Polarized Reflection and Absorption Spectra of the [2.2]-Paracyclophane Crystal

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The reflection spectra of a [2.2]-paracyclophane crystal were measured in the 17000—62000 cm^{-1} region with incident light polarized parallel and perpendicular to the a-axis. From analysis of the reflection spectra by the Kramers-Kronig method, the a-axis and c-axis polarized absorption spectra in the 38000—60000 cm^{-1} region were obtained. The c-axis polarized spectrum was obtained for the first time. The 43000 cm^{-1} band in the c-axis spectrum was assigned to the transitions to the $^1B_{1u}$ (p) and $^1B_{1u}$ (CT) states. The band around 48000 cm^{-1} was assigned to the transition to the $^1B_{3u}^-$ state, corresponding to the transition to the $^1E_{2g}^-$ state in benzene.

The electronic absorption spectra of [2.2]-paracyclophane (abbreviated hereafter to PC) in single crystal and in solution together with those of tetramethyl [2.2]-paracyclophane and multilayered cyclophanes in solution were reported previously.[1] Comparing the observed transition energies, oscillator strengths, and directions of transition moments with those obtained theoretically by considering the interaction between the ground, locally excited, and charge-transfer configurations, better assignments than those by others[2-4] were made.

It was difficult in the previous study,[1] however, to obtain the c-axis polarized absorption spectrum of the PC crystal in the region higher than 38000 cm^{-1} since the intensity was too strong for direct absorption measurement. In order to overcome this difficulty, we have undertaken to obtain polarized absorption spectra of PC single crystals by reflection measurement in the 17000—62000 cm^{-1} region and to verify our previous assignments by analysis of accurately determined polarization ratios.

Experimental

PC was purified by column chromatography on silica gel and then sublimed *in vacuo*. Single crystals were obtained by recrystallization from chloroform solution. The (011) faces of the crystals, on which reflection spectra were measured, were identified by optical conoscopy and X-ray analysis.

Reflection spectra at room temperature were measured with a reflection spectrophotometer.[5] Since PC sublimes gradually in high vacuum even at room temperature, reflection measurements in the vacuum ultraviolet region were performed under one atmosphere of dry nitrogen. The spectra shown in Fig. 1 are the averages of six determinations. Actual measurements of reflection spectra were made with the incident light polarized parallel and perpendicular to the a-axis. The refractive index, n, and the absorption index, k, were calculated by the Kramers-Kronig method.[6] The molar absorption coefficient, ε, for light polarized parallel or perpendicular to the a-axis was calculated with the formula

$$\varepsilon = \frac{4\pi nk\nu}{2.303M}$$

where ν is the frequency in cm^{-1} and M the molarity of the crystal (5.91 mol/l for PC). The c-axis polarized spectrum was obtained from the ε values for the light polarized paralell and perpendicular to the a-axis in the (011) plane,

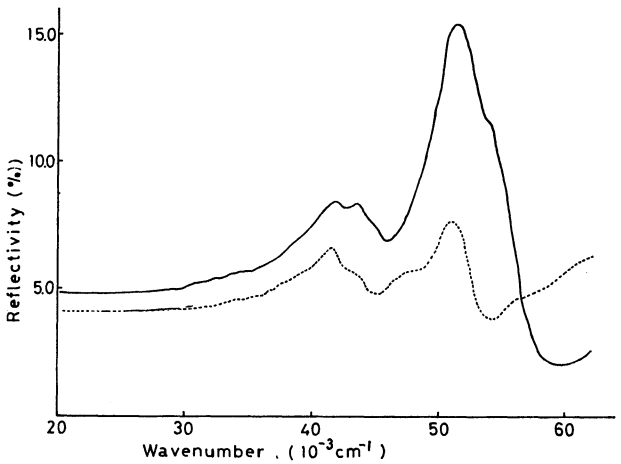


Fig. 1. Reflection spectra observed on the (011) face of the PC crystal. The solid and dotted cruves were obtained with the incident light polarized perpendicular and parallel to the a-axis, respectively.

the orientation of molecules in a unit cell being considered. In the actual evaluation the following equation was used:

$$\varepsilon_c = \frac{\varepsilon_{\perp a} - \cos^2 49°14' \, \varepsilon_a}{\cos^2 40°46'}$$

Results

Absorption spectra derived from the reflection spectra at room temperature are shown in Fig. 2. These spectra correspond fairly well to the absorption spectrum in solution. Here we are not concerned with the weak bands (bands I and II[1]) which appear in the 29500—38000 cm^{-1} region in solution but with bands III—VII which appear in the 38000—59400 cm^{-1} region.

