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Infra-Red Spectrum and Depolarization Factors of the Raman Lines of Spiropentane and the Raman and Infra-Red Spectra of 1,1-Dimethylcyclopropane,¹ 1-Methylcyclobutene, and Methylenecyclobutane

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The infra-red absorption spectrum in the region $700\text{--}4000\text{ cm}^{-1}$, both for the liquid and for the gas at various pressures, and precise values for the depolarization factors of the Raman lines of spiropentane are reported. Infra-red and Raman frequencies, estimated relative intensities, and qualitative depolarization data are reported also for 1,1-dimethylcyclopropane. Selection rules for the two hydrocarbons are discussed, and it is shown that the observed numbers of Raman frequencies are not inconsistent with the structures D_{2d} and C_{2v} for the spiropentane and 1,1-dimethylcyclopropane, respectively. In addition, Raman and infra-red data are included for the isomers, 1-methylcyclobutene and methylenecyclobutane. Tentative assignments of the fundamentals are made for each of the four hydrocarbons.

INTRODUCTION

MURRAY and Stevenson² synthesized a C_5H_8 hydrocarbon by the debromination of pentaerythrityl bromide with zinc dust, using acetamide as a solvent. On the basis of its Raman spectrum, chemical properties, and method of preparation, they assigned to the hydrocarbon the spiropentane structure (symmetry D_{2d}). This structure was later confirmed by an electron-diffraction investigation.³

In view of the symmetrical structure of spiropentane it seemed worth while to obtain precise depolarization factors for its Raman lines, to obtain its infra-red spectrum, and to attempt a correlation of these data by use of the group theory selection rules. As a possible aid to this analysis it appeared desirable also to obtain the Raman and infra-red spectra of the similar molecule, 1,1-dimethylcyclopropane. Infra-red and Raman spectra of the isomers, 1-methylcyclobutene and methylenecyclobutane are included.

¹ The Raman data for the first two compounds were presented at the American Physical Society Meeting, Columbus, Ohio, June 1945; abstract in *Phys. Rev.* **68**, 98 (1945).

² M. J. Murray and E. H. Stevenson, *J. Am. Chem. Soc.* **66**, 812 (1944).

³ J. Donohue, G. L. Humphrey, and V. Schomaker, *J. Am. Chem. Soc.* **67**, 332 (1945).

EXPERIMENTAL PROCEDURE

Raman

The depolarization factors for liquid spiropentane were obtained with a Hilger E-518 spectrograph by use of a previously described method.⁴ Calibration marks were placed upon each of the two spectrograms, and corrections were made for real or apparent polarization produced by the spectrograph, reciprocity failure of the plates, and convergence errors. Six independent determinations of the depolarization factor of each line were made; for the four more intense lines, half of these determinations were made from the 2-hr. spectrogram and half from the 5-hr. spectrogram; for the other, weaker lines, all six of the determinations were made from the 5-hr. spectrogram. Intensities were obtained by use of a Gaertner microdensitometer.

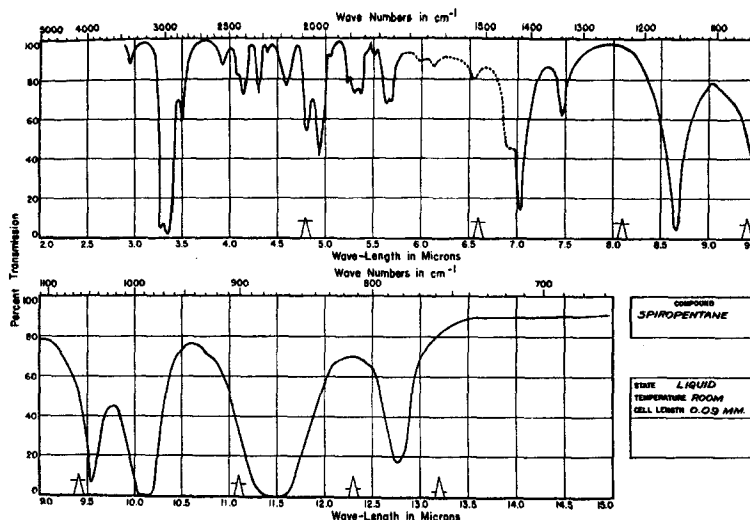
1,1-Dimethylcyclopropane

The sample of 1,1-dimethylcyclopropane was prepared by the reduction of $(CH_3)_2C(CH_2Br)_2$ by zinc in acetamide. The method is that described by Whitmore, Popkin, Bernstein, and Wilkins.⁵ Because the quantity of the reduction product at hand was too small to permit frac-

⁴ Forrest F. Cleveland, *J. Chem. Phys.* **13**, 101 (1945).

⁵ F. C. Whitmore, A. H. Popkin, H. I. Bernstein, and J. P. Wilkins, *J. Am. Chem. Soc.* **63**, 124 (1941).

FIG. 1. Infra-red absorption curve for liquid spiropentane.



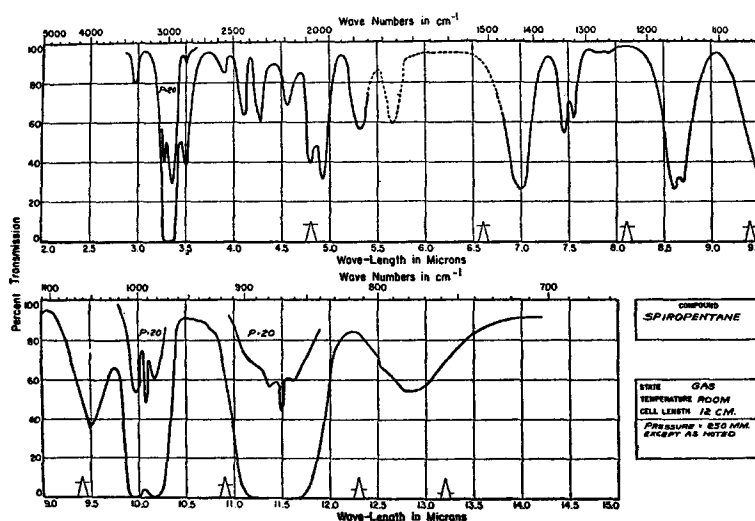
tiation in the equipment available, the Raman spectrum was obtained with the crude material. Weak Raman lines at 1652 and 3017 cm^{-1} (not included in Table II) are assigned to an olefinic impurity. Before the infra-red spectrum was taken, however, the olefinic contaminant was removed as follows: bromine was added to the crude product at about -40°C until a slight color showed that an excess of the halogen was present. On warming, the 1,1-dimethylcyclopropane vaporized directly into the absorption tube while the dibromides of the olefins remained as residue. Olefinic bands were absent in the spectrum of the sample thus purified.

1-Methylcyclobutene

It was stated by Philipov⁶ that the reduction of pentaerythrityl tetrabromide by zinc in alcohol produced methylenecyclobutane and 1-methylcyclobutene. Murray and Stevenson² found no spectroscopic (Raman) evidence for the presence of the latter compound, but since its spectrum was not available the conclusion needed verification. A sample of 1-methylcyclobutene was generously furnished by Dr. V. Schomaker. It was prepared as described by Shand, Schomaker, and Fischer.⁷

Even the most prominent unique lines found in

FIG. 2. Infra-red absorption curve for gaseous spiropentane.



⁶ O. Philipov, J. prakt. Chem. [2] 93, 162 (1916).

⁷ W. Shand, Jr., V. Schomaker, and J. R. Fischer, J. Am. Chem. Soc. 66, 636 (1944).

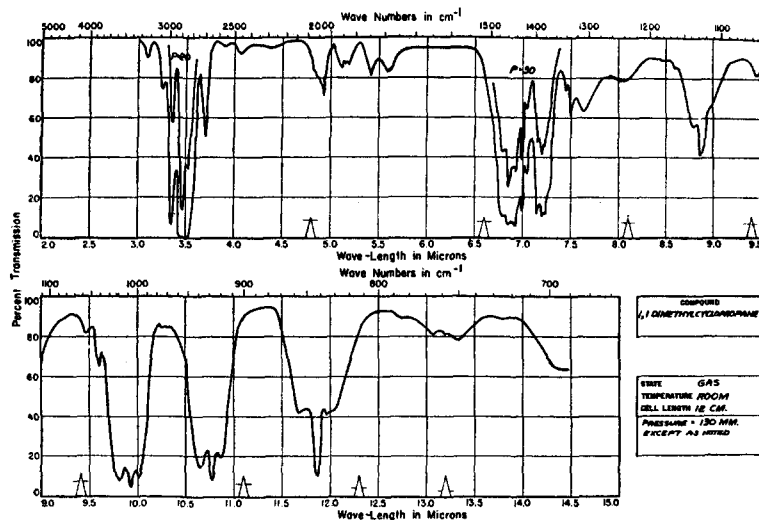


FIG. 3. Infra-red absorption curve for gaseous 1,1-dimethylcyclopropane.

the Raman spectrum of this hydrocarbon are absent from all reduction products of pentaerythrityl bromide so far examined by one of us (M.J.M.), hence it is thought that the concentration of this hydrocarbon in the crude product is probably less than one percent.

