[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICS OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES. ORGANO-MOLECULAR INVESTIGATIONS]

THE NEAR INFRA-RED ABSORPTION SPECTRA OF SOME ALDEHYDES, KETONES, ESTERS AND ETHERS

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The infra-red absorption spectra of a group of aldehydes, ketones and esters have been obtained in the wave length region shorter than 2.5 μ with the primary purpose of ascertaining whether there are any features in such spectra assignable to the carbonyl group. The spectra of ethyl sulfate, pentane and three ethers have also been recorded for comparison purposes. The technique adopted was similar to that followed in some previous investigations by the author.[1] A few changes in the procedure of securing these absorption records are perhaps worthy of mention.

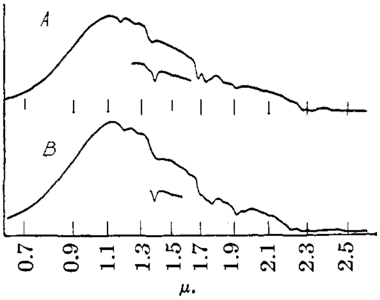

Fig. 1.—A, Acetaldehyde; B, propionaldehyde.

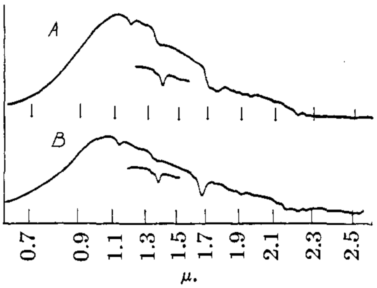

Fig. 2.—A, Butyraldehyde; B, benzaldehyde.

The tungsten lamp, rated at 7.5 amperes, was operated on much higher currents during this investigation. This permitted the use of narrower slits in the spectrograph. In obtaining the first set of records, Figs. 1–13, the initial slit and the one in front of the thermopile had a width of 0.152 mm. A slit of this width covers a spectral region of about 0.007 μ in the vicinity of 1.8 μ. The cell thickness, with two exceptions to be mentioned later, was 1 mm. The lamp source was operated on 9 amperes. The second set of records, Figs. 14–23, was for a cell thickness of 40 mm. The current was increased to 10 amperes and the slits narrowed to 0.127 mm., which is equivalent to about 0.006 μ at 1.8 μ.

With slits as narrow as this it was found impractical to adopt the previous method of using a visible emission spectrum line for a standard of reference. Consequently, it was decided to use the relatively sharp 1.39 μ absorption band of a 2-mm. cell of chloroform. To see whether it would be permissible to rack the plate-holder back to the vicinity of 1.4 μ

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[1] (a) Ellis, THIS JOURNAL, **49**, 347 (1927); (b) **50**, 685 (1928).

after an absorption record had been taken, for the purpose of tracing the chloroform band, several records of absorption curves were retraced on their original plates. The almost exact superposition of these records indicated that it would be practicable to rely upon this method of superposing a standard band upon the plate. This reference band is found in Figs. 1–13.

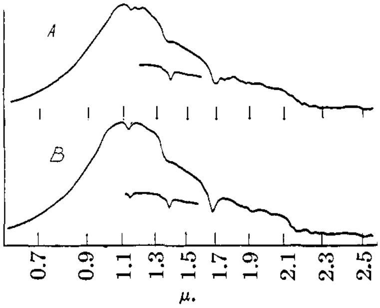

Fig. 3.—A, *p*-Tolualdehyde; B, cinnamaldehyde.

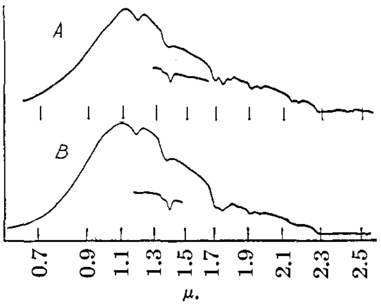

Fig. 4.—A, Acetone; B, methyl-*n*-propyl ketone.

