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Phosphorescence Spectra of *p*-Dichlorobenzene in Various Matrices at 1.4 K

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The phosphorescence spectra of *p*-dichlorobenzene have been obtained at 1.4 K in various hosts; benzene, *p*-xylene, *p*-dichlorobenzene, *p*-dichlorobenzene-d_4, and *p*-dibromobenzene. The long progressions in the b_{2g}, C–Cl bending vibration are indicative of a molecular distortion in the out-of-plane direction. With the aid of the technique of optical detection of zero-field magnetic resonance, the intense 1580 cm^{-1} band previously ascribed to the a_g, ν_{8a} vibration is found to be due to the b_{3g}, ν_{8b} vibration. The appearance of the b_{3g} band with strong intensity suggests a possibility of an additional in-plane distortion of phosphorescent *p*-dichlorobenzene.

The electronic structure and the molecular geometry of phosphorescent *p*-dichlorobenzene (DCB) have been the subjects of extensive studies in these years. It was first proposed from polarized T←S absorption spectra that the orbital symmetry of the lowest triplet state of DCB is B_{2u}.[1)] However, optically detected magnetic resonance (ODMR) experiments[2–6)] performed afterwards have shown that the symmetry is most probably described by B_{1u}.

The phosphorescence spectra of the exciton[7,8)] and the traps[3,8)] in a neat DCB crystal exhibit long progressions in the b_{2g}, C–Cl bending vibration. This suggests that the DCB molecule is distorted in the phosphorescent state. The out-of-plane position of the two chlorine atoms has been proposed by Buckley and Harris[2)] from the observation of somewhat large (≈8%) reductions in the ^{35}Cl quadrupolar coupling constant from −69.662 MHz in the ground state to −64.5 MHz in the triplet state. Furthermore, recent ODENDOR experiments[6)] also indicate that the C–H fragments are not positioned in the molecualr plane.

The phosphorescence spectrum of the 23 cm^{-1} trap-(x-trap) in a neat DCB crystal shows a strong vibrational band at 1579 cm^{-1} from the electronic origin.[3,8)] This band corresponds to the extremely strong band due to the e_{2g}, ν_8 skeletal vibration in the phosphorescence spectrum of benzene. In benzene, it has been shown that the appearance of this band with remarkable intensity is due to a strong vibronic coupling or the pseudo Jahn-Teller interaction between the lowest $^3B_{1u}$ state and the second lowest $^3E_{1u}$ state.[9–11)] This interaction causes potential curve distortions along the coordinate of the ν_8 mode in the interacting electronic states and a deviation of the triplet electron distribution from the hexagonal symmetry.

It is quite natural to expect that the strong 1579 cm^{-1} band in the DCB phosphorescence also results from a similar cause. In DCB, the ν_8 vibration splits into the a_g, ν_{8a} and the b_{3g}, ν_{8b} vibration. In most works, however, the band at approximately 1580 cm^{-1} was assigned as being due to the a_g vibration,[7,8)] but Buckley *et al.*[3)] ascribed it to a superposition of the a_g and the b_{3g} vibration. The PMDR(phosphorescence microwave double resonance) spectra by these authors clearly indicate a marked difference in the behaviour of this band and that of other a_g bands; this suggests a b_{3g} possibility. However, the relative radiative decay rates of the T_y and T_z spin sublevels are found to be $k_y^r/k_z^r=1.4$ in this band, which is unfavorable for the b_{3g} assignment.

The main purpose of this paper is to demonstrate that the band is superposed by the a_g and b_{3g} vibrations with vibrational frequencies slightly different from each other and that the b_{3g} band appears more strongly in most cases. The latter relates to a possibility of an in-plane distortion in the triplet spin distribution in addition to the out-of-plane distortion of the molecule proposed.[2)]

Experimental

p-Dichlorobenzene was purchased from Wako Pure Chemical Industries, Ltd. and purified by recrystallizations from ethanol and then by zone-refining (more than 150 passes). *p*-Dichlorobenzene-d_4 was purchased from Merck, Sharp & Dohme, Canada Ltd. and purified by zone-refining (more than 150 passes). Commercially available zone-refined *p*-dibromobenzene was used without further purification. Crystals were grown by the Bridgman method. Benzene and *p*-xylene were used after purification by vacuum distillation.