The Raman line at 1680 cm^{-1} in the spectrum of the sample of 1-methylcyclobutene is probably due to the presence of a small amount of the isomeric methylenecyclobutane. Likewise the infra-red spectrum of the liquid shows a band at 1670 cm^{-1} which could be assigned to the exocyclic olefin. The infra-red band of the liquid at 1720 cm^{-1} is probably due to carbonyl introduced either accidentally or by atmospheric oxidation. The Raman spectrum when obtained

some months earlier with the same sample had no line at this position.

Methylenecyclobutane

The sample of this hydrocarbon was obtained by careful fractionation of the olefins recovered from silver nitrate extraction of the crude reduction products of pentaerythrityl tetrabromide. The sample studied was taken from the middle of the plateau boiling at 41.8°C at 760-mm pressure.

Infra-Red

The infra-red spectra were obtained with a large Littrow spectrometer having a 60° prism of $10\times 15\text{-cm}$ faces and a collimating mirror of

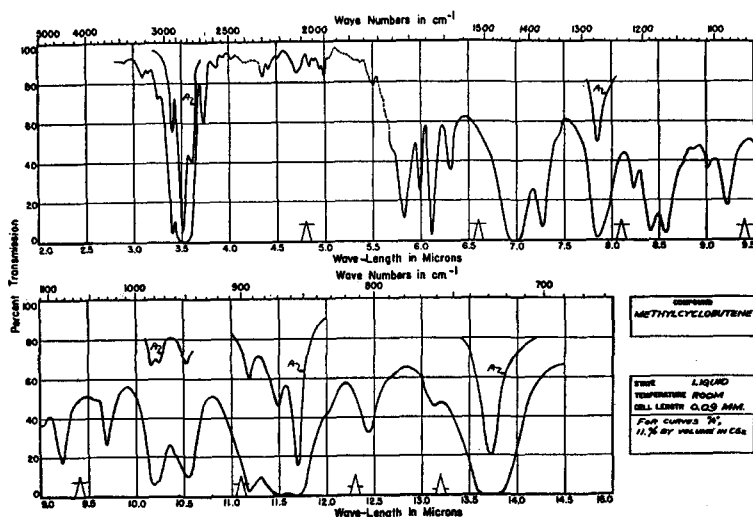
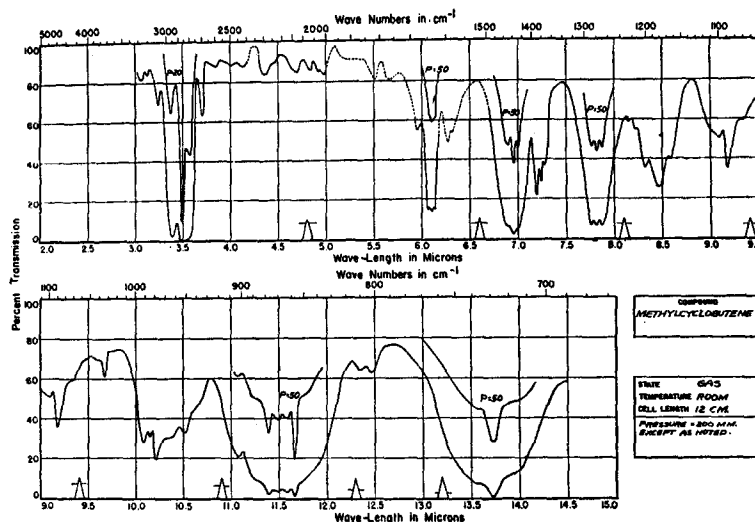


FIG. 4. Infra-red absorption curve for liquid 1-methylcyclobutene.

FIG. 5. Infra-red absorption curve for gaseous 1-methylcyclobutene.



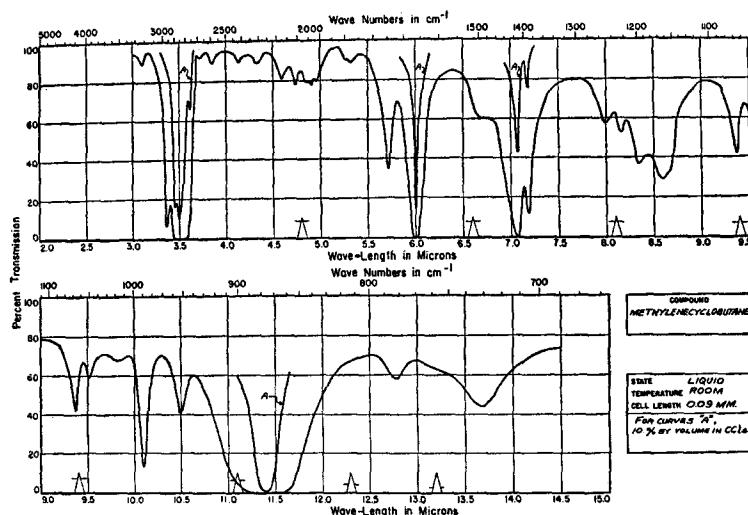
100-cm focal length. The spectrometer proper is nearly a duplicate of the instrument described by McAlister, Matheson, and Sweeney.⁸ The source used here, however, is a Nernst glower, and the photographic recordings of the thermocouple output are obtained by use of a two-galvanometer amplifier coupled by a conventional split-beam, photo-cell arrangement.

The spectra were recorded using rocksalt cells of the type described by Gildart and Wright⁹ and of the thicknesses noted on the spectrograms (Figs. 1-7). The final curve for each compound represents the result obtained by comparing the traces of the thermocouple output when the filled

cell is in the beam with that obtained with the evacuated cell.

Good stabilization of all circuits and elimination of sources of erratic disturbances have resulted in records that are reproducible to better than one percent of full-scale response and wave-length measurements to better than 0.01 micron. However, errors introduced in transposing from the records of thermocouple response *versus* dial reading to percent transmission *versus* wave-length may double these figures. To compensate for the variation of the intensity of the radiation emitted by the glower with wave-length, the slits of the spectrometer are manually operated in a

FIG. 6. Infra-red absorption curve for liquid methylenecyclobutane.



⁸ E. D. McAlister, G. L. Matheson, and W. J. Sweeney, Rev. Sci. Inst. 12, 314 (1941).

⁹ L. Gildart and N. Wright, Rev. Sci. Inst. 12, 204 (1941).

stepwise fashion. The effective slit widths are indicated on the curves (Figs. 1-7) at the appropriate wave-lengths.

Careful studies of the spectra of water vapor and of ammonia show that the optics of the instrument are of such sufficiently high quality that the resolving power is determined solely by the size of the slits used. Furthermore, the resolving power obtained is at least equal to or better than that reported by McAlister, Matheson, and Sweeney⁸ and by Oetjen, Kao, and Randall,¹⁰ except from 13 to 15 microns where the response of the thermocouple is below par, thus requiring the use of slits somewhat wider than normal. These data also show that the positions of the absorption maxima (as given in the tables) are reliable to 1 cm^{-1} at the longer wave-lengths. Band centers are given to the nearest 5 cm^{-1} for frequencies above 1300 cm^{-1} .

RESULTS

The depolarization data for spiropentane are given at the left in Table I. Depolarization factors were not obtained for the weak lines at 1150, 2836, and 2881 cm^{-1} , and the data for the weak 613- and 779- cm^{-1} lines are less precise than for the stronger lines. The lines at 1033 and 2991 cm^{-1} are strongly polarized, while the ones at 581, 613, and 779 cm^{-1} are only slightly polarized.

