MILLIMETERWAVE SPECTROSCOPY OF ETHANIMINE AND PROPANIMINE AND THEIR SEARCH IN ORION

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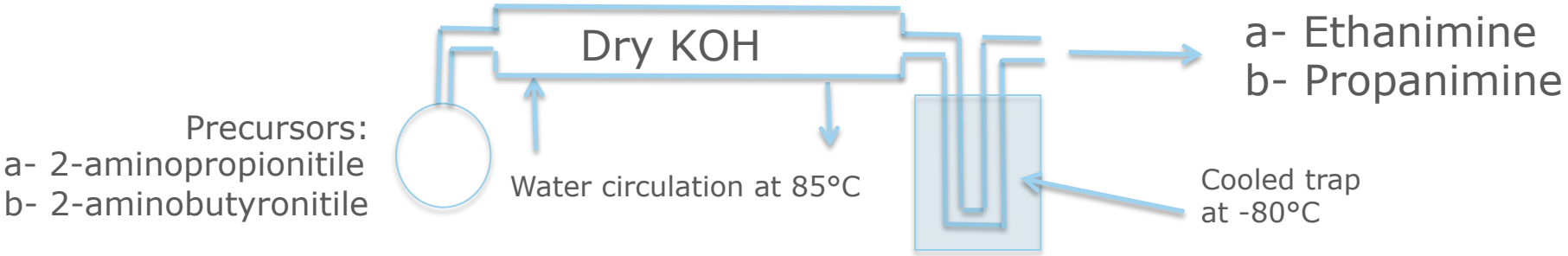
Motivation

- The aldimines are important to understand amino acids formation process as they appear in reaction scheme of Strecker-type synthesis.
- Methanimine (CH_2NH) was detected in 1973 (Godfrey et al., ApJL, 13, 119 1973)
- Beginning of the projet was studying ethanimine (CH_3CHNH) 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_3CH_2CHNH)

Synthesis method

- We did not used the production method from previous works
  - Ethanimine - Lovas et al. : Pyrolisis of $(CH_3CHNH)_3$
  - Ethanimine – Loomis et al.: Electric discharge of CH_3CN and H_2S
- 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.



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….

Spectra records

- 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
- Propanime:
  - 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_3CH_2CHNH

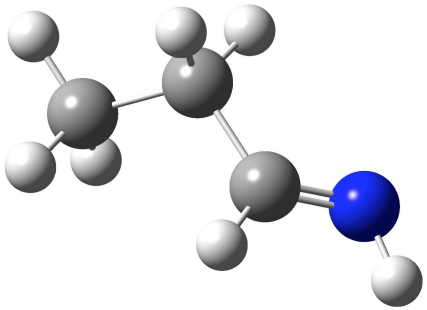
- No spectroscopie studies available up to now
- 2 conformers E and Z

