# Chemical processes in star forming regions

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- **Gas phase and surface chemistry (basic concepts)**
- **From cold gas to disks:**
  - **pre-stellar cloud cores**
  - **protostellar cores (hot cores and outflows)**
  - **protoplanetary disks**
- **Summary**

# Interstellar Molecules

$H_2$
$CH$
$CH^+$
$NH$
$OH$
$C_2$
$CN$
$CO$
$CSi$
$CP$
$CS$
$HF$
$NO$
$NS$
$SO$
$HCl$
$NaCl$

$KCl$
$AlCl$
$AlF$
$PN$
$SiN$
$SiO$
$SiS$
$CO^+$
$SO^+$
$H_3^+$
$CH_2$
$NH_2$
$H_2O$
$H_2S$
$C_2H$
$HCN$

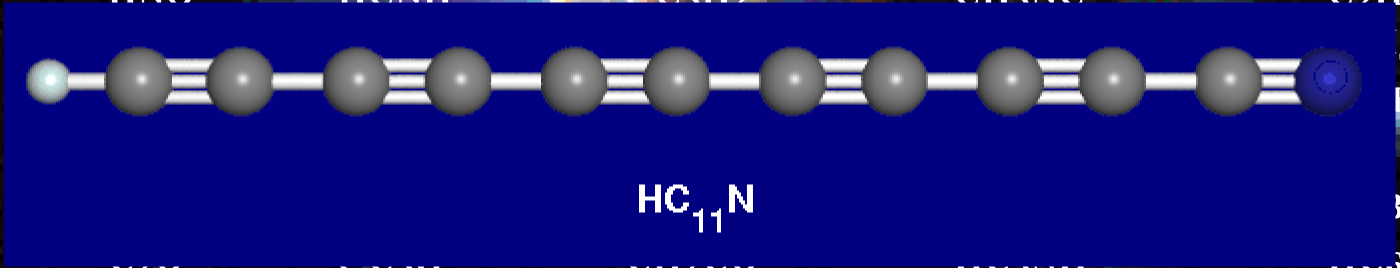
$HNC$
$HCO$
$HCO^+$
$HOC^+$
$HN_2^+$
$HNO$
$C_2O$
$CO_2$
$C_2S$
$AlNC$
$SiC_2$
$SiCN$
$SO_2$
$NaCN$
$OCS$
$MgNC$
$MgCN$
$N_2O$

$NH_3$
$CH_3$
$H_3O^+$
$H_2CO$
$H_2CS$
$HCCH$
$HCNH^+$
$c\text{-}C_3H$
$HCCN$
$HNCO$
$SiC_3$
$HOCO^+$
$HNCS$
$C_2CN$
$C_3O$
$NaCN$

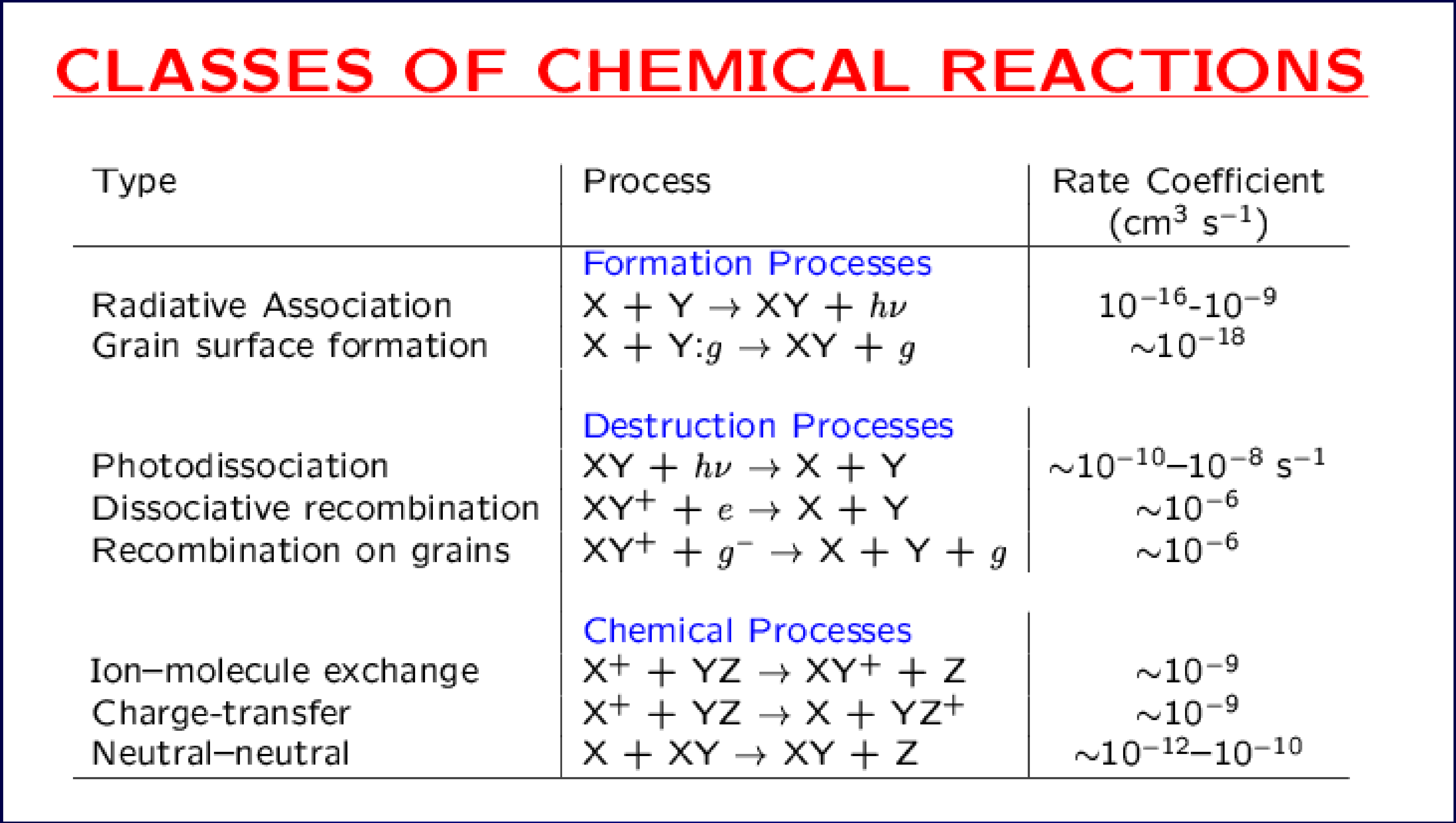
$C_3S$
$CH_4$
$SiH_4$
$CH_2NH$
$H_2C_3$(lin)
$c\text{-}C_3H_2$
$CH_2CO$
$HCOOH$
$C_4H$
$HC_2CN$
$HCCNC$
$HNCCC$
$C_4Si$
$H_2COH^+$

$C_5$
$CH_3OH$
$CH_3SH$
$C_2H_4$
$CH_3CN$
$CH_3NC$
$HC_3NH$
$C_4H_2$
$H_2C_4$(lin)
$C_5H$
$C_5N$
$CH_3NH_2$
$CH_2CHOH$
$CH_3CCH$
$CH_3CHO$
$CH_2CHCN$
$c\text{-}CH_2OCH_2$
$c\text{-}CH_2SCH$

$C_6H$
$HC_4CN$
$C_7H$, $C_6H_2$
$C_8H$
$HCOOCH_3$
$CH_3COOH$
$CH_3C_2CN$
$H_2C_6$(lin)
$C_6H_2$
$H_2COHCHO$
$C_2H_5OH$
$_3)_2O$
$H_5CN$
$_3C_4H$
$HC_6CN$
$(CH_2OH)_2$
$(CH_3)_2CO$
$CH_3C_4CN$?
$\boxed{NH_2CH_2COOH?}$
$HC_8CN$
$c\text{-}C_6H_6$
$HC_{10}CN$
+ *ISOTOPOMERS*



137 molecules have been detected in space (205 including isotopomers, 50 in comets)



# CLASSES OF CHEMICAL REACTIONS

| Type | Process | Rate Coefficient ($cm^3\ s^{-1}$) |
|---|---|---|
| | Formation Processes | |
| Radiative Association | $X + Y \rightarrow XY + h\nu$ | $10^{-16}$-$10^{-9}$ |
| Grain surface formation | $X + Y{:}g \rightarrow XY + g$ | $\sim 10^{-18}$ |
| | Destruction Processes | |
| Photodissociation | $XY + h\nu \rightarrow X + Y$ | $\sim 10^{-10}$–$10^{-8}\ s^{-1}$ |
| Dissociative recombination | $XY^+ + e \rightarrow X + Y$ | $\sim 10^{-6}$ |
| Recombination on grains | $XY^+ + g^- \rightarrow X + Y + g$ | $\sim 10^{-6}$ |
| | Chemical Processes | |
| Ion–molecule exchange | $X^+ + YZ \rightarrow XY^+ + Z$ | $\sim 10^{-9}$ |
| Charge-transfer | $X^+ + YZ \rightarrow X + YZ^+$ | $\sim 10^{-9}$ |
| Neutral–neutral | $X + XY \rightarrow XY + Z$ | $\sim 10^{-12}$–$10^{-10}$ |

Duley & Williams 1984, “Interstellar Chemistry”
Leung, Herbst & Huebner 1984, ApJS
Draine & Sutin 1987, ApJ
van Dishoeck et al. 1993, in “Protostars and Planets III”

# Rate Coefficients

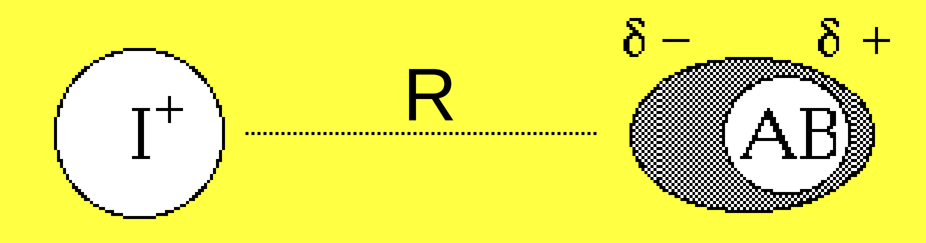
$$k = \langle \sigma\, v \rangle = a(T)\, \exp(-E/k_b T)\ \mathrm{cm^3\, s^{-1}}$$

$$E \sim \begin{cases} 1\ \mathrm{eV} & \text{for endothermic reactions} \\ 0.1\text{-}1\ \mathrm{eV} & \text{for exothermic reactions} \end{cases}$$

$k_b T < 0.01$ eV in molecular clouds

$$k \sim 10^{-44}\ \mathrm{cm^3\, s^{-1}}!\ \text{BUT...}$$

Exothermic ion-molecule reactions do not possess activation energy because of the strong long-range attractive force (Herbst & Klemperer 1973; Anicich & Huntress 1986):

