Potential Constants, Mean Amplitudes of Vibration, Shrinkage Constants and Coriolis Coupling Coefficients of Monohalo Acetylenes

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The potential constants are obtained for the monohaloacetylenes using the general valence force field. The theory of the mean-square amplitude matrices is applied to these molecules and the parallel and perpendicular mean-square amplitudes for the interatomic distances are calculated. The perpendicular amplitudes have been used for calculating the shrinkage effect. The Coriolis coupling coefficients are also obtained for all these molecules.

The infrared spectra of HC≡CF, HC≡CCL, HC≡CBr and their deuterocompounds. The molecular dimensions have been studied by Richardson and Goldstein. Hunt and Wilson have obtained the spectrum of one sample of monofluoroacetylene. Hunt and Wilson have studied the infrared spectra of gaseous HC≡CF, HC≡CCL, HC≡CBr and their deuterocompounds. The molecular dimensions have been determined by electron diffraction for HC≡CBr, by microwave spectroscopy for HC≡CF and by both techniques for HC≡CCL. All these molecules have got linear configuration.

The present investigation has been undertaken to obtain (1) the general valence potential constants, (2) the mean-square amplitude matrices which have proved to be very useful in electron-diffraction investigations and (3) the Bastiansen-Morino shrinkage effect and (4) the Coriolis coupling coefficients. The frequencies and the geometrical parameters used in the present investigation are the same as those used by Hunt and Wilson.

The normal modes of vibration for the monohaloacetylenes, assuming the \( C_{\infty v} \) point group, are distributed among the various symmetry species as \( 3 \Delta + 2 \Sigma \). The orientation of the cartesian coordinate axes and the numbering of the atoms are shown in fig. 1, where \( X \) represents the halogens.

**Kinetic energy matrix**

The elements of the kinetic energy matrix, obtained by the method of Fereigle and Meister, are as follows:

\[
\begin{align*}
G_{11} &= \mu \mu + \mu C, \\
G_{22} &= 2 \mu C, \\
G_{33} &= \mu C + \mu X, \\
G_{12} &= G_{23} = - \mu C, \\
G_{44} &= \mu \mu + \mu C \left( \frac{r_1}{r_2} + 2 \frac{r_1}{r_3} + 2 \right), \\
G_{45} &= \mu C \left( 2 \frac{r_1}{r_2} + \frac{r_1}{r_3} + 2 \right) + \mu X \left( \frac{r_1}{r_2} \right), \\
G_{46} &= - \mu C \left( 2 \frac{r_1}{r_2} \right) + \left( \frac{r_1}{r_2} \right)^3,
\end{align*}
\]

**Potential energy constants**

The potential energy constants are obtained using the general valence force field by the \( FG \) matrix method of Wilson. The final \( F \) matrix elements are

\[
\begin{align*}
F_{11} &= f_{11}, \\
F_{22} &= f_{22}, \\
F_{33} &= f_{33}, \\
F_{13} &= f_{13}, \\
F_{12} &= f_{12}, \\
F_{14} &= f_{14}, \\
F_{24} &= f_{24}, \\
F_{34} &= f_{34}, \\
F_{35} &= f_{35}, \\
F_{45} &= f_{45},
\end{align*}
\]

Mean amplitudes of vibration

The theory of the mean-square amplitudes of vibration is applied to these molecules and the mean amplitude values at 300 °K are evaluated, solving the secular equation,

\[ \Sigma G^{-1} - \Delta E = 0 \]

In order to compute the generalized mean-square amplitude, the symmetry coordinates are expressed in terms of cartesian displacement coordinates. The S-vectors in terms of the cartesian displacement coordinates are,

\[
S_1 = (z_1 - z_2), \quad S_2 = (z_2 - z_3), \quad S_3 = (z_3 - z_4),
\]

\[
S_{4a} = \sqrt{r_1 r_2} \left[ \frac{1}{r_1} x_1 - \left( \frac{1}{r_1} + \frac{1}{r_2} \right) x_2 + \frac{1}{r_2} x_3 \right],
\]

\[
S_{4b} = \sqrt{r_1 r_2} \left[ \frac{1}{r_1} y_1 - \left( \frac{1}{r_1} + \frac{1}{r_2} \right) y_2 + \frac{1}{r_2} y_3 \right],
\]

\[
S_{5a} = \sqrt{r_2 r_3} \left[ \frac{1}{r_2} x_1 - \left( \frac{1}{r_2} + \frac{1}{r_3} \right) x_2 + \frac{1}{r_3} x_3 \right],
\]

\[
S_{5b} = \sqrt{r_2 r_3} \left[ \frac{1}{r_2} y_1 - \left( \frac{1}{r_2} + \frac{1}{r_3} \right) y_2 + \frac{1}{r_3} y_3 \right].
\]

