The Infrared Absorption Spectra of p-Dichlorobenzene and p-Dichlorobenzene-d_4

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A report has previously been published by the author¹⁾ concerning the infrared absorption spectra of *p*-dichlorobenzene and *p*-dichlorobenzene-d_4 in the regions of the lithium fluoride, sodium chloride and potassium bromide prisms. Recently the author carried out the measurement of the infrared spectra in the farther region, that is, from 400 to 300 cm^{-1} which a cesium bromide prism and from 300 to 100 cm^{-1} with gratings. In addition, the shape of each absorption band observed between 1700 and 700 cm^{-1} was also measured by the aid of a high-temperature long-path cell. The results of these measurements and the new assignment determined on the basis of these experimental results are reported in this paper. The assignment proposed in the previous paper was revised in several points in the new assignment proposed here.

Experimental

Far Infrared Absorption Spectra.—The measurement in the cesium bromide prism region was carried out from 670 to 300 cm^{-1} using a Perkin-Elmer model 21 spectrophotometer and a 85 mm. high temperature gas cell almost identical with that described in the previous paper¹⁾, except that the window material was cesium bromide. The method of measurement need not be mentioned, since it was quite similar to the previous case¹⁾. The measurement was done at about 210°C. As a number of intense bands of atmospheric water vapor made the 100% line uneven, especially beyond 330 cm^{-1}, and as the infrared radiation from the cell and the hot sample vapor itself made the base line also uneven, it was necessary to measure the 100% and base lines, as well as the absorption curve for each measurement, in order to obtain a correct spectrum.

The spectra between 300 and 100 cm^{-1} were measured using the grating spectrophotometer installed in the laboratory of Professor Yoshinaga of Osaka University²⁾. As the construction of the spectrometer did not allow the measurement in a gaseous state, the spectra were taken in the state of Nujol mull sandwiched between two polyethylene sheets (1 mm. thick)*. As the specimen, on measurement, was placed in a vaccum in order to avoid disturbance by the strong absorption of atmospheric water, some extent of inhomogenity of thickness might occur in the layer of Nujol mull due to the insufficient rigidity of the polyethylene sheet. However, this inhomogenity, if any, gave rise to no obstacle to simple, accurate observation of the frequencies of absorption bands.

Observation of Band Shapes.—It is very desirable for the determination of the assignment to observe the correct shapes of the band envelopes. However, using the 85 mm. high temperature cell, it proved to be impossible to observe the clear band envelopes. This failure might be attributed to the high temperature at which the measurements were carried out more than to the poor resolution of the spectrometer. If the 85 mm. high temperature cell was used, it was necessary to raise the temperature over the boiling points of these sample substances, that is, at 200 or 300°C, to obtain an enough strong absorption curve. But at high temperatures the width of an absorption band becomes large**, and a clear envelope can not be observed, even if a small slit width is used. Also, because of the extremely low vapor pressures of the sample substances, the use of an ordinary long path cell of the multiple reflection type (for example, a ten-meter gas cell) at room temperature was not sufficient to obtain a strong enough absorption curve. Thus it proved necessary, in order to obtain a sufficiently clear spectrum, to carry out a measurement at a temperature not extremely high, using a high temperature long path cell.

The high temperature long path cell constructed in our laboratory has the same optical alignment as that of the Perkin-Elmer ten-meter cell, but all its mirrors were spattered with gold to secure them from corrosion by the heat and by the sample

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

2) H. Yoshinaga, S. Fujita, S. Minami, A. Mitsuishi, R. A. Oetjen and Y. Yamada, *J. Opt. Soc. Am.*, **48**, 315 (1958).

* To prepare the specimen, the method of compounding the substance with hot polyethylene was not available in this case because of the high volatility of the sample substance. The method of making the solid solution in paraffin was also found to be impossible.

