Raman Spectra of p-Dichlorobenzene and p-Dichlorobenzene-d_4

By Shinnosuke Saëki

(Received April 3, 1961)

The molecular spectra of *p*-dichlorobenzene have been studied by many investigators, and the author has reported on the infrared absorption spectra of ordinary and deuterated *p*-dichlorobenzene previously(1). In this paper, the Raman spectra of the same substances will be reported upon, for it is essential for the assignment of the molecular vibration to study the Raman spectra as well as the infrared spectra.

As the molecule of *p*-dichlorobenzene has the center of symmetry, the thirty normal vibrations are divided into two groups according to the rule of mutual exclusion. Consequently, fifteen vibrations are active in Raman effect and eleven vibrations are active in infrared absorption spectrum. Though this fact does much to simplify the molecular spectra of this substance, the Raman spectrum of this substance is still rather complicated with the appearence of the overtone lines, combination lines and lines due to the Fermi resonance in addition to the above-mentioned eleven fundamental lines.

Concerning the Raman spectrum of *p*-dichlorobenzene, a number of papers have been published since many years ago(2-4). In these papers, the assignment of the lines was carried out inductively, comparing the spectrum with those of other benzene derivatives of the same type and observing a frequency change between them for each corresponding band or line. Since the number and the variety of the treated substance were extensive, and since the conclusions were made after prudent examinations, one can put much confidence in most of the results obtained by this method. However, since in a different molecule the strength to the interatomic bonds (force constants) changes as well as the masses of atoms, a slight ambiguity appears to be left in the assignment which resulted from such inductive studies. Actually the proposed assignments of some Raman lines of *p*-dichlorobenzene seemed to be somewhat indefinite and arbitrary.

In the study reported here, as the Raman spectra were observed for completely deuterated *p*-dichlorobenzene as well as for the ordinary one, the product rule could be applied in order

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

2) A. Stojiljković and D. H. Whiffen, *Spectrochim. Acta*, 12, 47 (1958).

3) D. H. Whiffen, ibid., 7, 253 (1955).

4) C. Garrigon-Lagrange, J-M. Lebas and M-L. Josien, ibid., 12, 305 (1958).

to verify the assignment proposed. In addition to the frequencies, the qualitative depolarization ratio of each line was also observed by the two exposure method using the polaroid cylinders in order to obtain more definite assignments than previous ones.

Experimental

Ordinary *p*-dichlorobenzene of extra pure grade on the market was recrystallized three times from the ethanol solution, and then sublimed before being used for the measurement of the Raman spectra. The melting point of the obtained substance was 53°C.

The deuterated one was prepared and purified as follows. Ordinary *p*-dichlorobenzene was stirred at 105°C for six hours in heavy sulfuric acid. The reaction mixture was poured on ice and the precipitate filtered off and washed with water and dried. The exchange with heavy sulfuric acid was repeated until the strongest band of $C_6HD_3Cl_2$ could hardly be observed in the infrared absorption spectrum of the substance. It was necessary to repeat the exchange reaction two or three times in order to attain such purity. Then the obtained substance was further purified in the same way as that for ordinary *p*-dichlorobenzene, but because of the smallness of the quantity, the purification could not be carried out so thouroughly as in the case of ordinary *p*-dichlorobenzene. The deuterated substance was probably a little less pure than the ordinary one.

The Cary model 81 automatic recording Raman spectrophotometer was used for the measurements, of which the source was the mercury arc lamp of Toronto type, and the dispersion of the grating was 4 Å/mm. at 5000 Å.

The spectra were measured in the solution of 1 g. *p*-dichlorobenzene in 5 ml. carbon tetrachloride. The qualitative depolarization ratios were measured by placing the polaroid cylinder around the Raman tube and by polarizing the exciting light to the directions parallel or perpendicular to the axis of the tube.

Results

The observed Raman spectra are shown in Figs. 1—4. As are shown in Figs. 3 and 4, the base lines of the spectra of deuterated *p*-dichlorobenzene rose gradually towards the higher frequency ends of the spectra, showing remarkable backgrounds. It might probably be caused by the slight resinous impurity, which could not be removed completely by the purification because of the small quantity of deuterated substance available, as we mentioned previously.

