Millimeter and submm-wave spectroscopy of species of astrophysical importance

Luca Dore

Department of Chemistry “Giacomo Ciamician”
University of Bologna, Italy

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Main task: providing rest frequencies

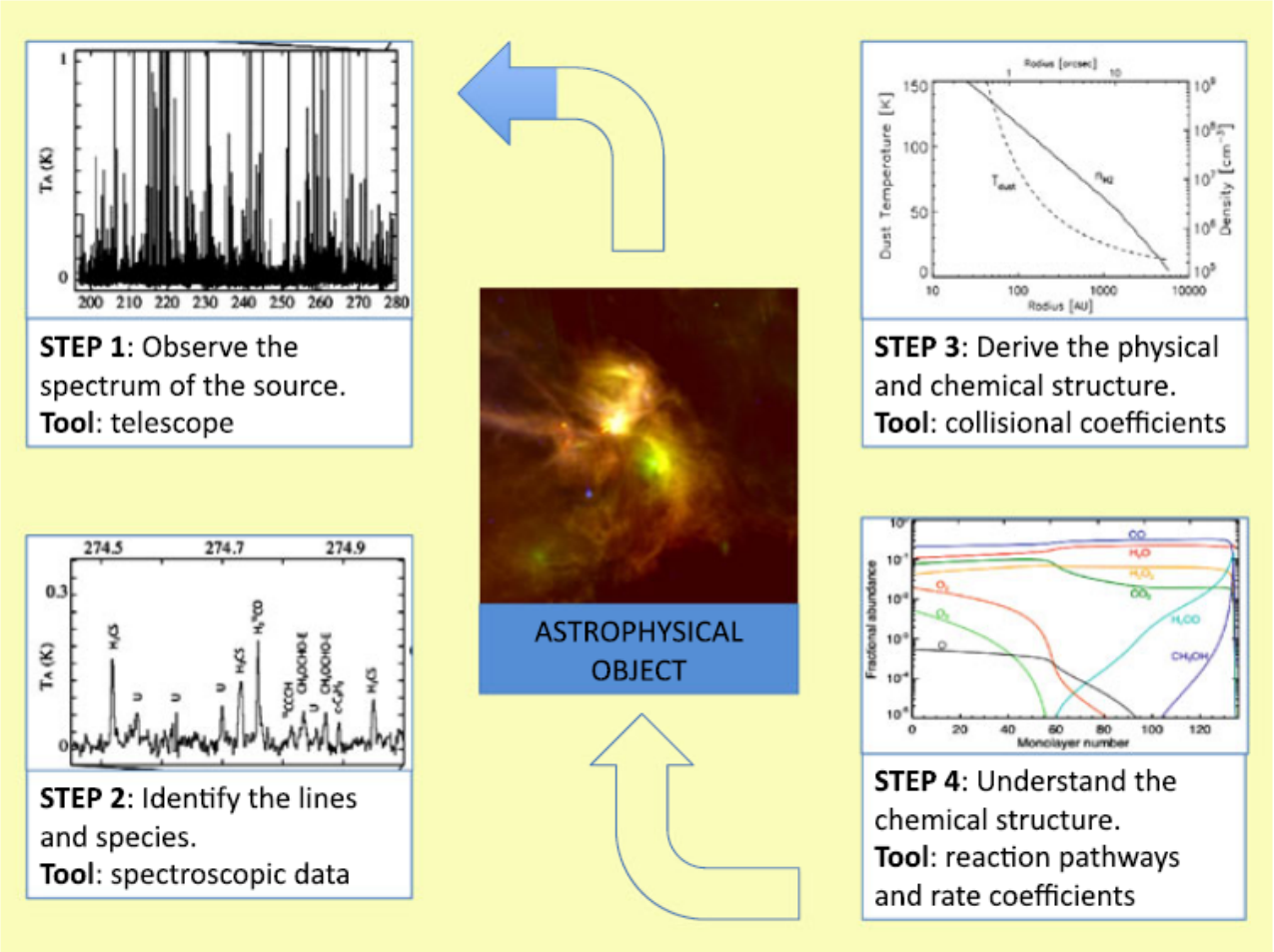
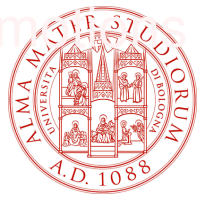


Figure: from P. Caselli & C. Ceccarelli, Astron Astrophys Rev (2012) 20:56

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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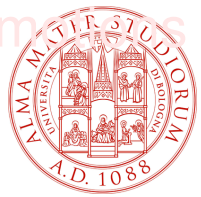

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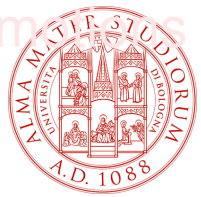

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Outline

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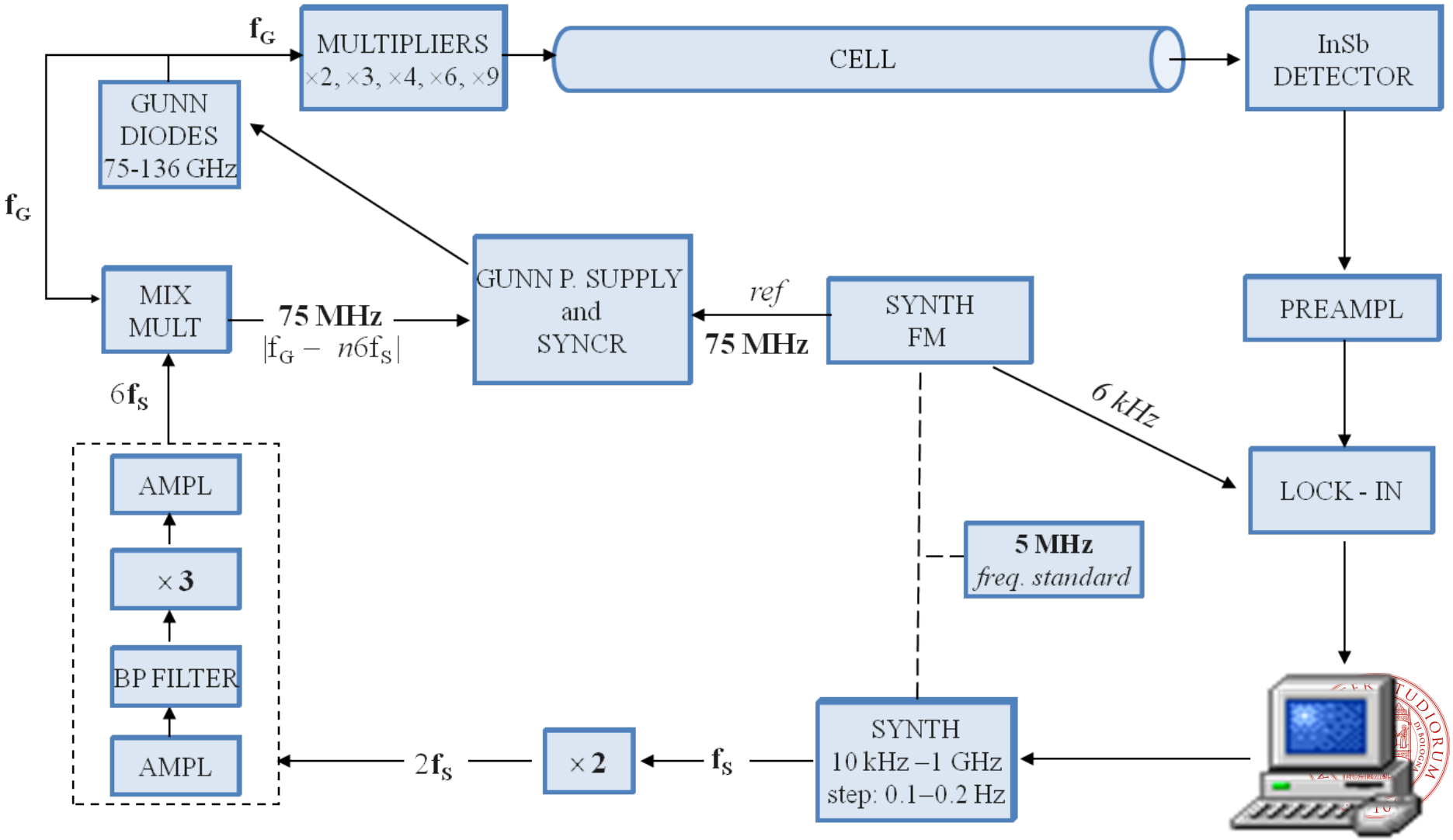
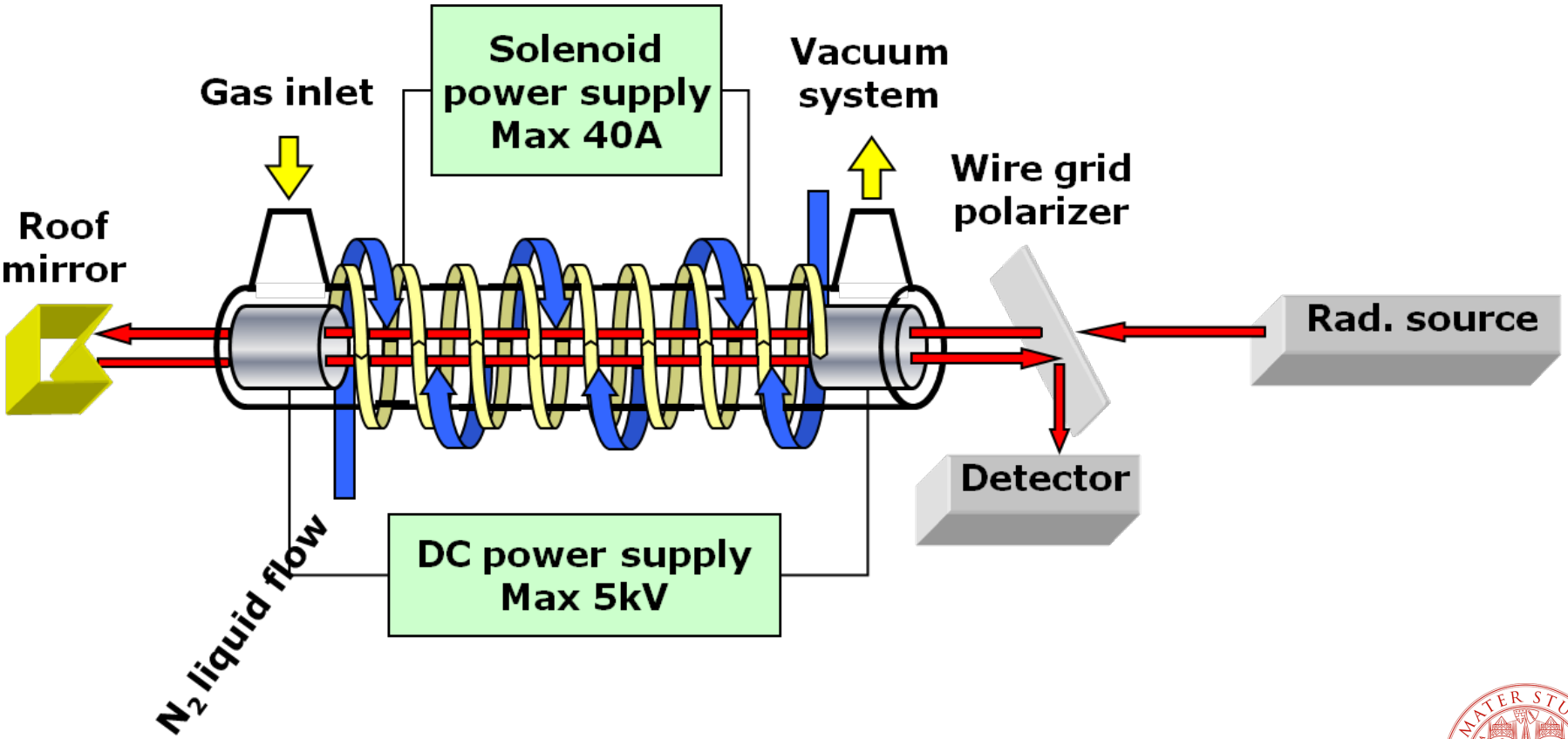
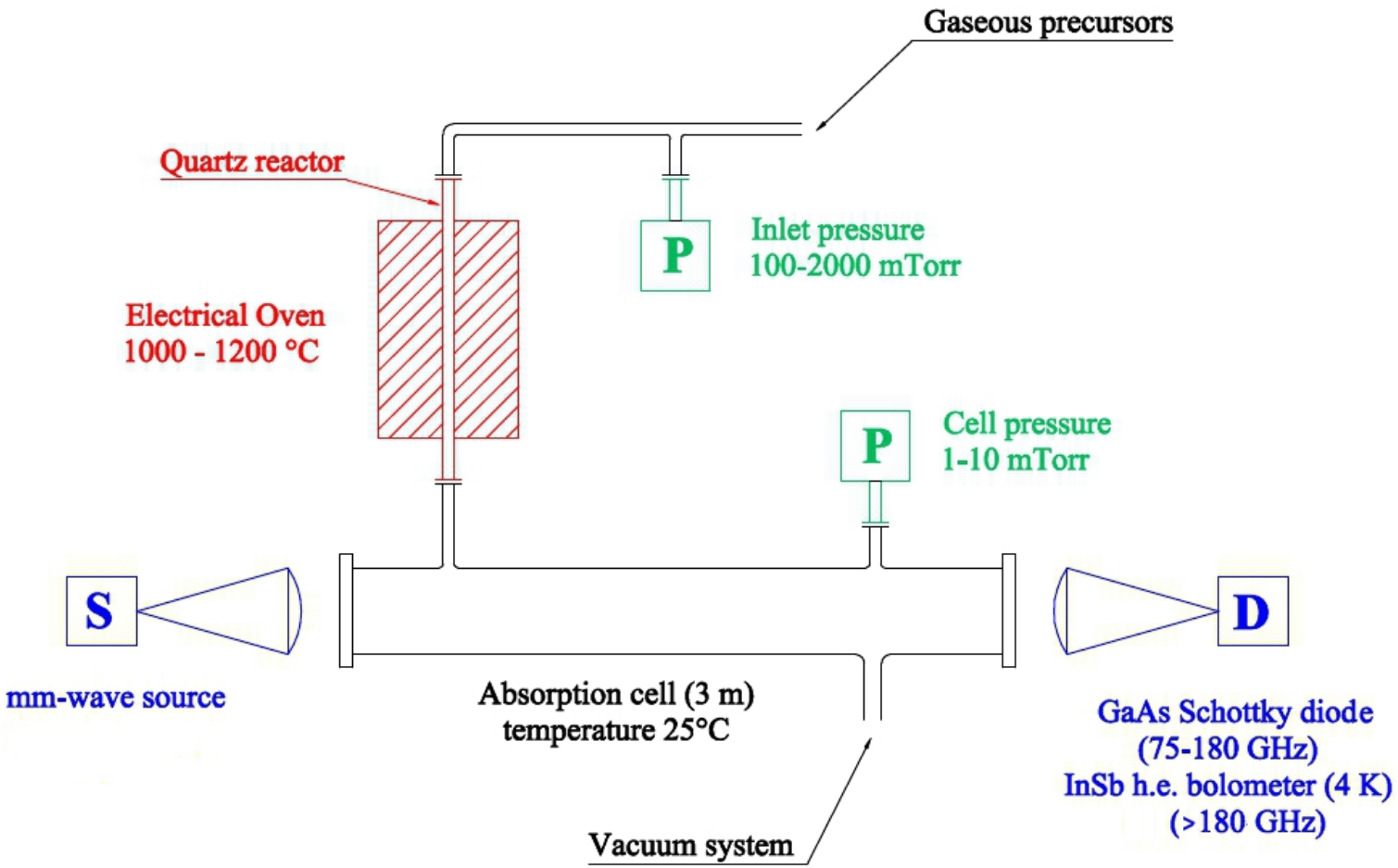
The spectrometer



