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Vibrational Spectra and Structure of Cyclopropane and Cyclopropane-d₆*

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Cyclopropane-d₆ has been synthesized from deuterium oxide and magnesium tricarbide in steps giving successively methyl acetylene- d_4 , propylene- d_6 , allyl chloride- d_5 , 3-bromo-1-chloropropane- d_6 , and cyclopropane- d_6 . Infrared spectra of cyclopropane and cyclopropane- d_6 have been obtained in the spectral region 350 to 3700 cm⁻¹ for the vapor and 650 to 3700 cm⁻¹ for the liquid. Raman spectra, including semiquantitative depolarization factors, have been determined for the liquid state. The spectroscopic results satisfy the Teller-Redlich product rule for a molecule of D_{3h} symmetry. All active fundamentals in cyclopropane- d_6 but one have been directly observed. The inactive fundamentals in both molecules have been located provisionally from overtone assignments. An attempt to determine the molecular geometry from rotational contours of the infrared bands was not successful, but high-resolution work on cyclopropane- d_6 shows that the C - C distance is 1.524 ± 0.014 A.

INTRODUCTION

HE interatomic distances and bond angles in cyclopropane are of considerable interest from the standpoint of valence theory, and there have been numerous structural studies of the molecule. The early work by means of infrared and Raman spectra has been summarized by Herzberg¹ and more recent investigations are discussed below. Since the molecule appears to have no dipole moment, it is presumably not directly accessible to study by microwave spectroscopy. There have been recent electron-diffraction studies² which support the D_{3h} structure generally accepted by chemists and give the C-C distance as 1.52 ± 0.02 A, the C-H distance as 1.08 A, and the HCH angle as 118°. Since interatomic distances involving hydrogen are more difficult to measure than those of heavier atoms, the latter two figures are somewhat more uncertain than the C-C distance.

The present work was undertaken in the hope that the additional information to be obtained from the deuterium derivative would not only enable a more complete and reliable vibrational analysis to be made, but might also provide further data from which to obtain the interatomic distances and angles.

EXPERIMENTAL DETAILS

Preparation of Cyclopropane- d_6

The six steps involved were:

- 1. Preparation of magnesium tricarbide, Mg_2C_3 .
- 2. Reaction of Mg_2C_3 with D_2O to give methyl acetylene- d_4 .

- 3. Reduction of methylacetylene- d_4 to propylene d_6 with D₂ gas.
- 4. High-temperature chlorination of propylene- d_6 to ally chloride- d_5 .
- 5. Addition of DBr to the double bond of allyl chloride- d_5 under proper conditions to obtain 3bromo-1-chloropropane- d_6 .
- 6. Ring closure with zinc dust.

By means of these reactions, most of which gave relatively high yields, about 6 g (0.125 mole) of cyclopropane- d_6 were prepared. Physical properties and infrared spectra indicated that chemical and isotopic purity were high, the latter about 99 atom-percent.³

The individual steps were carried out as follows:

1. Magnesium forms two carbides, either of which can be prepared pure by proper choice of conditions.⁴ If a suitable hydrocarbon such as *n*-pentane is passed over magnesium powder at 700°C, Mg_2C_3 is formed with little or no MgC_2 . The reaction was carried out in an asbestos-covered iron pipe wound with chromel heating coils. Vycor was used for one or two runs but disintegrated because of reaction with magnesium. Iron boats were used to contain the magnesium powder. Dry hydrogen was passed over the magnesium to displace the air in the system and subsequently to carry the *n*-pentane through the reaction chamber at the proper space velocity. Reaction was confined largely to the surface of the magnesium, necessitating broad, shallow boats. The estimated yield of Mg₂C₃ was 70 to 75%.5

2. The Mg₂C₃ was transferred rapidly after preparation to an all-Pyrex apparatus consisting of a 30-cm horizontal tube (about 40 mm diam) as reaction chamber, with a container for admitting D_2O at one end and a trap for collection of methyl acetylene- d_4 at the other. The reaction chamber was wound with heating coils and contained two thermocouple ports for following the reaction temperature. After Mg_2C_3 had been placed in the chamber, with glass wool plugs at each end to keep it from blowing around, the chamber was heated at 400°C for 8 to 10 hours under diffusionpump vacuum to decompose any Mg(OH)2 which might have been formed by atmospheric or other water vapor. The chamber was

^{*} This paper is based on a thesis submitted by A. W. Baker to the Graduate School of Massachusetts Institute of Technology in partial fulfillment of the requirements for the Ph.D. degree, September, 1950. A detailed account of the chemical procedures for preparation of cyclopropane d_6 is given in the thesis. † Present address: Spectroscopy Laboratory, Dow Chemical Company, Midland, Michigan.

<sup>Company, Michand, Michigan.
¹ G. Herzberg, Infrared and Raman Spectra (D. Van Nostrand</sup> Company, Inc., New York, 1945), pp. 351-353, 437.
² O. Bastiansen and O. Hassel, Tidsskr. Kjemi, Bergvesen Met.
6, 71 (1946); J. D. Dunitz and V. Schomaker, J. Chem. Phys. 20, 1703 (1952) (reference 19, p. 1705).

