May, 1976] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49 (5), 1221—1229 (1976) 1221

An Investigation of the Triplet State Dynamics of *p*-Chloroaniline by Microwave Induced Changes in the Phosphorescence Intensity and by Triplet ← Singlet Absorption

Nobuyuki Nishi and Minoru Kinoshita

The Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato-ku, Tokyo 106

(Received October 18, 1975)

The phosphorescent triplet state T_1 of *p*-chloroaniline (PCA) in a *p*-xylene host, in a neat crystal (n-trap), and in a PCA crystal doped with *p*-dichlorobenzene (x-trap) has been studied with the aid of phosphorescence spectra, optically detected zero-field magnetic resonance, and $T_1 \leftarrow S_0$ absorption spectra at temperatures below 4.2 K. The dynamic properties, particularly the radiative properties, of the individual spin states of T_1 are discussed in detail using the emission spectra for each spin state obtained with microwave techniques. For the x-trap system, the emissions from the T_y and T_z sublevels are found to be coincident in contrast to the other two systems. From this observation, it is suggested that the characters of the T_y and T_z states of normal PCA are mixed together in the x-trap.

The populating rates for the individual spin states were examined for the PCA crystal systems as a function of the excitation energy, when the excitation was induced by light having wavelengths in the $T_1 \leftarrow S_0$ absorption region. The relative populating rates thus obtained are dependent on the excitation energy. Therefore, it is concluded that the spin alignment produced by direct optical pumping from the ground state to the triplet manifold of the crystal is conserved during the vibrational relaxation and energy transfer processes. By using this unique wavelength dependence of the populating rates, the nature of the n- and x-traps is discussed and the vibrational structure of the $T_1 \leftarrow S_0$ spectrum is analyzed.

Detailed information on the static and dynamic properties of the phosphorescent triplet state of aromatic molecules has been successfully obtained in the past few years by using microwave techniques in combination with the conventional optical methods. In a previous paper,[1] it was shown that the emissions from the individual spin states in the lowest triplet state of *p*-chloroaniline (PCA) in *p*-xylene can be well separated at 1.3 K by applying the technique of microwave induced delayed phosphorescence (MIDP). This MIDP spectroscopy has proved to be useful in determining the mechanism of the $T_1 \rightarrow S_0$ radiative processes and in analyzing the vibrational structure of the phosphorescence. This work has been extended to two more PCA systems: a neat crystal and a PCA crystal doped with a small amount of *p*-dichlorobenzene. In these crystals, the phosphorescence is found to arise from the trap PCA molecules. It will be shown in this paper that the sublevel emissions of these traps are quite different from one system to another, although the phosphorescence spectra look much the same. From this observation the nature of the emitting centers will be deduced.

The $T_1 \leftarrow S_0$ absorption spectrum of a PCA crystal has also been observed and an attempt was made to analyze its vibrational structure using populating rates obtained by microwave techniques. Under the condition that spin-lattice relaxation is well suppressed, the spin directions produced by direct optical pumping into the triplet manifold are expected to be conserved during the vibrational relaxation, energy transfer, and phosphorescence decay processes. Therefore, the relative populating rates, if determined when the excitation is made by light of wavelengths corresponding to those of each vibronic band of the $T_1 \leftarrow S_0$ spectrum, are considered to be selective, and therefore, to be useful in the vibrational analysis of the spectrum.

Experimental

p-Chloroaniline, *p*-dichlorobenzene, and *p*-xylene were purchased from Tokyo Kasei Co. The former two materials were zone-refined (about 60 passes) and the purified portions were further sublimed in a vacuum. *p*-Xylene was purified by multiple distillation.

The light sources for the emission measurements were an Ork CH-612 1-kW mercury arc lamp and an Ushio UXL-1000D-O 1-kW DC xenon lamp. The exciting light was passed through a Corning 7-54 glass filter and a saturated $NiSO_4$ aqueous solution filter, and chopped with an Uniblitz L12 type electromagnetic shutter. The exciting light for photo-excitation experiments or the emission light from the sample was isolated by a Spex 1700-III 3/4-m spectrometer. The observing time was controlled by using an Uniblitz 26 type shutter in front of an EMI 6256-SA photomultiplier. The signal was fed into a low-pass filter and measured through a signal averager system (Nomura Electric Co. NP-800 or Ortec Model 4620/4623) or a PAR Model 128 lock-in amplifier. Hewlett-Packard Model 8620A and Weinschel Model 221 sweep oscillators were used as the microwave source with an appropriate microwave filter. The MIDP spectra were measured in a manner similar to that described in detail in a previous paper.[1] The repetition rate for the excitation and observation cycles was controlled to be 0.1—1 Hz by an Ortec 4653/4654 pulse generator system.

The light source for the absorption measurements was an Ushio UXL-500 500 W DC xenon lamp. The light transmitted through a 6 mm thick crystal was observed in the second order diffraction of the 3/4-m spectrometer.

The populating rate ratios for the triplet sublevels for each excitation energy were obtained by the fast passage PMDR method, first used by Winscom and Maki,[2] or a modified MIDP method. In the analysis of the signals, the values of the total decay and the relative radiative decay rate constants obtained by the ordinary MIDP techniques[3,4] were used.

Factor Group States

The crystal structure of PCA has been studied by

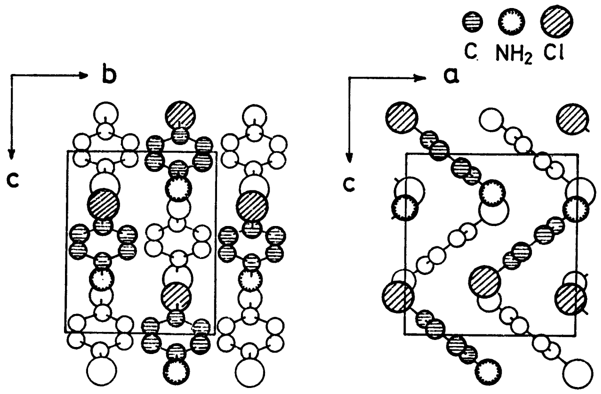

Fig. 1. The crystal structure of *p*-chloroaniline projected along the a and b axes.

Palm and was found to belong to the orthorhombic space group P_{nma} (D_{2h}^{16}),[5] as is shown in Fig. 1. The unit cell contains four PCA molecules. The long molecular axis (z: N–Cl direction) makes a larger projection on the a axis than on the c axis, and the medium in-plane axis (y: perpendicular to the long axis) is exactly parallel to the b axis. The molecular plane makes an angle of 39°40′ with the ab plane and the angle between the planes of two molecules is 79°20′. The coincidence of the molecular y axis with the crystal b axis offers many advantages in studying the optical properties of a PCA crystal.