** This might be due to the increasing collision between molecules and to the increasing population at the levels of higher *J* values.

gases. The cell was coiled with heaters on the whole outside surface and then covered with several layers of asbestors for the sake of heat insulation. The entrance and exit openings were doubly closed by potassium bromide plates in order to prevent the condensing of the sample gas on the inner surfaces of the windows. The temperature of the cell could be raised up to about 110°C without any risk of decomposing the binding and sealing materials. A slight leakage at the stopcock, however, did not allow the maintenance of the vacuum over the whole period of scanning the spectrum. The 720 cm. path length was used for the measurements, and the sufficiently clear spectra were obtained at 60~80°C for *p*-dichlorobenzene. Although the large amount of energy loss due to multiple reflections in the cell obliged the use of considerably wide slits, the obtained spectra were much clearer than those obtained using the 85 mm. high temperature cell, and many absorption bands which could not be resolved previously were newly observed by the aid of this 720 cm. cell. The absorption curves for the bands at 1417 and 1393 cm^{-1} of *p*-dichlorobenzene obtained using these two cells of different types are shown in Fig. 1 for comparison.

Fig. 1. The infrared absorption spectra of *p*-dichlorobenzene near 1400 cm^{-1} measured using the long path and short path gas cells.
The upper curve: spectrum measured using the 720 cm. cell (slit width: 70 μ)
The lower curve: spectrum measured using the 85 mm. cell (slit width: 40 μ)

Although every effort was made to reduce the absorption due to atmospheric water vapor, a remarkable amount of absorption, which necessarily remained because of the design of the long-path cell, made difficult the observation of band envelopes in the 6 μ region. The adsorption of the sample gas on the inner surface of the cell required the paying of a good deal of attention to the washing of the cell after measurements. It proved to be necessary in the case of *p*-dichlorobenzene, when measurement was over, to drive the sample gas out by nitrogen as completely as possible; then the cell was demounted and kept open for forty hours at a high temperature. Even after such a drastic washing, on the next use, the absorption bands of desorbed gas were often observed with considerable intensities when the measurement was carried out over a long period of time. Accordingly, on the analysis of the spectra taken under such conditions, much attention was required to rule out the undesired band.

Results

The observed spectra of *p*-dichlorobenzene and *p*-dichlorobenzene-d_4 are shown in Fig. 2. The curves beyond 300 cm^{-1} are fragmental because of the necessity of frequent exchanges of the gratings and filters with the decreasing frequency during the measurement.

The observation of band envelopes was successful for some of the bands observed in the region of cesium bromide prism, while it is impossible in principle in the region of the gratings, where the spectra were observed in the solid state.

The spectra of *p*-dichlorobenzene-d_4 observed using the 720 cm. high temperature cell are shown in Fig. 3 for the region where the principal bands appeared.

The frequencies, intensities and types of the observed bands are shown in Table I. However, it should be mentioned here that the strong band at 1170 cm^{-1} of *p*-dichlorobenzene-d_4 proved to originate in a substance other than *p*-dichlorobenzenes. A comparison with the spectrum of the solutions and an examination of the time dependent change of the spectrum revealed this. Accordingly, no further consideration should be given to this band.

Discussion and Assignment

Band Envelopes.—In the case of *p*-dichlorobenzene, the three principal axes of the moment of inertia coincide with the three symmetry axes of the molecule because of the high symmetry. Taking the x-axis perpendicular to the molecular plane, the z-axis along the line combining two chlorine atoms, and the y-axis perpendicular to these two, the moments of inertia are calculated to be:

	$C_6H_4Cl_2$	$C_6D_4Cl_2$	
I_x	823	848	
I_y	735	741	
I_z	88	106	(in physical atomic weight·Å^2)

Therefore, vibrations belonging to species B_{1u}, B_{2u} an B_{3u} give absorption bands of type A, B and C respectively. In the actual spectrum,

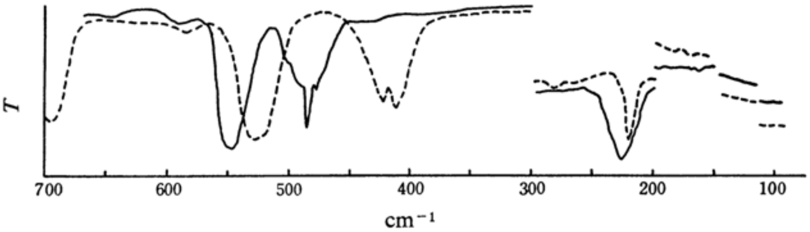

Fig. 2. Far infrared absorption spectra of ordinary and deuterated *p*-dichlorobenzenes.
$C_6H_4Cl_2$ —— $C_6D_4Cl_2$ ----

