

Introduction to Astrochemistry Part 2: Molecular Clouds and the Formation of Stars and Planets

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Observatory (NRAO)



GREEN BANK

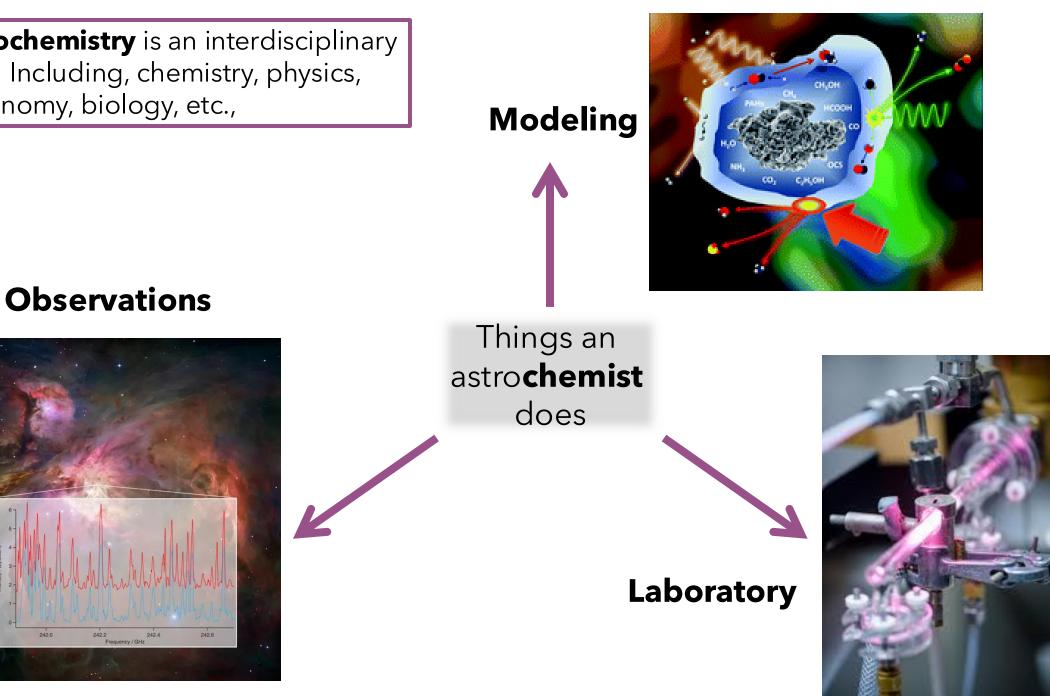
National Radio

Astronomy



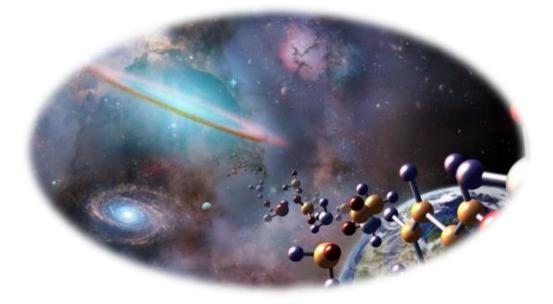
Astrochemistry is an interdisciplinary field! Including, chemistry, physics, astronomy, biology, etc.,

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Astrochemistry, or "Molecular Astrophysics"

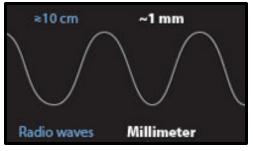
Definition: The study of the formation and destruction of molecules in the Universe, their interaction with radiation, and their feedback on physics of the environments



I write about molecules with great diffidence, having not yet rid myself of the tradition that **atoms are physics, but molecules are chemistry**, but the new conclusions that hydrogen is abundant seems to make it likely that the above mentioned elements H, O, and N will frequency form molecules

Submillimeter and Millimeter Radio Telescopes Probe Cool Molecular Gas!

Radio telescopes let us see objects we can't see in visible light – such as the dust and gas inside dense molecular clouds that will form stars like our Sun!



This is the type of object I study! >



Starless Core B68

✓ ✓ Visible light image

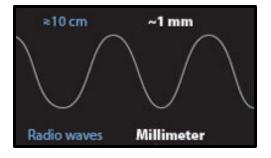


Starless Core: Birthplace of lowmass stars (M \leq a few M_{\odot}) Dense (10⁴ - 10⁵ cm⁻³) & cold (\leq 10K)

 $10K = -441.67^{\circ} F!$ Low temp. at poles of Mars -243 °F

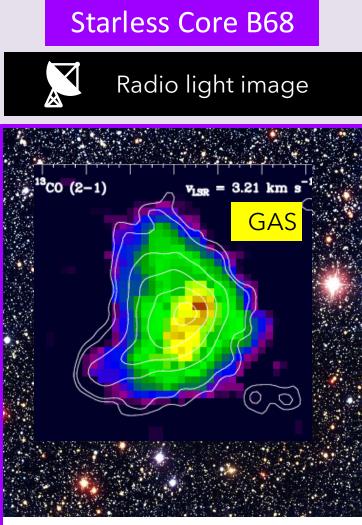
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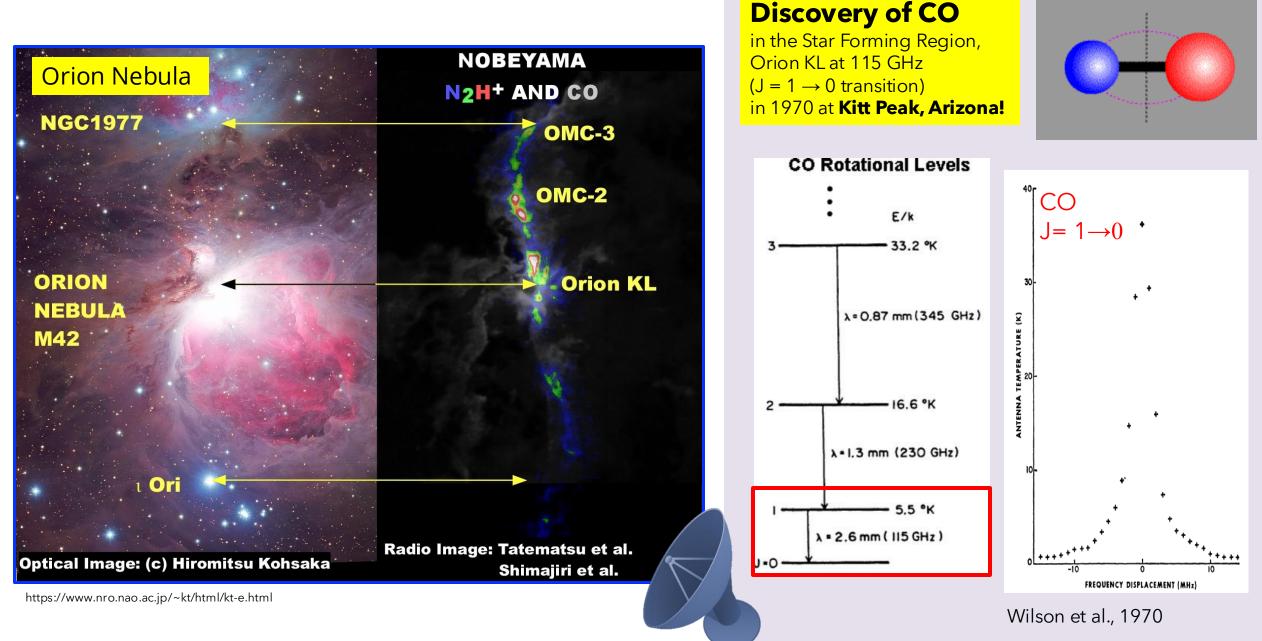
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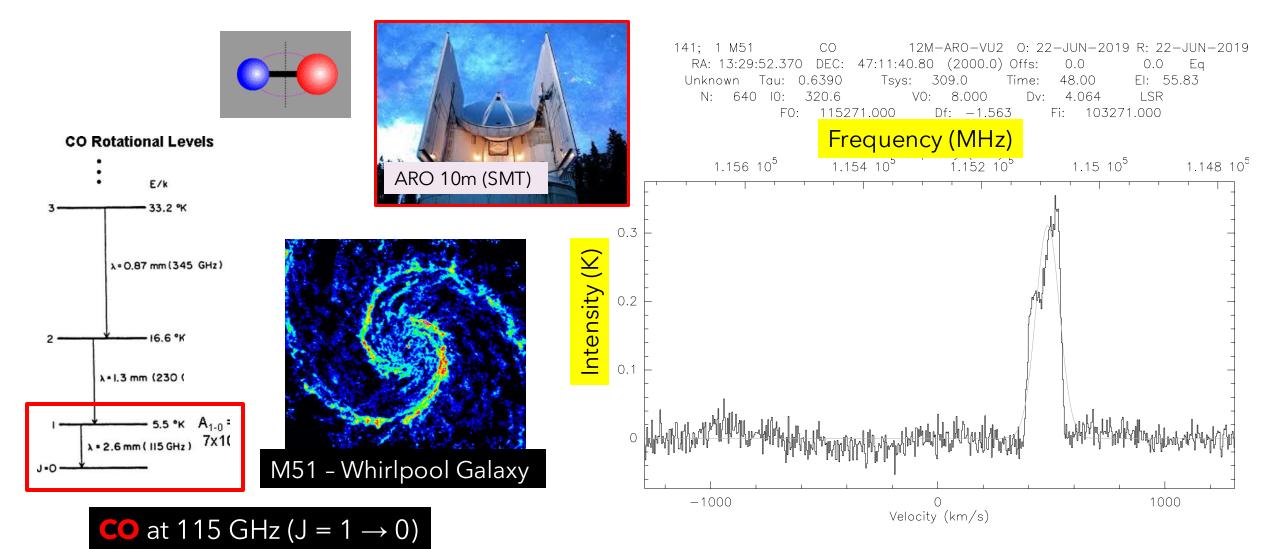


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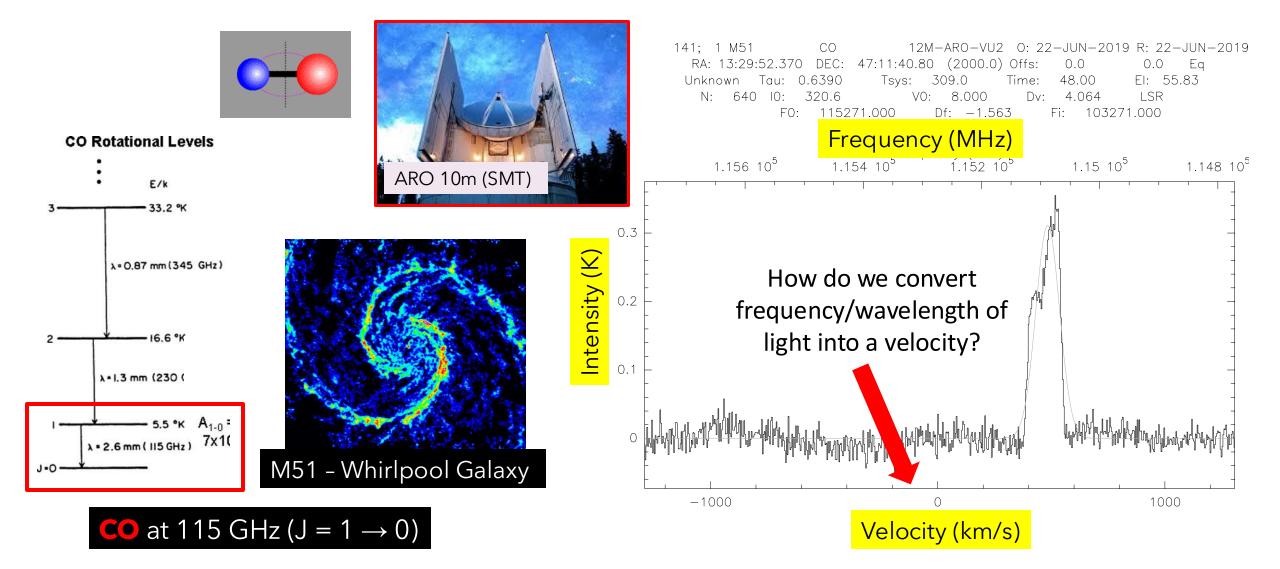
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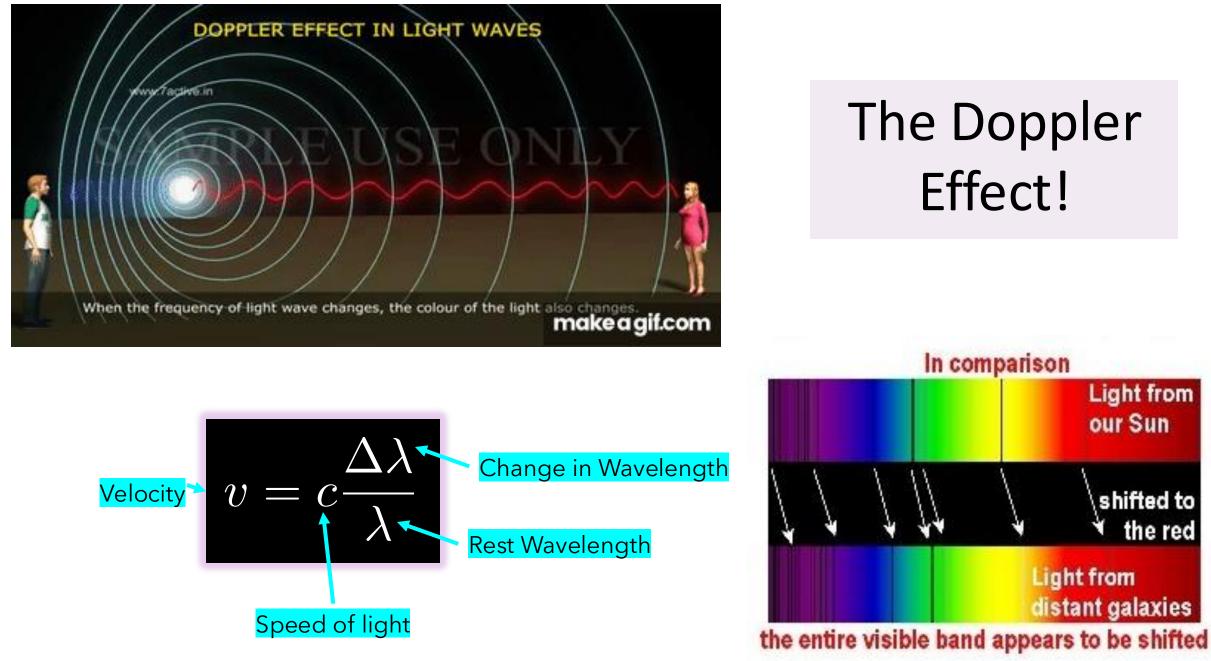


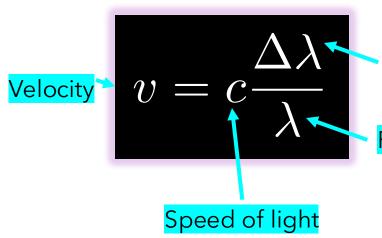
Measuring the Molecular **Gas Motions**!



Measuring the Molecular **Gas Motions**!



