

POLARIZED INFRARED SPECTRUM OF *p*-XYLENE-CARBON TETRABROMIDE COMPLEX

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Polarized infrared spectrum of *p*-xylene-carbon tetrabromide complex single crystals was investigated in the 400–3200 cm^{-1} region. Crystal structure of the compound is confirmed. Spectra of complex components are not affected by complex formation, the enhancement of A_{1u} forbidden transitions and suppression of A_{1g} and B_{2g} bands in the crystalline compound is explained by the crystal-field symmetry. Assignments of *p*-xylene infrared-active frequencies are discussed.

The interest of a spectroscopic study of the *p*-xylene-carbon tetrabromide complex consists in the fact that:

- i*) it offers a possibility to study the influence of charge-transfer interactions on the vibration spectra of components [1]. As it was shown by a study of ultraviolet spectra [2], CBr_4 forms very weak charge-transfer complexes with aromatic hydrocarbons.
- ii*) it is possible to check the assignment of infrared active frequencies of *p*-xylene (assignments proposed by different authors [3–5] differ in several points) as well, as some not elucidated details of the crystal structure by means of the polarized infrared spectra of single-crystal samples.

The crystal structure of the compound was determined by Strieter [6]: the space group is $D_{2h}^{17} - C_{mcm}$, $Z = 4$ in the centered unit cell, *i.e.* $Z = 2$ in the primitive cell. The site sym-

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meiry of the *p*-xylene molecule is C_{2h} , the plane of the benzene nucleus being perpendicular to the crystal (*bc*) plane. The crystal axis \mathbf{a} coincides either with the short molecular axis — V , or with the long one — U . The first alternative is believed to be more probable (Fig. 1).

The correlation diagram of infrared-active vibrational modes of *p*-xylene in the molecular point group, site group and factor group for the case ($V \equiv \mathbf{a}$) is given in Table I

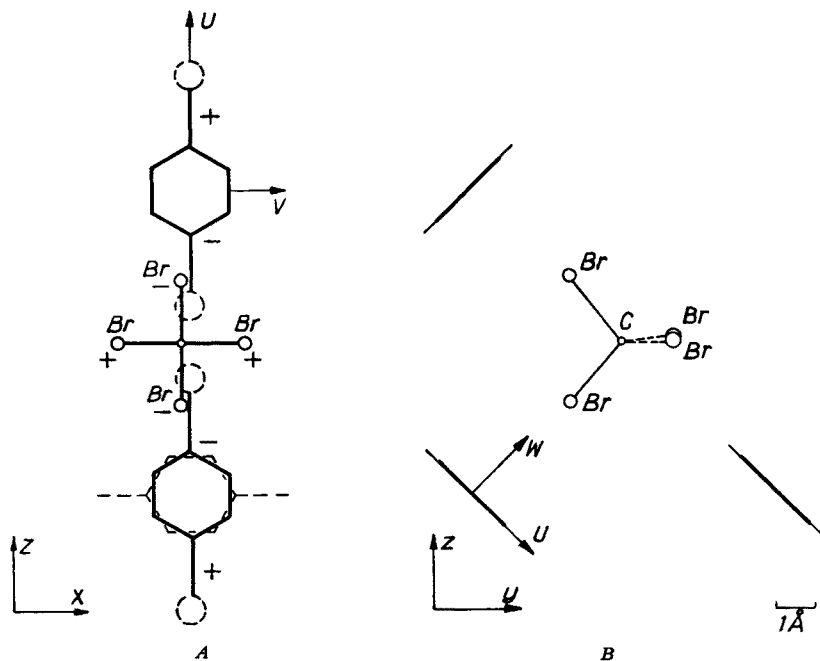


Fig. 1. Crystal structure of *p*-xylene-carbon tetrabromide complex. Projection on (010) plane (A) and (100) plane (B)

TABLE I

Correlation diagram for infrared-active vibrations of *p*-xylene in *p*-xylene-carbon tetrabromide complex crystal

