The Infrared Absorption Spectra of 1,3,5-Trichlorobenzene, 1,2,4,5-Tetrachlorobenzene and their Deuterated Derivatives

By Shinnosuke SAËKI

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The infrared absorption spectra of 1, 3, 5-trichlorobenzene[1], 1, 3, 5-trichlorobenzene-d_3[1], 1, 2, 4, 5-tetrachlorobenzene[2] and 1, 2, 4, 5-tetrachlorobenzene-d_2[2] have been studied from 4000 to 400 cm^{-1}, and the assignments of the observed bands have previously been proposed by the author. Also, recently the spectra of these substances have been measured in the far infrared region between 400 and 100 cm^{-1} using the cesium bromide prism and the gratings, and the spectra in the sodium chloride region have been reexamined with the aid of the high temperature long path cell described in a previous paper[3]. In this paper, the results of these measurements are reported, and, on the basis of this information, revised assignments for the infrared active normal vibrations of these molecules are proposed.

Experimental

As the method of the measurements was quite identical to that for *p*-dichlorobenzene and *p*-dichlorobenzene-d_4 which has been previously reported[3], any description of the measuring techniques is entirely omitted in this paper. The spectra obtained in the sodium chloride region using the high temperature long path cell were measured at different temperatures below 70°C for trichlorobenzenes and below 90°C for tetrachlorobenzenes, in order to observe the shapes of the bands of various intensities as accurately as possible. When the 85 mm. high temperature cell was used, the measurements were carried out at 240°C for trichlorobenzene and at 280°C for tetrachlorobenzene. The spectra in the far infrared region were measured in a solid state (Nujol mull) at room temperature using the grating spectrophotometer installed at the laboratory of Professor Yoshinaga of Osaka University.

Results

The far infrared absorption spectra of 1, 3, 5-trichlorobenzene and 1, 3, 5-trichlorobenzene-d_3 are shown in Fig. 1. The absorption curves are fragmental below 300 cm^{-1} because of the frequent exchanges of filters and gratings with the decreasing wave number. The spectra in the sodium chloride region measured by using the high temperature long path cell are shown in Fig. 2 for the range where the principal absorption bands appeared. In Figs. 3 and 4 the similar spectra for 1, 2, 4, 5-tetrachlorobenzene

1) S. Saëki, This Bulletin, 33, 1024 (1960).
2) S. Saëki, ibid., 34, 1552 (1961).
3) S. Saëki, ibid., 35, 326 (1962).

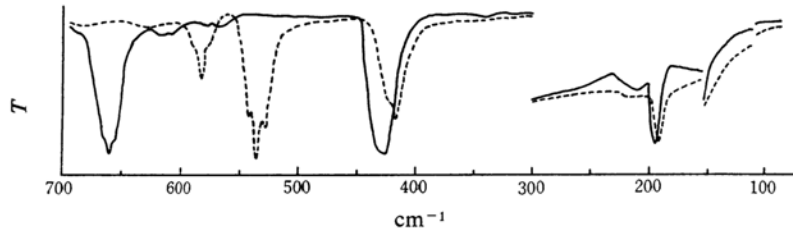

Fig. 1. Infrared absorption spectra of ordinary and deuterated 1,3,5-trichlorobenzenes.
$C_6H_3Cl_3$ ——, $C_6D_3Cl_3$ - - -

