THE NEAR INFRA-RED ABSORPTION SPECTRA OF SOME ORGANIC LIQUIDS

By Joseph W. Ellis

Abstract

Near infra-red absorption spectra of thirty-one organic liquids to 2.5μ.—*A self-recording prism spectrograph,* Littrow mounting, with dispersion equivalent to two 60° flint glass prisms—considerably greater than had hitherto been used in this region—was arranged so that the spot of light from the mirror of the galvanometer in the thermopile circuit, was focused on a sheet of bromide paper on a drum rotated in gear with the prism table. Curves thus obtained are reproduced which show the transmission through 11 mm of certain organic liquids: *ethyl, methyl, propyl, butyl, ethylene and methylene halides, butyl nitrite, benzene, toluene, pentane, hexane, heptane, octane, mesitylene, paraxylene, chloroform and bromoform.* In a table are given the wave-lengths of the absorption maxima accurate to about .01μ, and, in many cases, the percentage absorption, accurate to five per cent. Curves obtained by visual observations, are also given for eight of the above compounds and for *acetone and ethyl ether.* Bands near 0.90, 1.02, 1.17, 1.38 and 1.70μ occur in most if not all of these spectra. Hence these *bands are attributed to the C-H bond,* and appear to be, respectively the 7th, 6th, 5th, 4th, and 3rd harmonics of a fundamental frequency found by Coblentz at 6.9μ. There are also bands at 1.81, 1.91, 2.00 and 2.10μ which occur for several liquids. Shifts in the positions of the bands for different liquids, which may amount to ± .03μ, are not understood, but may be due to a change in the relation intensity of the two components of the band; for some of the bands are clearly double, like the infra-red bands due to gaseous compounds. The simple quantum theory of such gaseous spectra does not seem to hold directly for these liquid spectra, however, since the separation of the components of 1.38μ and also of 1.7μ is greater for the iodides than for the corresponding chlorides.

Introduction

While rock salt has proved to be the best prism material when investigations into the far infra-red region of the spectrum are desired, since it transmits as far as about 15μ, in studying the near infra-red region, prisms with a higher dispersive power, such as quartz, glass or carbon bisulfide may be used.[1] Puccianti,[2] using a single quartz prism, studied fifteen carbon compounds in this region and found that all the compounds in which there is a direct linkage of carbon and hydrogen have an absorption band at 1.71μ. Besides making investigations with a rock salt prism, Coblentz[3] studied the absorption of over

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[1] The relative dispersive powers of rock salt, quartz, fluorite and carbon bisulfide are given in Scientific Papers Bur. Stand. No. 401, 1920.

[2] Puccianti, Nuovo Cim., **11**, 141, 1900; Phys. Zeit. 1899–1900.

[3] W. W. Coblentz, Astrophys. J. **20**, 1904

twenty compounds in the region between the visible and 2.7μ with a quartz spectrograph. He also found the 1.71μ band wherever there was a C-H linkage. In all this work use was made of the heating effect of the infra-red rays falling on a bolometer, thermopile or radiometer. Abney and Festing,[4] the first investigators of infra-red absorption spectra, alone seem to have used a photographic method. They were able to produce a photographic plate sensitive to light of wave-lengths as great as 1.2μ. Their work shows a large number of absorption bands and lines up to this wave-length limit.

It was felt that an investigation in the near infra-red would yield valuable data provided a comparatively high dispersion could be obtained; consequently, a spectrograph with rather dense flint glass prisms was assembled. With the use of this instrument many organic compounds have been studied whose infra-red absorption spectra have heretofore been examined, if at all, only with the use of rock salt prisms; and as a result many absorption bands have been obtained which never could be resolved with such prisms.

Apparatus and Calibration

A brief discussion of the work begun and a brief description of the spectrograph used have already been given.[5] Since the publication of that article an automatic method has been adopted for the recording of the absorption curves. A diagram of this improved apparatus is given in Fig. 1. The source of radiation S was a 108-watt lamp, intended for a locomotive head-light, operating on six volts A.C. To insure a steady source, it was operated on a current supplied by a storage battery B,

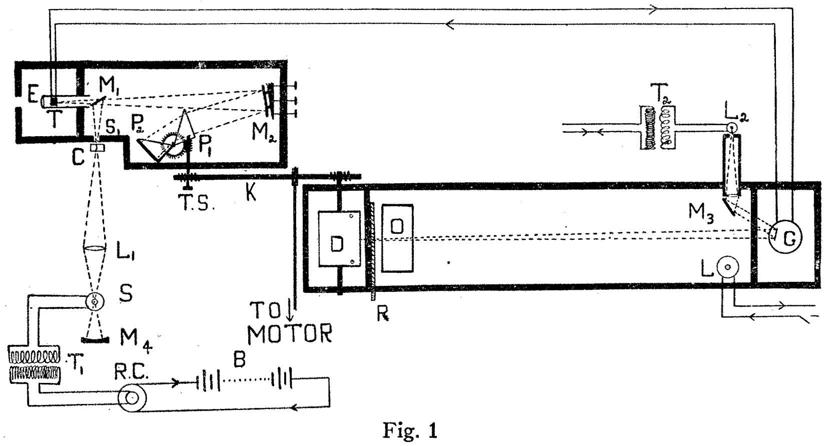

Fig. 1

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[4] Abney and Festing, Phil. Trans. **172**, 1881

[5] J. W. Ellis, Science, **54**, Sept. 15, 1922

after it had been properly converted and stepped down to the proper voltage by the rotary converter *RC* and the transformer T_1. By placing the concave mirror M_4 behind the source, about 40 per cent increase in transmission was obtained.

