RAMAN EFFECT IN MIXTURES OF ACETONE WITH ALCOHOLS

Hydrogen Bond Formation

By P. G. PURANIK

(*From the Physical Laboratories, Osmania University, Hyderabad*)

1. INTRODUCTION

RAMAN Effect and infra-red data have been successfully used in studying and explaining the intermolecular and intramolecular association caused by different processes. The formation of the hydrogen bond has received particular attention. Errera and Mollet (1936), Fox and Martin (1937), Williams, Hofstadter and Herman (1939) have studied the effect of polymerization in ethyl alcohol and phenol on the vibrations of the O—H linkage. Murthy and Sheshadri (1941) have recorded the Raman shifts in mixtures of esters and phenol, esters and alcohol, with a view to study the behaviour of carbonyl link. The bond formation in such mixtures is caused by the C = O group in the donor molecules and the O—H group in the acceptor molecules coming together. Consequently, the electron distribution gets readjusted and the carbonyl frequency in the donor gets reduced.

In the mixtures of acetone and phenol, the C = O frequency shifts from $1710 \, cm.^{-1}$ to $1695 \, cm.^{-1}$ Gordy (1938), from his study of infra-red absorption, has reported this shift of C = O absorption band. Koteswaram (1940) has studied the variation of the Raman Frequency due to the C = O linkage of acetone in aqueous solutions, and has reported a gradual decrease of the same with the reduction of acetone concentration.

Earlier workers had their attention generally confined to the C = O frequency, because hydrogen bond formation directly affects that linkage and weakens it, resulting in the decrease of the corresponding frequency. Koteswaram, however, has recorded a variation of the C—C frequency of acetone in aqueous solutions, and has mentioned that the admixture of acetone with methyl alcohol also indicates a decrease in the carbonyl frequency. But other investigators do not seem to have paid any attention to the variation in the C—C frequency, probably because the hydrogen bond formation effects this linkage only in an indirect manner. Even Koteswaram did not

499

proceed with higher alcohols and has not explained the implications of the increase in the C—C frequency.

The author, in a preliminary investigation, observed that both the C—C and C—H linkages in acetone are affected by the mixing of water and higher alcohols to a marked degree, in addition to the already well-known C = O linkage. This effect seems to be systematic, and not sporadic. It should, therefore, be regarded as consequential to the diminution of C = O frequency in mixtures. Thus, hydrogen bond formation can be studied with the help of a subsidiary effect, like that of the variation of C—C frequency, in addition to the direct effect on the carbonyl linkage. The C—C line has the added advantage of being twice as intense as the C = O line, particularly in acetone. It also occurs with visible excitation, in a region which is more convenient to study than the C = O frequency. Since the earlier work was done, more powerful techniques of getting intense Raman spectra have been developed, and the Raman lines can now be recorded within a few minutes. This enables one to study the finer features of the effect without taking recourse to prolonged exposures, and hence it is proposed by the author to examine some of these subsidiary effects, in their relation to hydrogen bond formation.

2. EXPERIMENTAL

Acetone, and all the alcohols used have been repeatedly distilled at their respective boiling points. Special care has been taken to render the alcohols free from water. Hilger Raman Source Unit, recently put on the market, has been used for illumination. There are four mercury vapour lamps (Mazda) in this Unit, arranged around a 22 cm. long Raman tube which can take in 7 c.c. of liquid. The lamps are arranged in series carrying a current of 10 amps. A Hilger E. 182 Littrow 2 metre spectrograph has been used to record the Raman spectra. A slit of 0·08 mm. width has been employed and comparison spectra obtained with the help of a Hartmann diaphragm. The plates are measured by direct comparison with a standard iron arc spectrum on a Hilger Comparator.

Moderately intense and sharp lines of 788 cm.$^{-1}$ (C—C) and 2925 cm.$^{-1}$ (C—H) for pure acetone are usually recorded in 30 minutes, and with the decrease of acetone content of the mixture, proportionately greater time is allowed for exposures, so that the intensity of the Raman lines in mixtures is almost the same as that of pure acetone. On account of such quick exposures, the broadening of the spectral lines due to prolonged photography and temperature variation has been eliminated.

3. RESULTS

Water and five alcohols—methyl, ethyl, *n*-propyl, *n*-butyl and *n*-amyl—have been chosen for studying the effect of their admixture with acetone. The results obtained by the author are given below. The C—C frequency and the C—H frequency of pure acetone, as obtained by the author, are 788 cm.$^{-1}$ and 2925 cm.$^{-1}$ respectively and these are in agreement with the average values of Kohlrausch.

