Ice chemistry:

Formation of complex organic molecules in interstellar ice

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KIDA workshop on interstellar and planetary atmosphere chemistry

5, 6 and 7 May 2015, Paris

Outline

1. Molecular complexity and solid-state chemistry
2. Formation of complex molecules
3. Dynamics of COMs formation

The solid-state formation of COM

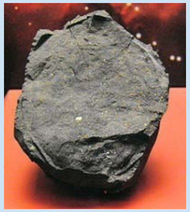
simple molecules

complex organic molecules

grain

organic residue

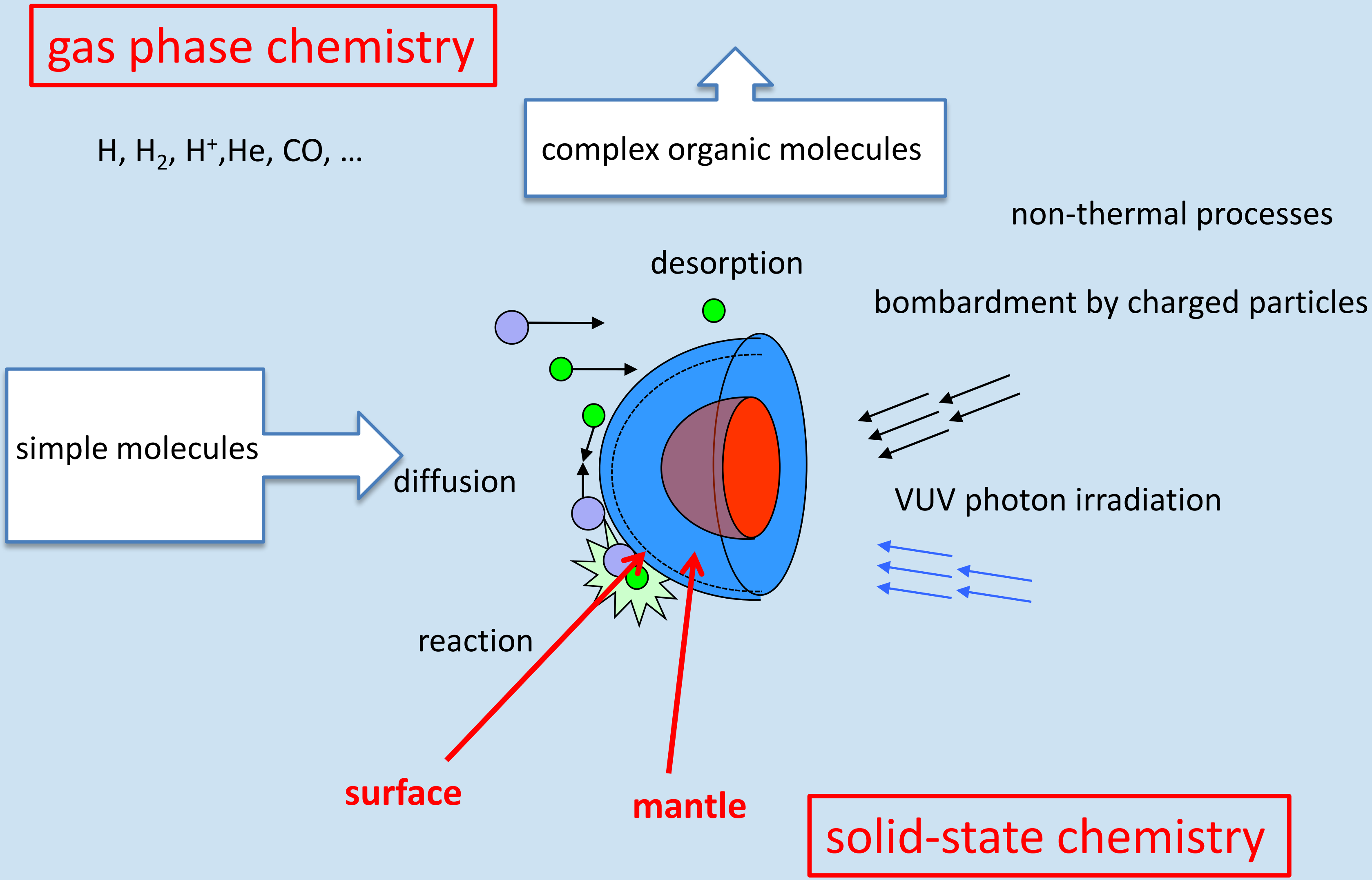
volatile species



refractory species

complexity

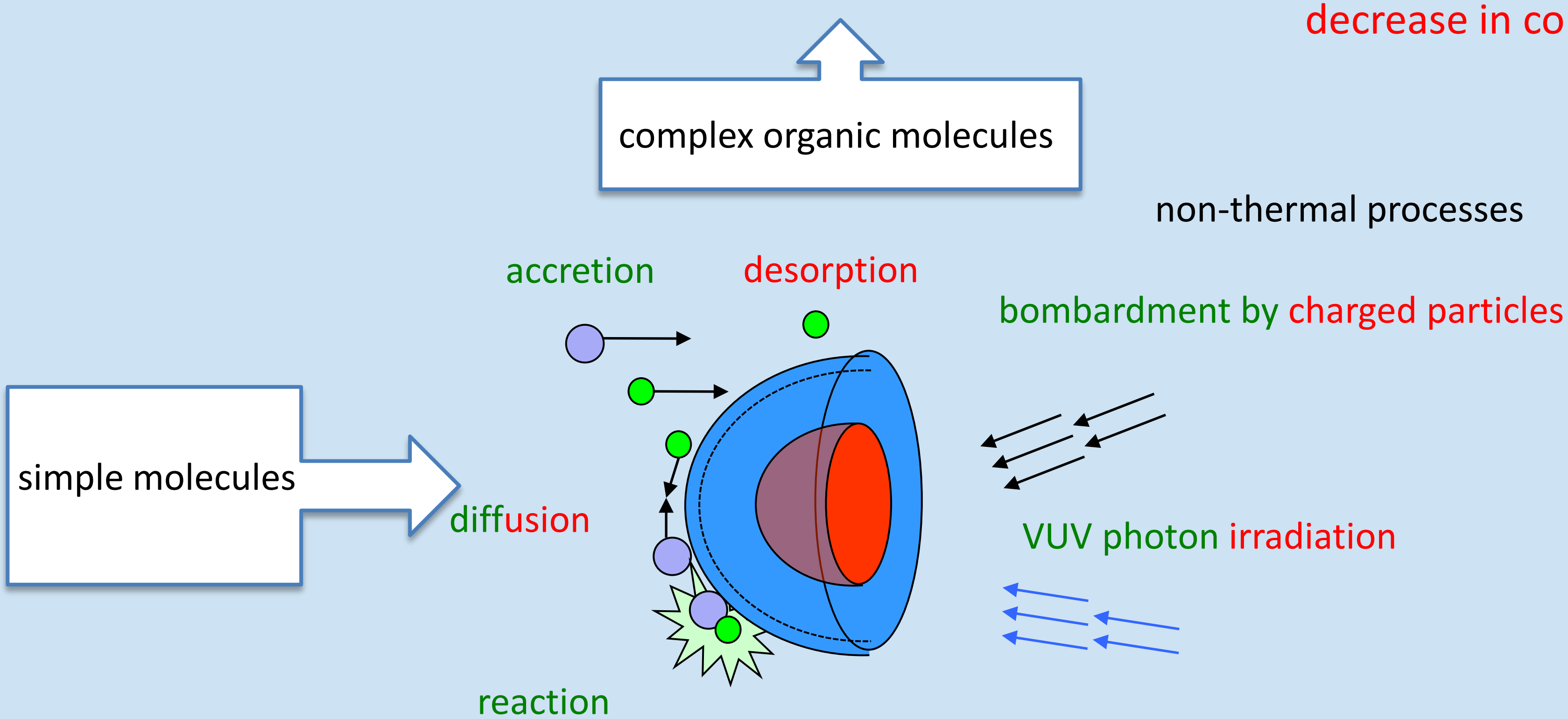
Modeling ice chemistry



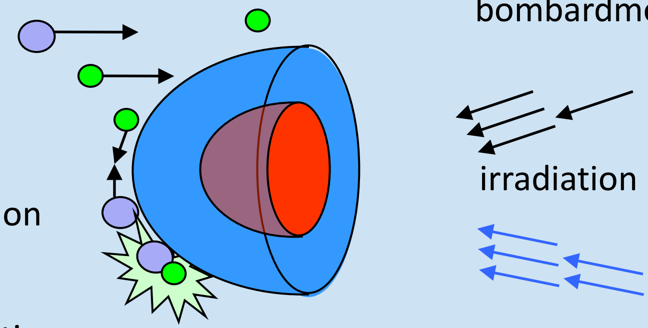
Modeling ice chemistry

increase in complexity (green arrow)

decrease in complexity (red arrow)



Modeling ice chemistry



$$\frac{dn_i}{dt} = \underbrace{\sum_j k_j n_j}_{\text{unimolecular reactions}} + \underbrace{\sum_{j,k} k_{jk} n_j n_k}_{\text{bimolecular reactions}} - \underbrace{n_i \sum_j k_j}_{\text{unimolecular reactions}} - \underbrace{n_i \sum_j k_{ij} n_j}_{\text{bimolecular reactions}}$$

- list of reactions
- reaction constants

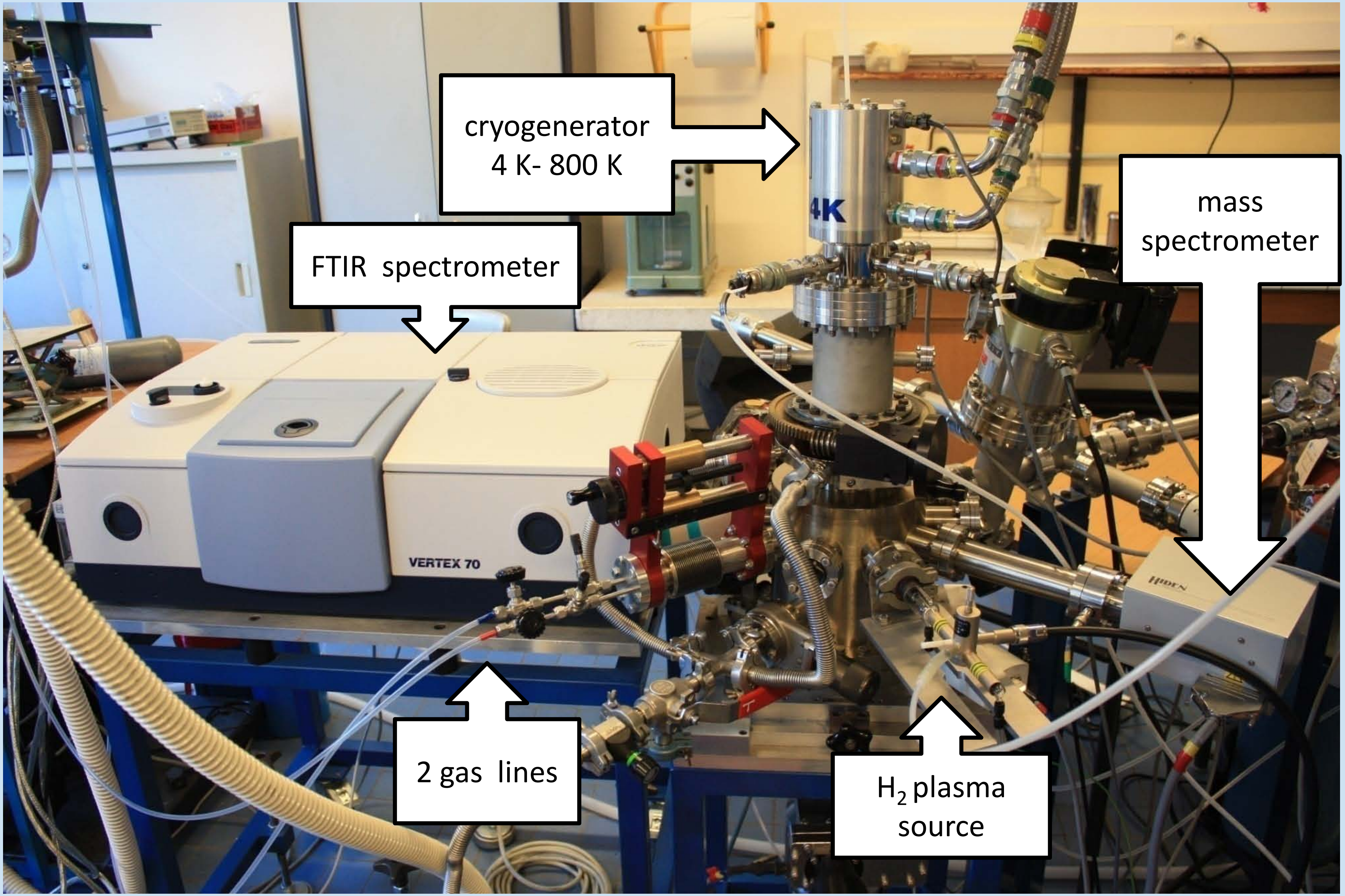
- accretion
- reactivity
- desorption
- photodissociation
- dissociation by CR and e$^-$
- reactivity

= a solid-state reaction network

a bottom-up (non-directed) approach , isolating each reaction and each process

Laboratory astrochemistry

(the RING experimental set-up)



Outline

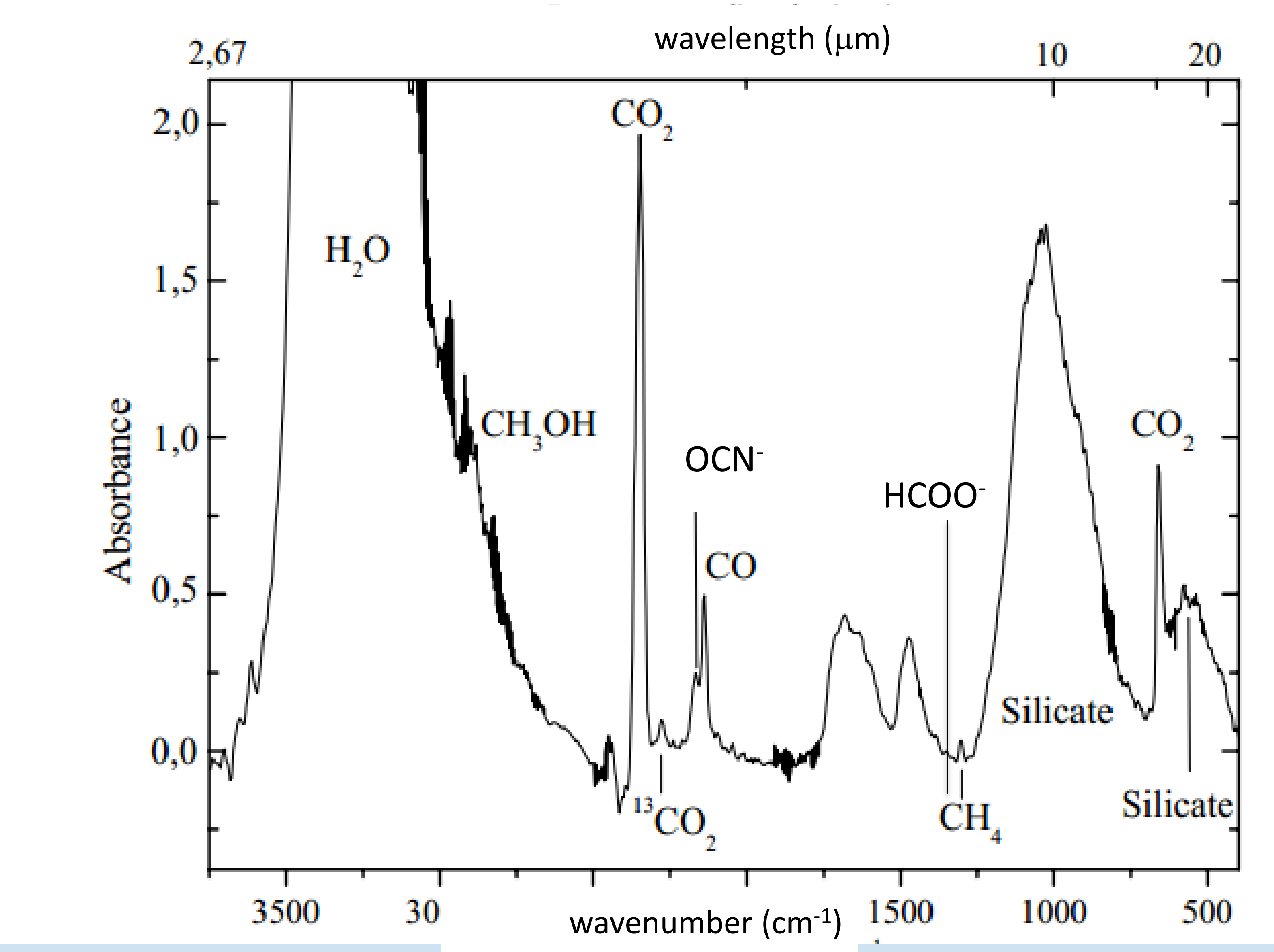
1. Molecular complexity and solid-state chemistry

2. Formation of complex molecules

   - Thermal formation of complex molecules
   - Photochemistry
   - Detection of COMS in the ISM

3. Dynamics of COMs formation

The initial molecules



NGC 7538 ISO spectrum

The initial molecules

(generation 0)

diffuse medium: H, C, O, N → molecular cloud

1. hydrogenation reaction of atoms

$H \rightarrow H_2$	Pirronello et al. (1997)
$C \rightarrow$ **CH_4**	Hiraoka et al. (1998)
$O \rightarrow$ **H_2O**	Hiraoka et al. (1998), Dulieu et al. (2010)
$OH^{\cdot} + H_2 \rightarrow$ **H_2O**	Oba et al. (2012) hydrogenation by molecular H_2
$N \rightarrow$ **NH_3**	Hiraoka et al. (1995)

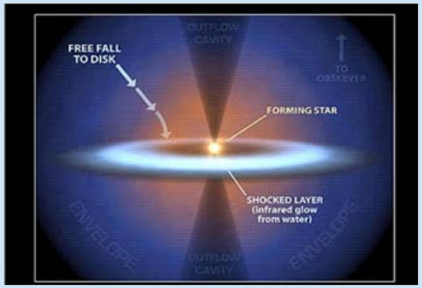
2. two heavy atom species and their hydrogenation products

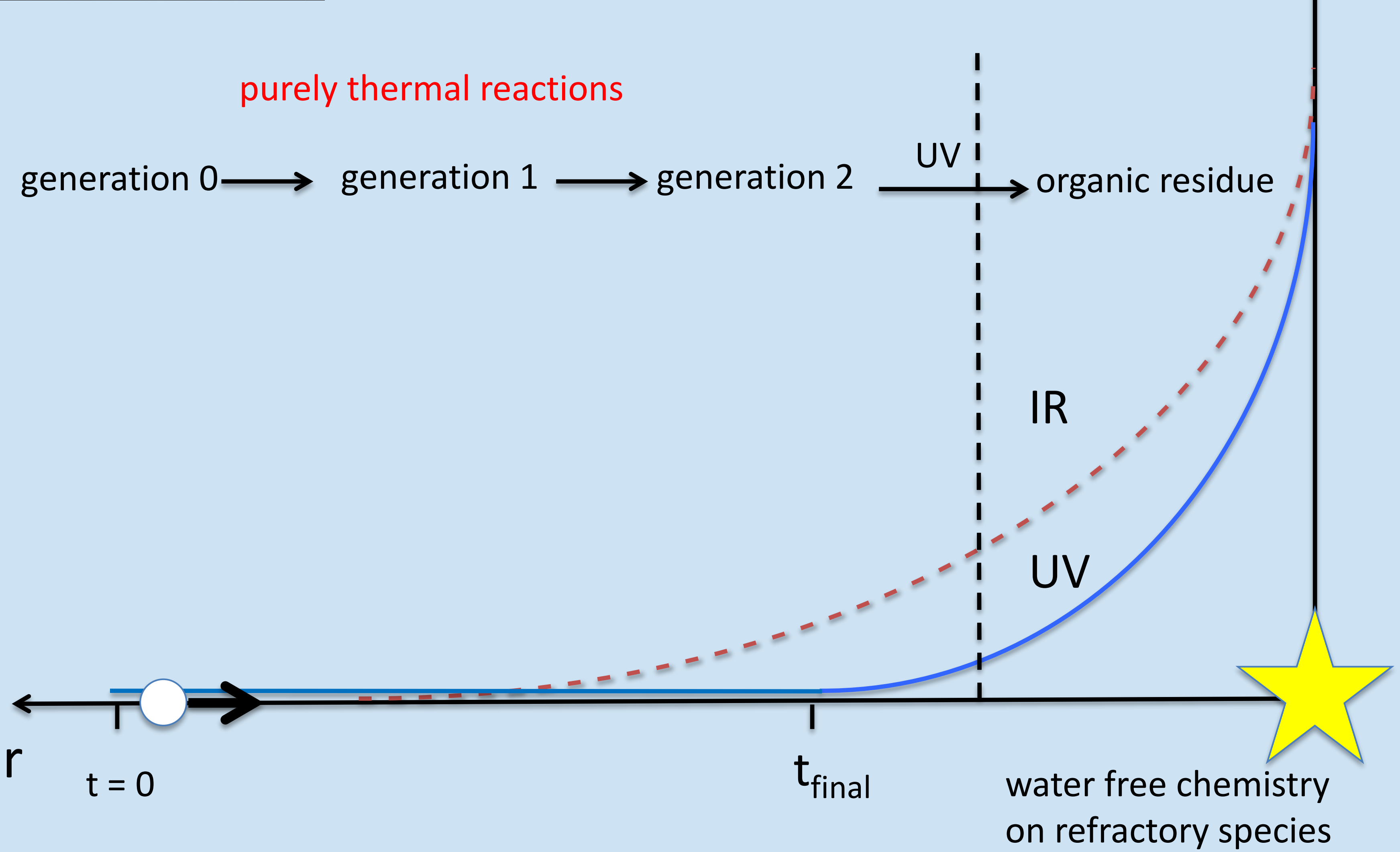
$C_2 \rightarrow$ **$C_2H_2 \rightarrow C_2H_4 \rightarrow C_2H_6$**	Hiraoka et al. (1999, 2000)
$O_2 \rightarrow$ **H_2O**	Ioppolo et al. (2008)
N_2	
$CO \rightarrow$ **$H_2CO \rightarrow CH_3OH$**	Hiraoka et al. (1994), Watanabe & Kouchi (2002)
$NO \rightarrow$ **NH_2OH**	Congiu et al. (2012)
$(CN^{\cdot} \rightarrow)$ **$HCN \rightarrow CH_2NH \rightarrow CH_3NH_2$**	Theule et al. (2011)
$CN^{\cdot} + H_2 \rightarrow$ **HCN**	Borget et al. (2015) hydrogenation by molecular H_2