It was discovered during the investigation, however, that there was an occasional record in which the 1.39 μ band was apparently shifted with respect to the spectrum recorded. This shift was ascertained from the following two observations. (1) As a result of a study of a considerable number of organic compounds, it becomes possible to predict fairly accurately the wave length positions of certain recurring bands. (2) A considerable increase in resolving power resulting from a narrowing of the slits revealed the identity of the so-called P, Q and R branches of the 1.87 μ atmospheric water-vapor band. The sharp Q branch is observable not only in the intensity distribution curve of Fig. 13A but also in all of the absorption records of Figs. 1–13. This band, therefore, was chosen as the reference line in these measurements. In obtaining the records of Figs. 14–23 the 40-mm. cell was removed near 1.5 μ although the record

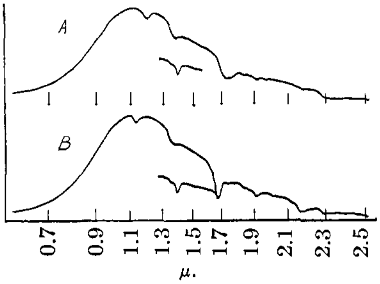

Fig. 5.—A, Methyl-*n*-amyl ketone; B, acetophenone.

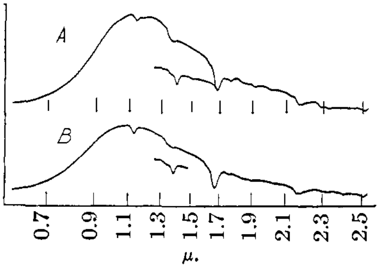

Fig. 6.—A, Propiophenone; B, benzophenone.

was continued to include the 1.87 μ water-vapor band. This reference band, however, has not been included in the figures.

Of the twenty-five compounds whose absorption curves are here presented eighteen contain a single carbonyl group, =C=O, while two others contain two such groups. Pentane and ethyl sulfate were included to show the behavior of a typical hydrocarbon and a typical alkyl radical, respectively. The three ethers were studied to see if any features appear which are characteristic of the oxygen atom in the chain.

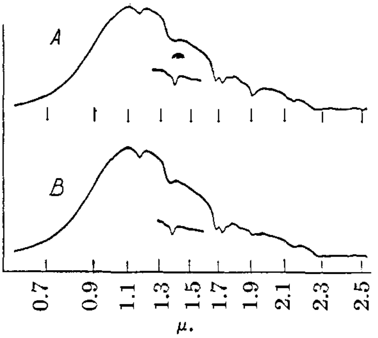

Fig. 7.—A, Methyl acetate; B, ethyl acetate.

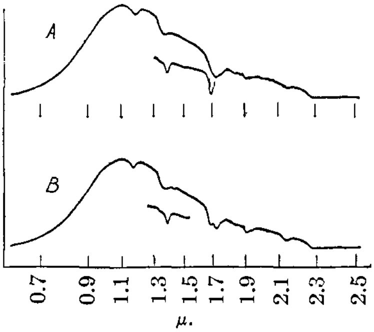

Fig. 8.—A, *n*-Butyl acetate; B, ethyl malonate.

All of the compounds are liquids at room temperature except quinone and benzophenone, which are solids. These latter two substances were therefore examined in carbon tetrachloride solution. A 40-mm. cell of the solution containing an amount of the solid equivalent to a 1-mm. thickness of the material in its crystalline state was used. Their spectra have been included with the 1-mm. cell records of the liquid compounds. All of the materials whose absorption spectra are here presented were purchased from the Eastman Kodak Company.

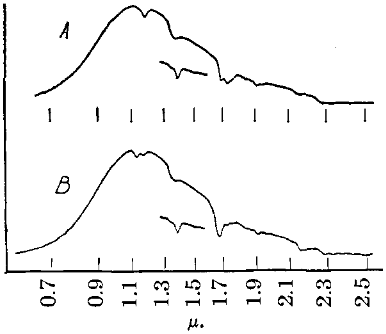

Fig. 9.—A, Ethyl propionate; B, ethyl benzoate.

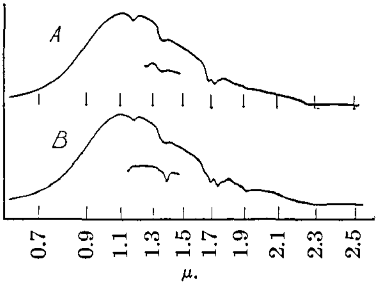

Fig. 10.—A, Ethyl sulfate; B, acetylacetone.

