

The ASAI View on the Evolution of Molecular Complexity along the Formation of Sun-Like stars

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ISWA - Campinas - July 2016







Outline

Introduction

Molecular complexity in the Prestellar phase

Feedback processes

Prebiotic chemistry

Protostars: from ASAI to SOLIS

Conclusions

Molecular Complexity in the Universe

2	3	4	5	6	7	8	9	10	11	12	13 atoms	
H_2	C ₃	c-C ₃ H	C ₅	C ₅ H	C ₆ H	CH ₃ C ₃ N	CH ₃ C ₄ H	CH ₃ C ₅ N	HC ₉ N	C ₆ H ₆	HC ₁₁ N	
AĪF	C_2H	1-C ₃ H	C_4H	$1-H_2C_4$	CH ₂ CHCN	HCOOCH ₃	CH ₃ CH ₂ CN	$(CH_3)_2CO$	CH ₃ C ₆ H	C ₂ H ₅ OCH ₃		
AlCl	$\overline{C_2O}$	C_3N	C ₄ Si	$C_2 H_4$	$CH_{3}C_{2}H$	CH ₃ COOH?	$(CH_3)_2O$	$(CH_2OH)_2$	C ₂ H ₅ OCHO	$C_{3}H_{7}CN$		
C2	$\tilde{C_2S}$	$C_{3}O$	$1-C_3H_2$	CH ₃ CN	HC ₅ N	C ₇ H	CH ₃ CH ₂ OH	CH ₃ CH ₂ CHO	CH ₃ OCOCH ₃	5 1		
CH	$\tilde{CH_2}$	C ₃ S	$c-C_3H_2$	CH ₃ NC	CH ₃ CHO	C_6H_2	HC ₇ N	CH ₃ CHCH ₂ O	5 5		$+ C_{60}, C_{70}$	
CH^+	HCN	$\tilde{C_{2}H_{2}}$	CH ₂ CN	CH ₃ OH	CH ₃ NH ₂	CH ₂ OHCHO	C ₈ H	5 2				
CN	HCO	NH ₃	$\tilde{CH_4}$	CH ₃ SH	$c-C_2H_4O$	1-HC ₆ H	CH ₃ CONH ₂	S				ŀ
CO	HCO^+	HCCN	HC ₃ N	HC ₃ NH ⁺	CH ₂ CHOH	CH ₂ CHCHO	C ₈ H ⁻					Ē
CO^+	HCS^+	HCNH ⁺	HC ₂ NC	HC ₂ CHO	$C_6 \tilde{H}^-$	CH ₂ CCHCN	$C_{3}H_{6}$	ec				E
CP	HOC^+	HNCO	HCOOH	NH ₂ CHO	Ũ	NH ₂ CH ₂ CN	5 0					E
CSi	H_2O	HNCS	H ₂ CNH	$C_5 N$		CH ₃ CHNH		L L				E
HCl	H_2S	HOCO ⁺	H_2C_2O	l-HC₄H		5		o 20		-		F
KCl	HNC	H_2CO	H ₂ NCN	1-HC ₄ N				0eI				E
NH	HNO	H_2CN	HNC ₃	$c-H_2C_3O$				E 10				F
NO	MgCN	H_2CS	SiH4	H ₂ CCNH				Nu		_	<u> </u>	F
NS	MgNC	H_3O^+	H_2COH^+	$C_5 N^-$				0	+			+
NaCl	N_2H^+	c-SiC ₃	C_4H^-	HNCHCN	[2 5	10	13 >13	
OH	N ₂ O	CH ₃	HCOCN						Number	r of constitu	ient atoms	
PN	NaCN	C ₃ N ⁻	HNCNH	•	0 1	1 1.	1					
SO	OCS	PH_3	CH ₃ O	20	0 molec	ules disc	overed					
SO^+	SO_2	HCNO	NH_4^+									
SiN	c-SiC2	HOCN	H_2NCO^+									
SiO	CO_2	C_3H^+		Co	mnley	Organic	Molecul	$ \mathbf{es} \cdot > 6 _{\mathbf{a}}$	toms + C	atoms		
SiS	NH_2	HMgNO	2		Complex Organic Molecules . < 0 atoms + C atoms							
CS	H_3^+			(Her	(Herbst & van Dishoeck, 2009)							
HF	SiCN			300	30% of molecules are COMs including.							
HD	AINC			507	50% of molecules are convis, meruding .							
FeO?	SiNC				Aminoacetonitrile : NH_2CH_2CN (Belloche, 2008)							
O_2	CCP				Branched alkyl molecules i C H CN (p. 1. 1. 2014)							
CF^+	AlOH				DI	ancheu an	xyi molect	1051-0311	CIN (Belloche	e, 2014)		
SiH	H_2O^+				Pro	opylene oz	$xyde CH_2C$	$CHCH_2O($	McGuire 2	2016)?		
PO	H_2Cl^+											
AlO,	KCN											
OH⁺,	FeCN			W	hat aho	ut I ow_	Mass Sta	r Formi	ng Regio	ms?		
CN-	HO_2			• • 1			11022 210		ing Kugiu	• •		