A small quartz lens L_1 focused the light upon the slit S_1 through a glass absorption cell *C*. After reflection from the plane speculum mirror M_1 and the concave speculum mirror M_2 the light entered the glass prism P_1. The back surface of the prism P_2 was silvered; so for any given position of P_2 only a small portion of the spectrum struck this silvered surface normally, and retraced its path to M_2 and then to the thermopile *T*. M_2 was slightly tilted so that this light on second reflection passed over M_1. The thermopile was of the Hilger type with ten bismuth-silver couples. *E* represents an eye-piece for the direct observation of visible light. The sensitive Leeds-Northrup galvanometer *G* used with the thermopile was placed on an isolated support to eliminate mechanical jarring.

The self-recording device consisted partly of a cylindrical drum *D*, 13 cm long and 48 cm in circumference, geared directly to the screw that also rotated P_2, by means of the shaft *K*. The thumbscrew *TS* enabled the gear at P_2 to be released at any time and P_2 brought back to its zero position. The gear ratios were so chosen that when P_2 had caused the region of the spectrum between 0.589μ and 2.7μ to pass before the thermopile, *D* had made one complete revolution. The shaft was driven by means of a slowed-down motor system so that it required fifteen minutes for one revolution of *D*. A strip of sensitized double-weight photographic paper was securely clamped around the drum. The light from the lamp L_2 was reflected from M_3 and the galvanometer mirror, and the magnified image of a single filament of L_2 was brought to a focus upon the screen in front of the drum. This screen was traversed by a narrow horizontal slit parallel to the axis of *D*, so that the intersection of the vertical image of the filament with this slit formed a spot of light on the photographic paper. The combination of the rotational motion of *D* and the horizontal motion of the image of the filament, caused by the swinging of the galvanometer mirror, traced a curve representing the absorption spectrum of the substance in *C*.

When a curve was to be taken, P_2 was set so that the *D*-lines of sodium fell upon the thermopile. The shutter *R* was then removed, and a lamp *L* within the dark box was thrown on for about a second, so as to give a dark line on the photographic paper which was taken as the zero line in all this work. A window of red glass *O* was used for observing the position of the image of the filament at any time. This was necessary because of the progressive shift of the galvanometer mirror at times.

The average dispersion obtained by means of these two 30° flint glass prisms, since the light traversed each prism twice, was between two and three times that obtained with a single 60° quartz prism, and between four and five times that obtained with a single 60° rock salt prism, considerably greater than that previously used in similar experiments.

The instrument was calibrated twice, both before and after the substitution of the self-recording device. The former calibration was more easily accomplished as the observing telescope was 2.5 meters distant from *G* while the distance *DG* was only one meter. Certain emission lines of lithium, sodium, thalium, strontium, and calcium, obtained by the use of cored carbons in a direct current arc, and several solar absorption bands were used for calibration. The greatest emission wave-lengths observed were at 1.85μ in sodium and 1.98μ in calcium. In the second calibration use was also made of the sharp absorption maxima in the spectrum of chloroform observed by the visual method.[6]

RESULTS AND DISCUSSION

Visual method. Twelve substances were studied by means of the visual method. The absorption curves of ten of these are given in Fig. 2. Percentage transmission is plotted against wave-length in microns. A differential method was used; observations were made for a given setting of the prism, first with an empty cell and then with a 3 mm cell of the substance. Because of decreased internal reflection with a filled cell the ratio of the deflections observed with the cell filled and with the cell empty, was greater than unity in regions of apparently perfect transmission. Corrections were made throughout, therefore, on the assumption that these were regions of one hundred per cent transmission.

These ten curves are strikingly similar in that they all have three absorption bands in common in the neighborhood of 1.17μ, 1.38μ, and 1.7μ. The band at 1.7μ, as was pointed out by Puccianti[2] and Coblentz,[3] is characteristic of all carbon-hydrogen compounds examined by them. There are shifts in the positions of these common absorption bands, however, which are greater than the limit of experimental error, but the slight irregularities in the region 0.8μ to 1.0μ are due largely to experimental errors, as the absolute deflections here were much smaller than at 1.5μ.

Self-recording method. Some thirty substances have been examined with the self-recording photographic device. These included chloroform, bromoform, certain ethyl, methyl, propyl, butyl, ethylene and methylene halides, as well as some simple hydro-carbons, such as benzene, toluene,

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[6] J. W. Ellis, Phys. Rev. **19**, May, 1922