The discharge cell

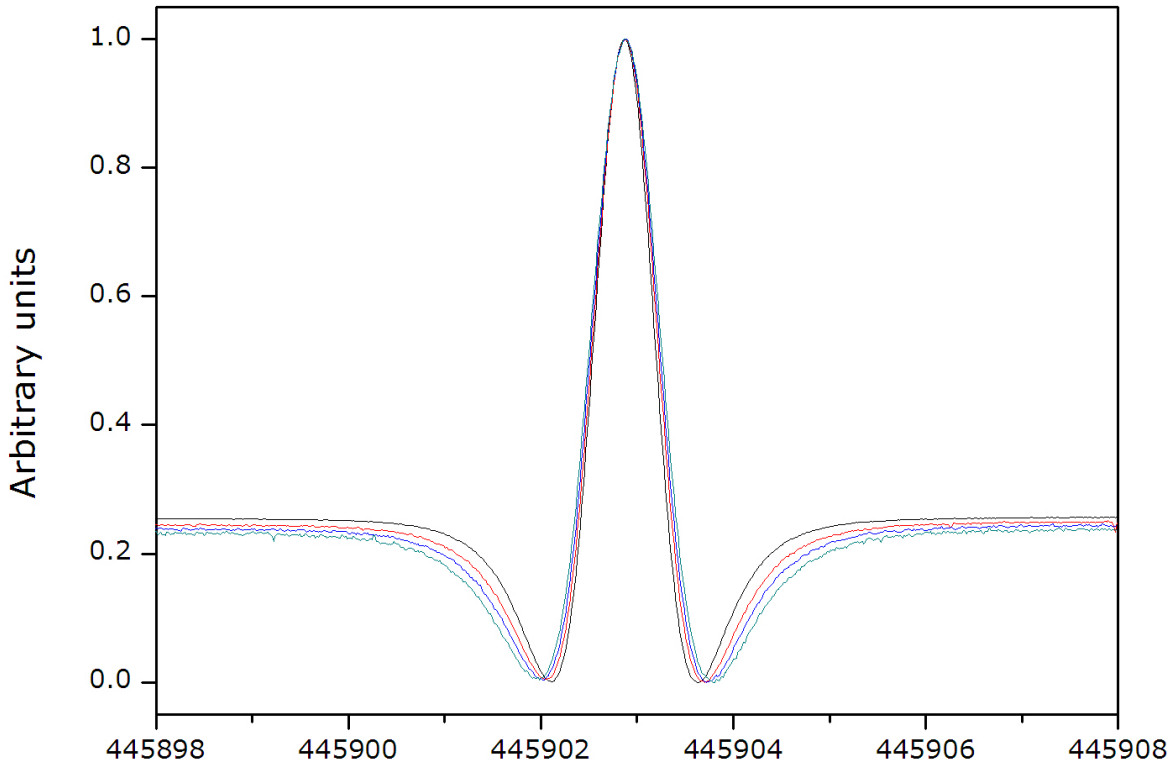


The pyrolysis cell



2^{nd} harmonic detection

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



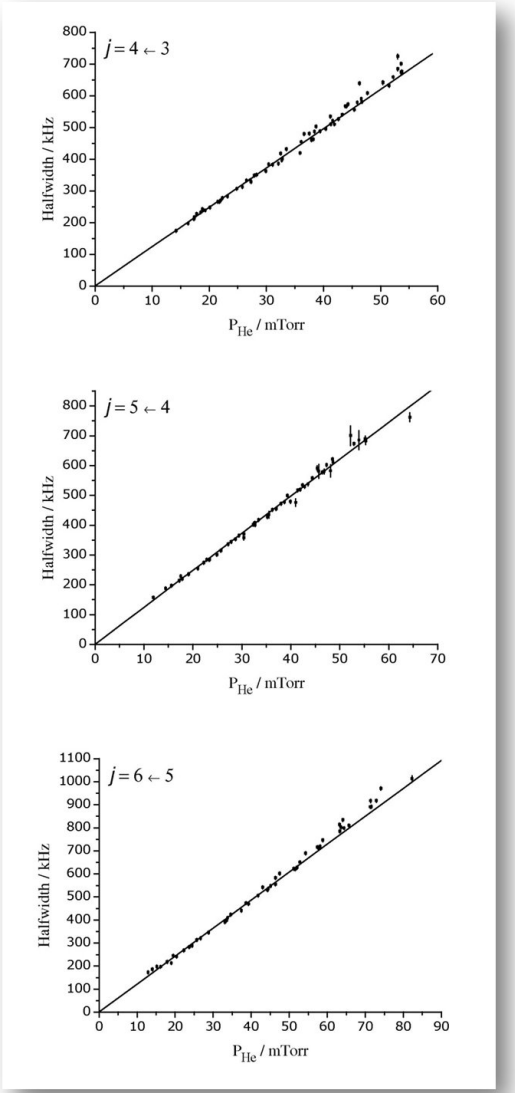
$$F_2(\omega) \propto \mathrm{Re} \int_0^{\infty} J_2(mT)\Phi e^{i\omega T} \mathrm{d}T$$

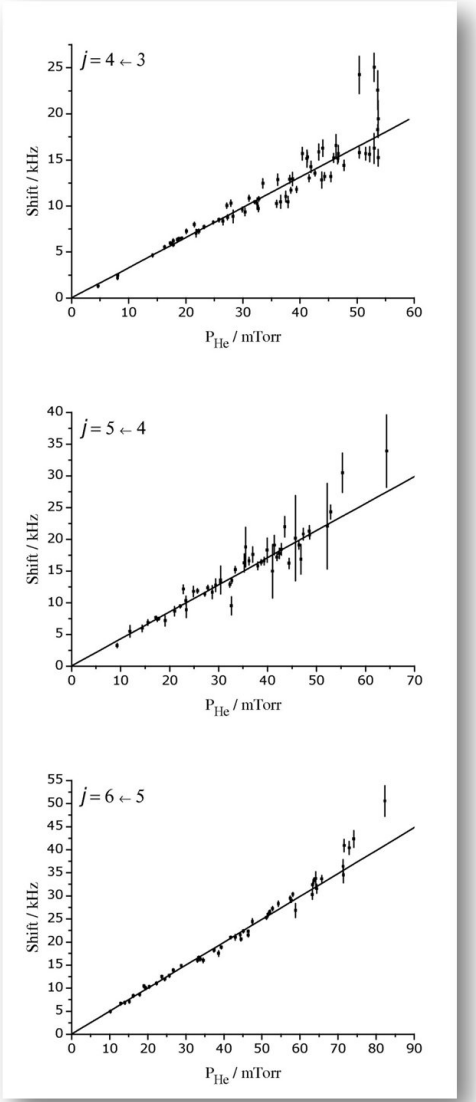
In case of weak absorptions, when the Beer-Lambert law can be linearized, the line shape resulting from second-harmonic detection is given by the real part of the Fourier transform of the correlation function (exponential decay) times a Bessel function of the first kind of order 2.

