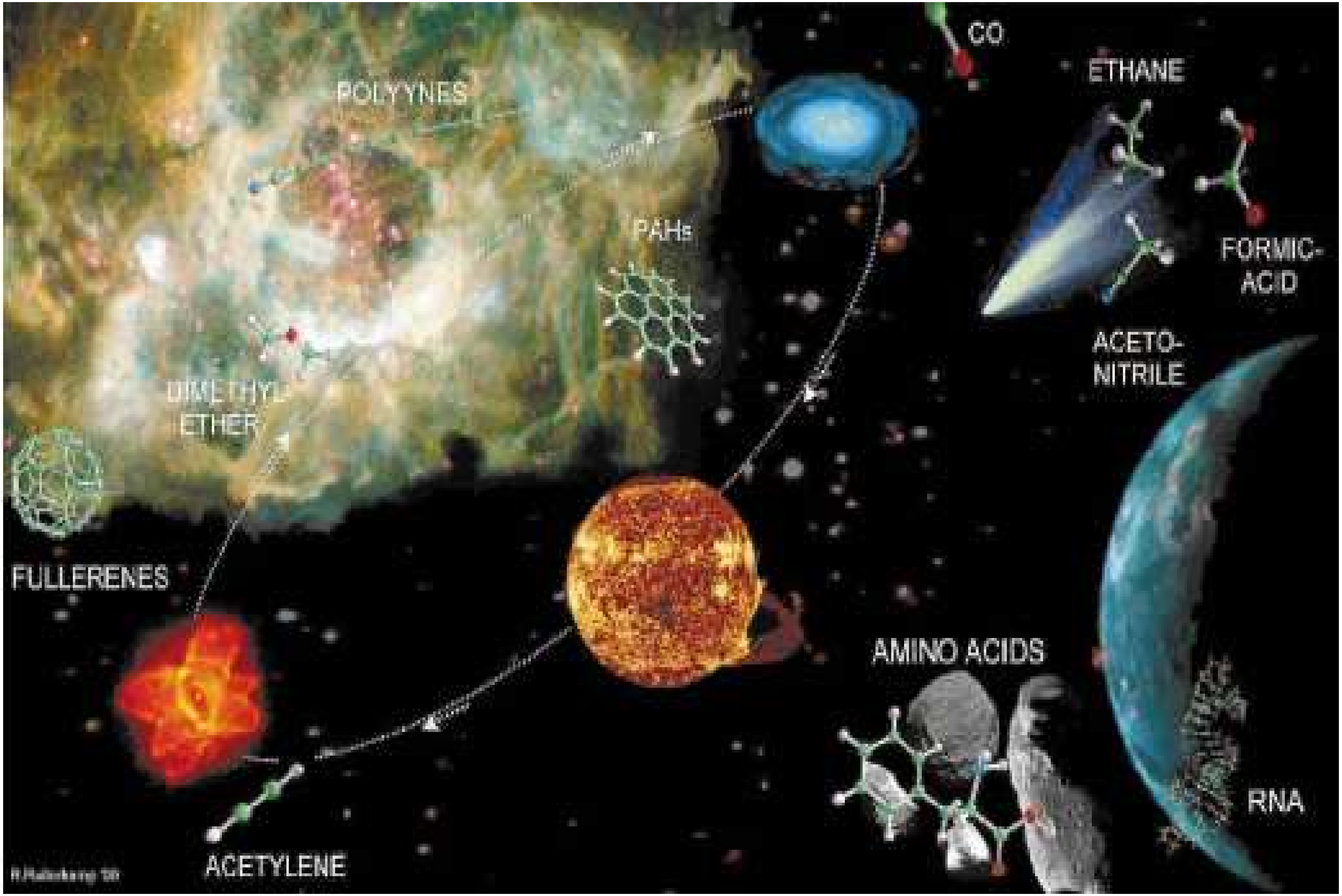
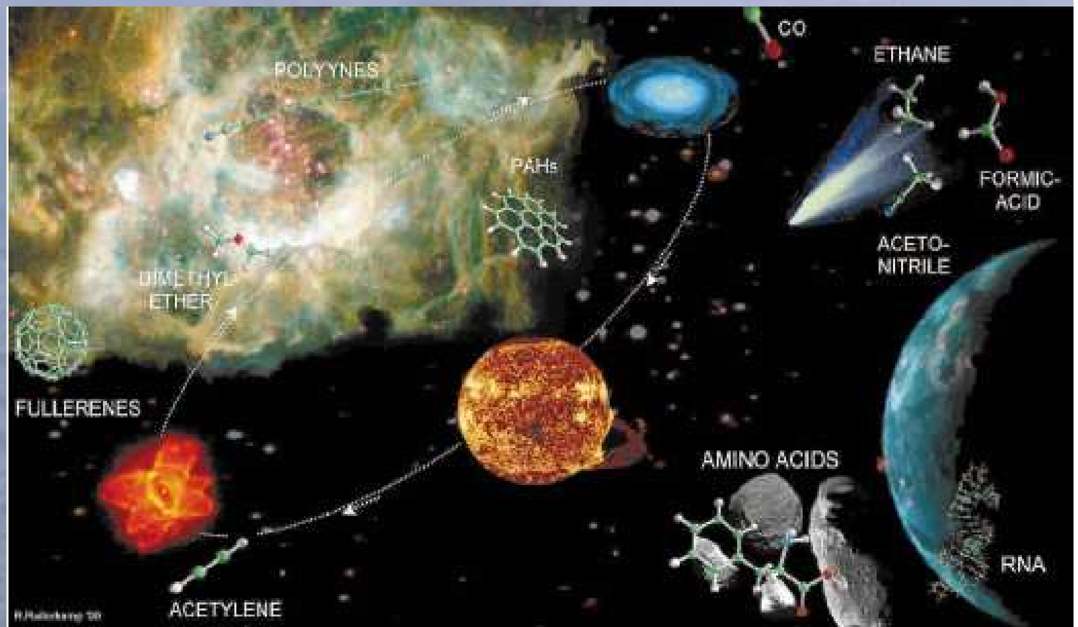
Chemistry of Star Formation



Outline

1. Chemistry of Star Formation
2. A Case Study : IRAS 16293-2422
3. Chemistry of Protoplanetary Disks



Chemical & Dynamical Time-scales

$t_{FF} = 4.3 \times 10^7 \, n^{-1/2}$ yr

$t_{AD} = 7.3 \times 10^{13} \, x_e$ yr

t_{SS} (diffuse) ~ 10^3 yr

t_{SS} (dense) ~ 10^7 yr

t_E (dense) ~ few x 10^5 yr

$t_{ACC} \sim 3 \times 10^9 \, n^{-1}$ yr

COLD PRE-STELLAR CORES

- **Observed in regions of low-mass star formation**
- **n> 10^6 cm^{-3}, T~10-20 K**
- **Depletion of heavy molecules : CO, CS, CCS, H_2CO (B 68, L1544)**
- **Selective depletion towards the centre: CO vs N_2**
- **Very high D/H : HDCO, D_2CO, NHD_2, ND_3, N_2D^+ (L1544, B1, IRAS 16293-2422, L134N)**

H_3^+ + HD --> H_2D^+ + H_2

H_2D^+ + HD --> D_2H^+ + H_2

D_2H^+ + HD --> D_3^+ + H_2

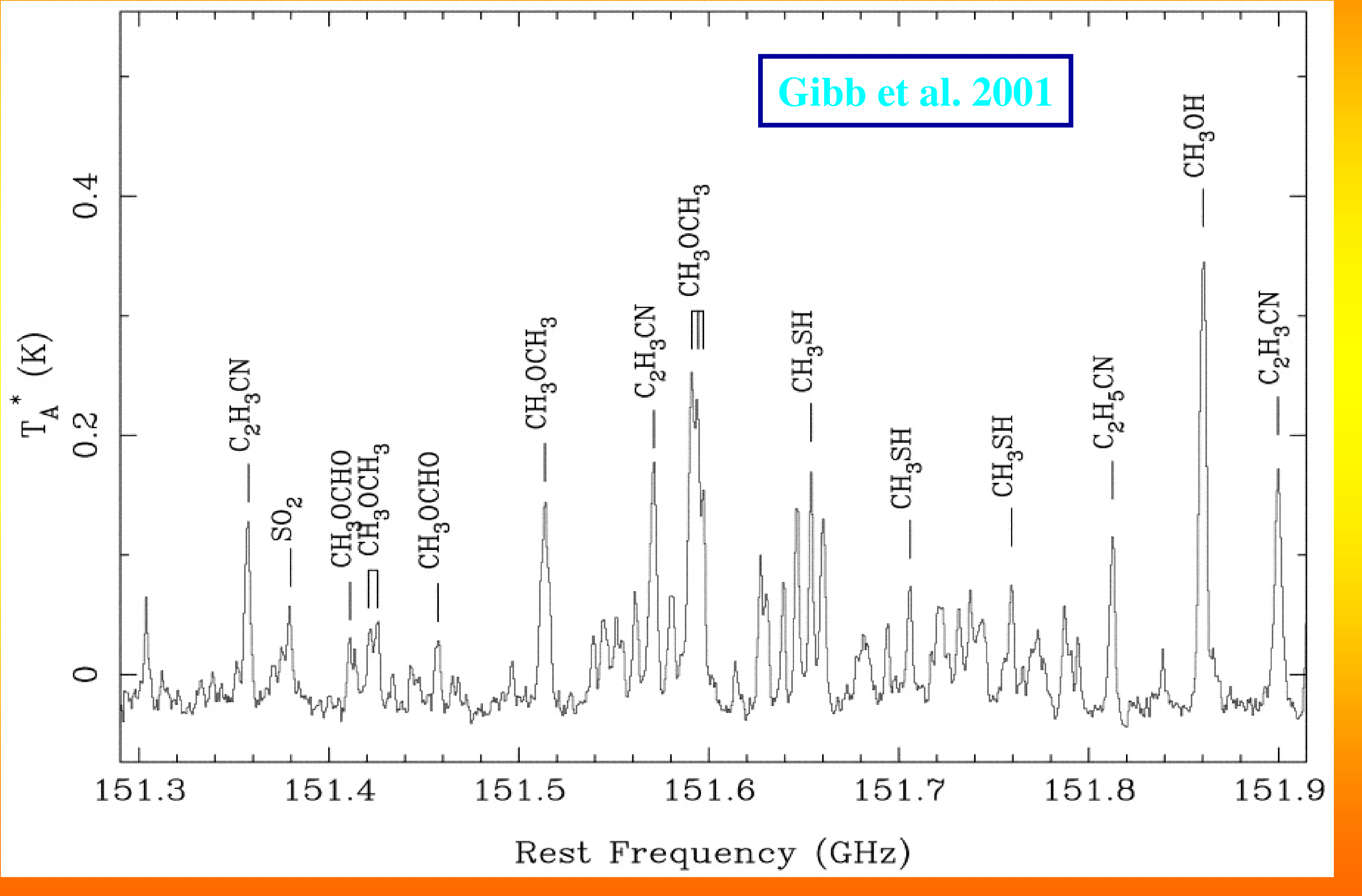
- **High gas phase DI/HI ratios, so enhanced D/H in surface reactions could explain CD_3OH, CHD_2OH, D_2S, D_2COetc, in later evolution**

