The InfraRed and Raman Spectra of Cyclopentane, Cyclopentaned1, and Cyclopentaned10

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The Infra-Red and Raman Spectra of Cyclopentane, Cyclopentane-d_1, and Cyclopentane-d_{10}

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The infra-red and Raman spectra of cyclopentane, cyclopentane-d_1, and cyclopentane-d_{10} have been determined for the purpose of establishing the symmetry of cyclopentane. D_{5h} selection rules are found to hold very well. This does not constitute a rigorous criterion for structure in this case, however, because drastic alteration of the symmetry by substituting groups such as D, OH, CH_3, or Cl for a hydrogen atom does not appreciably increase the complexity of the spectra. The data have provided two strong arguments against a D_{5h} structure. (1) An assignment could not be made which simultaneously satisfied the product rule and the expected band contours. (2) The entropy of the vapor demands a low frequency (near 140 cm^{-1} for the assignment in this paper) if the symmetry is D_{5h}. This is completely incompatible with the heat capacity of the solid.

It is concluded that cyclopentane definitely does not have D_{5h} symmetry. The actual geometry of the molecule is still not known. It is shown that a rigid structure of symmetry C_s, C_2, or C_1 is consistent with the available data. A decision between this and Kilpatrick, Pitzer, and Spitzer's model with a puckered ring and a pseudorotation in place of one of the genuine normal vibrations cannot be made at this time.

Analogous spectroscopic results for perfluorocyclopentane are mentioned briefly for comparison. This molecule is definitely non-planar.

The method of preparation of the deuterium compounds is given. A Pd-on-charcoal catalyst is described which promises to be useful in other hydrogen-deuterium exchange reactions.

INTRODUCTION

THIS study was undertaken in the hope of determining whether or not the carbon ring in cyclopentane is planar. Kilpatrick, Pitzer, and Spitzer[1] have pointed out that there are forces favoring both planar and non-planar structures. A regular pentagon has interior angles which are very close to the tetrahedral value (108° vs. 109° 28'), so the planar structure is stabilized by the forces tending to maintain tetrahedral bond angles. Conversely this structure is destabilized by repulsions between the hydrogen atoms of neighboring methylene groups. These repulsions are at a maximum for the planar structure. They produce torsional forces around the carbon-carbon bonds which tend to pucker the ring. The problem is to determine which of the two effects predominates.

There have been many earlier physical measurements pertaining to the structure of cyclopentane. The Raman spectrum[2-8] and the infra-red spectrum[9-13] have been

* From a dissertation submitted to the Graduate School of the University of Illinois in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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[1] Kilpatrick, Pitzer, and Spitzer, J. Am. Chem. Soc. **69**, 2483 (1947).

[2] J. Weiler, Zeits. f. Physik **72**, 206 (1931).

[3] Canals, Godchot, and Cauquil, Comptes Rendus **194**, 1574 (1932).

[4] K. W. F. Kohlrausch and R. Seka, Ber. **69**, 729 (1936).

[5] A. W. Reitz, Zeits. f. physik. Chemie **B-33**, 179 (1936); **B-38**, 381 (1938).

[6] E. J. Rosenbaum and H. F. Jacobson, J. Am. Chem. Soc. **63**, 2841 (1941).

[7] Bazhulin, Sterin, Bulanova, Solovova, Turova-Pollak, and Kazanskii, Izvest. Akad. Nauk. S. S. S. R. Otdel Khim. Nauk. 1946, No. 1, p. 7. Chem. Abs. **42**, 6238 i.

[8] Fenske, Braun, Wiegand, Quiggle, McCormack, and Rank, Anal. Chem. **19**, 700 (1947).

[9] Barca-Galateanu, Bull. soc. roumaine phys. **38**, No. 69, 109 (1938).

[10] P. Lambert and J. LeCompte, Ann. de physique **10** (11th series), 539 (1940).

[11] American Petroleum Institute Research Project 44 at the National Bureau of Standards. Catalog of Infra-Red Spectrograms. Serial No. 446, cyclopentane, contributed by the Shell Development Corporation.

[12] See reference 11, Serial Nos. 343 and 596, contributed by the Radiometry Laboratory of the National Bureau of Standards. Or see Plyler, Stair, and Humphreys, J. Research Nat. Bur.

1519

reported several times. Their simplicity suggests a high degree of symmetry. Electron diffraction studies give good agreement with an assumed planar ring.[14-16] Aston, Fink, and Schumann[17] measured the heat capacity of cyclopentane from 11.1°K to room temperature, and from this determined the entropy. This was compared with the entropy calculated from spectroscopic data. They found much better agreement for a puckered ring than for a planar ring, but many of their frequency assignments are dubious.

Kilpatrick, Pitzer, and Spitzer[1] have calculated the resultant potential energy due to the two opposing forces mentioned earlier, viz., the repulsions between hydrogen atoms on adjacent methylene groups, and the forces acting to preserve tetrahedral bond angles. The former was evaluated by using the potential barrier for the internal rotation in ethane, and the latter by employing a force constant carried over from other molecules. It was concluded that a puckered ring is more stable than a planar one. The calculations indicated: (a) that the maximum displacement of an equilibrium nuclear position out of the (hypothetical) D_{5h} plane is about 0.2A, and (b) that this maximum displacement is not localized at a given carbon atom, but rotates around the ring. These results make a non-planar ring appear reasonable, but hardly constitute convincing evidence for it because of the approximations involved. These authors also make a vibrational assignment and use it to calculate the entropy and heat capacity of the vapor at several temperatures. The agreement with calorimetric values is impressive, but is slightly misleading because two adjustable parameters were available for fitting the data (their q_0 and an anharmonicity coefficient).

The case for a non-planar ring rests almost entirely on the entropy argument. The most vulnerable point in this argument is the assignment of the vibrational frequencies. It therefore seemed worth while to study the vibrational spectrum in greater detail with the hope of obtaining a more reliable assignment, especially of the lower fundamentals. Still more important is the fact that one may reasonably hope to obtain completely independent evidence about the structure, since the selection rules for the planar and the non-planar forms are very different.

In this paper cyclopentane, cyclopentane-d_1, and cyclopentand-d_{10} will be referred to as d_0, d_1, and d_{10}, respectively, for the sake of brevity.

Stand. 38, 211 (1947); E. K. Plyler, J. Opt. Soc. Am. 37, 746 (1947).

[13] See reference 11, Serial No. 221, contributed by the Anglo-Iranian Oil Company, Ltd.; Serial No. 254, contributed by the Universal Oil Products Company. These spectra are definitely inferior to those of references 11 and 12.

[14] R. Wierl, Ann. d. Physik 8, 521 (1931); 13, 453 (1932).

[15] L. Pauling and L. O. Brockway, J. Am. Chem. Soc. 59, 1223 (1937).

[16] O. Hassel and H. Viervoll, Tids. Kjemi, Bergvesen, Met. 6, No. 3, 31 (1946).

[17] Aston, Fink, and Schumann, J. Am. Chem. Soc. 65, 341 (1943).

EXPERIMENTAL

A. Origin of the Compounds

The d_0 used for obtaining the infra-red and Raman spectra, and also employed as the starting material in the preparation of d_{10}, was the Phillips Petroleum Company's research grade product. Its purity was 99.95 ± 0.02 mole percent. The most probable impurity was 2,2-dimethylbutane, but no trace of this could be found in the infra-red spectrum.

Cyclopentane-d_1 was prepared by the Grignard reaction:

$$C_5H_9Cl \xrightarrow{Mg} C_5H_9MgCl \xrightarrow{DCl} C_5H_9D + MgCl_2(s).$$
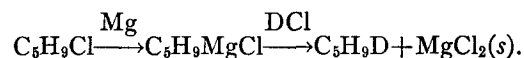
Cyclopentyl chloride was dissolved in thoroughly dried n-butyl ether and was treated with magnesium to form the Grignard reagent. The theoretical amount of deuterium chloride, prepared by adding heavy water dropwise to benzoyl chloride according to the method of Brown and Groot[18] was bubbled slowly into the ether solution under a dry nitrogen atmosphere. The resulting d_1 was removed from the mixture by distillation and was redistilled. The fraction boiling at 47.0 to 47.7°C (uncorr.) was taken.

Cyclopentane-d_{10} was prepared by exchange between d_0 and deuterium in the apparatus shown in Fig. 1. The d_0 was refluxed in the small reservoir so that its vapor mixed with the incoming deuterium gas. The mixture passed over the heated catalyst and then through a condenser which was cooled with acetone at dry ice temperature. The condensate returned to the reservoir through a 1-mm capillary. The exit hydrogen-deuterium mixture was passed through a cold trap to insure that no product would accidentally be lost through failure of the acetone circulating system.

