Laboratory millimeter-wave spectroscopy of organic molecules of astrophysical importance

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Life in a Cosmic Context
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An excerpt from Snyder (PNAS (2006) 103:12243)

- In 1970, Buhl and Snyder reported the detection of a strong unidentified emission line in five galactic sources. This line was labeled “X-ogen” simply because it was unidentified.
- Shortly thereafter, Klemperer argued that the best candidate for the carrier of the X-ogen line was HCO^+.
- Five years later, Klemperer’s proposed identification was confirmed by both the laboratory measurements of Woods et al. and the astronomical observations of Snyder et al. .
- Thus the X-ogen line is the $J = 1 - 0$ transition of HCO^+, which turned out to be the first detected rotational spectrum of a molecular ion.
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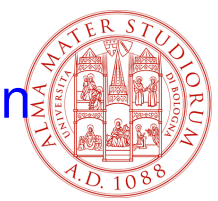


Main task: providing rest frequencies

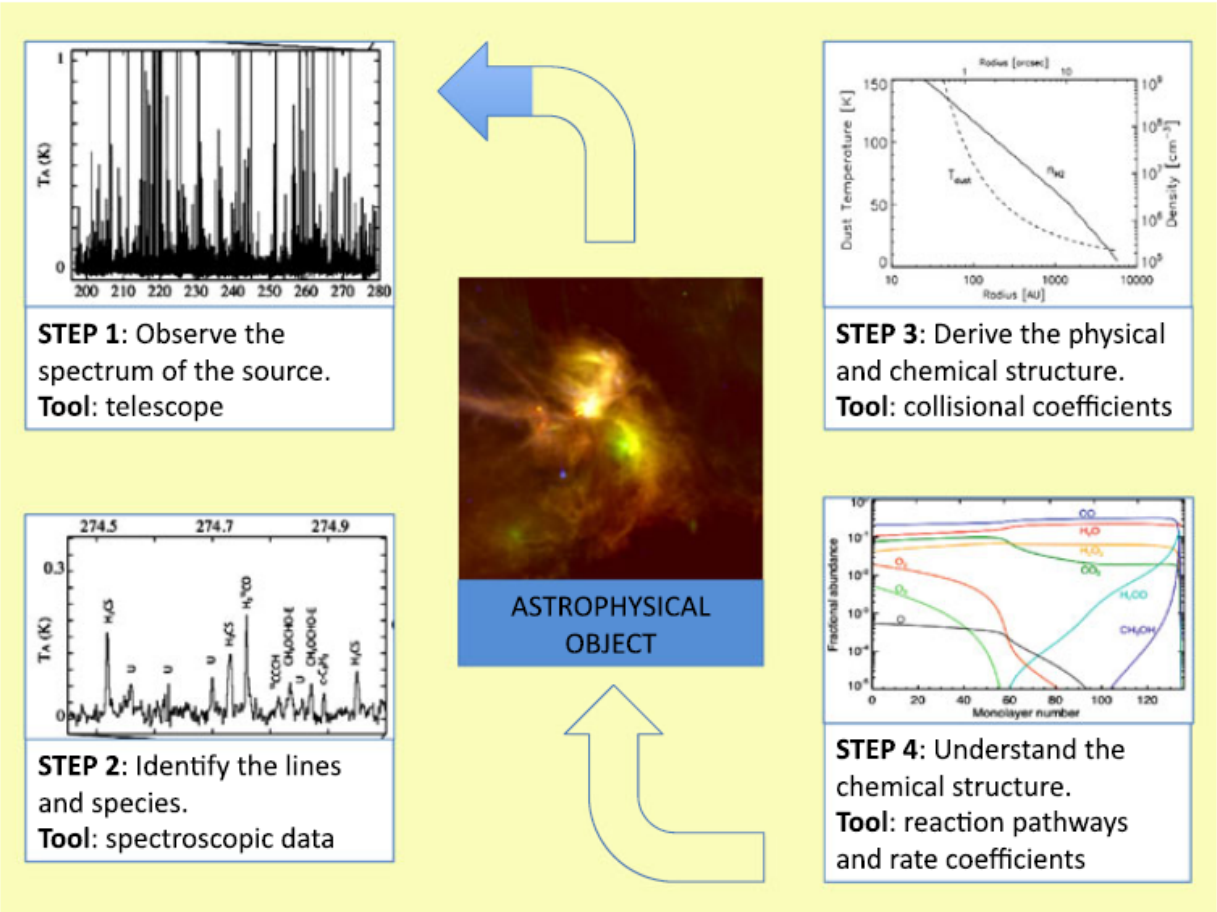
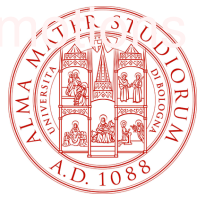


Figure: from P. Caselli & C. Ceccarelli, Astron. Astrophys. Rev (2012) 20:56

What do radio astronomers need from laboratory spectroscopy?

- Transition frequencies for the strongest molecular lines (i.e. for the vibrational ground state of the most abundant isotopologue). This is the most important information for the identification of new species in the interstellar medium.
- Transition frequencies for less abundant isotopologues (D, ^{13}C, ^{15}N, ^{18}O containing species). The detection of isotopic variants in space allows to investigate isotopic fractionation phenomena.
- Transition frequencies for molecules in vibrationally excited states. Their observation in space provides information on the IR radiation field of the observed "hot" sources.
- Very accurate rest frequencies for the best tracers of dynamical motions in narrow-line astronomical sources.



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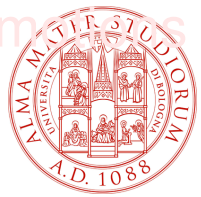

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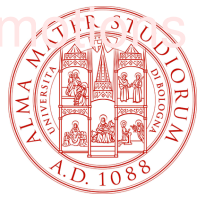

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Why THz spectroscopy?

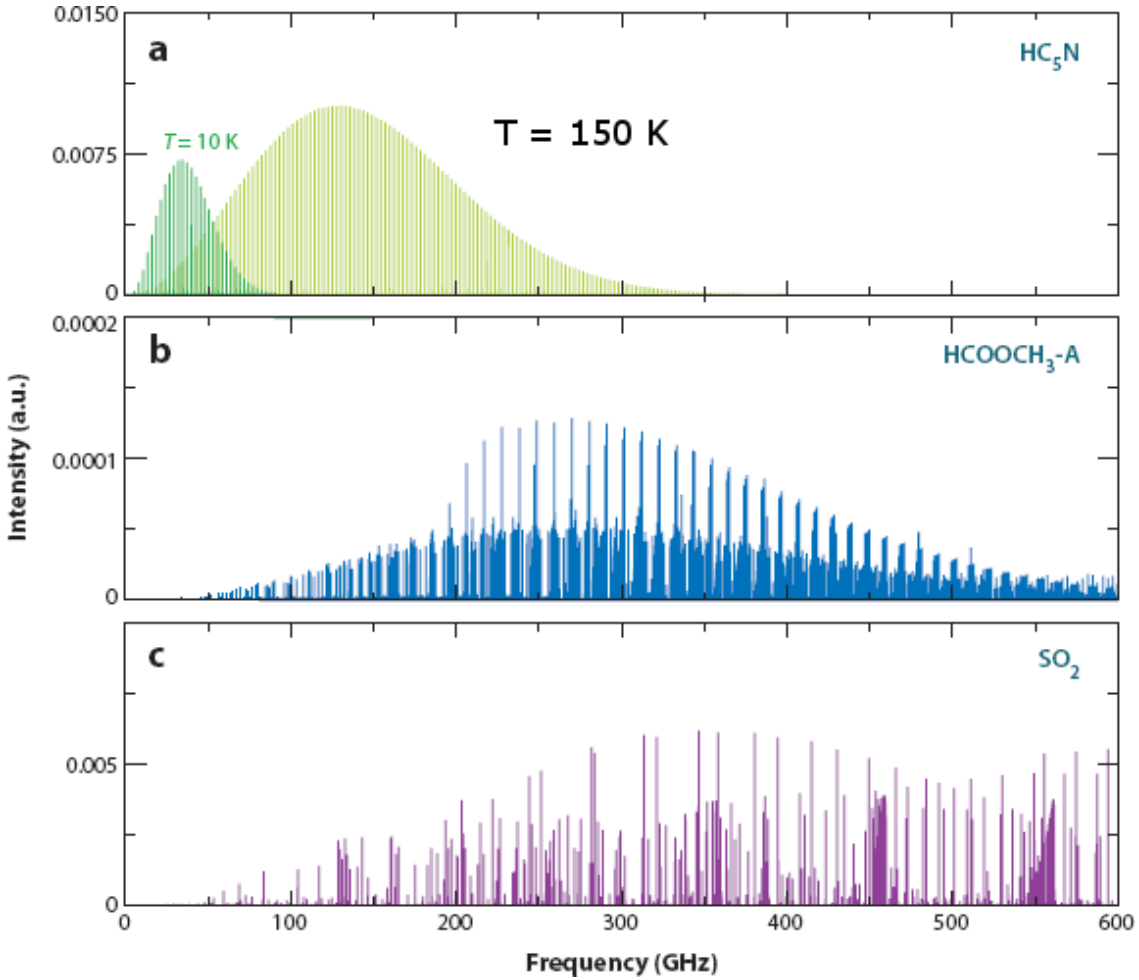

Figure: from E. Herbst & E.F. van Dishoeck, Annu. Rev. Astron. Astrophys. Rev (2009) 47:427

Outline

1. Experimental apparatus
   - Spectrometer
   - Performances
2. Organic molecules
   - Acrylic Acid
   - C_2HD
   - Imines
     - H_2NH
     - H_2CCNH

