KINETIC DATABASE FOR ASTROCHEMISTRY

Laboratory study of thermal and non-thermal desorption processes of interstellar ices

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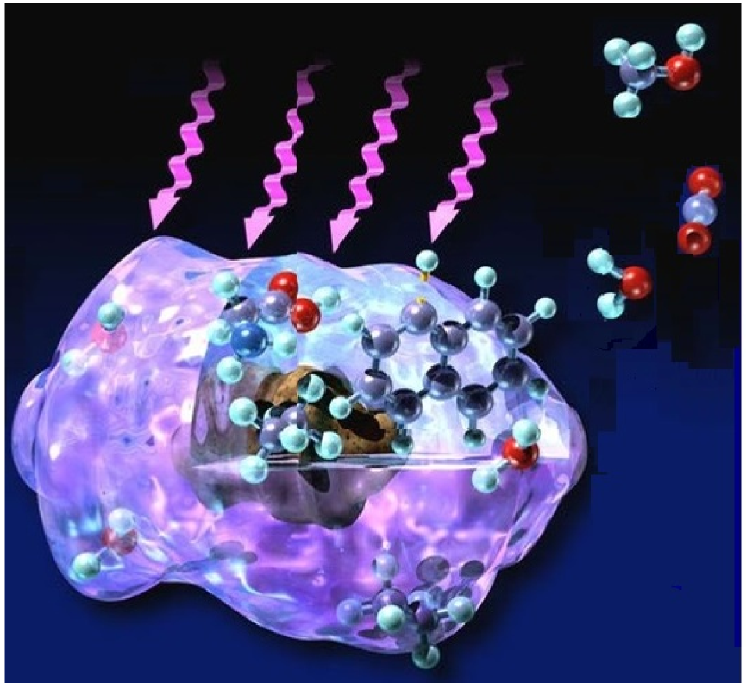
Motivations: Interstellar molecular ices

Cold regions of ISM (10 – 100 K) :

Rich variety of molecular species
- **H_2, CO, H_2O, CO_2**
- **$HCOOCH_3$, CH_3OH, CH_3CN…**



Molecules form or condense at the surface of micro-sized dust grains

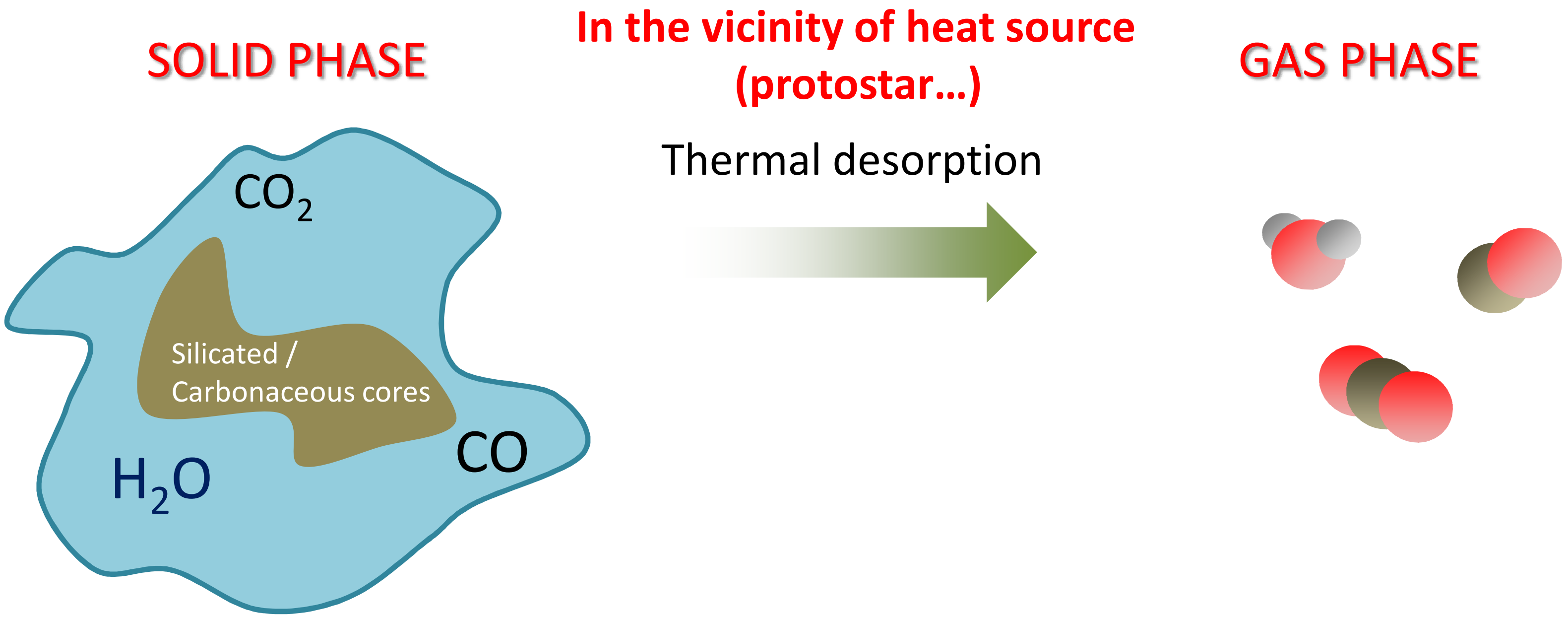
Ices = main reservoir of molecules in the cold interstellar region

Molecules are mainly detected in the gas phase

Solid-gas exchanges play a major role in gas phase abundance ratio and chemistry

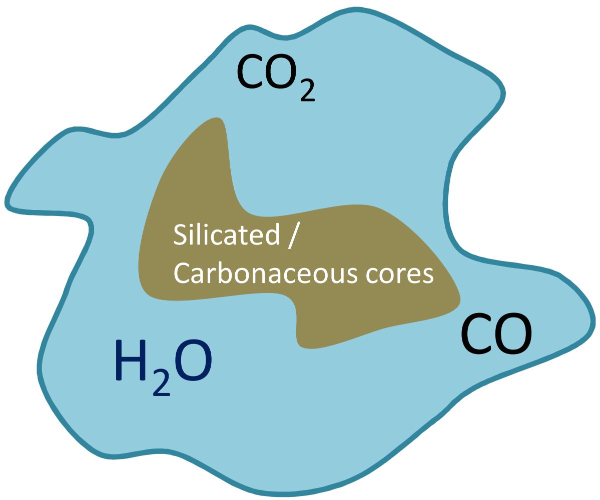
Desorption processes need to be quantified in order to be considered in astrochemical models

Motivations: Desorption processes



Motivations: Desorption processes

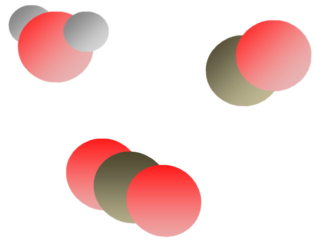
SOLID PHASE



In the vicinity of heat source (protostar…)

Thermal desorption

GAS PHASE



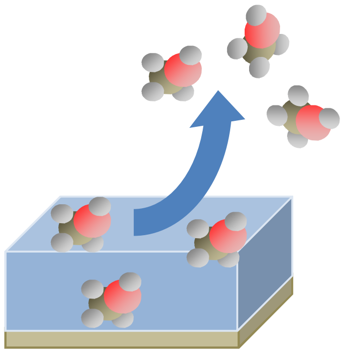
In cold regions (T ~ 10 K)

Non-thermal desorption

- Energetic particles
- Exothermic recombinations
- Shocks
- **UV photodesorption**

