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Singlet-Triplet Absorption Spectra of Crystalline Chrysene and Fluoranthene

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The precise measurement of the absorption spectra of the spin-forbidden $S_0 - T_1$ electronic transitions in aromatic molecular crystals is usually only possible if some indirect method is used. The mutual annihilation of mobile triplet excitons in such crystals can give rise to delayed fluorescence and the excitation spectrum of this kind of emission can be related to the $S_0 - T_1$ absorption spectrum[1]. In some cases, however, the quantum yield of delayed fluorescence may not be sufficiently high to allow measurement of the excitation spectrum. Such a low yield can be due either to a low value of the triplet exciton lifetime (due e.g. to impurity quenching) or to a low value of the quantum yield of fluorescence.

An alternative method of measuring the $S_0 - T_1$ absorption spectrum involves the introduction of a suitable guest material into the crystal and subsequent measurement of the excitation spectrum of the guest phosphorescence[2]. The guest is chosen so that it effectively traps triplet excitons i.e. its triplet level must lie sufficiently below the triplet exciton band of the host crystal. At the same time the guest substance itself should have a high quantum yield of phosphorescence in the matrix isolated state. At low guest concentrations direct excitation of the guest triplet state can be neglected and indirect population takes place via the triplet exciton band of the host crystal. Consequently the observed guest phosphorescence depends linearly on the $S_0 - T_1$ absorption of the crystal (at the low intensities of excitation considered here, triplet exciton kinetics are dominated by monomolecular processes).

Pyrene (T_1 16,800 cm^{-1} [3]) was employed as the guest substance in both chrysene and fluoranthene. The polycrystalline samples containing ca. 10^{-3} mole/mole pyrene were cooled in liquid nitrogen in order to reduce the rate of thermal release of trapped triplet states into the exciton band and the red pyrene phosphorescence was measured as a function of the excitation wavelength (slit width 2 nm) in a conventional phosphoroscope arrangement. The excitation spectra obtained in this way were normalised linearly to constant excitation quantum flux density. By way of comparison the phosphorescence spectra of both chrysene and fluoranthene in methyl cyclohexane were measured and corrected for monochromator and photomultiplier characteristics.

The spectra obtained are shown in Fig. 1 and the positions of the vibrational peaks are listed in Table 1. A small red shift in the $0-0$ transition on going from the isolated molecule to the crystal is

Table 1. Singlet-triplet transitions in chrysene and in fluoranthene (cm^{-1}).

Chrysene				*Fluoranthene*			
$T_1 \leftarrow S_0$		$T_1 \leftarrow S_0$		$S_0 \leftarrow T_1$		$S_0 \leftarrow T_1$	
ν	$\Delta\nu$	ν	$\Delta\nu$	ν	$\Delta\nu$	ν	$\Delta\nu$
19960	0	20060	0	18587	0	18518	0
20242	282	19782	273	18955	368	18215	303
20534	574	19493	567	19157	570	17953	565
21277	1317	18709	1351	19342	755	17730	788
21552	1592	18450	1610	19801	1214	17361	1157
21810	1850	18149	1911	20080	1493	17094	1424

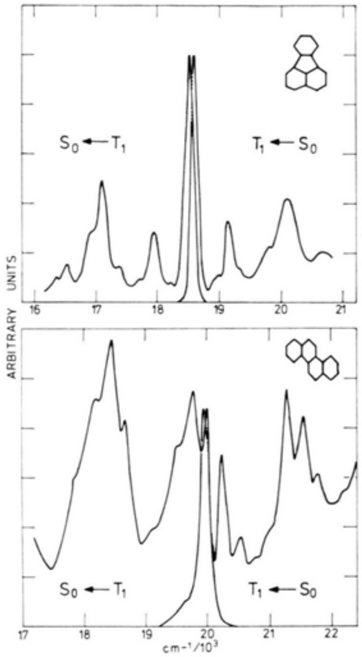

Fig. 1. Corrected excitation spectra of guest (pyrene) phosphorescene in crystalline chrysene and crystalline fluoranthene at 77 K. Also shown are the corrected phosphorescence spectra of the two substances in methyl cyclohexane at 77 K (see Table 1 for position of vibrational maxima).

evident in the case of chrysene, reflecting the intermolecular interaction in the crystal phase. The apparent blue shift observed for fluoranthene must be interpreted as a red shift of the phosphorescence relative to the absorption origin. Such behaviour is commonly attributed to a change in molecular geometry which follows electronic excitation. We have found a similar shift between the origin of the $S_1 \leftarrow S_0$ absorption and the $S_0 \leftarrow S_1$ emission in fluoranthene crystals[4]. In this case the shift is somewhat larger (ca. 250 cm^{-1}). These results provide evidence for the suggestion made by Berlman et al.[5] that fluoranthene and its derivatives may be nonplanar in the excited state.

The reported value of 18,316 cm^{-1} for the triplet origin in crystalline chrysene[6] (based on the phosphorescence at low temperatures) is incorrect. We have attempted to detect crystal phosphorescence in chrysene at room temperature but were unable to resolve the very weak emission from the flank of the delayed fluorescence. The difficulties involved in the detection of the phosphorescence of pure organic crystals have been discussed elsewhere[7]. The overlap between phosphorescence and delayed fluorescence is most severe for substances with a small energy difference between the S_1 and T_1 states and it is interesting to note at this point that we experienced no difficulty in detecting the exciton phosphorescence of crystalline pyrene using the same experimental arrangement[7]. By cooling the chrysene sample to 77 K we detected a weak emission centred at approximately 18,500 cm^{-1} and we attribute this to impurity centres which act as triplet exciton traps at low temperatures.

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