



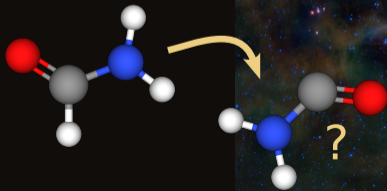
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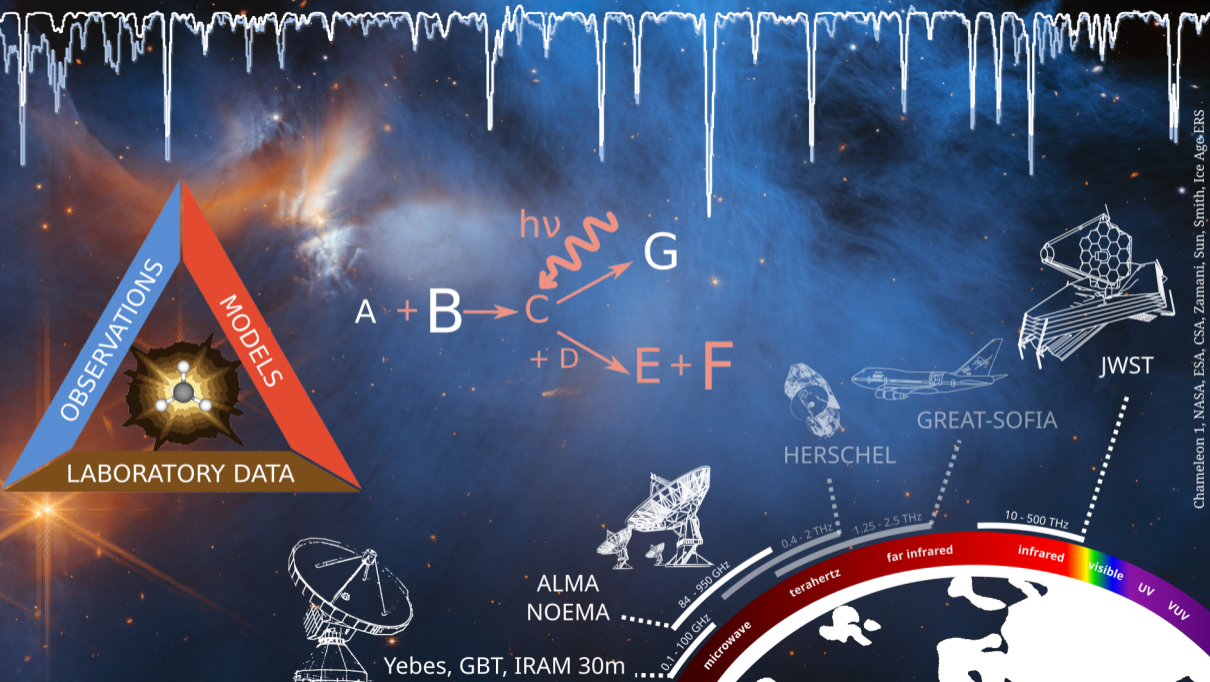


# Unveiling new reactive species of astrophysical relevance using laboratory rotational spectroscopy

*The case of the  $H_2NCO$  radical*

Marie-Aline Martin-Drumel

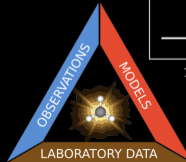
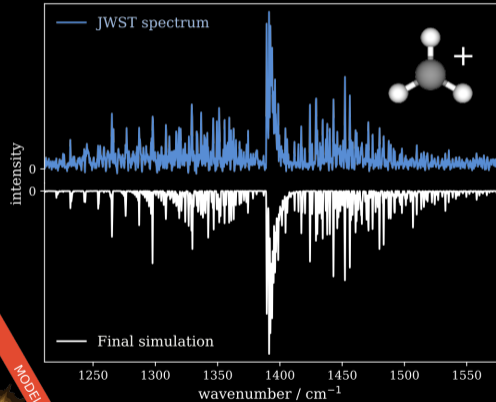




# The interstellar discovery of $\text{CH}_3^+$ results from a collaboration between astrophysicists, modellers, and laboratory spectroscopists