Several investigations, mainly in the infra-red, already described in the literature, have some bearing upon the present study. Smith and Boord[2] in an investigation apparently undertaken to test the present author's previous conclusion that there is a C–H series of absorption bands characteristic of carbon–hydrogen compounds, included in their group of substances several of which contain the carbonyl group. Their investigation did not extend beyond 2.5 μ. The resolution of bands which they secured was good in spite of the fact that they used a spectroscope equipped with a single 60° rock-salt prism. The region covered by them was the same as that covered in this investigation. However, the quartz prisms used here gave a dispersion and a resolution many times that secured by Smith and Boord. This is shown by a comparison of absorption curves of the three substances common to both investigations.

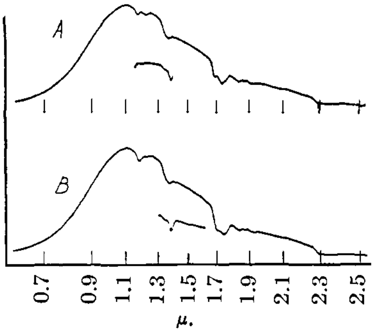

Fig. 11.—A, Ethyl ether; B, *n*-propyl ether.

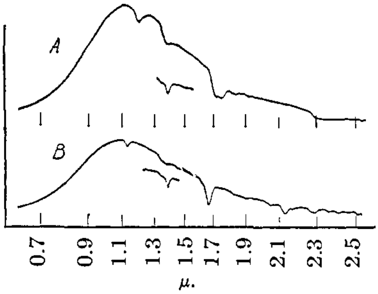

Fig. 12.—A, *n*-Butyl ether; B, quinone.

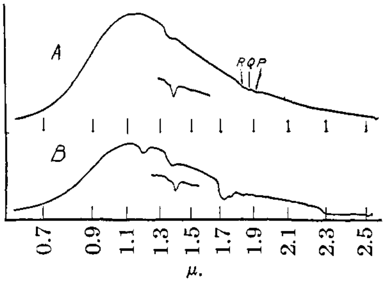

Fig. 13.—A, Intensity distribution; B, pentane.

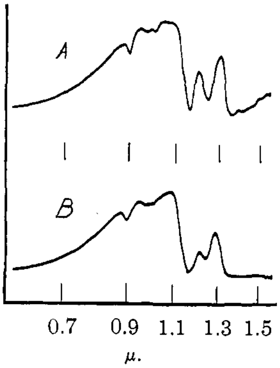

Fig. 14.—A, Acetaldehyde; B, propionaldehyde.

Several investigations made in the region beyond 2.5 μ include molecules

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[2] Smith and Boord, This Journal, **48**, 1512 (1926).

containing the carbonyl group. The extensive study made by Coblentz[3] includes several of these molecules. His records show in each case a strong band near 5.8 μ which he apparently refrains from definitely associating with the =C=O pair because the paraffin hydrocarbons also show a weaker band at this position.

Marsh[4] pointed out that in an investigation made by Spence[5] upon a number of alkaloids the presence or absence of a strong 5.8 μ band marks a distinguishing feature between those molecules containing the carbonyl group and those which do not contain it.

Henri[6] concluded from his study of several aldehydes, ketones and acids that three bands at 8.2–8.5, 5.7–5.85 and 4.9 μ are produced by the =C=O pair.

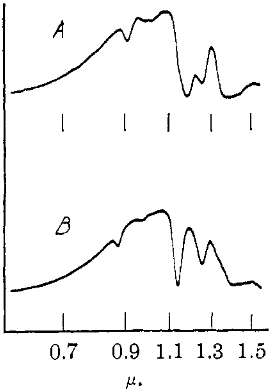

Fig. 15.—A, Butyraldehyde; B, benzaldehyde.

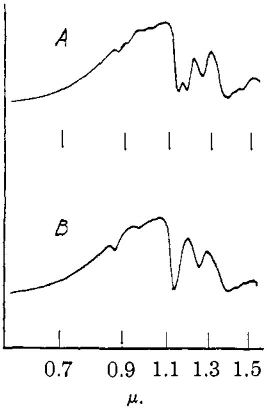

Fig. 16.—A, *p*-Tolualdehyde; B, cinnamaldehyde.

Bonino's[7] investigation of four homologous ketones was limited to the C–H band at 3.4 μ.

