SEPTEMBER 15, 1934 PHYSICAL REVIEW VOLUME 46

The Infrared Spectra of the Chlorine Derivatives of Ethylene C_2H_4

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(Received July 23, 1934)

The infrared absorption spectra of the molecules $C_2H_2Cl_2$, cis $C_2H_2Cl_2$, trans $C_2H_2Cl_2$, C_2HCl_3, C_2Cl_4 are studied in the region between 2 and 25μ. The difference of the spectra of the two symmetric isomers is shown. An attempt is made to analyze the absorption bands observed together with the Raman spectra into the fundamental vibrations of these molecules.

INTRODUCTION

At present the spectra of two molecules of the ethylene type, namely, ethylene and nitrogen tetroxide, are known. Next in simplicity come the chlorine derivatives of ethylene, C_2H_3Cl, cis $C_2H_2Cl_2$, trans $C_2H_2Cl_2$, C_2HCl_3, C_2Cl_4.[1] The Raman spectra of these molecules are known.[2] Of special interest is the work of Bonino and Brüll[3] who showed that the two symmetric isomers have distinctly different Raman spectra. From the difference of their geometric symmetry, one would expect their infrared absorption spectra to be different also. A study of the infrared spectra of these molecules will therefore be of some interest. As some fundamental vibrations of molecules are active in infrared absorption but are inactive in Raman scattering because of symmetry properties of the molecules, the combined data of infrared and Raman spectra may be necessary for obtaining all the fundamental vibrations of the molecules. Until now the only infrared data on these molecules are the absorption curve of C_2Cl_4 obtained by Coblentz[4] for the liquid state. In this work the vapors of these compounds were studied.

EXPERIMENTAL

In this investigation, the C_2HCl_3, C_2Cl_4, $C_2H_2Cl_2$ were obtained from the Eastman Kodak Laboratory. The cis and trans dichloroethylenes $C_2H_2Cl_2$ were separated by repeated fractional distillation, the original sample being very rich in the cis form (b.p..60°C).[5] Another sample of the trans $C_2H_2Cl_2$ was kindly furnished by Mr. G. A. Stone who obtained an enriched portion by heating the sample in a closed tube at 240°C for twelve hours in the course of experiments on the transformation of one isomer into another. As the amount of trans $C_2H_2Cl_2$ was small, it had not been possible to obtain pure trans $C_2H_2Cl_2$ which is free from the cis form. However, by varying the amount of the cis form there is no difficulty in distinguishing between the spectra of the two forms.

The vinyl chloride C_2H_3Cl was obtained by boiling a mixture of ethylene chloride $C_2H_4Cl_2$ (1.2 dichloroethane) with sodium hydroxide solution and alcohol. The vinyl chloride generated was separated in a fractionating column.

For the preliminary survey over the whole region from 2 to about 25μ, the recording spectrometer described by Randall and Strong[6] fitted with a 60° KBr prism was used. A big cell with KBr windows contained the substance at its saturated vapor pressure at room temperature and the radiation from a Nernst glower traversed a path of about 60 cm in the cell. Thus it is not likely that any fundamental band in this region may have been overlooked. For study of the individual bands, a prism-grating spectrometer was used. Shorter cells of 10 cm long with KBr or NaCl windows contained the vapor at the desired pressure for the mapping of the envelopes of the bands.

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* Now at National University of Peking. The work was done when holding a China Foundation Fellowship.

[1] The asymmetric isomer $CH_2 : CCl_2$ cannot be investigated on account of its ready polymerization under the action of light.

[2] Kohlrausch, *Smekal-Raman Effekt.* (1931).

[3] Bonino and Brüll, Zeits. f. Physik **58**, 194 (1929); Atti. accad. lincei **13**, 275 (1931).

[4] Coblentz, *Investigations on Infrared Spectra* (1905).

[5] There has been quite some confusion in the literature as to whether the high b.p. 60°C or the low b.p. 48°C is the cis form. By dielectric constant measurement, it is shown that the high b.p. form has a permanent moment, and hence is the cis isomer.

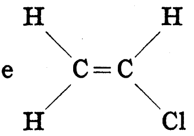
[6] Randall and Strong, Rev. Sci. Inst. **2**, 585 (1931).