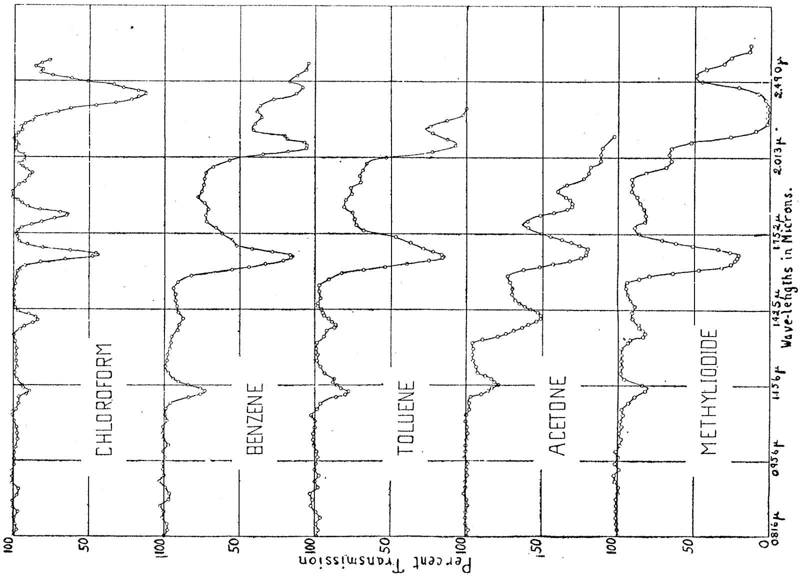
CHLOROFORM
BENZENE
TOLUENE
ACETONE
METHYLIODIDE
100
50
100
50
100
50
100
50
100
50
0
Percent Transmission
0.816μ
0.956μ
1.156μ
1.425μ
1.752μ
2.013μ
2.490μ
Wave-lengths in Microns.

Fig. 2a

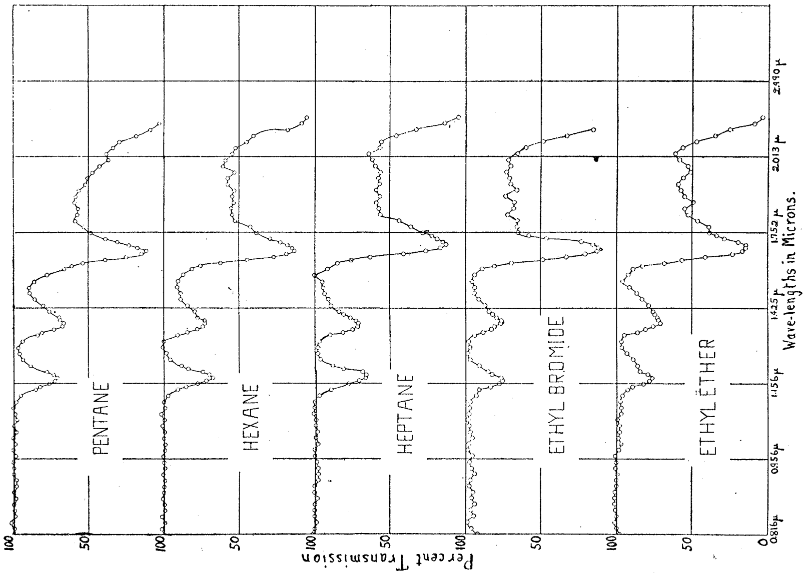
PENTANE
HEXANE
HEPTANE
ETHYL BROMIDE
ETHYL ETHER
100
50
100
50
100
50
100
50
100
50
0
Percent Transmission
0.816μ
0.956μ
1.156μ
1.425μ
1.752μ
2.013μ
2.490μ
Wave-lengths in Microns.

Fig. 2b

pentane, hexane, etc. Unless otherwise specified these compounds are the normal compounds. The thickness of the cell was 11 mm, or slightly more. The absorption curves, many times reduced, for most of the compounds are given in Figs. 3 and 4. The original records were 10 by 48 cm. The plain intensity distribution curve is shown in Fig. 3a. The regions of selective absorption in it are probably due to water vapor in the atmosphere.

Striking similarities among these spectra are evident. Besides the bands common to all in the neighborhood of 1.17μ, 1.38μ, and 1.7μ, in many of the compounds bands near 0.9μ and 1.0μ appear. The wave-lengths of the various maxima are recorded in Table I. In this table is also included the percentage absorption wherever its approximate measurement was found practicable. This was done by sketching the original intensity curve upon the spectrum curve, and taking the ratios of ordinates at the points of interest. The fair degree of consistency obtained in this manner indicates an average error of less than five per cent. The depth of these bands, however, is affected by the proximity of other bands and their lack of resolution.

In locating the positions of the absorption maxima, the intersection of a line drawn tangent to the absorption curve and having the slope of the original intensity distribution curve at that wave-length was taken as the minimum point of the curve. In the case, however, of the broad bands at 1.7μ, approximately the center of each band was chosen for the absorption maxima.

At least two curves were taken for nearly every substance. The details of the curves, such as points of inflection in the case of the resolution of two bands, were duplicated in almost every instance.

As carbon and hydrogen are the only elements which these substances have in common we must attribute these bands to them. Coblentz[7] studied the near infra-red absorption spectra of several vegetable and animal oils, and has found that they all have bands near 1.17μ, 1.39μ, and 1.75μ. Examination of the curves shows most of them to have selective absorption near 0.9μ and 1.0μ. Now it has been pointed out by other investigators and verified in this research, that substances such as CS_2 and CCl_4, which have carbon without hydrogen, have no absorption bands in this region. Compounds which have the hydrogen without the carbon do not show these bands. Consequently, we have to ascribe their presence to the C-H linkage in the compound. Although a quantitative comparison of the depths of these common bands among different sub-

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[7] W. W. Coblentz, Scientific Papers Bur. Stand., No. 418, 1921

stances would have to take into consideration the molecular concentration, one can see in a general way that the depth of the band is a direct function of the number of C-H groups in the molecule.

It is very apparent that the halogen in the aliphatic halides studied plays but a very small part in the selective absorption in this region. It would seem, however, that we should ascribe the progressive separation, or resolution, of the double band at 1.38μ in the case of the ethyl halides, Fig. 3a, and of the methylene halides, Fig. 4a, to the halogen. The order of these separations is also the order of the atomic weights of the halogen: chlorine, bromine, iodine. This band has a wide separation for methyl iodide also, but unfortunately methyl chloride and methyl bromide are gases at ordinary temperatures, and were not studied.