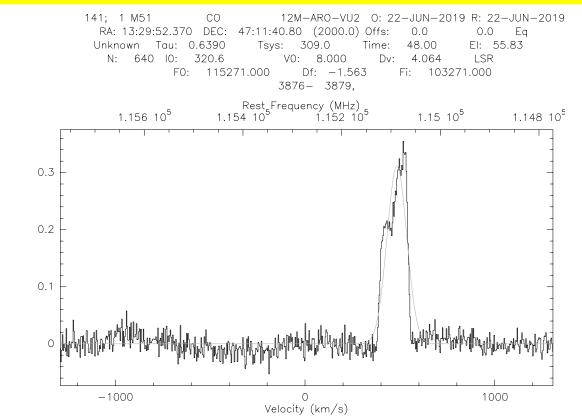




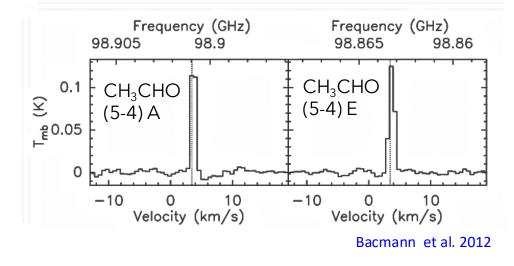
Change in Wavelength

Rest Wavelength

Extragalactic source, line-of-sight velocities a few hundred km/s

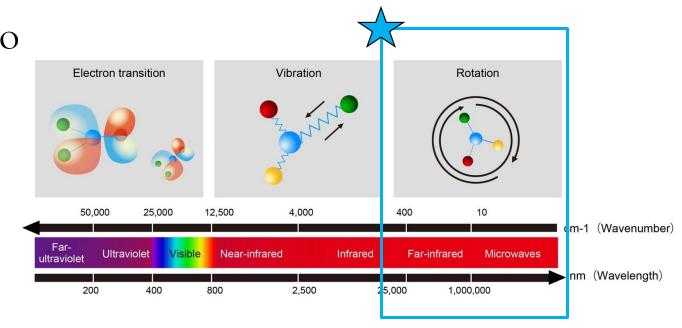


Galactic source, line-of-sight velocity a few km/s

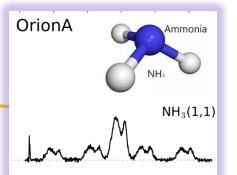


Submillimeter and Millimeter Radio Telescopes Identify Molecules via <u>Rotational Spectroscopy</u>!

> Radio waves let us see objects we can't see in visible light, like the cold gas in star forming regions



Dish acts like a mirror and focuses long wavelength radio light onto electronic device that receives it and records an objects' **spectrum**, i.e., it's intensity vs. frequency (or wavelength)



We know if a bright line occurs where a certain molecule is predicted to emit at, we have identified that molecule!

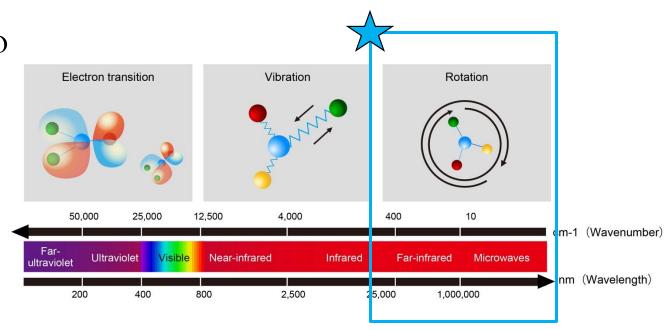
Submillimeter and Millimeter Radio Telescopes Identify Molecules via Rotational Spectroscopy!

How do we know what frequency? Online databases of laboratory measurements!

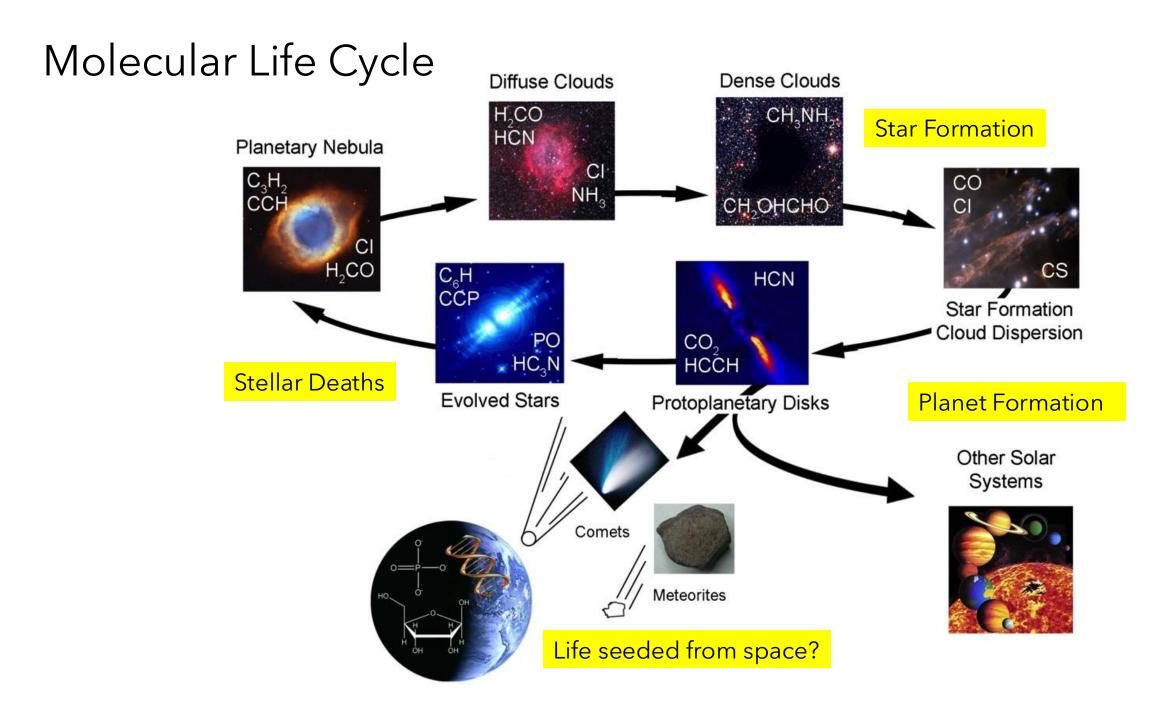
Hom

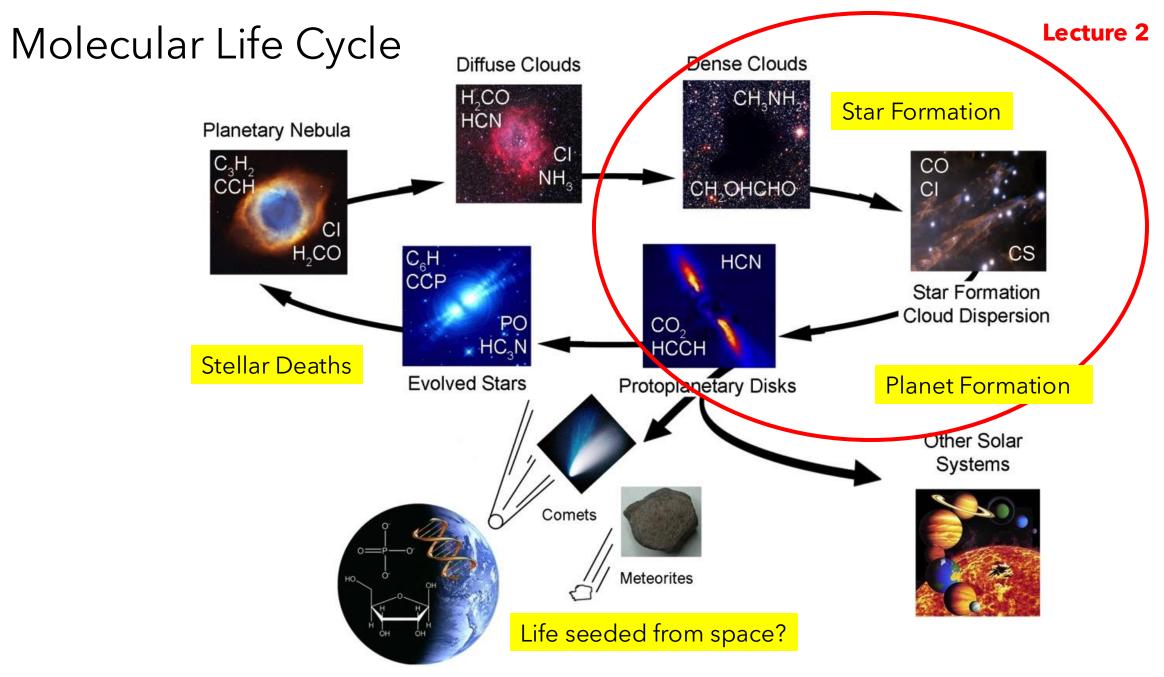
me	Basic	Advanced	FAQ	OSU	
					Splatalogue
			D	Databa	ase for Astronomical Spectroscopy
			Giv	ving yo	ou the right frequency one line at a time.

#	Species	Chemical Name	Ordered Frequency (GHz) (rest frame, <mark>redshifted)</mark>	Resolved QNs	CDMS/JPL Intensity	Lovas/AST Intensity	E _L (K)	E _U (K)	Linelist
1	<u>CO v = 0</u>	Carbon Monoxide	115.2712018, 115.2712018	1-0	-5.0105	60.00	0.000	5.53211	CDMS



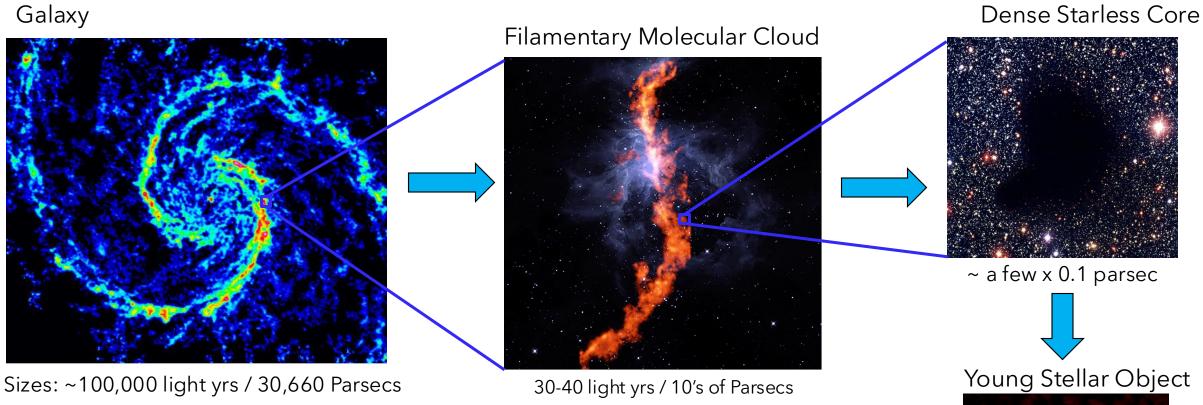
https://splatalogue.online





Cool clouds of gas: A birthplace for stars

Galaxy



Stars!



~ a few x 0.0001 parsec

40 au

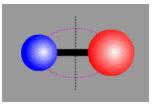
Cool clouds of gas: A birthplace for stars

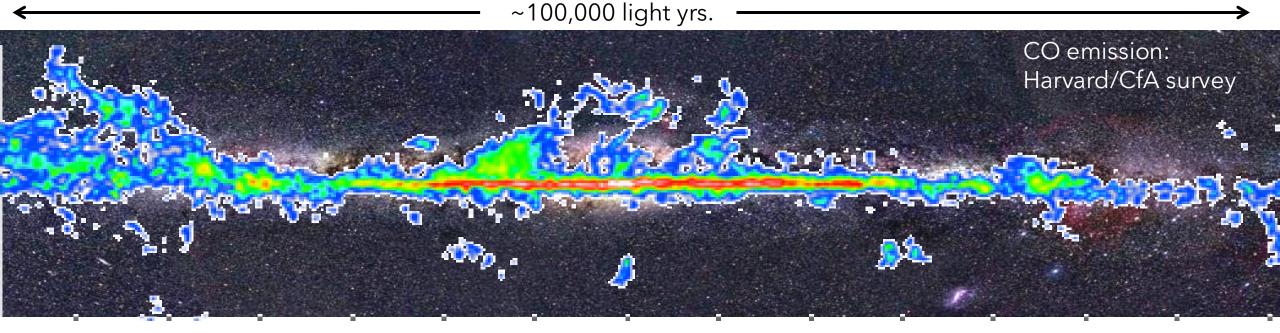
- Astronomers for centuries: Interstellar Space, realm of atomic material
 - ~100,000 light yrs.



Cool clouds of gas: A birthplace for stars and molecules!

- Astronomers for centuries: Interstellar Space, realm of atomic material
- Radio and MILLIMETER astronomy changed the paradigm!





 Molecular Gas widespread in the Galaxy (CO: J = 1-0 transition) 	• Molecules in massive, dense clouds: M ~ 1 - 10 ⁶ M_{\odot}
• Inner 10 kpc of Galaxy: 50% MOLECULAR \Rightarrow 10 ¹⁰ solar masses	• Typical Conditions: T ~ 10 - 50 K; n ~ 10 ³ - 10 ⁶ cm ⁻³ :
	COLD and DIFFUSE

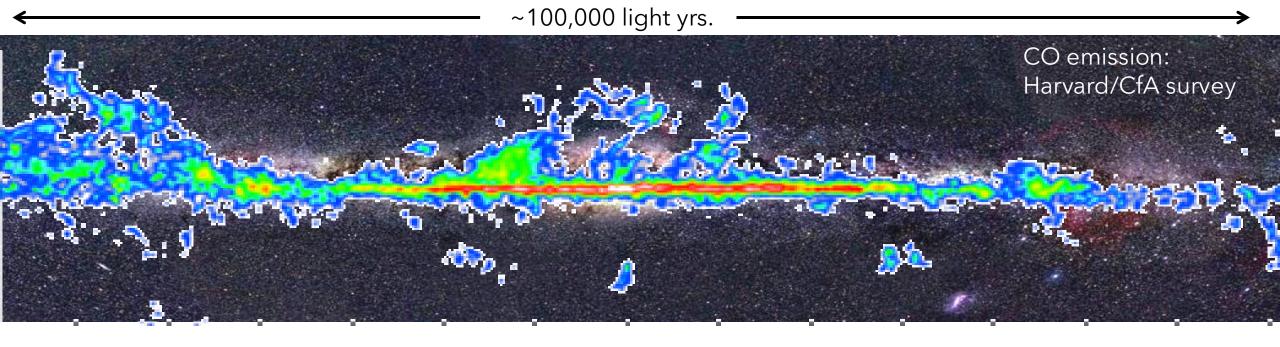
Cool clouds of gas: A birthplace for stars and molecules!

Astronomical scales different from our normal experience!

Molecular clouds live 1,000,000 - 10,000,000 yrs.

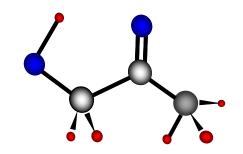
Motions/Speeds: 1 km/s ~ 3600 km/hour is about 5 x faster than a jet plane (at this speed, 4 days to Moon or 5 days to the Sun or 1 million years to the nearest star!

1 km/sec = 1 parsec (3.26 light yrs.) in 1 million years



Despite different physical conditions and timescales, molecules do form!

- Typical Conditions in molecular gas:
 - low Densities (10 10^7 cm^{-3} ; < 10^{-12} torr)
 - compared to Earth atmosphere ($\sim 10^{19}$ cm⁻³)
 - low Temperatures: T $\sim 10 100 \text{ K}$
- Severely restricts allowed chemical processes!

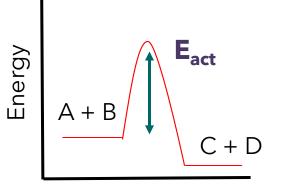


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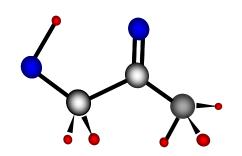
• Severely restricts allowed chemical processes!

- only two body collisions
 - i.e, three-body reactions such as
 - $A + B + C \rightarrow ABC * \rightarrow AB + C$
 - in majority of cases NOT POSSIBLE
- \bullet cannot overcome activation energy barriers $\mathsf{E}_{\mathsf{act}}$
- reactions must be **exothermic!**



Reaction coordinate

A reaction that results in products of greater stability (lower energy) than the reactants gives off energy and is said to be **exothermic**



Exothermic?

Molecule	Dissociation energy (eV)
H ₂	4.48
СН	3 47

CH	3.47
OH	4.39
CH+	4.09
OH+	5.10

Which reactions can form?

