Ural Federal University

Complex Organic Molecules as Companions of Forming Stars

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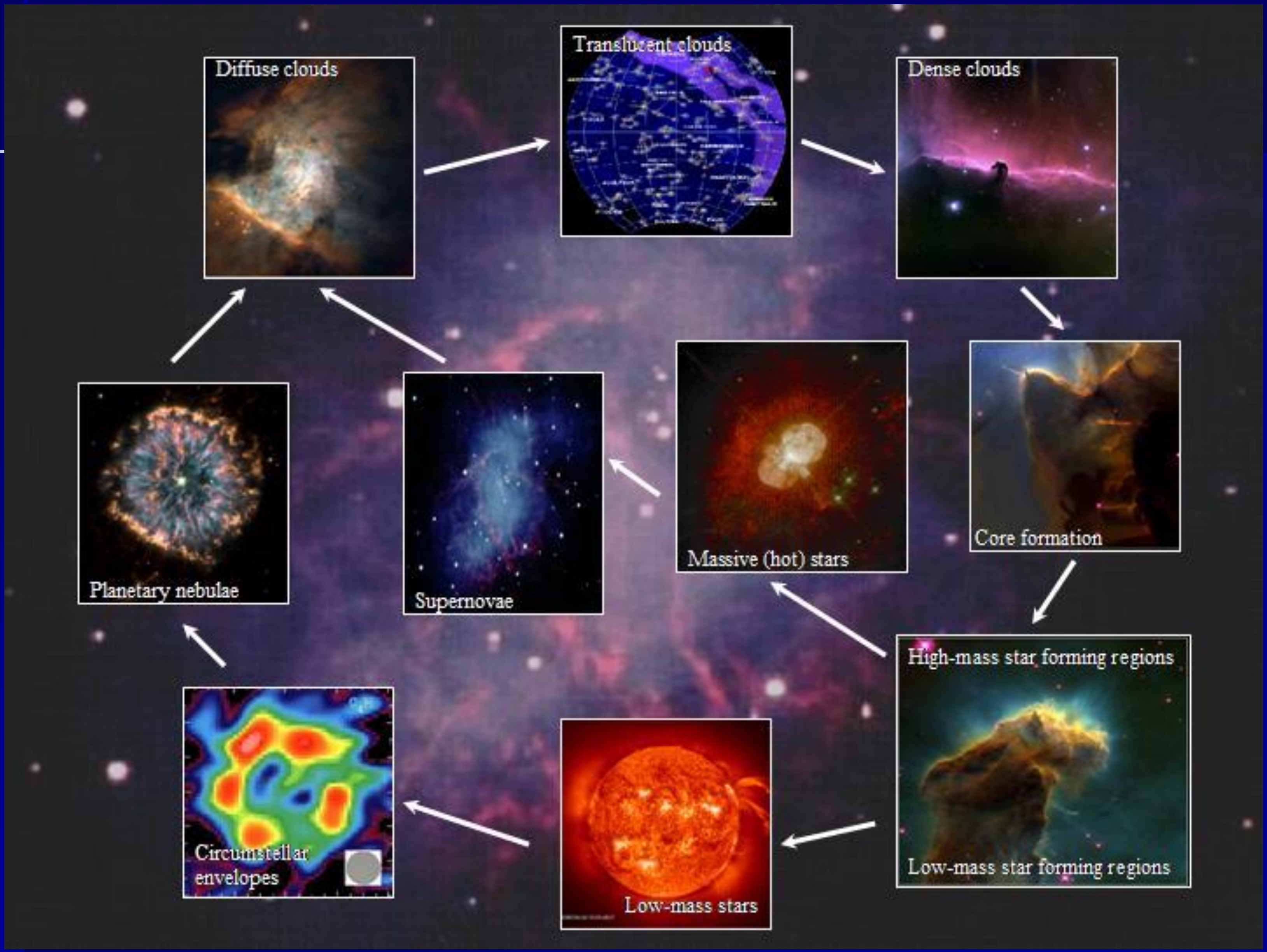
The Max Planck Partner Group

10.09.2019, XXI Mendeleev Symposium, Saint Petersburg

Matter cycle in Galaxy



Abundances of "metals" in diffuse ISM:

Element	n(X)/n(H)
N	7.60e-5
O	2.56e-4
C	1.20e-4
S	1.50e-5
Si	1.70e-6
Fe	2.00e-7
Na	2.00e-7
Mg	2.40e-6
Cl	1.80e-7
P	1.17e-7
F	1.80e-8

Fractional abundances of molecules cannot exceed ~ 1e-4 (except for H_2 and HeH+)

Interstellar and circumstellar molecules

Two atoms

AlF AlCl C_2 CH CH^+ CN CO CO^+ CP CS CSi HCl H_2 KCl NH NO NS NaCl OH PN SO SO^+ SiN SiO SiS HF SH

Three atoms

C_3 C_2H C_2O C_2S CH_2 HCN HCO HCO^+ HCS^+ HOC^+ H_2O H_2S HNC HNO MgCN MgNC N_2H^+ N_2O NaCN OCS SO_2 c-SiC_2 CO_2 NH_2 H_3^+ SiCN

Four atoms

c-C_3H l-C_3H C_3N C_3O C_3S C_2H_2 CH_2D^+? HCCN $HCNH^+$ HNCO HNCS $HOCO^+$ H_2CO H_2CN H_2CS H_3O^+ NH_3 SiC_3

Five atoms

C_5 C_4H C_4Si l-C_3H_2 c-C_3H_2 CH_2CN CH_4 HC_3N HC_2NC HCOOH H_2CHN H_2C_2O H_2NCN HNC_3 SiH_4 H_2COH^+

Six atoms

C_5H C_5O C_2H_4 CH_3CN CH_3NC CH_3OH CH_3SH HC_3NH+ HC_2CHO $HCONH_2$ l-H_2C_4 C_5N

Seven atoms

C_6H CH_2CHCN CH_3C_2H HC_5N $HCOCH_3$ NH_2CH_3 c-C_2H_4O CH_2CHOH C_7^-(?)

Eight atoms

CH_3C_3N $HCOOCH_3$ CH_3COOH C_7H H_2C_6 CH_2OHCHO

Nine atoms

CH_3C_4H CH_3CH_2CN $(CH_3)_2O$ CH_3CH_2OH HC_7N C_8H

Ten atoms

CH_3C_5N? $(CH_3)_2CO$

Eleven atoms HC_9N

Thirteen atoms c-C_6H_5CN

Discovery of space molecules since 1930s

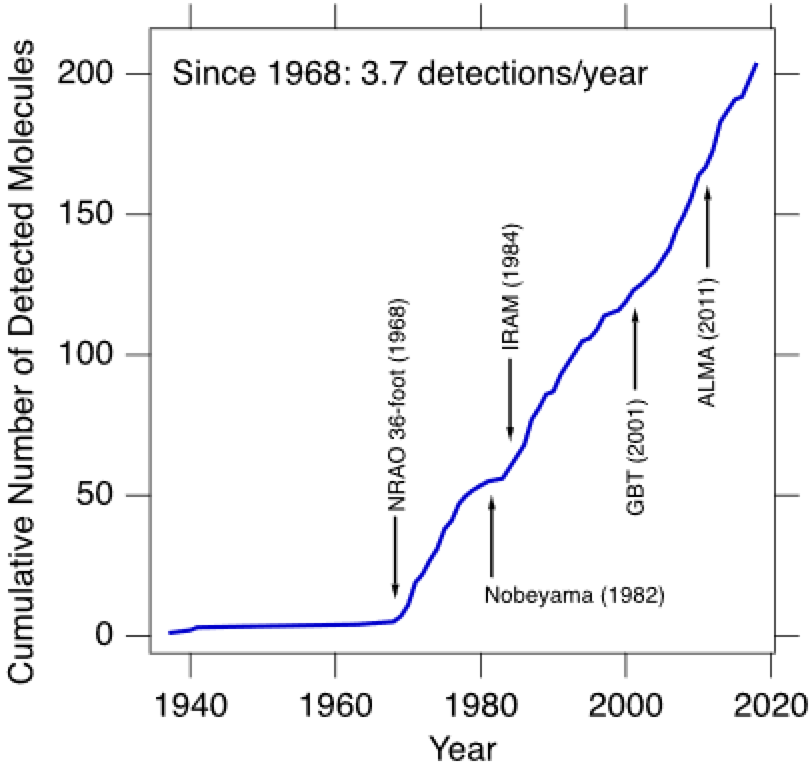


Figure 1. Cumulative number of known interstellar molecules over time. After the birth of molecular radio astronomy in the 1960s, there have been on average 3.7 new detections per year ($R^2 = 0.991$ for a linear fit beginning in 1968). The commissioning dates of several major contributing facilities are noted with arrows.

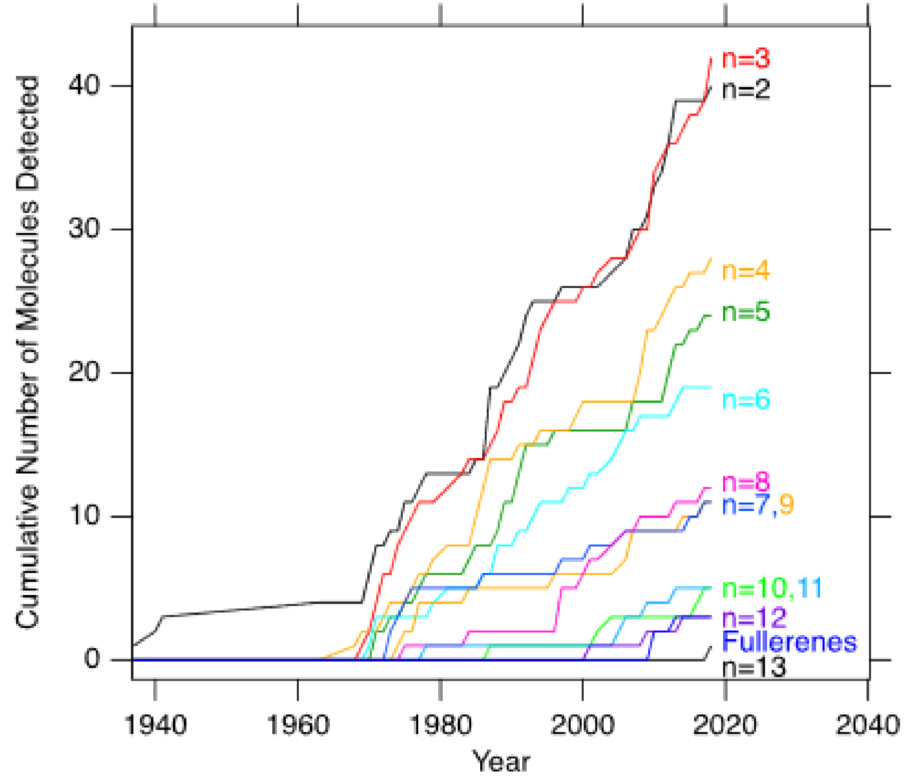
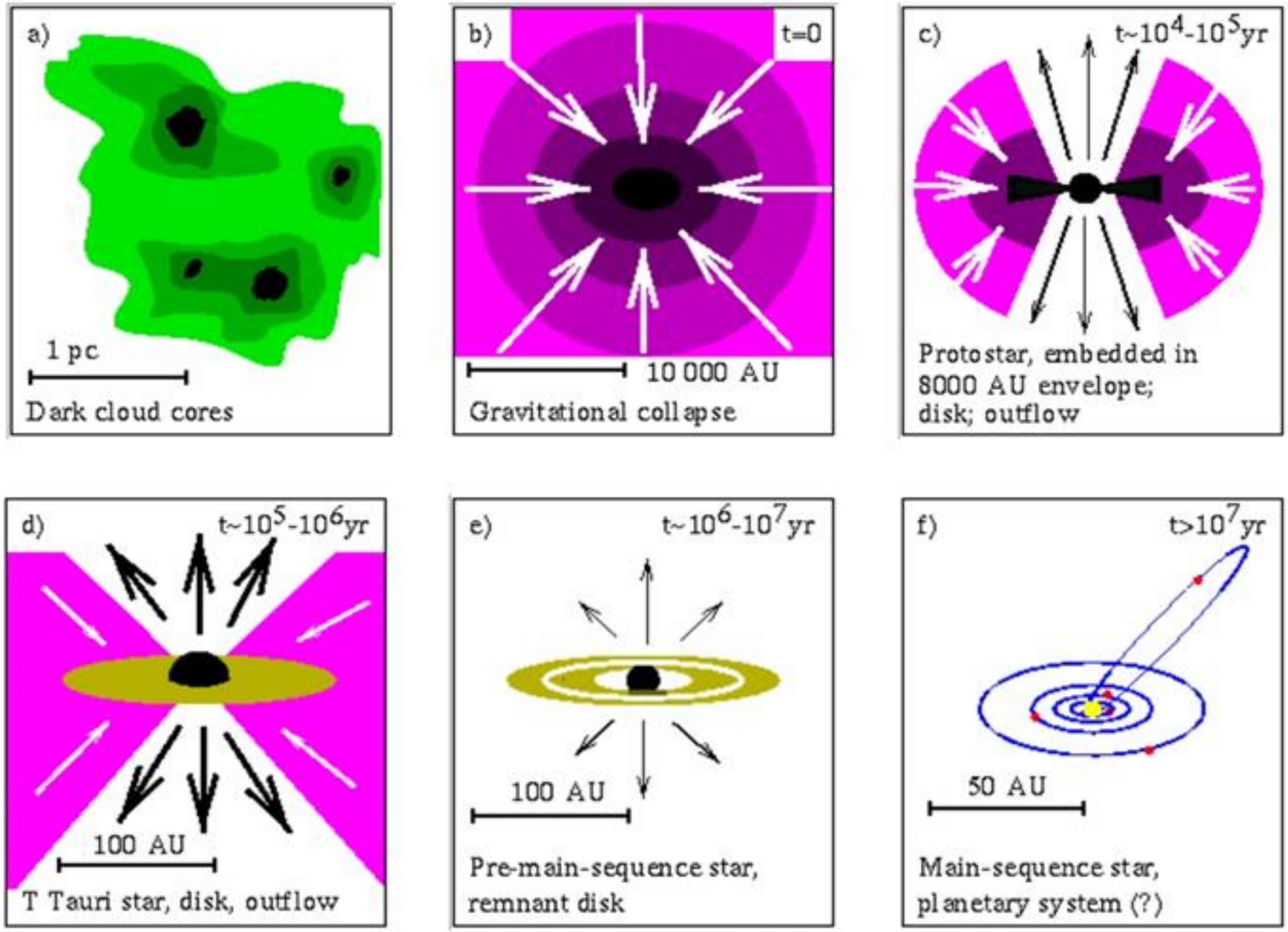


