Chemistry of ice: formation of complex molecules and photodesorption

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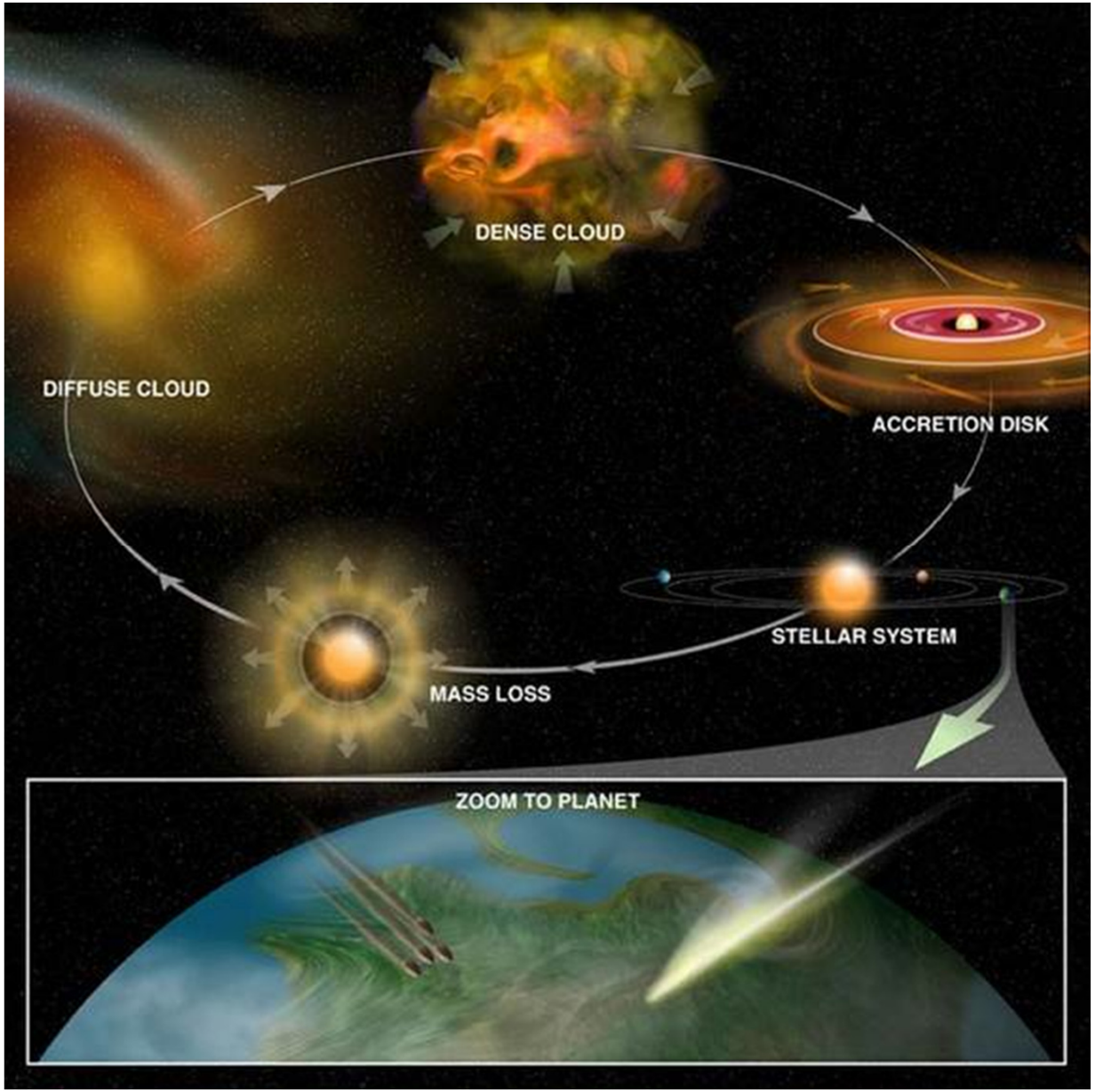
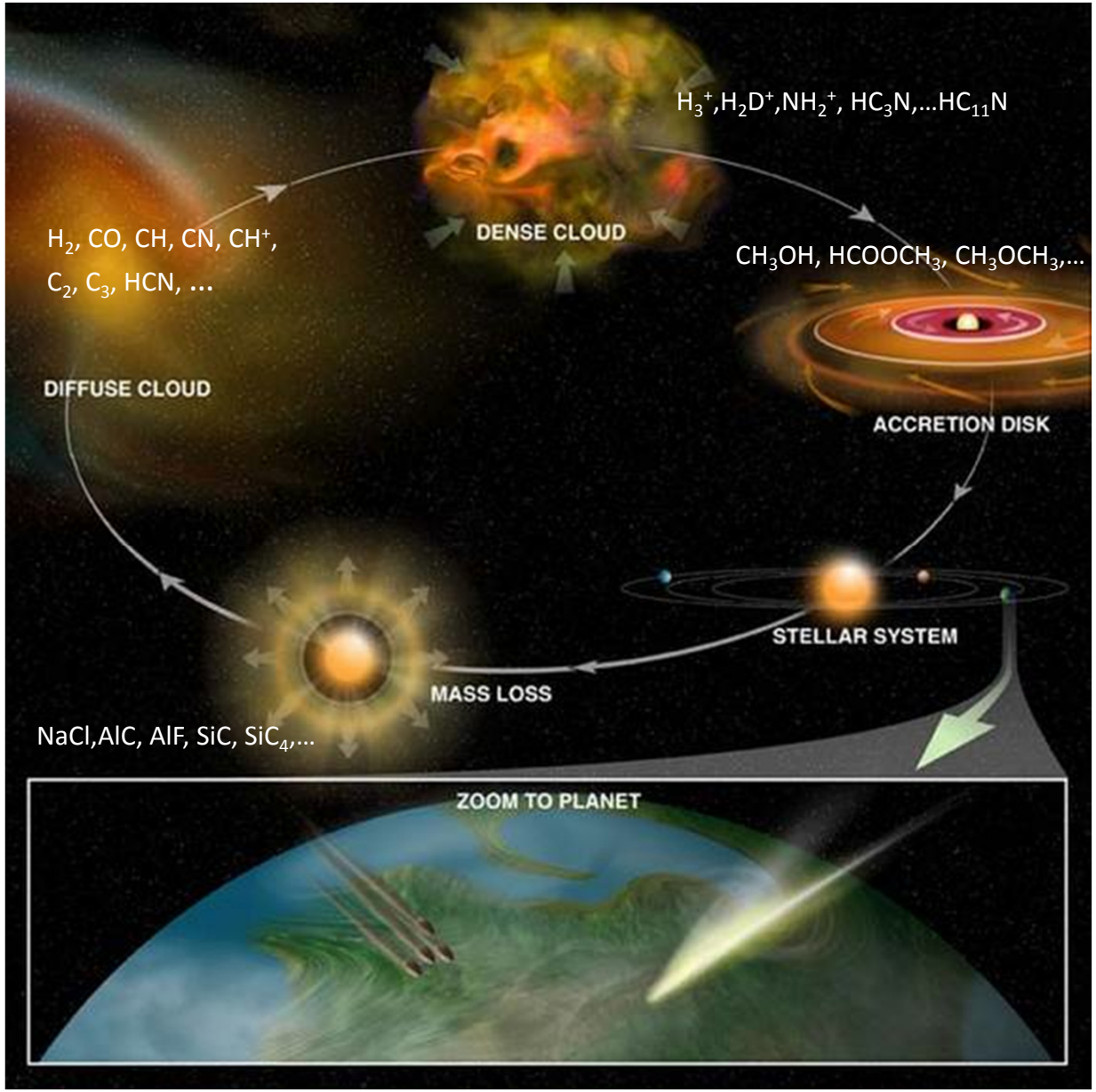
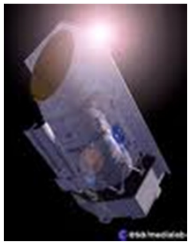
The life cycle of the interstellar matter



The life cycle of the interstellar matter



Ice chemistry



complex organic molecules

ice grain

atoms / simple molecules

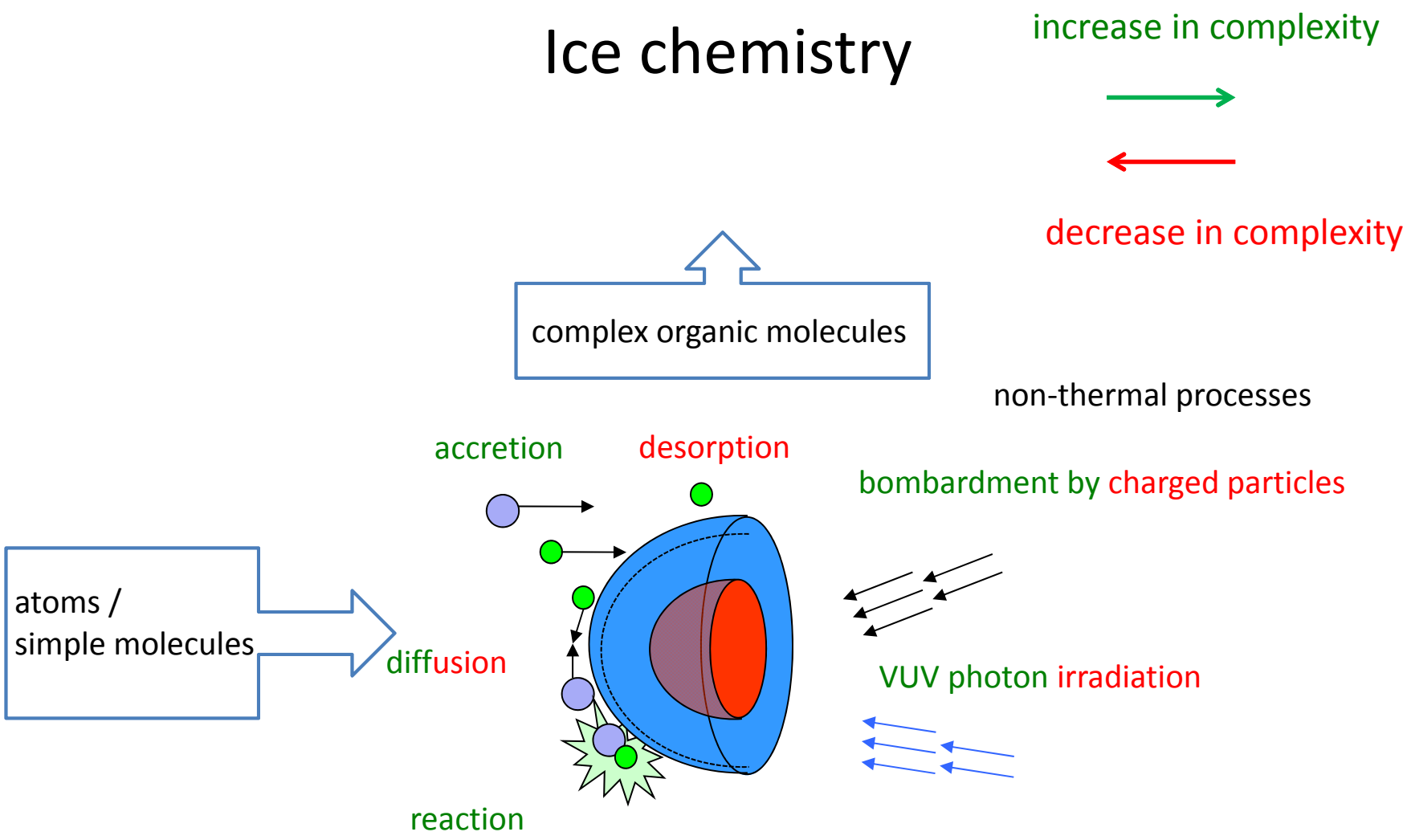
volatile species

organic residue

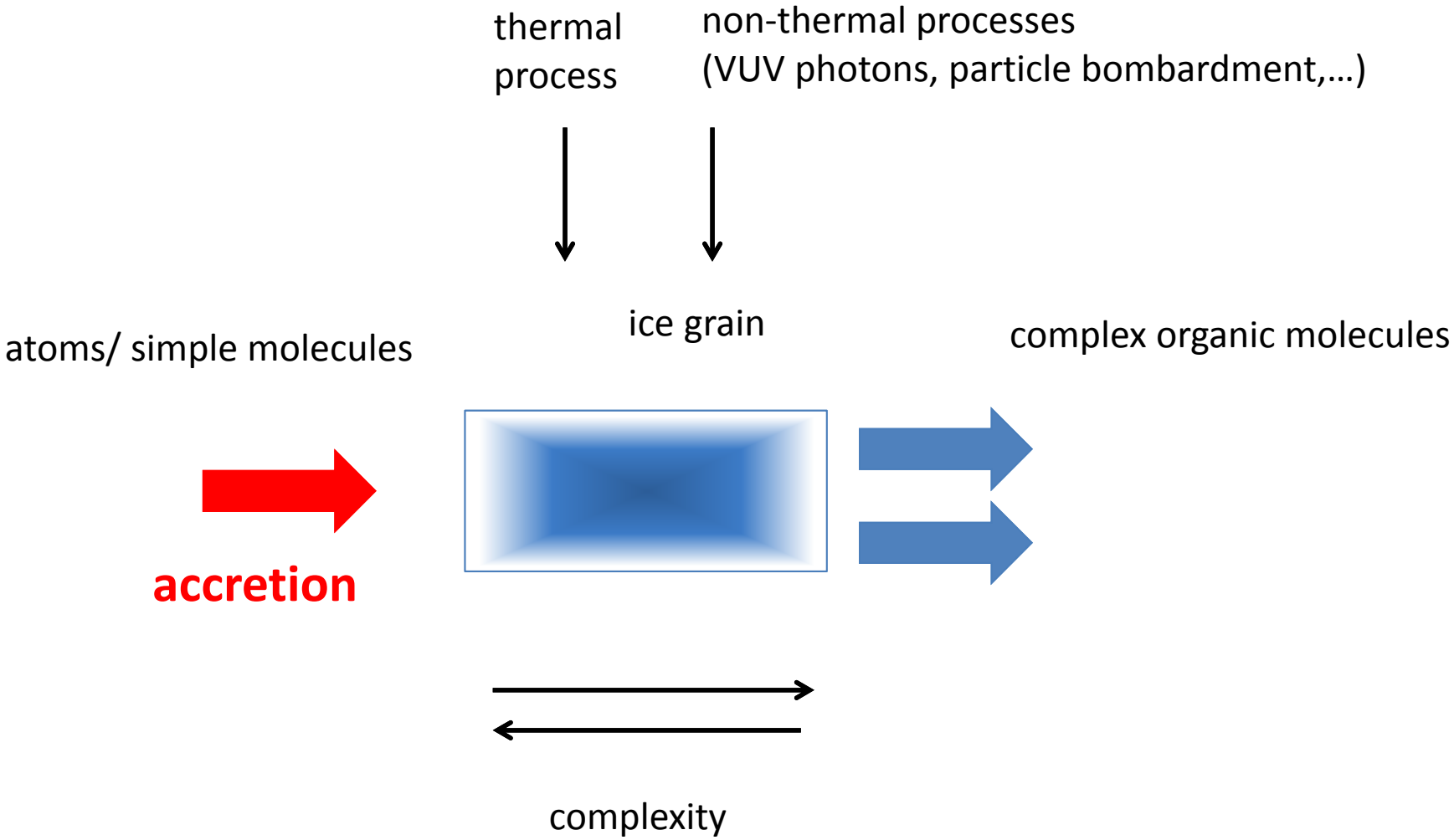
refractory species

complexity

Ice chemistry



Ice chemistry



Accretion of atoms and simple molecules

$$\frac{dn_i}{dt} = \underbrace{v_i * \sigma_d * n_d * S_i(T, T_g)}_{k_i^{acc}} * n_i$$

v_i speed of species i
σ_d geometrical cross-section of the grain
n_d grains density $n_d \approx 1.33\ 10^{-12} \times N_H cm^{-3}$

