IBER, Coimbra, September 2023

"INTERSTELLAR DETECTION OF CARBONIC ACID (HOCOOH) AT LAST"

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Image Credit: SARAO

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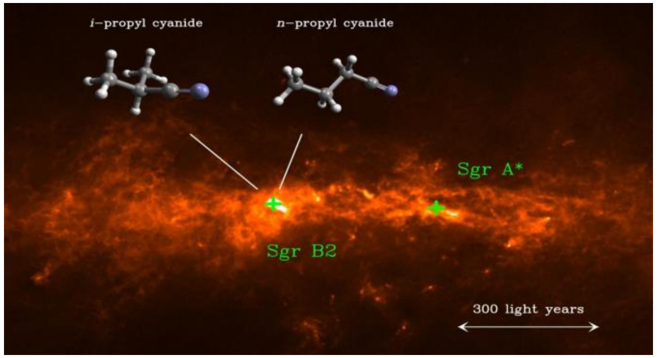
1.1. Exploring complex chemistry in the ISM

Interstellar medium (ISM): diluted mix of ions, atoms, molecules, dust particles and electromagnetic fields between stars.

Taurus Molecular Cloud (TMC). Credit: ESO/APEX (MPIfR/ESO/OSO)



Sgr B2 Molecular Cloud. Credit: A. Belloche.

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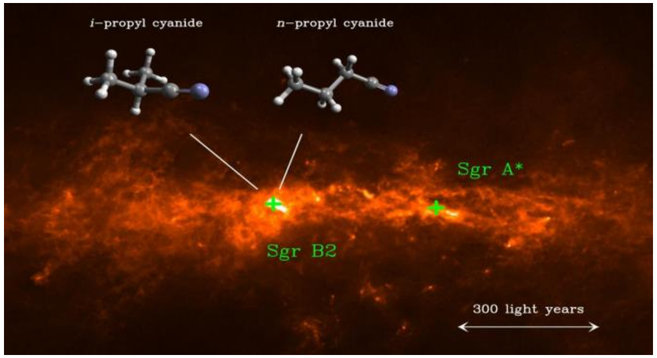

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Exploring complex chemistry:

- **How complex can molecules get in the ISM?**
- How do they form, grains, gas phase, which routes?
- Where do they form – cold dark clouds or hot molecular cores?

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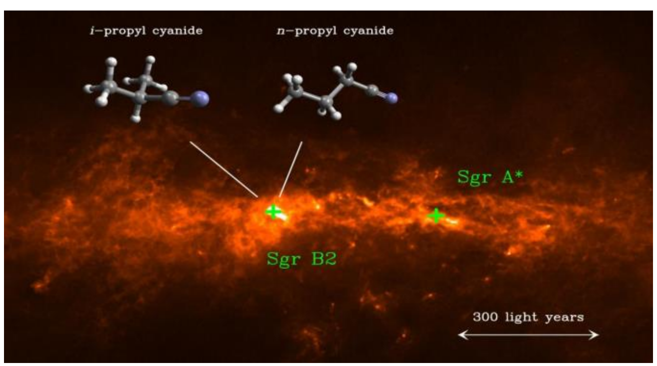

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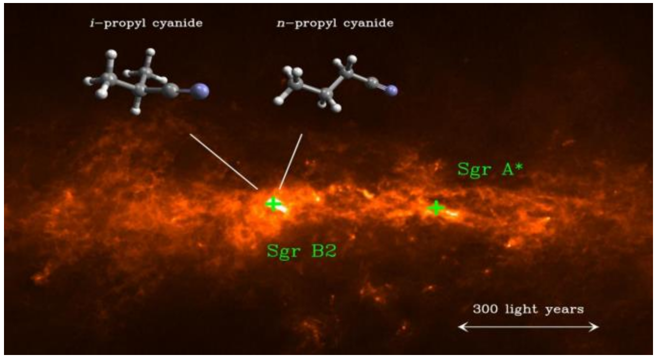

