

## InfraRed and Raman Spectra of Polyatomic Molecules. V. Cyclopropane and Ethylene Oxide

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## Infra-Red and Raman Spectra of Polyatomic Molecules. V. Cyclopropane and Ethylene Oxide

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The Raman and infra-red spectra of cyclopropane and ethylene oxide have been examined. The infra-red spectra were examined using a potassium bromide prism from 25 to  $11\mu$ , a rock-salt prism from 15 to  $7\mu$  and a fluorite prism from 8 to  $1.5\mu$ . Because of the greater dispersion of fluorite more bands than had previously been observed were resolved in the region in which this prism could be used. The nature, symmetry and selection rules of the vibrations of these two molecules are summarized. It was found possible to make a complete assignment of the fundamental frequencies of cyclopropane which accounts for all the features of the spectra. With ethylene oxide it was only possible to make a partial assignment. The frequencies of the corresponding fundamental modes of vibration of the two molecules are compared. On the basis of the frequency assignment described, values for the free energy, entropy and heat capacity of cyclopropane are calculated between  $100^\circ$  and  $1000^\circ\text{K}$ .

A COMPLETE knowledge of the vibration frequencies of cyclopropane and of ethylene oxide would be of considerable interest in relation to the theory of molecular vibrations. This necessitates a knowledge of the Raman and infra-red spectra and of the heat capacity at various temperatures. In this paper are described some measurements on the spectra and the results are discussed.

The Raman spectrum of cyclopropane has been examined by a number of workers,<sup>1</sup> the most complete investigations being those of Ananthakrishnan<sup>2</sup> and of Harris, Ashdown and Armstrong.<sup>3</sup> In the infra-red Bonner<sup>4</sup> examined the region  $15-1.5\mu$  using a rocksalt prism spectrograph and King, Armstrong and Harris<sup>5</sup> the region  $10-0.8\mu$  using both a rocksalt prism spectrograph and a quartz monochromator. Measurements on the Raman spectrum of ethylene oxide have been made by Lespiau and Bourguel,<sup>6</sup> by Timm and Mecke<sup>7</sup> and by Ananthakrishnan.<sup>2</sup> The infra-red spectrum has been studied by Bonner<sup>4</sup> from 15 to  $1.5\mu$ .

In this investigation photographs of the Raman

spectra of both cyclopropane and ethylene oxide were taken. More particularly, however, the infra-red spectra of both compounds were studied in the region  $25-1.5\mu$ . For this a potassium bromide prism was used from 25 to  $11\mu$ , a rock-salt prism from 15 to  $7\mu$  and a fluorite prism from 8 to  $1.5\mu$ . The potassium bromide prism enabled the spectra beyond  $15\mu$  to be studied. Fluorite gives better dispersion than rocksalt for wavelengths shorter than  $8\mu$  and is particularly valuable therefore for studying the fundamentals and combination levels from 1200 to  $3000\text{ cm}^{-1}$ . Above  $3000\text{ cm}^{-1}$  a quartz prism is to be preferred.

### CYCLOPROPANE

#### Experimental results

The Raman spectrum of liquid cyclopropane at  $-40^\circ\text{C}$  was examined using the apparatus described by Gershinowitz and Wilson.<sup>8</sup> The spectrum was excited by the 4047A and 4358A mercury lines. The results confirm entirely those of Ananthakrishnan who used the same means of excitation. No evidence was found for the  $382\text{ cm}^{-1}$  frequency observed by Harris, Ashdown and Armstrong using the 2537A mercury line, but this may arise because they employed more intense excitation.

The infra-red spectrum was studied using the apparatus described by Gershinowitz and Wilson<sup>9</sup>

<sup>1</sup> Lespiau, Bourguel and Wakeman, *Bull. Soc. Chim.* **4**, 51, 400 (1932). Kohlrausch and Köppl, *Zeits. f. physik. Chemie* **B26**, 209 (1934).

<sup>2</sup> Ananthakrishnan, *Proc. Ind. Acad. Sci.* **4**, 82 (1936).

<sup>3</sup> Harris, Ashdown and Armstrong, *J. Am. Chem. Soc.* **58**, 852 (1936).

<sup>4</sup> Bonner, *J. Chem. Phys.* **5**, 704 (1937).

<sup>5</sup> King, Armstrong and Harris, *J. Am. Chem. Soc.* **58**, 1580 (1936).

<sup>6</sup> Lespiau and Bourguel, *Bull. Soc. Chim.* **47**, 1365 (1930).

<sup>7</sup> Timm and Mecke, *Zeits. f. Physik* **97**, 221 (1935).

<sup>8</sup> Gershinowitz and Wilson, *J. Chem. Phys.* **6**, 247 (1938).

<sup>9</sup> Gershinowitz and Wilson, *J. Chem. Phys.* **6**, 197 (1938).

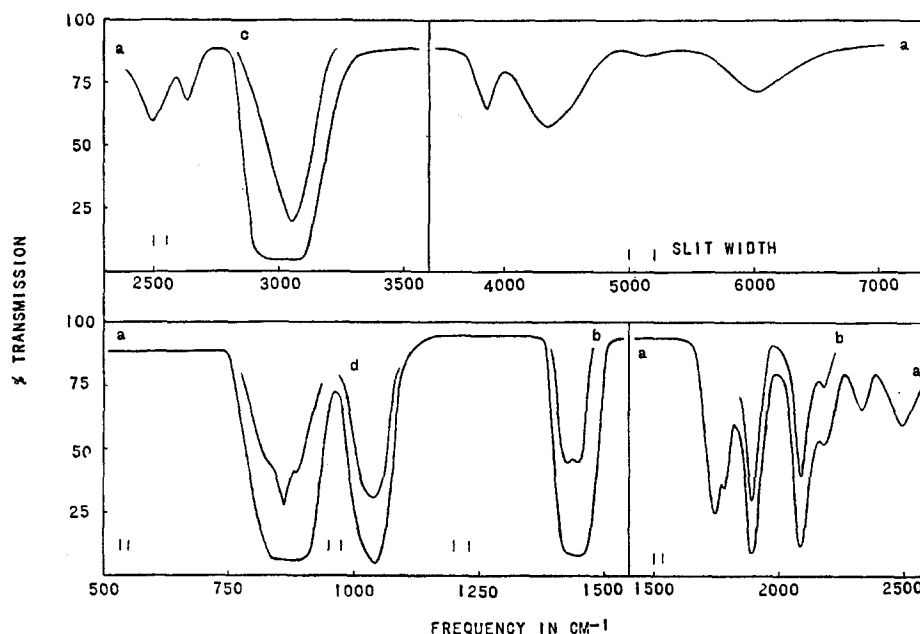


FIG. 1. Infra-red transmission of cyclopropane gas. Path length, 30 cm; pressures, (a) 750 mm, (b) 270 mm, (c) 120 mm, (d) 50 mm, (e) 30 mm.

only with the addition of a fluorite prism. The apparatus was calibrated by observing known bands of ethylene, benzene, acetylene and carbon dioxide. The gaseous cyclopropane was contained in cylindrical cells 20–30 cm in length and closed by windows of potassium bromide and rocksalt. Gas pressures from 30–750 mm were used.

