

The Absorption Spectrum of Benzene in the Region of 6.75μ

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(Received July 5, 1932)

The absorption band of benzene lying at 6.75μ has been investigated under high resolution for both liquid and gaseous states. The spectrum for the vapor shows three distinct branches with evidence of unresolved fine structure. The liquid shows a less regular spectrum with a definite shift towards longer wave-lengths. In addition, some new water vapor lines in the 6.26μ band are reported.

IN RECENT years an increasing amount of work has been done investigating the infrared absorption and Raman spectra of organic substances. The success which followed the unravelling of the fine structure of some of the more simple compounds led to attempts to resolve the spectra of molecules of increasing complexity. Among the group offering promise due to its complete symmetry is benzene, which has been investigated by a number of workers.^{1,2,3,4,5,6} Particularly in the last two or three years, considerable work has been done in the near infrared in this laboratory by Barnes⁶ and Leberknight.^{7*} Continued improvements in apparatus and resolving power, consisting chiefly of the employment of the Pfund anastigmatic spectrometer with echelette gratings of high resolution, have led to discovery of new bands, and increased complexity in some of the older ones. These studies have thus far been restricted primarily to the region in the neighborhood of 3μ . Bands which previously were so broad as to permit, at best, mere designation as combinations of various vibrational frequencies began to show some evidence of vibration-rotation structure. As a result of several discussions with Dr. C. E. Leberknight, the writer felt that it might be profitable to examine in great detail one of the bands somewhat farther out. The band at 6.75μ , which is quite intense and hence probably represents a fundamental vibration, offered excellent possibilities.

For the purpose of this investigation, the grating spectrometer employing the resonance radiometer, which was used in a recent mapping of the absorption and reflection spectrum of calcite,⁸ was found readily adaptable. The grating had 1364 lines per inch; the slit-width was 20A. As in this previous experiment, a magnesium-oxide filter was used to remove the higher

* In this work, which is soon to be published, the spectrum of benzene was investigated in solid, liquid and gaseous states in the region of 3μ under high resolution.

¹ Dougherty, Phys. Rev. **34**, 1549 (1929).

² J. Ellis, Phys. Rev. **27**, 298 (1926).

³ K. W. F. Kohlrausch, *Der Smekal-Raman Effekt* (Springer 1931).

⁴ Schaefer and Matossi, *Das Ultrarote Spektrum*. P. 270 ff.

⁵ R. B. Barnes, Phys. Rev. **35**, 1524 (1930).

⁶ R. B. Barnes, Phys. Rev. **36**, 296 (1930).

⁷ C. E. Leberknight, unpublished results.

⁸ S. Silverman, Phys. Rev. **39**, 72 (1932).

orders of shorter wave-lengths. The instrument was calibrated by means of visual observation of higher orders of the 5461 mercury line, and also by prominent atmospheric absorption lines.⁹ The vapor cell was prepared by sealing polished rock-salt windows to the ends of a brass tube. The cement used was a clear lacquer which was found to be almost completely unattacked by the benzene. The optimum cell length was found to be about 22 mm, which length of vapor absorbed 50 percent of the incident energy in the neighborhood of the absorption maximum. A free surface of liquid benzene was kept continually in the bottom of the cell in order to maintain constantly saturation pressure. No difficulty due to condensation on the windows was experienced. A dummy cell was prepared to give a comparison set of readings, as all measurements were taken *cell-in* and *cell-out*. The liquid cell consisted of two flat plates of rock salt, separated by thin strips of silver-foil 0.01 mm thick. This thickness of liquid gives the equivalent molecular path length of 22 mm of gas; this is desirable, as it is essential for direct comparison of gas and liquid to have very much the same *molecular thickness* to traverse. The cell was made tight on 3 sides with lacquer, and the 4th, open, side was fed occasionally with liquid from a pipette; an identical dummy cell was also prepared. The cells maintained their performance unaltered throughout the duration of the experiment.