L. Dore, JMS (2003) 221: 93

He broadening and shift of HCO^+ rotational lines

line widths

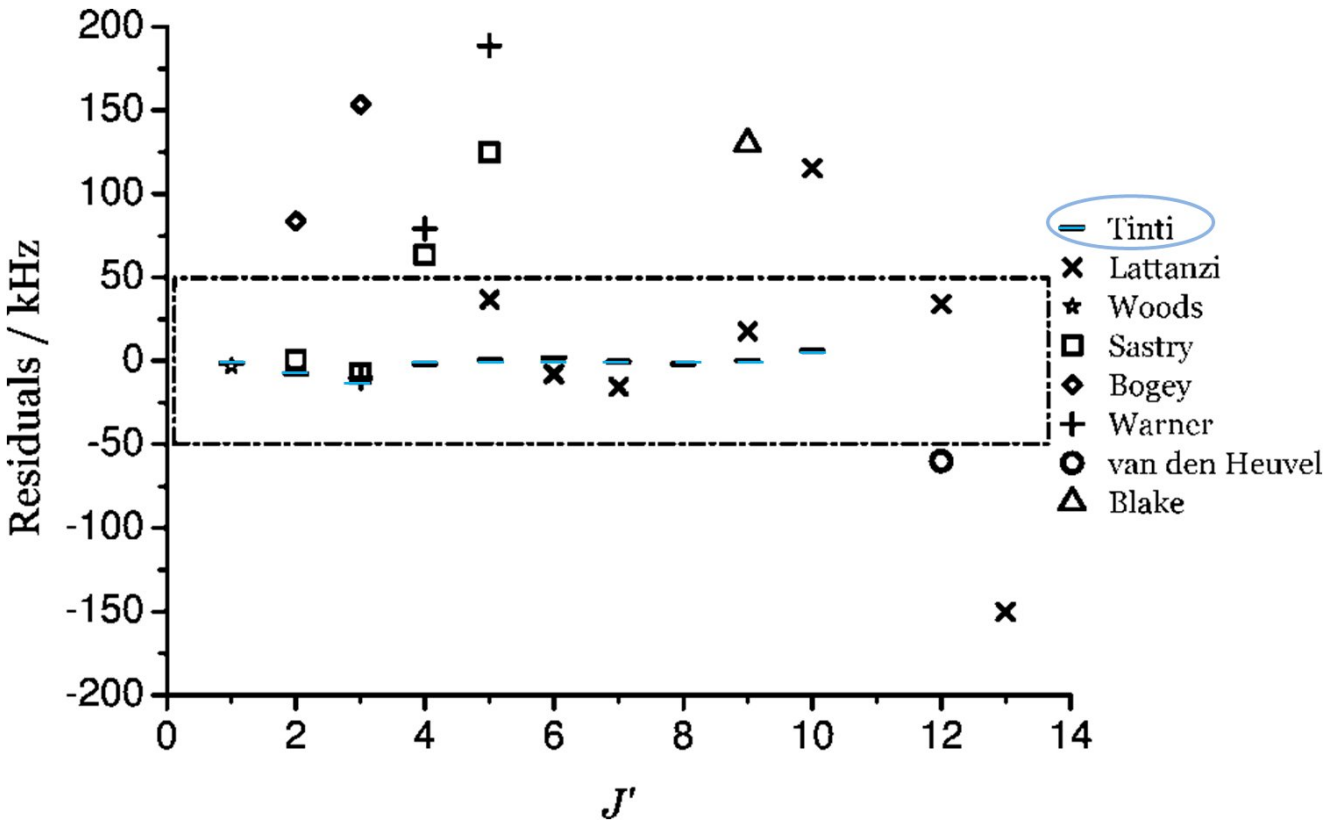




frequency shifts

High accuracy

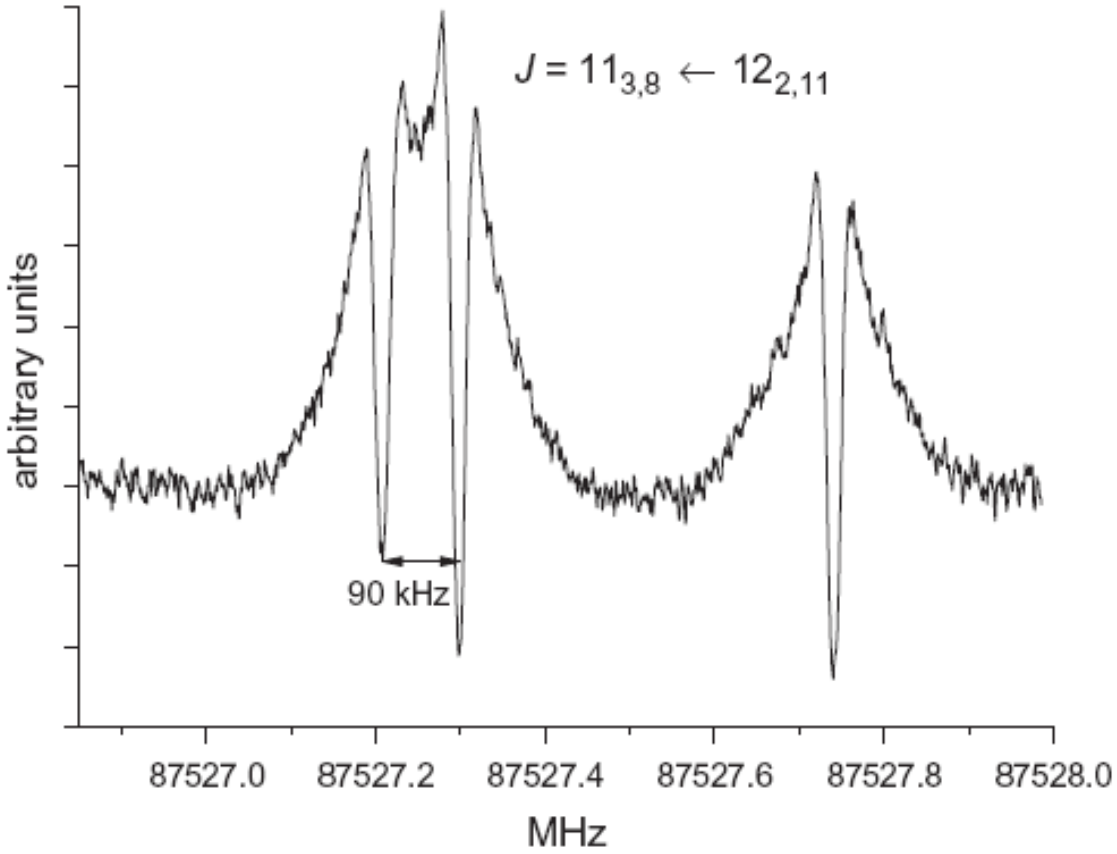
Figure: Residuals of transition frequencies of HCO^+ from different papers



