of a kinetic model which relates the localized state's rate of promotion and radiationless decay into the exciton band states to explicit features of the exciton and phonon band structure.

1. Introduction

In an attempt to more fully understand the long range transfer of triplet excitation energy between localized states via exciton band [1] intermediates, an experimental approach has been developed and employed which allows the first step in the indirect transfer process, the phonon assisted promotion of a localized excitation to a delocalized band state, to be isolated and studied. The technique which will be presented here involves the optical detection [2-4] of the loss of electron spin coherence of the localized excitation when the state is spin locked [5] in the rotating frame. In addition, the first experimental data on the temperature dependence of the rate of phonon assisted promotion of localized excitations to band states is reported. Finally, a model which includes the exciton band dispersion and density of states, phonon—localized excitation interactions (including single phonon, Raman, and multiple phonon processes), and the interaction of a localized state with the exciton band is presented and used to describe the promotion process and the radiationless decay of the phonon activated intermediate into the exciton band.

The importance of this initial step in the indirect transfer process cannot be underestimated, for it is one of the essential features which determines whether or not thermal equilibrium between delocalized band states and localized states can be achieved within the lifetime of the excited states and hence determines whether Boltzmann statistics apply to excited solids at low temperatures [6]. Furthermore, the kinetics of the macroscopic transport of electronic excitation energy in solids also depend in detail upon an understanding of this step, as well as upon the nature of the exciton propagation (coherent versus incoherent) in the band [7-9].

2. Discussion

The use of electron spin coherence to study kinetic phenomena associated with excited triplet states can be understood by viewing two of the excited triplet...
state spin sublevels in a reference frame rotating at the Larmor frequency (the interaction representation). The laboratory frame population of one of the two spin sublevels can be represented as a pseudomagnetization along the positive z-axis of the rotating frame and the laboratory frame population of the other spin sublevel is related to a pseudomagnetization along the negative z-axis of the rotating frame. It has been shown that when the time-dependent density matrix describing the dynamics of the electron spin ensemble is displayed through the electric-dipole transition moment operator responsible for phosphorescence, the projection of the magnetization onto the z-axis in the rotating frame is usually the only observable associated with a change in the intensity of phosphorescent emission [2].

Optically detected electron spin coherence can be used in the measurement of the rate of promotion of a localized state to a delocalized band state by determining the contribution of the promotion process to the loss of electron spin coherence when the spin ensemble is locked in the rotating frame. The loss of the spin locked pseudomagnetization, \( M \), as a function of time, \( t \), can be given by the following equation

\[
M(t) = M_0 \exp\left[-(K^L + K^T_{1p} + K^P) t\right]
\]

where \( K^L \) is the average of the rate constants for decay to the ground state of the two spin sublevels involved, \( K^T_{1p} \) is the rate constant for longitudinal spin relaxation along the spin locking field, and \( K^P \) is the rate constant for the phonon assisted promotion of localized states to delocalized states. The rate constant for the total decay of spin coherence, \( K_{T_{1p}} \), is the sum of these rate constants.

Specifically by applying a \( \pi/2 \) microwave pulse to one of the three zero-field transitions associated with an ensemble of localized triplet states, two of the spin sublevel populations become saturated in the laboratory frame but are still evolving coherently in time. The pseudomagnetization in the rotating frame is simply tilted 90° into the \( x-y \) plane. Spin locking [5] by phase shifting the applied microwave field 90° immediately after the \( \pi/2 \) pulse prevents the spin coherence from being lost for a time corresponding to \( T_{1p} \). \( T_{1p} \) can be measured by turning off the spin locking field and immediately restoring the pseudomagnetization to the z-axis by a final \( \pi/2 \) pulse having the same phase as the initial pulse and measuring the resulting change in the phosphorescence intensity as a function of the spin locked time.