It is known from earlier work that exchange between cyclohexane and deuterium occurs over a platinum-black-on-platinum-foil catalyst.[19, 20] This catalyst was therefore employed in the initial experiments with d_0. It worked very well at first, but its activity rapidly declined until it was useless at the end of 12 to 18 hr. An attempt to reactivate it was only slightly successful. It was realized later that the poisoning may have been due to the deposition of a film of SiO from the silicone stopcock grease used on the joints of the apparatus.[21]

Another catalyst consisting of a thin coating of palladium on activated charcoal was then tried and was found to be quite satisfactory. Measurable exchange occurred at 150°C over this catalyst, but the temperature was maintained at 190 to 210°C throughout the reaction in order to obtain a much higher rate. The

[18] H. C. Brown and C. Groot, J. Am. Chem. Soc. 64, 2223 (1942).

[19] Horrex, Greenhalgh, and Polanyi, Trans. Faraday Soc. 35, 511 (1939).

[20] A. Farkas and L. Farkas, Trans. Faraday Soc. 35, 917 (1939).

[21] R. H. Savage, J. Chem. Phys. 16, 237 (1948).

catalyst has been used for a total of 90 hr. with no lessing of activity.[22]

Eight milliliters of d_0 were exchanged with deuterium of 99.7 percent purity.[23] The rate of d_0 evaporation was kept at approximately 0.02 mole/min., and the deuterium flow at approximately 0.001 mole/min. The progress of the reaction was measured by following the disappearance of the C−H stretching band at 2950 cm^{-1}. The exchange was continued for a total of 66 hr. A yield of 5.5 ml of approximately 96 percent pure d_{10} was obtained. The chief impurity was d_9.

In order to insure that only C−H bonds were being ruptured in the exchange process, a test was carried out with d_0 and ordinary hydrogen at 250°C for an 8-hr.
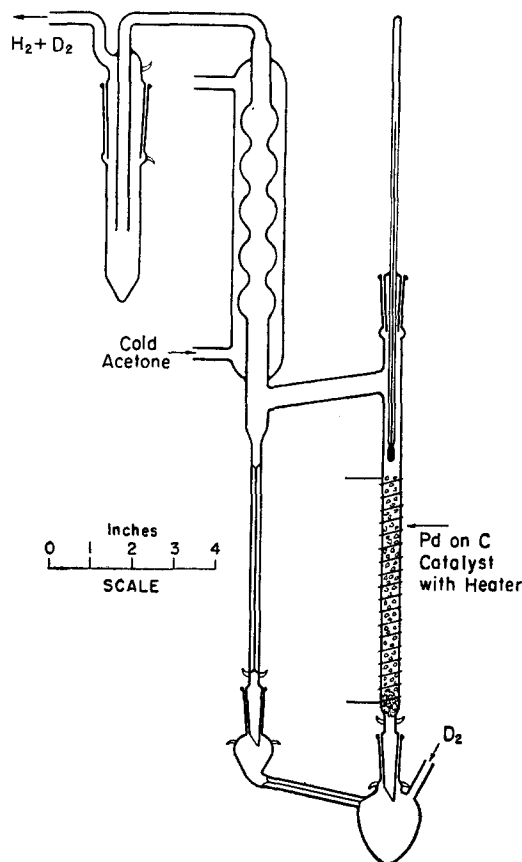

FIG. 1. Exchange apparatus.

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[22] The catalyst may be prepared as follows. Make up a two or three percent aqueous solution of sodium chloropalladite (Na_2PdCl_4), and adjust its pH to 5±1. Immerse Columbia SW activated carbon, 4/14 mesh, in this solution. Upon conclusion of the evolution of gas, decant the liquid and dry the catalyst. It is now ready for use.

Most charcoals are not suitable for this purpose, although other brands than the one mentioned can be employed. It is important that the charcoal possess a large percentage of fractures with a high metallic luster. The finished catalyst will appear to be brightly metallic.

[23] The deuterium was obtained from the Stuart Oxygen Company on allocation by the U. S. AEC. The mass spectrometer analysis was obtained through the courtesy of Mr. A. G. Sharkey and Dr. R. A. Friedel, U. S. Bureau of Mines .Bruceton, Pennsylvania.

period. It was thought that the elevated temperature would greatly increase both the C−H rupture and any C−C rupture that might be taking place. The infra-red spectrum of the hydrocarbon was checked before and after the test and the amount of any impurity formed was below the limits of spectroscopic detection.

B. Spectroscopic Measurements

The infra-red spectra presented in this paper were obtained with a modified Model 12-A Perkin-Elmer instrument equipped with a wave-length drive, a General Motors amplifier, and a Brown recorder. Prisms of KBr, NaCl, and CaF_2 were used for each sample. In addition gaseous d_0 was examined in the region from 2800 to 3000 cm^{-1} with a LiF prism.[24] Liquid d_0 was surveyed from 250 to 400 cm^{-1} with a thallium bromoiodide prism, using a 1.5-mm cell.[25] No bands were found in this range.

Band positions are estimated to have the following accuracies: 400 to 1000 cm^{-1}, ±1 cm^{-1}; 1000 to 2000, ±2; 2000 to 3100, ±3. Each sample was examined in the liquid state (0.08 mm thick), and as a vapor (10- and 100-cm cells).

The spectrograph used to obtain the Raman spectra was built at Mellon Institute by Dr. A. L. Marston. It is of the type designed by Lord,[26] and described in greater detail by Stamm.[27] The collimator is a 7° off-axis parabola of 16 cm diameter and 100 cm focal length. The plane echelette grating has 15,000 lines/in. with a total ruled area 4 in. high and 6 in. wide. The blaze is in one of the first-order blue-green regions. Ghost lines are rather bad with this grating, and make it very difficult to observe Raman displacements of less than 300 cm^{-1} unless they are intense. The camera lens, obtained from the Perkin-Elmer Corporation, is $f/5.4$ with an effective focal length of 27 in. The reciprocal dispersion at the plate is 25.4A/mm.

The illuminator was closely similar to that described by Crawford and Horwitz,[28] except that each arc was backed by an elliptical reflector. Twelve General Electric Type H-11 mercury arcs were employed. The power supply was stabilized by two Sola constant voltage transformers, each one supplying six lamps.

Wave-length measurements were made by the method described by Stamm.[27] The Raman displacements were corrected to vacuum and are accurate to ±2 cm^{-1} for sharp lines and about ±5 cm^{-1} for diffuse lines. Depolarization ratios were obtained by the method of

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[24] The authors are indebted to Dr. N. D. Coggeshall of the Gulf Research and Development Laboratory, Harmarville, Pennsylvania, for placing facilities for the LiF work at our disposal.

[25] These measurements were made by the Radiometry Section of the National Bureau of Standards through the courtesy of Dr. C. J. Humphreys and Dr. E. K. Plyler.

[26] Harrison, Lord, and Loofbourow, *Practical Spectroscopy* (Prentice-Hall, Inc., New York, 1948), p. 515.

[27] R. F. Stamm, Ind. Eng. Chem., Anal. Ed. **17**, 318 (1945).

[28] B. L. Crawford, Jr. and W. Horwitz, J. Chem. Phys. **15**, 268 (1947).

Crawford and Horwitz.[28] The high background on most of the plates made it difficult to get accurate numerical results, but there is seldom any doubt concerning whether a line is polarized or depolarized.

Sample size was 25 ml for d_0, and 4 ml for d_1 and d_{10}. Exposure times were 1 to 6 hr. for the qualitative plates, and 24 hr. for each of the polarization exposures. All the spectra were obtained on Eastman 103a-J spectroscopic plates. Mercury 4358A was isolated as the exciting line by using a Wratten 2A filter and 1 cm of 0.005 percent aqueous solution of Dupont Rhodamine 5 GDN Extra. One spectrum of each compound was also taken using both Hg 4047 and Hg 4358 excitation in order to test the effectiveness of the Wratten 2A filter. None of the Raman lines due to 4047 appeared on plates when the Wratten 2A filter was employed.

