Exciton Dynamics Probed by Single Molecule Spectroscopy

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Triplet exciton dynamics in isotopically mixed naphthalene crystals are investigated on a molecular scale using single terrylene molecules as local probes. Upon triplet excitation of the matrix, the resonance frequencies of the probe molecules show reversible frequency excursions on the time scale of seconds. The analysis based on localized and diffusing triplet excitations indicates that the frequency fluctuations are induced by excitations migrating in an energy funnel of trap states in the vicinity of the probe. [S0031-9007(99)08640-8]

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Single molecule spectroscopy (SMS), a recently developed technique that removes the ensemble averaging inherent to classical optical methods like spectral hole burning of photon echoes, provides information about structure and dynamics of solids in unprecedented detail [1]. In particular, insight into dynamical processes in the local environment of a chromophore can be gained and single events of the microscopic dynamics can be traced. Effects like the spectral diffusion of single molecule optical absorption lines caused by structural rearrangements in the matrix have been unveiled using SMS [2–4]. Transport, conversion, trapping, and relaxation of electronic excitations in solids have been studied for several decades and are phenomena of continuing importance. Molecular crystals provide ideal systems for their basic analysis. In this paper, we demonstrate for the first time that SMS can be applied to study electronic energy transport processes in solids on the molecular scale. We show that the experimental observations obtained for naphthalene crystals can tentatively be assigned to trapping, jumping, and relaxation of electronic excitations.

Our studies have concentrated on triplet exciton dynamics in isotopically mixed naphthalene crystals at 1.8 K using single terrylene molecules as local probes. Triplet excitation transport in such crystals [5] takes place primarily by migration between naphthalene h_8 trap states that lie 95.5 cm^{-1} below the exciton band of the deuterated host crystal [6]. The migration dynamics depend sensitively on temperature, on the naphthalene h_8 concentration, and on the presence of impurity trap states. Delayed fluorescence through triplet-triplet annihilation and phosphorescence from trap states are the dominant decay channels [7–10]. The phosphorescence lifetime of 2.7 s for naphthalene h_8 at 1.6 K [11] constitutes an upper temporal limit for excitation transport. Because of the sensitivity of single molecule optical absorption lines to dynamical processes in the environment, SMS can be applied to measure the spatial triplet-excitation configurations and their temporal evolution in the vicinity of single probes. Excitation and relaxation of the triplet states are expected to induce reversible frequency fluctuations in the single terrylene transition frequencies.

Naphthalene d_8 crystals doped with different concentrations of naphthalene h_8 (0, 0.3, 5.1, 16.8 mol %) and terrylene ($<10^{-9}$ M) were obtained by cosublimation of the components. Crystal platelets a few tens of microns thick were mounted on a sample holder at the working distance of a microscope objective and immersed in a superfluid helium bath at 1.8 K. A single mode dye laser was used to excite terrylene and the fluorescence light was detected by a photomultiplier. One spectroscopic site centered at 574.3 nm with an inhomogeneous bandwidth of about 220 GHz was observed. A distribution of single molecule linewidths peaked at 60 MHz with a FWHM of 20 MHz was determined. Most molecules were stable even under strong illumination. The naphthalene crystals were excited into their singlet manifold in the UV using a water filtered Xe lamp for a few seconds in order to reach a steady state triplet exciton population. Neither a temperature rise of the cryostat nor single molecule line broadening were observed subsequent to matrix excitation. Fast frequency scans over the absorption band of single terrylene molecules were performed after matrix excitation.

