171. *The Vibrational Spectra of Esters and Ketones.*

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The vibrational spectra of a number of ketones and esters have been measured between 5—20 μ. Correlation of strong bands found in related series suggests assignments of some of the frequencies to vibrations of particular parts of the nuclear frameworks, which may be useful in disentangling the spectra of complex molecules containing these groupings. The results are also useful in suggesting key bands for infra-red analysis of mixtures of these compounds, or for the detection of impurities.

THE use of infra-red spectra for both analysis and structural diagnosis demands the measurement of the spectra of many compounds differing in type over a wide spectral range. By this means, characteristic differences may be found giving key absorption bands for analysis, but at the same time the comparison of spectra of related compounds may lead to an assignment of vibration frequencies which are characteristic of particular types of nuclear skeleton. Such data can only be applied successfully in the study of complex or macro-molecules if measurements are first made, for purposes of reference, on relatively simple molecules, where the assignment of frequencies can be made with conviction. Compilations of this kind have been published recently, and some important correlations obtained (Barnes, Liddel, and Williams, *Ind. Eng. Chem. Anal.*, 1943, **15**, 83; Thompson and Torkington, *Proc. Roy. Soc.*, 1945, *A*, **184**, 3; *Trans. Faraday Soc.*, 1945, **41**, 246).

In connexion with the elucidation of the vibrational spectra of some polymers containing ester groupings, we have measured the spectra of many esters and ketones between 2 μ and 20 μ. Some of the results are collected here, and the spectra are discussed briefly from the standpoint of molecular structure. A complete correlation of the infra-red absorption frequencies with the corresponding Raman intervals would at present become unwieldy, and will therefore be deferred until the most important features can be disentangled from the much larger number of molecules under examination.

The compounds employed were usually commercial products, purified by fractionation. A few were prepared in this laboratory. In many cases two or more samples of the same compound were examined, the identity of the spectra serving as a check on purity. Benzophenone was measured as a solid film on rock-salt; the remainder were measured as liquids in an absorption cell made by separating plates of rock-salt by a washer about 0·08 mm. thick. The spectrometers have already been described (Thompson and Whiffen, this vol., p. 268).

The spectra are shown as charts, Figs. 1—7, in which bands are shown as lines of varying intensity covering the spectral range 500—1750 wave numbers. The disadvantage of this form of representation is that it does not reveal the relative breadths of the bands, and the intensities can only be regarded as approximate, but it

is more convenient if correlations of frequencies are to be derived by visual inspection of the spectra of a series of related molecules.

Fig. 1 shows the spectra of some ketones. In saturated alkyl ketones the frequency of the stretching vibration of the carbonyl link lies close to 1710 cm.$^{-1}$. When one radical attached to the carbonyl group is aryl, the frequency falls to about 1685, and when both the attached radicals are aryl, it falls still further to about 1655. In mesityl oxide, where there is also conjugation of double bonds, the carbonyl group frequency is below " normal."

