Polarized Raman and Infrared Spectra of 1,2,3- and 1,3,5-Trichloro- and Tribromobenzenes

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Assignment of the normal vibrations of 1,2,3- and 1,3,5-trichloro- and tribromobenzenes was made through the vibrational analyses of the polarized Raman and infrared spectra and also through the normal coordinate calculation. Substitutional effect on the vibrational frequencies and modes of the hydrogen bending and wagging vibrations induced by the halogen atoms is discussed.

Very recently the assignment of the normal vibrations of 2,6- and 3,5-dichloro- and 2,6- and 3,5-dibromopyridines was studied and a characteristic substitutional effect on the hydrogen bending and wagging vibrations was found.[1] The hydrogen bending and wagging vibrations of 2,6-dihalopyridines are of the ν_{18a}, ν_{18b}, and ν_{15} modes, and the ν_{17a}, ν_{17b}, and ν_{11} modes, respectively. In 3,5-dihalopyridines the frequency separation between the ν_{18a} and ν_{18b} vibrations and that between the ν_{17a} and ν_{17b} vibrations become very small and the bending ν_{15} and wagging ν_{11} vibrations change the vibrational modes to the ν_3 and ν_5 having higher frequencies than those of the ν_{15} and ν_{11} modes, respectively. In order to study the origin of such a substitutional effect on the frequencies and modes of the hydrogen bending and wagging vibrations, the normal vibrations of 1,2,3- and 1,3,5-trichloro- and tribromobenzenes are investigated.

Several studies have been made on the normal vibrations of trihalobenzenes,[2–4] but the reliable assignment based on enough experimental evidence such as polarization measurements of the Raman and infrared spectra has not been made. Since the orientation of the trihalobenzene molecules in crystal has been already studied, vibrational analyses of the polarized Raman and infrared spectra in single crystal can be easily made. In this paper, the assignment of the normal vibrations of 1,2,3- and 1,3,5-trichloro- and tribromobenzenes is discussed first on the basis of the polarization behavior of the Raman and infrared bands observed in single crystal and of the normal coordinate calculation, and then the substitutional effect on the normal vibrations is discussed.

Experimental

Material. 1,2,3-Trichloro-, 1,3,5-trichloro-, and 1,3,5-tribromobenzenes (1,2,3-TCB, 1,3,5-TCB, and 1,3,5-TBB) were obtained from Wako, Tokyo Kasei, and Nakarai Chemical Companies, respectively. 1,2,3-Tribromobenzene (1,2,3-TBB) was synthesized from *p*-nitroaniline following the method reported by Furuyama and Fukushi.[5] The samples were purified by repeated vacuum distillations followed by zone-refining of about 100 passages.

Optical Measurements. The polarized Raman spectrum was observed in single crystal with a JEOL 400 T Laser Raman Spectrophotometer. A well grown single crystal obtained by the Bridgman method was cut in a cube of about (5 mm)^3. The cleavage plane was selected as one of the planes of the cube and the edges of the cube were cut along the crystal growth direction, which is on the cleavage plane, and the directions perpendicular to it. The sample was excited with the 514.5 nm line from an Ar-ion laser. The method of observation of the polarized Raman spectrum was the same as described previously.[6] Depolarization measurement of the Raman spectrum was also made in molten phase.

The infrared spectrum was observed in vapor and single crystal phases with a Hitachi Infrared Spectrophotometer

Table 1. Force Constants for the In-Plane and Out-of-Plane Vibrations of 1,2,3- and 1,3,5-Trichloro- and Tribromobenzenes

