Raman Spectra of 1, 2, 4, 5-Tetrachlorobenzene and 1, 2, 4, 5-Tetrachlorobenzene-d_2

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Concerning the infrared absorption spectra of 1, 2, 4, 5-tetrachlorobenzene and 1, 2, 4, 5-tetrachlorobenzene-d_2, a report⁽¹⁾ was previously presented by the author in which tentative assigments were proposed for the observed infrared absorption bands. In this paper the Raman spectra of these substances will be presented, and the assignment of these observed lines will be discussed.

The Raman spectra of ordinary 1,2,4,5-tetrachlorobenzene have already been reported on by several investigators⁽²⁾. But all of their papers have been concerned with a group of similarly substituted benzenes, 1, 2, 4, 5-tetrachlorobenzene was treated simply as a member of this group. Consequently, the molecular spectra of 1, 2, 4, 5-tetrachlorobenzene itself do not appear to have been fully studied. In this paper, instead of adopting such an inductive method, the Raman spectrum was observed for deuterated as well as for ordinary 1, 2, 4, 5-tetrachlorobenzene, and the assignment was carried out by comparing the Raman spectra for both species of the substance.

Since the molecule contains four chlorine atoms, the normal vibrations were expected to be concentrated in a lower frequency region compared with those of *p*-dichlorobenzene and 1, 3, 5-trichlorobenzene, which have been studied in previous papers⁽³⁻⁶⁾. As the observation of low frequency vibrations is much easier in Raman effect than in infrared spectroscopy, the product rule can be applied more completely to Raman lines. However, since a Raman line belonging to a species other than the totally symmetric one generally has a relatively low intensity and can often escape observation, this might become a new obstacle for the assignment.

Experimental and Results

Ordinary commercial 1, 2, 4, 5-tetrachlorobenzene of extra pure grade was recrystallized from ethanol three times, and then further purified by sublimation.

The deuterated substance was prepared in the following way: 1, 2, 4, 5-tetrachlorobenzene was stirred with deuterated sulfuric acid for eight hours at 150°C. The reaction mixture was then poured on ice and the precipitate filtered off and dried. The degree of substitution was checked by the infrared absorption spectrum after each substitution reaction, and the reaction was repeated until the strongest absorption band of C_6HDCl_4 could hardly be recognized. The obtained $C_6D_2Cl_4$ was purified in the same way as that of ordinary tetrachlorobenzene.

The Raman spectra were measured by using a Cary model 81 automatic recording spectrophotometer, and the qualitative depolarization ratios were measured by the two-exposure method, using polaroid cylinders.

The measurements were carried out for the solutions in carbon tetrachloride and in benzene.

Although the Raman spectra of *p*-dichlorobenzene and 1, 3, 5-trichlorobenzene were measured for the solutions in methanol and carbon tetrachloride⁽⁵,⁶⁾, the solubility of 1, 2, 4, 5-tetrachlorobenzene in

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1) S. Saëki, This Bulletin, 34, 1552 (1961).

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

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

4) S. Saëki, ibid., 33, 1024 (1960).

5) S. Saëki, ibid., 34, 1658 (1961).

6) S. Saëki, ibid., 34, 1851 (1961).

methanol is so low that the spectra could not be measured in methanol solutions. Since the solubility of chlorobenzene decreases with the increasing number of chlorine atoms contained in the molecule, the concentrations of the sample solutions were not very high in this case. In the carbon tetrachloride solution, about 0.7 g. solute was dissolved in 5 ml. of solvent, while in the benzene solution about 0.6 g. solute was dissolved in 5 ml. of solvent. Irrespective of these low concentrations, the solute was not entirely dissolved at room temperature, and it was necessary to keep the Raman tube in the lamp compartment for almost an hour in order to dissolve the entire solute*.

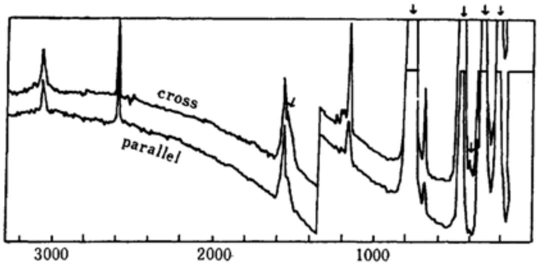

Fig. 1. Raman spectra of 1,2,4,5-tetrachlorobenzene (0.7 g. in 5 cc. carbon tetrachloride).

