

The infra-red absorption spectrum of methylene chloride

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The absorption spectrum of methylene chloride has been studied over limited regions in the infra-red by several workers (Ellis 1926; Lecomte 1933; Corin 1936; Emschwiller and Lecomte 1937). So far as we are aware it has never been investigated between 2.5 and 7μ , although this is a very important region. The present paper describes a study of the absorption of this substance in the liquid state between 2 and 12μ , which was undertaken with the following objects in view. First, it was hoped that it might be possible to resolve certain difficulties in the correlation of the infra-red with the Raman spectrum of this molecule. Thus Trumpy (1934) from a very careful examination of the Raman spectrum had made an assignment of the nine fundamental frequencies which did not admit of a reasonable explanation of a very strong absorption observed in the infra-red by Lecomte (1933) near 8μ . Before any reinterpretation of existing data could be attempted it was obviously necessary to complete the map of the spectrum between 2.5 and 7μ and to confirm Lecomte's work at 8μ . It was also important to observe as many overtone and combination bands as possible to provide data for verifying and testing any new assignment of the fundamental frequencies. Secondly, it was chosen as a suitable molecule for the further study of the assumption of independent groups (Sutherland and Dennison 1935; Mecke 1932) in computing the frequencies of a polyatomic molecule from a simplified but still very general potential function. Thus it is well known that certain groups (such as CH_2 or CH_3) in a molecule give rise to certain characteristic frequencies in the infra-red and Raman spectra of these molecules, being apparently practically independent of the rest of the molecule. Such frequencies are easy to identify in analysing the vibration spectrum of a polyatomic molecule but the frequencies which arise from the vibrations of those semi-independent groups as wholes are not at all easy to assign and it is just those "inter-group" frequencies as opposed to the "intra-group" frequencies for which we have found a new method of treatment in this case. Yet the method,

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which depends on an application of the isotope effect, is a very general one and should be applicable to many classes of polyatomic molecules.

EXPERIMENTAL

The spectrometer used was the well-known Hilger instrument D83. The source of radiation was a Nernst glower, while the currents from the thermopile were measured directly on a very sensitive Paschen type galvanometer. The spectrometer was carefully enclosed in a wooden box to minimize thermal disturbances. The dispersing prism was of fluorite between 2 and 9μ , and of rock salt between 8 and 12μ . The wave-length readings on the drums were checked with reference to the well-known atmospheric bands due to water vapour and carbon dioxide, the prisms being set in position initially by using the sodium *D* lines. No special precautions were taken to prevent variations in the current through the Nernst filament since the latter was operated from a battery supply which was very constant. For the majority of measurements the Paschen galvanometer mentioned above was employed; occasionally, however, the thermo-electric current was taken to a Kipp and Zonen *Zc* moving coil galvanometer the deflexions of which were amplified by a photo-electric relay of the type described by Moss (1935). This made it possible to work with very fine slits in the examination of the contours of certain bands.

The absorption cell employed is shown diagrammatically in fig. 1. It enabled one to vary the thickness of the layer of CH_2Cl_2 from 0.007 to 1 mm. The liquid is contained in the space *A* between the rock salt windows *B* and *C*, which were 5 mm. thick and 20 mm. in diameter.* These windows are surrounded by two rings, *D* and *E*, the latter being separated by a third ring, *F*, the thickness of which determines that of the layer of liquid to be examined. The ring *D* is provided with two tubes *G* and *H* which allow the liquid to flow into the cell through the openings *I* and *J*. The ring *F* (the internal diameter of which is a shade less than that of *D* or *E*) is placed against the ring *D* so that the openings *I'* and *J'* of the former correspond to *I* and *J* of the latter. The ring *E* is identical with *D* except that it has no tubes. These three rings are held together by screws through *K*₁, *K*₂, *K*₃ and *K*₄. The rock salt plates are next placed on either side of *F* and the whole pressed together tightly by means of two larger metal rings *L* and *M*, lead washers being put between *D* and *L* on one side and *E* and *M* on the other. The thickness of *D* (and of *E*) was just a little less than

* We are much indebted to Professor Errera of the University of Brussels for the loan of these rock salt plates.

that of the rock salt plate. The cell was filled through either *G* or *H*, one being the entrance tube, the other the exit for the air. This method proved very satisfactory even for the smallest thicknesses. The whole was made of brass, except for the washer *F* which was made from brass, aluminium or copper according to the thickness required.

