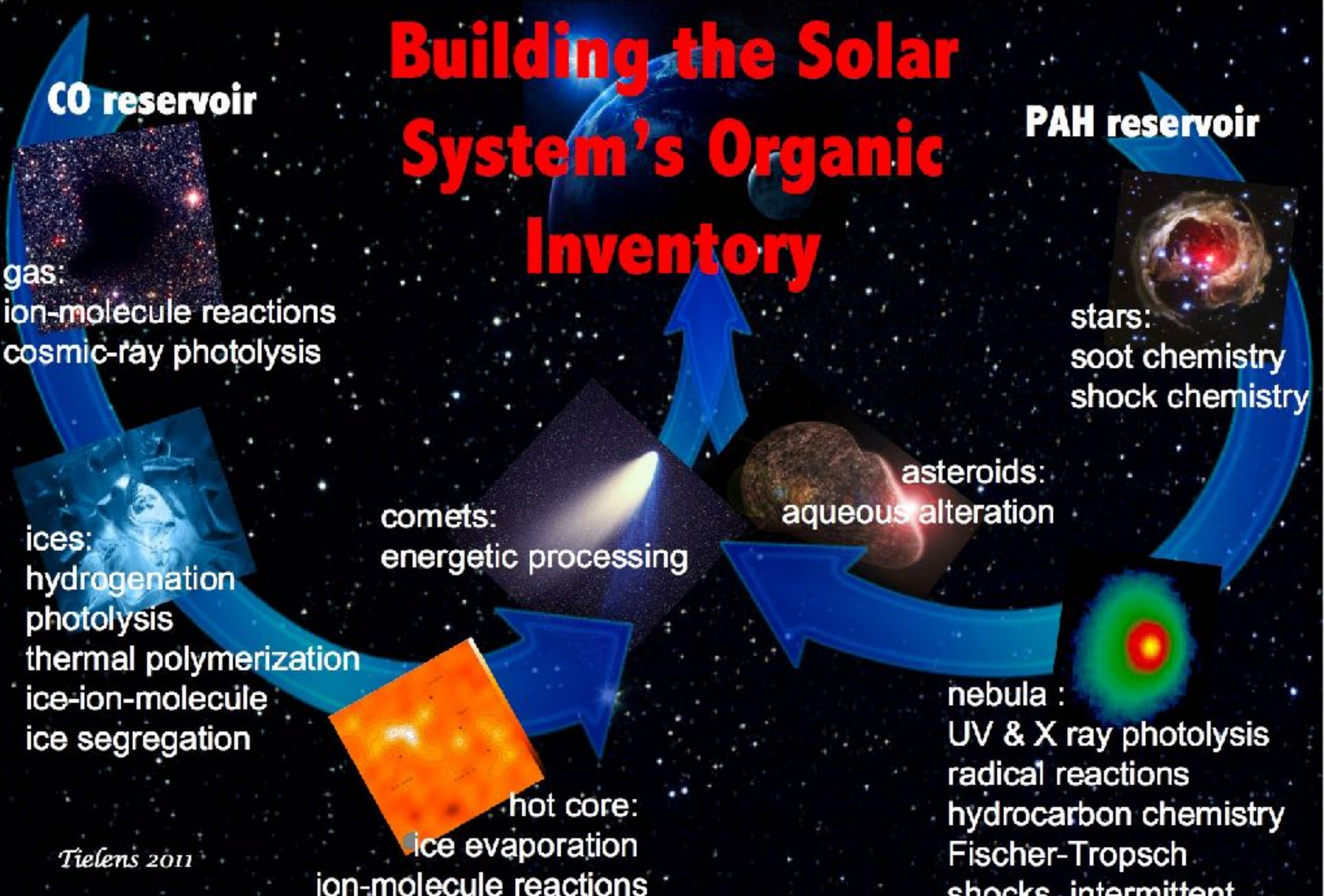
Surface Chemistry

Xander Tielens
Leiden Observatory & Astronomy Department, University of Maryland

Tielens, 2005, Physics and chemistry of the interstellar medium, (Cambridge University Press, Cambridge UK)
Tielens, 2021, Molecular Astrophysics, (Cambridge University Press, Cambridge UK)

Building the Solar System's Organic Inventory



CO reservoir

gas:
ion-molecule reactions
cosmic-ray photolysis

ices:
hydrogenation
photolysis
thermal polymerization
ice-ion-molecule
ice segregation

hot core:
ice evaporation
ion-molecule reactions

comets:
energetic processing

asteroids:
aqueous alteration

PAH reservoir

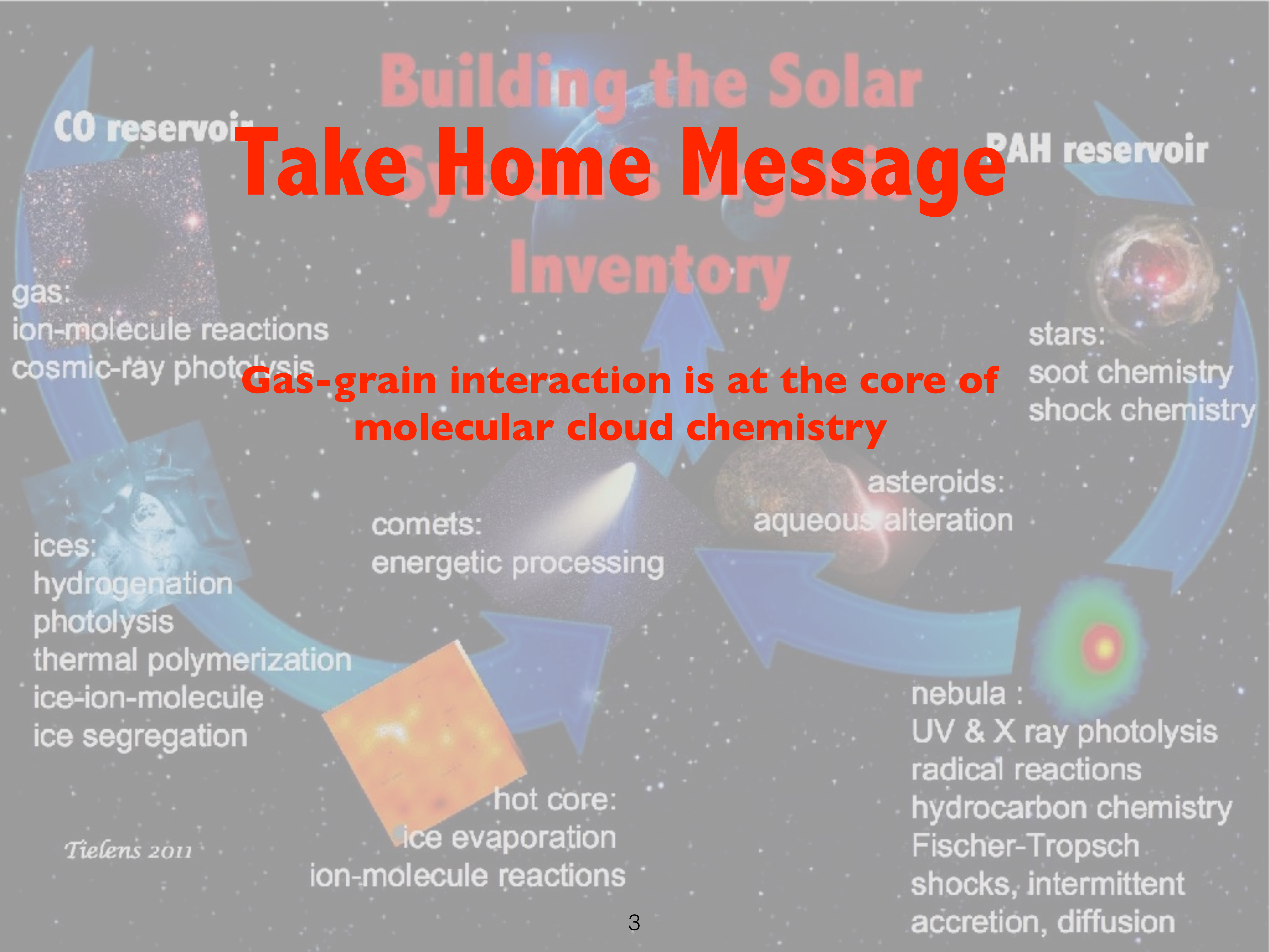
stars:
soot chemistry
shock chemistry

nebula :
UV & X ray photolysis
radical reactions
hydrocarbon chemistry
Fischer-Tropsch
shocks, intermittent
accretion, diffusion

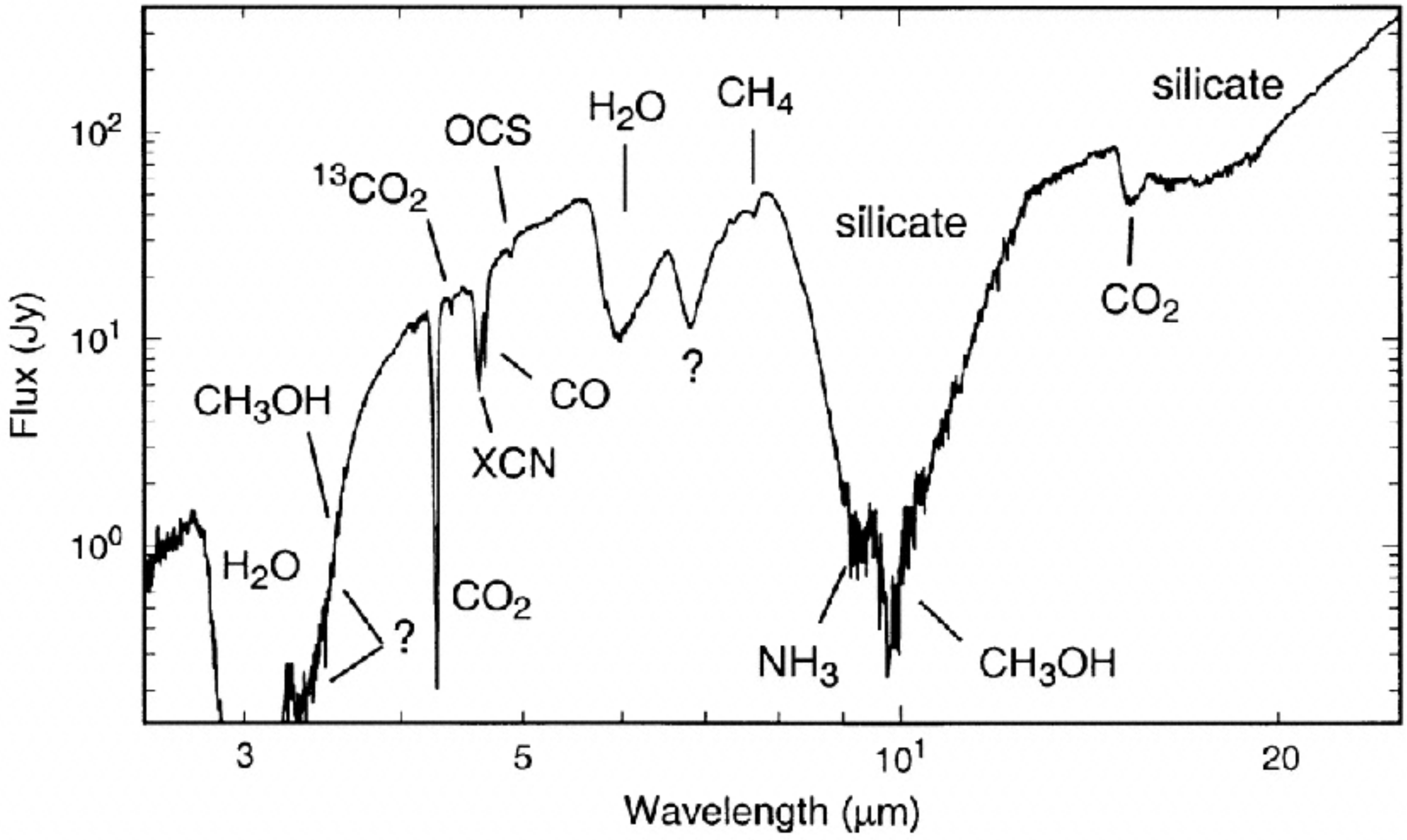
Tielens 2011

Take Home Message

Gas-grain interaction is at the core of molecular cloud chemistry



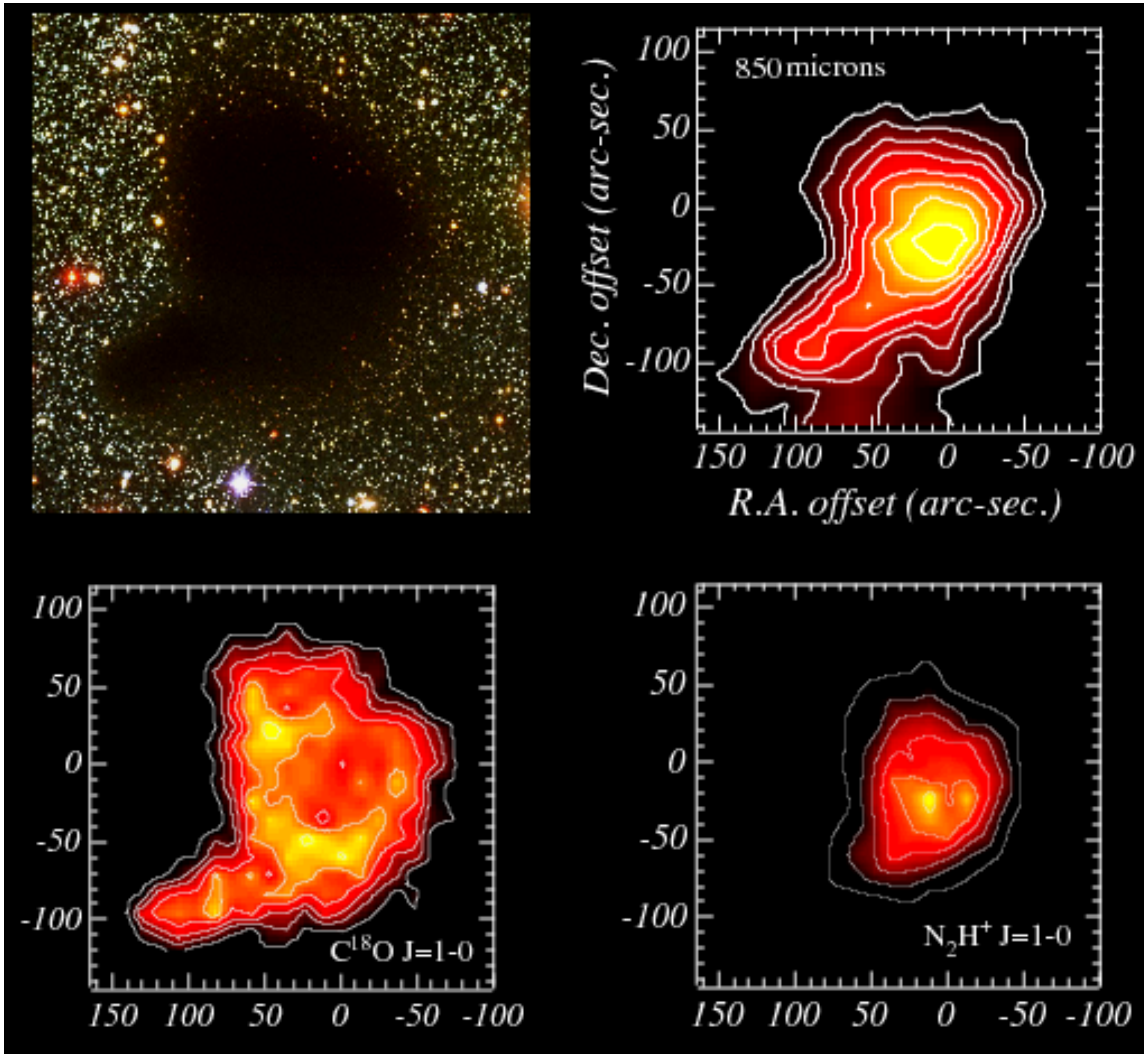
The Role of Dust



Ice as (cold) repository of material

Gibb et al, 2004, ApJS, 151, 35; Boogert et al 2015, ARAA, 53, 541

Gas Phase Depletion

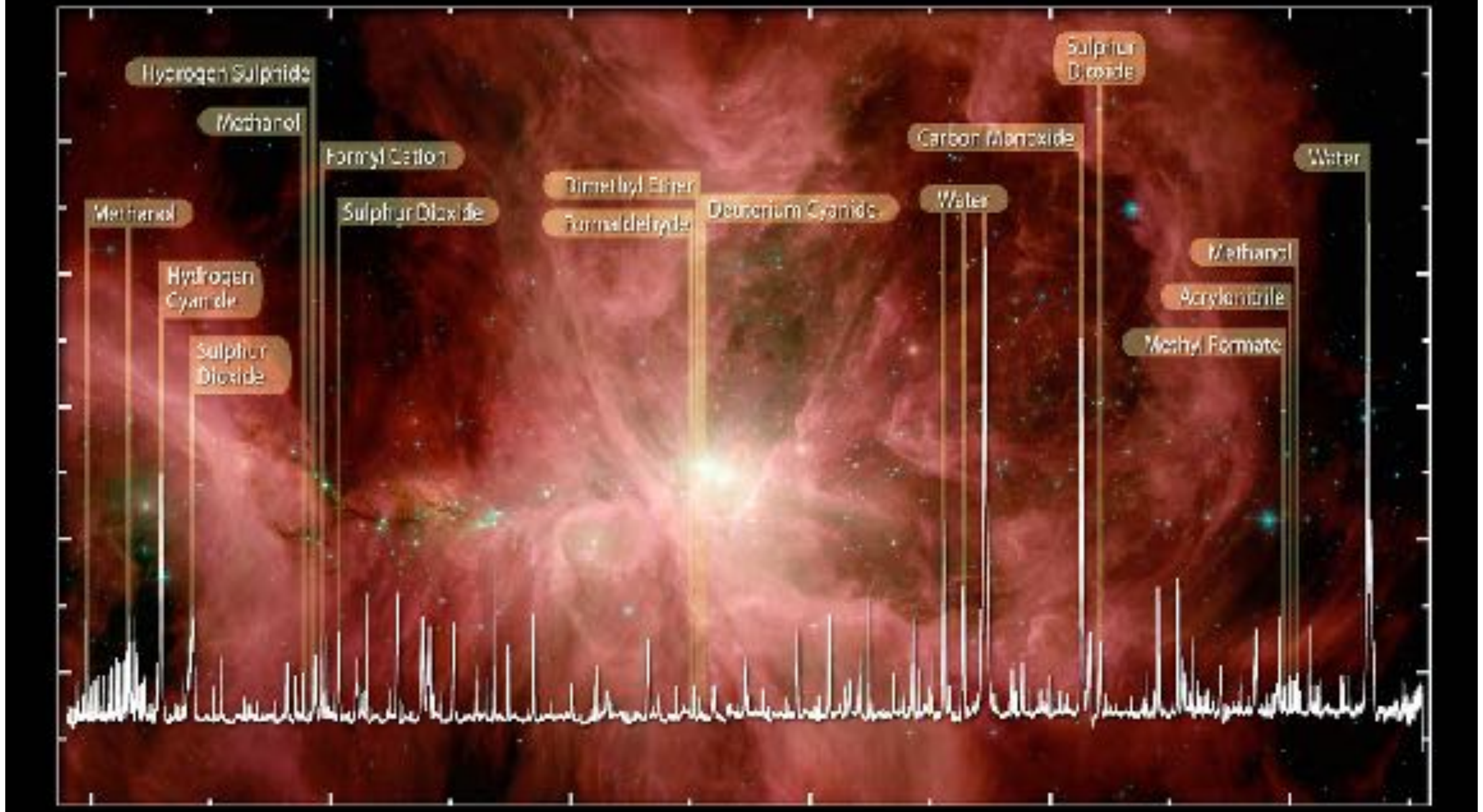


Depletion of many species in the densest cores

Caselli et al, 1999, ApJ, 523, L165 & Bergin et al, ApJ, 2001, 570, L101

Simple Organic Molecules ("SOM")