In-plane vibrations			
$K_{\mathrm{C'-C'}}$[a]	5.0 hN m^{-1}	$H_{\mathrm{C'-C'-X}}$	0.35 (0.3) hN m^{-1}
$K_{\mathrm{C'-C}}$	5.0	$H_{\mathrm{C-C'-X}}$	0.35 (0.3)
$K_{\mathrm{C-C}}$	5.0	$H_{\mathrm{C'-C-H}}$	0.2
$K_{\mathrm{C'-X}}$[b]	2.5 (2.2)[c]	$H_{\mathrm{C-C-H}}$	0.2
$K_{\mathrm{C-H}}$	4.65	$F_{\mathrm{C\cdots C}}$[d]	0.5
$H_{\mathrm{C'-C'-C'}}$	0.25	$F_{\mathrm{C\cdots X}}$[d]	0.5 (0.4)
$H_{\mathrm{C-C'-C}}$	0.25 (0.2)	$F_{\mathrm{C\cdots H}}$[d]	0.46
$H_{\mathrm{C'-C'-C}}$	0.25	ρ	0.25
$H_{\mathrm{C'-C-C}}$	0.3	$f^{\mathrm{o}}_{\beta_\mathrm{X},\beta_\mathrm{X}}$	0.3 aN m rad^{-2}
$H_{\mathrm{C-C-C}}$	0.3	$f^{\mathrm{o}}_{\beta_\mathrm{H},\beta_\mathrm{H}}$	0.04
$H_{\mathrm{C'-C-C'}}$	0.3		
Out-of-plane vibrations			
$Q_{\mathrm{C'-C'}}$	0.28 aN m rad^{-2}	$p^{\mathrm{o}}_{\mathrm{X,X}}$	0.06 aN m rad^{-2}
$Q_{\mathrm{C'-C}}$	0.28	$p^{\mathrm{o}}_{\mathrm{X,H}}$	0.03
$Q_{\mathrm{C-C}}$	0.2	$p^{\mathrm{o}}_{\mathrm{H,H}}$	0.03
P_{X}	0.36 (0.37)	$p^{\mathrm{m}}_{\mathrm{X,X}}$	−0.03
P_{H}	0.3	$p^{\mathrm{m}}_{\mathrm{H,H}}$	−0.02
$q^{\mathrm{o}}_{\mathrm{C'-C'}}$	−0.06	$t^{\mathrm{o}}_{\mathrm{X}}$	−0.01
$q^{\mathrm{o}}_{\mathrm{C-C}}$	−0.05	$t^{\mathrm{o}}_{\mathrm{H}}$	−0.02
q^{m}	0.03		

a) C′ is the carbon atom bonded to the halogen atom. b) X refers to the Cl or Br atom. c) The first number is the value for trichlorobenzenes and the number in parentheses is that for tribromobenzenes. d) Values of the force constants involving the C′ atom are taken to be the same as those involving the C atom.

Table 2. Normal Vibrations of 1,2,3-Trichloro- and Tribromobenzenes

Sym Spec	Mode	1,2,3-Trichlorobenzene						1,2,3-Tribromobenzene				
		Raman			Infrared		Calcd	Raman			Infrared	Calcd
		$\tilde{\nu}$ /cm^{-1}	pol		pol		$\tilde{\nu}$ /cm^{-1}	$\tilde{\nu}$ /cm^{-1}	pol		pol	$\tilde{\nu}$ /cm^{-1}
			liq	cry	vap	cry			liq	cry	cry	
a$_1$	ν_{7a}						3084					3084
	ν_2	3072	p				3077	3060	p			3077
	ν_{8a}	1562	p				1565	1550	p			1550
	ν_{19a}	1420			B	I	1434	1395	p		I	1418
	ν_{18a}	1158	p		B	I	1135	1128	p		I	1116
	ν_{12}	1087	p			I	1109	1071	p		I	1070
	ν_1	1048	p			I	1055	1016	p		I	1034
	ν_{6a}	731	p			I	712	700	p		I	683
	C–X str (ν_{20a})$^{a)}$	507	p		B	I	483	393	p			384
	C–X str (ν_{13})	345	p				315	220	p			201
	X bend (ν_{9a})	223	dp				214	135	p			132
b$_2$	ν_{7b}	3078	dp				3080	3068	dp			3080
	ν_{8b}	1566	dp	ww			1578	1555	dp	ww		1562
	ν_{19b}	1435	dp	ww	A	II	1417	1435	dp	ww	II	1409
	ν_{14}	1362				II	1352					1342
	ν_{15}	1257	dp	ww		II	1241	1250	dp	ww	II	1236
	ν_{18b}	1193	dp	ww	A	II	1168	1146	dp	ww	II	1154
	ν_{6b}	797			A	II	805	720			II	746
	X bend (ν_3)	487	dp	ww		II	497	422	dp	ww		442
	C–X str (ν_{20b})	395	dp	ww			393	325	dp	ww		313
	X bend (ν_{9b})	207	dp	ww			212					126
a$_2$	ν_{17a}	907	dp	vv			931	910	dp	vv		930
	ν_{16a}	518	dp	vv			521	518	dp	vv		518
	X wag (ν_{10a})	204	dp	vv			202	200	dp	vv		191
b$_1$	ν_{17b}	990	dp	uu		III	981	980	dp	uu	III	980
	ν_{11}	775	dp	uu	C	III	790	775	dp	uu	III	790
	ν_4	690			C	III	672	680			III	678
	ν_{16b}	425				III	451	437			III	448
	X wag (ν_{10b})	262	dp	uu			255	237	dp	uu		239
	X wag (ν_5)	89$^{b)}$					91	70	dp			61

a) X refers to the Cl or Br atom. b) Value taken from the combination band.