From the results of a study of twenty-five aldehydes and ketones Lecomte[8] concluded that a band occurring between 5.90 and 6.03 μ characterizes the =C=O group, while a weaker one at 2.90–3.05 μ is its first overtone. (Lecomte's values are obviously consistently too high, as is evidenced by a comparison of the values in this and others of his papers with numerous determinations by various investigators.)

In his visible Tesla emission spectra of some aldehydes and ketones, Marsh[9]

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[3] Coblentz, *Carnegie Inst. Pub.*, No. 35 (1905).

[4] Marsh, *Phil. Mag.*, **49**, 1206 (1925).

[5] Spence, *Astrophys. J.*, **39**, 243 (1914).

[6] Henri "Études de Photochimie," Gauthier-Villars, Paris, **1919**.

[7] Bonino, *Gazz. chim. ital.*, **55**, 335 (1925).

[8] Lecomte, *Compt. rend.*, **180**, 1481 (1925).

[9] Marsh, *Phil. Mag.*, **49**, 971 (1925).

found certain "blue bands" which showed a constant frequency separation of 172 mm.$^{-1}$. This frequency he associated with a molecular vibration which also gives rise under the proper conditions to the 5.8 μ infra-red absorption bands of these substances.

A conclusion by Bell[10] derived from his examination of the infra-red absorption of several tropine alkaloids is of interest. He is unwilling to conclude that the 5.8 μ band which he observed in those compounds containing the =C=O groups is a unique characteristic of this group inasmuch as the simple chain hydrocarbons also show absorption in the same region. Bell[11] still retains this attitude in his recent interpretation of the appearance of a strong 5.75 μ band in his spectra of seven organic carbonates.

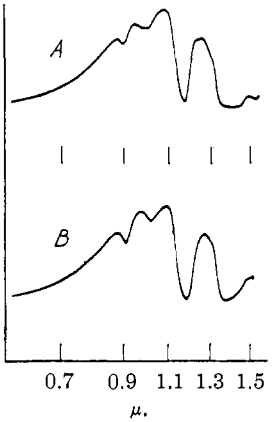

Fig. 17.—A, Acetone; B, methyl-*n*-propyl ketone.

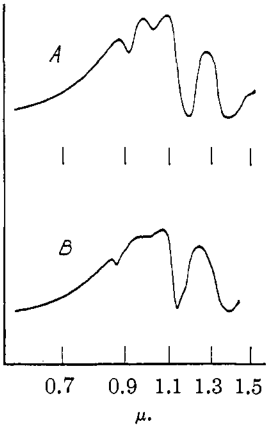

Fig. 18.—A, Methyl-*n*-amyl ketone; B, Acetophenone.

Bennett and Daniels[12] have recorded the absorption of acetic acid, mono-, di- and trichloro-acetic acids, methyl acetate and acetic anhydride in the regions 2–6 μ and 7–8 μ. They observed a strong band at 5.9 μ for acetic acid which progressively shifts to 5.75 μ upon successive substitutions of chlorine atoms. Their conclusion that this absorption maximum arises from the hydroxyl pair of the carboxyl group is not supported by the appearance of equally intense bands at 5.8 μ and 5.6 μ in their spectra of methyl acetate and acetic anhydride, respectively. It seems more probable that the bands in all six substances arise from the =C=O pair.

On the assumption that the 5.8 μ absorption maximum which is commonly observed is a fundamental band originating in a change of vibration

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[10] Bell, *J. Pharm. Exptl. Therap.*, **29**, 533 (1926).

[11] Bell, This Journal, **50**, 2940 (1928).

[12] Bennett and Daniels, *ibid.*, **49**, 50 (1927).

of the $=\mathrm{C}=\mathrm{O}$ atoms and that the 2.9 μ band found by Lecomte is its first overtone, it might be reasonably anticipated that higher overtones could be found below 2.5 μ provided cells of sufficient thickness were used. Now in the records of the absorption by the 1-mm. layers of the compounds containing the carbonyl group, Figs. 1–13, eighteen out of twenty of these substances show definite absorption at 1.9–2.0 μ, which is not characteristic of ordinary hydrocarbons. The other two examples, *p*-tolualdehyde and benzophenone, are doubtful. If the bands do occur in their records they are weak. The uncertainty in these two instances is increased by the fact that the band in question falls upon the P branch of the 1.87 μ water-vapor band. The weakness of the band in benzophenone, assuming that it really is present, could possibly be explained by the fact that the molecular weight of this molecule is relatively high, thus reducing the number of $=\mathrm{C}=\mathrm{O}$ absorbing centers per cubic centimeter; and also perhaps by the fact that this substance was one of the two examined in carbon tetrachloride solution. Its weakness, or absence, in *p*-tolualdehyde is not so easy to understand.

