

The Hot Molecular Core G331.512-0.103:  
Detection of CH<sub>2</sub>NH and its implications for NH<sub>2</sub>CH<sub>2</sub>COOH

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## Outline and Themes

- Introduction
  - Elements and molecules
- Scientific case
  - 'The penultimate step'
- Method
  - Observations and calculations
- Results
  - Detection and formation
- Future



The vicuña and the antenna.

(Credit: Jaime Guarda/ESO)

## A Production of Amino Acids Under Possible Primitive Earth Conditions

Stanley L. Miller<sup>1, 2</sup>

*G. H. Jones Chemical Laboratory,  
University of Chicago, Chicago, Illinois*

The idea that the organic compounds that serve as the basis of life were formed when the earth had an atmosphere of methane, ammonia, water, and hydrogen instead of carbon dioxide, nitrogen, oxygen, and water was suggested by Oparin (1) and has been given emphasis recently by Urey (2) and Bernal (3).

<sup>1</sup> National Science Foundation Fellow, 1952-53.

<sup>2</sup> Thanks are due Harold C. Urey for many helpful suggestions and guidance in the course of this investigation.

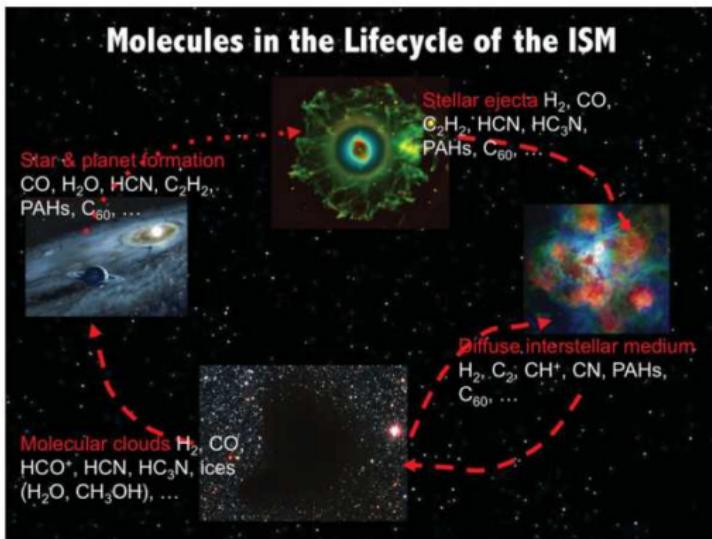
Science 1953.

Vol. 117, Issue 3046, pp. 528-529



Lazcano & Bada 2003. Origins of Life and Evolution of the Biosphere.

Vol 33, pp. 235-242



- Molecular formation include bottom-up and top-down routes;
- The whole cycle takes few billion years, with each phase characterized by distinctive molecules.

Tielens A. G. G. M. 2013. The Molecular Universe.

Rev. Mod. Phys. 85, 1021.

# Elements and molecules

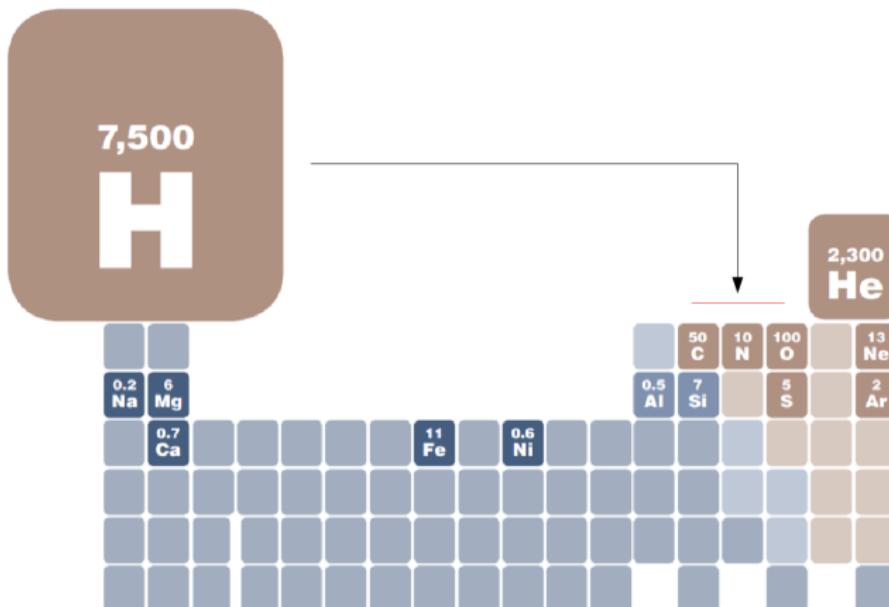
## ✓ The Chemical Universe

CHANDRA X-ray Observatory.

[http://chandra.harvard.edu/resources/illustrations/chemistry\\_universe.html](http://chandra.harvard.edu/resources/illustrations/chemistry_universe.html)

## ✓ The Molecular Universe

McCarthy & Thaddeus 2001. Chem. Soc. Rev., 30, 177.



# Elements and molecules

- ✓ The Chemical Universe

CHANDRA X-ray Observatory.