3. three heavy atom molecules and their hydrogenation products

HCOOH	Ioppolo et al. (2011)
CO_2	Oba et al. (2010), Ioppolo et al. (2011b), Noble et al. (2011)
$CH_3CHO \rightarrow C_2H_5OH$ (and CH_4 and CH_3OH)	Bisschop et al. (2007)

Star formation and the warm-up of the ices



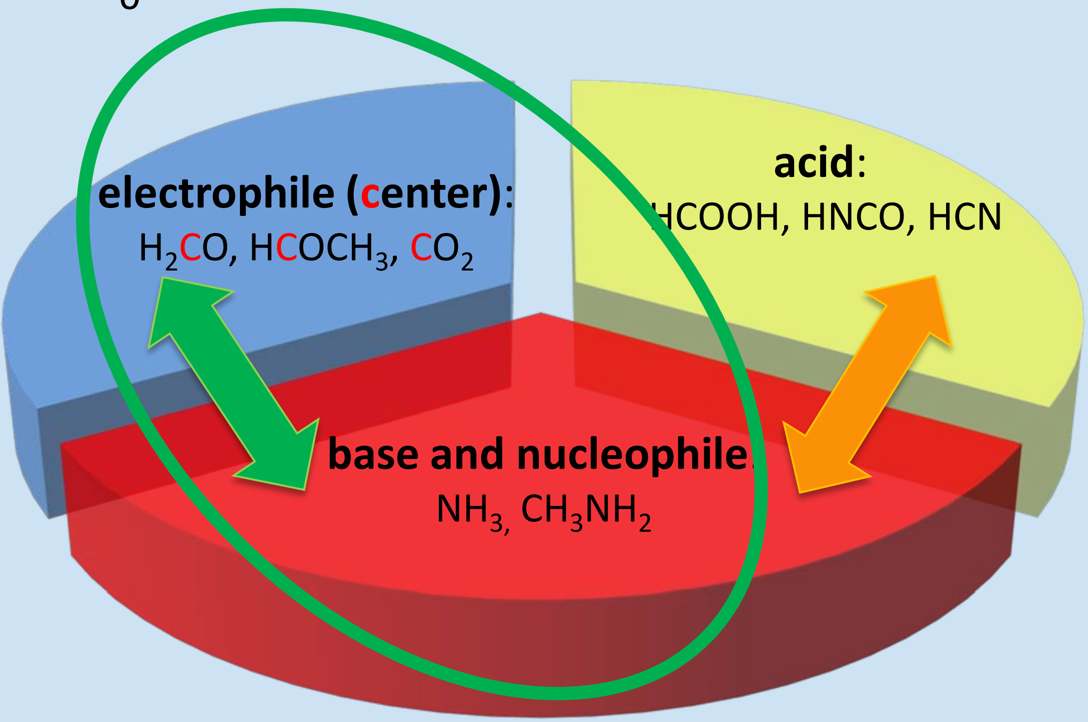


Inventory of the thermal reactions in the ice mantle

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											
…											

Thermal reactivity in the ice mantle

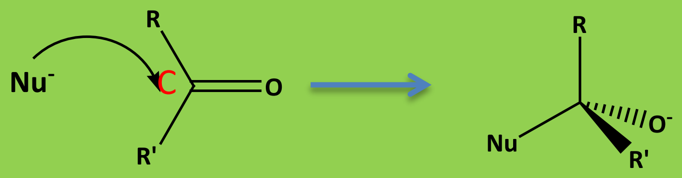
G_0 molecules:



acid-base reaction:

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

nucleophilic addition:



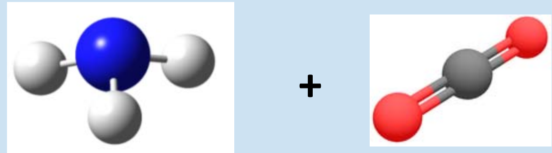
$G_0 \xrightarrow{+G_0} G_1 \xrightarrow{+G_0, G_1} G_2 \xrightarrow{+G_0, G_1, G_2} \ldots\ldots$

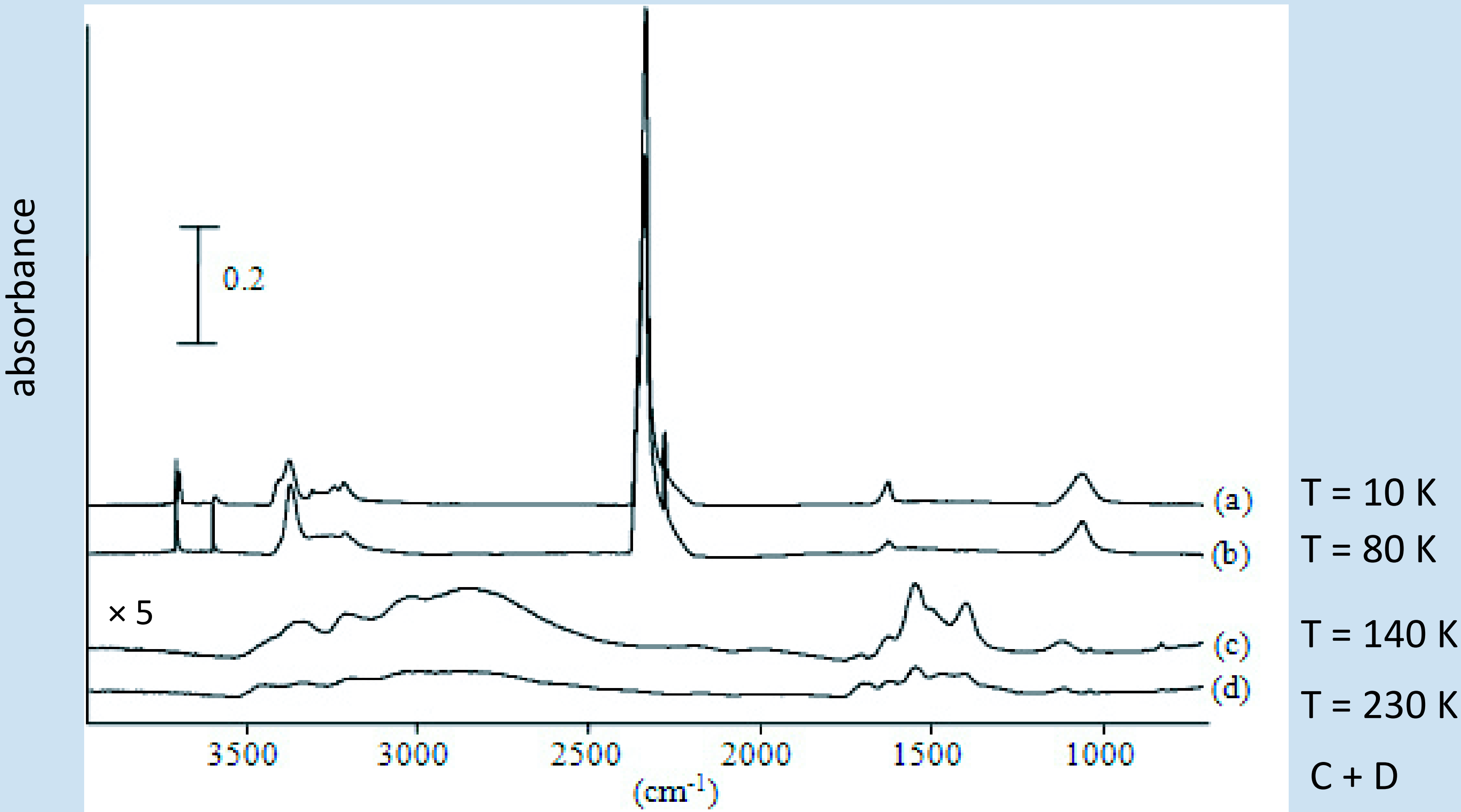
initial molecules | complex molecules

Inventory of the thermal reactions in the ice mantle

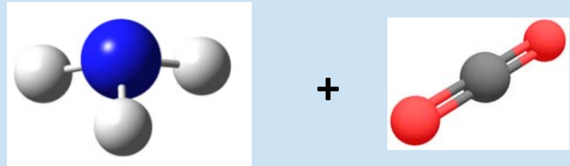
G0 molecules	H_2O	CO	CO_2	NH_3	CH_4	OCS	H_2CO	CH_3OH	$HCOOH$	$HNCO$	…
H_2O											
CO											
CO_2											
NH_3			?								
CH_4											
OCS											
H_2CO											
CH_3OH											
$HCOOH$											
$HNCO$											
…											

The NH_3 + CO_2 thermal solid-state reaction





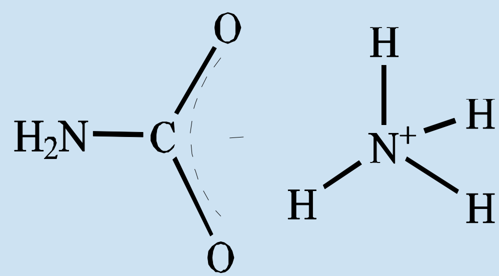
The NH_3 + CO_2 thermal solid-state reaction



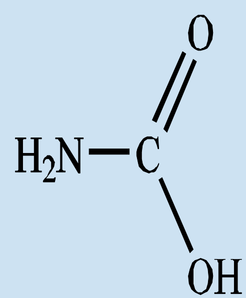
thermally produced species above 80K :

first-generation molecules
G1

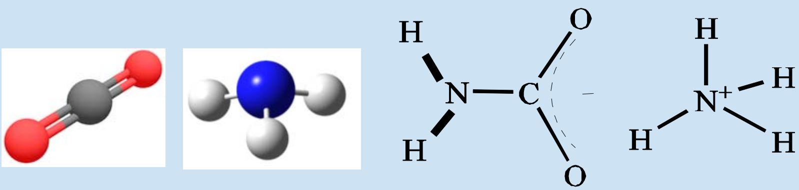
- C = ammonium carbamate (NH_4^+ NH_2COO^-)



- D = carbamic acid (NH_2COOH)

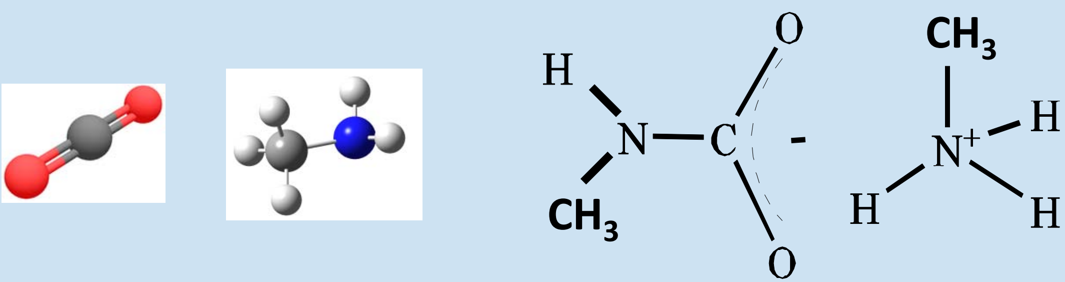


The NH_3 + CO_2 thermal solid-state reaction



J.B. Bossa, F. Duvernay, P. Theulé, F. Borget, T. Chiavassa, Chem. Phys.354(3), 211, 2008
Bossa, J.B.; Theule, P.; Duvernay, F.; Borget, F.; Chiavassa, T. *A&A,* 2008, *492*, 719

$$CO_2 + 2NH_3 \xrightarrow{80\ K} NH_2COO^-NH_4^+$$



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

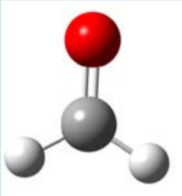
Inventory of the thermal reactions in the ice mantle

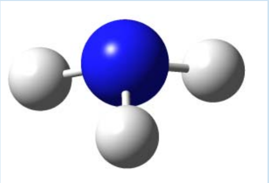
G0 molecules	H_2O	CO	CO_2	NH_3	CH_4	OCS	H_2CO	CH_3OH	HCOOH	HNCO	…
H_2O											
CO											
CO_2											
NH_3			$NH_4^+NH_2COO^-$								
CH_4											
OCS											
H_2CO											
CH_3OH											
HCOOH											
HNCO											
…											

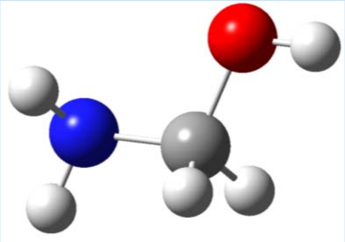
Inventory of the thermal reactions in the ice mantle

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											
…											

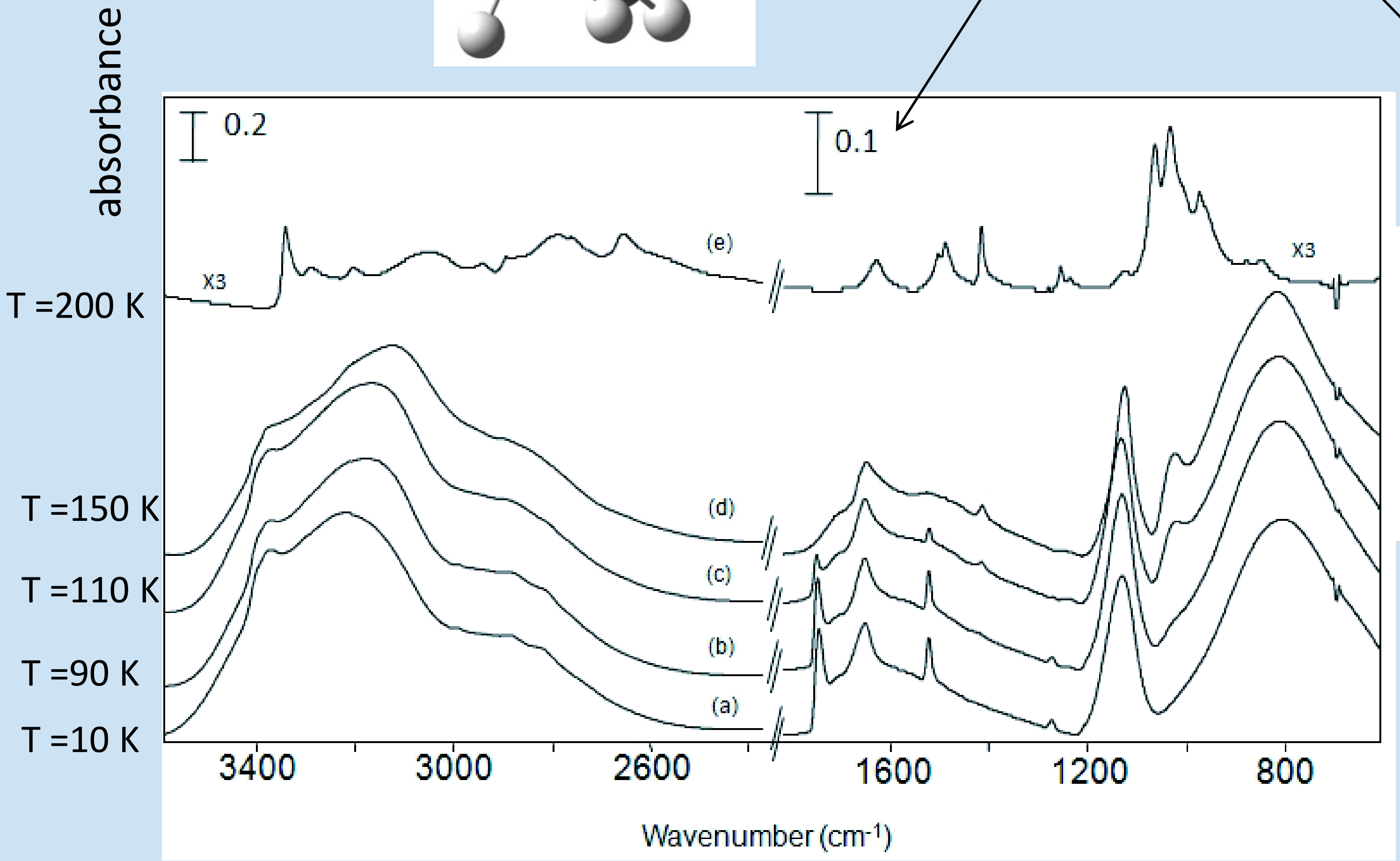
Thermal reaction in a $H_2CO:NH_3:H_2O$ ice

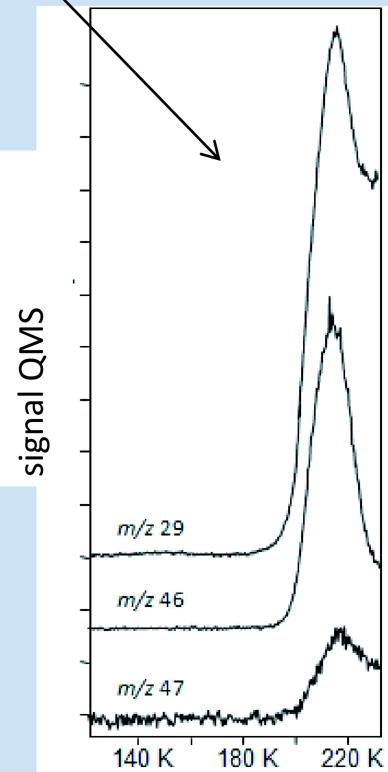






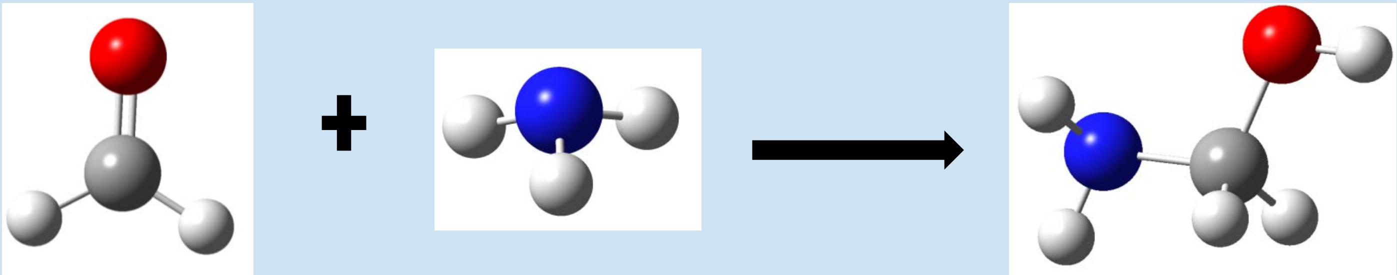
IR and mass spectra of NH_2CH_2OH





mass spectrum

Thermal reaction in a $H_2CO:NH_3:H_2O$ ice

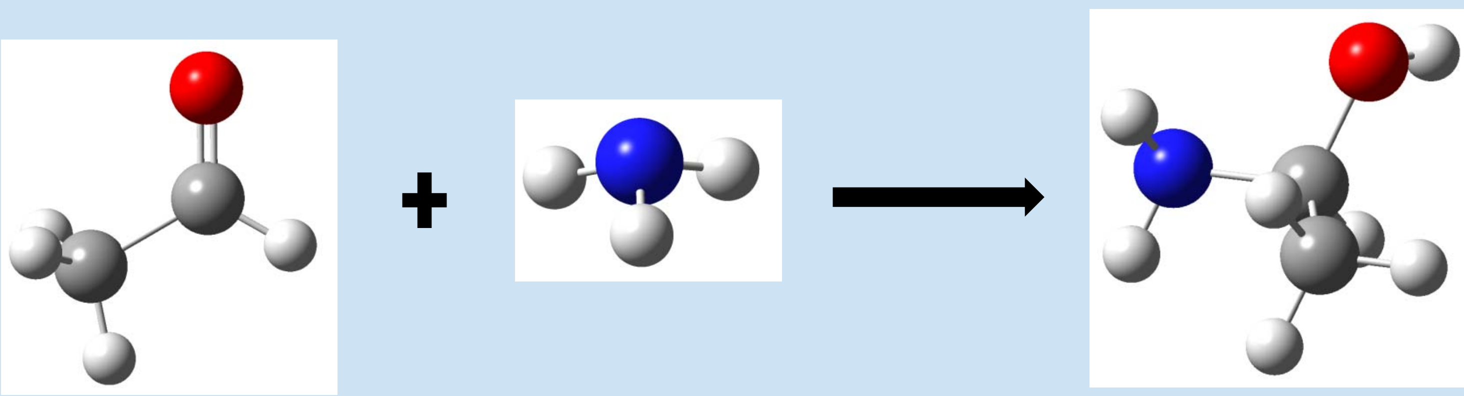


NH_2CH_2OH

H_2CO

aminomethanol

Bossa, J. et al. *ApJ* 2009, *707*, 1524



$NH_2CH(CH_3)OH$

CH_3CHO

alpha-aminoethanol (chiral)