S_i sticking coefficient of species i

H, He

for H on a amorphous ice surface:

Matar et al. JCP2010

$$S_H(T) = S_0 \frac{\left(1+\beta\frac{T}{T_0}\right)}{\left(1+\frac{T}{T_0}\right)^{\beta}}$$

S_0=1, β=2.5, T_0= 52 K

S_H(10K) ≈95%

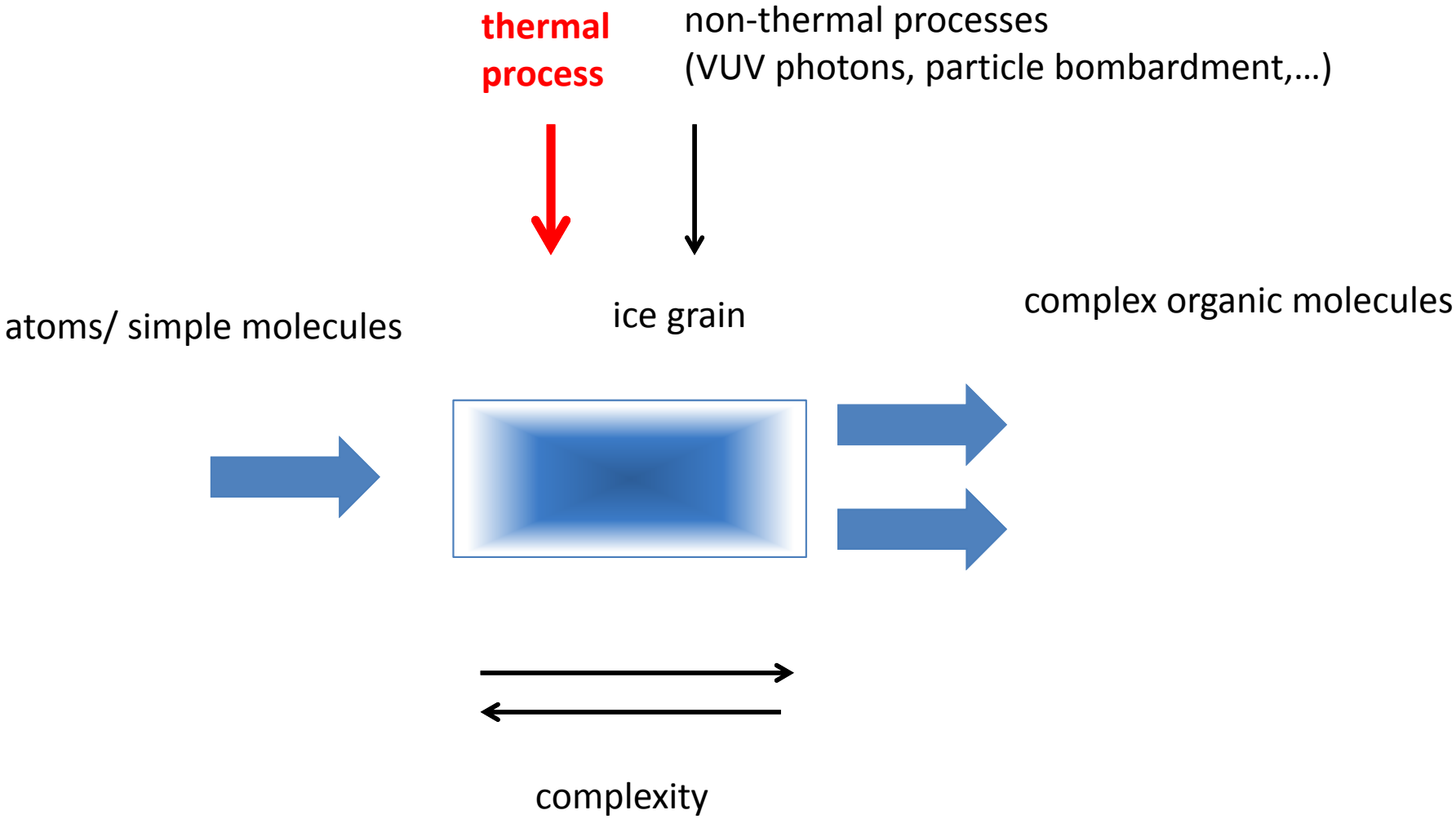
other species (H_2O, CO, N_2, …),

for H_2O:
Batista et al. Phys.Rev.Lett., 2005
Hundt et al. J.Chem.Phys., 2012
(≈100%)
for CO, N_2 :
Bisschop A&A 2006 (87% à 14 K)

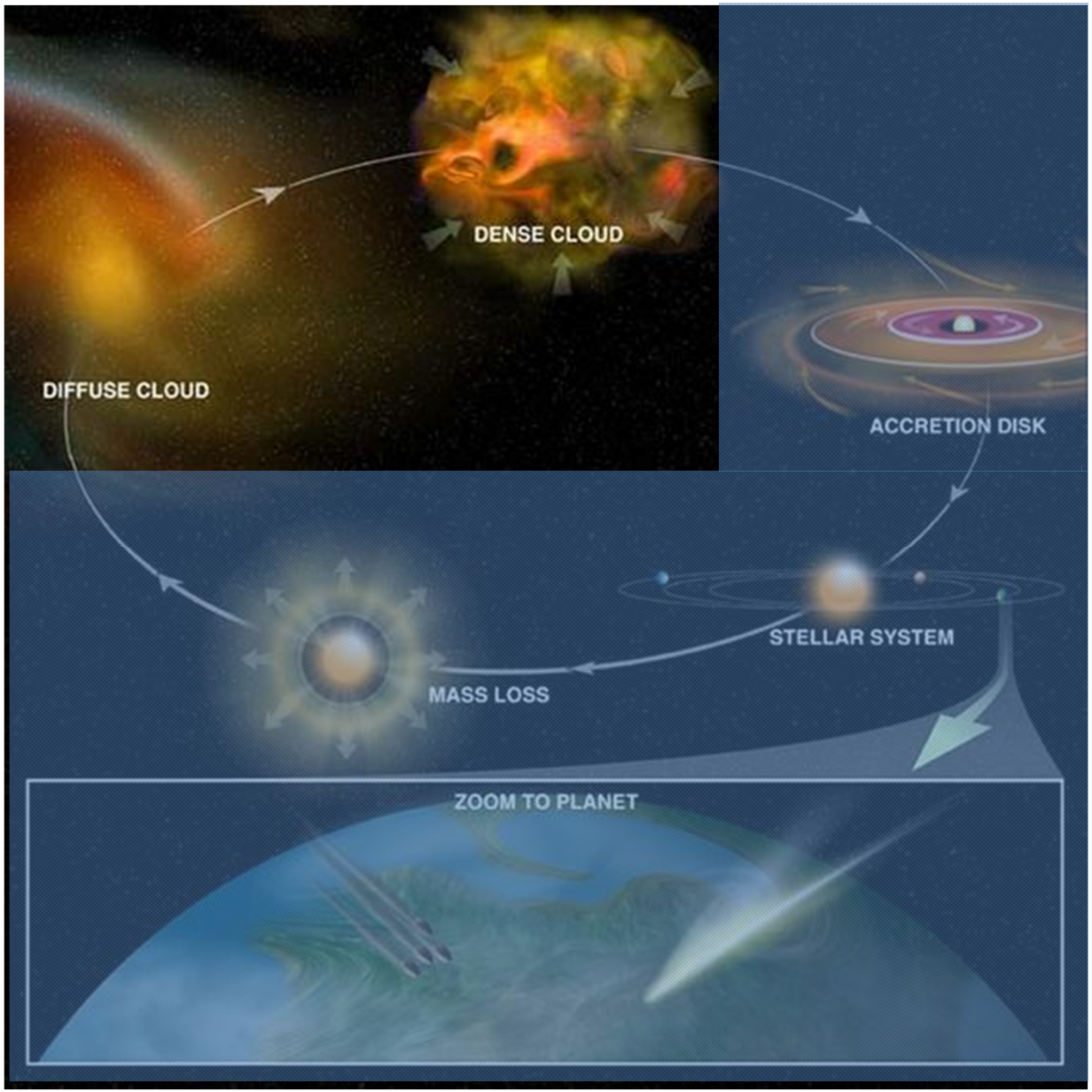
charged species
(on a neutral or charged surface)

?

Ice chemistry



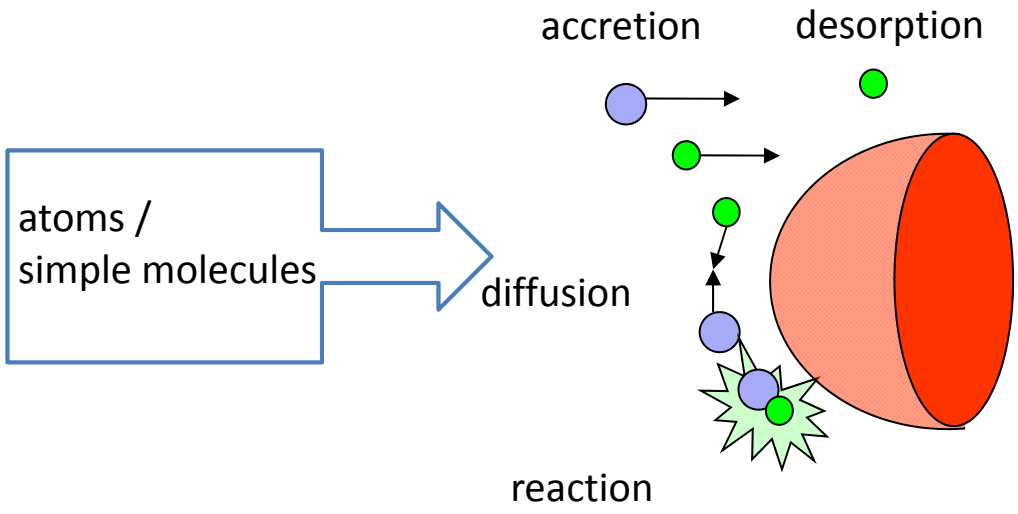
The ice mantle build-up

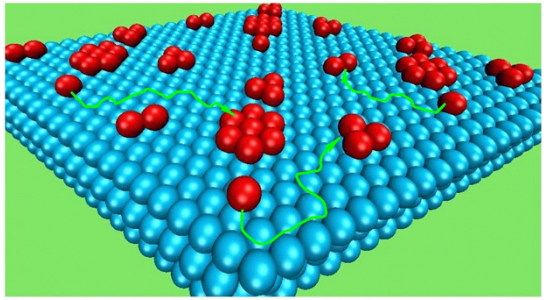


early and late prestellar ice formation

The ice mantle build-up

surface reactivity involving atoms (C, N, O, H) or small molecules





The interstellar ice CNO budget

C budget

CO, CO_2, OCN^-, H_2CO, CH_3OH, $HCOO^-$, CH_4

8-15 % wrt C_{total}

14-27 % wrt $C_{volatile}$

O budget

H_2O, CO, CO_2, OCN^-, H_2CO, CH_3OH, $HCOO^-$

12-16 % wrt O_{total}

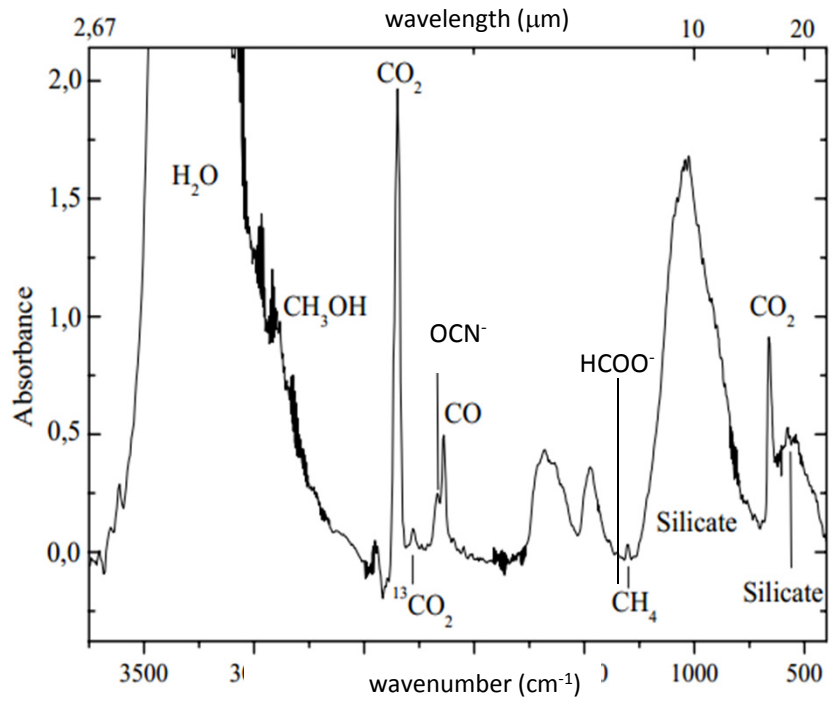
25-34 % wrt $O_{volatile}$

N budget

NH_3, NH_4^+, OCN^-, ?

10-12 % wrt N_{total}

10-12 % wrt $N_{volatile}$



NGC 7538 ISO spectrum

+ complex organic molecules (COMs)
in low abundances (< 0.1 % wrto H_2O)

The zeroth generation molecules

The ice mantle build-up

C

The formation of CH_4

$$C \xrightarrow{+H} CH_4$$

Hiraoka et al., ApJ 1998

The formation of carbon chains

$$C_2 \xrightarrow{+H} C_2H_2 \rightarrow C_2H_4 \rightarrow C_2H_6$$

Hiraoka et al., ApJ 1999, ApJ 2000

N

The formation of NH_3

$$N \xrightarrow{+H} NH_3$$

Hiraoka et al., ApJ 1995

The ice mantle build-up

O

The formation of H_2O

$O \xrightarrow{+H} H_2O$ — Hiraoka et al., ApJ 1998, Dulieu et al. , A&A 2010, Jing et al. ApJL, 2011

$O_2 \xrightarrow{+H} H_2O$ — Ioppolo et al., ApJ 2008, Miyauchi CPL, 2008

$O_3 \xrightarrow{+H} H_2O$ — Romanzin JCP 2011, Mokrane ApJL, 2009

$OH + OH \rightarrow H_2O_2 \xrightarrow{+2H} 2\ H_2O$ — Oba et al., PCCP 2011

$O + H_2 \rightarrow H_2O$ — Lamberts et al., arXiv 2014

$OH + H_2 \rightarrow H_2O + H$ — Oba et al., ApJ 2012, He and Vidali ApJ 2014

The formation of O_2

$O + O \rightarrow O_2$ $E < 1.25\ kJ.mol^{-1}$ — Minissale et al. ,J. Chem. Phys 2014

The formation of O_3

$O + O_2 \rightarrow O_3$ $E < 1.25\ kJ.mol^{-1}$ — Minissale et al., J. Chem. Phys 2014

The ice mantle build-up

C/O

The formation of CO_2

$CO + O \rightarrow CO_2$ E = 5.2 □ 1.5 kJ.mol^{-1} — Roser et al. ApJ 2001, Madzunkov PRA 2006, Minissale et al., A&A 2013

$CO + OH \rightarrow CO_2 + H$ — Ioppolo et al., MNRAS 2011 a

The formation of more complex molecules

$CO + OH \rightarrow HCOOH$ — Ioppolo et al., MNRAS 2011 b

$CO_2 \xrightarrow{+H}$ nothing — Bisschop et al., A&A 2007

$HCOOH \xrightarrow{+H}$ nothing — Bisschop et al., A&A 2007

$CH_3CHO \xrightarrow{+H} C_2H_5OH, CH_4, H_2CO, CH_3OH$ — Bisschop et al., A&A 2007

