La photodésorption d'analogues de glaces interstellaires en laboratoire : apport du rayonnement synchrotron SOLEIL

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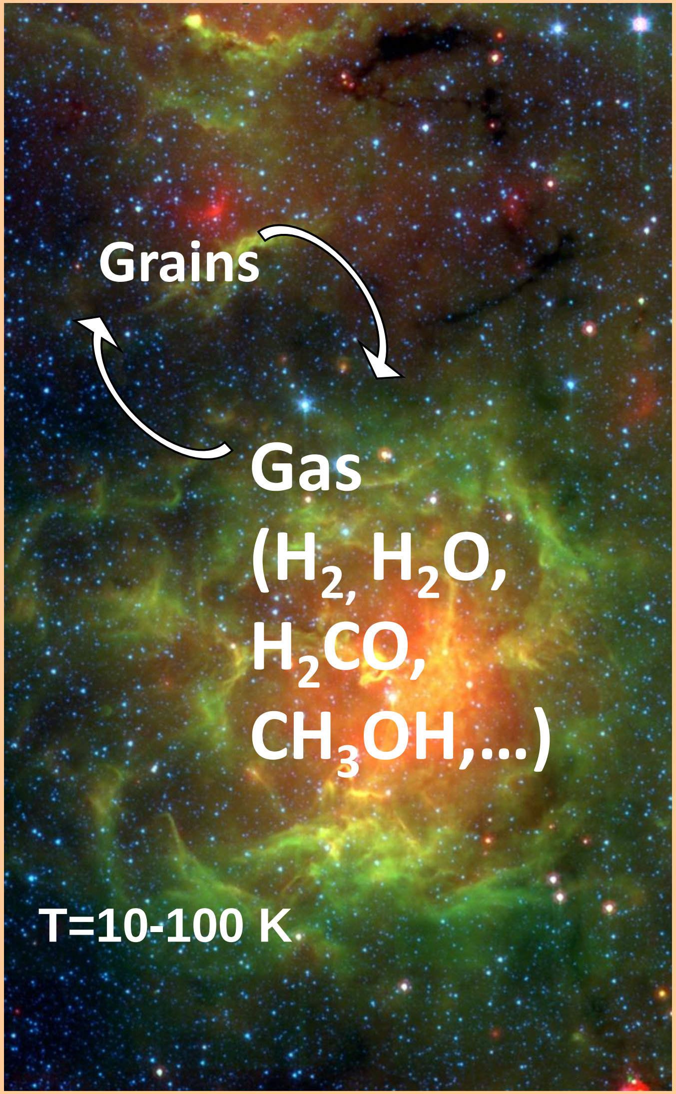
Gas and Ices

Molecular Clouds

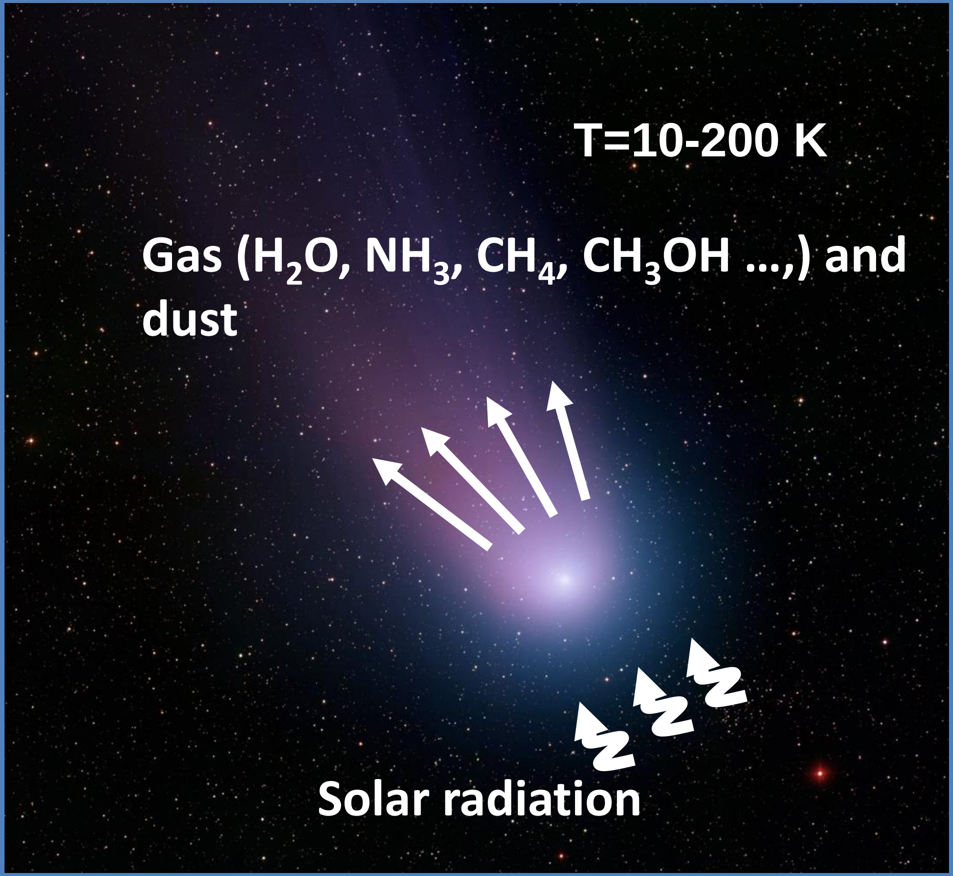


Grains

Gas (H_2, H_2O, H_2CO, CH_3OH,…)

T=10-100 K

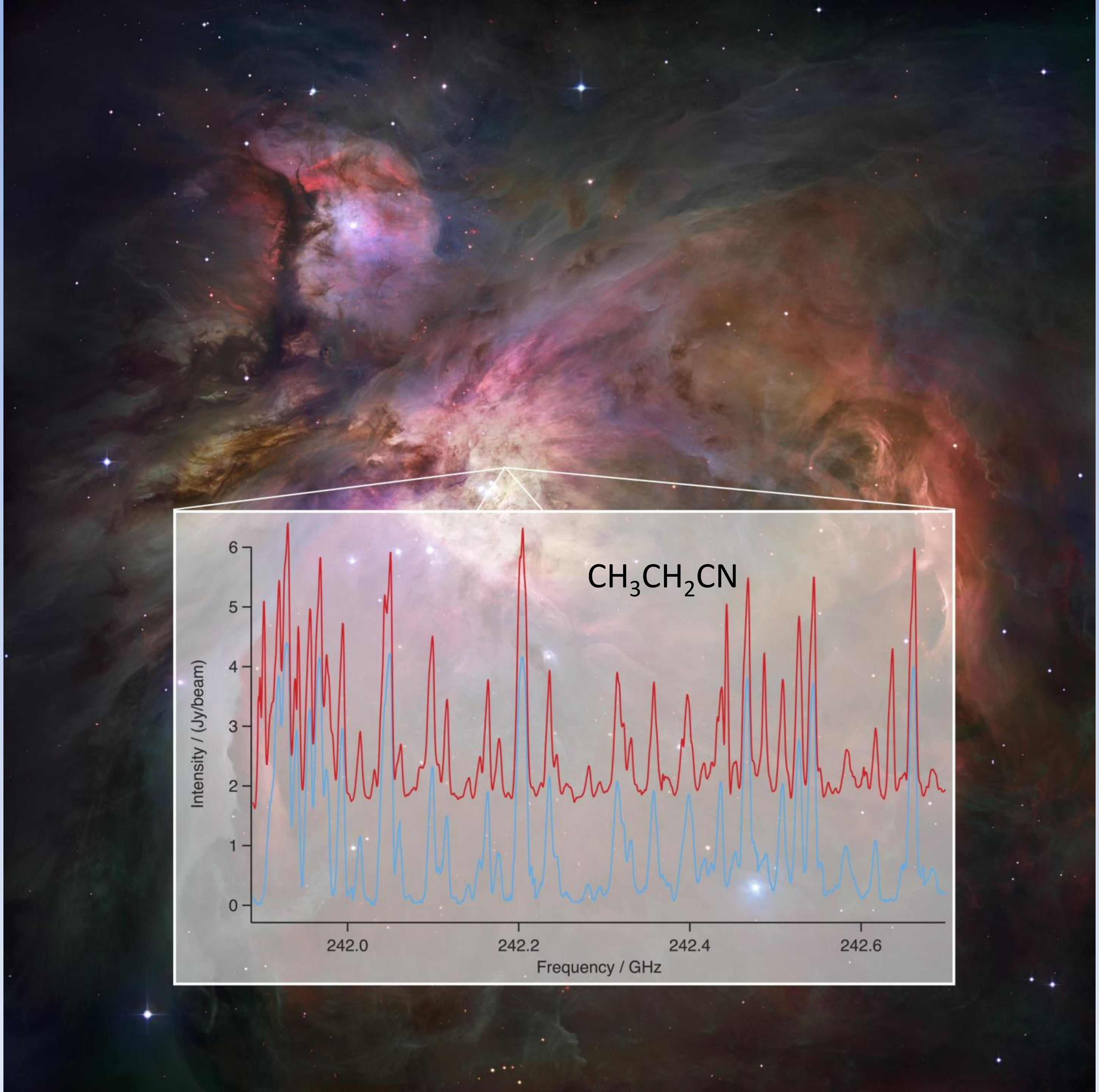
Comets



T=10-200 K

Gas (H_2O, NH_3, CH_4, CH_3OH …,) and dust

Solar radiation



CH_3CH_2CN

Intensity / (Jy/beam)
0
1
2
3
4
5
6
242.0
242.2
242.4
242.6
Frequency / GHz

Elemental Abundances

≈ 180 neutral IS et CS molecules (2013) (without isotopologues)

25 molecular ions (without isotopologues)

22 positive molecular ions

6 negative molecular ions

H, He

C, N, O

S, Si, P, F, Cl, Na, K, Mg, Al, *Ar*

Species	Abundance /H nuclei
H_2	0.5
HD	1.6×10^{-5}
He	0.09
C	1.2×10^{-4}
N	7.6×10^{-5}
O	2.6×10^{-4}
S	8.0×10^{-8}
Fe	1.5×10^{-8}

N = 2		N=3		N=4	N=5	N=6	N=7	N=9	N=12
H_2	AlCl	CH_2	SiCN	HNCO	CH_4	CH_3OH	CH_3NH_2	$(CH_3)_2O$	C_6H_6
CH	SiC	NH_2	SiNC	HOCN	SiH_4	CH_3SH	CH_3CCH	C_2H_5OH	
NH	SiO	H_2O	HCP	HCNO	CH_2NH	C_2H_4	CH_3CHO	C_2H_5CN	
OH	SiN	HCO	H_3^+	HCCN	C_5	H_2C_4	c-CH_2OCH_2	CH_3C_4H	
C_2	SiS	HCN	HCO^+	HNCS	c-C_3H_2	CH_3CN	H_2CCHOH	C_8H	
O_2	PO	HNC	HOC^+	HSCN	l-C_3H_2	CH_3NC	CH_2CHCN	HC_6CN	
CO	PN	HNO	HCS^+	C_3N	H_2CCN	NH_2CHO	HC_4CN	CH_3CONH_2	
CN	FeO	C_3	N_2H^+	C_3O	H_2NCN	H_2CCHO	C_6H	CH_2CHCH_3	
CS	CH^+	C_2H	CCP	C_3S	CH_2CO	C_5H	C_6H^-	C_8H^-	
N_2	CO^+	C_2O		SiC_3	HCOOH	C_5N		**N=10**	**N=13**
NO	SO^+	C_2S		H_3O^+	C_4H	C_5O	**N=8**	$(CH_3)_2CO$	$HC_{11}N$
NS	CF^+	OCS	**N=4**	$HCNH^+$	HC_2CN	C_5S	C_6H_2	C_2H_5CHO	
SH		CO_2	NH_3	$HOCO^+$	HC_2NC	c-C_3H_2O	CH_2CHCHO	$(CH_2OH)_2$	
SO		c-SiC_2	H_2CO	C_3N^-	C_4Si	CH_2CNH	$HCOOCH_3$	CH_3C_4CN	
HF		SO_2	H_2CS		C_4N	HC_3NH^+	$HOCH_2CHO$		
HCl		N_2O	H_2CN		H_2COH^+	C_5N^-	CH_3COOH	**N=11**	
NaCl		MgCN	c-C_3H		C_4H^-		C_7N	CH_3C_6H	
KCl		MgNC	l-C_3H				$H_2CCCHCN$	HC_8CN	
AlF		NaCN	C_2H_2				CH_3C_2CN		

ASTROCHIMIE

GRANDES QUESTIONS

❑ Gaz
  - réactions ion- molécules
  - modèles astrochimique: X 1000 réactions

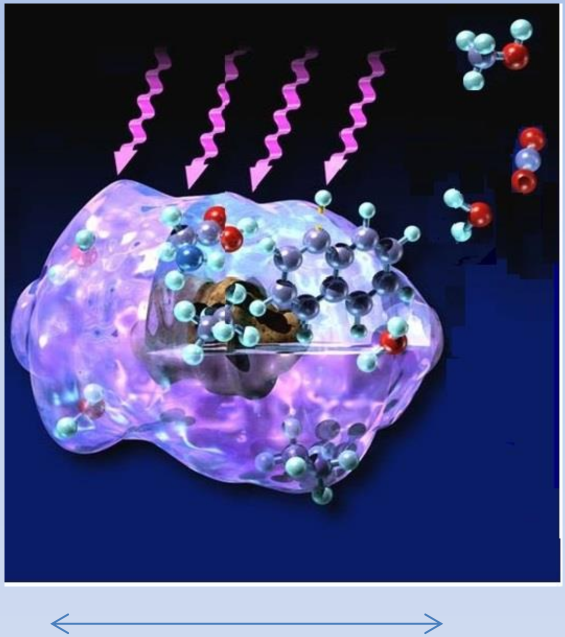
❑ Quelle chimie de surface des « poussières »
Faut-il apporter de l'énergie ?

  - diffusion (thermique/effet tunnel) des atomes
  - probabilité de réaction ?
  - effet isotopiques ?

❑ Origine et évolution des molécules observées ?

❑ Comment libérer les molécules en phase gazeuse
désorption thermique / non thermique

H_2O, CO_2, CH_4, NH_3, H_2CO, CH_3OH



5-250 nm

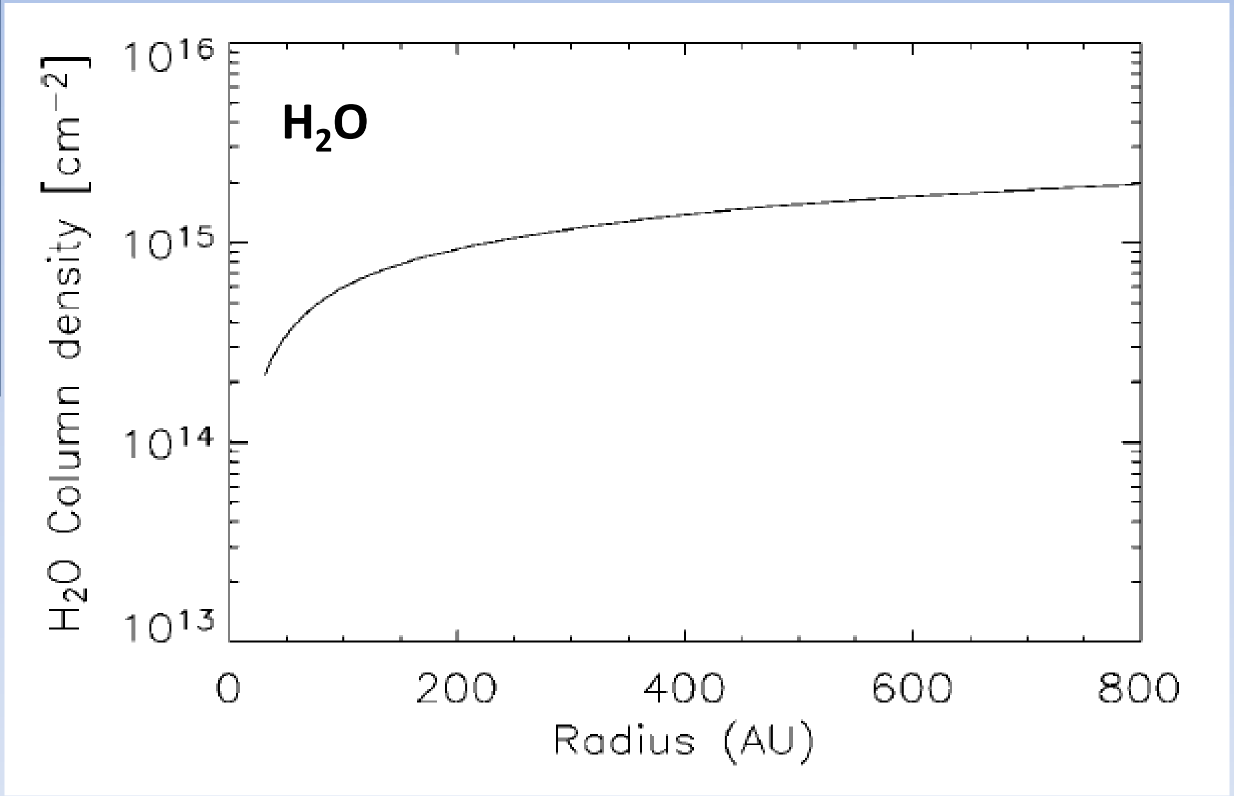
CONDITIONS PHYSIQUES

❑ Densité : $10 – 10^6$ cm^{-3}

❑ T_{gaz} : 10 K – x 100 K, milieu faiblement ionisé

❑ Bombardement de photons (UV, X) et particules énergétiques (rayons cosmiques)

Water Vapor and Water Ice in protoplanetary disks

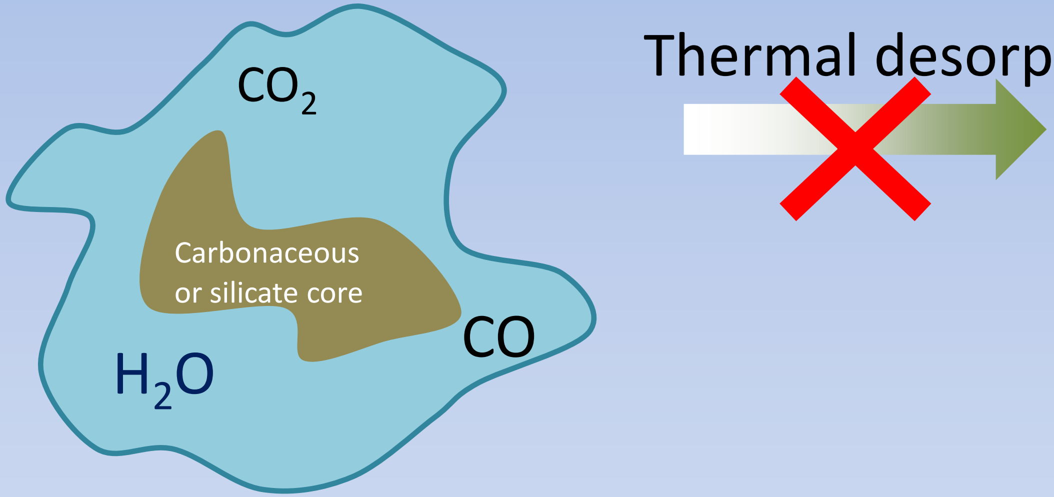


Dominik *et al.* 2005

Motivations: gas-to-ice balance

SOLID PHASE

GAS PHASE



Thermal desorption

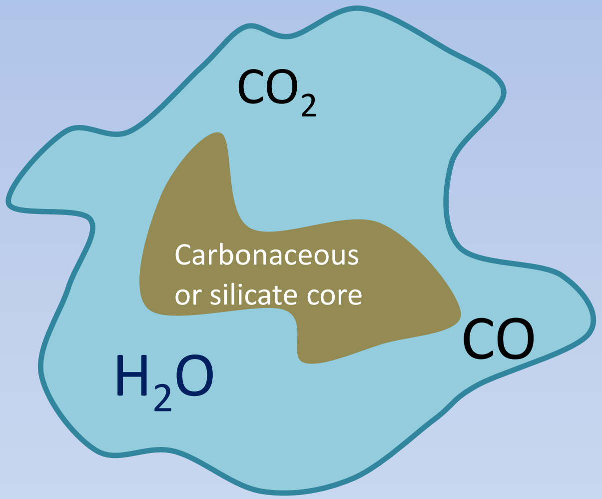
In cold regions

T =10-30 K

Motivations: gas-to-ice balance

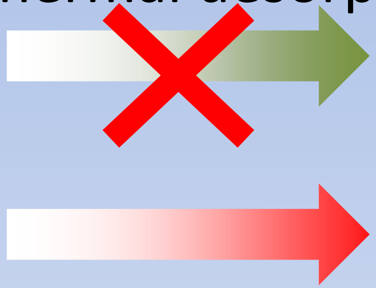
SOLID PHASE

GAS PHASE



T =10-30 K

Thermal desorption

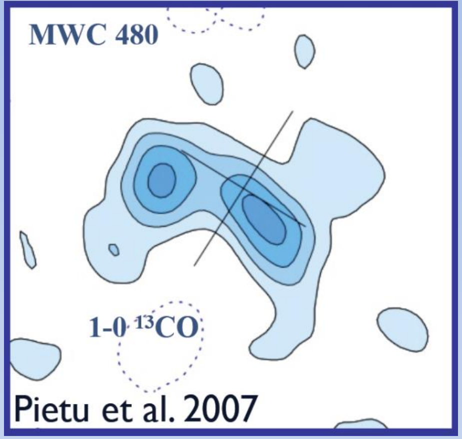


In cold regions

Non-thermal desorption

- Energetic particles
- Chemistry
- Sputtering in shocks
- **UV photodesorption**

UV Photodesorption desorption in the Interstellar Medium

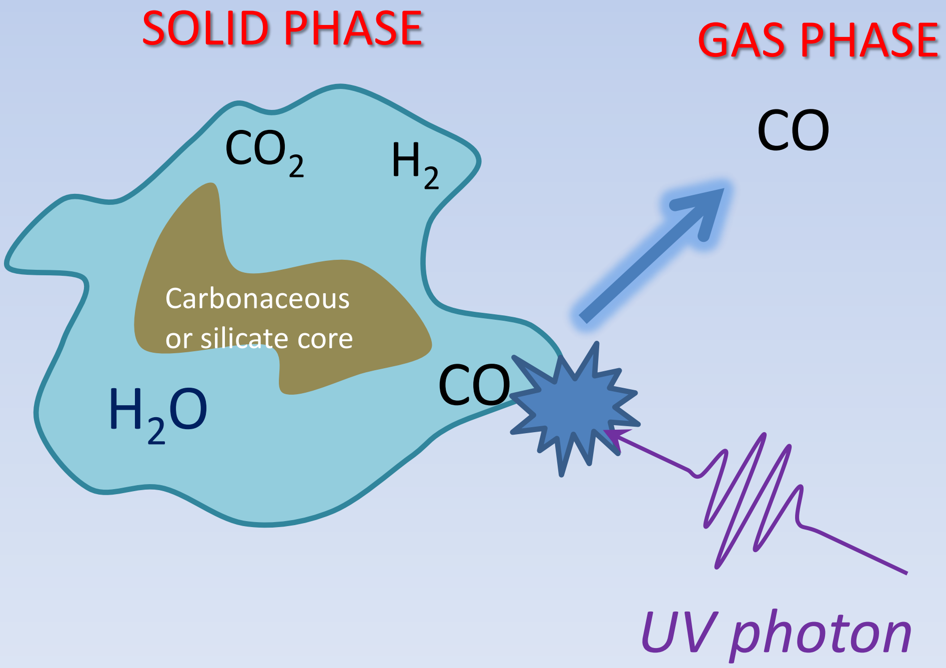


Pietu et al. 2007

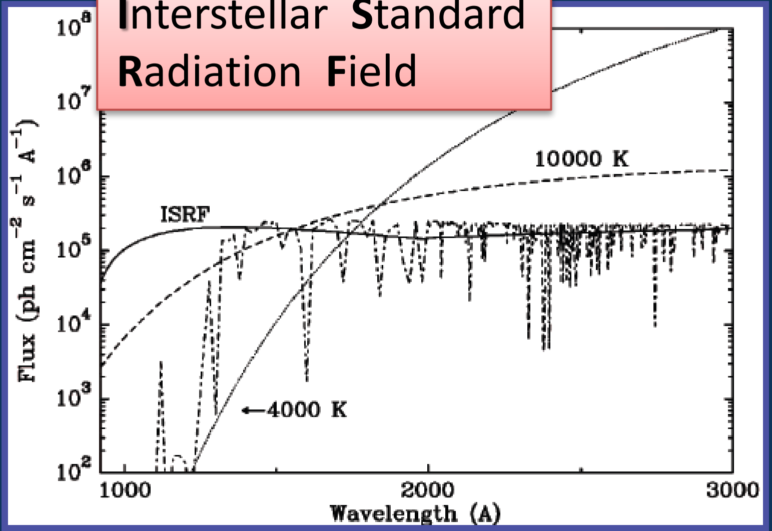
Dominik 2005
Hersant *et al.* 2009
Hollenbach 2009
Oka *et al.* 2012
Guzman *et al.* 2011