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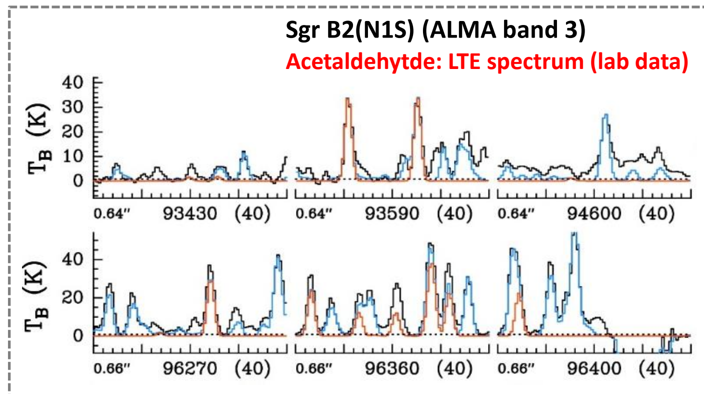
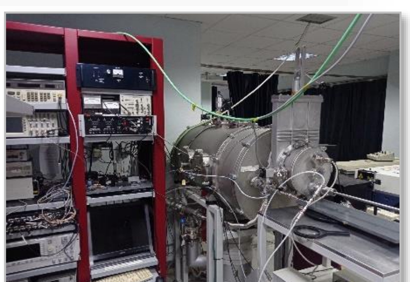
1.2. Synergy between radio astronomy and rotational spectroscopy

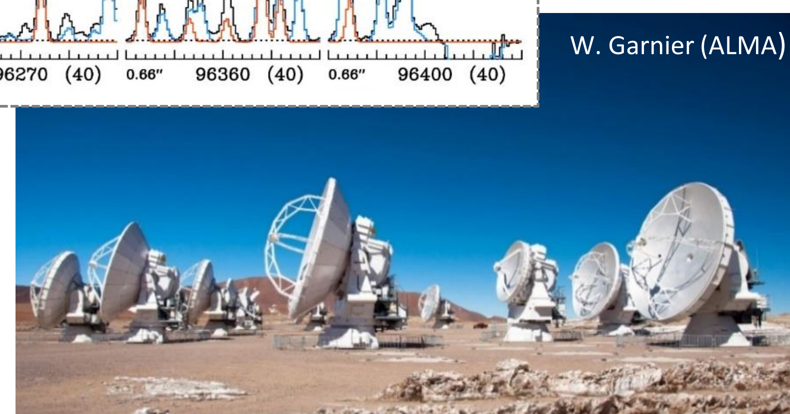
To answer this questions:

Symbiotic relationship between **radio astronomy** and laboratory experiments by means of **rotational spectroscopy:** ***need of accurate rotational data*.**



GEM ALONSO RESEARCH GROUP





Atacama Large Millimeter/Submillimeter Array - ALMA

McGuire, B. A. 2022, *ApJS*, 259, 30 (census)

1.3. Systems under study and fundamental goals

Background: **Significant experimental efforts have been made to study the so-called COMs.**

Carboxylic acids (R-COOH) are some of the most widespread species in nature, being **precursors of many biologically relevant molecules (i.e., amino acids).**

Zuckerman et al. 1971	Detection of **formic acid** (HCOOH; 50 yrs ago)
Mehringer et al. 1997	**Acetic acid** (CH_3COOH; 25 yrs ago)

The **census** of identified interstellar species has remained **untouched** for almost **a quarter century**

⇩

Need of new and dedicated observational effort

1.3. Systems under study and fundamental goals

Final goal:

Holy Grail: precursors of life

Relevance of Carbonic acid (HOCOOH):

On earth:

- Important role in various biological and geochemical processes

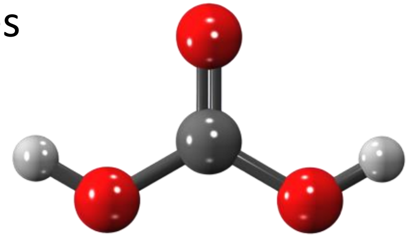
(Adamczyk et al. 2009; Loerting et al. 2000)

- Implications in the global carbon cycle

(Jones et al. 2014; Wang et al. 2016)

- Anthropogenic carbon and ocean pH

(Caldeira & Wickett 2003)



Cis-cis carbonic acid (HOCOOH)

In space: Its presence has been suggested in different astronomical environments:

- The Galilean icy moons

(Delitsky & Lane 1998; Jones et al. 2014; Bennett et al. 2014)

