[Contribution from the Spectroscopy Laboratory and Department of Chemistry, Massachusetts Institute of Technology]

The Vibrational Spectra and Structure of Cycloöctatetraene[1]

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After unsuccessful attempts to prepare cycloöctatetraene-d_8 by various exchange procedures, of which a brief summary is given, the compound was made by polymerization of acetylene-d_2 over a nickel cyanide catalyst. The infrared absorption spectra of cycloöctatetraene and the deuterium analog have been measured in both liquid and vapor phases over the spectral range 240-3500 cm.$^{-1}$. Their Raman spectra have been measured in the liquid phase with a plane-grating spectrograph and green excitation (Hg-5461). Qualitative depolarization factors for the more intense Raman lines were also determined. Interpretation of the spectra with the help of the product rule leads unequivocally to the crown structure with alternating single and double bonds (D_4 symmetry). A second interpretation is made on the basis of the tub structure (D_{2d} symmetry), but the serious obstacle is encountered that this structure should have all infrared-active fundamentals present also in the Raman effect, contrary to the observation of several strong infrared bands with no Raman counterparts. Structures of either higher or lower symmetry than D_4 or D_{2d} are inconsistent with the gross features of the spectra. In particular there is no spectroscopic indication of the presence of a structure having fused four- and six-membered rings (bicyclo(4.2.0)-octa-2,4,7-triene).

The discovery in 1940 by Reppe and co-workers[4] that acetylene can be polymerized catalytically to cycloöctatetraene has led to a renewed interest in both the chemistry and the molecular structure of this substance. It is now well established[5] that the classical cycloöctatetraene synthesis of Willstätter[6] gives a product identical with that obtained from acetylene. Moreover, an alternative synthesis[7] that partially overlaps the one of Willstätter leads to the same product. These syntheses indicate that the product deserves the name 1,3,5,7-cycloöctatetraene, but do not permit conclusions as to the exact geometrical form of the molecule.

Because of the insufficiency of present chemical evidence, determination of the structure by physical methods is desirable. Infrared and Raman spectra are potentially valuable in this connection because of the prospective high symmetry of the molecule and the possibility of extending the spectroscopic study to the deuterium derivative. The purpose of the present paper is to report our spectroscopic work on cycloöctatetraene and its deuterium derivative, and to draw conclusions concerning the geometrical form of the molecule.

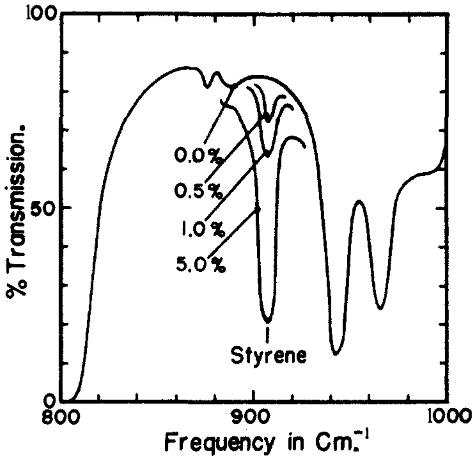

Fig. 1.—Variation with concentration of the 908 cm.$^{-1}$ infrared band of styrene dissolved in cycloöctatetraene.

Preparation and Properties of Cycloöctatetraene and Cycloöctatetraene-d_8

1. **Cycloöctatetraene.**—Inasmuch as the details of the polymerization of acetylene over a nickel cyanide catalyst to yield cycloöctatetraene have now been published in widely available form,[4,8,9] we shall not describe our preparative procedure. About 10 g. of acetylene was polymerized in a 0.2-liter high-pressure reaction bomb, the yield being about 2 g. of benzene, 6 g. of cycloöctatetraene and 1.5 g. of high-boiling residue. This mixture was fractionally distilled and then fractionally crystallized to remove possible small amounts of styrene (b.p. 146°). Examination of the infrared spectrum of the unpurified material shows weak bands at places where styrene has strong absorption, notably at 697, 777, 908 and 991 cm.$^{-1}$. The appearance of the 908 cm.$^{-1}$ styrene band for different concentrations of styrene in cycloöctatetraene is shown in Fig. 1. The marked difference in the freezing points of these two isomers (−31° *vs.* −4.7°) makes possible their separation by fractional crystallization. The final crystal fraction usually had a melting point between −6 and −5°, although the purification could be continued until the freezing point was as high as −4.7°. Infrared curves were run on the various fractions obtained, and the progressive diminution of the weak absorption bands due to impurities was observed. All bands whose intensity changed with fractionation were weak bands coincident with the above-mentioned frequencies of the strong styrene bands. The styrene present in the cyclooctatetraene before fractional crystallization ran from 3 to 7% in different polymerizations. It is of interest to note that about this amount of styrene was also present in the material prepared by the Willstätter and by the Cope and Bailey syntheses. The purified samples used in the study of the infrared and Raman spectra contained less than 1% of styrene.[10]

The physical properties of purified cycloöctatetraene were: freezing point −4.7, b.p. 140-142°; n^{25}_D 1.5341. These

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[4] Reppe, Schlichting, Klager and Toepel, *Ann.*, **560**, 1 (1948).

[5] Cope and Overberger, This Journal, **69**, 976 (1947); **70**, 1433 (1948).

[6] Willstätter and Waser, *Ber.*, **44**, 3442 (1911); Willstätter and Heidelberger, *ibid.*, **46**, 517 (1913).

[7] Cope and Bailey, This Journal, **70**, 2305 (1948).

[8] (a) Karl Kammermeyer, "Polymerization of Acetylene to Cyclooctatetraene," Hobart, Washington, D. C., 1947; (b) Copenhaver and Bigelow, "Acetylene and Carbon Monoxide Chemistry," Reinhold Publ. Corp., New York, N. Y., 1949.

[9] Cope and Estes, This Journal, **72**, 1128 (1950).

[10] Styrene-free cycloöctatetraene can readily be obtained by making use of the cycloöctatetraene–silver nitrate complex discovered by Reppe[4] (*cf.* Cope and Hochstein, This Journal, **72**, 2515 (1950)). At the time our work was in progress we were unaware of this possibility.

values are consistent with those reported by other investigators.[4,8,9,11,12a,b,c]

2. **Exchange between Cycloöctatetraene and Deuterium Compounds.**—Although our attempts to make the deuterium analog by exchange were not successful, it appears worthwhile to give a brief summary of the exchange studies.[13] The chemical properties and certain frequencies in the Raman spectrum indicate that the molecule is olefinic in nature. However, there is also evidence for high symmetry, which might imply a resonating system analogous to that in aromatic hydrocarbons. The spectral data are also inconsistent with the presence of functional groups of an aliphatic or acetylenic nature. For this reason most of the exchange reactions attempted were similar to, or modifications of, studies made by investigators of aromatic or olefinic substances.[14–17]

Two general precautions were to carry out attempted exchange in an all-glass system whenever possible and to work with a catalyst whose activity with respect to exchange in some other molecule was checked before each experiment. Two methods—pycnometric and spectroscopic—were used to determine whether exchange had occurred.

Liquid and vapor phase exchange studies of cycloöctatetraene with D_2O and D_2 were carried out with a variety of catalysts under a wide range of conditions. The following catalysts were employed for the vapor phase experiments: reduced nickel on kieselguhr, reduced nickel on celite, supported reduced platinum oxide, supported reduced palladium oxide, fresh copper turnings, platinized silica gel, platinized-platinum foil. In addition, catalysts used for the liquid phase studies were: Raney nickel, Adams platinum-platinum oxide and palladium-palladium oxide. The pressure in these experiments was varied from one atmosphere to fifteen, the work at higher pressures being performed in thick walled tubing. The temperature of that part of the exchange system containing the catalyst was varied in most cases from 50 to 350° for the lower pressures and 100 to 175° for the higher pressures. In the liquid phase experiments the liquid media were cycloöctatetraene itself, ether, dioxane and D_2O.

When working with D_2 we found that cycloöctatetraene was hydrogenated by those catalysts which would hydrogenate olefinic hydrocarbons such as amylene under the same conditions. With the other catalysts no exchange was observed. With all catalysts the compound appeared not to decompose appreciably except at temperatures greater than about 250°. None of the catalysts used were found to be active for exchange with D_2O, although a number of them were active for exchange between D_2O and both benzene and olefinic hydrocarbons under the same conditions.

Previous investigators[18] have found that deuterium derivatives of certain aromatic compounds can be made by exchange between these compounds and D_2O in an acid medium. If hydrogen exchange between D_2O and cycloöctatetraene should proceed through an electrophilic substitution process it would be possible to prepare the deuterium derivative in the same way. To determine the conditions for exchange in acid medium, the action of various concentrations of D_2SO_4 up to 40 mole per cent. was investigated. In every case no evidence of exchange was found. With solutions of D_2SO_4 greater than 40 mole per cent. it was observed that cycloöctatetraene underwent reaction and decomposition.

From the above experiments it was concluded that the exchange of hydrogen between cycloöctatetraene and D_2O is not effected by catalysts that are active for the analogous exchange in aromatic and olefinic compounds. The explanation may be that the substance itself or one of its decomposition products behaves as a poison for the exchange reactions. The poisoning may be due to such strong adsorption of cycloöctatetraene that water molecules cannot come into effective contact with the active points of the catalytic surfaces. We know from various experiments that cycloöctatetraene is very strongly adsorbed by many catalytic surfaces. It was concluded further that exchange with D_2 appears to proceed at best only simultaneously with hydrogenation, under the same conditions in which exchange occurs in benzene without hydrogenation. No exchange reaction was found to take place between the hydrogen atoms of cycloöctatetraene and deuterium ion in an acid medium below acid concentrations at which the molecule undergoes reaction or decomposition.

3. **The Polymerization of Acetylene-d_2.**—Cycloöctatetraene-d_8 was prepared from acetylene-d_2 by modification of the procedure used for the light compound.[19] The changes were necessitated by the limited supply of acetylene-d_2 and of deuterated solvent. The use of a deuterated solvent was considered worthwhile, for those solvents which have been found most suitable for the polymerization show evidence of the introduction of hydrogen into the acetylene-d_2 in the presence of the polymerization catalyst. Because of the apparent difficulty of making tetrahydrofuran-d_8, acetone-d_6 was used. It was made by base-catalyzed exchange with D_2O, and had a D-content of 97 atom -per cent. In view of the observed slowness of exchange between acetone containing no deuterium and C_2D_2 under the conditions of the polymerization, this was known to be a sufficiently high D-content.

Dry 99+% C_2D_2 suitable for polymerization was made from D_2O and CaC_2 freshly roasted at 250°. The C_2D_2 was collected in a large test-tube containing the dry solvent (20–25 cc. of acetone-d_6) at Dry Ice temperature. The amount of acetylene-d_2 generated could be determined by weighing the test-tube and solvent before and after the preparation. From 25 g. of D_2O 12–13 g. of acetylene-d_2 could be prepared.

The acetylene-d_2 was used immediately by pouring the solvent and C_2D_2 rapidly from the test-tube into the reaction bomb precooled to Dry Ice temperature, followed by the addition of 0.1 g. of catalyst, and rapid closing and sealing off of the bomb. At no time was the solvent exposed to the air longer than a few seconds. As the bomb warmed slightly, enough C_2D_2 was released from solution to allow the bomb to be vented for the purpose of displacing most of the oxygen. The C_2D_2 lost by this procedure (about 1 g.) was considered a small price to pay for a successful polymerization. From this point on, the procedure of preparation was the same as that for the light compound. To eliminate loss of heavy solvent, the cycloöctatetraene-d_8, acetone-d_6 and by-products were vacuum distilled from the bomb and the low-boiling components separated by fractionation. Cycloöctatetraene-d_8 was purified by fractional recrystallization in the same manner as the light compound. The material thus prepared contained less than one atom-per cent. of hydrogen as shown by the infrared absorption curves and had the following physical properties: b.p. 140–143°; f.p., −4.5°; $n^{25}\text{D}$ 1.522.

The Infrared and Raman Spectra of Cycloöctatetraene and Cycloöctatetraene-d_8

The earliest work on the vibrational spectra of cyclooctatetraene was apparently carried out in Germany between 1941 and 1944 but no account of it was published. The paper of Reppe, *et al.*,[4] gives a schematic diagram of the Raman spectrum that shows only seven lines, several of whose wave numbers disagree markedly with all subsequent publications. Reppe, *et al.*, also give an infrared curve (ref. 4, p. 11) on a small scale with no information as to how it was obtained. This curve, which covers the range 2–11.5 microns, apparently indicates a considerable amount of styrene because of the intensity of a band at 11 microns (909 cm.$^{-1}$) where cycloöctatetraene shows no absorption peak (see Fig. 1).

The first published Raman spectrum was that of the

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(11) Flett, Cave, Vago and Thompson, *Nature*, **159**, 739 (1947).