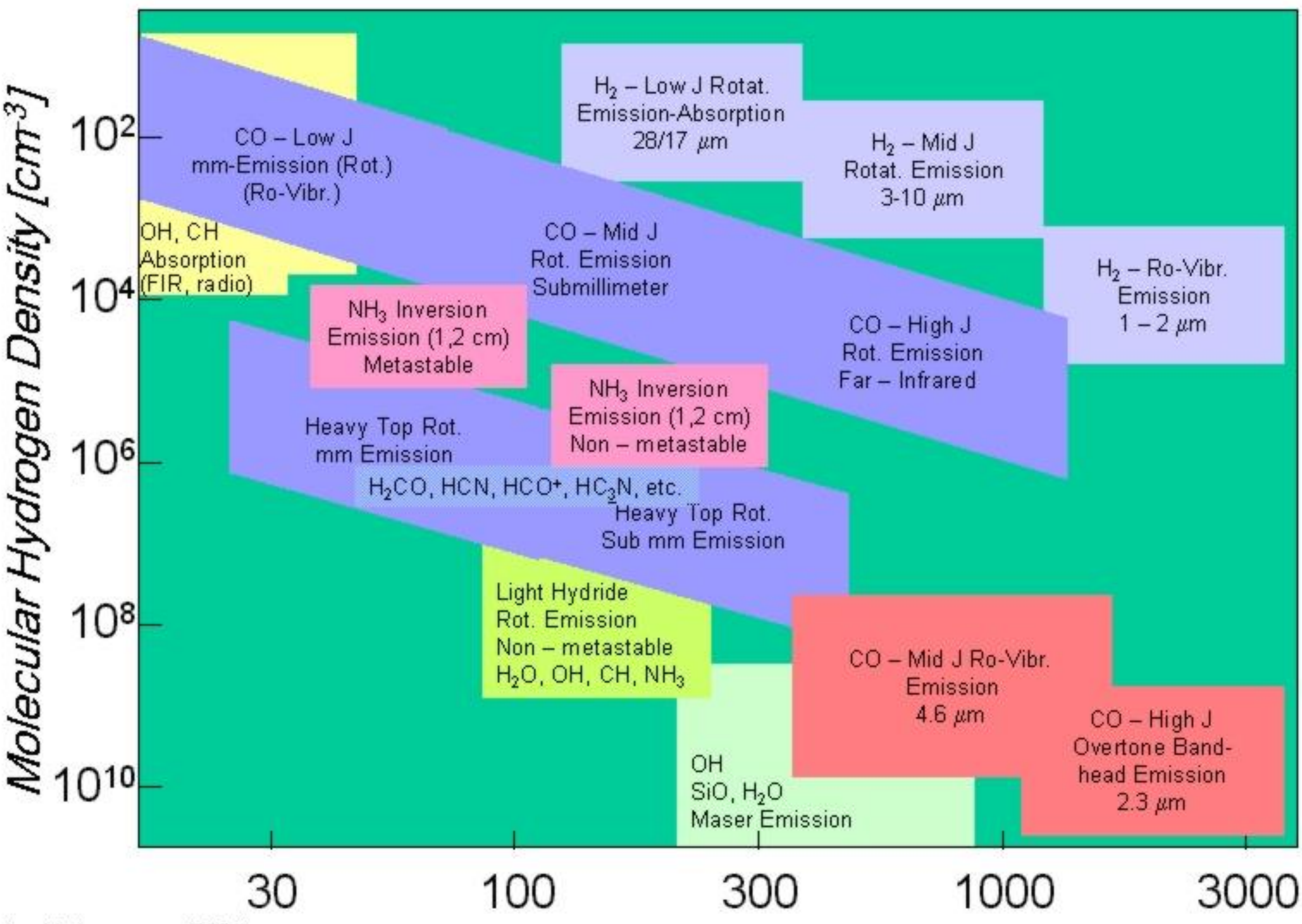
Figure 2. Cumulative number of known interstellar molecules with 2–13 atoms, as well as fullerene molecules, as a function of time. The traces are color-coded by number of atoms, and labeled on the right.

McGuire 2018

Sketch of a low-mass star formation



M.Hogerheijde 1998, after Shu et al. 1987



Jes K. Jørgensen (2001)

Based on figure by R. Genzel (1991)

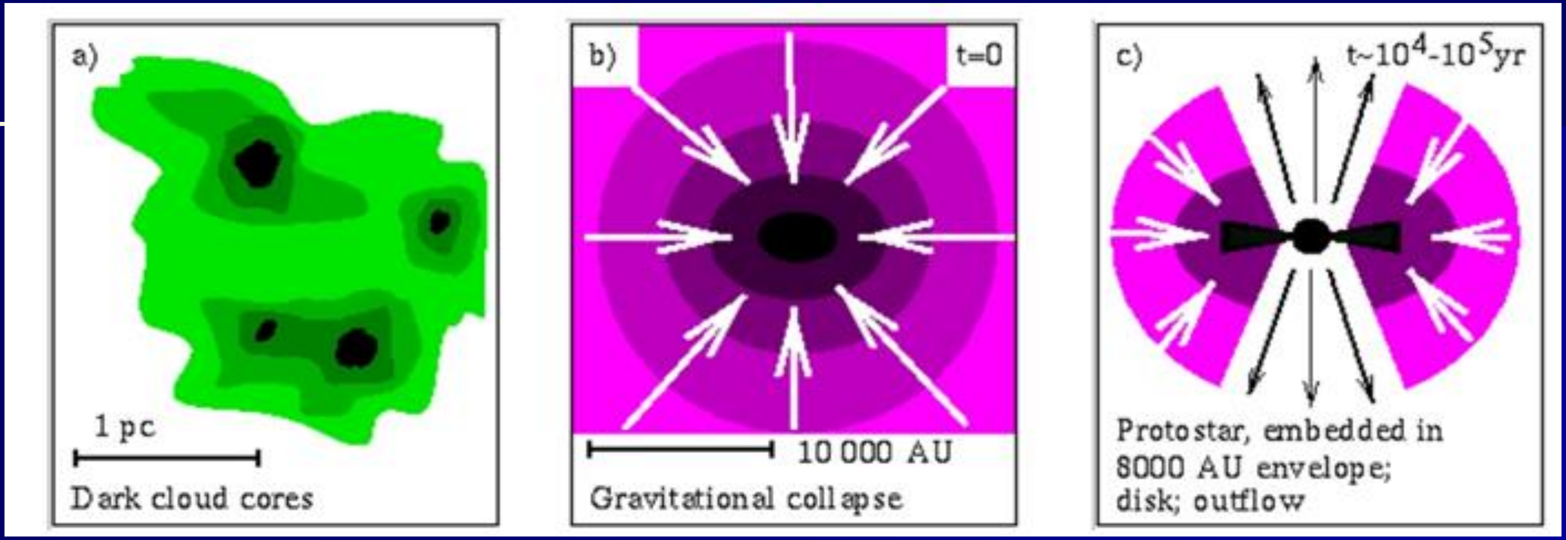
Complex organic molecules (COMs)

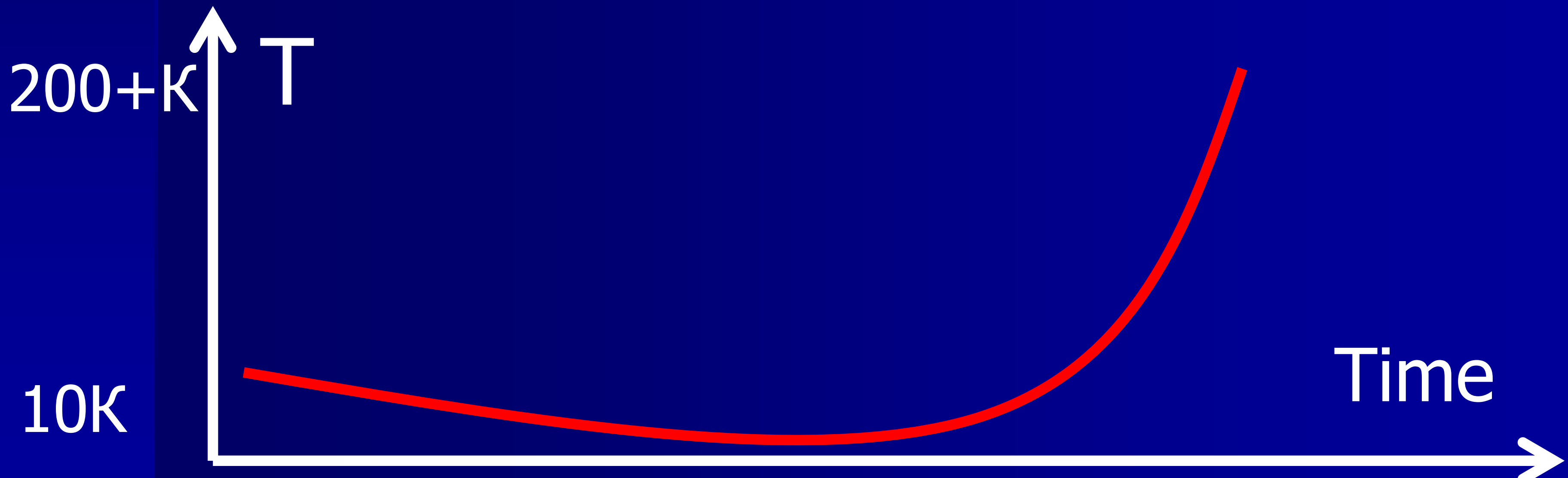
Species	Name	Source	Species	Name	Source
Hydrocarbons			**N-Containing**		
C_2H_4	Ethene	circ	CH_3CN	Acetonitrile	cc, hc, of
HC_4H	Butadiyne	circ	CH_3NC	Methylisocyanide	hc
H_2C_4	Butatrienylidene	circ, cc, lc	CH_2CNH	Keteneimine	hc
C_5H	Pentadiynyl	circ, cc	HC_3NH^+	Prot. cyanoacetylene	cc
CH_3C_2H	Propyne	cc, lc	C_5N	Cyanobutadiynyl	circ, cc
C_6H	Hexatriynyl	circ, cc, lc	HC_4N	Cyanopropynylidene	circ
C_6H^-	Hexatriynyl ion	circ, cc, lc	CH_3NH_2	Methylamine	hc, gc
H_2C_6	Hexapentaenylidene	circ, cc, lc	C_2H_3CN	Vinylcyanide	cc, hc
HC_6H	Triacetylene	circ	HC_5N	Cyanodiacetylene	circ, cc
C_7H	Heptatriynyl	circ, cc	CH_3C_3N	Methylcyanoacetylene	cc
CH_3C_4H	Methyldiacetylene	cc	CH_2CCHCN	Cyanoallene	cc
CH_3CHCH_2	Propylene	cc	NH_2CH_2CN	Aminoacetonitrile	hc
C_8H	Octatetraynyl	circ, cc	HC_7N	Cyanotriacetylene	circ, cc
C_8H^-	Octatetraynyl ion	circ, cc	C_2H_5CN	Propionitrile	hc
CH_3C_6H	Methyltriacetylene	cc	CH_3C_5N	Methylcyanodiacetylene	cc
C_6H_6	Benzene	circ	HC_9N	Cyanotetraacetylene	circ, cc
O-Containing			C_3H_7CN	N-propyl cyanide	hc
CH_3OH	Methanol	cc, hc, gc, of	$HC_{11}N$	Cyanopentaacetylene	circ, cc
HC_2CHO	Propynal	hc, gc	**S-Containing**		
c-C_3H_2O	Cyclopropenone	gc	CH_3SH	Methyl mercaptan	hc
CH_3CHO	Acetaldehyde	cc, hc, gc	**N,O-Containing**		
C_2H_3OH	Vinyl alcohol	hc	NH_2CHO	Formamide	hc
c-CH_2OCH_2	Ethylene oxide	hc, gc	CH_3CONH_2	Acetamide	hc, gc
$HCOOCH_3$	Methyl formate	hc, gc, of			
CH_3COOH	Acetic acid	hc, gc			
$HOCH_2CHO$	Glycolaldehyde	hc, gc			
C_2H_3CHO	Propenal	hc, gc			
C_2H_5OH	Ethanol	hc, of			
CH_3OCH_3	Methyl ether	hc, gc			
CH_3COCH_3	Acetone	hc			
$HOCH_2CH_2OH$	Ethylene glycol	hc, gc			
C_2H_5CHO	Propanal	hc, gc			
$HCOOC_2H_5$	Ethyl formate	hc			

Six+ atoms including carbon

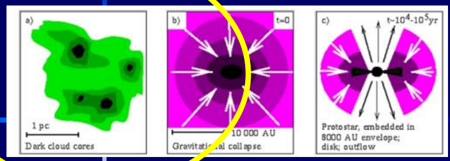
Herbst & van Dishoeck (2009)