³ Analyses were made by infrared absorption and mass spectrometry. We are indebted to Dr. F. L. Mohler, National Bureau of Standards, for the mass-spectrometric analysis.

of Standards, for the mass-spectrometric analysis. ⁴ J. Novak, Z. physik. Chem. **A73**, 513 (1910). ⁵ Further details are given in the Ph.D. thesis of A. W. Baker. L. C. Leitch and R. Renaud [Can. J. Chem. **30**, 79 (1952)] have also published detailed directions for preparation of Mg_2C_3 and methyl acetylene-d4.

allowed to cool to 140° and D₂O was admitted to the side tube. No free space was allowed above the magnesium carbide so that the D_2O was forced to diffuse through the carbide, reacting completely as the reaction progressed down the tube. Only a slight excess of D₂O was necessary for almost quantitative conversion of the carbide. The evaporation of the D₂O, which governed the rate of the reaction, was controlled by the pressure maintained in the reaction chamber and by the temperature of the side tube. Because of the liberation of large amounts of heat, with subsequent danger of fires and explosions, the passage of D₂O over Mg₂C₃ must be carefully regulated.

In addition to methyl acetylene- d_4 , small amounts of allene- d_4 were generated. The yield of allene- d_4 could be increased by raising the reaction temperature.6

3. A catalyst of activated cocoanut charcoal containing 0.5% palladium was used for the reduction of methyl acetylene- d_i to propylene- d_6 . The catalyst was placed in an eight-foot Pyrex tube (12 mm i.d.) wound with a heating element and was outgassed at high vacuum and 400°C for five days. Deuterium gas was then admitted at room temperature and atmospheric pressure, and the catalyst again baked out under vacuum. This precaution was necessary to minimize the effect of any hydrogen-containing substances initially present on the catalyst. A mixture of methyl acetylene- d_4 and deuterium, the latter in slight excess, was passed very slowly over the catalyst at 150°C. The infrared spectrum of the product⁷ showed that the conversion to propylene- d_6 was complete.

4. Allyl chloride- d_5 was prepared by high-temperature chlorination⁸ of propylene- d_6 . The latter was mixed at 550°C with chlorine (from a cylinder) in a Vycor oven which provided for pre-heating of the reactants. The ratio of propylene- d_6 to chlorine was followed by means of flow meters, the rate of flow being controlled by pressure regulation at the condensing trap on the output side. Space velocity of the gases was critically important. If the gases passed too slowly through the oven, excessive pyrolysis occurred, and if too rapidly, the reaction occurred partly outside the oven, with the production of undesired products such as 1,2 dichloropropane. Optimum total pressure for the reaction with propylene d_6 was about 50 mm. The allyl chloride- d_5 was purified by a trapto-trap distillation to remove DCl, followed by distillation through an efficient column of low hold-up to separate the organic chlorides.

5. The addition of DBr to all chloride- d_5 to form 3-bromo-1-chloropropane- d_6 was carried out in a thick-walled Pyrex tube of 15-ml capacity and capable of withstanding pressures in excess of 30 atmospheres. The tube was fitted with a standard-taper stopper sealed in with a high-melting wax. Anhydrous DBr, prepared by suitable modification of the method of Ruhoff et al.9 was distilled into the tube to 30% excess, after which benzoyl peroxide and oxygen were admitted.¹⁰ After the tube was sealed, it was slowly allowed to warm to room temperature and to stand for 15 hours. It was then chilled to liquid nitrogen temperature and opened. The 3-bromo-1-chloropropane-d₆ (80% yield) was fractionated with great care to obtain a clean-cut separation from any 2-bromo-1-chloropropane- d_6 formed, since the latter would cause contamination of the cyclopropane- d_6 with propylene- d_6 .

6. The conversion of 3-bromo-1-cyclopropane-d₆ to cyclopropane-d₆ was effected by the procedure of Ort.¹¹ The 3-bromo-1-chloropropane- d_6 (24.5 g) was added dropwise to a mixture of 59 ml absolute alcohol, 8.7 ml of water, 1.2 ml of 5% aqueous FeCl₃, 20 g of zinc dust, 5.5 g MgO and 2.7 g KBr. The mixture was refluxed at 85°C until evolution of gas ceased (10 to 15 hours), After separating water and alcohol from the condensed product. 7 ml of pure liquid cyclopropane- d_6 were obtained. The infrared spectrum of the product gave no evidence of impurities such as propylene- d_6^7 and the spectroscopically estimated isotopic purity was in excess of 99 atom-percent deuterium.

Prior to the synthesis described above, other routes to cyclopropane- d_6 were investigated. Although they were not successful, they are listed here for completeness.

