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THE ABSORPTION SPECTRUM OF LIQUID BENZENE

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Abstract

A precision method is described for measuring the wave-lengths of radiation in the near infra-red region of the spectrum using a six-foot Rowland concave grating with a Thalofide cell. The results obtained are believed to be accurate within 0.001μ. With this method the wave-length of an outstanding absorption band of liquid benzene was determined. The frequency of this band together with those of other bands previously measured by the authors substantiate the theory that the absorber of these radiations is a linear anharmonic oscillator, whose energy states are represented by odd multiples of half quanta.

The wave-lengths of the outstanding absorption bands of liquid benzene in the near infra-red region of the spectrum have been measured in recent years by Ellis,[1] Driesch[2] and Márton.[3] They used prism spectroscopes with thermopiles and their results, which are generally recorded to 0.01μ, are far from being in good agreement. In recent papers the authors[4] have reported their results which were obtained with gratings and by photography in the region less than 1μ in wave-length. With a recording densitometer[5] the wave-lengths of the centers of two outstanding bands of benzene were measured. The values obtained were 0.8744μ and 0.7133μ. Since this was published another band at 0.6060μ was observed and measured. To obtain a satisfactory photograph of this band a column of liquid 4.3 meters in length was used. The above values are believed to be accurate within 0.001μ.

On account of some theoretical considerations we were anxious to extend our measurements into the region greater than 1μ in wave-length and still retain the same degree of accuracy by using the same concave grating which had a radius of six feet and a dispersion of 0.000933μ per millimeter in the first order. Eastman's "Infra-red Sensitive" plates were found to be unsatisfactory in this region. A Hilger thermopile having ten bismuth-silver couples in air was next tried with a sensitive Coblentz galvanometer and a slit width of 1 mm. No measurable deflections of the galvanometer were obtained between 1 and 1.5μ. The work of Case[6] and of Kaplan[7] with the "Thalofide cell" suggested that this detector might be sufficiently susceptible to radiations in this region to use with the grating. It proved to be most satisfactory and the results described below were obtained with

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[1] Ellis, Phys. Rev. **23,** 48 (1924).

[2] Driesch, Zeits. f. Physik, **30,** 200 (1924).

[3] Márton, Zeits. f. Phys. Chem. **117,** 97 (1925).

[4] Barnes and Fulweiler, Journ. Am. Chem. Soc. **49,** 2034 (1927), and **50,** 1033 (1928).

[5] Barnes and Fulweiler, J.O.S.A. and R.S.I. **15,** 331 (1927).

[6] Case, Phys. Rev. **15,** 289 (1920).

[7] Kaplan, J.O.S.A. and R.S.I. **14,** 251 (1927).

one of these cells which was kindly loaned to us by Captain H. B. Ely of the Frankford Arsenal, to whom we wish to express our thanks.

Apparatus and Methods

The source of continuous radiation was a 100 C.P. "Pointolite" lamp. The absorption cells, screens and lenses, as well as their disposition in front of the slit of the spectroscope were the same as described in an earlier paper.[4]

The Thalofide cell was rigidly mounted behind an adjustable slit on the camera stand of the Rowland grating mounting. As the stand was moved along its linear track its position was read on a fixed scale. This was calibrated in terms of wave-lengths by means of the second order arc lines of copper and mercury. The linear relationship obtained indicated the accuracy of the adjustments. The whole mounting with slit, grating and cell was enclosed in a large light-proof box. By adjusting the sizes of the holes in the screens in front of the slit the entering beam was limited so that it just covered the ruled portion (5×3.5 cm) of the grating.

The Wheatstone bridge method for observing the change in the resistance of the cell when radiation fell upon it was employed. The circuit which is shown in Fig. 1 was earthed at A. T is the Thalofide cell which had a resistance of 210 megohms in the dark at room temperature. R_1, R_2, and R_3 are resistances comparable in value with that of T. They were made in the usual way by drawing thin lines with india ink on paper between metal clips. E is a Dolezalek electrometer. With 100 volts on the needle the sensitivity was 620 mm per volt at a scale distance of 2 meters—the distance used. With slit widths of 1 mm on the spectroscope and on the cell a battery potential, B, of 45 volts was sufficient to give deflections from 50 to 450 mm in the region between 1.11 and 1.17μ. The results recorded below were obtained in this region as a preliminary run showed that it contained a strong absorption band.

