The Raman Spectra of 1,3,5-Trichlorobenzene and 1,3,5-Trichlorobenzene-d_3

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A report on the infrared absorption spectra of ordinary and deuterated 1,3,5-trichlorobenzene has been previously presented by the author[1], but the Raman spectra of these substances have not yet been studied in detail. In this paper the Raman spectra of these substances are reported on, and the assignment of the observed Raman lines is presented, including that of the overtones and combinations.

As the molecule of 1,3,5-trichlorobenzene has a high symmetry, ten pairs of degenerate vibrations are contained in its thirty normal vibrations, and twenty fundamental frequencies are expected to be observed in the molecular spectra of this substance. Of these twenty frequencies, fourteen are active to the Raman effect.

Hitherto the assignments of the normal vibrations of the various aromatic derivatives have been made by collecting a large number of data for many similarly substituted benzenes and by comparing and systematizing these data. In the present report, instead of referring to the data of other substances, the assignment is determined by taking the spectra of both ordinary and deuterated substances, by applying the product rule, and by referring to the results of qualitative measurements of the depolarization ratios.

Experimental

Commercial 1,3,5-trichlorobenzene was recrystallized from ethanol solution three times, and was then further purified by sublimation. Deuterated material was prepared by stirring the ordinary 1,3,5-trichlorobenzene with deuterated sulfuric acid for eight hours at 105°C. The reaction mixture was poured on ice and recrystallized from ethanol. The progress of substitution was checked by the infrared absorption spectrum after each substitution reaction, and the reaction was repeated until the strongest absorption band of $C_6HD_2Cl_3$ could hardly be recognized. It was found that the absorption bands of $C_6H_3Cl_3$ almost completely disappeared after the first reaction, and that three repetitions of the reaction were sufficient to complete the substitution reaction*.

The instrument used for the measurements was a Cary model 81 Raman spectrophotometer. The source was a mercury arc lamp of Toronto type; the dispersion of the grating was 4 Å/mm. at 5000 Å wavelength.

Raman spectra were taken of the solution in carbon tetrachloride (1 g. solute dissolved in 5 ml. solvent) and in methanol (0.5 g. solute dissolved in 5 ml. solvent) for both ordinary and deuterated substances. As the solubilities of the substances in methanol are not sufficiently large, it was impossible to make the concentration of both solutions equal.

The depolarization ratio was measured by surrounding the Raman tube by polaroid cylinders and by polarizing the exciting light in directions parallel and perpendicular to the axis of the Raman tube.

Results

The observed Raman spectra are shown in Figs. 1—4. In the spectrum of the methanol solution of ordinary trichlorobenzene, as the base line rose gradually with increasing frequency, it was necessary to reset the zero

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[1] S. Saëki, This Bulletin, 33, 1024 (1960).

* The substance in which a given band originated was easily known by following the intensity changes of that band with the repetition of the substitution reactions.

suppression of the amplifier at 1800 cm^{-1}. Although the cause of the shift of the base line was not found, this gave rise to no obstacle for the measurement of the frequencies of Raman lines. In the figures, the peaks pointed out by the small arrows are due to the solvents or the source lamp (D line, 2602 cm^{-1}).

The frequencies and intensities of the observed lines are listed in Tables I and II. The intensities are shown for the spectra excited by the polarized lights in both directions (cross and parallel). The scale of the intensity is simply the height of a Raman line measured on the chart. The notation "masked" in the tables means that the line was not observed in that solution, being masked by a strong Raman line of the solvent, while it was observed in the other solution. The notation "unobserved" means that the line was not observed in that solution, while it was observed

TABLE I. RAMAN SPECTRUM OF 1,3,5-TRICHLOROBENZENE

$\tilde{\nu}$ cm^{-1}	Methanol soln. intensity		$\tilde{\nu}$ cm^{-1}	Carbon tetrachloride soln. intensity		Depolarization ratio
	Cross	Parallel		Cross	Parallel	
188	–	17		Masked		
209	+	7		Masked		
373	26	9	374	42	14	p.
425	5	5		Unobserved		
	Unobserved		526	1	1	
994	57	20	994	99	35	p.
	Masked		1060	6	2	p.
1147	26	12	1146	38	15	p.
	Masked		1536	10	3	
1565	12	15	1565	21	24	dep.
	Unobserved		2150	1	—	
	Unobserved		2211	3	0	
	Unobserved		2263	3	1	
3076	17	15	3081	33	24	dep.
3130	3	0	3132	7	2	p.

