

## The Ultraviolet Absorption of Simple Hydrocarbons IV. Unsaturated Cyclic Hydrocarbons in the Schumann Region

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## The Ultraviolet Absorption of Simple Hydrocarbons

### IV. Unsaturated Cyclic Hydrocarbons in the Schumann Region

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(Received November 6, 1937)

The absorption spectra of cyclohexene, cyclopentene, 1-3 cyclohexadiene and benzene have been examined in vapor phase in the region  $\lambda = 2300\text{--}1600\text{\AA}$ . The electronic excitation responsible for the first group of bands in this region is practically independent of the cyclic structure of the molecule since the wave number of the first band agrees closely with that obtained for olefins having the same arrangement of hydrogen-atoms around the double bond. Characteristic vibrational frequencies and different electronic levels have been identified.

EARLIER papers in this series have reported absorption spectra measurements between  $\lambda = 2300\text{\AA}$  and  $1600\text{\AA}$  for sixteen ethylenic hydrocarbons<sup>1</sup> and the present paper extends this investigation to include three cyclic hydrocarbons—cyclopentene, cyclohexene and 1-3-cyclohexadiene. The spectrum of benzene has been re-examined under conditions which give a better definition of the vibrational bands than was obtained in the earlier work and these results are used to compare with the measurements for the other cyclic hydrocarbons.

#### EXPERIMENTAL

Cyclohexene was prepared by dehydration of cyclohexanol<sup>2</sup> according to the method outlined

<sup>1</sup> E. P. Carr and M. K. Walker, *J. Chem. Phys.* **4**, 751 (1936); E. P. Carr and H. Stücklen, *Zeits. f. physik. Chemie* **B25**, 57 (1934); *J. Chem. Phys.* **4**, 760 (1936).

<sup>2</sup> The preparation and purification of all the compounds used for spectrographic examination are under the direction of Professor Mary L. Sherrill of this laboratory. The purification of the cyclic hydrocarbons has been made by fractionations through a 35 cm Fenske column. The purity of the material is tested not only by the usual physical constants—boiling point, index of refraction and density

by Kistiakowsky and co-workers<sup>3</sup> and had a boiling point of  $82.70^\circ \pm .05$  at 760 mm; an index of refraction,  $n_D^{20}$  1.4465; a density,  $d_4^{20}$  0.8101. A part of the cyclohexene was converted into 1-3-cyclohexadiene as described by these authors. The diene used for the spectrographic work was a highly purified product obtained directly from the dibromide and its physical constants, b.p.  $80.13^\circ \pm 0.05^\circ$ ,  $n_D^{20}$  1.4742,  $d_4^{20}$  0.8413, were in satisfactory agreement with the cyclohexadiene of Kistiakowsky prepared by way of the cyclohexenyl ether.

Cyclopentene was prepared from cyclopentanone which in turn had been prepared from adipic acid according to the method used by Kistiakowsky and co-workers.<sup>4</sup> Cyclopentanone

but also by absorption spectrum measurements of the liquid hydrocarbon and its hexane solution with the quartz spectrograph. Cyclopentene was prepared by Elizabeth S. Matlack of this laboratory; cyclohexene and cyclohexadiene by Kate Wilkins. This latter work was done in partial fulfillment of the requirements for the M.A. degree at Mount Holyoke College.

<sup>3</sup> G. B. Kistiakowsky *et al.*, *J. Am. Chem. Soc.* **58**, 140 (1936).

<sup>4</sup> G. B. Kistiakowsky *et al.*, *J. Am. Chem. Soc.* **59**, 832 (1937).

TABLE I.

CYCLOHEXENE		
1/λ	1/λ	1/λ
47420	48560	49810
760	930	50110
48010	49245	430
260	510	730
51100	52240	53680
230	500	970
360	630	54305
465	860	630
580	965	55020
710	53215	
870	320	
52100	560	
55435	57820	59100
990	58220	270
56990	670	610
57350	970	60160
		510

TABLE II.