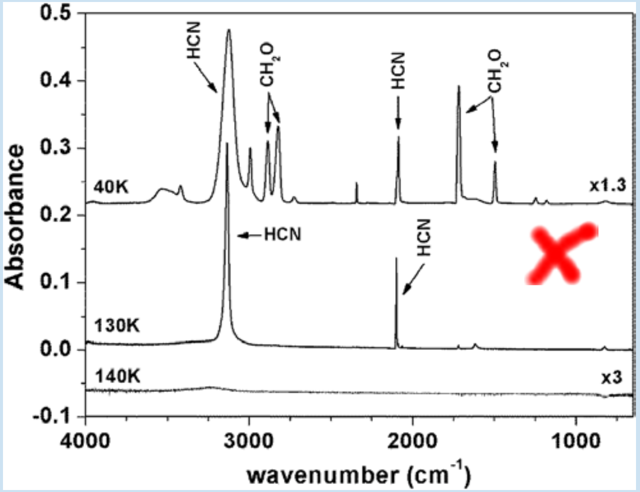
Duvernay et al., *A&A*, 2010 (523), 79

Inventory of the thermal reactions in the ice mantle

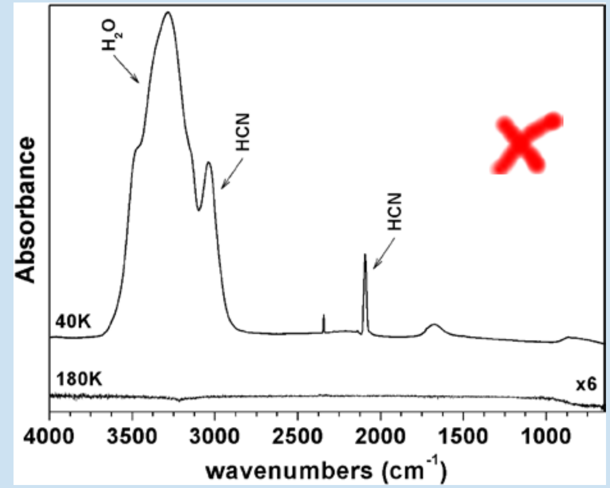
G0 molecules	H_2O	CO	CO_2	NH_3	CH_4	OCS	H_2CO	CH_3OH	HCOOH	HCN	…
H_2O											
CO											
CO_2											
NH_3											
CH_4											
OCS											
H_2CO										?	
CH_3OH											
HCOOH											
HNCO											
…											

The H_2CO + HCN thermal solid-state reaction

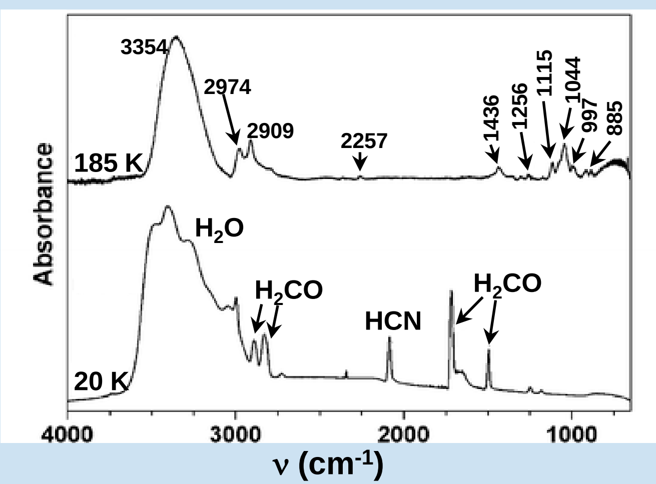
HCN + H_2CO

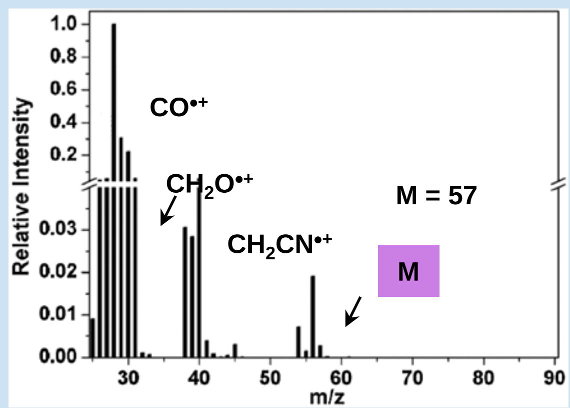


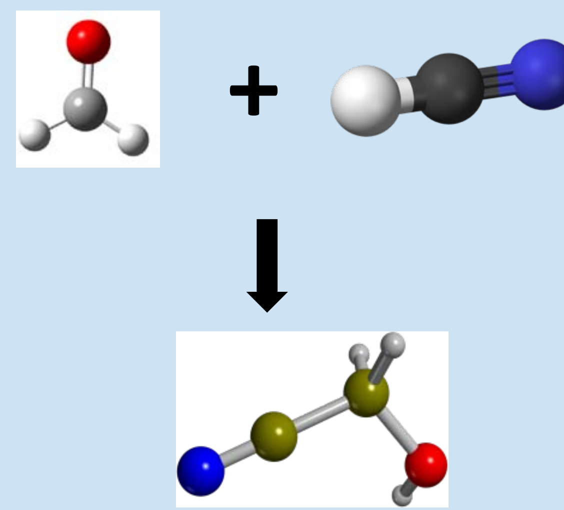
HCN + H_2O



HCN + H_2CO + H_2O (1:1:1)



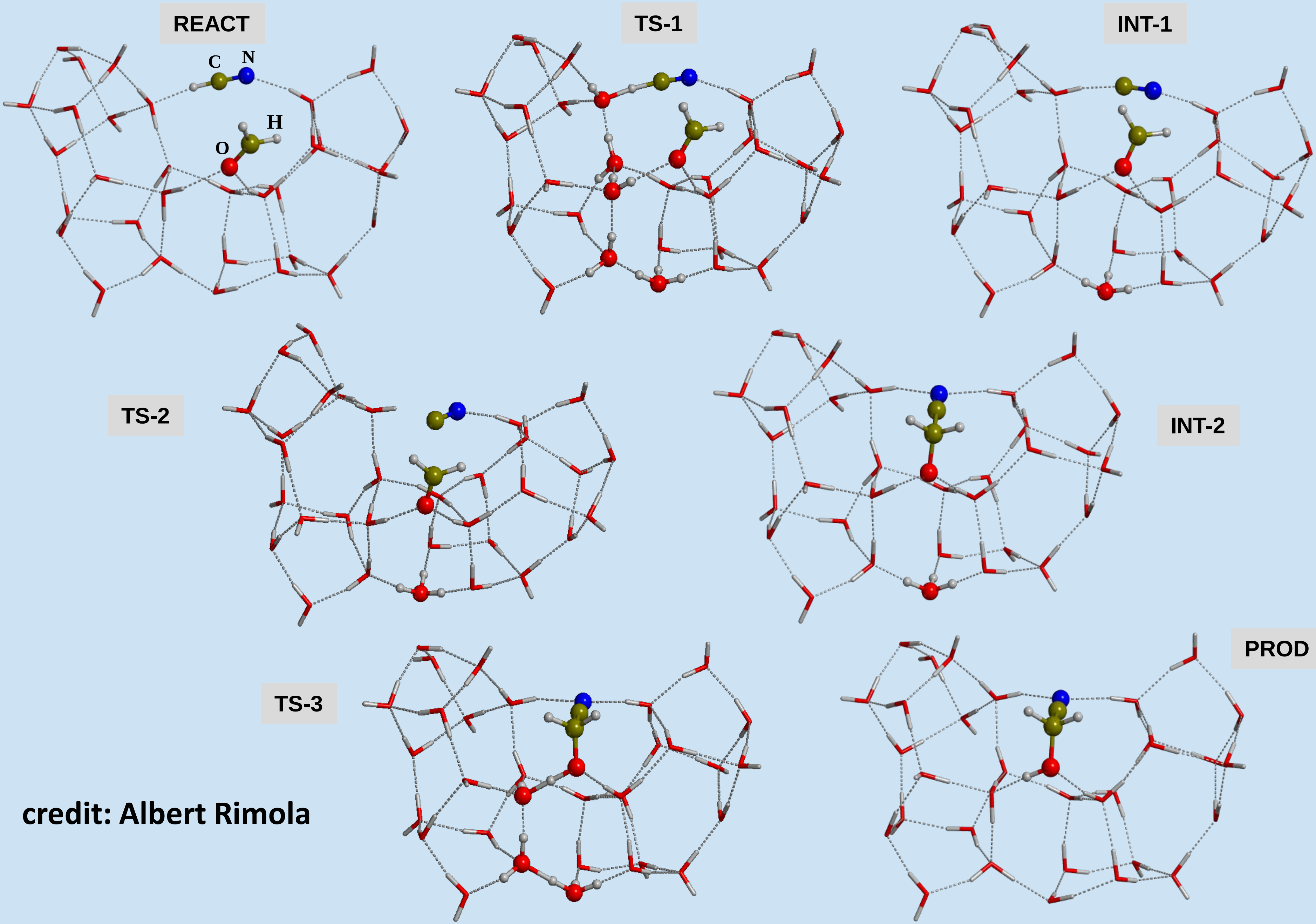




hydroxyacetonitrile $HOCH_2CN$

Danger et al., 2013

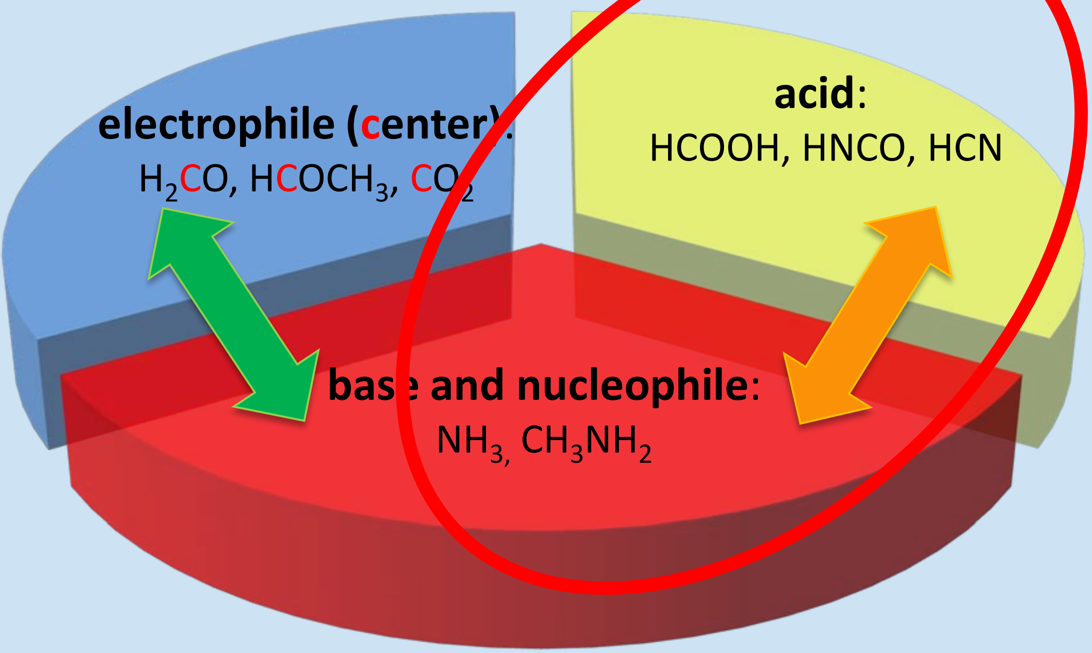
Atomistic interpretation of hydroxyacetonitrile formation



credit: Albert Rimola

Thermal reactivity in the ice mantle

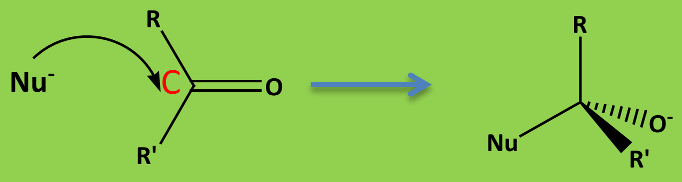
G_0 molecules:



acid-base reaction:

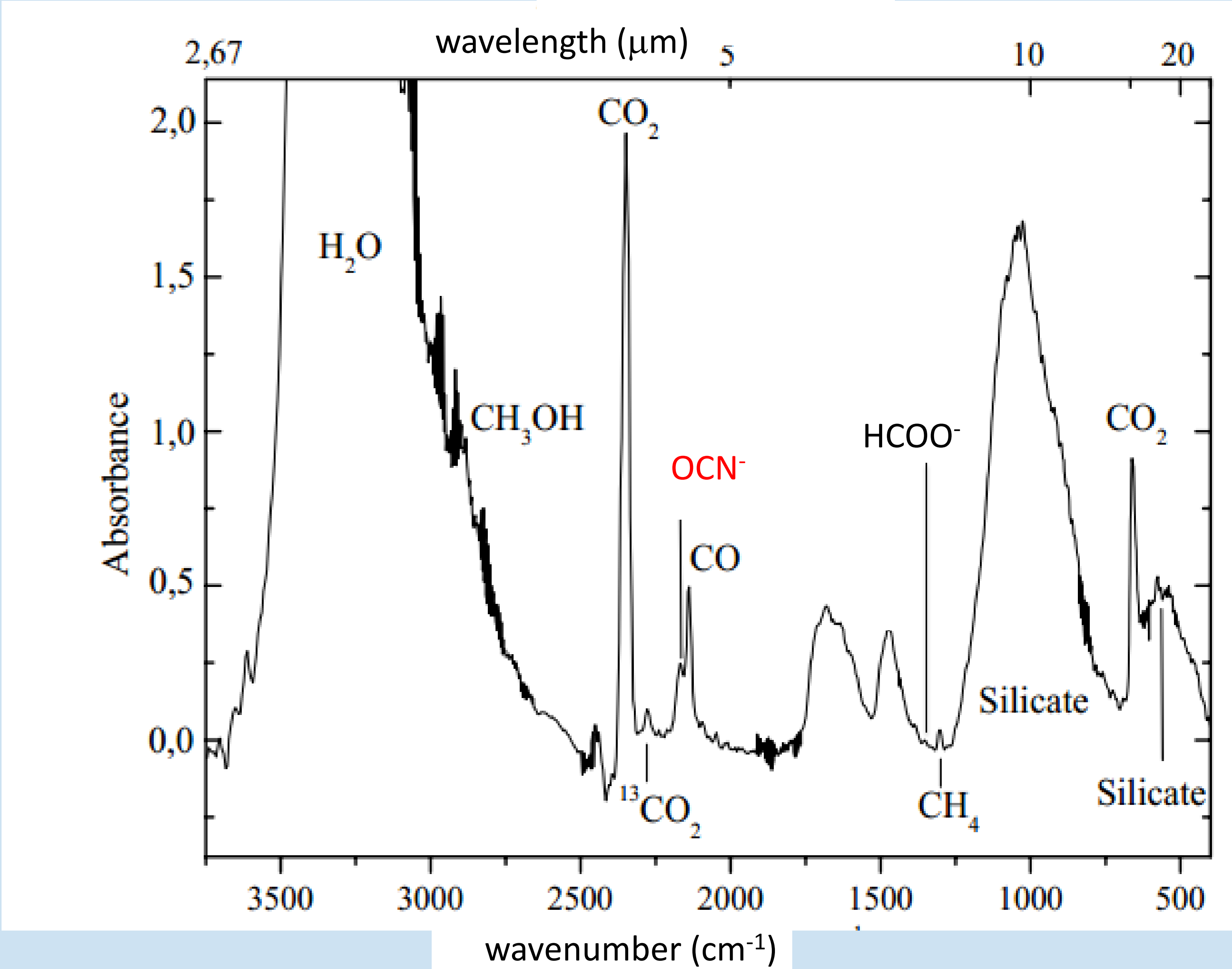
$AH + B \rightarrow A^- + BH^+$

nucleophilic addition:



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

initial molecules | complex molecules



NGC 7538 ISO spectrum

OCN^- formation and destruction

acid-base thermal reactions:

Formation

$$HNCO + NH_3 \rightarrow OCN^- + NH_4^+$$

Demyk et al. A&A 1998, Raunier et al., JCP 2004, Van Broekhuizen et al., A&A 2004, Mispelaer A&A 2012

$$HNCO + H_2O \rightarrow OCN^- + H_3O^+$$

Raunier S. et al., JCP, 2003, Theule A&A 2011

Destruction

$$OCN^- + H_3O^+ \rightarrow HOCN + H_2O$$

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										$H_3O^+OCN^-$	
CO											
CO_2											
NH_3											
CH_4											
OCS											
H_2CO											
CH_3OH											
HCOOH											
HNCO											
…											

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											
CO											
CO_2											
NH_3										$NH_4^+OCN^-$	
CH_4											
OCS											
H_2CO											
CH_3OH											
HCOOH											
HNCO											
…											

Thermal reactivity in the ice mantle

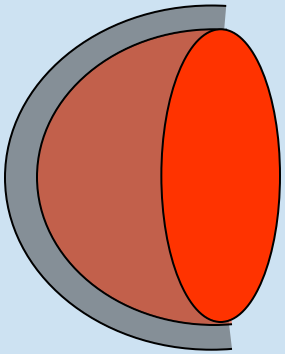
G0 molecules	H_2O	CO	CO_2	NH_3	CH_4	OCS	H_2CO	CH_3OH	HCOOH	HCN	…
H_2O											
CO											
CO_2											
NH_3										$NH_4^+CN^-$	
CH_4											
OCS											
H_2CO											
CH_3OH											
HCOOH											
HNCO											
…											

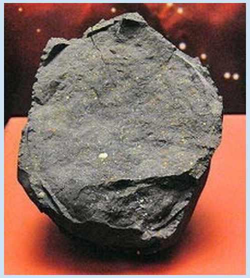
Thermal reactivity in the ice mantle

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	$H_3O^+OCN^-$			$NH_4^+OCN^-$							
…											

Toward more and more complexity: the organic residue

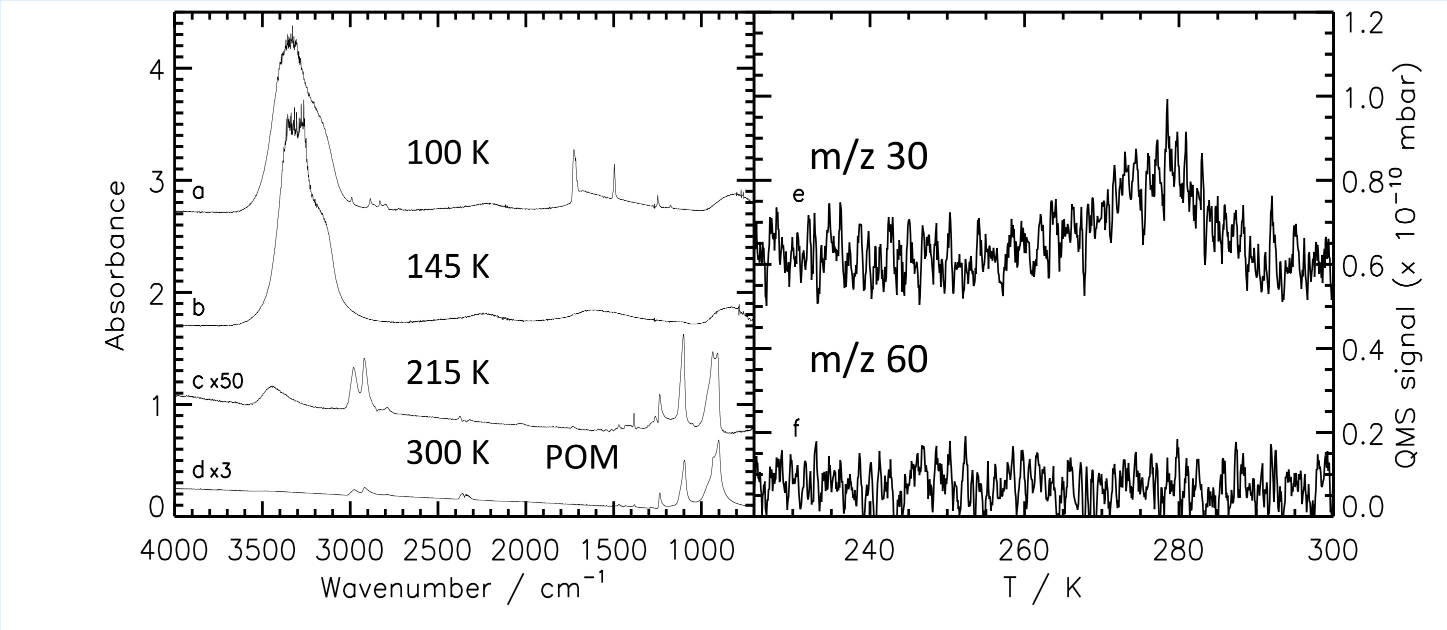
non-volatile organic matter



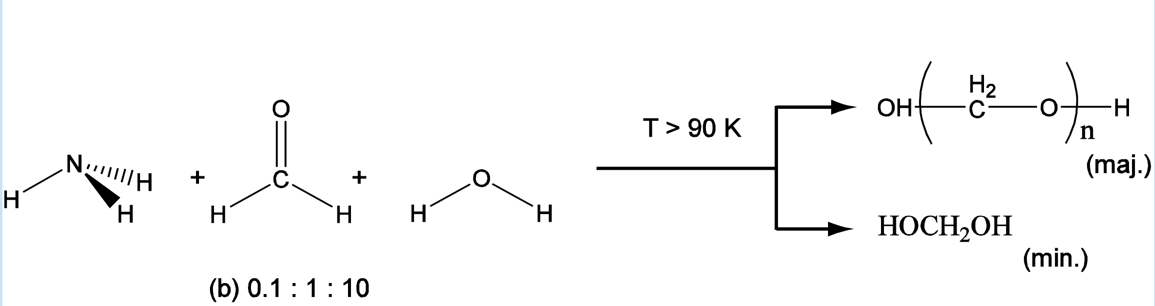


Condensation reactions in the ice mantle

H_2CO : H_2O thermal reactivity



H_2CO : H_2O mixture (1:14)



polyoxymethylene (POM)

