The Infrared Absorption Spectrum of 1, 2, 4, 5-Tetrachlorobenzene in Vapor State

By Shinnosuke SAËKI*

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The molecular spectra of 1, 2, 4, 5-tetrachlorobenzene have been studied by some investigators[1]. All of these studies were, however, mainly concerned with a number of benzene derivatives to find the relation between the position of substituents in the benzene ring and C–H out-of-plane characteristic frequencies. Also 1, 2, 4, 5-tetrachlorobenzene was treated only as a member of the substituted benzenes. The assignment of the observed bands of this substance has been little discussed with the exception of its out-of-plane C–H vibration. Besides, all the spectra were taken in solid or liquid state or in solution, and the spectra taken in these states are not suitable to be used for the assignment of the bands. We measured the spectra of ordinary and deuterated 1, 2, 4, 5-tetrachlorobenzene in vapor state with the aid of a high temperature cell to make some tentative assignments of the observed infrared absorption bands.

Experimental and Results

The measurements were carried out on ordinary and deuterated 1, 2, 4, 5-tetrachlorobenzenes, from 5000 to 2000 cm^{-1} with a lithium fluoride prism, from 2000 to 700 cm^{-1} with a sodium chloride prism and from 700 to 400 cm^{-1} with potassium bromide prism using the Perkin-Elmer 112 infrared spectrometers. As the boiling points of these substances are considerably high, in order to observe the spectra in vapor state we used the high temperature cell which was described in a previous paper[2]. The partial pressure of each substance was not measured. The substance was simply put in the cell which has been previously heated but not evacuated, and regulated the quantity of the substance in the cell so that it might give a good spectrum.

The ordinary 1, 2, 4, 5-tetrachlorobenzene used in this experiments was extra pure grade on the market, and the deuterated one was kindly provided by Dr. Leitch in Canada.

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* Present address: Government Chemical Industrial Research Institute, Shibuya-ku, Tokyo.

[1] For example, E. K. Plyler, H. C. Allen, Jr. and E. D. Tidwell, *J. Research Nat. Bur. Standards*, **58**, 255 (1957).

[2] S. Saëki, This Bulletin, 33, 1021 (1960).

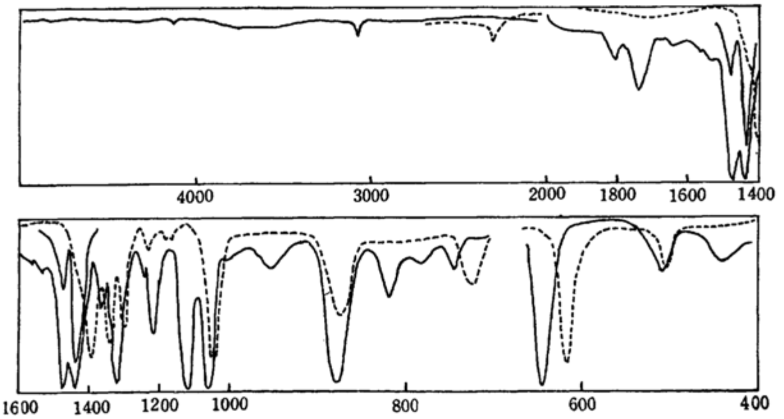

Fig. 1. Infrared absorption spectra of ordinary and deuterated 1,2,4,5-tetrachlorobenzenes.
$C_6H_2Cl_4$ —— $C_6D_2Cl_4$ ----

TABLE I. INFRARED ABSORPTION BANDS OF 1,2,4,5-TETRACHLOROBENZENES

$C_6H_2Cl_4$	$C_6D_2Cl_4$	$C_6H_2Cl_4$	$C_6D_2Cl_4$
3094 m	2300 m		1175 w
2775 w		1116 s	$\left\{\begin{matrix}1054\\1047\end{matrix}\right.$ s
2680 w		1060 s	
2630 w		947 w	
1802 w		880 s	874 s
1740 w		820 m	725 m
1474 m	1425 w	782 w	
1436 s	1392 s	745 w	
1367 m	1345 s	645 s	617 s
1319 s	1297 s	509 m	504 m
1241 w	1235 m	440 w	
1218 m	1187 w		

TABLE II. INFRARED ACTIVE NORMAL VIBRATIONS OF 1,2,4,5-TETRACHLOROBENZENES

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

The observed spectra of each substance are shown in Fig. 1, and the observed frequencies are shown in Table I.

Assignment

The symmetry of this substance belongs to the point group V_h as *p*-dichlorobenzene does. So it has thirteen infrared active normal vibrations of which five belong to the species B_{1u} (in-plane), five to the species B_{2u} (in-plane) and three to the species B_{3u} (out-of-plane)*. These expected vibrational modes are listed in Table II.