FIG. 1.
Ketones.
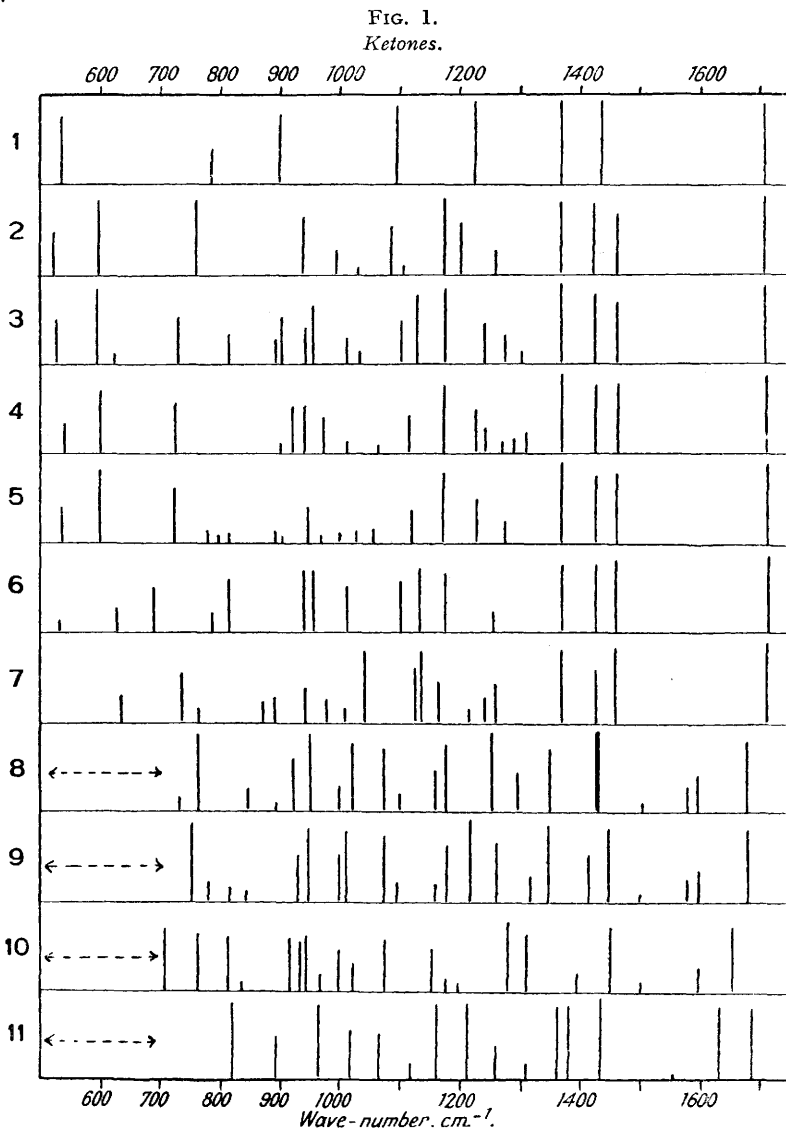
1. *Acetone.*
2. *Methyl ethyl ketone.*
3. *Methyl* n-*propyl ketone.*
4. *Methyl* n-*amyl ketone.*
5. *Methyl* n-*hexyl ketone.*
6. *Diethyl ketone.*
7. *Di-*n-*butyl ketone.*
8. *Acetophenone.*
9. *Propiophenone.*
10. *Benzophenone.*
11. *Mesityl oxide.*

With all the methyl ketones examined, other than acetone, fairly strong bands occur at the following approximate frequencies : 595, 1170, 1370, 1420, 1460. The band at 1370 is associated with a deformational mode of CH_3 radicals, as found with hydrocarbons. The bands at 1420 and 1460 are also due to deformational motions of CH_2 groups. It may be noted that acetone shows only a single band of this class at about 1435. In the other methyl ketones there are two kinds of CH_2 group, either adjacent to, or removed from, the carbonyl group. There are interesting changes of intensity with these bands between 1370 and 1460 cm.$^{-1}$ as the radicals attached to the carbonyl group are varied.

Diethyl ketone and di-*n*-butyl ketone show no strong band near 595. This suggests that this band with the methyl ketones is connected with the acetyl group, of which 595 might be a deformational frequency.