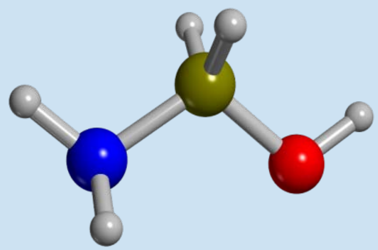
methanediol

Formation of methanediol $HOCH_2OH$

Duvernay et al., ApJ 2014

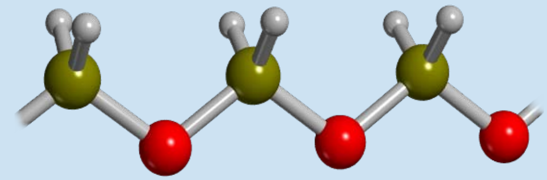
H_2O-dominated with $[NH_3]/[H_2CO] > 2$

$$NH_3 + H_2CO \rightarrow NH_2CH_2OH$$



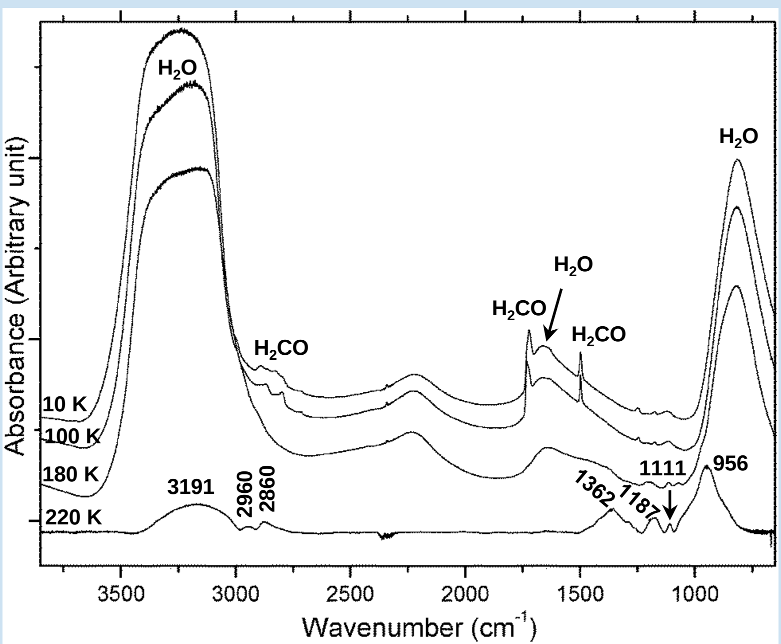
H_2O-dominated with $[NH_3]/[H_2CO] < 0.03$

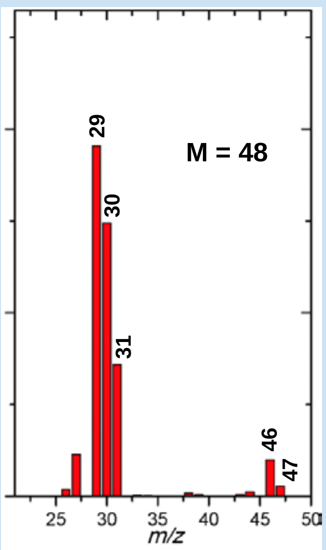
$$n\ H_2CO \rightarrow [\text{-O-}CH_2]_n$$

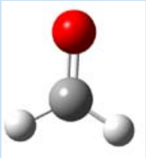


H_2O-dominated with $0.2 > [NH_3]/[H_2CO] > 1$

$H_2O:NH_3:H_2CO$ at 10:0.1:0.4







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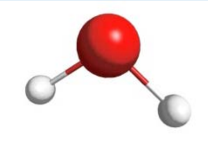
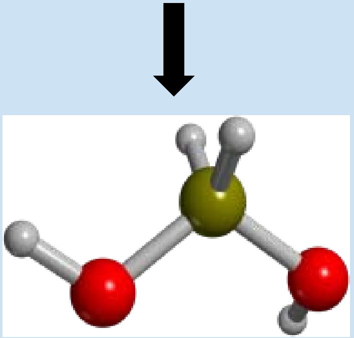
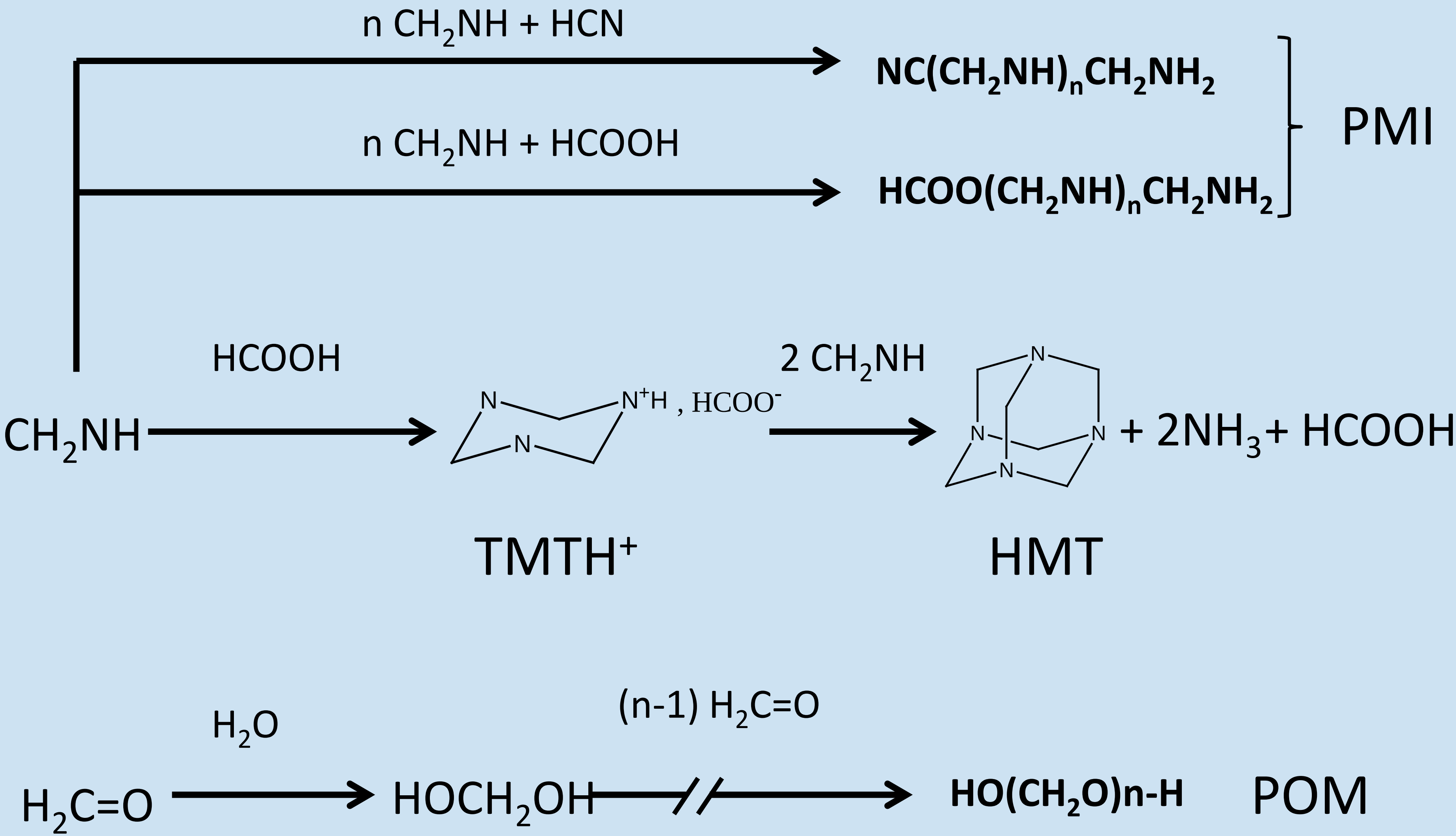




methanediol $HOCH_2OH$

Condensation reactions in the ice mantle



Outline

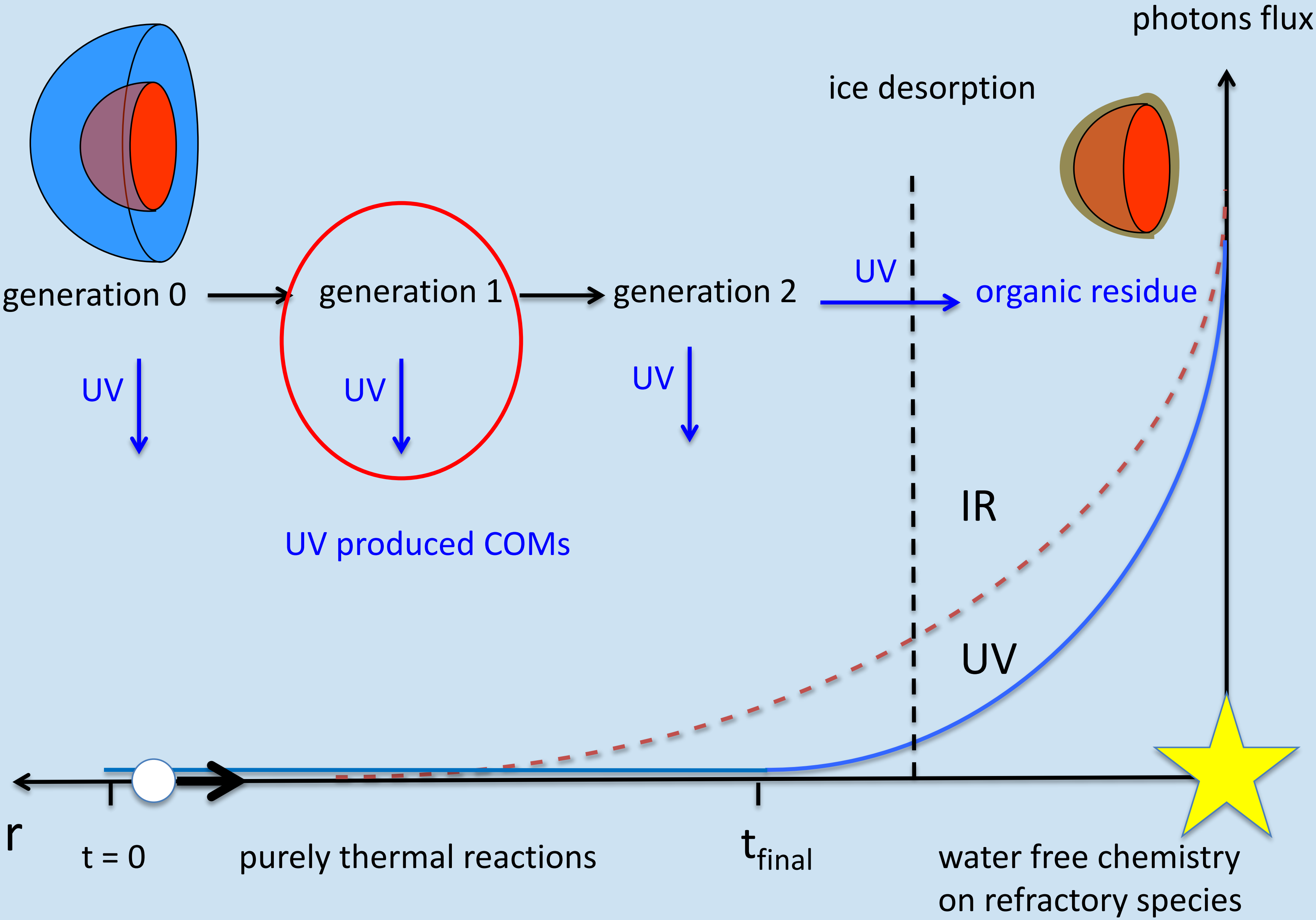
1. Molecular complexity and solid-state chemistry

2. Formation of complex molecules

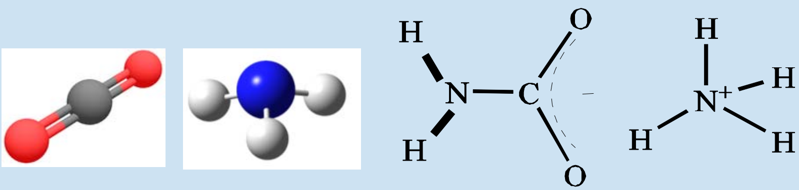
   - Thermal formation of complex molecules
   - Photochemistry
   - Detection of COMS in the ISM

3. Dynamics of COMs formation

Toward more complex molecules: ice photochemistry

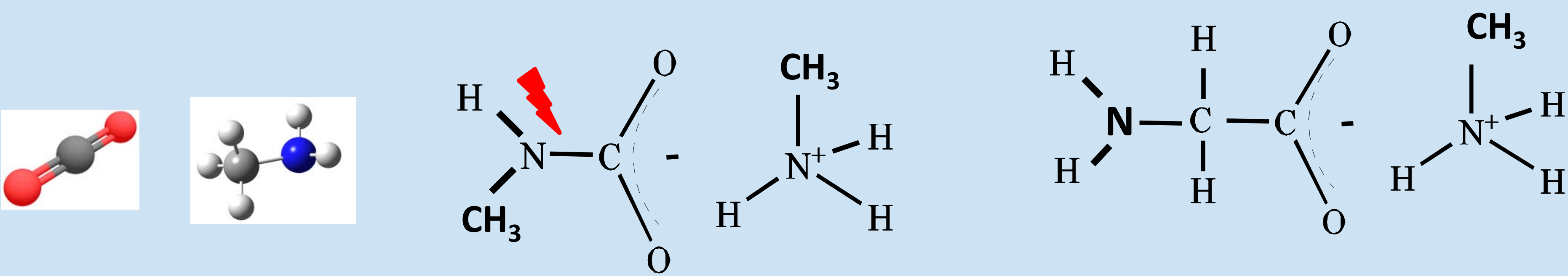


The NH_3 + CO_2 thermal solid-state reaction



J.B. Bossa, F. Duvernay, P. Theulé, F. Borget, T. Chiavassa, Chem. Phys.354(3), 211, 2008
Bossa, J.B.; Theule, P.; Duvernay, F.; Borget, F.; Chiavassa, T. *A&A,* 2008, *492*, 719

$$CO_2 + 2NH_3 \xrightarrow{80\ K} NH_2COO^-NH_4^+$$



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

a way to form glycine

Bossa, J.B.; Duvernay, F.; Theule, P.; Borget, F.; d'Hendecourt, L.; Chiavassa, T. *A&AS*2009, *506*, 601-608.

Outline

1. Molecular complexity and solid-state chemistry

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3. Dynamics of COMs formation

