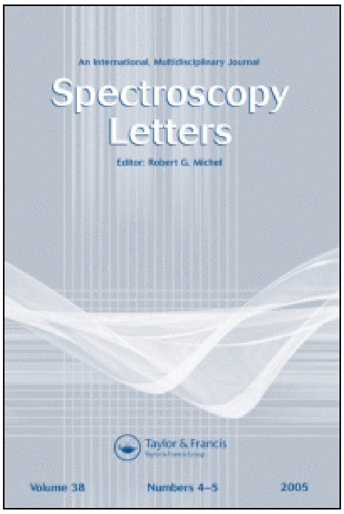

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MAGNETIC RESONANCE ON LOCALIZED EXCITED TRIPLET STATES IN 1,4-DIBROMONAPHTHALENE

KEY WORDS: Triplet excitons, 1,4-dibromonaphthalene,
linear systems, ODMR.

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ABSTRACT

Kinetic parameters of localized excited triplet states in 1,4-dibromonaphthalene have been determined from ODMR and MIDP experiments. The results show that no Boltzmann equilibrium exists over the triplet exciton sublevels at the moment of trapping. These experiments are in agreement with our previously reported findings, that in 1,4-dibromonaphthalene excitons exist with a very short lifetime.

INTRODUCTION

Different spectroscopical approaches have been used to study triplet exciton dynamics in molecular crystals. When the lifetime of the triplet excitons is long enough, electron spin resonance (ESR) and optically detected magnetic resonance (ODMR) techniques can probe directly the excitonic behaviour.[1] Other methods that have been used include detailed optical absorption measurements and time resolved optical emission measurements.[2] Two systems that have enjoyed especially great interest are 1,2,4,5-tetrachlorobenzene (TCB) and 1,4-dibromonaphthalene (DBN), both exhibiting one-dimensional transport topology. In contrast to the findings in TCB, triplet exciton ODMR spectra of DBN, remarkably, can only be obtained in a magnetic field.[3] Whether or not the presence of various different excitons and trap-like states, very close to the exciton origin as reported in previous letters,[4] play a crucial role in this peculiar behaviour is not immediately clear. We have shown the coexistence of excitons in DBN with very different lifetimes. Species responsible for phosphorescence emission have a relatively long lifetime (~ 150 μs). Excitons with a very short lifetime (< 1 μs) do not contribute to phosphorescence emission, but are very effectively trapped. In addition to zero-field ODMR work on localized states in DBN by other authors[5] we want to present in this letter zero-field ODMR and microwave induced delayed phosphorescence (MIDP) data on DBN traps that provide extra proof for the existence of excitons with an extremely short lifetime. It will be shown that the relative trap populating rates, p_i, are very different for the different triplet sublevels. Since the fine structure tensor axes of traps and exciton are almost coincident, these populating rates depend solely on the relative populations in the exciton sublevels at the moment of trapping. Therefore it will be concluded that the excitons live so short that the exciton sublevels cannot reach a Boltzmann equilibrium during their lifetime.

EXPERIMENTAL

The preparation of DBN single crystals has been described elsewhere.[4] The crystals are immersed in liquid helium in a 4-window Leybold Heraeus stainless steel cryostat. The sample is irradiated by means of a high pressure 200 W Osram mercury arc. The optical path from the arc to the crystal can be interrupted by a Uniblitz model 3100 shutter. A Hewlett Packard HP 8620 C microwave oscillator with different plug-ins for the various frequency ranges acts as the microwave-source. The optical path proceeds from the crystal through a 0.85 m Spex double monochromator 14018 (2400 grooves/mm holographic gratings) to a Peltier cooled photomultiplier RCA C31034. The photomultiplier is coupled to a Nicolet 1170 signal averager. A home-built pulseprogrammer controls all pulse sequences. Ultra low temperatures were reached by pumping on the helium bath with a large capacity Leybold-Heraeus pump, model D30A.

RESULTS

Fig. 1 shows the phosphorescence emission spectrum of a vapour grown (A) and a Bridgman grown (B) crystal of DBN at 1.2 K.

