is that on-surface damage to the bound group as opposed to sputtering of intact species. ESD spectra are observed to be sensitive to the chemical nature of the substrate (whereas SIMS fragmentation patterns appear to be relatively insensitive to the substrate material). TMS modified SiO₂ exhibits a trimethylsilyl parent ion signal as well as methyl-deficient fragment ions under 1.0-eV electron bombardment. The modified TiO₂ surface, however, appears to be more stable toward electron bombardment, yielding no detectable parent ion and exhibiting a disappearance cross section for intact surface groups 3.7 times smaller than that for modified SiO₂. We have suggested a mechanism operative in the TiO₂ system which involves quenching of the initial adsorbate excited state (by an electron originating within the TiO₂ valence band) before desorption of an intact group or extensive fragmentation can occur. The large bandgap of SiO₂ would tend to inhibit this process and so may explain the comparatively rapid decrease in surface concentration of trimethylsiloxy groups on SiO₂. A thorough analysis of this problem, however, requires variable primary energy ESD studies, including the low-energy (10-100 eV) region.

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Dynamics of Anisotropic Exciton Hopping in Molecular Crystals

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We investigate excitonic energy transfer in molecular crystals including the effect of anisotropic interactions and we apply our approach to the first singlet excited state of naphthalene. This is done through a random-walk formalism similar to our previous work, but incorporating here the weaker out-of-plane interactions explicitly. The problem is also treated via numerical simulations, which turn out to be consistent with the analytical formalism. Comparing the results with the experimental time decay curves, we find good agreement. The derived stepping time is of the order of 1 ps.

I. Introduction

The problem of the spatial extent of intermolecular interactions is very important in understanding the dynamics of energy or charge transfer in molecular solids. It has been long realized that for energy-transfer purposes real crystals sometimes behave two-dimensionally, or even one-dimensionally. As examples, tetrachlorobenzene and dibromonaphthalene are assumed to be one-dimensional, while naphthalene behaves rather two-dimensionally, even though these designations are not to be taken strictly. We notice here that integral dimensions have model character only, since cases in between can also happen, so that in the actual situation the effective dimensionality may be a fractional number.

In a series of papers Argyrakis and Kopelman have been able to explain experimental optical spectra of the isotopically mixed naphthalene system using properties of random walks and a kinetic formalism. In the calculations of ref 4-6, for simplicity, a strictly two-dimensional lattice was assumed. The most important result from these studies was that low-temperature spectra could be explained in terms of symmetric jumping rates (no activated behavior) only if a coherency was invoked (a mean free path of excitonic motion much longer than the lattice constant). Incoherent motion calculations (only the mean free path is of the order of the lattice constant) were in strong disagreement with experiment. In this paper we present our results on the same system, but now taking into account the anisotropic interactions in the three-dimensional lattice. It is well-known that for naphthalene the out-of-plane singlet exciton interactions are about 1 order of magnitude smaller than the in-plane ones. We develop here a formalism that takes into account such anisotropic interactions and we apply it to the naphthalene system. The formalism is based on the distribution of distinct sites visited by a random walker in a given number of steps and gives exact and approximate expressions for the decay law due to trapping. We point out

the equivalence between this approach and the kinetic formalism of ref 3–6 and test our procedure through Monte Carlo simulations for its validity. We show that our results agree with the experimental spectra of crystals that are slightly doped with impurities. The present formalism does not necessarily contradict earlier analyses for heavily doped crystals. Section II describes the model and the analytical formalism, while section III contains the simulation methods, the comparison with experiments, and the discussion.

II. The Model

In many recent works random walks were applied successfully to the description of energy-transfer processes in lattices containing several molecular species. In this work we consider a binary lattice, composed of two molecular species: active molecules and traps. The traps are taken to occupy the lattice sites substitutionally with probability \( p \). An energy-transfer event starts by having an active molecule excited; the excitation is exchanged resonantly between the active sites until a trap molecule is reached. An exact decay law is obtained, if trapping occurs at first encounter of a trap and if the interactions between active molecules and traps are identical with those between the active molecules themselves: the expression for the decay law \( \Phi_0 \) of the excitation due to trapping involves the cumulants of the distribution of the number \( R_n \) of distinct sites visited in \( n \) steps. Approximate forms to \( \Phi_0 \) follow, by restricting the expression for \( \Phi_0 \) to the first few cumulants. To wit, for small concentrations of traps, \( p \ll 1 \) one has

\[
\Phi_0 \approx \exp[-\sigma n]
\]

as a good approximation in three dimensions, or even better

\[
\Phi_0 \approx \exp[-\sigma p n^{3/2}]
\]