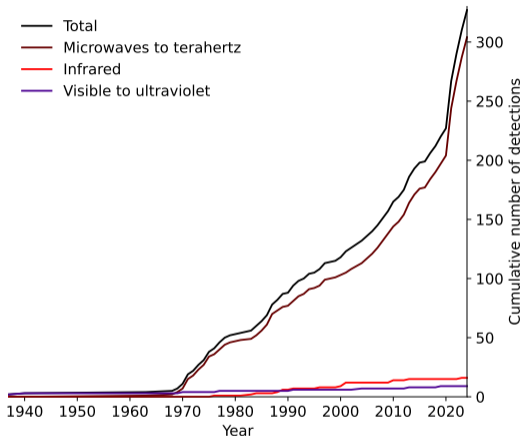


PIs: O. Berné, E. Habart, E. Peeters



Berné *et al.* *Nature* **621**, 56 (2023)  
Changala *et al.*, *A&A* **680**, A19 (2023)

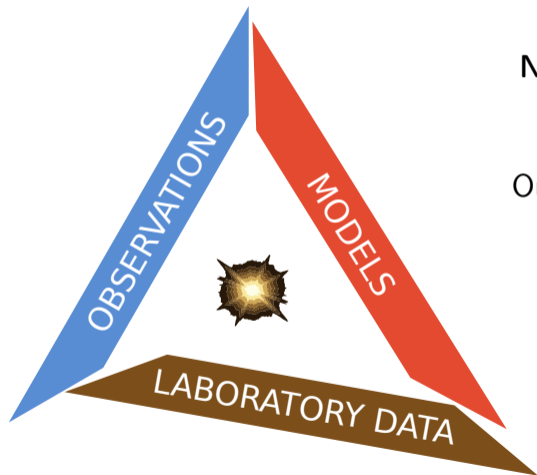
# Current ISM surveys allow for a wealth of molecular detections



Data from <http://www.astrochymist.org/>  
maintained by David Woon (U. Illinois),  
parsed using Kelvin Lee's scripts  
(<https://github.com/laserkelvin/Astrochymist>).  
As of Oct 25th, 2024

- $\sim 330$  known interstellar molecules
- $\sim 100$  new detections since 2020
- Many more molecules to be found
- Spectral ranges of interest for interstellar discoveries
  - ▶ Microwave to terahertz (polar molecules)
  - ▶ Infrared
  - ▶ Visible to ultraviolet

The availability of laboratory data is currently limiting the rate of molecular discoveries in the ISM



**Need for laboratory spectroscopic data on many molecules**

Our targets:

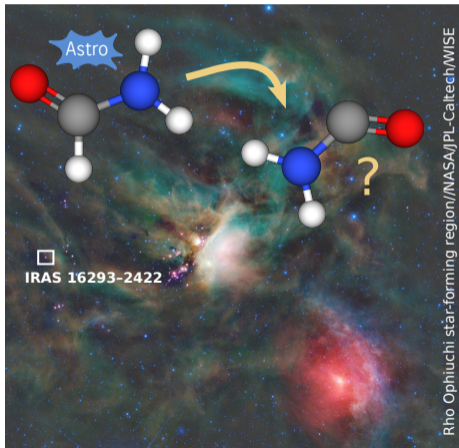
- Rest frequencies (*ISM detections*)
- Rotationally resolved (*molecule specific*)
  - ▶ pure rotation
  - ▶ ro-vibration
- Reactive species (*understudied*)
  - ▶ radicals, ions, metastable species

# Unveiling new reactive species of astrophysical relevance using laboratory rotational spectroscopy

The H<sub>2</sub>NCO radical: Laboratory rotational spectroscopy and interstellar searches

Laboratory  
Observations  
Models

The carbamoyl radical ( $\text{H}_2\text{NCO}$ ) is central to many astrochemical networks, but remains elusive in the gas phase



### Astrochemical models:

- Central to ice-grain chemistry networks
- Postulated key precursor of iCOMs (formamide, urea, acetamide...)

e.g., Ligterink *et al.*, *MNRAS* **480**, 3628 (2018)

