INTENSITY OF RAMAN LINES IN CARBOXYLIC
ACIDS, ESTERS AND NITRILES

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A good deal of work has been done in both Raman effect and infra-red on the assignment of characteristic frequencies in carbonyl compounds and nitriles. In majority of cases the Raman and infra-red frequencies are very nearly the same although occasionally large differences are also observed. In the infra-red, some work has been done on the intensity of carbonyl absorption of carboxylic acids and also of nitrile absorption but very little work has been done in Raman effect.

In the present investigation, the intensities of the characteristic bonds of type C = O, C = H bending, C = H stretching, C = C and C = N whose frequencies lie in the region 1700, 1400, 2900, 800 and 2300 cm. respectively, have been studied.

EXPERIMENTAL

Extra pure samples of the substances distilled at constant boiling-points have been used in the present investigation. A Hilger E 612 two-prism glass spectrograph in conjunction with a Hilger Raman Source Unit was used. The spectra of various substances have been recorded under identical conditions. A set of graded intensity marks were also given on the same plate and the intensities were computed using a Moll Microphotometer. The intensity values obtained have been reduced to standard intensity values (S) by making use of the expression suggested by Bernstein and Allen.

RESULTS

<table>
<thead>
<tr>
<th>Substance</th>
<th>Nature of vibration</th>
<th>Frequency cm.</th>
<th>I/I_{1668} cm.</th>
<th>Standard intensity (S)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid</td>
<td>C = O</td>
<td>1669</td>
<td>0.063</td>
<td>0.151</td>
</tr>
<tr>
<td>Propionic acid</td>
<td>C = O</td>
<td>1669</td>
<td>0.073</td>
<td>0.233</td>
</tr>
<tr>
<td>Butyric acid</td>
<td>C = O</td>
<td>1670</td>
<td>0.107</td>
<td>0.434</td>
</tr>
</tbody>
</table>

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### Table I—(Contd.)

<table>
<thead>
<tr>
<th>Substance</th>
<th>Name of vibration</th>
<th>Frequency cm$^{-1}$</th>
<th>$I/I_{450}$ cm$^{-1}$</th>
<th>Standard intensity (S)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid</td>
<td></td>
<td>1435</td>
<td>0.124</td>
<td>0.242</td>
</tr>
<tr>
<td>Propionic acid</td>
<td>C - H bending</td>
<td>1448</td>
<td>0.207</td>
<td>0.552</td>
</tr>
<tr>
<td>Valeric acid</td>
<td></td>
<td>1430</td>
<td>0.171</td>
<td>0.690</td>
</tr>
<tr>
<td>Acetic acid</td>
<td></td>
<td>2934</td>
<td>0.211</td>
<td>1.131</td>
</tr>
<tr>
<td>Propionic acid</td>
<td>C - H$_{as}$</td>
<td>2956</td>
<td>0.354</td>
<td>2.576</td>
</tr>
<tr>
<td>Butyric acid</td>
<td></td>
<td>2944</td>
<td>0.329</td>
<td>3.009</td>
</tr>
<tr>
<td>Valeric acid</td>
<td></td>
<td>2956</td>
<td>0.484</td>
<td>5.416</td>
</tr>
<tr>
<td>Acetic acid</td>
<td></td>
<td>895</td>
<td>0.325</td>
<td>0.355</td>
</tr>
<tr>
<td>Propionic acid</td>
<td>C - C</td>
<td>842</td>
<td>0.232</td>
<td>0.316</td>
</tr>
<tr>
<td>Valeric acid</td>
<td></td>
<td>826</td>
<td>0.144</td>
<td>0.295</td>
</tr>
</tbody>
</table>