Among these vibrations, the C–Cl bending vibration of each species is expected to be unobservable under the experimental conditions because of its low frequency, and some of the ring deformation frequencies might also exist beyond the experimental region. Therefore we should expect to observe from seven to ten fundamental frequencies under the experimental conditions. In the spectra nine or ten strong bands were observed for $C_6H_2Cl_4$ and eight strong bands for $C_6D_2Cl_4$. In addition to these strong bands a medium or weak band in shorter wavelength region was observed; that is, a band at 3094 cm^{-1} of $C_6H_2Cl_4$ and at 2300 cm^{-1} of $C_6D_2Cl_4$ which are evidently the fundamental bands of C–H and C–D stretching vibrations respectively.

Between 1500 and 1200 cm^{-1} three fundamental bands, might be expected that is, the ring stretching vibrations of the species B_{1u} and B_{2u} and the ring in-plane deformation vibration of the species B_{2u}. It should be mentioned here that the third vibration, which is called a ring deformation vibration, might probably have a considerably high frequency, because the mode of this ring deformation is necessarily accompanied by a ring stretching mode. Taking into account the relative intensities of these bands and the product rule, we consider that the

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* In this case, x axis was taken along the symmetry axis perpendicular to the molecular plane, and z axis along the symmetry axis combining two hydrogen atoms.

three bands at 1474, 1436 and 1319 cm^{-1} of $C_6H_2Cl_4$ correspond to the three bands at 1345, 1392 and 1297 cm^{-1} of $C_6D_2Cl_4$ respectively, and assigned the first pair of bands to the ring stretching vibration of species B_{2u}, the second to the ring stretching vibration of species B_{1u} and the third to the ring in-plane deformation vibration of species B_{2u}.

It appeared somewhat curious that in the region between 1200 and 1000 cm^{-1} we found two bands of $C_6H_2Cl_4$ at 1116 and 1060 cm^{-1}, but only one band of $C_6D_2Cl_4$ at 1051 cm^{-1} corresponding to them. The intensities of both of the two bands of $C_6H_2Cl_4$ were too remarkable to be considered as overtone or combination bands. On closer examination of the shape of the band at 1051 cm^{-1} of $C_6D_2Cl_4$, we found the two absorption maxima at 1054 and 1047 cm^{-1} which were not known to be the branches of a single band or to be the peaks of two independent bands. Badger and Zumwalt[3] gave the band envelopes of several types of unsymmetrical rotator molecules. The ρ[*1] and S values of the molecule of $C_6D_2Cl_4$ are 1.8 and -0.7 respectively for which the band envelope is not given in their paper. But the estimation from the different band envelopes described in their paper told us that the splitting of the two maxima would not be greater than 3 cm^{-1}.

Dennison[4] also showed that the diagrams of the fine structure of the band, but it was difficult to estimate the splitting of the two absorption maxima from these diagrams. If one approximates the molecule of 1, 2, 4, 5-tetrachlorobenzene by a symmetric rotator[*2], the approximate value of the splitting can be found to be about 5 cm^{-1}[*3]. Actually this splitting distance was found to be about 7 cm^{-1}, a little larger than the above-mentioned estimated and calculated values. But such an amount of discrepancy between the observed and calculated (or estimated) values is not enough to favor the supposition that these two absorption maxima would be caused by the two independent bands. However, we shall take this supposing at present, for it appears to explain more easily the correspondence between the absorption bands of each substance. Thus we assigned the band at 1116 and 1060 cm^{-1} of $C_6H_2Cl_4$ to the C–H in-plane bending vibration of species B_{2u} and to the ring deformation vibration of species B_{1u} respectively, and for their corresponding bands of $C_6D_2Cl_4$ we considered that the band at 1047 cm^{-1} of $C_6D_2Cl_4$ corresponds to the former band and the band at 1054 cm^{-1} of $C_6D_2Cl_4$ to the latter.

In the region below 1000 cm^{-1} were found four remarkable bands of each substance, that is, 880, 820, 645 and 509 cm^{-1} for $C_6H_2Cl_4$, and 874, 725, 617 and 504 cm^{-1} for $C_6D_2Cl_4$. Kakiuchi[5] assigned the band at 867 cm^{-1} of $C_6H_2Cl_4$ to the out-of-plane C–H bending vibration. It is evident that this is the band which was observed at 880 cm^{-1} in our experiments[*4]. But we found in the spectrum of $C_6D_2Cl_4$ a remarkable band at 874 cm^{-1} which evidently corresponds to the band at 880 cm^{-1}. It means that the frequency shift caused by the replacement of hydrogen atoms by deuterium atoms is only 6 cm^{-1}. This frequency shift is too small for a vibration mainly concerned with the C–H bond. Thus we assigned the band at 820 cm^{-1} to the out-of-plane C–H vibration, for its corresponding band of $C_6D_2Cl_4$ was found at 725 cm^{-1}, showing a great frequency shift. But the intensities of these bands appear to be too weak for the out-of-plane C–H and C–D vibrations, and we have not found a plausible explanation for this fact. As for the above-mentioned band at 880 cm^{-1} (874 cm^{-1} for $C_6D_2H_4$) we assigned it to the C–Cl stretching vibration of species B_{1u}. And to the other C–Cl stretching vibration which belongs to species B_{2u}, we assigned the band at 645 cm^{-1} (617 cm^{-1} for $C_6D_2Cl_4$). The last pair of bands which were found at 509 cm^{-1} (for $C_6H_2Cl_4$) and at 504 cm^{-1} (for $C_6D_2Cl_4$) were assigned to the out-of-plane deformation vibration of the ring. The assignment given above is shown in Table III.

