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# The Infrared Absorption of Benzene in the Liquid, Solid and Vapor States

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The $2.19\mu$, $2.46\mu$, and $3.25\mu$ infrared absorption regions of benzene were investigated in the liquid, solid and vapor states with a grating spectrograph whose theoretical resolving power was almost 15,000. For all the bands measured the solid absorption was approximately the same as that of the liquid but with the bands shifted slightly towards longer wave-lengths; the $3.25\mu$ and $2.46\mu$ bands showed a shift of about 13A, and the bands lying in the $2.19\mu$ region showed a shift of about 20A. In the vapor the absorption was quite different from that of the liquid. The $3.25\mu$ region had two strong bands in the vapor, each showing evidences of three components, while the liquid had three bands; interpreting the three components of the vapor bands as the envelopes of the vibration-rotation bands the value, $14\times10^{-39}$ g cm$^2$, is obtained for the moment of inertia of the benzene molecule. The $2.46\mu$ region showed a doublet in the vapor while the liquid had a single strong band. The $2.19\mu$ region showed two bands incompletely resolved in the vapor, but the liquid and solid showed a group of five bands with indications of a sixth.

## INTRODUCTION

IN investigating the problem of the structure of molecules, it is customary to proceed from the dynamical standpoint, that is, by the determination of the modes of vibration of the atoms or radicals within the molecule. These vibrations, being of comparatively low frequency, give rise to absorption bands in the infrared portion of the spectrum and can be determined from an analysis of the absorption spectrum of the molecule. Much work has been done with powerful instruments on the absorption of substances in the gaseous state, but little has been done on the absorption bands of a substance in the liquid, solid and vapor states with instruments of high resolving power.

In the case of benzene, few studies have been conducted with particular regard to its infrared absorption in the three states. Also, the region between $2\mu$ and $4\mu$ has been only meagerly explored with instruments of high resolving power. Barnes[1] studied the $3.25\mu$ band of liquid benzene and Meyer,[2] the same band in the vapor state. Dreisch[3] measured the absorption of liquid and gaseous benzene up to $2.7\mu$. He reports bands at $2.188\mu$ and $2.488\mu$, and a change in the magnitude of the absorption accompanied by a slight shift of the bands towards shorter wave-lengths in the vapor. This work was done with a prism spectrograph whose resolving power above $2\mu$ was low. Using a grating spectrograph of high resolving power, Barnes found the $3.25\mu$ band of liquid benzene to consist of three components of approximately the same intensity lying close together. Meyer, with a grating spectrograph, found a broad doublet in the vapor in the same region. Since the shift in the absorption bands as found by Dreisch between the liquid and vapor states is small and since there is no experimental information concerning the infrared absorption of solid benzene, this work was undertaken to measure the $2.188\mu$, $2.488\mu$, and $3.25\mu$ bands of benzene in the three states with a grating spectrograph of high resolving power which would enable a careful study to be made of the changes in the absorption involved in the change of state.

## APPARATUS

A diagram of the apparatus used in this investigation is shown in Fig. 1a. *G* is an echelette grating; two gratings were used, both being 3600 line gratings with a ruled surface of four inches thus giving a theoretical resolving power of almost 15,000. One of these gratings concentrated the energy at $4\mu$ while the other had its region of concentration at $2.7\mu$. The optical system has been described by Barnes.[1] The path of light

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[1] Barnes, Phys. Rev. **35**, 1528 (1930); Phys. Rev. **36**, 296 (1930).

[2] Meyer, J. O. S. A. **15**, 257 (1927).

[3] Dreisch, Zeits. f. Physik **30**, 200 (1924).

