

RAMAN EFFECT AND HYDROGEN BONDS

Part I. Mixtures of Esters and Acceptor Molecules

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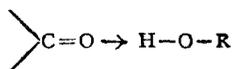
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THE hydrogen bond or the binding of two atoms by means of an atom of hydrogen has been successfully employed to give concreteness to such indefinite terms as partial valence, secondary forces, co-ordination, association and ortho-effect. Such a role of hydrogen (secondary forces) seems to have been first postulated by Moore and Winnill¹ to account for the differences in strength between tertiary and quaternary ammonium bases. The idea was developed into 'the hydrogen bond' within the scope of Lewis valence theory by Huggins² and Latimer and Rodebush³ to account for the association of water and for the formation of ions such as HF_2^- . It was extended to organic compounds with special reference to chelate structures by Sidgwick,⁴ who considered it as a particular case of Werner's co-ordination theory. This concept of hydrogen bond implies the capacity of hydrogen to assume a co-valency of two. Association between two molecules is represented as $-\text{A} : \text{H} : \text{A}'-$ where A and A' are the electronegative atoms of the two molecules which the 'H' atom holds together. The physical objections to this idea of co-valency of two for hydrogen, which implies a group of four shared electrons are very strong. The difficulties, however, seem to have been overcome by introducing the idea of resonance⁵ between two structures in the first of which the 'H' atom is attached to one and in the second to the other of the two atoms which it holds together ($\text{R} : \text{H} : \text{R}'$, $\text{R} : \text{H} : \text{R}'$). Whatever may be the exact details regarding the mechanism of the hydrogen bond, its occurrence is beyond doubt and there is good evidence for the capacity of a hydrogen atom to hold two other atoms together.

Newer methods of investigation have provided extensive experimental material which supports the theory of hydrogen bonds in a remarkable manner. The importance of this subject and the interest evinced by workers in various fields of investigation is clearly indicated by the recent discussions of the Faraday Society.⁶ Studies on the crystal structure of both inorganic and organic compounds have revealed several features indicating the existence of hydrogen bonds. The work of Pauling and Brockway,⁷ employing the method of electron diffraction, has definitely established the existence

of dimers of carboxylic acids involving hydrogen bonds. But by far the most important contribution to our knowledge of the subject has been made by the investigations of infra-red absorption spectra. Wulf and collaborators⁸ have examined the spectra of many organic compounds in solution and noticed the absence of the second harmonic of the OH band in cases where hydrogen bonds were to be anticipated. An account of similar work turned out in Cotton's laboratories in Paris since 1932 is given by Freyman.⁹ Buswell, Dietz and Rodebush¹⁰ investigated a large number of compounds using the region of the fundamental hydroxyl band and found the important generalisation that the presence of hydrogen bonds is accompanied by a considerable increase in the absorption and a marked change in the frequency of the band, the shift being in the direction of longer wavelengths. This work has been confirmed by other investigators¹¹ independently. Walter Gordy and co-workers¹² have made an extensive series of investigations on liquids and binary liquid mixtures and thus obtained information regarding the formation of hydrogen bonds between similar as well as dissimilar molecules. No attempt has, however, been made in this paper to give any exhaustive account of the infra-red studies; only items relevant to the discussion on Raman effect and hydrogen bonds have been included.

In regard to the application of the Raman effect to the study of hydrogen bonds no systematic investigation has so far been reported, though the concept has been utilised by some workers¹³ in the past to explain certain peculiarities in the Raman spectra of compounds and binary mixtures observed by them. Since the potentialities of this method are obviously great, the investigations described in this series of communications have been undertaken. The usual procedure adopted in infra-red spectroscopy is to determine the effect of hydrogen bond formation on the absorption of the group which carries the hydrogen, as for example the OH group of alcohols and phenol. It is relatively in very few cases that the effects of the bond on the second group involved, such as the C=O in carbonyl compounds, have been examined. The large amount of data obtained from infra-red studies seems to indicate that hydrogen bond formation is more or less universal in liquids and liquid mixtures of molecules having donor and acceptor atoms. In our investigations attention is confined to cases of hydrogen bond formation where the oxygen of the C=O group of various carbonyl compounds acts as the donor. Such cases may be represented as below:—



It readily follows that there should be a weakening of the C=O bond resulting in a lowering of the frequency of the line attributable to this linkage.