In eq 1 and 2 \( S_n \) is the mean number of sites visited and \( \sigma \) is the mean number of sites visited and \( \sigma_n \) is the variance. In this work we center on the approximate form, eq 1. To stress its dependence on \( n \) we consider the efficiency \( \epsilon \) defined as \( \epsilon = S_n/n \), so that

\[
\Phi_0 \approx \exp[-\sigma \epsilon n]
\]

Such a form is very convenient in three dimensions, where \( S_n \) has the following asymptotic expansion

\[
S_n = a_n + a_n n^{1/2} + a_3 n^{-1/2} + O(n^{-1/2})
\]

so that \( \epsilon_n = a_1 + a_2 n^{-1/2} + \ldots \). Thus, \( \epsilon_n \) tends for larger \( n \) to a constant value, \( \epsilon \approx a_1 \), which is independent of \( n \). For a regular nearest-neighbor random walk on a simple cubic lattice one has \( \epsilon = 0.659 \), vide infra. Taking a fixed stepping frequency \( \tau^{-1} \), the time-dependent decay \( \Phi(t) \) is then

\[
\Phi(t) \approx \exp[-\epsilon \tau t]
\]

with \( n = \tau t/\tau \). From the last expression a constant trapping rate for longer times follows:

\[
k(t) = -\Phi(t)/\Phi(t) \approx \epsilon \tau \implies k(t)
\]

In the region where the dependence of \( S_n \) (or \( \epsilon_n \)) on \( n \) is relevant [short times in three dimensions, or the two-dimensional case, for which \( S_n = an/(cn)^{1/2} \) the right-hand side of eq 6 has to be changed to

\[
k(t) = -\Phi(t)/\Phi(t) \approx \frac{dS(t)}{dt} = \frac{p}{\tau}[\epsilon(t) + \frac{dS(t)}{dt}]
\]

In eq 7 we used the expression \( S(t) \approx (\tau/\tau)\epsilon(t) \).

Up to now, our considerations hold for trapping at the first encounter. In general, the probability \( \gamma \) of getting trapped at the encounter of a trapping site may be less than unity. Such a case can be handled approximately by changing eq 6 to

\[
k(t) \approx \gamma \epsilon \tau
\]

(valid for three dimensions and longer times), and eq 7 to

\[
k(t) \approx \gamma (\epsilon \tau)[\epsilon(t) + \tau(d\epsilon(t)/dt)]
\]

In the more general case. An alternate derivation of eq 9 was given in ref 6 and 12. Evidently, for \( \gamma \ll 1 \), the trapping becomes less and less sensitive to the peculiarities of the random walk, so that the decay rate turns out to be simply \( k \approx \gamma \epsilon \tau \). However, as long as \( \epsilon \) is comparable to unity (as is the case in the following), and \( \gamma \) is not very small, eq 8 and 9 are certainly very reasonable approximations.

To make the connection to the experimental quantities, one has only to remark that, additional to the trapping channel, also radiative and nonradiative processes occur. Setting \( k_n \) for the decay rate of the isolated excited molecule, one has for the density \( N(t) \) of moving excitations

\[
dN(t)/dr = -[k_0 + k(i)]N(t)
\]

Equation 10 has the following solution:

\[
N(t) = N_0 e^{k_0 t} \exp[-\int_0^t k(i) dr']
\]

where we used \( k(i) \) of eq 9.

In section III we will use eq 11 for a fit to experimental data. Note that in eq 11 \( k_0, p \), and \( \gamma \) are material parameters and that, due to our approximations, the random walk enters solely through \( S(t) \). We continue here with a discussion of this quantity.

For a fixed stepping frequency \( \tau^{-1} \), as assumed previously, one can identify to a very good approximation \( S(t) \) and \( S_n \) by setting \( n = \lceil \tau t \rceil \); here \( \lceil x \rceil \) denotes the largest integer smaller than \( x \). Examples are given in ref 13, where also the connection to the exact procedure of the continuous-time random walk is made. We have thus only to consider \( S_n \).