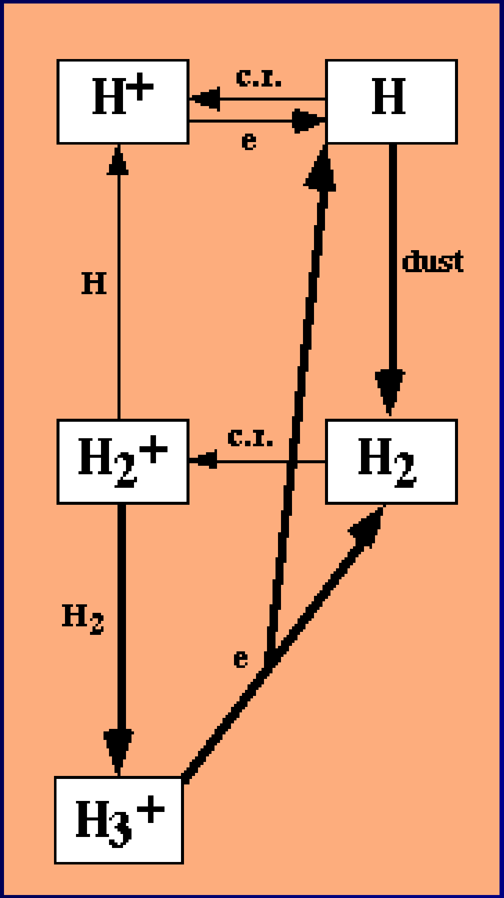


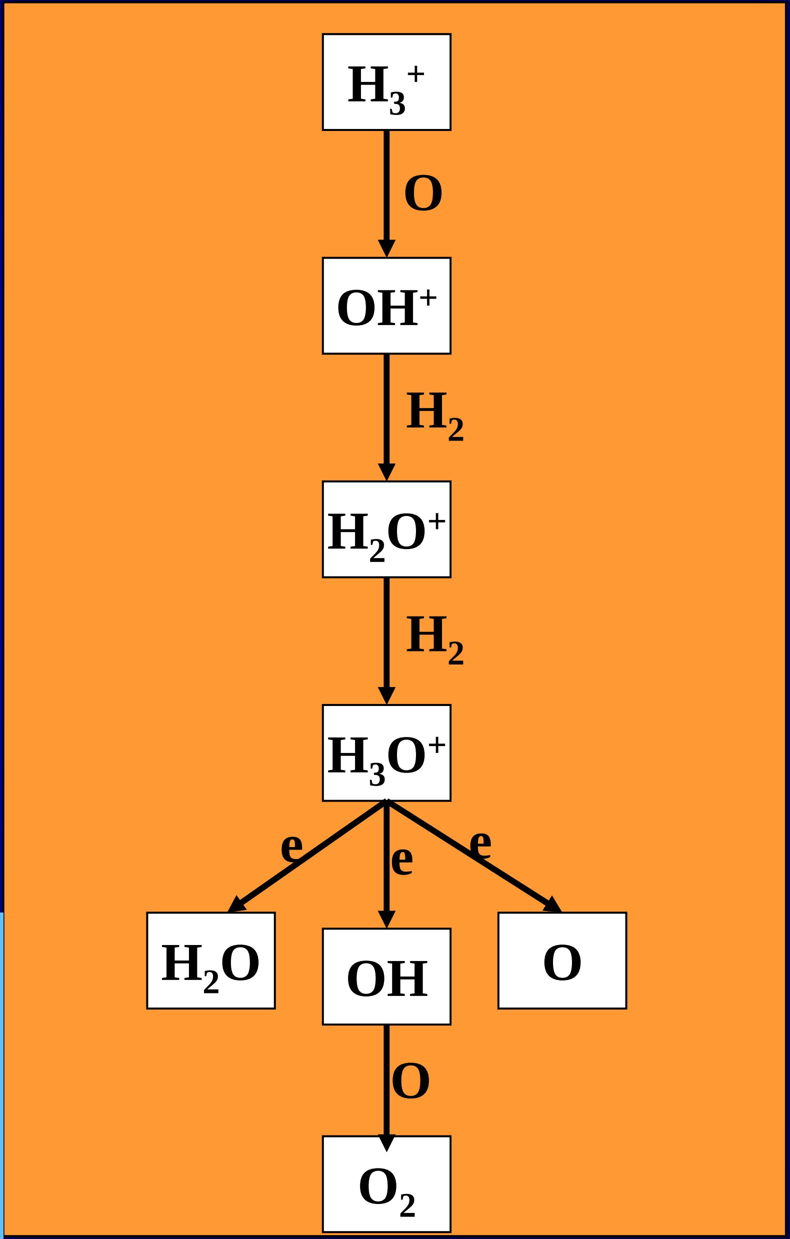
$$V(R) = -e^2/2\alpha R^4$$

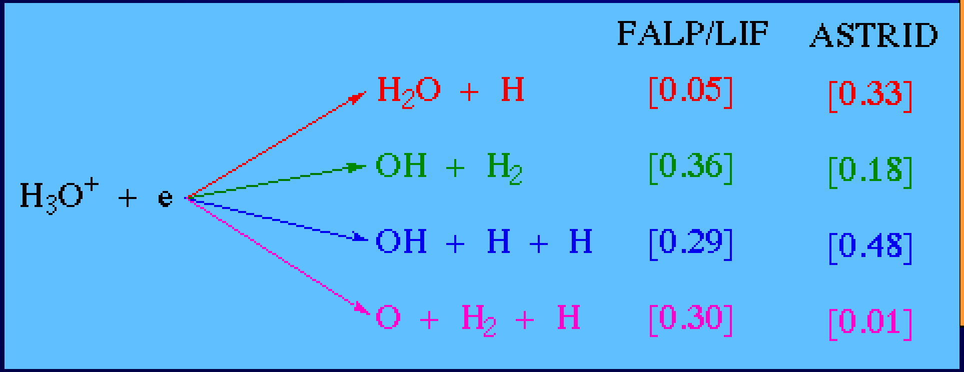
$$k_{LANGEVIN} = 2\,\pi e(\alpha/\mu)^{1/2} \sim 10^{-9}\ \mathrm{cm^3\, s^{-1}}$$

*independent on T !!!*

# Examples of gas phase chemistry







| | | FALP/LIF | ASTRID |
|---|---|---|---|
| $H_3O^+ + e$ | $H_2O + H$ | [0.05] | [0.33] |
| | $OH + H_2$ | [0.36] | [0.18] |
| | $OH + H + H$ | [0.29] | [0.48] |
| | $O + H_2 + H$ | [0.30] | [0.01] |

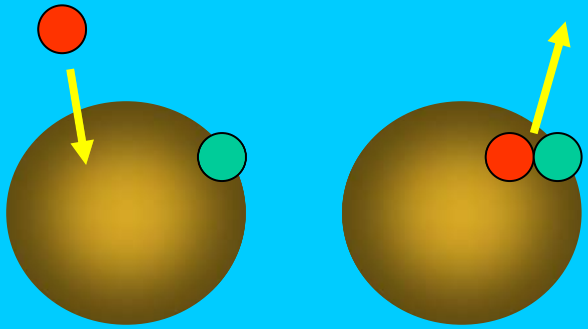
# Surface Chemistry

## (i.e. the chemistry on the surface of dust grains)

# Why do we need surface chemistry?

- Formation of $H_2$ (Gould & Salpeter 1963; Hollenbach & Salpeter 1970; Pirronello et al. 1999; Katz et al. 1999; Cazaux & Tielens 2002; Habart et al. 2003)

$R \sim 10^{-17}\ \mathrm{cm}^3\ \mathrm{s}^{-1}$

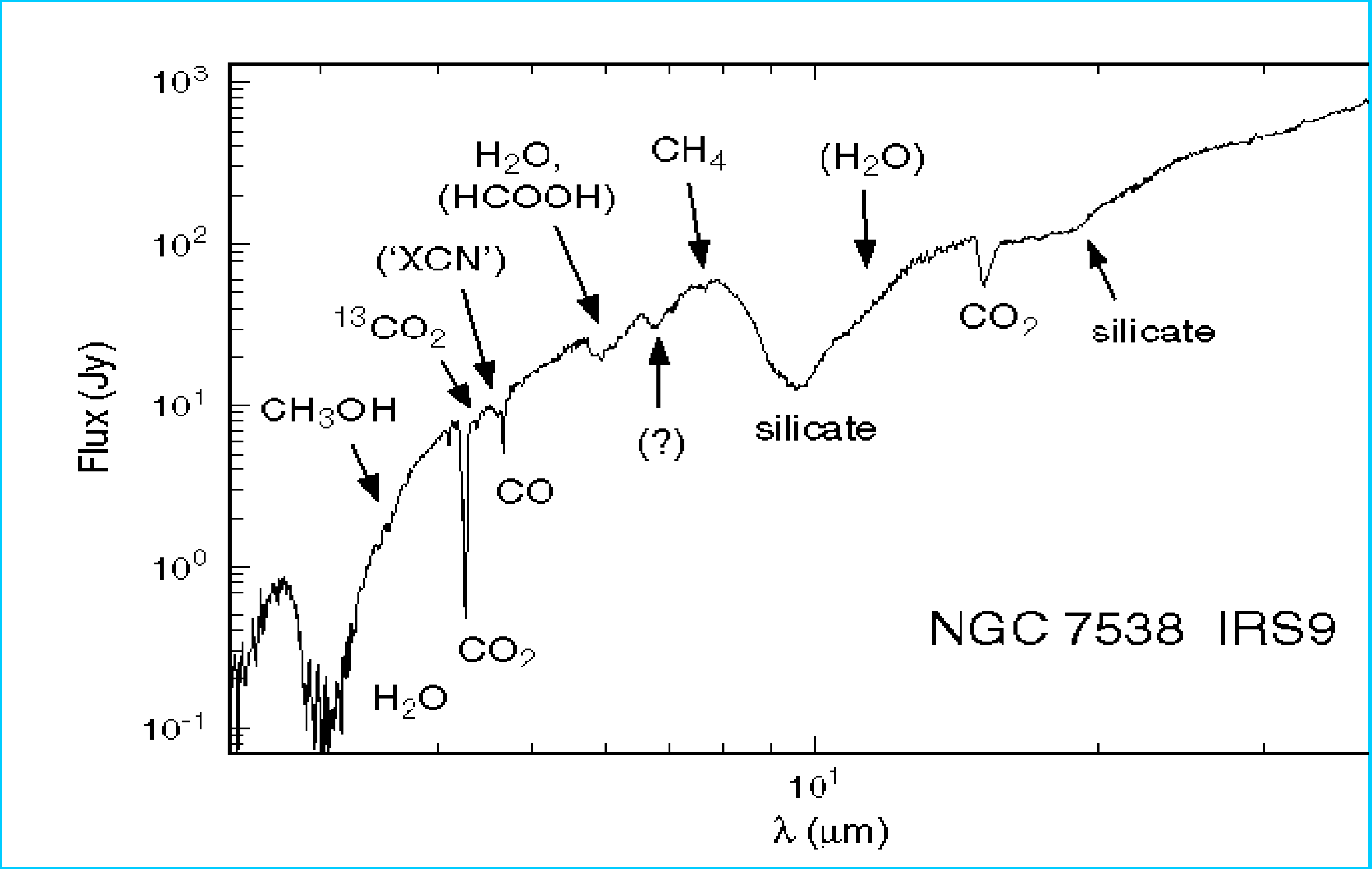


In gas phase:

$H^- + H \Rightarrow H_2 + e \quad R \sim 10^{-21} - 10^{-20}\ \mathrm{cm}^3\ \mathrm{s}^{-1}$

$H + H \Rightarrow H_2 + h\nu \quad R \sim 10^{-29} - 10^{-31}\ \mathrm{cm}^3\ \mathrm{s}^{-1}$

# Why do we need surface chemistry?



- Chemically rich icy mantles (e.g. Gibb et al. 2000; van Dishoeck et al. 1998)

# Why do we need surface chemistry?

- Large abundances of multiply deuterated species (Tielens 1983; Charnley et al. 1997; Caselli et al. 2002)

**D2CO/H2CO = 0.1**

**CHD2OH/CH3OH = 0.02**

**D2S/H2S = 0.02**

**ND3/NH3 = 0.001**

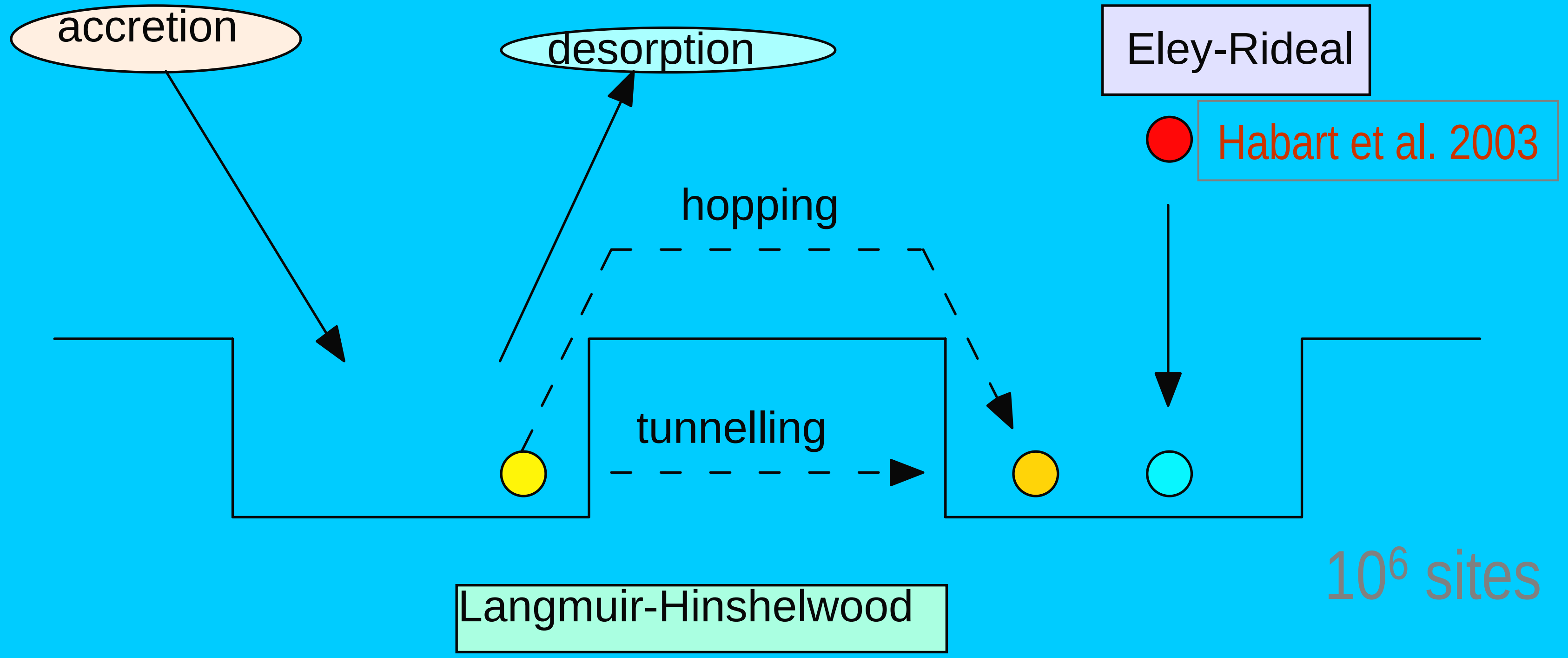
D2CO/H2CO = 0.1
CHD2OH/CH3OH = 0.02
D2S/H2S = 0.02

**CD3OH/CH3OH = 0.02**

Ceccarelli et al. 1998
Parise et al. 2002, 2004
van der Tak et al. 2002
Vastel et al. 2003

D/H = $1.5 \times 10^{-5}$ !!