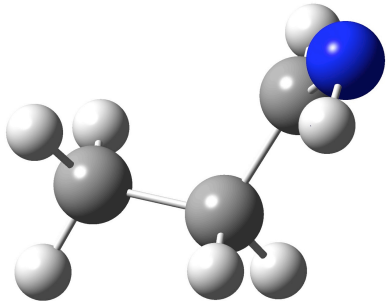
E conf

μ_a= 1.12 D

μ_b= 0.75 D

μ_c= 1.57 D





Z conf

ΔE^a = 264.25 cm^{-1}

μ_a= 2.49 D

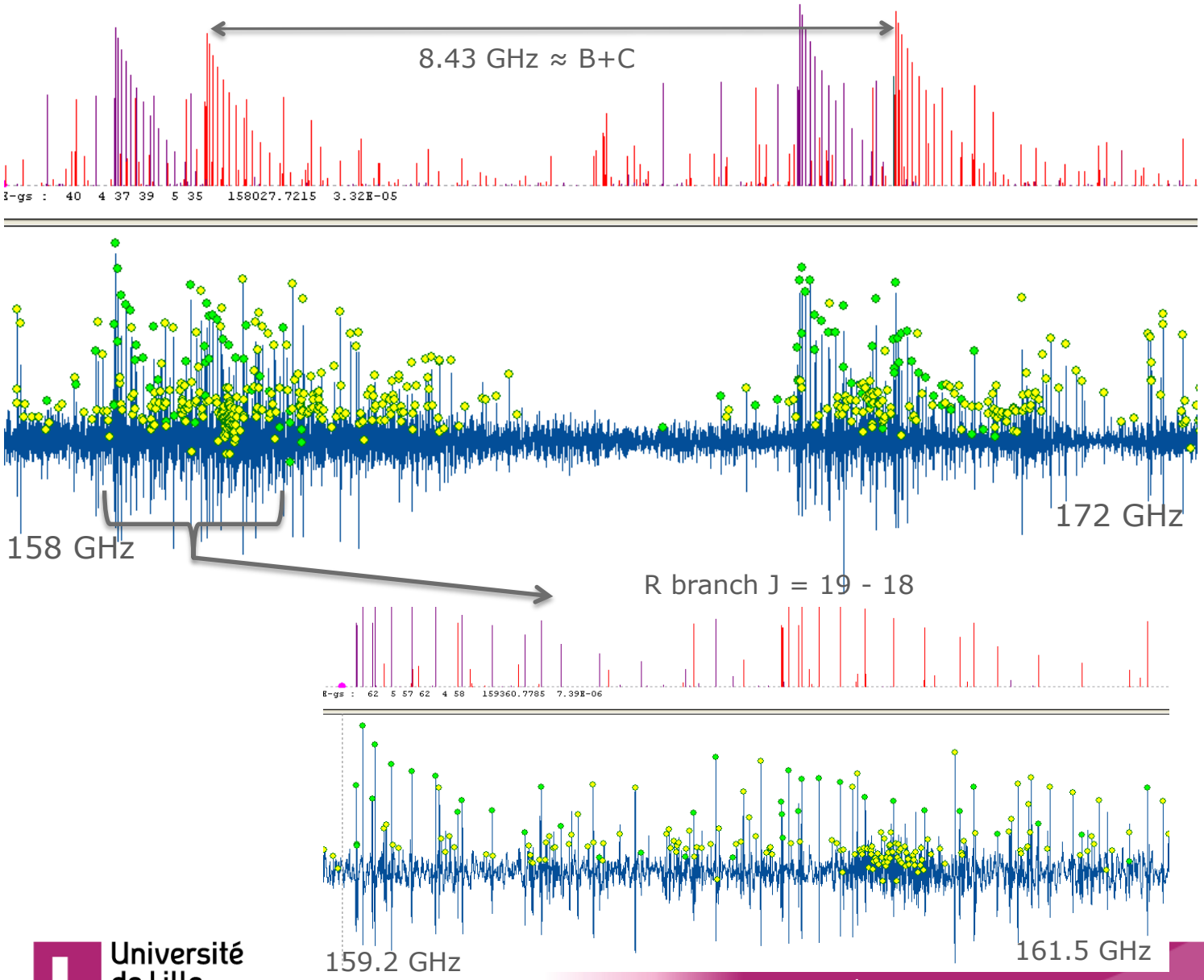
μ_b= 1.00 D

μ_c= 0.00 D

- Z is the less stable but Z_{conf} μ_a dipole moment is two times bigger than E_{conf} one
  - At lab temperature (Boltzman factor is 0.28 for Z_{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