The ice mantle build-up

N/O

The formation of hydroxylamine

$NO \xrightarrow{+H} NH_2OH$ Congiu et al., ApJ, 2012

$NH_3 + OH \rightarrow NH_2OH$ ➡ talk by Lahouari Krim

The formation of nitrogen oxides

$NO + O_2 \rightarrow NO_2, N_2O_3, N_2O_4$ Minissale et al., Chem. Phys. Lett., 2013

$NO + OH \rightarrow HONO, NO_2, N_2O, HNO, HNO_3$ Joshi et al., MNRAS, 2012

C/N

$HCN + H \rightarrow CH_2NH$

$CH_2NH + H + H \rightarrow CH_3NH_2$ Theule et al., A&A, 2011

$CN + H_2 \rightarrow HCN$ Borget et al., to be submitted

The ice mantle build-up

hydrogenation by <u>molecular</u> hydrogen

$OH + H_2 \rightarrow H_2O + H$ Oba et al., ApJ 2012

$O + H_2 \rightarrow H_2O$ Lamberts et al., arXiv 2014

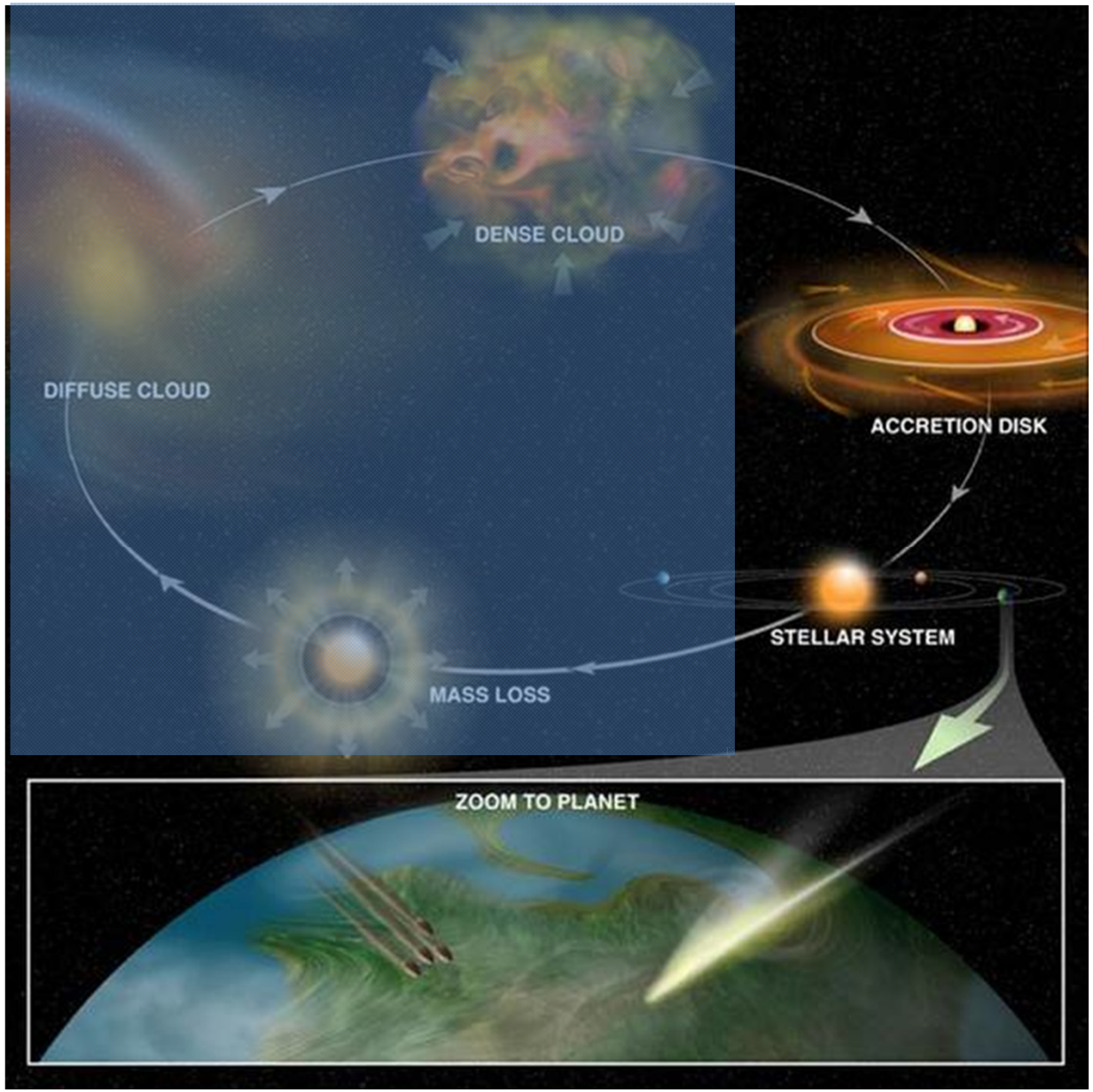
$CN + H_2 \rightarrow HCN$ Borget et al., to be submitted

activation energy vs abundance of the H_2 reactant ($H/H_2 \approx 10^{-4}$) ?

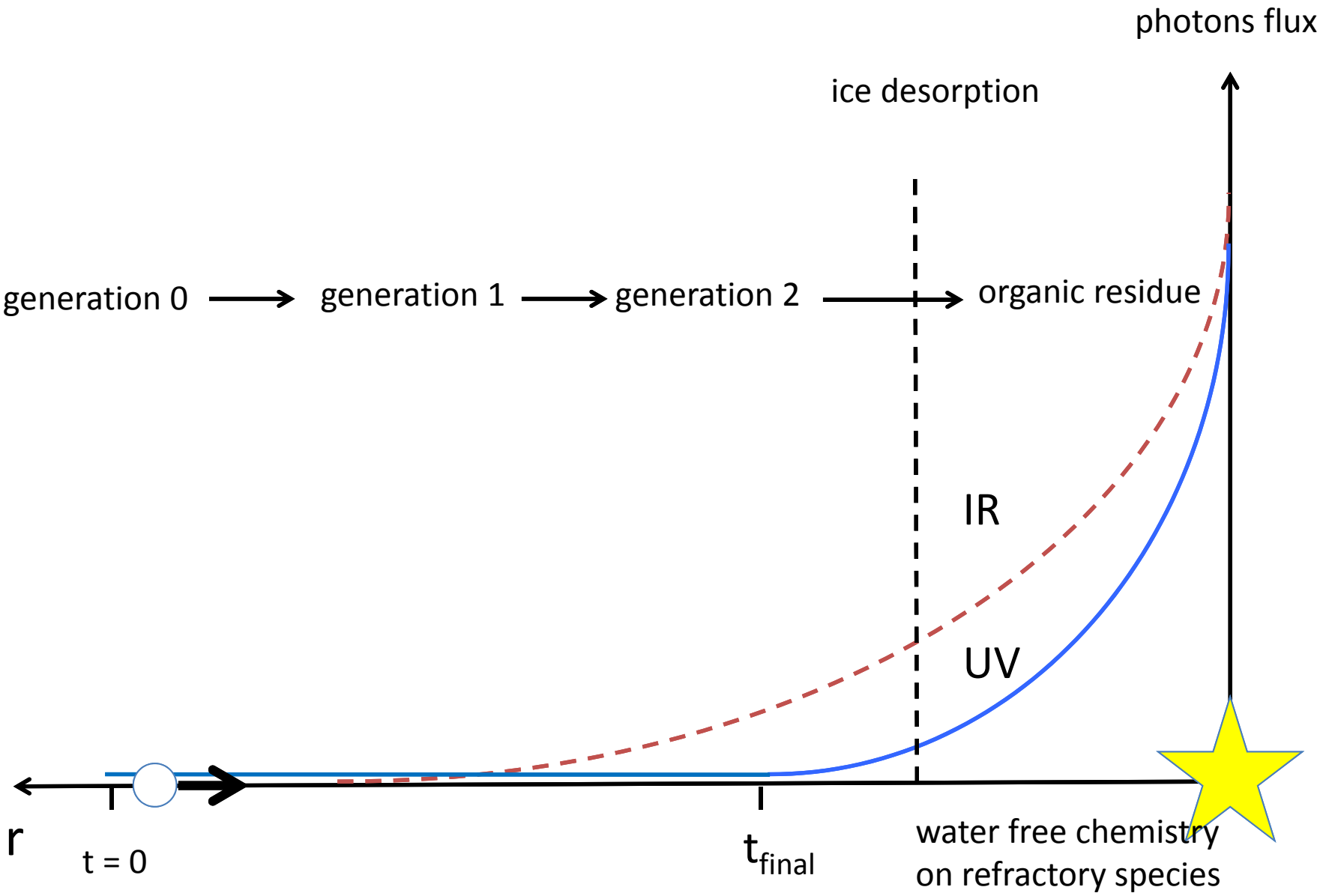
effect of an H_2 coating on grain surface and the radical life time ?

The formation of COMs

the protostellar stage



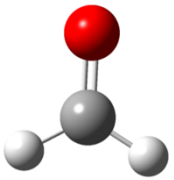
Purely thermal reactivity

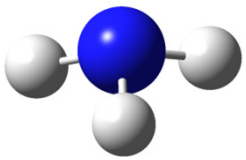


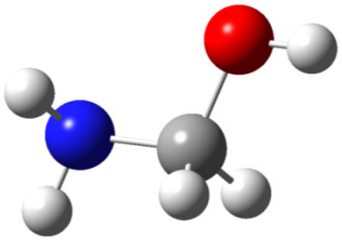
Purely thermal reactivity

G0 molecules	H_2O	CO	CO_2	NH_3	CH_4	OCS	H_2CO	CH_3OH	HCOOH	HNCO	…
H_2O											
CO											
CO_2											
NH_3							?				
CH_4											
OCS											
H_2CO											
CH_3OH											
HCOOH											
HNCO											
…											

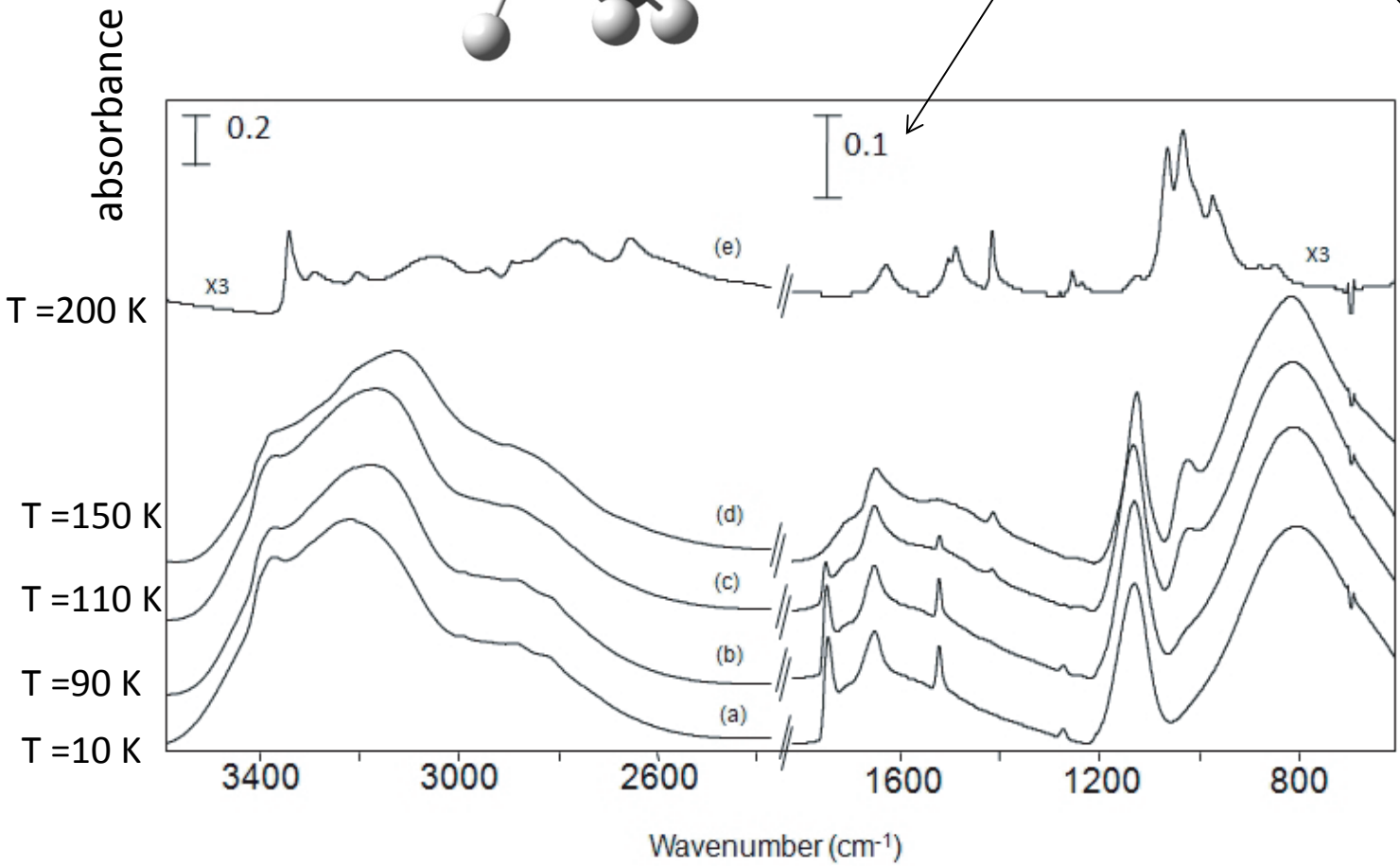
Purely thermal reactivity

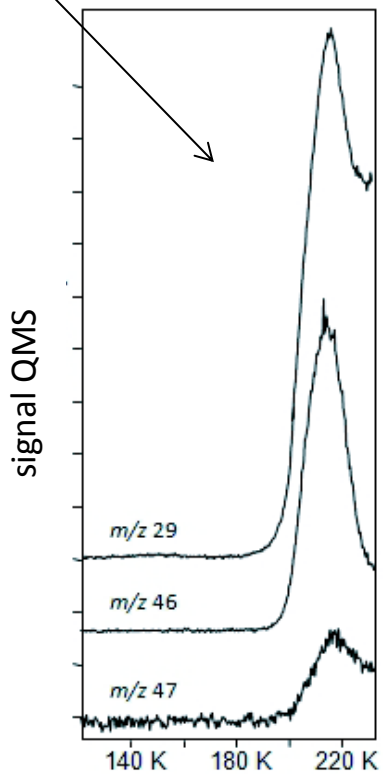






IR and mass spectra of NH_2CH_2OH

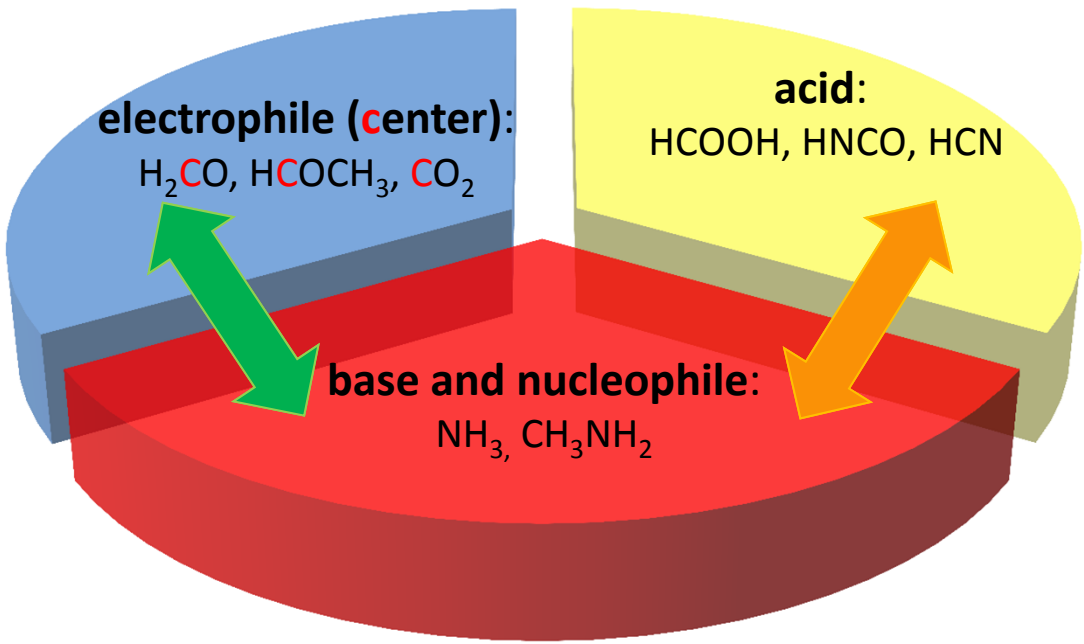




mass spectrum

Purely thermal reactivity

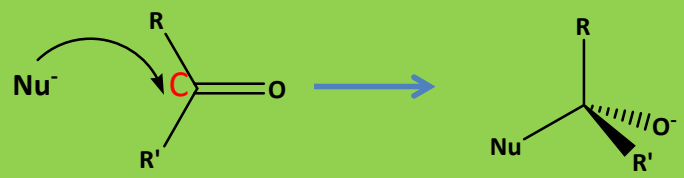
G_0 molecules:



acid-base reaction:

