

Vibration Spectra and Molecular Structure. III The Infrared Absorption Spectra of Cyclopropane and Ethylene Oxide

Lyman G. Bonner

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Vibration Spectra and Molecular Structure. III

The Infrared Absorption Spectra of Cyclopropane and Ethylene Oxide

LYMAN G. BONNER*

Palmer Physical Laboratory, Princeton, New Jersey

(Received June 3, 1937)

With a rocksalt prism spectrometer, the infrared absorption spectra of gaseous cyclopropane and ethylene oxide have been mapped in the region 1–15.5 μ . Cyclopropane shows bands at 6250, 4425, 3086, 2525, 2088, 1887, 1739, 1429, 1021, 860, and 671 cm^{-1} , while ethylene oxide absorbs at 6211, 4310, 3891, 3021, 2632, 2304, 2024, 1733, 1626, 1493, 1255, 1134, 862, 804 and 696 cm^{-1} . In addition to these infrared measurements, a redetermination was made of the Raman spectrum of liquid ethylene oxide. Raman lines appeared at 807, 867, 1123, 1269, 1488, 2914, 2958, and 3007 cm^{-1} .

IN a recent paper¹ the author presented the results of approximate force constant calculations on a number of the simpler organic molecules. In the course of this work it was necessary to obtain the spectra of two of the compounds investigated and it is the purpose of the present article to discuss this experimental work. The infrared absorption spectra of cyclopropane and ethylene oxide vapors were obtained in the region 1–15.5 μ and in addition a redetermination was made of the Raman spectrum of liquid ethylene oxide.

APPARATUS AND METHODS

The spectrometer used for the infrared measurements was a low dispersion rocksalt prism instrument, which has already been described.²

The light source for Raman effect determinations consisted of two water-cooled Pyrex mercury arcs of the conventional hairpin design, and a saturated sodium nitrite solution was used as filter. This restricted the exciting light essentially to the $\lambda 4358\text{\AA}$ line. A Steinheil high speed three-prism spectrograph was used. This

* National Research Fellow.

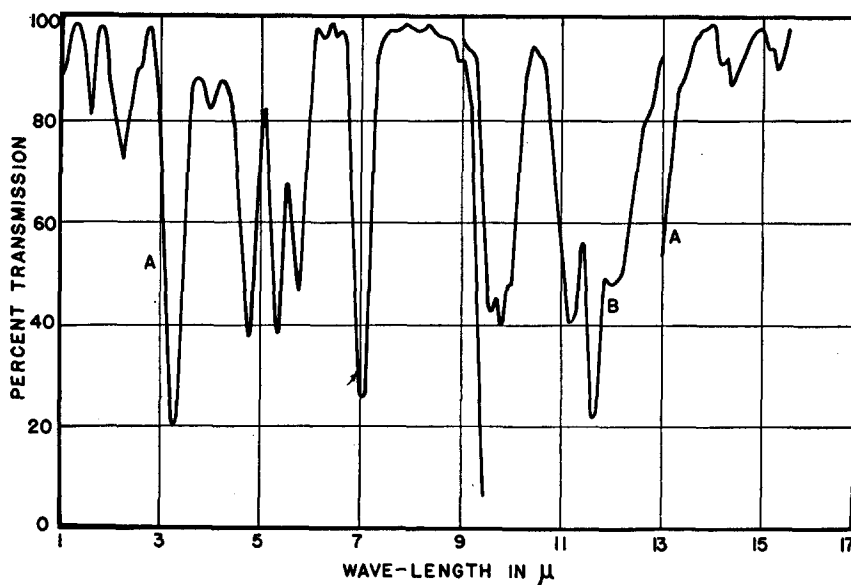
¹ L. G. Bonner, *J. Chem. Phys.* **5**, 293 (1937).² R. B. Barnes, R. R. Brattain, and F. Seitz, *Phys. Rev.* **48**, 582 (1935).

FIG. 1. The absorption of a 15 cm layer of cyclopropane vapor at A, 700 mm and B, 50 mm pressure.