TABLE I

Near infra-red absorption maxima for some organic liquids to 2.4μ.
Wave-length in μ; per cent absorption of 11 mm cell in brackets.
Values obtained by Puccianti, Iklé or Coblentz indicated thus (1.15P) etc.

Ethyl chloride C_2H_5Cl	.905	1.02	1.175(58)	1.37 (58)	1.70 (96)
Ethyl bromide C_2H_5Br	.90	1.01	1.165(54)	1.365(52)	1.69 (96)
Ethyl iodide C_2H_5I	.90	1.015	1.17 (54)	1.37(47)	1.70 (94)
	(.83P)	(.96P)	(1.15P)	(1.40P)	(1.72P)
Methyl iodide CH_3I	.895		1.15	1.35 (45)	1.66 (29)
	(.89P)		(1.15P)	(1.39P)	(1.70P)
Propyl bromide $CH_3\cdot CH_2\cdot CH_2Br$	.905	1.015	1.175(56)	1.365(53)	1.70 (96)
Propyl iodide $CH_3\cdot CH_2\cdot CH_2I$	.905		1.75 (57)	1.365(51)	1.69 (97)
Iso-propyl iodide $(CH_3)_2\cdot CHI$	.915		1.175(59)	1.365(50)	1.70 (97)
Butyl chloride $CH_3\cdot (CH_2)_2\cdot CH_2Cl$	.925		1.18 (59)	1.375(58)	1.70 (95)
Iso-Butyl chloride $(CH_3)_2\cdot CH\cdot CH_2Cl$	.915		1.175(56)	1.37 (63)	1.70 (96)
Butyl bromide $CH_3\cdot (CH_2)_2\cdot CH_2Br$	.915	1.025	1.18 (60)	1.37 (56)	1.70 (97)
Iso-Butyl bromide $(CH_3)\cdot CH\cdot CH_2Br$	.915		1.175(58)	1.365(56)	1.70 (96)
Butyl iodide $CH_3\cdot (CH_2)_2\cdot CH_2I$	.920		1.18 (59)	1.37 (55)	1.705(95)
Iso-Butyl iodide $(CH_3)_2\cdot CH\cdot CH_2I$	.915		1.175(53)	1.37 (48)	1.70 (95)
Butyl nitrite $(CH_3\cdot (CH_2)_2 CH_2NO_2$	.920		1.185(56)	1.37 (54)	1.705(97)
Butyl ether $(C_4H_9)_2\cdot O$	.920		1.19 (64)	1.375(67)	1.70 (98)
Pentane $CH_3(CH_2)_3CH_3$	.915	1.015	1.185(56)	1.375(54)	1.705(94)
Hexane $CH_3(CH_2)_4 CH_3$	.925	1.03	1.195(70)	1.38 (63)	1.72 (96)
Heptane $CH_3(CH_2)_5 CH_3$	.925	1.035	1.19 (67)	1.38 (60)	1.72 (92)
Octane $CH_3(CH_2)_6 CH_3$	.930	1.035	1.195(66)	1.385(60)	1.72 (94)
Mesitylene $(C_6H_3)_3$	.915	1.015	1.18 (54)	1.37 (56)	1.705(94)
Methylene chloride $CH_2 Cl_2$	.890, .935	1.03	1.15 (36)	1.39 (41)	1.675(92)
Methylene bromide $CH_2 Br_2$	.890	1.035	1.15 (38)	1.365(32)	1.68 (90)
Methylene iodide CH_2I_2	.895	1.03	1.15 (28)	1.37 (26)	1.68 (18)
Chloroform $CHCl_3$	.890	1.015	1.145(19)	1.385(36)	1.66 (65)
	(.84C)	(.99C)	(1.12, 1.21C)		(1.671, 1.71C)
Bromoform $CHBr_3$	.89	1.015	1.15 (23)	1.40 (57)	1.67 (74)
Ethylene bromide $C_2H_4Br_2$	.895		1.16 (42)	1.38 (39)	1.685(95)
Ethylene chloride $C_2H_4Cl_2$	.90		1.16 (46)	1.39 (47)	1.685(91)
Benzene C_6H_6	.885	(.99P)	1.145(51)	1.39 (22)	1.66 (93)
	(.86P)	(1.02C)	(1.13P)	(1.43C)	(1.68P)
Toluene $C_6H_5CH_3$	.885-.915		1.145(48)	1.375(37)	1.70 (93)
	(.87P)	(1.03P)	(1.16P)	(1.44P)	(1.70P, 1.71C)
Para-xylene $C_6H_4 (CH_3)_2$	.895-.915	1.02	1.155(46)	1.38(48)	1.705(94)
	(.86P)	(.94P)	(1.22P)	(1.41P)	(1.71PC)
Cotton-seed oil	.93	1.04	1.195(70)	1.395(70)	1.73 (95)
			(1.18C)	(1.39C)	(1.75C)