Molecular point group	Crystal	
	site group	factor group
D_{2h}	C_{2h}	D_{2h}
$B_{1u}(p_W)$	→ $B_u(p_U + p_W)$ ←	$B_{1u}(p_b)$
$B_{2u}(p_U)$		$B_{2u}(p_c)$
$B_{3u}(p_V)$	→ $A_u(p_V)$ ←	$B_{3u}(p_a)$
$A_{1u}(i_a)$		$A_{1u}(i_a)$

It follows therefrom that:

1) B_{1u} and B_{2u} frequencies split in the crystal into two infrared-active components polarized along the \mathbf{b} - and \mathbf{c} - axes, respectively. If Davydov splittings are not resolved, the resulting bands are polarized in the (bc) plane,

2) B_{3u} frequencies are polarized along the \mathbf{a} — axis,

3) A_{1u} frequencies, forbidden in the free molecule, are allowed and \mathbf{a} — polarized in the crystal, while Raman-active frequencies (A_{1g} , B_{1g} , B_{2g} , B_{3g}) remain infrared-forbidden,

4) in the case ($U \equiv \mathbf{a}$) the correlation diagram must be changed in the way, that B_{1u} and B_{3u} frequencies will show the identical polarization in the (bc) plane, while B_{2u} and A_{1u} will be polarized along the \mathbf{a} — axis.

Since the assignments of some frequencies are well established, it was possible to determine the symmetry type of the others and the real orientation of molecular axes in the unit cell.

Experimental

Analytical grade CBr_4 was purified by vacuum sublimation. Single crystals of the complex compound were grown by slow cooling of a saturated solution of CBr_4 in p -xylene and oriented by means of a study of interference patterns in polarized light.

The oriented single-crystal samples were sealed between two NaCl (or KBr) windows. Very thin crystal films, perpendicular to the crystal \mathbf{b} — axis may be grown directly from the melted substance between two NaCl plates.

Infrared spectra were recorded in the 400–3200 cm^{-1} region by means of a H 800 Hilger spectrometer equipped with a NaCl prism and of an Unicam SP 100 prism-grating instrument. A Perkin–Elmer AgCl polarizer was used. The accuracy in frequency determination was of the order of 2 cm^{-1} for sharp bands and of 5–10 cm^{-1} for weak and diffuse bands.

Raman spectra were studied by photographic methods with oriented single-crystal samples. The compound is however unstable even when cooled to -5°C and well protected against the ultraviolet radiation. The spectra obtained were of bad quality and only the CBr_4 frequencies could be detected.

Results

The observed absorption bands (their frequencies, polarization states and intensity estimations) are listed in Table II, spectrometer recordings are given in Fig. 2.

The spectrum consists of some 60 bands polarized either along the \mathbf{a} — axis or in the (bc) plane. Depolarization effects due to experimental errors are negligibly small.

Discussion

Crystal structure and crystal-field effects. The detailed analysis of polarized spectrum shows (see later) that the characteristic B_{1u} and B_{2u} ring frequencies are polarized in the (bc) plane, while B_{3u} bands are totally \mathbf{a} — polarized. The crystal structure proposed by Strieter [6] is thus confirmed: the V — axis of the molecule is directed along the \mathbf{a} — axis of the crystal.

The frequencies of the components are practically unchanged in the complex. The shifts of *p*-xylene bands do not exceed 5 cm^{-1} , such changes may be due to the change in the dielectric constant of the medium. The same is true for the Raman spectrum of CBr_4 : the frequencies are almost identical with those of crystalline CB_4 [7], no splitting of degenerate frequencies was found, although CBr_4 molecules occupy sites of C_{2v} symmetry. Our results agree with those of Hooper [8] obtained by means of *EQR* measurements: the amount of the charge transfer in the ground state must be negligible.