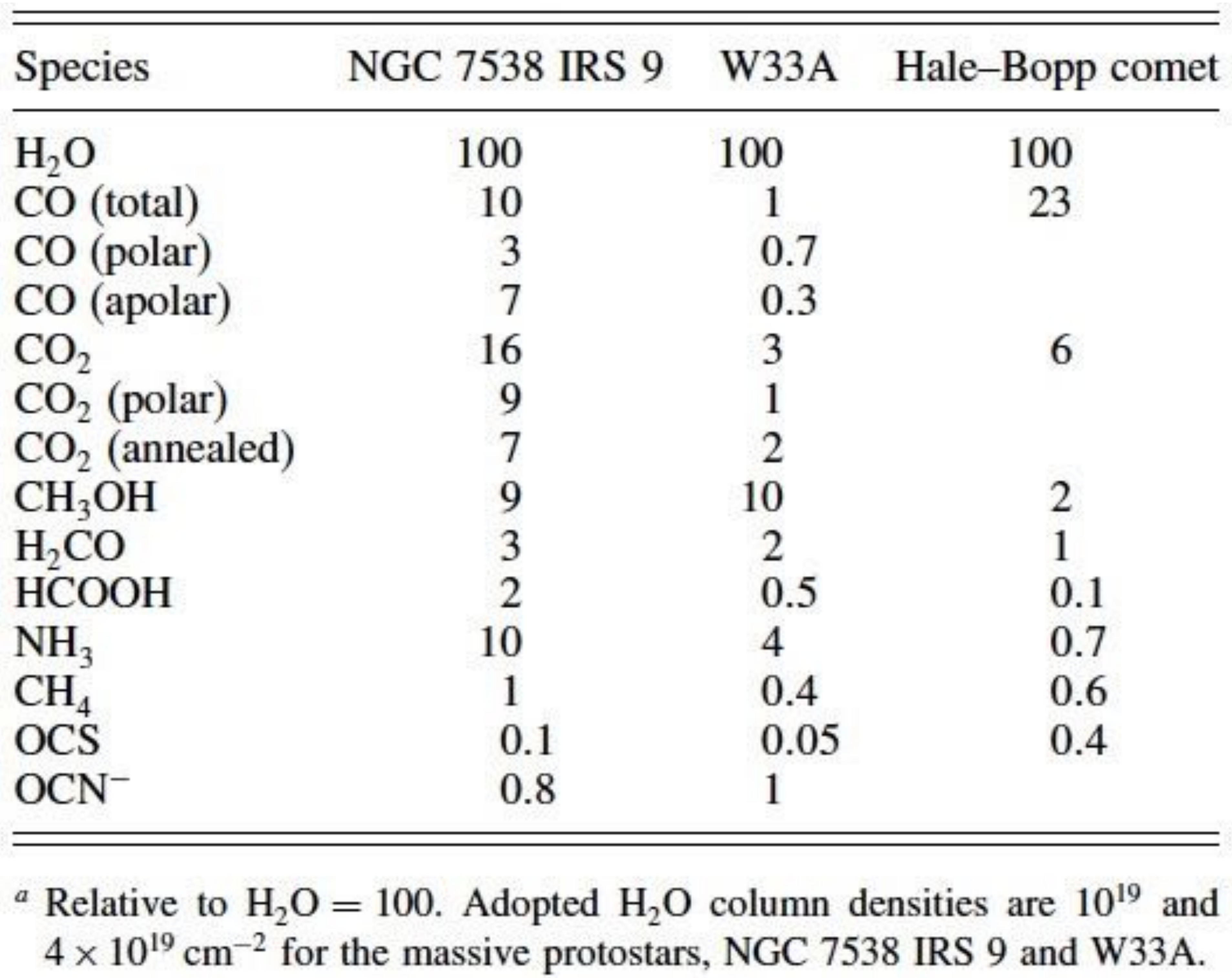
- Warm dense gas with rich organic inventory of relatively simple organic molecules
  - CH_3OH, CH_3CH_2OH, CH_3OCH_3, H_2CO, CH_3CHO, $HCOOH$, NH_2CHO, ...
  - HCN, CH_3CN, CH_3CH_2CN, ...
- **Large deuterium fractionations**
- Driven by evaporation of ice mantles formed in cold phase



HIFI Spectrum of Water and Organics in the Orion Nebula

© ESA, HEXOS and the HIFI consortium
E. Bergin

Blake et al, 1987, ApJ, 315, 621
Ceccarelli et al, 2007, PPV, 47
Bergin et al 2010, A&A, 521, L20



Species	NGC 7538 IRS 9	W33A	Hale–Bopp comet
H_2O	100	100	100
CO (total)	10	1	23
CO (polar)	3	0.7	
CO (apolar)	7	0.3	
CO_2	16	3	6
CO_2 (polar)	9	1	
CO_2 (annealed)	7	2	
CH_3OH	9	10	2
H_2CO	3	2	1
HCOOH	2	0.5	0.1
NH_3	10	4	0.7
CH_4	1	0.4	0.6
OCS	0.1	0.05	0.4
OCN^-	0.8	1	

[a] Relative to $H_2O = 100$. Adopted H_2O column densities are 10^{19} and 4×10^{19} cm^{-2} for the massive protostars, NGC 7538 IRS 9 and W33A.

Composition of interstellar ices
Very different from the gas phase !

Grain Surface Chemistry: In a Nutshell

- Dust grains are the “watering holes” of astrochemistry where species come to meet and mate.

- In a way, collisions on a grain surface can take very long (up to hours or days)

- Tunneling is key to hydrogenation (and deuteration)

- Initial conditions play a key role

  - O goes to H_2O through e.g., O_2 and O_3

  - C (e.g., CO) goes to H_2CO and CH_3OH

  - N goes to NH_3 while N_2 is inert

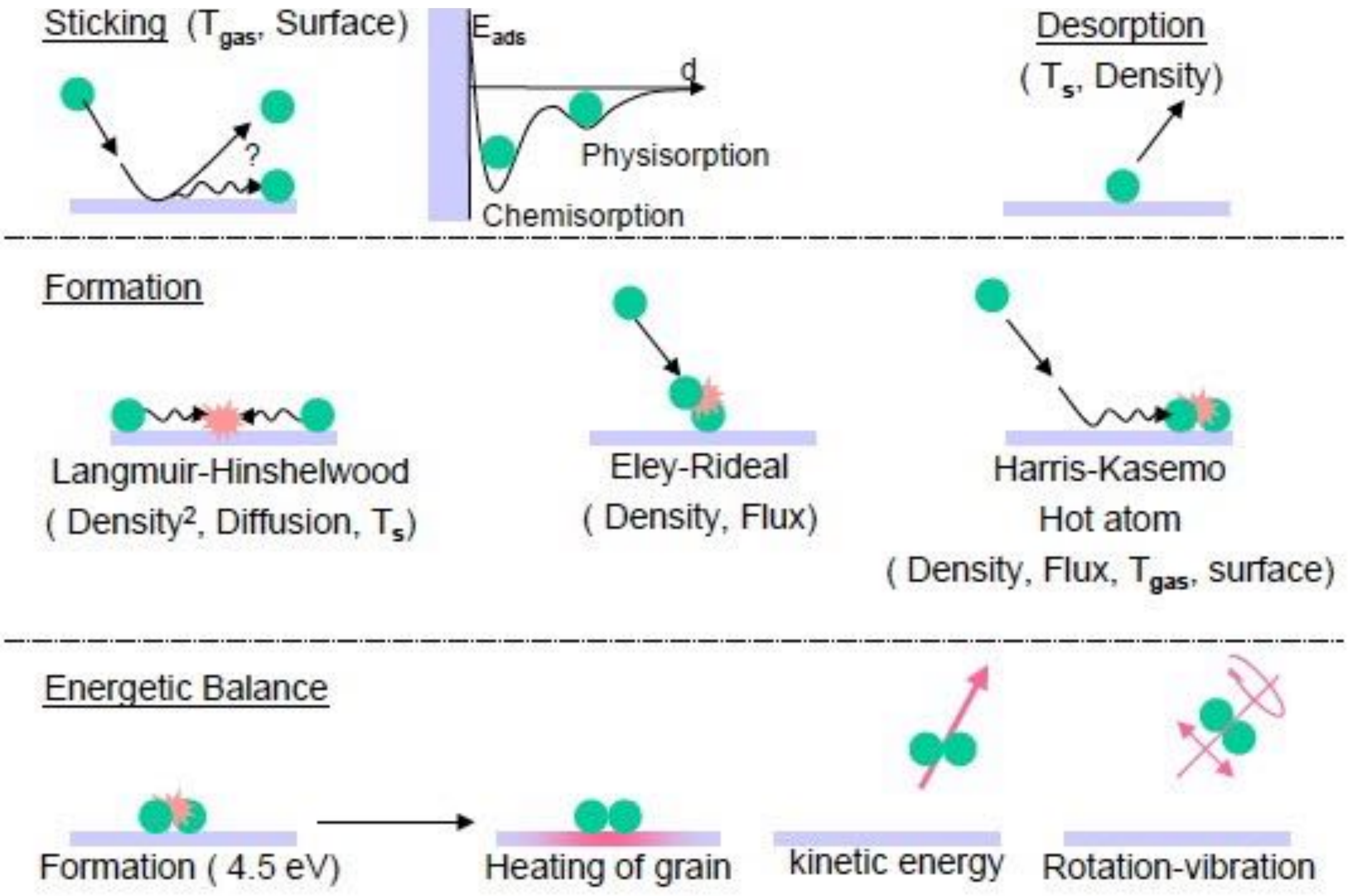
  - S goes to SO/SO2 and CS goes to OCS (?)

  - D enrichment is driven by high D/H (gas) and high HD/H_2 on the grain

Characteristics of Interstellar Surface Chemistry

- Low pressures: 10^{-17} – 10^{-13} mbar (UHV= 10^{-9} mbar)
- Low temperatures: 10–100 K
- Low densities: 10–10^{4} cm^{-3}
- Silicate grains + graphitic grains (diffuse clouds)
- Ice grains (molecular clouds)
  - Sizes: 5-1000 Angstrom & surface areas: $3x10^{2}$ – 10^{8} $Å^{2}$
  - Limited # sites: 10^{2} – 10^{7}

Processes involved in Surface Chemistry



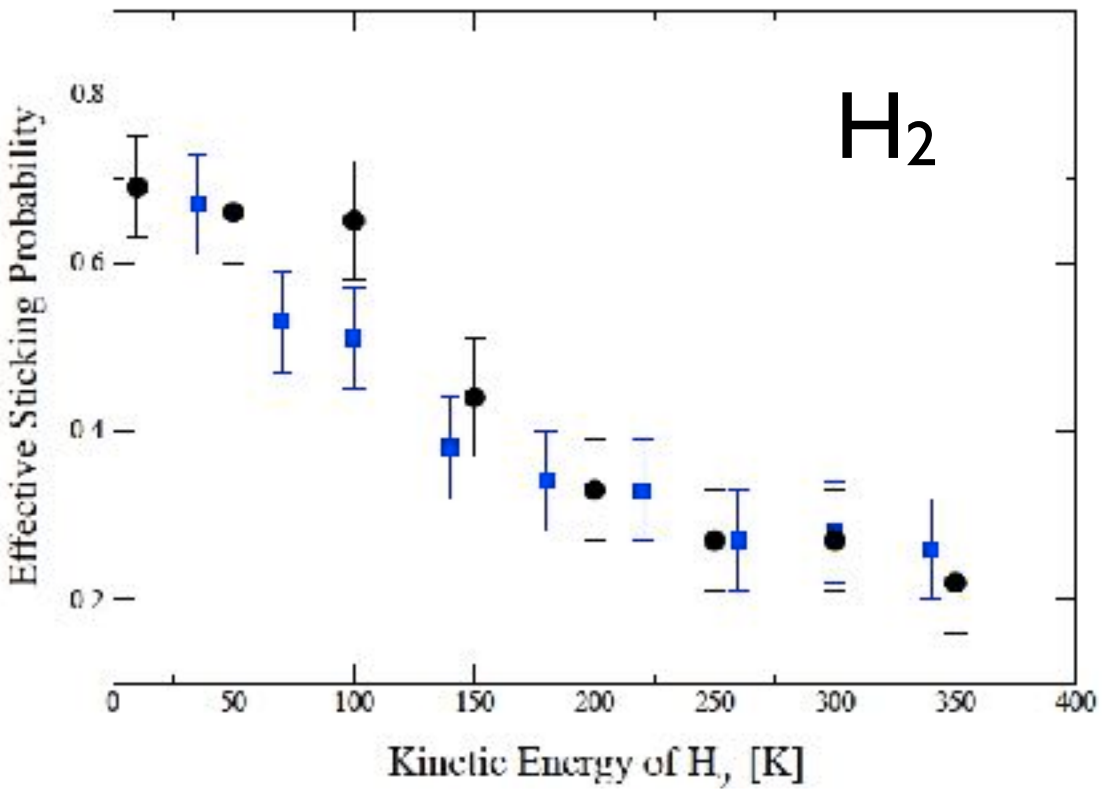
Sticking & Binding

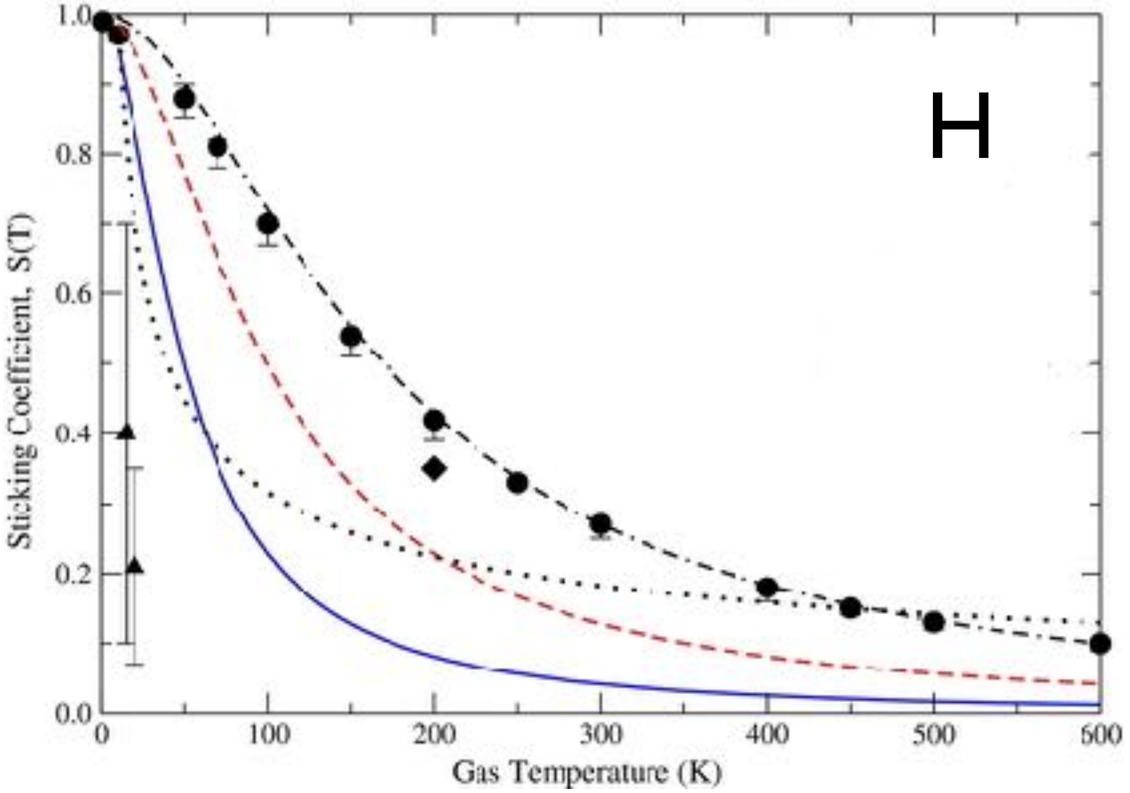
Timescales

Accretion timescale: grain size, *a*, abundance X_i, and mass m_i

$$\tau_{ac} = (\pi a^2 v_i n_i)^{-1} = 7 \left(\frac{300\,\text{Å}}{a}\right)\left(\frac{10^4\,cm^{-3}}{n}\right)\left(\frac{10^{-4}}{X_i}\right)\left(\frac{m_i}{1\,amu}\right) \quad \text{days}$$

Sticking





Have to transfer the kinetic energy, E_{kin}, to the surface atom in the collisions (hopping process). Energy transferred, ΔE, is related to:

$$\frac{\Delta E}{E_{kin} + E_b} = \frac{4\mu}{M}$$

where μ and M are the reduced and total mass

At 10K, sticking coefficient ~1, even for H/H_2

Timescales

Accretion timescale: grain size, *a*, abundance X_i, and mass m_i

$$\tau_{ac} = (\pi a^2 v_i n_i)^{-1} = 7 \left(\frac{300\,\text{Å}}{a}\right)\left(\frac{10^4\,cm^{-3}}{n}\right)\left(\frac{10^{-4}}{X_i}\right)\left(\frac{m_i}{1\,amu}\right) \quad \text{days}$$

Evaporation timescale: binding energy, E_b

$$\tau_{ev} = \nu_0^{-1} \exp\left[E_b/kT\right] \qquad \nu_0 = 1 - 4 \times 10^{12} \quad \text{s}^{-1}$$

Thermal/tunneling migration timescale: barrier width, *d*

$$\tau_m \simeq \nu_0^{-1} \exp\left[0.3E_b/kT\right] \qquad \tau_m = \nu_0^{-1} \exp\left[\frac{2d}{\hbar}\sqrt{E_b m_i}\right]$$

