RAMAN EFFECT IN MIXTURES OF BENZALDEHYDE WITH ALCOHOLS AND PHENOL

Hydrogen Bond Formation

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1. INTRODUCTION

In an earlier communication by the author (1953), Raman spectra in mixtures of acetone with alcohols have been studied. It was found that the diminution of C = O frequency in acetone due either to hydrogen bond formation or to certain other changes in chemical constitution is always accompanied by a corresponding increase in the C—O frequency, suggesting that the vibrations of the whole group C—O—C are to be regarded as affected thereby

and not of the C = O linkage alone. Such investigations have been extended by the author to other Ketones as well and the results obtained furnish further evidence in support of the new ideas that have been put forward. Details will be published in due course but in the Plate accompanying this paper, a picture of benzophenone with arrow marks on the lines that are shifted, is reproduced. In continuation of that work it is programmed to study a few aldehydes as well and the results obtained in mixtures of benzaldehyde with alcohols and phenol are now given with a view to bring out similar effects due to hydrogen bond formation, this time on the group C — C — H, one of the carbons being in the benzene ring itself.

Murty and Seshadri (1942) studied the Raman spectrum of the mixture of benzaldehyde and phenol and reported a diminution of C = O frequency from 1698 cm.−1 to 1670 cm.−1. Their attention was, however, confined only to the C = O link because of its direct bearing on the hydrogen bond formation. Besides, the data published by them do not contain information regarding the concentrations of the mixtures studied.

2. EXPERIMENTAL

Benzaldehyde has been purified by repeated distillation at constant boiling point of 179° C. Phenol has been purified by the usual process of
distilling, allowing it to solidify by cooling the distilled matter and absorbing the moisture. By a repetition of this process, pure colourless phenol crystals are obtained. Fuss glass spectrograph and a Hilger’s Raman Source Unit are used to record the spectra. Intense and complete Raman spectra of benzaldehyde could be obtained in 20 minutes. With mixtures containing the scattering liquid only as a fraction, proportionate time is allowed for the exposures. In the case of benzophenone, an exposure of a few seconds reveals practically all the prominent lines. On account of such quick exposures, the aldehyde or the phenol or benzophenone do not get coloured which would have been the case if prolonged exposures had to be used.

3. RESULTS WITH PURE LIQUIDS

The Raman frequencies of benzaldehyde and phenol, as obtained by the author are given below:

(1) Benzaldehyde

135 (6 b), 250 (2), 436 (6 b), 611 (6), 644 (2), 824 (8), 993 (10), 1017 (3), 1159 (5 b), 1197 (9), 1292 (8 b), 1378 (0 b), 1448 (0 s), 1493 (1 d), 1591 (10), 1641 (3 d), 1694 (10), 3060 (3).

(2) Phenol

240 (2), 504 (1), 532 (2), 620 (4), 750 (2), 812 (2), 826 (2), 1000 (10), 1028 (6), 1064 (0), 1160 (4), 1170 (3), 1258 (2), 1592 (8), 1601 (2), 3014 (1), 3046 (5), 3060 (10).

In all the spectrograms of benzaldehyde, the relative intensities of the lines 1159 cm$^{-1}$ and 1197 cm$^{-1}$ do not conform to the results reported by earlier workers. Kohlrausch and Pongratz (1934) record them as having equal intensities, and Murty and Seshadri (1942) estimate them as 10 and 8. A broad band at 1641 ± 10 cm$^{-1}$ is now recorded for the first time and it appears to be an overtone of 824 cm$^{-1}$

4. IDENTIFICATION OF GROUP FREQUENCIES

In Table I are given the important frequencies of benzene and some of its derivatives.

We need not comment on the assignment of the well known frequencies of the benzene ring which are easily recognisable in the above table. The first point of interest is the presence of 1209 in toluene, 1197 in benzaldehyde and 1190 in benzonitrile. This may, therefore, be regarded as arising from the C—C linkage between the ring carbon on the one hand and the aliphatic
Raman Effect in Mixtures of Benzaldehyde

**TABLE I**

<table>
<thead>
<tr>
<th>Important Raman Frequencies of Benzene and Some of Its Derivatives</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Benzene $\text{C}_6\text{H}_6$</td>
</tr>
<tr>
<td>2. Toluene $\text{C}<em>8\text{H}</em>{10}\text{CH}_3$</td>
</tr>
<tr>
<td>3. Benzaldehyde $\text{C}_6\text{H}_5\text{CHO}$</td>
</tr>
<tr>
<td>4. Benzonitrile $\text{C}_6\text{H}_5\text{CN}$</td>
</tr>
</tbody>
</table>

... carbon on the other. Similarly 1430 in toluene and 1448 and 1493 in benzaldehyde suggest that they are due to transverse oscillations of the aliphatic C—H linkage. Their absence in benzene and benzonitrile is naturally to be expected. A frequency due to the longitudinal oscillation of the aliphatic C—H, like the 2920 of toluene, should have appeared in benzaldehyde but has not appeared.

Therefore, the frequencies of benzaldehyde which we may associate with the group C—C—H are 1197, 1448, 1694 with the probability that a frequency in the neighbourhood of 2940 has not been observed.

5. RESULTS WITH MIXTURES

Methyl, ethyl and $n$-propyl alcohols are chosen for studying the effect of their admixture with benzaldehyde.

