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THE INFRA-RED ABSORPTION OF SOME ORGANIC LIQUIDS

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Abstract

The infra-red absorption spectra of fourteen organic compounds, including seven alcohols and seven miscellaneous compounds, have been studied in the region from 1μ to 7.5μ. The bands in the region from 1μ to 3μ have been classified as overtones or combination bands of the assumed fundamental bands for the alcohols at about 3.00μ, 3.4μ, 6.8μ, and 9.8μ. By the use of Sappenfield's work for the region from 1μ to 2μ and that of Weniger from 7.5μ to 10μ and the present work a fairly complete idea of the infra-red absorption spectra of the alcohols has been obtained. The intensity relations have been discussed briefly and it was shown that they were in general in accordance with combinations attributed to the different bands. The bands of the miscellaneous organic compounds have been classified, but all the bands have not been included as only the fundamentals at 3.4μ and 6.8μ were used. A probable reason for the similarity of the infra-red spectra of many organic compounds in the region from 1μ to 3μ has been suggested.

Introduction

An EXPERIMENTAL study has been made of the infra-red absorption bands of fourteen organic liquids in the region from 1μ to 8μ. The materials used were methyl, ethyl, propyl, butyl, iso-propyl, iso-amyl, and iso-butyl alcohols and m-nitrotoluene, o-nitrotoluene, methyl sulphate, ethyl sulphate, nitromethane, nitrobenzene and ethyl acetoacetate. The purpose of this investigation was to see what similarities existed in the near infra-red absorption bands of some organic liquids of quite different type. Also, it was hoped that several of the more intense bands of each material could be classified as combination bands of the fundamentals.

The infra-red absorption spectra of nearly all the alcohols studied in this work have already been investigated by Weniger[1] in the region from 1μ to 14μ and by Sappenfield[2] from 1μ to 2μ. The work of Weniger gives one a good representation of the bands to 14μ, but as he used a very thin cell for the entire region many of the smaller bands were not observed. Sappenfield was able, by using cells of different thickness and spectrometer of high resolution, to detect many bands in the region from 1μ to 2μ which had not previously been observed. He classified some of the bands observed by him on the basis of the work of Gapon.[3] It was believed that a modification of his classification would be more in accordance with intensity relations. It was thought that it would be of value to extend the experimental observations under high

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[1] Weniger, Phys. Rev. **31**, 388 (1910).

[2] Sappenfield, Phys. Rev. **33**, 37 (1929).

[3] Gapon, Zeit. f. Physik **44**, 600 (1927).

resolution beyond the region of 2μ and to classify the bands found by Sappenfield with those of this region.

EXPERIMENTAL PROCEDURE

The apparatus and the method of measurement were essentially the same as used by the writer in a previous investigation.[4] It was found necessary to use cells of different thickness in order to observe the weaker bands. These cell thicknesses and the effective slit widths are tabulated in Table 1. The thickness of the cells in the region from 2.80μ to 3.50μ and from 5.50μ to 7.50μ varied somewhat for each material studied. For example, in the cases of the alcohols it was necessary to have cells about 0.001 mm in order that 20 percent of the incident beam might be transmitted. These thin cells were made by placing a small drop of the liquid on a microscopic cover glass and then placing another cover glass over this. The cell formed in this manner was then pressed very thin and glued around the edges. An approximate value of the thickness was obtained by observing the change in the interference fringes when the cover glasses were pressed together at the center of the cell. The thicker cells were made by separating glass or rock-salt windows with lead foil or sheet lead. All the materials used in this study except two of the alcohols, which were prepared in the chemical laboratory, were obtained from the Eastman Kodak Laboratories.

TABLE I. *The cell thicknesses and the effective slit-width at the thermopile for the different parts of the region studied.*

Region	Thickness of cell	Prism used	Effective slit-width
$1\ 00\mu-1.25\mu$	1.50 mm	Quartz	0.0060μ
$1.25\mu-2.00\mu$	.7 mm		$.0075\mu$
$2.00\mu-2.80\mu$	.4 mm		$.0150\mu$
$2.80\mu-3.50\mu$	.01 to .001		$.0150\mu$
$5.50\mu-7.50\mu$	.01	Rock-salt	$.155\mu$

RESULTS AND DISCUSSION

The experimental results are represented in Figs. 1 to 6 and a list of the observed bands is given in Table II. The region from 2.8μ to 3.6μ was measured with the rock-salt prism in Fig. 3 and with the quartz prism in Fig. 2. Due to the great effective slit width in the region of 3μ for the rock-salt prism, it was not possible to resolve the bands at 3.00μ and 3.40μ. For the alcohols the region from 3.6μ to 5μ has been included in Fig. 3, but it does not contain any intense bands. Also, any bands of much intensity were not observed for the other materials in this region and results obtained were not included in Fig. 6. The relations found to exist between some of the bands of the alcohols are shown in Table III. The combinations given were calculated on the basis that the intense bands observed at 3.00μ, called ν_1^1, 3.40μ, ν_1, 6.90μ, ν_2, and

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[4] Plyler and Steele, Phys. Rev. **34**, 599 (1929).