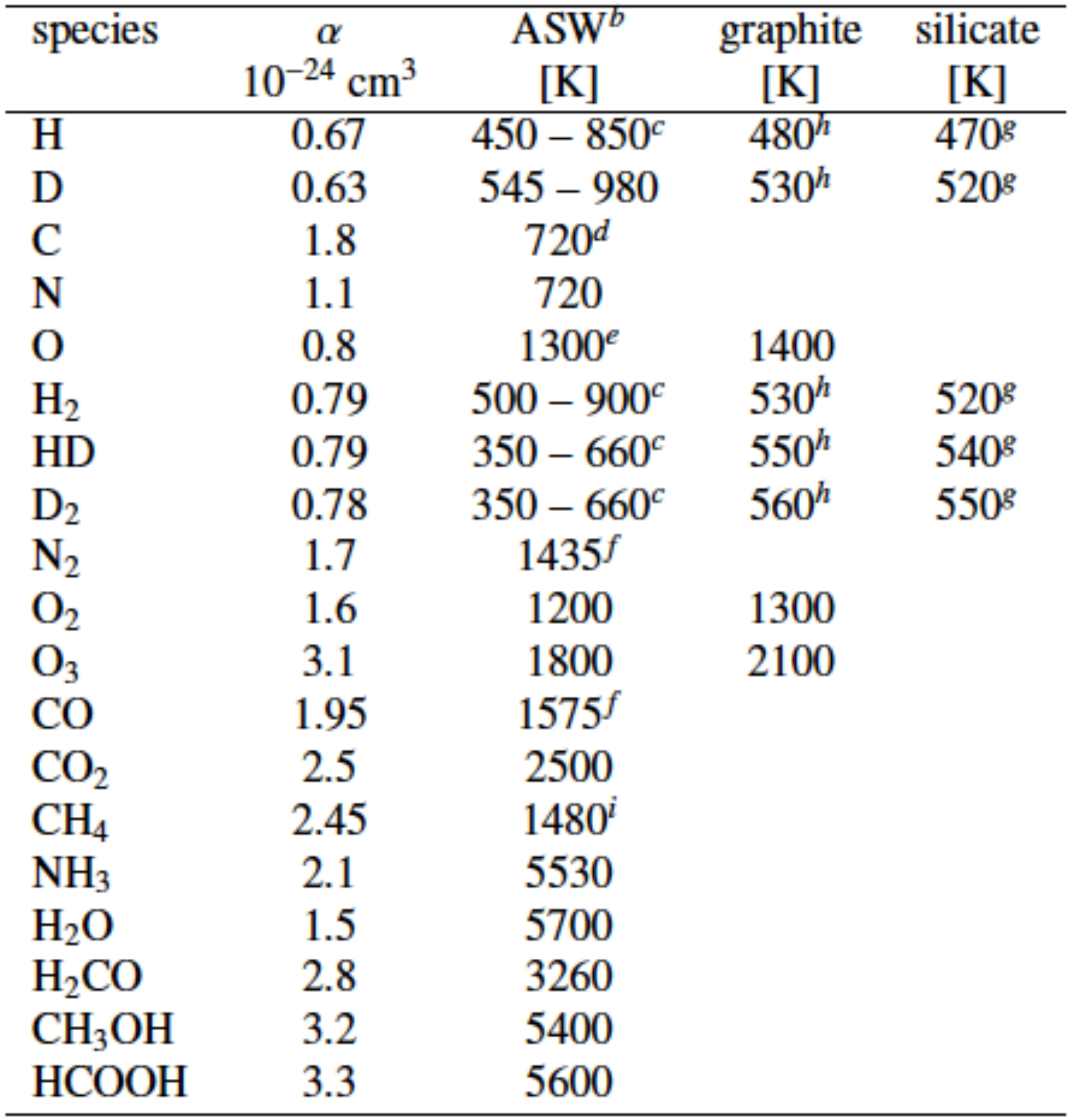


Table 7.2: Binding energies of astrophysically relevant species and surfaces[a]

species	α 10^{-24} cm^3	ASW[b] [K]	graphite [K]	silicate [K]
H	0.67	450 – 850[c]	480[h]	470[g]
D	0.63	545 – 980	530[h]	520[g]
C	1.8	720[d]		
N	1.1	720		
O	0.8	1300[e]	1400	
H_2	0.79	500 – 900[c]	530[h]	520[g]
HD	0.79	350 – 660[c]	550[h]	540[g]
D_2	0.78	350 – 660[c]	560[h]	550[g]
N_2	1.7	1435[f]		
O_2	1.6	1200	1300	
O_3	3.1	1800	2100	
CO	1.95	1575[f]		
CO_2	2.5	2500		
CH_4	2.45	1480[i]		
NH_3	2.1	5530		
H_2O	1.5	5700		
H_2CO	2.8	3260		
CH_3OH	3.2	5400		
HCOOH	3.3	5600		

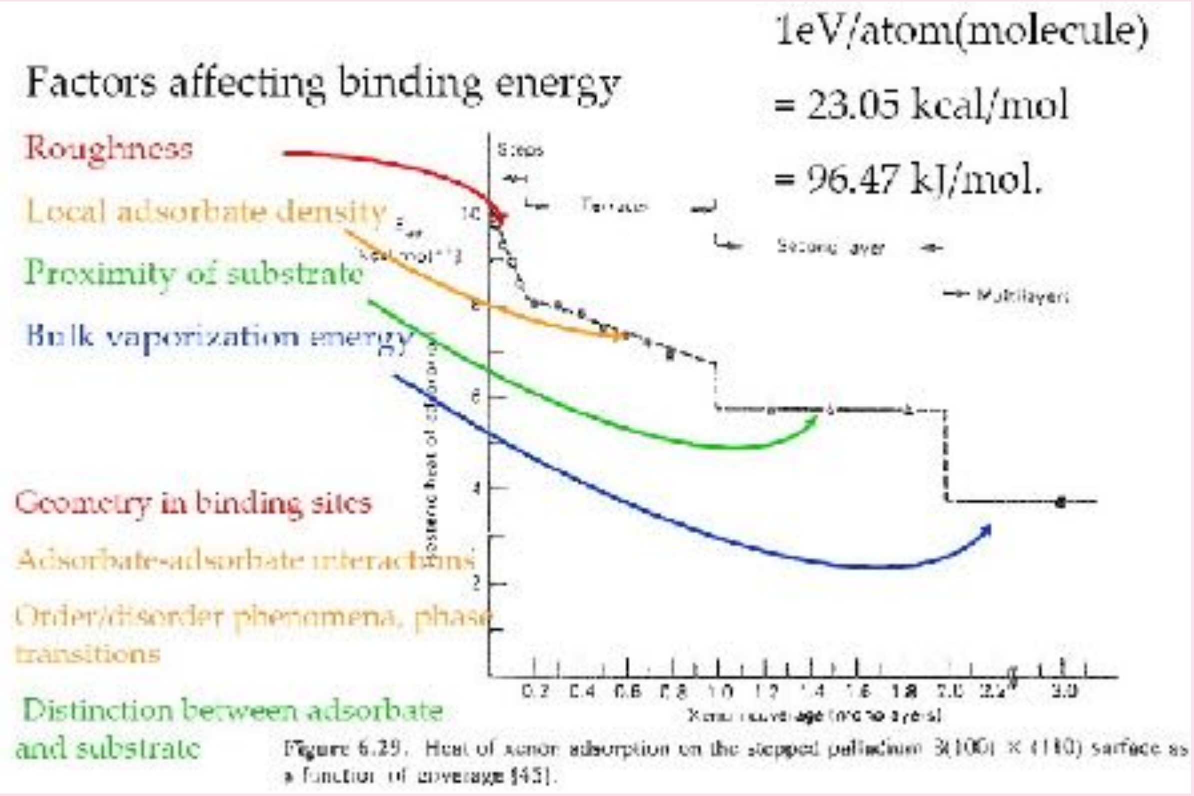
species	evaporation τ_{ev} [s]	migration τ_m [s]
H_2	9 (6)	3 (-6)
H	4 (2)	2 (-8)
D	1 (4)	3 (-8)
O	–	2 (-1)
C	–	2 (-3)
CO	–	–

Some species are highly mobile (H, D, H_2), some are sort of mobile (C,N, (O)), most are immobile (CO, OH, H_2O, …) at low T

Binding energy

Factors influencing binding energy

- Disorder (distribution of binding sites)
- Steps/kinks
- Interaction with adsorbates



Factors affecting binding energy

Roughness

Local adsorbate density

Proximity of substrate

Bulk vaporization energy

Geometry in binding sites

Adsorbate-adsorbate interactions

Order/disorder phenomena, phase transitions

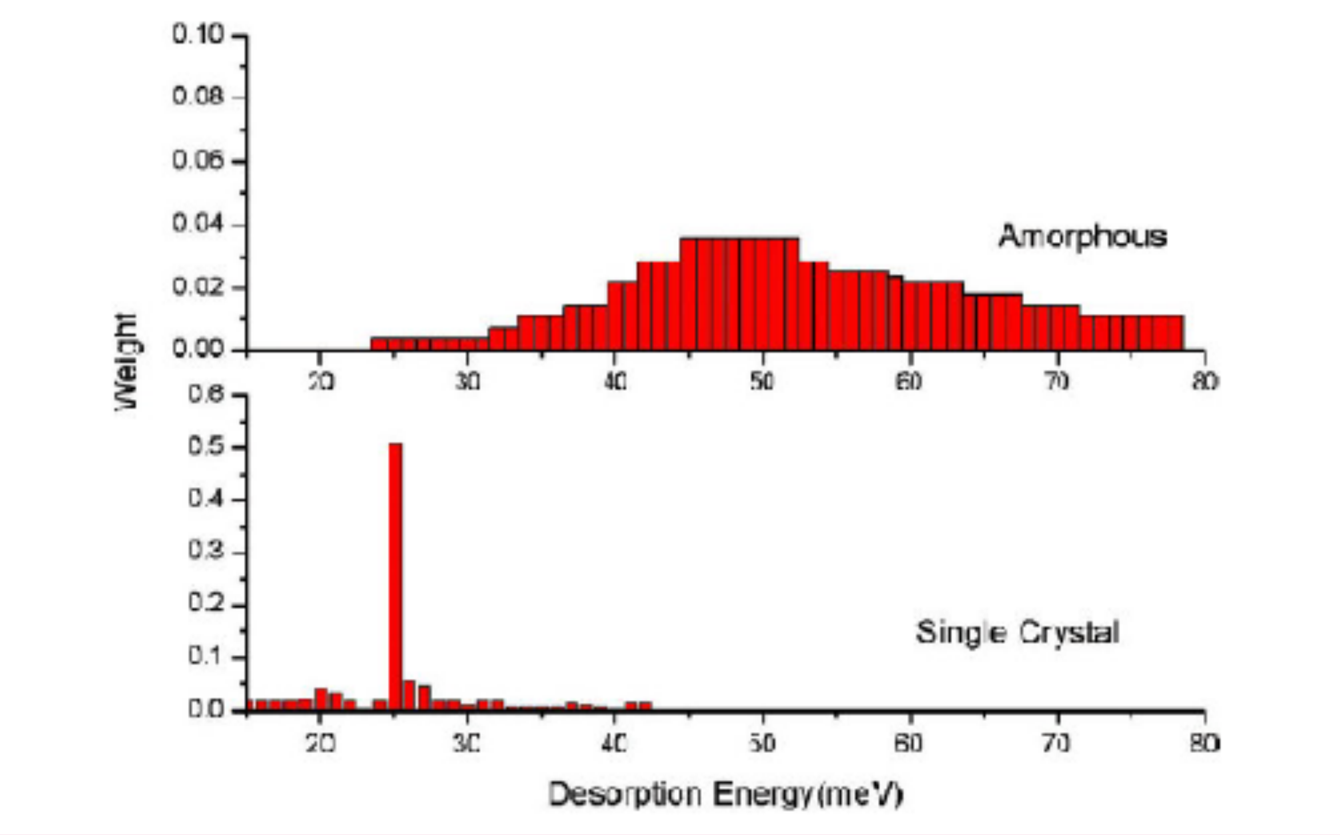
Distinction between adsorbate and substrate

1eV/atom(molecule)

= 23.05 kcal/mol

= 96.47 kJ/mol.

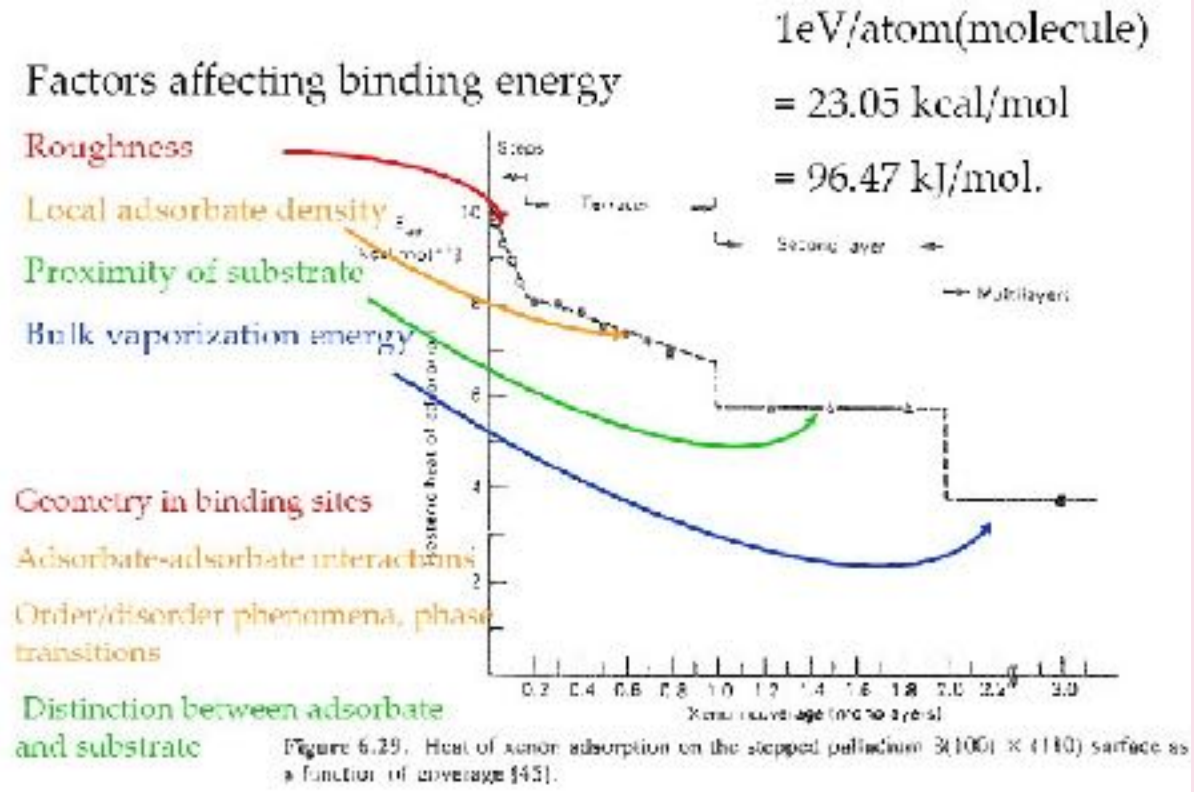
Figure 6.29. Heat of xenon adsorption on the stepped palladium 3(100) × (110) surface as a function of coverage [45].



Binding energy

Factors influencing binding energy

- Disorder (distribution of binding sites)
- Steps/kinks
- Interaction with adsorbates



1eV/atom(molecule)
= 23.05 kcal/mol
= 96.47 kJ/mol.

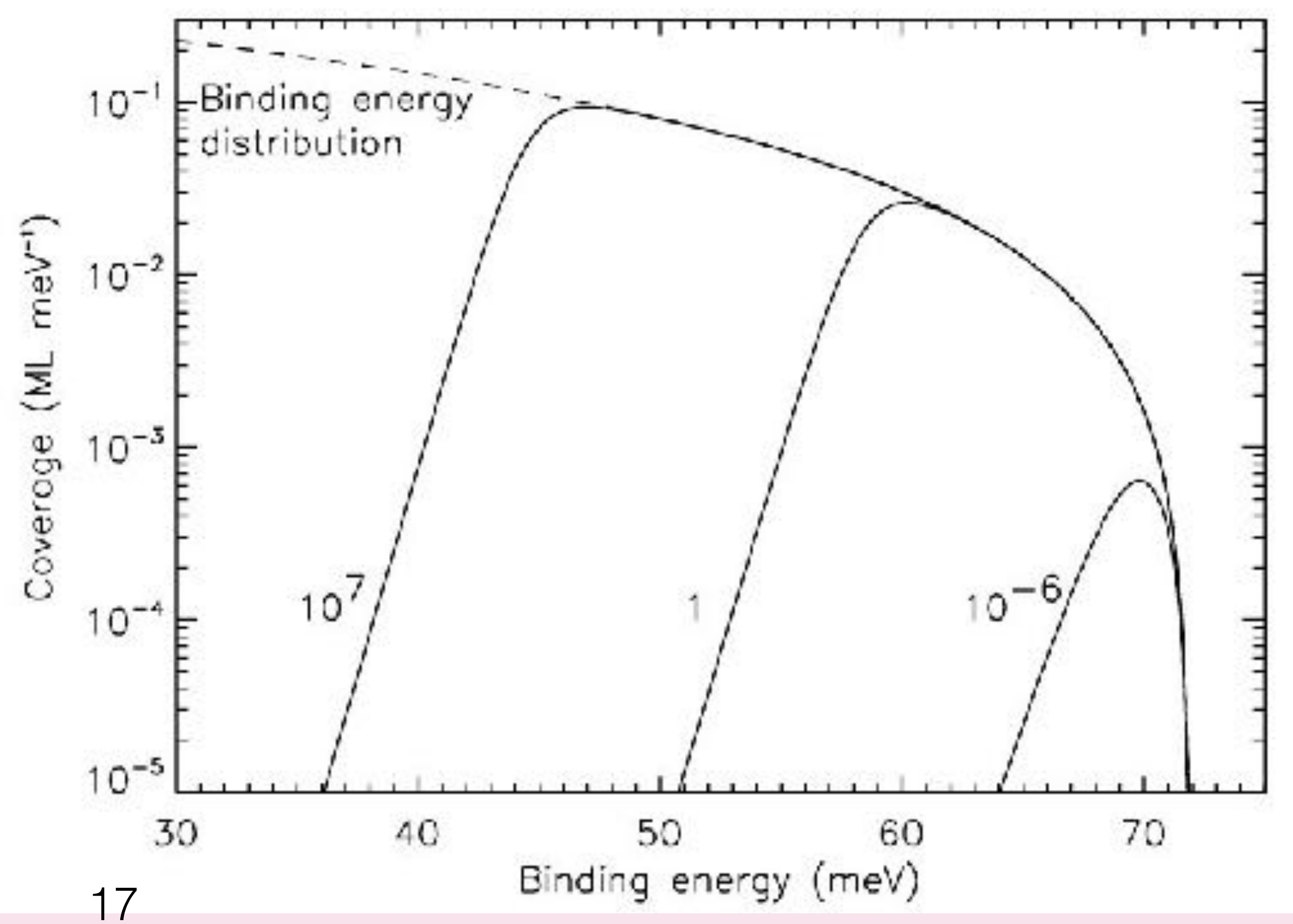
Figure 6.29. Heat of xenon adsorption on the stepped palladium 3(100) × (110) surface as a function of coverage [45].