(12) (a) Prosen, Johnson and Rossini, THIS JOURNAL, **69**, 2068 (1947); **72**, 626 (1950); (b) Scott, Gross, Oliver and Huffmann, *ibid.*, **71**, 1634 (1949); (c) Eccleston, Coleman and Adams, *ibid.*, **72**, 3866 (1950).

(13) A complete account is given in the Ph.D. dissertation of E. R. Lippincott (Johns Hopkins University, 1947). The exchange studies and most of the Raman work were carried out in the Department of Chemistry at the Johns Hopkins University.

(14) Farkas, Farkas and Rideal, *Proc. Roy. Soc.* (*London*), **A146**, 630 (1934).

(15) (a) Horiuti, Ogden and Polanyi, *Trans. Faraday Soc.*, **30**, 663 (1934); (b) Horiuti and Polanyi, *ibid.*, **30**, 1164 (1934).

(16) Zwigg, *ibid.*, **35**, 934 (1939).

(17) Bowman, Benedict and Taylor, THIS JOURNAL, **57**, 960 (1935).

(18) See, for example, Ingold, *et al.*, *J. Chem. Soc.*, 915 (1936).

(19) The deuterium used in this preparation was obtained as D_2O on allocation from the Isotopes Division, U. S. Atomic Energy Commission. We are grateful for their coöperation.

authors.[20a] Later Thompson and co-workers[10] and Bastiansen, Hassel and Langseth[20b] also reported the Raman spectrum. There is substantial agreement among these three workers on the prominent Raman lines, but more lines were reported by Lippincott and Lord than by the others. With the exception of two weak lines, we have verified all those previously reported and have found many additional lines.

The rock-salt infrared spectrum was first reported in numerical form by Thompson and co-workers,[11] and later by ourselves[21] with the addition of the potassium bromide region. The spectrum has also been reported in curve form in the American Petroleum Institute series.[22] The agreement among the various investigators is again quite good, there being minor differences attributable mainly to variable small amounts of styrene. In the present paper the infrared spectrum is reported to 240 cm.$^{-1}$ (42 microns).

No spectra have been reported for cycloöctatraene-d_8 except those in our note.[21]

Infrared Techniques.—The infrared spectra were obtained with a modified Perkin-Elmer Model 12B single-beam infrared spectrometer equipped with a d.c. vacuum thermocouple. The thermocouple output was amplified by a General Motors breaker-type d.c. amplifier and recorded on a Brown Instrument Co. "Electronik" recorder. The modification of the spectrometer consisted of a rearrangement of the external optical system to permit the ready introduction of a multiple-path vapor cell of considerable size. Prisms of various materials were used over the appropriate spectral ranges as follows: fluorite, 1200–3800 cm.$^{-1}$; rock salt, 650–1200 cm.$^{-1}$; potassium bromide, 400–650 cm.$^{-1}$; and thallium bromoiodide, 240–400 cm.$^{-1}$. Windows in the spectrometer system including the optical path from the source to the slit, were of potassium bromide except for the spectral region 240–400 cm.$^{-1}$, where films of polyethylene (0.025 mm. thick) were employed. The amplifier gain was such that 0.5 microvolt gave full-scale deflection in the 400-3800 cm.$^{-1}$ region, and 0.2 microvolt in the 240–400 cm.$^{-1}$ region. The signal-to-noise ratios realized in these two regions were respectively better than 100-to-1 and approximately 50-to-1.

Scattered light was minimized in the low-frequency regions by means of selective reflection filters of the type described by White.[23] These consisted of a plane echelette grating of 3600 lines per inch placed after the exit slit during study of the region from 240 to 900 cm.$^{-1}$ and an additional grating of 1000 lines per inch placed in the external optical system from 240 to 400 cm.$^{-1}$. Shutters of lithium fluoride and rock salt were used over the ranges 350–900 cm.$^{-1}$ and 240–350 cm.$^{-1}$, respectively. The excellence of the optics of the spectrometer, coupled with these measures, kept the residual stray radiation below 5% at all wave numbers, though of course it was far below 5% at most places. Atmospheric absorption due to water vapor was greatly reduced and that due to carbon dioxide eliminated by causing dry nitrogen at atmospheric pressure to stream through the entire optical path except the interior of the absorption cell. By this means it is relatively easy to reduce the absorption at the strong peaks of the 6 μ water band *as resolved by the fluorite prism* to less than 5%.

The wave number calibration of the instrument was carried out with the help of published frequency values for the vapors of H_2O, D_2O, HCl, DCl, HBr, NH_3 and CH_3OH, all of which have been studied with grating spectrometers. Absorption peaks are accurate to 2 cm.$^{-1}$ or better in the region 240–1700 cm.$^{-1}$ and 5 cm.$^{-1}$ or better from 1700 to 3800 cm.$^{-1}$. Overlapping of bands can interfere with the accuracy with which individual band frequencies are determined.

Absorption Measurements.—Spectra were obtained for both the liquid and the vapor state. The liquid absorption cells were of standard design,[24a] using spacers of amalgamated lead foil. The vapor cell possessed an internal optical system[24b] by means of which the effective path length could be varied in steps of 0.8 meter from 0.8 to 4 meters. Long optical paths through the vapor were necessary because of the low vapor pressure of cycloöctatetraene (5–6 mm. in the neighborhood of room temperature). When first used with cycloöctatetraene, the vapor cell gave rise to a little trouble because of its large internal surface area. The compound is strongly adsorbed on metal and glass surfaces, a property which makes difficult the complete removal of the vapor sample by pumping. In order to avoid contamination of the cell, lead gaskets were used in place of rubber ones, and after each run, the stop-cock grease was changed and the cell was dismantled and aired out. With these precautions, no further trouble was experienced.

Inasmuch as the Model 12B spectrometer does not record per cent. transmission directly, per cent. transmission *versus* wave number curves were obtained as follows: the spectrum was recorded from high to low wave numbers in a series of steps. At the outset of each step the slit width was set to give full-scale deflection with the blank cell in the path, and the spectrum was scanned until the deflection had fallen to about half of full scale with the blank cell. The slit was then opened to give full scale and the scanning continued. A single KBr plate was used as a blank liquid cell for the region 400–3800 cm.$^{-1}$. The evacuated vapor cell was used throughout as the blank for the vapor spectra. Per cent. transmission values were calculated from the ratio of the deflections measured on the sample cell to the corresponding deflections for the blank cell. The per cent. transmission curves determined in this way are shown for the liquid and vapor states of cycloöctatetraene and cycloöctatetraene-d_8 in Fig. 2. Tables I to IV list, respectively, the frequencies of bands considered strong enough in the vapor to be assigned as active fundamentals and frequencies of bands assigned as overtones or otherwise for the two compounds. The basis for the allocation of the bands to these categories is discussed later.

Raman Techniques.—The Raman spectra were studied with the plane grating spectrograph in the Department of Chemistry at the Johns Hopkins University. This type of instrument, of which detailed descriptions have been given elsewhere,[25] is particularly suited to the study of Raman spectra excited by Hg-5461 radiation because of its excellent dispersion at the longer wave lengths. Green excitation must be employed with cycloöctatetraene because of the compound's absorption in the blue region. The camera with which most of the spectra were photographed contained a Petzval lens of 685 mm. focal length (f/5.4) and produced a linear dispersion of about 0.040 mm. to the ångstrom. Resolution of sharp atomic lines 2 cm.$^{-1}$ apart is achievable without difficulty with the photographic emulsions used, although of course the limit of resolution of Raman lines is larger than this and highly dependent on the line shape.

Six General Electric AH-2 mercury arcs with elliptical reflectors served as a source of radiation. Between the arcs and the Raman tube were placed concentric cylindrical filter cells containing aqueous solutions of various inorganic salts. A 10 mm. thickness of 0.3 molar sodium chromate removes the short wave length region without noticeably reducing the intensity of Hg-5461. Five mm. of saturated neodymium chloride solution greatly reduces the continuous background in the source spectrum from 5600 to 6000 Å., and in addition almost completely eliminates the strong yellow lines Hg-5770 and Hg-5790. With these filters Raman lines must fall within 10 cm.$^{-1}$ of the yellow lines, whose separations from Hg-5461 are 980 and 1042 cm.$^{-1}$, respectively, to be obscured. For reduction of the continuum in the region 6000–6600 Å., a saturated cupric chloride solution of 5 mm. thickness is useful. Its cut-off is not sharp, however, and it has an appreciable effect on the intensity of the exciting line.

When the saturated neodymium chloride filter was used, two lines were found in cycloöctatetraene that are on the borderline of detectability (967 and 994 cm.$^{-1}$, respectively). It seemed desirable to verify these, and to look for others possibly concealed by Hg-5770 and Hg-5790. Accordingly, several spectra were taken with the yellow lines for excitation. A dilute aqueous solution of a cyanosine

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(20) (a) Lippincott and Lord, This Journal, **68**, 1868 (1946); (b) Bastiansen, Hassel and Langseth, *Nature*, **160**, 128 (1947).

(21) Lippincott, Lord and McDonald, *J. Chem. Phys.*, **16**, 548 (1948).

(22) Curves No. 595 and 739 in American Petroleum Institute Catalog of Infrared Spectral Data, issued by Research Project 44 at U. S. National Bureau of Standards. See also ref. 12c.

(23) White, *J. Opt. Soc. Am.*, **37**, 713 (1947).

(24) (a) See, for example, Harrison, Lord and Loofbourow, "Practical Spectroscopy," Prentice-Hall, New York, N. Y., 1948, pp. 486–488 and Fig. 17.5.

(24) (b) White, *J. Opt. Soc. Am.*, **32**, 285 (1942).

(25) Reference 24, pp. 515–517 and Fig. 18.4.

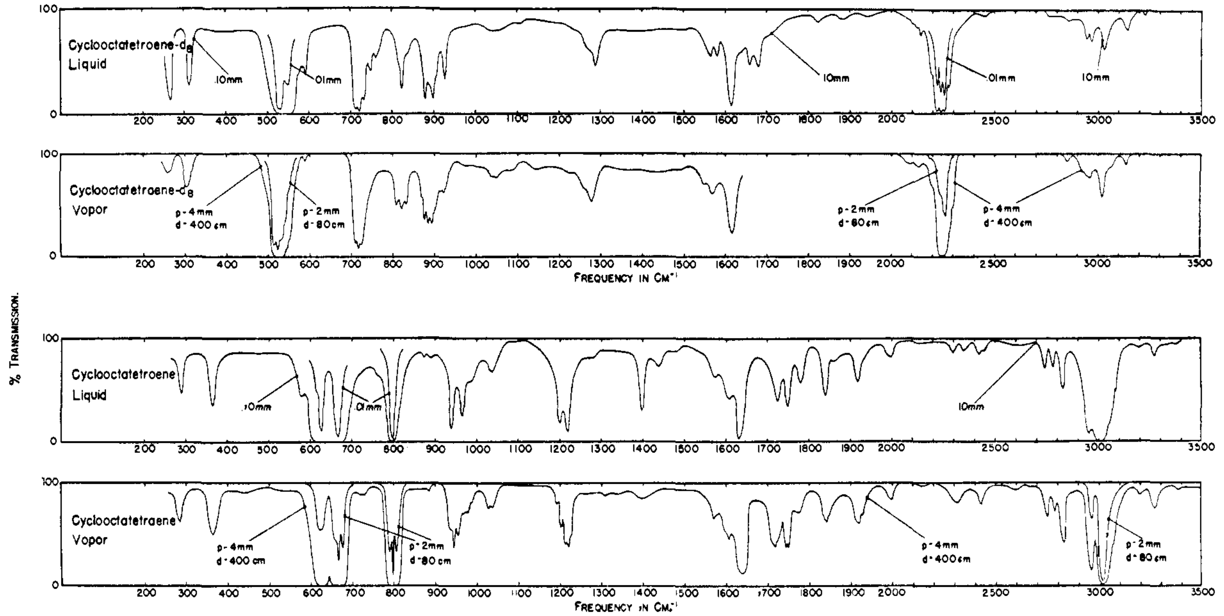

Fig. 2.—Infrared absorption of liquid and gaseous cycloöctatetraene and cycloöctatetraene-d_8.