TABLE I (*Continued*). Additional absorption maxima

Ethyl chloride C_2H_5Cl		1.81 (70)	1.90(40)	1.995(45)	2.085(33)	
Ethyl bromide C_2H_5Br		1.815(63)	1.90(51)	2.00(53)		
Ethyl iodide C_2H_5I		1.84(50)	1.93(45)	2.04(42)		
		(1.85P)				(2.3P)
Methyl iodide CH_3I	1.45(42)	1.86(32)			2.10(54)	
	(1.49P)	(1.85P)			(2.13P)	(2.37P)
Propyl bromide $CH_3 \cdot CH_2 \cdot CH_2Br$			1.90(70)			
Propyl iodide $CH_3 \cdot CH_2 \cdot CH_2I$			1.90(64)	2.005(53)		
jso-propyl iodide $(CH_3)_2 \cdot CHI$			1.90(55)	1.985(53)		
Butyl bromide $CH_3 \cdot (CH_2)_2 \cdot CH_2C_1$				1.99(64)		
Iso-butyl bromide $(CH_3)_2CH \cdot CH_2C_1$			1.90(68)	1.985(57)		
Pentane $CH_3(CH_2)_3\ CH_3$		1.82	1.90			
Hexane $CH_3(CH_2)_4\ CH_3$		1.81(90)				2.42
Heptane $CH_3(CH_2)_5\ CH_3$		1.80(88)				
Octane $CH_3(CH_2)_6\ CH_3$		1.80(91)				(2.38C)
Mesitylene $(C_6H_3)\ (CH_3)_3$		1.86(60)	(1.95C)	2.025(61)	(2.2C)	(2.3C)
Methylene chloride $CH_2\ Cl_2$		1.86(49)	1.98(20)	2.095(29)		
Methylene bromide $CH_2\ Br_2$	1.405(40)	1.875(47)	1.925(38)	2.045(23)		
Methylene iodide CH_2I_2	1.425(34)	1.835(32)	1.94(24)	2.07(47)	2.14	
Chloroform $CHCl_3$	1.50(12)	1.835(56)	(1.916I)	2.105(20)		2.425(2.38C)
Bromoform $CHBr_3$	1.535(30)	1.89(60)	(1.92I)	2.07(65)		
Ethylene bromide $C_2H_4Br_2$		1.86(58)		2.01(35)		
Ethylene chloride $C_2H_4Cl_2$		1.86(57)		2.01(35)		
Benzene C_6H_6	1.73, 1.79	1.85(47)	1.90(38)		2.18(95)	
			(1.95P)	(2.05P)	(2.18CP)	
Toluene $C_6H_5CH_3$		1.86(48)		2.02(50)	(2.18P)	(2.34P)
Para-xylene $C_6H_4\ (CH_3)_2$		1.86(53)		2.025(53)		
		(1.84P)		(2.06P)	(2.18P)	(2.34P)

It seems quite probable that the 1.7μ band for at least most of the compounds is not a single band. In many cases at least two distinct bands are seen, and the breadth of others would indicate a combination of two or more bands. This band seems to be triple in the case of methylene iodide and also perhaps in the cases of methylene chloride and, bromide. Comparison with the results of the visual observations and also of the curves for toluene, pentane, hexane and heptane shows there is a tendency for the minima to be displaced toward a longer wave-length in many substances when a thicker cell is used. Since absorption follows a logarithmic law, we should expect such a shift only when the longer wave-length component of a double band is more intense.

The spectra of chloroform and bromoform, Fig. 4a, are very similar. However, there is a shift toward the longer wave-lengths in the case of bromoform. These two compounds have the best defined bands of all the substances examined. They are also the most transparent. This fact is in accordance with the observation made by Iklé[8] that the presence of a greater amount of any halogen in a compound increases its diathermancy.

In Figs. 3b and 3c are given the curves of the propyl and of the butyl compounds. No appreciable differences are observed between the normal

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[8] Max Iklé, Dissertation, Berlin, 1903

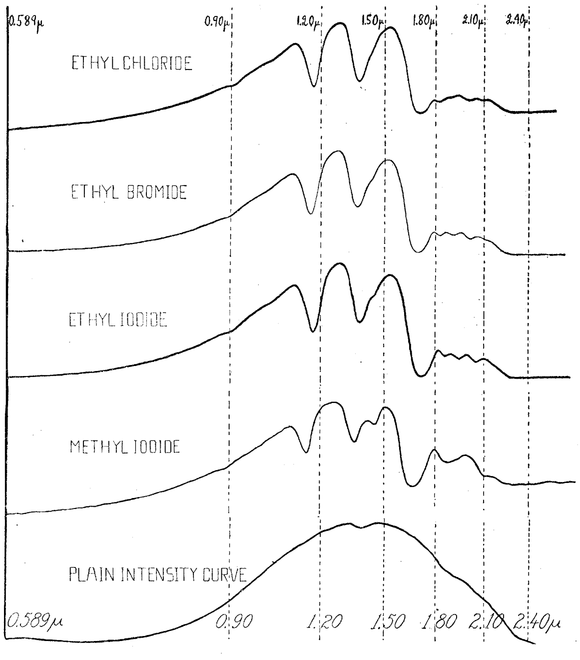
0.589μ
0.90μ
1.20μ
1.50μ
1.80μ
2.10μ
2.40μ
ETHYL CHLORIDE
ETHYL BROMIDE
ETHYL IODIDE
METHYL IODIDE
PLAIN INTENSITY CURVE
0.589μ
0.90
1.20
1.50
1.80
2.10
2.40μ