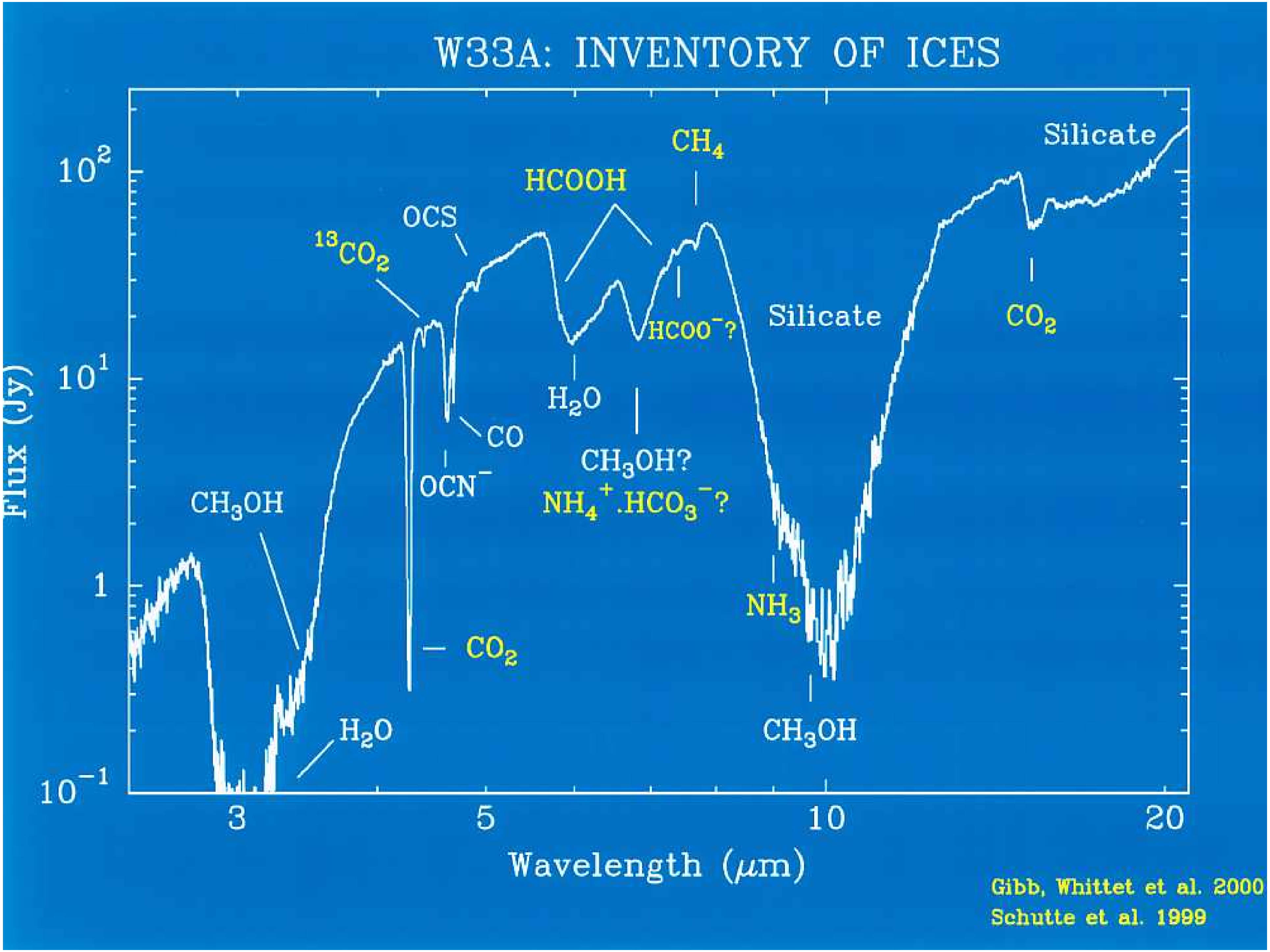
- **Also evidence for massive prestellar cores (e.g. MSX IRDC clouds)**

MASSIVE HOT MOLECULAR CORES

- **Embedded protostar; precursors of UCHII regions**
- **Lifetime ~ 10^5 yr**
- **n> 10^6 cm^{-3}, T~100-300 K**
- **High abundances of H_2O, NH_3, CH_3OH …**
- **Enhanced D/H ratios: HDO, DCN, CH_3OD …**
- **Rich in complex molecules:** HCOOH, HC_3N, CH_3CN, CH_3OH, CH_3CCH, CH_3CHO, C_2H_5OH, $HCOOCH_3$, CH_3OCH_3, CH_3COCH_3, C_2H_3CN, C_2H_5CN and CH_3COOH.

Survey of organic molecules in G327




W33A: INVENTORY OF ICES
Flux (Jy)
Wavelength (μm)
Silicate
CH4
HCOOH
OCS
13CO2
HCOO−?
Silicate
CO2
H2O
CO
OCN−
CH3OH?
NH4+.HCO3−?
CH3OH
NH3
CO2
H2O
CH3OH
Gibb, Whittet et al. 2000
Schutte et al. 1999

HOT CORE EVOLUTION

- **Theory: Brown et al. (1988)**

I. Static dense cloud $n \sim 10^3$ cm^{-3}, T= 10 K;
isothermal free-fall collapse to $n \sim 10^7$ cm^{-3} ;
gas phase chemistry + accretion on grains

II. Short (?) period of total depletion

III. Warm-up to ~ 100-300K and mantle evaporation.

ORIGIN OF HOT CORE MOLECULES

1. **Accreted during static/collapse phase I: CO, C_2H_2, HCN**

2. **Formed on grains during phases I & II: H_2O, NH_3, CH_3OH, CO_2**

3. **Formed in Phase III by post-evaporation gas chemistry:**

methanol … $(CH_3)_2O$, $HCOOCH_3$

$$CH_3OH_2^+ + CH_3OH \; \text{-->} \; (CH_3)_2OH^+ + H$$

ammonia … HCN, CH_3CN, HC_3N,

Complex molecules from radiative associations?

Ethanol

$$H_3O^+ \; + \; C_2H_4 \longrightarrow C_2H_7O^+ \xrightarrow{e^-} C_2H_5OH$$

Acetone

$$\left.\begin{array}{l} H_3O^+ + C_2H_2 \\ HCO^+ + CH_4 \\ H_2CO^+ + CH_4 \end{array}\right\} \longrightarrow C_2H_5O^+ \xrightarrow{e^-} CH_3CHO \xrightarrow{CH_3^+} C_3H_6OH^+ \xrightarrow{e^-} C_2H_6CO$$

Dimethyl ether

$$\left.\begin{array}{l} CH_3^+ + CH_3OH \\ CH_3OH_2^+ + CH_3OH \end{array}\right\} \longrightarrow C_2H_6OH^+ \xrightarrow{e^-} CH_3OCH_3$$

Methyl formate

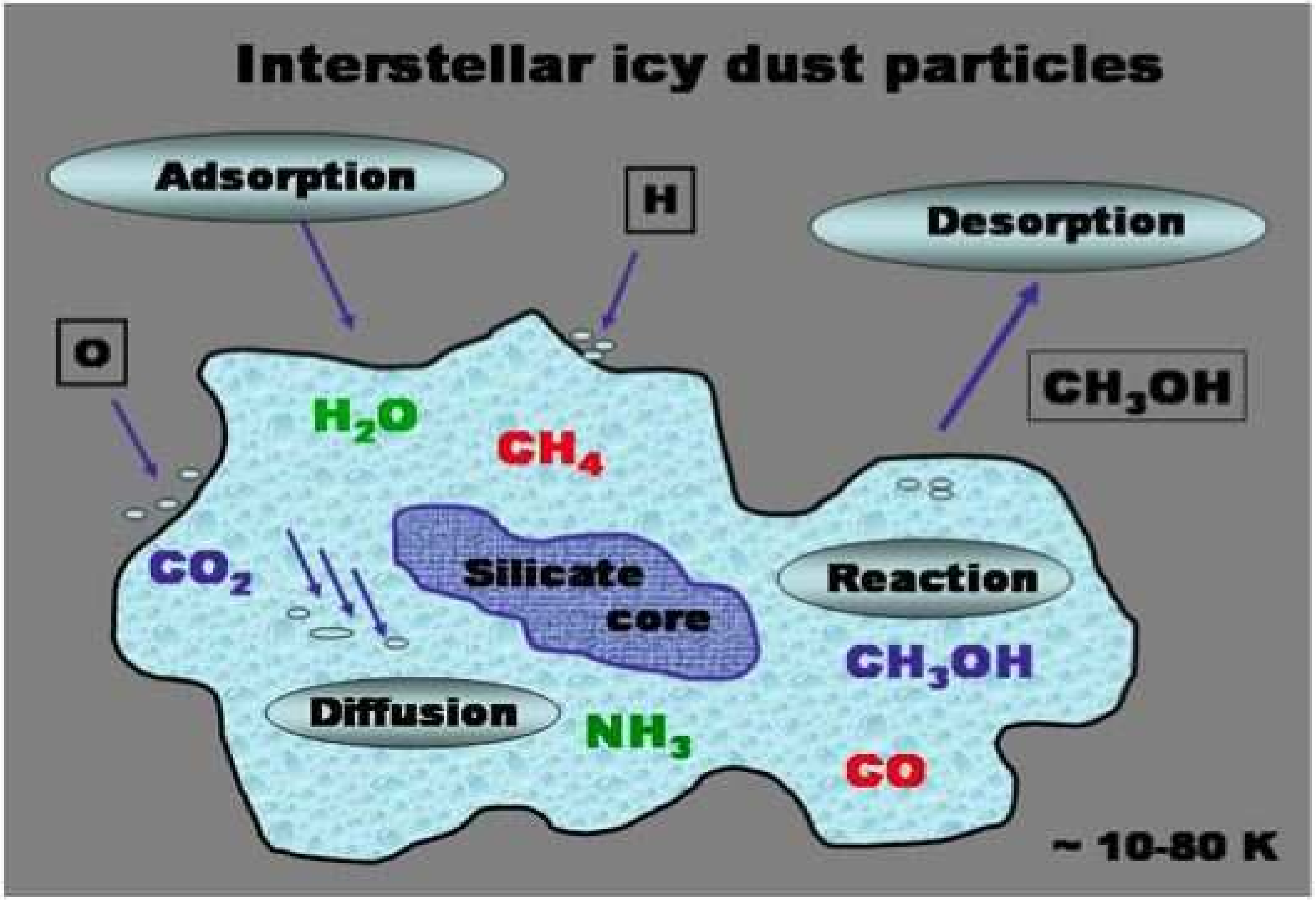
$$\left.\begin{array}{l} H_3^+ + CH_3OH \\ H_3O^+ + CH_3OH \\ CH_3^+ + H_2O \\ HCO^+ + CH_3OH \\ CH_4^+ + CH_3OH \\ CH^+ + CH_3OH \end{array}\right\} \longrightarrow CH_3OH_2^+ \xrightarrow{H_2CO} H_5C_2O_2^+ \xrightarrow{e^-} HCOOCH_3$$

CONSTRAINING SURFACE CHEMISTRY

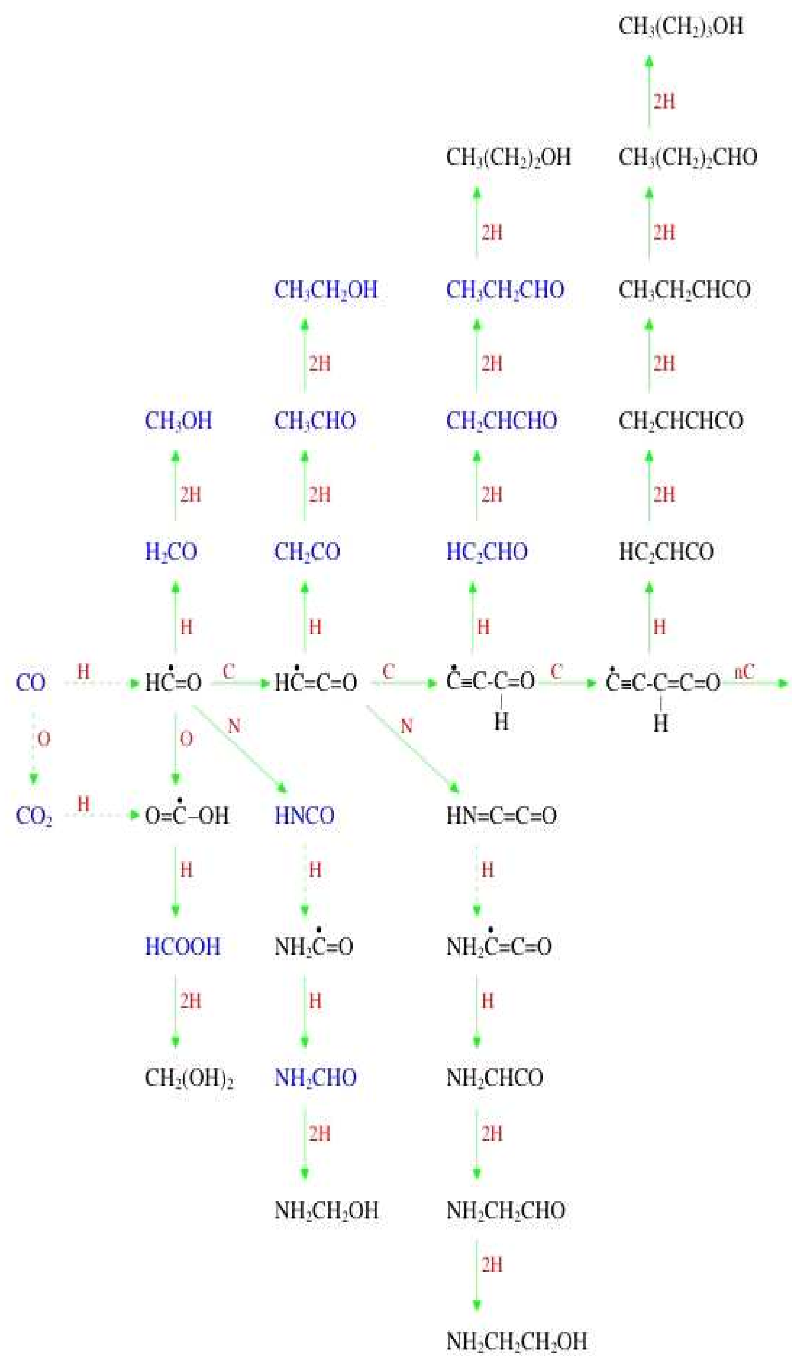
- **STRATEGY: observe hot core composition and develop models of post-evaporation chemistry, then determine if**