RESULTS

The infra-red spectra of the three samples in the vapor phase are shown in Figs. 2a and 2b, and in the liquid phase in Figs. 3a and 3b. Table I lists the frequencies. Intensities are estimated on a scale of 0 to 10, with the pressure and cell length taken into account. The frequencies for d_0 are in reasonably good agreement with those reported by the Shell Development Corporation for the vapor,[11] and by the National Bureau of Standards for the liquid.[12] Because the infra-red spectrum of d_{10} in the region near 2900 cm^{-1} still showed evidence of hydrogen in the sample, bands appearing above 2500 cm^{-1} are not listed. A sample of the liquid was removed from the exchange apparatus before completion of the exchange and its spectrum was measured on the Perkin-Elmer spectrometer with the
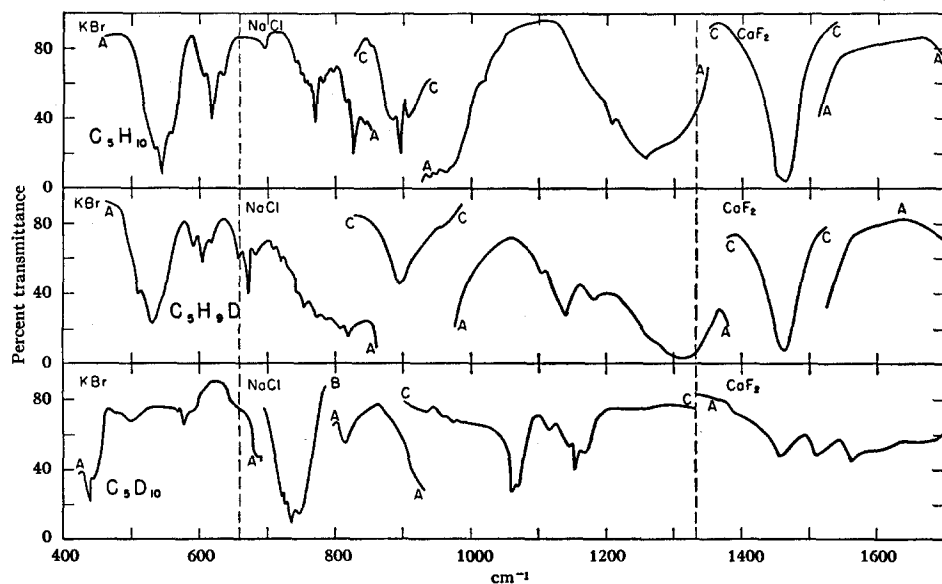

FIG. 2a. Infra-red spectra (vapor state). $A = 100$-cm cell, 220-mm pressure. $B = 100$-cm cell, 50-mm pressure. $C = 10$-cm cell, 220-mm pressure. $D = 10$-cm cell, 100-mm pressure. $E = 10$-cm cell, 25-mm pressure. $F = 10$-cm cell, 15-mm pressure. $G = 10$-cm cell, 5-mm pressure.
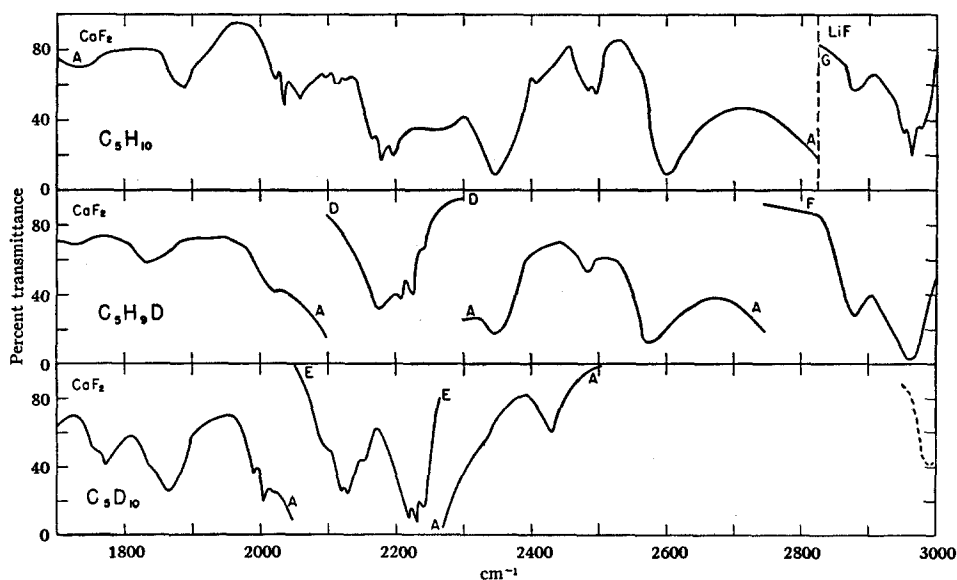
FIG. 2b. Infra-red spectra (vapor state) (continued).

KBr, NaCl, and CaF_2 prisms under the same conditions with which the final sample was measured. All bands that diminished in intensity were attributed to a molecular species containing hydrogen. All such bands were in the region above 2500 cm^{-1}.

Table II gives the best values for the Raman displacements of the three compounds. Each value is an average from several plates chosen for low background and high line intensity. The Raman lines in many cases are broad and diffuse, and the centers of the lines are difficult to determine. This is particularly true of the 1207-cm^{-1} line of d_0. The low frequency lines 283, 281, and 270 in the three compounds are of very low intensity and are obscured by grating ghosts of the exciting line

Hg 4358. The frequencies, and even the existence, of these lines on our plates are open to question. There was no evidence of hydrogen in any of the Raman plates of d_{10}. Table II also compares the Raman spectrum of d_0 obtained in this work with three previous spectra of high quality. The agreement is satisfactory.

INTERPRETATION OF RESULTS

A. General Remarks

Four point groups must be considered as possibilities for cyclopentane: D_{5h}, C_2, C_s, and C_1. Table III gives the symmetry properties, number of normal vibrations, and selection rules for D_{5h} symmetry according to the conventions of Herzberg.[29] It can be seen that three

FIG. 3a. Infra-red spectra (liquid state). Cell=0.08 mm.

FIG. 3b. Infra-red spectra (liquid state) (continued).

[29] G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), pp. 117, 138, 253.

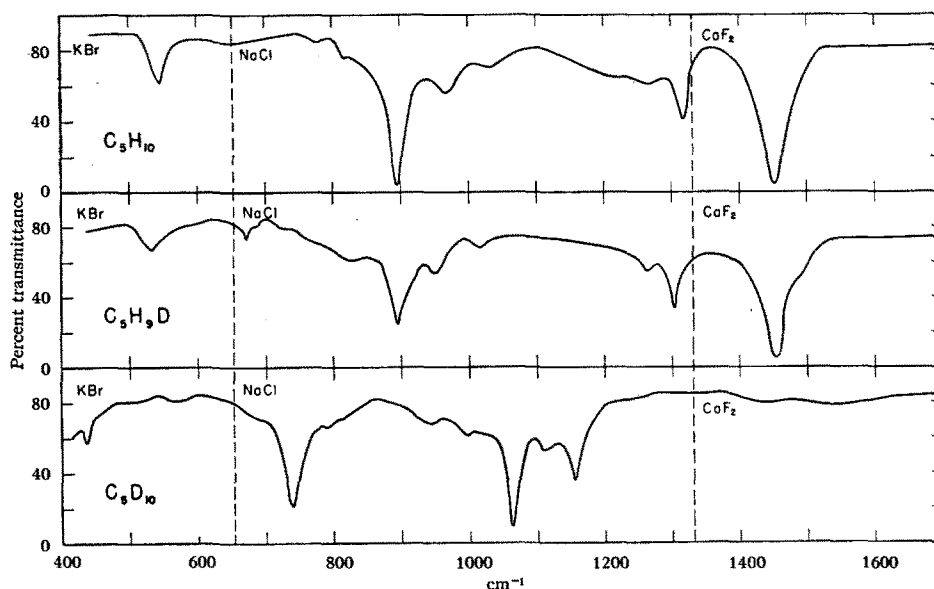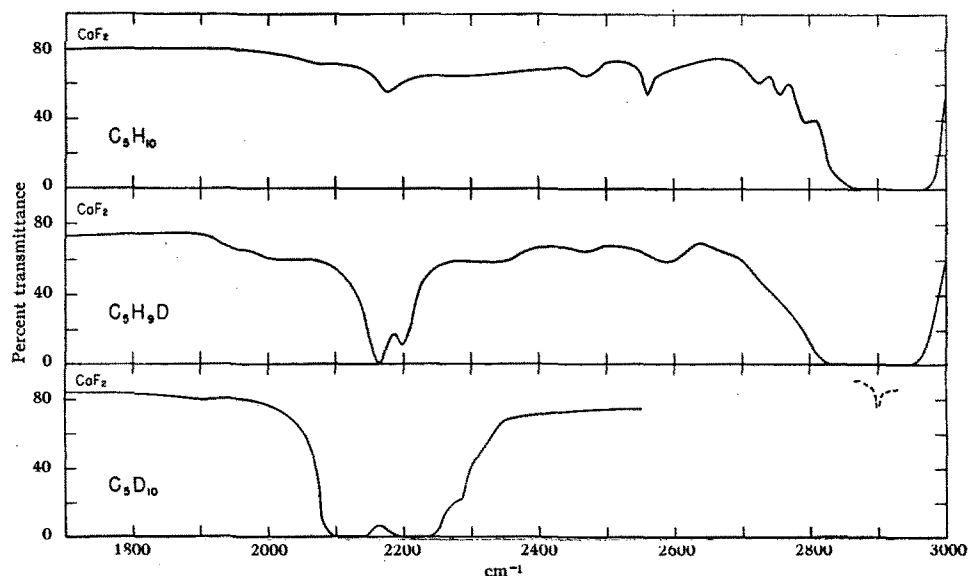TABLE I. The infra-red spectra of the cyclopentanes.

