

DIRECT MEASUREMENT OF THE QUANTUM YIELD FOR THE CREATION OF MOBILE EXCITONS FROM LOCALIZED STATES USING OPTICALLY DETECTED ELECTRON SPIN COHERENCE

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Optically detected spin locking and adiabatic demagnetization in the rotating frame are used to directly measure the rate constants for trap-to-band *promotion* and trap-to-trap energy *migration* in 1,2,4,5-tetrachlorobenzene. Comparison of these rate constants at a given temperature gives the quantum yield for the decay of a promoted localized state into a mobile exciton state. Its dependence on temperature is also determined.

1. Introduction

Propagation of Frenkel excitons [1] as a coherent wavepacket is an important prediction [2] about properties of solids at low temperatures and has recently been experimentally observed [3,4] for molecular crystals. An important aspect of wavepacket or coherent migration of electronic excitation is that it provides a very efficient means whereby localized impurity states can be maintained in thermal equilibrium with the band states [5]. In addition to facilitating long range energy transfer, it determines whether statistical or kinetic models govern the relative populations of the localized states and band states [5]. Central to the dynamics of these phenomena is the means by which a localized excitation is promoted to a state isoenergetic with the exciton band, with a subsequent evolution to a mobile exciton [5,6]. In this communication we report a series of experiments which demonstrate a few of the essential features of this process. Specifically, we will show that (a) it can be viewed as a radiationless decay from a phonon-activated intermediate to the states comprising the exciton band, and (b) that a "quantum yield" for the creation of a

mobile exciton from a localized state can be defined which experimentally approaches unity at low temperatures and decreases significantly as the temperature is raised.

2. Results and discussion

Two separate experimental techniques were combined to elucidate these results and to examine the fate of the localized excitations upon detrapping to the band states. The first, optically detected [7] spin locking [8], was used to measure the total promotion rate of the localized state to the band by monitoring the rate at which the Larmor frequency of the spin-locked ensemble fluctuated in excess of the locking field strength, γH_1 (≈ 5 MHz in these experiments).

The essential features of the spin-lock experiment as applied to a particular zero-field transition of an ensemble of molecules in their excited triplet state is best viewed in the rotating frame where the population difference between the two zero-field triplet spin sublevels is represented as a pseudomagnetization initially directed along the z axis [9,10]. It has been shown that the projection of this pseudomagnetization upon the z axis is generally the only observable related to changes in the phosphorescence intensity [11], and hence the only observable in an optically

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detected spin locking experiment. Application of a $\pi/2$ pulse and spin locking results in a coherent superposition of the ensemble of triplet spins that is destroyed whenever a fluctuation of the Larmor frequency occurs which is large relative to γH_1 , where H_1 is the spin locking field. The loss of spin coherence can be monitored optically by the application of a second $\pi/2$ "probe" pulse which rotates the remaining pseudomagnetization locked in the x - y plane to the z axis and causes a corresponding change in the phosphorescence. The loss of the spin-locked pseudomagnetization, M , as a function of time, t , can be given by the following equation [6]

$$M(t) = M_0 \exp \left\{ - \left[\frac{1}{2} (K_x + K_y) + K^T 1_{\rho m} + K_P \right] t \right\} \\ = M_0 \exp (-K_{T_{1\rho}} t), \quad (1)$$

where K_x and K_y are the rate constants for decay to the ground state of the two spin sublevels involved, $K^T 1_{\rho m}$ 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 exciton band states. The rate constant for the total decay of spin coherence, $K_{T_{1\rho}}$, is the sum of these rate constants.

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) and h_2 -1,2,4,5-tetrachlorobenzene in h_{14} -durene, which are examples of a "shallow" localized $^3\pi\pi^*$ state and a "deep" localized $^3\pi\pi^*$ state, respectively. The preparation [5,12], band structure [5] and characterization of the samples [5,12,13], as well as the experimental details [6,14], are presented elsewhere. h_2 -TCB is 23.5 cm^{-1} below the $k=0$ state of the d_2 -TCB triplet exciton band, and h_2 -TCB is 1456 cm^{-1} below the $k=0$ state of the h_{14} -durene triplet exciton band.

The results of the spin locking experiment for the h_2 -TCB trap in durene have been reported elsewhere [6]. Since the trap depth is very large relative to kT , K_P is assumed to be negligible. $K_{T_{1\rho}}$ was equal to 42 s^{-1} for the $2|E|$ transition and temperature independent between 1.5 and 4.2 K. From previous studies [15], $(K_x + K_y)/2$ was known to be 27.1 s^{-1} ; thus $K^T 1_{\rho m}$ was $\approx 15 \text{ s}^{-1}$.