$AH + B \longrightarrow A^- + BH^+$

nucleophilic addition:



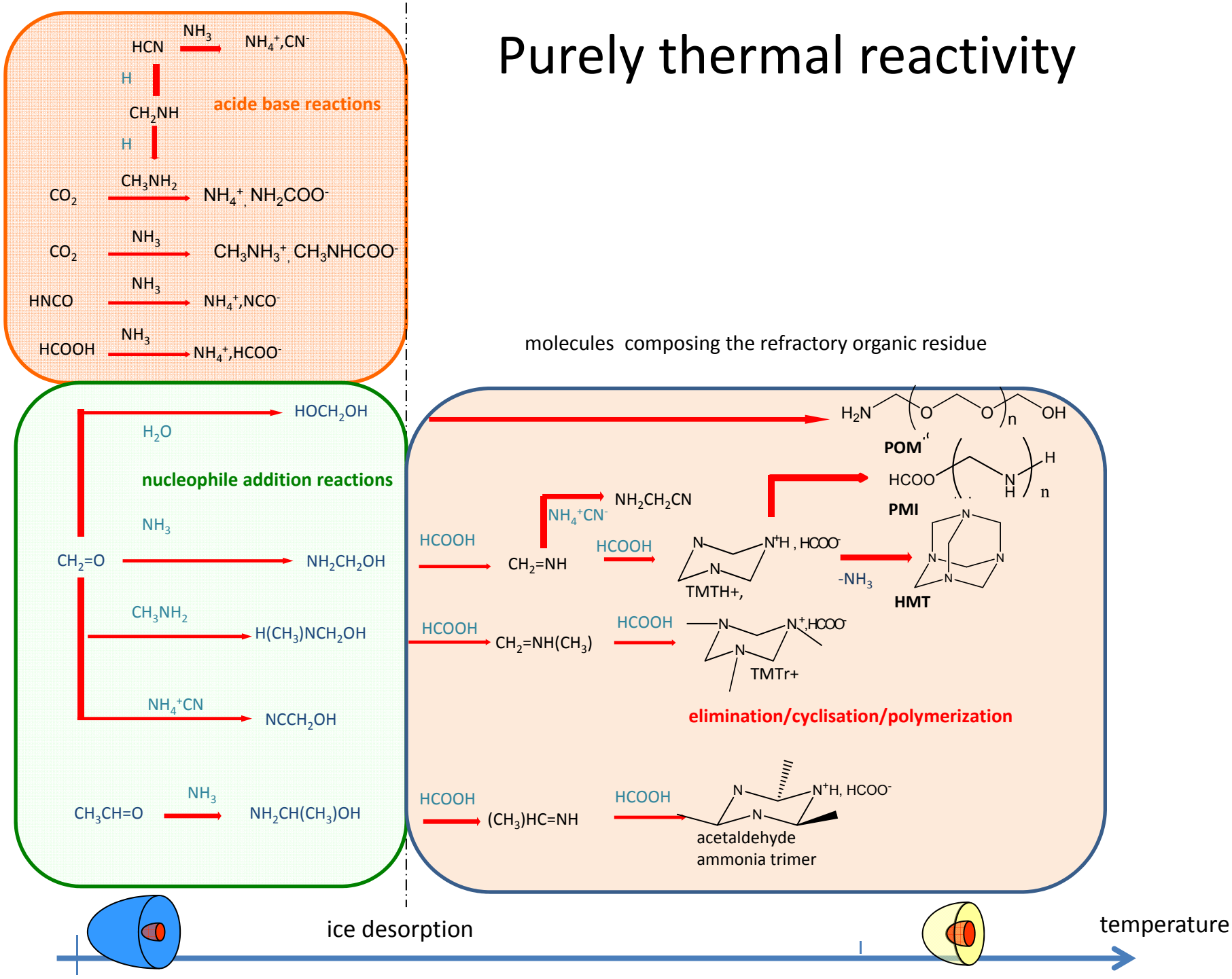
$G_0 \xrightarrow{+\,G_0} G_1 \xrightarrow{+\,G_0,G_1} G_2 \xrightarrow{+\,G_0,G_1,G_2} \cdots\cdots$

primitive molecules | complex molecules

Thermal reactivity in the ice mantle

G0 molecules	H_2O	CO	CO_2	NH_3	CH_4	OCS	H_2CO	CH_3OH	HCOOH	HNCO	…
H_2O							$HOCH_2OH$			$H_3O^+OCN^-$	
CO											
CO_2				NH_2COOH							
NH_3			NH_2COOH				NH_2CH_2OH		NH_4^+ $HCOO^-$	$NH_4^+OCN^-$	
CH_4											
OCS											
H_2CO	$HOCH_2OH$			NH_2CH_2OH			POM				
CH_3OH											
HCOOH				NH_4^+ $HCOO^-$							
HNCO	$H_3O^+OCN^-$			$NH_4^+OCN^-$							
…											

Purely thermal reactivity



Purely thermal reactivity

a solid-state chemical sub-network of purely thermal reactions

reactants				products					ν_0, E_a, [T interval, K]	references
acid-base reactions										
generation 0		generation 0		generation 1						
H_2O	+	HNCO	→	$H_3O^+ OCN^-$					(3 10^8, 26)[110K-130K]	Raunier et al. (2004); Theule et al. (2011a)
NH_3	+	HCOOH	→	$NH_4^+ HCOO^-$						Schutte et al. (1999)
NH_3	+	HNCO	→	$NH_4^+ OCN^-$					(4 10^{-3}, 0.4) [8K-40K]	Demyk et al. (1998); Raunier et al. (2003) van Broekhuizen et al. (2004); Mispelaer et al. (2012)
NH_3	+	HCN	→	$NH_4^+ CN^-$					(1.6 10^{-2}, 2.7)[60K-105K]	Clutter & Thompson (1969); Noble et al. (in prep.)
generation 1		generation 0		generation 2						
NH_2COOH	+	NH_3	→	$NH_4^+ NH_2COO^-$						Bossa et al. (2008)
$CH_3NHCOOH$	+	CH_3NH_2	→	$CH_3NH_3^+ CH_3NHCOO^-$						Bossa et al. (2009)
nucleophilic additions										
generation 0		generation 0		generation 1						
CO_2	+	NH_3	→	NH_2COOH						Frasco (1964); Hiratsuna (1984); Bossa et al. (2008)
CO_2	+	CH_3NH_2	→	$CH_3NHCOOH$						Bossa et al. (2009)
H_2CO	+	H_2O	→	$HOCH_2OH$						Noble et al. (2012 a)
H_2CO	+	NH_3	→	NH_2CH_2OH					(5 10^{-2}, 4.5)[80K-100K]	Bossa et al. (2009)
H_2CO	+	CH_3NH_2	→	CH_3NHCH_2OH					(2 10^{-2}, 1.1)[30K-120K]	Vinogradoff et al. (2012 a)
CH_3CHO	+	NH_3	→	$NH_2CH(CH_3)OH$					(7 10^{10}, 33)[115K-125K]	Duvernay et al. (2010)
generation 1		generation 0		generation 2						
$NH_4^+ CN^-$	+	CH_2NH	→	NH_2CH_2CN						Danger et al. (2011)
$NH_4^+ CN^-$	+	H_2CO	→	$HOCH_2CN$	+	NH_3			(2.8 10^{-1}, 3.8)[50K-130K]	Danger et al. (2012)
elimination reaction										
generation 1										
NH_2CH_2OH	+	HCOOH	→	$CH_2{=}NH$	+	H_2O	+	HCOOH		Vinogradoff et al. (2011, 2012 b)
$NH_2CH(CH_3)OH$	+	HCOOH	→	$CH_3CH{=}NH$	+	H_2O	+	HCOOH		Vinogradoff et al. (2012 a)
CH_3NHCH_2OH	+	HCOOH	→	$CH_2{=}NCH_3$	+	H_2O	+	HCOOH		Vinogradoff et al. (2012 a)

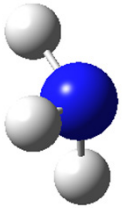
Theule et al. Adv. Spac. Res. 2013

Purely thermal reactivity

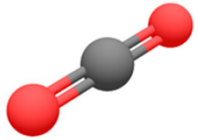
Thermal condensation reactions

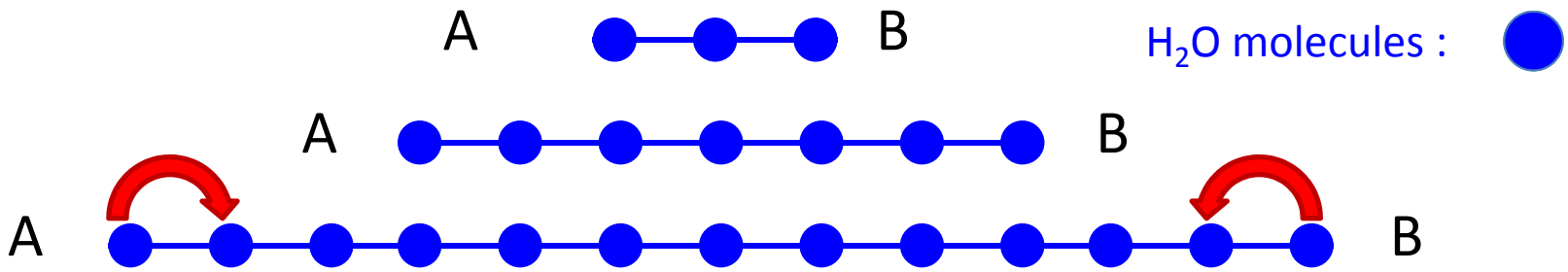
Reactants						Products			References
The formation of POM[a]									
H_2CO	+	H_2O			→	$HOCH_2OH$			Noble et al. (2012)
H_2CO	+	$HOCH_2OH$			→	$HOCH_2OCH_2OH$			Noble et al. (2012)
H_2CO	+	$HOCH_2OCH_2OH$			→	$HOCH_2OCH_2OCH_2OH$			Noble et al. (2012)
H_2CO	+	$HO–(CH_2–O)_{n-1}–H$			→	$HO–(CH_2O)_n–H$			Noble et al. (2012)
or									
H_2CO	+	$NH_4^+CN^-$			→	$NCCH_2OH$	+	NH_3	Danger et al. (2012)
H_2CO	+	$NCCH_2OH$			→	$NCCH_2OCH_2OH$			Danger et al. (2012)
H_2CO	+	$NC–(CH_2–O)_{n-1}–H$			→	$NC–(CH_2O)_n–H$			Danger et al. (2012)
or									
H_2CO	+	$NH_4^+HCOO^-$			→	$HCOOCH_2OH$	+	NH_3	Vinogradoff et al. (2012)
H_2CO	+	$HCOOCH_2OH$			→	$HCOOCH_2OCH_2OH$			Vinogradoff et al. (2012)
H_2CO	+	$HCOO–(CH_2–O)_{n-1}–H$			→	$HCOO–(CH_2O)_n–H$			Vinogradoff et al. (2012)
The formation of PMI[a]									
CH_2NH	+	$NH_4^+CN^-$			→	$NCCH_2NH_2$	+	NH_3	Danger et al. (2011)
CH_2NH	+	$NC(CH_2NH)_{n-1}H$			→	$NC(CH_2NH)_nH$			Danger et al. (2011)
or									
CH_2NH	+	$NH_4^+HCOO^-$			→	$HCOOCH_2NH_2$	+	NH_3	Vinogradoff et al. (2012)
CH_2NH	+	$HCOO(CH_2NH)_{n-1}H$			→	$HCOO(CH_2NH)_nH$			Vinogradoff et al. (2012)
The formation of HMT[b]									
CH_2NH	+	$HCOOH$			→	$CH_2NH_2^+HCOO^-$			Vinogradoff et al. (2012)
$CH_2NH_2^+HCOO^-$	+	CH_2NH	+	CH_2NH	→	$C_3N_3H_9H^+HCOO^-$			Vinogradoff et al. (2012)
$C_3N_3H_9H^+HCOO^-$	+	$C_3N_3H_9H^+HCOO^-$			→	$C_6H_{12}N_4$ (HMT)	+	2 $NH_4^+HCOO^-$	Vinogradoff et al. (2012)
The formation of AAT[b]									
CH_3CHNH	+	$HCOOH$			→	$CH_3CHNH_2^+HCOO^-$			Vinogradoff et al. (2013a)
$CH_3CHNH_2^+HCOO^-$	+	CH_3CHNH	+	CH_3CHNH	→	$C_6H_{15}N_3$ (AAT)	+	$HCOOH$	Vinogradoff et al. (2013a)
The formation of FMT[b]									
CH_2NCH_3	+	$HCOOH$			→	$[CH_2NHCH_3]^+HCOO^-$			Vinogradoff et al. (2013a)
$[CH_2NHCH_3]^+HCOO^-$	+	CH_2NCH_3	+	CH_2NCH_3	→	$C_6H_{15}N_3$ (FMT)	+	$HCOOH$	Vinogradoff et al. (2013a)

