DECEMBER, 1928 PHYSICAL REVIEW VOLUME 32

VISIBLE ABSORPTION BANDS OF COLORLESS LIQUIDS AND THEIR RELATION TO INFRA-RED BANDS

By Joseph W. Ellis

Abstract

The absorption of ten representative organic liquids has been studied in the visible spectrum by photographic means. Cell lengths up to 6½ meters were employed. The near infra-red spectra of these same substances have been obtained. A good correlation of the bands of the two regions has been secured; the bands of the visible region seem to be higher members of series previously detected in the infra-red.

There seems to have been no recent extensive study of the absorption bands of colorless liquids in the visible region of the spectrum. Nearly fifty years ago Russell and Lapraik[1] published the results of an investigation of the absorption of twenty-nine substances, mainly organic liquids, in the region between 0.73μ and 0.5μ. By using cell thicknesses varying from 2 to 8 ft. they were able to observe one or more absorption band for each substance. Their observations were made visually with a prism spectroscope and their results were presented through drawings.

The writer's apparent ability to formulate certain bands in the infra-red absorption spectra of various organic compounds into series which approach the red of the visible spectrum has caused him to attempt to correlate the bands of the visible region with those of the near infra-red. It seemed advisable to check some of the observations of Russell and Lapraik and also to extend the study to other compounds not examined by those investigators.

A large Hilger quartz spectrograph of the E1 type was used in the photography of these spectra. The source for a continuous spectrum was a 400 watt lamp. The absorption cells, ranging in length from 78 cm to 650 cm, were made by joining together sections of Pyrex glass tubing of about 20 mm inside diameter. These sections were silvered inside to increase the amount of light transmitted through the tube and to remove the possibility of introducing extraneous bands due to absorption by the glass walls. The ends of each tube were faced with bakelite cemented to the glass with deKhotinsky cement. The sections were held together with inside threaded brass sleeves and outside threaded brass collars cemented to the opposite tube. The two end sections were equipped with removable quartz end-plates. The light was rendered parallel before traversing the cell, but no condensing lens was used between the cell and the spectrograph slit.

Three types of photographic plate were used: orthochromatic, panchromatic and extreme red sensitive. No one type of plate is sensitive to the whole region under investigation. The use of extreme red sensitive plates permitted photography in the region of 0.75μ, a region not attained by Russell and Lapraik.

---

[1] Russell and Lapraik, Nature **22**, 368 (1880); Jour. Chem. Soc. **39**, 168 (1881).

The substances used for this study were chosen to include certain definite types of molecules. One purpose of the investigation was to observe the effects of unsaturation and of substitution in the molecule. Since great cell lengths were employed the number and types of compounds studied were limited by the cost of materials. Those used are discussed individually in the following paragraphs.

The plates were measured with a specially constructed measuring box equipped with a scale with a vernier attachment reading to 1/20 mm. Hartmann's dispersion formula was used to measure the lines by interpolation between helium and Fraunhofer lines. The sensitiveness of the instrument was equivalent to about 0.0002 and 0.0004μ in the regions 0.6μ and 0.75μ respectively, but because of the finite widths of the bands an accuracy of only about 0.001μ can be claimed.

Hexane, C_6H_{14} (E. K. Co. #P1135); 78 and 355 cm cell. This was chosen as the most readily obtained saturated chain hydrocarbon. A single band at 0.558μ (probably one component of a doublet) and two double bands at 0.635, 0.649μ and 0.744, 0.760μ were recorded. The shorter wave-length members of the double bands were the more intense.

Cyclohexane, C_6H_{12} (E. K. Co. #P702); 78 and 445 cm cell. This is a saturated cyclic hydrocarbon. It showed three double bands of approximately equal intensity components: 0.567, 0.575μ; 0.644, 0.653μ; and 0.753, 0.763μ. Bands characteristic of benzene appeared and were assumed to be due to this substance as an impurity.

Benzene, C_6H_6 (thiophene free); 78, 355 and 650 cm cell. This unsaturated cyclic hydrocarbon gave the following bands, all of which were single: 0.476, 0.532, 0.608 and 0.712μ. The 0.476μ band was extraordinarily weak even with the 6.5 m cell, but was detected on two different plates by several observers. It is of a shorter wave-length than any band observed by Russell and Lapraik.

