

RAMAN EFFECT AND HYDROGEN BONDS

Part II. Mixtures of Aldehydes and Ketones with Acceptor Solvents

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IN Part I¹ of this series a study of the mixtures of esters with various acceptor solvents was made and the results discussed. In continuation of the work a few typical ketones and aldehydes have now been employed. The Raman spectra of these substances and their mixtures with phenol, methyl and ethyl alcohols and chloroform have been investigated.

The following is the record of the Raman spectra of the aldehydes and ketones as obtained by us and used as standards for comparison.

(1) *Acetone*.—Purified by slow distillation at 56–58°.

386 (0) 480 (0) 535 (1) 790 (7) 1060 (1) 1225 (1) 1352 (0) 1420 (2)
1440 (4) 1710 (5 *b*) 2838 (0) 2922 (10) 2960 (4) 3005 (2).

(2) *Methyl ethyl ketone*.—Purified by slow distillation at 80°.

260 (0) 410 (2) 594 (2) 760 (6) 954 (1) 1000 (1) 1090 (2) 1160 (0)
1414 (2) 1712 (3 *b*) 2917 (1) 2980 (6 *b*).

Whitelaw² has reported 1734 cm.⁻¹ as the C=O frequency of this substance. Ganesan and Venkateswaran³ have given 1729 cm.⁻¹ whereas Kohlrausch⁴ and co-workers have recorded 1712 cm.⁻¹ Our value of the C=O frequency agrees with that of Kohlrausch and this appears to be quite reasonable because it is very close to the C=O frequency of acetone as may be expected.

Acetophenone.—Purified by distillation under reduced pressure.

165 (7 *b*) 365 (2) 470 (0) 590 (1) 619 (3) 725 (5) 764 (0) 946 (1)
1000 (10) 1024 (5) 1076 (4) 1160 (2) 1189 (0) 1264 (6) 1420 (1) 1450 (1)
1596 (10) 1678 (10 *b*) 2923 (2 *b*) 2970 (1) 3066 (8 *b*).

Benzaldehyde.—Purified by distillation under reduced pressure in an atmosphere of nitrogen.

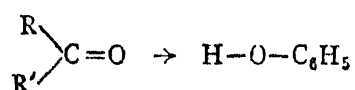
140 (10 *b*) 290 (4 *b*) 440 (6) 610 (6) 650 (2) 825 (4) 1002 (10)
1025 (2) 1164 (10) 1200 (8) 1290 (1) 1456 (1) 1487 (1) 1591 (10) 1698 (10)
3050 (4).

Cinnamic aldehyde.—Distilled under reduced pressure in an atmosphere of nitrogen.

170 (1) 317 (3) 400 (0) 490 (2) 576 (2) 602 (6) 846 (4) 972 (3)
 995 (8) 1028 (1) 1068 (2) 1122 (8) 1150 (1) 1180 (7) 1193 (5) 1242 (8) 1300 (2)
 1330 (6) 1388 (8) 1450 (2) 1490 (5) 1592 (10) 1624 (10) 1670 (10).

Mixtures with Phenol

Just as in the case of the esters, mixtures of aldehydes and ketones with phenol give prominent effects. Besides the original C=O lines with considerably diminished intensity new lines with smaller frequencies are obtained. The shifts are in general smaller than in the case of the esters. The new lines are attributable to the formation of hydrogen bonds as below :—



where R and R' are alkyl or aryl groups or hydrogen atoms.

The C=O frequencies in the carbonyl compounds and in the mixtures are embodied in Table I.

TABLE I

Name of the Carbonyl Compound	C=O frequency of the pure substance	C=O frequency of the phenol mixture	Difference
Acetone	1710	1695, 1710	15
Methyl ethyl ketone	1712	1690, 1712	22
Acetophenone	1678	1660, 1678	18
Benzaldehyde	1698	1670, 1698	28
Cinnamic aldehyde	1672	*diffuse	

*The diffuseness in the case of cinnamic aldehyde mixture is towards shorter wavelengths and it definitely indicates that there is a tendency to form molecular associates.