Cyclopentane Vapor cm^{-1}	I	Type	Cyclopentane Liquid cm^{-1}	I	Cyclopentane-d_1 Vapor cm^{-1}	I	Cyclopentane-d_1 Liquid cm^{-1}	I	Cyclopentane-d_{10} Vapor cm^{-1}	I	Type	Cyclopentane-d_{10} Liquid cm^{-1}	I
535 P					511 P				P obscured				
545 Q	3	?	546	3	533 Q	3	535	3	438 Q	2	⊥(?)	438	1
558 R					R obscured				446 R				
602 P					590 P				502	0			
617 Q	2	||			604 Q	1			567 P				
631 R					616 R				578 Q	0	||	572	0
697	0				659 P				590 R				
748	0	.			671 Q	2	672	2	686	0			
740 P					683 R				722	1			
753 Q	0	?			708 P				728 P				
764 R					720 Q	0			737 Q	6	⊥(?)	738	6
759 P					730 R				748 R				
770 Q	1	⊥(?)	776	0	743	0			—			791	0
779 R					753	0			814	1			
796	0				773	0			935	0		943	1
					788	0			974	0			
812 P					808 P				—			997	1
827 Q	1	||	817	1	820 Q	1			1061	6	?		
843 R					R obscured				1070			1064	6
882 P					895	5	895	5	1119	1		1111	1
896 Q	8	||	896	8	949	1	951	2	1146 P				
909 R					—		1018	1	1156 Q	6	⊥	1155	3
					1107	0			1165 R				
937 P					1140	2							
949 Q	3	?			1180	0							
962 R					—		1264	1	1315	0			
—			964	3	1315	3	1308	4	1458	1			
1020	0				1462	6	1454	8	1510	1			
—			1033	1	1727	0			1562	1			
1206	0				1867	1			1772	2			
1258	3 v.b.		1264	3 v.b.	2021	1			1867	2			
—			1316	4									
1462	9		1456	9	2172	7	2166	9	1990 P				
1739	0				2210	7			2005 Q	2	||(?)		
1884	0				2228	7	2199	8	2021 R				
2021	0				2346	3			2099	5			
2036	1 ?				2481	1	2468	0	2119	9	?		
2060	1				2597	3	2579	1	2130			2125	10
2095 P					2878	9	2870	10	2155	5			
2114 Q	0	||			2962	10	2950	10	2203	0			
2128 R					3191	3			2219 P				
2169 P					3488	3	3452	2	2230 Q	10	?	2220	10
2181 Q	1	?	2175	1					2239 R				
2194 R									—			2283	2
2346	1								2428	2			
2405	0								~3000	5	(C–H)	~2900	2
2481													
2492	1												
—			2585	1									
2610	2												
—			2725	1									
—			2753	1									
—			2793	2									
2876	9		2890	10									
2953 P													
2965 Q	10		2960	10									
2977 R													
3196	0												
—			3202	0									
3476	1		3481	1									

Note.—v.b. =very broad.

Raman lines are polarized, six fundamentals are totally inactive, and that there are no coincidences between Raman-active and infra-red-active vibrations. On the other hand the three lower symmetries allow all thirty-nine of the fundamentals to be active in both the infra-red and Raman spectrum, and twenty or more Raman lines are polarized. Thus the results expected for a planar ring are markedly different from those for a non-planar ring. This is indicated in greater detail in Table IV for the fundamentals below 1600 cm^{-1}. It is evident that one may reasonably expect to be able to determine whether or not the molecule has D_{5h} sym-

TABLE II. The Raman spectrum of the cyclopentanes (including a comparison with earlier work).

K. and S.[a]		Reitz[b]			Cyclopentane R. and J.[d]			Present work			Cyclopentane-d_1			Cyclopentane-d_{10}		
cm⁻¹	I	cm⁻¹	I	ρ	cm⁻¹	I	ρ	cm⁻¹	I	ρ[f]	cm⁻¹	I	ρ[f]	cm⁻¹	I	ρ[f]
165	0 ?	—	—	—	—	—	—	—	—	—	281?	0	—	270?	0	—
—	—	—	—	—	207	0	—	—	—	—	884	8	0.43	778	1	0.88
285	1 b.	285	1 b.	—	288	1	—	283(?)	0	—	1028	4 b.	0.92	802	9	0.49
589	00	—	—	—	—	—	—	—	—	—	1194	2 v.b.	—	937	5 b.	0.93
—	—	—	—	—	712	0	—	—	—	—	1280	2 b.	—	1021	1	—
886	9	886	9	0.08	888	10	p	886	9	0.25	1451	3 b.	0.91	1064	3 b.	—
973	½	967	0	—	—	—	—	—	—	—	1473	1	—	1124	4 b.	0.60
1028	4 b.	1028	4 b.	1.00	1032	4 b.	dp	1030	5 b.	0.86	2166	2 b.	0.69	2048	2	0.69
1102	1	1102	1	0.90	—	—	—	1104	1	—	2203	1 b.	0.75	2108	8	0.42
1216	1	1216	1	1.00[e]	—	—	—	1207[e]	3 v.b.	—	2868	9	0.46	2130	2	—
1284	2	1283	2 b.	1.04[e]	1298	1	—	1283	2 b.	—	2916	4 b.	—	2151	8	0.42
1446	5	1446	4 b.	0.92	1448	5 b.	dp	1453	4 b.	0.87	2940	9 v.b.	0.68	2214	6 v.b.	0.87
1480	1	1479	½	dp	1482	1 b.	—	1487	1	0.81	2962	9 v.b.	0.59	2304	2	0.73
2866	10	2866	10	0.26[a]	2869	10	p	2868	10	0.30						
2898	4	2898	4	—	2901	4	—	2904	4 b.	0.52						
2941	12 b.	2941	12 ⎫ 0.36		2943	7		2944	10 v.b.	0.46						
2964	10	2964	10 ⎭		2970	6		2966	9 v.b.	0.43						

Note.—b. =broad; v.b. =very broad.
[a] See reference 4.
[b] See reference 5.
[c] Said by Reitz to be unsatisfactory.
[d] See reference 6.
[e] Exceptionally broad and diffuse. Difficult to locate center.
[f] See section on Spectroscopic Measurements.

metry. On the other hand the choice between C_2, C_s, and C_1 would be very difficult. The number of observed frequencies has been added to Table IV for comparison.

The spectra clearly suggest D_{5h} symmetry except for two features. The first is that fifteen infra-red bands are found below 1600 cm⁻¹ for d_0 rather than about four. However, many of these are weak and were observed only in a meter gas cell at 220-mm pressure. Consequently one could hope to explain most of them as combination tones. The second difficulty is the spectrum of d_1. It was expected that if d_0 is D_{5h}, the substitution of one deuterium atom would lower the symmetry to C_s and would permit many more frequencies to be active. This has been found to happen with such molecules as benzene[30, 31] and cyclohexane,[32] where the substitution of one deuterium atom approximately doubles the number of observed bands in the Raman spectrum of the liquid or in the infra-red spectrum of the vapor. Cyclopentane-d_1 was therefore prepared with the expectation that it might exhibit an enriched spectrum which would provide some evidence for a high symmetry in the parent molecule. At the same time degenerate frequencies and forbidden fundamentals might be located. Actually, however, the spectrum of d_1 is of about the same complexity as that of d_0 or d_{10}, and the experiment is inconclusive. It seems strange that one deuterium atom can produce a marked effect in cyclohexane, and virtually no effect in cyclopentane. This might be taken as evidence against high symmetry for the latter.

Nevertheless the spectra on the whole strongly

[30] A. Langseth and R. C. Lord, Jr., Kgl. Danske Vid. Sels. Math. Fys. Medd. 16, 6 (1938).
[31] Bailey, Gordon, Hale, Herzfeld, Ingold, and Poole, J. Chem. Soc. 1946, 299; Herzfeld, Ingold, and Poole, *ibid.* 324.
[32] A. Langseth and B. Bak, J. Chem. Phys. 8, 410 (1940).