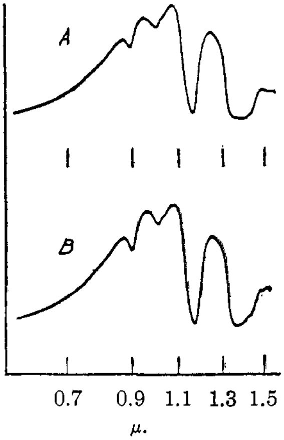

Fig. 19.—A, Methyl acetate; B, ethyl acetate.

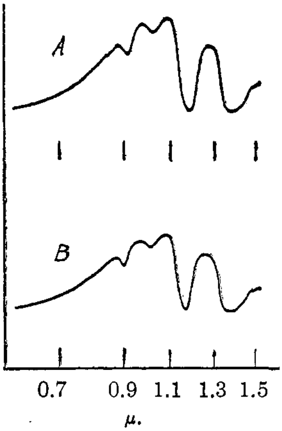

Fig. 20.—A, Butyl acetate; B, ethyl malonate.

The region 1.9–2.0 μ is the one in which a second overtone band of the 5.8 μ band would be sought. Because of the variation in the location of this longer wave length band as recorded by different observers, it is a little difficult to decide whether there is an exact integer relationship between it and the 1.9 μ band. A slight deviation from an exact one-to-three ratio between their frequencies would be anticipated as a result of numerous observations made upon infra-red absorption series. Thus the wave length of this possible harmonic band should be slightly greater than one-third of the wave length of the fundamental. A deviation comparable to the 1.5% variation from a 1:3 relationship found by Schaefer and Thomas[13] and calculated by Birge[14] between the fundamental carbon monoxide band at 4.67 μ and its second overtone at 1.57 μ would be expected. The much larger variation, 4%, found by the writer[15] for infrared absorption bands produced by C–H and N–H groups is doubtless due to the greater amplitudes of vibration resulting from the lightness of the hydrogen atom.

The inability to ascertain the exact nature of the overtone relationship existing between the 5.8 μ and the 1.9 μ bands is increased by the fact that the latter band appears double in a majority of the spectra. Whether this doubling has any bearing upon a similar phenomenon in many hydrocarbon bands[15] cannot be decided at this time.

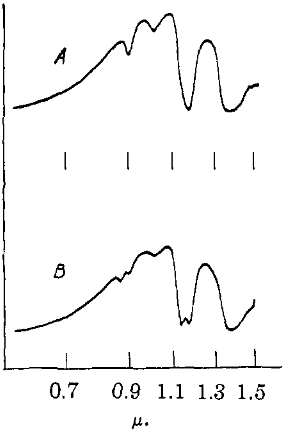

Fig. 21.—A, Ethyl propionate; B, ethyl benzoate.

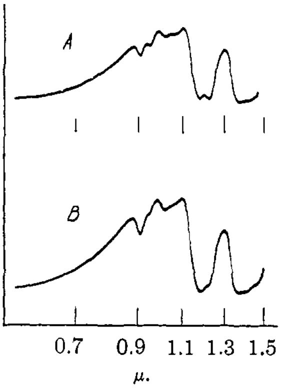

Fig. 22.—A, Ethyl ether; B, propyl ether.

As an example of the uncertainty which arises we may consider the spectrum of acetone, Fig. 4A. It shows prominent bands at 1.91 and 1.97 μ. Now the long wave length absorption maximum has been located by Coblentz[3] at 5.75 μ and by Henri[6] at 5.7 μ. Thus an *exactly harmonic* band would be expected between 1.90 and 1.92 μ. The question remains whether this overtone band is to be sought in the observed 1.91 μ or the 1.97 μ band or in their weighted mean. The writer inclines toward the latter point of view.