UV PHOTODESORPTION

Protoplanetary disks, *Photon-Dominated Regions, inner and outer regions of molecular clouds*



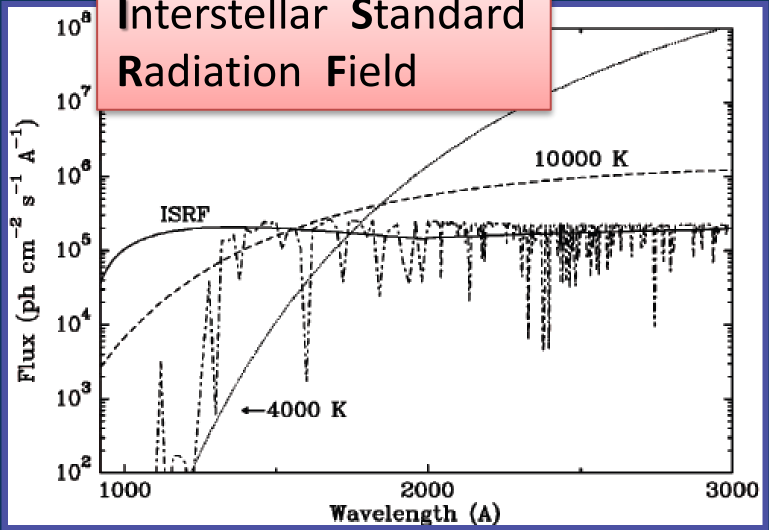
UV Profiles in Astrophysical Environments



Interstellar **S**tandard **R**adiation **F**ield

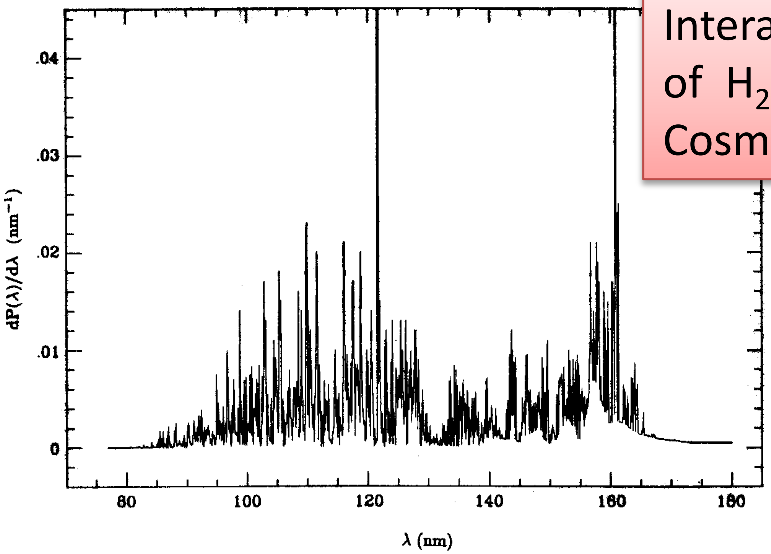
van Dishoeck et al. 2006

UV Profiles in Astrophysical Environments



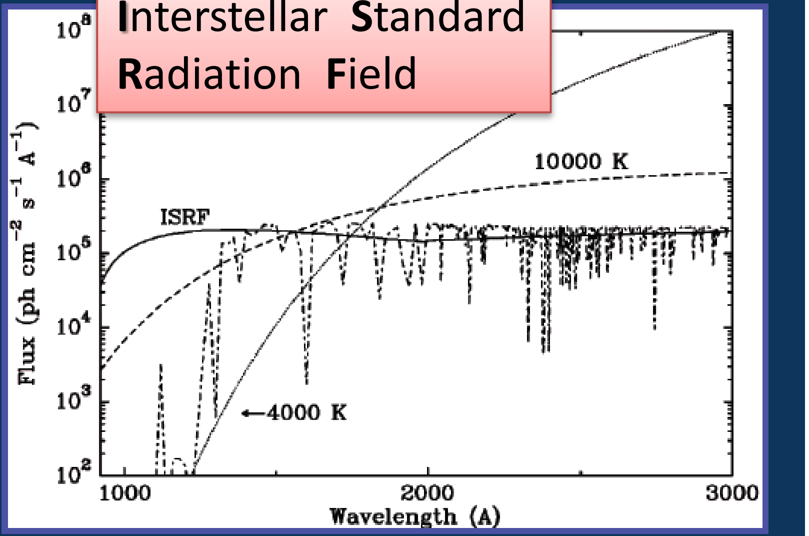
Interstellar **S**tandard **R**adiation **F**ield

van Dishoeck et al. 2006



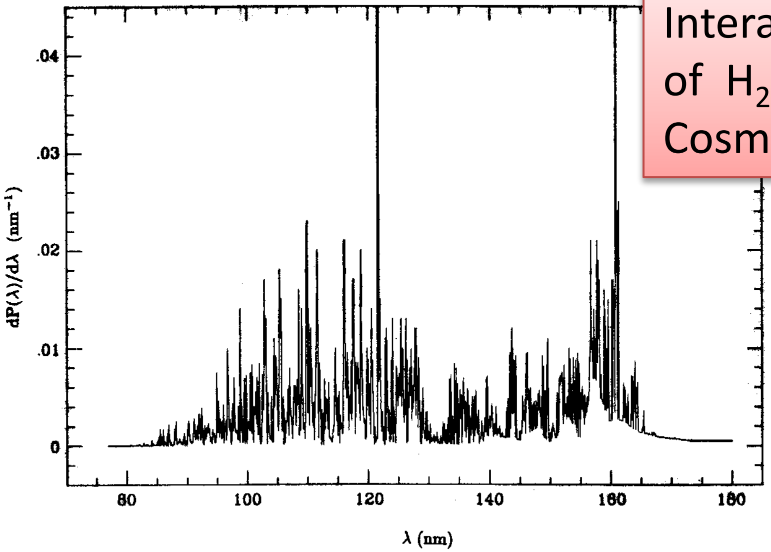
Interaction of H_2 with Cosmic rays

UV Profiles in Astrophysical Environments



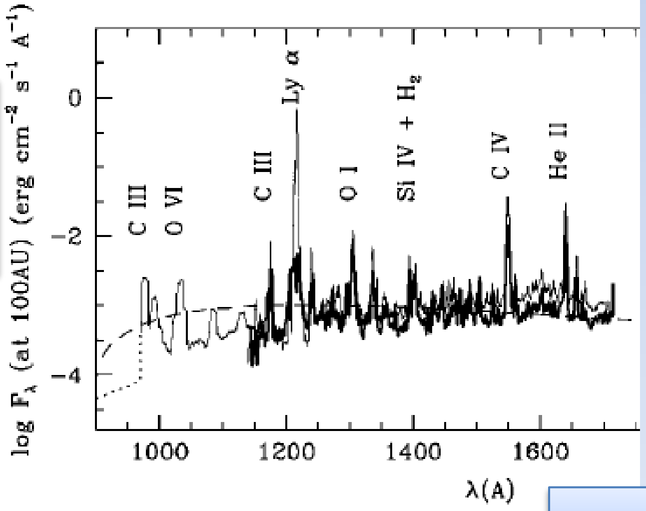
Interstellar **S**tandard **R**adiation **F**ield

van Dishoeck et al. 2006



Interaction of H_2 with Cosmic rays

UV spectrum of a T Tauri Star



Bergin 2003

UV-Photodesorption in the Laboratory

First theoretical estimate : $10^{-5} – 10^{-8}$ molecules /UV Photon (CO)

Hartquist & Williams 1990

Photodesorption rates

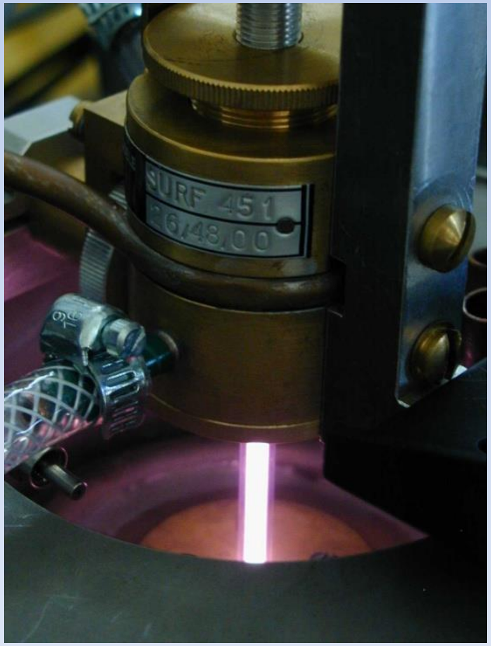
Microwave-Discharge Hydrogen-Flow Lamp

- **Absolute Yields (Lyα)**

Westley 1995, Öberg 2007, 2009a, 2009b, Muñoz Caro 2010 , Bahr & Baragiola 2012, Yan & Yates 2013 etc…

H_2O (D_2O), CO, N_2, O_2 @ low T

10^{-3} molecules / UV photon



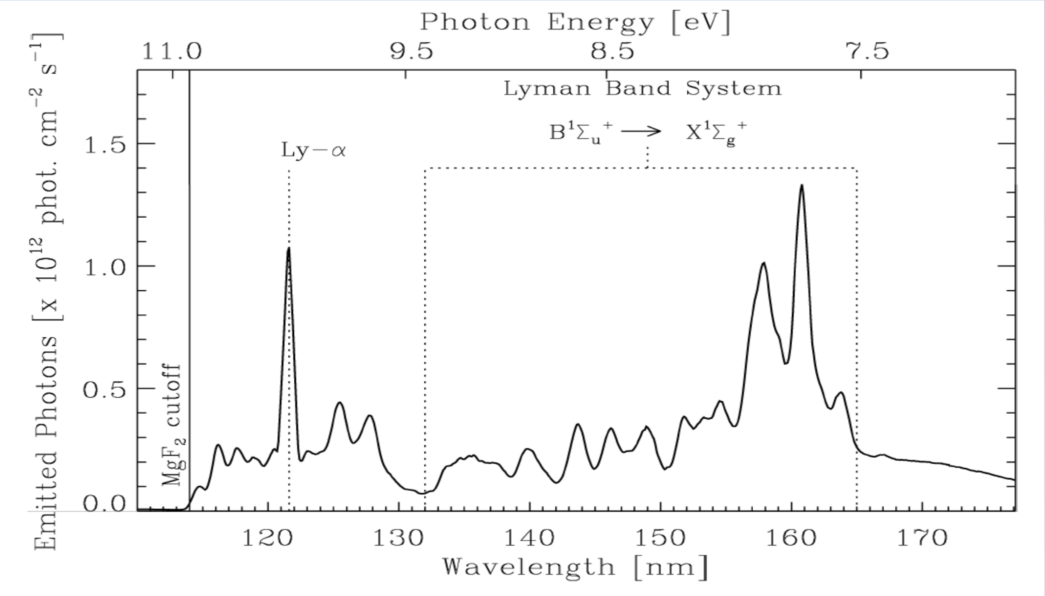
Experimental Conditions

✓ Photon Flux : 10^{14} photons cm^{-2} s^{-1}

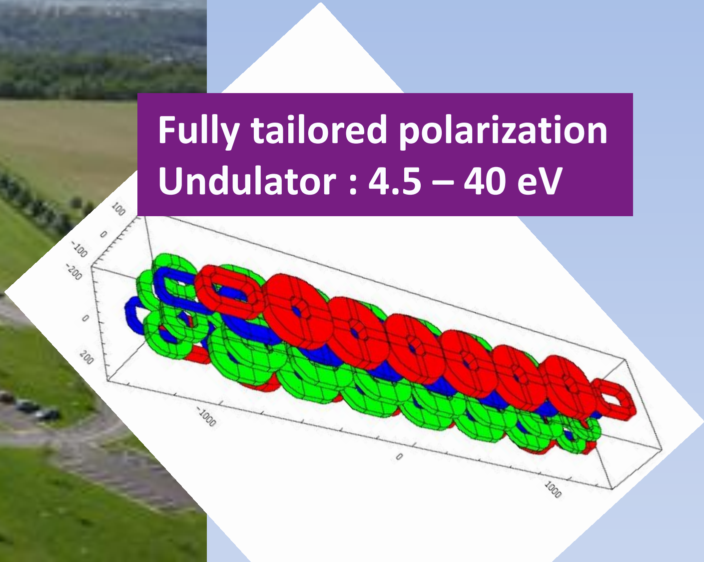
✓ Photon Fluence : 10^{15}- 10^{17} photons cm^{-2}

✓ Methods : IR absorption or Microbalance
Molecule generally not detected into the gas phase

✓ VUV spectrum depends on experimental operating conditions

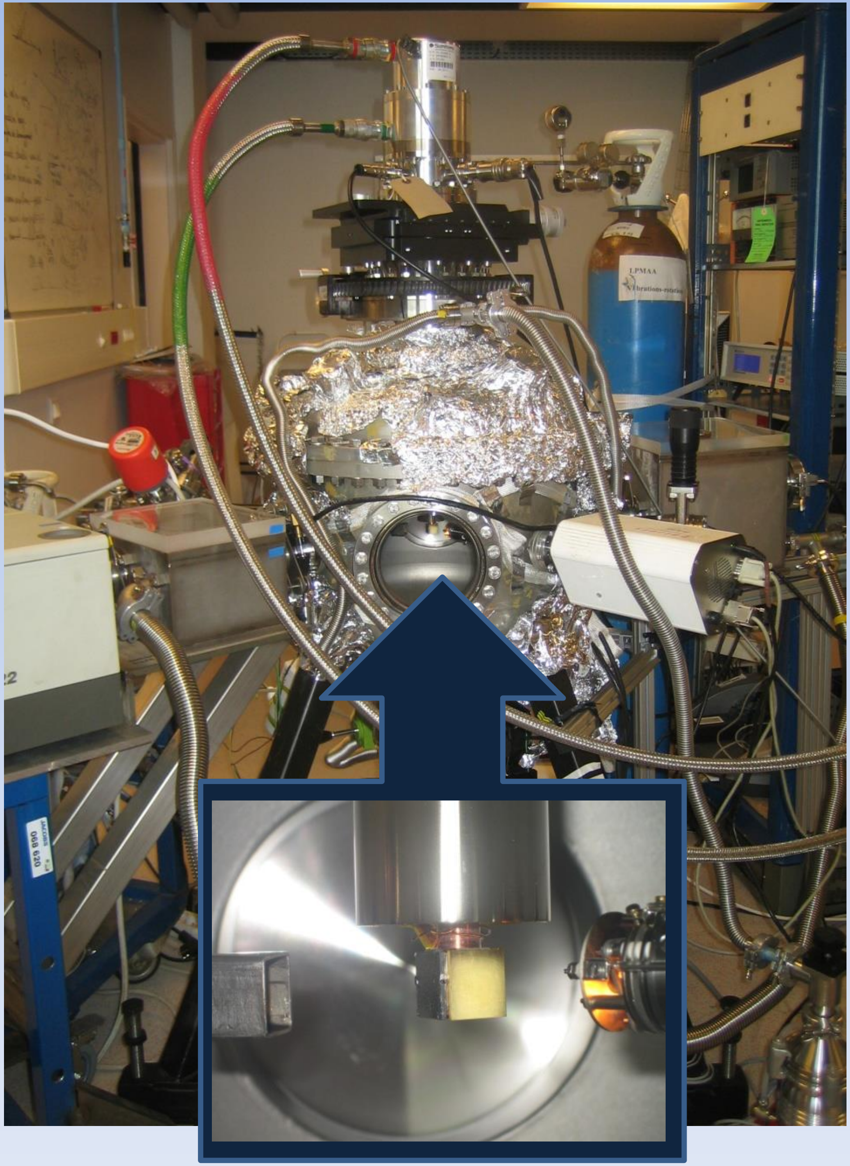


From Chen *et al. 2013*
APJ, in press



Fully tailored polarization
Undulator : 4.5 – 40 eV

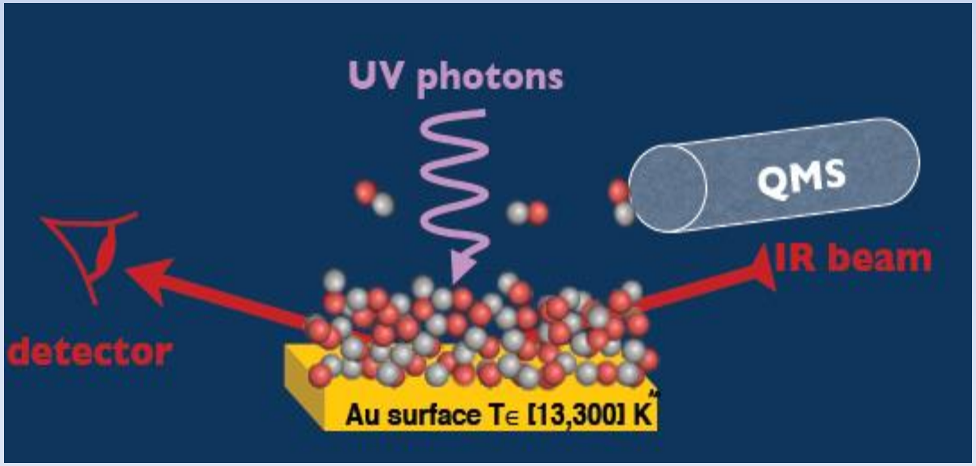
« SPICES » set-up : Surface Processes and ICES



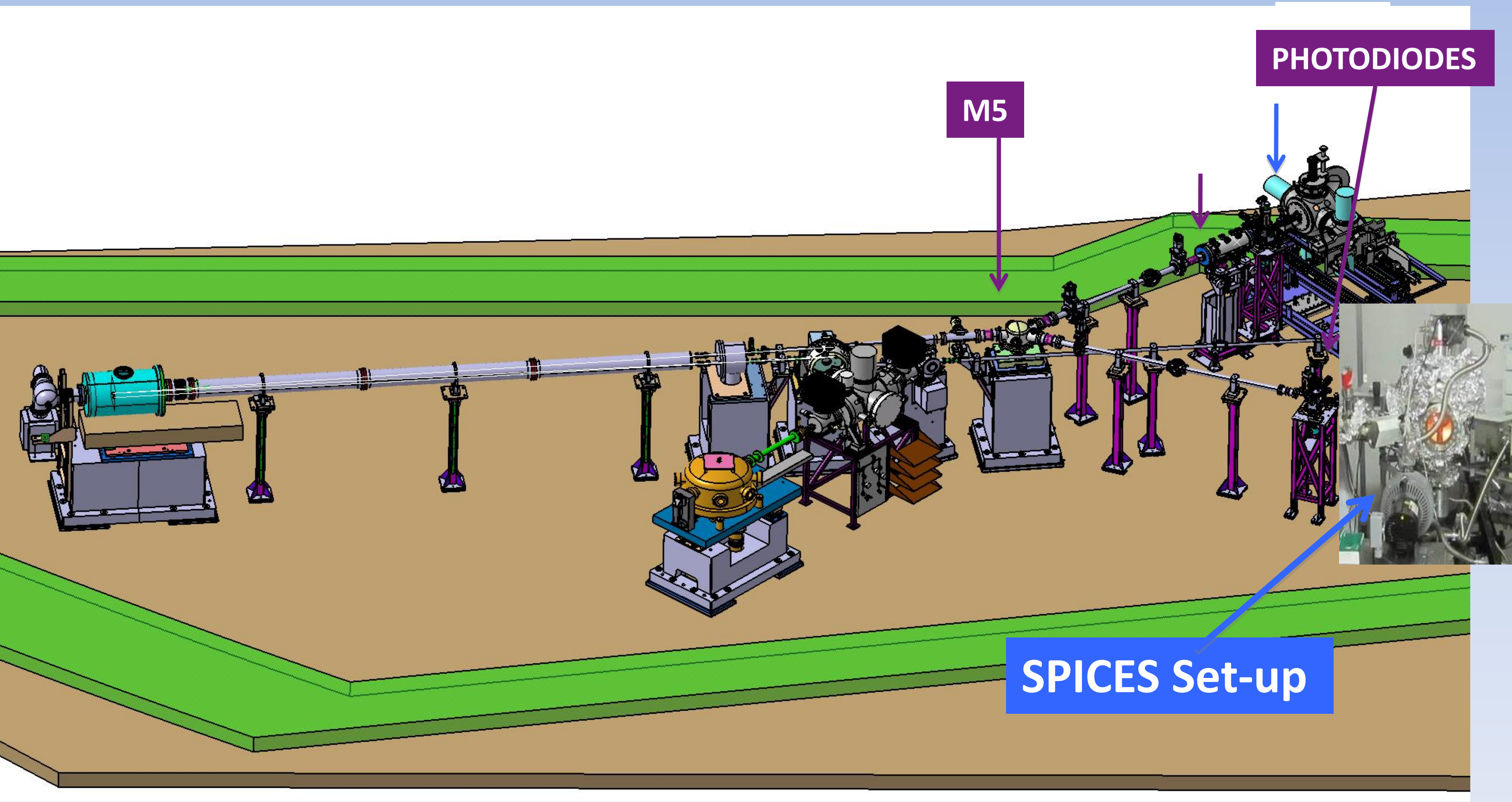
- ☐ UHV - 8-200 K

- ☐ Gas Phase
  Mass spectrometry

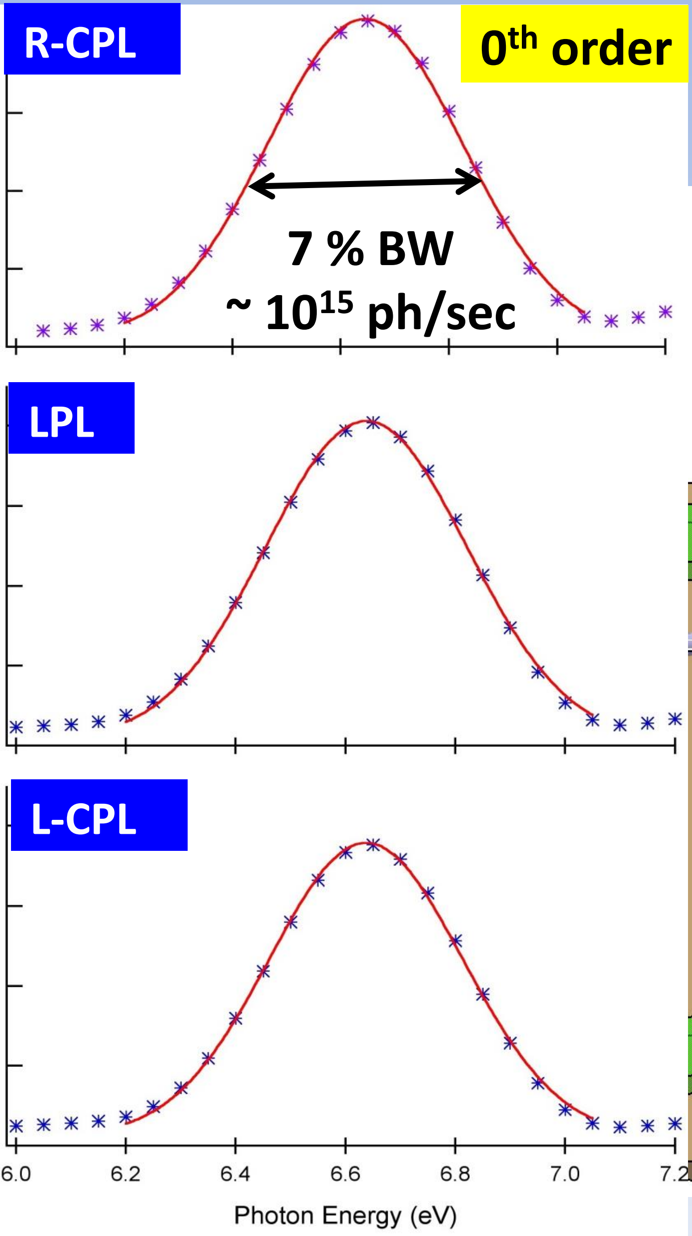
- ☐ Surface
  Reflexion Absorption Infrared Spectroscopy



« SPICES » @ SOLEIL (DESIRS beamline)



« SPICES » @ SOLEIL (DESIRS beamline)