The samples were excited with light of 313 nm from a super-high pressure mercury arc lamp (Orc CH-612, 1 kW) through a saturated $NiSO_4$ aqueous solution filter and a Toshiba UV-D33S filter. The phosphorescence emission from a sample was isolated by a Spex 1700-III 3/4 m spectrometer in conjunction with a pair of rotating disk choppers and detected by an EMI-9789SB photomultiplier tube and a PAR-128A lock-in amplifier.

ODMR experiments were carried out at 1.4 K with an HP-8620A sweep oscillator equipped with appropriate plug-ins and a Weinschell model 221 sweep oscillator with an H-408 plug-in. Details of the ODMR experiments were described in previous papers.[12,13)]

Phosphorescence Spectra

The phosphorescence spectra of DCB in various hosts were detected at 1.4 K. The spectra obtained in *p*-dibromobenzene (DBB) and in DCB-d_4 are shown in Fig. 1. It is to be noted that the position of the 0,0 band in the spectrum of DCB in DCB-d_4 coincides with that of the exciton phosphorescence origin[7)] and the T←S absorption origin[1)] of crystalline DCB. The phosphorescence spectra of DCB in *p*-xylene and 23 cm^{-1} trap in the neat crystal are found to be essentially

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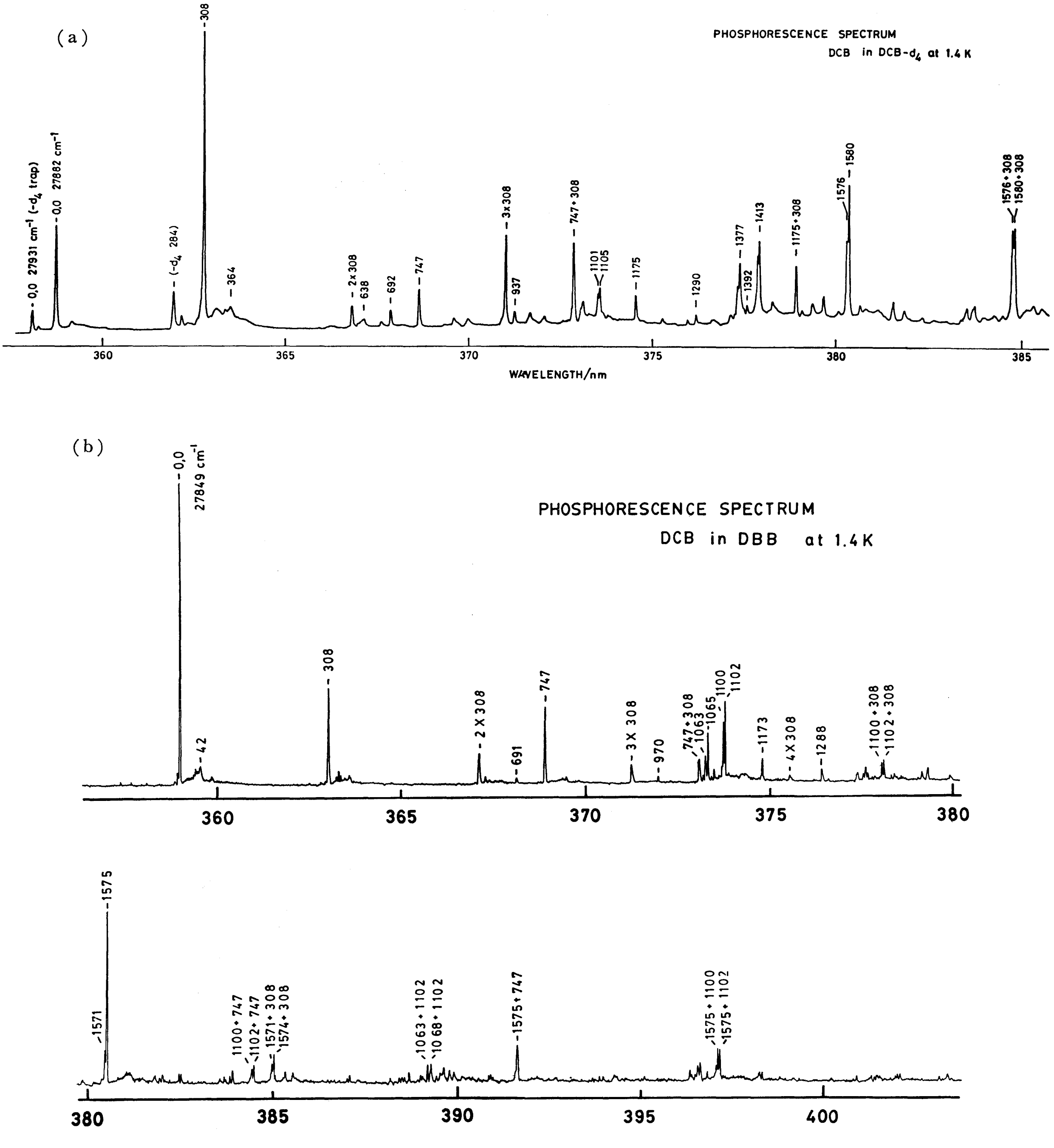