TABLE I. *Infrared and Raman spectra of C_2H_3Cl. s, m, w denote that the band is strong, medium, weak in intensity.*

Infrared absorption band in cm^{-1}	3130 (s)		1616 (s)	1390 (s)		1300 (s)	1160 (m)	1053 (s)	910 (s)	935 (s)	719 (s)	617 (s)		
Raman scattering in cm^{-1}	3134 (s)	3036 (s)	1608 (m)		1355 (m)	1271 (m)	1186 (?)	1048 w	909 w		715 (m)	610 w	535 w	400 (s)

As the rotational lines of these molecules are too close to be easily resolved, no attempt was made to obtain the fine structure of the bands and the width of the slits of the spectrometer was so adjusted that it included a spectral interval of about 1.5–2 wave numbers in the different regions of the spectrum.

(1) Vinyl chloride



Nine regions of absorption are located at 3.2μ, 6.2μ, 7.2μ, 7.7μ, 8.62μ, 9.5μ, 10.8μ, 13.9μ, 16.2μ. Of all these, the band at 8.62μ is of medium intensity, while all the others are very intense. The band at 10.8μ is a very broad one and examination under different vapor pressures indicates that there are two bands close to each other with maxima at 10.7μ and 11.0μ. As the molecule is highly unsymmetric, little information will be obtained from the contour of the bands and they have not been examined with the grating spectrometer. A comparison of the infrared and the Raman spectra is given in Table I.

(2) Cis $C_2H_2Cl_2$

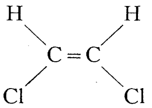
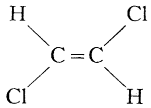
Six regions of intense absorption are observed with centers at 3.240μ, 6.28μ, 7.67μ, 11.7μ, 14.4μ and 17.55μ. The envelopes of these bands are given in Fig. 1.

(3) Trans $C_2H_2Cl_2$

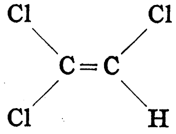
Five regions of intense absorption are located with centers at 3.236μ, 8.35μ, 10.91μ, 12.20μ, 16.15μ. The envelopes of these bands are given in Fig. 2.

The infrared and the Raman spectra of these two isomers are given in Table II for comparison.

TABLE II. *Infrared and Raman spectra of cis and trans $C_2H_2Cl_2$.*

			
Infrared	(cis) Raman	Raman	(trans) Infrared
	3161 ?	3141	
3087 s	3079 s	3079 s	3090 s
1591 s	1586 s	1581 s	
1303 s		1271 s	
	1186 s		1200 s
857 s			917 s
	714 s	846 s	
694 s			820 s
570 s	568 s	763 s	
	407 s		620 s
	173 s	251	

(4) Trichloroethylene



Seven regions of intense absorption are located with centers at 3.230μ, 6.4μ, 7.97μ, 10.63μ, 11.77μ, 12.76μ, 15.80μ. The envelopes of the bands and the comparison with the Raman spectra are given in Fig. 3 and Table III, respectively. The band at 6.4μ has not been examined with the grating spectrometer, for its overlapping with the strong absorption by water vapor in the atmosphere makes this difficult.

(5) Tetrachloroethylene C_2Cl_4

There are only 4 intense bands in the whole region between 2 and 25μ. They have centers at 10.95μ, 12.48μ, 12.80μ, 13.3μ. The bands at 5.6μ, 7.5μ, 9.0μ observed by Coblentz[3] for the

TABLE III. *Infrared and Raman spectra of C_2HCl_3.*

Infrared absorption bands in cm^{-1}	3096 m		1590 m			1250 m		940 s	850 s	784 s		633 s					
Raman lines in cm^{-1}		3082 s	1586 s	1385 s	1242 s		1226 w	947 w	845 w	786 m	765	628 s	449 m	381 s	274 s	212 s	165 s

