

THE INFRA-RED ABSORPTION SPECTRA OF BENZENE
AND ITS HALOGEN DERIVATIVESBY J. FENTON DAUGHERTY
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ABSTRACT

The infra-red absorption spectra of liquid benzene and its halogen derivatives have been measured from 1.00μ to 7.50μ . The near infra-red bands of benzene at 2.17μ , 2.45μ , and 2.71μ have been found to agree very well with the results of other observers, and several weak bands have been found which have not been previously noted. The region at 3.30μ has been studied in detail and different maxima have been found at 3.29μ , 3.32μ , and 3.44μ . The region from 5.00μ to 7.50μ shows five bands for benzene at 5.06μ , 5.56μ , 6.20μ , 6.74μ , and 7.16μ . The general absorption of the halogen derivatives is very much similar to that for benzene, however, the bands differ somewhat in position of the maxima, and in the weaker bands. The more intense bands in the near infra-red have been classified as overtones or combination bands, and the agreement between calculated and observed bands is satisfactory.

INTRODUCTION

THERE has been a large amount of work done in the study of the infra-red absorption of organic compounds, and some of the more important work has been done by Weniger,¹ who worked with forty-one alcohols, acids, and esters, also Johnson and Spence² studied twenty-four aniline dyes as far as 12μ , and Stang³ made a study of naphthalene and several of its monoderivatives in solution. More recent work by Bell⁴ has shown that in practically every case of eleven organic compounds studied a very strong band appears at 3.25μ . Ellis⁵ has investigated quite a number of organic compounds, and his results show great similarities among these spectra. From these investigations he was able to arrange the absorption bands in a series, and it was suggested that the origin of the different absorption bands may be traced to definite atoms, or pairs of atoms, as absorbing centers.

The present work was undertaken to obtain the complete absorption spectra from 1.00μ to 7.50μ , and to ascertain whether relationships could be found between the absorption bands. For this work benzene and the monohalogen derivatives, with the exception of mono-fluor-benzene, were studied. The object was twofold. First, to see if there existed any series relations between the bands of benzene, and second, to determine if there was any shifting of the maxima when a halogen was substituted for a hydrogen in the benzene ring.

¹ W. Weniger, *Phys. Rev.* **31**, 388 (1910).

² Johnson and Spence, *Phys. Rev.* **5**, 349 (1915).

³ A. H. Stang, *Phys. Rev.* **9**, 542 (1917).

⁴ F. K. Bell, *Jour. Amer. Chem. Soc.* **47**, 2192 (1925).

⁵ J. W. Ellis, *Phys. Rev.* **23**, 48 (1924); *Phys. Rev.* **27**, 298 (1926).

EXPERIMENTAL PROCEDURE

In the present work two different instruments were employed. For the investigation of the spectrum from 1.00μ to 3.50μ a Hilger D42 infra-red spectrometer of large aperture with quartz prism was used, and for the region from 3.50μ to 7.50μ a Hilger D35 instrument with rock-salt prism was employed. The thermopile, which was interchangeable with either instrument, was of the linear Rubens type. This was quite an advantage since once the galvanometer circuit was critically damped, it was just a matter of changing the thermopile when shifting from one instrument to the other. A Leeds and Northrup galvanometer of 10 ohms resistance and a sensitivity of 10 mm per microvolt was used.

Both spectrometers were first calibrated by setting the wave-length drum for the *D*-lines. A further check was used as a means of calibration. The positions of the water bands as determined by Collins⁶ were used to determine the accuracy of the calibration in the regions to be studied, and a very good agreement was found to exist. It was found that a small correction of the order of 0.01μ must be added to the observed readings in the region from 1.00μ to 3.50μ , when the D42 spectrometer was used. The D35 instrument was employed when investigating the region from 5.00μ to 7.50μ , and it was found on checking the calibration for the water vapor band at 6.26μ a correction of 0.04μ was necessary.