 $C + H_2 \Box CH + H ??$ $C_+ + H_2 \Box CH_+ + H ??$ $O + H_2 \Box OH + H ??$ $O_+ + H_2 \Box OH_+ + H ??$

energy ; bond length internuclear separation Dissociation energy or bond strength

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Credit: P. Caselli

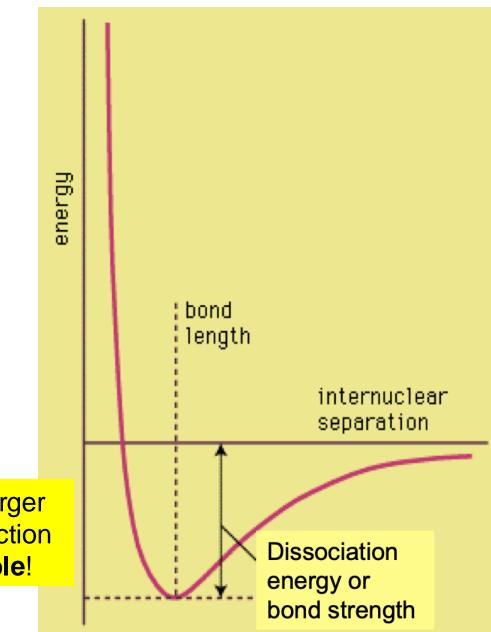
Exothermic?

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$$C + H_2 \Box CH + H ??$$

4.48eV vs. 3.47 eV

The bond strength of H₂ is larger than that of CH thus, the reaction is **not energetically favorable**!



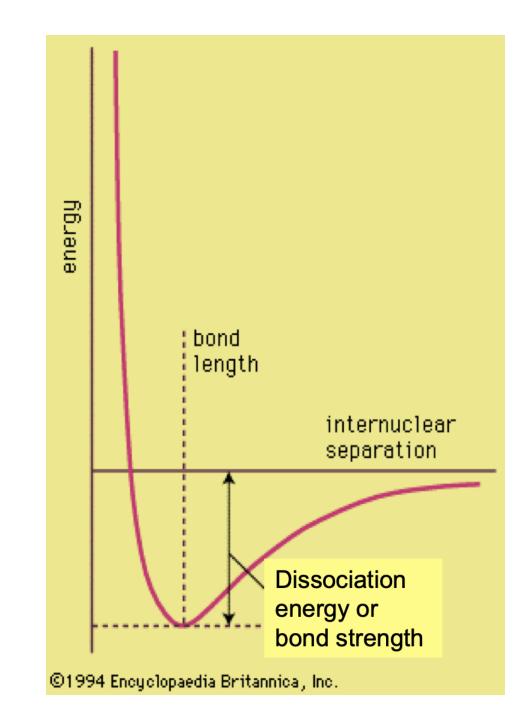
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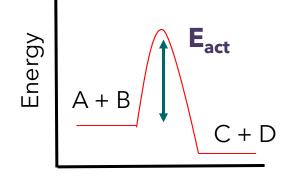
Credit: P. Caselli

Despite different physical conditions and timescales, molecules do form!

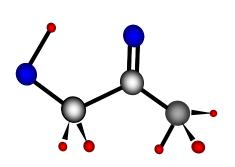
Reactions (gas-phase) that ARE possible:

* ION-MOLECULE

- $A + B^+ \rightarrow C + D^+$
- \bullet Two-body and typically exothermic with no $E_{\rm act}$
- roughly 50% have no reaction barriers
- proceed quickly (fast collisional rates)
- networks of Ion-Molecule reactions create interstellar molecules
- only reactions fast enough to form chemical species given cloud lifetimes ($t \sim 10^6 \ yrs.)$



Reaction coordinate



Despite different physical conditions and timescales, molecules do form!

Types of ION-MOLECULE reactions

1) Hydrogen Abstraction: $A^+ + H_2 \rightarrow AH^+ + H$

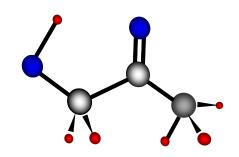
 $\begin{array}{c} \mathsf{O}^{+}+\mathsf{H}_{2}\rightarrow \; \mathsf{O}\mathsf{H}^{+}+\mathsf{H}\\ \mathsf{O}\mathsf{H}^{+}+\mathsf{H}_{2}\rightarrow \; \mathsf{H}_{2}\mathsf{O}^{+}+\mathsf{H}\\ \mathsf{H}_{2}\mathsf{O}^{+}+\mathsf{H}_{2}\rightarrow \; \mathsf{H}_{3}\mathsf{O}++\mathsf{H} \end{array}$

2) Heavy-Atom Synthesis: $AH^+ + CO \rightarrow ACO^+ + H$

 $CH_4^+ + CO \rightarrow CH_3CO^+ + H$

3) Carbon Addition: $C^+ + AH \rightarrow AC^+ + H$

 $\begin{array}{c} \mathsf{C^{+}+NH_{3} \rightarrow H_{2}CN^{+}+H} \\ \mathsf{C^{+}+H_{2}CO \rightarrow HCCO^{+}+H} \end{array}$



Despite different physical conditions and timescales, molecules do form!

Reactions (gas-phase) that ARE possible:

* Neutral-Neutral Reactions

 $A + B \rightarrow C + D$

- usually need **radical** atom or molecule

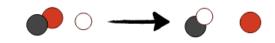
Example: NO + N \rightarrow N₂ + O

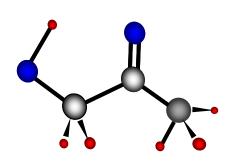
Example: the formation of water in hot (T > 400 K) gas is powered via

 $O + H_2 \rightarrow OH + H$, followed by, $OH + H_2 \rightarrow H_2O + H$

Bond rearrangement

Ion-molecule, neutral-neutral or charge transfer





Despite different physical conditions and timescales, molecules do form!

photon

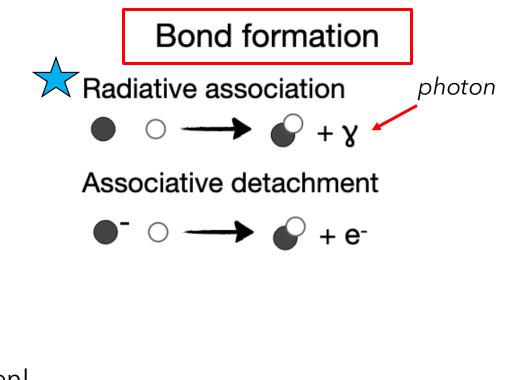
Reactions (gas-phase) that ARE possible:

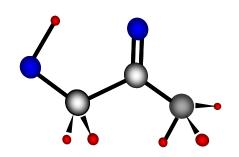
ive Association $A^+ + B \rightarrow AB^+ + hv$

* Radiative Association

- Tends to only be important for reactions where the reactants are very abundant and thus collisions are plentiful, which in practice implies that one of the reactants is the most common element in the Universe, i.e., hydrogen!

Example: $C^+ + H_2 \rightarrow CH_2^+ + hv$





Despite different physical conditions and timescales, molecules do form!

Reactions (gas-phase) that ARE possible:

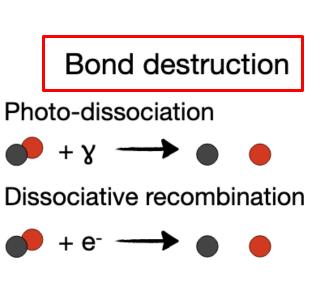
* Photo-dissociation

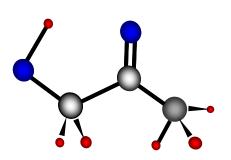
 $AB + hv \rightarrow A + B$

* Dissociative Electron Recombination

 $A^+ + e^- \rightarrow B + C$ (neutral products)

Example: $HCNH^+ + e^- \rightarrow HCN, HNC + H$



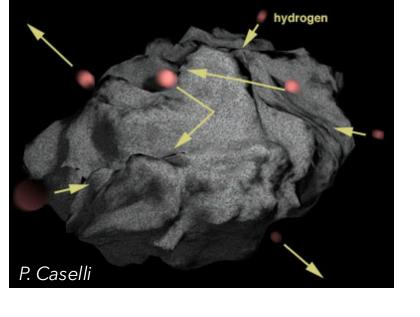


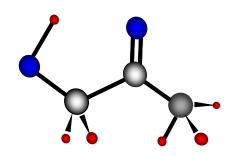
Despite different physical conditions and timescales, molecules do form!

Reactions on Grain Surfaces very important!

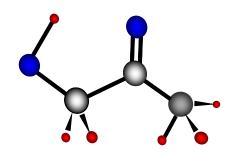
${\rm H} + {\rm H} \rightarrow {\rm H}_2$

- This reaction that starts the chemistry in the interstellar medium!
- Releases energy so H₂ can leave grain
- H₂ MUST form on grains!
- In general, less known (hard to discern processes on grains)
- Gas is cold: everything freezes on grains
- May create larger species on grains (> 6 atoms)





Basic Chemical Scheme:



1) H_2 formed on grain surfaces: $H + H + \text{grain} \rightarrow H_2 + \text{grain}$ 2) Gas-phase reactions in initiated by cosmic rays (photons)

$$\begin{array}{l} H_{2}+\gamma \rightarrow H_{2}^{+}+e +\gamma' \\ H_{2}^{+}+H_{2} \rightarrow H_{3}^{+}+H \\ H_{3}^{+}+CO \rightarrow HCO^{+}+H \\ H_{3}^{+}+N_{2} \rightarrow N_{2}H^{+}+H \\ etc. \end{array}$$

He⁺ + H₂ → does not occur at low T INSTEAD:

 $\begin{array}{rl} \mbox{He}+\gamma \rightarrow \mbox{He}^{+}+e \ +\gamma' \\ \mbox{He}^{+}+CO \rightarrow C^{+}+O + \mbox{He} \\ \mbox{C}^{+} & \rightarrow \mbox{ organic compounds} \end{array}$

Interstellar Chemistry Is KINETICALLY CONTROLLED, NOT THERMODYNAMICALLY

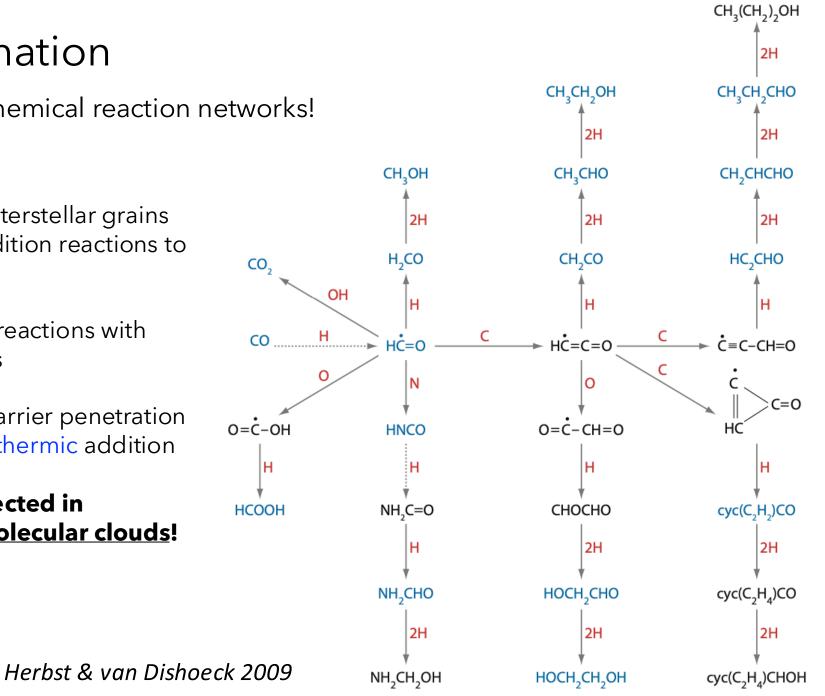
Large chemical reaction networks!

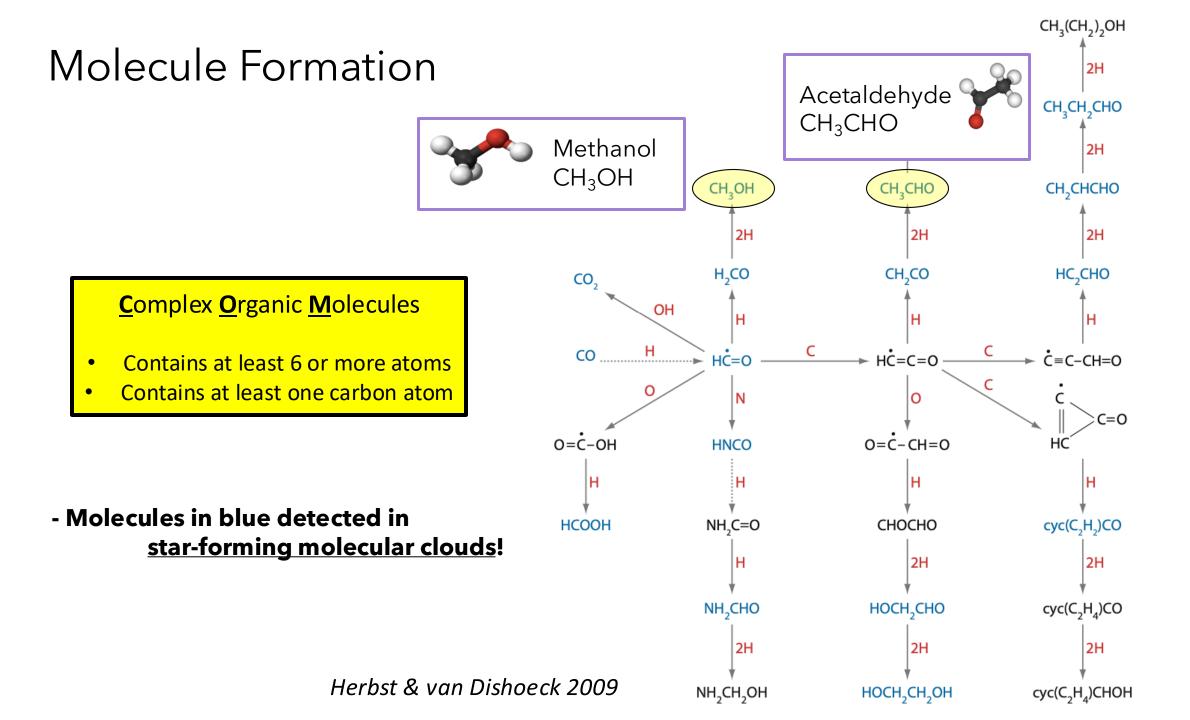
- Organic chemistry on interstellar grains resulting from cold H addition reactions to CO

- Broken arrows indicate reactions with activation energy barriers

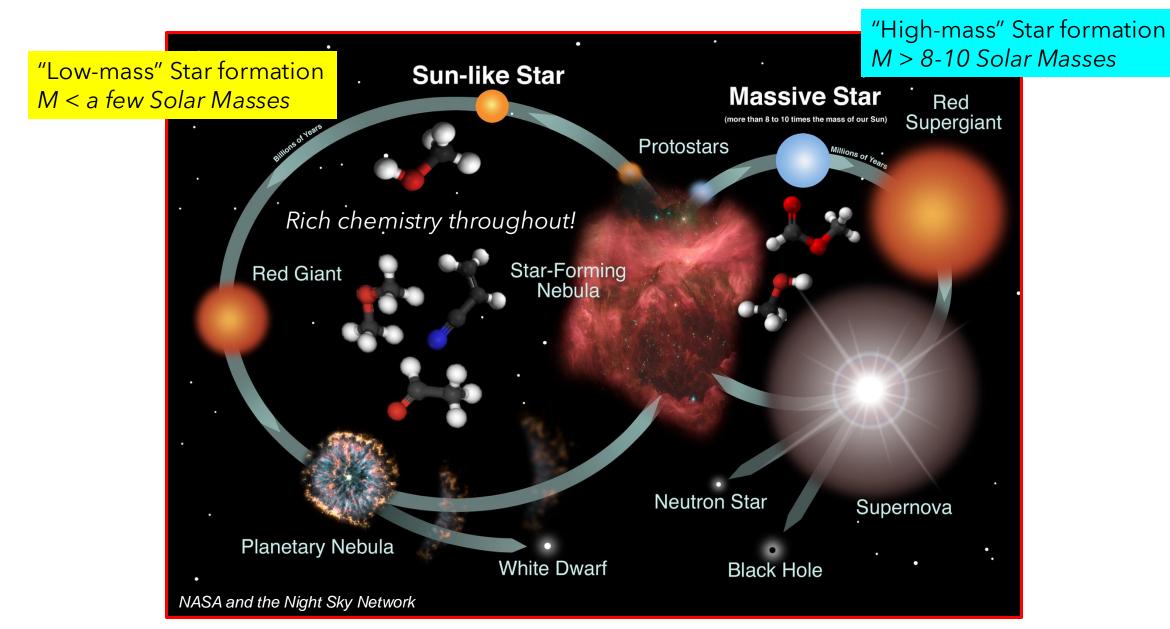
- Where 2H is shown, a barrier penetration reaction followed by exothermic addition

- Molecules in blue detected in star-forming molecular clouds!