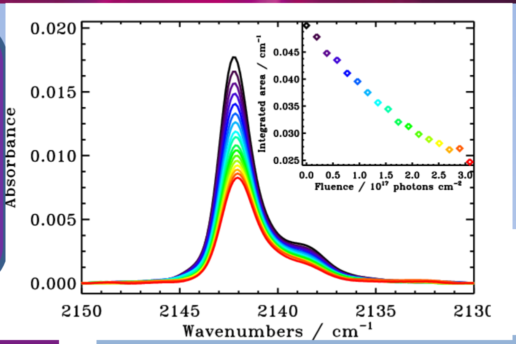


0th order

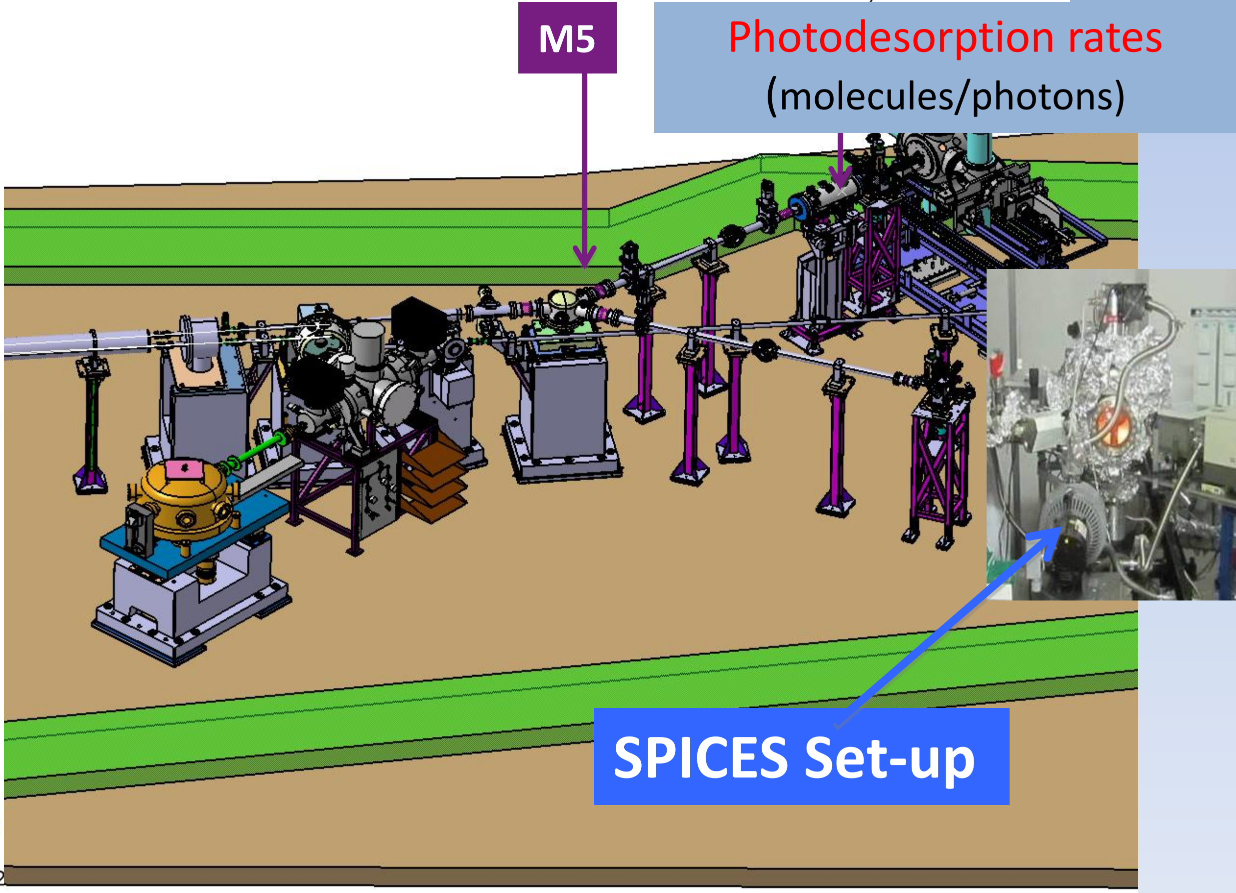
7 % BW

~ 10^{15} ph/sec

10^{15} photons/s
@ E between 5-40 eV
FWHM : 1 eV



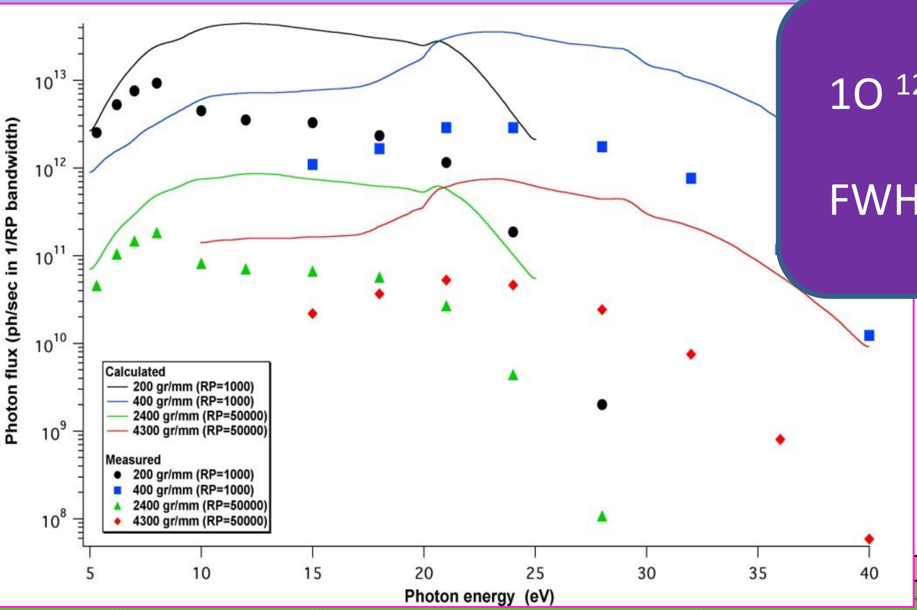
Photodesorption rates
(molecules/photons)



M5

SPICES Set-up

« SPICES » @ SOLEIL (DESIRS beamline)



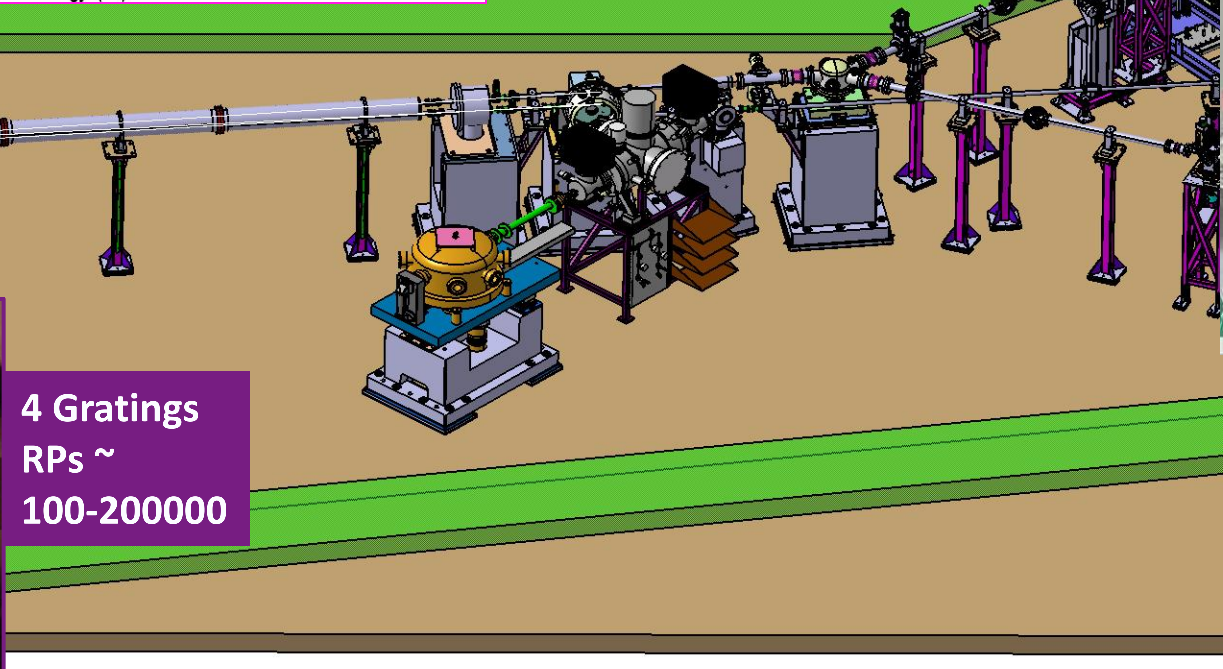
1O $^{12\text{-}13}$ photons/s

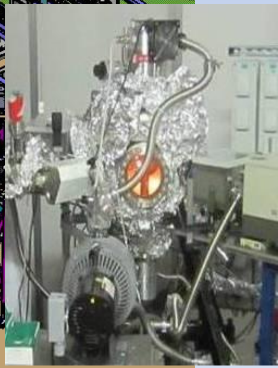
FWHM : 20-40 meV

Mass spectrometer

QMS = f(E)

Photodesorption spectra





4 Gratings
RPs ~
100-200000

New Experimental Approach

✓Monochromatic irradiation

Differential photodesorption yields

Y= f(E) => application to any FUV profiles

✓ Detection of molecules into GP

=> high sensitivity

✓ low Flux / Fluence

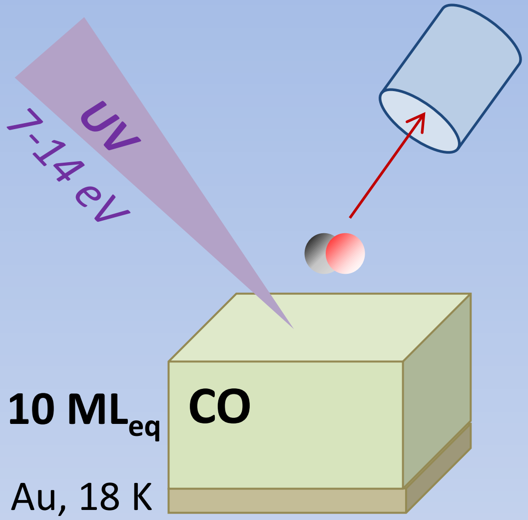
Favor identification of primary processes

✓ Understanding molecular processes

- Photodesorption mechanisms in pures ices
- Indirect desorption in binary ices
- Interconnection between photochemistry and photodesorption

Photodesorption of pure ices

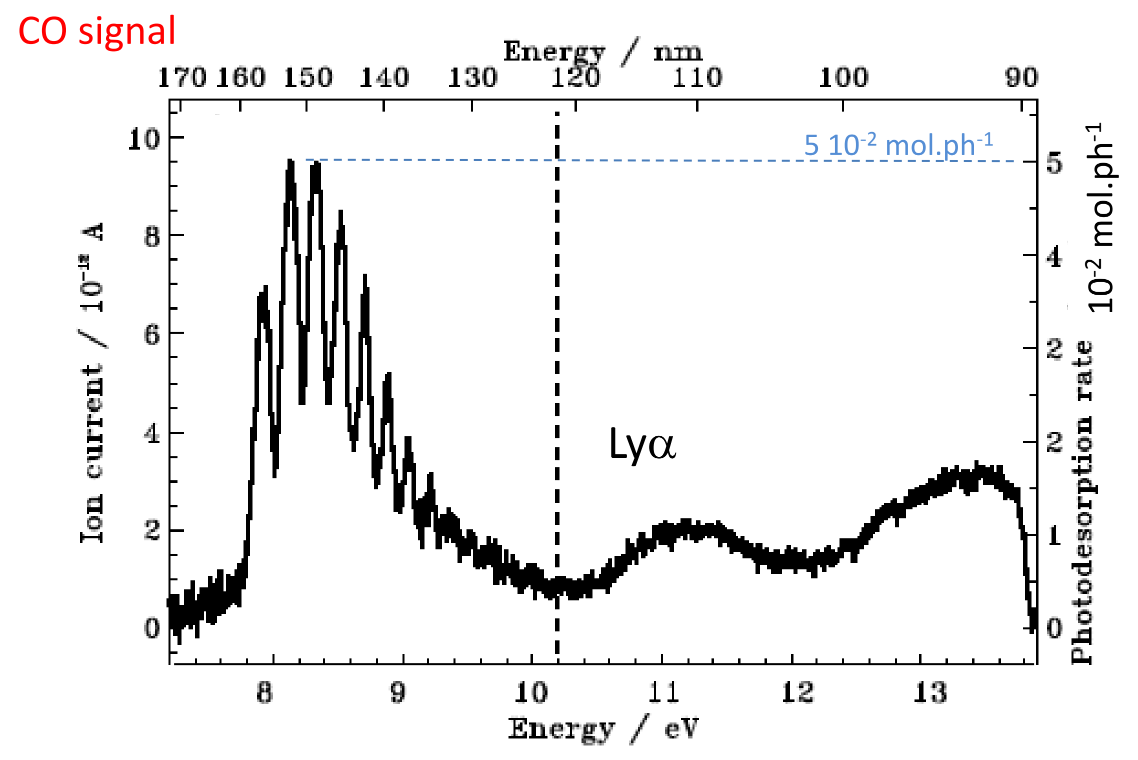
CO *Photodesorption Spectrum*



Mass spectrometer
QMS

10 ML$_{eq}$

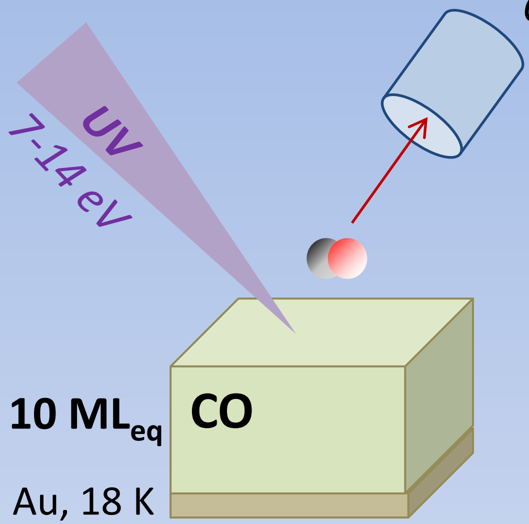
Au, 18 K



- ☐ Photodesorption of CO is strongly wavelenght-dependent
- ☐ Not very efficient @ Ly-α

CO Photodesorption mechanism

Layered ices : N_2 / CO

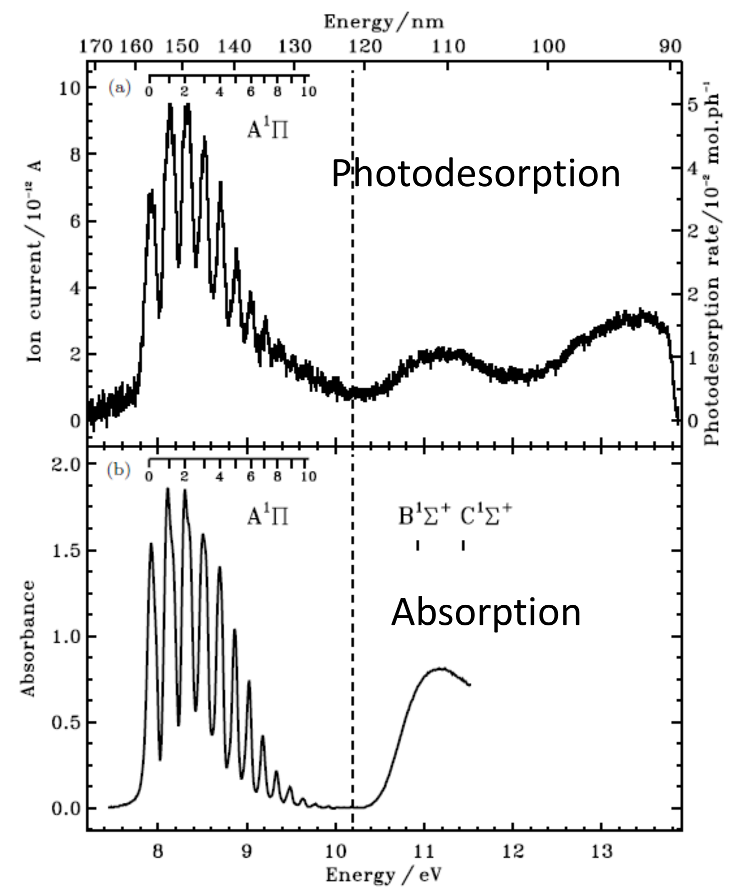


Mass spectrometer
QMS

10 $\mathrm{ML_{eq}}$ **CO**

Au, 18 K

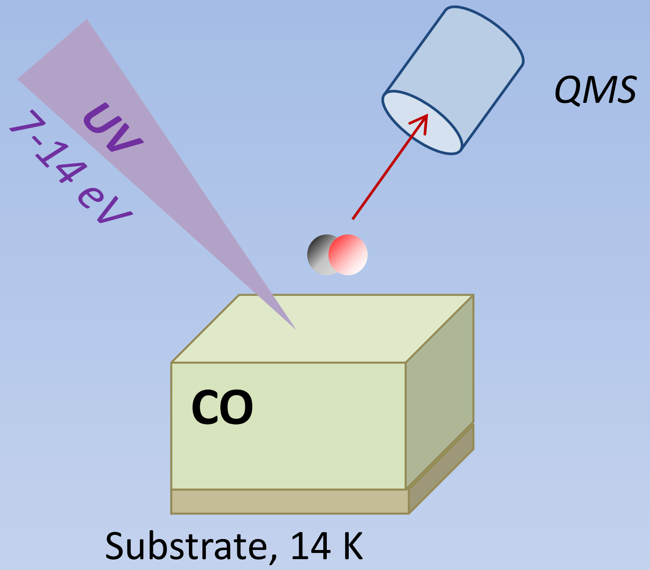
$A^1\Pi$ (v') ← $X^1\Sigma^+$(v=0)

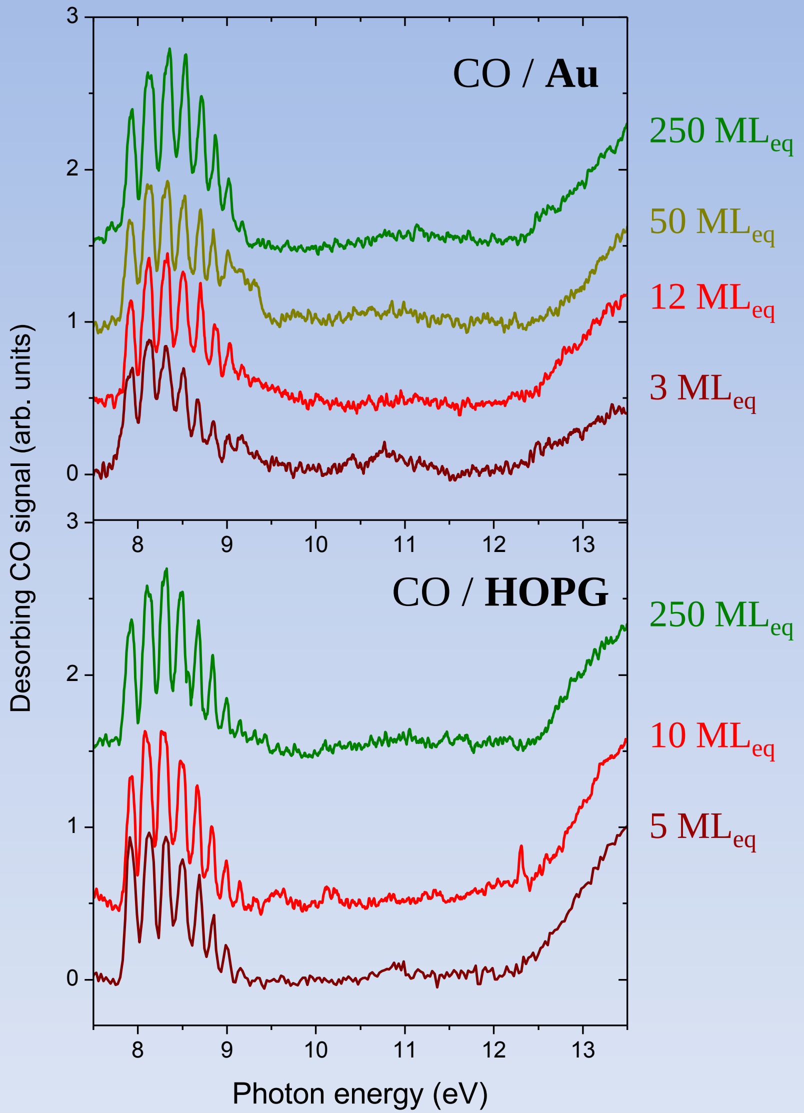


- Process triggered by the electronic excitation of the molecular ices: ***DIET***

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

CO photodesorption: molecular mechanism



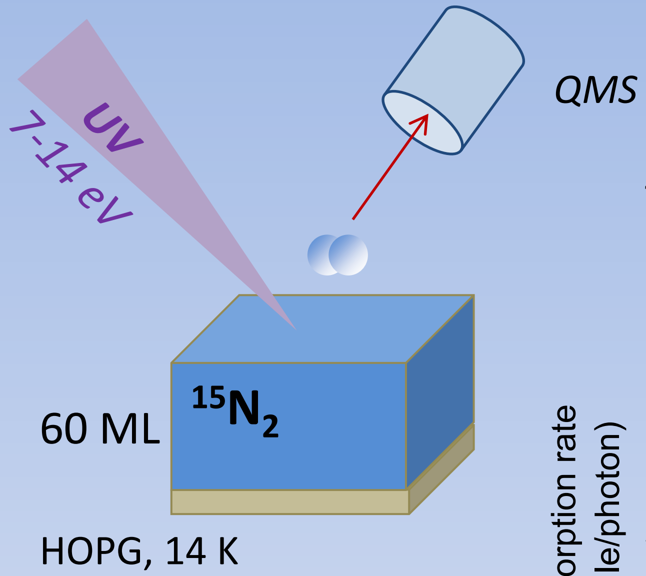


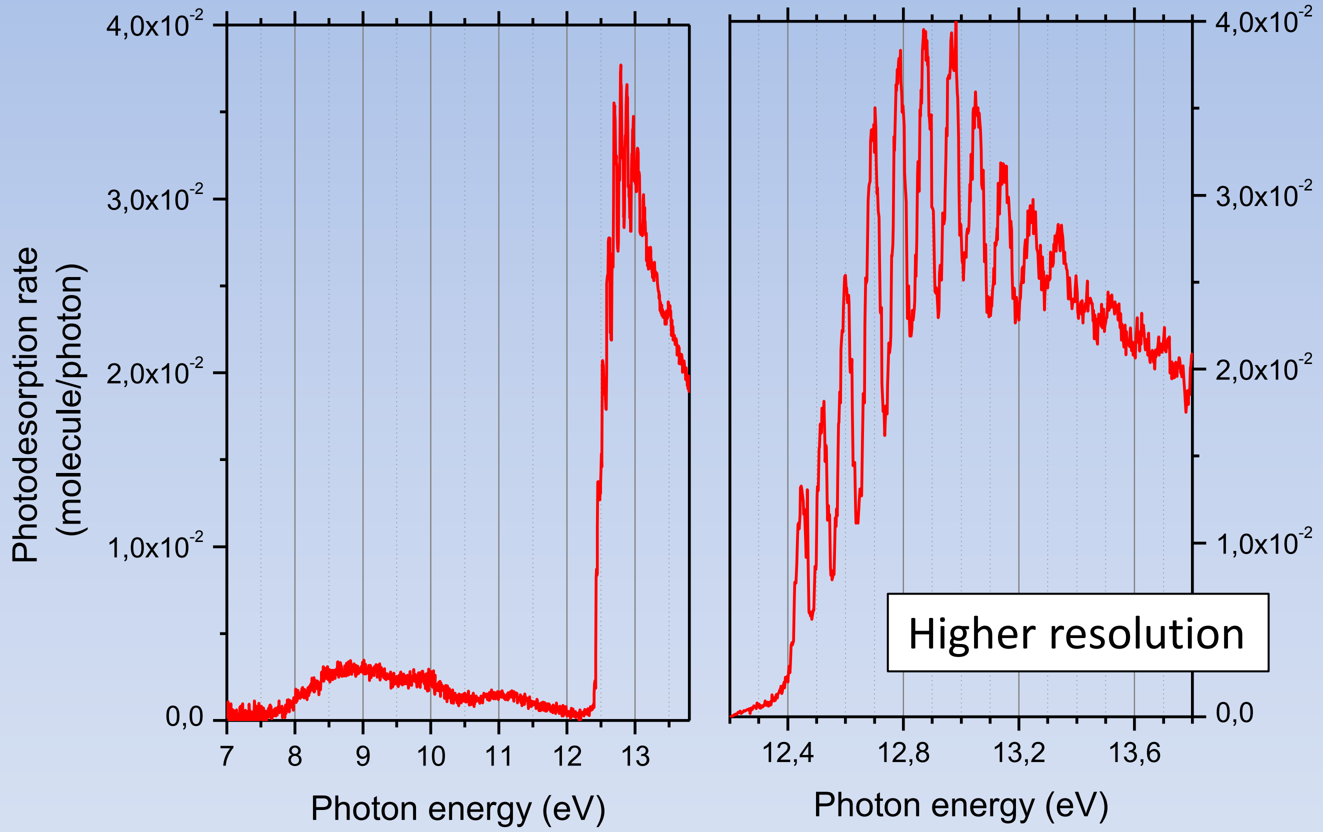
Not dependent on the nature of the substrate

