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In order to experimentally differentiate between coherent and diffusion limited triplet Frenkel[1] exciton migration in molecular crystals one must specify both the coherence time associated with the wave vector k and the correlation time associated with the particular experimental approach used. For experiments utilizing a time-dependent oscillating field such as visible electromagnetic radiation at one extreme and a microwave field at the other, the experimental correlation time is on the order of the reciprocal frequency of the applied field. If the lifetime of an exciton k state is much longer than the experimental correlation time, excitons associated with individual k states may be experimentally investigated by the applied field. With this experimental imposition, it is clear why a complete description of the dynamics of exciton migration in the Frenkel limit which allows an experimental probe into the correlation function associated with the dynamics requires that the electronic states, the phonon states, <u>and</u> phonon-exciton coupling all be explicitly considered in terms of the crystal states. Indeed, it is the latter interaction that determines the primary mechanism responsible for electronic energy transfer in solids at both high and low temperatures.[2,3] At low temperature the density of phonon states becomes sufficiently small that scattering between the exciton wave vector states k by the phonons is expected to be much less frequent than energy migration from lattice-site to lattice-site. In the limit that the time between scattering events approaches the radiative or radiationless lifetime of the excited electronic state, a Frenkel exciton can be thought of as a delocalized excitation propagating coherently as a wave packet at a velocity characteristic of both its energy and the linear combination of crystal k states which describe the wave packet. This velocity is termed the group velocity and is given by

$$V_g(k) = (2\pi/\hbar)(d\varepsilon/dk) \ . \tag{1}$$

For a one dimensional crystal,

$$\varepsilon(k) = E^o + 2\beta \cos ka \tag{2}$$

where $\varepsilon(k)$ is the band dispersion associated with translational equivalent interactions along a direction $\vec{a}$. E^o is the electronic energy of the localized molecular excited state while β is the effective intermolecular interaction in the nearest neighbor approximation. In a stocastic model the distance, $\ell(k)$, which an exciton propagates in a coherent fashion without changing either its direction or velocity is given by the lifetime of the coherent state, $\tau(k)$, times the group velocity of the wavepacket

$$\ell(k) = V_g(k) \cdot \tau(k) \ ; \tag{3}$$

$\ell(k)$ is thus equivalent to a mean-free path and $\tau(k)$ corresponds to a correlation time for the wave vector state k. From a dynamical point of view the important feature of coherent migration is that excitons can propagate in the crystal at a variety of velocities and a variety of distances depending upon the k states populated. For the case under consideration the group velocity is zero at the top and bottom of the band ($k = 0$ and $\pm\pi/a$) but $8\pi\beta/\hbar$ at the center of the band ($k = \pm\pi/2a$). The extent to which these states contribute to the propagation of electronic energy in a given situation is determined explicitly by the population distribution in the band. For a thermal distribution, the number of excitons, $N(k)$, propagating with a velocity, $V_g(k)$, at a given temperature is proportional to the density of states $\rho(\varepsilon)$ times the Boltzmann factor.

$$N(k) = \frac{\rho(\varepsilon)\ \exp(-\varepsilon(k)/kT)}{\int\rho(\varepsilon)\ \exp(-\varepsilon(k)/kT)} \tag{4}$$

One can show that k states in the center of the band can have velocities 10^6 - 10^7 times those associated with random walk migration for bands between 1 and 10 cm^{-1} and that the coherence length can approach macroscopic dimensions if phonon-exciton scattering is weak (i.e., $\tau(k)$ is long) and the excited states are long-lived (e.g., triplet states). In practice this is only achieved at very low temperatures where the distribution of phonon states approaches the $T\rightarrow 0$ limit. At intermediate temperatures the principal limitation of $\tau(k)$ is phonon-exciton scattering. In such cases an exciton initially in a k state scatters to other k' states via phonon interactions in a time short compared to the radiative or radiationless lifetime, but in a time long compared to intermolecular exchange. As a result the coherence time is shortened, the mean-free path or coherence length is reduced, and the individual k states acquire a width $\Gamma(k)$, given by the reciprocal of the coherence lifetime of the individual k states. $\Gamma(k)$ is given by

$$\Gamma(k) \equiv (\tau(k))^{-1} = \sum_{k'} (\tau_{kk'})^{-1} \qquad (5)$$

where $\tau_{kk'}$ is the probability of an exciton initially in the k<u>th</u> state scattering via phonon-exciton interactions to a final state k'.