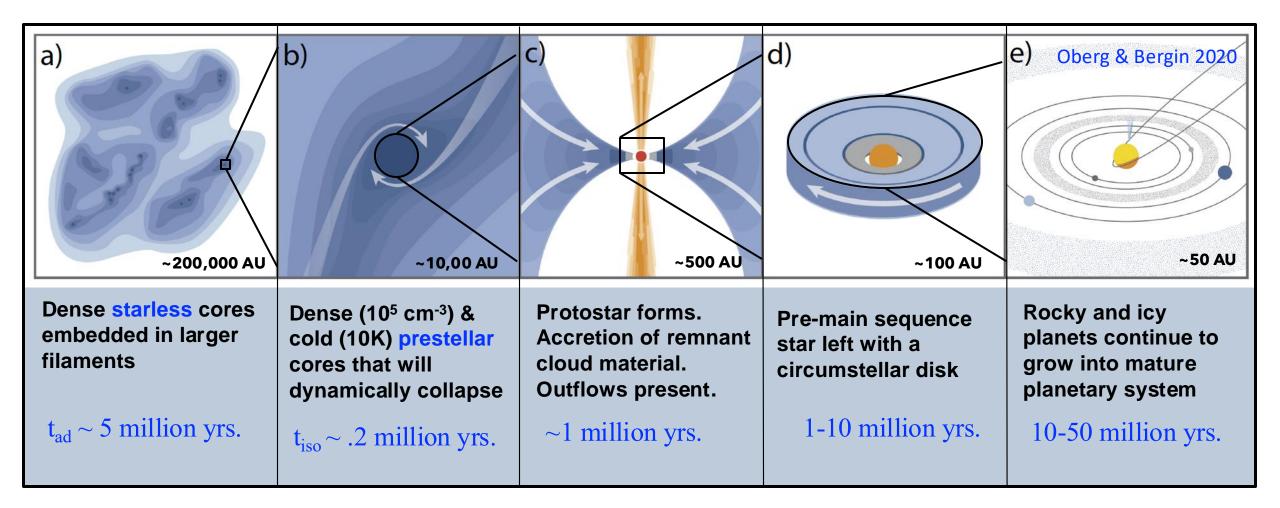




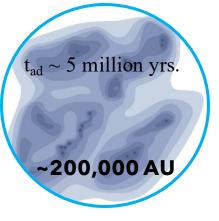
Cool clouds of gas: A birthplace for stars and molecules!



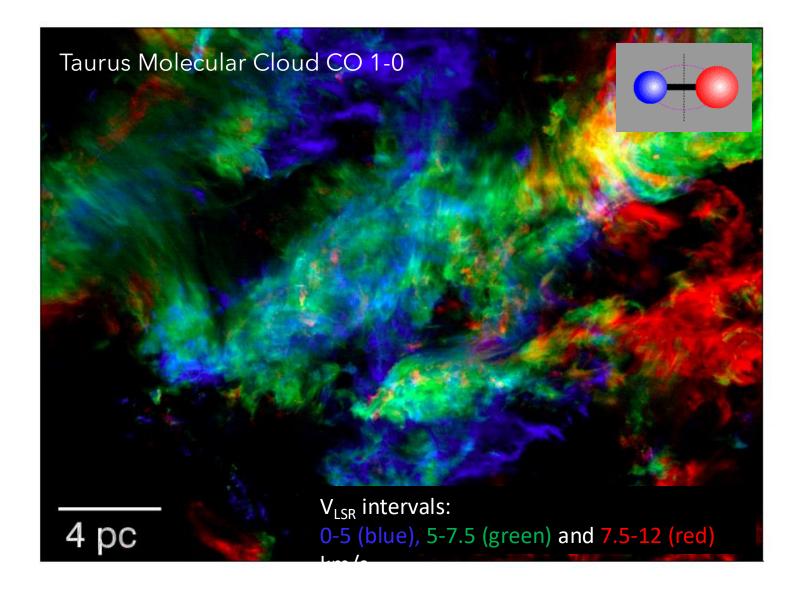
Astrochemistry in Low-mass ($M \leq a$ few M_{\odot}) Star Formation



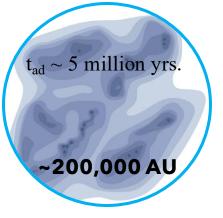
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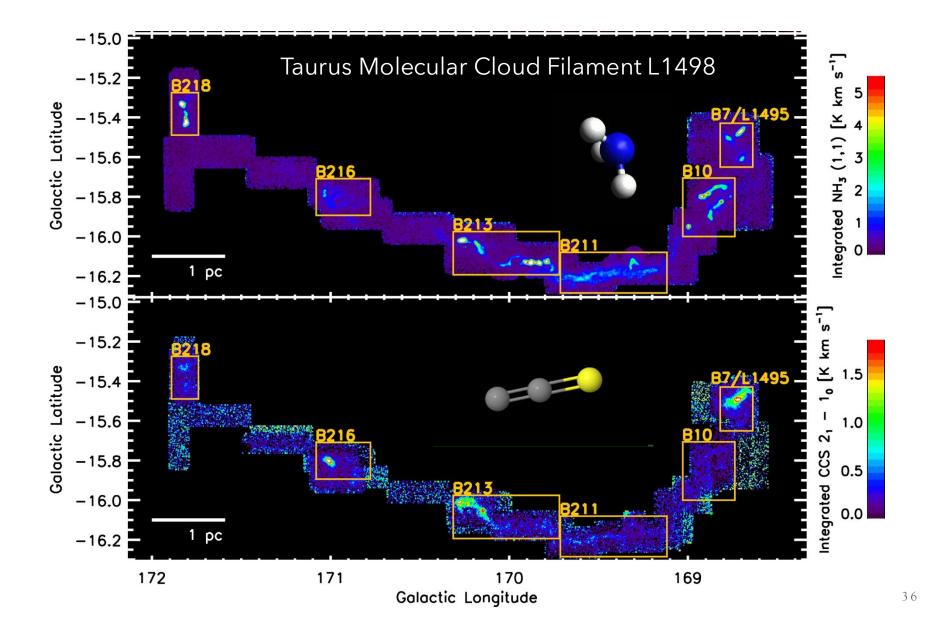
<u>Molecular</u> clouds are comprised of molecular gas (mostly H₂ and CO) and dust which form filamentary structures

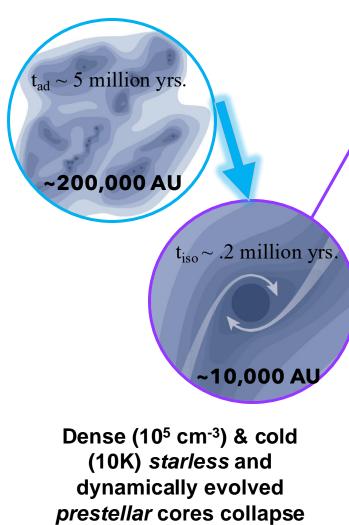


Astrochemistry in Low-mass ($M \leq a$ few M_{\odot}) Star Formation

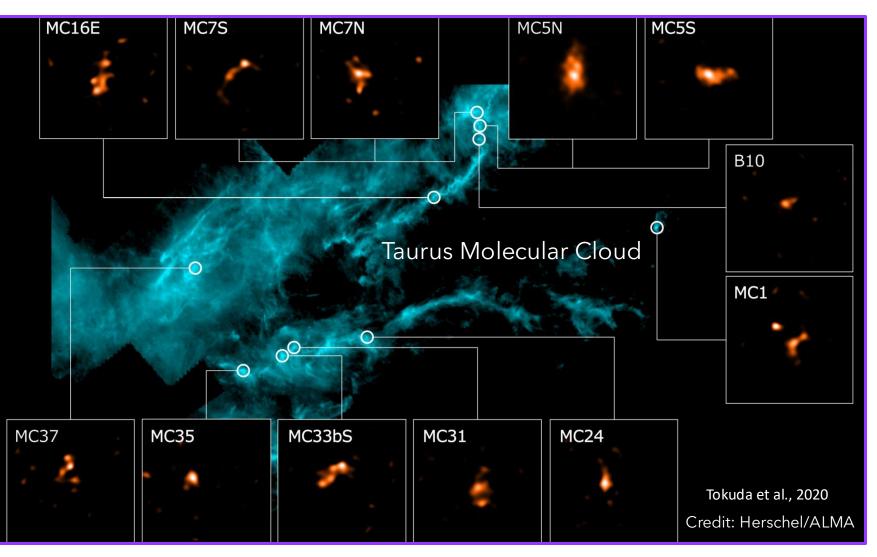


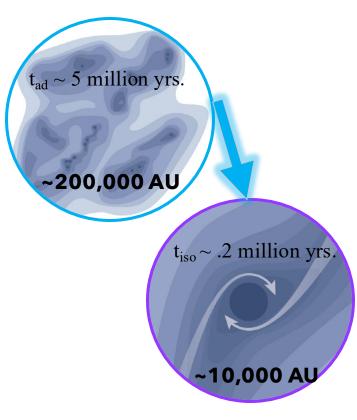
The filamentary structures are also traced by more 'exotic' molecular species, such as NH₃ and CCS





due to gravity and external cloud pressure





Dense (10⁵ cm⁻³) & cold (10K) *starless* and dynamically evolved *prestellar* cores collapse due to gravity and external cloud pressure

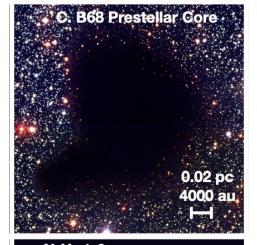
• DARK CLOUDS / Cold Cores

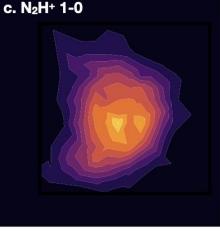
- indicated by absence of visible light
- Molecular lines characterized by **narrow, "sharp"**

line profiles

- Very **COLD**: T ~ 10 20 K
- **Dense**: $n \sim 10^3 10^5 \text{ cm}^{-3}$
- Typical masses: 1 M_{\odot} $10^3 \, M_{\odot}$
- Hydrogen in form of $\textbf{H}_{\textbf{2}}$
- Traced by dust extinction, far-IR dust emission, radio lines of molecules
- Most compact form known as "Bok Globules" \rightarrow
- Certain dark clouds known to be CARBON-RICH
- (C >O): Taurus
 - in general ISM, O/C ~ 1.5
- Quiescent: no violent outflows or energetic

motions





Oberg & Bergin 2020

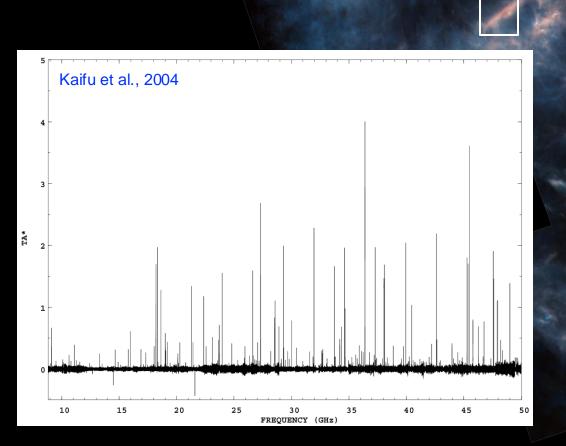
Credit: L. Ziurys

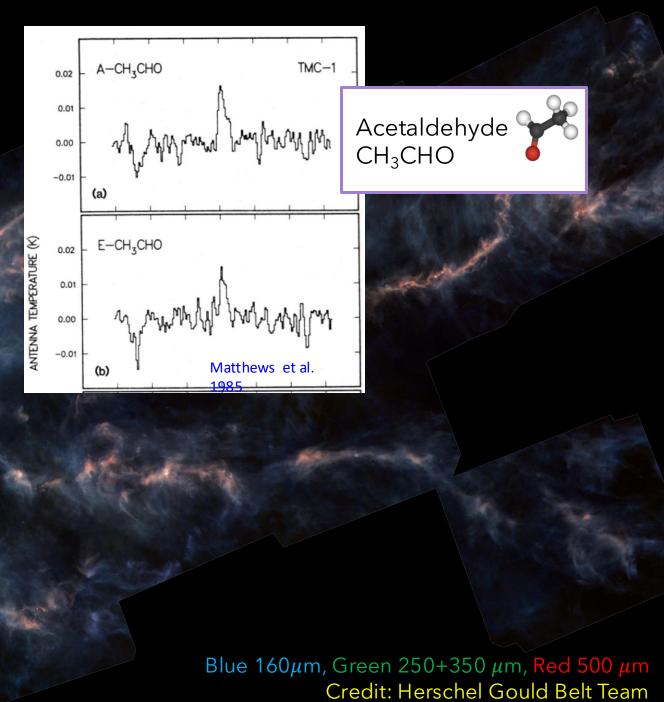
'Taurus Molecular Cloud 1' or TMC-1 is one of the most famous sites of complex chemistry – it is a cold (10 K) cloud with many COMs observed toward it from early observations (Matthews et al., 1985; Kaifu et al., 2004)

TMC-1

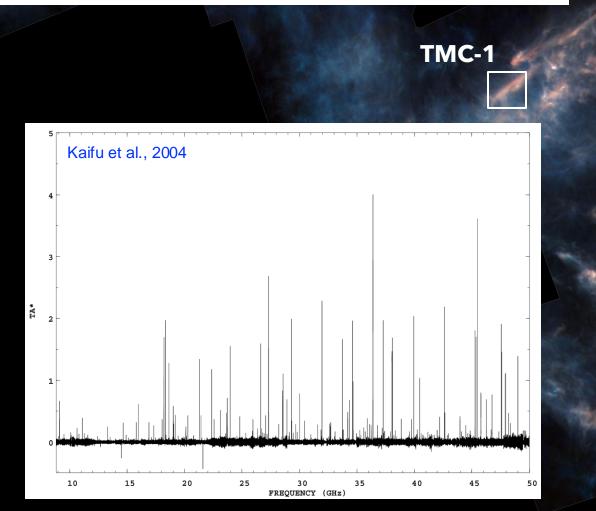
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TMC-1





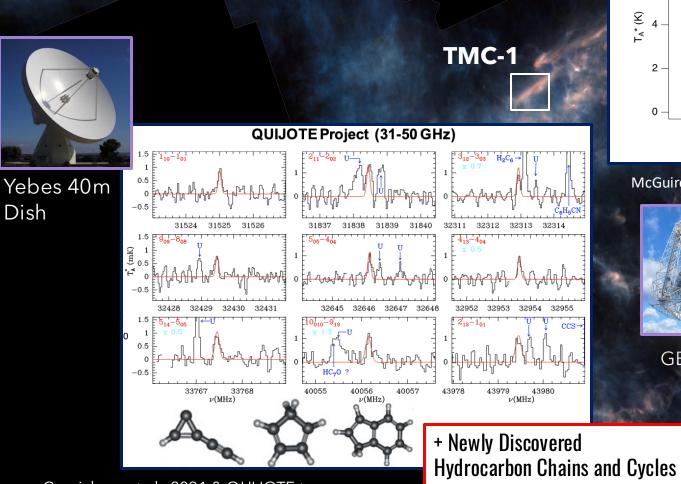
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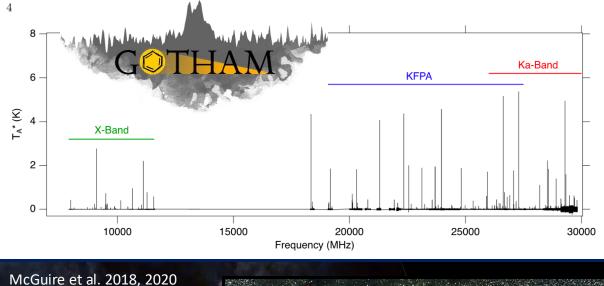
of molecule discoveries per source

Source	#	Source	#
Sgr B2	69	L1527	2
TMC-1	57	L1544	2
$\operatorname{IRC}+10216$	55	NGC 2024	2
LOS Cloud	42	NGC 7023	2
Orion	24	NGC 7027	2
L483	9	TC 1	2
W51	8	W49	2
VY Ca Maj	6	CRL 2688	1
B1-b	4	Crab Nebula	1
DR 21	4	DR 21(OH)	1
IRAS 16293	4	Galactic Center	1
NGC 6334	4	IC 443G	1
Sgr A	4	K3-50	1
CRL 618	3	L134	1
G+0.693-0.027	3	L183	1
NGC 2264	3	Lupus-1A	1
W3(OH)	3	M17SW	1
rho Oph A	3	NGC 7538	1
Horsehead PDR	2	Orion Bar	1
			McGuire 202

Sensitive, unbiased line surveys are ongoing and continually finding new molecules in TMC-1!