[http://chandra.harvard.edu/resources/illustrations/chemistry\\_universe.html](http://chandra.harvard.edu/resources/illustrations/chemistry_universe.html)

- ✓ The Molecular Universe

McCarthy & Thaddeus 2001. Chem. Soc. Rev., 30, 177.

Known Interstellar and Circumstellar Molecules (July 2000)							
2	3	4	5	6	7	8	9
H <sub>2</sub>	H <sub>2</sub> O	NH <sub>3</sub>	SiH <sub>4</sub>	CH <sub>3</sub> OH	CH <sub>3</sub> CHO	CH <sub>3</sub> CO <sub>2</sub> H	CH <sub>3</sub> CH <sub>2</sub> OH
OH	H <sub>2</sub> S	H <sub>2</sub> O <sup>+</sup>	CH <sub>4</sub>	NH <sub>2</sub> CHO	CH <sub>3</sub> NH <sub>2</sub>	HCO <sub>2</sub> CH <sub>3</sub>	(CH <sub>3</sub> ) <sub>2</sub> O
SO	SO <sub>2</sub>	H <sub>2</sub> CO	CHOOH	CH <sub>3</sub> CN	CH <sub>3</sub> CCH	CH <sub>3</sub> C <sub>2</sub> CN	CH <sub>3</sub> CH <sub>2</sub> CN
SO <sup>+</sup>	HN <sub>2</sub> <sup>+</sup>	H <sub>2</sub> CS	HC≡CCN	CH <sub>3</sub> NC	CH <sub>2</sub> CHCN	C <sub>7</sub> H	H(C≡C) <sub>3</sub> CN
SIO	HNO	HNCO	CH <sub>2</sub> NH	CH <sub>3</sub> SH	HC <sub>4</sub> CN	H <sub>2</sub> C <sub>6</sub>	H(C≡C) <sub>2</sub> CH <sub>3</sub>
SIS	SIH <sub>2</sub> ?	HNCS	NH <sub>2</sub> CN	C <sub>5</sub> H	C <sub>6</sub> H		C <sub>6</sub> H
NO	NH <sub>2</sub>	CCCN	H <sub>2</sub> CCO	CH <sub>2</sub> CHO	c-CH <sub>2</sub> OCH <sub>2</sub>		
NS	H <sub>3</sub> <sup>+</sup>	HCO <sup>±</sup>	C <sub>2</sub> H	CH <sub>2</sub> =CH <sub>2</sub>			
HCl	NNO	CCCH	c-C <sub>3</sub> H <sub>2</sub>	H <sub>2</sub> CCCC			
NaCl	HCO	c-CCCH	CH <sub>2</sub> CN	HC <sub>3</sub> NH <sup>+</sup>			
KCl	HCO <sup>+</sup>	CCCO	C <sub>5</sub>	C <sub>5</sub> N			
AlCl	OCS	CCCS	SIC <sub>4</sub>	C <sub>6</sub> S?			
AIF	CCH	HCCH	H <sub>2</sub> CCC				
PN	HCS <sup>+</sup>	HCNH <sup>+</sup>	HCCNC				
SIN	c-SICC	HCCN	HNCCC				
NH	CCO	H <sub>2</sub> CN	H <sub>3</sub> CO <sup>+</sup>				
CH	CCS	c-SIC <sub>3</sub>					
CH <sup>+</sup>	C	CH <sub>3</sub>					
CN	MgNC	CH <sub>2</sub> D <sup>+</sup> ?					
CO	NaCN						
CS	CH <sub>2</sub>						
C <sub>2</sub>	MgCN						
SIC	HOC <sup>+</sup>						
CP	HCN						
CO <sup>+</sup>	HNC						
HF	SICN						
	KCN?						

— Carbon chains  
— Complex Organic Molecules  
— Tracers of shocks and UV-irradiation



# Cometary Glycine: Comet 81P/Wild 2



Table 1. Summary of the amino acid concentrations in water extracts of Stardust flight foils<sup>a</sup>.

Amino acid	This study				Previous study <sup>b</sup>			
	C2103N,0	C2016N,2	C2017N,0	C2078N,0	C2125N,2		C2092S,0	
	Both sides (total)				Aerogel side (total)	Metal side (total)	Both sides (free)	Both sides (total)
Glycine	34	2	13	19	21	<3	27	68
β-alanine	2	1	1	3	<2	<2	1	7
D-alanine	<3	<3	<3	<3	<3	<3	<3	<4
L-alanine	2	<1	1	1	1	<3	6	12
EACA <sup>c</sup>	326	51	66	327	186	126	11	1,413

Elsila, Glavin & Dworkin 2009.