The infra-red data for the liquid and gaseous states are given in the central part of Table I, and the corresponding infra-red absorption curves are

shown in Figs. 1 and 2. The infra-red spectra of gaseous spiropentane and methylenecyclobutane have also been reported by Cleaves and Sherrick.¹¹ The data reported by them agree well with those obtained in the present investigation, except for differences in resolving power of the two instruments.

The Raman data obtained for liquid 1,1-dimethylcyclopropane are compared with the Raman data obtained for liquid spiropentane at the left in Table II; the corresponding infra-red data for the two compounds in the gaseous state are compared at the right in Table II. The infra-red absorption curve for the 1,1-dimethylcyclopropane is shown in Fig. 3.

The Raman spectrum of 1-methylcyclobutene and the infra-red spectra for the liquid and gaseous states are compared in Table III. The corresponding infra-red absorption curves are given in Figs. 4 and 5.

The Raman spectrum of methylenecyclobutane and the infra-red spectra for the liquid and gaseous states are compared in Table IV. The corresponding infra-red absorption curves are given in Figs. 6 and 7.

DISCUSSION OF RESULTS

Number of Frequencies Expected for the Bicyclic C_6H_8 Compound

The number of polarized and depolarized Raman lines to be expected in the Raman spec-

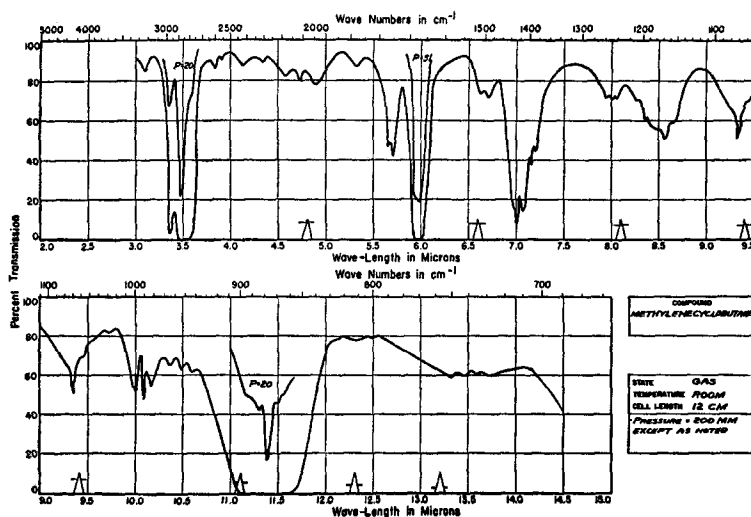


FIG. 7. Infra-red absorption curve for gaseous methylenecyclobutane.

¹⁰ R. A. Oetjen, C. L. Kao, and H. M. Randall, *Rev. Sci. Instr.* **13**, 515 (1942).

¹¹ A. P. Cleaves and M. E. Sherrick, N.A.C.A., Tech. Note No. 1160 (1946).

TABLE I. Raman and infra-red data for spiropentane (C₅H₈).*

Raman					Infra-red				Tentative assignment
$\Delta\nu$	Liquid				Liquid		Gas		
	<i>I</i>	ρ	a.d.	m.d.	ν_l	<i>I_l</i>	ν_g	<i>I_g</i>	
305	4	0.86	0.03	0.07					Fundamental, <i>E</i> , 305**
581	16	0.69	0.02	0.04					Fundamental, <i>A</i> ₁ , 581
613	4	0.71	0.04	0.11					Fundamental, <i>E</i> , 613
779	4	0.66	0.07	0.12	783	<i>s</i>	778	<i>m</i>	Fundamental, <i>E</i> , 779
							798	<i>vw</i>	1397-613=784, <i>B</i> ₁ × <i>E</i>
							861	<i>vs</i>	<i>P</i> branch or 1163-305=858, (<i>B</i> ₂ or <i>E</i>)× <i>E</i>
872	30	0.82	0.01	0.04	871	<i>vs</i>	870	<i>vs</i>	Fundamental, <i>B</i> ₂ or <i>E</i> , 870
							879	<i>vs</i>	<i>R</i> branch
							896	<i>w</i>	305+581=886, <i>A</i> ₁ × <i>E</i>
					(928)	<i>vw</i>	929	<i>vw</i>	3(305)=915, <i>E</i> ³
							940	<i>vw</i>	305+613=918, <i>E</i> × <i>E</i>
							983	<i>vs</i>	<i>P</i> branch
					990	<i>vs</i>	993	<i>vs</i>	Fundamental, <i>E</i> , 993
							1003	<i>vs</i>	<i>R</i> branch
1033	50	0.02	0.01	0.03					Fundamental, <i>A</i> ₁ , 1033
					1049	<i>s</i>	1053	<i>s</i>	Fundamental, <i>B</i> ₂ or <i>E</i> , 1053
1150	1	—	—	—	1155	<i>s</i>	1151	<i>s</i>	Fundamental, <i>B</i> ₂ or <i>E</i> , 1151
							1163	<i>s</i>	Fundamental, <i>B</i> ₂ or <i>E</i> , 1163
							1260	<i>vw</i>	2(613)=1226, <i>E</i> ²
							1280	<i>vw</i>	305+993=1298, <i>E</i> × <i>E</i>
							1325	<i>m</i>	Fundamental, <i>B</i> ₂ or <i>E</i> , 1325
					1340	<i>w</i>	1340	<i>m</i>	Fundamental, <i>B</i> ₂ or <i>E</i> , 1340
1397	5	0.81	0.03	0.04					Fundamental, <i>B</i> ₁ , 1397
1426	10	0.82	0.02	0.05	1420	<i>s</i>	1430	<i>s</i>	Fundamental, <i>B</i> ₂ or <i>E</i> , 1430
					1445	<i>w</i>			581+870=1451, <i>A</i> ₁ ×(<i>B</i> ₂ or <i>E</i>)
					1530	<i>w</i>			2(778)=1556, <i>E</i> ²
					1630	<i>w</i>			305+1325=1630, <i>E</i> ×(<i>B</i> ₂ or <i>E</i>)
					1675	<i>w</i>			613+1053=1666, <i>E</i> ×(<i>B</i> ₂ or <i>E</i>)
					1760	<i>w</i>			613+1151=1764, <i>E</i> ×(<i>B</i> ₂ or <i>E</i>)
					1775	<i>w</i>	1765	<i>m</i>	613+1163=1776, <i>E</i> ×(<i>B</i> ₂ or <i>E</i>)
					1815	<i>w</i>			1033+778=1811, <i>A</i> ₁ × <i>E</i>
					1825	<i>vw</i>			1053+778=1831, <i>E</i> ×(<i>B</i> ₂ or <i>E</i>)
					1860	<i>vw</i>			870+993=1863, <i>E</i> ×(<i>B</i> ₂ or <i>E</i>)
					1885	<i>vw</i>	1880	<i>m</i>	870+1033=1903, <i>A</i> ₁ ×(<i>B</i> ₂ or <i>E</i>)
					1915	<i>vw</i>			581+1340=1921, <i>A</i> ₁ ×(<i>B</i> ₂ or <i>E</i>)
					1985	<i>vw</i>			2(993)=1986, <i>E</i> ²
					2025	<i>m</i>	2030	<i>s</i>	993+1033=2026, <i>A</i> ₁ × <i>E</i>
					2085	<i>m</i>	2085	<i>s</i>	1033+1053=2086, <i>A</i> ₁ ×(<i>B</i> ₂ or <i>E</i>)
					2175	<i>w</i>	2190	<i>m</i>	1033+1151=2184, <i>A</i> ₁ ×(<i>B</i> ₂ or <i>E</i>)
					2275	<i>w</i>			870+1397=2267, <i>B</i> ₁ ×(<i>B</i> ₂ or <i>E</i>)
					2320	<i>m</i>	2345	<i>m</i>	993+1340=2333, <i>E</i> ×(<i>B</i> ₂ or <i>E</i>)
					2415	<i>m</i>			993+1430=2423, <i>E</i> ×(<i>B</i> ₂ or <i>E</i>)
					2450	<i>w</i>	2435	<i>m</i>	1053+1397=2450, <i>B</i> ₁ ×(<i>B</i> ₂ or <i>E</i>)
					2545	<i>w</i>			1151+1397=2548, <i>B</i> ₁ ×(<i>B</i> ₂ or <i>E</i>)
							2565	<i>w</i>	1163+1397=2560, <i>B</i> ₁ ×(<i>B</i> ₂ or <i>E</i>)
2836	0.4	—	—	—					Fundamental, <i>A</i> ₁ or <i>B</i> ₁ , 2836
					2860	<i>m</i>	2850	<i>s</i>	Fundamental, <i>B</i> ₂ or <i>E</i> , 2850
2881	<i>vw</i>	—	—	—					Fundamental, <i>B</i> ₁ or <i>A</i> ₁ , 2881
					2985	<i>vs</i>	2985	<i>vs</i>	Fundamental, <i>B</i> ₂ or <i>E</i> , 2985
2991	100	0.15	0.03	0.05					Fundamental, <i>A</i> ₁ , 2991
					3050	<i>vs</i>	3050	<i>vs</i>	Fundamental, <i>B</i> ₂ or <i>E</i> , 3050
3065	30	0.80	0.02	0.03					Fundamental, <i>B</i> ₁ , 3065
							3370	<i>w</i>	305+3065=3370, <i>B</i> ₁ × <i>E</i>
					3400	<i>w</i>			