Cernicharo et al., 2021 & QUIJOTE team

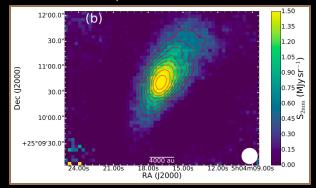


GBT 100m Dish



Beyond TMC-1, **L1544 is** a well-studied, very evolved core with a central density > 10⁷ cm⁻³ with evidence for active collapse (Bizzocchi et al. 2014, Spezzano et al. 2017, Caselli et al. 2019)

TMC-1

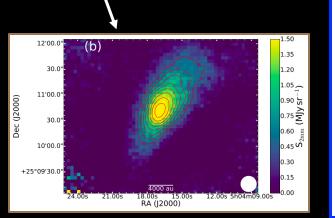


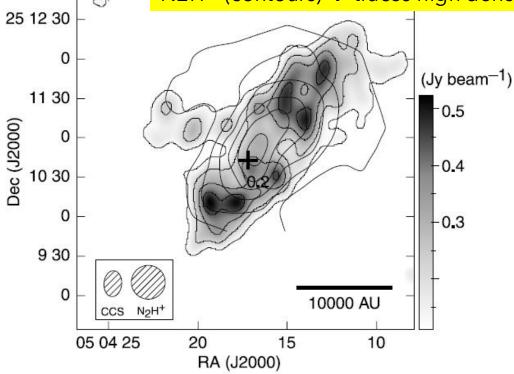
Chacón-Tanarro et al. 2019

L1544

Beyond TMC-1, **L1544** is a well-studied, very evolved core with a central density $> 10^7$ cm⁻³ with evidence for active collapse (Bizzocchi et al. 2014, Spezzano et al. 2017, Caselli et al. 2019)

CCS (greyscale) → freeze out towards denser and colder center N2H+ (contours) → traces high densities in and around core







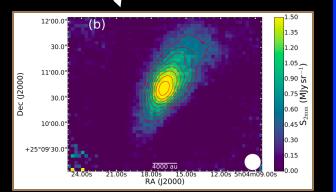
Blue 160 μ m, Green 250+350 μ m, Red 500 μ m Credit: Herschel Gould Belt Team

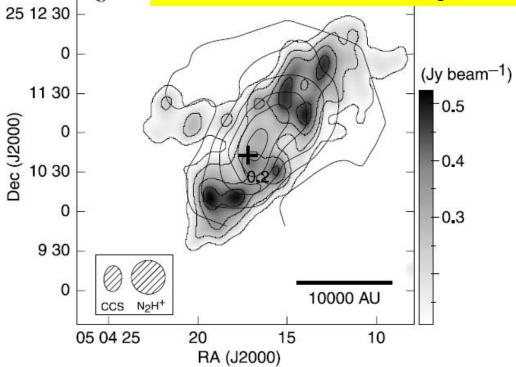
Chacón-Tanarro et al. 2019

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CCS (greyscale) → freeze out towards denser and colder center N2H+ (contours) → traces high densities in and around core





*Molecules are powerful probes of the physical conditions!

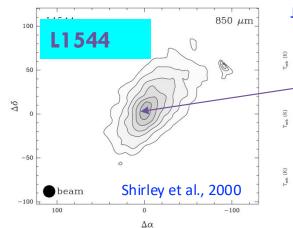
Blue 160 μ m, Green 250+350 μ m, Red 500 μ m Credit: Herschel Gould Belt Team

Chacón-Tanarro et al. 2019

L1544

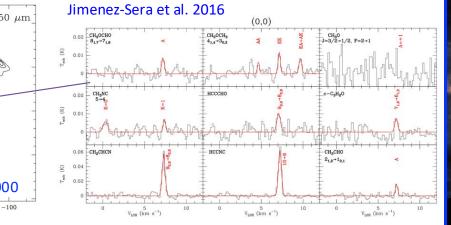
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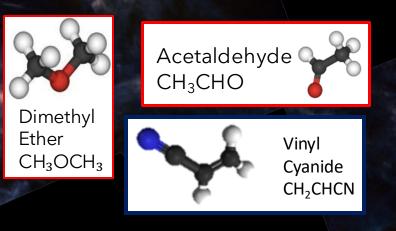
One of the first sites of COMs detections in isolated prestellar core!



L1544

100

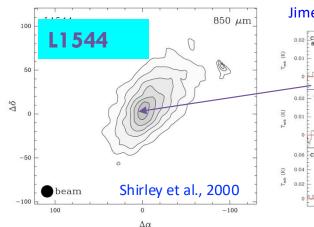


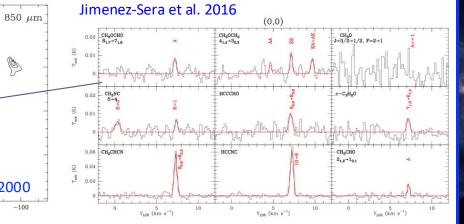


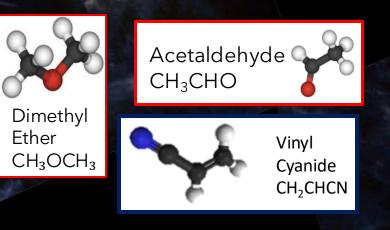
Beyond TMC-1, **L1544 is** a well-studied, very evolved core with a central density > 10⁷ cm⁻³ with evidence for active collapse (Bizzocchi et al. 2014, Spezzano et al. 2017, Caselli et al. 2019)

Are complex organic molecules (COMs) common at the earliest stages of lowmass star formation, i.e., in more 'typical' starless and prestellar cores?

One of the first sites of COMs detections in **isolated prestellar core**!

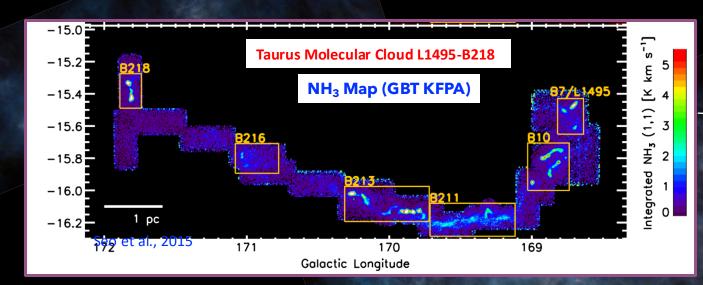






Blue 160 μ m, Green 250+350 μ m, Red 500 μ m Credit: Herschel Gould Belt Team

L1544



First night of PhD observing in 2017



In my PhD research, I studied 'typical' starless and prestellar cores in the Taurus Molecular Cloud!

12m Radio Telescope, Kitt Peak, AZ

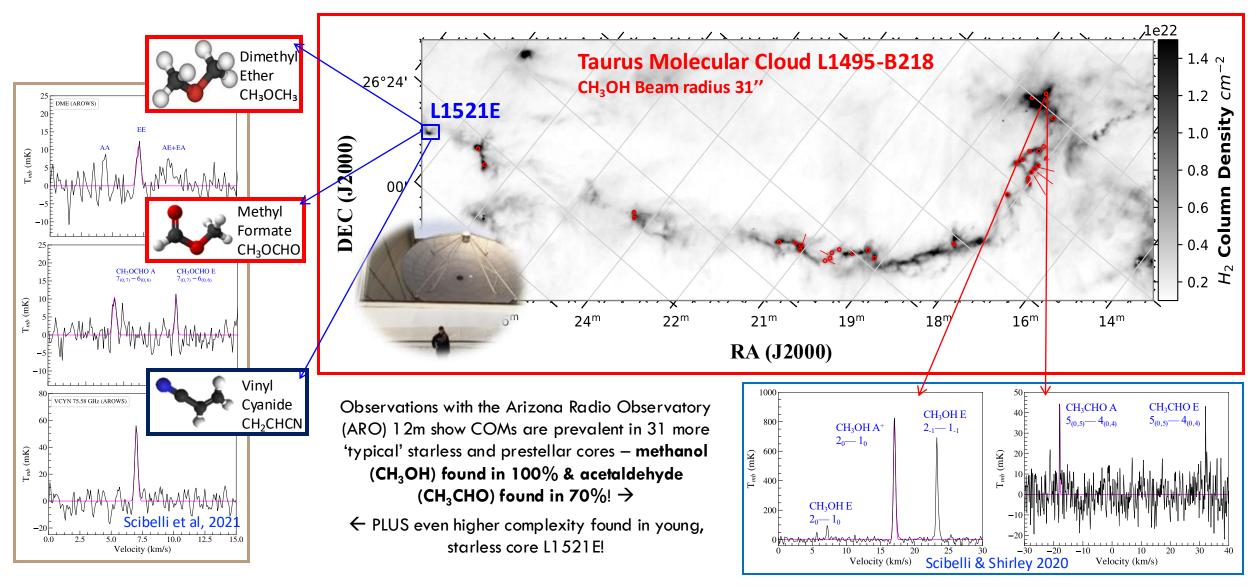
Blue 160 μ m, Green 250+350 μ m, Red 500 μ m Credit: Herschel Gould Belt Team