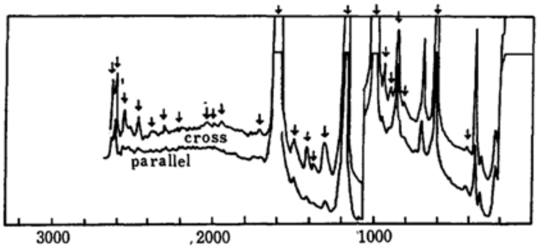

Fig. 2. Raman spectra of 1,2,4,5-tetrachlorobenzene (0.6 g. in 5 cc. benzene).

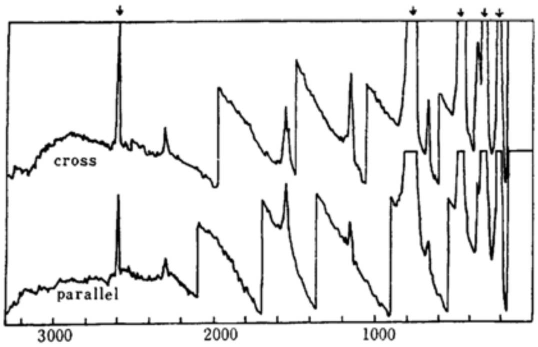

Fig. 3. Raman spectra of 1,2,4,5-tetrachlorobenzene-d_2 (0.5 g. in 4 cc. carbon tetrachloride).

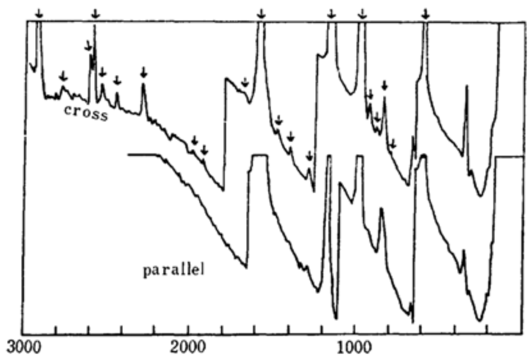

Fig. 4. Raman spectra of 1,2,4,5-tetrachlorobenzene-d_2 (0.6 g. in 5 cc. benzene).

TABLE I. RAMAN SPECTRUM OF 1,2,4,5-TETRACHLOROBENZENE

Carbon tetrachloride solution			Benzene solution		
	Intensity			Intensity	
$\tilde{\nu}$, cm^{-1}	Cross	Parallel	$\tilde{\nu}$, cm^{-1}	Cross	Parallel
			184	sh 1	sh 1
			226	16	17
			314	10	12
350	>70	sh 22	352	84	38
			467	1	–
			509	2	2
ca. 570	2	–	554	1	–
685	50	18	685	53	22
1162	72	27			
1190	7	6			
1206	10	5			
1236	3	3			
ca. 1535	+	–			
1567	33	35			
2502	6	3			
3075	25	17			
3137	4	–			

TABLE II. RAMAN SPECTRUM OF 1,2,4,5-TETRACHLOROBENZENE-d_2

Carbon tetrachloride solution			Benzene solution		
	Intensity			Intensity	
$\tilde{\nu}$, cm^{-1}	Cross	Parallel	$\tilde{\nu}$, cm^{-1}	Cross	Parallel
			184	sh 2	sh 4
			215	sh 5	sh 7
			315	6	7
351	63	sh 20 ?	351	49	22
667	41	16	665	34	14
			956	sh 10	
1155	54	21			
1180	6	5			
1208	4	+			
1410	2 ?	–			
1418	7	2			
1520	1 ?	sh +			
1552	44	45			
1675	3 ?	–			
2301	17	13			
ca. 2500	6	+			

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* The temperature was 36°C in the lamp compartment.

As the concentrations of the solutions were low, a relatively high gain was required for the measurements; consequently, the signal to noise ratio in the obtained spectra was about 25, a rather low value for this spectrometer. The obtained Raman spectra are shown in Figs. 1—4, where the noises could not be well represented because of the small sizes of the figures. The base line of each spectrum, especially of the spectra of deuterated substance, rose towards the higher frequency limit of the spectrum. This was probably due to a slight amount of resinous impurity, which was unavoidable in this case. The rapid rising of the base line made necessary its resetting at several frequencies, but it produced no obstruction to the measurement of the frequencies of Raman lines.

In the figures, the Raman lines marked with small arrows are those of the solvent or of the mercury arc lamp.

The observed Raman lines are listed in Tables I and II. In the tables, the intensities are simply represented by the heights of lines measured by the scale on the chart.