Wave number (cm~1) and intensity		Wave number (cm ⁻¹) and intensity			
Vapor	Liquid	Assignment	Vapor	Liquid	Assignment
720 O vw		$\nu_9 - \nu_{14}$?	2070.4 P)	······································	()
740 Ř vw		• •	2095.7 O m	2083 s	$v_4 + v_5$
	745 vw	V 14	2112.0 R		$(2\nu_{13})$
836.7 P)			2160 P		
854 O'	0//	V 7	2188.8 Q w	2172 m	$\nu_{9} + \nu_{14}$
868.5 0 VVS	800 VS	ν_{11}	? Ř		
898.0 Ř			Region of 1	2211 w	$\nu_3 + \nu_{10}$
1007.5 P			poorly de-	2303 w	$\nu_9 + \nu_{11}$
1028.7 Q vs	1024 vs	ν_{10}	fined band	2458 w	$\nu_9 + \nu_{10}$
1051.6 Ř			minima)	2500 w	$\nu_2 + \nu_{10}$
,	1 188 w	ν_3	2621 vw	2621 w	$\nu_3 + \nu_9$
1422.0 P)			2640 vw		?
1441.8 Q }m	1434 vs	ν_9	2850 P		
$1455.7 \ \bar{R}$			2873 Q }w	2863 m	$2\nu_{9}$
1480 sh vw		$2\nu_{14}$	-R		
1505 sh vw	1510 vw	?	-	2881 w	$\nu_2 + \nu_9$
1739.9 w	1727 m	$2\nu_{11}$	2937 vw	2933 ms	$2\nu_{14} + \nu_{9}$
	1765 m	$\nu_{10} + \nu_{14}$	3009.4 P		
1770		∫ v5+v11	3028.1 Q \vs	3019 vs	ν_8
1777 W		$v_{13} + v_{14}$	3050.6 R		
1865 vw		$\nu_4 + \nu_{14}$	$\sim 3075 P$		
1894 ms	1887 s	$\nu_{10} + \nu_{11}$	3102.9 Q }s	3090 vs	ν_6
1935.8 vw	1940 (sh)	$\nu_5 + \nu_{10}$?	3129 R		
		$\nu_3 + \nu_7$	3229 vw $\}$		∫ Ternary
2044 vw	2048 m	$\{ \nu_3 + \nu_{11} \}$	3241 vw∫		\ overtone

TABLE I. Infrared bands of cyclopropane.

⁶ R. C. Lord and J. Ocampo, J. Chem. Phys. 19, 260 (1951); R. C. Lord and P. Venkateswarlu, J. Chem. Phys. 20, 1237 (1952).
⁷ Cf. R. C. Lord and P. Venkateswarlu, J. Opt. Soc. Am. 43, 1079 (1953).
⁸ H. P. A. Groll and G. Hearn, Ind. Eng. Chem. 31, 1239, 1530 (1939).
⁹ Ruhoff, Burnett, and Reid, Org. Syntheses 2, 338 (1943).
¹⁰ M. S. Kharasch and F. R. Mayo, J. Am. Chem. Soc. 55, 2468 (1933).
¹¹ J. N. Ort, U. S. Patent 2,240,513.

Wave number (cm	1 ⁻¹) and intensity		Wave number (cm ⁻¹) a	nd intensity	
Vapor	Liquid	Assignment	Vapor	Liquid	Assignment
614 w 694.4 <i>P</i>)	(beyond range)	ν ₇	$ \begin{array}{c} -P \\ 1670 Q \\ 1692 R \end{array} $ vw	1667 w	$ \begin{cases} \nu_3 + \nu_{11} \\ 2\nu_{13} \end{cases} $
$720.1 Q \ vs \ 745.5 R$	720 vs	ν_{11}	1765.4 ms	1760 s	$2\nu_{10}$
,	750 sh?	2			
838 vvw 864.7 P	832 vw	ν_{13} ?	1773.7 m 1941.7 vw	1783 w 1935 vw	$\nu_9 + \nu_{11}$?
886.9 Q ms 907.9 R	883 s	ν_{10}	1965 sh	1951 w 2028 w	$ \nu_9 + \nu_{10} \\ \nu_3 + \nu_9 $
,	956 w 1002 vvw	ν ₃ ?	2141.4 w 2194 P	2132 m	$2\nu_9$
1055.3 <i>P</i>)	1019 vvw	;	2211.4 Q vs 2231.3 R	2204 vs	ν_8
1074.3 Q s 1090.0 R	1068 s	ν,	2316 P 2336 Q ys	2330 vs	Vs
1148 vw 1240 vw)	1141 vw	$\nu_7 + \nu_{14}$	2360 Ř) 2860 vw	2854 vw	$ \begin{cases} \nu_1 + \nu_7 \\ \nu_{12} + \nu_{14} \end{cases} $
1247 vw }	1244 w 1279 vw	$\nu_{11} + \nu_{14}$	2043 yw	2037 w	$ \begin{pmatrix} \nu_{12} + \nu_{14} \\ \nu_{6} + \nu_{14} \end{pmatrix} $
1329.6 vw	1330 vw	$\nu_4 + \nu_{14}$	3039 P	2957 ₩	$\int C_3 D_5 H$
1404 VW 1435.6 w	1402 VW 1434 W	$\nu_{10} + \nu_{14}$ $2\nu_{11}$	3073 R	3030 W	$\int \nu_{11} + \nu_{12}$
	15557 \$11	r		3087 W	$\nu_8 + \nu_{10}$
1571.4 P	1594			3162	$\begin{cases} \nu_3 + \nu_8 \\ \nu_{12} + \nu_{13} \end{cases}$
1602.3 R	1364 Ins	$\nu_4 + \nu_5$	3294 w	3291	$\nu_3 + \nu_6$
			3400 Q 3420 R	3391 m	$\nu_9 + \nu_{12}$
			3485 vw	3470 vw	$\nu_2 + \nu_8$
			3014 VW	3014 VW	$\nu_2 + \nu_6$