TABLE III. Symmetry properties, number of normal vibrations, and selection rules for cyclopentane (D_{5h} symmetry).

D_{5h}	Symmetry properties					No. of normal vibra-tions	Selection rules	
	C_5	σ_h	C_2	σ_v	T and R		Raman	IR
A_1'	1	1	1	1		3	+(p)	—
A_1''	1	−1	1	−1		1	—	—
A_2'	1	1	−1	−1	R_z	1	—	—
A_2''	1	−1	−1	1	T_z	2	—	+(‖)
E_1'	2 cos72°	2	0	0	T_{xy}	4	—	+(⊥)
E_1''	2 cos72°	−2	0	0	R_{xy}	3	+	—
E_2'	2 cos144°	2	0	0		5	+	—
E_2''	2 cos144°	−2	0	0		4	—	—

indicate D_{5h} symmetry, so the initial effort was to make an assignment on this basis. This assignment must satisfy three criteria: (1) the calculated band envelopes, (2) the product rule, and (3) the measured entropy. The first two of these require a knowledge of the moments of inertia. For this we have used the molecular dimensions of Hassel and Vierwoll,[16] namely a planar ring, an H−C−H angle of 109° 28', a C−H distance of 1.09A, and a C−C distance of 1.54A. The calculated moments of inertia are given in Table V.

Since a D_{5h} molecule is a symmetric top, the separation of the P and R maxima of the infra-red bands can be determined from the equations of Gerhard and Dennison.[33] The expected $P−R$ separations are included in Table V. The parallel bands will have a very intense Q branch, whereas perpendicular bands will have a less marked one. The exact appearance of the perpendicular bands cannot be predicted from the results of Gerhard and Dennison since this case is intermediate between two of theirs. The theoretical product rule ratios are

[33] S. L. Gerhard and D. M. Dennison, Phys. Rev. 43, 197 (1933).

TABLE IV. Number of allowed *vs.* number of observed bands of cyclopentane.

		Theory			Obsv'd freqs.
	C_1	C_s	C_2	D_{5h}	
1. No. of Raman-active fundamentals <1600 cm^{-1}	29	29	29	8	8
2. No. of polarized Raman fundamentals <1600 cm^{-1}	29	15	15	2	1
3. No. of infra-red-active fundamentals <1600 cm^{-1}	29	29	29	4	15
4. No. of Raman-infra-red coincidences <1600 cm^{-1}	29	29	29	0	1

TABLE V. Calculated moments of inertia (in atomic weight units $\times A^2$) and calculated $P-R$ separations for cyclopentane.

	I_x	I_y	I_z	$\Delta\nu(\perp$ bands$)$	$\Delta\nu(\parallel$ bands$)$
Cyclopentane	78.5	78.5	141	19–21 cm^{-1}	28 cm^{-1}
Cyclopentane-d_{10}	105	105	179	16–18	24

given later in Table VII. The entropy criterion will also be discussed later.

B. Analysis Based on D_{5h} Symmetry

The results of this section are summarized in Tables VI, VII, and IX. Table VI gives the numbering of the vibrations. The classification of methylene vibrations into deformations, waggings, twistings, and rockings is that defined by Linnett,[34] as modified slightly by Wilson.[35]

1. Raman-Active Species

a. *The totally symmetric vibrations (species A_1').*— The Raman spectrum of d_0 exhibits intense and highly polarized lines at 886 and 2868 cm^{-1} which can be assigned immediately to ν_3 and ν_1 respectively. In d_{10} there are polarized lines at 802, 1124, 2108, and 2151 cm^{-1}. We believe that the latter two, which have nearly the same intensities, are the results of Fermi interaction between 2×1064 (Raman) or 2×1066 (infra-red) and a fundamental very near 2130 cm^{-1}. The missing methylene frequency in d_0 can now be located by applying the product rule. It is calculated to be 1483 cm^{-1}. There is an observed Raman line at 1487 which we take to be this fundamental. Fenske, *et al.*[8] are the only workers who report it to be polarized. This may be due either to the fact that it is overlapped by the more intense depolarized line at 1453 cm^{-1}, or to an inherently high depolarization ratio.

All the assignments are collected in Table VI. The calculated and observed product rule ratios are compared in Table VII.

b. *The degenerate vibrations (species E_1'' and E_2').*— Most of the remaining Raman lines are unusually broad and diffuse. Rosenbaum and Jacobson[6] have suggested that this may be due to a slightly non-planar

[34] J. W. Linnett, J. Chem. Phys. **6**, 695 (1938).
[35] T. P. Wilson, J. Chem. Phys. **11**, 369 (1943).

TABLE VI. Assignment of fundamentals on the basis of D_{5h} symmetry.

Species	Sel. rules	Description	Notation	Cyclopentane	Cyclopentane-d_{10}
A_1'	R	C—H stretching	1	2868 cm^{-1}	2130 cm^{-1*}
		CH$_2$ deformation	2	1487	1124
		in-plane ring	3	886	802
A_1''	F	CH$_2$ twisting	4	—	—
A_2'	F	CH$_2$ wagging	5	—	—
A_2''	I	C—H stretching	6	2965	2230
		CH$_2$ rocking	7	(1462)	1066
E_1'	I	C—H stretching	8	2876	2125
		CH$_2$ deformation	9	(1462)	1156
		CH$_2$ wagging	10	896	737
		in-plane ring	11	545	438
E_1''	R	C—H stretching	12	2966	2214
		CH$_2$ twisting	13	1207	[965±7]
		CH$_2$ rocking	14	1104	778
E_2'	R	C—H stretching	15	2944	2130
		CH$_2$ deformation	16	1453	1064
		CH$_2$ wagging	17	1283	1021
		in-plane ring	18	1030	937
		in-plane ring	19	283	270
E_2''	F	C—H stretching	20	—	—
		CH$_2$ twisting	21	—	—
		CH$_2$ rocking	22	—	—
		out-of-plane ring	23	—	—

R—Raman active   [ ] —Calculated or estimated.
I—Infra-red active   Has not been observed experimentally.
F—Forbidden   ( )—Used twice.
       * —Inferred from resonance pair 2108–2151.

TABLE VII. Product rule ratios for D_{5h}.

	A_1'	A_1''	A_2'	A_2''	E_1'	E_1''	E_2'	E_2''
τ_{theor}	2.00	1.41	1.26	1.87	2.64	2.44	2.83	2.83
τ_{corr}	1.96	1.39	1.25	1.83	2.56	2.37	2.74	2.74
τ_{obs}	1.97	—	—	1.82	2.59	—	2.73	—

ring. However Herzberg[36] has pointed out that degenerate Raman frequencies of symmetrical-top molecules may be expected to be broad because the individual Q branches do not quite coincide in frequency.

It is surprising to find that the four Raman lines observed in the C—H stretching region for d_0 are all polarized, because there should be two depolarized fundamentals. There is little doubt that 2868 is the A_1' fundamental. The line at 2904 can be explained as $2\times1453=2906$, and 2966 as $2\times1487=2974$. The latter seems too intense not to be also a fundamental, and we believe that there is an accidental coincidence here. This would account for the intensity, the broad appearance, and the partial polarization. The polarization of 2944 is difficult to explain, although it may be due to overlapping with 2966. Its intensity certainly suggests a fundamental.

Considering the E_2' species first, we assign the line 283 in d_0 and 270 in d_{10} to one of the ring frequencies. This seems surprisingly low for an in-plane ring vibration. We feel, however, that it is probably an allowed fundamental frequency. We have been unable to explain it as a combination tone or difference tone. It seems improbable that it is the forbidden E_2'' out-of-plane

[36] See reference 29, p. 444.

ring vibration because it has been reported in almost every Raman study, even at moderate exposures. Considering how feeble the allowed Raman lines are, it does not seem likely that a forbidden line would be so universally found. We therefore assign 283 to one of the E_2' ring modes. The other ring vibration in d_0 is taken as 1030 because this is the lowest unassigned frequency. Since a ring vibration is expected to be about 10 percent lower in the heavy molecule, 937 is chosen as its counterpart in d_{10}. There is no doubt that the methylene deformation is 1453 in d_0 and 1064 in d_{10}. This leaves Raman frequencies at 1104, 1207, and 1283 in d_0 and at 778 and 1021 in d_{10} to be assigned to the remaining three methylene vibrations of species E_1'' and E_2'. The 778 frequency presumably has a counterpart in d_0; it can be only 1104 because either of the other two values requires a shift much larger than $2^{\frac{1}{2}}$. Furthermore the 1104–778 pair cannot belong to E_2' because there is no combination of observed $C-H$ and $C-D$ stretching frequencies which will satisfy the product rule. We therefore place it in E_1''. There is now only a limited number of combinations for the remaining assignments. With the help of the product rule it is readily found that two satisfactory alternatives are: (1) 1283 and 1021 belong to E_2', and 1207 and a calculated 965 ± 7 belong to E_1'', or (2) vice versa. We find no evidence for the 965 frequency beyond this product rule calculation. The first alternative seems more probable, because the second requires fundamentals for d_{10} at 937 and 965 in species E_2'. It is unlikely that two fundamental frequencies of a highly symmetrical molecule will be this close together when they are in the same species. Therefore the first assignment is given in Table VI.