* $\Delta\nu$ is the Raman displacement in cm⁻¹; *I* is the relative intensity of the Raman line determined with the microdensitometer; ρ is the mean of the six values of the depolarization factor; a.d. is the average deviation from the mean value of ρ ; m.d. is the maximum deviation from the mean value of ρ ; ν_l and ν_g are the infra-red frequencies in cm⁻¹ for the liquid and gaseous states, respectively; *I*_l and *I*_g are the corresponding intensities (*vs*=very strong, *s*=strong, *m*=medium, *w*=weak, *vw*=very weak); and the braces enclose branches belonging to one band.

** Assumed value of the fundamental. The type-*E* fundamentals are doubly degenerate, degeneracy=*d*=2, all other fundamentals are non-degenerate, *d*=1.

trum was worked out from the group theory formulas¹² for each of the five conceivable struc-

¹² See Arnold G. Meister, Forrest F. Cleveland, and M. J. Murray, Am. J. Phys. 11, 239 (1943).

tures listed by Murray and Stevenson.² This was done both for the entire molecule and for the carbon skeleton alone. The results are given in Table V. The five possible structures given by

TABLE II. Comparison of the Raman data for the liquid state and the infra-red data for the gaseous state for 1,1-dimethylcyclopropane (C_5H_{10}) and spiropentane (C_5H_8).*

Raman data (liquid)						Infra-red data (gas)			
Spiropentane			1,1-Dimethylcyclopropane			Spiropentane		1,1-Dimethylcyclopropane	
$\Delta\nu$	I	ρ	$\Delta\nu$	I_0	ρ_0	ν_0	I_0	ν_0	I_0
305	4	0.86							
			326	1	—				
			356	3	D				
			392	1	—				
581	16	0.69							
613	4	0.71							
			658	1	—				
			678	7	P				
								724	w
								750	w
								758	w
								766	w
								785	w
779	4	0.66	778	1	—	778	m		
						798	vw		
			836	5	D			(830)	m
								835	s
								842	vs
								857	s
872	30	0.82				861	vs		
						870	vs		
						879	vs		
						896	w		
			928	10	P			920	s
						929	vw	928	vs
						940	vw	939	vs
								(970)	vs
						983	vs	(976)	vs
						993	vs	999	vs
						1003	vs	1007	vs
								1019	vs
1033	50	0.02						1042	m
			1056	5	P	1053	s	1056	w
								(1112)	m
			1124	2	—			1127	m
								1137	m

Murray and Stevenson² are shown in the first column, and the observed numbers of lines are listed at the bottom. In determining these observed numbers of lines it was assumed that the carbon skeleton frequencies were those less than 1155 cm^{-1} and that the weak 613-cm^{-1} and 779-cm^{-1} lines were depolarized lines. The 581-cm^{-1} line was chosen as a polarized line, rather than the 779 line, because of the greater reliability of the ρ value of the 581 line, because polarized lines are usually more intense in Raman spectra than depolarized lines, and because there is an infra-red band near 779 cm^{-1} . Such a coincidence of Raman and infra-red bands is forbidden for polarized lines by the selection rules if the structure of the hydrocarbon is that indicated by the chemical and electron diffraction evidence.

The 1150-cm^{-1} line could reasonably be expected to correspond to a non-totally-symmet-

rical vibration involving the CCC rings, since the totally-symmetrical frequency involving these rings certainly corresponds to the highly polarized line at 1033 cm^{-1} and since the more unsymmetrical vibration frequently corresponds to a line having a higher frequency than that of the totally-symmetrical vibration; if this is the case, the 1150 line would be a depolarized line.

If these assumptions are made, the observed numbers and those predicted for the spiropentane or D_{2d} structure are in good agreement as far as the skeleton frequencies are concerned; in fact if the 1150 line is actually a depolarized line, as indicated above, the agreement would be perfect. But when the entire molecule is considered, the observed numbers are less than the predicted ones, presumably because of unresolved lines in the region of the carbon-hydrogen frequencies; such unresolved lines are to be expected since

TABLE II.—Continued.

Raman data (liquid)						Infra-red data (gas)			
Spiropentane			1,1-Dimethylcyclopropane			Spiropentane		1,1-Dimethylcyclopropane	
$\Delta\nu$	I	ρ	$\Delta\nu$	I_s	ρ_s	ν_0	I_s	ν_0	I_s
1150	1	—	1158	1	—	1151	<i>s</i>	1163	<i>w</i>
						1163	<i>s</i>	1180	<i>vw</i>
								1240	<i>w</i>
						1261	<i>vw</i>	(1270)	<i>vw</i>
			1319	8	<i>P</i>	1280	<i>vw</i>	1310	<i>m</i>
						1325	<i>m</i>	1335	<i>m</i>
			1382	2	—	1340	<i>m</i>	1340	<i>w</i>
								1380	<i>m</i>
1397	5	0.81						1385	<i>m</i>
1426	10	0.82						1395	<i>m</i>
			1433	4 <i>b</i>	<i>D</i>	1430	<i>s</i>	1420	<i>w</i>
			1465	4 <i>b</i>	<i>D</i>			1430	<i>m</i>
								1445	<i>s</i>
								1460	<i>vs</i>
						1765	<i>m</i>	1470	<i>s</i>
						1880	<i>m</i>	1785	<i>w</i>
								1850	<i>w</i>
								1930	<i>vw</i>
								1940	<i>vw</i>
								1955	<i>vw</i>
						2030	<i>s</i>	2030	<i>w</i>
								(2060)	<i>vw</i>
						2085	<i>s</i>	(2070)	<i>vw</i>
						2190	<i>m</i>		
								2285	<i>w</i>
						2345	<i>m</i>		
						2435	<i>m</i>	2460	<i>w</i>
						2565	<i>w</i>	2560	<i>w</i>
								2700	<i>m</i>
			2733	3	<i>P</i>			2840	<i>m</i>
2836	0.4	—	2863	6	<i>P</i>	2850	<i>s</i>	2890	<i>vs</i>
2881	<i>vw</i>	—	2892	5	<i>P</i>				
			2926	7	<i>P</i>				
			2950	5	<i>D</i>				
2991	100	0.15	2993	10	<i>P</i>	2985	<i>vs</i>	2985	<i>m</i>
						3050	<i>vs</i>	3075	<i>m</i>
3065	30	0.80	3061	4 <i>b</i>	<i>D</i>			3240	<i>w</i>
						3370	<i>w</i>		

* I_s = Estimated intensity on the basis of 10 for the strongest line; ρ_s is the qualitative depolarization data, *P* = polarized, *D* = depolarized; *b* = broad; other symbols have the same meaning as in Table I. Data in regard to which there is some uncertainty are enclosed in parentheses.

there should be 15C—H lines all of which involve, however, only one kind of C—H bond. These frequencies would give rise to Raman lines that would undoubtedly fall very close together on the spectrograms and which could well be unresolved.

One can conclude then that the observed Raman data are in reasonably good agreement with the spiropentane or D_{2d} structure. The predictions for the D_{3h} structure are not in as good an agreement with the observed Raman data, even if the 1150 line were considered to be a C—H frequency.

