THE ABSORPTION SPECTRA OF CERTAIN ORGANIC LIQUIDS IN THE NEAR INFRA-RED

By James W. Sappenfield

Abstract

Absorption spectra have been studied in the region from 0.8 to 2.5μ with an accuracy of 0.002μ for twenty-four organic liquids, including nine alcohols, six esters, two ethers, two aldehydes, and five miscellaneous compounds. The carbon-hydrogen linkage and other similar ones have been discussed as a probable source of the absorption. While certain inconsistencies are pointed out, no other explanation is available. The relative intensity of the various bands has been discussed and it is shown that the bands at 1.4 and 1.0μ and the two bands at 1.2 and 0.9μ evidently arise from different sources. The effect of homology is shown to be slight, which agrees with the conclusions of Weniger. An attempt has been made to get a relation between different band heads of a particular compound. The anharmonic series as suggested by Ellis, and the relation $\nu_n = \nu_0(n)^{1/2}$ suggested by Gapon were both used with moderate success. The latter equation was modified so as to read $\nu_n = \nu_0/(n)^{1/2}$ and applied to part of the data of Weniger with moderate success.

Introduction

DURING the last several years many investigations have been carried out to determine the relationship of absorption spectra to chemical constitution. These investigations include such work as that of Coblentz[1] and Weniger[2] who studied the region from the visible to 15μ. The region from the visible to 2.5μ has been examined in a number of cases with greater resolving power than that used by Coblentz and Weniger. Work of this kind has been done by Puccianti,[3] Abney and Festing,[4] and Ellis[5] using quartz and glass prisms. Easley, Fenner and Spence[6] have recently studied this region with a grating which gave much better resolution than any of the prisms.

Since there is still not much detailed information available between the visible and 2.5μ, the present investigation was undertaken for the purpose of supplying accurate data on a number of additional organic liquids. In selecting the compounds to be investigated several were chosen from the work of Weniger in order that Weniger's data for wave-lengths greater than 2.5μ might be used in any interpretations that might suggest themselves. In addition to these, several other organic compounds were chosen from different chemical families in order to study similarities and dissimilarities in them.

[1] Coblentz, Investigation of Infra-Red Spectra, Carnegie Inst. Pub. (1905).

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

[3] Puccianti, Phys. Zeits., **1,** 494, (1900).

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

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

[6] Easley, Fenner and Spence, Astrophys J., **67,** 185 (1928).

Apparatus

The spectrometer was specially designed and constructed in the department shop. A diagram is given in Fig. 1. The base $ABCDEF$ was a heavy iron plate mounted on six legs, one at each corner. The mirrors M_1 and M_2
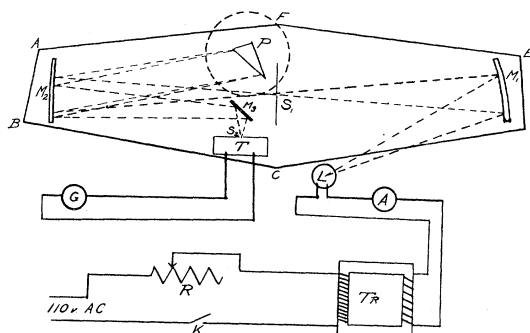

Fig. 1. Diagrammatic sketch of apparatus.

were concave and M_3 was plane. Each of these mirrors was silvered on the front side. The adjustable slits S_1 and S_2 were kept at the same width throughout the investigation; S_1 at 0.10 mm and S_2 at 0.14 mm. The linear thermopile, T, of ten couples of bismuth and silver was made by Coblentz. It was connected in series with a high sensitivity Leeds-Northrup galvanometer. The scale distance used was 4 meters. The glass prism P with an angle of 30° was silvered on the back side and mounted on a high grade divided circle which was divided into divisions of 5 minutes each and could be read accurately to 1 second of arc by a micrometer microscope. The source of radiation, L, was a straight tungsten filament lamp which carried 22 amps. at 11 volts. The power was supplied by a step-down transformer connected to the 110 volt a.c. circuit. Current through the lamp was read on the ammeter A and was regulated by the variable resistance R. A diagram of a
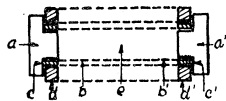