This completes the assignment of the Raman-active fundamentals. A few left-over lines are explained as overtones in Table IX.

2. Infra-Red-Active Species

There are 6 infra-red-active fundamentals. Far more than 6 bands were observed, but on the basis of intensity and the expected positions those at 2965, 2876, 1462, 1258, 896, and 545 are probably fundamentals for d_0. In d_{10} the bands at 2230, 2125, 1156, 1066, 737, and 438 suggest themselves as fundamentals.

The 2 parallel bands of A_2'', with their wide $P-R$ separation and their strong Q branch, should be readily apparent. The bands at 896 in d_0 and at 737 in d_{10} are obvious choices. This leaves 1462, 1258, and 545 for three of the E_1' vibrations of d_0, and 1156, 1066, and 438 for d_{10}, with the $C-H$ and $C-D$ frequencies still to be chosen. Unfortunately these assignments lead to serious disagreement between theoretical and observed product rule ratios for both species, regardless of what combination of the observed $C-H$ and $C-D$ stretching frequencies is used. This seems to be a real difficulty with the assumption of D_{5h} symmetry. If any of the observed bands are parallel fundamentals, they would

appear to be 896 in d_0 and 737 in d_{10}. These are among the most intense bands in their respective spectra, their $P-R$ separations are correct, and the Q branch (at least in 896) is very prominent. There is an additional reason for assigning 896 to the A_2'' methylene rocking mode; namely that the analogous frequency in cyclopropane has been assigned to 872,[34] and in cyclobutane to 902.[35] One might therefore abandon the 737 frequency and see if any other combination will satisfy the product rule. It is found that 2965 and 896 in d_0, and 2130 and 686 in d_{10}, give a good fit. This raises two more problems, however. Why does the intense 896 band of d_0 become the weak 686 of d_{10}? How should one now explain the intense 737 band of d_{10}?

At this point we note that the 2 strong bands in d_{10} at 1065 and 1156 have completely different contours, suggesting that they belong to different species. Since there are only 2 infra-red-active species, one band must be in A_2'' and the other in E_1'. Furthermore their intensity is strong indication that they are fundamentals. If then one of these is the A_2'' methylene rocking of d_{10}, it must be somewhere near 1460 cm^{-1} in d_0. The assignment of 2965 and 1462 to the A_2'' modes of d_0, and 2230 and 1066 to d_{10}, gives excellent agreement with the product rule. Similarly in E_1' the assignment of 2876, 1462, 896, and 545 as fundamentals in d_0, and 2125, 1156, 737, and 438 as fundamentals in d_{10} gives good agreement. Thus 1462 of d_0 is assumed to be accidentally degenerate, and to split to give 1065 and 1156 on going to d_{10}.

We have now used the strongest infra-red bands of both molecules to give an assignment that fits the product rule, but at the following cost.

1. The assignment of 1462 to a CH_2 rocking frequency and of 896 to a wagging mode is in disagreement with the assignments for cyclopropane and cyclobutane. This may not be a serious objection, for these latter two analyses have never been put to the test of satisfying the product rule. Had we not had the spectrum of cyclopentane-d_{10} available so that the product rule could be applied, we certainly would also have assigned the A_2'' rocking to 896. Furthermore in ethylene oxide, which is isoelectronic with cyclopropane, the analogous rocking mode is assigned to 1379 cm^{-1} (although somewhat dubiously).[37, 37a]

2. Band contours are ignored. The most likely parallel band, 896 of d_0, is placed in the species having perpendicular bands. In brief, the assignment which fits the criterion of band contours does not fit the product rule, and vice versa. Thus doubt is cast on the original assumption of D_{5h} symmetry. Conversely, there is some doubt as to how rigorous the band contour criterion is. Rasmussen, in a study of the infra-red spectrum of

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[37] See reference 29, pp. 341, 351.

[37a] *Note added in proof:* Professor R. C. Lord has recently completed a study of light and heavy cyclopropane. He has kindly informed us that the A_2'' methylene wagging frequency occurs at 854 and 614 cm^{-1} respectively in these two molecules. It is unexpectedly weak in both cases.

TABLE VIII. Estimation of the E_2'' out-of-plane ring frequency.

	260°K	298.16°K
$S_{trans}+S_{rotn}$ $(\sigma=1)$	62.73 e.u.	63.82 e.u.
S_{vibn} (minus out-of-plane ring vibn.)	4.11	5.42
$-R\ln\sigma$, with $\sigma=10$.	-4.57	-4.57
S_{calc} (minus ν_{23})	62.27	64.67
$S_{measured}$	67.60	70.06
Difference	5.33	5.39
Approximate value for out-of-plane ring vibn.	130 cm^{-1}	150 cm^{-1}

cyclohexane,[38] found that the contour of one of the five bands he observed below 1500 cm^{-1} was completely different from that predicted.

We feel that the product rule is the more rigorous of the two criteria, so we shall adopt the second assignment of the infra-red bands and proceed with the analysis to see what further evidence can be obtained for or against D_{5h} symmetry.

3. Totally Inactive Species

There are 6 totally inactive vibrations for D_{5h} symmetry. It is possible that some of these may appear in the infra-red spectrum of the liquid. Actually there are bands at 1316, 1033, and 964 in the infra-red spectrum of liquid d_0, and at 997 and 791 in d_{10} that have no clear counterparts in the vapor spectra. The 1033 band may be due to the 1030 Raman-active vibration in d_0. The remaining four bands are probably forbidden fundamentals, but we are unable to make specific assignments. It may be noted that the 964 frequency has also been reported in three earlier Raman studies.[4,5,7]

This completes the assignment as far as we are able to deduce it from the spectra. The results are collected in Table VI. Table VII compares the theoretical and the observed product rule ratios. This table also contains a "corrected" value of τ, in which an empirical anharmonicity correction of one percent for each hydrogen bending and stretching mode in the species has been subtracted from the theoretical product rule ratio.

4. Estimation of the E_2'' Out-of-Plane Ring Vibration (ν_{23})

A direct comparison of the entropy calculated statistically with that obtained from calorimetric measurements cannot be made because the vibrational assignment is incomplete. In particular the E_2'' out-of-plane ring vibration, which is probably the lowest of all the fundamentals, is missing. However one can use the measured entropy to estimate this low frequency. One can then examine the spectrum to see if there is any evidence for such a frequency in the form of an allowed combination or difference tone.

The entropy of d_0 has been measured by Aston, Fink,

and Schumann[17] and by Douslin and Huffman.[39] Kilpatrick, Pitzer, and Spitzer[1] have discussed these results critically and have introduced a small correction. We shall use their values.

The calculations are summarized in Table VIII. The assignments of Table VI have been used, plus the following estimated frequencies (and degeneracies) for the inactive fundamentals: 1316(2), 964(2), 2950(2), 1000(1), 1200(1). Although these frequencies are only guesses, they make such a small contribution to the entropy at the two temperatures employed that very little error is introduced. The formulas used to calculate the entropy of translation and rotation may be found in Herzberg.[40] The vibrational entropy was compiled from the tables in Taylor and Glasstone.[41]

It is seen that the out-of-plane ring frequency would have to be about 140±20 cm^{-1} to make our assignment consistent with the measured entropy. Presumably in d_{10} it would be somewhere in the range 125±20 cm^{-1}. The only prior experimental evidence supporting these values is the very faint Raman line found in d_0 by Kohlrausch and Seka[4] at 165 cm^{-1}. This line has not been reported by any other investigators, and can be assigned to ν_{23} only in violation of the selection rules.

5. Assignment of the Left-Over Frequencies

Table IX gives suggested assignments for the left-over frequencies. It was not possible to explain all of the observed bands, but this is to be expected because: (a) the totally inactive fundamentals are not known, (b) only binary combinations were tried, and (c) some of the weak lines in the d_{10} spectrum may actually be due to d_9.