- Mercury's north polar region

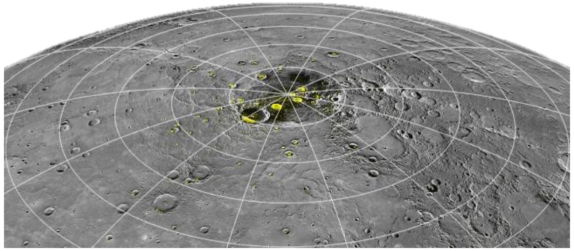
(Delitsky et al. 2017)

- The surface and/or atmosphere of Mars

(Strazzulla et al. 1996)

- Icy mantles of dust grains (vast amounts of H_2O and CO_2)

(Moore et al. 2001; Zheng & Kaiser 2007; Oba et al. 2010; Ioppolo et al. 2021)



Credit: NASA/Johns Hopkins University Applied Physics Laboratory

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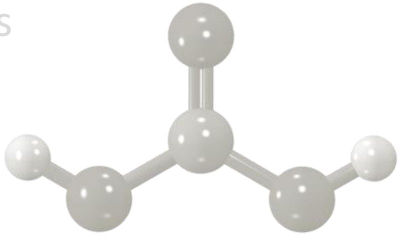

Despite being an **auspicious interstellar candidate** (-OH derivative of formic acid)

HOCOOH still **awaited detection** in the **ISM**

(Delitsky & Lane 1998; Jones et al. 2014; Bennett et al. 2014)

- Mercury's north polar region

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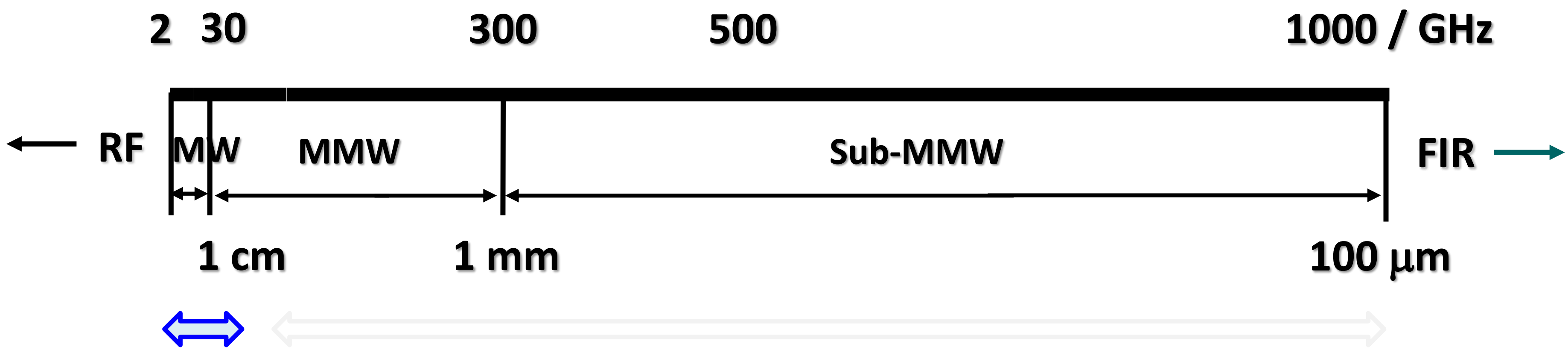
2.1. Rotational spectroscopy



FTMW techniques
(2 – 40 GHz)

Frequency modulation mmw and sub-mmw spectroscopy (50 – 1000 GHz)

First step: Rotational studies of COMs

Very robust technique for structural elucidation of molecules in the **gas-phase** that present a **permanent dipole moment:** accurate three-dimensional description.

