INVESTIGATION OF PURE ROTATION OF ETHYNYLBENZONITRILE ISOMERS USING CHIRPED-PULSE W-BAND SPECTROSCOPY

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Cyano-substituted molecules: an interesting family

Some already detected in interstellar medium

Benzonitrile (PhCN) \(^1\)

\[
\begin{array}{c}
\text{PhCN} \\
\includegraphics[width=0.2\textwidth]{benzonitrile.png}
\end{array}
\]

1-..2- cyanonaphthalene (C_{11}H_{7}N) \(^2\)

\[
\begin{array}{c}
\text{C_{11}H_{7}N} \\
\includegraphics[width=0.2\textwidth]{cyanonaphthalene.png}
\end{array}
\]

Some already studied by our team:

Phenylpropionitrile (PhC_{3}N)

\[
\begin{array}{c}
\text{PhC_{3}N} \\
\includegraphics[width=0.2\textwidth]{phenylpropionitrile.png}
\end{array}
\]

Investigation of 3 isomers of PhC$_3$N: 2-, 3-, 4-ethynylbenzonitrile (ETB)

DFT Geometry Optimization
($\omega$B97XD/cc-pVQZ, harmonic + scaled$^2$)

<table>
<thead>
<tr>
<th>Molecules</th>
<th>$A$ (MHz)</th>
<th>$B$ (MHz)</th>
<th>$C$ (MHz)</th>
<th>$\mu$ (Debye)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$a$</td>
<td>$b$</td>
<td>$c$</td>
<td></td>
</tr>
<tr>
<td>2-ETB</td>
<td>2002</td>
<td>1329</td>
<td>799</td>
<td>3.9 -2.3 0</td>
</tr>
<tr>
<td>3-ETB</td>
<td>2697</td>
<td>903</td>
<td>677</td>
<td>3.6 2.5 0</td>
</tr>
<tr>
<td>4-ETB</td>
<td>5647</td>
<td>705</td>
<td>627</td>
<td>-4.3 0 0</td>
</tr>
</tbody>
</table>

Acquisition set-ups available at ISMO

- **Chirped-pulse millimeter-wave spectrometer**
  - 75 - 110 GHz

- **Room temperature flow cell**
- **DC discharge + flow cell**
- **RF discharge + flow cell**
- **H abstraction + flow cell**
- **DC discharge + supersonic jet**

- **Frequency-multiplication-based (sub)millimeter-wave spectrometer**
  - 75 - 900 GHz
Acquisition set-ups available at ISMO

Chirped-pulse millimeter-wave spectrometer
75 - 110 GHz

Room temperature flow cell
DC discharge + flow cell
RF discharge + flow cell
H abstraction + flow cell
DC discharge + supersonic jet

Frequency-multiplication-based (sub)millimeter-wave spectrometer
75 - 900 GHz
**W-band Chirped-Pulse Spectroscopy**

**Characteristics:**
- Frequency range: 75-110 GHz
- Commercial (BrightSpec)
- Sequential chirp, 30 MHz segments (HDR mode)
- 1 million averages within 2h
- Pulse length: from 0.1 to 0.5 µs
- FID length: up to 4 µs

Laboratory acquisition

2-ETB

Settings:
- 1 million averages
- Pressure: $1.4 \times 10^{-3}$ mbar
- $\text{SNR}_{\text{max}} \approx 140$
- Pulse Length: 0.5 $\mu$s

3-ETB

Settings:
- 1 million averages
- Pressure: $1.2 \times 10^{-3}$ mbar
- $\text{SNR}_{\text{max}} \approx 90$
- Pulse Length: 0.25 $\mu$s

4-ETB

Settings:
- 1 million averages
- Pressure: $2.2 \times 10^{-3}$ mbar
- $\text{SNR}_{\text{max}} \approx 130$
- Pulse Length: 0.5 $\mu$s
Laboratory acquisition

2-ETB

Settings:
- 1 million averages
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- $\text{SNR}_{\text{max}} \approx 130$
- Pulse Length: 0.5 µs
Graphical exploitation of the spectra: principle

