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The Absorption, Fluorescence and Phosphorescence of Single Crystals of 1,2,4,5-Tetrachlorobenzene and 1,4-Dichlorobenzene at Low Temperatures

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Abstract—The emission spectra of ultra pure single crystals of 1, 2, 4, 5-tetrachlorobenzene (TCB) and 1, 4-dichlorobenzene (DCB) at temperatures from 4.2 °K upwards are reported. In addition, by use of the phosphorescence excitation technique the singlet-triplet absorption spectrum at 4.2 °K has been obtained.

The phosphorescence emission of TCB at 4.2 °K occurs predominantly from a defect origin " X " situated 48 cm^{-1} below the triplet exciton band. The triplet exciton energy level is at 26676 cm^{-1} from both emission and absorption studies. This is the triplet emission origin when the crystal is above 12 °K. The temperature dependence of the emission intensity from the defect has an activation energy of 40 ± 8 cm^{-1}. This value is consistent with our suggestion of thermal depopulation of the traps.

Single crystals of DCB show strong excimer emission and weak triplet exciton emission. There is no evidence for trapping levels. The triplet exciton origin is 27890 cm^{-1} from both emission and absorption studies.

Weak fluorescence ($\phi_F < 10^{-2}$) is detected from both TCB and DCB.

Vibrational analyses are reported for the absorption, fluorescence and phosphorescence spectra.

1. Introduction

Recent studies of the low lying triplet and singlet electronic excited states of single crystals of the p-dihalogenated benzenes⁽¹⁾ and hexachlorobenzene⁽²⁾ have led to an understanding of the symmetry of the triplet state, possible spin-orbit coupling routes, crystal field

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effects and triplet exciton band structure. In particular, the phosphorescence of hexachlorobenzene single crystals at 4.2 °K has been explained in terms of emission from localized exciton states approximately 40 cm^{-1} below the triplet exciton band.(2) Above this temperature, emission occurs from the triplet exciton origin and from lower lying traps. The only other detailed report of the phosphorescence spectrum from a halogenated benzene crystal is that for 1,4-dibromobenzene.(1) That spectrum was interpreted solely in terms of triplet exciton emission.

To extend these studies of singlet ↔ triplet transitions and, in particular, to understand the role of exciton trap levels in organic crystals, we have investigated the emission spectra of ultra pure single crystals of 1,2,4,5-tetrachlorobenzene and 1,4-dichlorobenzene. In addition, the phosphorescence excitation technique is used to obtain $T_1 \leftarrow S_0$ absorption spectra.

There is very little existing information on the absorption or emission properties of 1,2,4,5-tetrachlorobenzene (TCB). Hirota(3) and Marchetti and Kearns(4) have reported the $T_1 \leftarrow S_0$ absorption spectrum by phosphorescence excitation of naphthalene-doped crystals of TCB at 77 °K. The (0—0) band of phosphorescence from a frozen solution of TCB was established to be about 25400 cm^{-1} but no spectrum was published.(3) Pesteil *et al.*(5) have measured the unpolarized $S_1 \leftarrow S_0$ absorption of a single crystal of TCB and assigned the origin as 33855 cm^{-1}. No fluorescence has been reported.

The excited singlet and triplet states of *p*-dichlorobenzene (DCB) have been studied in detail by Castro and Hochstrasser.(1) While the phosphorescence origin is quoted as 27890 cm^{-1} (in agreement with the $T_1 \leftarrow S_0$ origin) details of the spectrum are not reported.

2. Experimental

1,2,4,5-tetrachlorobenzene (Eastman P1445) and 1,4-dichlorobenzene (B.D.H.) were recrystallized from purified absolute ethanol, vacuum sublimed and zone refined. After sixty zone passes the central fraction was transferred in vacuo to another zone refining tube and subjected to a further one hundred passes. Crystals were melt grown in a Bridgman furnace from the central fraction of the final material.

Freshly cleaved crystals were conoscopically examined, oriented and mounted in a liquid helium cryostat. Standard spectroscopic techniques as described in previous papers(2,6) were employed. Singlet-triplet absorption spectra were obtained from the excitation spectrum of pure crystal phosphorescence.

3. Molecular and Crystal Symmetry

Both DCB and TCB are planar with point group symmetry $D_{2h}(V_h)$.(1,7) DCB crystallizes in the space group $C_{2h}^5(P2_1/a)$ with $Z=2$.(8) At temperatures above 303.8 °K DCB exists in a triclinic (β) form. All investigations were carried out on the monoclinic (α) form. The principal cleavage plane is (100). At 300 °K TCB is monoclinic ($P2_1/a$) with $Z=2$. Below 188 °K it exists in a triclinic (α) form.(9) Crystal studies at 150 °K suggest that the space group is $C_i(P\bar{1})$ with $Z=2$.(10) All studies on TCB were carried out on the triclinic (α) form. Cleavage is expected to be (001).(10)

The orthogonal molecular axes L, M and N are chosen with $L(z)$ along the H–H axis (TCB) or Cl–Cl axis (DCB), $N(x)$ normal to the molecular plane and $M(y)$ in the plane of the molecule and perpendicular to the (xy) plane i.e. bisecting the C–C bond. This leads to the spectroscopically significant symmetry designations in D_{2h} of $B_{1u}[L(z)]$; $B_{2u}[M(y)]$; $B_{3u}[N(x)]$.

4. Results and Discussion

4.1. Phosphorescence Spectra

4.1.1. *Phosphorescence of* 1,2,4,5-*tetrachlorobenzene*. The $T_1 \rightarrow S_0$ emission spectrum of TCB is found to be very sensitive to temperature in the region 4.2 °K to 15 °K. A portion of the observed unpolarized spectrum at temperatures of 4.2 °K, 7.5 °K and 12 °K is shown in Fig. 1. Relative intensities and a tentative assignment of the bands are given in Table 1 for temperatures of 4.2 °K and 12 °K.

