Acknowledge:
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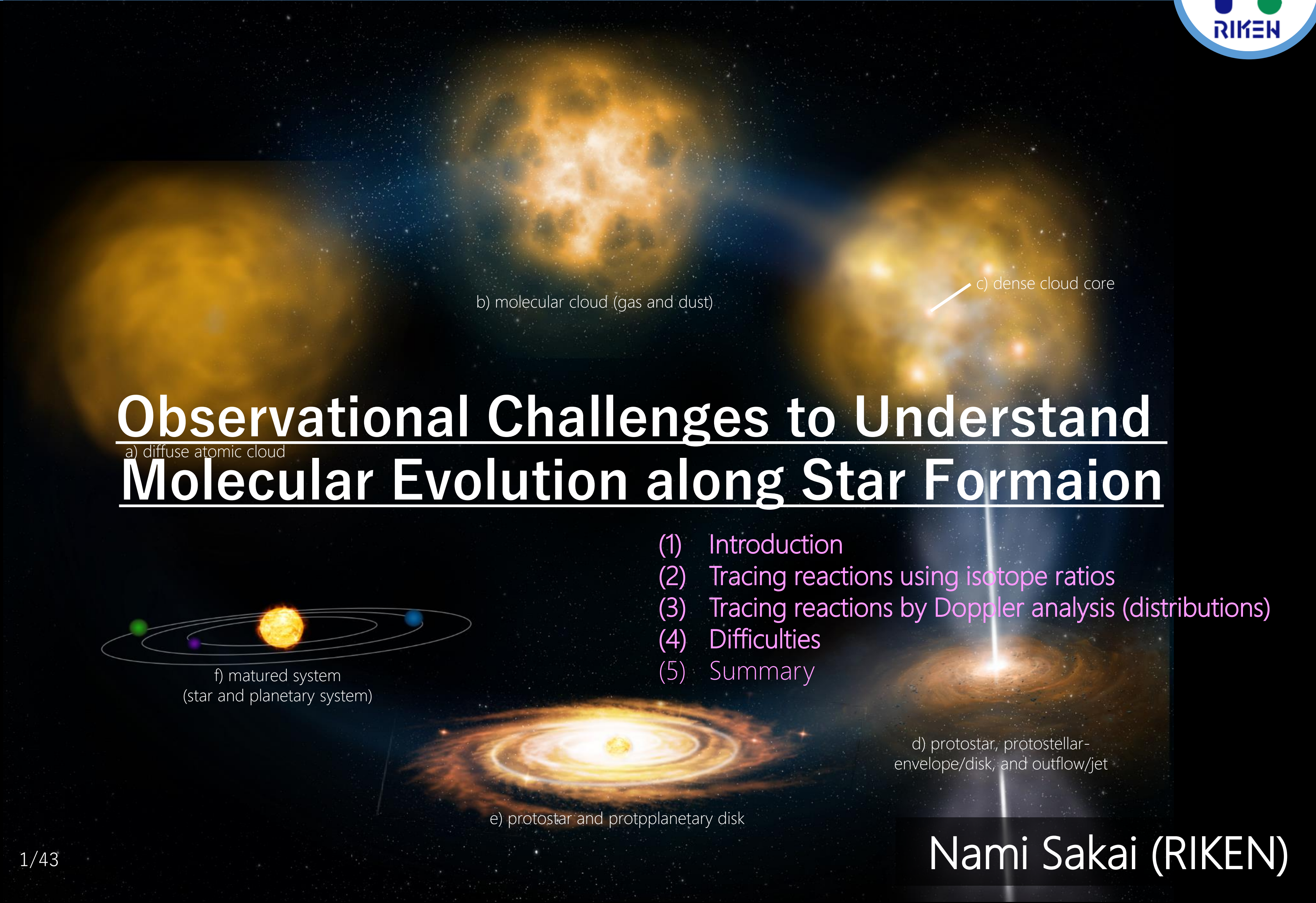
RIKEN

Observational Challenges to Understand Molecular Evolution along Star Formaion



(1) Introduction
(2) Tracing reactions using isotope ratios
(3) Tracing reactions by Doppler analysis (distributions)
(4) Difficulties
(5) Summary

Nami Sakai (RIKEN)

Molecules in Space (~200 species)

2 Atoms (42 Species)
H_2, CO, AlF, AlCl, C_2, C… CS, HF, HD, FeO (?),
O_2, CF^+, SiH (?), PO, Al…

3 Atoms (40 Species)
C_3, C_2H, C_2O, C_2S, CH_2, … CN, OCS, SO_2, c-SiC_2,
CO_2, NH_2, H_3^+, SiCN, Al…

4 Atoms (27 Species)
c-C_3H, l-C_3H, C_3N, C_3O, … iC_3, CH_3, C_3N^-, PH_3,
HCNO, HOCN, HSCN, H…

5 Atoms (23 Species)
C_5, C_4H, C_4Si, *l*-C_3H_2, c-… OH$^+$, C_4H^-, HC(O)CN,
HNCNH, CH_3O, NH_4^+, H…

6 Atoms (17 Species)
C_5H, *l*-H_2C_4, C_2H_4, CH_3… O, H_2CCNH (?), C_5N^-,
HNCHCN

7 Atoms (10 Species)
C_6H, CH_2CHCN, CH_3C_2H…

8 Atoms (11 Species)
CH_3C_3N, $HC(O)OCH_3$, C… CH_3CHNH

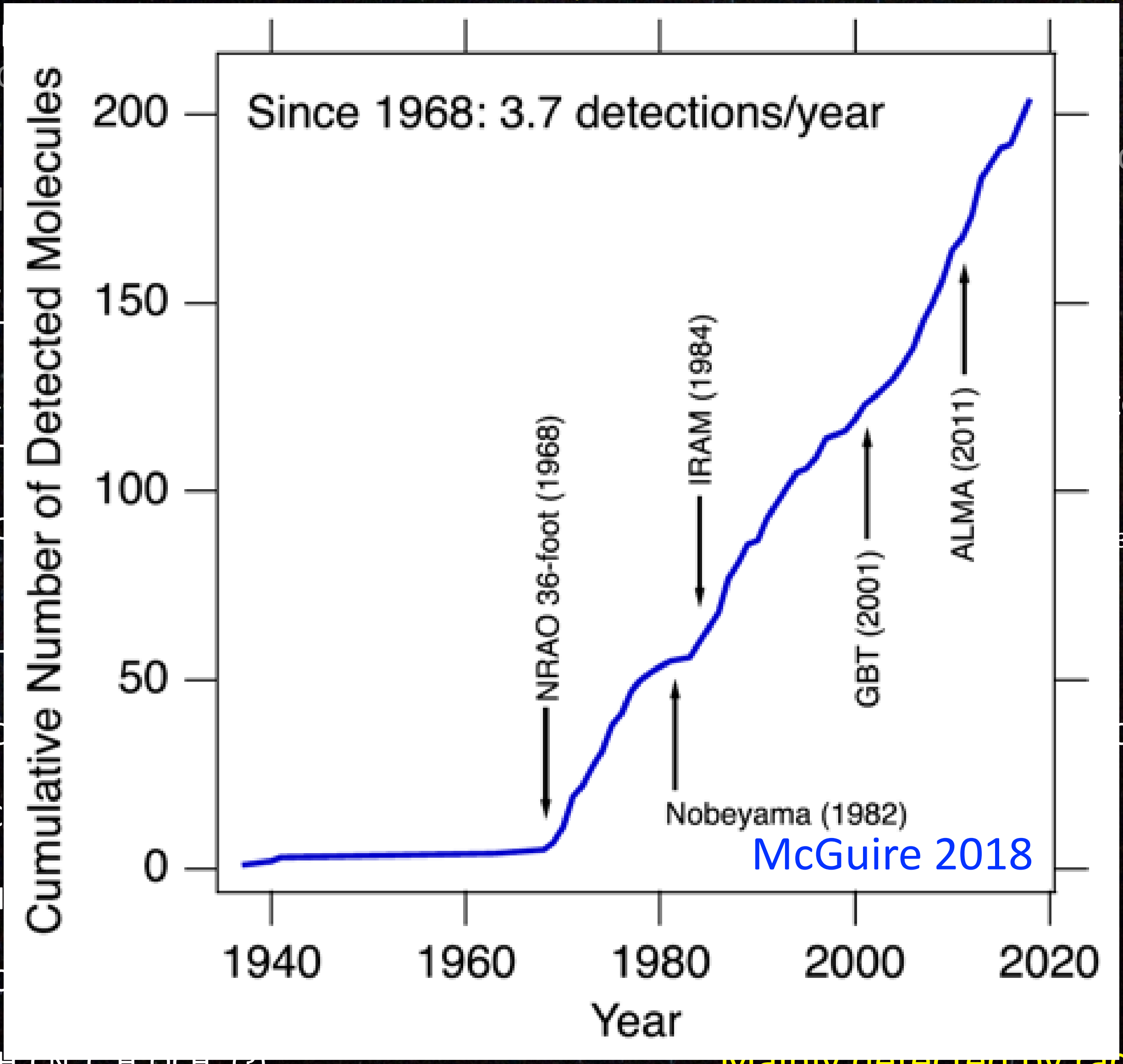
9 Atoms (10 Species)
CH_3C_4H, CH_3CH_2CN, (C…

10 Atoms (5 Species)
CH_3C_5N, $(CH_3)_2CO$, (CH…

11 Atoms (4 Species)
HC_9N, CH_3C_6H, C_2H_5OC…

12 Atoms (4 Species)
c-C_6H_6, n-C_3H_7CN, i-C_3H_7CN, $C_2H_5OCH_3$ (?)

>12 Atoms (3 Species)
C_{60}, C_{70}, C_{60}^+



Mainly detected by radio observations

(Gray: Detected toward AGB stars)
(The Cologne Database for Molecular Spectroscopy (CDMS): Nov. 2016.)

Non-equilibrium Chemistry

Formation of Molecules: H_3^+ chemistry (ex; CO)

$$H_3^+ + C \to CH^+ + H_2,$$
$$CH^+ + H_2 \to CH_2^+ + H,$$
$$CH_2^+ + H_2 \to CH_3^+ + H,$$
$$CH_3^+ + e \to (CH_2 + H) \text{ or } (CH + H + H),$$
$$CH + O \to CO + H.$$

$$\tau_f \sim \frac{1}{k[H_3^+]} = \frac{[CO]}{\zeta[H_2]} = \frac{f_{CO}}{\zeta} \sim 3\times10^5 \text{ yr}$$

⇒typically~10^6 yr

$$H_2 \xrightarrow{cr} H_2^+ + e$$
$$H_2^+ + H_2 \to H_3^+ + H$$
$$H_3^+ + CO \to HCO^+ + H_2.$$
$$\zeta[H_2] = k[CO][H_3^+].$$

$$\frac{d[H_3^+]}{dt} = k[H_2^+][H_2] - k[CO][H_3^+] = 0$$
$$\frac{d[H_2^+]}{dt} = \zeta[H_2] - k[H_2^+][H_2] = 0$$

Destruction : Reaction with He^+

$$\frac{d[He^+]}{dt} = \zeta[He] - k[He^+][CO] = 0$$

$$\tau_d \sim \frac{1}{k[He^+]} = \frac{[CO]}{\zeta[He]} \sim 1.4\times10^7 \text{ yr}$$

ζ: Cosmic ray ionization rate(~10^{-17} s^{-1})
k: Langevin rate(~10^{-9} cm^3 s^{-1})

~10^7 yr at Av > 5 cloud (Ionic Destruction: slow)
~10^2 yr at Av < 3 cloud (Photodissociation: fast)

$$A \underset{\tau_d}{\overset{\tau_f}{\rightleftarrows}} A'$$

→ $\tau \sim 10^6$ yr

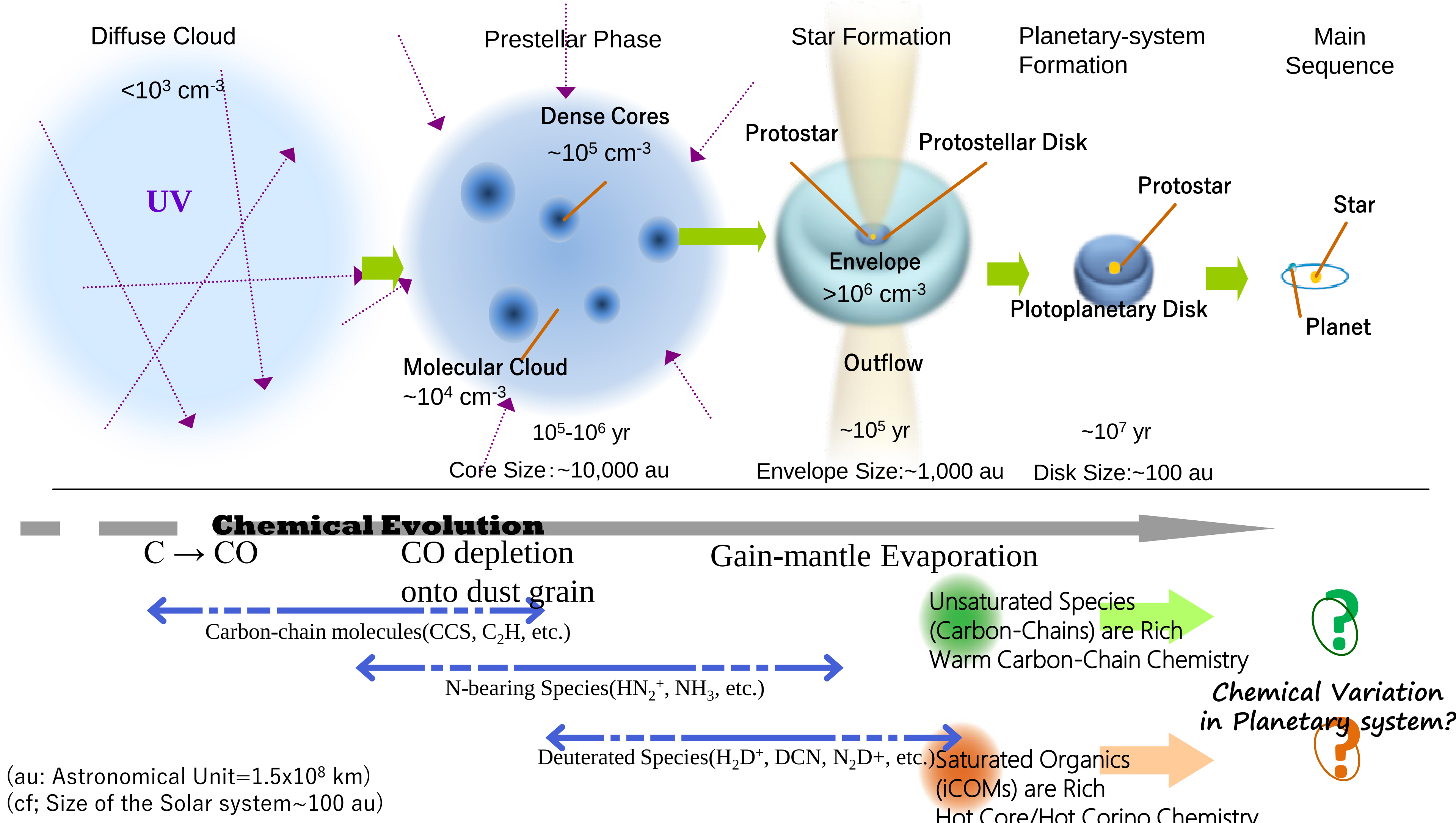
$$\frac{1}{\tau} = \frac{1}{\tau_f} + \frac{1}{\tau_d}$$

$$\tau \gtrsim \tau_{dyn}$$

Dynamical time (free-fall time)

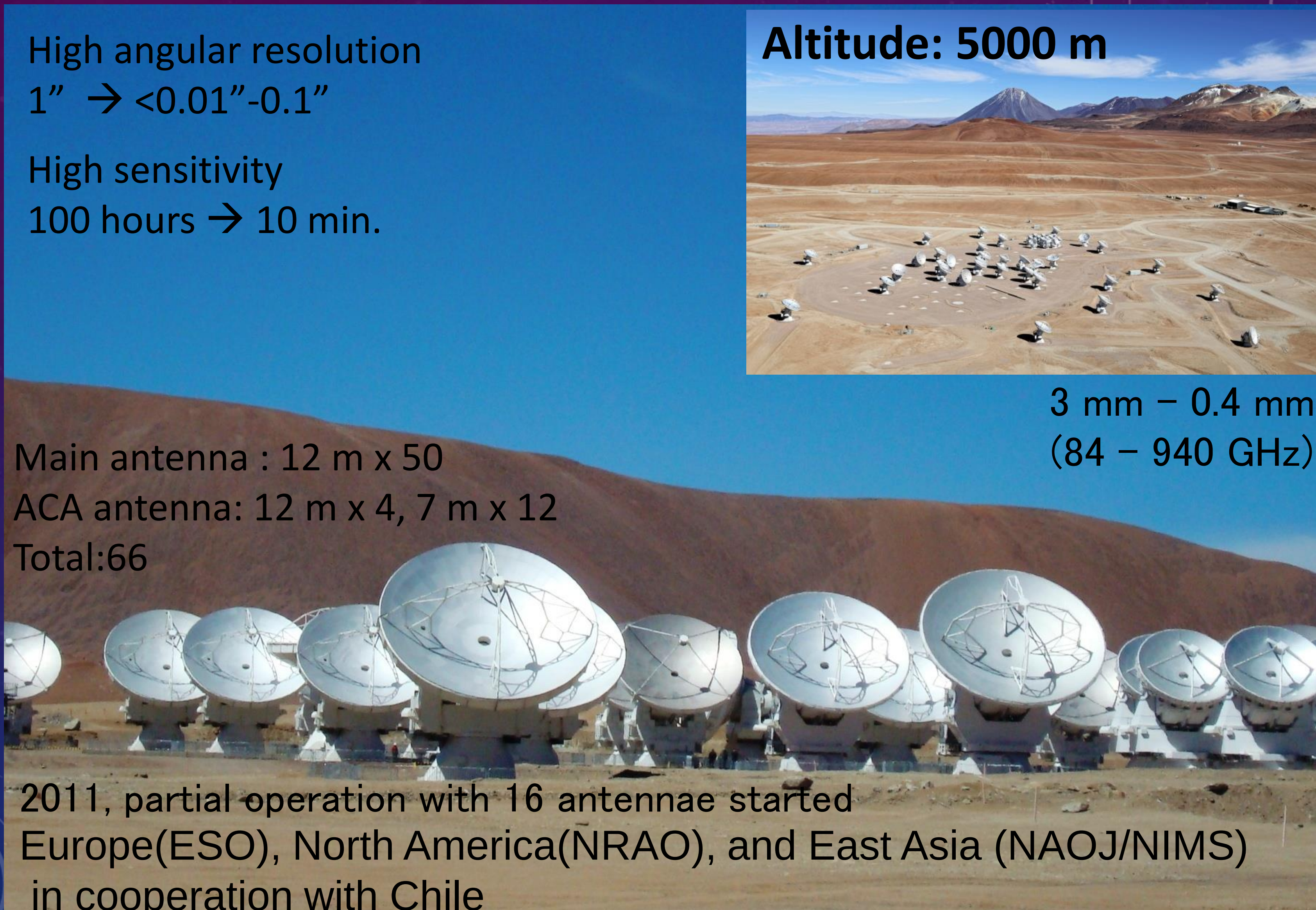
$$t_{\text{free fall}} = \frac{4\times10^5}{\sqrt{n/10^4 \text{ cm}^{-3}}} \text{ yr}$$

Chemical Evolution & Star Formation



GREY CHOW / CATERS NEW

アルマ望遠鏡(アタカマ 大型ミリ波/サブミリ波 干渉計)
(ALMA: Atacama Large Millimeter/sub-millimeter Array)



High angular resolution
1” → <0.01”-0.1”

High sensitivity
100 hours → 10 min.