TABLE I. INFRARED ABSORPTION BANDS OF 1,3,5-TRICHLOROBENZENE

$C_6H_3Cl_3$			$C_6D_3Cl_3$		
Wave number	Intensity	Type	Wave number	Intensity	Type
1724	3				
1608	1				
1575	15		1560	20	
ca. 1520	0		1543	8	
			1524	0	
1474	5		1396	4	
1412	10		1342	20	
1384	6		1266 1262	8	
			1245	3	
			1211 1208	10	
			1147	4	
			863.2	4	
1105 1101	10		843.2 839.3	12	
1059	5				
859.9 855.4 850.7	10	∥	771.6 767.0 763.5	12	∥
813.7	15		799.2	20	
795.1	6		591.0 583.4 577.4	m	∥
660.9	s	∥	542.0 535.3 527.4	s	∥
623.1	w				
571.4	w		422.8	sh w	
429.7	sb		416.7	s	
194.3	s		193.5	s	

and tetrachlorobenzene-d_2 are shown. The frequencies, the intensities and the types of the observed bands are listed in Tables I and II, in which the intensities are described by a rough visual estimation, and the types are presented only for the bands whose envelopes showed the typical features of any band type.

Comparing the absorption curves shown in Figs. 2 and 4 with those presented in the previous papers[1,2], one can easily see that the absorption bands are separated from each other

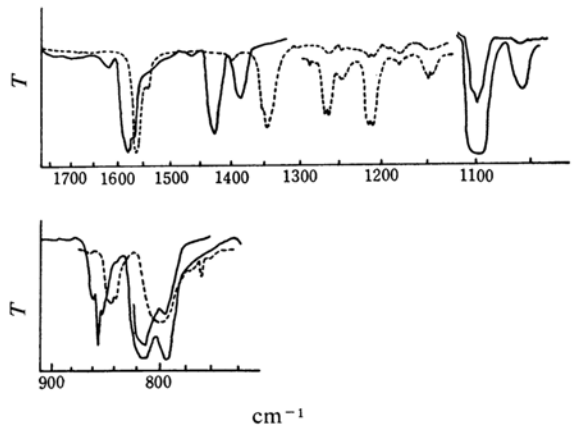

Fig. 2. Infrared absorption spectra of ordinary and deuterated 1,3,5-trichlorobenzenes.
$C_6H_3Cl_3$ ——, $C_6D_3Cl_3$ - - -

TABLE II. INFRARED ABSORPTION BANDS OF 1,2,4,5-TETRACHLOROBENZENE

$C_6H_2Cl_4$			$C_6D_2Cl_4$		
Wave number	Intensity	Type	Wave number	Intensity	Type
			1425	1	
1473	10		1396	20	A ?
1447	20	A	1355	10	A ?
1378	3				
1328	12		1307	9	A
			1243	5	A
1120	15		873.5	10	A
1071 1066	20	B	1060 1054	15	B
			743.6	1	
			738.9	2	
882.4	10	C	726.6	8	C
820.7	3				
767.2	w				
643.1	s		623.1	s	
510.2 504.2	s	B	505.9	s	
444.8 437.5	s		387.9 380.7	s	
140.4	s		140.4	s	

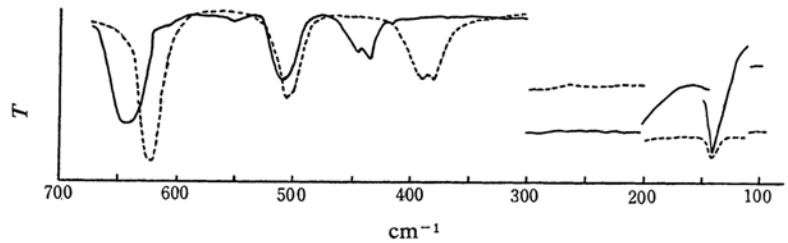

Fig. 3. Infrared absorption spectra of ordinary and deuterated 1,2,4,5-tetrachlorobenzenes.
$C_6H_2Cl_4$ ——, $C_6D_2Cl_4$ - - -