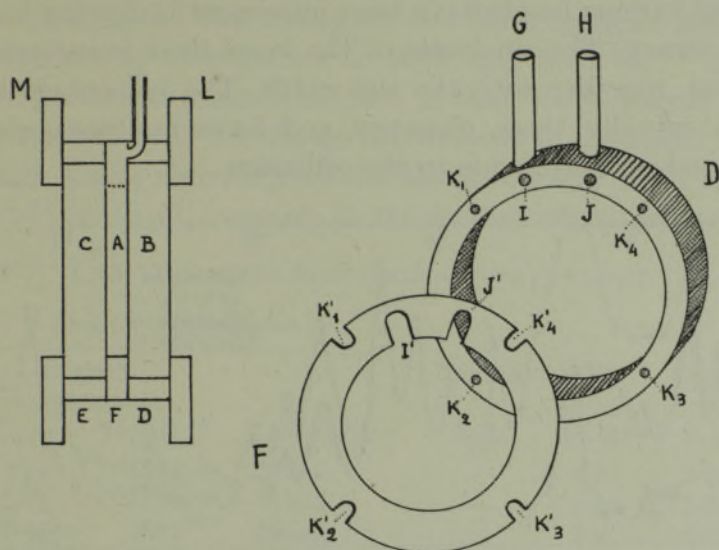


FIG. 1. The absorption cell.

In making the observations a preliminary run was done with the empty cell to ensure that the windows were perfectly clean and to get an estimate of the percentage loss due solely to them. This was of the order of 15 %. Readings were then taken of the energy falling on the thermopile with, and without, the cell in the path of the beam to give the percentage absorption at any particular wave-length. Beyond 4μ a glass shutter was always used for cutting off the radiation from the thermopile to ensure that only the long wave-length radiation was being measured. The thickness of the cell varied from place to place in the spectrum depending on the intensity of the absorption at the particular region. It was chosen to yield a maximum absorption at the centre of the band of from 60 to 90 %. All the important bands were plotted on at least two independent occasions and indications of weak bands were confirmed or disproved by using thicker layers of liquid. The width of the entrance and exit slits were always the same and were always as narrow as would still yield reasonable deflexions. They are indicated to scale for each region on its appropriate diagram.

RESULTS

Between 2 and 12μ we have observed altogether twenty-six absorption bands of which sixteen (occurring between 2.9 and 7μ) are new, the remaining ten having been already reported by earlier workers. The appearance of these bands is illustrated in figs. 2 and 3. For convenience of reference the various bands have been numbered beginning from those of highest frequency. The thickness of the layer used is indicated on each curve in mm. together with the slit width. The percentage absorptions plotted are actually those observed and have not been corrected for absorption and scattering due to the cell alone.

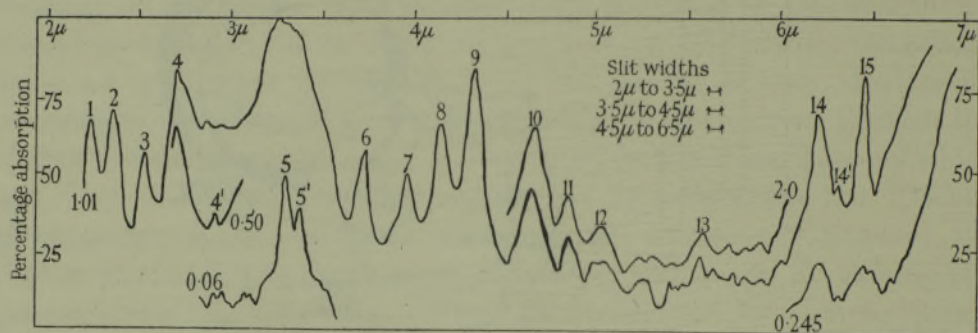


FIG. 2. Spectrum of methylene chloride from 2 to 6.5μ .