Meteoritics & Planetary Science 44, 9, 1323

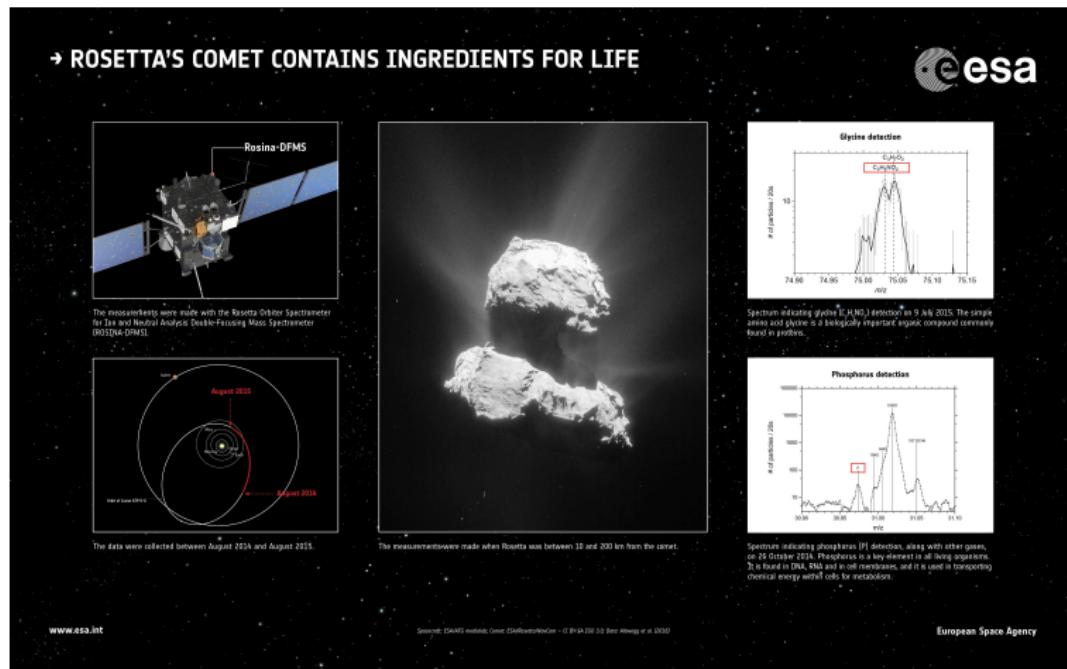
Mission: Stardust. Target: Wild 2. Spacecraft: Stardust.

Image credit: NASA/JPL-Caltech



# Cometary Glycine: Comet 67P/Churyumov-Gerasimenko

→ ROSETTA'S COMET CONTAINS INGREDIENTS FOR LIFE



The image is a composite of several panels from the Rosetta mission. At the top left is a diagram of the Rosetta spacecraft with its solar panels and the Rosina-DFMS instrument highlighted. Below it is a photograph of comet 67P/Churyumov-Gerasimenko with a bright, glowing nucleus and a long, luminous tail. To the right is the European Space Agency (esa) logo. The bottom section contains two scientific plots. The first plot, titled 'Glycine detection', shows a spectrum with peaks at 74.96 and 75.00 ppm, labeled 'Glycine'. The second plot, titled 'Phosphorus detection', shows a spectrum with a prominent peak at 31.00 ppm, labeled 'Phosphorus'. Both plots have axes for 'Number of detections / 25s' and 'ppm'.

Rosina-DFMS

The measurements were made with the Rosetta Orbiter Spectrometer for Ion and Neutral Analysis Double-Focusing Mass Spectrometer (ROSINA-DFMS).

August 2014

August 2015

The data were collected between August 2014 and August 2015.

The measurements were made when Rosetta was between 10 and 200 km from the comet.

Glycine detection

Number of detections / 25s

ppm

74.96 74.98 75.00 75.02 75.04 75.06 75.08 75.10 75.12

Glycine

Phosphorus detection

Number of detections / 25s

ppm

30.80 31.00 31.20 31.40 31.60 31.80 32.00 32.20

Phosphorus

Spectrum indicating glycine ( $\text{C}_2\text{H}_5\text{NO}_2$ ) detection on 9 July 2015. The simple amino acid glycine is a biologically important organic compound commonly found in proteins.

Spectrum indicating phosphorus (P) detection, along with other gases, on 26 October 2015. Phosphorus is a key element in all living organisms. It is found in DNA, RNA and in cell membranes, and it is used in transporting chemical energy within cells for metabolism.

[www.esa.int](http://www.esa.int)

Source: ESA/Hubble, Credit: ESA/Rosetta/OSIRIS - CC BY-SA 3.0; Balsiger et al. 2016

European Space Agency

Altwegg, Balsiger, Bar-Nun et al. 2016. Science Advances, Vol 2., no. 5  
Mission: Rosetta. Comet 67P/Churyumov-Gerasimenko

Image Credit: ESA/Rosetta/NAVCAM CC BY-SA IGO 3.0

# Shock synthesis: Impact events on early Earth

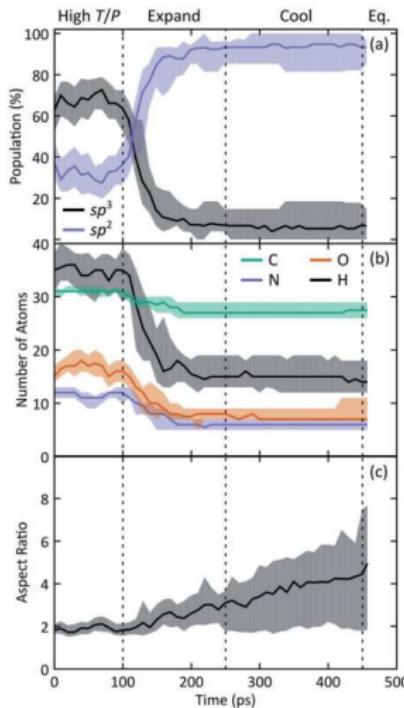
## Chemistry in shock

- \* ( $T$ ) 298 K  $\longrightarrow$  3000 K
- \* ( $\rho$ ) 1.0 g cm $^{-3}$   $\longrightarrow$  2.5 g cm $^{-3}$
- \* ( $P$ ) 48 GPa