It should be mentioned here that the assignment shown in Table III based on the assumption that the band at 1051 cm^{-1} of $C_6D_2Cl_4$ is composed of two closely positioned independent bands. If not, the assignment should be quite changed as follows.

We regarded the absorption maxima at 1054 and 1047 cm^{-1} observed in the spectrum of $C_6D_2Cl_4$ as the branches of one band which corresponds to the band at 1116 or at 1060 cm^{-1} of $C_6H_2Cl_4$. Then one of these two bands has no corresponding band of $C_6D_2Cl_4$ except the band at 874 cm^{-1}. If we consider the band

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[3] R. M. Badger and L. R. Zumwalt, *J. Chem. Phys.*, 6, 711 (1938).

[*1] Badger and Zumwalt defined $\rho=(a-c)/b$, where a, b and c are the reciprocals of three principal moments of inertia, I_A, I_B and I_C respectively.

[4] D. M. Dennison, *Rev. Mod. Phys.*, 33, 280 (1931).

[*2] For this molecule three principal moments of inertia were calculated as $I_A=688\times10^{-40}$, $I_B=1752\times10^{-40}$ and $I_C=2440\times10^{-40}$. Thus the approximation by the symmetric rotator is not very bold.

[*3] In this calculation we assumed that $I_B=2000\times10^{-40}$. This is the approximate mean value of the real I_B and I_C values.

[5] Y. Kakiuchi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), 80, 356 (1959).

[*4] He used the frequencies observed by Plyler and his collaborators[2]. Those frequencies were observed in the liquid state, so it is quite natural that there are small discrepancies between their frequencies and our frequencies observed in the vapor state.

TABLE III. ASSIGNMENT I

Species	$C_6H_2Cl_4$	$C_6D_2Cl_4$	Mode
B_{1u}	3094	2300	C-H or C-D stretching
	1436	1392	Ring stretching
	1060	1054	Ring deformation
	880	874	C-Cl stretching
	—	—	C-Cl bending
B_{2u}	1474	1345	Ring stretching
	1319	1297	Ring deformation
	1116	1047	C-H or C-D bending
	645	617	C-Cl stretching
	—	—	C-Cl bending
B_{3u}	820	725	C-H or C-D bending
	509	504	Ring deformation
	—	—	C-Cl bending

at 874 cm^{-1} of $C_6D_2Cl_4$ as corresponding to the band at 1116 or at 1060 cm^{-1}, this great frequency shift suggests that the pair is to be assigned to the C-H (C-D) in-plane bending vibration of species B_{2u}. Then there are two possible assignments of the other pair (the band at 1060 or at 1116 cm^{-1} of $C_6H_2Cl_4$ and the band at 1051 cm^{-1} of $C_6D_2Cl_4$), that is, an assignment to the ring deformation vibration and an assignment to the C-Cl stretching vibration of species B_{1u}. In the case of this molecule the frequency of the ring deformation vibration of species B_{1u} might be rather low, for it could occur without coupling with a stretching mode of the ring. The frequency of a C-Cl stretching vibration which is generally expected at about 700 cm^{-1} might easily couple with the vibrations of other modes in this case, and its frequency might change over a wide region. From these considerations we concluded that the pair of bands in question is to be assigned to the C-Cl stretching vibration of species B_{1u}. Concerning the question as to which of the above-mentioned two bands at 1116 cm^{-1} and at 1060 cm^{-1} of $C_6H_2Cl_4$ is to be assigned to C-H in-plane bending vibration of species B_{2u}, we decided to assign the former band to this normal vibration from the consideration of the product rule.

As for the other fundamental bands, we assigned the pair of bands at 509 cm^{-1} ($C_6H_2Cl_4$) and 504 cm^{-1} ($C_6D_2Cl_4$) to the ring in-plane deformation vibration of species B_{1u} and the pair of bands at 645 cm^{-1} ($C_6H_2Cl_4$) and 617 cm^{-1} ($C_6D_2Cl_4$) to the C-Cl stretching vibration of species B_{2u}. In addition to the above-mentioned change in the assignment, the correspondence of three pairs of ring stretching vibrations (in the region 1300$\sim$1500 cm^{-1}) is also changes from the consideration of the product rule as is shown in Table IV.