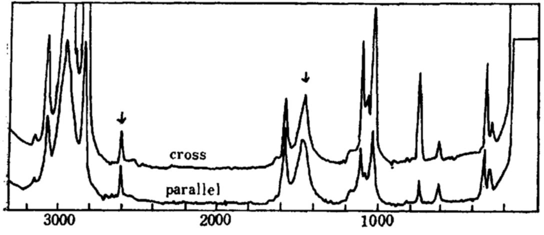

Fig. 1. Raman spectra of *p*-dichlorobenzene (1 g. in 5 ml. methanol).

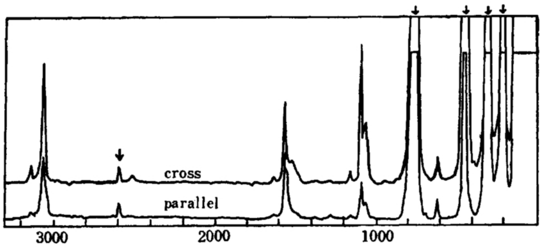

Fig. 2. Raman spectra of *p*-dichlorobenzene (1 g. in 5 ml. carbon tetrachloride).

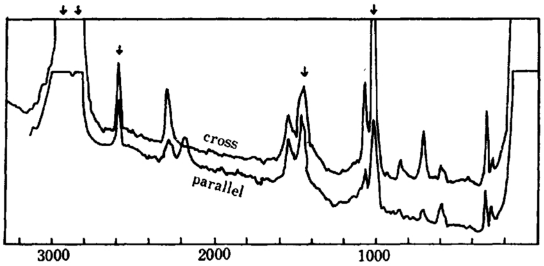

Fig. 3. Raman spectra of *p*-dichlorobenzene-d_4 (1 g. in 5 ml. methanol).

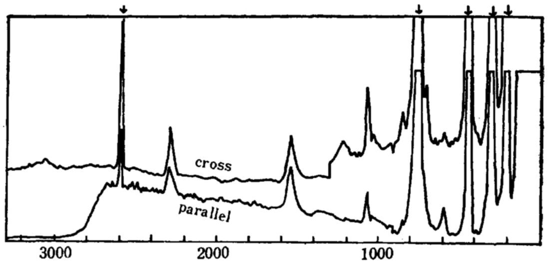

Fig. 4. Raman spectra of *p*-dichlorobenzene-d_4 (1 g. in 5 ml. carbon tetrachloride).

The observed frequencies and intensities of Raman lines are listed in Tables I and II. The intensities are described by the heights of lines measured on the chart. The notation "masked" means that the line could not be observed, due to the masking effect of a strong Raman line of the solvent in the spectra of that solution while it was observed in the other solution. Though the Raman spectra of the substances were observed in the solution in methanol or in carbon tetrachloride, there is no possibility that a Raman line is masked in both methanol and carbon tetrachloride solutions, for there is no frequency region

TABLE I. RAMAN SPECTRA OF *p*-DICHLOROBENZENE

Methanol soln.			Carbon tetrachloride soln.			Depolarization ratio
	Intensity			Intensity		
$\tilde{\nu}$	Cross	Parallel	$\tilde{\nu}$	Cross	Parallel	
295	14	17		Masked		dep.
329	54	27		Masked		p.
349	sh.	1		Masked		?
	Unobserved		400	4	2	?
623	13	14	625	16	16	dep.
744	56	16		Masked		p.
1067	19		1067	16	5	p.
1077	sh.	10	1080	25	5	p.
1103	80	35	1103	83	25	p.
1177	6	3	1163	8	3	p.
	Unobserved		1285	2	3	dep.
	Unobserved		1378	2	0	?
	Masked		1531	12b	sh.	p.
1571	38	39	1572	48	51	dep.
	Unobserved		1630	4	3	dep.
2520	4	0	2523	5	1	p.
3071	66	33	3071	75	39	p.
3147	8	5	3147	11	4	?