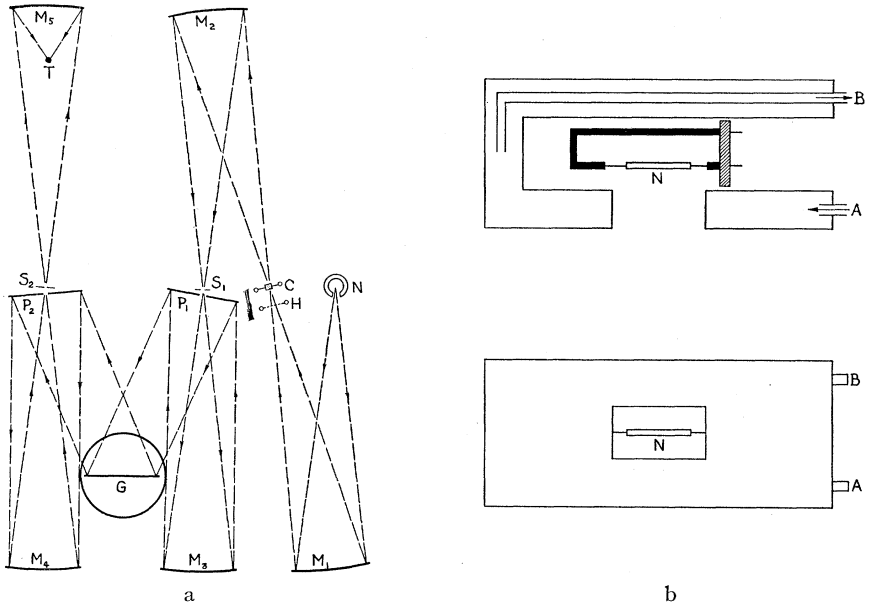

FIG. 1a. Diagram of the optical system; b. Diagram of the water cooler for the Nernst glower.

through the system is made clear in the diagram. By employing plane mirrors in the manner shown it is possible to use the concave mirrors along their axes and thus minimize the aberrations; in fact, with the width of the first slit equal to 0.1 mm the image of the visible mercury lines is formed straight and well defined.

A vacuum thermocouple was used in series with a high sensitivity Kipp and Zonen galvanometer to measure the intensity of the radiation. Although the thermocouple was not a compensating one, the drift of the galvanometer current was so very small that continuous readings could be taken without determining zero readings at each setting of the grating. The galvanometer deflections were read to 0.5 mm on a scale at a distance of five meters.

The source of radiation was a Nernst glower which operated at 220 volts and 0.6 amperes from a large storage battery. The glower was shielded with a water cooler to minimize convection currents. (Fig. 1b.)

## CALIBRATION

By observing the grating settings which directed the various orders of the visible mercury spectrum on the second slit, a calibration more accurate than 5A was obtained. The grating, mounted on a spectrometer table, could be rotated by the observer from a distance of three meters at which distance the rotation was measured by the motion of the image of an incandescent filament formed on a scale. The light from an incandescent lamp was reflected twice from a mirror fixed to the grating and then focussed on the scale so that the image of one of the filaments could be used as an indicator. A motion of the image on the scale of 1 mm corresponded to a change of wave-length falling on the slit $S_2$ of about 9A. In order to avoid the use of the long scale required to read from $2\mu$ to $3.5\mu$ a single scale 1 meter in length was used, but instead of a single mirror attached to the grating, two mirrors were used inclined at a small angle to each other in such a manner that when the image from the one mirror left the scale the image from the other came on. The instrument was calibrated before and after each set of readings by means of the higher orders of the visible mercury lines; in addition, the calibration was checked by taking readings on the third order of the $1.0140\mu$ emission line of mercury.

## PROCEDURE

In taking measurements in any part of the spectrum precautions had to be taken to eliminate the effect of superimposed orders on the thermocouple which results from the fact that the radiation falling on $S_1$ contains a wide range of wave-lengths. This effect was practically eliminated by the use of filters whose preparation has been described by Pfund.[4] A film of zinc oxide deposited on a quartz plate was found to be quite satisfactory for the region between $2\mu$ and $3.5\mu$. In Fig. 2 is shown the transmission curve of this filter whose efficiency is such that the contamination of lower wave-length energy is less than 2 percent at $2\mu$; about 7 percent at $2.6\mu$; and about 35 percent at $3.3\mu$, using the Nernst glower as the source. To be quite certain that the bands measured were not higher orders of lower wave-lengths, two other filters were used whose transmission curves are also shown on Fig. 2. As is seen from the curve, the transmission of the Corex glass filter is zero above $3\mu$ and high at $1.5\mu$; hence the bands at $3.25\mu$ should disappear when this filter is used, and such was the case. The same procedure was followed with the Pollopas filter to test the bands at $2.19\mu$ and $2.46\mu$. Pollopas is a urea-formaldehyde condensation product.