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



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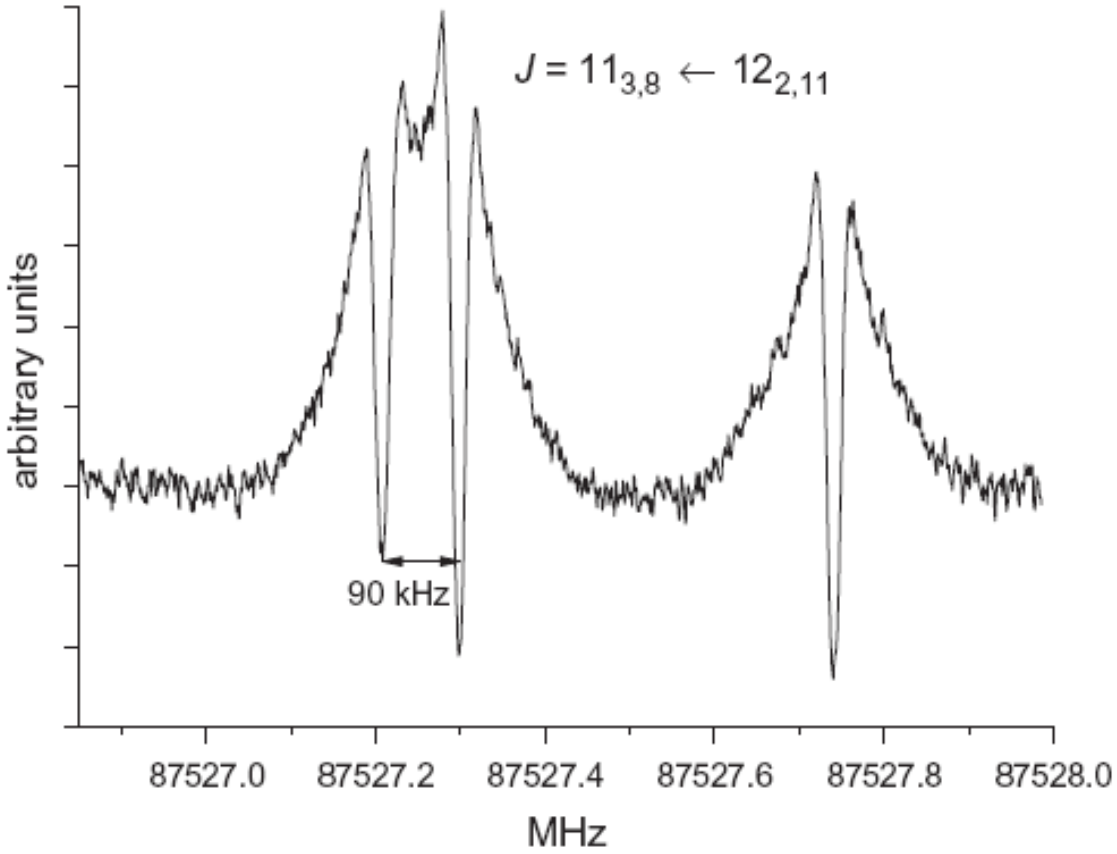
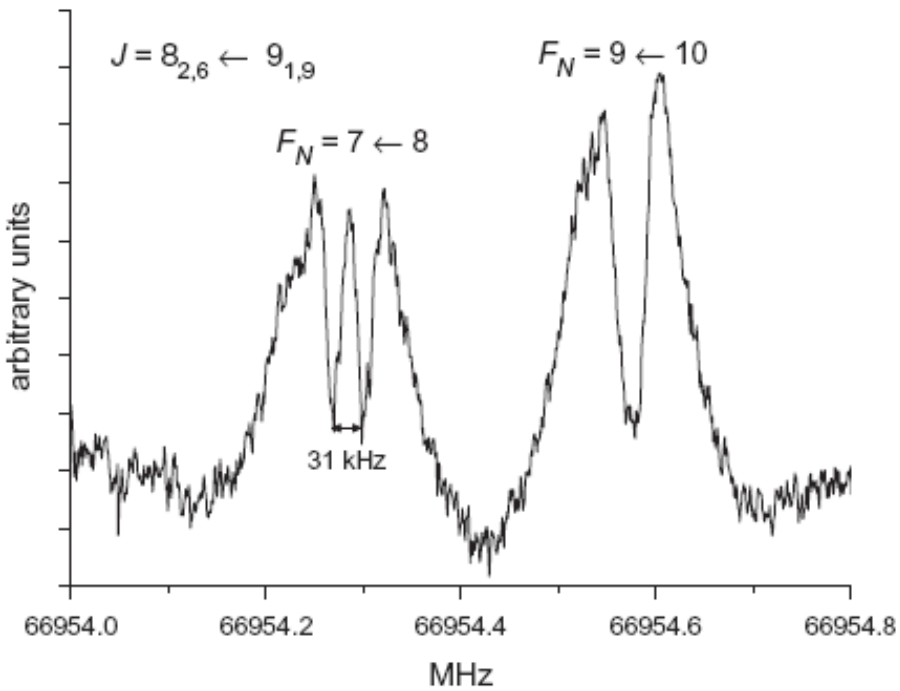
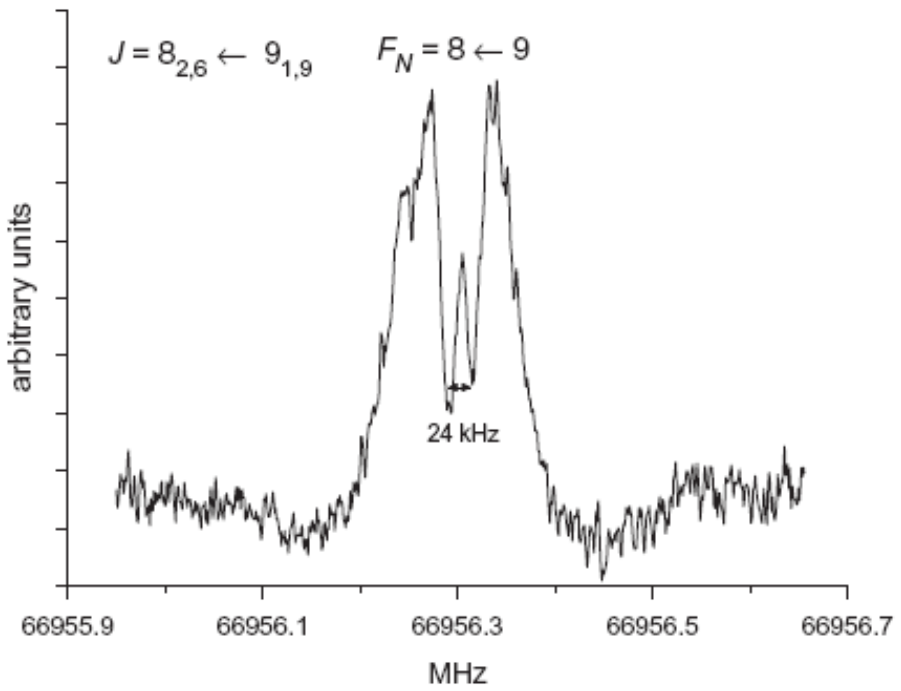


High resolution

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).

NCO$^-$

- There is now strong experimental and theoretical support to the assumption that the so-called XCN feature at 2165 cm^{-1} (4.62 μm) of interstellar ices observed toward various young stellar objects is due to NCO$^-$.
- There is a suggestion that “cyanate ion would also be a stable radiation product in any Titan region having both nitriles and H_2O-ice”.
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Spectroscopy of NCO$^-$

- The high-resolution ground state rotational spectrum of the cyanate ion has been observed from 23 to 368 GHz (from $J = 1 \leftarrow 0$ to $J = 16 \leftarrow 15$) at Harvard (Lattanzi et al. ApJ (2010) 720:1717).
- The first high-resolution spectrum of NCO$^-$ dated back to 1987, when Gruebele et al. measured 132 IR transitions in the CN-stretching fundamental and the corresponding bending and stretching hot bands.
- We extended the detection of the rotational spectrum of NCO$^-$ into the submillimeter-wave region by recording three additional lines up to 437.4 GHz, that is in band 8 (385 – 500 GHz) of ALMA.

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NCO^- production

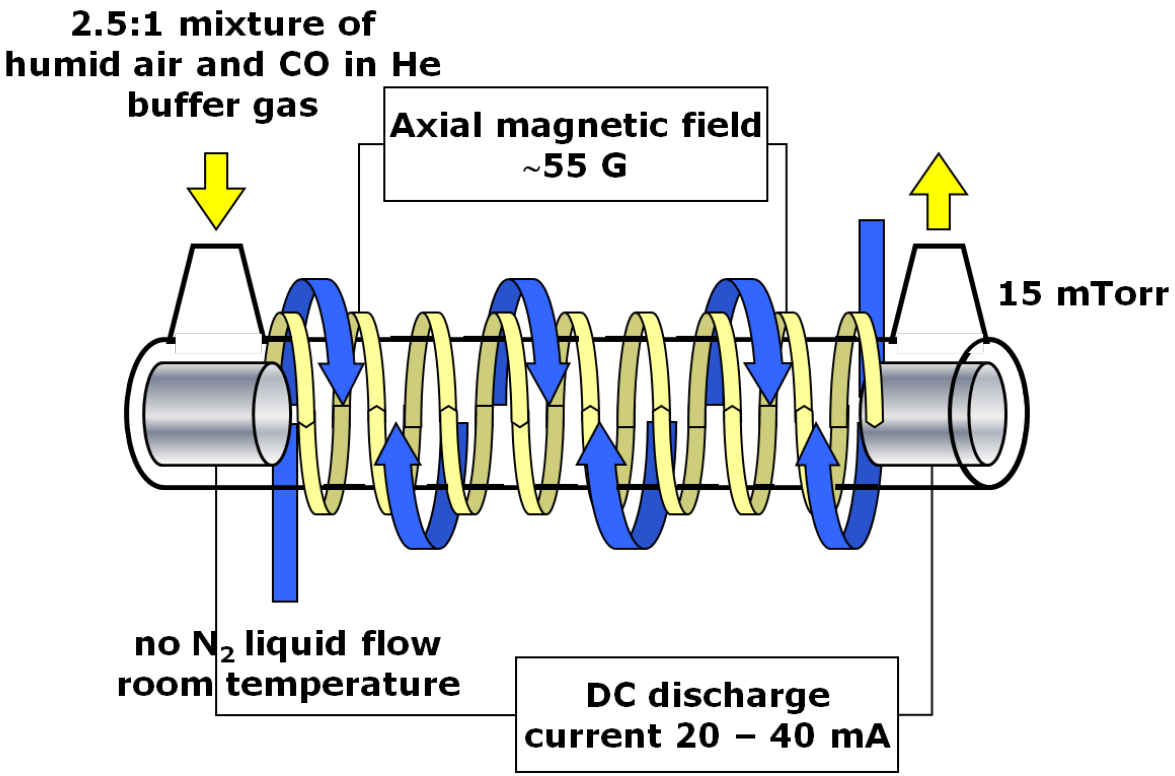

Figure: The best conditions for NCO^- production were found by looking for the most intense signal of the $J = 53_{0,53} \leftarrow 52_{1,52}$ transition of the isocyanic acid HNCO.

- NCO^- should be produced by dissociative electron attachment to HNCO (Lattanzi et al. ApJ (2010) 720:1717).
- We can confirm this hypothesis, because even using different precursors, for instance NH_3 and CO, the better was the production of HNCO, the stronger was the signal detected for NCO^-.

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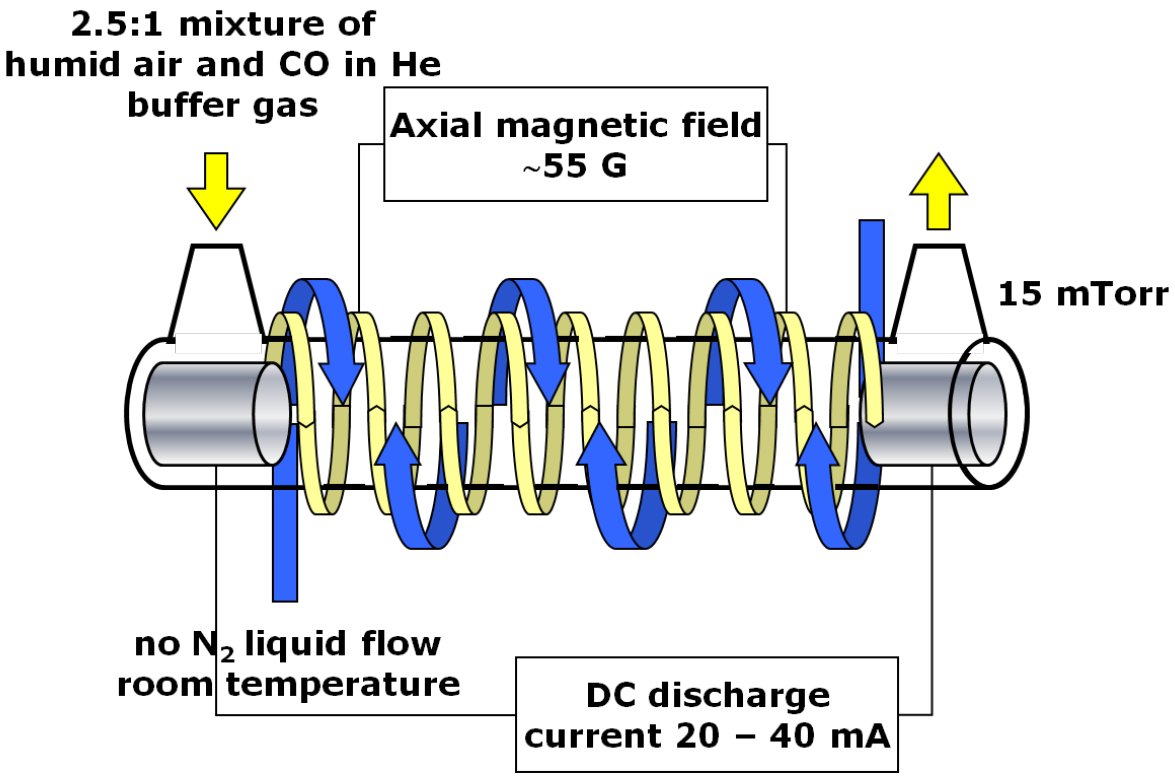

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Centrifugal analysis

Table . Spectroscopic constants of NCO^-.