Fig. 1. The phosphorescence spectra of *p*-dichlorobenzene in (a) *p*-dichlorobenzene-d_4 and in (b) *p*-dibromobenzene at 1.4 K.

the same as those reported previously.[3,4,8] The spectrum in benzene shows a multi-site emission consisting of broad vibrational bands.

The band at about 310 cm^{-1} from the electronic origin has been assigned as being due to the progression-forming b_{2g}, C–Cl out-of-plane bending vibration. The progression can be followed through the fifth member in all the spectra obtained but in benzene. The spectra shown in Fig. 1 display a marked contrast in the intensity of the fundamental band of this mode. The band at 0—308 cm^{-1} is the strongest band in the spectrum of DCB in DCB-d_4. A similar feature is observed in the spectra of DCB in *p*-xylene and in benzene. In the spectrum of DCB in DBB, on the other hand, the corresponding band is weaker than the 0,0 band. The spectrum of the x-trap in the neat crystal also exhibits a similar trend.

Zero-field Splitting and Decay Rates

The zero-field splitting and the molecular symmetry axes are shown in Fig. 2. The zero-field splittings and the decay rates of the individual spin states of

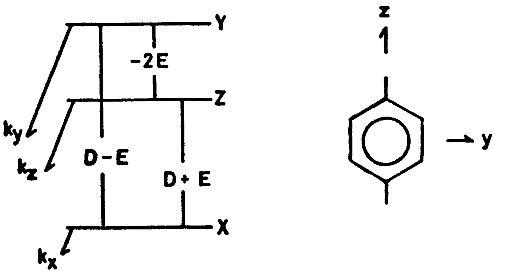

Fig. 2. The definition of the molecular symmetry axes and the zero-field splitting of *p*-dichlorobenzene.