In the same way the strong band near 1170 must be connected with the acetyl group. In both cases acetone appears to be anomalous.
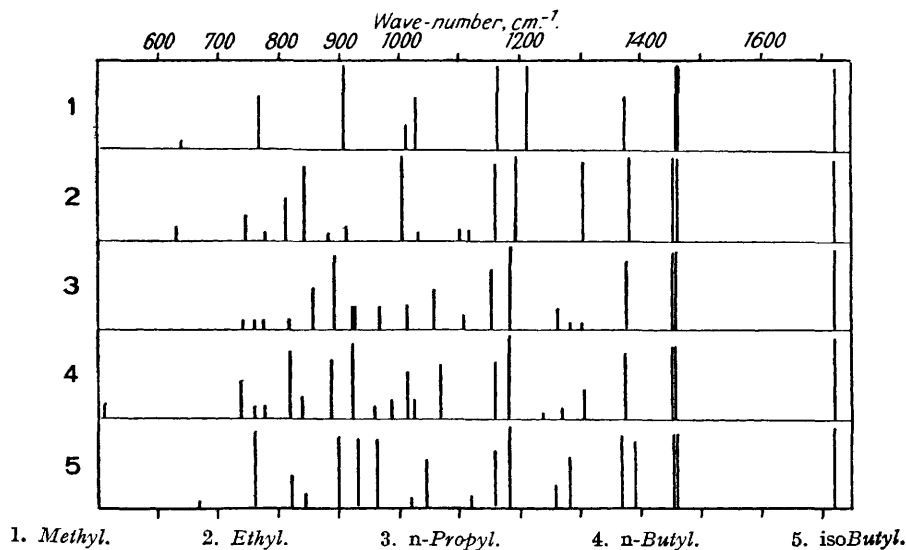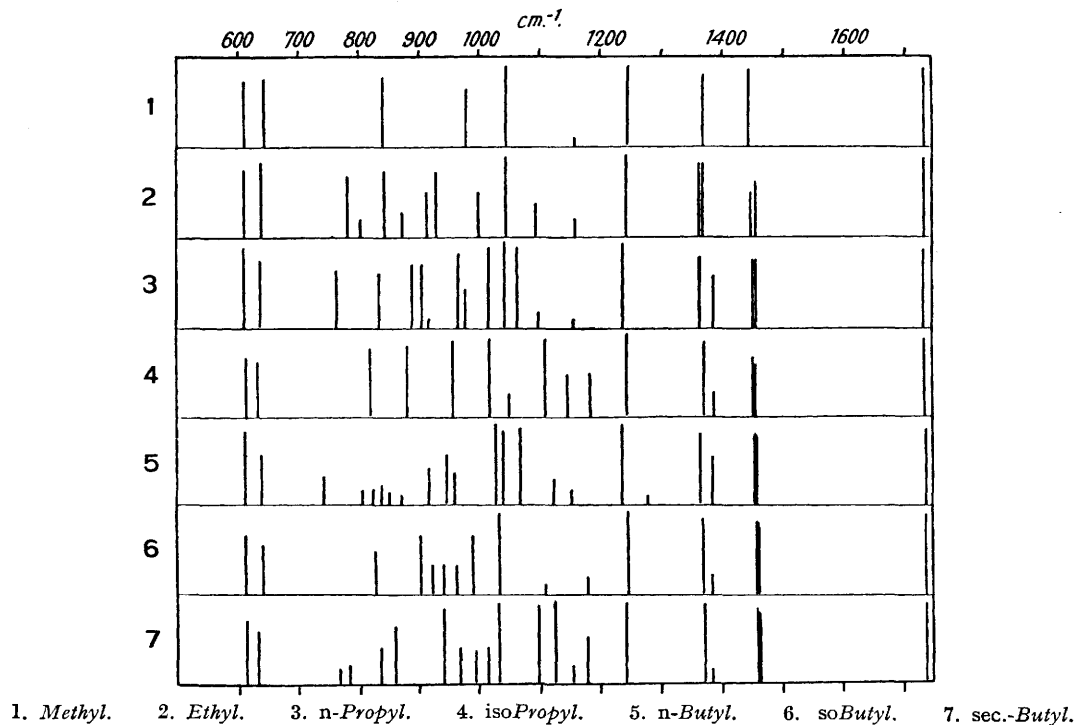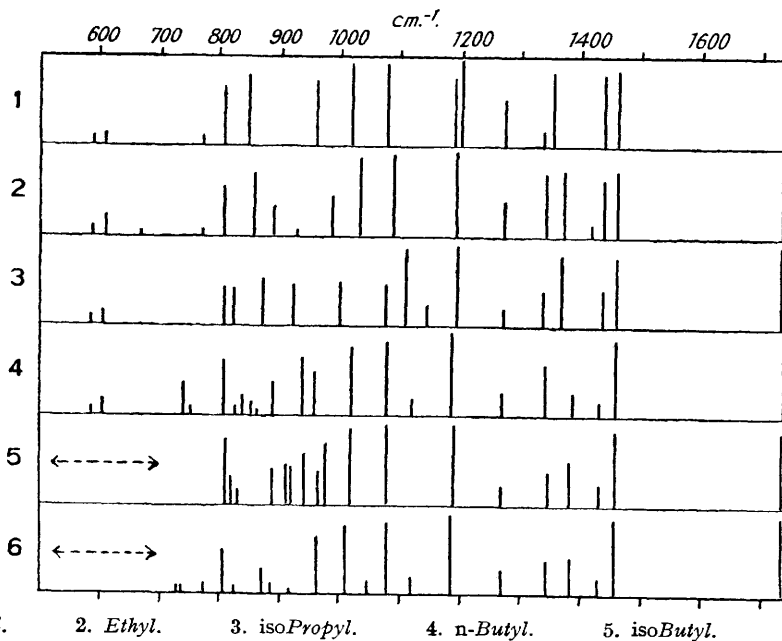
Fig. 2.