Thermal desorption: a joint experimental-theoretical approach

- **How to quantify thermal desorption?**



$$\phi(T) = Ae^{-\frac{E_{ads}}{kT}}$$

- **Aim: access reliable values for adsorption energies**

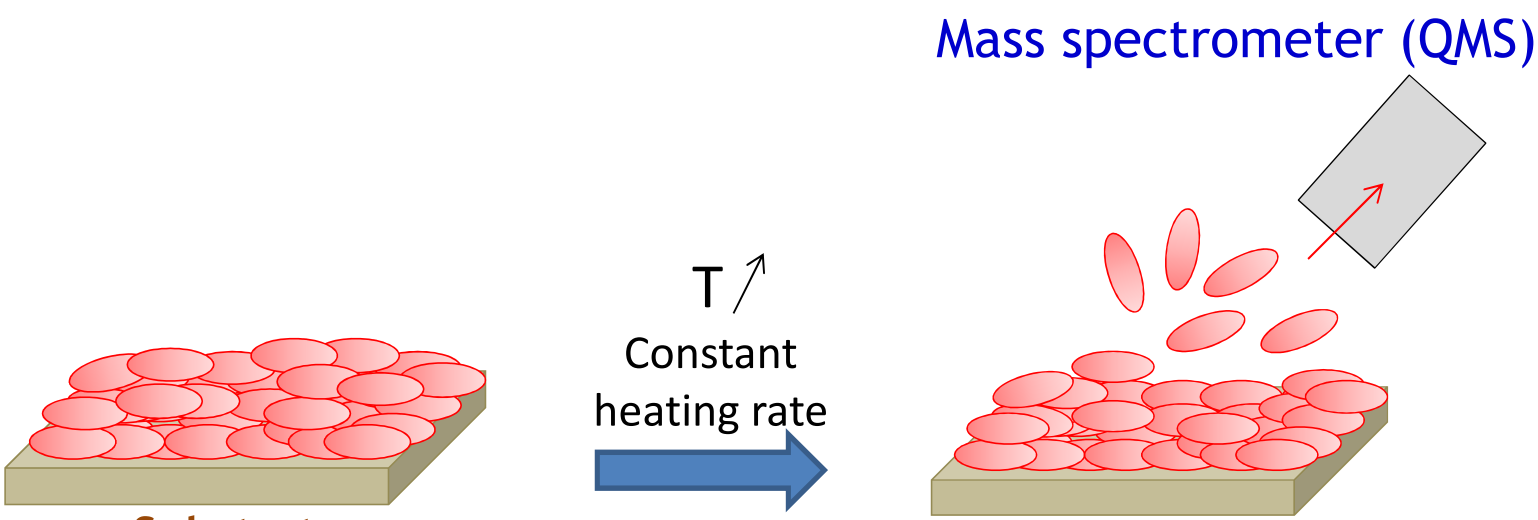
Experimental measurements: TPD technique in SPICES setup	*Intercomparisons* ⟷	Theoretical calculations: periodic DFT method

F. Pauzat, Y. Ellinger, A. Markovits

*PhD: **M. Doronin** (see poster)*

Organic molecules synthesis: ***J.-C. Guillemin***

Thermal desorption: Temperature Programmed Desorption method



Substrat

Highly Oriented Pyrolitic Graphite (HOPG)

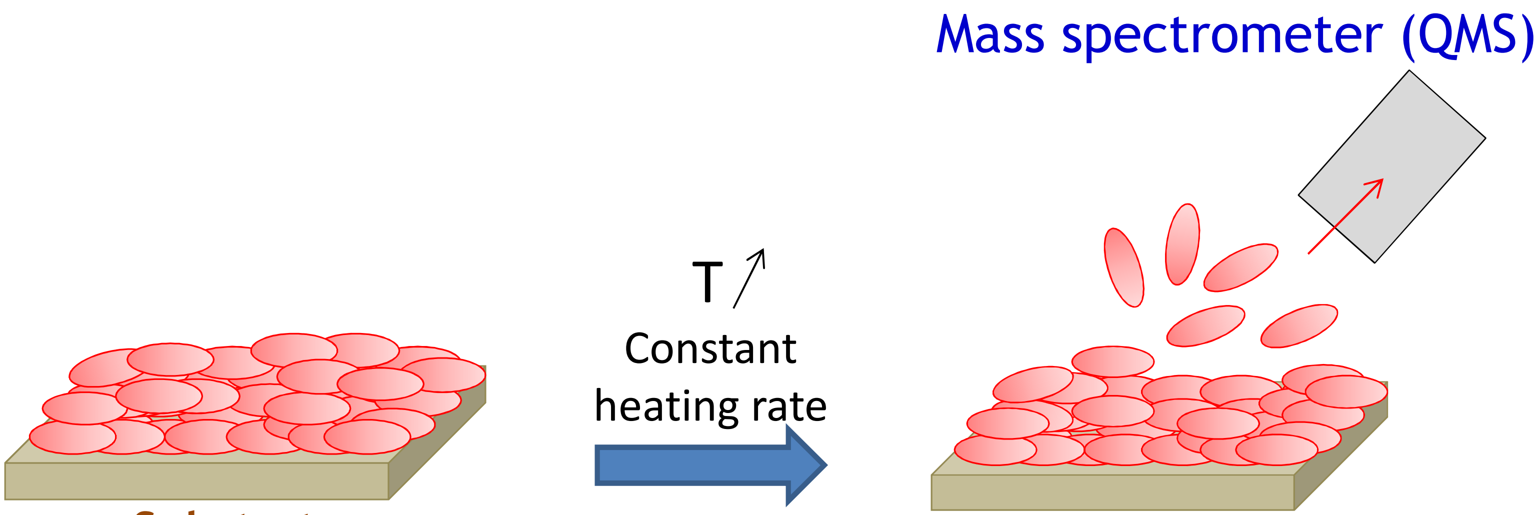
Quartz (0001)

Water ice (amorphous or crystalline)

T ~ 10 K

Desorbing flux : $$\phi = -\frac{d\theta_{surface}}{dT} = \frac{\nu}{\beta}.\theta^{n}.e^{-\frac{E_{ads}}{kT}}$$

Thermal desorption: *Temperature Programmed Desorption method*



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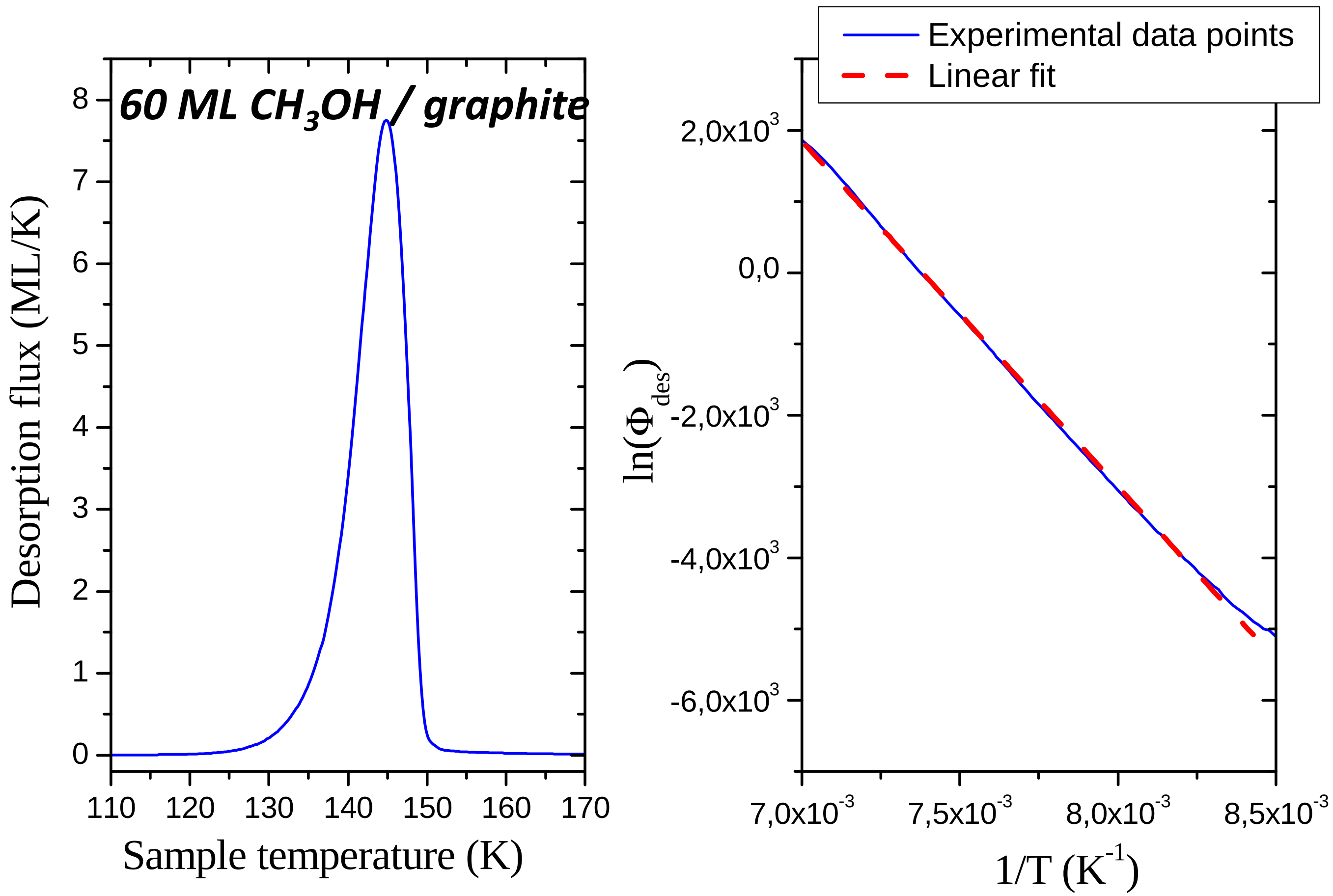
Thick ices: Multilayers