Figure 1 is a grey scale plot of time dependent fluorescence excitation scans covering a 2 GHz range at 574.3 nm. The spectra were recorded continuously at a rate of 0.5 s/scan in 40 MHz steps with 10 ms signal integration per point. Dark colors represent high fluorescence intensities. To improve the contrast of this plot, the decaying background originating from trap state phosphorescence overlapping with the detection bandwidth of terrylene was subtracted in every scan. The signal-traces A, B, and C of three single terrylene molecules can be identified in three consecutive matrix excitation cycles. These traces exhibit a variety of different behavior: Trace A shows spectral dynamics independent of the matrix excitation. The spectrum of molecule B is irreversibly shifted upon matrix excitation but otherwise stable. Of particular interest here are the spectral dynamics of molecule C. Before matrix
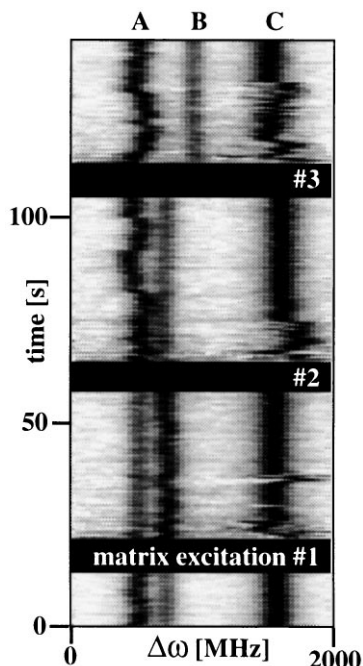
FIG. 1. Time dependent excitation spectra of three terrylene molecules denoted by *A*, *B*, and *C* in an isotopically mixed naphthalene crystal. The time between two consecutive scans is 0.5 s. The fast laser scans are interrupted by matrix excitations (#1–#3) for a few seconds, the corresponding periods are indicated by black bars. Molecule *C* exhibits reversible frequency excursions after every matrix excitation on the time scale of seconds.
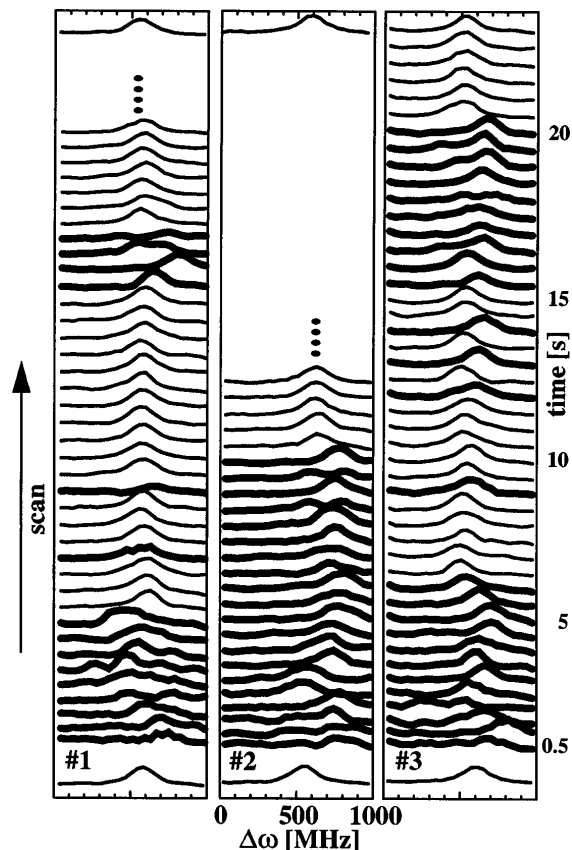

FIG. 2. Fluorescence excitation scans of molecule *C* right before (bottom) and after the matrix excitation cycles #1, #2, and #3. The time between two consecutive scans is 0.5 s. Scans showing spectral activity are plotted in boldface.

excitation, the transition frequency is stable. After matrix excitation, reversible frequency excursions on the time scale of seconds are observed. Such excursions could be induced for a sequence of 74 matrix excitations cycles. These data were recorded for a crystal having 5.1% naphthalene h_8. Spectral dynamics on the time scale of seconds have also been observed in crystals having 0%, 0.3%, and 16.8% naphthalene h_8. In the following, we focus on the analysis of the spectral dynamics of molecule *C* which, although representing a particular case, allows for general conclusions.

Figure 2 shows the fluorescence excitation scans of molecule *C* in Fig. 1 in detail. Plotted are scans recorded immediately after matrix excitations #1, #2, and #3. For comparison the last scan of the preceding excitation cycle is also given. Frequency excursions, unusual line shapes, and line broadening are observed in many laser scans after matrix excitation—the corresponding lines are plotted in bold style. Several seconds after matrix excitation, a stable Lorentzian line is recovered. The following recurring and characteristic properties of the spectral dynamics can be deduced: (i) The excursions are limited to the range of several times the linewidth. On average, the trace is shifted to the blue. (ii) The trace pattern is unique for each excitation cycle. (iii) For many scans, several frequency jumps occur during the

scan resulting in line broadening and unusual line shapes. This characteristic behavior lasts until a stable absorption line is suddenly recovered. (iv) In approximately 10% of the excitation cycles the traces relax intermittently to the equilibrium position. After stable periods, the spectral dynamics continue until a final relaxation takes place (see excitations #1 and #3 in Figs. 1 and 2).

