The Assignment of Infrared Absorption Bands of 1, 3, 5-Trichlorobenzene

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Several works have been published concerning the infrared spectra of 1, 3, 5-trichlorobenzene (for example, Ref. 1 and 2). However, all of these spectra were measured in solid state or in solution and we have no spectrum of this substance in vapor state. As we pointed out in our previous paper[3] chlorobenzenes show strong bands of overtones and combinations in solid state or in solution. So, one must be very cautious in trying the assignment of infrared bands of these substances using the spectra in these states. For this reason, we measured the infrared absorption spectra of deuterated and non-deuterated 1, 3, 5-trichlorobenzenes in vapor state to make the assignment of the absorption bands of these substances.

Experimental and Results

Spectral data were obtained by means of a Perkin-Elmer 112 spectrometer equipped with LiF, NaCl and KBr prisms. The measurements were carried out under ordinary pressure at high temperature. In these measurements we used the high temperatures cell which we described in detail in our previous paper[3]. The non-deuterated 1, 3, 5-trichlorobenzene used in our experiments was the " extra pure " one on the market, and the deuterated one was kindly provided by Dr. Leitch in Canada.

For the non-deuterated substance we made several measurements in various concentrations to obtain the correct frequencies and shapes of the strong bands and also to ascertain the existence of very weak bands. But, for the deuterated substance, we could not measure its spectra so attentively because of the smallness of the quantity, and it is possible that some weak bands were missed in our measurements. However, as we are going to assign only the fundamental bands of these spectra, this missing would not be very serious.

The spectra obtained by our measurements are shown in Fig. 1, and the frequencies of the observed bands are shown in Table I.

TABLE I. THE INFRARED ABSORPTION BANDS OF 1, 3, 5-TRICHLOROBENZENE (cm^{-1})

Non-deuterated		Deuterated		Non-deuterated		Deuterated	
4650	w	4550	w	1565	s	1549	s
4365	w	3256	w	1464	w		
4236	w	3105	w	1419	s	1333	s
4085	m	2800	w	1380	m	1257	m
3132	w	2687	w			1206	m
		2600	w	1261	w	1066	w
3089	m	(2310)				1024	w
2951	w	2274	w			950	w
2928	w					896	w
2838	w			1100	s		
2712	w			1055	m		
2632	w			889	w		
2592	m			853	s	843	s
2197	w			813	s	795	s
1944	w					769	w
1722	m			719	w		
1606	w			662	s	532	s

N. B. The value in the bracket is the frequencies observed in solid state by other authors. The indication of the intensities are not very precise.

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1) E. Herz, K. W. F. Kohlrausch and R. Vogel, *Monatsh.* 76, 200 (1947).

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

3) S. Saëki, This Bulletin, 33, 1021 (1960).

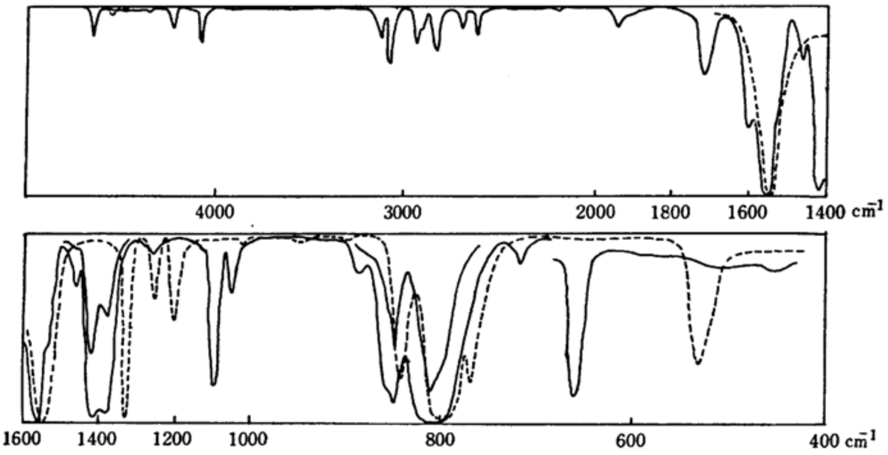

Fig. 1. Infrared absorption spectra of 1,3,5-trichlorobenzene.
—— non-deuterated ---- deuterated

Assignments

Assuming the molecular structure of 1,3,5-trichlorobenzene to be of D_{3h} form, it has ten infrared active fundamental frequencies, of which seven are doubly degenerate (species E′, in-plane) and three are non-degenerate (species A_2'', out-of-plane). The modes of these vibrations are shown in Table II. Of course we can not expect to observe all of these ten normal frequencies under our experimental conditions, because two C–Cl deformation frequencies (E′ and A_2'') are evidently too low to be measured, and two ring deformation frequencies might also exist below the observable region. Thus only from six to eight fundamental frequencies might be observed by our experiments. However, as is shown in Fig. 1 and Table I, there were too many strong bands in the spectra, but we could eliminate some of them by comparing the spectrum of non-deuterated substance with that of deuterated one.