Mixtures with Other Solvents

In regard to the mixtures with other solvents, methyl and ethyl alcohols and chloroform, no noticeable change existed in their spectra as the result of admixture. This is clearly brought out in Table II. There is thus no

TABLE II

Name of the Carbonyl Compound	C=O frequency of the pure substance	C=O frequencies of the mixture		
		With methyl alcohol	With ethyl alcohol	With chloroform
Acetone	1710	1710	1710	1710
Methyl ethyl ketone	1712	1712	1712	1712
Acetophenone	1678	1678	1680	1680
Benzaldehyde	1698	1696
Cinnamic aldehyde	1670	1670	1670	1670

evidence from the Raman spectra for the formation of hydrogen bonds in these cases.

In regard to the acetone-alcohol mixture it may be recalled here that from a study of the infra-red spectra Goody⁵ reported a shift of the C=O frequency of acetone as a result of admixture with alcohol. However, this observation is not very reliable, as Badger and Bauer⁶ have pointed out, because comparison was effected between the observed spectrum of the mixture and that calculated using Beer's law. Adopting the correct procedure, that is by comparison of the spectrum of the mixture with that obtained when the components were placed separately in two absorption cells in series in the absorption path, no difference was noticed by the latter workers. Our observations recorded in the above table support this contention and indicate that the C=O group is not affected.

Discussion

The results reported in this communication offer further support to the conclusions arrived at in Part I and the explanations that were offered. The large variations in the strengths of hydrogen bonds are again noticed in the phenol mixtures obviously depending upon the anionoid power of the donor atoms.

In regard to the other mixtures it is remarkable that no change in the C=O frequencies could be noted. Many examples of this type were reported even in Part I. In these cases it may be taken that the study of the phenomenon through the C=O frequencies indicates no hydrogen bond formation. However, as already stated by us, infra-red data relating to changes in the acceptor part show that hydrogen bond formation is more or less universal in mixtures having donor and acceptor atoms—the types that have been used by us. Thus it becomes necessary to visualise two types of molecular aggregates in one of which the donor group is definitely affected whereas in the other there is no effect on this group. In this connection the proposal of Bernal⁷ to classify hydrogen bonds under two types, namely the hydrogen and the hydroxyl bonds may be recalled. The distinction between them lay in a marked difference in the strengths. In the first category called hydrogen bonds the O—H····O distance was found to be 2.50–2.65 Å.U. corresponding to an energy of the bond of about 8000 cal./mole. The hydrogen atom was considered to be attached with almost equal firmness to the two oxygen atoms which it joins. This satisfies all the requirements of true hydrogen bonds exhibiting resonance as suggested by Sidgwick.⁸ Consequently both the centres, anionoid as well as cationoid, should be affected. In the second category called hydroxyl bonds the O—H··O distance was

found to be 2.7–2.9 Å.U. and the energy involved about 5000 cal./mole. In this bond the hydrogen atom was still regarded as belonging to its parent oxygen and hence it may be expected that the effect on the donor group will be small.

Though the above suggestions of Bernal could be satisfactorily applied for particular cases, owing to practical difficulties in effecting the distinction this classification could not be employed for the large number of cases of hydrogen bonds that have been investigated (mainly by infra-red studies). The criterion adopted by Bernal as feasible for ordinary work utilises the disappearance of the OH band for indicating the existence of hydrogen bonds and its shift towards longer wave-lengths for the hydroxyl bonds. But this has not been found to be satisfactory since later work⁹ employing improved methods has revealed the existence of the OH band even in well-established cases of hydrogen bonds in which the band was originally missed. Hence this criterion cannot be employed. Consequently the distinction between the two types of hydrogen bonds has not been widely adopted by workers in this field and both types are referred to only as hydrogen bonds in literature.

The results obtained in the course of the present work indicate the need and also a method for the recognition of two types of hydrogen bonds, (1) the stronger bonds that affect both the anionoid and cationoid centres (*i.e.*, C=O and OH groups) as obtained from Raman and infra-red spectra and (2) the weaker type whose effect is only exhibited in the O–H groups. However, since they are all hydrogen bonds the nomenclature of Bernal does not seem to be quite suitable and hence the following proposal is made for naming them:

- (1) True hydrogen bonds;
- (2) Hydrogen bonds.

Though there exists large variation in the bond strengths in each group (*vide* Venkateswaran,¹⁰ Murty and Seshadri¹) the distinction between these two main classes is marked.

