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Vibrational spectra of hexabromobenzene and hexaiodobenzene

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Abstract—Infrared and Raman spectra of polycrystalline C_6Br_6 and C_6I_6 are measured at both room temperature and liquid nitrogen temperatures. Vibrational assignment of fundamental modes as well as combination bands are established on the basis of normal coordinate analysis.

INTRODUCTION

Vibrational spectra of hexabromobenzene C_6Br_6 and hexaiodobenzene C_6I_6 have been studied by a few investigators [1–3]. DELORME *et al* [1] reported i.r. spectra of these molecules in the region from 4000–70 cm^{-1}, and MARSAULT *et al* [2] measured far i.r. spectra in the region from 200 to 15 cm^{-1}. Raman spectra of C_6Br_6 and C_6I_6 were studied by ABRAMOWITZ *et al* [3]. These authors were interested primarily in the planarity of these hexahalobenzenes. The assignments of intramolecular and lattice vibrations are yet to be settled. To establish the vibrational assignments consistent with those in other hexahalobenzenes, i.r. and Raman spectra of these molecules were remeasured. Normal coordinate analysis has been carried out, and the complete assignments are presented for C_6Br_6 and C_6I_6.

EXPERIMENTAL

The commercially available sample of C_6Br_6 was purified by repeated recrystallization from saturated benzene solution. C_6I_6 was prepared from benzene, fuming sulfuric acid and solid iodine and recrystallized from boiling nitrobenzene solution as described by RUPP [4] and DURAND *et al* [5]. Result of elementary analysis of C_6I_6 is as follows: expected C 8.65%, found C 8.76%.

Raman spectra of powder C_6Br_6 were taken on a JEOL JRS-400D double monochromator using 5145 and 4880 *A* excitation lines from an argon ion gas laser with an output of 700 mw. For orange polycrystalline C_6I_6, a Spex Model 1401 double monochromator with 6328 *A* excitation line from a He–Ne gas laser was used with an output of 50 mw. Raman lines scattered from the surface of C_6I_6 disc were detected.

Infrared spectra of C_6Br_6 and C_6I_6 were recorded on a Hitachi G2 (4000–400 cm^{-1}), EPI-L (700–200 cm^{-1}) and FIS-1 (500–60 cm^{-1}) spectrometers. Far i.r. spectra were also taken on a Hitachi 070 interferometer to check the reproducibility in the region from 200–60 cm^{-1}. Both spectra obtained by using different spectrometers match completely.

Low temperature measurements of i.r. and Raman spectra were made with a conventional cryostat holding liquid nitrogen. Infrared and Raman spectra of C_6Br_6 and C_6I_6 are given in Fig. 1 and 2, respectively.

NORMAL COORDINATE TREATMENT

The planarity of the C_6X_6 type molecules (X = F, Cl, Br, and I) has been the subject of a number of investigations. X-ray diffraction study (6, 7) indicates the puckered D_{3d} structure for the C_6I_6 crystal. However, six iodine atoms are located only 0.04 *A* off the plane of the benzene ring. An electron diffraction investigation of gaseous C_6Br_6 indicates a distorted configuration [8], while X-ray analysis [9] supported planar configuration in the crystalline state which is isomorphous to crystalline C_6Cl_6 [10, 11]. Since vibrational frequencies are insensitive to slight geometrical changes of configuration, normal coordinate treatments were undertaken on a planar D_{6h} model. The calculated frequencies may be compared with those for planar C_6Cl_6 [12].

According to the group theory, the irreducible representations for the normal modes of C_6X_6 molecule assuming D_{6h} symmetry are: $\Gamma\ (D_{6h}) = (2a_{1g} + a_{2g} + 4e_{2g} + 2b_{1u} + 2b_{2u} + 3e_{1u}) + (2b_{2g} + e_{1g} + a_{2u} + 2e_{2u})$, where the symmetry species enclosed in the first set of braces correspond to the

