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Abstract—Evidence is presented to confirm triplet excimer emission from halogenated benzene crystals. The emission is not due to photochemical impurities or other effects provided the samples are in vacuum. It is shown that the excimer phosphorescence maxima shifts substantially to lower energy from crystal to solid solution, probably due to a reduction in the repulsive potential in the dimer ground state from solution to crystal. The triplet excimer energy levels in solution and in single crystals are presented for several symmetrically substituted halogenated benzenes and some qualitative data presented for the distribution of the excitation energy in the monomer and dimer triplet manifold.

1. Introduction

The low temperature spin-forbidden emission spectra of the halogenated benzene single crystals show two distinct systems(1,2)

(i) a narrow band system with band widths (full width at half maximum) about 2 cm^{-1}. This system corresponds to emissions from triplet exciton energy levels. It is analysed in terms of ground state vibrational progressions built either on the triplet exciton origin level (identified by $T_1 \leftarrow S_0$ absorption spectra) or on trapped triplet exciton levels.(2,3)

(ii) a broad structureless band with full width at half maximum about 4000 cm^{-1}. This band has a maximum emission intensity several thousands of wavenumbers below the triplet exciton origin band.

Castro and Hochstrasser(1) (C–H) first reported this low energy emission from crystals and interpreted it as triplet excimer emission. Such an emission has been established for aromatic hydrocarbons in concentrated solution.(4) Further, there is recent evidence of excimer phosphorescence from pyrene crystals(5) as well as the well established excimer fluorescence.(6) However the C–H assignment of this emission from halobenzene crystals to a triplet excimer emission has been questioned by Lim and Chakrabarti(7) (L–C). On the basis of their emission spectra of frozen solutions of chlorobenzene and of *p*-dibromobenzene L–C concluded that (a) triplet excimer emission occurs at lower energy than reported for single crystals by C–H (b) the C–H crystal emission spectra results from photoproducts as evidenced by emission experiments on *p*-dibromobenzene in a rigid glass. These showed a time-dependent intensity which corresponded to a photoproduct emission.

In our studies of the properties of the triplet exciton in halobenzene crystals, we have data which clarifies the above important controversy. From our emission spectra of single crystals and frozen solutions of several symmetrically halogenated benzenes, we conclude that the broad structureless emission from the crystal does not result from photochemical impurities. Our results are consistent with a C–H model of triplet excimer emission, provided the experiments are carried out in high vacuum with ultra-pure crystals. In the case of 1,4-dibromobenzene, an emission lower in energy is observed when air is admitted to the crystal environment. Further, we present quantitative data on the triplet excimer energy level in solution and in the crystal.

2. Experimental

The apparatus and crystal purification and preparation have been described before.(2)

3. Results and Discussion

To assess possible photochemical effects on the low temperature emission properties of the halogenated benzene single crystals, studies have been carried out on ultrapure crystals after UV irradiation in a vacuum of 10^{-5} to 10^{-6} mm Hg, and also in air. Prolonged irradiation has already been reported to show no effect on the emission spectrum at 4.2 K.(2) In Fig. 1 are shown the phosphorescence decay curves of hexachlorobenzene (HCB) and *p*-dibromobenzene (DBB) single crystals at 293 K(a) under vacuum and (b) after air was admitted to the sample. A broad band (500 nm) of emission was monitored. Under vacuum conditions the experimental phosphorescence lifetimes are $t_p(\mathrm{HCB}) = 2.4$ ms; $t_p(\mathrm{DBB}) = 0.38$ ms. When air is admitted to the sample, the decay curve of HCB is unaltered, but the decay curve of DBB shows a much longer component in the emission with $t_p \simeq 20$ ms. This change in the emission properties of DBB is most striking, as the intense blue emission from the crystal in vacuo is replaced by a green emission in air. Such photochemical sensitivity of the *p*-dihalobenzenes is not unexpected. *p*-Diiodobenzene has been found (in studies of undegassed solutions at room temperature) to be photodissociative in the triplet state.(8)

The observation of the sensitivity of the emission spectrum of DBB to the surrounding atmosphere deserves more study but it is suggestive of needed care in data interpretation when undegassed solutions of DBB are used to study emission phenomena.