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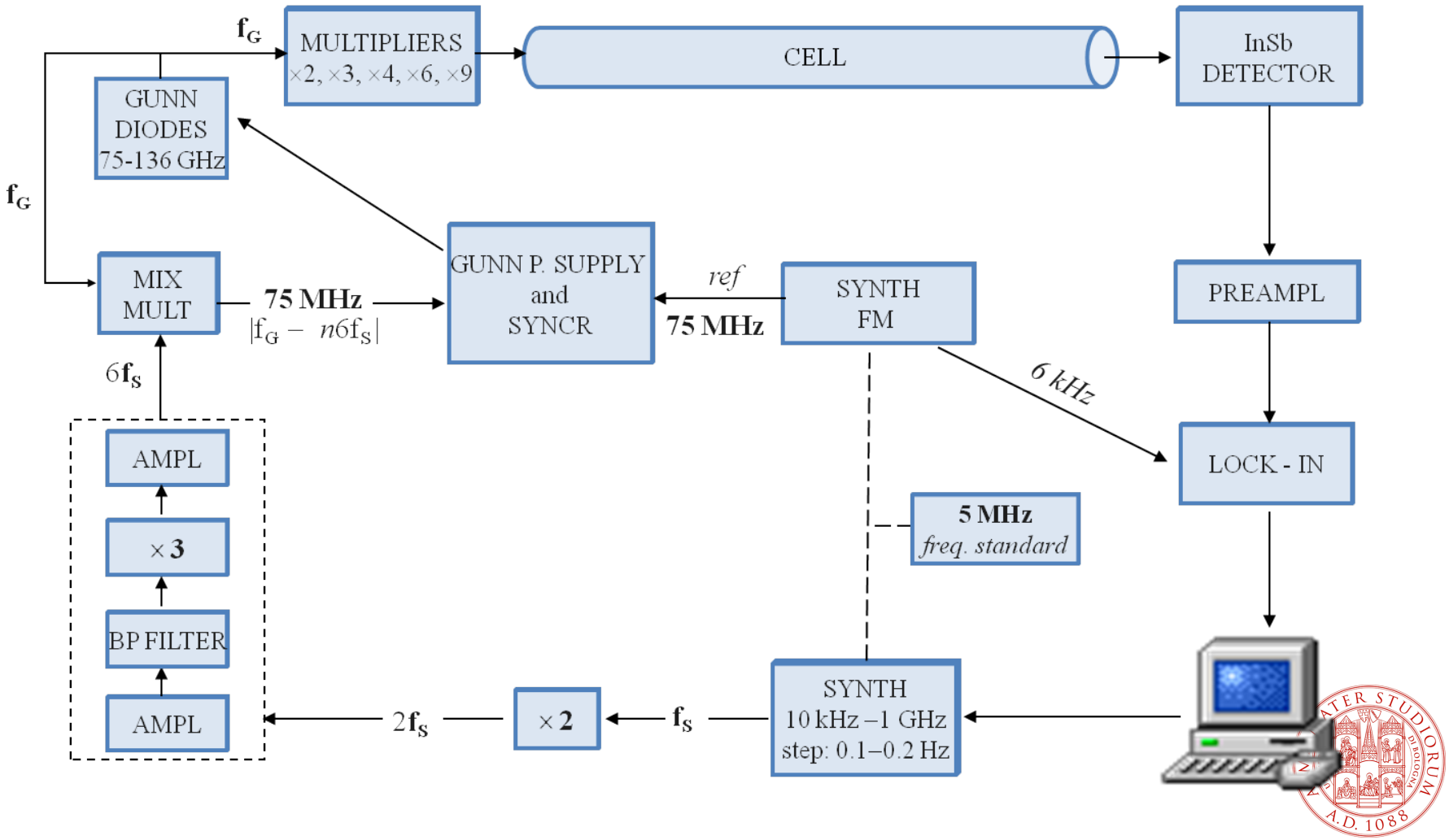
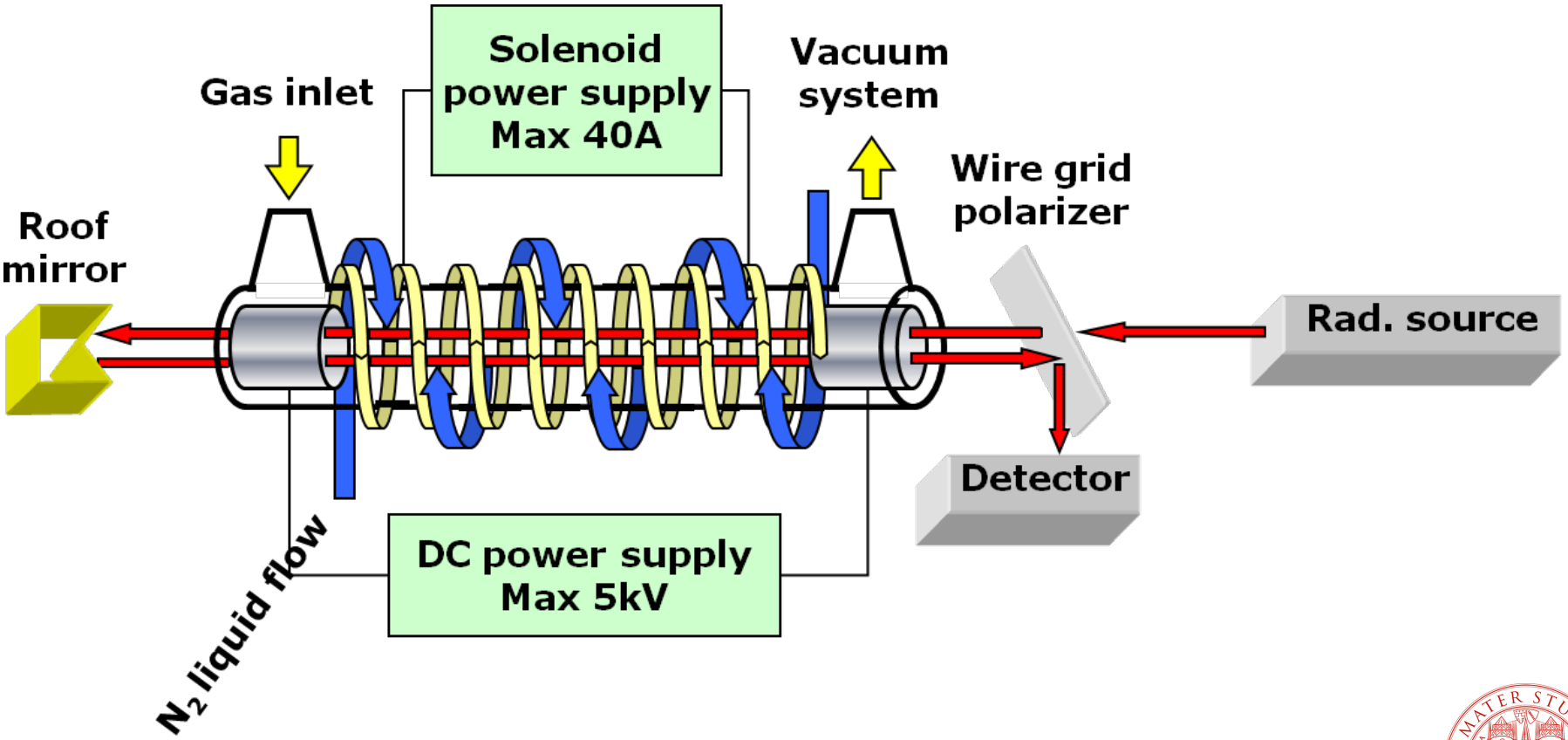
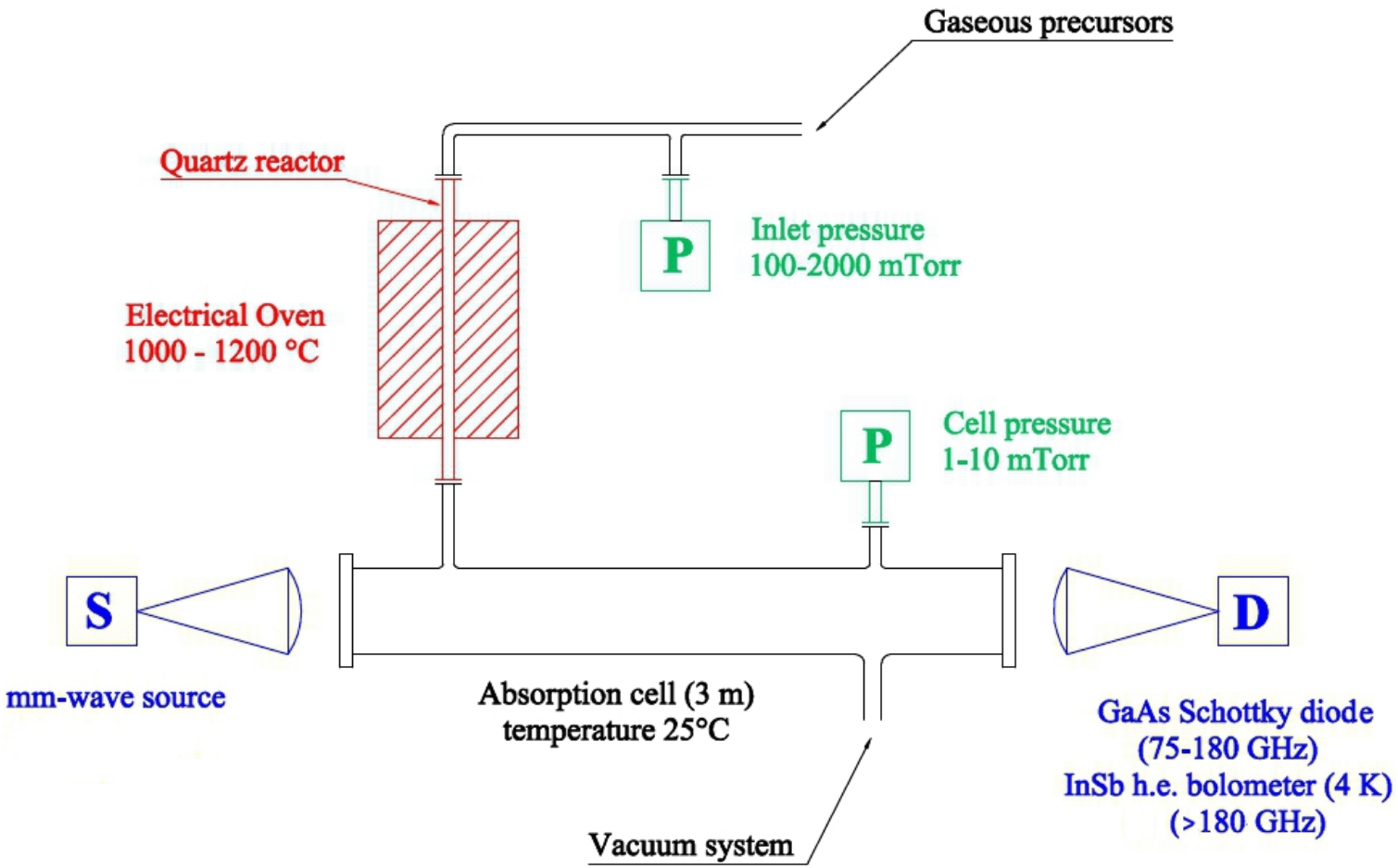
The spectrometer



The discharge cell

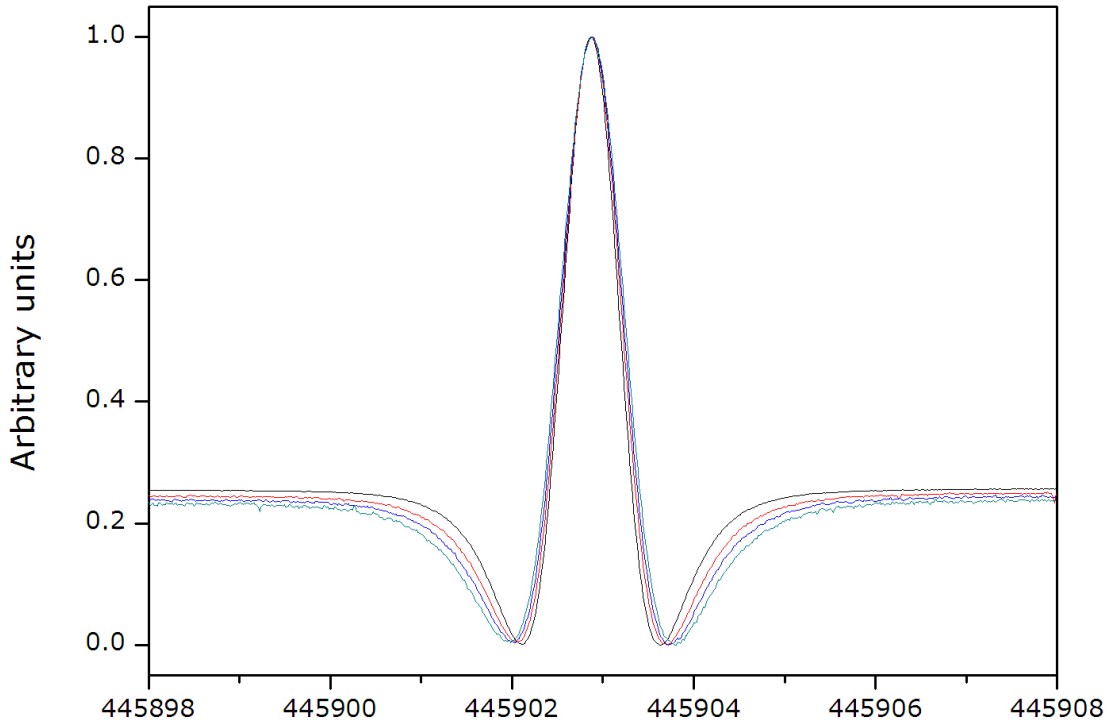


The pyrolysis cell



2^{nd} harmonic detection

Figure: Second harmonic spectra of HCO^+ recorded at increasing values of He pressure in a negative glow discharge cell