Zeroth order desorption: n = 0

$$ln(\phi) = -\frac{E_{ads}}{k}\frac{1}{T} + ln\left(\frac{\nu}{\beta}\right)$$



E_{ads} = 420 meV

$\nu = 5.10^{14}\ s^{-1}$

Thermal desorption: *the case of methanol on graphite*

Thin ices: (sub)Monolayers

Higher order desorption: $$\phi = -\frac{d\theta_{surface}}{dT} = \frac{\nu}{\beta}.\theta^n.e^{-\frac{E_{ads}}{kT}}$$

Our method :

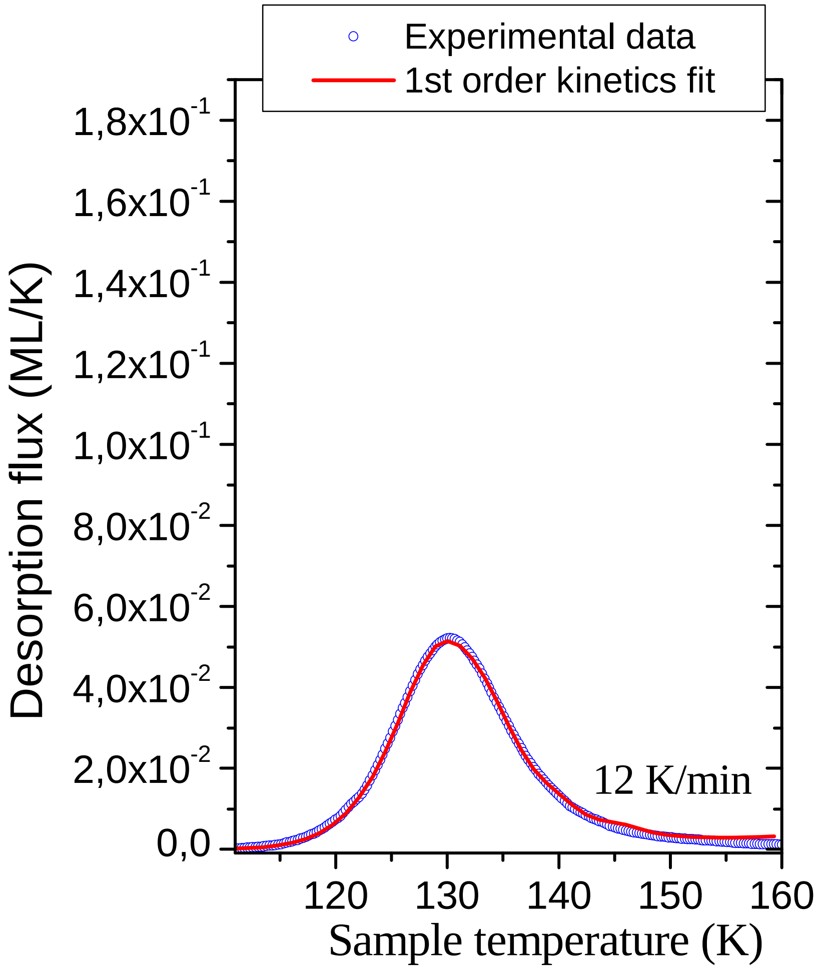
- **First order approximation (n = 1)**
- **Determination of ν from a set of TPD curves, made at different heating rates β**
- **Consideration of a distribution of adsorption energies**

$$\phi(T) = \frac{1}{\beta}\upsilon\sum_i \theta_i e^{-\frac{E_i}{kT}}$$

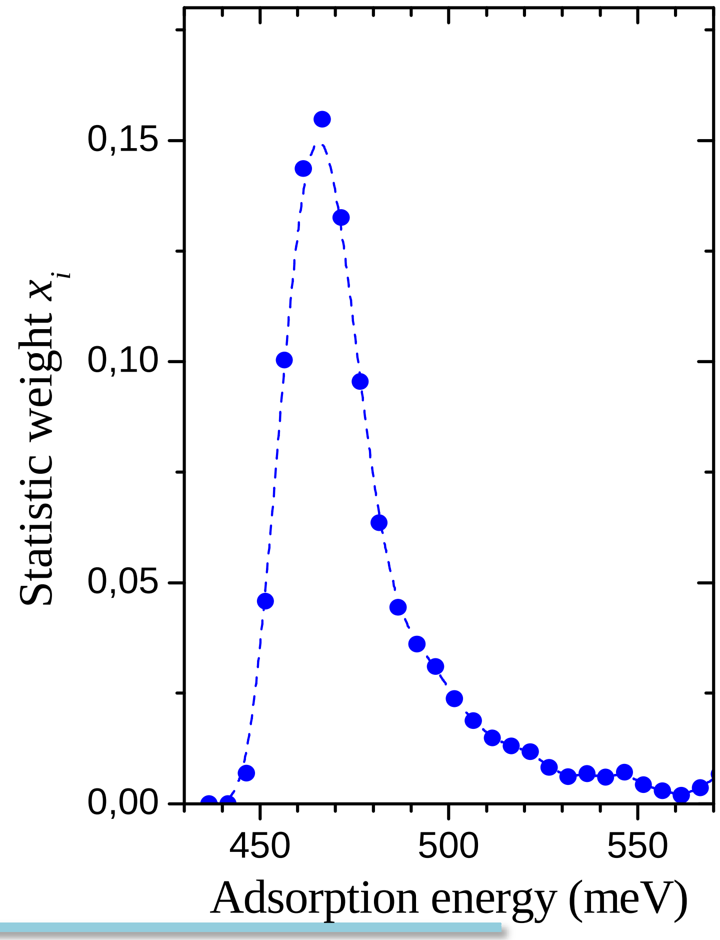
Thermal desorption: *the case of methanol on graphite*