In Table 1 are shown our results for the energies of the maxima

TABLE 1 Triplet Excimer Phosphorescence from Halogenated Benzenes

Sample†	$\bar{\upsilon}$(cm^{-1}) (" Monomer " Phos)	$\bar{\upsilon}$ (Excimer Phos)	$\Delta\bar{\upsilon}$ (" Monomer " Excimer)	1‡ (Å)	1 cos θ §
HCB	25684	22989	2695	3.87	3.64
HCB (Solution)	(25684)	20408	5276	—	—
DBB	27910	24558	3352	4.10	3.55
DBB (Solution)	(27910)	22000	5910	—	—
DCB	27890	22046	5844	3.90	3.60
TCB	26675	23923	2752	3.85	3.50‖
TBB	27457	23095	4362	4.08	3.83

† All samples are crystalline unless indicated.

‡ 1 is the crystal axis length along direction of planar overlap of molecules. (For HCB this is *b*, for all others *c*.)

§ θ is the angle between the *N* molecular axis and *1*.

‖ Based on data for monoclinic TCB. At 4.2 K, TCB is triclinic.

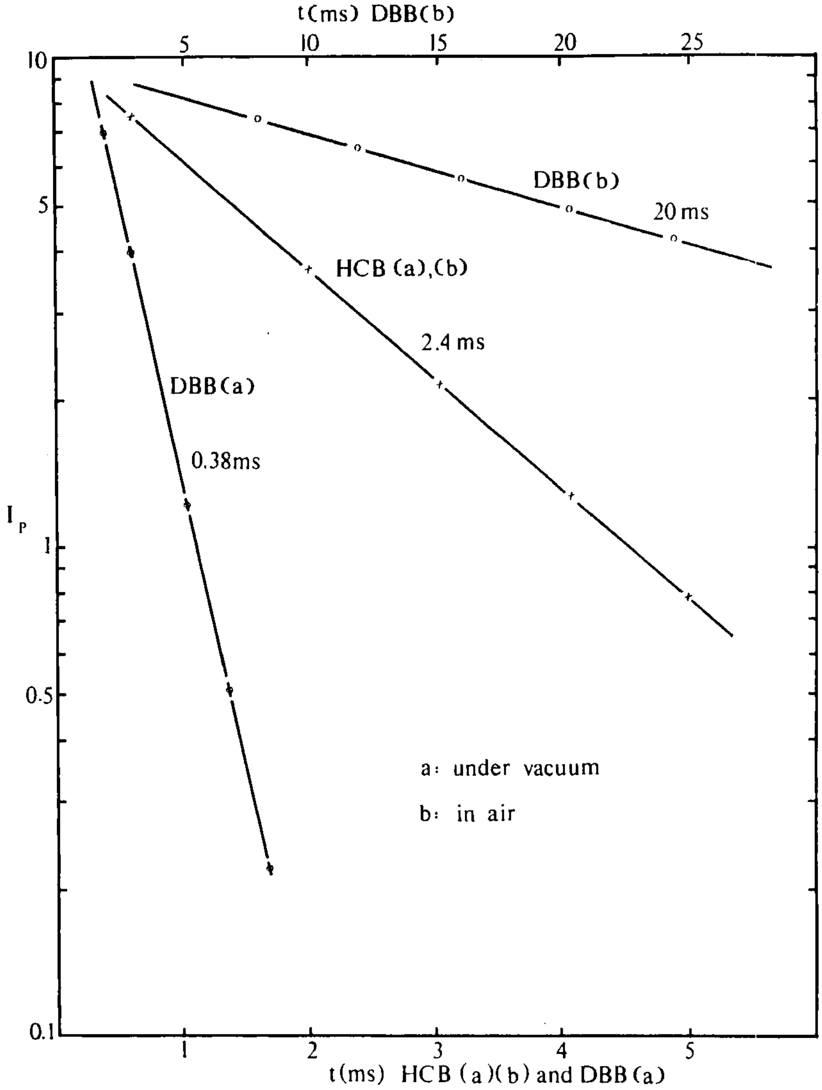

Figure 1. The time dependence of phosphorescence intensity from single crystals at 293 K of hexachlorobenzene (HCB) and 1,4-dibromobenzene (DBB) (a) under vacuum (b) in air.