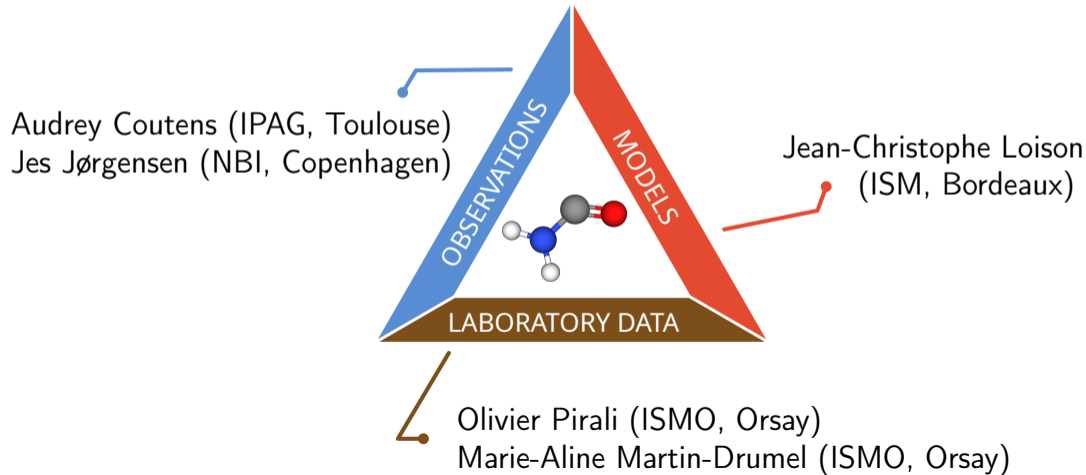
### Laboratory spectroscopic data:

- Quantum chemical calculations
- EPR spectroscopy
- IR detection on ice analogs

e.g., Haupa *et al.*, *JACS* **141**, 11614 (2019)

**No gas phase spectroscopic data**

We have undertaken laboratory and interstellar searches  
for  $\text{H}_2\text{NCO}$



# Unveiling new reactive species of astrophysical relevance using laboratory rotational spectroscopy

The H<sub>2</sub>NCO radical: Laboratory rotational spectroscopy and interstellar searches

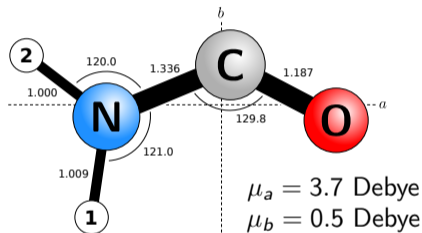
Laboratory

Observations

Models

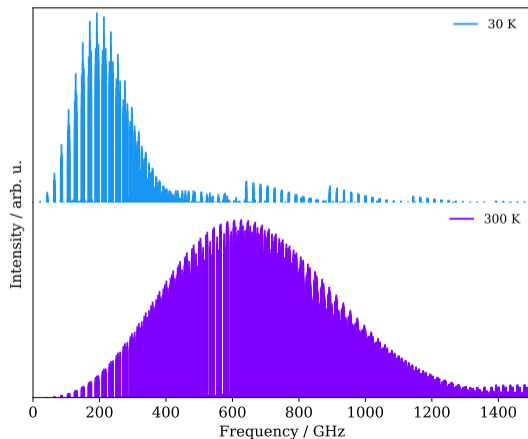
LABORATORY DATA

Quantum chemical calculations on  $\text{H}_2\text{NCO}$  show that  $\text{H}_2\text{NCO}$  rotational spectrum spreads over the millimeter- and submillimeter-wave domain, even at low temperatures

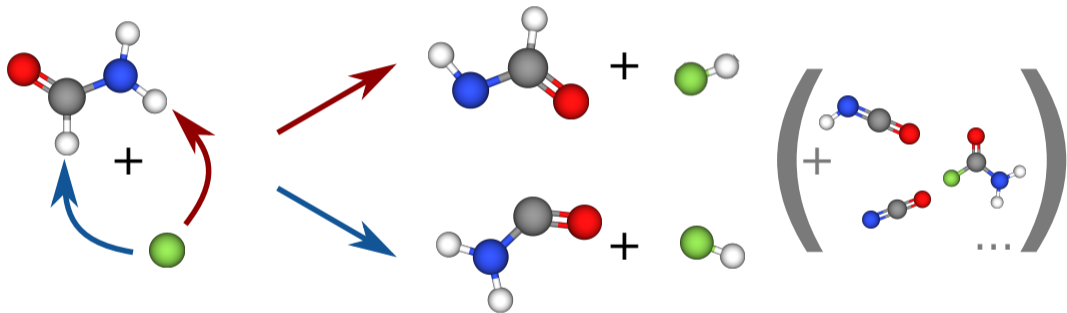


- $\omega\text{B97X-D/cc-pVQZ}$ 
  - ▶ Equilibrium geometry optimization
  - ▶ Harmonic and anharmonic frequency analysis