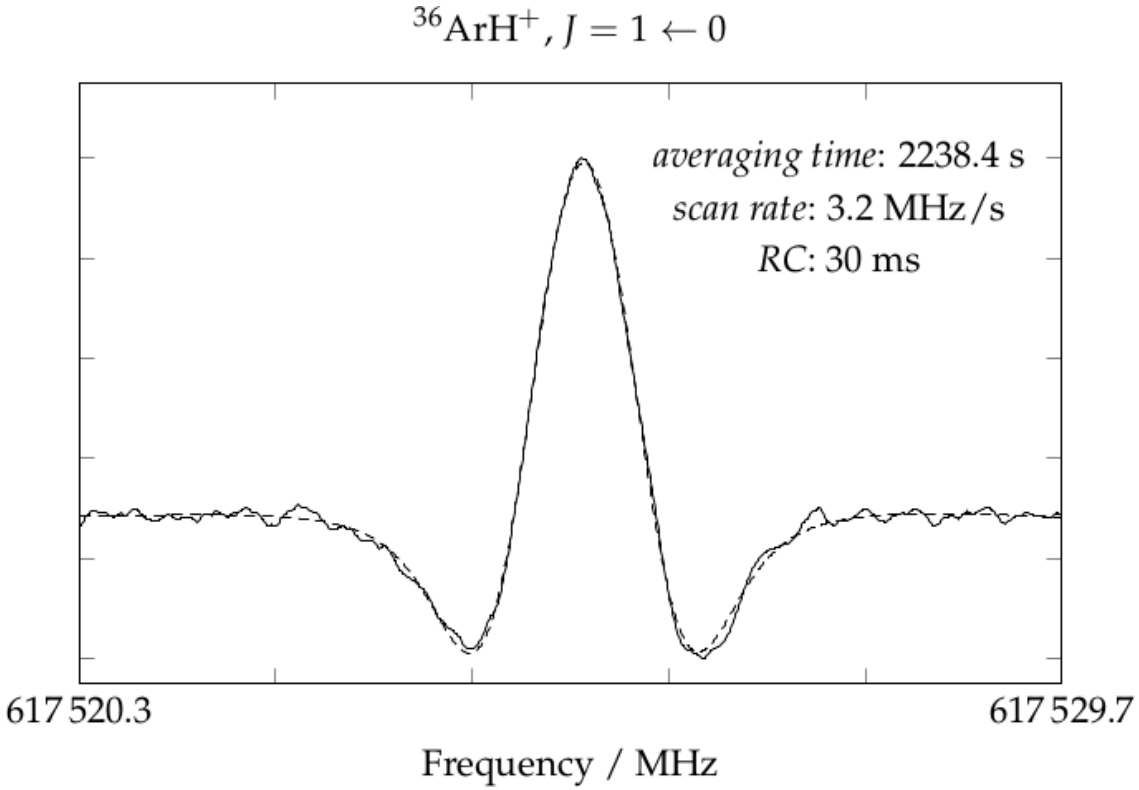
$$F_2(\omega) \propto \mathrm{Re} \int_0^{\infty} J_2(mT)\Phi e^{i\omega T} \mathrm{d}T$$

In case of weak absorptions, when the Beer-Lambert law can be linearized, the line shape resulting from second-harmonic detection is given by the real part of the Fourier transform of the correlation function (exponential decay) times a Bessel function of the first kind of order 2.

L. Dore, JMS (2003) 221: 93

Sensitivity

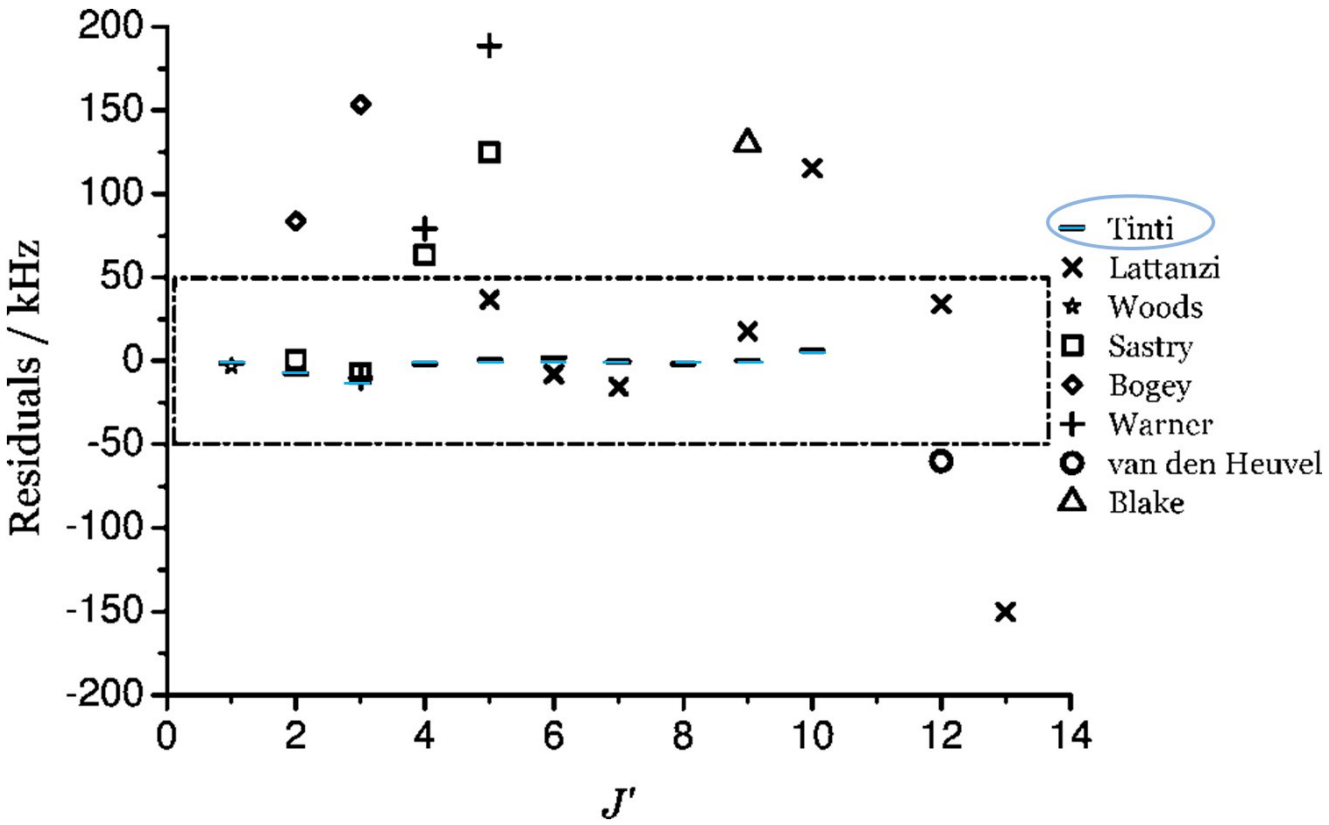
The abundances on Earth of ^{38}Ar, ^{36}Ar, and ^{40}Ar are 0.063%, 0.337%, and 99.600%, respectively. However, in the Sun, 84.6% of argon is ^{36}Ar.



The estimated abundance of ^{36}ArH$^+$ in the cell is 4 ppm.

High accuracy

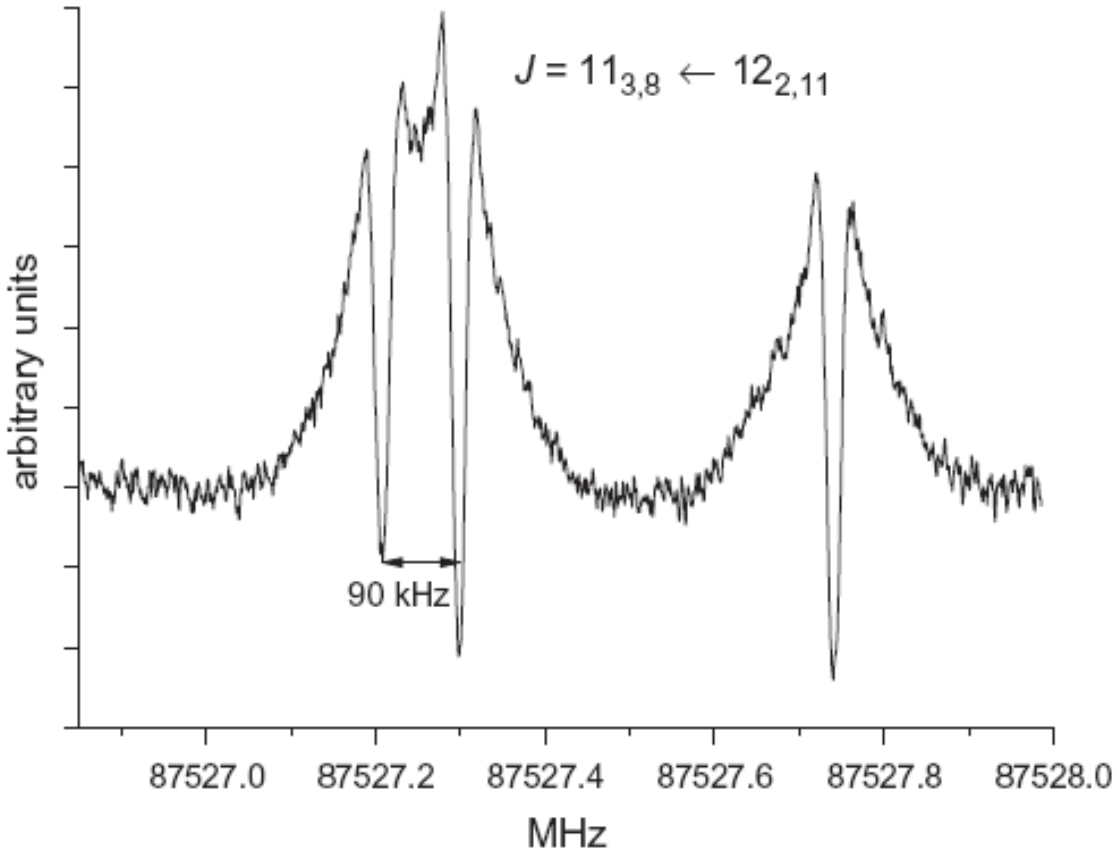
Figure: Residuals of transition frequencies of HCO^+ from different papers



The highest transition frequency measured by F. Tinti et al., ApJ (2007) 669: L113 is at 891.6 GHz

High resolution

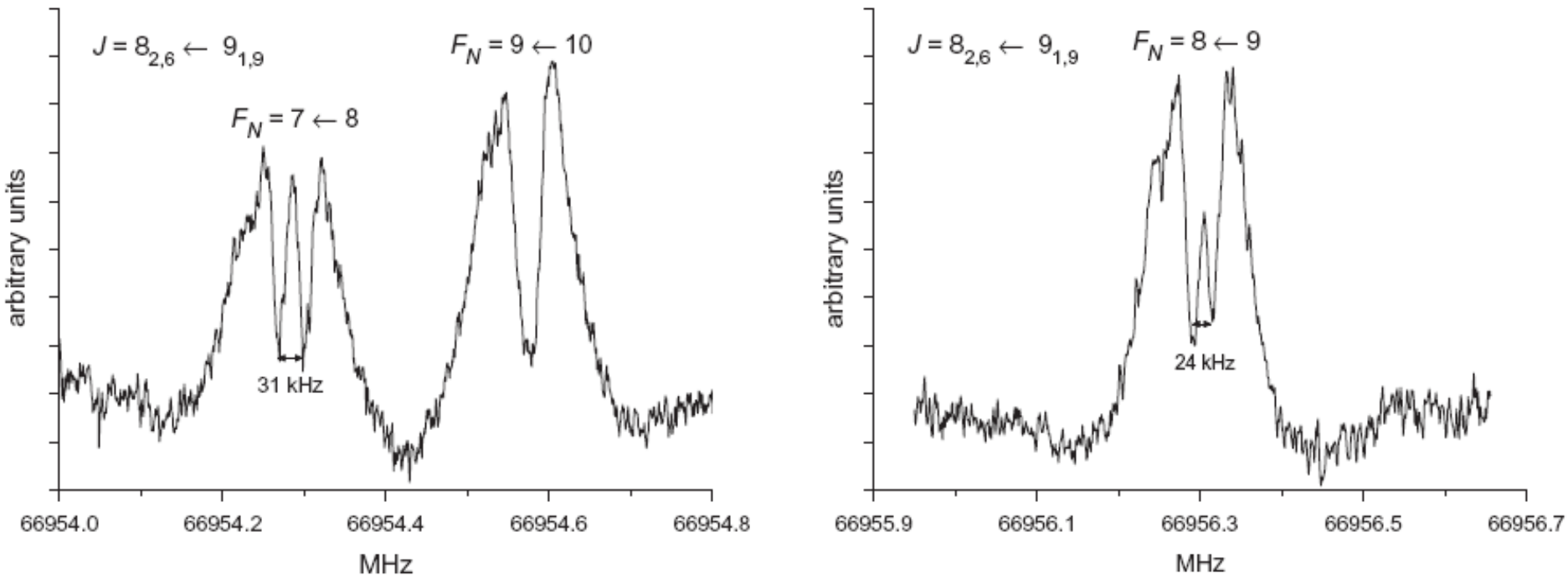
Figure: Closely spaced $\Delta F = -1$ hyperfine components due to N nucleus of a transition of methanimine (H_2CNH) resolved by Lamb-dip spectroscopy



Scan carried out in 205 s at ∼155 kHz/s with 10 ms as RC constant and 15 kHz as modulation depth.