TABLE 1. THE TOTAL SYMMETRIES OF THE THREE SPIN STATES IN THE FOUR ELECTRONIC FACTOR GROUP STATES

	T_a	T_b	T_c
^3A_g	B_{1g}	B_{2g}	B_{3g}
$^3B_{1u}$	A_u	B_{3u}(c)	B_{2u}(b)
$^3B_{2g}$	B_{3g}	A_g	B_{1g}
$^3B_{3u}$	B_{2u}(b)	B_{1u}(a)	A_u

The excited triplet A_1 (π,π^*) state of the free PCA molecule splits into the four factor group states of B_{1u}, B_{3u}, A_g and B_{2g} in the crystal. The three spin substates of the exciton level are designated by T_a, T_b and T_c, and their total symmetries are summarized in Table 1 with the polarization characteristics of the transition between the ground state and each substate. The crystal vectors a, b and c are designated as B_{1u}, B_{2u} and B_{3u}, respectively. Four of the twelve substates in Table 1 have the possibility of carrying dipole activity. If we assume that the one-center spin-orbit interaction between the (π,π^*) and (σ,π^*) states is predominant in acquiring the dipole activity, only two substates remain as strongly active substates: the $T_b(B_{3u})$ substate in the B_{1u} factor group state and the $T_b(B_{1u})$ substate in the B_{3u} factor group state. The transition involving the former state is polarized parallel to the c axis and the one involving the latter parallel to the a axis. By following the theoretical treatment of Hochstrasser and using the crystal geometry, the intensity ratio of the (0,0) transition of $^3B_{1u}\leftarrow{}^1A_g$ to that of $^3B_{3u}\leftarrow{}^1A_g$ is estimated to be about 1.5. In the high-resolution $T_1\leftarrow S_0$ absorption spectrum of a PCA crystal, the (0,0) band is found to split into two lines, the lower-energy component being 3–4 times stronger than the higher-energy one. Although this observed intensity ratio is larger than the ratio calculated on the basis of the crystal structure, we can safely conclude that the lowest dipole-allowed component has the strongest intensity and is assigned to the $^3B_{1u}$ state.

It has been found by Marchetti[6] that the ordering of the crystal zero-field levels of this state is $T_b > T_a > T_c$ and the top sublevel has the strongest dipole activity. This ordering in the crystal system leads to the following ordering of the molecular zero-field levels: $T_y > T_z > T_x$. These facts eliminate the possibility of the $^3B_2(\pi,\pi^*)$ state as the phosphorescent state of the free PCA molecule. The assignments of the $^3A_1(\pi,\pi^*)$ state to T_1 of isolated PCA and the $^3B_{1u}$ state to the lowest exciton state coincide well with the results presented below.

Results and Discussion

Phosphorescence Spectra, Zero-field Splittings and Kinetic Constants. The phosphorescence spectra of PCA were observed in three different systems: (1) in PCA molecules doped in a *p*-xylene crystal in which the PCA molecules are considered to be not too distorted by the host lattice, (2) in a neat PCA crystal the phosphorescence of which arises mainly from a trap 283 cm^{-1} below the $T_1\leftarrow S_0$ absorption origin, and (3) in a PCA crystal which has been doped with a small amount of *p*-dichlorobenzene. The phosphorescence origin of this latter crystal is lower by 67 cm^{-1} than the absorption origin of the crystal. The trap thus induced by *p*-dichlorobenzene is hereafter referred to in this text as an x-trap, because the appearnce of this trap resembles that of the so-called x-trap produced by doping quinoxaline in a naphthalene crystal[7]. The trap of the neat crystal is referred to as an n-trap for convenience. The phosphorescence spectra of these n- and x-traps are similar in shape to the spectrum reported previously for the PCA-doped xylene system[1].

The MIDP signals were observed at 4.559, 2.495 and 2.064 GHz for PCA isolated in *p*-xylene. The first two signals were strong but the latter was very weak. For the other systems, very strong PMDR and MIDP signals were observed. The x-trap phosphorescence produced signals at 4.539, 2.308 and 2.23 GHz and the n-trap at 4.063, 2.533 and 1.53 GHz.

The kinetic constants were obtained from an analysis of the MIDP signals by means of the method described by Schmidt *et al.*[3,4] with some modifications. The total decay rate constants of the sublevel emissions and

TABLE 2. ZERO-FIELD SPLITTINGS AND DECAY RATE CONSTANTS OF *p*-CHLOROANILINE

	PCA in *p*-xylene	n-trap	x-trap
D cm^{-1}	0.1176	0.1099	0.1128
E cm^{-1}	0.0344	0.0255	0.0385
k_y s^{-1}	9.5	42	16
k_z s^{-1}	6.8	20	12
k_x s^{-1}	0.1	1.1	0.5

the zero-field splitting constants in each system are summarized in Table 2. The zero-field microwave transitions were assigned according to the results stated in the previous section and the spin-orbit selection rule.

The D and E values are both positive for every system. Decreases in the D and E values of the n-trap system are noticeable. The latter value is reduced to about 66% of that observed in the x-trap system. While the total decay rate constant k_y for the n-trap is about four times larger than that for PCA in xylene, k_x increases by about 10 times in the n-trap. As will be seen, this increase in k_x for the PCA-crystal systems is attributed to the external heavy-atom effect. On the other hand, the changes in k_y and k_z in the n-trap may be correlated to the decrease in the E value.

Spin-Lattice Relaxation Rates. It has been shown that the spin-lattice relaxation rates in the phosphorescent triplet state in a zero magnetic field can be obtained from steady-state microwave induced phosphorescence experiments, if one knows the three total decay rates obtained in isolation.[8] Following the treatment of Antheunis,[8] one can derive the following equation for the spin-lattice relaxation rates, W_{xy} and W_{xz}* between the T_x and T_y sublevels and the T_x and T_z sublevels, respectively, as:

$$(k_x/k_y+1)W_{xy}+W_{xz}=\left(\frac{h_{x-y}(0;\,\mathrm{ISOL.})}{h_{x-y}(0;\,T;\,\mathrm{y}=\mathrm{z})}-1\right)k_x$$

where h_{x-y} (0;ISOL.) is the height of the microwave induced change in the steady-state phosphorescence intensity on sweeping through the T_x—T_y resonance in isolation and h_{x-y} (0;T; y=z) is the height under continuous microwave contact between T_y and T_z at temperature T. If $k_y \gg k_x'$ the left-hand side of the equation becomes the sum of the spin-lattice relaxation rates, *i.e.*, $W_{xy}+W_{xz}$.

In the n-trap system of the PCA crystal, $k_x/k_y=0.026$ and the approximation of $1+k_x/k_y \cong 1$ can be applied to within the error of the k_x value. The sum of the relaxation rates for the n-trap triplet state is plotted against the temperature in Fig. 2, which indicates that the isolation condition is well fulfilled below 1.8 K.

