293. *The Vibration Frequency of the Carbonyl Linkage.*

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Measurements have been collated of the vibrational frequency of the carbonyl group near 5·9 μ in the infra-red absorption spectra of different classes of compound.

The shift of this frequency has been considered in terms of the electronic structures. Shifts in the frequency which occur in different states of aggregation have also been measured for different classes of compound and the results have been interpreted in terms of the formation of hydrogen bridges or dipole aggregates.

IT has long been known that the vibration of a carbonyl link in organic compounds gives rise to absorption in the Raman and the infra-red spectra corresponding to a frequency around 5·9 μ, or 1700 cm.$^{-1}$. In some cases, such as keten, carbon dioxide or a carboxylate ion, where the vibration of this link involves a simultaneous strong interaction with the vibration of a contiguous bond, a very different value may arise. More generally, however, the frequency is regarded as characteristic, and for this reason it is important in structural diagnosis. Results from many laboratories with a wide variety of molecules have shown, however, that the exact value of the frequency depends upon the particular type of carbonyl link involved. This is to be expected since small differences in the ionic character of the carbonyl link will arise due to electronic effects induced by the attached groups. Some typical Raman data have been discussed by Kohlrausch (*e.g.*, " Der Smekal-Raman Effekt ", Vol. I, p. 157). Infra-red measurements are at present, however, being more widely applied for structural diagnosis, and a more careful examination of the shifts is therefore desirable. It should, moreover, lead to further knowledge about the electronic structure of the molecules concerned.

Results for many molecules are already available, notably those of Barnes, Liddel, and Williams (*Ind. Eng. Chem. Anal.*, 1943, **15**, 659; see Barnes, Gore, Liddel, and Williams, " Infrared Spectroscopy ", Reinhold, 1944), of Lecomte (series of papers in *Compt. rend.*, 1941—1945, and *Bull. Soc. chim.*, 1942—1944), and other unpublished data in this and other laboratories. However, many of these results are not ideally suited for detailed comparisons, owing to differences either in the instrumental resolving power, or in the conditions of measurement. We have therefore re-measured a large number of compounds, using the high resolving power of a prism of calcium fluoride in a double-beam recording spectrometer. The substances were examined where possible both in the vapour and in the condensed state, so that electronic displacement might be studied with a minimum of interference from intermolecular association, and also the effect of this molecular association in the different cases might be compared. Results are summarised below for most of the simpler molecules where special and more complex effects such as the splitting of frequencies do not arise.

EXPERIMENTAL.

The spectrometer was a double-beam instrument with fluorite prism as described elsewhere (Sutherland and Thompson, *Trans. Faraday Soc.*, 1945, **41**, 174; Thompson, Whiffen, Richards, and Temple, Report 17, Hydrocarbon Group, Inst. Petroleum). The positions of sharp bands could be fixed to within ± 2 cm.$^{-1}$, and as between different molecules in a series are probably comparable to within ± 1 cm.$^{-1}$. The contour found with some vapour bands makes it difficult to fix the band centre with high precision. For the vapours the absorption cell was a cylindrical glass tube 20 cm. in length, having flanged ends on to which rock-salt plates were fixed with a hard grease, the whole being enclosed in a small electric furnace with apertures at the two sides to allow passage of the beam of radiation through the cell. It could be used at temperatures up to 60°. In each case a pressure of about 2 mm. was used. Liquids and solutions were examined in cells of the conventional type about 0·05 mm. in thickness.

RESULTS AND DISCUSSION.

Table I summarises the results for the vapours of several groups of compounds in which the radicals attached to the carbonyl group are saturated. In some cases the band shows contour, the centre of which was chosen as band origin. The simple aliphatic acids show two bands, the relative intensity of which varies with temperature. At the higher temperatures the component at higher frequencies is strengthened and is correlated with the monomeric form (Herman and Hofstadter, *J. Chem. Physics*, 1938, **6**, 534; Davies and Sutherland, *ibid.*, p. 755). The striking feature is that, although the vibration frequency varies substantially among the different types of compound, yet within a given class of homologues it remains close to a particular value. Thus in the alkyl esters it lies near 1765 cm.$^{-1}$, although the formates appear definitely to have a

TABLE I.

Vapours.

(Position of bands in cm.$^{-1}$.)