TABLE II. RAMAN SPECTRA OF *p*-DICHLOROBENZENE-d_4

Methanol soln.			Carbon tetrachloride soln.			Depolarization ratio
	Intensity			Intensity		
$\tilde{\nu}$	Cross	Parallel	$\tilde{\nu}$	Cross	Parallel	
288	11	12		Masked		dep.
324	42	27		Masked		p.
607	12	14	606	11	17	dep.
708	30	9	710	sh.	sh.	p.
863	14	6	861	13	5	p.
937	?					
1078	54	28	1078	39	18	p.
ca. 1520	2	3	ca. 1520	sh.	0	p.
1553	24	22	1553	28	30	dep.
2285			2285	8?	12?	dep.
2301	36	15	2301	31	19	p.

where both methanol and carbon tetrachloride have a strong Raman line. The only exception is the region between a line at 1460 cm^{-1} of methanol and a line at 1530 cm^{-1} of carbon tetrachloride. But fortunately, as neither of these lines was very strong, there was little possibility that a line would escape observation even in this region, so long as its intensity is not extremely weak.

The notation "unobserved" in the tables means that the line was not observed in one of the solutions while it was observed in the other solution. As all of these lines had very small intensities, it was not unreasonable that they were unobservable in one of the solutions. However, they could still not be adopted uncritically as the Raman lines of solute.

The notation "sh." means a line observed as a shoulder of a strong Raman line of the solute itself or the solvent, and "p." and "dep." represent a line which apparently changed and apparently did not change its intensity when excited by incident light polarized parallel and perpendicular to the axis of the Raman tube, respectively.

Discussion

The molecule of *p*-dichlorobenzene belongs to a point group V_h, and its fifteen Raman active normal vibrations are factored into six of the species A_g (in-plane), five of the species B_{3g} (in-plane), one of the species B_{1g} (out-of-plane) and three of the species B_{2g} (out-of-plane). Therefore six polarized (and probably strong) lines and nine depolarized lines were expected to be observed in the Raman spectrum. The modes of these normal vibrations are shown in Table III.

TABLE III. THE MODES OF THE NORMAL VIBRATIONS OF *p*-DICHLOROBENZENE

Species	No.*	Mode
A_g	ν_1	C–H or C–D stretching
	ν_2	Ring stretching
	ν_3	C–H or C–D in-plane bending
	ν_4	Ring stretching
	ν_5	C–Cl stretching
	ν_6	Ring in-plane deformation
B_{1g}	ν_9	C–H or C–D 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}	C–H or C–D stretching
	ν_{24}	Ring stretching
	ν_{25}	C–H or C–D in-plane bending
	ν_{26}	Ring in-plane deformation
	ν_{27}	C–Cl in-plane bending

* The normal vibrations were numbered after Herzberg.

***p*-Dichlorobenzene.** — Seventeen Raman lines are observed in the spectrum of this substance. Therefore the number of observed lines exceedes the number of Raman active normal vibrations. However, since there were several lines which were apparently considered to be overtones or combinations, this fact does not mean that all of the Raman active normal vibrations have been observed.

As we mentioned previously, six polarized lines were expected to be observed, but actually nine polarized lines were found in the observed spectrum, as is shown in Table I. Considering its frequency value, one of these polarized lines observed at 2522 cm^{-1} [*1] must be explained as an overtone or a combination. The number of remaining observed lines was still more than the number of expected lines. Considering the vibrational modes shown in Table III, these six lines belonging to the species A_g, one was expected to appear near 3000 cm^{-1}, one at about 1500 cm^{-1}, and two between 1300 and 1000 cm^{-1}. Though the vibrational mode of ν_4 was described as the ring stretching, it proved to be the " breathing " vibration of the benzene ring on closer examination. Therefore its frequency might be relatively low and expected to appear in this region, and two below 1000 cm^{-1}. Accordingly it was clear that the line at 3071 cm^{-1} had to be assigned to C–H stretching vibration, the line at 1531 cm^{-1} to the ring stretching vibration, the line at 774 cm^{-1} to the C–Cl stretching vibration, and the line at 331 cm^{-1} to the ring in-plane deformation vibration.

