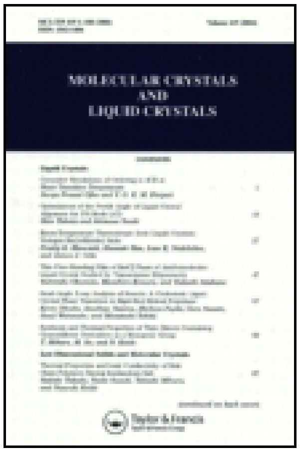

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Dephasing of Electron Spin Echo in the Triplet State of Orientationally Disordered Crystals

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Dephasing of Electron Spin Echo in the Triplet State of Orientationally Disordered Crystals

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Conventional and pulse optically detected magnetic resonance spectroscopy is used to study the dynamics of electronic energy transfer process in two orientationally disordered crystals, 1-bromo-4-chloronaphthalene and 4-bromo-4′-chlorobenzophenone.

Keywords: ODMR, coherence, spin echo, disordered crystals

INTRODUCTION

Interest in the experimental studies of excitons in molecular crystals has grown over the past decades as state-of-the-art instruments capable of measuring fast processes have become accessible. Initially, much of the thrust of experimentalists was on excitons of low dimensionality, especially one- and quasi one-dimensional, since the theory of one-dimensional excitons has been well understood.[1–15] In fact, even for crystals which should form models for one-dimensional excitons, such perfect crystals are rare and, to date, experimental studies have been limited to a few examples.

Energy transfer can also occur in other types of solids, including disordered crystals. Although appearing at first to be more complicated, energy migration in disordered crystals presents many interesting features worthy of studies. 1-bromo-4-chloronaphthalene (BCN)

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and 4-bromo-4′-chlorobenzophenone (BCB) are two examples of orientationally disordered crystals. The crystal structures of the molecules analogous to BCN, 1,4-dichloronaphthalene (DCN) and 1,4-dibromonaphthalene (DBN), are such that the molecules exhibit a stacking arrangement, allowing the excitons to travel along the stack almost perpendicular to the molecular plane.[16–18] Hence, excitons in these molecular crystals form excellent examples of one-dimensional motion. BCN, on the other hand, exhibits a random distribution of the orientation of the chlorine and bromine substituent groups and results in a relatively large inhomogeneous linewidth.

In a previous study, we reported the triplet state parameters of the BCN, DCN and DBN along with the results of a preliminary study involving exciton trapping in these crystals with varying acceptor trap concentrations.[19] Since that time, modifications which have been made in the optically detected magnetic resonance (ODMR) apparatus have resulted in a very versatile programmable pulse train generator and photon counter for coherence studies. In addition, our recent work on the theory and the method in differential saturation technique allows us to determine the relative homogeneous and inhomogeneous contributions to the ODMR linewidth. To date, pulse methods in ODMR have been applied to localized states in deep traps and to excitons of one-dimensional models, such as in tetrachlorobenzene and DBN. The orientationally disordered solid provides a novel system in which to test the applicability of pulse ODMR to the study of spectral diffusion in energetically more complicated solids.

EXPERIMENTAL

BCN was synthesized by the Sandmeyer reaction from 1-amino-4-chloronaphthalene. The ether extract from the diazotized mixture was washed, decolorized and dried over sodium sulfate and the ether was evaporated. The resulting solid residue was recrystallized from absolute ethanol, giving an approximate yield of 20%.

BCB was synthesized by the Friedal-Crafts reaction. About 100 ml of 4-benzoylchloride was mixed with twice that many moles of bromobenzene and 100 g of aluminum chloride. The mixture was refluxed at 156°C for 24 hours, and then quenched with ice-water and with concentrated HCl. The product was extracted with dichloromethane, and recrystallized three times from absolute ethanol. The reaction yield was about 20%.