Table 1. The positions of phosphorescence origin bands, zero-field splittings and phosphorescence decay rates of the individual spin sublevels of *p*-dichlorobenzene in various matrices at 1.4 K

	p-Xylene	Benzene (site II)	DBB	Neat cryst.	DCB-d_4
$\nu_{0,0}$/cm^{-1}	27415	27786	27849	27859	27882
D/GHz	4.324	4.421	4.472	4.483	4.505
$-2E$/GHz	1.369	(1.634)	(1.778)	1.758	1.849
k_y/s^{-1}	73.5	56.5	71.4	73.6	55.6
k_z/s^{-1}	7.0	21.7	57.1	35.6	18.8
k_x/s^{-1}	0.65	1.6	11.9	2.1	1.1

Table 2. Relative radiative decay rate constants of *p*-dichlorobenzene at 1.4 K

System	Band	Symmetry	k_y^r	k_z^r	k_x^r
In *p*-xylene	0, 0		1	0.008	0.008
	303 cm^{-1}	b_{2g}	1	0.04	0.01
	1573	b_{3g}	1	1.82	0.44
	1577	a_g	1	0.03	0.03
In benzene	0, 0		1	0.16	0.026
	307	b_{2g}	1	0.34	0.033
Neat crystal	0, 0		1	0.15	0.038
	314	b_{2g}	1	0.29	0.015
	1578	a_g	1	0.17	0.032
	1581	b_{3g}	1	1.0	0.045
In DCB-d_4	0, 0		1	0.04	0.01
	308	b_{2g}	1	0.17	0.04
	1576	a_g	1	0.16	0.10
	1580	b_{3g}	1	6.67	0.13
In DBB	0, 0		1	0.82	0.14
	308	b_{2g}	1	0.35	0.05
	1571	a_g	1	0.73	0.19
	1575	b_{3g}	1	1.54	0.33

DCB in these matrices are determined by the MIDP (microwave-induced delayed phosphorescence) method. The results are listed in Table 1. The sublevel ordering has been determined to be $T_y > T_z > T_x$ in the *p*-xylene and neat crystal systems.[3,4] The same ordering is deduced for the other systems from the similarity in the splitting and from the relation of $k_y > k_z > k_x$. This relation has been commonly observed in various mono- and 1,4-dihalobenzenes.[4,13]

The zero-field splitting parameters, D and E, vary slightly depending on the matrix used. It may be pertinent to point out that the variation of the zero-field splitting parameters exhibits a good correlation with the shift of the phosphorescence origin band as shown in Table 1, although a slight discrepancy is seen between the neat crystal system and the DBB host system. A similar correlation has also been observed in the case of pyrazine.[14]

The values of k_z and k_x are small in the *p*-xylene system, but become large in the other systems, even in benzene. The increase in k_z and k_x in the DCB and DBB crystalline systems are related to the external heavy atom effect. However, the k_z and k_x values for the trap in the neat crystal seem to have an influence from other sources in addition to the external heavy atom effect, because these values are about twice those for DCB in DCB-d_4. As a possible cause for this, we presently consider a distortion or a rotation of the trap molecules from the results of T←S excitation experiments.[15] The values for DCB in benzene seem to be affected by spin-lattice relaxation.

Relative Radiative Decay Rates

The relative radiative decay rate constants of the three spin sublevels of DCB in the hosts used are determined at 1.4 K in some of the main vibrational bands. The results are summarized in Table 2. The values for the 0,0 and b_{2g} bands in the spectrum of DCB in *p*-xylene are essentially in agreement with the results reported previously.[4] The assignments of the bands appearing at approximately 0—1580 cm^{-1} will be discussed in detail below.

If the electron distribution in DCB is retained in the D_{2h} symmetry in the triplet state, the transition from the T_z sublevel in the 0,0 band and the transitions from the T_x sublevel in the b_{2g} bands are strictly forbidden as shown in Table 3. The fact that these bands originate from all the spin sublevels suggests that the electron distribution is deformed from

Table 3. Polarizations of radiative transitions from the triplet state sublevels in four bands of the phosphorescence spectrum of *p*-dichlorobenzene as expected from group theoretical considerations

Orbital symmetry	Magnetc sublevel	Spin-orbit symmetry	Vibrationl band polarization			
			a_g	b_{1g}	b_{2g}	b_{3g}
$^3B_{1u}(\pi,\pi^*)$	T_y	B_{3u}	x	y	z	f[a]
	T_z	A_u	f	z	y	x
	T_x	B_{2u}	y	x	f	z

a) f = forbidden.