Concerning the assignment of the lines observed in the region 1000∼1300 cm^{-1}, there were some points of discussion. While only two of the totally symmetric normal vibrations were expected to appear in this region, four polarized Raman lines were actually observed at 1067, 1080, 1103 and 1163 cm^{-1} [*2]. As the line at 1103 cm^{-1} had much greater intensity than the other three, this line may the most plausibly be assigned to the breathing vibration of the ring. From the facts that the line at 1067 cm^{-1} was very close to the line at 1080 cm^{-1}, and that these two lines were hardly resolved in the spectrum of the methanol solution, these two lines might be considered to be brought out by a Fermi resonance between a fundamental and an overtone or a combination vibration (for example $545(b_{1u})^{1)} \times 2 = 1090\ (A_g)$, $744\ (a_g) + 331\ (a_g) = 1075\ (A_g)$). Then the frequency of the in-plane bending vibration of C–H bonds was estimated to be about 1075 cm^{-1}, the mean value of these two frequencies. Provided that the two normal vibrations were assigned in such a way, the line at 1163 cm^{-1} had to be considered as an overtone or a combination, or a fundamental which belongs to a species other than A_g. However it was also possible to take the line at 1163 cm^{-1} for the in-plane bending vibration of C–H bonds, and to take the lines at 1067 and 1080 cm^{-1} for the above-mentioned combination and overtone respectively. This alternative assignment seems to be somewhat unreasonable taking into account their relative intensities, nevertheless this could not be considered to be absolutely impossible. The superiority of one to the other will be revealed later by the application of the product rule.

The next step is to assign the other lines to the normal vibrations which belong to species other than A_g. These normal vibrations consist of four out-of-plane vibrations which belong to the species B_{1g} or B_{2g}, and five in-plane vibrations which belong to the species B_{3g}. As is shown in Table II, two of the four out-of-plane vibrations are those of C–H bonds, and their frequencies must be higher than 819 cm^{-1}, which is the frequency of the infrared active out-of-plane vibration of C–H bonds (species $B_{3u}$$^{1)}$) in which the four C–H bonds vibrate from the plane of the molecule up and down in the same phase. Though the frequencies of these vibrations were estimated to be between 819 and 1100 cm^{-1}, no depolarized line was observed in this region. Since naturally too much confidence should not be put in the observed degrees of depolarization, it would not be impossible to assign the lines at 1067 and 1080 cm^{-1} to these out-of-plane vibrations. However, since these lines had been well explained as a combination and as an overtone, as was mentioned above, and since the observed degrees of depolarization were not consistent with the above assignments, it appears better to consider that the normal vibrations in question were not observed and to assign the above lines to a combination and an overtone than to make a strained assignment. Further discussion concerning these lines will be seen later.

The other two out-of-plane vibrations are those of the ring and of the C–Cl bonds. Since the frequency of the former was expected to be about 400 cm^{-1}, the line observed at 400 cm^{-1} in the solution of carbon tetrachloride was assigned to it. But it should be mentioned here that there remained a little ambiguity in this assignment, since the intensity of the line was so weak that it was not observed in the solution of methanol. As the out-of-plane bending vibrations of C–Cl bonds were expected to be observed in lower frequency region —probably in the vicinity of 300 cm^{-1}, the line at 294 cm^{-1} was assigned to this vibration.

[*1] As a slight discrepancy was generally seen between the frequency observed in methanol solution and that oserved in carbon tetrachloride solution, the mean value of these two was used in this paper as a rule. However, in the case that an apparent difference existed between the accuracies of two observed frequencies, the more accurate one was used.

[*2] Since the second and the fourth lines were observed much more clearly in carbon tetrachloride than in methanol as is seen in Figs. 1 and 2, the frequencies observed in carbon tetrachloride solution were adopted as is mentioned in the last foot-note.

The last five normal vibrations to be assigned are those which belong to the species B_{3g}. The frequency of the stretching vibration of C–H bonds was naturally a little higher than 3000 cm^{-1}, and in the observed spectra a weak line was found at 3147 cm^{-1} in addition to the strong line at 3071 cm^{-1} which was already assigned to the vibration of the species A_g. The observation of the qualitative depolarization ratio showed that this weak line was considerably polarized. In addition to this fact, the frequency 3147 cm^{-1} appeared to be too high even for an aromatic C–H stretching vibration. Therefore this line had to be assigned not to the C–H stretching vibration, but to the overtone of the ring stretching vibration of 1572 cm^{-1} which will be discussed below. The C–H stretching vibration of the species B_{3g} should be considered to overlap with that of the species A_g at 3071 cm^{-1}.