# GRAIN SURFACE PROCESSES



accretion

desorption

Eley-Rideal

Habart et al. 2003

hopping

tunnelling

Langmuir-Hinshelwood

$10^6$ sites

Tielens & Hagen (1982); Tielens & Allamandola (1987); Hasegawa et al. (1992); Cazaux & Tielens (2004)

Herbst (2000)

# TYPES OF SURFACE REACTIONS

REACTANTS: MAINLY MOBILE ATOMS AND RADICALS

**$A + B \rightarrow AB$ association**

**$H + H \rightarrow H_2$**

**$H + X \rightarrow XH$ (X = O, C, N, CO, etc.)**

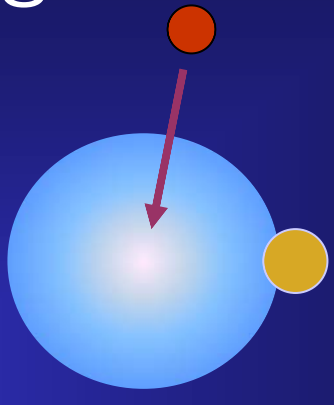
WHICH CONVERTS

$O \rightarrow OH \rightarrow H_2O$

$C \rightarrow CH \rightarrow CH_2 \rightarrow CH_3 \rightarrow CH_4$

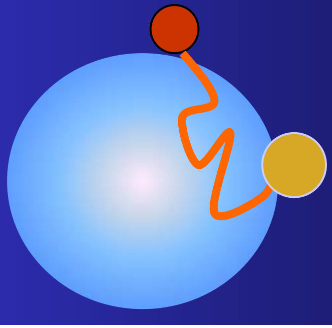
$N \rightarrow NH \rightarrow NH_2 \rightarrow NH_3$

$CO \rightarrow HCO \rightarrow H_2CO \rightarrow H_3CO \rightarrow CH_3OH$



Accretion

$\propto 10/[T_k^{1/2}\, n(H_2)]$ days



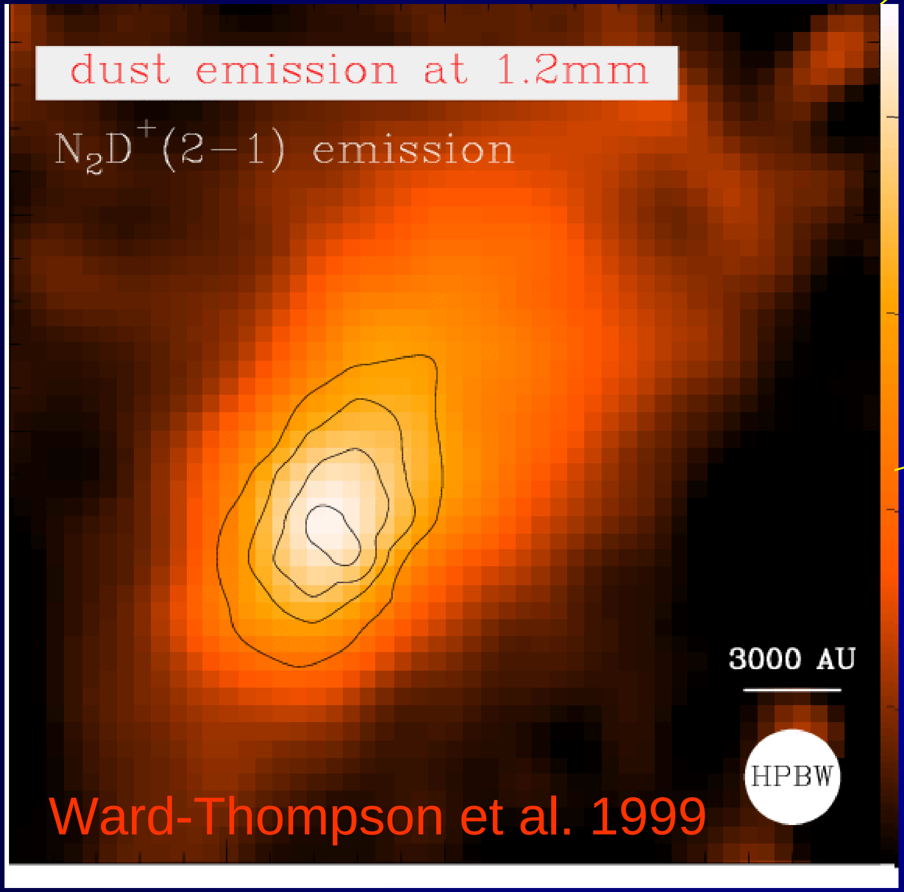
Diffusion + Reaction

$t_{qt}(H) \sim 10^{-5}-10^{-3}$ s

Watson & Salpeter 1972; Allen & Robinson 1977; Pickes & Williams 1977; Tielens & Hagen 1982; d'Hendecourt et al. 1985; Hasegawa et al. 1992

# Pre-stellar cores

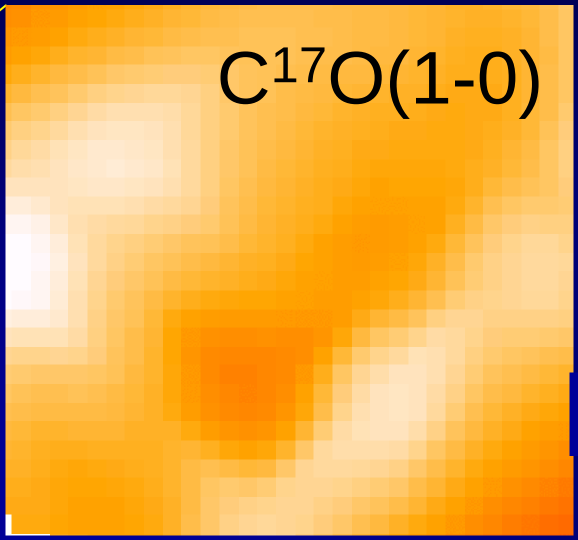
# Pre-stellar cores: chemical properties



Ward-Thompson et al. 1999

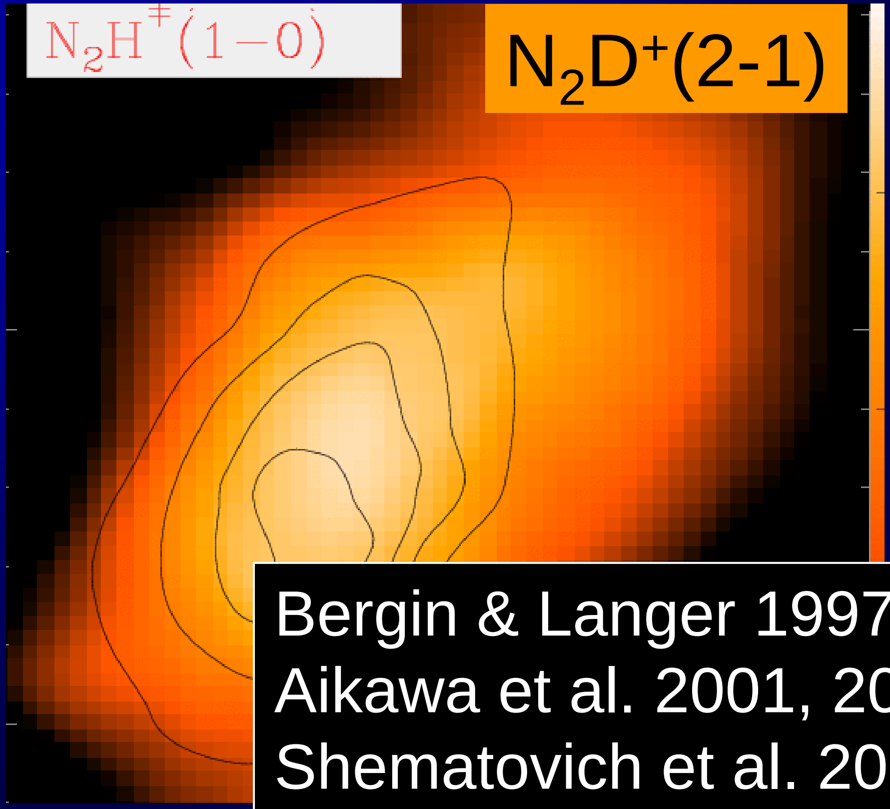
**$N_2H^+$ and $N_2D^+$ are good tracers of the core nucleus (Caselli et al. 2002b)**

**D-fractionation increases towards the core center.**



**CO disappears from gas phase at R < 7000 AU**

Caselli et al. 1999



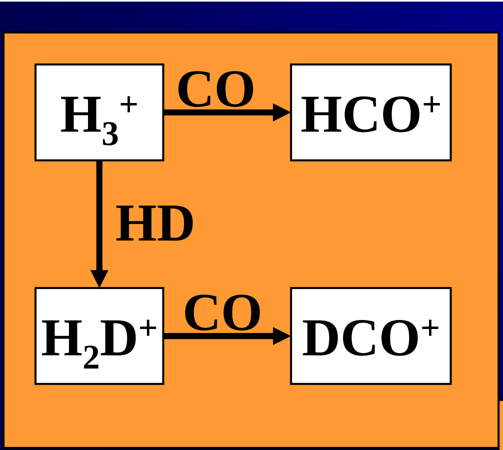
Bergin & Langer 1997
Aikawa et al. 2001, 2003
Shematovich et al. 2003

In pre-stellar cores: high degree of deuterium fractionation and molecular freeze out (Bacmann et al. 2003; Crapsi et al. 2004)

$H_3^+ + HD \Rightarrow H_2D^+ + H_2 + \Delta E$ (Watson 1976)

$H_2D^+ + N_2\ (CO) \Rightarrow N_2D^+\ (DCO^+) + H_2$

$H_2D^+ / H_3^+$ increases if the abundance of gas phase neutral species decreases (Dalgarno & Lepp 1984)