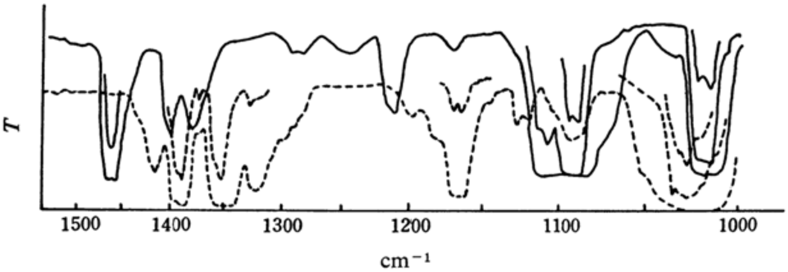

Fig. 3. Infrared absorption spectra of ordinary and deuterated *p*-dichlorobenzenes.
$C_6H_4Cl_2$ —— $C_6D_4Cl_2$ ----

TABLE I. INFRARED ABSORPTION BANDS OF *p*-DICHLOROBENZENE AND *p*-DICHLOROBENZENE-d_4

$C_6D_4Cl_2$			$C_6H_4Cl_2$		
Wave number	Type	Intensity	Wave number	Type	Intensity
3098	B	2	2301		3
3037	A	sh 1	2289		0
1888	B	4	1622	A	2
1758	A	3	1568	B	4
1656	B	sh 2			
1625	A	5	1434	A	4
1509	A or B	3	1405		12
1478	B or A	10	1366 1373	B or A	14
1417	A	8			
1393	A	5	1334 {1337 1331}	B	5
1297	B	1	1315 {1319 1310}	B	sh 1
1253	A	1	1205		sh 2
1217		4	1187		sh 1
1173	B?	1	1170 ?	B	12
1112 {1115 1109}	B	3	1127 {1131 1123}	B	3
1094 {1096 1091}	B	15	1096	A	4
1017 {1021 1014}	B	12	834.7 821.8 811.7		7
819.2	C	20	694.8	C	10
774.2	B	sh 1			
588	A	m	581.7	A	w
545.2	A or B	s	527.4	A	s
480.7	C	s	418.4	B ?	s
225.2		s	221.2		s

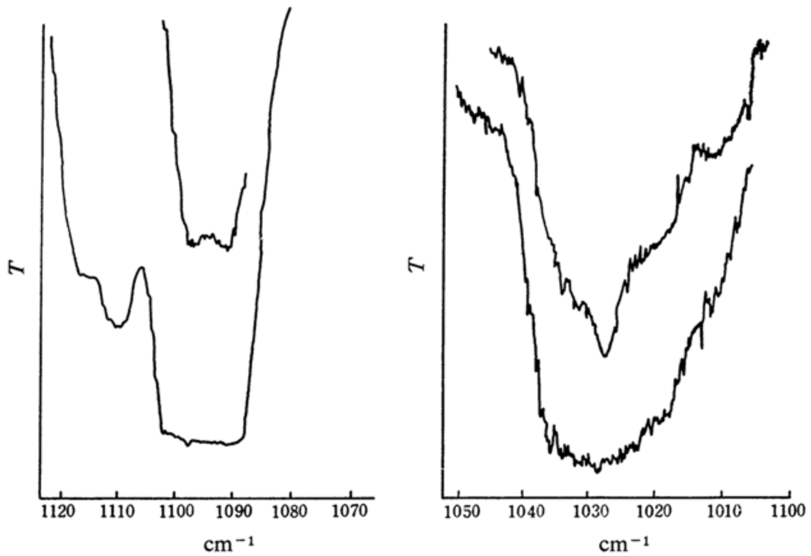

Fig. 4. The shapes of the bands at 1094 cm^{-1} of ordinary *p*-dichlorobenzene and at 1028 cm^{-1} of deuterated *p*-dichlorobenzene.

relatively clear band envelopes were observed for type C bands, for, as was expected from their vibrational modes, all of them appeared in a lower frequency region, where the resolution of the spectrometer is relatively high. However, for the bands of the other species, when they appeared in the higher frequency region, the observed envelopes were not adequately clear to distinguish them as type A or B. In Table I, bands having somewhat pointed peaks are descibed as type A bands, and bands having somewhat round peaks, as type B bands. On the contrary, envelopes were clearly observed for the bands which appeared in the region below 1100 cm^{-1}, except for a few bands. Examples will be shown below.