TABLE II. *List of observed bands.*

			Alcohols			
Methyl	Ethyl	Propyl	Butyl	Iso-propyl	Iso-amyl	Iso-butyl
2.06μ	2.03μ	2.07μ	2.07μ	2.06μ	2.05μ	2.05μ
2.27	2.23	2.16	2.18	2.28	2.27	2.10
2.46	2.42	2.27	2.30	2.42	2.39	2.25
2.56	2.54	2.43	2.44	2.54	2.56	2.38
2.92	3.01	2.62	2.60	3.00	3.01	2.50
3.02	3.39	3.01	3.00	3.38	3.42	2.99
3.29	4.31	3.43	3.43	4.22	4.61	3.41
3.42	5.00	4.55	3.22	4.44	5.16	4.52
4.22	5.75	4.91	4.67	5.72	5.69	4.78
4.70	6.11	5.18	5.07	5.98	5.92	5.18
5.42	6.62	5.81	5.93	6.10	6.80	5.86
5.84	6.89	6.06	6.13	6.71	6.96	6.86
6.14	7.04	6.67	6.83	6.91	7.14	7.00
6.73	7.40	6.81	6.95	7.24	7.79	7.88
6.99	7.81	7.91	7.98			
7.38						
7.82						

M-nitro-toluene	O-nitro-toluene	Methyl sulphate	Nitro-methane	Ethyl sulphate	Nitro-benzene	Ethyl acetoacetate
1.15μ	1.15μ	1.15μ	1.12μ	1.17μ	1.13μ	1.17μ
1.39	1.40	1.38	1.37	1.39	1.29	1.40
1.68	1.67	1.67	1.68	1.71	1.42	1.65
1.98	2.00	1.86	1.82	1.91	1.63	1.92
2.04	2.30	1.97	1.92	2.05	1.80	1.99
2.31	2.41	2.06	2.26	2.30	1.90	2.29
2.47	2.54	2.24	2.41	2.43	2.15	2.40
2.55	3.28	2.37	2.59	3.37	2.44	2.62
3.28	3.39	2.60	3.29	7.20	3.26	3.39
3.42	6.68	3.40	3.41		3.43	5.82
6.57	7.46	7.05	6.37		6.56	7.10
7.40		7.20	7.13		7.36	

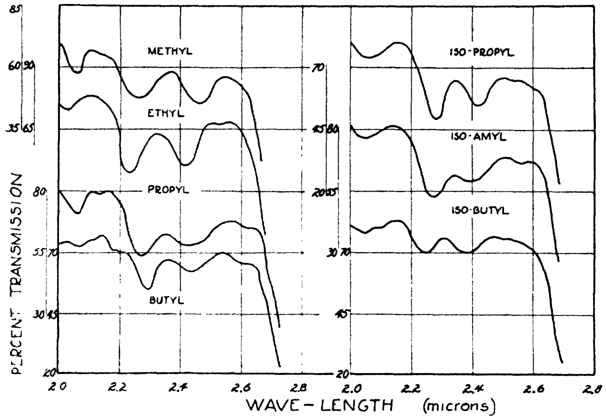

Fig. 1. The percent transmission of methyl alcohol, ethyl alcohol, propyl alcohol, butyl alcohol, iso-propyl alcohol, iso-amyl alcohol and iso-butyl alcohol in the region from 2μ to 2.7μ, the cell thickness being 0.4 mm.

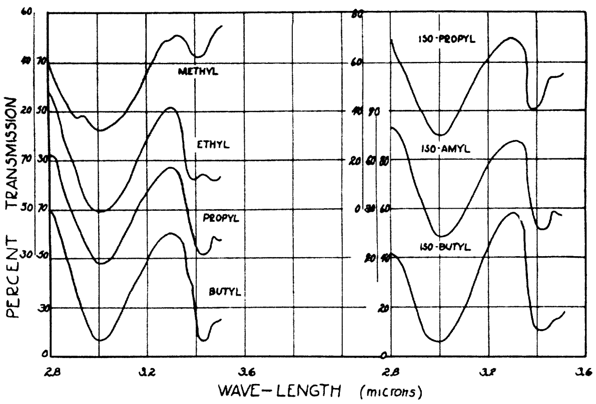

Fig. 2. The percent transmission of methyl alcohol, ethyl alcohol, propyl alcohol, butyl alcohol, iso-propyl alcohol, iso-amyl alcohol and iso-butyl alcohol in the region from 2.8μ to 3.5μ, the cell thickness being from 0.01 to 0.001 mm.