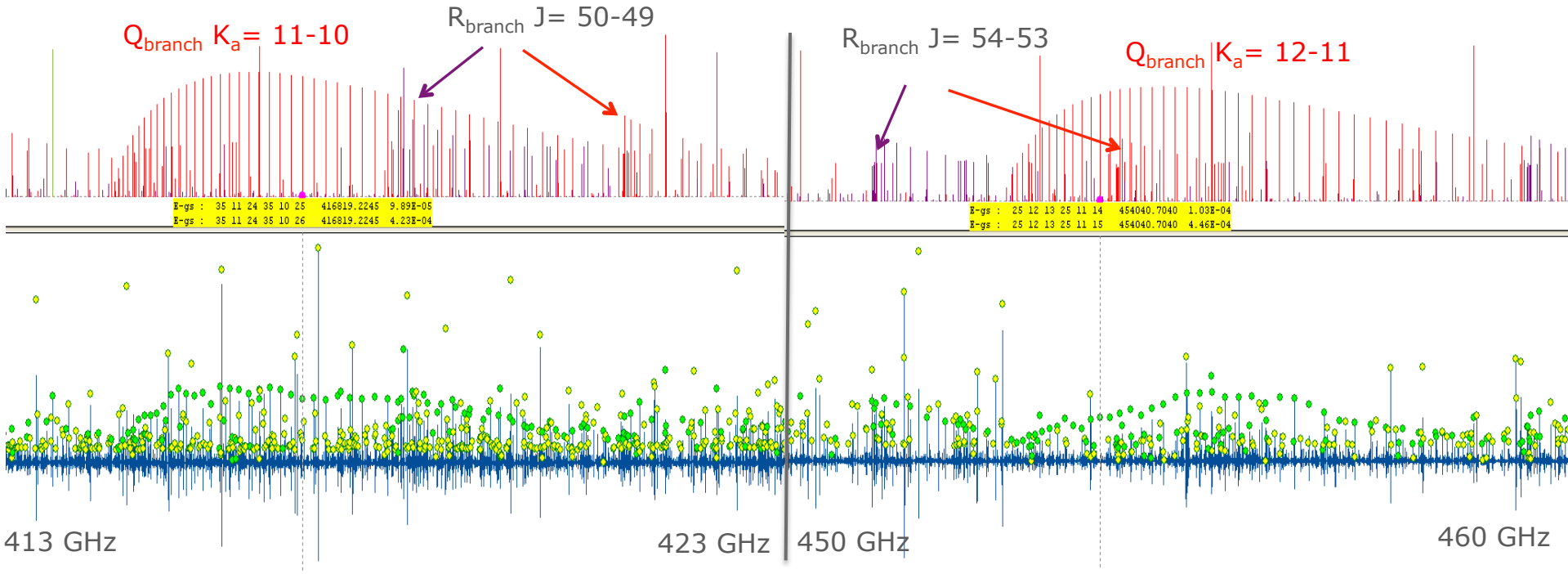
Propanimine spectra



E Conf

Z Conf

Propanimine spectra



- At high frequency, Q branch spectra for E conformer
- Due to small dipole moment along b axis, Only few μ_b line could be assign unambigously for Z conformer

Propanimine results

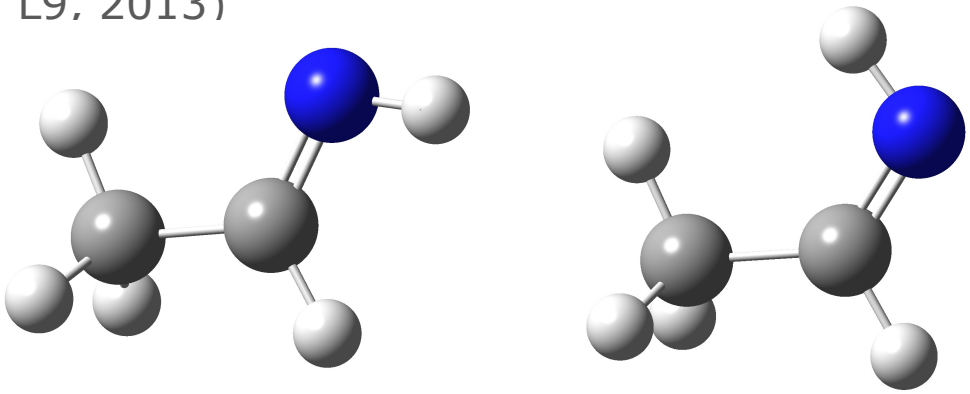
	E conf			Z conf	
Parameters (MHz)	Red A	Red S	b3lyp/6-311++g(3df,2pd)	Red S	b3lyp/6-311++g(3df,2pd)
A	24185.2684(54)	24185.2383(13)	24524.01435	23925.28(11)	24200.58727
B	4292.3639(11)	4292.55416(32)	4277.01166	4260.9797(14)	4250.25902
C	4156.7893(11)	4156.59879(32)	4147.17419	4129.2305(14)	4124.55433
N_{lines}/N_{param}	585/24	585/25		303/20	
$J_{max}/K_{a\ Max}$	73/21	73/21		49/19	
σ_{fit} (in kHz)	146.1	39.3		49.9	