Extinction directions and crystal orientation are initially determined for the monoclinic (β) form at room temperature. At low temperature these relations of the crystal absorption directions with the crystal axes will be altered. The absorption directions for the

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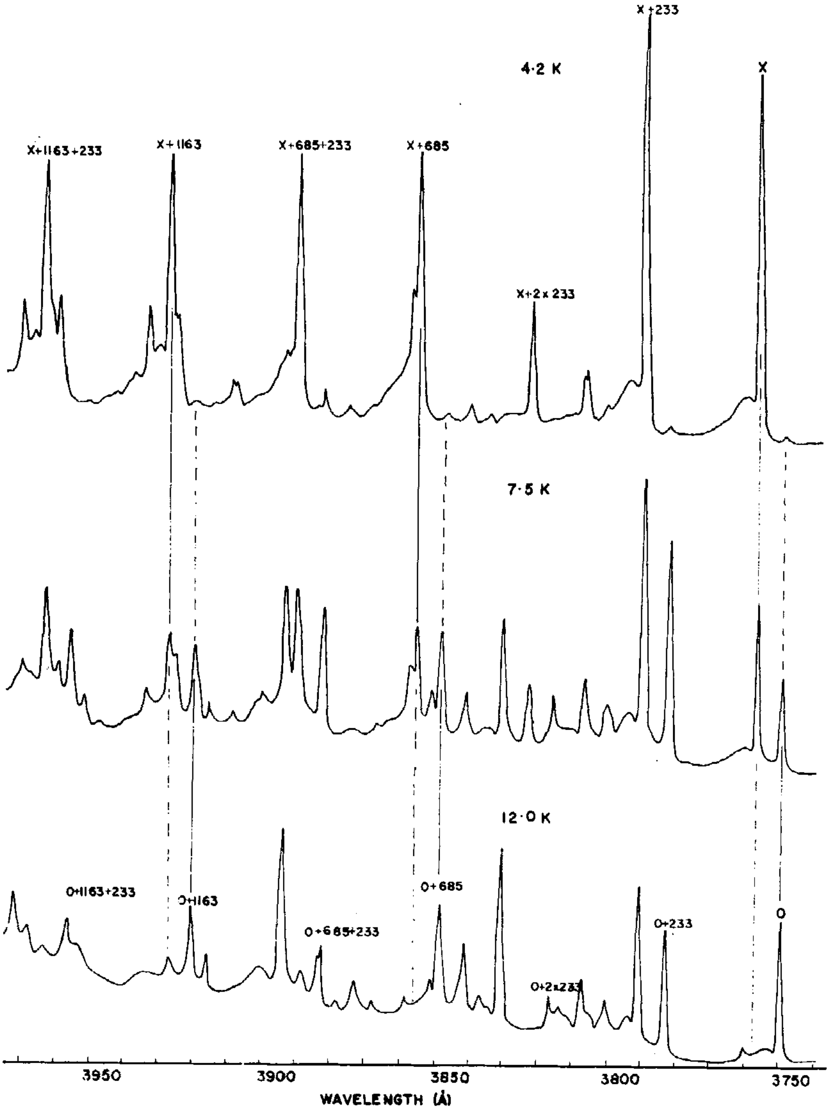

Figure 1. Phosphorescence spectrum of 1, 2, 4, 5-tetrachlorobenzene single crystal at 4.2 °K (a), 7.5 °K (b) and 12 °K (c). Note as the temperature increases the emission intensity redistributes from the trap level " X " (and bands built on this origin) to the triplet exciton origin (0—0) and bands built on this. The broad underlying emission intensity in region 3900–4100 Å in curve *C* results from triplet excimer emission.

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TABLE 1 Analysis of the Phosphorescence Spectrum of 1, 2, 4, 5-Tetrachlorobenzene at 4.2 °K and 12 °K

Rel. int. 4.2 °K	Rel. int. 12 °K	$\bar{\nu}$	$\Delta\bar{\nu}$	Tentative assignment
vvw	s	26676	0	" 0 " EXCITON ORIGIN
—	vvw	26635	41	0 + 41 lattice
vs	—	26628	48	" X " DEFECT ORIGIN
w(dif)	vw	25694	82	0 + 2 × 41
				X + 34 lattice
vw	s	26443	233	0 + b_{2g} fundamental [225]
vvw	—	26425	251	
vs	—	26394	282	X + b_{2g} fundamental [225]
w	vw	26363	313	0 + b_{3g} fundamental [312]
vvw	w	26323	353	0 + a_g fundamental [352]
vw	—	26313	363	X + b_{3g} fundamental [312]
mw	—	26278	398	X + a_g fundamental [352]
—	vvw	26243	433	0 + 353 + 2 × 41
vvw	vvw	26238	438	0 + b_{3u} fundamental [442]
vvw	vw	26208	468	0 + 2 × 233
m	—	26164	512	X + 2 × 233
vw	s	26119	563	
—	vvw	26099	577	0 + 233 + 353
vw	vw	26080	596	
vw	m	26044	632	0 + 2 × 313
vw	ms	25991	685	0 + a_g fundamental [684]
vw	vw	25973	703	0 + 2 × 353
s	—	25943	733	X + a_g fundamental [684]
m	vw	25932	744	X + 2 × 353
w	—	25912	764	
vw	—	25889	787	
—	vvw	25863	813	
—	vw	25823	853	
vw	—	25812	864	0 + 864 b_{2g} fundamental?
w	w	25759	917	0 + 685 + 233
vvw	vw	25743	933	0 + 4 × 233
s	—	25710	966	X + 685 + 233
w	vs	25689	987	0 + 685 + 313
vw	—	25676	1000	
		25642	1034	0 + 685 + 353
vvw	—	25633	1043	X + 685 + 313
vvw	w	25549	1127	0 + 2 × 563
vvw	m	25513	1163	0 + a_g fundamental [1165]
m	—	25480	1196	
s	vw	24467	1209	X + a_g fundamental [1165]
w	—	25441	1235	X + 1163 + 24
m	vvw	25422	1254	X + 1163 + 41
w	—	25398	1278	X + 1163 + 41 + 24
—	vw	25304	1372	0 + 2 × 685
—	w	25279	1397	0 + 1163 + 233
m	—	25258	1418	
s	vw	25233	1443	X + 1163 + 233
mw	vw	25210	1466	X + 1163 + 233 + 22

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triclinic (α) form were determined by rotating the polaroid analyser to give maximum emission intensity. Spectra were recorded parallel and perpendicular to this direction of maximum emission intensity. These directions were only a few degrees rotation from the extinction directions of the monoclinic form.

The unequivocal assignment of the observed vibrational structure is rendered difficult because of the constant polarization properties through the emission spectrum.

In view of this absence of polarization properties the unpolarized spectrum is considered here.