Figure 1 shows the transmission curve that was obtained experimentally. The positions of the bands together with the estimated intensities are summarized in Table I. This table also summarizes the available Raman data. As regards the individual bands, that at  $860\text{ cm}^{-1}$  appears to be unsymmetrical when plotted on a frequency scale and shows apparently a  $Q$  branch. The  $10\mu$  band showed maximum absorption at  $1041\text{ cm}^{-1}$ . Bonner gave the center as  $1020\text{ cm}^{-1}$ . The band seems to be somewhat unsymmetrical, the transmission curve rising more rapidly on the high frequency side. The fluorite prism resolved the band at  $1435\text{ cm}^{-1}$  into two branches, the doublet separation being  $20\text{ cm}^{-1}$ . The band at  $1739\text{ cm}^{-1}$  was found to have a shoulder on the high frequency side, the position of this being  $1779\text{ cm}^{-1}$ . Fairly intense bands were observed at  $1890$  and  $2083\text{ cm}^{-1}$  in agreement with Bonner. In the region from here

up to  $3000\text{ cm}^{-1}$ , whereas Bonner observed only one band the fluorite prism was able to resolve four. The band at  $3.3\mu$  appeared at  $3049\text{ cm}^{-1}$  compared with Bonner's value of  $3086\text{ cm}^{-1}$ . The band at  $3580\text{ cm}^{-1}$  described by King, Ashdown and Armstrong was not observed, but a band was found at  $3846\text{ cm}^{-1}$ . The band observed at  $4348\text{ cm}^{-1}$  (Bonner gives  $4425\text{ cm}^{-1}$ ) was separated by King, Ashdown and Armstrong into two bands at  $4200$  and  $4450\text{ cm}^{-1}$  presumably because a quartz prism was used by them in this region. A very weak band was observed at  $5128\text{ cm}^{-1}$  and faint broad band at about  $6020\text{ cm}^{-1}$ . Despite repeated investigation no band could be found at  $15\mu$  where faint absorption was observed by Bonner. Except for the absence of the  $15\mu$  band and the resolution of more faint bands because of higher dispersion, the results described here agree closely with those of Bonner.

### Symmetry properties

The cyclopropane molecule provides an example of the group  $D_{3h}$ . In Table II are summarized the number of vibrations in the various classes together with their symmetry and selection rules. In the first column are listed the symmetry classes forming the group  $D_{3h}$  and in the

second the number of vibrations of the cyclopropane molecule which belong to these various classes. Vibrations in the classes designated by the letter *A* are nondegenerate while those in the *E* classes are doubly-degenerate. In the third and fourth columns the selection rules for the Raman and infra-red spectra are given while the last two columns give the symmetry of the vibrations with respect to  $\sigma_h$ , the plane of the  $C_3$  ring and  $3\sigma_v$ , the three symmetry planes perpendicular to  $\sigma_h$ . It will be seen from Table II that there are two completely inactive fundamental vibration frequencies, four frequencies that should be active in both the Raman and infra-red spectra, two that should be active in the infra-red only and six in the Raman only. Of these last six the three in  $A_1'$  should lead to polarized Raman lines.

### Form of vibrations

There will be four distinct molecular vibrations which involve mainly changes in the carbon

TABLE I. *The observed wave-lengths and frequencies of the infra-red bands of cyclopropane and the Raman frequencies.*

INFRA-RED SPECTRUM			RAMAN FREQUENCIES
DESCRIPTION	WAVE-LENGTH ( $\mu$ )	FREQUENCY ( $\text{cm}^{-1}$ )	
very strong	<i>P</i> branch*	12.10	826
	<i>Q</i> branch	11.63	860
	<i>R</i> branch	11.29	886
		9.61	1041
medium strong	<i>P</i> branch	7.02	1425
	Center	6.97	1435
	<i>R</i> branch	6.92	1445
			1454
medium		5.75	1739
weak		5.62	1779
strong		5.29	1890
medium strong		4.80	2083
weak		4.59	2179
weak		4.29	2331
medium weak		4.01	2494
weak		3.80	2632
			2852 ( <i>P</i> )
			2952 ( <i>P</i> )
			3010 ( <i>P</i> )
			3028 ( <i>P</i> )
			3080
very strong	3.28	3049	
weak	2.60	3846	
medium weak	2.30	4348	
very weak	1.95	5130	
weak	1.66	6020	

\* The notation *P*, *Q*, *R* is used for convenience and is not intended to indicate that the band is a parallel one.  
 † (*P*) indicates that the line is polarized.

TABLE II. *The symmetry and selection rules for the vibrations of the cyclopropane molecule.*

SYM-METRY CLASS	NO. OF FUNDAMENTAL VIBRATIONS IN CLASS	PERMITTED TO APPEAR IN		SYMMETRY WITH RESPECT TO	
		RAMAN	INFRA-RED	$\sigma_h$	$3\sigma_v$
$A_1'$	3	Yes	No	<i>S</i>	<i>S</i>
$A_2'$	1	No	No	<i>S</i>	<i>A</i>
$E'$	4	Yes	Yes	<i>S</i>	degenerate
$A_1''$	1	No	No	<i>A</i>	<i>A</i>
$A_2''$	2	No	Yes	<i>A</i>	<i>S</i>
$E''$	3	Yes	No	<i>A</i>	degenerate