Constants	Lattanzi et al. [7]	This work[a]	Correlation matrix		
B_0/MHz	11 513.9683(8)	11 513.96777(43)	1.000		
D_J/kHz	4.561(2)	4.55907(87)	0.885	1.000	
eqQ/Hz	−1.0307(37)	−1.0302(37)	0.221	0.196	1.000
rms^b_{res}/kHz		12.7			
σ^c		0.724			

- The determined rotational and centrifugal distortion constants allow an accurate prediction of the transition frequencies in the ALMA bands 9 and 10.
- The predicted uncertainties, and the predicted transition frequencies as well, are model-dependent, because the sixth-order centrifugal distortion constant H_J is undetermined.
- We estimated H_J theoretically, obtaining a value of 0.129 mHz, which implies a sextic contribution to the transition frequencies below 1 THz lower than the experimental uncertainty.

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GeO: an astromolecule?

- Ge is mainly produced in TP-AGB stars through s-process (slow neutron capture process).
- After the TP-AGB phase is terminated, the remnant of the ejected stellar material form a Planetary Nebula (PNe), which is expected to host enhanced gas-phase abundances of heavy n-capture elements.
- Elevated Ge abundances ($\geq 3-10$ times solar) have been measured in several PNe (GeIII lines, far UV).
- GeO spectra might be detectable in post-AGB objects (Proto-PNe) deriving from an O-rich star.
- Determining accurate abundances of GeO can set constraints on models of stellar nucleosynthesis and provides insights on the pr of chemical enrichment of the ISM.

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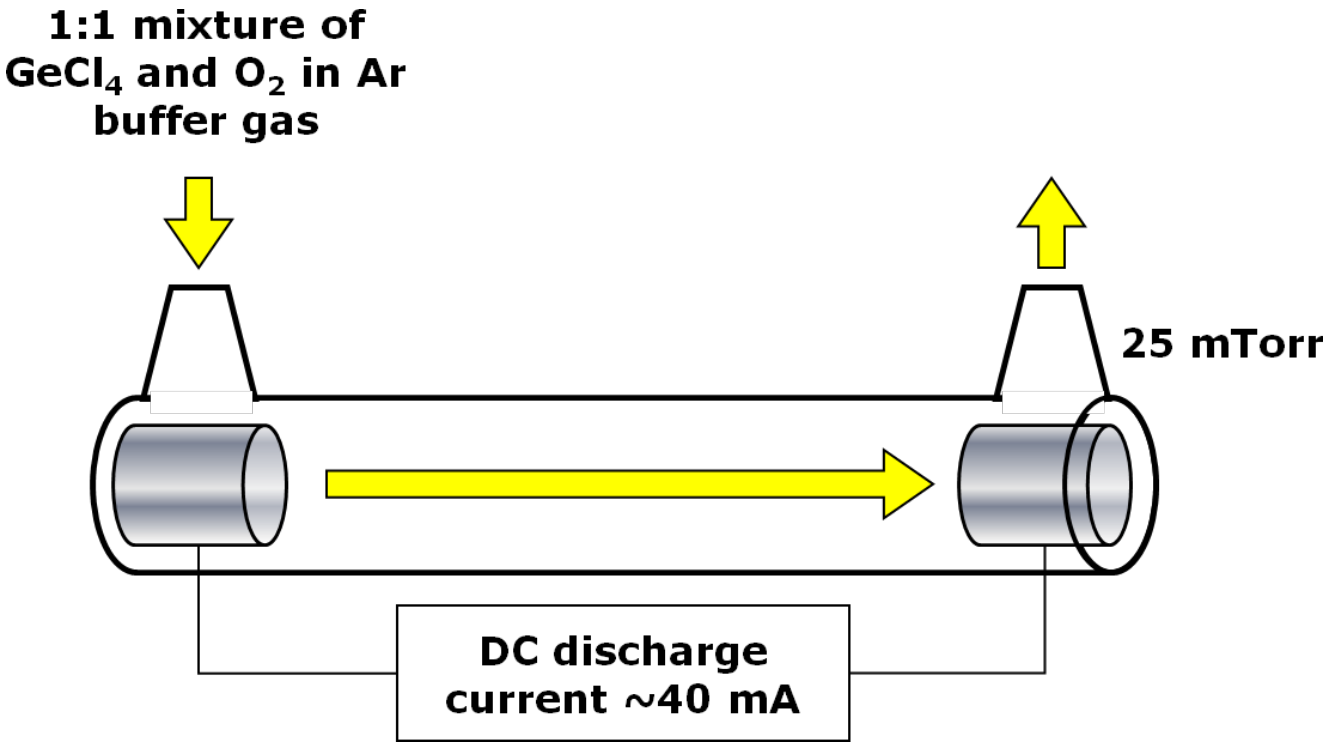
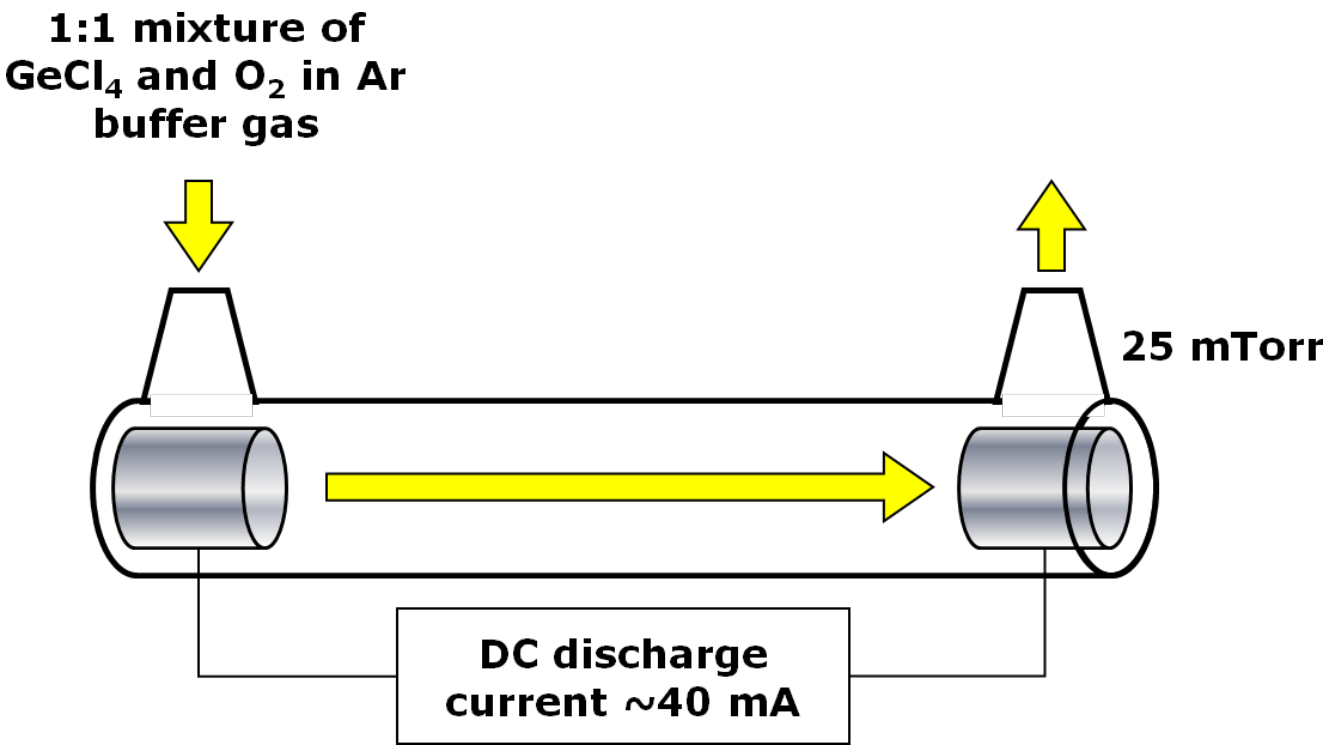


- Natural germanium is composed of ^{70}Ge (20.5%), ^{72}Ge (27.4%), ^{73}Ge (7.8%), ^{74}Ge (36.5%) and ^{76}Ge (7.8%).
- All the five common isotopologues of Ge^{16}O have been observed.

GeO production



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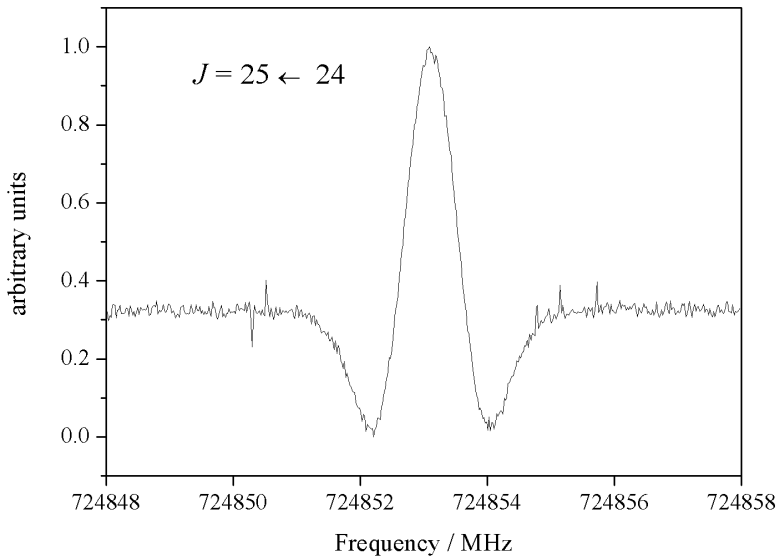
Submillimeter-wave spectrum

The ground state rotational spectra of the 5 isotopologues have been recorded in the range 115 – 732 GHz, with J ranging from 3 to 24. For the most abundant ^{74}GeO species, the rotational spectrum in the first excited vibrational state has been recorded in the same range.