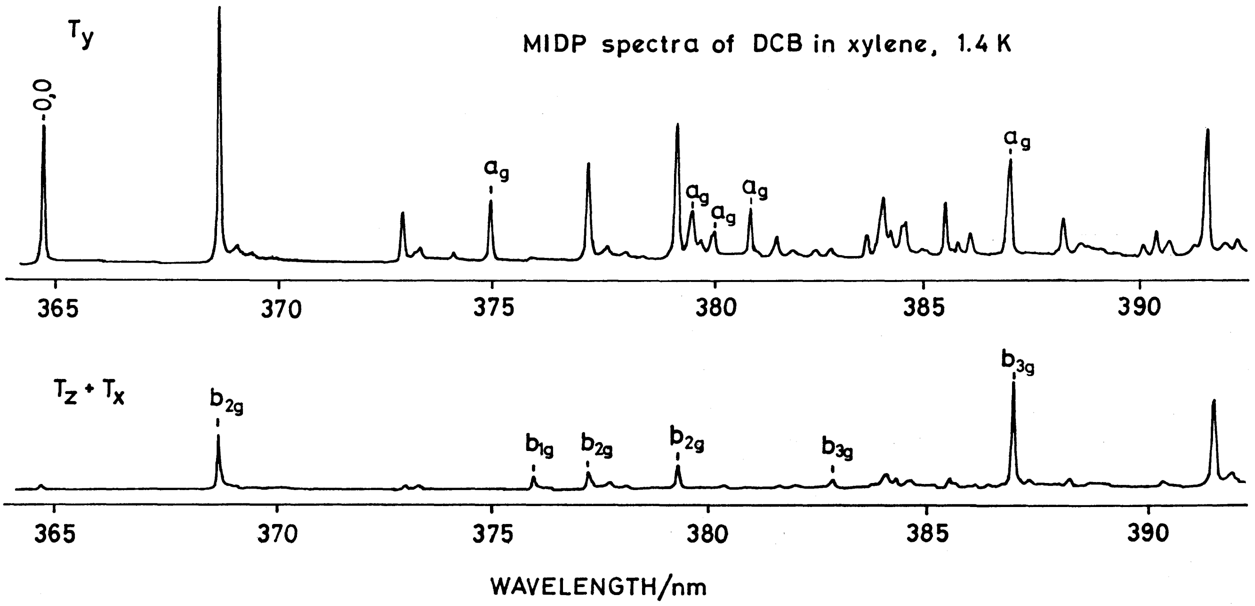

Fig. 3. The sublevel phosphorescence spectra of *p*-dichlorobenzene in *p*-xylene at 1.4 K.

Table 4. Fundamental vibrations identified in the phosphorescence spectrum of *p*-dichlorobenzene in cm^{-1}

Symmetry	Raman (crystal)	In *p*-xylene	In benzene		x-Trap neat crystal	In DCB-d_4	In DBB	x-Trap neat crystal$^{a)}$	Exciton$^{b)}$
			site I	site II					
a_g	327		313	307	333	337	330	327 331	330
	744	751	751	749	746	747	747	749	746
	1103	1098	1106	1105	1108	1101 1105	1100 1102	1103 1106	1103
	1174	1171			1180	1175	1173	1178	1173
	1577	1577	(1584)$^{c)}$	(1581)	1578	1576	1571	1576 1579	1578
	3071								
b_{1g}	814	821			818	815	816	816	
b_{2g}	306	303			314	308	308	309	310
	689	694			691	692	691	690	
	976	(938)			(938)	(937)	970		
b_{3g}	350				(355)	(364)	(326)		(355)
	628	637			636	638	628		(635)
	1293	1297			1292	1290	1288		
	1577	1573	(1584)	(1581)	1581	1580	1575		
	3064								

a) From Ref. 8. b) From Ref. 7. c) The assignment of the band in the parentheses is not certain.