Comet of the century: A horizon special

Graphic image: Weave VFX/BBC

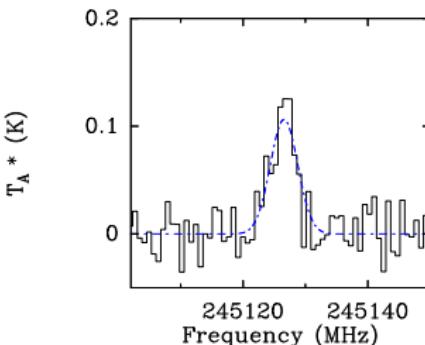


Kroonblawd, Lindsey & Goldman 2019.

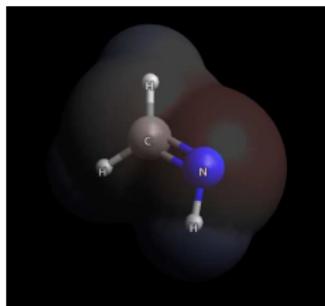
Chem. Sci., 10, 6091-6098



# Spectral survey Methanimine

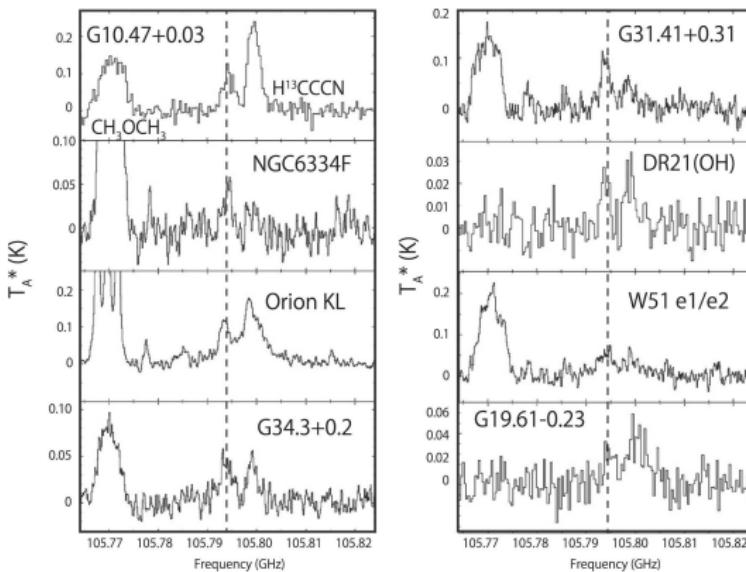


CH<sub>2</sub>NH in G331.512-0.103:  $4_{1,4}-3_{1,3}$  at 245126.014 MHz.



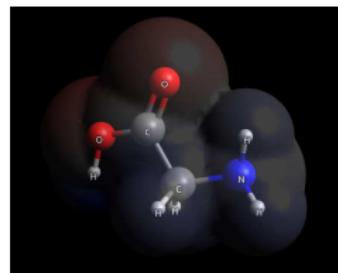
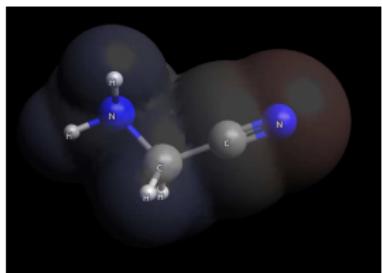
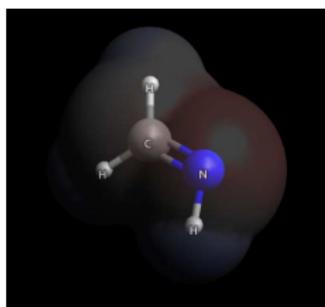
## Formation path for glycine

Suzuki et al. 2016 ApJ 825 79:  
CH<sub>2</sub>NH in 12 high-mass and 2 low-mass star forming regions