The a-axis spectrum in the 38000—50000 cm^{-1} region agrees with the spectrum of the (001) face obtained by direct absorption measurement.[1] In the region above 56000 cm^{-1}, the intensity of the a-axis spectrum is slightly increased with increasing wave number. The reliability of this result was confirmed by varying the trial reflection curve[7] for the frequency region higher than our experimental limit. With all the trial curves, we found an a-axis polarized transition band in this region.

The c-axis spectrum in the wave number region higher than 38000 cm^{-1} was obtained for the first time.

The absorption intensity in this region is too strong to be measured directly. The observed band positions and the oscillator strengths in solution and in crystal are listed in Table 1.

Discussion

The PC crystal belongs to the D_{4h}^{14} space group (tetragonal) and has two molecules per unit cell.[8] The molecular point group and the molecular site group are both D_{2h}. PC is thus an example in which the site symmetry is the same as the full molecular point group symmetry. The unique symmetry axis of two molecules in a unit cell and their benzene-ring planes are perpendicular to each other. Therefore, a Davydov splitting is expected neither for the transition to the $^1B_{2u}$ state polarized parallel to the y molecular axis nor for the transition to the $^1B_{3u}$ state polarized parallel to the x molecular axis. Both transition bands are expected to appear in the spectra polarized along the a and b crystal axes, while the band corresponding to the transition to the $^1B_{1u}$ state polarized parallel to the z molecular axis is expected to appear in the spectrum polarized along the c crystal axis.

In the a-axis component of the crystal spectrum derived from the observed reflection spectrum, a weak band appears at 39400 cm^{-1}, in agreement with the direct absorption measurement.[1] The oscillator strength of this band was roughly estimated to be 0.01_5 in the present study. These results support the previous assignment[1] that the band at 39400 cm^{-1} is due to the transition to the $^1B_{2u}$ (α-parentage) excited state.

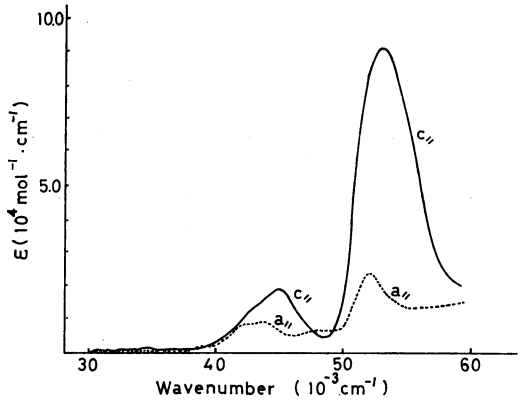


Fig. 2. Polarized absorption spectra of PC derived from the reflection spectra.

The 43000 cm^{-1} band in the a-axis spectrum and the 45000 cm^{-1} band in the c-axis spectrum (Fig. 2), correspond to the 44500 cm^{-1} band in solution. Two bands polarized along the long molecular axis are expected to appear in this region of the c-axis spectrum;[1] one of them corresponds to the *p*-band of *p*-xylene which is strongly polarized along the long molecular axis[9-11] and the other is due to the transition to the charge-transfer (CT) state stabilized by interaction with a locally excited configuration corresponding to the β-band of *p*-xylene. The former band is theoretically predicted to appear at 41400 cm^{-1} (f=0.220) and the latter at 46930 cm^{-1} (f=0.327). The band observed at 45000 cm^{-1} in the c-axis spectrum can be separated into two bands; a stronger band at higher frequencies and a weaker band at lower frequencies. Thus, the observed c-axis spectrum supports the prediction.