hydrogen bonds. These will belong to the classes  $A_1'$ ,  $E'$ ,  $A_2''$  and  $E''$  and will have frequencies in the neighborhood of  $3000 \text{ cm}^{-1}$ . Also there will be two vibrations which involve mainly distortions of the  $C_3$  ring. One of these will be in the  $A_1'$  class and the other in  $E'$ . The other eight fundamental frequencies will depend on motions of the methylene groups. These may be divided into four types: (a) deformation of the methylene groups symmetrical to  $\sigma_h$  and  $\sigma_v$  involving a change in the HCH angle; (b) bending of the methylene group against the ring with the HCH angle remaining the same, this also being symmetrical to  $\sigma_h$  but antisymmetrical to  $\sigma_v$ ; (c) rocking of the methylene groups, the HCH angle remaining constant and the motion being antisymmetrical to the  $\sigma_h$  plane but symmetrical to the  $\sigma_v$  plane; (d) twisting of the methylene groups, the motion being antisymmetrical to both  $\sigma_h$  and  $\sigma_v$ . The nature of these elementary motions is shown diagrammatically in Fig. 2. All actual motions of the methylene groups can be explained as combinations of these four elementary motions. The two methylene deformations will be in the classes  $A_1'$  and  $E'$ , the bending motions in  $A_2'$  and  $E'$ , the rocking motions in  $A_2''$  and  $E''$  and the twisting motions in  $A_1''$  and  $E''$ . Any actual motions of the cyclopropane molecule will, of course, not be simple. For example one of the individual vibrations in  $E'$  will involve a combination of a methylene deformation, a methylene bending and ring deformation. However, though not rigidly applicable, this simplification may assist in fixing the order of magnitude of various frequencies and will also be of help in comparing the results for cyclopropane and ethylene oxide. In Table III are

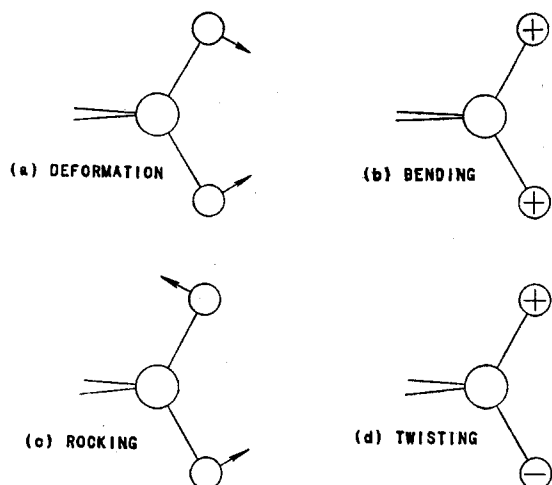


FIG. 2. Diagrammatic representation of the four elementary motions of the methylene group in cyclopropane, (a) Deformation, (b) bending, (c) rocking, (d) twisting.

given the types of distortions that will occur in the vibrations of the various classes.

### The vibration frequencies

Ananthakrishnan observed in the Raman effect polarized lines at 1503 and 1187 in addition to those in the neighborhood of 3000  $\text{cm}^{-1}$ . For the  $A_1'$  frequencies we should expect therefore, *ca.* 3000, 1503 and 1187  $\text{cm}^{-1}$ . The 3000  $\text{cm}^{-1}$  frequency corresponds, of course, to the carbon-hydrogen valency vibration and, by analogy with other molecules, the 1503  $\text{cm}^{-1}$  frequency may be supposed to result from a vibration involving largely methylene deformation. 1187  $\text{cm}^{-1}$  is then the ring frequency as has been postulated by Bonner.<sup>10</sup> The  $E'$  vibrations are active in both spectra. The carbon-hydrogen valency vibration frequency must be *ca.* 3000 and the methylene

TABLE III. Distortions occurring in the vibrations of the various symmetry classes for cyclopropane.

$A_1'$	$A_2'$	$E'$
CH valency CH <sub>2</sub> deformation ring deformation	CH <sub>2</sub> bending	CH valency CH <sub>2</sub> deformation CH <sub>2</sub> bending ring deformation
$A_1''$	$A_2''$	$E''$
CH <sub>2</sub> twisting	CH valency CH <sub>2</sub> rocking	CH valency CH <sub>2</sub> rocking CH <sub>2</sub> twisting

<sup>10</sup> Bonner, J. Chem. Phys. 5, 293 (1937).

deformation frequency 1435  $\text{cm}^{-1}$ . The latter appears in the Raman effect at 1434  $\text{cm}^{-1}$  and in the infra-red at 1435  $\text{cm}^{-1}$ . As has been suggested by Bonner, the ring frequency in this class must be 860  $\text{cm}^{-1}$  (Raman effect 863, Infra-red 860). For the fourth frequency in this class 1022  $\text{cm}^{-1}$  seems to be the most likely value since Harris, Ashdown and Armstrong observed a Raman shift of 1022  $\text{cm}^{-1}$  and there is an infra-red band at 1041  $\text{cm}^{-1}$ . This will be discussed in more detail later. For the remaining frequency symmetrical to  $\sigma_h$  there is the methylene bending vibration in  $A_2'$ . This is totally inactive but since the methylene bending frequency in  $E'$  has the value 1022 we should expect this to be at least of approximately the same order of magnitude.

As regards the vibrations antisymmetric to  $\sigma_h$  we may consider first those in  $A_2''$  which are infra-red active. One of these will be in the neighborhood of 3050  $\text{cm}^{-1}$ . For the other there are only two infra-red bands below 1400  $\text{cm}^{-1}$ , *viz.*, 860 and 1041. It seems likely that by comparison with the frequencies of similar motions in ethylene and formaldehyde the methylene rocking frequency is not as low as 860  $\text{cm}^{-1}$ . If the frequency is 1041  $\text{cm}^{-1}$ , the  $10\mu$  band would appear to be really two superimposed bands. This is in agreement with the appearance of this band. The appearance is, moreover, quite in keeping with the existence of a band at 1041  $\text{cm}^{-1}$  with a

TABLE IV. The magnitudes of the fundamental frequencies of cyclopropane with the corresponding Raman and infra-red frequencies.

SYMMETRY CLASS	SUGGESTED FUNDAMENTAL FREQUENCIES	RAMAN FREQUENCIES	INFRA-RED FREQUENCIES
$A_1'$	3000 1485 1187	2952, 3010, 3028 1503, 1454 1187	forbidden forbidden forbidden
$A_2'$	1070	forbidden	forbidden
$E'$	3000 1435 1022 860	(3008) 1434 1022 863	(3049) 1435 (1041) (860)
$A_1''$	1000	forbidden	forbidden
$A_2''$	3050 1041	forbidden forbidden	3050 1041
$E''$	3080 1250 740	3080 not observed 740	forbidden forbidden forbidden

less intense band at  $1022\text{ cm}^{-1}$ . Another possibility is that this fundamental does not appear in the infra-red spectrum although it is allowed. Data on other molecules however seem to indicate that fundamentals allowed in the infra-red usually appear. The fundamentals in  $E''$  should appear depolarized in the Raman effect. This indicates for the carbon-hydrogen valency vibrations  $3080\text{ cm}^{-1}$  and for the methylene twisting vibration  $740\text{ cm}^{-1}$ . The third fundamental in  $E''$ , the methylene rocking vibration, apparently does not appear. The remaining fundamental, which is in  $A_1''$ , is completely inactive.