The band of $C_6H_4Cl_2$ at 1094 cm^{-1}, which certainly corresponds to 1028 cm^{-1} of $C_6D_4Cl_2$*, is shown in Fig. 4. This appeared to be a type B band showing a clear absorption minimum at the center, while the band of $C_6D_4Cl_2$ at 1028 cm^{-1} could be explained only as a type A band because of its clear Q branch, as is seen in the figure. This fact suggests that too much significance should not be attached to the observed band envelopes on determining the assignment, at least when their apparent shapes are considered.

In the observed spectra, there were many asymmetrical absorption bands consisting of two branches of unequal intensity. The band of *p*-dichlorobenzene observed at 1217 cm^{-1} is shown in Fig. 5 as a typical example. Considering the existence of two branches, they might be regarded as type B bands, but if the stronger branch is regarded as an overlap of the Q and R branches, such a band should be considered as a type A or C band. As will be mentioned later, the band of $C_6D_4Cl_2$ at 414 cm^{-1} also showed such an envelope and appeared to be a type B band, but it was revealed to be a type C band by a consideration of the product rule and of the correspondence with a band of $C_6H_4Cl_2$. There were many other bands like this, of which the type could not be determined clearly.

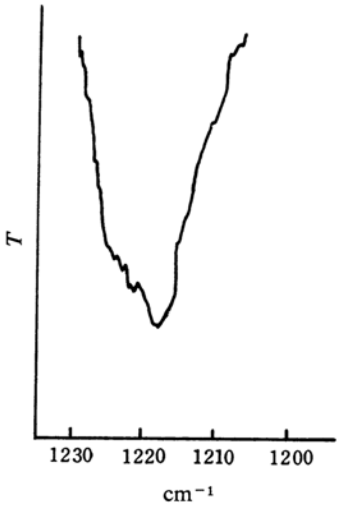

Fig. 5. The shape of the band at 1217 cm^{-1} of *p*-dichlorobenzene.

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* This correspondence between bands satisfied the product rule, as will be shown later.

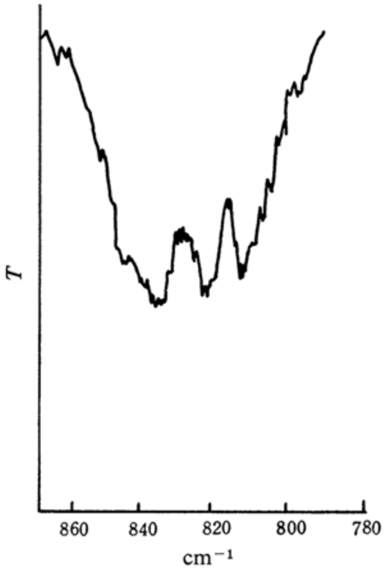

Fig. 6. The shape of the band at 820 cm^{-1} of *p*-dichlorobenzene-d_4.

Another difficult band was observed in the spectrum of deuterated *p*-dichlorobenzene. In Fig. 6 is shown a band observed around 820 cm^{-1}. The large spacing between the three absorption maxima (see the figure) could be explained neither as three branches of a single band, nor as three separate absorption bands, because of the resultant absence of the branches of each band. However, in the spectra of solutions, three closely positioned weak bands were observed in this frequency region; these may be separate bands, the branches of which overlap, one with the others.

Assignment.—Taking account of the product rule, and on the basis of the above-mentioned results concerning the envelopes of principal bands, the assignment of the observed bands was determined as is shown in Table II.

Some revisions of the previous assignment were required to be consistent with the above-mentioned new experimental results. In our previous paper¹⁾, the band at 483 cm^{-1} of $C_6H_4Cl_2$ (414 cm^{-1} for $C_6D_4Cl_2$) was assigned