Formates.

1. *Methyl.*   2. *Ethyl.*   3. n-*Propyl.*   4. n-*Butyl.*   5. iso*Butyl.*

Fig. 3.

Acetates.

1. *Methyl.*   2. *Ethyl.*   3. n-*Propyl.*   4. iso*Propyl.*   5. n-*Butyl.*   6. so*Butyl.*   7. sec.-*Butyl.*

In the spectra of methyl *n*-amyl and methyl *n*-hexyl ketone, the bands at 723 and 722 cm.$^{-1}$ are probably associated with a vibration of the long carbon–carbon chain. This has been found with all paraffins containing a straight chain of more than four carbon atoms. Many of the bands common to acetophenone and propiophenone are connected with vibrations of the phenyl group. In these compounds the methyl group deformation is at 1350, rather lower than usual. Also, on passing from acetophenone to propiophenone the band at 1435 connected with the CH_2 group deformation splits into a pair at 1410, 1445, presumably owing to the introduction of two types of CH_2 group as indicated above. With mesityl oxide the stretching vibration

of the carbon–carbon double bond is found at 1630 cm.$^{-1}$. There are two frequencies, 1360 and 1380 corresponding to methyl group deformations, which have been found in the case of hydrocarbons having two methyl groups attached to the same carbon atom.

FIG. 4.

Propionates.

1. *Methyl.* 2. *Ethyl.* 3. iso*Propyl.* 4. n-*Butyl.* 5. iso*Butyl.* 6. n-*Amyl.*

With alkyl formates (Fig. 2) the stretching vibration of the carbonyl group has a frequency 1722—1724 cm.$^{-1}$, somewhat higher than that of ketones. The methyl group deformational frequency of methyl formate at about 1375 is common to the series, but splits in the iso*butyl derivative, where two methyl groups are attached

FIG. 5.