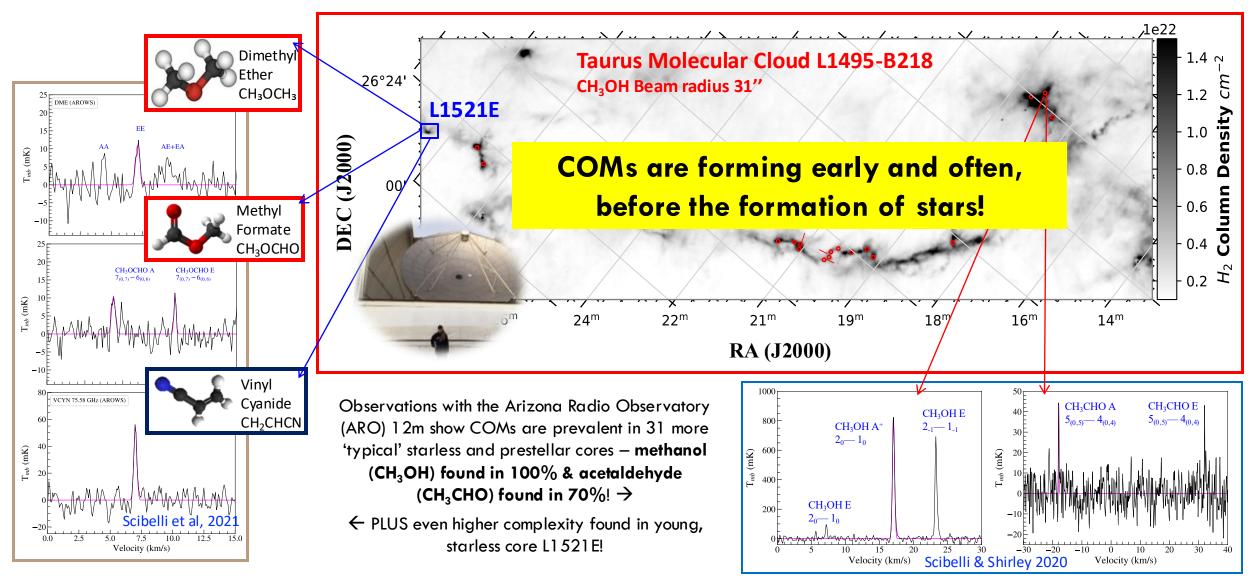
L1495/B18

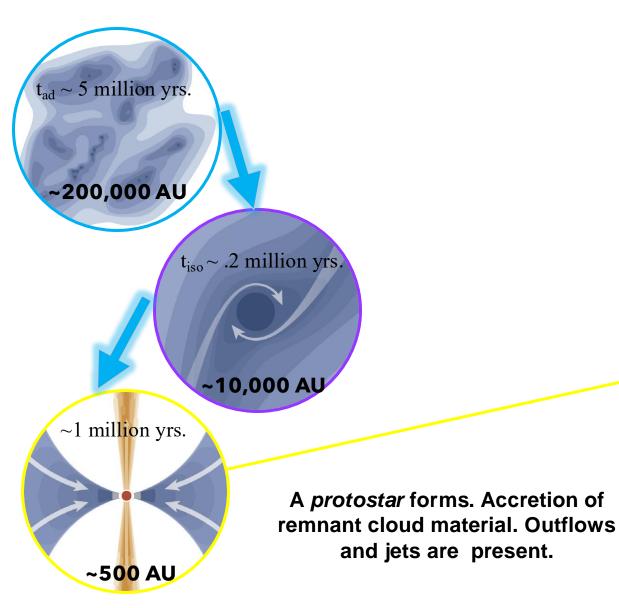
31 total cores

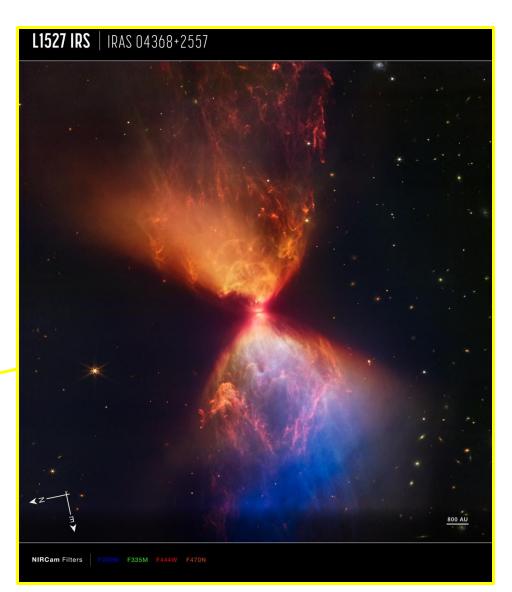
L1521E

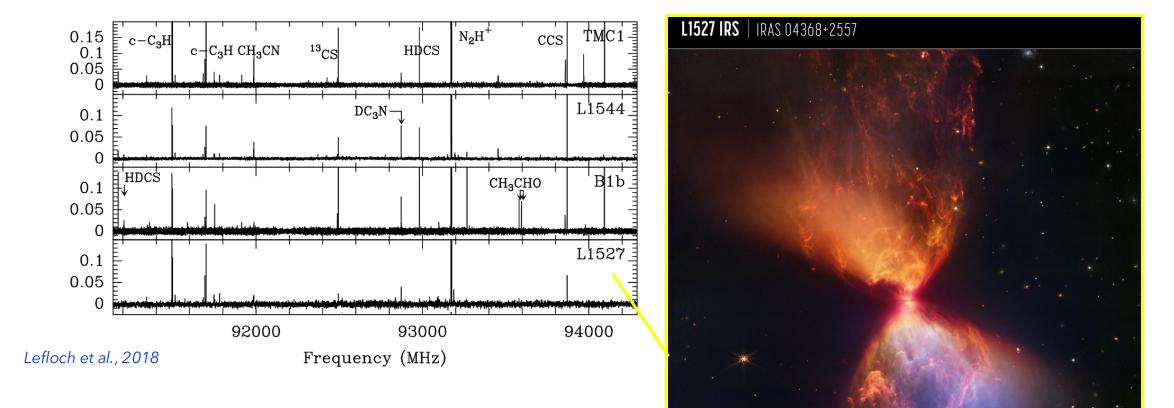
100







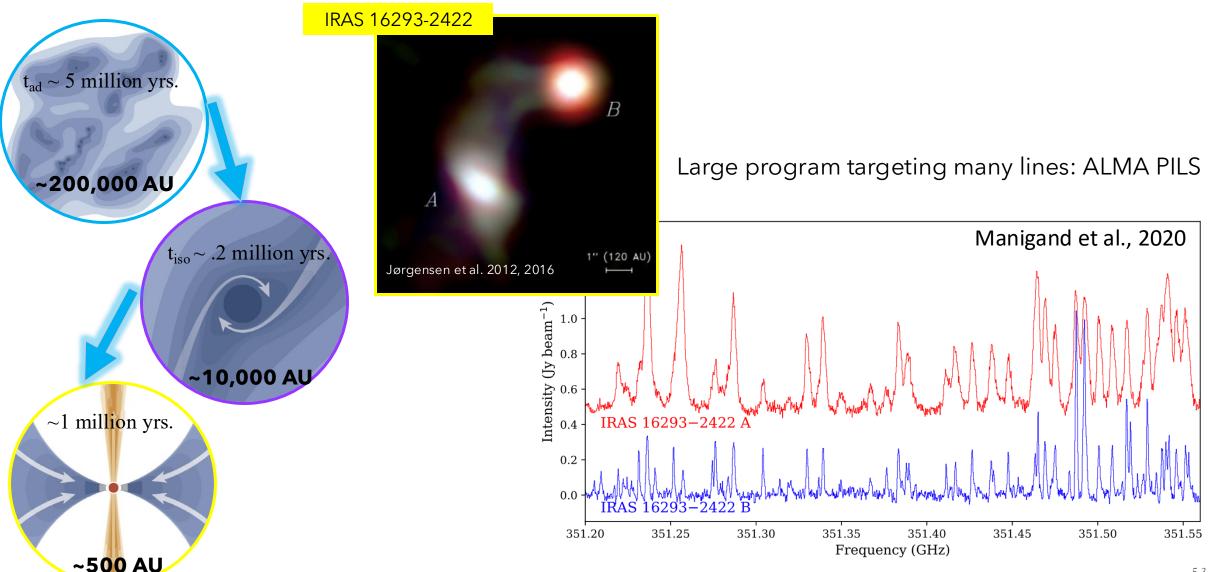


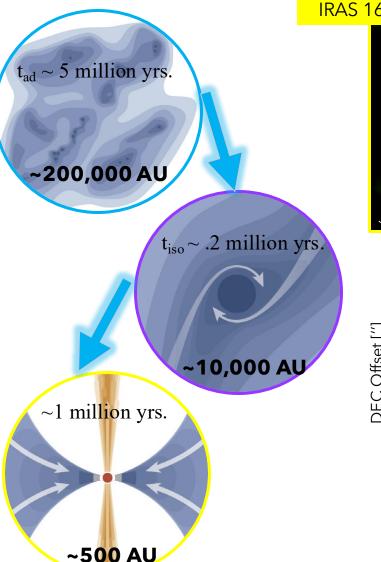


12

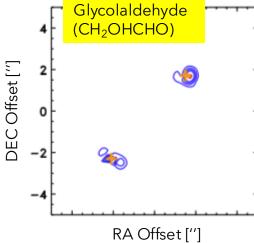
NIRCam Filters

800 AU





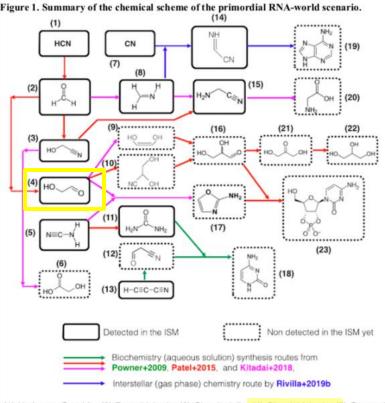






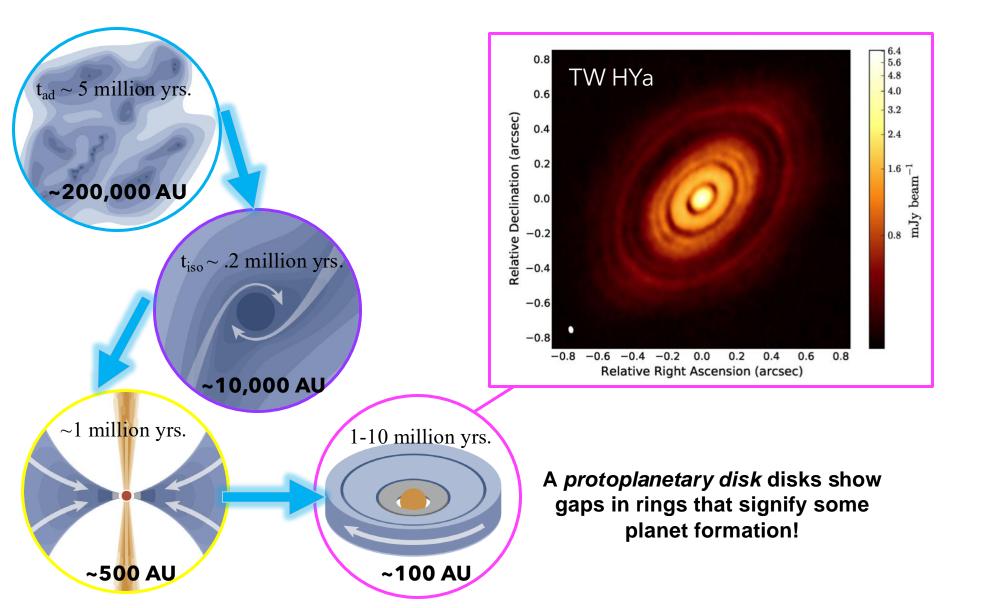
Life appeared on Earth about 4 billion years ago, but we do not know the processes that made it possible.

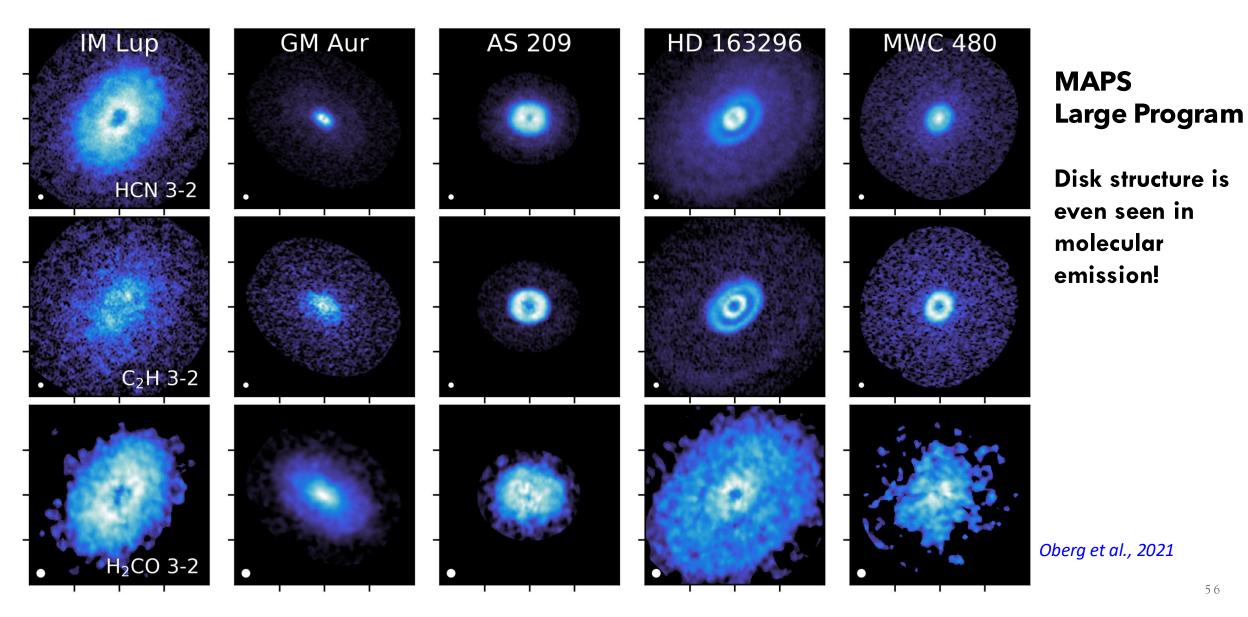
One of the proposed scenarios is the socalled ribonucleic acid RNA-world, which suggests that early forms of life relied solely on (RNA) to store genetic information and to catalyze chemical reactions.



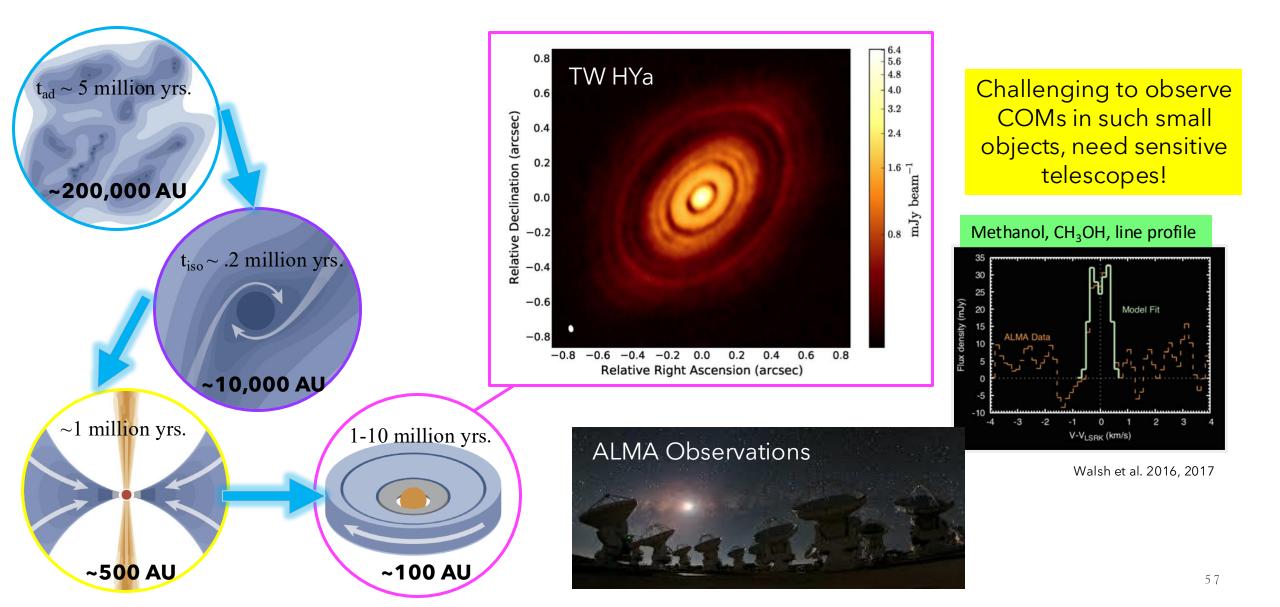
Hydrogen Cyanide; (2) Formaldehyde; (3) Glycolonitrile; (4) Glycolaldehyde; (5) Cyanamide;
 (6) Glycolic acid; (7) Cyanide; (8) Methanimine; (9) Enol form of glycolaldehyde; (10) Cyanohydrin;
 (11) Urea; (12) 3-Oxopropanenitrile; (13) Cyanoacetylene; (14) Cyanomethanimine; (15) Aminoacetonitrile; (16) Glyceraldehyde; (17) 2- amino-oxazole; (18) Cytosine; (19) Adenine; (20) Glycero; (21) Dihydroxyacetone (DHA); (22) Glycerol; (23) Beta-ribocytidine-2',3'-cyclic phosphate (pyrimidine ribonucleotide)