Selection Rules and Assignment of Frequencies for Spiropentane

The selection rules for fundamentals, overtones, and binary combinations¹² for the spiropentane or D_{2d} structure are given in Table VI and a tentative assignment of the frequencies is given at the right in Table I. Twenty-one of the expected 25 bands corresponding to fundamental frequencies were assigned. The fundamentals were selected upon the basis of their intensity, their appearance or non-appearance in the Raman and infra-red spectra, and in consideration of the selection rules for fundamentals, overtones, and

TABLE III. Raman and infra-red data for 1-methylcyclobutene (C_5H_8).*

Raman		Infra-red				Tentative assignment
Liquid		Liquid		Gas		
$\Delta\nu$	I_s	ν_l	I_l	ν_g	I_g	
318	4					Fundamental, 318**
390	3					Fundamental, 390
434	0					729-318=411 or 1091-651=440
520	1					890-390=500 or 1181-651=530
620	1					2(318)=636
651	6					Fundamental, 651
				716	<i>vs</i>	1034-318=716
723	1	728	<i>s</i>	729	<i>vs</i>	Fundamental, 729
				737	<i>vs</i>	1375-651=724
762	2	762	<i>m</i>			Fundamental, 762
		804	<i>s</i>	802	<i>w</i>	1181-390=791
		(833)	<i>w</i>	810	<i>w</i>	1217-390=827
860	4	854	<i>vs</i>	858	<i>vs</i>	Fundamental, 858
				864	<i>vs</i>	1181-318=863
		870	<i>vs</i>	870	<i>vs</i>	1202-318=884
				877	<i>vs</i>	1280-390=890
890	5	894	<i>vs</i>	890	<i>vs</i>	Fundamental, 890
				903	<i>vs</i>	1217-318=899
957	5	949	<i>vs</i>	951	<i>s</i>	Fundamental, 951
		976	<i>vs</i>	965	<i>s</i>	318+651=969
986	6	983	<i>vs</i>	979	<i>s</i>	Fundamental, 979
				986	<i>s</i>	1375-390=985
				993	<i>s</i>	1640-651=989
				1026	<i>w</i>	390+651=1041
1037	2	1032	<i>s</i>	1034	<i>m</i>	Fundamental, 1034
		(1046)	<i>vw</i>	1043	<i>w</i>	318+729=1047
				1070	<i>w</i>	1375-318=1057
1091	2	1085	<i>vs</i>	1090	<i>s</i>	Fundamental, 1090
		1110	<i>m</i>	1100	<i>w</i>	1435-318=1117
		1130	<i>vw</i>			390+729=1119
1144	2	1143	<i>vw</i>			Fundamental, 1144
		1167	<i>vs</i>	1164	<i>m</i>	318+858=1176
				1181	<i>s</i>	Fundamental, 1181
1185	1b	1189	<i>vs</i>	1202	<i>m</i>	Fundamental, 1202
1216	4	1214	<i>s</i>	1217	<i>w</i>	Fundamental, 1217
				1227	<i>w</i>	390+858=1248
				1270	<i>vs</i>	318+951=1269

binary combinations. Three of the five type- A_1 , two of the four type- B_1 , and four of the eight type- E fundamentals were definitely assigned. The twelve remaining ones could only be assigned to one or the other of two vibration types, ten as either B_2 or E , two as either A_1 or B_1 . Four of the fundamentals, the vibration type of which was at first ambiguous, were assigned to a particular vibration type while accounting for the weak bands as overtones or binary combinations. Only overtones or binary combinations allowed by the selection rules were used in accounting for the weaker bands, and difference bands were used only for the fundamentals below 700 cm^{-1} , for which the corresponding energy states can be expected to be sufficiently well populated to give rise to appreciable intensities. It was not possible to account for the weak infra-red band observed

for the liquid state at 3400 cm^{-1} . It could be accounted for as the combination $581+2836=3417$, except for the fact that this combination is forbidden by the selection rules. This weak band may owe its origin to a combination of three, or more, frequencies.

Of the four unassigned lines, three correspond to type- A_2 frequencies that are forbidden in both the Raman and infra-red spectra. These frequencies correspond to C-H vibrations and therefore at least some of them may be expected to fall in the 1400- or 3000-cm^{-1} regions.

For a revision of the present tentative and incomplete assignment, a normal coordinate treatment should be very valuable. Such a treatment should make it possible to remove much or all of the ambiguity inherent in the bands assigned to " B_2 or E " which must be done before reliable

TABLE III.—Continued.

Raman		Infra-red				Tentative assignment
Liquid		Liquid		Gas		
$\Delta\nu$	I_e	ν_l	I_l	ν_g	I_g	
1278	3	1276	<i>vs</i>	1280	<i>vs</i>	Fundamental, 1280
				1290	<i>vs</i>	390+890=1280 or 318+979=1297 or 2(651)=1302
		1345	<i>w</i>			390+951=1341 or 318+1034=1352
1378	4	1375	<i>vs</i>	1375	<i>m</i>	Fundamental, 1375
				1380	<i>s</i>	651+729=1380
				1390	<i>s</i>	318+1090=1408
				1430	<i>m</i>	390+1034=1424
1430	8 <i>b</i>	1435	<i>vs</i>	1435	<i>s</i>	Fundamental, 1435
				1450	<i>m</i>	2(729)=1458
1586	1	1585	<i>s</i>	1585	<i>m</i>	Fundamental, 1585
				1595	<i>m</i>	318+1280=1598 or 651+951=1602
				1630	<i>s</i>	651+979=1630
1641	8	1640	<i>vs</i>	1640	<i>s</i>	Fundamental, 1640
				1650	<i>s</i>	390+1280=1670
1680	3	1670	<i>s</i>	1675	<i>m</i>	729+951=1680 or 651+1034=1685 or 318+1375=1693 (or impurity)
		1720	<i>vs</i>			2(858)=1716 or 729+979=1708 (or impurity)
		1758	<i>w</i>			858+890=1748 or 318+1435=1753
				1765	<i>w</i>	729+1034=1763 or 390+1375=1765
		1820	<i>w</i>	1820	<i>w</i>	858+951=1809 or 729+1090=1819 or 390+1435=1825
				1905	<i>w</i>	2(951)=1902 or 318+1585=1903 or 729+1181=1910
		2000	<i>w</i>	2010	<i>w</i>	729+1280=2009 or 979+1034=2013
		2020	<i>w</i>	2035	<i>w</i>	651+1375=2026 or 390+1640=2030
		2045	<i>vw</i>			858+1181=2039 or 951+1090=2041
		2065	<i>vw</i>	2065	<i>w</i>	2(1034)=2068 or 979+1090=2069 or 890+1181=2071
		2125	<i>w</i>	2135	<i>w</i>	1034+1090=2124 or 951+1181=2132 or 858+1280=2138
		2220	<i>vw</i>			1034+1181=2215 or 951+1280=2231
		2270	<i>w</i>	2235	<i>w</i>	858+1375=2233 or 651+1585=2236
		2295	<i>w</i>	2290	<i>w</i>	651+1640=2291 or 858+1435=2293
		2400	<i>w</i>	2420	<i>w</i>	1034+1375=2409 or 979+1435=2414
		2480	<i>w</i>	2495	<i>w</i>	890+1585=2475 or 1217+1280=2495 or 858+1640=2498
		2540	<i>vw</i>			890+1640=2530 or 951+1585=2536
		2585	<i>w</i>	2600	<i>w</i>	951+1640=2591 or 1217+1375=2592
		2675	<i>m</i>			1034+1640=2674 or 1090+1585=2675
2723	2	2770	<i>m</i>	2700	<i>m</i>	Fundamental, 2700
2851	5 <i>vb</i>	2850	<i>vs</i>	2800	<i>vs</i>	Fundamental, 2800
2917	10 <i>vb</i>			2865	<i>vs</i>	Fundamental, 2865
		2940	<i>m</i>	2965	<i>vs</i>	Fundamental, 2917
3044	6					Fundamental, 2965
		3080	<i>vw</i>	3085	<i>w</i>	Fundamental, 3044
		3180	<i>vw</i>			1640+1435=3075
		3240	<i>vw</i>	3200	<i>w</i>	2(1585)=3170 or 318+2865=3183
		3450	<i>vw</i>	3270	<i>w</i>	1640+1585=3225 or 318+2917=3235
						318+2965=3283 or 2(1640)=3280
						651+2800=3451 or 390+3044=3434

* See reference 3, *vb*=very broad; other symbols have the same meaning as in Tables I and II.** Assumed value of the fundamental. All of the fundamentals are non-degenerate, degeneracy = $d=1$.

values of thermodynamic quantities can be calculated from the spectroscopic data. Then a high resolution investigation, especially in the 3000-cm⁻¹ region where the resolution was poorest, might lead to the discovery of the missing A_1 fundamental. A_1 frequencies usually give rise to strong lines in the Raman spectrum, and it seems more likely that the missing A_1 line should be attributed to an unresolved line than to a Raman line so weak that it escaped observation. If the normal coordinate treatment and the high resolu-

tion investigation should result in the establishment of the B_2 and E frequencies and in the discovery of the missing A_1 fundamental, the A_2 frequencies might then be located by a comparison of heat capacities calculated from the spectroscopic data with heat capacities experimentally determined.