Fig. 2. Absorption cells.

cell is given in Fig. 2 in which aa' is a cross section of the circular brass cell; bb' are mica windows, cc' are rubber gaskets and dd' are circular brass rings by means of which the mica windows were pressed against the brass shoulders. The liquid was enclosed in the space e and the entire cell was mounted in a cell holder. Two cells of this kind were mounted, one above the other, in the cell holder. They were identical in construction but one was filled with the liquid under investigation and the other was left empty. The cell holder and a shutter were mounted directly in front of the slit S_1. Six different cell thicknesses were used to bring out the different bands to best advantage. These thicknesses were 40, 10, 5, 2.5, 1.0, and 0.5 mm.

Method

The percentage transmission of the liquid for a particular wave-length was determined by reading the deflection of the galvanometer when the

radiation passed through the full cell and then the deflection when the radiation passed through the empty cell. The ratio of the first of these deflections to the second gives the percentage transmission after multiplying by 100. The corresponding wave-length was determined from the angular position of the prism from which the wave-length could be determined by a calibration curve.

Readings for percentage transmission were taken at intervals of about 15 seconds of arc on the divided circle. This interval amounted to about 0.005μ for the middle of the spectrum. A curve was then plotted on a large scale using percentage transmission as ordinates and angular position of the prism as abscissas. The minimum of the curve was accurately located and the wave-length corresponding to the position of the prism was then determined from the calibration curve. Under normal conditions only one observation was taken for each point on the curve since they could be duplicated to a fraction of a percent.

CALIBRATION

In order to determine the wave-lengths accurately an arbitrary zero position had to be established which could be checked from day to day. A visual observation on the D line was finally selected as most satisfactory. This observation on the D line was made by a telescope that was focused on the slit S_2. The source of light was a carbon arc cored with sodium chloride. It was substituted for the lamp L, Fig. 1.

The absorption bands of chloroform were used for the calibration. Their position was determined as indicated in the preceding section. The angle between these bands and the D lines was then plotted against the wave-length of these bands as given by Easley, Fenner and Spence.[6] A smooth curve was then drawn between these points. There were 19 points between 0.589 and 2.28μ and the accuracy was about 0.002μ. The position of the D lines was determined at least once a day so that the angle between the various bands and the D lines could always be known with certainty. This angle was then used for reading the wave-length from the calibration curve.