Model 345. The single crystal sample was grown between two KRS-5 plates in the same way as described previously.[7] Well grown single crystal portion of the crystal sample was selected under polarized light and other portion was covered with aluminum foil. The polarized infrared spectrum was observed with an AgBr wire-grid polarizer. The incident infrared light was polarized by the polarizer in such a way that the electric vector pointed in the direction of 45° from both the vertical and horizontal directions. The polarizer was rotatable by 90°. Although the spectrophotometer had some preferential sensitivity to the vertically polarized light, the two diagonally polarized components of the light beam behaved equally concerning the intensity. The sample crystal sandwiched between two KRS-5 plates was held in a cell holder in such a way that the crystal growth direction on the sample plane coincided with the polarization direction of the incident infrared light.

Normal Coordinate Calculation

The normal coordinate calculation was performed through the standard GF matrix method with a FACOM M-780/10S computer at the Computer Center of Fukuoka University. The geometric parameters of the 1,2,3-TCB, 1,3,5-TCB, and 1,3,5-TBB molecules were taken from the data determined by Hazell et al.[8] and Milledge and Pant.[9] The molecular structure of 1,2,3-TBB was assumed to be the same as that of 1,2,3-TCB except for the C–Br bond, whose length was assumed to be 0.185 nm. The F matrix elements for the in-plane vibrations were evaluated with the potential field of an improved modification of the Urey-Bradley force field described previously.[6,7] For the out-of-plane vibrations the valence force field and the ϕ type torsional coordinate were used.[6,7] Values of the force constants used for the calculations of the in-plane and out-of-plane normal vibrations are listed in Table 1. The notations of the force constants are exactly the same as those used previously.[6,7] The calculated frequencies and modes of the normal vibrations are given in Tables 2 and 3.

Calculation of Relative Intensities of the Raman and Infrared Bands in Single Crystal

1,2,3-TCB and 1,2,3-TBB crystallize in monoclinic space group $P2_1/c$ with eight molecules in the unit

Table 3. Normal Vibrations of 1,3,5-Trichloro- and Tribromobenzenes

Sym Spec	Mode	1,3,5-Trichlorobenzene						1,3,5-Tribromobenzene				
		Raman			Infrared		Calcd	Raman			Infrared	Calcd
		$\tilde{\nu}$/cm^{-1}	pol		pol		$\tilde{\nu}$/cm^{-1}	$\tilde{\nu}$/cm^{-1}	pol		pol	$\tilde{\nu}$/cm^{-1}
			liq	cry	vap	cry			liq	cry	cry	
a$_1'$	ν_2	3083	p				3082	3075	p			3093
	ν_{12}	1148	p				1173	1118	p			1131
	ν_1	997	p				997	987	p			985
	C–X str (ν_{13})$^{a)}$	376	p				350	230	p			221
e$'$	ν_7	3078				II	3079					3090
	ν_8	1569	dp	ww		II	1581	1555	dp	ww	II	1566
	ν_{19}	1422	dp	ww	A	II	1437	1412	dp	ww	II	1427
	ν_{18}	1103	dp	ww		II	1114	1095	dp	ww	II	1109
	ν_6	817				II	804	740			II	748
	C–X str (ν_{20})	426	dp	ww		II	409	345	dp	ww		336
	X bend (ν_9)	190	dp	ww			213	117	dp	ww		133
a$_2'$	ν_{14}						1348					1344
	ν_3						1312					1313
	X bend (ν_{15})						537					476
e$''$	ν_{17}	945	dp	vv			945	943	dp	vv		947
	ν_{16}	530	dp	vv			525	507	dp	vv		518
	X wag (ν_{10})	221	dp	vv			204	200	dp	vv		192
a$_2''$	ν_5	853$^{b)}$			C	III	865	854$^{b)}$			III	868
	ν_4	660$^{b)}$			C	III	665	660$^{b)}$			III	667
	X wag (ν_{11})	142$^{c)}$					140	122$^{c)}$				114

a) X refers to the Cl or Br atom. b) Taken from the infrared band. c) Taken from the combination band.

Table 4. Squares of the Relative Values of the Elements of the Raman Tensor for 1,2,3-Trichlorobenzene

	b$_2$	b$_1$	a$_2$
(Aaa)^2	0.71	1.22	0.66
(Abb)^2	0.28	0.61	1.32
(Ac$'$c$'$)$^{2a)}$	1.87	0.11	0.11
(Aab)^2	0.50	0.15	0.00
(Aac$'$)^2	0.04	0.19	0.53
(Abc$'$)^2	0.03	0.69	0.42

a) c$'$ axis is taken to be perpendicular to both the a and b axes.