PGOPHER\textsuperscript{1}:
Modelize and fit spectra using a set of constants

Loomis-Wood for Windows, Asymmetric top (LWWa)\textsuperscript{2}:
Graphical assignment of transitions

Graphical exploitation of the spectra: principle

1. **PGOPHER**
2. **LWWa**

- Quantum Chemical Calculations

- Set of rotational constants
Graphical exploitation of the spectra: principle

**PGOPHER**

**LWWa**

Quantum Chemical Calculations

Set of rotational constants

→

Predict energy levels
Graphical exploitation of the spectra: principle

- **Export assignments**
- **Graphical assignment of the experimental frequency to the transition**
- **Predict the frequency of transitions**

Quantum Chemical Calculations

- **Set of rotational constants**
- **Predict energy levels**

**PGOPHER**

**LWWa**
Graphical exploitation of the spectra: principle

**PGOPHER**

- Fit experimental observations
- Export assignments

**LWWa**

- Quantum Chemical Calculations
- Set of rotational constants
- Predict energy levels
- Predict the frequency of transitions

Graphical assignment of the experimental frequency to the transition
Exploitation of 4-ETB spectrum: starting point

\[ \Delta J = +1 \quad \Delta K'_c = 0 \quad \Delta K_a = +1 \quad \Delta K''_c = 0 \]

\[ J = 150 \quad J = 110 \quad J = 85 \quad J = 58 \]

-250 MHz from prediction
Exploitation of 4-ETB spectrum: finish line?

\[ \Delta J = +1 \quad dK'_c = 0 \quad \Delta K_a = +1 \quad dK''_c = 0 \]
Exploitation of 4-ETB spectrum: finish line?

Experiment

Simulation

Frequency (GHz)
Exploitation of 4-ETB spectrum: What’s left?

First vibrational excited states:

\[ \nu_{26} = 1 \, @ \, 74 \, \text{cm}^{-1} \] (oop bending)

\[ \nu_{39} = 1 \, @ \, 117 \, \text{cm}^{-1} \] (ip bending / wagging)

\[ \nu_{26} = 2 \, @ \, 148 \, \text{cm}^{-1} \]

DFT Frequency calculation
\((\omega B97XD/cc-pVQZ, \text{ anharmonic})\)
Exploitation of 4-ETB spectrum: What’s left?

First vibrational excited states:

\[ \nu_{26} = 1 \]
\[ \nu_{39} = 1 \]
\[ \nu_{26} = 2 \]
Exploitation of 4-ETB spectrum: What’s left?

\[ \nu_{26} = 1, \quad \nu_{39} = 1, \quad \nu_{26} = 2 \]
Results

4-ETB

- 20 743 lines assigned
- 4 states investigated
- Error ~ 0.046 MHz

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</tr>
<tr>
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<td>5647</td>
<td>5646</td>
<td>705</td>
</tr>
<tr>
<td>v_{26}=1</td>
<td>5529</td>
<td>5542</td>
<td>708</td>
</tr>
<tr>
<td>v_{29}=1</td>
<td>5732</td>
<td>5747</td>
<td>708</td>
</tr>
<tr>
<td>v_{26}=2</td>
<td>5425</td>
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Rk: scaled harmonic constants for GS, anharmonic constants for ES (scaled on GS)
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*Rk: scaled harmonic constants for GS, anharmonic constants for ES (scaled on GS)*

2-ETB
- 5 000 lines assigned
- Only ground state investigated
- Work in progress

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<td>2002</td>
<td>2027</td>
<td>1329</td>
</tr>
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3-ETB
- 14 036 lines assigned
- Only ground state investigated
- Work in progress

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<td>2705</td>
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- Assignment of lines to vibrational excited states of 2 and 3-ETB
- Interstellar searches
Acknowledgements

Collaborators:

Institut des Sciences Moléculaires d’Orsay, France
Olivier Pirali
Marie-Aline Martin-Drumel

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Kelvin Lee

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