Ice formed COMs detection

simple molecules

complex organic molecules

grain

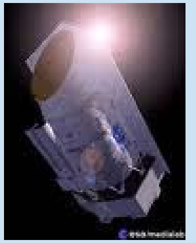
organic residue

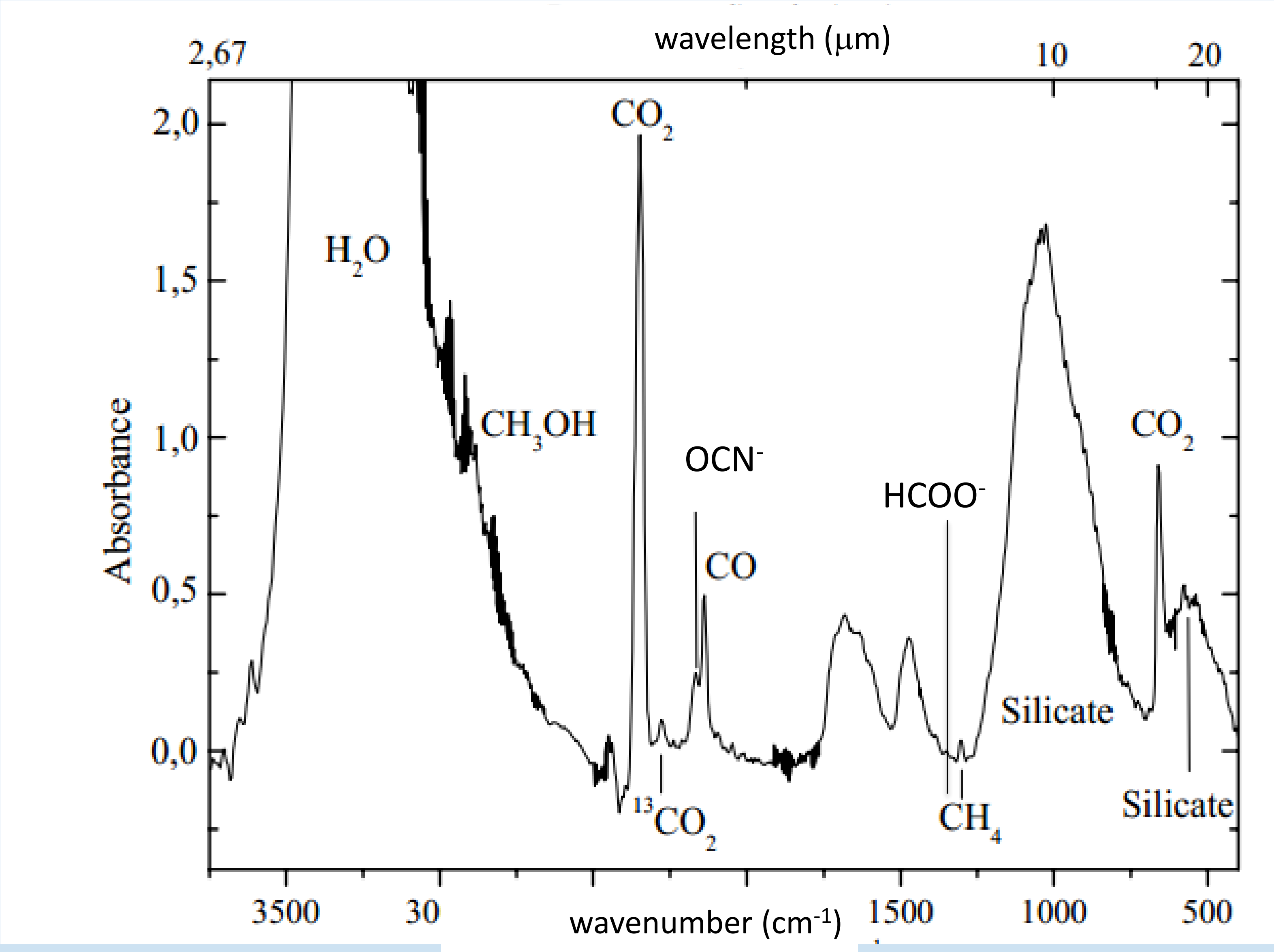
volatile species

refractory species

complexity

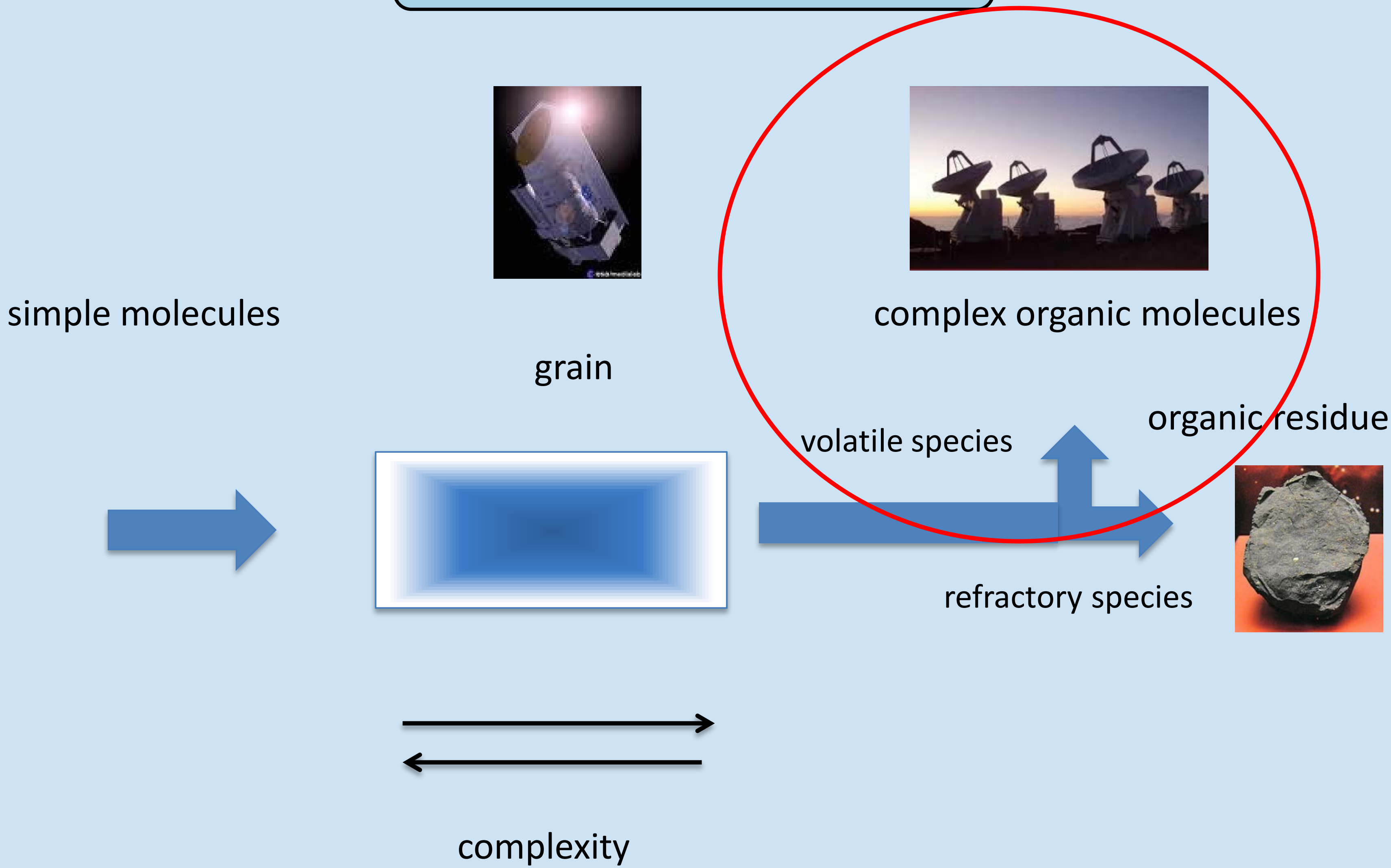
Ice formed COMs detection





NGC 7538 ISO spectrum

Ice formed COMs detection



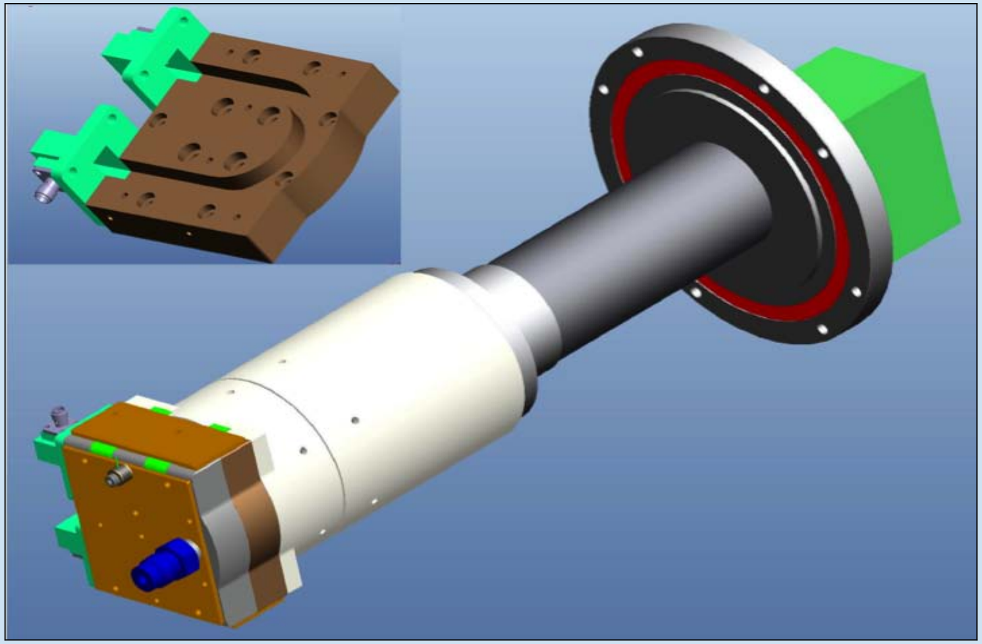
Ice formed COMs detection

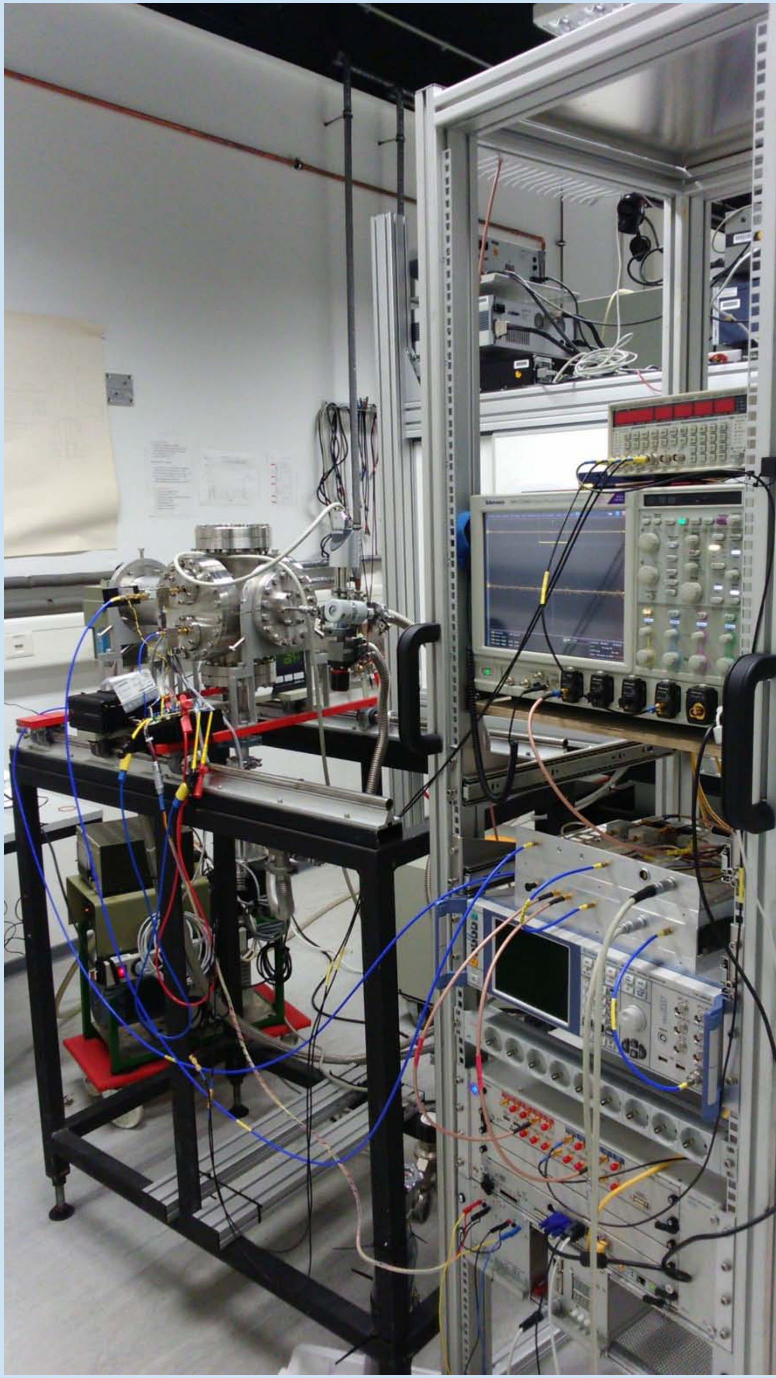
Prof. Stephan Schlemmer
Christian Endres, Marius Hermann, JB Bossa

formation of COMs in the ice

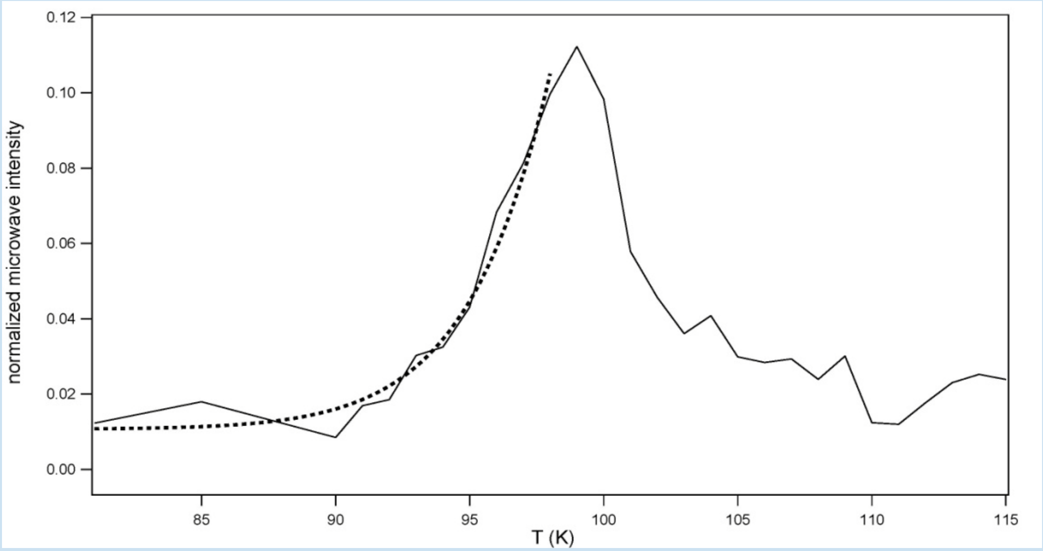
+

Chirped pulse Fourier transform microwave spectrometer

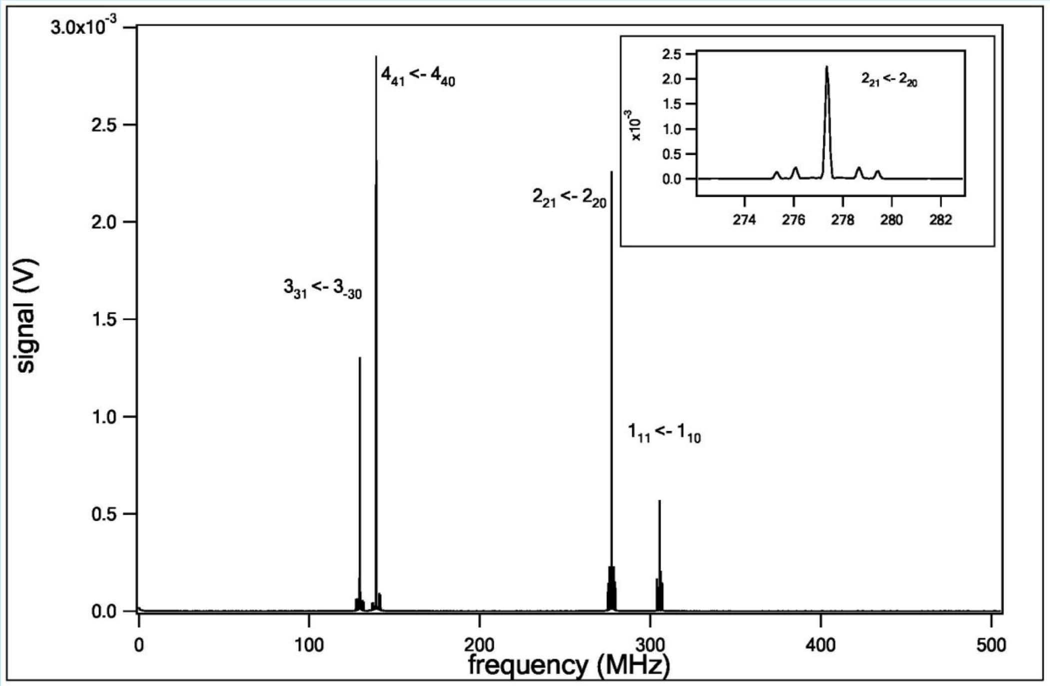




Ice formed molecules detection



NH_3 ice TPD



high-resolution and sensitivity

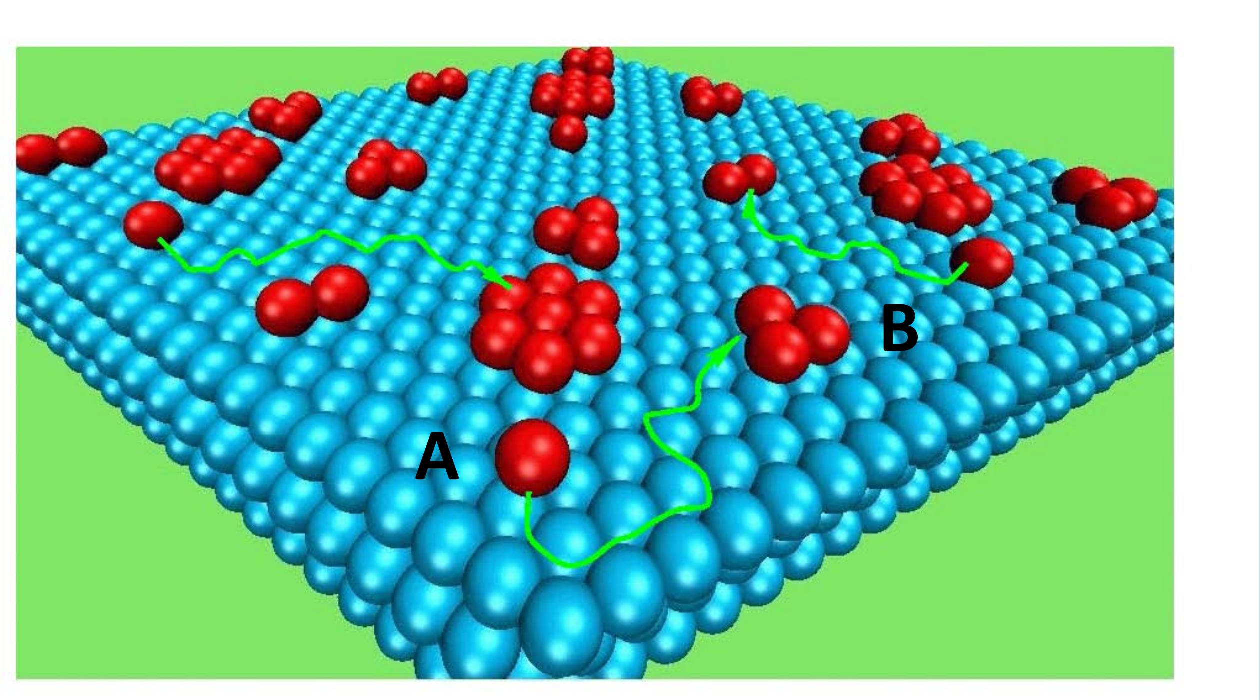
Outline

1. Molecular complexity and solid-state chemistry

2. Formation of complex molecules

3. Dynamics of COMs formation
   - diffusion limited reactivity
   - reaction rate constants
   - diffusion coefficients
   - desorption and trapping

Diffusion-limited reactivity



the diffusion-reaction equation

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

Outline

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

Reaction rate constants in the solid-phase

$k_{reaction}$?

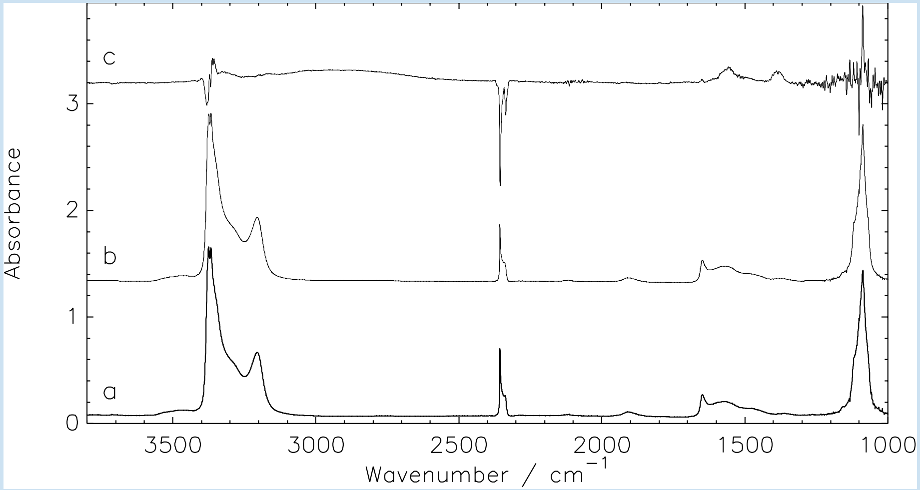
A = NH_3 B = CO_2

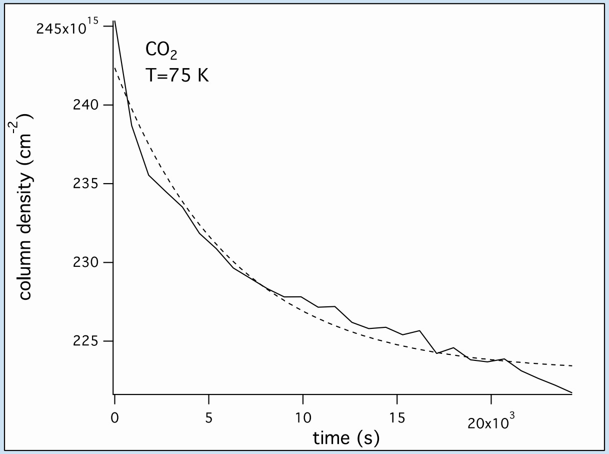
$$\frac{dN_i}{dt} = -k_{ij}(T_{const}) \; N_i^{\alpha} N_j^{\beta}$$

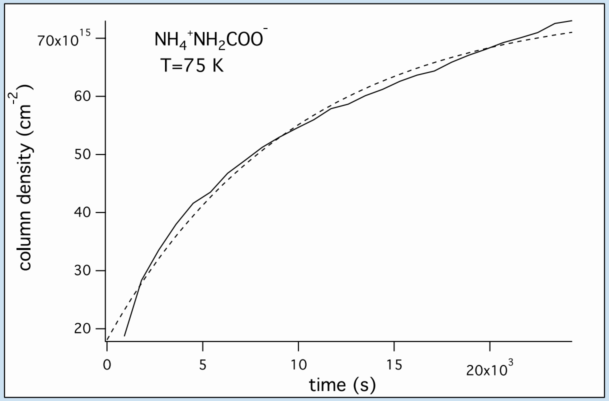
α, β partial orders
$\alpha + \beta$ total order

Reaction rate constants in the solid-phase

T constant



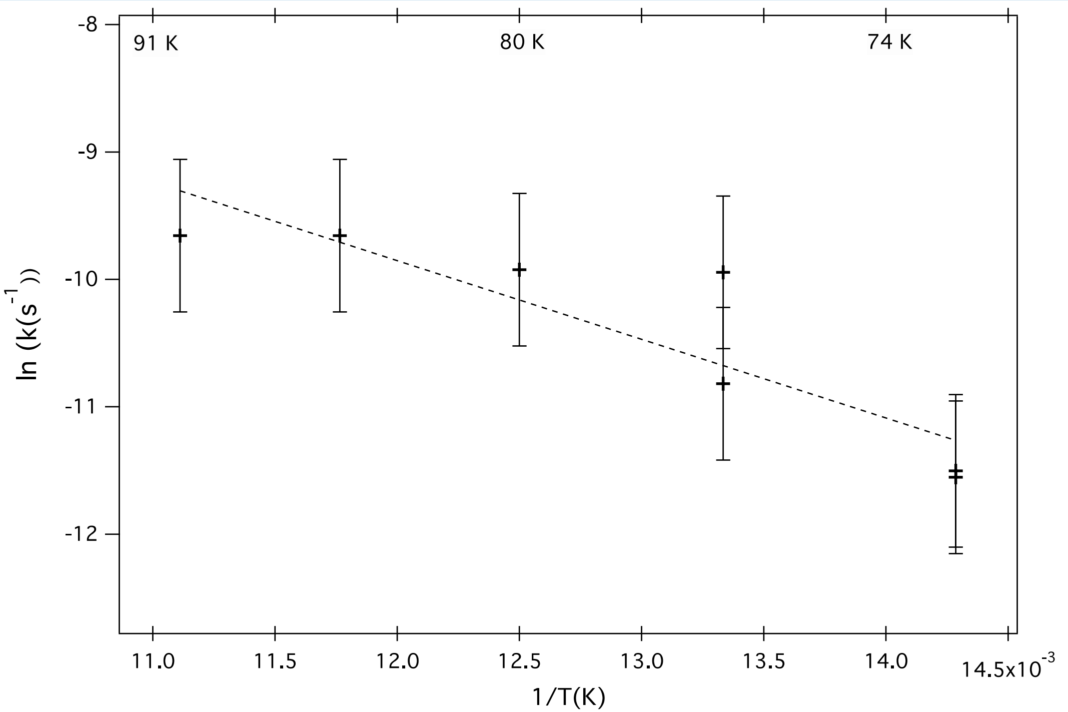




→ k_{ij} (T_{const})

Reaction rate constants in the solid-phase

The temperature dependence of the reaction rate constant



$$k(T) = A\,e^{-\frac{E_a}{k_B T}}$$

$$E_a = 5.1 \pm 1.6 \;\; kJ.mol^{-1}$$ (613 K, 53 meV)

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

Reaction rate constants in the solid-phase

ab-initio calculations

P. Ghesquière, T. Mineva, D. Talbi

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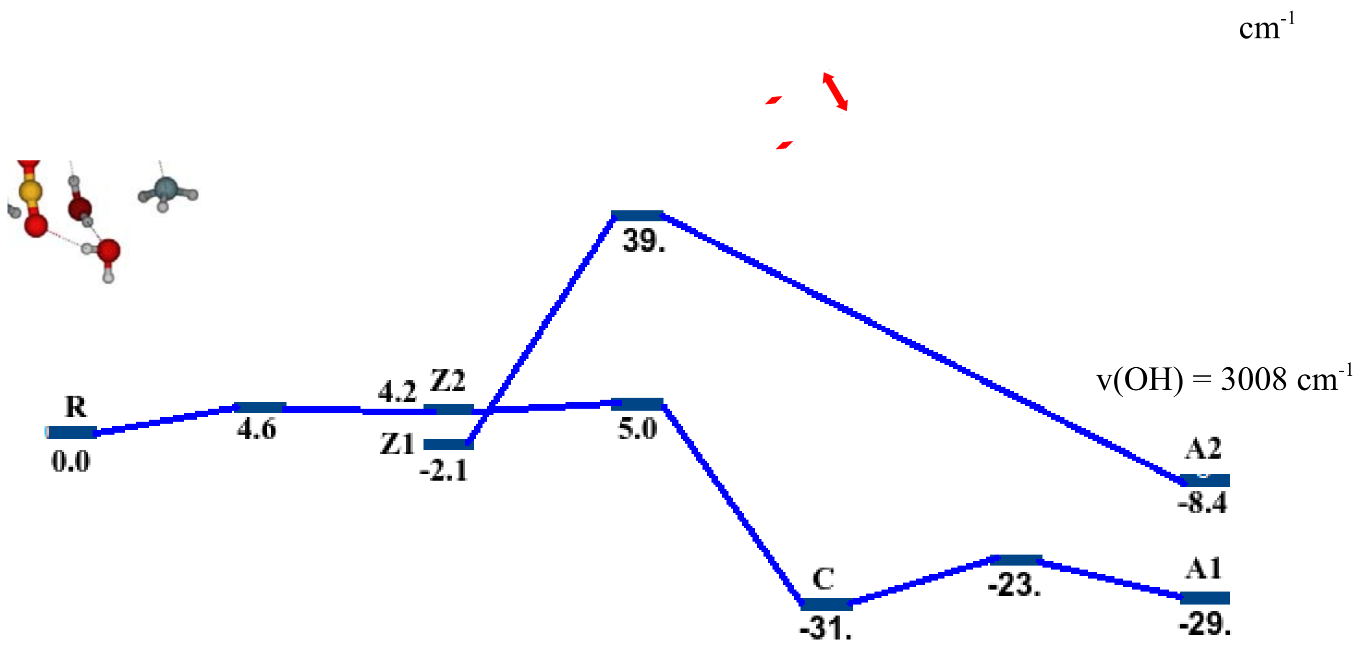
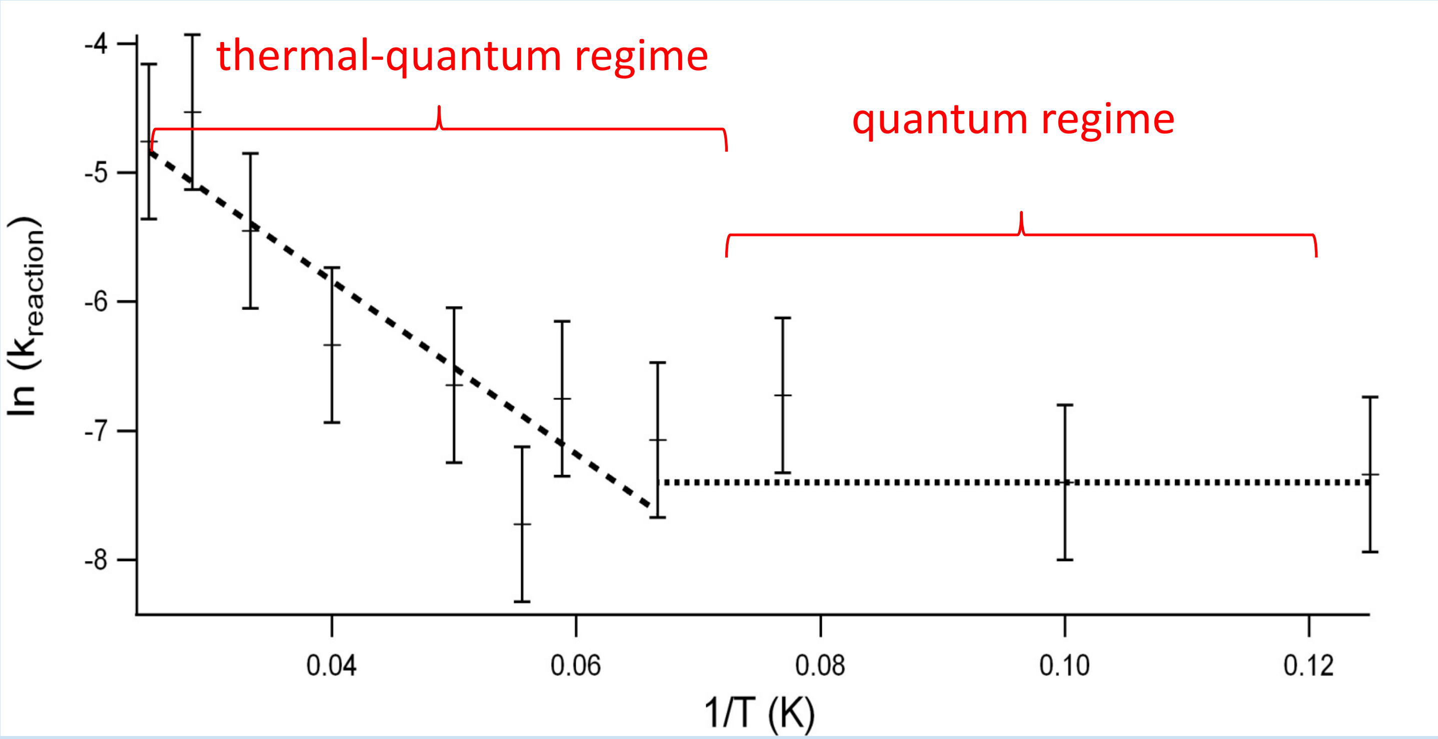