Altitude: 5000 m

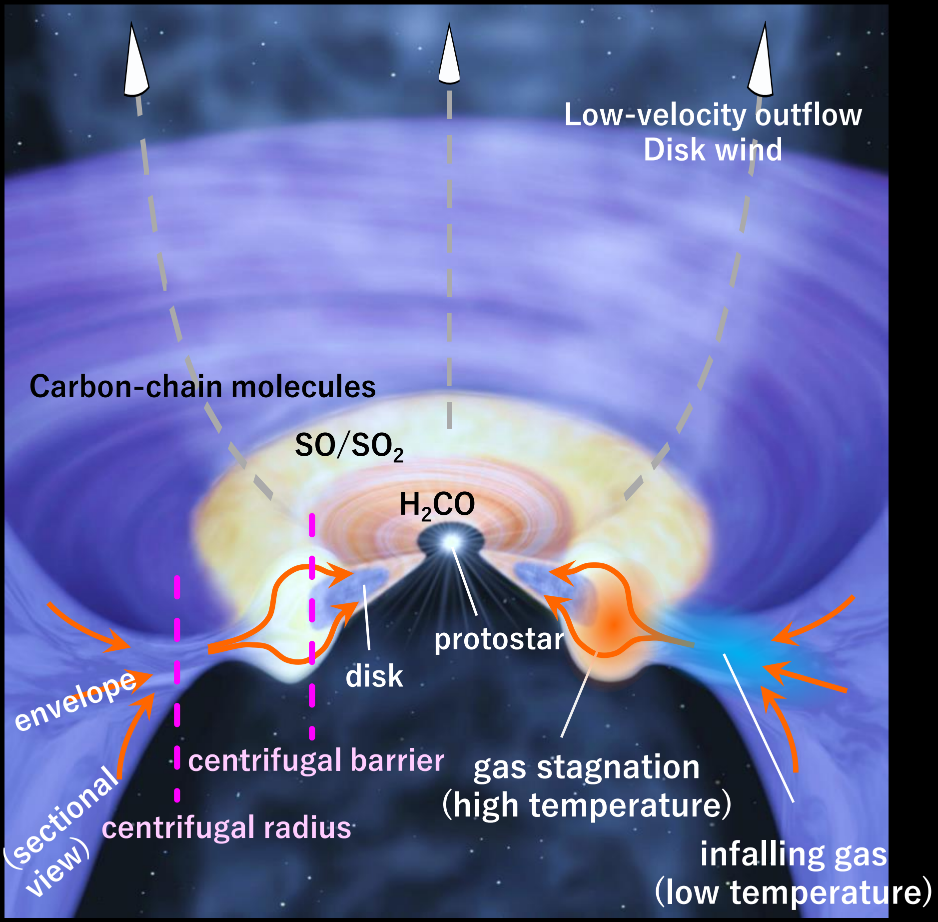
3 mm – 0.4 mm
(84 – 940 GHz)

Main antenna : 12 m x 50
ACA antenna: 12 m x 4, 7 m x 12
Total:66

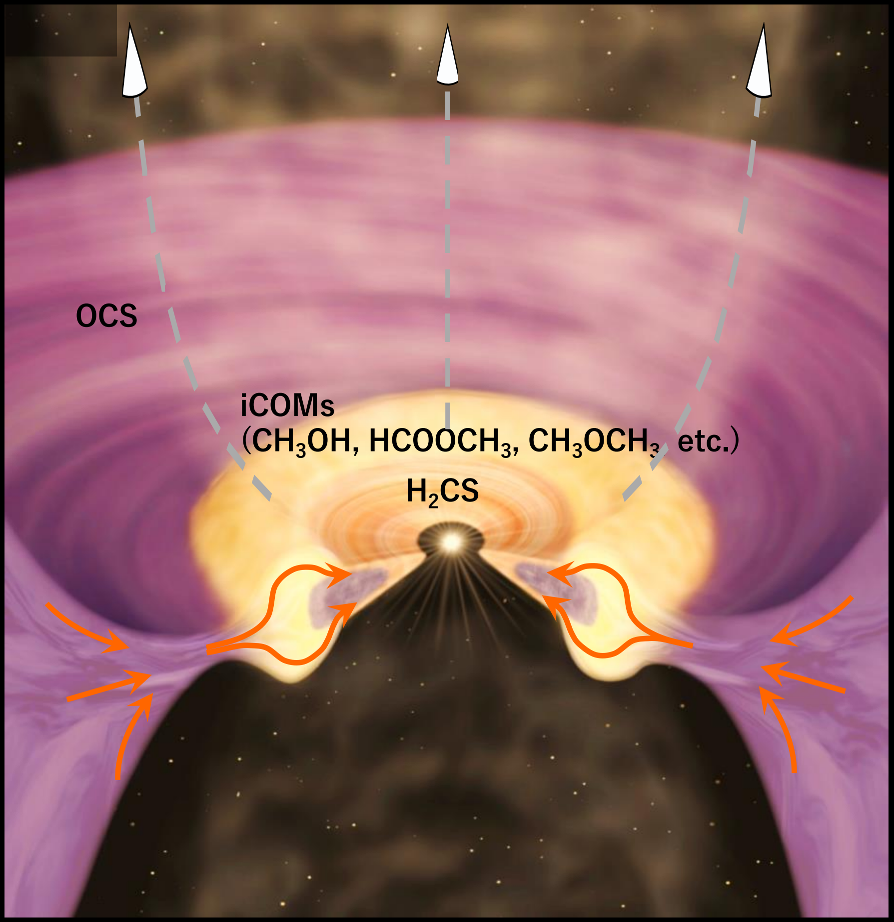
2011, partial operation with 16 antennae started
Europe(ESO), North America(NRAO), and East Asia (NAOJ/NIMS) in cooperation with Chile

- At least two different chemical environments are recognized
- Edge of the disk is highlighted by chemical change

Characterized by unsaturated species (ex: L1527)



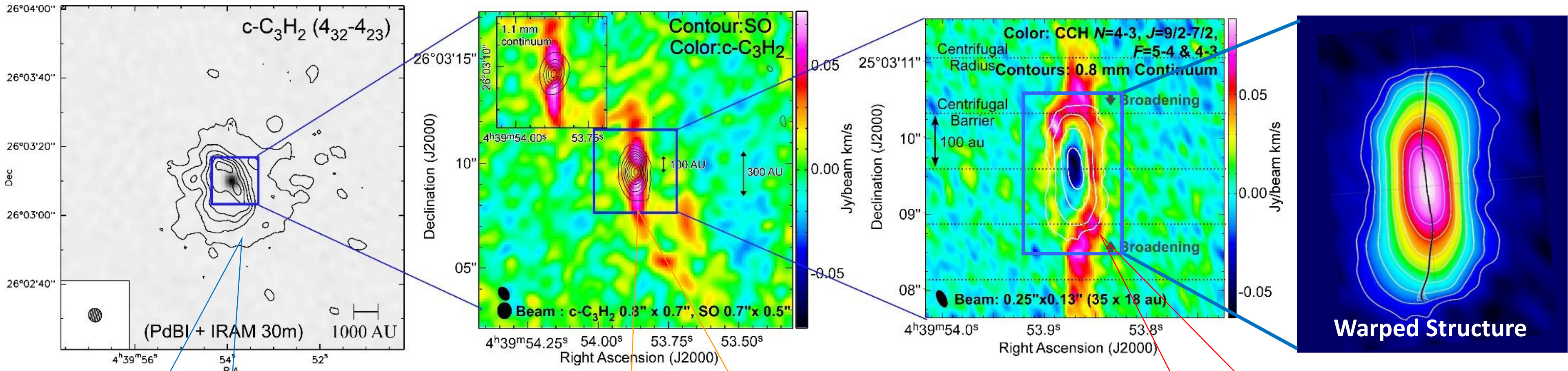
Characterized by saturated species (ex: IRAS16293-2422A/B)



(e.g. Sakai et al. 2014, Nature 507, 78; 2014, ApJ, 791, L38; 2017, MNRAS, 467, L76; Oya et al. 2016, ApJ, 824, 88; 2018, ApJ, 854, 96)

Progress in the last decade

<2010	2014	2017	2019
1,000 au:	100 au:	30 au:	10 au:
Before ALMA	ALMA Cycle 0	Cycle 2	Cycle 4



Outer Envelope
(Association of Carbon-Chain Molecules)

Identification of Centrifugal Barrier
(Drastic Chemical Change, Transition from the Envelope to Disk)

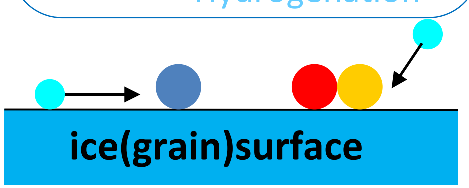
Gas Stagnation
in front of the Centrifugal Barrier
(Frontier of Disk Formation, Angular Momentum Extraction)

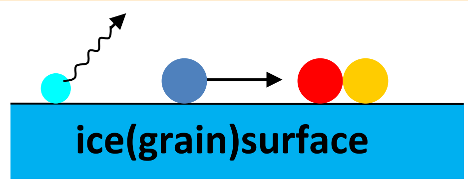
Dust Growth
Spiral/Ring Structure

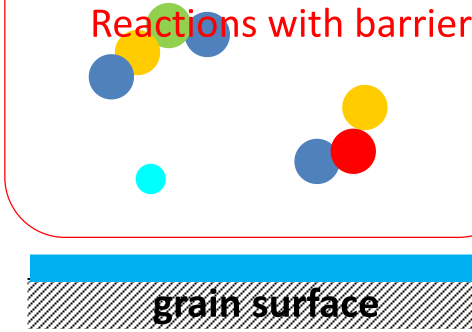
T ~ 10K
Density>10^5cm^{-3}
- Depletion
- Surface reactions
  e.g. CO → CH_3OH
  Hydrogenation

20K < *T*< 100K, Density>10^7cm^{-3}
Surface reactions of heavy elements
cosmic ray induced UV
gas-phase reactions
→ Complex organic molecules

T>100 K, Evaporation
Gas-phase reactions
Reactions with barrier?







(Sketch provided by Y. Aikawa)

(Sakai+2010, *ApJ*, 722, 1633;+2014, *Natur.* 507, 78; +2014, *ApJ*, 791, L38; +2017, *MNRAS*, 467, L76; +2019, *Natur.*. 565, 206)

How to Know the Details?

- How those molecules are formed ?
- Can we distinguish gas-origin and grain-surface-origin?
- Future of the ice composition in hot Corino vs WCCC
  CH_3OH/COMs vs (CH_4 or H_2CO)
- Polymerization of carbon-chain molecules after the depletion?
- Formation/destruction of Sulfur-bearing species are not known well.

→ Chemical Model? Lab. Experiment? **Observational constraints!**

Photo: Cygnus

Back to Starless Cores

-Molecular $^{12}C/^{13}C$ ratios-

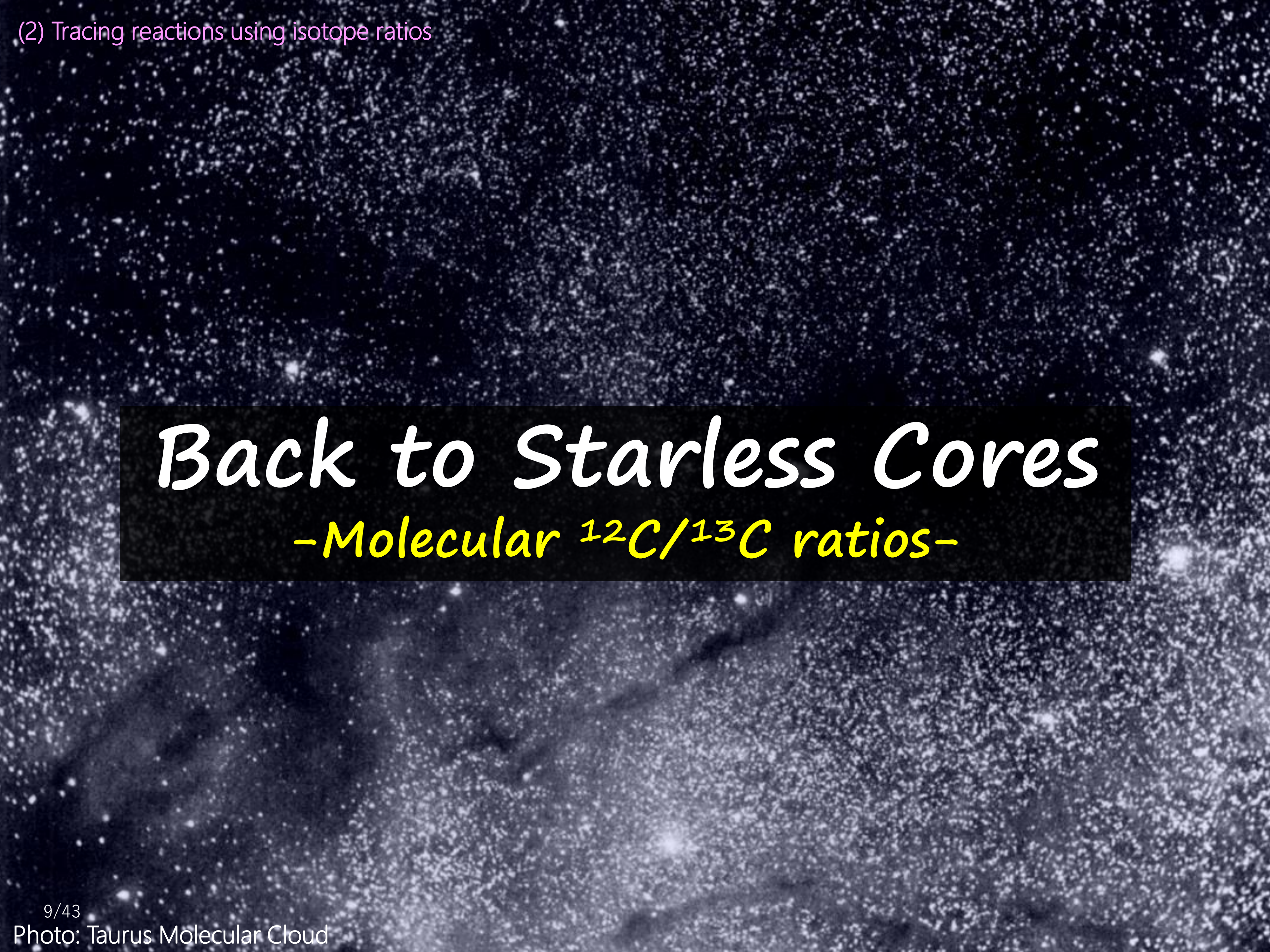
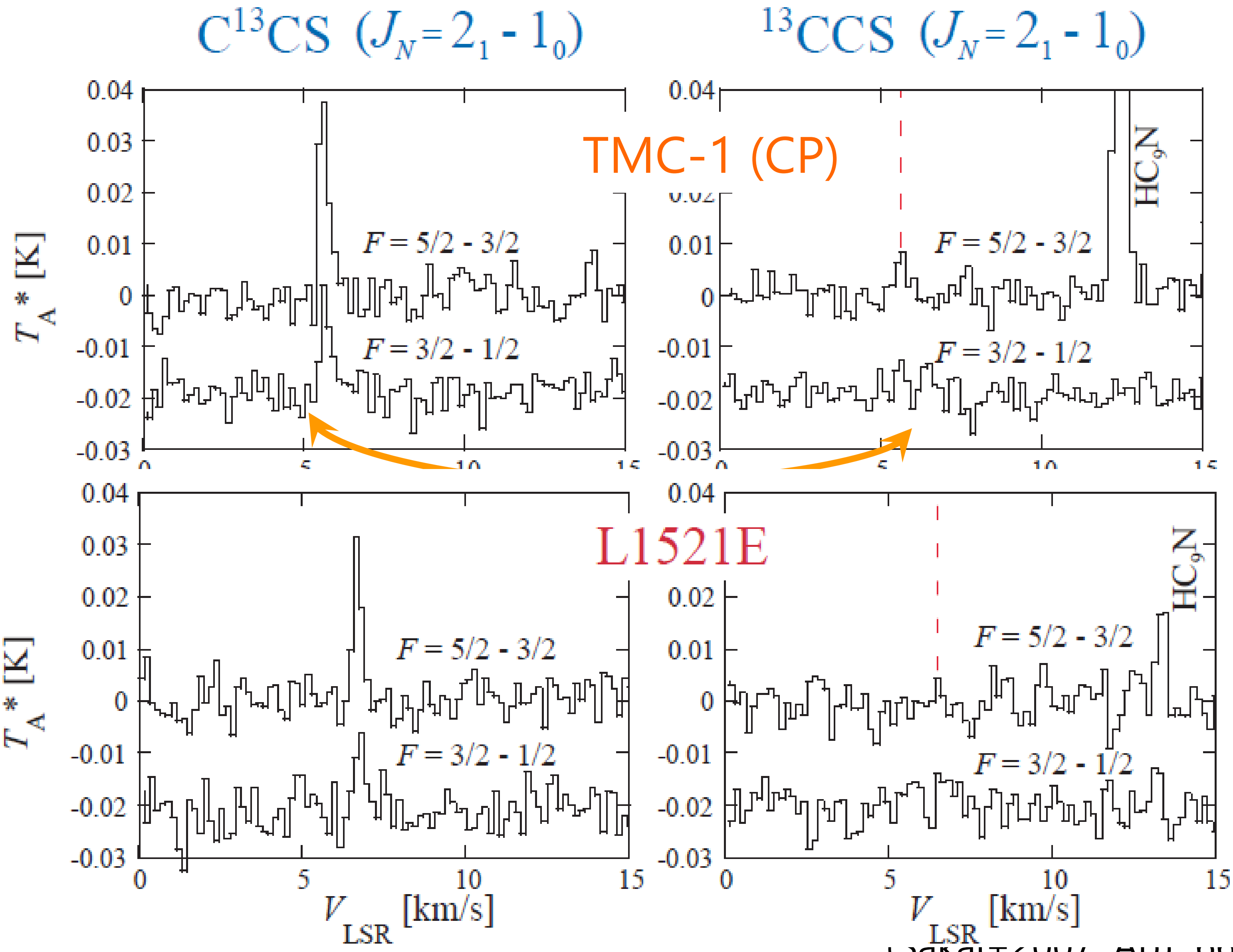