Thin ices: (sub)Monolayers

0.8 ML CH_3OH / graphite



Adsorption energies distribution for an arbitrary ν at 3 K/min



Thermal desorption: *the case of methanol on graphite*

Thin ices: (sub)Monolayers

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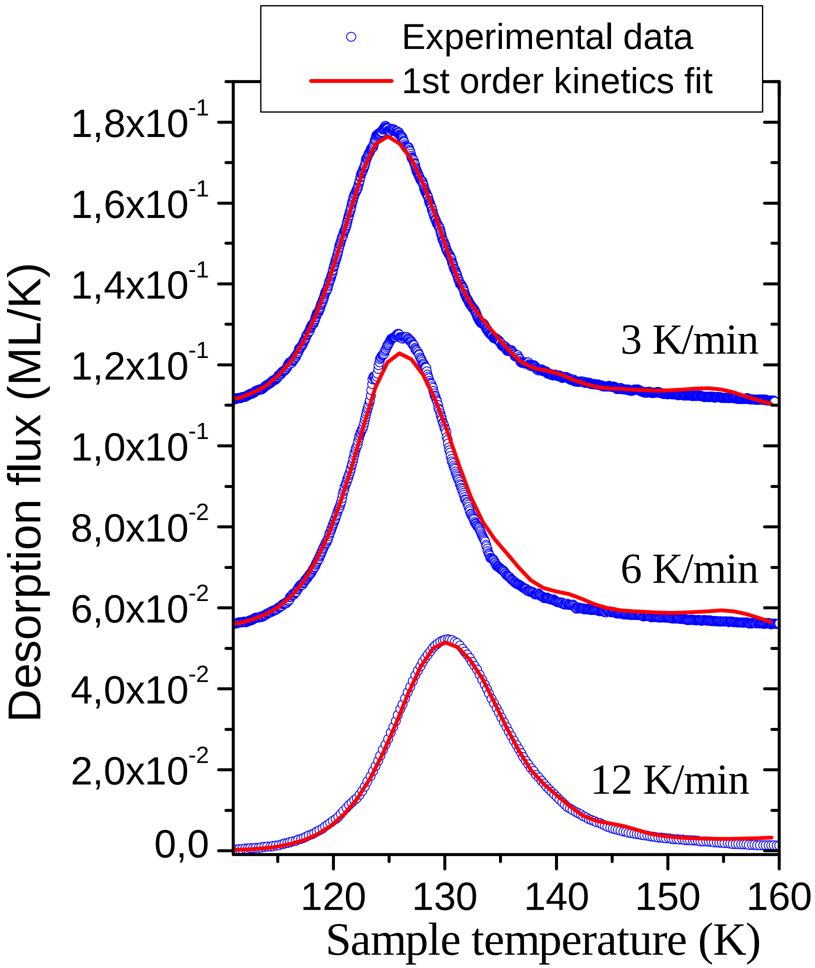

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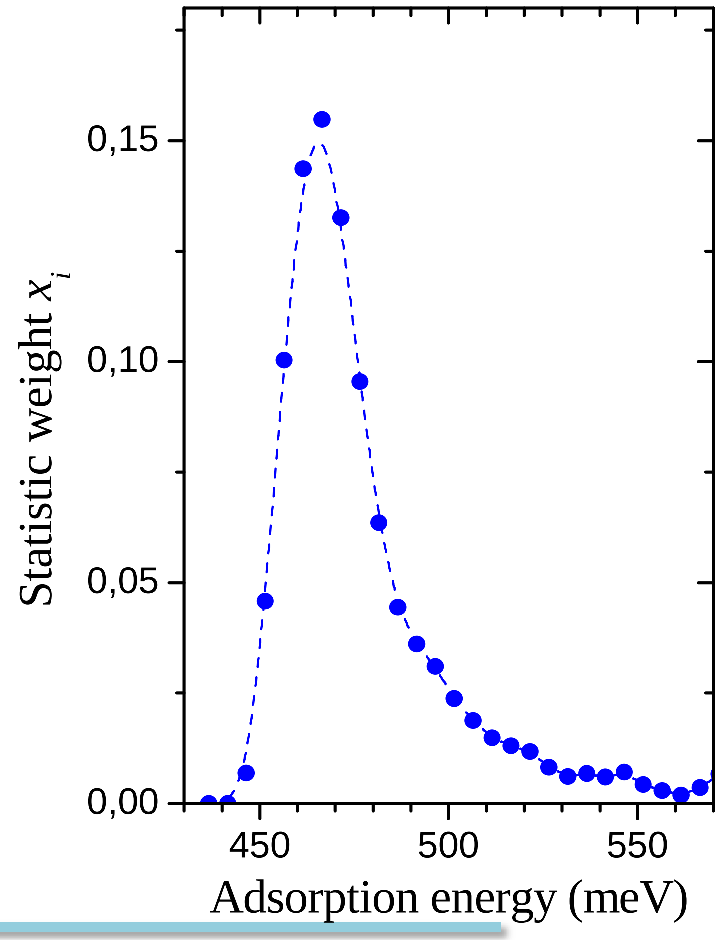
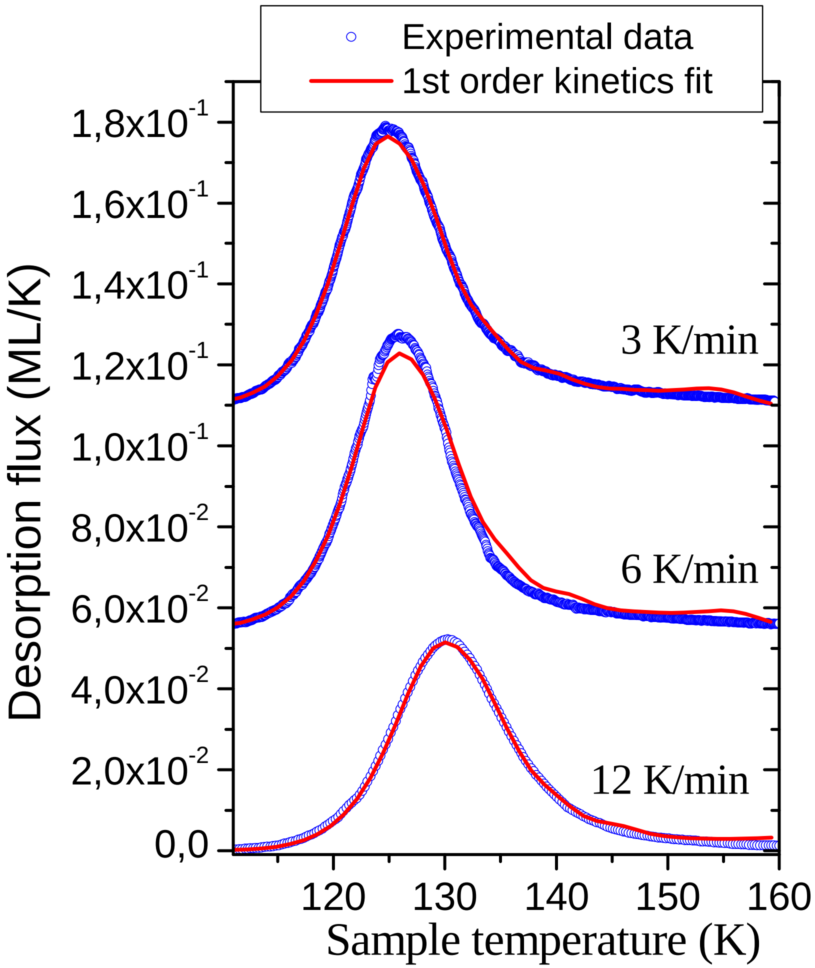


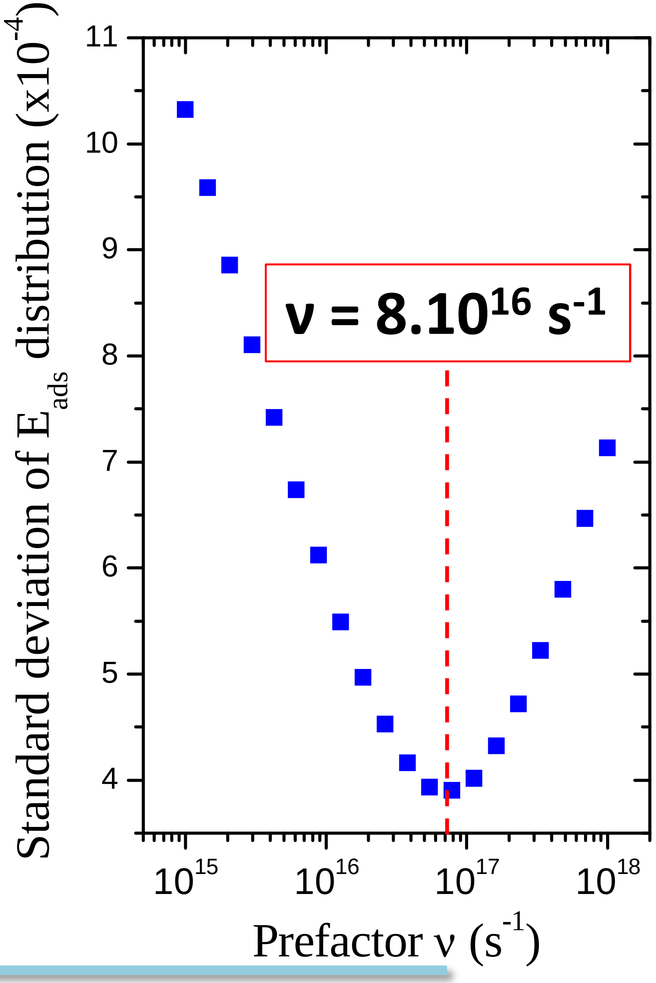
Thermal desorption: the case of methanol on graphite