Compound.	Sub-maxima.	Band centre.
Acid halides.		
Bromoacetyl bromide	1817, 1830	1824
Acetyl chloride	1815, 1829	1822
Chloroacetyl chloride	1805, 1835	1820
Acids.		
Formic acid (20°)	1745, 1794	1794
,, ,, (60°)	1758, 1794	1794
Acetic acid (20°)	1735, 1785	1785
,, ,, (60°)	1735, 1790	1790
Propionic acid (20°)	1736, 1787	1787
Chloroacetic acid	—	1794
Carbonates.		
Dimethyl carbonate	1770, 1784	1777
Diethyl ,,	—	1767
Aldehydes.		
Formaldehyde	—	1745
Acetaldehyde	1739, 1765	1752
Propaldehyde	1748, 1765	1757
Ketones.		
Acetone	—	1742
Methyl ethyl ketone	1736, 1748	1742
Diethyl ,,	—	1738
Methyl *n*-propyl ,,	—	1737
Methyl *n*-amyl ,,	—	1738
Methyl *n*-hexyl ,, (60°)	—	1738
Di-*n*-butyl ,, (60°)	—	1733
*cyclo*Pentanone	—	1772
*cyclo*Hexanone	—	1742
Amide.		
NN-Diethylformamide (formodiethylamide)	—	1710

Compound.	Sub-maxima.	Band centre.
Esters.		
Methyl formate	1746, 1769	1757
Ethyl ,,	1749, 1761	1755
n-Propyl ,,	—	1752
*iso*Propyl ,,	—	1752
n-Butyl ,,	—	1754
*iso*Butyl ,,	—	1754
*iso*Amyl ,,	—	1752
Methyl acetate	1767, 1780	1774
Ethyl ,,	—	1765
n-Propyl ,,	—	1768
*iso*Propyl ,,	—	1762
n-Butyl ,,	—	1768
*iso*Butyl ,,	—	1770
sec.-Butyl ,,	—	1764
*iso*Amyl ,,	—	1769
*cyclo*Hexyl ,,	—	1766
Methyl propionate	1765, 1770	1767
Ethyl ,,	—	1761
*iso*Propyl ,,	—	1758
n-Butyl ,,	—	1763
*iso*Butyl ,,	—	1764
n-Amyl ,,	—	1765
Ethyl *n*-butyrate	—	1760
*iso*Propyl ,,	—	1757
n-Butyl ,,	—	1758
Ethyl *iso*butyrate	—	1759
n-Propyl ,,	—	1758
*iso*Propyl ,,	—	1757
n-Butyl ,,	—	1759
*iso*Butyl ,,	—	1759
Methyl trimethylacetate	—	1758
Ethyl *iso*valerate	—	1759
Methyl hexoate	—	1765
Ethyl trichloroacetate	—	1786

lower value around 1755 cm.$^{-1}$. Ketones have a value close to 1740 cm.$^{-1}$, in acids and acid chlorides the frequency is usually higher, and in amides much lower.

Table II shows the trend of the mean values for the different classes.

TABLE II.

Vapours.

(Position of bands in cm.$^{-1}$.)

Acid halides	1820	Aldehydes	1755
Acids	1790	Alkyl ketones	1740
Alkyl esters	1765	*NN*-Dialkylamides	1710
Alkyl formates	1755		

TABLE III.

(Position of bands in cm.$^{-1}$.)

Esters.			Aldehydes.		
Methyl acrylate	1758	mean 1750	Benzaldehyde	1725	mean 1722
Ethyl crotonate	1746		Acraldehyde	1723	
Methyl benzoate	1754		Crotonaldehyde	1720	
Vinyl acetate	1787	mean 1790	Ketone.		
Phenyl acetate	1793		Phenyl methyl ketone	1707	

The α-conjugated esters, namely acrylates, crotonates, and benzoates (see Table III), have frequencies somewhat lower than the corresponding saturated esters, but when the unsaturated radical replaces the hydrogen atom of the carboxyl group, as in vinyl acetate, the frequency is much higher. In the same way with the aldehydes and ketones, conjugation lowers the vibration frequency of the carbonyl group.

The effect of halogen atoms as substituents should also be noted. Thus chloroacetic acid has the band at 1794 cm.$^{-1}$, whereas in acetic acid it lies at 1785 cm.$^{-1}$, and in ethyl trichloroacetate it lies at 1786 cm.$^{-1}$, but at 1765 cm.$^{-1}$ in ethyl acetate. α-Chloro-substitution therefore raises the frequency. In the acid chlorides, however, where the frequency is already much higher than in the corresponding carboxylic acid, further substitution of a halogen on the α-carbon atom appears to have little effect.