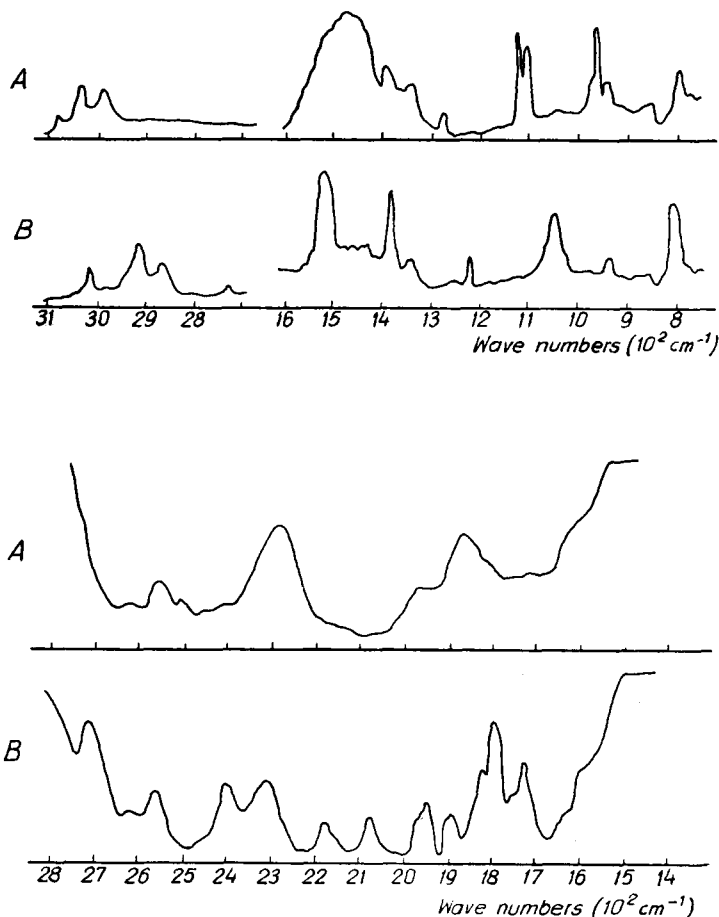


Fig. 2. Infrared spectrum of a single crystal sample: A) $E||a$, B) $E||c$

The intensity changes seem to be rather due to the crystal-field effects than to charge transfer interactions:

1) The band at 965 cm^{-1} absent in the spectrum of *p*-xylene vapour [9] and very weak in the liquid is strongly enhanced in the crystal. This frequency was assigned [3], [4] to an A_{1u} mode, forbidden in the free molecule and allowed in the site group. The band is fairly strong, but its polarization along the a — axis excludes the possibility of intensity-borrowing

TABLE II

Polarized infrared spectrum of the crystal (light beam perpendicular to the (ac) face)

ν cm ⁻¹	$E a$	$E c$	ν cm ⁻¹	$E a$	$E c$
486	v.w*	m	1896	m	—
670	v.s	v.s	1904	—	w
750	v.w	v.w	1915	—	v.w
796	w	v.s	1970	—	w
857	—	v.w	1982	—	m
866	—	sh	1997	w	—
935	—	w	2032	v.w	—
939	m	—	2090	—	w
955	s	—	2168	v.w	—
965	m	—	2200	—	v.w
1022	—	s	2230	v.w	—
1041	v.w	s	2300	w	—
1102	s	—	2325	—	w
1122	s	—	2414	—	w
1220	—	m	2430	v.w	—
1255	—	v.w	2460	—	v.w
1275	w	—	2530	w	—
1345	m	w	2570	—	w
1380	—	s	2585	w	—
1395	w	—	2612	—	v.w
1425	?	w	2648	v.w	—
1460	v.s	—	2689	v.w	—
1506	—	s	2730	—	w
1516	sh	v.s	2864	—	m
1604	—	v.w	2918	—	s
1640	w	—	2943	—	m
1720	—	w	2995	s	—
1735	—	m	3018	—	s
1764	v.w	—	3043	s	—
1784	—	m	3090	w	—
1830	—	w	3132	—	v.w

* v.s — very strong, s — strong, m — moderately strong, w — weak, v.w. — very weak, sh — shoulder

from the charge-transfer transition [1], which is (bc) polarized. The activation of g -frequencies by intensity-borrowing mechanism is impossible, because of the C_{2h} site symmetry [10]. 2) Three weak bands in the spectrum of liquid xylene: 833, 933 and 1182 cm⁻¹ assigned to A_{1g} and B_{3g} vibrations forbidden in the infrared spectrum of free molecules disappear in the spectrum of the crystal (very weak absorption at 937 cm⁻¹ is rather due to a combination CBr_4 band) (Fig. 3).