TABLE II. NORMAL VIBRATIONS OF 1,3,5-TRICHLOROBENZENE

E′ (in-plane)	A_2'' (out-of-plane)
C–H stretching	C–H deformation
ring stretching	ring deformation
ring stretching	C–Cl deformation
C–H deformation	
ring deformation	
C–Cl stretching	
C–Cl deformation	

We could easily assign the band at 3089 cm^{-1} of $C_6H_3Cl_3$ to the C–H stretching vibration (E′). The C–D stretching vibration of $C_6D_3Cl_3$ was not observed. It might be because of the unfortunate overlapping with the strong band of carbon dioxide near 2200 cm^{-1}. In solid state, it was observed at 2310 cm^{-1}[4].

We assigned two strong bands at 1565 and 1419 cm^{-1} of $C_6H_3Cl_3$ (1549 and 1333 cm^{-1} of C_6D_3Cl) to the ring stretching fundamental vibrations of species E′, and the strong band at 1380 cm^{-1} of $C_6H_3Cl_3$ to the C–H deformation vibration of E′ (in-plane). However, for the corresponding band of $C_6D_3Cl_3$, we observed two bands of considerable intensity at 1257 and 1206 cm^{-1}. These two bands were considered to be brought about by a Fermi resonance between a fundamental and an overtone or combination of species E′, and their nearly equal relative intensities suggested to us that the proper frequency of the concerned fundamental band might be about 1230 cm^{-1}. As for the overtone or combination band which interacts with the fundamental, we can say little of it because of the lack of data in the low frequency region and also of the lack of the Raman spectrum* of this substance.

We observed another strong band at 1100 cm^{-1} in the spectrum of $C_6H_3Cl_3$ but in the spectrum of $C_6D_3Cl_3$ we did not find any strong band corresponding to it. Although the intensity of the band at 1100 cm^{-1} of $C_6H_3Cl_3$ was very remarkable, this lack of corresponding band in the spectrum of $C_6D_3Cl_3$ kept us from assigning the band to a fundamental one.

The band at 853 cm^{-1} of $C_6H_3Cl_3$, was hitherto pointed out by many investigators[5] as an out-of-plane fundamental vibration band of C–H

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[4] J. Lecomte, unpublished.

* We have not yet succeeded in observing the Raman lines of this substance. For, when this substance was resolved in the solvents, the solution was slightly colored, and it prevented us from measuring the Raman spectrum.

[5] For example, Y. Kakiuchi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **80**, 356 (1959) and A. R. H. Cole and H. W. Thompson, *Trans. Faraday Soc.*, **46** 103 (1950).

bond. But, as is shown in our spectrum of Fig. 1, this band corresponds to the band at 843 cm^{-1} of $C_6D_3Cl_3$. That means, the frequency shift caused by the substitution of hydrogen atoms by deuterium atoms was only 10 cm^{-1}. If this is a band principally concerning the vibration of C–H bond, the frequency shift might be much greater than 10 cm^{-1}. Even if we dare to consider that it is the band at 769 cm^{-1} of $C_6D_3Cl_3$ that corresponds to 853 cm^{-1} of $C_6H_3Cl_3$, another difficulty would be caused. As we shall show later, we have a band in a lower frequency region which showed a large frequency shift by the substitution of hydrogen atoms, that is, the band at 662 cm^{-1} of C_6H_3 (532 cm^{-1} of $C_6D_3Cl_3$). If we assign the band at 853 cm^{-1} to the out-of-plane C–H vibration, there should be no way to explain the band at 662 cm^{-1} which was shifted widely to 532 cm^{-1} by the introduction of deuterium atoms. Therefore we did not assign this band at 853 cm^{-1} (at 843 cm^{-1} in the case of $C_6D_3Cl_3$) to the out-of-plane C–H (or C–D) vibration. One might also assign it to the in-plane ring deformation fundamental vibration (E′). But it is generally known that the frequency of this mode is very variable over a wide region, especially when there is a large possibility of coupling with other modes. So we are not sure that we could assign this band to the ring deformation fundamental vibration. After all we assigned it to no normal vibraton. After all we assigned it to no normal vibration, considering it as an overtone or combination band which was brought about by the Fermi resonances with a fundamental band at 813 cm^{-1} and which borrowed the intensity from the fundamental band. Thus we could get over the superabundance of the strong bands in the observed spectra.