Thin ices: (sub)Monolayers

0.8 ML CH_3OH / graphite

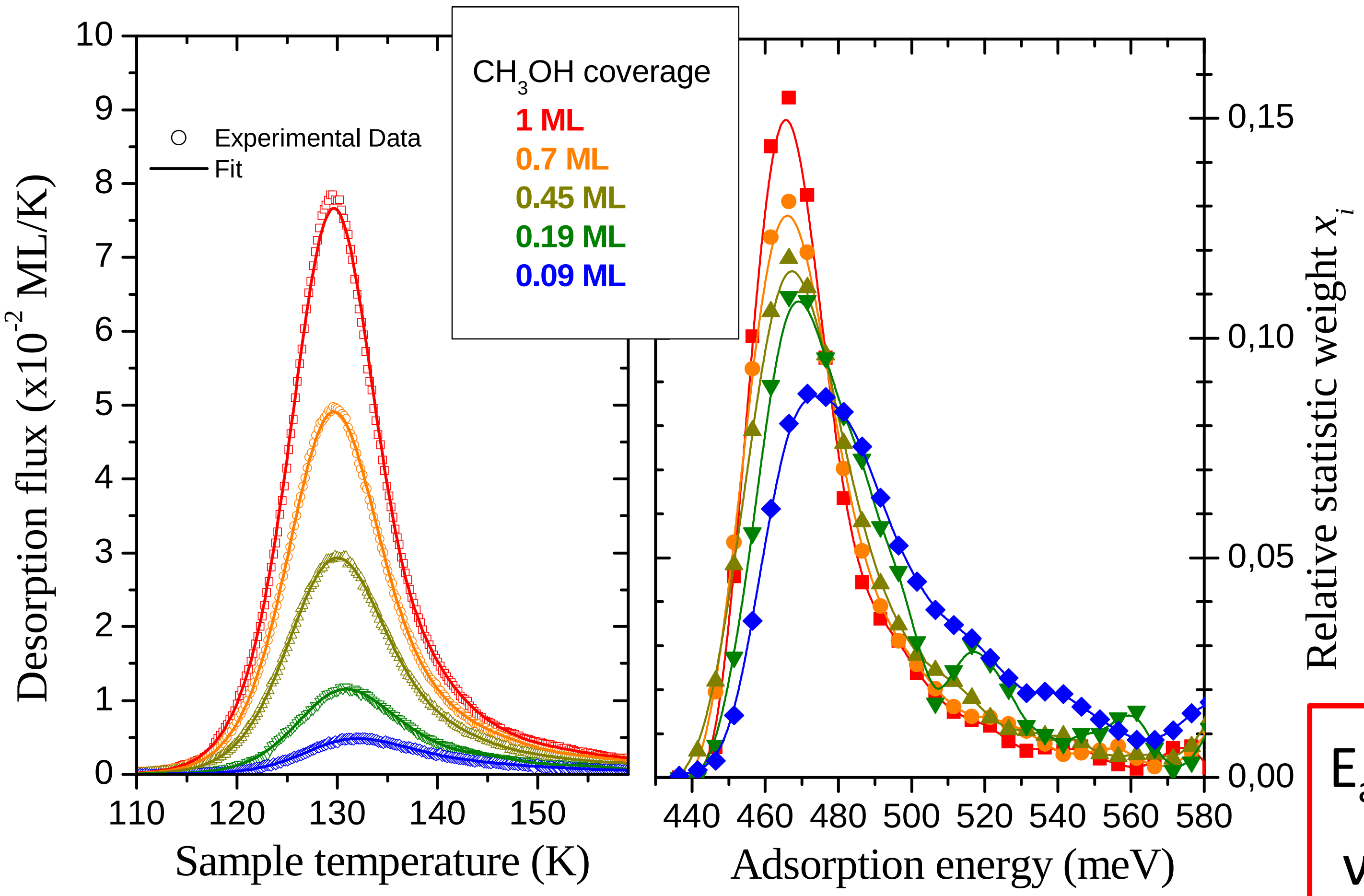


The 'good' value is the one for which the energy distribution is independent from the heating rate



Thermal desorption: the case of methanol on graphite

Thin ices: (sub)Monolayers



E_{ads} = 465±30 meV

ν = 1.10$^{17\pm0.5}$ s^{-1}

Thermal desorption: conclusions

- method to extract quantitative parameters (E_{ads}, ν) from experimental data

- good agreement with theoretical values of adsorption energies from the LCT team

- results compare well with previous experimental results from with Smith et al. 2014 et Bolina et al. 2005

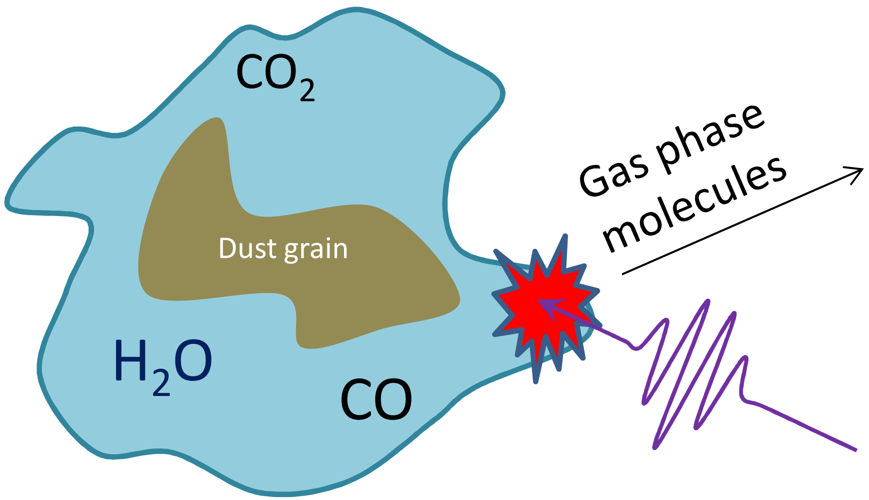
- limitations :
  - recquires to have a very good reproducibility on the ice growing method
  - diffusion is neglected

Thermal desorption: conclusions

Some systems studied so far (data for low coverage regime ~ 0.2 ML):

	Amorphous Water ice		Crystalline Water ice		Graphite		Quartz α (0001)	
	ν (s^{-1})	E_{ads} (meV)	ν (s^{-1})	E_{ads} (meV)	ν (s^{-1})	E_{ads} (meV)	ν (s^{-1})	E_{ads} (meV)
CH_3OH					10^{17}	465		
CH_3CN			10^{18}	> 570	2.10^{16}	480	10^{17}	540
CH_3NC			10^{18}	> 540	5.10^{17}	500	10^{17}	480
$HCOOCH_3$	10^{13-15}	370	10^{13-15}	380				
Ar			10^{10}	75				
Kr			2.10^{12}	125				
Xe			7.10^{12}	173				