In summary then, a proper description of the dynamics of exciton migration must include in addition to the stationary states of the crystal (a) the group velocities of excitons, (b) the population distribution over the k states of the band, and (c) the coherence times for the individual k states and hence an explicit model for phonon-exciton scattering. This stocastic description views the exciton as executing a random walk migration in a time on the order of the coherence lifetime but allows for long range propagation via coherent migration in between scattering events.

From an experimental point of view, this model requires that careful attention be given to the relationship between the correlation time associated with exciton migration and the time scale of the particular experimental approach being employed. If, for example, the experimental correlation time, which is on the order of the reciprocal of the radiation field, is much shorter than $\tau(k)$ (as is the case for optical absorption), only manifestations of the coherent model are apparent from the data.[4] Similarly, when the experimental correlation time is longer than $\tau(k)$ for all k, only the random walk processes are displayed. A reliable measure of phenomena connecting coherent migration and diffusion limited migration, such as phonon-exciton scattering, $V_g(k)$ and $\ell(k)$, can only be determined when the experimental correlation time is on the order of $\tau(k)$.

With this in mind three experimental approaches to the investigation of coherence in energy migration have been devised. The first, optically detected electron spin resonance of triplet excitons in zero-field[5] takes advantage of the fact that selective spin-orbit coupling between singlet bands and the individual triplet spin sublevel bands results in a k dependent Larmor frequency, ω_o^k, of the triplet exciton zero-field splittings.

The proper representation for electron spin resonance absorption in terms of the Bloch formalism[6] is a set of Bloch equations, one for each k state in the band, whose frequency components ω_o^k are coupled by phonon-exciton scattering. In the rotating frame, the presence of a weak oscillating rf field of the form

$$\mathcal{H}_1(t) = -\gamma H_1 \cdot \hat{S}_y \cos \omega t \qquad (6)$$

connecting τ_x with τ_z via the electron spin operator $\hat{S}_y$ results in an in-phase, u, and out-of-phase, v, component of a complex moment, G, given by

$$G_k = u_k + iv_k \ . \qquad (7)$$

Modified Bloch equations can be constructed from the complex moments[7] of each k state that include the effects of phonon-exciton scattering phenomenologically through the scattering rates $(1/\tau_{kk'})$. The $(2k + 1)$ equations are:

$$dG_k/dt + [1/T_2(k) - i(\omega_o^k - \omega)]G_k = -i\gamma H_1 N(k) + \sum_{k'} [G_{k'}/\tau_{kk'} - G_k/\tau_{kk'}] \qquad (8)$$

where N(k) is given by Equation (4). $T_2(k)$ is the homogenous spin-spin relaxation time for the kth exciton state. $1/\tau_{kk'}$, or the probability per unit time for an exciton being scattered by a phonon from k to k' is displayed as a "golden rule" rate:[8]

$$1/\tau_{kk'} = \rho_{\varepsilon}(k') \sum_{\lambda,q,q'} \rho_p(q') \exp[-E^{\lambda}(q)/kT]\, \rho_p(q)$$
$$\times\ |\langle kq|\mathcal{H}^{\lambda}_{ep}|k'q'\rangle|^2 \delta(k,k',q,q') \qquad (9)$$

