ASSIGNMENT OF THE RAMAN FREQUENCIES OF METHYL AND ETHYL BENZOATES AND ETHYL CINNAMATE

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1. INTRODUCTION

The Raman spectra of methyl and ethyl benzoates have been studied by several investigators—(1) Ghosh and Kar (1931), (2) Matsuo and Han (1933), (3) Kohlrausch and Pongratz (1933), (4) Murty and Seshadri (1939), (5) Herz et al. (1943) and (6) Hariharan (1954). The spectrum of ethyl cinnamate has been investigated by Harrand (1953) besides the earlier workers. Matsuo and Han have assigned the different frequencies observed in a series of alkyl esters of benzoic acid. Hariharan differs in his assignments of frequencies of methyl and ethyl benzoates from those of Matsuo and Han. In his studies of hydrogen bond formation in the mixtures of esters with phenol or methyl alcohol, the author has proposed to assign the various frequencies of esters. The assignments proposed by the author do not agree substantially with those of either Matsuo and Han or Hariharan.

2. EXPERIMENTAL

The experimental technique adopted has been described in the earlier communications by the author (1953).

3. RESULTS

The Raman frequencies as recorded by the author are given below.

Table I

(i) Methyl Benzoate

138 (0), 170 (0), 217 (5), 359 (6), 535 (1), 619 (6), 676 (2), 812 (1 b), 825 (7), 968 (2), 988 (2), 1004 (10), 1027 (3), 1114 (2), 1161 (2), 1181 (2), 1280 (8 b), 1323 (1 b), 1450 (2 b), 1500 (2), 1603 (10), 1724 (7), 3067 (1 b).

(ii) Ethyl Benzoate

192 (7), 331 (5), 384 (2), 617 (7), 670 (4), 785 (2), 810 (2), 850 (7), 985 (5), 1002 (10), 1026 (2), 1109 (3), 1160 (3), 1278 (9), 1314 (2), 1367 (2),
Raman Frequencies of Methyl and Ethyl Benzoates and Ethyl Cinnamate

TABLE I—(Continued)

1397 (2), 1454 (5), 1498 (2), 1603 (10), 1719 (8), 2934 (1), 2978 (1), 3066 (1).

(iii) Ethyl Cinnamate

178 (1 b), 273 (1 b), 341 (1), 408 (2), 458 (0), 580 (1), 594 (1), 622 (4), 722 (2), 740 (1), 774 (2), 843 (3), 871 (3 b), 928 (1), 991 (2), 1005 (7), 1029 (2), 1169 (3), 1184 (5), 1205 (5), 1270 (3 b), 1307 (3), 1335 (2), 1369 (2), 1395 (1), 1453 (4), 1498 (4), 1541 (3), 1577 (4), 1601 (8), 1639 (9), 1711 (5), 2829 (1), 2938 (1).

Three lines at 535, 988 and 1500 cm$^{-1}$ in methyl benzoate 985 cm$^{-1}$ in ethyl benzoate and six lines at 178, 341, 458, 740, 774 and 2829 cm$^{-1}$ in ethyl cinnamate have been recorded for the first time by the author.

4. ASSIGNMENT OF THE LINES

The shifts at 615, 1001, 1025, 1158, 1177, 1595 and 3070 cm$^{-1}$ are identified as the well-known frequencies of the phenyl group, because of the approximate constancy of the characteristic frequencies of the phenyl group shown by Murray and Cleveland (1941). Therefore the lines at 619, 1004, 1027, 1161, 1181, 1603 and 3067 cm$^{-1}$ in methyl benzoate and 617, 1002, 1026, 1160, 1172, 1603 and 3066 cm$^{-1}$ in ethyl benzoate can be identified as the frequencies arising out of the vibrations of the ring. The frequencies due to the C—H valence and deformation oscillations of the aliphatic group, 1450, 1500 cm$^{-1}$ in methyl benzoate and 2934, 2978, 1367, 1454 and 1498 cm$^{-1}$ in ethyl benzoate.

The low frequency lines at 138, 170, 217, 359 and 535 cm$^{-1}$ in methyl benzoate and 192 (7), 331 (5) and 384 in ethyl benzoate can be attributed to the intermolecular oscillations.