With a view to sum up the results obtained with mixtures forming heteromolecular hydrogen bonds Table III is presented here. The notation employed is as follows:—

- (a) shift of the C=O frequency. Shifts in cm.^{-1} are given as a_{20} etc.;
- (b) the appearance of a new line with a shorter frequency. The frequency differences are given as b_{20} etc.;
- (c) diffuseness of the frequency towards shorter wave-lengths (< 15 wave numbers);

(d) no change in the C=O frequency.

TABLE III

Name of the Carbonyl Compound	C=O frequency of the pure substance	Effect of admixture			
		With phenol	With methyl alcohol	With ethyl alcohol	With, chloroform
1. Ethyl acetate	1739	b_{39}	c	c	d
2. Ethyl benzoate	1720	b_{25}	d	d	d
3. Ethyl cinnamate	1712	b_{27}	d	d	c
4. Phenyl acetate	1766	b_{50}	b_{20}	b_{20}	b_{20}
5. Phenyl propionate	1760	b_{50}
6. Phenyl benzoate	1740	b_{36}	c
7. Benzylacetate	1745	b_{30}	d
8. Coumarin	1742	a_{32}	a_{15}	a_{22}	a_{22}
9. Acetone	1710	b_{32}	d	d	d
10. Methyl ethyl ketone	1712	b_{22}	d
11. Acetophenone	1678	b_{18}	d	d	d
12. Benzaldehyde	1745	b_{28}	d
13. Cinnamic aldehyde	1672	..	d	d	d

From the above table the following points regarding the influence of constitutive factors on the strengths of hydrogen bonds may be noted:—

(a) Esters in general form stronger hydrogen bonds than ketones.

(b) Phenyl esters as a rule produce stronger bonds than the corresponding alkyl esters.

(c) Esters of aliphatic acids give rise to stronger hydrogen bonds than the corresponding esters of aromatic acids.

(d) Benzyl esters are similar to the corresponding alkyl esters in this respect.

(e) Aliphatic ketones form stronger bonds than aromatic ketones.

(f) The conjugation of a C=C with the C=O reduces the hydrogen bond forming capacity as in cinnamates and cinnamic aldehyde.

(g) Coumarin forms strong hydrogen bonds and resembles the phenyl esters in this respect. Further, the original C=O frequency completely disappears thus indicating that the association is almost complete.

The abovementioned influences of the constitutive factors on the hydrogen bonds could be readily understood from their effect on the C=O frequency of the compounds concerned. The C=O frequency of esters is higher than that of ketones indicating, thereby, that their C=O bond is stronger and that the group is more powerful as an anionoid centre. The

effect of the phenyl group varies with its location. When it is attached to the 'C' of the C=O through an oxygen atom, as found in phenyl esters, it enhances the C=O frequency and enables it to form stronger hydrogen bonds. If the phenyl group, however, is attached directly to the 'C' of the C=O, as in the case of esters of aromatic acids and in aromatic ketones, the C=O frequencies are lowered and the hydrogen bonds that are formed become weaker. When the phenyl group is separated from the C=O by means of a CH₂ group, as found in the benzyl esters the influence of this group is lost and hence the benzyl esters behave like the alkyl esters. Greater details regarding the influence of constitutive factors on the C=O group have been given in our previous publications.¹¹

Summary

The Raman spectra of a few typical aldehydes and ketones and their mixtures with acceptor solvents such as phenol, methyl and ethyl alcohols and chloroform are recorded and the results are discussed. They support the general conclusion arrived at in Part I that large variations in hydrogen bond strengths exist and that they depend upon two factors (1) the anionoid power of the donor atom and (2) the cationoid power of the acceptor atom. The question of distinguishing between two types of hydrogen bonds, the hydrogen and hydroxyl bonds, as suggested by Bernal is discussed in the light of our results. It is shown that there is justification for division into two categories and a proposal is made to effect the classification as below:

- (1) True Hydrogen Bonds. (2) Hydrogen Bonds.

In Class (1) both the cationoid (C=O) and anionoid (OH) centres are affected whereas in class (2) only the cationoid group indicates change.

The influences of constitutive factors on the capacity of the carbonyl compounds to form hydrogen bonds are explained as due to their effect on the strength of the C=O group. Similar explanation has already been given in Part I regarding the behaviour of the solvents containing cationoid atom (H atom) in hydrogen bond formation.

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