LAM’s LAMs

Low barrier methyl internal rotation in 3-pentyn-1-ol
as observed by microwave spectroscopy

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Motivation

- Many methyl internal rotation problems, but only few very low barrier cases ($V_3 < 30 \text{ cm}^{-1}$), e.g. acetamide ($V_3 \approx 25 \text{ cm}^{-1}$).\(^1\)

- Why?
  - Low barriers are hard to calculate
  - Rotational spectra are hard to assign and to fit
  - No simple intuitive rules to predict the barrier height
  - $V_3$ and $V_6$ components might become comparable in magnitude \(\rightarrow\) complicates the spectral analysis (e.g. meta-fluorotoluene\(^2\) or trans-methyl nitrite\(^3\))

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Low barrier ($V_3 < 10 \text{ cm}^{-1}$) cases

Triple bond – a low barrier guarantee

\[
\text{CH}_3 - \text{CH}_3
\]
Ethane
about 1000 cm\(^{-1}\)

\[
\text{CH}_3 - \text{C} \equiv \text{C} - \text{CH}_3
\]
Dimethylacetylene
almost free internal rotation

\[
\text{CH}_3 - \text{C} \equiv \text{C} - \text{R}
\]
Propynyl methyl group
< 10 cm\(^{-1}\)
Low barrier ($V_3 < 10 \text{ cm}^{-1}$) cases

$$\text{CH}_3-\text{C}≡\text{C}-\text{R}$$

<table>
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<tr>
<th>Compound</th>
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<th>3rd</th>
<th>4th</th>
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3-Pentyn-1-ol

\[ \text{CH}_3-C\equiv C-R \]

- \( R = \text{CH}_2\text{CH}_2\text{OH} \)
- The conformational landscape is completely determined by \( \varphi_1 \) and \( \varphi_2 \) (rotation about the \( C_7-C_{10} \) and \( C_{10}-O_{13} \) bonds)
- MP2/6-311++G(d,p) level of theory
- \( \varphi_3 = (C_{10}, C_7, C_1, H_2) \): \( V_3 \) barrier of the propynyl methyl group
Conformational analysis

- $(\varphi_1,\varphi_2), (-\varphi_1,-\varphi_2)$: same potential energy due to the linearity of the CH$_3$CCCH$_2$ moiety $\rightarrow \frac{1}{2}$ of the calculations
## Conformational analysis

<table>
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<th></th>
<th>ΔE</th>
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<th>C</th>
<th>μ_α</th>
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Microwave spectrum

Molecular beam FT microwave spectroscopy, 2 – 26.5 GHz

High resolution
- Line widths in the range 10 – 25 kHz → measurement accuracy better than 2 kHz
- Doppler effect; carrier gas: helium

Broadband scan
- Series of automatically recorded spectra in the high resolution mode
- 250 kHz step width, 50 decays per step
- Frequency range : 11.0 – 17.0 GHz
# Molecular parameters

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<tr>
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<th>Fit BELGI</th>
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<tr>
<td>B</td>
<td>GHz</td>
<td>1.68514380(81)</td>
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$^a$ Parameters

$^b$ Calculated

$^c$ Estimated from spectrum parameter $F_0$
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Molecular parameters

- **BELGI-C₁** considers the interaction between different torsional states and includes more higher order terms.
- **XIAM**: well-suited for the assignment step (fast, user-friendly, parameters with physical meaning and small correlations).
- Larger **XIAM** deviations in other internal rotation problems with higher barriers, i.a. ethyl acetate (101.606(23) cm⁻¹, 85.3 kHz), allyl acetate (98.093(12) cm⁻¹, 54.0 kHz), vinyl acetate (151.492(34) cm⁻¹, 92.3 kHz)

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# Molecular parameters

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$^a$ Represents the parameter being fit.

$^b$ Standard deviation.

$^c$ Standard deviation

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3-Pentyn-1-ol vs. 3-Butyn-1-ol

Structure comparison