The uniqueness of spin locking to the measurement of kinetic phenomena is that once the triplet spin states have been locked in the \( x-y \) plane, any additional population entering the ensemble of localized states at later times via incoherent processes such as intersystem crossing or trapping of delocalized band states, enters along the + or - z-axis of the rotating frame because of the random phases of the entering spins relative to the spin locked ensemble. Consequently, this additional population is driven by the microwave field in a plane perpendicular to the \( x-y \) plane during the spin lock period. The net effect is that this incoming population results in a coherent disk of spins in a plane perpendicular to the \( x-y \) plane and has no net pseudomagnetization along the z-axis. When the final \( \pi/2 \) pulse is applied, this disk is tipped into the \( x-y \) plane and still has no net projection along the rotating frame z-axis. The result in the laboratory frame is that any population entering the localized state after the initial \( \pi/2 \) pulse is incoherently and equally distributed between the two spin sublevels.

If the two spin sublevels coupled by the microwave field have the same phosphorescent emission polarization, then, in principle the emitted radiation will have a quantum beat modulation at the Larmor frequency as discussed in ref. [2].

\( K^T_{1p} \) is the rate constant for the loss of spin locked pseudomagnetization due to relaxation along the rotating frame magnetic field and is to be distinguished from \( K_{T_{1p}} \) which is the total rate constant for the loss of spin locked population due to all mechanisms.

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\( K^P \) is the rate constant for the phonon assisted promotion of localized states to delocalized states.

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OPTICALLY DETECTED SPIN LOCKING IN THE PRESENCE OF FLUCTUATING SPIN SUBLEVEL POPULATIONS
(The Relationship between the Laboratory Frame and the Interaction Representation)

Fig. 1. (A) A diagrammatical representation of the rotating frame pseudomagnetization for a system in which intersystem crossing occurs only to one level. (a) Pseudomagnetization before the application of microwaves; (b) after initial \( \pi/2 \) pulse applied along the rotating frame \( x \)-axis; (b') the field is shifted 90° to the \( y \)-axis spin locking the initial pseudomagnetization. The partial disk indicates incoming population being driven in a plane perpendicular to the spin locked population; (c) a component of pseudomagnetization developing along the negative \( y \)-axis due to longitudinal relaxation along the spin locking field is indicated by the double headed arrow. The disk represents entering population after several hundred nanoseconds incoherently distributed and precessing about the spin locking field; (d) after the application of the final \( \pi/2 \) pulse along the \( x \) direction, the remaining spin locked population is restored to the \( z \)-axis. (B) An illustration of the spin sublevel population change in the laboratory frame under the application of the spin locking pulse sequence. (a) All population in the middle spin sublevel; (b) microwaves couple the middle and bottom sublevel for a time which produces a \( \pi/2 \) pulse. The sublevel populations are equalized; (b') the system is spin locked. The coherent population is equally distributed between the two spin sublevels but incoherent population begins to enter; (c) the coherent population decreases and the incoherent population becomes equally distributed; (d) the final \( \pi/2 \) pulse increases the bottom sublevel population. No changes occur due to the incoherent population. (C) A representation of the 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 \( \tau \).
3. Experimental

The basic experimental design for optically detected magnetic resonance (ODMR) is similar to that described previously [10]. Microwave pulses of the appropriate phase were obtained as follows. The microwave output of a Hewlett Packard Model 8690B sweep oscillator was amplified by a one watt microwave traveling wave amplifier. The output of this amplifier was then divided into two separate parallel channels by use of Anaren Corp. 90° hybrid coupler. Each channel contained a 10 cm General Radio adjustable sliding coaxial line, a Narda variable attenuator, 20 dB isolators, and two Hewlett Packard 33124A PIN diodes in series which were used to produce microwave pulses of the desired duration. The pin diodes were driven by National Semiconductor DH0035CG current drivers which were controlled by TTL logic circuits designed and constructed in this laboratory. The two channels were then recombined by an Anaren 180° hybrid coupler, and the resultant microwave pulse sequence was passed through a Hewlett Packard 8430A band pass filter to remove low frequency switching transients. Finally, the microwave pulses were amplified by a 20 watt TWT amplifier whose output was directed into a 50 Ω coaxial cable and terminated into a slow wave helix which contained the sample. Phase adjustments were made by observing the response of a crystal diode detector to the incident power from the individual signals when separate channels were switched on and to the resultant signal when two channels were opened concurrently and added together.