There appears to be some uncertainty about the assignment of the frequencies of the group C—OR. Matsuo and Han attribute the lines 1720, 1270 and 670 cm$^{-1}$ as the characteristic vibrations of the above group, but Herz et al. have assigned 1720, 1120, 966 and 828 cm$^{-1}$ to the inner vibrations of CO.OCH$_3$ group. Paranjpe and Savnur (1933) attribute the lines 1730, 1030 and 630 cm$^{-1}$ as characteristic of the same group. Hariharan assigns 1720, 1110 and 670 cm$^{-1}$ as the frequencies of the group C=O. Except
Matsuo and Han none of the earlier workers assign the intense line at 1270 cm\(^{-1}\) as one of the frequencies of the group C=O, although this line occurs in all the benzoates. Hariharan suggests this line to arise out of some deformation oscillations involving the hydrogen atoms in the attached aliphatic group.

In an earlier communication (1953) the author, in identifying the frequencies of benzaldehyde, has assigned 1197, 1448, 1493, 1694 cm\(^{-1}\) to the group C—C—H. In this assignment it is obvious that 1694 cm\(^{-1}\) is due to C=O and 1493 is due to C—H\(^{11}\) and C—H\(^{14}\). Therefore 1197 cm\(^{-1}\) can be associated with C—C linkage between the ring carbon on the one hand and the aliphatic carbon on the other. Similarly the lines at 1181 cm\(^{-1}\) in methyl benzoate and 1172 cm\(^{-1}\) in ethyl benzoate, can be assigned to C—C link formed by the ring carbon and the aliphatic carbon of the group C—OCH\(_3\).

It is difficult to assign either of the lines 619 and 676 cm\(^{-1}\) to the group C—OCH\(_3\) because these frequencies with comparable intensities are found in the spectrum of benzene.

Regarding the line at 1280 cm\(^{-1}\) in methyl benzoate and 1279 cm\(^{-1}\) in ethyl benzoate, Hariharan does not agree with the assignment made by Matsuo and Han as to their being one of the group frequencies of the group C—OR.

**Table II**

*Some Frequencies of Benzene and Substituted Compounds*

<table>
<thead>
<tr>
<th>Compound</th>
<th>1178</th>
<th>1584</th>
<th>1600</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Frequencies of Methyl and Ethyl Benzoates and Ethyl Cinnamate

TABLE II—(Continued)

<table>
<thead>
<tr>
<th>Name</th>
<th>ν (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzaldehyde</td>
<td>1159, 1197, 1448, 1493, 1591, 1694</td>
</tr>
<tr>
<td>Methoxy Benzene</td>
<td>1177, 1244, 1452, 1587, 1603</td>
</tr>
<tr>
<td>Methyl Benzoate</td>
<td>1181, 1280, 1450, 1603, 1724</td>
</tr>
</tbody>
</table>

Some of the relevant frequencies of benzene and some of the substituted compounds are given in Table II. When the aldehydic group C—H is substituted in one of the hydrogens of benzene, some new frequencies, 1197, 1448, 1591, 1694 cm⁻¹ are recorded which can reasonably be assigned to the new group that has entered the compound by way of substitution. Similarly by the substitution of the methoxy group in place of one of the hydrogens, an intense line at 1244 cm⁻¹ is recorded, which was not recorded either in benzene or benzaldehyde. This line can therefore be assigned to the vibrations of C—O bond which exists in methoxy benzene only.

Therefore 1280 cm⁻¹ in methyl benzoate and 1278 cm⁻¹ in ethyl benzoate can be ascribed to the vibrations of the C—O link in the group C—OR.

Thus the lines at 1181, 1280 and 1724 cm⁻¹ in methyl benzoate and 1172, 1278 and 1719 cm⁻¹ in ethyl benzoate can be assigned to the frequencies of the group C—OR where R is either CH₃ or C₆H₅.

Similar assignments can be made in the case of ethyl cinnamate. The
group \(-\text{C} = \text{C}\) gets linked to the phenyl group through one of the carbons.

Therefore 1205 cm\(^{-1}\) in ethyl cinnamate can be assigned to the \(\text{C} = \text{C}\) link formed by the \(\text{C}\) of the ring and \(\text{C}\) of the vinyl group and 1639 cm\(^{-1}\) can be ascribed to the vibrations of the \(\text{C} = \text{C}\). A line at 1270 cm\(^{-1}\) is due to the vibrations \(\text{C} - \text{O}\) in the aliphatic side-chain. The assignment of the other frequencies are well known.

**Summary**

The Raman spectra of methyl and ethyl benzoates, and ethyl cinnamates have been recorded in the liquid state at 42° C. Some new lines are reported. The lines at 1181, 1280 and 1724 cm\(^{-1}\) in methyl benzoate, and 1172, 1278 and 1719 cm\(^{-1}\) in ethyl benzoate are assigned to the group \(\text{C} - \text{OR}\) and 1205, 1270 and 1639 cm\(^{-1}\) are assigned to the group \(-\text{C} = \text{C}\) in ethyl cinnamate.

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**References**