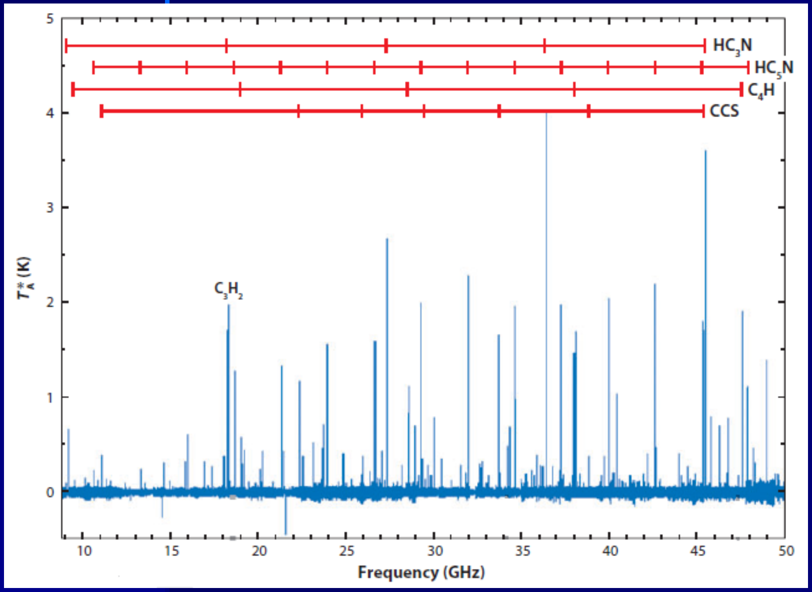
Temperature in a developing protostar





1. Organic molecules in cold cores





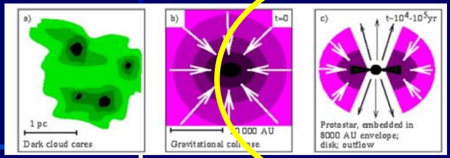
TMC-1 spectrum, Kaifu et al. (2004)

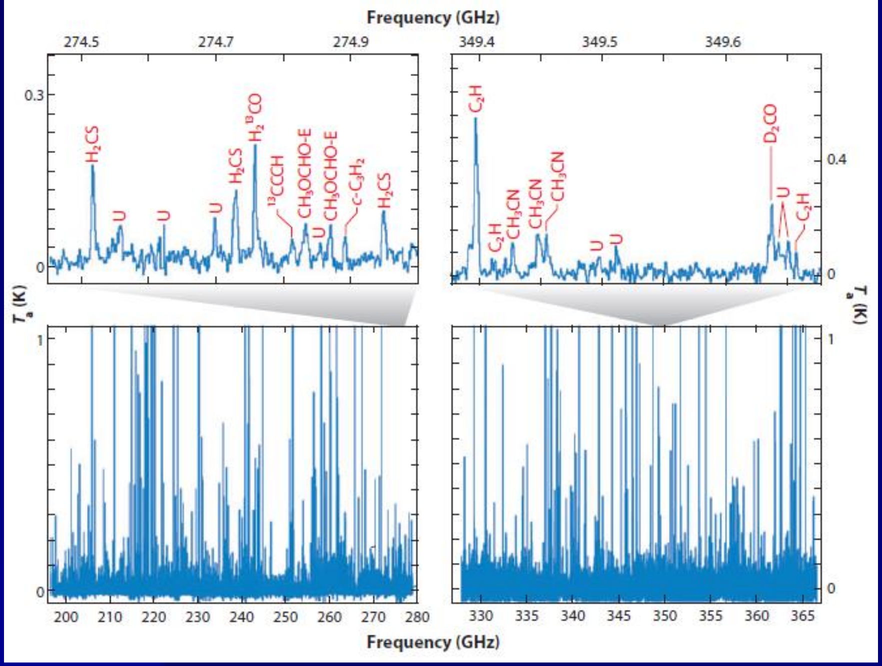
HC_xN – cyanopolyynes,
C_xH – unsaturated hydrocarbon radicals,
CH_3OH – methanol

Abundances of unsaturated species are higher than of saturated ones;

Dispersion in abundances between the sources

2. Organic species in hot cores/corinos



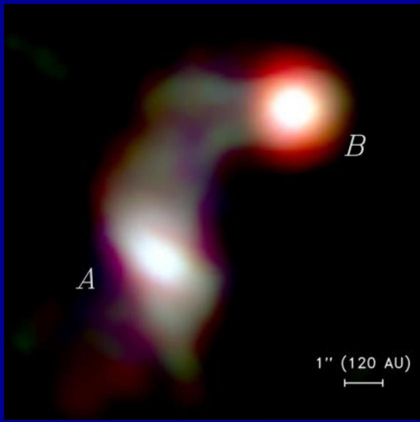


IRAS16293-2422 spectrum, Caux et al. (2005)

Predominantly saturated molecules:
CH_3CN, CH_3OH, $HCOOCH_3$, CH_3OCH_3, CH_3C_2H,
fractional abundances ~ 10^{-8} – 10^{-7}

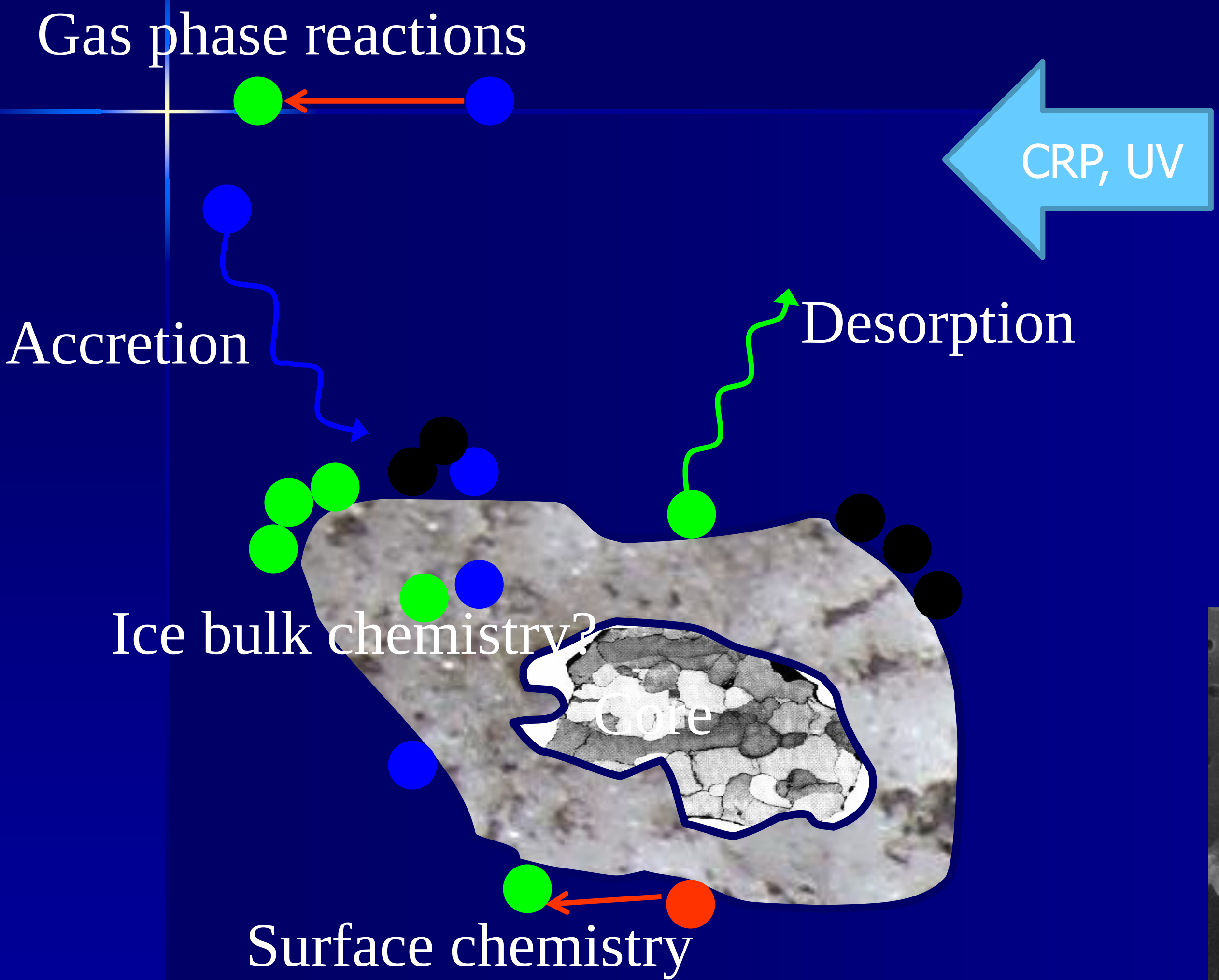
Abundances are similar in different objects

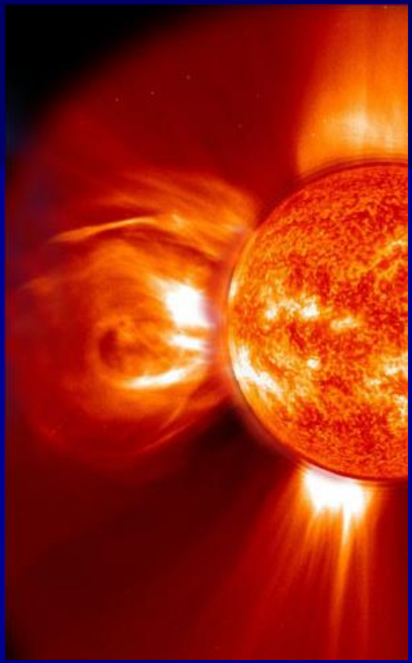
«Prebiotic» molecules:
Aminoacetonitrile (NH_2CH_2CN) – found
Ethylene glycol ($HOCH_2CH_2OH$) – found
Glycine (NH_2CH_2COOH) – not found (yet?)

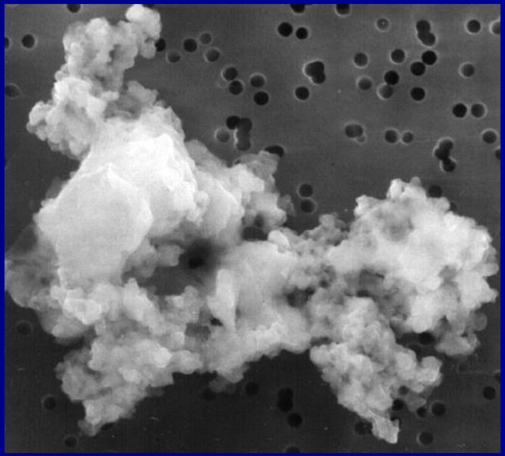


IRAS16293-2422, image from Jorgensen et al. (2016)

Formation and destruction of molecules in the ISM



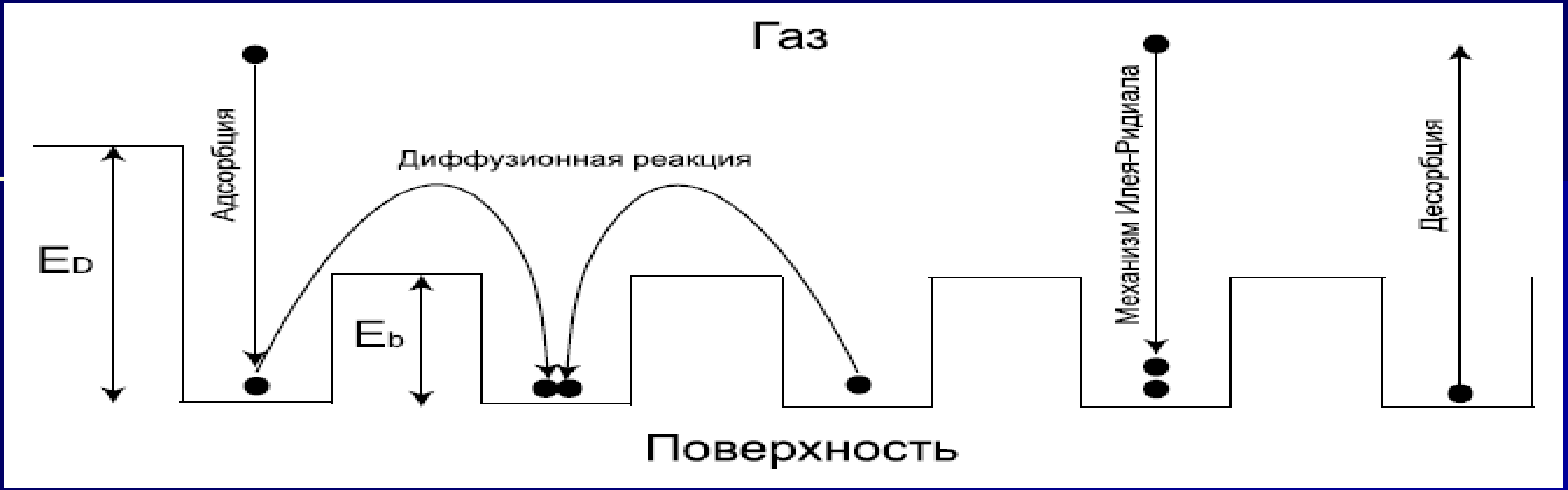




$N(r) \sim r^{-3.5}$, $10^{-6} < r < 10^{-4}$ cm

Based on a slide by D. Semenov

Diffusive surface chemistry



Molecular hydrogen formation: H + H → H_2

Hydrogenation:

CO → HCO → H_2CO → H_3CO → CH_3OH

CH → CH_2 → CH_3 → CH_4

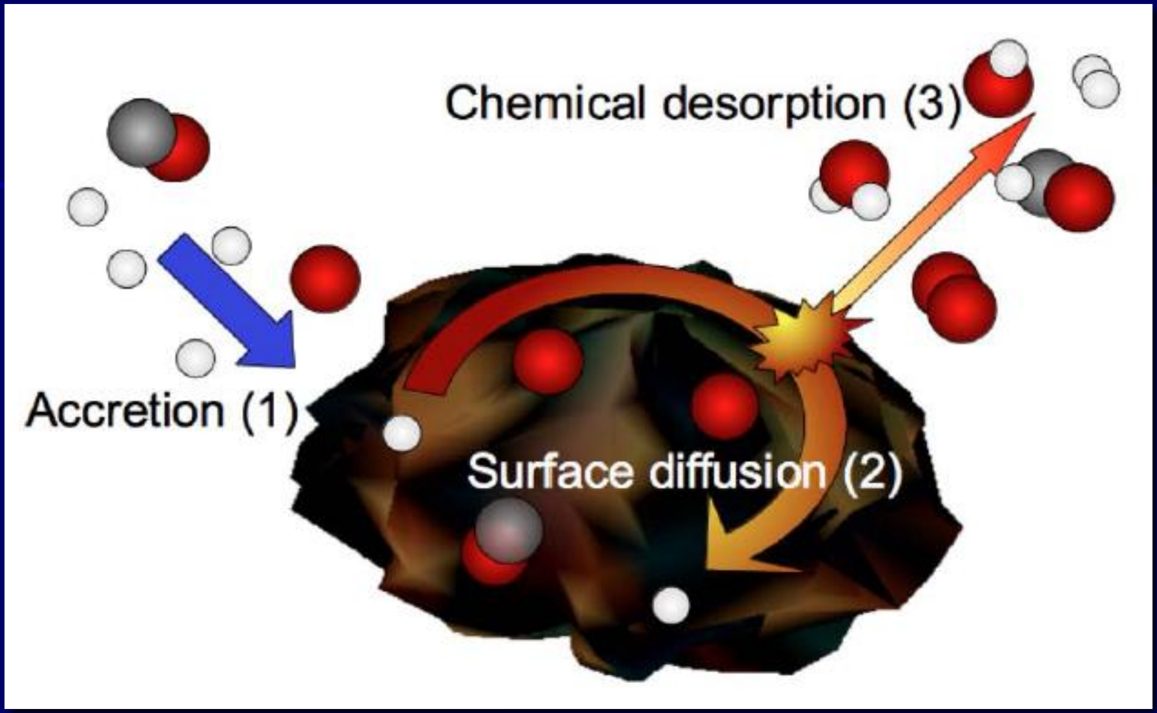
NH → NH_2 → NH_3

COMs formation:

HCO + H_3CO → $HCOOCH_3$ etc.