Table 5. Proportionality Factors of the Intensity of the Infrared Bands along the a, b, and c axes of the 1,2,3-Trichloro-, 1,3,5-Trichloro-, and 1,3,5-Tribromobenzene Crystals

	Pol	a$_1$	b$_2$	b$_1$
1,2,3-TCB	// a	0.81	0.44	0.75
	// b	0.25	0.56	1.19
	// c	1.13	1.21	0.07
	Pol			a$_2''$
1,3,5-TCB (1,3,5-TBB)	// a			0.18 (0.22)$^{a)}$
	// b			0.00 (0.00)
	// c			0.81 (0.77)

a) The first number is the value for 1,3,5-TCB and the number in parentheses is that for 1,3,5-TBB.

cell[8,10] and 1,3,5-TCB and 1,3,5-TBB crystallize in orthorhombic space group $P2_12_12_1$ with four molecules in the unit cell.[9] The relationship between the Raman tensor for the free molecule and that for the crystal was derived based on the simple oriented gas model, and the matrix elements of the Raman tensor were evaluated in the same way as described previously.[6] The direction cosines between the crystal and molecular axes were calculated usig the crystal data.[8] The squares of relative values of the elements of the Raman tensor, which are proportional to the relative intensities of the Raman bands, are given in Table 4 for 1,2,3-TCB. The calculation of the Raman tensor for 1,2,3-TBB could not be made because sufficient crystal data needed for the calculation were not available. The quantitative discussion can not be made on polarization behavior of the Raman bands of 1,3,5-TCB and 1,3,5-TBB, because the molecular structures of these molecules belong to the D_{3h} point group and plural polarizability elements belong to the degenerate symmetry species.

In order to carry out the vibrational analysis of the polarized infrared spectrum, the crystal axes in the sample plane sandwiched between two KRS-5 plates have to be determined. Since the two extinction directions found on the sample plane of 1,2,3-TCB were perpendicular to each other, proportionality factors of the intensities of the infrared bands along the crystal a, b, and c axes were calculated assuming that the sample plane is the ab or bc plane. In 1,3,5-TCB and 1,3,5-TBB, the quantitative analysis of the polarized infrared spectra can be made only for the out-of-plane vibrations because the infrared active in-plane e' vibrations are polarized in the molecular plane while the out-of-plane a_2'' vibrations are polarized along the direction normal to the molecular plane in these molecules. The results are listed in Table 5.

Results and Discussion

The moments of inertia calculated from the molecular structure suggest that the infrared bands belonging to a_1, b_2, and b_1 symmetry species show the B, A, and C band contours, respectively, in 1,2,3-TCB and 1,2,3-TBB and those belonging to e' and a_2'' species show the A (or B) and C contours, respectively, in 1,3,5-TCB and 1,3,5-TBB. The polarized infrared spectra of the 1,2,3-TCB, 1,2,3-TBB, 1,3,5-TCB, and 1,3,5-TBB single crystals are shown in Fig. 1. The infrared spectra measured with the incident light beams polarized parallel and perpendicular to the crystal growth direction in the sample plane are referred to as the // and ⊥ spectra and were drawn with the solid and dotted lines in the figure, respectively. As can be seen in Fig. 1, polarization behavior of the infrared bands in the 1,2,3-TCB and 1,2,3-TBB crystals can be classified into three types. The intensity of the bands showing the first type polarization is stronger in the // spectrum than in the ⊥ one, while the second type bands are observed with almost equal intensity in the // and ⊥ spectra. The intensity of the third type bands observed in the ⊥ spectrum is about twice of that in the // spectrum. These three types of polarization behavior are referred to as the type I, II, and III, respectively. Figure 1 shows that polarization behavior of the infrared bands observed for the 1,3,5-TCB and 1,3,5-TBB crystals can be classified into two types. The bands showing the first type polarization have almost equal intensity in the // and ⊥ spectra and the intensity of the second type bands is stronger in the ⊥ spectrum than in the // one. These two types of polarization behavior are referred to as the type II and III, respectively, following the case of 1,2,3-TCB and 1,2,3-TBB.

The polarized Raman spectra of the 1,2,3-TCB, 1,2,3-TBB, 1,3,5-TCB, and 1,3,5-TBB single crystals are shown in Figs. 2 and 3. Since the crystallographic analysis for the cleavage planes of the single crystals of these molecules has not been reported yet, the crystal growth direction and the direction perpendicular to it in the cleavage plane were taken to be the u and v axes, respectively, and the w axis was taken to the direction perpendicular to both the u and v axes. The polarized Raman spectrum was denoted by two characters such as uv, where the first letter refers to the direction of polarization of the excitation light and the latter to that of the scattering light.