Assignment

Since the 1, 2, 4, 5-tetrachlorobenzene molecule has the symmetry V_h, as does the *p*-dichlorobenzene molecule, fifteen of thirty normal vibrations are active to the Raman effect. Also, as this molecule has a center of symmetry, there is no vibration which is active in both the Raman effect and infrared absorption, according to the mutual exclusion law. The fifteen Raman active normal vibrations are classified as six vibrations belonging to species A_g (in-plane), five to species B_{3g} (in-plane), one to species B_{1g} (out-of-plane), and three to species B_{2g} (out-of-plane)*. These normal vibrations and their modes are shown in Table III.

TABLE III. SPECIES AND MODES OF NORMAL VIBRATIONS OF 1,2,4,5-TETRACHLOROBENZENE

Species	No.	Mode
A_g	ν_1	C-H or C-D stretching
	ν_2	Ring stretching
	ν_3	Ring stretching
	ν_4	C-Cl stretching
	ν_5	Ring deformation
	ν_6	C-Cl in-plane bending
B_{1g}	ν_9	C-Cl out-of-plane bending
B_{2g}	ν_{15}	C-H or C-D out-of-plane bending
	ν_{16}	Ring out-of-plane deformation
	ν_{17}	C-Cl out-of-plane bending
B_{3g}	ν_{23}	Ring stretching
	ν_{24}	C-H or C-D in-plane bending
	ν_{25}	C-Cl stretching
	ν_{26}	Ring in-plane deformation
	ν_{27}	C-Cl in-plane bending

Sixteen Raman lines were observed for ordinary as well as for deuterated 1, 2, 4, 5-tetrachlorobenzene, but, considering their frequencies, some of them apparently do not correspond to normal vibrations. Therefore, it seems that some of the Raman active normal vibrations were not observed on account of very low frequencies or intensities.

1, 2, 4, 5-Tetrachlorobenzene. — *Species A_g.* — The six normal vibrations belonging to species A_g are seen in Table III. In the spectra obtained, the polarized and strong lines were observed in the regions expected from their modes, except for ν_2 and ν_6 (see Figs. 1 and 2), and the following assignment was unambiguously decided upon: ν_1: 3075 cm^{-1}, ν_3: 1162 cm^{-1}, ν_4: 685 cm^{-1} and ν_5: 350 cm^{-1}. Considering the high intensities and low depolarization ratios of these lines, no point of discussion exists in the above assignment.

In the region around 1500 cm^{-1} where the ring stretching vibration was expected to appear, a remarkable line was observed at 1567 cm^{-1}. However, the large depolarization ratio of this line clearly showed itself to correspond to the ring stretching vibration of species B_{3g}. In addition to this line, a much weaker line was with difficulty observed at 1535 cm^{-1} only in the carbon tetrachloride solution. As this line was observed as a shoulder of the Raman line of the solvent at 1550 cm^{-1} only in the spectrum excited by perpendicularly polarized light, its accurate frequency was difficult to measure. However, it was clear that this was a polarized line, since it entirely disappeared when excited by parallelly polarized light.

It might be indeed unusual for a line belonging to species A_g to show such a weak intensity, but since no other polarized line was found in this region, this line had to be considered to correspond to the totally symmetric ring stretching vibration.

As for the last vibration of species A_g, ν_6, the in-plane bending vibration of the C-Cl bonds, two weak lines were observed near 200 cm^{-1}, one at 226 cm^{-1} and the other at 184 cm^{-1}. In the carbon tetrachloride solution, these lines were masked by a strong line of the solvent, but in the benzene solution they were observed as a shoulder of the exciting line. However, neither of these lines could be assigned to ν_6, for both of them had considerable depolarization ratios. Therefore, it was concluded that ν_6 might have a lower frequency and be completely masked by the Rayleigh line. By estimating from the width of the Rayleigh line, the frequency should be lower than 175 cm^{-1}.

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* The x-axis was taken along the two-fold axis perpendicular to the molecular plane, and the z axis was taken along the line combining the two hydrogen atoms.

Species B_{1g}.—As is seen in Table III, the only vibration belonging to species B_{1g} is the out-of-plane bending vibration of C–Cl bonds, ν_9. As there are four Raman active bending vibrations of C–Cl bonds, that is, ν_6, ν_9, ν_{17} and ν_{27}, it is very difficult to determine the assignment of the two observed lines at 184 and 226 cm^{-1}. However, these lines were shifted to 184 and 215 cm^{-1} respectively, by the deuteration; this fact suggests that the line at 226 cm^{-1} of ordinary tetrachlorobenzene could not correspond to ν_9, which belongs to species B_{1g}, for the product rule requires that the ratio of the ν_9's of ordinary and deuterated tetrachlorobenzene be 1. Consequently, the conclusion was drawn that the vibration ν_9 corresponds to the line at 184 cm^{-1} or lies in the unobservable low frequency region.