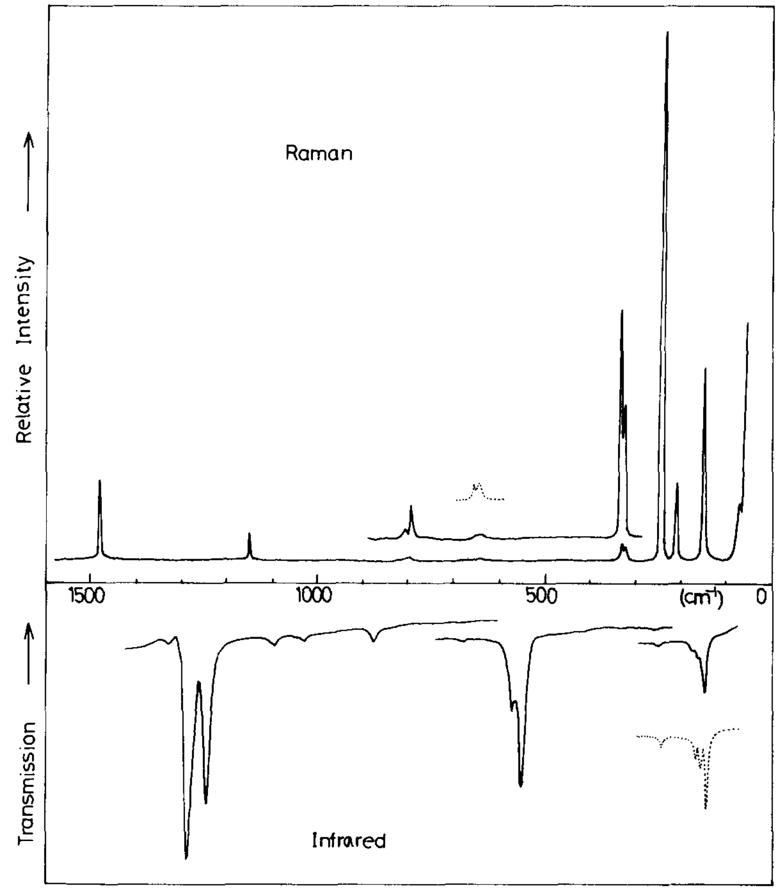

Fig. 1. Raman and i.r. spectra of solid C_6Br_6 at room temperature. (Dotted curves indicate the spectra obtained at liquid nitrogen temperature.)

in-plane modes, and the species in the second braces correspond to the out-of-plane modes. Of these twenty normal modes, seven modes $(2a_{1g} + 4e_{2g} + e_{1g})$ are Raman active, and four $(3e_{1u} + a_{2u})$ are i.r. active. The correlation between D_{6h} and D_{3d} indicates that two b_{2g} modes are Raman active and two b_{1u} and two e_{2u} modes are i.r. active in a puckered D_{3d} structure. Hereafter the notation of symmetry species in D_{6h} symmetry will be used.

Internal symmetry coordinates chosen are the same as those of HARADA *et al.* in the calculation of the benzene molecule [13]. The potential energy is given as [13]:

$$\begin{aligned}2V_{in} &= 2V_{UBFF} \\ &+ 2\left(o_{cx}\sum^{6} s_i s_{i+1} + m_{cx}\sum^{6} s_i s_{i+2}\right. \\ &\left.+ p_{cx}\sum^{3} s_i s_{i+3}\right) + 2\left(o_{ccx}\sum^{6} \psi_i \psi_{i+1}\right. \\ &\left.+ m_{ccx}\sum^{6} \psi_i \psi_{i+2} + p_{ccx}\sum^{3} \psi_i \psi_{i+3}\right) \\ &+ 2\left(o_{cc}\sum^{6} t_i t_{i+1} + m_{cc}\sum^{6} t_i t_{i+2}\right. \\ &\left.+ p_{cc}\sum^{3} t_i t_{i+3}\right) + 2\left(o_{ccc}\sum^{6} \phi_i \phi_{i+1}\right. \\ &\left.+ m_{ccc}\sum^{6} \phi_i \phi_{i+2} + p_{ccc}\sum^{3} \phi_i \phi_{i+3}\right)\end{aligned}$$

