The Assignment of the Molecular Vibrations of Hexachlorobenzene

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The Raman spectrum of hexachlorobenzene has been studied by Dadieu and his colleagues[1] and by Murray and Andrews[2], and the infrared absorption spectrum of the same substance, by Plyler and his collaborators[3]. But, in all of these papers, only the results of observations (vibrational frequencies, intensities, depolarization ratios of Raman lines, etc.) have been presented, and no discussion has been given concerning the assignment of the observed lines or bands. In this paper, the Raman spectra of hexachlorobenzene in various solutions, the qualitative depolarization ratio of each Raman line, and infrared absorption spectra in gaseous state are reported on, and an assignment of these observed lines and bands is proposed.

Experimental and Results

Hexachlorobenzene of extra pure grade on the market was recrystallized from ethanol three times and used for the measurement of the spectra.

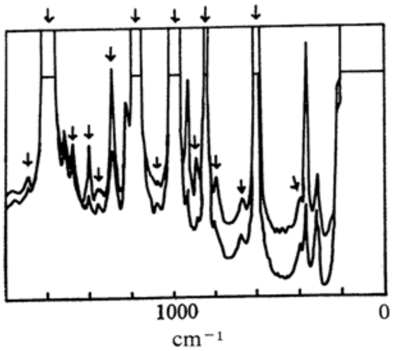

Fig. 1. Raman spectra of hexachlorobenzene (0.25 g. in 5 ml. benzene).
The upper curve : cross
The lower curve : parallel

The Raman spectra were measured using a Cary model 81 Raman spectrophotometer. The qualitative depolarization ratios were observed by the two-exposure method, using polaroid cylinders. As the solubility of this substance is not enough to obtain an adequately clear spectrum, not only benzene and carbon tetrachloride, but also carbon disulfide were used as the solvents in order to make the measurements as accurate as possible. To prepare the

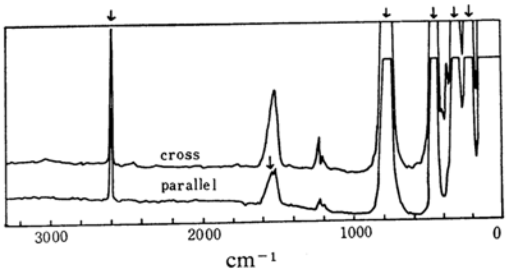

Fig. 2. Raman spectra of hexachlorobenzene (0.2 g. in 5 ml. carbon tetrachloride).

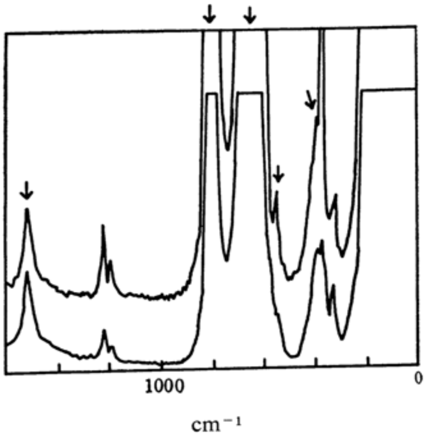

Fig. 3. Raman spectra of hexachlorobenzene (0.2 g. in 5 ml. carbon disulfide).
The upper curve : cross
The lower curve : parallel

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[1] A. Dadieu, K. W. F. Kohlrausch and A. Pongratz, *Monatsh.*, **61**, 426 (1932).

[2] J. W. Murray and D. H. Andrews, *J. Chem. Phys.*, **2**, 119 (1934).

[3] E. K. Plyler, H. C. Allen, Jr. and E. D. Tidwell, *J. Res. Nat. Bur. Standards*, **58**, 255 (1958).