$\rho_e(k')$, $\rho_p(q')$ and $\rho_p(q)$ are the exciton (subscript e) or phonon (subscript p) density of states functions evaluated at the energy of the wave vector k', q', or q, respectively. λ is the index which runs over the phonon branches and $E^{\lambda}(q)$ is the energy of the <u>qth</u> wave vector of the phonon branch. The sum over phonon states q and q' is restricted to collisions that conserve both the total energy and momentum of the initial and final exciton-phonon states $\langle kq|$. H_{ep} is the exciton-phonon coupling Hamiltonian. In weak oscillating rf fields and steady state ($dG_k/dt = 0$) the electron spin resonance line shape function, $g(\omega)$, is given by:

$$g(\omega) = \mathrm{Im} \sum_k G_k \quad . \qquad (10)$$

The function, $g(\omega)$, can be easily solved in two limits. The first, termed the strong scattering case, occurs when $(\omega_o^{k} - \omega_o^{k'})\tau_{kk'} \ll 1$ and yields a homogeneously narrowed line centered at $k = \pm\pi/2a$ at high temperatures and corresponds to the random walk limit.[9] The second, when $(\omega_o^{k} - \omega_o^{k'})\tau_{kk'} \gg 1$, corresponds to the coherent limit in which phonon-exciton scattering causes a change in the exciton states on a time ($\tau_{kk'}$) slow compared to the differences in the Larmor frequencies ($\omega_o{}^k - \omega_o{}^{k'}$). In such cases the individual k states of the triplet band can be sampled by the rf field. Assuming phonon-exciton scattering to be uniform in k, i.e., $\tau_{kk'}$'s are equal for all k and k', the electron spin resonance absorption, $g(\omega)$, is the sum of (2k + 1) independent Lorentz lines each centered at $\omega_o{}^k$ and weighted by the number of excitons occupying the state k with group velocity $V_g(k)$. The width of each Lorentz line has a contribution from both a finite coherence lifetime $\tau(k)$ and the homogeneous line with parameter $T_2(k)$. When a thermal distribution characterizes the triplet band

$$g(\omega) = \frac{\delta}{\pi}\int_0^{\pi/a} \frac{\exp[4\beta(1 - \cos ka)/kT]}{[\omega + \Delta_{ST}^{\xi} \cos ka]^2 + \delta^2}\, dk \qquad (11)$$

Δ_{ST}^{ξ} is related to spin orbit, T is temperature, δ is the half width at half height of an individual k state electron spin transition and is a measure of $\tau(k)$.

Some specific features of equation (11) are that: (a) the Larmor frequencies are directly related to band energy insofar as a prescribed $\omega_o{}^k$ couples the spin sublevels of an exciton whose energy is $\varepsilon(k)$; (b) the intensity of the transition is directly related to the density of states function times a Boltzmann factor. Thus, both the distribution function over the k states and hence the band width are experimentally obtained.[10] (c) The broadening function, δ, gives an estimate of the phonon-exciton scattering, and hence a measure of the coherence length, $\ell(k)$, and insight into the mechanism of phonon-exciton scattering. The dependence of $g(\omega)$ on H_{ep}^{λ} via $(\tau_{kk'})^{-1}$ might, for example, allow linear[2] and quadratic phonon-exciton coupling[3] to be distinguished experimentally. (d) The overall width of the $g(\omega)$ is determined by the spin-orbit coupling parameter, Δ_{ST}^{ξ}, hence the selectivity of spin-orbit coupling to the triplet spin sublevels can be determined. (e) The microwave field selectively perturbs the electron spin of excitons whose group velocity is $V_g(\underline{k})$, and therefore the k dependence of other processes such as the dynamics of trapping,[11] exciton-exciton annihilation,[12] etc., can be potentially studied in the coherent limit.