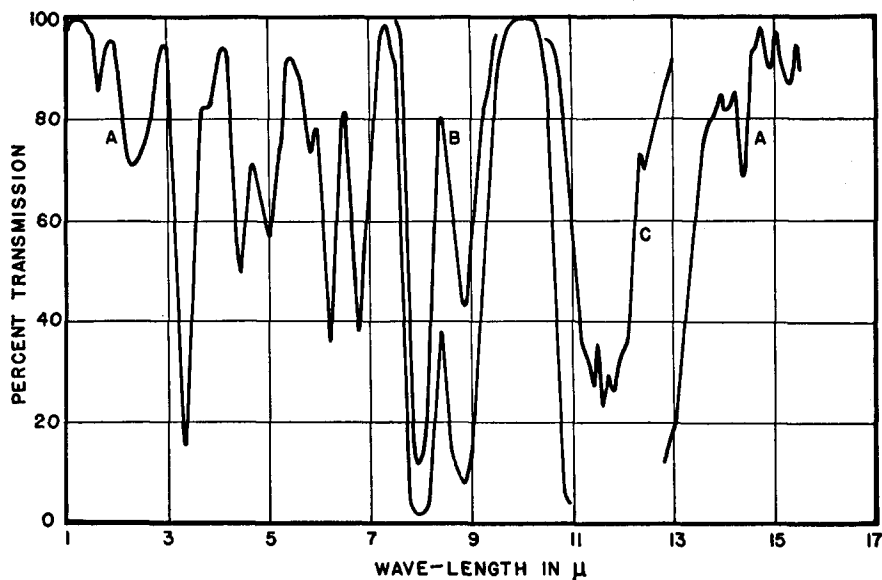


FIG. 2. The absorption of a 15 cm layer of ethylene oxide vapor at A, 700 mm, B, 200 mm, and C, 25 mm pressure.

instrument had a dispersion of about 50Å/mm in the region of interest.

In obtaining the infrared curves the fractional transmission of the gas cell was determined at 0.1μ intervals throughout the region 1–15.5 μ . In all cases a 15 cm glass cell, sealed at the ends with rocksalt plates, was used. In order to bring out bands with greatest clearness, gas pressures ranging from 25 to 700 mm were used in different spectral regions. After obtaining the above rough curve, the regions of all band centers were gone over again, taking points at 0.02μ intervals in order to locate more accurately the absorption centers, and also to bring out more clearly any structure in the bands.

Since no dummy cell was used in these measurements there was a small and constant background absorption, which was allowed for in the following way. The experimental curve was first plotted, and in this the transmission in regions of no absorption by the gas always reached a definite maximum value, usually 70–80 percent. This was then assumed to be the zero transmission of the cell and the scale of the ordinate changed accordingly.

CYCLOPROPANE

The cyclopropane used in these experiments was a particularly pure product prepared in the

Harvard Chemical Laboratories and very kindly supplied to me by Dr. E. Bright Wilson, Jr., for which I wish to thank him at this time. Fig. 1 shows the infrared spectrum of cyclopropane and Table I gives the positions of the band centers, together with the probable accuracy with which they have been determined. The bands at 9.8 and 11.6 μ seem to be resolved into *P*, *Q*, and *R* branches, with *P*–*R* separations of 42 and 66 cm^{-1} respectively. Due to experimental difficulties, measurements beyond 14 μ are somewhat uncertain but there seems to be no doubt about the reality of the two minima at 14.4 and 15.3 μ . These may be taken as components of a doublet

TABLE I. Positions of cyclopropane bands.