Narrowband FTMW spectroscopy (pulsed discharge nozzle) + **DR**

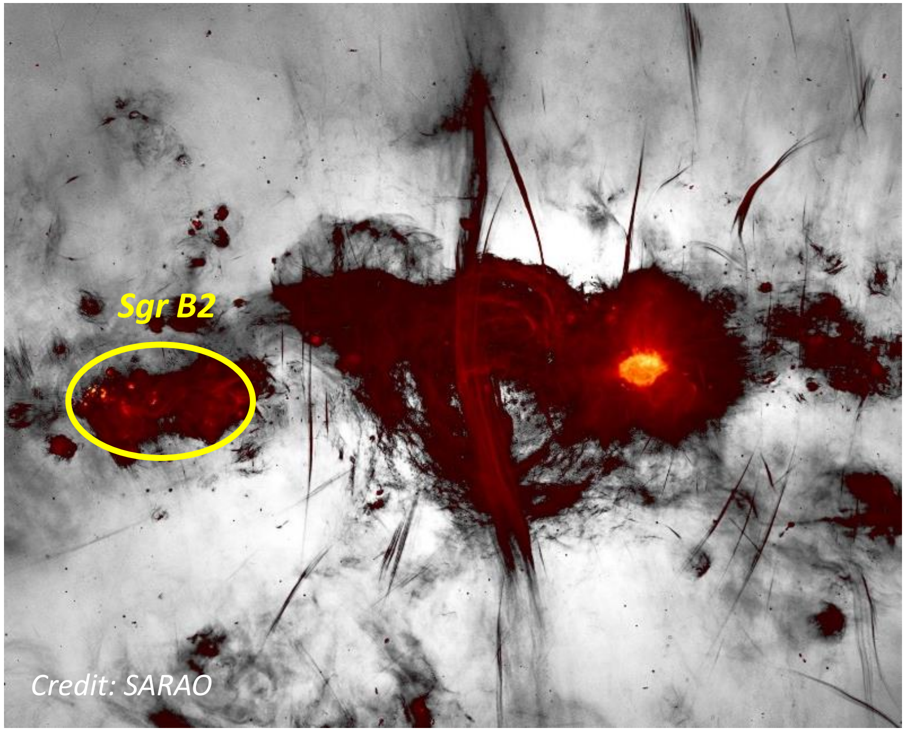
- Experimental work by Mori et al. *JChPh,* 139 (2009); *JChPh,* 134 (2011).

2.1. Observational radioastronomy

Single dish astronomical observations:

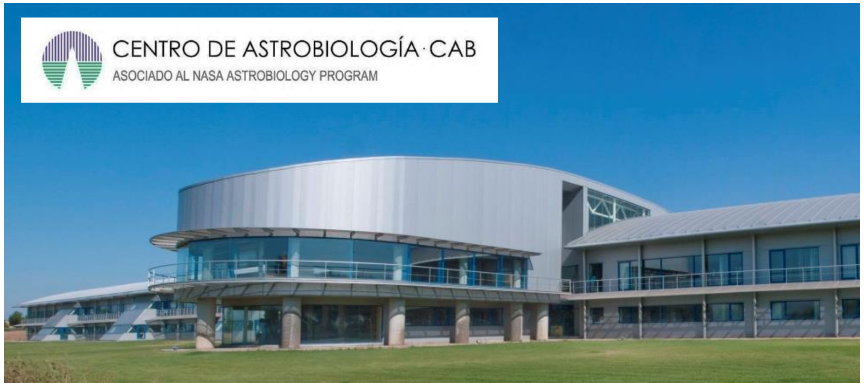
Search toward the **G+0.693-0.027** molecular cloud with IRAM 30m (3-mm) and Yebes 40m (7-mm) observations.

Observational Project lead by Víctor M. Rivilla (CAB, CSIC-INTA)



First identification in the ISM of a dozen of molecules:

- **ethanolamine** (Rivilla, V. M. et al., 2021)
- **1,2-ethenediol** (Rivilla, V. M. et al., 2022)
- **hydroxylamine** (Rivilla, V. M., et al., 2020)



2.1. Observational radioastronomy

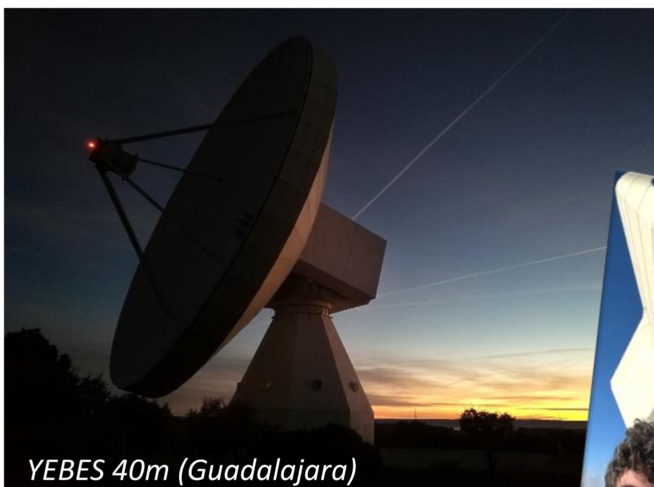
NEW OBSERVING RUNS: Ultra-deep spectral survey of G+0.693

Yebes-40m sub-mK survey (new observations, March 2021 and March 2022)***:***

Final noise levels between 0.25 – 0.9 mK across the whole Q-band

IRAM-30m (new observations, February 1−18 2023):

Final noise levels between 0.5 – 2.5 mK at 3 mm, and 1.0−1.6 mK at 2 mm.