The spin lock experiment was performed on two systems, \(h_2\)-1,2,4,5-tetrachlorobenzene (\(h_2\)-TCB) in \(d_2\)-1,2,4,5-tetrachlorobenzene (\(d_2\)-TCB) [6] and \(h_2\)-1,2,4,5-tetrachlorobenzene in \(h_{14}\)-durene [11, 12] which are examples of a "shallow" localized \(3\pi\pi^*\) state and a "deep" localized \(3\pi\pi^*\) state, respectively. The preparation and characterization of the samples are described elsewhere [6]. \(h_2\)-TCB is 23.5 cm\(^{-1}\) below the \(k = 0\) state of the \(d_2\)-TCB triplet exciton band [6] and \(h_2\)-TCB is 1456 cm\(^{-1}\) below the \(k = 0\) state of the \(h_{14}\)-durene [13] triplet exciton band. The \(D-E\) and the \(2E\) transitions were used for these systems, respectively. The transition frequencies for \(h_2\)-TCB in \(d_2\)-TCB and \(h_2\)-TCB in \(h_{14}\)-durene are 3.578 GHz and 1.746 GHz. The sam-
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Fig. 3. The lower portion is a semilogarithmic plot of the rate constant for the loss of spin locked population versus $1/T$ for the $h_2\cdot 1,2,4,5$-tetrachlorobenzene in $h_{14}$-durene system. This is an example of a deep localized state ($\Delta \approx 1450$ cm$^{-1}$) and the rate constant is temperature independent. The upper portion is a plot of the rate constant for the loss of the localized state spin locked population due only to the promotion to delocalized band states for $h_2$-TCB in $d_2$-TCB ($\Delta = 23.5$ cm$^{-1}$). A model for the observed temperature dependence is presented in the text.

4. Results

Fig. 1 illustrates in a purely schematic fashion the relationship of the phosphorescence intensity to state of the electron spin ensemble in the laboratory frame and in the interaction representation. Experimental data for the $h_2\cdot 1,2,4,5$-tetrachlorobenzene $\tau_z \rightarrow \tau_y$ transition in a $d_2\cdot 1,2,4,5$-tetrachlorobenzene host is presented in fig. 2. An example of the change in phosphorescence intensity, $\Delta I$ (cf. fig. 1), induced by the final $\pi/2$ pulse as a function of the spin lock time $\tau$ at 1.8°K is presented in the lower portion of fig. 2. The signal to noise of the data illustrated is representative of 600 time averaged accumulations at a rate of 5 per second. A semilog plot of $\Delta I$ versus the spin lock time $\tau$ reveals an exponential decay with a $T_{1\rho}$ of 4.95 msec at 1.8°K. This is illustrated in the upper portion of fig. 2. When the same experiment is repeated with $h_2$-TCB doped into $h_{14}$-durene (1% m/m), $T_{1\rho}$ is found to be significantly longer [$\tau(1/\epsilon) = 24$ msec]. Moreover, when the temperature dependence of $h_2$-TCB in $h_{14}$-durene was investigated, $T_{1\rho}$ was found to be invariant within experimental error throughout the range from 4.2°K to 1.5°K. This is illustrated in the lower portion of fig. 3 in which $K_{T_{1\rho}}$ is plotted against $1/T$. 
On the other hand, for h$_2$-TCB in d$_2$-TCB, the data revealed a dramatic temperature dependence. $T_{1\rho}$ varied more than an order of magnitude in the limited range from 1.4°K to 2.1°K. Due to the unavailability of fast transient averaging equipment, the results of these preliminary experiments could not be extended to higher temperatures. A semilog plot of $K^P$ for h$_2$-TCB in d$_2$-TCB versus $1/T$ is given in the upper portion of fig. 3. $K^P$ was obtained by subtracting $K^L$ and $K^{2\mu\mu\nu}$ measured in the durene host from $K_{1\mu\rho}$ measured in d$_2$-TCB. $K^P$, the phonon assisted rate constant, is seen to be a rapidly changing non-exponential function of temperature.