Necessary to use reduction S

Ethanimine: CH_3CHNH

- Stark spectroscopy
  - up to 140 GHz: E_{conf} g.s., v_t=1 and Z_{conf} g.s. (Lovas et al., J. Chem. Phys. 72, 4964, 1980)
  - from 18 to 76 GHz: Z_{conf} g.s. and v_t=1(Brown et al., AJCh, 33, 1, 1980)
- Zeeman MW (Krause et al., Z. Naturfosch. 46, 785, 1991)
- CP-FTMW measurements from 6.5 to 40 GHz (Loomis et al., ApJL. 765, L9, 2013)

E_{conf} (cis)
μ_a= 0.834 D
μ_b= 1.882 D



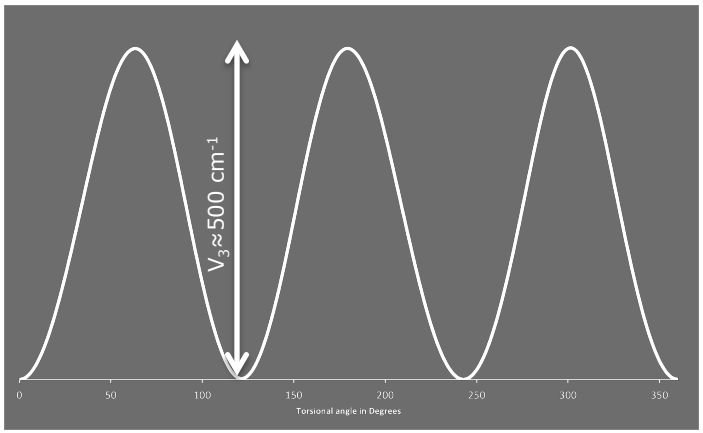
Z_{conf} (trans)
ΔE^a = 282 cm^{-1}
μ_a= 2.380 D
μ_b= 0.445 D