As shown in a series of publications by Montroll and Weiss[4,15] for random walks on regular lattices, \( S_n \) is obtained readily from its generating function \( S(z) = \sum_{n=0}^{\infty} S_n z^n \), where \( S(z) \) is connected to the generating function \( P(z) \) of the walk

\[
P(z) = \frac{1}{(2\pi)^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{dk}{1 - z \lambda(k)}
\]

Here we applied this to the three-dimensional cubic case and denoted by \( k \) the vector \( (k_1, k_2, k_3) \). We have for anisotropic steps \( \lambda(k) = \lambda_1 \cos k_1 + \lambda_2 \cos k_2 + \lambda_3 \cos k_3 \), where a step in the direction \( x, y, \) or \( z \) occurs with probability \( \lambda_1, \lambda_2, \) or \( \lambda_3 \), respectively. Again following Montroll,[16] we remark that \( P(1) \)

\[
\begin{array}{cccc}
\lambda_1 & \lambda_2 & \lambda_3 & \gamma \\
0.3333 & 0.3333 & 1.00 & 0.65946 \\
0.4548 & 0.1304 & 0.3 & 0.60858 \\
0.4762 & 0.0476 & 0.1 & 0.52698 \\
0.4926 & 0.0148 & 0.03 & 0.44628 \\
0.4975 & 0.0050 & 0.01 & 0.38804 \\
0.4993 & 0.0015 & 0.003 & 0.33841 \\
0.4998 & 0.0005 & 0.001 & 0.30276 \\
\end{array}
\]

\[\text{Table I: Mean Number of Distinct Sites } S_n \text{ Visited in } n \text{ Steps}^a\]

\[\begin{array}{cccc}
\lambda_1 & \lambda_2 & \lambda_3 & \gamma \\
0.3333 & 0.3333 & 1.00 & 0.65946 \\
0.4548 & 0.1304 & 0.3 & 0.60858 \\
0.4762 & 0.0476 & 0.1 & 0.52698 \\
0.4926 & 0.0148 & 0.03 & 0.44628 \\
0.4975 & 0.0050 & 0.01 & 0.38804 \\
0.4993 & 0.0015 & 0.003 & 0.33841 \\
0.4998 & 0.0005 & 0.001 & 0.30276 \\
\end{array}\]

\[\text{a The steps occur to nearest neighbors on the simple cubic lattice with probabilities } \lambda_1, \lambda_2, \text{ and } \lambda_3 \text{ for the } x, y, \text{ and } z \text{ directions. Here } S_n = a_n + a_n n^{1/2}, \text{ eq 4; the efficiency is } \gamma = a_1 + a_2 n^{1/2}.\]

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TABLE II: Mean Number of Distinct Sites Visited, \( S_n \), Obtained from Numerical Simulation\(^a\)

<table>
<thead>
<tr>
<th>( \lambda_3/\lambda_1 )</th>
<th>( a_1 )</th>
<th>( a_2 )</th>
<th>( a_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.660</td>
<td>0.55</td>
<td>0.89</td>
</tr>
<tr>
<td>0.1</td>
<td>0.527</td>
<td>0.74</td>
<td>0.88</td>
</tr>
<tr>
<td>0.01</td>
<td>0.385</td>
<td>1.25</td>
<td>0.89</td>
</tr>
<tr>
<td>0.001</td>
<td>0.300</td>
<td>2.31</td>
<td>0.23</td>
</tr>
</tbody>
</table>

\(^a\) \( S_n = a_1 n + a_2 n^{1/2} + a_3 \); the efficiency is \( \epsilon_n = a_1 + a_2 n^{1/2} + a_3 / n \).

Figure 1. Plot of the efficiency \( \epsilon_n \) as a function of the number of steps \( n \). Curves A refer to the isotropic simple cubic lattice (\( \lambda_3 = \lambda_1 \), i.e., six equal interactions), while curves B refer to an anisotropic lattice (\( \lambda_3/\lambda_1 = 0.1 \), i.e., four equal in-plane interactions and two out-of-plane equal to 1/10 of the in-plane ones). The smooth curves are analytical, \( \epsilon_n \), while curves B refer to an anisotropic lattice (and also \( \lambda_3 = \lambda_1 \)).