Table I

Infrared Absorption Spectrum of Cycloöctatetraene: Principal Absorption Bands

Liquid spectrum Frequency in cm.⁻¹	Liquid spectrum Relative intensity	Vapor spectrum Frequency in cm.⁻¹	Relative intensity
290	m	285 (broad)	m
366	m	365 (broad)	m
628	vs	625 (broad)	s
		661-P	s
667	vs	669-Q	vs
		678-R	s
		792-P	s
800	vs	800-Q	s
		808-R	s
		937-P	m
942	s	945-Q	m
		(955)-R	(m)
		955-P	m
966	m	967-Q	w
		976-R	w
		1194-P	w
1202	s	1204-Q	m
		(1214)-R	(m)
		1214-P	m
1221	s	1223-Q	m
		1231-R	m
1399	m	1400	vvw
1609	m	1608	w
1635	s	1640	s
1725	w	1718	m
1750	m	1745	m
		1752	m
2830	w	2830	m
2955	m	2965	s
3004	vs	3015	vs

Table II

Infrared Absorption Spectrum of Cycloöctatetraene-d_8: Principal Absorption Bands

Liquid spectrum Frequency in cm.⁻¹	Liquid spectrum Relative intensity	Vapor spectrum Frequency in cm.⁻¹	Relative intensity
265	m	265	w
313	m	308	w
		518-P	vs
527	vs	527-Q	vs
		537-R	vs
551	m	551	w
		712-P	s
720	s	720-Q	s
		727-R	s
		816-P	m
822	m	823-Q	m
		831-R	m
		870-P	m
879	s	879-Q	m
		(888)-R	(m)
		888-P	m
899	s	898-Q	m
		905-R	m
		920-P	w
926	m	927-Q	w
		934-R	w
1286	m	1282	m
1614	s	1619	s
2220	s	2240	vs
2236	vs		
2252	vs	2270 (broad)	vs

dye served to remove wave lengths below the yellow, and satisfactory spectra were obtained.

The Raman tube, of conventional design, had an effective length of 10 cm. and a volume of 3–4 cc. although smaller volumes (down to 1 cc.) were occasionally used. An image of the tube was thrown on the spectrograph slit by a condensing lens of appropriate focal length and aperture.

The spectra were photographed on Eastman spectroscopic plates of emulsion type 103a-E. This emulsion is sensitized in the yellow and red, and enables the photography of Raman lines of absolute wave length as high as 6600 Å. Exposure times of one-half to two hours were used, the longer of these times being required to bring out the weaker lines. Eastman D-19 developer and F-5 fixer were used. The plates were enlarged twelve times and printed on du Pont Defender Velour Black B.T. 3 paper. It was usually found necessary in printing to expose for the weak lines separately from the stronger lines. The Raman lines, together with reference iron and mercury lines, were

TABLE III

INFRARED ABSORPTION SPECTRUM OF CYCLOÖCTATETRAENE: WEAK ABSORPTION BANDS

Liquid spectrum		Vapor spectrum	
Frequency in cm.$^{-1}$	Relative intensity	Frequency in cm.$^{-1}$	Relative intensity
582	w	590	vw
873	w	. .	. .
890	w	895	vvw
. .	. .	980	w
993	w	991	w
1036	w	1028 1039	w w
1036	vw		
		1427	vvw
1573	w	1572	w
1781	w	1777 (broad)	w
1842	w	1842 (broad)	w
1865	vvw	. .	. .
1922	w	1922 (broad)	w
2007	w	2004	w
2308	vw	2315	w
2425	w	2430	w
2450	vw	. .	. .
2745	w	2750	w
2784	w	2788	w
		3270	w

TABLE IV

INFRARED ABSORPTION SPECTRUM OF CYCLOÖCTATETRAENE-d_8: WEAK ABSORPTION BANDS

Liquid spectrum		Vapor spectrum	
Frequency in cm.$^{-1}$	Relative intensiy	Frequency in cm.$^{-1}$	Relative intensity
592	w	592	vvw
711	w	. .	. .
730	w	. .	. .
747	w	. .	. .
759	w	. .	. .
813	w	. .	. .
838	w	. .	. .
889	w	. .	. .
1379	w	. .	. .
1438 (broad)	w	1450	vw
1483	vw	. .	. .
1564	w	1567	w
1582	w	1575	w
1658	w	. .	. .
1680	w	. .	. .
1824	vw	. .	. .
1889	vw	. .	. .
2141	vw	2140	vw
. .	. . .	2190	w
2940	w	2930	vw
2965	w	2965	w
3025	w	3030	w
3135	w	3140	vw

measured from these prints with an X-ray film recorder. Many plates were measured by two additional means: by a microcomparator and by a Leeds and Northrup recording microdensitometer. Intensities of Raman lines were estimated by eye on an arbitrary scale from 1 to 10.

The self-consistency of the wave numbers for lines measured on several plates by the three methods indicates that lines of intensity 2 or greater are in general reliable to 2 cm.$^{-1}$ or better, whereas the very weak lines may be in error by as much as 5 cm.$^{-1}$. Lines of intensity 1 were verified on at least two plates.

Semi-quantitative depolarization factors were determined by a method similar to that of Cleveland and Murray.[26] In this method the Raman tube is illuminated successively from two mutually perpendicular directions, and the light entering the spectrograph is analyzed by means of a Polaroid film at the slit. Because the relative intensities of the two polarized components were measured without preliminary calibration of the emulsion, our depolarization factors are only approximate, except for lines whose depolarization factors are close to 6/7. For these latter, the depolarization factors should be accurate to 10-15%. This means that a Raman line with a depolarization factor 15% or more below 6/7 should definitely be detected as polarized. The depolarization factors of the polarized lines may be in error by 15%, or even more for the strongly polarized lines. The intensities of the two components were measured both as integrated intensities from a Leeds and Northrup microdensitometer record and as peak intensities with a Hilger model H451 non-recording microdensitometer. The two procedures gave depolarization factors which agreed well within the above limits of error.

Three determinations of the depolarization factors for the stronger lines of cycloöctatetraene and two for those of cycloöctatetraene-d_8 were carried out. Exposure times of 24 hours for each component in the light compound and 40 hours in the deuterium derivative were required. For certain of the lines in both compounds, the overlapping of polarized and depolarized lines renders measurement of depolarization factors very difficult. The strong line at 3013 cm.$^{-1}$ in cycloöctatetraene is certainly highly polarized, as is shown by the reproduction of the microdensitometer records in Fig. 3, but the closeness of the depolarized line at 3003 cm.$^{-1}$ prevents quantitative measurement of the depolarization factor. A similar situation exists in the heavy compound for the lines at 2250 and 2255 cm.$^{-1}$.

Tables V to VIII list the frequencies, estimated intensities and depolarization factors (when measured) of lines

TABLE V

RAMAN SPECTRUM OF CYCLOÖCTATETRAENE IN LIQUID STATE: PRINCIPAL LINES

Frequency in cm.$^{-1}$	Relative intensity	Depolarization factor	Frequency in cm.$^{-1}$	Relative intensity	Depolarization factor
194	10	1/2	1202	9	6/7
249	9	6/7	1221	4	. . .
292	9	6/7	1399	2	. . .
366	10	6/7	1439	9	6/7
655	5	. .	1601	7	6/7 ?
758	2	. .	1631	8	6/7 ?
873	10	1/10	1651	10	1/5
908	3	. .	1743	4	<6/7
948	9	6/7	2954	9	6/7
967	7	. .	3003	10	6/7
976	4	. .	3013	10	≪6/7
994	6	<6/7	3048	4	. . .

TABLE VI

RAMAN SPECTRUM OF CYCLOÖCTATETRAENE-d_8 IN LIQUID STATE: PRINCIPAL LINES

Frequency in cm.$^{-1}$	Relative intensity	Depolarization factor	Frequency in cm.$^{-1}$	Relative intensity	Depolarization factor
172	10	1/2	890	2 broad	. .
238	8	6/7 ?	930	2	. .
265	9	6/7 ?	1287	2	. .
312	10	6/7	1297	8	6/7
576	8	. . .	1579	6	. .
591	3	. . .	1615	6	. .
761	8	6/7	1636	9	1/6
812	4	1/3	1653	10	1/10
822	10	1/6	2225	9	6/7
838	3	6/7	2250	10	≪6/7
872	4	6/7	2255	8 broad	. .
881	8	6/7			

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(26) Cleveland and Murray, *J. Chem. Phys.*, **7**, 396 (1939).

TABLE VII

RAMAN SPECTRUM OF CYCLOÖCTATETRAENE IN LIQUID STATE: WEAK LINES

Frequency in cm.$^{-1}$	Relative intensity	Frequency in cm.$^{-1}$	Relative intensity	Frequency in cm.$^{-1}$	Relative intensity
380	1	1890	1	2576	1
488	1	1916	2	2598	1
497	1	1929	1	2610	1
513	2	1940	2	2627	1
728	1	1970	1	2681	1
1461	1	1999	1	2692	1
1528	1	2026	1	2708	1
1548	1	2190	1	2726	1
1570	1	2201	1	2746	1
1677	1	2302	1	2793	2
1769	1	2339	1	2832	2
1800	1	2472	1	2853	2
1820	1	2489	1	2872	2
1836	2	2524	1		
1857	1	2551	1		

TABLE VIII

RAMAN SPECTRUM OF CYCLOÖCTATETRAENE-d_8 IN LIQUID STATE: WEAK LINES

Frequency in cm.$^{-1}$	Relative intensity	Frequency in cm.$^{-1}$	Relative intensity
327	1	1355?	2
565	1	1542	2
745	1	1554	1
791	1	1597	1
		1675	1

assigned as fundamentals and as overtones (or otherwise) for the two compounds. The basis for the distribution of the various frequencies among these tables is discussed below.

Comments on Experimental Results

The spectra listed in Tables I–VIII have been divided for convenience of discussion into stronger and weaker bands and lines. The infrared spectra have been assigned qualitative intensities according to the convention: very strong, less than 5% transmission; strong, 5–20%; medium, 20–50%; weak, 50–90%; very weak, greater than 90% transmission.[27] Bands of medium and higher intensity in the liquid are included in Table I for cycloöctatetraene and in Table II for cycloöctatetraene-d_8, and the remaining bands in Tables III and IV. Two weak bands on the borderline between weak and medium have been included in Table I because these bands (overtones at 1725 and 2830 cm.$^{-1}$) show medium intensity in the vapor.

The division of the Raman lines has been made at the intensity level 2, those of higher intensity than this being included in Table V for the hydrogen compound and in Table VI for the deuterium derivative, and the remainder being placed in Tables VII and VIII, respectively. Two lines (758 and 1399) of borderline intensity are included in Table V and three (890, 930, and 1287) in Table VI. Because of the well-known fact that in the Raman effect combination tones of various kinds are of a different order of intensity from that of allowed fundamentals, the division of the observed Raman lines on an intensity basis may be regarded as a preliminary separation of fundamentals from overtones. Unfortunately, the same kind of division for the infrared bands is much less certain in this respect. However, those bands of medium intensity or higher in the vapor spectrum can usually be taken as fundamentals in the absence of definite evidence to the contrary.

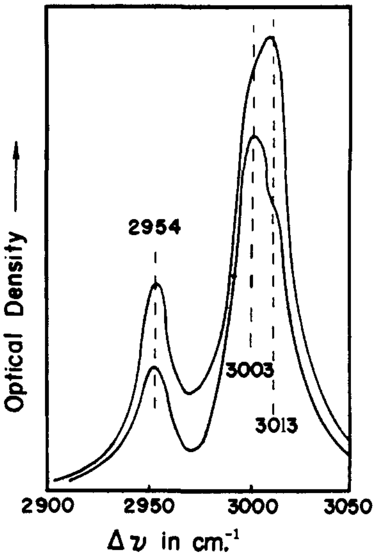

Fig. 3.—Smoothed microdensitometer tracings of perpendicular (lower curve) and parallel (upper curve) polarized components of the Raman lines in the C–H stretching region of cycloöctatetraene.

A remarkable feature of the cycloöctatetraene spectra is the considerable number of frequencies that coincide with those of styrene, which shows strong Raman lines at 999, 1204, 1601 and 1632 cm.$^{-1}$ and intense infrared absorption at 991, 1203 and 1633 cm.$^{-1}$. The reality of these frequencies in cycloöctatetraene cannot be doubted, however, because of the circumstance that their intensity does not alter upon purification of the material to such an extent that the very strong styrene infrared band at 908 cm.$^{-1}$ disappears completely. In the deuterium derivative, one must be prepared for a corresponding set of close coincidences with the frequencies of styrene-d_8. Our procedure in this case was to purify the cycloöctatetraene-d_8 samples by distillation and by fractional crystallization until the infrared spectra showed no further change. While the limited amount of the crude material was something of a handicap in obtaining sufficient very pure compound for spectroscopic study, we estimate from the infrared spectra that the cycloöctatetraene-d_8 with which most of the spectra were obtained was 99^{+} mole per cent. pure with respect to all impurities except cycloöctatetraene-d_7.

The deuterium oxide from which the deuterium derivative was made was stated by the supplier (U. S. Atomic Energy Commission, Stuart Oxygen Company, Agent) to be 99.87 atom per cent. deuterium. If no hydrogen was introduced during the synthesis, this percentage corresponds to 1 mole per cent. of cycloöctatetraene-d_7 in the final product. It is difficult to estimate from the spectra whether the figure is actually larger than this. No C–H stretching frequencies were observed in the Raman

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[27] These percentages apply to a thickness of 0.1 mm. in the liquid and 4 m. in the vapor at a pressure of 4 mm. (see Fig. 2).

effect, but the weak infrared bands at 2965 and 3025 are very possibly due to the d_7-compound. The great sensitivity of the infrared to small amounts of hydrogen in deuterium compounds makes the observed intensities of these bands compatible with two mole per cent. or less of cycloöctatetraene-d_7.

