Spectroscopic Studies on Molecular Vibrations and Coriolis Coupling in Acetylenes, Diodoacetylene, and Cyanogen

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Spectroscopic calculations are reported for some linear symmetrical \(X_2Y_2\) type molecules. For diodoacetylene the following quantities are given numerically:

(a) Force constants,
(b) mean-square amplitude matrix elements,
(c) parallel and perpendicular mean-square amplitudes,
(d) mean amplitudes of vibration,
(e) Bastiansen–Morino shrinkage effects,
(f) L-matrix elements, and
(g) Coriolis coupling coefficients.

The calculated L-matrix elements and Coriolis coupling coefficients are also given for acetylene, acetylene-\(d_4\), and cyanogen.

Our studies on mean amplitudes of vibration\(^1\) and Bastiansen–Morino shrinkage effects\(^2\) in linear molecules\(^3\)–\(^5\) have been continued by the presently reported study on diodoacetylene. This molecule is of the same type as cyanogen\(^6\) and acetylene\(^4\), viz. linear symmetrical \(X_2Y_2\) (symmetry group \(D_{\infty h}\)). The work has been actuated by the scheduled electron-diffraction study on diodoacetylene (Bastiansen \textit{et al}.

In addition to the mean amplitudes of vibration, shrinkage effects and related quantities, the Coriolis coupling coefficients\(^6,7\) of linear symmetrical \(X_2Y_2\) type molecules have been studied\(^8\). In the present work numerical \(\zeta\)-values are reported for acetylene, acetylene-\(d_4\), diodoacetylene, and cyanogen.

DIIDOACETYLENE

Experimental data. We used the experimental vibrational frequencies from Cleveland and Meister\(^9,10\) \textit{viz.} \((\Sigma_{c}^+: 191, 2109, (\Sigma_{u}^+:) 710, (\Pi_{c}^+:) 310, \text{and} (\Pi_{u}^+:) 115\), all in cm\(^{-1}\). As equilibrium distances we had to use the old data\(^11\) of \((C\equiv C)\) \(D = 1.18\) Å, and \((C\equiv I)\) \(R = 2.03\) Å because of the lack of more recent
**Table 1. Force constants and mean-square amplitude matrix elements for diodoacetylene***

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Force constant (mdyne/Å)</th>
<th>Symbol</th>
<th>Mean-square amplitude (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_1$</td>
<td>2.78201</td>
<td>$\Sigma_1$</td>
<td>0.00130947</td>
</tr>
<tr>
<td>$F_2$</td>
<td>15.799</td>
<td>$\Sigma_2$</td>
<td>0.00133440</td>
</tr>
<tr>
<td>$F_{12}$</td>
<td>1.03984</td>
<td>$\Sigma_{12}$</td>
<td>-0.00096594</td>
</tr>
<tr>
<td>$F_3$</td>
<td>3.25579</td>
<td>$\Sigma_3$</td>
<td>0.00216567</td>
</tr>
<tr>
<td>$F_4$</td>
<td>0.058986</td>
<td>$\Sigma_4$</td>
<td>0.0521920</td>
</tr>
<tr>
<td>$F_5$</td>
<td>0.146943</td>
<td>$\Sigma_5$</td>
<td>0.00777209</td>
</tr>
</tbody>
</table>

* For explanation of symbols, see Refs.5,4

measurements. The same data have also been applied by Cleveland and Meister 6, and are hoped to be sufficiently accurate for our purpose.

**Force constants.** The considered model contains six harmonic force constants, whereas the number of vibrational frequencies is five. Since no data on different isotopic molecules are available in the present case, one assumption must be made in order to calculate the force constants from the frequencies. Cleveland and Meister 6 transferred the force constant of CC stretching from methylidoacetylene. This assumption seems to be very reasonable, and we followed the same procedure, putting $F_2$ equal to 15.799 mdyn/Å. The present recalculated force constants are given in Table 1. The calculations confirm the results of Cleveland and Meister 6, as the small differences certainly may be ascribed to slightly different physical constants. We used $\mu_C = 0.0833065$ (based on C$^{12}$) and $\mu_I = 0.0078790$ (Amu)$^{-1}$ for the inverse masses of the C and I atoms, respectively. The squared wave numbers ($\omega$ in cm$^{-1}$) were converted to $\lambda$ values (in mdyne/ÅÅm$^{-1}$) by the factor 0.0588932 ($\lambda = 4\pi^2\omega^2$). In Table 1 the force field is given in terms of the symmetrized force constants. They are based on a set of symmetry coordinates, which have been specified elsewhere 6. To compare our result with that of Cleveland and Meister 6, we performed the transformation of our force constants to those in the notation of the mentioned investigators. The result is given in the following.