By contrast, the decay of $M(t)$ of the shallow

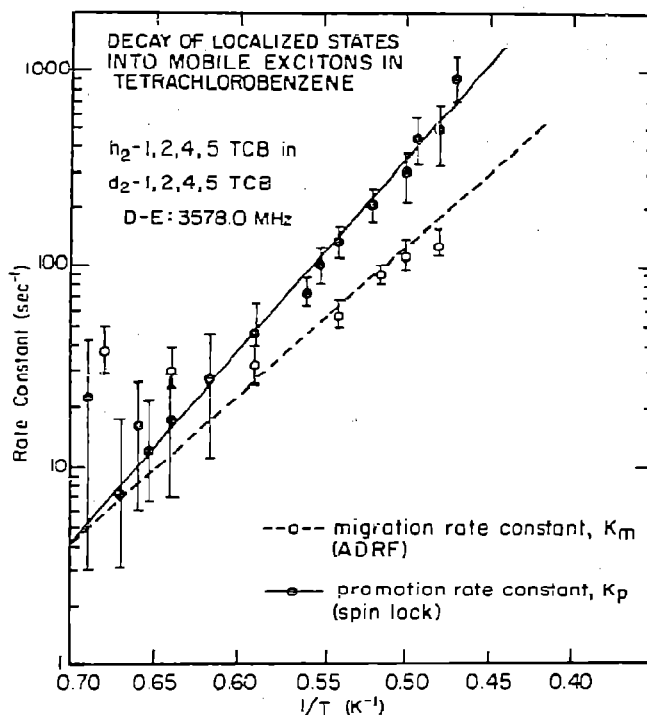


Fig. 1. Experimentally measured values of the rate constants for promotion of h_2 -TCB localized trap states in d_2 -TCB to the d_2 -TCB exciton band (solid circles), and for h_2 -TCB trap-to-trap migration (open circles). The rate constants K_P and K_M were measured versus temperature by means of optically detected spin locking and adiabatic demagnetization in the rotating frame, respectively.

h_2 -TCB in d_2 -TCB trap is strongly temperature dependent. Using values of $(K_x + K_y)/2$ and $K^T 1_{\rho m}$ obtained from the deep trap durene system (both equal to $\approx 15 \text{ s}^{-1}$) [6,15], K_P was evaluated at different temperatures. The resulting values are plotted in fig. 1 for the $D - |E|$ transition. K_P varies more than an order of magnitude in the limited range 1.5 K to 2.1 K. Furthermore, in this range K_P is exponential with temperature.

To understand this temperature dependence, we have constructed a model for the detrapping process, in which the promotion of a localized trap state to the exciton band is viewed as a "two" step process \ddagger .

\ddagger We do not wish to imply here that the detrapping process can be resolved into two discrete steps, but rather that it is a concerted process with a total probability given by the golden rule expression (2). Recurrence of the intermediate to the localized trap state is negligible when the exciton density of states is high and the k state lifetimes are short.

In the first step, a phonon scatters with the trap state to produce an activated intermediate isoenergetic with one or more k states of the band. In the second step, this intermediate relaxes radiationlessly into the exciton band.

Quantitatively, the probability per unit time of a localized state $|\tau\rangle$ interacting with a single phonon $P(\epsilon)$ of energy ϵ and decaying into a specific band state $|k\rangle$ via an intermediate state $|\tau_i\rangle$ having energy E_i is given to the second order by [5,16]

$$K_{k\epsilon} = (2\pi/\hbar) \langle n(\epsilon) \rangle_T |\langle \tau P(\epsilon) | H_{\tau P} | \tau_i P(\epsilon - E_i) \rangle|^2 \times |\langle \tau_i P(\epsilon - E_i) | H_{\tau E} | k P(\epsilon - E_i) \rangle|^2 \rho(E_i). \quad (2)$$

The term $\langle n(\epsilon) \rangle_T |\langle \tau P(\epsilon) | H_{\tau P} | \tau_i P(\epsilon - E_i) \rangle|^2$ gives the probability for creating the intermediate τ_i . $\langle n(\epsilon) \rangle_T$ is the average number of phonons having energy ϵ at temperature T given by the Planck distribution function [17] times $\rho(\epsilon)$, which is the density of phonon states as given by the phonon dispersion. The radiationless decay into the exciton manifold of k states at an energy E_i above the localized state is given by

$$|\langle \tau_i P(\epsilon - E_i) | H_{\tau E} | k P(\epsilon - E_i) \rangle|^2 \rho(E_i), \quad (3)$$

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 $\epsilon \geq E_i$ 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.,

$$K_P = \sum_k \sum_{\epsilon \geq E_i} K_{k\epsilon}. \quad (4)$$

At low temperatures, however, the phonon distribution function will weight the values of $K_{k\epsilon}$ so that K_P will effectively represent detrapping to a relatively narrow range of k states whose energies are nearest the trap state.