TABLE I. RAMAN LINES OF HEXACHLOROBENZENE

Benzene soln.			CCl_4 soln.			CS_2 soln.		
ν, cm^{-1}	Intensity		ν, cm^{-1}	Intensity		ν, cm^{-1}	Intensity	
	Cross	Parallel		Cross	Parallel		Cross	Parallel
213	sh 1	sh 1						
322	31	35				322	25	22
342	1	1						
373	80	30	371	26	sh 10 ?	371	>60	20
			572	2	—			
			1196	8	3	1194	12	5
1224	27	12	1226	22	9	1225	27	11
1248	sh 1	—						
1522	15	17	1521	masked	15	1518	33	32
			2453	2	+			
			3042	1	—			

sample solutions, 0.2~0.25 g. solute was dissolved in 5 ml. solvent in all cases. The obtained Raman spectra are shown in Figs. 1—3, and the frequencies of the observed lines are shown in Table I. The small arrows in the figures point out the Raman lines of the solvent and the mercury lines from the source lamp.

The infrared absorption specta were measured using a Perkin-Elmer model 21 spectrophotometer equipped with sodium chloride or a cesium bromide prism over the region of 4000~300 cm^{-1}. The far infrared spectrum was measured in the region of 300~100 cm^{-1} using the grating spectrophotometer installed at the laboratory of Professor Yoshinaga of Osaka University⁴⁾.

As the vapor pressure of hexachlorobenzene is quite low, a high temperature and long path length cell was necessary to measure the spectrum in a gaseous state. The spectra in the sodium chloride region were measured using a long path and high temperature cell of the multiple reflection type. This cell has an optical system quite similar to that of the Perkin-Elmer long path gas cell, but all its mirrors are spattered with gold to prevent corrosion. The path length used in the measurements was 720 cm. The cell can be used at any desired temperature below 120°C by the aid of a transformer and the heaters which are coiled over the outside surface of the cell body. In the measurement, the specimen was put in the cell, and the air in the cell was replaced by nitrogen from the bomb in order to make the absorption by the atmospheric water vapor as weak as possible*. Then, after keeping the cell at a desired temperature for two or three hours in order to saturate the vapor pressure of the sample substance, the spectrum was measured.

The spectrum in the cesium bromide region was measured using the 85 mm. high temperature cell with cesium bromide windows 50 mm. in diameter. The design of this cell is almost the same as that described previously⁵⁾.

In the far infrared region, since a high temperature cell could not be used because of the complete difference in the type of spectrometer, the spectrum was taken as the Nujol mull sandwiched between two thick sheets of polyethylene. However, no absorption band was observed in this region. Since this molecule certainly has some vibrations of low frequency which are active to the infrared

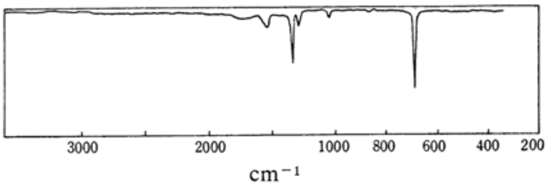

Fig. 4. Infrared absorption spectrum of hexachlorobenzene (in gaseous state).

TABLE II. INFRARED ABSORPTION BANDS OF HEXACHLOROBENZENE

ν, cm^{-1}	Intensity
1396	m
1350	s
1307	m
1053	w
1012	w
874.4	w
696.2	s
687.6	w

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4) H. Yoshinaga, S. Fujita, S. Minami, A. Mitzuishi, R. A. Oetjen and Y. Yamada, *J. Opt. Soc. Am.*, **48**, 315 (1958).

* Because of a slight leakage of the cell, the spectra could not be observed in vacuo.

5) S. Saëki, This Bulletin, **33**, 1021 (1960).

TABLE III. NORMAL VIBRATIONS OF HEXACHLOROBENZENE

Species	Activity	No.	Mode	Observed frequency cm^{-1}
A_{1g}	Raman	ν_1	C–Cl stretching	1225
		ν_2	Breathing	372
A_{2u}	Infrared	ν_4	C–Cl out-of-plane bending	—
E_{1g}	Raman	ν_{11}	C–Cl out-of-plane bending	213
E_{1u}	Infrared	ν_{12}	Ring stretching	1350
		ν_{13}	C–Cl stretching	696
		ν_{14}	C–Cl in-plane bending	—
E_{2g}	Raman	ν_{15}	Ring stretching	1522
		ν_{16}	C–Cl stretching	—
		ν_{17}	Ring in-plane deformation	340
		ν_{18}	C–Cl in-plane bending	322

absorption, this fact might be because the intensity of these vibrations is too low to be observed.