SOURCE AND PURITY OF THE LIQUIDS

For the most part the materials were obtained from the Eastman Kodak Company and were of the highest purity obtainable. These were iso-propyl alcohol, n-butyl alcohol, iso-butyl alcohol, secondary butyl alcohol, tertiary butyl alcohol, n-propyl amine, n-butyl acetate, n-propyl acetate, pyridine, cyclohexanone, methyl ethyl ketone, n-propyl n-propionate, ethyl-n-butyrate, benzyl methyl ether, benzyl ether, butyraldehyde, and cinnamaldehyde. The chloroform used for calibrating was from Squibb. The ethyl alcohol was marked 99.71 percent pure. The following products were marked "chemically pure": methyl alcohol from the American Chemical Products Company of Rochester, N. Y., and n-propyl alcohol, n-butyl alcohol, iso-butyl alcohol and iso-amyl alcohol from the Coleman and Bell Company of Norwood, Ohio. The methyl acetate was obtained from the General Chemical Company of Easton, Pa., and the ethyl acetate was obtained from
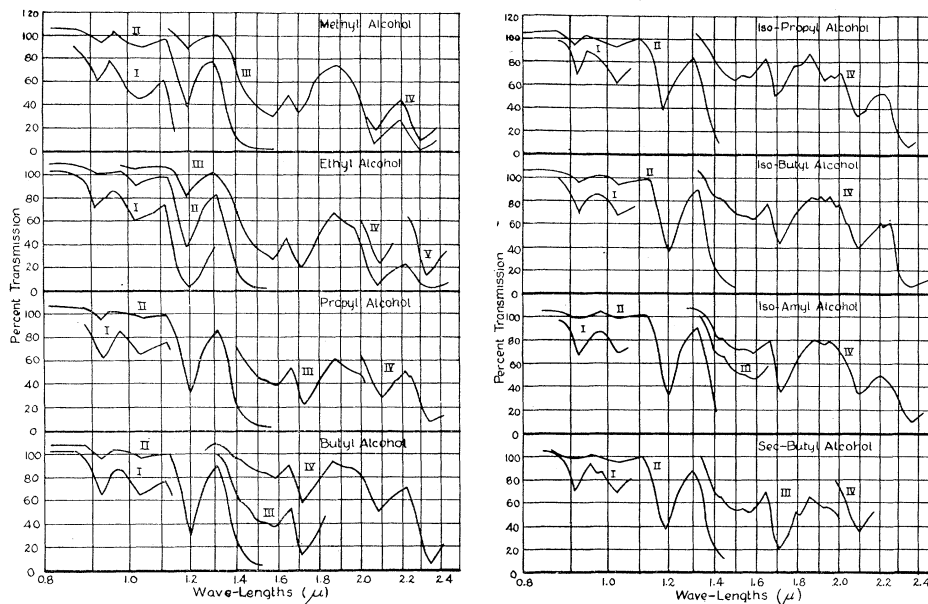
Fig. 3. Percentage transmission in methyl alcohol, ethyl alcohol, propyl alcohol, butyl alcohol, iso-propyl alcohol, iso-butyl alcohol, iso-amyl alcohol and secondary butyl alcohol for cell thickness of I–40 mm; II–10 mm; III–2.5 mm; IV–1.0 mm; and V–0.5 mm.

Fig. 4. Percentage transmission in tertiary butyl alcohol, propyl propionate, ethyl butyrate, methyl ethyl ketone, methyl acetate, ethyl acetate, propyl acetate, and butyl acetate for cell thicknesses of I–40 mm; II–10 mm; III–2.5 mm; IV–1.0 mm; V–0.5 mm.

the Kauffman-Lattimer Company of Columbus, Ohio. The butyric acid was made by Merck and was marked "Absolute Technical."

RESULTS

A complete curve is given for each of the twenty-four compounds studied. The curves were plotted originally with the angular position of the prism as abscissas and the proper wave-length scale was then superposed but only the wave-length scale has been recorded on these figures.
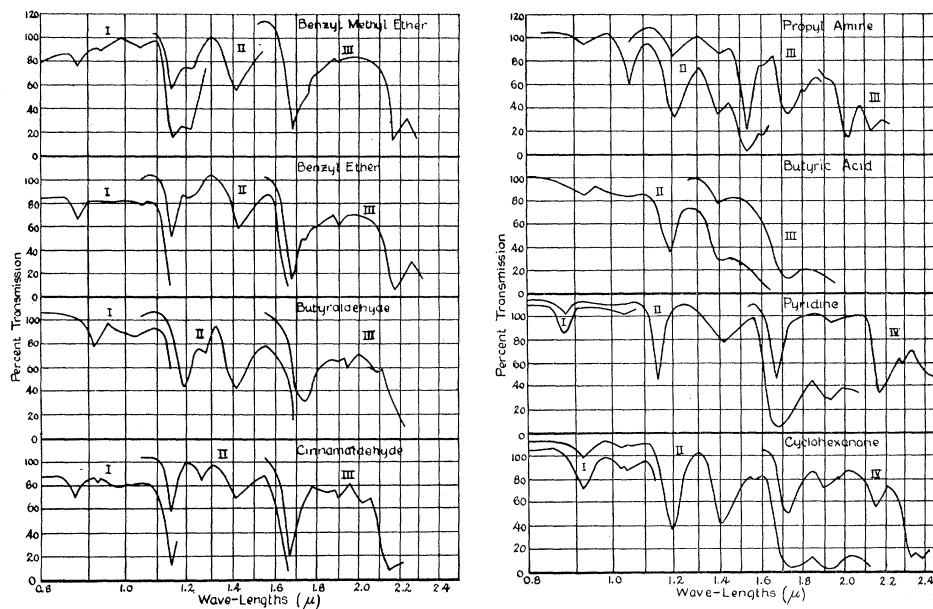
Fig. 5. Percentage transmission in benzyl methyl ether, benzyl ether, butyraldehyde, cinnamaldehyde, propyl amine, butyric acid, pyridine and cyclohexanone for cell thicknesses of I–40 mm; II–10 mm; III–2.5 mm; IV–1.0 mm; V–0.5 mm.

