Bending Energy Minimisation Criterion for Molecular Geometry in XY₃ Pyramidal Systems

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A study of the variation of the vibrational potential energy contribution with interbond angles in XY₃ pyramidal molecules confirms the observation previously made for XY₂ bend symmetric systems that the actual equilibrium configuration lies in the premises of minimum \( V_{\text{bend}} \) and zero \( V_{\text{stretch-bend}} \).

An analysis of the variation of the vibrational potential energy with geometry in simple molecules can be of fundamental interest and a mathematical formalism for this purpose has been developed recently [1]. The plots of various contributions to the potential energy \( V \) with semi interbond angle \( \theta \) in XY₂ bend symmetric systems seem to suggest that the actual equilibrium configuration lies in the premises of minimum for \( V_{\text{bend}} \) and zero for \( V_{\text{bend-stretch}} \). Extension of the analysis to XY₃ pyramidal systems is discussed below.

XY₃ pyramidal molecules belong to the \( C_{3v} \) point group, have the vibrational representation \( T = 2A_1 + 2E \), and contributions to the potential energy come from stretching, bending, and different mutual interactions between the two. The recipe for plotting the potential energy contributions as a function of the semi interbond angle \( \theta \) is almost the same as given in the earlier work [1] except that here one has to deal with two vibrational species viz., \( A_1 \) and \( E \), both of order two (as against one vibrational species of order two and one vibrational species of order one viz., \( A_1 \) and \( B_1 \) in XY₂ bend symmetric systems).

Fortunately, there are a few XY₃ pyramidal molecules in the literature for which the interbond angles are uniquely fixed and the normal and isotopic frequencies have been exactly determined [2]. Moreover, these happen to be hydrides where the isotopic fre-

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Fig. 1. Variation of the vibrational potential energy with the semi interbond angle in SbH₃ molecule.

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quency shifts are comparatively large. This has enabled us to draw the $V - \theta$ plots for such molecules which verify the criterion of $V_{\text{bend}}$ minimum for the equilibrium configuration.

The results are given in Table 1 along with a typical plot in Figure 1. The values of interbond angles corresponding to the $V_{\text{bend}}$ minimum show even better agreement than in the case of $XY_2$ bend symmetric systems [1].

Table 1. Semi interbond angle determined from energy considerations.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Semi interbond angle</th>
<th>Experimental value [2]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$V_e = \text{min}$</td>
<td>$V_{\theta} = 0$</td>
</tr>
<tr>
<td>SbH$_3$, SbD$_3$</td>
<td>45.75° 46°</td>
<td>45.75°</td>
</tr>
<tr>
<td>AsH$_3$, AsD$_3$</td>
<td>45.25° 44°</td>
<td>46°</td>
</tr>
<tr>
<td>PH$_3$, PD$_3$</td>
<td>45.75° 44.75°</td>
<td>46.75°</td>
</tr>
<tr>
<td>NH$_3$, ND$_3$</td>
<td>53.6° 53.6°</td>
<td>53.5°</td>
</tr>
</tbody>
</table>