Reaction dynamics

A = 

A + B

B = 

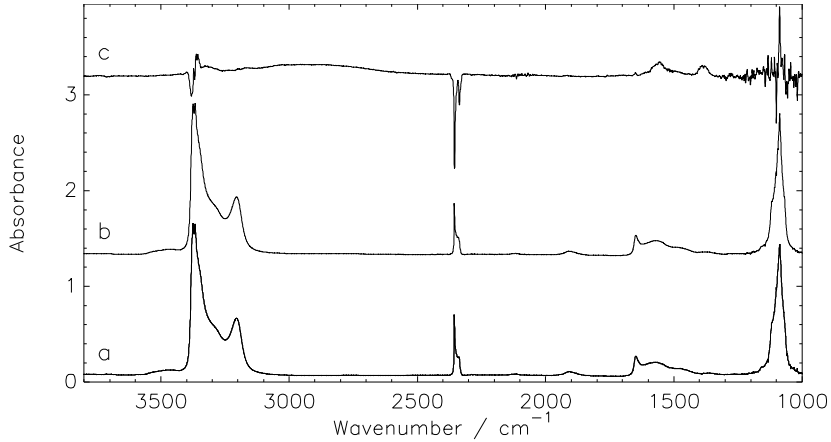


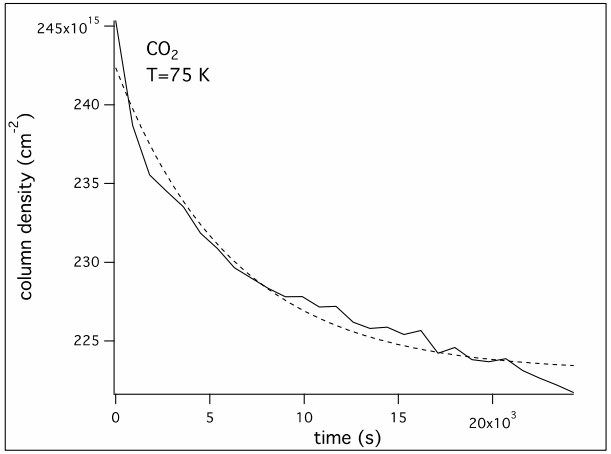
diffusion limited reactivity

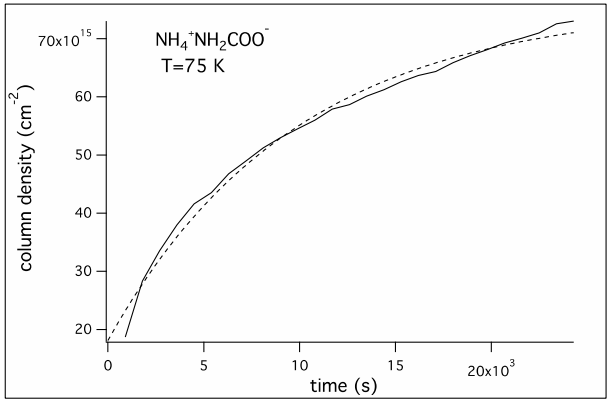
$$\frac{\partial n_A}{\partial t} - \boxed{D(T)} \times \nabla^2 n_A + \boxed{k(T)} \times n_A n_B = 0$$

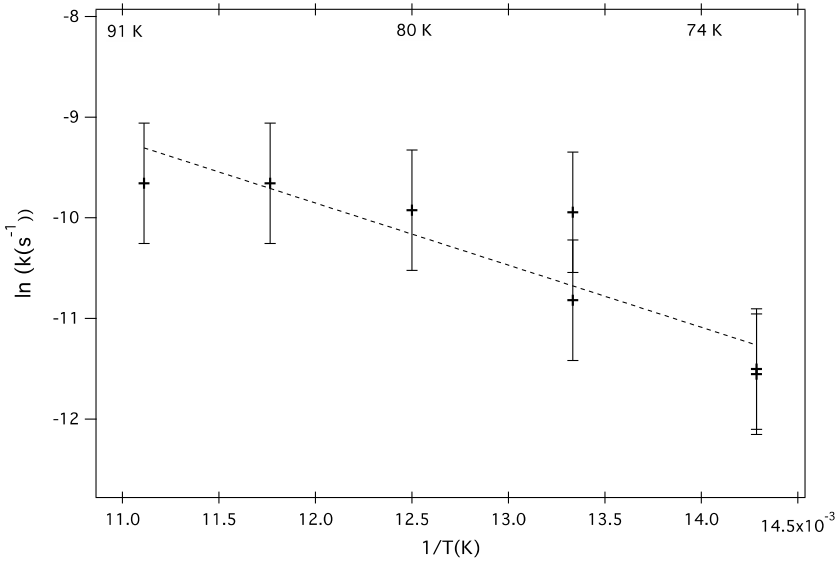
next talk by Pierre Ghesquiere

The reaction rate constant k(T)







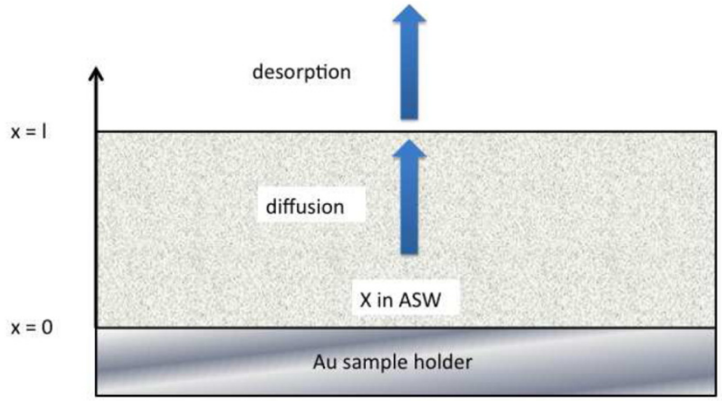


$$\frac{\partial n_A}{\partial t} + k(T) \times n_A n_B = 0 \quad \rightarrow \quad k(T) = A\, e^{-\frac{E_a}{k_B T}}$$

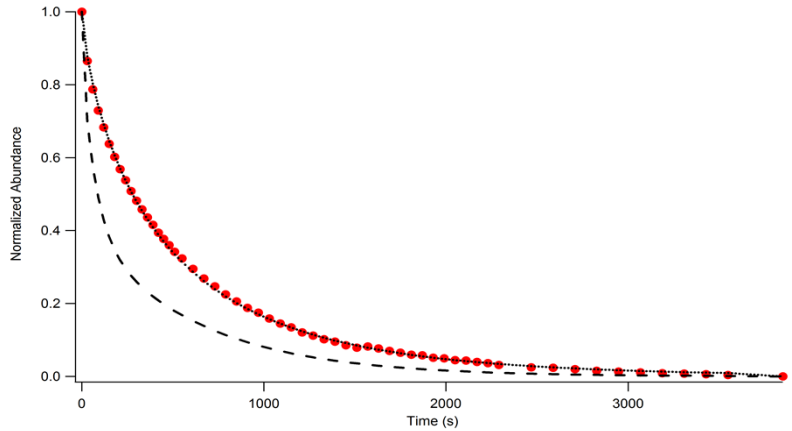
$$E_a = 5.1 \pm 1.6 \;\; kJ.mol^{-1}$$

$$A = 0.09^{+1.1}_{-0.08} \; s^{-1}$$

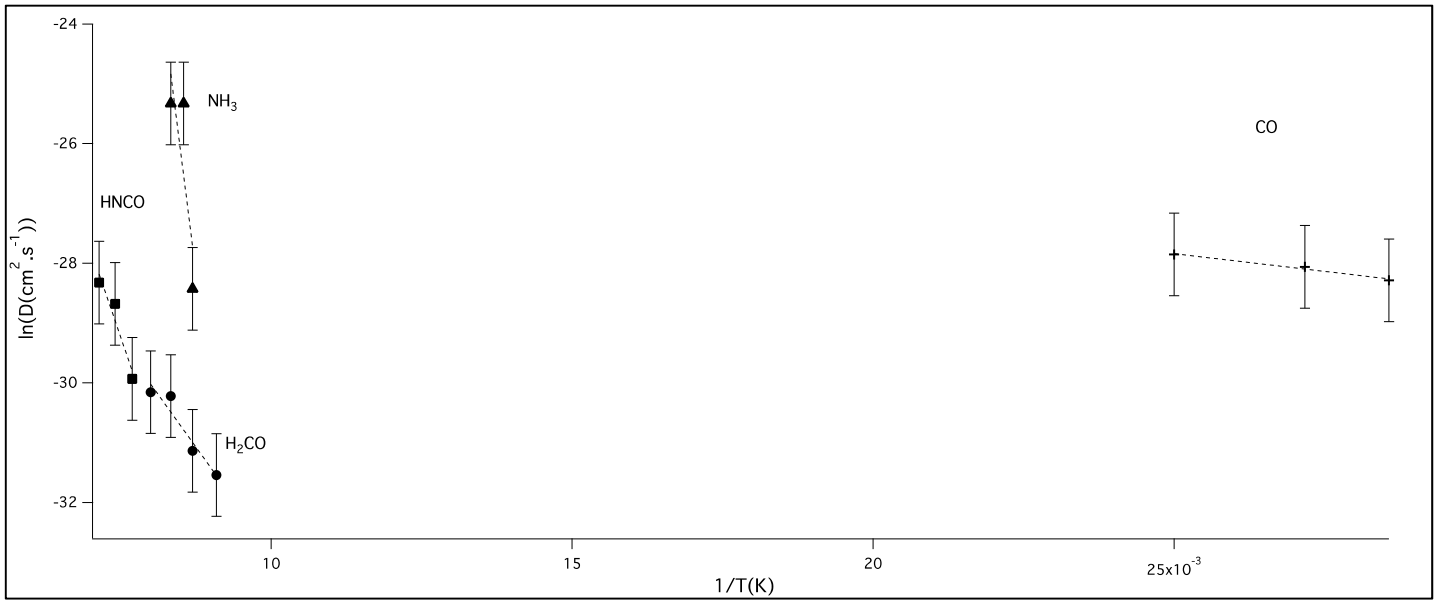
The diffusion coefficient D(T)



T fixed



Mispelaer et al., A&A 2013



$$\frac{\partial n}{\partial t} - D(T) \times \frac{\partial^2 n}{\partial z^2} = 0$$

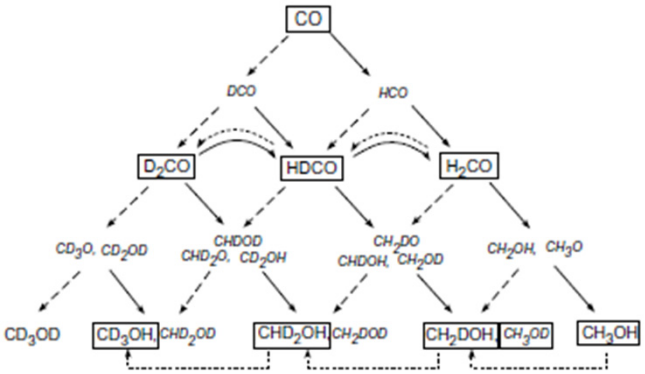
➔ $D(T_{fixed})$

The isotopic H/D exchange

what is the deuteration pathway ?

How can we use the D/H ratio as a chemical clock ?

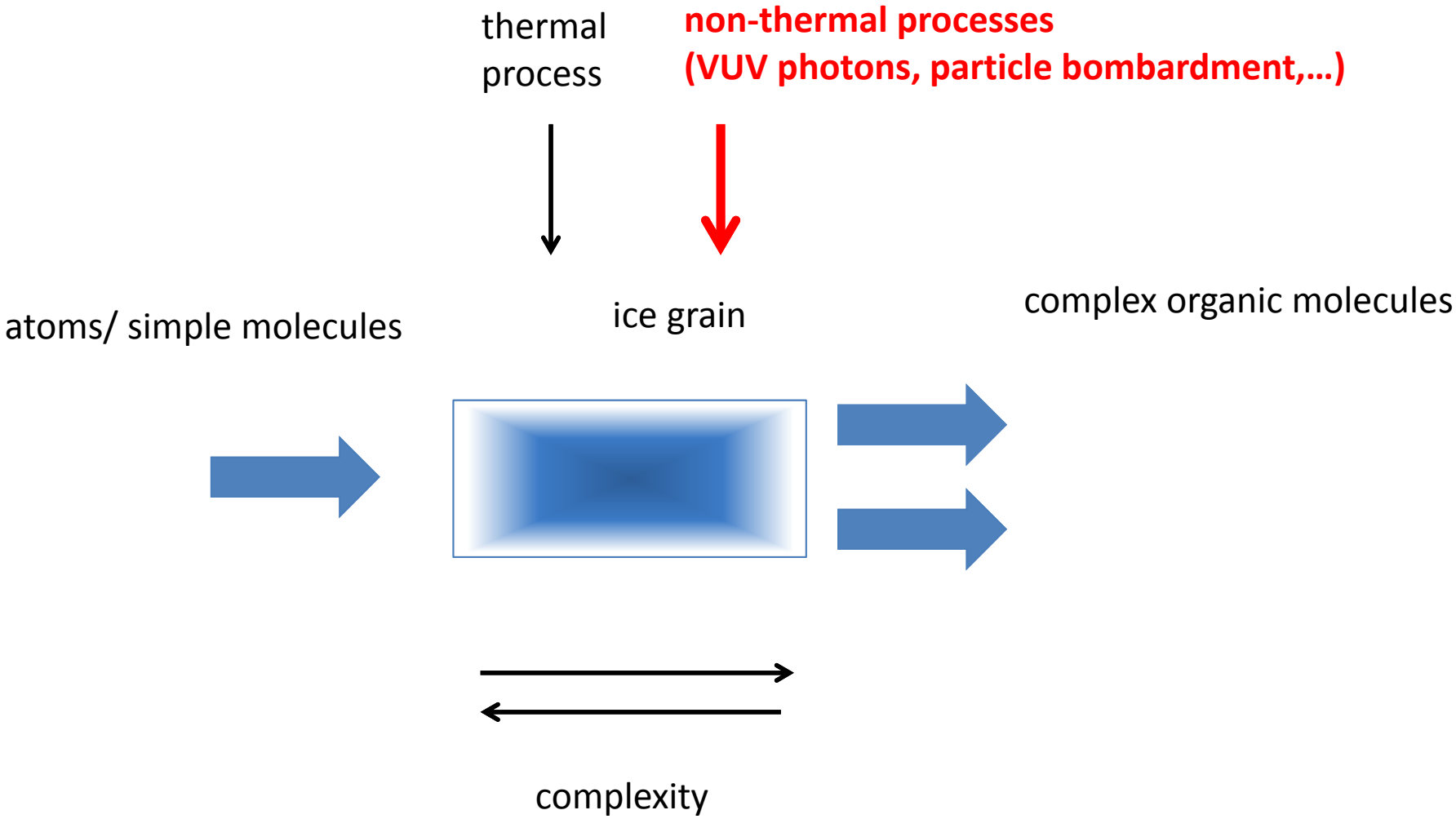
N. Watanabe, A. Kouchi / Progress in Surface Science 83 (2008) 439–489