The assignment at 4.2 °K is made in terms of emission occurring predominantly from a " defect " origin, " X ", situated 48 cm^{-1} below the triplet exciton band. The triplet exciton origin is assigned as the very weak emission peak at 4.2 °K at 26676 cm^{-1}. This is confirmed by $T_1 \leftarrow S_0$ absorption (Sec. 4.3). The vibrational progression built on " X " is shown in Table 1. (Ground state Raman frequencies(11,12) are given in brackets.) The most intense bands correspond to the ground state a_g modes 685 cm^{-1} (*C–Cl* stretch) and 1163 cm^{-1} (Ring stretch) and a b_{2g} mode of 233 cm^{-1} (*C–Cl* out of plane bend). Other definite assignments are an a_g fundamental at 353 cm^{-1} and a b_{3g} fundamental at 313 cm^{-1}.

As the temperature is increased from 4.2 °K the origin intensity increases relative to the " defect " origin until at 12 °K almost entirely pure triplet exciton phosphorescence is being observed (see Fig. 1). From Table 1 it is seen that the observed spectrum may be analysed in terms of molecular and lattice vibrations built on the exciton origin " O ". Again the predominant vibrations are two a_g modes and one b_{2g} modes.

The phosphorescence spectrum of *p*-dibromobenzene(1) shows a prominent $n \times b_{2g}$ progression of alternating intensity which indicates the molecule is distorted to C_{2h} symmetry in the triplet state. Similar behaviour might be expected in TCB as the b_{2g} (δC–Cl) vibration carries the molecule to C_{2h} symmetry. This is not observed. The intensity of the (0–$0 + n \times 233$) and ($X + n \times 233$) progressions decrease very rapidly to VVW by $n = 3$ to 4. Other b_{2g} vibrations are not seen e.g. the b_{2g} vibration at 681 cm^{-1} would be obscured by the strong 685 cm^{-1} a_g mode. It is noted that the band 282 cm^{-1} distant from the exciton origin which has been assigned

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as $(X+233)\,(b_{2g})$ does not decrease in intensity on warming from 4.2 °K to 12 °K to the extent that intensity of the defect origin or the a_g vibrations built on this origin decrease. This band could indicate an underlying molecular vibration of 282 cm^{-1} built on the exciton origin " O " or it could mark a lower lying trapping level.

The temperature dependence of the emission intensity from the defect origin " X " is such that a plot of log $(1/I_p)$ against $(1/T)$ is linear [I_p is the phosphorescence intensity of the defect origin " X " and T the crystal temperature in °K]. Taking a relation of the form $1/I_p = C \exp(-\Delta E/kT)$ where C is a constant, an activation energy of 40 ± 6 cm^{-1} is obtained. This value is in reasonable agreement with the energy separation of 48 cm^{-1} between the triplet exciton and defect origins. The temperature dependence of the spectrum in Fig. 1 would seem to be explained in terms of thermal population of the intrinsic triplet exciton band from localized trapped excitons 40–50 cm^{-1} below the exciton band.

This behaviour is very similar to that reported for hexachlorobenzene(2) although in the latter case the presence of a deeper trapping level complicated the interpretation. Various studies have been carried out of trapping levels in the phosphorescence of crystals of pyrazine,(13) naphthalene doped with β-methyl naphthalene, thiophene and durene(14) and biphenyl doped with carbazole and dibenzothiophene.(15) In no case has the triplet exciton origin been observed in emission, presumably because of the rapid triplet exciton-triplet exciton annihilation after the trap is depopulated. In the halogenated benzenes, biexcitonic annihilation is minimized because of the short triplet radiative lifetime (typically 10^{-2} seconds) resulting from enhanced intramolecular spin-orbit coupling from the heavy atom. The increase in triplet exciton origin band intensity is accompanied by the decrease in intensity of the band associated with the trapping level. The activation energy for the process of depopulating the trap is just the spectroscopic separation of the two bands in the emission spectrum.

It is noted that in both hexachlorobenzene and 1,2,4,5-tetrachlorobenzene a similar localized exciton trap depth was observed (40–50 cm^{-1}). The physical interpretation of these traps has been discussed previously.(2)

4.2.2. *Phosphorescence of* 1,4-*dichlorobenzene.* Pure single crystals

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of 1,4-dichlorobenzene show strong triplet excimer emission but weak triplet exciton phosphorescence. This renders a detailed vibrational investigation and polarization study difficult. The phosphorescence spectrum is presented here for comparison with spectra obtained from other halogenated benzenes of D_{2h} point group symmetry TCB and 1,4-dibromobenzene.(1)

In Fig. 2(a) is shown the complete emission spectrum consisting of exciton phosphorescence and triplet excimer(16) emission from the *bc* face of a single crystal of *p*-dichlorobenzene at 4.2 °K. An expanded region of the exciton phosphorescence spectrum is shown in Fig. 2b. A vibrational analysis of the bands in Fig. 2(b) is given in Table 2. Relative intensities are indicated; ground state molecular vibrations from Raman studies(11,17) are included in brackets. As a result of the low emission intensity a greater effective slit width was employed. This results in a loss in resolution and a lower assignment accuracy (± 6 cm^{-1}).

From temperature dependence studies no evidence has been found for trapping levels in the emission spectrum and it is concluded that triplet exciton phosphorescence originates from the first band in the spectrum at 27890 cm^{-1} as shown. This is confirmed by the $T_1 \leftarrow S_0$ absorption spectrum, (Ref. 1 and Sec. 4.3.1).

The most intense vibration is the b_{2g} mode at 310 cm^{-1} which corresponds to the *C–Cl* out-of-plane bend appearing in *p*-dibromobenzene phosphorescence as discussed before. The $n \times 310$ cm^{-1} progression observed alternates in intensity (*cf.* *p*-dibromobenzene) but falls off in intensity much more rapidly and can be followed only to $n=6$. The Franck Condon maximum occurs at $n=1$. The a_g vibrations recognized (330 cm^{-1}, 746 cm^{-1}, 1103 cm^{-1}, 1173 cm^{-1} and 1578 cm^{-1}) are built both on the origin and on the 310 cm^{-1} vibration. Possible b_{3g} vibrations expected to occur at 350 cm^{-1} and 628 cm^{-1}(17) are obscured by the lattice and vibrational structure built on the b_{2g} (310 cm^{-1}) vibration.