Vibrational Analysis of the $T_1 \rightarrow S_0$ Spectrum. The phosphorescence spectrum of each system was decomposed into the three sublevel emission spectra using MIDP techniques. The MIDP spectra for the three systems at 1.3 K are shown in Figs. 3–5.

For the PCA-doped xylene system, the vibrational

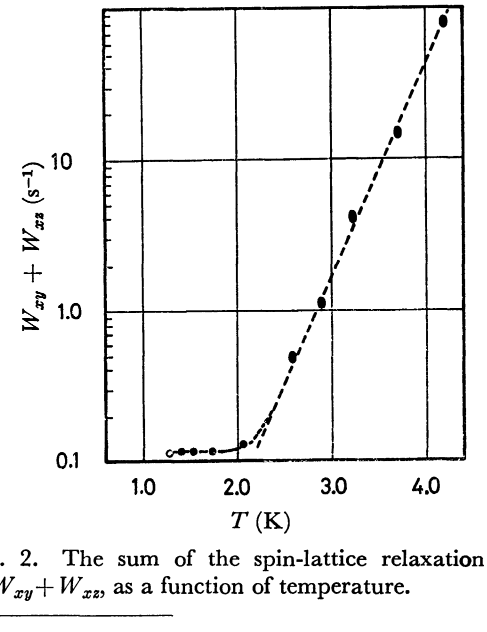

Fig. 2. The sum of the spin-lattice relaxation rates, $W_{xy}+W_{xz}$, as a function of temperature.

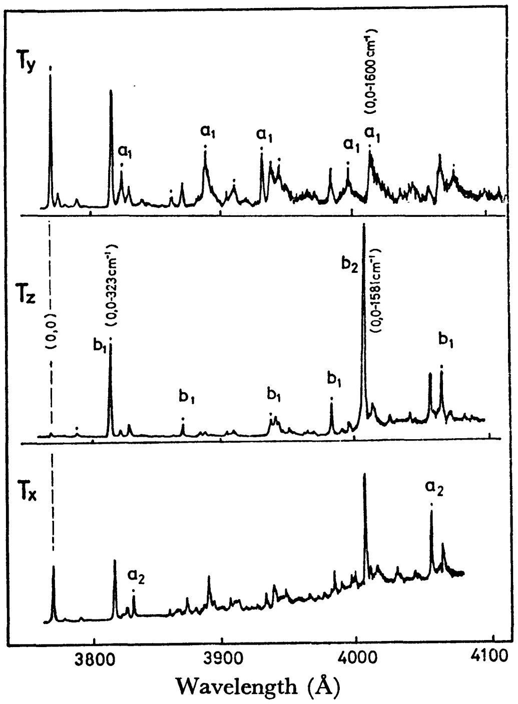

Fig. 3. The MIDP spectra of *p*-chloroaniline in *p*-xylene at 1.3 K. The spectrum denoted by T_u is the emission from the T_u sublevel (u=x, y, and z).

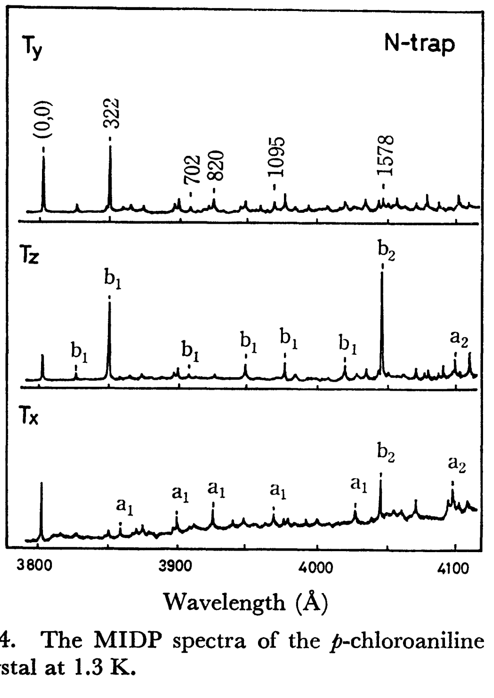

Fig. 4. The MIDP spectra of the *p*-chloroaniline neat crystal at 1.3 K.

---

* The approximation, $W_{xy}=W_{yx}$ and $W_{xz}=W_{zx}$, are used.

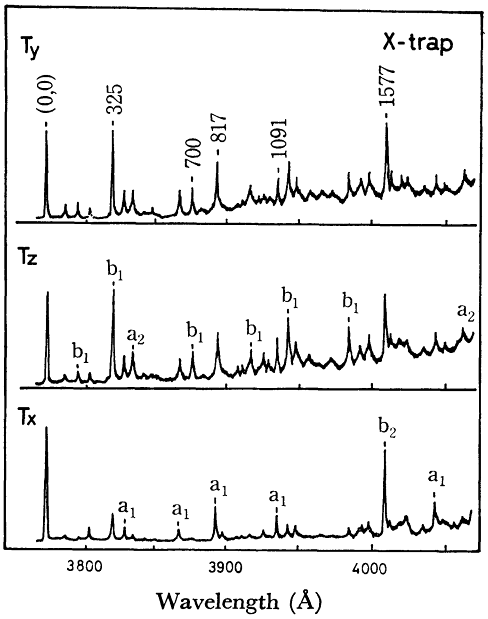

Fig. 5. The MIDP spectra (at 1.3 K) of the x-trap induced by doping *p*-dichlorobenzene into the *p*-chloroaniline crystal.

TABLE 3. VIBRATIONAL ANALYSIS OF THE PHOSPHORESCENCE SPECTRUM OF *p*-CHLOROANILINE IN *p*-XYLENE AT 1.5 K[a]

ν (cm^{-1})	$\Delta\nu$ (cm^{-1})	Relative intensity	Assignment
26513		s	(0, 0)
26470	43	w	lattice
26372	141	w	b_1
26189	323	s	b_1 (C–Cl bend. o.p.)
26129	384	m	a_1 (C–C bend. i.p.)
26097	416	m	a_2
25864	649	w	a_1 (2×323)
25811	702	m	b_1 (323+384)
25694	818	m	a_1 (C–C str.)
25583	930	vw	b_1
25415	1098	m	a_1
25376	1137	w	b_1 (323+818)
25338	1175	w	a_1 (C–H bend.)
25091	1421	m	b_1 (323+1098)
25016	1497	w	a_1 (C=C str.)
24932	1581	m	b_2 (C=C str.)
24913	1600	w	a_1 (C=C str.)
24609	1904	vw	a_2 (323+1581)
24592	1921	w	a_1 (818+1098)
24549	1964	w	b_2 (384+1581)

a) Relative intensity: s > m > w > vw, bend: bending mode, str: stretching mode, o.p.: out-of-plane, i.p.: in-plane.

analysis indicated in Table 3 has been reported previously.[1] First, the band at 0—323 cm^{-1} was assigned to the out-of-plane b_1 vibration and that at 0—1581 cm^{-1} to the in-plane vibration of b_2 symmetry. Then the other bands were analyzed using the following characteristics of the MIDP spectra of Fig. 3:

1) The bands involving totally symmetric vibrations are active in the emission from the T_y spin state.