All the materials studied were first run with slit-widths of 0.25 mm, except in the case of the D35 spectrometer where the collimator slit was 0.39 mm. This gave the general outline of the absorption curves. Having thus located the approximate positions of the absorption maxima, the thermopile slit of the D35 spectrometer was reduced to 0.203 mm, and the collimator slit to 0.303 mm. For the D35 instrument the spectrum embraced by the thermopile in the region of 6.26μ , when the thermopile slit is at 0.25 mm, was 0.155μ , and with the thermopile slit at 0.203 mm, the region exposed to the thermopile would be 0.124μ . When the D42 spectrometer was used with slit-widths of 0.25 mm, the portion of the spectrum embraced by the thermopile in the region of 2.70μ , was 0.015μ , and when the thermopile slit was reduced to 0.125 mm, the portion of the spectrum exposed to the thermopile would be 0.0075μ .

The cells employed in this work were made by gluing, with Le Page's liquid glue, the windows of glass, polished fused quartz, fluorite, or rock-salt as the case might be, to pieces of lead foil or lead sheet depending upon the thickness of cell desired. One window was glued to the lead, glue put on the outer edge of the other window, the hollow part of the lead was then filled with the liquid to be studied, by means of a pipette, and the second window slipped into place. The cell was then clamped in its mount which consisted of two brass disks held together by four bolts. This mount was then placed on a board which was free to move in guides, between fixed limits, and was so arranged that a mirror focused an image of the source on the cell, and a

⁶ J. R. Collins, Phys. Rev. **26**, 771 (1925).

second mirror focused this image on the collimator slit of the spectrometer. A diaphragm, with aperture slightly smaller than the diameter of the cell, was placed immediately in front of the cell. The whole assembly was so arranged that the observer could move the cell in and out of the beam of radiation, read the galvanometer deflections, and set the spectrometer wavelength drum without leaving his position.

In Table I will be found cell thicknesses, material of cell windows, and the intervals at which readings were taken for different parts of the spectrum studied.

TABLE I. Shows cell thicknesses for different parts of the spectrum studied; materials of which cell windows were made; and intervals at which readings were taken for the different parts of the spectrum.

Portion of spectrum	Thickness of cell	Material of cell windows	Intervals at which readings were taken
From 1.00 μ to 1.25 μ	5.25 cm	Ordinary glass	Every 0.01 μ over the whole range and every 0.005 μ at the center of the bands.
1.25 μ to 2.00 μ	3.35 cm	Polished fused quartz	
2.00 μ to 2.80 μ	0.074 cm	Polished fused quartz	
2.80 μ to 3.50 μ	0.012 cm	Microscope cover glasses	
5.00 μ to 7.50 μ	0.024 cm	Fluorite and rock-salt	Every 0.02 μ and at the center of bands every 0.01 μ .

The source of radiation was a Globar element (55 volts) about three inches long. The center of the element was ground away to about one half the diameter of the original piece. This prevented the ends from becoming overheated and reduced sparking at the end contacts to a minimum. In order to have the source as steady as possible it was operated from a bank of storage batteries. By means of a variable resistance, in series with the Globar element, the desired intensity could be obtained. In the present work currents from 2.4 to 3.0 amperes were employed. In a single run, however, the current was kept very nearly constant.

The benzene was obtained from the Chemistry Department of the University of North Carolina, and was known to contain 0.003 percent of carbon disulphide. This small trace should cause no serious difficulty, as carbon disulphide is very transparent for the region of the spectrum studied, except for one large maximum at about 4.60 μ . The other substances were obtained from the Eastman Kodak Laboratories. A boiling point test was made for all the substances and the results checked well with the true boiling points.

RESULTS AND DISCUSSION

The infra-red absorption spectra of benzene, and its mono-halogen derivatives were studied from 1.00μ to 7.50μ . Table II gives a list of all the maxima observed for the four materials, some of which appear only as slight inflections of the curves being marked by an (*), some other regions which appear only as slight inflections, and may be considered as bands, are not given in the list. Twenty-eight absorption maxima are listed for benzene, and about the same number for each of the halogen derivatives. The more in-