Chemical (reactive) desorption

Dulieu et al. (2013)



Heat of reaction = Σ Heats of formation of reactants - Σ Heats of formation of products

Heat of reaction ejects certain fraction of products to the gas:
grX+grY -> grZ + Z(gas)

The efficiency of RD was measured in experiments. Its dependence on the heat of reaction and surface coverage is quantified, although the results are controversial (e.g., Minissale et al. vs. Chuang et al.)

Astrochemical databases

Lister - [C:\projects\reduction\red2\rec\newnsm.rec]

Файл Правка Вид Справка 21 %

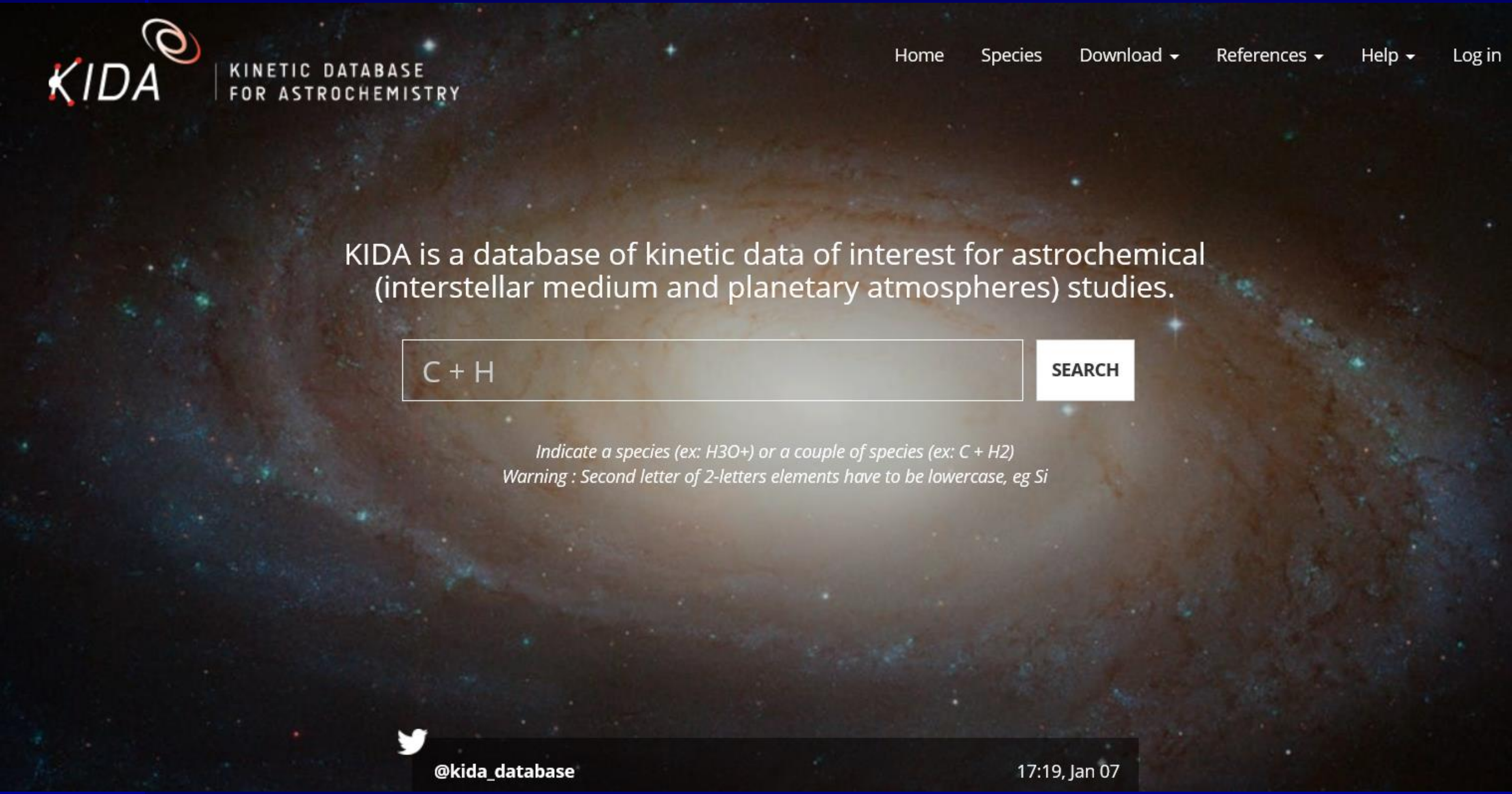
902	He+	CH5N	HCNH+	H	H2	He	6.70E-10	-0.50	0.00
903	He+								
904	He+								
905	He+								
906	He+								
907	He+								
908	He+								
909	He+								
910	He+								
911	He+								
912	He+								
913	He+								
914	He+								
915	He+								
916	He+								
917	He+								
918	He+								
919	He+								
920	He+								
921	He+								
922	He+								
923	He+								

Lister - [c:\projects\reduction\red2\rec\rate95.rec]

Файл Правка Вид Справка 0 %

1	H	H2	H	H	H	4.67E-07	-1.00	55000.0	CDA	
2	H	C	CH	PHOTON		1.00E-17	0.00	0.0	NAA	PH80
3	H	CH	C	H2		4.98E-11	0.00	0.0	MNEA	NIST
4	H	CH	C	H	H	6.00E-09	0.00	40200.0	CDA	
5	H	CH2	CH	H2		2.70E-10	0.00	0.0	MNEA	NIST
6	H	NH	N	H2		1.73E-11	0.50	2400.0	NEA	
7	H	CH3	CH2	H2		1.00E-10	0.00	7600.0	MNEA	NIST
8	H	O	OH	PHOTON		9.90E-19	-0.38	0.0	NAA	
9	H	NH2	NH	H2		5.25E-12	0.79	2200.0	NEA	
10	H	CH4	H2	CH3		5.82E-13	3.00	4045.0	MNEA	NIST
11	H	OH	H2	O		7.00E-14	2.80	1950.0	MNEA	NIST
12	H	OH	O	H	H	6.00E-09	0.00	50900.0	CDA	
13	H	NH3	NH2	H2		7.80E-13	2.40	4990.0	MNEA	NIST
14	H	H2O	OH	H2		6.83E-12	1.60	9720.0	MNEA	NIST
15	H	H2O	OH	H	H	5.80E-09	0.00	52900.0	CDA	
16	H	C2	CH	C		4.67E-10	0.50	30450.0	NEA	
17	H	CO	C	OH		1.10E-10	0.50	77700.0	NEA	
18	H	C2H3	C2H2	H2		2.00E-11	0.00	0.0	MNEA1	NIST
19	H	HCN	CN	H2		6.31E-10	0.00	12400.0	MNEE	NIST
20	H	H2CN	HCN	H2		1.00E-10	0.50	0.0	MNEA	NM90
21	H	HCO	CO	H2		1.50E-10	0.00	0.0	MNEA	NIST
22	H	NO	NH	O		9.29E-10	-0.10	35220.0	MNEA	NIST

- ~ 5000 – 7000 reactions, ~ 100 – 1000 surface reactions
- rates of only 10 – 20 % reactions measured/evaluated



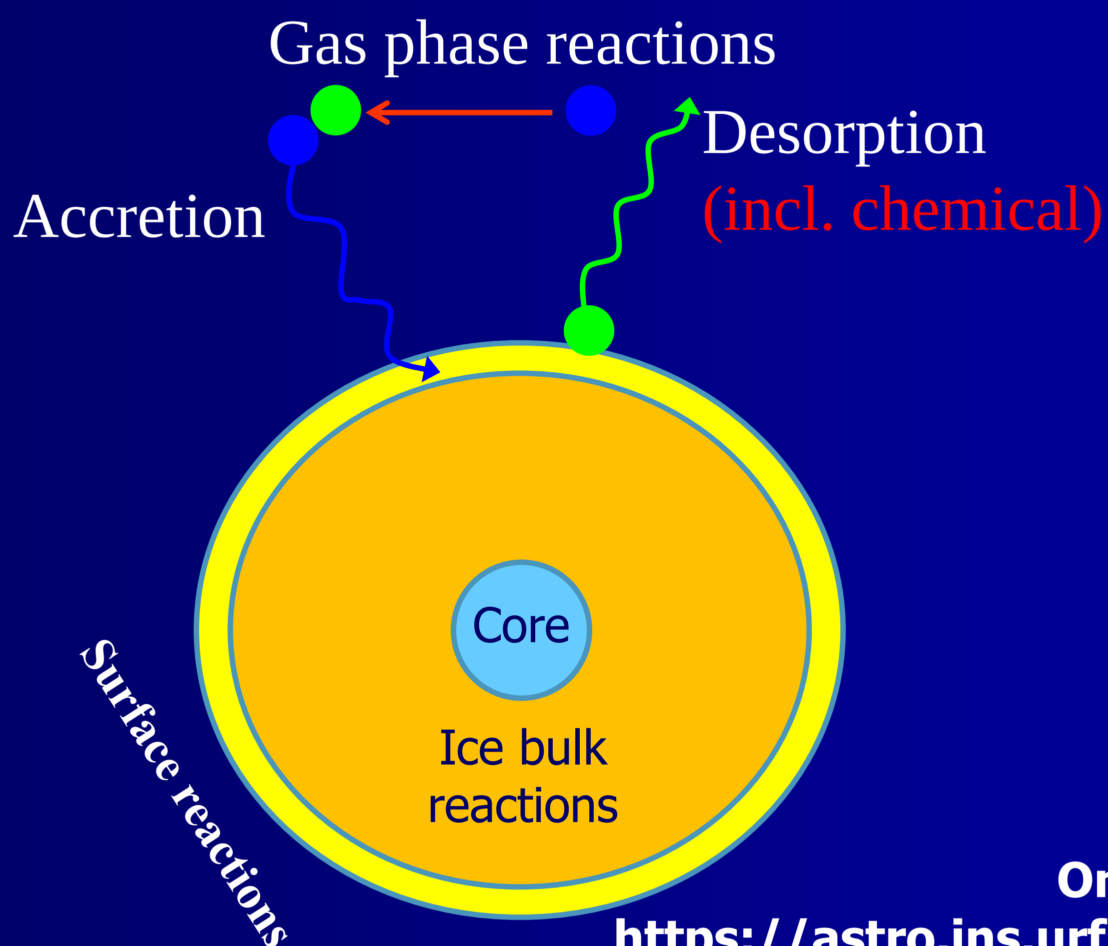
http://kida.obs.u-bordeaux1.fr/

Numerical modeling

Chemical rate equations:

$$\begin{cases} \dfrac{dn_i}{dt} = \sum\limits_{l}\sum\limits_{m} K_{lm} n_l n_m - n_i \sum\limits_{s} K_{is} n_s - k_{acc} n_i + k_{des} n_i^{dust} & \textbf{Gas} \\ \dfrac{dn_i^{dust}}{dt} = \sum\limits_{l}\sum\limits_{m} K_{lm} n_l^{dust} n_m^{dust} - n_i^{dust} \sum\limits_{s} K_{is} n_s^{dust} + k_{acc} n_i - k_{des} n_i^{dust} & \textbf{Surface} \end{cases}$$

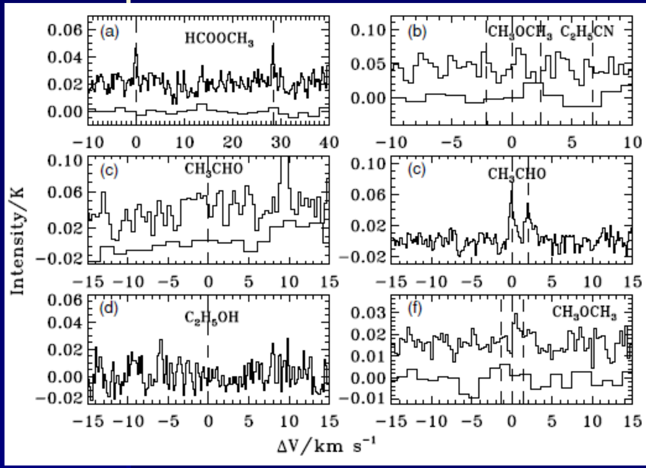
Rate equations-based code MONACO for the numerical simulations of gas-grain chemistry in the ISM (Vasyunin&Herbst 2013, Vasyunin et al. 2017)



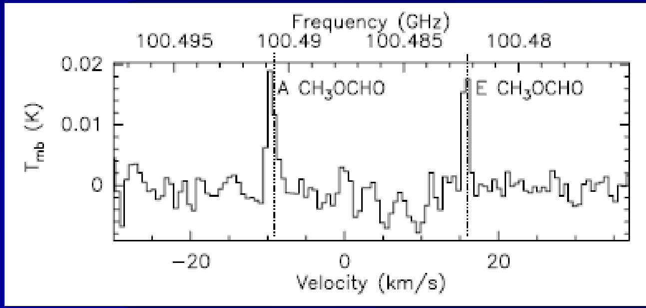
Online version:
https://astro.ins.urfu.ru/monaco

COMs typical for hot cores in cold clouds:

Fractional abundances:
$10^{-10} – 10^{-11}$ w.r.t. H.



