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The Near Infrared Spectrum of Benzene- d_6

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The transmission spectrum of C_6D_6 has been studied from 1μ to 13.25μ and the shifts of three of the four infrared active vibrations determined. The results obtained are in substantial agreement with the assumption of a plane symmetrical molecule as outlined by Wilson.

Measurements on C_6H_6 and thiophene extending from 1μ to 15μ are also presented.

ACCORDING to present theoretical considerations¹ the benzene molecule is best represented by a regular plane hexagon model with the carbons and hydrogens all lying in the same plane. Of the thirty possible modes of vibration of such a model only four are infrared active. These have been observed and carefully studied by many investigators and are found at 3.25, 6.75, 9.78 and 14.90μ , respectively. In addition to these fundamentals several other weaker bands are usually found, which are thought of as combination bands.

With the advent of heavy hydrogen it was immediately evident that infrared measurements upon molecules prepared from it would furnish important data concerning the structure of these molecules. This has been shown to be true by the work of various authors in which the vibrations and in some cases the rotations of heavy methane, ammonia, acetylene, etc., have been studied. As a result of these successes we were particularly glad to receive from Professor Taylor a sample of heavy benzene prepared as described in a previous paper,² and to be able to measure its near infrared spectrum. Since a discussion of the theoretical significance of these measurements with regard to the general properties and the structure of the benzene molecule is to be presented in a subsequent paper by Dr. Benedict and Mr. Bowman, the present paper will be concerned only with the experimental side of the problem.

The chief purpose of this investigation was to map the positions of the vibration bands of C_6D_6 with particular reference to the frequencies corresponding to the four active vibrations of C_6H_6 mentioned above. From a comparison of these

observed values with those calculated by Benedict, the validity of the present assumptions regarding the ordinary benzene molecule may be

TABLE I. Observed and calculated frequencies of C_6H_6 and C_6D_6 .

C_6H_6		C_6D_6		
λ in μ (Obs.)	ν in cm^{-1} (Obs.)	λ in μ (Obs.)	ν in cm^{-1} (Obs.)	ν in cm^{-1} (Calc.)
0.84	11,905	1.01	9901	
1.08	9259	1.375	7272	
1.25	8000	1.56	6410	
1.65	6061	1.90	5263	
2.03	4926	2.28	4386	
2.35	4255	2.88	3472	
2.75	3636	3.06	3268	
3.25	3077	3.20	3125	
3.75	2667	3.55	2817	
4.00	2500	3.95	2532	
4.45	2247	4.36	2294	2310
5.15	1942	5.18	1930	
5.60	1786	5.45	1835	
6.02	1661	5.70	1754	
6.18	1618	6.03	1658	
6.77	1477	6.22	1608	
7.32	1366	6.95	1439	
7.91	1264	7.57	1321	1320
8.35	1198	8.09	1236	
8.65	1156	8.72	1147	
8.94	1119	9.25	1081	
9.17	1090	9.47	1056	
9.76	1025	9.89	1011	
10.46	956	10.15	985	
10.67	937	10.46	956	
10.95	913	10.70	935	
11.20	893	10.85	922	
11.32	883	11.13	998	
11.66	858	11.45	873	
11.86	843	11.56	865	
11.97	835	11.96	836	
12.07	829	12.20	820	
12.22	818	12.38	808	
12.41	806	12.55	797	817
12.64	791	12.76	785	
12.75	784	13.04	767	
12.91	775			
13.02	768			
13.35	749			
13.60	735			
13.90	719			
14.14	707			
14.41	694			
14.70	680			
14.95	669			485

¹ E. Bright Wilson, Jr., Phys. Rev. **45**, 706 (1934).

² Bowman, Benedict and Taylor, J. Am. Chem. Soc. **57**, 960 (1935).