Since the curves are on a very small scale the bands cannot be located from these curves with accuracy. A list of all the bands found between 0.8 and 2.5μ is given in Table I.

The alcohols. This group is composed of nine members, six primary alcohols, two secondary and one tertiary alcohol.

By comparing the curves for the four normal alcohols, one finds certain characteristics developing. The band which appears at 1.4μ is almost completely overshadowed by a band at about 1.55μ. In butyl alcohol a break actually occurs at 1.429μ but in the others this band shows itself only by a broadening of the band. The band at about 1.55μ is broad and shows two definite components except in methyl alcohol when they are both evidently present but unresolved. A band appears at about 1.94μ for all except the methyl alcohol and its intensity increases somewhat with the higher members of the series. Various small bands appear in each.

TABLE I.   *List of all observed absorption bands between 0.8 and 2.5μ.*
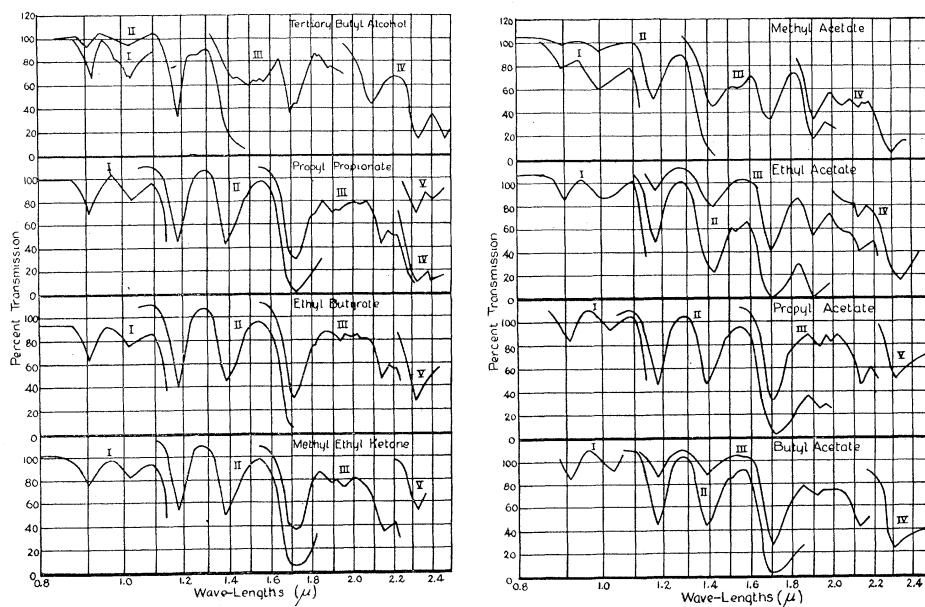
Methyl Alcohol	Ethyl Alcohol	Propyl Alcohol	Butyl Alcohol	Iso Propyl Alcohol	Iso Butyl Alcohol	Iso Amyl Alcohol	Sec. Butyl Alcohol
0.916μ	0.886μ	0.923μ	0.923μ	0.910μ	0.918μ	0.918μ	0.912μ
1.030	0.910	1.028	1.032	1.023	1.025	1.030	0.971
1.193	0.939	1.198	1.203	1.187	1.196	1.204	1.029
1.575	1.022	1.529	1.429	1.497	1.412	1.428	1.195
1.707	1.072	1.585	1.533	1.574	1.530	1.528	1.428
2.068	1.190	1.715	1.588	1.698	1.582	1.585	1.505
2.305	1.530	1.949	1.718	1.803	1.714	1.715	1.572
	1.577	2.091	1.931	1.934	1.890	1.931	1.712
	1.711	2.167	2.085	1.984	1.933	2.087	1.766
	1.948	2.232	2.360	2.094	1.967	2.367	1.821
	2.087	2.340		2.125	2.044		1.934
	2.336			2.350	2.085		2.105
					2.218		
					2.372		