YEBES 40m (Guadalajara)

IRAM 30m (Granada)

NEW THRILLING SCIENCE!!!

Sanz-Novo, M. Rivilla, V. M., et al., ApJ, 954 3, 2023

Rivilla, V. M., Sanz-Novo, M. et al., ApJL, 953, L20, 2023

LINK TO THE PAPER

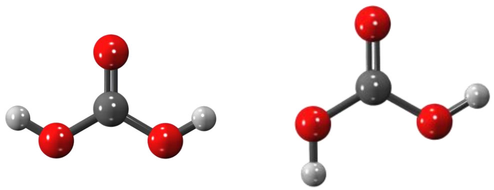
3.1. Rotational spectroscopy: generation of line catalogues and initial search

Scarce rotational spectroscopic data

Very unstable molecule (rapidly decomposes into CO_2 and H_2O under the presence of water).

Laboratory detection and conformational identification

- Cavity-based FTMW (and DR) rotational study (Mori et al. 2009, 2011)



Cis-cis *Cis-trans*

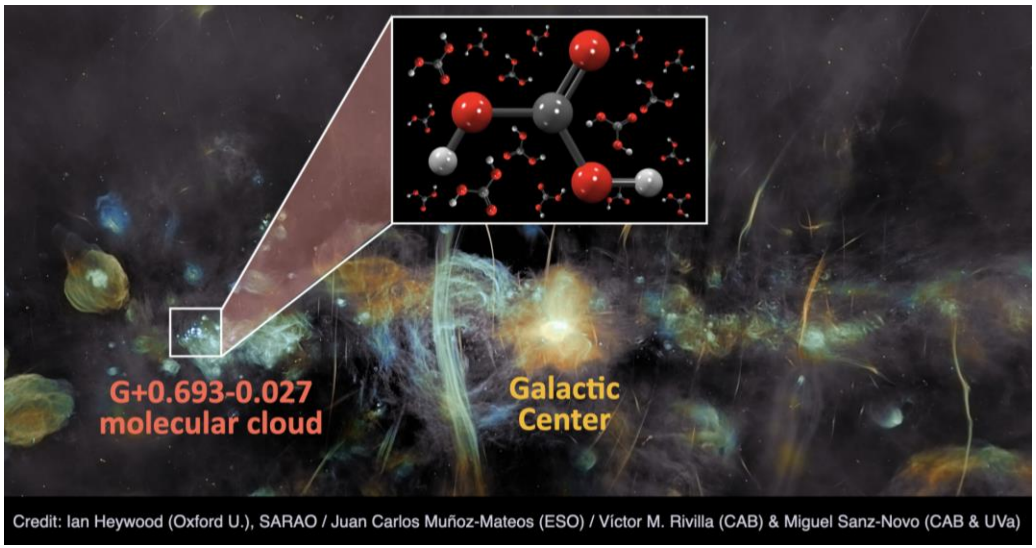
- Two conformers well-characterized in the lab (up to 41 and 65 GHz, respectively).
- The lower-energy conformer, *cis-cis* HOCOOH: **extremely low dipole moment** (fifteen times lower), which will hamper its detection.

