LETTERS

Energy Trapping and Funnels in Mixed Naphthalene Crystals

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From singlet energy transport studies in several mixed molecular crystals, at liquid helium temperatures, we deduce relative trapping efficiencies for several β-methylnaphthalenes and anthracene in naphthalene, and compare these to the efficiency of naphthalene in perdeuterionaphthalene ($C_{10}H_8/C_{10}D_8$). We find that all these species are more efficient than naphthalene, but only by a factor of 2–8, with small energy funnels (order of 4 molecules) being generated around these trap molecules. We also discuss the possible contributions to trapping from phonon (and localized phonon) effects.

Introduction

Over the past few years several groups in molecular crystals have used many chemically and isotopically mixed systems for studying the energy dynamics, i.e., transport, trapping, exciton interactions, etc. in both singlet and triplet states at low temperatures. In particular, trapping is a very useful experimental tool and it has been used extensively as an excitation sensor.[1-6] This is achieved by including in the system one species in minute concentrations that has an excited state energy level lower than all other components, thus acting as an ultimate trap or energy sink (and appropriately labeled *supertrap*). One can then probe the transport properties by monitoring the supertrap emission, its time evolution, etc. In this work we focus on the trapping stage.

In a hopping model, it has often been assumed that in order to achieve trapping it is necessary to have an excited donor molecule adjacent to a trap site. Then, a transfer to the trap site would result in trapping with a probability of 1.0. Similarly, a hop that takes place between two sites *next* to a trap but not *onto* the trap has a trapping probability of 0. One realizes that these two are only extreme cases, and the actual truth is somewhere in the middle. There is also enough evidence from various experiments to suggest that this trapping efficiency depends strongly upon the nature of the system and the nature of the trap, and that not all supertraps have the same efficiency. For example, it is claimed[2] that anthracene has a considerably

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greater trapping efficiency than 1 (at low temperatures), while for naphthalene it is of the order of 1. It is also well-known that such supertraps may have different efficiencies at room temperature.[1] We note that all our results are limited to liquid helium temperatures.

We have investigated experimentally the isotopic mixed naphthalene system ($C_{10}H_8/C_{10}D_8$) doped with the following traps: β-methylnaphthalene (BMN), deuterated BMN (d-BMN), partially deuterated BMN ($C_{11}D_9H$), and anthracene. Since each crystal has at least two of the three impurities present, we estimate the ratios of their trapping efficiencies, noting that the existing models and experimental data are not adequate to estimate absolute values for these efficiencies.

Experimental Section

We have prepared over the course of several studies many mixed naphthalene ($C_{10}H_8/C_{10}D_8$) crystals covering a wide concentration range, using zone-refined $C_{10}H_8$ from Materials Limited (99.999% pure) and $C_{10}D_8$ (99 atom % D) from Merck Sharp and Dohme. The BMN was either naturally abundant in it (d-BMN, $C_{11}D_9H$) or added in the crystal (BMN) in very small amounts, for the $C_{10}D_8/C_{10}H_8/$BMN systems. For the $C_{10}H_8/$anthracene/BMN crystals, anthracene was added by directly weighing the amounts while BMN was naturally abundant in the naphthalene material. The excitation light was a high-pressure Xe lamp appropriately filtered, and all spectra were taken at liquid helium temperatures. The details of the experimental setup and apparatus can be found elsewhere.[7]

Results

We recorded the steady-state absorption and fluorescence originating from all species in each system (if measurable) at liquid helium temperature. The absorption spectra were also used to calculate analytically the dopant concentrations for each sample. The relative absorbances, integrated over the bands, provide the ratio of concentrations, while the integrated emissions provide a measure of efficiency for the relative trapping of excitonic energy. The emission observed at a particular energy is proportional to the trapping efficiency of the species (γ), the absolute concentration of it (C), the radiative quantum yield (Q), and the Franck–Condon factors (F) for the bands utilized for its monitoring. Therefore, the emission ratio (E/E') for two isotopic BMN species should be