Toluene, $C_6H_5 \cdot CH_3$ (E. K. Co. #P325); 78, 170 and 631 cm cell. The effect of substitution of a methyl group was sought in this instance. Bands of the benzene type were observed at 0.608μ and 0.713μ. In addition a weak double band at 0.737, 0.748μ was found. The rather nebulous absorption recorded by Russell and Lapraik around 0.63μ could not be brought out.

m-Xylene, $C_6H_4 \cdot (CH_3)_2$ (E. K. Co. #T275); 78, 170 and 436 cm cell. The bands characteristic of the benzene ring were found shifted to 0.611μ and 0.713μ. A doublet at 0.738, 0.748μ was much more intense than the one analogous to it in toluene. Absorption occurs near 0.63μ but, because of the low sensitivity of the plates, no measurements could be made upon it. There seems, however, to be evidence of doubleness there.

Chlorobenzene, C_6H_5Cl (E. K. Co. #70); 70 and 353 cm cell. The benzene bands appeared, shifted to shorter wave-length values, 0.604μ and 0.707μ.

Chloroform, $CHCl_3$ (Eastman practical and U.S.P.); 78, 170 and 445 cm cell. The following bands were found: 0.614, 0.622, 0.665, 0.690 and 0.721μ.

Acetone, $CH_3 \cdot CO \cdot CH_3$ (E. K. Co. #P297); 78, 170 and 449 cm cell. Two doublets with the shorter wave component slightly more intense were observed: 0.618, 0.631μ and 0.727, 0.741μ.

Ethyl acetate, $CH_3COOC_2H_5$ (E. K. Co. #300); 78 and 263 cm cell. This compound showed two doublets, the shorter wave members being the weaker: 0.617, 0.626μ and 0.723, 0.735μ.

Aniline, $C_6H_5 \cdot NH_2$; 78, 172 and 353 cm cell. This sample was obtained from the chemistry department. It was twice distilled before using but retained a slightly yellow color. Light transmitted through it varied in color from a deep red to a bright orange for cell lengths ranging from 353 to 78 cm. This compound was included in order to observe the effects due to the substitution of an amino group. Bands were found at 0.608, 0.648 and 0.712μ. A prominent one at 0.630μ found in Russell and Lapraik's spectrum of aniline, as well as in certain of their other records, does not appear in this investigation. The absence of this band is of interest since it is one of the few among all of those observed by these investigators which finds no place in the correlation described later in this article.

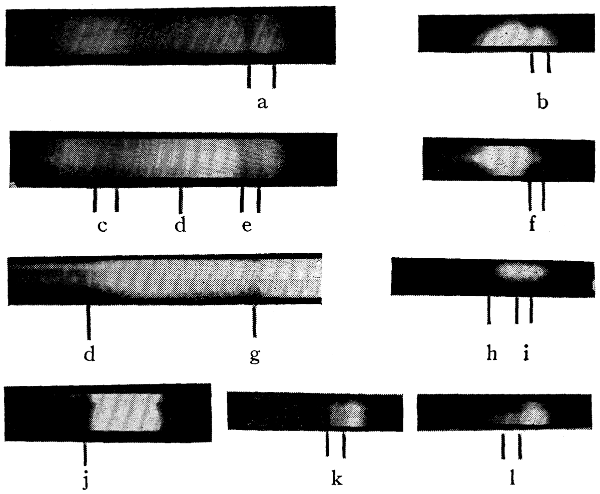

Fig. 1. Typical visible absorption bands—*a*, Hexane 0.635, 0.649μ; *b*, Hexane 0.744, 0.760μ; *c*, Cyclohexane 0.567, 0.575μ; *d*, Benzene 0.608μ; *e*, Cyclohexane 0.644, 0.653μ; *f*, Cyclohexane 0.753, 0.763μ; *g*, Benzene 0.608μ; *h*, m-Xylene 0.713μ; *i*, m-Xylene 0.738, 0.748μ; *j*, Chlorobenzene 0.707μ; *k*, Acetone 0.727, 0.741μ; *l*, Ethyl acetate 0.723, 0.735μ.