The results for \( a_1 \) and \( a_2 \) in eq 4 (and also \( \epsilon \)) is known exactly, in closed form. In order to obtain also \( a_2 \) in eq 4 we have inverted the series \( P(z) = \sum P_{\lambda} a_{\lambda} \). The results for \( a_1 \) and \( a_2 \) for \( \lambda_3/\lambda_1 \) between 1 (isotropic case) and 10\(^{-3} \) are given in Table I. Remarkably, even for the very anisotropic case \( \lambda_3/\lambda_1 = 10^{-3} \), the \( S_n \) are well described by eq 4. Thus, the system behaves three-dimensionally\(^1\) and does not yet show the two-dimensional behavior \( S_n = an/ln \) (eqn)\(^9\). We should mention that also in the study of one-dimensional crystals use has been made of eq 12 and expressions akin to it\(^1\)\(^-\)\(^3\).

From Table I, one can obtain \( S(t) \) directly by use of eq 4 and replacing \( n \) by \( r/t \). We remark that the \( \lambda_3/\lambda_1 \) range exhibited covers our experimental condition \( \lambda_3/\lambda_1 \approx 0.1 \). The approximate analytical decay law \( N(t) \) follows then from our eq 11.

Figure 2. Experimental and calculated decay curves. The experimental line is the radiation intensity at 4.2 K from a crystal of 0.95 mole fraction of C\(_{10}\)D\(_8\), 0.05 mole fraction of C\(_{10}\)D\(_4\), and 3.3 \( \times \) 10\(^{-3} \) mole fraction of BMN (\( \delta \)-methyl-naphthalene), excited at 31 000 cm\(^{-1} \). The smooth curve is the fitted result from eq 11.

The numerical methods described in ref 6. The results are given in Figure 1 for the efficiency \( \epsilon_n \). The simulations were carried out for 200 000 steps and involved 100 walks each. Presented are the isotropic random walk \( \lambda_3/\lambda_1 = 1 \), as well as the \( \lambda_3/\lambda_1 = 0.1 \) case. The curves lie near the exact asymptotic values of 0.66 and 0.53 but they decay slightly more rapidly than the analytical expressions also indicated in Figure 1. The reason for this discrepancy may be due to the procedure of ref 6, which uses a lattice of size 153 \( \times \) 153 \( \times \) 153 (3.6 \( \times \) 10\(^6 \) sites) and cyclical boundary conditions. Thus, sites related by cyclical symmetry are not distinguished and for very long walks some undercounting follows.

In the previous section we have determined the dependence of the excitation decay on the anisotropy. In the model considered the random walk takes place on a simple cubic lattice. In more general cases (many-component systems, long-range steps) exact forms for \( P(z) \) and \( S(z) \) are not available, so that in order to derive the decay law one has to perform simulation calculations. Here we present (as additional support of the data and as a check for

the numerical methods) such simulation results.

Following the procedures of refs 8-10 we have generated (for several \( \lambda_3/\lambda_1 \) values) 1000 different walks of 5000 steps each. Our findings for \( S_n \) are summarized in Table II and are given in the form \( S_n = a_1 n + a_2 n^{1/2} + a_3 \). The values for \( a_1 \), \( a_2 \), and \( a_3 \) were obtained as a least-squares fit to the data. Comparison to the exact expressions of Table I shows that \( a_1 \) is obtained correctly well within 1%, whereas the uncertainty on \( a_2 \) is about 10% and the values are better for isotropic walks.

To show some very long walks we have used the Monte Carlo methods described in ref 6. The results are given in Figure 1 for the efficiency \( \epsilon_n \). The simulations were carried out for 200 000 steps and involved 100 walks each. Presented are the isotropic random walk \( \lambda_3/\lambda_1 = 1 \), as well as the \( \lambda_3/\lambda_1 = 0.1 \) case. The curves lie near the exact asymptotic values of 0.66 and 0.53 but they decay slightly more rapidly than the analytical expressions also indicated in Figure 1. The reason for this discrepancy may be due to the procedure of ref 6, which uses a lattice of size 153 \( \times \) 153 \( \times \) 153 (3.6 \( \times \) 10\(^6 \) sites) and cyclical boundary conditions. Thus, sites related by cyclical symmetry are not distinguished and for very long walks some undercounting follows.