Frequency ν_{23} can combine only with the E_1'', E_2', or E_2'' fundamentals to give infra-red-active combinations. By assuming that ν_{23} is in the range 100–200 cm^{-1}, one can compare these fundamentals with the left-over bands to see if any consistent indication is given for the value of ν_{23}. Two bands suggest that it is near 155 cm^{-1} in d_0, and 2 more suggest either 155 or 125 cm^{-1} in d_{10}. There are alternative explanations for 2 of these 4 left-over bands. The evidence is thus so slight that these values have not been entered in Tables VI and IX.

6. Summary of the Spectroscopic Case for D_{5h} Symmetry

The evidence favoring D_{5h} symmetry is the following. (a) The observed spectrum of d_0 is exceedingly simple, and agrees well with what is expected from the selection rules. There are very few strong bands in either infra-red or Raman spectrum, and very few coincidences between the two. The few coincidences which do occur can be reasonably explained as accidental degeneracies.

[38] R. S. Rasmussen, J. Chem. Phys. 11, 249 (1943).

[39] D. R. Douslin and H. M. Huffman, J. Am. Chem. Soc. 68, 173 (1946).

[40] See reference 29, p. 522.

[41] Taylor and Glasstone, Treatise on Physical Chemistry (D. Van Nostrand Company, Inc., New York, 1942), Vol. I, p. 654.

The number of polarized Raman lines agrees with expectations. (b) An assignment can be made which fits the product rule quite satisfactorily. (c) Left-over frequencies can be explained rather well, considering the three handicaps enumerated above.

The evidence against D_{5h} symmetry is the following. (a) Either band contours or the product rule has to be ignored in making the assignment. (b) To fit the product rule, the assignment places a methylene rocking frequency at 1462 and a wagging frequency at 896 cm⁻¹. This does not agree with assignments in cyclopropane and cyclobutane. (c) An in-plane ring vibration is assigned to 285 cm⁻¹, which seems surprisingly low. (d) There is no good independent evidence for the out-of-plane ring vibration at 140 ± 20 cm⁻¹ which is required to fit the entropy. (e) The selection rule argument favoring D_{5h} is weakened by the fact that: (1) the spectrum of d_1 is not markedly richer in bands than is that of d_0, (2) the Raman spectrum of the isoelectronic tetrahydrofuran is remarkably similar to that of d_0,[42] and (3) the Raman spectra of C_5H_9X, where X is OH, NH₂, CH₃, SH, Cl, Br, or I, are not much more complex than that of d_0 itself.[43] Apparently the effective selection rules are not sensitive to rather severe changes in symmetry. This largely nullifies one of the main arguments for D_{5h} symmetry.

Our tentative conclusion from the spectral evidence is that cyclopentane does not have strict D_{5h} symmetry, although it is certainly close enough so that D_{5h} selection rules hold very well.

C. The Heat Capacity of Solid Cyclopentane

The assignment for the D_{5h} structure postulates a doubly degenerate vibration (ν_{23}) at 140 ± 20 cm⁻¹ in order to fit the entropy. Professor R. C. Lord has suggested to us that the heat capacity of the solid might provide definite evidence concerning the reality of this value. This has proved to be the case. The results show that there is no such frequency.

The general method was that developed by Lord,[44] and used by Lord, Ahlberg, and Andrews,[45] and by Brucksch and Ziegler.[46] The basic equation is:

$$C_{v(I)} = C_p - (C_p - C_v) - C_{v(L)}, \qquad (1)$$

where $C_{v(I)} =$ "internal" heat capacity, caused by vibrations within the molecules; and $C_{v(L)} =$ "lattice" heat capacity, caused by translations and rotations of the molecules as units.

[42] K. W. F. Kohlrausch and A. W. Reitz, Zeits. f. physik. Chemie B45, 249 (1939).

[43] K. W. F. Kohlrausch, "Ramanspektren" Hand- und Jahrbuch der Chemischen Physik, Vol. 9, VI (1943). (Reprinted by Edwards Brothers, Inc., Ann. Arbor, Michigan), p. 331.

[44] R. C. Lord, J. Chem. Phys. 9, 693 (1941).

[45] Lord, Ahlberg, and Andrews, J. Chem. Phys. 5, 649 (1937). This paper does for benzene precisely what we shall do for cyclopentane—namely, eliminate the possibility of a low doubly degenerate frequency near 160 cm⁻¹.

[46] W. F. Brucksch, Jr. and W. T. Ziegler, J. Chem. Phys. 10, 740 (1942).

TABLE IX. Assignment of left-over frequencies (D_{5h} selection rules).

Cyclopentane				Cyclopentane-d_{10}			
cm⁻¹	I	Assignment	Active species	cm⁻¹	I	Assignment	Active species
Raman						Raman	
2904	4	$2\nu_{16} = 2906$	A_1'	2048	2	$2\nu_{17} = 2042$	A_1'
				2304	2	$2\nu_9 = 2312$	A_1', E_2'
Infra-red						Infra-red	
617	2(∥)	$\nu_{10} - \nu_{19} = 613$	E_1'	502	0	$\nu_{18} - \nu_{11} = 499$	E_1'
697	0	—		578	0(∥)	$\nu_{13} - \nu_{11} = 583$	A_2''
748	0	$\nu_{18} - \nu_{19} = 747$	E_1'	686	0	$\nu_2 - \nu_{11} = 686$	E_1'
753	0	$\nu_{18} - \nu_{19} = 747$	E_1'			$\nu_{17} - \nu_{19} = 691$	E_1'
770	1(⊥)	$\nu_5 - \nu_{11} = 771$	E_1'	722	1	—	
796	0	—		814	1	—	
827	1(∥)	$\nu_{11} + \nu_{19} = 828$	A_2''	935	0	—	
949	3	$\nu_2 - \nu_{11} = 942$	E_1'	974	0	—	
1020	0	—		1119	2	—	
1206	0	—		1315	0	—	
1258	3	$\nu_{19} + 964 = 1247$	?	1458	1	$\nu_{11} + \nu_{14} = 1459$	A_2''
1739	0	$\nu_{16} + \nu_{19} = 1736$	E_1'	1510	1	$\nu_{10} + \nu_{14} = 1515$	A_2''
1884	0	—		1562	1	$\nu_2 + \nu_{11} = 1562$	E_1'
2021	0	—		1772	2	—	
2036	1	$\nu_2 + \nu_{11} = 2032$	E_1'	1867	2	$\nu_3 + \nu_7 = 1868$	A_2''
2060	1	$2\nu_{18} = 2060$	E_1'	2005	2	$\nu_6 + \nu_{18} = 2001$	E_1'
2114	0	—		2099	5	$\nu_9 + \nu_{18} = 2093$	E_1'
2181	1	$\nu_{10} + \nu_{17} = 2179$	E_1'	2155	5	—	
2346	1	$\nu_3 + \nu_7 = 2348$	A_2''	2203	0	$\nu_5 + \nu_9 = 2206$	E_1'
		$\nu_3 + \nu_9 = 2348$	E_1'	2428	2	—	
2405	0	$2\nu_{17} = 2414$	E_1'				
2486	1	$\nu_9 + \nu_{18} = 2492$	E_1'				
		$\nu_{16} + \nu_{18} = 2483$	E_1'				
2610	2	—					
3196	0	—					
3476	1	—					

$C_{v(I)}$ was first calculated from Eq. (1). For this purpose the observed values of C_p were employed.[17,39] The quantity $(C_p - C_v)$ was determined from the Nernst-Lindemann equation: $C_p - C_v = 0.0214 C_p^2 T / T_{m.p.}$. $C_{v(L)}$ was evaluated from a Debye function with six degrees of freedom in place of the usual three. The characteristic θ was calculated at 15°K from the low temperature form of the Debye equation, $C_v = 928(T/\theta)^3$, and was found to be 152°. An alternative value of 155° was obtained by fitting the heat capacity curve between 0°–50°K. The former value was employed because it is free from any suspicion of being empirically adjusted. $C_{v(L)}$ was obtained at various temperatures from the usual tables.

$C_{v(I)}$ was then independently calculated from the vibrational assignments, using Einstein functions. The following frequencies (and their degeneracies) are the only ones which make any appreciable contribution at the temperatures employed: 283(2), 545(2), 886(1), 896(2), ν_{23}(2). No value was included for ν_{23}. The difference between this statistical value of $C_{v(I)}$ and the value calculated from Eq. (1) is the contribution due to ν_{23}.

The results are summarized in Table X. It is seen that a frequency in the range 140–160 cm⁻¹ would contribute far too much to the heat capacity to give agreement between the two $C_{v(I)}$'s.

Similar calculations were carried out for chlorine and cyanogen to get some estimate of how accurately $C_{v(I)}$'s calculated by the two methods would agree.[47] Although the agreement in some cases was not as close as might be desired, the errors were such that there is still no doubt that a frequency of 140–160 cm⁻¹ in

[47] Data and pertinent references may be found in reference 46.