Set by H_2 coverage:

$$\pi a^2 \upsilon_{\mathrm{H}_2} n_{\mathrm{H}_2} = \nu \exp\left[-E_b\left(\theta\left(\mathrm{H}_2\right)\right)/kT\right]$$

$$E_b(\mathrm{H}) = \frac{\alpha(\mathrm{H})}{\alpha(\mathrm{H}_2)} E_b\left(\theta\left(\mathrm{H}_2\right)\right)$$

At $n = 10^4\ \mathrm{cm}^{-3}$, $E_b\left(\theta\left(\mathrm{H}_2\right)\right) = 450\ \mathrm{K}$ $(\theta(\mathrm{H}_2) \approx 0.2)$ and $E_b(\mathrm{H}) = 350\ \mathrm{K}$.



Surface Migration

Surface diffusion is a random walk:

Timescale to visit each site (at least) once:

$\tau_{scan} = N^2 \ln[N] \tau_m \ll \tau_{ev}$ at 10 K.

with N the number of sites.

If there is a coreactant radical, reaction will occur.

Note that low-T ice is highly porous and N may be as large as 10^{16} cm^{-2}.

Formation

Langmuir-Hinshelwood Reaction

Radical-radical reactions

reactants		products	reactants		products
H + H	⟶	H_2	O + O	⟶	O_2
H + O	⟶	OH	O + N	⟶	NO
H + OH	⟶	H_2O	O + C	⟶	CO
H + C	⟶	CH	O + CN	⟶	OCN
H + CH	⟶	CH_2	O + HCO	⟶	HCOO
H + CH	⟶	CH_3	C + N	⟶	CN
H + CH_3	⟶	CH_4	C + HCO	⟶	CCHO
H + N	⟶	NH	N + N	⟶	N_2
H + NH	⟶	NH_2	N + NH	⟶	N_2H
H + NH_2	⟶	NH_3	N + HCO	⟶	HNCO
H + O_2H	⟶	H_2O_2			
H + NO	⟶	HNO			
H + CN	⟶	HCN			
H + CN	⟶	HNC			
H + CNO	⟶	HNCO			
H + HCO	⟶	H2CO			
H + HCOO	⟶	HCOOH			
H + CH_3O	⟶	CH_3OH			
H + NCHO	⟶	NHCHO			
H + NHCHO	⟶	NH_2CHO			
H + CCHO	⟶	CHCHO			
H + CHCHO	⟶	CH_2CHO			
H + CH_2CHO	⟶	CH_3CHO			
H + N_2H	⟶	N_2H_2			

reactions between radicals with unpaired electrons will occur on “collision”

Radical-Molecule Reactions

Some radical-molecule reactions can occur as they have no or submerged barriers:

- $H + O_2$ —> HO_2
- $H + O_3$ —> $OH + O_2$

Reactions with Activation Barriers

Competition between reaction and diffusion:

p, p_0, p_m is reaction, barrier penetration, migration probability

$$p = \frac{p_0}{p_0 + p_m}, \text{ with } p_0 \ll p_m$$

$$p_0 = \nu_0 \exp\left[-\frac{2a}{\hbar} \sqrt{2mE_a} \right]$$

Number of times a site is visited that can lead to a reaction is: $n_r = \dfrac{\tau_{ev}}{\tau_m} \theta_i$

Probibility for reaction in the k^{th} visit,

$p_k = (1 - p)^{k-1} p$ and probability for reaction before evaporation:

$$p_r = \sum_1^{n_r} p_k = 1 - (1 - p)^{n_r} \approx n_r p = \tau_{ev} \theta_i p_0$$

With more than 1 possible coreactant, this probability becomes

$$\varphi_i = \frac{\theta_i p_0(i)}{\sum \theta_j p_0(i)}$$

Reactions with Activation Barriers

θ_r	E_a [K]
10^{-6}	3400
10^{-1}	7500

Activation barrier for a H reaction probability of p_r=0.5 and surface coverage, θ_r

H Reactions with Activation Barriers

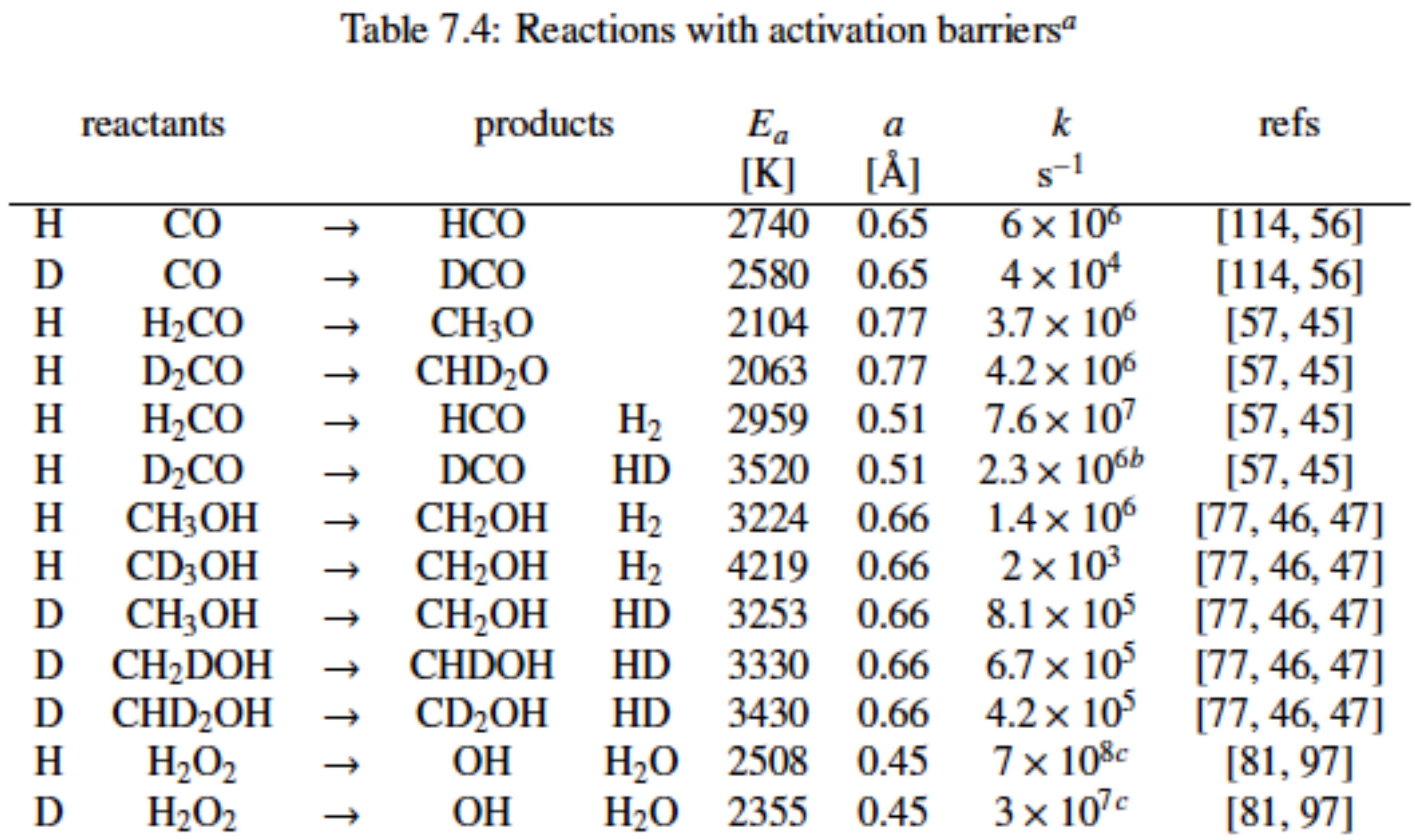


Table 7.4: Reactions with activation barriers[a]

reactants			products		E_a [K]	a [Å]	k s^{-1}	refs
H	CO	→	HCO		2740	0.65	6×10^{6}	[114, 56]
D	CO	→	DCO		2580	0.65	4×10^{4}	[114, 56]
H	H_2CO	→	CH_3O		2104	0.77	3.7×10^{6}	[57, 45]
H	D_2CO	→	CHD_2O		2063	0.77	4.2×10^{6}	[57, 45]
H	H_2CO	→	HCO	H_2	2959	0.51	7.6×10^{7}	[57, 45]
H	D_2CO	→	DCO	HD	3520	0.51	2.3×10^{6}[b]	[57, 45]
H	CH_3OH	→	CH_2OH	H_2	3224	0.66	1.4×10^{6}	[77, 46, 47]
H	CD_3OH	→	CH_2OH	H_2	4219	0.66	2×10^{3}	[77, 46, 47]
D	CH_3OH	→	CH_2OH	HD	3253	0.66	8.1×10^{5}	[77, 46, 47]
D	CH_2DOH	→	CHDOH	HD	3330	0.66	6.7×10^{5}	[77, 46, 47]
D	CHD_2OH	→	CD_2OH	HD	3430	0.66	4.2×10^{5}	[77, 46, 47]
H	H_2O_2	→	OH	H_2O	2508	0.45	7×10^{8}[c]	[81, 97]
D	H_2O_2	→	OH	H_2O	2355	0.45	3×10^{7}[c]	[81, 97]

Reactions with H_2

At low T, surface coverage of H_2 is high. H_2 can also readily tunnel through activation barriers. Reaction has to occur before a mobile coreactant (H or O) accretes and finds and reacts with the species. Probability is:

$$p_r = \tau_{ac}\theta\left(\mathrm{H}_2\right)p_0$$

with $\tau_{ac} = 10^5$ s and $\theta\left(\mathrm{H}_2\right) = 0.2$, the limiting $E_a \simeq 4700$ K.

This includes $\mathrm{OH} + \mathrm{H}_2 \rightarrow \mathrm{H}_2\mathrm{O} + \mathrm{H}$ (note possible cascade).

Reactions with H_2

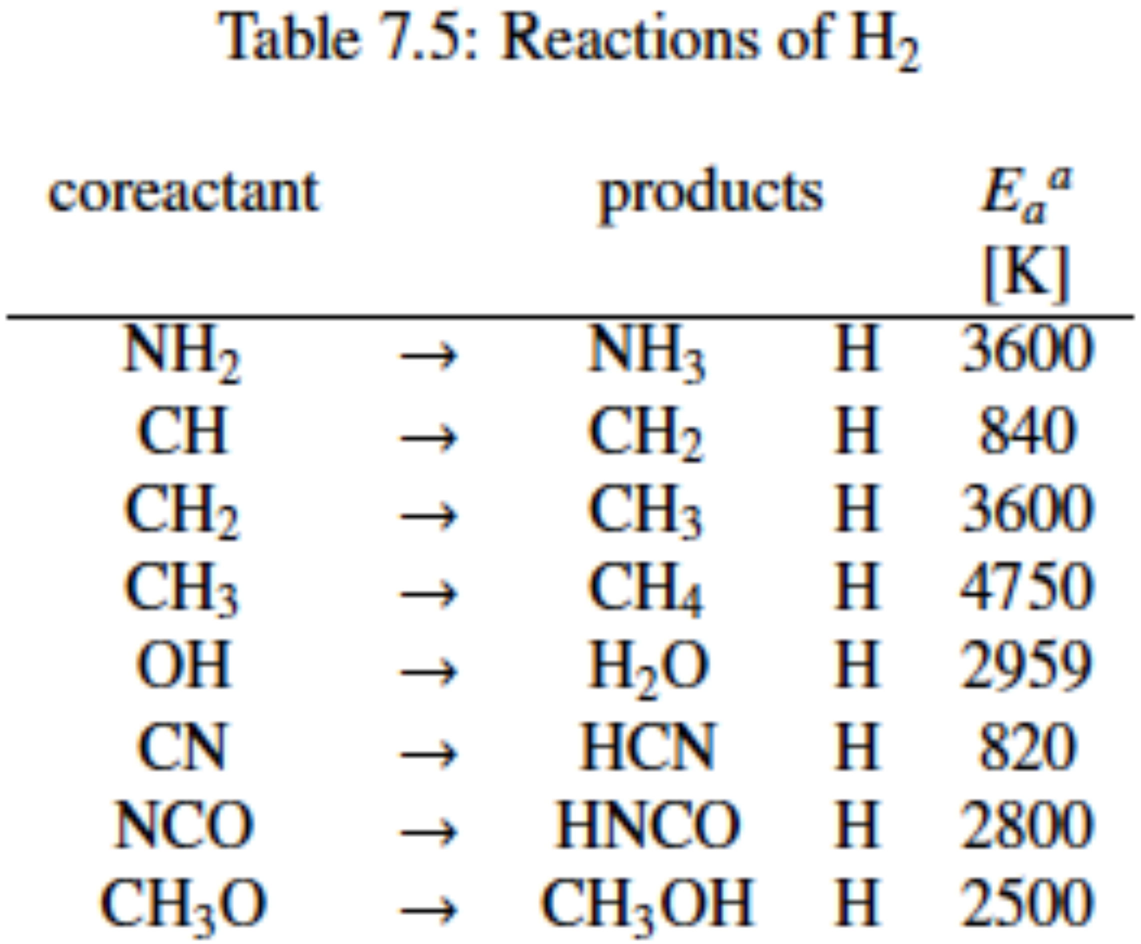


Table 7.5: Reactions of H_2

coreactant		products		$E_a{}^a$ [K]
NH_2	→	NH_3	H	3600
CH	→	CH_2	H	840
CH_2	→	CH_3	H	3600
CH_3	→	CH_4	H	4750
OH	→	H_2O	H	2959
CN	→	HCN	H	820
NCO	→	HNCO	H	2800
CH_3O	→	CH_3OH	H	2500

Reactions involving atomic O

$$O + O \rightarrow O_2 \quad \text{(radical-radical)}$$

$$O + H \rightarrow OH \quad \text{(radical-radical)}$$

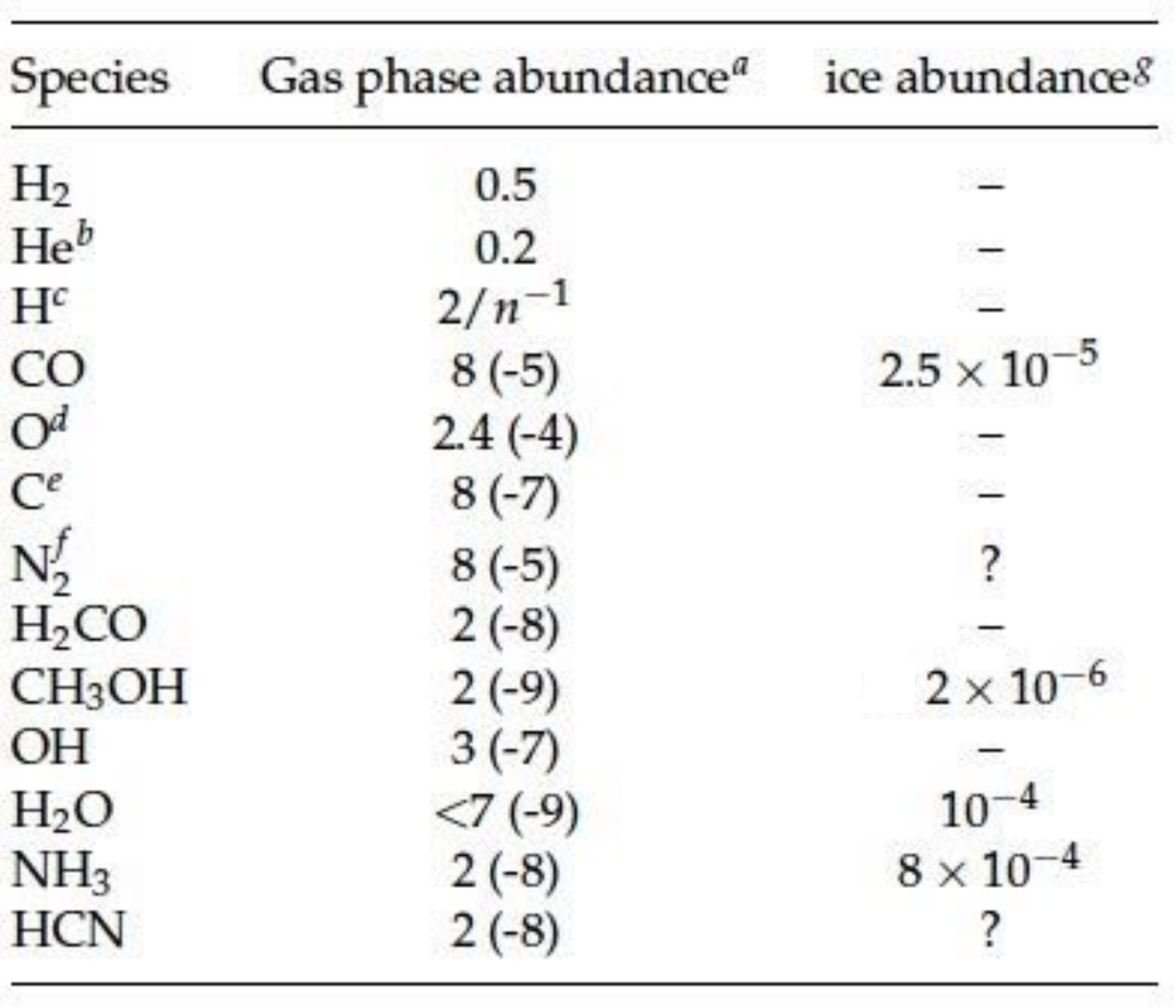
$$O + O_2 \rightarrow O_3 \quad \text{(barrierless)}$$

$$O + CO \rightarrow CO_2 \quad \text{(slow)}$$

$$O + SO \rightarrow SO_2 \quad (?)$$

$$O + CS \rightarrow OCS \quad (?)$$

Composition of Gas Phase

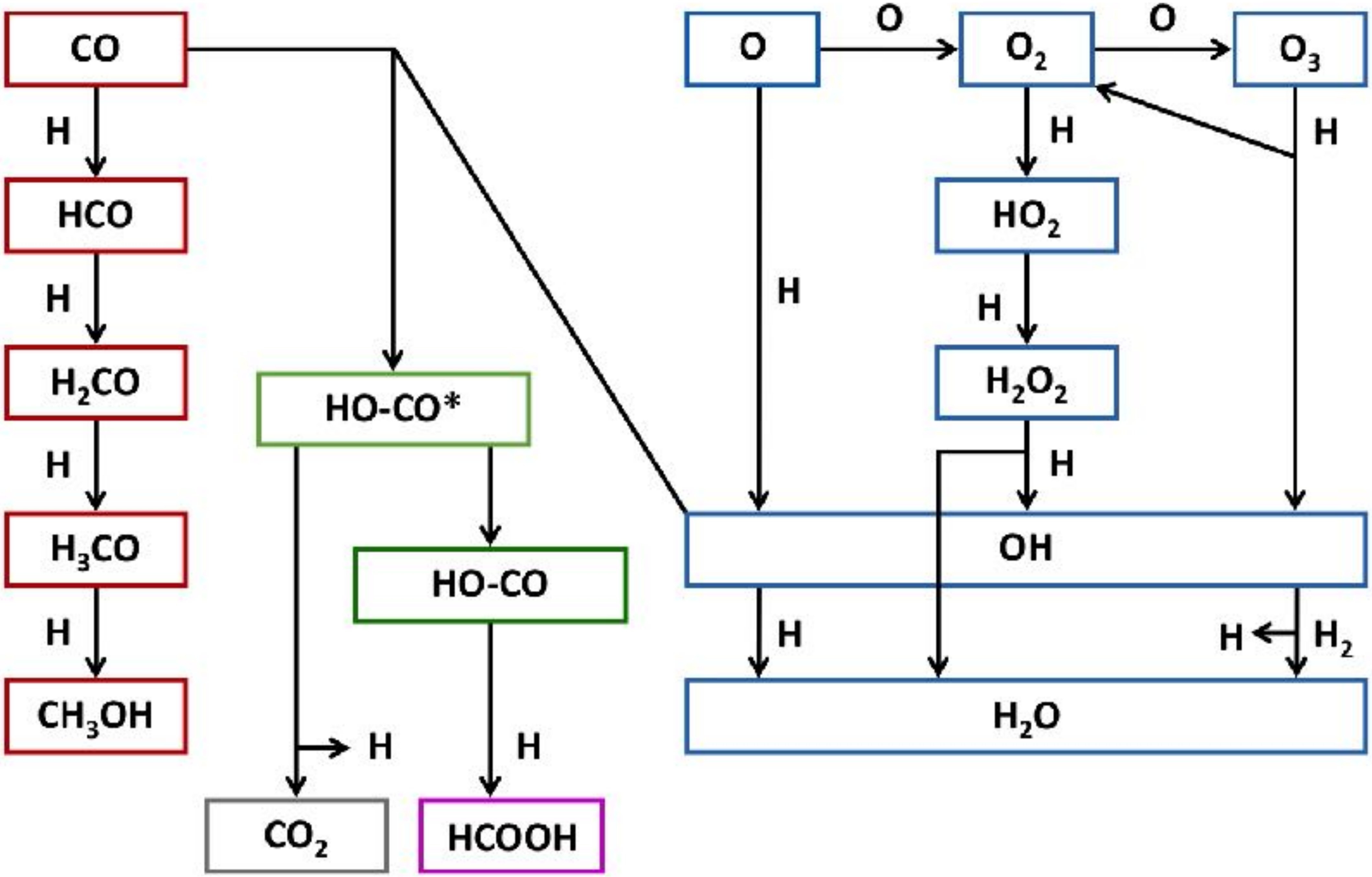


Species	Gas phase abundance[a]	ice abundance[g]
H_2	0.5	–
He[b]	0.2	–
H[c]	$2/n^{-1}$	–
CO	8 (-5)	2.5×10^{-5}
O[d]	2.4 (-4)	–
C[e]	8 (-7)	–
N_2[f]	8 (-5)	?
H_2CO	2 (-8)	–
CH_3OH	2 (-9)	2×10^{-6}
OH	3 (-7)	–
H_2O	<7 (-9)	10^{-4}
NH_3	2 (-8)	8×10^{-4}
HCN	2 (-8)	?