Another characteristic of the spectra is the marked intensity change that occurs on passing from the light to the heavy compound. This change was encountered in both the infrared and the Raman effect. It was apparent in the greatly lengthened exposure times required to get usable polarization spectra for the heavy compound, and in the much smaller number of overtones observed. The same exposure times which produced the large number of overtones listed in Table VII for the light compound yielded the very small number given in Table VIII for the deuterium derivative. In order to produce a comparable number of overtones, lengthened exposures could have been used. This procedure was not followed because the interpretation of extremely faint lines would be difficult and of doubtful value in view of the presence of small amounts of extraneous compounds such as the d_7-derivative. The smaller number of overtones in the heavy compound is entirely compatible with the smaller anharmonicity of deuterium vibrations and with the drop in frequency. The latter change not only reduces the intensity in both types of spectra but also moves the overtones from between 2000 and 3000 cm.$^{-1}$ to much lower values.

In Table IX are listed the observed coincidences. The precision of the infrared and Raman frequencies imposes the requirement that an infrared frequency measured in the liquid must fall within 4 cm.$^{-1}$ that of a Raman line below 1700 cm.$^{-1}$ and 7 cm.$^{-1}$ above 1700 cm.$^{-1}$ in order to be called a coincidence. In actuality the observed coincidences agree more closely than this. Only one of eleven major coincidences in cycloöctatetraene and three of eleven in the deuterium compound disagree by more than 2 cm.$^{-1}$

TABLE IX

SUMMARY OF COINCIDENCE FREQUENCIES

C_8H_8				C_8D_8			
Infrared cm.$^{-1}$	I	Raman cm.$^{-1}$	I	Infrared cm.$^{-1}$	I	Raman cm.$^{-1}$	
A Major coincidences							
290	m	292	9	265	m	265	9
366	m	366	10	313	m	312	10
966	m	967	7	592	w	591	3
993	w	994	6	822	m	822	10
1202	s	1202	9	879	s	881	8
1221	s	1221	4	926	m	930	2
1399	m	1399	2	1286	m	1287	2
1439	w	1439	9	1582	w	1579	6
1635	s	1631	8	1614	s	1615	6
2955	m	2954	9	2220	s	2225	9
3004	s	3003	10	2252	vs	2254	8
B Coincidences between lines weak in liquid or absent in vapor							
873[a]	s	873	10	747[a]	w	745	1
1573	w	1570	1	759[a]	w	761	8
1842	w	1836	2	813[a]	w	812	4
1865[a]	vw	1857	1	838[a]	w	838	3
1922	w	1916	2	889[a]	w	890	2
2308	vw	2302	1	1658[a]	w	1653	10
2745	w	2746	1	1680[a]	vw	1675	1
2784	w	2793	2				
2830	w	2832	2				

[a] Not observed in vapor spectrum.

Because the changes in frequency observed in passing from liquid to vapor spectra in the infrared are often larger than our coincidence criterion, coincidences must be determined from the liquid spectra. This raises the difficulty that an excessive number of coincidences may be found because bands often appear in the infrared spectra of liquids in contravention of selection rules. The difficulty is avoided by removing from the list of coincidences those infrared bands that are absent from the vapor spectrum. On this basis the observed coincidences have been divided in Table IX into "major coincidences" and secondary coincidences that either disappear in the vapor or correspond to obvious overtones.

A number of coincidences in cycloöctatetraene-d_8 that disappear in the vapor occur in the range 740–900 cm.$^{-1}$, which is the range of the C–D bending frequencies. One or two of these may be genuine despite our failure to observe the band in the vapor, because of the notably weak vapor spectrum of the deuterium compound. The remainder, however, are surely spurious. The lack of similar coincidences in the light compound appears to be due to the concentration of the C–H bending frequencies in the narrow range 1200–1225 cm.$^{-1}$. As a result, genuine and spurious coincidences overlap and cannot be disentangled by study of the vapor spectrum.

The principal features of the vibrational spectra on which structural conclusions will be based are summarized in Table X. This table is so drawn as to enable a general comparison between the observed spectra on the one hand and the spectra predicted on the basis of various structures on the other. Because a rigorous interpretation of the spectroscopic data necessitates a much more detailed consideration, the purpose of Table X is simply to enable the elimination of structures whose vibrational selection rules conflict with the main outlines of the observed spectra and which can therefore scarcely be expected to explain the spectra in detail.

TABLE X

SUMMARY OF SPECTROSCOPIC DATA

Number of:	Cyclo-octa-tetraene	Cyclo-octa-tetraene-d_8
Principal Raman lines	24	23
Polarized Raman lines	6	6
Principal infrared bands	17	14
Major coincidences	11	11
Principal lines in Raman effect only	13	12
Principal bands in infrared only	7	5

It must be pointed out that the figures in Table X are arbitrary to some extent. The number of principal Raman lines and infrared bands would change somewhat if the minimum intensity level for such bands were raised or lowered. The number of major coincidences would decrease slightly if these were limited to coincidences between principal Raman lines and infrared bands. Actually Table IX lists one major coincidence for cycloöctatetraene (1439 cm.$^{-1}$) and two for cycloöctatetraene-d_8 (592 and 1582) between weak infrared bands and principal Raman lines. In all these cases, however, the weak infrared band is readily found in the vapor, and the intensity of the Raman line is larger than is expected for an overtone. The number of polarized lines represents a lower limit, inasmuch as any of those lines too weak to measure might be polarized. The fact that the sum of the number of principal bands in the infrared only and the number of major coincidences does not equal the total number of principal infrared bands is due to the above-mentioned inclusion of one or two weak bands among the major coincidences.

Within the latitude allowed by these considerations, however, the selection rules for any structure must predict the numbers given in Table X. For example, a highly-symmetrical structure which predicts only two polarized lines is irreconcilable with the six observed. A structure that has a center of symmetry would permit no coincidences, which again is incompatible with the eleven observed. In this way one can eliminate many structures without attempting to make a detailed interpretation of the observed spectra. In the following section our first step will be a consideration of various plausible structures for cycloöctatetraene, and the consequent elimination of most of them with the help of Table X.

Interpretation of the Spectra and Structural Conclusions Therefrom

Since the cycloöctatetraene molecule had been suggested to have various structures, among them a cubic cage, a fused benzene and cyclobutene ring system and a cyclohexadiene ring with two fused cyclopropane rings, one of the first objectives of the spectroscopic investigation was to decide whether the structure is 1,3,5,7-cycloöctatetraene or not.

Either the Raman spectrum or the infrared alone is essentially adequate for this purpose. The absence from either spectrum of certain benzene frequencies fairly well rules out those structures involving a fused benzene ring. The lack of frequencies characteristic of $-CH_2-$ groups eliminates certain others and the presence of a typical olefinic double-bond frequency is incompatible with a polycyclic saturated hydrocarbon structure. Negative evidence of this sort coupled with the relative simplicity of both spectra for so large a molecule favors a true cycloöctatetraene structure of comparatively high symmetry. In addition, the simplicity of the spectra rules out the existence of structural isomers in equilibrium unless one isomer is present in very small amount or both have exceedingly high symmetry. The latter possibility is in conflict with the experimentally indicated absence of a symmetry center, since the highly symmetrical forms O_h (cubic cage), D_{8h} and D_{4h} all have symmetry centers, and the form D_{4d}, although it does not possess a center, acts spectroscopically as though it does.

In the following interpretation of the spectra, no initial assumptions about the structure of the molecule are made beyond the empirical formula C_8H_8 and the usual restrictions of quadrivalent carbon and univalent hydrogen. In Table XI are summarized the selection rules for the infrared and Raman spectra of the molecular configurations compatible with these assumptions.[28] For most of these structures the geometrical form of the molecule is fairly well determined by the symmetry properties of the point group and by valence requirements. For some of the groups of lower symmetry, however, several structures of the same symmetry are possible. In these cases the selection rules will sometimes give slightly different numbers in certain of the columns of Table XI for the different structures. These differences are never large and are not of importance for the following discussion.

A comparison of Tables X and XI shows immediately that the observed spectra are incompatible with a structure of very high symmetry. The large number of observed polarized lines, the total number of observed frequencies, and especially the number of coincidences between infrared and Raman frequencies rule out any structure belonging to the eight groups of highest symmetry in Table XI. It is conceivable, of course, that we may be dealing with a superposition of the spectra of two isomers of very high symmetry. Detailed examination of the various combinations of selection rules for the above eight groups shows, however, that these combinations do not fit the observed spectra much better than any one of the groups alone. Moreover, the frequencies of corresponding modes of vibration in two isomers tend to occur at about the same place in the spectrum, and as a result lines from these vibrations show a doublet character in the spectrum of a mixture of two isomers. The observed spectra of cycloöctatetraene and cycloöctatetraene-d_8 do not exhibit this feature, especially in the polarized lines, and therefore it is highly implausible to interpret the spectra in terms of two structures.

TABLE XI

SUMMARY OF THE SPECTROSCOPIC ACTIVITY OF THE VIBRATIONAL FREQUENCIES IN DIFFERENT STRUCTURES OF CYCLOÖCTATETRAENE

Point group	Total distinct frequencies	Raman activity		Infrared activity total	Coincidences		Silent frequencies
		Total	Polarized		Total	Polarized	
O_h	18	8	2	3	0	0	7
T_d	18	15	4	7	7	0	3
D_{8h}	26	7	2	4	0	0	15
C_{8h}	26	8	3	4	0	0	14
C_{8v}	26	13	3	7	7	3	13
C_8	26	14	4	8	8	4	12
S_8	26	16	5	10	0	0	0
D_{4d}	26	15	4	8	0	0	3
D_{4h}	32	15	4	8	0	0	9
D_4	32	28	6	14	10	0	0
C_{4h}	32	18	7	10	0	0	4
C_{4v}	32	27	5	15	15	5	5
C_4	32	32	12	20	20	10	0
S_4	32	32	11	21	21	11	0
$D_{2d} \equiv V_d$	32	27	6	15	15	0	5
D_{3h}	28	20	6	12	7	0	3
D_3	28	22	8	20	14	0	0
C_{3h}	28	21	7	14	7	0	0
C_{3v}	28	25	11	25	25	11	3
C_3	28	28	14	28	28	14	0
$D_{2h} \equiv V_h$	42	21	6	15	0	0	6
$D_2 \equiv V$	42	42	12	30	30	0	0
C_{2v}	42	42	11	31	31	11	0
C_{2h}	42	21	11	21	0	0	0
C_2	42	42	22	42	42	22	0
C_i	42	21	21	21	0	0	0
C_s	42	42	21	42	42	21	0

On the other hand, structures of low symmetry are in even greater conflict with the observed spectra. Too many active frequencies and too many coincidences are permitted for all structures lacking a threefold or fourfold axis except for those with a center of symmetry. These latter, however, exclude coincidences altogether, which is in contradiction with observation. It is thus possible to eliminate the last

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[28] The details of the methods for working out these rules may be found in the monographs on the subject of infrared and Raman spectra, *e.g.* Herzberg, "Infrared and Raman Spectra," Van Nostrand and Co., New York, N. Y., 1945.

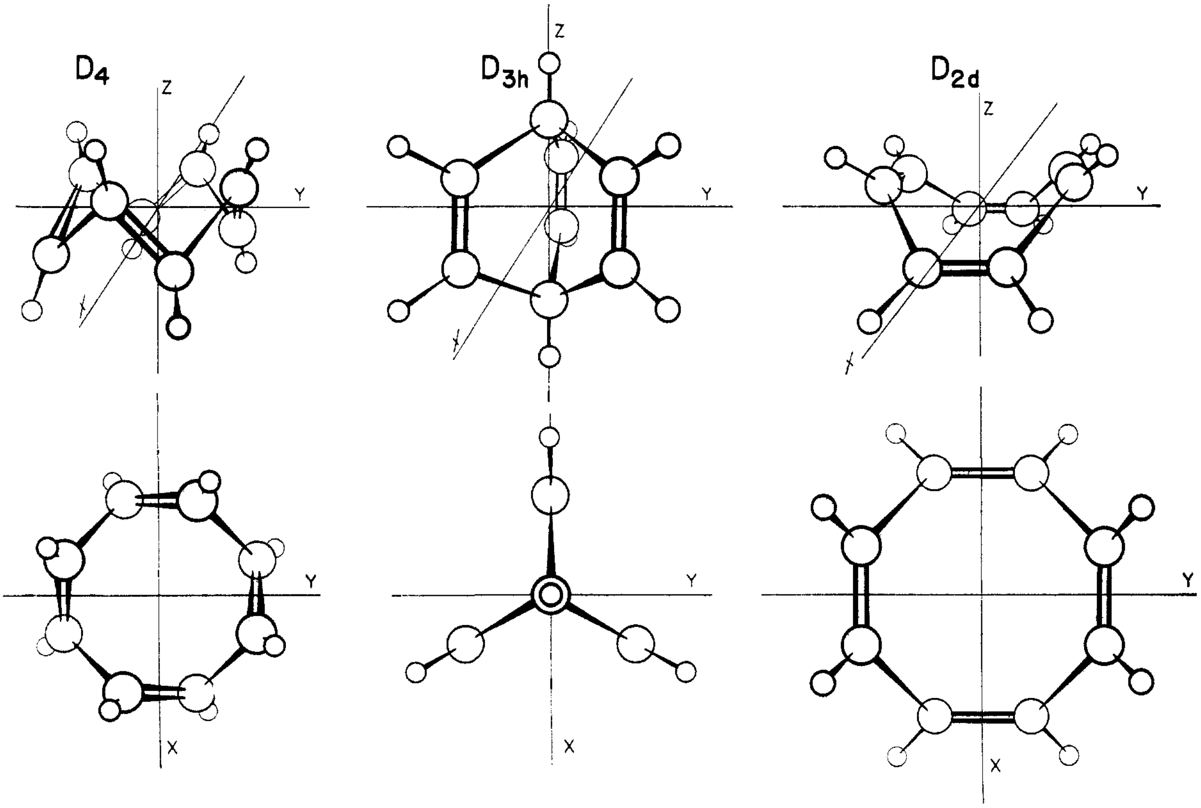

Fig. 4.—Cycloöctatetraene structures that fit the observed spectra most closely.

seven structures in Table XI, that is, all structures belonging to point groups with no axes of threefold or higher.