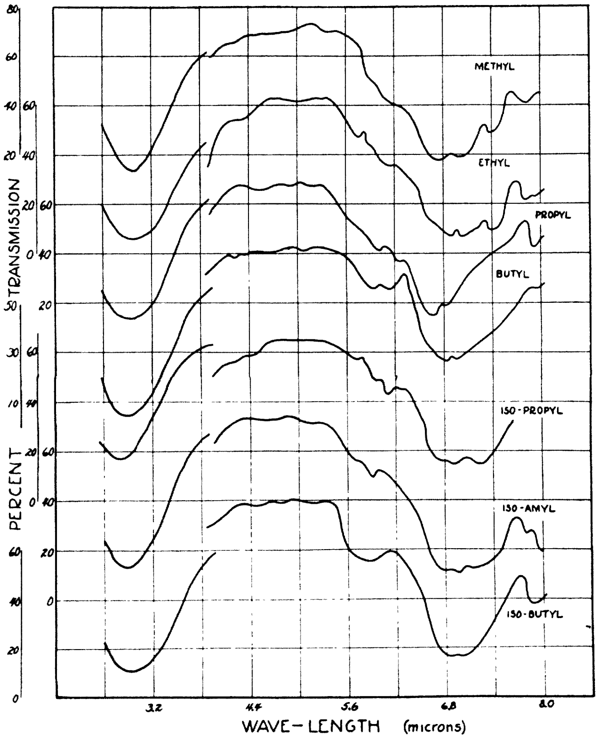

Fig. 3. The percent transmission of methyl alcohol, ethyl alcohol, propyl alcohol, butyl alcohol, iso-propyl alcohol, iso-amyl alcohol and iso-butyl alcohol in the region from 2.8μ to 8μ, the cell thickness being from 0.01 to 0.001 mm.

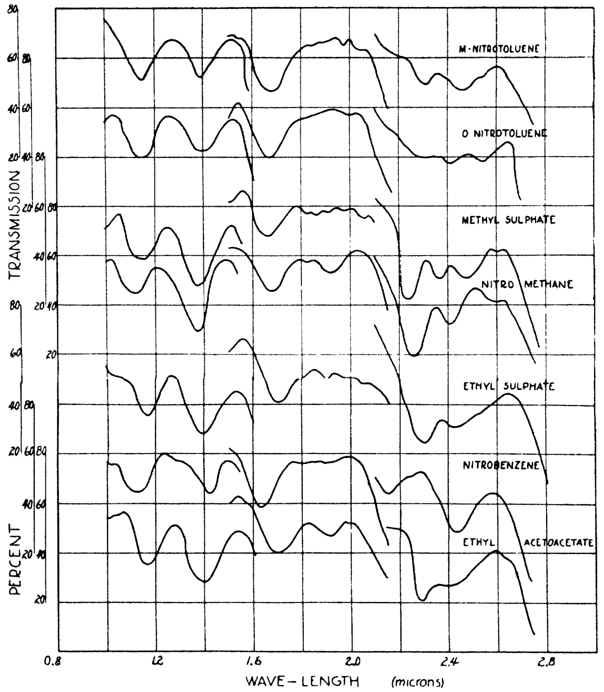

Fig. 4. The percent transmission of m-nitrotoluene, o-nitrotoluene, methyl sulphate, nitromethane, ethyl sulphate, nitrobenzene, and ethyl acetoacetate in the region from 1μ to 2.8μ, the cell thickness being 15 mm from 1μ to 1.25μ, 0.7 mm from 1.25μ to 8.2μ, and 0.4 mm from 2.00μ to 2.8μ.