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Molecular Complexity and Star Formation

An astrochemical view of solar-type star formation



Molecular Complexity and Star Formation

An astrochemical view of solar-type star formation



Composition of Hale-Bopp // L1157



X]/[CH30H] (ISM)

Bockelee-Morvan et al. (2000)

Open Issues

Are meteoritic and cometary amino-acids pristine interstellar molecules ? Are such molecules widespread in the Galaxy and in star-forming regions ? Which memory is kept by the small bodies of the Solar System ?

Our view of chemical evolution is incomplete

- Molecular composition of the prestellar phase is poorly known e.g. : CH_3CHCH_2 was discovered as abundant as $c-C_3H_2$ (Marcelino et al. 2007)

- Some protostars do not exhibit a hot corino BUT a rich content in C-chains sakai et al. (2008) \rightarrow Is there any other "chemical class" of protostars and why?

- Not many protostars are "well known" ?... Are they freaks ?

Which molecular complexity along SF can be reached and how does it evolve ?

Which role do Feedback processes play ? outflow/shocks, UV radiation

Which processes drive the formation/destruction of molecular species ?

Why Line Surveys ?



Unbiased Spectral Line Surveys

- A large number of lines: large frequency coverage to probe a wide range of A_{ij} , E_{up} n, T, v + isotopologues
- No (important) missing line(s) : unbiased
- Full chemical census : parent, daughter molecules, radicals, etc...

Serendipitous discoveries: CH₃COOCH₃ (Tercero et al. 2013), CH₃CHCH₂ (Marcelino et al. 2007), ...

Secure identification requires

- Good knowledge of the source structure (gradients (X, T, n, v) should be consistent)
 Emission may be extended (filtered ?)... → Mapping
- No conflict with other molecules : model emission of various molecules (consistent relative intensities and line blending)

Recent Advances in Radioastronomy



2011 : A few GHz bandwidth ③

Broad band Low-Trec 2SB receivers (+ backends) IRAM 30m : Spectal range 70 – 360 GHz Bandwidth : 32 GHz instantaneous (soon 64 GHz) Resolution : 50 to 200 kHz

Observational uncertainties (rel. calibration/pointing) are less

Full mm line survey : 200hrs \rightarrow 50hrs !

Spectral Line Surveys are becoming the reference tool



PI: B. Lefloch (IPAG) & R. Bachiller (OAN)



ASAI (400hrs) : a Legacy Chemical Survey of Solar-Type SFRs 1- to obtain an evolutive view of chemistry 2 - to constrain the influence of environmental conditions

Unbiased spectral surveys 70-272 GHz of a sample of 10 template sources of the different stages of solar-type star formation with the IRAM 30m telescope (+Herschel)

Prestellar cores: young / evolved

Class 0/I/II : Early / Hot Corino / WCCC + 2 Int. Mass protostars: Isolated/Cluster

Shocks



- Census of the molecular composition: source intercomparison → time, env. conditions
 Derive chemical composition/structure of the sources: comparison with models → quantify chemical differentiation : how and when
- 3. Characterize the physical and chemical processes at work





Time

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The Prestellar Phase

L1544 as prototype of prestellar cores

A prestellar core in Taurus (d=140pc)



Ward-Thompson et al. (1999)