1-3 CYCLOHEXADIENE		
1/λ	1/λ	1/λ
47780-47975	48560	49000
48070-48210	680	100
48235-48365	790	200
48475	885	300
49400	49870	50410
480	970	525
580	50100	635
680	200	765
760	305	
		53650
		820
51185	52605	950
280	700	54355
380	810	440
500	900	540
615	53000	650
710	100	730
820	200	820
945	310	940
52050	430	55045
500	540	
57875	58125	58415
960	220	510
58035	315	

was reduced, using a copper-chromium oxide catalyst,<sup>5</sup> and the resulting cyclopentanol had a boiling point of 140–141° at 759 mm. The cyclopentanol was dehydrated by means of fused potassium acid sulphate, dried over lime and

purified by distillation. The resulting cyclopentene had a boiling point of 44.02° ± .02°,  $n_D^{20}$  1.4420,  $d_4^{20}$  0.7716.

Benzene, Kahlbaum special for molecular weight determinations, was fractionated and the middle fraction boiling at 80.0–80.1° was used for spectrographic examination.

The apparatus and experimental procedure for the absorption spectra measurements have been described in detail.<sup>6</sup> For the earlier study of benzene a 12 cm absorption tube was used; all of the measurements reported in this paper were made with a 60 cm tube. The exposure time varied from 4 min. to 10 min. and all of the

TABLE III.

BENZENE		
1/λ	1/λ	1/λ
48800	50320	52480
49035	570	670
205	850	940
355	51030	53220
670	300	475
780	690	700
970	870	54040
50140	52030	430
55330	56740	57550
420	830	635
772	57020	735
860	095	840
56130	260	955
215	350	58120
505		220
590		
55420	56220	57115

TABLE IV.

CYCLOPENTENE		
1/λ	1/λ	1/λ
47603	48348	49168
720	490	285
815	645	400
935	772	520
48062	915	653
204	49040	788
		900
50090	50870	51470
320	51200	645
405	260	825
700	310	52370
		710
53140	54120	55610
685	660	

<sup>5</sup> This reduction was kindly carried out for us at the University of Wisconsin through the courtesy of Dr. Homer Adkins.

<sup>6</sup> E. P. Carr and H. Stücklen, reference 1.

bands which are given in the tables were photographed while the vapor was kept flowing through the absorption cell. When the vapor is stationary or flowing very slowly photochemical decomposition takes place and new absorption bands appear. With each compound a series of plates were taken after irradiation of the material from 10–45 min. in order to distinguish clearly between the bands of the original material and those due to the presence of disintegration products.

### RESULTS

The spectra of the cyclic unsaturated hydrocarbons show the same general regions of absorption as were evident with the olefins and may be classified into regions *A–D* as was done in the earlier work. The present study is concerned primarily with the absorption between 2300 and 1650 Å which is the region previously discussed as region *C*, the long wave portion and *B*, the short wave. This subdivision is quite arbitrary and was made to simplify the discussion. Each of the cyclic hydrocarbons has been examined also in pure liquid and hexane solution phase with the quartz spectrograph, and these curves will be published in a separate paper in connection with a study of photochemical decomposition of these hydrocarbons.

The results of measurements with the fluorite vacuum spectrograph are presented in the form of tables and graphs. The most striking difference in the spectra of the aliphatic and cyclic hydrocarbons in this region is the presence of sharp, narrow bands in the latter, whereas, with the exception of *cis*- and *trans*butene-2 and isobutene all of the olefins show only diffuse bands. Tables I–IV give the wave numbers of the center of the absorption bands, which can be measured with an error of less than 10  $\text{cm}^{-1}$  for intense narrow bands. The values for each compound are subdivided into groups depending upon similarity in structure of the bands.

As in the previous work, the intensities of the bands as given in the curves are estimated from their appearance on the photographic plate since the Schumann plates do not admit of quantitative photometric measurement. The vapor pressure of the hydrocarbon in the absorption tube was varied from 40 mm to less than 0.1 mm.