Fig. 3a

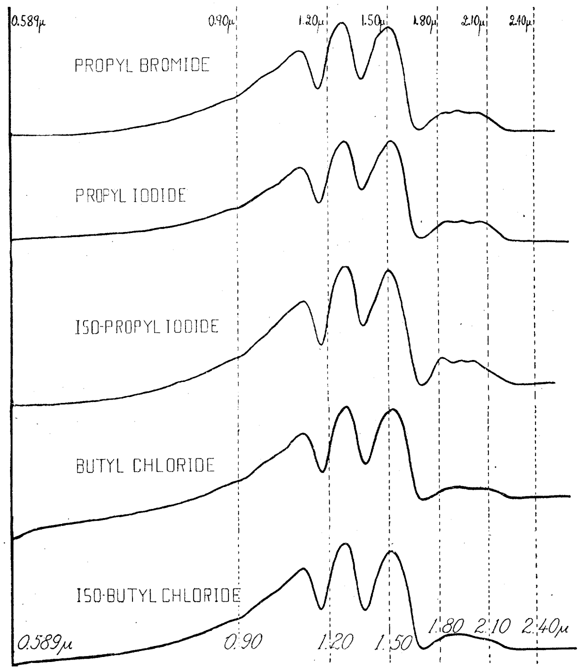
0.589μ
0.90μ
1.20μ
1.50μ
1.80μ
2.10μ
2.40μ
PROPYL BROMIDE
PROPYL IODIDE
ISO-PROPYL IODIDE
BUTYL CHLORIDE
ISO-BUTYL CHLORIDE
0.589μ
0.90
1.20
1.50
1.80
2.10
2.40μ

Fig. 3b

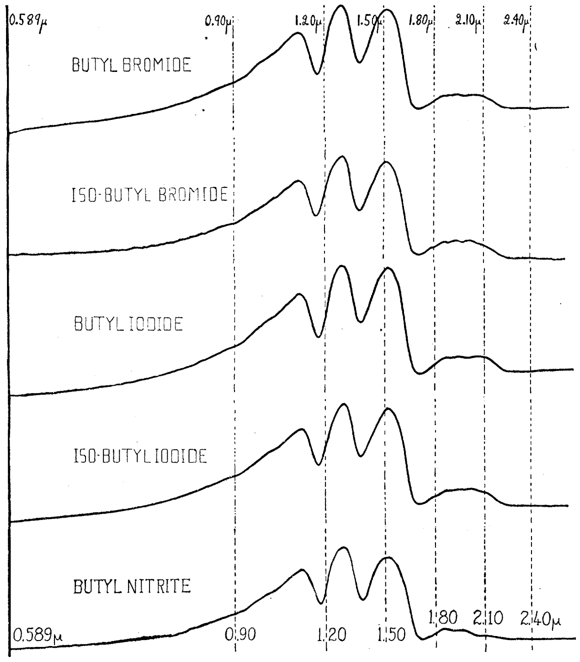
0.589μ
0.90μ
1.20μ
1.50μ
1.80μ
2.10μ
2.40μ
BUTYL BROMIDE
ISO-BUTYL BROMIDE
BUTYL IODIDE
ISO-BUTYL IODIDE
BUTYL NITRITE
0.589μ
0.90
1.20
1.50
1.80
2.10
2.40μ

Fig. 3c

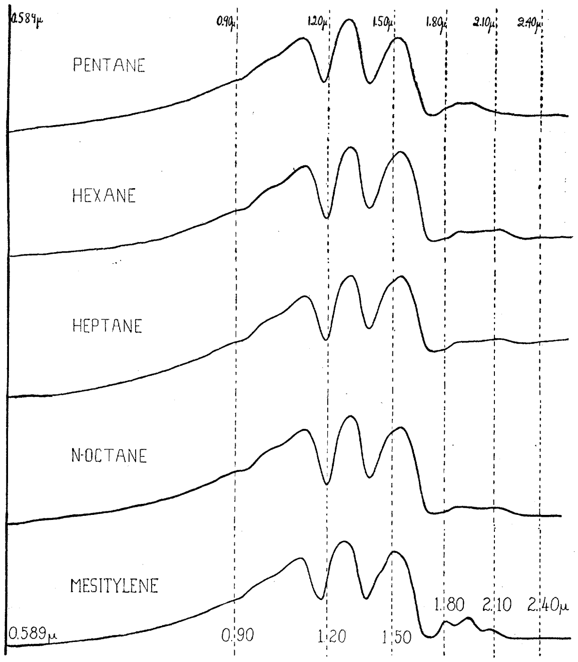
0.589μ
0.90μ
1.20μ
1.50μ
1.80μ
2.10μ
2.40μ
PENTANE
HEXANE
HEPTANE
N-OCTANE
MESITYLENE
0.589μ
0.90
1.20
1.50
1.80
2.10
2.40μ

Fig. 3d

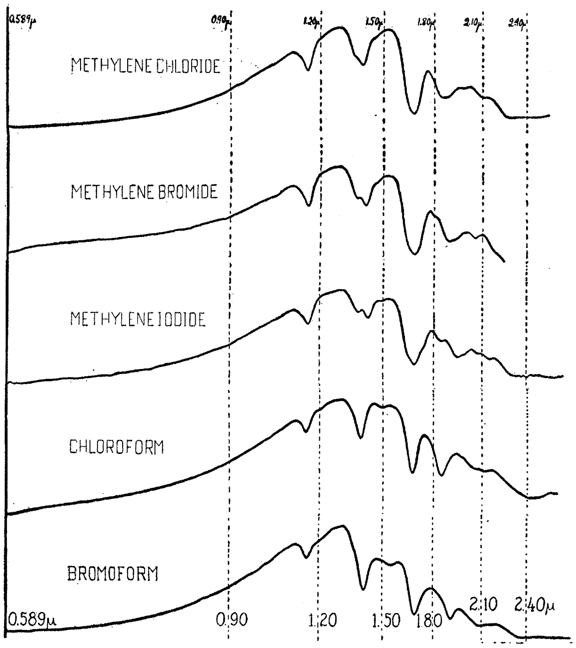
0.589μ
0.90μ
1.20μ
1.50μ
1.80μ
2.10μ
2.40μ
METHYLENE CHLORIDE
METHYLENE BROMIDE
METHYLENE IODIDE
CHLOROFORM
BROMOFORM
0.589μ
0.90
1.20
1.50
1.80
2.10
2.40μ

