NORMAL COORDINATE ANALYSIS OF DICYANODIACETYLENE

By K. RAMASWAMY* and K. SRINIVASAN*

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Introduction

In earlier papers1-3 we determined the molecular constants of various conjugated linear systems using the “characteristic set of valence coordinates” introduced by Herranz and Castano.4,5 The present communication deals with the normal coordinate analysis of dicyanodiacetylene—the longest known linear molecule with four conjugated triple bonds.

Results and Discussion

The vibrational assignments given by Miller and Lemmon6 on the basis of D_{2h} symmetry were made use of in the present calculations. Since no microwave or electron diffraction data are available the structural parameters were transferred from dicyanoacetylene. These are given in Table 1.

**Table 1**

<table>
<thead>
<tr>
<th>Vibrational Frequencies (cm⁻¹) and Bond Lengths (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>σ_v̇  1 2235</td>
</tr>
<tr>
<td>2 2183</td>
</tr>
<tr>
<td>3 1287·5</td>
</tr>
<tr>
<td>4 571</td>
</tr>
</tbody>
</table>

The orthonormal set of symmetry coordinates,7 transforming according to the irreducible representations of D_{2h} point group, were constructed from the internal coordinates defined in Figure 1.

* Department of Physics, Annamalai University, Annamalainagar, South India.

The symmetry coordinates for the \( \sigma_g^+ \) and \( \sigma_u^+ \) species are given below:

\[
\begin{align*}
\sigma_g^+ \text{ species} & \\
S_1 & = 2^{-1/2}(\Delta d_1 + \Delta d_2) \\
S_2 & = 2^{-1/2}(\Delta D_1 + \Delta D_2) \\
S_3 & = 6^{-1/2}(2\Delta r_2 - \Delta r_1 - \Delta r_3) \\
S_4 & = 3^{-1/2}(\Delta r_1 + \Delta r_2 + \Delta r_3)
\end{align*}
\]

\[
\begin{align*}
\sigma_u^+ \text{ species} & \\
S_5 & = 2^{-1/2}(\Delta d_1 - \Delta d_2) \\
S_6 & = 2^{-1/2}(\Delta D_1 - \Delta D_2) \\
S_7 & = 2^{-1/2}(\Delta r_1 - \Delta r_3)
\end{align*}
\]

The \( F \) matrix elements were obtained in the usual way.\textsuperscript{1-5} The computed valence constants are given in Table 2.

![Fig. 1.—Inter-bond distances and inter-bond angles.](image)

Table 2

<table>
<thead>
<tr>
<th>Elements</th>
<th>Valence Force Constants for Elements</th>
<th>Valence Force Constants for Elements</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Set I</td>
<td>Set II</td>
</tr>
<tr>
<td>( f(d) )</td>
<td>40·2984\textsuperscript{a}</td>
<td>28·3509</td>
</tr>
<tr>
<td>( f(r_1) ) or ( f(r_2) )</td>
<td>28·8024</td>
<td>12·8664</td>
</tr>
<tr>
<td>( f(r_2) )</td>
<td>18·4987</td>
<td>21·6459</td>
</tr>
<tr>
<td>( f(D) )</td>
<td>46·2432</td>
<td>10·4044</td>
</tr>
<tr>
<td>( f(dr_1) )</td>
<td>26·8087</td>
<td>6·6492</td>
</tr>
</tbody>
</table>

\textsuperscript{a}This number of significant figures is retained to secure internal consistency in the calculations.

Table 3

| Potential Energy Distribution for the Various Normal Modes of \( \sigma_g^+ \) |
|-------------------|---|---|---|---|---|---|---|---|
|                  | 1 | 2 | 3 | 4 | 1 | 2 | 3 | 4 |
| \( S_1 \) | 1·2479 | 0·2170 | 0·1240 | 0·0235 | \( S_1 \) | 1·0246 | 0·0053 | 0·0200 | 0·0132 |
| \( S_2 \) | 0·0459 | 1·5627 | 0·8642 | 0·4587 | \( S_2 \) | 0·0256 | 1·1311 | 0·2732 | 0·0067 |
| \( S_3 \) | 0·0243 | 0·9338 | 1·4532 | 0·6039 | \( S_3 \) | 0·0034 | 0·3279 | 1·1256 | 0·0036 |
| \( S_4 \) | 0·0324 | 0·2127 | 0·5108 | 1·3274 | \( S_4 \) | 0·0025 | 0·0082 | 0·3474 | 1·0032 |

As seen from Table 2, abnormal values for the valence constants are obtained for this set. The potential energy distribution\textsuperscript{8} for this set, given in Table 3, also

indicates very high mixing between the $S_2$, $S_3$, and $S_4$ coordinates of $\sigma_g^+$ species. Hence the following symmetry coordinates transforming according to the irreducible representation were constructed for the $\sigma_g^+$ and $\sigma_u^+$ species:

$$\begin{align*}
\sigma_g^+ \text{ species} & \quad \sigma_u^+ \text{ species} \\
S_1 & = 2^{-1/2}(\Delta d_1 + \Delta d_2) \\
S_2 & = 20^{-1/2}(4\Delta r_2 - \Delta r_1 - \Delta r_3 - \Delta D_1 - \Delta D_2) \\
S_3 & = 5^{-1/2}(\Delta r_1 + \Delta r_2 + \Delta r_3 + \Delta D_1 + \Delta D_2) \\
S_4 & = 2^{-1}(\Delta r_1 + \Delta r_3 - \Delta D_1 - \Delta D_2) \\
S_5 & = 2^{-1/2}(\Delta d_1 - \Delta d_2) \\
S_6 & = 2^{-1}(\Delta r_1 - \Delta r_3 - \Delta D_1 + \Delta D_2) \\
S_7 & = 2^{-1}(\Delta r_1 - \Delta r_3 + \Delta D_1 - \Delta D_2)
\end{align*}$$

The $F$ matrix elements were computed and the valence force constants for this set are given in Table 2. As seen from Table 2 the potential energy distribution, computed for this set, justifies our choice of symmetry coordinates.

The $f(d)$ value of $28.35$ mdyn/Å of dicyanodiacylene compares well with the value of $27.62$ mdyn/Å and $26.78$ mdyn/Å obtained in the case of dicyanoacetylene and cyanoacetylene respectively. In the case of the three C-C bonds, $r_1$, $r_2$, and $r_3$, the value obtained for the $f(r_1)$ and $f(r_3)$ is $12.87$ mdyn/Å while the $f(r_2)$ value is $21.65$ mdyn/Å. The value obtained for $f(D)$ is $10.40$ mdyn/Å. While the triple bonds on either side of the central single bond appear to have weakened out, the central single bond has strengthened to such a value as to be attributed a triple bond character.

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