TABLE II. Infrared bands of cyclopropane- d_6

1. Exchange between D_2O and cyclopropane. No exchange could be effected using D_2O and a variety of catalysts such as platinum-on-asbestos, palladium-on-charcoal, nickel-on-kieselguhr, PtO₂, and slightly poisoned nickel-on-kieselguhr. The temperatures ranged from 25°C up to the decomposition temperature of cyclopropane (about 280°C for the conditions used). In some instances contact of D_2O and cyclopropane with the catalyst was maintained for 3 to 4 days.

2. Exchange between D_2 and cyclopropane. Under any conditions of catalysts and temperature that seemed likely to promote exchange, deuterium opened the ring to give propane- d_2 . There was a slight indication of exchange when a very low $D_2/cyclo$ propane ratio was used but complete deuteration was impractical by this method.

3. Synthesis from malonic ester. An attempt was made to reduce malonic ester- d_2 to 1,3-dihydroxy propane- d_8 with lithium aluminum deuteride. None of the desired compound could be obtained.

4. Synthesis from malononitrile. This procedure is a modification of No. 3. Malononitrile- d_2 is synthesized and then reduced to the completely deuterated diamine with lithium aluminum deuteride. Benzoyl chloride is added to the diamine to form dibenzoyl propylene diamine, and addition of phosphorus pentabromide will give 1,3-dibromopropane- d_6 . It was found that malononitrile could not be reduced by lithium aluminum deuteride.

5. Synthesis from malononitrile. An electrolytic method is said to reduce malononitrile to the diamine in 50% yield.¹² Although this method would open the way for the application of the remaining steps of procedure No. 4, no work was attempted along these lines.

Infrared Spectra

The infrared absorption spectra were obtained over the spectral range 350 to 3700 cm^{-1} for the vapor and 650 to 3700 cm⁻¹ for the liquid with a Perkin-Elmer 12B single-beam spectrometer modified as previously described.¹³ Prisms of CaF₂, NaCl, and KBr were used in their respective regions of best resolution, which seldom was much worse than 3 cm^{-1} except in the 3000 cm⁻¹ region. Two absorption cells for the vapor were respectively 6 cm and 4 m in path length, while the liquid was measured in the low-temperature cell of Lord, McDonald, and Miller.13 The wave numbers (vac) of sharp bands are probably accurate to $\pm 2 \text{ cm}^{-1}$ except above 2500 cm^{-1} , where the accuracy may change to as much as ± 5 cm⁻¹. Reproducibility is somewhat better than this, being 1 cm⁻¹ or less below 2000 cm^{-1.13} The results of the infrared studies are given numerically in Tables I and II and graphically in Figs. 1 and 2. Qualitative intensities are denoted by symbols whose meanings are: s=strong, m=medium, w=weak, v = very, sh= shoulder. When two or three adjacent peaks are believed to be rotational maxima for the same vibration they are labeled P, Q, R.

It is believed that the infrared results for cyclopropane vapor are a considerable improvment in completeness, resolution and accuracy over those hitherto

¹³ Lord, McDonald, and Miller, J. Opt. Soc. Am. 42, 149 (1952).

¹² Ohta, J. Chem. Soc. Japan 63, 1762-5 (1942).



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Wave num-ber (cm⁻¹) Int. and Pol. Assign- Wave num-ment ber (cm⁻¹) Int. and Pol. Assign-ment $2\nu_{14}$ 741 (1) dep 1504.2 (1) pol V14 866 (8) dep 2859 (2) pol $2\nu_9$ ν_{11} 1023 $(0) \cdots$ 2954(6) pol 202 V10 1188.2 (9) pol 3009 (10) pol) (PI ν_3 1433.6 (5) dep 3027 (9) pol 2 28 ν_0 1453.3 (3) pol 3075 (9) dep

y,

TABLE III. Raman spectrum of liquid cyclopropane.

published for the region up to 3500 cm^{-1} . This is due partly to the improved performance of the Model 12B spectrometer equipped with a CaF_2 prism, and partly due to the removal of absorption by atmospheric water and carbon dioxide.14

The infrared spectrum of liquid cyclopropane and the vapor and liquid spectra of cyclopropane- d_6 have not been reported previously.