1. **Formed pre-warm-up by gas reactions and simple accretion?**
   CO
2. **Formed in hot post-evaporation gas chemistry?**
   CH_3OCH_3
3. **Formed on grains during phases I & II ?**
   C_2H_5OH

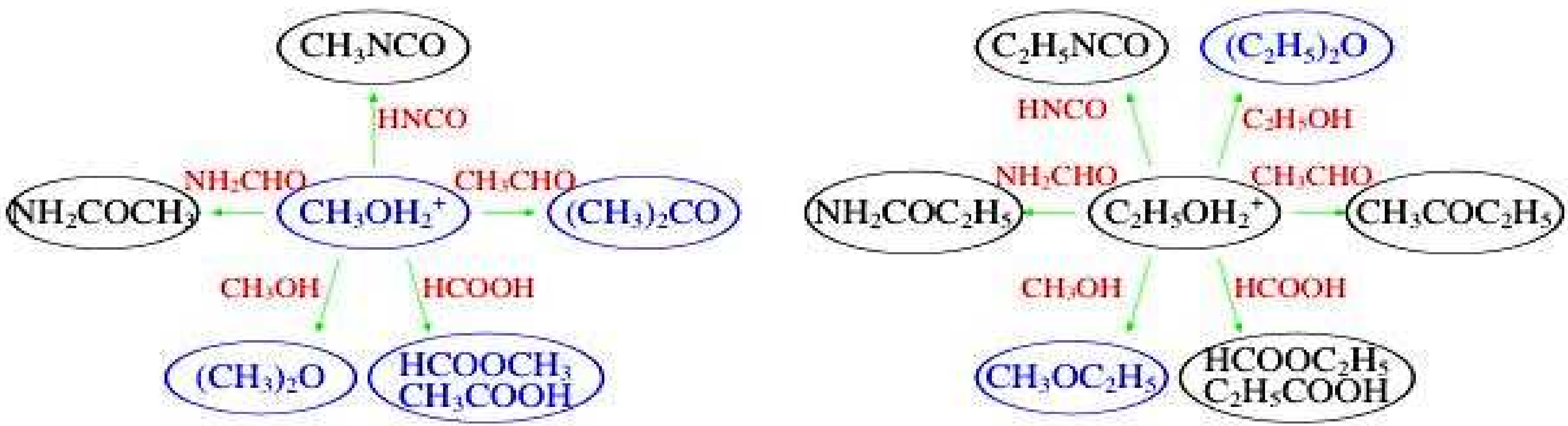
If so, look for viable reaction pathways …



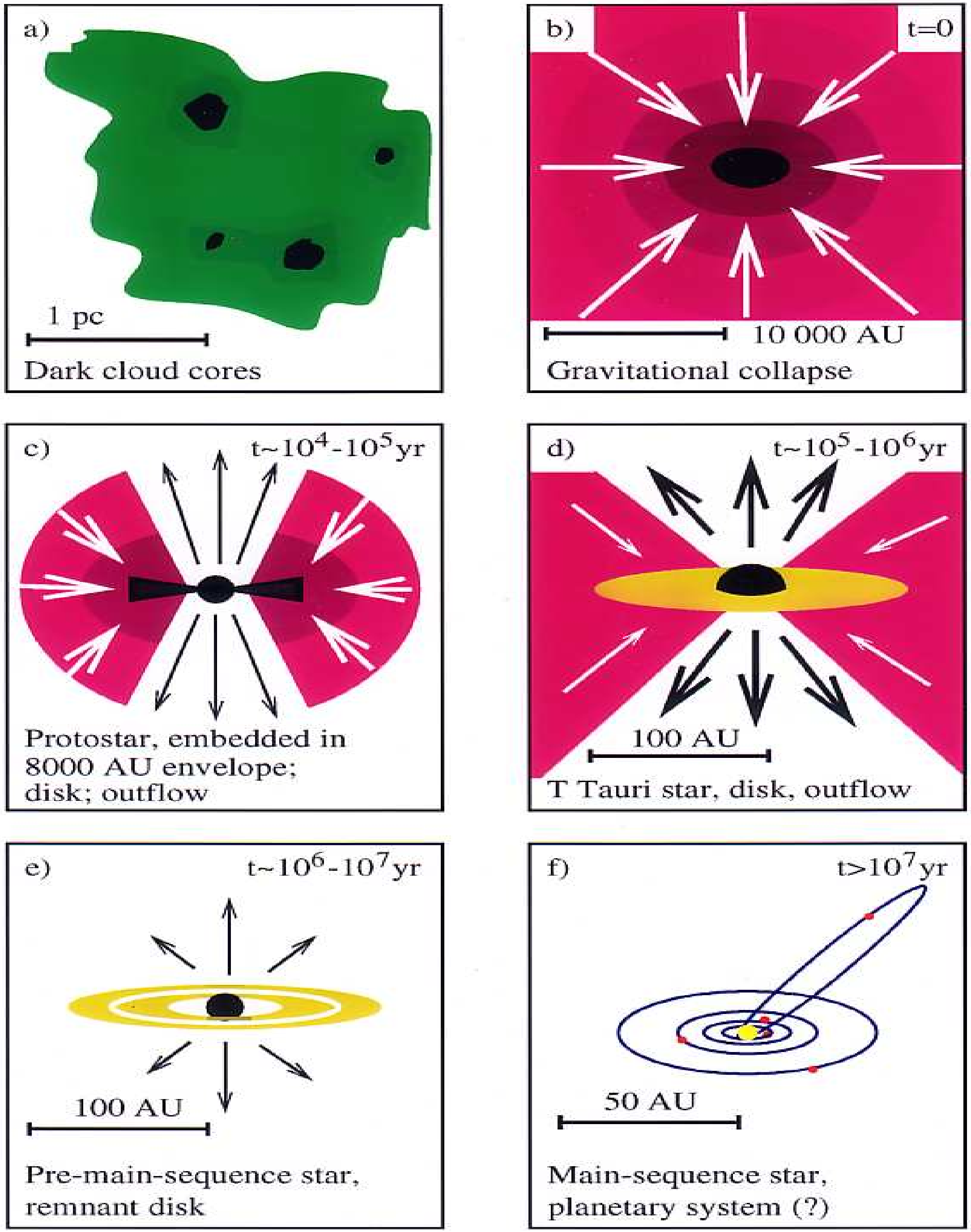
Ehrenfreund, Charnley & Botta (2005)


CO
CO2
HC=O
O=C-OH
HC=C=O
C≡C-C=O
C≡C-C=C=O
H2CO
CH3OH
CH2CO
CH3CHO
CH3CH2OH
HC2CHO
CH2CHCHO
CH3CH2CHO
CH3(CH2)2OH
HC2CHCO
CH2CHCHCO
CH3CH2CHCO
CH3(CH2)2CHO
CH3(CH2)3OH
HCOOH
CH2(OH)2
HNCO
NH2C=O
NH2CHO
NH2CH2OH
HN=C=C=O
NH2C=C=O
NH2CHCO
NH2CH2CHO
NH2CH2CH2OH
H
O
C
N
2H
nC

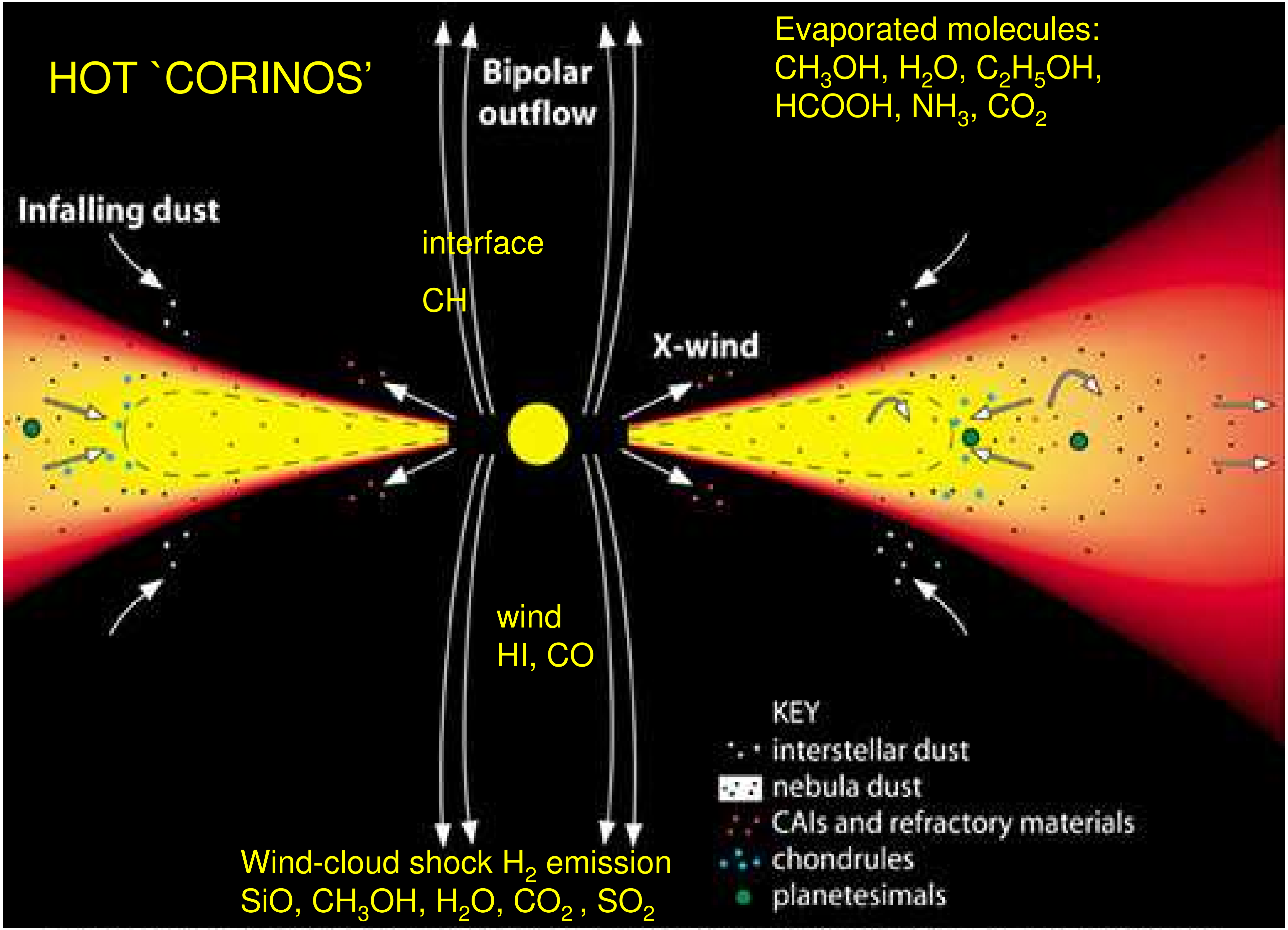
ALKYL CATION TRANSFER REACTIONS



LOW-MASS STAR FORMATION



Hogerheijde 1998, after Shu et al. 1987



(PSRD graphic by Nancy Hulbirt, based on a conceptual drawing by Edward Scott, Univ. of Hawaii.)

Organic Molecules
in the
IRAS 16293-2422 Hot Corino

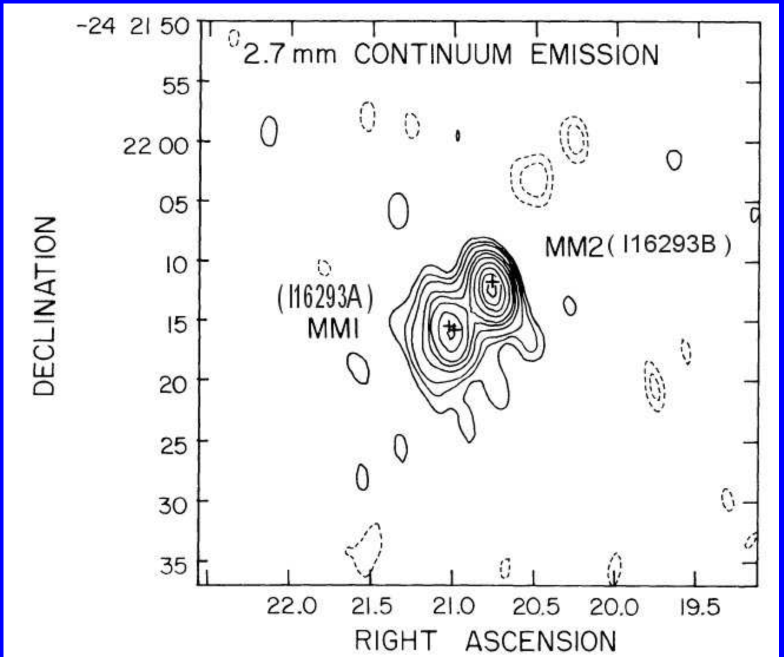
Observations with the SMA (Kuan et al. 2004)

Theory and Experiments

Predictions

IRAS 16293-2422

- Low-mass protostellar core located in Rho Ophiuchus; D ~ 160 pc.
- High spatial resolution continuum observations show it is a protobinary system (A & B) with a projected separation of ~840 AU.
- 30 different molecular species - excluding isotopes - detected in single-dish observations; including HCOOH, HC_3N, CH_3CN, CH_3OH, CH_3CCH, CH_3CHO, $HCOOCH_3$, CH_3OCH_3, C_2H_5CN and CH_3COOH.