Rules of Engagement

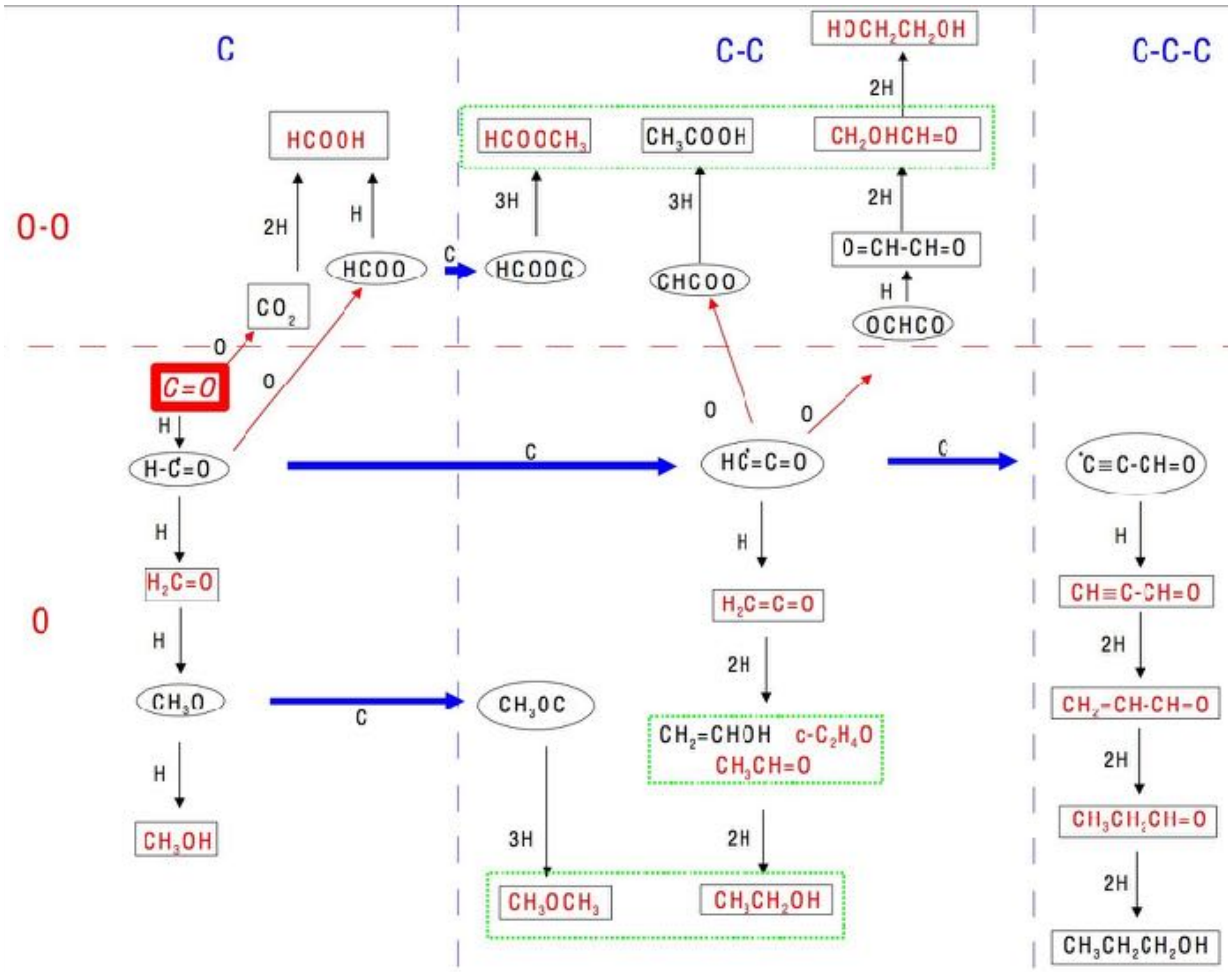
- Diffusion limit (limited by the rate at which species can be brought to the surface)
- At most 1 highly mobile species (H, D) present on any grain surface but lots of H_2.
- Hydrogenation reactions are highly favored. If no coreactant, H/D will evaporate (unlikely as H/D can react with CO, H_2CO, …).
- C,N & O can scan part of the surface and react with radicals and potentially abundant species (e.g., CO)
- atomic C and N are not very abundant and formation of large molecules is inhibited.
- Immobile species (e.g., CO) will have to wait for roaming atoms and if that takes too long, they will get buried ($\tau_{bur} = 10^4$ yr)
- Newly formed radicals may "hop" around (Harris-Kasemo) and find a coreactant ($OH + CO \text{—>} CO_2 + H$)

Surface Reaction Network



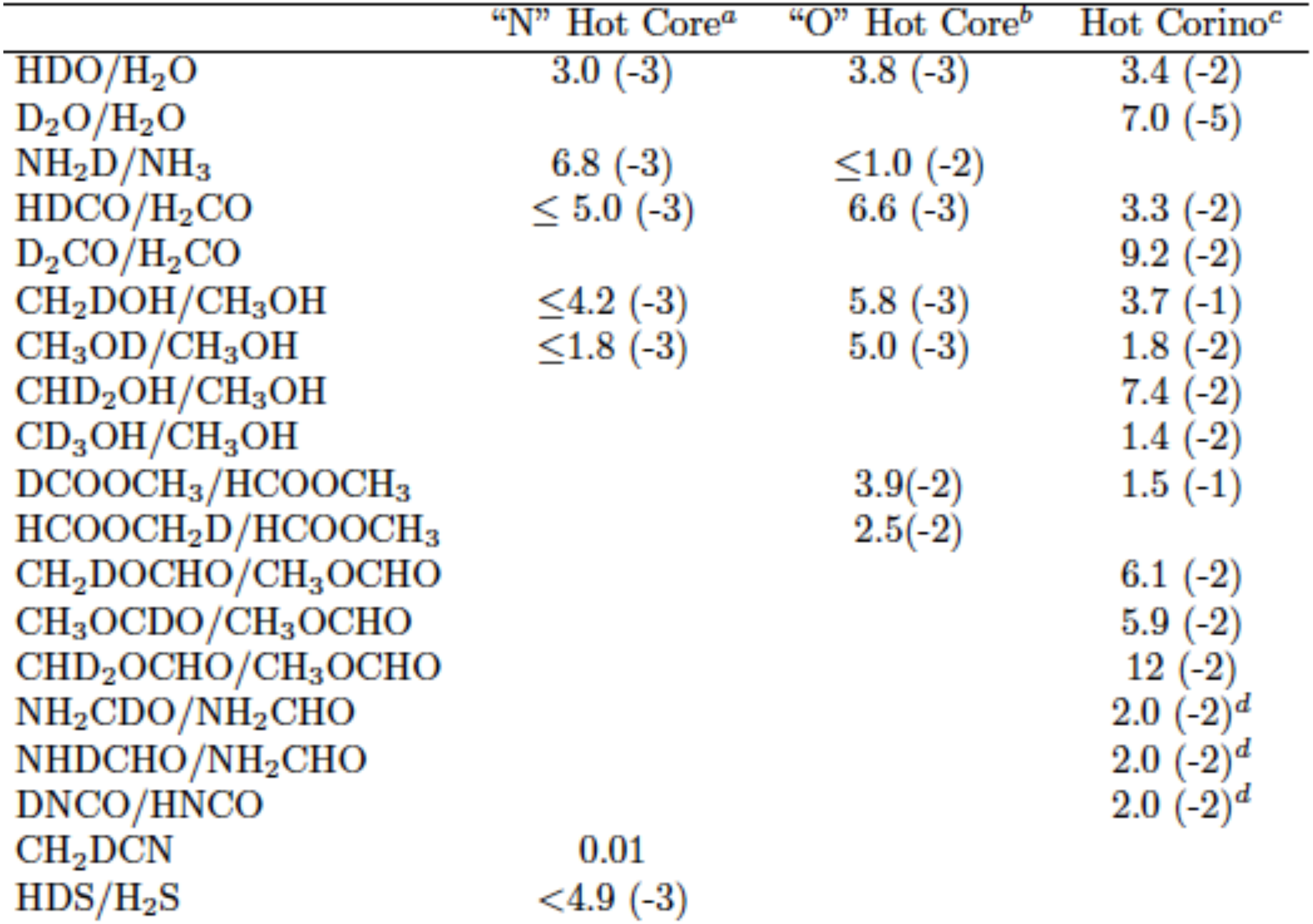
Tielens & Hagen 1982, A&A, 114, 245
Ioppolo et al, 2008, ApJ, 686, 1474

Building up complex species



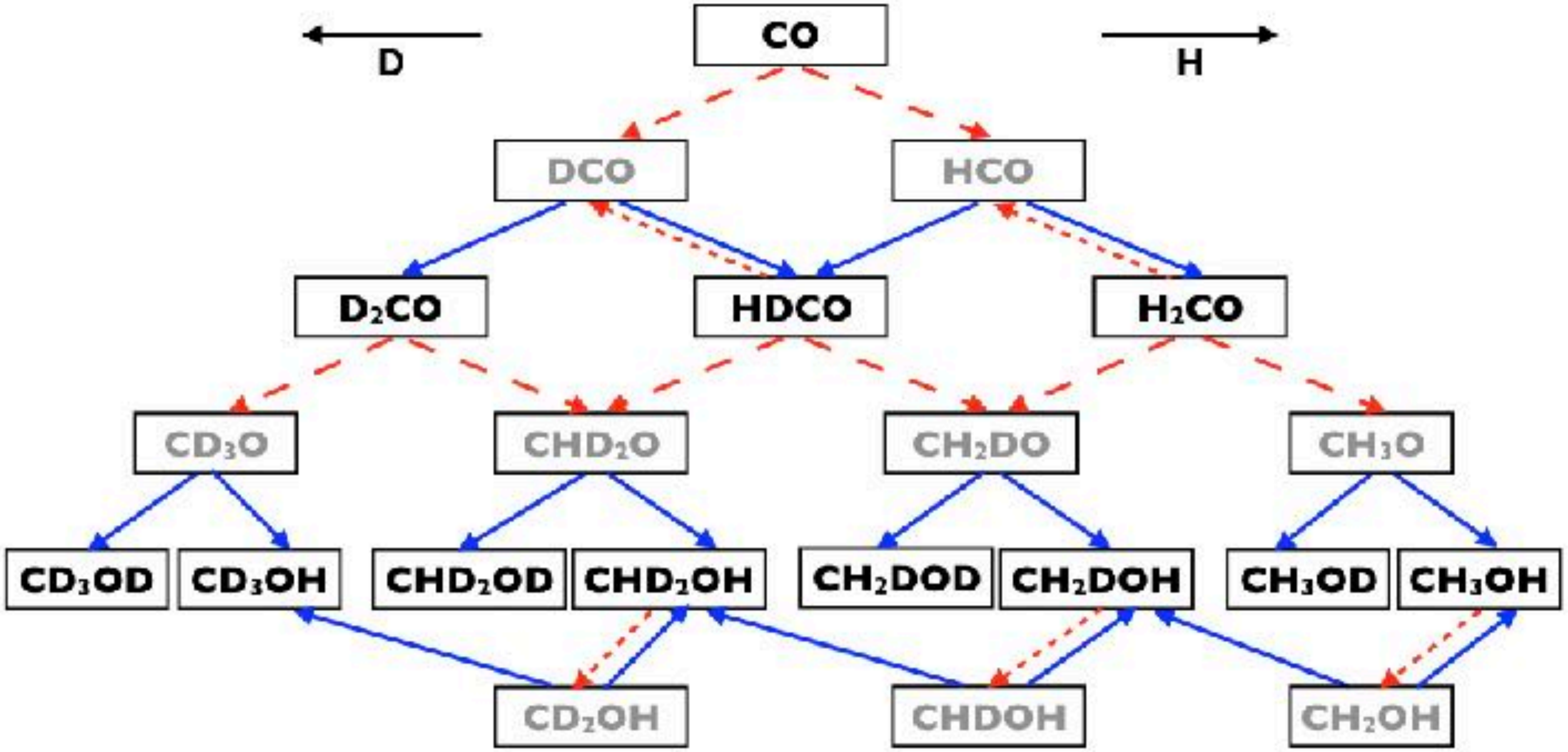
CO is “inert” in the gas phase but readily “activated on a grain surface. Can we build more complex species ? Accretion of C is slow

Deuterium Fractionation



	"N" Hot Core[a]	"O" Hot Core[b]	Hot Corino[c]
HDO/H_2O	3.0 (-3)	3.8 (-3)	3.4 (-2)
D_2O/H_2O			7.0 (-5)
NH_2D/NH_3	6.8 (-3)	$\leq$1.0 (-2)	
$HDCO/H_2CO$	$\leq$ 5.0 (-3)	6.6 (-3)	3.3 (-2)
D_2CO/H_2CO			9.2 (-2)
CH_2DOH/CH_3OH	$\leq$4.2 (-3)	5.8 (-3)	3.7 (-1)
CH_3OD/CH_3OH	$\leq$1.8 (-3)	5.0 (-3)	1.8 (-2)
CHD_2OH/CH_3OH			7.4 (-2)
CD_3OH/CH_3OH			1.4 (-2)
$DCOOCH_3/HCOOCH_3$		3.9(-2)	1.5 (-1)
$HCOOCH_2D/HCOOCH_3$		2.5(-2)	
CH_2DOCHO/CH_3OCHO			6.1 (-2)
CH_3OCDO/CH_3OCHO			5.9 (-2)
CHD_2OCHO/CH_3OCHO			12 (-2)
NH_2CDO/NH_2CHO			2.0 (-2)[d]
$NHDCHO/NH_2CHO$			2.0 (-2)[d]
$DNCO/HNCO$			2.0 (-2)[d]
CH_2DCN	0.01		
HDS/H_2S	<4.9 (-3)		

Deuterium Chemistry


D
CO
H
DCO HCO
D_2CO $HDCO$ H_2CO
CD_3O CHD_2O CH_2DO CH_3O
CD_3OD CD_3OH CHD_2OD CHD_2OH CH_2DOD CH_2DOH CH_3OD CH_3OH
CD_2OH $CHDOH$ CH_2OH

- High deuteration:
- atomic D/H in accreted gas is high (e.g., $DCO^+/HCO^+ >> A_D$)
- HD/H_2 ratio on grains is high
- H-abstraction, D-addition (only on CH_n not with OH)

- HDO/CH_3OD controlled by HD/H_2
- H-D exchange on OH group in H-bonded system (at “high” temperatures)

Tielens 1983, A&A, 119, 177
Charnley et al, 1997, ApJ, 482, L203
Watanabe & Kouchi 2008, Prog Surf Sci, 83, 439
Hidaka et al 2009, ApJ, 702, 291
Nagaoka et al 2007, J Phys Chem A, 111, 3016
Souda et al 2003, J Chem Phys, 119, 6194
Souda et al 2004, Phys Rev Lett, 93, 235502
Ratajczak et al 2009, A&A, 496, L21

