EXPERIMENTAL DETERMINATION OF THE TRIPLET EXCITON INTERMOLECULAR INTERACTION MATRIX ELEMENT AND THE EXCITON–PHONON SCATTERING RATE IN MOLECULAR CRYSTALS

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An experimental method involving the temperature dependence of the intensity of trap emission is employed to determine the sign and magnitude of the nearest-neighbor intermolecular interaction matrix element responsible for triplet exciton transport and the number of wave vector states comprising the triplet exciton band in 1,2,4,5-tetrachlorobenzene. These quantities are utilized to obtain $T_2(T)$ from previously reported ESR data. Using $T_2(T)$ which is related to the rate of exciton inelastic scattering, the exciton transport coherence length is calculated.

1. Introduction

In order to elucidate the mechanism of energy transport in a molecular solid, both the strength of the intermolecular interactions which are responsible for Frenkel exciton [1] transport and the rate of exciton–phonon scattering must be determined [2–5]. An exciton wave packet composed of a linear combination of wave vector states centered about the state $|k\rangle$ propagates through the lattice with a well defined group velocity which is dependent upon the strength of the intermolecular interactions. The distance traveled by this wave packet, its mean free path, is determined by the rate of exciton–phonon scattering and exciton–impurity scattering. If the distance traversed is large relative to a lattice spacing, i.e. if the wave packet's group velocity divided by the scattering rate yields a distance large relative to the molecular spacing, then the migration is said to have a "coherent" [4,6–10] component. On the other hand, if the scattering time is short relative to the time required for the exciton to travel one lattice site, the rapid change in the linear combination of wave vector states will result in diffusive "incoherent" [5] transport of a localized excitation. In a highly purified crystal, impurity scattering may shorten the mean free path of a coherently migrating wave packet, but only exciton–phonon scattering events can occur frequently enough to totally dampen coherent propagation.

In this paper experimental results are presented which permit the triplet exciton coherence length to be determined for the molecular crystal 1,2,4,5-tetrachlorobenzene (TCB). TCB is a particularly interesting system since it is an example of a "one dimensional" solid, i.e. it has a crystal structure which produces significant excited state intermolecular interactions only between molecules arrayed along linear chains [11–14]. Thus exciton delocalization and transport will occur in one dimension. At liquid helium temperatures, analysis of the intensity of phosphorescent emission from a shallow intrinsic trap in the TCB crystal as a function of temperature permits the sign and magnitude of the exciton transport intermolecular interaction matrix element, β, to be accurately determined. In addition, the average number of states comprising the exciton band is obtained.

Previously a theoretical treatment of triplet exciton ESR band-to-band transitions has been given which relates the ESR line shape to the rate of exciton–phonon scattering [10,12,15,16]. At low temperatures, TCB falls into "the narrow band coherent limit". In this case, each exciton wave vector state, $|k\rangle$, has associated with it a lorentzian line. The sum of these individual lorentzian lines yields an envelope which is the observed experimental ESR line shape. In an elegant experiment, Francis and Harris have recorded exciton band-to-band ESR spectra for TCB at 3.2 K [13].

From this data they were able to determine the absolute value of β. However, in order to determine the exciton–phonon scattering rate, which is related to T_2, the transverse relaxation time associated with the individual Lorentz lines comprising the band-to-band transition envelope, it is necessary to know the number of k states in the band. Thus combining the number of band states reported here with the literature ESR data, T_2 is determined and related to the exciton–phonon scattering rate. Finally, using the rate of exciton inelastic scattering and the thermal average exciton group velocity, the coherence length is determined.

2. Discussion

For an ensemble of exciton bands and localized trap states in thermal equilibrium, the temperature dependent intensity of trap emission [9] is given by

$$I(T) = k_r N(T) P(T). \tag{1}$$

k_r is the radiative rate constant for the particular emission line under observation. $N(T)$ is the temperature dependent total number of excitations in the ensemble of excitons and traps. $P(T)$ is the temperature dependent probability that an excitation in the ensemble will be in the trap. For systems in which there is only one type of trap, taking the trap energy as the zero of energy, $P(T) = 1/Z(T)$ where $Z(T)$ is the partition function for the system. The partition function for one dimensional exciton–trap systems in which only nearest neighbor intermolecular interactions are important is