The wave number at which absorption begins in the Schumann region was found for the olefins to be dependent upon the number of hydrogen atoms bound to the carbon atoms of the double bond. All of the cyclic compounds which have been studied, including benzene and diphenyl, have the grouping  $\text{C}-\text{CH}=\text{CH}-\text{C}$  and the analogous group for the olefins,  $\text{R}-\text{CH}=\text{CH}-\text{R}$ , was designated as *IIa*. For this group the beginning of absorption for the olefins was between 48,200 and 49,200  $\text{cm}^{-1}$ ; for benzene this is at 48,800  $\text{cm}^{-1}$  and for the other cyclic hydrocarbons it is between 47,400 and 47,900  $\text{cm}^{-1}$ . While there is a slight shift toward the visible of the first absorption band of all of the cyclic compounds except benzene in comparison with the olefins the close parallelism of the aliphatic and cyclic compounds is of interest. Evidently the energy of this electronic excitation which is common to all of the hydrocarbons containing the  $\text{C}=\text{C}$  linkage is not only independent of the nature of the alkyl substituent, as was shown previously, but it would seem also to be practically independent of whether the molecule has a cyclic or an open chain structure.

The variation in breadth of the narrow bands which are characteristic of these cyclic compounds is no doubt of significance but it seems premature to attempt any theoretical explanation. In the first group of bands of cyclohexene and *cis*butene-2 the breadth of the bands is of the order of 100  $\text{cm}^{-1}$ , while in *trans*butene-2, cyclopentene and cyclohexadiene it is from 40–50  $\text{cm}^{-1}$ . In benzene these bands have broadened to such an extent that they overlap and give the effect of shallow diffuse bands and only in a narrow range of pressures are the single maxima sharp enough to be measured. In the short wave region benzene has a doublet band system in which the average width of a band is 40  $\text{cm}^{-1}$  and cyclohexene shows a comparable band system at somewhat longer wave-lengths.

### DISCUSSION OF RESULTS

The first absorption bands in the Schumann region for ethylenic derivatives were ascribed to an electronic excitation corresponding to the transition  ${}^1A_1 \rightarrow {}^1B_1$ <sup>7</sup> which had been predicted

<sup>7</sup> E. P. Carr and H. Stücklen, J. Chem. Phys. **4**, 760 (1936).

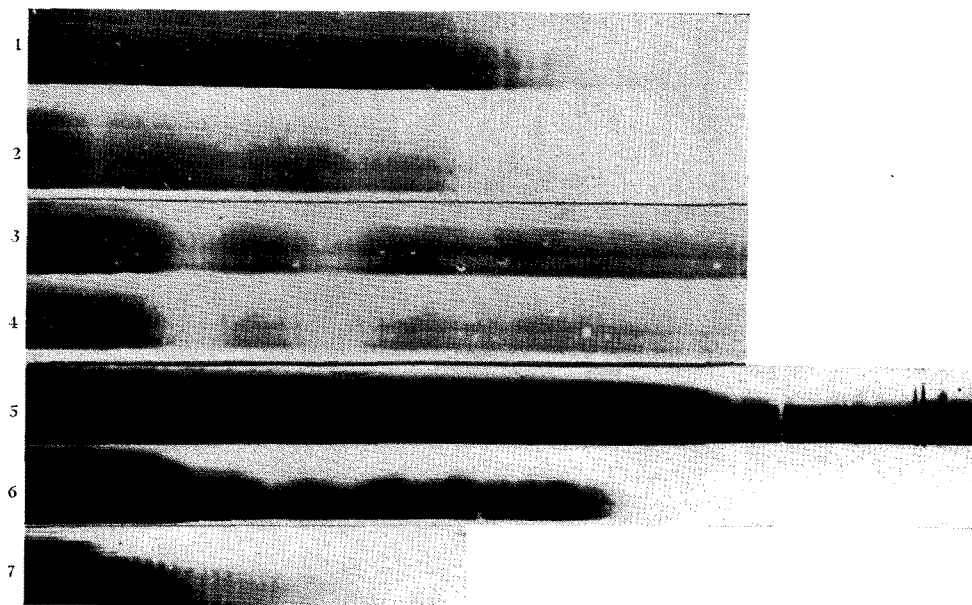


FIG. 1. 1,2, Cyclohexene; 3,4, cyclohexadiene; 5,6, benzene; 7, cyclopentene.