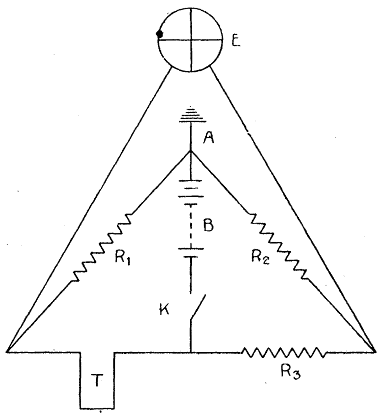

Fig. 1. Diagram of circuit used with Thalofide cell.

When the battery key, K, was closed there was always a small deflection of the needle because of the fact that it was impossible to make the ratio of the resistances T/R_1 exactly equal to R_3/R_2 and also on account of the resistance of the Thalofide cell being slightly lowered when a small current is passed through it. However, within fifteen minutes a position of equilibrium was reached and then the cell worked remarkably satisfactorily under the influence of the small intensities of radiation used. It responded quickly, the zero point remained surprisingly constant and the deflections produced by radiation of a definite wave-length agreed with one another within one percent.

Preliminary observations with red and infra-red filters placed in front of the spectroscopic slit showed that the influence of second order radiation on the cell was negligible compared to that of the first order in the region investigated. No filters were, therefore, used. It was also observed that the glass windows of the absorption cells had no selective absorption bands but because of reflection and general absorption the transmitted radiation was uniformly cut down about twenty percent for all wave-lengths.

The method of taking observations was to close the key, K, and leave it closed throughout a run, then to set the pointer connected with the cell T on a scale division corresponding to a definite wave-length falling on the cell. A shutter was then raised allowing the radiation to pass through the spectroscopic slit and the maximum deflection read. Dropping the shutter the absorption cell was lowered into place between the screens, the shutter raised and the deflection noted. This observation was repeated. Then the absorption cell was removed and the first observation repeated. The mount was then moved along the scale a few millimeters or less and another set of readings taken and so on throughout the range investigated.

The ratio of the mean of the two middle readings to the mean of the first and last readings gives what we shall call the "transmission ratio" rather than the "transmission percentage" of the liquid in the cell. To calculate the latter it would be necessary to know the amount of radiation lost and gained by internal and external reflection produced by the cell when empty and full. The transmission ratio is, however, sufficient for the determination of the wave-length of the center of an absorption band.

The benzene was purified by washing it ten times with 95% sulphuric acid and once with a caustic soda solution. Then it was steam distilled and fractionated and the middle 70% shaken with mercury. It was then fractionated by freezing until the freezing point was constant which was 5.483°C.

Results and Discussion

The results obtained are recorded by small circles on the curves of Fig. 2. These curves show the variation in the transmission ratio with wave-length for three lengths of benzene with different slit widths as given in Table I.

Table I. *Slit widths and absorption lengths used in obtaining the curves in Fig. 2.*

Curve	Width of slits of Spectroscope and Thalofide cell	Absorption length
A	1 mm	1 mm
B	0.5 mm	11 mm
C	1 mm	20 mm

The broad absorption band shown by these curves has its center at 1.1409μ within $\pm 0.001\mu$. The small rise in the curves at the bottom of these graphs indicates that the band is a doublet. Although the shape and intensity of the components are not known a rough estimate gives 0.008μ as their separation. This corresponds to a frequency difference of 2×10^{12} sec^{-1} which agrees within the limits of measurement with the frequency difference of the components of the absorption band[8] at 0.8744μ. It is also interesting to note that the shorter wave-length component appears to have the greater intensity. The curves also indicate a very weak absorption band at 1.164μ.