In this procedure possibilities of accuracy and definiteness are greater since the Raman line of the C=O is usually bright and sharp and any modifications undergone by it can be easily recorded. On the other hand the utilisation of the OH group is difficult for two reasons, *viz.*, (i) the difficulty of recording the OH band and (ii) the non-existence of any hydroxylic compound devoid of hydrogen bond in it for use as the correct standard.

Hydrogen bonds can be classified broadly under two heads namely, intermolecular and intramolecular hydrogen bonds. In the former, the two atoms linked by the hydrogen belong to different molecules whereas in the latter they are present in the same molecule. Intermolecular hydrogen bonds may further be subdivided as the homo- and the hetero-molecular types according as the union is brought about between similar and dissimilar molecules respectively. These bonds are represented by many American workers by means of dotted lines joining the donor atom and the hydrogen. It seems to be more reasonable to represent them by means of arrows pointing in the direction of the pull of electrons as $> \text{C}=\text{O} \rightarrow \text{H}-\text{O}-\text{R}$. The terms donor and acceptor are used by some¹⁴ in connection with the proton but it appears to be more correct to refer them to the electrons since, according to the ideas advanced by Sidgwick,⁵ it is only the electrons that change their positions in the resonance condition. Further, this will be in accordance with the accepted usage of these terms in connection with co-ordinate valency.

The essential requisites for the formation of hydrogen bonds are (i) the existence of 'H' atoms with the capacity to serve as acceptors and (ii) the presence of atoms having free pairs of electrons, enabling them to act as donors. As examples may be mentioned 'H' atoms present in hydroxylic and amino compounds under category (i) and oxygen, nitrogen and chlorine atoms under category (ii). Consequently the strength of hydrogen bonds will depend upon the anionoid power of the donor and the cationoid power of the acceptor atoms and a large variation in bond strength is possible.

In this connection it may be recalled that Bernal¹⁵ proposed to distinguish between two types of hydrogen bonds and to call them the hydrogen and the hydroxyl bonds respectively. "In the hydrogen bond the hydrogen atom is attached with almost equal firmness to the two oxygen atoms which it joins, the O—H···O distance being 2·50–2·65 Å corresponding to an energy of the bond of about 8000 cal./ mol. The O–H links in these conditions are greatly weakened and the characteristic OH band is not found in the normal spectral region. In the 'hydroxyl bond' the hydrogen atom is still regarded as belonging to its parent oxygen, although the O–H link is somewhat weakened

and the band is observed at a lower frequency. The distance O—H··O in this type of bond is taken to be 2·7 to 2·9 Å and the energy involved about 5,000 cal./mol. Venkateswaran¹⁶ in the course of his work on the Raman spectra of some inorganic acids came to the conclusion that, in view of the fact that the hydrogen bonds are capable of exhibiting varying bond strengths, the distinction between the two types as proposed by Bernal is too artificial.

With a view to test the validity of the generalisation namely 'the anionoid power of the donor atoms and the cationoid power of the acceptor atoms determine the strength of hydrogen bonds' and to examine the need for division into different categories as proposed by Bernal, a large number of organic compounds containing C=O groups of different types and mixtures of these with phenol, alcohol, and chloroform have been investigated. Incidentally it was expected that the results would supplement data obtained from the study of infra-red spectra.