Mundy, et al., 1992

Sample images of large organic molecules

Crosses mark the positions of Source A and Source B, as denoted in the continuum image.

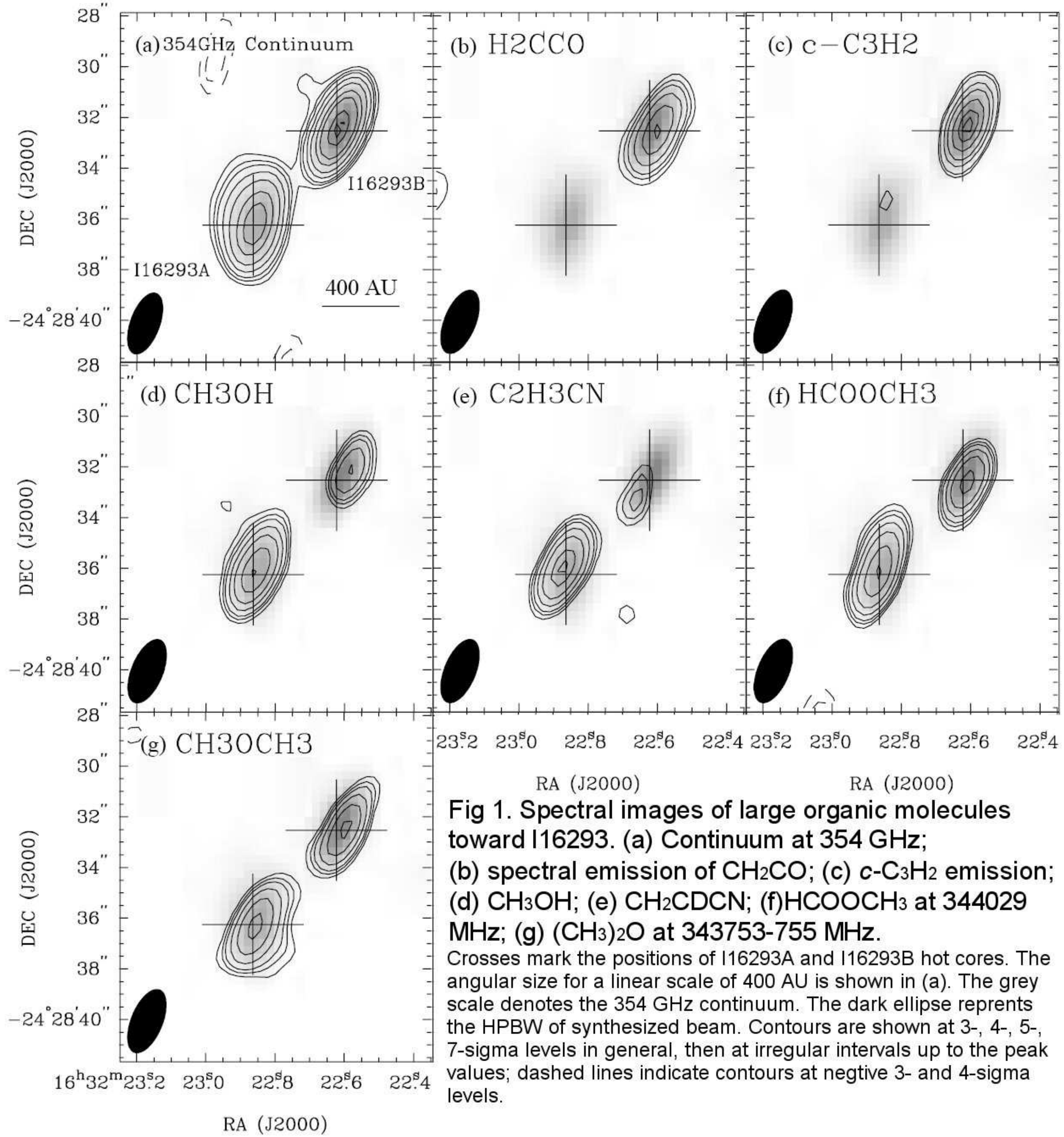


Fig 1. Spectral images of large organic molecules toward I16293. (a) Continuum at 354 GHz; (b) spectral emission of CH_2CO; (c) *c*-C_3H_2 emission; (d) CH_3OH; (e) CH_2CDCN; (f)$HCOOCH_3$ at 344029 MHz; (g) $(CH_3)_2O$ at 343753-755 MHz.

Crosses mark the positions of I16293A and I16293B hot cores. The angular size for a linear scale of 400 AU is shown in (a). The grey scale denotes the 354 GHz continuum. The dark ellipse reprents the HPBW of synthesized beam. Contours are shown at 3-, 4-, 5-, 7-sigma levels in general, then at irregular intervals up to the peak values; dashed lines indicate contours at negtive 3- and 4-sigma levels.

Molecular Column Densities and Fractional Abundances

Molecular column densities and fractional abundances toward IRAS 16293-2422.

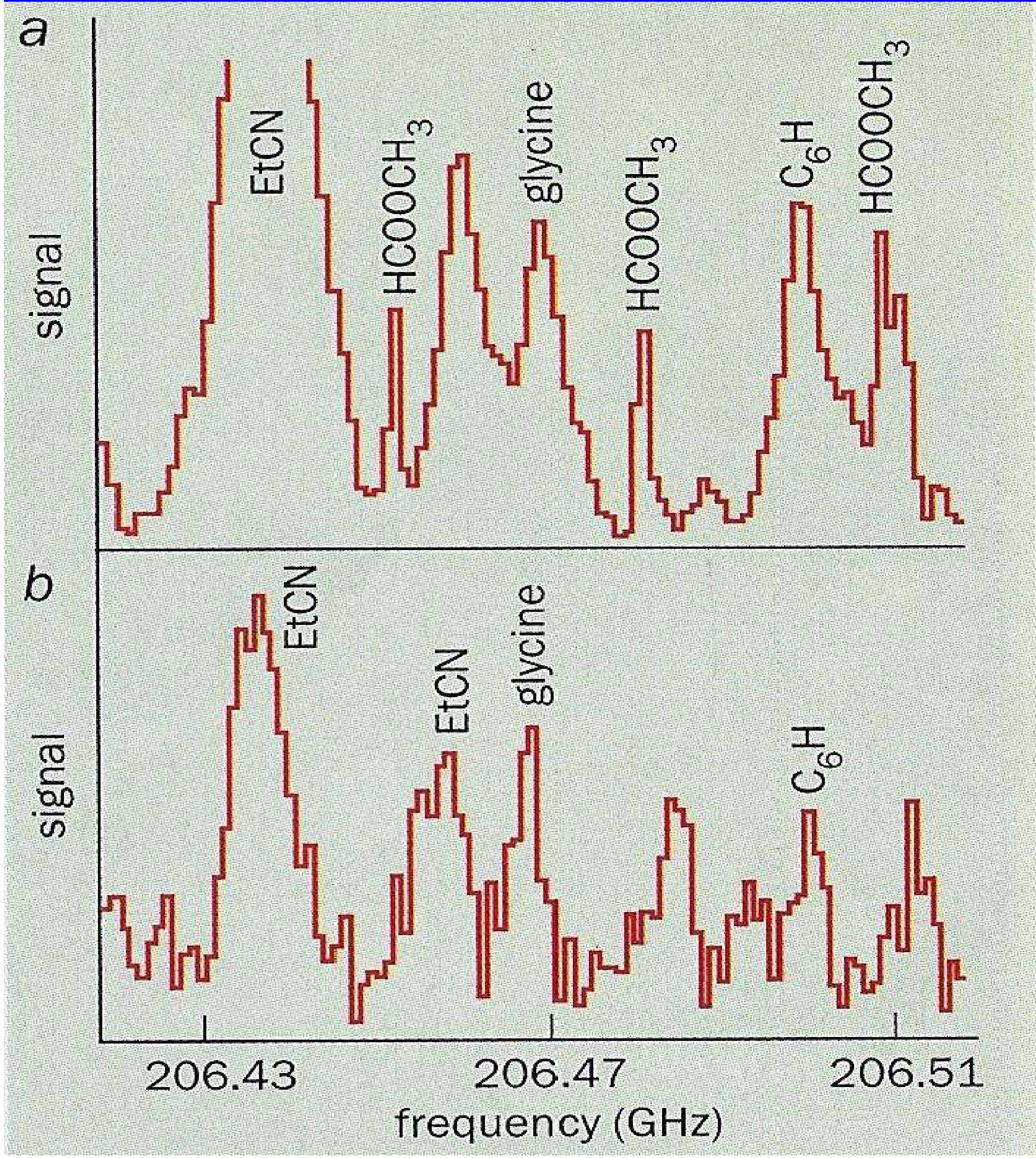
Molecule	I16293A $\int I_\nu dV$ (Jy $bm^{-1}km\ s^{-1}$)	I16293A N (cm^{-2})	I16293A X (N/N_{H_2})	I16293B $\int I_\nu dV$ (Jy $bm^{-1}km\ s^{-1}$)	I16293B N (cm^{-2})	I16293B X (N/N_{H_2})	HMC X
SO	2.69	4.2(+16)	2.6(-8)	—	——	——	1.9(-7)[a]
SO_2	4.42	2.2(+17)	1.4(-7)	3.00	1.5(+17)	9.2(-8)	1.2(-7)[a]
$^{34}SO_2$	2.50	2.3(+16)	1.4(-8)	—	——	——	—
$OC^{34}S$	12.36	4.7(+15)	3.0(-9)	8.32	3.2(+15)	2.0(-9)	—
HCN	270.58	9.2(+14)	5.8(-10)	161.86	5.5(+14)	3.4(-10)	3.2(-9)[b]
HCN (v_2=1)	9.89	2.7(+15)	1.7(-9)	2.15	5.8(+14)	3.6(-10)	3.2(-9)[b]
$HC^{15}N$	42.86	1.2(+14)	7.4(-11)	6.97	1.9(+13)	1.2(-11)	—
H_2CS	5.94	1.5(+15)	9.4(-10)	5.31	1.3(+15)	8.4(-10)	8.(-10)[a]
$C^{13}CCS$	—	——	——	3.75	9.6(+13)	6.2(-11)	—
c-C_3H_2	—	——	——	10.03	7.2(+15)	4.5(-9)	6.3(-11)[b]
CH_2CO	—	——	——	3.22	1.9(+15)	1.2(-9)	3.(-10)[a]
HC_3N	16.73	6.7(+14)	4.2(-10)	4.86	2.0(+14)	1.2(-10)	1.8(-9)[a]
CH_3OH	13.62	1.1(+18)	6.8(-7)	6.20	5.0(+17)	3.1(-7)	1.4(-7)[a]
$^{13}CH_3OH$	5.34	8.1(+16)	5.0(-8)	—	——	——	—
CH_2CHCN	8.58	1.5(+16)	9.4(-9)	2.34	4.1(+15)	2.6(-9)	1.5(-9)[a]
CH_2CDCN	....	5.9(+14)	3.7(-10)	....	8.8(+14)[c]	5.5(-10)	—
$HCOOCH_3$	....	1.2(+16)[c]	7.5(-9)	....	8.7(+15)[c]	5.4(-9)	1.4(-8)[a]
$(CH_3)_2O$	8.49	6.6(+15)	4.1(-9)	10.32	8.0(+15)	5.0(-9)	8.(-9)[a]

[a] Orion KL hot core; from Sutton *et al.* (1995).

[b] Sgr B2(M) hot core; from Sutton *et al.* (1991).

[c] The averaged column density from all transitions observed.