1,2,3-Trichlorobenzene. Since the infrared bands having the A, B, and C band contours showed the type II, I, and III polarization in crystal, respectively, the infrared bands showing the type I, II, and III polarization were assigned to the vibrations belonging to the symmetry species a_1, b_2, and b_1, respectively. Comparison of these observed polarization behavior of the

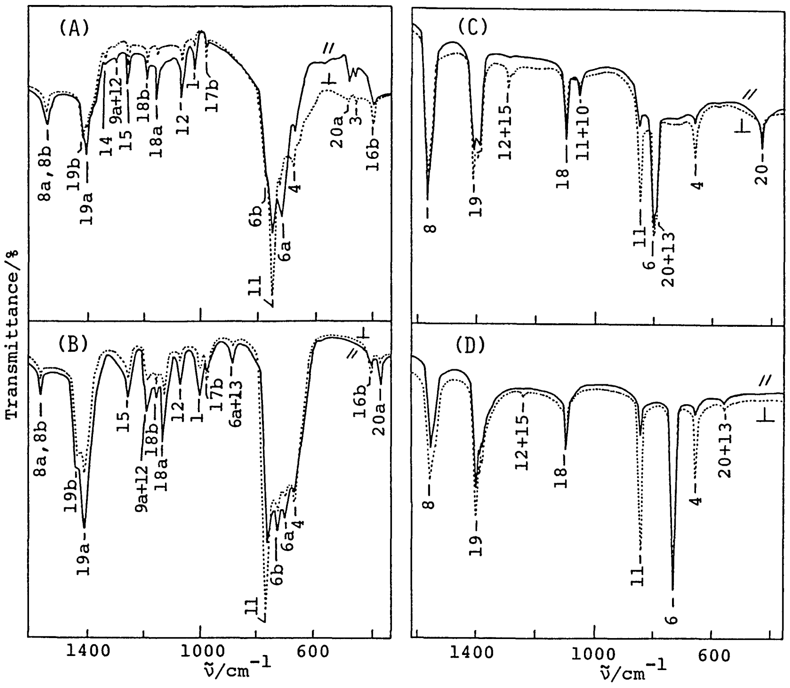

Fig. 1. Polarized infrared spectra of 1,2,3-trichlorobenzene (A), 1,2,3-tribromobenzene (B), 1,3,5-trichlorobenzene (C), and 1,3,5-tribromobenzene (D) in single crystal. For the definition of the symbols // and ⊥, see text.

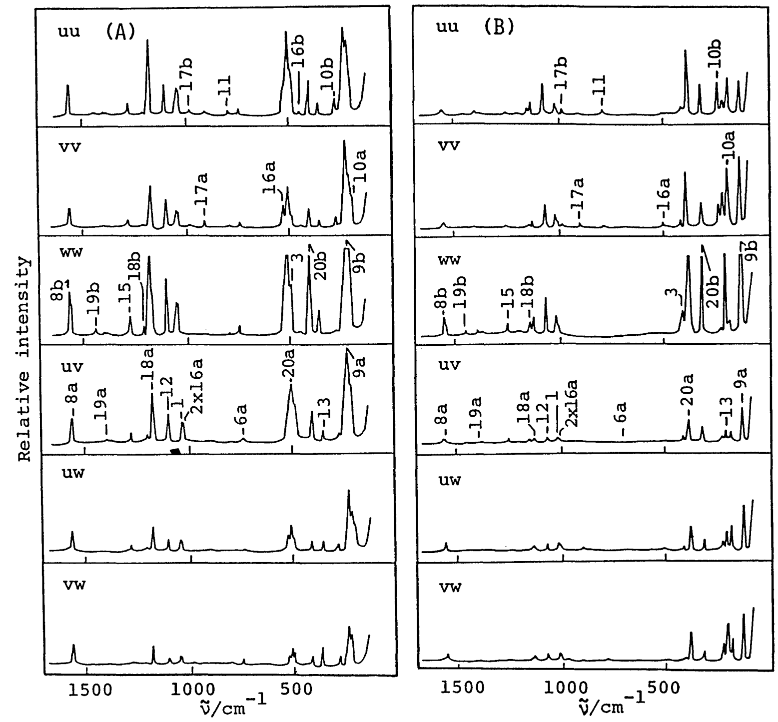

Fig. 2. Polarized Raman spectra of 1,2,3-trichlorobenzene (A) and 1,2,3-tribromobenzene (B) in single crystal. For the definition of the symbols of spectra such as uu, see text.