5. Model for the decay of localized states into the delocalized band states

Qualitatively, we view the decay of the localized state into the delocalized exciton band as follows. One or more phonons interact with a localized state to produce an intermediate state which is degenerate with one or more of the wavevector states of the exciton band. This localized intermediate then decays radiationlessly into the band, and the radiationless relaxation process is displayed in the form of a golden rule rate [15]. The assumptions implicit in this model are that the creation of the intermediate state is a stochastic process [16] and that the decay into the band is irreversible in the sense that recurrence [17] is negligible because of the high density of band states and the finite lifetime of the $k$ states into which the intermediate evolves.

Quantitatively, the probability per unit time of a localized state, $|\tau_i\rangle$, interacting with a single phonon, $P(e)$, of energy $e$ and decaying into a specific band state $|k\rangle$, via an intermediate state, $|\tau_i\rangle$ having energy $E_i$ is given by

$$K_{ke} = \frac{(2\pi/h)}{(\langle n(e) \rangle_T)} |\langle \tau_i | P(e) | H_{\tau_i} | P(e-E_i) \rangle|^2 \times |\langle P(e-E_i) | H_{\tau_i} | P(e-E_i) \rangle|^2 \rho(E_i). \tag{2}$$

* Delocalized exciton band is taken to mean any linear combination of the stationary $k$ states of the exciton band. In general, the decay will take place into an admixture of a small number of $k$ states which form a mobile wave packet state. However the possibility exists that the admixture will contain all $k$ states and therefore will be described by a Wannier function which is centered about a particular lattice site [14].

$$\langle n(e) \rangle_T$$ is the average number of phonons having energy $e$ at temperature $T$ given by the Planck distribution function [18]*. $|\langle n(e) \rangle_H | \langle P(e-E_i) | H_{\tau_i} | P(e-E_i) \rangle|^2 \rho(E_i)$ is the probability of creating the intermediate $|\tau_i\rangle$. Matrix elements of $H_{\tau_i}P$ depend explicitly on spatial coordinates but are taken to be spin independent in the sense that the electron spin dipolar interactions do not effect the overall promotion rate. Both direct and Raman single phonon processes are included by taking $e = E_i$ and $e > E_i$, respectively. Unless multiphonon processes are included, $P(e)$ must have energy greater than or equal to $E_i$. The radiationless decay of the intermediate $|\tau_i\rangle$ into the exciton manifold of $k$ states at an energy $E_i$ above the localized state is given by

$$|\langle \tau_i | P(e-E_i) | H_{\tau_i} E | kP(e-E_i) \rangle|^2 \rho(E_i) \tag{3}$$

where $\rho(E_i)$ is the exciton density of states function evaluated at $E_i$.

The total probability per unit time for the phonon assisted promotion of a localized state to the exciton band, $K^P$, is obtained by summing over all phonons with energy $e \geq E_i$ and then summing over all intermediate states $|\tau_i\rangle$ which have energies $E_i$ equal to the energies of the band $k$ states, i.e.,

$$K^P = \sum_k \sum_{e \geq E_i} K_{ke} \tag{3}$$

If the multiple phonon processes are important, then the matrix elements in eqs. (2) and (3) are modified to include the interaction of the localized state with the additional phonons. For the two phonon case, one must include the two phonons, $P(e)$ and $P(e')$. $\langle n(e) \rangle_T$ is replaced with $\langle n(e) \rangle_T \langle n(e') \rangle_T$ and a summation over all pairs of initial and final phonons which conserve the energy of the overall process must be performed in eq. (3). Extension to higher order processes is straightforward.