D_{2h} to C_{2h} or a lower symmetry by small perturbations. In particular, the b_{2g} progression alternates in intensity with the members of odd quanta being the strongest. Therefore, a distortion along the out-of-plane direction is most probable. Possible perturbations for this have already been discussed by Buckley *et al.*3)

Sublevel Spectra and Vibrational Analysis

The phosphorescence spectrum of DCB in *p*-xylene is resolved into two sublevel spectra as shown in Fig. 3. The T_y spectrum recorded by phase-sensitively detecting the MIDP signals produced 100 ms after the excitation cutoff by irradiating the microwaves resonant with the $T_y \leftrightarrow T_z$ transition. The T_z+T_x spectrum was taken by sampling the tail portions(100—150 ms) of the phosphorescence decay. As the contribution from the T_x emission is small, the T_z+T_x spectrum can be regarded as consisting mainly of the emission from T_z.

The 0,0 band and the band at 0—303 cm^{-1} appear very strongly in the T_y spectrum, but weakly in the T_z+T_x spectrum. Therefore, the bands appearing strongly in the T_y spectrum and weakly in the other can be ascribed to a_g or b_{2g} vibrations. Referring to the results of the Raman studies16) and the previous phosphorescence works,3,4,7,8) we assigned the bands at 0—751, 0—1112, 0—1171, and 0—1577 cm^{-1} as being due to the a_g fundamentals and the bands at 0—303 and 0—694 cm^{-1} as being due to the b_{2g} fundamentals. The assignment of the 1577 cm^{-1} band will be described in the following section. One of the bands at 0—938 and 0—965 cm^{-1} may also be ascribed to b_{2g}. Although the latter is consistent with the Raman results, we tentatively assign the former to the band due to the b_{2g} vibration, because the former band appears relatively strongly in all the spectra studied. In addition to the bands assigned above, there are many overtone and combination bands of a_g and b_{2g} symmetries. Of these, the band at 0—1078 cm^{-1} ($2\times b_{1u}$) is in Fermi resonance with the 1112 cm^{-1} a_g vibration.

The bands at 0—821, 0—1297, and 0—1573 cm^{-1} differ in behavior in the sublevel spectra from the bands due to a_g and b_{2g} vibrations. These bands appear relatively strongly in the T_z+T_x spectrum. The band at 0—637 cm^{-1} is also stronger than the 0,0 band in the T_z+T_x spectrum, but is much weaker than the 0,0 band in the T_y spectrum. Therefore, these bands may be attributed to either b_{1g} or b_{3g} vibration.

The MIDP sublevel spectra for the x-trap were also obtained in a similar manner. The MIDP signals due to the $T_y\leftrightarrow T_x$ and $T_z\leftrightarrow T_x$ transitions were sampled in this case to obtain the T_y and T_z spectra. The spectra showed essentially the same feature as the am-PMDR subspectra obtained by Buckley *et al.*[3] The results of the vibrational analysis are given in Table 4 for the fundamentals identified. The results for the x-trap and DCB in *p*-xylene are used for the analyses of the other systems.

The 1580 cm^{-1} Vibrations

In this work, a particular attention is paid to the assignment of the band appearing at approximately 0—1580 cm^{-1} in all the systems studied. In Fig. 4(a), the 1573 cm^{-1} band in the spectrum of DCB in *p*-xylene is shown under magnification. The band seems to have a shoulder at 0—1577 cm^{-1}. The same band recorded under different conditions are shown in Figs. 4(b) and 4(c). The band in Fig. 4(b) was taken by sampling the emission between 100 and 150 ms after the excitation cutoff. The intensity of the shoulder band is diminished. As the population in T_y has been almost completely exhausted before the sampling time, the shoulder band is regarded as the band originating mainly from T_y. The band shown in Fig. 4(c) was recorded in the same sampling time but with the microwave pulses which initiate the $T_y\leftrightarrow T_z$ transition 100 ms after the excitation cutoff. The peak decreases in intensity, but the shoulder increases. This can be seen clearly in Figs. 4(d) and 4(e), where the MIDP signals produced by the microwave pulses($T_y\leftrightarrow T_z$) at about 190 ms for the peak and for the shoulder position are shown, respectively. The changes in intensity result from the population transfer from T_z to T_y. Thus the peak emission has its origin in the T_z sublevel, whereas the shoulder emission in the T_y sublevel.