→ **Reliable set of spectroscopic constants**



$\text{H}_2\text{NCO}$  was produced at room temperature in flow cells  
by H-abstraction from formamide



$\text{CH}_2\text{OH}$ : Chitarra *et al.*, *A&A* **644**, A123 (2020)  
Coudert *et al.*, *JCP* **156** 244301 (2022)

$\text{CH}_3\text{O}$ : Martin-Drumel *et al.*, *in prep.*

$\text{CH}_2\text{CN}$ : Chitarra *et al.*, *JPCA* **126** 7502 (2022)

& more...

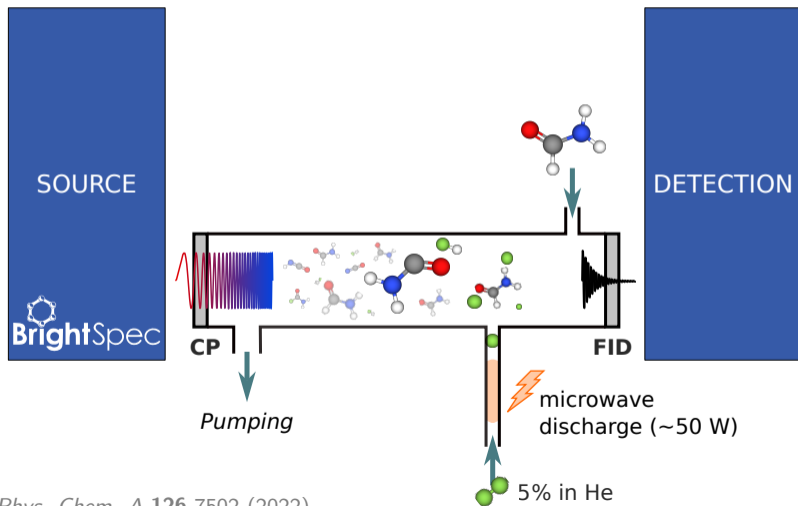
$\text{CH}_2\text{CHO}$ : Chahbazian *et al.*, *JPCA* **128** 370 (2024)

$\text{CH}_3\text{CO}$ : Coudert *et al.*, *in prep.*

$\text{CH}_3\text{COCH}_2$ : Chahbazian *et al.*, *JPCL* **15** 9803 (2024)

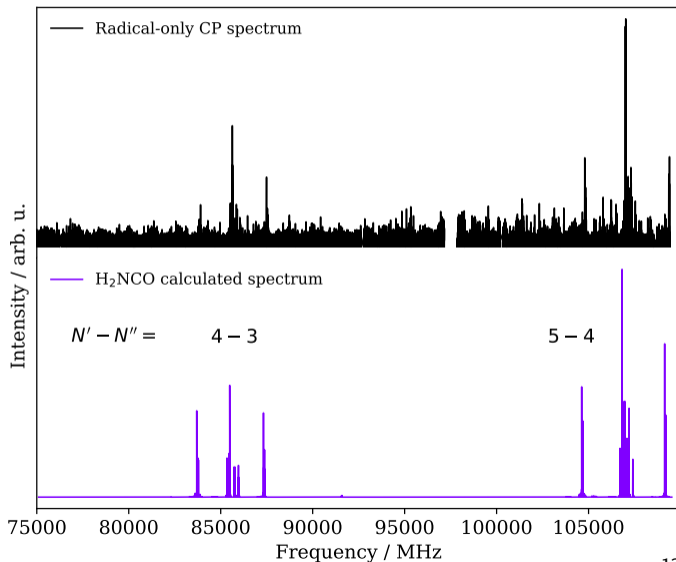
$\text{H}_2\text{NCO}$ : Martin-Drumel *et al.*, *A&A* **687** A233 (2024)

Initial searches have been undertaken using a chirped-pulse Fourier-transform millimeter-wave spectrometer

