Grain surface chemistry and its impact on the gas phase

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H_2 FORMATION ON GRAIN SURFACES

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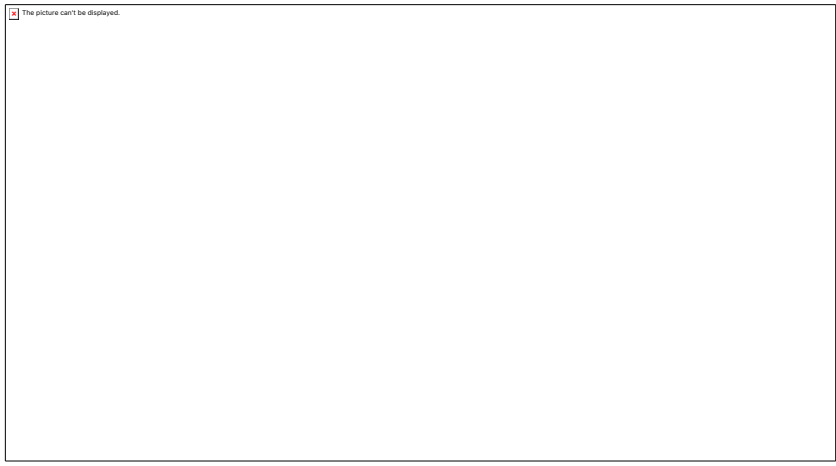
Overview

- The interplay between ice and gas in space
  - Prestellar cores
  - Hot cores and corinos
  - Icy moons
- From ice to gas:

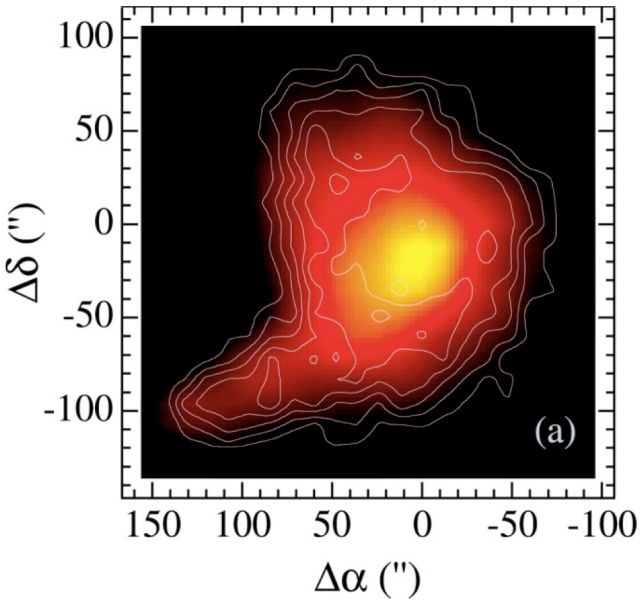
  thermal desorption

  chemical desorption
- Astrophysical applications
- Conclusions



Courtesy F. Dulieu

From gas to ice



B68 IRAM 30m;
Caselli 1999, Bergin et al. 2002
Keto & Caselli 2010
Extinction Av~27
$C^{18}O$ J=1-0

Prestellar cores: CO depleted from the gas

~ 90% of CO molecules should leave the gas phase, on average along the line of sight

~99% of them must deplete in the core nucleus

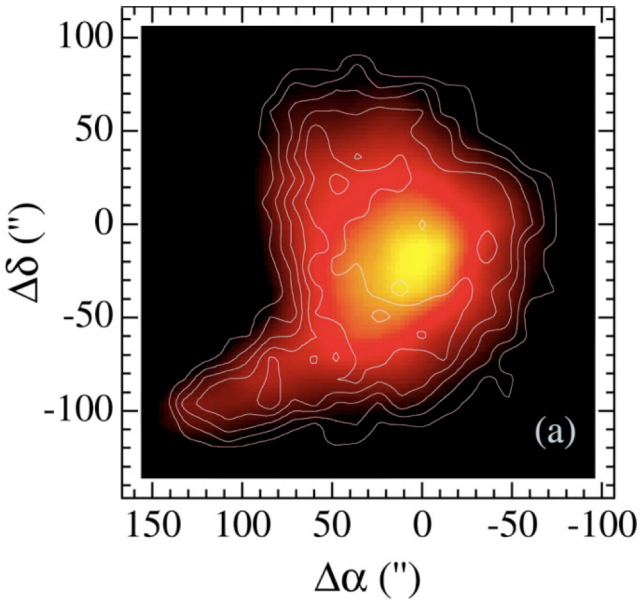
Caselli et al. 1999

CO freeze-out onto dust particles → form thick icy mantles *Ossenkopf & Henning 1994; Pontoppidan et al. 2008.*

Many cold cores

Willacy et al. 1998; Tafalla et al. 2002, 2004; Pagani et al. 2005, 2012; Brady-Ford & Shirley 2011

From ices to gas



Prestellar cores:

CO depleted from the gas

Hot corino: complex molecules

IRAS16293: *Botinelli 2004; Bisschop 2008; Cazaux et al. 2003; Pineda 2012*

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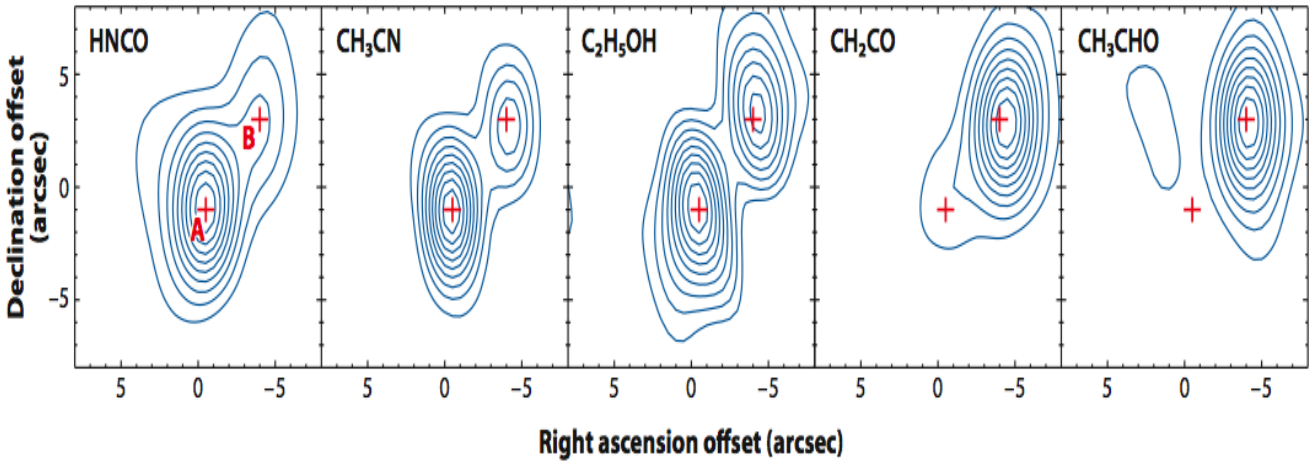
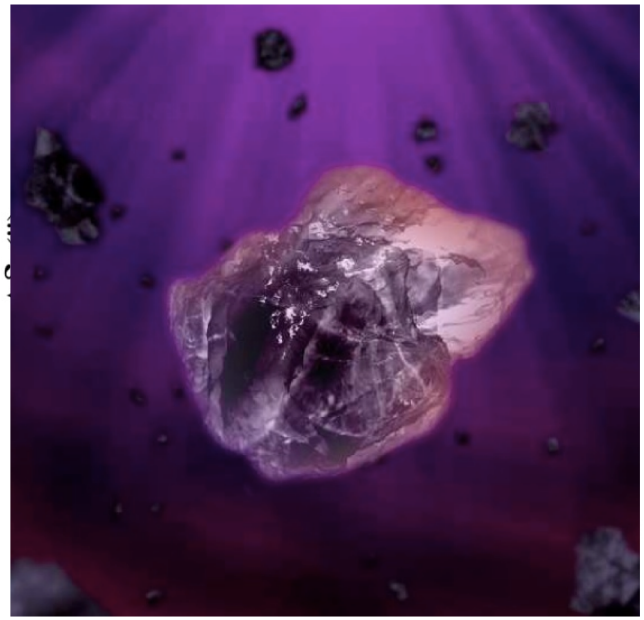