Photo: Taurus Molecular Cloud

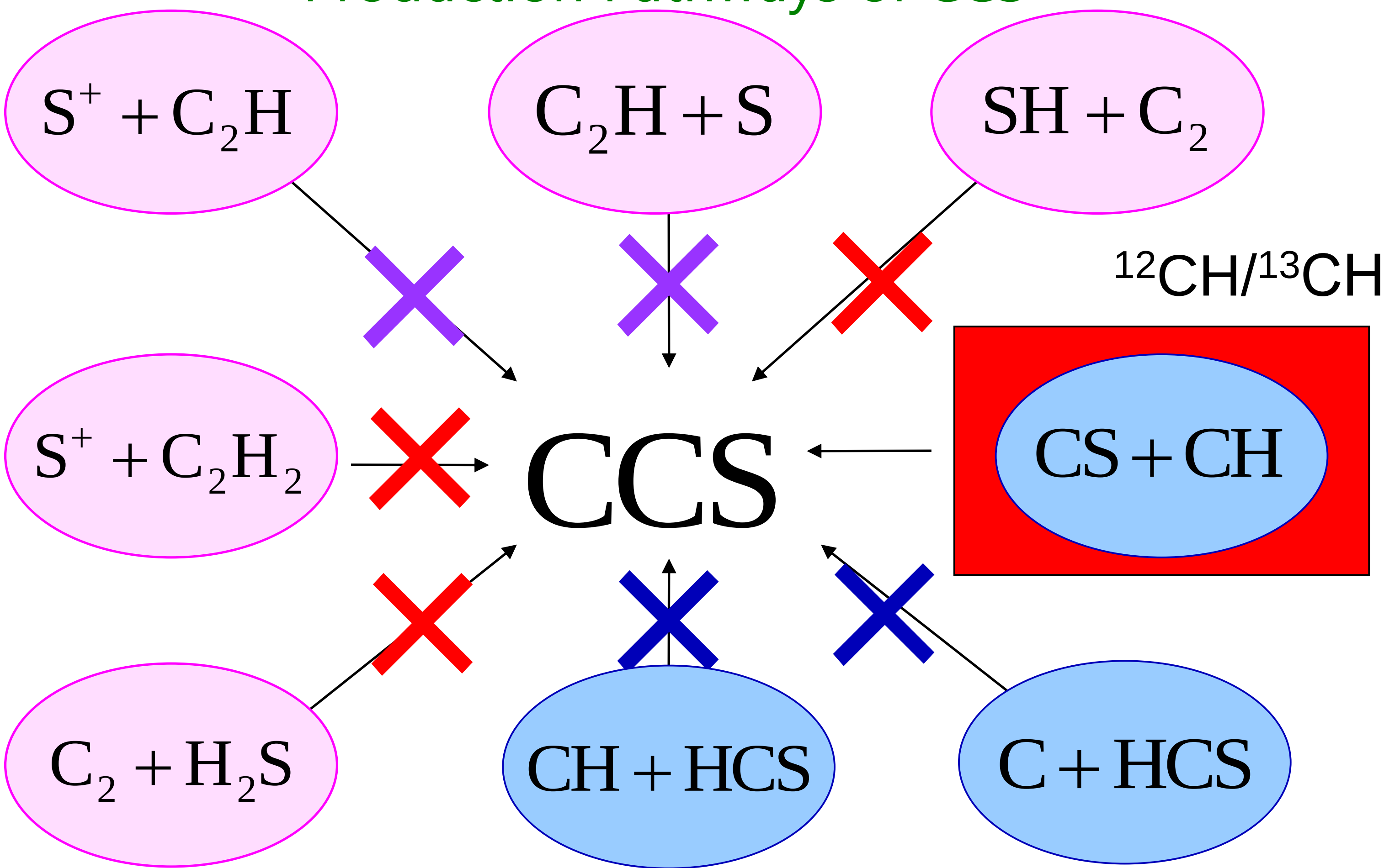
Abundance Anomaly: ^{13}C species of CCS



(Sakai+2007, ApJ 663, 1174)

Case study: CCS

Production Pathways of CCS



$^{12}CH/^{13}CH$ > 70 (3σ)

> 210 (1σ)

Most Probable Route

(Millar & Herbst.1990, Petrie+1996, Yamada+2002)

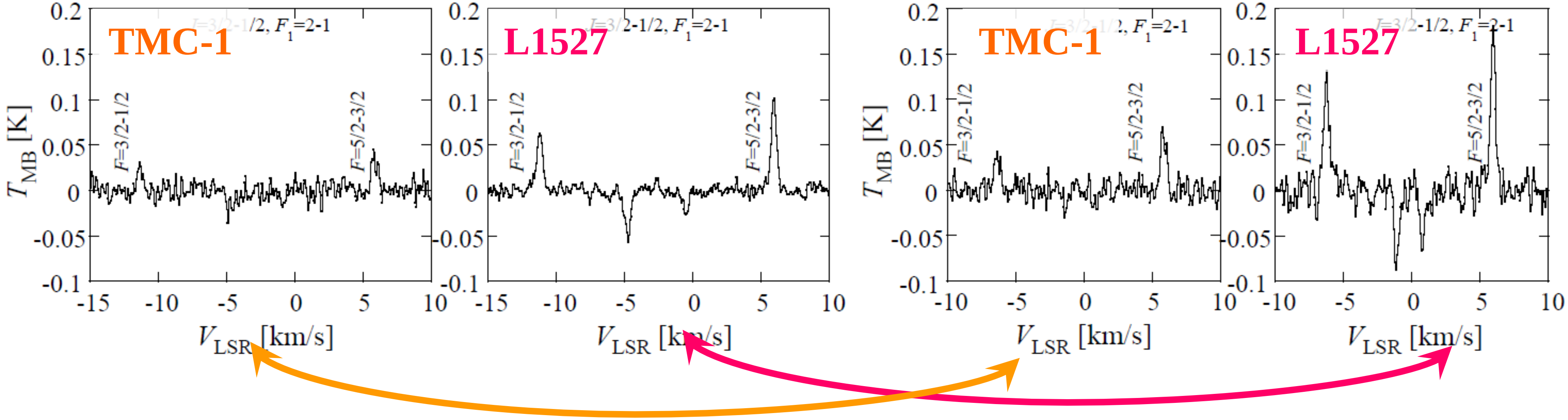
Nonequivalent route 76%↑

~~Equivalent routes~~

 (Sakai+2007, ApJ 663, 1174)

Abundance Anomaly: ^{13}C species of CCH

^{13}CCH $\qquad\qquad$ C^{13}CH



R = 1.6 ± 0.4 (3σ) $\qquad$ R = 1.6 ± 0.1 (3σ)

If CCS is formed via S$^+$ +CCH…

$$S^+ + {}^{13}CCH \rightarrow C^{13}CS + H$$

$$S^+ + C^{13}CH \rightarrow {}^{13}CCS + H$$

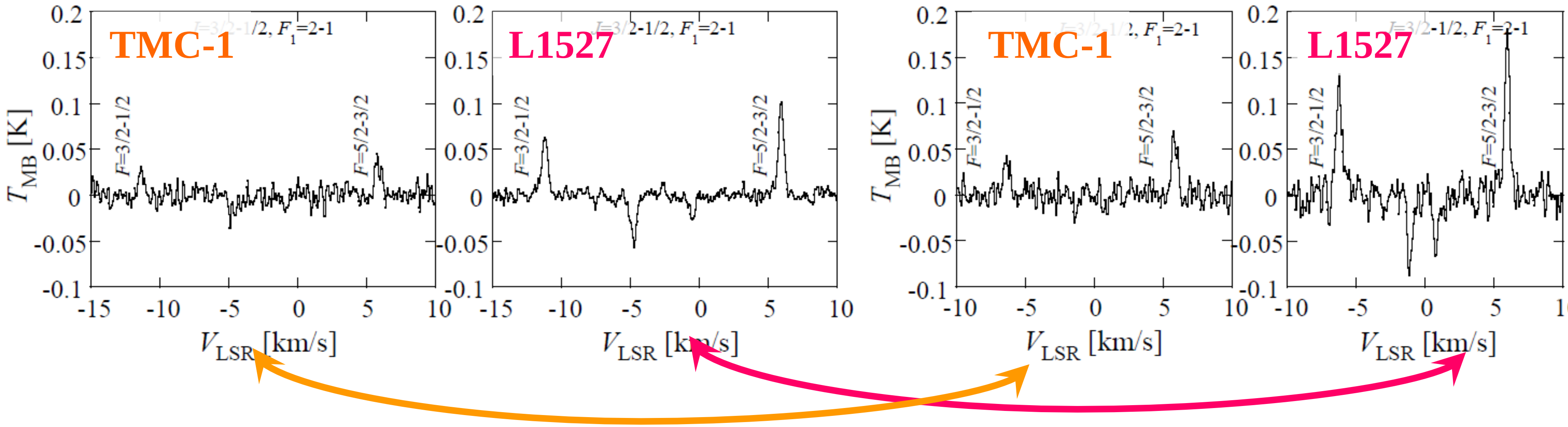
Opposite !

IRAM 30 m

(Sakai+2010, A&A, 512, A31)

Abundance Anomaly: ^{13}C species of CCH

^{13}CCH | C^{13}CH



R = 1.6 ± 0.4 (3σ) | R = 1.6 ± 0.1 (3σ)

Production pathways of CCH

$HCCH^+ + e \rightarrow CCH + H$

$C_2H_3^+ + e \rightarrow CCH + H_2$

$CH_2 + C \rightarrow CCH + H$

IRAM 30 m

(Sakai+2010, A&A, 512, A31)

$^{12}C/^{13}C$ Ratio to Trace the Reactions

Anomaly of the $^{12}C/^{13}C$ ratios in the starless core, TMC-1(CP)

$CH/^{13}CH$	>71 (3σ)	$CCCCH/^{13}CCCCH$	141 ± 44 (3σ)
$CCH/^{13}CCH$	>250	$CCCCH/C^{13}CCCH$	97 ± 27 (3σ)
$CCH/C^{13}CH$	>170	$CCCCH/CC^{13}CCH$	82 ± 15 (3σ)
$CCS/^{13}CCS$	230 ± 130 (3σ)	$CCCCH/CCC^{13}CH$	118 ± 23 (3σ)
$CCS/C^{13}CS$	54 ± 5 (3σ)	$HCCCN/H^{13}CCCN$	79 ± 11 (1σ) (Takano+1997)
$CCCS/^{13}CCCS$	>206 (3σ)	$HCCCN/HC^{13}CCN$	75 ± 10 (1σ) (Takano+1997)
$CCCS/C^{13}CCS$	48 ± 15 (3σ)	$HCCCN/HCC^{13}CN$	55 ± 7 (1σ) (Takano+1997)
$CCCS/CC^{13}CS$	30–206	HC_5N/HC_5N ^{13}C isotopomers	82-103 (Takano+1990, Taniguchi+2016)
(*e.g.* Sakai et al. 2013, JPC, 117, 9831)		HC_7N/average ^{13}C isotopomers	87^{+35}_{-19} (1σ) (Langston & Turner 2007)

Interstellar $^{12}C/^{13}C$ ratio : 60-70

e.g.
Lucas & Liszt (1998): 59, derived from HCO^+, HCN, & HNC
Milam+(2005): 68, derived from CO, CN, & H_2CO

Different ratios in the same species.
Dilution of ^{13}C in molecules.

^{13}C-Dilution Mechanism in Molecules

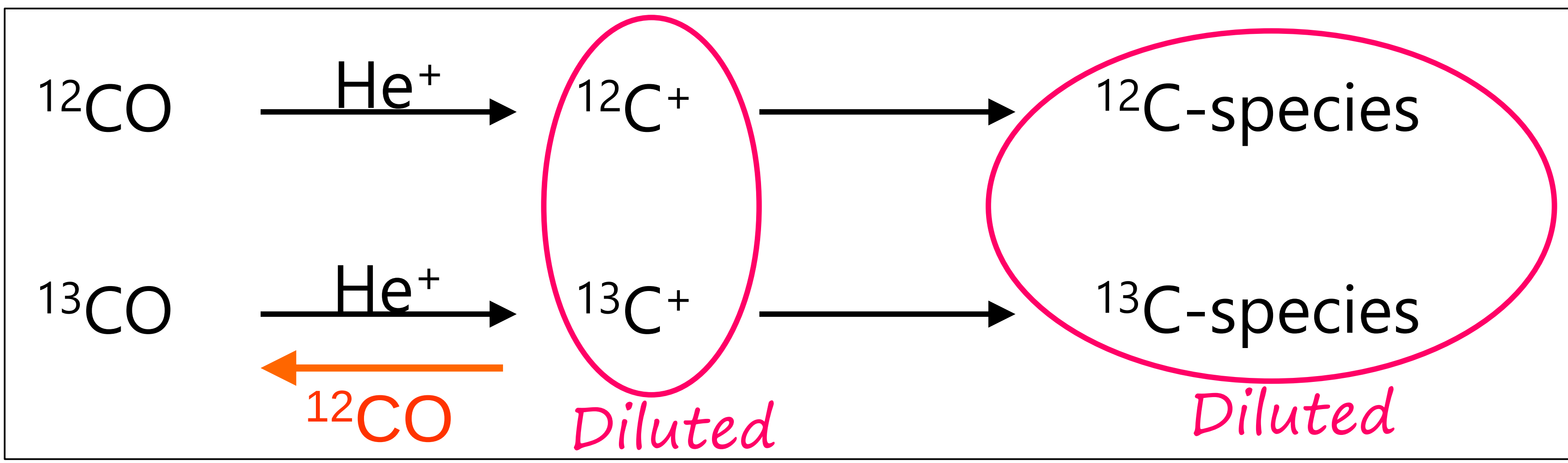
- Main reservoir of ^{13}C in molecular cloud → ^{13}CO
- Source of $^{13}C^+$ for production of molecules

  $CO + He^+ \rightarrow C^+ + O + He$ (→Original $^{12}C^+/^{13}C^+$=60-70)

- Main loss process of $^{13}C^+$

  $^{13}C^+ + {}^{12}CO \rightarrow C^+ + {}^{13}CO + 35$ K

  ⇨ High ^{12}C/^{13}C ratio in various molecules



R ~ 60-70 R > 60-70 R > 60-70

(*c.f.* Langer+1984, ApJ, 277, 581).