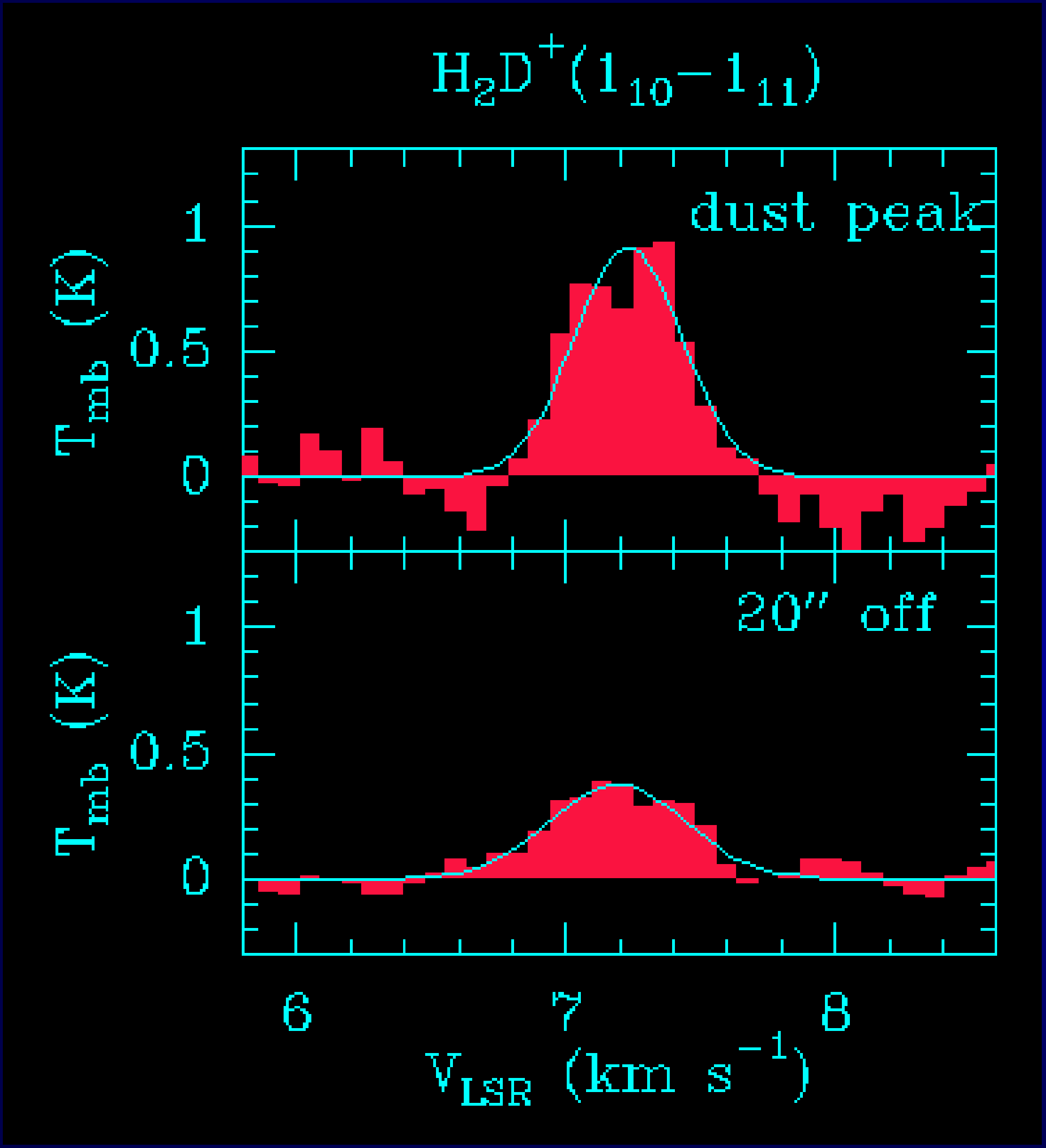
CO freeze-out

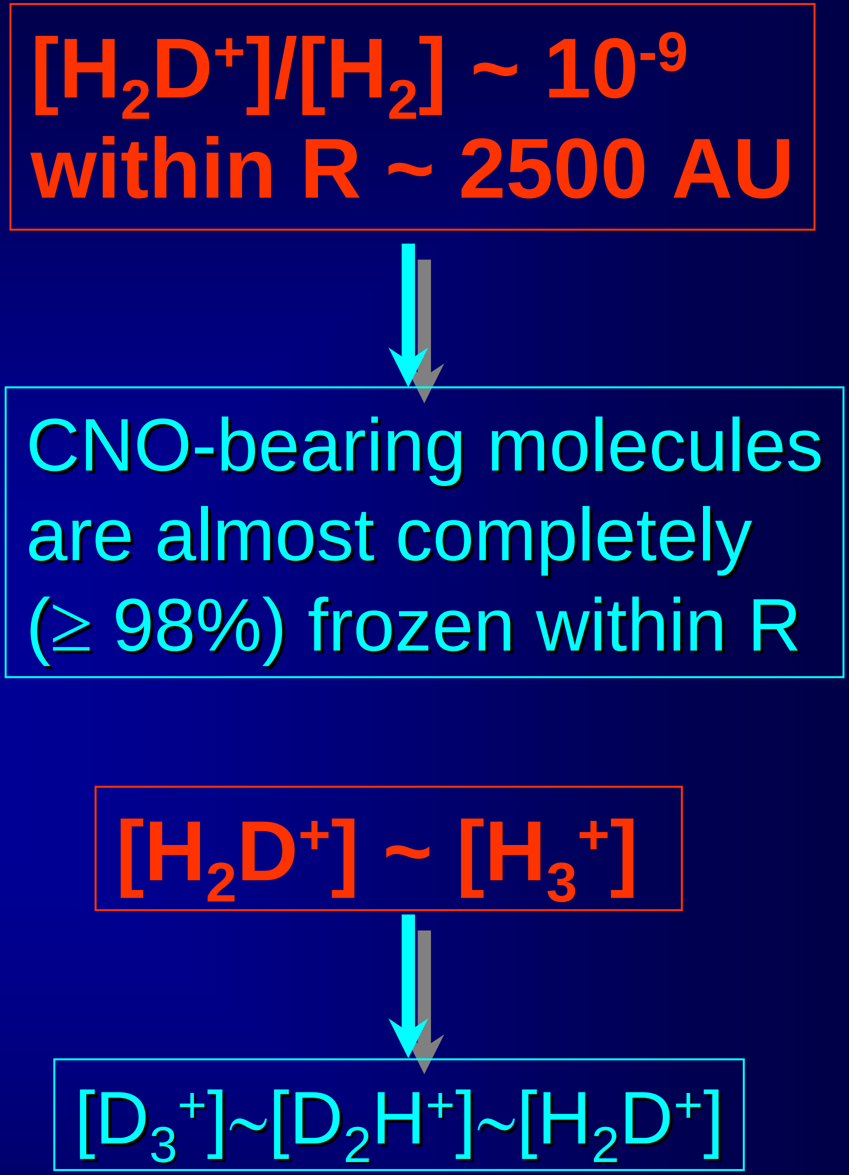
**LOWER**
$H_3^+$ and $H_2D^+$ destruction rates

**HIGHER**
$H_2D^+$ formation rate

**LARGER**
$H_2D^+/H_3^+$ abundance ratio and deuterium fractionation

# Strong *ortho*-$H_2D^+$ emission:





**$[H_2D^+]/[H_2] \sim 10^{-9}$ within R ~ 2500 AU**

CNO-bearing molecules are almost completely (≥ 98%) frozen within R

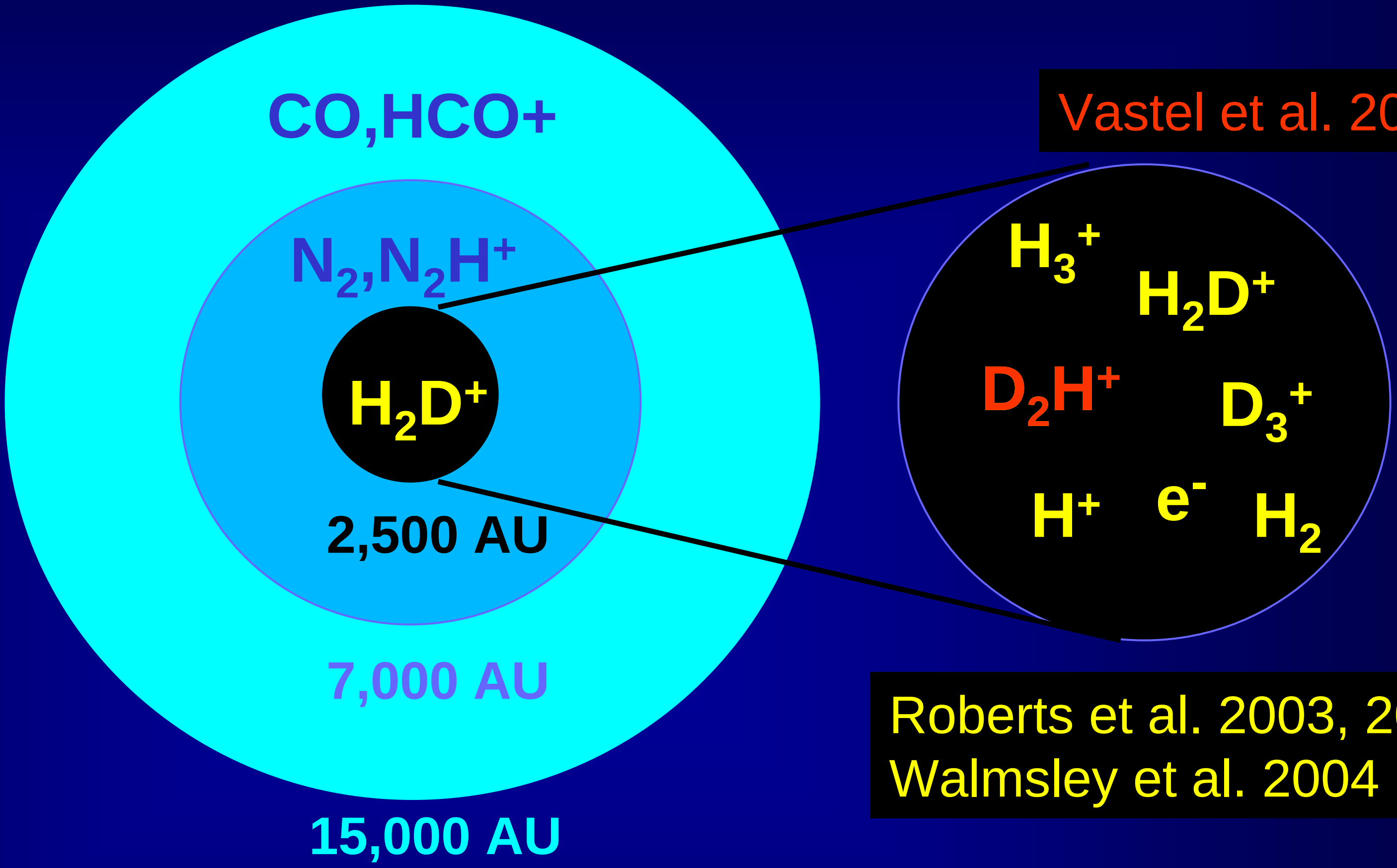
**$[H_2D^+] \sim [H_3^+]$**

$[D_3^+] \sim [D_2H^+] \sim [H_2D^+]$

**Roberts et al. 2003, 2004**
**Walmsley et al. 2003, 2004**

Caselli, van der Tak, Ceccarelli, Bacmann 2003, A&A, 403, L37

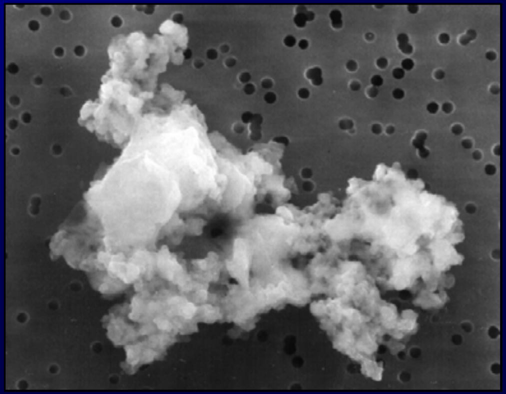
# Summary on pre-stellar cores



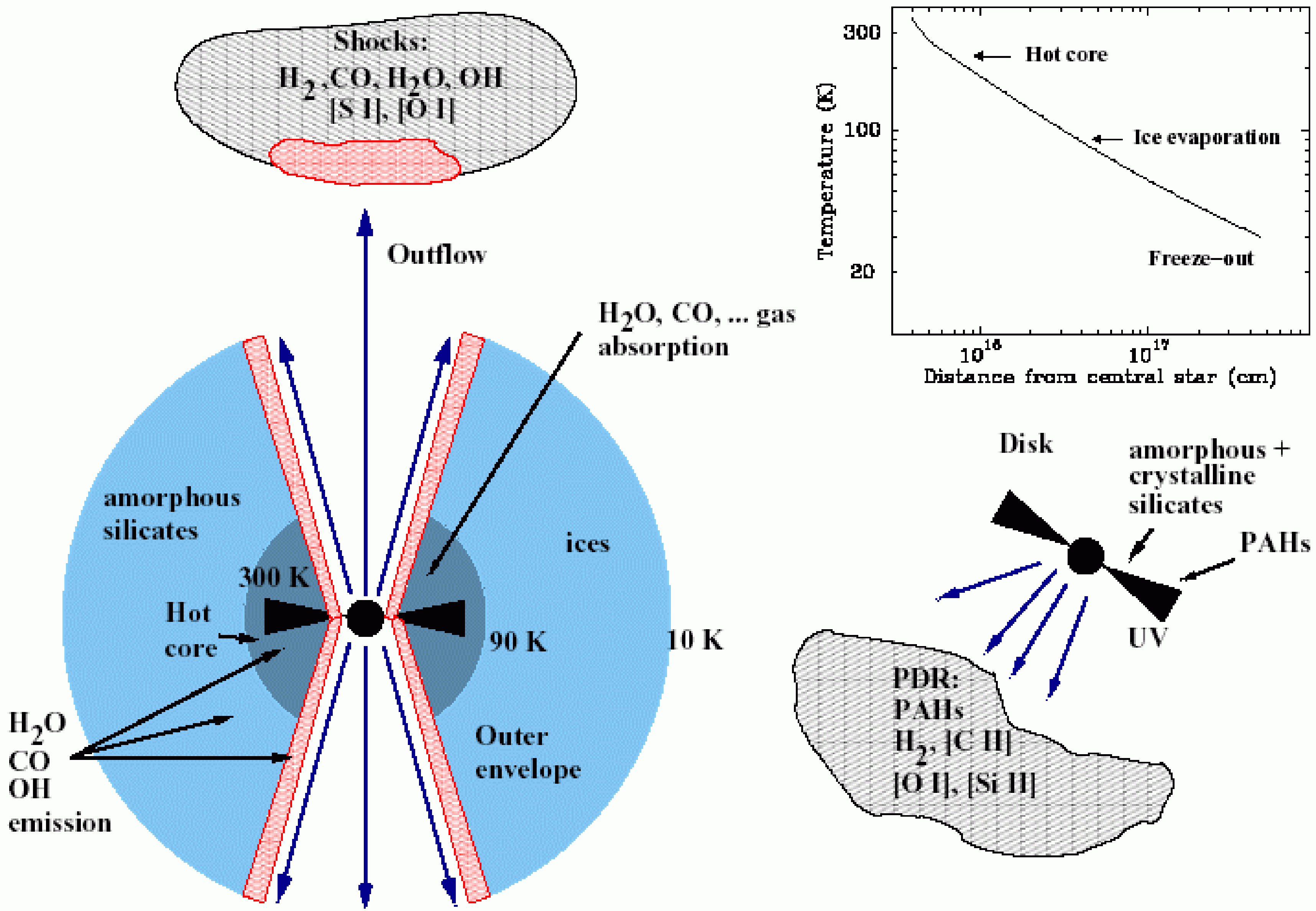
Vastel et al. 2004

Roberts et al. 2003, 2004
Walmsley et al. 2004

Within the “molecular hole” (r ~ 2500 AU), dust grains are probably covered by *thick iced mantles*, which boost grain coagulation