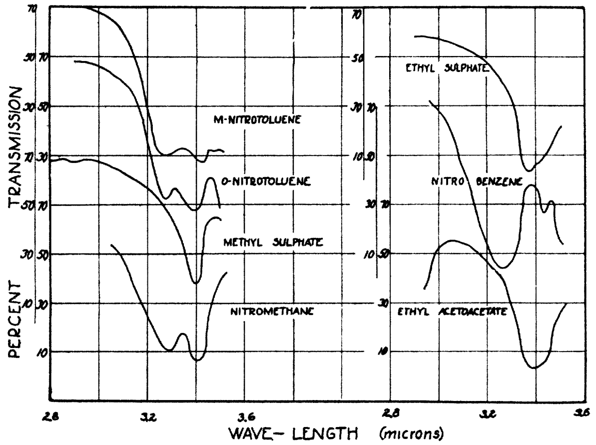

Fig. 5. The percent transmission of m-nitrotoluene, o-nitrotoluene, methyl sulphate, nitromethane, ethyl sulphate, nitrobenzene, and ethyl acetoacetate in the region from 2.8μ to 3.5μ, the cell thickness being about 0.01 mm.

9.8μ, ν_3, were the fundamental bands. The combinations which the bands are attributed to are made up of only two or three of the fundamentals or their overtones as it is probable that more intense bands will be produced by simple combinations. All the observed bands have not been assigned to combinations as it was found necessary to include up to the fifth or sixth overtone as one of the terms to obtain good agreement between the observed and calculated results. It was believed that the bands at about 1.94μ and 2.60μ which were omitted, were due to a combination including a fundamental beyond 12μ which had not been observed rather than to a combination of the known fundamentals. Fundamental bands have been observed for several

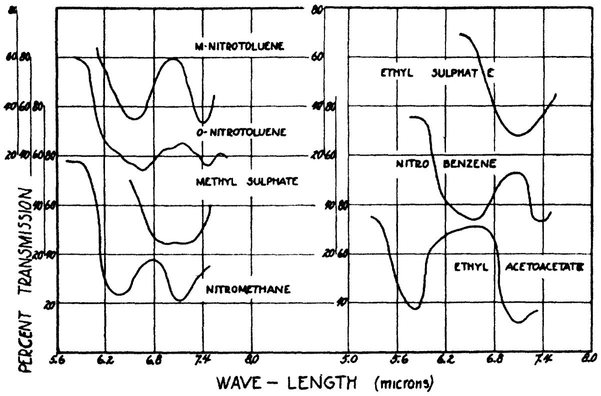

Fig. 6. The percent transmission of m-nitrotoluene, o-nitrotoluene, methyl sulphate, nitromethane, ethyl sulphate, nitrobenzene, and ethyl acetoacetate in the region from 5.5μ to 7.5μ, the cell thickness being about 0.01 mm.

Table III. *Calculated and observed bands in the alcohols.*

	Propyl alcohol		Butyl alcohol		Iso-butyl alcohol	
	obs.	calc.	obs.	calc.	obs.	calc.
$4\nu_1$	0.923μ	0.923μ	0.929μ	0.929μ	0.918μ	0.918μ
$3\nu_1^1$	1.028	1.028	1.032	1.032	1.025	1.025
$\nu_1+2\nu_1^1$		1.06		1.06		1.06
$\nu_1^1+2\nu_1$		1.11		1.10		1.11
$3\nu_1$	1.198	1.198	1.203	1.203	1.196	1.196
$\nu_1^1+\nu_1+\nu_3$		1.37	1.43	1.37	1.41	1.37
$2\nu_1$	1.53	1.53	1.53	1.53	1.53	1.53
$\nu_1^1+\nu_1$	1.58	1.60	1.59	1.60	1.58	1.60
$\nu_1^1+\nu_2+\nu_3$	1.71	1.71	1.72	1.72	1.71	1.72
$2\nu_1$	1.71	1.76	1.72	1.75	1.71	1.77
$\nu_1+\nu_2+\nu_3$		1.84		1.82		1.83
$\nu_1^1+\nu_2$	2.07	2.08	2.07	2.09	2.10	2.09
$\nu_1+\nu_2$	2.27	2.27	2.30	2.29	2.25	2.28
$\nu_1^1+\nu_3$	2.27	2.29	2.30	2.29	2.25	2.29
ν_1^1	3.01	3.05	3.00	3.03	2.99	3.03
ν_1	3.43	3.44	3.43	3.40	3.41	3.47
ν_2	6.73	6.73	6.83	6.85	6.86	6.90
ν_3	9.60	9.60	9.75	9.75	9.75	9.75

organic compounds in this region and it is probable that they exist for these materials, and if they were known, probably a more complete classification could be made.

By a study of the experimental results it is seen that there is considerable overlapping of the bands in the near infra-red region. Unless high resolution is used the less intense maxima are not observed. Also often a weak band occurs near an intense one and changes the shape of the more intense absorption curve, but does not cause the absorption curve to change sufficiently for it to be detected. This effect is especially noticeable in the alcohols in the region from 1.4μ to 1.6μ.