Tert. Butyl Alcohol	Propyl Propion-ate	Ethyl Butyr-ate	Methyl Ethyl Ketone	Methyl Acetate	Ethyl Acetate	Propyl Acetate	Butyl Acetate
0.913μ	0.910μ	0.910μ	0.909μ	0.900μ	0.903μ	0.913μ	0.914μ
0.980	1.026	1.020	1.024	1.000	1.012	1.026	1.033
1.022	1.188	1.186	1.183	1.175	1.180	1.187	1.189
1.184	1.389	1.393	1.386	1.442	1.430	1.392	1.396
1.248	1.717	1.718	1.453	1.534	1.538	1.709	1.504
1.421	1.814	1.821	1.727	1.716	1.711	1.790	1.720
1.498	1.937	1.939	1.900	1.921	1.907	1.938	1.929
1.536	2.035	1.989	1.968	2.050	2.061	1.990	2.137
1.574	2.145	2.041	2.163	2.132	2.126	2.140	2.316
1.697	2.209	2.142	2.335	2.173	2.347	2.316	
1.735	2.330	2.201		2.313			
1.830	2.408	2.330					
1.883							
2.100							
2.337							
2.485							

Benzyl Methyl Ether	Benzyl Ether	Butyr-Alde-hyde	Cinnam-Aldehyde	Propyl Amine	Butyric Acid	Pyridine	Cyclo-Hex-anone
0.875μ	0.875μ	0.918μ	0.873μ	0.922μ	0.920μ	0.877μ	0.923μ
0.929	1.052	0.995	0.926	1.055	1.018	1.034	1.024
1.045	1.149	1.033	0.984	1.206	1.190	1.145	1.042
1.143	1.208	1.196	1.030	1.409	1.392	1.428	1.199
1.220	1.428	1.273	1.146	1.534	1.729	1.678	1.417
1.421	1.682	1.418	1.266	1.604		1.937	1.575
1.683	1.747	1.742	1.418	1.729		2.176	1.730
1.759	1.803	1.899	1.683	1.807		2.44	1.907
1.814	1.904	1.943	1.855	1.923		2.56	1.983
1.898	2.176	2.080	1.907	2.025			2.154
2.170			2.022	2.130			2.340
			2.160				2.407

A comparison of the iso-alcohols with the corresponding normal alcohols shows a general, though small, shift toward shorter wave-lengths. In general an iso-alcohol closely resembles the normal alcohol just preceding it in the series.

The secondary butyl alcohol is very much like the iso-butyl alcohol in structure and the absorption curves are very much alike. The tertiary butyl

alcohol is considerably different from the other butyl alcohols in structure since one carbon atom acts as a center and three methyl (CH_3) groups and one hydroxyl group (OH) are attached to it. The absorption curve is different in several respects. An actual minimum occurs at 1.421μ while in the others it was only a point of inflection. The components of the 1.55μ band are much more widely separated than usual. The bands at 1.022 and 1.698μ both appear double but with one component quite weak.

The acetates and related compounds. This group includes four primary acetates, methyl, ethyl, propyl, and butyl, and the related compounds n-propyl n-propionate, ethyl butyrate and methyl ethyl ketone. These liquids show more interesting differences than did the alcohols. The band at 1.92μ which appeared weakly in the alcohols, is one of the major bands in methyl acetate and appears with diminishing intensity in the higher members of the series and is quite small again in the butyl acetate, the propionate and the butyrate. The band at 2.050μ in the methyl acetate is gradually overshadowed and does not show at all in the propyl and butyl acetates although it is present to a small degree in the propionate and the butyrate. The relative intensity of the bands will be discussed later but here it is to be pointed out that the band at 1.4μ decreases rapidly in intensity in passing from methyl acetate to ethyl acetate, decreases less rapidly in passing from ethyl acetate to propyl acetate and remains practically constant in passing from propyl acetate to butyl acetate.