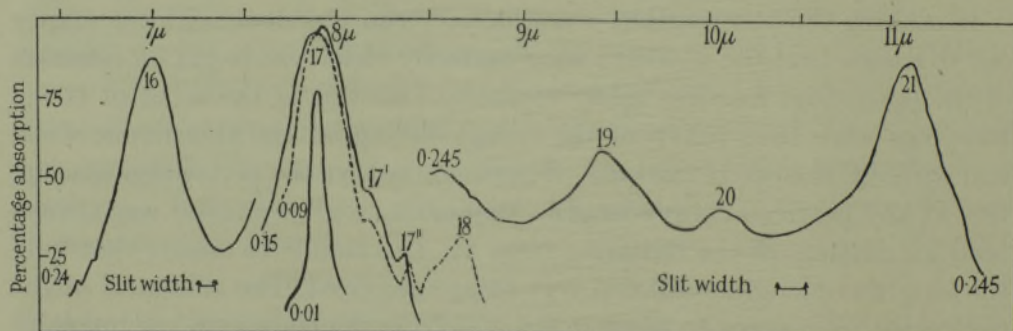


FIG. 3. Spectrum of methylene chloride from 6.5 to 11.5μ .

It will be observed that the most intense absorption bands occur at 3.3 , 7 , 7.9 and 11.1μ , bands of medium intensity were found at 4.3 , 6.3 , 6.5 and 9.4μ , while seventeen very much weaker bands were observed at the positions given in Table I. The band at 3.3μ was found on using a smaller thickness of liquid and very narrow slits to consists of two bands having their maxima at 3043 and 2985 cm.^{-1} . These observations are compared with the existing data on the infra-red and Raman spectrum of

this molecule in Table I. It will be noticed that in cases where the observations overlap the agreement between the positions of the centres of the bands as reported by the different authors is quite satisfactory, with the exception of the weak bands near 8.6 and 9.5μ . Even in these two cases it probably does not exceed the experimental error, since the bands in question are rather broad and do not have a well-defined maximum. The coincidence between the two strong Raman lines lying at 3043 and 2985 cm.^{-1} and the strong absorptions at 3049 and 2985 cm.^{-1} is especially satisfactory. The most remarkable fact is that the strongest absorption band of all, viz. that at 7.9μ , has no counterpart in the Raman spectrum. It is this which makes necessary the detailed discussion of the fundamental frequencies of the CH_2Cl_2 molecule in the section which follows.

TABLE I. THE VIBRATION SPECTRUM OF METHYLENE CHLORIDE

	Present investigation			Lecomte	Ellis	Corin	Raman spectrum				
	Position		Intensity					in μ	in μ	in μ	in cm.^{-1}
	In μ	In cm.^{-1}									
1	2.24	4464	Weak	—	2.27	2.24	—				
2	2.36	4237	Weak	—	2.42	2.33	—				
3	2.54	3937	Weak	—	2.57	2.57	—				
4	2.70	3704	Weak	—	2.76	—	—				
4'	2.92	3425	Very weak	—	2.80	—	—				
5	3.28	3049	Strong	—	—	—	3043				
5'	3.35	2985	Strong	—	—	—	2985				
6	3.74	2674	Weak	—	—	—	—				
7	3.96	2525	Weak	—	—	—	—				
8	4.14	2415	Weak	—	—	—	—				
9	4.32	2315	Medium	—	—	—	—				
10	4.68	2137	Weak	—	—	—	—				
11	4.86	2058	Weak	—	—	—	—				
12	5.04	1984	Very weak	—	—	—	—				
13	5.58	1792	Very weak	—	—	—	—				
14	6.20	1613	Weak	—	—	—	—				
14'	6.32	1582	Very weak	—	—	—	—				
15	6.46	1548	Weak	—	—	—	—				
16	7.00	1429	Strong	7.00	—	—	1419				
17	7.90	1266	Very strong	8.02	—	—	—				
17'	8.18	1222	Weak	—	—	—	—				
17''	8.39	1192	Weak	—	—	—	—				
18	8.66	1155	Weak	8.83	—	—	1149				
19	9.43	1060	Weak	9.59	—	—	1060				
20	10.14	985	Weak	10.28	—	—	—				
21	11.12	899	Medium	11.20	—	—	898				
22	—	737	Very strong	13.60	—	—	735				
23	—	704	Very strong	14.20	—	—	700				
24	Not observed in infra-red up to the present						284				