# The various phases after protostellar birth



Van Dishoeck 2004, ARA&A

# Shock chemistry along YSO's outflows

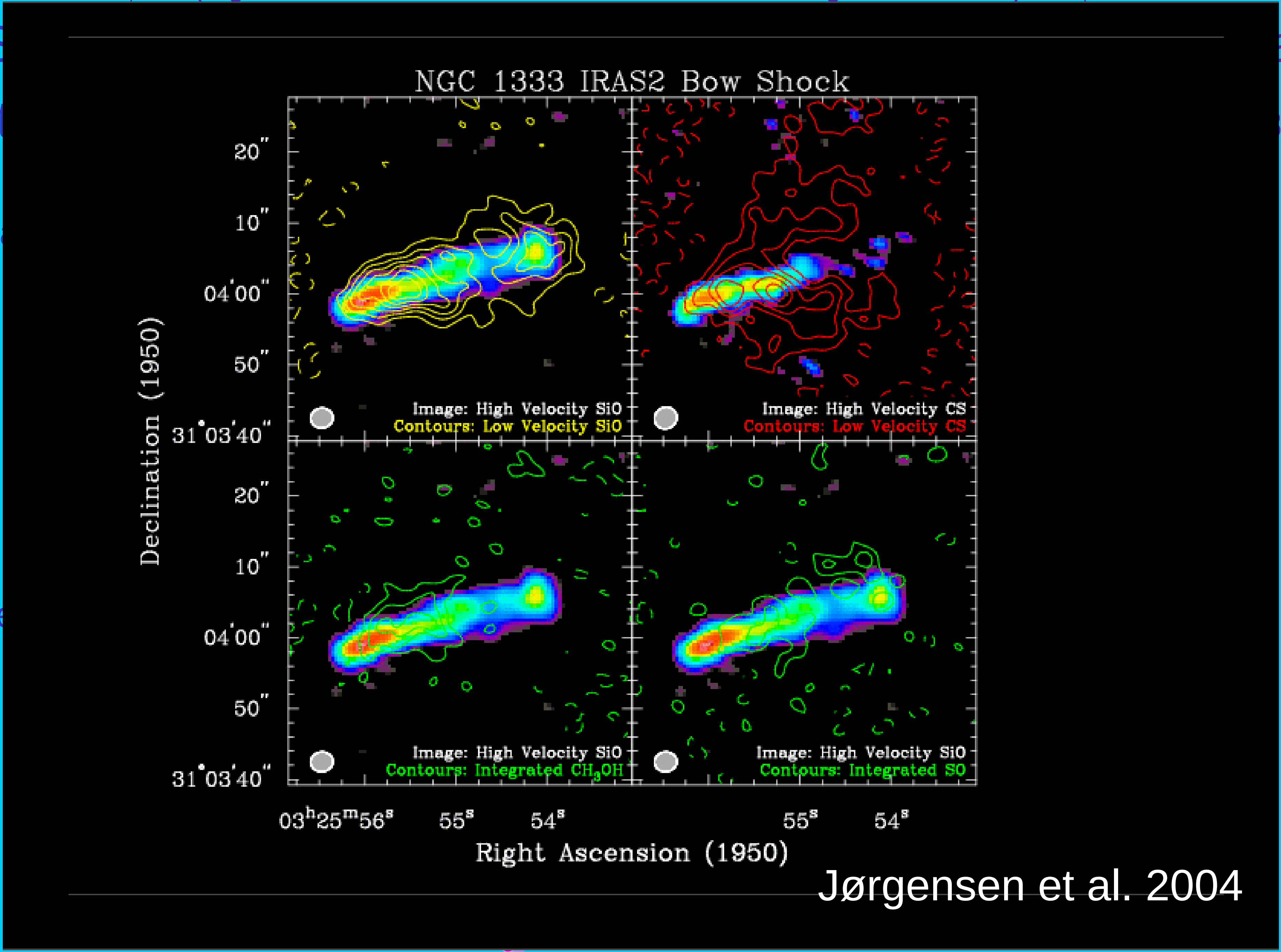
(e.g. Caselli et al. 1997; Schilke et al. 1997; Bergin et al. 1998)

- S ar

out 3)

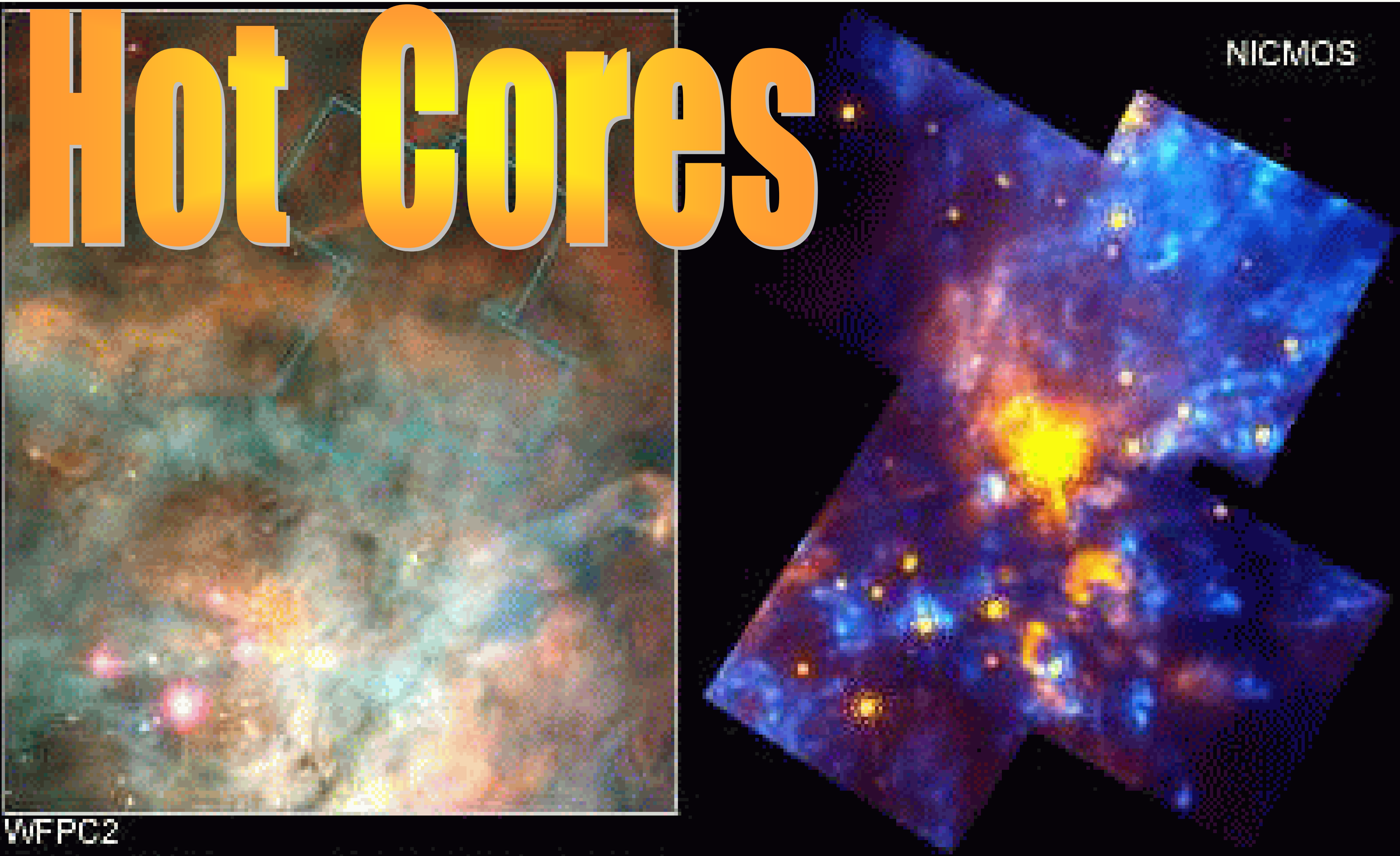
1. M

2. Re



Jørgensen et al. 2004

# Hot Cores



**Orion Nebula • OMC-1 Region**

Hubble Space Telescope

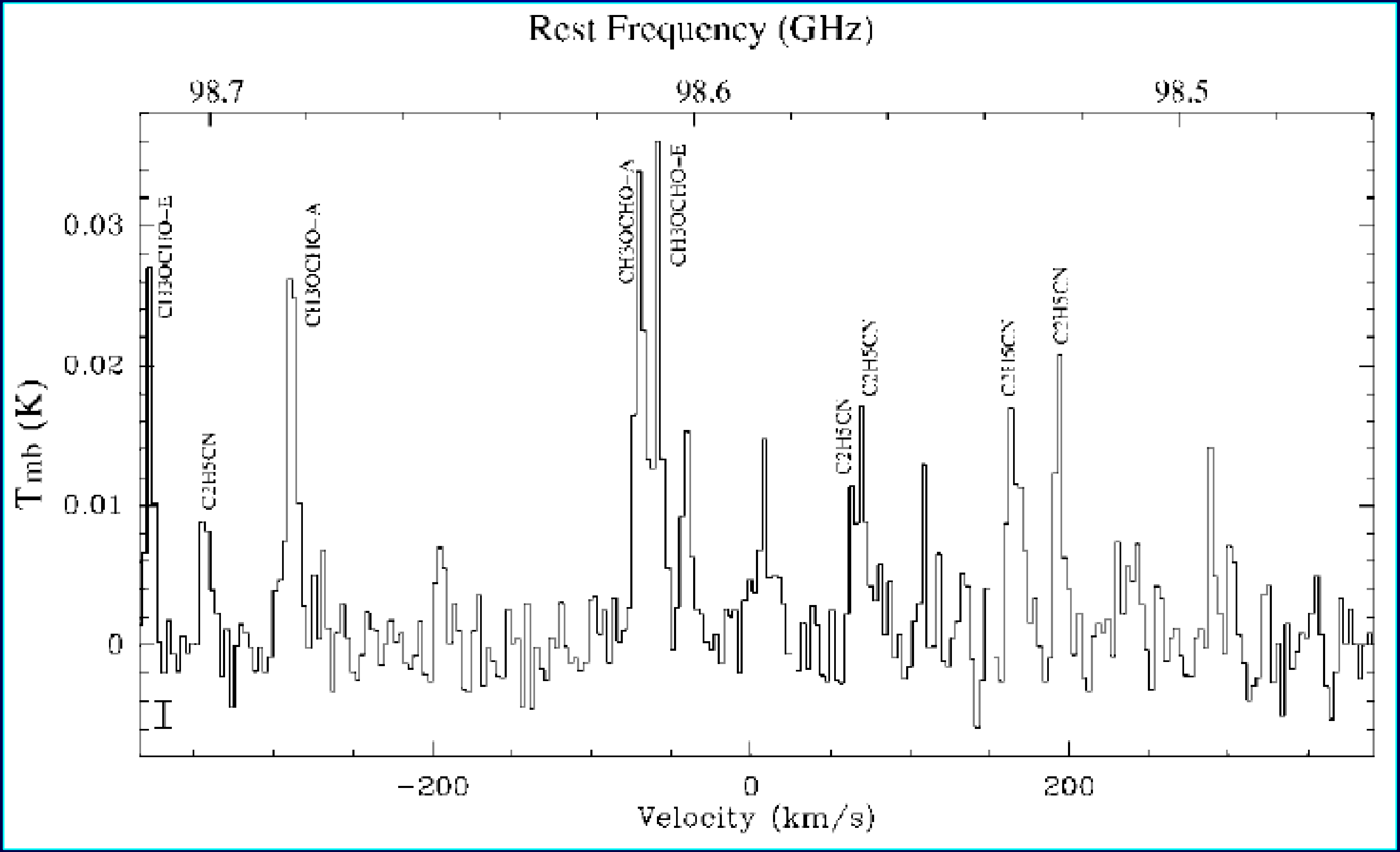
PRC97-13 • ST ScI OPO • May 12, 1997

R. Thompson (Univ. Arizona), S. Stolovy (Univ. Arizona), C.R. O'Dell (Rice Univ.) and NASA

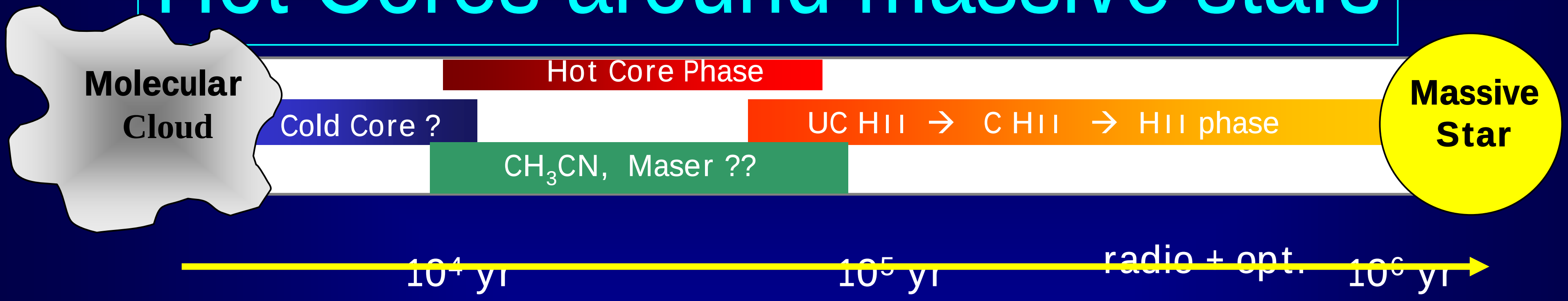
# Hot Cores around low mass protostars

## $r \sim 100$ AU, $T \geq 50$ K, $n(H_2) \geq 10^6$ cm$^{-3}$

IRAS 16293-2422 (*Cazaux et al. 2003; Bottinelli et al. 2004; Kuan et al. 2004*):
"Hot-core" within central 150 AU. Rich chemistry (HCOOH, $CH_3CHO$, $CH_3OCHO$, $CH_3OCH_3$, $CH_3COOH$, $CH_3CN$, $C_2H_5CN$, $CH_3CCH$).