Not dependent on the thickness of the ice

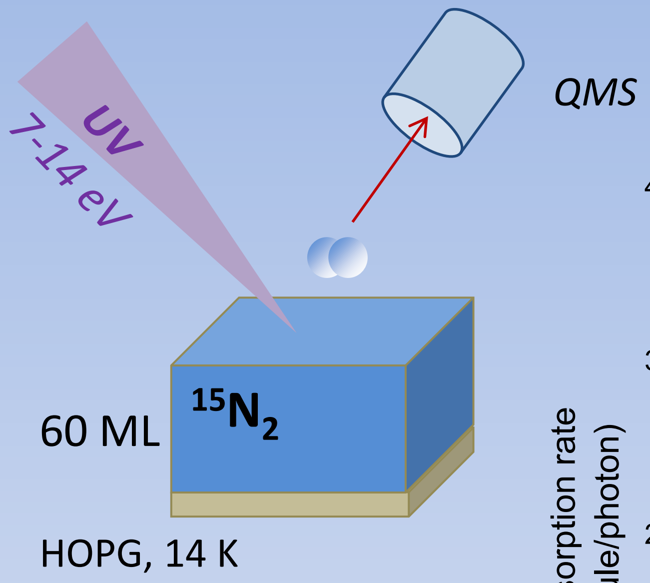
⇨ **A surface process ?**

Pure N_2 photodesorption

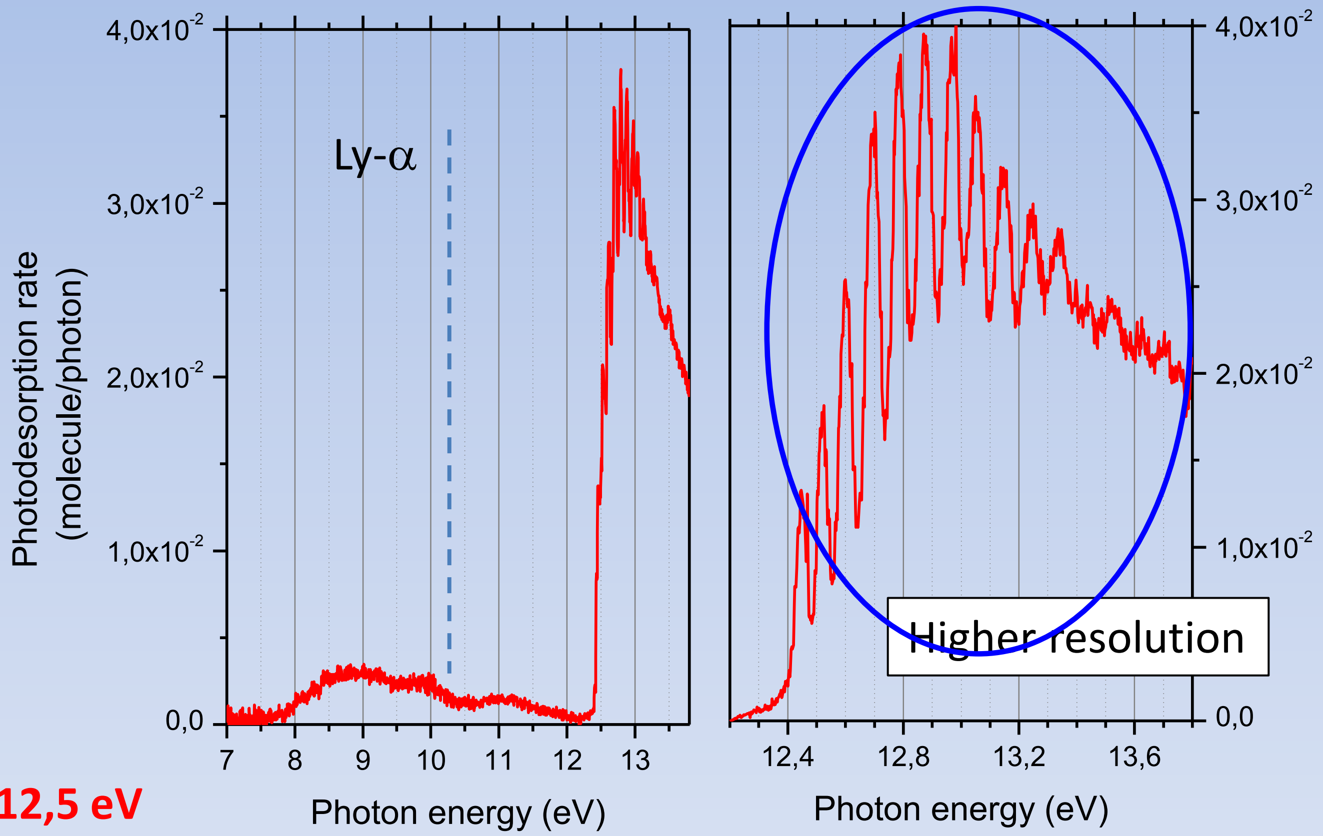




Pure N_2 photodesorption



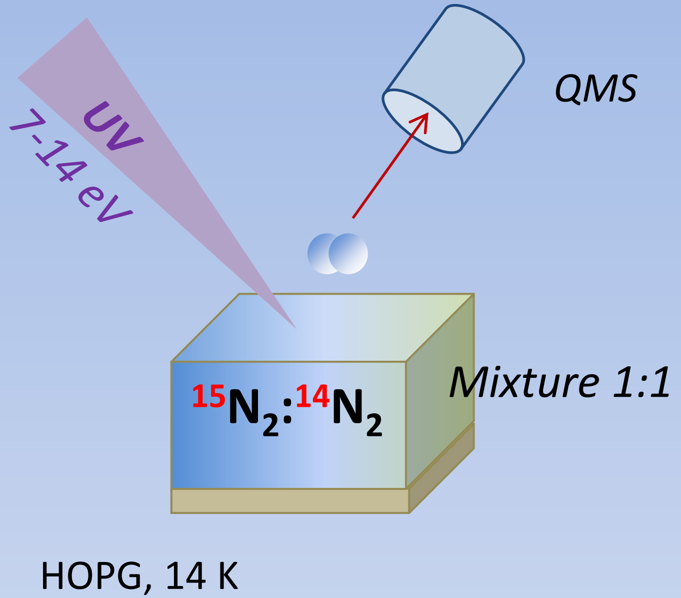
$b^1\Pi_u\ (v') \leftarrow X^1\Sigma_g^+(v=0)$

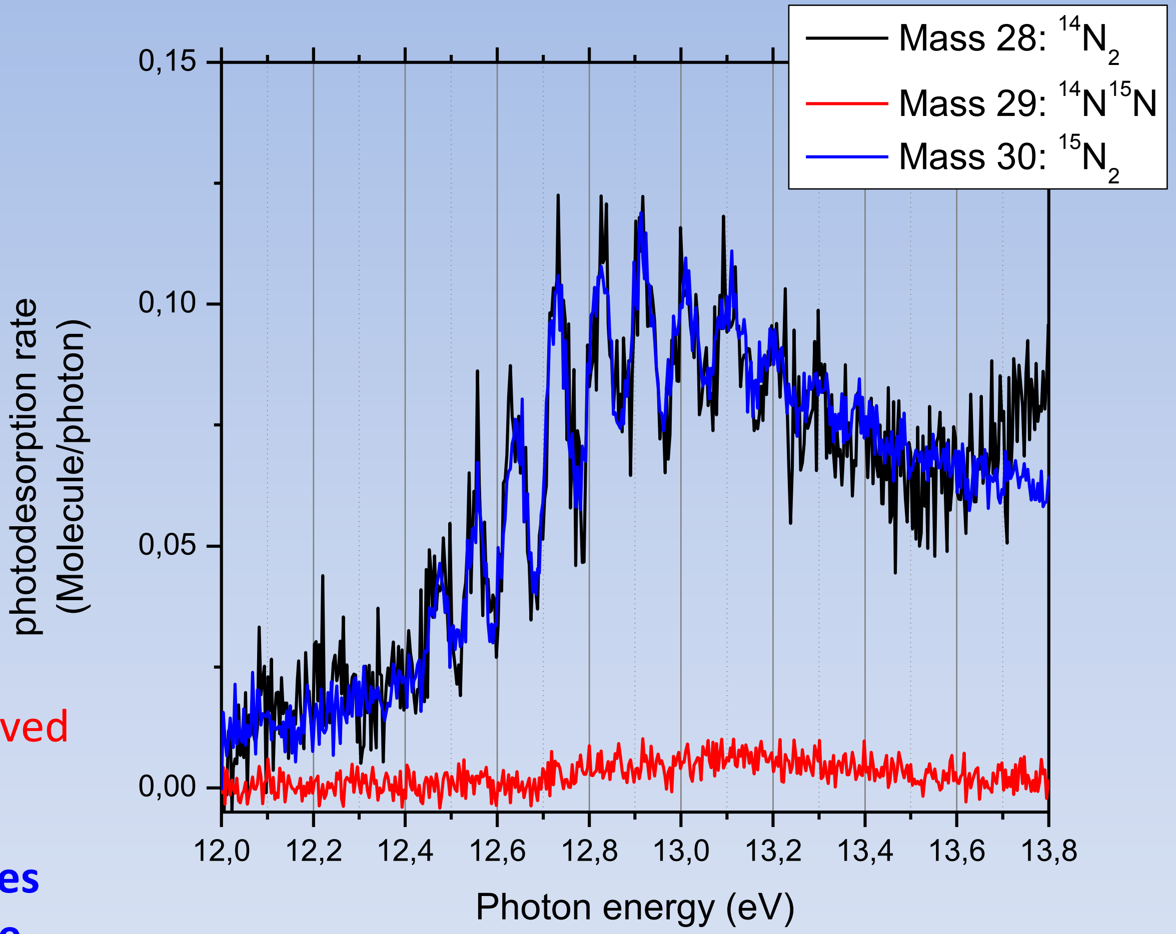


Very high efficiency above 12,5 eV

First event leading to the desorption: excitation to an electronic bound state

Photodesorption of pure N_2: induced by N + N recombination ?





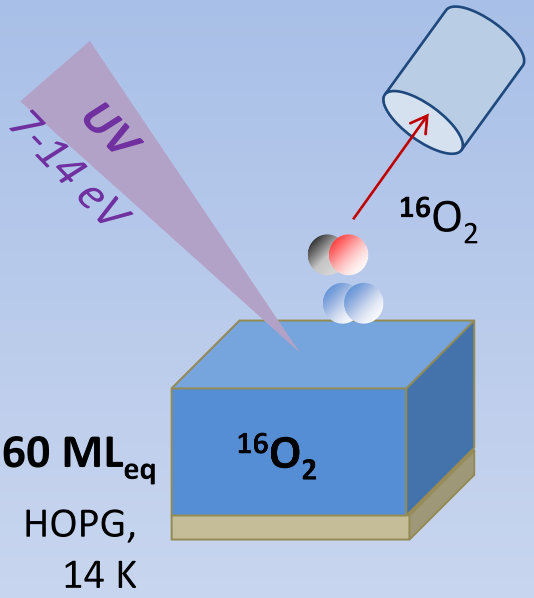
Desorption of $^{14}N_2$ and $^{15}N_2$ is observed

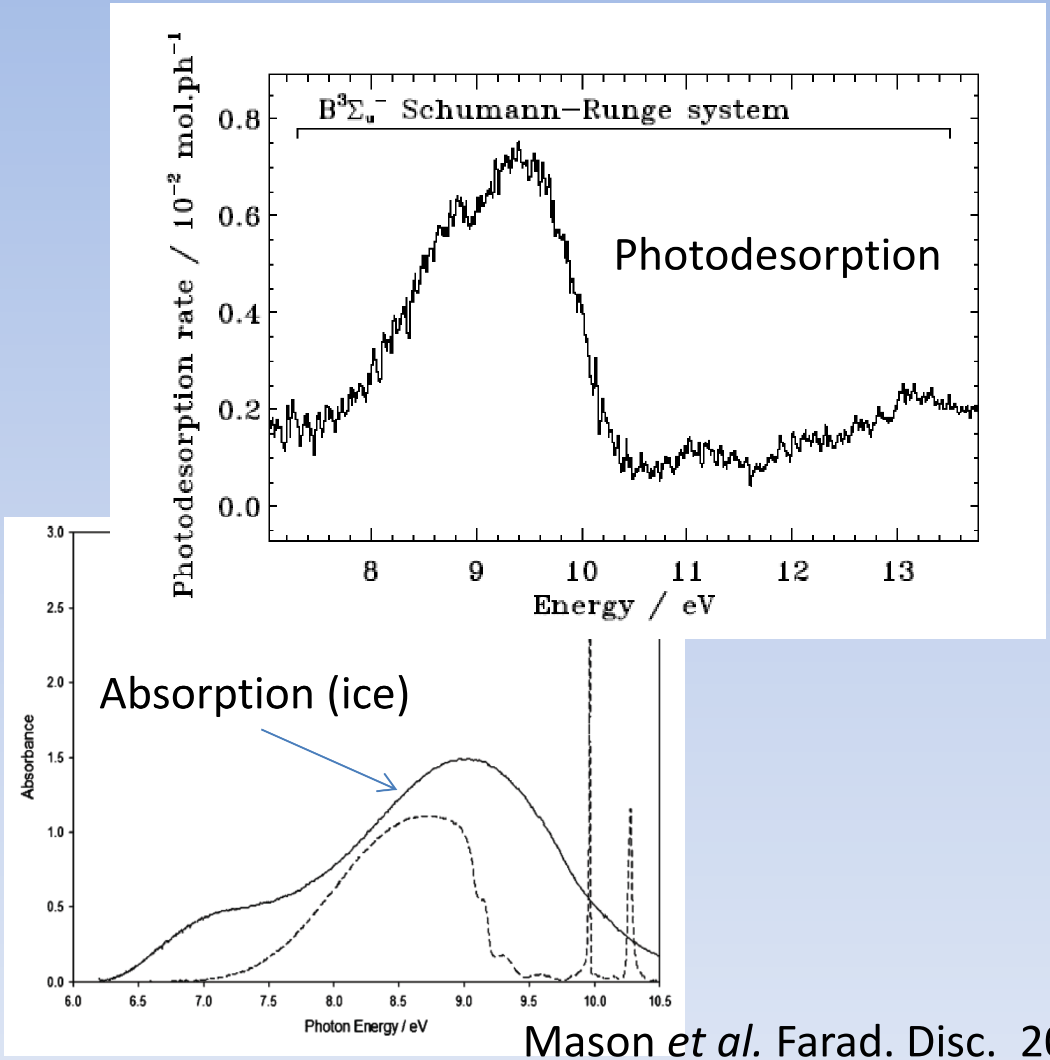
Desorption ^{14}N-^{15}N is not seen

⇨ **Recombination of N_2 does not seem to be operative for the photodesorption**

Fayolle et al., A&A. 2013

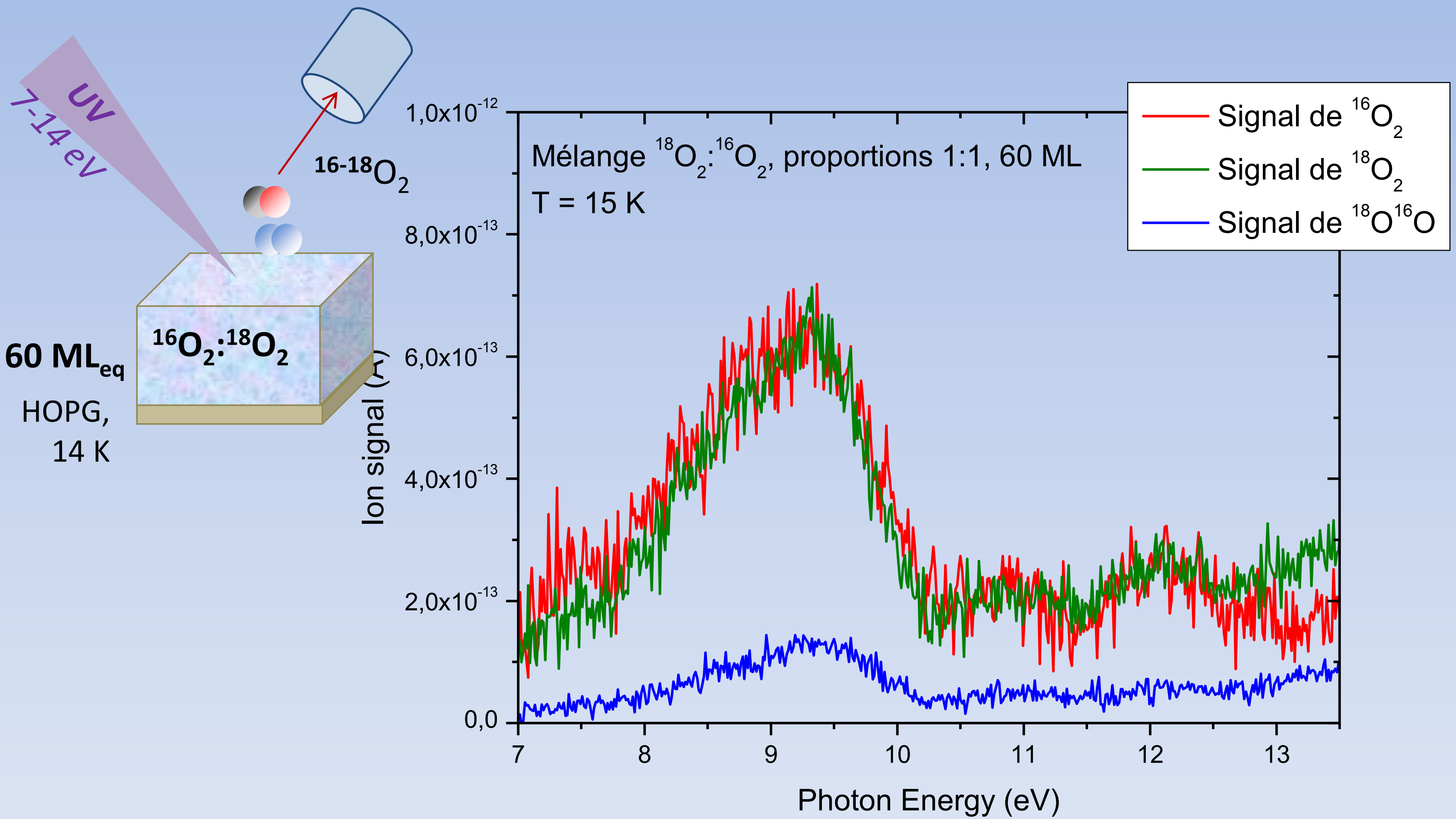
O_2





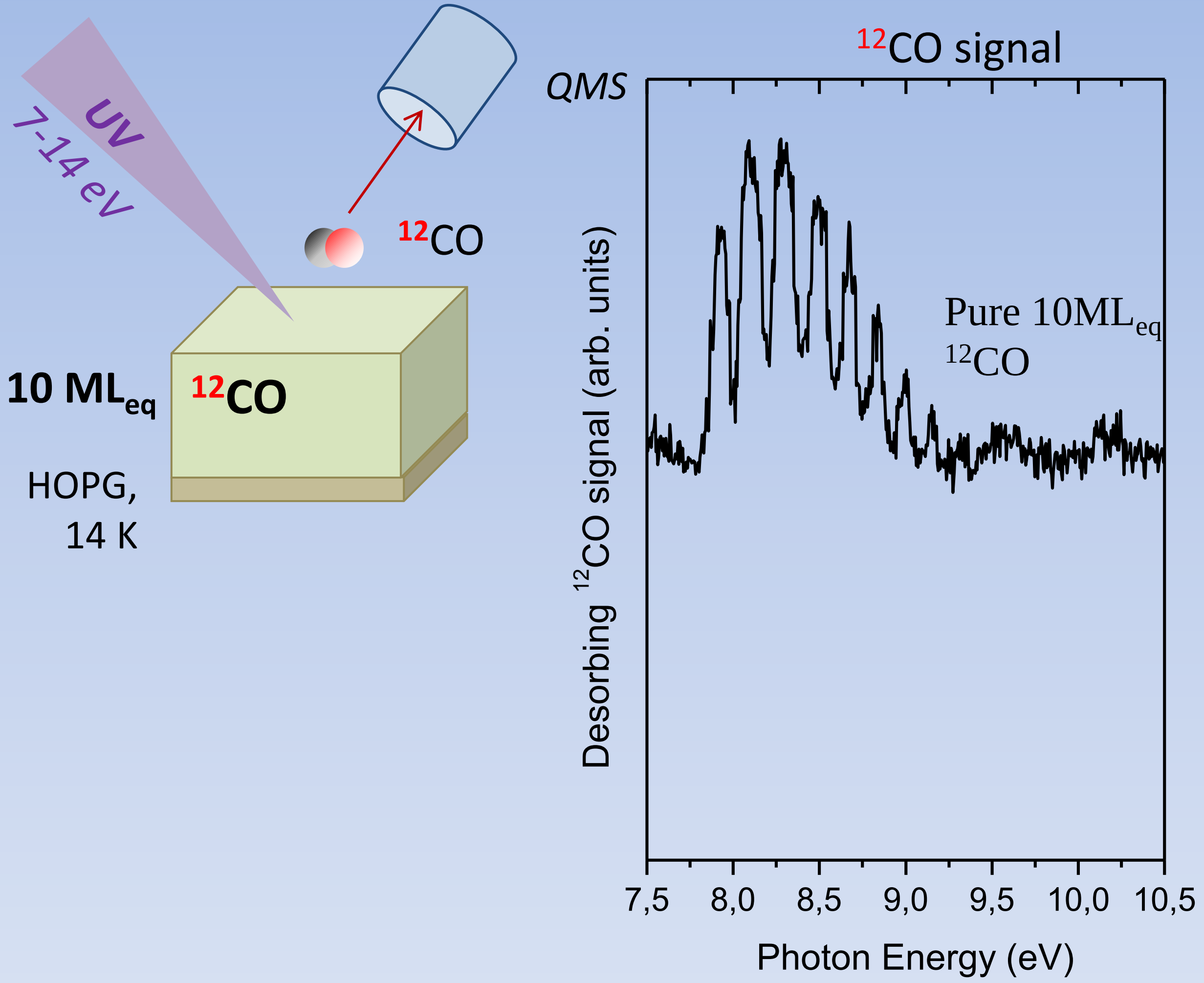
Mason *et al.* Farad. Disc. 2006

Photodesorption and Photochemistry



Photodesorption of Layered and mixed ices (without chemistry)

CO photodesorption: molecular mechanism



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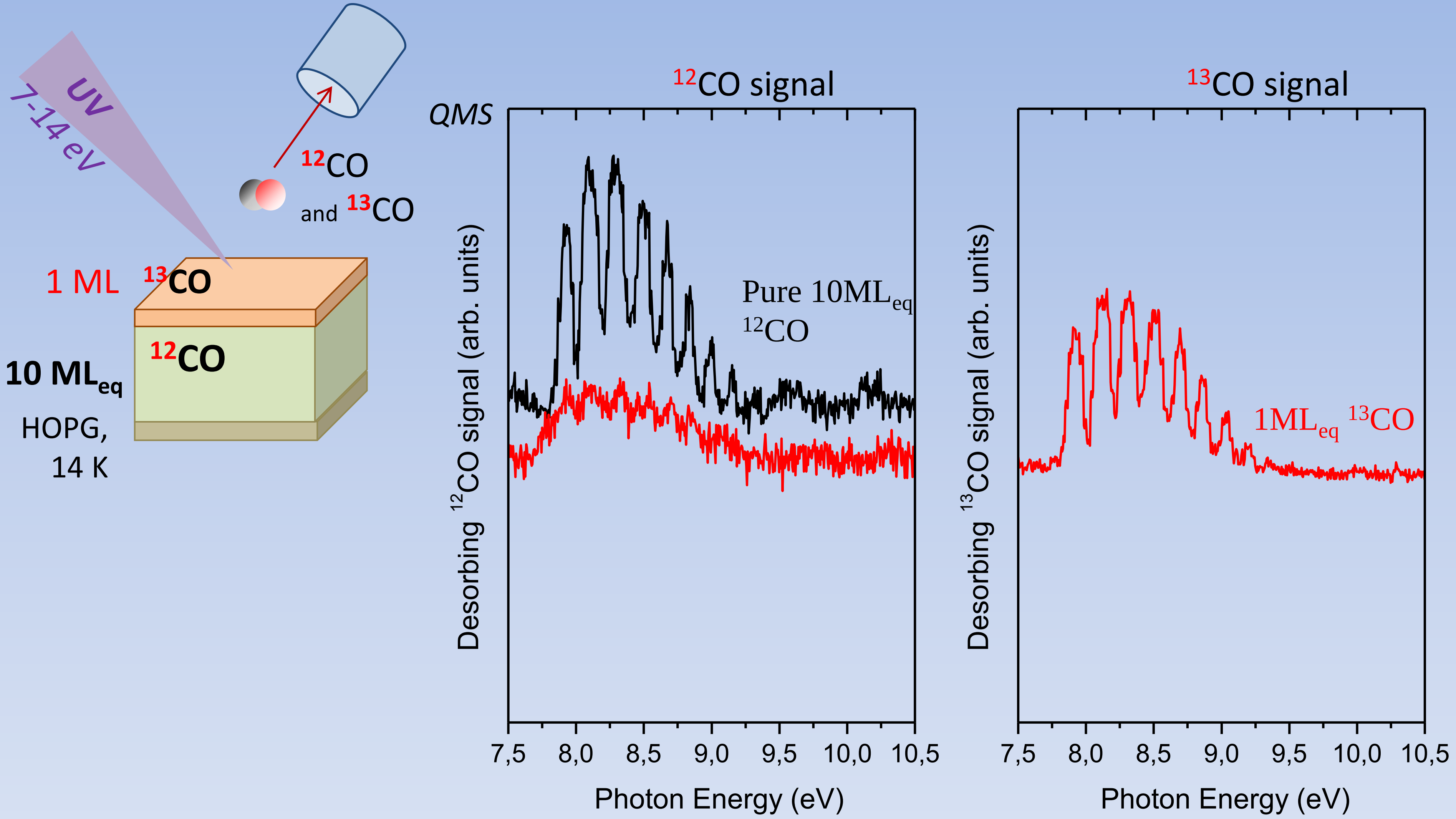