Other compounds. The other compounds were more or less unrelated. The wave-lengths are given in Table I and the curves are shown in the figures. The important characteristics of these curves will be discussed under certain general headings.

DISCUSSION OF RESULTS

Chemical bonds and absorption. Probably the most fundamental question that can be asked concerning absorption spectra of this kind is, what is the nature of the absorbing unit. Since a certain set of bands appear in almost all organic materials at approximately the same wave-lengths, it has been assumed that the vibrations take place between certain atoms or atom groups that are common to all these substances. This is obviously a carbon and hydrogen linkage. This viewpoint has been strengthened by such investigations as that by Easley, Fenner and Spence.[6] As halogen atoms are substituted for hydrogen in methane the absorption bands disappear. This seems to show rather conclusively that hydrogen is an essential part of the absorbing system. Ellis has undertaken to show that a C-H bond is the cause of one of the most prominent series of bands in these compounds. He has also found evidence for thinking that N-H[7] and S-H[8] bonds cause characteristic absorption bands. Following this point of view the bands at 1.55μ in the alcohols should be attributed to O-H. This seems reasonable since Weniger's curves show a band at 3.0μ which is the approximate multiple

[7] Ellis, Phys. Rev., **31**, 314 (1928).
[8] Ellis, Phys. Rev., **31**, 916 (1928).

of the one at 1.55μ. However this is contradicted by the fact that the bands at 1.55μ and 3.0μ do not occur in butyric acid. One may say that the alcohols and acids are quite different chemically but one at least loses some of his confidence in a simple bond theory.

The band at 1.2μ has a very interesting characteristic. In the chain molecules this band is located at about 1.20μ. However the benzene ring derivatives apparently show the same band at 1.15μ. Molecules of combined ring and chain systems may show both bands as shown in the curves of benzyl methyl ether and benzyl ether. The band at 1.15μ is the stronger because the C_6H_5 group is the predominant part of the molecule. This relation is shown in the two aldehydes also. The butyraldehyde is a straight chain molecule and gives the band at 1.196μ. The cinnamaldehyde gives the band at 1.146μ. Since this molecule has only a small chain the absence of the band at 1.2μ is not surprising.

A similar set of conditions arise in the neighborhood of 0.9μ. In the chain molecules the band is at about 0.92μ and in the benzene derivatives it is located at about 0.875μ. In benzyl methyl ether and cinnamaldehyde two bands appear, one at about 0.92μ and the other at 0.875μ with the band at 0.875μ much stronger. In benzyl ether only the band at 0.875μ occurs and in butyraldehyde only the band at 0.918μ is found.

One is not to conclude from this that the difference is entirely between chain and ring formations. Pyridine (C_5H_5N) and cyclohexanone ($C_6H_{10}O$) are both ring molecules. Pyridine gives the typical benzene bands at 0.877 and 1.145μ. Cyclohexanone gives bands at 0.923 and 1.199μ which are characteristic of the regular chain. This fact seems to indicate that the benzene bands are not due to the cyclic arrangement but rather to the C_6H_5 group. This is very possible since this is a very stable chemical group. It should also be mentioned here that bands at 0.878 and 1.153μ appear in chloroform so that bands may be located at these positions without the presence of a benzene ring.