→ Z_{conf} spectra could be more intense even at ISM temperature

[a]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

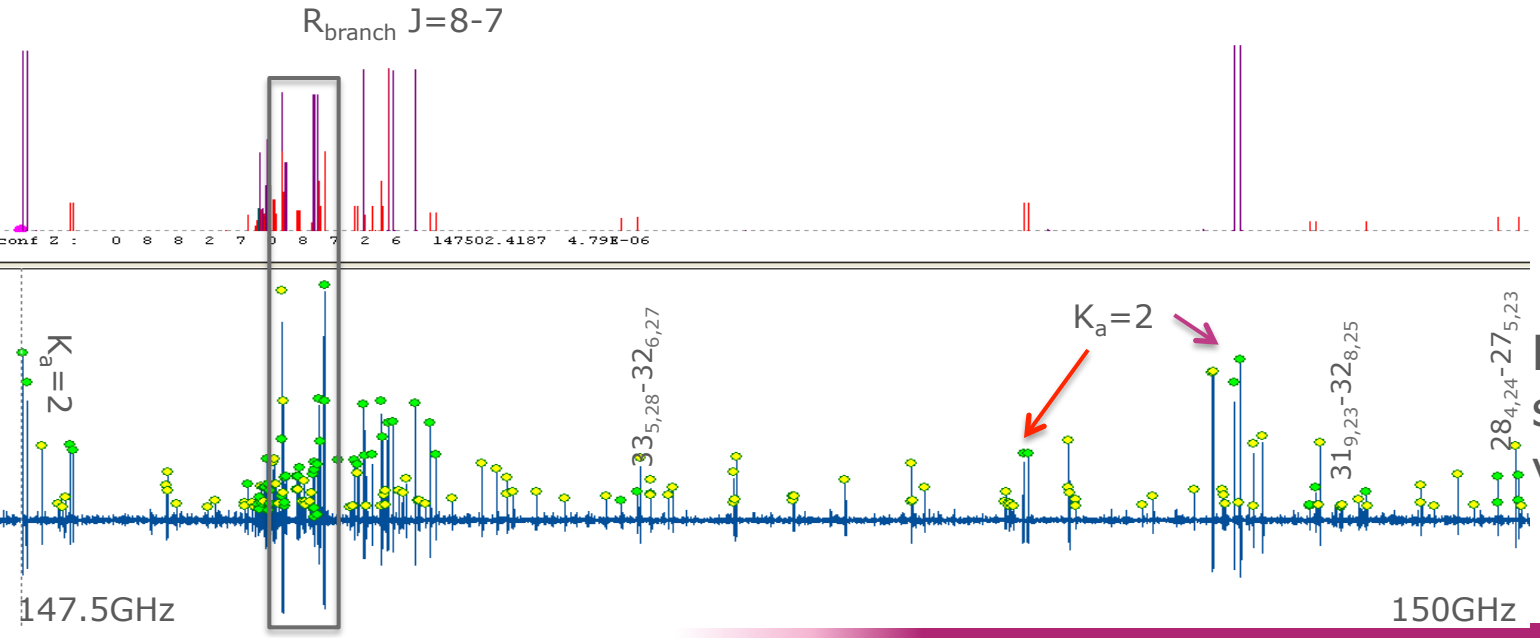
$$V(\alpha) = \frac{V_3}{2}(1 - \cos 3\alpha) + \frac{V_6}{2}(1 - \cos 6\alpha) + \ldots$$

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

- Even if the barriers have medium values: ≈ 500 cm-1. The analysis of the spectra was not obvious for 2 reasons:
  - Strong coupling between torsion and rotation: ρ = 0.28. This as high as acetaldehyde.
    - not possible to fit A lines with Watson's Hamiltonian
    - not possible tu use XIAM for Ka > 4