The generalized mean-square amplitudes of vibration for the monohaloacetylenes can be expressed in terms of the relations connecting the cartesian displacement coordinates and the symmetry coordinates. The mean-square parallel amplitudes will be given by the relation \( (z_A - z_B)^2 \). The expressions for the perpendicular mean-square amplitudes can be written as \( r_{AB} = ((z_A - z_B)^2) \) and \( (Ax \cdot Ay) = (Ax \cdot Az) = (Az \cdot Ax) = 0 \). The \( \Sigma \) matrix elements in terms of the mean-square amplitude quantities are

\[
\Sigma_{11} = \sigma_1; \quad \Sigma_{22} = \sigma_2;
\]

\[
\Sigma_{33} = \sigma_3; \quad \Sigma_{12} = \sigma_{12};
\]

\[
\Sigma_{13} = 0; \quad \Sigma_{23} = \sigma_{23};
\]

\[
\Sigma_{44} = \sigma_5; \quad \Sigma_{55} = \sigma_5 \text{ and } \Sigma_{45} = \sigma_6.
\]

The additional mean-square amplitude quantities, introduced for the non-bonded distance deviations of the molecule in terms of the \( \Sigma \) matrix elements, are

\[
\sigma_{H...C} = \Sigma_{11} + \Sigma_{22} + 2 \Sigma_{12},
\]

\[
\sigma_{H...X} = \Sigma_{11} + \Sigma_{22} + \Sigma_{33} + 2 \Sigma_{12} + 2 \Sigma_{23},
\]

\[
\sigma_{C...X} = \Sigma_{22} + \Sigma_{33} + 2 \Sigma_{23}.
\]

The relations for the perpendicular mean-square amplitude quantities in terms of the \( \Sigma \) matrix elements can be obtained using the methods of Morino and Hirota 10, by substituting for \( x_A \) and \( x_B \) from the \( A \) matrix, which is given as \( A = M^{-1} B'G^{-1} \), where \( M \) is a diagonal matrix of \( 3N \) dimensions, consisting of the masses \( m_i \) of all the atoms. The following expressions are obtained for the generalized mean-square amplitudes of the different bonded and nonbonded atom-pairs.

\[
H - C_1:
\]

\[
\langle (Ax)^2 \rangle = \langle (z_A - z_B)^2 \rangle,
\]

\[
\langle (Ax)^2 \rangle = \langle (Ay)^2 \rangle = \langle (z_A - z_B)^2 \rangle = \langle (y_A - y_B)^2 \rangle.
\]

\[
C_1 - C_2:
\]

\[
\langle (Ax)^2 \rangle = \langle (z_A - z_B)^2 \rangle,
\]

\[
\langle (Ax)^2 \rangle = \langle (Ay)^2 \rangle = \langle (z_A - z_B)^2 \rangle = \langle (y_A - y_B)^2 \rangle.
\]

\[
C_2 - C_3:
\]

\[
\langle (Ax)^2 \rangle = \langle (z_A - z_B)^2 \rangle,
\]

\[
\langle (Ax)^2 \rangle = \langle (Ay)^2 \rangle = \langle (z_A - z_B)^2 \rangle = \langle (y_A - y_B)^2 \rangle.
\]

\[
H \ldots X:
\]

\[
\langle (Ax)^2 \rangle = \langle (z_A - z_B)^2 \rangle,
\]

\[
\langle (Ax)^2 \rangle = \langle (Ay)^2 \rangle = \langle (z_A - z_B)^2 \rangle = \langle (y_A - y_B)^2 \rangle.
\]

\[
C_1 \ldots X:
\]

\[
\langle (Ax)^2 \rangle = \langle (z_A - z_B)^2 \rangle,
\]

\[
\langle (Ax)^2 \rangle = \langle (Ay)^2 \rangle = \langle (z_A - z_B)^2 \rangle = \langle (y_A - y_B)^2 \rangle.
\]

Shrinkage Effect

The "shrinkage" in linear molecules, which has been observed from electron-diffraction data by Bastiansen et al. 11 may be calculated spectroscopically by means of the mean-square perpendicular amplitudes as has been pointed out by Morino 12.