Ring strain may also markedly affect the vibration frequency of the carbonyl group. Thus in *cyclo*hexanone it lies at 1742 cm.$^{-1}$, but in *cyclo*pentanone at 1772 cm.$^{-1}$. This point is discussed further below.

Table IV summarises results for compounds measured in the condensed state. A detailed survey of ketones and esters has already been published (Thompson and Torkington, *J.*, 1945, 640). The changes in the spectra of amides under different conditions of measurement have also been described * (Richards and Thompson, *J.*, 1947, 1248).

The results of Table IV show that (1) there is a general lowering of the frequency of the carbonyl group in passing from the vapours to the liquid and the solid states, (2) with most compounds the lowering is about 20 cm.$^{-1}$, but with acids, amides, and monosubstituted amides, where hydrogen bridge formation is more directly possible, it is much more pronounced.

Table V shows some results for compounds containing unsaturated radicals. As found with the vapours, conjugation with the carbonyl group leads to a lowering of its vibration frequency whereas in vinyl acetate or phenyl acetate it is raised. In all cases, however, there is a lowering of about 20 cm.$^{-1}$ as compared with the vapour.

Many other compounds have been examined containing a carbonyl group as part of a heterocyclic ring, such as lactones, oxazolones, and lactams. With these compounds the value of the frequency of this carbonyl group appears to be a complex function of ring strain, of the nature of side chains attached to the ring, of the presence of conjugation, and of other factors. These will be considered in a later paper.

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* Our work on amides, amino-acids, and related substances was carried out several years ago as a preliminary to infra-red measurements on peptides and protein materials, which have since been continued. Similar work on amides was carried out independently at about the same time in America by Brattain and Rasmussen of the Shell Development Company, and by Randall and Fowler of the University of Michigan, in connection with investigations on penicillin to which some of our own work was later applied. Much of the American work overlapped ours, although there were important differences of approach and different aspects were examined in greater detail. Although their work has hitherto only been available in confidential reports it is hoped that it will soon be published without loss of priority. We would repeat the appreciation already expressed in our paper of valuable discussions with them several years ago on some aspects of these subjects.

TABLE IV.

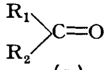
(l = liquid, s = solid, sol. = solution.)

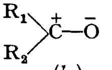
Compound.	State.	Carbonyl group frequency (cm.$^{-1}$).	Decrease (cm.$^{-1}$) from vapour.
Acetyl chloride	l	1808	14
Ethyl trichloroacetate	l	1768	18
Acetic acid	l	1717	68
Propionic acid	l	1722	65
Methyl acetate	l	1747	27
*cyclo*Hexyl acetate	l	1740	26
Acetaldehyde	l	1729	23
Propaldehyde	l	1735	22
Acetone	l	1718	24
Methyl ethyl ketone	l	1721	21
Methyl *n*-propyl ketone	l	1721	16
Methyl *n*-hexyl ketone	l	1720	18
Diethyl ketone	l	1718	20
Di-*n*-butyl ketone	l	1718	15
*cyclo*Hexanone	l	1714	28
*cyclo*Pentanone	l	1744	28
Hexoamide	s	1652	—
,,	sol., methanol	1672	—
,,	sol., chloroform	1682	—
,,	sol., dioxan	1692	—
N-*tert*.-Amylphenylacetamide	s	1645	—
,, ,,	sol., methanol	1657	—
,, ,,	sol., chloroform	1668	—
,, ,,	sol., dioxan	1682	—
NN-Diethylacetamide	l	1645	—
,,	sol., methanol	1615	—
,,	sol., chloroform	1629	—
,,	sol., dioxan	1647	—
NN-Diethylformamide	l	1670	40

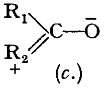
TABLE V.

Compound.	State.	Carbonyl group frequency (cm.$^{-1}$).	Decrease (cm.$^{-1}$) from vapour.
Vinyl acetate	l	1762	25
Phenyl acetate	l	1766	27
Methyl acrylate	l	1732	26
Methyl benzoate	l	1727	27
Benzaldehyde	l	1705	20
Phenyl methyl ketone	l	1687	20

Although it is not yet possible to explain quantitatively the shifts described above, a qualitative framework for most of the effects can be set up in terms of known structural characteristics. The close concordance of the frequency of the carbonyl group in esters having widely different alkyl groups shows, at least, that mass effects are of minor significance, and differences between the different classes must arise primarily from differences in electronic structure, and reveal differences in the force constant in the different case.

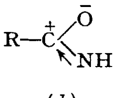

(*a*.)