TABLE II. RAMAN SPECTRUM OF 1,3,5-TRICHLOROBENZENE-d_3

$\tilde{\nu}$ cm^{-1}	Methanol soln. intensity		$\tilde{\nu}$ cm^{-1}	Carbon tetrachloride soln. intensity		Depolarization ratio
	Cross	Parallel		Cross	Parallel	
188	70	70		Masked		dep.
374	38	14	373	63	21	p.
418	10	10	417	—	13	dep.
495	5	5	492	—	sh.	
	Unobserved		711	sh.	sh.	
950	86	31	952	100	54	p.
	Masked		993	21	6	p.
	Masked		1058	4	1	
1144	18	8	1142	45	16	p.
	Masked		1337	2	2	
	Masked		1418	4	1	
	Masked		1528	+	–	
1550	25	25	1548	47	43	dep.
1767	3	2		Unobserved		
1883	4	3		Unobserved		
2027	3	3		Unobserved		
2283	—	2 sh.	2282	sh.	5	
2303	17	10	2303	41	25	
	Unobserved		2389	2	2	
	Unobserved		2537	6	3	p.
	Unobserved		3079	2	2	
	Unobserved		3094	3	2	

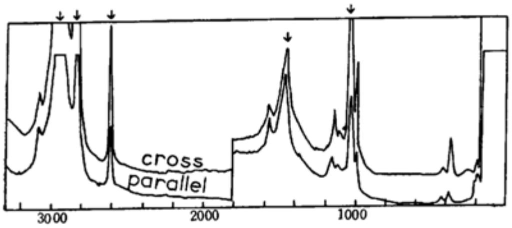

Fig. 1. Raman spectra of 1,3,5-trichlorobenzene (0.5 g. in 5 ml. methanol).

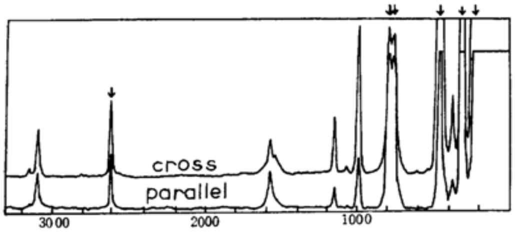

Fig. 2. Raman spectra of 1,3,5-trichlorobenzene (1 g. in 5 ml. carbon tetrachloride).

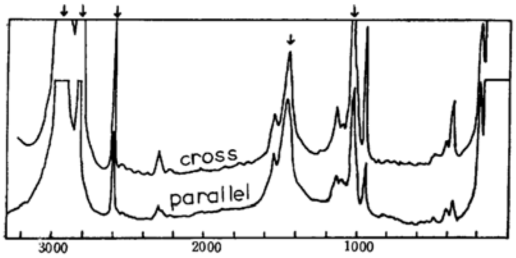

Fig. 3. Raman spectra of 1,3,5-trichlorobenzene-d_3 (0.5 g. in 5 ml. methanol).

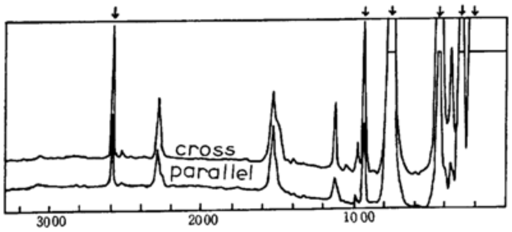

Fig. 4. Raman spectra of 1,3,5-trichlorobenzene-d_3 (1 g. in 5ml. carbon tetrachloride).

in the other solution. This inconstancy of observation might be due to the unequal concentrations or to different solvent effects in both solutions. In any case, it should be remembered that there might be a little ambiguity in such lines.

Assignment

1, 3, 5-Trichlorobenzene.—*Species* A_1'. — It is universally known that the vibrations belonging to totally symmetric species give the most intense Raman lines. In the case of 1, 3, 5-trichlorobenzene, four normal vibrations belong to species A_1', as is shown in Table III.