TABLE II. ASSIGNMENT OF THE INFRARED ABSORPTION BANDS OF *p*-DICHLOROBENZENE AND *p*-DICHLOROBENZENE-d_4

Wave number		Assignment	Mode
$C_6H_4Cl_2$	$C_6D_4Cl_2$		
3098	2301	$\nu_{10}(b_{1u})$	C–H or C–D stretching
3098	2289	$\nu_{18}(b_{2u})$	C–H or C–D stretching
1888	1622	$\nu_7(a_u)+\nu_{15}(b_{2g})$	
1758		$\nu_2(a_g)+\nu_{30}(b_{3u})$	
1656		$\nu_4(a_g)+\nu_{14}(b_{1u})$	
1625		$\nu_9(b_{1g})+\nu_{28}(b_{3u})$	
	1568	$\nu_3(a_g)+\nu_{28}(b_{3u})$	
1509		$\nu_{12}(b_{1u})+\nu_{16}(b_{2g})$	
	1434	$\nu_{13}(b_{1u})+\nu_{26}(b_{3g})$	
1478	1370	$\nu_{11}(b_{1u})$	Ring stretching
1417	1405	$\nu_{19}(b_{2u})$	Ring stretching
1393	1334	$\nu_{20}(b_{2u})$	Ring stretching
	1315	$\nu_{13}(b_{1u})+\nu_{17}(b_{2g})$	
1297		$\nu_9(b_{1g})+\nu_{29}(b_{3u})$	
1253		$\nu_7(a_u)+\nu_{17}(b_{2g})$	
1217		$\nu_4(a_g)+\nu_{29}(b_{3u})$	
	1205	$\nu_{13}(b_{1u})+\nu_{16}(b_{2g})$	
1173		$\nu_{14}(b_{1u})+\nu_{26}(b_{3g})$	
	1127	$\nu_4(a_g)+\nu_{29}(b_{3u})$	
1112	811.7	$\nu_{21}(b_{2u})$	C–H or C–D in-plane bending
	1096	$\nu_3(a_g)+\nu_{30}(b_{3u})$	
1094	1028	$\nu_{12}(b_{1u})$	Ring in-plane deformation
1017	821.8	$\nu_{13}(b_{1u})$	C–H or C–D in-plane bending
819.2	694.8	$\nu_{28}(b_{3u})$	C–H or C–D out-of-plane bending
774.2		$\nu_{17}(b_{2g})+\nu_{29}(b_{3u})$	
588	581.7	$\nu_6(a_g)+\nu_{22}(b_{2u})$ or $\nu_{22}(b_{2u})+\nu_{27}(b_{3g})$	
545.2	527.4	$\nu_{14}(b_{1u})$	C–Cl stretching
480.7	418.4	$\nu_{29}(b_{3u})$	Ring out-of-plane deformation
225.2	221.2	$\nu_{30}(b_{3u})$	C–Cl out-of-plane bending

to ν_{14} of the species B_{1u}, and the band at 544 cm^{-1} of $C_6H_4Cl_2$ (526 cm^{-1} for $C_6D_4Cl_2$) was assigned to ν_{29} of species B_{3u}. However, as the bands at 481 cm^{-1} of $C_6H_4Cl_2$ and at 418 cm^{-1} of $C_6D_4Cl_2$ proved to be type C bands in this study, it became clear that the 481 cm^{-1} and the 418 cm^{-1} should be assigned to ν_{29} and the 545 cm^{-1} and 527 cm^{-1} should be assigned to ν_{14}, inverting the previous assignment.

Furthermore, in our previous assignment, the pair of bands at 1014 and 800 cm^{-1} was assigned to the ring deformation vibration ν_{20} of species B_{2u}. However, as is clear from a consideration of the vibrational mode, this vibration is necessarily accompanied with the ring stretching one, and, consequently, the frequency of this vibration must be relatively high. From this viewpoint, the bands at 1393 cm^{-1} of $C_6H_4Cl_2$ and at 1334 cm^{-1} of $C_6D_4Cl_2$ were assigned to this vibration, ν_{20}.

As the large frequency shifts observed for the bands at 1017 and 1112 cm^{-1} of $C_6H_4Cl_2$ on the deuteration (to 821.8 and 811.7 cm^{-1} of $C_6D_4Cl_2$ respectively) suggest that these vibrations mainly concern the motions of the C–H bonds, they are assigned to the C–H in-plane bending vibrations.