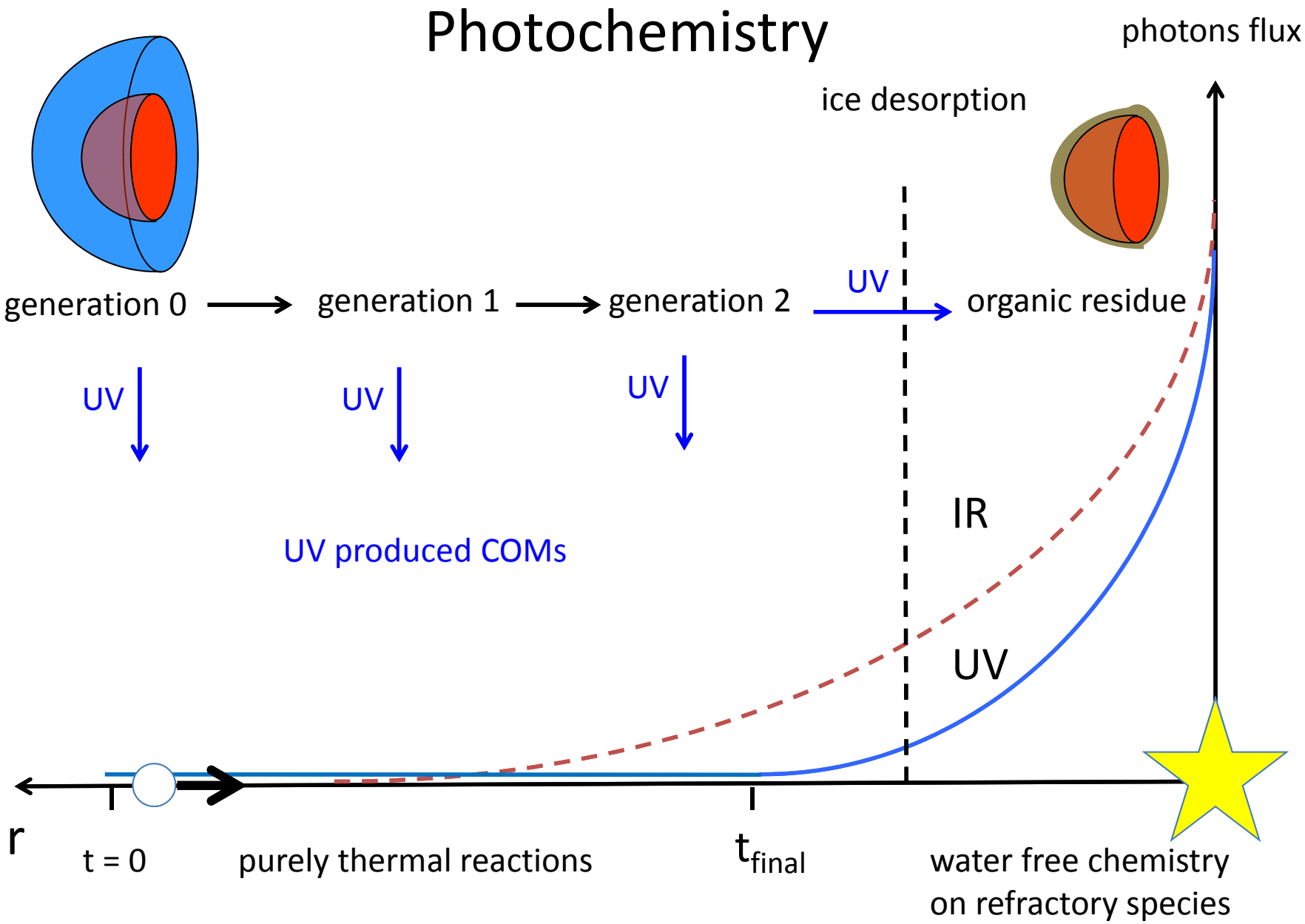


the deuteration of methanol in star-formation regions, the CH_2DOH / CH_3OD ratio

talk by Mathilde Faure

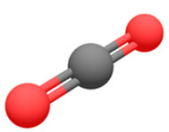
Ice chemistry

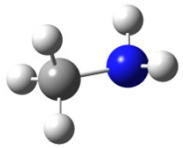


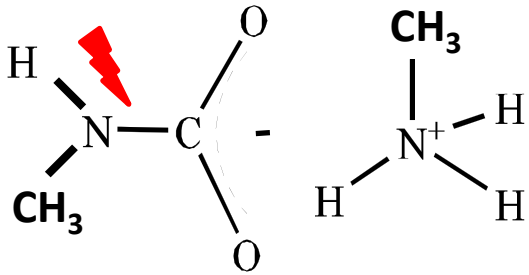

Photochemistry
photons flux
ice desorption
generation 0
generation 1
generation 2
UV
organic residue
UV
UV
UV
UV produced COMs
IR
UV
r
t = 0
purely thermal reactions
t final
water free chemistry
on refractory species

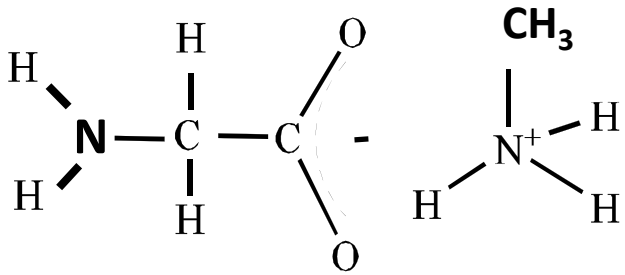
Photochemistry

✓ Formation of COMs from complex molecules irradiation









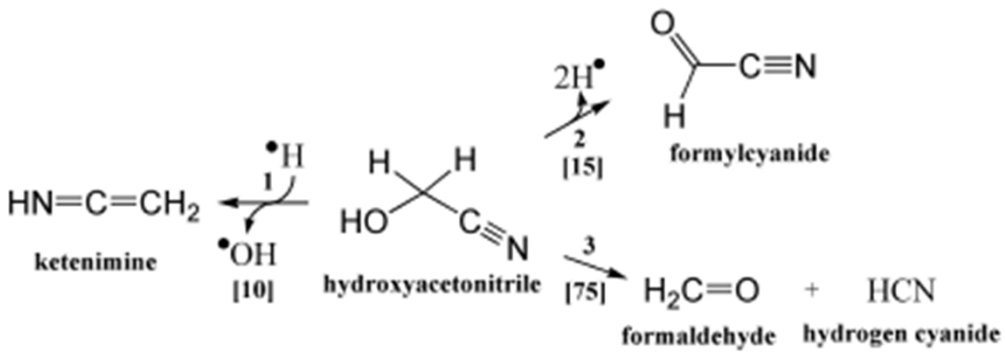
$$CO_2 + 2CH_3NH_2 \xrightarrow{50\ K} NH(CH_3)COO^-CH_3NH_3^+ \xrightarrow{h\nu} NH_2CH_2COO^-CH_3NH_3^+$$

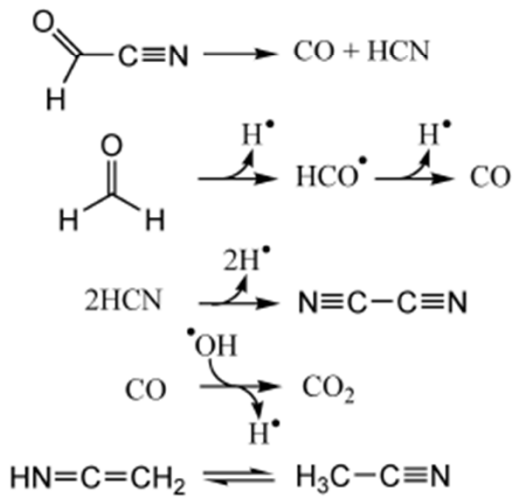
a way to form glycine

Bossa, J.B.; Duvernay, F.; Theule, P.; Borget, F.; d'Hendecourt, L.; Chiavassa, T. *A&AS* 2009

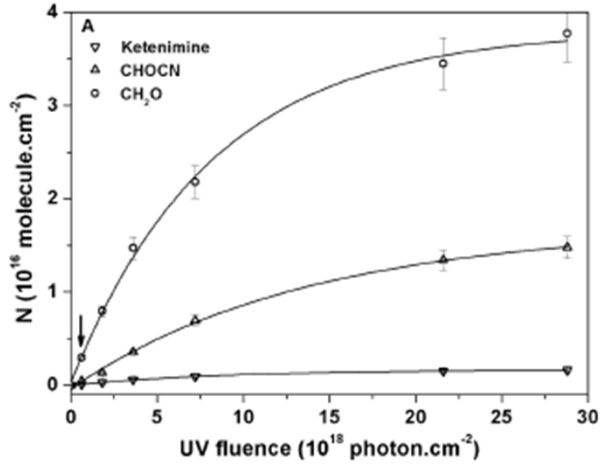
Photochemistry

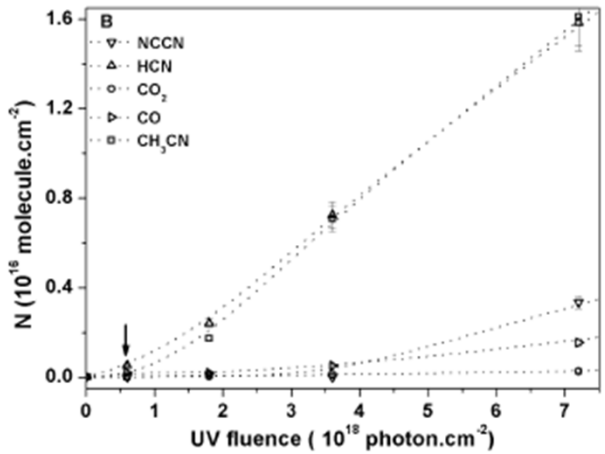
✓ destruction of COMs (photodissociation) and photo equilibrium





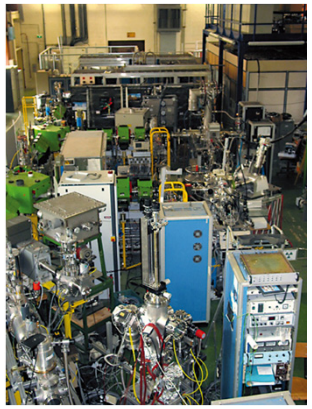
Danger et al., A&A, 2013





talk by Jean-Baptiste Bossa

Ion induced chemistry



GANIL

heavy-ion beams to mimic solar and stellar winds or galactic cosmic-rays

ice analogues bombardment by ions C^{q+} , O^{q+}, Fe^{q+}, S^{q+}, Ni^{q+}, $Zn^{q+,}$ with (q=1, 2, 3,…11) at kev- GeV

✓ destruction of molecules (dissociation cross-sections)

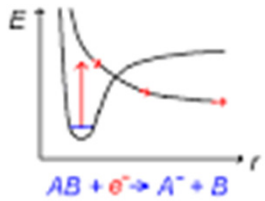
✓ production of molecules (production yields)

✓sputtering yields (heavy ions induced desorption)

- Dissociation cross-section ~ electronic stopping power $^{3/2}$,
  de Barros et al. MNRAS 2014
- Heavy ions induced chemistry
  Lv et al. A&A 2012, Andrade et al. MNRAS 2013, Mejia et al. MNRAS 2013,
  Bordalo et al. ApJ 2013, Ding et al. Icarus 2013, de Barros et al., MNRAS 2014, Lv et al., MNRAS 2014
  Baratta and Palumbo et al.,A&A 2014
- Ion bombardment products roughly similar to those by photons, protons or electrons,
  Munoz Caro et al., A&A 2014
- Compactification of the ice by ion bombardment
  Dartois A&A 2013

Electron induced chemistry

✓ chemical reactions



dissociative electron attachment $AB + e^- \rightarrow AB^{-*} \rightarrow A^- + B$

Formation of O_3 from 5 keV electron bombardment of solid oxygen
Bhalamurugan et al., ApJ 2007, Bennet and Kaiser, ApJ 2007

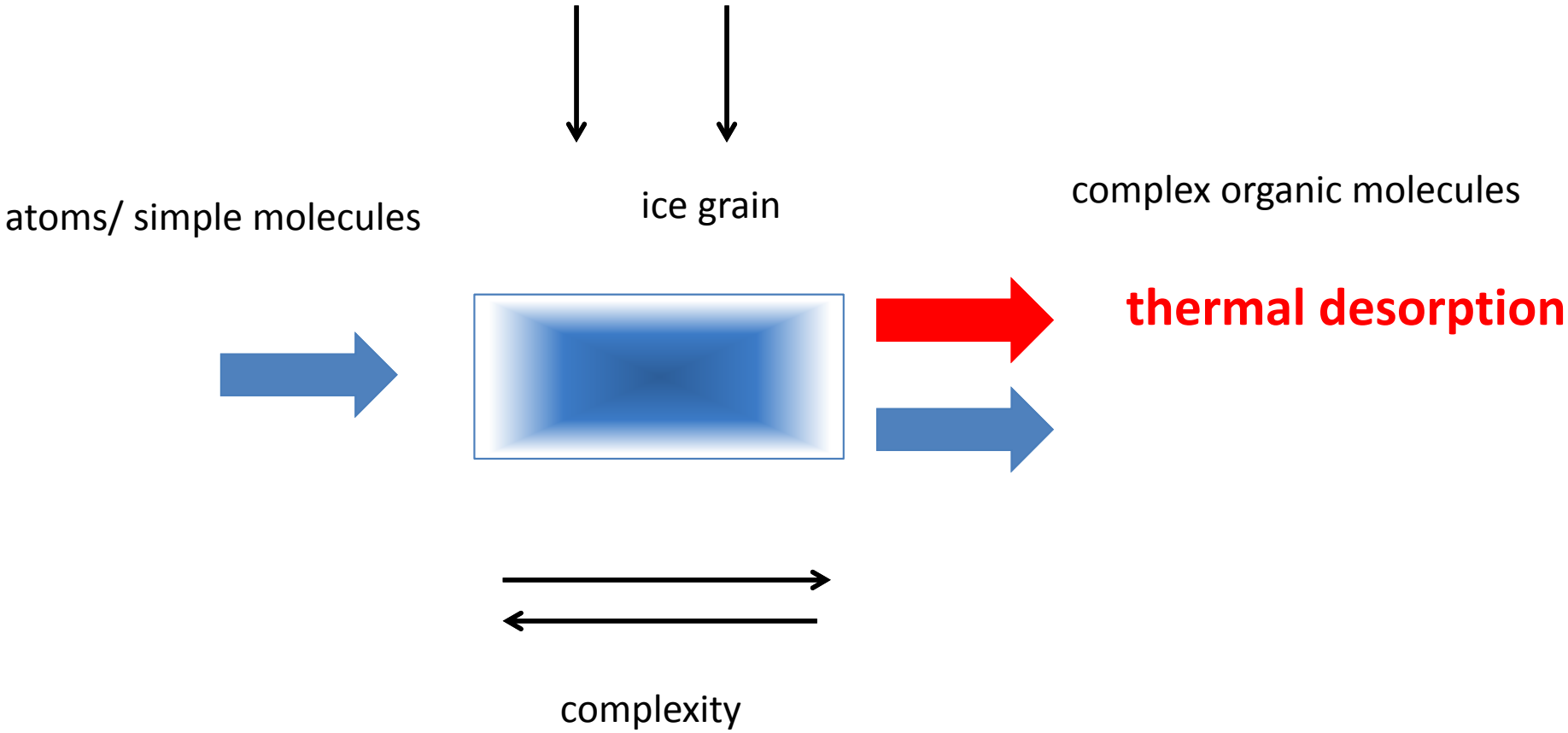
Electron bombardment of ice analogues and formation of COMs
Brant et al. ApJ 2014, Zhou et al., ApJ 2014, Surajit and Kaiser ApJ 2013, Kim and Kaiser, ApJ 2012, Kim and Kaiser, ApJ 2011

Role of low-energy electrons (few eV) in ice chemistry through resonant dissociative electron attachment
Lafosse et al., Surface Science, 2009 Bertin et al., PCCP 2009, Martin et al., Int.J. Mass Spec. 2008

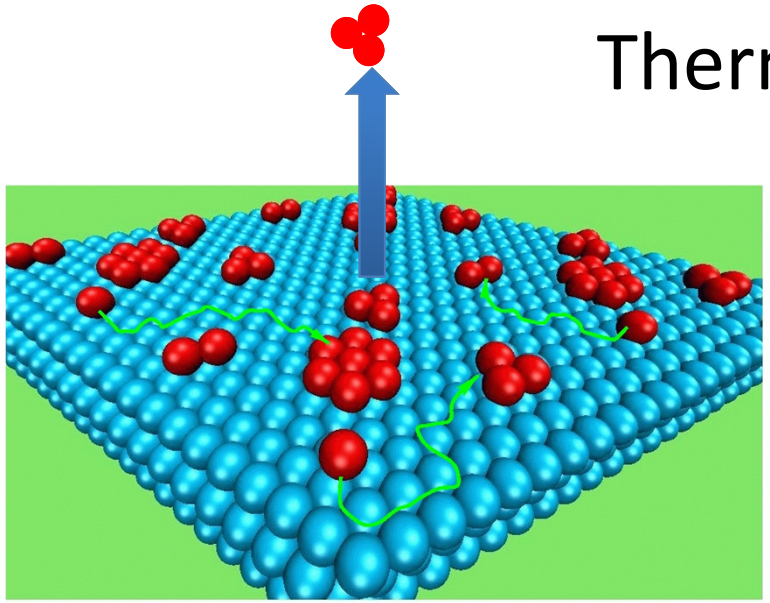
✓ charge transfer review in Baragiola R, Nuc. Inst. Meth.Phys.Res. B., 2005