Both BCN and BCB were zone refined for an equivalent of over

200 passes. The middle sections of the material in the zone refining tubes were then sealed under vacuum and single crystals were grown from the melt by the standard Bridgman method. The crystals were carefully annealed for 24 hours at just below the melting temperature.

The annealed crystals were cleaved and inserted in a helical antenna made of flattened silver wire. A cone-shaped reflector, the position of which was adjustable to 1/4 λ from the helical sample holder, allowed the use of 10–20 W TWT microwave amplifiers with resultant π pulse lengths of 30–40 ns, as determined by transient nutation experiments. The entire helix assembly was immersed in a liquid helium bath and temperatures of 1.4 K, as determined by a calibrated diode, were achieved by rapidly pumping the helium vapor above the liquid.

The sample in the microwave helix was optically pumped with a broad-band excitation source and the surface emission monitored with a Jarrell-Ash 1 m scanning double monochromator equipped with a thermoelectrically cooled photomultiplier tube. The microwave source was a Hewlett-Packard model 8350 microwave sweep oscillator. Signal averaging was performed on a Tracor-Northern instrument and the data transferred to a Hewlett-Packard 9816 microcomputer for interactive analysis. The dynamic parameters of the depopulation process from the zero field states were observed via the adiabatic rapid passage of the zero field transitions as first described by Winscom and Maki.[20]

The various spin relaxation times were obtained with the use of a microcomputer-assisted pulse train generator and photon counter, the details of which are described elsewhere.[21,22] The pulse train generated output from the computer was fed to several high isolation PIN diodes which switched the appropriately phase-shifted microwave source. The phase shift of the microwave was done by inserting a −3 db, 90° hybrid coupler followed by two −3 db, 180° hybrid couplers in the microwave line. In this way, all four phases, 0°, 90°, 180°, and 270°, were generated. In each of these lines, a variable attenuator and a phase shifter were placed in series. Then, by means of four PIN diodes inserted in each of the four lines, any combination of the phase-shifted microwave could be selected by the pulse programmer interface.

Initially, a transient nutation experiment was done to determine the pulse widths necessary for $\pi/2$ and π, i.e. saturation and inversion, pulses for subsequent coherence experiments. These pulse widths were thus calibrated for each of the phase shifted microwave power. The homogeneous lifetimes were determined by monitoring the decay of the Hahn spin echo.[23] In addition, a computer assisted routine was used to empirically fit the echo shape data to expressions describing Lorentzian and Gaussian shapes using trial dephasing times.[24] A two pulse rotary echo experiment was also used to measure spin–spin relaxation. The pulse sequence is a 180° phase shifted pulse immediately following the 0° pulse. The time duration of both pulses is varied simultaneously and the intensity of the phosphorescence is detected immediately after the cessation of the final pulse.

The use of the microcomputer assisted pulse train generator allowed for much more precise control of the pulse timing than was possible in our earlier work. The use of a 100 MHz clock and ECL circuits throughout the pulse programmer interface were found to be a minimum requirement in the operation of the pulse train generator, because of the extremely short spin relaxation times encountered in the triplet state of these molecules.

In order to determine the nature of line broadening in ODMR, van der Velden and Veeman devised a method in which the slowly swept microwave power was amplitude modulated to a depth of less than 100%.[25] The appearance of the resulting differentially saturated spectra determined whether the zero field resonance was homogeneously or inhomogeneously broadened. A more recently developed method, which is complementary, but more convenient, was used in this study, the details of which were reported elsewhere.[26] In this method, a very low power pre-saturating microwave source, which is frequency distributed through the entire zero field linewidth, is used in addition to the slowly swept pulse microwave power, and the resulting phosphorescence change is detected. The microwave pulse width was adjusted for a pulse as determined from transient nutation data. In this way, a twofold enhancement in the signal intensity could be achieved as compared to the differential saturation method, since in the later technique, the maximum signal would be achieved at saturation. The presence or the absence of the characteristic dip in the resulting ODMR spectra indicates that the linewidth is homogeneously or inhomogeneously broadened.