### Table II

**Carboxylic esters**

<table>
<thead>
<tr>
<th>Substance</th>
<th>Nature of vibration</th>
<th>Frequency cm$^{-1}$</th>
<th>$I/I_{450}$ cm$^{-1}$</th>
<th>Standard intensity (S)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl butyrate</td>
<td>C = O</td>
<td>1740</td>
<td>0.104</td>
<td>0.540</td>
</tr>
<tr>
<td>Ethyl butyrate</td>
<td>C = O</td>
<td>1739</td>
<td>0.171</td>
<td>1.025</td>
</tr>
<tr>
<td>Methyl acetate</td>
<td></td>
<td>1455</td>
<td>0.201</td>
<td>0.601</td>
</tr>
<tr>
<td>Amyl acetate</td>
<td>C - H bending</td>
<td>1452</td>
<td>0.270</td>
<td>1.471</td>
</tr>
<tr>
<td>Methyl butyrate</td>
<td></td>
<td>1453</td>
<td>0.230</td>
<td>0.942</td>
</tr>
<tr>
<td>Ethyl butyrate</td>
<td></td>
<td>1455</td>
<td>0.234</td>
<td>1.111</td>
</tr>
<tr>
<td>Methyl acetate</td>
<td></td>
<td>2942</td>
<td>0.163</td>
<td>1.314</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td></td>
<td>2940</td>
<td>0.183</td>
<td>1.633</td>
</tr>
<tr>
<td>Amyl acetate</td>
<td>C - H$_{as}$</td>
<td>2940</td>
<td>0.256</td>
<td>3.761</td>
</tr>
<tr>
<td>Methyl butyrate</td>
<td></td>
<td>2940</td>
<td>0.443</td>
<td>4.902</td>
</tr>
<tr>
<td>Ethyl butyrate</td>
<td></td>
<td>2941</td>
<td>0.486</td>
<td>6.242</td>
</tr>
<tr>
<td>Methyl acetate</td>
<td>C - C</td>
<td>646</td>
<td>0.161</td>
<td>0.176</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>C - C</td>
<td>633</td>
<td>0.125</td>
<td>0.151</td>
</tr>
<tr>
<td>Amyl acetate</td>
<td></td>
<td>620</td>
<td>0.072</td>
<td>0.136</td>
</tr>
</tbody>
</table>
Intensity of Raman Lines in Carboxylic Acids, Esters and Nitriles

TABLE III

Nitriles

<table>
<thead>
<tr>
<th>Substance</th>
<th>Nature of vibration</th>
<th>Frequency cm$^{-1}$</th>
<th>I/I$_{488}$ cal</th>
<th>Standard intensity (S)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aceto nitrile</td>
<td></td>
<td>2250</td>
<td>0.282</td>
<td>0.852</td>
</tr>
<tr>
<td>Propio nitrile</td>
<td></td>
<td>2245</td>
<td>0.175</td>
<td>0.750</td>
</tr>
<tr>
<td>Butyro nitrile</td>
<td>C=N</td>
<td>2244</td>
<td>0.092</td>
<td>0.511</td>
</tr>
<tr>
<td>Benzo nitrile</td>
<td></td>
<td>2224</td>
<td>2.119</td>
<td>17.440</td>
</tr>
</tbody>
</table>

DISCUSSION

From Tables I and II the following general conclusions regarding the characteristic vibrations in both carboxylic acids and esters may be arrived at:

1. The intensity of the lines due to C=O vibration is found to increase as we go from lower to higher members of the series.

2. The intensities of lines in the regions 1400 cm$^{-1}$ and 2900 cm$^{-1}$ characteristic of C-H bending and C-H$_{\text{a}}$ stretching vibrations also behave in the same way as in (1).

3. The addition of a CH$_6$ group in a homologous series has a different effect on the low frequency region characteristic of C-C vibration in the sense that the intensities show a gradual decrease from lower to higher members of the series.

From Table III it can be seen that (1) the intensity of the line due to C=N vibration is found to be decreasing from the lower to the higher members of the homologous series. This conclusion is in agreement with the observation in the infra-red. (2) The large intensity in aromatic conjugated substance of benzo nitrile compared to the aliphatic unconjugated nitriles may be explained as due to the combined effect of the general increase in intensity to be expected from aliphatic to aromatic and also from unconjugated to conjugated substances. This observation is in conformity with that made by Cross and Rolfe in infra-red absorption.
Summary

The intensities of characteristic vibrations in carboxylic acids, esters and nitriles have been studied. In both carboxylic acids and esters the intensities of Raman lines due to C = O, C − H bending and C − H stretching vibrations are found to increase from lower to higher members of the series while there is a decrease in intensity of C − C frequency. The intensity of the lines due to C = N vibration is found to be decreasing from lower to higher members of the series. The intensity in aromatic conjugated nitrile is found to be abnormally great when compared to that in unconjugated aliphatic nitriles.

Acknowledgement

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References

10. .. Ibid., 1959, 156, 561.