Let us consider the 43000 cm^{-1} band in the a-axis spectrum. From the polarization, this band can be ascribed to a transition to the $^1B_{2u}$ or $^1B_{3u}^-$ state. Two bands polarized along the a-axis are theoretically predicted to appear in this region. They are due to transitions to the $^1B_{3u}^-$ and $^1B_{2u}$ (CT) states. The transition energies and oscillator strengths are calculated to be as follows: 46680 cm^{-1}, 0.425 for the transition to the $^1B_{2u}$ state and 45300 cm^{-1}, 0 for the transition to the $^1B_{3u}^-$ state. The observed spectrum (Fig. 2) shows that another band (band V in the previous paper) polarized along the a-axis appears at 48700 cm^{-1} as a shoulder. It is therefore reasonable to consider that the a-axis polarized bands at 43000 and 48700 cm^{-1} are due to the predicted transitions to the $^1B_{2u}$ and $^1B_{3u}^-$ states. Since the calculated transition energies are close to each other for both transitions, it is difficult to determine which transition corresponds to the 43000 cm^{-1} band. By comparing the observed and predicted intensities, however, it is more probable that the 43000 and 48700 cm^{-1} bands are due to the transitions to the $^1B_{2u}$ and $^1B_{3u}^-$ states, respectively.

The $^1B_{3u}^-$ state is mainly composed of a locally excited configuration corresponding to the excitation to the $^1E_{2g}^-$ state of benzene. A number of studies have been made on the band corresponding to the transition to the $^1E_{2g}^-$ state which is forbidden for benzene.[12-21] Quite recently, a band at 46300 cm^{-1} was assigned to this transition.[19,20] Thus it is reasonable to assign the 48700 cm^{-1} band of PC to the $^1B_{3u}^- \leftarrow {}^1A_{1g}$ transition.

The 52000 and 53200 cm^{-1} bands polarized along the a- and c-axis, respectively, correspond to the 53000 cm^{-1} band in solution. From the consideration of the absorption intensities and polarizations, the 52000 cm^{-1} band can be assigned to a transition to a $^1B_{2u}$ state (theoretically at 62380 cm^{-1} and β-parentage) and the 53200 cm^{-1} band to a $^1B_{1u}$ state (theoretically at 62610 cm^{-1} and β-parentage). Both bands correspond to the strong β bands of *p*-xylene.

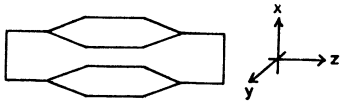
The a-axis spectrum has an absorption band at 59000 cm^{-1}. This band may correspond to a shoulder at 58000 cm^{-1} in solution. In view of the polarization, the 59000 cm^{-1} band is tentatively assigned to a transition to a $^1B_{3u}^+$ excited state (theoretically predicted to appear at 62270 cm^{-1}). This transition band corresponds to the $^1E_{2g}^+ \leftarrow {}^1A_{1g}^-$ transition band of benzene which appears at 169—172 nm.[19] In the crystal, however, a transition to the conduction band is also possible in the region above 55000 cm^{-1}. This makes the assignment of the 59000 cm^{-1} band ambiguous.

All the assignments are listed in Table 1. The transition energies for observed bands in the crystal show consistent trends; the bands of the a-axis spectrum show a red shift, while those of the c-axis spectrum show no shift or a small blue shift compared with those of the solution spectrum. These results can be qualitatively

TABLE 1. OBSERVED AND CALCULATED TRANSITION ENERGIES (ΔE in 10^3 cm^{-1}), OSCILLATOR STRENGTHS (f), AND POLARIZATIONS OF PC