DISCUSSION

The molecule CH_2Cl_2 has nine fundamental frequencies. These may be separated into three groups of three in a rough physical way by considering the molecule to be built up from a CH_2 group and a CCl_2 group. If we look at the molecule in this way then it is clear that the CH_2 group and the CCl_2 group will have each three fundamental frequencies, while the vibrations of the CH_2 group as a whole with respect to the CCl_2 group as a whole form the third group of three (Group 3). This method of splitting the molecule into semi-independent vibrating groups has been shown to be justified by Sutherland and Dennison (1935) and by other authors (Mecke 1932; Kohlrausch 1935). Its great value is that it enables some of the fundamental frequencies to be immediately identified. Thus the CH_2 group is well known to possess three fundamental frequencies, two of which fall near 3000 cm.^{-1} and the other near 1450 cm.^{-1} . We are therefore fairly sure that the bands at 3049 , 2985 and 1430 cm.^{-1} are the first group of three fundamentals. In a similar way one may pick out the three frequencies at 700 , 735 and 284 cm.^{-1} as the second group of three, consisting essentially of the vibrations of the CCl_2 group. The real difficulty comes when we try to say which are the other three fundamentals. When the Raman spectrum of CH_2Cl_2 was examined in great detail by Trumphy (1934) he found, in addition to the above six fundamentals (which he assigned in the same way as we have done), three other Raman lines at 898 , 1060 and 1149 cm.^{-1} . Since all of the nine fundamental frequencies of this molecule are permitted in the Raman effect, Trumphy concluded very naturally that these frequencies represented the other three fundamentals. The objection to this assignment is that it leaves quite unexplained the most intense infra-red absorption at 1266 cm.^{-1} . This absorption is so strong that it can scarcely be considered to be other than a fundamental frequency. Even if one attempts to interpret it as a combination band of Trumphy's fundamentals one meets with very serious difficulties since the only combination which it might be is $\nu_1 + 2\delta_1$.^{*} That such a combination band should have powerful absorption is extremely unlikely and we propose to accept the strong infra-red frequency at 1266 cm.^{-1} as one of the three frequencies of Group 3. The problem is now to decide the other two.

We first notice that of the three Raman frequencies of Trumphy at 898 , 1060 and 1149 cm.^{-1} only one appears with any marked intensity in the infra-red: this is the one at 898 cm.^{-1} . If we accept this as the second of

^{*} See Table III for explanation of this notation.

the missing fundamentals then it remains to decide between 1060 and 1149 cm.^{-1} as the last. One must not neglect the possibility that both of those frequencies (being relatively weak in absorption and in scattering) may be overtone or combination frequencies due to a low fundamental in the neighbourhood of 500–600 cm.^{-1} and Emschwiller and Lecomte (1937) have in fact made a suggestion of this kind. Since this region of the spectrum has not been investigated in the infra-red and was beyond the range of our spectrometer we have tackled the problem from the theoretical side and have been able to show that the possibility of such a low fundamental is most unlikely (see next section). If we rule out Lecomte's suggestion, we consider that the frequency at 1060 cm.^{-1} is the correct one to choose as the remaining fundamental for the following reasons. First of all, it is quite impossible to interpret it in terms of any simple combination of the other eight frequencies; secondly, it is possible to interpret the frequency at 1149 cm.^{-1} in terms of the other eight frequencies in at least two simple and reasonable ways; finally, we have been able to estimate the approximate value of this frequency as somewhere between 1100 and 1110 cm.^{-1} by a calculation which we shall now describe.