Ejection

Thermal Desorption

Sublimation set by binding energy but remember long timescales in space

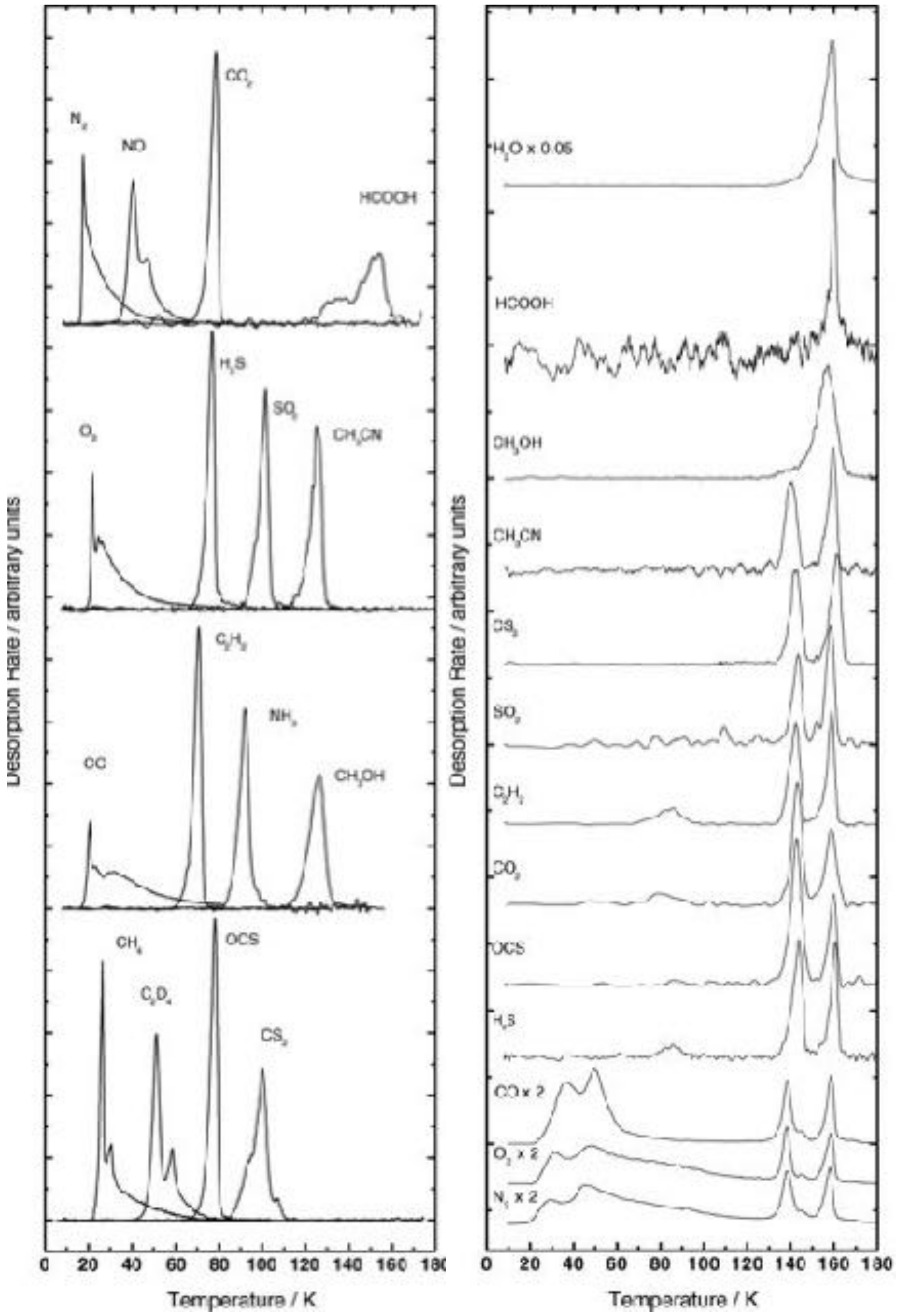
Sublimation temperature pure ices. T_{sub}: $CO/N_2/O_2 < CO_2 < NH_3 < H_2O/CH_3OH$

Mixed ices: multiple peaks as trace species can be encapsulated

1) Pure ice temperature

2) Volcano desorption when amorphous H_2O ice crystalizes

3) At $T_{sub}(H_2O)$: clathrate species



Photodesorption

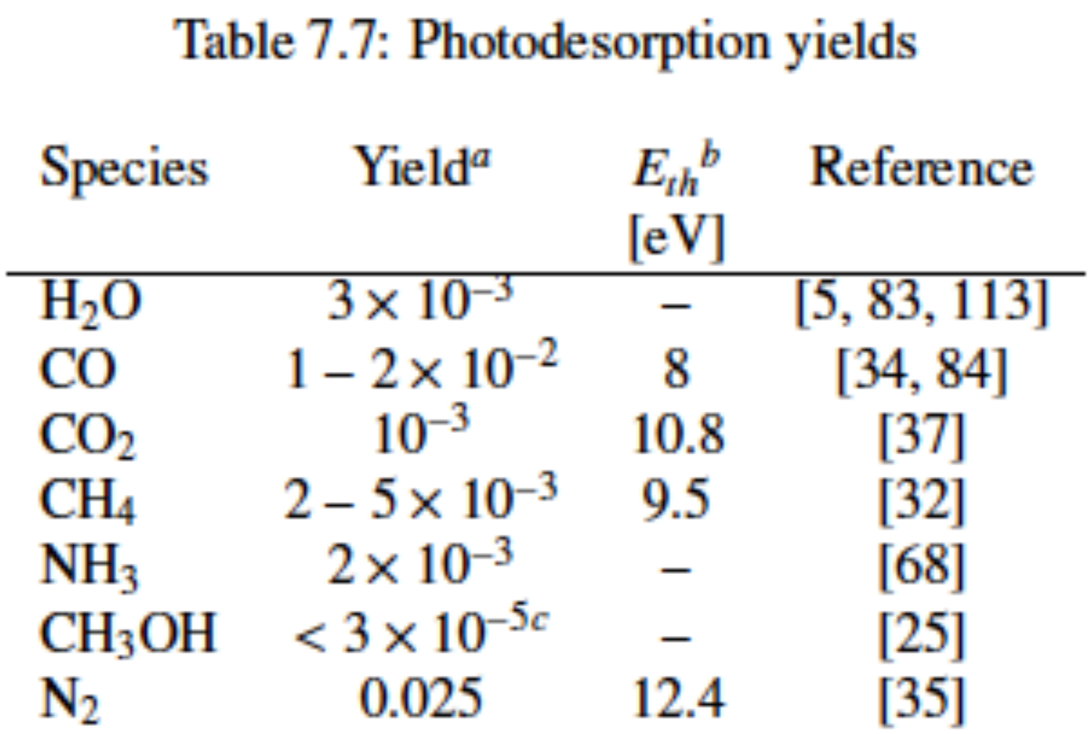
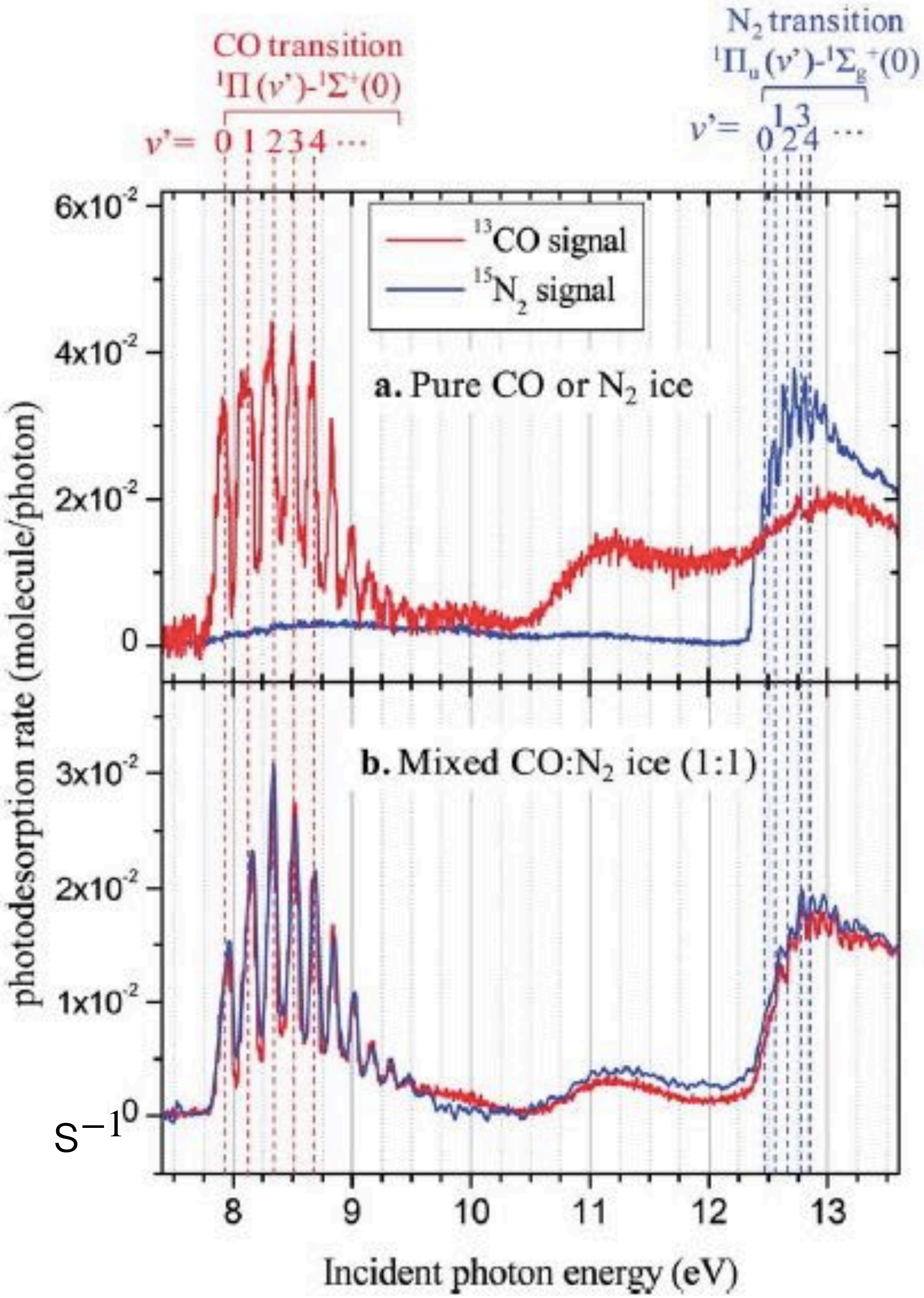


Table 7.7: Photodesorption yields

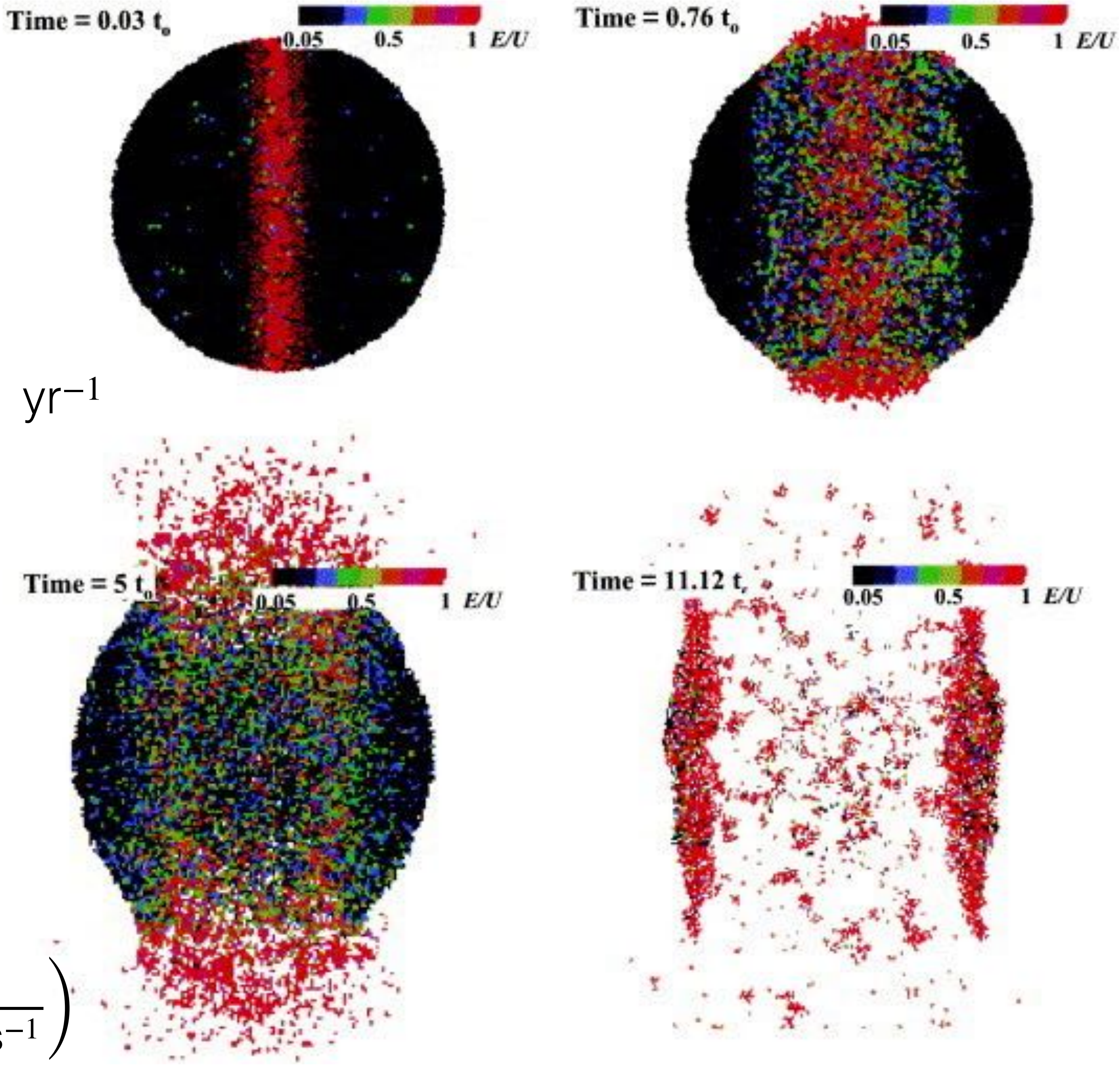
Species	Yield^a	$E_{th}{}^b$ [eV]	Reference
H_2O	3×10^{-3}	–	[5, 83, 113]
CO	$1-2\times10^{-2}$	8	[34, 84]
CO_2	10^{-3}	10.8	[37]
CH_4	$2-5\times10^{-3}$	9.5	[32]
NH_3	2×10^{-3}	–	[68]
CH_3OH	$<3\times10^{-5c}$	–	[25]
N_2	0.025	12.4	[35]

$$k_{pd} = \mathcal{N}_{uv}\,\pi a^2\,Y_i\,\theta_i \simeq 3\times10^{-11}\left(\frac{Y_i}{10^{-3}}\right)\left(\frac{\theta_i}{10^{-1}}\right)\,\mathrm{s}^{-1}$$

$$X(\mathrm{H_2O}) = 10^{-7}\left(\frac{10^4\,\mathrm{cm}^{-3}}{n}\right)\left(\frac{\zeta_{CR}}{3\times10^{-17}\,\mathrm{s}^{-1}}\right)\left(\frac{Y}{10^{-3}}\right)$$



Cosmic Rays



$$k_{cr} = 4\pi \mathcal{N}_{cr} \pi a^2 \simeq 10^{-5} \left(\frac{a}{1000\,\text{Å}}\right) \quad \text{yr}^{-1}$$

$$X\left(\text{H}_2\text{O}\right) = 6 \times 10^{-9} \left(\frac{10^4\,\text{cm}^{-3}}{n}\right) \left(\frac{\zeta_{CR}}{3 \times 10^{-17}\,\text{s}^{-1}}\right)$$

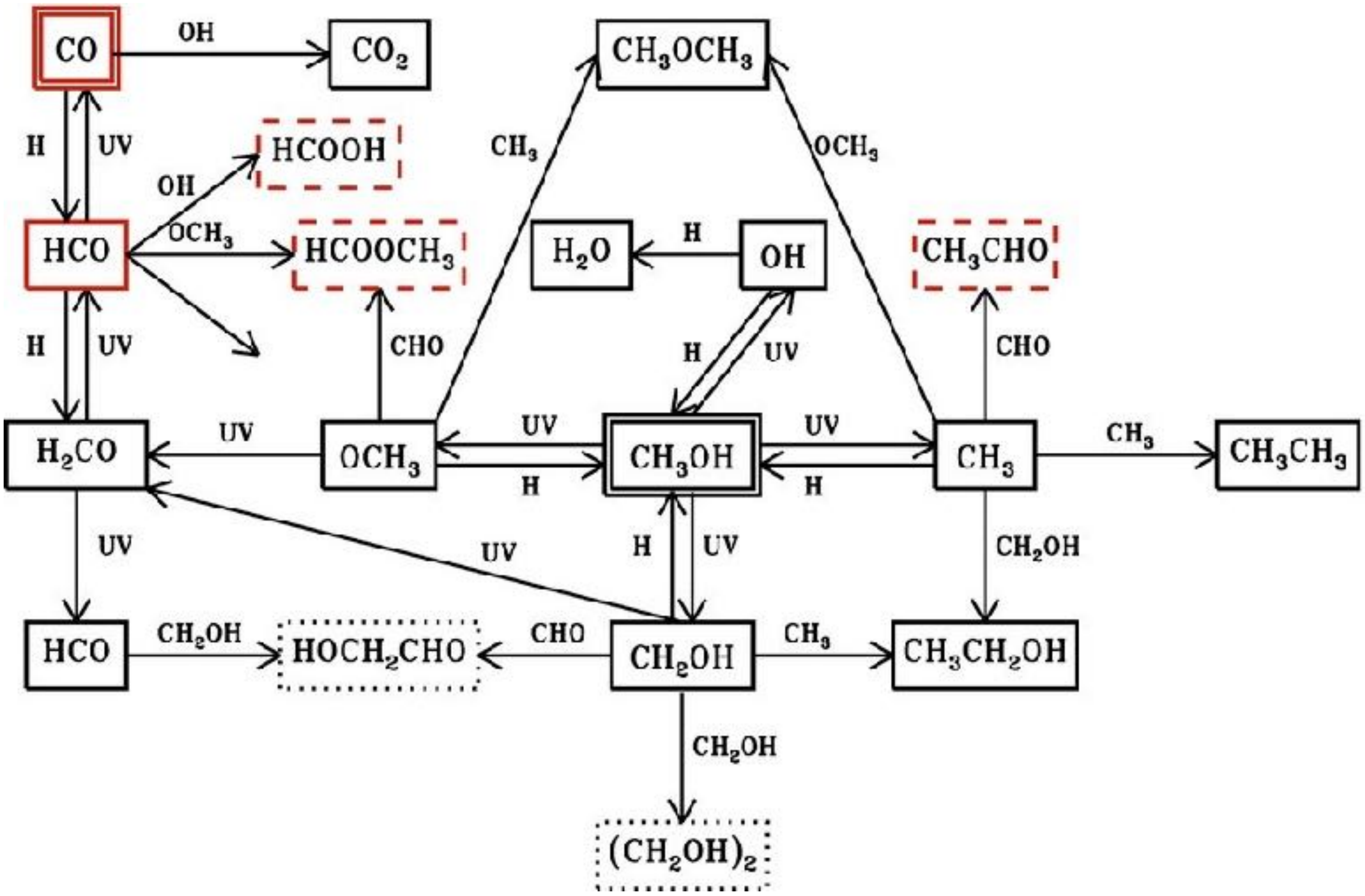
$$X\left(\text{CO}\right) = 3 \times 10^{-6} \left(\frac{10^4\,\text{cm}^{-3}}{n}\right) \left(\frac{\zeta_{CR}}{3 \times 10^{-17}\,\text{s}^{-1}}\right)$$

Ejection upon Formation

Reaction heat may be transferred to surface bond and cause ejection

$$X\left(\mathrm{H_2O}\right) = 10^{-6}\left(\frac{10^4\,\mathrm{cm}^{-3}}{n}\right)\left(\frac{\zeta_{CR}}{3\times10^{-17}\,\mathrm{s}^{-1}}\right)\left(\frac{f_{ej}}{10^{-3}}\right)$$

f_{ej} is not well known:
Theory (H_2O): $f_{ej} = 10^{-3}$
Experiments (H_2S): $f_{ej} > 10^{-3}$