4.3. Singlet Triplet Absorption Spectra

4.3.1. $T_1 \leftarrow S_0$ *of 1,4-dichlorobenzene*. The $T_1 \leftarrow S_0$ absorption spectrum of the *bc* face of a single crystal of 1,4-dichlorobenzene at 4.2 °K is shown in Fig. 3. The observed band intensities, polarizations, and vibrational assignments are given in Table 3. Ground state fun-

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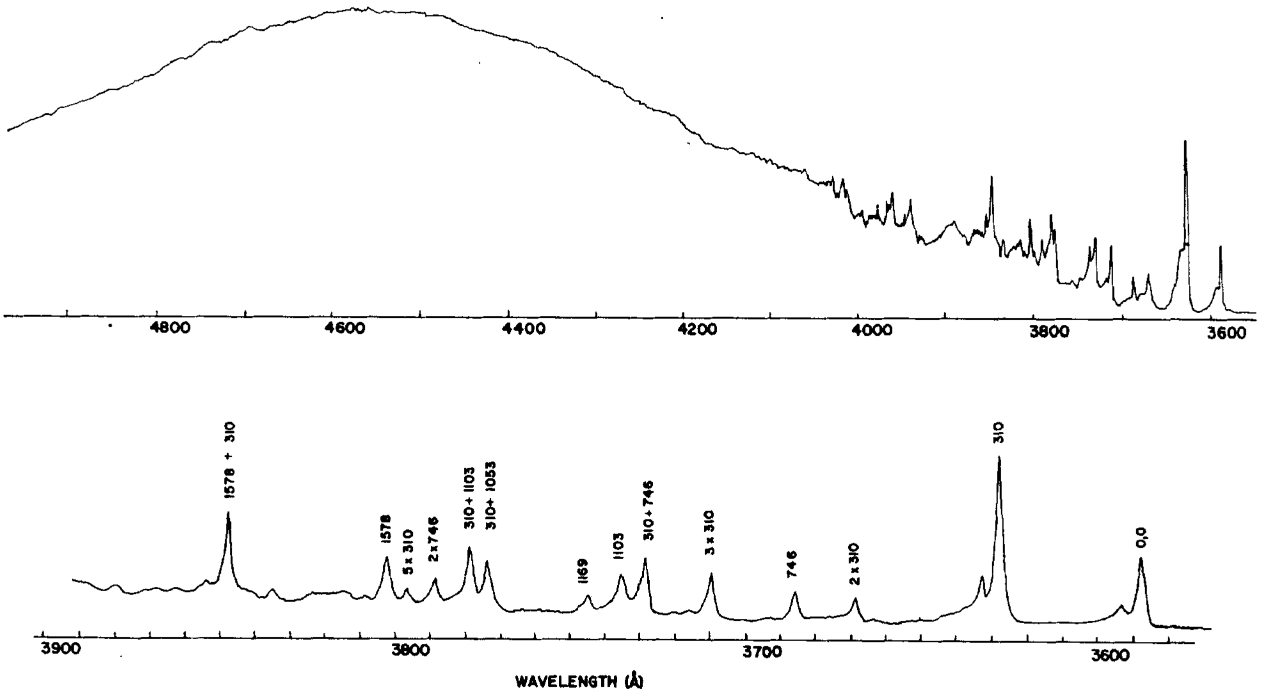

Figure 2. Phosphorescence spectrum of 1, 4-dichlorobenzene single crystal at 4.2 °K. (a) Complete emission spectrum showing the triplet exciton emission and bands associated with this transition and the broad triplet excimer emission centered at 4530 Å. (b) The triplet exciton emission spectrum from 3580 Å to 3900 Å.

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TABLE 2 Analysis of the Phosphorescence Spectrum of 1, 4-Dichlorobenzene Single Crystal at 4.2 °K

Rel. int.	$\bar{\nu}$	$\Delta\bar{\nu}$	Assignment
m	27890	0-0	EXCITON ORIGIN
vw	27840	50	lattice
s	27580	310	b_{2g} fundamental [306]
w	27560	330	a_g fundamental [327]
w	27535	355	310 + 45 or b_{3g} fundamental [350]
vw	27474	416	310 + 2 × 50
w	27274	616	2 × 310
w	27255	635	310 + 330 or b_{3g} fundamental [628]
w	27144	746	a_g fundamental [744]
vvw	27093	797	746 + 50
m	26969	921	3 × 310
vvw	26925	965	310 + 2 × 330
m	26937	1053	746 + 310
m	26787	1103	a_g fundamental [1096]
w	26717	1173	a_g fundamental [1169]
m	26511	1379	1053 + 310 or 1053 + 327 or 635 + 746
m	26474	1414	310 + 1103
w	26403	1487	2 × 746 or 1173 + 310
w	26350	1540	5 × 310
m	26312	1578	a_g fundamental [1577]
vw	26269	1621	1578 + 50
vw	26226	1664	746 + 3 × 310
vw	26175	1715	2 × 310 + 1103
vw	26088	1802	310 + 2 × 746 or 1173 + 2 × 310
vw	26042	1848	6 × 310
m	26008	1882	1578 + 310
w	25957	1933	1578 + 310 + 50
vw	25893	1997	
vw	25867	2023	
vw	25783	2107	2 × 1053
w	25566	2324	
w	25392	2498	1578 + 3 × 310
w	25259	2631	
vw	25208	2682	

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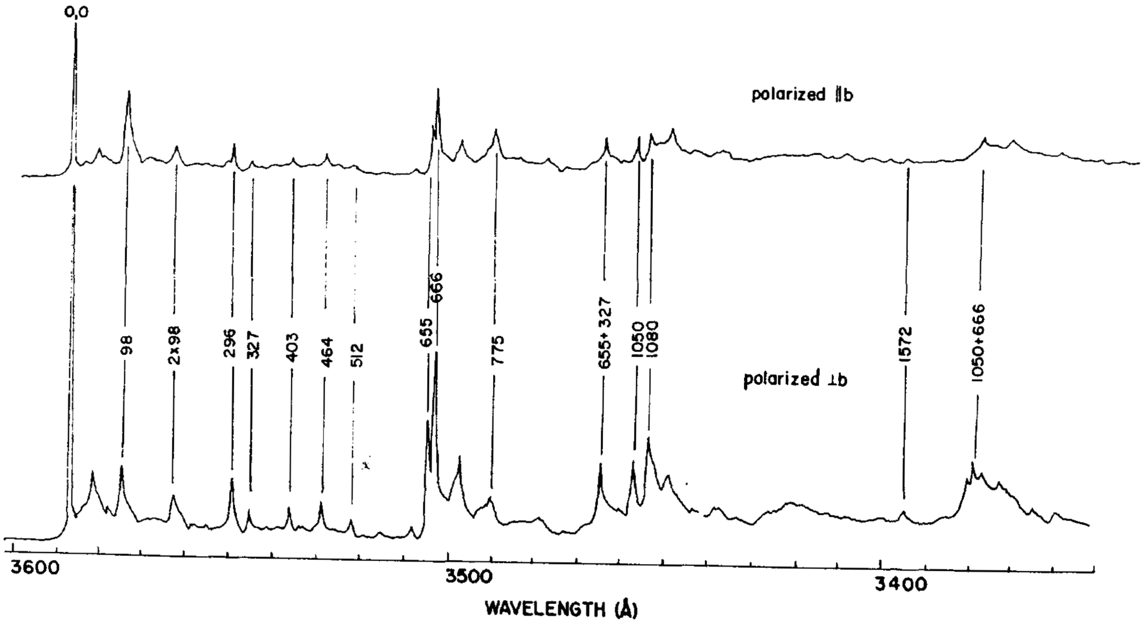

Figure 3. The polarized singlet-triplet exciton absorption spectrum of a single crystal of 1, 4-dichlorobenzene at 4.2 °K (*bc* face).