By the above considerations, therefore, the values of eleven of the fourteen fundamental frequencies have been fixed. The others must be determined by a consideration of the overtone and combination levels. At this stage it may be mentioned that it seems probable that resonance would occur between the first overtone of  $740\text{ cm}^{-1}$  and the methylene deformation fundamental in  $A_1'$ . This would indicate that this fundamental has the unperturbed frequency of

TABLE V. Suggested interpretation of overtone and combination levels of cyclopropane.

OBSERVED FREQUENCY	OBSERVED IN:	SUGGESTED COMBINATION	SYMMETRY CLASS
382	Raman	$1250 - 865 = 385$	$[A_1'' + A_2'' + E'']$
1454	Raman	$2 \times 740 = 1480$	$A_1' + E'$
1503		1485	$A_1'$
1739	Infra-red	$1000 + 740 = 1740$	$E'$
1779	Infra-red	$1041 + 740 = 1781$	$E'$
1890	Infra-red	$1020 + 865 = 1885$	$A_1' + A_2' + E'$
1873	Raman	$1020 + 1070 = 2090$	$E'$
2083	Infra-red	$1435 + 740 = 2175$	$A_1'' + A_2'' + E''$
2179	Infra-red		
2331	Infra-red	$1485 + 865 = 2350$	$E'$
2494	Infra-red	$1485 + 1020 = 2505$	$E'$
		$1435 + 1070 = 2505$	$E'$
2632	Infra-red	$1435 + 1187 = 2622$	$E'$
2856	Raman	$2 \times 1435 = 2870$	$A_1'$
2952	Raman	$4 \times 740 = 2960$	$A_1'$
3010		$2 \times 1485 = 2970$	$A_1'$
3028		3000	$A_1'$
3846	Infra-red	$3000 (A_1') + 865 = 3865$	$E'$
		$3000 (E') + 865 = 3865$	$A_1' + E'$
4200*	Infra-red	$3000 (E') + 1187 = 4187$	$E'$
		$3050 + 1187 = 4237$	$A_2''$
		$3000 (E') + 1250 = 4250$	$A_1'' + A_2'' + E''$
4450*	Infra-red	$3000 (A_1') + 1435 = 4435$	$E'$
		$3000 (E') + 1435 = 4435$	$A_1' + A_2' + E'$
		$3000 (E') + 1485 = 4485$	$E'$
		$3000 (A_1') + 2 \times 740 = 4480$	$A_1' + E'$
		$3000 (E') + 2 \times 740 = 4480$	$A_1' + A_2' + 2E'$
5128	Infra-red	$3000 (E') + 2 \times 1070 = 5140$	$E'$
		$3080 + 2 \times 1022 = 5124$	$A_1'' + A_2'' + 2E''$
		$3050 + 1041 + 1022 = 5113$	$E'$
		$3000 + 1250 + 860 = 5110$	$A_1'' + A_2'' + E''$
6020	Infra-red	First overtones of $E'$ and $E''$ 3000 fundamentals. Also combinations	

\* Observed by King, Armstrong and Harris.<sup>5</sup>

ca.  $1485\text{ cm}^{-1}$  rather than  $1503\text{ cm}^{-1}$ , resonance giving rise to two neighboring levels leading to the Raman frequencies at  $1503$  and  $1454\text{ cm}^{-1}$ . On this basis the Raman lines with  $\Delta\nu = 1454\text{ cm}^{-1}$  should be polarized as are those with  $\Delta\nu = 1503\text{ cm}^{-1}$ . The closeness of the  $1434\text{ cm}^{-1}$  Raman line has prevented the determination of this. The fundamentals still to be determined are the two in  $A_2'$  and  $A_1''$ , and one of the  $E''$  vibrations.

In Table IV is given an assignment of all the fundamentals together with the manner of their appearance in the spectra which seems to explain most satisfactorily all the observed overtones. In cases where the fundamental is the member of a resonance doublet or triplet the frequencies of all the components have been listed. Also where the fundamental may be obscured by another the value of the latter has been included in brackets. It will be seen that only one Raman line is definitely absent and there are no infra-red bands certainly missing.

### Overtone and combination levels

Table V summarizes the suggested interpretation of the observed overtone levels. The first and second columns give the observed frequency and the spectrum in which it is detected. The third column gives the suggested combination together with the calculated frequency and the last the symmetry class to which the level belongs. In the large majority of cases only binary combinations of fundamental frequencies have been used in interpreting the observed levels and for the exceptions there are circumstances which render such postulates acceptable. In the first case one component of the resonance triplet  $2952$ ,  $3010$ ,  $3028\text{ cm}^{-1}$  has been ascribed to  $4 \times 740$ , that is, the third overtone. The prominence of the overtone presumably is to be explained because of resonance with the first overtone of  $1485\text{ cm}^{-1}$  and the  $A_1'$  fundamental, just as the first overtone appears because of resonance with the  $A_1'$  fundamental at  $1485\text{ cm}^{-1}$ . In the second case certain overtones above  $4000\text{ cm}^{-1}$  have been ascribed to ternary combinations but only when a number of such overtones are coincident. This superposition may lead to a piling up of absorption and hence the appearance of an otherwise rather improbable band.