UV Photodesorption: wavelength-resolved studies



- **UV photodesorption as a source for gas phase molecules in cold media:**

  Dominik et al., 2005
  Hersant et al., 2009
  Guzman et al., 2011
  …

- **UV photodesorption of simple molecules has been studied in laboratory mainly using discharge lamp, with varying spectra, as UV sources:**

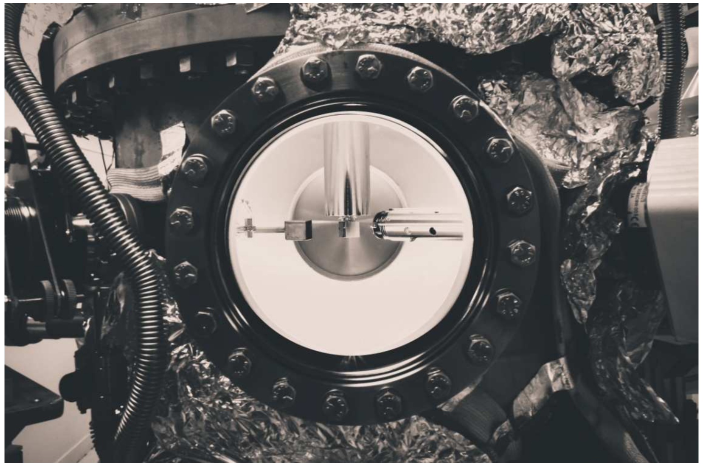
  Westley et al., 1995
  Öberg et al., 2007, 2008, 2009
  Muñoz-Caro et al., 2010
  …

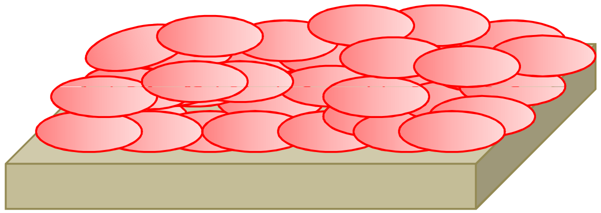
Our approach: determniation of photodesorption rate **as a function of the photon energy**

- to take into account different UV fields
- to access molecular mechanism responsible for the desorption

UV Photodesorption: wavelength-resolved studies

Experiments in the SPICES instrument (UPMC)
P ~ 10^{-10} Torr





Substrate
Highly Oriented Pyrolitic Graphite (HOPG)
Au polycristallin
Quartz (0001)

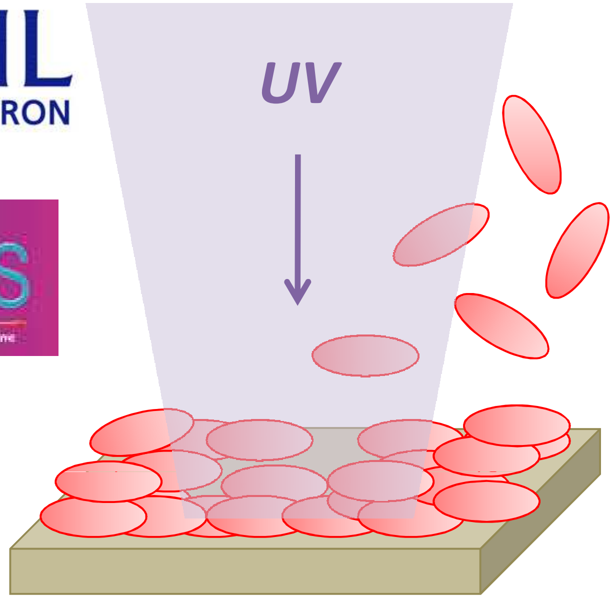
T ~ 10 K

***UV Photodesorption**: wavelength-resolved studies*

SOLEIL SYNCHROTRON

Beamline

DESIRS



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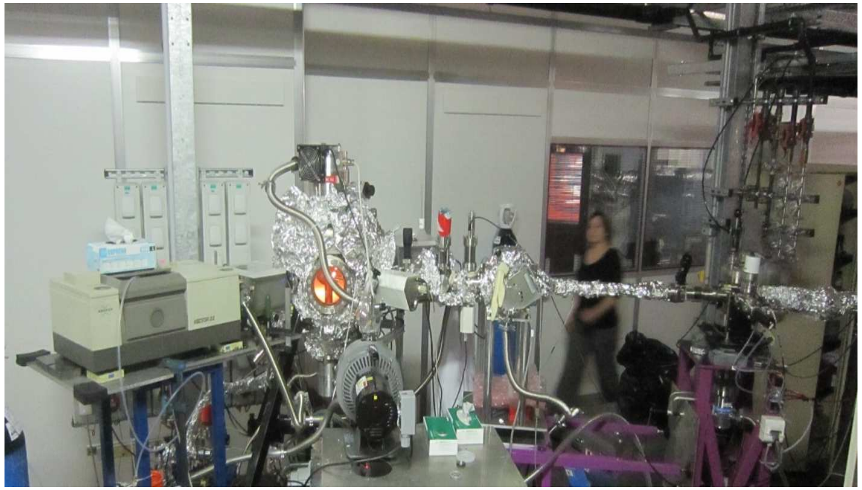
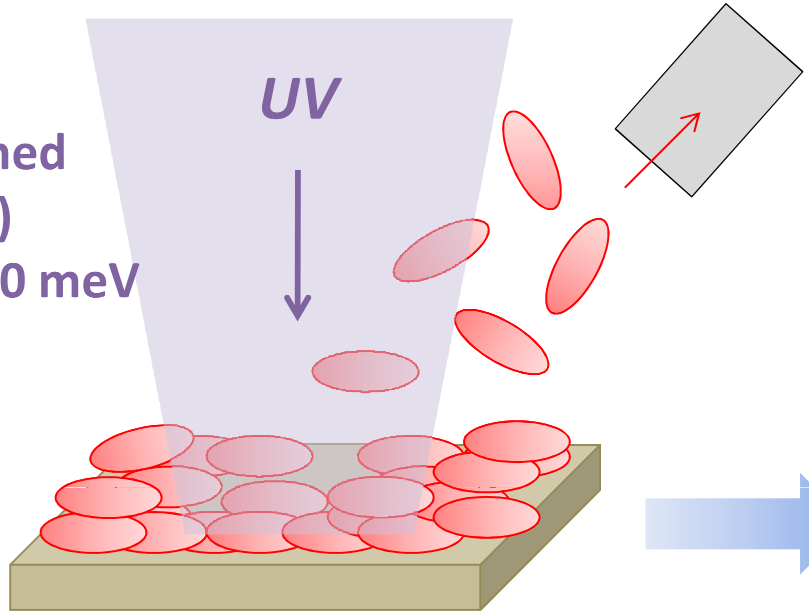


UV Photodesorption: *wavelength-resolved studies*

Mass Spectrometer (QMS)

Desorbed molecules ***as a function of*** $\boldsymbol{E_{photon}}$

E_{photon} scanned
(7-14 eV)
Resolution < 40 meV



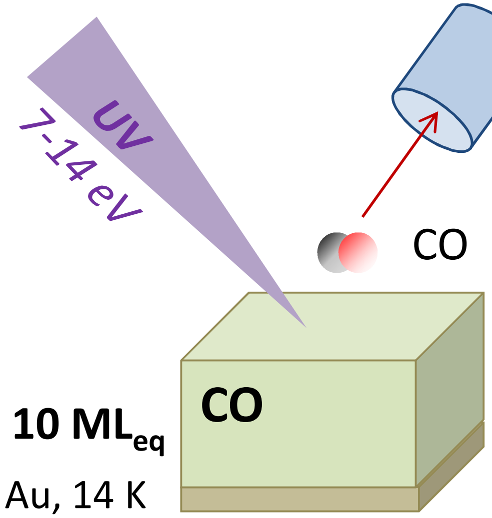
Photon Stimulated Desorption Spectrum (PSD)