Interstellar Glycine

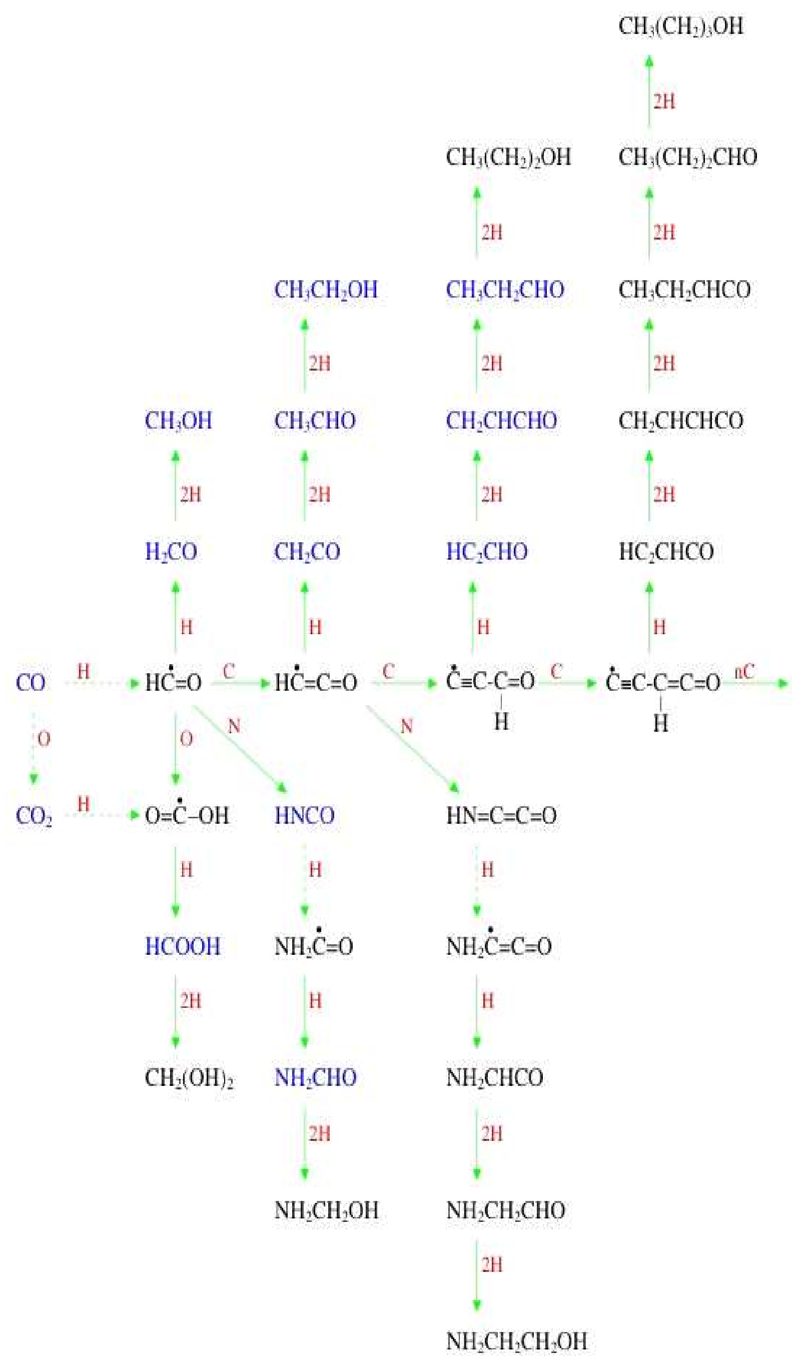


Detected in three hot molecular cores

- **Sgr B2(N-LMH)**
- **Orion KL**
- **W51 e1/e2**

27 glycine lines were detected in 19 different spectral bands in one or more sources

Kuan et al. 2003


CO
H
HC=O
C
HC=C=O
C
C≡C-C=O
C
C≡C-C=C=O
nC
O
CO2
O=C–OH
HNCO
N
HN=C=C=O
H2CO
CH3OH
2H
CH2CO
CH3CHO
CH3CH2OH
HC2CHO
CH2CHCHO
CH3CH2CHO
CH3(CH2)2OH
HC2CHCO
CH2CHCHCO
CH3CH2CHCO
CH3(CH2)2CHO
CH3(CH2)3OH
HCOOH
CH2(OH)2
NH2C=O
NH2CHO
NH2CH2OH
NH2C=C=O
NH2CHCO
NH2CH2CHO
NH2CH2CH2OH

Amino Acids via Ion-Molecule Reactions

From surface-formed aminoalcohols ?

$NH_2CH_2OH_2^+ + HCOOH \longrightarrow NH_2CH_2COOH_2^+ + H_2O$

$NH_2(CH_2)_2OH_2^+ + HCOOH \longrightarrow NH_2(CH_2)_2COOH_2^+ + H_2O$

Ices rich in NH_2OH ?

Then, from hydroxlamine (Blagojevic et al. 2003):

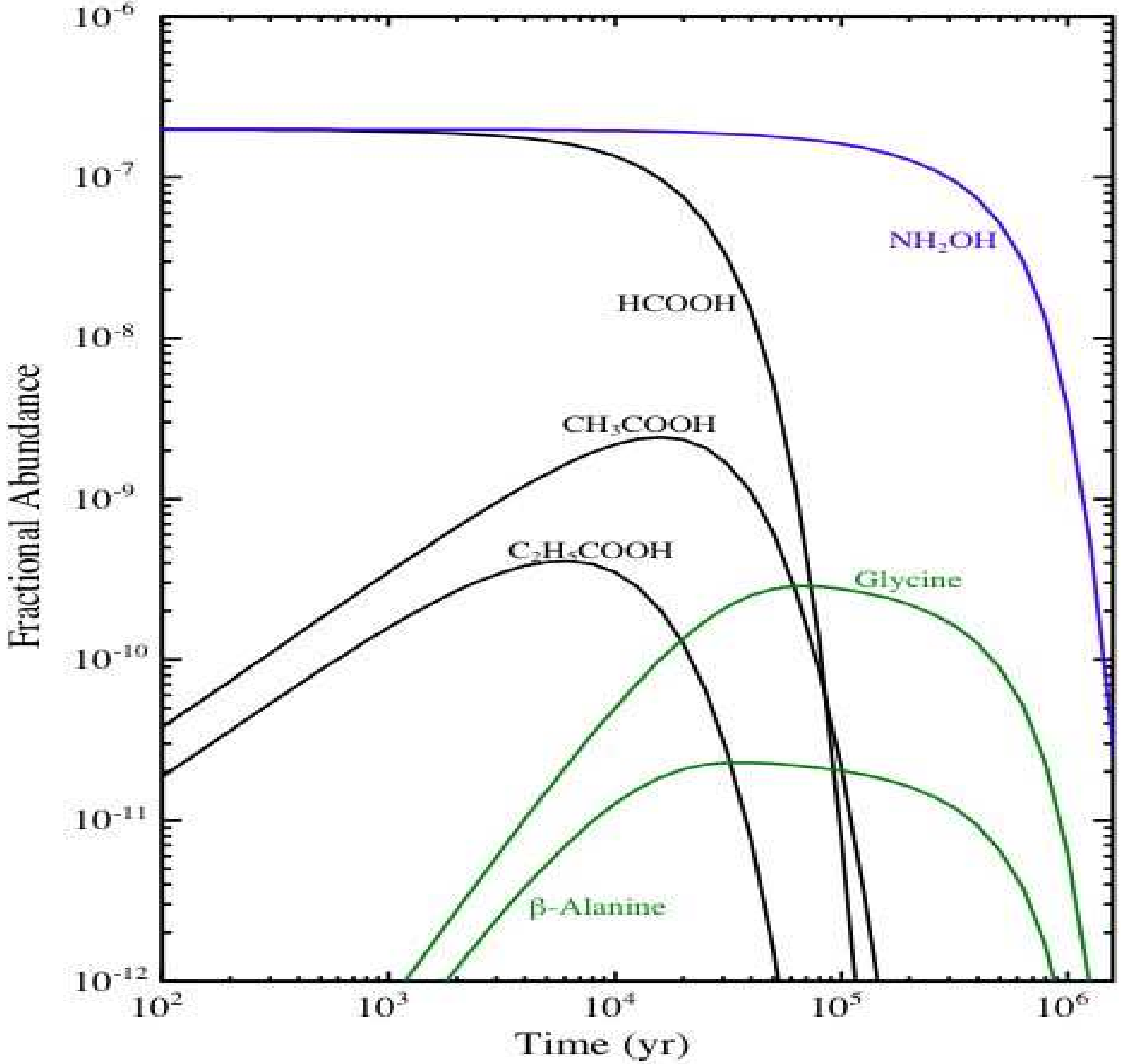
$NH_2OH_2^+ + CH_3COOH \longrightarrow NH_2CH_2COOH_2^+ + H_2O$

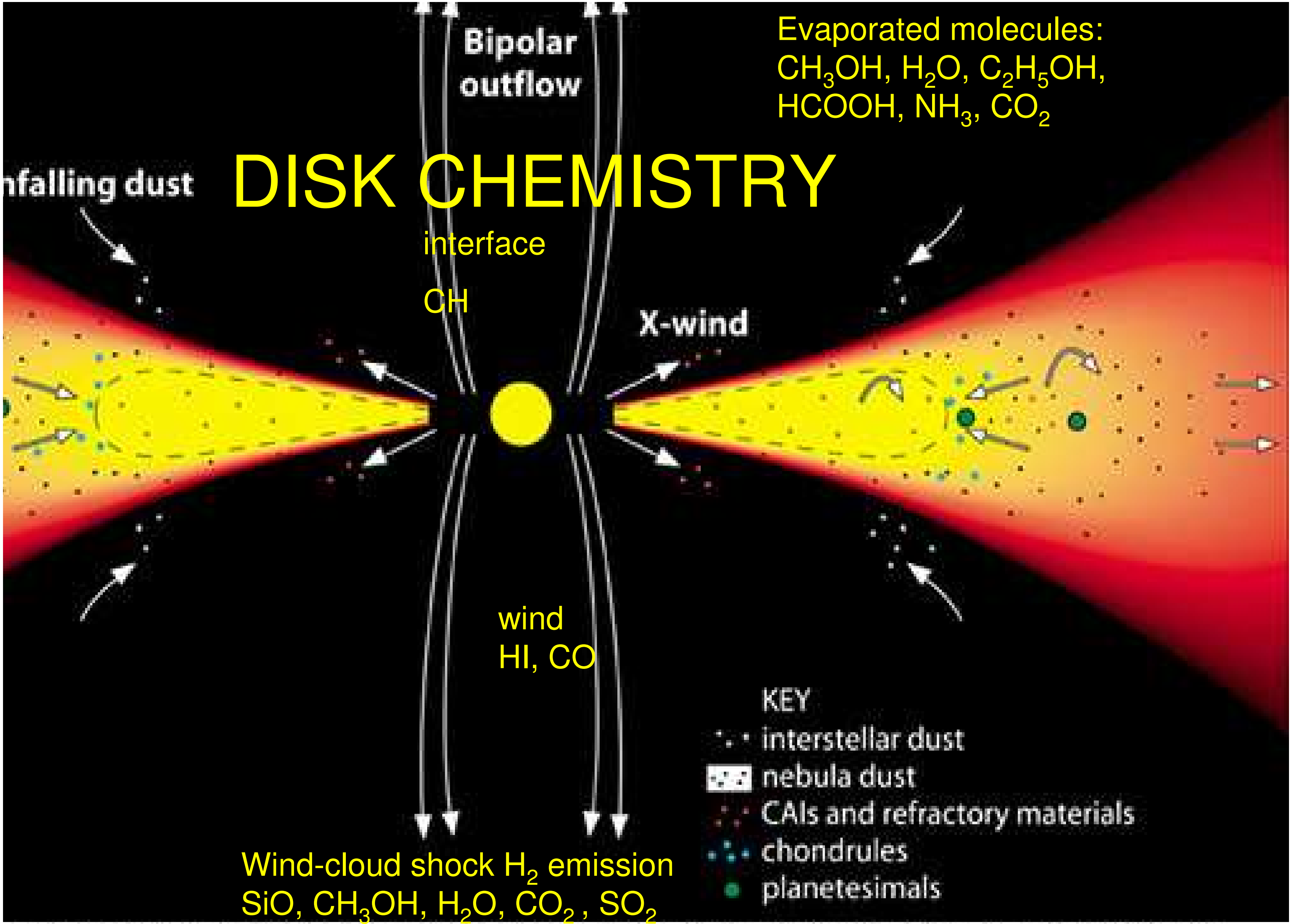
$NH_2OH_2^+ + CH_3CH_2COOH \longrightarrow NH_2(CH_2)_2COOH_2^+ + H_2O$

SIFT experiments (Blagojevic & Bohme) determine reaction efficiency & structure of product molecular ions (e.g. alpha-Alanine vs. beta-Alanine)

Quantum-chemical studies (Petrie) used to investigate reactions involving highly unstable reactants (NH_2CH_2OH).