1,1-Dimethylcyclopropane

The equilibrium configuration of the 1,1-dimethylcyclopropane molecule will depend upon

TABLE IV. Raman and infra-red data for methylenecyclobutane (C_4H_6).*

Raman		Infra-red				Tentative assignment
Liquid		Liquid		Gas		
$\Delta\nu$	I	ν_L	I_L	ν_g	I_g	
354	23					Fundamental, 354**
373	13					Fundamental, 373
657	20					Fundamental, 657
		731	<i>m</i>	728	<i>w</i>	Fundamental, 728
				736	<i>w</i>	354+373=727
				743	<i>w</i>	2(373)=746
				751	<i>w</i>	1415-657=758
		782	<i>m</i>			Fundamental, 782
				800	<i>w</i>	1155-354=801
				812	<i>w</i>	1167-354=813
				825	<i>w</i>	1197-373=824
				865	<i>vs</i>	1197-354=843
				870	<i>vs</i>	1248-373=875
873	14	877	<i>vs</i>	879	<i>vs</i>	Fundamental, 879
				884	<i>vs</i>	1248-354=894
907	20			895	<i>vs</i>	Fundamental, 895
				944	<i>w</i>	Fundamental, A_1 , 954
957	72	952	<i>m</i>	954	<i>w</i>	
				966	<i>w</i>	
				983	<i>m</i>	
		990	<i>vs</i>	991	<i>m</i>	Fundamental, 991
				1001	<i>m</i>	354+657=1011
		1018	<i>w</i>	1029	<i>w</i>	Fundamental, 1029
		1051	<i>m</i>	1059	<i>w</i>	Fundamental, 1059
		1067	<i>m</i>	1070	<i>m</i>	Fundamental, 1070
		1155	<i>m</i>	1155	<i>m</i>	Fundamental, 1155
		1164	<i>s</i>	1167	<i>m</i>	Fundamental, 1167
				1183	<i>m</i>	Fundamental, 1197
1191	11	1198	<i>s</i>	1197	<i>m</i>	
				1210	<i>m</i>	
		1226	<i>m</i>			
				1240	<i>m</i>	354+879=1233
		1250	<i>m</i>	1248	<i>m</i>	354+895=1249 or 373+879=1252
				1260	<i>m</i>	Fundamental, ($XXC=CH_2$), 1248
				1385	<i>m</i>	373+895=1268
						657+728=1385

the orientations of the two methyl groups with respect to rotation about the C—C single bond. A qualitative consideration of the possible interactions between the *H* and *C* atoms indicates that only one of two structures, of symmetry C_1 and C_{2v} , is probable.

For the structure C_1 all of the frequencies would be allowed to appear in the Raman spectrum and should all be polarized. For the structure C_{2v} the frequencies allowed in the Raman spectrum are: twelve polarized, type- A_1 frequencies, four of which are frequencies of the carbon skeleton; and 27 depolarized (10 type B_1 , 8 type A_2 , and 9 type B_2) frequencies, five of which (two type B_2 , one type A_2 , and two type B_1) are carbon skeleton frequencies. The selection rules allow all of the fundamentals to appear in the Raman spectrum and all except the A_2 fundamentals to appear in the infra-red. All overtones and binary combinations are allowed

in the Raman spectrum and all except A_2^n (n odd), $A_1 \times A_2$, and $B_1 \times B_2$ are allowed in the infra-red.

From the qualitative depolarization data given in Table II it does not appear probable that all of the lines are polarized and, consequently, it seems more reasonable to suppose that the structure is C_{2v} rather than C_1 . Assuming the C_{2v} structure, a comparison of the expected and observed numbers of lines for the 1,1-dimethylcyclopropane with the corresponding numbers for spiropentane is given in Table VII. Skeleton frequencies were, as for spiropentane, taken as those less than 1155 cm^{-1} ; when this is done, the total number of skeleton frequencies observed (10) is one greater than the expected number (9) in this region. The additional frequency could well be a C—H frequency similar to the "rocking frequency" of the methyl group which in dimethyl-

TABLE IV.—Continued.

Raman		Infra-red				Tentative assignment
Liquid		Liquid		Gas		
$\Delta\nu$	I	ν_l	I_l	ν_g	I_g	
1391	20	1390	<i>vs</i>	1395	<i>s</i>	Fundamental, ($XXC=CH_2$), 1395
		1415	<i>vs</i>	1415	<i>vs</i>	Fundamental, 1415
1428	20			1425	<i>vs</i>	Fundamental, ($XXC=CH_2$), 1425
		1485	<i>m</i>	1490	<i>w</i>	Fundamental, 1490
				1510	<i>w</i>	354 + 1155 = 1509 or 728 + 782 = 1510
1679	48	1665	<i>vs</i>	1675	<i>vs</i>	Fundamental, ($XXC=CH_2$), 1675
		1750	<i>s</i>	1750	<i>m</i>	354 + 1395 = 1749 or 728 + 1029 = 1757 or 2(879) = 1758
				1770	<i>m</i>	373 + 1395 = 1768
		1880	<i>w</i>	1880	<i>w</i>	728 + 1155 = 1883
		1900	<i>w</i>			2(954) = 1908
		2015	<i>w</i>			954 + 1059 = 2013
		2040	<i>w</i>	2045	<i>w</i>	879 + 1167 = 2046
		2060	<i>w</i>			991 + 1070 = 2061 or 896 + 1167 = 2063
		2115	<i>w</i>	2115	<i>w</i>	2(1059) = 2118 or 954 + 1155 = 2109
		2180	<i>w</i>	2185	<i>w</i>	782 + 1395 = 2177 or 991 + 1197 = 2188
		2310	<i>w</i>	2305	<i>w</i>	879 + 1425 = 2304 or 2(1155) = 2310
		2420	<i>w</i>	2420	<i>w</i>	1425 + 991 = 2416
				2560	<i>w</i>	879 + 1675 = 2554
		2590	<i>w</i>	2605	<i>w</i>	1197 + 1395 = 2592
		2690	<i>w</i>			1248 + 1425 = 2673
		2770	<i>s</i>	(2785)	<i>m</i>	Fundamental, 2770
2826	4					Fundamental, A_2 , 2826
2861	4	2860	<i>vs</i>	2880	<i>vs</i>	Fundamental, 2860
2902	60	2900	<i>s</i>			Fundamental, 2902
2921	75					Fundamental, A_2 , 2921
2952	88					Fundamental, A_2 , 2952
2986	100	2980	<i>s</i>	2985	<i>vs</i>	Fundamental, (ring and $XXC=CH_2$), 2985, 2985
3072	18					Fundamental, A_2 , 3072
		3225	<i>w</i>	3235	<i>w</i>	2860 + 373 = 3233

* See reference 3. For meaning of symbols, see footnotes to Tables I, II, and III.

** Assumed value of the fundamental. All of the fundamentals are non-degenerate, degeneracy = $d = 1$.






acetylene¹³ appeared at 1029 cm^{-1} . While the observed numbers of frequencies for the carbon skeleton are in fairly good qualitative agreement with the values expected for the C_{2v} structure, definite conclusions cannot be drawn on the basis of the present qualitative depolarization data.