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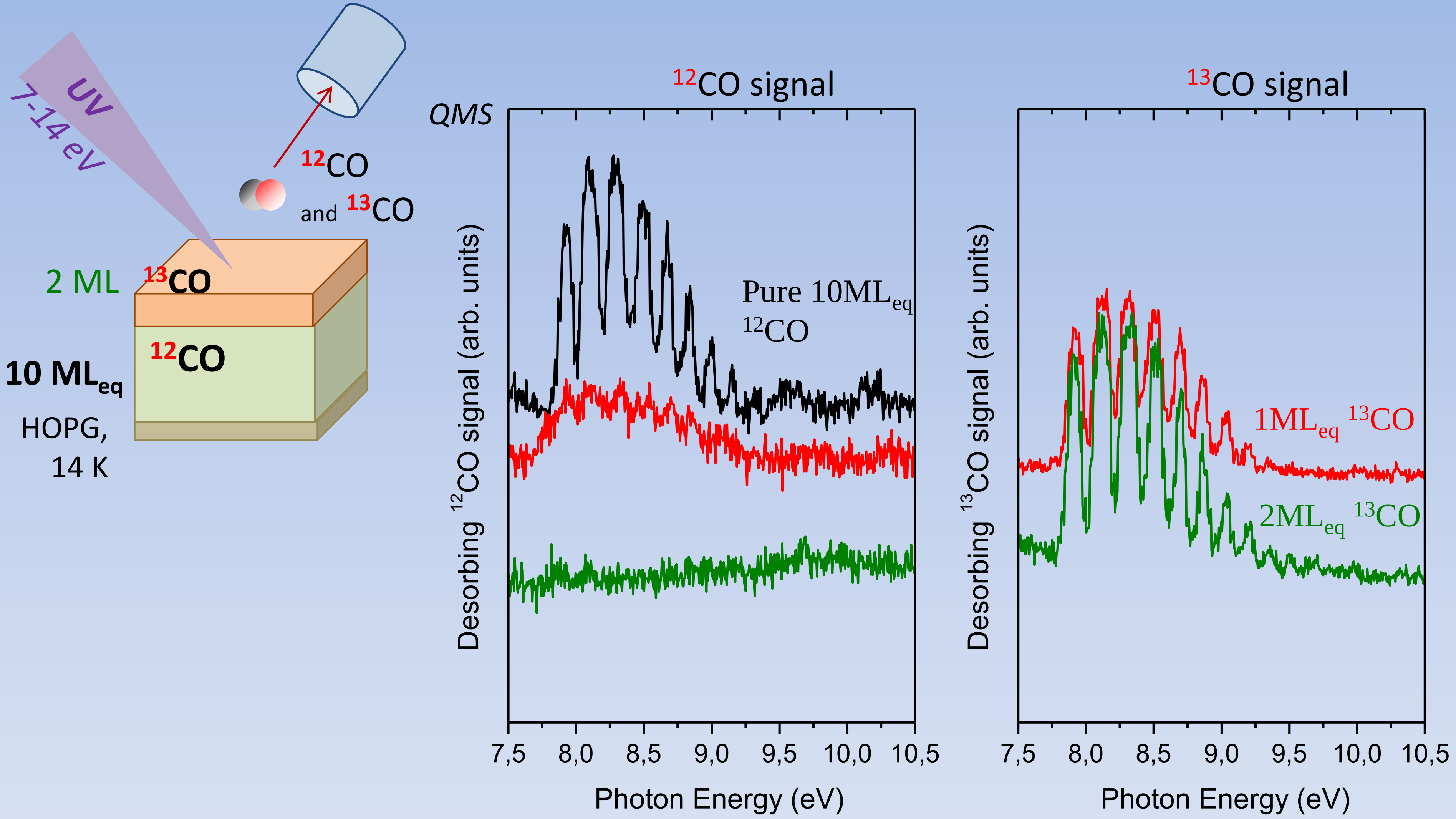
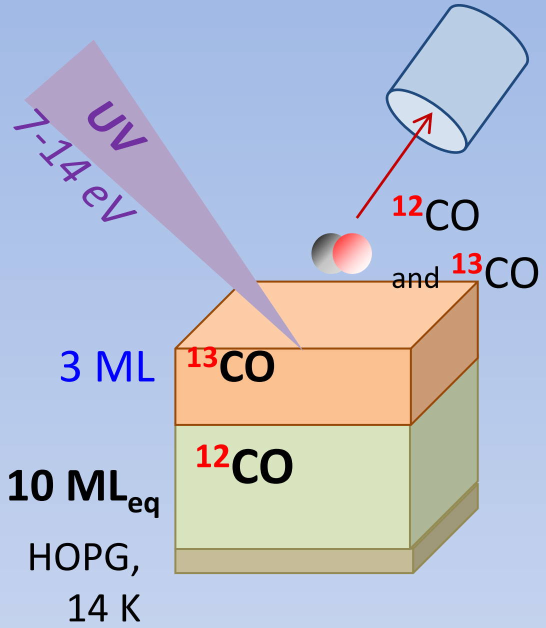
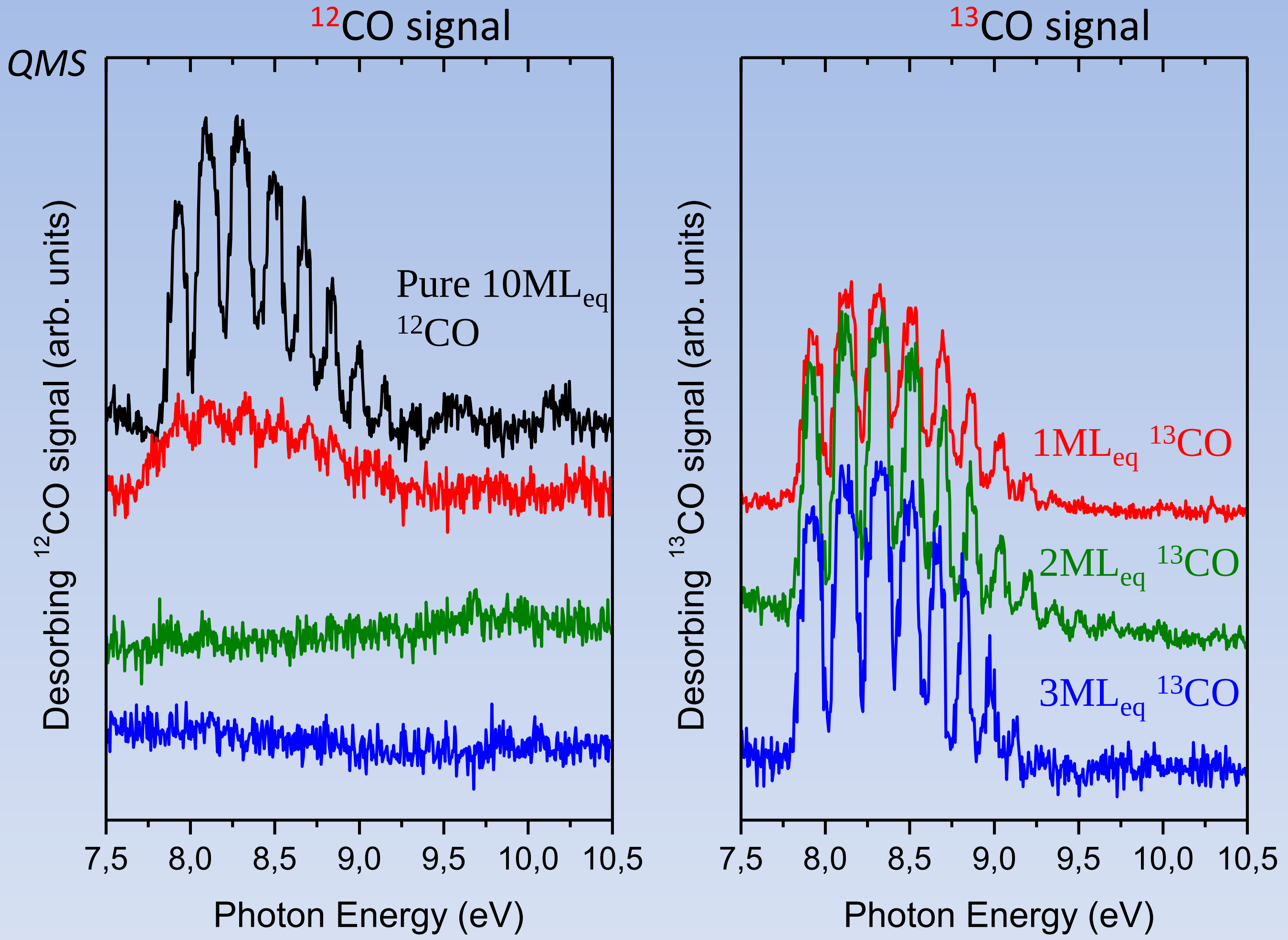


CO photodesorption: molecular mechanism



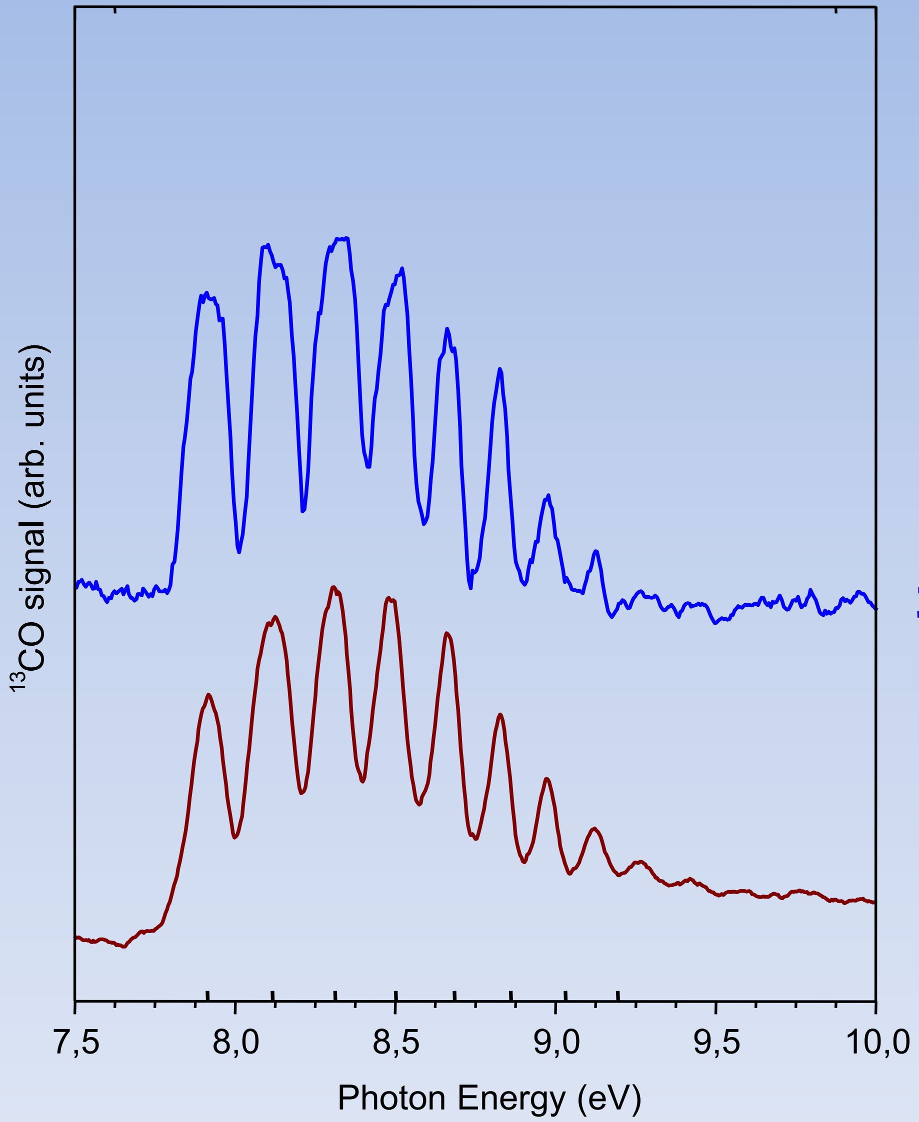


Bertin et al., PCCP 2012

A surface process: only the topmost molecules are desorbing

Only the upper 1-3 layers are affected with photodesorption

CO photodesorption: molecular mechanism

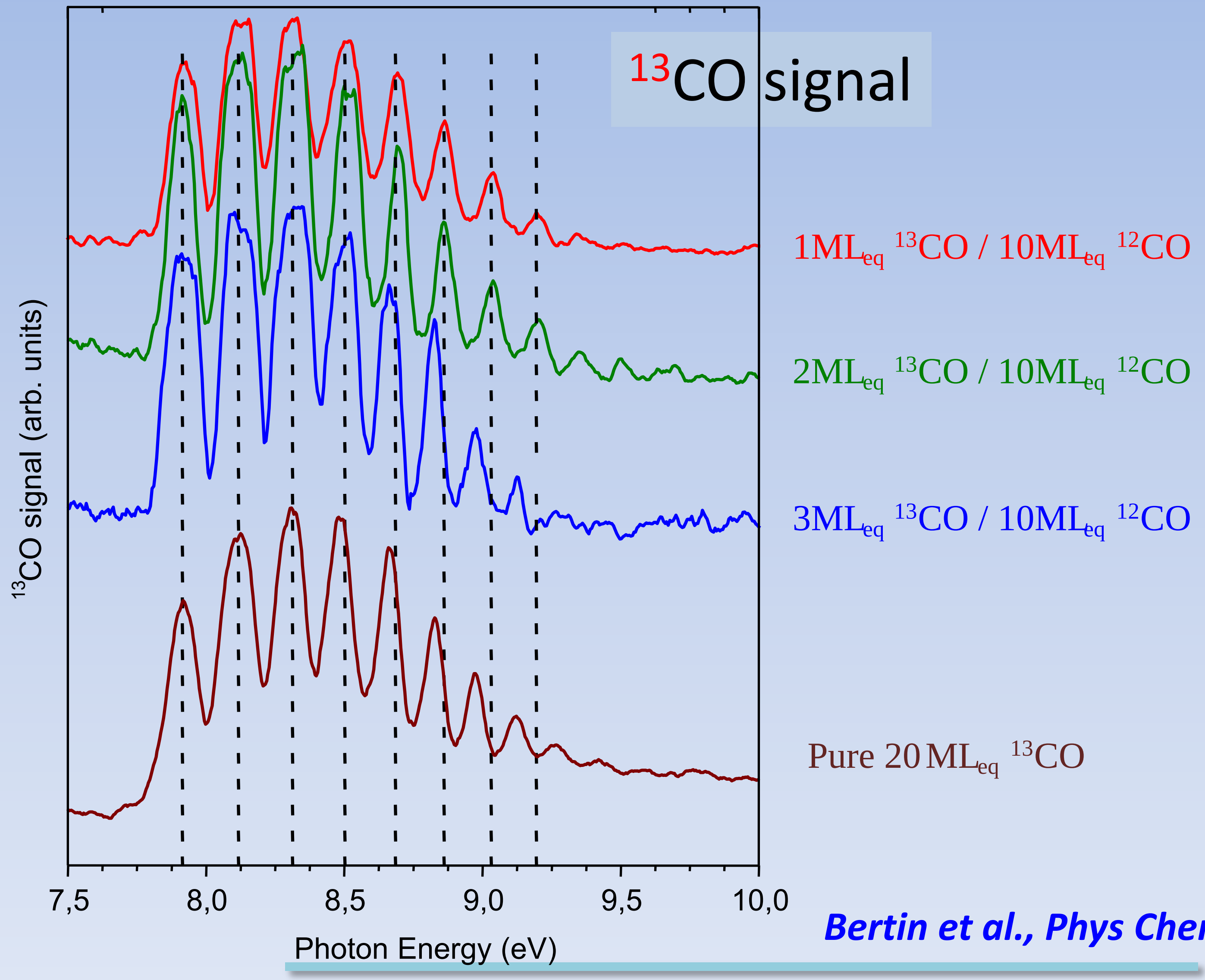


^{13}CO signal

3ML$_{eq}$ ^{13}CO / 10ML $_{eq}$ ^{12}CO

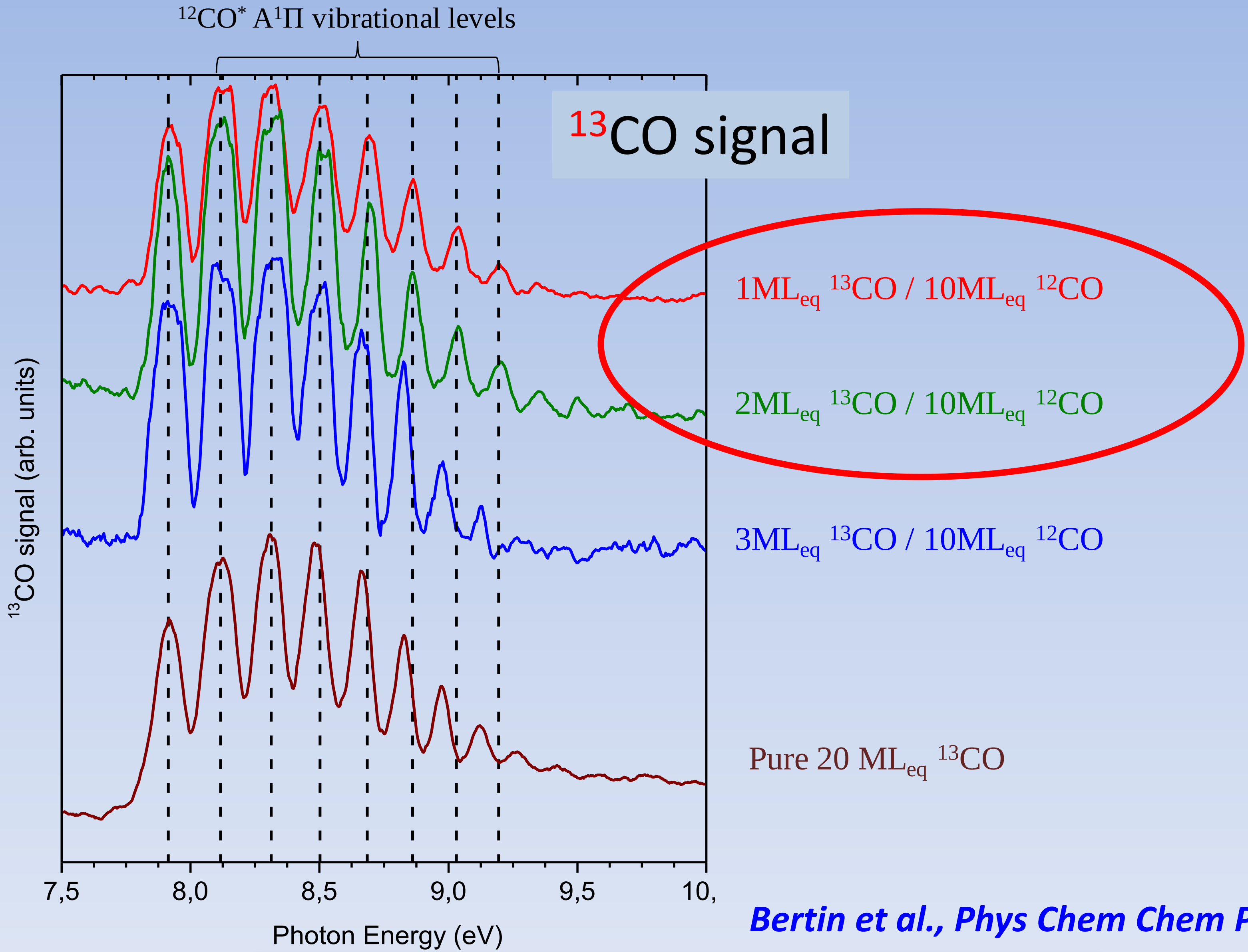
Pure 20 ML$_{eq}$ ^{13}CO

CO photodesorption: molecular mechanism



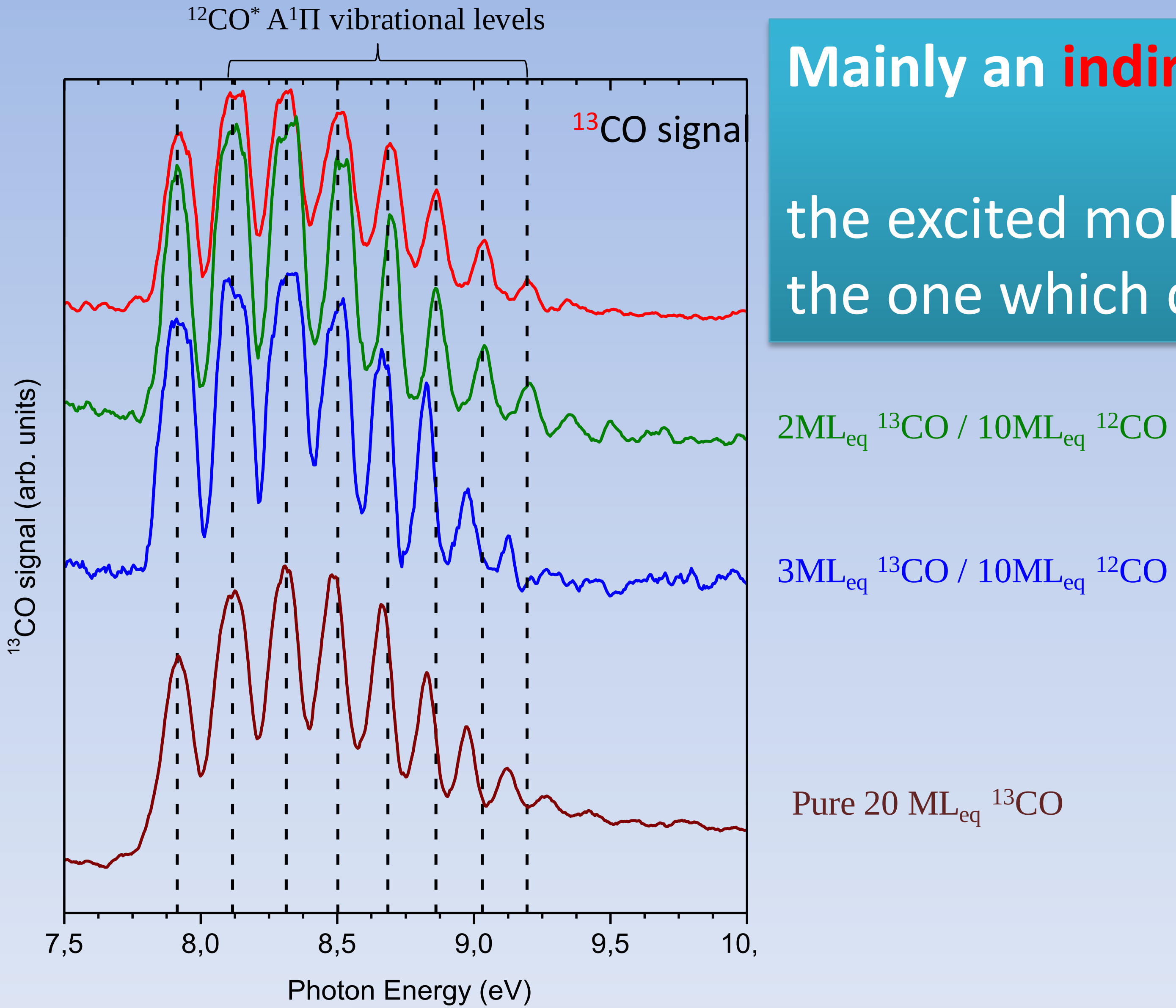
Bertin et al., Phys Chem Chem Phys 2012

CO photodesorption: molecular mechanism



Bertin et al., Phys Chem Chem Phys 2012

CO photodesorption: molecular mechanism

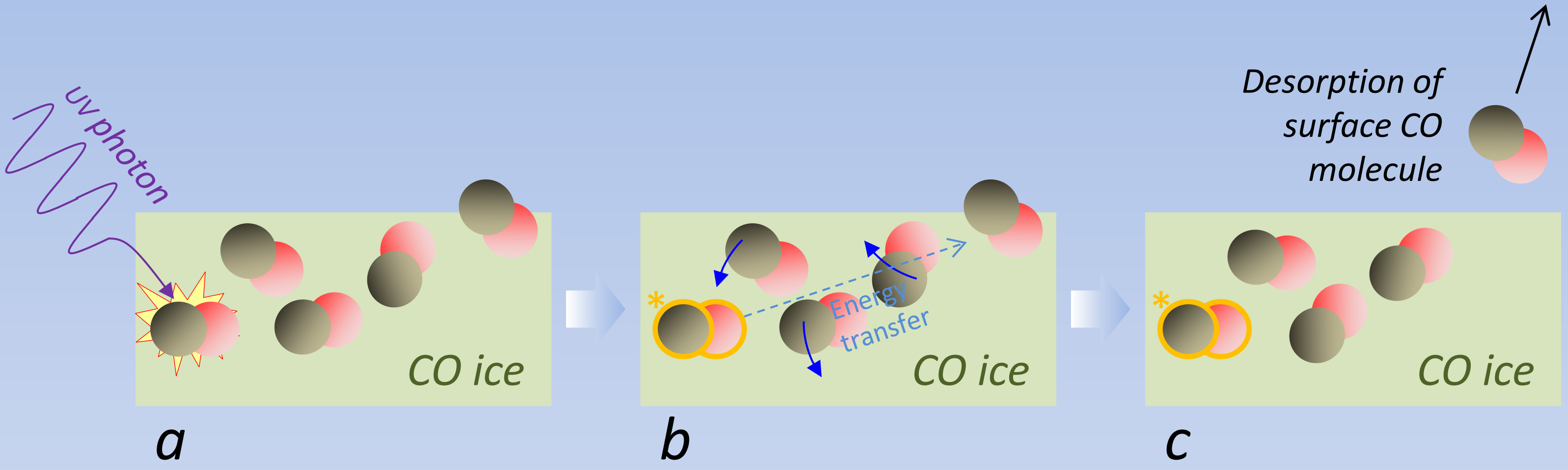


Mainly an indirect process:

the excited molecule is not the one which desorbs

CO photodesorption: molecular mechanism

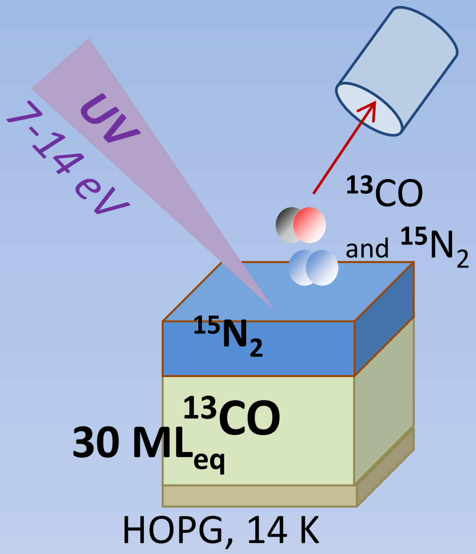
Indirect – surface DIET mechanism



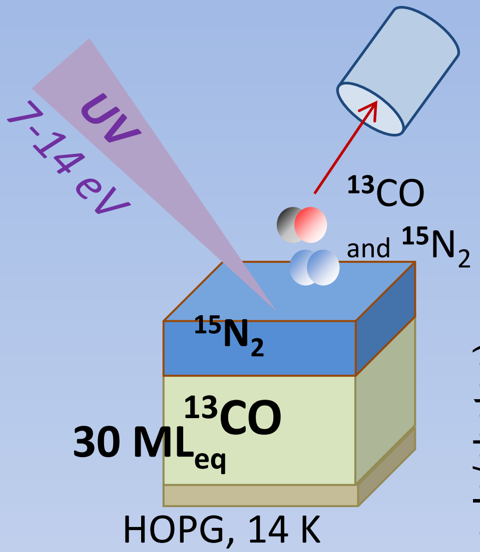
Important role inter-molecular energy coupling