RESULTS AND DISCUSSION

Prasad, Morgan and El-Sayed proposed a model of energy transfer in orientationally disordered solids when the acceptor concentration is high.[27,28] When initially prepared by a short wavelength, *but within* the absorption linewidth, the dominant mechanism for energy transfer is a one-dimensional exchange. The energy cascades from high to low energy sites irreversibly until the transfer of energy is slower than the radiative rate. During the cascade process, the energy settles into potential wells of varying depths and the energy transfer switches to a three-dimensional dipole–dipole type. From the analysis of the lineshapes, the number of sites experienced by an excitation was determined to be 365 with a dipole–dipole nearest neighbor energy transfer time of 2.6 μs.

Energy transfer processes can be most optimally studied by spin locking.[12] However, the relaxation times in the orientationally disordered solids studied here were found to be shorter than the times conveniently accessible by spin locking. In addition, for these crystals, the contribution to spectral diffusion time from hyperfine field fluctuation was found to be at least an order of magnitude longer than the energy transfer processes.[29] For these two reasons, the rotary echo experiment was chosen to study the energy migration in the solids.

A summary of the zero field parameters for the phosphorescent triplet state for BCN neat and in single crystals of durene and naphthalene are shown in Table I. It should be noted that the zero field transitions reported here do not correspond to those observed by Niederwald et al.[30] The spin dephasing times of BCN for the 3156 MHz transition were determined and the results are summarized in Table II. For comparison, the inhomogeneous lifetimes, as calculated from the slow passage ODMR linewidths are shown. From the aforementioned models of energy transfer in orientationally disordered crystals, the decay of the rotary echo is not predicted to be a simple exponen-

TABLE I

Zero field parameters for the phosphorescent triplet state of BCN at 1.4 K. (The error limits are: ±5 cm^{-1}, ±20%, and ±2 MHz for the 0,0 band, decay constants, and zero-field transitions, respectively.)

	0,0 band (cm^{-1})	Decay rate constants (s^{-1})	Zero field transitions (MHz)
neat	20214	170	3165
		110	2675
		6.9	
in durene	20222	160	3164
		60	2670
		2.0	
in naphthalene	20218	180	3157
		75	2647
		2.2	

TABLE II

Spin dephasing times ($\pm 20\%$) of BCN neat single crystals for the 3165 MHz zero field transition in μsec at 4.2 and 1.4 K

	4.2 K	1.4 K
echo decay	0.30	0.35
rotary echo	0.30	0.30
	2.0	3.0
ODMR linewidth	0.074	0.066
echo shape	0.080	0.080

tial.[27,28] Nevertheless, experimentally, the observed decay is close enough to an exponential that the decay constant can be estimated. In fact, in BCN, the best fit was a biexponential curve and the two l/e times are presented in Table II. The longer of the two spin diffusional times, as measured by the rotary echo experiment, corresponded well with what has been assigned to dipole–dipole triplet–triplet energy transfer times as reported by El-Sayed et al.[27,28] The shorter component may be due to the short range exchange energy transfer processes which were observed by El-Sayed.[27,28] The somewhat shorter dipole–dipole transfer time which was observed by rotary echo decay at the higher temperature might be explained by the larger contribution to the total dephasing time by thermal repopulation of higher energy sites and subsequent cascading into lower energy sites.

Homogeneous lifetimes from echo decay measurements are a composite of all spin–spin relaxation processes and the faster processes which contribute to the total dephasing time mask the slower components. Hence, the echo decay should be the fast limit. The good agreement found between the echo decay and the shorter components in the rotary echo decay was very satisfying.