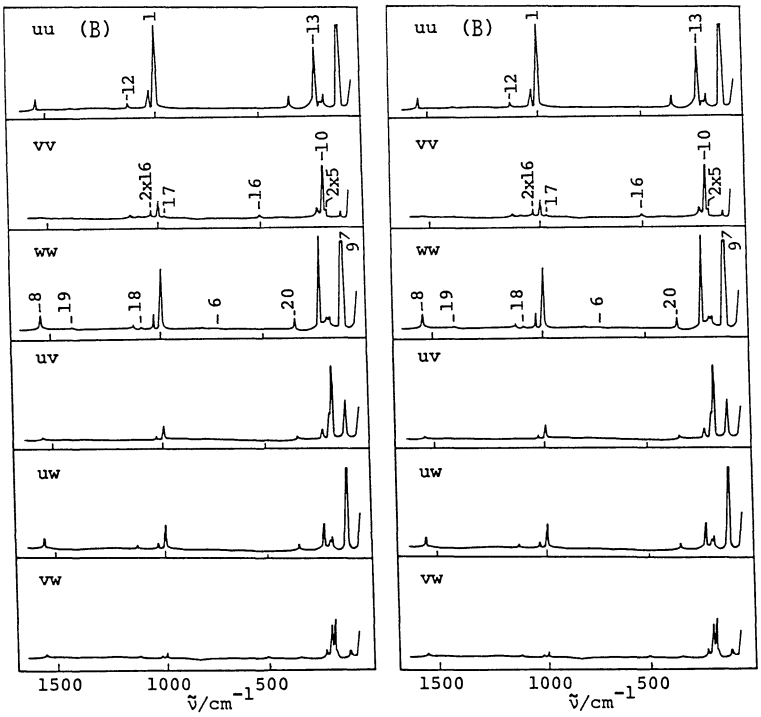

Fig. 3. Polarized Raman spectra of 1,3,5-trichlorobenzene (A) and 1,3,5-tribromobenzene in single crystal.

infrared bands with the proportionality factors given in Table 5 suggests that the plane of the crystal sample is to be the ab plane.

Species a_1: The highly polarized Raman bands in the depolarization measurement in molten phase and the infrared bands having the B band contour in vapor and the type I polarization in crystal were assigned straightforwardly to the vibrations of species a_1. The depolarized Raman band observed at 223 cm^{-1} in molten phase was assigned to the Cl bending (ν_{9a})

vibration of a_1 species, because the polarization behavior of this Raman band in single crystal could not be ascribed to any of the non-totally symmetric vibrations.

Species b_2: The infrared bands having the A band contour in vapor and the type II polarization in crystal were assigned to the vibrations of species b_2. The observed intensity of the corresponding Raman bands in single crystal is the strongest in the ww spectrum and decreases in the uu and uv spectrum in order. Therefore, the Raman bands having such polarization were assigned to the vibrations of species b_2. Table 4 shows that the relative intensity of the Raman bands to be assigned to the b_2 vibration is the strongest in the $c'c'$ polarized spectrum and decreases in the aa, ab, and bb spectra in order. Comparison of the observed polarization behavior with the expected one suggests that the u, v, and w axes correspond to the crystal a, b, and c' axes, respectively.

Species b_1: The infrared bands having the C band contour in vapor and the type III polarization in crystal were assigned to the vibrations of species b_1. The corresponding Raman bands in single crystal were observed with the strongest intensity in the uu spectrum and with almost equal intensity in the vv and vw spectra. Thus the Raman bands having such polarization were assigned to the b_1 vibrations. This observed polarization agrees with the result given in Table 4 if the u, v, and w axes correspond to the crystal a, b, and c' axes, respectively, as in the case of the vibrations of species b_2. The weak infrared band observed at 820 cm^{-1} having the type III polarization could be assigned to the combination band of the ν_{6a} and ν_5 vibrations. This gives the frequency of 89 cm^{-1} for the ν_5 vibration.

Species a_2: Table 4 indicates that the intensity of the Raman bands to be assigned to the a_2 vibrations is the strongest in the bb(vv) spectrum and decreases in the aa(uu), ac'(uw), and bc'(vw) spectra in order. The Raman bands having such polarization in crystal were assigned to the vibrations of species a_2.

1,3,5-Trichlorobenzene. The infrared bands having the A and C band contours show the type II and III polarization behavior in crystal, respectively. This suggests that the infrared bands having the type II and III polarization can be assigned to the vibrations of species e' and a_2'', respectively.

Species a_1': The strongly polarized Raman bands in molten phase were assigned to the vibrations of species a_1'.

Species e': The infrared bands having the A band contour in vapor and the type II polarization in crystal were assigned to the vibrations of species e'. It is interesting to observe that the relative intensity of the all corresponding Raman bands is the strongest in the ww spectrum although the quantitative treatment cannot be made for the analysis of the polarized Raman bands of the molecules belonging to the D_{3h} point group. The Cl bending vibration was assigned based on the polarization behavior of the Raman band.

Species e'': The depolarized Raman bands in molten phase whose corresponding infrared bands could not be observed were assigned to the vibrations of species e''. It is interesting to find that the polarization behavior of these Raman bands was quite similar to each other as observed in the case of the vibrations of species e'.

Species a_2'': The infrared bands having the C band contour in vapor and the type III polarization in crystal were assigned to the vibrations of species a_2''. The very weak infrared band observed at 1290 cm^{-1} having the type III polarization could be assigned to the combination band of the ν_{12} and Cl wagging (ν_{11}) vibrations. This gives the frequency of 142 cm^{-1} for the ν_{11} vibration.

Species a_2': The vibrations belonging to a_2' species could not be determined experimentally because the a_2' vibrations are Raman and infrared inactive.

