

## WAVELENGTH-DEPENDENT TRIPLET STATE POPULATING MECHANISMS OF NAPHTHALENE IN HEAVY-ATOM HOSTS

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We have made zero-field optically-detected magnetic resonance measurements on the triplet state of naphthalene- $d_8$  incorporated in the heavy-atom host crystals *p*-dichlorobenzene, *p*-dibromobenzene, and *s*-tetrachlorobenzene. The dependence of the relative triplet sublevel populating rates on the exciting wavelength is interpreted in terms of the electronic excitation transfer mechanisms. We find that upon excitation of the host  $S_1 \leftarrow S_0$  transition in *p*-dichlorobenzene, energy transfer to the guest  $T_1$  takes place via the guest  $S_1$ , whereas in the other host crystals the intermediate is mainly the host  $T_1$  band. Upon host  $T_1 \leftarrow S_0$  excitation, trapping takes place from a spin-aligned exciton band in *s*-tetrachlorobenzene, whereas the initial alignment is lost prior to trapping in the dihalobenzene hosts.

### 1. Introduction

In recent years, the method of optically detected magnetic resonance (ODMR) of phosphorescent triplet states [1–4] has been extensively used for measuring the kinetic parameters of individual sublevels [5–11]. In particular, the determination of the relative populating rate constants of the triplet sublevels gives important information about the selective intersystem crossing pathways in isolated molecules. In this communication, we report on the use of relative populating rate constants of the triplet sublevels to distinguish between different triplet populating mechanisms. The system which we will focus on most closely is naphthalene- $d_8$  dissolved in a single crystal of 1,4-dichlorobenzene (DCB). The ordering of the energies is  $T_1(G) < T_1(H) < S_1(G) < S_1(H)$ , where G is the guest, and H is the host. In this system, depending upon the exciting wavelength, it is possible to populate  $T_1(G)$  either by energy transfer from the host  $T_1$  band, or by internal intersystem crossing.

These two mechanisms are expected to lead to differing relative populating rates of the sublevels of  $T_1(G)$ . Having established different populating patterns from the two populating mechanisms, it is then possible to assess the principal populating mechanism of  $T_1(G)$  which results from direct excitation of the host singlet,  $S_1(H)$ . In this case, the possibilities are  $S_1(H) \rightarrow T_1(H) \rightarrow T_1(G)$ , and  $S_1(H) \rightarrow S_1(G) \rightarrow T_1(G)$ . We find that the latter mechanism dominates in our samples of naphthalene- $d_8$  in *p*-dichlorobenzene, while the former mechanism appears more important for naphthalene- $d_8$  in *p*-dibromobenzene (DBB), and in *s*-tetrachlorobenzene (TCB). We also observe that spin alignment of the triplet excitons in TCB is maintained during the time interval required for trapping, whereas spin alignment is lost in the triplet exciton bands of the *p*-dihalobenzenes prior to trapping.

### 2. Experimental

All materials were purified by extensive zone refining (200–300 passes) and single crystals were grown by the Bridgman method. Samples were mounted in a helical slow-wave structure which terminates a coaxial microwave transmission line and is immersed

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in a liquid helium dewar kept at ca. 1.3°K by pumping. The sample was optically pumped either continuously using a PEK, Inc. 100 W high pressure Hg lamp filtered by a 1/4 meter Bausch & Lomb monochromator, or using flash excitation from a PEK, Inc. X-80 xenon flashlamp filtered with the appropriate interference filter. The 0,0-band of the naphthalene phosphorescence was selected with a McPherson, Inc. Model 2051 one meter grating monochromator fitted with a cooled EMI, Inc. Model 9558QA photomultiplier. The measurement of relative populating rate constants using microwave-induced phosphorescence transients during cw optical pumping has been described previously [10] as has their measurement using flash excitation methods [11]. All measurements were made in the absence of an externally applied magnetic field.

### 3. Results and discussion

The relative populating rates of the individual triplet sublevels of naphthalene- $d_8$  in DCB resulting from cw excitation and flash excitation methods are summarized in table 1. In the cw excitation method [10], the relative populating rates are calculated using the observed decay constants of the individual triplet sublevels (which will be reported in a forthcoming communication [12]) assuming that spin-lattice relaxation (SLR) effects are absent. The relative steady-state populations, however, are given correctly by this method even if SLR affects the decay constants. On the other hand, the flash excitation method [11] gives the relative populating rate constants correctly even in the presence of SLR. The

steady-state populations are calculated assuming negligible SLR. A comparison of the steady-state populations arising from 310 nm cw excitation with those calculated from flash excitation (assuming negligible SLR) shows that significant  $T_z \leftrightarrow T_y$  relaxation occurs at 1.3°K. The striking result, however, is the strong dependence of the relative populating rate constants on the exciting wavelength. Excitation at 340 nm (host  $T_1 \leftarrow S_0$ ) leads to approximately equal populating rates of the guest triplet sublevels, whereas excitation at 310 nm (guest  $S_1 \leftarrow S_0$ ) and at 280 nm (host  $S_1 \leftarrow S_0$ ) leads to experimentally indistinguishable results with  $p_y > p_z > p_x$ . Any significant competition of the energy transfer process  $S_1(H) \rightarrow T_1(H) \rightarrow T_1(G)$  with the predominant process,  $S_1(H) \rightarrow S_1(G) \rightarrow T_1(G)$ , would have resulted in distinguishable rates using 310 nm and 280 nm excitation.