Raman Spectra

The Raman spectra of liquid cyclopropane and cyclopropane- d_6 were obtained at about -90° C with a Zeiss three-prism spectrograph. The techniques employed have been described in some detail by Lord and Nielsen.¹⁵ Depolarization measurements were made only on cyclopropane- d_6 . They were semiquantitative, but were adequate to distinguish polarized lines with $\rho < 0.75$ from depolarized lines. Wave number accuracy is $\pm 2 \text{ cm}^{-1}$ except for weak or fuzzy lines, for which it may be ± 5 cm⁻¹. Measured wave numbers (vac), visually estimated intensities on an arbitrary scale of 10, and state of polarization (for cyclopropane- d_6 only) are listed in Tables III and IV, and the spectra are shown photographically in Fig. 3.

The spectrum of cyclopropane agrees with the one summarized in Herzberg,¹ except that the lines at 382 and 1873 could not be found. The former is difficult to explain reasonably, and the latter, if real, must

TABLE IV. Raman spectrum of liquid cyclopropane- d_6 .

Wave num- ber (cm ⁻¹)	Int. and Pol.	Assign- ment	Wave num- ber (cm ⁻¹)	Int. and Pol.	Assign- ment
528	(1) dep	V14	1338	(0)	v7+v11
721	(4) dep	V11	1587	$(0) \cdots$	$\nu_9 + \nu_{14}$
884	(6) dep	ν_{10}	2131	(3) pol	$2\nu_{9}$
956	(7) pol	ν_3	2204	(3) dep	ν_8
1068	(1) dep	ν_9	2236	(10) pol	ν_1
1229	(2) pol	$2\nu_{7}$	2329	(7) pol	ν_{12}
1274	(8) pol	ν_2			

¹⁴ The authors have had the opportunity of seeing unpublished spectra of the strong bands of cyclopropane measured by Dr. L. G. Smith with a grating instrument. They have also had the privilege of examining the 1953 thesis of Dr. H. W. Neill, describing work carried out under the direction of Professor G. B. B. M. Sutherland at the University of Michigan. This thesis reports a very complete study of the infrared spectrum of cyclopropane vapor at both grating and prism resolution. The present results are in good agreement with the prism spectra of Neill and Sutherland. ¹⁵ R. C. Lord and E. Nielsen, J. Opt. Soc. Am. 40, 655 (1950);

J. Chem. Phys. 19, 1 (1951).

surely be an overtone, and hence is not likely to be of significance in the assignment of fundamentals. The remarkable intensity changes caused by deuterium substitution will be discussed later.

INTERPRETATION OF THE SEPCTRA

Discussion of the vibrational spectra of cyclopropane by all previous investigators, including Herzberg,¹ has been based on the D_{3h} structure. This basis will be used here, since it will be shown that there is a considerable amount of spectroscopic evidence in favor of it and none to the contrary. The distribution of the modes of vibration of cyclopropane among the various D_{3h} symmetry species and their spectroscopic activities are shown in Table V. The qualitative descriptions¹⁶ of the modes of vibration are those in rather general use, but it is perhaps worthwhile to say that CH2 deformation refers to the symmetrical scissors-like bending of the CH₂ bonds, CH₂ wagging to the "fan-



FIG. 3. Raman spectra of cyclopropane and cyclopropane- d_6 .

ning" motion of the CH₂ group perpendicular to its own plane, CH₂ twisting to a torsion of the CH₂ group about the bisector of the HCH angle, and CH₂ rocking to the rotary motion of the CH_2 group as a unit about an axis perpendicular to its own plane. Since there are three CH_2 groups, the symmetry species of a given type of motion is determined not only by the nature of the motion of the individual groups but also by their mutual phase relationships.

From Table V the assignment of the observed infrared and Raman frequencies is straightforward in principle. Polarized Raman lines must belong to A_1' , depolarized Raman lines not coincident with infrared bands should belong to E'', infrared bands not coincident with Raman lines to A_2'' (these bands should also have "parallel" structure, if this can be determined), and Raman lines coincident with infrared bands (of perpendicular structure) to E'. The two vibrations of species A_2' and A_1'' are inactive in both spectra. These characteristics are satisfactory for the assignment of

¹⁶ See reference 1, Table 108, p. 351.