Three of the remaining normal vibrations are the stretching vibration of the ring, the in-plane deformation vibration of the ring and the in-plane bending vibration of C–H bonds. There might be no objection to assigning three depolarized lines observed at 1572, 1285 and 623 cm^{-1} to them respectively. As for the last remaining normal vibration, that is, the C–Cl in-plane bending vibration, there was no observed line except a very weak line at 349 cm^{-1} to be assigned to it. Though the intensity of this line was very low, this line had been observed also by Whiffen et al.[2] And since there were no lines observed in the spectra to be assigned to the C–Cl bending vibrations except the two lines observed at 349 and at 294 cm^{-1}, it appeared to be quite plausible to assign the former line to the in-plane, and the latter line to the out-of-plane bending vibration of C–Cl bonds respectively.

A brief discussion should be given here concerning the lines which had not yet been treated above that is, the weak lines at 2520, 1630 and 1378 cm^{-1}, of which the degrees of depolarization could not be measured with adequate certainty. The line at 2520 cm^{-1}, though observed to be polarized, could not be explained as a line belonging to the species A_g. This line might probably be a combination line of the species B_{3g}, that is, 1405 (b_{2u}) + 1091 (b_{1u}). The line at 1630 cm^{-1} was measured as a depolarized line, and explained as being 1091 (b_{1u}) + 545 ($_{3u}$). The line at 1378 cm^{-1} was easily explained as 819(b_{3u}) + 544(b_{3u}).

Deuterated *p*-Dichlorobenzene. — The Raman lines observed for deuterated *p*-dichlorobenzene was not so many as for an ordinary one. The observed eleven lines were shown in Table II. According to the measurement of the qualitative polarization ratios, six of these lines were polarized. But the result obtained for the line at about 1520 cm^{-1} was a little ambiguous, because its intensity was so weak that the observation of the depolarization ratio was very difficult even qualitatively. However, these six polarized lines were unambiguously assigned to the six normal vibrations of the species A_g, as is shown in Table IV. The comparison of this assignment with that for ordinary *p*-dichlorobenzene will be given later.

The remaining five observed lines are to be assigned to the remaining nine normal vibrations, of which four out-of-plane vibrations belong to the species B_{1g} or B_{2g}, and five in-plane vibrations belong to the species B_{3g}. It might be apparent that two of the out-of-plane vibrations concerning C–D bonds have frequencies higher than 695 cm^{-1}, the frequency of the C–D out-of-plane vibration of the species B_{3u} observed in the infrared absorption spectrum[1]. However no corresponding line was observed in such a region of frequency, so it had to be concluded that these vibrations had too low intensities to be observed. The other two out-of-plane vibrations were expected to appear from 350 to 400 cm^{-1} and at about 250 cm^{-1} respectively, considering their vibrational modes (Table III). But there was no line to correspond to the former vibration. The line corresponding to the latter vibration was observed at 288 cm^{-1} with remarkable intensity, but it was difficult to determine whether this line was to be assigned to the out-of-plane or in-plane vibration of C–Cl bonds.

Concerning the in-plane normal vibrations belonging to the species B_{3g}, there might be no difficulty in assigning the line at 2285 cm^{-1} to the C–D stretching vibration and the line at 1553 cm^{-1} to the ring stretching vibration. As for the in-plane bending vibration of C–D bonds, since the corresponding vibration of ordinary *p*-dichlorobenzene was observed at 1285 cm^{-1} with relatively low intensity, the frequency was expected to be a little lower than 1000 cm^{-1} in the case of a deuterated one. No distinct line was observed in this frequency region at first sight, but the closer examination of the spectra revealed a very weak line at 937 cm^{-1}, the intensity of which was so weak that the line could hardly be distinguished from the noises. It might be a little questionable to consider it as a real Raman line. but if we remember that the line at 1285 cm^{-1} of ordinary *p*-dichlorobenzene was also very weak and that the corresponding line of deuterated *p*-dichlorobenzene has to appear in the region of 900~1000 cm^{-1}, this line could be assigned to the C–D in-plane bending vibration.