L1544 as prototype of prestellar cores

A prestellar core in Taurus (d=140pc)



Vastel (2006)

Ward-Thompson et al. (1999)



HOCO⁺ Vastel et al. (2016),
+ hyperfine CH₂CN Vastel et al. (2015)
(stay tuned: more is coming soon)

Complex Organic Molecules:

N-, C-, O-bearing

A large degree of molecular complexity degree is already present in the prestellar phase

Complex Organic Molecules in L1544

Census of O-bearing COMs





Complex Organic Molecules in L1544



Jimenez-Serra et al. (2016)

Deeper integration (1 mK rms) : CH_3OCHO , CH_3OCH_3 + N-bearing COMs



Caselli et al. (2012) Keto et al. (2014)



Gravitational contraction of the envelope

-4 -4 $H_{2}O ice$ -6 -6 -6 -6 -8 -10 3.0 3.5 4.0 4.5 Log Radius (AU)

 H_2O : Abundances Xi $\approx 10^{-9}$ Xe $\approx 10^{-7}$

Photodesorption of H₂O ices due to : FUV photons in the external envelope (r > 5000 AU) CR-H₂ interaction \rightarrow dim FUV field $\approx 10^{-3}$ G₀





CH₃OH arises

- from the low-density, outer layers at 7000-10000 AU from the core center Keto et al. (2014)
- from the region of strong water ice UV-photodesorption

CH₃OH is produced in the outer layers of L1544: likely to be (photo?) desorbed from the ice mantles of dust grains



The detection of COMs at T=10K is a challenge for models

NAHOON: time-dependent gas phase chemistry code (Wakelam et al. 2012; Loison et al. (2014)

 $[CH_3OH]$ and $[C_2H_4]$ are increased and released in the gas phase



CH₃CHO

Non-thermal desorption of CH_3OH and C_2H_4 from grain mantles + gas phase reactions could account for the formation of some COMs *in the gas phase* : CH_3OH , H_2CCO

CH₃OH : 1(-8) C₂H₄ : 5(-9)

Non-Thermal desorption mechanism ?

Feedback processes



Outflows interact with the parental cloud through *shocks*

L1157 : Distance: 250 pc Driving source: Class 0 L1157-mm (L= 4-11 L_0) Precessing molecular outflow associated with several bow shocks seen in CO and in H₂.



L1157 is the prototype of Chemically Active Outflows

Spitzer 8 µm: grey CO: contours)ec (J2000) L1157-mm 02 01 (ATA) Bachiller et al. (2001), Looney et al. (2007), 20^s 10^s 39^m0^s 50^s 40^s RA (J2000) Neufeld et al. (2009)



L1157-B1 : bright molecular shock → Evidence for grain mantle/core sputtering and dust shattering : CH₃OH/SiO → high-temperature gas phase reactions : HCN

Chemically active outflows are ideal laboratories to study shock chemistry.



L1157-B1 : Prototype of chemically active outflow shock (Bachiller et al. 2001)



80 – 116 GHz : $1\sigma \simeq 1.5$ mK 330 lines detected (3 σ) spectral line density $\langle s \rangle = 9$ GHz ⁻¹

45 molecular species identified (+ rare isotopologues) 10% of U lines

A New View on outflow shock gas Physical conditions : n, T, ζ pre-shock dust and gas composition

Full Census of Molecular Ions (Podio et al. 2014; Codella et al. 2014) HCO^+ , $HOCO^+$, SO^+ , HCS^+ , N_2H^+

Cyanopolyynes : Talk by E. Mendoza

NH_2 CHO around solar-type protostars



Detections: B1:23 lines B2:6 lines

 $X \sim 10^{-9} - 10^{-8}$ similar to high-mass!



First discovery of NH₂CHO in protostellar shocks

Mendoza et al. (2014)



Shocks are an excellent laboratory to study COMs

- a chemical diversity comparable to hot corinos !
- Abundances are higher by x10 or more
- Mixed "cold/hot" abundance ratios...