# Hot Cores around massive stars



Molecular Cloud

Hot Core Phase

Cold Core ?

UC H II → C H II → H II phase

$CH_3CN$, Maser ??

Massive Star

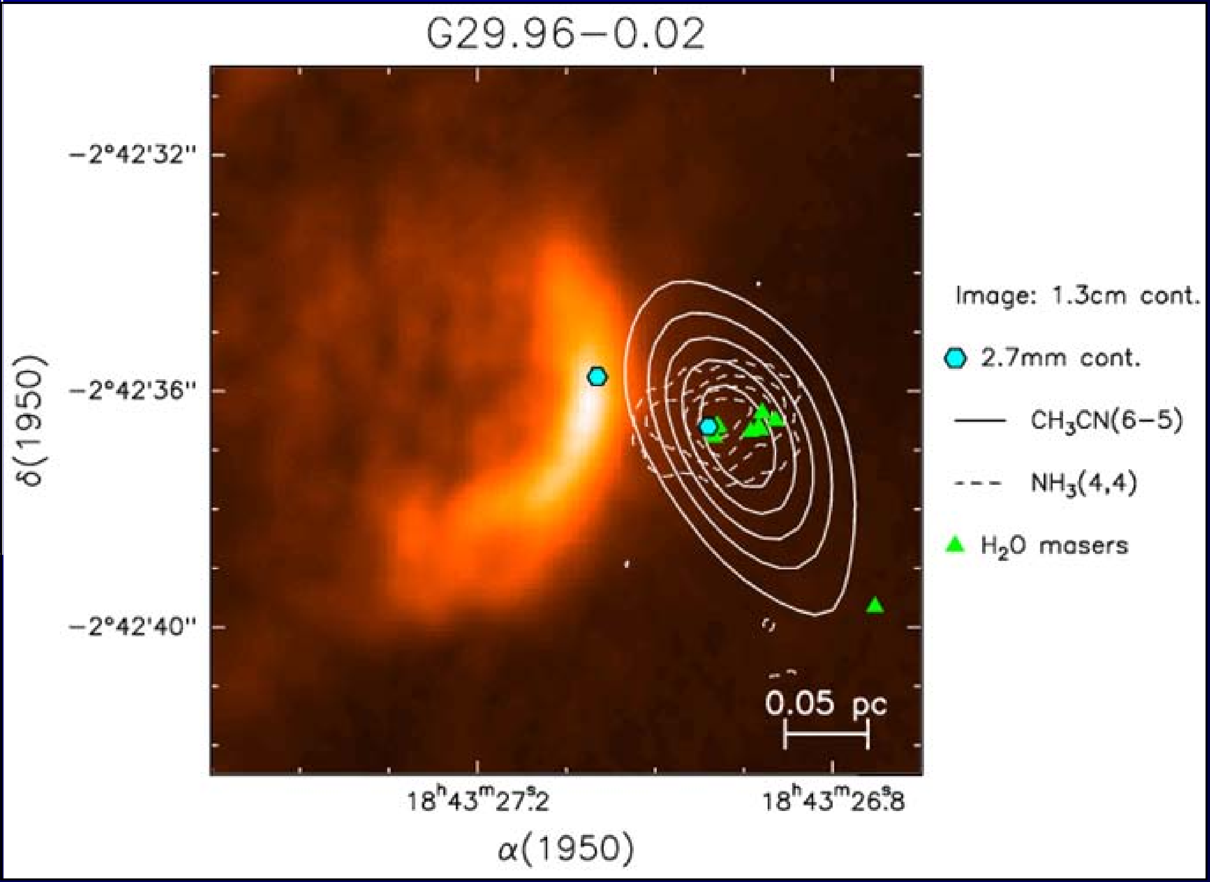
$10^4$ yr

$10^5$ yr

radio + opt.

$10^6$ yr

Hot Cores represent a stage in the star formation process earlier than ultracompact (UC) HII regions (Kurtz et al. 2000)



**$D \leq 0.1$ pc**

**$n(H_2) \geq 10^7$ cm$^{-3}$**

**$T \geq 100$ K**

(Cesaroni et al. 1998; Olmi et al. 2003)

# Chemical signatures of Hot Cores

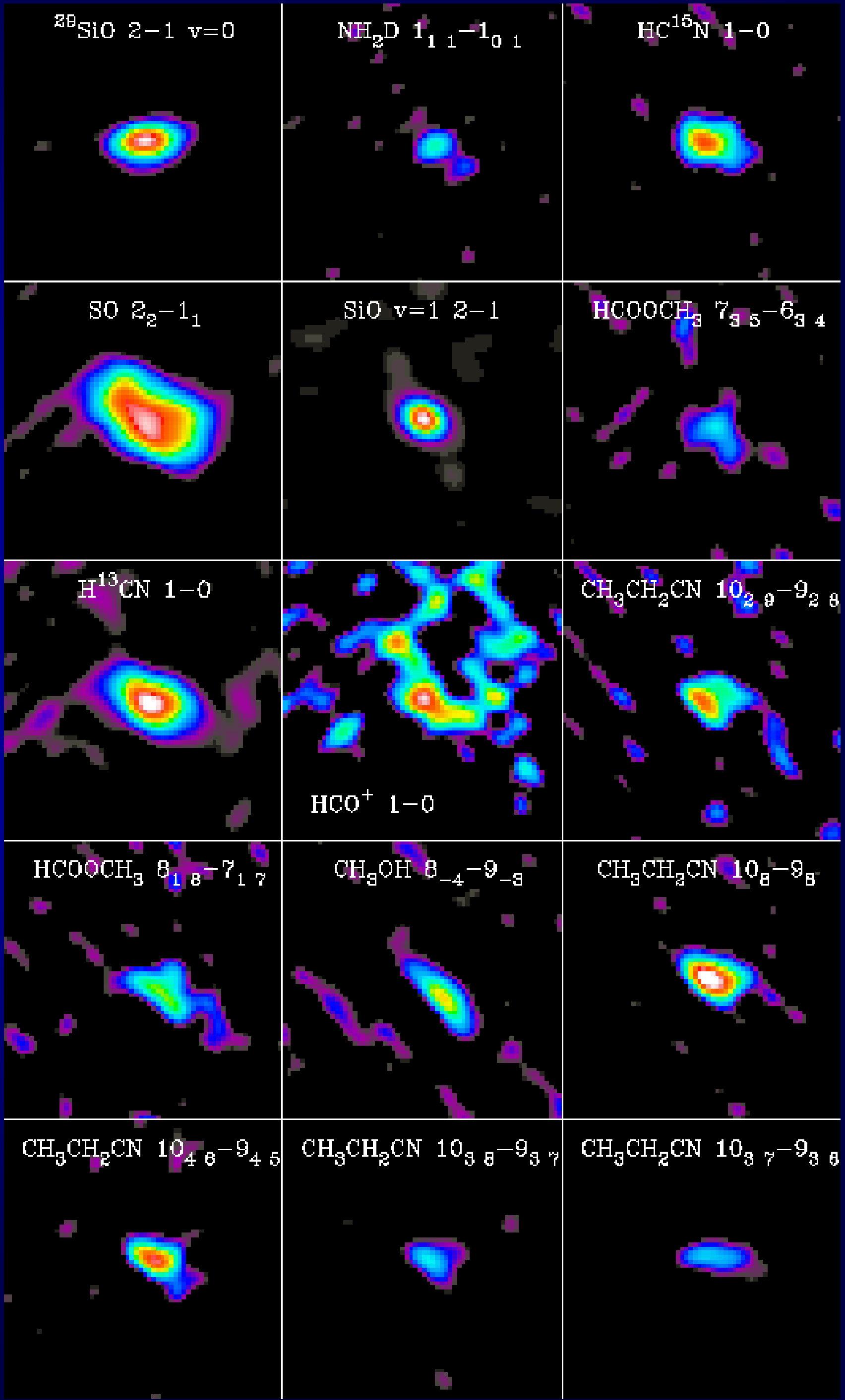
**Orion KL**

- Saturated molecules:
$H_2O$, $NH_3$, $H_2S$, $CH_3OH$
(e.g. Pauls et al. 1983; Menten et al. 1986)

- H-rich complex N-bearing and O-bearing molecules:
$CH_3CN$, $CH_2CHCN$, $CH_3CH_2CN$, $CH_3OCH_3$, $HCOOCH_3$, $C_2H_5OH$..
(e.g. Blake et al. 1987; Mehringer & Snyder 1996)

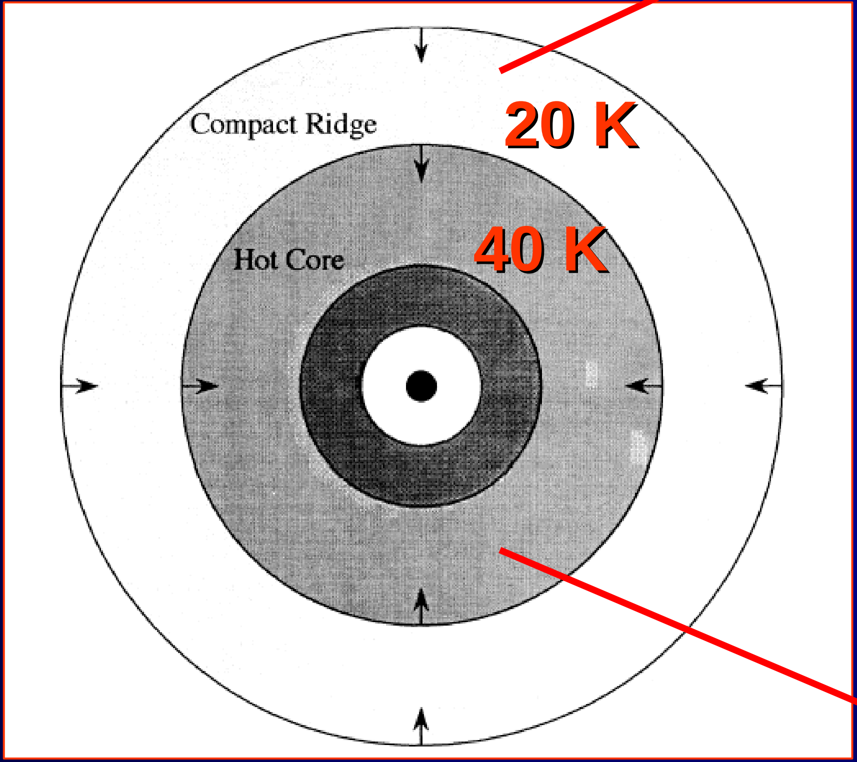
- Relatively large deuterium fractionation (e.g. Olofsson 1984; Turner 1990)

- Chemical differentiation
(e.g. Wright et al. 1996; Wyrowski et al. 1997)



# The Orion Hot Core and Compact Ridge

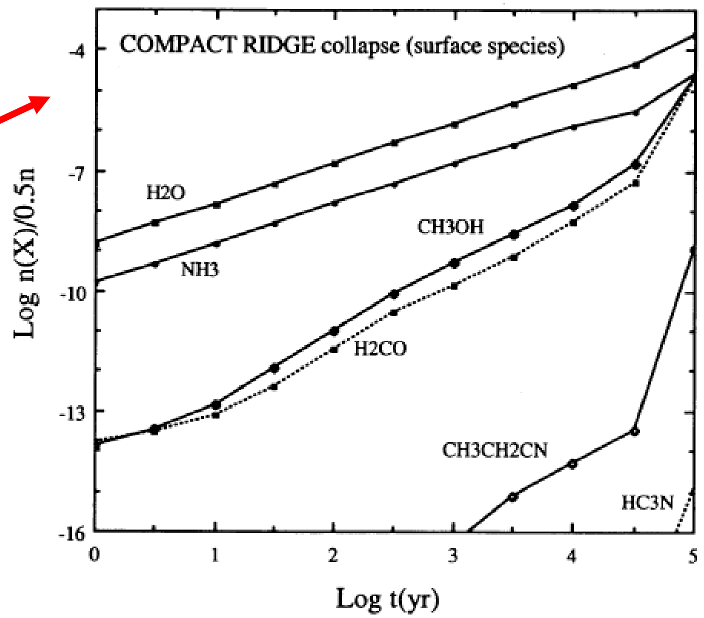
(Caselli, Hasegawa & Herbst 1993)