The experimental methods are essentially the same as those described by us in our former publications in these *Proceedings*. In this part the results of investigation of the Raman spectra of various esters and their mixtures with acceptors like phenol, methyl alcohol, ethyl alcohol and chloroform are dealt with. The following esters have been employed :

(1) Ethyl acetate, (2) Ethyl benzoate, (3) Ethyl cinnamate, (4) Phenyl acetate, (5) Phenyl propionate, (6) Phenyl benzoate, (7) Phenyl cinnamate and (8) Benzyl-acetate. In addition to the above, coumarin has been also included in this part because, as shown by us previously it behaves very much like a phenyl ester.¹⁷

Pure substances were available in most cases and they were further purified by repeated distillation or crystallisation. High boiling liquids were as a rule distilled under reduced pressure. Phenyl propionate was prepared by heating dry phenol with sodium propionate and propionic anhydride at 160° C. in an oil bath for six hours. It was repeatedly washed with sodium carbonate solution, ether extracted, dried over anhydrous calcium chloride and distilled under reduced pressure after the ether had been driven off. Phenyl cinnamate was prepared by the action of phenol on cinnamoyl chloride in the presence of pyridine. It was recrystallised several times from alcohol. Phenol was dried over calcium chloride and distilled perfectly out of contact with air and moisture and fresh samples were employed, because on keeping, it acquires a reddish colour which is likely to absorb much of the exciting radiation, viz., 4358 Å. Methyl and ethyl alcohols were purified by distillation over calcium turnings. Chloroform was subjected to slow distillation.

A description of the spectra of the substances as recorded by us is given below and subsequently the effects of mixing the esters and the acceptor solvents on the carbonyl frequencies are dealt with. No attempt is made to give any exhaustive list of references to the previous work on the Raman Spectra of the substances because they could easily be obtained from the recent book published by Hibben.¹⁸ However, select references relevant to the discussions are given in proper places.

Spectra of the Donor Substances in the Pure State

(Figures within brackets indicate visual estimates of the relative intensities).

(1) *Ethyl acetate*.—376 (9) 633 (9) 784 (3) 846 (10) 916 (1) 938 (1) 999 (1) 1045 (2) 1096 (1) 1114 (3) 1452 (6*b*) 1739 (6*b*) 2880 (1) 2940 (8*b*) 2982 (7*b*).

(2) *Ethyl benzoate*.—193 (3) 214 (2) 326 (4) 395 (1) 488 (1) 588 (1) 619 (6) 677 (4) 783 (2) 809 (2) 852 (5) 1004 (10) 1029 (3) 1112 (3) 1160 (2) 1178 (2) 1277 (5) 1314 (2) 1371 (2) 1381 (2) 1453 (3) 1493 (1) 1602 (10) 1720 (8) 2935 (2) 2972 (2) 3076 (6).

(3) *Ethyl cinnamate*.—274 (1) 357 (1) 580 (1) 618 (1) 715 (2) 840 (2) 945 (2) 974 (2) 1000 (7) 1030 (3) 1153 (2) 1180 (4) 1202 (6) 1255 (2) 130 (1) 1450 (2) 1578 (2) 1598 (7) 1634 (10) 1712 (5*b*) 2940 (1) 3066 (1).

(4) *Phenyl acetate*.—185 (1) 239 (4) 272 (4) 341 (1) 529 (5) 597 (1) 618 (4) 664 (4) 694 (2) 744 (5) 815 (5) 829 (1) 892 (2) 926 (1) 1004 (10) 1027 (3) 1079 (1) 1163 (6) 1195 (6) 1262 (1) 1311 (1) 1369 (1) 1429 (1) 1448 (1) 1596 (8) 1766 (3) 2912 (2) 3047 (2) 3070 (7).

(5) *Phenyl propionate*.—186 (1) 230 (2) 268 (2) 338 (1) 529 (3) 618 (2) 660 (2) 740 (3) 820 (4) 890 (0) 926 (0) 1004 (10) 1030 (2) 1163 (3) 1195 (3) 1598 (6) 1760 (3) 2912 (1) 3072 (5).

(6) *Phenyl benzoate*.—340 (3) 610 (3) 674 (1) 850 (2) 1000 (10) 1030 (2) 1115 (2) 1158 (2) 1176 (1) 1274 (3) 1310 (1) 1365 (1) 1450 (2) 1604 (10) 1740 (7) 2930 (1) 3070 (5).

(7) *Phenyl cinnamate*.—(The spectrum was studied in solution in carbon tetrachloride.)