In the monohaloacetylenes, the following shrinkage effects can be calculated.

\[
- \delta_{1-3} = \frac{\tau_{13} - \tau_{12} - \tau_{23}}{(r_1 + r_2)},
\]

\[
- \delta_{2-4} = \frac{\tau_{24} - \tau_{23} - \tau_{34}}{(r_2 + r_3)},
\]

\[
- \delta_{1-4} = \frac{\tau_{14} - \tau_{12} - \tau_{23} - \tau_{34}}{(r_1 + r_2 + r_3)},
\]

Where \( \tau_{ij} = \frac{\langle (d_{ij})^2 \rangle + \langle (d_{ij})^2 \rangle}{2} \)

8. E. B. Wilson, J. chem. Physics 7, 1047 [1939]; 9, 76 [1941].
Coriolis Coupling Coefficients

Coriolis constants are evaluated for the $\Sigma^+ \times \pi$ and $\pi \times \pi$ couplings. Using Meal and Polo's \(^{13}\) vector method, the following non-vanishing $C^\alpha$ matrix elements are obtained in the present case.

### $\Sigma^+ \times \pi$

\[
\begin{align*}
C_{1,4}^{x, b} &= -C_{1,4}^{y, a} = -\mu_Y \left( \frac{r_2}{r_1} - \mu_c \left( \frac{r_5}{r_4} + \frac{r_1}{r_2} \right) \right), \\
C_{1,5}^{x, b} &= -C_{1,5}^{y, a} = \mu_c \left( \sqrt{\frac{r_5}{r_4}} \right), \\
C_{2,4}^{x, b} &= -C_{2,4}^{y, a} = \mu_c \left( \sqrt{\frac{r_5}{r_4}} + 2 \sqrt{\frac{r_5}{r_2}} \right), \\
C_{2,5}^{x, b} &= -C_{2,5}^{y, a} = -\mu_c \left( 2 \sqrt{\frac{r_5}{r_2}} + \sqrt{\frac{r_5}{r_3}} \right), \\
C_{3,4}^{x, b} &= -C_{3,4}^{y, a} = -\mu_c \left( \sqrt{\frac{r_5}{r_2}} \right), \\
C_{3,5}^{x, b} &= -C_{3,5}^{y, a} = \mu_c \left( \sqrt{\frac{r_5}{r_2}} + \sqrt{\frac{r_5}{r_3}} + \mu_x \sqrt{\frac{r_5}{r_3}} \right).
\end{align*}
\]

### $\pi \times \pi$

\[
\begin{align*}
C_{4}^{a, 4 b} &= \mu_Y \left( \frac{r_2}{r_1} + \mu_c \left( \frac{r_5}{r_4} + 2 \frac{r_1}{r_2} + 2 \right) \right), \\
C_{5}^{a, 5 b} &= \mu_c \left( 2 \frac{r_5}{r_2} + \frac{r_5}{r_3} + 2 \right) + \mu_x \left( \frac{r_5}{r_2} \right), \\
C_{4}^{a, 5 b} &= \mu_c \left( \frac{r_5}{r_2} \right) \left( \frac{r_1}{r_2} \right)^2 + \mu_x \left( \frac{r_5}{r_2} \right) \left( \frac{r_1}{r_2} \right).
\end{align*}
\]

Using the above $C$ elements and the $L$ matrix derived from the force field, the zeta elements are calculated. For the $\pi \times \pi$ coupling $\zeta_{4}^{a, 4 b} = \zeta_{5}^{a, 5 b} = 1$ and $\zeta_{4}^{a, 5 b} = \zeta_{5}^{a, 4 b} = 0$.

### Results and discussion

The potential constants obtained using the general valence force field are presented in Table I. Table II gives the mean amplitudes of vibration of the various bonded and nonbonded atom pairs. The generalized mean-square amplitudes are given in Table III. The mean amplitudes obtained in the present study are compared with those obtained in methyl halides \(^9\) in Table IV. The $\equiv C - H$ link in monohaloacetylene is shorter than the $C - H$ link in methane. This shortening may be due to the use of a carbon orbital differing from that of tetrahedral orbital. Accordingly the $C - H$ force constant is larger and the mean amplitudes smaller than the normal value. The same explanation stands good in the case of $\equiv C -$ halogen bond also, where the force constant is significantly larger and the mean amplitudes smaller than the corresponding values in methyl halides, as shown in Table IV. From the consideration of force