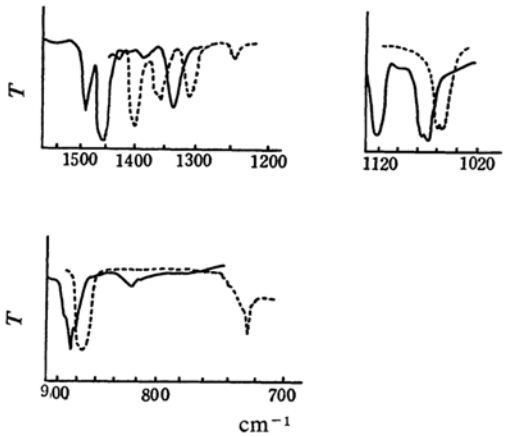

Fig. 4. Infrared absorption spectra of ordinary and deuterated 1,2,4,5-tetrachlorobenzenes.
$C_6H_2Cl_4$ ——, $C_6D_2Cl_4$ - - -

much more distinctly by the use of the high temperature long path cell, and also that the shape of each band can be much more clearly observed by means of this cell.

Band Shapes and Assignment

1, 3, 5-Trichlorobenzene and 1, 3, 5-Trichlorobenzene-d_3. — The vibrations of these molecules, which are active in infrared absorption, belong to species A_2'' or E' because of the high symmetry of the molecule, D_{3h}. Three of the ten infrared active normal vibrations are out-of-plane vibrations belonging to species A_2'', and the other seven are in-plane vibrations belonging to species E'. Furthermore, as the molecule is a symmetric top, the out-of-plane vibrations give parallel bands which show remarkable Q branches under proper resolution of the spectrometer, and the in-plane vibrations are perpendicular, showing less remarkable Q branches.

The bands which actually showed a clear Q branch in the observed spectra were those at 660.9 and 855.4 cm^{-1} of $C_6H_3Cl_3$ and those at 535.3, 583.4 and 767.0 cm^{-1} of $C_6D_3Cl_3$. Of these five bands, the last two were less intense than the first three. The three normal vibrations of species A_2'' are the out-of-plane vibrations of C–H (or C–D), C–Cl and the ring. Therefore, the pair of bands with the highest frequencies, that is, the bands observed at 855.4 and 767.0 cm^{-1}, were assigned to the out-of-plane bending vibrations of C–H and C–D bonds respectively, and the second highest pair of bands, at 660.9 and 535.3 cm^{-1}, were assigned to the ring deformation vibration. To the C–Cl out-of-plane bending vibrations, the pair of bands at 194.3 and 193.5 cm^{-1} which were observed in the grating region were quite confidently assigned. In the above correspondences between the bands of each species of the substance, the bands at 767.0 cm^{-1} of the deuterated substance seems to be too weak to correspond to the band at 855.4 cm^{-1} of the ordinary substance, even if the difference in the concentrations of the sample solutions is taken into account. The explanation for this fact will be seen later. The band at 583 cm^{-1} of the deuterated substance was ruled out from the fundamental bands because it has a relatively low intensity and did not satisfy the product rule.

There is a very noticeable fact in the abovementioned assignment of the parallel vibrations. According to the above assignment, the band at 855.4 cm^{-1} of the ordinary substance (the out-of-plane bending vibration of the C–H bonds) should show a large frequency shift on the deuteration, and the frequency shift of the band at 660.9 cm^{-1} (the out-of-plane deformation vibration of the ring) should be much smaller than that. But, in practice, the behavior of these bands on the deuteration was quite contrary. While the band at 855.4 cm^{-1} of the ordinary substance shifted to 767.0 cm^{-1} on the deuteration, showing only a 10% decrease in frequency, the band at 660.9 cm^{-1} shifted to the band at 535.3 cm^{-1} on the deuteration, showing a 19% decrease in frequency. However, these experimental results, which appeared to be inconsistent with the assignment, can be explained as follows. As the out-of-plane C–H bending vibration of this molecule has been observed at 855 cm^{-1}, that