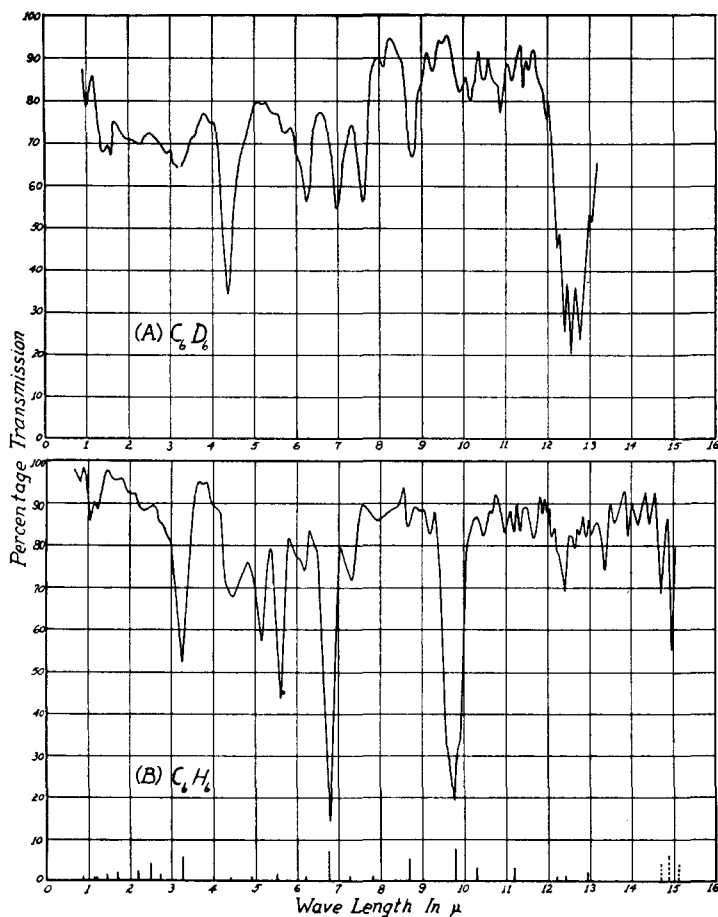


FIG. 1. Comparison of the near-infrared spectra of light and heavy benzene. (a) C_6D_6 (b) C_6H_6 . The vertical lines in (b) show the positions and intensities of the absorption bands as given by Coblenz. The group around 15μ are by Kettering and Sleator.

tested. At the present time the fine structure of these bands was not considered, hence a rocksalt spectrometer employing a 60° prism and 40 cm focal length mirrors was used. The slits were kept 0.35 mm wide throughout all of the measurements, some 10 to 20 points being taken to each μ . The source was a hot platinum strip operated at 20 amperes by a 22-volt transformer and the receiving device a Moll linear thermopile connected to a photo-relay system.

The gas was contained in a 15 cm glass cell having rocksalt windows. The cell was filled by

placing a few drops of the liquid in a side tube, freezing it with liquid air, evacuating the cell and then removing the liquid air. The percentage transmission of the benzene was arrived at by employing the following procedure. First a complete run was taken throughout the entire spectral range, in which readings were taken of the filled cell against the energy. These gave the percentage transmission of the cell plus the benzene. The latter was then frozen out completely and a similar run taken in order to get the percentage transmission of the cell alone. Upon making the

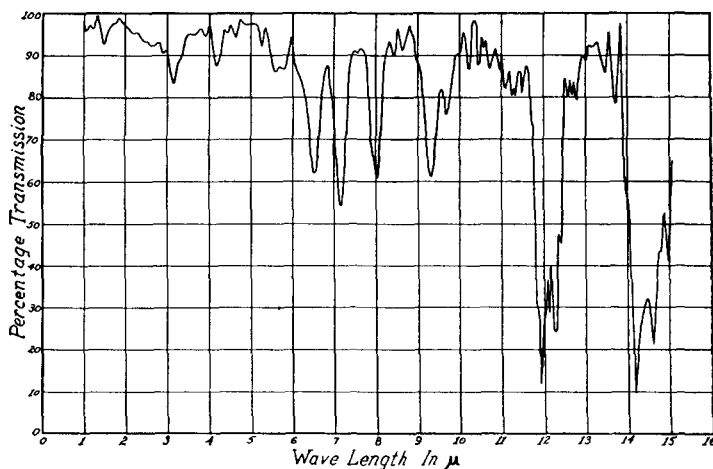


FIG. 2. Near-infrared spectrum of thiophene.

proper corrections the transmission of the benzene alone was then obtained. No experimental points are shown in the curves, the values given being the averages of several runs. No absorption band has been indicated which has not been found on at least two separate runs.

In order to complete the story similar measurements were made upon ordinary benzene, in spite of the fact that these values are well known.* The sample used was furnished us by Mr. Bowman and was the same benzene from which the C_6D_6 was prepared. Thiophene, C_4H_4S , is very hard to remove from benzene and so, although we did not suspect its presence in our benzene, a careful run was made on pure thiophene in order to be sure that none of the bands came from this source. The results showed that the benzene was thiophene free.

The instrument was calibrated empirically, by locating carefully the well-known absorption bands of H_2O , CO_2 and the reflection bands of SiO_2 . This calibration curve was then checked by mapping the spectra of toluene cyclo-hexane and cyclo-hexene. None of the known bands of these substances was off by as much as 0.10μ . All of the values listed in Tables I and II are probably accurate to $\pm 0.05\mu$. In each of the curves, every

minimum which was found to agree in the separate runs taken upon that substance was plotted. The interpretation of the weak bands is uncertain.

In Fig. 1, curve (a) shows the C_6D_6 results. This series of measurements was extended only as far as 13.25μ , since the calculated values indicated

TABLE II. Observed frequencies of C_4H_4S .