High resolution

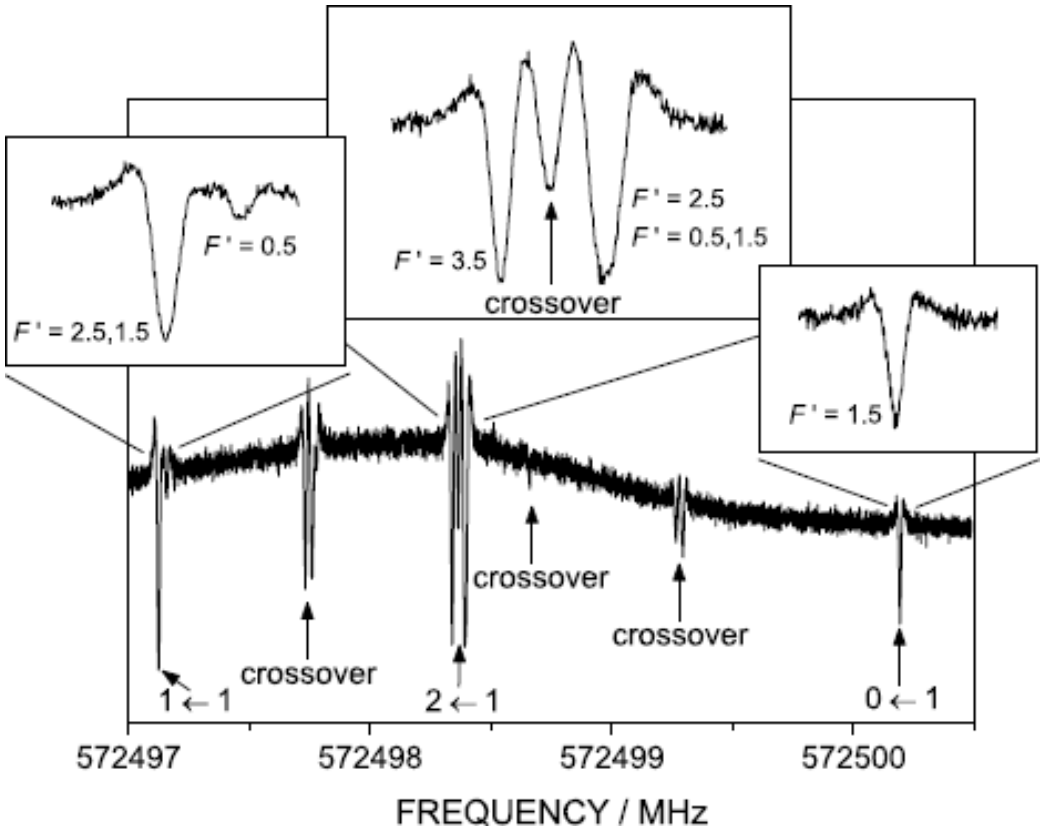
Figure: Further splitting in N-quadrupole hyperfine components due to protons magnetic interactions.



Scans carried out with 10 ms as RC constant and 15 kHz as modulation depth: in 469 s at ∼158 kHz/s (left) and in 421 s at ∼198 kHz/s (right). L. Dore et al., JMS (2010) 263: 44

High resolution

Lamb-dip spectrum of the transition $J_K = 1_0 - 0_0$ of NH_3 showing ^{14}N hfs and H hfs.

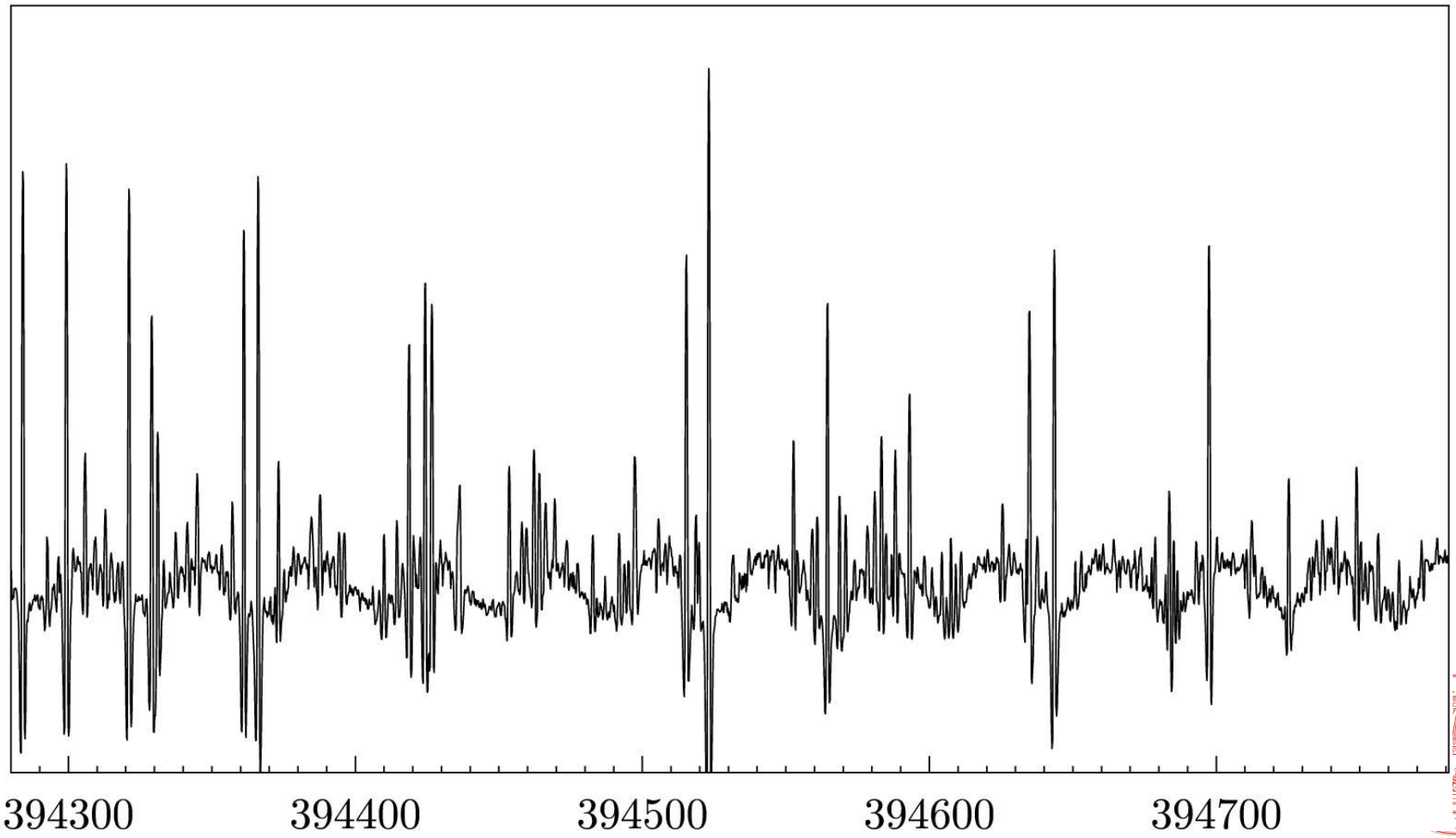


The magnified windows show the splittings due to the proton spin interactions.

Cazzoli, Dore & Puzzarini, A&A (2009) 507: 1707

Long scans

Figure: Acrylic Acid, RC=10ms, step=20 kHz



Acrylic Acid: an interstellar molecule?

- The two smallest carboxylic acids, formic (HCOOH) and acetic acid (CH_3COOH), have been detected.
- Two substituted propenes, acrylonitrile (CH_2=CH–CN) and acrolein (CH_2=CH–CHO) have been detected.
- A possible formation pathway of acrylic acid in methane and carbon dioxide containing interstellar ices could be:

$$\begin{aligned} H + CO_2 &\rightarrow HOCO \\ C_2H_3 + HOCO &\rightarrow C_2H_3COOH \end{aligned}$$

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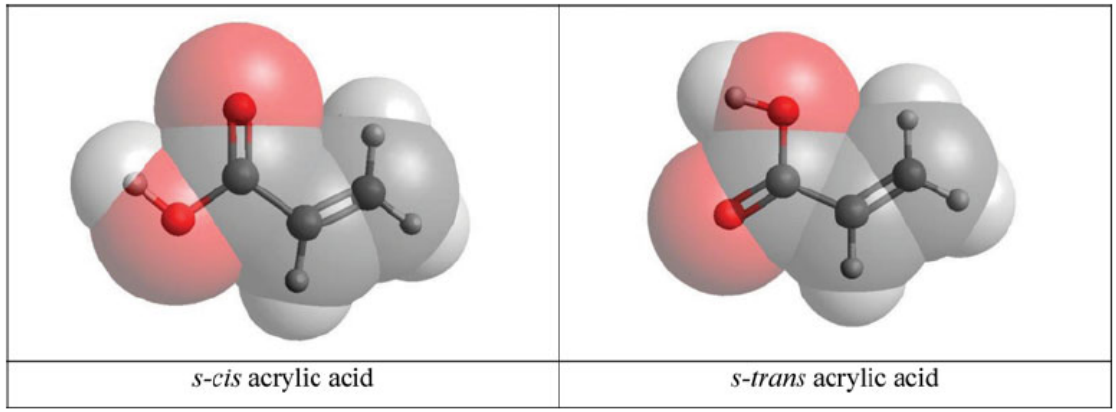

- AA is the smallest carboxylic acid containing a carbon-carbon double bond; two conformers (s-*cis* and s-*trans*) have been observed in supersonic expansions in the 6–18.5 and 52–74.4 GHz frequency ranges. (Calabrese et al., JMS (2014) 295:37)
- The ^{13}C mono-substituted isotopologues were observed in natural abundance and for the first time. Low frequency, high resolved microwave measurements on acidic deuterated AA allowed for the determination of nuclear quadrupole coupling constants.

