MILLIMETERWAVE SPECTROSCOPY OF ETHANIMINE AND PROPANIMINE AND THEIR SEARCH IN ORION

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Motivation

• The aldimines are important to understand amino acids formation process as they appear in reaction scheme of Strecker-type synthesis.

• Methanimine (CH$_2$NH) was detected in 1973 (Godfrey et al., ApJL, 13, 119 1973)

• Beginning of the projet was studying ethanimine (CH$_3$CHNH) in 02/2013. But at the same time it was detected in SgrB$_2$ with Primos survey (Loomis et al., ApJL, 765, L9, 2013)

• We decided to study the next one in the serie: propanimine (CH$_3$CH$_2$CHNH)
Synthesis method

• We did not used the production method from previous works
  – Ethanimine - Lovas et al. : Pyrolysis of \((\text{CH}_3\text{CHNH})_3\)
  – Ethanimine – Loomis et al.: Electric discharge of \(\text{CH}_3\text{CN}\) and \(\text{H}_2\text{S}\)

• We used a synthesis method to obtain pure samples. E,Z-Ethanimine and E,Z Propanimine has been prepared in the following way (Guillemin, et al. *Tetrahedron*, 44, 4431, 1988):
  – The precursors 2-aminopropionitile or 2-aminobutyronitile (5 mmol), were synthesized
  – They have been slowly vaporized in a reactor containing dry KOH in powder (50 g) in half section and heated to 85-100°C.
  – A trap cooled at -80°C removed high boiling compounds and the gaseous flow was then trapped at nitrogen temperature.

Dry KOH

Precursors:
- 2-aminopropionitile
- 2-aminobutyronitile

Water circulation at 85°C

Cooled trap at -80°C

a- Ethanimine
b- Propanimine
Synthesis method

- Ethanimine: was trapped after the synthesis in Rennes, evaporated in Lille at -78°C then introduced in the pyrex cell of the spectrometer in slow flow mode.
- Propanimine was found to be less stable: it is a surprise. Logically stability increase with complexity of the molecule. 3 trials were necessary to record the spectra:
  - 05/2013: like ethanimine it was trapped after the synthesis in Rennes, evaporated in Lille at -65/-68°C. Mistrial
  - 01/2014: pyrolysis in situ at 650°C. Beautiful spectra of ... Ethyl cyanide!
  - 04/2014: The synthesis was done directly before the cell – Success. More difficult for long time recording...
At recording time, Fast DDS « solid state » spectrometer was not ready (see talk RI06 ISMS 2015)

Ethanimine:
- Fast DDS BWO’s spectrometer 110-170 GHz (1ms per point/step: 30 kHz).
- Usual solid state devices (35 ms per point/step: 36 kHz), 36GHz were recorded in the 238-300 GHz range

Propanimine:
- Our BWO’s mixer was down: not possible to use fast spectrometer
- Spectra was recorded only in « slow motion » mode: 110 GHz were recorded in the 150-465 Ghz.
- Due tu in situ synthesis, in order to speed up recording: « large » frequency step was used (120 to 210 kHz). Signal to noise is not that great....
Propanimine: CH$_3$CH$_2$CHNH

- No spectroscopic studies available up to now
- 2 conformers E and Z

E$_{\text{conf}}$
- $\mu_a = 1.12$ D
- $\mu_b = 0.75$ D
- $\mu_c = 1.57$ D

Z$_{\text{conf}}$
- $\Delta E^a = 264.25$ cm$^{-1}$
- $\mu_a = 2.49$ D
- $\mu_b = 1.00$ D
- $\mu_c = 0.00$ D

- Z is the less stable but Z$_{\text{conf}}$ $\mu_a$ dipole moment is two times bigger than E$_{\text{conf}}$ one
  - At lab temperature (Boltzmann factor is 0.28 for Z$_{\text{conf}}$: intensities are the same
  - At ISM temperature (150-250 K): both should be detected

$^a$ab initio calculation at B3LYP/6-311G++(3df,2pd) level including ZPE correction
Propanimine spectra