Species B_{2g}.—Although the out-of-plane bending vibration of C–H bonds was expected to appear in the region from 800 to 1000 cm^{-1}, no Raman line was observed in this region, as is seen in Table I. Since the Raman active out-of-plane vibrations of C–H bonds were not observed in the spectrum of *p*-dichloro- and 1, 3, 5-trichlorobenzene, as was reported in the previous papers[2,3], it appeared to be unobservable, in this case also on account of its low intensity.

To the out-of-plane deformation vibration of the ring, ν_{16}, the line at 314 cm^{-1} could be assigned. However, since there is another ring deformation vibration belonging to species B_{3g} (ν_{26}), it seemed also possible to assign the line at 314 cm^{-1} to it. However, this latter possibility must be ruled out for a reason which will be mentioned later.

As for the out-of-plane bending vibration of C–Cl bonds, ν_{17}, it is possibly unobserved. However, provided that it were observed in the spectra, the line at 184 cm^{-1} or 226 cm^{-1} might be regarded as the corresponding line.

Species B_{3g}.—As the stretching vibration of the benzene ring, ν_{23}, was expected to appear at about 1500 cm^{-1}, it was clear that the above-mentioned remarkable line at 1567 cm^{-1} corresponded to this vibration. This assignment is consistent with the observed qualitative depolarization ratio.

In the region 1000$\sim$1200 cm^{-1} where the in-plane bending vibration of C–H bonds, ν_{24}, was expected to appear, two lines of medium intensity were observed at 1190 and 1206 cm^{-1}. Since the latter line was polarized, as is shown in Table I, the former was assigned to ν_{24}.

Although the C–Cl stretching vibration, ν_{25}, was expected to appear in the vicinity of 700 cm^{-1}, no line was observed in this region except the strong line at 685 cm^{-1} which had already been assigned to ν_4. But if lines are looked for over a wider frequency region, two weak lines are found at 509 and 554 cm^{-1}. Although the former was a little stronger than the latter, the latter combining with the line at 685 cm^{-1} (a_g), gave a combination line at 1236 cm^{-1} which could not be explained as any other combination. Therefore, the line at 554 cm^{-1} was assigned to ν_{25}.

To the in-plane deformation vibration of the benzene ring, ν_{26}, either the line at 467 cm^{-1} or at 509 cm^{-1} might be assigned. It appeared to be a little strained to assign the line at 314 cm^{-1} to ν_{26}, for ν_{26} probably has a frequency higher than 351 cm^{-1}, which was the frequency of the totally symmetric in-plane deformation vibration of the benzene ring. However, since the lines at 467 and 509 cm^{-1} were both very weak, it was difficult to determine which was to be assigned to ν_{26}. If one was taken for the fundamental, the other had to be explained as an overtone or a combination. However, if necessary, both of them could be explained as an overtone or a combination, that is, $467=226$ $(b_{2g})\times2$ and $509=184$ (b_{1g} or b_{3g}) $+314$ (b_{2g}).

However, there was another, more plausible explanation for the line at 509 cm^{-1}. As was reported in our previous paper[4], a strong absorption band was observed at 507 cm^{-1} in the infrared absorption spectrum of this substance. Taking account of this fact, the Raman line at 509 cm^{-1} was explained as the forbidden line which was brought out by the breakdown of the rule of mutual exclusion in solution. Since it is quite probable that the rule of mutual exclusion breaks down in the condensed system, the above explanation appeared to be the most plausible. Accordingly, the line at 467 cm^{-1} was assigned to ν_{26}.

For the C–Cl in-plane bending vibration, ν_{27}, there were two lines to be assigned, that is, the lines at 184 cm^{-1} and at 226 cm^{-1}. As has been mentioned above, it is impossible to determine definitely the assignment of these lines. It might as possibly be that ν_{27} was not observed as that ν_{27} corresponds to one of these two lines.

Overtones and Combinations.—There were five observed lines which were not assigned to the fundamentals, that is, the lines at 3137, 2502, 1236, 1206 and 509 cm^{-1}. The lines at 1236 and 509 cm^{-1} have already been explained as 685 (a_g) $+$ 554 (b_{3g}) and as a forbidden line which was brought out by the breakdown of the mutual exclusion law respectively.