The breaking off of the $g \leftrightarrow g$ selection rule in the liquid state must be due to the interaction of randomly oriented xylene molecules. In the crystal, the site group being C_{2h} , the $g \leftrightarrow g$ rule must hold rigorously.

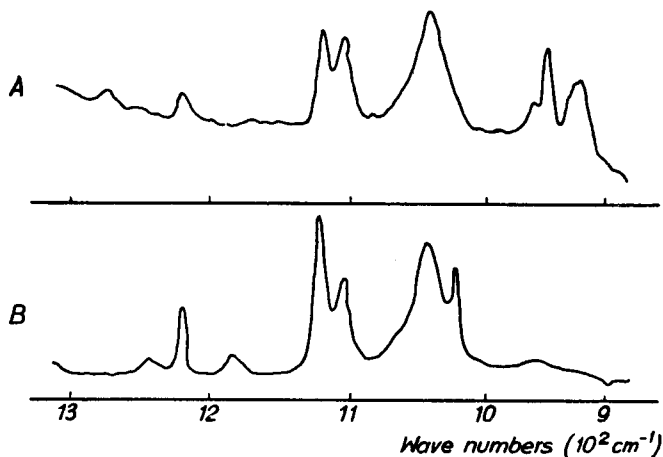


Fig. 3. Infrared spectra of A) solid complex (crystal powder) and B) *p*-xylene (liquid)

Assignments of *p*-xylene frequencies

Ring frequencies. The assignments of infrared-active vibrations [3], [4] are in good agreement with polarization data, except in the case of two bands: at 1421 and 1629 cm^{-1} . The first of them is very weak and shows rather the B_{2u} polarization (instead of B_{3u} , as proposed by Brandmuller [3]), but the result is not quite certain, because of a strong overlap with very strong methyl absorption. The assignment of 19*b* vibration to the 1346 cm^{-1} band, proposed by Garrigou-Lagrange seems to be more plausible. The 1629 cm^{-1} band was not found in the crystal spectrum; two weak bands in this region at 1604 and 1640 cm^{-1} seem to be rather due to combination vibrations.

Aromatic C—H stretching vibrations. Two strong bands at 3017 and 3044 cm^{-1} were alternatively assigned to 20*a* and 20*b* vibrations. The polarized spectrum shows clearly that the first of them corresponds to the 20*a* (B_{2u}) mode, the second one — to the 20*b* (B_{3u}) mode.

Methyl group frequencies. The spectrum of a free (C_{3v}) methyl group consists of two stretching $\nu(A+E)$, two bending $\delta(A+E)$ and one rocking $r(E)$ vibration. If the free rotation of methyl groups is assumed, *A* bands would be polarized along the molecular *U* — axis (*i.e.* in the (*bc*) plane of the crystal) and *E* bands in the (*VW*) molecular plane (completely depolarized in the spectrum of crystals). If the rotation is hindered, every *A* vibration would give one infrared-active B_{2u} (*bc* — polarized) frequency and an *E* vibration would split into one B_{1u} (*bc* — polarized) and one B_{3u} (*a* — polarized) component.