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

Wave number $C_6H_3Cl_3$	Wave number $C_6D_3Cl_3$	Assignment	Mode
1724		?	
1608		$\nu_{13}(e')+\nu_{20}(e'')$	
1575	1560	$\nu_{12}(e')$	Ring stretching
	1543	$\nu_{14}(e')+\nu_{18}(e'')$	
1520		$\nu_{14}(e')+\nu_{16}(e')$	
1474		$\nu_4(a_1')+\nu_{14}(e')$	
	1396	?	
1412	1342	$\nu_{13}(e')$	Ring stretching
1384	1264	$\nu_8(a_2'')+\nu_{19}(e'')$	
	1245	$\nu_9(a_2'')+\nu_{18}(e'')$	
	1209	$\nu_4(a_1')+\nu_{14}(e')$ or $\nu_{15}(e')+\nu_{16}(e')$	
	1147	$\nu_4(a_1')+\nu_8(a_2'')$	
	863.2	?	
1103	841.3	$\nu_{14}(e')$	C-H or C-D in-plane bending
1059		$\nu_{19}(e'')\times 2$	
855.4	767.0	$\nu_8(a_2'')$	C-H out-of-plane bending / Ring out-of-plane deformation
813.7	799.2	$\nu_{15}(e')$	C-Cl stretching
795.1		$\nu_4(a_1')+\nu_{16}(e')$	
	583.4*	$\nu_4(a_1')+\nu_{10}(a_2'')$ or $\nu_{16}(e')+\nu_{20}(e'')$	
660.9	535.3	$\nu_9(a_2'')$	Ring out-of-plane deformation / C-D out-of-plane bending
623.1		$\nu_{16}(e')+\nu_{20}(e'')$	
571.4		$\nu_4(a_1')+\nu_{10}(a_2'')$	
429.7	416.7	$\nu_{16}(e')$	Ring in-plane deformation
194.3	193.5	$\nu_{10}(a_2'')$	C-Cl out-of-plane bending

* Note in proof: This band may be more confidently assigned to the second overtone of the fundamental at 193.5 cm^{-1} (a_2'', C-Cl out-of-plane bending) which borrows the intensity from the foundamental at 535.3 cm^{-1} of species A_2''. In the case of ordinary trichlorobenzene, this overtone is not observed, because it has no fundamental of the same species in its vicinity.

of the C-D bands can be expected to appear in the vicinity of 650 cm^{-1}. Consequently, in the case of the deuterated molecule, an extreme coupling must be expected between the C-D bending vibration and the ring deformation vibration, and, provided that the proper frequency of the ring deformation vibration exists a little higher than that of a C-D bending vibration, the coupling might push up the former and push down the latter by many wave numbers. The apparently contradictory phenomenon mentioned above is probably brought about in such a way. One can easily see from this consideration that the mode of these vibrations of the deuterated molecule are not simple but an almost fifty-fifty mixture of the C-D bending and the ring deformation modes, and, from the consideration of the intensity shown below, it might be better to assign the band of higher frequency to the ring deformation vibration and the lower to the C-D bending vibration.

This supposition for the vibrational modes appeared to be justified by the inversion of the relative intensities of these bands on the deuteration, that is, the fact that while the band at 855.4 cm^{-1} is stronger than the band at 660.9 cm^{-1} in the case of an ordinary molecule, the band at 767.0 cm^{-1} is weaker than the band at 535.3 cm^{-1} in the case of a deuterated molecule.

Among the seven vibrations belonging to species E', the C-H (or C-D) stretching vibration (ν_{11}) was not observed, being beyond the high frequency limit of the region of this investigation*, and the C-Cl in-plane bending vibration (ν_{17}) was not found in the observed spectra, in spite of being expected to appear between 200 and 300 cm^{-1}**.

* It has already been reported in our previous paper[1] that this vibration was found at 3089 and 2310 cm^{-1} for the ordinary and deuterated 1,3,5-trichlorobenzene respectively.

** In the grating region, only one absorption band was found and was assigned to ν_{10} of the species A_2'', as has already been mentioned.