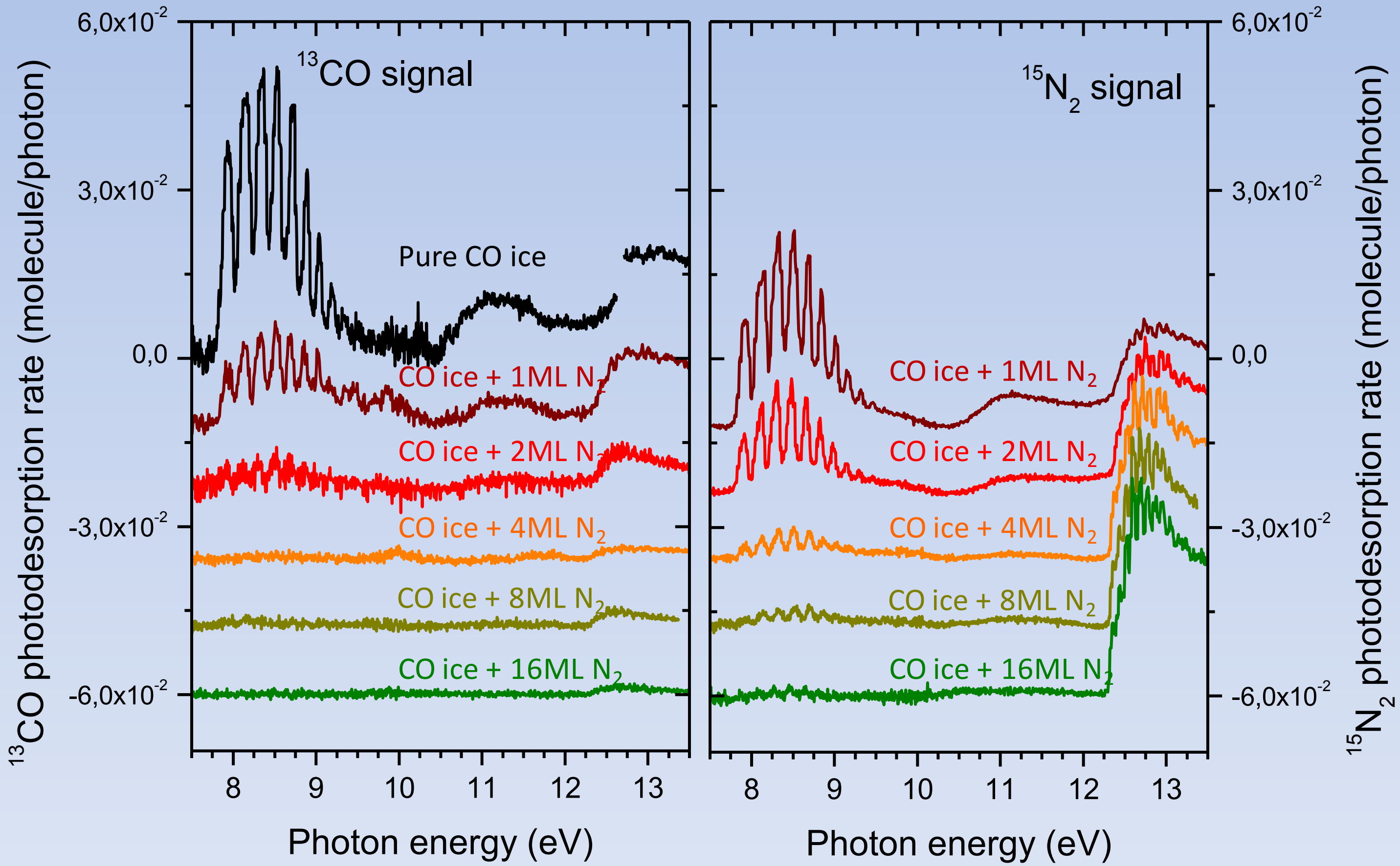
Bertin et al., Phys Chem Chem Phys 2012

Layered ices : N_2 / CO

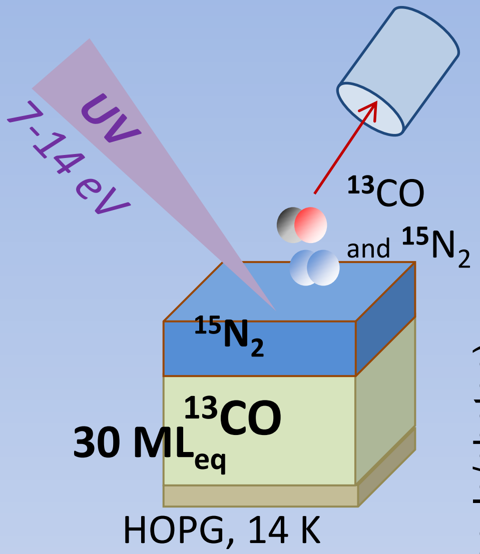


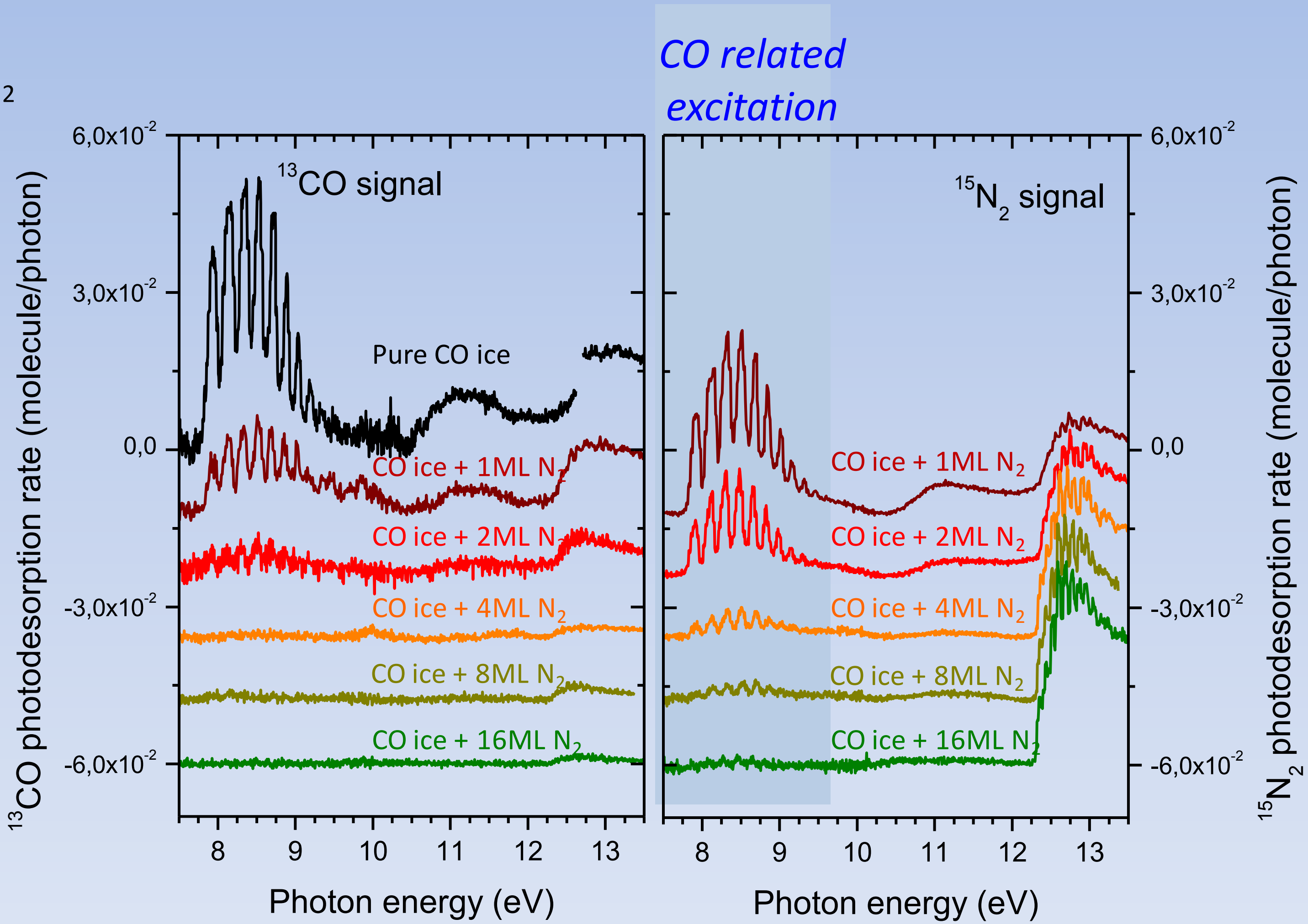
Layered ices : N_2 / CO



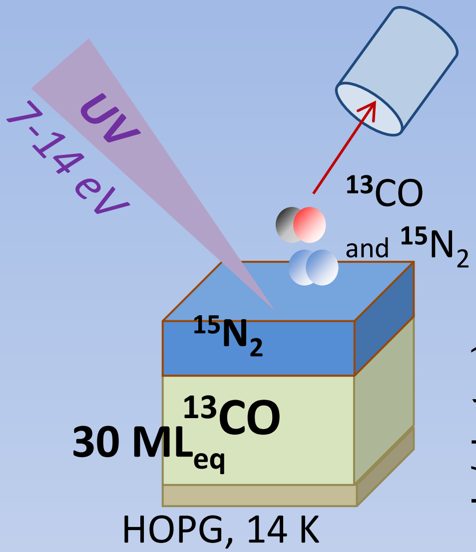


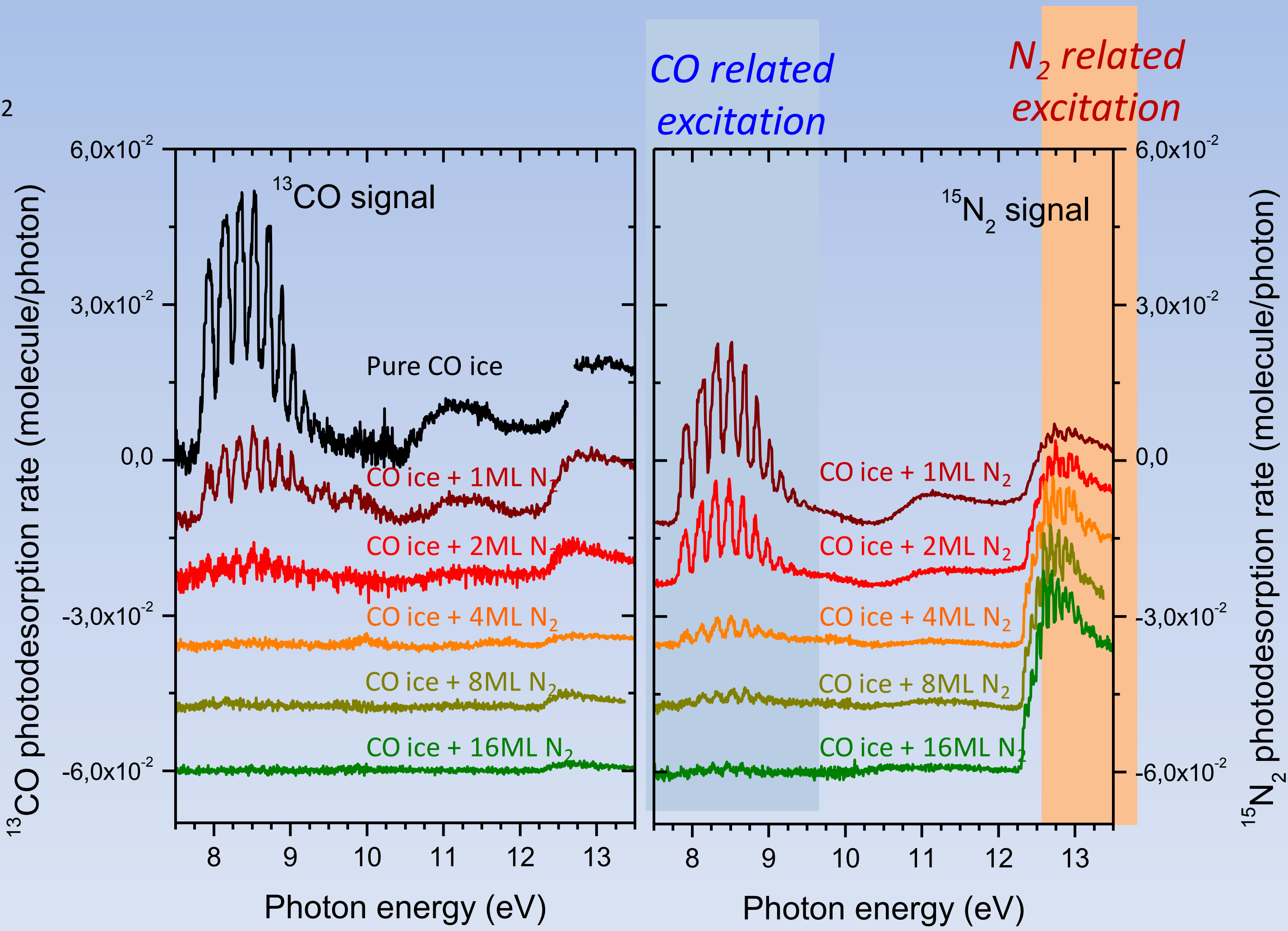
Layered ices : N_2 / CO



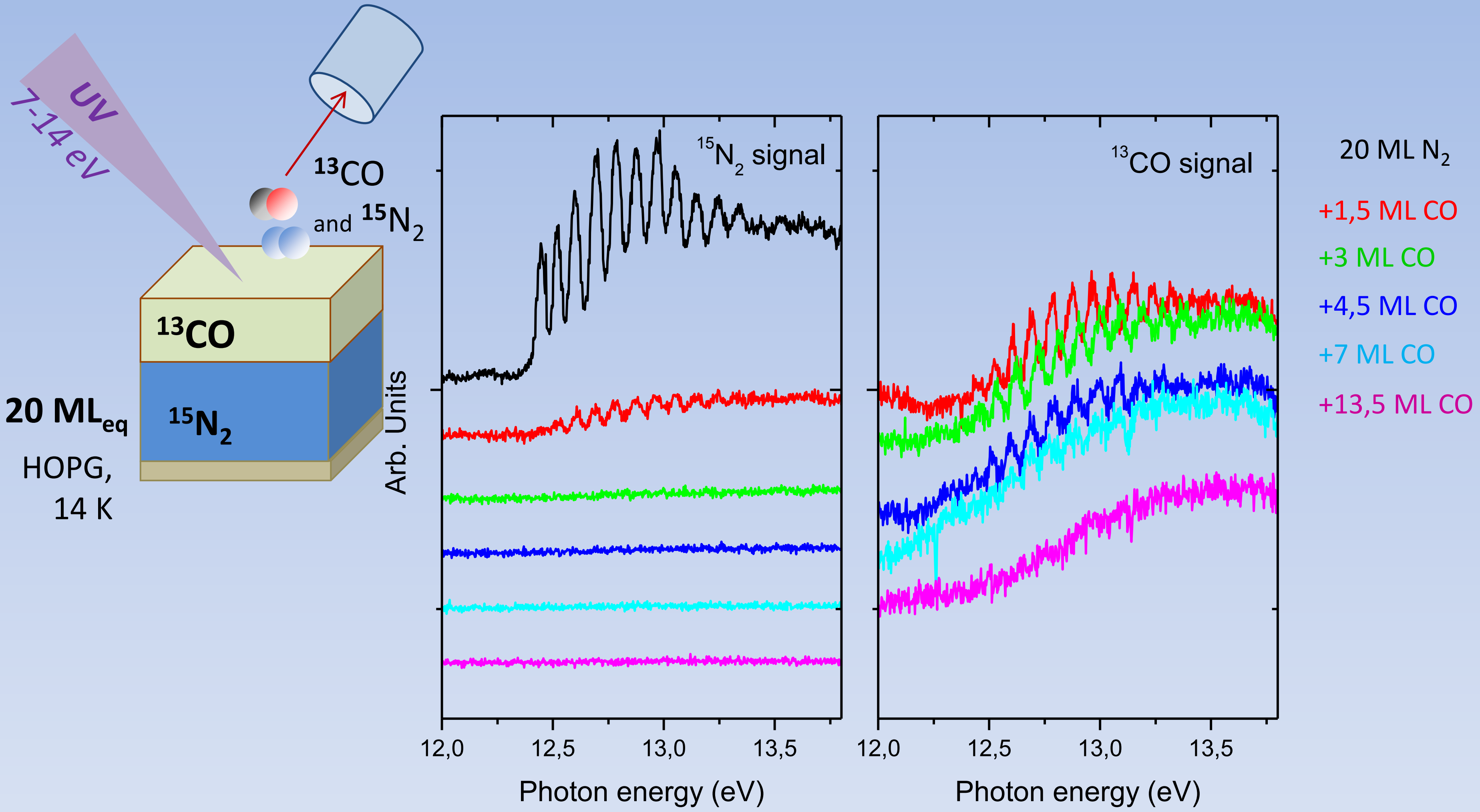

CO related excitation

Layered ices : N_2 / CO

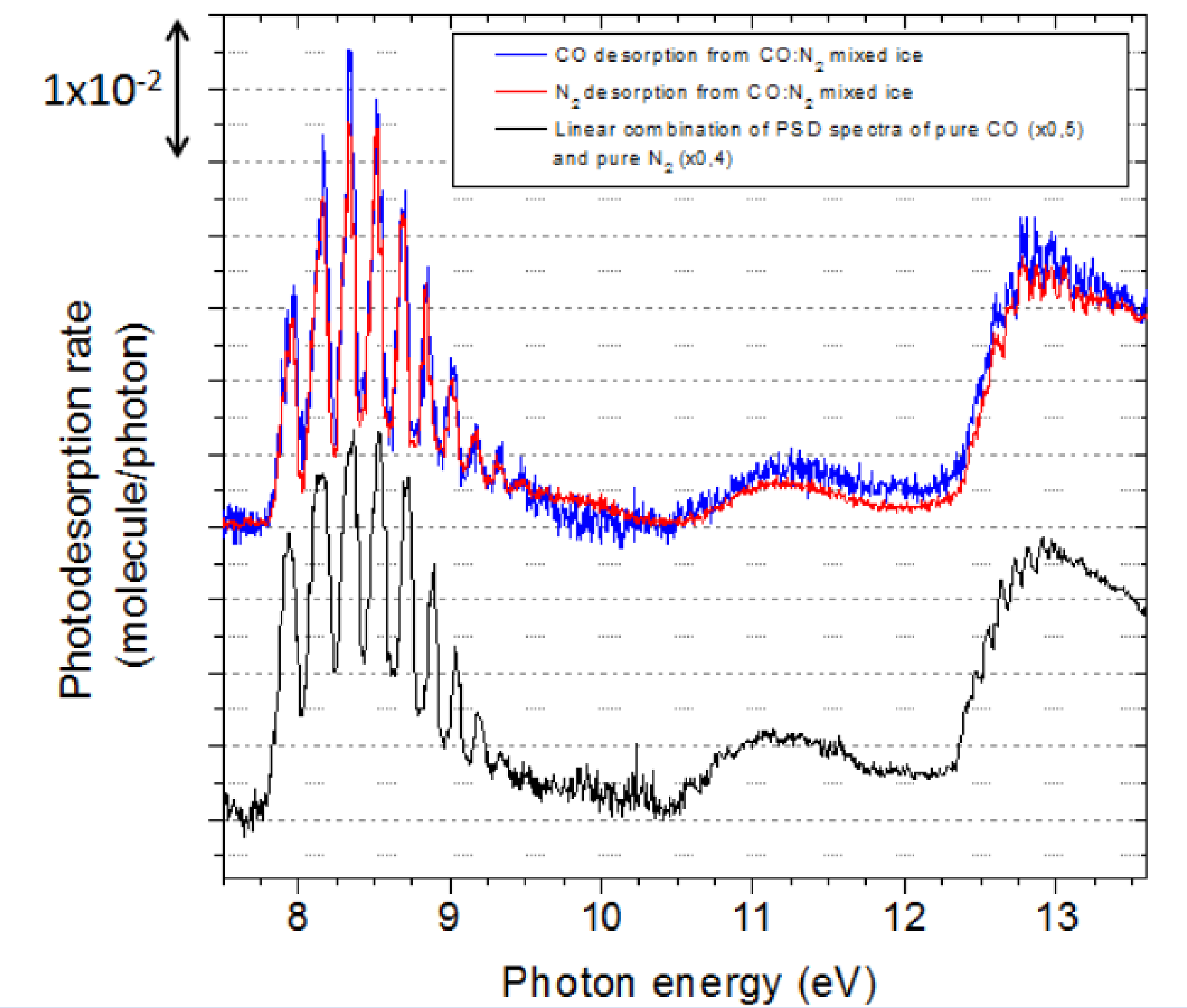




Layered ices : CO / N_2

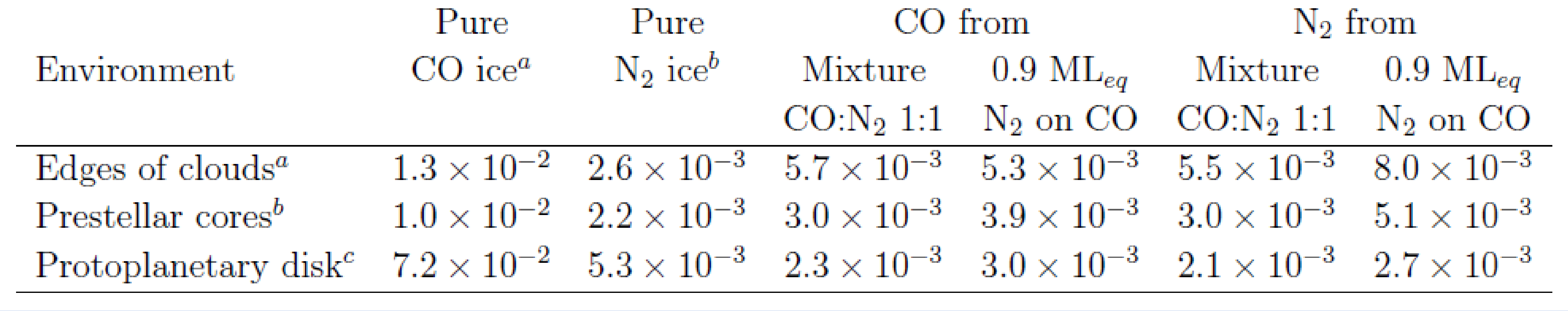


Photodesorption from a homogeneous mixture – CO : N_2 ice



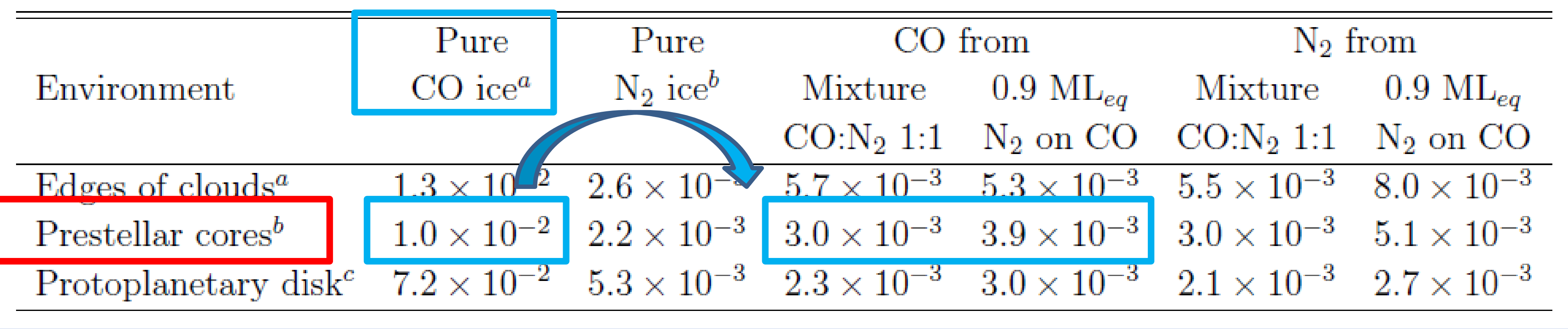
Bertin et al., 2013 APJ. In press

Integrated Photodesorption rates (mol.ph^{-1})



