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Coherent Triplet Exciton Trapping in Molecular Crystals

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We have reported the results of several phosphorescence-microwave double resonance experiments¹ using single crystals of zone-refined 1,2,4,5-tetrachlorobenzene (TCB) which exhibit trap and exciton emission² over the temperature range 1.3-4.2°K. This communication is concerned with a recent aspect of this work in which a microwave induced perturbation of the spin-alignment of the exciton spin-manifolds³ is transmitted to trapping sites via triplet exciton migration. The resulting change in the trap spin-alignment is subsequently detected as a change in the intensity of trap phosphorescence.

TCB Y-trap emission (0-0; 3755.7 Å) may be enhanced by doping in low concentration with a wide variety of halogenated benzenes whose lowest triplet states lie at higher energies than that of the host. The microwave ($D+|E|$) transition obtained monitoring the enhanced trap phosphorescence is shown in Figure 1. All features which correspond to an

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increase in phosphorescence intensity are associated with the ESR spectrum of the trap sites and include both electron and chlorine nuclear spin transitions. An important feature of the spectrum in Figure 1 is the decrease in phosphorescence intensity spanning the full linewidth of the exciton electron spin transition.¹ The linewidth and intensity of this transition is insensitive to a homogeneous, but arbitrarily oriented, magnetic field of approximately 200 gauss, consistent with motional averaging of the nuclear spin states in exciton electron spin transitions. The same field causes a three-fold broadening of the trap ESR signal due to Zeeman mixing of nuclear and electron spin states. An additional feature of the trap-monitored exciton electron spin transition, bearing directly upon the coherent nature of the exciton migration, is the loss of the central band minimum⁴ that is observed monitoring the exciton phosphorescence.¹ The loss of this feature is, in fact, predicted by an extension of the one-dimensional band model.

In view of a lamellar packing arrangement and short intermolecular separation between translationally equivalent nearest neighbors,⁵ TCB is expected to provide a model structure for one-dimensional exciton interactions.⁶ The following relation has been derived for the microwave induced change in the spin-alignment between two of the three exciton spin-manifolds, $\Delta N^e(\omega)$, for one-dimensional Frenkel excitons:⁴

$$\Delta N^e(\omega) \sim \rho(\omega) \{ \exp(-E(\omega)/kT) \}. \quad (1)$$

$\rho(\omega)$ is the density of exciton states connected by the microwave frequency, ω , and $E(\omega)$ is the energy dispersion of the spin-manifolds.

The microwave induced change in the trap spin-alignment, $\Delta N^t(\omega)$, is given by:

$$\Delta N^t(\omega) \sim K \Delta N^e(\omega) (K_i^{-1} + K_j^{-1}) \quad (2)$$

where K is an effective rate constant for the trapping of triplet excitons and K_i and K_j are total depletive rate constants for the trap spin sublevels.⁷

If the principal limitation on the coherence lifetime of the triplet exciton is trapping rather than phonon scattering, then the effective trapping rate constant is taken to be proportional to the product of the group velocity of the excitons perturbed by the microwave field, $V_g(\omega)$, and the density of trapping sites, D_T . Since $V_g(\omega) = \rho(\omega)^{-1}$, Equation (2) becomes:

$$\Delta N^t(\omega) \sim D_T \{ \exp(-E(\omega)/kT) \} (K_i^{-1} + K_j^{-1}). \quad (3)$$

The essential feature of Equation (3) is that the change in trap spin-alignment as a function of microwave frequency depends only upon the Boltzmann distribution of the population within the exciton spin-manifolds. This dependence is illustrated by the trap-monitored exciton electron spin transition in Figure 1 and will be referred to as the concentrated trap limit.

In another limit,⁷ the dilute trap limit, when exciton-phonon scattering is faster than trapping, the effective trapping rate constant $K \sim \bar{V}_g D_T$, where $\bar{V}_g$ is the average group velocity taken over the distribution within the exciton spin-manifold. In this limit, $\Delta N^t(\omega)$ depends

upon both the Boltzmann population distribution and the density of states $\rho(\omega)$. Consequently, the trap-monitored exciton electron spin transitions exhibit a central band minimum associated with the minimum in $\rho(\omega)$ at $k = \pm \pi/2$.⁴

Experiments within the above limits should be extremely valuable for investigation of the dynamics of exciton migration insomuch as intrinsic phosphorescence from exciton states of molecular crystals has been observed in only a few cases.

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Figure 1. Zero-field optically detected ($D+|E|$) transition in 1,2,4,5-tetrachlorobenzene obtained at 1.35°K monitoring Y-trap emission. Y-trap emission was enhanced by doping zone-refined tetrachlorobenzene with paradichlorobenzene (1% m/m).

Fig. 1

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