From ices to gas



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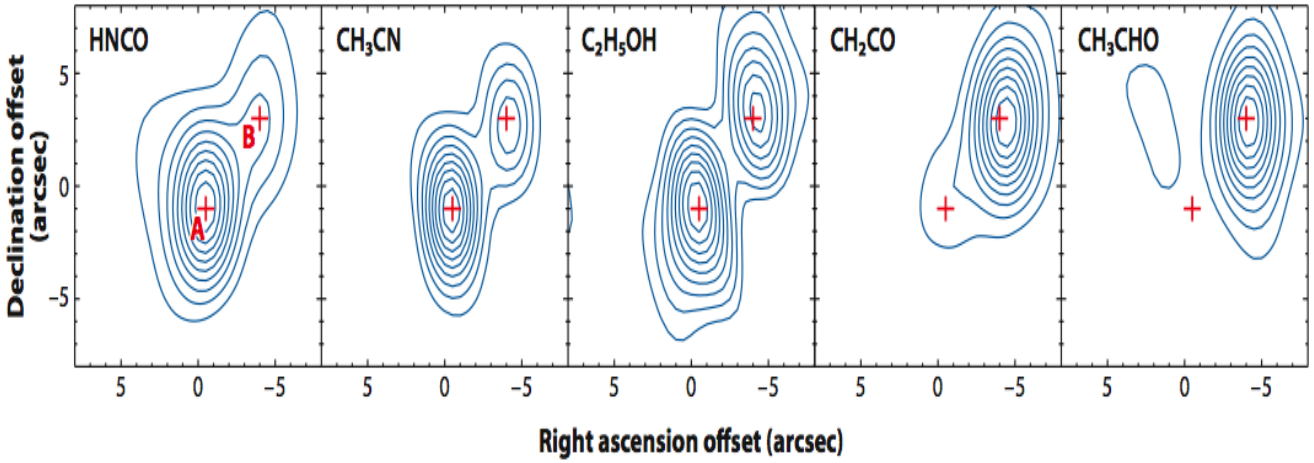
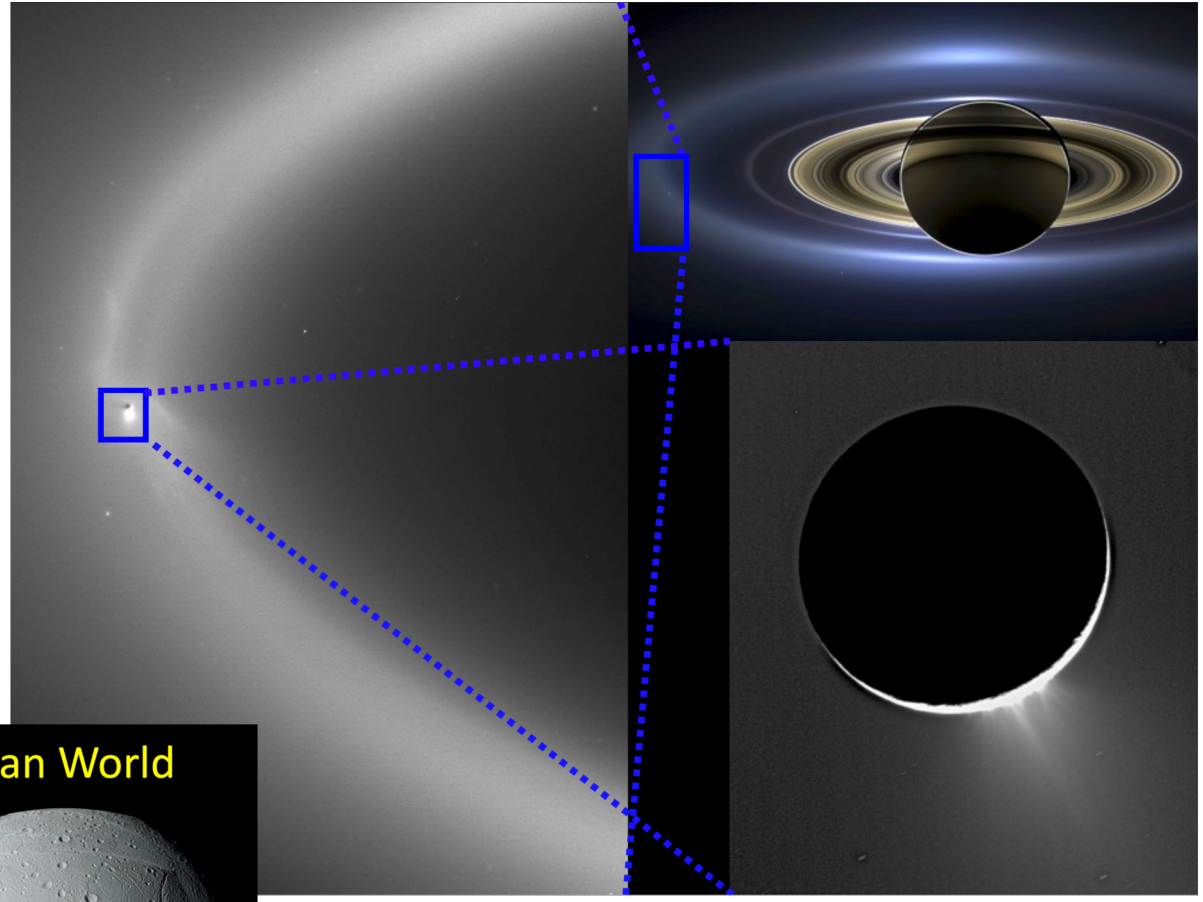
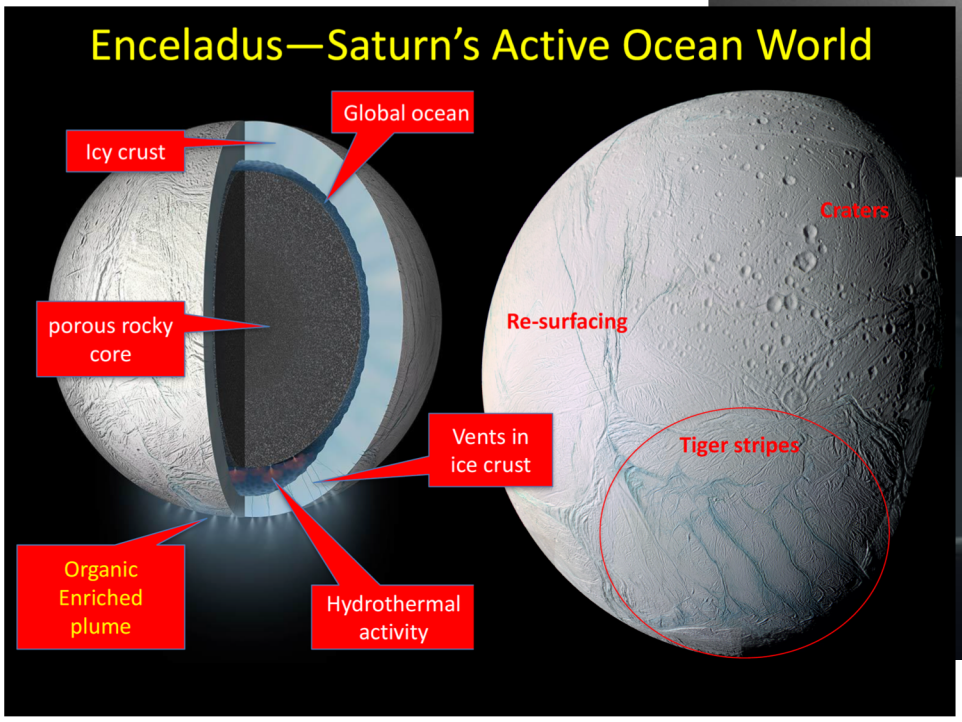
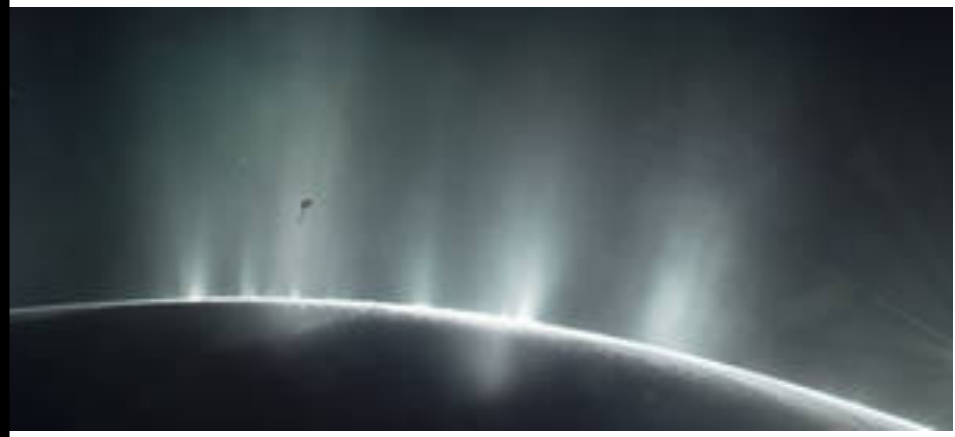