Intensities of bands. The relative intensity of the bands has received very little attention up to the present time. Ellis[9] arranges the bands at 6.9, 3.3, 2.2, 1.7, 1.4, 1.2, 1.0, and 0.9μ in a series and makes the general statement that the intensity decreases with the wave-length with certain exceptions. There are certain cases of relative intensity which seem worthy of consideration. In the first place consider the band at 1.55μ in the normal alcohols. Its intensity remains practically constant in these alcohols. On the other hand its neighbor at 1.71μ grows stronger with each succeeding member of the series. This would indicate that one arises from a part of the molecule which is the same for all members of the series and the other arises from a part that is being altered in passing from one of the normal alcohols to another. These variations in intensity would suggest that the band at 1.55μ is due to an O-H bond and the one at 1.71μ is due to a C-H bond.

[9] Ellis, Phys. Rev., **27**, 298 (1926).

There is reason to suppose that the members of a series of bands should show some kind of consistent relative intensity but there is no such relation for the bands at 1.4 and 1.2μ or at 1.0 and 0.9μ. Furthermore the relative intensity of the bands at 1.0 and 0.9μ may be approximately predicted by knowing the relative intensity of the bands at 1.4 and 1.2μ. It may be said without exception that as the band at 1.4μ decreases in intensity in proportion to the band at 1.2μ the band at 1.0μ decreases in intensity in proportion to the band at 0.9μ. (Compare the curves for methyl acetate, propyl acetate, and pyridine.) If the bands at 1.0 and 0.9μ have about equal intensities, e.g. ethyl acetate, the ratio of intensity of the band at 1.4μ to the band at 1.2μ is about 1.6. If the intensity of the band at 1.4μ is equal to that at 1.2μ, e.g. propyl acetate, the ratio of intensity of the band at 0.9μ to the band at 1.0μ is 1.55. This indicates that the bands at 1.4 and 1.0μ are closely related and that they differ in origin from the bands at 1.2 and 0.9μ.

The variation in intensity of the band at 1.92μ in the acetates is unexplainable. The assumption of a C-H bond or any other kind of bond seems to give negative results. No other kind of explanation is available. Weniger called attention to a similar set of conditions arising in the primary alcohols. A minor band appeared at 4.9μ in methyl alcohol and shifted to longer wave-lengths and faded out until it was not observable in the amyl alcohol. Another band at 5.9μ in the methyl alcohol did the same thing. Weniger offered no suggestions.

Effect of chemical substitutions. Since the absorption spectra of chemically similar compounds are known to be similar, a study of the variations of the spectra of homologous series is interesting. Homologous compounds are compounds which are structurally similar and differ by a CH_2 group. Weniger studied the effects of homology in the primary alcohols, secondary alcohols, certain acids and esters. He concluded that in ascending the series in the alcohols several of the bands shifted to longer wave-lengths; in the esters the effect was very slight. His conclusions are both verified for bands between 0.8 and 2.5μ. In the alcohols there seems to be a general tendency toward a shift to longer wave-lengths although it is quite small. In the acetates, which are a class of esters, there seems to be no general systematic changes.

Ethyl acetate differs from propyl propionate by an additional CH_2 in both the acid and basic parts of the molecule. The result is a general shift to longer wave-lengths except the band at 1.430μ shifts to 1.398μ and the band at 2.347μ shifts to 2.330μ.

Butyl acetate, propyl propionate and ethyl butyrate have the same molecular weight and general formula. The structure of one may be changed into the next by transposing a CH_2 group from the acid part of the molecule to the basic part. The shifts are all quite small and are not consistent in the two transformations available for consideration.

Ethyl acetate ($CH_3COOC_2H_5$) differs in structural formula from methyl ethyl ketone ($CH_3COC_2H_5$) by one oxygen atom in the central chain. This

change in structure results in a shifting of the bands to longer wave-lengths except the band at 1.430μ shifts to 1.386μ and the band at 2.347μ shifts to 2.335μ.

THEORETICAL DISCUSSION

It seems probable that the different bands of a compound should be related and that their position might be expressed by an equation. Kratzer[10] developed the theory of the anharmonic oscillator and Ellis has applied it to his data. Kratzer showed that $\nu_n = n\nu_0(1 - nx)$ or $\nu_n = An - Bn^2$ where x, A and B are constants, n is an integer, ν_n is the frequency of the band and ν_0 a fundamental frequency. Ellis[9] originally used the frequency of the band at 6.8μ as the fundamental but he recently[7] revised it and used the band at 3.3μ.