for the ethylene molecule.<sup>8</sup> Since the excitation involves an ( $x$ ) orbital, localized in the region of the C=C bond, it would be reasonable to expect the vibrational bands which are characteristic of this linkage. Because of the breadth and diffuseness of the bands in the spectra of the higher olefins it was not possible to identify any of the vibrational bands with certainty but the appearance of fine structure in the butenes and in the cyclic compounds enables the measurement of band separations with an error of not more than  $10\text{ cm}^{-1}$ . Vibrational frequencies of  $1510\text{ cm}^{-1}$  for the excited molecule of cisbutene-2,  $1570\text{ cm}^{-1}$  for transbutene-2, and  $1485\text{ cm}^{-1}$  for cyclohexene have already been pointed out<sup>9</sup> together with their relation to the Raman frequencies of  $1658$  and  $1674$  for cis- and transpentene-2 and  $1646\text{ cm}^{-1}$  for cyclohexene. The spectrum of cyclopentene in the Schumann region shows only a long series of equally spaced narrow bands of gradually increasing intensity with increasing wave number, whereas in the other cyclic compounds there are groups of bands with sharply marked maxima (Fig. 1). In cyclohexene and

cyclohexadiene the separation between the most intense band in the first and second groups (Fig. 2) is of the order of that which is characteristic for this vibration in ethylenic compounds and seems, without question, to be related to the vibration along the axis of the C=C bond. In the spectrum of benzene (Fig. 2) the corresponding separation is  $935\text{ cm}^{-1}$  and this frequency must be ascribed to the C=C vibration which constitutes the so-called "breathing" frequency of the benzene molecule and corresponds to the  $992\text{ cm}^{-1}$  in the normal molecule.

In cyclohexene and cyclohexadiene there is a strong band, the separation of which from the strongest or 0-0 band of the first group is of

TABLE V.

COMPOUND	$1/\lambda$ RAMAN*	$1/\lambda$ ULTRAVIOLET
Cyclohexene	$1646\text{ cm}^{-1}$	$1485\text{ cm}^{-1}$
	2912	2670
	3024	
1-3-Cyclohexadiene	1574	$1360 \pm 50^\dagger$
	3042	2920
Benzene	992	935
	3060	2835

\* K. W. Kohlrausch and R. Seka, Ber. A68, 528 (1935).

† There are two bands of almost equal intensity in the center of the second group. In measuring the separation of the maxima of different groups an error of  $\pm 50\text{ cm}^{-1}$  is therefore possible.

<sup>8</sup> Mulliken, Phys. Rev. 41, 751 (1932); J. Chem. Phys. 3, 517 (1935).

<sup>9</sup> E. P. Carr and H. Stücklen, J. Am. Chem. Soc. (in publication).

the order of  $2700\text{--}2900\text{ cm}^{-1}$ . This band is present in the benzene spectrum also where it is one of the intense bands in the fourth group and has been found in cisbutene-2 in the third group. A second member of the  $\text{C}=\text{C}$  vibrational series is clearly separated from it in all of the compounds except cyclohexadiene. This band could be ascribed to a  $\text{C}-\text{H}$  stretching vibration, the frequency of which for hydrocarbons in their normal state is known to be of the order of  $3000\text{ cm}^{-1}$ . Considering intensities, this assignment would be allowed. The band is equal or stronger than the neighboring higher member of the  $\text{C}=\text{C}$  vibrational series, while this again is weaker than the preceding member of its series. A comparison of these vibration frequencies for the excited molecule with the corresponding ones for the normal molecule from the Raman spectra is given in Table V.