2) The bands involving the vibrations of b_1 symmetry are active in the emissions from T_y, T_z and T_x.

3) The bands involving the vibrations of b_2 symmetry are active in the emissions from T_z and T_x.

The mechanisms whereby each sublevel of the isolated PCA molecule acquires its dipole activity are summarized in Table 4 along with the observed intensities of the individual vibronic species in the sublevel spectra.

For the other two systems, the analysis was also performed in a similar manner. For the n-trap, the characteristics of the MIDP spectra are almost identical to those described for isolated PCA with the exception of the fact that the b_1 vibrations are less active than the a_1 vibrations in the T_x spectrum. The same statement holds for the T_x spectrum of the x-trap. However, the T_y and T_z spectra of the x-trap are quite different from those of the n-trap. They are considered to be a mixture of the T_y and T_z spectra of the n-trap. Using these features and the results in Table 3, a vibrational analysis of the phosphorescences of the n- and x-traps was completed as shown in Tables 5 and 6.

Radiative Properties of the Triplet Sublevels. The relative radiative decay rates for the main vibronic bands were examined by the method of Schmidt *et al.*[4] and the results obtained for the (0,0), (0,0—320 cm^{-1}) and (0,0—1580 cm^{-1}) bands are tabulated in Table 7. Since the height of each vibronic band in the sublevel spectra of Figs. 3—5 is nearly proportional to the radiative decay rate k_u^r for that band (u=x, y and z), the relative values of k_u^r for the other bands may be estimated from Figs. 3—5 and Table 7.

Although the phosphorescence spectra are not shown here, the T_y spectrum of each system is almost identical to the phosphorescence spectrum of the respective system except for the intensity of the (0,0—1580 cm^{-1}) band. The intensity of this band in the phosphorescence spectra of the isolated PCA and of the n-trap results from the T_z emission, as can be seen from Table

TABLE 4. MAIN PERTURBING MECHANISMS FOR THE $^3A_1 \rightarrow {}^1A_1$ RADIATIVE TRANSITION FOR *p*-CHLOROANILINE IN *p*-XYLENE

Triplet sublevel	Vibrational symmetry	Observed intensity	Intermediate state	Perturbing state
$^3A_1(T_y)$	a_1	very strong	first order	$^1B_1(\sigma, \pi^*)$
	b_1	very strong	$^{3,1}B_1(\sigma, \pi^*)$	$^1A_1(\pi, \pi^*)$
$^3A_1(T_z)$	b_2	very strong	$^3B_2(\pi, \pi^*)$, $^1A_2(\sigma, \pi^*)$	$^1B_1(\sigma, \pi^*)$
	b_1	strong	$^3B_1(\sigma, \pi^*)$, $^1A_2(\sigma, \pi^*)$	$^1B_2(\pi, \pi^*)$
	a_2	medium	$^{3,1}A_2(\sigma, \pi^*)$	$^1A_1(\pi, \pi^*)$
$^3A_1(T_y)$	a_2	weak	$^3A_2(\sigma, \pi^*)$, $^1B_2(\pi, \pi^*)$	$^1B_1(\sigma, \pi^*)$
	b_2	weak	$^3B_2(\pi, \pi^*)$, $^1B_2(\pi, \pi^*)$	$^1A_1(\pi, \pi^*)$

TABLE 5. VIBRATIONAL ANALYSIS OF THE PHOSPHORESCENCE SPECTRUM OF *p*-CHLOROANILINE n-TRAP AT 1.3 K[a)]

ν (cm^{-1})	$\Delta\nu$ (cm^{-1})	Relative intensity	Assignment
26295		s	(0, 0)
26140	155	w	b$_1$
25992	303	vw	a$_1$ (2×155)
25973	322	s	b$_1$ (C–Cl bend. o.p.)
25920	375	w	a$_1$ (C–C bend. i.p.)
25874	421	w	a$_2$
25822	473	w	a$_1$ (155+322)
25673	622	vw	b$_1$ (2×155+322)
25652	643	m	a$_1$ (2×322)
25593	702	vw	b$_1$ (322+375)
25497	798	w	
25475	820	m	a$_1$ (C–C str.)
25350	945	w	b$_1$
25333	962	m	b$_1$ (3×322)
25200	1095	w	a$_1$
25173	1122	vw	b$_2$ (C–H bend.)
25153	1142	m	b$_1$ (322+820)
25116	1179	w	a$_1$ (C–H bend.)
24882	1413	m	
24792	1503	m	a$_1$ (C=C str.)
24717	1578	s	b$_2$ (C=C str.)
24694	1601	mw	a$_1$ (C=C str.)
24624	1671	w	
24565	1720	w	
24399	1896	m	a$_2$ (322+1578)
24337	1958	m	b$_2$ (375+1578)

a) Relative intensity: s > m > mw > w > vw, bend.: bending mode, str.: stretching mode, o.p.: out-of-palne, i.p.: in-plane.

TABLE 6. VIBRATIONAL ANALYSIS OF THE PHOSPHORESCENCE SPECTRUM OF *p*-CHLOROANILINE X-TRAP AT 1.3 K[a)]

ν (cm^{-1})	$\Delta\nu$ (cm^{-1})	Relative intensity	Assignment
26511		s	(0, 0)
26460	51	vw	
26422	89	w	
26360	151	w	b$_1$
26186	325	s	b$_1$ (C–Cl bend. o.p.)
26132	379	m	a$_1$ (C–C bend. i.p.)
26104	407	vw	
26092	419	m	a$_2$
26033	478	vw	a$_1$ (151+325)
25867	644	m	a$_1$ (2×325)
25811	700	m	b$_1$ (325+379)
25694	817	ms	a$_1$ (C–C str.)
25578	933	w	b$_1$
25541	970	m	b$_1$ (3×325)
25463	1048	vw	b$_1$
25420	1091	m	a$_1$
25370	1141	ms	b$_1$ (325+817)
25338	1173	m	a$_1$ (C–H bend.)
25095	1416	m	
25056	1455	mw	
25009	1506	m	a$_1$ (C=C str.)
24934	1577	s	b$_2$ (C=C str.)
24913	1598	m	a$_1$ (C=C str.)
24841	1670	m	
24779	1732	w	
24605	1906	m	a$_2$ (325+1577)
24555	1956	m	b$_2$ (375+1577)

a) Relative intensity: s > ms > m > mw > w > vw, bend.: bending mode, str.: stretching mode, o.p.: out-of-plane, i.p.: in-plane.