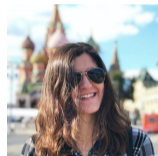
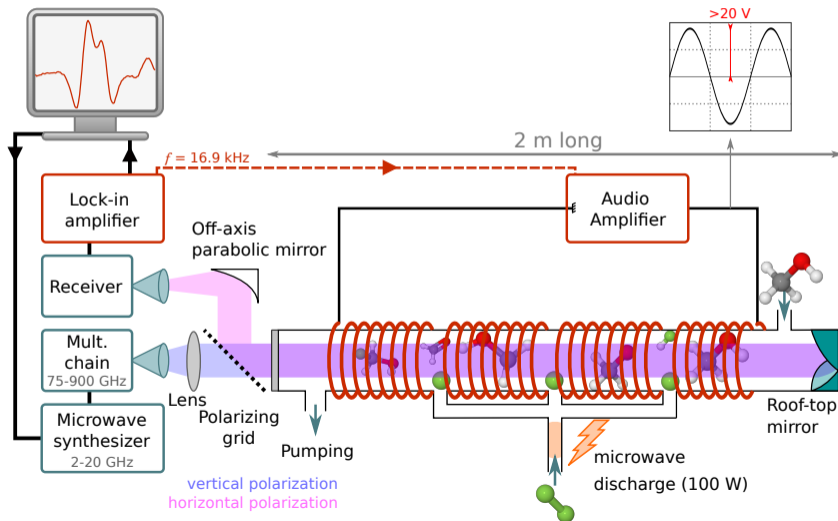


Transitions corresponding to what expected for H<sub>2</sub>NCO were readily observed

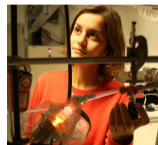
- 2 clusters of *a*-type lines
- Partially resolved hyperfine structure



# Higher frequency measurements were performed using the Zeeman-modulation submillimeter-wave spectrometer



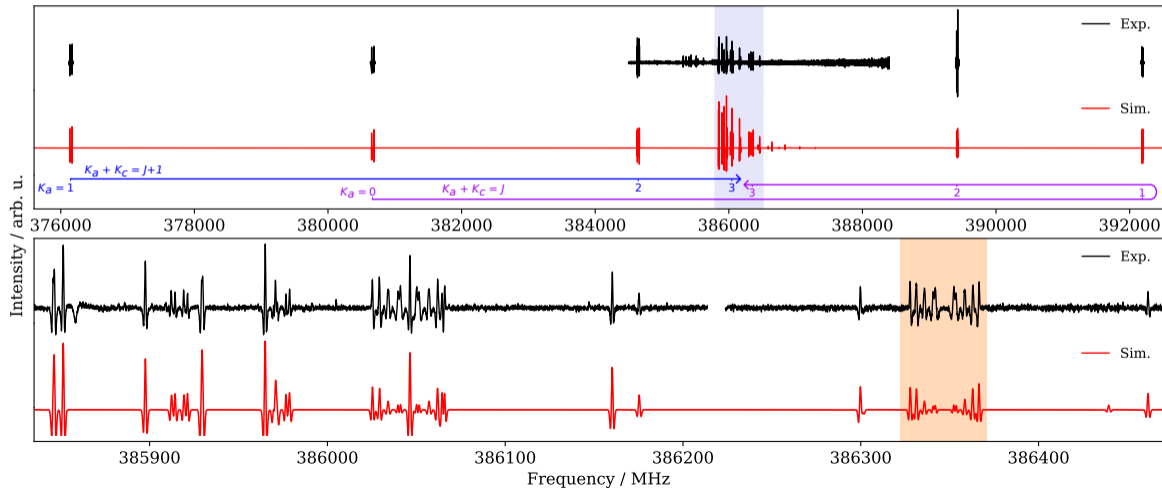
Olivia Chitarra



Rosemonde Chahbazian

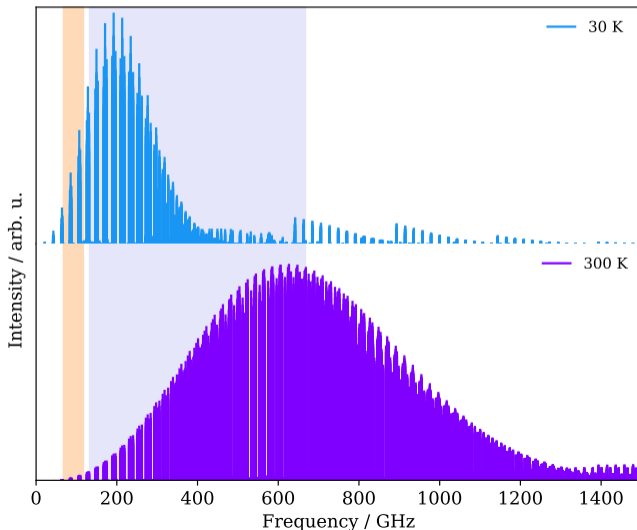
# Only transitions arising from open-shell species are visible