We assigned the very strong bands at 813 cm^{-1} of $C_6H_3Cl_3$ and at 795 cm^{-1} of $C_6D_3Cl_3$ to the C–Cl stretching vibration. But it should be mentioned here that this designation of the vibrational mode is used just as a convention. For, as we showed in our previous paper[3], the mixing of the vibrational modes is extreme in this region of frequency, and it might not be very correct to designate the modes of these normal vibrations by simple terms as C–Cl stretching vibration and so forth.

We observed only one strong band in KBr region in each spectrum of $C_6H_3Cl_3$ and $C_6D_3Cl_3$, that is, the bands at 662 cm^{-1} and at 532 cm^{-1} respectively. As there was no other strong absorption band, it is quite certain that these two bands correspond to each other. Further, the fact that the ratio of their frequencies is considerably apart from 1 (1.24) suggests to us that these vibrational bands are concerned with the hydrogen and deuterium atoms respectively. For the spectrum of mesitylene Whiffen[6] assigned the band at 928 cm^{-1} to the out-of-plane vibration of C–H bond. In the case 1, 3, 5-trichlorobenzene, since no appropriate strong band was found in the neighbourhood of 900 cm^{-1}, we assigned the band at 662 cm^{-1} (at 532 cm^{-1} for $C_6D_3Cl_3$) to the C–H (C–D) out-of-plane vibration. The above-mentioned assignment is shown in Table III.

TABLE III. THE ASSIGNMENT OF THE INFRARED BANDS OF 1,3,5-TRICHLOROBENZENE

Type	$C_6H_3Cl_3$	$C_6D_3Cl_3$	Mode
E′	3089	(2310)	C–H stretching
	1565	1549	ring stretching
	1419	1333	ring stretching
	1380	1230*	C–H deformation
	813	795	C–Cl stretching
	—	—	ring deformation
	—	—	C–Cl deformation
A_2''	662	532	C–H deformation
	—	—	ring deformation
	—	—	C–Cl deformation

* This is the average value of the two observed frequencies, i. e., 1257 and 1206 cm^{-1}.

Discussion

The theoretical values of the ratios of products of normal frequencies of each substance (deuterated and non-deuterated) are 1.972 for the species E′ and 1.402 for the species A_2''. For the species A_2'' we could observe only one frequency of each substance, and it was impossible to apply the product rule to this species. The only one observed frequency of species A_2'' was 662 cm^{-1} of $C_6H_3Cl_3$ (532 cm^{-1} of $C_6D_3Cl_3$) which we assigned to the out-of-plane C–H (or C–D) fundamental vibration by reason of the large shift of frequency accompanying the substitution of hydrogen atoms by deuterium atoms. As was mentioned in the previous section, this assignment is quite different from that which is generally admitted now. We can not get to a definite conclusion on this point at present, but if we succeed in measuring the spectra of these substances in the far infrared region, and if we observe the other two out-of-plane fundamental bands, we shall be able to determine the correct assignment.

For the species E′ too, there were some frequencies that were left unobservable under our experimental conditions, and it is also impossible to apply the product rule perfectly. But, in this case, five or six normal frequencies (seven in all) were observed, so it is not

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[6] D. H. Whiffen, *Spectrochim. Acta*, 7, 253 (1955–6).

completely meaningless to calculate the ratio of products of observed frequencies alone. This calculated ratio was 1.650, when we excluded the pair of frequencies at 853 cm^{-1} (for $C_6H_3Cl_3$) and at 843 cm^{-1} (for $C_6D_3Cl_3$) from this calculation. It means that the ratio of products by the other two unobserved frequencies is to be about 1.19, and this is quite an appropriate value. But if we include the above-mentioned pair of frequencies into this calculation, the ratio increases only a little and becomes 1.670. It requires that the ratio of the last unobserved frequency of each substance is 1.18. This value seems to be too great to attribute to the ratio of only one pair of frequency. This is another reason why we have not dared to assign this pair of bands to the fundamental ones.

Summary

The infrared absorption spectra of deuterated nd non-deuterated 1,3,5-trichlorobenzenes were measured in the vapor state from 5,000 to 400 cm^{-1}. The results of our measurements allowed us the assignment of the fundamental bands of this substance by the aid of the product rule. As we could not observe all of the fundamental bands of this substance, the perfect application of the product rule was not possible. But we proved that our assignment did not conflict with the product rule.

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