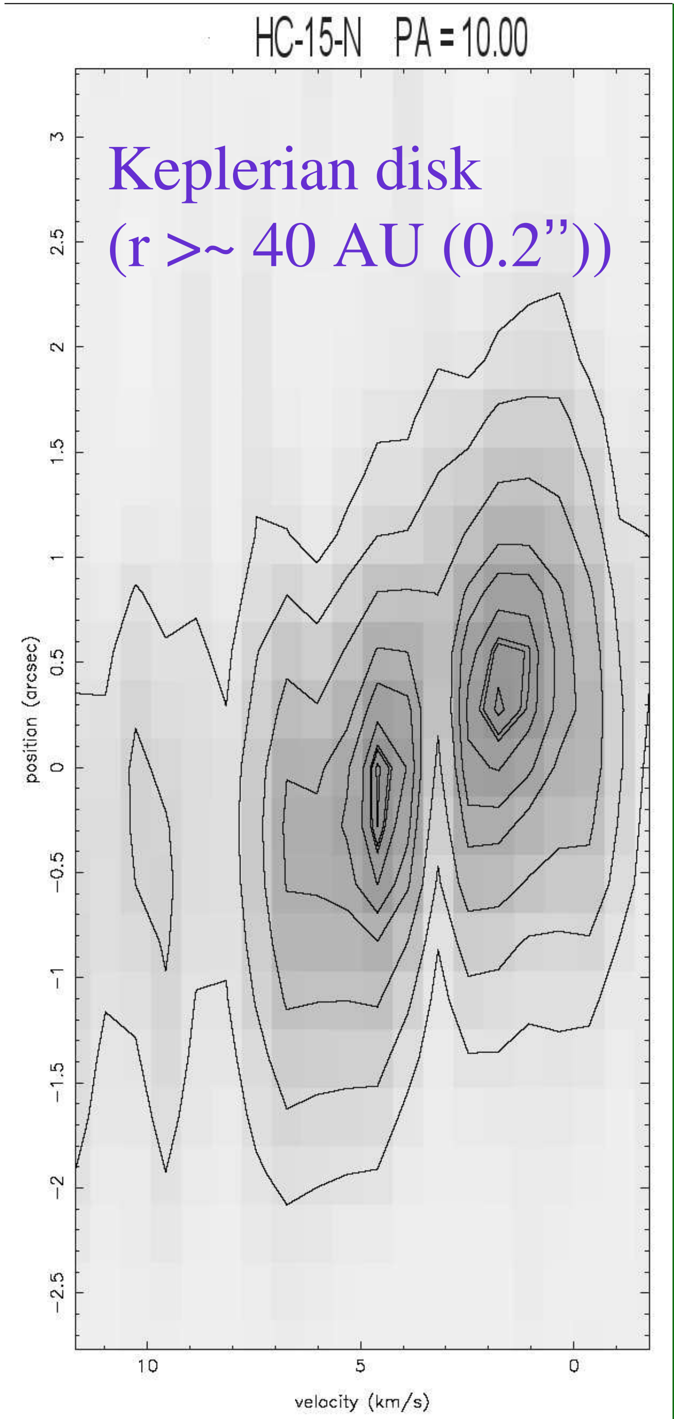
Gas Phase Synthesis of Protostellar Amino Acids



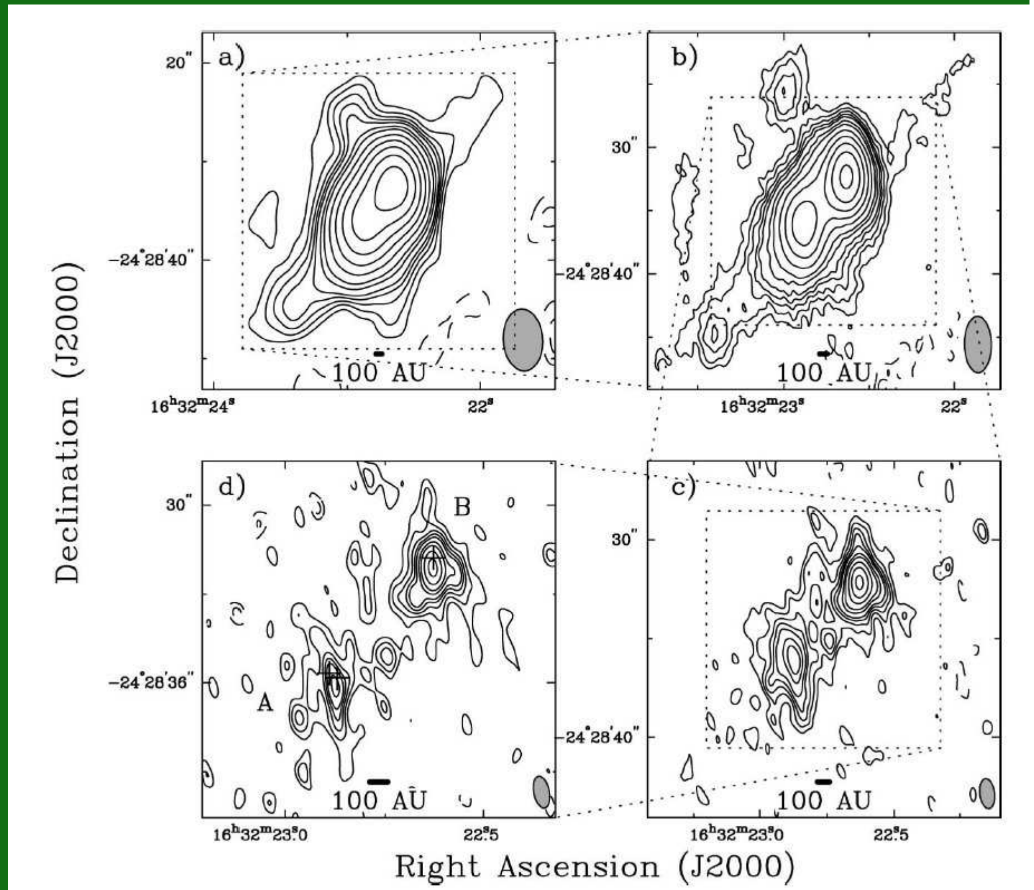


(PSRD graphic by Nancy Hulbirt, based on a conceptual drawing by Edward Scott, Univ. of Hawaii.)

I16293A: a protostellar disk



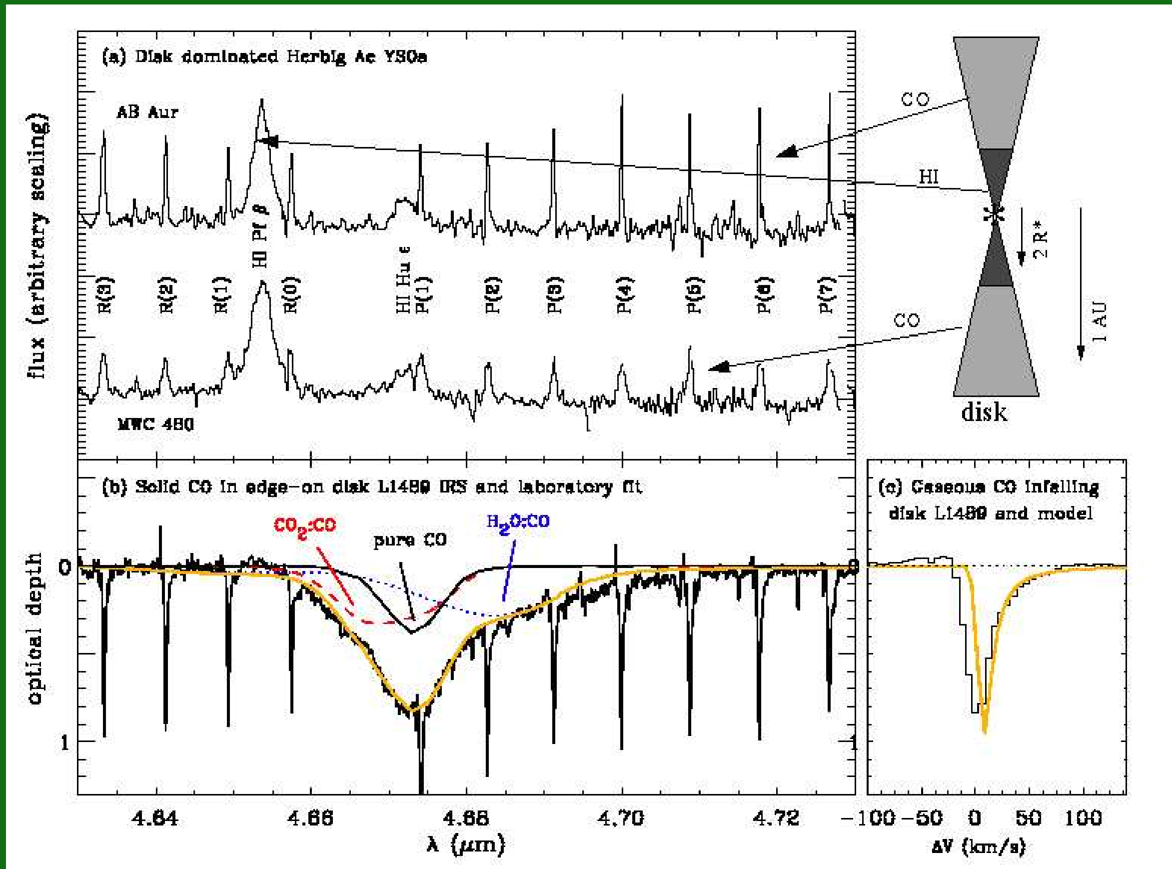
Takakuwa et al. (2004)



Looney & Mundy 2000, ApJ

CO Gas and Ice in CS Disks

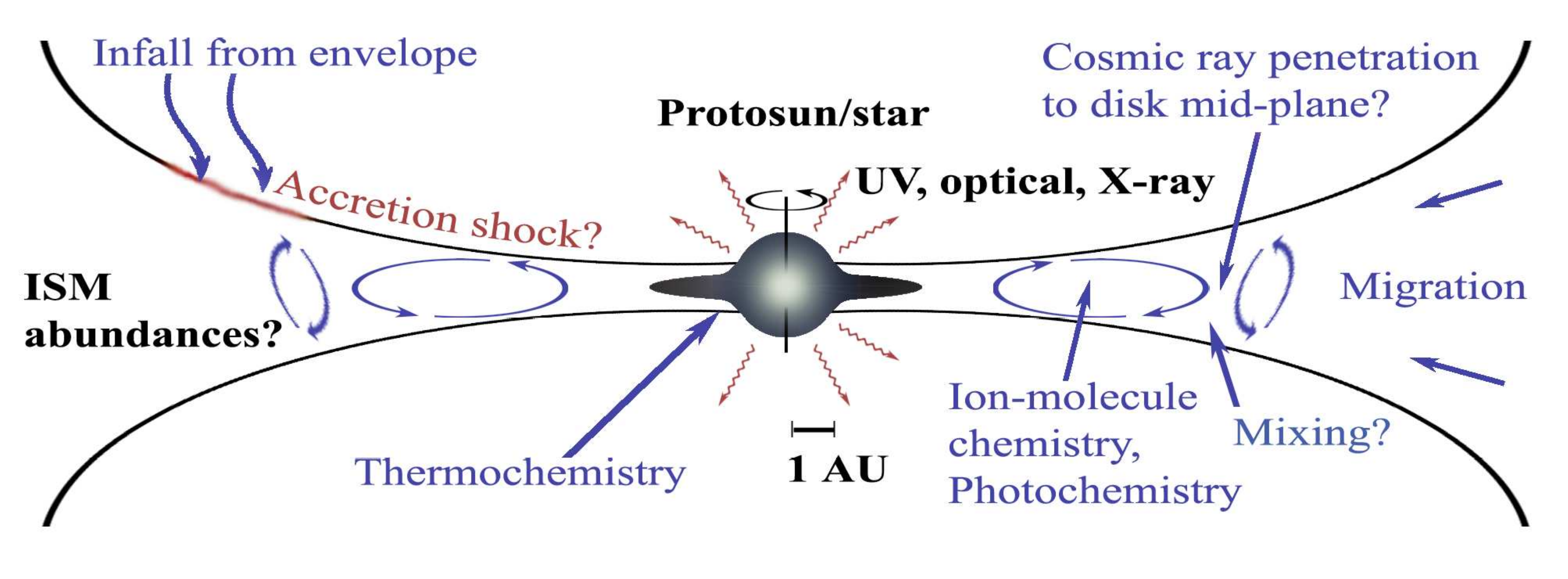
G. Blake et al. 2003 (personal communication)



Chemical Characteristics of Circumstellar Disks

- DM Tau, GG Tau, L1157, LkCa15, TW Hya (Dutrey et al, 1997, 2000)
- Molecules detected: CO, $C^{18}O$, ^{13}CO, HCN, HNC, CN, CS H_2CO, HCO^+, $H^{13}CO^+$, C_2H, CH_3OH, N_2H^+, DCO^+
- Depletion by factors of 3-100 relative to molecular cloud abundances (TMC-1) - sticking on grains important
- Radical and ion emission originates in disk surface photochemistry.

Processes affecting ices and dust in Protoplanetary Disks.