<table>
<thead>
<tr>
<th>Force Constant</th>
<th>HC=CF</th>
<th>DC=CF</th>
<th>HC=CCl</th>
<th>DC=CCl</th>
<th>HC=CBr</th>
<th>DC=CBr</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f_1$</td>
<td>5.9870</td>
<td>6.0190</td>
<td>5.9610</td>
<td>6.0980</td>
<td>5.9280</td>
<td>6.0420</td>
</tr>
<tr>
<td>$f_2$</td>
<td>16.6200</td>
<td>16.6200</td>
<td>15.8100</td>
<td>15.8100</td>
<td>15.4900</td>
<td>15.6700</td>
</tr>
<tr>
<td>$f_3$</td>
<td>8.2130</td>
<td>8.2130</td>
<td>5.2550</td>
<td>5.2340</td>
<td>5.4770</td>
<td>4.4750</td>
</tr>
<tr>
<td>$f_{rx}$</td>
<td>0.2636</td>
<td>0.2770</td>
<td>0.3319</td>
<td>0.3248</td>
<td>0.3035</td>
<td>0.3172</td>
</tr>
<tr>
<td>$f_{rx^2}$</td>
<td>0.3035</td>
<td>0.3097</td>
<td>0.3084</td>
<td>0.3008</td>
<td>0.3119</td>
<td>0.3172</td>
</tr>
<tr>
<td>$f_\phi$</td>
<td>0.1271</td>
<td>0.1219</td>
<td>0.1672</td>
<td>0.1835</td>
<td>0.1787</td>
<td>0.1953</td>
</tr>
<tr>
<td>$f_\theta$</td>
<td>0.2032</td>
<td>0.2337</td>
<td>0.2405</td>
<td>0.2181</td>
<td>0.2195</td>
<td>0.2913</td>
</tr>
<tr>
<td>$f_\phi\theta$</td>
<td>0.0205</td>
<td>0.0364</td>
<td>0.1346</td>
<td>0.1418</td>
<td>0.1418</td>
<td>0.1418</td>
</tr>
</tbody>
</table>

Table I. Potential energy constants of monohaloacetylenes and their deuterocompounds (10$^5$ dynes/cm).

<table>
<thead>
<tr>
<th>Atom pair</th>
<th>HC=CF</th>
<th>DC=CF</th>
<th>HC=CCl</th>
<th>DC=CCl</th>
<th>HC=CBr</th>
<th>DC=CBr</th>
</tr>
</thead>
<tbody>
<tr>
<td>C—H or C—D</td>
<td>0.07291</td>
<td>0.06381</td>
<td>0.07375</td>
<td>0.06383</td>
<td>0.07461</td>
<td>0.06387</td>
</tr>
<tr>
<td>C=C</td>
<td>0.03552</td>
<td>0.03562</td>
<td>0.03593</td>
<td>0.03533</td>
<td>0.03593</td>
<td>0.03566</td>
</tr>
<tr>
<td>C—X</td>
<td>0.04308</td>
<td>0.04277</td>
<td>0.04414</td>
<td>0.04370</td>
<td>0.04578</td>
<td>0.04471</td>
</tr>
<tr>
<td>H...C$_2$ or D...C$_2$</td>
<td>0.07696</td>
<td>0.06832</td>
<td>0.07823</td>
<td>0.06858</td>
<td>0.07903</td>
<td>0.06852</td>
</tr>
<tr>
<td>H...X or D...X</td>
<td>0.04193</td>
<td>0.04015</td>
<td>0.04383</td>
<td>0.04366</td>
<td>0.04411</td>
<td>0.04451</td>
</tr>
<tr>
<td>C$_1$...X</td>
<td>0.08013</td>
<td>0.07082</td>
<td>0.08217</td>
<td>0.07311</td>
<td>0.08307</td>
<td>0.07355</td>
</tr>
</tbody>
</table>

Table II. Mean amplitudes of vibration of monohaloacetylenes and their deuterocompounds [Å].

\(^{13}\) J. H. Meal and S. R. Polo, J. chem. Physics 24, 1126 [1956].
Table III. Generalised mean-square amplitudes of vibration [Å²] in monohaloacetylenes and their deuterocompounds.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>C-H or C-D</th>
<th>C-X</th>
</tr>
</thead>
<tbody>
<tr>
<td>bond length</td>
<td>mean amplitude</td>
<td>bond length</td>
</tr>
<tr>
<td>CH₃Cl</td>
<td>1.11</td>
<td>0.0761</td>
</tr>
<tr>
<td>HC=CCl</td>
<td>1.0587</td>
<td>0.0738</td>
</tr>
<tr>
<td>CD₂Cl</td>
<td>1.11</td>
<td>0.0652</td>
</tr>
<tr>
<td>DC=CCl</td>
<td>1.0587</td>
<td>0.0638</td>
</tr>
<tr>
<td>CH₃Br</td>
<td>1.11</td>
<td>0.0759</td>
</tr>
<tr>
<td>HC=CBr</td>
<td>1.0587</td>
<td>0.0651</td>
</tr>
<tr>
<td>CD₂Br</td>
<td>1.11</td>
<td>0.0651</td>
</tr>
<tr>
<td>DC=CBr</td>
<td>1.0587</td>
<td>0.0639</td>
</tr>
</tbody>
</table>

Table IV. Comparison of the mean amplitudes of monohaloacetylenes and methyl halides.

Table V. Shrinkage constants [Å] in monohaloacetylenes and their deuterocompounds.

Table VI. Coriolis coupling coefficients of monohaloacetylenes and their deuterocompounds.