The absorption spectrum of cyclopentene (Fig. 3) is unique among the twenty-two hydrocarbons that have been examined in this laboratory. The beginning of absorption at  $47,600\text{ cm}^{-1}$  is in accord with that for the other cyclic hydrocarbons and the ethylenic derivatives of group IIa but the spectrum in this region shows only a series of about twenty equally spaced narrow bands, the average separation of which is  $130\text{ cm}^{-1}$ . The intensity of these bands increases gradually but there is no evidence in this electronic level of the discrete bands which have been ascribed to vibrations of the  $\text{C}=\text{C}$  bond in other molecules. It would seem as if an electronic excitation which is analogous to that found for the other unsaturated hydrocarbons is, in the case of cyclopentene, unaccompanied by

the characteristic  $\text{C}=\text{C}$  vibration. It should be noted, however, that quite clearly marked band separations of  $1520$  and  $2470\text{ cm}^{-1}$  are shown in the higher electronic level which begins at about  $53,000\text{ cm}^{-1}$  although it has not been possible to identify corresponding vibrational bands in this electronic transition for other hydrocarbons

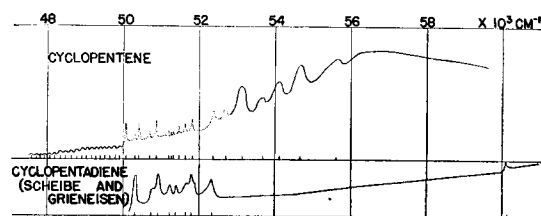


FIG. 3.

except isobutene. A comparative table of Raman spectrum measurements for cyclopentene by various investigators is given by Reitz.<sup>10</sup> There is a strong Raman line at  $1610\text{ cm}^{-1}$  and a group of lines at  $2846$ ,  $2902$ ,  $2947$  and  $3060\text{ cm}^{-1}$ , all of high intensity.

The doublet system in cyclopentene which appears at  $50,000\text{ cm}^{-1}$  is undoubtedly due to the presence of cyclopentadiene. This band system appears very faintly when the ordinary exposures of from 4 to 6 minutes are made but comes out very strongly on longer irradiation. The curve for cyclopentadiene given by Scheibe and Grieneisen<sup>11</sup> is reproduced below that for cyclopentene (Fig. 3) and shows quite clearly that this system in our measurements of cyclopentene must be due to the diene which has been formed by photochemical decomposition. Further discussion of the cyclopentene spectrum must be postponed until the spectrum of cyclopentane and cyclopentadiene can be examined.

From the general character of the bands in cyclohexene and their intensity relationships there would seem to be from 4–5 different electronic levels in the region between  $47,000$  and  $61,000\text{ cm}^{-1}$ . The first excitation beginning at  $47,750\text{ cm}^{-1}$  seems to be completely analogous to that in the ethylenic derivatives which has been ascribed to a  ${}^1A_1 \rightarrow {}^1B_1$  transition. The curves for cis- and transbutene-2 are given in

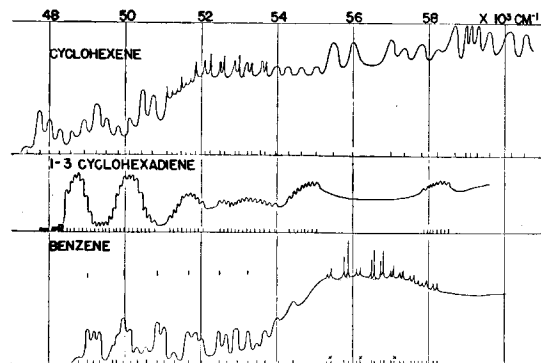


FIG. 2.

<sup>10</sup> A. W. Reitz, *Zeits. f. physik. Chemie* **B33**, 182 (1936).

<sup>11</sup> Scheibe and Grieneisen, *Zeits. f. physik. Chemie* **B25**, 52 (1934).