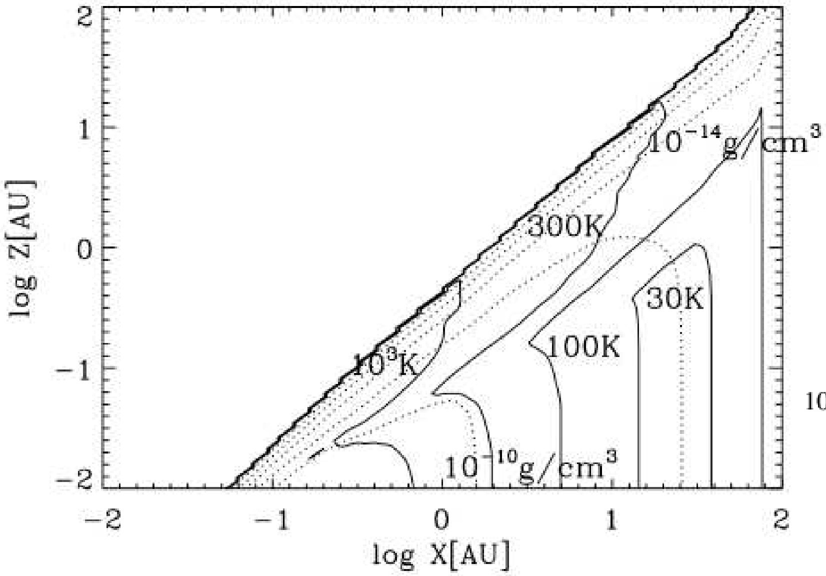
The composition of disk material is extremely sensitive to initial composition, nebular processing, and nebular dynamics.

some recent models of disk chemistry and their ingredients

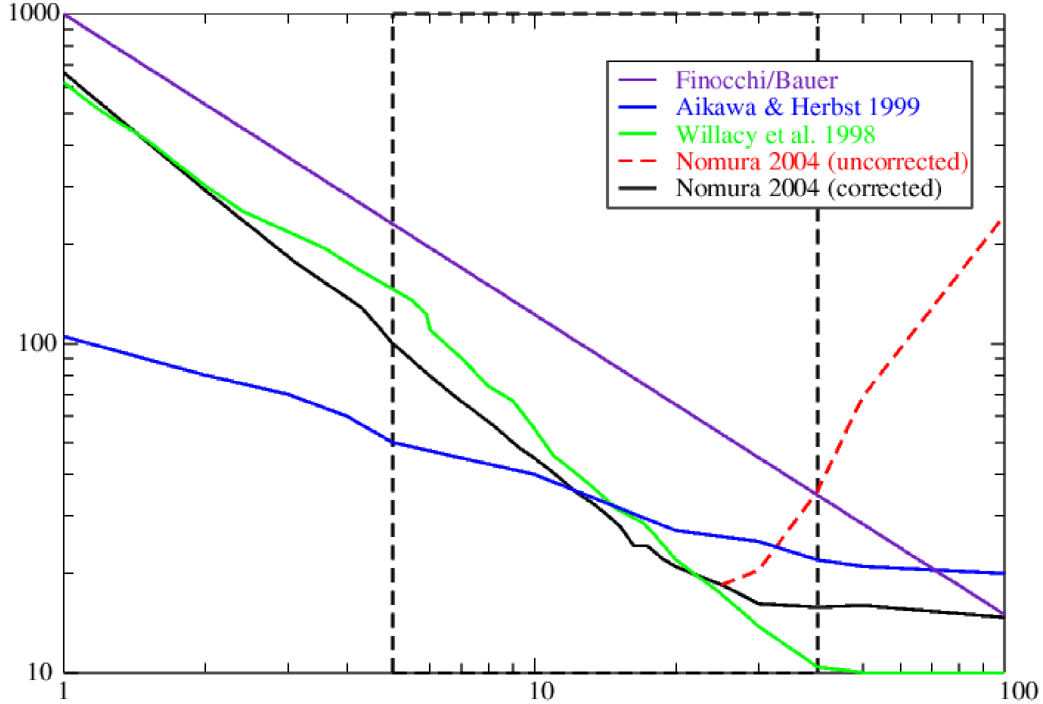
Table 1.2. Recent models of chemistry in protoplanetary disks. A comparison of the main features of some prominent models in the literature. The columns are as follows. (1) Physics: the underlying description of the disk structure; Semi-Analytical (S); Bell et al. (1997; B); Hayashi minimum mass solar nebula (Hayashi 1981; H); Steady Accretion Disk (A; Lynden-Bell & Pringle 1974); D'Alessio et al. (D; 1998); Chiang & Goldreich (1997, 1999; C); Nomura (N; 2002). (2) Chemistry: Prasad & Huntress (1980; PH); Mitchell (1984), Baulch et al. (1992) (MB); explicit grain surface reactions, not including gas-grain interaction, H_2 formation or recombination of ions (S); UMIST reaction kinetics (U; Le Teuff et al. 2000; Millar et al. 1997); Ohio State reaction kinetics (O; Terzieva & Herbst 1998); deuterium fractionation reactions (D). (3) Dimension: 1-D midplane model, or 1+1D vertical structure calculation. (4) Ionisation: cosmic ray (C), UV photon (U), X-ray photon (X), ionisation due to the decay of extinct radionuclides (R). (5) Gas-grain interaction: freeze-out and thermal/non-thermal desorption. (6) Dust destruction (carbon, troilite, silicate). (7) Observables reported; column densities (CD); D/H ratios; line profiles resulting from radiative transfer calculations. (8) Coupling: true coupling of chemistry and dynamics.

Model	P	Chem	D	I	G	D	Obs	C
Aikawa et al. (1996)	H	PH	1	U,C	Y	N	CD	N
Bauer et al. (1997)	S	MB	1	-	N	Y	No	N
Finocchi & Gail (1997)	S	MB	1	-	N	Y	No	N
Willacy et al. (1998)	B	U,S	1	C,R	Y	N	No	N
Aikawa & Herbst (1999)	H	O	1+1	X,C,U	Y	N	CD	N
Aikawa et al. (1999)	A	U	1	C	Y	N	No	N
Aikawa & Herbst (1999b)	A	O,D	1	C	Y	N	D/H	N
Willacy & Langer (2000)	C	U,S	1+1	U,C,R	Y	N	CD	N
Aikawa & Herbst (2001)	H	O,D	1+1	X,C,U	Y	N	CD,D/H	N
Aikawa et al. (2002)	D	O	1+1	U,C	Y	N	CD,Line	N
Markwick et al. (2002)	B	U	1+1	X,C,U,R	Y	N	CD	N
van Zadelhoff et al. (2003)	D	O	1+1	U,C	Y	N	Line	N
Millar et al. (2003)	N	U	1+1	U,C,R	Y	N	CD	N
Ilgner et al. (2003)	B	U	1+1	U,C,R	Y	N	No	Y

Structure of a Disk for R < 100 AU.

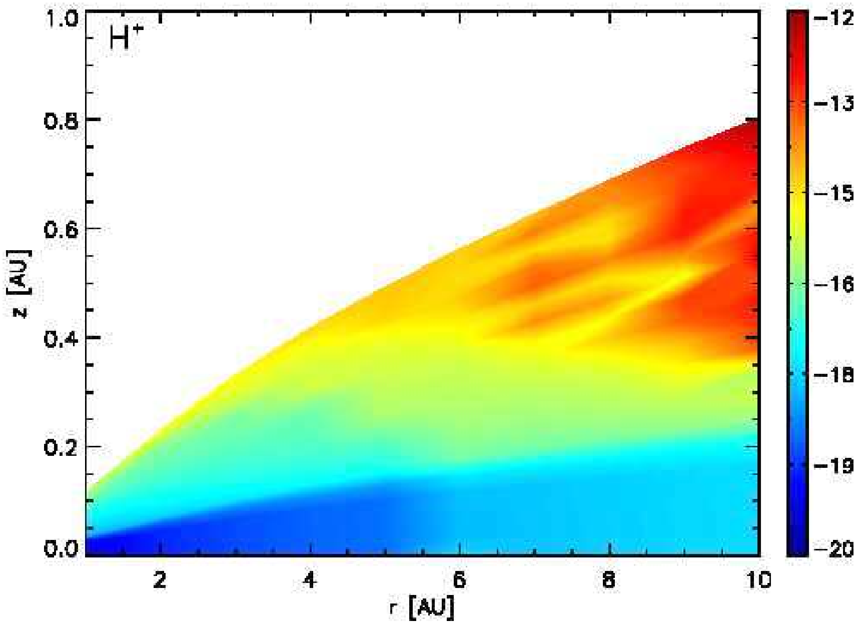


After Markwick et al. (2002)

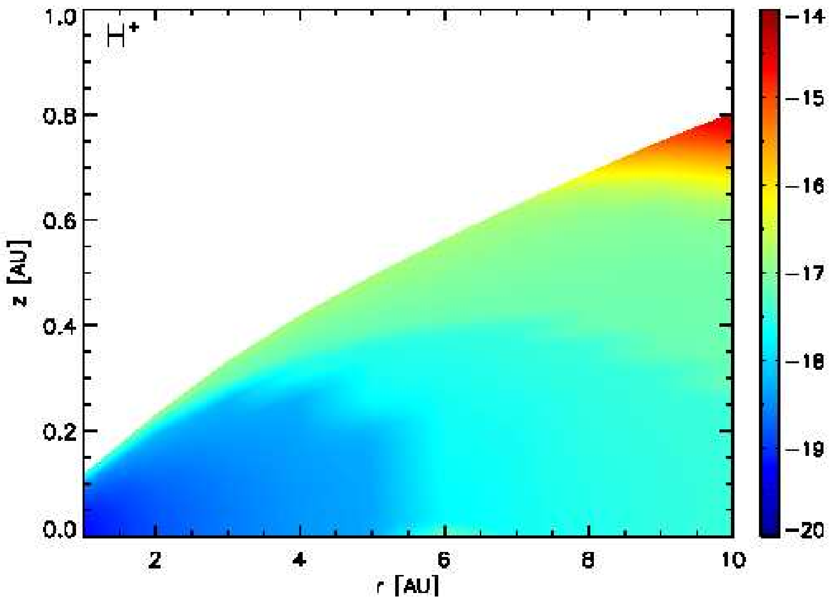


X-rays in Disk Chemistry

High X-ray flux



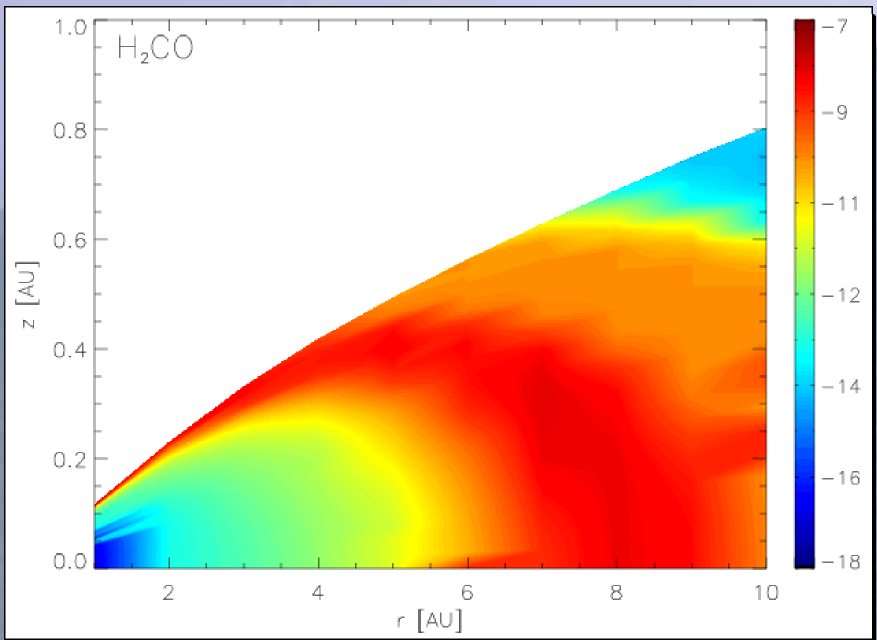
No X-ray flux

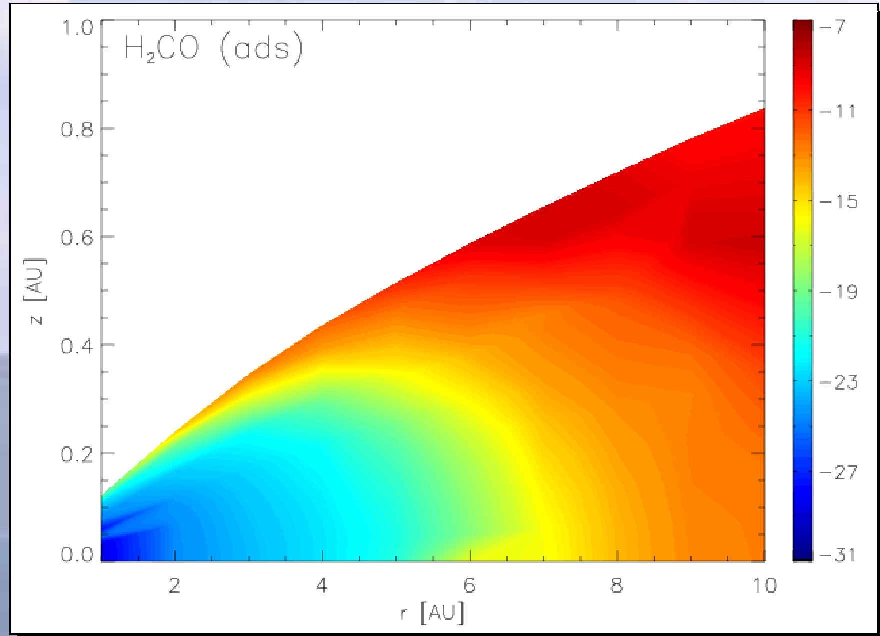


After Markwick et al. A & A 385:632-646 (2002)