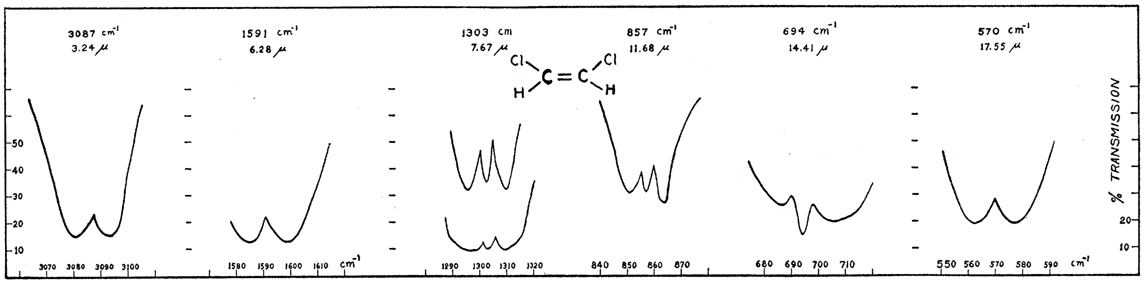


FIG. 1. Infrared absorption bands of cis $C_2H_2Cl_2$.

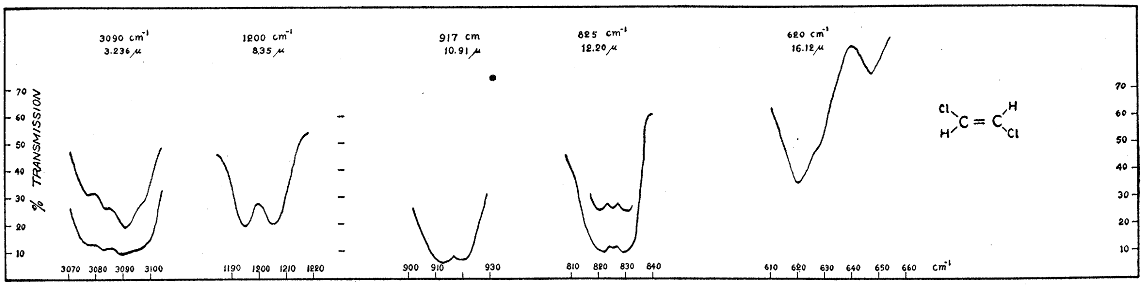


FIG. 2. Infrared absorption bands of trans $C_2H_2Cl_2$.

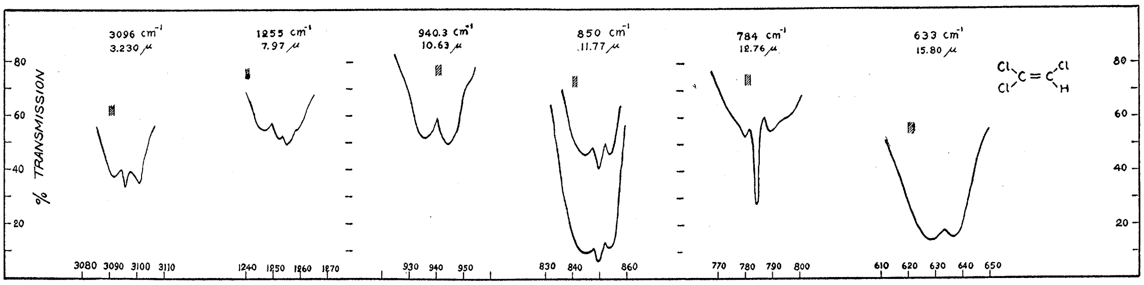


FIG. 3. Infrared absorption bands of C_2HCl_3. The width of spectrometer slits used in mapping the different bands is indicated by the shaded strips.

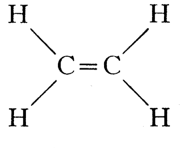
liquid cannot be found with radiation travelling 60 cm of path of saturated C_2Cl_4 vapor at room temperature, while the bands at 10.95μ, 12.48μ, 12.80μ show about 70 percent absorption for a path of 10 cm at 2 cm pressure. Thus it is unlikely that any one of the bands at 5.6μ, 7.5μ, 9.0μ is a fundamental band. (See Table IV and Fig. 4.)

TABLE IV. *Infrared and Raman spectra of* C_2Cl_4.