\[
\begin{align*}
    k_a &= F_2 = 15.799 \ (15.799) \\
    k_i &= (1/2) (F_1 + F_3) = 3.0189 \ (3.0186) \\
    k_q &= (D/2K) (F_1 + F_3) = 0.059851 \ (0.05967) \\
    k_{ia} &= 2^{-1/2} K_2 = 0.73528 \ (0.7350) \\
    k_{qp} &= (D/2K) (F_5 - F_4) = 0.025564 \ (0.02538) \\
    k_{ii} &= (1/2) (F_1 - F_3) = -0.23689 \ (-0.2372)
\end{align*}
\]

The values from Cleveland and Meister are given in parentheses. $r_i$ and $r_a$ in the notation of Cleveland and Meister corresponds to our $R$ and $D$, respectively.

**Mean-square amplitude matrix.** The $\Sigma$-matrix elements have been determined by means of the relation 12

\[
\Sigma = L A \tilde{L}
\]

and are included in Table 1.

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Table 2. Mean-square parallel ($\sigma$) and perpendicular ($\tau$) amplitudes for diiodoacetylene at $T = 0$ and 298 °K

<table>
<thead>
<tr>
<th>Distance</th>
<th>Symbol</th>
<th>$T = 0$ (Å units)</th>
<th>298 °K</th>
</tr>
</thead>
<tbody>
<tr>
<td>C—I</td>
<td>$\sigma_r$</td>
<td>0.00173757</td>
<td>0.00223201</td>
</tr>
<tr>
<td></td>
<td>$\tau_r$</td>
<td>0.00759139</td>
<td>0.0261377</td>
</tr>
<tr>
<td>C≡C</td>
<td>$\sigma_d$</td>
<td>0.00133440</td>
<td>0.00133775</td>
</tr>
<tr>
<td></td>
<td>$\tau_d$</td>
<td>0.00901976</td>
<td>0.0142280</td>
</tr>
<tr>
<td>C...I</td>
<td>$\sigma_{r+d}$</td>
<td>0.00179077</td>
<td>0.00236251</td>
</tr>
<tr>
<td></td>
<td>$\tau_{r+d}$</td>
<td>0.00884521</td>
<td>0.0281155</td>
</tr>
<tr>
<td>I...I</td>
<td>$\sigma_{br+d}$</td>
<td>0.00139095</td>
<td>0.00322888</td>
</tr>
<tr>
<td></td>
<td>$\tau_{br+d}$</td>
<td>0.00000409</td>
<td>0.00000645</td>
</tr>
</tbody>
</table>

Table 3. Mean amplitudes of vibration and shrinkage effects for diiodoacetylene

<table>
<thead>
<tr>
<th>Distance</th>
<th>Symbol</th>
<th>Mean amplitude of vibration (Å)</th>
<th>Shrinkage effect</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$T = 0$</td>
<td>$T = 0$</td>
</tr>
<tr>
<td>C—I</td>
<td>$u_r$</td>
<td>0.0417</td>
<td>0.0472</td>
</tr>
<tr>
<td>C≡C</td>
<td>$u_d$</td>
<td>0.0365</td>
<td>0.0366</td>
</tr>
<tr>
<td>C...I</td>
<td>$u_{r+d}$</td>
<td>0.0423</td>
<td>0.0486</td>
</tr>
<tr>
<td>I...I</td>
<td>$u_{br+d}$</td>
<td>0.0373</td>
<td>0.0568</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$T = 0$</td>
<td>298 °K</td>
</tr>
<tr>
<td>C...I</td>
<td>$\delta_{r+d}^F$</td>
<td>0.0086</td>
<td>0.0162</td>
</tr>
<tr>
<td>I...I</td>
<td>$\delta_{br+d}^F$</td>
<td>0.0151</td>
<td>0.0378</td>
</tr>
</tbody>
</table>

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The mean-square parallel and perpendicular amplitudes (\(\sigma\) and \(\tau\), respectively) are defined for the here considered molecular model in Ref.3, where these quantities are given in terms of the \(\Sigma\)-matrix elements. They are given numerically for diiodoacetylene in Table 2.