The above assignment therefore accounts in a

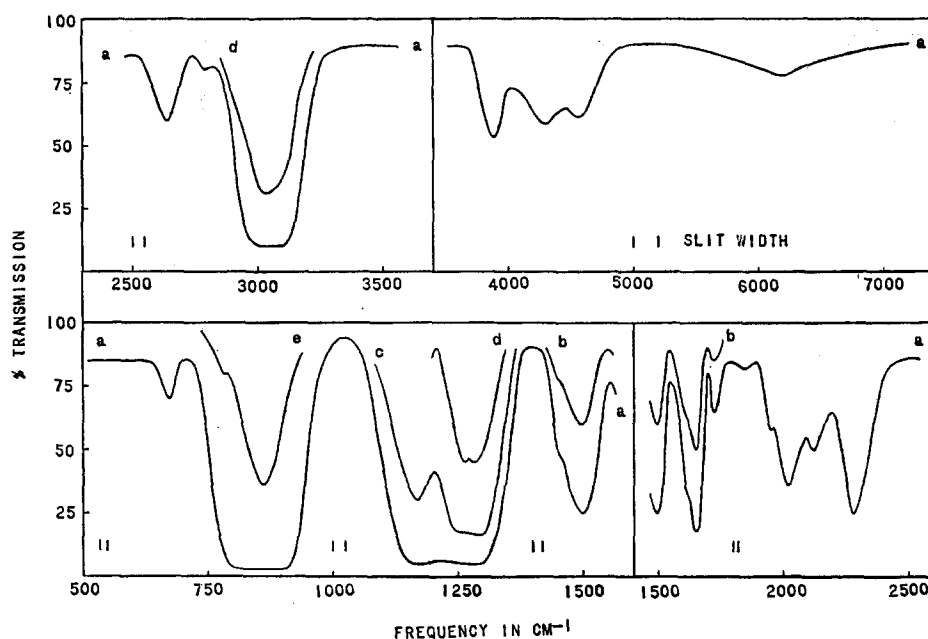


FIG. 3. Infra-red transmission of ethylene oxide gas. Path length 30 cm; pressures, (a) 750 mm, (b) 270 mm, (c) 220 mm, (d) 40 mm, (e) 10 mm.

completely satisfactory manner for the observed spectroscopic evidence. Moreover, added support is given for this assignment since heat capacities calculated from the above frequencies are in agreement with experimental values over the temperature range from  $0^{\circ}$ – $70^{\circ}$ . These have been determined in this laboratory and I wish to thank Professor Kistiakowsky for allowing me to use these results prior to their publication.

#### ETHYLENE OXIDE

##### Experimental results

The Raman spectrum of liquid ethylene oxide has been examined with results that are in agreement with those of Ananthakrishnan. The results for the infra-red spectrum agree in general with those obtained by Bonner. There are, however, minor differences some of which can be ascribed to the varying dispersion of the different prisms employed.

Figure 3 shows the transmission curve that was obtained experimentally. The positions and intensities of the bands are summarized in Table VI together with Ananthakrishnan's figures for the Raman frequency shifts. The band at  $11.6\mu$ , very intense as in cyclopropane, overlaps a

TABLE VI. The observed wave-lengths and frequencies of the infra-red bands of ethylene oxide and the Raman frequencies.

INFRA-RED SPECTRUM			RAMAN FREQUENCIES
DESCRIPTION	WAVE-LENGTH ( $\mu$ )	FREQUENCY ( $\text{cm}^{-1}$ )	
weak	14.86	673	807 869 1122 (P) 1159
weak	12.33	811	
very strong	11.54	867	
strong	8.56	1168	
strong { P branch Center R branch	7.91	1264	1270 (P)
	7.87	1271	
	7.81	1280	
weak	6.88	1453	1492 (P?)
medium	6.68	1497	
weak	6.19	1616	
medium	6.06	1650	
weak	5.81	1721	2917 (P) 2952 (P) 3028 (P) 3080
very weak	5.42	1845	
weak	5.13	1949	
medium	4.95	2020	
weak	4.72	2119	
medium	4.39	2278	
medium weak	3.79	2639	
weak	3.59	2786	
very strong	3.30	3030	
medium weak	2.58	3876	
medium weak	2.33	4292	
weak	2.18	4587	
weak	1.62	6173	

(P) indicates that the line is polarized.

TABLE VII. *The symmetry and selection rules for the vibrations of the ethylene oxide molecule.*

SYM- METRY CLASS	NUMBER OF FUNDAMENTAL VIBRATIONS IN CLASS	PERMITTED TO APPEAR IN		SYMMETRY WITH RESPECT TO	
		RAMAN	INFRA-RED	$\sigma_h$	$\sigma_v$
$A_1$	5	Yes	Yes	$S$	$S$
$B_1$	4	Yes	Yes	$S$	$A$
$B_2$	3	Yes	Yes	$A$	$S$
$A_2$	3	Yes	No	$A$	$A$

fainter band, the position of which, as of all partially obscured bands, is difficult to determine. However, it seems to be at about  $811\text{ cm}^{-1}$ . In the potassium bromide region only one faint band was observed, this being at  $673\text{ cm}^{-1}$ . Bonner describes a faint band at  $696\text{ cm}^{-1}$ . The discrepancy between the two figures is surprising. Bonner, using a rocksalt prism, was working towards the very limit available with this substance and this might lead to some inaccuracy in the determination of the position of the band. Towards higher frequencies a band was observed at  $1168\text{ cm}^{-1}$ . Bonner gives  $1134\text{ cm}^{-1}$  for the position of this band. The intense band at  $7.9\mu$  was observed both with the rocksalt and fluorite prisms. The measured values for the position of the center were  $1275$  and  $1271\text{ cm}^{-1}$ , respectively, with the two prisms. This agreement is quite satisfactory. As the fluorite prism has the greater dispersion, the value of  $1271\text{ cm}^{-1}$  is taken to be the better one. Bonner gave  $1255\text{ cm}^{-1}$  but the existence of a Raman shift of  $1270\text{ cm}^{-1}$  lends support to the value of  $1271\text{ cm}^{-1}$ . Over the region from  $1400$  to  $3100\text{ cm}^{-1}$  Bonner's observations agree as regards the main features with those described here, but whereas he observed only seven bands, this examination revealed thirteen as may be seen by reference to Fig. 3 and Table VI. Beyond  $3100\text{ cm}^{-1}$  bands were observed at  $3876$ ,  $4292$ ,  $4587$  and  $6173\text{ cm}^{-1}$ . Bonner observed three bands at  $3891$ ,  $4310$  and  $6211\text{ cm}^{-1}$ , in satisfactory agreement.