Noble et al., PCCP 2014

Reaction rate constants in the solid-phase

$$HNCO + NH_3 \rightarrow OCN^- + NH_4^+$$

Mispelaer et al., A&A 2011



1/40 K 1/15 K 1/8 K

$$k(T) = k_0 * e^{-\frac{E_a}{k_B T}} \quad k_0 = 0.0035 \pm 0.0015 (s^{-1}) \quad E_a = 0.4 \pm 0.1 \ kJ\ mol^{-1}$$ (36 K)

Reaction rate constants in the solid-phase

pre-exponentiel coefficient

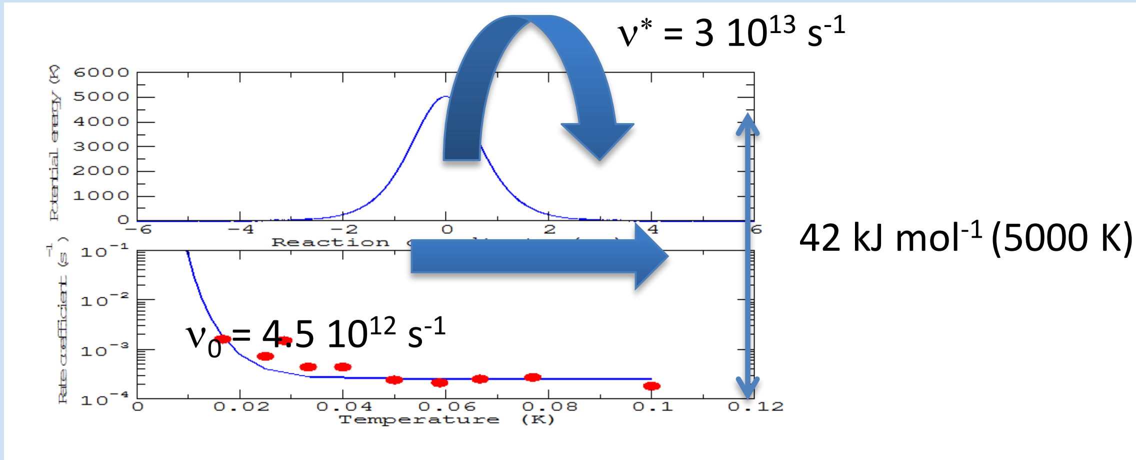
reactants				products					ν_0, E_a, [T interval, K]
acid-base reactions									
generation 0		generation 0		generation 1					
H_2O	+	HNCO	→	$H_3O^+ OCN^-$					(3 10^{8}, 26)[110K-130K]
NH_3	+	HCOOH	→	$NH_4^+ HCOO^-$					
NH_3	+	HNCO	→	$NH_4^+ OCN^-$					(4 10^{-3}, 0.4) [8K-40K]
NH_3	+	HCN	→	$NH_4^+ CN^-$					(1.6 10^{-2}, 2.7)[90K-105K]
generation 1		generation 0		generation 2					
NH_2COOH	+	NH_3	→	$NH_4^+ NH_2COO^-$					
$CH_3NHCOOH$	+	CH_3NH_2	→	$CH_3NH_3^+ CH_3NHCOO^-$					
nucleophilic additions									
generation 0		generation 0		generation 1					
CO_2	+	NH_3	→	NH_2COOH					
CO_2	+	CH_3NH_2	→	$CH_3NHCOOH$					
H_2CO	+	H_2O	→	$HOCH_2OH$					
H_2CO	+	NH_3	→	NH_2CH_2OH					(5 10^{-3}, 4.5)[80K-100K]
H_2CO	+	CH_3NH_2	→	CH_3NHCH_2OH					(2 10^{-2}, 1.1)[30K-120K]
CH_3CHO	+	NH_3	→	$NH_2CH(CH_3)OH$					(7 10^{10}, 39)[115K-125K]
generation 1		generation 0		generation 2					
$NH_4^+CN^-$	+	CH_2NH	→	NH_2CH_2CN					
$NH_4^+CN^-$	+	H_2CO	→	$HOCH_2CN$	+	NH_3			(2.8 10^{-1}, 3.8)[50K-130K]
elimination reaction									
generation 1									
NH_2CH_2OH	+	HCOOH	→	$CH_2{=}NH$	+	H_2O	+	HCOOH	
$NH_2CH(CH_3)OH$	+	HCOOH	→	$CH_3CH{=}NH$	+	H_2O	+	HCOOH	
CH_3NHCH_2OH	+	HCOOH	→	$CH_2{=}NCH_3$	+	H_2O	+	HCOOH	

Theule et al., Adv. Space Res. 2013

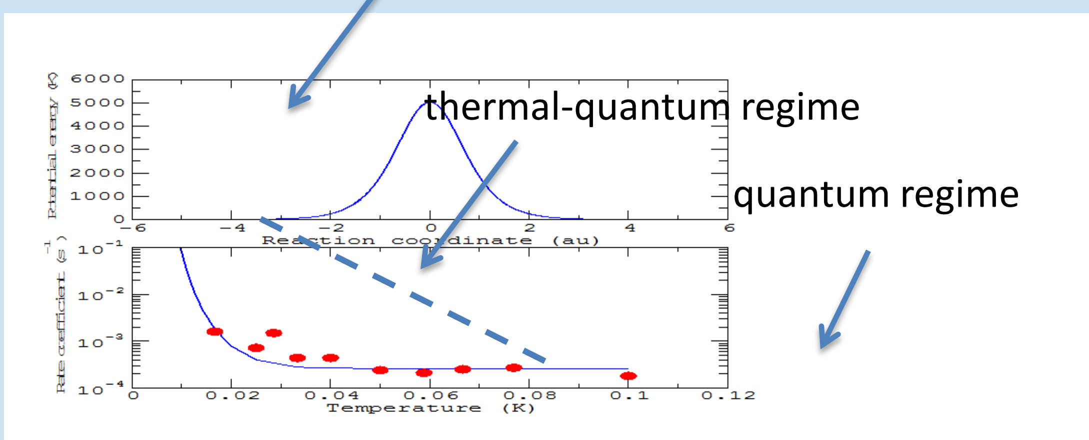
The pre-exponential factor issue

the influence of quantum tunneling

credit: Alexandre Faure



thermal (Arrhenius) regime

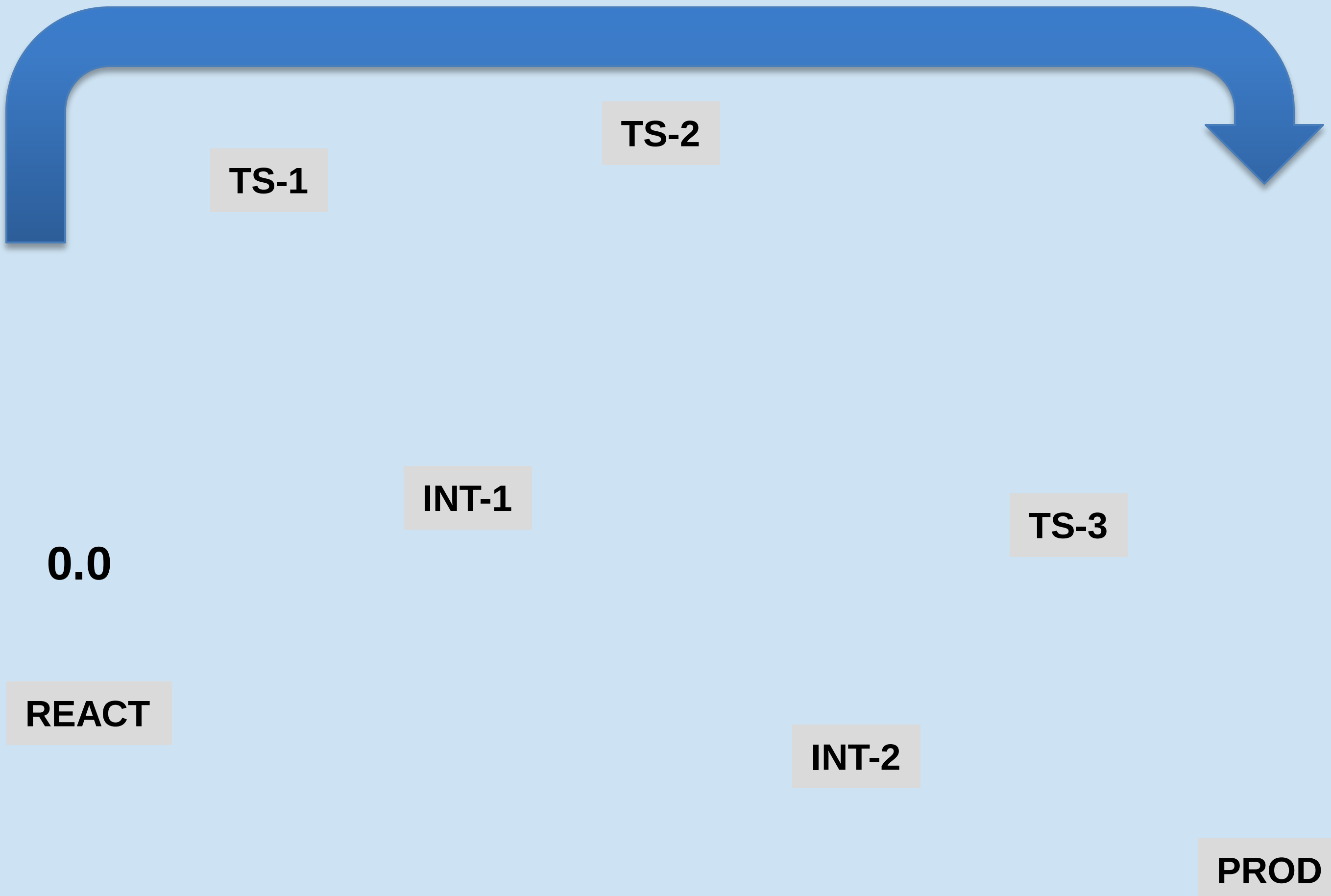


50 K 10 K 1/T

The pre-exponential factor issue

what are we measuring ?

$$k(T) = k_0 * e^{-\frac{E_a}{k_B T}}$$



usefullness of quantum calculations to understand the microphysics

Laboratory data into model

[cm⁻³.s⁻¹] [cm⁻³] [cm⁻³] [cm³.s⁻¹]

$$\frac{dN_i}{dt} = -k_{ij} N_j N_i$$

$$n_d \approx 1.33\ 10^{-12} \times N_H cm^{-3}$$

grain density

$$N_s \approx 10^6 grain^{-1}$$

nb of sites on a grain

[cm³.s⁻¹] [Ø] [s⁻¹] [cm³]

$$k_{ij} = k_{chem} \times \max\left(\frac{1}{t_{\substack{thermal\\hopping}}}, \frac{1}{t_{tunnelling}}\right) \times \frac{1}{N_s * n_d}$$

$$\frac{1}{10^6 * 10^{-8}} = 10^2$$

reaction rate constant A + B

diffusion factor

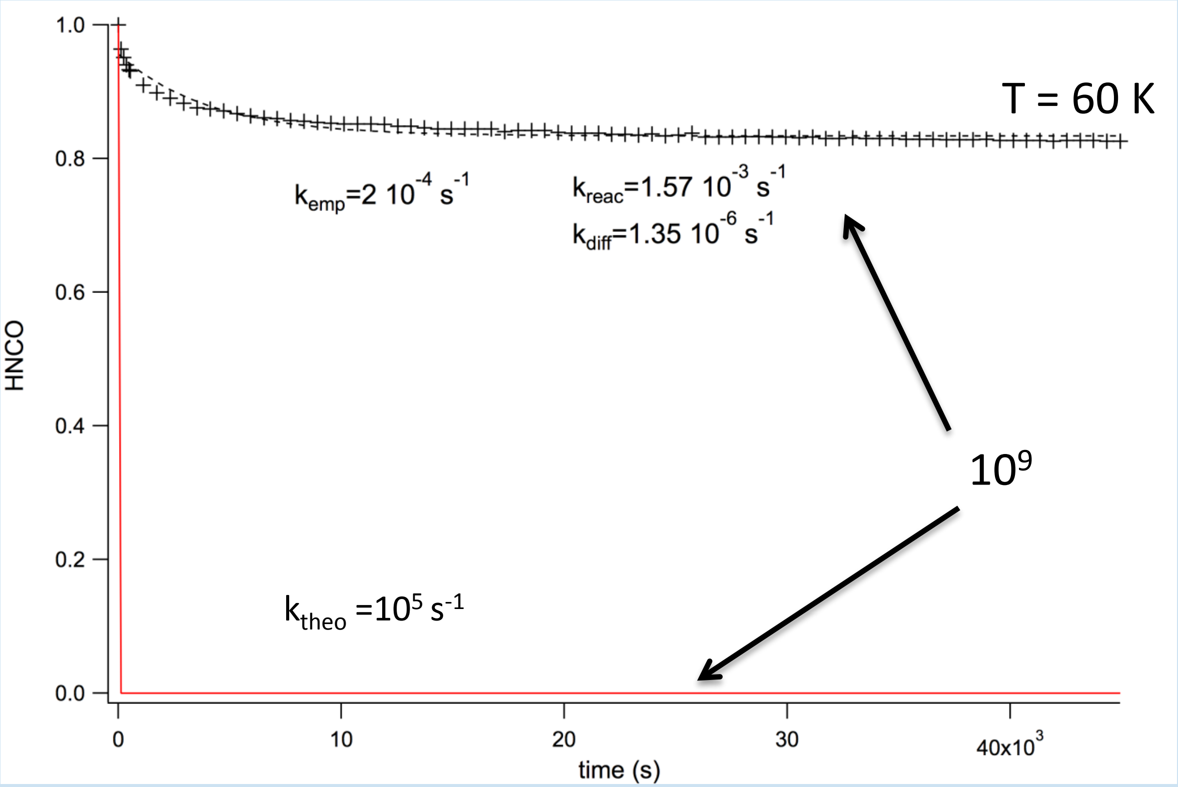
$$k_{chem} = \exp\left(-\frac{2a}{\hbar}\sqrt{2\mu E_a}\right) = 3.3\ 10^{-2}$$

[Ø]

μ: masse réduite
a= 1 Å

Laboratory data into model

$HNCO + NH_3 \rightarrow OCN^- + NH_4^+$ in $HNCO: NH_3: H_2O$



- problem of formalism
- temperature dependence of the reactions (tunneling effect not appropriated for all reactions)
- problem of the yield

Reaction rate constants in the solid-phase

M. Faure et al., Icarus, submitted + A. Faure A&A submitted

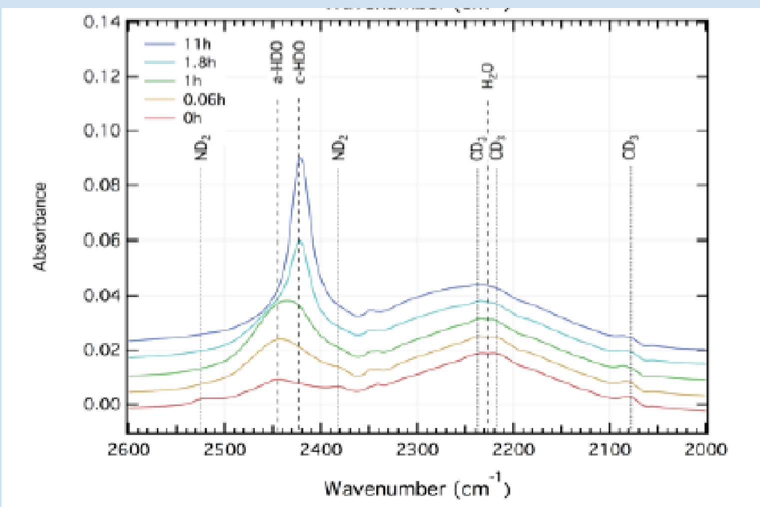
<u>deuteration rate constants</u>: the time evolution of the COMs D/H ratio in ice

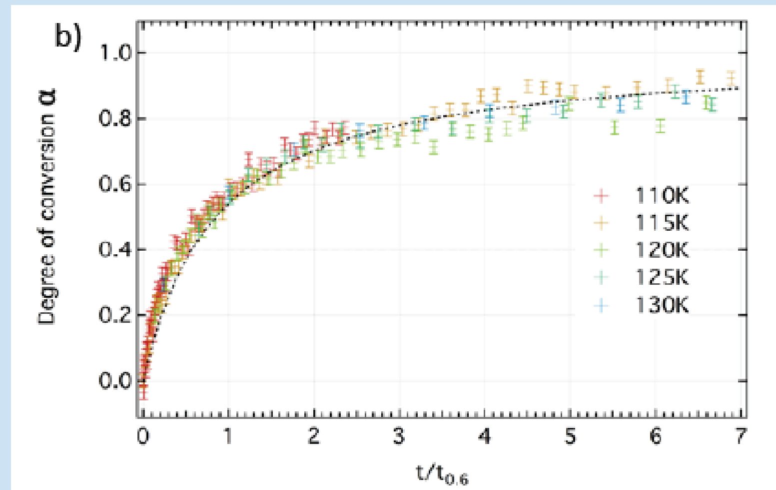
$H_2O + CD_3OD \rightarrow CHD_2OD/CH_2DOD/CH_3OD/\ CHD_2OH/CH_2DOH/CH_3OH + HOD/D_2O$

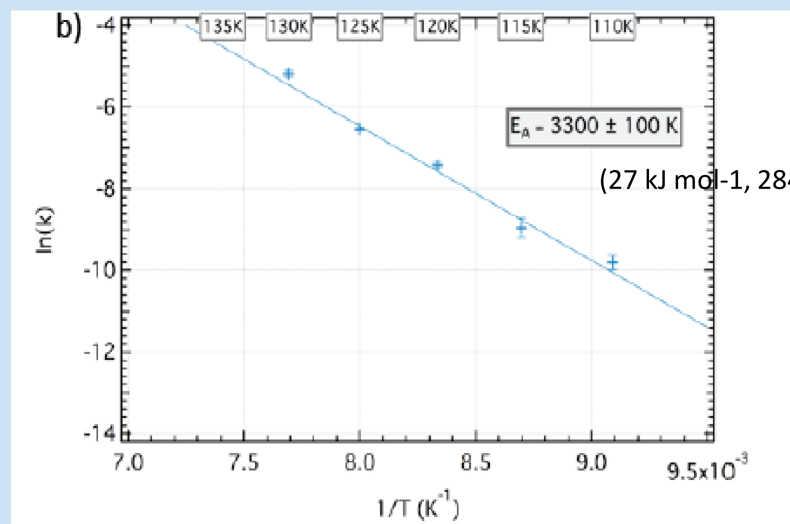
$H_2O + CD_3ND_2 \rightarrow CH_2DND_2,\ CHD_2ND_2,\ CH_3ND_2/\ldots$