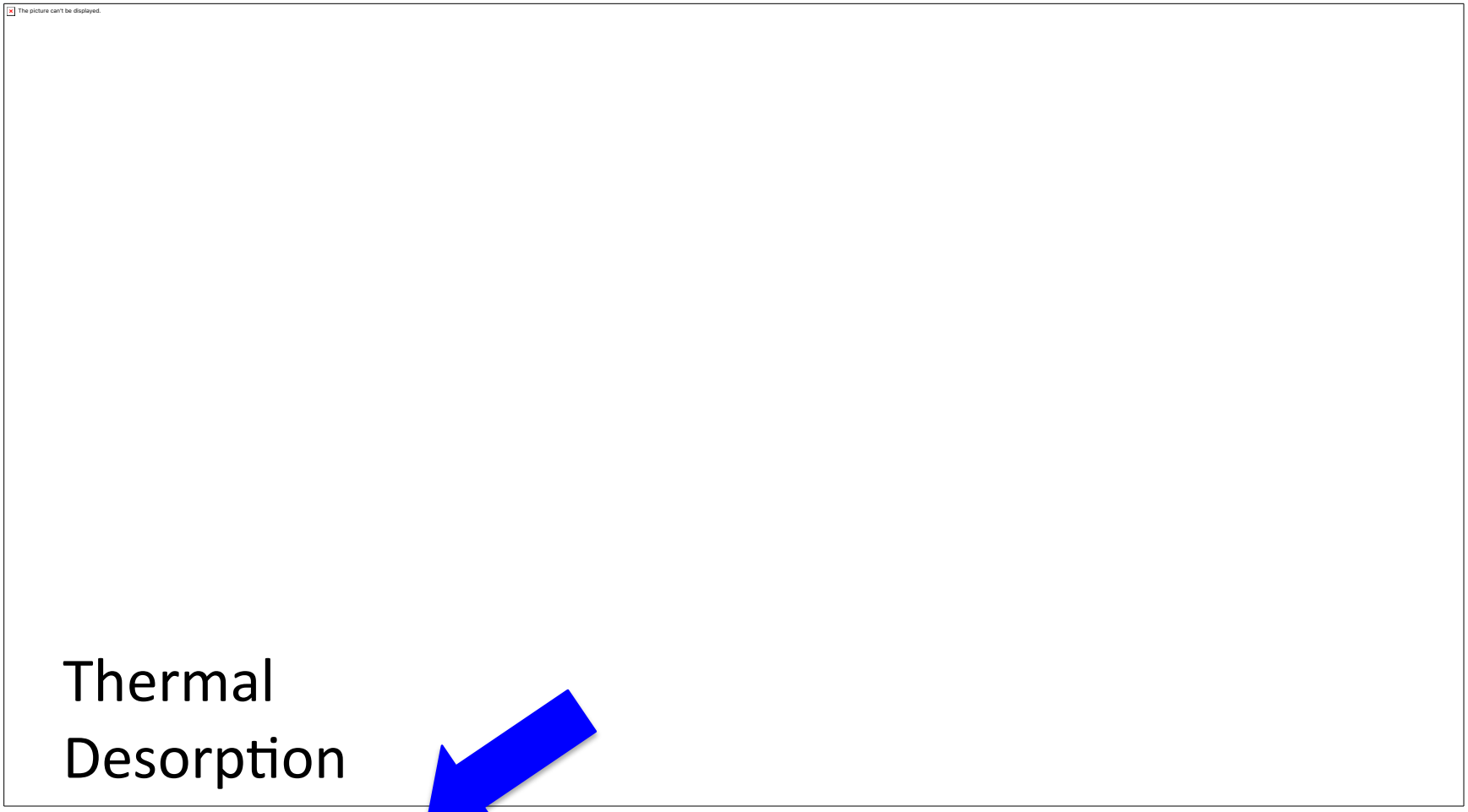
Icy moon: Enceladus, the moon with a plume







Accretion and thermal desorption: From gas to ice and back to gas



Binding of simple molecules:
Experiments CO adsorption and desorption

Spain:

InterStellar Astrochemistry Chamber

Munoz Caro et al. 2010

CO accretion from 80 K to 8 K

Accretion → CO solid by Fourier transform infrared (FTIR) spectroscopy in transmittance

Taiwan:

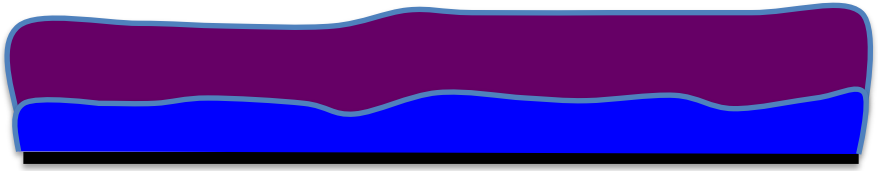
Interstellar Photoprocess System

Chen et al. 2014

CO accretion at 14 K

TPD→Laser reflective interference system counts with a He-Ne laser (λ = 632.8 nm)

TPD → Mass spectrometer to follow CO desorbing with T

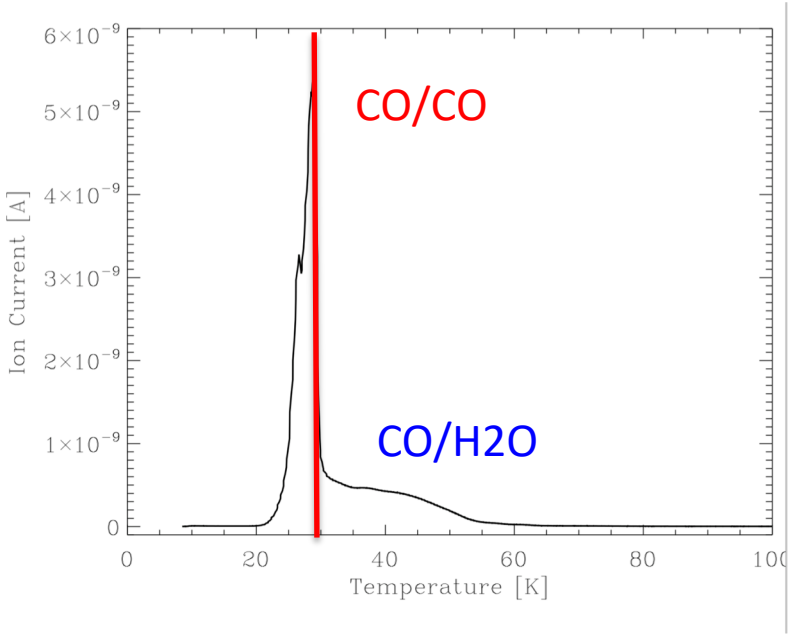


CO

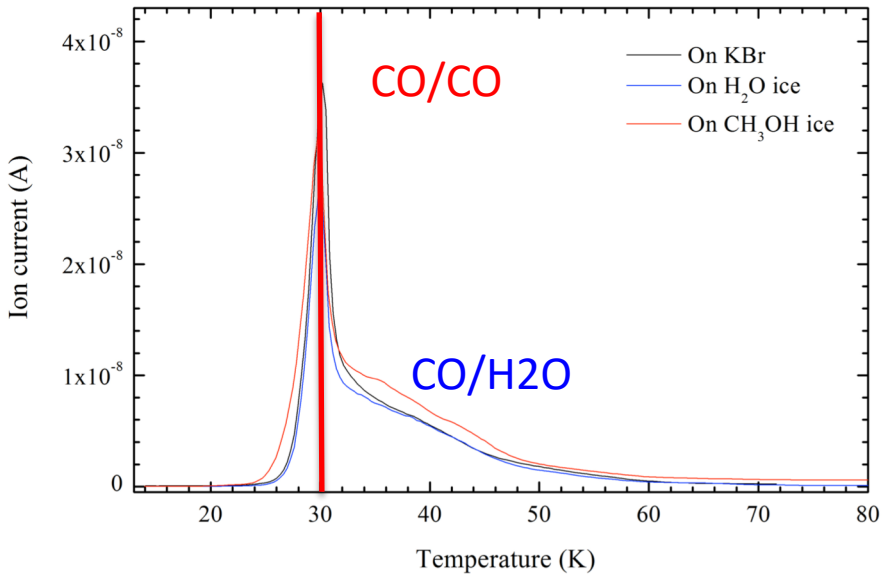
water

CO desorption

Spain: CO accretion 80 K to 8 K + TPD



Taiwan: CO accretion at 14 K + TPD



Multilayer CO/CO at ~30K; Monolayer CO/H2O until ~50-60K

Noble et al. 2014; Collings et al. 2004; Marťın-Domenech et al. 2014

CO desorption: determining binding energies

Monolayer: CO on water

From TPD: 30-50 K corresponds to binding energies ranging between 900 and 1500 K (Ebin= 30.9 * T_{des}; *Luna et al. 2017*)

He et al. 2016; Martin Domenech 2014; Noble et al. 2012

Multilayer: CO on CO

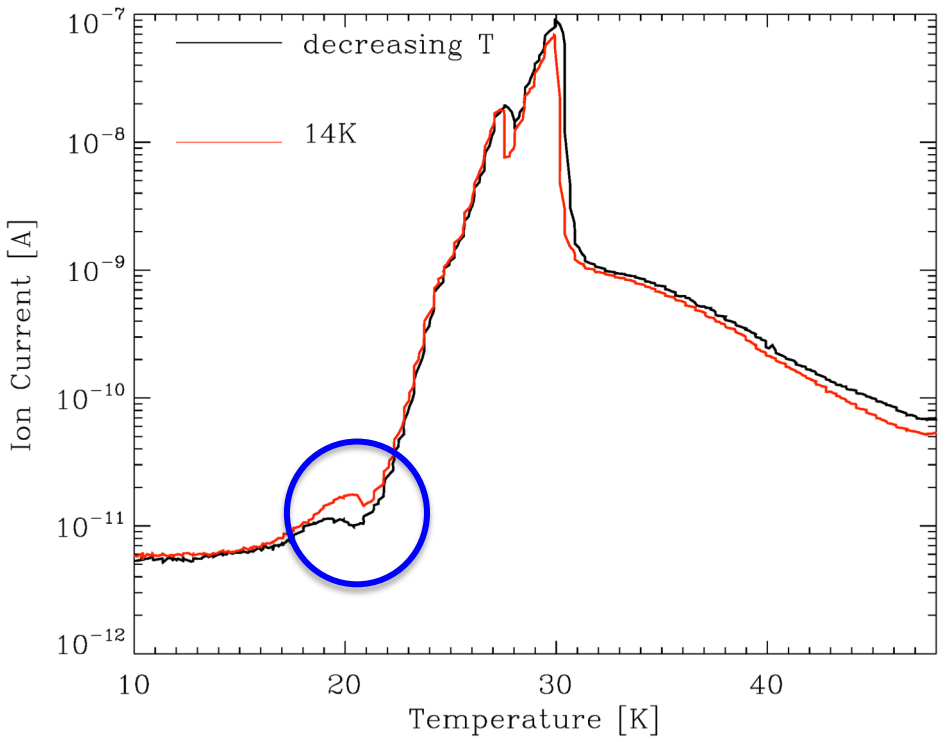
Interaction CO with a CO surface:

~830 K *Luna et al. 2014; Noble et al. 2012; Munoz Caro et al 2010; Pontoppidan et al. 2006, Acharyya et al. 2007, Collings et al. 2003*

CO desorption

TPD from 1) CO accretion from 80 K to 8 K 2) CO accretion at 14K
Look similar → accretion does not change the CO ice?