TABLE 3 Analysis of the Singlet-Triplet Exciton Absorption Spectrum of 1, 4-Dichlorobenzene Single Crystal at 4.2 °K

Rel. int.	Polarization $I_c : I_b$	$\bar{\nu}$	$\Delta\bar{\nu}$	Assignment
vvw	2.9	27890	0-0	EXCITON ORIGIN
w		27894	4	
vw		27899	9	
vw		27911	21	21 lattice
vw		27923	33	33 lattice
w	2.2	27936	46	2 × 21 or 46 lattice
w		27945	55	21 + 33
vw		27963	73	46 + 21 or 73
w(sh)		27984	94	3 × 33 or 2 × 46
m	0.75	27988	98	lattice or V. low fundamental
w		27999	109	109 lattice
vw(dif)		28032	142	98 + 46
vw(dif)		28046	156	98 + 55
vvw		28058	168	98 + 3 × 21
w	1.6	28084	194	2 × 98
vvw(dif)		28114	224	2 × 98 + 30 or b_{2u} fundamental [226]
vvw		28130	240	2 × 98 + 46
vw		28177	287	
w	2.3	28186	296	b_{2g} fundamental [306]
vvw		28198	308	
vvw		28206	316	296 + 21 lattice
vw	1.0	28217	327	a_g fundamental [327]
vvw		28233	343	327 + 21
vvw(dif)		28266	376	327 + 50
vw(sh)		28286	396	296 + 98
w	2.3	28293	403	a_u fundamental
vvw		28316	426	403 + 21
vw		28344	454	2 × 224 (b_{2u} + b_{2u})
w	2.3	28354	464	b_{3u} fundamental [485]
vvw		28382	492	296 + 2 × 98
vw	1.5	28402	512	b_{1u} fundamental [550]
vvw		28410	520	306 + 224
vvw		28422	532	
vvw(dif)		28454	564	306 + 224 + 44
vvw		28471	581	
vvw		28486	596	296 + 3 × 98 or 2 × 296
vw	1.5	28519	629	296 + 327 or b_{3g} fundamental [628]
m	2.2	28545	655	b_{2g} fundamental [689]
s	2.10	28556	666	a_g fundamental [744]

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Rel. int.	Polarization $[I_c : I_b]$	$\bar{\nu}$	$\Delta\bar{\nu}$	Assignment
vw		28576	686	666 + 21
w		28593	703	296 +403
m	2.42	28605	715	666 + 46
w		28646	756	655 + 98
w	0.60	28665	775	b_{1g} fundamental [814]
vw		28708	818	775 + 46
vw		28724	834	
vvw		28748	858	
vw		28768	878	775 + 98
vvw		28785	895	775 + 98 + 21
vvw		28813	923	775 + 98 + 46
vvw		28840	950	296 + 655 (b_{2g} + b_{2g})
vvw		28857	967	296 + 666
mw	2.0	28877	987	655 + 327
vw		28892	1002	
vw		28903	1013	
vw		28917	1027	2 × 512
mw	2.10	28940	1050	a_g fundamental (1096]
m	2.10	28970	1080	a_g fundamental [1169]
mw	1.20	29007	1117	655 + 464
vw		29028	1138	666 + 464?
vw		29056	1166	
vw		29099	1209	3 × 403
vw		29113	1223	
vvw		29142	1252	655 + 2 × 296
vvw		29168	1278	
vw		29202	1312	2 × 655
vw		29249	1359	
vw		29283	1393	3 × 464
vvw		29350	1460	
vvw		29400	1510	
vw		29462	1572	a_g fundamental [1577]
vvw		29554	1664	
vw		29595	1705	1050 + 655
w		29616	1726	1050 + 666
w		29633	1743	1080 + 666
w		29669	1779	
vw		29783	1893	

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damentals(17) are indicated in brackets. The spectrum was obtained from the phosphorescence excitation spectrum of the pure crystal at 4.2 °K. A broad band pass of triplet exciton and triplet excimer phosphorescence was monitored allowing an effective slit width of 2 cm^{-1} in the excitation monochromator.

The $T_1 \leftarrow S_0$ spectrum of 1,4-dichlorobenzene single crystals has been reported previously in detail.(1) From our results, we note the following.

(i) The increased sensitivity of the phosphorescence excitation technique has enabled more bands to be located in the excitation spectrum of a 1 mm thick DCB crystal than were obtained from a 20 mm thick crystal by direct absroption.(1)

(ii) The increased number of bands resolved correspond mostly to lattice structure built on the origin and a_g vibrations, and combinations of molecular vibrations. The lattice vibrations are summarised in Table 4 where they are compared with the Raman data of Ito *et al.*(18) The 21 cm^{-1} mode not previously assigned is observed both in lattice combination bands and also built on molecular vibrations (Table 3). The band (0–0 + 109) cm^{-1} is assigned as a high lying lattice frequency.(18) The band (0–0 + 98) cm^{-1} is unusual in the intensity it carries and its polarization properties. These suggest it is not a lattice mode.(1)

TABLE 4 Observed Crystal Lattice Vibrations of 1, 4-Dichlorobenzene (cm^{-1})

$T_1 \leftarrow S_0$ [4.2 °K] This investigation	$T_1 \leftarrow S_0$ [4.2 °K]^1	Raman [77 °K]^{18} A_g	B_g
21			
33			32
46	46		
73 (or 46 + 21)	55	58	65
109		114	117

(iii) The assignment(1) of the bands at (0–0 + 403) cm^{-1}, (0–0 + 464) cm^{-1} and (0–0 + 512) cm^{-1} as corresponding to a_u, b_{3u} and b_{1u} fundamentals would appear valid. Although the bands are weak, they are narrow and cannot be assigned in terms of g-symmetry fundamentals. The very weak band at 224 cm^{-1} could be a b_{2g}

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fundamental [226 cm^{-1}]. This band is not narrow as are the other u modes, but it does appear later in the spectrum at (O–O + 454) cm^{-1} as $b_{2u} \times b_{2u} = a_g$.