n-*Butyrates.*

1. *Methyl.* 2. *Ethyl.* 3. iso*Propyl.* 4. n-*Butyl.* 5. n-*Amyl.*
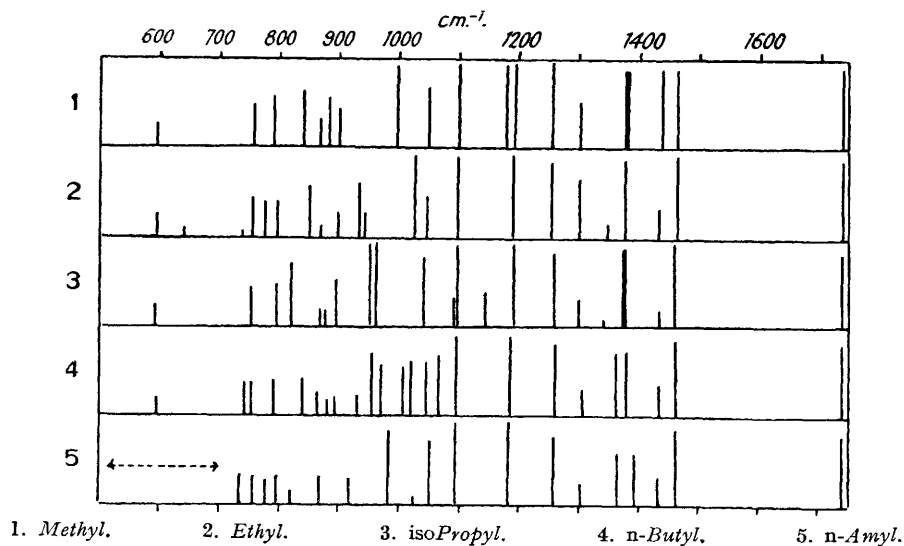
to the same carbon atom, giving the pair 1370, 1390. Also the other CH_2 group deformation of methyl formate at about 1460 is split in the other formates, presumably owing to the presence of CH_2 groups which differ in their internal molecular environment, as found with the ketones above. In iso*butyl formate the strong band at about 760 cm.$^{-1}$ may, by analogy with results on hydrocarbons, be associated with the iso*propyl group.

The most interesting bands with formates are those at about 1160 and 1185. The former remains almost

unchanged in value throughout the series, although it diminishes in intensity as the alkyl group increases in size; the latter band falls from about 1214 in methyl formate and 1195 in ethyl formate to a steady value of about 1185 in the higher homologues. The origin of these bands is discussed below.

In acetates (Fig. 3), the stretching vibration frequency of the carbonyl group lies at about 1740 cm.$^{-1}$, higher than in alkyl ketones or formates. The region 1300—1500, in which the frequencies of CH_3 and CH_2 deformations appear, is again interesting. With methyl acetate there appear to be two bands at 1375 and 1450, but with higher homologues splitting of both bands occurs, again presumably owing to the introduction of CH_2 and CH_3 groups whose immediate environment is different. It would be premature to discuss these frequencies in detail, since they are now being examined more closely with the increased resolving power provided by a fluorite prism. It seems likely, however, that there may be here a sensitive method for the differentiation of different kinds of CH_2 and CH_3 groups.

The other most strikingly constant frequencies of acetates are found at 612, 640, and 1245 cm.$^{-1}$. Formates showed no correspondingly strong band in the region of 600, and for this reason the frequencies 612, 640 appear to arise from $CH_3 \cdot CO$ groups, of which they would be deformational vibrations of the nuclear framework. As

FIG. 6.
isoButyrates.