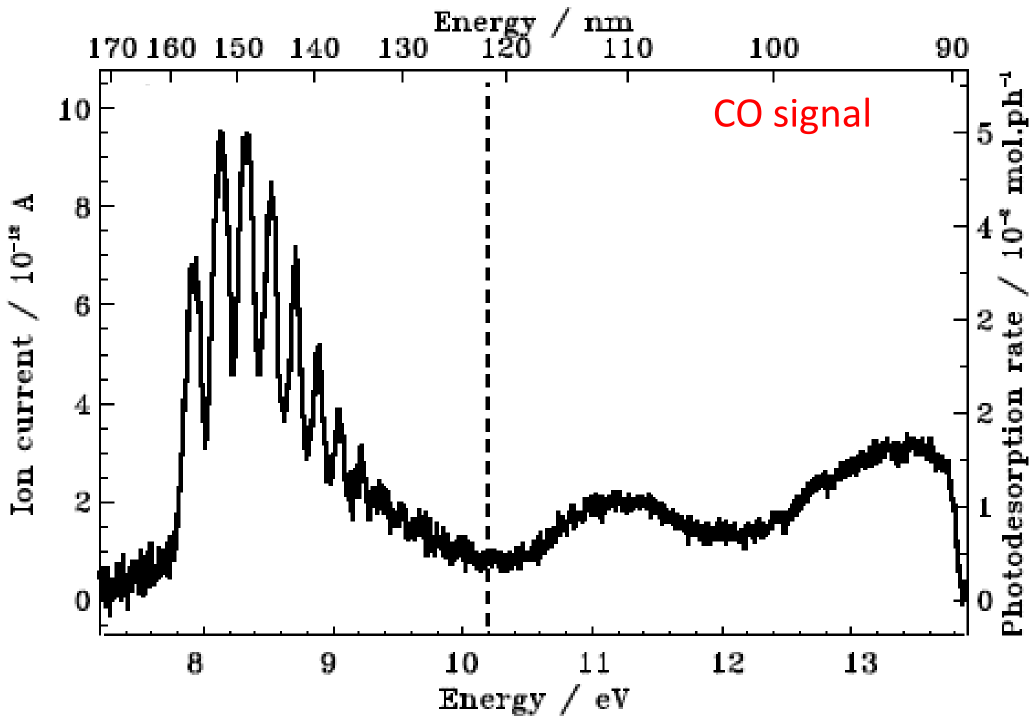
Substrate
Highly Oriented Pyrolitic Graphite (HOPG)
Au polycristallin
Quartz (0001)

T ~ 10 K

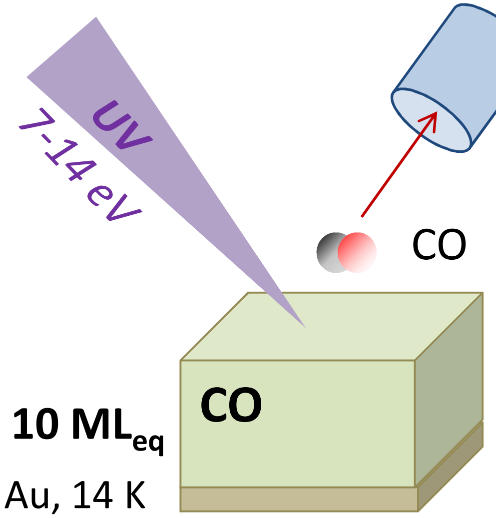
UV Photodesorption: the case of CO

Fayolle et al., Astrophys. J. Lett. 2011

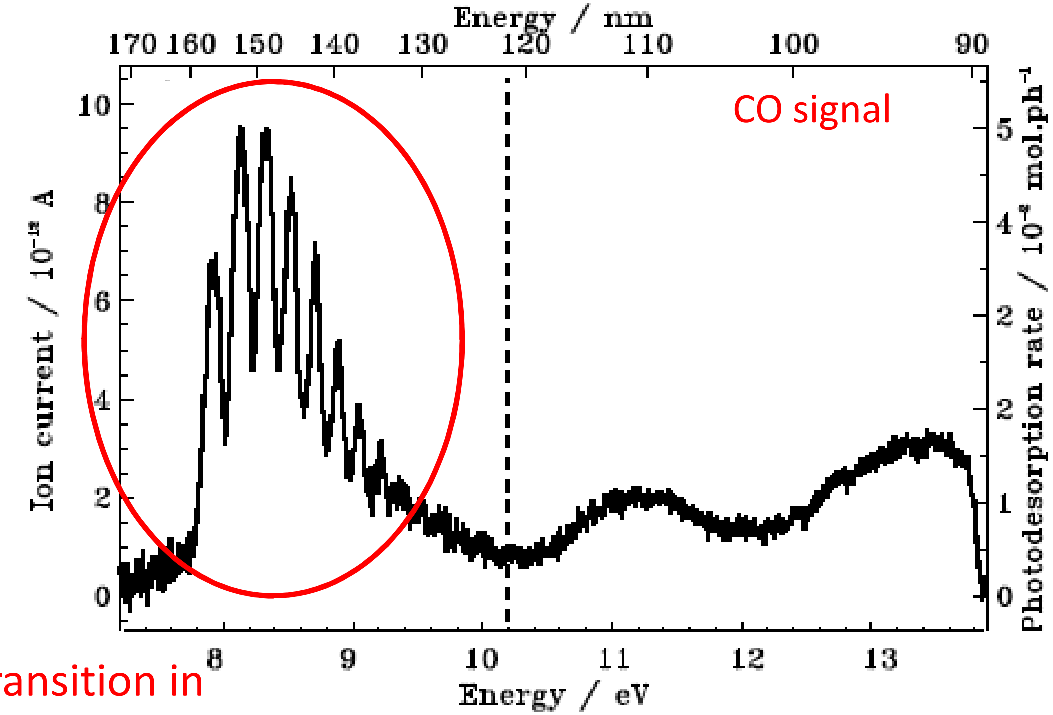




Photodesorption efficiency very dependent on photon energy



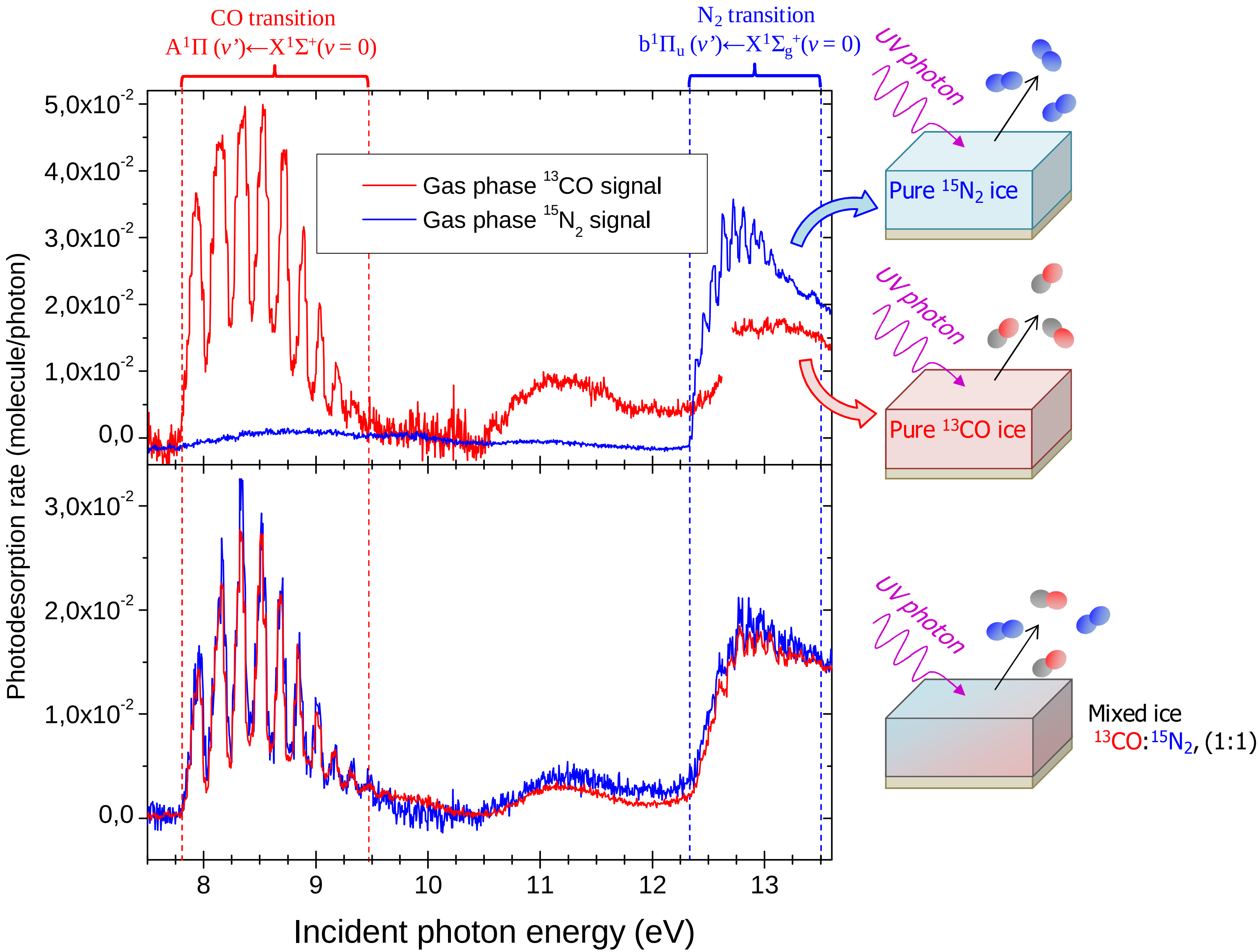
$A^1\Pi$ (v') ← $X^1\Sigma^+$(v=0)