$$\begin{aligned}2V_{out} &= A\sum^{6} \gamma_i^2 + B\sum^{6} \delta_i^2 \\ &+ 2C\left(\sum^{6} \gamma_i \delta_i - \sum^{6} \gamma_i \delta_{i-1}\right) + 2D\left(\sum^{6} \gamma_i \delta_{i+1}\right. \\ &\left.- \sum^{6} \gamma_i \delta_{i-2}\right) + 2\left(a_0\sum^{6} \gamma_i \gamma_{i+1}\right. \\ &\left.+ a_m\sum^{6} \gamma_i \gamma_{i+2} + a_p\sum^{3} \gamma_i \gamma_{i+3}\right) \\ &+ 2\left(b_0\sum^{6} \delta_i \delta_{i+1} + b_m\sum^{6} \delta_i \delta_{i+2}\right. \\ &\left.+ b_p\sum^{3} \delta_i \delta_{i+3}\right).\end{aligned}$$

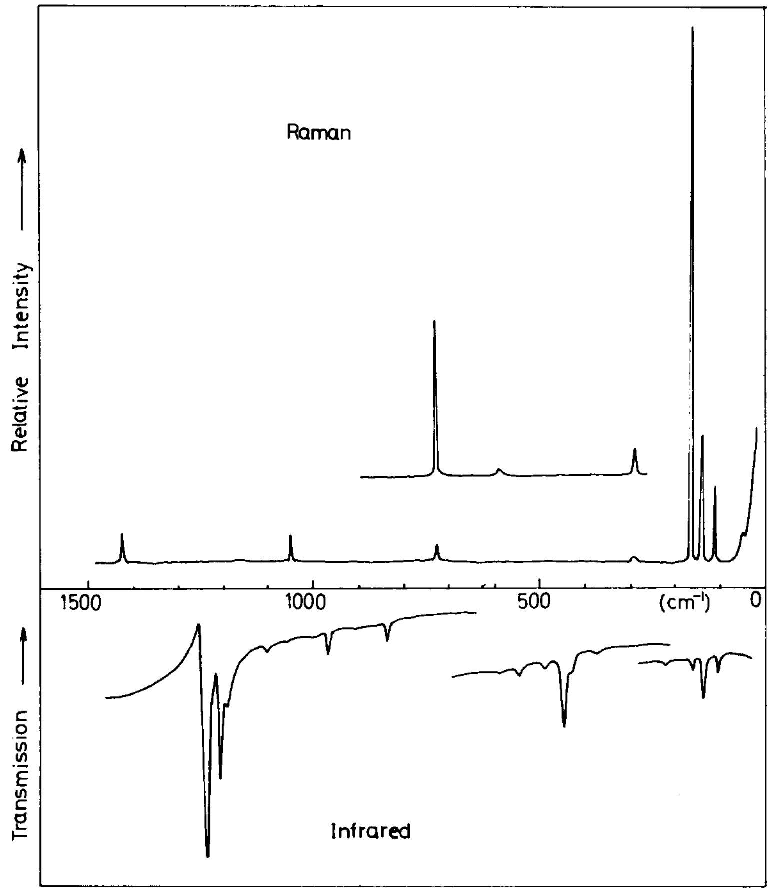

Fig. 2. Raman and i.r. spectra of solid C_6I_6 at room temperature.

In the preliminary calculation, the values of force constants adopted are the same as those used for the benzene molecule [13] except K_{cx}, H_{cx}, and F_{cx}, which are listed in Table 1. These values are transferred from CH_3Br, C_2Br_4 and CH_3I [14]. Calculated frequencies are also shown in Table 1.