The infrared absorption spectra in the sodium chloride and cesium bromide regions are shown in Fig. 4, and the frequencies of the observed bands are listed in Table II.

Assignment

Assuming the symmetry D_{6h} for the molecule of hexachlorobenzene, the normal vibrations are classified as:

$$\text{In-plane vibrations}: 2A_{1g}+A_{2g}+2B_{1u}+2B_{2u}+3E_{1u}+4E_{2g}$$

$$\text{Out-of-plane vibrations}: A_{2u}+2B_{2g}+E_{1g}+2E_{2u}$$

Among these vibrations, those belonging to the species A_{1g}, E_{1g} and E_{2g} are active in the Raman effect, and those belonging to the species A_{2u} and E_{1u} are active in the infrared absorption spectrum. Consequently, seven Raman lines and four infrared absorption bands are expected for this molecule. These are listed in Table III.

Raman Spectrum.—*Species A_{1g}.*—Two vibrations belong to this species. One is the breathing vibration of the molecule as a whole, and the other is the symmetric stretching vibration of the C–Cl bands. Though the former would empirically be expected to have a frequency about 1000 cm^{-1} and the latter about 600 cm^{-1}, this expectation is not realized in this case. As is shown in Table I, two strong and polarized lines were observed at 372 and 1225 cm^{-1}. The third polarized line at 1195 cm^{-1} was much weaker than the first two and should be considered as an overtone or a combination. The observed frequencies of both ν_1 and ν_2 are completely different from the above, expected values. Since the two totally symmetric vibrations can be regarded as linear combinations of the breathing vibrations of two rings, that is, the rings consisting of six carbon atoms and six chlorine atoms respectively, the line at 1225 cm^{-1} can be assigned to the antiphase linear combination of these breathings, namely, the symmetric stretching vibration of the C–Cl bonds (ν_1), while the line at 372 cm^{-1} can be assigned to the same-phase linear combination of these breathings, namely, the breathing vibration of the molecule as a whole.

Species E_{1g}.—Only one vibration, ν_{11}, belongs to this species. As this is the out-of-plane bending vibration of the C–Cl bonds, the line observed at 213 cm^{-1} was assigned to it.

Species E_{2g}.—The line at 1522 cm^{-1} was apparently assigned to the stretching vibration of the benzene ring, ν_{15}. Though this line was not very clearly observed in the carbon tetrachloride and carbon disulfide solutions because of the overlapping with lines of solvents, it was clearly observed in benzene solution and its depolarization ratio could be confirmed to be large.

The C–Cl stretching vibration, ν_{16}, was expected to appear near 700 cm^{-1}, but no line was observed around there. In the carbon tetrachloride solution a weak line was observed at 572 cm^{-1}, but this line was found to be polarized and could not be regarded as a fundamental. Though no fundamental line was found which might give an overtone at 572 cm^{-1}, it might possibly still be an overtone since there are many fundamentals inactive in both Raman and infrared spectra.

The weak line at 340 cm^{-1} was assigned to the deformation vibration of the ring, ν_{17}. This line probably corresponds to a fundamental vibration irrespective of its extremely low intensity, for its frequency is too low to be considered as an overtone or a combination.

The remarkable line at 322 cm^{-1} was assigned to the in-plane bending vibration of the C–Cl bonds, ν_{18}.

Overtones and Combinations.—The five lines at 3042, 2452, 1248, 1195 and 572 cm^{-1} which were not assigned to fundamentals are all polarized and were considered to be overtones. The first two are apparently the overtones of ν_{15} (1522 cm^{-1}) and ν_1 (1225 cm^{-1}). The other three are not overtones of observed fundamentals, but they might be the overtones of inactive fundamentals of the frequencies about 624, 598 and 286 cm^{-1}. However, of course, the above-mentioned observed bands can by no means be adequate evidence for the existence of these fundamental frequencies.