$$Z(T) = 1 + e^{-\Delta/kT} + e^{(4\beta-\Delta)/kT}$$

$$+ 2e^{(2\beta-\Delta)/kT} \sum_k e^{-2\beta\cos ka/kT}, \tag{2}$$

where Δ is the trap depth, i.e. the spectroscopically observable difference in energy between the trap state and the $k = 0$ state of the exciton band, and β is the intermolecular interaction matrix element. The one dimensional nearest neighbor exciton band dispersion is given by [17]

$$E(k) = E^0 - 2\beta \cos ka. \tag{3}$$

The summation in eq. (2) is over each of the doubly

degenerate band wave vector states in the first Brillouin zone. When the number of states is large, the sum can be converted to an integral and evaluated, yielding the following expression:

$$Z(T) = 1 - e^{-\Delta/kT} - e^{(4\beta-\Delta)/kT}$$

$$+ Ne^{(2\beta-\Delta)/kT} I_0(y). \tag{4}$$

N is the number of states in the band and $I_0(y)$ is the zeroth order modified Bessel function with argument $y = 2\beta/kT$.

Under steady state conditions, the temperature dependent total population of the system $N(T)$ is a function of $Z(T)$ and the exciton and trap rate constants for decay to the ground state, K_E and K_T, respectively, in addition to various other parameters such as the intensity of the excitation source, and the first excited singlet state lifetime. If the intensity of trap emission as a function of temperature is normalized to the emission intensity at a single reference temperature, all constants divide out with the exception of K_E, K_T, and the parameters contained in $Z(T)$. Thus the final form for the intensity of trap emission is

$$I(T) = I(T_r) \left[\frac{K_T \chi(T_r) + K_E [1 - \chi(T_r)]}{K_T \chi(T) + K_E [1 - \chi(T)]} \right] \frac{\chi(T)}{\chi(T_r)}, \tag{5}$$

where $\chi(T) = 1/Z(T)$ and $\chi(T_r) = 1/Z(T_r)$. T_r is the reference temperature and $I(T_r)$ is the experimentally observed trap emission intensity at the reference temperature, T_r. In eq. (5), K_T and K_E can be determined experimentally. This leaves the values of N, the number of states in the exciton band and β, the intermolecular interaction matrix element, as the unknown parameters contained in χ which determine the nature of $I(T)$. N is equivalent to the average number of molecules in an exciton linear chain. This is in turn determined by the trap concentration.

As mentioned above, ESR data for the TCB triplet exciton band-to-band transition has been reported in the literature. More recently a theoretical treatment of the band-to-band ESR line shapes has been given [10]. The appropriate line shape expression for the TCB case is

$$G^T(\omega) = \sum_k 2e^{-2\beta\cos ka/kT} \frac{T_2(T)/\pi}{1 + [T_2(T)]^2(\omega - \omega_k^0)^2}. \tag{6}$$

This expression describes the envelope of a collection of lorentzian lines, one for each k state. Each line is centered at a frequency ω_k^0, which varies as $\cos(ka)$ and mirrors the band dispersion on a reduced scale [12,15,16]. The Lorentz line associated with each k state is weighted by the k state probability, i.e. its Boltzmann factor. The observed line shape, $G^T(\omega)$, is determined by the number of terms in the summation, i.e. the number of band states N, the intermolecular interaction matrix element β, the temperature T, and the relaxation time $T_2(T)$ associated with the individual Lorentz lines forming the envelope. In the narrow band limit appropriate for TCB, $T_2(T)$ is taken to be k independent and given by [10]

$$1/T_2(T) = 1/T_2^p + 1/\tau(T), \qquad (7)$$

where $1/T_2^p$ is an intrinsic linewidth and $\tau(T)$ is the exciton inelastic scattering time which at low temperatures primarily involves exciton—acoustic phonon scattering [2—10]. It should be noted that elastic scattering processes which admix $+$ and $- k$ will not affect $T_2(T)$ since k states with opposite signs are degenerate in energy. Therefore scattering between $+$ and $- k$ will not contribute to line broadening. Using eq. (5) to analyze the temperature dependence of trap phosphorescence, β and N are determined. These are then used in conjunction with eq. (6) and the ESR data to determine the remaining parameter, $T_2(T)$. In the limit that $T_2^p \gg \tau(T)$, $T_2(T)$ is the time between exciton inelastic scattering events.

3. Experimental

Two separate batches of TCB were recrystallized from ethanol, vacuum sublimed, and zone refined for 200 passes. Small quantities of each batch of TCB were grown into single crystals under vacuum by the standard Bridgeman technique. The single crystals were cleaved and small transparent pieces were used as experimental samples. The temperature of the samples immersed in liquid He was monitored by measuring the pressure of the He vapor with a digital manometer. The measured temperatures was in error by less than 0.01 K and was varied in the range 4.2 K to 1.52 K.