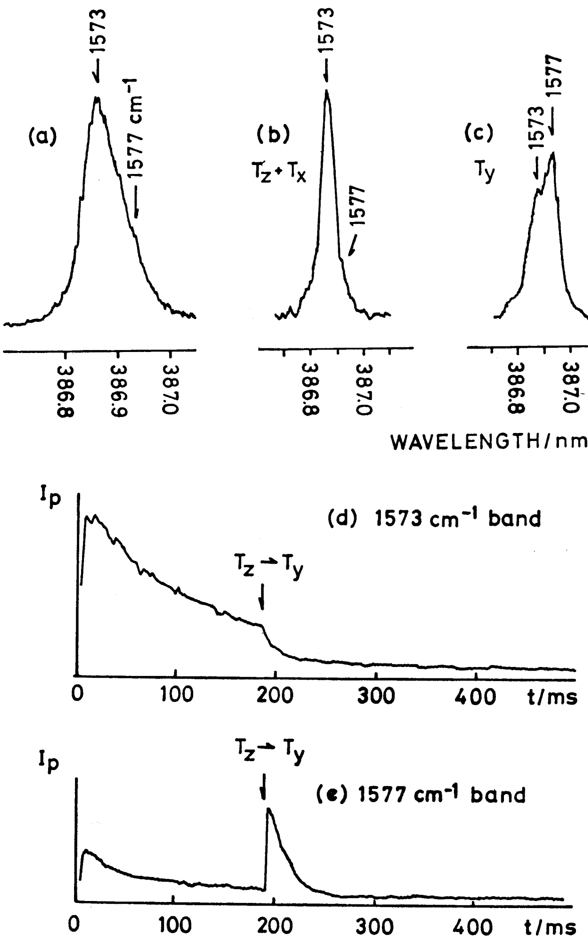

Fig. 4. The 1573 cm^{-1} band in the phosphorescence spectrum of *p*-dichlorobenzene in *p*-xylene at 1.4 K under various conditions(a—c; see the text) and the MIDP signals obtained by monitoring the emission at slightly different wavelengths (d and e).

Similar results have also been obtained in all the other systems but in benzene. As another example, the 1581 cm^{-1} band observed in the spectrum of the x-trap is shown in Fig. 5. In this case, the T_y and T_z spectra were taken by applying the microwaves resonant with the $T_y\leftrightarrow T_x$ and the $T_z\leftrightarrow T_x$ transitions, respectively. It is clear from the figure that the peak band originates mainly from T_z while the shoulder from T_y.

In the system of DCB in DCB-d_4, a splitting of the band is recognized even in the phosphorescence spectrum in Fig. 1. The MIDP experiments on this system and the system of DCB in DBB also showed that the peak band originates mainly from T_z. The spectrum in benzene is too broad to obtain conclusive results.