Infrared absorption in cm⁻¹		913 s	802 s	782 s	755 m					
Raman lines in cm⁻¹	1570 s					512 m	447 s	383 w	341 m	234 s

DISCUSSION

While the molecules C_2H_3Cl and C_2HCl_3 have no simple symmetry, and all the twelve fundamental vibrations are expected to be active both in infrared absorption and in Raman scattering, it is not so with cis $C_2H_2Cl_2$, trans $C_2H_2Cl_2$ and C_2Cl_4. Assuming the forms of these molecules to be that of the ethylene type[7]



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[7] The form of these molecules seems to be well established by the electron interference measurements of Weirl, Ann. d.

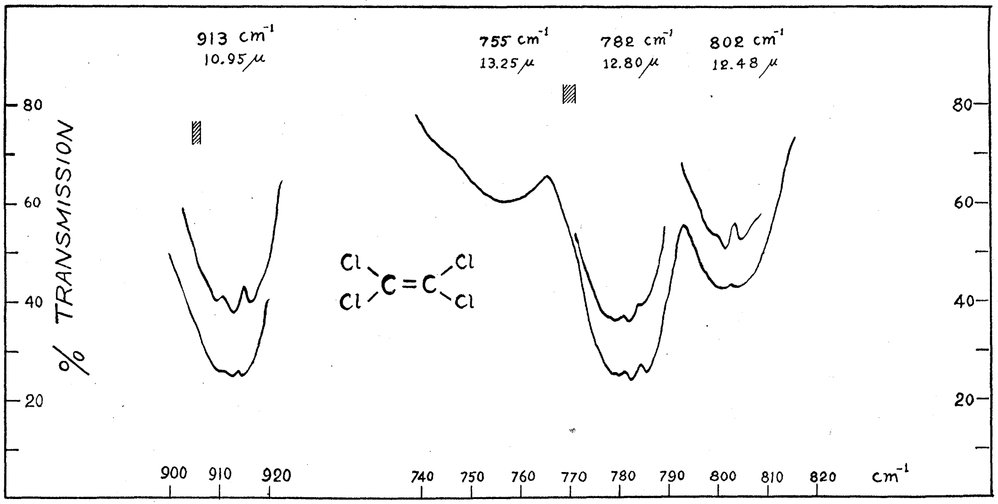
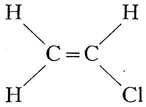
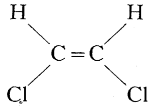
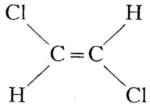
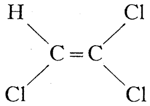
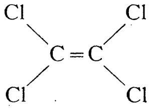


FIG. 4. Infrared absorption bands of C_2Cl_4. The width of spectrometer slits is indicated by the shaded stripes.

TABLE V. *Fundamental frequencies of the chlorine derivatives of C_2H_4.* The crosses indicate inactive infrared and inactive or weak Raman frequencies. The notations under the columns (S) and (M) are those of Sutherland[9] and Mecke, respectively.

Modes of vibration												
	(S)	(M)	Infra-red	Raman	Infra-red	Raman	Infra-red	Raman	Infra-red	Raman	Infra-red	Raman
ν_1	(ν_2)	$\nu_{\pi s}$	1615	1608	1591	1586	X	1581	1590	1586	X	1570
ν_2	(ν_1)	$\nu_{\pi a}$	1390		1303	X	1200	X	1250		913	X
ν_3	(ν_4)	$\delta_{\pi s}$		1355		1186	X	1271		1241	X	446
ν_4	(ν_3)	$\delta_{\pi a}$	1300	1271	857	X	917	X				X
ν_5	(ν_8)	$\nu_{2\pi s}$	1160	1186	X	714	X	763		384	X	235
ν_6	(ν_7)		617	610	X	X		X		449	X	X
ν_7	(ν_6)	$\nu_{\sigma s}$	3130	3134		X	X	3141	3096		X	X
ν_8	(ν_5)	$\nu_{\sigma a}$		3036	3087	3079	3090	X		3082	862	X
ν_9	(ν_{10})	$\delta_{\sigma s}$	910	909		X	X	846	850	845	X	X
ν_{10}	(ν_9)	$\delta_{\sigma a}$	719	715	570	568	620	X	633	628	755	X
ν_{11}	(ν_{12})	$\delta_{\sigma' s}$	1053	1048	X	X	X	X	940	947	X	X
ν_{12}	(ν_{11})	$\delta_{\sigma' a}$	935		694	X	820	X	784	786	782	X

one can easily obtain the selection rules in infrared absorption and Raman scattering for these molecules, as given in Table V. The twelve modes of vibrations are represented in Fig. 5.