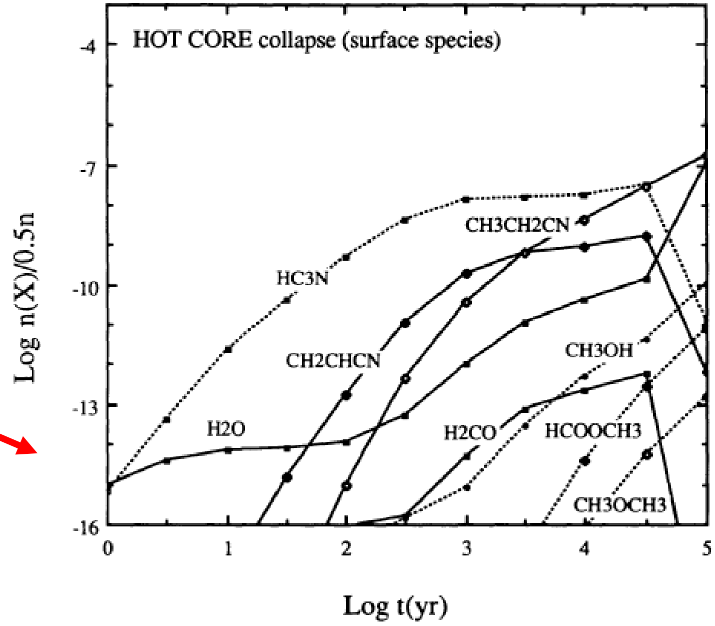
20 K

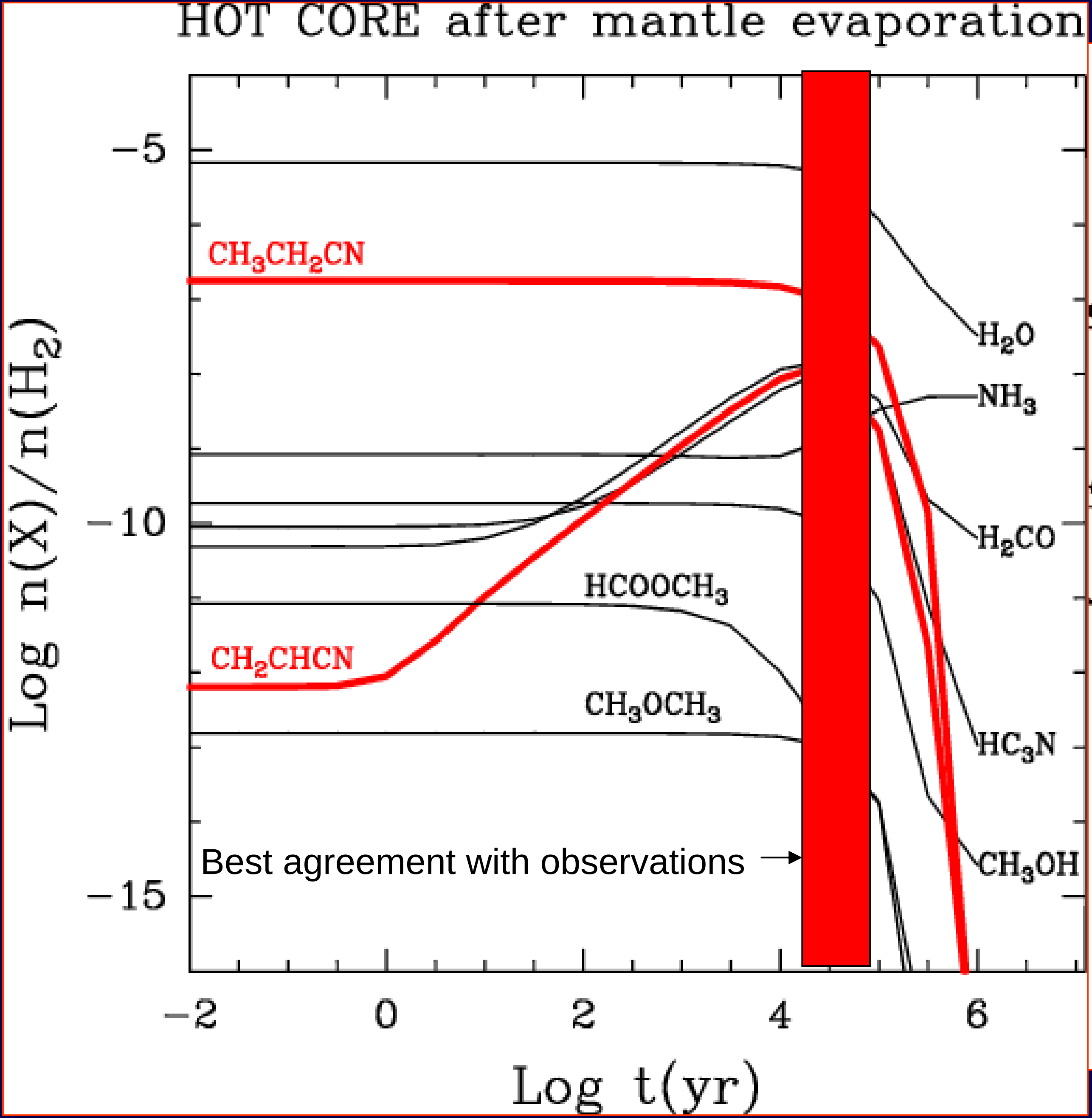
40 K

Mostly simple saturated species

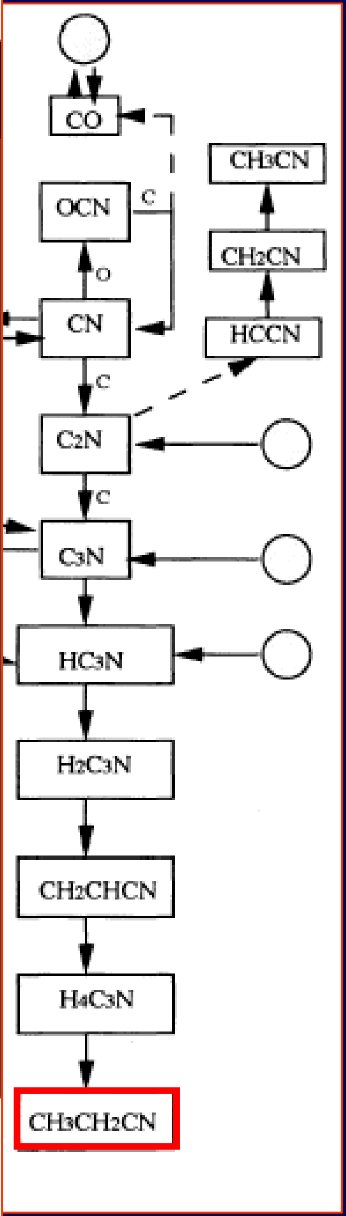


Mostly complex N-bearing species





Best agreement with observations →



# Current models

**Rodgers & Charnley 2003:** chemistry in a cloud undergoing "inside-out" collapse (Shu 1977). Predictions for low-mass protostellar envelopes: simple chemistry.

**Nomura & Millar 2004 + Doty et al. 2004 + Lee et al. 2004**: detailed physical and radiative transfer models coupled with the chemistry.

**Viti et al. 2004**: In treating the thermal evaporation of dust grain mantles, one has to take into account the molecular trapping of volatile species in water ice.

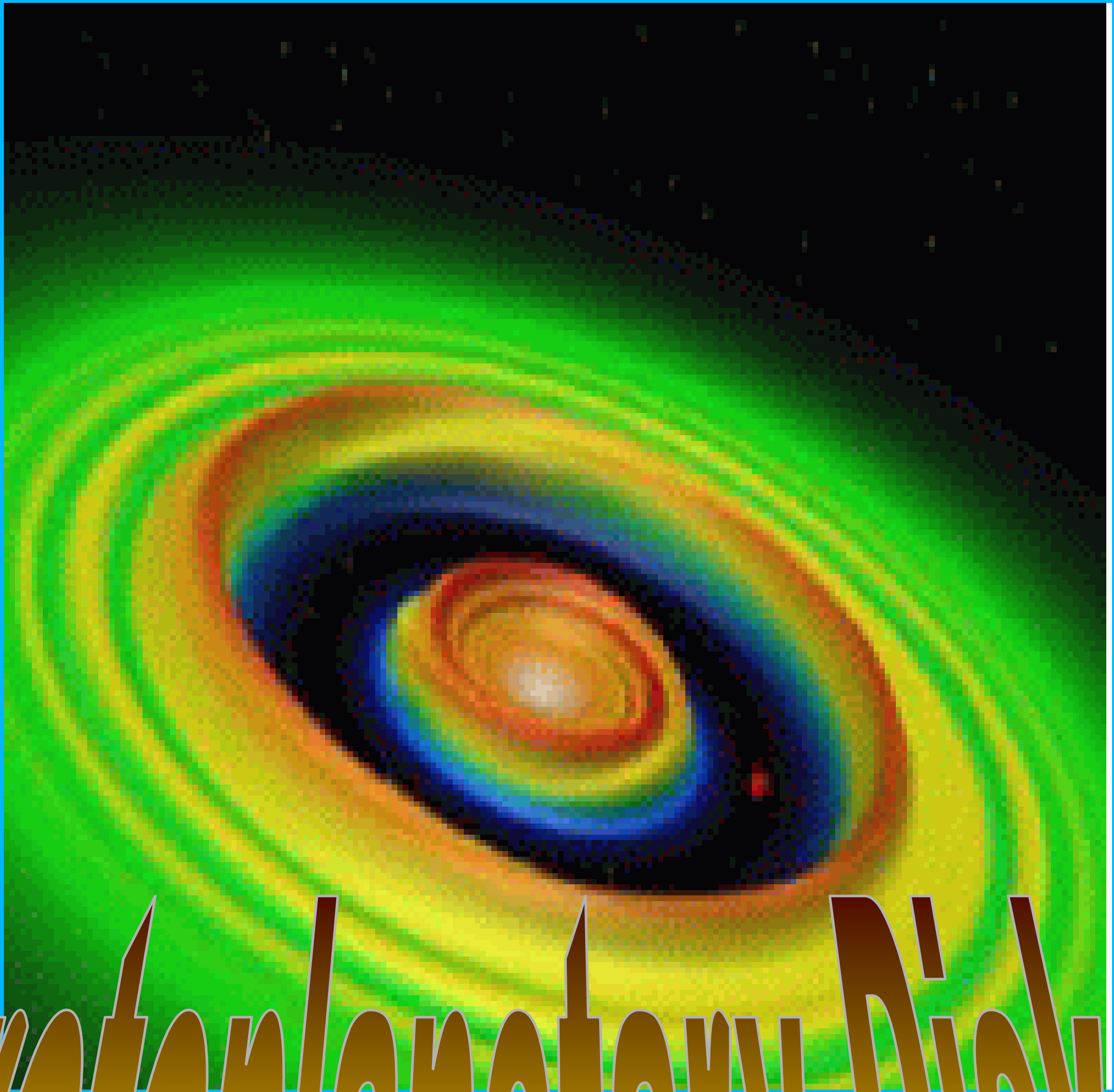
# …and (some of) their problems

1. Gas phase chemistry cannot explain the large abundance of $HCOOCH_3$ (Horn et al. 2004). Its formation route on the surface is not yet understood.

2. Dynamical processes are not yet well defined. So the inclusion of dynamics is another source of uncertainty for the chemical evolution of star forming regions.

3. Grain mantle composition (i.e. binding energies) changes during cloud evolution. The grain-size distribution changes too. Both arguments are neglected.