The samples were illuminated by a high-pressure mercury arc lamp in the region 2700—3600 Å [18]. Excitation takes place into the singlet manifold and after intersystem crossing the first excited triplet state is created. Phosphorescence from the triplet state was detected at right angles to the exciting light using a 3/4 m Spex Czerny—Turner scanning spectrometer. The characteristic emission of TCB as reported earlier [14,19] was observed from each sample, and was independent of the orientation of the sample. The emission consists of two electronic—vibronic progressions, one originating from the exciton band origin at 3748.7 Å and the other from a trap 17.3 cm^{-1} lower in energy. The trap (referred to as the X-trap) is thought to be associated with a crystal lattice imperfection [13,19]. The trap depth was measured by scanning a calibrated 10 Å region 60 times. The results were averaged. The intensity of trap emission was monitored from 4.2 K to 1.52 K. There was an increase of intensity when the liquid He underwent the λ-transition. Independent observations of the increase of intensity when light was intentionally scattered off a crystal confirmed that the increase was due solely to the cessation of bubbling at 2.17 K. Observed intensities were therefore corrected to compensate for the λ-transition.

The phosphorescent lifetimes of both the band and trap in steady state were measured at 4.35 K and 1.53 K respectively. At 4.35 K exciton emission accounts for virtually 100% of the phosphorescent emission. Therefore the exciton lifetime can be obtained free of modifications due to trapping [20—23] and detrapping [24,25] processes. At 1.53 K, although exciton emission can still be observed, flash excitation experiments on this system have shown that exciton trapping is complete within 10 m1 s and that detrapping is negligible at these temperatures [26]. Therefore the trap lifetime can be determined. Fast mechanical shutters were used to determine the exciton and trap lifetimes. The shuttered phosphorescent signal was fed into a 1024-channel CAT, averaged 200 times and read out digitally into a NOVA 210 computer. Finally, the trap intensity versus temperature was fit to the calculated functional form, eq. (5), using a nonlinear regression routine, N1HH23 [27] on an IBM 370 computer.

4. Results and conclusions

Table 1 lists the experimentally determined phos-

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Species	Lifetime (t 1/e)	Δ
TCB exciton	6.7 ms	0
TCB X-trap	38 ms [a]	17.3 cm^{-1}
TCB in durene	36 ms [a]	1456 cm^{-1} [b]

[a] From ref. [28]. [b] From ref. [29].

phorescent lifetimes obtained for the TCB exciton band and X-trap in addition to the lifetime reported in the literature for another TCB trap species, TCB isolated in a durene host. The localized X-trap has virtually the identical lifetime as TCB in durene, while the exciton lifetime is considerably shorter. Both the exciton and X-trap decays from steady state consisted of single exponentials. These were extrapolated to $t = 0$, i.e. the time when the shutter began to close, using a numerical procedure for the deconvolution of the decay from the shutter closing. In both cases, the observed single exponentials contained, within experimental accuracy, 100% of the steady state intensity. Thus the shutter could not have masked a fast decay which contained any significant percentage of the steady state light intensity. K_E and K_T of eq. (5) are 149.3/s and 26.3/s, respectively.

Fig. 1 shows the experimentally measured temperature dependence of X-trap emission[+] and the best calculated curve using eq. (5). The first thing to be noted is that the excellent agreement between the experimental and the calculated curves overwhelmingly supports the assumption that the system is in thermal equilibrium, a necessary condition for the use of eq. (5). The values obtained for the intermolecular interaction matrix element, β, and the number of band states, N, are

$$\beta = +0.34 \pm 0.05 \text{ cm}^{-1}, \qquad N = 5550 \pm 300 \text{ states}.$$

The error limits were assigned by a standard propagation of errors treatment. The values obtained were independent of the reference temperature T_r. The major uncertainty in β resulted from the error in the measur-