Fig. 4a

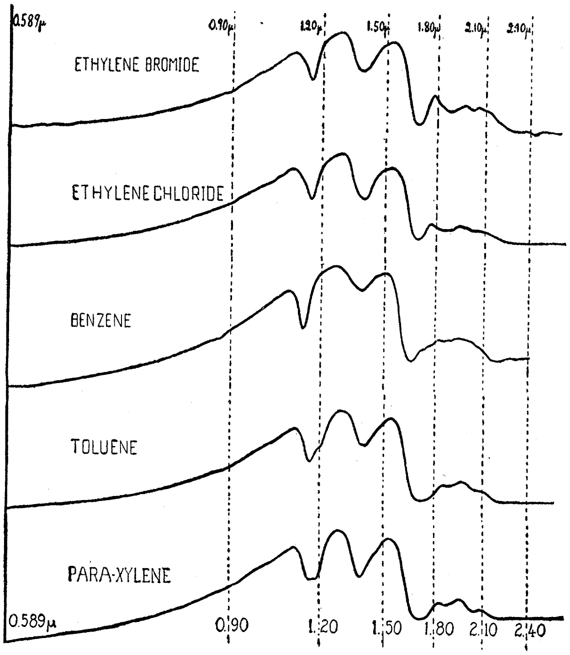
0.589μ
0.90μ
1.20μ
1.50μ
1.80μ
2.10μ
2.40μ
ETHYLENE BROMIDE
ETHYLENE CHLORIDE
BENZENE
TOLUENE
PARA-XYLENE
0.589μ
0.90
1.20
1.50
1.80
2.10
2.40

Fig. 4b

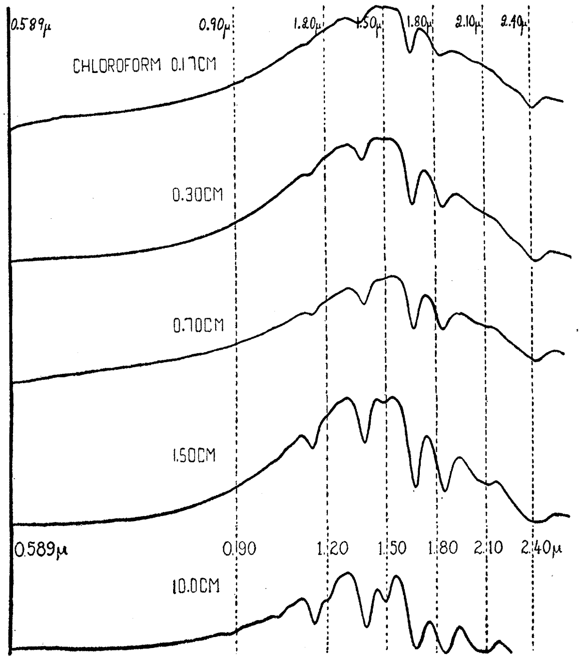
0.589μ
0.90μ
1.20μ
1.50μ
1.80μ
2.10μ
2.40μ
CHLOROFORM 0.17CM
0.30CM
0.70CM
1.50CM
0.589μ
0.90
1.20
1.50
1.80
2.10
2.40μ
10.0CM

Fig. 4c

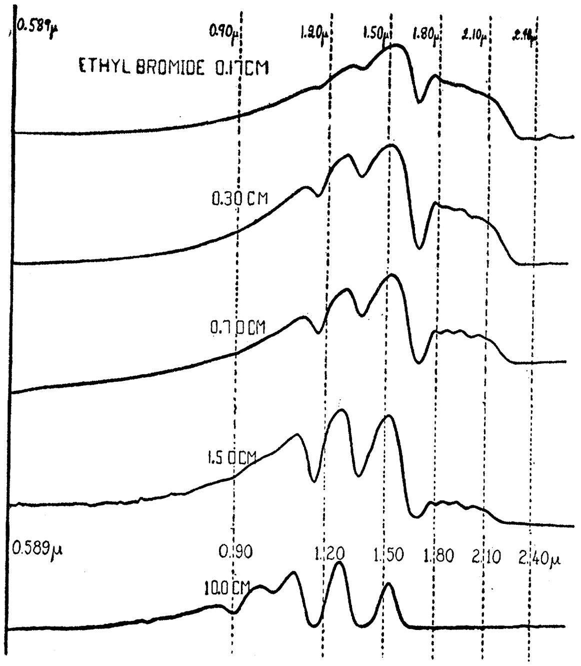
0.589μ
0.90μ
1.20μ
1.50μ
1.80μ
2.10μ
2.40μ
ETHYL BROMIDE 0.17CM
0.30 CM
0.70CM
1.50CM
0.589μ
0.90
1.20
1.50
1.80
2.10
2.40μ
10.0CM

Fig. 4d

and the iso- compounds; nor between the curve for butyl nitrite and those for the butyl halides.