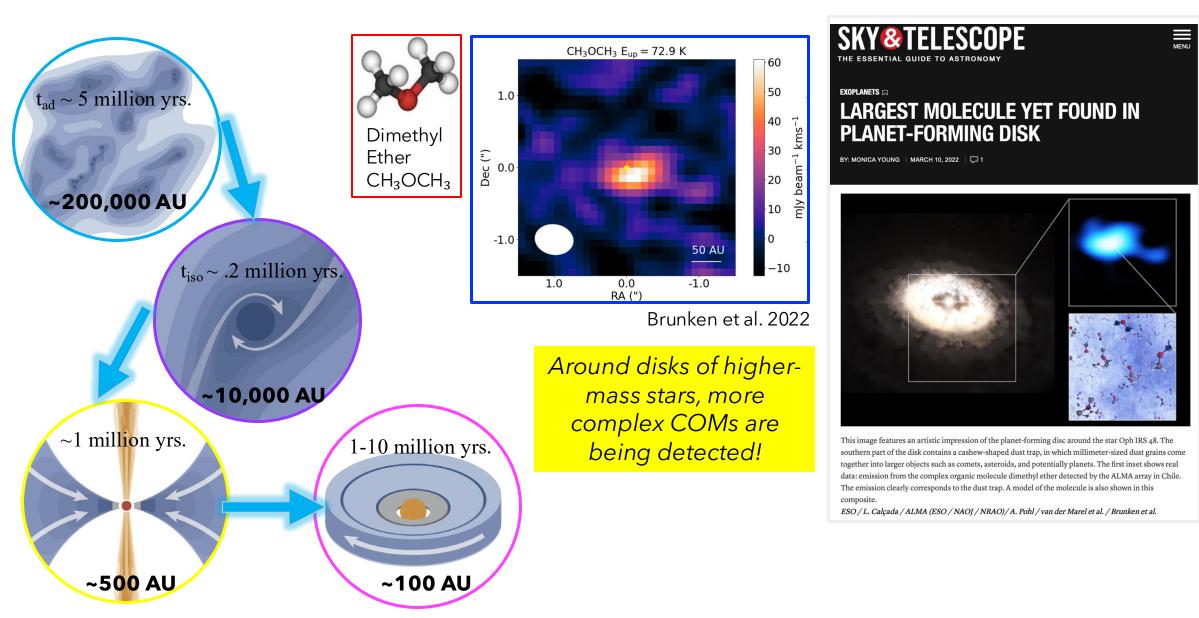
Jimenez-Serra et al. 2020

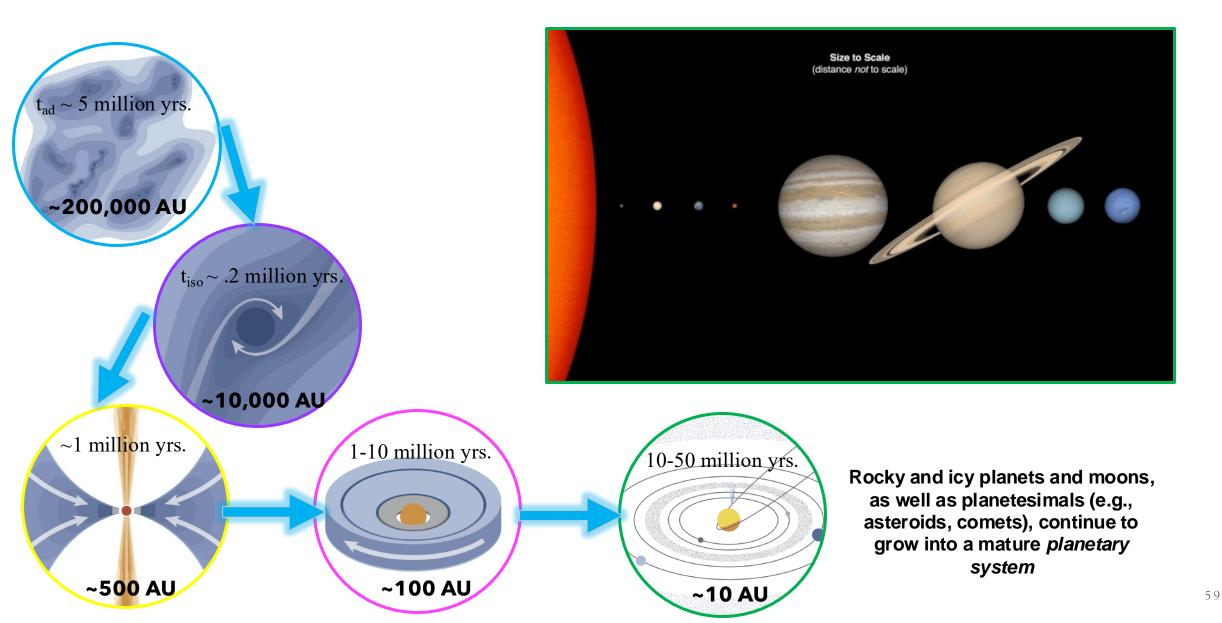


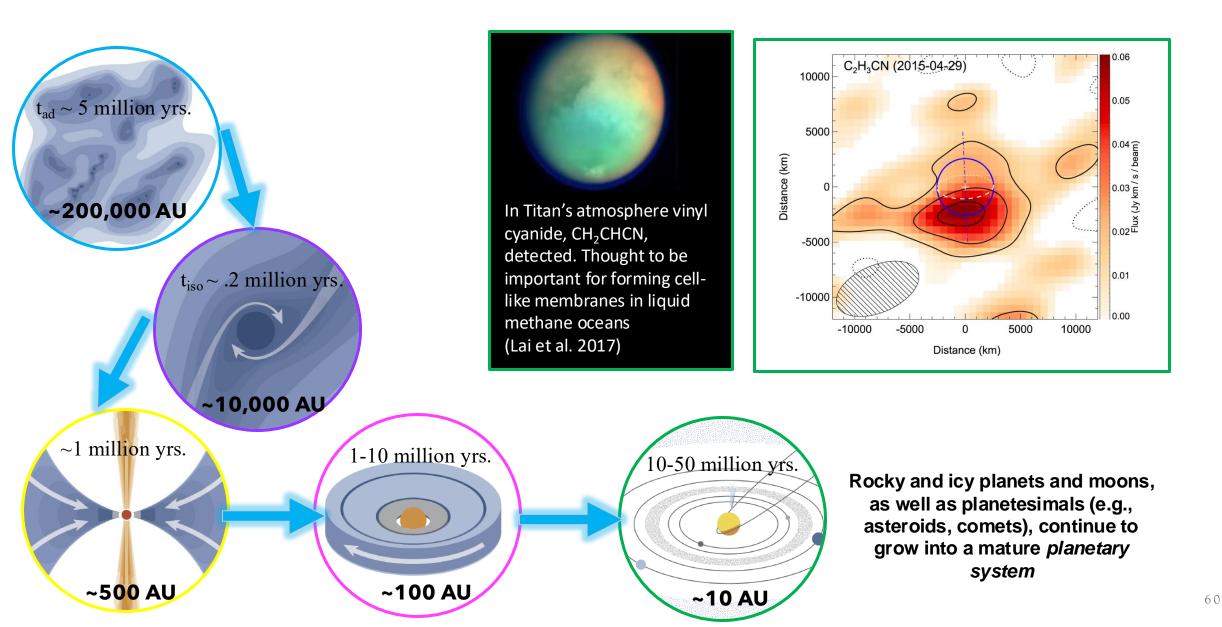


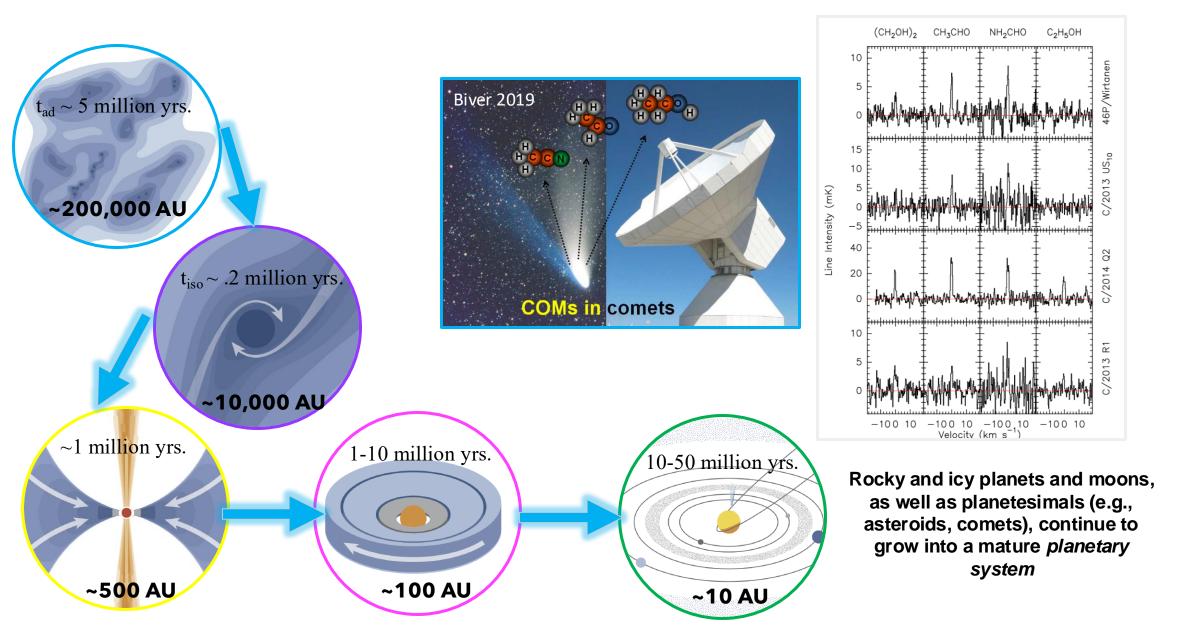
56

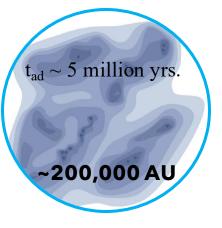




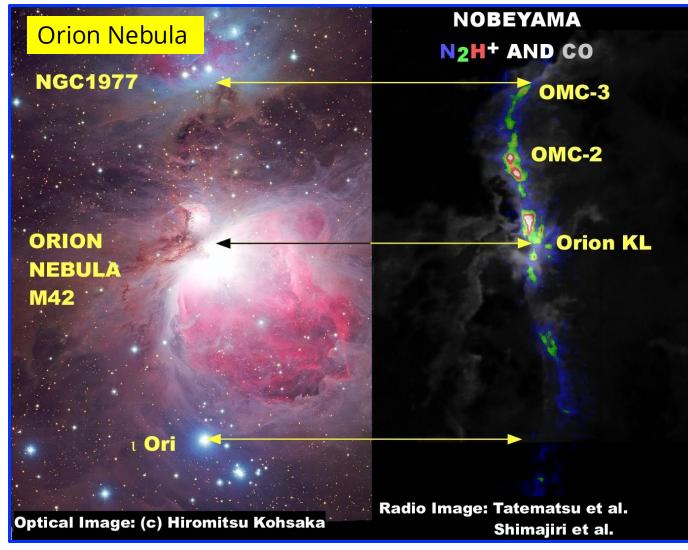








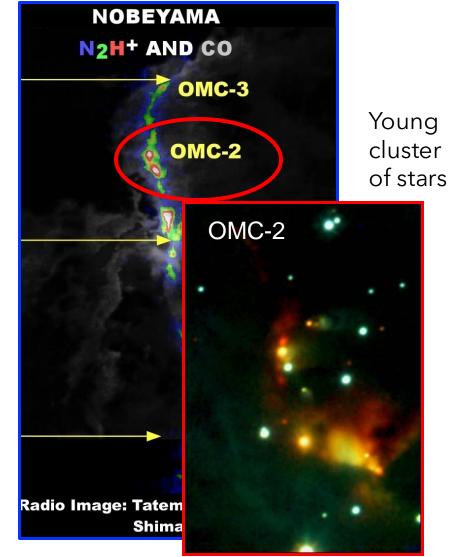
Molecular clouds (CO) and filaments (N₂H+) also present in high-mass regions



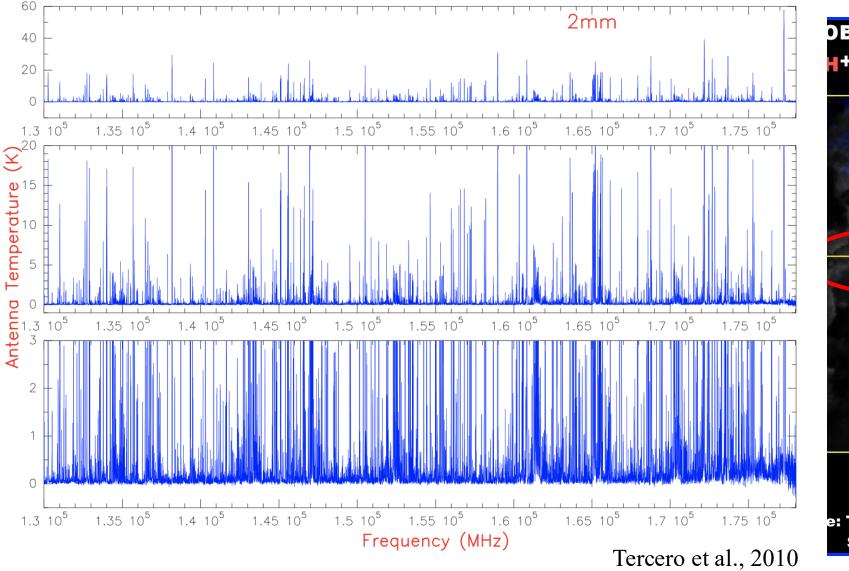
https://www.nro.nao.ac.jp/~kt/html/kt-e.html

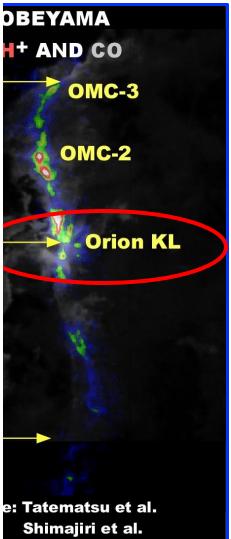
GIANT MOLECULAR CLOUDS

- Denser and warmer than low-mass dark clouds
- T ~ 50 100 K
- n ~ $10^4 10^6$ cm⁻³
- Masses of 10^4 $10^6~M_{\odot}$
- Not gravitationally stable
 - \Rightarrow Collapse to form stars and solar systems
 - \Rightarrow Lifetimes of ~ 10⁶-10⁷ years
- Often contain protostellar cores
 - T ~ 100 200 K
 - n ~ 10⁷ 10⁸ cm⁻³
 - emit intensely in infrared and heat up surrounding gas
- Can be traced in IR, radio and infrared lines of molecules
 - both rotational and ro-vibrational transitions
- Sites of most massive star formation (Hot OB stars)

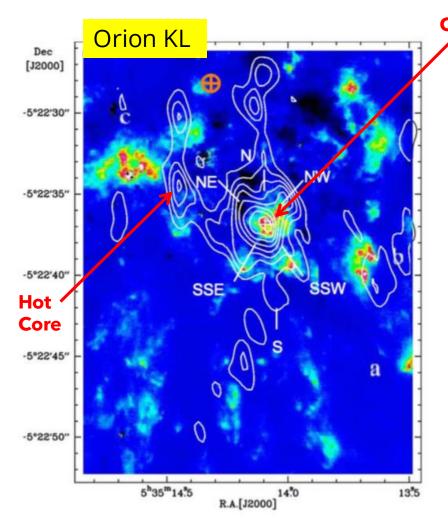


Credit: L. Ziurys



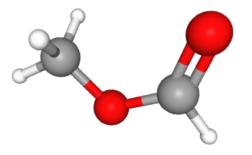


A 'hotspot' for complex chemistry!

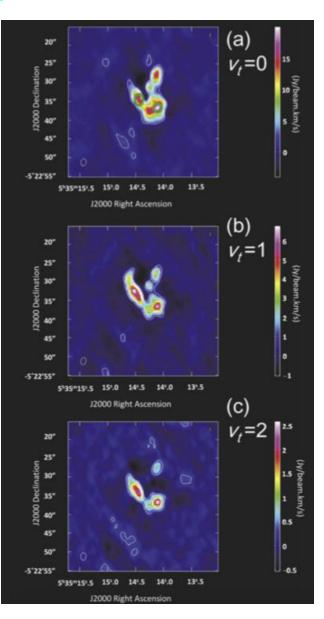


Compact Ridge

8-atom molecule, Methyl Formate, HCOOCH₃, tracing the star-forming 'hot core'

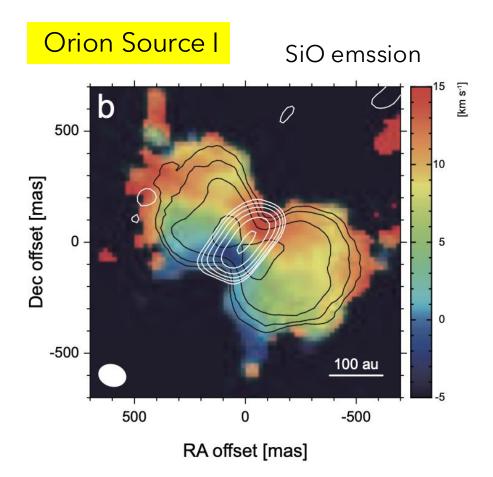


First identification of rotational transitions in the second vibrationally excited state!

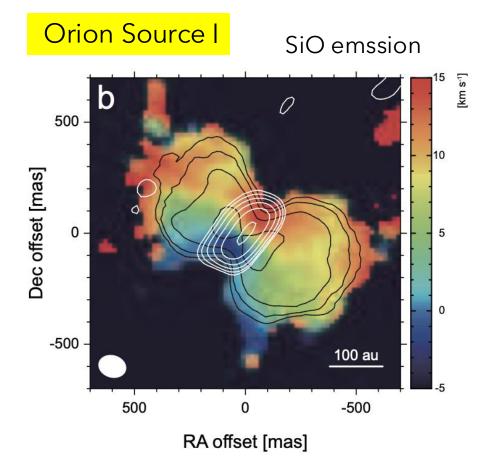


Contours: Methyl Formate 8.6 km/s channel map (Favre et al. 2011) Emission: 2.12 micron excited H_2 emission (Lacombe et al. 2004)

Sakai et al. 2015



The presence of a **disk-outflow** system (Hirota et al. 2017) indicates that "Orion source I" is accreting, confirming its nature as a young, forming star.

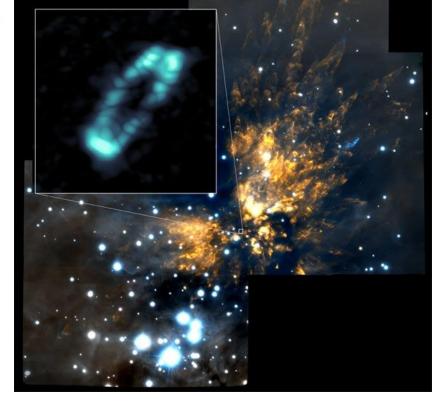


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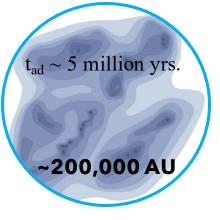
First detection of salts in star forming core!