7 and Figs. 3 and 4. For the x-trap system, on the other hand, the spectra of the T_y and T_z emissions resemble each other as is seen in Fig. 5 and the emissions contribute nearly equally to the phosphorescence, as is shown in Table 7. For the T_x spectra, the non-totally symmetric vibrations appear relatively strongly in the isolated PCA system, while the totally symmetric vibrations are dominant in the n- and x-trap systems.

For the isolated PCA system, the characteristic appearance of the (0,0−323 cm^{-1}) b$_1$ band in each sublevel spectrum can be understood in terms of the internal heavy-atom effect which enhances the spin-orbit coupling between the $^{3,1}A_1$ (π,π^*) and $^{1,3}B_1$ (σ,π^*) states. The b$_2$ band at 0−1581 cm^{-1} which has a notable intensity in the T_z spectrum was assigned to the ν_{8b} type C=C stretching vibration. The ν_{8b} vibration was also observed in the phosphorescence spectra of benzene[9)] and toluene[10)]. The notable appearance of this vibration has been discussed in relation to the pseudo-Jahn-Teller interaction between the phosphorescent $^3(\pi,\pi^*)$ state and nearby $^3(\pi,\pi^*)$ state. The fact that this in-plane non-totally symmetric vibration bands has a considerable intensity in the phosphorescence spectrum indicates that the second order spin-orbit vibronic process plays a role comparable to the first order process producing the (0,0) band intensity. However, the oscillator strength of the $^1B_1$ $(\sigma,\pi^*)\leftarrow{}^1A_1$ transition is considered to be smaller by a factor of 10^{-2}–10^{-4} than that of the $^1B_2$ $(\pi,\pi^*)\leftarrow{}^1A_1$ transition. It is therefore concluded that a strong vibronic interaction exists between the $^3A_1$ (π,π^*) and $^3B_2$ (π,π^*) states *via* the ν_{8b} type vibration, which leads to the pseudo-Jahn-Teller distortion.

The sublevel spectra for the x-trap have structures quite different from those for isolated PCA. The T_y

TABLE 7. RELATIVE VALUES OF RADIATIVE DECAY RATE CONSTANTS OF *p*-CHLOROANILINE

System	PCA in *p*-xylene			n-trap			x-trap		
Symmefry	a$_1$	b$_1$	b$_2$	a$_1$	b$_1$	b$_2$	a$_1$	b$_1$	b$_2$
$\Delta\nu$	(0, 0)	323 cm^{-1}	1581 cm^{-1}	(0, 0)	322 cm^{-1}	1578 cm^{-1}	(0, 0)	325 cm^{-1}	1577 cm^{-1}
k_y^r	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
k_z^r	0.007	0.22	9.0	0.12	0.26	0.83	1.0	0.9	0.8
k_x^r	0.001	0.001	0.07	0.02_6	0.006	0.05	0.09	0.02	0.06_6

The maximum experimental error is estimated to be 25%.

and T_z spectra resemble each other except for the small intensity difference in the individual vibronic bands. These are considered to be a mixture of the T_y and T_z characters of isolated PCA. Each spectrum contains the strong (0,0), (0,0−325 cm^{-1}) and (0,0−1577 cm^{-1}) bands which belong to the a_1, b_1 and b_2 symmetries, respectively. On the other hand, the T_y and T_z spectra of the n-trap system seem to show a feature similar to those of isolated PCA. The (0,0) band in the T_z spectrum is weaker than the (0,0−322 cm^{-1}) band, but the relative intensity of the (0,0−1578 cm^{-1}) band is extremely strong compared with that in the T_y spectrum. This anomalous behavior of the two types of traps in the PCA crystals is considered to originate from a distortion of the electronic structure induced by impurity molecules (*p*-dichlorobenzene for the x-trap) or by defects in the crystal.

The lifetime of the T_x sublevel emission of isolated PCA in *p*-xylene is about 10 s or about 100 times longer than that of the T_y emission. Although the presence of the out-of-plane vibrations is well understood by the mechanisms given in Table 4, the strong appearance of the ν_{8b} type vibration and the (0,0) band in the T_x spectrum cannot be explained by the selection rule for the C_{2v} symmetry, because the spin-orbit coupling between the $^3A_1$ (π,π^*) and $^1B_2$ (π,π^*) states is small. The emission from the weakly radiative T_x sublevel seems to be sensitively affected by the crystal field.

The T_x spectra of the n- and x-traps contain strong (0,0) and (0,0−1577 cm^{-1}) bands and have similar stuctures except for the quasi-continuum background intensity. The intensities of the totally symmetric vibration bands apparently exceed those of the out-of-plane vibronic bands. This phenomenon can be attributed to the external heavy-atom effect due to the chlorine atoms of the nearby PCA molecules.

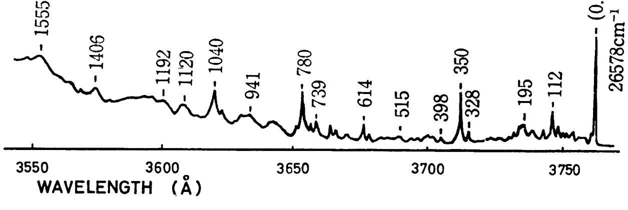

Fig. 6. The $T_1 \leftarrow S_0$ absorption spectrum of the *p*-chloroaniline crystal.

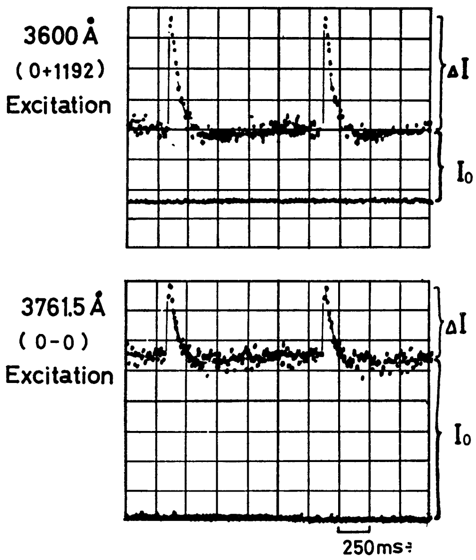

Fig. 7. Typical examples of the fast passage PMDR signals obtained by observing the total phosphorescence of the x-trap when the sample was excited at the (0,0) band (bottom) and at the (0,0+1192 cm^{-1}) band (top) of the $T_1 \leftarrow S_0$ spectrum.