As discussed above, the shoulder band originating from T_y has to be assigned as being due to the a_g, ν_{8a} vibration. The vibration involved in the peak band is therefore unambiguously assigned to the b_{3g}, ν_{8b} vibration. It is to be noted that in all these systems the peak positions correspond to the band due to the b_{3g} vibration. In this regard, the previous assignment[7,8] to the a_g vibration should be revised. In the high resolution spectrum of the x-trap reported

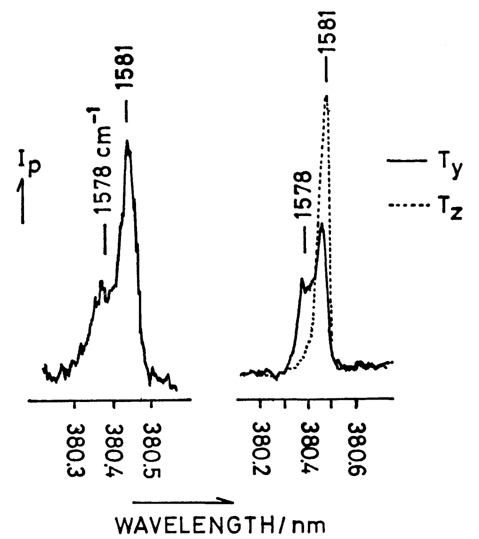

Fig. 5. The 1581 cm^{-1} band in the phosphorescence spectrum of the x-trap (23 cm^{-1}) in the neat *p*-dichlorobenzene crystal(left) and the same band observed with microwave perturbations (right; see the text).

by Gash *et al.*,[8] the band of present interest is clearly split, but they ascribed the both components to the a_g vibration, since they observed some of other a_g bands as doublets. However, they also observed the 749 and 1178 cm^{-1}, a_g bands without splitting. In view of this and our present results, the band at 0—1579.0 cm^{-1} in their spectrum is to be attributed to the b_{3g} vibration.

In the case of benzene, the ν_8 band in the phosphorescence spectrum appears with remarkable intensity, because of the strong vibronic coupling between the $^3B_{1u}$ and $^3E_{1u}$ states through the ν_8 mode. It seems that a similar situation is retained in DCB. Therefore, the main mechanism by which the ν_{8b}, b_{3g} band acquires the dipole activity is described by the second order spin-orbit vibronic coupling scheme of $^3B_{1u} \leftsquigarrow b_{3g} \rightsquigarrow {}^3B_{2u} \leftsquigarrow H_{so}(T_z) \rightsquigarrow {}^1B_{3u}$. The emission to the b_{3g} vibrational levels steals its intensity mainly from the $^1B_{3u} \rightarrow {}^1A_g$ transition as the emission to the a_g vibrational level does. The differentiation of a_g and b_{3g} vibrations are therefore not feasible from the phosphorescence polarization measurements. A similar situation has also been found in *p*-chloroaniline.[13]

As mentioned above, the coupling between the $^3B_{1u}$ and $^3E_{1u}$ states through the ν_8, e_{2g} mode in benzene results in pseudo Jahn-Teller instability, which combined with the crystal field of lower symmetry causes a distortion of the hexagonal symmetry of both the nuclei and the electronic structure. Indeed, various experiments[17–25] have shown that the lowest triplet state of benzene has a non-hexagonal electronic structure; *i.e.*, the in-plane distortion along the e_{2g} mode. Therefore, it is very probable that the DCB molecule is also subject to a similar distortion along the b_{3g} mode.

This kind of distortion would result in a deviation of the in-plane principal axes of the fine structure tensor from the molecular symmetry axes. Vergragt *et al.*[26,27] have demonstrated that the in-plane principal axes of toluene and *p*-xylene are skew in the triplet state by approximately 70(π/180) rad with respect to the axes expected for an undistorted molecule. In DCB, such a large deviation of the principal axes may not be expected, because the radiative decay rate ratio, k^r_z/k^r_y, for the 0,0 band is small in *p*-xylene and in DCB-d_4 as shown in Table 2. Recently, it has been shown from NQR experiments for DCB in DBB[28,29] that the in-plane principal axes are rotated by about 10 (π/180)—12(π/180) rad about the axis normal to the molecular plane. Furthermore, an out-of-plane deviation of the principal axis, y, by about 20(π/180) rad is also deduced from the NQR experiments.[28] These results, though somewhat large in the DBB host, are consistent with our present expectations.

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