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Model for Trapping Rates for Sensitized Fluorescence in Molecular Crystals

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Expressions for trapping (and detrapping) rates, which describe transitions from (and to) the k -states of the host crystal to (and from) the trap states, and which serve as inputs in a theory of sensitized fluorescence in molecular crystals, are derived from the point of view of their k -dependence. They are shown to be consistent with experimental observations.

Ausdrücke für die Anhaft- (und Anregungs)raten, die die Übergänge von (und zu) den k -Zuständen des Wirtskristalls zu (und von) Haftstellen beschreiben und die als Eingangswerte in eine Theorie der sensibilisierten Fluoreszenz in Moleküllkristallen dienen, werden vom Standpunkt ihrer k -Abhängigkeit abgeleitet. Es wird gezeigt, daß sie mit experimentellen Beobachtungen konsistent sind.

1. Introduction

Sensitized fluorescence in molecular crystals has been actively studied for many years [1, 2]. We have recently developed a theoretical formalism [3] for this phenomenon, which is based on a Boltzmann equation in k -space. This is suggested by the translational periodicity of crystals and is in contrast with most theoretical treatments of this and related subjects [2, 4] which use transport equations in real space (for a review see, e.g., [5]). Our formalism is based on the equations

$$\frac{df_k}{dt} + \left(\frac{1}{\tau} + \alpha_k^- \right) f_k = \alpha_k^+ f_\theta + \sum_{k'} (Q_{kk'} f_{k'} - Q_{k'k} f_k), \quad (1)$$

$$\frac{df_\theta}{dt} + \left(\frac{1}{\tau_\theta} + \sum_{k'} \alpha_{k'}^+ \right) f_\theta = \sum_{k'} \alpha_{k'}^- f_{k'} \quad (2)$$

and it describes the excitation dynamics in a doped crystal after pulse excitation. Here f_k is the probability that the state k in the band of the host crystal is excited, f_θ the probability that the trap (the guest molecules) is excited, the τ 's are radiative lifetimes, the Q 's describe scattering in the host band, and the α 's are trapping and detrapping rates associated with specific k -states.

The general program consists of solving (1) and (2) under suitable initial conditions which are usually $f_\theta(0) = 0$, $f_k(0) = \delta_{k,0}$, the latter reflecting the selection rules for light absorption. The quantities $f_\theta(t)$ and $F(t) \equiv \sum_k f_k(t)$ are then to be computed.

Being proportional to the guest and the host emission, respectively, they are experimentally relevant quantities. To carry out this program values of the various parameters in (1) and (2) must be determined. The τ 's are well known and the Q 's may be obtained from investigations [6] of exciton scattering mechanisms. The evaluation of the trapping rates α_k^- and the detrapping rates α_k^+ poses an important problem [2] which we attempt to tackle in this paper in terms of a simple model.

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2. Evaluation of the Rates

The trapping and detrapping rates will be given by the "golden rule" prescription for transition rates and will thus be proportional to the square of the matrix element of the Hamiltonian H between the trap state $|\theta\rangle$ and the host k -state $|k\rangle$ under consideration. With the help of the identity operator involving $|m\rangle$, $|n\rangle$ etc., which are host crystal states localized on sites m , n , etc., we write

$$\langle\theta|H|k\rangle = \langle\theta|H|\theta\rangle\langle\theta|k\rangle + \sum_m \langle\theta|H|m\rangle\langle m|k\rangle. \quad (3)$$

Either by assuming the trap state to be orthogonal to the k -states or by taking the energy of the trap state to be zero, the first term on the right-hand side of (3) is made zero. The definition $\langle\theta|H|m\rangle \equiv V_m$ then yields from (3)

$$\lambda_k = \text{const} \left| \sum_{m,n} V_m V_n^* e^{-ik(m-n)} \right| \quad (4)$$

for the trapping or detrapping rates. The constant includes the density of states and other proportionality factors and differs by the Boltzmann factor $\exp(-\omega/k_B T)$ in the trapping case from the detrapping case. Here ω , k_B , and T are the energy difference between the k -state and the trap state, the Boltzmann constant, and the temperature, respectively. We emphasize that the relevant density of states to be included in the constant in (4) is not the one obtained from the k -derivative of the band energy and other band parameters. We are here interested in transition rates from (and to) *individual* k -states and not those from (and to) the entire band. The density of states in the band is therefore of no concern in the rate expressions. The density of states of relevance here refers to the states of a bath such as phonons which must assist in the transition. This should be particularly clear in the light of energy conservation required by the "golden rule". Obviously the trap state is lower in energy than the band state and requires energy compensation by the bath. The actual states that should enter the "golden rule" are thus the outer products of $|k\rangle$ and $|\theta\rangle$ with the bath states. It is also the density of states of the latter that accounts for the Boltzmann factors relating the trapping rates to the detrapping rates.