ODMR spectra were taken using the differential saturation method as described above. The comparison of the ODMR linewidth and the echo decay indicate that the characteristic dip in the differentially saturated ODMR spectra should be observed. However, this dip has not been observed even with microwave pulses as short as 10 ns. From a careful analysis of the echo shapes, the inhomogeneous T_2 times were found to be consistent with those calculated from ODMR linewidths. Hence, in BCN, unlike some carbonyl containing molecules for which such comparisons have been made, the ODMR linewidths are not as susceptible to power broadening.[24]

Table III presents the zero field parameters for the triplet state of BCB, in addition to those of the analogous dihalobenzophenones,

TABLE III

Zero field parameters for the phosphorescent triplet state of BCB at 1.4 K. (The error limits are: ±5 cm^{-1} and ±2 MHz for the 0,0 origin and the zero field transitions, respectively. The rate constants and relaxation times are ±20%.)

	0,0 origin (cm^{-1})	Decay rate constants (s^{-1})	Zero field transitions (MHz)	T_2 (μs)	Rotech (μs)
BCB	24,480	890	5540	0.23	0.19
neat		60	4075	0.28	0.29
		170	1462	0.28	0.40
BCB	23,810	590	4358		
in benzophenone		47	2625		
		110	1733		
DCB	24,181	688	5130		
neat		51	3645		
		57	—		
DCB	24,100	600	5266		
in benzophenone		50	3930		
		100	—		
DBB	23,930	1500	5130		
neat		630	3693		
		530	—		
DBB	24,100	660	5140		
in benzophenone		160	4007		
		70	—		
BP	24,100	624	5377	4.0	3.7
		62	4110	5.0	4.3
		40	—		

4,4′-dichloro- (DCB) and 4,4′-dibromo-benzophenones (DBB). These were also doped in a single crystal of benzophenone BP for comparison with the neat samples. It is noteworthy that, similar to the BCN study, the dephasing times observed from Hahn spin echo decay and the two-pulse rotary echo decay were very similar. The decays were single exponentials and the decay times correspond well with those for BCN. Unlike BCN, however, a long component in the rotary echo decay was not observed. The preliminary conclusion is that in BCB, the excitation migrates rapidly via exchange type energy transfer, and settles into deep traps. The trap-to-trap distances appear to be much larger than those for BCN, because of the absence of the longer decay. This conclusion is consistent with results from spectral diffusion studies by Talapatra et al.[31] Another tentative explanation for the lack of the long range energy transfer in BCB might be orientational constraints in such processes. In addition, the similarity in the decay times measured by the Hahn echo and rotary echo pulse sequences leads one to conclude that, as was the case for BCN, the dephasing by nuclear spin flips during the excitation transfer process is much longer than the energy transfer times.

In the symmetrical dihalobenzophenones, the zero field transitions and the total phosphorescence rate constants are not appreciably different as neat crystals or doped in benzophenone. The much larger phosphorescence rate constants for neat DBB are consistent with the intermolecular external heavy atom effect. In BCB, the difference in the largest zero field transitions between BCB neat and BCB doped in benzophenone is almost 1200 MHz. In the disordered crystal, energy migration would ultimately lead to population of the trap state of the lowest energies, from which luminescence occurs. Hence, the monitored emission favors particular states which are not necessarily those which are more representative in the distribution of state energies.

Finally, whereas the triplet states in DBB and DCB are not appreciably different than that in benzophenone, the zero field transitions of BCB in benzophenone are very different. In the former cases, the halogen substitutions in the para position of the benzoyl moiety do not greatly distort the triplet state; in the latter case, however, spin-orbit contribution to the zero field splittings appear to be important. The observed overall increase in the phosphorescence rate constants for BCB neat and BCB in benzophenone can be attributed to intermolecular heavy atom effect.

CONCLUSION

The two systems which were studied here provide a good sampling of the orientationally disordered crystal. Although studies using pulsed excitation sources tend to yield dynamical information in energy transfer processes more directly, conventional and pulse ODMR techniques appear to promise complementary and new information in the study of the inherently complex processes of energy transfer in orientationally disordered crystals.

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