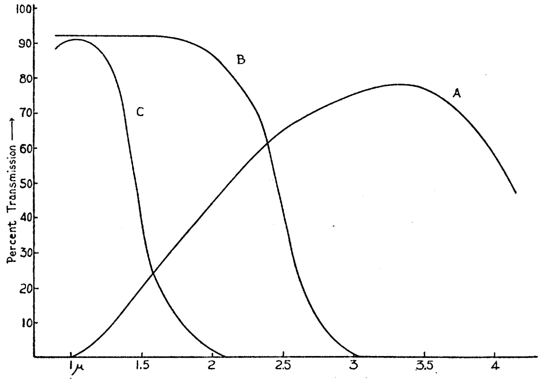

FIG. 2. Transmission curves of the filters; *A*, zinc oxide deposited on a quartz plate; *B*, corex "A" glass, 5.37 mm thick; *C*, pollopas, 4.45 mm thick.

In taking readings, settings were made at 1 mm intervals on the scale which corresponded to a change of wave-length of about 9A; tenths on the scale could be estimated easily. With the exception of the measurements on the solid and those on the vapor at $2.19\mu$, at each setting of the grating a zero reading was taken, and then readings were taken with the cell in the light path and with the radiation passing through a dummy cell. In the case of the measurements on the solid and those with the long cell required for the vapor at $2.19\mu$ this method was not feasible. In these cases continuous readings were taken; this procedure being justified because of the fact that there was little drift in the thermocouple current. To be certain of the small shifts occurring between the bands in the liquid and solid states measurements were made with the liquid, then solid, then liquid, etc.

The benzene used was obtained from Merck and was dried by distilling it with phosphorus pentoxide. For the liquid measurements the benzene was contained in small cells with microscope cover glass windows; these cells have been described by Barnes.[1] In the case of the frozen benzene these same cells were placed in a brass tube which was packed in carbon dioxide snow; at first there was trouble with moisture condensing on the windows but this was eliminated by blowing a stream of dry air on the windows. For the measurements in the vapor state the benzene was contained in brass tubes with quartz windows; the length of the cell being so chosen with respect to the thickness of the liquid cell that there were approximately the same number of molecules in the light path in the two cases.

## RESULTS

The absorption curves of benzene in the three states for the bands lying in the $2.19\mu$, $2.46\mu$ and $3.25\mu$ regions are shown in Figs. 3–5; and the wave-lengths of the absorption bands are listed in Table I. In this table column 1 gives the wave-lengths of the absorption bands for the liquid, column 2 gives the shifts of the bands in passing from the liquid to the solid at the temperature of carbon dioxide snow, and column 3 gives the wave-lengths of the bands in the vapor state. For all the bands measured it is evident that there is no difference in the type of absorption in passing from the liquid to the solid; in each of the regions of absorption the relative intensity of the individual bands is approximately the same in the two states, but there is a small shift in the position of the bands towards longer wave-

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[4] Pfund, Phys. Rev. **36**, 71 (1930).

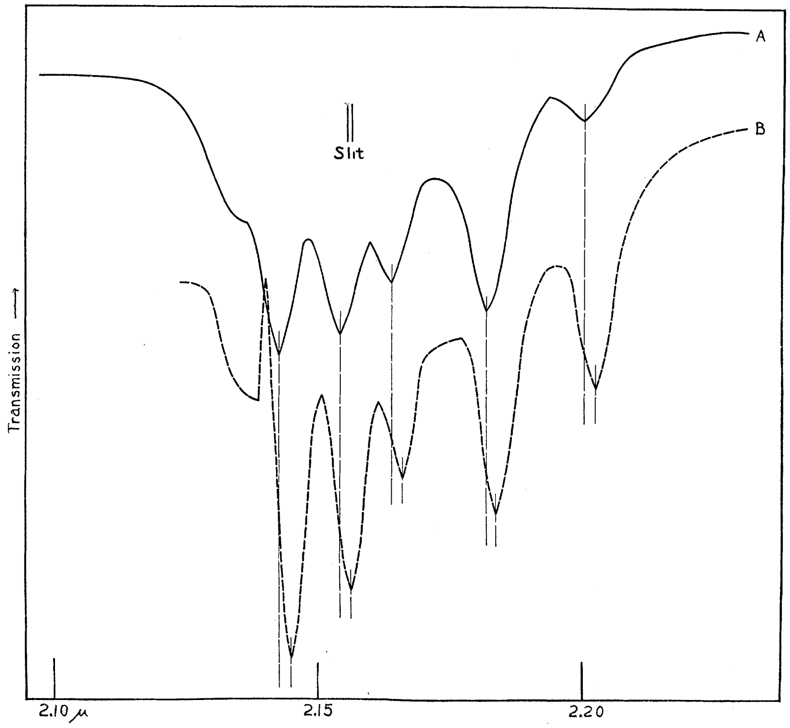

FIG. 3. Absorption curves for the 2.18μ band in the liquid and solid states; *A*, liquid cell = 0.15 mm; *B*, solid cell = 0.15 mm; slit = 12A.