Case study: CH_3OH

Gas phase Formation

$CH_3^+ + H_2O \rightarrow CH_3OH_2^+ + h\nu$

$CH_3OH_2^+ + e \rightarrow CH_3OH + H$

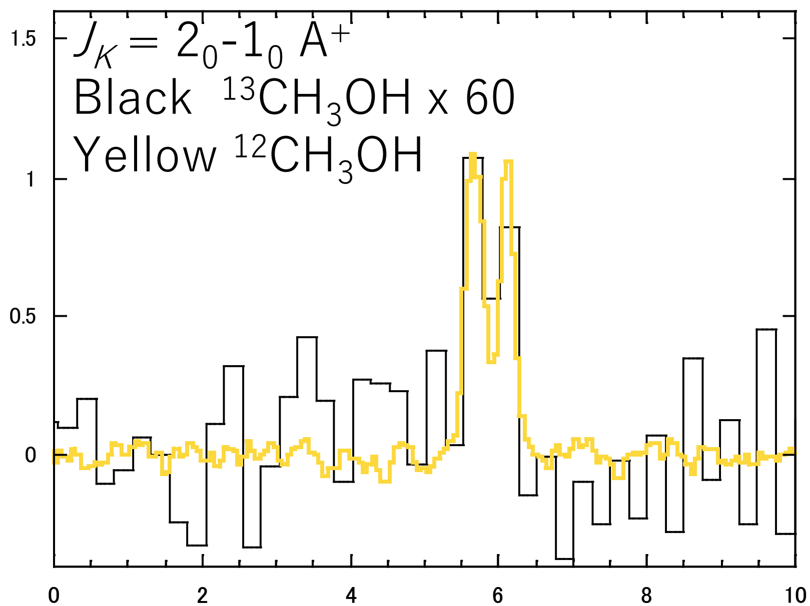
$^{12}C/^{13}C >> 60\text{-}70$

Formation on Grains

$CO \rightarrow HCO \rightarrow H_2CO$

$\rightarrow CH_3O \rightarrow CH_3OH$

$^{12}C/^{13}C = 60\text{-}70$



TMC-1(CP): Starless core

$^{13}CH_3OH$:

$J_K = 1_0\text{-}0_0$ A$^+$, $2_0\text{-}1_0$ A$^+$, $2_{-1}\text{-}1_{-1}$ E

$^{12}CH_3OH$:

$J_K = 1_0\text{-}0_0$ A$^+$, $2_0\text{-}1_0$ A$^+$, $2_{-1}\text{-}1_{-1}$ E, $3_0\text{-}2_0$ A$^+$, $3_{-1}\text{-}2_{-1}$ E

$^{12}C/^{13}C = 62 \pm 10$ (LVG)

Non-thermal desorption (Reaction-Excess energy, Cosmic-induced UV, etc.)

(Soma+2015, ApJ, 802, 74, cf; Soma+2018, ApJ, 854, 116)

How to constrain the pathways?

Chemical Models

~5000 reactions

~500 species

compare

Observations

abundance ratios

Macroscopic Approach

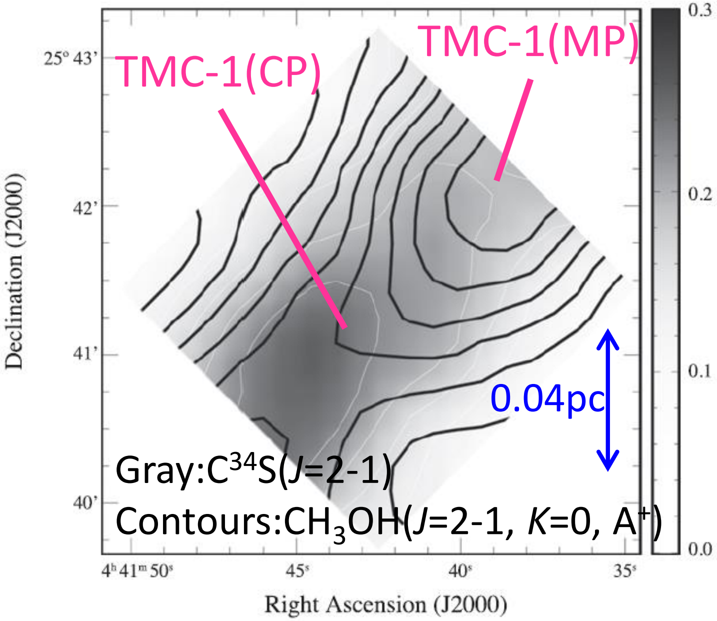
Microscopic Approach
(Isotopic Species)
(Like data assimilation..?)

-Doppler analysis of the lines-

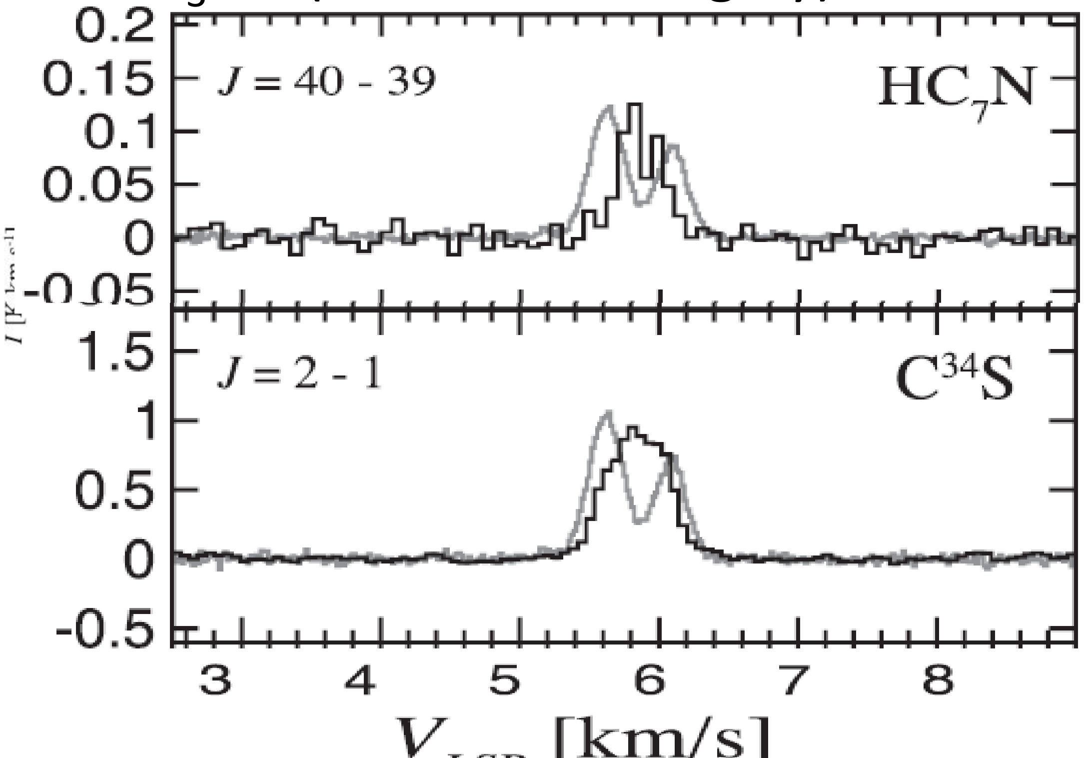
Photo: Taurus Molecular Cloud

Origin of COMs in TMC-1

$C^{34}S$ anti-correlate with CH_3OH



High velocity resolution observation of CH_3OH (J=1-0, K=0, A^+, gray)



- CH_3OH is released into gas-phase in core peripheries (starless core case).
- Line shapes of carbon-chain molecules are different from that of CH_3OH

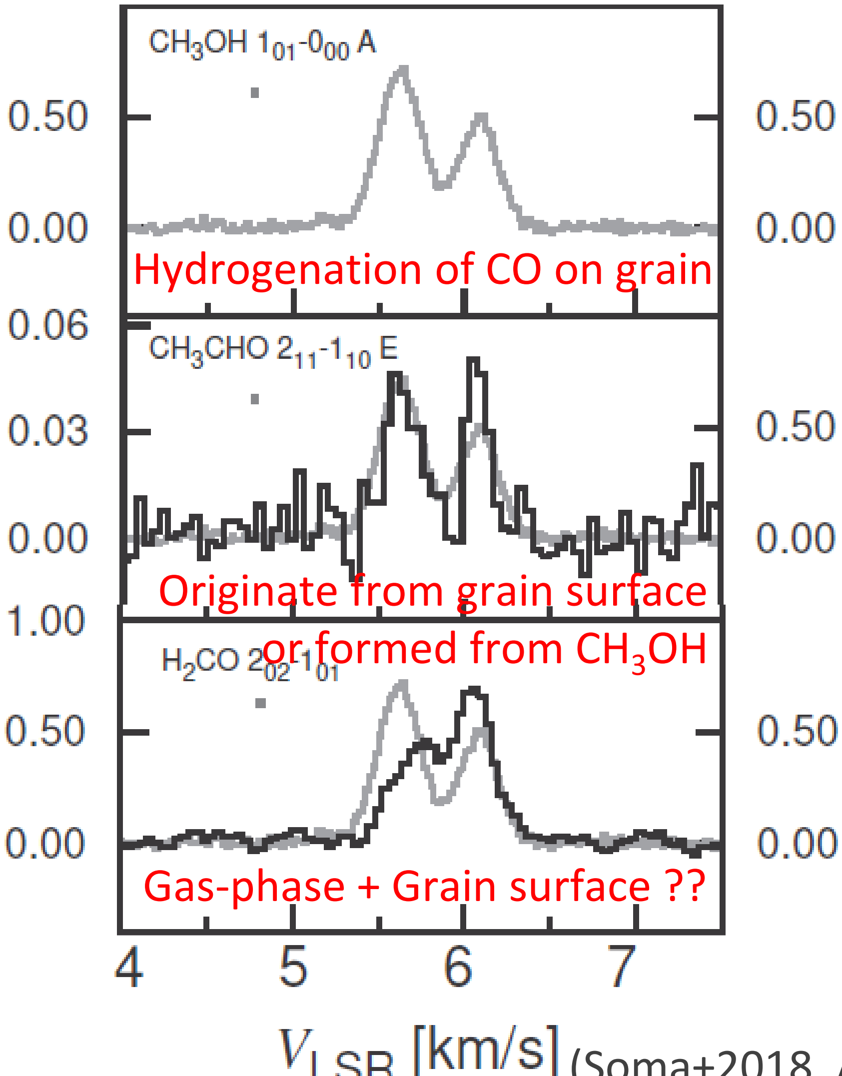
→Always narrower in carbon-chain molecules

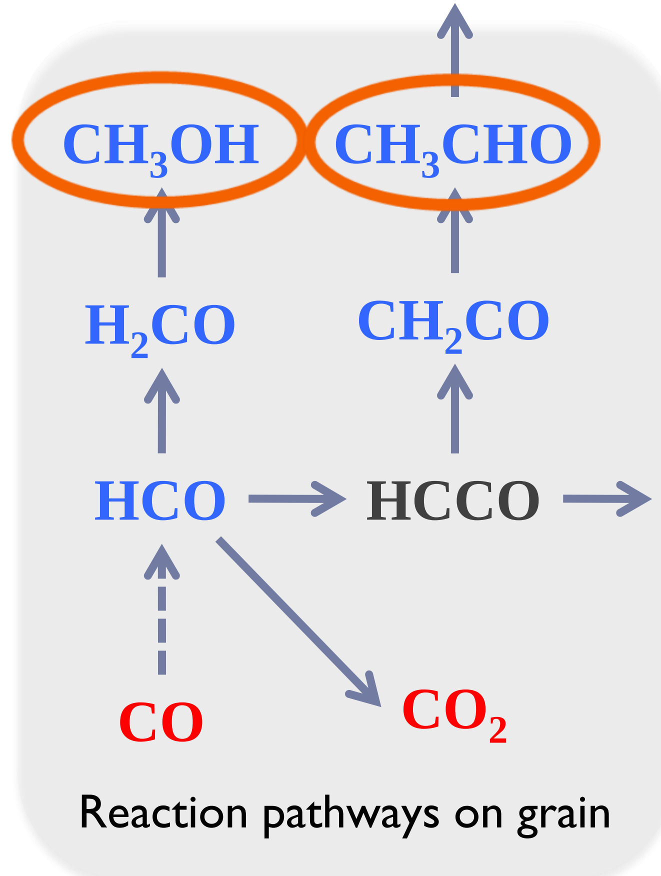
→Narrower in gas-phase species

(Soma+2015, ApJ 802, 74)

Origin of COMs in TMC-1

TMC-1 (CP)

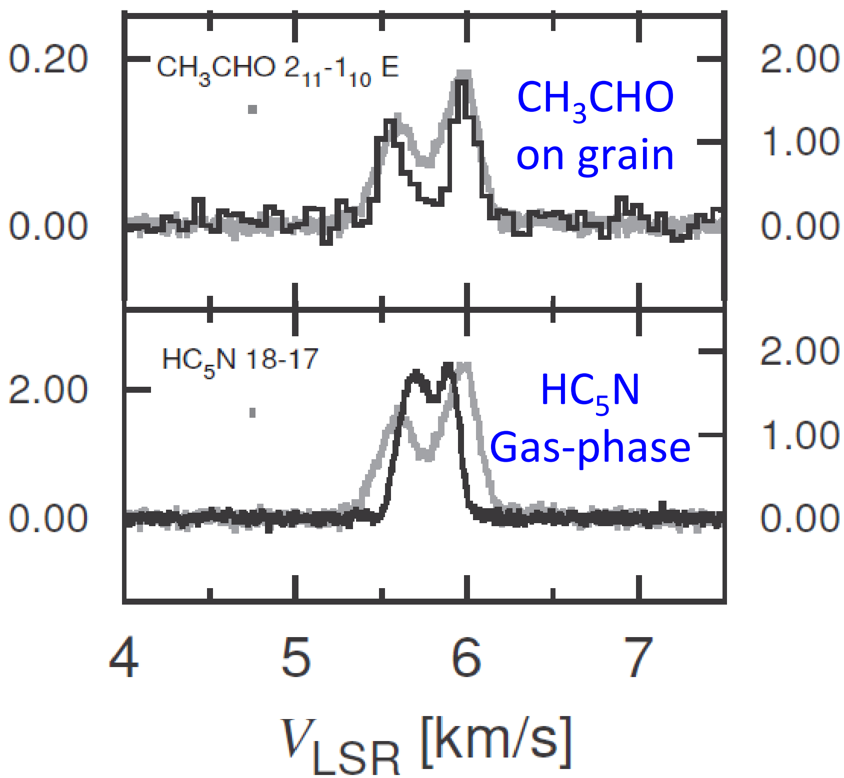




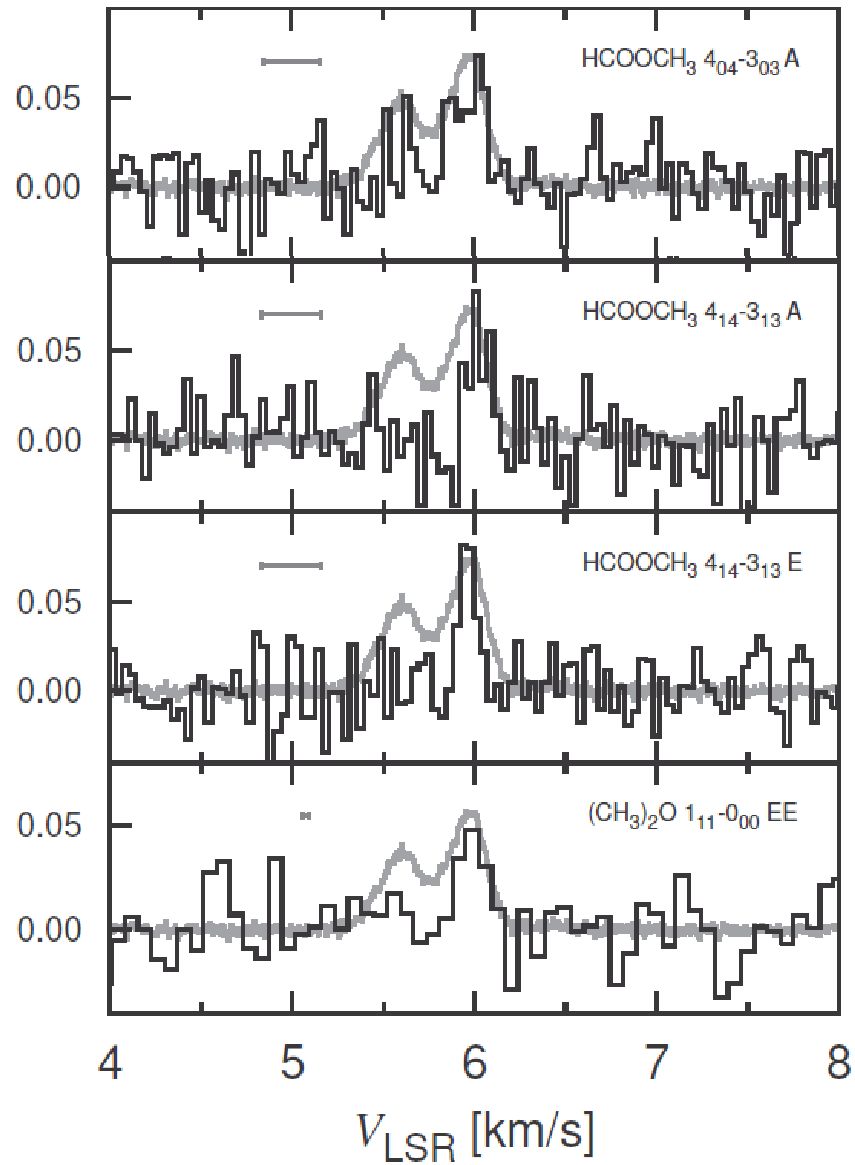
(Soma+2018, ApJ, 854, 116)

Origin of COMs in TMC-1

TMC-1 (Methanol Peak)



Detections of $HCOOCH_3$ and $(CH_3)_2O$ lines



CH_3CHO, $HCOOCH_3$, and $(CH_3)_2O$ could originate from grain surface or formed from CH_3OH

(Soma+2018, ApJ, 854, 116)

Difficulties

1) Interpretation: Effect of isotope exchange reaction?

2) Identification/Observation: Rest frequency accuracy

    2-1) Isotopic species
    2-2)-<0.1 km/s accuracy required even for major species
    2-3) Higher excitation lines

3) Many unidentified lines

Photo: Cygnus

Other Possibilities

Isotope exchange reactions??