TABLE III. THE NORMAL MODES OF 1,3,5-TRICHLOROBENZENE

Species	Mode
A_1'	C–H or C–D stretching
	Ring breathing
	C–Cl stretching
	Ring deformation
E′	C–H or CD stretching
	Ring stretching
	Ring stretching
	C–H or C–D in-plane bending
	C–Cl stretching
	Ring in-plane deformation
	C–Cl in-plane bending
E″	C–H or C–D out-of-plane bending
	Ring out-of-plane deformation
	C–Cl out-of-plane bending

The C–H stretching vibration is expected to appear about 3000 cm^{-1}, the breathing of the benzene ring is expected to appear about 1100 cm^{-1} judging from the case of *p*-dichlorobenzene (which was reported on in our previous paper[2]), the C–Cl stretching vibration is expected to be observed in the region 700∼800 cm^{-1}, and the deformation of the ring is expected to be observed at 300∼400 cm^{-1}. From these estimations of the frequencies, four lines with remarkable intensities were selected from the observed Raman lines, that is, the lines at 3079, 1147, 994 and 374 cm^{-1}. However, as is seen in Table I, the line at 3079 cm^{-1} was not very definitely polarized. In the vicinity of this line, another line was observed at 3130 cm^{-1} which was apparently polarized. Therefore, it might be considered that this line corresponded to the C–H symmetric stretching vibration of the species A_1' and that the above-mentioned line at 3079 cm^{-1} corresponded to the C–H degenerate stretching vibration of the species E′. But this assignment conflicts with the empirical knowledge that a line belonging to a totally symmetric species is generally more intense than a line belonging to other species, and that the frequency of a degenerate stretching vibration of the C–H bonds is higher than that of a symmetric one as a general rule. Therefore, it seems to be more plausible to assign the line at 3079 cm^{-1} to both degenerate and symmetric stretching vibrations of C–H bonds. Then the line at 3130 cm^{-1} might well be explained as an overtone of the line at 1563 cm^{-1} (e′), which will be discussed later.

The other three polarized lines were easily assigned to the other three normal vibrations

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[2] S. Saëki, ibid., 34, 1658 (1961).

TABLE IV. THE ASSIGNMENTS OF RAMAN LINES OF 1,3,5-TRICHLOROBENZENE

Species	No.	$\tilde{\nu}$		Mode
		$C_6H_3Cl_3$	$C_6D_3Cl_3$	
A_1'	ν_1	3079	2303	C–H or C–D stretching
	ν_2	1147	1143	Ring breathing
	ν_3	994	951	C–Cl stretching
	ν_4	374	374	Ring deformation
E'	ν_{11}	3079	2303	C–H or C–D stretching
	ν_{12}	1565	1548	Ring stretching
	ν_{13}	(1412)	1337	Ring stretching
	ν_{14}	(1103)	(843)	C–H or C–D in-plane bending
	ν_{15}	(814)	(795)	C–Cl stretching
	ν_{16}	425	418	Ring in-plane deformation
	ν_{17}	209 or 188 ?	188 ?	C–Cl in-plane bending
E''	ν_{18}	—	711	C–H or C–D out-of-plane bending
	ν_{19}	526	494	Ring out-of-plane deformation
	ν_{20}	188 ?	188 ?	C–Cl out-of-plane bending

N. B. The values in parentheses are the wave number which were observed in the infrared spectra.

of species A_1', as is shown in Table IV. Since these lines had remarkable intensities, and no alternate lines were observed in their vicinities, the assignment was quite unambiguous. Although the frequency of the ν_3, the C–Cl stretching vibration, to which the line at 994 cm^{-1} was assigned, was a little higher than the expected value, it is nevertheless a quite probable value for such a vibration, considering the fact pointed out in our previous paper[3] that the strong coupling between the normal vibrations of such frequencies may often cause a large frequency shift from the empirically expected one. Consequently, this molecule might not have a normal vibration which could be called a C–Cl stretching vibration in its proper sense. However, at present such a vibration will be called a C–Cl stretching vibration for convenience.