RESULTS

The absorption in the vapor cell shows the 6.75μ band to be clearly divided into three distinct bands lying at 6.683 ; 6.743 ; 6.790μ respectively; the band at 6.743 being somewhat broader and slightly more intense than

TABLE I. *Absorption maxima for benzene.*

Vapor λ	ν	Liquid λ	ν
$6.683 \pm 0.0015\mu$	1496.3 ± 0.4	6.643μ	1505.3 ± 0.4
6.743	1483.0	6.683	1496.3
6.790	1472.8	6.753	1480.8
		6.830	1468.1

its companions. All three of the branches show clear evidence of unresolved fine structure, with small but distinct maxima separated by intervals as small as 2 wave numbers. It is entirely probable, however, that the true fine structure of the band is such as to defy resolution by the instrument at our disposal; in which case these small maxima would have no meaning other than to indicate the presence of other fine structure. Inasmuch as the benzene is so complex and has such a large moment of inertia (in the neighborhood of $11 \times 10^{-39} \text{g} \times \text{cm}^2$) one would expect the structure to be very complicated and the lines to be densely packed.

The absorption of the liquid presented a less attractive map. The central band from the vapor absorption is sharpened slightly with a shift from 6.743 to 6.753μ . The band at 6.683 has been so altered as to bear little resemblance

⁹ Plyler and Sleator, Phys. Rev. **37**, 1493 (1931).

to the gaseous state. It is much weaker, being nearly washed out, and shows two maxima: one at 6.643 and one at 6.683μ . The 3rd band has also changed so as to present an entirely new picture. It is much broader than its counterpart in the vapor state, and it is quite irregular in outline, with its maximum at 6.830μ . Its intensity is about that of the corresponding vapor band.

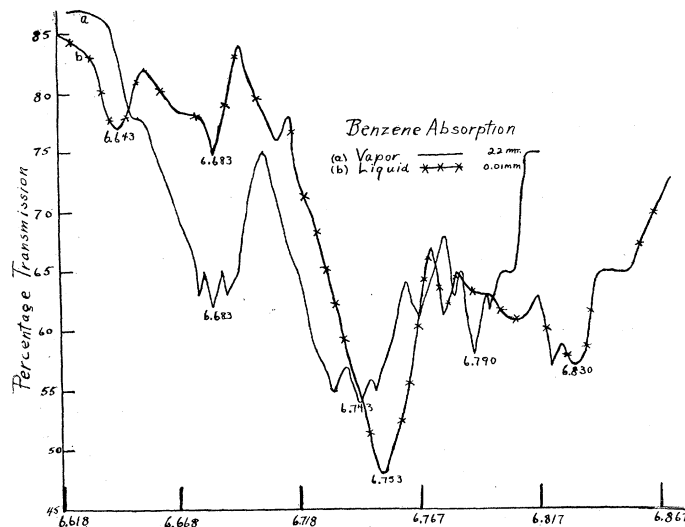


Fig. 1.

It is perhaps worthy of note that in the plotting of this spectrum many runs of the atmospheric absorption bands were obtained. An admirable check of many lines found recently by Plyler and Sleator⁹ was obtained. In addition some new ones, marked by the above authors as missing, were observed. These are listed in Table II.

TABLE II. *New absorption lines in water vapor.*

λ	ν	λ	ν
$6.284 \pm 0.0015\mu$	1591.3 ± 0.4	$6.367 \pm 0.0015\mu$	1570.6 ± 0.4
6.294	1588.8	6.480	1543.2
6.299	1587.6	6.485	1542.0
6.313	1584.0	6.583	1519.1

In conclusion, it might be remarked that at present it appears impossible to derive a detailed description of the quantum states of the benzene molecule from the data at hand. The present investigation has shown the existence of hitherto undiscovered fine structure, and it is planned further to probe the spectrum with instruments of still higher resolution in an attempt to unravel the fine detail.

The writer takes great pleasure in expressing his thanks to Dr. C. E. Leberknight for many fruitful discussions concerning this experiment. He also wishes to acknowledge a Grant-in-aid of the National Research Council which has helped make this investigation possible.