Band[a]	Obsd: Soln ΔE_{soln}	Obsd: Soln f	Obsd: Cryst ΔE_{cryst}	Obsd: Cryst Pol	Obsd: Cryst f[b]	Calcd[d] $\Delta\nu$[c]	Calcd[d] ΔE_{calcd}	Calcd[d] f[f]	Upper state
III	41.0	0.05	39.4	*a*	0.02[e]	1.6	34.3	0.010 (y)	$^1B_{2u}(\alpha)$
IV	44.5	0.26	43.0	*a*	0.12[e]	1.5	46.7	0.425 (y)	$^1B_{2u}$(CT)[g]
			44.8	*c*	0.13	−0.3	41.3	0.220 (z)	$^1B_{1u}(\beta)$
							46.9	0.327 (z)	$^1B_{1u}$(CT)[g]
V	48.7	0.12	48.0	*a*	0.07[e]	0.7	45.3	0.0 (x)	$^1B_{3u}^-$
VI	53.3	1.07	52.0	*a*	0.26[e]	1.3	63.0	0.619 (y)	$^1B_{2u}(\beta)$
			53.2	*c*	0.72	0.1	63.0	0.667 (z)	$^1B_{1u}(\beta)$
VII	57.8	0.20	~58.0	*a*	0.16[e]	—	62.4	0.0 (x)	$^1B_{3u}^+$

a) We are concerned here with absorption bands in the frequency region higher than 38000 cm^{-1}, so bands I and II have been omitted from this table. b) For comparison with the solution values, these values were obtained by multiplying observed oscillator strengths of the c- and a-axes polarized bands by 1/3 and 2/3, respectively. c) $\Delta\nu=\Delta E_{soln}-\Delta E_{cryst}$. d) Theoretical values taken from Ref. 1. e) Roughly estimated because of overlapping of the corresponding bands. f) Polarization direction is indicated in parentheses:



g) Transitions to these states are mainly caused by intensity borrowing from the β states of the benzene ring.

interpreted by the simple exciton theory of molecular crystals[20] as follows.

In the case of the PC crystal, there are two translationally nonequivalent molecules per unit cell located at (0,0,0) and (1/2, 1/2, 1/2). Exciton states are given by the following linear combinations of $\mathbf{k}=0$:

$$\Psi_i^f = (2N)^{-1/2} \quad (\varphi_1^f \pm \varphi_2^f) \tag{1}$$

where i refers to the irreducible representation in the factor group ($i=1$ and 2 refer to E_u and A_u, respectively). φ_i^f is a one-site exciton function of Site i and State f. To first order, the energy of the i-th factor group component of the f-th electronic state of the crystal is given by:

$$E_i^f - E_0 = \varepsilon^f + D^f + J_i^{ff}(\mathbf{k}). \tag{2}$$

ε^f is the excitation energy of the free molecule from the ground state to the f-th excited state, D^f the environmental shift, and J_i^{ff} the sum of intermolecular excitation exchange integrals usually taken to be a sum of dipole-dipole interactions. In the case of the PC crystal, we have $J_i^{B_{2u},B_{2u}}=J_i^{B_{3u},B_{3u}}=0$, and $J_i^{B_{1u},B_{1u}}\neq 0$ because of the orientation of the two molecules in the unit cell. The calculated excitation exchange integrals are listed in Table 2. We see that the crystal states from the B_{2u} and B_{3u} excited states of the free molecule have zero Davydov splittings. The band shifts between solution and crystal are interpreted by the second term of Eq. (2). The B_{1u} molecular excited state splits in the crystal into the A_u and E_u exciton states with an energy difference of 325 cm^{-1}/Å^2. However, since the unique symmetry axis of the crystal (c-axis) is parallel to the long axis of all molecules, only the transition to the A_u state is optically allowed (c-axis polarized). The D^f term usually has a negative value for a crystal of an aromatic compound. This is easily seen from the a-axis spectrum. Thus the shift of each absorption band in the c-axis spectrum results from cancellation of the second and third terms in Eq. (2).

TABLE 2. EXCITATION EXCHANGE INTEGRALS (J_i^{fg}, cm^{-1}/Å^2)

	$^1B_{1u}$	$^1B_{2u}$	$^1B_{3u}$
$^1B_{1u}$	163	0	0
$^1B_{2u}$	0	0	−75
$^1B_{3u}$	0	−75	0

These values were obtained by the summation of dipole-dipole interaction terms within 50 Å spheres.

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