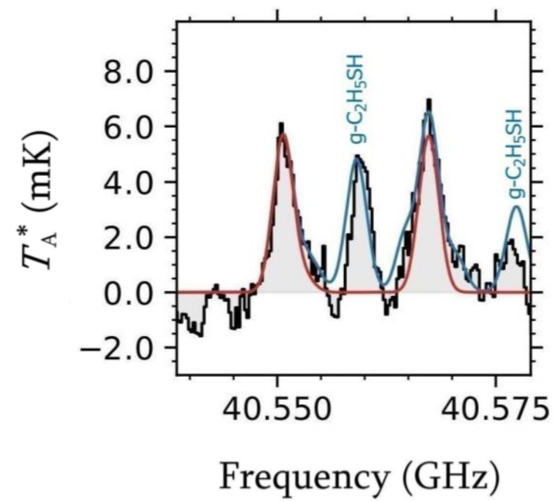
Our work approach

- *Preparation of **line catalogues** and implementation in **MADCUBA***
- *First **inspection of the Q-band data** (31-50 GHz) → Detection of several lines*
- *Exploration of the **3mm data** → Systematic frequency shifts at high frequencies.*
- ***New global fit** including the **newly measured astronomical lines***

3.1. Rotational spectroscopy: generation of line catalogues and initial search

Initial search: ***cis-trans* conformer** of HOCOOH





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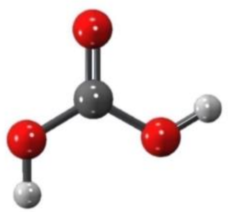
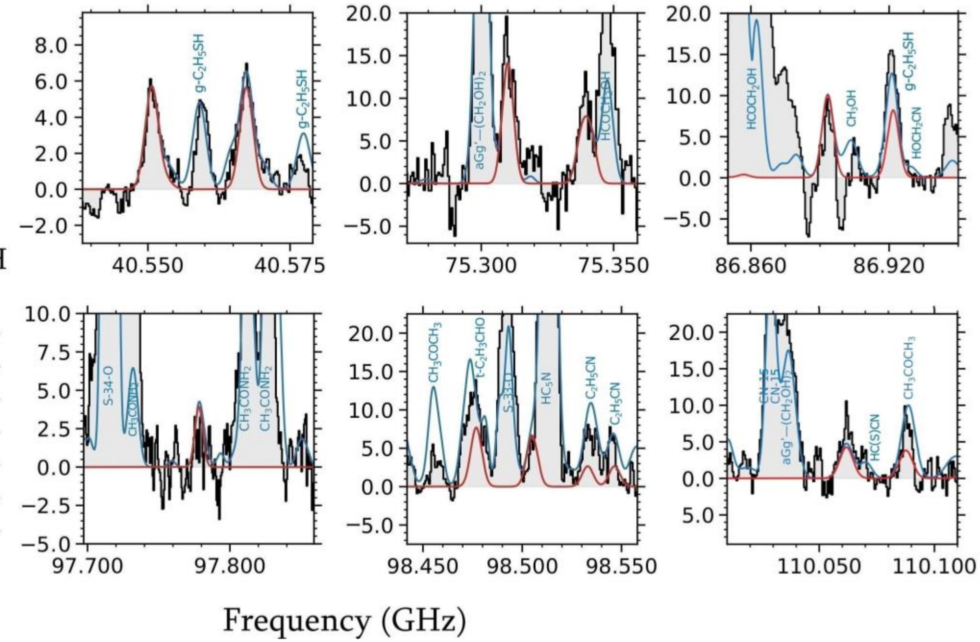
- *Exploration of the **3mm data** (<120 GHz)* ⇨ *Systematic frequency shifts.*
- ***New global fit** including the **newly measured astronomical lines***

3.2. Astronomical search for HOCOOH

Search for cis-trans **HOCOOH** *toward the G+0.693 molecular cloud*



cis-trans HOCOOH



LTE spectra overlayed with the observations

FIRST INTERSTELLAR MOLECULE WITH 3 OXYGEN ATOMS

Column density:

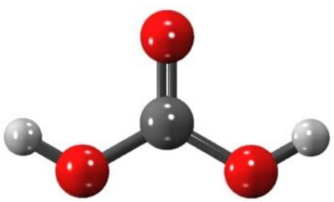
$N = (6.4 \pm 0.4)\times10^{12}\ \mathrm{cm}^{-2}$

$T_{ex} = 7.2 \pm 0.6$ K

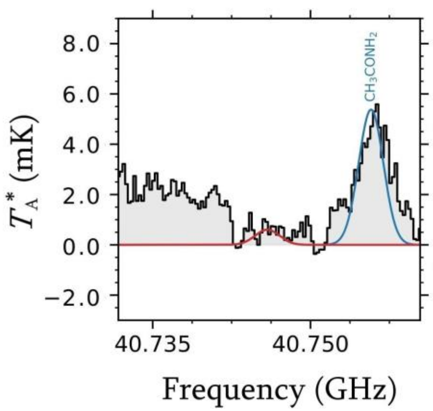
We detected several **clear and unblended spectroscopic features** with **S/N ratio > 6** , highlighting **four pairs of lines** of *cis-trans* HOCOOH corresponding to different K_a = 0,1 and 2 progressions.