$$E/E' = (\gamma/\gamma')(C/C')(Q/Q')(F/F') \qquad (1)$$

We assume that the ratio $C/C' = A/A'$, where A is the absorbance, and that the F and F' factors and the molar absorptions are the same for all isotopic BMN. This also gives equal *radiative* lifetimes, resulting in $Q/Q' = \tau/\tau'$. Then eq 1 becomes

$$E/E' = (\gamma/\gamma')(A/A')(\tau/\tau') \qquad (2)$$

From eq 2 the ratio emission/absorbance is

$$(E/E')/(A/A') = (\gamma/\gamma')(\tau/\tau') \qquad (3)$$

This particular equation is correct also for two nonisotopic traps, due to practical cancellations of F/F' and of molar absorptivities with radiative lifetimes. (The only corrections are due to frequency and index of refraction changes, which are minor.) We have experimentally determined that the lifetime ratio is very close to one.[3] Therefore, we are left only with the trapping efficiency ratio. Table I summarizes the results for four crystals, 0.99, 0.95, 0.60 and

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TABLE I: Absorbance and Emission Ratios for BMN and d-BMN

C_N	A/A'	E/E'	ratio (eq 3)
0.99	2.9	8.2	2.8
0.95	2.0	5.8	2.9
0.60	1.4	2.9	2.1
0.30	0.5	0.6	1.2

TABLE II: Absorbance and Emission Ratios for d-BMN and $C_{11}D_9H$

C_N	A/A'	E/E'	ratio (eq 3)
0.92	1.7	2.1	1.2
0.89	1.9	1.8	0.95
0.84	1.8	2.6	1.4
0.77	2.0	2.9	1.5
0.64	2.3	3.4	1.5
0.57	1.9	2.6	1.4
0.46	2.7	2.7	1.0
0.38	2.0	3.9	2.0
0.28	2.3	4.5	2.0

0.30 mole fraction $C_{10}H_8$, for the BMN and d-BMN, while Table II contains the data for d-BMN and the partially deuterated BMN species, $C_{11}D_9H$, for several crystals.

From these tables one can deduce that, within a factor of 2 or 3, all trapping efficiencies are the same. From Table I it appears that BMN is consistently a factor of about 2 more efficient than d-BMN, while from Table II it appears that d-BMN may be slightly more efficient than $HC_{11}D_9$. Unfortunately, this does not set any trend between the three different species, and we thus conclude that within experimental uncertainty there are no order-of-magnitude changes in trapping efficiency among the three mentioned species. This indicates that the exciton–phonon coupling factors are not sensitive to exact energy matchings (i.e., based on vibrational frequencies) but are most probably a result of multiphonon factors, which are fairly smooth at the energies of 300–400 cm^{-1}, which are the naphthalene–BMN mismatch energies.

We also compared the naphthalene and BMN (protonated and deuterated) efficiencies when the two are in a $C_{10}D_8$ host crystal, i.e., compared the efficiencies of the following transfers: $C_{10}D_8 \rightarrow C_{10}H_8$ and $C_{10}D_8 \rightarrow$ BMN. We have experimentally established the following quantities:

$$E_{\text{d-BMN}}/E_N = 0.88 \qquad (4)$$

$$A_{\text{d-BMN}}/A_N = 0.73 \qquad (5)$$

$$\tau_{\text{d-BMN}}/\tau_N = 0.30 \qquad (6)$$

$$\tau_{\text{BMN}}/\tau_N = 0.33 \qquad (7)$$

Therefore, from eq 1 $(E_{\text{d-BMN}}/E_N)/(A_{\text{d-BMN}}/A_N) = 0.88/0.73 = 0.30\gamma_{\text{d-BMN}}/\gamma_N$, and thus $\gamma_{\text{d-BMN}}/\gamma_N = 4.0$.

Using the ratio $\gamma_{\text{d-BMN}}/\gamma_{\text{BMN}} = 2.2$ from the previous calculations (average from Table I), we now have $\gamma_{\text{BMN}}/\gamma_N = 1.8$, thus establishing that BMN is about twice as efficient than $C_{10}H_8$ in trapping $C_{10}D_8$ excitonic energy.