B1-b, Oeberg et al. 2010



L1689b, Bacmann et al. 2012

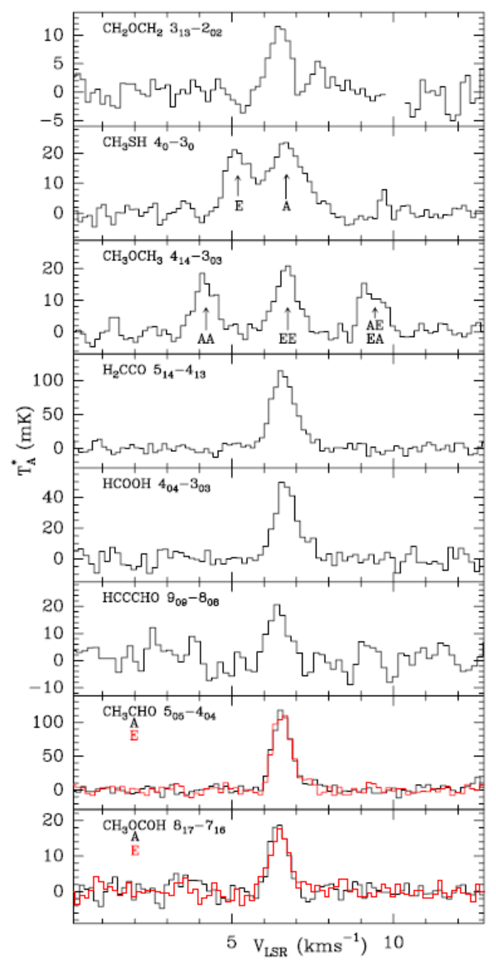
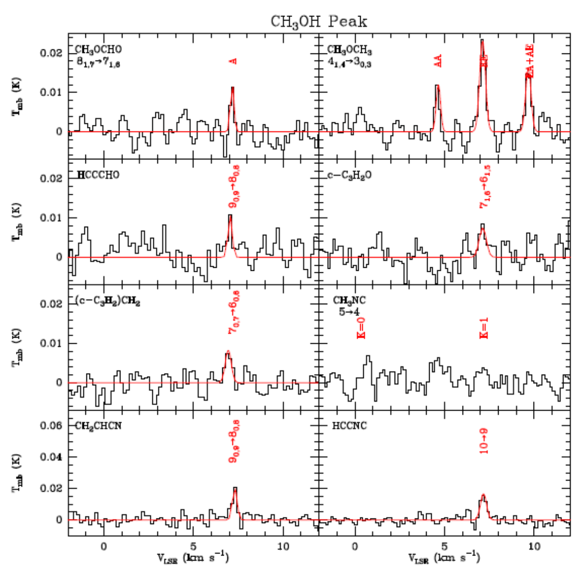


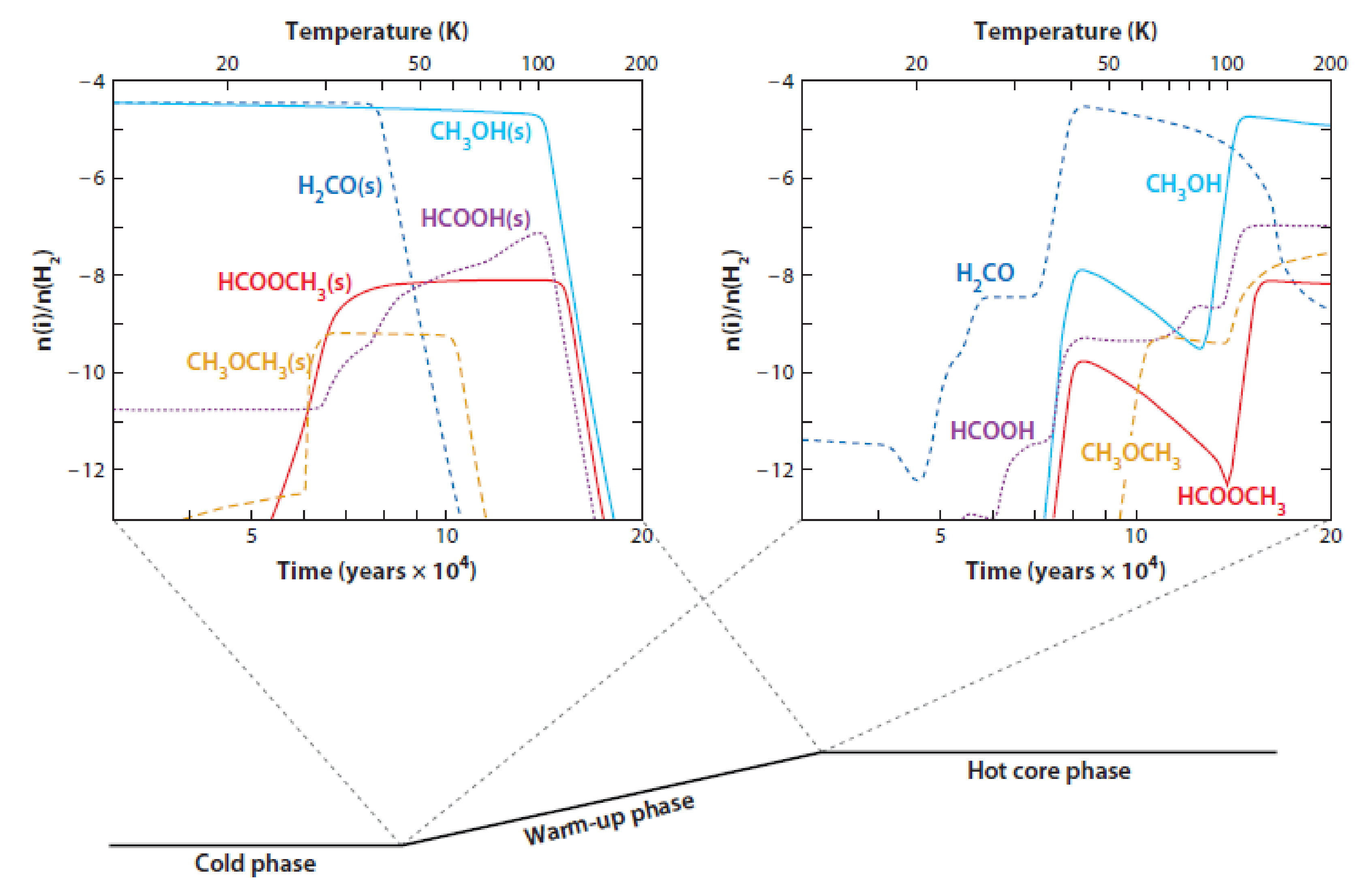
Figure 2. Selected lines of hot core-type molecules detected toward B1-b. For oxirane we have only detected the ortho line shown in the upper panel.
(A color version of this figure is available in the online journal.)

B1-b, Cernicharo et al. 2012



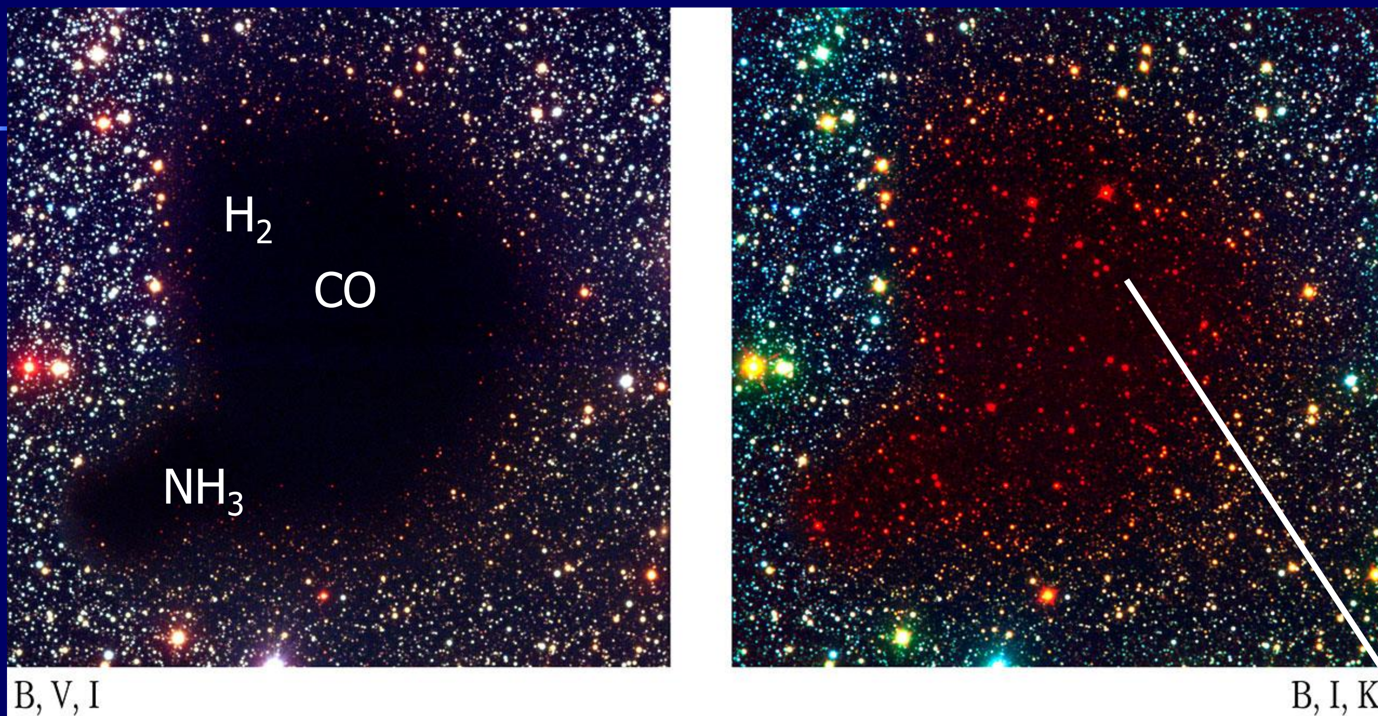
Jiménez-Serra, Vasyunin et al. 2016

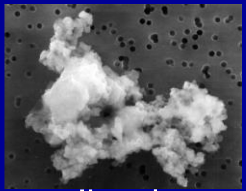
Formation of COMs during the warm-up of a hot core



Garrod & Herbst (2006)

Physical conditions at the earliest stages of star formation





Interstellar dust grains
<a> ~ 10^{-5} cm

T ~ 10K, n(H) ~ 10^4 – 10^5 cm^{-3}
Molecular freeze-out on a timescale
t_{depl} ~ 10^9 / n(H) years

“Cold” COMs vs. “Hot” COMs: a modeler’s perspective

Hot:

Found in hot cores/corinos

Abundances wrt.H ~ 10^{-8} – 10^{-7}

Formed in radical-radical surface chemistry during warm-up phase from 10 K to > 100 K, at 30-40 K, then thermally evaporated to gas

(Garrod&Herbst 2006)

Cold:

Found in cold clouds (pre-stellar cores), Tdust, Tgas ~ 10 K

Abundances wrt.H ~ 10^{-11} – 10^{-10}

Cannot be formed during warm-up phase because of no warm-up phase!

Proposed scenarios of cold COMs formation:

Vasyunin & Herbst (2013)

Reboussin et al. (2014)

Ruaud et al. (2015)

Fedoseev et al. (2015)

Balucani etl al. (2015)

Ivlev et al. (2015)*

Chuang et al. (2016)

Vasyunin et al. (2017)

Shingledecker et al. (2018)

Scenario by Vasyunin&Herbst (2013) :

Efficient chemical desorption + reactions in the cold gas

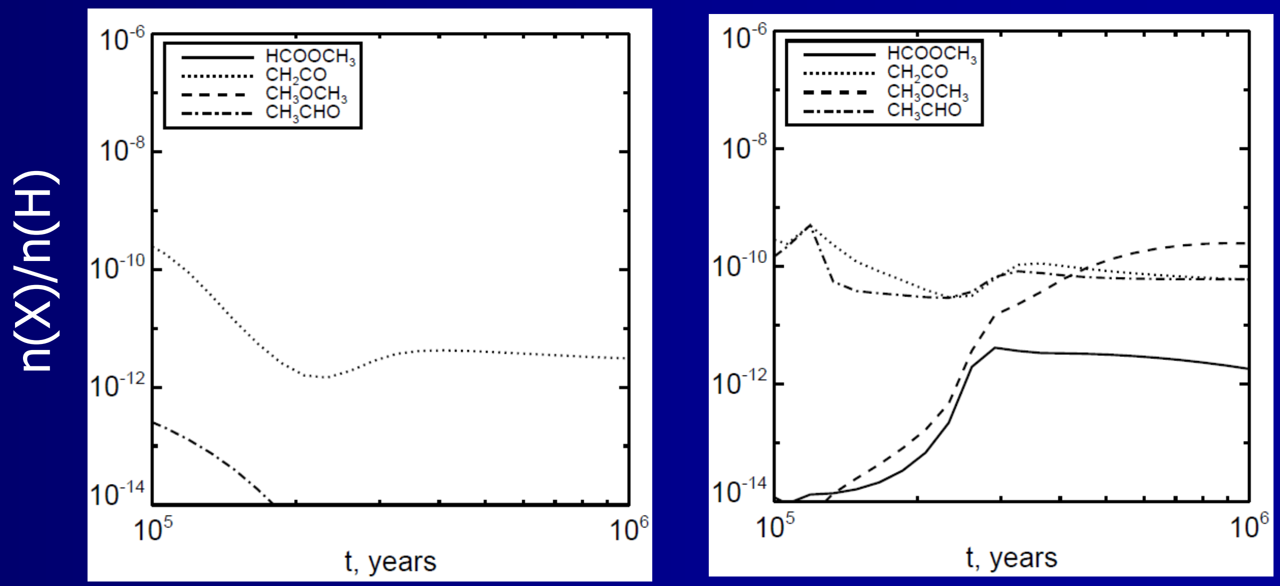
$grH + grH_2CO \rightarrow grCH_3OH$ (90%)
$grH + grH_2CO \rightarrow CH_3OH$ (10%) – ejected to gas via chemical desorption