Normal vibrations of 1,2,3- and 1,3,5-TCB thus determined based on the polarization behavior of the

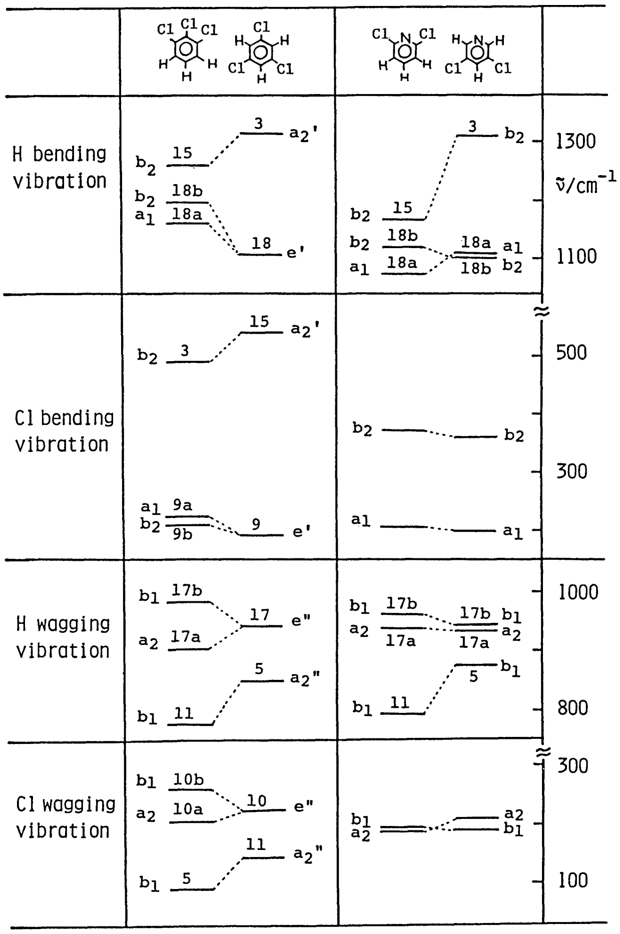

Fig. 4. Correlation diagrams for the H and Cl bending and wagging vibrations of 1,2,3- and 1,3,5-trichlorobenzenes and of 2,6- and 3,5-dichloropyridines.

Raman and infrared bands are summarized in Tables 2 and 3 and Figs. 1—3. The vibrational modes were determined through the normal coordinate calculation.

1,2,3-Tribromobenzene and 1,3,5-Tribromobenzene. The observed polarization behavior of the Raman and infrared bands of the 1,2,3-TBB and 1,3,5-TBB single crystals was exactly the same as that observed for the 1,2,3-TCB and 1,3,5-TCB single crystals, respectively. The assignment of the normal vibrations of 1,2,3-TBB and 1,3,5-TBB was carried out based on exactly the same criterion as that of 1,2,3-TCB and 1,3,5-TCB, respectively, and the results are given in Tables 2 and 3 and Figs. 1—3.

The normal coordinate calculation made on 1,2,3-TCB and 1,2,3-TBB indicates that ν_{6a} and ν_{6b} vibrations mix largely with the ϕ-X stretching (ν_{13}) and (ν_{20b}) vibrations, respectively, and the ϕ-X stretching (ν_{13}) vibration interacts with the ϕ-X stretching (ν_{20a}) vibration, where X refers to the Cl or Br atom. The calculation also indicates that the ν_{16a} and ν_{16b} vibrations mix with the X wagging (ν_{10a}) and (ν_5) vibrations, respectively, where the ν_{16b} vibration interacts with the ν_4 vibration and the X wagging (ν_5) vibration with the X wagging (ν_{10b}) vibration. These mixings are found by the experimental fact that the frequencies of the ν_{6a}, ν_{6b}, and ν_{16a} vibrations increase largely from the frequencies of the ν_6 and ν_{16} vibrations of benzene (606 and 405 cm^{-1}). The same mixings are also found in 1,3,5-TCB and 1,3,5-TBB, that is, the ν_6 and ν_{16} vibrations mix largely with the ϕ-X stretching (ν_{20}) and X wagging (ν_{10}) vibrations, respectively.