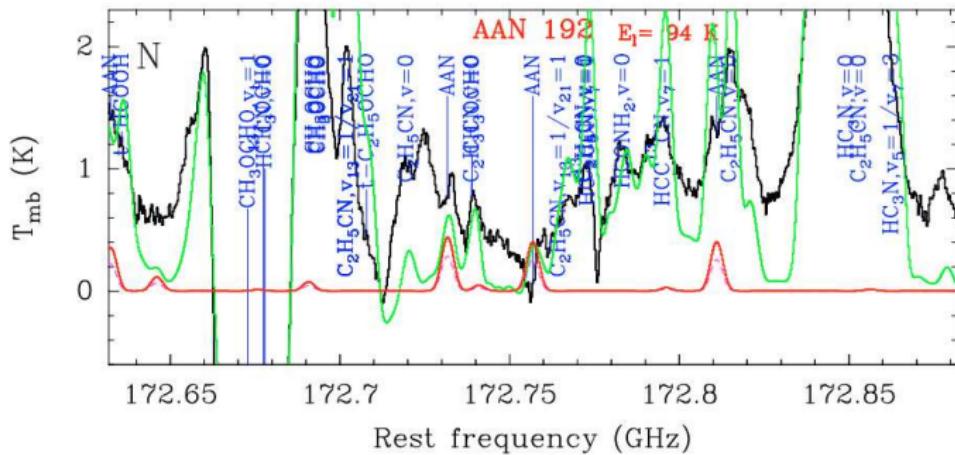


- e.g. Kim & Kaiser 2011; Theule et al. 2011 and Woon 2002; Holtom et al. 2005; Peltzer et al. 1984; Danger et al. 2011.

# $\text{CH}_2\text{NH}$ , $\text{NH}_2\text{CH}_2\text{CN}$ and $\text{NH}_2\text{CH}_2\text{COOH}$



# Amino acetonitrile in Sgr B2(N)

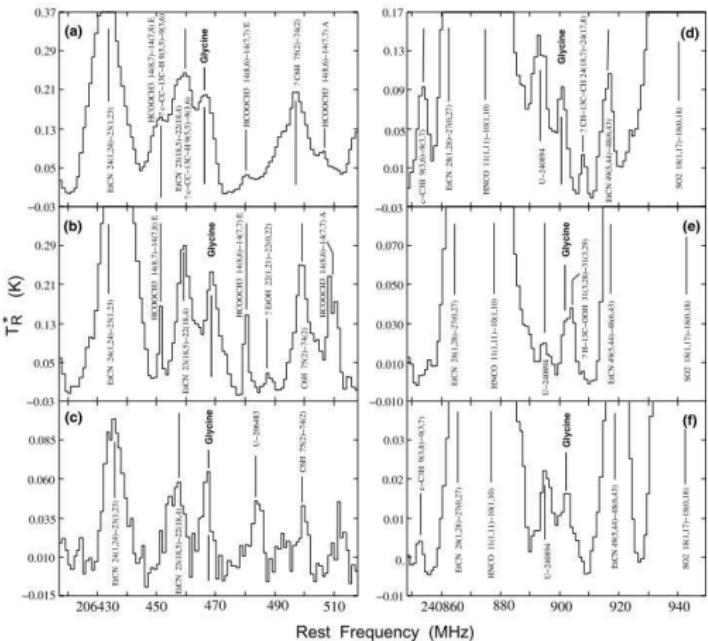


Belloche et al. 2008 A&A 482, 179

(also Belloche et al. 2008. A&A 492, 769)

# Search for interstellar glycine

Kuan et al. 2003. ApJ, 593, 848



## Observations

Instruments: APEX-I, -II, -III and SEPIA-B5 (around 50 hs)

- **(2019)** Cyanoacetylene and their isotopologues in G331.512-0.103;
- **(2018–2019)** Hot molecular core candidates across the southern Milky Way;
- **(2016–2019)** Glycolaldehyde and pre-biotic molecules in the powerful outflow/hot core G331.512-0.103 (I, II, III)

(Bronfman et al. 2008; Merello et al. 2014; Mendoza et al. 2018; Hervías-Caimapo et al. 2019; Duronea et al. 2019)



Pic credits: ALMA, APEX gallery <http://www.almaobservatory.org/en/images/>

## Making a detection: databases

Without considering the spectroscopy, the filter by databases

**Search Filter** +/-

- Exclude atmospheric species
- Exclude potential interstellar species
- Exclude probable interstellar species
- Exclude known AST species
- Show ONLY astronomically-observed transitions
- Show ONLY NRAO Recommended Freq

**Line List Display** +/-

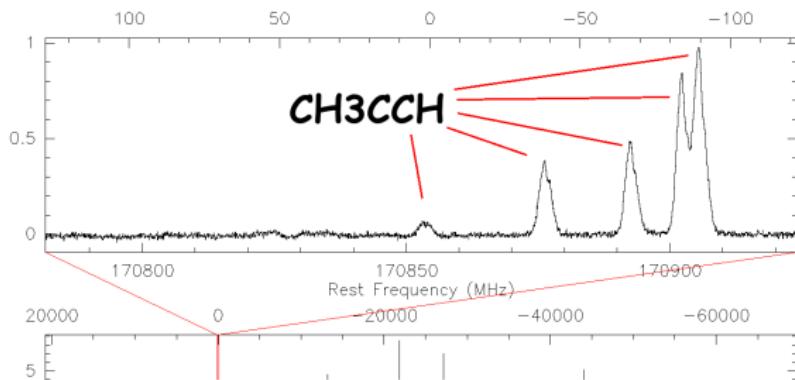
- JPL     CDMS
- Lovas/NIST     SLAIM
- ToyaMA     OSU
- Recombination Lines
- TopModel Lines
- RFI Lines