Vib'n. Species no.	Approximate form	Selection rules		Assignment		Product rule		
	no.	of vibration	Raman	Infrared	C ₃ H ₆	$C_{3}D_{6}$	$ au_{ m obs}$	τ_{calo}
$A_{1'}$	1	CH stretching	pol	f	3009	2236	1.94	2,000
-	2	CH_2 deformation	1		1475°	1270ª		
	3	Ring breathing			1188	956		
A_1''	4	CH ₂ twisting	f	f	(1125) ^b	(800)	(1.40)	1.414
A_{2}'	5	CH ₂ wagging	Ĩf	f	(975)	(790)	(1.23)	1.235
$A_{2}^{\prime\prime}$	6	CC stretching	f	Parallel	3102.9	2338	(1.85)	1.871
-	7	CH ₂ rocking	Ĩf	bands	(854)	614	· · ·	
E'	8	CH stretching	depol	Perpen-	3028.1	2211.4	2.57	2.646
	9	CH ₂ deformation	-	dicular	1441.8	1074.3		
	10	Ring deformation		bands	1028.7	886.9		
	11	CH ₂ wagging			868.5	720.1		
$E^{\prime\prime}$	12	CH stretching	depol	f	3075	2329	(2.30)	2.351
	13	CH ₂ twisting	*	•	(1050)	(835)	· · ·	
	14	CH ₂ rocking			741	528		

TABLE V. Symmetry species, selection rules, and frequency assignments (D_{3h} structure).

Corrected approximately for Fermi resonance.
 Parentheses indicate estimated values.

all observed infrared bands and Raman lines, and the ease with which the assignment can be made is adequate confirmation of the D_{3h} structure.

Species A_1'

The totally symmetrical frequencies are easily located in both cyclopropane and cyclopropane- d_6 , although the frequency changes observed in the latter are rather surprising. There are two weak polarized Raman lines at 1453 and 1504 cm⁻¹ in cyclopropane. On the basis of the D_{3h} structure, they are best explained as a Fermi-resonance doublet resulting from interaction between a fundamental expected at about 1475 cm⁻¹ and the first overtone of the Raman-active fundamental at 741 cm⁻¹. The intensity ratio of the two lines indicates that the lower component lies nearer to the "unperturbed" fundamental, which must be very close to 1475. The other two A_1 frequencies are readily placed at 1188 and 3009 cm⁻¹, though the exact position of the latter is undoubtedly influenced by Fermi resonance also, in view of the polarized companion of lesser intensity at 3027.

In cyclopropane- d_6 the frequencies and intensities of the A_1' lines change remarkably. No Raman lines occur between 1068 and 1229, whereas one might expect both the 1188 ring frequency and the 1475 CH₂ deformation frequency of cyclopropane to be displaced to this range. Instead the 1188 line shifts 24% to 956 and the 1475 frequency moves by 16% to 1274. The intensity change in the latter is even more remarkable, from a weak line (estimate 3) to the second strongest line (8) in the spectrum. However, the product rule for species A_1' is well satisfied with the expected small deviation (3%).

The explanation of these changes is straightforward. There is strong (first-order) coupling between the CD_2 deformation and the ring breathing vibrations in cyclopropane- d_6 because of the close proximity of their frequencies. This coupling causes a mixing of the two modes to such an extent that it is no longer accurate to describe one of them as the "CD₂ deformation vibration" and the other as the "ring breathing vibration." The mixing also results in a transfer of Raman intensity from the latter to the former and accounts for the increased intensity of the former. The phenomenon is observed in many deuterium compounds, an exactly analogous effect having been found, for instance, in the A_1 frequencies of allene and allene- d_4 .⁶ Other examples have been reported in the spectra of deuterated propanes by McMurry and Thornton,¹⁷ who give the same explanation. Since the observed mixing is the direct result of coupling between deuterium deformation and heavy-atom vibrations when their frequencies are nearly equal, one concludes that such coupling should also exist under comparable circumstances between any hydrogen bending vibrations and skeletal vibrations. A contrary view has been put forward recently by I. Nakagawa.¹⁸

Species A_2''

The parallel rotational structure expected for infrared bands of this species enables the CH and CD stretching fundamentals to be located at 3102.9 and 2336 cm^{-1} respectively. The other frequency $(CH_2 \text{ rocking})$ was placed by Smith¹⁹ at 872 cm⁻¹, where it was said to be observed underlying the fine structure of the very strong perpendicular band at 868. Since there is considerable doubt about this, it is helpful that a weak infrared band, apparently of parallel structure, is observed at 614 cm⁻¹ in cyclopropane- d_6 . This band has no counterpart in the Raman effect, and hence should be assigned to A_2'' . If the assignment is correct, the product rule indicates that Smith's estimate of 872 is somewhat high. A more compatible value is 854 cm⁻¹, at which point a weak maximum is observed between the P and O branches of the 868 band (see Fig. 1). This maximum may be the sharp Q-branch of the A_2''

¹⁷ H. L. McMurry and V. Thornton, J. Chem. Phys. 19, 1014 (1951).

¹⁸ I. Nakagawa, J. Chem. Soc. Japan **75**, 178 (1954); Chem. Abst. **48**, 4975b (1954). ¹⁹ L. G. Smith, Phys. Rev. 59, 924 (1941).

fundamental or perhaps part of the structure of the 866 band. In any event, if the cyclopropane- d_6 band is correctly assigned, the A_2'' band in the light compound must be very close to 854.