VIBRATIONAL ASSIGNMENTS

Raman spectra

Although general features of the Raman spectra of C_6Br_6 and C_6I_6 are similar to those reported by ABRAMOWITZ *et al.* [3], we observe a few additional bands at 648, 637, 68, 47, 41, 34, 22, and 20 cm^{-1} for the C_6Br_6 molecule at room temperature. Also, the bands at 489 cm^{-1} and 125 cm^{-1} they reported are completely missing. For C_6I_6, a weak band at 592 cm^{-1} was observed, while a sharp band at 383 cm^{-1} [3] was not recorded even at low tempera-

Table 1. Vibrational frequencies and force constants of C_6Br_6 and C_6I_6 in preliminary calculation

	Calculated frequencies (cm^{-1})	
	C_6Br_6	C_6I_6
a_{1g}	1104, 229	1090,173
b_{2g}	748, 61	746, 45
e_{1g}	300	290
e_{2g}	1559, 797, 197, 96	1547, 769, 152, 69
a_{2u}	117	107
b_{1u}	1142, 230	1122, 173
e_{1u}	1300, 539, 118	1284, 487, 86
e_{2u}	561, 46	555, 34
	Force constants (md/A)	
	C_6Br_6	C_6I_6
K_{cx}	1.757	1.547
H_{ccx}	0.08	0.07
F_{ccx}	0.68	0.60

Values of other force constants are the same as used for benzene molecule [13].

ture. No splitting was observed around 592 cm^{-1} at low temperature.

Bates *et al.* [15] determined the assignments of molecular and lattice vibrations of the C_6Cl_6 crystal from the polarized Raman spectra. They assigned the six bands at 56, 54, 45, 38, 25, and 21 cm^{-1} at 300 K to the lattice vibrations about the three principal axes of a molecule. X-ray diffraction studies [6, 7, 9, 10, 11] indicate that C_6Cl_6, C_6Br_6, and C_6I_6 crystals have isomorphic structures with space group $P21/c$ and that each contains two molecules in a unit cell with the same packing. Therefore, the patterns of lattice vibrations in C_6Br_6 and C_6I_6 are expected to be parallel to that of C_6Cl_6. As intermolecular forces differ hardly in C_6Cl_6 and in C_6Br_6, the librational frequencies are determined mainly by the principal moments of inertia. The lower librational frequencies, therefore, are expected for C_6Br_6. This consideration leads us to the assignment that four sharp bands at 47, 41, 22, and 20 cm^{-1} as well as a broad band at 34 cm^{-1} are due to the librational modes. The band at 68 cm^{-1} is assigned to an intramolecular vibration, namely the b_{2g} CX out-of-plane bending mode which corresponds to the C_6Cl_6 band at 103 cm^{-1} [15].

The corresponding b_{2g} band for C_6I_6 as well as the librational bands located at lower frequencies were not observed. This is probably due to the different experimental conditions used for C_6Br_6 and C_6I_6.

Another b_{2g} fundamental is harder to assign. Normal coordinate analysis indicates that this is a chair type deformation and halogen atoms scarcely move in this mode. The frequency shifts from C_6Cl_6 to C_6I_6 are expected to be small. **Bates** [15] assigned a band at 678 cm^{-1} of C_6Cl_6 to this mode. Therefore, the doublet located at 648 and 637 cm^{-1} of C_6Br_6 and the C_6I_6 band at 592 cm^{-1} may be assigned to this fundamental. This assignment is less unambiguous, since overtones of the e_{1g} doublet at 326 and 319 cm^{-1} for C_6Br_6 and/or the C_6I_6 band at 295 cm^{-1} may also appear in the same frequency range.

In other spectral regions, the present assignment is identical to that given in [3].

Infrared spectra

The i.r. spectra in Figs. 1 and 2 are essentially identical to those obtained by **Delorme** [1] above 600 cm^{-1}. The spectra also match with the far i.r. spectra of **Marsault** [2] in the region of 200–15 cm^{-1}. There are, however, considerable discrepancies between our spectra and those of Delorme below 500 cm^{-1}. We observed a band at 246 cm^{-1},

Table 2. Assignment of fundamental frequencies of C_6X_6 molecules (in cm^{-1})