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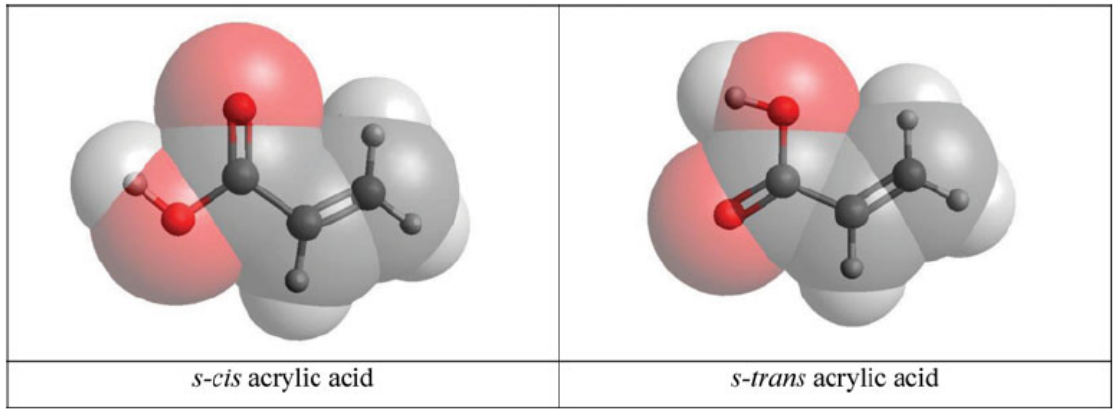

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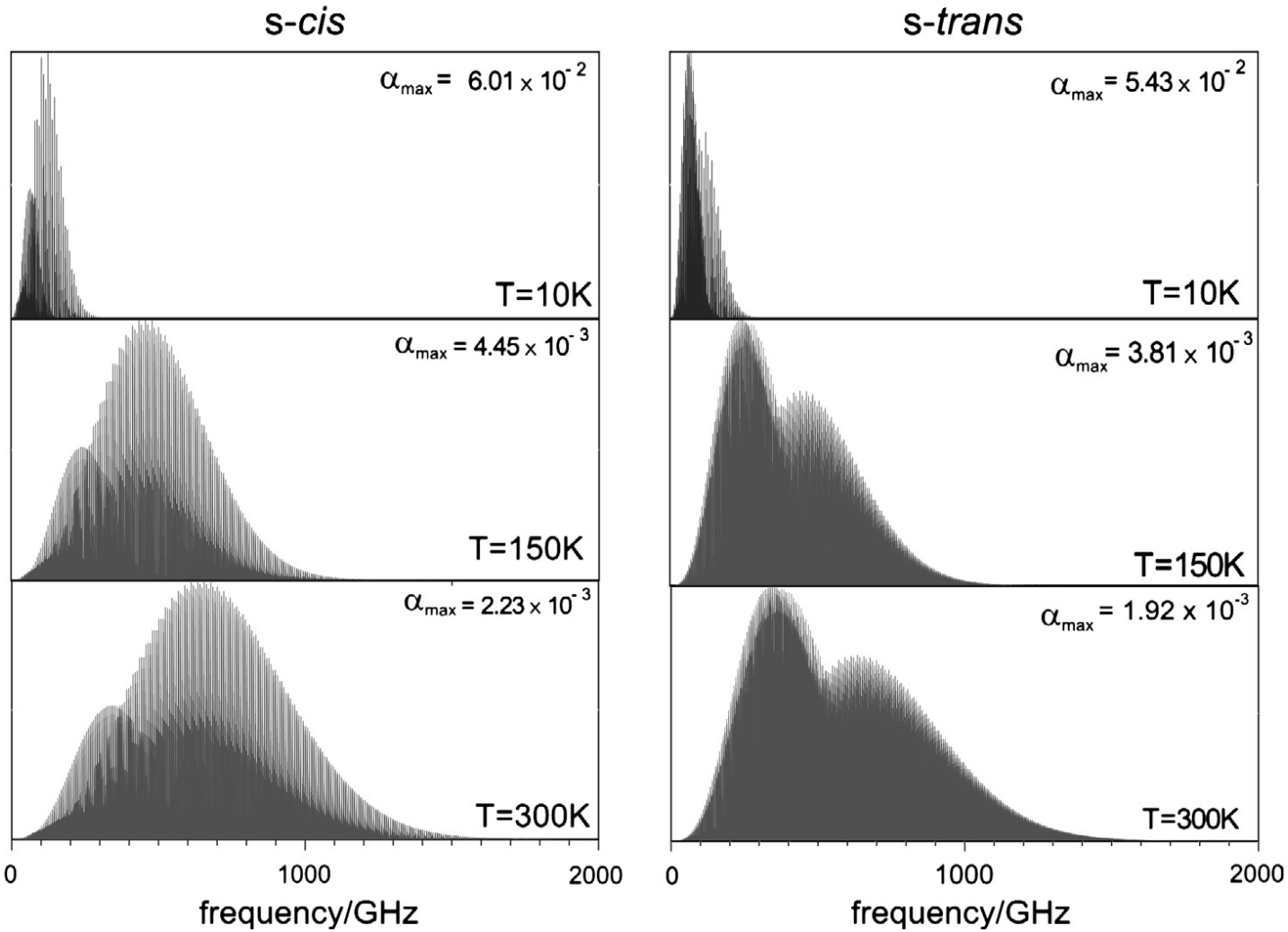
Need for the mmw spectrum



Spectrum assignment

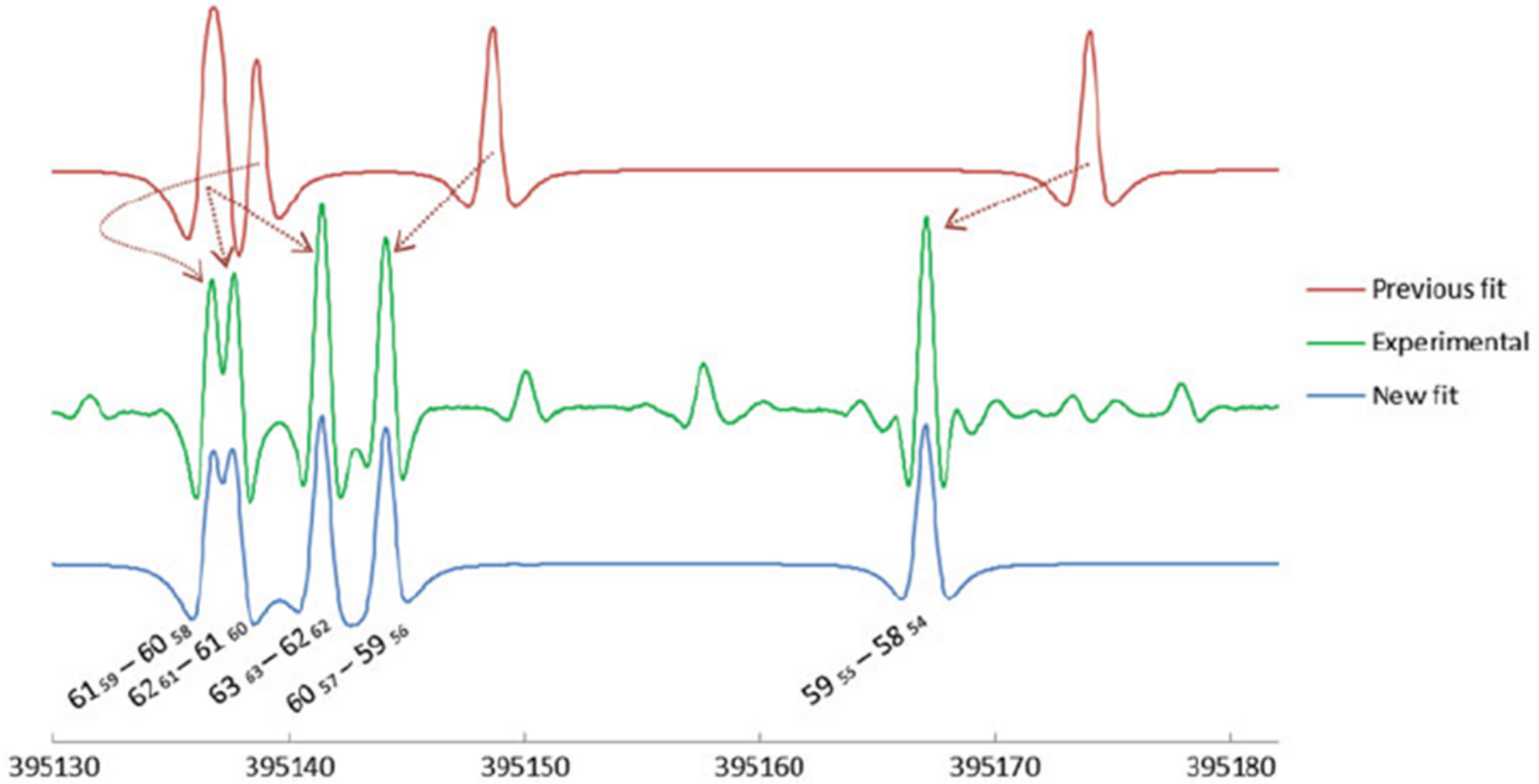


Figure: Portion of the millimetre spectrum of *s-trans* AA showing the actual position of the lines compared to the prediction form the previous millimetre wave work.

Calabrese et al., Mol. Phys. (2015) 113: 2290

Spectrum prediction

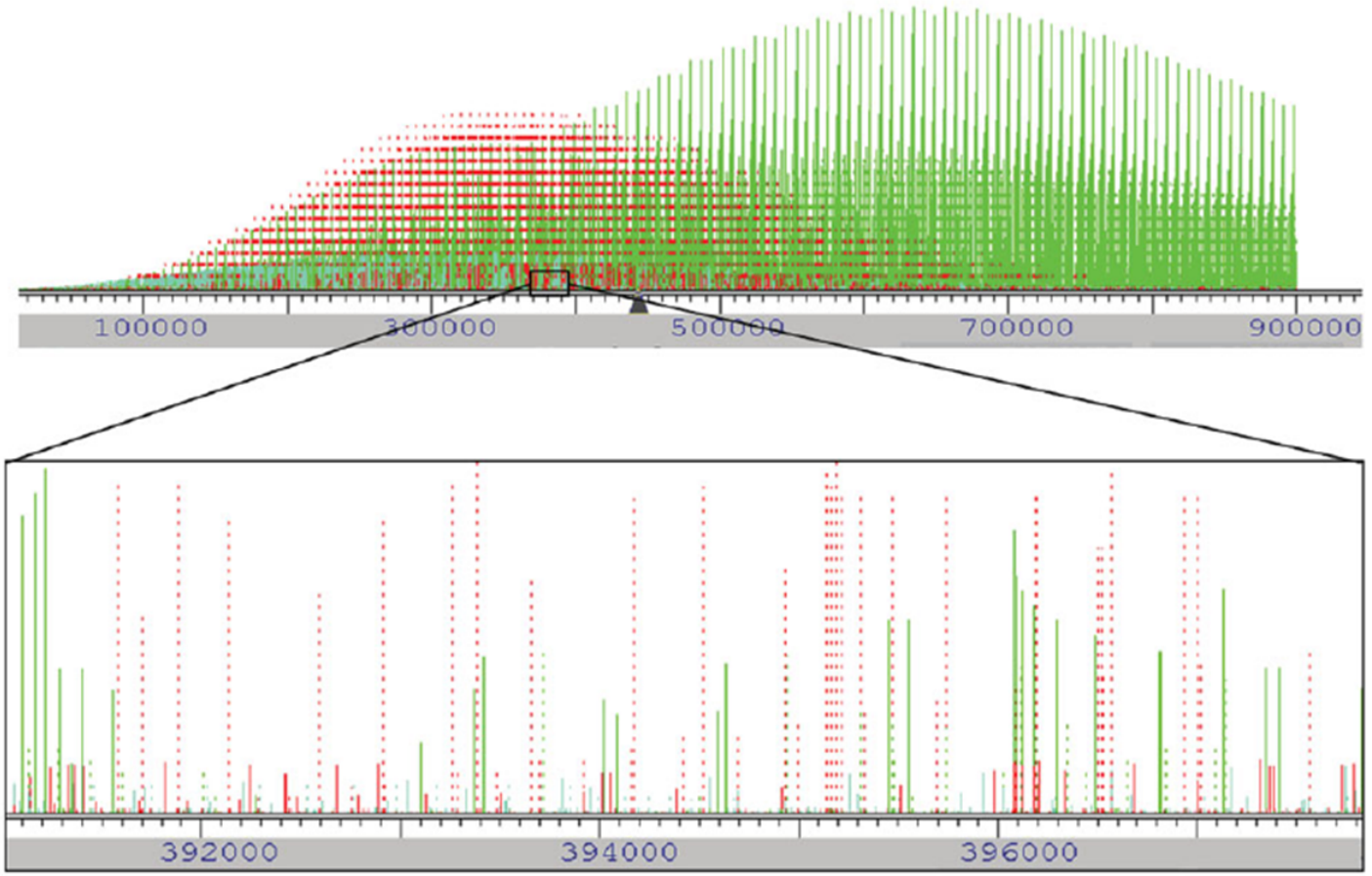


Figure: Overall spectrum prediction @ 298 K with the expanded region. Continuous lines, *s-cis* AA; dashed lines *s-trans* AA. Red, μ_a-type spectrum; green μ_b-type spectrum.