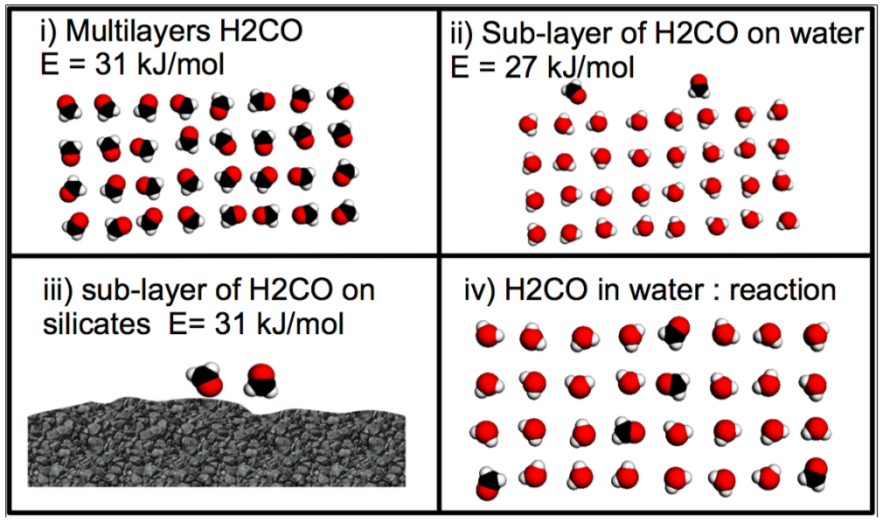
✓ electronic desorption (sputtering) by dissociative attachment or Auger desorption

Ice chemistry



Thermal desorption





crédit : F. Dulieu

the Wigner-Polanyi equation

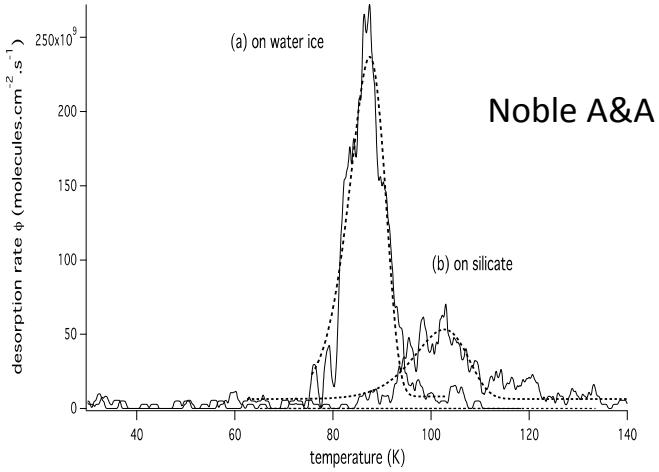
$$\frac{dX}{dt} = -k_{des} X^n$$

n= 0,1

$$k_{des}(T) = \nu \, e^{-\frac{E_a}{k_B T}}$$

$\nu \approx 10^{12}$-10^{13} s^{-1}

➔ (ν, E_{des})

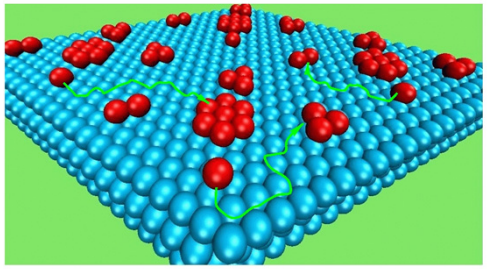


Noble A&A 2012

F. Dulieu, E. Congiu, Cergy-Pontoise

Thermal desorption

in the monolayer regime (surface coverage $\theta < 1$)



✓ dependence on the surface nature
(silicate, non-porous ice, crystalline ice)

✓ dependence on the surface coverage θ

Mol.	Surface	$E(\theta)$ / K				
		$E(0.1)$	$E(0.2)$	$E(0.5)$	$E(0.9)$	$E(1.0)$
O_2	$H_2O_{(np)}$	1161	1082	972	928	914
	$H_2O_{(c)}$	1149	1092	1017	975	969
	SiO_x	1255	1146	1019	945	930
CO	$H_2O_{(np)}$	1307	1247	1135	956	863
	$H_2O_{(c)}$	1330	1288	1199	1086	1009
	SiO_x	1418	1257	1045	896	867
CO_2	$H_2O_{(np)}$	2346	2258	2197	2197	2236
	$H_2O_{(c)}$	2514	2451	2364	2341	2361
	SiO_x	3008	2798	2487	2317	2271

formation of islands

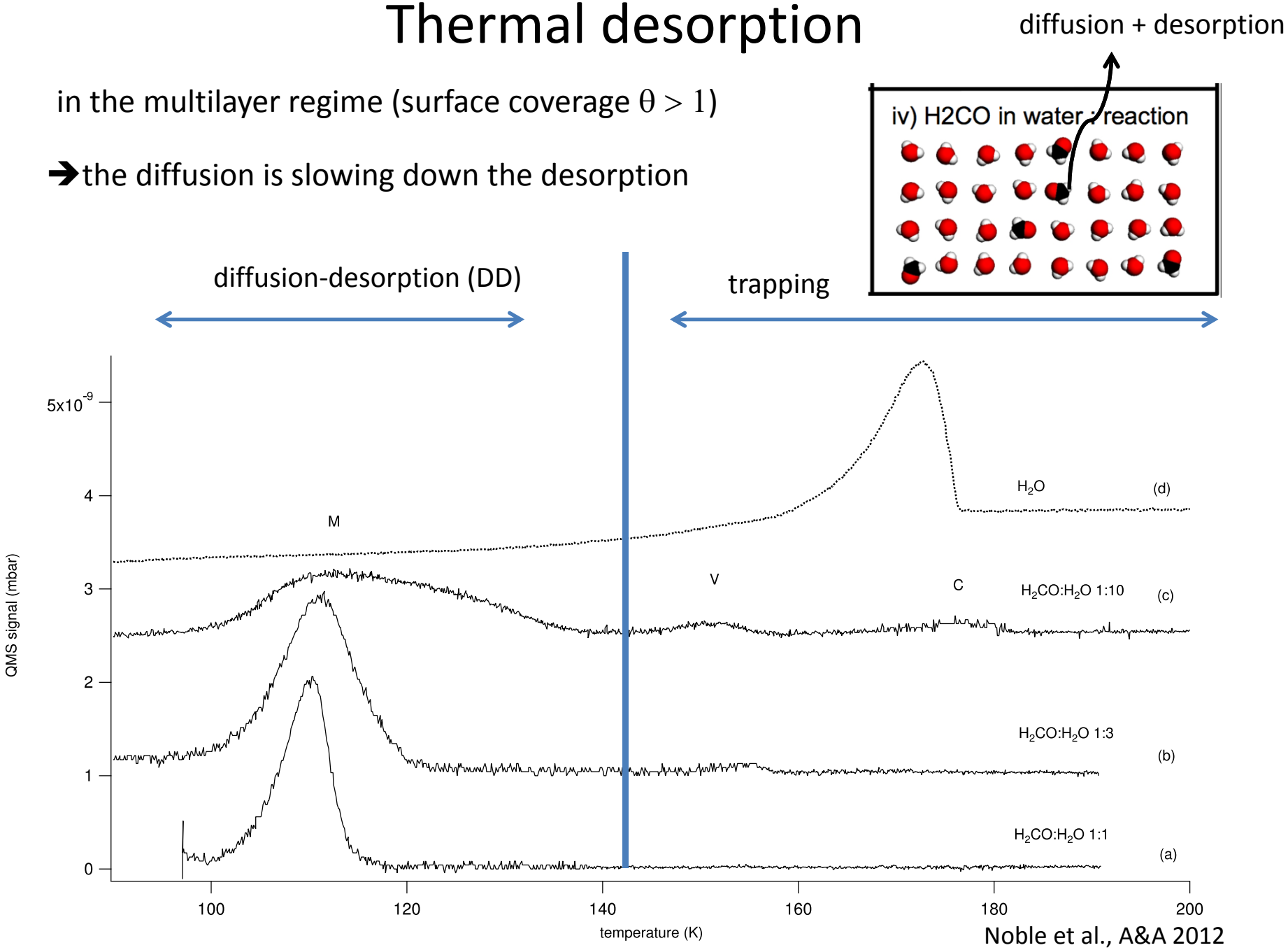
Molecule	Surface	Calculated values[a]	
		ν 10^{26} molec $cm^{-2}s^{-1}$	E_{ads} K
O_2	$H_2O_{(np)}$	6.9	898(30)
	$H_2O_{(c)}$	7.0	936(40)
	SiO_x	6.9	895(36)
	Au	*6.9*	*912(15)*[b]
		...	*925(25)*[c]
CO	$H_2O_{(np)}$	7.1	828(28)
	$H_2O_{(c)}$	7.1	849(55)
	SiO_x	7.1	831(40)
	Au	*7.2*	*858(15)*[b]
		...	*826(24)*[d]
		...	*855(25)*[e]
CO_2	$H_2O_{(np)}$	9.3	2267(71)
	$H_2O_{(c)}$	9.5	2356(83)
	SiO_x	9.3	2269(80)
	porous ASW	...	*2690(50)*[f]
	HOPG	...	*2982(-)*[g]

Noble et al., MNRAS 2012

Thermal desorption

in the multilayer regime (surface coverage $\theta > 1$)

➔the diffusion is slowing down the desorption

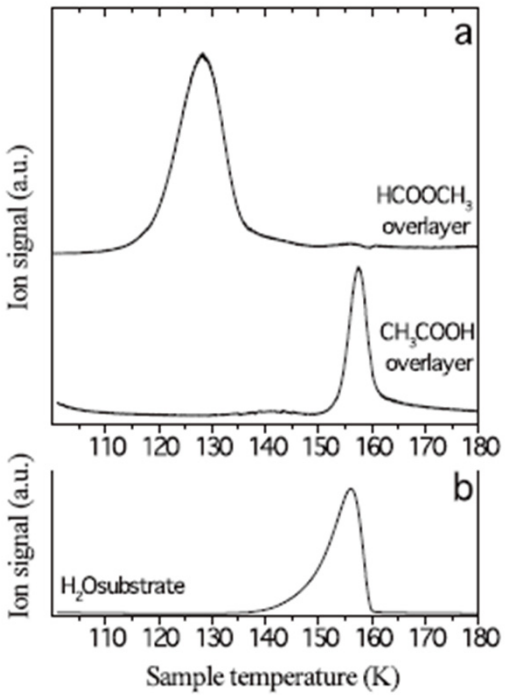


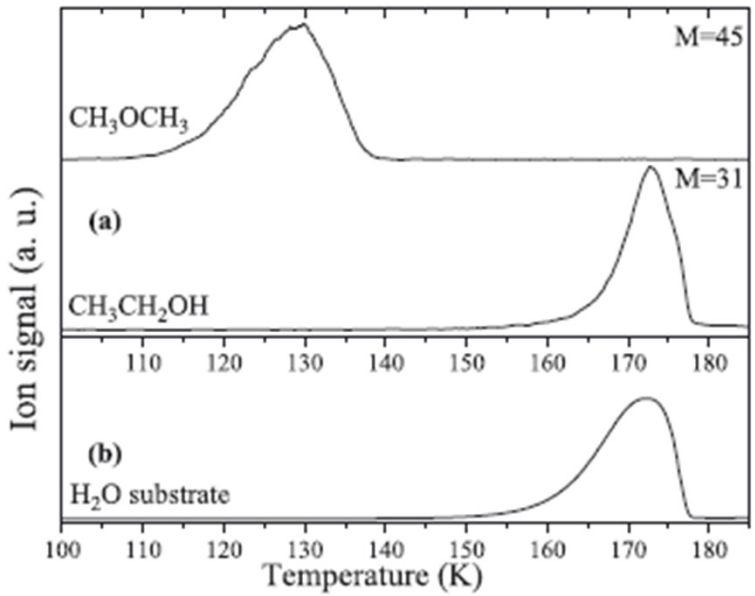
Noble et al., A&A 2012

Thermal desorption

in the multilayer regime (surface coverage $\theta > 1$)

Lattelais et al. A&A 2011
Bertin et al. J.Phys.Chem. 2011





methylformate $HCOOCH_3$

E_{des}= 37.4 □4.2 kJ.mol^{-1}

acetic acid CH_3COOH

E_{des}= 68 kJ.mol^{-1} (calc.)

dimethyl ether CH_3OCH_3

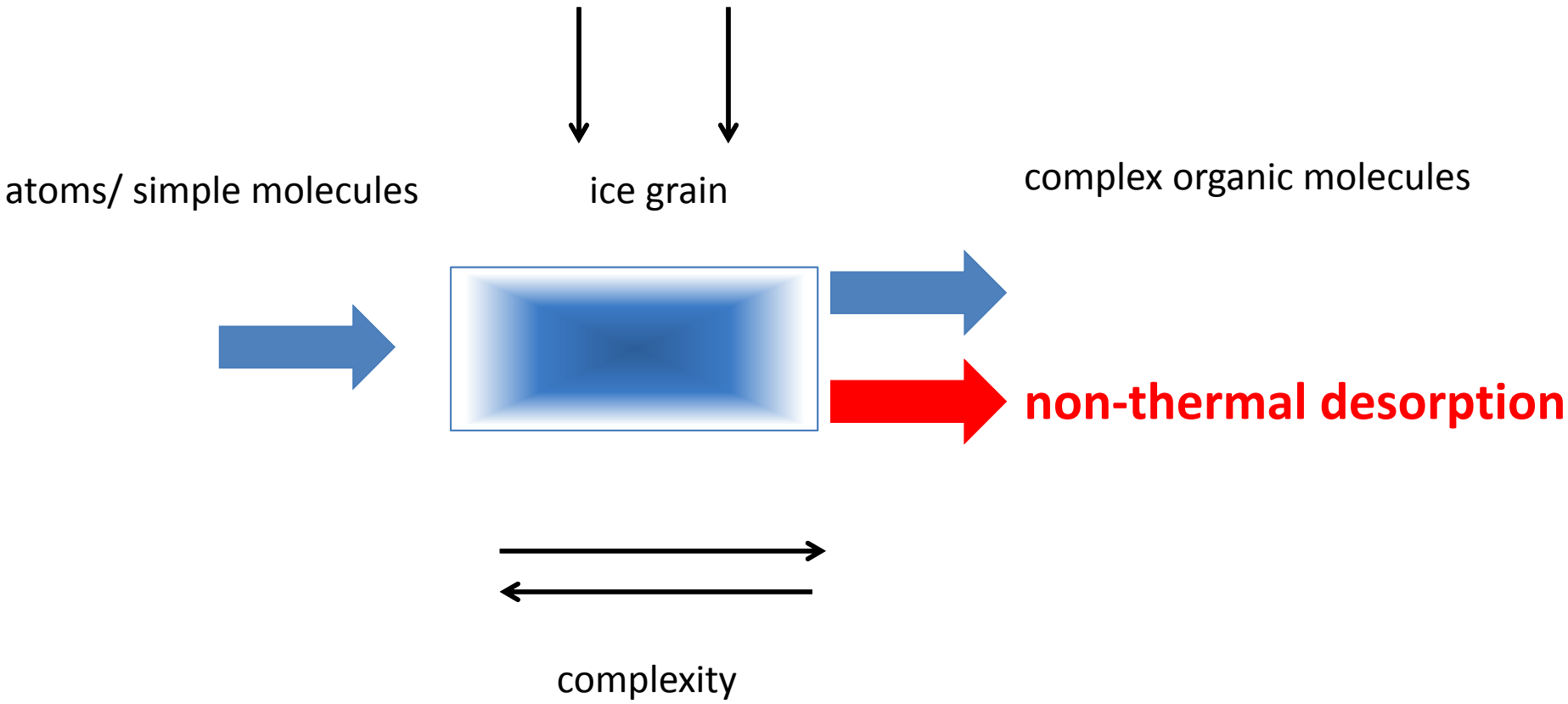
E_{des}= 34.0 □4.2 kJ.mol^{-1}

ethanol CH_3CH_2OH

E_{des}= 57 kJ.mol^{-1} (calc.)