Fig. 4 in order to show the striking parallelism between the spectra of cisbutene-2 and cyclohexene in the region between  $47,000\text{ cm}^{-1}$  and  $51,000\text{ cm}^{-1}$ . These results have served as a confirmatory test for the assignment of molecular configurations to the isomers of butene-2.<sup>9</sup> The

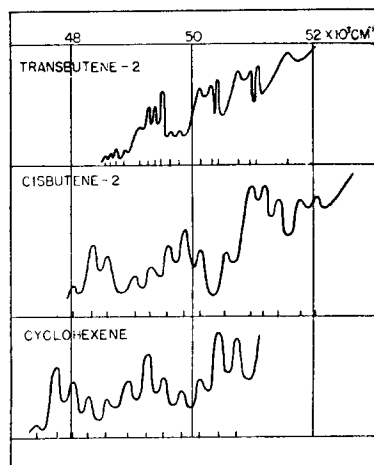


FIG. 4.

only other electronic excitation in this spectrum which shows a marked resemblance to anything which has been found in the spectra of other unsaturated hydrocarbons is the doublet system which begins about  $52,000\text{ cm}^{-1}$  and extends to  $55,000\text{ cm}^{-1}$ , the last four groups not being resolved. This system is quite similar to that found in benzene between  $55,500$  and  $58,500\text{ cm}^{-1}$ ; in each case the short wave component of the doublet is much stronger than the other; the separation between the two bands in the doublet is of the order of  $100\text{ cm}^{-1}$  in benzene and  $130\text{ cm}^{-1}$  in cyclohexene. In both spectra the separation between successive doublets seems to remain fairly constant although the separation is somewhat larger in cyclohexene ( $350\text{ cm}^{-1}$ ) than in benzene ( $250\text{ cm}^{-1}$ ).

In cyclohexadiene a series of more than fifty narrow bands, with an average separation of  $100\text{ cm}^{-1}$  extends with but slight interruption from  $48,500$  to  $55,000\text{ cm}^{-1}$ . Underlying this series of bands are the diffuse bands whose separations correspond to vibrational frequencies of the  $\text{C}=\text{C}$  and  $\text{C}-\text{H}$  bonds. The narrow band spectrum reappears again in another electronic level in the region of  $58,000\text{ cm}^{-1}$  but the separa-

tion here seems to be slightly less than in the longer wave region. It is not possible at this time to attempt any theoretical discussion of these narrow bands which seem to be so characteristic a part of the spectra of cyclopentene and 1-3-cyclohexadiene.

In the earlier discussion of the benzene spectrum<sup>12</sup> very little could be said about the region between  $48,500$  and  $54,000\text{ cm}^{-1}$  since the experimental conditions were not such that the narrow bands in this region were resolved and with the exception of the first two bands where some splitting was evident only the maxima of groups of diffuse bands were given. The results of the present investigation of the benzene spectrum show that the strongest bands of each of the first six groups, as indicated in Fig. 2, fit into a vibrational series of the form:  $1/\lambda = 49035 + 960\nu - 25\nu^2$ , the average deviation of  $\pm 3\text{ cm}^{-1}$  being within the limits of experimental error. The lower intensity of the first, or 0-0 band, would be explained by the Franck-Condon principle; after the second the intensity decreases as must be expected for a vibrational series. In the case of cyclohexene and cyclohexadiene it is of interest to note that in each spectrum the first two bands have the same intensity.

The general characteristics of the spectra of benzene, cyclohexene, cyclohexadiene in the region beginning about  $48,000\text{ cm}^{-1}$  and their analogy to the spectra of the ethylenic derivatives point to the conclusion that the electronic transition involved is similar in all of the molecules. In the ethylenic hydrocarbons this transition was tentatively assigned to the transition  ${}^1A_1 \rightarrow {}^1B_1$  and the much weaker absorption in the quartz region to a  ${}^1A_1 \rightarrow {}^3B_1$  transition. The olefins show a step-out indicating a broad absorption band of very low intensity in the quartz region so that no study of fine structure is possible but the analogy to the benzene spectrum is shown by the fact that the absorption of the group II hydrocarbons in liquid and hexane solution is in precisely the same region as that of benzene solutions.<sup>13</sup> The sharp bands of

<sup>12</sup> E. P. Carr and H. Stücklen, *Zeits. f. physik. Chemie* **B25**, 57 (1934).