Acetylene

- C_2H_2 can be found in several astronomical environments:
  - in molecular clouds,
  - in massive young stellar objects and planet forming zones,
  - in circumstellar envelopes of AGB stars,
  - in cometary comae.
- C_2H_2 is a precursor for molecular complexity:
  for instance, its reaction with cyanogen radical to form cyanoacetylene is the first step in the cyanopolyyines synthesis:

$$CN + C_2H_2 \rightarrow HC_3N + H$$

- However, $^{12}C_2H_2$ has no permanent electric dipole moment and cannot be detected by (sub-)millimeter telescopes, but by detecting some P-branch high-J transitions of its $\nu_5 \leftarrow \nu_4$ difference band in the region.

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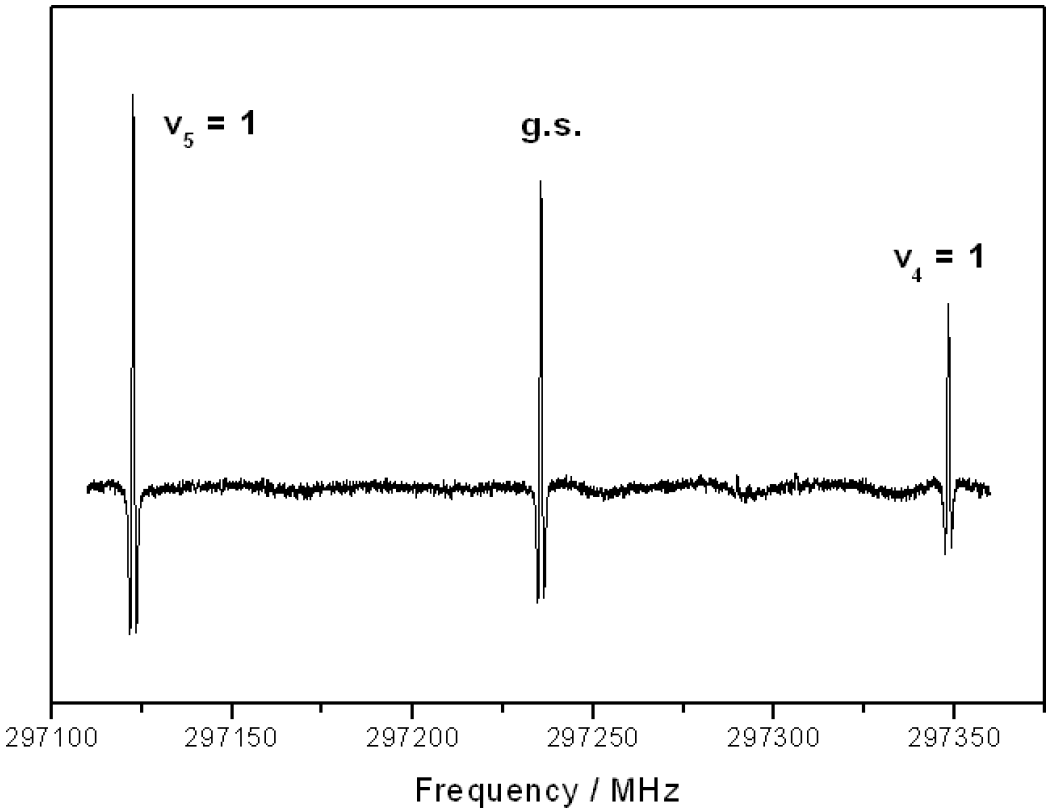
$^{12}C_2HD$ do have a small permanent dipole moment (0.01 D)

Figure: Low frequency components of the ℓ-doublet of the $J = 5 \leftarrow 4$ transition in the $\nu_5 = 1$, ground, and $\nu_4 = 1$ vibrational states.

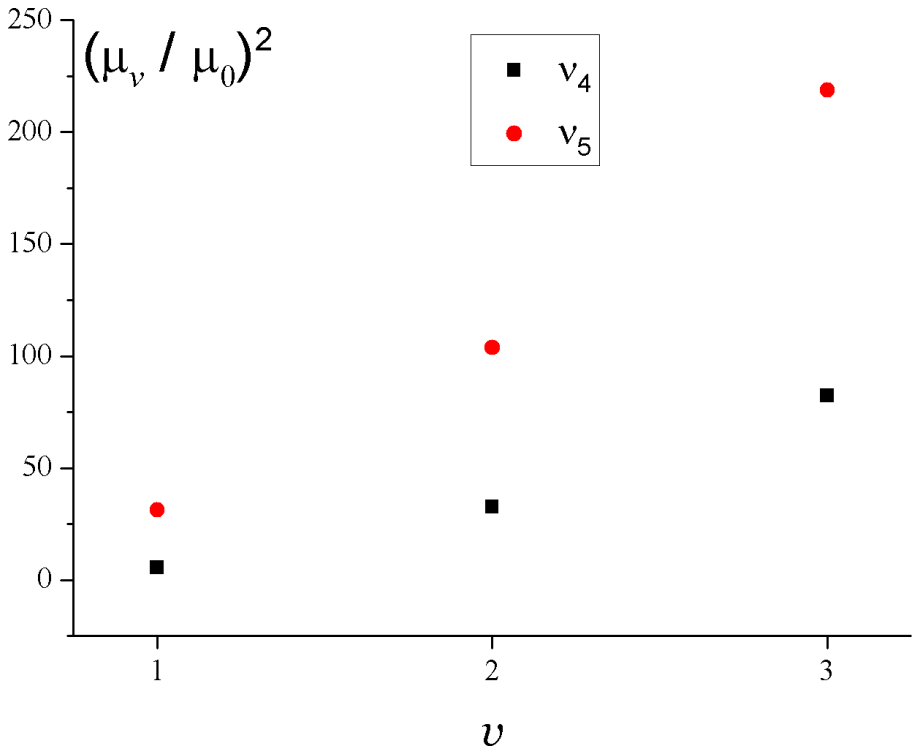


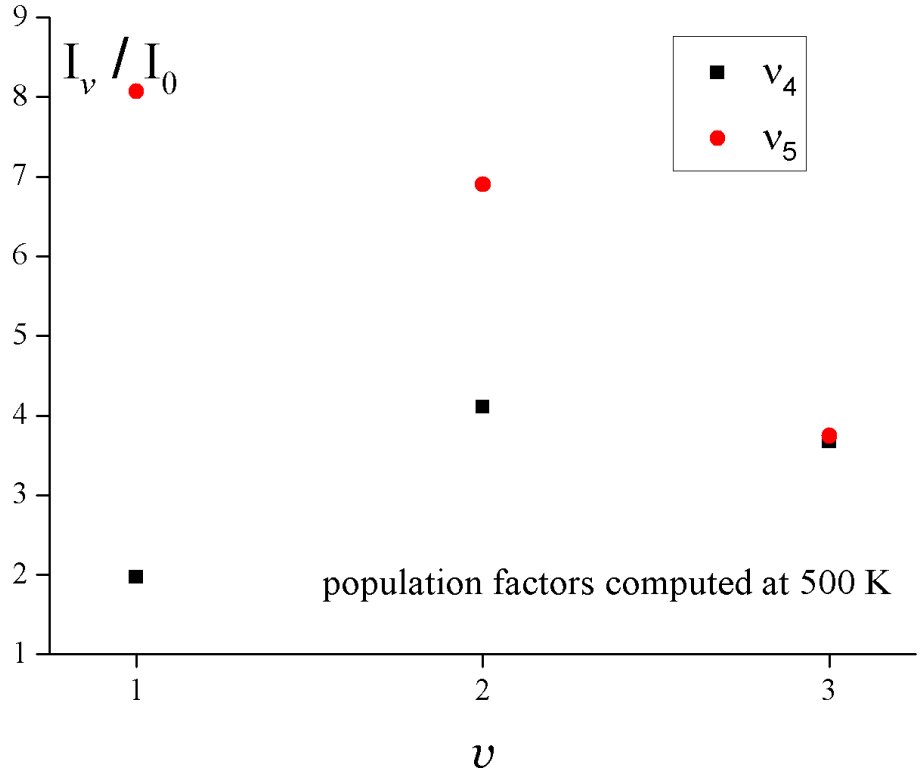
The dipole moment value is larger in the excited bending modes than in the ground state.

ν_5 is the *cis* bending mode ($678\,\mathrm{cm}^{-1} \equiv 975$ K) and ν_4 is the *trans* bending mode ($519\,\mathrm{cm}^{-1} \equiv 745$ K).

C. Degli Esposti et al., A&A 559, A125 (2013)

The dipole is strongly enhanced by the bending vibrations





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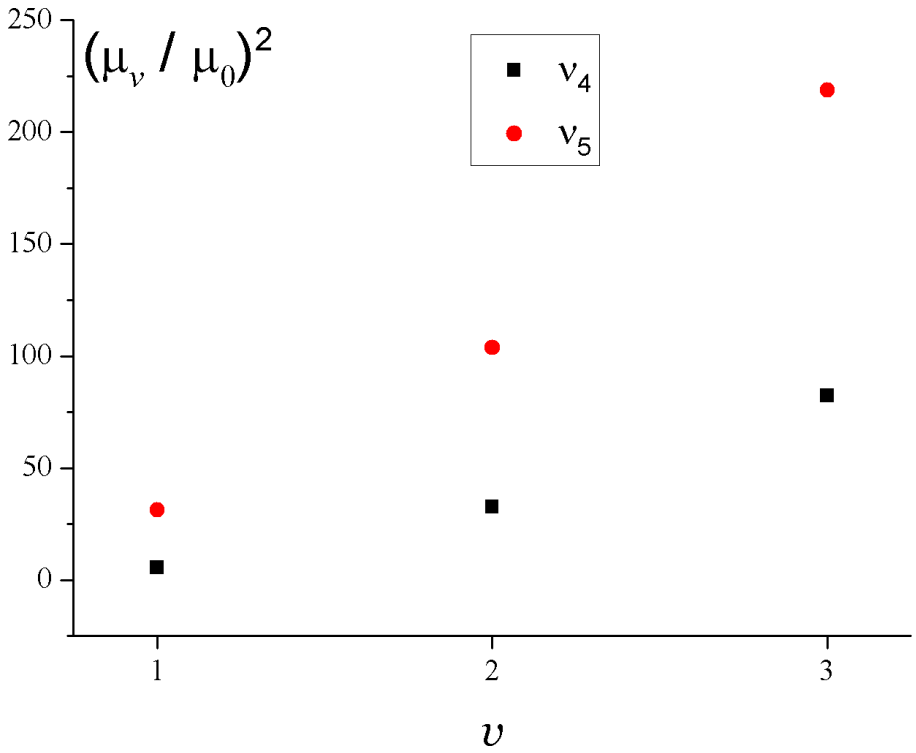