From symmetry considerations, the cis $C_2H_2Cl_2$ should have nine active vibrations in infrared absorption, five intense lines in the Raman spectrum; while the trans $C_2H_2Cl_2$ should have six infrared active vibrations, five intense Raman lines. C_2Cl_4, possessing a higher symmetry, should have only five infrared active vibrations and three[8] intense Raman lines.

The assignment given in the table is partly based on mechanical considerations, partly on the shape of the envelopes of the individual bands, and on considering their relation with the

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Physik **13**, 453 (1932) and R. W. Dormte, Chem. Phys. **1**, 566 (1933).

[8] For C_2Cl_4, the vibrations ν_7, ν_9, ν_{11} will be active in Raman scattering, according to the considerations of Placzek, Leipziger Vorträge (1931), but they are very weak and will probably not be observed experimentally. Similarly such weak lines are here considered inactive for cis and trans $C_2H_2Cl_2$.

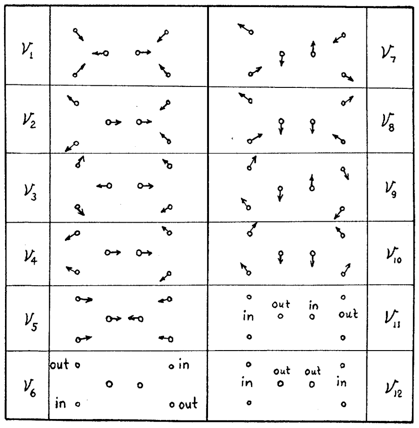

FIG. 5. Fundamental vibrations of ethylene type molecules.

Raman spectra as indicated by the selection rules. The intensity of the four observed bands of C_2Cl_4 shows that they are fundamental bands; the other active one has not been observed up to 25μ. It is possible that it lies beyond 25μ. The scarcity of lines in the Raman spectrum and the intensities of the 1570, 446, 235 cm^{-1} lines show that they are the three active frequencies ν_1, ν_3, ν_5. From electron diffraction data[7] one finds that the principal moments of inertia of C_2Cl_4 stand roughly in the ratio 2 : 1 : 1 and one would not expect the envelopes of the bands to exhibit distinct doublet structure or intense Q branch. This agrees with the observed envelopes where the insufficiently resolved maxima might not be real. This makes the distinction between ν_2, ν_4, ν_8, ν_{10} inpracticable. Assuming ν_2 is 913 cm^{-1}, a calculation for ν_4 from a relation among ν_1, ν_2, ν_3, ν_4, ν_5 obtained on the simplifying assumption that only neighboring atoms act on each other[9] gives $\nu_4 \sim 385$. This is very rough, as the force constant between the two C carbons so calculated does not agree with that obtained by similar considerations from C_2H_4.

For cis $C_2H_2Cl_2$, the principal moments of inertia calculated on electron diffraction data stand approximately in the ratio 1 : 6.5 : 7.5. Reference to Dennison's diagram[10] shows that ν_1, ν_3, ν_8, ν_{10} would possess a doublet structure and ν_2, ν_4, ν_7, ν_9 would possess something like a Q branch. In the case of trans $C_2H_2Cl_2$, as the directions of changes of electric moment do not coincide with the principal axes of moments of inertia, the above considerations no longer apply, and the assignment of the active frequencies is mainly guided by reference to its Raman spectra and the spectra of the cis molecule. The scheme in Table V may be regarded as tentative; a final assignment can be made only with the aid of additional data on the combination and harmonic bands of these molecules.

On similar considerations, the fundamental vibrations of C_2H_3Cl and C_2HCl_3 are also given in Table V.

The writer wishes to acknowledge his deep appreciation to Professor H. M. Randall whose courtesy in extending him the privilege of working in this Laboratory makes this study possible.

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[9] G. B. B. M. Sutherland, Proc. Roy. Soc. **A141**, 342 (1933).

[10] D. M. Dennison, Rev. Mod. Phys. **3**, 280 (1931).