$N' - N'' = 18 - 17$  *a*-type transition



$\text{H}_2\text{NCO}$  has been observed in the laboratory  
for the first time in the gas phase

- Experimentally-determined spectroscopic constants in  $\nu = 0$
- Reliable predictions up to about 700 GHz, for  $T = 0 - 300$  K



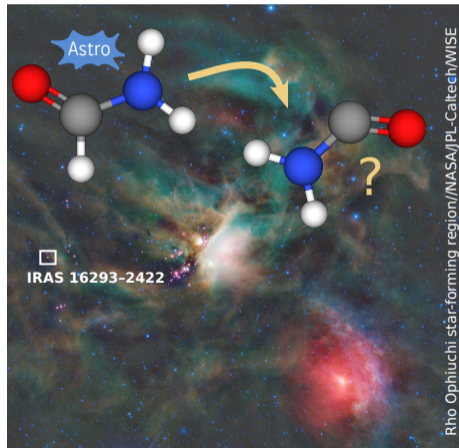
# Unveiling new reactive species of astrophysical relevance using laboratory rotational spectroscopy

The  $\text{H}_2\text{NCO}$  radical: Laboratory rotational spectroscopy and interstellar searches

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Models



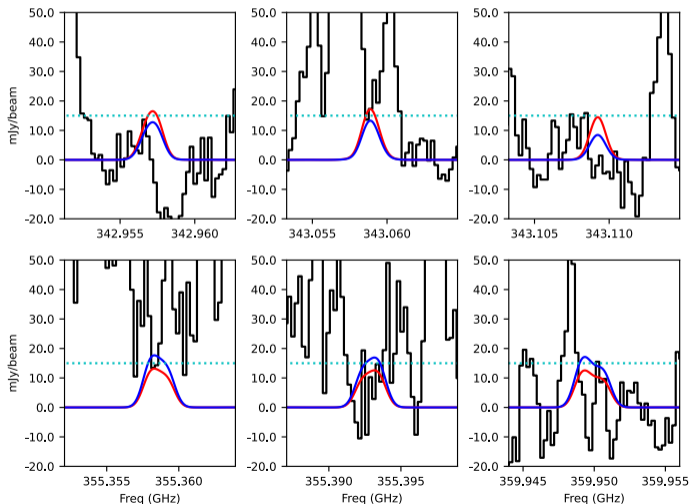
Interstellar searches have been undertaken toward the solar-type protostar IRAS 16293–2422



- ALMA PILS survey
- Formamide abundant in that source  
Coutens et al., *A&A* 590, L6 (2016)
- $T \sim 125 - 300$  K
- Search for transitions around 340 – 360 GHz

The radical is undetected and much less abundant than formamide in the gas phase in that protostar

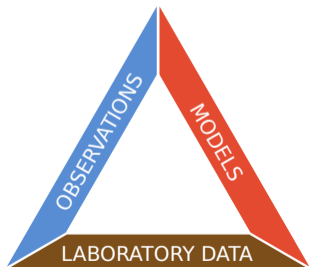
$\text{H}_2\text{NCO}$  is at least  
**90 times** less abundant  
than formamide



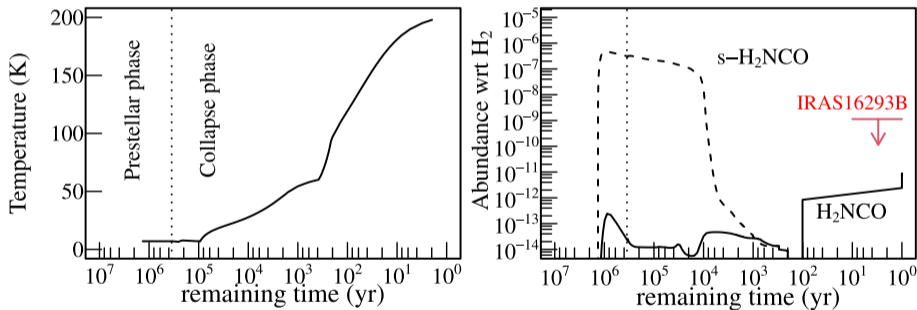
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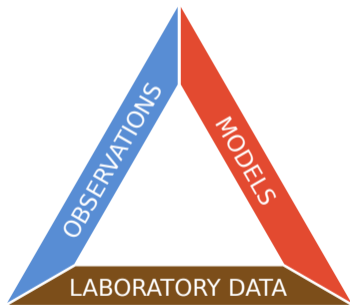