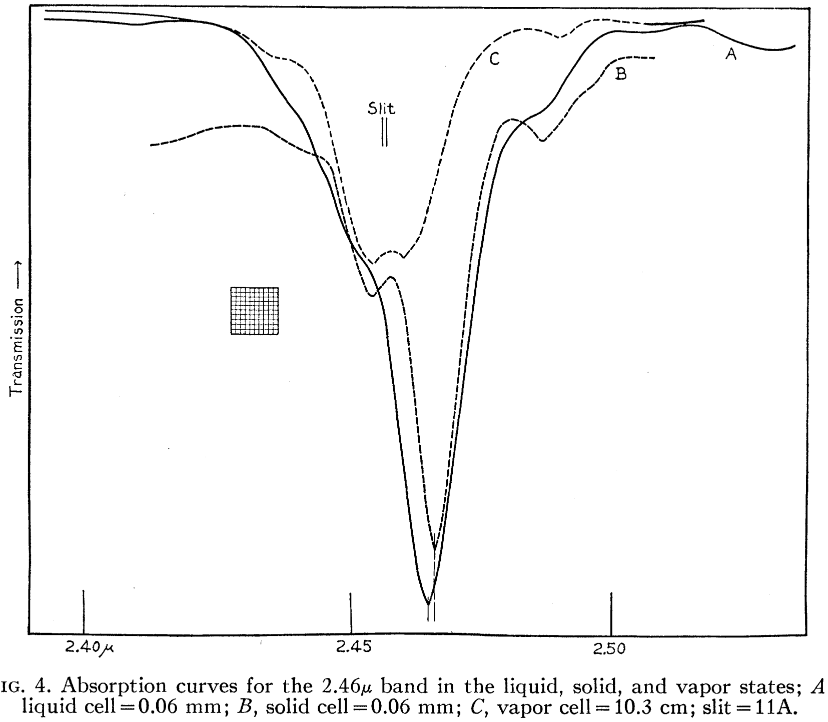

FIG. 4. Absorption curves for the 2.46μ band in the liquid, solid, and vapor states; *A*, liquid cell = 0.06 mm; *B*, solid cell = 0.06 mm; *C*, vapor cell = 10.3 cm; slit = 11A.