TABLE I

Mixtures of Acetone with Water and Alcohols

% age by volume of acetone	C—C Frequency cm.$^{-1}$			C—H Frequency cm.$^{-1}$			C = O Frequency cm.$^{-1}$		
	80%	50%	20%	80%	50%	20%	80%	50%	20%
1. Water H·OH	795	799	801	2929	2935	2933	1704	1702	1696
2. Methyl alchhol CH$_3$·OH	794	795	799	2929	2934	2932	..	..	..
3. Ethyl alcohol C$_2$H$_5$·OH	788	788	788	2925	2925	2925	1710	1710	1710
4. *n*-Propyl alcohol C$_3$H$_7$·OH	788	792	794	2925	(2930)	(2930)	1710	1710	1706
5. *n*-Butyl alcohol C$_4$H$_9$·OH	788	794	789	2925	(2926)	(2935)	1710	1710	1707

Note.—In the case of higher alcohols (4 and 5), there are Raman lines in the vicinity of C—H line of acetone. Such frequencies of acetone in mixtures, falling in the vicinity of the alcohol lines, are given in brackets. As the values may not be very reliable on account of possible overlapping, no detailed comments are made on these frequencies.

From the results detailed in Table I it is seen that

(i) The admixture of ethyl alcohol with acetone has no effect on any one of the acetone frequencies. This effect is being recorded for the first time in respect of C—C and C—H frequencies, but had been noticed in the case of C = O frequency, by earlier workers. Since ethyl alcohol is strongly polymerized by inter-molecular association between two molecules of the alcohol, presumably there are no single molecules left for permitting any bond formation with the acetone molecules.

(ii) In the mixtures of methyl alcohol and water with acetone, the 788 cm.$^{-1}$ line and 2925 cm.$^{-1}$ line shift towards greater frequencies, with the lowering of the acetone concentration of the mixtures.

(iii) Higher alcohols like n-propyl alcohol and n-butyl alcohol, when mixed with acetone affect no shift in the C—C frequency of acetone, when the acetone content is very high. With the decrease in acetone concentration the C—C line shifts towards greater frequencies.

(iv) In the case of mixtures of n-amyl alcohol, the 788 line does not show any shift at higher concentrations of acetone. With the decrease in the acetone concentration the intensity of the acetone line becomes extremely weak.

(v) Spectrum of the scattered light in the case of mixtures exhibits a continuous background although the scattered beam in each of the pure substances separately does not give any continuous spectrum.

(vi) The phenomenon of concentration scattering, by which a mixture shows a disproportionate increase in the Rayleigh scattering but not in Raman scattering, is also shown very clearly in all the experiments with the mixtures. A quantitative investigation of this aspect is proposed to be made later.

4. DISCUSSION OF THE RESULTS

The author has observed, that in the mixtures studied, wherever there is a diminution of C = O frequency, there is always an increase in the C—C frequency. This means that the weakening of the carbonyl link due to the hydrogen bond formation, results in a strengthening of the C—C linkage, as is evidenced by the enhanced C—C frequency.

Exactly the same phenomenon is seen to occur when the carbonyl frequency is lowered similarly, though by a different process such as substitution of a benzene ring and such other groups in the ketone.

The Raman frequencies of C—C and C = O lines of a few substituted ketones studied by earlier workers are given in Table II.

A good number of substituted ketones other than those listed in Table II have been studied by earlier workers, but with only the C = O linkage in view, and not the C—C link. They will have to be re-examined from this point of view. The data given show that the diminution of the C = O frequency due to the substitution of certain radicals, is attended by an increase in the C—C frequency. The phenomenon now observed by the author in mixtures of acetone, with water and alcohols, with the exception of ethyl alcohol, is similar to such an effect. Only the shifts in the Raman frequencies of the C—C line are comparatively smaller. The larger shifts

TABLE II

Raman Frequencies of Acetone and Substituted Ketones

Name of the Ketone	Formula	Frequency	Frequency	Investigator
1. Acetone ..	$H_3C-C-CH_3$ $\diagup O$	788	1706	Kohlrausch (1934)
2. Methyl benzyl ketone	$H_3C-C-CH_2C_6H_5$ $\diagup O$	816	1697	Kohlrausch and Pongratz (1934)
3. 3. Octyn–2–one ..	$H_3C-C-C\equiv C-C_4H_9$ $\diagup O$	809	1675	Murray and Cleaveland (1944)
4. 4. Nonyn–3–one ..	$H_5C_2-C-C\equiv C-C_4H_9$ $\diagup O$	804	1675	do

in the substituted ketones can be attributed to a greater change in the magnitudes of valence forces. In the case of mixtures, the hydrogen bond formation being the cause, the effects are not so prominent.

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5. SUMMARY

The diminution of the C = O frequency in acetone due to hydrogen bond formation, when it is mixed with water or an alcohol, wherever it exists, is always accompanied by a corresponding increase of the C—C frequency. These phenomena appear to be related to each other because both of them are again noticed in substituted ketones, when the substitution is such that it lowers the frequency of the C = O line. It is suggested that these secondary changes may also be conveniently used for studying effects like hydrogen bond formation by Raman spectrum methods.

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