Prebiotic Chemistry

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An important molecule for prebiotic chemical processes:

the simplest molecule with a peptide bond with the four most abundant elements of biological systems: C,N,O,H

NH₂CHO could drive the synthesis of more complex, pre-biotic molecules involved in pre-genetic and pre-metabolic processes (Saladino et al. 2012; *Ferus et al. 2015*)



 Detected in Comets: Hale-Bopp (Bockelee-Morvan et al. 2000), 81P/Wild2 (Elsila 2009): Exogeneous delivery on Earth (Ferus et al. 2014) ?
 Detected in high-mass SFRs (Bisschop et al. 2007) and IRAS16293-2422 (Kahane et al. 2013).



NH_2 CHO in solar-type SFRs

ASAI: Systematic search for NH₂CHO in solar-type environments

	Source	d	M	$L_{ m bol}$	Type	
		(pc)	(M_{\odot})	(L_{\odot})		
	TMC1	140	21		PSC - young	
	L1544	140	2.7	1.0	PSC - evolved	
Not detected	B1	200	1.9	1.9	Class 0 - early	-
	L1527	140	0.9	1.9	Class 0, WCCC	
	L1157-mm	325	1.5	4.7	Class 0, WCCC?	
	IRAS 4A	235	5.6	9.1	Class 0, HC	
	SVS 13A	235	0.34	21	Class $0/1$	
Detected	OMC-2 FIR 4	420	30	100	IM proto-cluster	
	Cep E	730	35	100	IM protostar	
	L1157-B1	250	_	_	outflow shock	

Lopez-Sepulcre et al. (2015)



cold sources X < a few 10⁻¹²

hot sources

NH₂CHO is detected only in hot corino protostars and shocks.



Search for $NH_2COCH_3 \otimes : X(NH_2COCH_3)/X(NH_2CHO) < 0.15$ in L1157-B1 > 1 in SgrB2 (Halfen 2011)

Search for HNCO \bigcirc



NH₂CHO and HNCO are chemically related (α =1) HNCO is *also* detected in cold sources (see Marcelino et al. 2009)

NH_2 CHO formation routes

Gas Phase



Grain Mantles

- Irradiation of CO and NH₃ rich icy mantles on grains: $NH_3 \rightarrow NH_2 + H$ $H + CO \rightarrow HCO$ $HCO + NH_2 \rightarrow NH_2CHO$ Jones et al. (2011)
 - Hydrogenation of HNCO on dust grains: $\frac{\text{HNCO} + \text{H} \rightarrow \text{H}_2\text{NCO}}{\text{H}_2\text{NCO} + \text{H} \rightarrow \text{NH}_2\text{CHO}}$ Raunier et al. (2004), Garrod et al. (2008)

Experimentally Inefficient (Noble et al. 2015)



Gas phase scenario

 $\rm NH_2 + H_2CO \rightarrow \rm NH_2CHO + H$

Garrod et al. (2008) Barone et al. (2015)





L1157-B1 : 2000 yrs L1157-B2 : 4000 yrs (Gueth et al. 1996)

Step 1 : cold cloud chemical abundances Step 2 : Passage of the shock \rightarrow increase of (n,T) \rightarrow release of H₂CO and NH₂ in the gas



H₂CO (ASAI) NH₂ (CHESS) NH₂CHO (ASAI)

Reasonable agreement

L1157-B2, I16293-2422 : OK ((Barone et al. 2015)

P- Chemistry in Solar-type SFRs

Phosphorus is one of the main biogenic elements CHONPS: [P]= 3x10⁻⁷

Solar system:

Ubiquitous in meteorites (Macia 2005) Identified in comet 67P/Churuymov-Gerasimenko (Altwegg et al. 2016)

Interstellar Medium:

Thorne (1984) : *PO is the main gas phase reservoir of Phosphorus in molecular clouds ?* Very few (sometimes uncertain) detections:

 \rightarrow Evolved stars: HCP, PH₃, CP, CCP, PO, PN (Agundez et al. 2007; DeBeck)

→ High-Mass SFRs: PN (Ziurys et al. 1987; Fontani et al. 2016), PO (Rivilla in press).