$CH_3OH + H_3O^+ \rightarrow CH_3OH_2^+ + H_2O$

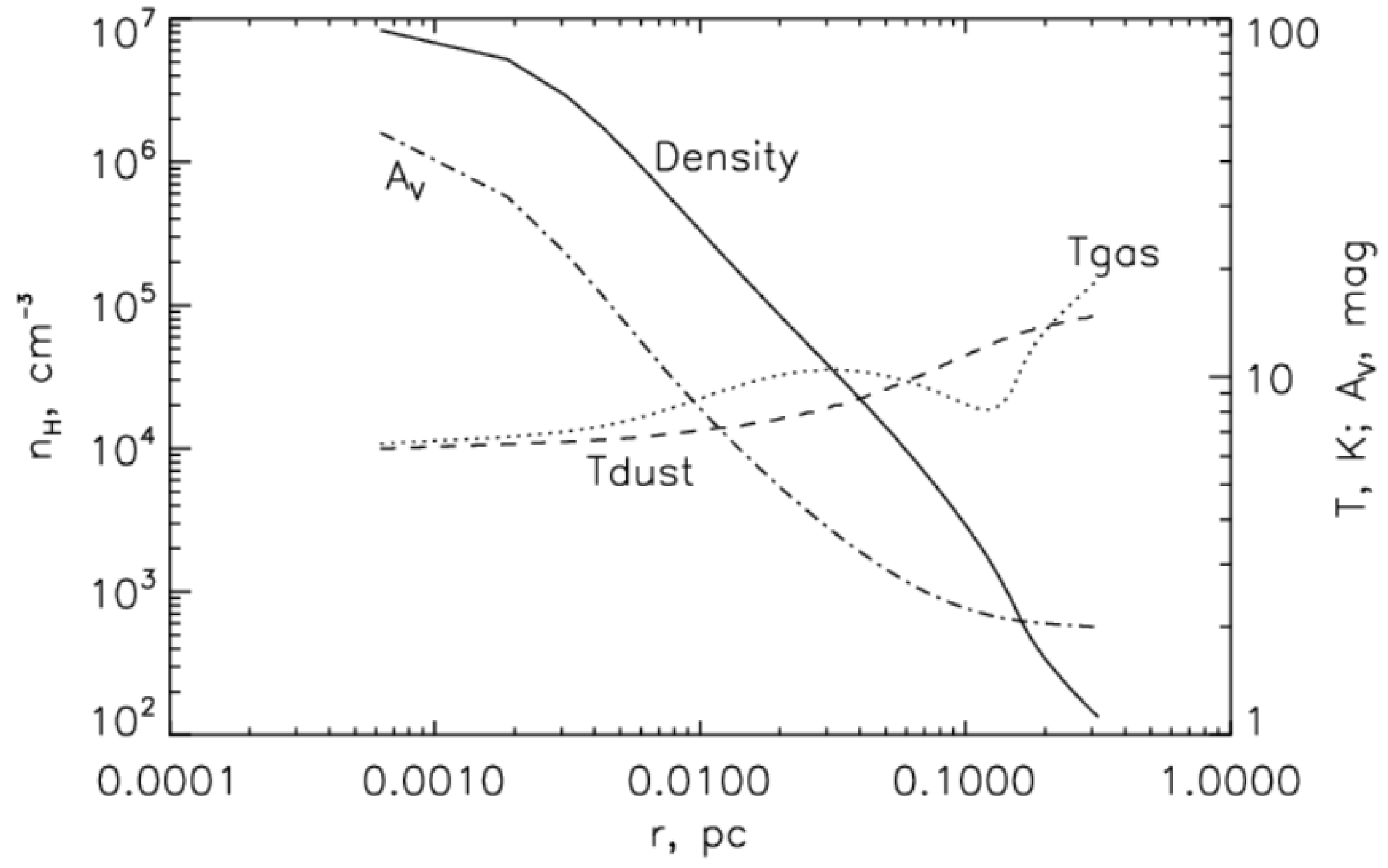
$CH_3OH_2^+ + CH_3OH \rightarrow CH_3OHCH_3^+$

$CH_3OHCH_3^+ + e^- \rightarrow CH_3OCH_3 + H$

COMs at 10 K



L1544 physical model:

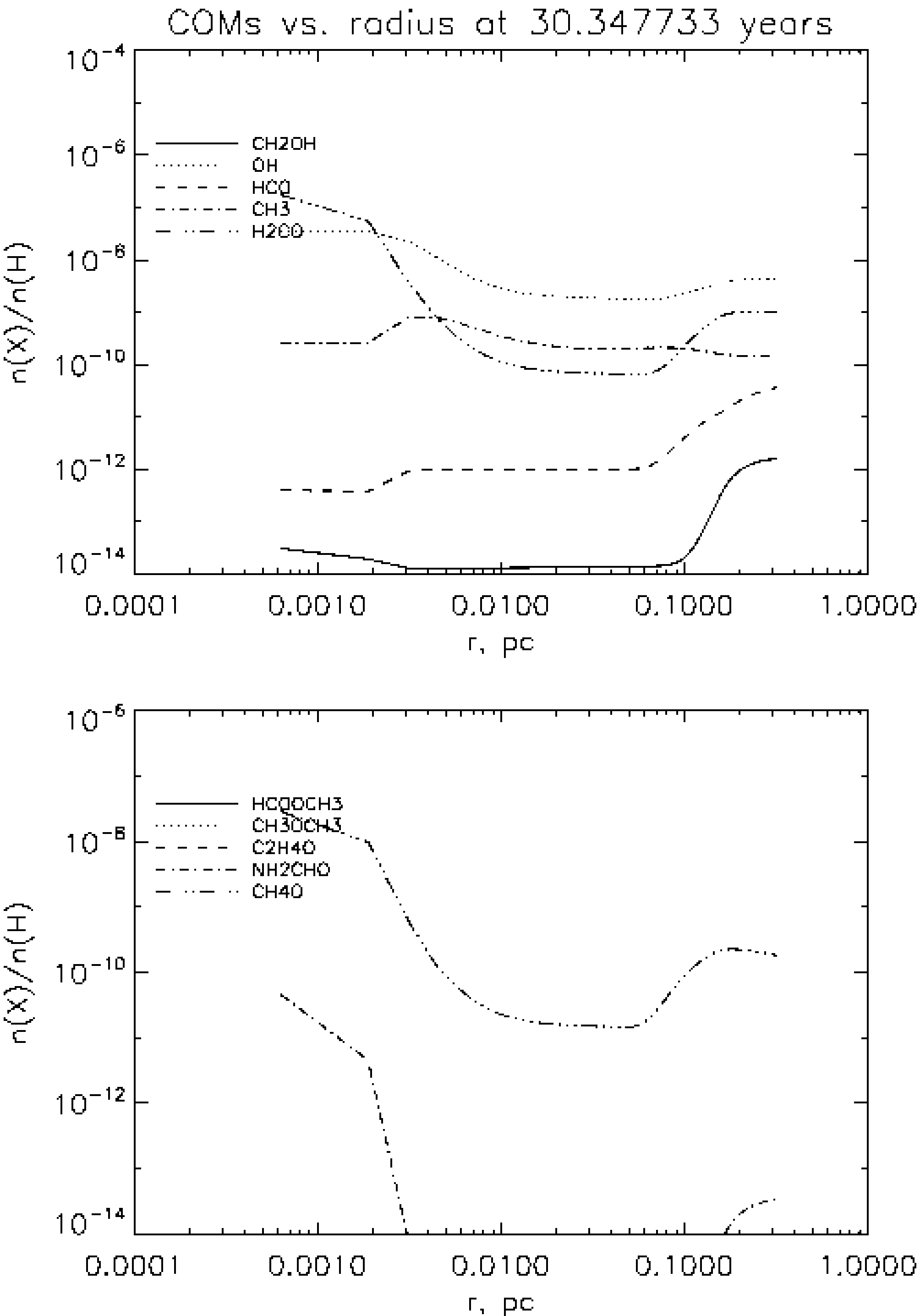


Keto&Caselli (2012)

1D modeling of COMs in L1544

"Methanol peak":
Bizzocchi et al. (2014),
Vastel et al. (2014),
Jimenez-Serra,
Vasyunin et al. (2016)

Vasyunin et al., ApJ (2017)



What about ices? Case of L1544

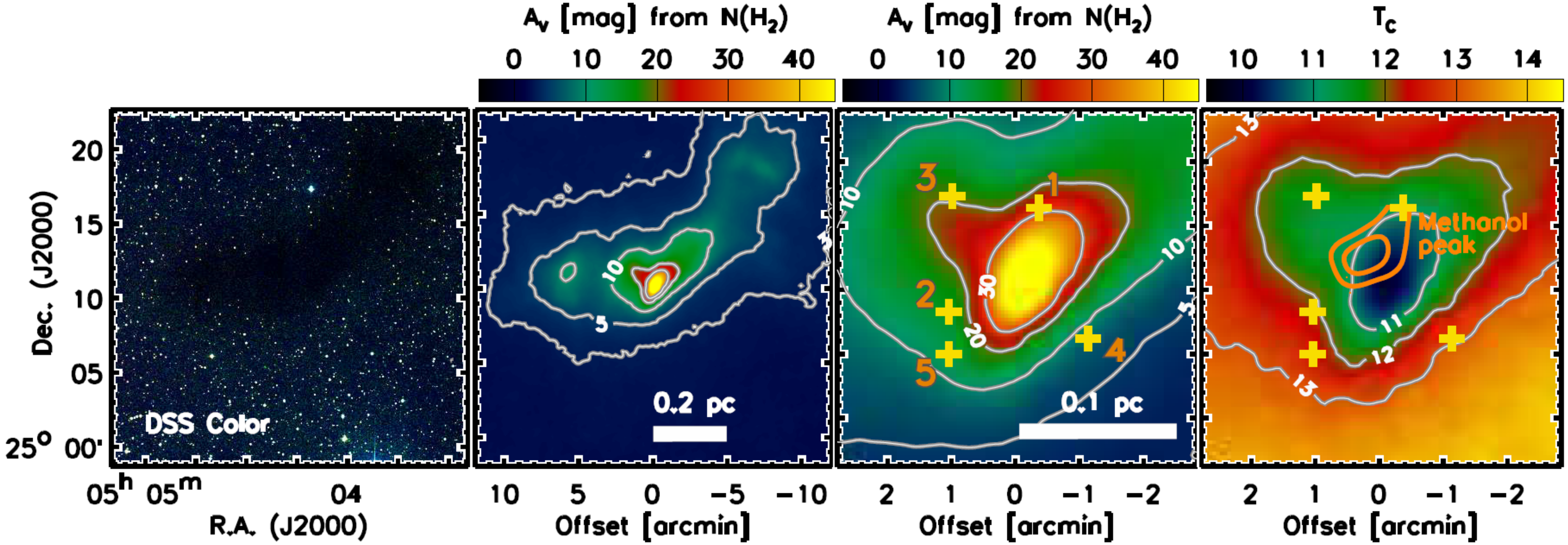


Fig. 1. The locations of the sources in L 1544 observed in the present study. First panel from the left : DSS color image of L 1544 to delineate the dark patch of the starless core. Second : the extinction map based on the Herschel/SPIRE far-infrared imaging. Third: a close-up view of the central part of L 1544, enclosed in the orange rectangle on the second panel. The positions of the 2MASS/WISE sources are marked with crosses. Fourth: the dust color temperature based on Herschel/SPIRE imaging. The methanol peak observed by Bizzocchi et al. (2014) is shown in the orange contours.

Goto, Vasyunin et al., submitted

Methanol and water ice in L1544 with SpeX IRTF

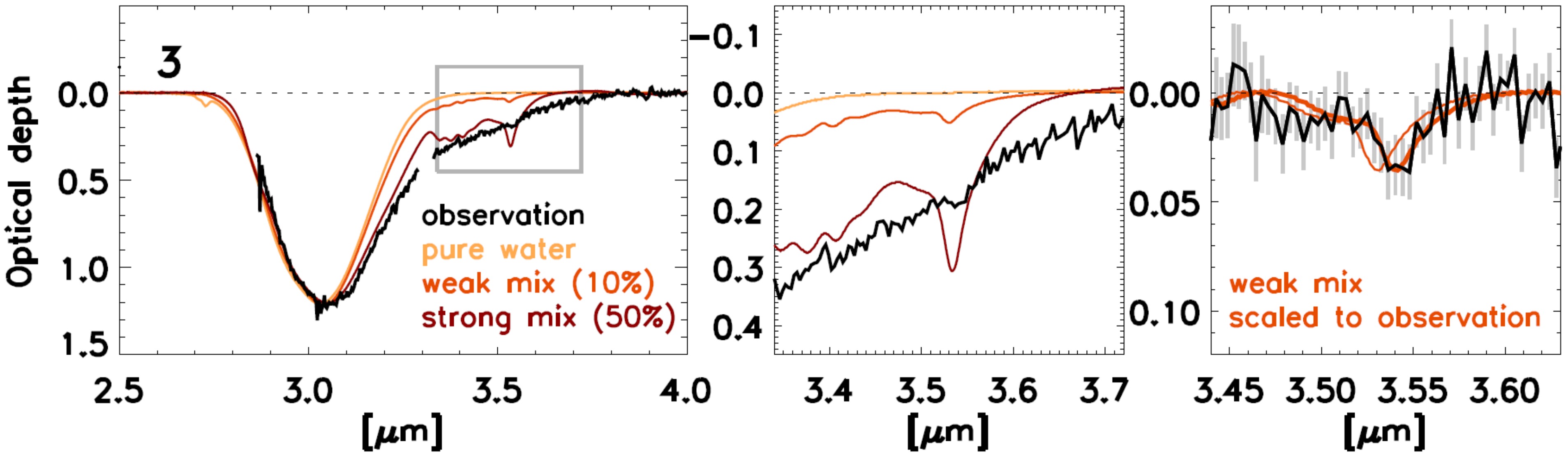


Fig. 3. Left: the spectrum of the source #3 (in black trace) compared to the laboratory ice spectra from Hudgins et al. (1993). The pure water ice