274 (1) 375 (1) 580 (1) 618 (1) 715 (2) 840 (2) 945 (2) 974 (2) 1000 (7) 1030 (3) 1153 (2) 1180 (4) 1202 (6) 1255 (2) 1301 (1) 1450 (2) 1540 (2) 1570 (2) 1596 (7) 1633 (10) 1742 (4) 2940 (1) 3067 (1).

(8) *Benzyl acetate*.—187 (2) 223 (2) 263 (1) 300 (1) 329 (1) 426 (0) 499 (1) 580 (5) 619 (3) 642 (2) 751 (5) 820 (1) 839 (3) 919 (2) 1002 (10) 1028 (4)

1077 (3) 1119 (3) 1157 (3) 1181 (2) 1213 (1) 1244 (1) 1263 (2) 1452 (2) 1585 (2) 1606 (8) 1745 (4) 2940 (2) 3070 (7).

(9) *Coumarin*.—(a) Solution in carbon tetrachloride, Frequencies between 1000–2000 cm^{-1} are given below :—

1030 (1) 1102 (3) 1125 (3) 1158 (3) 1178 (10) 1228 (4) 1257 (2) 1330 (4) 1457 (2) 1492 (2) 1570 (8) 1610 (6) 1625 (6) 1742 (6).

(b) Pure solid melted and resolidified.—1030 (1) 1100 (3) 1128 (3) 1156 (3) 1181 (10) 1228 (4) 1260 (4) 1328 (6) 1457 (2) 1486 (4) 1567 (8) 1604 (6) 1620 (6) 1708 (6) 1731 (6).

Spectra of Acceptor Substances

(1) *Phenol*.—236 (3) 532 (1) 624 (2) 750 (1) 812 (1) 826 (1) 1000 (10) 1028 (6) 1070 (0) 1158 (2) 1167 (3) 1255 (1) 1595 (5) 1601 (5) 3014 (0) 3046 (3) 3060 (10).

(2) *Ethyl alcohol*.—434 (1) 880 (6) 1051 (3) 1095 (3) 1453 (5) 2875 (5) 2930 (10) 2972 (4).

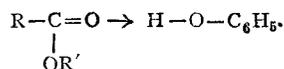
(3) *Methyl alcohol*.—1030 (4) 1464 (5) 2838 (5) 2945 (6).

(4) *Chloroform*.—264 (5) 367 (5) 688 (10) 765 (5b) 1220 (1).

In general the esters were mixed with the solvents in the proportion, 1:1 and the spectra of the mixtures compared with those of the pure substances. When solids like coumarin and phenol were concerned the two molten substances were mixed and the Raman tube containing the molten mixture was kept at about 80° C. by means of an electric heater. In many cases it was observed that the spectra of the mixtures showed conspicuous changes as far as the C=O frequency was concerned.

Mixtures of Esters with Phenol

The results obtained with these mixtures are presented in Table I. The most striking effects are noticed here; in all cases new C=O lines which are bright make their appearance and these are attributable to hydrogen bond formation as represented below :—



Except the case of coumarin mixture, in which the original C=O frequency has completely disappeared, the others continue to exhibit the unchanged frequencies of the esters with considerably diminished intensity. Obviously the mixtures contain a portion at least of the uncombined esters. The larger

TABLE I

Name of the substance	C=O frequency in the pure state	C=O frequency in mixtures with phenols	Difference
Ethyl acetate	1739	1700, 1739	39
Ethyl benzoate	1720	1695, 1720	25
Ethyl cinnamate	1712	1685, 1712	27
Phenyl acetate	1766	1716, 1766	50
Phenyl propionate	1760	1710, 1760	50
Phenyl benzoate	1740	1704, 1740	36
Benzyl acetate	1745	1715, 1745	30
Coumarin	1742 (in CCl ₄)	1710	32

shifts are noticed with esters having high C = O frequencies and *vice-versa*; the range in the values lies between 50 and 25 wave numbers.

