The Assignment of Infrared Absorption Bands of p-Dichlorobenzene

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Many works have been published by a number of investigators concerning the vibrational spectra of *p*-dichlorobenzene (for example Ref. 1 and 2). But all of these measurements were done in solid state or in solution, and we have not yet any molecular spectrum of this substance in gaseous state. Since the spectrum of *p*-dichlorobenzene in solid or solution shows many strong overtones and combination liable to lead to an erroneous assignment, we have measured the gaseous spectra of deuterated and non-deuterated *p*-dichlorobenzenes to obtain the correct assignment.

Experimental

The measurements were carried out using Perkin-Elmer model 112 spectrometer, for the region from 5,000 to 2,000 cm^{-1} with a LiF prism, from 2,000 to 700 cm^{-1} with an NaCl prism and from 700 to 400 cm^{-1} with a KBr prism.

As the boiling points of these substances are considerably high (173.4°C for $C_6H_4Cl_2$), it was necessary to use a high temperature cell to obtain their gaseous spectra. An ordinary gas cell 85 mm. thick with pyrex bracelets of 15 mm. height on the KBr windows was coiled by a fine nichrome wire, then covered by a thick layer of asbestos for the sake of thermal insulation. The bracelets prevented the sample gas from condensing on the KBr windows and made sure to obtain the real gas phase spectra. This cell was usable at any temperature below 300°C by the aid of a slide wire resistor. We did not use any binding agent either to fix the KBr windows to the cell body, or to attach the pyrex rings to the windows, in order to avoid introduction of any impurity which might result from the thermal decomposition of the binding agent. The design of the cell is shown in Fig. 1. The inequality of the diameters at both ends of the cell might cause an inhomogeneity of the temperature in the cell to some extent, but it was not considered to have any effect on the spectra obtained.

The powder of the substance was put in the cell which was previously heated to a temperature sufficiently higher than its boiling point, and the measurement was carried out for the mixture of the vapor and the air at one atmospheric pressure.

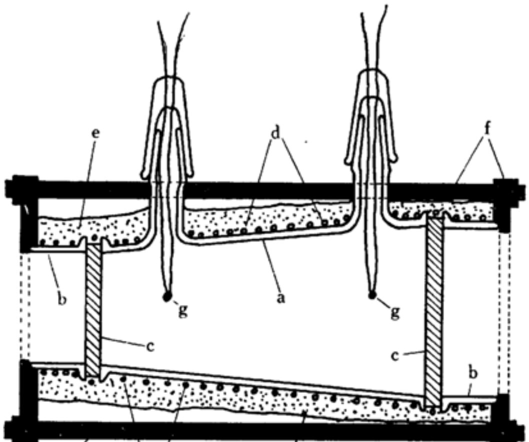

Fig. 1. Description of the high temperature cell

a: cell body
b: bracelets
c: KBr windows
d: nichrome wire
e: asbestos
f: supporting frame work
g: thermocouples

Results

The spectra obtained are shown in Fig. 2, and the observed frequencies of the absorption bands are shown in Table I. The spectra of deuterated *p*-dichlorobenzene were not so clear as those of ordinary *p*-dichlorobenzene because of the small available quantity of the substance. Thus we could detect no overtone nor combination band of deuterated *p*-dichlorobenzene

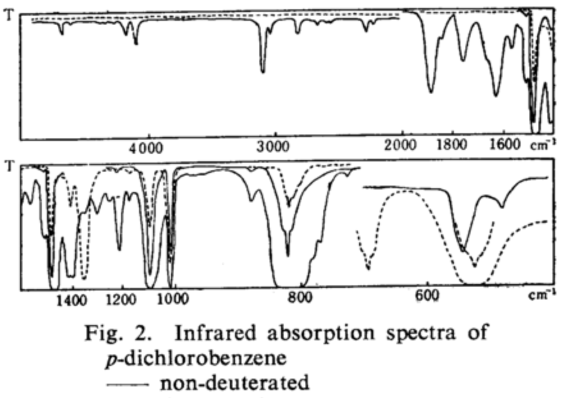

Fig. 2. Infrared absorption spectra of *p*-dichlorobenzene
—— non-deuterated
---- deuterated

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1) D. H. Whiffen, *Spectrochim. Acta*, **7**, 253 (1955).

2) E. K. Plyler, H. C. Allen, Jr. and E. D. Tidwell, *J. Research Natl. Bur. Standards*, **58**, 255 (1957).