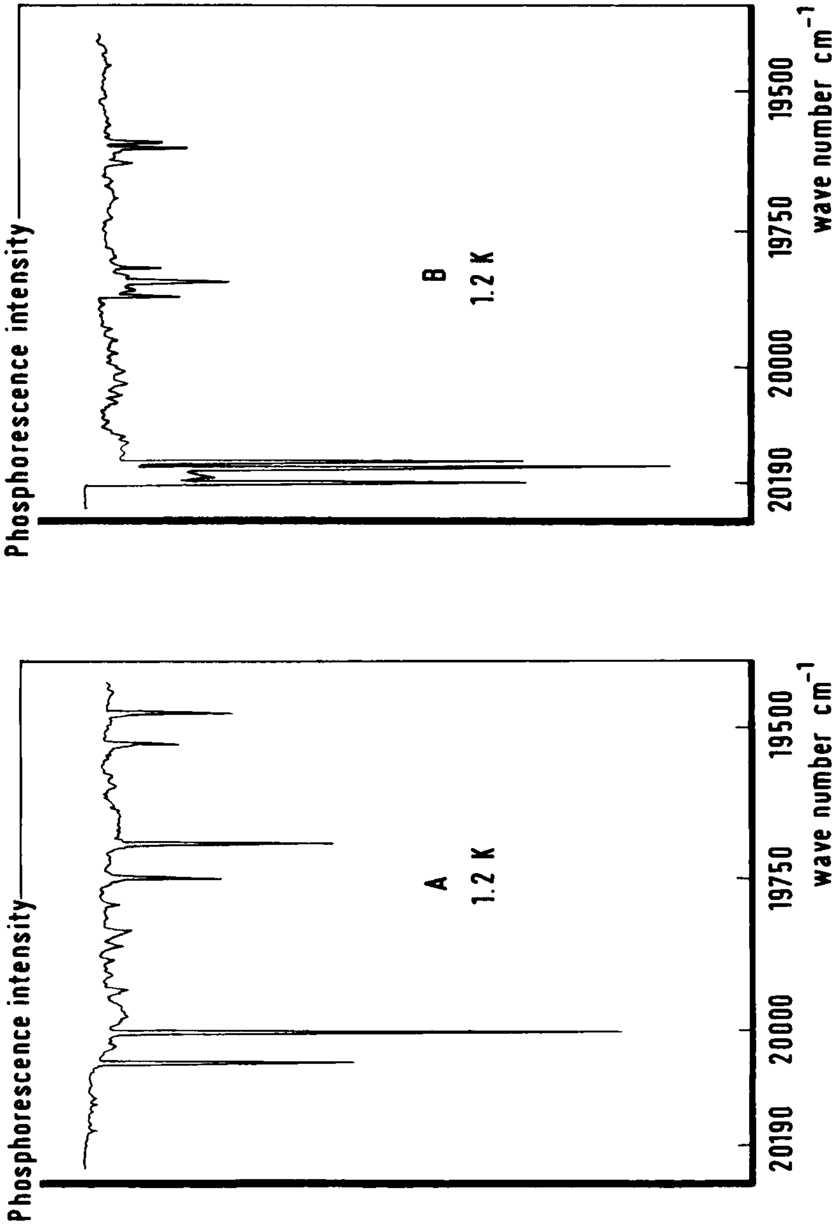

FIG. 1 Phosphorescence emission spectrum of a vapour grown (A) and Bridgman grown crystal of DBN (B).

In the vapour grown crystal no exciton emission can be detected at temperatures between 4.2 K and 1.2 K. Only two traps are observed at 20056.1 cm^{-1} and 20006.1 cm^{-1}. Spectrum 1B is quite different, exhibiting shallow traps at 20166.7 cm^{-1} and 20157.4 cm^{-1}. Furthermore at 1.2 K strong emission is observed from trap-like states very close to the exciton origin (20190.6 cm^{-1})[4]. No zero-field ODMR signals could be obtained from these states. In order to obtain additional information with regard to the trapping dynamics ODMR and MIDP experiments were performed on the states at 20056.1 cm^{-1}, 20006.1 cm^{-1}, 20166.7 cm^{-1} and 20157.4 cm^{-1} in the vapour grown and Bridgman grown crystals, respectively. The experiments were performed via standard methods described elsewhere.[6] Table 1 gives the zero-field splitting parameters at 1.4 K (in MHz) observed for the four traps mentioned above.

