THE EQUIVALENCE OF THE METHYL GROUPS IN PUCKERED 3,3-DIMETHYL OXETANE

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The classical concept of structure which assigns definite bond lengths and angles is not always meaningful in flexible molecules.

- The molecular structure is not always unique:
  - Conformers identifiable as minima in the potential energy surface
  - Large amplitude vibrations connect the different minima
- It is sometimes more realistic to investigate the potential energy surface and the large amplitude motion dynamics
INTRODUCTION

*Ring-Puckering* and 3,3-dimethyloxetane.

\[ \phi_{\text{min}} = 17.5^\circ \]
INTRODUCTION

Ring-Puckering and 3,3-dimethyloxetane.

INTRODUCTION

3,3-DMO isotopologues in natural abundance

Ring atoms

$^{13}\text{C}_\alpha$ - Intensity 2% with respect to parent

$^{13}\text{C}_\beta$ - Intensity 1% with respect to parent

$^{18}\text{O}$ - Intensity 0.2% with respect to parent

The data are consistent with a slight non planar structure

## INTRODUCTION

### 3,3-DMO isotopologues in natural abundance

<table>
<thead>
<tr>
<th></th>
<th>$^{13}\text{C}_m^1$ 3,3-DMO</th>
<th>$^{13}\text{C}_m^3$3,3-DMO</th>
<th>$^{13}\text{C}_m^2$ 3,3-DMO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Predicted.</td>
<td>Obs.</td>
<td>Predicted.</td>
</tr>
<tr>
<td>A/MHz</td>
<td>5102.24</td>
<td>5088.938(11)</td>
<td>5075.46</td>
</tr>
<tr>
<td>B/MHz</td>
<td>3130.76</td>
<td>3138.7898(2)</td>
<td>3145.96</td>
</tr>
<tr>
<td>C/MHz</td>
<td>2790.27</td>
<td>2792.6970(2)</td>
<td>2794.25</td>
</tr>
<tr>
<td>Int (%)</td>
<td>1</td>
<td>2</td>
<td>1</td>
</tr>
</tbody>
</table>

Both $^{13}\text{C}_m^1$, and thus both methyl groups are equivalent

AIM

➢ To explain the equivalency of the methyl group $^{13}$C atoms

1. The ring puckering motion interchanges both methyl groups.

2. Calculation of the dynamics of this motion along its minimum energy path on the basis of theoretical computations

3. Prediction of the rotational parameters for the parent molecule and methyl group $^{13}$C isotopologues
METHODS

Isotopic substitution only affects to kinetic energy terms.

\[ H = T + V \]

Rotational constants  Vibrational Reduced Mass G Matrix
METHODS

Hamiltonian for ring puckering motion

- The potential energy function is symmetric
- It only contains even terms in powers of the ring-puckering coordinate.

\[ V(\phi) = a\phi^4 - b\phi^2 \]

- It is not affected by isotopic substitution.
METHODS

Hamiltonian for ring puckering motion

\[ H_v = - \frac{\hbar^2}{2} \mathbf{p} \cdot \mathbf{G} \mathbf{p} + V \]

\[ H(\phi) = - \left( \frac{\hbar^2}{2} \right) \left( \frac{d}{d\phi} \right) G_\phi(\phi) \left( \frac{d}{d\phi} \right) + a\phi^4 + b\phi^2 \]

\[ G_\phi(\phi) = \frac{1}{\mu_\phi} \]

\[ = G^{(0)}_\phi + G^{(1)}_\phi \phi + G^{(2)}_\phi \phi^2 + G^{(3)}_\phi \phi^3 + G^{(4)}_\phi \phi^4 + G^{(5)}_\phi \phi^5 + G^{(6)}_\phi \phi^6 \]

\[ G^{(i)}_\phi = \frac{1}{i!} \left( \frac{d^i G_\phi(\phi)}{d\phi} \right)_{\phi=0} \]
METHODS

Rotational constants prediction.

- Dependence with vibrational coordinate:

\[ B(X) = B^0 + B^{(1)}X + B^{(2)}X^2 + B^{(3)}X^3 + B^{(4)}X^4 + B^{(5)}X^5 + B^{(6)}X^6 \]

\[ B^{(i)} = \frac{1}{i!} \left( \frac{d^i B}{dX^i} \right)_{X=0} \]

- Dependence with vibrational quantum number:

\[ B_v = B^{(0)} + B^{(1)} < X^1 >_v + B^{(2)} < X^2 >_v + B^{(3)} < X^3 >_v + B^{(4)} < X^4 >_v \]
RESULTS

Computational method selection (B3LYP, MP2, CCSD)

- Basis sets: 6-311(d,p), 6-311++G(d,p), 6-311++G(2d,p), cc-pVDZ y cc-pVTZ.
- CCSD/6-311++G(d,p)
RESULTS

CCSD/6-311++G(d,p), $^{13}\text{C}_m$ rotational constants
RESULTS

CCSD/6-311++G(d,p), $^{13}C_m$ Reduced mass
CONCLUSION

- Both methyl group $^{13}$C of 3,3-DMO are effectively equivalent.
- This conclusion seems no to be in agreement with our conventional way to think in the molecular structure.
- Instead it easily reached from consideration of the ring-puckering potential energy function and its dynamics to predict the spectroscopic parameters.
Thank you for your attention!