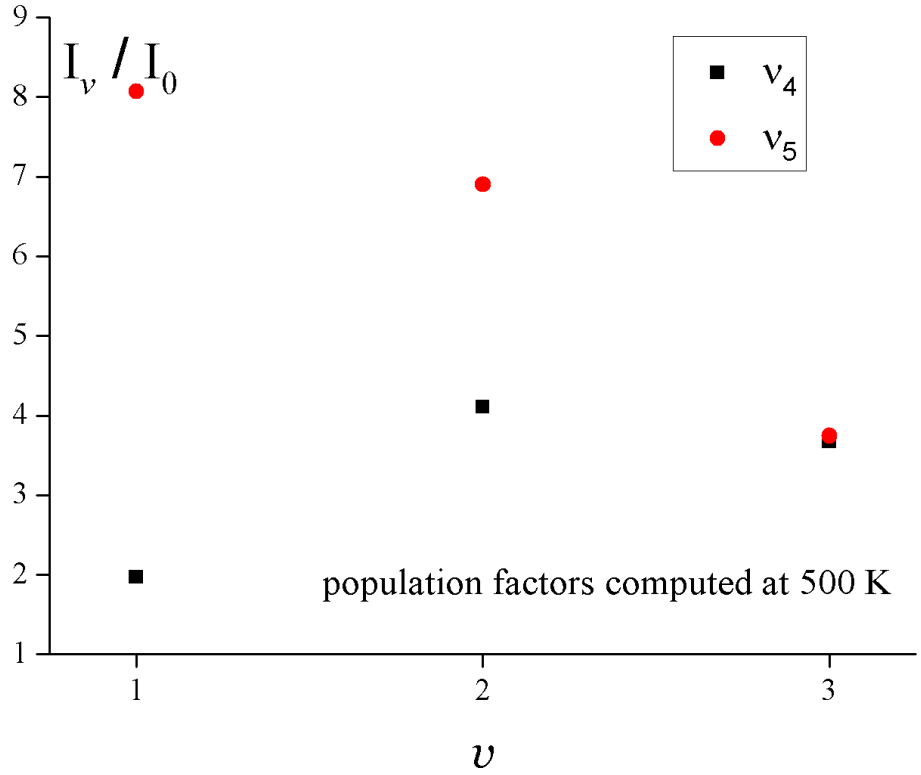

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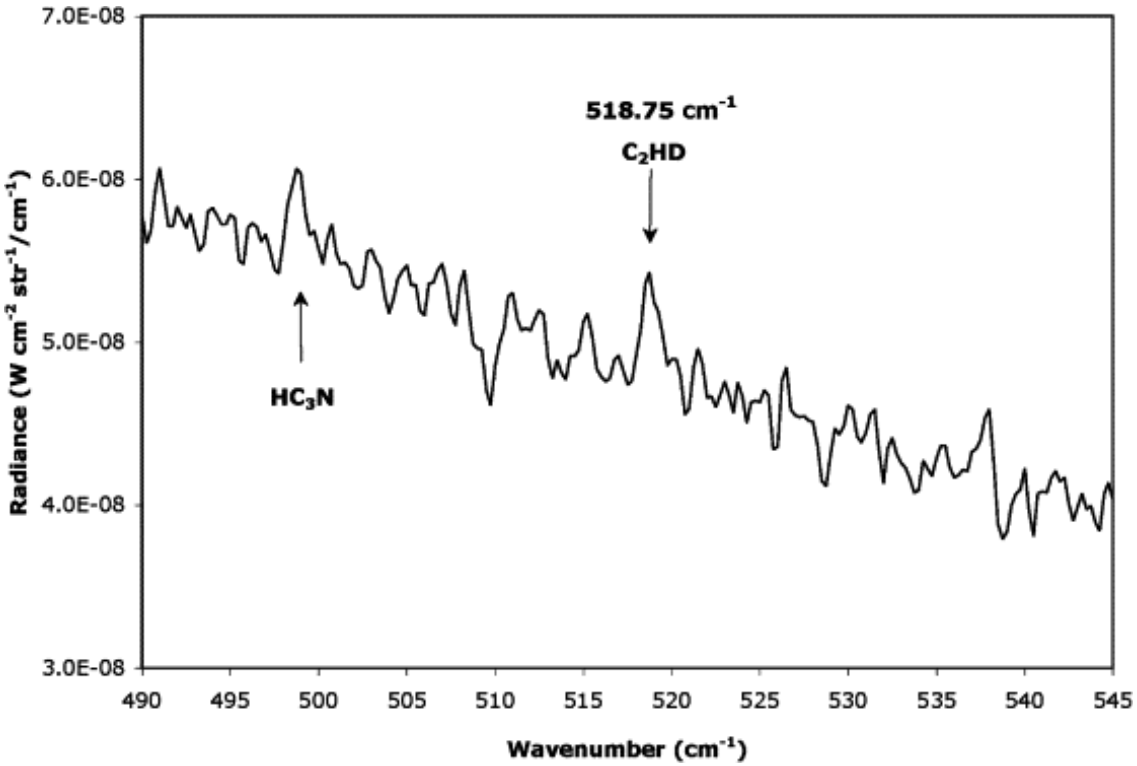
$^{12}C_2HD$ has been observed in Titan

Figure: Detection of the ν_4 Q-branch of C_2HD at 519 cm^{-1}



From these observations it was possible to derive the D/H ratio on Titan.

A. Coustenis, Icarus (2008) 197: 539

The rotational spectrum of $^{12}C_2HD$

- Rotational transitions were recorded in the range $100 - 700$ GHz for the vibrational ground state and for the bending states $v_4 = 1$ (Π), $v_5 = 1$ (Π), $v_4 = 2$ (Σ^+ and Δ), $v_5 = 2$ (Σ^+ and Δ), $v_4 = v_5 = 1$ (Σ^+, Σ^- and Δ), $v_4 = 3$ (Π and Φ) and $v_5 = 3$ (Π and Φ).
- The transition frequencies measured in this work were fitted together with all the infrared ro-vibrational transitions involving the same bending states available in the literature. The global fit allowed a very accurate determination of the vibrational, rotational and ℓ-type interaction parameters for the bending states up to $v_4 + v_5 = 3$.
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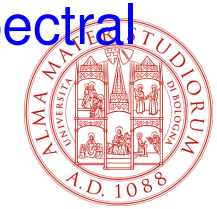

Five imines discovered in space

1. On 1973, methanimine (CH_2NH) detected in the molecular cloud Sgr B2.
2. On 1992, 1,2-propadienylidene (CCCNH) detected in TMC 1.
3. On 2006, ketenimine (CH_2CNH) detected in absorption toward the star-forming region Sagittarius B2 North (Sgr B2(N)).
4. On 2013, two conformers of ethanimine (CH_3CHNH) detected in Sgr B2(N).
5. On 2013, E-cyanomethanimine (E-HNCHCN) detected toward Sagittarius B2(N).

- Recent laboratory studies on interstellar ice analogues have shown that hydrogenation reactions of CN-bearing molecules on the grain surface lead to the formation of methylamine and amino-acetonitrile, which are important building-blocks for biomolecules.
- In these processes, imines (molecules containing the C=NH moiety) play a prime role as either hydrogenation intermediate of nitriles or precursors of saturated amine compounds.

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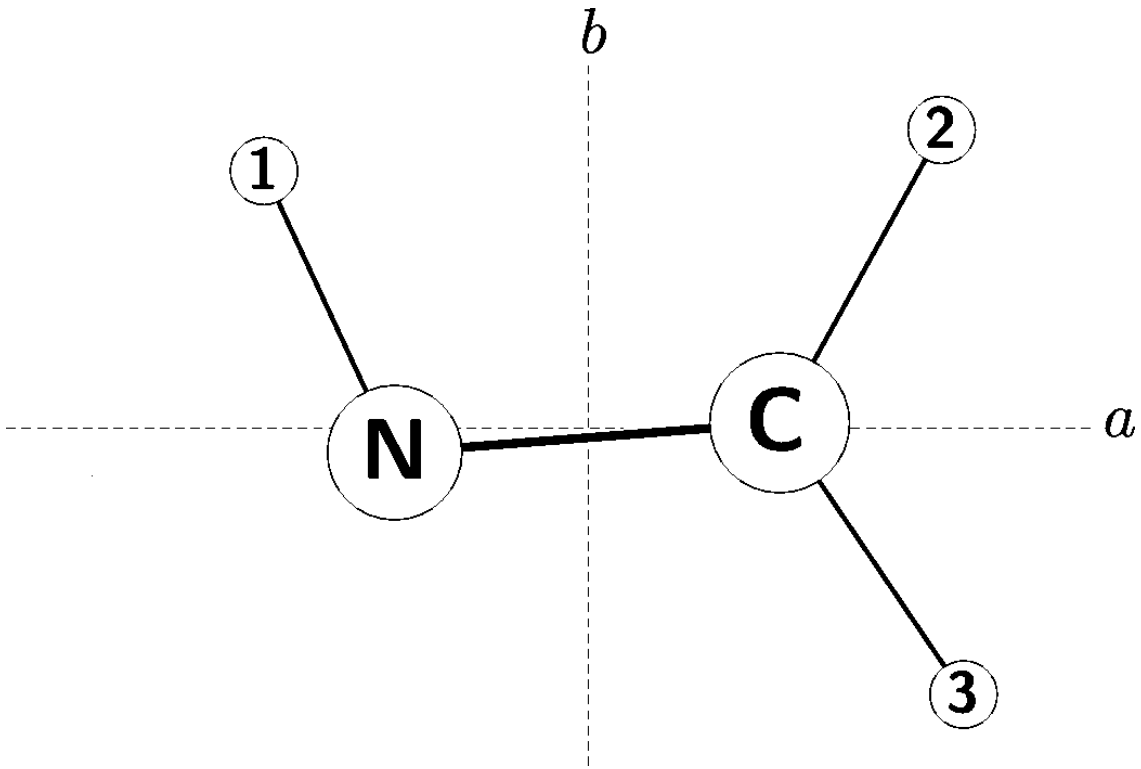
Methanimine

Figure: $H_2C{=}NH$ is a near prolate asymmetric rotor. The dipole moment has two components, along *a* and *b* principal axes



Methanimine: an interstellar molecule

- On 1973, first detection in the molecular cloud Sgr B2.
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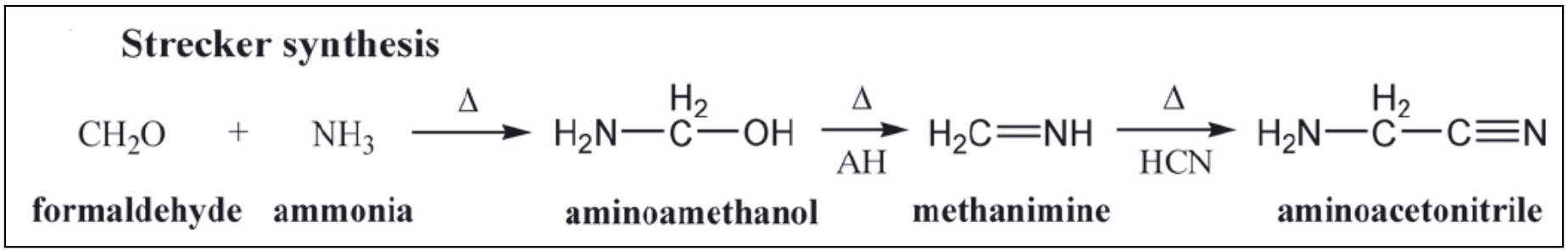
Methanimine: a pre-biotic interstellar molecule

Danger et al. (A&A (2011) 535: A47) prove that, by warming ice analogues in astrophysical-like conditions, methanimine participates in the Strecker synthesis to form aminoacetonitrile (NH_2CH_2CN; recently detected in Sgr B2(N)), which is a possible precursor of glycine, the simplest amino acid.