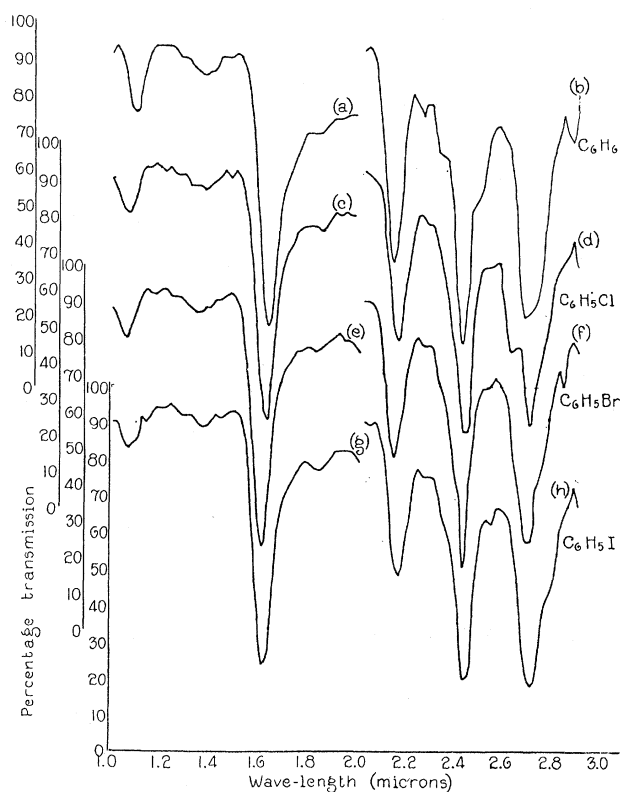


Fig. 1. Curves (a) and (b), benzene; curves (c) and (d), mono-chloro-benzene; curves (e) and (f), mono-bromo-benzene; curves (g) and (h), mono-iodo-benzene.

tense maxima, which are set forth in curves (a) and (b), Fig. 1, are in good accord with those found by other workers in this region.⁷ The values of the maxima observed by the writer in every case are slightly less than those given by other observers. This may be due to a difference in calibration or a temperature effect.

A very thorough study was made of the bands for benzene in the region from 1.00μ to 1.90μ , the results of which are shown in curves (a) and (b), Fig. 2. It appears that the maximum at 1.12μ has associated with it a smaller

⁷ Th. Dreisch, *Zeits. f. Physik* 30, 200 (1924).

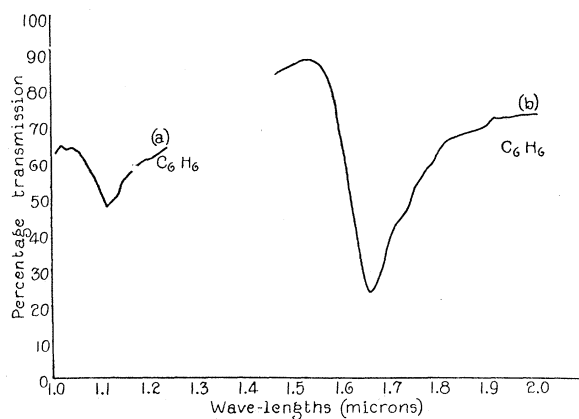


Fig. 2. Curves (a) and (b), benzene.

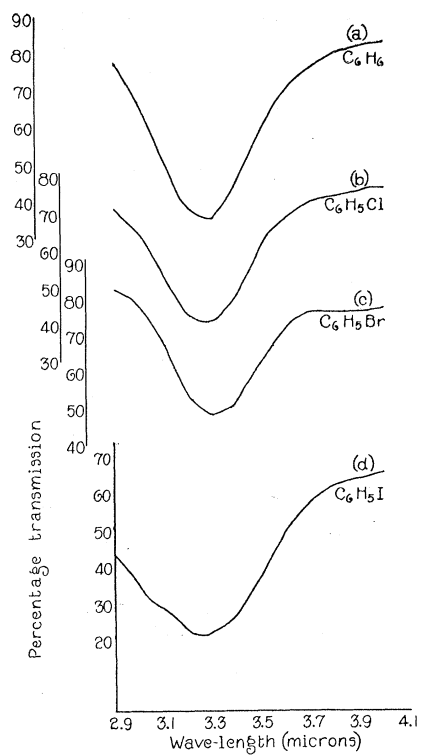


Fig. 3. Curve (a), benzene; curve (b), mono-chloro-benzene; curve (c), mono-bromo-benzene; curve (d), mono-iodo-benzene.

maximum at 1.14μ . Barnes and Fulweiler⁸ have made a study of this region with a grating and have found maxima at 1.1372μ and 1.1445μ for this band.