Gapon[11] suggested the equation $\nu_n = \nu_0(n)^{1/2}$ where ν_n was the frequency of the band, ν_0 the fundamental frequency, and n an integer. In applying this equation the author noticed that the equation $\nu_n = \nu_0(n)^{-1/2}$ gave results that agree with the bands recorded by Weniger. In both cases the ν_0 was the frequency of the band at about 3.3μ.

TABLE II.

Butyl Alcohol							Ethyl Acetate						
Wave-lengths, $\lambda_n = 3.415n^{\pm 1/2}$			Wave-numbers $\nu_n = 2964n - 63n^2$			Wave-length	Wave-lengths $\lambda_n = 3.390n^{\pm 1/2}$			Wave-numbers $\nu_n = 3074n - 77n^2$			Wave Length
λ Obs.	n	λ Calc.	ν Obs.	n	ν Calc.	λ Calc.	λ Obs.	n	λ Calc.	ν Obs.	n	ν Calc.	λ Calc.
0.923μ	14	0.913μ	10834.2	4	10848	0.922μ	0.902μ	14	0.906μ	11074	4	11056	0.904μ
1.032	11	1.030					1.012	11	1.022				
1.203	8	1.217	8312.6	3	8325	1.201	1.180	8	1.199	8475	3	8523	1.173
1.429	6	1.394					1.430	6	1.384				
1.533	5	1.527					1.538	5	1.516				
1.588							1.711	4	1.695	5845	2	5836	1.713
1.718	4	1.708	5820.7	2	5676	1.762	1.907	3	1.957				
1.931	3	1.972					2.061						
2.085							2.126						
2.360	2	2.415					2.347	2	2.397				
3.0							2.65						
3.5	1	3.415	2857.1	1	2901	3.45	2.8						
4.9	2	4.83					3.05						
5.6							3.45	1	3.390	2899	1	2995	3.389
5.8	3	5.91					4.3						
6.1							4.95	2	4.8				
6.9	4	6.82					5.35						
7.2							5.85	3	5.87				
7.45	5	7.63					6.6	4	6.78				
7.75							7.3	5	7.6				
8.0							8.1	6	8.3				
8.45	6	8.35					8.9	7	9.0				
9.15	7	9.04					9.7	8	9.6				
9.45							10.05	9	10.2				
9.6	8	9.65					10.50						
10.0	9	10.25					10.75	10	10.7				
10.5		10.8					11.05	11	11.25				
11.3	11	11.3					11.8	12	11.75				
11.8	12	11.8					12.2	13	12.2				
12.0							12.7	14	12.7				
12.15	13	12.3					13.8	16	13.6				
12.45													
12.8	14	12.8											
13.1	15	13.2											
13.5	16	13.65											
13.8													

The calculated results from these equations are given in Table II for butyl alcohol and ethyl acetate. In making the calculations ν_0 was deter-

[10] Kratzer, Zeits, f. Physik, **3,** 289 (1920).

[11] Gapon, Zeitz. f. Physik. **44** 600 (1927).

mined by substituting known values of ν_n and n in the equation $\nu_n = \nu_0(n)^{1/2}$. The agreement between calculated and observed values is about the same in the other compounds studied in this investigation. In each case the agreement is fair but in no case is it nearly perfect. The square root relation has the advantage of fitting many more bands but it lacks the ease of physical interpretation that comes in case the molecule is considered as an anharmonic oscillator. While other series of a similar nature suggest themselves they are not nearly so long and the accuracy is not good. It is recognized that these suggestions are purely empirical.

In conclusion the author wishes to express his appreciation to Professor Alpheus W. Smith for suggesting the problem and for his advice and assistance in the work. He is also indebted to Professor C. E. Boord and Dr. R. K. Summerbell for advice on the chemical part of the work.

MENDENHALL LABORATORY OF PHYSICS,
OHIO STATE UNIVERSITY.
September 20, 1928.