Process initiated by electronic transition in the condensed molecules (**DIET**)

UV Photodesorption: *case of mixed ices*

Bertin et al., ApJ 2013



UV Photodesorption: indirect effects on photodesorption rates

- **CO and N_2 co-adsorbed** ***Bertin et al., ApJ 2013***

	Pure Ices	Mixed Ice (1:1)	Layered ice (1ML N_2 / CO)
CO photodesorption (molecule/photon)	$1.0 \cdot 10^{-2}$	$3.0 \cdot 10^{-3}$	$2.9 \cdot 10^{-3}$
N_2 photodesorption (molecule/photon)	$2.2 \cdot 10^{-3}$	$3.0 \cdot 10^{-3}$	$5.1 \cdot 10^{-3}$

UV spectra in dense cores from Gredel 1987

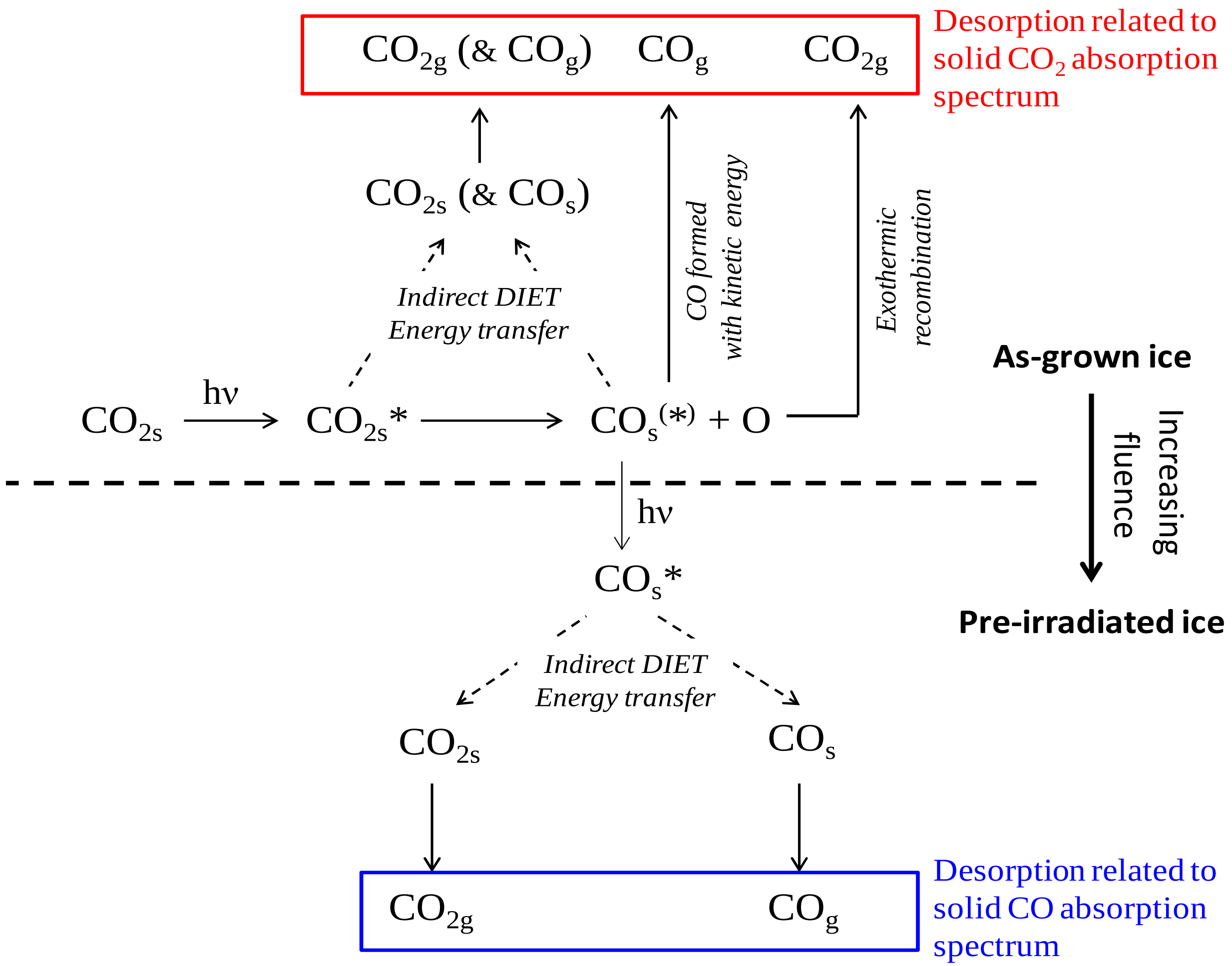
- **CO co-adsorbed with H_2O** ***Bertin et al., Phys Chem Chem Phys 2012***

Photodesorption of CO interacting with H_2O molecules is strongly suppressed

UV Photodesorption: What about photodissociation?

- **Cases of pure O_2 and pure CO_2**

Fayolle et al., A&A 2013
Fillion et al. Faraday Disc 2014



Photochemistry can participate to the overall photodesorption process

- **The case of methanol**

Recent data from last SOLEIL beamtime
Treatment still in process

The main desorbing signal comes from the photofragments of methanol (CH_3, OH, CO, HCO, H_2CO…)

No dependency in the CO/methanol ratio is observed for the fragments desorption

- **The case of methanol**

Recent data from last SOLEIL beamtime
Treatment still in process

Desorption of the intact methanol is only observed for pure CH_3OH ices, and is comparatively weaker than the desorption of the fragments

UV Photodesorption: conclusions and open questions

- **How to take into account wavelength dependency**

  Wavelength-dependent Photodesorption ***spectra can be used with any UV spectra to obtain integrated photodesorption rates***

- **How to take into account indirect effects: Important role of the ice composition**

  Measures of photodesorption ***rates in CO-rich / H_2O-rich ices*** *with different stoechiometries*

  Only the ***composition of the top-layers*** *needs to be considered*

- **Photodissociating molecules: photofragments *vs* intact molecules**

  Photodesorption of 'complex' molecules is ***dominated by the fragments desorption***

  Photodesorption rates of photofragments/photoproducts *can be measured*

  Photodesorption of ***reactive fragments may participate to the origin of COMs in the gas*** *of the cold regions*

Acknowledgments

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J.-C. Guillemin

Supports

SOLEIL synchrotron, Beamline DESIRS

DIM – Astrophysique et Conditions d'Apparition de la Vie

PHC program Van Gogh

Labex MiChem

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