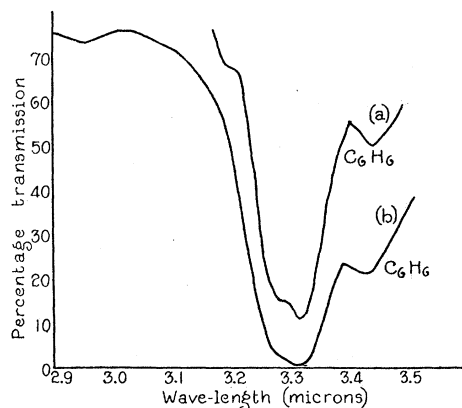


Fig. 4. Curves (a) and (b), benzene.

In addition to the more intense maximum at 1.66μ there appear three smaller maxima, one at 1.72μ , one at 1.78μ and another at 1.88μ .

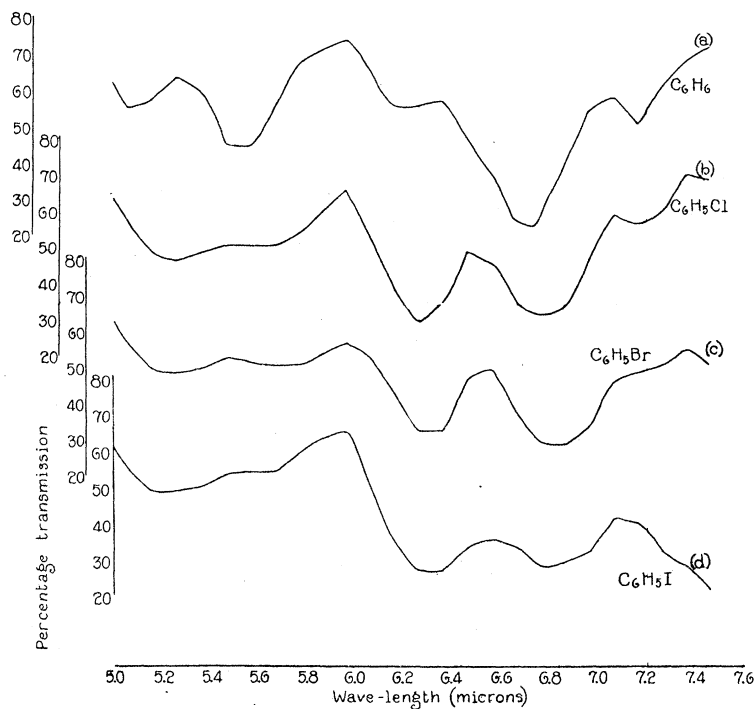


Fig. 5. Curve (a), benzene; curve (b), mono-chloro-benzene; curve (c), mono-bromo-benzene; curve (d), mono-iodo-benzene.

⁸ Barnes and Fulweiler, Phys. Rev. **32**, 618 (1928).

It will be noted from the curves of Figs. 1, 3, and 5, that the infra-red absorption spectra for the four materials studied show great similarity throughout the whole region. There are some instances where a shifting of the bands occurs, but it does not appear, from the observed results, that this shifting follows any definite rule. For instance, consider the maximum which occurs at 1.66μ for benzene. If by substituting in the benzene ring a heavier atom for a lighter hydrogen atom causes any shifting of the bands, one would expect mono-iodo-benzene to show the greatest shift as this is the heaviest molecule studied. For mono-chloro-benzene the band occurs at 1.65μ which indicates a slight shift toward the shorter wave-length region. For mono-bromo-benzene which is heavier than mono-chloro-benzene, there appears to be a slight shift again as the band is found at 1.63μ . But in the case of mono-iodo-benzene the maximum occurs at the same position, 1.63μ , as the maximum for mono-bromo-benzene. By comparison of the absorption spectra of the different materials studied, it is seen that the intensity of the observed maxima does not seem to be greatly affected when a halogen is substituted in the molecule.