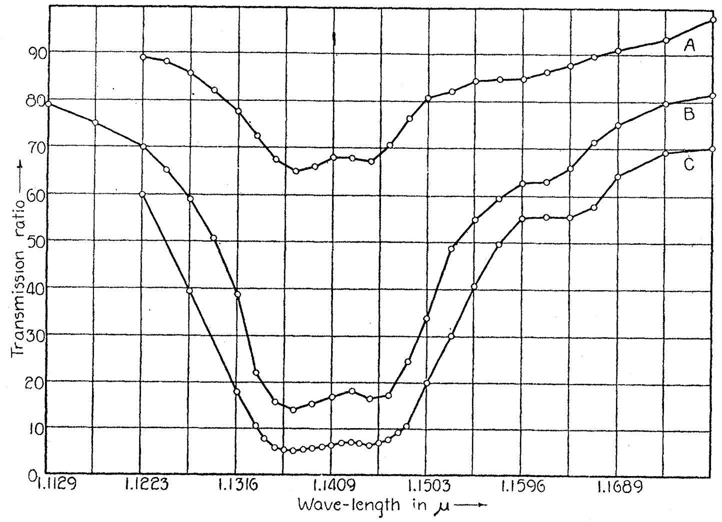

Fig. 2. Variation of transmission ratio with wave-length for three lengths of liquid benzene.

In Table II, the first column, λ, contains the authors' values of the wave-length of the outstanding absorption bands of benzene in the region so far investigated. The second column, 1/λ, gives their wave-numbers reduced to vacuum as obtained from Kayser's "Tabelle der Schwingungszahlen" and by extrapolation for the longest wave-length. The third column gives the differences of the successive wave-numbers. These differences decrease as the wave-numbers increase and, therefore, as the frequencies increase. This is characteristic of radiations emitted or absorbed by an anharmonic oscillator.

Table II. *Wave-lengths and wave-numbers of absorption bands of liquid benzene.*

$\lambda(\mu)$	$1/\lambda(\text{cm}^{-1})$	Consecutive difference
1.1409	8762	
.8744	11433	2671
.7133	14015	2582
.6060	16497	2482

Extending, by inspection, this approximately harmonic series into the longer wave-length region we get two more bands near 1.7μ and 3.2μ where the series appears to stop. Assuming that 3.2μ is the wave-length of the radiation associated with the fundamental frequency of the oscillator then the

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[8] Barnes and Fulweiler, Journ. Am. Chem. Soc. 50, 1035 (1928).

orders, m, of the harmonics are those given in the first column of Table III. Now the formula[9] for an anharmonic oscillator is

$$\omega_m = m\omega_0(1 - mx)$$

where ω_m is the wave-number of the radiation absorbed by the oscillator, ω_0 and x are constants. Applying this expression to the four observations given in Table II we get by the method of least squares the following values for the constants.

$$\omega_0 = 3085.8 \text{ cm}^{-1}, \quad x = 0.01823$$

Columns three and four of Table III give the values of the wave-numbers and of the wave-lengths calculated by the above equation. The last column shows the differences between the calculated and the observed values. The agreement is very satisfactory. The wave-lengths of the first two bands as measured by Coblentz[10] (C), Ellis (E), Driesch (D), and Márton (M) and our measurements of the last four bands are given in the fifth column.

TABLE III. *Calculated and observed bands of liquid benzene.*

Order m	Transition quanta	Calculated wave-numbers $\omega_m = 1/\lambda(\text{cm}^{-1})$	Calculated wave-lengths $\lambda(\mu)$	Observed wave-lengths $\lambda(\mu)$	Calc.-Obs. wave-lengths
1	1/2→ 3/2	3030	3.300	3.25 (C) 3.30 (M)	
2	3/2→ 5/2	5947	1.682	1.68 (C) 1.66 (E) 1.688 (F) 1.70 (M)	
3	5/2→ 7/2	8751	1.1422	1.1409	+0.0013
4	7/2→ 9/2	11443	0.8736	0.8744	−0.0008
5	9/2→11/2	14023	0.7129	0.7133	−0.0004
6	11/2→13/2	16490	0.6062	0.6060	+0.0002

If we assume that there exists an absorption band further out in the infra-red than the one at 3.3μ and thereby increase by unity each value of the m's assigned above to the bands we get a negative value for x. This seems unreasonable so we believe that the band with a wave-length approximately 3.3μ, corresponding to a frequency of 90.9×10^{12} sec^{-1}, is the fundamental of this outstanding absorption series of liquid benzene.