We have made cw measurements on naphthalene- $d_8$  dissolved in DBB, and in TCB single crystal hosts. In the DBB host we find no excitation wavelength dependence of the steady-state populations of the triplet sublevels. We find  $p_x:p_y:p_z \approx 4:3:3$ , although these values which are obtained from cw measurements are undoubtedly influenced by SLR. The naphthalene  $S_1 \leftarrow S_0$  could not be excited in DBB due to the intense overlapping host  $T_1 \leftarrow S_0$  absorption. Since excitation of the host  $S_1 \leftarrow S_0$  transition leads to the same steady-state naphthalene sublevel populations as does excitation of the host  $T_1 \leftarrow S_0$  transition, it is reasonable to assume that energy transfer to the guest occurs mainly by the route,  $S_1(H) \rightarrow T_1(H) \rightarrow T_1(G)$ .

Excitation of the host  $T_1 \leftarrow S_0$  transition (330 nm) in TCB doped with naphthalene- $d_8$  gives the relative

Table 1  
Relative populating rates and steady-state populations of naphthalene- $d_8$  triplet sublevels in *p*-dichlorobenzene <sup>a)</sup>

$\lambda_{exc}^{b)}$ (nm)	Steady-state populations (%)			Populating rates (%)		
	$n_x^0$	$n_y^0$	$n_z^0$	$p_x$	$p_y$	$p_z$
340 (cw)	12.4	55.4	32.2	31.7	32.1	36.2
310 (cw)	4.6	64.2	31.2	14.2	44.2	41.6
280 (cw)						
310 (flash)	4.4	73.4	22.2	14.4	54.1	31.5

<sup>a)</sup> Principal axes of naphthalene are:  $x$  – out-of-plane,  $y$  – in-plane long axis; <sup>b)</sup> for cw measurements,  $n_{\mu}^0$  are correct while  $p_{\mu}$  are inferred assuming negligible SLR; for flash measurements,  $p_{\mu}$  are correct, while  $n_{\mu}^0$  are inferred assuming negligible SLR.

populating rates  $p_x:p_y:p_z \approx 1:1:4$  of the guest triplet sublevels, whereas excitation at 314.5 nm (primarily guest  $S_1 \leftarrow S_0$ ) leads to  $p_x:p_y:p_z \approx 1:5:6$ . Excitation at 280 nm (host  $S_1 \leftarrow S_0$ ) results in populating rates which are qualitatively in agreement with those found for excitation at 330 nm, which is in contrast with the results of the 1,4-dichlorobenzene host. It can be concluded that energy transfer to the triplet state of naphthalene in the TCB host occurs to a significant extent via  $S_1(H) \rightarrow T_1(H) \rightarrow T_1(G)$ . TCB is an example of a 1-dimensional exciton crystal [13] in that the strongly interacting molecules are translationally equivalent. Since the triplet energy propagates via an exchange interaction primarily between equivalent molecules, the loss of spin alignment with respect to the molecular axis system is expected to be inefficient\*. It is interesting to note that in TCB doped with naphthalene, 65–70% of the energy transfer from the triplet exciton band occurs to the  $T_z$  sublevel, indicating that trapping occurs more rapidly than the loss of spin alignment of the exciton†. Since the naphthalene concentration is estimated as  $\approx 0.5\%$ , the triplet exciton can move over at least 100 sites (along a chain) while retaining spin alignment. These results are in contrast with those found for the 1,4-

\* Francis and Harris [14] have observed the retention of spin alignment in the TCB triplet exciton band by observing the effect of saturating the exciton magnetic resonance on the  $\gamma$ -trap emission.

† The preference of the populating rate for the  $T_z$  sublevel of naphthalene in TCB is surprising in light of some recently reported work on TCB assigning the orbital symmetry of  $T_1$  as  ${}^3B_{1u}$  [15]. We would expect then that the  $T_y$  sublevel of TCB is mainly responsible for the electronic  $T_1 \leftarrow S_0$  absorption intensity. Since our crystals show no exciton phosphorescence, the alignment of the exciton triplet should prefer  $T_y$ ; the corresponding spin sublevel of naphthalene should have the highest populating rate. There are several possible explanations for this discrepancy: (i) the naphthalene axes may be rotated relative to TCB; (ii) the TCB  $T_1 \leftarrow S_0$  absorption could have considerable  $b_{3g}$  vibronic activity, which would result in  $T_z$  alignment; (iii) trapping might occur preferentially to guest molecules in adjacent chains; and (iv) excitation at 330 nm could possibly be mainly  $T_2 \leftarrow S_0$ , where  $T_2$  might reasonably be  ${}^3B_{2u}$ , resulting in  $T_z$  activity (the origin of  $T_1$  is at  $\approx 370$  nm). Further experiments are in progress to help clarify this point.

dihalobenzene hosts in which considerable exchange interaction between translationally non-equivalent sites is expected ††.

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†† Cheng et al. [16] have reported also that the populating rates of naphthalene- $d_8$  sublevels in DBB are approximately equal indicating that the DBB spin alignment is relaxed prior to trapping.

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