- Splatalogue: <https://www.cv.nrao.edu/php/splat>
- <https://spec.jpl.nasa.gov>
- <https://cdms.astro.uni-koeln.de>
- <https://physics.nist.gov/cgi-bin/micro/table5/start.pl>

## Essential criteria for (new) detections

- 1) First of all, think in contamination
- 2) Rest frequencies → Laboratory work, high-precision Hamiltonian models
- 3) Frequency agreement → Agreement between the rest frequency and the LSR velocity of the source
- 4) Beam dilution effects
- 5) Relative intensities → Consistency of dipole moments, line strengths, frequencies, energy levels, rotational temperatures

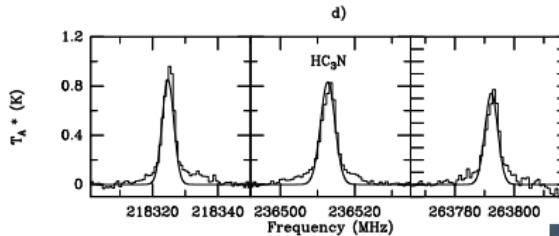
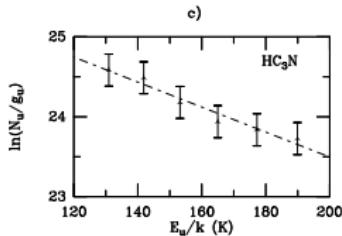
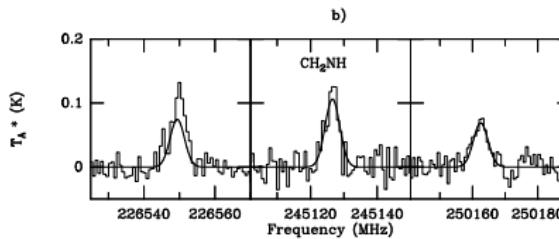
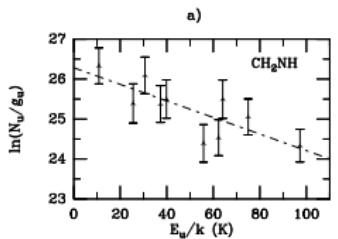


(e.g. Snyder, Lovas & Hollis et al. 2005. ApJ, 619:914-930)

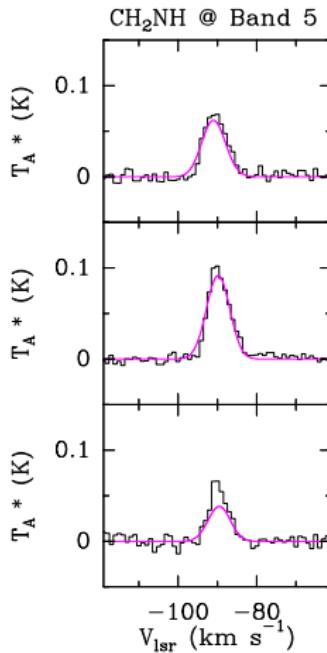
# The case of G331.512-0.103: CH<sub>2</sub>NH and HC<sub>3</sub>N

Prediction and observation: APEX/Sepia band 5 (Mendoza et al. in prep)

- a) and b): CH<sub>2</sub>NH  
 $T_{\text{exc}} \approx 40 \text{ K}$  and  $N \approx 1.2 \times 10^{14} \text{ cm}^{-2}$
- c) and d): HC<sub>3</sub>N  
 $T_{\text{exc}} \approx 85 \text{ K}$  and  $N \approx 6.9 \times 10^{14} \text{ cm}^{-2}$