Search for cis-cis HOCOOH toward the G+0.693 molecular cloud

Nondetecton of the low-lying *cis-cis* conformer:



cis-cis HOCOOH



Upper limit of cis-trans HOCOOH:
$N \leq 1.6 \times 10^{14}$ cm^{-2}

Molecular abundance compared to H_2 of $\leq 1.2 \times 10^{-9}$

Constrains on the abundance of *cis-cis* HOCOOH in the ISM

Its **abundance** is expected to be of **the same order** as that of ***trans*-HCOOH.**

Carbonic acid possibly emerges as an **abundant O-bearing COM** in the ISM although it went unnoticed so far.

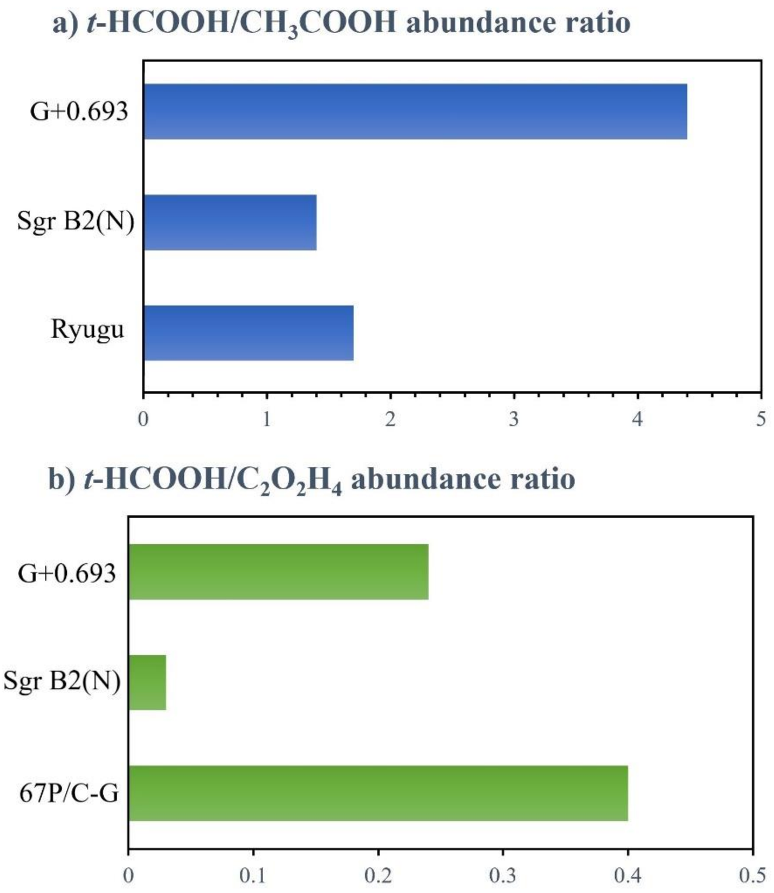
3.3. Discussion

Abundance of carboxylic acids in different astronomical environments:

- Molecular cloud: G+0.693 (This work)
- Star forming-regions: Sgr B2(N) (Belloche et al. 2013)
- Asteroids: Ryugu material (Naraoka et al. 2023)
- Comets: 67P/Churyumov-Gerasimenko (Altwegg et al. 2016; Drozdovskaya 2019)

Relationship between their **relative molecular abundances** in the ISM and that found in **minor bodies of the Solar System**

Carboxylic acids seem to **survive** the **star-formation process.**



Chemical inheritance of inteterstellar carboxylic acids

3.3. Discussion

Formation pathways of HOCOOH: Plethora of experimental and theoretical studies

⇨ **Surface of dust grains: OH radical addition** to **HOCO**, which can be formed:

- Through the reaction of CO and the radical species OH

(Lester et al. 2001; Noble et al. 2011; Nguyen et al. 2012; Ruaud et al. 2015; Tachikawa & Kawabata 2016; Ioppolo et al. 2021).