TABLE I. OBSERVED FREQUENCIES (cm^{-1})

Non-deuterated	Deuterated	Non-deuterated	Deuterated
4675 m		1626 s	1479 s
4605 w		1567 m	
4384 w		1509 m	
4328 w		1478 s	1404 m
4258 w		1417 s	
4170 m		1395 s	1357 s
4095 m		1348 w	
3094 s	(2290)	1301 m	
3035 m	(2283)	1251 w	1174 w
2816 m		1217 m	1090 s
2665 w		1175 w	
2590 w		1091 s	1020 s
2556 w		1014 s	800?*m
2273 w		878 w	
2220 w		819 s	695 s
1882 s		725 w	
1837 w		544 s	526 s
1758 m		483 s	(436)
1664 w			(414)

N. B. The values in the brackets are the frequencies observed in solid state by other author (J. Lecomte, unpublished).
The indication of the intensities are not very precise.

* This band was covered by the strong band at 819 cm^{-1} of ordinary *p*-dichlorobenzene, and observed as a shoulder.

in the LiF region, and further it is necessary to mention here that the shapes of bands of deuterated *p*-dichlorobenzene in the figure are not so precise as those of ordinary *p*-dichlorobenzene.

Several measurements were repeated for non-deuterated *p*-dichlorobenzene to observe the correct shapes of the absorption bands, but were not successful except for those in the lower frequency part of NaCl region, that is, for the bands at 1013 cm^{-1} and at 819 cm^{-1} which were found to be type B and type C (or A) bands respectively. The other bands did not show any definite feature of the envelopes by which the types of the bands might be decided.

Assignment

The molecular structure of *p*-dichlorobenzene has the V_h symmetry, and we can expect for the molecule thirteen infrared active fundamental vibrations which are shown in Table II. Among those vibrations the frequencies of the C–Cl deformation vibrations are obviously too low to be measured under our experimental conditions, and it is possible that the frequencies of the ring deformation vibrations are also too low to be observed. Consequently only from nine to eleven bands are expected to be observed by our measurements.

TABLE II. INFRARED ACTIVE NORMAL VIBRATIONS OF *p*-DICHLOROBENZENE

- Species B_{1u} (in-plane)
  - C–H stretching
  - C–H bending
  - C–C stretching
  - ring deformation
  - C–Cl stretching
- Species B_{2u} (in-plane)
  - C–H stretching
  - C–H bending
  - C–C stretching
  - ring deformation
  - C–Cl deformation
- Species B_{3u} (out-of-plane)
  - C–H bending
  - ring deformation
  - C–Cl deformation

TABLE III. ASSIGNMENT OF INFRARED FUNDAMENTAL BANDS OF *p*-DICHLOROBENZENE

Species	Non-deuterated cm^{-1}	Deuterated cm^{-1}	Mode
B_{1u}	3094	2290	C–H stretching
	1478	1404	ring stretching
	1217	1090	C–H deformation
	1091	1020	skeletal vibration
	483	414	skeletal vibration
B_{2u}	3035	2283	C–H stretching
	1626	1479	ring stretching
	1405*	1357	C–H deformation
	1014	800	ring deformation
	—	—	C–Cl deformation
B_{3u}	819	695	C–H deformation
	544	526	ring deformation
	—	—	C–Cl deformation

N. B. Concerning the notations for symmetry species, we remark that we have chosen x-axis to be perpendicular to the plane of molecule and z-axis in the direction of the line combining two chlorine atoms.

* The mean value of 1395 and 1417 cm^{-1} in Table I.

We can easily assign the absorption bands at 3094 cm^{-1} (2290 cm^{-1} for $C_6D_4Cl_2$) and 3035 cm^{-1} (2283 cm^{-1} for $C_6D_4Cl_2$) to the two C–H (or C–D) stretching frequencies. The absorption band at 819 cm^{-1} of $C_6H_4Cl_2$ (695 cm^{-1} for $C_6D_4Cl_2$) is assigned to the out-of-plane vibration of C–H (or C–D) by many authors (for example, by D. H. Whiffen[1]) and Y. Kakiuchi[3])). We have assigned a strong band at 544 cm^{-1} of $C_6H_4Cl_2$ (526 cm^{-1} for $C_6D_4Cl_2$) to the out-of-plane vibration of benzene ring. This band might be assigned to the in-plane deformation vibration of the ring,

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3) Y. Kakiuchi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), 77, 1572 (1956).

but, as shown later, this assignment does not satisfy the product rule.