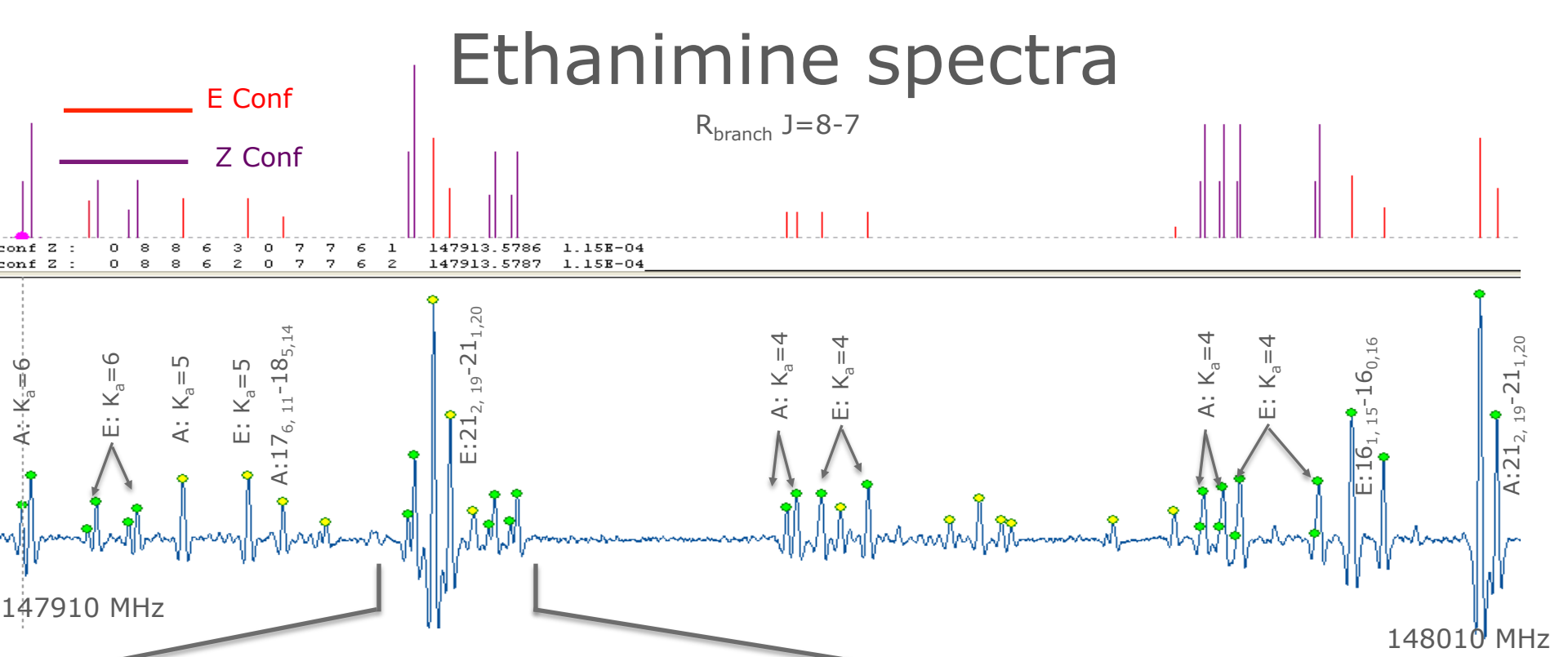
Ethanimine spectra

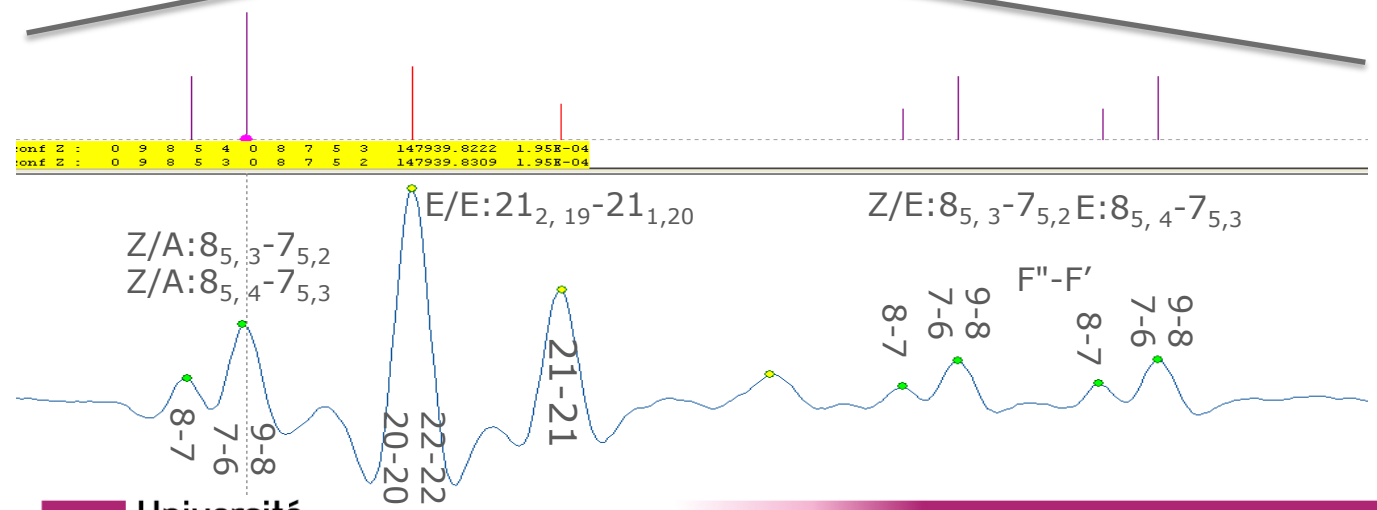
- Usually in millimeterwave spectra ^{14}N nuclear electric quadrupole hyperfine splittings are no observed with doppler limited resolution or only for high K_a values. (cf. Ethyl cyanide)
- These splittings are enhanced by internal rotation and should be take into account, especially for μ_b type lines.
- 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)