The other five vibrations are two stretching vibrations of the ring (ν_{12}, ν_{13}), an in-plane bending vibration of the C–H (or C–D) bonds (ν_{14}), a stretching vibration of the C–Cl bonds (ν_{15}) and an in-plane deformation vibration of the ring (ν_{16}). The observed remarkable absorption bands were unambiguously assigned to these vibrations by taking account of the observed frequencies and intensities, as shown in Table III.

The next step to be done is the applying of the product rule to the assignment determined above. In species E′, although the C–Cl bending vibration (ν_{17}) was observed for neither species of the substance, the ratio of the frequencies of such a low frequency vibration as ν_{17} can well be assumed to be nearly 1. With this assumption, the ratio of the products of the frequencies for each species of the substace was calculated to be 1.956 for species E′. The ratio calculated for species A_2'' was 1.383. As the theoretical values are 1.972 and 1.402 for species E′ and A_2'' respectively, the agreement between the observed and theoretical values are quite satisfactory, verifying the correctness of the proposed assignment.

On the basis of the assignment previously determined for the Raman active normal vibrations[4] and the above-mentioned assignment for the infrared active normal vibrations, the assignment of overtone and combination bands observed in the infrared absorption spectra could be determined. However, since there are three normal vibrations belonging to species A_2' for which there is no way of knowing the frequencies because of the inactivity in both of the Raman effect and infrared absorption, there might unavoidably be some overtone and combination bands for which the determination of assignment is impossible.

Among the observed overtone and combination bands, the three bands of ordinary trichlorobenzene at 1384, 1059 and 795.1 cm^{-1} have unusually high intensities. As an explanation of this fact could be found only in the Fermi resonances with the fundamental bands at 1412, 1103 and 813.7 cm^{-1} respectively, and as all of these fundamental bands belong to species E′, the species of these overtone or combination vibrations should also be E′. On the contrary, the fact that the combination band at 1543 cm^{-1} of the deuterated substance has a relatively low intensity in spite of the close existence of the fundamental band at 1560 cm^{-1} (E′), indicated that the species of this combination band should be A_2''. By taking into account such facts, as well as the frequencies and activities, the assignment of overtone and combination bands was determined as shown in Table III.

1, 2, 4, 5-Tetrachlorobenzene and 1, 2, 4, 5-Tetrachlorobenzene-d_2. — As the symmetry of these molecules is V_h, as in the case of *p*-dichlorobenzene, thirteen of thirty normal vibrations are active in infrared absorption; five of them belong to species B_{1u} (in-plane), five belong to species B_{2u} (in-plane), and three belong to species B_{3u} (out-of-plane)*.

This molecule is an asymmetric top, three moments of the inertia of which are as follows (in physical atomic weight·A^2):

	$C_6H_2Cl_4$	$C_6D_2Cl_4$
I_x:	1470	1482
I_y:	412	423
I_z:	1059	1059

Accordingly, the vibrations belonging to species B_{1u}, B_{2u} and B_{3u} give type B, A and C bands respectively.

The three out-of-plane normal vibrations belonging to species B_{3u} are the C–H (or C–D) and C–Cl bending vibrations and the deformation vibration of the ring. The C–Cl bending vibration appeared at 140.4 cm^{-1} in the grating region. However, since the spectra were measured in a solid state in this region, observation of the band envelope of this vibration was impossible. For the other two vibrations, the observation of the band envelopes was as had been expected. But, in practice, only one band of each substance, that is, the band at 882.4 cm^{-1} of $C_6H_2Cl_4$ and the band at 726.6 cm^{-1} of $C_6D_2Cl_4$, showed the remarkable Q branch which is the feature of the type C band. This pair of bands was assigned to the out-of-plane C–H (or C–D) bending vibration by considering their frequencies. The out-of-plane deformation vibration of the ring was expected to appear between 400 and 600 cm^{-1}. In this region of frequency, three remarkable bands were observed for each substance, that is, the bands at 643.1, 506 and 441 cm^{-1} of ordinary tetrachlorobenzene, and at 623.1, 505.9 and 384 cm^{-1} of the deuterated substance. All of these three pairs of bands have remarkable intensities, but their band envelopes were not clearly observed. Therefore, it was impossible to determine which of these three pairs of bands is to be assigned to the out-of-plane deformation vibration of the ring. However, as the assignment of the other two pairs of normal vibrations of species B_{3u} had already been

4) S. Saëki, This Bulletin, 34, 1851 (1961).