We finally turn to the naphthalene–anthracene–BMN system. Table III summarizes results for several crystals at different concentrations and temperatures. Here we compare the eq 3 ratios of BMN and anthracene, which vary from about 0.5 to 2.5 (1.8 K), and from 0.7 to 2.6 (4.2 K), for several different concentrations. We attribute the scatter, in part, to polarization effects, having used a variety of crystal orientations. We do not believe that these polarization effects go outside this scatter (factor of 2 from mean). We also notice that the phonon sidebands cause

TABLE III: Absorbance and Emission Ratios for Anthracene/BMN in Naphthalene

C_N	$10^3 C_A$	A_{BMN}/A_A	E_{BMN}/E_A		$(E_{BMN}/E_A)/(A_{BMN}/A_A)$	
			4.2 K	1.8 K	4.2 K	1.8 K
1.00	3.51	1.0	0.72	0.70	0.72	0.70
1.00	1.57	1.39	1.77	1.89	1.27	1.36
1.00	2.26	1.60	4.2	4.1	2.63	2.56
0.96	1.26	2.0	2.91	4.02	1.46	2.01
0.88	1.21	1.3	1.44	1.7	1.11	1.31
0.71	2.49	0.705	1.50	0.82	2.13	1.16
0.61	1.46	0.89	1.52	0.72	1.7	0.8
0.51	3.86	1.2	1.0	0.6	0.83	0.5
0.31	1.48	0.55	0.403	0.396	0.73	0.72

a significant "depolarization" of the "oriented gas" transitions.[8]

Discussion

Relative trapping efficiencies may be related to at least three distinct factors: (1) electronic effects on the transfer integral (J); (2) phonon (including vibron) effects [$\rho(\omega)$] related to energy mismatches[4] and relaxation; (3) perturbation of the donor molecules by the acceptor, resulting in energy shifts (D) and effective energy funnels (or energy ridges) in the immediate environment of the acceptor.

The results of Table I indicate that there is an isotopic effect, albeit it is barely outside the experimental scatter. We do not expect that a deep and large energy funnel would show an isotope effect (the van der Waals perturbations should be essentially isotope independent). We note that independent work[8] has indicated that the energy funnel around BMN in naphthalene contains only 0-4 molecules. This is consistent with our present results. Barring J and $\rho(\omega)$ effects (see above) we expect the funnel (D) effect to be given roughly by the number of host molecules it contains. It appears that the BMN in naphthalene case is a combination of $\rho(\omega)$ and D effects, with

a possible J contribution. There may be partial cancellations among these effects. We also note that there are *no* localized phonons around a BMN impurity,[8,9] while they do exist around anthracene.[10]

We believe that it is a safe assumption to consider that the $C_{10}H_8$ in $C_{10}D_8$ traps are isotopic in nature, and thus *no* funnel is created around the trap ($C_{10}H_8$). Also, the BMN in $C_{10}H_8$ trapping efficiency is of the order of two. Thus the funnel around the BMN trap is of the order of one (neighboring) molecule. Due to uncertainties (factor of 2) we estimate a lower limit of zero and an upper limit of four. This agrees with the direct observations[8] on this "funnel".

Turning now to the anthracene case, as its trapping efficiency is only about four times larger than that of BMN, it appears that, if there is a funnel around it, it would be limited to nearest and possibly next-nearest neighbors. It thus appears that for the singlet naphthalene exciton (band half-width = 80 cm^{-1}) no *large* energy funnels are created by substituents such as BMN or anthracene.

Conclusions

The singlet exciton trapping efficiencies of BMN and anthracene in naphthalene are comparable to each other and also to that of naphthalene in $C_{10}D_8$. We conclude that (1) "funnel effects" do not extend much beyond the four nearest-neighbor shells in these systems; (2) phonon effects are of some importance, at least for the BMN in naphthalene case; (3) localized phonons (anthracene in naphthalene) do not significantly aid trapping, unless they are cancelled by an unknown compensating transfer integral effect.

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