The effect of the change of thickness of the cell upon the form of the curves is well shown for chloroform and ethyl bromide in Figs. 4c and 4d. Thicknesses varying from 0.17 cm to 10.0 cm were used for each. Since the bands at 0.9μ and 1.0μ show plainly for the 10 cm cells, although they were entirely obscured for the 1.1 cm cell for chloroform, the probability that these two bands are also common to all C-H compounds is increased.

The spectrum of cotton-seed oil also was taken. Its absorption maxima are tabulated in Table I and agree well with those given by Coblentz.[7]

Correction to Puccianti's values. More accurate determinations of the indices of refraction for quartz for infra-red light have been made since Puccianti[2] made his investigations. Fortunately, he recorded the refracting angle of his prism and also the deviation for several absorption bands. When the new values of these indices of refraction as given by the Bureau of Standards[1] are applied, somewhat different values from those computed by Puccianti are obtained (see Table II).

TABLE II

Corrections to Puccianti's values

Puccianti's values	Corrected values	Difference
1.150μ	1.146μ	0.004μ
1.440	1.388	0.052
1.710	1.690	0.020
2.180	2.156	0.024

The corrected values agree more closely with those of the present investigation.

The duplicity of the bands. It is a well known theory that absorption bands in the near infra-red spectra of gases should not be single but rather triple bands, the center corresponding to an oscillation frequency and the two outer components to a combination of oscillation and rotational frequencies. However, in the case of gases the central component is always missing, i.e. the oscillation frequencies do not exist alone. Thus the bands are double rather than triple. The duplicity of many of the bands shown above and the possibility that many of the other bands may be unresolved would suggest the possible application of the above theory to liquids.

Of all the bands shown above in Figs. 3 and 4, the 1.38μ band for the methylene halides and for methyl iodide shows the greatest separation. It has been pointed out that this separation is greatest for the iodide. Under the newer quantum theory the rotational frequencies of the gas molecule occur only in whole multiples, n, of $h/4\pi^2 I$, where h is Planck's constant and I the moment of inertia of the molecule. Thus

$$\nu_r = nh/4\pi^2 I \tag{1}$$

This combination of rotational frequencies with an oscillation frequency gives to the two components of the double band a structure of equally spaced narrow bands, or lines, which under high resolution have been discovered in the cases of some diatomic gases by Imes[9] and others. The separation of these lines is given by ν_r. Now according to Kemble[10] the value of n which gives the line of maximum intensity is given by

$$n_{max} = 2\pi\sqrt{KIT}/h \tag{2}$$

where K is the gas constant and T the absolute temperature. Combination of Eq. (1) and Eq. (2) gives for the maximum frequency in one of these components

$$\nu_{max} = \sqrt{kT/I}/2\pi \tag{3}$$

Since I varies directly with the mass of the molecule, and since I occurs in the denominator of the expression for ν_{max}, we should expect the heavier methylene iodide molecule to have a smaller separation $2\nu_{max}$ between its two components than the bromide or chloride, provided the theory worked out for gases is also applicable for liquids. This, however, is contrary to observation. If the theory does apply to liquids, we have to assume the heavier molecules of methylene iodide to have smaller effective dimensions than the methylene bromide or chloride molecules.

Harmonic relationship with far infra-red bands. An examination of the curves given by Coblentz shows that all the C-H substances have a band at approximately 6.9μ. Out of the large number of characteristic absorption bands this and the one at 3.4μ alone seem to be common to all C-H compounds. This fact has led the writer to conclude that the 6.9μ band is probably a fundamental oscillation band for the carbon-hydrogen linkage. Coblentz has ascribed it and also the 3.4μ band to a CH_2 or a CH_3 group, while Weniger[11] ascribed it to O-H in the case of the numerous alcohols which he investigated.

Possible harmonics in the near infra-red are given in Table III. These values from the third to the seventh check well with the wave-number values for the five bands mentioned above as being characteristic of all the compounds tabulated in Table I.

In computing this table the average values for the wave-numbers of all the substances examined were taken. A progressive variation between

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[9] Imes, Astrophs. J. **50,** 1919

[10] Kemble, Phys. Rev. (2), **8,** 1916

[11] Weniger, Phys. Rev., **31,** 1910

the calculated and the observed values is noticed. The second harmonic at 2.3μ shows up in some of Coblentz' curves, much weaker than the first. It lies at one end of the region of the present investigation, and because of the comparatively thick cell used was not clearly defined.

TABLE III

Harmonic	ν*(calc.)*	ν*(obs.)*	λ*(calc.)*	λ*(obs.)*	*Diff. (per cent)*
1	290		3.450μ		
2	435		2.300		
3	580	590	1.725	1.696μ	2
4	725	727	1.380	1.375	–
5	870	855	1.150	1.171	−2
6	1015	980	0.975	1.023	−3
7	1160	1105	0.863	0.906	−5

A regular diminution in the intensities would be expected among these bands. In Coblentz' curves the intensities fall off regularly from the fundamental to the first and second harmonics. The present investigation shows a regular diminution with the exception that the fourth and fifth harmonics are of approximately equal intensities, while the seventh is a little stronger than the sixth. The two latter, however, are much weaker than the two former.

In conclusion, the writer wishes to express his thanks to Professor E. P. Lewis, out of whose suggestion this research originated, for his advice throughout the progress of the work. He also wishes to express his appreciation to Professor R. T. Birge for his suggestions concerning the applications of the quantum theory to band spectra.

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