Laboratory data in support of astronomical detection of molecules

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Rotational spectroscopy

- The research of molecules in space is essential to understand the chemistry of the Universe
- Astrochemical models are based on:
  - identification of the molecules
  - abundance
  - isotopic variations and other details
- Rotational spectroscopy is one of the main techniques for observation and identification of molecules in space

(*including: tautomers; isotopomers; conformers; vibrational and electronic excited states; ionized species)
Molecules in space
(184+deuterated+unconfirmed)

Line surveys in the 1 mm atmospheric window toward two massive young stellar objects, I(N) (top) and I (bottom), in the NGC 6334 star-forming region.

If \( P_0 \gg P_b \text{ (ca. }10^5\text{)} \)

**Supersonic expansion**

- Cooling of the degrees of freedom
- Stop of the intermolecular collisions
- Depopulation of the excited vibrational states
- More intense, more simple rotational spectra
- Longer lifetime of kinetically unstable species

**Mix of sample (ca. 1-2%) in rare gas**

- \( P_0 = 0.2 - 4 \text{ bar} \)
- \( P_b \approx 10^{-6} \text{ bar} \)

**Zone of silence**

**Direction of flux**
Free Jet Absorption Millimeter Wave spectrometer (FJ-AMMW, 52-74.4 GHz)

- Sweep rate: 10 GHz per day
- Sensitivity: $10^{-7}$ - $10^{-8}$ cm$^{-1}$
- Resolution: 200 kHz
- Accuracy: < 50 kHz

- Typical conditions:
  - $P_0$=200-500 mbar, $P_b$=0.001 mbar
  - $T_{\text{rot}} \approx 10$ K, $T_{\text{sample}}$ up to 160°
  - Jet length: 16 cm

- C. Calabrese et al. JPC-A 117 (2013) 13712
Molecular Beam Fourier Transform MW spectrometer (MBFTMW, 6-18 GHz)

- Sweep rate: 0.2 GHz per day
- Sensitivity: $10^{-11} - 10^{-12}$ cm$^{-1}$
- Sub Doppler resolution: few kHz
- Accuracy: $< 3$ kHz
- $T_{rot} \approx 1$ K

- Operated according to: Jens-Uwe Grabow, Habilitationsschrift, Universität Hannover (2004)
Experimental Perspective: MBFTMW + Laser ablation/desorption

- Laser Nd-YAG (Quanta Systems) 532 nm 10 ns:
- Vaporization without decomposition of solid compounds and biomolecules
- Vaporization of metals
Atacama Large Millimeter/submillimeter Array
ALMA: 31 - 950 GHz

- High sensitivity and resolution
- The interpretation of the plethora of data that will be obtained requires a large number of laboratory data

Examples of transitions of propyl cyanide toward the northern hot core of Sgr B2(N):
- **Black**: continuum-subtracted spectrum observed with ALMA
- **Green**: preliminary model including all identified molecules
- **Red**: synthetic spectra of i-PrCN and n-PrCN

- Belloche et al. Science 345 (2014) 1584
- Müller et al. J. Mol. Spectr. 267 (2011) 100
- Durig & Li, J. Mol. Struct. 21 (1974) 289
Polycyclic Aromatic Hydrocarbon Molecules

Microwave spectrum of fluorene:
Fluorene and fluorenone: infrared spectra prediction (B3LYP/cc-pVTZ)

Irreducible representations of the fundamental vibrational normal modes ($I'_v$) and of the 1:1 combination bands ($I'_c$):

<table>
<thead>
<tr>
<th></th>
<th>9HF</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th>F9O</th>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>$I'_v$</td>
<td>22 $a_1$</td>
<td>10 $a_2$</td>
<td>11 $b_1$</td>
<td>20 $b_2$</td>
<td></td>
<td>$I'_c$</td>
<td>21 $a_1$</td>
<td>9 $a_2$</td>
<td>10 $b_1$</td>
<td>20 $b_2$</td>
</tr>
<tr>
<td>22 $a_1$</td>
<td>231 $a_1$</td>
<td>220 $a_2$</td>
<td>242 $b_1$</td>
<td>440 $b_2$</td>
<td></td>
<td>21 $a_1$</td>
<td>210 $a_1$</td>
<td>189 $a_2$</td>
<td>210 $b_1$</td>
<td>420 $b_2$</td>
</tr>
<tr>
<td>10 $a_2$</td>
<td>45 $a_1$</td>
<td>110 $b_2$</td>
<td>200 $b_1$</td>
<td></td>
<td></td>
<td>9 $a_2$</td>
<td>36 $a_1$</td>
<td>90 $b_1$</td>
<td>180 $b_1$</td>
<td></td>
</tr>
<tr>
<td>11 $b_1$</td>
<td>55 $a_1$</td>
<td>220 $a_2$</td>
<td></td>
<td></td>
<td></td>
<td>10 $b_1$</td>
<td>45 $a_1$</td>
<td>200 $a_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20 $b_2$</td>
<td></td>
<td>190 $a_1$</td>
<td></td>
<td></td>
<td></td>
<td>20 $b_2$</td>
<td></td>
<td></td>
<td></td>
<td>190 $a_1$</td>
</tr>
<tr>
<td>$I'_c$</td>
<td>521 $a_1$</td>
<td>440 $a_2$</td>
<td>442 $b_1$</td>
<td>550 $b_2$</td>
<td></td>
<td>$I'_c$</td>
<td>481 $a_1$</td>
<td>389 $a_2$</td>
<td>390 $b_1$</td>
<td>510 $b_2$</td>
</tr>
</tbody>
</table>
Acrylic acid