Of the above substances Russell and Lapraik give records for benzene, toluene, xylene, chlorobenzene, aniline and chloroform. There seems to be a good agreement among the results of the two investigations; however, it is evident that there is a systematic error of calibration in the red on the part of the earlier investigators. That their published values for the region 0.7μ are too low is evident by comparing their 0.708μ value for benzene and toluene with the 0.713 and 0.714μ values for these substances obtained by Barnes and Fulweiler[2] through the use of a diffraction grating. The values of the present investigation are nearly in agreement with those of Barnes and Fulweiler,

[2] Barnes and Fulweiler, Jour. Amer. Chem. Soc. **49**, 2034 (1927).

but differ consistently from those of Russell and Lapraik in this particular portion of the spectrum.

Since the present investigation includes an attempt at correlation of these visible bands with infra-red bands, the spectra below 2.5μ of all of the above

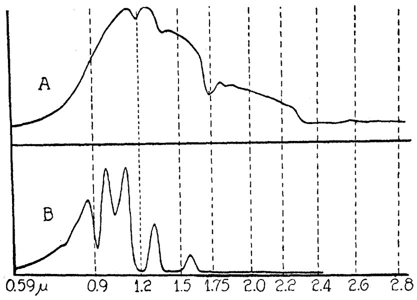

Fig. 2. Hexane. *A*, 1 mm; *B*, 155 mm.

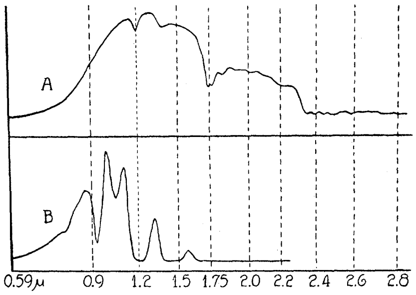

Fig. 3. Cyclohexane. *A*, 1 mm; *B*, 155 mm.

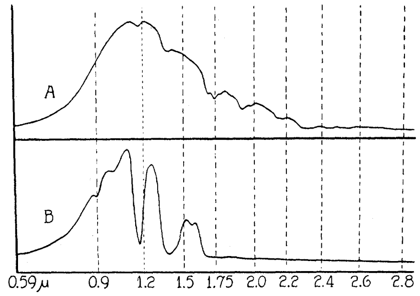

Fig. 4. Acetone. *A*, 1 mm; *B*, 155 mm.

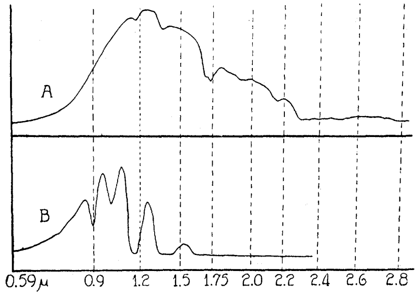

Fig. 5. Ethyl acetate. *A*, 1 mm; *B*, 155 mm.

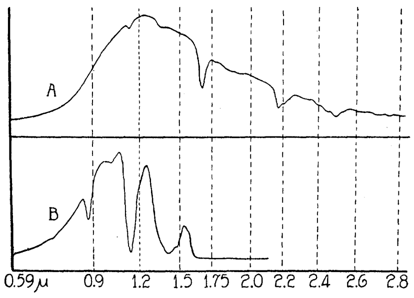

Fig. 6. Chlorobenzene. *A*, 1 mm; *B*, 155 mm.

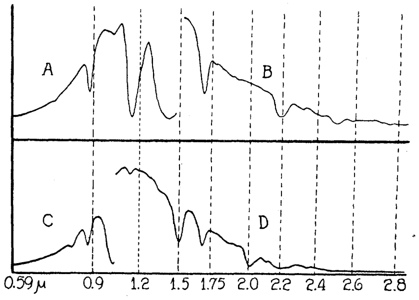

Fig. 7. *A*, Benzene, 1 mm; *B*, Benzene, 155 mm; *C*, Aniline, 1 mm; *D*, Aniline, 155 mm.

compounds were carefully recorded on a registering quartz spectrograph. Two cell thicknesses, 155 mm and 1 mm, were used to bring out the bands most advantageously. The records of all of these substances, with the exception of chloroform, are shown in Figs. 2–8. Where data for wave-lengths greater than 2.5μ were needed, the values were taken from the published papers of other investigators, references to which are given in connection with Table I.