Spectroscopic parameters of ^{74}Ge^{16}O from a global fit adopting a Dunham-type energy level expression.

Parameter	Fit[a]
Fitted values	
$U_{01}\mu^{-1}$/MHz	14,562.06462(94)[b]
δ_{01}^{Ge}/MHz	−0.16352(91)
Y_{02}/kHz	−14.12023(33)
Y_{03}/mHz	−1.92(26)
Y_{11}/MHz	−92.29323(16)
Y_{21}/kHz	[d]
Y_{31}/kHz	[d]
Y_{12}/Hz	−16.63(17)
Derived values	
Y_{01}/MHz	14,560.86227(15)[e]
B_e/MHz	14,560.86802(22)[f]
Δ_{01}^{Ge}	−1.5131(84)[g]
δ_{01}^{O}/MHz	−1.0388[i]
Δ_{01}^{O}	

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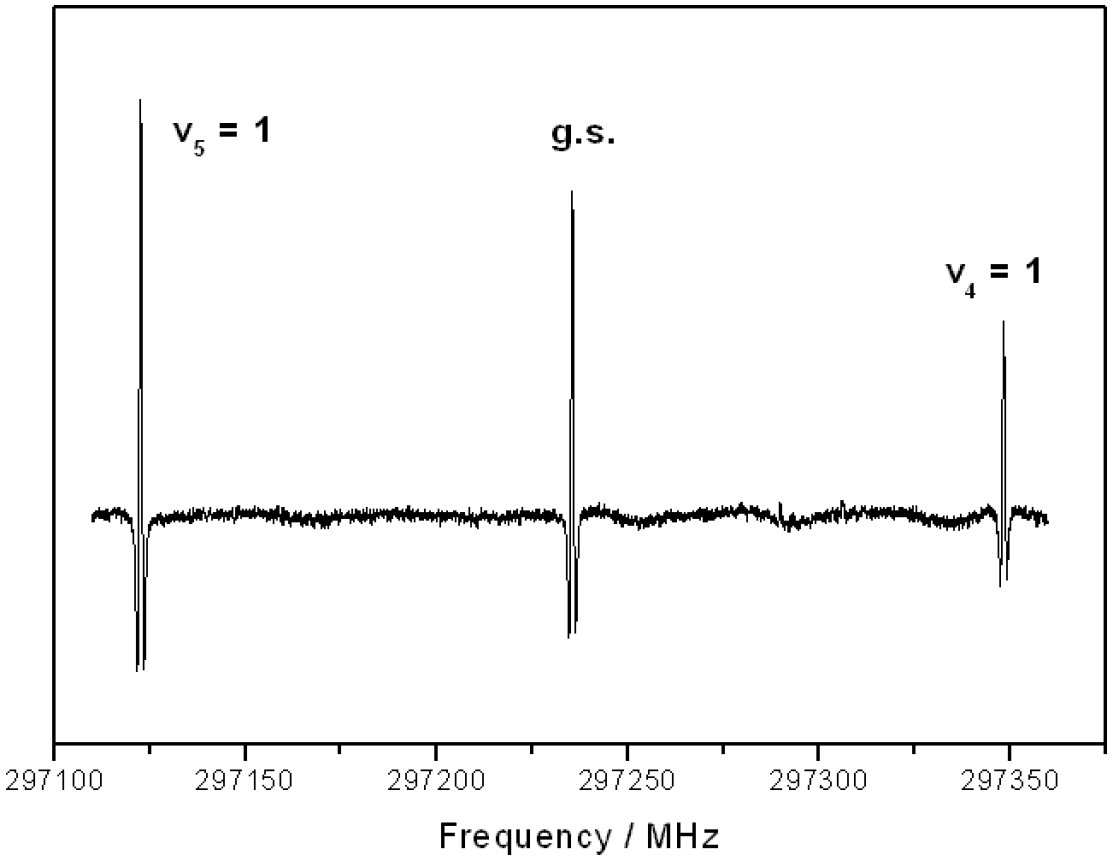
$^{12}C_2HD$ do have a small permanent dipole moment (0.01 D)

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.

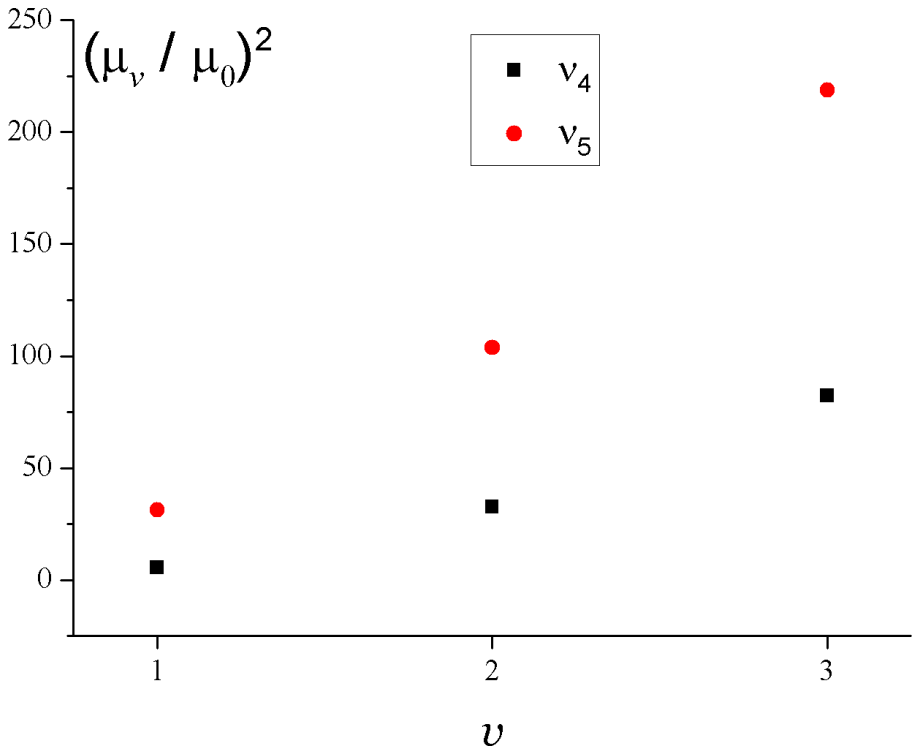


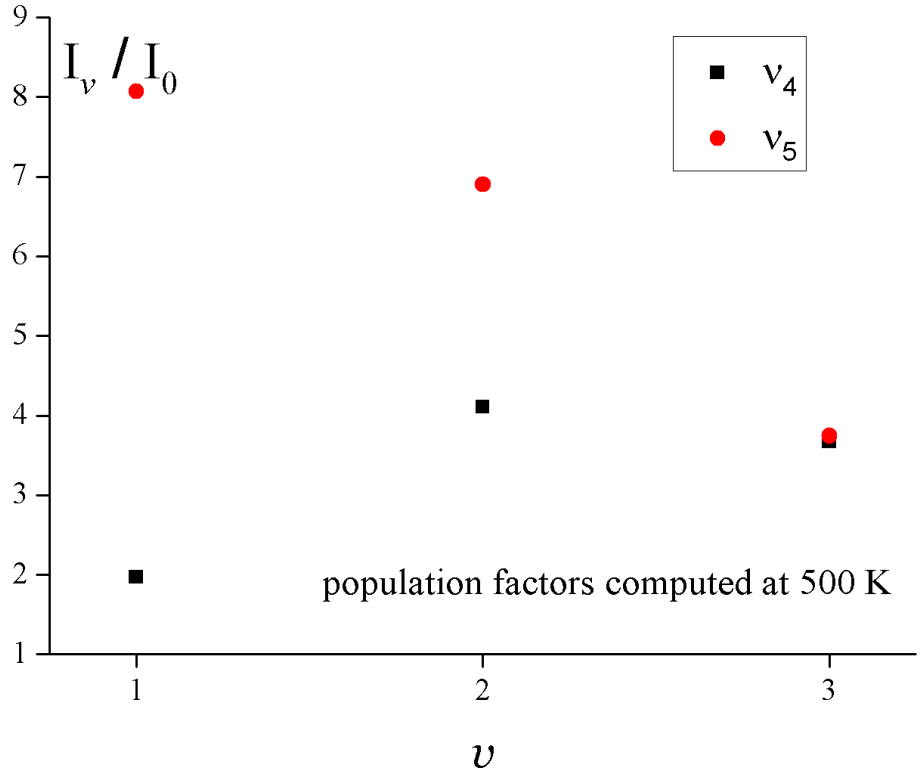
The dipole moment value is larger in the excited bending modes than in the ground state.

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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This will facilitate the detection of emission lines in the bending states in chemically rich regions, like IRC+10216, which show a high degree of vibrational excitation.