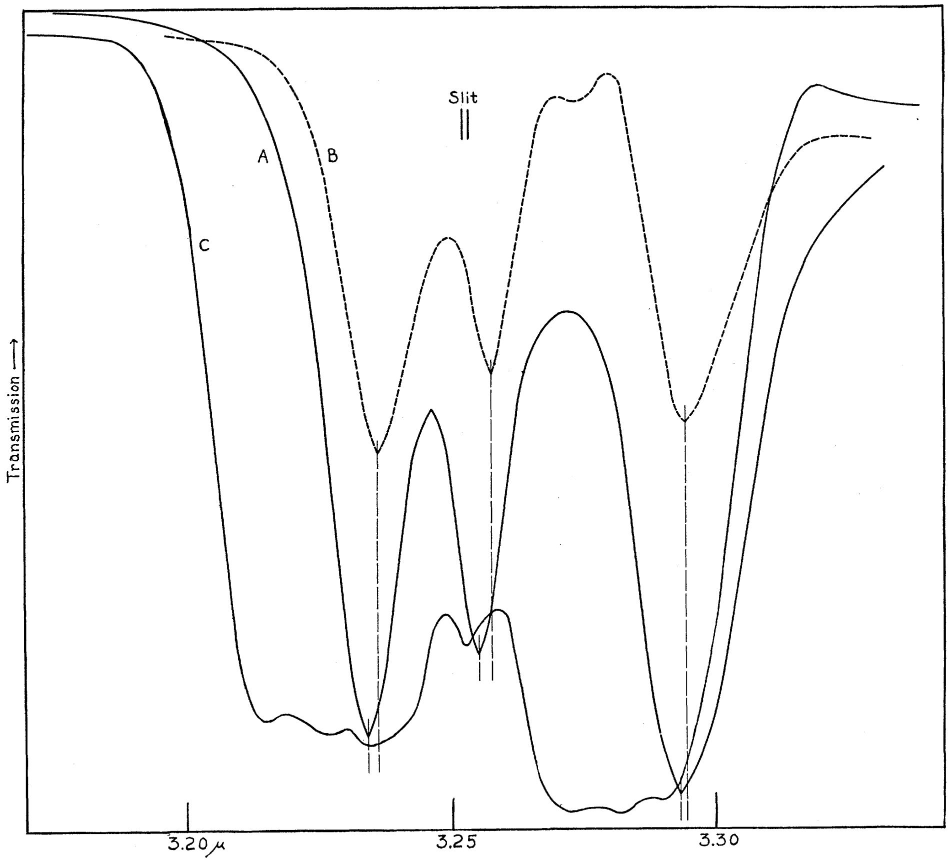

FIG. 5. Absorption curves for the 3.25μ band in the liquid, solid, and vapor states; *A*, liquid cell =0.02 mm; *B*, solid cell=0.02 mm; *C*, vapor cell=4 cm; slit=13A.

TABLE I.

| Liquid | Liquid to Solid | Vapor |
|---|---|---|
| 3.235μ | +0.0013μ | 3.217μ<br>3.226<br>3.236 |
| 3.256 | +0.0024 | |
| 3.294 | +0.0012 | 3.273<br>3.283<br>3.292 |
| | 2.454μ | |
| 2.464 | +0.0013<br>2.486μ | 2.452<br>2.462 |
| 2.144 | +0.0020 | |
| 2.155 | +0.0020 | 2.148 |
| 2.164 | +0.0020 | |
| 2.183 | +0.0019 | 2.175 |
| 2.202 | +0.0020 | |

lengths in the solid absorption. The curves show very clearly, however, that there is a difference in absorption in passing from the liquid to the vapor state, and also that in the vapor the envelope of the vibration-rotation bands appears.

### 3.25μ region

The absorption curves for the bands lying in this region are shown in Fig. 3. The measurements on the liquid and solid were made with cells of 0.02 mm in thickness while those on the vapor were made with a cell of 4 cm in length. In the liquid there are three absorption bands of approximately the same intensity as has been reported by Barnes. The solid shows the same type of absorption as the liquid, having three bands of approximately the same intensity but there is a small average shift of 13A towards longer wave-lengths. In the vapor the absorption is quite different from that of the liquid; there are two strong absorption bands and these in turn show evidences of finer structure, each band, in fact, showing evidences of three components. If these components are interpreted as the envelopes of the vibration-rotation bands of the benzene molecule they show a doublet separation of 0.019μ. Considering the benzene molecule to be plane and the vibrational frequency to be due to the vibration of the C–H atoms then these bands will be of the perpendicular type and the results of the calculations of Gerhard and Dennison[5] can be applied to the calculation of the moment of inertia about an axis lying in the plane of the molecule; this calculation gives the value, $14\times10^{-39}$ g cm$^2$, which is in agreement with the value obtained by Kettering and Sleator[6] from measurements on the 9.5μ band of benzene.

### 2.46μ region

Fig. 4 shows the absorption curves for the band lying in this region. The thickness of the absorption cell was 0.06 mm for the liquid and solid measurements and 10.3 cm for those on the vapor. In the liquid there is a strong absorption band at 2.464μ with indications of two weaker bands, one on each side of the strong band. In the solid the strong band shows a shift of 13A towards longer wave-lengths and two weaker bands appear, caused, no doubt, by the narrowing of the lines by the low temperature. The vapor shows towards shorter wave-lengths a band which is double.

### 2.19μ region

In this region the curves (Fig. 5) show that instead of a single band, as reported by Dreisch, there is a group of five bands with indications of a sixth. In the solid state all these bands are shifted towards longer wave-lengths by approximately 20A. These measurements were made with cells of 0.15 mm in thickness. The sharp upward break in the solid absorption curve seemed to be due to some emission line in the particular Nernst glower used in the experiment since it did not occur when this part of the curve was repeated with an incandescent lamp as the source. The vapor appeared to have two main absorption bands incompletely resolved, lying at 2.148μ and 2.175μ.

In conclusion the writer wishes to express his appreciation to Professor A. H. Pfund for his assistance during the course of the investigation of the problem.

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[5] Gerhard and Dennison, Phys. Rev. **43**, 197 (1933).

[6] Kettering and Sleator, Physics **4**, 39 (1933).