Environment	Pure CO ice[a]	Pure N_2 ice[b]	CO from Mixture $CO:N_2$ 1:1	CO from 0.9 ML_{eq} N_2 on CO	N_2 from Mixture $CO:N_2$ 1:1	N_2 from 0.9 ML_{eq} N_2 on CO
Edges of clouds[a]	1.3×10^{-2}	2.6×10^{-3}	5.7×10^{-3}	5.3×10^{-3}	5.5×10^{-3}	8.0×10^{-3}
Prestellar cores[b]	1.0×10^{-2}	2.2×10^{-3}	3.0×10^{-3}	3.9×10^{-3}	3.0×10^{-3}	5.1×10^{-3}
Protoplanetary disk[c]	7.2×10^{-2}	5.3×10^{-3}	2.3×10^{-3}	3.0×10^{-3}	2.1×10^{-3}	2.7×10^{-3}

Integrated Photodesorption rates (mol.ph^{-1})



Environment	Pure CO ice[a]	Pure N_2 ice[b]	CO from Mixture $CO:N_2$ 1:1	CO from 0.9 ML_{eq} N_2 on CO	N_2 from Mixture $CO:N_2$ 1:1	N_2 from 0.9 ML_{eq} N_2 on CO
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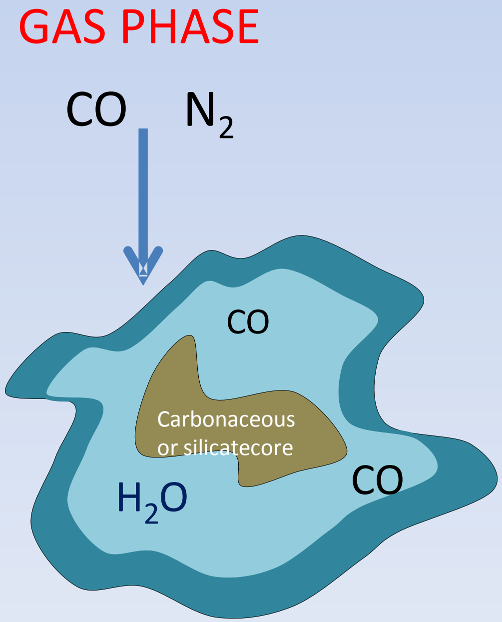


GAS PHASE

CO N_2

CO

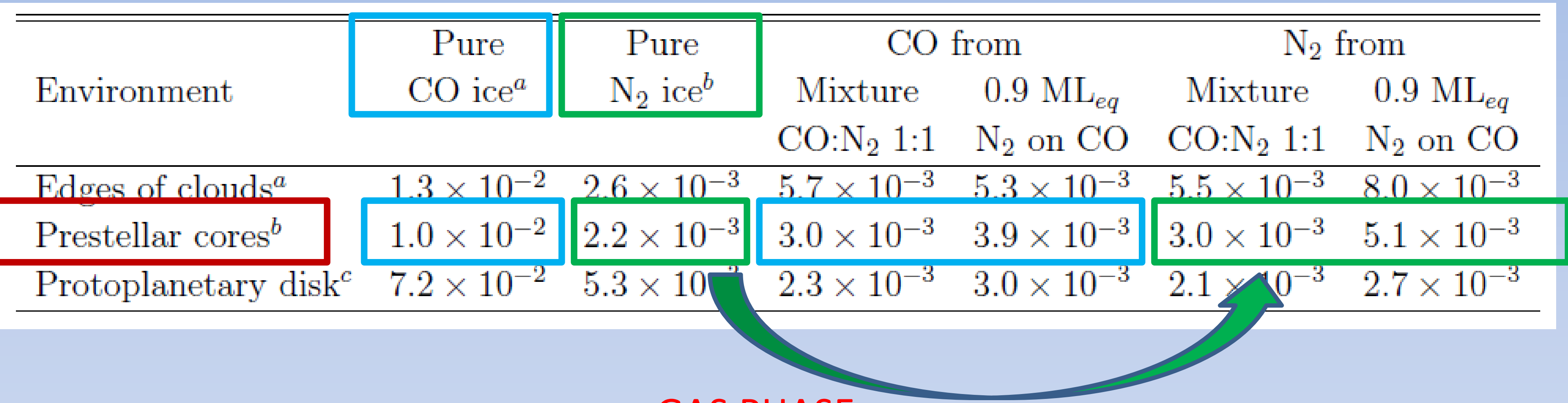
Carbonaceous or silicatecore

H_2O

CO

Prestellar Cores

Integrated Photodesorption rates (mol.ph^{-1})



Environment	Pure CO ice[a]	Pure N_2 ice[b]	CO from		N_2 from	
			Mixture CO:N_2 1:1	0.9 ML_{eq} N_2 on CO	Mixture CO:N_2 1:1	0.9 ML_{eq} N_2 on CO
Edges of clouds[a]	1.3×10^{-2}	2.6×10^{-3}	5.7×10^{-3}	5.3×10^{-3}	5.5×10^{-3}	8.0×10^{-3}
Prestellar cores[b]	1.0×10^{-2}	2.2×10^{-3}	3.0×10^{-3}	3.9×10^{-3}	3.0×10^{-3}	5.1×10^{-3}
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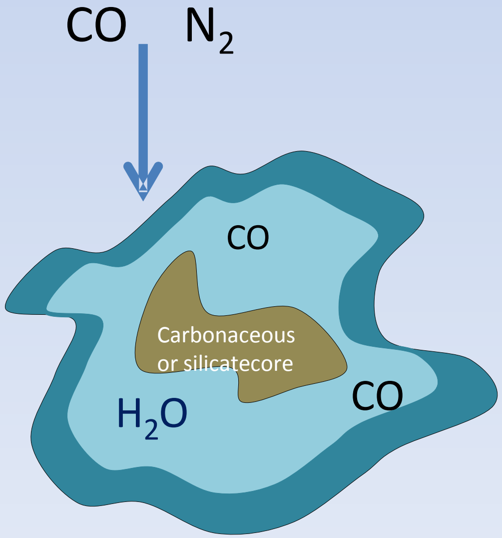
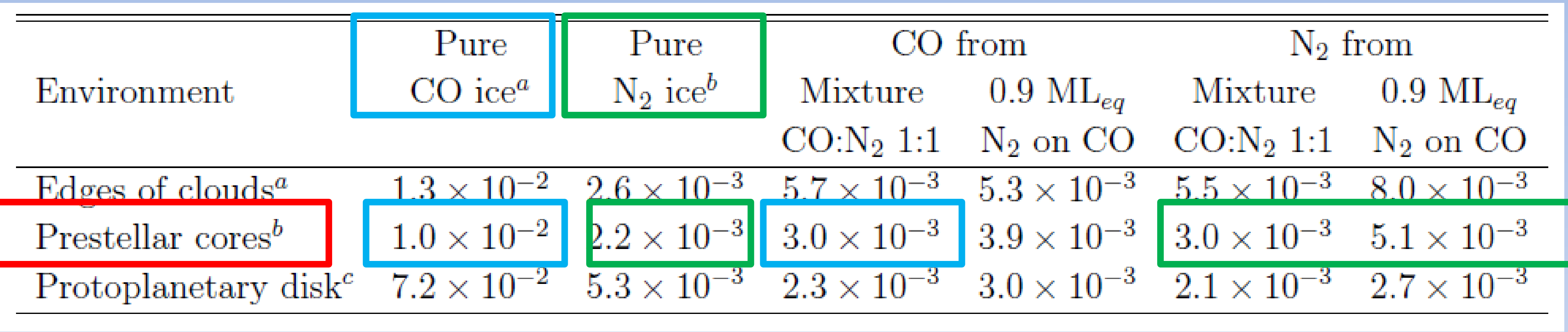
GAS PHASE



Prestellar Cores

Integrated Photodesorption rates (mol.ph^{-1})



Environment	Pure CO ice[a]	Pure N_2 ice[b]	CO from Mixture CO:N_2 1:1	CO from 0.9 ML_{eq} N_2 on CO	N_2 from Mixture CO:N_2 1:1	N_2 from 0.9 ML_{eq} N_2 on CO
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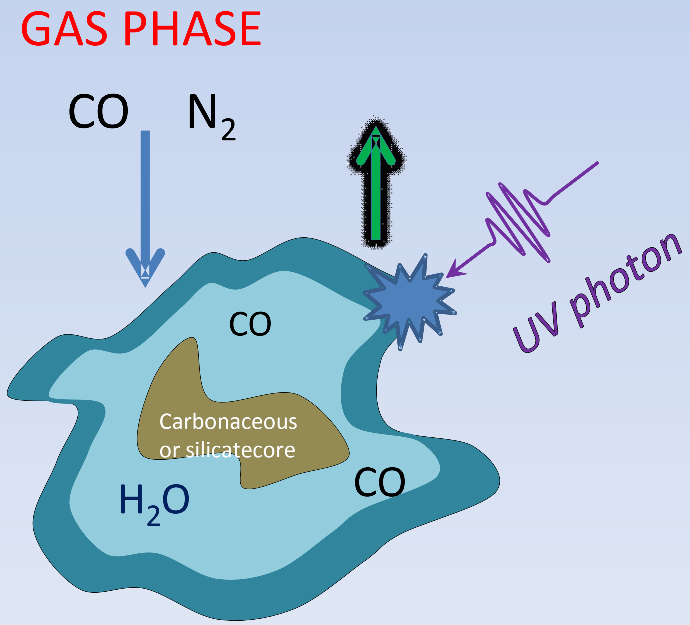
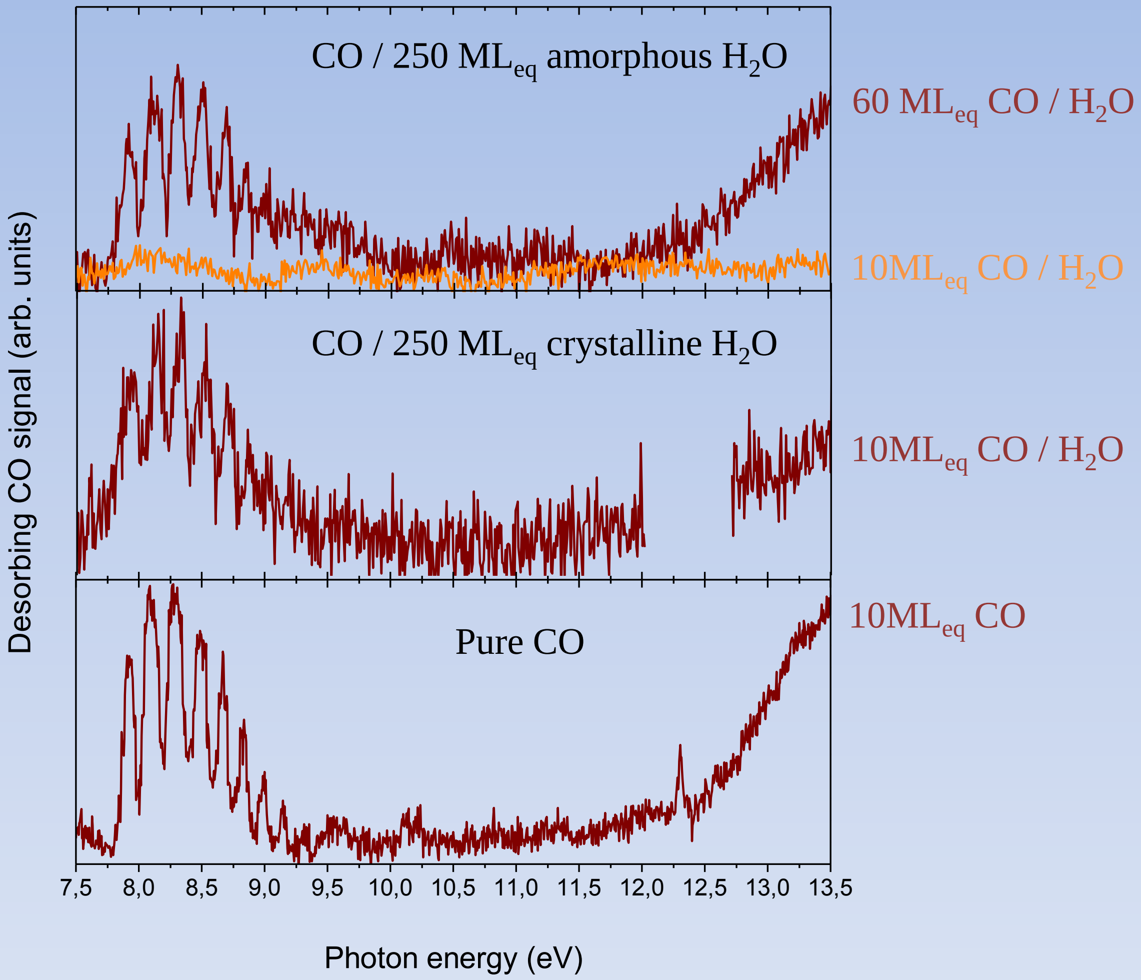
Prestellar Cores

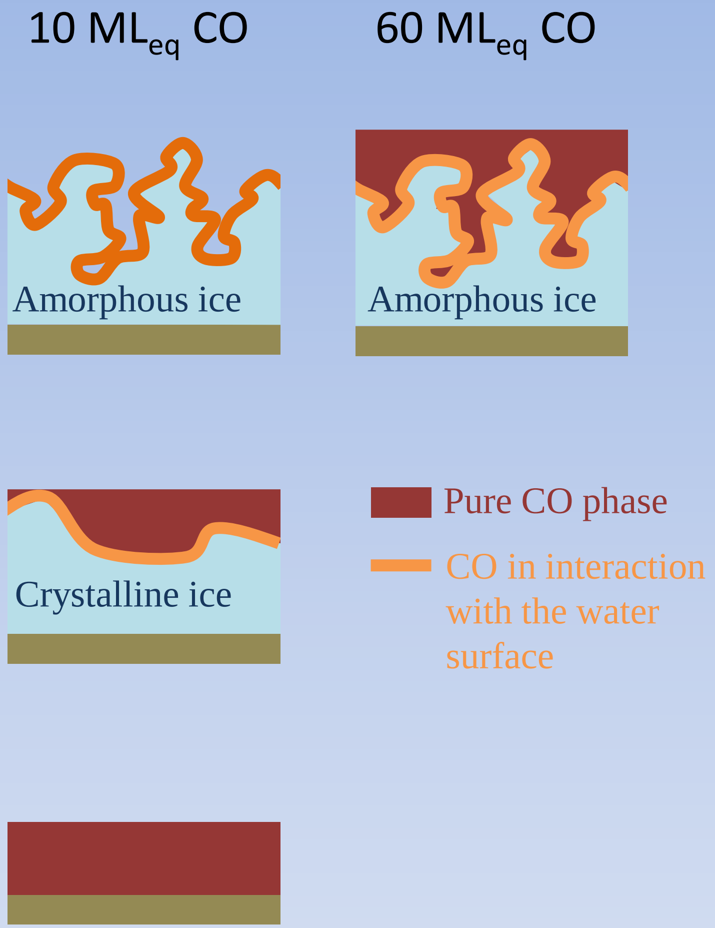


Why
[N_2] > [CO] ?

CO : H_2O layered ice

Bertin et al., Phys Chem Chem Phys 2012





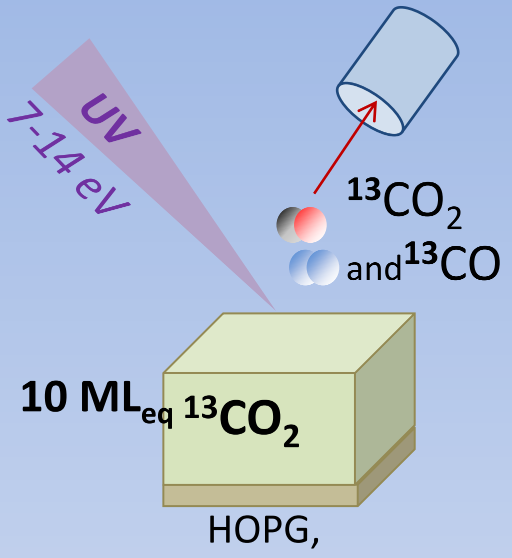
🟥 Pure CO phase

▬ CO in interaction with the water surface

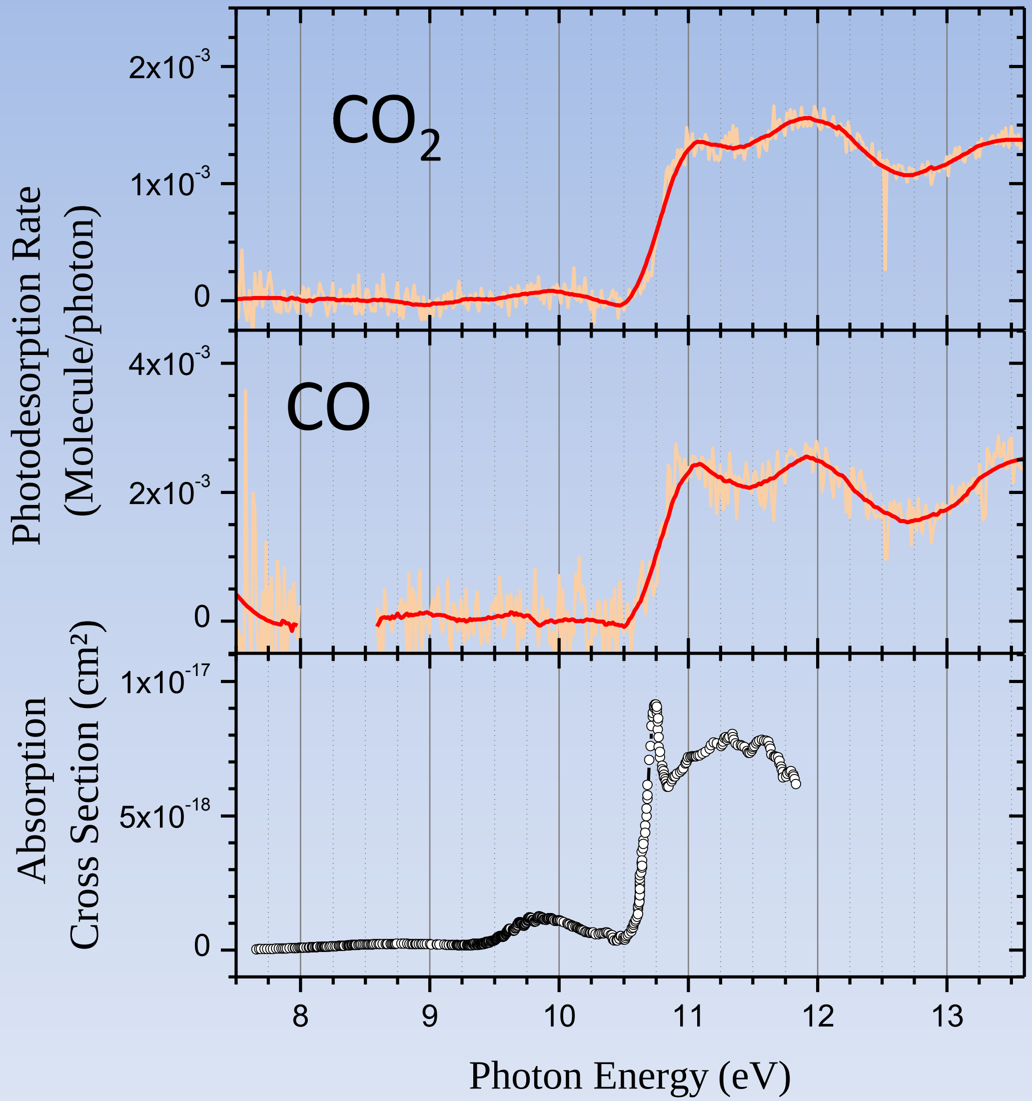
Interactions of CO-H_2O quench the photodesorption process by *at least* a factor of 15

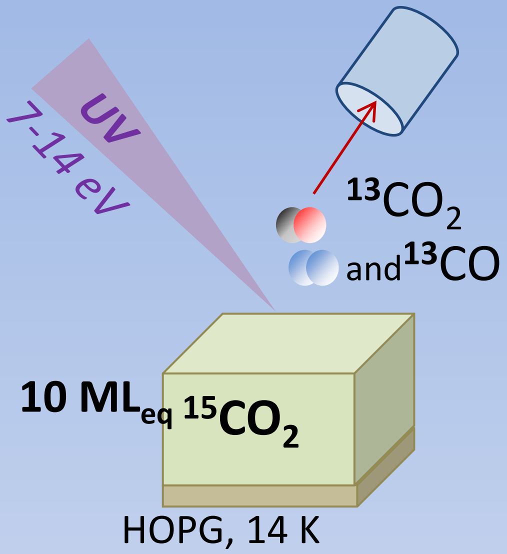
Photodesorption and photochemistry
The CO_2 case
(New Results)