Have a look at TPD in logarithmic scales:



Multilayer CO/CO at ~30K;
Monolayer CO/H_2O until ~50-60K

Noble et al. 2014; Collings et al. 2004; Martín-Domenech et al. 2014

What is the small peak at 20K???

CO molecules with binding energies ~600K

More for deposition at 14K than for decreasing T

CO desorption: determining binding energies

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Interaction between 2 CO molecules: van der Waals

~200 K *Karssemeijer & Cuppen 2014; Tang et al. 2002; Krupskii et al 1973;*

How does the binding energy increase with the number of neighbors as CO interact with 1 CO (dimer; ~200K) or with > 3 CO (surface)?

Building CO ices

Multilayer: CO on CO

Interaction between 2 CO molecules: van der Waals

~200 K *Karssemeijer & Cuppen 2014*

Interaction CO with a CO surface:

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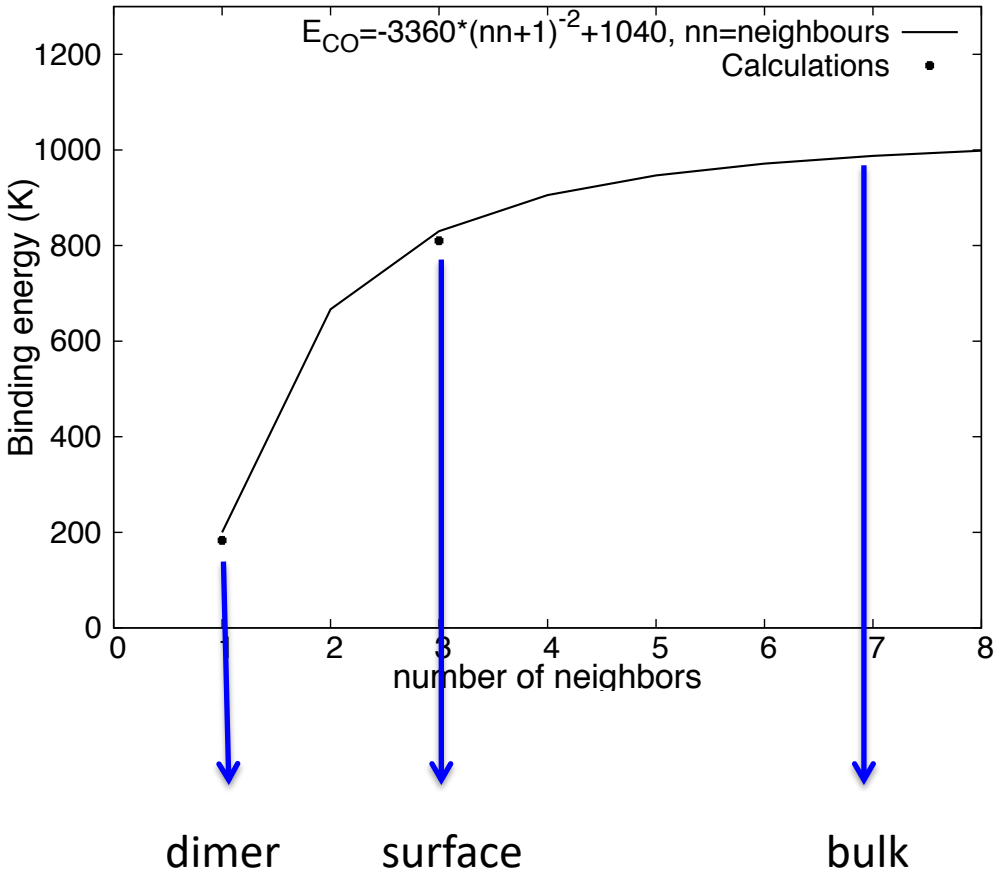


Improvement in the future F. Dulieu

Simulations

Step-by-step Monte Carlo simulation to follow the formation of CO ices

Cazaux et al. 2016

Follow the fate of individual CO molecules

Accretion

Diffusion

Evaporation

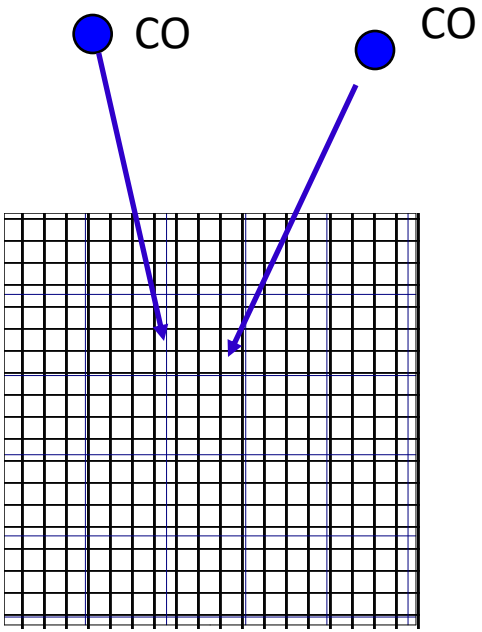
CO arrive randomly on the surface + a random walk

Cuppen & Herbst (2007) KMC

Garrod (2013) off lattice KMC

Lamberts (2014) KMC

binding energy of one species is the sum of the pair-wise interaction potentials with its neighbours.



grid sizes of 20*20 sites

Flux to mimic the experiments:

Deposition 14K:

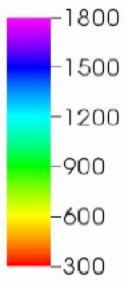
7.8 ML/min ~ 52 molecules/s

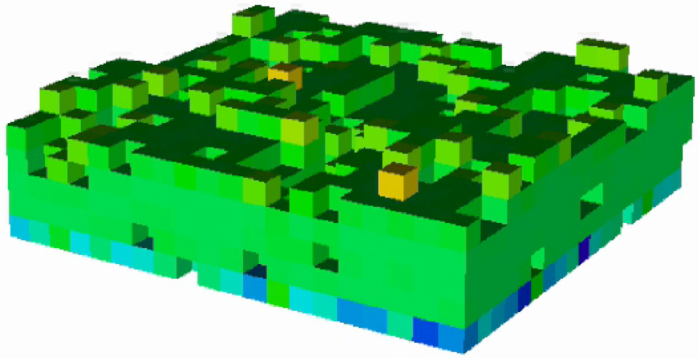
Deposition 80 down to 8K

1.5 ML/min ~ 10 molecules/s

Building CO ices

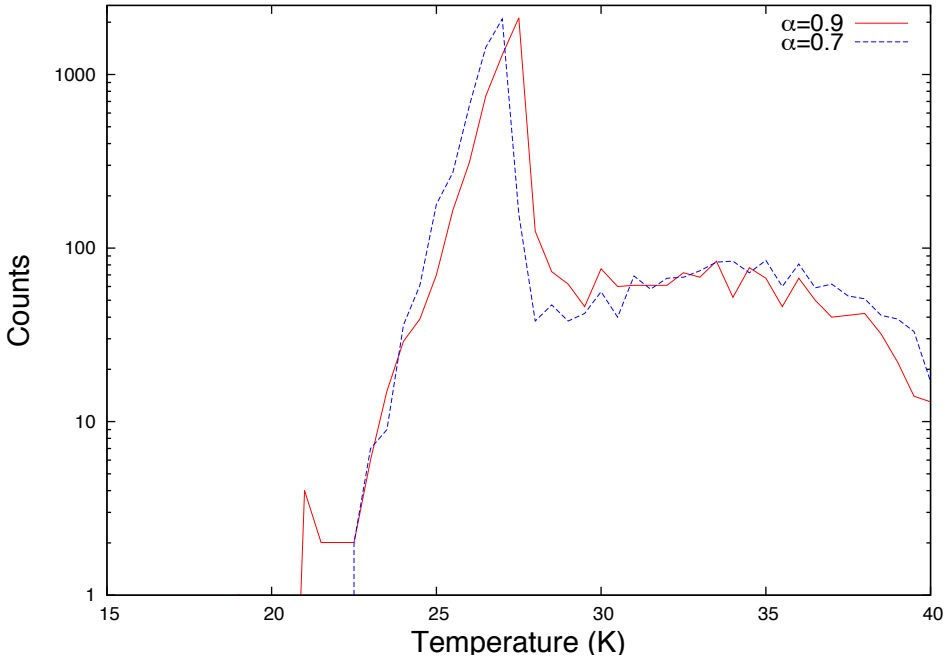
- Monte Carlo simulations of the formation of the CO ices.
- Reproduce accretion + TPD