The line at 607 cm^{-1} was easily assigned to the ring in-plane deformation vibration.

To the C–Cl in-plane bending vibration, it is possible to assign the line at 288 cm^{-1}, but, as is mentioned above, it might also be possible to assign it to the in-plane bending vibration of C–Cl bonds. As in the case of ordinary *p*-dichlorobenzene, the decision of the assignment for these vibrations appear to be impossible at this point.

The Product Rule.—According to the Teller-Radlich product rule, the theoretical ratios of the products of the frequencies for each substance are 1.998 for the species A_g, 1.249 for the species B_{1g}, 1.408 for the species B_{2g} and 1.969 for the species B_{3g}, where the calculations were carried out using the following values for molecular constants:

$m_H = 1.0081$ (in physical atomic weight)
$m_D = 2.0147$ (in physical atomic weight)
$m_C = 12.0038$ (in physical atomic weight)
$m_{Cl} = 34.9801$ (in physical atomic weight)
$r_{C-H} = 1.08$ (Å)
$r_{C-Cl} = 1.68$ (Å)
$r_{C-C} = 1.39$ (Å)

and 120° for all of the bond angles.

The assignments for the six normal vibrations of the species A_g were unambiguously determined in the case of ordinary *p*-dichlorobenzene, but in the case of a deuterated substance there remained a question which of the two lines at 1163 cm^{-1} and 1075 cm^{-1} was to be assigned to the in-plane vibration of C–H bonds. If the ratio of the products of the frequencies was calculated assuming the latter assignment, the result was 1.825, a little less than the theoretical value 1.998. On the contrary, if the former assignment was assumed, the ratio became 1.991, in good accordance with the theoretical value. This result led us to the conclution that it was the line at 1163 cm^{-1} to be assigned to the C–H bending vibration of the species A_g.

Here, in connection with this assignment a comment should be mentioned about the exchange of the vibrational modes. As was stated above, according to this assignment, ν_3's were 1163 and 1078 cm^{-1} for ordinary and deuterated *p*-dichlorobenzene respectively, and ν_4's were 1103 and 863 cm^{-1} for ordinary and deuterated ones respectively. The fact that the line at 1103 cm^{-1} was much more intense than the line at 1163 cm^{-1} in the spectra of ordinary *p*-dichlorobenzene suggests to us that the mode of the former is the breathing of the benzene ring and that of the latter is the C–H in-plane bending vibration. However, in the case of a deuterated substance, it was clear from the consideration of the frequency that the line at 1078 cm^{-1} was the breathing of the benzene ring and that the line at 863 cm^{-1} was the C–D in-plane bending vibration. Thus the exchange of the vibrational modes shown in Fig. 5 took place in the case of these molecules. This consideration suggested that the breathing vibration of the benzene ring strongly couples with the C–H or C–D in-plane bending vibration in these molecules, and that the modes of these vibrations are by no means simple, but rather complicated combinations of some simple modes.

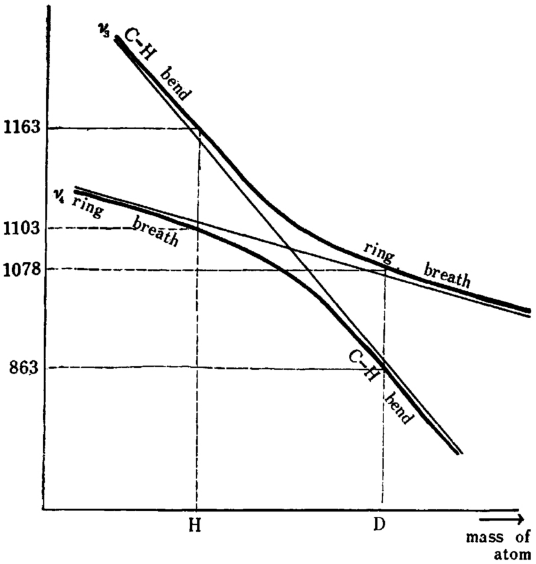

Fig. 5. The variation of vibrational mode with atomic mass.