6. Conclusions

(i) The fact that the $T_{1\rho}$ for h$_2$-TCB in $h_{14}$-durene is long and temperature independent makes it reasonable to conclude that $K^P$, the phonon assisted promotion rate constant, for this system is zero and that

* The Planck distribution function may be employed, provided that anharmonic contributions to the phonon potential are not large, and is certainly adequate for a first order calculation.
$K_{T_{1p}}$ is just the sum of $K^L$ and $K^{T_{1pm}}$. This is not surprising in view of the large (1456 cm$^{-1}$ [13]) energy difference between the localized $h_2$-TCB $3\pi\pi^*$ state and the durene triplet band. From an independent measurement of the $\tau_y$ and $\tau_z$ sublevel decay rate constants ($K_y = 27.8$ sec$^{-1}$; $K_z = 26.3$ sec$^{-1}$ [11]) in this system, a value of 27.1 sec$^{-1}$ for $K^L$, the rate constant for decay to the ground state from the spin lock state is obtained. Thus, the spin lattice relaxation time in the rotating frame can be determined from eq. (1) and fig. 3. $T_{1p} = (K^{T_{1pm}})^{-1} = 67$ msec and appears to be temperature independent over the limited range investigated.

(ii) In an independent investigation [6] of the $h_2$-TCB $3\pi\pi^*$ state in the $d_2$-TCB host it has been shown that in the temperature region 1.38°K to 2.1°K, the phonon assisted promotion of the $h_2$-TCB state to the $d_2$-TCB exciton band is becoming appreciable, although a quantitative measurement of the rate was not determined. This was established from the explicit temperature dependence of the $h_2$-TCB and $hd$-TCB phosphorescence in a $d_2$-TCB crystal and the relationship of this dependence to the Boltzmann thermal equilibrium between exciton states and multiple trap states in this system. From these investigations, we have established that in the temperature region 1.3°K to 1.9°K the localized states are not in thermal equilibrium with the $d_2$-TCB band states but that there is promotion to the band and that the phonon assisted promotion rate for $h_2$-TCB to the $d_2$-TCB band must be rapidly increasing with temperature to account for Boltzmann equilibrium between the localized and delocalized states above $\approx 2.4$°K. Making the assumption that $K^L$ and $K^{T_{1pm}}$ are approximately the same for $h_2$-TCB in the two hosts ($h_{14}$-durene and $d_2$-TCB), $K^P$ can be determined as a function of temperature. This is illustrated by the semilog plot of the data in the upper portion of fig. 3. Since $K^P$ is large relative to $K^L$ and $K^{T_{1pm}}$, changes in these latter two rate constants due to the $d_2$-TCB host will not significantly affect the magnitude of $K^P$ determined at each temperature and will certainly not alter the steep temperature dependence of the promotion rate constant. A significant feature of the temperature dependent promotion rate is that it is clearly non-exponential.

For the temperatures over which the experiments were performed, it is expected that only the acoustic phonon branches will have appreciable population. Unfortunately, experimental acoustic phonon dispersions are unavailable for this system, and only a limited amount of data is available on other molecular crystals [19, 20]. We expect, however, on the basis of the neutron scattering results in $d_8$-naphthalene [20] and anthracene [19], that the acoustic branch is essentially linear up to $\approx 10$ cm$^{-1}$; hence, the optic branch and the nonlinear region of the acoustic branch do not significantly change their populations between 1.4 and 2.1°K.

It can be seen from eqs. (2) and (3) that the phonon assisted rate of promotion is governed in first order by the phonon distribution function. For temperatures where $K_B T$ is much less than $\Delta$, the energy difference between the localized state and the exciton band, one expects an exponentially increasing rate constant with temperature when only single phonon processes are considered and when only the linear regions of the acoustic branch are populated. Moreover, when $K_B T \ll \Delta$, the functional relationship between the rate constant and temperature (exponential versus non-exponential in the range relevant to the experimental data) is relatively insensitive to the exciton band dispersion, and theory predicts an exponential behavior if one assumes that the coupling of the localized state to the phonons is equally probable for all phonon wavevectors $q$ (i.e., $\left< q \right> \left< H_{ph} \right| \tau_T \left| q - \epsilon \right> = q$ independent).