Gas-grain interaction

Observed molecules;
CN, CO, NH_3, H_2CO, HCN, HNC, CS, HCO^+, HCS^+





In the inner regions, ice mantles are evaporated

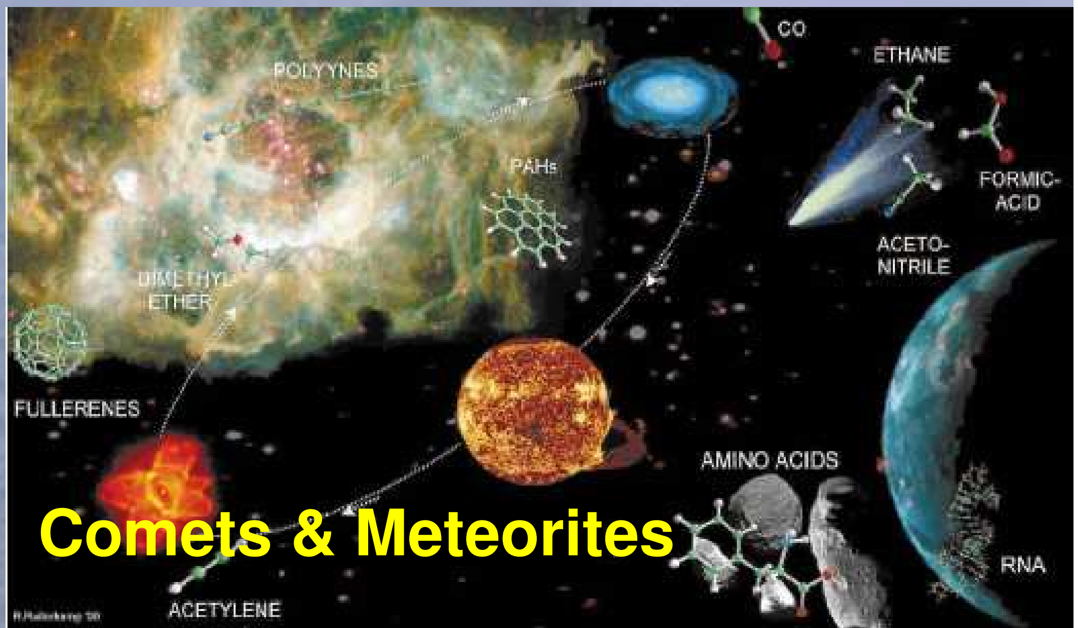
Summary

1. Studying gas phase chemistry in SF constrains possible grain processes

2. High resolution observations, expts. & models can combine to help understand molecular composition of SF cores

3. Disk Chemistry - the next frontier with ALMA

Tomorrow:



What happens to interstellar matter ?

- Large-scale inward transport of most of the gas and dust and outward transport of most of the angular momentum

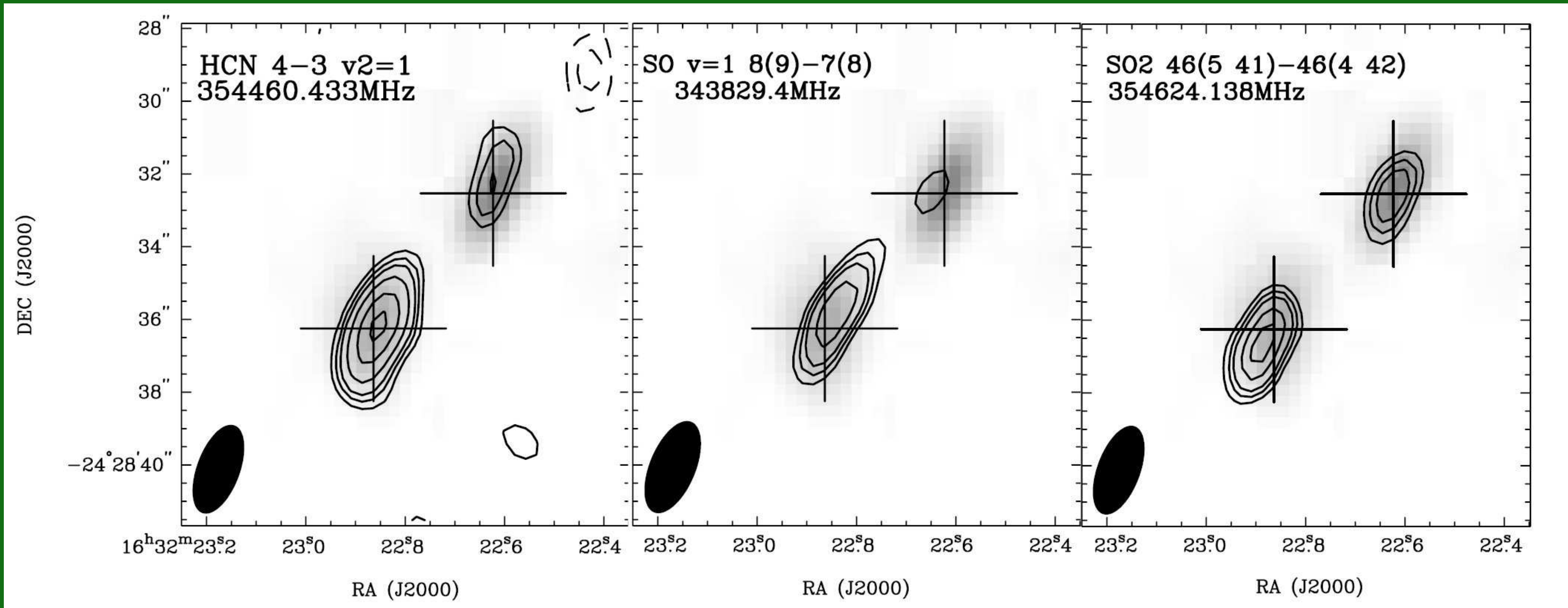
- Turbulent motions produced an outward diffusion of material from the inner nebula

- This led to radial mixing of the products of two chemistries:

✓ the cold outer protosolar nebula, where accretion favours retention of ISM integrity, was in fact a chemically active region cosmic rays (beyond about 10 AU) and other sources of ionization such as X-rays, UV photons and radioactive decay (e.g., ^{26}Al and ^{60}Fe,) can drive a non-equilibrium chemistry involving ion-molecule and neutral-neutral reactions

✓ in the hot inner nebula (within about 1 AU), material can be completely destroyed and lose its interstellar integrity

Highly-Excited Vibrational Transitions

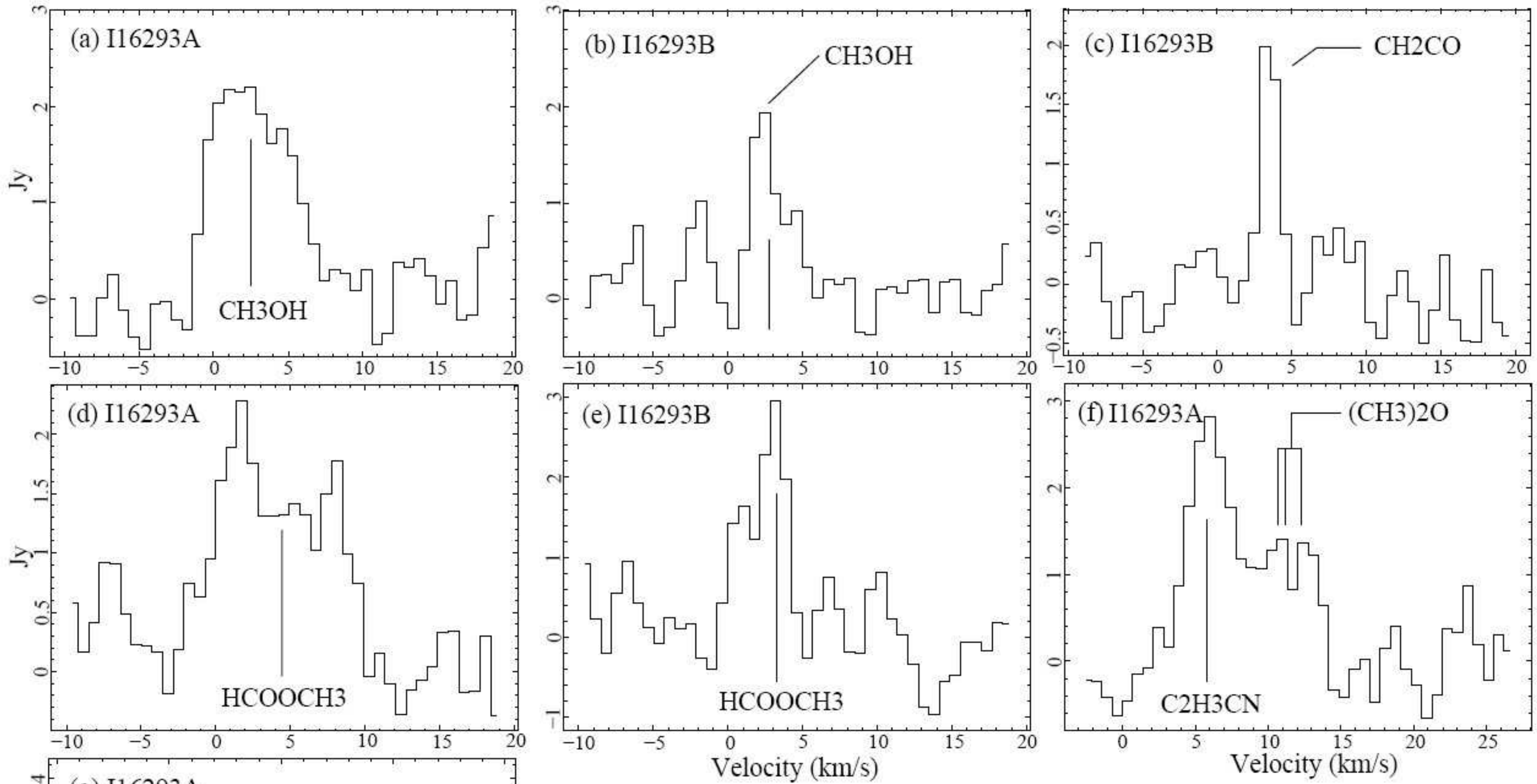


- Highly excited transitions of HCN, SO and SO_2 (lower energy levels 1050 K, 1660 K and 1800 K above ground)

For IRAS 16293, the arcsecond resolution of the Submillimetre Array (1″ = 160 AU), provides the perfect tool for imaging highly-excited submillimetre molecular emission

343.55 - 344.22 GHz (LSB) and 354.21- 354.88 GHz (USB). Angular resolution is 2.6″ x 1.2″(~200 x 400 AU).

Sample Spectra of Complex Organic Molecules



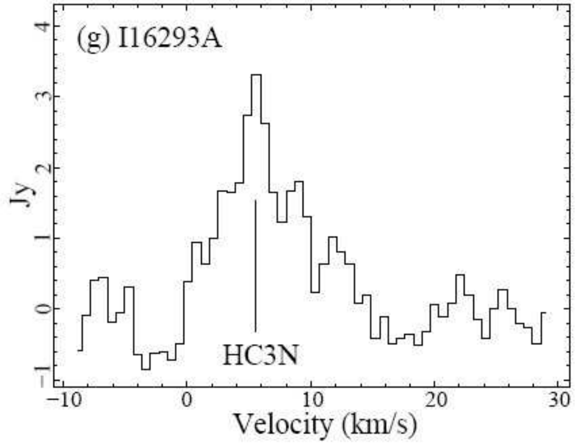


Fig2. Sample spectra of large organic molecules toward IRAS 16293-2422. CH_3OH line at I16293A and I16293B are shown in (a) and (b), respectively; CH_2CO line at I16293B is in spectrum (c); (d) and (e) display $HCOOCH_3$ spectra (344029 MHz) at I16293A and I16293B, respectively; (f)-(g) give CH_2CHCN and HC_3N lines. $(CH_3)_2O$ transitions at 343753-343755 MHz can also be seen in (f), and its weaker appearance of spectral profile is due to the fact that the spectrum is taken at the peak emission position of integrated CH_2CDCN line. All spectra were Hanning smothed for better S/N ratios.