Of the remaining structures, those belonging to point groups D_{4h} and C_{4h} are ruled out by the observed coincidences, while those of point groups C_{4v}, C_4, S_4, C_{3v} and C_3 are eliminated by the absence of coincidences between polarized Raman lines and infrared bands. Structures of symmetry C_{3h} and D_3 cannot be rejected on qualitative grounds, but the number of polarized Raman lines, infrared-active fundamentals and coincidences called for by these structures disagrees sufficiently with the experimental summary of Table X that we feel justified in eliminating them also. In addition both C_{3h} and D_3 structures are derived from the D_{3h} structure, which is eliminated by detailed arguments given below. These arguments can also be applied to C_{3h} and D_3, and accordingly we will give no further consideration to these two structures.

We are therefore left with the structures D_4, D_{2d} and D_{3h}, which are shown in Fig. 4. It will be seen on comparison of Tables X and XI that each of these fits the observed spectra fairly well, having about the right number of total lines, polarized lines and coincidences. A decision among them must therefore be made by examination of the details of the spectra.

Although the D_{3h} structure has not been proposed to our knowledge, its plausibility from a valence-bond standpoint makes it a worthwhile structure to consider.[29] We believe it can be ruled out on spectroscopic grounds for the following reasons, among others. The two C–H bonds along the threefold axis should be aliphatic rather than olefinic in character and should therefore exhibit frequencies in the neighborhood of 2900 cm.$^{-1}$. No fundamental frequencies of this value occur in the spectrum. If one ascribes the frequency at 2454 cm.$^{-1}$ to such bonds, one encounters the difficulty that the line should be polarized, which is not the case. The six polarized frequencies, in fact, should all occur above 800 cm.$^{-1}$ (one C–C stretching frequency at about 800–1000 cm.$^{-1}$, one "cage breathing" frequency in the same region, one C–H bending frequency at about 1200–1400 cm.$^{-1}$, one C=C stretching frequency at about 1650 cm.$^{-1}$, two C–H stretching frequencies at 2900 and 3000 cm.$^{-1}$), and certainly none should be as low as the observed polarized line at 194 cm.$^{-1}$. This line of reasoning, along with other arguments such as the small number of expected coincidences (seven *vs.* eleven observed), is sufficient to enable the rejection of the D_{3h} model.

We are therefore left with the D_4 and D_{2d} structures. The selection rules for these two structures are remarkably similar, and both fit the observed spectra about equally well with one important exception. The D_{2d} structure requires that all infrared-active frequencies also occur in the Raman effect, whereas four infrared bands are excluded from the Raman effect in the D_4 structure. The strongest bands in the infrared spectra of both cycloöctatetraene and cycloöctatetraene-d_8 have no counterparts in the Raman spectrum, and on this basis we reject the D_{2d} model in favor of the D_4, and proceed to interpret the spectra in terms of the latter. Because X-ray[30a] and electron-diffraction[30b] evidence has been put forward on behalf of the D_{2d} structure however, we shall also consider the observed spectra in terms of the D_{2d} structure, and shall see that, apart from the above-mentioned feature of the absence of strong infrared frequencies from the Raman effect, the D_{2d} structure serves nearly as well as the D_4 for interpretation of the spectra.

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(29) The D_{3h} structure is unlikely in view of the method of synthesis of cycloöctatetraene[4] and of the reactions of the compound. It is not cycloöctatetraene, of course, but rather bicyclo[2.2.2.]octa-2,5,7-triene. In view of the various valence-bond angles allowed by such a structure, it might well be stable, and its synthesis represents an interesting problem in organic chemistry.

(30) (a) Kaufman, Fankuchen and Mark, *Nature*, **161**, 165 (1947); *J. Chem. Phys.*, **15**, 414 (1947); (b) Hedberg and Schomaker, Abstracts, San Francisco Meeting, American Chemical Society, March, 1949. It is to be noted that the electron-diffraction data have also been interpreted as consistent with the D_4 structure (see ref. 41).

Assignment of Frequencies on the Basis of the D_4 Structure

The distribution of the various frequencies of cycloöctatetraene among the different vibrational species of the point group D_4 is given in Table XII. The species are defined in terms of the behavior of the normal vibrations with respect to the symmetry elements of the D_4 group, namely the fourfold axis C_4 (taken as the z-axis) and two pairs of twofold axes. One of these pairs ($C_2^{x,y}$), passing through the centers of the double bonds (Fig. 4) consists of the x- and y-axes, and the other pair (C_2^{dia}), passing through the centers of the single bonds, lies in the xy-plane at an angle of 45° to the x- and y-axes. The symbols in the columns headed "Symmetry of Species" show the behavior of vibrations of the different species of vibrations with respect to the three axes C_4^z, $C_2^{x,y}$ and C_2^{dia}. A plus-sign means that the vibrational displacements are unchanged by rotation about the axis through the appropriate angle (90° for C_4^z, 180° for the others), a minus-sign that rotation changes the sign but not the magnitude of the displacements, the symbol $e^{\pm}$ that the displacements of the degenerate (E species) vibrations are changed in a more complex fashion[31] and the double symbol $\pm$ that the two independent sets of displacements for a doubly-degenerate vibration can be so chosen that one set does not change and the other changes into its negative when the indicated rotation is carried out.

Table XII

Distribution of Vibrations Among Species and the Selection Rules for D_4 Structure of Cycloöctatetraene

Vibrl. species	Symmetry of species C_4^z	$C_2^{x,y}$	C_2^{dia}	No. of vibrations C	H	Total	Selection rules Raman	Infra-red
A_1	+	+	+	3	3	6	Polar.	f
A_2	+	−	−	1	3	4	f	$M_{\parallel}$
B_1	−	+	−	3	3	6	Depol.	f
B_2	−	−	+	3	3	6	Depol.	f
E	$e^{\pm}$	$\pm$	$\pm$	4	6	10	Depol.	$M_{\perp}$

The vibrations of the molecule can be fairly well divided into "carbon-atom"—or ring—vibrations and "hydrogen-atom" vibrations. The number of each kind is indicated in the columns marked "C" and "H," respectively, in Table XII. The spectroscopic activity of these is shown in the column "selection rules." Here we see that there are six totally-symmetrical vibrations (species A_1), three hydrogen and three ring, that these appear polarized in the Raman effect and that they are forbidden (f) in the infrared. The species A_2 has four vibrations, all forbidden in the Raman effect, but allowed in the infrared, the vibrating electric moment, $M_{\parallel}$, being parallel to the z-axis. There are six vibrations each in species B_1 and B_2, all of which appear depolarized in the Raman effect and absent from the infrared. The doubly-degenerate species E contains ten frequencies, to each of which correspond two vibrations, so that this species accounts for twenty of the forty-two vibrational degrees of freedom. Each of these ten frequencies shows up in both the Raman effect and the infrared, the Raman lines appearing depolarized and the electric moment, $M_{\perp}$, being perpendicular to the z-axis. It can be readily verified that these figures add up to those listed for the point group D_4 in Table XI.

Totally-symmetrical Species.—The assignment of the observed frequencies to the different species is best commenced with the six A_1 vibrations. Since all these vibrations should give rise to polarized Raman lines, most of them are easy to find. The three ring vibrations correspond roughly to a ring puckering, a C–C single-bond stretching and a C–C double-bond stretching, and we assign to them the polarized lines in cycloöctatetraene at 194, 873 and 1651 cm.$^{-1}$, respectively. Two of these frequencies shift as expected in cycloöctatetraene-d_8 to 172 and 822 cm.$^{-1}$., but there is an unexpected increase in the double-bond frequency in the heavy compound to 1653. Such an increase can only result from anharmonicity[32] and we therefore look for the origin of this. It is found in the Fermi resonance[33] between the fundamental double-bond frequency and the first overtone of the totally symmetrical ring frequency at 822 cm.$^{-1}$. The coincidence of these two frequencies before Fermi interaction must be very nearly exact because of the closely similar intensities of the two lines (1636 and 1653) after interaction. The unperturbed double-bond frequency should therefore have a value of about 1644 cm.$^{-1}$. The shift from 1651 in the light compound to 1644 is surprisingly small, but is of course in the proper direction. It may be mentioned that the first overtone of the corresponding ring frequency at 873 in the light compound also interacts with the double-bond frequency, but because of the large frequency separation in this case, the interaction is small. The overtone occurs, with relatively high intensity for an overtone, at 1743 cm.$^{-1}$ and is definitely polarized.

The location of the three A_1 hydrogen frequencies is less straightforward. To facilitate the frequency assignment, the motion of the hydrogen atoms can be considered in terms of a hypothetical plane drawn through the C–H bond line parallel to the z-axis. In one type of hydrogen motion (called "parallel C–H bending" hereafter), the atom moves within this plane and in a direction normal to the C–H bond line. In the second type (to be called "perpendicular C–H bending"), the motion takes place perpendicular both to the bond line and to the plane. In the third (C–H stretching), the hydrogen atom vibrates within the plane and along the bond line. In species A_1 there is one vibration of each type. It is easy to assign the C–H and C–D stretching frequencies, for the Raman lines at 3013 and 2250 cm.$^{-1}$, respectively, are polarized, and in fact are separable on polarization plates from nearby depolarized lines on this account (see Fig. 3). The bending frequencies, however, can only be located with the help of the spectrum of the heavy compound. In this compound a polarized line appears at 812 cm.$^{-1}$ which is presumed to arise from a parallel C–D bending vibration. If this assignment is correct, the corresponding vibration in the light compound should have a frequency in the range 1000–1150 cm.$^{-1}$. The only line near this range occurs at 994 cm.$^{-1}$, and, because of its proximity to the yellow mercury line at 5770 Å., is difficult to measure for polarization characteristics when excited by Hg-5461. We have found it polarized, although quantitative measurement of the depolarization factor was unreliable. This line has also been verified by excitation with the yellow lines Hg-5770 and -5790.

The remaining C–H frequency by analogy with other olefinic and aromatic hydrocarbons should occur in the range 1000–1500 cm.$^{-1}$. While there should be six such frequencies of various species in this range, only four are observed and of these, two must be regarded with suspicion because of the small shift they display on passing from cyclooctatetraene to cycloöctatetraene-d_8. We are forced by the barrenness of the region to the conclusion that some of the C–H perpendicular bending vibrations have very nearly the same frequency, just as do the C–H stretching vibrations, and accordingly "pile up" in the spectrum in a similar way. This may result from the possibility that the potential energy function for hydrogen vibrations approximates a D_{4d} symmetry. The D_{4d} symmetry differs from the D_4 in the presence of planes of symmetry through the fourfold axis and the carbon and hydrogen atoms, these planes being eliminated in D_4 by the difference between the alternate C–C bonds. However, the alternate C–C bond distances are not greatly different (0.1 Å. or less according to electron diffraction evidence[30]) and therefore the symmetry of the potential function for the various C–H vibrations may approximate D_{4d}.

In the D_{4d} structure for cycloöctatetraene, there are no Raman-active perpendicular C–H bending frequencies except in the degenerate species. The totally-symmetrical D_4 frequency of this type, however, is derived from a non-degenerate D_{4d} frequency and should therefore be expected to be weak in the Raman effect compared to the other totally-symmetrical lines and to have a high depolarization factor. This expectation, coupled with the observation that in both the infrared and Raman spectra the region 1000–1500 cm.$^{-1}$ contains remarkably few bands, gives us a basis for interpreting the depolarized Raman line at 1202 cm.$^{-1}$ as a superposition of a weak, slightly polarized line from a totally-symmetrical C–H perpendicular vibration and a strong depolarized line from a non-totally symmetrical vibration.