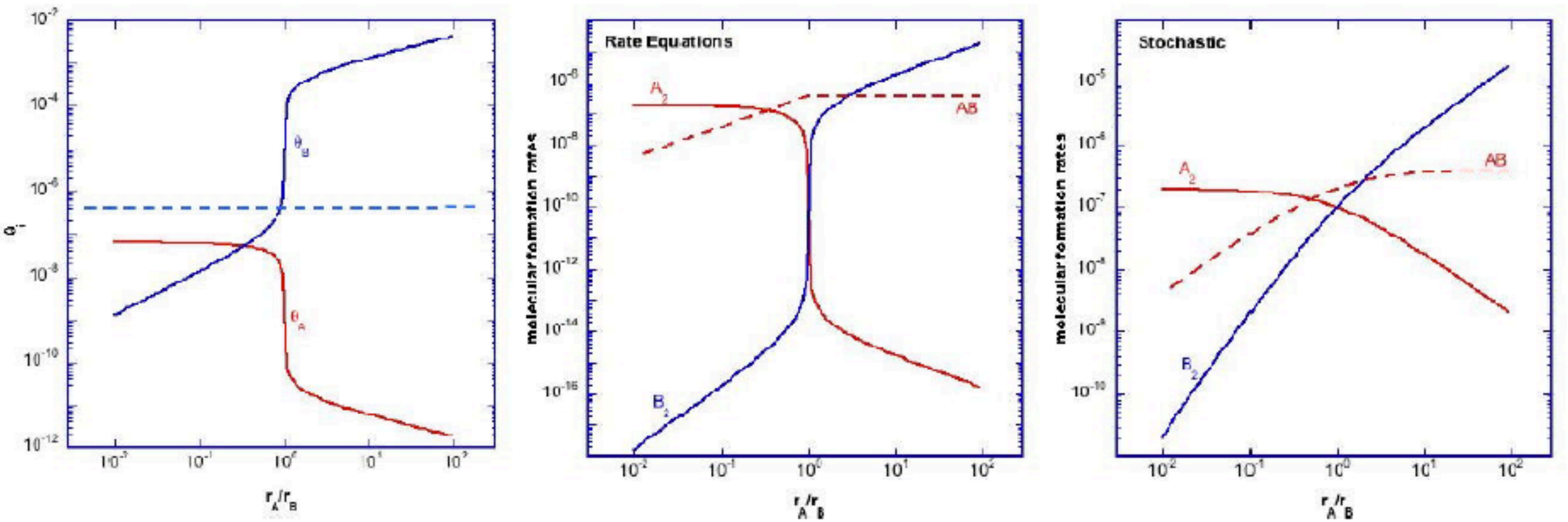
Reaction networks driven by photolysis of interstellar ices

Garrod et al, 2008, ApJ, 682, 283
Oberg et al, 2010, ApJ, 718, 832

Thermal Processing

- Diffusion of stored radicals (produced by UV photolysis), followed by reaction
- Segregation of ice components
- Polymerization reactions: formation of polyoxymethylene and related compounds

Solution methods: need for stochastic approach



Cannot blindly use rate equation approaches:
Concentration of mobile species is either 0 or 1, never 2.

Consider system consisting of A & B that accrete and can form A_2, B_2, and AB.

Stochastic Nature of Surface Chemistry

Rate Equations: $\frac{dn_i}{dt} = -n_i \sum_j n_j k_{ij} + \sum_{j,l} n_{jl} k_{jl} - n_i k_{ev} n_i + k_{ac} n_i^{gas}$

For simplicity, consider only reactions without activation barriers

(e.g., k's are migration rates). Say, H_2 formation:

$$R\left(\mathrm{H}_2\right) = \frac{1}{2} k_m n_{\mathrm{H}}^2$$

In reality, we have to evaluate the probability to have m species H present

$$\frac{dP_m\left(\mathrm{H}\right)}{dt} = k_{ac}\left(\mathrm{H}\right)\left[P_{m-1}\left(\mathrm{H}\right) - P_m\left(\mathrm{H}\right)\right] - k_{ev}\left(\mathrm{H}\right)\left[mP_m\left(\mathrm{H}\right) - \left(m+1\right)P_{m+1}\left(\mathrm{H}\right)\right]$$

$$\frac{1}{2} k_H \left[\left(m+2\right)\left(m+1\right)P_{m+2}\left(\mathrm{H}\right) - m\left(m-1\right)P_m\left(\mathrm{H}\right)\right]$$

$$\left\langle n_{\mathrm{H}} \right\rangle = \sum_{m=1}^{\infty} mP_m\left(\mathrm{H}\right), \quad \left\langle n_{\mathrm{H}}^2 \right\rangle = \sum_{m=1}^{\infty} m^2 P_m\left(\mathrm{H}\right), \quad \sigma_{\mathrm{H}}^2 = \left\langle n_{\mathrm{H}}^2 \right\rangle - \left\langle n_{\mathrm{H}} \right\rangle^2$$

$$R\left(\mathrm{H}_2\right) = \frac{dN\left(\mathrm{H}_2\right)}{dt} = k_{\mathrm{H}} \left\langle n_{\mathrm{H}}\left(n_{\mathrm{H}} - 1\right)\right\rangle \approx k_{\mathrm{H}} \left\langle n_{\mathrm{H}}^2 \right\rangle \approx k_{\mathrm{H}} \left\langle n_{\mathrm{H}} \right\rangle^2, \text{ only if } n_{\mathrm{H}} \gg 1$$

Surface Chemistry Methods

method	advantage	disadvantage
Rate Equations	Easy to integrate with gas phase chemistry	Incorrect when fluctuations are large Semi-empirical correction factors have to be validated every time
Monte Carlo	Correct in stochastic limit Versatile: can include many characteristics of the surface	Difficult to combine with gas phase chemistry Time-consuming
Master equation	Correct in stochastic limit Can evolve grains surface chemistry and gas phase chemistry simultaneously	Very time consuming for all but the simplest systems
Moments equation	Correct in stochastic limit	Need to truncate the moments Very time consuming
Hybrid approaches	Master equation approach for mobile species Rate equations for immobile species	

Grain Surface Chemistry: In a Nutshell

- Dust grains are the “watering holes” of astrochemistry where species come to meet and mate.
- In a way, collisions on a grain surface can take very long (up to hours or days)
- Tunneling is key to hydrogenation (and deuteration)
- Initial conditions play a key role
  - O goes to H_2O through e.g., O_2 and O_3
  - C (e.g., CO) goes to H_2CO and CH_3OH
  - N goes to NH_3 while N_2 is inert
  - S goes to SO/SO2 and CS goes to OCS (?)
  - D enrichment is driven by high D/H (gas) and high HD/H_2 on the grain

Exercises

- Calculate the H_2 binding energy and surface coverage at 20 K (see slide 7).

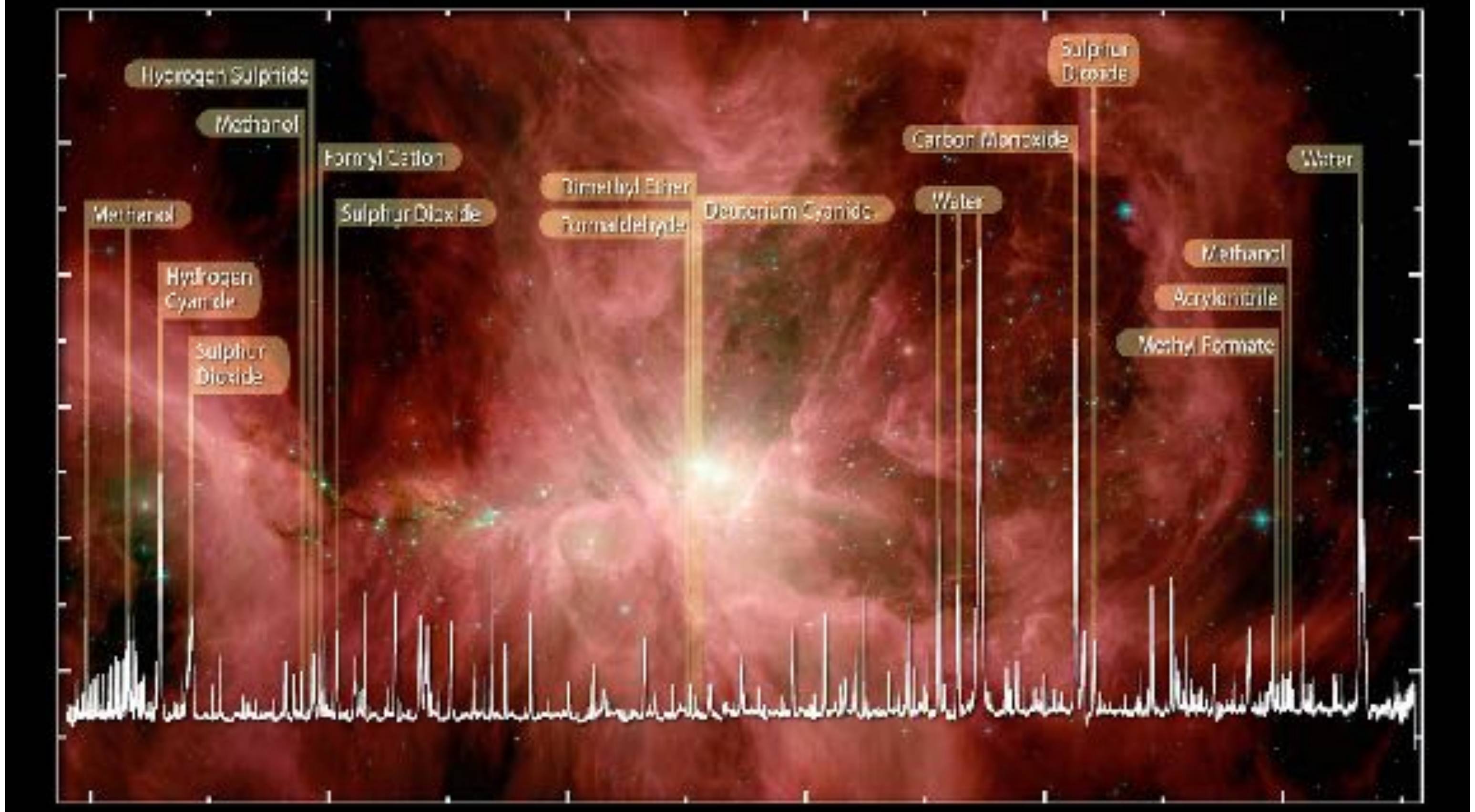
- If the diffusion barrier is 30% of the binding energy, calculate the timescale to scan the whole surface for H at 10K and compare graphically with the accretion time and evaporation timescale as a function of grain size. Do the same for atomic O.

- If the reaction barrier for H with CO is 1000 K and for H with H_2CO is 1200 K, calculate the relative probabilities for CO and H_2CO to react with H. Why could CH_3OH still be the dominant reservoir of carbon in interstellar ice ?

SOM in Hot Cores/Corinos

Simple Organic Molecules ("SOM")

- Warm dense gas with rich organic inventory: of relatively simple organic molecules
  - CH_3OH, CH_3CH_2OH, CH_3OCH_3, H_2CO, CH_3CHO, $HCOOH$, NH_2CHO, ...
  - HCN, CH_3CN, CH_3CH_2CN, ...
- Large deuterium fractionations
- Driven by evaporation of ice mantles formed in cold phase



HIFI Spectrum of Water and Organics in the Orion Nebula

© ESA, HEXOS and the HIFI consortium
E. Bergin

Blake et al, 1987, ApJ, 315, 621
Ceccarelli et al, 2007, PPV, 47
Bergin et al 2010, A&A, 521, L20

Origin of “SOM”

Deuterium fractionation implies formed from cold-reservoir-progenitors

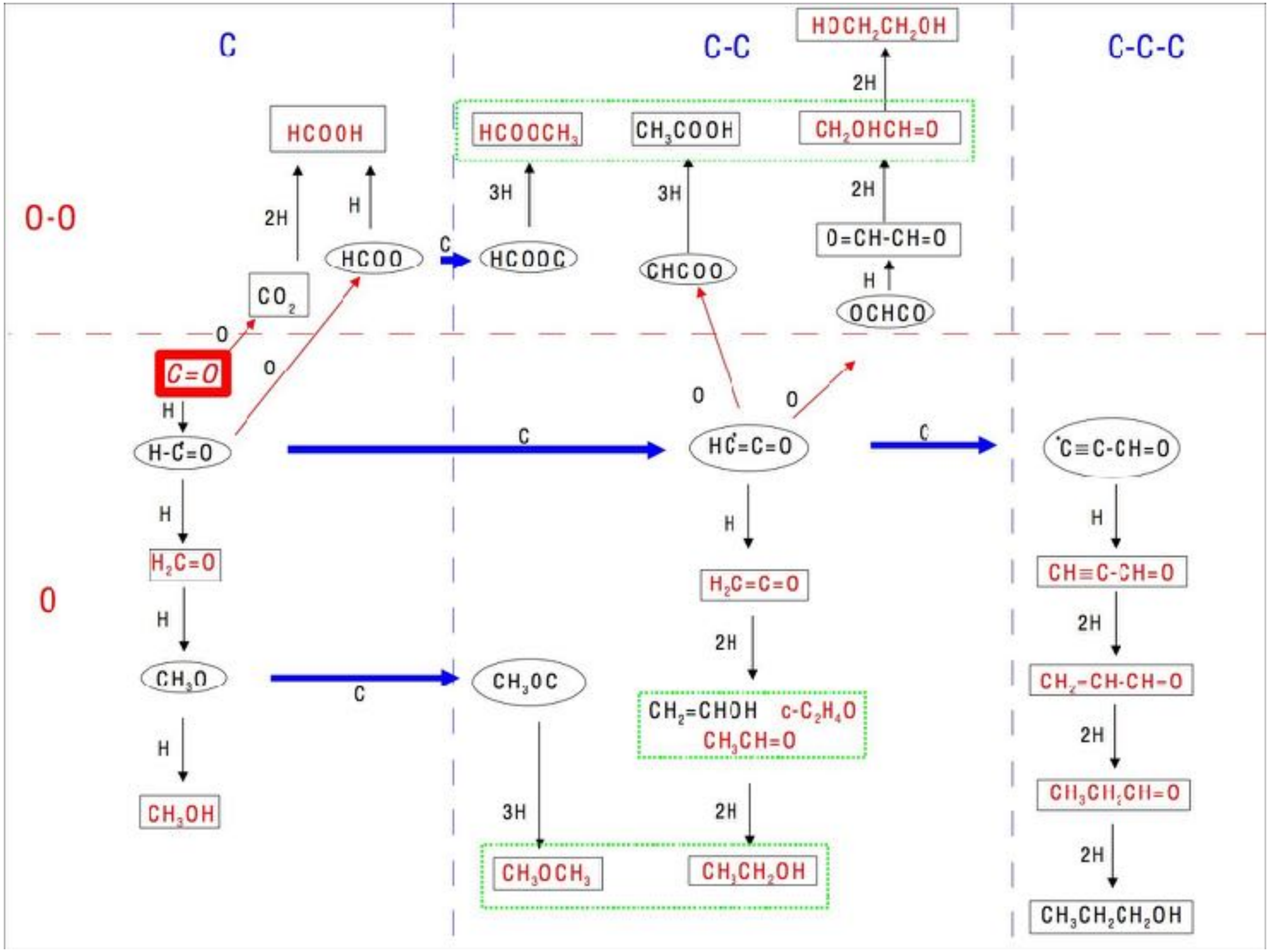
- Surface chemistry in cold regions
- Photolysis of ices
- Evaporation followed by gas phase reactions
- Ion molecule chemistry in ices

Gas phase chemistry: Charnley et al 1992, ApJ, 399, L71, Caselli et al, 1993, ApJ, 408, 538; Geppert et al, Faraday discussions, 133, 177, Horn et al, 2004, ApJ, 611, 605

Grain surface chemistry: Charnley & Rodgers 2007 Bioastronomy

Charged ices: Bouwman et al, 2011, A&A, 529, 46; Schutte et al, 2003, 398, 1049; Demyk et al, 1998, A&A, 339, 553, Balog et al 2009, Phys Rev Lett, 201, 73003

Photolyzed ices: Garrod et al, 2008, ApJ, 682, 283; Oberg et al, 2010, ApJ, 718, 832