Species E'. — Contrary to the easy assignment of the normal vibrations belonging to species A_1', the assignment of the observed lines to the seven normal vibrations of this species was very difficult. Since the normal vibrations belonging to species E′ are active in both the Raman and infrared spectra, the assignments would appear to be easily achieved by looking for the frequencies which were commonly observed in the Raman and infrared spectra. However, this could not be done so easily in practice. Actually only four frequencies were commonly observed in Raman and infrared spectra, that is, 3079 (3098), 1565 (1565), 1060 (1100 or 1055) and 425 (430). (in cm^{-1}. The frequencies put between parentheses are those observed in the infrared absorption spectrum in a gaseous state.) The fact that only four vibrations appeared commonly in both spectra, while seven were expected, suggested that the intensities of the Raman lines or the infrared absorption bands of the other three vibrations were to weak to be observed. But, on the other hand, the above-mentioned four lines could definitely be assigned to species E′. However, the line at 1060 cm^{-1} was somewhat questionable. Since the infrared absorption spectrum of the substance was measured in the gaseous state, the frequency of an observed band must be a little higher than that of the corresponding line observed in the Raman spectrum. From this consideration, it was not reasonable to consider the infrared absorption band at 1055 cm^{-1} to correspond to the Raman line at 1060 cm^{-1}. And the other infrared band observed at 1103 cm^{-1} seemed too high to be regarded as the corresponding band of this Raman line. Moreover, its depolarization ratio shown in Table I suggested that it belongs to species A_1'. These facts might rule out the assignment of the line at 1060 cm^{-1} to the normal vibration of species E′.

As for the other three commonly observed frequencies, the line at 3079 cm^{-1} was assigned to the degenerate stretching vibration of C–H bonds (ν_{11}), as was mentioned above, and the line at 1565 cm^{-1} was assigned to the stretching vibration of the benzene ring (ν_{12}), and the line at 425 cm^{-1} to the deformation vibration of the benzene ring (ν_{16}), all with sufficient certainty.

As for the remaining four normal vibrations

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[3] S. Saĕki, ibid., 33. 1021 (1960).

of this species (ν_{13}, ν_{14}, ν_{15} and ν_{17}), the assignment of the lines was very difficult. The stretching vibration of the benzene ring, ν_{13}, is empirically expected to appear in the frequency region 1400~1600 cm^{-1}. But, as is seen in Fig. 1 and in Table I, no Raman line was clearly observed in this region except for the line at 1565 cm^{-1}. A weak line observed only with difficulty at 1536 cm^{-1} for the solution in carbon tetrachloride was polarized and had to be considered as an overtone or a combination belonging to species A_1' (for example 1147 $(a_1')+374(a_1')$). As was already reported in our previous paper[1)], the infrared absorption spectrum of this substance showed many intense absorption bands in this region of the spectrum (1412 (s), 1398 (m), 1384 (m) and 1341 (s)). The band at 1412 cm^{-1} was especially clearly assigned to a fundamental because of its outstanding intensity. Consequently, although the Raman line was not observed, it appears to be plausible to assign this band to ν_{13}.

The C–H in-plane bending vibration was expected to appear in the vicinity of 1000 cm^{-1}, where only the above-mentioned polarized line at 1060 cm^{-1} was observed. In the infrared absorption spectrum[1)], a remarkable band was observed at 1103 cm^{-1} which showed a large frequency shift on the substitution for hydrogen atoms by deuterium atoms. Accordingly, we assigned this band to the C–H in-plane bending vibration (ν_{14}).

As for the C–Cl stretching vibration ν_{15}, since the coupling with other vibrational modes might shift its frequency from its usual value, as in the case of ν_3, it would be necessary to examine it over a relatively wide region of frequency, such as 600~1000 cm^{-1}. However, no Raman line was found in spite of taking such an extremely wide region. In the infrared absorption spectrum, two intense bands were observed, that is, bands at 855 and 814 cm^{-1}. The former was clearly identified from the shape of its envelope* to be a band which did not belong to species E$'$. Consequently, the band at 814 cm^{-1} was assigned to the C–Cl stretching vibration of species E$'$ (ν_{15}).