The data presented in this table qualitatively agree with the values obtained by other authors[5] for similar traps in DBN. Except for the trap at 20157.4 cm^{-1} a very small $|E|$ value is observed (46 - 56 MHz). By means of the MIDP method we determined the total decay rate constants (k_i), the relative radiative rate constants (k_i^r), the relative populations ($N_i(0)$), and the relative populating rates (p_i) of the triplet sublevels at 1.4 K. These are listed in table 2. The labels of the triplet sublevels are chosen according to Mulliken's notation for C_{2v}-symmetry. The out-of-plane molecular axis is therefore taken to be the x-axis, whereas the z-axis is the C_2-symmetry axis. The DBN molecule in the ground state is known to be absolutely planar.[7] If the molecule in the excited

TABLE 1

Zero-field splitting parameters (in MHz) for several DBN traps in neat crystals at 1.4 K

0-0 band cm^{-1}	20056.1	20006.1	20166.7	20157.4
$\|D\| + \|E\|$	2856	2839	2816	2994
$\|D\| - \|E\|$	2764	2761	2704	2686
$\|D\|$	2810	2800	2760	2840
$\|E\|$	46	39	56	154

state would retain C_{2v}-symmetry, then simple symmetry and spin-orbit coupling considerations would predict only τ_z to be radiative. However, it is found that also k_y^r is not negligible which shows that the molecule in the excited state is distorted.[5] The values for the radiative decay constants vary drastically for the different traps. This is not unexpected when structural distortions in the excited state play such an important role.

The most interesting conclusions may be drawn from the values for the relative populating rates, p_i. The spin-populations in a particular triplet exciton sublevel is transferred to the different sublevels in a trap at a rate, which is proportional to the squared direction cosines relating the fine structure axes of the exciton to the axes of the trap, when the trapping proces occurs randomly with respect to the Larmor precession.[8] In DBN the trap fine structure tensor axes are almost coincident with those of the exciton. Our trap populating rates p_i are defined, as usual,[10] as the product of the trap steady state population $N_i(0)$ and the trap

TABLE 2

Kinetic parameters for different DBN traps at 1.4 K

0-0 band, cm^{-1}		20056.1	20006.1	20166.7	20157.4
k_z, s^{-1}		288	315	340	238
k_y, s^{-1}	(±10%)	320	410	355	214
k_x, s^{-1}		10.8	13.9	10.8	7.3
k_z^r		110	8	70	6
k_y^r	(±20%)	80	27	71	8
k_x^r		1	1	1	1
$N_z(0)$		0.3	0.1	0.5	0.8
$N_y(0)$	(±20%)	0.4	0.8	0.7	1
$N_x(0)$		1	1	1	1
p_z		8	10	15	25
p_y	(±20%)	12	23	22	29
p_x		1	1	1	1

total decay rate k_i. With this definition the relative trap populating rates p_i in DBN are proportional to the relative steady state populations in the exciton sublevels. Table 2 shows that for all traps $p_z \sim p_y$ but very different from p_x. Therefore we may conclude that the triplet sublevel populations of the excitons which are trapped at these traps are about equal for the z and y sublevels but very different from the populations of sublevel x.

Consequently no Boltzmann equilibrium can exist between the exciton spin levels, proving that the lifetime of these levels is shorter than the spin-lattice relaxation time for transitions between them. In fact the relative populating rates of the trap are very much like what is expected for the populating rates of the exciton sublevels on the basis of selective spin-orbit coupling, assuming that also in the exciton state C_{2v}-symmetry no longer describes the molecule. However, is was concluded from magnetic field experiments on the triplet exciton phosphorescence emission[9] that a Boltzmann equilibrium does exist over the magnetic sublevels in a magnetic field. This apparent contradiction can be explained by our earlier finding[4] that in DBN different triplet excitons exist with very different lifetimes. Long lived excitons are responsible for the phosphorescence emission. A Boltzmann distribution exists between the triplet sublevels of these excitons. As shown by our time-resolved experiments, also triplet excitons exist with an extremely short lifetime (< 1 μs). It was proved that the latter species are mainly responsible for populating the traps studied here. Therefore these findings are completely in agreement with the conclusions obtained now from the values of the relative populating rates, showing that these excitons are trapped so quickly that no Boltzmann equilibrium over the triplet sublevels can be reached within their lifetime. These experiments therefore support our previous conclusion that excitons exist in DBN with an extremely short lifetime.

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