P- Chemistry in Solar-type SFRs

Systematic search for P-bearing species between 80 and 350 GHz with the IRAM 30m towards solar-type protostars and associated outflow/shocks

First detection of PO and PN in solar-type star forming region L1157



Emission from molecular-rich shock B1



PO and PN are produced in the shock (from sputtered PH_3): PO/PN= 3 X ~ 10⁻⁹ : Phosphorus depleted by 100 Modelling (UCL_CHEM) : atomic N plays a key₆ role in the chemistry of PO and PN

Protostars: from ASAI to SOLIS

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COMs around Solar-Type Protostars



One solar-type protostar investigated in detail: IRAS16293-2422

3 mm surveys since 1994 (also interferometric): Blake et al. (1994), Jorgensen et al. (2011), Caux et al. (2011)

TIMASS (Caux et al. 2011): 300 hrs of telescope time : IRAM 30m + JCMT : 80 - 365 GHz : 10" – 30" **CHESS** (Ceccarelli et al. 2010): HIFI/Herschel : 480 – 1900 GHz : 10" – 40"



Spectral Line Density : s= 20 GHz⁻¹

1000 Lines identified 32 chemical species

Line forest : CH₃CN, CH₃CCH, HCOOCH₃

Comparable to High-Mass SFR

Chemical Differentiation in I16293-2422

I16293, PdBI (Bottinelli et al. 2007)





A multiple system different signatures/sources

A rich content in COMs in the hot corino region : size ≈ 1.5 ": Td > 100K



2.5" – 5" resolution Acetaldehyde and Ketene peak at B S-bearing, N-Bearing peak at A

Outflow influences chemistry

No significant excitation gradients

Chemical differentiation studies will benefit a lot from ALMA and NOEMA



IRAS16293-2422



Ketene/Methyl Formate : Cold / Hot objects

(Jaber et al. 2014, Kahane et al. 2013, Jorgensen et al. 2012)

A rich content in COMs and pre-biotic material H₂CCO, CH₃CHO, NH₂CHO, HCOOCH₃,

 CH_3OCH_3 , CH_3CN , $HOCH_2CHO$ ($E_{up} < 150K$)

Two components:

Hot corino $(Td \ge 100K)$: X= 1(-9) – 1(-8) Cold envelope : X= 3(-12) – 2(-10)



Correlation between species abundant in Hot objects

Tight linear correlation between MF and DME

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Models (<2012) are unable to reproduce the observed abundances

Taquet et al (2012)

Are they synthesized through gas phase chemistry Or at the icy surface of grain mantle?

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SOLIS

http://solis.osug.fr



First Galactic Large Program with NOEMA

375 hrs - PIs : C. Ceccarelli (IPAG) & P. Caselli (MPE) Summer 2015 – 2017

(1) Understanding organic chemistry in space and (2) how it evolves during the process of formation of Solar-type systems are the two complementary goals of the proposed project, SOLIS.

Observing COMs down to 0.3 " resolution (40AU) in ASAI sources

- prestellar to evolved protostars (cold/warm gas/dust)
- environmental conditions (shocks, UV radiation)

Five "key" COMs : CH_3O , CH_3OH , CH_3OCH_3 , $HCOOCH_3$, NH_2CHO



Abundance maps of COMs in each source

- → Test gas phase vs grain surface chemistry
- \rightarrow Assess formation/destruction routes
- → Desorption mechanims : UV/CR/thermal

New insight from SOLIS



(Codella et al. in prep)

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Conclusions

ASAI illustrates the power of unbiased line surveys

- New molecular species were detected : NO⁺, p-CH₂CN, PO, PN.
- 10% of U lines in the database : more to come !
- Families of chemically related species are evidenced: DME/MF, NH₂CHO/HNCO, ...
- More work is needed to establish their formation routes: SOLIS

Molecular Complexity:

- is present to a wide degree in the prestellar phase. A scenario combining non-thermal desorption of simple species on icy mantles + subsequent gas phase reactions is proposed
- is widespread (enhanced) by feedback processes such as shocks

Many results to come out in the next months !