The vibrations of 296 cm^{-1} and 655 cm^{-1} assigned as b_{2g} appear in combination only with the very weak a_g fundamental 327 cm^{-1} (*νC–Cl*) but not with other strong a_g fundamentals corresponding to carbon framework modes. The identification of non totally symmetric vibrations and accurate polarization ratios are critical in any attempt to determine triplet state symmetry from a vibronic analysis.

(iv) The polarization ratios (Table 3) are in all cases less than the calculated oriented gas polarization ratio, in disagreement with other work.⁽¹⁾ However, the origin value, $I \mid b : I \mid\mid b = 2.9$, does agree with that of Castro and Hochstrasser, and this value is consistent with a small amount of in-plane polarization in a predominantly out-of-plane [N (x)] polarized transition.

4.3.2. $T_1 \leftarrow S_0$ *of* 1,2,4,5-*Tetrachlorobenzene*. The $T_1 \leftarrow S_0$ origin is assigned as the first intense peak in the spectrum (Fig. 4) at 26 675 cm^{-1}. The observed bands, intensities, and vibrational assignments are summarised in Table 5. Most of the intensity in the spectrum is carried by the origin and the totally symmetric vibration at 596 cm^{-1} (684 cm^{-1} in the ground state). This is characteristic of a symmetry allowed transition. Well resolved lattice structure is also seen built on the origin and the a_g modes. The strong band at 106 cm^{-1} could be analogous to the band at 97 cm^{-1} in $T_1 \leftarrow S_0$ of *p*-dichlorobenzene discussed in Sec. 4.3.1. In TCB the first ground state a_g fundamental occurs at 190 cm^{-1}. It is possible that the peak at 106 cm^{-1} is this vibration. Unfortunately, the absence of polarization properties (Sec. 4.1.1) prevents a definite assignment of this and other bands. The band appearing at 1176 cm^{-1} is interpreted as the combination (868 + 312 cm^{-1}, $b_{3g} + b_{3g}$). The only active b_{2g} vibration is *δC–Cl* [225 cm^{-1}] which is prominent in the phosphorescence spectrum.

4.4. FLUORESCENCE SPECTRA

Substitution of a heavy atom for hydrogen on the framework of an aromatic hydrocarbon results in an enhancement of the $S_1 \rightarrow T_1$ intersystem crossing quantum yield. As a result, ϕ_p is enhanced but ϕ_F is typically reduced to zero (especially in the case of bromine or iodine substitution). It has been shown⁽²⁾ that weak fluorescence

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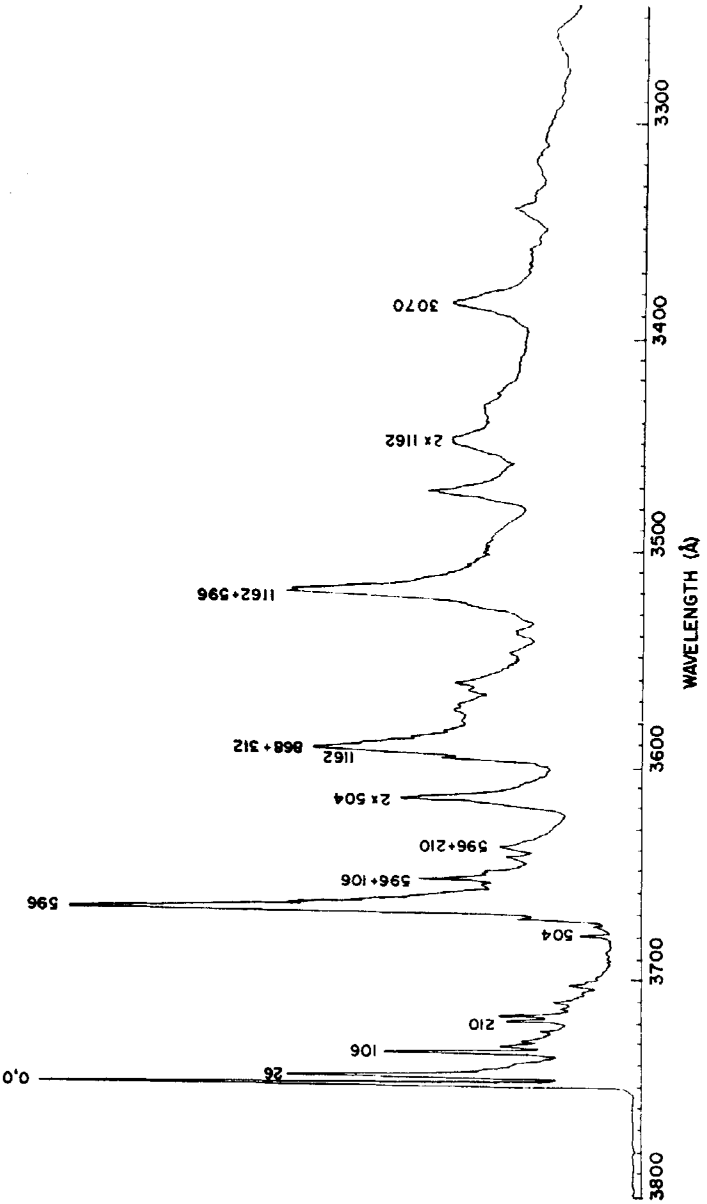

Figure 4. The unpolarized singlet-triplet exciton absorption spectrum of a single crystal of 1, 2, 4, 5-tetrachlorobenzene at 4.2 °K (*ab* face).