	Sym. species D_{6h}	C_6Cl_6 Ref. [15] obs.	C_6Cl_6 Ref. [12] calc.	C_6Br_6 This work obs.	C_6Br_6 This work calc.	C_6I_6 This work obs.	C_6I_6 This work calc.	Sym. species D_{3d}	
a_{1g}	ν_1	1226	1165	1159	1130	1057	1039	ν_1	a_{1g}
	ν_2	372	383	232	243	166	177	ν_2	
b_{2g}	ν_7	678	677	648 637	648	592	601	ν_3	
	ν_8	103	98	68	68	59	48	ν_4	
e_{1g}	ν_{11}	345	389	326 319	300	295	290	ν_{13}	e_g
e_{2g}	ν_{15}	1523	1585	1485	1485	1430 1423	1430	ν_{11}	
	ν_{16}	883	837	795	785	731	706	ν_{12}	
	ν_{17}	323	303	208	178	148	134	ν_{14}	
	ν_{18}	218	204	148	130	119	99	ν_{15}	
a_{2u}	ν_4	170	197	145	145	144	144	ν_8	a_{2u}
b_{1u}	ν_5	1080	1067	1031	1036	968	978	υ_9	
	ν_6	395	368	246	216	167	154	ν_{10}	
e_{1u}	ν_{12}	1344†	1356	1292	1310	1238	1248	ν_{16}	e_u
	ν_{13}	694†	661	558	580	455	485	ν_{17}	
	ν_{14}	215	215	162 155	141	113	108	ν_{18}	
e_{2u}	ν_{19}	521	581	567	560	543	555	ν_{19}	
	ν_{20}	79	79	48.8* 46.4*	46	45.8* 41.6*	34	ν_{20}	

† Ref. [18]. * Ref. [3].

a weak doublet at 162 and 155 cm^{-1}, and a strong band at 145 cm^{-1} in the spectrum of C_6Br_6, while DELORME *et al.* [1] reported bands at 433, 246, 145, and 135 cm^{-1}. The last band is missing from the spectrum of Marsault. Reversal of intensity is also observed for the bands at 558 and 526 cm^{-1}.

Three bands are observed at 167, 144, and 113 cm^{-1} for C_6I_6. This agrees with the observation by Marsault, while only a band at 113 cm^{-1} was recorded by Delorme. Below 600 cm^{-1} we used the combined data of Marsault's and our own.

From the normal coordinate analysis of C_6Br_6 two bands at 1292 and 558 cm^{-1} and a weak doublet at 162 and 155 cm^{-1} are assigned, respectively, to the ring distortion, the CBr stretching, and the CBr deformation vibrations in the e_{1u} species. The strong band at 145 cm^{-1} is assigned to the a_{2u} CBr bending vibration. Preliminary calculation indicates that two e_{2u} and two b_{1u} vibrations have frequencies around 561, 46, 1142, and 230 cm^{-1}, respectively. These modes are i.r. active in D_{3d} symmetry, and the observed band at 565 cm^{-1} is assigned to the e_{2u} boat type deformation, while the bands at 1031 and 246 cm^{-1} are assigned to the b_{1u} triangular deformation and CBr stretching modes respectively. The doublet observed at 48.8 and 46.4 cm^{-1} by Marsault is assigned to the e_{2u} CBr bending mode.

Normal coordinate treatment also indicates that the displacements of halogen atoms in the a_{2u} vibration are very small,* while those in the e_{1u} CX deformation vibrations are comparable to the displacements of carbon atoms. The latter mode is expected to be much more sensitive to the halogen substitutions. The band at 144 cm^{-1} is assigned to the a_{2u} vibration for C_6I_6 (which corresponds to the 145 cm^{-1} band in C_6Br_6) and the band at 113 cm^{-1} to the e_{1u} mode. The bands at 1238 and 455 cm^{-1} are assigned to the other e_{1u} modes, i.e. the ring distortion and the CI stretching vibrations. The weak band at 229 cm^{-1} may arise from a combination of 113 cm^{-1} (e_{1u}) and 119 cm^{-1} (e_{2g}) bands. The above assignments differ considerably from earlier workers.

The preliminary calculation also indicates that the observed bands at 968, 167, and 543 cm^{-1} are assigned, respectively, to the triangular deformation and the CI stretching vibrations in the b_{1u} species and to the boat type deformation in the e_{2u} species. It is very hard to assign the 167 cm^{-1} band to the e_{1u} mode as indicated by Marsault. The calculation shows that the doublet at 45.8 and 41.6 cm^{-1} observed by MARSAULT [2] is due to the e_{2u} CX bending mode. The final assignments are listed in Table 2 along with the assignments for C_6Cl_6 [15].