THE ISOTOPIC METHOD

The mathematical treatment of the normal vibrations of a system of the type YX_2Z_2 has not yet been given, and although it would be possible to extend the treatments given of simpler molecules to this type, the process would be extremely laborious and of no small difficulty since it would involve the solving of a ninth order determinantal equation. The results obtained would also be dependent on the type of potential function assumed so that at best one might only obtain a somewhat forced agreement between calculated and observed frequencies. It occurred to us that a relatively simple approximate treatment might be made to yield rough values for the frequencies by regarding the Cl atoms as heavy "isotopes" of hydrogen of mass 35 and then employ the equations for the isotope effect in CH_4 which have been derived by Rosenthal (1934). Of course the values one obtains for the three frequencies will be too high since the C-Cl force constant is appreciably smaller than the C-H force constant which has been taken in its place. To get over this difficulty we have also calculated the same three frequencies looking on the hydrogen atoms as light "isotopes" of the Cl atoms and using the potential constants of the CCl_4 molecule given by Voge and Rosenthal (1936). This will give too low a value for the frequencies since the C-Cl force constant has been used

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for two bands in which the real force constant is somewhat higher. We hoped that the difference between the upper and lower limits thus obtained would not be too great so that a correlation might be made with the observational data. Table II shows that the experiment has been more successful than one might have imagined. Thus, using Rosenthal's notation, we find that the highest of the three (ω_{4a}) should lie between 1295 and 1081 cm.^{-1} . This we identify with the strong infra-red band at 1266 cm.^{-1} . The lowest (ω_{4c}) is to be expected between 720 and 843 cm.^{-1} ; this we associate with the frequency at 898 cm.^{-1} . The middle one (ω_{2a}) should appear between 910 and 1108 cm.^{-1} and would therefore correspond more closely to the frequency at 1060 cm.^{-1} than to that at 1150 cm.^{-1} . While this evidence for the assignment of the three group frequencies could not be regarded as conclusive in itself, when taken into consideration with the remarks above concerning intensities, it would appear to be the most consistent correlation of the spectrum yet offered.

TABLE II. THE METHYLENE CHLORIDE FREQUENCIES OF GROUP 3

Designation		Calculated values		Experimental values
Rosenthal's notation	Present notation	Upper limit	Lower limit	
ω_{4a}	ω_3	1295	1081	1266
ω_{2a}	ω_2	1108	910	1060
ω_{4c}	ω_1	843	720	896

It remains to show that the other bands can be interpreted in terms of the nine fundamentals we have now chosen. That this can readily be done is shown in Table III. The main difficulty is to account for the frequency at 1150 cm.^{-1} . This would appear to be either the addition band $\omega_1 + \delta_1$ or the difference band $\delta_2 - \delta_1$ cm.^{-1} or possibly a superposition of both of them, since the band appears to have two maxima in the infra-red and in the Raman spectrum there seems to be more uncertainty about its exact magnitude than is the case with the other frequencies. Why this should be the only combination band to appear in the Raman spectrum is not at all clear. All that we can say here is that a similar phenomenon has been observed for other polyatomic molecules (e.g. ethylene), and that the conditions determining the appearance of overtone and combination frequencies in Raman spectra are not yet understood. As regards the other assignments in Table III we might remark that all of the bands with the exception of 4' and 8 have been accounted for as simple combinations of not more than two fundamentals. Since such simple addition bands are

those which are most likely to appear, our assignment of the fundamentals appears to gain additional evidence. Our attempts to account for all of our observed bands in terms of Trumpy's fundamentals had not an equal measure of success. In several cases we have given only one assignment where alternative interpretations were possible. For instance, band 11 might equally well be interpreted as $2\omega_2$ and we have no reason for preferring the assignment given in Table III unless that it gives a slightly