* In the case of the point group V_h, the notation of the species depends on which of the three principal axes is taken for the x axis, which for the y, and which for the z. In this case, the axis perpendicular to the molecular plane is taken as the x axis, the axis combining two hydrogen (or deuterium) atoms as the z, and the third axis perpendicular to the first two as the y axis.

TABLE IV. THE ASSIGNMENT OF INFRARED ABSORPTION BANDS OF 1,2,4,5-TETRACHLOROBENZENE

Wave number		Assignment	Mode
$C_6H_2Cl_4$	$C_6D_2Cl_4$		
	1425	?	
1473	1396	$\nu_{11}(b_{1u})$	Ring stretching
1447	1355	$\nu_{18}(b_{2u})$	Ring stretching
1378		$\nu_{12}(b_{1u})+\nu_{16}(b_{2g})$	
1328	1307	$\nu_{19}(b_{2u})$	Ring stretching
	1243	$\nu_{12}(b_{1u})+\nu_{16}(b_{2g})$	
1120	873.5	$\nu_{20}(b_{2u})$	C-H or C-D in-plane bending
1069	1057	$\nu_{12}(b_{1u})$	C-Cl stretching
882.4	726.6	$\nu_{28}(b_{3u})$	C-H or C-D out-of-plane bending
820.7		$\nu_{13}(b_{1u})+\nu_{16}(b_{2g})$	
767.2		?	
	743.6	?	
	738.9	?	
643.1	623.1	$\nu_{21}(b_{2u})$	C-Cl stretching
507.2	505.9	$\nu_{13}(b_{1u})$	Ring in-plane deformation
441.2	384.3	$\nu_{29}(b_{3u})$	Ring out-of-plane deformation
140.4	140.4	$\nu_{30}(b_{3u})$	C-Cl out-of-plane bending

determined, the assignment of the third pair could be determined by applying the product rule. Among the observed three pairs of bands, the pair of 441.2 cm^{-1} (of $C_6H_2Cl_4$) and 384.3 cm^{-1} (of $C_6D_2Cl_4$) proved best to satisfy the product rule, and so was assigned to the ring deformation normal vibration, ν_{29}.

The in-plane vibrations of these molecules belong to species B_{1u} or B_{2u}, as was mentioned above. There exist three stretching vibrations of the benzene ring, one of which belongs to species B_{1u}, while the other two belong to species B_{2u}. In the observed spectra, three intense bands were actually found between 1300 and 1500 cm^{-1} for each substance (see Fig. 4 and Table II). Accordingly, these three pairs could apparently be assigned to $\nu_{11}(b_{1u})$, $\nu_{18}(b_{2u})$ and $\nu_{19}(b_{2u})$, and, by analogy to the case of *p*-dichlorobenzene[3], the pair of bands at 1473 and 1396 cm^{-1} was assigned to ν_{11} (b_{1u}) and the other two pairs were assigned to $\nu_{18}(b_{2u})$ and $\nu_{19}(b_{2u})$.

To the C–H and C–D in-plane bending vibration (ν_{20}'s), the bands at 1120 and 873.5 cm^{-1} were assigned respectively. Although, considering the frequency only, the band observed at 1069 cm^{-1} appears to correspond to the C–H in-plane bending vibration better than the band at 1120 cm^{-1}, this pairing must be ruled out, for the band at 1069 cm^{-1} was found to be a type B band showing two clear absorption maxima, as has been shown in Fig. 4 and Table II. As the spectrum of the deuterated substance also shows a type B band at 1057 cm^{-1} which apparently corresponds to the band in question at 1069 cm^{-1} of the ordinary substance, this pair of bands must be considered to originate in vibrations belonging to species B_{1u}. Furthermore, apart from the band envelope, this pair of bands could not be taken for ν_{20} because of the small frequency shift (12 cm^{-1}) on duteration. Thus it was determined that the pair of bands at 1120 and 873.5 cm^{-1} was to be assigned to the C–H (or C–D) in-plane bending vibration, ν_{20}.