The C–Cl in-plane bending vibration ν_{17} was expected to be found about 200 cm^{-1}. In the neighborhood of 200 cm^{-1} a remarkable line was observed at 188 cm^{-1}, and a less intense line was observed at 209 cm^{-1}. Since there exists another Raman active bending vibration of C–Cl bonds which belongs to species E$''$ (out-of-plane), the above-mentioned two observed Raman lines apparently originate in these two C–Cl bending vibrations. However, it was difficult to find the correspondence between these lines and these normal vibrations. It was imagined, by analogy to C–H vibrations, that the line of the higher frequency (209 cm^{-1}) might probably correspond to the in-plane bending vibration, and the lower one to the out-of-plane vibration. Of course, however, this was not certain.

Species E$''$.—Three out-of-plane normal vibrations belong to this species, as listed in Table III. To the C–Cl out-of-plane bending vibration ν_{20}, as was mentioned above, either the line at 209 cm^{-1} or the line at 188 cm^{-1} —probably the latter—was to be assigned. The out-of-plane deformation vibration of the benzene ring ν_{19} was expected to be observed from 400 to 500 cm^{-1}, where a very weak and depolarized line was found at 526 cm^{-1}. Disregarding its low intensity, we assigned this line to ν_{19} for the following reasons: 1. An overtone or combination belonging to a species other than A_1' might not appear in the spectrum with an observable intensity. 2. The frequency of this line (526 cm^{-1}) could not be derived by combining or multiplying the frequencies of other fundamentals. 3. The line at 1060 cm^{-1} which was mentioned in previous paragraphs was well explained as the overtone of this line.

The C–H out-of-plane vibration ν_{18} was expected to appear in the vicinity of 800 cm^{-1}, but no corresponding Raman line was observed in this frequency region. This might be because the intensity of the line was probably too low to be observed.

Overtones and Combinations.—The overtones and combinations which have already been explained are as follows:

3132 cm^{-1} (A_1'): 1565 cm^{-1} (e')×2
1536 cm^{-1} (A_1'): 1147 cm^{-1} (a_1')
+374 cm^1 (a_1') three weak lines
1060 cm^{-1} (A_1'): 526 cm^{-1} (e'')×2

In addition to these lines three weak lines were observed between 2100 and 2300 cm^{-1}, as is shown in Table I. Though two of these lines were easily explained as

2263 cm^{-1} (A_1'): 1147 cm^{-1} (a_1')×2
2211 cm^{-1} (A_1'): 1103 cm^{-1} (e')×2

the third line observed at 2150 cm^{-1} was difficult to explain. It might probably originate. in a slight amount of impurity.

The assignment determined above is shown in Table IV.

1, 3, 5-Trichlorobenzene-d_3.—*Species A_1'.*—The strong and polarized Raman line at 2303 cm^{-1}

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* Concerning the envelopes of the infrared absorption bands of these substances, a report will be presented soon.

was easily and definitely assigned to the symmetric stretching vibration of C–D bonds. The remaining three vibrations are the breathing and the deformation of the benzene ring, and the symmetric stretching of the C–Cl bonds, all of which are not much influenced by the substitution for hydrogen atoms by deuterium atoms. Therefore, these vibrations of deuterated 1, 3, 5-trichlorobenzene were expected to be observed at frequencies only a little lower than those of the corresponding lines of 1, 3, 5-trichlorobenzene, that is, at 1147, 994 and 374 cm^{-1} respectively. In fact, as is shown in Table II, three strong and polarized lines were found at 1143, 951 and 374 cm^{-1} in the Raman spectra of deuterated trichlorobenzene. So, the lines at 1143, 951 and 374 cm^{-1} were unambiguously assigned to the ring breathing (ν_2), C–Cl stretching (ν_3) and ring deformation vibration (ν_4) respectively. In the Raman spectrum of deuterated substance, a line was observed at 993 cm^{-1} which appeared to correspond to the line at 994 cm^{-1} of ordinary substance better than the line at 951 cm^{-1} did. However, the requirement of fulfilling the product rule and the definite inferiority in the intensity of the line at 993 cm^{-1} to the line at 951 cm^{-1} ruled out the assignment of the former line to ν_3. It seemed that this line should be explained as the overtone of the line at 492 cm^{-1} (e''), which will be discussed later, just as the line at 1060 cm^{-1} was the overtone of the line at 526 cm^{-1} in the case of ordinary substance. Its unusually strong intensity might well be explained by the Fermi resonance with the line at 951 cm^{-1}.