Sodium chloride (NaCl), potassium chloride (KCl), and their ³⁷Cl and ⁴¹K isotopologues,

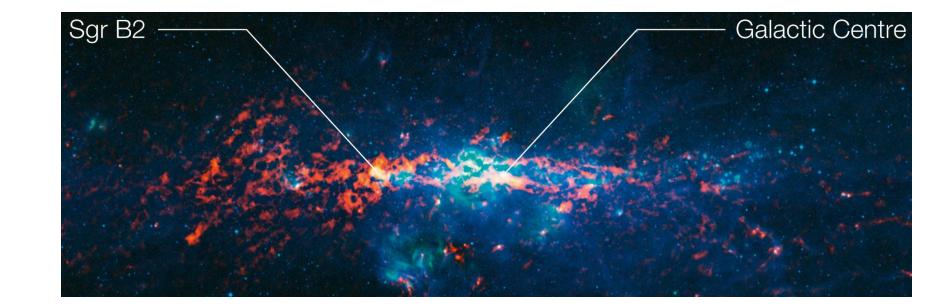


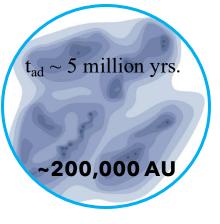


Adam Ginsburg et al. 2019.

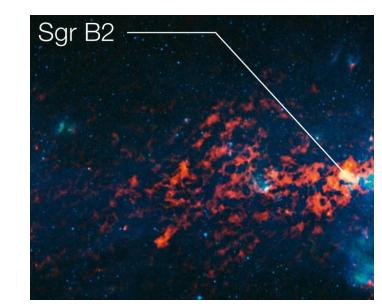


At the center of our galaxy, high mass clouds are chemically rich!





At the center of our galaxy, high mass clouds are chemically rich!

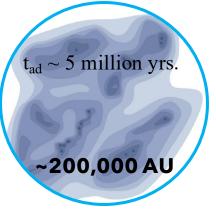


"Famous" cloud Sgr B2 is the #1 source of new molecule detections! Lots of complex chemistry!

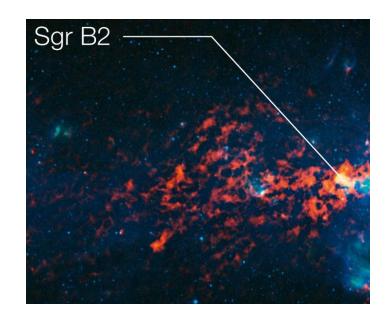
of molecule discoveries per source

Source	#	Source	#
Sgr B2	69	L1527	2
TMC-1	57	L1544	2
IRC+10216	55	NGC 2024	2
LOS Cloud	42	NGC 7023	2
Orion	$\overline{24}$	NGC 7027	2
L483	9	TC 1	2
W51	8	W49	2
VY Ca Maj	6	CRL 2688	1
в1-b	4	Crab Nebula	1
DR 21	4	DR 21(OH)	1
IRAS 16293	4	Galactic Center	1
NGC 6334	4	IC 443G	1
Sgr A	4	K3-50	1
CRL 618	3	L134	1
G+0.693-0.027	3	L183	1
NGC 2264	3	Lupus-1A	1
W3(OH)	3	M17SW	1
rho Oph A	3	NGC 7538	1
Horsehead PDR	2	Orion Bar	1

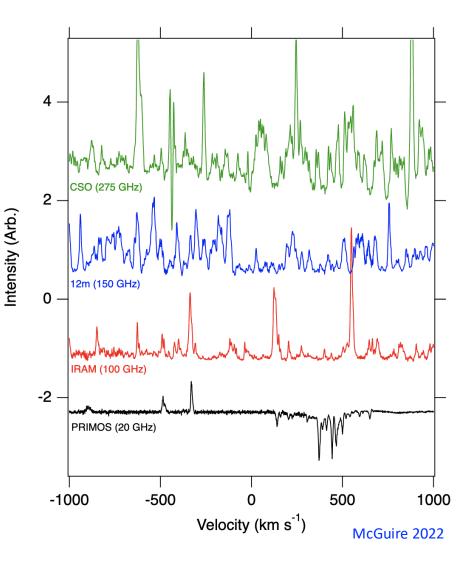
McGuire 2022

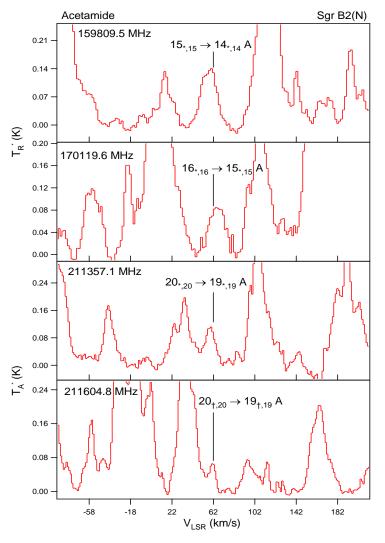


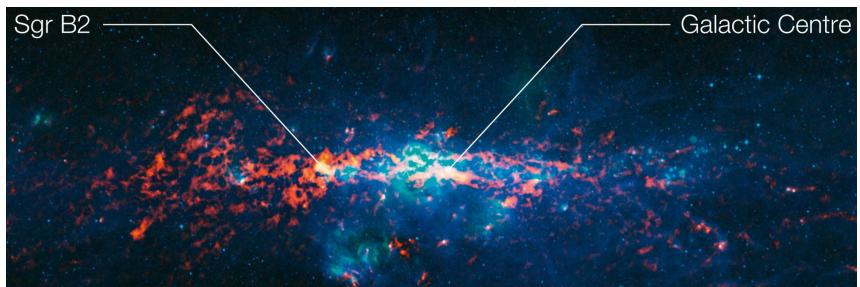
At the center of our galaxy, high mass clouds are chemically rich!



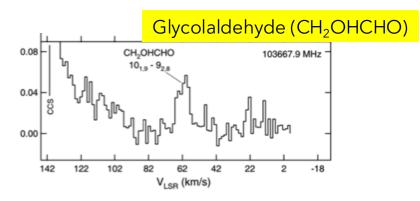
Many line surveys done at different frequencies, across the millimeter and submillimeter spectrum ->







- Much broader lines
- Asymmetric line profiles
- Multiple velocity components
- Line confusion

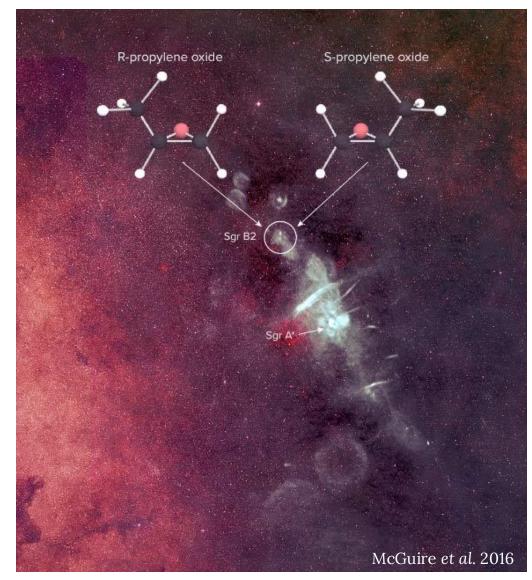


(Hollis et al. 2000, Halfen et al. 2006)

(Halfen et al. 2011; 2013)

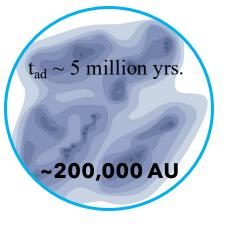
~200,000 AU At the center of our galaxy, high mass clouds are chemically rich!

 $t_{ad} \sim 5$ million yrs.

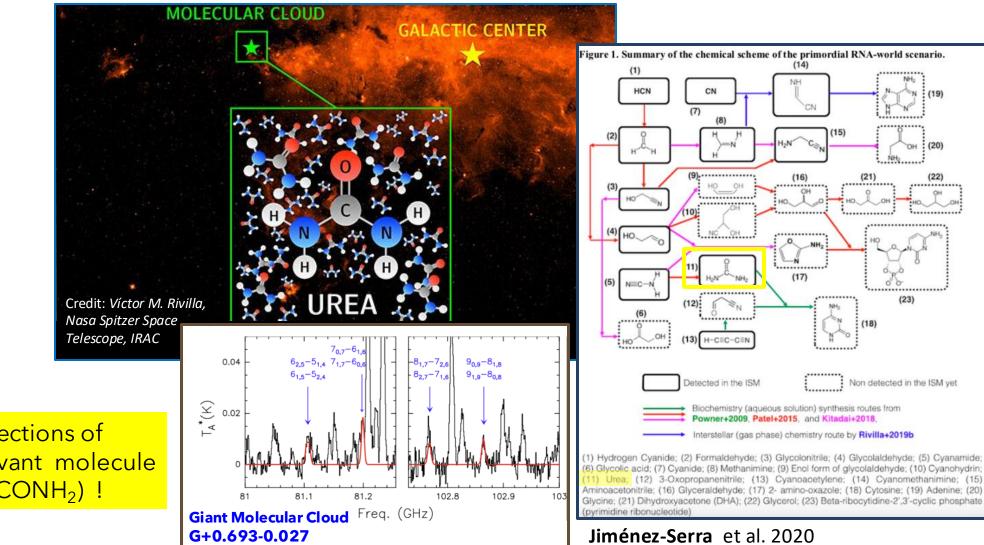


First chiral molecule detected in interstellar space toward the Sgr B2 star forming cloud!

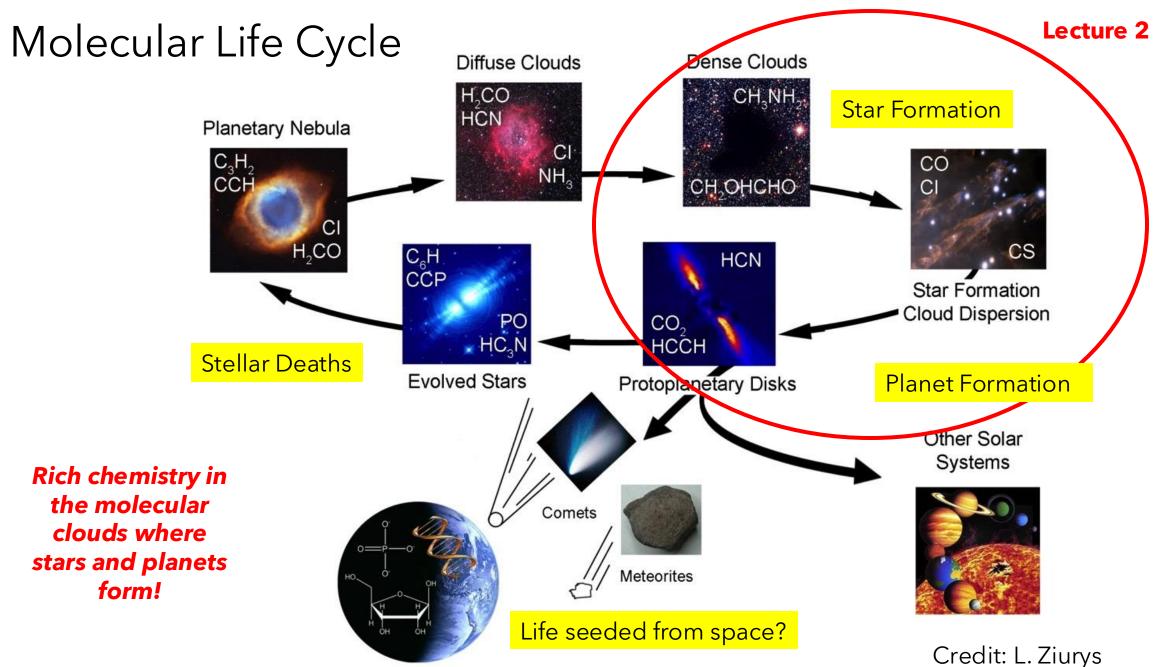
Propylene oxide, CH₃CHCH₂O

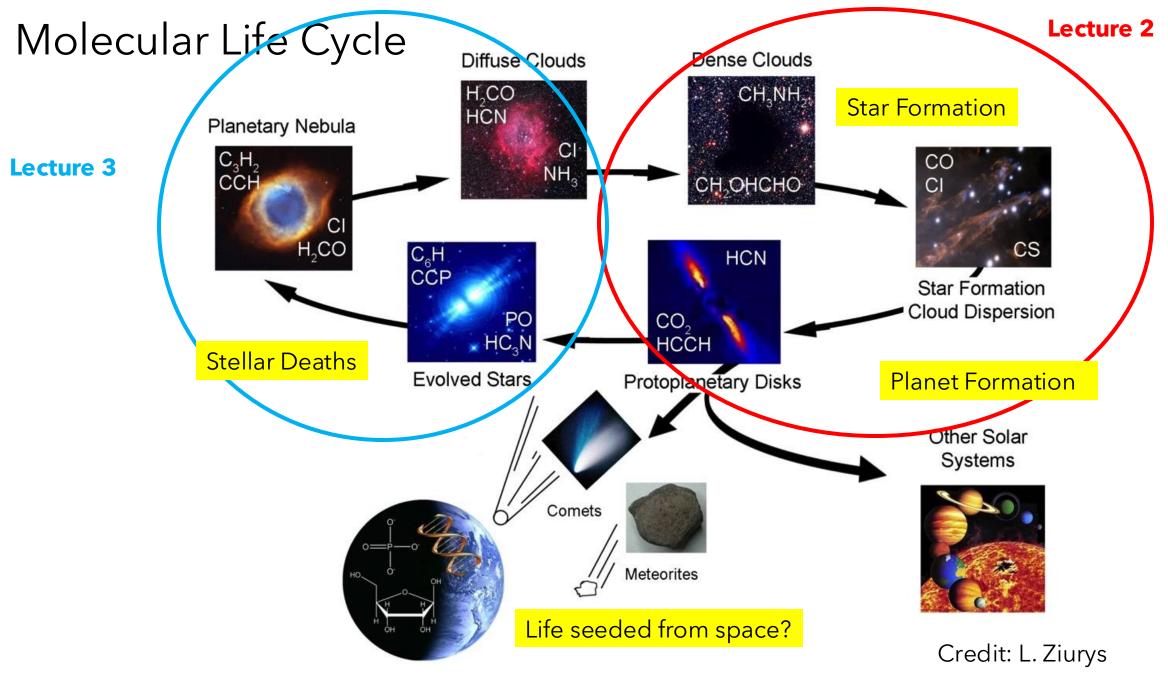


At the center of our galaxy, high mass clouds are chemically rich!



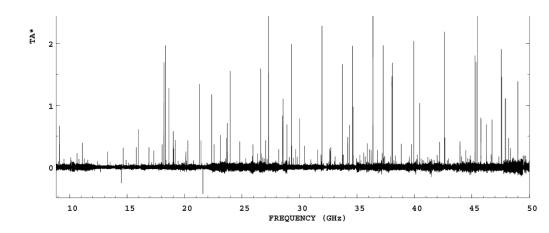
Recent Detections of biologically relevant molecule UREA (NH₂CONH₂) !





SUMMARY:

• Reminder! Submillimeter and millimeter radio telescopes are powerful instruments that let observational astrochemists (like myself) study the rotational spectra of interstellar molecules in high detail!



- Cold molecular clouds are the birthplaces of stars and planets. Within molecular clouds, the rotational
 spectra of molecules can be used to trace the motions of the gas, as well as the densities and
 temperatures.
- Within molecular clouds H₂ forms on the surfaces of interstellar dust grains and is released into the gas this is the start of chemistry in the interstellar medium!
- Molecule formation proceeds via **exothermic reactions** (where the products are at lower energy than the reactants) and is usually done via ion-molecule reactions initiated by cosmic rays (high energy photons).
- A rich inventory of **complex organic molecules (COMs**) have been detected in virtually **all stages of lowmass and high-mass star formation**!



Questions?