In order for detrapping to occur, ϵ must be at least equal to Δ , the energy difference between the localized state and the exciton band. At liquid helium temperatures, kT is much less than Δ in this system, so that one can approximate $\langle n(\epsilon) \rangle_T$ by $\rho(\epsilon) \exp(-\epsilon/kT)$. Furthermore, only linear regions of the acoustic phonon branch are likely to be populated at these temperatures, so that $\rho(\epsilon)$ will be a constant in the tem-

perature range of interest. The net result of the above considerations is that one expects the experimentally measured promotion rate constant to increase exponentially with temperature, and that the exponential factor would yield the value of Δ , the apparent activation energy for detrapping.

As shown in fig. 1, K_P is exponential with temperature \ddagger and the slope gives $\Delta = 16 \pm 4 \text{ cm}^{-1}$, approximately equal to the separation between the energies of the trap state and the bottom of the exciton band.

Having established the essential features of the promotion process, the question remains as to whether or not upon promotion an excitation remains localized and eventually retraps on the same site or forms a mobile exciton, which migrates to another site via the band before retrapping occurs. Taking α as the fraction of promoted excitations that migrate to other traps, we may define a migration rate constant K_M equal to αK_P ; similarly βK_P is the localized retrapping rate constant and μK_P is the rate constant for decay from the band to the ground state. Assuming that μ is small [5] relative to α and β , the problem reduces to distinguishing between promoted excitations that either remain localized (β) or become delocalized (α). This can be distinguished in an experiment which monitors the time evolution of an ordered electron-spin state created in the traps by means of adiabatic demagnetization in the rotating frame (ADRF) [18,19].

The essential features of the "ordered" state are as follows. As is well-known, triplet ODMR lines are broadened in zero field by hyperfine and crystal field interactions. A typical linewidth for the systems of interest is $\approx 2 \text{ MHz}$ [14,20]. One can define an average resonance frequency, ω_0 , which divides the total spin ensemble into "fast" spins whose resonance frequency $\omega > \omega_0$, and "slow" spins for which

\ddagger In the preliminary investigation reported in ref. [6], a non-exponential temperature dependence of K_P was observed. The values of K_P measured at the higher temperatures ($\approx 1.85 - 2.1 \text{ K}$) agreed within limits of error with the values reported in the present work, but the values observed below 1.8 K were significantly larger. The discrepancy may be a result of peculiar characteristics of the sample or of errors due to off-resonance effects in the earlier work. In several subsequent experimental runs, an exponential dependence within limits of error of the results reported here has been observed.

$\omega < \omega_0$. In a frame rotating at ω_0 , the quantity $(\omega - \omega_0)$ appears as a local field H_{loc} directed along the positive or negative z axis.

The experimental optically detected ADRF technique has been described in detail previously [19]. Briefly, one starts with a spin lock state with $H_1 \gg H_{loc}$ and then reduces the H_1 field slowly enough so that each isochromat remains parallel to its effective field, $H_{eff} = H_1 + H_{loc}$. When H_1 is reduced to zero, each isochromat is then aligned along its own local field. The resulting "ordered" state is one in which the polarization of the slow spin ensemble is now inverted relative to the fast spin ensemble.

The unique feature of the ADRF experiment is that after the trap spins are aligned along their local fields, the pseudomagnetization is distributed along the z axis in the rotating frame and hence the "order" is not necessarily lost irreversibly by fluctuations in the Larmor frequency, as is the case in a spin-locked ensemble. Instead, the order is lost by a redistribution of local fields which in the present case requires that the excitation be propagated to a different lattice site after promotion from the localized state. Simply retrapping on the same site will not alter the local field of the spin.

To measure the rate of migration, the order can be monitored with an adiabatic remagnetization-probe pulse sequence [21], performed at a variable time after the ordered state has been prepared. The ability to remagnetize depends on the local field order remaining at that time. It can be shown from simple geometrical considerations that only spins which undergo exchange between the fast ($\omega > \omega_0$) and slow ($\omega < \omega_0$) spin ensembles will contribute to the loss of order, and that each of these migration events makes a double contribution to the order decay. Using the assumption that the distribution of local fields in the crystal is random[‡], it is clear that one half of the migration events will make no contribution to ordered decay, while the other half makes a double contribution. Hence the migration rate constant, K_M , will appear directly in the expression for the decay of the ordered state:

[‡] 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.

$$I \propto \{ \exp [-(K_x + K_M)t] + \exp [-(K_y + K_M)t] \}. \quad (5)$$

Here I represents the contribution of the ordered component to the total phosphorescence intensity and K_x and K_y are the rate constants for decay from the two sublevels.