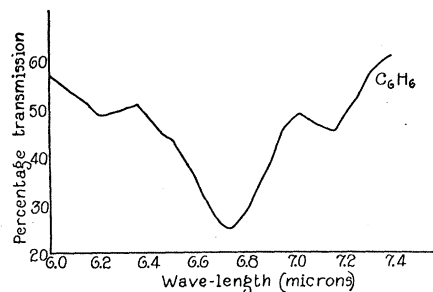


Fig. 6. Curve for benzene.

On the basis of theory benzene is symmetrically constituted and is composed of six carbon atoms and six hydrogen atoms. The most probable arrangement, according to Beckenkamp⁹ is that the centers of gravity of the carbon atoms form a spacial six membered ring, while the hydrogen atoms which lie with their axis perpendicular to the main axis of the molecule form a plane ring. This arrangement permits of a possibility of thirty modes of vibration since there are twelve particles. It is likely, however, that some of the vibrations have the same frequency or are inactive.

While the number of actual modes of vibration is not known, due to their intensity and location the following maxima were assumed to be fundamentals, 3.30μ , 6.74μ , 9.80μ ; the last value is taken from the work of Coblenz.¹⁰ Also a band at 15.5μ which was calculated from observed maxima, is considered to be a fundamental band. These fundamentals were given the following frequency notation ν_1 , ν_2 , ν_3 , and ν_4 respectively.

By means of the formula $\nu_n = n\nu_0 (1 - nx)$, where ν_n and ν_0 are expressed in wave numbers and (x) is a constant, a check for the position of the funda-

⁹ J. Bechenkamp, *Zeits. f. Anorg. Chem.* **139**, 220 (1924).

¹⁰ W. W. Coblenz, *Investigations of Infra-red Spectra*, Carnegie Bull. 35, (1905).

mental at 3.30μ was obtained. Assuming that the 1.66μ maximum is the first overtone of the above fundamental, and 1.12μ is the second overtone, a calculated value of ν_1 in good agreement with the observed value was found.

Since the maximum at 2.71μ is not identified as a fundamental or overtone, it is assumed to be due to a combination of two fundamental frequencies. This combination, on account of its intensity, probably includes (ν_1) as one of

TABLE II. Observed bands for benzene and its halogen derivatives.

Benzene	Mono-chloro-benzene	Mono-bromo-benzene	Mono-iodo-benzene	Benzene	Mono-chloro-benzene	Mono-bromo-benzene	Mono-iodo-benzene
1.06 μ^*				2.45	2.46	2.45	2.45
1.12	1.09 μ	1.08 μ	1.08 μ	2.51*	2.65*	2.55*	2.57
1.14*	1.17*	1.19*	1.16*	2.71	2.73	2.72	2.73
1.31*	1.24*	1.28*	1.22*	2.91*	2.87*	2.87*	
1.40	1.30*		1.32*	2.95*			
1.43	1.40	1.37	1.39	3.29*			
1.48*	1.50*	1.45*	1.46*	3.32	3.28	3.30	3.26
1.66	1.65	1.63	1.63	3.44			
1.72*				4.43*	4.43*	4.43*	4.43*
1.78*		1.78*		5.06	5.26	5.26	5.20
1.88*	1.87*	1.85*	1.86*	5.56	5.56	5.70	5.60
2.17	2.19	2.17	2.19	6.20	6.26	6.30	6.30
2.29*	2.31*	2.31*	2.31*	6.74	6.76	6.86	6.76
2.37*				7.16	7.16	7.16	7.28*

the component bands. By subtracting the frequency of (ν_1), a value is obtained which corresponds to a band at 15.5μ , this being assumed as a fundamental band. In the work of Coblenz¹⁰ it is noticed that for benzene a very broad region of absorption begins at about 14.4μ and continues to 15.0μ , where his observations end. It is difficult to say where the center of the absorption band is located. If a thinner cell were used, it is very likely from the appearance of the other fundamentals observed, that the center of the band would be located in the region from 15.0μ to 16.0μ . This gives considerable evidence that there exists an intense fundamental for benzene in this region. A list of all the fundamentals, overtones, and combinations which the other bands are attributed to are given in Table III.