Goto, Vasyunin et al., submitted

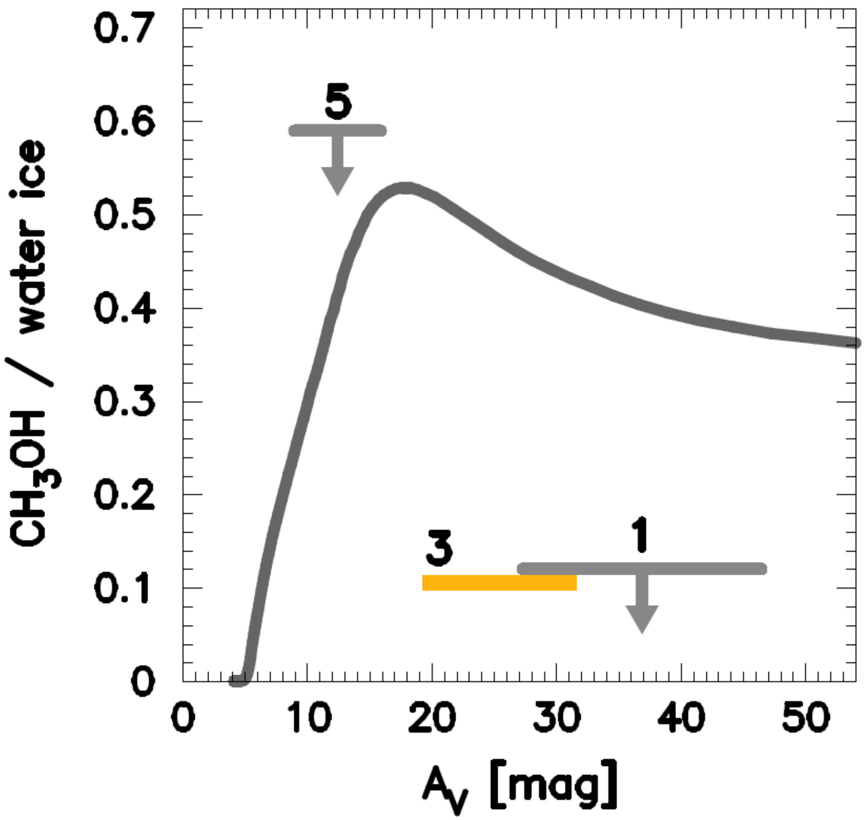


Fig. 6. Fraction of methanol-ice with respect to water-ice column density plotted as a function of the visual extinction A_V on the line of sight through the cloud. The gray curve is the model calculation by Vasyunin et al. (2017). The methanol to water ice ratio observed on source #3 is marked by a horizontal yellow line, with the extent of the line denoting the full range of A_V measured by different methods. The upper limits on the methanol ice abundance are shown with downward arrows in light gray for sources #1 and #5. The fraction of the methanol ice detected on #3 is 4.5 times smaller than is expected.

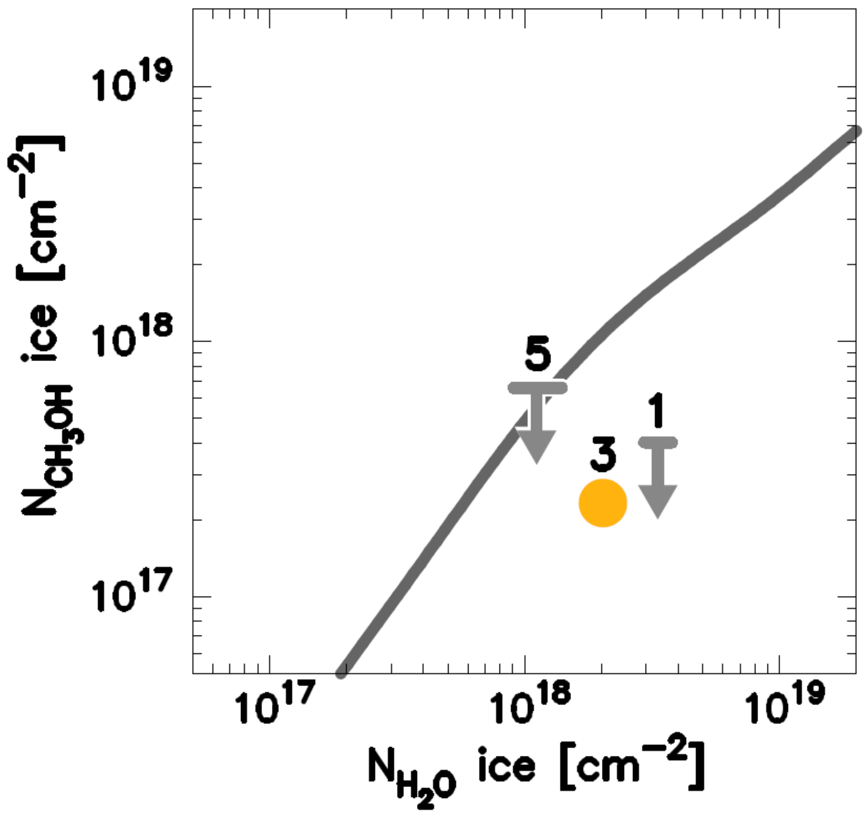
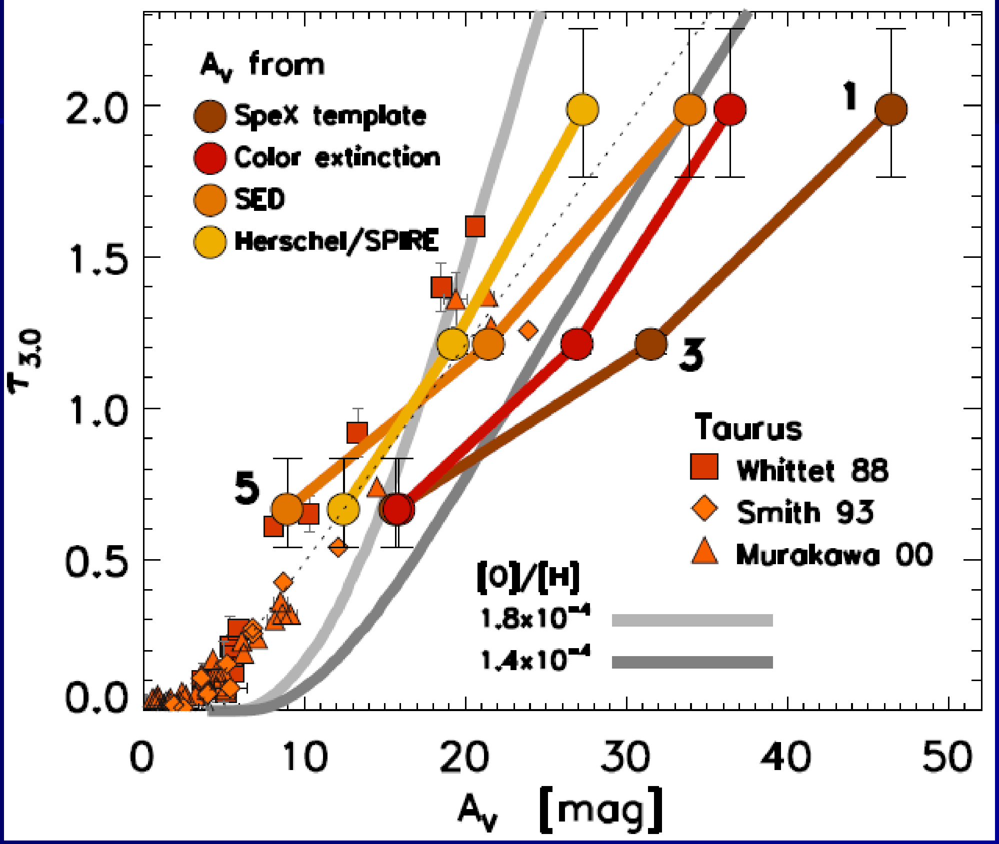


Fig. 7. Column density of methanol ice plotted against that of water ice. The gray curve is the model calculated by Vasyunin et al. (2017). The methanol ice column density on source #3 is shown in yellow circle. The uncertainty of the column densities are smaller than the size of the symbol. The upper limits on source #1 and #5 are shown in downward arrows. The extent of the horizontal bars denotes the uncertainty in $N(H_2O)^{ice}$. The methanol ice detected on source #3 and the upper limit set on source #1 are smaller than that of the model predictions by factors of 5.0 and 4.1, respectively.

Optical depth of water ice at 3 um vs. visual extinction



Goto, Vasyunin et al., submitted

Additional depletion of elemental oxygen is needed to fit observational trend

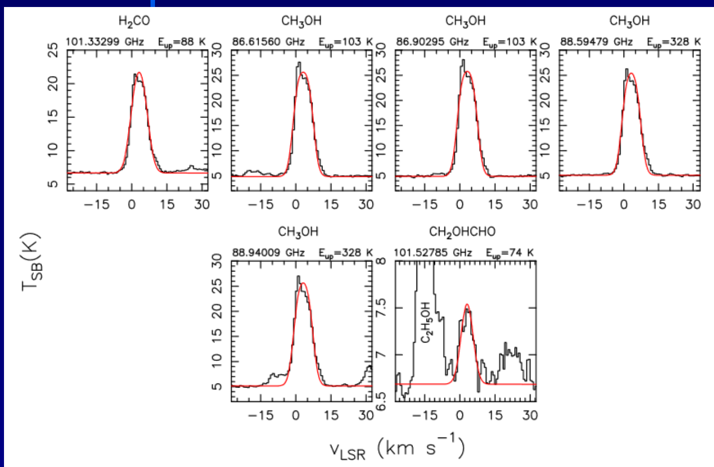
Hot core chemistry: IRAS16293 with ALMA

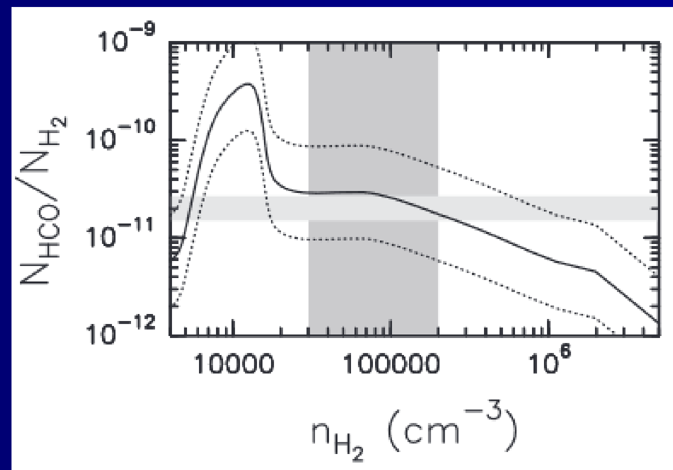
MNRAS 483, 806–823 (2019)
doi:10.1093/mnras/sty3078
Advance Access publication 2018 November 16

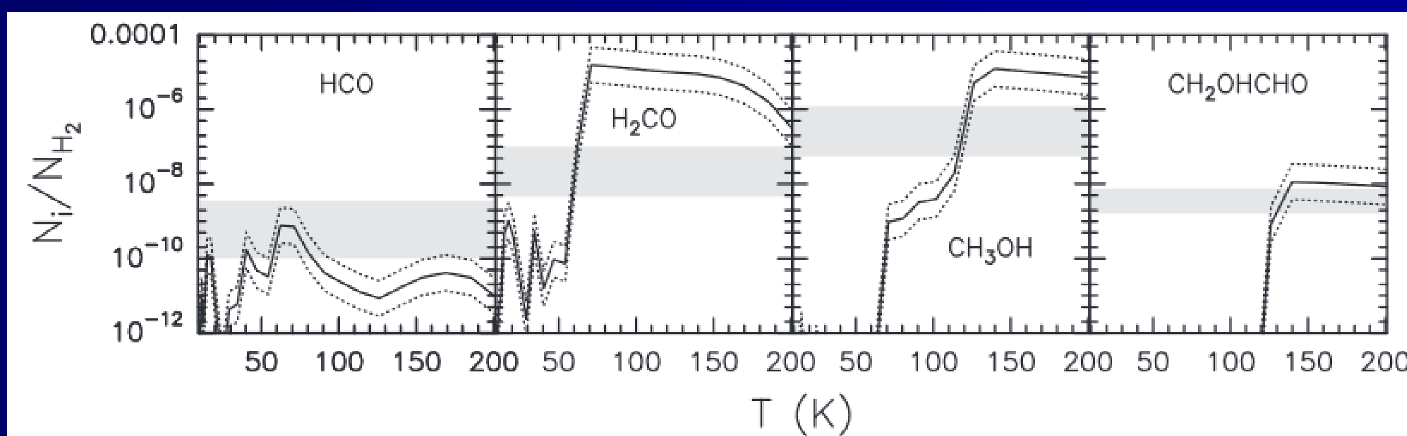
First ALMA maps of HCO, an important precursor of complex organic molecules, towards IRAS 16293–2422

V. M. Rivilla,[1★] M. T. Beltrán,[1] A. Vasyunin,[2,3,4] P. Caselli,[2] S. Viti,[5] F. Fontani[1] and R. Cesaroni[1]

A combination of hot and cold chemistries







Prebiotic but not organic?
PO in high-mass star-forming regions

The Astrophysical Journal, 826:161 (8pp), 2016 August 1
doi:10.3847/0004-637X/826/2/161