The derived upper limit on the column density is in agreement with predictions from a physico-chemical model

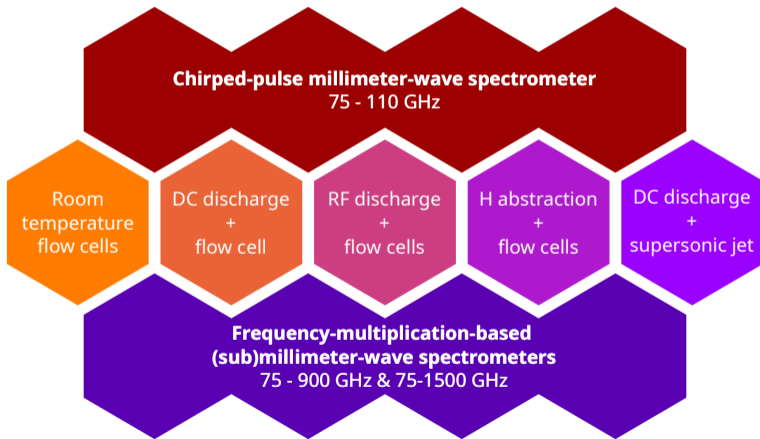


# Unveiling new reactive species of astrophysical relevance using laboratory rotational spectroscopy

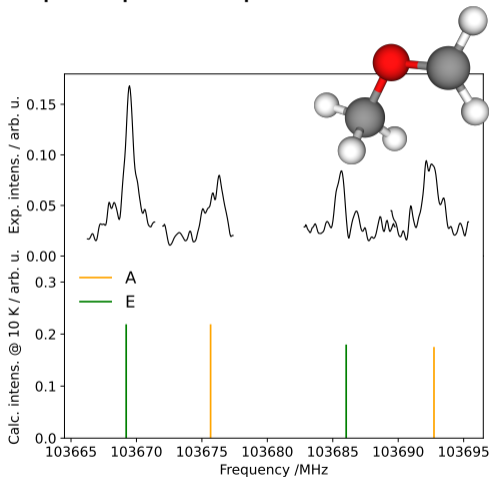
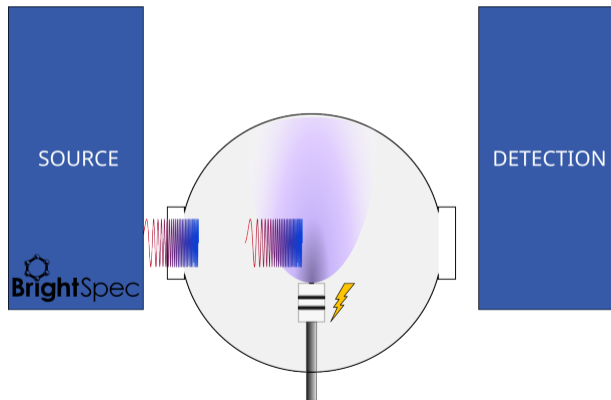
- H<sub>2</sub>NCO is *not* an abundant gas phase molecule in IRAS 16293–2422
- H<sub>2</sub>NCO may still be an important reaction intermediate, but likely on grain surfaces
- Reliable predictions are available for searches in other sources



Several experimental set-ups are now available @ISMO  
to investigate astronomically-relevant species



We are finalizing the development of a supersonic jet experiment that has recently be coupled to the chirped-pulse spectrometer



# Acknowledgments

## Rotational spectroscopy @ISMO

- Olivier Pirali (Senior Researcher)
- Rosemonde Chahbazian (PhD)
- Luan Juppet (PhD)

## Collaborators

- Jean-Christophe Loison (ISM, Bordeaux)
- Audrey Coutens (IPAG, Toulouse)
- Jes Jørgensen (Niels Bohr Institute, Copenhagen)



# Unveiling new reactive species of astrophysical relevance using laboratory rotational spectroscopy

- New laboratory data are mandatory to assign current astronomical surveys and better understand the astrochemistry at play
- Molecular searches in the ISM are a collaborative effort