Fortunately this situation is altered in the heavy compound, probably because the frequencies of the C–D bending vibrations coincide with ring frequencies of appropriate

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[31] Compare, for example, Herzberg, ref. 28, pp. 98–99.

[32] Halverson, *Rev. Mod. Phys.*, **19**, 87 (1947).

[33] Compare Herzberg, ref. 28, p. 215.

symmetry species. The resulting interactions vary from species to species and hence the C–D bending frequencies differ from one another. The region 800–900 cm.$^{-1}$ is rich in infrared bands and Raman lines, at least two of the latter being polarized. These two, at 812 and 822 cm.$^{-1}$, correspond to the 994 and 873 cm.$^{-1}$ lines in the light compound. There are three other Raman lines, at 838, 872 and 890 cm.$^{-1}$, which do not appear in the infrared vapor spectrum and which therefore belong to one of the three infrared-silent species. It is not a matter of critical importance which of the three is assigned to class A_1. The 872 line is selected because it fits the product rule best (see below), but it is depolarized, as are the other two. Possibly the high depolarization factor arises from the quasi-D_{4d} symmetry for the hydrogen potential function, as postulated above for the corresponding Raman line in the light compound.

The foregoing assignments are listed in Table XIV.

Degenerate Species

The infrared- and Raman-active doubly-degenerate species E is conveniently considered next. Bands and lines of this species should be easily located because only this species is active in both spectra. Ten such frequencies are expected and in Table IX eleven major coincidences are listed both for cycloöctatetraene and for cycloöctatetraene-d_8. For the former the coincidences at 994 and 1439 are rejected. The 993 band in the infrared coincides with a polarized Raman line, which renders the coincidence in the liquid suspect, and the weak vapor band can be well explained as an overtone (194 (A_1) + 800 (A_2) = 994 (A_2)). The line at 1439 is extremely weak in the vapor and shows a large liquid-to-vapor shift of 12 cm.$^{-1}$, as though the liquid coincidence were a real one resulting from violation of the infrared selection rules, and the vapor phase infrared band were a weak overtone which accidentally comes within 12 cm.$^{-1}$ of the Raman line.

In cycloöctatetraene-d_8, the coincidences at 592 and 1582 are rejected as spurious, the former because of the vanishingly small intensity of the vapor band at that point. The 1582 coincidence is ruled out because only one fundamental of the E species is to be expected in the neighborhood of 1600 cm.$^{-1}$, and this is observed as an intense band at 1619 cm.$^{-1}$ in the infrared vapor spectrum and at 1615 cm.$^{-1}$ in the Raman effect. The 1582 coincidence is explained as the accidental coincidence of an infrared overtone [761 (E) + 822 (A_1 or E) = 1583 (E) is one of several possibilities] with a Raman fundamental. The Raman line is too intense for an overtone unless Fermi resonance is involved. Fermi resonance with the fundamental at 1615 cm.$^{-1}$ is of course possible, but the large separation of 30 cm.$^{-1}$ or more between this line and the *unperturbed* overtone makes it doubtful that the intensity of the Raman line at 1579 cm.$^{-1}$ can be accounted for on such grounds.

We are therefore left with nine coincidences believed to be genuine, whereas the selection rules demand ten (Table XII). In cycloöctatetraene the tenth coincidence is thought to lie at 942 cm.$^{-1}$. There is a strong infrared band at this point, and a strong Raman line at 948 cm.$^{-1}$. The discrepancy of 6 cm.$^{-1}$ is beyond experimental error, and repeated measurements in both spectra have confirmed this. However, the Raman line seems slightly asymmetrical in shape, with evidence of a shoulder on the low frequency side. It is therefore our assumption that the Raman line is an unresolved doublet, one component of which coincides with the infrared band.

In the heavy compound there are several coincidences in the range 700–900 cm.$^{-1}$ between infrared bands of the liquid and Raman lines. As is indicated in Table IX, however, none of these persists in the infrared of the vapor. The product rule for class E points to either the 745 or 761 Raman line as the appropriate one, and the latter is selected on intensity grounds. No explanation is offered for the failure to observe this band in the infrared vapor spectrum.

It should be remarked that the coincidence with the polarized line at 822 cm.$^{-1}$ is certainly accidental. A real coincidence here is not only incompatible with the D_4 structure but is also inconsistent with the remainder of the spectrum, since coincidences are not observed for numerous other polarized lines in the spectra of both the light and heavy compounds. We presume that a Raman line of species E is superimposed on the 822 totally-symmetrical line of higher intensity, because the infrared band must be either A_2 or E, the former being ruled out by later discussion.

The assignments to the E species are summarized in Table XIV.

Infrared-active Species A_2

The existence of several strong infrared bands in the spectra of both cycloöctatetraene and cycloöctatetraene-d_8 that have no Raman counterparts is the strongest spectroscopic evidence for the D_4 structure. As we have pointed out earlier,[21] careful search of the Raman spectrum for lines coinciding with these strong bands has produced only negative results. The search has been aided by the fact that the Raman spectrum is quite open in the light compound for the bands at 630, 667 and 800 cm.$^{-1}$ and in the deuterium compound at 527 and 720 cm.$^{-1}$. Moreover, the presence of impurities is not a consideration, since small amounts of impurities would merely add weak lines and could not cause genuine lines to disappear.

The previously-mentioned congestion of perpendicular C–H bending frequencies affects the A_2 species, since it contains one such vibration. In the deuterium compound, however, there is a clear-cut strong C–D bending band at 899 cm.$^{-1}$ that has no Raman counterpart within a factor of two of the experimental error allowed for coincidences. It is therefore straightforward to select four strong bands from the spectrum of cycloöctatetraene-d_8 at 527, 720, 899 and 2236 cm.$^{-1}$. The four corresponding frequencies in the light compound occur at 648, 800, 1221 and 3004 cm.$^{-1}$. The third of these is located with the help of the product rule, while the first is determined from the doublet 630–669 in the following way.

In cycloöctatetraene there are two very intense bands at 630 and 669 cm.$^{-1}$, while in the heavy compound only one intense band is found below 700 cm.$^{-1}$. This could be explained as a drastic intensity change on the part of one band, as a superposition of two intense bands (of different vibrational species) in the heavy compound or as a doubling in the light compound because of Fermi resonance. The first explanation is unlikely in view of the intensity changes usually produced by deuterium[32,34] and the second is inconsistent with the failure to observe a Raman line coincident with the single intense band in cycloöctatetraene-d_8. We therefore ascribe the doublet in the light compound to Fermi resonance between an A_2 fundamental at about 648 cm.$^{-1}$ and the overtone 292 (E) + 366 (E). The 10 cm.$^{-1}$ deviation of the sum of these two frequencies from 648 is ascribed to anharmonicity.

The two bands at 630 and 669 definitely have different rotational structures in the vapor phase. We believe the explanation of this is given by the possibility of another A_2 overtone at 629 (380 (B_1) + 249 (B_2)) and that the overlap of the two overtone bands washes out their rotational structures. In the heavy compound the single intense band has a clear-cut rotational structure analogous to that of the 669 band. The overtones responsible for the Fermi resonance have shifted to 565 (B_1 + B_2) and 577 cm.$^{-1}$ (E + E), respectively, in cycloöctatetraene-d_8. These are 38 and 50 cm.$^{-1}$ removed from the fundamental at 527 cm.$^{-1}$, and hence little Fermi resonance is to be expected. At 551 cm.$^{-1}$ on the shoulder of the intense 527 band, there is a band that can be assigned to the B_1 + B_2 combination on the assumption that the 14 cm.$^{-1}$ discrepancy arises from anharmonicity and from inaccuracy in the 551 value. This latter is certainly lower than the actual position of the band because of the influence of the 527 band, but the extent of the shift is hard to estimate. It is not likely that the error is larger than 5 cm.$^{-1}$. From 551 to 592 no additional bands are resolvable.

The Raman-active Species B_1 and B_2.—The remaining unassigned Raman lines should be either fundamentals of these two species or overtones. The B_1 and B_2 species are closely analogous, the former being symmetric to the twofold axes through the midpoints of the C–C double bonds and the latter to the twofold axes through the midpoints of the C–C single bonds. This definition of the species is arbitrary, of course, and could just as well be reversed.

The principal Raman lines not hitherto assigned are listed in Table XIII. There are eight for cycloöctatetraene and seven for the deuterium derivative, to which must be added with certainty two C–H stretching frequencies, one each

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(34) Lord and Teller, *J. Chem. Soc.*, 1728 (1937).

for species B_1 and B_2, and with high probability an additional low ring-puckering frequency. The C-H stretching frequencies both occur in the neighborhood of 3013 cm.$^{-1}$ (2250 cm.$^{-1}$ in the deuterium compound) and from Tables VII and VIII we select 380 and 327 as the respective values of the puckering frequency. After these additions there remain to be located one frequency for the light compound and two for the heavy. In the table of weak Raman lines for cycloöctatetraene (Table VII) there is only one additional line—that at 728 cm.$^{-1}$—which is reasonably eligible for the B_1 and B_2 classes. The others are all too high or, with the exception of the above-mentioned 380 line, too low. In Table VIII for the deuterium compound, the lines at 565, 745 and 791 cm.$^{-1}$ are candidates for the two missing frequencies.

TABLE XIII

PRINCIPAL RAMAN LINES NOT ASSIGNED TO SPECIES A_1 OR E

Cycloöctatetraene	Cycloöctatetraene-d_8
249	238
655	576
758	591
908	838
(948)	890
976	1297
1439	1579
1601	

We can now assign six frequencies to the B_1 and six to the B_2 species as follows. Each species must have one C-H stretching and two C-H bending frequencies which can be recognized by their large shifts in the deuterium derivative. The ring puckering frequencies are the very lowest and are readily assigned. The double-bond frequency must correspond to a mode of vibration that is symmetrical to the two-fold axis through the double-bond midpoint, and therefore can be assigned to species B_1. With the help of these considerations and the product rule, the assignment given in Table XIV is made. The assignment shown rejects the 890 frequency in favor of 791 in C_8D_8 in order to obtain best agreement with the product rule. The 890 frequency is not significantly more intense than 791 and can readily be explained as an overtone (*e.g.*, 576 (B_2) + 312 (E) = 888 (E), which can interact with 881 (E)). The B_1-B_2 assignment is not unique, since an interchange of the pair of frequencies 728–565 with 758–591 would not impair the product-rule agreement.

TABLE XIV

ASSIGNMENT OF FREQUENCIES FOR D_4 STRUCTURE

Species	Freq. no.	Type of vibration	C_8H_8	C_8D_8	τ_0	τ_c
A_1	1	C—H stretching	3013	2250	2.72	2.828
	2	C═C stretching	1651	1645^a		
	3	C—H bending (⊥)	1202	872		
	4	C—H bending (‖)	994	812		
	5	C—C stretching	873	822		
	6	Ring puckering	194	172		
A_2	7	C—H stretching	3004	2236	2.49	2.533
	8	C—H bending (⊥)	1221	899		
	9	Ring distortion	800	720		
	10	C—H bending (‖)	648^a	527		
B_1	11	C—H stretching	3013	2250	2.77	2.828
	12	C═C stretching	1601	1579		
	13	C—H bending (⊥)	948	791		
	14	C—H bending (‖)	728	565		
	15	Ring distortion	655	576		
	16	Ring puckering	380	327		
B_2	17	C—H stretching	3013	2250	2.83	2.828
	18	Ring distortion	1439	1297		
	19	C—H bending (⊥)	976	745		
	20	C—C stretching	908	838		
	21	C—H bending (‖)	758	591		
	22	Ring puckering	249	238		
E	23	C—H stretching	3003	2254	6.56	7.11
	24	C—H stretching	2954	2225		
	25	C═C stretching	1635	1615		
	26	Ring distortion	1399	1287		
	27	C—H bending (⊥)	1221	930		
	28	C—H bending (⊥)	1202	881		
	29	C—H bending (‖)	967	761		
	30	C—C stretching	942	822		
	31	C—H bending (‖)	366	312		
	32	Ring puckering	292	265		

^{a} Denotes the estimated unperturbed position of a fundamental that is affected by Fermi resonance.

Table XIV summarizes the foregoing assignments. The description of the various vibrational modes given in Column 3 is of course very rough in many cases and is based on the assumption that the vibrations follow a valence-force potential system. It is further assumed that ring vibrations parallel to the fourfold axis ("ring puckering") are distinguishable from ring vibrations roughly perpendicular to the fourfold axis ("ring distortion") as well as from other ring vibrations associated primarily with compression of the single or double bonds. The columns τ_0 and τ_c give, respectively, the experimental and theoretical values for the ratios of the products of the frequencies in cycloöctatetraene to those in cycloöctatetraene-d_8 for each species.