This is the second assignment which seems to us to be as plausible as the former one. This assignment is shown in Table IV.

TABLE IV. ASSIGNMENT II

Species	$C_6H_2Cl_4$	$C_6D_2Cl_4$	Mode
B_{1u}	3094	2300	C-H or C-D stretching
	1474	1392	Ring stretching
	1060	1047	Ring deformation
	509	504	C-Cl stretching
	—	—	C-Cl bending
B_{2u}	1436	1345	Ring stretching
	1319	1297	Ring deformation
	1116	874	C-H or C-D bending
	645	617	C-Cl stretching
	—	—	C-Cl bending
B_{3u}	880	725	C-H or C-D bending
	—	—	Ring deformation
	—	—	C-Cl bending

Discussion

According to the product rule the theoretical value of the ratio of products of the frequencies is 1.407 for all three species (B_{1u}, B_{2u} and B_{3u}) in the case of this molecule. As we could not observe all of the fundamental frequencies under our experimental conditions, it was not possible to apply the product rule to the results obtained perfectly, but it was possible to ascertain whether the ratio of products calculated from the observed frequencies alone exceeds the theoretical value or not. We carried out this calculation for every species of both of the above-mentioned assignments. The results are shown in Table V.

TABLE V. CALCULATED RATIOS OF THE PRODUCTS OF OBSERVED FREQUENCIES

	Species	Calculated ratio	Number of observed frequency
Assignment I	B_{1u}	1.405	4 of 5
	B_{2u}	1.242	4 of 5
	B_{3u}	1.142	2 of 3
Assignment II	B_{1u}	1.456	4 of 5
	B_{2u}	1.449	4 of 5
	B_{3u}	1.214	1 of 3

None of the calculated ratios of assignment I exceeded the theoretical value 1.407, while two of the three calculated ratios of assignment II exceed the theoretical values. From the theoretical point of view assignment I shows no contradiction. But on closer examination one will find some points of discussion. In the first place the value of the ratio for species B_{1u} of assignment I is almost equal to the theoretical value, so the ratio of the unobserved fifth frequencies must be nearly 1. As the fifth frequency is that of the C–Cl bending vibration (or skeletal vibration), this requirement will probably be fulfilled. In the second place those ratios for the species B_{2u} and B_{3u} of the assignment I are so small that the ratios of the last unobserved frequency of these species must be considerably great, that is, 1.144 and 1.232 for the species B_{2u} and B_{3u} respectively. Considering the fact that both of these values are ratios of the frequencies of C–Cl bending vibrations, they are evidently too great to attribute to the single ratios of frequencies. This appears to be an absolute defect of assignment I as well as of the above-mentioned ambiguity in the explanation of the band at 1051 cm^{-1} of $C_6D_2Cl_4$.

As for assignment II, as we mentioned previously, there are two ratios exceeding the theoretical values. However, a discrepancy of a few per cent must be expected between the observed and theoretical ratios, as there are various factors which cause the deviation, such as small mechanical errors of the spectrometer, the unharmonicity of the vibrations, Fermi resonance, etc. Therefore, provided that the ratios of C–Cl bending frequencies are nearly 1, the discrepancies found for species B_{1u} and B_{2u} might not absolutely deny assignment II.

In the case of species B_{3u}, since only one of the three frequencies was observed, the application of the product rule was quite impossible. But the ratio of 1.214 obtained for the first pair of frequencies of this species seems to be perfectly plausible for the C–H (or C–D) out-of-plane bending vibration, and this assignment appears to be strongly preferable to that for species B_{3u} of assignment I.

After all, although we could not find an adequate difference between two assignments shown in Table V to draw out any unambiguous conclusion, assignment II seems to us a little more plausible than the other. In order to remove this ambiguity it may be necessary to carry out the measurement of the spectra of these substances in the far infrared region or to observe the precise shape of each fundamental band or to find out the exact force constants which will allow us to calculate the normal frequencies of these molecules with sufficient accuracy.

Summary

The infrared absorption spectra of ordinary and deuterated 1, 2, 4, 5-tetrachlorobenzenes were measured in the vapor state using the high temperature cell. For the results obtained by the measurements we proposed two possible assignments of the fundamental infrared bands, and made the discussion comparing these two tentative assignments. However, at present we have no experimental base upon which we can decide the superiority of one to the other. In order to solve this difficulty we are going to make an investigation of the spectra of these molecules in the far infrared region as well as the calculation of the exact force constants of the chlorobenzenes.

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Laboratoire des Recherches Physiques
Faculté des Sciences de Paris