To quantitatively analyze the dynamics, we have determined the number of frequency jumps for each scan. In Fig. 3, corresponding histograms are displayed for the excitation cycles #1, #2, and #3. They were obtained by counting the number of frequency jumps in each scan and by adding one if a jump is present with respect to the previous scan. A total of 27, 12, and 24 jumps were counted for the excitation cycles #1, #2, and #3, respectively. Such histograms were calculated for 21 excitation cycles for which trace *C* was clearly separated from traces *A* and *B*. All histograms looked similar; 18 jumps occurred on average. In order to grasp the characteristic property of all histograms, we have performed a conditional average. For each scan (bin), the average was taken over those of the 21 histograms that show dynamics for the same or later scans. The resulting averaged histogram
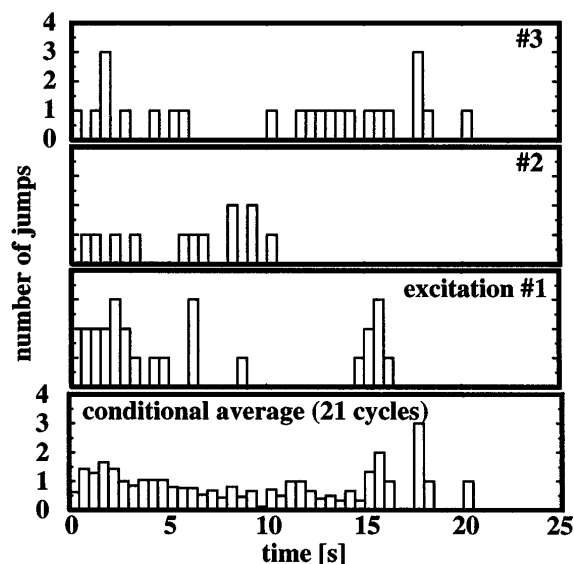
FIG. 3. The number of frequency jumps as a function of time for the excitation cycles #1–#3. The conditional average taken from 21 excitation cycles is given on the bottom.

is also shown in Fig. 3. It shows that there is a weakly decreasing activity at early times followed by a period of approximately constant activity.

Interestingly, the almost constant activity followed by the sudden recovery of a stable line shape allows for the determination of a further quantity, namely the final recovery time. Figure 4 shows the corresponding histogram that has been obtained from the analysis of all 74 excitation cycles. The histogram is slightly asymmetric with a tail towards longer times; the FWHM is about 7 s. On average, a stable absorption line is recovered after 9 s (18 scans).

Since the presence of naphthalene h_8 traps is no prerequisite for exciton induced spectral dynamics and heating effects can be excluded, it is natural to assume that these fluctuations result mainly from triplet excitations located on distorted matrix molecules (X traps) in the vicinity of the probe. Impurity generated X traps are well known in naphthalene crystals [12,13]. We assume that terrylene re-
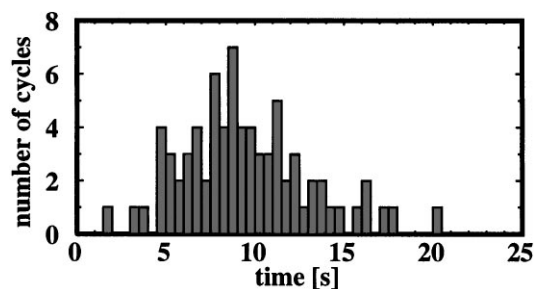

FIG. 4. Histogram of the recovery times for a stable line shape obtained from 74 excitation cycles.

places three naphthalene molecules in the host lattice and might thus generate a large number of lattice defects beyond the 16 matrix molecules of the first solvent shell. The lattice disorder is considered to decrease with the distance from the impurity; accordingly, the trap depths would also decrease resulting in an energy funnel of trap states with respect to the host exciton band [13].

For the interpretation of the experimental observations we have considered two models based either on stationary or migrating excitations. In the first case, triplet excitations are localized on lattice trap sites. They interact with the probe and induce frequency fluctuations upon spontaneous decay. We have simulated such a mechanism assuming a cubic lattice and dipolar interactions between the probe and the trap molecules. Dipolar coupling ensures positive and negative frequency shifts independent of the actual mechanism, that might involve both elastic and electrostatic contributions. The conclusions drawn below hold generally irrespective of the details of the lattice geometry. We set the equilibrium transition frequency of the probe to $\omega_0 = 0$ and write for the time dependent frequency

$$\omega(t) = \sum_k \varepsilon(\mathbf{r}_k)\rho_k\xi_k u_k(t), \qquad \lim_{t\to\infty} \omega(t) = 0, \quad (1)$$