### Symmetry properties

The ethylene oxide molecule provides an example of the group  $C_{2v}$ . In Table VII are summarized the number of vibrations in the various symmetry classes together with their symmetry and selection rules. This is similar to Table II for cyclopropane. In the last two columns of the

TABLE VIII. *Distortions occurring in the vibrations of the various symmetry classes for ethylene oxide.*

$A_1$	$B_1$	$B_2$	$A_2$
CH valency CH <sub>2</sub> deformation CH <sub>2</sub> bending ring deformation ring deformation	CH valency CH <sub>2</sub> deformation CH <sub>2</sub> bending ring deformation	CH valency CH <sub>2</sub> rocking CH <sub>2</sub> twisting	CH valency CH <sub>2</sub> rocking CH <sub>2</sub> twisting

table the symmetries with respect to  $\sigma_h$ , the plane of the ring, and with respect to  $\sigma_v$ , the symmetry plane perpendicular to the ring, are listed. It will be seen from the above table that all the fifteen fundamental frequencies may appear in the Raman effect and all but three in the infra-red. This renders an assignment of the observed frequencies to individual vibrations more difficult than in cyclopropane, where the selection rules were of real assistance. The five vibrations in  $A_1$  lead to polarized Raman lines.

### Form of vibrations

It is possible to make a table similar to Table III for cyclopropane in which the molecular distortions occurring in the vibrations of the different symmetry classes are summarized. This is done in Table VIII. These various distortions may be described in the same way with ethylene oxide as with cyclopropane. Since the two molecules are so similar it is to be expected that frequencies which depend largely on similar distortions will have approximately the same value in ethylene oxide and cyclopropane.

TABLE IX. *Suggested values for the fundamental frequencies of ethylene oxide with the corresponding Raman and infra-red frequencies.*

SYMMETRY CLASS	SUGGESTED FUNDAMENTAL FREQUENCY	RAMAN FREQUENCIES	INFRA-RED FREQUENCIES
$A_1$	3000 1494 1122 1270 811	3008, 2960 1492 1122 1270 (807)	(3030) 1497 (1168) 1271 811
$B_1$	3000 1453 1163 868	(3008) not observed 1159 869	(3030) 1453 1168 867
$B_2$	3062 1172 673	(3062) not observed not observed	(3030) (1168) 673
$A_2$	3062 — 807	(3062) not observed 807	forbidden forbidden forbidden



### The vibration frequencies

One of the  $A_1$  vibrations will have a frequency *ca.* 3000  $\text{cm}^{-1}$  and there will be four with frequencies lower than this. Below 2000  $\text{cm}^{-1}$  Ananthakrishnan observed only three polarized lines.\* These had shifts of 1492, 1270 and 1122  $\text{cm}^{-1}$ . On this basis, therefore, the methylene deformation vibration has a frequency of 1492, the methylene bending 1122 and one of the ring frequencies 1270  $\text{cm}^{-1}$ , the value of the other frequency in this class remaining in doubt. Bonner<sup>10</sup> assigned to it the value 807  $\text{cm}^{-1}$ . If this were correct, however, it would be expected that lines with this shift would be polarized instead of being depolarized. The frequencies 1492 and 1270 appear also in the infra-red spectrum at 1497 and 1271. The band at 1168  $\text{cm}^{-1}$  may obscure the band corresponding to 1122  $\text{cm}^{-1}$  if the latter is faint.

One of the four vibrations in the class  $B_1$  will have a value *ca.* 3000  $\text{cm}^{-1}$  and there will be three vibrations with smaller frequencies. The methylene deformation frequency is presumably 1453  $\text{cm}^{-1}$ , being observed in the infra-red spectrum; and the methylene bending frequency 1163  $\text{cm}^{-1}$ , observed in the Raman spectrum at 1159 and in the infra-red at 1168  $\text{cm}^{-1}$ . The fourth vibration in this class consists mainly of ring distortion and by analogy with the similar vibration in cyclopropane may be assigned the frequency 868  $\text{cm}^{-1}$ . The infra-red band falls at 867 and the Raman shift at 869  $\text{cm}^{-1}$ .

In the class  $B_2$  there is one vibration which has a frequency around 3000  $\text{cm}^{-1}$ . This may be assigned the value 3062  $\text{cm}^{-1}$  observed in the Raman effect. There are also two smaller frequencies. The methylene twisting frequency is presumably 673  $\text{cm}^{-1}$ . The value for the rocking frequency cannot be determined from the evidence available.

The carbon-hydrogen valency vibration in  $A_2$  may be expected to have about the same frequency as that in  $B_2$  since both are antisymmetrical to  $\sigma_h$ . The rocking frequency apparently does not appear. There is still the depolarized

TABLE X. Suggested interpretation of overtone and combination levels of ethylene oxide.

OBSERVED FREQUENCY	OBSERVED IN:	SUGGESTED COMBINATION	SYMMETRY CLASS
1616	Infra-red	$2 \times 807 = 1614$	$A_1$
		$2 \times 811 = 1622$	$A_1$
1650	Infra-red	$807 + 868 = 1675$	$B_2$
		$811 + 868 = 1678$	$B_1$
1721	Infra-red	$2 \times 868 = 1736$	$A_1$
1845	Infra-red	$1172 + 673 = 1845$	$A_1$
1949	Infra-red	$1270 + 673 = 1943$	$B_2$
2020	Infra-red	$1163 + 868 = 2031$	$A_1$
2119	Infra-red	$1270 + 868 = 2138$	$B_1$
2278	Infra-red	$1122 + 1163 = 2285$	$B_1$
2639	Infra-red	$1494 + 1163 = 2657$	$B_1$
2786	Infra-red	$1494 + 1270 = 2764$	$A_1$
2917	Raman	$2 \times 1453 = 2906$	$A_1$
2960	Raman	$2 \times 1494 = 2988$	$A_1$
3008		3000	$A_1$
3876	Infra-red	$3000 (A_1) + 868 = 3868$	$B_1$
		$3000 (B_1) + 868 = 3868$	$A_1$
		$3062 (B_2) + 811 = 3873$	$B_2$
		$3062 (B_2) + 807 = 3869$	$B_1$
		$3062 (A_2) + 807 = 3869$	$A_1$
4292	Infra-red	$3000 (A_1) + 1270 = 4270$	$A_1$
		$3000 (B_1) + 1270 = 4270$	$B_1$
4587	Infra-red	$3062 (B_2) + 1495 = 4557$	$B_2$
6173	Infra-red	Binary combinations of 3000 frequencies	—

Raman line at 807  $\text{cm}^{-1}$  which might be assigned to the twisting frequency in this class. However, there is an infra-red band at 811  $\text{cm}^{-1}$  and an  $A_2$  fundamental is inactive in the infra-red spectrum. It may be that the infra-red band corresponds to the  $A_1$  fundamental and that the polarized Raman line expected to correspond to it is obscured by the line arising from the  $A_2$  fundamental.