of the broad emission bands from crystals of hexachlorobenzene (HCB); 1,4-dibromobenzene (DBB); 1,4-dichlorobenzene (DCB); 1,2,4,5-tetrachlorobenzene (TCB) and 1,3,5-tribromobenzene (TBB) as well as frozen solutions of DBB and HCB at 77 K. The emission spectra were independent of the excitation wavelength within the $T_1 \leftarrow S_0$ or $S_1 \leftarrow S_0$ regions. The monomer emissions at 77 K in the rigid glass [methylcyclohexane : isopentane (5 : 1)] have $T_1 \leftarrow S_0$ origins which agree to within 3 cm^{-1} with the $T_1 \leftarrow S_0$ absorption origins at 4.2 K. However, the *excimer phosphorescence maxima shifts substantially to lower energy on passing from the crystal to a rigid glass* for those systems (HCB and DBB) studied. This shift (~2560 cm^{-1}) from crystal to solution is identical for DBB and HCB within the experimental uncertainty of measuring the peak of a broad emission band. Such a shift to lower energy is opposite to the shift observed for the singlet energy levels on passing from solution to crystal for aromatic hydrocarbons and haloaromatics.(9) But a similar shift to lower energies of the singlet excimer energy level on going from crystal to solution has been observed for anthracene(10) and pyrene.(11) This suggests to us that the shift to lower energies from crystal to solution is a characteristic of both triplet and singlet excimer emission, and is not, as Lim and Chakrabarti suppose, an indication of spurious emission from the crystal.

The lower energy shift is probably due to a reduction in the repulsive potential in the dimer ground state on passing from solution to crystal. In Fig. 2 is shown the total delayed emission spectrum of a $5 \times 10^{-4} M$ solution of DBB in a methylcyclohexane : isopentane glass (5 : 1) at 77 K. Also shown is the potential energy of the ground and the excited states of an excimer, E, as a function of r, the monomer separation.(12) R and R' represent the repulsive potentials in the dimer ground and excited state respectively; V' is the excimer attractive potential (for a singlet excimer V' would be expected to result from dipole–dipole and charge resonance interactions, while in the triplet excimer these would be electron exchange and charge transfer interactions); D_M and D_0 are the energies of the emission maximum and the band edge respectively. The net excimer binding energy, B, [$= (V' - R)$ at $r = r_m$] is related to the experimental observables D_M and D_0 by $B = D_M - D_0$. This is indicated on the experimentally observed spectrum. Using the

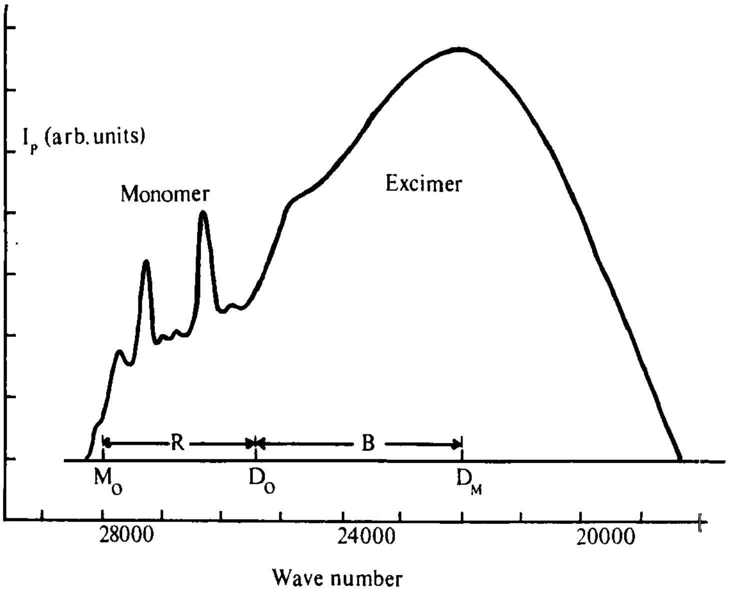

Figure 2 (a). The phosphorescence spectrum of 1,4-dibromobenzene (DBB) in a methylcyclohexane: isopentane glass (5 : 1) at 77 K. The symbols are explained in the text.