The line at 3137 cm^{-1} was clearly explained as 1567 $(b_{3g})\times2$.

Although the lines at 2502 and 1206 cm^{-1} were both polarized, these could be well explained neither as an overtone nor as a combination belonging to species A_g. Since these two lines were observed also in the carbon tetrachloride solution of the deuterated substance, as is shown in Table II, they should be regarded as lines due to the slight impurity contained in the solvent. Although these lines were not observed in the Raman spectrum of the pure solvent, they might quite probably appear in the spectra of sample solutions because of the extremely high gain required on the measurement of the sample solutions. Thus, these lines were removed from discussion.

1, 2, 4, 5-Tetrachlorobenzene-d$_2$.—*Species A_g.*—The line at 2301 cm^{-1} corresponded apparently to ν_1, the stretching vibration of the C–D bonds. Although the depolarization ratio of this line was observed to be unusually high*, there was no other remarkable line in its vicinity. Since there is no other Raman active stretching vibration of C–D bonds, there is no room for doubting this assignment.

A very weak line observed at 1520 cm^{-1} was assigned to ν_2, for it was apparent from the frequency and the intensity that this line corresponds to the line at 1535 cm^{-1} (ν_2) of ordinary 1, 2, 4, 5-tetrachlorobenzene.

For $\nu_3 \sim \nu_5$, the assignment could unambiguously be determined, as is shown in Table IV. No line was observed for ν_6. This might be because its frequency was too low to be observed, as in the case of ordinary substance. A combination line was observed at 1675 cm^{-1} which could well be explained by assuming the frequency of ν_6 to be 155 cm^{-1}, as will be shown later. But, of course, this was not strong enough support for assigning 155 cm^{-1} to ν_6.

Species B_{1g}.—Only ν_9 belongs to this species. As was already mentioned, it is not certain that the frequency of this vibration is high enough to be observed. Provided that this vibration can be observed, the line at 184 cm^{-1} could be assigned to it.

Species B_{2g}.—The C–D out-of-plane bending vibration of this species, ν_{15}, was not observed as in the case of the ordinary substance.

To the deformation vibration of the ring, ν_{16}, the line at 315 cm^{-1} was assigned. Although it is impossible that the frequency of the deuterated substance is higher than that of the ordinary substance (314 cm^{-1}), this might be attributed to a slight error in the measurement of the frequency because of excessive noise.

As for ν_{17}, the line at 184 cm^{-1} might be assigned to it. However, the assignment for such C–Cl bending vibrations is not very certain for the reason which has already been stated in the case of ordinary tetrachlorobenzene.

Species B_{3g}.—The line at 1552 cm^{-1} was easily assigned to ν_{23}, the stretching vibration of the ring.

As for ν_{24}, since it was observed at 1190 cm^{-1} in the case of the ordinary substance, it was expected to appear near 1000 cm^{-1} in the deuterated substance. But in this region only a weak and diffuse line was observed at 956 cm^{-1}. Since, irrespective of its low depolarization ratio, this line could not be explained as an overtone or as a combination belonging to species A$_g$, it might be assigned to ν_{24}. It will be seen later that this assignment facilitates the explanation of some combination lines.

Although ν_{25} and ν_{26} of ordinary tetrachlorobenzene were observed at 554 and 467 cm^{-1} respectively, those of deuterated one were not observed.

As for ν_{27}, since the line at 226 cm^{-1} was assigned to it in the case of 1, 2, 4, 5-tetrachlorobenzene, the line at 215 cm^{-1} should be assigned to it in the case of deuterated substance.

Overtones and Combinations.—There were six observed lines which were not assigned to the fundamentals, that is, 1180, 1208, 1410, 1448, 1675 and 2500 cm^{-1}. Of these six, the two lines at 1208 cm^{-1} and 2500 cm^{-1} should be regarded as lines of the impurity contained in the solvent (carbon tetrachloride), as was pointed out in the previous paragraphs, and removed from discussion.

The line at 1180 cm^{-1} was explained as 956 (b$_{3g}$)+215 (b$_{2g}$). The existence of this combination line appeared to justify not only the assignment of the weak line at 956 cm^{-1} to a fundamental, but also the determination of species B$_{2g}$ for the fundamental line at 215 cm^{-1}. For, by assuming that this line corresponds to the fundamental of species B$_{3g}$ (ν_{27}), the species of the combination line at 1180 cm^{-1} should be A$_g$, while the observed depolarization ratio was relatively high. However, it should be mentioned here that the certainty of this determination of the species depends on the reliability of the measurement of the depolarization ratio.