Direct Pumping of Each Triplet Vibronic Level, Energy-Transfer and Nature of the Traps. The $T_1 \leftarrow S_0$ absorption spectrum of a PCA crystal is shown in Fig. 6. The spectrum exhibits a relatively strong (0,0) band at 26578 cm^{-1} and resembles that of a symmetry allowed transition. On the shorter wavelength side of 3650 Å, it becomes much broader. The excitation spectrum was also observed with a high-pressure mercury arc lamp and nearly the same band widths as those in the absorption spectrum were obtained. Under the same conditions as those for the observation of the excitation spectrum, the dependence of the relative populating rates for the three sublevels on the excitation energy was examined by means of the MIDP and fast passage PMDR techniques. Typical fast passage PMDR signals for the two different excitation energies are shown in Fig. 7. The quantity, $\Delta I/I_0$, in Fig. 7 is a measure of the population difference between the sublevels connected by the resonant microwave pulse. After some manipulation, it yields the relative populating rate.

The transition probability for excitation to each sublevel in the triplet manifold is expected to change with the electronic and geometrical stucture of the excited vibronic state. In other words, the populating rate obtained by pumping one of the vibronic levels in the lowest triplet state of the crystal and by monitoring the trap emission is expected to reflect the transition probability for excitation to one of the individual spin states in that vibronic level, if spin alignment is conserved during the processes of vibrational relaxation, energy transfer and phosphorescence decay.

The vibrational relaxation to the lowest exciton level is believed to be fast enough to preserve the selective pumping probabilities. For the triplet-triplet energy transfer process, El-Sayed *et al.* have shown that the spin directions are conserved in the case of the x-trap emission of a naphthalene crystal doped with quinoxaline.[11,12] These authors have concluded that the triplet-triplet energy transfer takes place by the electron exchange mechanism and the probability of transfer between one spin direction in the molecular framework of a donor and the three spin directions in the molecular framework of an acceptor is proportional to the squares of the projection of the spin direction of the donor onto the spin directions of the acceptor.

The dependence of the relative populating rates on the excitation energy for both the n- and x-traps are shown in Fig. 8. As can be seen from the figure, the populating rate ratios change dynamically from one vibronic band to another. Figure 8 shows the following important facts:

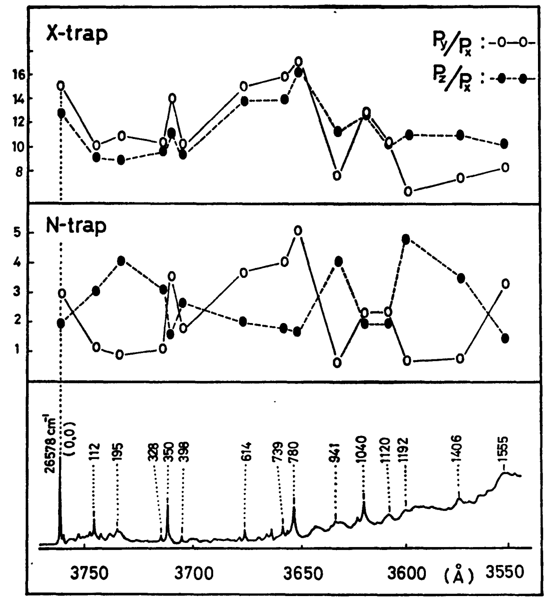

Fig. 8. The populating rate ratios obtained at 1.3 K by pumping each of the vibronic levels in the triplet manifold of the neat crystal (middle) and the *p*-chloroaniline crystal doped with *p*-dichlorobenzene (top) are plotted against the excitation energy. At the bottom, the $T_1 \leftarrow S_0$ absorption spectrum is shown for convenience.

1) The ratios P_u/P_x (u=y and z) change in a similar way with the excitation energy in the x-trap system, while they change in a different manner in the n-trap system.

2) The P_u/P_x ratios for (0,0) band excitation are in good agreement with the (0,0) band $k_u{}^r/k_x{}^r$ ratios for the x-trap, while for the n-trap they are much smaller than the $k_u{}^r/k_x{}^r$ ratios.

In order to check the growing process of the sublevel population, the phosphorescence rise curves for the respective exciting energies were examined under the same conditions as those for the observation of the excitation spectrum. Typical examples are shown in Fig. 9, where the initial part of the phosphorescence decay is also recorded after the observation of the growth curve for about 860 ms. The two curves in Fig. 9 apparently indicate that the growing rate of the longer lifetime component is considerably faster than the decay rate and that the optical pumping of the crystal spin state from which the relaxation occurs mainly to the T_x sublevel is fairly enhanced on the excitation in the (0,0+1192 cm^{-1}) band compared with that in the (0,0) band.

The marked changes in the rise curves and the populating rates for trap molecule systems suggest that the spin-lattice relaxation in the exciton spin states scarcely affects the deactivation processes to the sublevels of the emitting trap molecules. The fact that the x- and n-traps in the PCA crystals have different populating rate ratios for the same exciting energy is considered to give support to the conclusion obtained by El-Sayed *et al.*[11,12]

In the x-trap system, the characters of the T_y and T_z sublevels are different from those in isolated PCA. The sublevel spectra and the ratios of the radiative decay rates of the x-trap can be explained by the mixing of the T_y and T_z states of isolated PCA. If *p*-dichlorobenzene molecules are substituted into the PCA crystal, one of the two chlorine atoms of the *p*-dichlorobenzene is found at a position otherwise occupied by an amino group, and is expected to interact with the two neighboring chlorine atoms of the nearby PCA molecules, because these three chlorine atoms are located closely together on a plane nearly paralled to the bc plane of the crystal, as is shown in Fig. 10. Therefore, repulsive forces act between the chlorine atoms, and the chlorine