The spectrum of stretching vibrations corresponds to the case of hindered rotation. It consists of four strong bands, one of them: 2995 cm^{-1} is *a* — polarized and must be assigned to the B_{3u} (in plane) component of the ν_E vibration. Three others, polarized in the (*bc*) plane may correspond: 2946 cm^{-1} — to the B_{1u} (out-of-plane) component of ν_E and a doublet: 2863+2918 — to the Fermi resonance between $\nu_A(B_{2u})$ and the B_{2u} component of the $2 \times \delta_E$ vibration. If it is assumed, that the high-frequency component of the degenerate vibration corresponds always to ν'_s and the lower one — to ν_a [11], the conformation of the

TABLE III
Assignment of fundamentals

Mode*	Symmetry	Frequency		Symmetry type (from dichroic ratio)
		liquid	complex	
16 <i>b</i>	B_{1u}	483	486	B_{1u} (or B_{2u})
6 <i>a</i> [3]	A_{1g}	742	750 ?	?
11	B_{1u}	795	796	B_{1u} (or B_{2u})
6 <i>a</i> [4]	A_{1g}	833	<i>ia</i>	
5	B_{2g}	933	?	
17 <i>a</i>	A_{1u}	961	955	A_{1u} (or B_{3u})
—		—	965	A_{1u} or B_{3u} (rCH_3 ?)
18 <i>a</i>	B_{2u}	1022	1022	B_{2u} (or B_{1u})
rCH_3 [4]	$B_{1u} + B_{3u}$	1041	1042	B_{1u} (or B_{2u})
15	B_{3u}	{1102 1118}	{1102 1122}	B_{3u} (or A_u)
9 <i>a</i>	A_{1g}	1182	<i>ia</i>	
13	B_{2u}	1218	1220	B_{2u} (or B_{1u})
19 <i>b</i> ([4]	B_{3u}	1346	1345	B_{3u} (or A_{1u})
$\delta_A CH_3$ [4]	B_{2u}	1379	1380	B_{2u} (or B_{1u})
19 <i>b</i> [3]	B_{3u}	1421	1425	?
$\delta_E CH_3$	$B_{1u} + B_{3u}$	{1453 1458}	1460	B_{3u} (or A_{1u})
19 <i>a</i>	B_{2u}	1516	{1506 1516}	B_{2u} (or B_{1u})
14	B_{3u}	1629	1604? 1640?	B_{2u} (or B_{1u}) B_{3u} (or A_{1u})
$\nu_A CH_3$	B_{2u}	{2867 2921}	{2863 2918}	B_{2u} (or B_{1u})
$\nu_E CH_3$	$B_{1u} + B_{3u}$	{2945 2972}	2943 <i>ia</i>	B_{1u} (or B_{2u})
overtone		2995	2995	B_{3u} (or A_{1u})
20 <i>a, b</i>	B_{2u} and B_{3u}	{3017 3044}	3018 3043	B_{2u} (or (B_{1u}) 20 <i>a</i>) B_{3u} (or A_{1u}) 20 <i>b</i>

* in Wilson's notation [13].

methyl group may be deduced: one of its hydrogen atoms in the plane of the benzene ring, two other — in symmetrical positions at the both sides of the plane.

The assignment of the 2995 cm^{-1} band given in [4] is not consistent with its polarization state and the 2972 cm^{-1} band of the liquid is missing in the crystal spectrum. It is quite possible, that the conformation of methyl groups is different in the liquid and in the crystal-line complex compound [12].

In the low-frequency region, the symmetric bending vibration band $\delta_A = 1380 cm^{-1}$ is polarized in the (*bc*) plane in good agreement with the theory. The polarization states of degenerate frequencies seem to be anomalous: $\delta_E = 1460 cm^{-1}$ is simple and *a* — polarized, while $\nu_E = 1043 cm^{-1}$ band is strongly (*bc*) polarized. We are obliged to assume that in