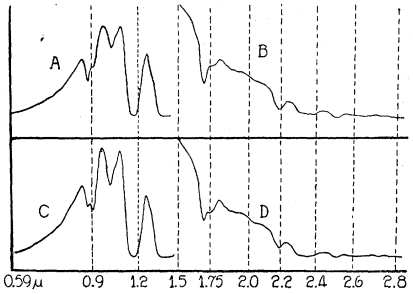

Fig. 8. *A*, Toluene, 1 mm; *B*, Toluene, 155 mm; *C*, m-Xylene, 1 mm; *D*, m-Xylene, 155 mm.

In 1881 Abney and Festing[3] published the results of a photographic investigation of the spectra of a group of compounds in the short wave portion of the infra-red. Although it is possible to associate certain of their bands with those usually found below 1μ by thermal means, the complexity of the spectra which they record seems not to be in general agreement with the observations of others. Because of this no use is made of their data in the present paper, even in those few instances in which a substance was studied in both investigations.

In earlier papers[4] the writer attempted to arrange certain of the near infra-red absorption frequencies of a few organic compounds into a series whose constants were evaluated from an average of the frequencies observed for several compounds. Variations in the positions of these bands which are quite certainly due to molecular structure make this method of formulation extremely inadvisable. This series included nine members ranging from about 6.5μ to 0.76μ. A later note,[5] preliminary to the present paper, attempted to reformulate for individual compounds certain of these bands into new parabolic series which include most of the bands observed in the visible spectrum. The new series, with initial members near 3.3μ and 3.4μ respectively for aryl and alkyl compounds, include only alternate bands of the older series. There are three main reasons for this reformulation. (1) Only the alternate bands chosen bear a similarity in structure to one another. (2) Only under these circumstances does a series yield a sequence of bands of gradually diminishing intensities. (3) The bands of the visible region fit into this arrangement.

In Table I are tabulated the wave-length values of the members of these series. The values of n refer to the series member number; this reaches the maximum value of 8 for the 0.476μ band found in the visible blue of the benzene spectrum. Data from observations by others have been included in this table.

The notion initially advanced in the writer's earlier papers that these bands originate in characteristic oscillation frequencies of the carbon-hydrogen bond is retained here. Infra-red bands other than those tabulated recur in the spectra of these compounds and doubtless are somehow associated with the C-H linkage. They will not be discussed in this article. The above series, however, include all of the observed visible bands with the exception of the 0.622, 0.665 and 0.690μ values of chloroform and the 0.648μ value for aniline.

---

[3] Abney and Festing, Phil. Trans. **172**, 887 (1881).

[4] Ellis, Phys. Rev. **23**, 48 (1924); **27**, 298 (1926); J.O.S.A. and R.S.I. **8**, 1 (1924).

[5] Ellis, Phys. Rev. **31**, 310 (1928).

TABLE I. *Wave-length values in μ of infra-red and visible absorption bands.*

	n=1	2	3	4	5	6	7	8
Hexane	3.48 3.39 a 3.43 b	1.76 1.73 1.73 c	1.195 1.19 c	0.92	0.760 0.744	0.649 0.635	..... 0.558	.....
Cyclohexane	3.49 c	1.765 1.735 1.74 c	1.20 1.19 c	0.93	0.763 0.753	0.653 0.644	0.575 0.567	
Benzene	3.26 a 3.25 b 3.30 c 3.30 d	1.68 1.68 b 1.70 c	1.145 1.14 b 1.19 c 1.13 e 1.18 f	0.875 0.874 g	0.712 0.713 g 0.708 h	0.608 0.611 h	0.532	0.476
Toluene	3.46 3.41 a 3.27 3.34 b 3.38 c	1.77 1.75 1.69 1.71 b 1.71 c	1.19 1.15 i 1.19 c	0.910 0.875 ..... 0.877 g	0.748 0.737 0.713 ..... 0.714 g 0.708 h	..... 0.608 0.612 h	.....	.....
m-Xylene	3.38 b 3.39 c	1.77 1.75 1.70 1.71 b 1.71 c	1.19 1.15 i 1.19 c	0.910 0.885 0.879 g	0.748 0.738 0.713 0.710 h	..... 0.611 0.613 h	.....	.....
Chlorobenzene	3.14 c	1.67 1.60 c	1.14	0.87	0.707 0.708 h	0.604 0.611 h	.....	.....
Chloroform	3.32 b 3.10 c	1.69 1.69 b 1.66 c 1.72 f	1.15 i 1.14 c 1.19 f	0.88	0.721 0.714 h	0.614 0.612 h	.....	.....
Acetone	3.42 b 3.26 c	1.74 1.695 1.77 c	1.18 1.15? 1.14 c	0.90	0.741 0.727	0.631 0.618	.....	....
Ethyl acetate	.....	1.73 1.695	1.18	0.90	0.735 0.723	0.626 0.617	.....	.....
Aniline C-H	3.25 b 3.20 j	1.68	1.145	0.87	0.712 0.704 h	0.608 0.611 h	.....	.....
Aniline N-H	2.80 j	1.50	1.03	0.79	0.648 0.649 h	.....	.....	.....