C_4H_4S		C_4H_4S	
λ in μ (Obs.)	ν in cm^{-1} (Obs.)	λ in μ (Obs.)	ν in cm^{-1} (Obs.)
1.10	9091	9.67	1034
1.25	8000	10.00	1000
1.50	6667	10.23	978
1.75	5714	10.45	957
2.20	4545	10.57	946
2.45	4082	10.71	934
2.67	3745	10.97	912
2.91	3436	11.08	903
3.18	3145	11.25	889
3.35	2985	11.28	887
3.65	2740	11.50	870
3.92	2551	11.92	839
4.19	2387	12.13	824
4.45	2247	12.27	815
4.65	2150	12.41	806
4.87	2053	12.59	794
5.27	1898	12.69	788
5.59	1789	12.80	781
5.82	1718	13.01	769
6.52	1534	13.17	759
7.16	1397	13.46	743
7.56	1323	13.72	729
8.01	1248	14.19	705
8.43	1186	14.61	684
8.64	1157	14.77	677
9.32	1073	14.98	668

* Schaefer and Matossi, *Das Ultrarot Spectrum* (Breslau, 1930).

that the fourth fundamental would lie around 20μ , which was beyond the limit of our instrument. The measurements on C_6H_6 , curve (b), were extended only as far out as 15.05μ since this was very near the limit of our instrument and since the wavelength of this last absorption was well known. The vertical lines at the bottom of the graph give the wavelengths and intensities as listed in *Das Ultrarot Spectrum*. The agreement of these two sets of data is very good, however attention is called to several new bands in our curves and to the large discrepancy in the intensities of the band at 8.65μ . A comparison of curves

(a) and (b) shows the absence of C_6H_6 in the C_6D_6 , in complete agreement with the results of the ultraviolet measurements to be discussed in a later paper. The good agreement between the observed and calculated frequencies of the fundamentals of C_6D_6 is, as will be shown below, excellent support for the present theoretical assumptions concerning the structure of the benzene molecule. Table I presents a summary of the benzene results. The calculated values are by Benedict.

In Fig. 2 and Table II the results on a sample of Eastman Kodak thiophene are presented.

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The Raman Spectra of Arsenic Trichloride and of Its Mixtures

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The Raman spectra from mixtures of AsCl_3 with benzene, carbon tetrachloride, methyl and ethyl alcohol have been investigated. The strong deviations from additivity have been observed for AsCl_3 in alcohols. The shifts are correlated with the strength of the bond $\text{As}-\text{Cl}$. A computation of the constants of the molecule AsCl_3 is made which agrees with electronographic data. The geometrical configuration of the molecule AsCl_3 in mixtures undergoes only a slight deformation, but the bond $\text{As}-\text{Cl}$ is considerably weakened in alcoholic solutions.

1.

INVESTIGATION of Raman spectra of liquid mixtures did not give definite results. In certain cases, the spectrum of mixtures is a strict superposition of the spectra of the components,¹ in other ones various changes have been observed, e.g., the splitting of Raman lines, their shifts and the variation of relative intensities, the disappearance of some frequencies or the appearance of new ones.² These deviations from additivity are ascribed to polymerization, to

formation of complexes or to solvation. Up to now it has not been possible to establish a clearly expressed connection between the deviations of Raman spectra of mixtures from additivity and the properties of the components of the mixture. In particular, there is no parallelism between deviations from additivity and dipole moments;³ in certain cases the mixtures with dipole components behave additively, in others additivity is broken in the presence of nonpolar components of the mixture. The question requires thus additional experimental research.

We have examined the Raman spectra of mixtures of arsenic trichloride with benzene, carbon tetrachloride, methyl and ethyl alcohols. The method and detailed results for the two

¹ A. Dadiou and K. W. F. Kohlrausch, *Physik. Zeits.* **30**, 384 (1929); E. H. L. Meyer, *ibid.* **32**, 293 (1931); R. E. Whiting and W. H. Martin, *Trans. Roy. Soc. Canada* **25**, 87 (1931); E. A. Cragler, *Phys. Rev.* **38**, 1387 (1931); H. H. Voge, *J. Chem. Phys.* **2**, 264 (1934); S. Leitmann and S. Uchodin, *Comptes rendus Acad. USSR* **4**, 14 (1934).

² A. Dadiou and K. W. F. Kohlrausch, *Wien. Ber.* **138**, 335 (1929); **139**, 77, 439 (1930); **140**, 293 (1931); E. H. L. Meyer, reference 1; P. Krishnamurti, *Ind. J. Phys.* **6**, 401 (1931); S. Parthasarths, *ibid.* **6**, 287 (1931) etc.

³ For once, such a parallelism was observed for HCl in dipole solvents (W. West and P. Arthur, *J. Chem. Phys.* **2**, 215 (1934)).