DISCUSSION

Since the assignments for the fundamental frequencies were settled, the least-squares refinement of force constants has been attempted to reproduce the frequencies in the a_{1g}, e_{2g}, e_{1u}, a_{2u}, and b_{2g} species as nearly as possible. The force constants K_{cx}, K_{cc}, H_{cx}, H_{cc} as well as c_{xx}, a cis interaction constant introduced by MANN *et al* [16, 17] in the normal coordinate analysis in C_2X_4, are treated as adjustable parameters in the in-plane modes. As for out-of-plane force constants, A, B, a_0, a_m, a_p, b_0, b_m, and b_p are taken as variables with the constraints of $\Delta A = \Delta a_m$, $\Delta a_o = \Delta a_p$, $\Delta B = \Delta b_m = -\Delta b_0 = -\Delta b_p$. The constraints leave the e_{2u} and e_{1g} frequencies unchanged: the frequency fits in these species are good in the preliminary calculation. The final results are given in Table 2 and the final set of force constants is given in Table 3.

The overall agreements of the calculated and observed frequencies are quite satisfactory. It is encouraging that the frequency fits in the b_{1u} species are improved considerably in the refinement process which supports the present revised assignments. Some frequencies are interpreted as combination bands, and they are listed in Table 4.

The obtained value of K_{CBr} for C_6Br_6 is reasonable considering the corresponding value for fluorobromobenzenes is reported to be 2.9314 md/*A* [19]. It is in-

Table 3. Values of force constants (final set)

	In-plane f. c. (md/A)			Out-of-plane f. c. (md·A)	
	C_6Br_6	C_6I_6		C_6Br_6	C_6I_6
K_{cc}	4.699	4.313	A	0.4082	0.4129
K_{cx}	2.578	1.656	B	0.4064	0.4409
H_{cx}	0.260	0.239	C	0.0398	0.0398
F_{cx}	0.387	0.387	D	−0.0027	−0.0027
H_{ccc}	0.098	0.115	a_o	0.0696	0.1016
F_{ccc}	0.241	0.241	a_m	−0.0018	0.0029
o_{cc}	0.481	0.481	a_p	0.0591	0.0912
m_{cc}	−0.204	−0.204	b_o	−0.0258	−0.0603
p_{cc}	0.377	0.377	b_m	0.0680	0.1025
o_{cx}	0.024	0.024	b_p	−0.0396	−0.0741
m_{cx}	0.0	0.0			
p_{cx}	−0.006	−0.006			
o_{ccx}	0.005	0.005			
m_{ccx}	−0.014	−0.014			
p_{ccx}	0.007	0.007			
o_{ccc}	−0.018	−0.018			
m_{ccc}	0.0	0.0			
p_{ccc}	0.0	0.0			
c_{xx}	0.373	0.423			

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* 0.14 for C_6Br_6 and 0.09 for C_6I_6 relative to the displacements of carbon atoms.

Table 4. Assignment of combination bands of C_6Br_6 and C_6I_6 (in cm^{-1})