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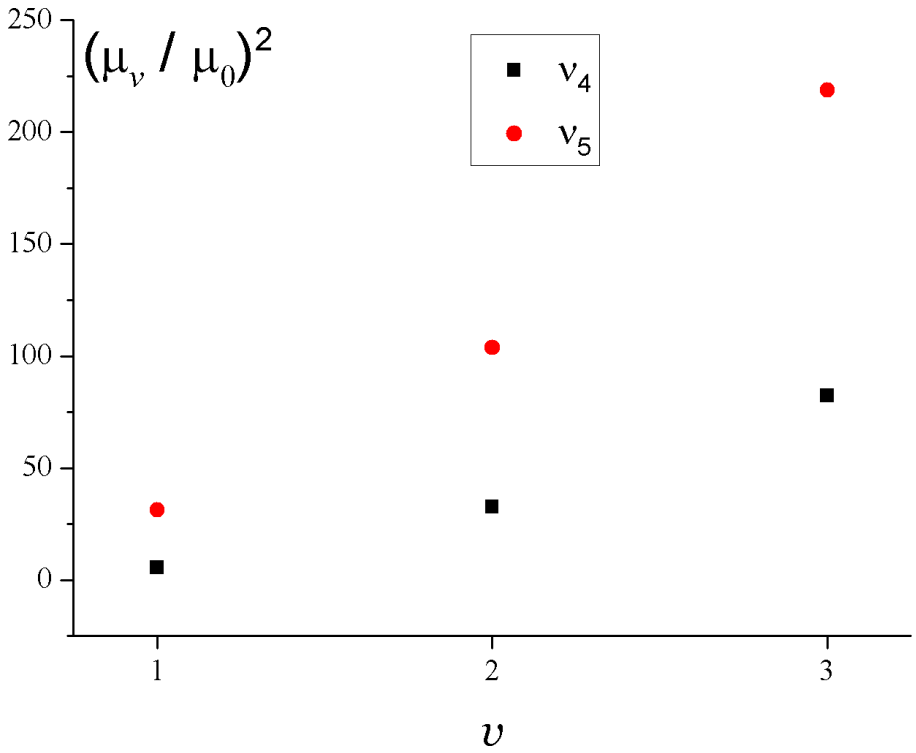

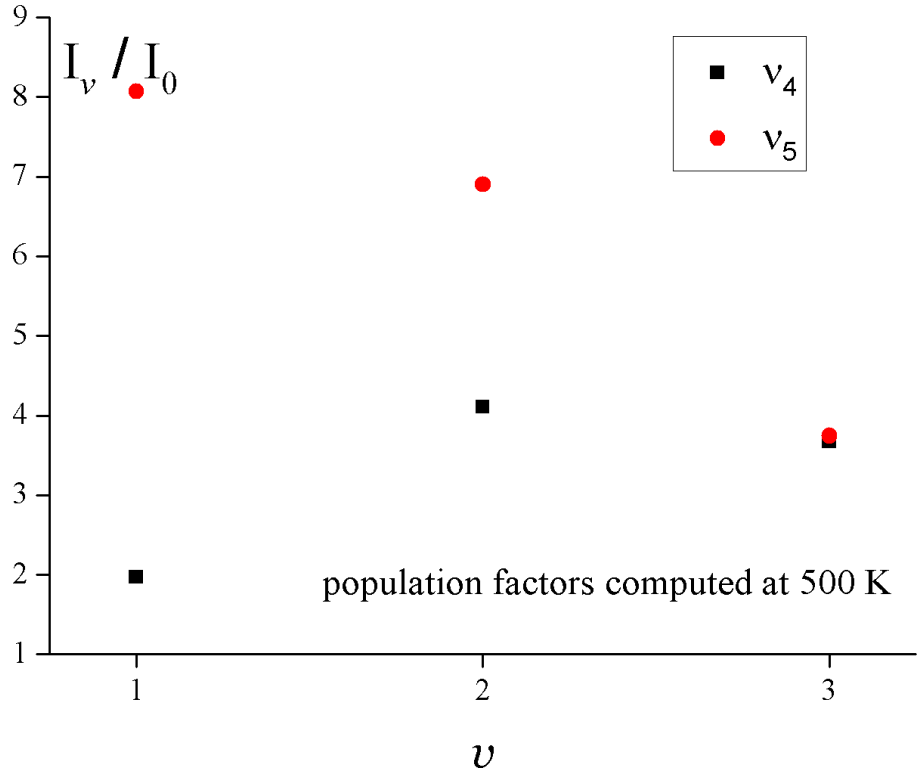

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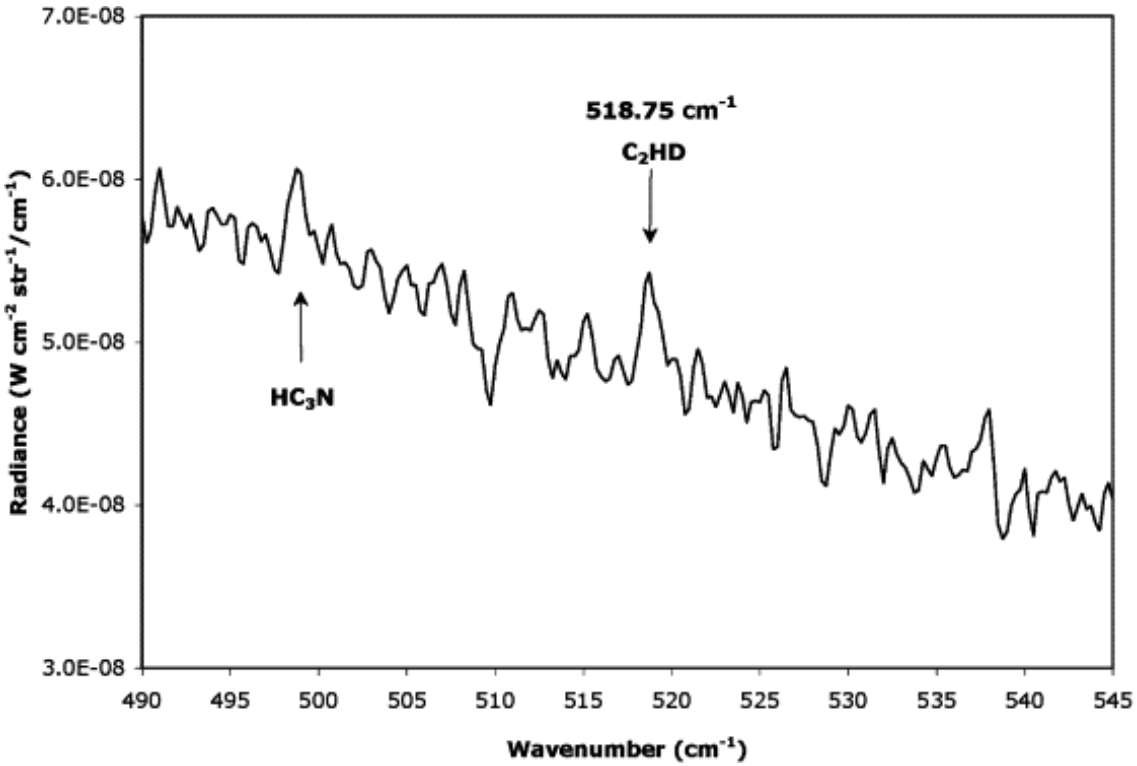
$^{12}C_2HD$ has been observed in Titan

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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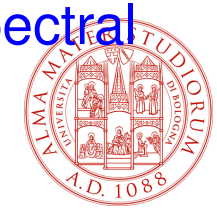

Four imines discovered in space

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).

- 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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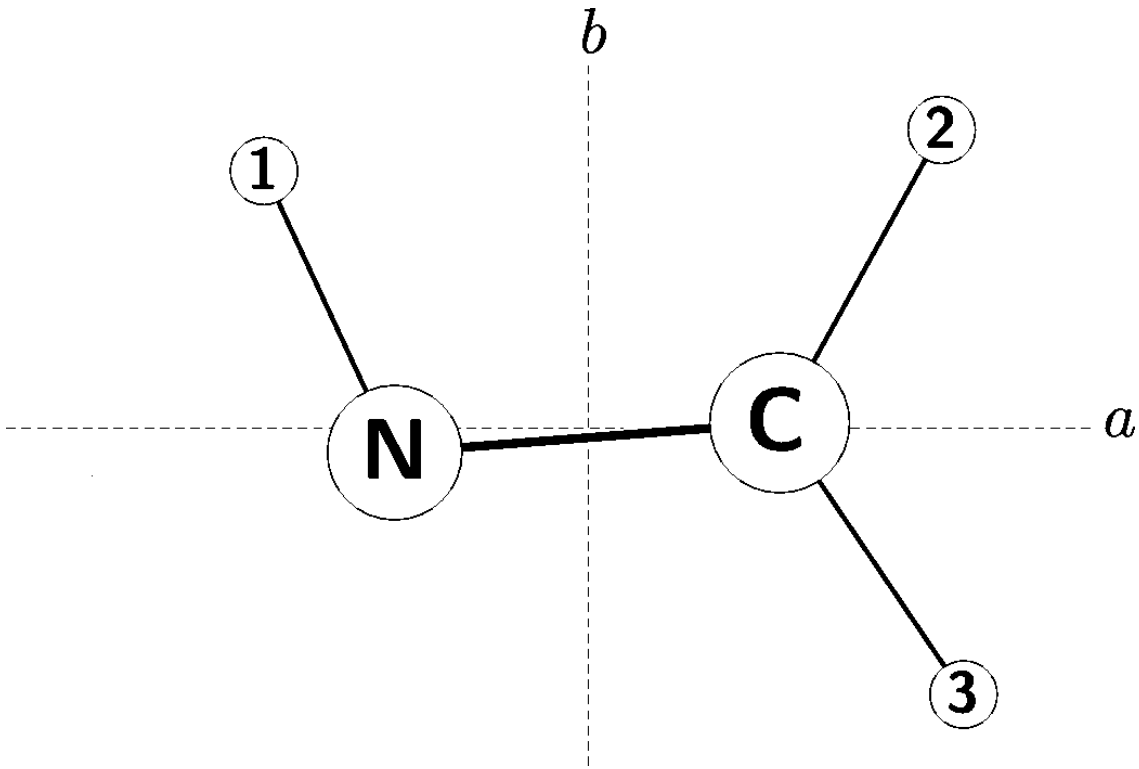
Methanimine

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

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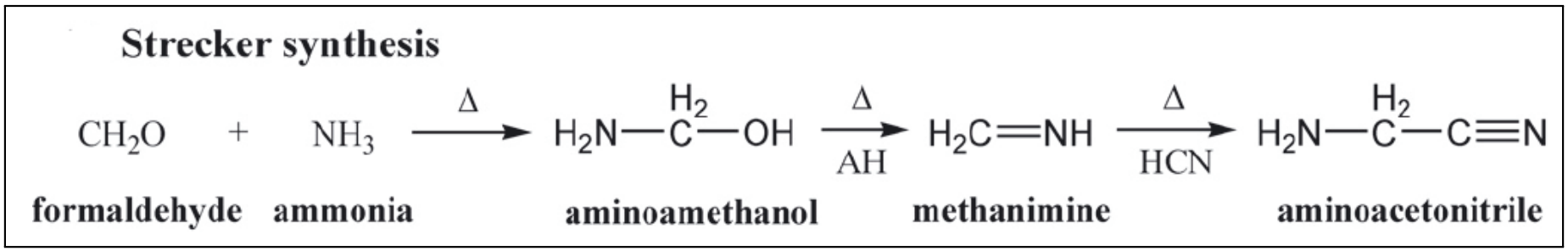
Methanimine: a pre-biotic interstellar molecule

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.