The values of thirteen of the fifteen fundamental frequencies have now been determined. Estimates can be made of the possible order of magnitude of the two remaining frequencies by comparison with cyclopropane. The methylene rocking frequency of cyclopropane in the symmetry class  $A_2''$  had the frequency 1041  $\text{cm}^{-1}$ . This vibration is similar to that of the missing frequency in  $B_2$ . However, it must be remembered that the methylene bending frequencies in cyclopropane of *ca.* 1050  $\text{cm}^{-1}$  are raised in ethylene oxide to *ca.* 1150  $\text{cm}^{-1}$ . If there is a similar increase in this case, a frequency between 1100 and 1200 would be expected for the missing  $B_2$  fundamental. Moreover, if this frequency does lie in this region, its absence in the infra-red spectrum would be accounted for since the band at 1168  $\text{cm}^{-1}$  which has been assigned to the  $B_1$

\* In Ananthakrishnan's paper<sup>2</sup> there is a discrepancy between the table for individual lines observed and the final table of Raman shifts. According to the first the 1492  $\text{cm}^{-1}$  shift leads to polarized lines, but according to the second, to lines which are depolarized. The line has been taken to be polarized.

fundamental would perhaps obscure it. It is found that all the observed overtone and combination levels can be accounted for in terms of the thirteen determined fundamentals and a value of 1172 for the missing  $B_2$  fundamental. The spectroscopic data do not, therefore, allow a determination of all the fifteen fundamental frequencies. In Table IX are summarized the figures for the fundamental frequencies with the manner in which they appear in the spectra. It will be seen that according to this table there are only four of the allowed frequencies which are definitely absent. In the infra-red none of the allowed fundamentals are definitely absent. In Table X it is shown how the observed overtone and combination frequencies can be interpreted in terms of these fundamentals. All the observed infra-red bands and Raman frequency shifts have

been accounted for by means of fundamentals or binary combinations.

The available data on ethylene oxide do not therefore allow a complete determination of the fundamental frequencies. Because of the nature of the selection rules for this molecule any assignment is of necessity only tentative since there are several assignments possible. Nevertheless with the facts at present at our disposal that described above seems to be the most probable. Further data that are required to determine the complete assignment must be obtained with a grating spectrograph so that bands which are not separated with a prism spectrograph may be resolved. A grating spectrograph would also allow a determination of the type of the individual bands and this might assist in the assignment. Heat capacity data would also be of great value.

TABLE XI. *A comparison of the vibration frequencies of cyclopropane and ethylene oxide.*

CYCLOPROPANE				ETHYLENE OXIDE		
SYMMETRY	FREQ.	VIBRATION		VIBRATION	FREQ.	SYMMETRY
[S, S] $A_1'$	3000	CH valency		CH valency	3000	$A_1$ [S, S]
	1485	CH <sub>2</sub> deform.		CH <sub>2</sub> deform.	1494	
	1187	ring deform.		CH <sub>2</sub> bending	1122	
[S, A] $A_2'$				ring deform.	1270	
	1070	CH <sub>2</sub> bending		ring deform.	811	$B_1$ [S, A]
[S, —] $E'$	3000	CH valency		CH valency	3000	
	1435	CH <sub>2</sub> deform.		CH <sub>2</sub> deform.	1453	
	1022	CH <sub>2</sub> bending		CH <sub>2</sub> bending	1163	
	860	ring deform.		ring deform.	868	
[A, S] $A_2''$	3050	CH valency		CH valency	3062	$B_2$ [A, S]
	1041	CH <sub>2</sub> rocking		CH <sub>2</sub> rocking	1172	
[A, S] $A_1''$	1000	CH <sub>2</sub> twisting		CH <sub>2</sub> twisting	673	
[A, —] $E''$	3080	CH valency		CH valency	3062	$A_2$ [A, A]
	1250	CH <sub>2</sub> rocking		CH <sub>2</sub> rocking	—	
	740	CH <sub>2</sub> twisting		CH <sub>2</sub> twisting	807	

TABLE XII. Calculated values\* for the free energy, entropy and heat capacity of cyclopropane.

T °K	TRANSLATIONAL AND ROTATIONAL		VIBRATIONAL		TOTAL		C <sub>p</sub> <sup>0</sup>
	$\frac{(F-E_0^0)}{T}$	S	$\frac{(F-E_0^0)}{T}$	S	$\frac{(F-E_0^0)}{T}$	S	
100	38.71	46.66	0.00	0.00	38.71	46.66	7.96
150	41.93	49.88	0.00	0.04	41.93	49.92	8.25
200	44.22	52.17	0.03	0.25	44.25	52.42	9.26
250	45.99	53.94	0.12	0.73	46.11	54.67	11.03
300	47.44	55.39	0.28	1.48	47.72	56.87	13.27
350	48.67	56.62	0.52	2.48	49.19	59.10	15.66
400	49.73	57.68	0.84	3.67	50.57	61.35	18.07
500	51.50	59.45	1.67	6.40	53.17	65.85	22.34
600	52.95	60.90	2.70	9.35	55.65	70.25	25.88
700	54.18	62.13	3.87	12.34	58.05	74.47	28.81
800	55.24	63.19	5.11	15.29	60.35	78.48	31.25
900	56.18	64.13	6.39	18.17	62.57	82.30	33.39
1000	57.01	64.96	7.73	20.95	64.74	85.91	35.22

\* The units used in this table are calories per mole and degrees absolute.

### Comparison with cyclopropane

In Table XI the frequencies of the comparable modes of vibration of ethylene oxide and cyclopropane are compared. In this table the types of vibration together with the suggested values for the frequencies are described. The symmetry with respect to the symmetry planes is described by the bracketed letters. The first letter indicates the symmetry with respect to the plane of the ring,  $\sigma_h$ , and the second the symmetry with respect to the three  $\sigma_v$  planes in cyclopropane and the one  $\sigma_v$  plane in ethylene oxide. For the degenerate vibrations of cyclopropane the symmetry with respect to the three  $\sigma_v$  planes cannot be given. Because of this it cannot be stated whether the  $E'$  vibrations are related to those in  $A_1$  or to those in  $B_1$  in ethylene oxide or whether the  $E''$  vibrations are related to those in  $B_2$  or to those in  $A_2$ . In addition certain of the ethylene oxide vibrations are related to two cyclopropane frequencies since cyclopropane has six more vibrational degrees of freedom. The lines in the center of the table indicate the manner in which the vibrations are related.