The lines at 1410 and 1448 cm^{-1} were well explained as the overtones of the infrared active fundamentals of 719 and 725 cm^{-1} respectively. These two overtones might perhaps resonate and be shifted away from each other.

The line at 1675 cm^{-1}, with a low depolarization ratio, could not be explained as an overtone, but, provided that the frequency of the unobserved ν_6 of species A$_g$ is 155 cm^{-1}, it can be explained as a combination, 1520 (a$_g$) +155 (a$_g$).

The assignments determined above are shown in Table IV.

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* The measurement was repeated three times, and the high depolarization ratio was observed every time.

TABLE IV. THE ASSIGNMENTS OF RAMAN LINES OF ORDINARY AND DEUTERATED 1, 2, 4, 5-TETRACHLOROBENZENE

Species	No.	$\tilde{\nu}$		Mode
		$C_6H_2Cl_4$	$C_6D_2Cl_4$	
A_g	ν_1	3075	2301	C–H or C–D stretching
	ν_2	ca. 1535	1520	Ring stretching
	ν_3	1162	1155	Ring stretching
	ν_4	685	667	C–Cl stretching
	ν_5	351	351	Ring in-plane deformation
	ν_6	—	—	C–Cl in-plane bending
B_{1g}	ν_9	184 ?	184 ?	C–Cl out-of-plane bending
B_{2g}	ν_{15}	—	—	C–H or C–D out-of-plane bending
	ν_{16}	314	315	Ring out-of-plane deformation
	ν_{17}	226	215	C–Cl out-of-plane bending
B_{3g}	ν_{23}	1567	1552	Ring stretching
	ν_{24}	1190	956	C–H or C–D in-plane bending
	ν_{25}	554	—	C–Cl stretching
	ν_{26}	467	—	Ring in-plane deformation
	ν_{27}	184 ?	184 ?	C–Cl in-plane bending

Discussion

According to the product rule, the theoretical values of the product of the ratios of the frequencies for each substance are 1.414, 1, 1.393 and 1.408 for species A_g, B_{1g}, B_{2g} and B_{3g} respectively.

For species A_g, although the frequencies of ν_6's were observed for neither species of substance, these could with enough security be assumed to be nearly equal*. With this assumption, the ratio calculated from the observed frequencies for species A_g was 1.394 in good accordance with the above-mentioned theoretical value, showing the correctness of the proposed assignment.

For species B_{1g}, the assignment was determined so that the product rule might be fulfilled.

For species B_{2g}, as the bending vibrations of C–H and C–D bonds were not observed, the application of the product rule was impossible.

For species B_{3g}, the application of the product rule was also impossible because, while all normal vibrations were observed for 1, 2, 4, 5-tetrachlorobenzene (assuming that ν_{27} is 184 cm^{-1}), some of those for 1, 2, 4, 5-tetrachlorobenzene-d$_2$ were not observed.

Generally speaking, in the case of 1, 2, 4, 5-tetrachlorobenzene, it was difficult to observe Raman lines of low intensity because of its poor solubility to the solvents. Furthermore, it is impossible, because of the mutual exclusion law, to look for these unobserved normal frequencies in the infrared absorption spectrum. Consequently, for some of the normal vibrations of this substance, there was no way of knowing their frequencies; this fact prevented the application of the product rule to verify the proposed assignment for most of the species. However, the clear explanation of observed weak lines as overtones or combinations appears to suggest that the proposed assignments might be the most reliable one at present.

Summary

The Raman spectra of 1, 2, 4, 5-tetrachlorobenzene and 1, 2, 4, 5-tetrachlorobenzene-d$_2$ were measured in their dissolved states in methanol and carbon tetrachloride. The depolarization ratio of each Raman line was also observed qualitatively by the two-exposure method, using polaroid cylinders. On the basis of these experimental results, the assignment of normal vibrations was determined. The verification of the proposed assignments by means of the product rule was impossible for most of the species because of some unobserved normal vibrations. But, for species A_g, good agreement was obtained between the theoretical and observed values of the product of the frequencies for each substance, and the correctness of the assignment was thus verified.

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* The fact that the normal vibrations with low frequency were scarcely influenced by the substitution for hydrogen atoms of deuterium ones has been seen in the cases of *p*-dichlorobenzene and 1, 3, 5-trichlorobenzene (Refs. 5 and 6).