(cf: T_{kin}~10 K@TMC-1)
(T_{rot}<10 K, not thermalized)

CCH i) H + *CCH → H*CC + H (ΔE=8 K)

1 : 1.6 (Observation)

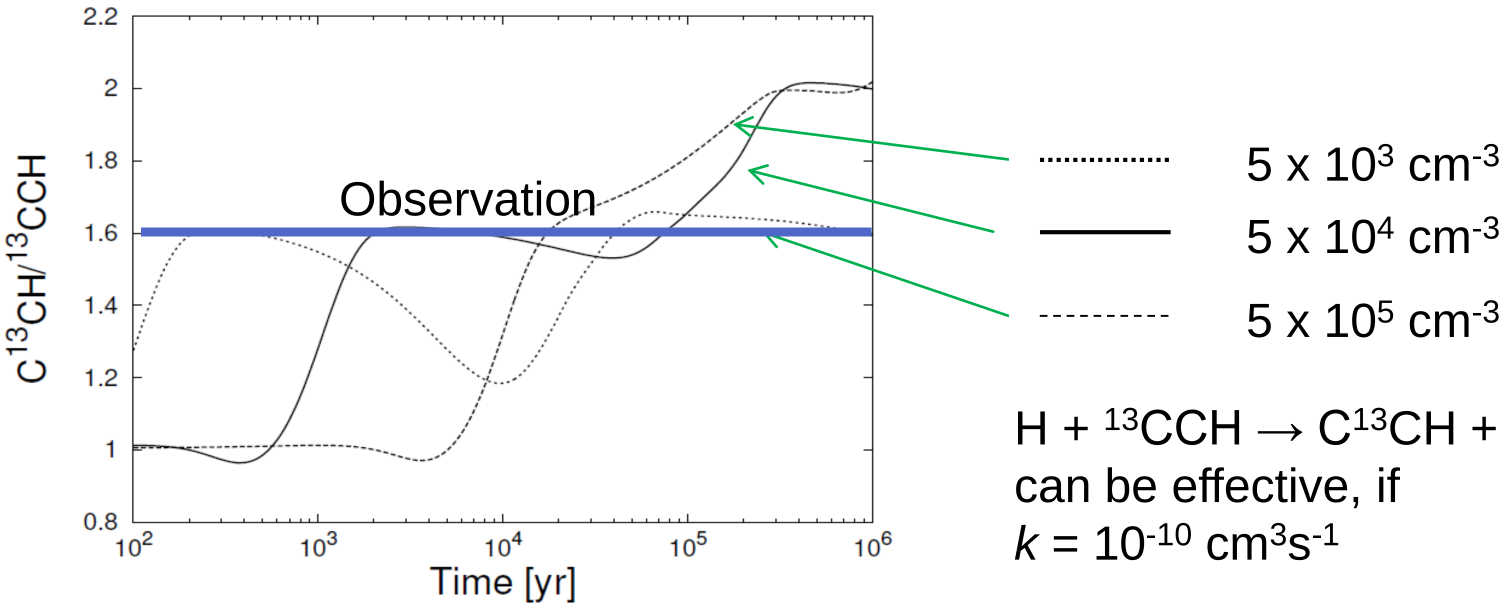
CCS ii) S + *CCS → S*CC + S (ΔE=17 K)

1 : 4.2 (Observation)

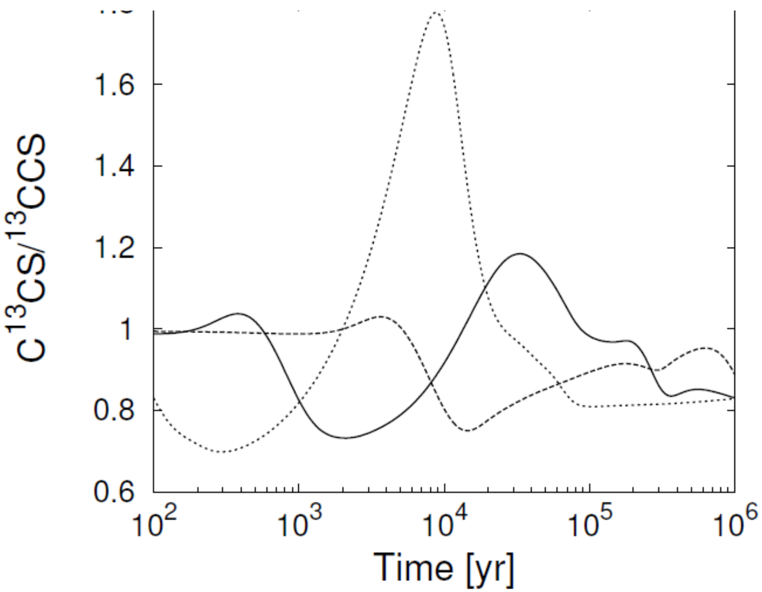
S is less abundant than H.
Is this possible ???

(CCH: Tarroni, private communication)
(CCS: Osamura, private communication)

Chemical Model Calculation (Furuya et al. 2011, ApJ)



$H + {}^{13}CCH \rightarrow C^{13}CH + H$
can be effective, if
$k = 10^{-10}$ cm^3s^{-1}



$S + {}^{13}CCS \rightarrow C^{13}CS + S$
is not effective.

The ratio 4.2 can not be realized.

Other Possibilities

Isotope exchange reactions??

(cf: T_{kin}~10 K@TMC-1)
(T_{rot}<10 K, not thermalized)

CCH i) H + *CCH → H*CC + H (ΔE=8 K)

1 : 1.6 (Observation)

CCS ii) S + *CCS → S*CC + S (ΔE=17 K)

1 : 4.2 (Observation)

S is less abundant than H.
Is this possible ???

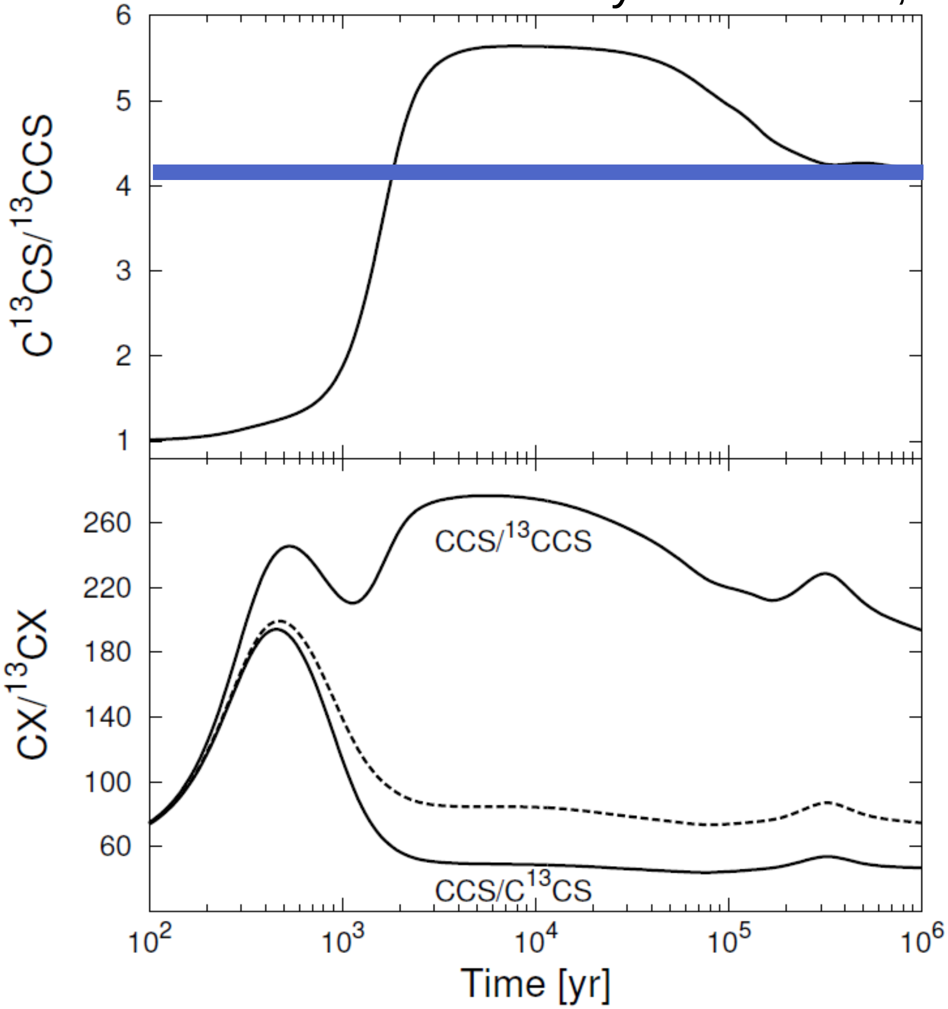
iii) H + *CCS → C*CS + H ??

The simplest catalyst !?

(CCH: Tarroni, private communication)
(CCS: Osamura, private communication)

Chemical Model Calculation (Furuya et al. 2011, ApJ)

Furuya et al. 2011, ApJ



$[HCCS]^*$

$H + {}^{13}CCS \rightarrow C^{13}CS + H$

explains the result, if $k = 10^{-10}$ cm^3s^{-1} .

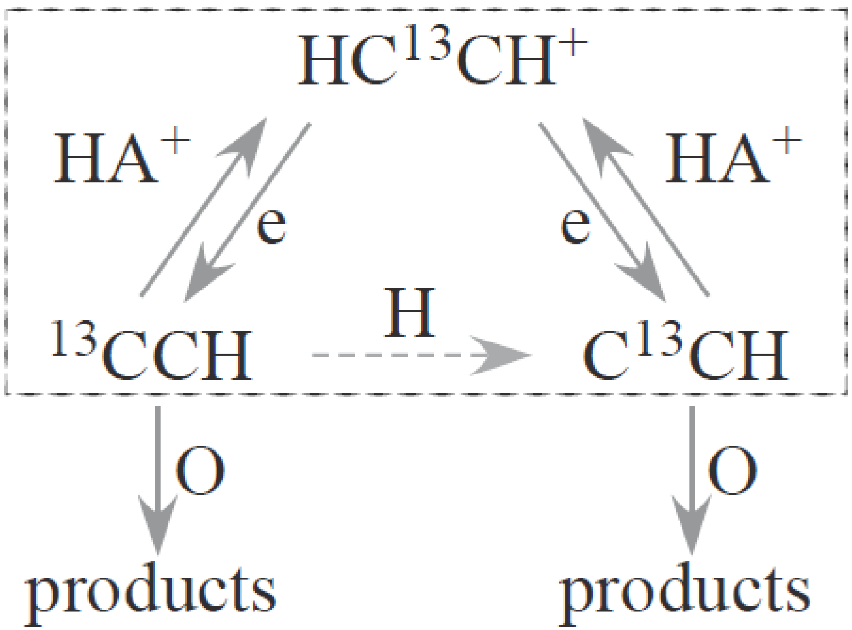
Exothermic with no barrier (Yamada et al. 2002)

H as the simplest catalyst??

But how efficient ???

Exchange Reaction; CCH Case

ΔE is only 8 K



R

$$\frac{[\mathrm{C^{13}CH}]}{[\mathrm{^{13}CCH}]} = \frac{2k_{ex}^{(f)}[\mathrm{H}] + k_d[\mathrm{O}]}{2k_{ex}^{(b)}[\mathrm{H}] + k_d[\mathrm{O}]}$$

$$k_{ex}^{(b)} = k_{ex}^{(f)} \exp\left(-\frac{\Delta G}{kT}\right)$$

	TMC-1			L1527	
$n(\mathrm{H_2})$/cm^{-3}	10^4	3×10^4	10^5	10^5	10^6
R	1.51	1.23	1.07	1.16	1.02
R(obs)	1.6 ±0.4 (3σ)			1.6 ±0.1 (3σ)	

Other Possibilities

(cf: T_{kin}~10 K@TMC-1)

Isotope exchange reactions??

CCH i) H + *CCH → H*CC + H (ΔE=8 K)

1 : 1.6

CCS ii) S + *CCS → S*CC + S (ΔE=17 K)

S is less abundant than H.
Is this possible ???

1 : 4.2

The simplest catalyst !?

iii) H + *CCS → C*CS + H ??

c-C_3H_2 ^{13}C on-axis : ^{13}C off axis =1:5 in L1527

(expected to be 1:2)

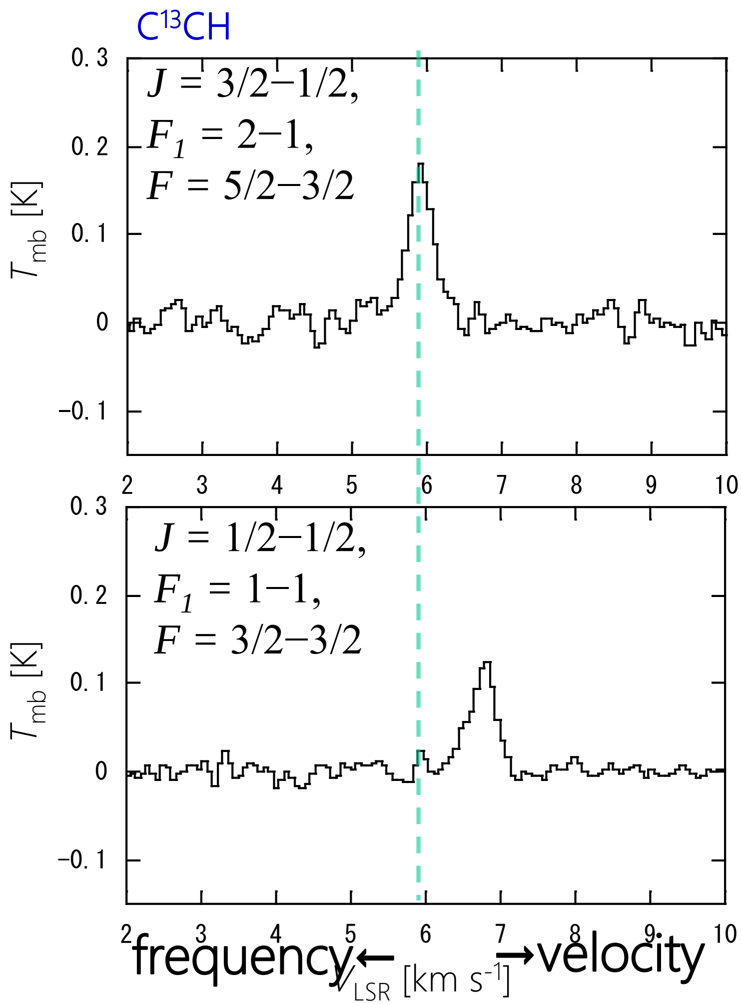
Closed-shell molecule

If it happens for C_3H_2, l-C_3H_2 ⇔ c-C_3H_2 would happen.

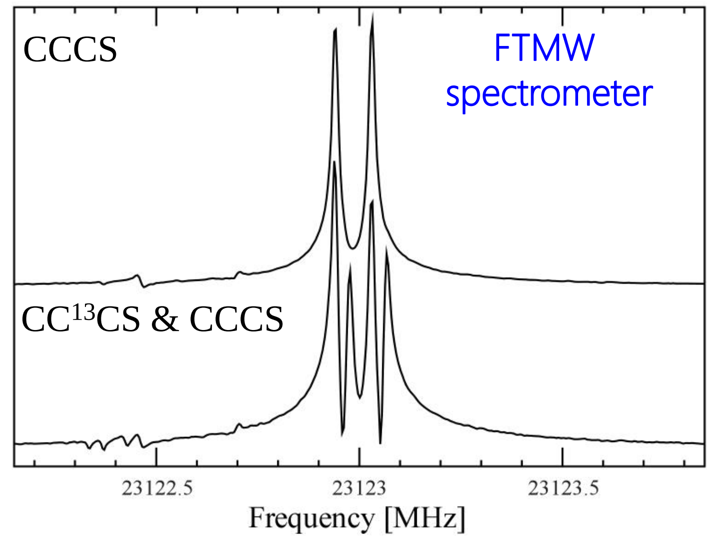
In this case, l-C_3H_2would be killed…..