<sup>13</sup> E. P. Carr and G. F. Walter, *J. Chem. Phys.* **4**, 760 (1936); *International Critical Tables*, Vol. 5, p. 363.

the latter spectrum are well known and the vapor phase spectrum has been exhaustively investigated. If, therefore, the assumption that closely corresponding electronic transitions are involved in the excitation of all the molecules having the  $-C-CH=CH-C-$  grouping is valid the absorption spectrum of benzene in the long wave region between 37,000 and 44,000  $\text{cm}^{-1}$  would be ascribed to a singlet-triplet transition. Some justification for this assumption is given by the recent interpretation of the fluorescence spectrum of benzene by Ingold and Wilson<sup>14</sup> in which a complete analysis of the spectrum was possible on the basis of transitions from three excited electron states to the zero level of the ground state.

<sup>14</sup> C. K. Ingold and C. L. Wilson, J. Chem. Soc. 941 (1936).

The vapor pressure of the benzene was too high and the absorption tube too short to resolve the benzene spectrum sufficiently to permit detailed analysis of the bands but the general characteristics of the spectrum between 48,800 and 54,400  $\text{cm}^{-1}$  and in the quartz region are sufficiently similar to indicate closely related electronic transitions. The probability of the singlet $\rightarrow$ triplet transition for ethylene was estimated by Mulliken to be of the order of  $10^{-4}$  of that for the singlet $\rightarrow$ singlet transition and the ethylenic derivatives showed close agreement with that prediction. If the assumption of corresponding states for benzene is correct, comparison of the intensities in the two regions would show that the probability of the transition to the triplet state in benzene is about  $10^{-2}$  of that for the singlet $\rightarrow$ singlet transition.

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## Infrared Absorption Studies

### IV. The Infrared Spectrum of Water in an Inert Solvent

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(Received November 22, 1937)

The infrared absorption spectrum of  $\text{H}_2\text{O}$ , HDO and  $\text{D}_2\text{O}$  in dilute solution in carbon tetrachloride and carbon bisulfide has been investigated with a grating of high resolving power, in the region 2.6–3.8 $\mu$ . Several bands have been identified as  $\nu_3$  bands and the hitherto unobserved  $\nu_1$  band for  $\text{H}_2\text{O}$  is believed to have been found. The frequencies observed are compared with the same frequencies in the vapor and a displacement of frequency which is proportional to the frequency itself is observed in solution. A fine structure is observed in the case of  $\text{H}_2\text{O}$  which may be ascribed to rotation unless some other explanation is found. The spectrum in carbon bisulfide appears to be identical with that in carbon tetrachloride.

THE infrared vibration rotation spectrum of water vapor was investigated by Plyler and Sleator<sup>1</sup> and that of heavy water vapor has been recently studied by Barker and Sleator.<sup>2</sup> They have located the principal vibration frequencies for water and the two deuterium substituted molecules with the exception of  $\nu_1$  which has not been observed in the symmetrical molecule and  $\nu_3$  for HDO.  $\nu_1$ , however, has been observed

in the Raman spectrum for  $\text{H}_2\text{O}$ .<sup>3</sup> Studies of hydrogen chloride absorption in solution have been made by Plyler and Williams,<sup>4</sup> and West and Edwards.<sup>5</sup> Recently Kinsey and Ellis<sup>6</sup> have observed the infrared absorption spectrum of water in carbon bisulfide solution with a prism spectrograph.

<sup>3</sup> D. Bender, Phys. Rev. **47**, 252 (1935).

<sup>4</sup> E. K. Plyler and D. Williams, Phys. Rev. **49**, 215 (1936).

<sup>5</sup> W. West and R. T. Edwards, J. Chem. Phys. **5**, 14 (1937).

<sup>6</sup> E. L. Kinsey and J. W. Ellis, Phys. Rev. **51**, 1074 (1937).

<sup>1</sup> E. K. Plyler and W. W. Sleator, Phys. Rev. **37**, 1493 (1931).

<sup>2</sup> E. F. Barker and W. W. Sleator, J. Chem. Phys. **3**, 660 (1935).