8.43 GHz ≈ B+C

R branch J = 19 - 18

E Conf

Z Conf

158 GHz

161.5 GHz

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• At high frequency, Q branch spectra for E conformer
• Due to small dipole moment along b axis, Only few $\mu_b$ line could be assign unambiguously for Z conformer
# Propanimine results

<table>
<thead>
<tr>
<th>Parameters (MHz)</th>
<th>E conf</th>
<th>Z conf</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Red A</td>
<td>Red S</td>
</tr>
<tr>
<td></td>
<td>24185.2684(54)</td>
<td>24185.2383(13)</td>
</tr>
<tr>
<td>B</td>
<td>4292.3639(11)</td>
<td>4292.55416(32)</td>
</tr>
<tr>
<td>C</td>
<td>4156.7893(11)</td>
<td>4156.59879(32)</td>
</tr>
<tr>
<td>(N_{\text{lines}}/N_{\text{param}})</td>
<td>585/24</td>
<td>585/25</td>
</tr>
<tr>
<td>(J_{\text{max}}/K_{a\text{ Max}})</td>
<td>73/21</td>
<td>73/21</td>
</tr>
<tr>
<td>(\sigma_{\text{fit}}) (in kHz)</td>
<td>146.1</td>
<td>39.3</td>
</tr>
</tbody>
</table>

Necessary to use reduction S
Ethanimine: \( \text{CH}_3\text{CHNH} \)

- **Stark spectroscopy**
  - up to 140 GHz: \( E_{\text{conf}} \) g.s., \( \nu_t = 1 \) and \( Z_{\text{conf}} \) g.s. (Lovas et al., J. Chem. Phys. 72, 4964, 1980)
  - from 18 to 76 GHz: \( Z_{\text{conf}} \) g.s. and \( \nu_t = 1 \) (Brown et al., AJCh, 33, 1, 1980)

- **Zeeman MW** (Krause et al., Z. Naturforsch. 46, 785, 1991)

- **CP-FTMW measurements** from 6.5 to 40 GHz (Loomis et al., ApJL. 765, L9, 2013)

\[
E_{\text{conf}} \text{ (cis)} \\
\mu_a = 0.834 \text{ D} \\
\mu_b = 1.882 \text{ D}
\]

\[
Z_{\text{conf}} \text{ (trans)} \\
\Delta E^a = 282 \text{ cm}^{-1} \\
\mu_a = 2.380 \text{ D} \\
\mu_b = 0.445 \text{ D}
\]

\( Z_{\text{conf}} \) spectra could be more intense even at ISM temperature

\(^a\text{ab initio calculation at MP2/aug-cc-pvqz level including ZPE correction}\)
Ethanimine spectra

- Ethanimine exhibits large amplitude: internal rotation of methyl group.

- Methyl group is $C_3v$ symmetry

  $$V(\alpha) = \frac{V_3^3}{2}(1 - \cos 3\alpha) + \frac{V_6^6}{2}(1 - \cos 6\alpha) + ...$$

- Due to tunnel effect, the transitions are splitted into two components: A and E

- Even if the barriers have medium values: $\approx 500 \text{ cm}^{-1}$. The analysis of the spectra was not obvious for 2 reasons:
  - Strong coupling between torsion and rotation: $\rho = 0.28$. This as high as acetaldehyde.
  - not possible to fit A lines with Watson’s Hamiltonian
  - not possible to use XIAM for $K_a > 4$
Ethanimine spectra

- Usually in millimeterwave spectra $^{14}$N nuclear electric quadrupole hyperfine splittings are no observed with doppler limited resolution or only for high $K_a$ values. (cf. Ethyl cyanide)
- These splittings are enhanced by internal rotation and should be take into account, especially for $\mu_b$ type lines.
- Due to interaction with internal rotationn the hyperfine analysis needs specific code. Test version of « RAM36-code » from V. Ilyushin (Karkhov-Ukraine) which include treatment of hyperfine components was used (Ilyushin et al. J. Mol. Spectrosc. 259, 26, 2010)
Ethanimine spectra

R_{branch} J=8-7

- $\mu_a$: hyperfine quadrupole structure for high Ka Values and low J
- $\mu_b$: bigger splitting and $K_a$ is only 1..