$D_2O + HCN \rightarrow HDO + DCN$

<u>example</u>: a $H_2O:CD_3ND_2$ mixture at T constant





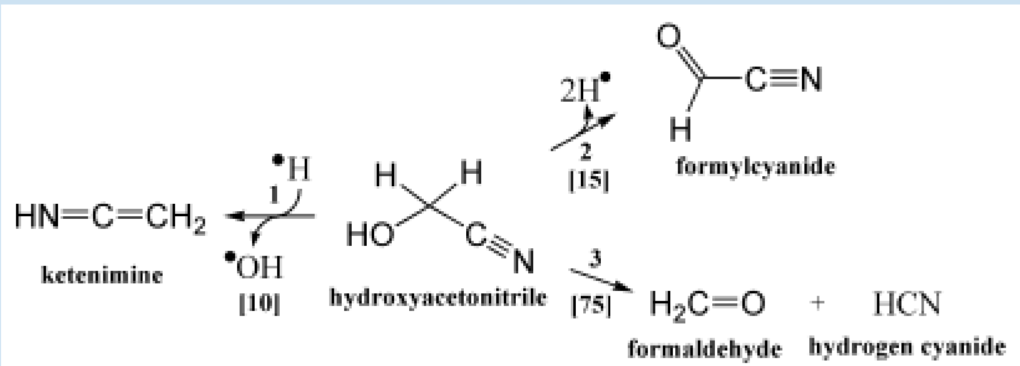


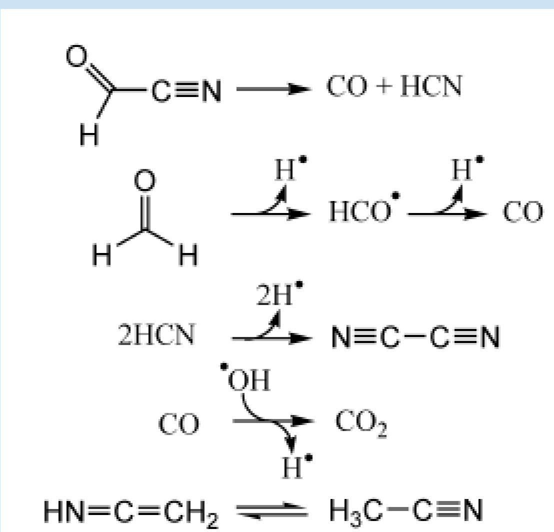
(27 kJ mol-1, 284 meV)

D/H exchanges between -OH and $-NH_2$/NH functional groups

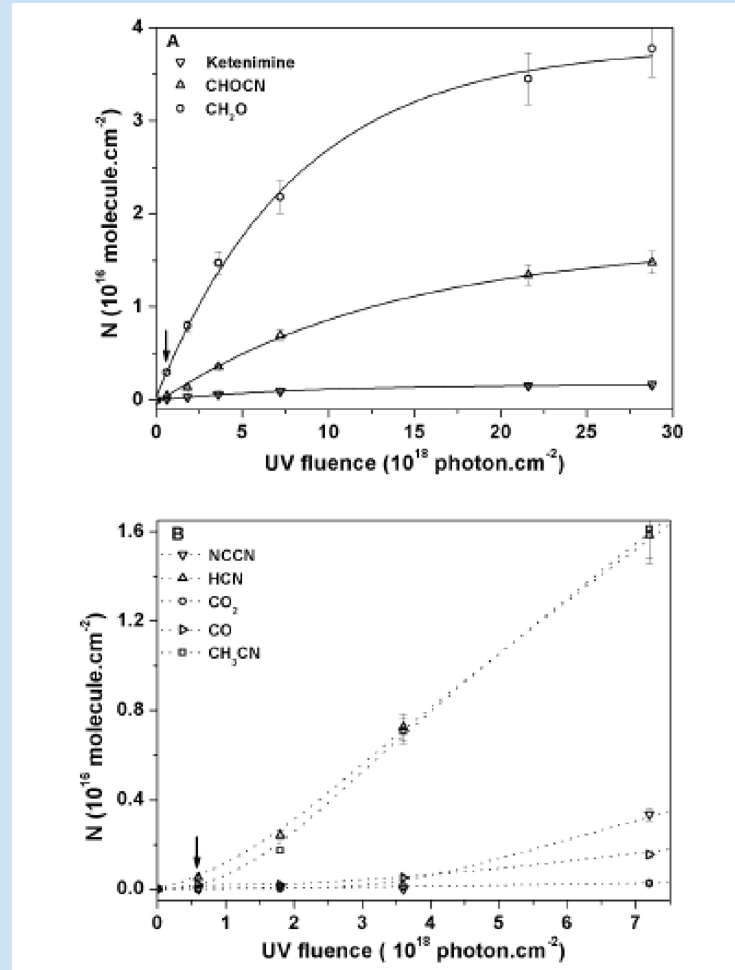
Reaction rate constants in the solid-phase

Photochemistry rate constants: photo- production/destruction of COMs and photo equilibrium





Danger et al., A&A, 2013



$\sigma \sim 10^{-19}$ cm^2

Reaction rate constants in the solid-phase

in the gas phase:

$$AB \xrightarrow{k_{photo}} A + B$$

$$k_{photo} = \int \Phi(\nu) * \sigma(\upsilon) d\nu$$

$\sigma_{gas} \sim 10^{-17}$ cm^2

in the solid phase :

$$AB \underset{k_{recomb}(T)}{\overset{k_{photo}}{\rightleftarrows}} A + B$$

$$AB(t) = \frac{k_{recomb} + k_{photo} e^{-(k_{photo} + k_{recomb})*t}}{k_{recomb} + k_{photo}} * AB_{(t=0)}$$

$$K(T) = \frac{A_\infty}{B_\infty} = \frac{k_{photo}}{k_{recomb}(T)}$$

k_{eff}(flux, ν, T)

$\sigma_{solid} \sim 10^{-19}$ cm^2

the « cage effect »

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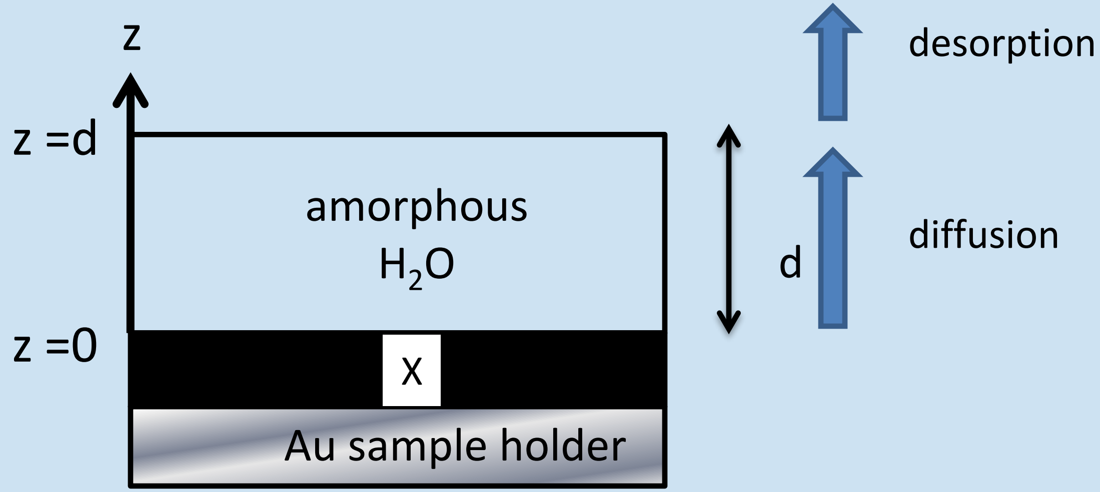
    - desorption and trapping

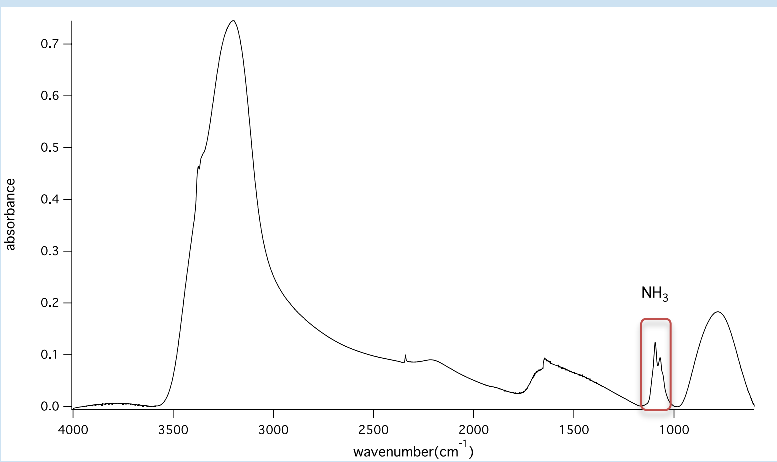
$$\frac{\partial n_A}{\partial t} - D(T) \times \nabla^2 n_A + k(T) \times n_A n_B = 0$$

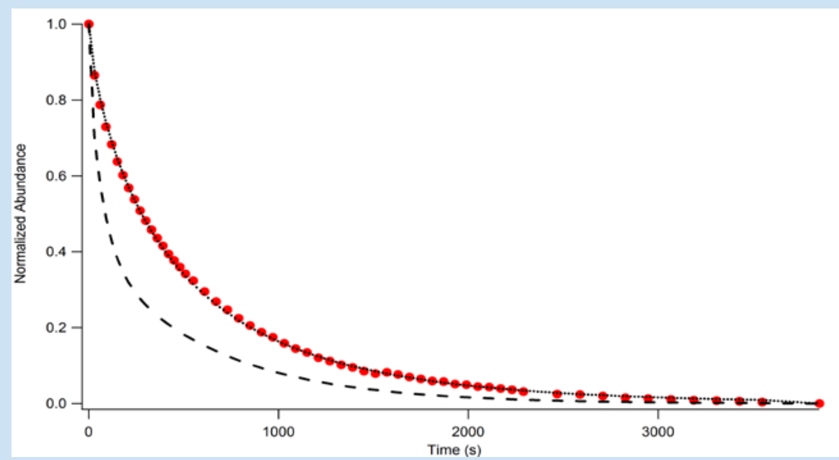
Diffusion coefficients of molecules in amorphous ice

T constant



X = CO, HNCO, H_2CO or NH_3





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

➔ D(115K)

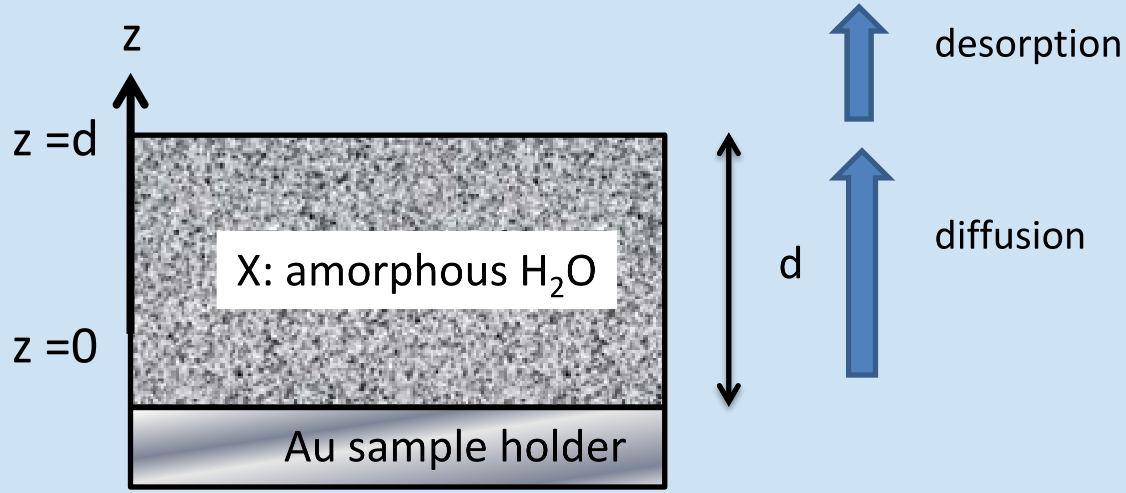
Mispelaer et al., A&A 2013

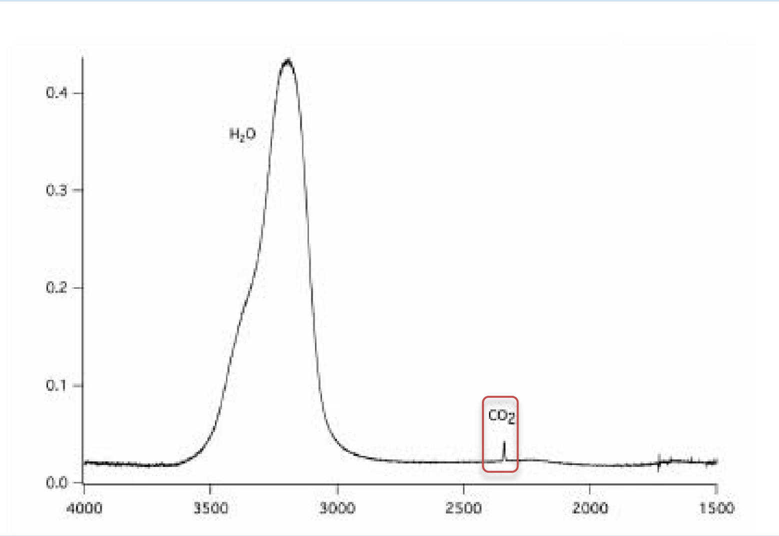
Diffusion coefficients of molecules in amorphous ice

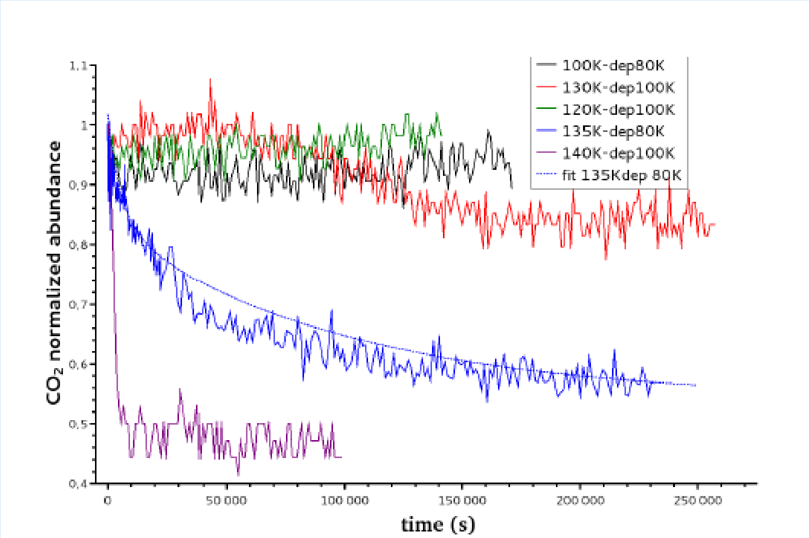
T constant

X = CO_2

Ghesquière et al., PCCP 2015







+ molecular dynamics calculations in low-density amorphous ice (LDA)

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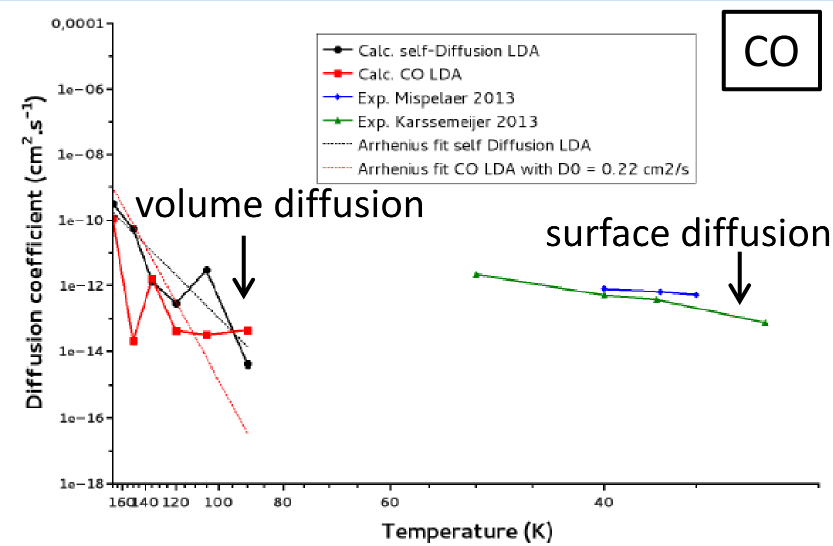
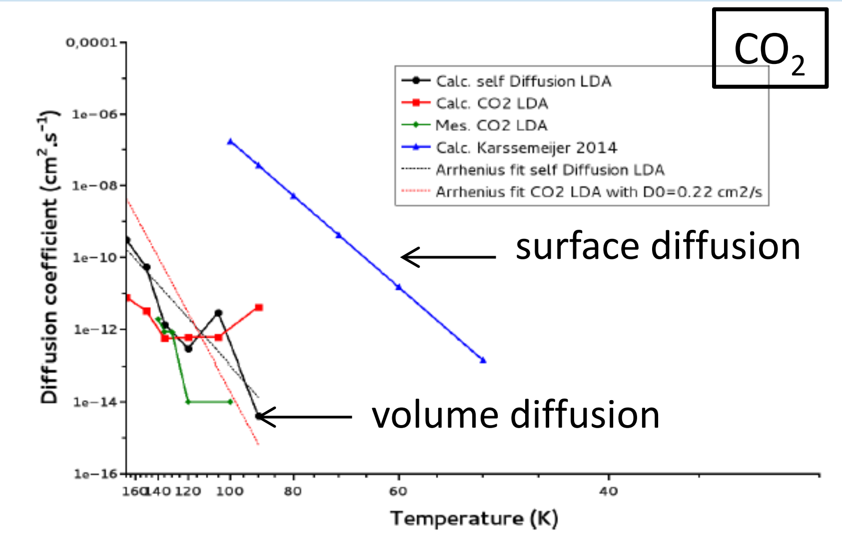
P. Ghesquiere, T. Mineva, D. Talbi

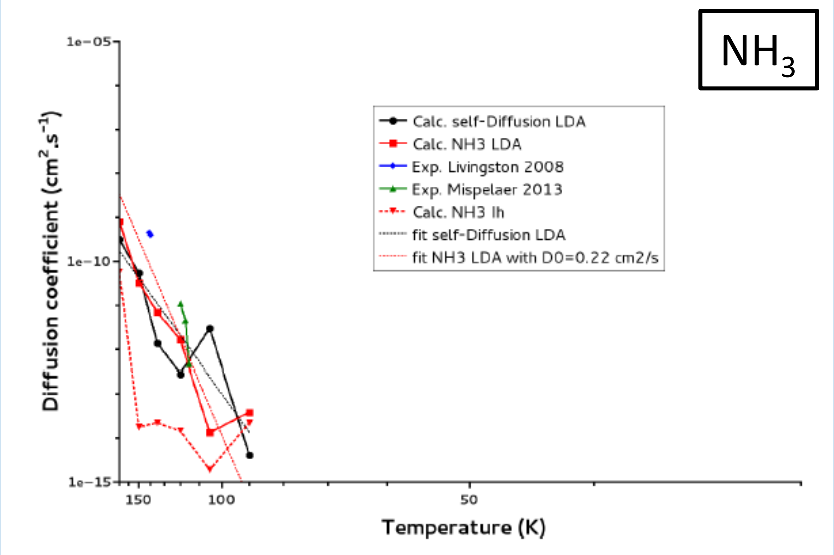
Diffusion coefficients of molecules in amorphous ice

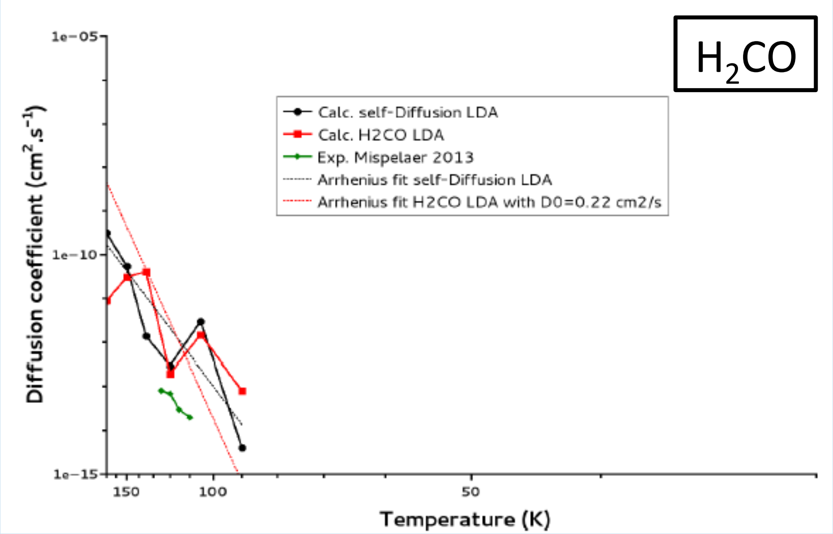




good agreement experiment and MD calculations

surface diffusion faster than volume diffusion





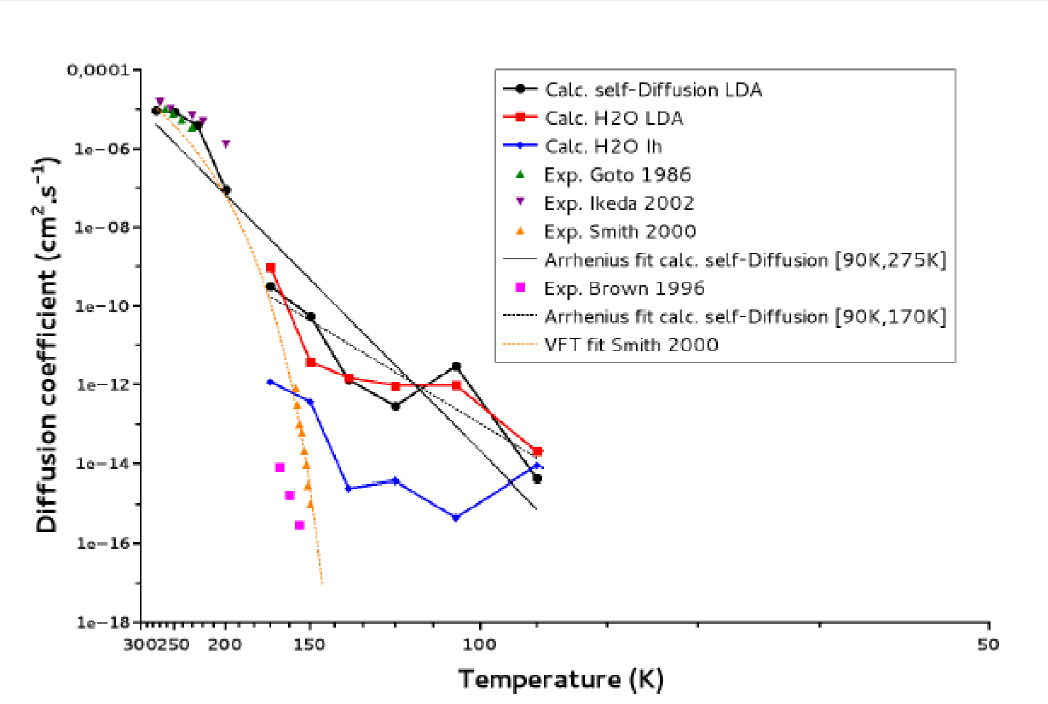
correlation with water self-diffusion for both hydrogen bonded and non hydrogen bonded molecules