DESCRIPTION	WAVE-LENGTH (μ)	FREQUENCY (cm^{-1})
	1.60	6250 \pm 100
	2.26	4425 \pm 75
	3.24	3086 \pm 20
	3.96	2525 \pm 30
	4.79	2088 \pm 8
	5.30	1887 \pm 7
	5.75	1739 \pm 6
	7.00	1429 \pm 4
<i>R</i> Branch	9.58	1044 \pm 2
<i>Q</i> "	9.79	1021 \pm 2
<i>P</i> "	9.98	1002 \pm 4
<i>R</i> "	11.18	894 \pm 2
<i>Q</i> "	11.63	860 \pm 2
<i>P</i> "	12.07	828 \pm 2
<i>R</i> "	14.4	694 \pm 5
Center	14.9	671 \pm 5
<i>P</i> Branch	15.3	654 \pm 5

type band with center at 14.9μ and a $P-R$ separation of 40 cm^{-1} . For purposes of comparison it is interesting to note that Harris, Ashdown, and Armstrong³ report Raman lines of cyclopropane at 382, 745, 869, 1022, 1191, 1437, 1454, 1505, 1873, 2856, 2953, 3013, 3030, and 3079 cm^{-1} . The frequencies used in the previous analysis¹ were 869 and 1191 cm^{-1} .

ETHYLENE OXIDE

The material used was a commercial product supplied by the Carbide and Carbon Chemical Company and used without further purification. Fig. 2 shows the infrared spectrum and Table II gives the positions of the band centers. Under higher dispersion the band at 8.0μ seems to resolve into a doublet with center at 7.97, while the 11.6μ band appears to be of the Q branch type. The sharp minimum at 14.35μ may perhaps be taken as another Q branch, the corresponding P and R branches being lost in the general background.

Measurements on two Raman plates showed lines at 807, 867, 1123, 1269, 1488, 2914, 2958, and 3007 cm^{-1} . This is in good agreement with

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

TABLE II. Positions of ethylene oxide bands.

DESCRIPTION	WAVE-LENGTH (μ)	FREQUENCY (cm^{-1})
	1.61	6211 ± 100
	2.32	4310 ± 70
	2.57	3891 ± 40
	3.31	3021 ± 20
	3.80	2632 ± 20
	4.34	2304 ± 10
	4.94	2024 ± 8
	5.77	1733 ± 6
	6.15	1626 ± 5
	6.70	1493 ± 5
R Branch	7.90	1266 ± 3
Center	7.97	1255 ± 3
P Branch	8.04	1244 ± 3
	8.82	1134 ± 3
R Branch	11.42	875 ± 2
Q "	11.60	862 ± 2
P "	11.80	847 ± 2
	12.43	804 ± 2
	14.35	696 ± 3

recent work of Ananthakrishnan,⁴ except that this author finds, in addition, lines at 1159 and 3062 cm^{-1} . The frequencies assumed for the heavy particle vibrations were 807, 869, and 1270 cm^{-1} .

In conclusion I wish to express my thanks to Dr. R. Bowling Barnes, formerly of this university, for his advice in connection with these measurements.

⁴ R. Ananthakrishnan, Proc. Ind. Acad. Sci. **4**, 82 (1936).

Chemical Applications of the Raman Effect: I. Polymerization

JAMES H. HIBBEN

Geophysical Laboratory, Carnegie Institution of Washington, Washington, D. C.

(Received June 16, 1937)

The Raman spectra of methyl methacrylate and similar compounds have been investigated and interpreted. The changes in the molecular constitution on polymerization indicate the

disappearance of a $\begin{array}{c} \text{H} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{H} \end{array}$ linkage and the like disappearance of the $\text{C}=\text{C}$ linkage. Lower

frequencies appear indicating an increased chain length and a slight decrease in the complexity of the intermediate frequency would seem to indicate an increase in the symmetry of the molecule. The force constants of the more characteristic groups are closer to the *cis*- than the *trans*-modification of the isomer. Unlike inorganic glasses, the polymer exhibits at least some sharp lines. These permit an explanation of the continuing structure present throughout the solid and the mechanism by which this structure comes into existence.

THE Raman spectra of methyl methacrylate as the monomer and in different stages of polymerization were investigated in order to

obtain some information concerning the mechanism of polymerization and the molecular constitution of an amorphous compound having the