The experimental setup has been reported elsewhere,\(^4\) and therefore the detailed discussion on the apparatus and techniques will not be given here. Briefly, we have measured the time-dependent fluorescence of crystals immersed in liquid helium \((T = 4.2 \text{ K})\) and illuminated with a nitrogen-pumped dye laser at a wavelength of 325 nm. The excitation pulse of Gaussian shape with a full width at half-height of 5 ns was repeated with a frequency of 10 Hz. The emitted signal was averaged by a boxcar integrator and processed in digital form on a computer. In Figure 2 we show the experimental time decay curve for a crystal containing 0.95 mole fraction of C\(_{10}\)D\(_8\) 0.05 mole fraction of C\(_{10}\)D\(_4\), and 3.3 \( \times \) 10\(^{-3} \) mole fraction of BMN (\( \delta \)-methyl-naphthalene). Since C\(_{10}\)D\(_8\) is the exciton carrier and BMN the exciton trap, we chose a crystal that has high carrier and low trap concentrations, so as to ensure almost uninhibited mobility.

In Figure 2 we also plot the predictions from the decay law, eq 11. Notice that in order to make a comparison we have to convolute the calculated solution with the excitation source, i.e., the laser signal. When this is done, we see that the analytical expression is in reasonable agreement with the experimental result. This means that including three-dimensional anisotropic interactions (which lead to quasi-exponential time behavior, i.e., to mainly one adjustable parameter) one can adequately explain the
observations. From the fit we get an overall decay rate of about 50 ns, in agreement with similar results on neat naphthalene crystals (doped with $10^{-5}$ M BMN) by Braun et al.\(^{(20)}\) Since $a_1 \approx 0.5$ and $\gamma$ is of the order unity,\(^{(21)}\) the same holds for the product $a_1 \gamma$; thus, the hopping time in the plane turns out to be of the order of 1 ps.

The crystal examined was doped with minute amounts of impurities and we paid special attention to the characteristics of the excitation decay. The theoretical extension to ternary crystals, and thus a study of the total concentration range of the ratio $\frac{C_{10H_8}}{C_{10D_8}}$, calls for additional methods (analytical and simulation procedures) beyond the scope of the present paper (see also ref 6 for interesting results). We also cannot exclude the presence of coherence (such as direct trap excitation from the bottom of the $k = 0$ band\(^{(22)}\)), which was inferred by evidence from measurements of heavily mixed crystals; from the present work we find, however, that an anisotropic three-dimensional random-walk model offers a good explanation of the observed decay behavior of lightly doped crystals without invoking coherence.

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Registry No. Naphthalene, 91-20-3.

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Picosecond Laser Spectroscopy of Dual Excited Electronic States of 4-(9-Anthryl)-N,N-dimethylaniline

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Quantitative measurements of $S_2 \leftrightarrow S_1$ absorption spectra of 4-(9-anthryl)-N,N-dimethylaniline (ADMA) in various solvents have been carried out by means of picosecond laser spectroscopy at room temperature. The results have been approximately explained by assuming the existence of closely lying dual excited states with different electronic structure, and the equilibrium constant between them has been obtained as a function of solvent polarity. Dipole moments of these two states have been estimated to be 12.5 and 20.5 D, respectively. In low-viscosity polar solvents, the equilibrium between the two states is attained immediately after picosecond pulsed ($\sim 30$ ps) excitation. In 2-propanol solution, however, both a rapid process and a much slower process of the interconversion between the two states have been observed, the mechanisms of which have been examined. Importance of the wide-band picosecond time-resolved absorption spectroscopy for investigating the change of electronic structure in the excited state, of which the studies by means of time-resolved fluorescence spectroscopy is rather difficult, has been demonstrated clearly.

Introduction

The dual fluorescence phenomena observed for compounds with electron donor and acceptor groups separated by a single bond have been a subject of lively investigations by means of stationary as well as time-resolved measurements. Especially intensive investigations including picosecond time-resolved fluorescence measurements have been made for $p$-(dimethylamino)benzimidazole (DMABN),\(^{(1,2)}\), while 4-(9-anthryl)-N,N-dimethylaniline (ADMA) is also a typical compound showing a similar phenomenon and has been investigated to elucidate the relevant mechanisms.\(^{(3-8)}\)

The dual fluorescence spectra of DMABN are considered to be emitted from a strongly polar and a less polar excited state respectively, the former state emitting at a longer wavelength be emitted from a strongly polar and a less polar excited state. According to Grabowski et al., the $\pi$-systems of donor and acceptor groups are perpendicular to each other in the excited state with higher polarity.\(^{(8)}\) On the other hand, an alternative model based on the electrooptical emission and absorption measurements on ADMA has been proposed by Baumann et al.\(^{(7)}\) According to their results, the spectra of ADMA can be understood in terms of a solvent-induced polarizability effect without assuming any conformational change in the excited state even in polar solvents.

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