Species E'. — As was done in the case of ordinary substance, four frequencies which were observed commonly in the Raman and infrared absorption spectra were picked up. These were 2303 (2310), 1548 (1560), 1337 (1342) and 418 (420)cm^{-1}. The line at 2303 cm^{-1} was a polarized line and was already assigned to the C–D symmetric stretching vibration of species A_1'. In the neighborhood of this line was observed another weak depolarized line at 2282 cm^{-1}. It was difficult to determine which of these two lines was to be assigned to the C–D degenerate stretching vibration. However, since the line at 2282 cm^{-1} might be explained as a combination, 952 (a_1')+1342 (e', gaseous infrared band), the line at 2303 cm^{-1} was assigned to the C–D degenerate stretching vibration, assuming that its frequency was equal to that of the symmetric vibration as in the case of trichlorobenzene.

The lines at 1548 and at 418 cm^{-1} were assigned to the stretching and deformation vibrations of the benzene ring respectively. As these line definitely corresponded to the lines at 1565 and 425 cm^{-1} of ordinary substance, there is no point of discussion in the assignment.

The line at 1337 cm^{-1}, though weak in Raman spectra, corresponded to the intense band at 1342 cm^{-1} in the infrared absorption spectrum, and it was plausibly assigned to the stretching vibration of the ring, ν_{13}, by taking account of its frequency and depolarization ratio. Other weak lines observed in its vicinity, that is, lines at 1528, 1455 and 1418 cm^{-1}, could not be assigned to ν_{13} from a consideration of their depolarization ratios and of correspondencies with the infrared absorption bands.

The remaining three vibrations are the in-plane bending vibration of C–D bonds, the stretching vibration and the in-plane bending vibration of C–Cl bonds. As the first two vibrations were not observed in the Raman spectra, probably because of their weak intensities, as in the case of trichlorobenzene, the frequencies of observed in the infrared spectrum had to be adopted. To the in-plane bending vibration of C–D bonds was assigned the absorption band at 843 cm^{-1} observed in the infrared spectrum, for the corresponding band of the ordinary substance was observed at 1103 cm^{-1}. The absorption band at 799 cm^{-1} was assigned to the C–Cl stretching vibration, because the band at 814 cm^{-1} was assigned to the corresponding vibration of ordinary substance.

The in-plane bending vibration of C–Cl bonds was expected to be observed near 200 cm^{-1}, and only a remarkable line at 188 cm^{-1} was observed in this region for deuterated substance. From both the intensity and the depolarization ratio, this line was considered to correspond to the line at 188 cm^{-1} of ordinary substance, but it was not known at this point whether this line was to be assigned to the in-plane or to the out-of-plane vibration of C–Cl bonds. Concerning this alternate assignment, some discussion will be given later.

Species E''. — The frequency of the out-of-plane bending vibration of C–D bonds is estimated to be lower than 800 cm^{-1}, and a diffuse line was observed at 711 cm^{-1} as a shoulder of a strong Raman line of the solvent in the spectrum of carbon tetrachloride solution of deuterated substance. This line seemed to be recognizable also in the methanol solution, but due to its low intensity it could not be clearly distinguished from the noise. However, a polarized line which seemed to correspond to the first harmonic of this vibration was observed at 1418 cm^{-1}. Since this line could not be explained as an overtone or as a combination of other vibrations, the line at 711 cm^{-1} could be considered as a normal vibration.

It was apparent from the frequency and

the depolarization ratio that the line at 494 cm^{-1} corresponds to the line at 526 cm^{-1} of ordinary substance. Accordingly the line at 494 cm^{-1} was assigned to the out-of-plane bending vibration of the benzene ring of deuterated substance.

As for the out-of-plane vibration of C–Cl bonds, the line at 188 cm^{-1} might be assigned to it. However, as was mentioned above, it is difficult to determine whether this line is to be assigned to the in-plane or out-of-plane vibration of C–Cl bonds.

The above assignment is shown in Table IV.

Overtones and Combinations.—More overtones and combinations were observed in the spectra of deuterated substance than in that of ordinary substance. As was stated above, the line at 993 cm^{-1} was explained as 495 (e$''$) ×2, the line at 2282 cm^{-1} as 952 (a_1') + 1337 (e$'$), and the line at 1418 cm^{-1} as 711 (e$''$) ×2. For the other observed Raman lines, the following explanations were possible:

1058: 535 (a_2'') ×2

1455: ?