# $\text{CH}_2\text{NH}$ in G331 as seen with APEX/Band5



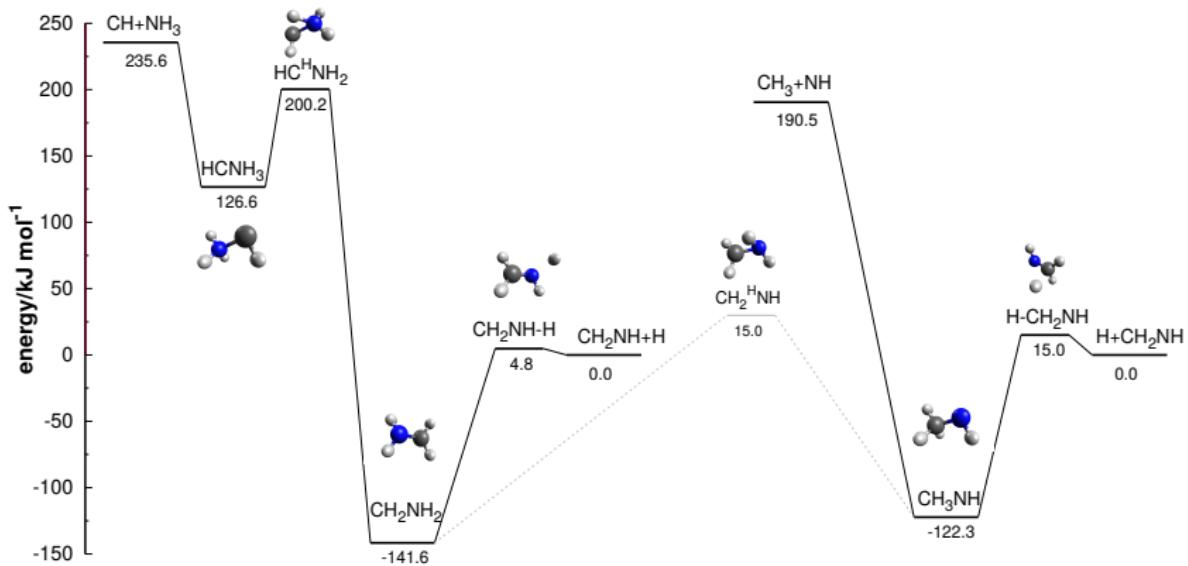
## Spectral analysis

- \* 16 lines of  $\text{CH}_2\text{NH}$  between 160 - 352 GHz;
- \* Excitation components  $10 < E_u(\text{K}) < 200$ ;
- \* Emission origin in discussion  $T < 70 \text{ K}$ .  $N \simeq 10^{14} \text{ cm}^{-2}$ ;

Frequency (MHz)	$E_u$ (K)	$A_{ij}$ ( $1 \times 10^{-5} \text{s}^{-1}$ )
166852.248	11.0789	21.1
172267.519	17.4749	10.3
178073.945	45.8521	31.4

# Theoretical studies on the CH<sub>2</sub>NH formation

- Precursors: CH, NH<sub>3</sub>, CH<sub>3</sub> and NH
- Reaction: CH + NH<sub>3</sub> → CH<sub>2</sub>NH + H



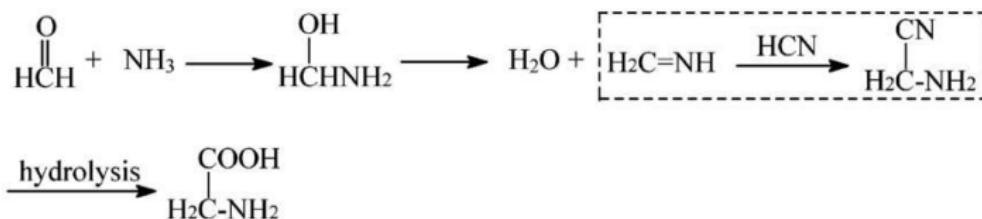
Mendoza et al. in prep

e.g. Mallard et al. 1994. Bocherel et al. 1996. Blitz et al. 2012. Suzuki et al. 2016

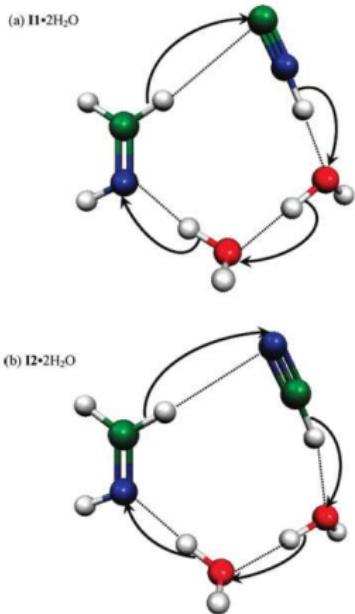
## The penultimate step: Strecker synthesis

- The role of CH<sub>2</sub>NH, H<sub>2</sub>O, HCN and HNC in a Strecker synthesis to produce glycine (Koch et al. 2008. J. Phys. Chem. C, 112, 2972-2980)

**SCHEME 1**



## The penultimate step: Strecker synthesis



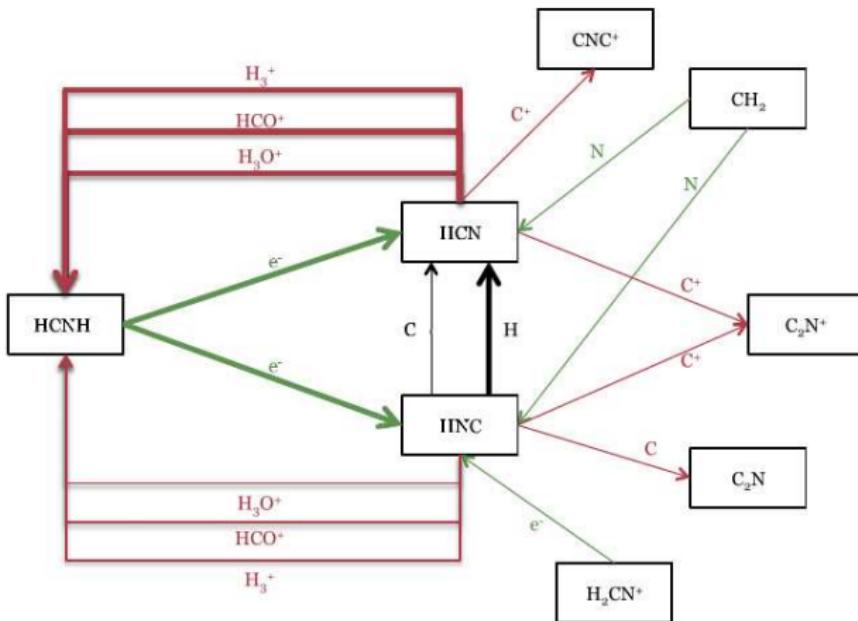
### Interstellar ice models

- Reaction between  $\text{CH}_2\text{NH}$  and  $\text{HCN}$  and  $\text{HNC}$  to produce  $\text{NH}_2\text{CH}_2\text{CN}$
- Isomerization  
 $\text{HCN} \rightarrow \text{HNC}$  vs  $\text{HNC} \rightarrow \text{HCN}$
- ✓ The reaction with  $\text{HNC}$  is sufficiently low in comparison with  $\text{HCN}$

Of course: observations and simulations suppose (diverse) complex systems  
 $\text{H}_2\text{O}$ ,  $\text{HCN}$ ,  $\text{HNC}$ ,  $\text{CH}_2\text{NH}$ ...