The above-mentioned pair of bands at 1069 and 1057 cm^{-1} was assigned to the C–Cl stretching vibrations of species B_{1u}, ν_{13}'s. To the C–Cl stretching vibrations of species B_{2u} (ν_{21}'s), the pair of bands observed at 643.1 623.1 cm^{-1} was assigned. Though the frequency difference between these two pairs of C–Cl stretching vibrations appears to be too large, it is really quite probable considering that the C–Cl stretching vibration has a strong tendency to couple with other vibrations, that is, for example, with a ring deformation vibration or a C–H (or C–D) bending vibration.

The last pair of the observed strong bands, at 507.2 and 505.9 cm^{-1}, was assigned to the deformation vibration of the ring belonging to species B_{1u}.

The remaining two normal vibrations are C–Cl in-plane bending vibrations belonging to species B_{1u} and B_{2u} respectively. Although they were expected to appear around 200 cm^{-1}, no absorption band except the above-mentioned one at 140.4 cm^{-1} was observed in the grating region.

The next step is to prove the assignment determined above by making use of the product rule. The theoretical values of the ratios of the products of frequencies for both species of substance are 1.407 for all three vibrational

species (B_{1u}, B_{2u} and B_{3u}). In the proposed assignment, the frequencies of two C–Cl in-plane bending vibrations of species B_{1u} and B_{2u} are wanted. However, as the ratios of these frequencies could be assumed to be 1 without any serious error, the ratio of the products of the observed frequencies could be calculated based on the proposed assignment as follows:

Species B_{1u}:	1.439
Species B_{2u}:	1.436
Species B_{3u}:	1.394

The calculated values for species B_{1u} and B_{2u} exceeds the theoretical values by about 2%, while that for species B_{3u} is lower than the theoretical value by 1%. The accordances can be said to be satisfactory enough to show the correctness of the assignment.

On the basis of the assignment of the infrared active normal vibrations determined above and the assignment of the Raman active normal vibrations reported previously[5], some of the combination bands observed in the infrared absorption spectra could well be explained. However, since this molecule has two normal vibrations (the out-of-plane vibrations of the C–Cl bonds and the ring) belonging to species A_u which are inactive in both the Raman effect and infrared absorption, and since, even among active normal vibrations, some had not been observed, there were necessarily some combination bands which could not be explained. The assignment of the combination bands is shown in Table IV, together with the assignment of the fundamental bands.

5) S. Saëki, This Bulletin, 34, 1858 (1961).

Summary

The infrared absorption spectra of 1, 3, 5-trichlorobenzene, 1,3,5-trichlorobenzene-d_3, 1,2,4,5-tetrachlorobenzene and 1, 2, 4, 5-tetrachlorobenzene-d_2 were observed in a gaseous state from 700 to 300 cm^{-1} with a cesium bromide prism and in a solid state from 300 to 100 cm^{-1} using a grating spectrometer. Furthermore, the spectra in the sodium chloride region were carefully observed in the ranges where the main absorption bands appear, using a long path (720 cm.) high temperature cell. The obtained accurate frequencies and envelopes of the absorption bands have been reported on.

On the basis of these results, the assignments of the infrared active normal vibrations of these substances have been determined and checked by the product rule.

The assignments of the overtone and combination bands have also been determined using the assigned frequencies and species of infrared active and Raman active fundamental vibrations.

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Government Chemical Industrial Research Institute, Tokyo
Shibuya-ku, Tokyo