STRUCTURAL ANALYSIS OF $AXY_2$ TYPE MOLECULES [LINEAR VERSUS BENT SYMMETRIC] BASED ON BENDING ENERGY MINIMIZATION CRITERION

Abstract

The method of the minimum bending energy for correct geometry is applied to the case of $AXY_2$ type linear symmetric molecules treating them as bent symmetric structure. Examples with linear molecules like $CO_2$ and $CN_2$ indicate that these have minimum contribution from bending energy while the interbond angle $Y-X-Y$ is exactly $180^\circ$.

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§4.1 Introduction

In general, a molecule of \( X_2 \) symmetric type may assume a linear structure like \( CO_2 \) or a bent symmetric structure like \( ClO_2 \) or \( SO_2 \). A linear symmetric \( \textit{XY}_2 \) system has the following symmetry properties:

1. \( C^\infty \): Infinite number of rotation axes.
2. \( \sigma_v^m \): Infinite number of vertical planes.
3. \( \sigma_h \): One reflection plane passing through the \( X \) atom and perpendicular to the \( Y-X-Y \) axis.
4. A centre of symmetry point at \( X \).
5. Identity operation.

A molecule with the above symmetry properties is identified with \( D_{2h} \) point group. It is well established from Raman and infrared studies that \( CO_2 \) and \( CS_2 \) belong to \( D_{2h} \) point group and have a centre of symmetry. \( ClO_2 \) and \( SO_2 \) like molecules belong to the \( C_2 \) point group with interbond angle quite different from 180°.
It has been established in the previous chapter that molecules prefer a geometry for which the contribution of bending energy of vibration to the potential energy is a minimum. This finding opens a new route to determine the structure of simple molecules. In this chapter the principle is applied to CO$_2$ and CS$_2$ molecules.

§4.2 Mathematical formalism

As already explained in chapter 2 the average potential energy of a vibrating molecule is expressed in symmetry coordinates as,

$$
\langle 2V \rangle = \sum_{ij} \sigma_{ij} \Sigma_{ij}
$$

(4.1)

This may also be written in terms of the valence force field and mean square amplitude as

$$
\langle 2V' \rangle = \sum_{ij} \sigma_{ij} \sigma_{ij}
$$

(4.2)
The various contributions to the potential energy are separated from the above expression and the bending energy contribution alone studied in this case.

To begin with, it is assumed that CO₂ molecule has an interbond angle \( \alpha \) and behaves like a bent symmetric structure. Then from the average potential energy expression

\[
(2V) = f_u \sigma_u + 2f_r \sigma_r + 2f_n \sigma_n + 4f_\sigma \sigma_\sigma
\]

the contribution from the bending energy alone is

\[
V_{\text{bend}} = \frac{1}{2}(f_u \sigma_u)
\]

\( f_u \) and \( \sigma_u \) are related to the \( F \) and \( \Sigma \) elements as explained in chapter 2. Equations [2.15-2.22].

For the evaluation of the bending energy contributions it is required to evaluate first the \( l \) matrix. This is possible through the \( G \) matrix elements which is explained in detail in chapter 2. Equations [2.24-2.27]. The \( F \) and \( \Sigma \) elements are related to the \( l \) matrix. For the evaluation of the \( l \) matrix we employ the parametric approach as already mentioned in chapter 2 [47].
\[ L = \tilde{L}_n C \] which satisfies the Wilson condition \([1,6]\) that \[ LL^T \approx \tilde{G} \]
demanding \( f_{al} f_{al}^T \approx \tilde{G} \).

To begin with an arbitrary value for the inter bond angle is assigned to the CO\(_2\) molecule. Then the isotopically invariant force field matrix \( F \) is fixed using the vibrational frequencies of the normal molecule and its isotopic substituents \([43]\). The mean square amplitude matrix \( \Sigma \) is computed by the method described by Cyvin\([10]\). The bending energy contribution \( (V_{\alpha}) \) is determined. The interbond angle is varied in regular steps each time the bending energy contributions evaluated. The variation of the bending energy with interbond angle is plotted in a graph. The CS\(_2\) molecule has also been studied. For comparison an SO\(_2\) molecule also been used for investigation. The graphs are plotted. The spectroscopic data used for the analysis are shown in Table IV.1.