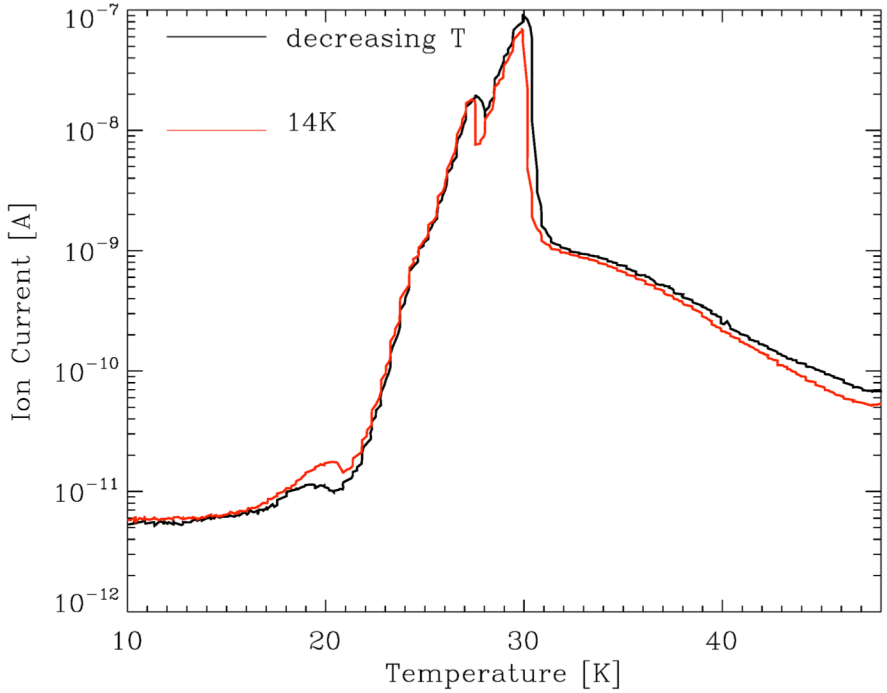




Evaporating CO ices

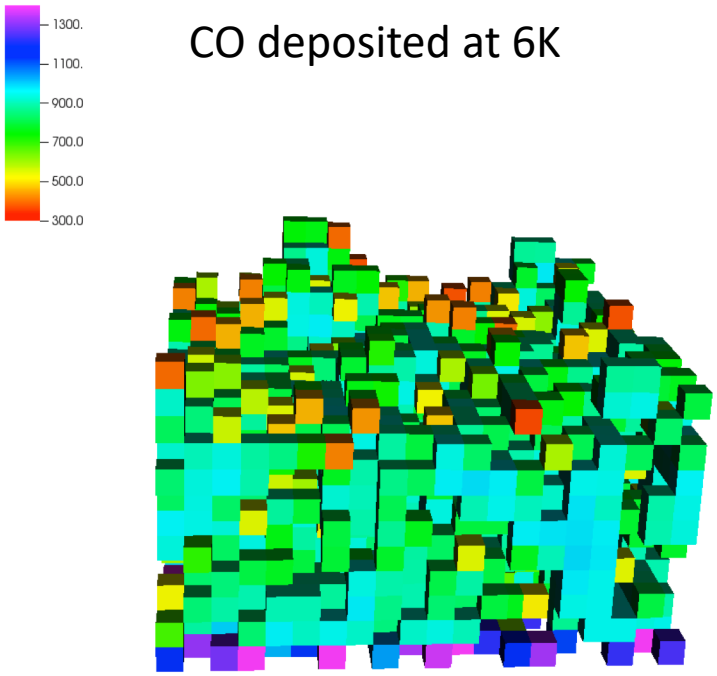
- Can TPD experiments constrain the diffusion?
- The presence of weakly bound CO molecules can only be reproduce if the diffusion is low.





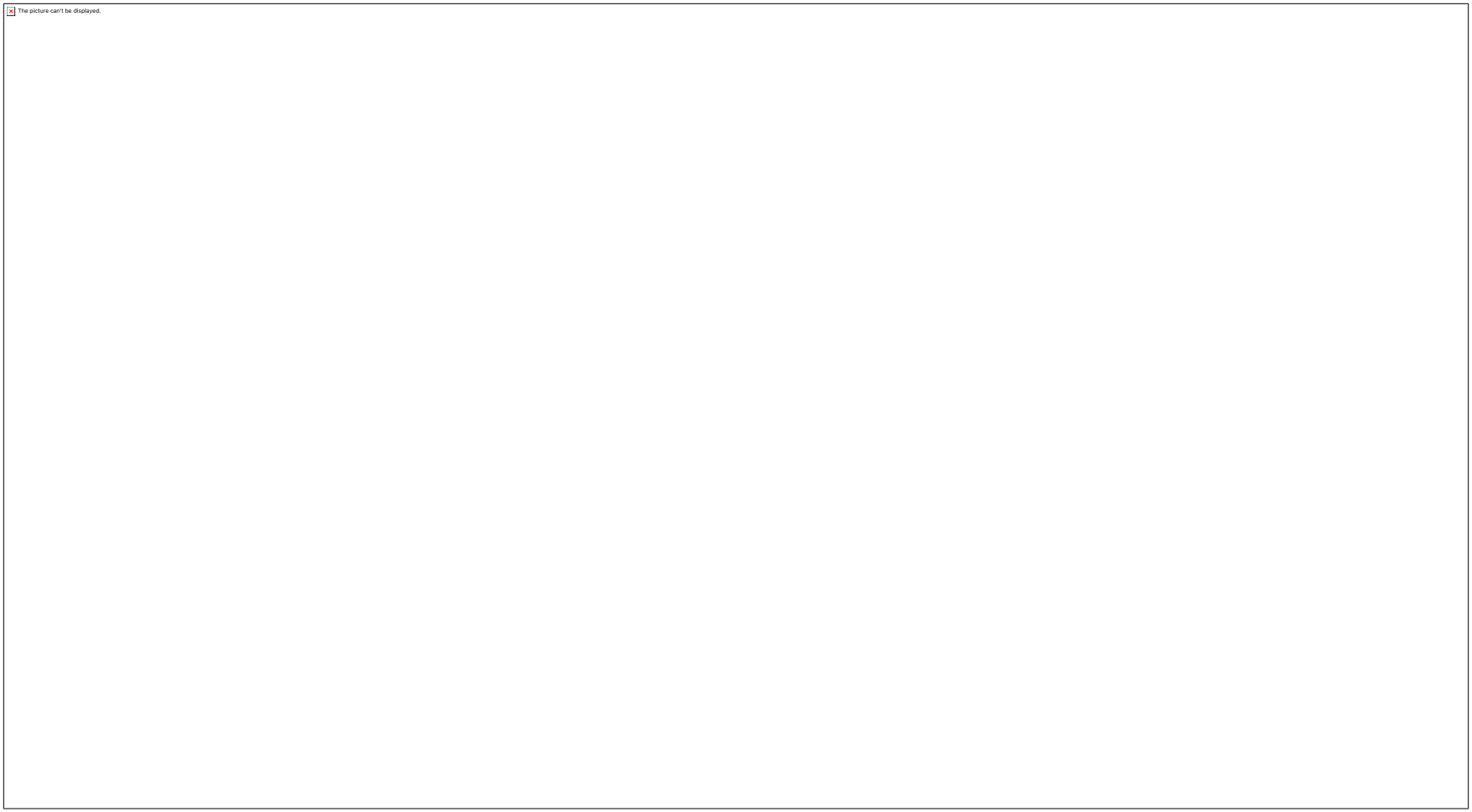
Ice in space versus TPD

- Laboratory: TPD show binding energies of already reorganized ices. Looking at details → some constrains on binding energies and mobility
- MC simulations → weakly bound CO are present and show slow diffusion
- CO depletion in dense core → higher gas phase CO because lower binding energy?