Diffusion coefficients of molecules in amorphous ice

temperature dependence of the diffusion coefficient

$$D(T) = D_0 e^{-\frac{E_d}{k_B T}}$$

System	D_0 ($cm^2.s^{-1}$)	E_a ($kJ.mol^{-1}$)	E_a ($kJ.mol^{-1}$) with $D_0 = 0.22$ $cm^2.s^{-}$	Edes (($kJ.mol^{-1}$)
H_2O Self-D LDA	(7 ± 1) e-06	15 ± 5	24.9 ± 2.9	46.6 [44]
H_2O Self-D Ih	(1 ± 0.2) e-10	9 ± 5		
NH_3 LDA	(3 ± 0.5) e-05	17 ± 5	25.4 ± 1.0	25 [61]
NH_3 Ih	(7 ± 2) e-10	9 ± 5		
CO_2	(3 ± 0.5) e-10	3 ± 3	25.0 ± 2.4	22.4 [61]
CO	(2 ± 0.5) e-09	8 ± 5	27.2 ± 2.1	9.8 [61][62]
H_2CO	(1.7 ± 0.5) e-08	9 ± 5	25.0 ± 1.7	27 [57]
H_2O	(9 ± 1) e-07	13 ± 5	25.3 ± 1.3	46.6 [44]



diffusion of small molecules probably driven by the water self-diffusion in the ice

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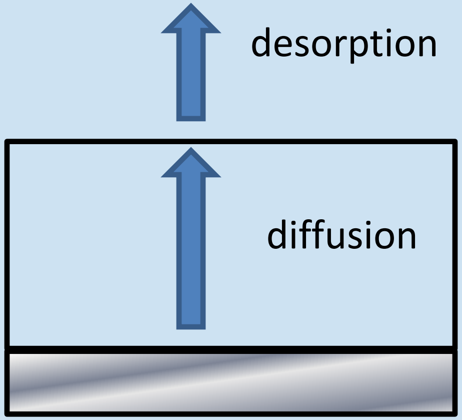
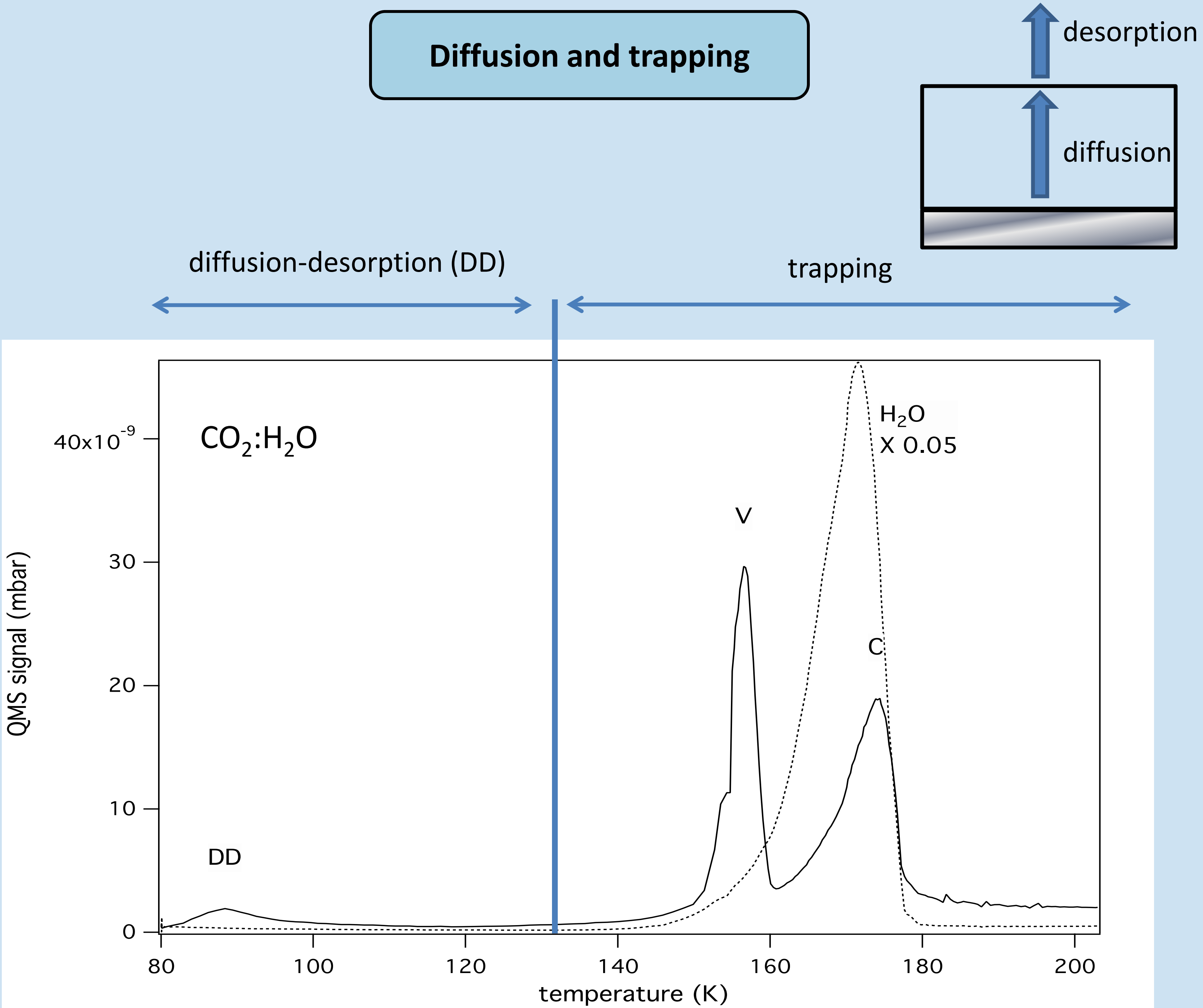
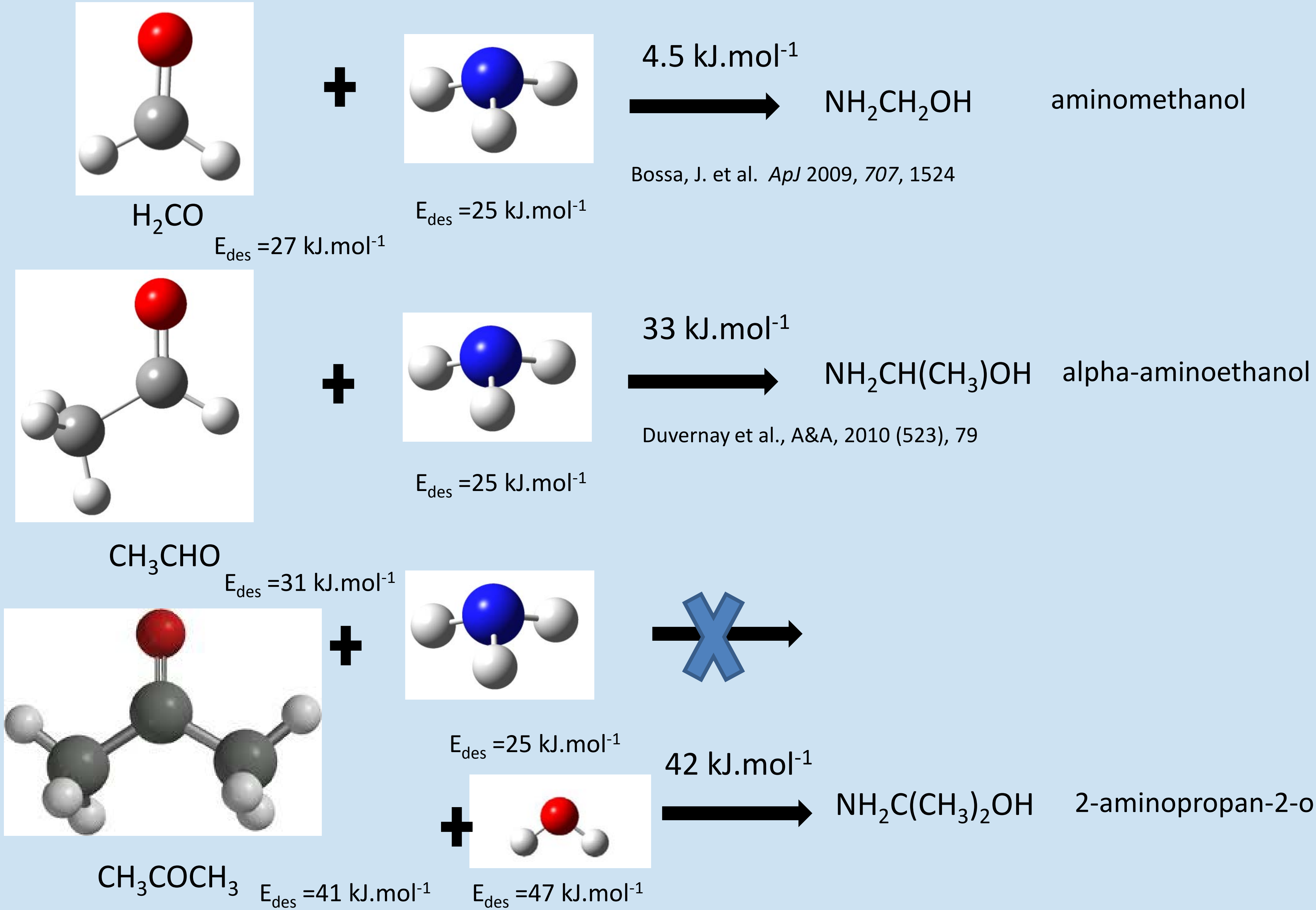


Diffusion and trapping



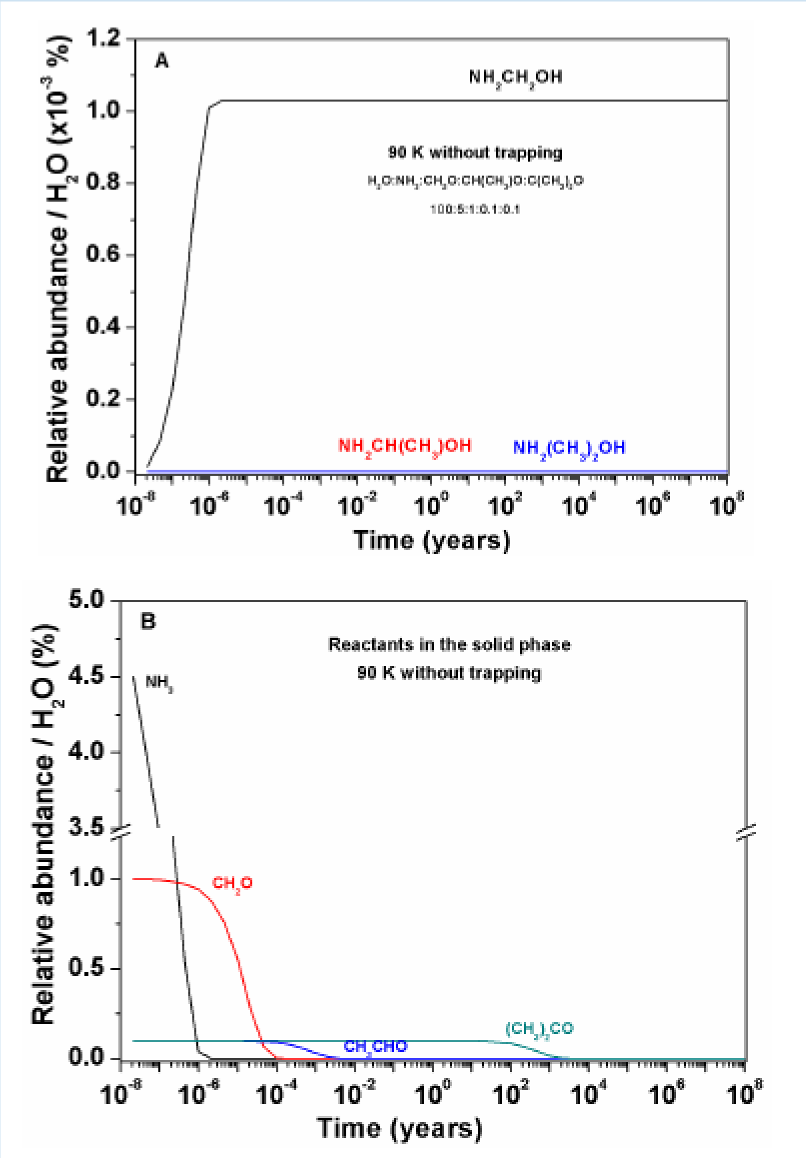
Diffusion and trapping

Fresneau et al., *MNRAS*, 2014

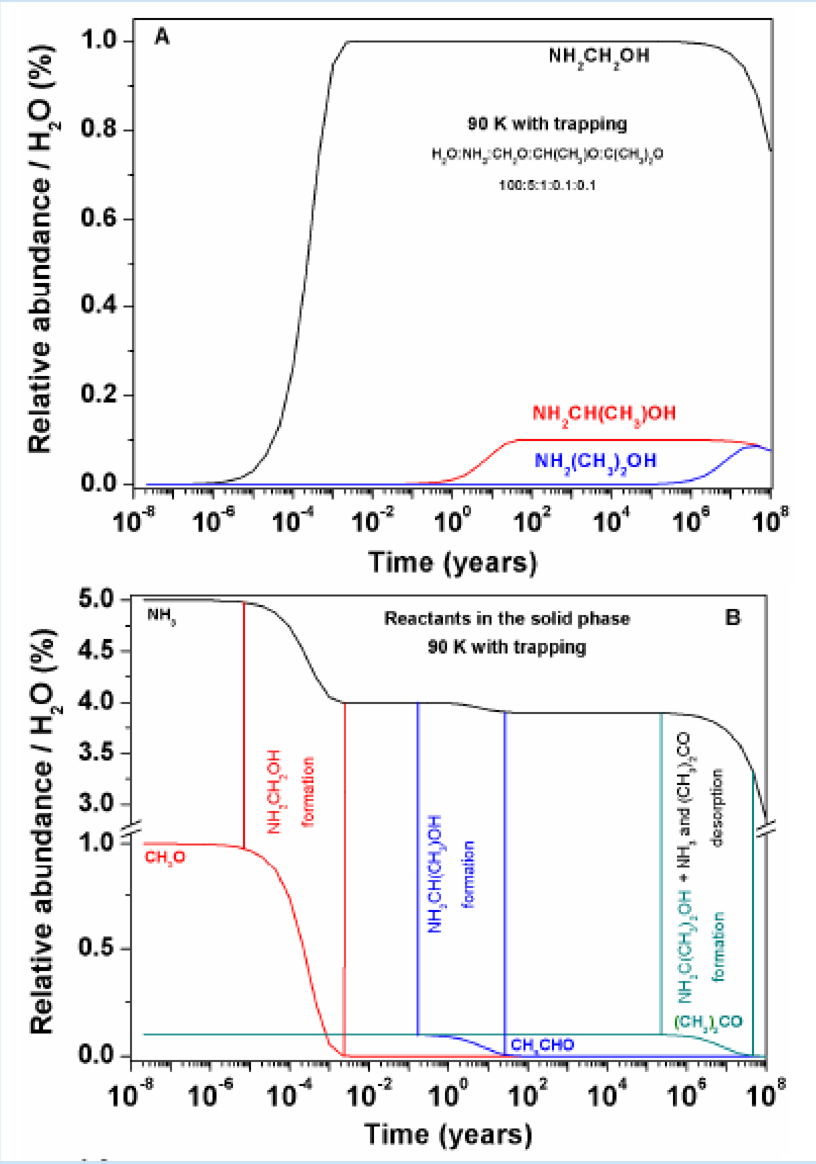


Diffusion and trapping

no trapping



trapping



trapping important for « mild » chemistry and COM formation (role of the water solvent)

Conclusion and perspectives

- laboratory experiments and theoretical studies enable to understand solid-state chemistry

- important to quantify each competing process (activation energies, cross sections,…)

  to understand the dynamics

- challenge to input the microphysics in a gas-grain code with the required level of details (and not too much)

Thanks

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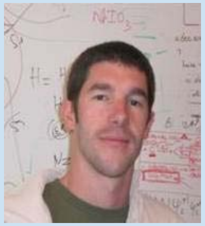
Prof. Thierry Chiavassa

Fabien Borget

Isabelle Couturier

Grégoire Danger



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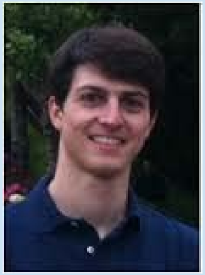

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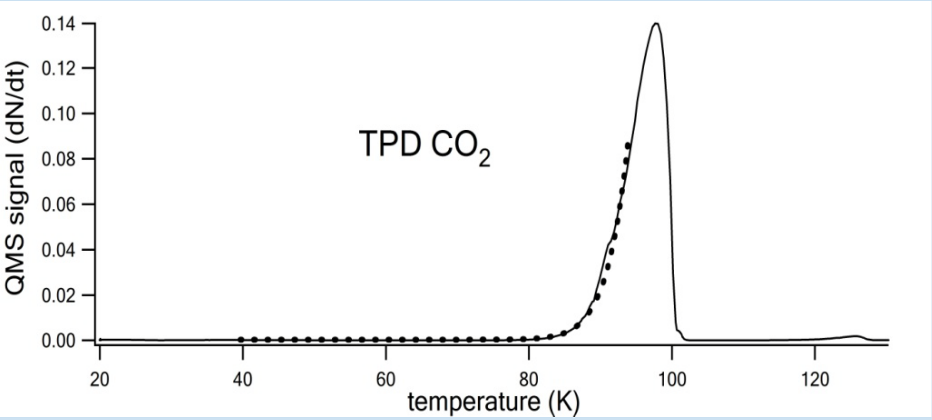
Thank you for your attention

lab

The pre-exponential factor issue

// desorption



ν_0= 5 10^{10} s^{-1} E_{des}=21.22 kJ mol^{-1}

ν_0= 10^{12} s^{-1} E_{des}=23.48 kJ mol^{-1}

ν_0=10^{13} s^{-1} E_{des}=25.26 kJ mol^{-1}

correlation between ν_0 et E_{des}

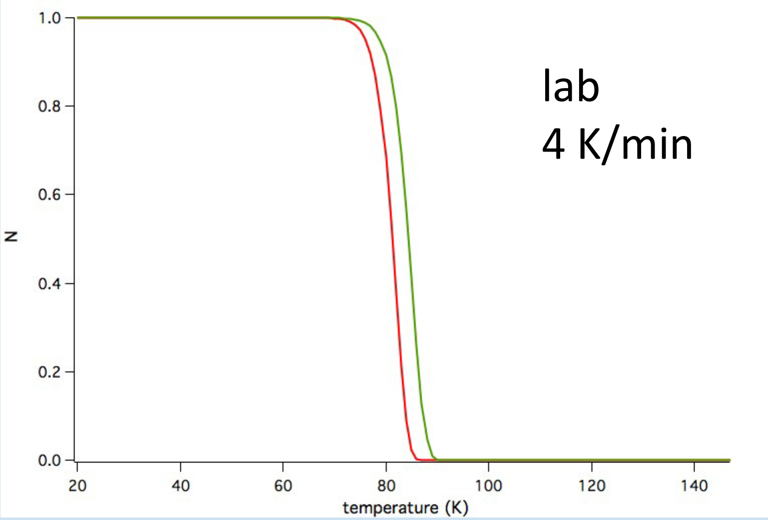
k_{des}=f(ν_0 ,E_{des}) desorption kinetic doublet

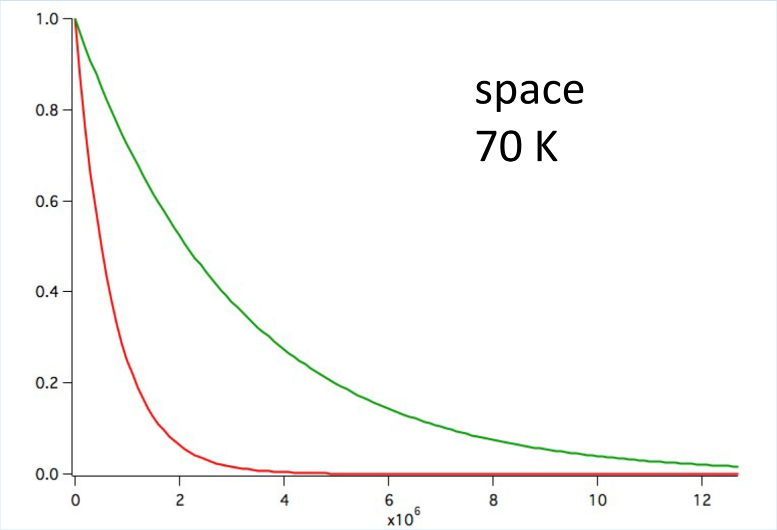
model

$$\nu_0 = \sqrt{\frac{2n_s E_{des}}{\pi m}}$$

E_{des} = 25.26 kJ/mol -> ν_0=2.34 10^{12} s^{-1}

(ν_0=2.34 10^{12} s^{-1} , E_{des}=25.26 kJ mol^{-1})





see M. Bertin's talk and Misha Doronin's poster