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TABLE 5 Analysis of the Singlet-Triplet Exciton Absorption Spectrum of 1, 2, 4, 5-Tetrachlorobenzene Single Crystal at 4.2 °K

Rel. int.	$\bar{\nu}$	$\Delta\bar{\nu}$	Assignment
vs	26675	0	EXCITON ORIGIN
w(sh)	26679	4	4
s	26701	26	26 lattice
m	26706	31	31 lattice
w	26720	45	45 lattice
w	26731	56	56 (26 + 31)
w	26742	67	67 (26 + 45)
s	26781	106	a_g fundamental [190] or lattice
w	26805	130	106 + 26
w	26827	152	106 + 45
vw	26836	161	106 + 56
vs	26856	181	106 + 3 × 26
vw	26871	196	106 + 26 + 67 or b_{1u} fundamental [218]
mw	26892	210	b_{2g} fundamental [225] or 2 × 106
mw	26910	235	210 + 26
vvw	26926	251	210 + 41
vvw	26937	262	210 + 52
vw	26958	283	b_{3g} fundamental [312]
vvw	26983	308	283 + 26
vvw	26990	315	106 + 210 or 3 × 106
vw	27015	340	106 + 210 + 26 or a_g fundamental [352]
vw	27179	504	b_{3g} fundamental [511]
vvw	27212	537	504 + 31
w	27237	562	2 × 283 (b_{3g} + b_{3g})
s	27271	596	a_g fundamental [684]
m	27292	617	596 + 21
m(sh)	27305	630	596 + 34
mw(sh)	27326	651	596 + 55
w	27349	674	596 + 3 × 26
mw	27375	700	596 + 106
w	27401	726	596 + 106 + 26
vw	27451	776	596 + 106 + 3 × 26
w	27488	813	596 + 2 × 106 or 596 + 210
m	27668	993	2 × 504
vw	27689	1014	993 + 21
vw	27735	1060	993 + 67
mw	27814	1139	
mw	27837	1162	a_g fundamental [1165]
m	27851	1176	868 + 312 [b_{3g} + b_{3g}]
mw	27913	1238	2 × 596 + 46
w	27984	1309	2 × 596 + 67
w	28078	1403	
vw	28110	1435	
vw	28197	1522	a_g fundamental [1549]
vw	28277	1602	
vw(sh)	28341	1666	
s	28425	1750	1162 + 596
mw	28816	2141	
w	29019	2344	2 × 1162
vw	29146	2471	
w	29581	2906	a_g fundamental [3070]

($\phi_F \simeq 10^{-2}$) can be detected from the hexachlorobenzene single crystal at 4.2 °K. A full vibrational analysis and polarization study of this emission was possible. Other chloro-substituted benzenes might also be expected to emit fluorescence.

4.4.1. $S_1 \rightarrow S_0$ *of* 1,2,4,5-*Tetrachlorobenzene.* The observed fluorescence of TCB (Fig. 5) commences with a weak, diffuse region around 33795 cm^{-1}. The first intense emission peak is observed at 33144 cm^{-1}. If this is chosen as the first totally symmetric vibration (O–O − 684 cm^{-1}) the $S_1 \rightarrow S_0$ origin is assigned as 33829 cm^{-1}. Other peaks in the spectrum may be assigned on this basis in terms of molecular and lattice vibrations built on this origin at 33829 cm^{-1} (Table 6). The origin is almost totally reabsorbed, and the weak diffuse region around 33795 cm^{-1} is interpreted as phonon structure built on this origin. Significant reabsorption of the emission origin is to be expected as the ${}^1B_{2u} \leftarrow {}^1A_{1g}$ transition of TCB has an oscillator strength, in solution, of 0.013 (*cf.* Hexachlorobenzene, $f_{S_0-S_1} =$ 0.002—No reabsorption is observed: Anthracene, $f_{S_0-S_1} = 0.10$—Total reabsorption is observed). Pesteil *et al.* from crystal absorption studies at 4.2 °K have placed the origin at 33855 cm^{-1}. Their reported absorption spectrum is quite broad and shows no phonon structure. The origin is taken as the first intense peak. However it is not possible to analyse the observed fluorescence spectrum in terms of an origin at 33855 cm^{-1}. This suggests that the observed emission origin is a defect origin or the absorption peak does not represent the O–O transition. There is no evidence that the emission originates from an exciton trap level about 26 cm^{-1} below the exciton band. From the intensity of the $S_1 \rightarrow S_0$ transition it could be expected that singlet exciton migration to trapping levels below the singlet exciton band could be sufficiently rapid to permit observation of these levels in the fluorescence spectrum. As has been seen (Table 6) the emission can be assigned in terms of emission arising from a single (reabsorbed) origin. On warming from 4.2 °K the bands broaden uniformly and no evidence is found for singlet exciton trapping levels, as has been found for anthracene for example.(19,20) Whilst there is strong evidence for triplet exciton traps in this (see Sec. 4.1.1) and other halobenzenes,(2) the absence of detectable singlet exciton traps may indicate, not the absence of trapping levels, but rather the lack of population of these levels during the exciton

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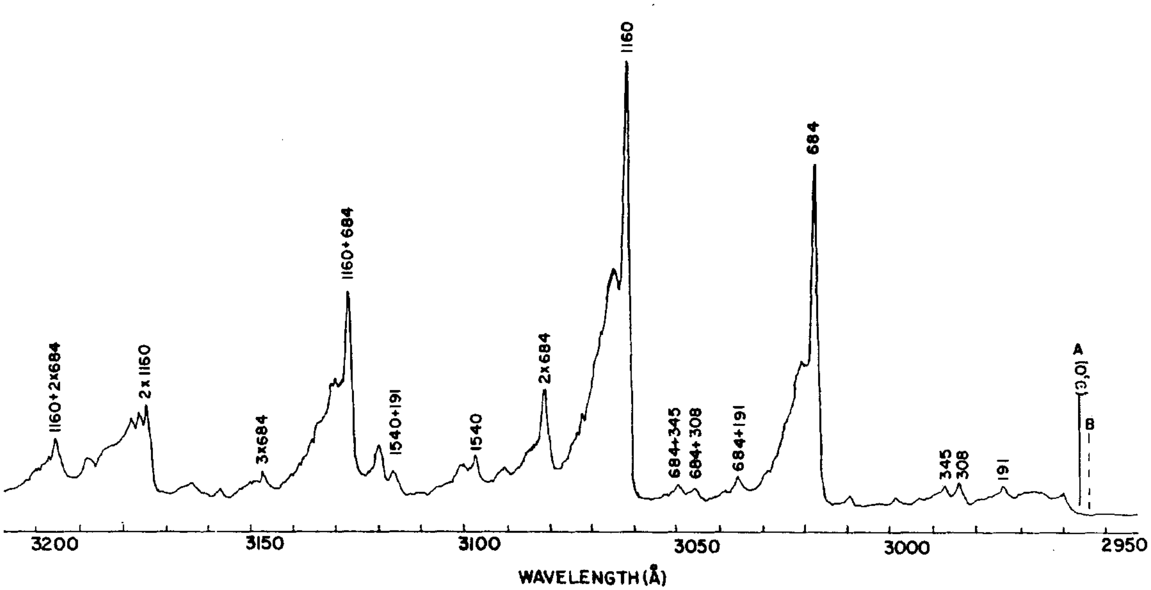

Figure 5. The fluorescence spectrum of 1, 2, 4, 5-tetrachlorobenzene single crystal at 4.2 ° K. The peak (A) of the absorption spectrum from Ref. (5) is also shown. Note its separation of 26 cm^{-1} from the emission origin, B.