Ester Alcohol Mixtures

Anhydrous ethyl and methyl alcohols were employed and it was noticed that the two gave identical results as far the C = O frequency shift was concerned. Here also coumarin mixtures gave a new C = O frequency, the original one having disappeared. In regard to the others the effects are not so prominent as in the case of phenol. The results are presented in Table II and the changes are attributed to the formation of hydrogen bonds of the following type :

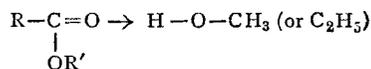


TABLE II

Name of the substance	C=O frequency in the pure state	C=O frequency in mixtures with alcohol
Ethyl acetate	1739	diffuse
Ethyl benzoate	1720	1722
Ethyl cinnamate	1712	1712
Phenyl acetate	1766	1746, 1766
Phenyl cinnamate	1742	diffuse
Coumarin	1742 (in CCl ₄)	1720

Diffuseness of the lines mentioned above is towards shorter wavelengths and does not exceed 15 wave numbers.

Ester-Chloroform Mixtures

The tendency to form hydrogen bonds is, in general, as weak as in the case of the alcohol mixtures as will be evident from Table III.

However, coumarin, phenyl cinnamate and phenyl acetate exhibit marked shifts in the C=O frequencies even here due to complex formation as below :

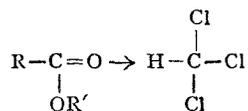


TABLE III

Name of the substance	C=O frequency in the pure state	C=O frequency in mixtures with chloroform
Ethyl acetate	1739	1736
Ethyl benzoate	1720	1722
Ethyl cinnamate	1712	diffuse
Phenyl acetate	1766	1746, 1766
Phenyl benzoate	1740	diffuse
Phenyl cinnamate	1740	1722
Benzyl acetate	1745	1740
Coumarin	1742 (in CCl ₄)	1720

Diffuseness of the lines mentioned above is towards shorter wavelengths and does not exceed 15 wave numbers.

All the observed results may be consolidated and classified as follows:—

(i) Those in which a shift of the C=O frequency towards shorter wavelength is observed. The unmodified C=O frequency of the ester does not make its appearance at all in these cases. These are denoted as (*a*) in Table IV and the shifts of the C=O frequencies are given in cm.⁻¹ as (*a*₂₀) etc. Examples of this category are phenyl cinnamate in chloroform and coumarin in various solvents.

(ii) Those in which the appearance of a modified C=O frequency (towards shorter wavelengths) is noted in addition to the original C=O frequency of the ester. These are denoted by (*b*) in Table IV and the frequency differences between the two are given in cm.⁻¹ as (*b*₂₀) etc. Mixtures of most of the substances with phenol belong to this class.

(iii) This represents the cases where the C=O frequencies of the esters are found to become diffuse towards the shorter wavelengths. Cases of ethyl acetate in alcohol, phenyl benzoate in chloroform etc. belong to this group and they are represented as (*c*).

(iv) This group embodies the cases where no change has been observed in the C=O frequency of the carbonyl compound. These are denoted as (*d*).

Among the examples of this type may be mentioned the mixtures of ethyl benzoate and chloroform, ethyl benzoate and ethyl alcohol, etc.

The following table gives a consolidated statement of the changes undergone by the C = O frequencies.

TABLE IV

Name of the compound	C=O frequency of the pure substance	In chloroform	In methyl alcohol	In ethyl alcohol	In phenol
Ethyl acetate	1739	<i>d</i>	<i>c</i>	<i>c</i>	..
Ethyl benzoate	1720	<i>d</i>	<i>d</i>	<i>d</i>	<i>b</i> ₂₅
Ethyl cinnamate	1712	<i>c</i>	<i>d</i>	<i>d</i>	<i>b</i> ₂₇
Phenyl acetate	1766	<i>b</i> ₂₀	<i>b</i> ₂₀	<i>b</i> ₂₀	<i>b</i> ₅₀
Phenyl propionate	1760	<i>b</i> ₅₀
Phenyl benzoate	1740	<i>c</i>	<i>b</i> ₃₆
Phenyl cinnamate	1742	<i>a</i> ₁₈	<i>c</i>	<i>c</i>	..
Benzyl acetate	1745	<i>d</i>	<i>b</i> ₃₀
Coumarin	1742	<i>a</i> ₂₈	<i>a</i> ₂₂	<i>a</i> ₂₂	<i>a</i> ₃₂

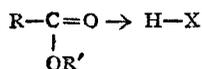
With a view to make sure that the changes observed in the C = O frequencies are not due to the effect of mere dilution, mixtures of some of the esters with the solvents benzene and carbon tetrachloride which act only as diluents were studied and Table V gives the results. The C = O frequencies are unaffected in these solvents.