TABLE III. OVERTONE AND COMBINATION BANDS OF METHYLENE CHLORIDE

Fundamentals arising from the CCl_2 group	$\left\{ \begin{array}{l} \nu_1 = 700 \\ \nu_2 = 736 \\ \delta_1 = 284 \end{array} \right.$	Fundamentals arising from the CH_2 group	$\left\{ \begin{array}{l} \nu_3 = 2985 \\ \nu_4 = 3046 \\ \delta_2 = 1425 \end{array} \right.$	Fundamentals of Group 3	$\left\{ \begin{array}{l} \omega_1 = 896 \\ \omega_2 = 1060 \\ \omega_3 = 1266 \end{array} \right.$
	Observed frequency	Assignment		Predicted frequency	
	20 985	$\nu_1 + \delta_1$		984	
	18 1155	$\nu_4 - \delta_1$		1141	
	17'' 1192	$\omega_1 + \delta_1$		1180	
	17' 1222	$\nu_1 + 2\delta_1$		1268	
	15 1548	$\omega_3 + \delta_1$		1550	
	14' 1582	$\nu_1 + \omega_1$		1596	
	14 1613	$\nu_2 + \omega_1$		1632	
	13 1792	$\nu_2 + \omega_2$		1796	
	12 1984	$\nu_2 + \omega_3$		2002	
	11 2058	$2\omega_1 + \delta_1$		2076	
	10 2137	$\omega_3 + \omega_1$		2162	
	9 2315	$\delta_2 + \omega_1$		2321	
	8 2415	$\omega_3 + \omega_1 + \delta_1$		2421	
	7 2525	$2\omega_3$		2532	
	6 2674	$\delta_2 + \omega_3$		2691	
	4' 3425	$\nu_3 + \nu_2 - \delta_1$		3420	
	4 3704	$\nu_3 + \nu_2$		3721	
	3 3937	$\nu_4 + \omega_1$		3942	
	2 4237	$\nu_3 + \omega_3$		4251	
	1 4464	$\nu_4 + \delta_2$		4471	

All frequencies are given in cm.^{-1} .

better numerical agreement with the observed frequency. This is not a sufficiently good reason, however, for excluding one assignment in favour of another, since exact numerical agreement is not to be expected because of anharmonicity and interactions. We have not given all the possible ways of interpreting each band because we were only interested in showing that all the observed bands could be accounted for very easily in terms of our

fundamentals. In actual fact there are only another two simple alternative assignments in addition to the one just quoted; they are:

Band 13 as $2\omega_1$,

Band 10 as $\nu_2 + \delta_2$.

It will be noticed that the numerical agreement between an observed and a predicted frequency is within 1 or 2 %, except the band 17' the exact position of which is impossible to determine since it appears as a shoulder on the very intense band 17.

ACKNOWLEDGEMENTS

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SUMMARY

The infra-red absorption spectrum of methylene chloride has been investigated in the liquid state between 2 and 12μ with a prism spectrometer. Twenty-six bands have been observed of which sixteen have not been recorded before; the positions and intensities of the remaining ten agree well with the works of other observers. The most important fact which emerges is that one of the very intense absorption bands has no counterpart in the Raman spectrum of this molecule. This has necessitated a new assignment of the fundamental frequencies, which has been done partly by the method of independent groups and partly by applying the theory of the isotope effect in a molecule of the type YX_4 . The latter is a new and surprisingly successful method of forming a rough numerical estimate of the magnitude of certain of the frequencies of the YX_2Z_2 molecule from a knowledge of the potential constants of the YX_4 and YZ_4 molecules. The twenty-six observed bands are accounted for very simply in terms of the new set of fundamental frequencies.

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On the velocity and temperature distributions in the turbulent wake behind a heated body of revolution

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INTRODUCTION

1. The calculation of the distribution of mean velocity in the turbulent wake behind a body of revolution in a uniform stream of an incompressible fluid was first carried out by Swain (1929) by using Prandtl's momentum transport theory of turbulent motion. The uniform stream was considered to be parallel to the axis of revolution of the body and the mean motion was assumed to be symmetrical about the same axis. Swain further adopted Prandtl's assumptions that for sufficiently high Reynolds numbers and at a sufficient distance downstream, there is geometrical and mechanical similarity in different sections of the wake, and that the values of the mixing length, l , at corresponding points in different sections are proportional to the breadths of the sections. She also assumed, as done by Schlichting (1930) in his discussion of the two-dimensional wind-shadow problem, that the mixing length l is constant over any one section of the wake.

Now, taking the x -axis along the axis of revolution of the body and the r -axis perpendicular to it, let the undisturbed velocity be denoted by U . Then, the x -component of velocity, u , in the wake may be written as

$$u = U - u^*. \quad (1)$$