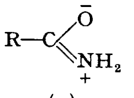

(*b*.)

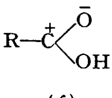

(*c*.)

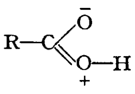
In ketones (*a*), the double-bond character may be reduced by participation in the actual molecule of the ionic forms (*b*) and (*c*). The extent to which (*b*) and (*c*) will play a part will depend on the nature of the groups R_1 and R_2, (*b*) being determined by the electron-attracting or electron-repelling character of R_1 and R_2, and (*c*) being a possible mesomeric form contributing to the true form.

In alkyl ketones, having a frequency (vapour) close to 1740 cm.$^{-1}$, the structure (*b*) must be partially concerned. In the aldehydes the presence of the polarisable hydrogen atom leads to diminution of the ionic character, *i.e.*, a smaller proportion of (*b*), so that the frequency rises. In the esters, the electrophilic inductive properties of the alkoxy-group (OR) again reduce the contribution of (*b*). Evidently in this case the contribution of the mesomeric form is too small to overcome the former effect. That the inductive effect of alkoxy-groups exceeds the mesomeric effect is suggested by the relative dissociation constants of alkoxy-substituted acetic and benzoic acids. The peculiar small lowering of the frequencies in formates is not easily explained. In the acid chlorides, the powerfully electron-attracting halogen atom diminishes the contribution of form (*b*), and this far exceeds the effect from the mesomeric form (*c*), so that the frequency rises. In the amides, the NH_2 group has a strong inductive effect favouring the form (*d*), and the mesomeric form (*c*), namely (*e*), is also possible, so that there is a marked lowering of the carbonyl frequency.


(*d*.)


(*e*.)


(*f*.)


(*g*.)

The results with carboxylic acids are more difficult to interpret. As compared with esters, the smaller inductive effect of OH than OR should favour the form (*f*), and the greater mesomeric effect should favour (*g*). Both these effects should lower the frequency, which is, however, raised.

In α-chloro-acids the inductive effect towards the chlorine atom should decrease the ionic character and raise the frequency slightly, as found.

With the conjugated esters, electronic drifts lead to a weakening of the carbonyl link, *i.e.*, there is a greater contribution of the mesomeric ionic form in the hybrid. The frequency therefore falls. The increase in vinyl esters probably arises from the electron affinity of the sp^2 hybridised carbon atom of the vinyl group discussed by Walsh (*Trans. Faraday Soc.*, 1947, **43**, 75) which effectively increases the electron-attracting power of the oxygen atom in the $-O-CH=CH_2$ group, thus diminishing the ionic character of the carbonyl link.

As already shown, the shifts found to occur on change of state appear to be of two kinds. Acids, amides, and monosubstituted amides show large shifts, the magnitude of which varies in solvents of different dielectric constants. The most important feature here is the formation of very strong hydrogen bridges, as previously described for the amides (Richards and Thompson, *J.*, 1947, 1248). Other compounds, such as ketones, esters, acid chlorides, and disubstituted amides, show smaller shifts, and the carbonyl group frequency does not vary appreciably in solvents of different dielectric constants, as the results of Table VI show.

TABLE VI.

Value of carbonyl group frequency (cm.$^{-1}$).

Solvent.	Dielectric constant.	Acetone.	Methyl Acetate.	Coumarin.	Didecyl ketone.
(Vapour)	—	1742	1774	1776	1740
*cyclo*Hexane	2	1728	1756	1758	1724
Carbon tetrachloride	2·2	1724	1749	1738	1718
Dioxan	2·2	1720	1747	1738	1718
Bromoform	4·5	1712	1738	1730	1709
Chloroform	5·0	1717	1742	1738	1715
Ethylene dichloride	10·5	1718	1743	1735	1717
Pyridine	12·5	1718	1743	—	—
Acetone	21·4	1718	—	—	—
Propionitrile	26·5	1718	1743	1735	1717
Acetonitrile	38·8	1748	1745	1732	1717
Nitromethane	39·4	1718	—	—	—

With these compounds it seems probable that dipolar association occurs in the liquid state and in solution. Some support for this hypothesis is found in the fact that the shift on passing from vapour to liquid increases along the series acetyl chloride (14), esters (20—30), disubstituted amides (40), since the frequency decreases, *i.e.*, the ionic character increases, in this order.

It seems likely that further light may be thrown on the nature of the electronic structures discussed above by measurement of the intensities of the vibration bands, and such measurements are in progress.

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