where the sum runs over all lattice sites denoted by the index k. $\varepsilon(\mathbf{r}_k)$ is the frequency jump induced by the trap excitation at the displacement $\mathbf{r}_k$. ρ_k and ξ_k are two indicator variables telling whether a site is occupied by a trap and whether this trap is initially excited, respectively. The two variables take the value 1 with probabilities p_s and p_e and the value zero otherwise. $u_k(t)$ is a stochastic variable indicating the trap state. It is 1 for $0 < t < t_f$ and 0 otherwise, where t_f is a random relaxation time. The excitations relax independently and exponentially with a rate constant γ so that $u_k(t) = 1$ with probability $e^{-\gamma t}$. ρ_k guarantees for a random realization of spatial trap configuration. ξ_k and $u_k(t)$ guarantee for a unique initial excitation configuration and frequency relaxation pathway, respectively. Using Eq. (1) we have simulated time dependent frequency trajectories from which we also calculated fluorescence excitation scans. Shown in Fig. 5(a) is a grey scale plot of a simulation realization. For the calculation we set $p_s = 0.1$ and $p_e = 1$, and the lattice was spherically restricted to 500 sites resulting in approximately 50 traps. For such conditions the spectral dynamics of the probe is typically dominated by the relaxation of a few close trap excitations that induce large jumps. In the example of Fig. 5(a), the absorption line jumps between a few discrete frequency positions and almost no dynamics are observed during the scans. In addition, the spectral dynamics is stronger at earlier times and on average, approximately 10 jumps can be identified. In contrast, the spectral dynamics of trace C shown for comparison in Fig. 5(b) is much richer. The experimental data show, as mentioned above, many frequency jumps
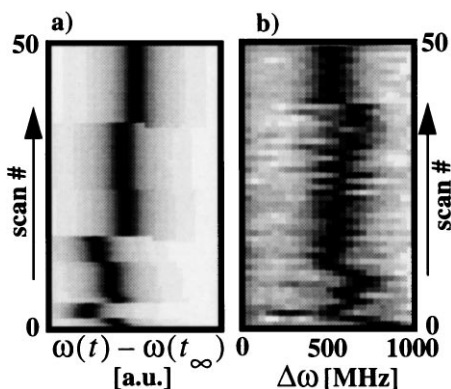
FIG. 5.   Comparison of time dependent excitation spectra. (a) Simulation calculation according to Eq. (1). (b) Data from cycle #3 of Fig. 1 on an enlarged time scale.

during and between the scans until the dynamics suddenly vanish. It is apparent that such a behavior is incompatible with that of the model. Irrespective of the choice of the parameters in the model, the jump activity would decay exponentially. From this observation we conclude that the model based on stationary excitations has to be ruled out for the interpretation of the experimental data.

In the second model we consider excitations that are mobile. We assume that the spectral dynamics are induced by excitations migrating between the X traps of a funnel in the immediate vicinity of the probe. Excitons migrating in the funnel would give rise to a rich dynamics with many frequency jumps of comparable size until suddenly a stationary state is recovered because of spontaneous excitation relaxation. The resurgent dynamics observed in some cases could result from excitation relaxation followed by repopulation of the funnel, for example, from naphthalene h_8 triplet exciton trap states. Relaxation and repopulation would also ensure an almost constant number of excitations in the funnel. Triplet-triplet annihilation would limit the number of excitations simultaneously present in the funnel and thus would further ensure a constant triplet occupation of the funnel. A funnel would also give rise to a large trap cross section (exciton harvesting cross section) so that singlet and triplet excitations would be efficiently captured by the funnel. This would explain why spectral dynamics were explicitly observed for each excitation cycle. The shape of the histogram in Fig. 4 indicates that several excitations are involved on average. Assuming for simplicity an initial population of the funnel followed by excitation migration and decay, approximately ten excitations with a decay time on the order of 3 s are required to explain such a histogram.

To give support to the interpretation that terrylene interacts with excitations localized on neighboring naphthalene molecules, we have estimated the electric dipolar coupling from independent measurements. From Stark-shift experiments a difference between the dipole moments of

the two lowest terrylene singlet states of approximately 0.01 debye was determined. Assuming a similar dipole-moment difference for the T_1 and S_0 states of disturbed naphthalene molecules in the first solvent shell at a distance of about 0.5 nm, we calculated frequency shifts of a few hundred MHz. These shifts are in agreement with the experimental observations, however, other type of interactions, for instance elastic forces, might cause frequency jumps of similar magnitude.

Concluding, we have demonstrated that SMS can be applied to investigate transport, trapping, and relaxation steps of electronic excitation dynamics in solids on a molecular scale. The extension of such investigations to energy transport in disordered and amorphous solids seems to be feasible.

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