§4.3 Results and discussions

A glance at the results show a clear minimum value for the bending energy occurs for both the molecules which corresponds to an interbond angle \(180^\circ\). This confirms that their structures are linear. For comparison the curve for SO\(_2\) molecule is also plotted. For this the minimum bending energy corresponds
to an interbond angle 120°, indicating bent symmetric structure. The experimentally determined value for the interbond angle is 119.5±0.5°. The bending energy versus interbond angle for these molecules is given in Fig 4.1.

The above results confirm that the bending energy minimisation criterion can be applied to visualise the geometry of simple molecules with the help of available spectroscopic data and also assuming a known point group.
Table IV.1: Data table for CO\textsubscript{2} and CS\textsubscript{2} molecules

<table>
<thead>
<tr>
<th>Molecule</th>
<th>ω\textsubscript{1}</th>
<th>ω\textsubscript{2}</th>
<th>ω\textsubscript{3}</th>
<th>Λ\textsubscript{1}</th>
<th>Λ\textsubscript{2}</th>
<th>Λ\textsubscript{3}</th>
<th>Λ\textsubscript{4}</th>
<th>Δ\textsubscript{1}</th>
<th>Δ\textsubscript{2}</th>
<th>Δ\textsubscript{3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>^{14}\text{CO}_2</td>
<td>1354.4</td>
<td>672.2</td>
<td>2396.4</td>
<td>1.0819</td>
<td>0.2664</td>
<td>3.387</td>
<td>0.1249</td>
<td>0.22716</td>
<td>0.00704</td>
<td></td>
</tr>
<tr>
<td>^{12}\text{CO}_2</td>
<td>1354.4</td>
<td>636.23</td>
<td>2268.3</td>
<td>0.8195</td>
<td>0.23874</td>
<td>3.0346</td>
<td>0.1249</td>
<td>0.2291</td>
<td>0.00743</td>
<td></td>
</tr>
<tr>
<td>^{12}\text{CS}_2</td>
<td>671.4</td>
<td>398.6</td>
<td>1351.9</td>
<td>2.659</td>
<td>0.937</td>
<td>1.4205</td>
<td>0.3495</td>
<td>0.5698</td>
<td>0.01088</td>
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</tr>
<tr>
<td>^{14}\text{CS}_2</td>
<td>671.4</td>
<td>373.8</td>
<td>1455.5</td>
<td>2.659</td>
<td>0.824</td>
<td>1.2493</td>
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<td></td>
<td></td>
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</tr>
</tbody>
</table>

Table IV.2: Inter bond angle determined from Bending Energy considerations

<table>
<thead>
<tr>
<th>MOLECULE</th>
<th>INTER BOND ANGLE BASED ON V\textsubscript{1}, min</th>
<th>EXPERIMENTAL VALUE</th>
<th>REF</th>
</tr>
</thead>
<tbody>
<tr>
<td>^{12}\text{CO}_2</td>
<td>180°</td>
<td>180°</td>
<td>43</td>
</tr>
<tr>
<td>^{14}\text{CO}_2</td>
<td>180°</td>
<td>180°</td>
<td>43</td>
</tr>
<tr>
<td>^{12}\text{CS}_2</td>
<td>180°</td>
<td>180°</td>
<td>43</td>
</tr>
<tr>
<td>^{14}\text{CS}_2</td>
<td>120°</td>
<td>119.56±0.5°</td>
<td>41</td>
</tr>
</tbody>
</table>

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Fig 4 shows the variation of bending energy with inter bond angle for $CO_2$, $CS_2$, and $SO_2$.

X axis Inter bond angle (in degrees)

Y axis Bending energy ($V_\text{in cm}^{-1}$)