$$CO + OH \rightarrow \textit{trans}\text{-}HOCO \qquad (1)$$

$$CO + OH \rightarrow \textit{cis}\text{-}HOCO \qquad (2)$$

$$\textit{trans}\text{-}HOCO + OH \rightarrow HOCOOH \qquad (3)$$

$$\textit{cis}\text{-}HOCO + OH \rightarrow HOCOOH \qquad (4)$$

- Through energetic processing of H_2O/CO_2 icy mixtures

(Zheng & Kaiser 2007)

$$H_2O + e^- \rightarrow H + OH + e^- \qquad (5)$$

$$H + CO_2 \rightarrow \textit{cis}\text{-}HOCO \qquad (6)$$

TAKE-HOME MESSAGES:

- **Discovery** of **HOCOOH**, the **third insterstellar carboxylic acid** and the **first interstellar molecule** with **more than two oxygen atoms** detected so far.
- Relevant insight into the **actual degree of chemical complexity of the ISM**, significant implications to unravel the **role of HOCOOH** within **interstellar C- and O- chemistry.**
- **Overall good correlation** between the **relative molecular abundance of carboxylic acids** in **different astronomical environments.**
- We open the door to achieve **indirect interstellar identifications of conformers** that **remained undetectable to radioastronomy**.

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Image Credit: SARAO

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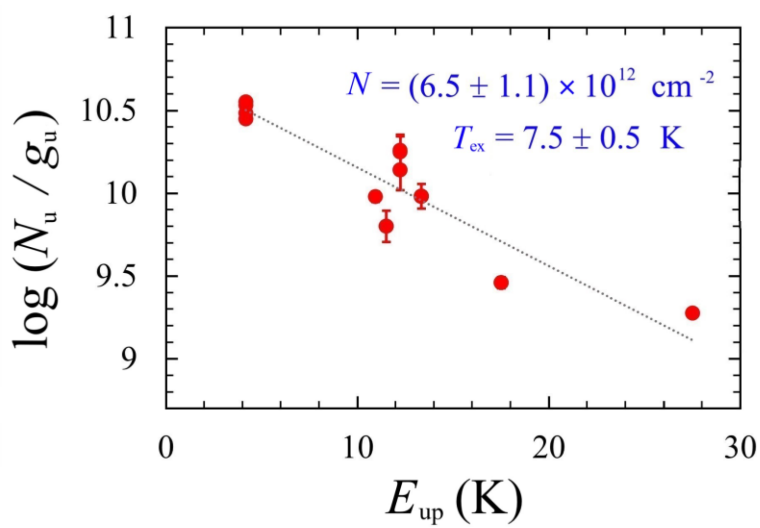
Search for cis-trans HOCOOH toward the G+0.693 molecular cloud



Rotational diagram of cis-trans HOCOOH

Autofit results of cis-trans HOCOOH:

N = $(6.4 \pm 0.4) \times 10^{12}$ cm^{-2}
T_{ex} = 7.2 ± 0.6 K

Molecular abundance compared to H_2 of ~ 4.7×10^{-11}

Consistent with the rotational diagram analysis

cis-trans **HOCOOH** is ~**31** and **7 times less abundant** than ***trans*** **HCOOH** and **CH_3COOH**, respectively, toward G+0.693, but it is also ~**4 times more abundant** than ***cis*** **HCOOH**.

3.3. Discussion

HOCOOH can also **exhibit *trans/cis*** rotational or **conformational isomerism:**
(Pettersson et al. 2002; Macôas et al. 2005; Tsuge & Khriachtchev 2015; García de la Concepción et al. 2022)

We obtain a ***cis-cis/cis-trans* HOCOOH abundance ratio** of **≤25**, rationalized in terms of the different relative electronic energies:

Molecule	ΔE / kcal mol^{-1}	Abundance ratio	Rerefence
HC(O)SH	0.68	~3.7	(García de la Concepción et al. 2022)
HOCOOH	1.71	≤25	(Mori et al. 2009)
HCOOH	4.04	~ 117	(García de la Concepción et al. 2022)

These **isomerization processes** are **feasible** under **ISM conditions** due to **multi-dimensional ground-state quantum tunnelling effects.**
(García de la Concepción et al. 2022)