The correspondence between the carbon-hydrogen valency and the methylene deformation vibrations is immediately apparent. As regards the ring vibrations it is to be noted that the frequency of  $1187\text{ cm}^{-1}$  for cyclopropane increases to  $1270$  for ethylene oxide. Likewise, the methylene bending frequencies in ethylene oxide are about  $100\text{ cm}^{-1}$  higher than in cyclopropane. The methylene twisting frequencies are a little lower in ethylene oxide than in cyclopropane. The evidence regarding the rocking frequencies is

more indefinite though it appears that they may be higher in ethylene oxide than in cyclopropane. This comparison would lead us to expect for the methylene rocking frequency in  $A_2$ , missing in the Raman spectrum of ethylene oxide, a value in the neighborhood of  $1300\text{ cm}^{-1}$ . It is unfortunate that no direct evidence can be obtained as to the magnitude of this frequency. In general, therefore, the fundamental frequencies deduced for cyclopropane and ethylene oxide agree in a most satisfactory manner, lending support to the individual assignments. These facts, in addition, indicate a greater rigidity in ethylene oxide compared with cyclopropane with reference to all distortions except that involving methylenetwisting.

### Calculation of thermodynamic quantities

Since a complete assignment of the vibration frequencies of cyclopropane has been made, it is possible to calculate the free energy,  $F$ , the entropy,  $S$ , and the heat capacity,  $C$ , of this substance. The inadequate knowledge for ethylene oxide does not warrant such a calculation in this case. The molecular dimensions of cyclopropane that have been used in the calculation of the translational and rotational contributions to the free energy and entropy are  $1.53\text{Å}$  for the carbon-carbon link,  $1.09\text{Å}$  for the carbon-hydrogen link and  $116^\circ 56'$  for the HCH angle. The figure for the carbon-carbon link is obtained from electron diffraction data,<sup>11</sup> that for the carbon-hydrogen distance is that in methane<sup>12</sup> which is likely to be close to the value here. The methylene angle has been chosen so that it and the four HCC angles round any single carbon atom are the same, thus dividing the strain between all the angles. This value for the angle cannot be far from the real one. Table XII summarizes the results of the calculations. In the second and third columns are given the translational and rotational contributions to  $-(F-E_0^0)/T$  and  $S$  at the temperatures,  $T$ , in the first column. The fourth and fifth give the vibrational contributions to these quantities while the sixth and seventh give their total values. The last column gives the value of the heat capacity at constant pressure,  $C_p^0$ .\*

<sup>11</sup> Pauling and Brockway, J. Am. Chem. Soc. **59**, 1223 (1937).

<sup>12</sup> Ginsburg and Barker, J. Chem. Phys. **3**, 668 (1935).

\* The constants used in calculating the above quantities were obtained from the *International Critical Tables*. It was assumed that the vibrations were harmonic.

Murphy<sup>13</sup> has given analytical expressions for describing the free energy, entropy and heat capacity as functions of the temperature. The application of these to allene has been discussed by Linnett and Avery,<sup>14</sup> where it was found that the more complicated molecule necessitated the introduction of an extra term into the expressions for  $-(F-E_0^0)/T$  and  $S$  and that the heat capacity required an even more complicated expression. Expressions similar to those for allene were used for cyclopropane. The equations for the translational and rotational parts of  $-(F-E_0^0)/T$  and  $S$  are:

$$-(F-E_0^0)/T = 18.300 \log T + 2.112,$$

$$S = 18.300 \log T + 10.060$$

and for the vibrational parts:

$$-\frac{(F-E_0^0)}{T} = 131.60 - \frac{34.757 \log T}{T}$$

$$- 51.386 \log T + 4.395T \times 10^{-2}$$

$$- 0.686T^2 \times 10^{-5} + \frac{36.289 \times 10^2}{T},$$

$$S = 109.28 - 51.386 \log T$$

$$+ 8.791T \times 10^{-2}$$

$$- 2.058T^2 \times 10^{-5} - \frac{15.095 \times 10^2}{T}.$$

The equations for the complete values of

<sup>13</sup> Murphy, J. Chem. Phys. 5, 637 (1937).

<sup>14</sup> Linnett and Avery, J. Chem. Phys. 6, 686 (1938).

$-(F-E_0^0)/T$  and  $S$  are then:

$$-\frac{(F-E_0^0)}{T} = 133.71 - \frac{34.757 \log T}{T}$$

$$- 33.086 \log T + 4.395T \times 10^{-2}$$

$$- 0.686T^2 \times 10^{-5} + \frac{36.289 \times 10^2}{T},$$

$$S = 119.34 - 33.086 \log T$$

$$+ 8.791T \times 10^{-2}$$

$$- 2.058T^2 \times 10^{-5} - \frac{15.095 \times 10^2}{T}.$$

The equations for the vibrational components of  $-(F-E_0^0)/T$  and  $S$  reproduce the values in Table XII very well between 200 and 1000°K, but not so well between 100 and 200°. Nevertheless the equations for the total values of  $-(F-E_0^0)/T$  and  $S$  reproduce the tabulated values within 0.2 percent over the whole range between 100° and 1000°.\*

I wish to thank Professor E. Bright Wilson, Jr., who suggested my studying these compounds, for his advice during this work.

\* Uncertainty in the calculated values of the thermodynamic quantities may arise from several causes. In the first place there is uncertainty in our knowledge of the frequencies both from experimental inexactitude and also because Raman measurements were made on the liquid. Another source of error comes from our lack of knowledge regarding the anharmonicities of vibrations in polyatomic molecules.

## A Partial Analysis of Some Infra-Red Absorption Spectra of Organic Molecules in Dilute Solution\*

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An attempt is made to resolve into component parts a number of relatively complex infra-red absorption coefficient curves for several OH-containing organic molecules in the region of the first overtone absorption of the OH group. Such analyses suggest certain relations between the structure of the molecule and its effect upon the character of the absorption of the absorbing group.

**I**N dilute solution of a nonpolar solvent such as carbon tetrachloride, the absorption in the

near infra-red characteristic of the presence of a single OH or NH group in an organic molecule is often relatively simple, the curve of the absorption coefficient consisting of one or two absorption peaks which are narrow and fre-

\* Material presented at the Rochester meeting of the American Chemical Society, September 1937, and at the Indianapolis meeting of the American Association for the Advancement of Science, December 1937.