TABLE IV

Assignment of overtone and combination bands

ν	Symmetry type	Assignment
935	?	$\text{CBr}_4 \nu_1 + \nu_3 = 934$
939	B_{1u} or B_{2u}	$6b + 18b = 935(B_{2u})$ or $1 + 11 = 940(B_{1u})$
1102 } 1120 }	B_{3u}	15 and $6a + 18b = 1116(B_{3u})$ FR*
1255	B_{1u} or B_{2u}	$17b + 1 = 1253(B_{1u})$
1275	A_{1u} or B_{3u}	$10b + 17a = 1270(B_{3u})$
1395	A_{1u} or B_{3u}	$9b + 18 = 1411(B_{3u})$
1506 } 1516 }	B_{2u}	$19a(B_{2u})$ and $9b + 15 = 1509(B_{2u})$ FR
1604	B_{1u} or B_{2u}	$17a + 6b = 1603(B_{1u})$ or $17b + 6a = 1620(B_{1u})$
1640	A_{1u} or B_{3u}	$17a + 4 = 1657(B_{3u})$
1720	B_{1u} or B_{2u}	$18 + 4 = 1720(B_{1u})$
1735	B_{1u} or B_{2u}	$17 + 5 = 1730(B_{2u})$
1764	A_{1u} or B_{3u}	$9b + \delta_A \text{CH}_3 = 1770(B_{3u})$
1784	B_{1u} or B_{2u}	$6 + 15 = 1763(B_{1u})$?
1830	B_{1u} or B_{2u}	$10b + 19a = 1826(B_{1u})$
1896	A_{1u} or B_{3u}	$9b + 19a = 1907(B_{3u})$
1904	B_{1u} or B_{2u}	$4 + 13 = 1918(B_{1u})$
1915	B_{1u} or B_{2u}	$10a + 15 = 1926(B_{1u})$
1970	B_{1u} or B_{2u}	$1 + 19a = 1975(B_{2u})$
1997	A_{1u} or B_{3u}	?
2032	A_{1u} or B_{3u}	$6b + \delta_A \text{CH}_3 = 2023(B_{2u})$
2090	B_{1u} or B_{2u}	$8a + 11 = 2103(B_{1u})$
2168	A_{1u} or B_{3u}	$6b + 19a = 2160(B_{3u})$
2200	B_{1u} or B_{2u}	$9a + 18a = 2204(B_{2u})$
2230	A_{1u} or B_{3u}	?
2300	A_{1u} or B_{3u}	$9a + 15 = 2302(B_{3u})$
2325	B_{1u} or B_{2u}	$5 + 18a = 2315(B_{1u})$
2414	B_{1u} or B_{2u}	$7a + 13 = 2423(B_{2u})$
2430	A_{1u} or B_{3u} }	$\delta_E^- \text{CH}_3 + 18a = 2466(B_{1u} + B_{3u})$
2460	B_{1u} or B_{2u} }	
2530	A_{1u} or B_{3u}	$3 + 4 = 2538(B_{2u})$
2570	B_{1u} or B_{2u}	$9a + \delta_A \text{CH}_3 = 2585(B_{2u})$
2585	A_{1u} or B_{3u}	$86 + 18a = 2598(B_{3u})$
2612	B_{1u} or B_{2u}	$8a + 18a = 2637(B_{2u})$
2648	A_{1u} or B_{3u}	$7a + \delta_E \text{CH}_3 = 2663(B_{1u} + B_{3u})$
2689	A_{1u} or B_{3u}	$3 + \delta_A \text{CH}_3 = 2698(B_{3u})$
2730	B_{1u} or B_{2u}	$2 \times \delta_A \text{CH}_3 = 2756(B_{2u})$
2864 } 2918 }	B_{2u}	$\gamma_A \text{CH}_3$ and $2 \times \delta_E \text{CH}_3(B_{2u})$ FR*
3090	A_{1u} or B_{3u}	$8b + 19a = 3094(B_{3u})$
3132	B_{1u} or B_{2u}	$8a + 19a = 3134(B_{2u})$

* FR — Fermi resonance

both cases one of the components: $\delta(B_{3u})$ and $r(B_{1u})$ is much stronger than the other or that the splitting of degenerate frequencies is increased in the crystal: $\delta_E \rightarrow 1460 + 1425$, $r_E \rightarrow 1042 + 965$. The first assumption seems to be much more plausible.

Overtone and combination bands. A tentative assignment of weak absorption bands of the *p*-xylene spectrum is given in Table IV. Frequencies of the fundamentals are taken from [3] and [4]; it is assumed that Raman frequencies, like the infrared ones are not affected by complex formation. Good agreement of calculated and observed frequencies of the same symmetry type seems to confirm the assignment of Raman-active fundamentals.

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