In the work of Ellis⁵ there was a classification of the bands of benzene and it is interesting to make a comparison with the classification in the present work. Ellis considered the spectrum of benzene to consist of two fundamentals, one at 28μ and another at 6.44μ , and that all near infra-red bands were overtones or combinations of these two frequencies. Thus a band at 1.03μ was attributed to the twenty-eighth overtone of the band at 28.0μ . Several observed bands in the region from 1.00μ to 5.00μ are attributed to combinations. The intense band, for example, at 2.18μ is identified as the combination of one fundamental and the eighth overtone of the other. In the present work the bands in the near infra-red are assumed to arise from four fundamentals instead of two and the combinations do not include any overtones above the third. The present classification appears to be more in accord with the ob-

¹¹ J. E. Purvis, Proc. Cam. Phil. Soc. **21**, 556 (1922-23).

served intensities, but a careful study has not been made of the intensities of the bands.

In conclusion from the present work the experimental data seems to indicate for benzene in the liquid state, that there exists only minor differences in the general absorption from its halogen derivatives. However, when the individual bands are considered in detail, they are found to occur at slightly different wave-lengths, and the weak bands occur in some of the liquids that are not observed in the others. It is probable that if these materials were studied in the gaseous state under high resolution, so that the individual lines

TABLE III. Calculated and observed wave-lengths for benzene and its mono-halogen derivatives.

Combination	Observed wave No.	Calculated λ	Observed λ	Observed wave No.	Calculated λ	Observed λ
	For benzene			For mono-chloro-benzene		
ν_1	3052.6	3.28 μ	3.30 μ	3016.7	3.32 μ	3.28 μ
ν_2	1483.7		6.74	1479.3		6.76
ν_3	1020.4		9.80*	1077.6		9.28*
ν_4	644.2	15.50		653.0	15.30	
$2\nu_1$	6042.3		1.66	6060.6		1.65
$3\nu_1$	8968.8		1.12	9174.3		1.09
$\nu_1 + \nu_2$	4536.3	2.20	2.17	4496.0	2.22	2.19
$\nu_1 + \nu_3$	4073.0	2.46	2.45	4094.3	2.44	2.46
$\nu_1 + \nu_4$	3696.8		2.71	3669.7		2.73
$2\nu_1 + \nu_2$	7526.0	1.33	1.31	7539.9	1.32	1.30
$2\nu_1 + \nu_3$	7062.7	1.42	1.43	7138.2	1.40	1.40
$2\nu_1 + \nu_4$	6686.5	1.50	1.48	6713.6	1.49	1.50
$3\nu_1 + \nu_4$	9613.0	1.04	1.06			
	For mono-bromo-benzene			For mono-iodo-benzene		
ν_1	3053.0	3.26 μ	3.30 μ	3053.0	3.26 μ	3.26 μ
ν_2	1457.7		6.86	1479.3		6.76
ν_3	1061.6		9.42*	1052.6		9.50**
ν_4	630.2	15.80		616.7	16.20	
$2\nu_1$	6153.9		1.63	6153.9		1.63
$3\nu_1$	9302.5		1.08	9302.5		1.08
$\nu_1 + \nu_2$	4510.7	2.22	2.18	4532.3	2.21	2.19
$\nu_1 + \nu_3$	4114.6	2.43	2.45	4105.6	2.44	2.45
$\nu_1 + \nu_4$	3683.2		2.72	3669.7		2.73
$2\nu_1 + \nu_2$	7611.6	1.32	1.28	7633.2	1.31	1.32
$2\nu_1 + \nu_3$	7215.5	1.39	1.37	7206.5	1.39	1.39
$2\nu_1 + \nu_4$	6784.1	1.47	1.45	6770.6	1.48	1.46

* Indicate values taken from work of Coblentz.¹⁰

** Indicates value taken from work of Purvis.¹¹

in the vibration rotational bands would appear, that considerable differences would be noticed.

It has been possible to classify all the more intense bands in the near infra-red region as observed by the writer and other workers. No doubt all the bands could have been classified if the wave-lengths of all the fundamentals were known.

The writer wishes to express his appreciation and thanks to Dr. E. K. Plyler, of the University of North Carolina, for suggesting the original problem, and for his encouragement throughout the duration of the work.