a. Meyer, Bronk and Levin, J. O. S. A. and R. S. I. **15,** 257 (1927).
b. Coblentz, Publication of the Carnegie Institution of Washington, No. 35 (1905).
c. Márton, Zeits. f. Phys. Chem. **117,** 97 (1925).
d. Bell, Jour. Amer. Chem. Soc. **47,** 2811 (1925).
e. Puccianti, Phys. Zeits. **1,** 48 (1899).
f. Dreisch, Zeits. f. Physik **30,** 200 (1924).
g. Barnes and Fulweiler, Jour. Amer. Chem. Soc. **49,** 2034 (1927); J. O. S. A. and R. S. I. **15,** 331 (1927).
h. Russell and Lapraik, Jour. Chem. Soc. **39,** 168 (1881).
i. Ellis, Phys. Rev. **23,** 48 (1924).
j. Bell, Jour. Amer. Chem. Soc. **47,** 2192 (1925).

Since the infra-red spectrum of chloroform contains exceptionally strong bands apparently associated with the presence of the chlorine atoms we may credit the above three visible absorption regions to the presence of the halogen. The 0.648μ band for aniline fits well into a second series of bands originating at 2.80 or 2.90μ which is apparently due to the N-H linkage.[6] This special series is included at the bottom of Table I. The new record for aniline yields a value of 1.50μ for $n=2$. Using a 155 mm cell a band, not characteristic of the phenyl radical appears at 0.79μ. This fits the N-H sequence as $n=4$.

A further evidence which supports the new series formulation is to be found in a succeeding paper which attempts to use these series in the evaluation of the heats of linkage of the C-H and N-H bonds.

The writer wishes to acknowledge the helpful assistance of Mr. Kenneth Stoddard in this investigation.

DEPARTMENT OF PHYSICS
[ORGANO-MOLECULAR INVESTIGATIONS]
UNIVERSITY OF CALIFORNIA AT LOS ANGELES.
AUGUST 14, 1928.

---

[6] Ellis, Jour. Amer. Chem. Soc. **50**, 685 (1928).

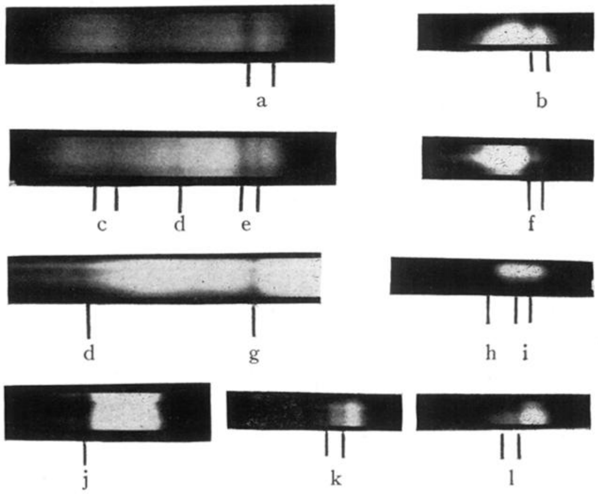

Fig. 1. Typical visible absorption bands—*a*, Hexane 0.635, 0.649μ; *b*, Hexane 0.744, 0.760μ; *c*, Cyclohexane 0.567, 0.575μ; *d*, Benzene 0.608μ; *e*, Cyclohexane 0.644, 0.653μ; *f*, Cyclohexane 0.753, 0.763μ; *g*, Benzene 0.608μ; *h*, m-Xylene 0.713μ; *i*, m-Xylene 0.738, 0.748μ; *j*, Chlorobenzene 0.707μ; *k*, Acetone 0.727, 0.741μ; *l*, Ethyl acetate 0.723, 0.735μ.