1528: 1337 (e$'$, from the infrared spectrum) + 188 (e$'$ or e$''$)

1767: 1337 (e$'$) + 418 (e$'$)

1883: 1143 (a_1') + 767 (e$'$) or 1337 (e$'$) + 535 (a_2'')

2029: 1550 (e$'$) + 841 (e$'$, from the infrared spectrum)

2537: 950 (a_1') + 1550 (e$'$)

3079, 3094: 1549 (e$'$) ×2, 2303 (a_1' and e$'$) + 801 (a_2'')

Though the line observed at 1455 cm^{-1} could not be well explained, the existence of such a line is quite natural, since the molecule has three normal vibrations belonging to species A_2' which are active to neither the Raman nor the infrared spectrum. Some of the above-mentioned explanations of overtones and combinations were not consistent with the observed qualitative depolarization ratios* But this inconsistency might not be very significant. If too much confidence was put in the observed results of the depolarization ratio, it might sometimes lead to an erroneous assignment. However, it should be mentioned here that the above explanation of the overtones and combinations may not be absolutely correct because of the existence of the unobservable normal vibrations.

Discussion

The product rule was applied to the assignment given above. For species A_1', the ratio of the products of the frequencies of the ordinary and deuterated trichlorobenzenes was calculated from the observed frequencies, such as 1.401 in good agreement with the theoretical value 1.414, showing that the assignment was correct.

In species E$'$, it has previously been pointed out that the assignment of ν_{17} was somewhat questionable. The theoretical value of the ratio is 1.982. Assuming that the line at 209 cm^{-1} of ordinary trichlorobenzene and the line at 188 cm^{-1} of deuterated correspond to the in-plane bending vibrations of C–Cl bonds, ν_{17}'s, the ratio calculated from the observed frequencies was 2.162, exceeding the theoretical value by about 9%. On the other hand, assuming that the line observed at 188 cm^{-1} of both trichlorobenzenes corresponds to ν_{17}, the calculated ratio was found to be 1.944, lower than the theoretical value by about 2%. This discrepancy of 2% could be expected from the accumulation of small errors in frequency measurements, from the shift of the fundamental lines due to Fermi reasonance, etc., but that of 9% had to be regarded as inexplicable and might suggest an erroneous assignment. Thus, it was decided that the lines at 188 cm^{-1} in both substances had to be assigned to ν_{17}. However, it should be mentioned here that, since there exists a possibility that an unobservably weak line corresponding to the line at 209 cm^{-1} does exsist at a suitable frequency (about 205 cm^{-1}) in the spectrum of deuterated substance, the above assignment can not be considered absolutely correct.

For species E$''$, the theoretical value is 1.402. However, since ν_{18} (C–H out-of-plane bending vibration) of ordinary trichlorobenzene was not observed, the observed ratio could not be compared with the theoretical one. Accordingly, the above-mintioned question concerning the assignment of the C–Cl in-plane bending vibration could not be solved. However, if the frequency of ν_{20}'s were assumed to be 188 cm^{-1} for both ordinary and deuterated substances, the frequency of ν_{18} of ordinary substance could be calculated to be 936 cm^{-1} by applying the product rule. However, as was stated in the previous paragraphs, no Raman line was observed in the neighborhood of this frequency.

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* For example, the combination of two fundamental vibrations belonging to species E$'$ brings out four vibrations belonging to species A_1', A_2' and E$'$ respectively, of which the one belonging to species A_1' might have the highest intensity in Raman effect. Therefore, the depolarization ratio of the observed line corresponding to this combination has to be considerably small.

Summary

The Raman spectra and the qualitative depolarization ratio of each line were observed for the solutions of 1, 3, 5-trichlorobenzene and 1, 3, 5-trichlorobenzene-d_3. The assignments of Raman active normal vibrations of these substances were carried out from the results of these measurements. The assignments for species A_1' and E' proved to be correct from the application of the product rule, showing a good accordance between theoretical and calculated ratios of products of the frequencies. However, the application of the product rule was impossible for species E'' because of unobserved frequencies.

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