CO deposited at 6K

Chemical desorption

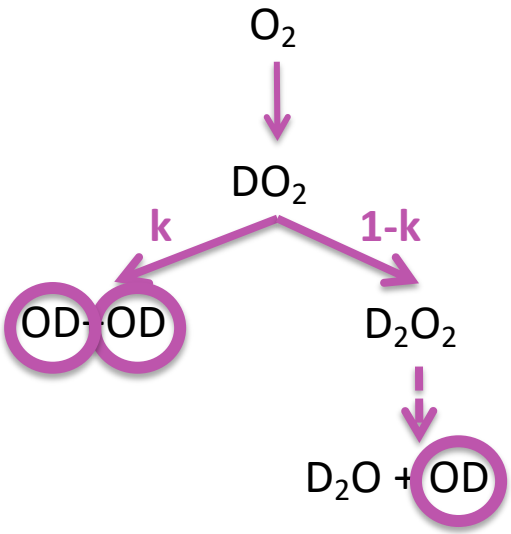


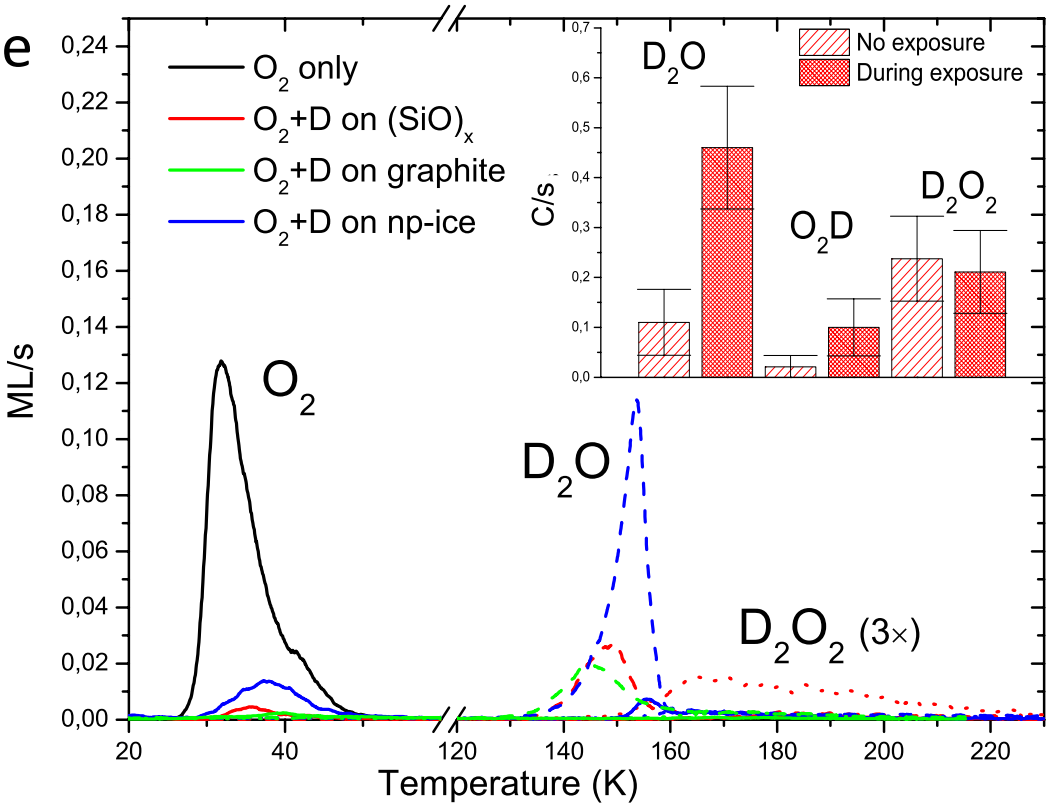
Quantifying the chemical desorption process

1st step: O_2 deposited on surface

2nd step: D deposited

→ most of the O_2 is missing.





D_2O (gas)

OD + D → D_2O (ice)

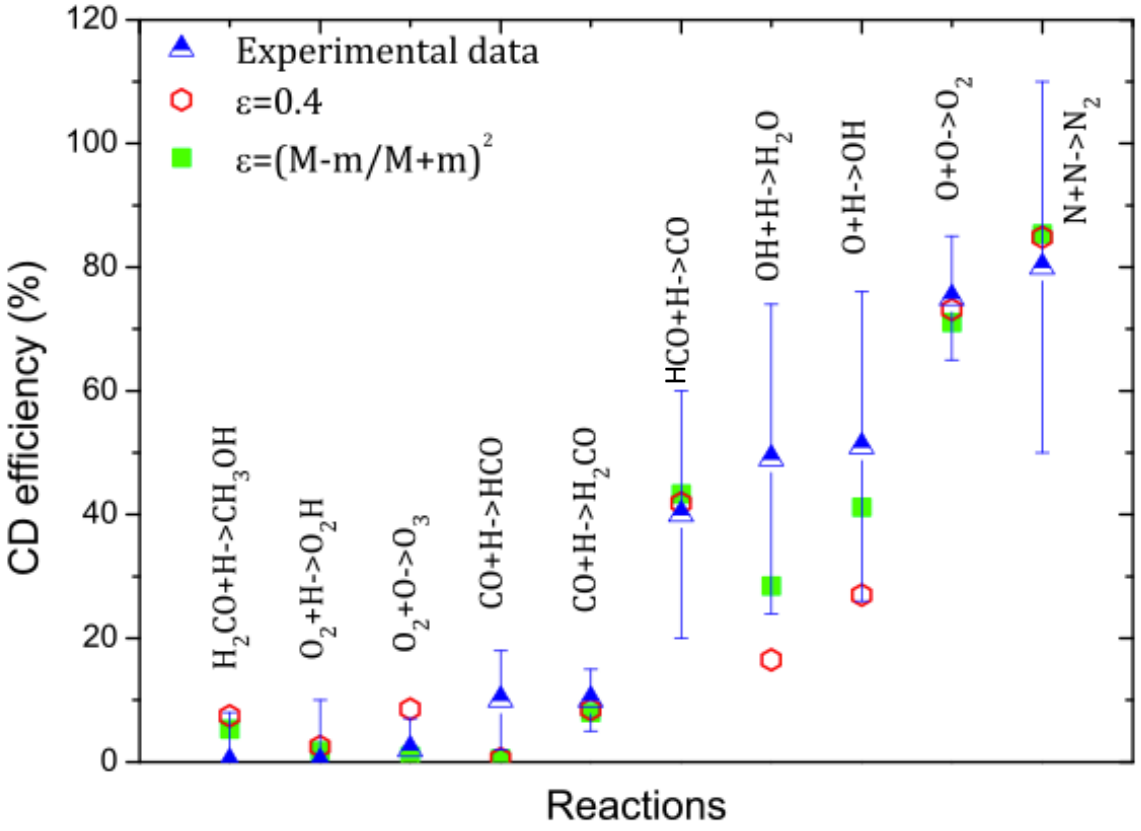
Best fit to the measurements → ~**50%** of D_2O desorb from OD +D

Dulieu et al. 2012
Chaabouni et al. 2012

Quantifying the chemical desorption process

Experiments	Surface temperature	Coverage range	Method DED	Method TPD	Reaction	Desorbing product	ΔH_R	Experimental CD efficiency np-ASW	Experimental CD efficiency Amorphous silicate	Experimental CD efficiency Oxidized HOPG	Theoretical
	(K)	(ML)					eV	%	%	%	%
[O+H]	10	<1	√	√	O+H	OH	4.44	25±15*	–	50±25*	39
					OH+H	H_2O	5.17	30±15*	–	50±25*	27
					OH+H	H_2O	5.17	<40±20[a]	<70±20[a]	<80±20[b]	27
[O_2+H]	10	0.5-1	√	√	O_2+H	O_2H	2.24	<8*	10±10[b]	–	1.4
					O_2H+H	H_2O_2	3.69	<8*	<5[b]	–	0.5
					O_2H+H	2 OH	1.47	<8*	<5[b]	–	0.3
					H_2O_2+H	H_2O+OH	2.95	<5*	<5[b]	–	2.1
[O_3+H]	10 and 45	0.5-1	√	√	O_3+H	O_2+OH	3.33	–	<10[b]	<8*	8
					OH+H	H_2O	5.17	–	80±20[b]	–	27
[O+O]	8 to 25	<1	√	√	O+O	O_2	5.16	<5[c]	40±10[#d]	80±10[#e]	68
					O_2+O	O_3	1.1	<5[c]	<5[d]	<5[e]	0
[N+N]	10	<1	√	√	N+N	N_2	9.79	>50[&*]	>70[&*]	>70[&*]	89
[CO+H]	10	0.8-2.5	√	√	CO+H	HCO	0.66	–	–	10±8*	0.7
					HCO+H	$CO+H_2$	3.85	–	–	40±20*	47
					HCO+H	H_2CO	3.91	–	–	<8*	7
[H_2CO+H]	10 and 55	0.8-2	√	√	H_2CO+H	CH_3O	0.88	–	–	<8*	0
					H_2CO+H	HCO+H_2	0.61	–	–	10±5*	0
					HCO+H	$CO+H_2$	3.85	–	–	40±20*	47
					HCO+H	H_2CO	3.91	–	–	10±5*	7
					CH_3O+H	CH_3OH	4.56	<8*	–	<8*	2.3
[Ar+H]	10	1	√	√	Ar+H	Ar		–	<5*	–	
[NO+H/O/N]	10	0.5-5	X	√	many	many		<8*	<8*	<8*	
[CO+O]	10	0.5-4	√	√	CO+O	CO_2	5.51	<5*	–	<5*	22
[H_2CO+O]	10 and 55	0.8-2	X	√	H_2CO+O	CO_2+H_2	5.45	<10*	–	<10*	8
[CH_3OH+H]	10	0.5-2	√	√	CH_3OH+H	CH_3OH		<8*	–	<8*	
[CH_3OH+O]	10	0.5-2	√	√	CH_3OH+O	CH_3OH		<8*	–	<8*	