**Mean amplitudes of vibration and shrinkage effects.** The calculated mean amplitudes of vibration \(u\) and Bastiansen-Morino shrinkage effects \(\delta\) for diiodoacetylene are reported in Table 3.

**L-Matrices**

Because of the wide applicability of the normal coordinate transformation matrix, \(L\) (\(S = LQ\)), it seems justified to specify its elements for the presently considered molecules. The L-matrix has been used in the present computations on diiodoacetylene (cf. the \(\Sigma\)-matrix above), as well as in our previous computations on acetylene 4, and cyanogen 3. The L-matrix elements from our calculations are given numerically for acetylene, acetylene-\(d_4\), diiodoacetylene, and cyanogen in the following. Units: Å\(\text{m}^{-1}\).

**Acetylene.**

\[
\begin{align*}
L_{11} &= 0.774617 & L_{12} &= -0.689355 \\
L_{21} &= 0.175761 & L_{22} &= 0.368403 \\
L_{33} &= 1.036939 & L_{44} &= 1.360063 & L_{55} &= 1.106234
\end{align*}
\]

**Acetylene-\(d_4\).**

\[
\begin{align*}
L_{11} &= 0.279561 & L_{12} &= -0.708168 \\
L_{21} &= 0.294525 & L_{22} &= 0.282609 \\
L_{33} &= 0.761351 & L_{44} &= 1.133903 & L_{55} &= 0.812230
\end{align*}
\]

**Diiodoacetylene**

\[
\begin{align*}
L_{11} &= 0.085022 & L_{12} &= -0.289752 \\
L_{21} &= 0.005279 & L_{22} &= 0.408148 \\
L_{33} &= 0.301969 & L_{44} &= 0.979536 & L_{55} &= 0.230227
\end{align*}
\]

**Cyanogen**

\[
\begin{align*}
L_{11} &= 0.383545 & L_{12} &= 0.087179 \\
L_{21} &= -0.353533 & L_{22} &= 0.204027 \\
L_{33} &= 0.393315 & L_{44} &= 1.120054 & L_{55} &= 0.429550
\end{align*}
\]

**Coriolis coupling coefficients**

The Coriolis coefficients of rotation-vibration interaction (\(\zeta\)-values) for the linear symmetrical \(X_2Y_2\) molecular model have been treated theoretically.

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Table 4. Coriolis coupling coefficients ($\zeta$) in some molecules

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$\zeta_{14}$</th>
<th>$\zeta_{24}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetylene</td>
<td>0.436</td>
<td>-0.900</td>
</tr>
<tr>
<td>Acetylene-d$_4$</td>
<td>-0.081</td>
<td>-0.997</td>
</tr>
<tr>
<td>Diiodoacetylene</td>
<td>0.056</td>
<td>-0.998</td>
</tr>
<tr>
<td>Cyanogen</td>
<td>0.982</td>
<td>-0.189</td>
</tr>
</tbody>
</table>

* Notice the relation $8 \zeta_{14}^2 + \zeta_{24}^2 = 1$.

elsewhere$^8$. There are two different non-trivial (i.e. force-constant dependent) $\zeta$-values in the considered case, viz.

\[
\begin{align*}
\zeta_{14} &= \zeta_{1,4a} - \zeta_{1,4b} \\
\zeta_{24} &= \zeta_{2,4a} - \zeta_{2,4b}
\end{align*}
\]

They may be calculated again by means of the L-matrix in various ways. We have found the application$^6,7 \zeta^a = \tilde{L} G^{-1} C^a \tilde{L}^{-1}$ to be the most useful one of the methods, and we obtained the simple equations:

\[
\begin{align*}
\zeta_{14} &= L_{44}^{-1} [(D/R)^{1/2} L_{11} - (2R/D)^{1/2} L_{21}] \\
\zeta_{24} &= L_{44}^{-1} [(D/R)^{1/2} L_{12} - (2R/D)^{1/2} L_{22}]
\end{align*}
\]

The numerical results for the four molecules in question are given in Table 4.

Note The digits as given in this report are not necessarily significant. They have been included to preserve mathematical consistency.

REFERENCES


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