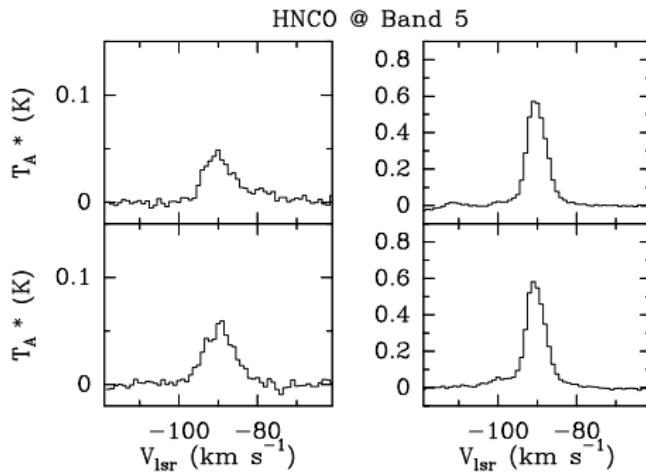
Koch et al. 2008. J. Phys. Chem. C, 112,  
2972–2980

# The importance of HCN and HNC in Star-Forming Regions



Loison, Wakelam & Hickson 2014. MNRAS, 443, Issue 1,  
 Graninger, Herbst, Öberg, Vasyunin 2014. ApJ, 787:74

# HNCO in G331 as seen with APEX/Band5



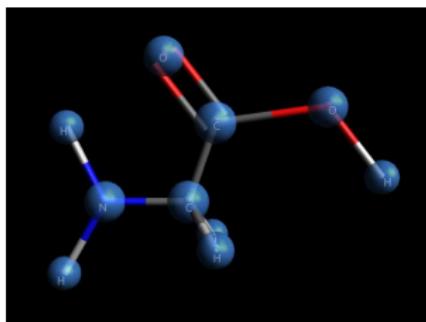
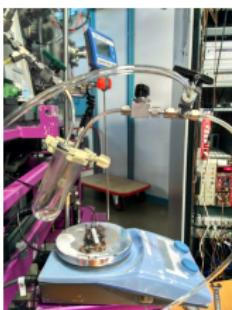
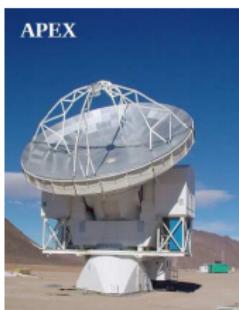
Frequency (MHz)	$E_u$ (K)	$A_{ij}$ ( $1 \times 10^{-5} \text{s}^{-1}$ )
175792.3332( $\pm 0.014$ )	211.07	0.127
175843.701( $\pm 0.03$ )	37.98	7.64
197764.7327( $\pm 0.0167$ )	220.56	0.144
197821.39( $\pm 0.03$ )	47.47	10.8

Mendoza et al. in prep

# Summarizing

## (Partial) conclusions

- CH<sub>2</sub>NH: Prediction and confirmation in G331
- CH<sub>2</sub>NH: as an key building block for pre-biotic chemistry
- $N(\text{CH}_2\text{NH}) \simeq 10^{14} \text{ cm}^{-2}$ ,  $T < 70\text{K}$
- CH<sub>2</sub>NH lines comparable with those observed in other HMCs



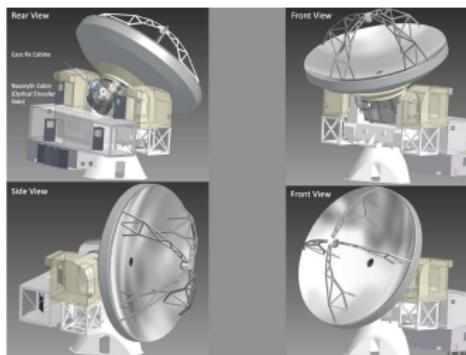
observations + experiments + models

# Perspectives

## LLAMA Project

Interesting science with the band 5

- Maser of HCN at 177 GHz
- Maser of H<sub>2</sub>O at 183 GHz
- Typical spectral tracers as CH<sub>3</sub>CN, CH<sub>3</sub>OH, CH<sub>3</sub>CCH and HC<sub>3</sub>N
- Pre-biotic chemistry: NH<sub>2</sub>CHO and HNCO



[www.llamaobservatory.org/english.html](http://www.llamaobservatory.org/english.html)



thank you!