Light molecule: spectra is not very dense

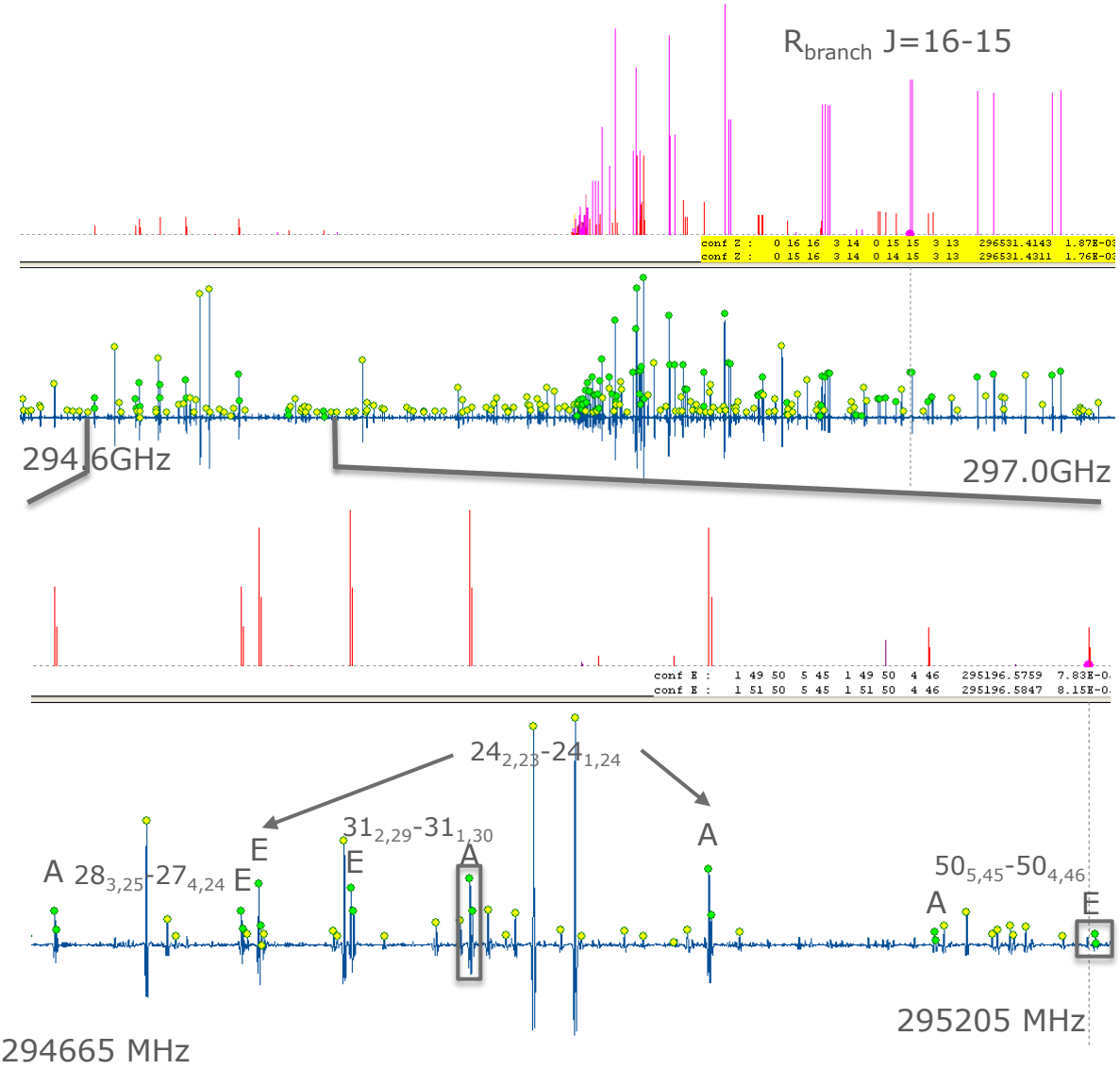
Ethanimine spectra



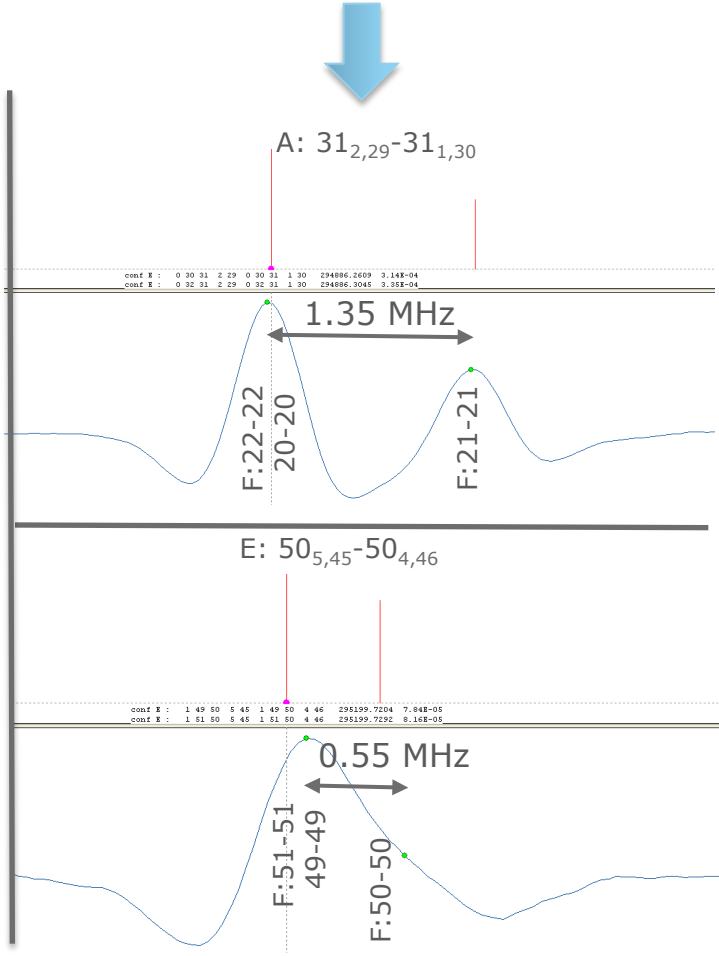


- μ_a:hyperfine quadrupole structure for high Ka Values and low J
- μ_b: bigger splitting and K_a is only 1..

Ethanimine spectra



- Still splittings at 300 GHz and J=50



Ethanimine results

	E conformer		Z conformer	
	This work	Lovas +Loomis	This work	Lovas +Loomis
A (GHz)	52.83537(29)	52.81854(45)	495815(48)	49.666(13)
B (GHz)	10.07601(15)	10.08613(45)	1015214(14)	10.1490(40)
C (GHz)	8.70427(13)	8.6956781(24)	8.644814(12)	8.64485(19)
F (GHz)	182.85(51)	219.764	225.6(27)	217.972
ρ	0.308606(23)	0.306205(31)	0.286090(76)	0.2861(33)
V_3 *(cm^{-1})*	451.9(15)	557.970(24)	535.6	515.0(11)
$2D_{ab}$ *(MHz)*	-7226.50(29)	-7224.8(53)	-7134.4(16)	-7101(46)
X_{aa}	1.066(16)	1.040(13)	-3.7628(98)	-3.726(22)
X_{bb}	-4.127(10)	-4.1161(86)	0.605(23)	0.585(57)
N_{param}/N_{lines}	27/829	13/108	18/270	12/63
J_{max}, $K_{a\ max}$	50/13	13/4	26/15	7/6
σ_{fit} (kHz)	39.3	95.7	44.7	127.5

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

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