Quantifying the chemical desorption process



Minissale et al. 2016
Cazaux et al. 2016

CD: Higher than previous studies *Garrod 2007*

Problems with methanol in dense cores: *Wakelam 2017*

Quantifying the chemical desorption process

- Chemical desorption depends on:
  - Enthalpy of reaction
  - Degrees of freedom
  - Binding energies
  - Surface coverage

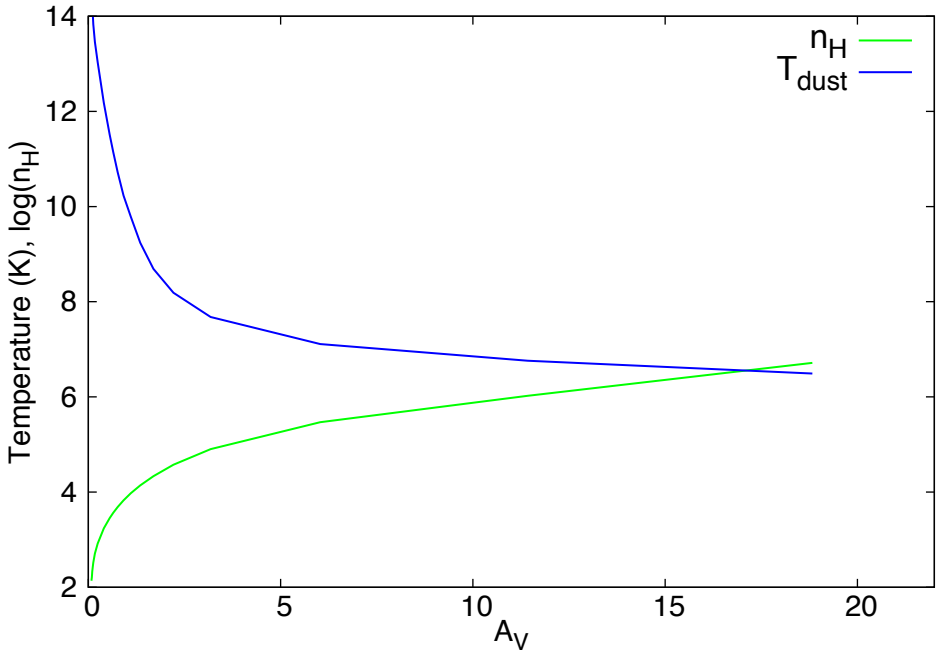
- For icy surfaces, the chemical desorption is much smaller than on bare surfaces (under detection limits). New measurements *(Oba et al. 2018 H+HS → H_2S on water ice CD=80%.)*

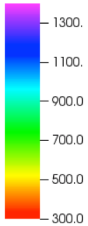
CO in starless and prestellar cores

- CO depletion in the center of the B68 and L1544 dense clouds ≥99% of CO missing from the gas phase; *Caselli et al. 1999; Bergin et al. 2002*
- Keto & Caselli (2010) found that the desorption rate due to cosmic ray strikes, *Hasegawa & Herbst (1993)*, should be increased by a factor of 30.
- Other mechanisms to release CO:
  - Photodesorption with UV photons *Oberg et al. 2007, 2009; Muñoz Caro et al. 2010; Fayolle et al. 2011; Muñoz Caro et al. 2016*
  - formation of H2 *Takahashi & Williams 2000*
  - non canonical explosions *Rawlings et al. 2013*
  - direct cosmic ray sputtering *Dartois et al. 2015*
  - cosmic ray induced explosive chemical desorption *Shen et al. 2004*
  - chemical desorption Dulieu et al. 2013
  - impulsive spot heating on grains *Ivlev et al. 2015*
  - **Binding energies?**

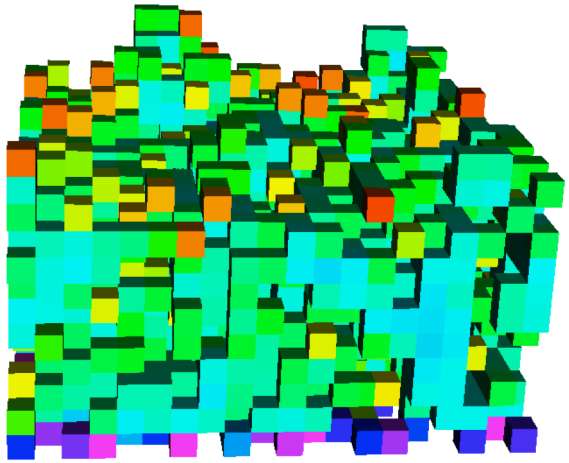
CO in starless and prestellar cores

- Density, temperature profile of pre-stellar core, from *Keto & Caselli 2010*
- CO ices deposited at 6K → weakly bound + holes
- Binding energy is set by the deposition temperature.



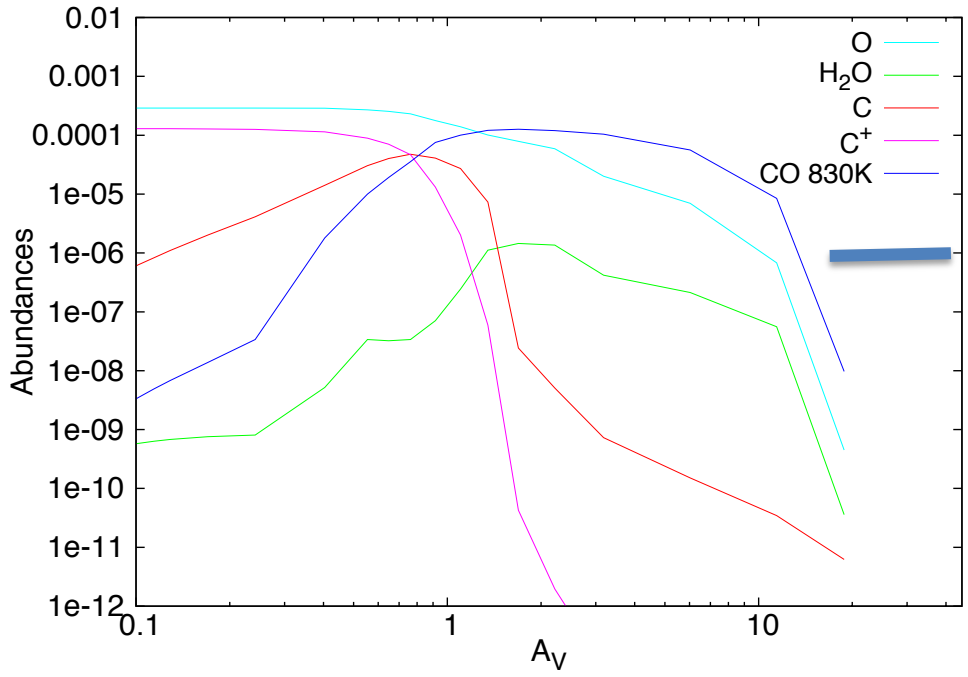


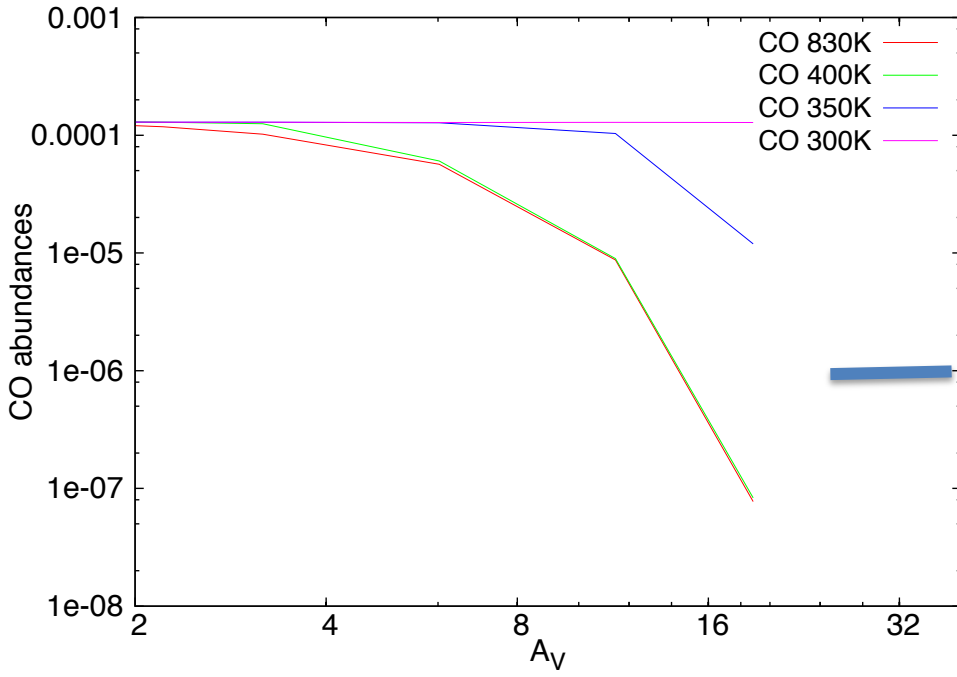
CO deposited at 6K



CO in prestellar cores

- Chemical model following density/temperature *Keto & Caselli 2010*
- Nahoon time dependent model + adsorption and desorption of CO **(ONLY!!! NO REACTIONS WITH CO OR OTHER DESORPTION MECHANISMS!!!)**
- CO with different binding energies/ **$t=10^4$ years**