It was impossible to apply the product rule to the species B_{1g} and B_{2g} because of the insufficient number of the observed lines. As was already stated above, only one normal vibration—the C–H or C–D out-of-plane vibration—belongs to the species B_{1g}. Therefore, provided that the line at 1067 or 1080 cm^{-1} of ordinary *p*-dichlorobenzene corresponds to this vibration, the frequency of the corresponding vibration of deuterated substance could be estimated at about 850 cm^{-1} by utilizing the product rule. As is shown in Table II, a remarkable line was indeed observed at 863 cm^{-1} in the spectra of deuterated substance, but it was already assigned to a vibration of the species A_g, because the measurement of the depolarization ratio showed it to be polarized. In addition to such a lack of a corresponding line, both lines at 1067 and 1080 cm^{-1} of the ordinary substance were themselves polarized, and so it seemed to be unreasonable to assign either of them to the vibration of the species B_{1g}.

As the C–Cl in-plane bending vibration of

TABLE IV. ASSIGNMENTS OF RAMAN LINES OF ORDINARY AND DEUTERATED *p*-DICHLOROBENZENES

Species	No.	$\tilde{\nu}$		Mode
		$C_6H_4Cl_2$	$C_6D_4Cl_2$	
A_g	ν_1	3071	2301	C–H or C–D stretching
	ν_2	1531	ca. 1520	Ring stretching
	ν_3	1163	1078	C–H in-plane bending Ring breathing
	ν_4	1103	863	Ring breathing C–D in-plane bending
	ν_5	744	708	C–Cl stretching
	ν_6	329	324	Ring in-plane deformation
B_{1g}	ν_9	—	—	C–H or C–D out-of-plane bending
B_{2g}	ν_{15}	—	—	C–H or C–D out-of-plane bending
	ν_{16}	400?	—	Ring out-of-plane deformation
	ν_{17}	295	288	C–Cl out-of-plane bending
B_{3g}	ν_{23}	3071	2285	C–H or C–D stretching
	ν_{24}	1572	1553	Ring stretching
	ν_{25}	1285	937?	C–H or C–D in-plane bending
	ν_{26}	623	607	Ring in-plane deformation
	ν_{27}	349	—	C–Cl in-plane bending

deuterated *p*-dichlorobenzene, which corresponds to the line at 349 cm^{-1} of the ordinary substance, was not observed, the exact application of the product rule was impossible for the species B_{3g} also. However, the ratio of products of the frequencies calculated from four pairs of observed frequencies alone was 1.963, which was very near to the theoretical value 1.969 irrespective of the omission of the fifth pair. Generally speaking, a vibration directly concerned with C–H bonds naturally shows the sensitive frequency shift with the substitution of the hydrogen atoms by deuterium atoms. The other vibrations—especially when their frequencies are very different from the frequency of C–H vibration—show little frequency shift. Therefore the C–Cl bending vibration of deuterated *p*-dichlorobenzene was expected to have a frequency nearly equal to that of the corresponding vibration of ordinary *p*-dichlorobenzene, 349 cm^{-1}. This means that the ratio of the frequencies for the fifth vibration of the species B_{3g} is probably little larger than 1, and therefore, if the above-mentioned calculation had been carried out taking account of this pair of frequencies, the result would be still in good accordance with the theoretical value. This consideration means that the application of the product rule could prove the correctness of the assignment for the species B_{3g} too.

The assignment which was determined above is shown in Table IV.

Summary

The Raman spectra of ordinary and deuterated *p*-dichlorobenzene were measured in solutions. The qualitative depolarization ratios of observed Raman lines were also measured by the two exposure method using the polaroid cylinders. On the basis of these results, the assignments of normal vibrations for these substances were determined. The assignments for the in-plane normal vibrations (species A_g and B_{3g}) were verified applying the product rule.

The author gratefully acknowledges the encouragement and advice given him by Dr. Y. Mashiko.

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