Species E'

This species is easily assigned because its fundamentals are both Raman and infrared active. All are observed in both spectra for both compounds. In Table V the vapor-phase infrared frequencies are used to calculate the product rule, but the liquid-phase Raman frequencies are all within 10 $\rm cm^{-1}$ (usually much less) of the vapor frequencies. The product rule is well satisfied. The assignment agrees with that of Herzberg¹ and various earlier investigators, but the additional evidence furnished by the spectrum of cyclopropane d_6 is considerable. It enables a clear-cut rejection of the suggestion of Scott et al.,20 based on normal-coordinate calculations for cyclopropane and spiropentane, that 868 be assigned to E'' and the Raman-active frequency at 741 be put in E' in its place. The analog of 741 in cyclopropane- d_6 is clearly the line at 528, which is also Raman-active and silent in the infrared. If these two frequencies be substituted for 868 and 720 respectively, the observed E' frequency-product ratio deviates from the theoretical product rule by 17% in a direction opposite to that expected from anharmonicity. To be sure, the infrared band at 614 can be paired with the 741 Raman line to preserve the product-rule value, but this would be objectionable on the ground that 741 is Raman-active but infrared-forbidden while 614 is just the reverse.

Finally it may be commented that species E', which contains both CH₂ deformation and wagging modes, as well as a ring vibration, also exhibits unusual frequency shifts. Here, however, the CH₂ deformation shows a "normal" shift (34%), while the ring and CH₂ wagging vibrations couple strongly and shift about 16% and 20% respectively. Moreover, it appears that considerable coupling prevails in both cyclopropane and cyclopropane- d_6 .

Species E''

There are only hydrogen degrees of freedom in E'', which is Raman-active and infrared-forbidden. Depolarized Raman lines without counterparts in the infrared spectrum of the vapor are found at 3075 and 741 cm⁻¹ in cyclopropane and at 2329 and 528 cm⁻¹ in cyclopropane- d_6 , and may be assigned to this species. The higher frequencies belong to CH and CD stretching modes and the lower to CH₂ and CD₂ rocking. The rocking assignment is different from that of Herzberg,¹ but is indicated by a considerable amount of evidence of various sorts. The A_2'' rocking frequency at 614 in cyclopropane- d_6 is not far removed from 528. In

²⁰ Scott, Finke, Hubbard, McCullough, Gross, Williamson, Waddington, and Huffman, J. Am. Chem. Soc. 72, 4664 (1950). ethylene oxide, cyclobutene, and cyclobutane, and their deuterium derivatives,²¹ the band types of certain infrared bands of comparable frequency (in the range 630–850 for the *H*-compound), indicate clearly their species, from which it may be concluded that the vibration in question is either a twisting or a rocking. In cyclobutane, however, for symmetry reasons, the band must be due to a rocking mode (A_{2u} of D_{4h}). This is true even though the symmetry of cyclobutane may actually be D_{2d} , for the selection rules obeyed by the infrared and Raman spectra are closely those of D_{4h} , and the band is quite strong in both light and heavy cyclobutane.

No twisting frequency is directly observed in cyclopropane, but by analogy with the corresponding observed twisting frequencies in ethylene oxide and cyclobutene, these should lie near 1100 in the light compound and 830 in the heavy. With the help of the product rule for the A_1'' and E'' species and the overtone band assignments (see below), the estimates given in Table V were made.

Species A_1'' and A_2'

Each of these contains one spectroscopically inactive frequency. The twising frequency (A_1'') was located from overtones 1125 and 800 cm⁻¹ (see below) and the A_2' wagging at 975 and 790 cm⁻¹ in cyclopropane and cyclopropane- d_6 . While these values are uncertain, they are about what one expects and fit the product rules satisfactorily.

COMBINATION TONE ASSIGNMENTS

The high symmetry of cyclopropane imposes considerable restriction on the infrared activity of combination tones. The inactive fundamentals, however, may combine with others to give rise to allowed overtones and it might reasonably be expected that such overtones could be used to locate the inactive fundamentals. This turns out to be the case, but the evidence is not very extensive, and confirmation of these values from other sources (infrared spectra of single crystals, higher overtones, normal coordinate calculations) is needed.

There are about sixty allowed binary summation tones. In cyclopropane half of these lie above 3700 cm⁻¹ and half below 3000 cm⁻¹, none being calculated for the intermediate region. The present investigation did not extend above 3700 cm⁻¹.²² Below 3000 cm⁻¹, bands have been found at spectral locations where 21 of the 31 binary summation tones were expected. In cyclopropane- d_6 the corresponding bands lie below 2200 cm⁻¹, and 13 of the expected 30 are observed. Of these 13, 11 correspond to the same combinations observed

²¹ R. C. Lord and B. Nolin, succeeding paper on ethylene oxide; D. G. Rea, thesis, MIT, 1954, for cyclobutene and cyclobutane.

²² S. P. Sinha [J. Chem. Phys. 18, 217 (1950)] investigated the region above 4100 cm⁻¹ in a long-path cell, but came to no conclusions about the positions of the inactive fundamentals.

for cyclopropane. There are nine overtones found in cyclopropane- d_6 in the range 2700–3700 cm⁻¹ and all of these can be explained readily as binary summation tones.