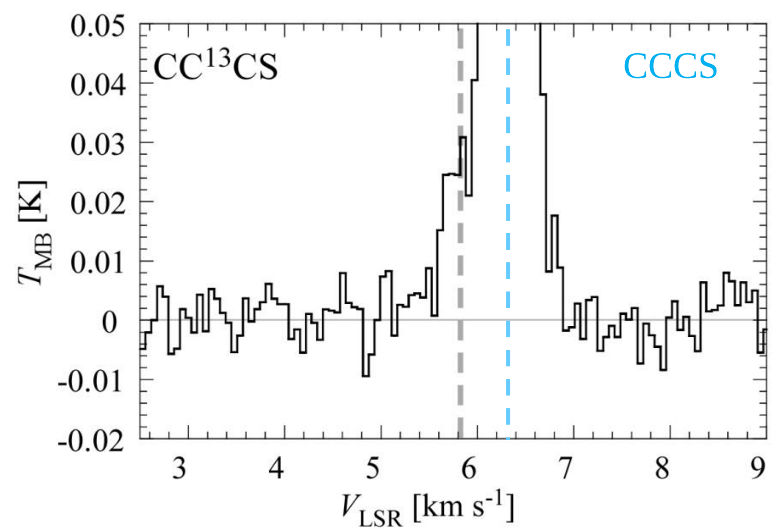
(Yoshida+2015, ApJ, 807, 66)

Spectral Line Frequency of ^{13}C Species



Required accuracy:
a few ~ a few 10 kHz

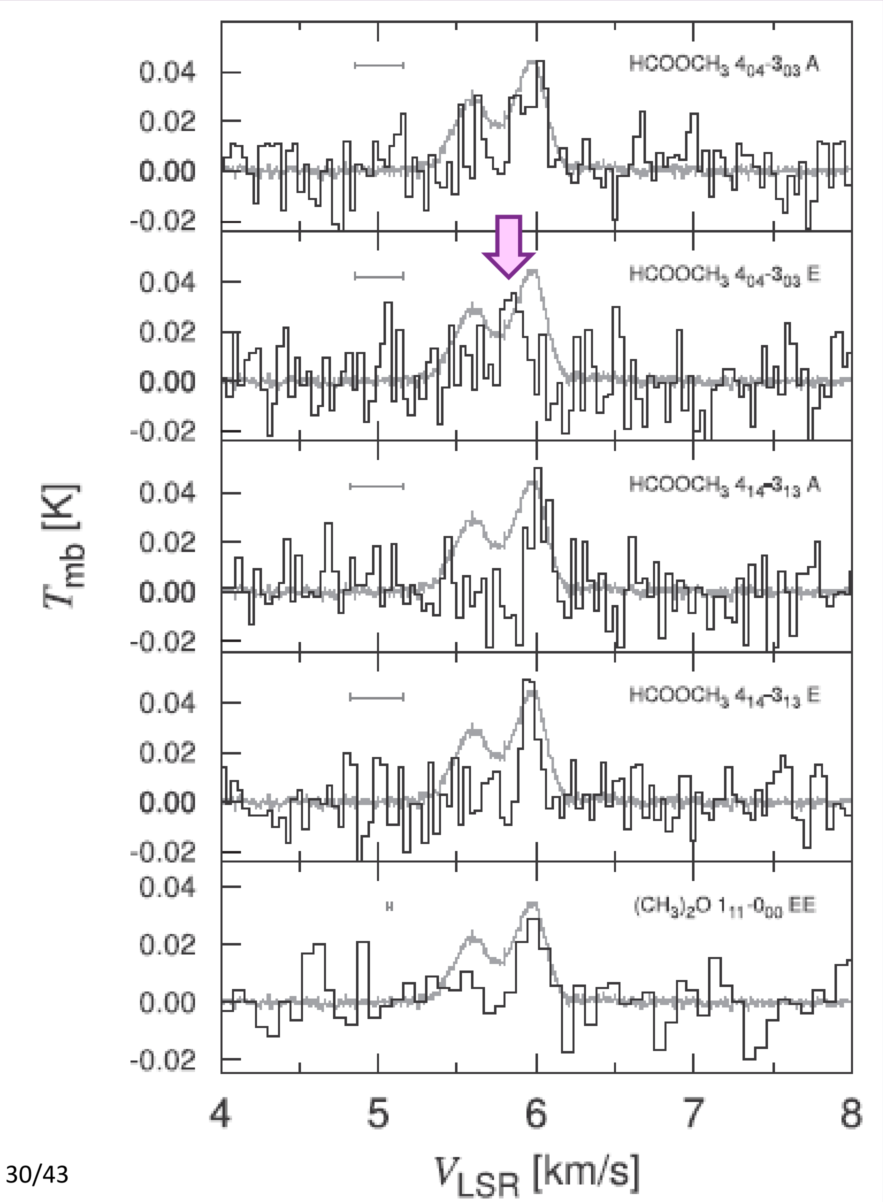




Observed spectra toward TMC-1

(Sakai et al. 2013, JPC, 117, 9831)

Required accuracy for Doppler analysis



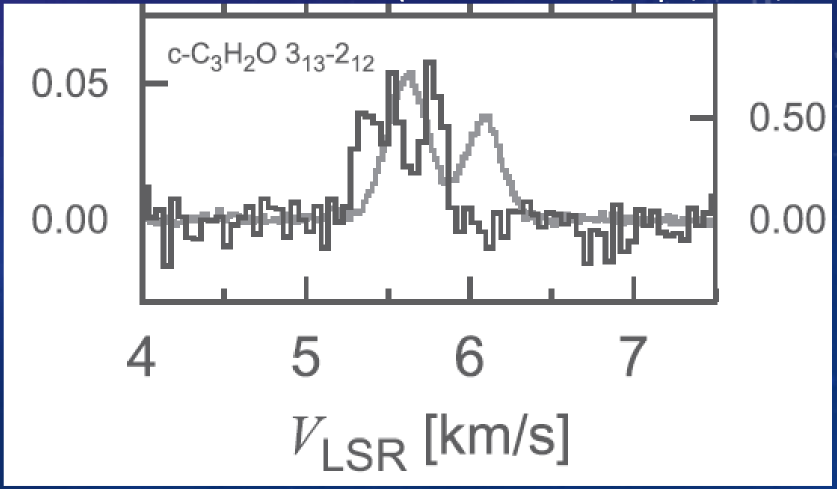
Thermal line width ~ 0.1 km/s

→<300 kHz @ 1 THz
(Various high excitation lines)

→ <30 kHz @ 100 GHz
(Various "complex" species)

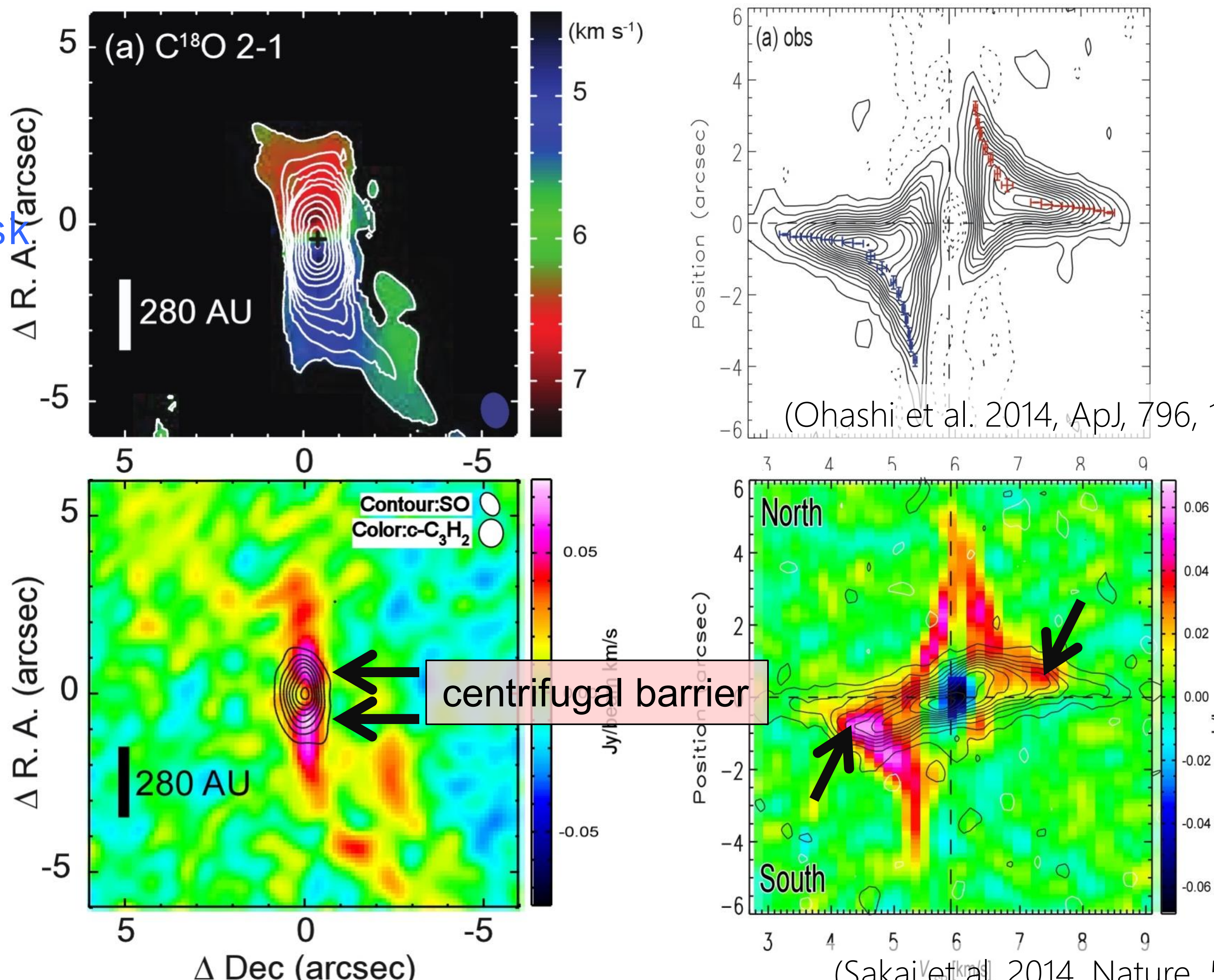
→ <0.5 kHz @ 1.6 GHz
(OH ground state transitions)

(Soma+2018, ApJ, 854, 116)



Required accuracy for Doppler analysis

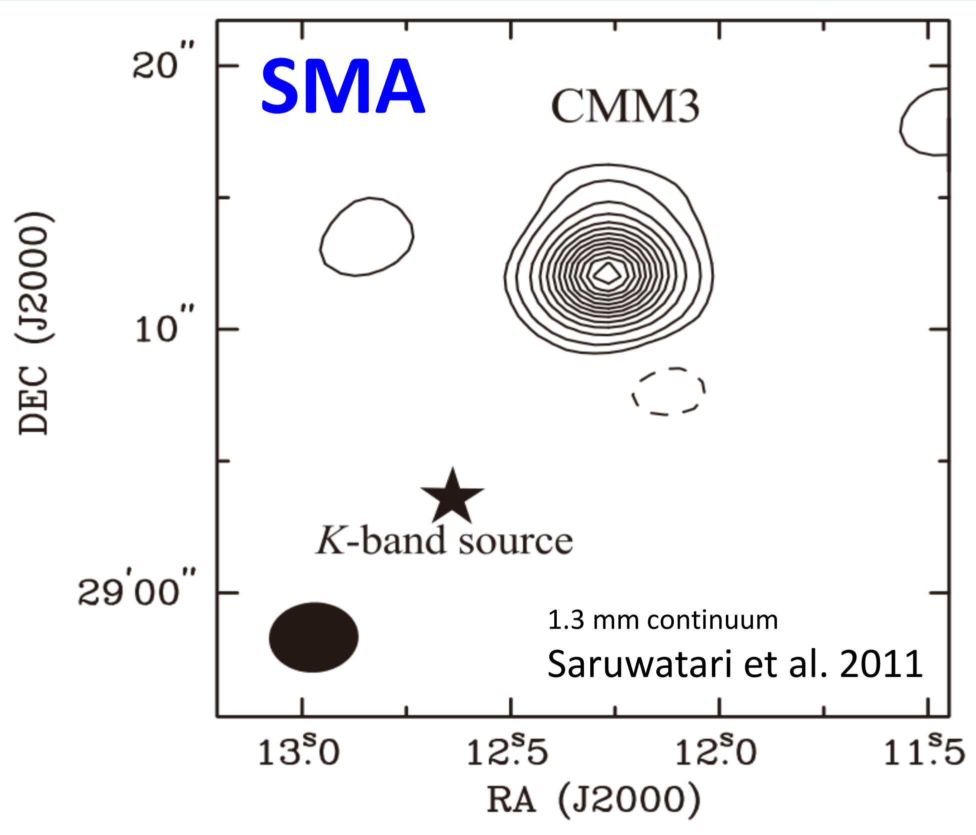
L1527
Class 0
Taurus
Edge-on
Infant Disk

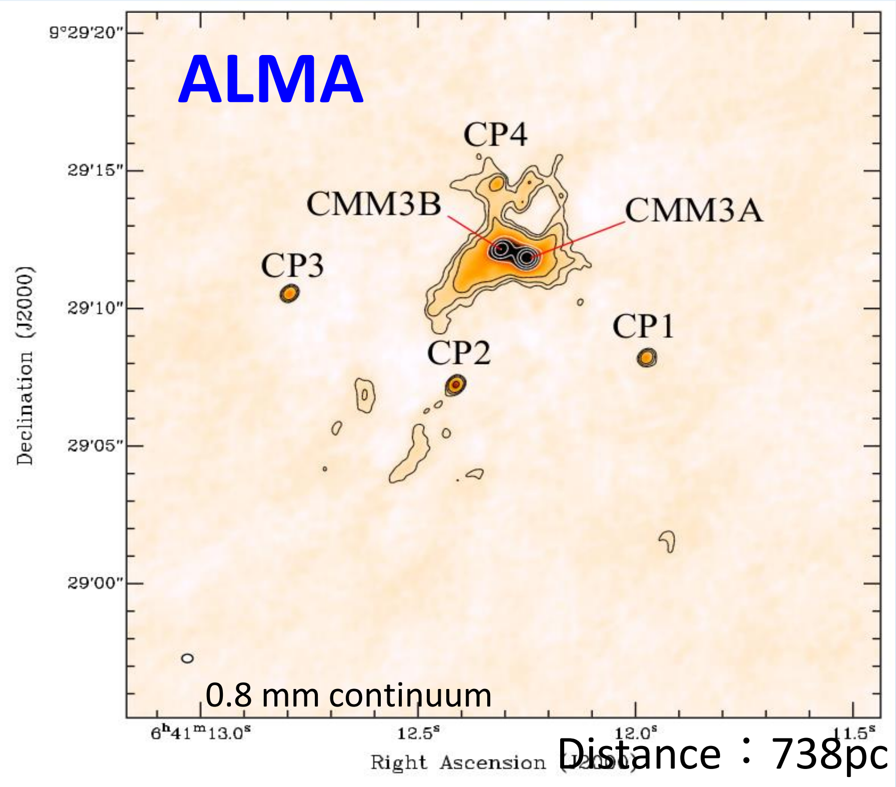


(Ohashi et al. 2014, ApJ, 796, 131)

(Sakai et al. 2014, Nature, 507, 78)

"High-Mass" Protostar: NGC 2264 CMM3





CMM3 is resolved into two sources.

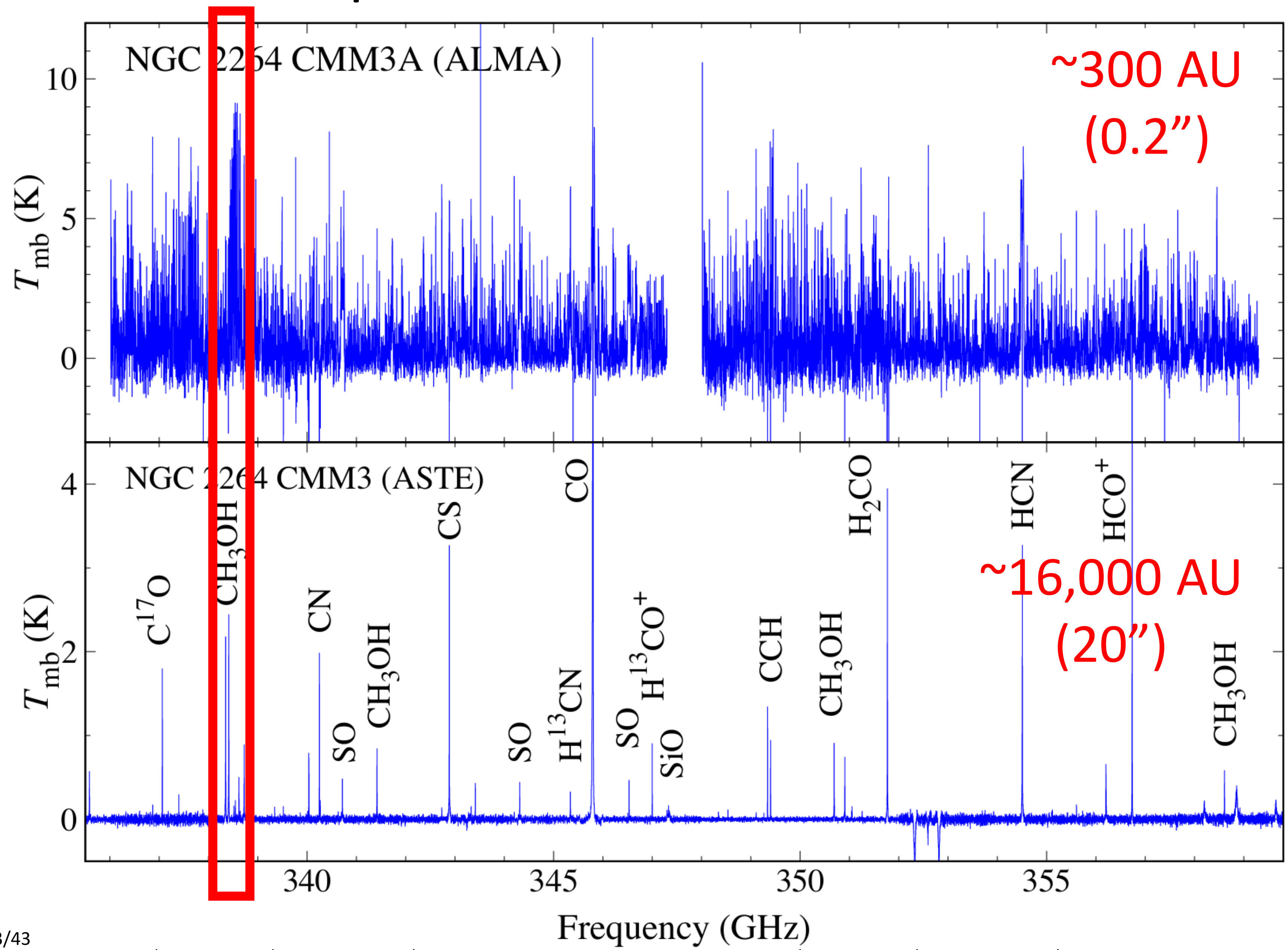
- Separation: ~ 1 arcsec
- Binary system (CMM3A and CMM3B)

→ Intermediate-mass protostellar binary?