A correlation diagram for the H and Cl bending and wagging vibrations of 1,2,3-TCB and 1,3,5-TCB is shown in Fig. 4 together with a diagram for the 2,6- and 3,5-dichloropyridines (2,6-DCP and 3,5-DCP). A question arising from the correlation diagram is why the H bending and wagging vibrations of the ν_3 and ν_5 modes in 1,3,5-TCB change to the vibrations of the ν_{15} and ν_{11} modes in 1,2,3-TCB, respectively. The modes of the H and Cl bending and wagging vibrations of 1,2,3-TCB and 1,3,5-TCB are given in Fig. 5. The normal coordinate calculation indicates that the degenerate H and Cl bending vibrations are of the ν_{18} and ν_9 modes, respectively, in 1,3,5-TCB. These vibrations split into the ν_{18a} and ν_{18b}, and the ν_{9a} and ν_{9b} vibrations in 1,2,3-TCB. The displacements of the three Cl atoms in the ν_{9a} and ν_{9b} modes given in Fig. 5 suggest that in the third Cl bending vibration the three Cl atoms in both the 1,2,3-TCB and 1,3,5-TCB molecules should rotate in the same direction (clockwise in Fig. 5) about a line normal to the molecular plane and passing through the center of mass, and the H and C atoms rotate simultaneously in the opposite direction (counterclockwise in Fig. 5) in order to keep the center of mass unchanged. These displacements of the atoms give the ν_3 mode to 1,2,3-TCB and the ν_{15} mode to 1,3,5-TCB for the third Cl bending vibration. Thus the third H bending vibration is of the ν_{15} mode in 1,2,3-TCB and of the ν_3 mode in 1,3,5-TCB.

The calculation also shows that the degenerate H

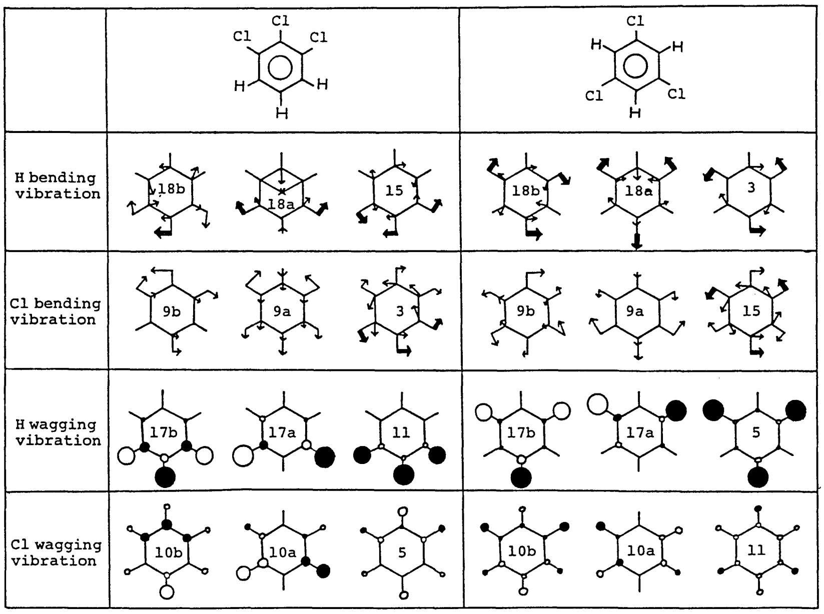

Fig. 5. Modes of the H and Cl bending and wagging vibrations of 1,2,3- and 1,3,5-trichlorobenzenes. Value of the L_x vector is represented by length of the arrow and area of the circle for the in-plane and out-of-plane vibrations, respectively. The bold arrow represents five times large value of the fine arrow. The marks ○ and ● represent the upward and downward displacements from the molecular plane, respectively.

and Cl wagging vibrations are of the ν_{17} and ν_{10} modes, respectively, in 1,3,5-TCB and the degeneracy is released in 1,2,3-TCB. The displacements of the three Cl atoms in the ν_{10a} and ν_{10b} modes suggest that in the third Cl wagging vibration the Cl atoms bonded to the C atoms on the 1 and 3 positions should displace in the same direction and the Cl atom bonded to the C atom on the 2 position should displace in the opposite direction in the 1,2,3-TCB, while the three Cl atoms should displace in the same direction and the H and C atoms should displace simultaneously in the opposite direction in the 1,3,5-TCB in order to keep the balance. These displacements of the atoms give the third Cl wagging vibration of the ν_5 mode to 1,2,3-TCB and of the ν_{11} mode to 1,3,5-TCB. Thus the third H wagging vibration is of the ν_{11} mode in 1,2,3-TCB and of the ν_5 mode in 1,3,5-TCB. The same argument can be made for 1,2,3-TBB and 1,3,5-TBB, and also for 2,6-DCP, 2,6-DBP, 3,5-DCP, and 3,5-DBP.

Figure 4 shows that the correlation diagram for the H bending and wagging vibrations of 2,6-DCP and 3,5-DCP is quite similar to that for 1,2,3-DCB and 1,3,5-DCB. This fact suggests that the three H atoms in the 3,5-DCP molecule behave as if the molecular symmetry belongs to the pseudo D_{3h} point group for the H bending and wagging vibrations. The very small frequency separations between the H bending ν_{18a} and ν_{18b} vibrations and between the H wagging ν_{17a} and ν_{17b} vibrations in 3,5-DCP can be thus explained.

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