The details of the method for obtaining τ_c will not be given here,[35] except to state that the moments of inertia used in finding τ_c for species A_2 and E were: in C_8H_8 $I_{xy} = 303$ and $I_z = 580$, and in C_8D_8 $I_{xy} = 356$ and $I_z = 672$, all $\times 10^{-40}$ gram-cm.^{2}. These values follow from the D_4 geometry and the interatomic distances[30b] C═C = 1.34 Å., C–C = 1.45 Å., C═C—C angle = 127°, C-H = 1.08 Å. and C-C-H angle = 116.5°. It should be noted that minor changes in these values will have virtually no effect on τ_c because the percentage changes in the moments of inertia for the light and heavy compounds will be nearly the same. The discrepancies between τ_0 and τ_c are those to be expected from anharmonicity.[36] The close agreement between the values of τ_0 and τ_c for species B_2 is unusual, and is perhaps to be ascribed to anharmonicities of different sign for the C-H stretching and C-H bending vibrations.

In view of the large number of vibrational degrees of freedom of the cycloöctatetraene molecule and the attendant complexity of the spectra, it is too much to expect that all the assignments in Table XIV are correct. It is more reasonable, however, to hope that the fundamental frequencies have been located, and that any error lies in the assignment of these to the several species. Fortunately the location of the type E frequencies, whose assignment is most important for the calculation of thermodynamic functions, is fairly straightforward, and therefore the assignments of Table XIV can be used with some confidence in such calculations. We have calculated the thermodynamic functions for the vapor state and have also made a semi-empirical calculation[37] of the

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(35) See Halverson, ref. 32, pp. 93–96 or Herzberg, ref. 28, pp. 231–238.

(36) Halverson, ref. 22, p. 94.

(37) Lord, *J. Chem. Phys.*, **9**, 693 (1941).

heat capacity of the crystal. The agreement of the latter over a wide temperature range with the measured values,[12b,c] as well as the agreement between the third-law and spectroscopic entropy values, indicates that the assignment of fundamentals, especially the degenerate ones, is not seriously in error. These calculations are to be reported in a succeeding paper.[38]

Interpretation of the Spectra on the Basis of a D_{2d} Structure

For the reasons mentioned earlier, it is important to examine in detail the interpretation of the observed spectra in terms of the D_{2d} structure. Table XV gives the distribution of fundamental frequencies among the various vibrational species of this structure, together with the selection rules. Comparison of Table XV with Table XII for the D_4 structure shows how remarkably similar are the two structures from a spectroscopic standpoint. This similarity, and the points at which it no longer holds, will appear in the following discussion.

Just as for the D_4 model, interpretation of the spectra on the D_{2d} basis is best begun with the totally-symmetrical species A_1. The number of vibrations of this species, their approximate expected frequencies in both the light and heavy compounds, and the product-rule ratio are identical both for the D_4 and D_{2d} models. The A_1 discussion for D_4 can thus be carried over more or less unchanged to the D_{2d} case, the difficulty with the location of the sixth polarized Raman line being equally acute for both.[39] The assignment should be the same, so that the A_1 frequencies listed in Table XIV are logical ones for a D_{2d} structure.

Table XV

Distribution of Vibrations Among Species and the Selection Rules for D_{2d} Structure of Cycloöctatetraene

Vibrl. species	Symmetry of species S_4^z	$C_2^{x,y}$	σ_v	No. of vibrations C	H	Total	Selection rules Raman	Infrared	Product rule r_c
A_1	+	+	+	3	3	6	Polar.	f	2.828
A_2	+	−	−	2	3	5	f	f	2.624
B_1	−	+	−	3	3	6	Depol.	f	2.828
B_2	−	−	+	2	3	5	Depol.	$M_{\parallel}$	2.724
E	$e^{\pm}$	±	±	4	6	10	Depol.	$M_{\perp}$	7.120

The next assignments to be considered are those to species B_2 and E, since these species include the infrared-active fundamentals, all of which are also Raman-active. There are five of species B_2 and ten of species E. There is some difficulty in deciding to which of the two species a given band belongs, because the only general difference expected between the two is a more clearly defined P-Q-R structure for the non-degenerate species B_2. It is certainly true that the very strong infrared bands at 669 and 800 cm.$^{-1}$ in cyclooctatetraene and 527, 720 and 823 cm.$^{-1}$ in the deuterium compound show a well-defined P-Q-R spacing entirely compatible with the moments of inertia of the D_{2d} structure. However, many other bands, such as those at 945, 967, 1204 and 1223 cm.$^{-1}$ in the light compound and at 879, 898 and 927 cm.$^{-1}$ in the heavy, give good evidence of structure but because of overlapping it is difficult to determine the P-Q-R peaks reliably.

On the other hand, there is no discernible structure in the two bands at 1608 and 1640 in cycloöctatetraene, one of which on the D_{2d} basis must belong to B_2 and the other to E. This lack is not due to experimental difficulty, for the resolution achieved at 1600 cm.$^{-1}$ with the fluorite prism is far better than is needed for this purpose. A decision might be made on the basis that the E vibration should be more intense, since in this case the electric moment vibrates perpendicularly to z-axis, as do the double bonds in this vibration. In the B_2 vibration, the electric moment vibrates parallel to the z-axis, while the vibration itself should have little amplitude in the z-direction, and therefore should produce only a small value of the electric moment. On this basis the strong band at 1640 is assigned to E and the weak band at 1608 to B_2. The 1640 band has its counterpart in the Raman effect (1631 *vs.* 1635 in infrared liquid spectrum) but the weak band shows an unusually large discrepancy (1601 in Raman effect *vs.* 1609 in infrared liquid spectrum) that we regard as definitely outside experimental error. Such a difficulty does not arise in the D_4 interpretation, inasmuch as the 1601 frequency should not appear in the infrared and the 1609 frequency can be interpreted as an overtone of species E (669 (A_2) + 942 (E)), which should be accompanied by a weaker companion at 1570 (628 (A_2) + 942 (E)). A weak overtone is indeed found at 1573 in the infrared and at 1570 in the Raman effect, which agrees with the E species assignment. Both these overtones persist in the infrared of the vapor. The Raman counterpart of the 1609 overtone would be concealed by the much stronger 1601 fundamental.

This difficulty with the D_{2d} structure is relieved in the heavy compound, for the infrared band which would be assigned to the B_2 vibration (1582) no longer disagrees unduly with the Raman line (1579). Conversely, with the D_4 structure it is necessary to call this coincidence accidental, and moreover to find a new explanation for the infrared band, because the fundamentals used in the light compound have shifted so much in the heavy that the overtone comes below 1400 cm.$^{-1}$. On the D_4 basis the band can be attributed to 822 (A or E) + 761 (E), or to other combinations which fit within the 10 cm.$^{-1}$ or so that might reasonably be allowed for anharmonicity.

The remainder of the infrared-active bands can be assigned in the following way: The non-degenerate B_2 species should have one non-planar and one planar C–H bending vibration,[40] to which the bands at 669 and 1221 in the light compound and at 527 and 899 in the heavy can be ascribed. In addition a ring-distortion vibration must be accounted for, and the band at 800 in cycloöctatetraene and at 720 in the deuterium derivative is a reasonable assignment. All these bands show a well-defined P-Q-R structure, as expected for B_2 vibrations, and fit the product rule reasonably well (see Table XVI). The complication that the 669 band is double in the light compound and single in the heavy can be explained as for the D_4 structure by Fermi resonance. The difficulty that the strong bands at 629, 669 and 800 in cycloöctatetraene and at 527, 720 and 899 in the deuterium derivative do not appear in the Raman effect will be considered later.

After making the B_2 assignment, we put the remainder of the principal infrared-active frequencies into species E. This procedure results in a set of E frequencies identical with those of the E species in the D_4 structure (Table XIV), and since the E-species product rules for the two structures are virtually identical, the product rule is satisfied equally well for both. The only special comment on this species concerns the double use of the two frequencies at 1202 and 1221 in the light compound. For the D_{2d} as well as the D_4 structure the number of C–H bending frequencies observed in the 1000–1400 cm.$^{-1}$ region is smaller than expected, and therefore two or more such vibrations of different species must have about the same frequency. It should also be remarked that our failure to find precise coincidence between the Raman line at 948 and the infrared band at 942 may be interpreted, as in the D_4 structure, to imply two superimposed Raman lines of different species, one E and the other B_1.

The last spectroscopically active species (B_1) contains those vibrations that are silent in the infrared and active but depolarized in the Raman effect. A list of these is given in Table XIII, with the additional comment, as made for the D_4 structure, that the species must contain a C–H stretching vibration. In view of their intensities and on grounds of where the frequencies of this species should lie, we select 249, 655, 1439 and 3013 for cycloöctatetraene and 238, 576, 1297 and 2250 for the deuterium compound. This leaves two frequencies to be found, one for a C–H planar bending vibration and the other for a C–C stretching vibration. The best compromise between the anticipated locations of these frequencies, the product rule and the numbers

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[38] Lippincott and Lord, This Journal, **73**, in press (1951).

[39] The explanation of a high depolarization factor for the sixth A_1 line in the D_4 structure no longer holds for a D_{2d} structure, but this is hardly a strong argument against the latter.

[40] In the D_{2d} structure, any two carbon atoms joined by a double bond and the four atoms connected to them presumably lie in a plane. C–H bending vibrations that take place approximately within this plane are called planar, and those that do not are called non-planar.

furnished by Tables VIII and XIII is obtained if one sets the first of these vibrations at frequencies of 976 and 745 in the light and heavy compounds, and the second at 948 and 838 cm.$^{-1}$. While the agreement with the product rule is probably within the limits that anharmonicity might impose, it is not very good. In addition, there are left over several Raman lines that must now be explained as overtones, some of which are rather strong for such an explanation. These are 758 and 908 in the light compound and 591 and 890 in the heavy.

The remaining D_{2d} species (A_2) contains five spectroscopically silent vibrations. In Table XVI the approximate nature of these vibrations and rough estimates of their frequencies in the two compounds are given.

Comparison of the Spectroscopic Evidence for the D_4 (Crown) and D_{2d} (Tub) Structures

As is readily apparent from the foregoing discussion and from a comparison of Tables XIV and XVI, the close similarity of the selection rules for the two structures leads to closely parallel interpretations of the spectra. Among other results, this similarity makes it virtually impossible to decide between the two structures on the basis of heat capacities or other thermodynamic data, as is discussed in detail in our paper[38] on the thermodynamic properties of cycloöctatetraene. Therefore, if a decision is to be made from the vibrational spectra, it must be made directly from the spectroscopic data. Such a decision is particularly important in view of an unresolved conflict between the electron-diffraction results of different investigators, one group of workers[30b] favoring the D_{2d} structure and another[41] the D_4 model.

TABLE XVI

D_{2d} STRUCTURE: ASSIGNMENT OF FREQUENCIES

Species	Freq. no.	Type of vibration	C_8H_8	C_8D_8	τ_0	τ_c
A_1	1	C—H stretching	3013	2250	2.72	2.828
	2	C=C stretching	1651	1645[a]		
	3	C—H bending (planar[b])	1202	872		
	4	C—H bending (non-planar)	994	812		
	5	C—C stretching	873	822		
	6	Ring puckering	194	172		
A_2	7	C—H stretching	(3000)	(2250)	..	2.624
	8	C—H bending (planar)	(1200)	(880)		
	9	C—H bending (non-planar)	(1000)	(800)		
	10	Ring distortion	(700)	(650)		
	11	Ring puckering	(300)	(275)		
B_1	12	C—H stretching	3013	2250	2.62	2.828
	13	Ring distortion	1439	1297		
	14	C—H bending (planar)	976	745		
	15	C—C stretching	948	838		
	16	C—H bending (non-planar)	655	576		
	17	Ring puckering	249	238		
B_2	18	C—H stretching	3003	2250	2.52	2.724
	19	C=C stretching	1608	1582		
	20	C—H bending (planar)	1221	899		
	21	Ring distortion	800	720		
	22	C—H bending (non-planar)	648[a]	527		
E	23	C—H stretching	3003	2254	6.56	7.12
	24	C—H stretching	2954	2225		
	25	C=C stretching	1635	1615		
	26	Ring distortion	1399	1287		
	27	C—H bending (planar)	1221	930		
	28	C—H bending (planar)	1202	881		
	29	C—C stretching	942	822		
	30	C—H bending (non-planar)	967	761		
	31	C—H bending (non-planar)	366	312		
	32	Ring puckering	292	265		

[a] Denotes the estimated unperturbed position of a fundamental that is affected by Fermi resonance. [b] In the D_{2d} structure, any two carbon atoms joined by a double bond and the four atoms connected to them presumably lie in a plane. C-H bending vibrations that take place approximately within this plane are called planar, and those that do not are called non-planar.