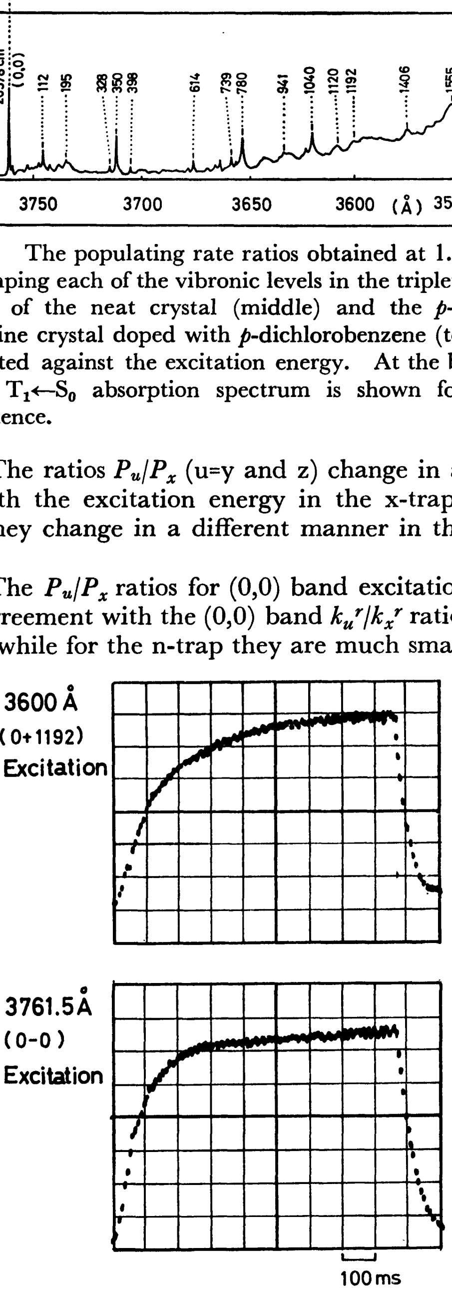

Fig. 9. The phosphorescence rise curves for the x-trap obtained by exciting at the (0,0) band (bottom) and at the (0,0+1192 cm^{-1}) band (top) of the $T_1 \leftarrow S_0$ absorption. After the excitation for about 860 ms, the exciting light was removed to observe the initial part of the decay.

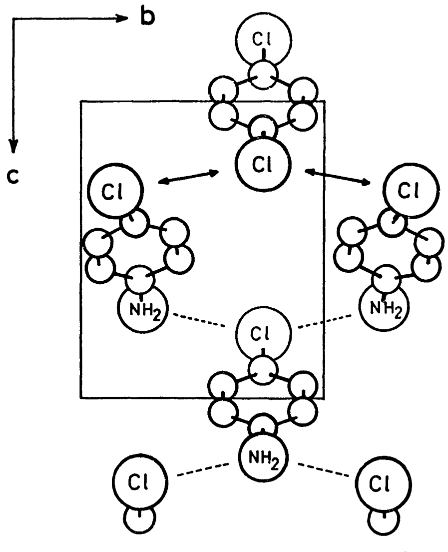

Fig. 10. Illustration of a possible structure of the x-trap induced in the *p*-chloroaniline crystal by doping *p*-dichlorobenzene. The solid arrow indicates the repulsive force and the dotted line shows attractive force.

atoms of these PCA molecules approach the neighboring amino groups. The y axes of the PCA molecules are thus expected to be distorted so as to be bent from the crystal b axis, which otherwise coincides with the y axis. Electronic distortion of these molecules is also expected to occur mainly in the molecular yz plane. This model seems to explain well the observed results for the x-trap system, where the z spin axis is considered to change its direction from the molecular long (N–Cl) axis toward the crystal b axis.

By using the conclusion of El-Sayed *et al.*, the spin directions or, equivalently, the populating rates for the trap sublevels under (0,0) band excitation are explained by the squares of the direction cosines between the crystal spin axes and those in the trap molecules. The (0,0) band pumping is expected to excite the crystal selectively to the T_b spin state, and also to a small extent to the T_a and T_c states by means of the external heavy-atom effect. Spin-orbit coupling which gives the transition intensity for the (0,0) band excitation of the $T_a \leftarrow S_0$ and $T_c \leftarrow S_0$ transitions comes from three-center integrals and is weaker than the external heavy-atom perturbation in the PCA crystal as mentioned above. However, the transition probability to the T_a or T_c spin state is not considered to exceed 10% of that to the T_b state, because the $k_y{}^r/k_x{}^r$ values in the n- and x-trap systems are large enough for the (0,0) band emission. Since excitation at the (0,0) origin of the $^3B_{1u}$ or $^3B_{3u}$ factor group state results mostly in the population of the T_b spin state, the observed ratio of $P_y/P_z \cong 1.2$ is then expected to represent the ratio $\cos^2\theta_{by}/\cos^2\theta_{bz}$, where $\cos\theta_{by}$ and $\cos\theta_{bz}$ are the projections of the crystal b axis onto the y- and z-spin axes of the x-trap molecule, respectively. By assuming that the angle between the y- and z-spin axes is 90° and the yz plane includes the b axis, θ_{by} and θ_{bz} are estimated to be about 42° and 48°, respectively. Spin axis rotation of 45° has been recently reported for the case of tetramethylpyrazine in durene.[13)]

The populating rate ratios P_u/P_x are small in the n-trap or, equivalently, the populating rate P_x is relatively large. This cannot be explained by the external heavy-atom effect alone, as mentioned previously. The large P_x is considered to be caused by the trapping process from the crystal T_b state to the trap T_x state. Considering the experimental errors in the populating rate ratios obtained, one may roughly estimate the range of the angles of the n-trap molecule to be $35° \lesssim \theta_{by} \lesssim 45°$, $53° \lesssim \theta_{bz} \lesssim 63°$ and $60° \lesssim \theta_{bx} \lesssim 70°$. We already know that the radiative decay rate ratios for the n-trap molecules are not so different from those of the isolated PCA molecules in *p*-xylene. Therefore, we can conclude that the deviation in orientation of the n-trap molecules does not affect its electronic structure as much as in the case of the x-trap, where the intermolecular interaction between the trap PCA and the neighboring *p*-dichlorobenzene is considered to play an important role in determining its electronic structure. Probably, the n-trap is not induced by a chemical impurity, but is produced by a crystal defect characteristic of the PCA crystal, because the n-trap is produced quite generally and no strong emissions from other traps can be found in the same spectral region.

Vibrational Analysis of the $T_1 \leftarrow S_0$ Spectrum. The variations of the P_u/P_x ratios with the excitation energy reflect the characteristics of the vibronic levels in the triplet manifold, and are thus utilized for the vibrational analysis of the $T_1 \leftarrow S_0$ absorption spectrum of the PCA crystal. Although the vibronic selection rule for the $T_1 \leftarrow S_0$ transition of the crystal depends on the representations of the factor group states, it is expected that the selection rule is correlated with the vibronic characteristics of the emission spectrum.

From the feature described for the n-trap system in the section on the vibrational analysis of the phosphorescence spectrum and the results shown in Fig. 8, it can be said that the transitions involving totally symmetric vibrations give a relatively large P_y/P_x ratio and a small P_z/P_x ratio, while the transitions involving the vibrations of b_2 symmetry give a relatively small P_y/P_x ratio and a large P_z/P_x ratio for the populating processes in the n-trap. On the other hand, it seems rather difficult to predict the P_u/P_x ratios for transitions involving the out-of-plane a_2 and b_1 vibrations.

The out-of-plane vibrations are expected to have low frequencies in the T_1 state. The bands at 0+112, 0+195, 0+328 and 0+398 cm^{-1} show small P_y/P_x ratios and large P_z/P_x ratios, and all of these low-frequency vibrations appear to have little possibility of belonging to the b_2 in-plane mode. If we attach considerable importance to the facts that they have relatively large P_u/P_x values and low-vibrational frequencies, these bands could be assigned to transitions to the out-of-plane vibronic levels.