Four new continuum sources (CP1-CP4)

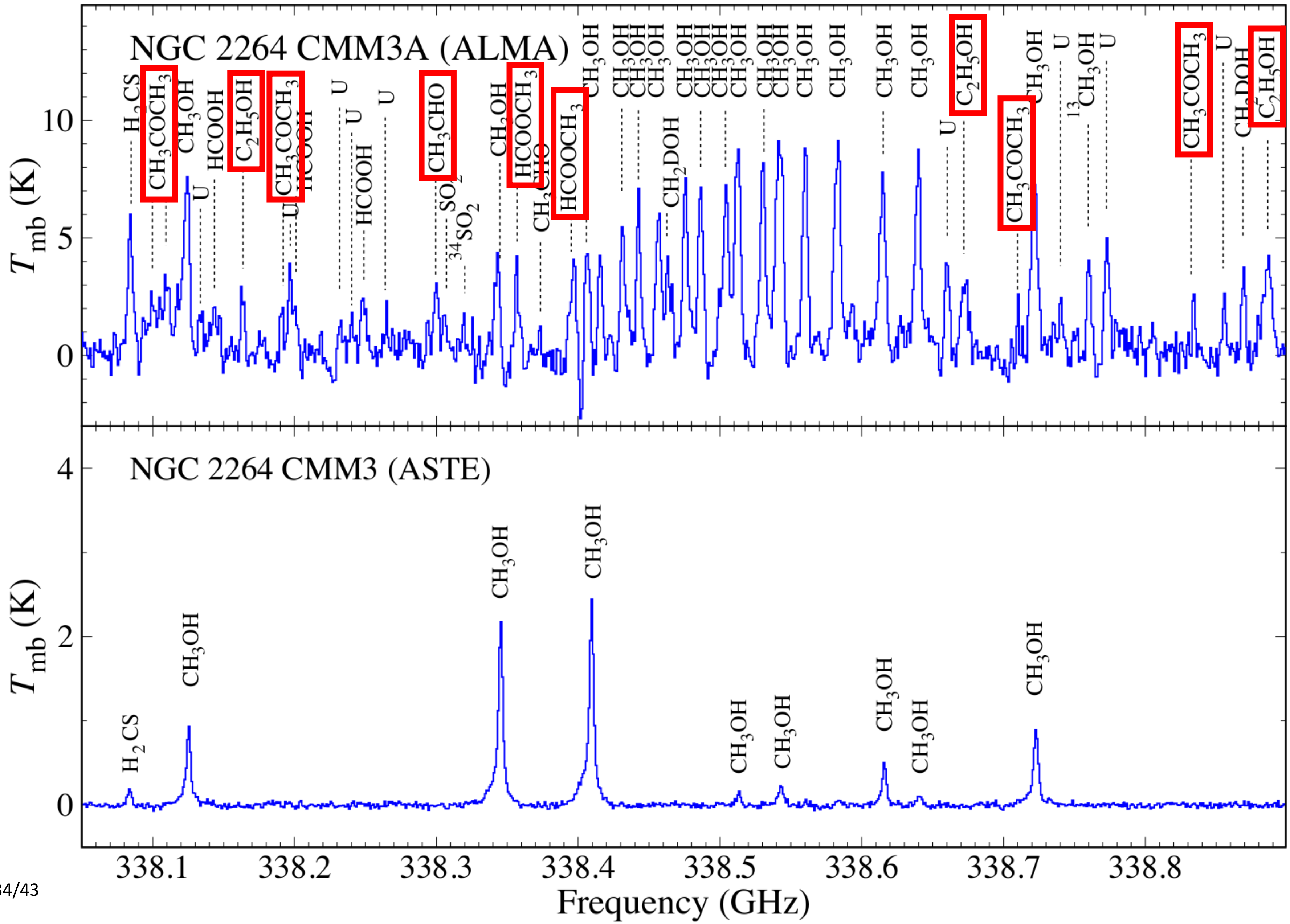
(Watanabe, Y., Sakai, N. et al. 2017, ApJ, 847, 108)

Spectrum toward CMM3A

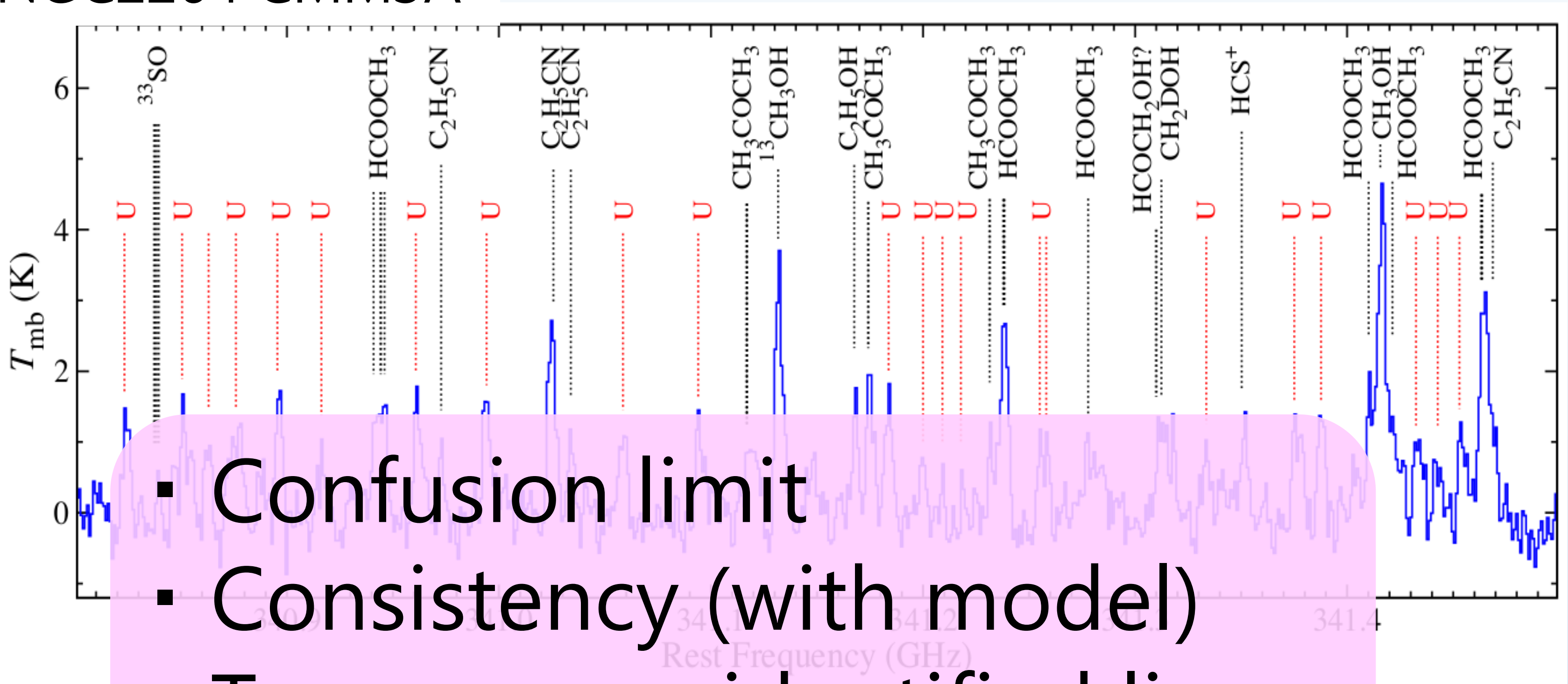


(Watanabe, Y., Sakai, N. et al. 2015, ApJ, 809, 162; Watanabe, Y., Sakai, N. et al. 2017, ApJ, 847, 108)

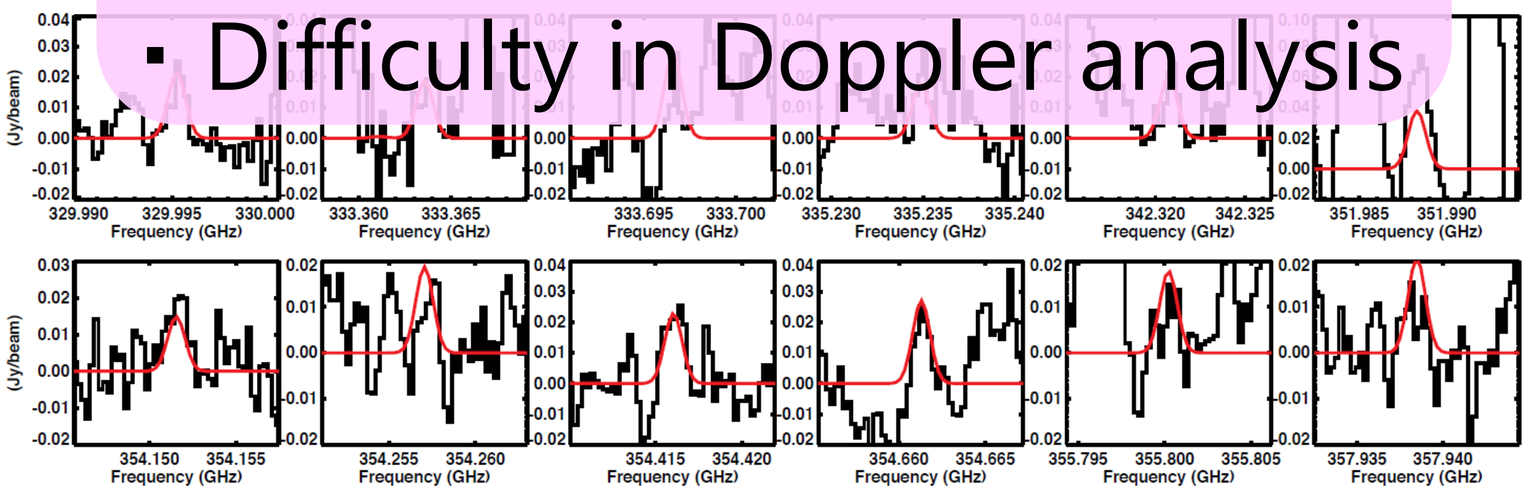
Expanded Spectrum toward CMM3A



NGC2264 CMM3A



IRAS16293-2422B



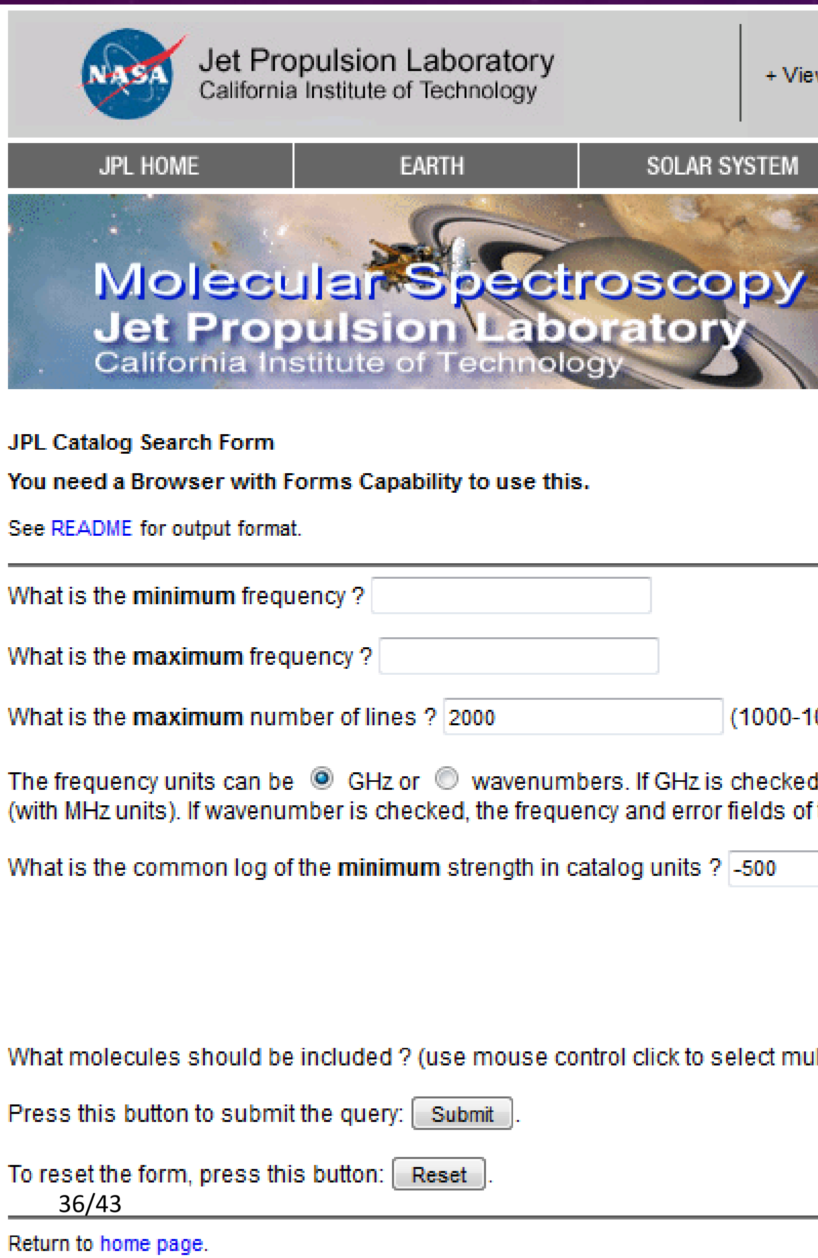
- Confusion limit
- Consistency (with model)
- Too many unidentified lines
- Difficulty in Doppler analysis

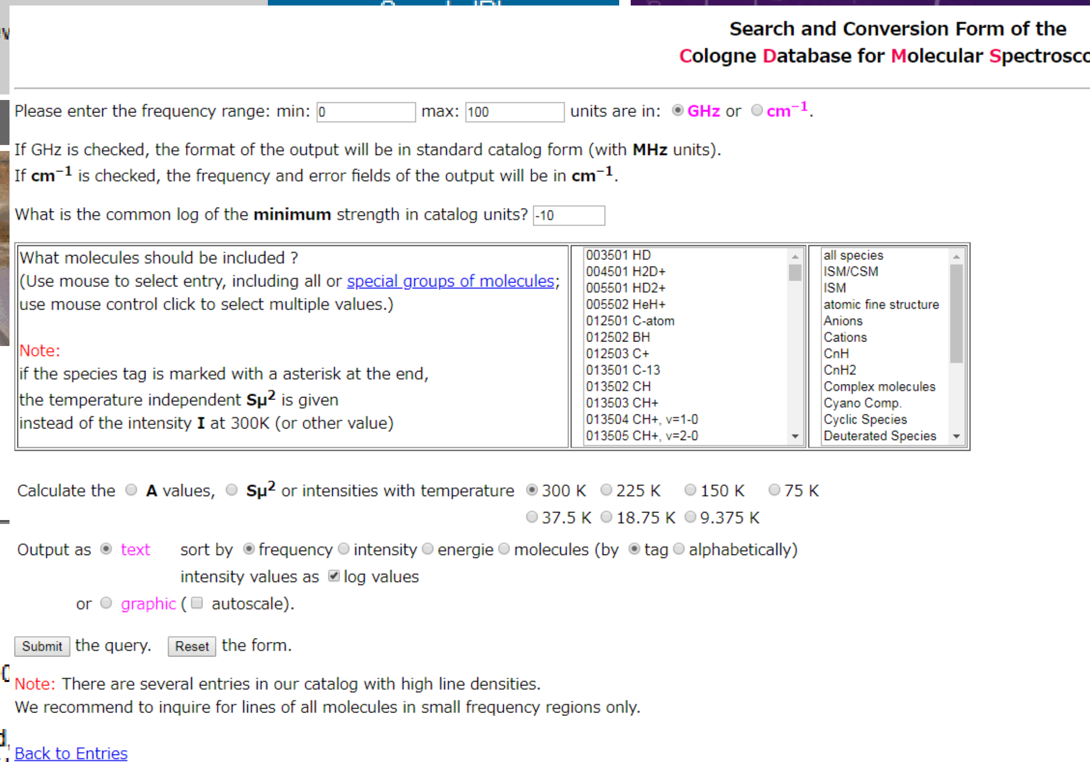
Fig. B.1. Black: detected lines of NH_2CDO. Red: best-fit model for T_{ex} = 300 K.

(Coutens, A. et al. A&A, 590, L6)

(4) Difficulties 2&3

Rest Frequencies of Molecules→ Spectral Line Database





↑Koln Univ.