The values of inactive frequencies in cyclopropane and cyclopropane- d_6 obtained from the interpretation of combination tones are: ν_4 , 1125 and 800, and ν_5 , 975 and 790. However, the value for ν_5 in cyclopropane is based mainly on a band (2095.7, $\nu_4 + \nu_5$) for which there is an alternate explanation ($2\nu_{13}$). In the event that the latter is correct, the value for ν_5 becomes very doubtful, but ν_{13} is evaluated as 1050 or thereabouts. A similar ambiguity about ν_{13} exists in cyclopropane- d_6 .

Assignments of the overtone bands have been given in Tables I and II. Ternary combinations have not been considered (with one exception) because few will fall below 3000 cm⁻¹ in cyclopropane and 2000 cm⁻¹ in cyclopropane- d_6 , and because they are expected to be less intense than the binary summation tones. Similarly binary difference tones have been omitted because the Boltzmann factors are expected to be small. The interpretation has not apparently suffered thereby with one exception.

The exception is the very weak and sharp band at 720 cm^{-1} in cyclopropane. This band, of which a broader companion at 740 cm⁻¹ may be the *R*-branch, has not been reported previously. This is understandable, even if the band is genuine, because it coincides with a carbon dioxide band of moderate intensity. However, all trace of atmospheric carbon dioxide absorption was removed from our instrument by flushing with dry nitrogen, as was indicated by the complete absence of the powerful 667 cm⁻¹ band, and contamination of the sample itself by carbon dioxide is ruled out by the same evidence.

The only infrared-active binary difference frequency near 720 cm⁻¹ and with a reasonably large Boltzmann factor is $\nu_9 - \nu_{14}$, for which the frequency calculated from the gas-phase value of ν_9 and liquid-phase value of ν_{14} is 701 cm⁻¹. The difference is well beyond experimental error. Unless it be assumed that the gas-phase value of v_{14} is 15–20 cm⁻¹ smaller than the liquid-phase value (there is some evidence to the contrary), that the value of ν_9 is in error, or that the very intense band at 866 cm⁻¹ (ν_{11}) causes a displacement in the position of the Q-branch of the overtone, this explanation must be rejected. In view of the absence of any corresponding band in the spectrum of cyclopropane- d_6 which is in accord with the product rule, the band is left without definite assignment. Possibly it should be rejected as not belonging to cyclopropane.

Geometrical Configuration of Cyclopropane

It was hoped at the outset of this work that the rotational contour of a parallel band in cyclopropane- d_6

might be used in the evaluation of the double moment of inertia for that molecule with the help of the treatment of Gerhard and Dennison.²³ The expression for the double moment I_{xy} of cyclopropane is:

$$I_{xy} = m_{\rm C} r^2_{\rm CC} / 2 + m_{\rm H} [(r_{\rm CC} + \sqrt{3} r_{\rm CH} \cos \phi)^2 + 6 r_{\rm CH}^2 \sin^2 \phi]$$

where $m_{\rm C}$ and $m_{\rm H}$ are the carbon and hydrogen masses, $r_{\rm CC}$ and $r_{\rm CH}$ the carbon-carbon and carbon-hydrogen internuclear distances, and 2ϕ , the HCH bond angle. Since the first term and the quantity in square brackets are the same for both cyclopropane and cyclopropane d_6 , measurements of I_{xy} for both molecules enables evaluation of the quantity in square brackets without detailed determination of $r_{\rm CC}$, $r_{\rm CH}$, and ϕ . Hence $r_{\rm CC}$ can be obtained directly once the two values of I_{xy} are known.

Unfortunately the P-R separation in the only parallel band which could be accurately measured in the spectrum of cyclopropane- d_6 ($\Delta v_{P-R} = 43.1 \text{ cm}^{-1}$ for the band at 2336 cm⁻¹) gives a highly implausible value for I_{xy} and hence for r_{CC} . The correct values of I_{xy} as determined from high-resolution studies²⁴ are 41.82 and 60.48, $\times 10^{-40}$ g-cm², from which it follows that $r_{CC} = 1.524$ A.

Thermodynamic Functions

The fundamental frequencies of Table V and the moments of inertia implied by the foregoing values of I_{xy} coupled with a reasonable assumption about r_{CH} are closely similar to those used by Ruhrwein and Powell²⁵ in the calculation of the entropy of cyclopropane vapor, as indicated by their *Note added in proof.* The difference in the entropy which would result from use of the present values would be about -0.05 eu at the boiling point, 240.3°K. Recalculation of the thermodynamic functions scarcely seems worthwhile.

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²³ S. L. Gerhard and D. M. Dennison, Phys. Rev. 43, 197 (1933). ²⁴ Günthard, Lord, and McCubbin (unpublished).

²⁵ R. A. Ruhrwein and T. M. Powell, J. Am. Chem. Soc. 68, 1063 (1946).