As for the other normal frequencies, we measured seven strong bands between 1000 and 2000 cm^{-1} in the spectrum of $C_6H_4Cl_2$ (six bands for $C_6D_4Cl_2$), while there remain six normal vibrations to assign them. As there were too many absorption bands in the spectrum of $C_6H_4Cl_2$, we assumed that the two bands at 1417 and at 1395 cm^{-1} are caused by a Fermi resonance between a fundamental and a combination* near by it. Taking into account of the fact that the intensities of these two bands were nearly equal, we estimated that the position of the fundamental would be 1405 cm^{-1} (mean value of these two observed frequencies) if it were not for the Fermi resonance. We assigned the highest two of these six bands to the stretching vibrations of the ring, and the next two frequencies (one of which is the above-mentioned 1405 cm^{-1}) to the in-plane bending vibrations of C-H, and 1015 cm^{-1} and 1091 cm^{-1} to the deformation vibration of the ring and the stretching vibration of C-Cl respectively. As for the C-Cl stretching vibration, we could easily imagine from its abnormal frequency that this mode might be extremely mixed with some other modes. Although assignments of the last two frequencies seem to be mutually exchangeable, the exchange would result the larger deviation from the product rule.

In addition to the above-mentioned bands, we observed a strong band at 483 cm^{-1} in the spectrum of the $C_6H_4Cl_2$. This band corresponds to the band at 414 cm^{-1} in the spectrum of the $C_6D_4Cl_2$. We assigned these bands to the skeletal vibration of the molecule, i. e., the mixed vibration of ring deformation and C-Cl stretching.

Thus we assigned eleven of thirteen fundamental vibrations, and the remaining two fundamentals are the vibrations of C-Cl deformation, the frequencies of which are expected to be too low to be measured. The present assignments are shown in Table III.

Discussion

According to the product rule, the ratio of the products of the frequencies of non-deuterated and deuterated *p*-dichlorobenzene is 1.972 for the species B_{1u} and B_{2u}, and 1.388 for the species B_{3u}. In the case of the species B_{1u} we found that the ratio calculated from the observed frequencies was 1.970 which is in good accordance with the theoretical value. But in the case of the other species, the unobserved bands of low frequencies prevented us from applying the product rule perfectly, and all that we were able to do was to verify that the ratios calculated from the observed frequencies alone did not exceed the theoretical value. Actually these ratios were calculated as 1.917 and 1.219 for species B_{2u} and B_{3u} respectively, and these were quite plausible values.

As for the band envelopes, as mentioned in the previous chapter, for non-deuterated *p*-dichlorobenzene the band at 1014 cm^{-1} was found to be a type B band showing an apparent absorption minimum at the center of the band, while the band at 819 cm^{-1} was found to be type A or C band showing a prominent Q branch accompanied by P and R branches at its both sides. Considering that the axis of the largest moment of inertia of this molecule is perpendicular to the molecular plane, and that the axis of the smallest moment of inertia combines the two chlorine atoms, it would be easily shown that the type A, B and C bands belong to the species B_{1u}, B_{2u} and B_{3u} respectively, and that the band at 1014 cm^{-1} belongs to species B_{2u} and the band at 819 cm^{-1} belongs to the species B_{1u} or B_{3u}. The assignment shown in Table III is in good accordance with these results. The observed envelopes of the other bands were not adequately clear to give some suggestions for their assignments. Further for the spectra of deuterated *p*-dichlorobenzene we could not find any absorption band which showed a clear band envelope. The band at 819 cm^{-1} the envelope of which showed a clear feature of type A or C band was apparently to be considered as the extremely strong band of ordinary *p*-dichlorobenzene contained in deuterated *p*-dichlorobenzene as a slight impurity.

We had tried many other assignments which seemed to be compatible with the empirical knowledge. But they did not satisfy the product rule so well as the one shown in Table III.

The present assignment is different at some points from those given by other authors for their spectra in solid state or in solution. Comparing our gaseous spectra with those spectra of solid or solution, we saw that many strong bands in the latter spectra disappeared entirely or partially in the former. Thus we believe that the spectrum measured in solid state or in solution is not suitable for the assignment of the absorption bands.

Summary

The infrared absorption spectra of deuterated and non-deuterated *p*-dichlorobenzene were measured in the vapor state using a high

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* We observed a strong Raman line at 331 cm^{-1}. The combination of this vibration with the infrared active vibration at 1090 cm^{-1} would appear in the neighborhood of 1405 cm^{-1} We shall present a paper on the Raman spectra of *p*-dichlorobenzene in near future.

temperature cell. The results obtained by the measurements permitted us the assignment of the observed fundamental bands with the aid of the product rule. For some frequencies which we could not measure under our experimental conditions, we used the frequencies observed by other workers in the solid state which enabled us to apply the product rule.

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