Attributing this series to a linear oscillator which may be the molecule as a whole or better a CH group and applying the quantum theory we get for the phase integral over a complete vibration

$$\oint pdq = \oint mvdx = \pi m v_0 x_0 = nh \tag{1}$$

where m, v_0 and x_0 are the mass, maximum linear velocity and maximum linear displacement respectively of the oscillator and n an integer.

The total energy (kinetic and potential) of the oscillator is given by

$$E = mv_0^2/2$$

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[9] Cf. Page "Molecular Spectra in Gases" Bulletin National Research Council, pp. 42–45 (1926).

[10] Coblentz, Carnegie Inst. Pub. 35, pp. 76 and 231 (1905).

Hence from Eq. (1)

$$E = n^2h^2/2\pi^2mx_0^2 \tag{2}$$

Now by Bohr's frequency condition

$$E_1 - E_0 = h\nu \tag{3}$$

If x_0 be considered constant, *whatever the linear velocity*, we get from Eqs. (2) and (3) that

$$\nu = (n_1^2 - n_0^2)h/2\pi^2mx_0^2 \tag{4}$$

where ν is the frequency of the radiation absorbed and n_0 and n_1 the quantum numbers associated with the energy levels E_0 and E_1. If only energy changes of one unit at a time are permitted, that is $n_1 = n_0 + 1$, $n_2 = n_1 + 1$, etc, then Eq. (4) becomes

$$\nu = (2n_0 + 1)h/2\pi^2mx_0^2 \tag{5}$$

which shows that the frequencies absorbed should be proportional to certain integers. That this is almost true is shown by the results given in Table II. If the zero energy state is designated by $n_0 = 0$ and the next state by $n_1 = 1$, then by Eq. (5) the fundamental frequency, ν_1, absorbed in the transition 0→1 is equal to $h/2\pi^2mx_0^2$. Let us call this quantity A. The second harmonic which is given by the transition 1→2 where $n_1 = 1$ and $n_2 = 2$ has by Eq. (5) a frequency, ν_2 equal to $3A$, and so on for the higher harmonics. We, thus, obtain the relation that

$$\nu_1:\nu_2:\nu_3:\cdots::1:3:5:\cdots$$

which certainly is not the sequence of frequencies and, therefore, of wave-numbers as given in the third column of Table III. If, however, we assign, to the quantum numbers, n, odd multiples of 1/2 as in the "new" wave-mechanics, then Eq. (5) for the transition (1/2→3/2) from zero energy state where now $n_0 = 1/2$ to state where $n_1 = 3/2$, gives for the fundamental frequency, ν_1, the value of $2A$. For the second harmonic, (3/2→5/2), $\nu_2 = 4A$, and so on for the higher harmonics. Then we get the relation that

$$\nu_1:\nu_2:\nu_3:\cdots::1:2:3:\cdots$$

which agrees with the observations above except for the small correction term on account of the oscillator vibrating anharmonically. The transition quanta for the various frequencies are given in the second column of Table III.

In conclusion, it may be of interest to calculate the maximum amplitude, x_0 of the oscillator, which is assumed to be approximately constant for the various harmonics. Taking, for example, the fundamental (1/2→3/2) where $\nu_1 = 90.9 \times 10^{12}$ sec^{-1} and for h, 6.55×10^{-27} erg·sec and assuming that the oscillator is the CH group, then $m = 21.58 \times 10^{-24}$ g, we get for x_0 from Eq. (5) the value $5.8. \times 10^{-10}$ cm which is of the order of 1/100 of the average dimension of the molecule of solid benzene as determined by Bragg.

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