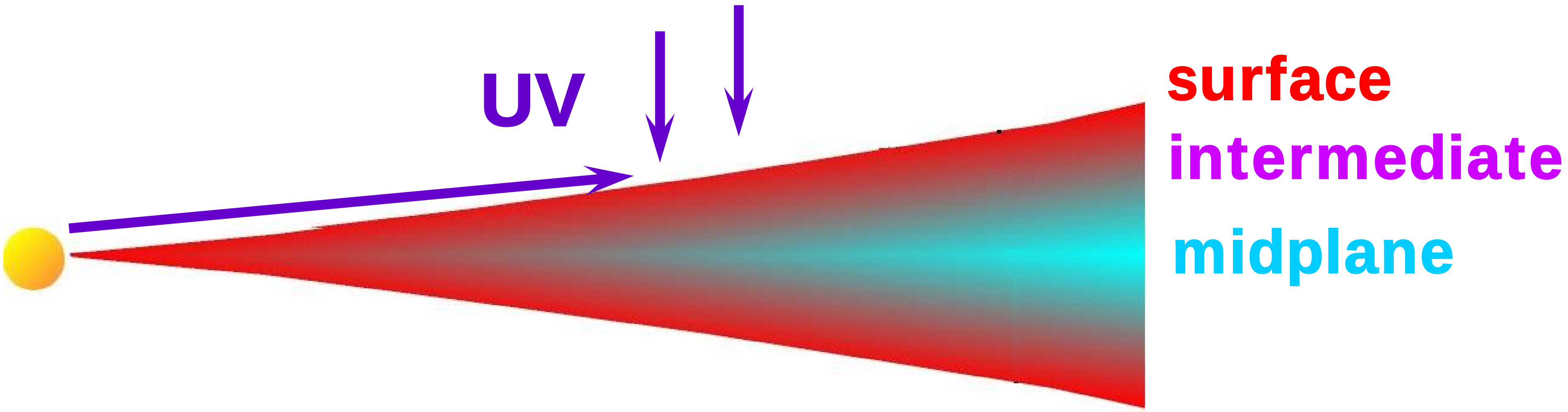
4. Sulphur chemistry (e.g. Wakelam et al. 2004)



# Protoplanetary Disks

Protoplanetary Disks

# Chemical Structure of PPDs



**Surface layer** : n~$10^{4-5}$cm$^{-3}$, T>50K

Photochemistry

**Intermediate** : n~$10^{6-7}$cm$^{-3}$, T>40K

Dense cloud chemistry

**Midplane** : n>$10^{7}$cm$^{-3}$, T<20K

Freeze-out

Aikawa et al. 2002; Markwick & Charnley 2003

# Molecular Abundances of PPD

| Molecules | TMC1 | DM Tau | $f_{deplete}$ |
|---|---|---|---|
| CO | 7.0(-5) | 1.4(-5) | - |
| $C_2H$ | 8.0(-8) | 1.1(-8) | 7 |
| CN | 3.0(-8) | 3.2(-9) | 10 |
| HCN | 2.0(-8) | 5.5(-10) | 40 |
| HNC | 2.0(-8) | 2.4(-10) | 90 |
| CS | 1.0(-8) | 3.3(-10) | 30 |
| $H_2CO$ | 2.0(-8) | 5.0(-10) | 50 |
| $HCO^+$ | 2.0(-8) | 5.0(-10) | 50 |

**(Dutrey et al. 1997)**

**DCO+ (van Dishoeck et al. 2003) and H2D+ (Ceccarelli et al. 2004) detected.**

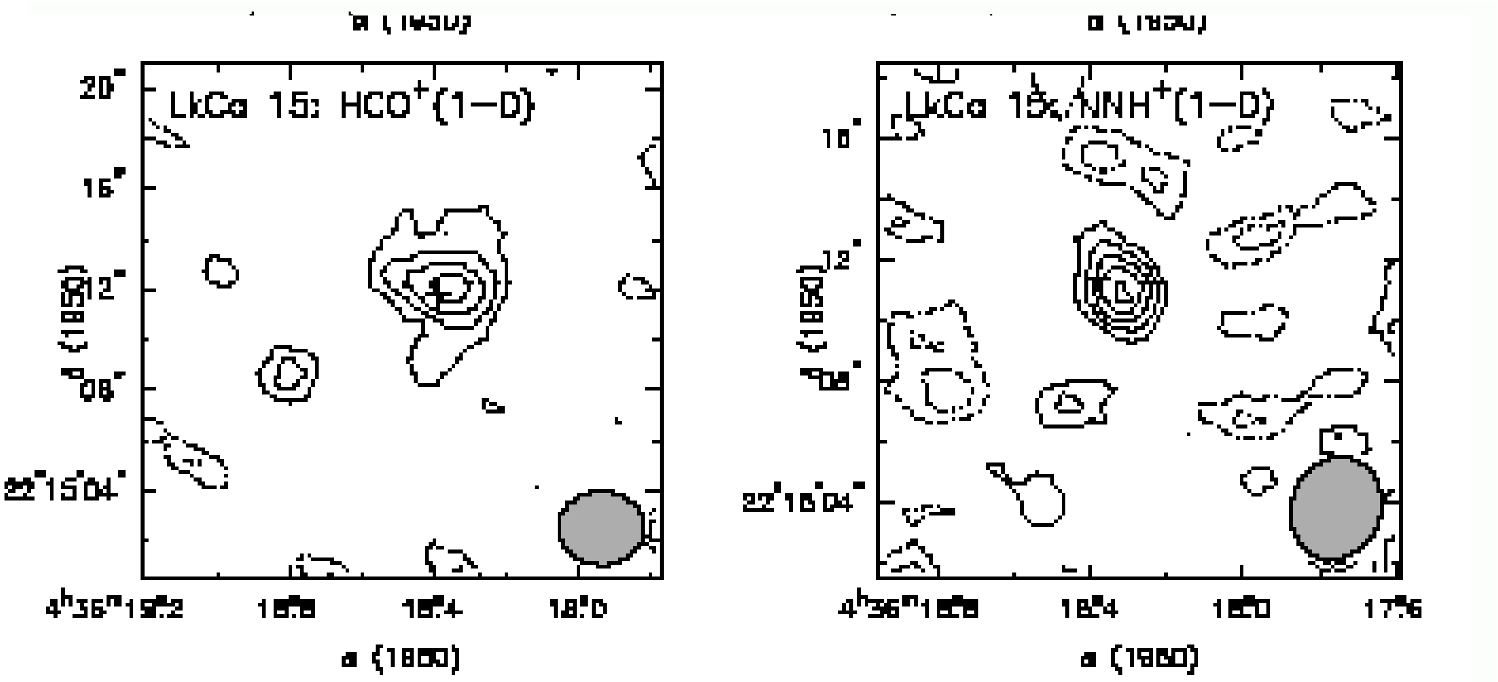
**Low molecular abundances**

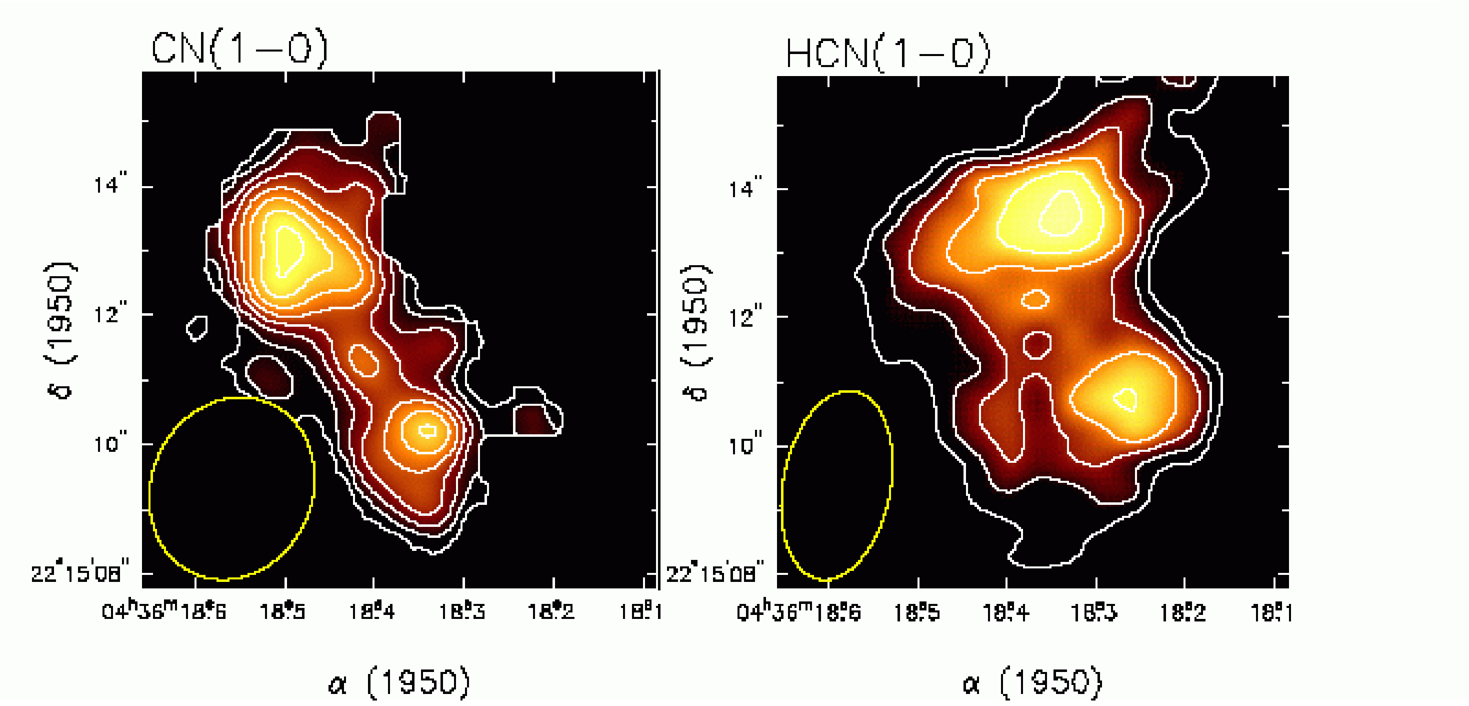
← **Freeze-out @ cold dense region**

**High CN / HCN ratio**

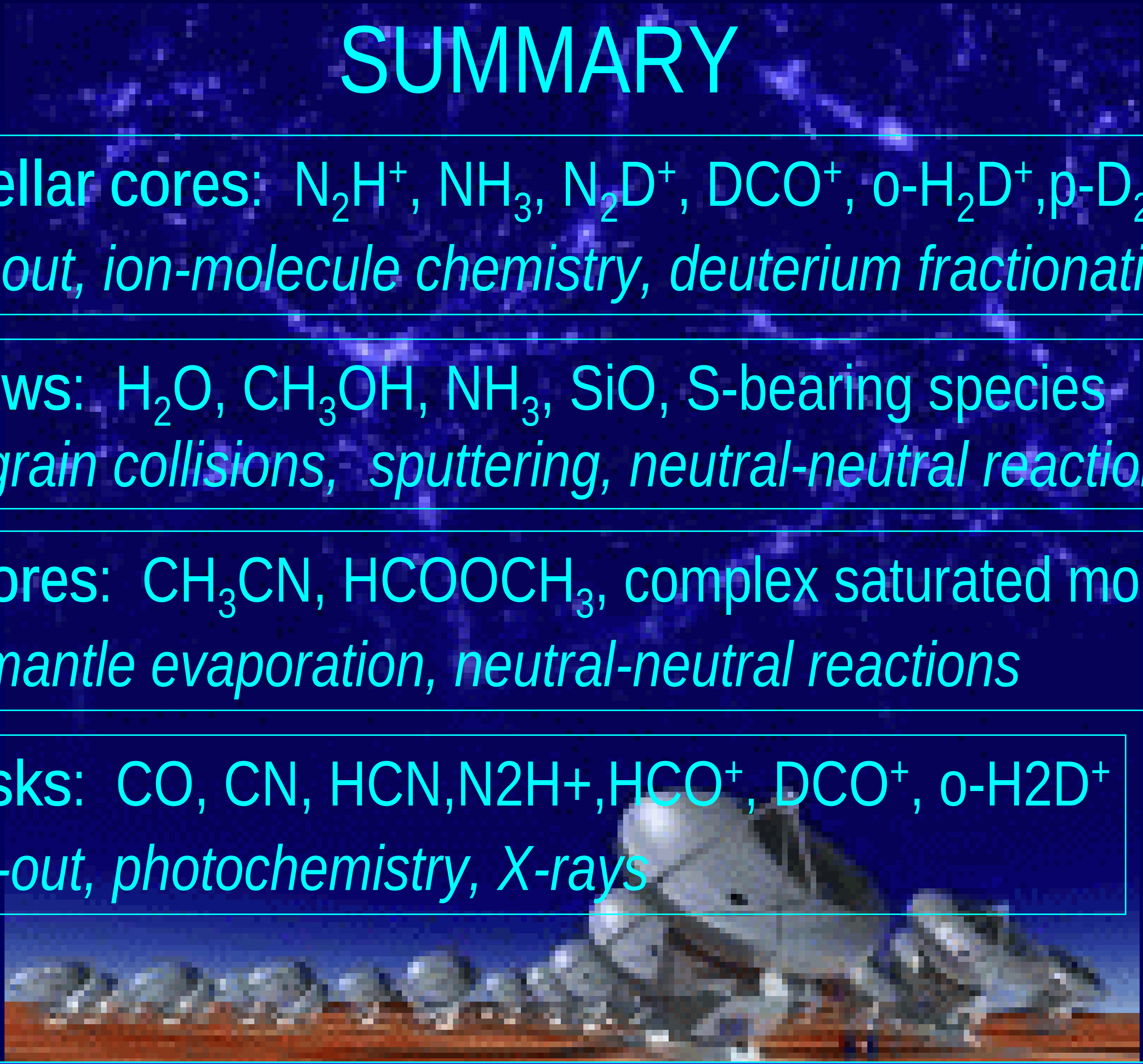
← **Photochemistry @ disk surface**

# LkCa 15 @ OVRO (Qi et al. 2003)





# SUMMARY



Pre-stellar cores: $N_2H^+$, $NH_3$, $N_2D^+$, $DCO^+$, o-$H_2D^+$,p-$D_2H^+$

*freeze-out, ion-molecule chemistry, deuterium fractionation*

Outflows: $H_2O$, $CH_3OH$, $NH_3$, SiO, S-bearing species

*grain-grain collisions, sputtering, neutral-neutral reactions*

Hot Cores: $CH_3CN$, $HCOOCH_3$, complex saturated molecules

*grain mantle evaporation, neutral-neutral reactions*

PP Disks: CO, CN, HCN,N2H+,$HCO^+$, $DCO^+$, o-H2D$^+$

*freeze-out, photochemistry, X-rays*

APEX; Herschel ($H_2O$, $H_3O^+$, o-$D_2H^+$); SOFIA (p-$H_2D^+$); ALMA