If one compares the selection rules of the D_4 and D_{2d} structures for cycloöctatetraene, one finds the following main differences: number of coincidences between infrared and Raman fundamental frequencies, 10 for D_4 *vs.* 15 for D_{2d}; number of Raman-active, infrared-silent, 4 *vs.* 0. The most critical of these differences is the last, for it means that in the D_{2d} structure all infrared bands should have counterparts in the Raman effect. In the infrared vapor spectra, three intense bands in cycloöctatetraene (at 628, 667 and 800) and four in the deuterium derivative (527, 720, 899 and 2236) occur at places in the spectrum where no Raman lines are found.

Irrespective of the detailed interpretation of these bands on the assumption of one structure or the other, they are in direct contradiction to the selection rules for the D_{2d} structure. Because of their intensities and spectral locations, it is impossible to dismiss them as overtones, nor can they be attributed to impurities. For most of the bands the coincidental Raman lines would be easy to find because of the "open" character of the Raman spectrum in the neighborhood of the expected lines. The deviations from the selection rules cannot be ascribed to "liquid forces" because the infrared bands are observed in the vapor and "liquid forces" might be postulated to explain the presence of weak Raman lines but could not account for the absence of lines that should be there.

There is no way of reconciling this aspect of the spectra with the D_{2d} structure short of denying that the aspect does not exist, that is, saying that the Raman lines are present but are unobservably weak. This is of course possible, but should at least have some rational explanation. One might presume that the low intensity results from an approximation to higher symmetry, in this case D_{4h}. Apart from the fact that there is no other evidence in the spectra for such an approximation, all but one of the infrared-active B_2 vibrations in D_{2d} are derived from Raman-active vibrations in D_{4h}, while the E vibrations give ample evidence of Raman activity. Another possible explanation might be worked out on an *ad hoc* basis by supposing that in the B_2 vibrations the polarizability changes associated with the motion of the carbon atoms are just cancelled by those of the hydrogen atoms.[42] The difficulty with this kind of proposal is that adjustment of the parameters to give cancellation in cycloöctatetraene cannot simultaneously result in cancellation for all the B_2 vibrations in the deuterium derivative. The reason for this is that several different kinds of vibration correspond to the infrared-active, Raman-silent frequencies (as is shown by the shifts in the deuterium spectrum). Thus the ratios of carbon atom to hydrogen atom amplitudes of vibration vary widely not only from one vibration to another in the same compound, but especially from a vibration in cycloöctatetraene to the analogous vibration in the deuterium derivative.

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(41) Bastiansen and Hassel, *Acta Chem. Scand.*, **3**, 209 (1949).

(42) The details of such a possibility are considered for a vibration of E_g^- symmetry in benzene in ref. 34.

TABLE XVII

ASSIGNMENTS OF COMBINATION TONES BELOW 2000 CM.$^{-1}$

In Table XVII the columns headed "*I*" contain the intensities, letter symbols referring to infrared bands and numbers to Raman lines in accordance with the usage of Tables I-VIII. The notation (L) means that an infrared band is observed only in the liquid phase, in which case it is possible for the band to appear in contravention of the selection rules. The numbers in the columns headed "Assignment" refer to the fundamental frequencies listed in Table XIV.

Cycloöctatetraene

$\bar{\nu}$ in cm.$^{-1}$	*I*	Assignment
488	1	6 + 32
497	1	$2\nu_{22}$
513	2	21-22; 5-31; 9-32
582	w	$2\nu_{32}$
728	1	$2\nu_{31}$
873	w(L)	ν_5
890	w	15 + 22
993	w	6 + 9
1028 1036	w w	14 + 32 15 + 31 21 + 32
1427	vvw	?
1439	vw(L)	ν_{18}
1461	1	$2\nu_{14}$ 9 + 15 22 + 27
1528	1	5 + 15 9 + 14
1548	1	9 + 21
1573	1 and w	15 + 20; 28 + 31[a]
1677	1	13 + 14; 18 + 22; 26 + 32
1725	w	21 + 29; 18 + 32
1750	m	9 + 30
1769	1	9 + 29; 26 + 31
1781	w	4 + 9
1800	1	6 + 12; 18 + 31
1820 1836	1 2	5 + 13 5 + 29 6 + 25 2 + 6
1842	w	12 + 22
1857	1	15 + 28
1865	vvw(L)	15 + 27
1890	1	$2\nu_{13}$; $2\nu_{30}$
1916 1922	2 w	25 + 32
1929	1	4 + 30; $2\nu_{29}$
1940	2	2 + 32; 4 + 13
1970	1	4 + 19; 21 + 27
1999	1	3 + 9; 25 + 31
2007	w	2 + 31

Cycloöctatetraene-*d*$_8$

$\bar{\nu}$ in cm.$^{-1}$	*I*	Assignment
551	m	16 + 22
592	w	16 + 32
711	w(L)	?
730	w(L)	6 + 14
813	w(L)	ν_4
890	2	15 + 31
1355	2	10 + 30; 13 + 14; 21 + 29
1379	w(L)	13 + 21
1438	w	14 + 28
1483	vw(L)	9 + 29
1542	2	9 + 30; 18 + 22
1554	1	4 + 19; 13 + 29; 26 + 32
1564	w	18 + 32; 19 + 30
1582	w	29 + 30[a]
1597	1	4 + 13; 9 + 28; 26 + 31
1658	w(L)	8 + 29; 9 + 27; 20 + 30
1675	1 and w(L)	13 + 28; 19 + 27; $2\nu_{20}$
1824	vw(L)	8 + 27; 10 + 26
1889	vw(L)	12 + 31; 25 + 32

[a] See also text, p. 3382.

The conflict of the observed spectrum with the selection rules of the D$_{2d}$ structure extends beyond the failure to find all infrared fundamentals in the Raman effect, but the additional evidence, while definite, is by no means inescapable. However, in the event of a close balance of other evidence between the two structures, it could serve as a basis for decision. The D$_{2d}$ model requires only six depolarized Raman lines that are not in coincidence with infrared bands, while the number of unassigned lines of this sort listed in Table XIII is larger than this, and must be increased by at least one C–H stretching frequency. To be sure, one or two of these lines are weak and could possibly be interpreted as overtones but all of them were regarded as of sufficient intensity to be placed in the list of principal lines before the interpretation was undertaken.

We thus arrive at the conclusions: (1) the vibrational spectra of cycloöctatetraene can be interpreted on the basis of the D$_4$ structure without major difficulty and with only one or two minor ones; (2) the spectra can be interpreted on the basis of the D$_{2d}$ structure apart from the major difficulty that, contrary to expectation from the D$_{2d}$ selection rules, certain very strong infrared bands have no counterpart in the Raman effect, and apart from certain other less important difficulties; (3) if a decision between these two structures is to be made on the basis of the spectroscopic data, the evidence is strongly in favor of the D$_4$ form.

Overtones

The interpretation of those infrared bands and Raman lines that have not been assigned to fundamental frequencies might be expected to assist in the elucidation of the structure. Unfortunately the laxity of the combination-tone selection rules for both D$_4$ and D$_{2d}$ structures, the large number of fundamental frequencies and the inexact agreement between calculated and observed frequency values because of anharmonicity all work together to make the interpretation of combination tones of little significance. In Table XVII are given interpretations of all bands listed in Tables I-VIII below 2000 cm.$^{-1}$ that have not been discussed previously. The calculated values of the combination tones agree with the observed ones within the limits of accuracy of measurement of weak lines (usually 3-4 cm.$^{-1}$) and of anharmonicity (usually less than 10 cm.$^{-1}$). In several cases other assignments nearly as good as those in Table XVII can be made, but we have not listed them for various reasons, on grounds either of excessive anharmonicity or of expected low intensity or for some reason pertinent to the particular assignment.

The bands above 2000 cm.$^{-1}$ must be overtones except for the hydrogen and deuterium stretching vibrations, and thus do not concern us as possible fundamentals. In view of the fact that most of them can be explained in a variety of ways, we have not bothered to list the explanations in Table XVII.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF SOUTHERN CALIFORNIA]

Spectral Study of Long Chain Quaternary Ammonium Salts in Brom Phenol Blue Solutions

BY EUGENE L. COLICHMAN[1]

The absorption spectra of the acidic and basic forms of brom phenol blue have been determined in the visible and also in the ultraviolet region of the spectra, previously unreported. Changes in these spectra, observed when long chain quaternary ammonium salts are added to the solutions, permit evaluation of the "quaternary-dye" micellar phenomenon.

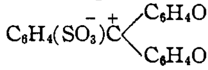
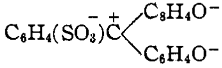
The reaction between long chain quaternary ammonium salts and brom phenol blue has received considerable attention.[2-7] The influence of colloidal agents on the color of indicators was reported only qualitatively in the first report.[2] Empirical analytical methods[3,4,5] for quantitative analyses of surface active agents then followed based on these initial observations. The nature of this reaction has been investigated by conductance[6] and surface and interfacial tension methods.[7] These later results indicate ion-pair formation in aqueous solutions followed by micellization. Considerably lower critical micelle concentrations, for the quaternary ammonium salts when in the presence of either acidic or basic forms of brom phenol blue, have been indicated, but quantitative proof has been lacking. The present spectrophotometric investigation was undertaken with this in mind.

The spectral change method of locating critical micelle concentrations, proposed by Corrin, Klevens and Harkins[8,9] and later studied in detail by two of these investigators,[10,11] is used in the present study.

Results and Discussion

Spectrophotometric data in the visible and ultraviolet regions of the spectra were obtained with a Beckman quartz spectrophotometer, model DU, using 1-cm. quartz cells. Temperature was 30 ± 2° in all measurements. The quaternary ammonium salts used were described previously.[6,7,12] Brom phenol blue samples from both National Aniline Co. and Eastman Kodak Co. gave similar results. *p*H 1.00 solutions were obtained by using the appropriate dilution of hydrochloric acid. The *p*H 6.50 solutions were Sorenson's phosphate buffer.[13] The measurements in the visible region were made according to accepted procedure.

The spectrum of brom phenol blue in the presence of cetyltrimethylammonium bromide was studied, also, in the ultraviolet region. The blank solutions, set automatically at one hundred per cent. transmission, were cetyltrimethylammonium bromide-buffer solutions. Therefore, the spectrum under these conditions is that of the brom phenol blue alone, but influenced by the quaternary ammonium salt present. The effect of the other quaternary ammonium salts could not be investigated, similarly, in this region due to their much higher absorption.

Brode's work[13,14] and a later investigation[15] prove that two and only two colored forms can be responsible for the tautomeric equilibrium in the *p*H range investigated due to the sharp isosbestic point exhibited. The yellow or acidic form  $C_6H_4(\overset{-}{SO_3})\overset{+}{C}\begin{smallmatrix}\diagup C_6H_4OH\\ \diagdown C_6H_4O^-\end{smallmatrix}$, present at *p*H 1.00 in ordinary aqueous solutions, and the purple or basic form,  $C_6H_4(\overset{-}{SO_3})\overset{+}{C}\begin{smallmatrix}\diagup C_8H_4O^-\\ \diagdown C_6H_4O^-\end{smallmatrix}$, found at *p*H 6.50, are symbolized here simply as: HD^- and $D^=$.

The spectral change method[8-11] of locating critical micelle concentrations (C.M.C.) in the brom phenol blue (B.P.B.)-quaternary ammonium salt systems is illustrated in Fig. 1. The abrupt change in the spectrum occurs at the C.M.C. The minimum concentration of quaternary ammonium salt which yields a constant value for the extinction coefficient is defined here as the stable micelle point (S.M.P.). This leveling off point corresponds to complete extraction of the dye into the micelle. These results are presented in Table I. Only cetyltrimethylammonium bromide gave clear solutions at concentrations as low as the C.M.C. values. The C.M.C. values for the other quaternary ammonium salts could not be determined accurately and are not given.

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(1) Department of Chemistry, University of Portland, Portland, Oregon.

(2) Hartley, *Trans. Faraday Soc.*, **30**, 444 (1934).

(3) Hartley and Runnicles, *Proc. Roy. Soc.* (*London*), **168A**, 420 (1938).

(4) (a) Auerbach, *Anal. Chem.*, **15**, 492 (1943); (b) **16**, 739 (1944).

(5) Colichman, *ibid.*, **19**, 430 (1947).

(6) Colichman, THIS JOURNAL, **72**, 1834 (1950).

(7) Colichman, *ibid.*, **73**, 1795 (1951).

(8) Corrin, Klevens and Harkins, *J. Chem. Phys.*, **14**, 216 (1946).

(9) Corrin, Klevens and Harkins, *ibid.*, **14**, 480 (1946).

(10) Corrin and Harkins, THIS JOURNAL, **69**, 679 (1947).

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(13) Clark, "The Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore, Md., 1928.

(14) Brode, THIS JOURNAL, **46**, 581 (1924)

(15) Haring and Heller, *ibid.*, **63**, 1024 (1941).