Since all of the fundamentals, overtones, and binary combinations are allowed in the Raman spectrum, whether the structure is C_1 or C_{2v} , and all of them, if the structure is C_1 , or most of them, if the structure is C_{2v} , are allowed in the infra-red spectrum, it seemed worth while to attempt a tentative assignment of the frequencies for this molecule. Such an assignment, even if incomplete, is of value to those who may wish to estimate the heat capacity or other thermodynamic quantities, estimates even as far off as 10 percent frequently being of value in work of a practical nature. The tentative assignment finally decided upon is given at the right in Table VIII. The nine fundamental frequencies of the carbon skeleton were

assumed to be those at 326, 356, 392, 658, 678, 836, 842, 928, and 1056 cm^{-1} . These are the frequencies that make the greatest contribution to the thermodynamic quantities, and the assignment of these skeleton frequencies is complete. Nineteen other frequencies were chosen as fundamentals (see Table VIII), thus making a total of 28 assigned fundamentals out of the 39 possible ones. The 785- cm^{-1} band was assumed to be a CH_2 deformation frequency, in line with Mecke's results¹⁴ for the isomeric paraffins; he found such a frequency near 750 cm^{-1} for these compounds (at 762 cm^{-1} for n -pentane). The intense, polarized Raman lines at 928 and 1056 cm^{-1} correspond to totally symmetrical (A_1) vibrations of the open and closed CCC triangles, respectively. For comparison, one may note that the frequency of the open CCC triangle in n -propane is at 867 cm^{-1} , while the frequency of the CCC ring in spiro-pentane and cyclopropane is 1033 and 1187 cm^{-1} , respectively. The strong, polarized Raman

¹³ B. L. Crawford, Jr., J. Chem. Phys. 7, 555 (1939).¹⁴ R. Mecke, Zeits. f. physik. Chemie B36, 347 (1937).

TABLE V. Comparison of the expected numbers of Raman lines for the five conceivable structures of the bicyclic C_5H_8 hydrocarbon with the experimental results.*

Structure	Symmetry	Number of fundamentals					
		Molecule			Skeleton		
		<i>P</i>	<i>D</i>	<i>T</i>	<i>P</i>	<i>D</i>	<i>T</i>
	C_s	18	15	33	5	4	9
	C_s	19	14	33	6	3	9
	C_s	20	13	33	6	3	9
	D_{3h}	5	11	16	2	3	5
	D_{2d}	5	17	22	2	5	7
Observed		3	7	13	2	4	7

* *P* = number of polarized lines, *D* = number of depolarized lines, *T* = total number of lines allowed in the Raman spectrum.

line at 678 cm^{-1} also seems certain to correspond to an A_1 fundamental. In the region of the C—H vibrations, where the resolution was poorest, the broad Raman line observed at 3061 cm^{-1} was assumed to correspond to two unresolved fundamentals, one at 3045 , the other at 3075 cm^{-1} .

All of the remaining bands observed in the Raman and infra-red spectra were accounted for, in this tentative assignment, as *P* or *R* branches, overtones, or binary combinations. Frequencies corresponding to difference bands were calculated only for fundamentals below 700 cm^{-1} , for which the corresponding energy states can be expected

TABLE VII. Comparison of the expected and observed numbers of Raman lines for 1,1-dimethylcyclopropane and spiropentane.

Hydrocarbon	Symmetry		Number of frequencies					
			Molecule			Skeleton		
			<i>P</i>	<i>D</i>	<i>T</i>	<i>P</i>	<i>D</i>	<i>T</i>
Spiropentane	D_{2d}	Expected:	5	17	22	2	5	7
		Observed:	3	7	13	2	4	7
1,1-Dimethylcyclopropane	C_{2v}	Expected:	12	27	39	4	5	9
		Observed:	9	6	22	3	2	10

to be sufficiently well populated to give rise to appreciable intensities.

Of the eleven unassigned fundamentals, it seems likely that several of them may lie in the $2700\text{--}3100\text{ cm}^{-1}$ region and have escaped observation because of insufficient resolution in this region. Fundamentals falling in this region make a relatively small contribution to the thermodynamic quantities. A high resolution investigation in this region, quantitative values for the depolarization factors of the Raman lines, and an experimental measurement of the heat capacity at various temperatures would provide useful data for a revision of the present tentative and incomplete assignment.

1-Methylcyclobutene

Depending upon the orientation of the methyl group, the structure of 1-methylcyclobutene is

TABLE VI. Selection rules for fundamentals, overtones, and binary combinations for the spiropentane or D_{2d} structure.*

Number of fundamentals			Number of allowed fundamentals				Forbidden overtones		Forbidden binary combinations	
Type	Molecule	Skeleton	Molecule		Skeleton		i.r.	<i>R</i>	i.r.	<i>R</i>
			i.r.	<i>R</i>	i.r.	<i>R</i>				
A_1	5	2	0	5 <i>P</i>	0	2 <i>P</i>	All	None	$A_1 \times A_1$ $A_1 \times A_2$ $A_1 \times B_1$	$A_1 \times A_2$
A_2	3	0	0	0	0	0	All	A_2^n (<i>n</i> odd)	$A_2 \times A_1$ $A_2 \times A_2$ $A_2 \times B_2$	$A_2 \times A_1$
B_1	4	1	0	4 <i>D</i>	0	1 <i>D</i>	All	None	$B_1 \times A_1$ $B_1 \times B_1$ $B_1 \times B_2$	$B_1 \times B_2$
B_2	5	2	5 <i>M_z</i>	5 <i>D</i>	2 <i>M_z</i>	2 <i>D</i>	B_2^n (<i>n</i> even)	None	$B_2 \times A_2$ $B_2 \times B_1$ $B_2 \times B_2$	$B_2 \times B_1$
<i>E</i>	8	2	8 <i>M_P</i>	8 <i>D</i>	2 <i>M_P</i>	2 <i>D</i>	None	None	None	None

* i.r. = infra-red, *R* = Raman, *P* = polarized, *D* = depolarized, *M_z* = parallel band, *M_P* = perpendicular band.

TABLE VIII. Tentative assignment of frequencies for 1,1-dimethylcyclopropane.*

$\Delta\nu$	Raman		Infra-red		Tentative assignment
	Liquid	ρ	Gas	I_0	
326	1	—			Fundamental, 326**
356	3	<i>D</i>			Fundamental, 356
392	1	—			Fundamental, 392
658	1	—			Fundamental, 658
678	7	<i>P</i>			Fundamental, 678, A_1
			724	<i>w</i>	326+392=718
			750	<i>w</i>	356+392=748
			758	<i>w</i>	1429-678=751
			766	<i>w</i>	1445-678=767
778	1	—	785	<i>w</i>	Fundamental, 785
836	5	<i>D</i>	(830)	<i>m</i>	Fundamental, 836
			835	<i>s</i>	<i>P</i> branch or 1163-326=837
			842	<i>vs</i>	Fundamental, 842
			857	<i>s</i>	<i>R</i> branch
			920	<i>s</i>	1310-392=918 or <i>P</i> branch
928	10	<i>P</i>	928	<i>vs</i>	Fundamental, 928, A_1
			939	<i>vs</i>	<i>R</i> branch
			(970)	<i>vvw</i>	1310-356=954
			(976)	<i>vvw</i>	326+658=984 or 3(326)=978
			999	<i>vs</i>	<i>P</i> branch or 1380-392=988
			1007	<i>vs</i>	Fundamental, 1007
			1019	<i>vs</i>	356+658=1014 or <i>R</i> branch
			1042	<i>m</i>	1430-392=1038 or 392+658=1050
1056	5	<i>P</i>	1056	<i>w</i>	Fundamental, 1056, A_1
			(1112)	<i>m</i>	326+785=1111
1124	2	—	1127	<i>m</i>	Fundamental, 1127
			1137	<i>m</i>	356+785=1141 or 1460-326=1135
1158	1	—	1163	<i>w</i>	Fundamental, 1163
			1180	<i>vw</i>	392+785=1177
			1240	<i>w</i>	392+842=1234
			(1270)	<i>vw</i>	326+928=1254

either C_1 or C_s , the only possible symmetry element being a plane of symmetry. If the structure is C_1 , with no symmetry, there would be 33 fundamentals, of which nine are vibrations of the carbon skeleton. All of these would be allowed in both the Raman and infra-red spectra, and all of the Raman lines should be polarized.

If the structure is C_s , all of the 33 fundamentals are again allowed in both the Raman and infra-red spectra and, as before, nine of them are frequencies of the carbon skeleton. Of the 33 expected Raman lines, 20 should be polarized and 13 depolarized. Of the nine Raman lines corresponding to frequencies of the carbon skeleton, seven should be polarized and two depolarized. Since some depolarized lines are to be expected for the C_s structure, but not for the C_1 structure, precise values of the depolarization factors of the Raman lines should enable one to decide between these two structures.