- Already detected in the interstellar medium or circumstellar shells:
  - formic acid $\text{H-COOH}$
  - acetic acid $\text{CH}_3\text{-COOH}$
  - acrylonitrile $\text{CH}_2=\text{CH-CN}$
  - acrolein $\text{CH}_2=\text{CH-CHO}$

- A possible formation pathway of acrylic acid in interstellar ices containing CH4 and CO2 could be:
  - $\cdot\text{H} + \text{CO}_2 \rightarrow \cdot\text{COOH}$
  - $\cdot\text{CH}=\text{CH}_2 + \cdot\text{COOH} \rightarrow \text{CH}_2\text{CHCOOH}$

$\Delta E \approx 60 \text{ cm}^{-1}$

$s\text{-trans aa}$
- $\mu_a 0.66 (10) \text{ D}$
- $\mu_b 1.35 (5) \text{ D}$

$s\text{-cis aa}$
- $\mu_a 1.70 (4) \text{ D}$
- $\mu_b 1.10 (5) \text{ D}$

Acrylic acid

Laboratory rotational spectrum of acrylic acid and its isotopologues in the 6–18.5 GHz and 52–74.4 GHz frequency ranges


ABSTRACT

In order to facilitate the detection of acrylic acid in space, for which a possible mechanism of formation is proposed, we extended the measurements of the rotational spectrum of this molecule to the 6–18.5 GHz (three-distant Fourier transform) and 52–74.4 GHz (frequency domain) ranges in supersonic expansions. 77 new lines were assigned to the s-cis conformer and 83 new lines to the s-trans conformer. In addition, the rotational spectra of the three singly 13C isotopologues have been measured in natural abundance for both conformers. High resolution measurements of the nuclear quadrupole and hyperfine transitions allowed for the determination of the deuterium nuclear quadrupole coupling constants. All the spectroscopic experimental parameters were compared to the ones obtained with quantum chemical methods at the MP2(Sing-ci-pVTZ and B3LYP/Sing-ci-pVTZ levels of calculation).

s-cis acrylic acid

$\alpha_{\text{max}} = 6.01 \times 10^{-2}$

$T=10K$

$\alpha_{\text{max}} = 2.23 \times 10^{-3}$

$T=300K$
Acrylonitrile (vinyl cyanide) - water

MP2/6-311++G** results:

\[ \Delta H_0 = 17.8 \text{ kJ/mol} \]
\[ \Delta H_0 = 15.5 \text{ kJ/mol} \]
\[ \Delta H_0 = 14.7 \text{ kJ/mol} \]

A = 5225 MHz       A = 6669 MHz       A = 27674 MHz
B = 3517 MHz       B = 2701 MHz       B = 1241 MHz
C = 2105 MHz      C = 1924 MHz       C = 1196 MHz

\[ \Delta H_0 = 5282.022 (2) \text{ MHz} \]
\[ \Delta H_0 = 3422.840 (3) \text{ MHz} \]
\[ \Delta H_0 = 2074.858 (4) \text{ MHz} \]

\[ J = 8.74 (1) \text{ kHz} \]
\[ J = -4.00 (3) \text{ kHz} \]
\[ K = 15.79 (6) \text{ kHz} \]
\[ d_1 = -4.089 (2) \text{ kHz} \]
\[ d_2 = -0.758 (2) \text{ kHz} \]

\[ \chi_{aa} = -0.38 (10) \text{ MHz} \]
\[ \chi_{bb} = -1.47 (9) \text{ MHz} \]
\[ \chi_{cc} = 1.84 (9) \text{ MHz} \]

Experimental results:

\[ M_{cc} = -0.12 \text{ uÅ}^2 \text{ H}_2 \text{O} \]
\[ M_{cc} = -0.13 \text{ uÅ}^2 \text{ H}_{18}\text{OH} \]
\[ M_{cc} = -0.08 \text{ uÅ}^2 \text{ D}_B \text{OH}_F \]
\[ M_{cc} = -0.12 \text{ uÅ}^2 \text{ D}_2 \]

\[ \Delta H_0 = 2.406 \text{ Å} \]
\[ \Delta H_0 = 2.330 \text{ Å} \]
\[ \Delta H_0 = 2.583 \text{ Å} \]
\[ \Delta H_0 = 2.572 \text{ Å} \]

\[ \Delta H_0 = 2.116 \text{ Å} \]
(1S,2S)-trans-1,2-Cyclohexanediol

B3LYP/6-31G* PES

<table>
<thead>
<tr>
<th>$\Delta E_01$ / MHz</th>
<th>1278.88 (4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A0/A1 / MHz</td>
<td>2793.655/6.671 (1)</td>
</tr>
<tr>
<td>B0/B1 / MHz</td>
<td>1946.339/3.07 (2)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>C / MHz</th>
<th>1238.933 (4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DJ / kHz</td>
<td>0.040 (9)</td>
</tr>
<tr>
<td>DJK / kHz</td>
<td>0.19 (2)</td>
</tr>
<tr>
<td>DK / kHz</td>
<td>0.26 (1)</td>
</tr>
<tr>
<td>d1 / kHz</td>
<td>-0.056 (8)</td>
</tr>
<tr>
<td>d2 / kHz</td>
<td>0.011 (9)</td>
</tr>
</tbody>
</table>

cm$^{-1}$
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Organic and prebiotic molecules

Uscendo: primo poster a destra