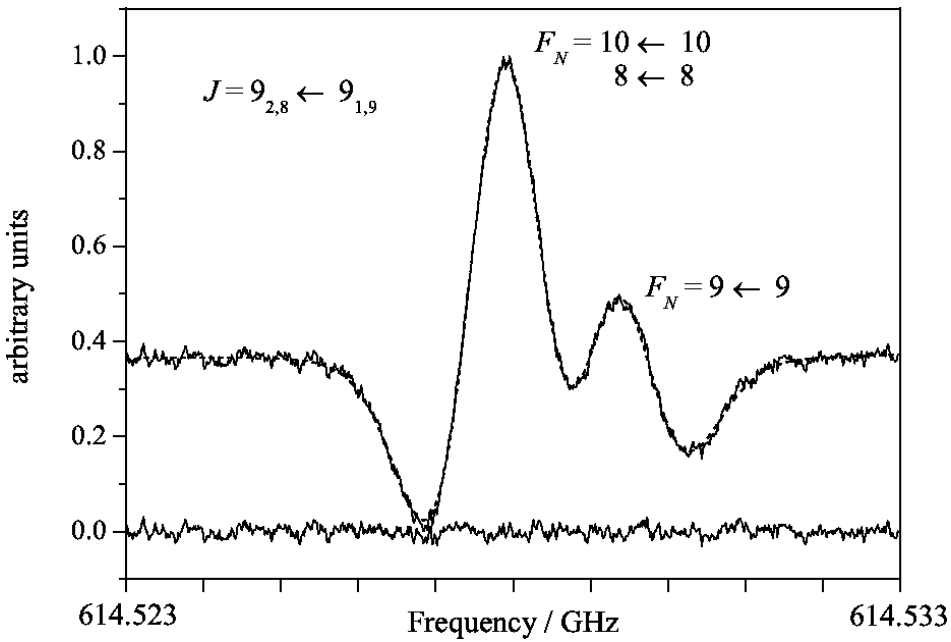
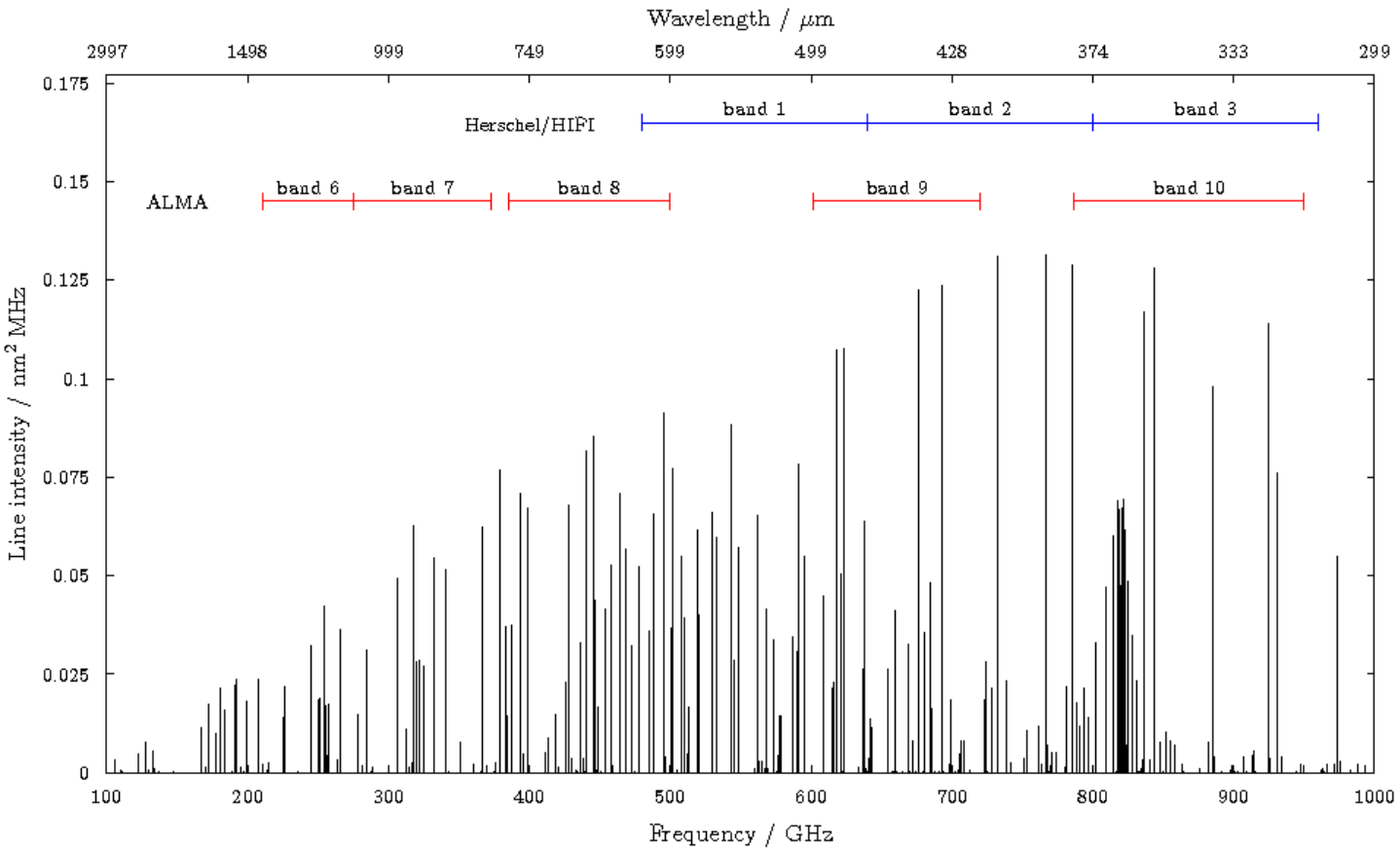


Figure: Hyperfine doublet recorded in 310 s with a time constant of 10 ms. The spectral profile has been fitted to a sum of three hyperfine components.

Rest-frequencies for astrophysical purposes

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

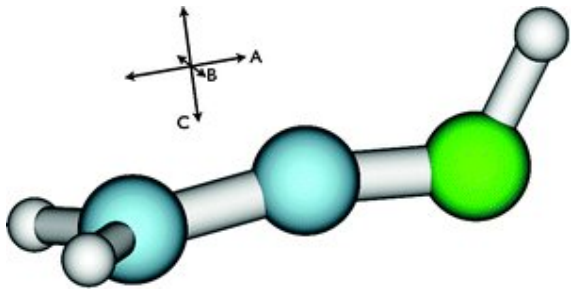


The frequency precision of the predictions in ALMA band 10 is of the order of a few parts in 10^9 (0.0003 km s^{-1} in radial velocity)

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).

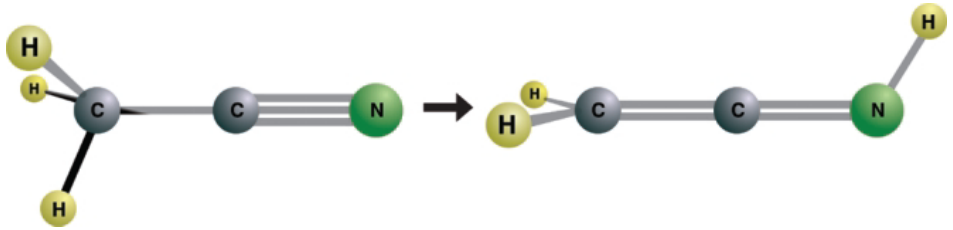


Figure: This isomer conversion reaction may be driven by shocks (Lovas et al. ApJ (2006) 645: L137)

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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Submillimeter-wave spectrum

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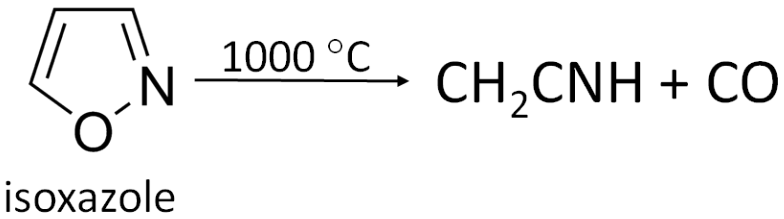


The ground state rotational spectrum has been recorded in the range 80 – 620 GHz. 207 new rotational transitions have been recorded, which are R ($\Delta J = +1$) and Q ($\Delta J = 0$) a-type lines, and R, Q, and P ($\Delta J = -1$) c-type lines, spanning J values from 0 to 67 and K_a values from 0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

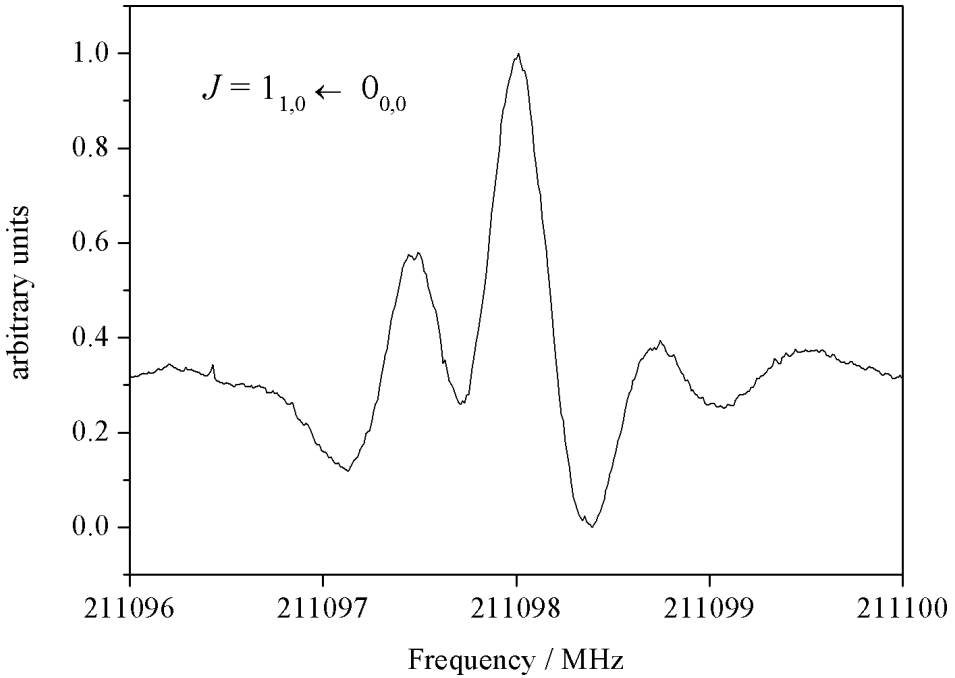


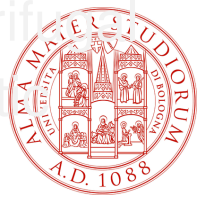
Figure: A fairly large number of the recorded transitions show an hyperfine structure due to the electric quadrupole coupling of the ^{14}N nucleus ($I = 1$). The $1_{1,0} \leftarrow 0_{0,0}$ transition is an example.

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.

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

- In addition to the rotational constants, all quartic and sextic centrifugal distortion constants could be determined, together with a few octic terms.



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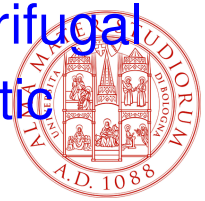

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