The decay of the ordered state has been measured in two systems, d_2 -TCB in durene and h_2 -TCB in d_2 -TCB. The durene host results have been reported previously [19]. K_M was essentially zero in this system and the order lifetime was nearly equal to the triplet lifetimes (36 and 38 ms) and was temperature independent.

In the shallow trap system, h_2 -TCB in d_2 -TCB, the order decay is strongly temperature dependent. Using values of K_x and K_y obtained for the deep trap durene system [15], one can solve for a value of K_M at each temperature by fitting eq. (5) to the order decay. The resulting values are presented in fig. 1 along with the data for K_P . Both migration and detrapping increase rapidly with temperature, but the increase of migration is significantly slower.

The ratio of K_M to K_P at a given temperature gives α , the fraction of spins which migrate to the other traps upon detrapping. Thus K_M is actually a rate constant for the composite process of detrapping, trap-to-trap migration and retrapping at a trap other than the trap of origin. Promotion to the band is a required first step in this process so that we express K_M as

$$K_M = K_P (\alpha_{int}) (\alpha_{mig}), \quad (6)$$

where α_{int} is the fraction of intermediate states τ_i which evolve to mobile excitons (as opposed to localized excitons) and α_{mig} is the fraction of mobile excitons which migrate away from the original trap and are ultimately trapped at another site. The ratio of K_M to K_P is

$$K_M/K_P \equiv \alpha = (\alpha_{int}) (\alpha_{mig})$$

and represents the fraction of trap spins which migrate to other traps after promotion to the band and is more or less related to a quantum yield for the creation of an exciton wavepacket.

The behavior of α with temperature will depend on both α_{int} and α_{mig} . Experimentally, α is observed to decrease very sharply with increasing temperature in the range investigated here ($\approx 1.5 - 2.1$ K) as shown in fig. 2. Within experimental limits of error, the

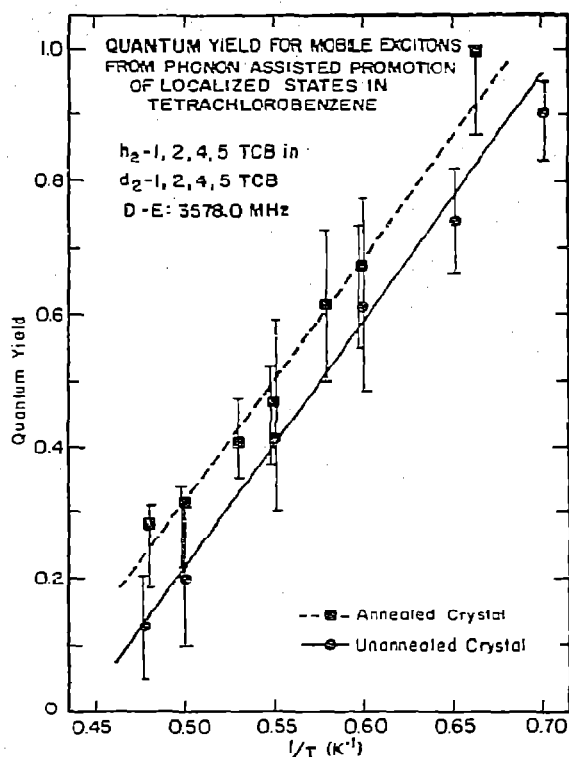


Fig. 2. Quantum yield for h_2 -TCB trap-to-trap migration in d_2 -TCB. The quantum yield, given by the ratio of the migration rate constant to the promotion rate constant, represents the fraction of trap spins which migrate to other traps after promotion to the exciton band.

decrease is linear in the reciprocal temperature. This trend was observed for the two separate samples represented in fig. 2. A preliminary understanding of the temperature dependence of α is provided by some qualitative features of phonon-exciton scattering [22]. It is expected that increased phonon-exciton scattering at the higher temperatures will diminish both α_{int} and α_{mig} . For example, as the temperature is increased, the excitons are scattered among their k states so strongly that the promoted intermediate state τ_1 decays into a state where the superposition of k states fluctuates rapidly. This state tends to be localized in the vicinity of the trap, and as a result, α_{int} , the probability for the creation of mobile excitons, is decreased.

We expect increasing temperature to have a similar effect on α_{mig} . Several experimental studies have provided evidence for coherent exciton migration in these

systems [3,5,23], although the temperature dependence of the coherence lifetime and coherence length have not yet been investigated in detail. It is reasonable to expect that as the temperature is increased, the migration becomes less coherent and more random walk-like, with the result that retrapping of mobile excitons at the original trap becomes more likely. Thus α_{mig} would decrease. These qualitative considerations must certainly be incorporated into any complete description of low temperature migration, particularly in the light of previous theoretical [22] and experimental [3] studies. Nevertheless the results reported here, to the best of our knowledge, provide the first experimental probe into the explicit time dependence of the creation of a mobile state from a stationary localized state.

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