The assignment of the combination bands is also shown in Table II. Of these combination bands, a brief discussion should be given about the assignment of the band at 588 cm^{-1} of $C_6H_4Cl_2$ which appearently corresponds to the band at 581.7 cm^{-1} of $C_6D_4Cl_2$. This pair of bands is difficult to explain as any combination of the observed fundamentals. The unobserved low frequency fundamental of the gerade species is ν_{27} of $C_6D_4Cl_2$* (b_{3g}, Raman active), and those of ungerade species are $\nu_8(a_u)$ and $\nu_{22}(b_{2u})$ of each substance. Therefore, the possible assignments for 588 and 581.7 cm^{-1} are as follows:

$$\nu_6(a_g)+\nu_{22}(b_{2u})$$
$$\nu_{22}(b_{2u})+\nu_{27}(b_{3g})$$
$$\nu_8(a_u)+\nu_{17}(b_{2g})$$
$$\nu_8(a_u)+\nu_{27}(b_{3g})$$

However, as $\nu_8(a_u)$, being the out-of-plane deformation vibration of the ring, may have a frequency higher than 300 cm^{-1} at the lowest, the last two assignments appear to be impossible. The remaining two assignments seem to have similar possibilities. If the first assignment is taken up, the frequencies of ν_{22}'s are calculated from the frequencies of ν_6's to be 259 and 258 cm^{-1} for $C_6H_4Cl_2$ and $C_6D_4Cl_2$ respectively. If the second assignment is taken up, 239 cm^{-1} is obtained as the frequencies of ν_{22} for $C_6H_4Cl_2$, while the frequency of ν_{22} for $C_6D_4Cl_2$, can not be calculated, for the frequency of ν_{27} was not observed for $C_6D_4Cl_2$. However, if the above-mentioned frequency of 340 cm^{-1} for the ν_{27} of $C_6D_4Cl_2$ (see the last footnote) is used, ν_{22} can be calculated to be 242 cm^{-1} for $C_6D_4Cl_2$. Since, from a theoretical viewpoint, the frequency must be lower for $C_6D_4Cl_2$ than for $C_6H_4Cl_2$, the frequencies of ν_{22} and ν_{27} for $C_6D_4Cl_2$ should be determined to be 239 and 343 cm^{-1}. After all, two possible pairs of ν_{22} for each substance are obtained, that is, 259 and 258 cm^{-1}, and 239 and 239 cm^{-1}. As both of these two pairs are plausible for the C–Cl in-plane bending vibrations, it is very difficult to distinguish which pair is the true one, while one of these two pairs is certainly true. Since the influence of these two assignments on the ratio of the products of the frequencies is very small, even the product rule sheds little light on the determination of this question.

Product Rule.—The ratios of products of the frequency required by the theorem of Teller and Redlich are as follows:

1.972	for species B_{1u}
1.972	for species B_{2u}
1.395	for species B_{3u}

The ratios calculated from the observed frequencies are 1.977 for species B_{1u} and 1.379 for species B_{3u}, showing good accordances with the above theoretical values. As for species B_{2u}, since ν_{22} was observed for neither $C_6H_4Cl_2$ nor $C_6D_4Cl_2$, the perfect application of the product rule was impossible. However, taking account of the fact that a low frequency vibration such as ν_{22} is little influenced by deuteration, the ratio of ν_{22}'s for both substance could be estimated to be little larger than 1. This estimation seems to be justified by the calculated pairs of frequencies for ν_{22}'s in the previous paragraphs. With this assumption, the ratio of the products of the frequencies can be calculated to be 1.953 for species B_{2u}; the accordance with the theoretical value is also very good in this case. From such considerations, the assignment proposed here proves to have much reliability.

Summary

The infrared absorption spectra of *p*-dichlorobenzene and *p*-dichlorobenzene-d_4 were measured from 300 to 700 cm^{-1} in a gaseous state with cesium bromide prism, from 300 to 100 cm^{-1} in a solid state with gratings, and, using a newly constructed long path (720 cm.) high

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* ν_{27} of $C_6H_4Cl_2$ was observed at 349 cm^{-1}. Applying the product rule using this frequency, the frequency of ν_{27} of $C_6D_4Cl_2$ is calculated to be about 340 cm^{-1}.

temperature cell, from 1700 to 700 cm^{-1} in a gaseous state with a sodium chloride prism. The frequencies and band envelopes of observed absorption bands were reported.

On the basis of these results, the assignment of the infrared active normal vibrations of these molecules was determined. The assignment was checked by means of the application of the product rule, and the correctness was verified by the good agreement between the theoretical and experimental values.

The assignment was also determined for the observed combination bands, using the Raman fundamental frequencies presented in the previous paper as well as infrared frequencies.

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