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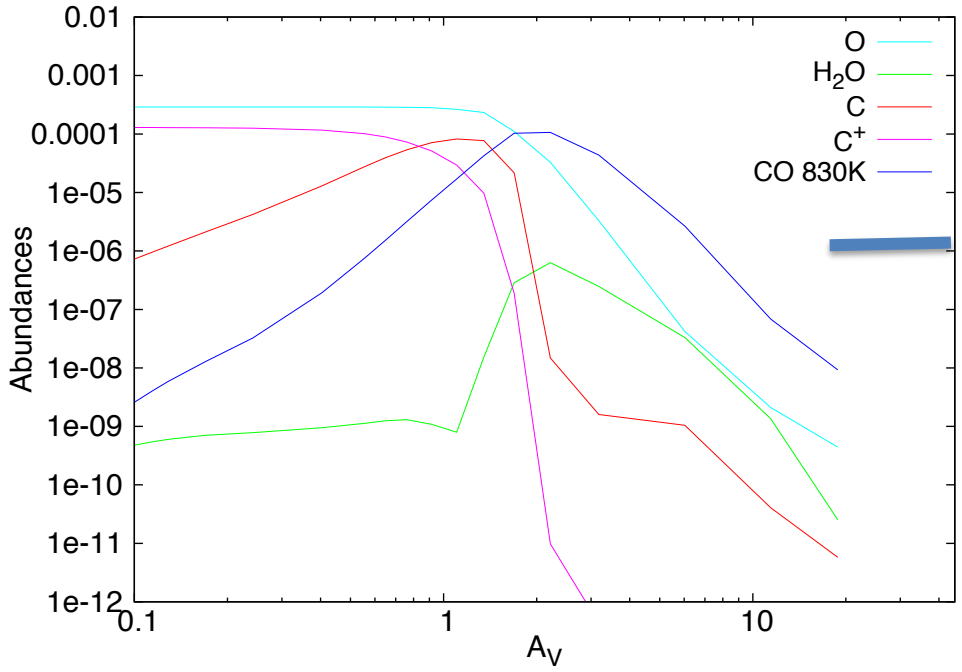
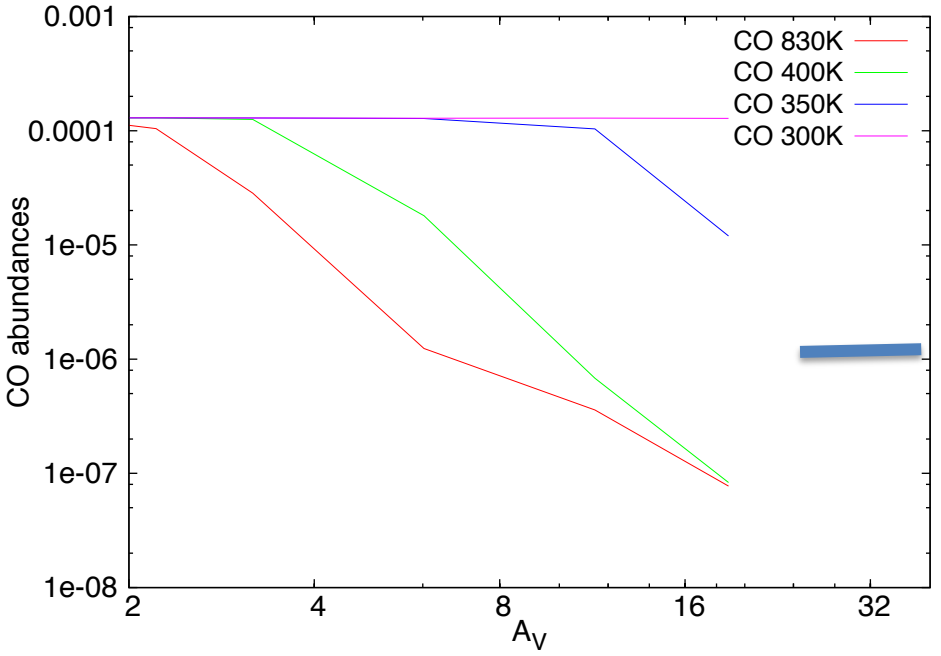
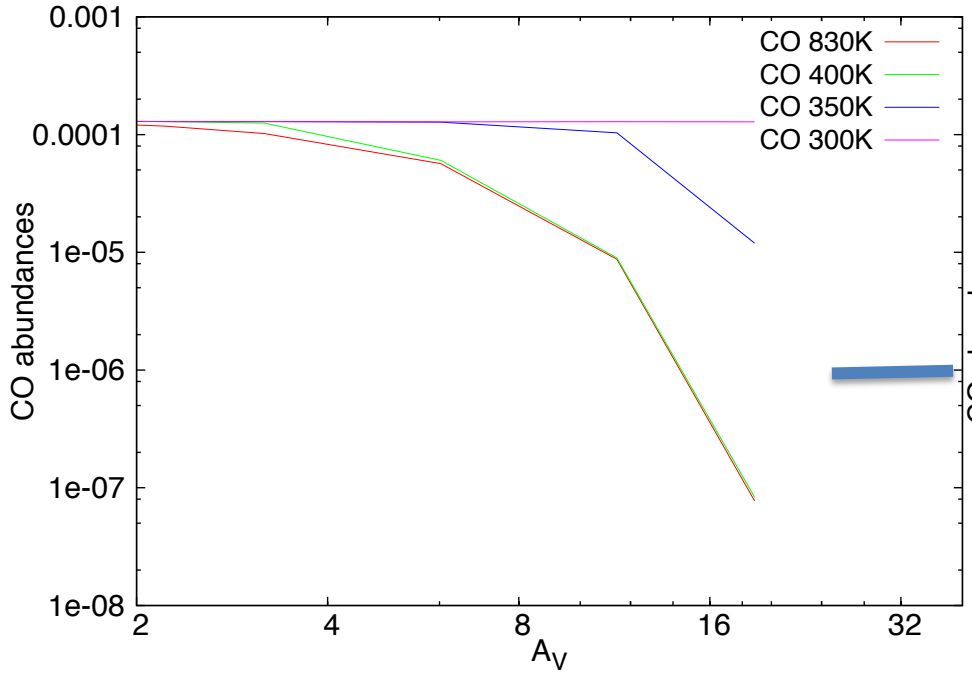
- CO with different binding energies/ **$t=10^5$ years**

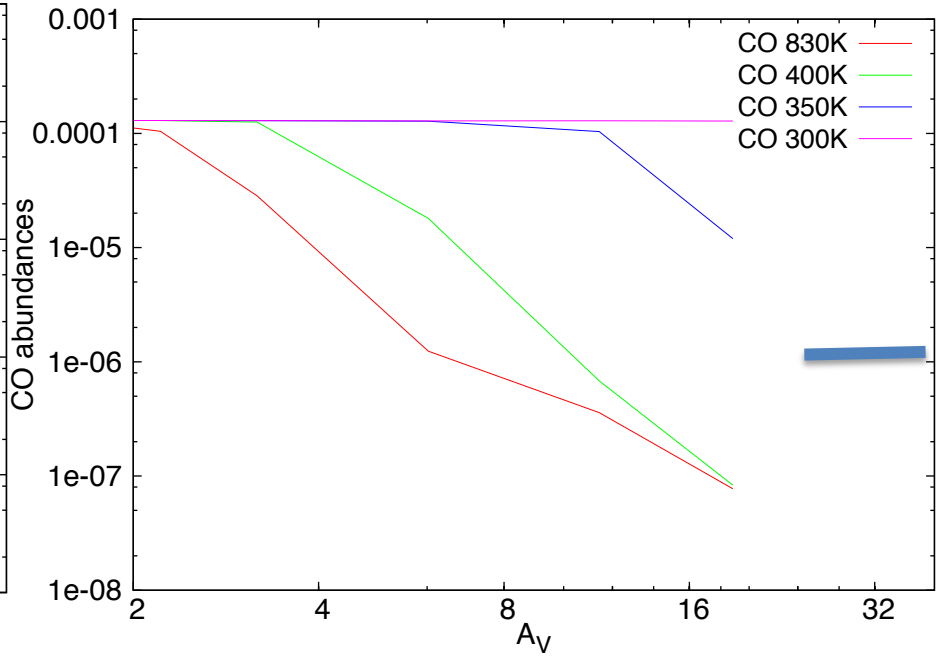




CO in prestellar cores

- low binding energies for CO→ changes the depletion of CO in dense cores
- rate equation model → cannot compute the depletion of CO due to the distribution of binding energies on the last layer of the ices.
- Models more details are needed (layers, *Taquet et al. 2012*)





Conclusions

- Laboratory: TPD show binding energies of already reorganized ices. Looking at details → some constrains on binding energies and mobility
- MC simulations → weakly bound CO are present and show slow diffusion?
- Deposition temperature sets the binding energies

→ Reproducing TPD for other species. Thesis M. Minissale & F. Dulieu

→ estimate binding energies with number of neighbors.

- CD depends on 1) enthalpy of formation 2) binding energy 3) degrees of freedom 4) mass of the products
- bare surfaces → measurements
  on icy surfaces → upper limits? And we are missing the binding energies of intermediate *(Wakelam 2016)* → CD is not efficient for methanol on ice.

Thank you

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