The observation of a non-exponential behavior and the steep temperature dependence in this limited temperature range suggests that some or all of the following considerations are important. (a) Multiphonon processes dominate the promotion process; (b) $d_2$-TCB has an acoustic phonon dispersion that becomes significantly nonlinear at very low energies ($\approx 5$ cm$^{-1}$) or (c) the coupling of the phonons to the localized states are strongly $q$ dependent.

Further experimental data and a detailed comparison of the data to the above model should establish the relative importance of the above considerations.

(iii) Although these experiments have demonstrated

* If there is a low temperature phase transition a soft phonon mode will be produced which will facilitate multiphonon processes. This possibility is currently being experimentally investigated.
the temperature dependence of the phonon assisted promotion of localized states to the exciton band, we do not yet know quantitatively what fraction of the promoted intermediates decays radiationlessly into the exciton band, nor do we know whether or not there is a strong $k$ dependence to the process other than the obvious effect of a large exciton density of states at the top and bottom of the triplet band in these systems [6].

In addition to the decay of a localized state into a mobile exciton state, a second possible mechanism for the loss of spin coherence is the creation of a localized bound phonon-exciton state. This bound state can evolve into a mobile state in which case it may be viewed merely as a short-lived intermediate, or it can relax back into the ensemble of non-phonon excited localized states after a time period long enough for it to have lost phase coherence with the spin locked ensemble. The principal factor determining whether electron spin phase coherence is lost, if a bound phonon-exciton intermediate relaxes back into its original lattice site, is the life time of the intermediate. In this system we expect a difference in the $D-E$ transition frequency of the exciton band and the localized trap state to be about 60 MHz; hence phase coherence in these experiments will be lost in the promotion-relaxation process if the excited intermediate has a life time of greater than $\approx 10^{-8}$ seconds. Earlier experiments have demonstrated the redistribution of the $h_{2}\text{-TCB}^{3\pi\pi}$ state energy to other (hd-TCB) localized states via the $d_{2}\text{-TCB}$ band [6, 8].

The peaking of the density of states function at the top and bottom of the exciton band occurs for one-dimensional bands: cf. ref. [21]. Crystals of $h_{2}\text{-1,2,4,5-tetrachlorobenzene}$ and 1,4-dibromonaphthalene have been shown to have one-dimensional band structures (cf. refs. [6, 8, 22]). For $d_{2}\text{-1,2,4,5-tetrachlorobenzene}$ discussed in this paper, it is reasonable to assume a one-dimensional band since deuteration will not greatly alter the crystal structure.

The time dependence of the loss of electron spin coherence with the spin locked ensemble is determined by the difference in the Larmor frequencies of the two states relative to the life time of the bound phonon-exciton intermediate. In these experiments $\gamma H_{1} \approx 5$ MHz while the difference between the band and localized states Larmor frequencies ($\Delta \omega$) is about 60 MHz [23]. Thus the spin when promoted will dephase with the ensemble in a time of the order of $\Delta \omega^{-1}$ provided $\gamma H_{1} < \Delta \omega$. This is the case in these experiments implying that the production of mobile excitons must account for a significant part of the measured values of $K_{P}$. Furthermore, a $10^{-8}$ second lifetime for a vibrationally excited (phonon-excited) intermediate seems very long in view of data available for phonon relaxation rates in solids [24]. To date there is no experimental evidence to demonstrate the existence of bound phonon-exciton states which relax back to the same lattice site. However, if they exist, they will contribute in part to $K_{P}$. Additional experiments are currently being pursued in this laboratory to determine the extent of these contributions to the magnitude of $K_{P}$.

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References

    J.C. Slater, Phys. Rev. 76 (1949) 1552; 87 (1952) 807.