RAMAN SPECTRUM OF ACETONITRILE

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1. INTRODUCTION

The acetonitrile (methyl cyanide, CH₃CN) molecule belongs to the point group C₃ᵥ and as such it has eight distinct modes of vibrations ν₁, ν₂, ν₃, ν₄, ν₅, ν₆, ν₇, and ν₈, 4 of which come under the A₁ class and the remaining 4 under the E class. All these eight modes are active in Raman effect and in infra-red absorption. Although in infra-red absorption eight principal absorption maxima corresponding to ν₁ to ν₈ have been recorded (Venkateswarlu, 1951, 1952, Nakagawa and Shimanauchi, 1962 and Millegan and Jacobse, 1962), in Raman effect the line corresponding to the mode ν₇ has not been recorded so far (Evans and Bernstein, 1955). The Raman spectrum of acetonitrile (liquid) has therefore been reinvestigated using the very intense helical arc of Toronto type constructed in our Laboratory. The λ4046 radiation of the arc was suppressed by using a filter containing a saturated solution of NaNO₂. With the Hilger two-prism spectrograph exposures of the order of 36 hours were given to get an intense spectrogram.

2. RESULTS AND DISCUSSION

An enlarged photograph of the Raman spectrum of acetonitrile is reproduced in Fig. 1 (a) and the corresponding microphotometer record in Fig. 1 (b). 19 distinct Raman lines have been recorded for this substance and their frequency shifts have been entered in Table I. The lines with frequency shifts 483, 1178 and 1244 cm⁻¹ which are marked on the microphotometer record are the intense modes ν₁ and ν₂ excited by λ4046 radiation. In the second and third columns of the same table are entered the frequency shifts of the Raman lines reported by Evans and Bernstein (1955) and frequencies of infra-red absorption maxima observed by P. Venkateswarlu (1952). There is a very close correspondence between the Raman effect data of the present author and the infra-red absorption data of Venkateswarlu. This is what should be expected for the molecule belonging to C₃ᵥ point group.
## Table I

Raman spectrum of acetonitrile

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Author</th>
<th>Infra-red</th>
<th>Mode</th>
<th>Class</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Evans &amp; Bernstein</td>
<td>379</td>
<td>379</td>
<td>$\nu_6$</td>
<td>$E$ C–C ≡ N bending</td>
</tr>
<tr>
<td>1</td>
<td></td>
<td>380</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>674</td>
<td>674</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>754</td>
<td>750</td>
<td>2 $\nu_6$</td>
<td>$A_1 + E$ Octave</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>920</td>
<td>919</td>
<td>$\nu_4$</td>
<td>$A_1$ CC stretching</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>1044</td>
<td>1047</td>
<td>$\nu_7$</td>
<td>$E$ CH$_3$ rocking</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>1378</td>
<td>1371</td>
<td>$\nu_8$</td>
<td>$A_1$ CH$_3$ deformation</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>1414</td>
<td></td>
<td>$\nu_7 + \nu_8$</td>
<td>Combination</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>1449</td>
<td>1443</td>
<td>$\nu_6$</td>
<td>$E$ CH$_3$ deformation</td>
</tr>
<tr>
<td>9</td>
<td></td>
<td>1558</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td></td>
<td>2197</td>
<td></td>
<td>2 $\nu_4 + \nu_8$</td>
<td>Combination</td>
</tr>
<tr>
<td>11</td>
<td></td>
<td>2248</td>
<td>2248</td>
<td>$\nu_2$</td>
<td>$A_1$ C≡N stretching</td>
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<tr>
<td>12</td>
<td></td>
<td>2289</td>
<td>2289</td>
<td>2 $\nu_6 + \nu_4$</td>
<td>Combination</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2293</td>
<td>$\nu_6 + \nu_4$</td>
<td>Combination</td>
</tr>
<tr>
<td>13</td>
<td></td>
<td>2460</td>
<td></td>
<td>$\nu_6 + \nu_7$</td>
<td>Combination</td>
</tr>
<tr>
<td>14</td>
<td></td>
<td>2644</td>
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<td>$\nu_7 + \nu_8$</td>
<td>Combination</td>
</tr>
<tr>
<td>15</td>
<td></td>
<td>2736</td>
<td></td>
<td>2 $\nu_5$</td>
<td>$A_1$</td>
</tr>
<tr>
<td>16</td>
<td></td>
<td>2841</td>
<td></td>
<td>$\nu_5 + \nu_6$</td>
<td>Combination</td>
</tr>
<tr>
<td>17</td>
<td></td>
<td>2887</td>
<td>2882</td>
<td>2 $\nu_6$</td>
<td>$A_1$  Octave</td>
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<td>18</td>
<td></td>
<td>2942</td>
<td>2941</td>
<td>$\nu_1$</td>
<td>$A_1$ Symmetric C–H stretching</td>
</tr>
<tr>
<td>19</td>
<td></td>
<td>2999</td>
<td>3001</td>
<td>$\nu_6$</td>
<td>$E$ Asymmetric C–H stretching</td>
</tr>
</tbody>
</table>
By comparison with infra-red data and the assignments given by the earlier workers, all the eight fundamental modes have been identified (Table I). The mode $v_7$ which was missing in the Raman spectra recorded by the earlier workers can be seen very clearly in the microphotometer record at 1044 cm.$^{-1}$ [see Fig. 1 (b)]. It is comparatively a weaker line. There is also a continuous background which extends from 0 cm.$^{-1}$ up to about 1200 cm.$^{-1}$ with the intensity falling off as one proceeds away from the exciting line. Besides, there is the usual intense rotational wing accompanying the Rayleigh which extends up to 120 cm.$^{-1}$ The presence of the continuous background has made the 1044 line scarcely visible on the photograph. The intensity of the 1044 line is definitely less than the intensity of some of the octaves and combinations. It is surprising to note that all the fundamental modes except $v_7$ appear with considerable intensity in Raman effect. The modes $v_1$, $v_2$, $v_3$ and $v_4$ which come under symmetric $A_1$ class are more intense and sharper than the degenerate modes $v_5$, $v_6$, $v_7$ and $v_8$.

The Raman spectrum exhibits eleven lines belonging to the second-order spectrum. Nine of them have been explained as octaves and combinations (summations) of the fundamental modes.

3. SUMMARY

Raman spectrum of acetonitrile has been re-examined. 19 Raman lines have been recorded which include all the eight fundamental modes, three octaves and six summations. The fundamental mode $v_7$ which has not been recorded before appears very weakly in the Raman spectrum.

4. ACKNOWLEDGEMENT

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5. REFERENCES

1. Evans, J. C. and Bernstein, H. J.
3. Nakagawa, I. and Shimanauchi, T.
4. Venkateswarlu, P.

EXPLANATION OF PLATE VI

Fig. 1 (a) Raman spectrum of acetonitrile taken with $\lambda$ 4358 excitation and two-prism spectrograph.

(b) Microphotometer record of the above.
Fig. 1 (a) Raman Spectrum of Acetonitrile taken with λ 4358 Excitation and Two-Prism Spectrograph.

(b) Microphotometer Record of the above.