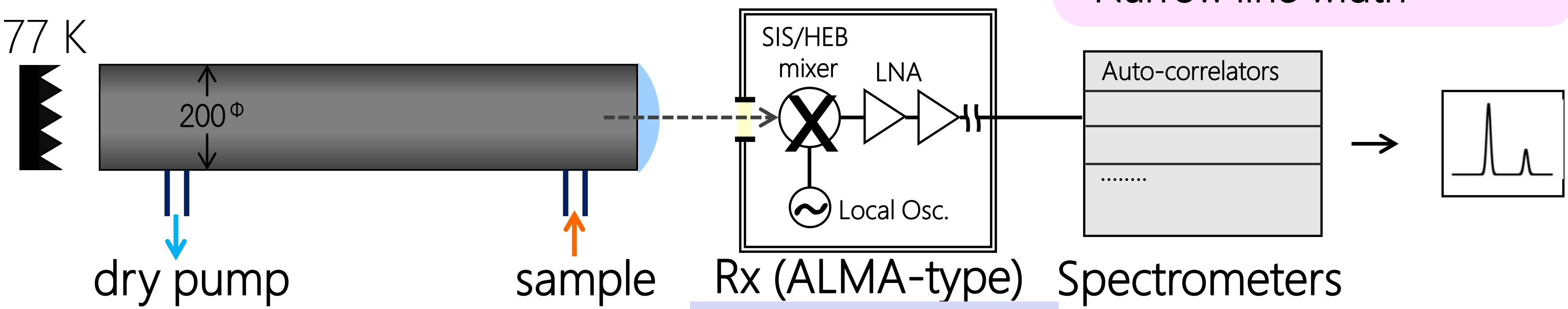
←NASA

~400 species

Observing Gas Cells instead of the Sky

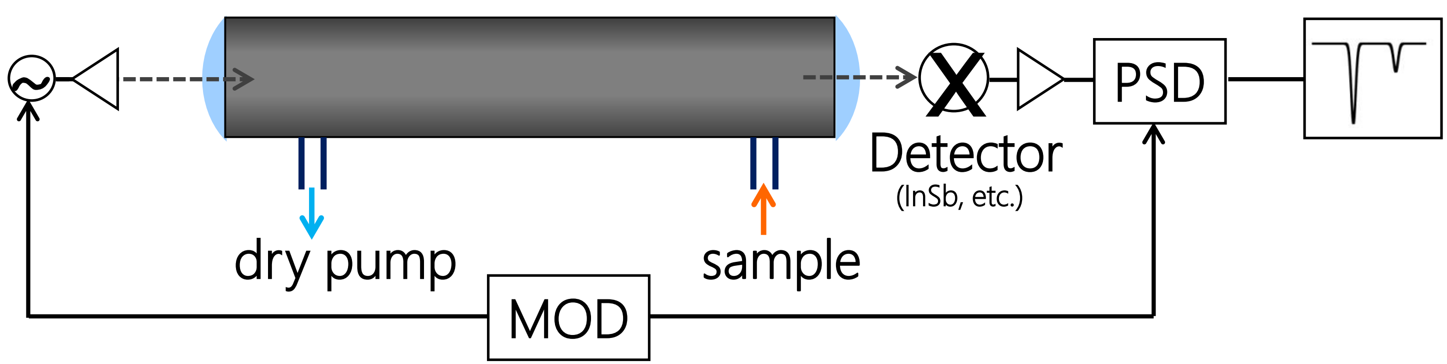
Emission Spectrometer

- Wide frequency coverage
- Reliable intensity
- Narrow line width



--UEC, UT, NAOJ--

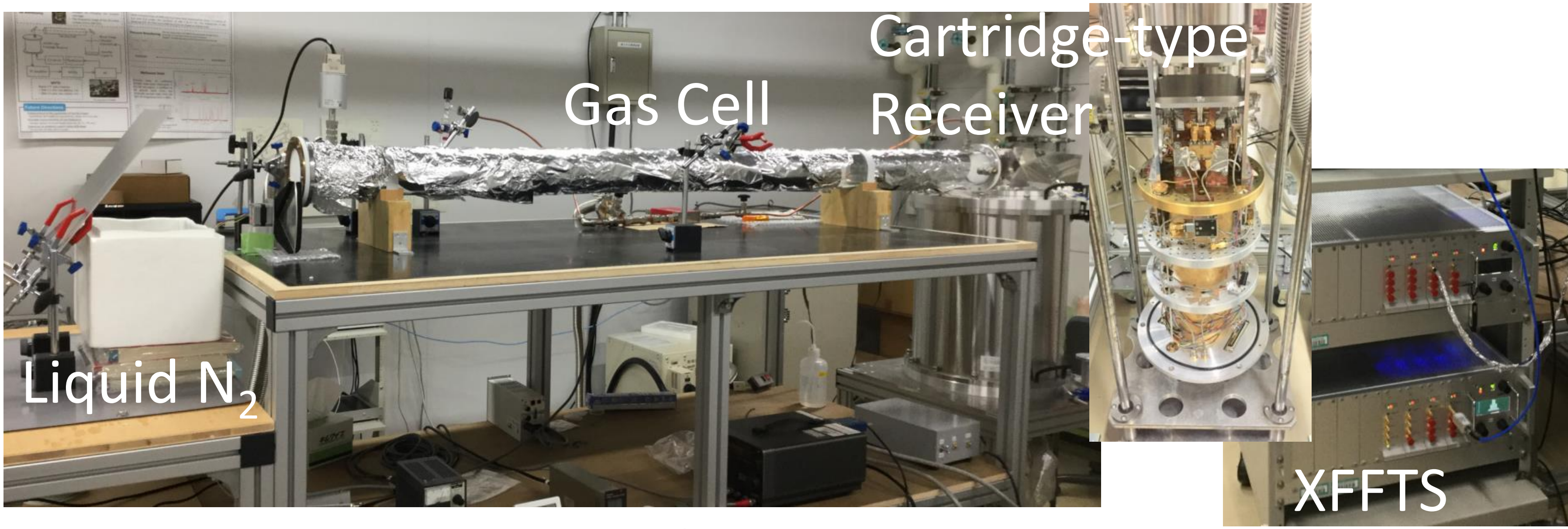
Conventional Absorption Spectrometer

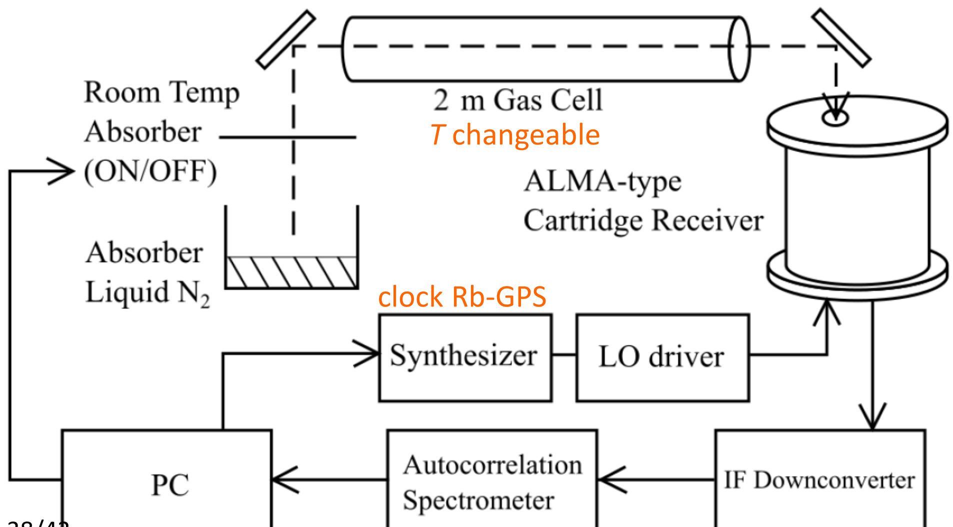


(T)SUMIRE

すみれ

(THz) Spectrometer Using superconductor MIxer REceiver





Receivers

- 210-270 GHz (band 6) (SIS)

(- 300-500 GHz (band7+8) (SIS))

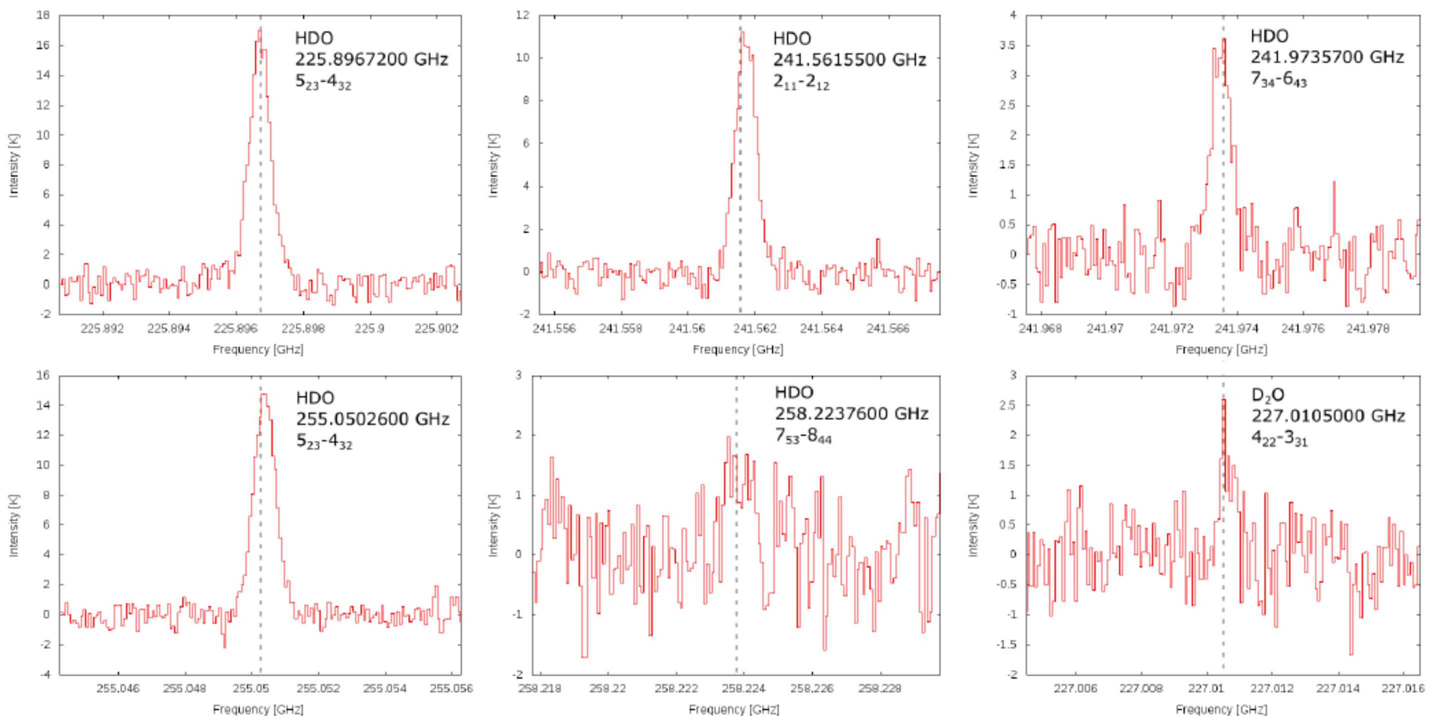
- 0.9 THz band (HEB)

Spectrometers

XFFTS 2.5 GHz (0.075 MHz res.) x 4
0.5 GHz (0.015 MHz res.) x 4
(32,768 ch)

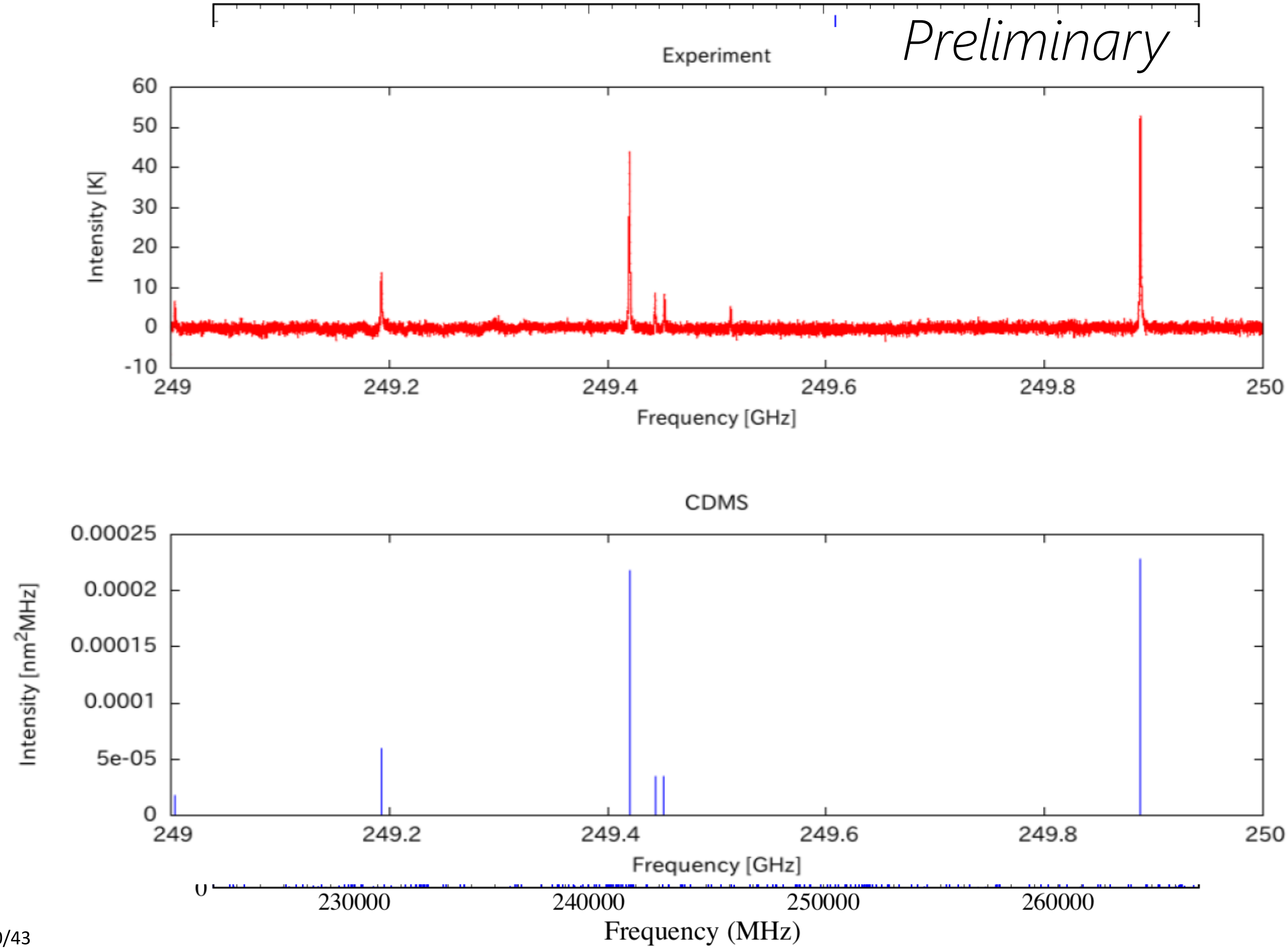
(Watanabe, Y., Sakai, N.+2019, in prep. Collaboration with UT, NAOJ, and UEC.)

HDO/D_2O lines



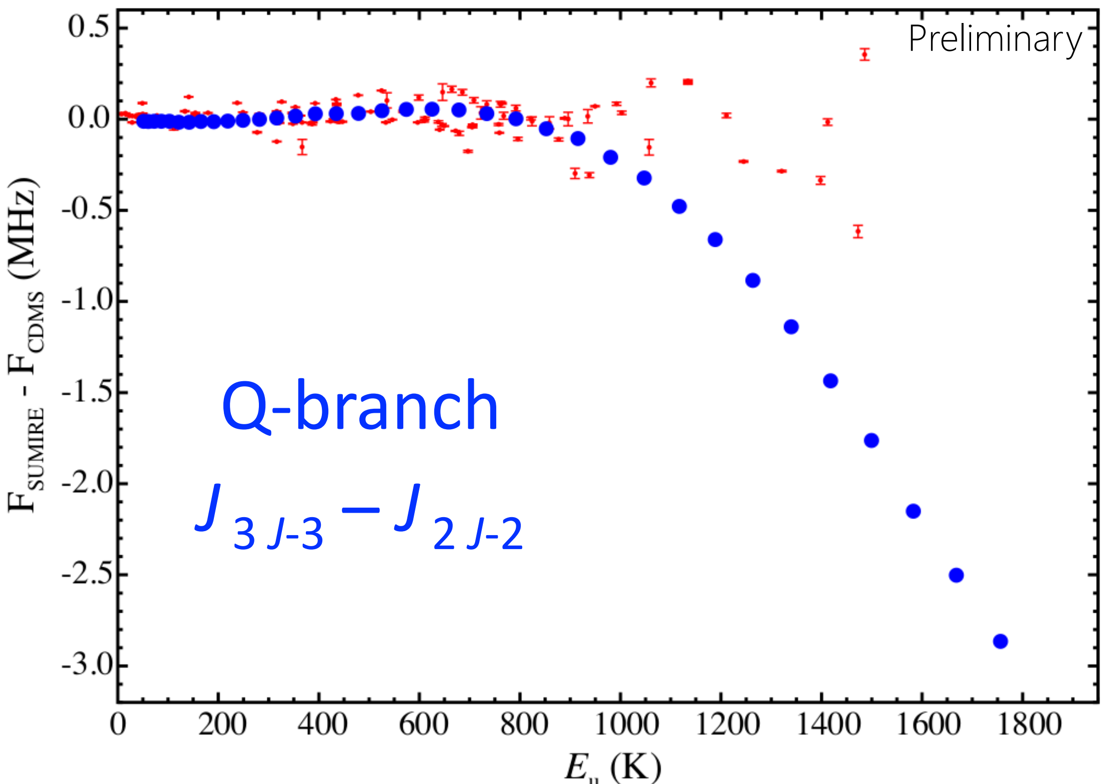
	量子数	文献値 (MHz)	実験値 (MHz)	実験値ー文献値 (kHz)
HDO	3_{12}-2_{21}	225896.720±0.038	[redacted]	[redacted]
	2_{11}-2_{12}	241561.550±0.037	[redacted]	[redacted]
	7_{34}-6_{43}	241973.570±0.039	[redacted]	[redacted]
	5_{23}-4_{32}	255050.260±0.059	[redacted]	[redacted]
	7_{53}-8_{44}	258223.76±0.10	[redacted]	[redacted]
D_2O	4_{22}-3_{31}	227010.50±0.050	[redacted]	[redacted]

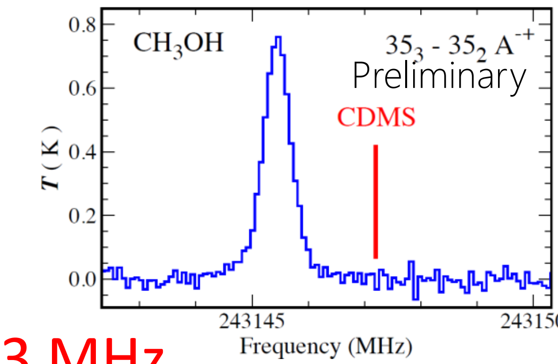
CH_3OH Test Spectrum taken by SUMIRE



(Watanabe, Y., Sakai, N.+2019, in prep. Collaboration with UT, NAOJ, and UEC)

CH_3OH Test Spectrum taken by SUMIRE





$\Delta f \sim 3$ MHz

$\Delta v \sim 3.6$ km/s

Database: Extrapolation from low-frequency measurements

=> Significant error (Effect of higher order perturbation)

=> Miss-Assignment, Systematic error in Doppler velocities

Importance of direct spectroscopic measurement

(Watanabe, Y., Sakai, N.+2019, in prep. Collaboration with UT, NAOJ, and UEC)

Summary

- ALMA can now study molecular evolution in disk forming region.

→Initial chemical composition of protoplanetary disk have large variety

Interactive reaction processes between gas and dust
(reaction rate, branching ratio, binding energy, desorption mechanism, diffusion mechanism.....etc.)
Insufficiency of knowledge in molecular science.

- Isotope fractionation & Doppler analysis tells us fruitful information.

We need "Data assimilation".
Effect of Exchange reaction should be explored more.

- Importance of accurate rest frequencies.

→Higher excitation lines, rare species have large errors.

Important for understanding formation pathways
& for deriving column densities, identifications

→Lines of normal species still have errors.

Important for Doppler analysis!