[+] A preliminary discussion of this system was used to demonstrate that band–trap equilibrium exists at these temperatures [9]. However, the necessary lifetime corrections contained in eq. (5) were not employed and the trap depth Δ, incorrectly reported in ref. [14] was used. This resulted in a substantial error in both β and N.
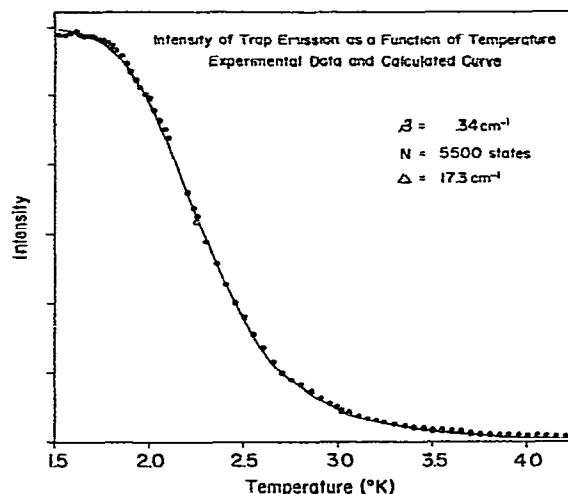

Fig. 1. The experimental data and calculated curve for the temperature dependence of the intensity of phosphorescent emission from the 17.3 cm^{-1} deep X-trap in TCB. The best fit to the experimental data was obtained for the intermolecular interaction $\beta = 0.34$ cm^{-1} and the number of band states $N = 5500$ states.

ed trap depth, $\Delta = 17.27 \pm 0.15$ cm^{-1}. The error in the number of states for a particular sample is considerably smaller than ±300 assigned to N, however there seemed to be a small but real variation in the number of band states in the samples obtained from the separately grown single crystals. The value of N and its error limits were obtained by averaging N for the different samples. The value of β obtained using the trap intensity method is remarkably close to the value ($|\beta| = 0.32$ cm^{-1}) obtained by Francis and Harris from ESR measurements. The positive sign associated with β implies that the TCB triplet exciton band is inverted, the $k = 0$ state being the highest energy state. The spectroscopically determined trap depth Δ is in this case the difference in energy between the trap and the top of the band. This is due to the $\Delta k = 0$ selection rule which applies to exciton band emission [30].

The nearly identical values of β obtained from two widely differing experimental methods allows us to use these values and the value obtained for N with confidence. The band-to-band ESR line shape, described by eq. (6), is determined by the temperature T, the intermolecular interaction matrix element β, the number of band states N, and the temperature dependent relaxation time $T_2(T)$. Since we now know T, β, *and*
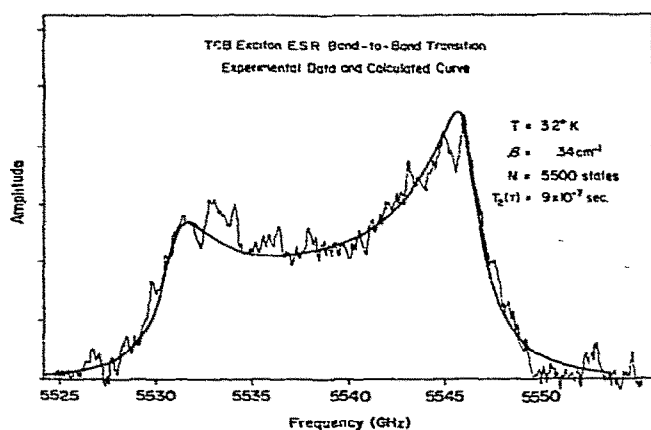
Fig. 2. The experimental ESR triplet exciton band-to-band transition data, taken from ref. [13], for TCB at 3.2 K. The solid line is calculated using eq. (6) with $\beta = 0.34$ cm^{-1}, $N = 5500$, and $T_2(T) = 9 \times 10^{-7}$ s. $T_2(T)$, the transverse relaxation time for the individual lorentzian line associated with each band wave vector state, is equivalent to the exciton inelastic scattering time.

N for the ESR experiment, eq. (6) can be used to analyze the data in detail and $T_2(T)$ can be obtained. (The temperature dependent intensity of trap emission of samples from the crystal of TCB used in the ESR experiments is in all appearances identical to that reported here [9]. Therefore the assumption that the N obtained here also applies to the ESR experiments is reasonable.)
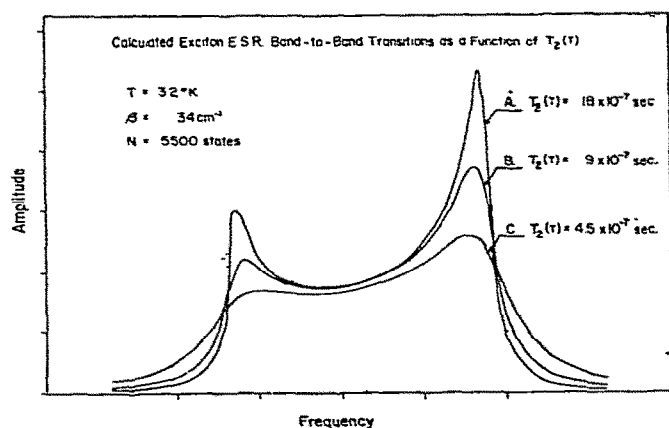