3. Expressions in a Simple Model

Consider now the guest molecule to be placed substitutionally at, or at least interstitially close to, one of the host sites, and assume the matrix element $\langle\theta|H|m\rangle$ connecting the trap to the host molecules to be so short-ranged that the nearest-neighbour approximation is valid. For the sake of simplicity the matrix elements will be assumed to be real and expressions valid for one dimension will be written down; their generalization to two or three dimensions is straightforward. Denoting by V_0 , V_1 , and V_{-1} the matrix elements connecting the trap to the nearest host site and the two sites on both its sides, (4) is seen to give

$$\lambda_k = \text{const} [(V_0^2 + V_1^2 + V_{-1}^2) + 2V_0(V_1 + V_{-1}) \cos k + 2V_1 V_{-1} \cos 2k]. \quad (5)$$

If the guest molecule is placed substitutionally or generally in such a way that $V_1 = V_{-1}$,

$$\lambda_k = \text{const} (V_0 + 2V_1 \cos k)^2. \quad (6)$$

Several conclusions follow. If the trap communicates with only one host site, (5) or (6), or more generally (4), shows that the trapping rate is constant over the band. In the general case the rate always has its maximum value at the $k = 0$ edge of the band. The value at the other edge ($k = \pm\pi$) depends on the relative values of V_0 and $2V_1$ (in the context of (6)). Thus if $V_0 \geq 2V_1$, the rate has its minimum value at $k = \pm\pi$. But the value is larger than the minimum if $2V_1 > V_0$. In fact for the case $V_0 = 0$

signifying communication of the trap with only the two side sites, the $k = \pm\pi$ value of the rate is a maximum and equals the $k = 0$ value. The matrix elements V_m basically describe *transfer* interactions between the trap and the host sites. Therefore, they will drop off with an increase in the distance from the trap and it appears likely that $\Gamma_0 \cong 2\Gamma_1$ will be often satisfied. Fig. 1 shows the variation over the band of the trapping or the detrapping rate for this case.

4. Discussion

Powell and Soos [2] have emphasized that one of the least understood areas in sensitized fluorescence concerns the specification of the trapping and detrapping phenomena. This note attempts to make a contribution in this direction. Our model and arguments are trivially simple and the expressions we have derived do not connect the rates to the microscopic parameters of the bath (such as phonons) which assist the trapping and detrapping phenomena. This is in contrast to the analysis given by Fayer and Harris [7] which does specify such a connection. On the other hand, our rates are more "fine-grained" than the ones in [7] in that they describe transitions between individual k -states and the trap. The rates in [7] concern transitions from and to the entire host band.

The primary aim of the present analysis is to arrive at the k -dependence of the rates. This is given generally in (4), for particular cases in (5) and (6), and is plotted in Fig. 1. We point out that the basic feature of this k -dependence, the maximum at $k = 0$, is borne out by available experimental observations [1, 2]. It is possible to derive [3] from (1) and (2) the following expression for the energy transfer rate [1, 2] $k(t)$, a well-known quantity in sensitized fluorescence, which describes transfer of excitation from the host to the trap:

$$k(t) = \frac{\Gamma\alpha e^{-t\alpha} + (\alpha_0^- - \alpha)(\alpha_0^- + \Gamma) e^{-t(\alpha_0^- + \Gamma)}}{\Gamma e^{-t\alpha} + (\alpha_0^- - \alpha) e^{-t(\alpha_0^- + \Gamma)}} \quad (7)$$

Here $(1/\Gamma)$ is a relaxation time describing scattering in the host band, α_0^- the trapping rate α_k^- at $k = 0$, and α an average of the trapping rates over the band. This expression has the qualitative features [1, 2] of the experimentally observed quantity. In particular it is easily verified from (7) that $k(t)$ begins with the value α_0^- at $t = 0$, decreases in time, and ends up as α at long times. Unless the trapping rates have a maximum at $k = 0$ this cannot happen. If the maximum were to lie elsewhere in the band, (7) or even straightforward physical considerations would show that $k(t)$, which must always begin with the value α_0^- because of the selection rules in light absorption, would tend to *increase* beyond its initial value. Group velocities in the band have been recently employed in the analysis of exciton transport. One might be tempted to take them to be proportional to the trapping rates on the basis of the

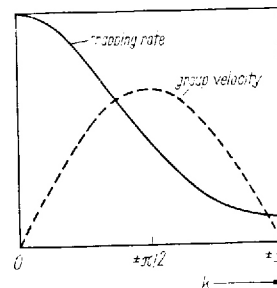


Fig. 1. The k -dependence of the trapping or detrapping rates showing the maximum at $k = 0$ which is excited as a result of light absorption. The dashed line shows the variation of the group velocity for a tight-binding band for comparison

argument that the higher the group velocity is, the faster would the exciton reach the trap from a fixed distance away from the trap. Such an analysis would not be valid. It is also in clear contradiction with experiment. For group velocities (see Fig. 1) with their maximum in the middle of the band and α_k^- proportional to them, the energy transfer rate would not be maximum at $t = 0$.

An analysis similar to the one in [7] but relevant to individual k -states which establishes the connection of the trapping and detrapping rates to microscopic phonon quantities, such as their occupation numbers, will be given elsewhere. Microscopic expressions for the rates may also be written down by a straightforward combination of the present analysis with that in [7] if one assumes their mechanism. These expressions are identical to those in [7] except for the introduction of the k -dependent factor in (4) above and the omission of the factor denoting the exciton density of states.

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