The transitions corresponding to the band at 0+350 cm^{-1} is active in the processes to T_y and T_x and this vibration can possibly be assigned to the a_1 or b_1 vibration in the crystal system. By assuming a mirror-image relation of the spectral features for emission and absorption, this strong band might be assigned to the transition to the b_1 vibrational level. The corresponding emission band appears at 0−323 cm^{-1} in the PCA-doped xylene system. However, it should be noted that this ν_{10} type out-of-plane mode in *p*-dichlorobenzene shows no frequency change in the triplet and ground states and the frequencies of other vibrations also change very little[14)]. If the band at 0+350 cm^{-1} is due to the ν_{10} type vibration, which involves an out-of-plane C–Cl bending, the increment in frequency becomes about 8% upon transfer to the excited state. This seems to be too large. The line at 0+350 cm^{-1} is more reasonably assigned as being due to a totally symmetric C–Cl bending vibration that is at 379 cm^{-1} in the ground state in the *p*-xylene solution, since the populating rate ratios for excitation to this level are close to those obtained for the (0,0) band excitation, and the strong totally symmetric vibration band has been observed at 0+356 cm^{-1} in the $^1B_2\,(\pi,\pi^*) \leftarrow {}^1A_1$ spectrum by Marchetti.[15)]

In the wavelength region shorter than 3650 Å, the spectrum becomes broader and the bands, which can be assigned to b_2 vibrations, appear. The intensities of these b_2 bands, however, are not too strong. Burland, Castro and Robinson have studied the $^3B_{1u} \leftarrow {}^1A_{1g}$ absorption spectrum of benzene using the phosphorescence photo-excitation method.[16] They concluded that the ν_8 type vibration, the direction of which is related to the direction of the molecular distortion, is shifted by the pseudo-Jahn-Teller interaction from 1600 cm^{-1} in the ground state to 250 cm^{-1} in the excited triplet state.[16] In PCA, this normal mode splits into the ν_{8a} (a_1) and ν_{8b} (b_2) vibrations. The frequencies of these normal modes in the ground state are 1600 and 1581 cm^{-1}, respectively, in the *p*-xylene solution.[1] The absorption band at 0+1555 cm^{-1} is reasonably assigned as being due to the a_1 fundamental corresponding to the ν_{8a} type vibration. The frequency change is about -3%, but larger than those found in *p*-dichloro- and *p*-dibromo-benzenes, where the frequency changes are $+0.3$ and $+0.2\%$, respectively.[14]

This ν_{8a} assignment leads to the conclusion that the force constants for the C=C stretching vibration in the excited state is much the same as in the ground state and does not produce such a low frequency for the antisymmetric ν_{8b} type vibration as in the case of benzene. The geometrical change caused by the pseudo-Jahn-Teller interaction is not expected to be large. This conclusion seems to be consistent with the fact that the (0,0) band in the T_z sublevel spectrum of PCA in *p*-xylene is extremely weak. The most probable band due to the ν_{8b} type mode is the one at 0+1406 cm^{-1}.

TABLE 8. VIBRATIONAL ANALYSIS OF THE $T_1 \leftarrow S_0$ ABSORPTION SPECTRUM OF *p*-CHLOROANILINE CRYSTAL AND COMPARISON OF THE VIBRATIONAL FREQUENCIES (IN UNITS OF cm^{-1})

T_1		S_0[a)]	S_1[b)]	T_1 of DCB[c)]
(0, 0)				
112	b_1 or a_2	145	144(ac)	97
195		223		192
328	b_1	318		299(b_{2g})
350	a_1(C–Cl bend.)	379	356(abc)	330(a_g)
398	a_2	(416)[d)]	408(ac)	406(a_u)
614	a_1(C–Cl str.)	637	631(ac)	
739	(a_1)	—	696(ac)	668(a_g)
780	a_1(C–C str.)	826	797(abc)	
941	b_2(C–H bend.)	1118		
1040	a_1(C–H bend.)	1090	1059(abc)	1051(a_g)
1120	(a_1)	1171	1132(ac)	1081(a_g)
1192	b_2(C–H bend.)	1380	1208(b)	
1406	b_2(C=C str.)	1596	1400(b)	
1555	a_1(C=C str.)	1602		1578(a_g)

a) V. B. Singh, R. N. Singh, and I. S. Singh, *Spectrochim. Acta*, **22**, 927 (1966). b) Ref. 15. c) DCB= *p*-dichlorobenzene, Ref. 14. d) This value is from the phosphorescence spectrum in the *p*-xylene solution.

The final results of the analysis of the main bands observed in the absorption spectrum of the PCA crystal are summarized in Table 8, where the frequencies of each state are compared. The frequency changes in the observed normal modes in the ground state, in the first excited singlet and triplet states are relatively small and the structural difference of the molecule between the first excited singlet and triplet states is also regarded as being very small.

References

1) E. Kanezaki, N. Nishi, M. Kinoshita, and K. Niimori, *Chem. Phys. Lett.*, **29**, 529 (1974).

2) C. J. Winscom and A. H. Maki, *Chem. Phys. Lett.*, **12**, 264 (1971).

3) J. Schmidt, W. S. Veeman, and J. H. van der Waals, *Chem. Phys. Lett.*, **4**, 341 (1969).

4) J. Schmidt, D. A. Antheunis, and J. H. van der Waals, *Mol. Phys.*, **22**, 1 (1971).

5) J. H. Palm, *Acta Crystallogr*, **21**, 473 (1966).

6) A. P. Marchetti, *J. Chem. Phys.*, **57**, 5475 (1972).

7) H. Port and H. C. Wolf, *Z. Naturforsch.*, **23a**, 315 (1968).

8) D. A. Antheunis, Thesis, University of Leiden, The Netherlands (1974).

9) E. R. Bernstein, S. D. Colson, D. S. Tinti, and G. W. Robinson, *J. Chem. Phys.*, **48**, 4632 (1968).

10) D. M. Haaland and G. C. Nieman, *J. Chem. Phys.*, **59**, 4423 (1973).

11) M. A. El-Sayed, D. S. Tinti, and E. M. Yee, *J. Chem. Phys.*, **51**, 5721 (1969).

12) M. A. El-Sayed, *J. Chem. Phys.*, **54**, 680 (1971).

13) D. A. Antheunis, B. J. Botter, J. Schmidt, and J. H. van der Waals, *Mol. Phys.*, **29**, 49 (1975).

14) G. Castro and R. M. Hochstrasser, *J. Chem. Phys.*, **46**, 3617 (1967).

15) A. P. Marchetti, *J. Chem. Phys.*, **56**, 5101 (1972).

16) D. M. Burland, G. Castro, and G. W. Robinson, *J. Chem. Phys.*, **52**, 4100 (1970).