Fig. 3. Calculated ESR band-to-band spectra. Curve B uses the parameters determined for TCB: $\beta = 0.34$ cm^{-1}, $N = 5500$ states and $T_2(T) = 9 \times 10^{-7}$ s. Curves A and C use twice and half the measured $T_2(T)$ respectively. The sensitivity of the line shape to $T_2(T)$ can be seen. $T_2(T)$ is equivalent to the temperature dependent exciton inelastic scattering rate.

In fig. 2, the exciton band-to-band ESR data is reproduced along with the best fit obtained by using the known values of T, β, and N and varying $T_2(T)$. Considering the amount of noise in the spectrum, the fit is quite good. The calculated curve works well for the wings, the peaks, and the valley. Fig. 3 displays the same calculated curve as fig. 2 in addition to curves calculated using half the value and twice the value of $T_2(T)$ obtained from the experimental data. It can be seen that the line shape is extremely sensitive to the value of $T_2(T)$.

The ESR data has been reported for $T = 3.2$ K only. The best fit of the data was obtained with

$$T_2(3.2 \text{ K}) = 9 \times 10^{-7} \text{ s}.$$

Since $T_2(T)$ has a contribution from the intrinsic relaxation time T_2^p in addition to the inelastic exciton scattering time $\tau(T)$, the value cited corresponds to a time *equal* to or *shorter* than the inelastic scattering time. At the low temperatures under consideration, the predominate mechanism for inelastic scattering should be exciton—acoustic phonon scattering with possibly a contribution from spontaneous emission of acoustic phonons by the exciton state. Optical phonons, with energies large compared to kT, should be unimportant in low temperature scattering although they may be involved in the initial "dressing" of the bare exciton state [4]. As mentioned above $T_2(T)$ will not be affected by elastic scattering processes, such as reflection from an impurity site, since states with the same absolute values of k are degenerate in energy and therefore scattering between two such states will not contribute to line broadening.

The value $T_2(T)$ obtained here is equivalent to the exciton coherence time determined by exciton—phonon scattering. An estimate of the average exciton coherence length $\langle l(T) \rangle$, i.e. the exciton—phonon mean free path can be obtained from

$$\langle l(T) \rangle = \langle V_g(T) \rangle T_2(T), \tag{8}$$

where $\langle V_g(T) \rangle$ is the average group velocity of an exciton wave packet at temperature T, given by [9]

$$\langle V_g(T) \rangle = (2\beta a/\hbar)(2kT/\pi\beta)^{1/2}[I_{1/2}(y)/I_0(y)], \tag{9}$$

where a is the lattice spacing and $I_{1/2}(y)$ and $I_0(y)$ are modified Bessel functions with $y = 2\beta/kT$. Substituting the appropriate values for $\langle V_g(T) \rangle$ and $T_2(T)$, a coherence length of 60 000 lattice sites is obtained.

Therefore coherent migration of excitons should be the dominant transport mechanism for triplet excitons in TCB at low temperatures. Coherent migration provides the necessary mechanism for the rapid establishment of the observed thermal equilibrium which exists between band and localized excited states.

In summary: analysis of the temperature dependence of the intensity of trap emission has been used to determine the static triplet exciton band parameters, i.e. β, the intermolecular interaction matrix element, and N, the number of band states for the one dimensional TCB crystal. This method may prove to be generally useful since it is not dependent upon resolving small spectroscopic splittings and unlike ESR it can be used on excited states of any spin multiplicity. In addition to the static band parameters, $T_2(T)$ which should be equivalent to the exciton—acoustic phonon scattering time at 3.2 K was determined from previously reported ESR data. If ESR spectra at other temperatures become available, the temperature dependence of exciton—phonon scattering in this system could be deduced from the temperature dependent exciton band-to-band line shapes (see fig. 3). Finally the value of $T_2(3.2\,\mathrm{K}) \approx 1\,\mu\mathrm{s}$ implies that coherent migration is the dominant mode of exciton transport at low temperature in the TCB system.

Acknowledgement

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