cm.$^{-1}$

1. *Methyl.*   2. *Ethyl.*   3. *n-Propyl.*   4. *isoPropyl.*   5. *n-Butyl.*   6. *isoButyl.*
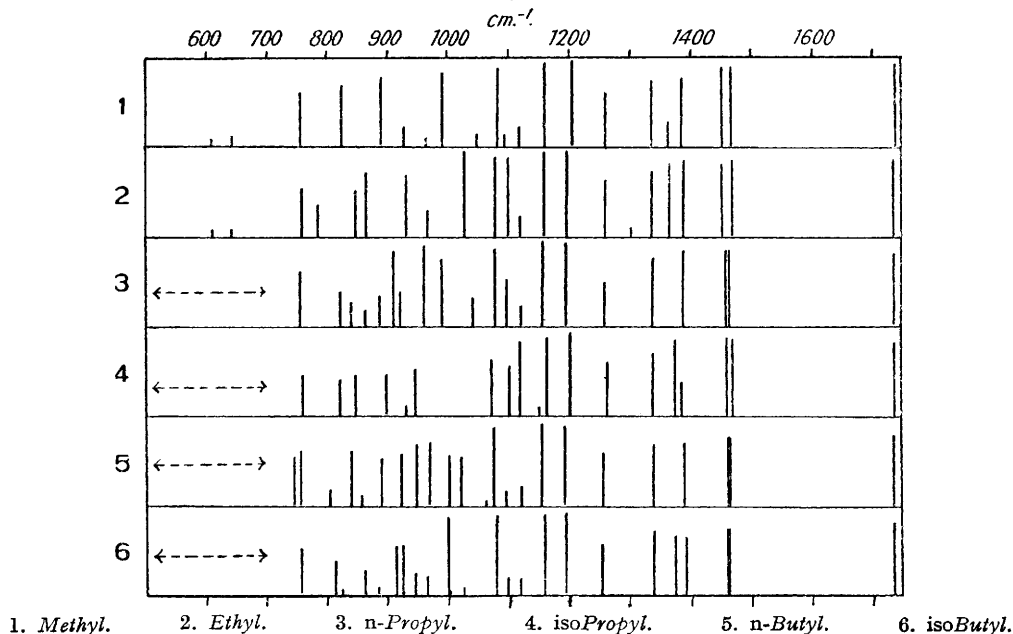
explained above, methyl ketones have a fairly strong band at 595. The latter may therefore correspond to 612 in the acetates and be connected with the acetyl part of the skeleton, whilst that at 640 might be due to the entire framework $CH_3 \cdot CO \cdot O$, in which the extra oxygen atom becomes important.

The strong band of acetates at about 1245 is perhaps more significant. By virtue of its intensity and frequency it is analogous to those of formates at 1160 and 1185. It is discussed below. The strong bands of acetates in the region of 1000 cm.$^{-1}$ are noteworthy, although no obvious correlation suggests itself. Acetates from normal alcohols have a strong band near 1050 which appears to split as the alkyl chain is lengthened. When the alkyl chain is branched, the strong bands are much less bunched around 1050.

The spectra of some propionates are shown in Fig. 4. The carbonyl group frequency lies at 1735—1740, as with acetates. Again the region 1300—1500, where the deformational frequencies of CH_2 and CH_3 groups are absorbed, is interesting and a more detailed study of both the frequencies and intensities is being carried out with the aid of the fluorite prism. The remainder of the spectral range provides a series of correlations. First, propionates show two weak bands at 590, 610. There is marked correspondence in frequency between these and the pair found with acetates at 612, 640, but in propionates both bands are very much reduced in intensity. It was suggested above that these bands in the case of acetates are connected with motions of the nuclear framework $C \cdot CO \cdot O$, and it seems probable that this conclusion is correct, and that in the propionates which have the skeleton $C \cdot C \cdot CO \cdot O \cdot$ the addition of the extra carbon atom does not much affect the frequencies which are primarily determined by the rest of the skeleton. On the other hand, it is quite plausible that this change may influence the intensities.

The characteristic feature of propionates is a very intense band between 1190 and 1200 cm.$^{-1}$. This is the analogue of the acetate band at 1245. Other bands which seem to occur throughout the series lie at 810, 1275, and except for the *iso*propyl derivative, there appears to be a fairly constant pair at 1020, 1080.

Fig. 5 shows the spectra of some normal butyrates. The ester carbonyl frequency remains at about 1735, and again the region of CH_2 and CH_3 group absorption, *viz.*, 1300—1500, shows particularly interesting features which are left for later detailed analysis. Otherwise, the following frequencies persist throughout the series : 590, 750, 1100, 1190, 1255, 1300. Of these, the group of three intense bands at 1100, 1190, 1255 is the most striking feature.

The band at 590 might at first sight be correlated with one of the pair found with acetates, but this seems unlikely. It is more probable that the pair of acetate bands near 600, connected with the skeleton C·CO·O, which was suppressed in intensity in the propionates C·C·CO·O·, is still more suppressed in the butyrates C·C·C·CO·O·, and the band at 590 may be due to some other vibration altogether.