□ the most stable isomer interacts more efficiently with the water ice than the higher energy isomer

Ice chemistry

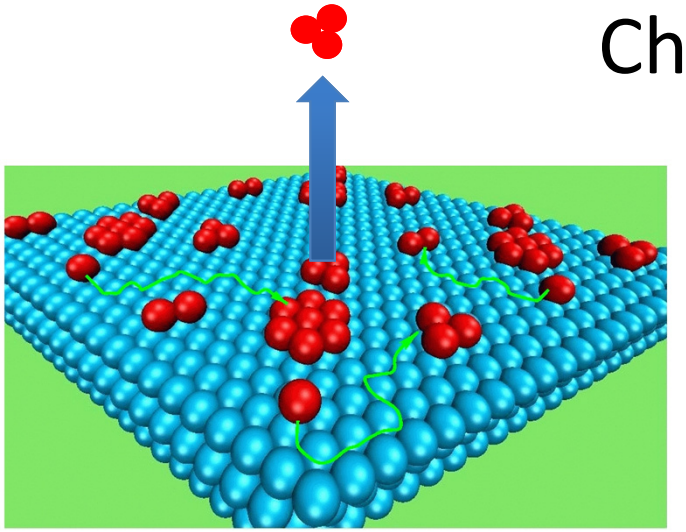


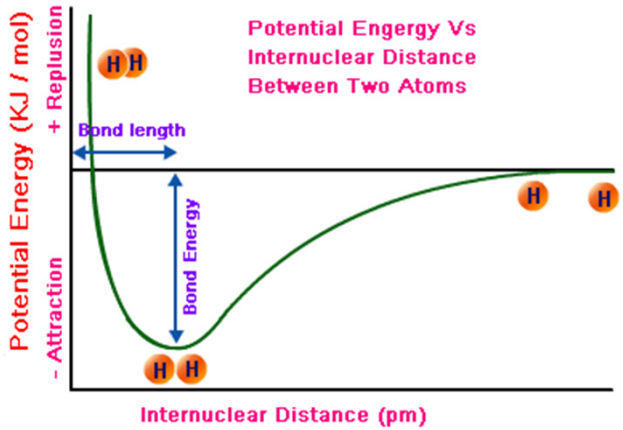
Non-thermal desorption

problem in accounting for the presence of COMs in cold media

- ✓ collisions with cosmic rays (heavy ions $m > m_{Fe}$)
- ✓ chemical desorption
- ✓ photodesorption

Chemical desorption





Chemical desorption efficiency of different reactions

the exothermicity of the chemical bond

in the monolayer regime (surface coverage $\theta < 1$)

Reaction	Exothermicity (eV)	Fraction released in gas phase
$OD + D \rightarrow D_2O$	5.2	>90%
$O_2 + D \rightarrow DO_2$	2.3	<10%
$DO_2 + D \rightarrow D_2O_2$	3.7	<10%
$DO_2 + D \rightarrow OD + OD$	1.6	
$D_2O_2 + D \rightarrow D_2O + OD$	3.1	<10%
$O + O \rightarrow O_2$	5.2	60% Dulieu et al. in prep.
$O + O_2 \rightarrow O_3$	1.1	≤10% Minissale et al. in prep.

Dulieu et al. Nature Scientific Reports, 2013

Photodesorption

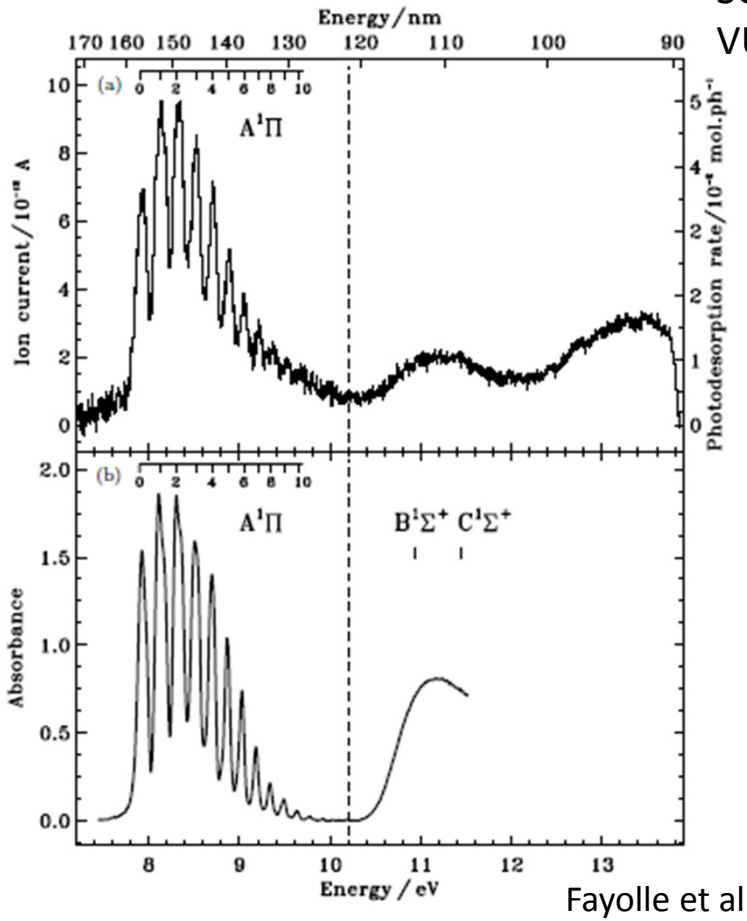
SOLEIL/DESIRS
VUV light source

a wavelength dependent mechanism

Ly α

the solid CO
photodesorption spectrum
at 18 K

the solid CO
absorption spectrum
at 10 K



Fayolle et al., ApJ Letters 2011

correlation of the desorption features with the transition $A^1\Pi \leftarrow X^1\Sigma^+(\upsilon', \nu''=0)$ vibronic bands

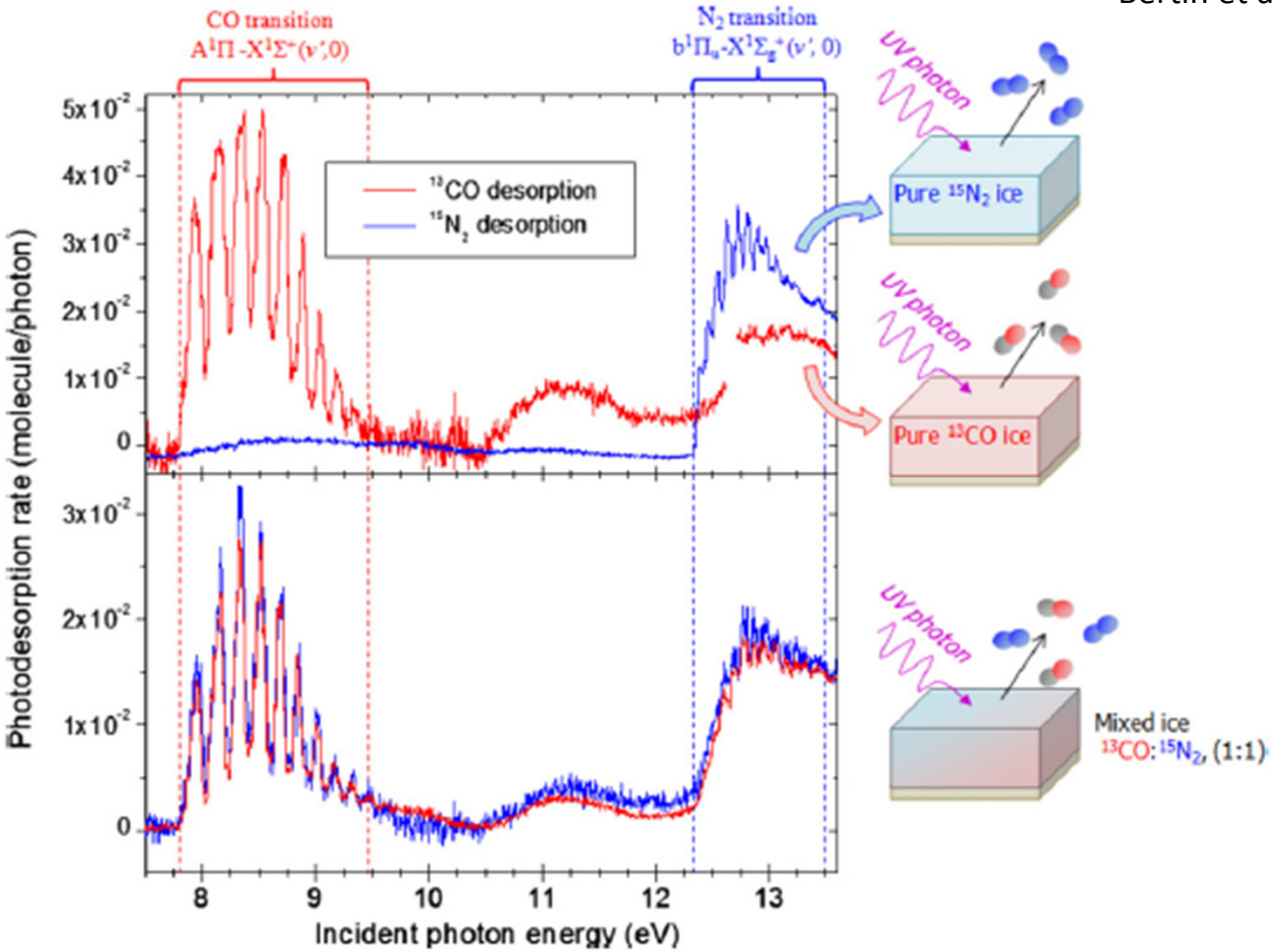
➔ Desorption Induced by Electronic transition (DIET)

Photodesorption

a mixture-dependent mechanism

the photodesorption spectrum is the sum of its components photodesorption

Bertin et al. ApJ 2013

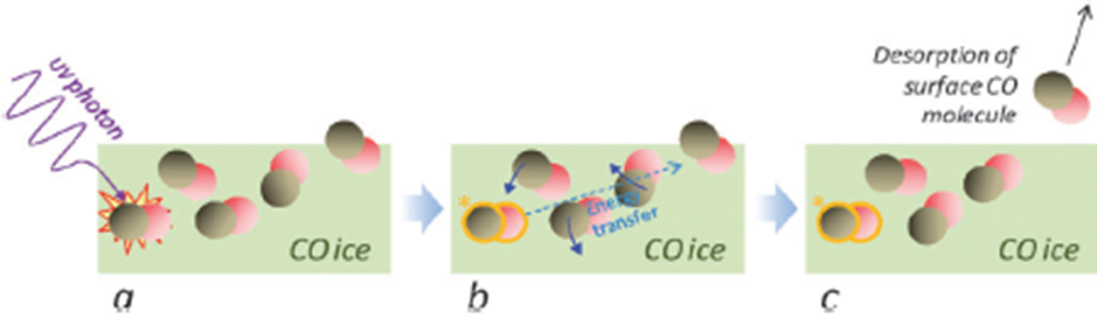


➔ the desorbing molecule is not necessarily the one which absorbs

Photodesorption

DIET : a three-step mechanism

Bertin et al. PCCP 2012



a : a sub-surface CO molecule is promoted into it $A^1\Pi$ state by a resonant VUV photon

b: the photodesorption efficiency depends on the energy distribution through:

- intramolecular vibrational energy relaxation (IVR)
- dissociation (w/o indirect desorption)
- intermolecular energy relaxation (EVR)

c : a surface CO receives enough kinetic energy and is ejected from the surface

Photodesorption

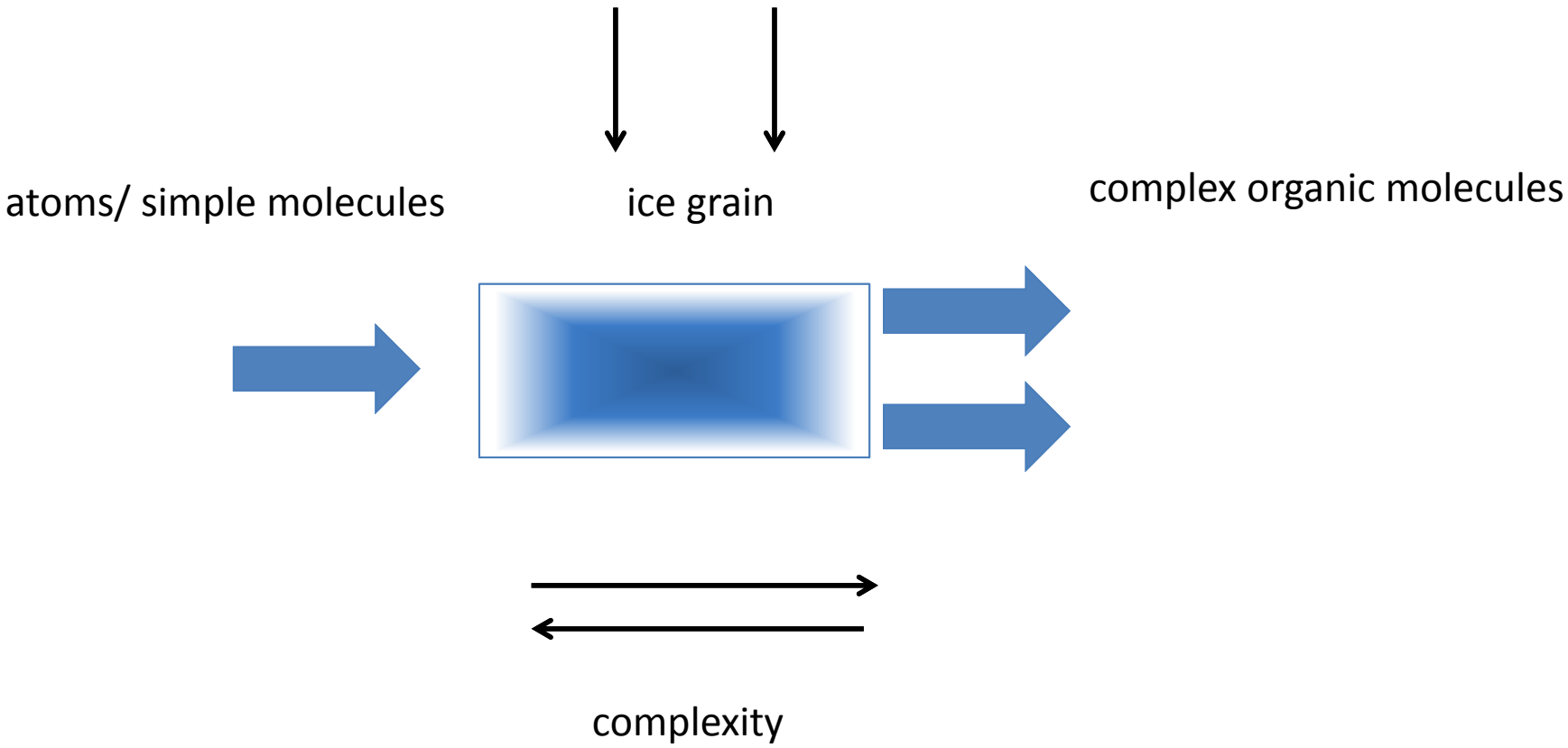
- ✓ photodesorption rates are wavelength dependent
  10^{-4} – 10^{-2} molecules /UV photons
  photodesorption from Lyα not efficient for CO, N_2, CO_2

- ✓ differential photodesorption yields available for any distinct insterstellar regions

- ✓ photodesorption and photochemistry interconnected (CO_2, COMs ?)

➡ poster by Mathieu Bertin

Conclusion


atoms/ simple molecules
ice grain
complex organic molecules
complexity

Conclusion

- increasing contribution of laboratory experiments and theoretical studies
- still a lot of work, but we are making progress in understanding solid-state chemistry
- efforts in quantifying each competing process (activation energies, cross sections,…)
- challenge to input the microphysics in a gas-grain code with the required level of details