	obs.	assignment		obs.	assignment
		C_6Br_6			
i.r.	447 (2)	$208 (e_{2g}) + 246 (b_{1u})$		1249 (8)	$1485 (e_{2g}) - 246 (b_{1u})$
	630 (3)	$68 (b_{2g}) + 567 (e_{2u})$		1336 (4)	$1485 (e_{2g}) - 145 (a_{2u})$
	677 (3)	$637 (b_{2g}) + 48.8 (e_{2u})$		1520 (2)	$1292 (e_{1u}) + 232 (a_{1g})$
	865 (2)	$319 (e_{1g}) + 558 (e_{1u})$		1952 (2)	$1292 (e_{1u}) + 648 (b_{2g})$
	880 (5)	$1031 (b_{1u}) - 148 (e_{2g})$			
	965 (2)	$1031 (b_{1u}) - 68 (b_{2g})$	R		
	1057 (2)	$1292 (e_{1u}) - 232 (a_{1g})$		819 (1)	$246 (b_{1u}) + 567 (e_{2u})$
	1098 (2)	$68 (b_{2g}) + 1031 (b_{1u})$		1215 (1)	$1159 (a_{1g}) + 68 (b_{2g})$
		C_6I_6			
	obs.	assignment		obs.	assignment
i.r.	229 (4)	$119 (e_{2g}) + 113 (e_{1u})$		702 (4)	$166 (a_{1g}) + 543 (e_{2u})$
	249 (3)	$295 (e_{1g}) - 45.8 (e_{2u})$		773 (4)	$731 (e_{2g}) + 41.6 (e_{2u})$
	267 (3)	$119 (e_{2g}) + 144 (a_{2u})$		834 (5)	$295 (e_{1g}) + 543 (e_{2u})$
	280 (2)	$\begin{cases} 166 (a_{1g}) + 113 (e_{1u}) \\ 119 (e_{2g}) + 167 (b_{1u}) \end{cases}$		862 (4) 897 (2)	$968 (b_{1u}) - 119 (e_{2g})$ $731 (e_{2g}) + 167 (b_{1u})$
	315 (4)	$\begin{cases} 166 (a_{1g}) + 144 (a_{2u}) \\ 148 (e_{2g}) + 167 (b_{1u}) \end{cases}$		921 (2) 980 (3)	$1057 (a_{1g}) - 144 (a_{2u})$ $1430 (e_{2g}) - 455 (e_{1u})$
	339 (2)	$455 (e_{1u}) - 119 (e_{2g})$		1009 (3)	$1057 (a_{1g}) - 45.8 (e_{2u})$
	385 (4)	$543 (e_{2u}) - 166 (a_{1g})$		1074 (3)	$1238 (e_{1u}) - 166 (a_{1g})$
	440 (4)	$295 (e_{1g}) + 144 (a_{2u})$		1089 (3)	$968 (b_{1u}) + 119 (e_{2g})$
	491 (4)	$543 (e_{2u}) - 59 (b_{2g})$		1119 (4)	$1238 (e_{1u}) - 119 (e_{2g})$
	564 (4)	$731 (e_{2g}) - 167 (b_{1u})$		1171 (2)	$1057 (a_{1g}) + 113 (e_{1u})$
	574 (3)	$119 (e_{2g}) + 455 (e_{1u})$		1205 (8)	$1057 (a_{1g}) + 144 (a_{2u})$
	609 (2)	$148 (e_{2g}) + 455 (e_{1u})$		1316 (3)	$1430 (e_{2g}) - 113 (e_{1u})$
	663 (2)	$119 (e_{2g}) + 543 (e_{2u})$			
	676 (3)	$968 (b_{1u}) - 295 (e_{1g})$	R		
	692 (2)	$148 (e_{2g}) + 543 (e_{2u})$		1349 (1)	$1057 (a_{1g}) + 295 (e_{1g})$

Numbers in the parentheses indicate the relative intensities.

teresting to note that the values of K_{CC} for C_6Br_6 and C_6I_6 are smaller than the value for C_6H_6 (5.237 md/A) [13], and that the force constant c_{xx}, which was completely ignored in C_6H_6, has rather large values for C_6Br_6 and C_6I_6. As for out-of-plane force constants A and B, they are slightly larger than those found for C_6H_6 (A = 0.3970 mdA, B = 0.3668 mdA) [13]. In order to make more quantitative discussion, it is necessary to study a complete set of brominated and iodinated benzenes, as were attempted for that of fluorinated benzenes [20, 21] and that of chlorinated benzenes [22].

In conclusion, all the observed i.r. and Raman bands are assigned to fundamentals as well as combination bands on the basis of normal coordinate analysis assuming a planar D_{6h} configuration. The present assignments for the b_{2g}, a_{2u}, b_{1u}, e_{1u}, and e_{2u} modes differ from those given earlier [1–3]. A few bands can be interpreted as due to i.r. inactive (b_{1u}, e_{2u}) or Raman inactive (b_{2g}) bands in D_{6h} symmetry. This supports a slightly puckered molecular model of D_{3d} symmetry for C_6Br_6 and C_6I_6 crystals as were proposed by previous investigators [1–3].

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