SOLIS is taking over: we will map the distribution of COMs at excellent sensitity level down to x10 AU.scale

Thank You

The ASAI Team:

M. Benedettini, R. Bachiller, E. Bianchi, G. Busquet, S. Cabrit, P. Caselli, C. Ceccarelli, J. Cernicharo, C. Codella, A. Faure, F. Fontani, A. Fuente, A. Gomez-Ruiz, M. Gonzalez, P. Hily-Blant, I. Jimenez-Serra, C. Kahane, A. Lopez-Sepulcre, E. Mendoza, K. Yoshida, T. Monfardini, L. Podio, E. Roueff, N. Sakai, M. Tafalla, M. Vasta, S. Viti, S. Yamamoto

Beyond ASAI

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Molecules in Meteorites and Comets

Meteorites and Comets

More than **80 amino acids** were found in meteorites on Earth, with specific isotopic composition and racemic distribution: extraterrestrial origin (Botta & Bada 2002)

+ several other classes of organic compounds: carboxylic acids, , alcohols, amines, amides, ... High D fractionation ratio.



Stardust: **glycine** (NH₂CH₂COOH) and amines were detected in samples returned from comet 81P/Wild 2 (Elsila, 2009) *despite evidence for terrestrial contamination*



Altwegg et al. (2016)

Glycine detected in the coma with Rosina

→ UV photochemistry of CH₃NH₂ and CO₂ ice on grain mantles (e.g. Bossa 2010) ?
 → Gas phase formation in the ISM ?



Species	Tex (K)	N (cm ⁻²)	X
C ₃ O	10	2(11)	5(-11)
CH₃CHO	17 ± 1	5(11)	1(-10)
t-HCOOH	10	5(11)	1(-10)
H ₂ CCO	27 ± 1	5(12)	1(-9)
нсссно	12 ± 1	2.7(11)	7(-11)
E-CH ₃ CCH	11 ± 2	2(13)	5(-9)
CH ₃ OCH ₃	11	1(12)	1(-10)
HCOOCH ₃	4	≤ 6(12)	7(-10)
CH₃OH	10	3(13)	6(-9)

Excitation and physical conditions are similar to those of CH₃OH

The emission of Complex Organic Molecules probably arises from the same region as CH₃OH and H₂O

Seeds Of Life In Space (SOLIS) Formamide NH₂CHO (prebiotic molecule)

L1157

50

IRAS 4A



25/35

Β1

-20

IMS chiral molecule: propylene oxide (CH₃CHCH₂O)

211 - 202 20 ō -20 11.0 - 10.1 100 5n 150 v [km/s]

McGuire et al. (2016)



Fig. 1. The molecular structure of *S*-propylene oxide and *R*-propylene oxide. (A) *S*-propylene oxide. (B) *R*-propylene oxide. Carbon, hydrogen, and oxygen atoms are indicated by gray, small white, and red spheres, respectively.

amino acids are chirals (S-form)!

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The Hyperfine Structure of CH₂CN

U Lines at 106 GHz ?

Vastel , Yamamoto, Lefloch, Bachiller (2015) **Full hyperfine transition series of CH₂CN identified in L1544**

LTE analysis : Tex= 10 – 12K X(CH₂CN) \simeq 10 ⁻¹² to 10 ⁻¹¹ OPR = 1

Dark cloud : TMC1 : $X \simeq 10^{-9}$

A tracer of chemical evolution ?





Early-type protostar (Class 0/I)

Complex Organic Molecules in the cold envelope

CH₃OH, H₂CCO, CH₃CHO, HC₂CHO (propynal), CH₃CN : seen in I16293 c-H₂C₃O, C₂H₃CN : not seen in I16293 CH₃OCH₃, HCOOCH₃ : not detected

Strongly differs from hot corino



105

1.2 10° 1.4 10⁵ Rest Frequency (MHz)

narrow (< 1km/s) : COMs broad (> 1.5 km/s) : SO, CH₃CN

1.6 105







Early-type protostar (Class 0/I) Complex Organic Molecules in the cold envelope CH₃OH, H₂CCO, CH₃CHO, HC₂CHO (propynal), CH₃CN : seen in I16293 c-H₂C₃O, C₂H₃CN : not seen in I16293 CH₃OCH₃, HCOOCH₃ : not detected

Strongly differs from hot corino

ALMA (0.6" resolution)



Chemical differentiation at the centrifugal barrier

- SO and CH_3OH emission at the centrifugal barrier, in the disk?
- $c-C_3H_2$ in the envelope