Since all of the fundamentals and all of the overtones and combinations (for either structure)

are allowed in both the Raman and infra-red spectra, it seemed worth while to attempt an assignment of the fundamentals. The tentative assignments finally decided upon are listed at the right in Table III. The nine fundamental frequencies of the carbon skeleton were assumed to be those at 318, 390, 651, 729, 858, 890, 951, 979, and 1640. These are the frequencies that make the greatest contribution to the thermodynamic quantities and the assignment of these skeleton frequencies is complete. Seventeen other frequencies were chosen as fundamentals (see Table III), thus making a total of 26 assigned fundamentals out of the 33 possible ones. The 762-cm⁻¹ band was again, as for 1,1-dimethylcyclopropane, assumed to be a CH₂ deformation frequency. The 1202-cm⁻¹ infra-red band, unresolved from the 1181 band in the Raman spectrum, was chosen as a fundamental in order to explain the infra-red band at 870 cm⁻¹ as a difference band.

All of the remaining frequencies observed in

TABLE VIII.—Continued.

$\Delta\nu$	Raman		Infra-red		Tentative assignment
	Liquid	ρ	Gas	I_g	
1319	8	P	1310	m	Fundamental, 1310
			1335	m	$326+1007=1333$
			1340	w	$658+678=1336$
1382	2	---	1380	m	Fundamental, 1380
			1385	m	$326+1056=1382$
			1395	m	$392+1007=1399$
			1420	w	$356+1056=1412$
			1430	m	Fundamental, 1430
1433	4b	D	1445	s	Fundamental, 1445
			1460	vs	Fundamental, 1460
1465	4b	D	1470	s	Fundamental, 1470
			1785	w	$326+1460=1786$ or $785+1007=1792$
			1850	w	$842+1007=1849$
			1930	vw	$928+1007=1935$ or $785+1127=1912$
			1940	vw	$785+1163=1948$
			1955	vw	$836+1127=1963$
			2030	w	$2(1007)=2014$
			(2060)	vw	$678+1380=2058$
			(2070)	vw	$1007+1056=2063$
			2285	w	$842+1445=2287$
			2460	w	$1007+1460=2467$
			2560	w	$1127+1430=2557$
			2700	m	$1310+1380=2690$ or $3045-326=2719$
2733	3	P			Fundamental, 2733
2863	6	P	2840	m	Fundamental, 2840
2892	5	P			Fundamental, 2863
2926	7	P	2890	vs	Fundamental, 2890
2950	5	D			Fundamental, 2926
2993	10	P	2985	m	Fundamental, 2950, A_2
					Fundamental, 2985
***3061	4b	D	3075	m	Fundamental, 3045, A_2
			3240	w	Fundamental, 3075
					$356+2890=3246$

* For meaning of symbols, see footnotes to Tables I, II, and III.

** Assumed value of the fundamental. All of the fundamentals are non-degenerate, degeneracy = $d = 1$.

*** 3061 is assumed to be two unresolved fundamentals, one at 3045, the other at 3075 cm^{-1} .

the Raman and infra-red spectra were accounted for as overtones or binary combinations. Frequencies corresponding to difference bands were again calculated only for the three lowest fundamentals, 318, 390, and 651. While the frequency near 1675 cm^{-1} may be due to the presence of an olefinic impurity, at least part of its intensity may be due to one of the combination bands given in Table III, the intensity of the combination band being enhanced by its nearness to the 1640 fundamental. Likewise, while the 1720 band may be due to an impurity containing a carbonyl group, at least part of its intensity may be accounted for as an overtone or combination.

Of the seven unassigned fundamentals, it seems likely that most of them lie in the 2700–3100- cm^{-1} region and escaped observation because of insufficient resolution, although it is, of course, possible that a few of the bands assigned as overtones or

combinations may in reality be fundamentals. A high resolution investigation in the 3000- cm^{-1} region would probably lead to an improved assignment. An experimental measurement of the heat capacity at various temperatures and a quantitative determination of the depolarization factors of the Raman lines would also provide useful data for a revision of the present tentative and incomplete assignment.

Methylenecyclobutane

If the five carbon atoms and the two hydrogen atoms of the methylene group lie in a plane, as seems probable in view of Wilson's analysis of cyclobutane,¹⁵ the symmetry of methylenecyclobutane is C_{2v} . For this structure, there should be eleven type- A_1 frequencies (of which four are

¹⁵ T. P. Wilson, J. Chem. Phys. 11, 369 (1943).

frequencies of the carbon skeleton), polarized in the Raman spectrum, parallel bands in the infra-red; five type- A_2 frequencies (none of which are carbon skeleton frequencies), depolarized in the Raman spectrum, forbidden in the infra-red; eight type- B_1 frequencies (two of which are carbon skeleton frequencies), depolarized in the Raman spectrum, perpendicular bands in the infra-red; and nine B_2 type frequencies (three of which are carbon skeleton frequencies), depolarized in the Raman spectrum, perpendicular bands in the infra-red. The type- B_2 frequencies are symmetrical with respect to the plane of the ring. There are thus a total of 33 fundamentals, of which 9 are carbon skeleton frequencies and 24 are C—H frequencies.

A tentative assignment of the fundamentals is given at the right in Table IV. Frequencies selected as carbon skeleton fundamentals were those at 354, 373, 657, 728, 879, 895, 954, 991, and 1675 cm^{-1} . The 954- cm^{-1} frequency, because of its great intensity in the Raman spectrum, certainly corresponds to the totally symmetrical, type A_1 , "breathing" frequency of the ring. The corresponding frequency for cyclobutane itself appears¹⁶ at 1010 cm^{-1} .

Twenty-one of the C—H frequencies were tentatively assigned; they are the ones at (782), 1029, 1059, 1070, 1155, 1167, 1197, 1248, 1395, 1415, 1425, 1490, (2770), 2826, 2860, 2902, 2921, 2952, 2985, 2985, and 3072 cm^{-1} , the ones in the parentheses being relatively less certain than the others.

Previous results¹⁶ for olefins showed that for molecules containing an $XXC=CH_2$ group Raman lines were generally observed near 1300, 1410, 1650, 2980, and 3075 cm^{-1} . Observed frequencies for the methylenecyclobutane that probably correspond to these are the ones at 1248, 1415, 1675, 2985, and 3072 cm^{-1} . The 1675- cm^{-1} frequency is the skeleton frequency associated with the stretching of the carbon-carbon double bond.

The olefinic frequency at 2985 cm^{-1} is believed to be coincident with a ring C—H frequency, for cyclobutane itself has a strong Raman line at 2988 cm^{-1} . Furthermore, for cyclobutane the most intense C—H Raman line is at 2962 cm^{-1} ,

while for the present compound the strongest Raman line is the one at 2986 cm^{-1} . This change in the relative intensities is understandable if one supposes that the band observed near 2985 cm^{-1} is in reality two unresolved bands, one due to the ring hydrogens, the other to the olefinic hydrogens. This is the basis for assigning two C—H fundamentals with the same frequency at 2985 cm^{-1} .

The five, type- A_2 , C—H frequencies are allowed in the Raman spectrum, but are forbidden in the infra-red spectrum. Four of these five type- A_2 frequencies can be ascribed to the four Raman lines observed at 2826, 2921, 2952, and 3072 cm^{-1} . The remaining one could be one of the supposedly coincident lines at 2985 cm^{-1} .

The remaining observed bands can be accounted for as P and R branches, binary combinations, or overtones. While the overtones A_2^n (n odd) and the binary combinations $A_1 \times A_2$ are forbidden in the infra-red, this would not affect any of the overtones or binary combinations used here, since the assigned A_2 fundamentals were all in the 3000- cm^{-1} region. The only other binary combinations forbidden in the infra-red are the $B_1 \times B_2$ ones, and it is possible that some of the binary combinations used may have involved a type- B_1 and a type- B_2 frequency. In many cases, however, there were several binary combinations that could have been used to account for the observed band, so that the elimination of the $B_1 \times B_2$ combinations if and when the B_1 and B_2 frequencies are identified would probably not be difficult. All overtones and binary combinations are allowed in the Raman spectrum.

It seems likely that the three unassigned C—H fundamentals exist as unresolved lines, probably in the 3000- cm^{-1} region where the resolution was poorest, although it is of course possible that some of the bands accounted for as overtones or combinations may actually be fundamentals. Precise depolarization factors of the Raman lines and high resolution studies, particularly in the 3000- cm^{-1} region, should provide useful information for a revision of the present tentative and incomplete assignment.

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¹⁶ Forrest F. Cleveland, J. Chem. Phys. 12, 53 (1944).

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