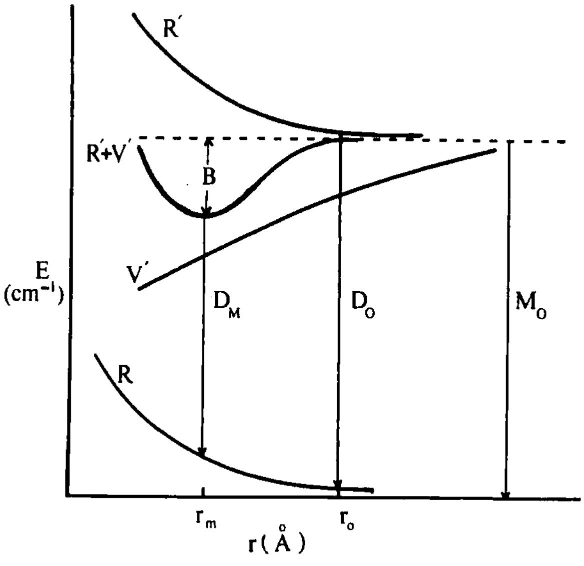

Figure 2 (b). Potential energy diagram for an excimer. The symbols are explained in the text.

assumption of Birks and Christophorou(12) that $R(r_m) \approx R(r_0)$ the excimer binding energies B, and the repulsive potential, R, may be compared for the crystal and solution (Table 2).

TABLE 2 Net Excimer Binding Energies ($D_0 - D_m$) and Repulsive Energies (R) in cm^{-1}

	Solution		Crystal	
	$D_0 - D_m$	R	$D_0 - D_m$	R
DBB	3500	2560	3350	0
HCB	2690	2560	2695	0
DCB	—	—	3432	2410

We note that for DBB and HCB, the net excimer binding energies in the frozen solution and the crystal are identical and that the shift in the broad band maximum results from a difference in the repulsive potential in the dimer ground state on passing from the solution to the crystal. The attractive potential in the dimer ground state (due to long range dispersion forces) may be of similar magnitude to R and thus reduce the potential(12) in the crystal. In not all crystals studied, however, was R observed to be approximately zero.

Excimer emission in frozen solutions is most readily observed when there is a slightly distorted sandwich configuration of the solute molecules.(13,14) For halobenzene single crystals, such a configuration of molecules is best achieved by molecules stacked along the *b* crystal axis (HCB) and *c* crystal axis (other halobenzenes), as seen from Table 1. In view of the overlap possible, intermolecular interaction energies between these translationally equivalent molecules will be large and rapid triplet exciton migration will occur along this axis. Since the excimer triplet energy level is lower than the monomer triplet energy level, then, following absorption, a radiationless process to the excimer energy level must occur.(13) Energy localization on a discrete pair of molecules must occur within the radiative lifetime of the triplet exciton. This might occur at a defect site or similar point in the crystal,(15) where the triplet exciton may be trapped. Although we have not studied in detail all the quantitative aspects of the degradation paths of the excitation energy in these crystals, some pertinent results have been obtained. Thus at 4.2 K, in HCB, TCB and DBB, the observed phosphorescence originates from trap levels 20 to 50 cm^{-1} below the triplet exciton energy level, but in DCB and TCB triplet exciton phosphorescence is observed.⁽³⁾ The striking feature is that the triplet *excimer* emission from DCB and TBB is *intense* at 4.2 K while that from HCB, TCB and DBB is much weaker at 4.2 K. But on warming these latter crystals above 4.2 K and so depopulating the triplet trap levels, triplet exciton emission is observed and the *triplet excimer emission intensifies relative to the monomer* emission. Obviously, the exciton has to be mobile prior to strong excimer phosphorescence.

In conclusion then, we believe there is no reason to doubt that triplet excimer emission is observed in these crystal systems. The observed low temperature phosphorescence spectrum of halogenated benzene single crystals is explicable by competition between:

(i) triplet exciton trapping leading to defect phosphorescence;
(ii) triplet exciton localization leading to excimer phosphorescence;
(iii) intrinsic triplet exciton phosphorescence.

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