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Table 6 Analysis of the Fluorescence Spectrum of 1, 2, 4, 5-Tetrachlorobenzene Single Crystal at 4.2 :K

Rel. int.	$\bar{\nu}$	$\Delta\bar{\nu}$	Assignment
	33829	0-0	Reabsorbed Origin
vvw	33795	34	lattice
vvw	33777	52	lattice
vw	33727	102	2 × 52
vw	33638	191	a_g fundamental [190]
vw	33521	308	b_{3g} fundamental [312]
vw	33484	345	a_g fundamental [352]
vw	33234	595	233 + 352
s	33145	684	a_g fundamental [684]
m	33118	711	684 + 26
m	33086	743	684 + 58
vw	32949	880	684 + 191 or b_{3g} fundamental [868]
vw	32835	994	684 + 308
vvw	32790	1039	684 + 345
vvw	32755	1074	684 + 345 + 35
vs	32669	1160	a_g fundamental [1165]
s	32639	1190	1160 + 34
m(sh)	32552	1277	1160 + 1153
w	32478	1351	1160 + 191
m	32464	1365	2 × 685
w	32428	1401	2 × 685 + 36
vw	32357	1472	1160 + 308
vvw	32316	1513	1160 + 345
w	32289	1540	a_g fundamental [1549]
vw	32260	1569	1540 + 29
w	32092	1737	1540 + 191 or 2 × 868
w	32056	1773	
ms	31985	1844	1160 + 684
m	31949	1880	1160 + 684 + 36
vw	31778	2051	3 × 684
vw	31605	2224	
mw	31509	2320	2 × 1160
mw	31486	2343	2 × 1160 + 23
w	31415	2414	
w	31397	2432	1160 + 685 + 595
mw	31298	2531	1160 + 2 × 685

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radiative lifetime. The singlet radiative lifetime ($\sim 10^{-7}$ sec), is greater than that for anthracene ($\sim 10^{-8}$ sec,) but the intermolecular interaction energy determining the exciton velocity operator is much less.† It would appear then that the singlet exciton in TCB is relatively immobile compared with that for anthracene.

We note that there is an energy gap of 26 cm^{-1} between the absorption peak(5) and the emission origin interpreted by us as the singlet exciton emission origin. We suggest that this gap is explicable in terms of the absorption peak not coinciding with the absorption origin. The absorption band width(5) at 4.2 °K (full width at half maximum) is about 60 cm^{-1}. Until one knows the nature and extent of the broadening processes operative e.g. exciton phonon scattering, exciton defect scattering, radiationless broadening, we doubt that the true absorption origin can be located precisely within this broad band. In particular we suggest that the absorption peak is not necessarily the absorption origin. A similar situation holds for anthracene where an energy gap of about 90 cm^{-1} exists between the assigned emission origin(19) and the singlet absorption peak (b-polarized).(21)

The strongest bands appearing in the spectrum are the a_g modes 684 cm^{-1} and 1160 cm^{-1} and combinations and overtones of these. Only one b_{3g} vibration is assigned (308 cm^{-1}). Low lying a_g vibrations at 191 cm^{-1} and 345 cm^{-1} are identified, but carry little intensity. The b_{3g} vibrations and the a_g vibrations built on it, are very weak. An unassigned vibration at 595 cm^{-1} could possibly also be a b_{3g} vibration. The phonon structure built on the a_g vibrations consists of a broad continuum of overlapping vibrations from which only one or two modes may be resolved. The continuum tails to lower energies for $\sim$ 100 to 200 cm^{-1} from the intense bands so obscuring some possible molecular vibration combinations.

The general features of the fluorescence correspond to those expected for a symmetry allowed ${}^1B_{2u} \rightarrow {}^1A_{1g}$ transition—strong a_g fundamentals built on the origin and on a b_{3g} vibration $[B_{2u} \times b_{3g} = B_{1u}(L, z)]$.

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† The factor group splitting for example for TCB is not known, but presumably is less than a few cm^{-1} judging from the unpolarized absorption spectrum of Pesteil *et al.*(5) The value for anthracene is about 200 cm^{-1} (see Ref. (21)). However, the interaction energy between translationally equivalent molecules will probably be greater for TCB because of the layered structure along the short c axis.

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4.4.2. $S_0 \rightarrow S_3$ *of* 1,4-*Dichlorobenzene.* The fluorescence of DCB was very weak and was partially obscured by the tail of the filtered exciting light. A low resolution spectrum only was obtained and fifteen bands identified. While the weak nature of the emission prevents a vibrational analysis being presented at this stage, certain features can be identified.

The $S_1 \rightarrow S_0$ spectrum at 4.2 °K commences with a very weak (partially reabsorbed?) origin at 35663 cm^{-1}. The principal progression forming modes are the a_g vibrations 747 cm^{-1} and 1073 cm^{-1}. A weak b_{3g} vibration at 637 cm^{-1} and a_g vibrations built on this are identified.

5. Conclusions

The study of the temperature dependence of the phosphorescence from 4.2 °K to 20 °K of DCB and TCB has indicated that only in TCB can emission from trapped triplet excitons be observed. At the same time the triplet excimer emission is very strong from DCB at 4.2 °K and very weak from TCB. Only when $T \simeq 12$ °K and intrinsic triplet exciton phosphorescence is predominant can strong excimer emission be observed from TCB (Fig. 1). Localization of the triplet exciton in shallow traps below the exciton band competes with formation of the triplet excimer (which has been presumed to occur at a defect site in the crystal).(1,16)

The halogen enhancement of the $S_1 \rightarrow T_1$ intersystem crossing quantum yield has not prevented observation of weak fluorescence ($\phi_F < 10^{-2}$) from both TCB and DCB crystals. The observed 4.2 °K fluorescence spectra seem to indicate intrinsic singlet exciton fluorescence although the weak emission could restrict identification of trapped exciton states.

No definitive statement can be made concerning the triplet state symmetry of these molecules. The $T_1 \leftarrow S_0$ data reported here for DCB are in general agreement with the observations of Castro and Hochstrasser.(1) A detailed single crsytal polarization study alone is insufficient in view of the uncertain spin-orbit coupling routes and crystal field effects.

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