A second approach to the study of exciton dynamics is <u>based upon a statistical model for the probability of trapping excitons in the coherent and random walk limits[12] and includes a detailed consideration of the energy dispersion of the band, the number of k states comprising the band and the partitioning of energy between the band and trap states when a Boltzmann distribution characterizes the ensemble</u>. Basically, in any "real" crystal, where the energy separation between the impurity (trap) states and the exciton (k = 0) states can be spectroscopically measured, it is expected that the temperature dependent emission from the band states and impurity states would be a sensitive function of the energy dispersion of the band. Furthermore, the ability for exciton migration between trap sites to thermally equilibrate the excitation within the lifetime of the state depends in detail upon the average velocity of exciton migration which in turn is related to the extent of coherence. For a one-dimensional crystal the partition function z for band and trap states can be written as

$$z = 1 + e^{-\Delta/kT} + \sum_{k=\pi/na}^{(n-1)(\pi/an)} 2e^{-[\Delta-2\beta(1-\cos ka)]/kT}$$

The zero of energy is taken at the energy of the trap which is Δ below the k = 0 state of the band. The dispersion is restricted to a nearest neighbor approximation with an intermolecular interaction β along a translation equivalent direction $\vec{a}$. The leading and second terms in the partition function characterize the Boltzmann factor for the trap level and the nondegenerate exciton k = 0 state from which emission occurs. The remaining doubly degenerate terms include the non k = 0 exciton states. This model views the exciton states and trap states in thermal equilibrium where the trap probability is taken to be $P_{trap} = 1/z$, and hence the intensity of trap emission is given by $I_{trap} \propto 1/z$. An important feature necessary for this description to be valid is that the system must reach equilibrium within the lifetimes of the excited states, implying that the average excitation migrates between many trap sites via the exciton states in a time less than the lifetime of the excitation. In the coherent model the average velocity at a temperature T for the exciton is given by

$$\langle V_g \rangle = \frac{2\beta a}{\hbar} \frac{\sum_k \sin(ka) e^{-(2\beta \cos ka)/kT}}{\sum_k e^{-(2\beta \cos ka)/kT}}$$

For a 1 cm^{-1} band at 4.2°K, $\langle V_g \rangle \simeq 2500\ cm^{-1}/sec$ while in the hopping model the median velocity, $\bar{V}_{hop} = \frac{3}{8}\left(\frac{4\beta}{h}\right)^{1/2} a$, is a factor of 10^6 smaller. When the impurity density becomes low $\bar{V}_{hop}$ is too small to allow the sample to come into thermal equilibrium within the lifetime of the states, and the temperature dependent emission "appears" bottlenecked. On the other hand, coherent migration is more than adequate to insure equilibrium. The latter description has been found to give excellent agreement with experiment at low temperatures and agrees well with the results of the spin resonance experiments[10] for two crystals which have been studied and which can be considered models for one dimensional exciton migration. They are 1,2,4,5-tetrachlorobenzene[10] and 1,4-dibromonaphthalene.[13]

The third experimental approach devised to study exciton dynamics is based upon some <u>new optically detected magnetic resonance pulse methods that are capable of studying any state of the spin coherence of mobile and nonmobile triplet states utilizing virtually all of the phosphorescence emission</u>. Specifically, by viewing zero field optically detected magnetic resonance in an interaction representation which removes the zero-field splitting it can be shown that the populations in the individual spin sublevels in the laboratory frame are related to a pseudo-magnetization along z in the rotating frame.[14] Further, when the density matrix in the interaction representation is displayed thru the electric dipole transition moment responsible for phosphorescence usually only ±z components in the interaction representation are experimentally observable via a microwave induced modulation of the phosphorescence intensity.[14]

The net result is that spin echoes,[15] spin echo trains,[16] spin locking,[16] and other coherent electron spin experiments can be detected optically on as few as 10^4 spins by restoring the spin ensemble from the x,y-plane to the ±z axis and observing the resulting change in phosphorescence as it reflects the instantaneous spin coherence in the interaction representation x,y-plane.

The importance of these techniques to the study of exciton migration and other phenomena associated with molecular crystals is that they provide in principle a method of extracting the full correlation function for the dephasing of the electron spin ensemble. Because different phenomena such as coherent vs. incoherent migration, trapping and detrapping, dephase the electron spins with dramatically different correlation times, the contribution of each can be determined from the Fourier spectrum of the electron spin relaxation function. Experiments which have been recently completed such as optically detected spin echoes and echo trains, spin locking and spin polarization transfer in trap and excitation states in the rotating frame will be presented to illustrate these points.

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