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Ethanamine spectra

- Still splittings at 300 GHz and J=50

A: $31_{2,29}-31_{1,30}$

F: $50_{5,45}-50_{4,46}$

0.55 MHz

1.35 MHz

R$_{\text{branch}}$ J=16-15

$A$ 28$_{3,25}$-27$_{4,24}$ $E$

$31_{2,29}-31_{1,30}$

$24_{2,23}-24_{1,24}$

$A$ 50$_{5,45}$-50$_{4,46}$

$E$

294.6 GHz

297.0 GHz

294 665 MHz

295205 MHz

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### Ethanimine results

<table>
<thead>
<tr>
<th></th>
<th>E conformer</th>
<th></th>
<th>Z conformer</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>This work</td>
<td>Lovas + Loomis</td>
<td>This work</td>
<td>Lovas + Loomis</td>
</tr>
<tr>
<td><strong>A (GHz)</strong></td>
<td>52.83537(29)</td>
<td>52.81854(45)</td>
<td>49.5815(48)</td>
<td>49.666(13)</td>
</tr>
<tr>
<td><strong>B (GHz)</strong></td>
<td>10.07601(15)</td>
<td>10.08613(45)</td>
<td>10.15214(14)</td>
<td>10.1490(40)</td>
</tr>
<tr>
<td><strong>C (GHz)</strong></td>
<td>8.70427(13)</td>
<td>8.6956781(24)</td>
<td>8.644814(12)</td>
<td>8.64485(19)</td>
</tr>
<tr>
<td><strong>F (GHz)</strong></td>
<td>182.85(51)</td>
<td>219.764</td>
<td>225.6(27)</td>
<td>217.972</td>
</tr>
<tr>
<td><strong>ρ</strong></td>
<td>0.308606(23)</td>
<td>0.306205(31)</td>
<td>0.286090(76)</td>
<td>0.2861(33)</td>
</tr>
<tr>
<td><strong>V₃ (cm⁻¹)</strong></td>
<td>451.9(15)</td>
<td>557.970(24)</td>
<td>535.6</td>
<td>515.0(11)</td>
</tr>
<tr>
<td><strong>2Dₐₜ (MHz)</strong></td>
<td>-7226.50(29)</td>
<td>-7224.8(53)</td>
<td>-7134.4(16)</td>
<td>-7101(46)</td>
</tr>
<tr>
<td><strong>Xₐₐ</strong></td>
<td>1.066(16)</td>
<td>1.040(13)</td>
<td>-3.7628(98)</td>
<td>-3.726(22)</td>
</tr>
<tr>
<td><strong>Xₐₜ</strong></td>
<td>-4.127(10)</td>
<td>-4.1161(86)</td>
<td>0.605(23)</td>
<td>0.585(57)</td>
</tr>
<tr>
<td><strong>Nₚₐᵣₙ/Nₗᵢₙ</strong></td>
<td>27/829</td>
<td>13/108</td>
<td>18/270</td>
<td>12/63</td>
</tr>
<tr>
<td><strong>Jₘₐₓ, Kₐₘₐₓ</strong></td>
<td>50/13</td>
<td>13/4</td>
<td>26/15</td>
<td>7/6</td>
</tr>
<tr>
<td><strong>σₕᵢₙ (kHz)</strong></td>
<td>39.3</td>
<td>95.7</td>
<td>44.7</td>
<td>127.5</td>
</tr>
</tbody>
</table>
Conclusions

• Spectra of ethanimine was extended in the millimeterwave domain, the analysis include the treatment of the internal rotation and the quadrupole hyperfine structure

• First spectroscopic study of propanimine

• These works permit to generate accurate line list for these two molecules in the millimeter wave domain

• Their searches are actually in progress in Orion
Acknowledgements

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