Sappenfield[2] has used the suggestion of Ellis[5] that the organic liquids may be arranged as a series of overtones of the 3.4μ band and thus four of the bands are classified. This classification appears probable and the writer has included it in the present arrangement. The band at 0.92μ was classified as $4\nu_1$ and the band at 1.20μ as $3\nu_1$, and $2\nu_1$ and ν_1 were calculated from these bands. However, as a small error in $4\nu_1$ and $3\nu_1$ would cause a large error in ν_1 it was thought that the observed value of ν_1 was more accurate and it was used in the calculation of the combination bands. In like manner ν_1^1 was checked by using the bands at 1.02μ as $3\nu_1^1$ and 1.53μ as $2\nu_1^1$, but in combination bands the observed value of ν_1^1 was used. It should be noted in some cases there is a considerabel difference between the calculated and observed bands in the case of $2\nu_1$ at about 1.75μ. This difference is probably brought about by the fact that the combination $\nu_1^1+\nu_2+\nu_3$ also gives rise to a band at near the same wave-length. In the case of tertiary butyl alcohol and secondary butyl alcohol both maxima were found.

By an examination of the results obtained in this work and those obtained by Weniger[1] the intensities of the assumed fundmentals are in the order ν_3, ν_1^1, ν_2, and ν_1. Of the combination bands obtained by adding two fundamental bands $\nu_1^1+\nu_3$ should probably be the most intense and $\nu_1+\nu_2$ the least intense. However, these two bands fall in the same region of the spectrum and were not separated. The intensity of $\nu_1^1+\nu_1$ in the region of 1.60μ is somewhat less than the intensity of $\nu_1^1+\nu_2$ at 2.09μ and the intensity of $\nu_1^1+\nu_1+\nu_3$ is less than that of $\nu_1^1+\nu_1$. The decrease in intensity of the successive overtones of ν_1^1 and ν_1 is large. Due to the considerable overlapping in the bands, it is not possible to made a careful comparison of the intensities of the different combinations, but in the bands where the intensities could be checked the combinations given in Table III were upheld.

In Table IV the assumed fundamentals ν_1 at 3.40μ and ν_2 at 6.80μ and combination bands of M nitrotoluene, methyl sulphate, nitromethane are given. Only slight differences occur for the other materials studied and they have not been included. Since only two fundamentals are known, several of the bands in the near infra-red could not be attributed to simple combinations. They have been omitted for they are possibly due to combinations of ν_1 and ν_2 with bands in the region of 10μ to 12μ and 15μ to 18μ. In these

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[5] Ellis, Phys. Rev. 31, 916 (1928).

regions bands have been shown to exist for several of methyl and ethyl compounds by different observers.[6]

While it must be recognized that the infra-red absorption spectra of each substance are different even though they may be only slightly different chemically, yet the great similiarity in the absorption spectra of quite different organic compounds in the region from 1μ to 3μ is readily observed. This similarity in the near infra-red region is probably due to the fact that many organic compounds have fundamentals at about 3.3μ and 6.8μ, and in several cases also, fundamental bands are in the region from 8μ to 12μ and from 12μ to 18μ. By the combinations of these bands the near infra-red spectra are somewhat similar in appearance, but in the region from 8μ to longer wavelengths a considerable difference is found in the spectra of similar organic compounds. An examination of the results of Coblentz[6] shows this for a large number of organic compounds.

TABLE IV. *Combination bands in nitrotoluene, methyl sulphate and nitrobenzene.*

	M-nitro-toluene obs.	calc.	Methyl sulphate obs.	calc.	Nitro-benzene obs.	calc.
$3\nu_1$	1.15μ	1.15μ*	1.15μ	1.15μ*	1.13μ	1.13μ*
$2\nu_1+\nu_2$	1.39	1.35	1.38	1.35	1.29	1.32
$2\nu_1$	1.68	1.68*	1.67	1.67*	1.63	1.63*
$\nu_1+\nu_2$	2.21	2.21	2.24	2.29	2.15	2.21
ν_1	3.28	3.27	3.40	3.24	3.26	3.13
$2\nu_2$	3.42		3.40		3.43	
ν_2	6.80	6.80*	7.05	7.05*	6.90	6.90*

* Experimental values used as calculated values.

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[6] Coblentz, Investigations of Infra Red Spectra, Part 1–2, Carnegie Institution of Washington, (1905).