CrossMark

THE FIRST DETECTIONS OF THE KEY PREBIOTIC MOLECULE PO IN STAR-FORMING REGIONS

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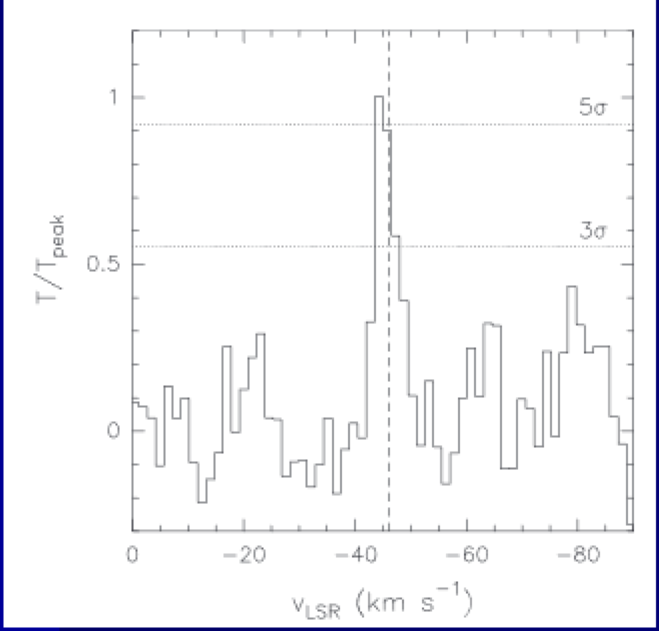
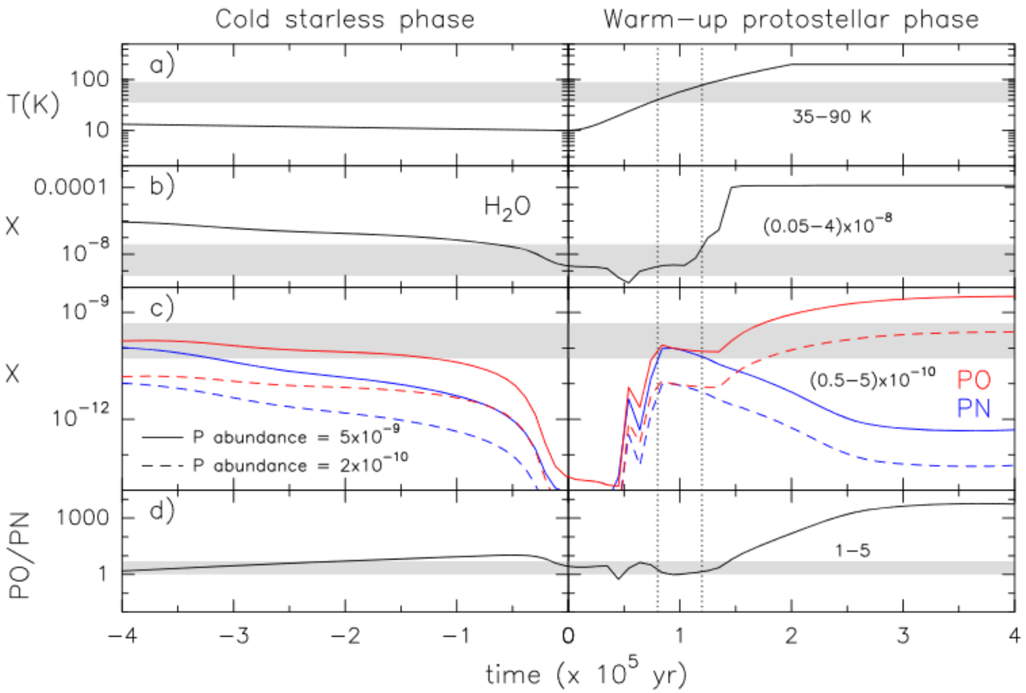
Received 2016 April 28; revised 2016 May 14; accepted 2016 May 17; published 2016 July 28





Conclusions

1. Studies of molecular inventory of star-forming regions is one of the most active fields in astrophysics/astrochemistry. The formation of COMs is one of the topics that attract most interest.

2. COMs are found at different stages of low-mass star formation: from the earliest stages represented by prestellar cores and up to protoplanetary disks

3. Modern observational facilities, already working and those to be launched soon (JWST) are the key driver of the progress in the field

4. A variety of physical and chemical mechanisms lead to the formation of COMs in Space. Many of those mechanisms are yet to be explored in details

5. Laboratory studies are very valuable for the understanding of chemistry in space.

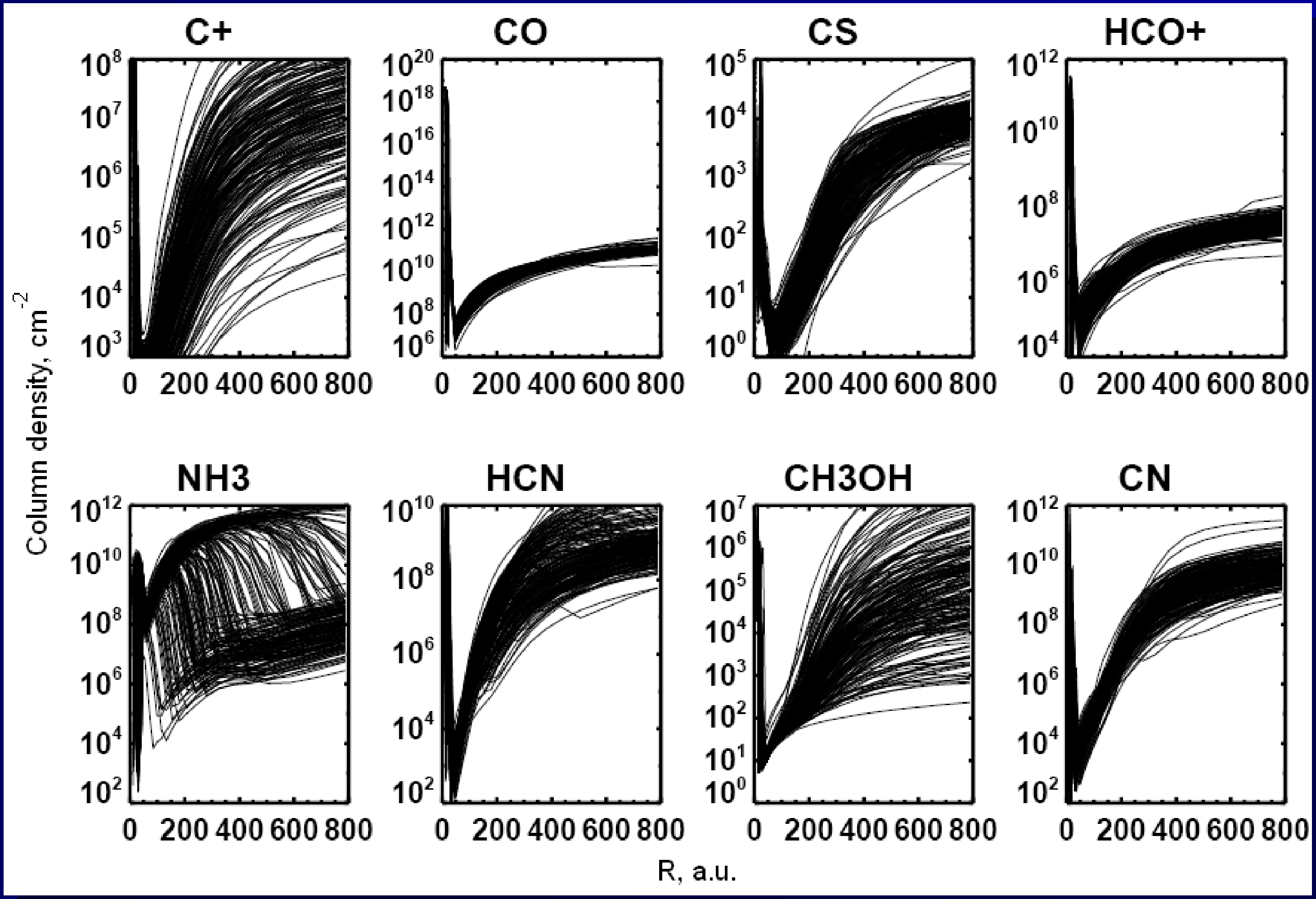
Thank you for your attention!

Financial support by

UrFU («5-100»)
RScF, project 18-12-00351
LZP, project lzp-2018/1-0170

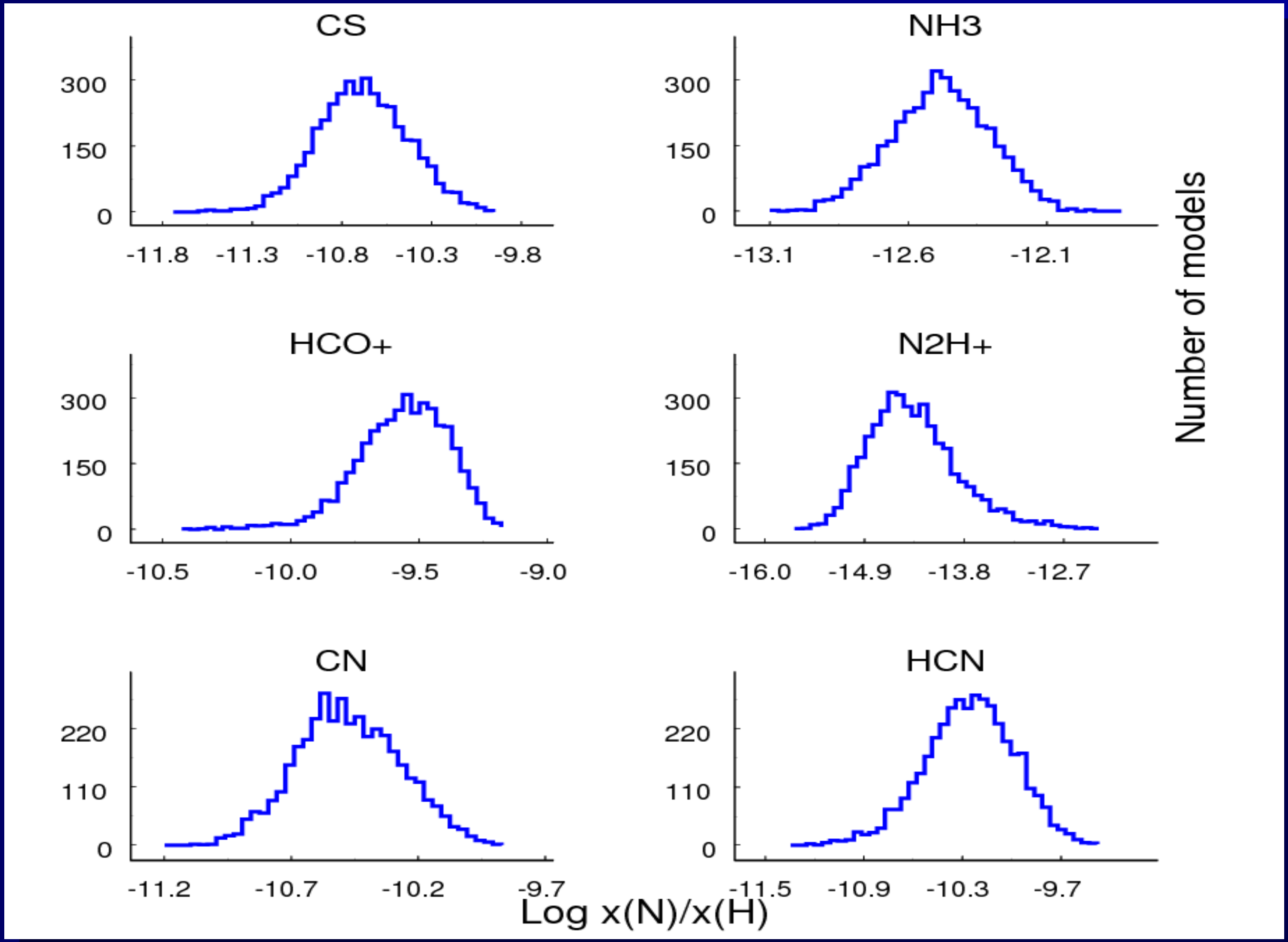
Extra slides

Uncertainties in astrochemical modeling (Vasyunin et al., 2004, 2008)



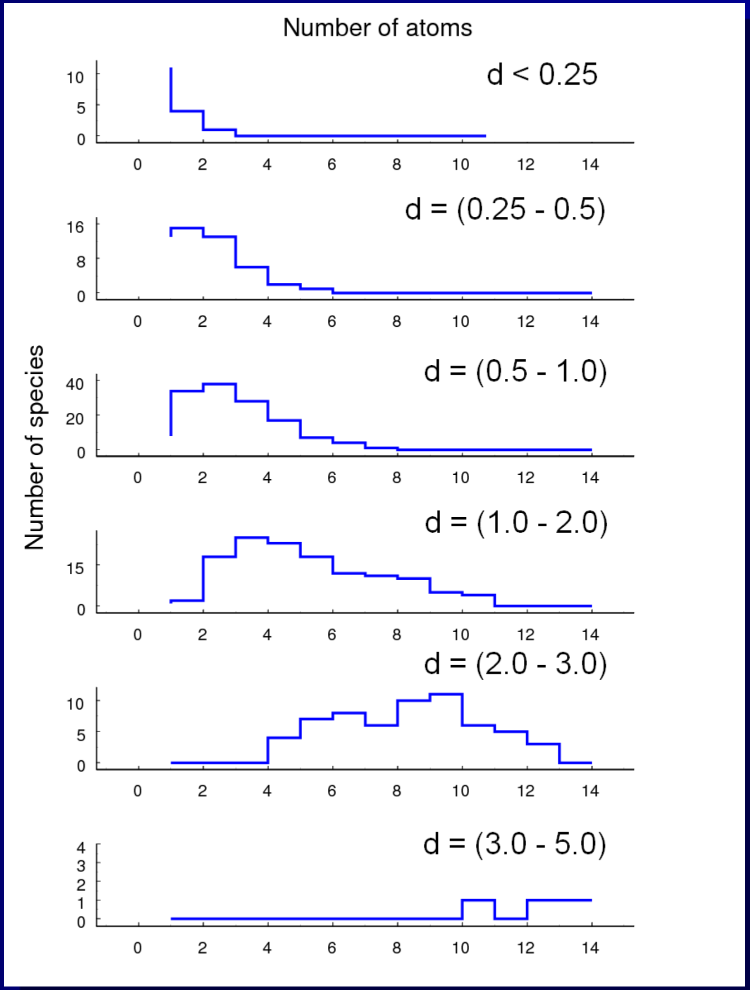
Uncertainties in astrochemical modeling (Vasyunin et al., 2004, 2008)

Shape of abundance distributions is almost Gaussian:



Uncertainties in astrochemical modeling (Vasyunin et al., 2004, 2008)

Uncertainty grows up with complexity of a species:



Uncertainties in astrochemical modeling (Vasyunin et al., 2004, 2008)

Identification of most "uncertain" reactions:

H_2 + C.R.P. -> H_2^+ + e^- N + CH -> CN + H