A third overtone of the 5.8 μ band would occur near 1.45 μ. The records of the 40-mm. cells, Figs. 14–23, show absorption at this point, indications of doubling appearing in several instances. Again, uncertainty

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[13] Schaefer and Thomas, *Z. Physik*, **12**, 330 (1923).

[14] Birge, *Phys. Rev.*, **28**, 1157 (1926).

[15] Ellis, *ibid.*, **33**, 27 (1929).

is introduced because of the proximity of the complicated 1.4 μ band characteristic of hydrocarbons.

A fourth overtone, if present, should occur near 1.16 μ. This again falls upon or near a C–H band. The asymmetry of the deep 1.14–1.20 μ absorption band in many instances indicates the possible presence of such an overtone.

A fifth overtone would be found near 0.97 μ. Such a band does appear in the records of the aldehydes. If it is present in many of the other curves it is either very weak or has shifted to merge with the 1.0 μ hydrocarbon band.

Absorption near 0.9, 1.0, 1.18, 1.4, 1.7 and 2.18 μ (benzene and phenyl radical), 2.3 μ (paraffins and alkyl radicals) is characteristic of hydrocarbons. In addition to these bands and those mentioned above as probably belonging to the carbonyl pair, there are other special features of these records which seem to be introduced by the presence of the carbonyl pair. Thus in the six aldehyde curves, Figs. 14–16, there appears a strong band at 1.25 μ. Again, in the records of most of the substances, excluding the three ethers, there is absorption near 2.15 μ, in many instances the band being noticeably double. If there are other fundamental absorption bands assignable to the =C=O group, as claimed by Henri, then combination bands obtained from these and the 5.8 μ band and its overtones might be expected in this shorter wave length region. Thus if we add the frequency of Henri's 8.3 μ band to the frequency of the 2.9 μ overtone of Lecomte we obtain a frequency of a band at 2.15 μ. Again, a combination of the 8.3 μ and our 1.45 μ band yields a value of 1.23 μ. These values are in good agreement with those mentioned above.

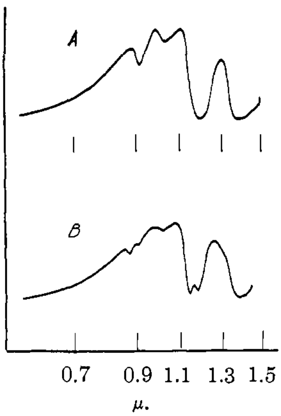

Fig. 23.—A, Butyl ether; B, propiophenone.

In Table I have been assembled the values for the absorption bands which are here assumed to arise from the carbonyl group. Determinations by other investigators have been included also.

There are features of these spectra other than those apparently originating in the =C=O pair which are of interest. Most of the remaining prominent absorption maxima are characteristic of hydrocarbons. The bands near 1.7, 1.2 and 0.9 μ can now fairly certainly be identified[15] as the first, second and third overtones, respectively, of a 3.3–3.4 μ band, all of which arise from oscillations of the carbon–hydrogen atom pair. They may be referred to as C–H bands. Bands near 1.0, 1.4 and 2.3 μ (or 2.18 μ) also always appear in the spectra of hydrocarbons and may be