Submillimeter-wave spectrum

Pyrolysis reaction

$$NH_2CH_2CH_2NH_{2\,(g)} \xrightarrow{1150\,^{\circ}C} 2H_2CNH_{(g)} + H_{2\,(g)}$$

The ground state rotational spectrum has been recorded in the ranges 64 – 172 GHz and 329 – 629 GHz, allowing the determination of fairly accurate rotational constants and the complete sets of quartic and sextic centrifugal distortion constants, in addition to two octic constants.

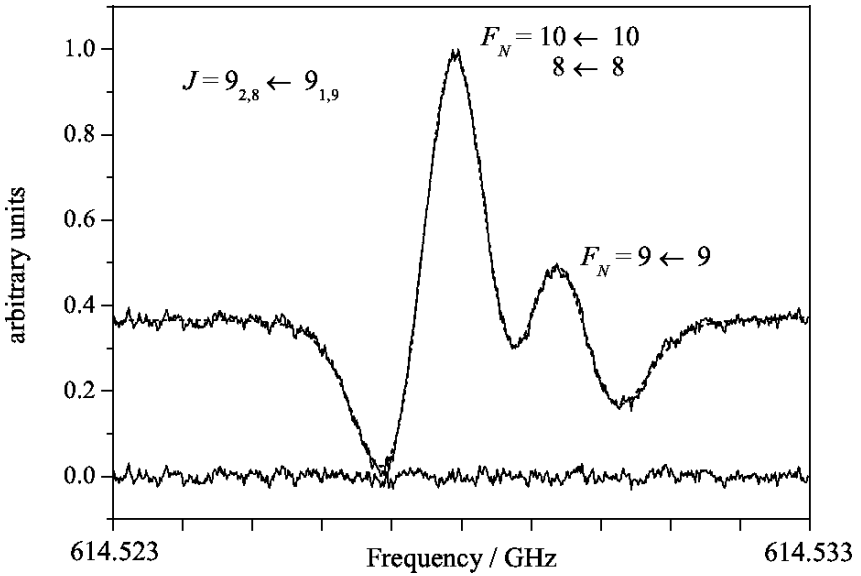
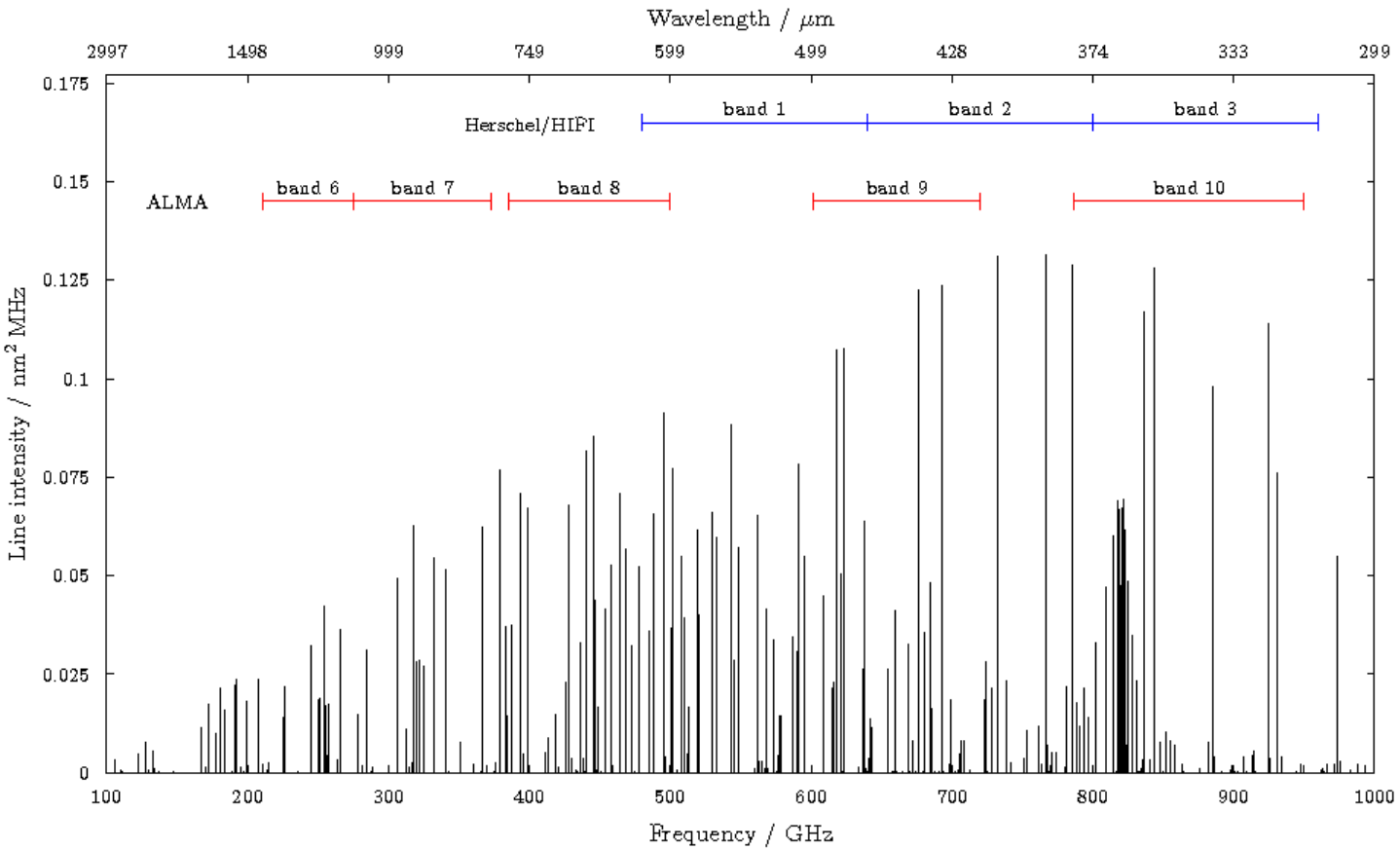


Figure: Hyperfine doublet recorded in 310 s with a time constant of 10 ms. The spectral profile has been fitted to a sum of three hyperfine components.

Rest-frequencies for astrophysical purposes

Figure: Simulation of the rotational spectrum of CH_2NH. Intensities are computed at 50 K.

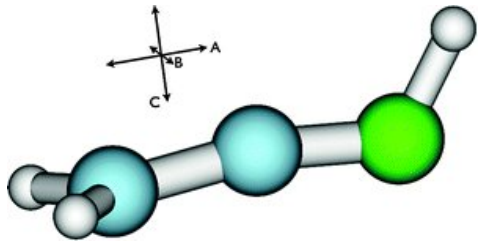


The frequency precision of the predictions in ALMA band 10 is of the order of a few parts in 10^9 (0.0003 km s^{-1} in radial velocity)

At 50 K the strongest transitions lie in the ALMA bands 9 and 10.

Ketenimine

Figure: $H_2CC{=}NH$ is a near prolate asymmetric rotor. The dipole moment has two components, along *a* and *c* principal axes



Ketenimine is a member of the interstellar C_2H_3N isomer triad comprised also of methyl cyanide (CH_3CN) and methyl isocyanide (CH_3NC).

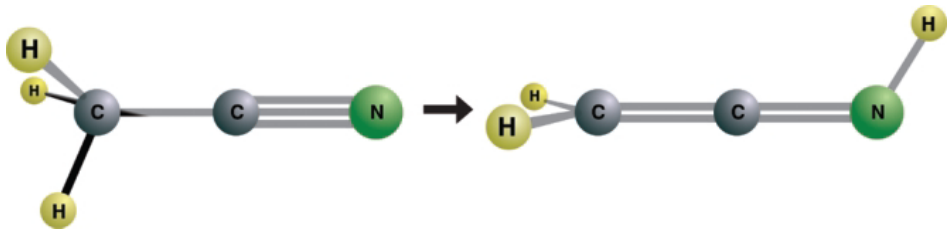


Figure: This isomer conversion reaction (tautomerization) may be driven by shocks that pervade the Sgr B2(N) star-forming region (Lovas et al. ApJ (2006) 645:L137).

Are the three isomers cospatial?

- Interferometric observations with the Atacama Large Millimetre Array (ALMA) are clearly a well suited tool to provide deep insights on the imine chemistry in massive star forming regions.
- The availability of very accurate rest frequencies is of prime importance, particularly if one aims at carrying out studies on chemically-rich regions, where extremely crowded spectra are usually observed at millimeter and sub-millimeter wavelengths.
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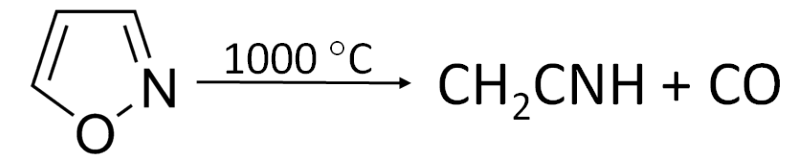

isoxazole

The ground state rotational spectrum has been recorded in the range 80 – 620 GHz. 207 new rotational transitions have been recorded, which are R ($\Delta J = +1$) and Q ($\Delta J = 0$) a-type lines, and R, Q, and P ($\Delta J = -1$) c-type lines, spanning J values from 0 to 67 and K_a values from 0 to 9.

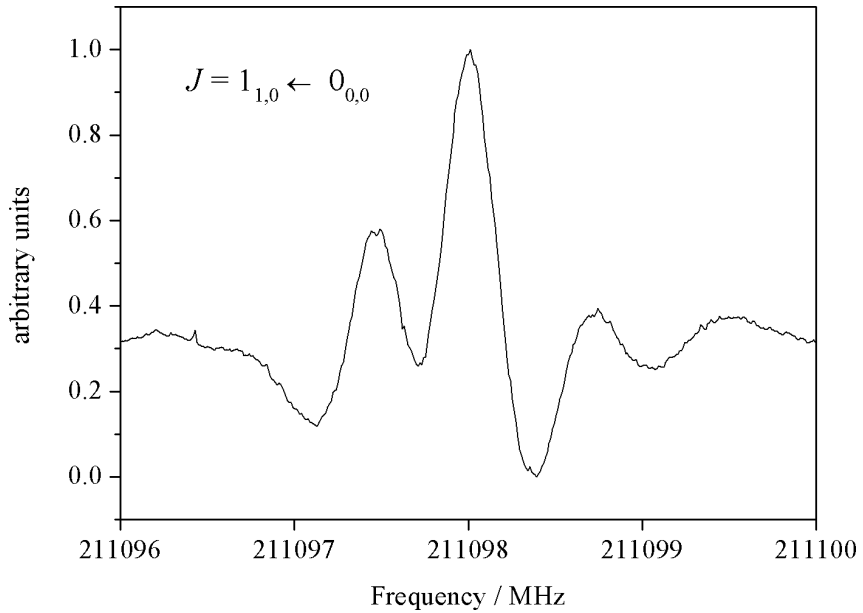

Figure: A fairly large number of the recorded transitions show an hyperfine structure due to the electric quadrupole coupling of the ^{14}N nucleus ($I = 1$). The $1_{1,0} \leftarrow 0_{0,0}$ transition is an example.

Centrifugal resonance

- Nearly all of the analysed rotational transition frequencies could be well fitted using a single-state Hamiltonian.
- A weak centrifugal resonance couples the ground state to the lowest energy modes ν_8 and ν_{12}, and affects the frequency of a few *a*-dipole transitions with $K_a \geq 7$.
- These transitions could be properly fitted adopting an interaction scheme where off-diagonal matrix elements originating from the H_{12} ro-vibrational Hamiltonian are considered.

$$H_{12} = -\omega_8 q_8 C_8^{ab} \left[J_b, J_a\right]_+ - \omega_{12} q_{12} C_{12}^{ac} \left[J_c, J_a\right]_+$$

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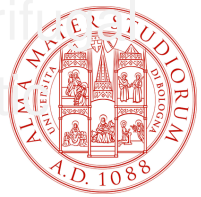

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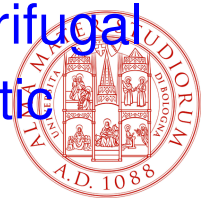

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