Infrared Absorption Specta.—*Species* A_{2u}.—Only the out-of-plane bending vibration of C–Cl bonds, ν_4, belongs to this species. Though this vibration was expected to appear near 200 cm^{-1}, no absorption band was observed in the far infrared region, as has already been mentioned. This might be due to the difficulty in the measuring technics* and to the low intensity of this band.

Species E_{1u}.—Three vibrations, ν_{12}, ν_{13} and ν_{14}, belong to this species. The modes of these vibrations might be rather complicated in this case, and it is difficult to visualize these modes because of extreme mixing of the stretching and deformation vibrations of the ring and the C–Cl bonds. Though the simple modes are given for these vibrations in Table III, this is simply for the sake of convenience; actually such simple notations might by no means describe the true modes faithfully. On account of such complexity in the vibrational mode, the empirical estimation of the normal frequencies might be very difficult for this species. However, one can find an analogy in the case of the species E_{1u} of benzene. The mode of ν_{12} of benzene is nearly the stretching vibration of C–H bonds, that of ν_{13} is nearly the stretching vibration of the carbon ring, and that of ν_{14} is the vibration between the carbon ring and the ring consisting of six hydrogen atoms⁶⁾. The observed frequencies for these vibrations are 3099, 1485 and 1037 cm^{-1} respectively. The first two are just the frequencies to be expected from the modes, but it is interesting that the third is the frequency empirically expected for a C–H in-plane bending vibration. Provided that the analogy can be applied to the case of hexachlorobenzene, irrespective of the large difference between the masses of hydrogen and chlorine atom, the vibration ν_{12}, ν_{13} and ν_{14} might have the frequencies of the ring stretching vibration, of C–Cl stretching vibration and of C–Cl in-plane bending vibration respectively. In the infrared absorption spectrum, two strong absorption bands were really observed at 1350 and 696.2 cm^{-1}. Consequently, the former can be assigned to ν_{12} and the latter to ν_{13}. However, though ν_{14} could be expected to appear at 200～300 cm^{-1} according to the above-mentioned analogy, no band was observed in the far infrared region, as has already been mentioned. This is probably because ν_{14} has a very low intensity.

Combination Bands.—A considerable number of combination bands were observed in the infrared absorption spectra, as is shown in Table II. As this molecule has a center of symmetry, only the vibrations belonging to the ungerade species are active to the infrared absorption. Since the first overtone of a fundamental of any species belongs to a gerade species, and since second overtones and higher might not have observable intensities, the observed absorption bands not corresponding to fundamentals should be regarded as combination bands between a gerade fundamental and an ungerade fundamental. However, the clear explanation of these combination bands is not easy in this case. The molecule of hexachlorobenzene has ten fundamental frequencies belonging to the ungerade species, but only two of them were observed; the others were inactive or unobserved. Also, of the vibrations belonging to the gerade species, only a few were observed. Under such conditions, it is not possible to explain all of the combination bands, and it seems to be rather insignificant to present the explanations for only a few combination bands. Thus, discussion of the combination bands has been entirely omitted.

The above-mentioned assignment for the normal vibrations is shown in the last column of Table III.

Summary

The infrared absorption spectra of hexachlorobenzene were measured in a gaseous state from 4000 to 300 cm^{-1}, and in solid state from 300 to 100 cm^{-1}. The Raman spectra of the same substance were measured in solutions in benzene, carbon tetrachloride and carbon disulfide. The depolarization ratio of each Raman line was also observed qualitatively. The assignment of the observed absorption bands and Raman lines was determined, partly by referring to that of benzene.

The author wishes to express his appreciation to Professor H. Yoshinaga and Dr.

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* The measurement had to be carried out in vacuo in order to avoid the extreme masking effect of the strong absorption of water vapor in the atmosphere. However, as the window material of the sample holder was polyethylene, it was not certain that the proper thickness and homogeneity of the Nujol paste layer was preserved even in vacuo.

6) G. Herzberg, "Molecular Spectra and Molecular Structure II", D. Van Nostrand Co. (1954), p. 118.

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