In the *iso*butyrates (Fig. 6), the carbonyl ester frequency again lies close to 1735, and the region of absorption of the CH_2 and CH_3 deformations is interesting. Other frequencies which persist are 755, 1080, 1160, 1200, 1260, of which those at 1160 and 1200 are the strongest.

FIG. 7.
Miscellaneous esters.
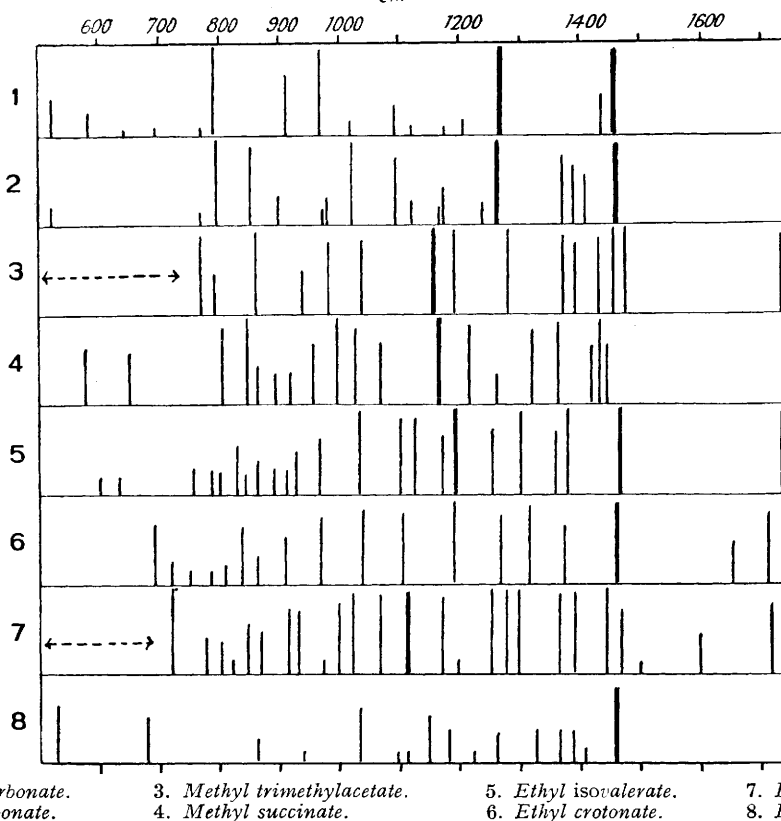
1. *Methyl carbonate.*   3. *Methyl trimethylacetate.*   5. *Ethyl* iso*valerate.*   7. *Ethyl benzoate.*
2. *Ethyl carbonate.*   4. *Methyl succinate.*   6. *Ethyl crotonate.*   8. *Ethyl malonate.*

A few other esters examined are shown in Fig. 7. The influence of neighbouring groups on the carbonyl group stretching frequency will be discussed in detail in a forthcoming paper by Mr. Trotter.

The esters being taken as a whole, the most intense and interesting bands are those in the region 1050—1250 cm.$^{-1}$, and particularly the following :

| Formates | 1185 | Propionates | 1190 | *iso*Butyrates | 1200 |
| Acetates | 1245 | *n*-Butyrates | 1190 | *iso*Valerates | 1195 |

These bands are almost certainly connected with a vibration which is primarily controlled by a ·C·O· bond, and indeed many ethers are found to have a strong band in this region. In the esters there are two such

R_1—C—$\overset{1}{\underset{\underset{O}{\|}}{\text{C}}}$—O—$\overset{2}{}$$R_2$ bonds, one contiguous to the carbonyl group and the other between the oxygen and alcohol residue (see inset). It seems probable that the very strong bands just listed are connected mainly with the first of these C–O bonds; and that the other strong bands found between 1000 and 1200 in the different cases are more related with the other C–O link and with C–C bond vibrations.

A more detailed analysis of all these results will be made when other related molecules have been examined.

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