In the case of methyl alcohol mixture, from 100% benzaldehyde, the concentration of the aldehyde is reduced to 10% by volume, by gradual steps, care being taken to use freshly distilled aldehyde every time. In the 50:50 mixture, there is a slight shift of 1694 cm$^{-1}$ line towards shorter frequency. When the concentration of the aldehyde is reduced to 20% by volume, the phenomenon of critical opalescence is observed. The intensity of the Rayleigh lines becomes so great that there is a general blackening of the spectrum.

The admixture of ethyl alcohol with benzaldehyde does not affect any of the frequencies of the aldehyde, but strong opalescence sets in when the concentration of the aldehyde is reduced to 20% by volume.
The mixing of propyl alcohol does not produce any effect whatsoever.

Raman frequencies of the mixtures of benzaldehyde and phenol which show displacements with varying concentrations are given in Tables II (a) and II (b). In Table II (a) the variations of the low frequencies of benzaldehyde are recorded. With the increase of the phenol content of the mixture, the Raman line at 135 cm.\(^{-1}\) shifts to a marked extent and reaches 151 cm.\(^{-1}\) at high concentrations. In Table II (b), variations in respect of the two higher frequencies are given.

### Table II (a)

*Low Frequencies of Benzaldehyde in Mixtures with Phenol*

<table>
<thead>
<tr>
<th></th>
<th>Pure</th>
<th>0.87 : 1</th>
<th>1.81 : 1</th>
<th>2.92 : 1</th>
<th>3.98 : 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzaldehyde</td>
<td>mol.</td>
<td>mol.</td>
<td>mol.</td>
<td>mol.</td>
<td>mol.</td>
</tr>
<tr>
<td>Phenol</td>
<td>mol.</td>
<td>mol.</td>
<td>mol.</td>
<td>mol.</td>
<td>mol.</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>135</td>
<td>143</td>
<td>139</td>
<td>145</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>233</td>
<td>238</td>
<td>243</td>
<td>.</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>436</td>
<td>442</td>
<td>437</td>
<td>447</td>
</tr>
</tbody>
</table>

### Table II (b)

*Frequencies of the C -- C -- H Group*

<table>
<thead>
<tr>
<th>Link</th>
<th>Pure</th>
<th>0.87 : 1</th>
<th>1.81 : 1</th>
<th>2.92 : 1</th>
<th>3.98 : 1</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Benzaldehyde</td>
<td>mol.</td>
<td>mol.</td>
<td>mol.</td>
<td>mol.</td>
</tr>
<tr>
<td></td>
<td>Phenol</td>
<td>1197</td>
<td>1201</td>
<td>1204</td>
<td>1694</td>
</tr>
</tbody>
</table>

The shifts in case of all the above frequencies marked with arrows in the figure, are easily noticeable and quite marked.

6. **Discussion of the Results**

Table II (b) shows the outstanding feature of this investigation that while the C = O frequency decreases, the C -- C frequency increases. This effect is similar to the one noticed by the author in acetone mixtures and
Raman Effect in Mixtures of Benzaldehyde

suggests that the hydrogen bond formation has its effect on the aldehydic group as a whole and not merely on the C = O linkage.

As in acetone, the same phenomenon is seen to occur again when the carbonyl frequency is lowered, by an altogether different process, such as the substitution of one of the hydrogens in the ring by a suitable group. The Raman frequencies of C—C and C = O linkages in a few substituted aldehydes, studied by earlier workers, and illustrating the above point are given below in Table III.

<table>
<thead>
<tr>
<th>Name of the aldehyde</th>
<th>Formula</th>
<th>C — C Frequency cm.(^{-1})</th>
<th>C = O Frequency cm.(^{-1})</th>
<th>Investigator</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Benzaldehyde</td>
<td>C(_6)H(_6)CHO</td>
<td>1201</td>
<td>1696</td>
<td>Kohlrausch and Pon-gratz (1934)</td>
</tr>
<tr>
<td>2. O. Chloro-benzaldehyde</td>
<td>Cl-C(_6)H(_4)-CHO</td>
<td>1262</td>
<td>1682</td>
<td>Bonino and Ansidei (1934)</td>
</tr>
<tr>
<td>3. Salicylaldehyde</td>
<td>OH-C(_6)H(_4)-CHO</td>
<td>1230</td>
<td>1663</td>
<td>S. Venkateswaran and S. Bhagavantam (1930)</td>
</tr>
</tbody>
</table>

The data given in Table III show that the diminution of the C = O frequency is accompanied by an enhancement of the C — C frequency.

In the case of acetone and alcohol mixtures, an increase in the C—H frequency has been noticed. In the benzaldehyde spectrum the two lines due to the C—H linkages in the aldehyde group—1448 cm.\(^{-1}\) and 1493 cm.\(^{-1}\)—are very weak and as such, variations in their frequencies could not be measured.

The author expresses his sincere thanks to Professor S. Bhagavantam for suggesting the problem and giving necessary guidance.

7. SUMMARY

The 1197 cm.\(^{-1}\) line in benzaldehyde is attributed to the C—C linkage between the aldehyde and the phenyl groups. The admixture of methyl and ethyl alcohols does not affect the C—C and C = O frequencies in benzaldehyde. Mixtures with phenol show the formation of hydrogen bond resulting in the weakening of the C = O link and a lowering of the relative frequency.
This is accompanied by an increase of the C—C frequency in the group C—C—H. This phenomenon is analogous to what has been observed when hydrogen bonds are formed between acetone and alcohol molecules.

REFERENCES

Raman Spectra

Fig. I. (a) Pure benzaldehyde, (b) benzaldehyde with phenol

Fig. II. (a) Benzophenone in CCl₄, (b) benzophenone with phenol