TABLE X. Vibrational heat capacity of solid cyclopentane.

T(°K)	C_p	$(C_p - C_v)$	$C_v(L)$	$C_v(I)$ Eq. (1)	$C_v(I)$ Statis.*	Diff.	Contrib'n. if ν_{23} were 140 cm^{-1}	Contrib'n. if ν_{23} were 160 cm^{-1}
50°	8.55	0.44	7.82	0.29	0.08	0.21	1.20	0.86
100	14.40	2.46	10.64	1.30	1.26	0.04	2.86	2.60
140	21.60	7.76	11.24	2.60	2.57	0.03	3.36	3.20

* Contribution of ν_{23} not included.

cyclopentane is completely incompatible with the heat capacity.

Thus the assumption of D_{5h} symmetry leads to an insurmountable dilemma. On the one hand the entropy of the vapor at room temperature demands the existence of a very low fundamental. No revision of the D_{5h} assignments can alter this fact. On the other hand the existence of such a fundamental is definitely incompatible with the heat capacity of the crystal. The only possible conclusion is that cyclopentane cannot have D_{5h} symmetry.

D. Consideration of Lower Symmetries

The other possible symmetries for cyclopentane—C_s, C_2, C_1—allow all 39 fundamentals to appear in both the infra-red and Raman spectra. The observed spectra cannot in any case be made to fit this. Kilpatrick, Pitzer, and Spitzer[1] have pointed out that if the warping of the ring away from D_{5h} symmetry is small, the hydrogen vibrations will be virtually unaffected. Their degeneracies will not be split, and they will follow the selection rules for D_{5h} fairly closely. For the ring vibrations, however, the effective symmetry is probably so low that the degeneracies are removed, and there are no forbidden fundamentals.

Table XI gives a suggested assignment for cyclopentane and cyclopentane-d_{10} based on these assumptions. The hydrogen assignments are the same as for D_{5h} except that the methylene rocking formerly put at 1492 has been changed to 896, and the methylene wagging formerly at 896 has been made 1258. Also hydrogen frequencies which are totally forbidden for D_{5h} have been assigned to weak observed bands. The ring vibrations are quite different from the D_{5h} assignments. One component of the out-of-plane mode is assigned to 285 cm^{-1}; the other component will be located with the help of the entropy. The 545 band has been split into 545 and 617. The Raman-active in-plane ring vibration ν_{19} is taken to be 769 and 827, and the 1030 band has been split into 1030 and 949.

In brief, all the observed frequencies for cyclopentane below 1500 cm^{-1} with the exceptions of 697 and 1206 are assigned to fundamental vibrations. Certain of the assignments should doubtless be interchanged, but these permutations will have no effect on the calculated entropy because all the low frequencies are taken to be singly degenerate.

The value of ν_{23b} is now estimated by comparing the

measured entropy at 298°K with the entropy calculated from 38 of the 39 frequencies. The difference indicates that ν_{23b} is about 215 cm^{-1}. The only observed frequency near this value is a very faint Raman line at 207 cm^{-1} reported by Rosenbaum and Jacobson.[6] We cannot confirm this value because it is in a region where the Rowland ghosts from our grating are too intense. Nevertheless this will be taken as the value of ν_{23b}.

The assignments of Table XI provide the following calculated values for some of the thermodynamic properties.

1. Entropy of the vapor

	260°K	298°K
$S_{spectros}$	67.46 e.u.	70.14 e.u.
$S_{calorimetric}$	67.60	70.06
Diff.	−0.14	+0.08

The experimental error in the calorimetric value is about ±0.10 e.u. Considering that many liquid phase frequencies were used in calculating the entropy, and also that moments of inertia for a D_{5h} structure were employed, the agreement is reasonable.

2. Heat capacity of the solid

	50°K	100°K	140°K
C_p(calc.)	8.48 e.u.	14.74	21.90
C_p(obs.)	8.55	14.40	21.60
Diff.	−0.07	+0.34	+0.30

This is within the accuracy of the calculations.

3. Heat capacity of the gas

	353°K	539°K
C_p(calc.)	25.13 e.u.	39.46
C_p(obs.)	24.42	38.3
Diff.	0.71	1.2

These differences are rather large, but this is not unexpected. The assignments of the moderately high frequencies are critical, since they make large contributions to C_p at these temperatures. It is quite possible that there may be errors in some of these assignments. Furthermore anharmonicity is assuming importance. This would cause the observed C_p to be lower than the calculated value, which is found to be the case. It may be noted that the assignments of the very low frequencies are not critical, because the contribution of the low frequencies is approaching the classical value. Consequently the heat capacity of the gas at these temperatures is rather insensitive to the particular choice of ν_{23b}.

The assignments of Table XI thus fit the observed data moderately well. It is interesting to compare them with those of Kilpatrick, Pitzer, and Spitzer.[1] The agreement is not very good for the hydrogen vibrations, because these authors give only average values for groups of hydrogen frequencies. The agreement for the ring vibrations is excellent except for ν_{23}. Kilpatrick,

Pitzer, and Spitzer picture the out-of-plane ring vibration ν_{23} of D_{5h} as splitting into two parts in the puckered molecule: a vibration in which the nuclei move perpendicularly to the (hypothetical) σ_h plane, and a pseudo rotation in which the position of maximum displacement rotates slowly around the ring. This latter mode does not possess an angular momentum because any given atom moves only perpendicularly to the plane. Nevertheless it can be regarded as a kind of free rotation because the potential energy associated with this motion is zero (see their Eqs. (4) and (5)). A plane rotator energy expression is used to evaluate the contribution of this mode to the partition function.

In effect, Kilpatrick, Pitzer, and Spitzer propose that only 38 of the 39 vibrational modes are genuine vibrations, and that the remaining one is a free rotation. In this paper, all 39 have been assumed to be genuine vibrations, and a spectroscopically-observed frequency has been assigned to each. It does not seem possible to decide at this time which alternative is correct. One would have to decide in favor of the second one if the existence of ν_{23b} in the spectrum could be proved. We hope to investigate this possibility.

The conclusions of this paper may be summarized as follows.

1. Cyclopentane definitely does not have D_{5h} symmetry.

2. Its exact symmetry and geometry are not known.

3. It is not necessary to adopt Kilpatrick, Pitzer, and Spitzer's model of a puckered ring with a pseudo rotation in order to interpret the data.

COMPARISON WITH PERFLUOROCYCLOPENTANE

It may be of interest to mention the results for perfluorocyclopentane, C_5F_{10}, for comparison. One would expect this molecule to have a greater tendency to be non-planar than cyclopentane, because repulsions between fluorine atoms on neighboring carbons are probably greater than between hydrogen atoms. This is borne out experimentally. Electron diffraction results indicate that C_5F_{10} does not have D_{5h} symmetry.[48] This

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[48] Bastiansen, Hassel, and Lund, Acta Chem. Scand. 3, 297 (1949).

TABLE XI. Assignment of fundamental frequencies for a non-planar ring.

Mode of vibration	D_{5h} notation	C_5H_{10}	C_5D_{10}
C—H stretching	1	2868	2130
	6	2965	2230
	8a, 8b	2876	2125
	12a, 12b	2966	2214
	15a, 15b	2944	2130
	20a, 20b	[~2900]	[~2150]
CH$_2$ deformation	2	1487	1124
	9a, 9b	1462	1156
	16a, 16b	1453	1064
CH$_2$ wagging	5	1316	[1060]
	10a, 10b	1258	1065
	17a, 17b	1283	1021
CH$_2$ twisting	4	1306	943
	13a, 13b	1207	[965]
	21a, 21b	1033	791
CH$_2$ rocking	7	896	737
	14a, 14b	1104	778
	23a, 23b	964	[710]
Ring	3	886	802
	11a	545	438
	11b	617	502
	18a	1030	937
	18b	949	814
	19a	827	728
	19b	769	687
	23a	283	270
	23b	207	?

[ ] Estimated.

is confirmed by the vibrational spectrum. In contrast to the case of cyclopentane, the effective selection rules are certainly not those for D_{5h} symmetry. The Raman spectrum has approximately twice as many lines below 1400 cm^{-1} as does cyclopentane, and there are eight coincidences between the infra-red and Raman spectra in this range.[49]

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[49] Dr. Don C. Smith of the Naval Research Laboratory very kindly furnished these spectra in advance of publication. They are now available in Naval Res. Lab. Report 3567, pp. 85, 128–129. The infra-red spectrum is also available as A.P.I. curves 992 and 993. (Reference 11.)