Table I

Absorption Bands Assigned to the =C=O Pair

Wave lengths in μ

Acetaldehyde	....	....	....	....	1.91	...	1.46	1.41	0.96	..	..	1.24
Propionaldehyde	....	....	5.90L	2.93L	1.91	1.96	1.46	..	.96	..	..	1.24
Butyraldehyde	....	....	5.90L	....	1.91?	1.96	1.44	1.40	.98	..	..	1.25
Benzaldehyde	....	5.97L	5.8H	....	1.92	1.99	1.48	1.42	.97	..	..	1.25
							1.41					
p-Tolualdehyde	....	....	....	....	1.91?	1.99	1.46	1.42	.97	..	..	1.25
					2.04?							
Cinnamaldehyde	....	....	....	....	1.92	2.02	1.49	1.42	.97	..	..	1.25
Acetone	5.75C,	5.7H	5.90L	2.90L	1.91	1.97	1.44		.96	2.15	2.18	..
Methylpropyl ketone	....	....	5.92L	2.90L	1.91	1.97	..		..	2.15	2.18	..
Methyl-*n*-amyl ketone	....	....	....	....	1.91	1.97	..		..	2.15	2.18	..
Acetophenone	....	6.03L	5.8H	2.97L	1.91	2.01	..		..	..	..	..
Propiophenone	....	....	6.03L	2.97L	1.91	2.01	..		..	..	..	..
Benzophenone	....	....	....	....	?		..		..	..	..	..
Methyl acetate	....	5.8C	5.8BD	....	1.91	1.93SB	1.42		..	2.12	2.16	..
Ethyl acetate	....	....	....	....	1.91	1.94	1.42		..	2.12	2.16	..
n-Butyl acetate	....	....	....	....	1.91	1.94	..		..	2.12	2.16	..
Ethyl malonate	....	....	....	....	1.91	1.94	..		..	2.14		..
Ethyl propionate	....	....	....	....	1.91	1.94	..		..	2.16		..
					1.91SB							
Ethyl benzoate	....	....	....	....	1.91	1.95	..		..	..		..
Acetylacetone	....	....	....	....	1.91		..		..	..		..
Quinone	....	....	....	....	1.90?		..		..	2.14		..

L = Lecomte, ref. 8; H = Henri, ref. 6; C = Coblentz, ref. 3; SB = Smith and Boord, ref. 2; BD = Bennett and Daniels, ref. 12.

referred to as hydrocarbon bands. Their origins are probably more complicated than those giving rise to the 3.4 μ fundamental and its harmonics. A possible interpretation of their origins, which further study may show to be only partially correct, has already been suggested by the writer.[1b]

The author[15] has already commented upon the doubleness of the C–H bands of certain compounds, suggesting that this doubleness may arise from two types of C–H linkages. Such an hypothesis is supported by the conclusions of Mrs. Lonsdale[16] in her critical study of the physical evidences pointing toward an anisotropy of the carbon atom. She has concluded that carbon will in general exhibit two each of two types of valency. This doubleness is evident in the 1.75 μ band of many of the alkyl compounds. It always appears when a methyl or ethyl group is present and sometimes when a propyl radical occurs. The breadth of the band when higher radicals are used, for example butyl, suggests that the doubleness is still there but that it is partially obscured. The 1.68 μ band, which appears clearly separated from the 1.75 μ doublet in the spectra of alkyl derivatives in which the radical is relatively light, but which merges into this latter band when the alkyl radical is heavy, seems to be a characteristic feature of paraffins and alkyl radicals. Its exact nature is not understood.

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[16] Lonsdale, *Phil. Mag.*, **6**, 433 (1928).

The two molecules benzophenone and quinone, containing aryl groups without alkyl groups, show a single band at 1.68 μ corresponding to the alkyl doublet at 1.75 μ. Those compounds containing both types of radical show the alkyl doublet and single aryl band clearly separated.

The resolving power of the instrument is probably insufficient to reveal a doubling of the 1.2 μ and the 0.9 μ alkyl C–H bands if it exists. A distinct separation in these bands, however, is found between the alkyl and aryl components.

An unexpected and widely separated doubling of the 1.2 μ and the 0.9 μ bands occurs in the spectra of the three ethers. Since the changes in the intensity ratio of the two components are similar as one goes from ethyl ether to *n*-butyl ether, it seems that both members are C–H bands. The only explanation which the author can offer for this doubling is a possible weakening of the C–H bonds in the cases of carbon atoms adjoining the oxygen atom.

The increased resolving power obtained in these records has revealed the fact that the 2.18 μ hydrocarbon band of the phenyl radical is double. A new record taken of benzene, not reproduced in this paper, shows a corresponding doubling.

The writer wishes to acknowledge the assistance of Mr. Charles Shaw in a portion of this investigation.

Summary

1. The infra-red absorption spectra below 2.5 μ have been recorded for a group of aldehydes, ketones, esters and ethers.

2. An absorption band, often double, between 1.9 and 2 μ is interpreted as a second overtone of a prominent 5.8 μ band previously recorded by many observers. Both are assigned to the carbonyl group.

3. Evidence pointing toward the existence of third, fourth and fifth overtones of the 5.8 μ band is found near 1.45, 1.16 and 0.97 μ in the spectra of some of the compounds.

4. Features characterizing hydrocarbons and their derivatives are found in these spectra at positions where they were anticipated.

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