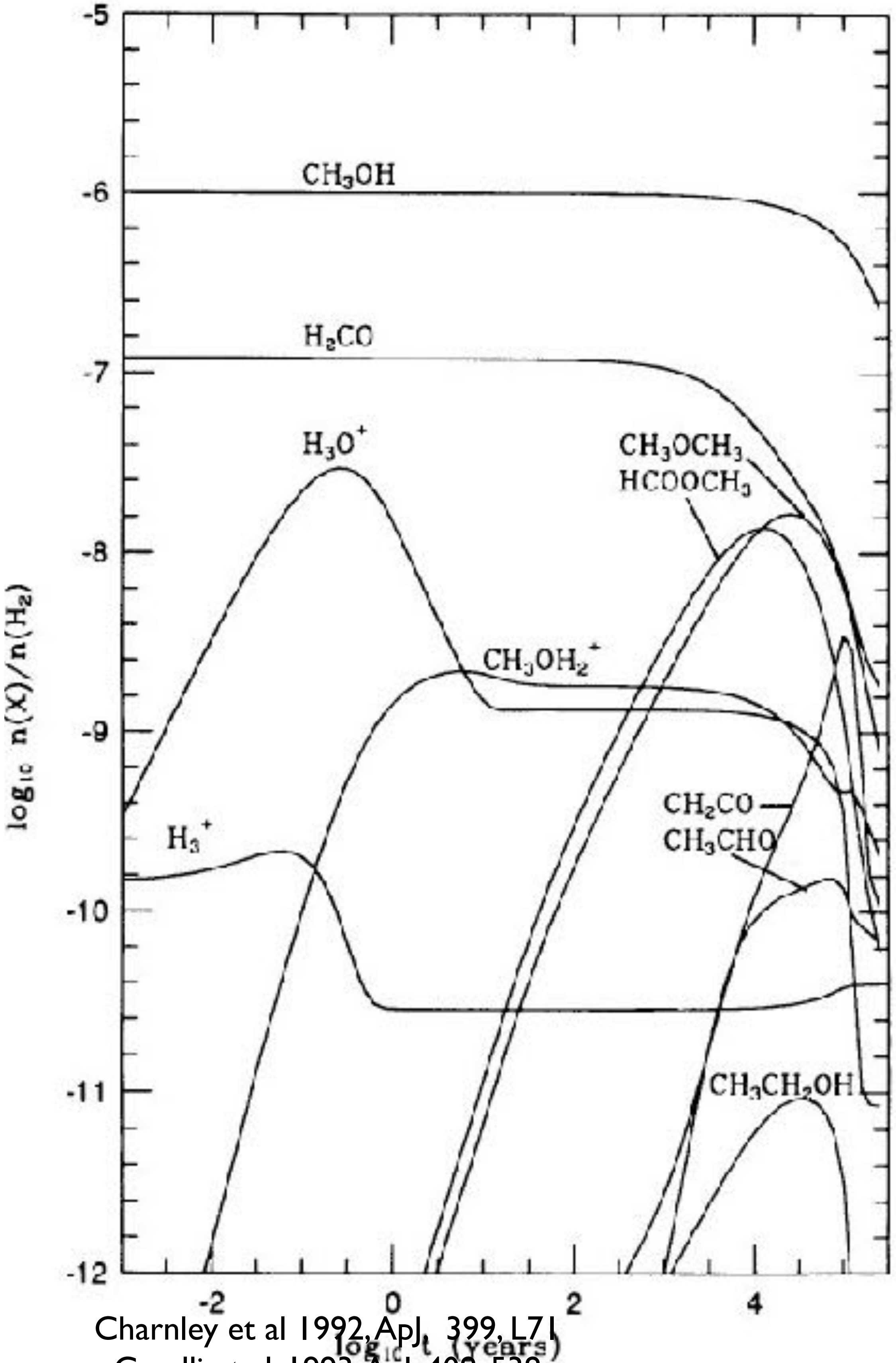


Building up complex species

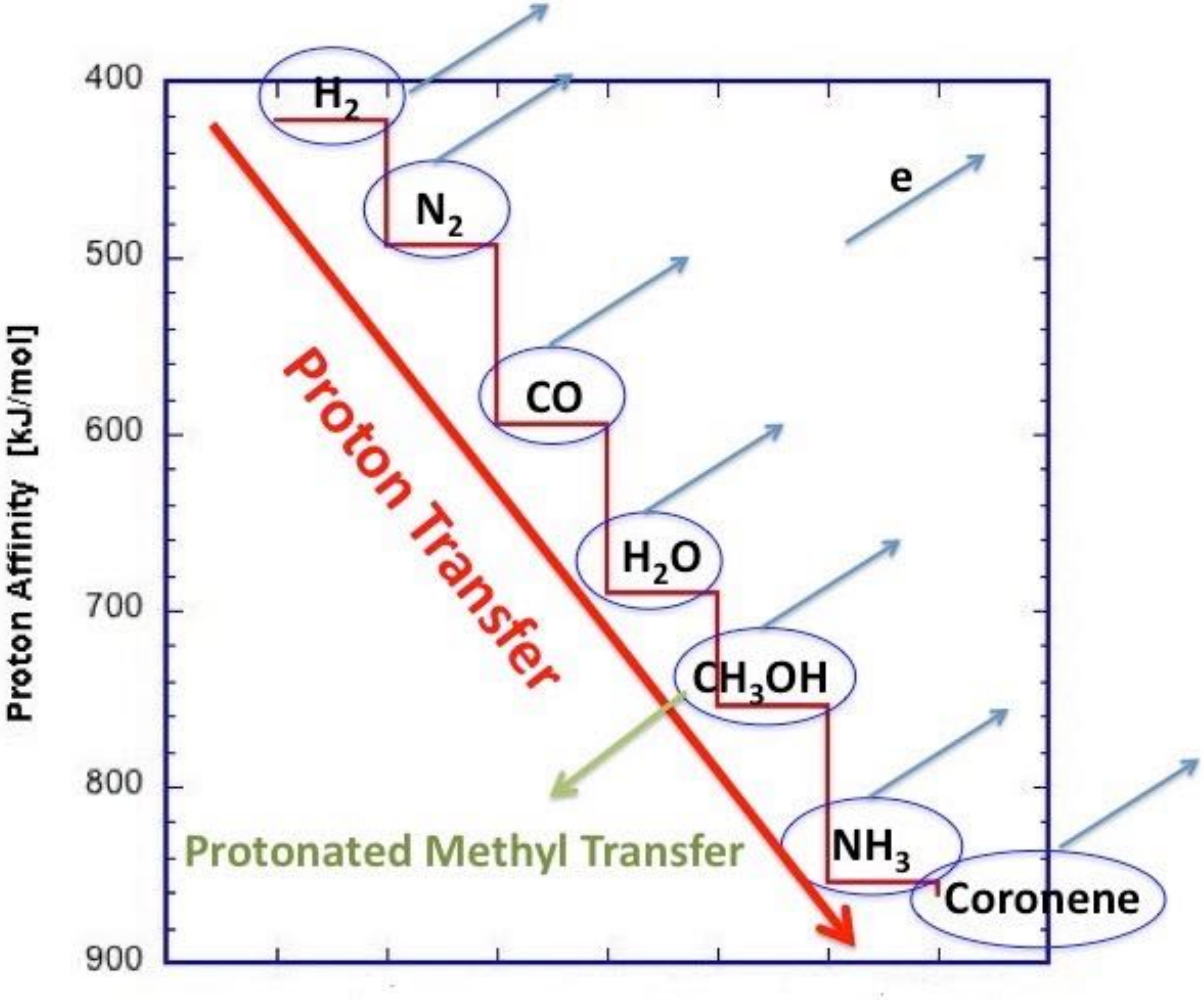
But C/CO=10^{-2} (CR-induced photon field dissociates CO)

Evaporating Ices

- Evaporating ice molecules drive rich chemistry
- Protonated methanol & methyl transfer
- Issues:
    - Experimental studies disagree
        - formation of intermediaries inhibited
        - Recombination leads to fragmentation
        - Ammonia may “save” the day as a proton scavenger
    - Chemical clock ~3x10^4 yr incompatible with hot corinos

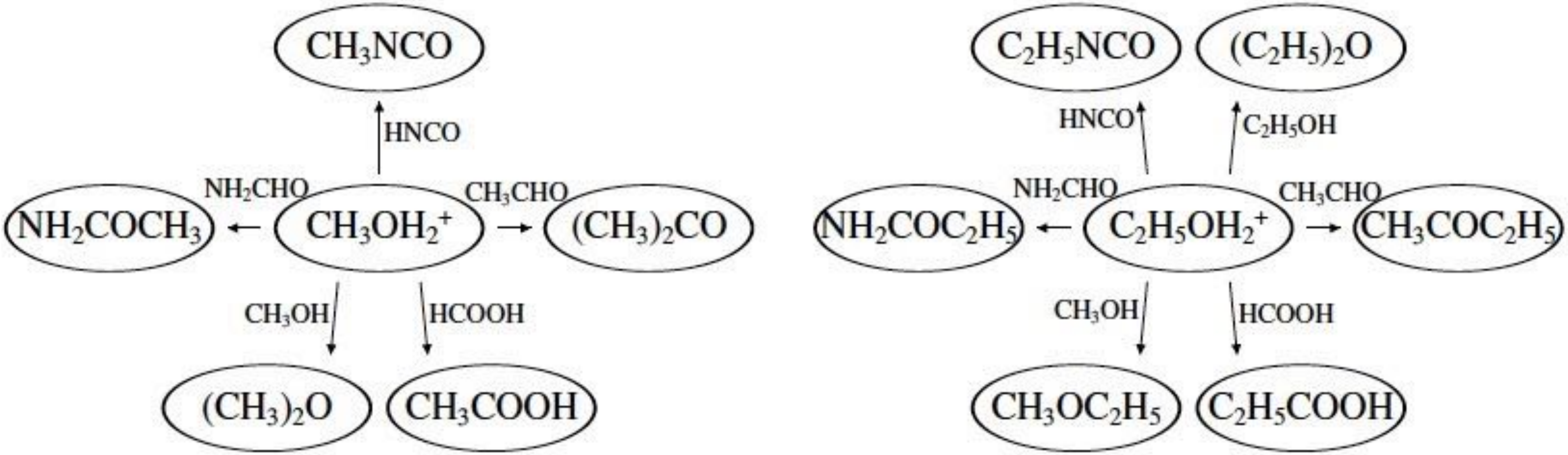


Charnley et al 1992, ApJ, 399, L71
Caselli et al, 1993, ApJ, 408, 538
Geppert et al, Faraday discussions, 133, 177
Horn et al, 2004, ApJ, 611, 605



Proton Transfer

$$X_i = \frac{k_e X_e}{k_i} \simeq 10^{-5}\left(\frac{X_e}{10^{-8}}\right)$$



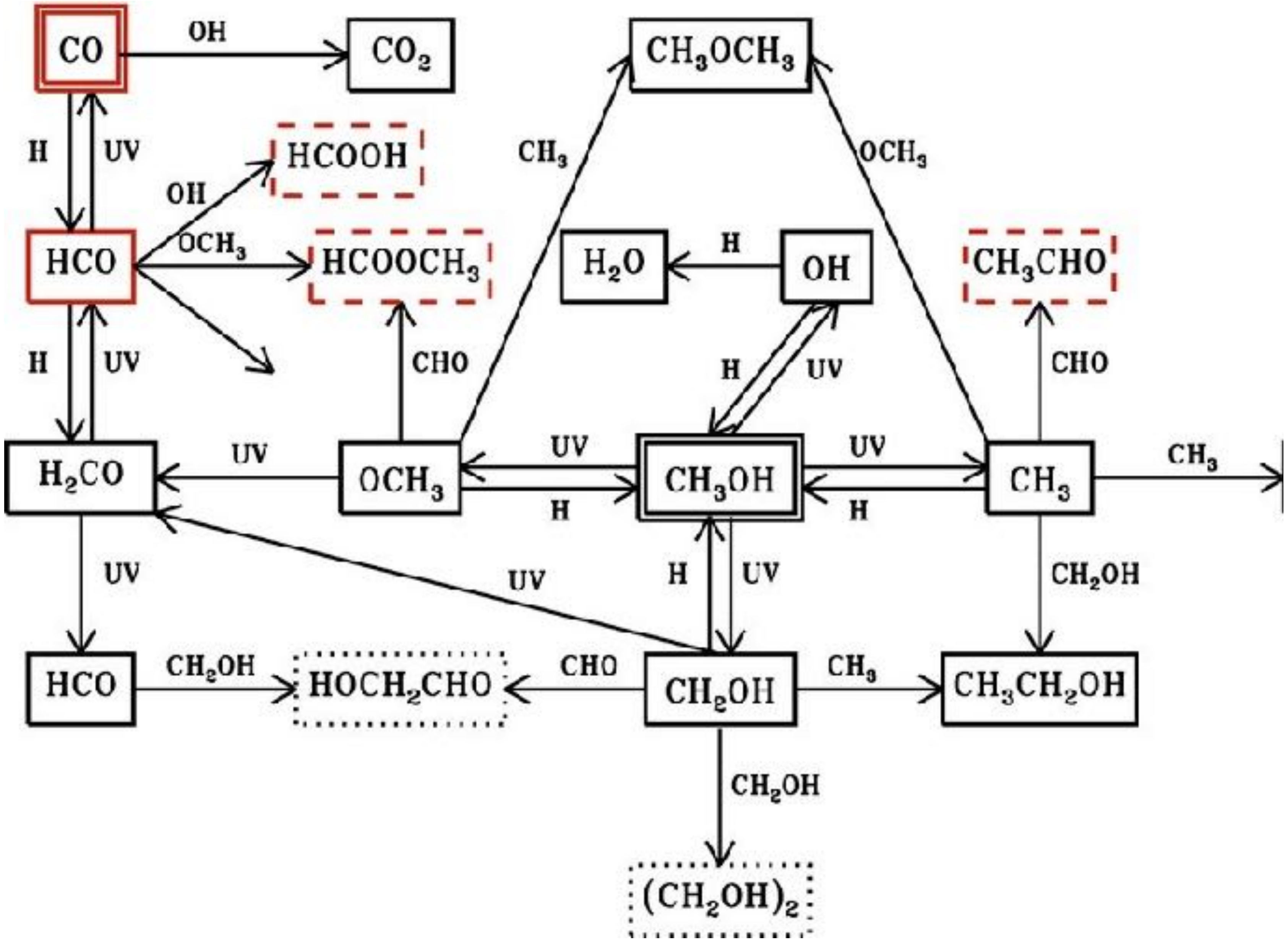
Alkyl Transfer from Alcohols

Charnley et al 1992, ApJ, 399, L71

Photolyzed Ices

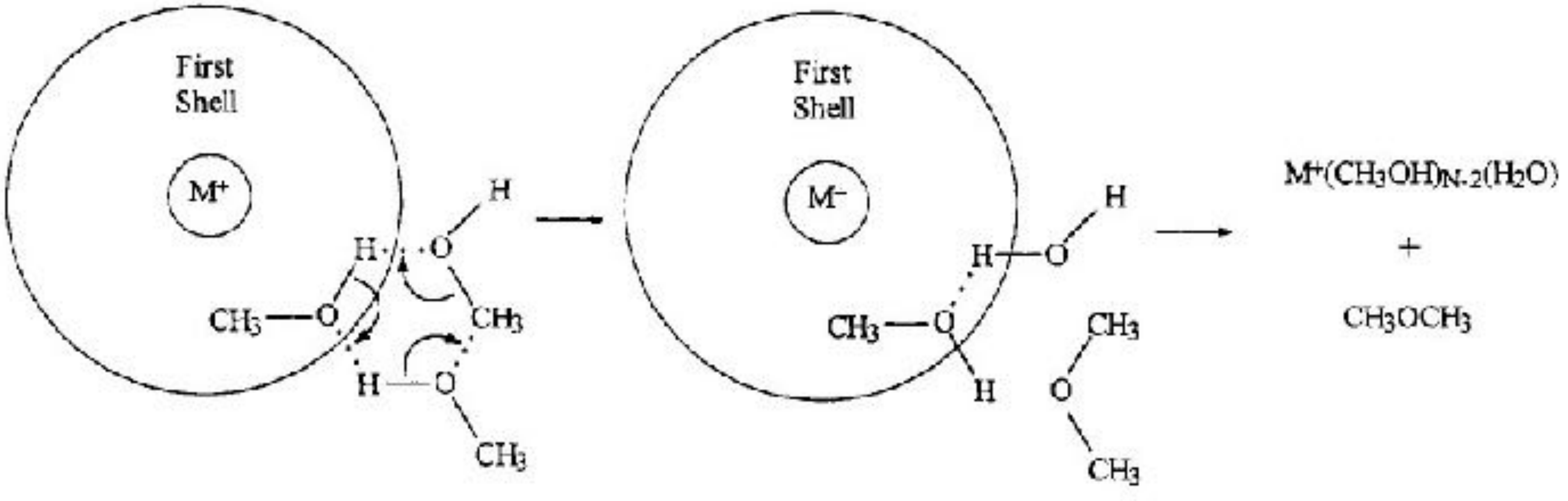
UV photolysis/ion bombardment & warm up

- Radical production (CH_3 & others)
- Recombination
- Issues:
  - Chemical specificity
  - Polymerization



Garrod et al, 2008, ApJ, 682, 283
Oberg et al, 2010, ApJ, 718, 832

Charged Ices



Ion-molecule Chemistry in Ices

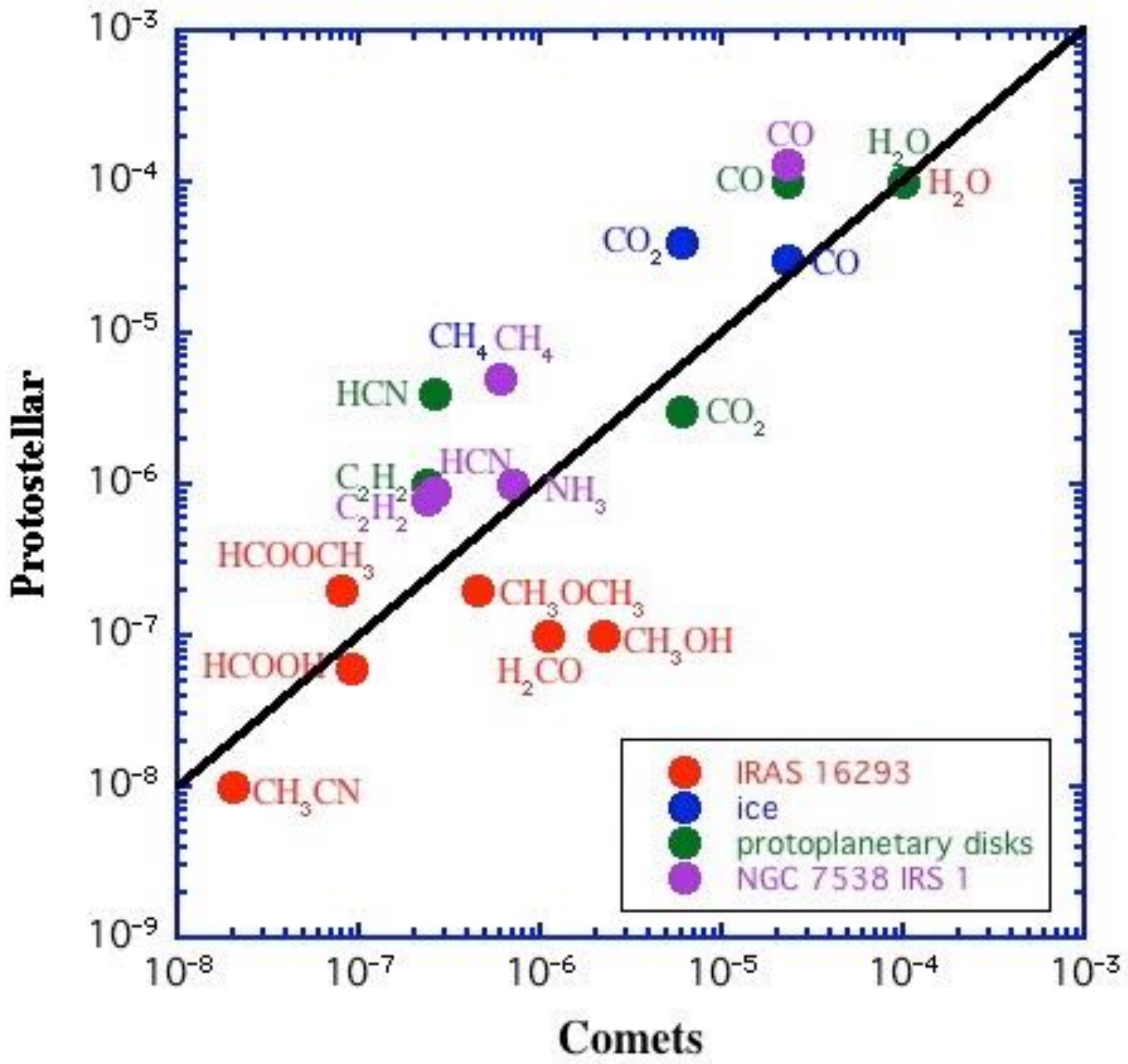
- Ices are charged & charges are localized:
  - Na, PAHs
  - OCN^-
  - Polarization charge
- Warm-up leads to segregation
- H-bonding
- Stereochemistry
- Methanol drives chemistry
- Near evaporation, “droplets” may conduce methyl transfer without fragmentation

charged ices: Bouwman et al, 2011, A&A, 529, 46; Schutte et al, 2003, 398, 1049; Demyk et al, 1998, A&A, 339, 553, Balog et al 2009, Phys Rev Lett, 201, 73003

The Organic Inventory of Comets

Comets, and hence the Earth, sampled many reservoirs with a diverse chemical history

ice chemistry
Hot Core chemistry
Warm gas photochemistry



Tielens, 2013, Rev Mod Phys and refs therein