TABLE V

Name of the substance	C=O frequency in pure state	C=O frequency in CCl ₄ solution	C=O frequency in benzene solution
Ethyl acetate	1739	1740	1740
Ethyl benzoate	1720	1718	1721
Ethyl cinnamate	1712	1712	1712
Phenyl acetate	1766	1763	1760
Phenyl cinnamate	1742	1740

Discussion of the Results

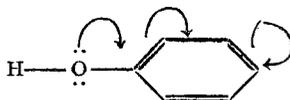
From the results presented in Table IV it is clear that in a large number of cases the Raman line attributable to the C = O group has been affected. The influence of the mixture is felt in one of three ways, *viz.*, (1) a shift of the C = O line, (2) an appearance of a new line and (3) a diffuseness of the same, all taking place towards shorter wavelengths. These changes can be taken as evidences for the formation of hydrogen bonds as represented below:—



It is reasonable to assume that the extent of the lowering of the C=O frequency gives an indication of the weakening of the C=O link due to hydrogen bond formation and consequently it affords a measure of the strength of the hydrogen bond involved. From the large number of cases examined it is clear that these bonds vary very widely in strength depending upon the components of the mixtures.

Taking the series of mixtures with phenol it is evident that hydrogen bonds are formed very markedly. The strongest bonds are noticed with esters having the highest C=O frequencies. It is consequently definite that the higher the anionoid power of the C=O, *i.e.*, the greater its capacity to act as donor, the stronger is the hydrogen bond formed. Methyl and ethyl alcohols behave very similar to one another. Though as a rule the hydrogen bonds formed with these solvents are weaker than in the case of phenol, similar gradation in the strengths of the bonds with the change in the C=O frequencies are noticeable. In the case of chloroform the number of examples of hydrogen bond formation are fewer and the bonds are weaker. It is only with esters of very high C=O frequencies that any effect is noticed.

These differences in the capacities of the different solvents to form hydrogen bonds is obviously due to the differences in the cationoid power of the hydrogen atoms involved. Phenol is, of course, the best and this is to be attributed to the presence of a phenyl ring producing a positive field by withdrawing electrons as represented below :



This explains also why it behaves as a weak acid. Alcohols are comparatively weaker due to the lack of such an electron sink. However, owing to the capacity of the oxygen atom to take a negative charge the hydrogen atom attached to it is sufficiently cationoid to form hydrogen bonds. The weakness of chloroform is to be attributed to the linking of hydrogen with carbon, an atom which shows very little tendency to take a charge. In spite of the existence of three chlorine atoms which produce positive inductive effect, the cationoid power of the hydrogen is small compared with some of the hydroxylic compounds. This agrees with the general behaviour of carbon compounds wherein even the reactive methylene groups exhibit very little tendency to produce hydrogen ions. Thus the general expectation that the strengths of hydrogen bonds depend upon (1) the anionoid power of the donor and (2) the cationoid power of the acceptor is amply substantiated.

Further cases of hydrogen bond formation leading to a full discussion of the results will be described in the subsequent communications.

Summary

A brief survey of the existing literature on hydrogen bonds is made. The advantages of employing the Raman effect for investigations in this field are discussed. The results not only supplement those obtained from infra-red studies but they become more definite, particularly when such groups as the C=O, which yield sharp Raman lines, are employed.

Hydrogen bond formation between various esters as donor molecules and phenol, alcohols and chloroform as acceptor molecules has been studied and the results are presented in this paper. The changes in the C=O frequencies are classified. It is shown that there are large variations in the strengths of hydrogen bonds. The generalization that the strengths of hydrogen bonds depend on the anionoid power of the donor and the cationoid power of the acceptor atoms is made as a logical consequence of the mechanism of hydrogen bonds and is supported by the experimental results that are recorded.

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