Pure CO_2



T= 10 K





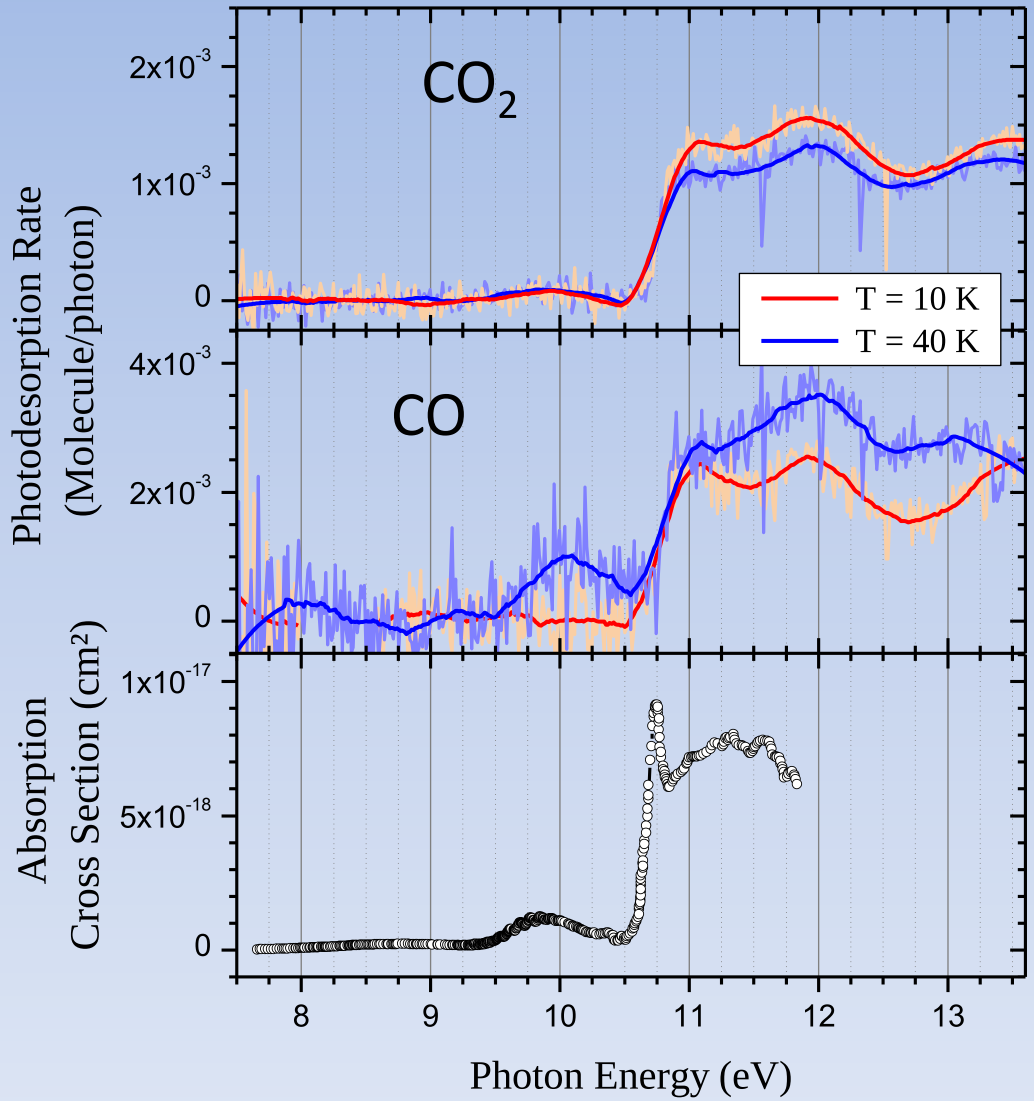
UV

7-14 eV

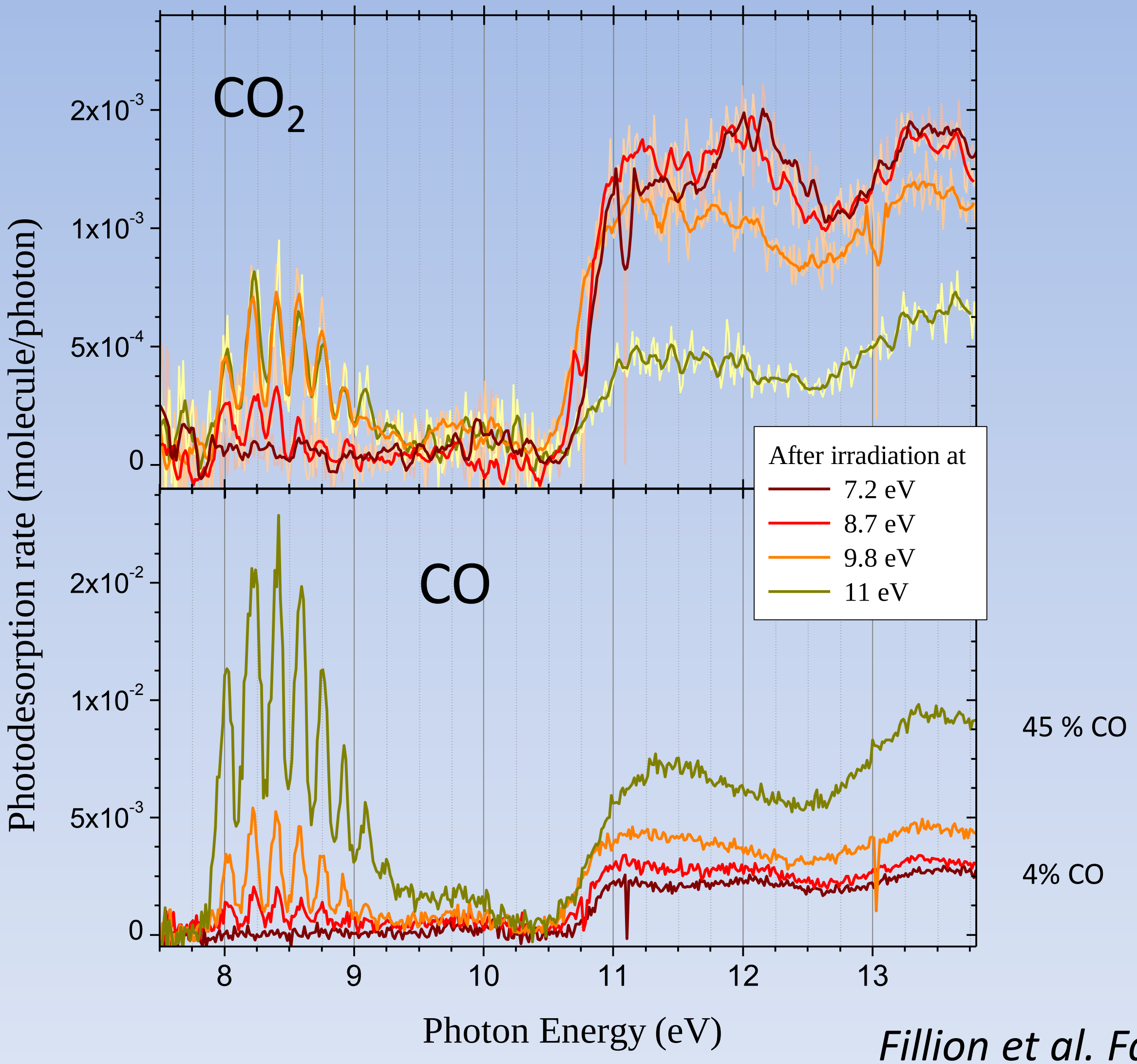
$^{13}CO_2$ and ^{13}CO

10 ML_{eq} $^{15}CO_2$

HOPG, 14 K



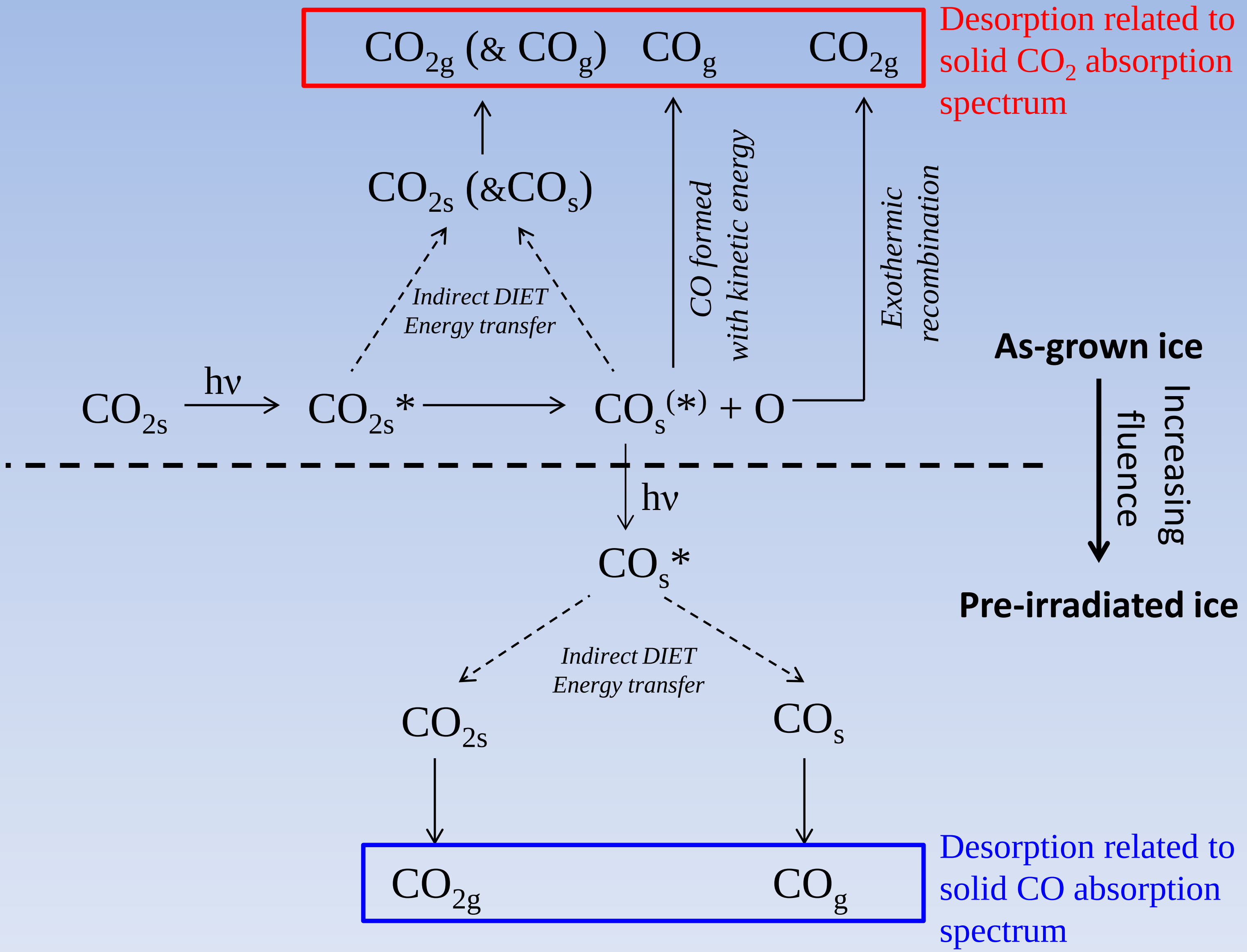
Pre-irradiated CO_2



Fillion et al. Faraday Discuss., 2014

DOI: 10.1039/C3FD00129F

Mechanisms



CO_{2g} (& CO_g) CO_g CO_{2g}

Desorption related to solid CO_2 absorption spectrum

CO_{2s} (&CO_s)

Indirect DIET Energy transfer

CO formed with kinetic energy

Exothermic recombination

$CO_{2s} \xrightarrow{h\nu} CO_{2s}^* \longrightarrow CO_s^{(*)} + O$

As-grown ice

Increasing fluence

Pre-irradiated ice

$h\nu$

CO_s^*

Indirect DIET Energy transfer

CO_{2s} CO_s

CO_{2g} CO_g

Desorption related to solid CO absorption spectrum

Summary and conclusions

☐ photodesorption without chemistry

	N_2	CO
Ly man-alpha	1,5 10^{-3}	4 10^{-3}
Edge of Clouds	2,6 10^{-3}	1,2 10^{-2}

- ✓ Energy dependent, High absolute rates
- ✓ Indirect desorption from electronic excitation
- ✓ Rates depends on the chemical composition and ice structure

☐ CO_2: photodesorption and Photochemistry interconnected
CO photoproduced induce the photodesorption of CO_2 below 10 eV

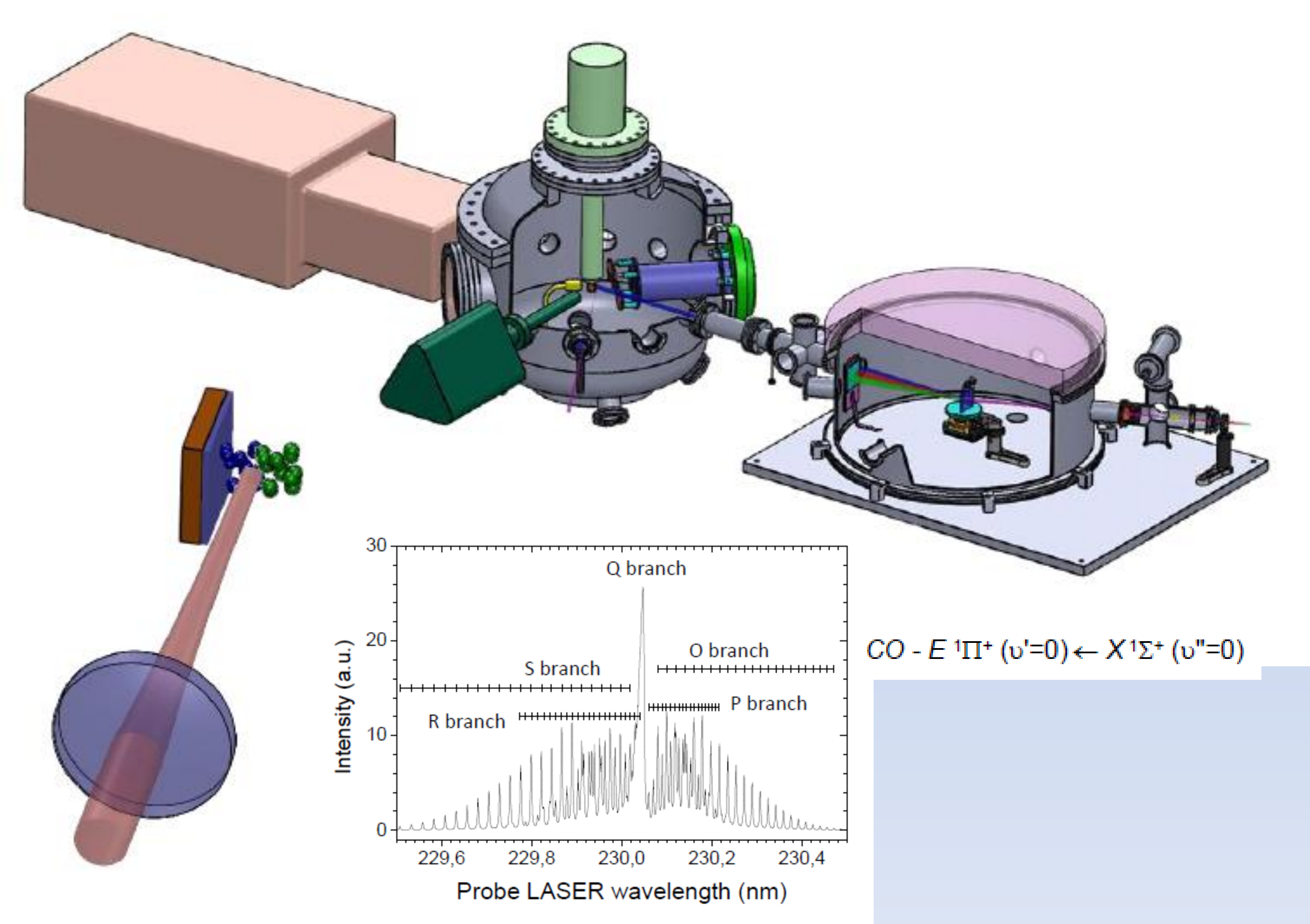
FUTURE DIRECTIONS

- ✓ **Indirect desorption ?**

  CO: H_2CO and CO : CH_3OH

- ✓ **Competitive photodissociation**
- ✓ **Energy partitioning**

FUTURE DIRECTIONS



$CO - E\,^1\Pi^+ (\upsilon'=0) \leftarrow X\,^1\Sigma^+ (\upsilon''=0)$

Acknowledgments

M.Bertin

X. Michaut

L. Philippe

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C. Romanzin (Univ-Paris-sud-LCP)
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A Moudens (Univ-Cergy-LERMA)
U. Poderoso (UPMC)

E Fayolle

H. Linnartz

K. Öberg

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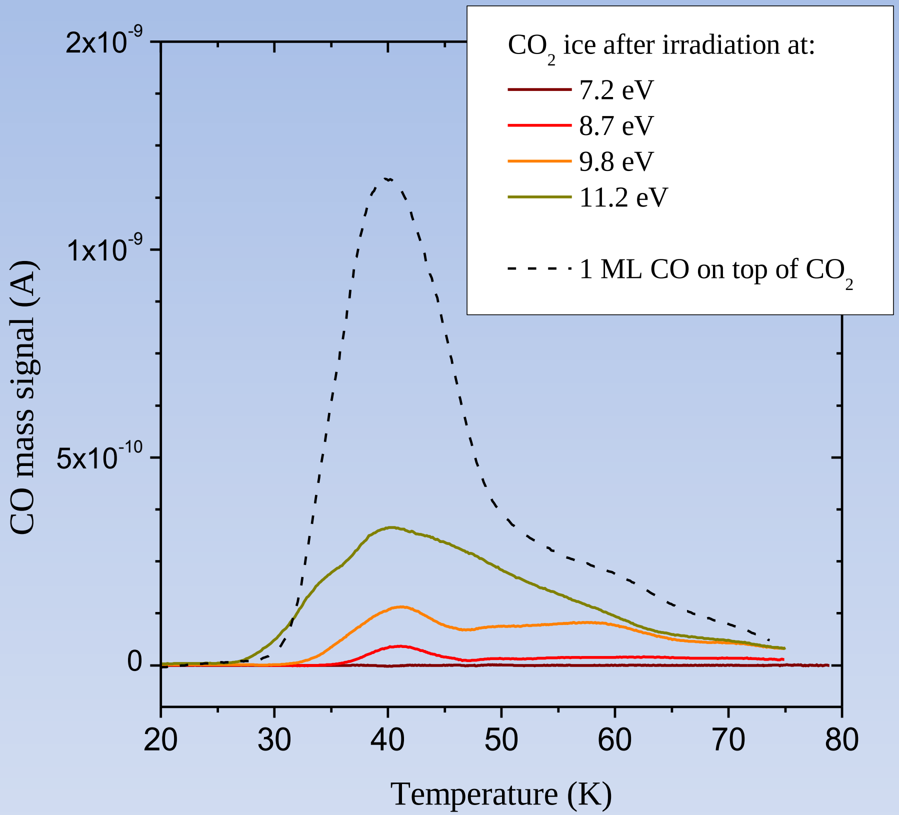
☐ SOLEIL –DESIRS

☐ Programme PCMI « Physique et Chimie du Milieu Interstellaire » & Université Pierre & Marie Curie

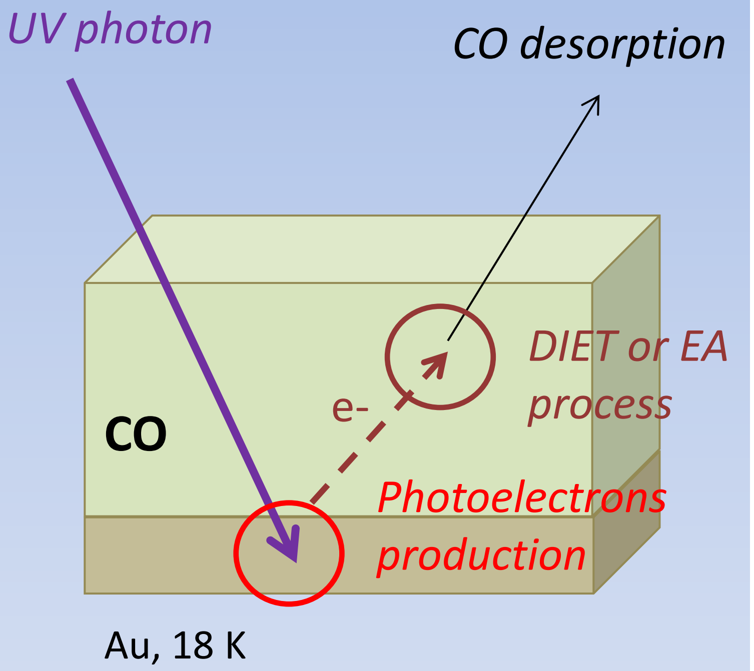
☐ Partenariat Hubert Curien « Van Gogh » - Collaboration H Linnartz & K Öberg

☐ European COST action « the chemical COSMOS »


2x10^{-9}
1x10^{-9}
5x10^{-10}
0
CO mass signal (A)
20
30
40
50
60
70
80
Temperature (K)
CO$_2$ ice after irradiation at:
7.2 eV
8.7 eV
9.8 eV
11.2 eV
1 ML CO on top of CO$_2$

CO photodesorption: mechanism

Fayolle et al., ApJ 2011



UV photon

CO desorption

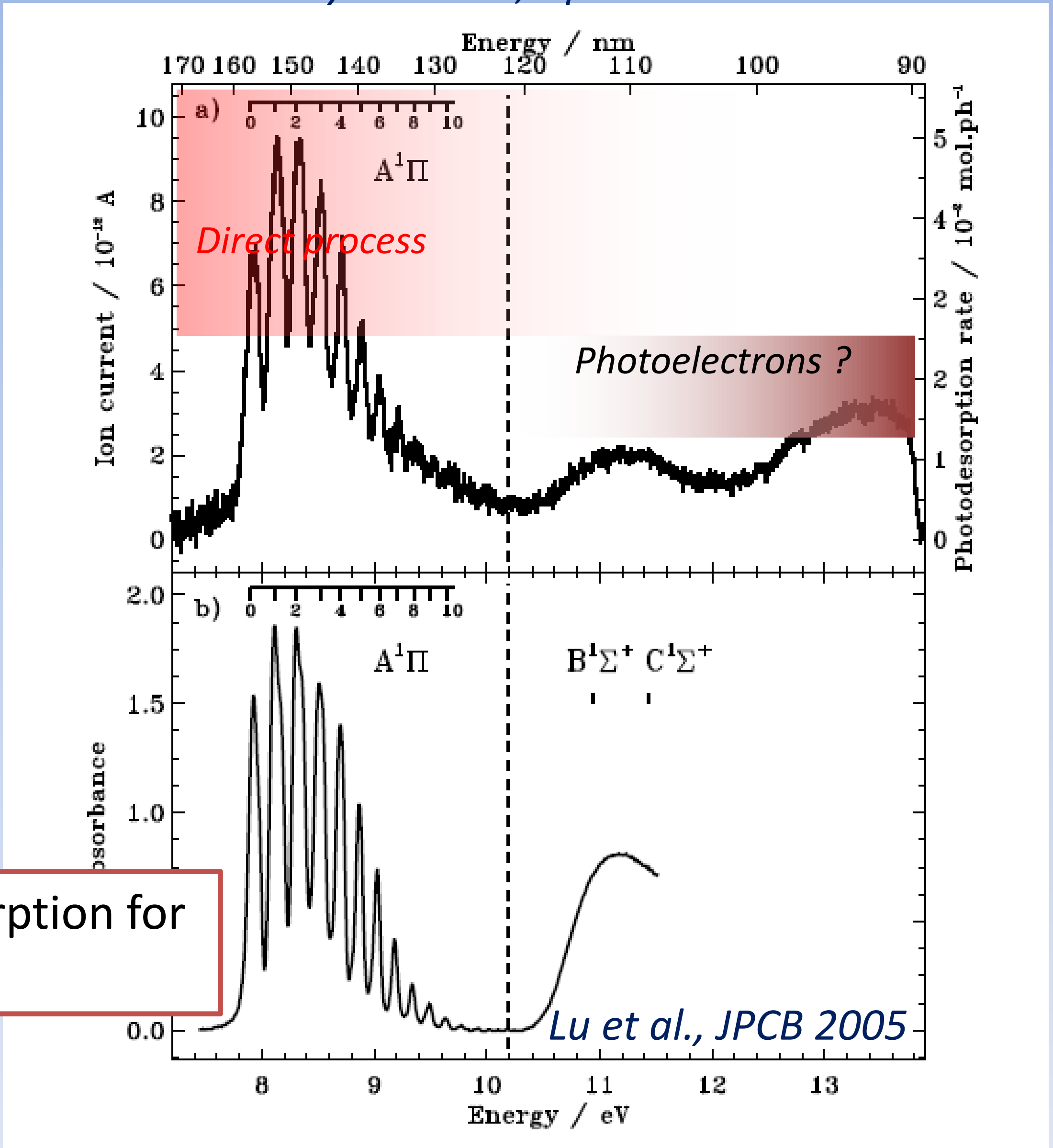
DIET or EA process

e-

CO

Photoelectrons production

Au, 18 K

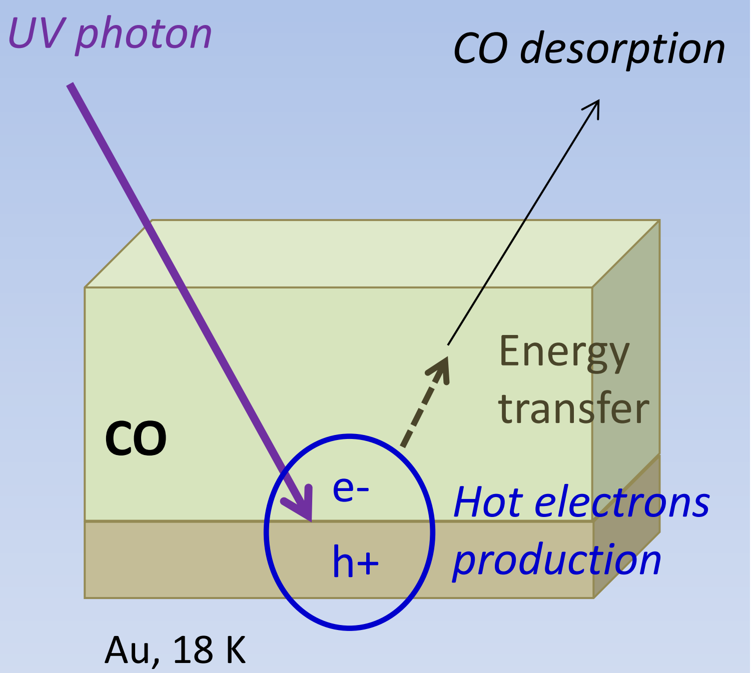


Lu et al., JPCB 2005

Photoelectrons can trigger desorption for E_{photon} > 10.5 eV

CO photodesorption: mechanism

Fayolle et al., ApJ 2011



UV photon

CO desorption

Energy transfer

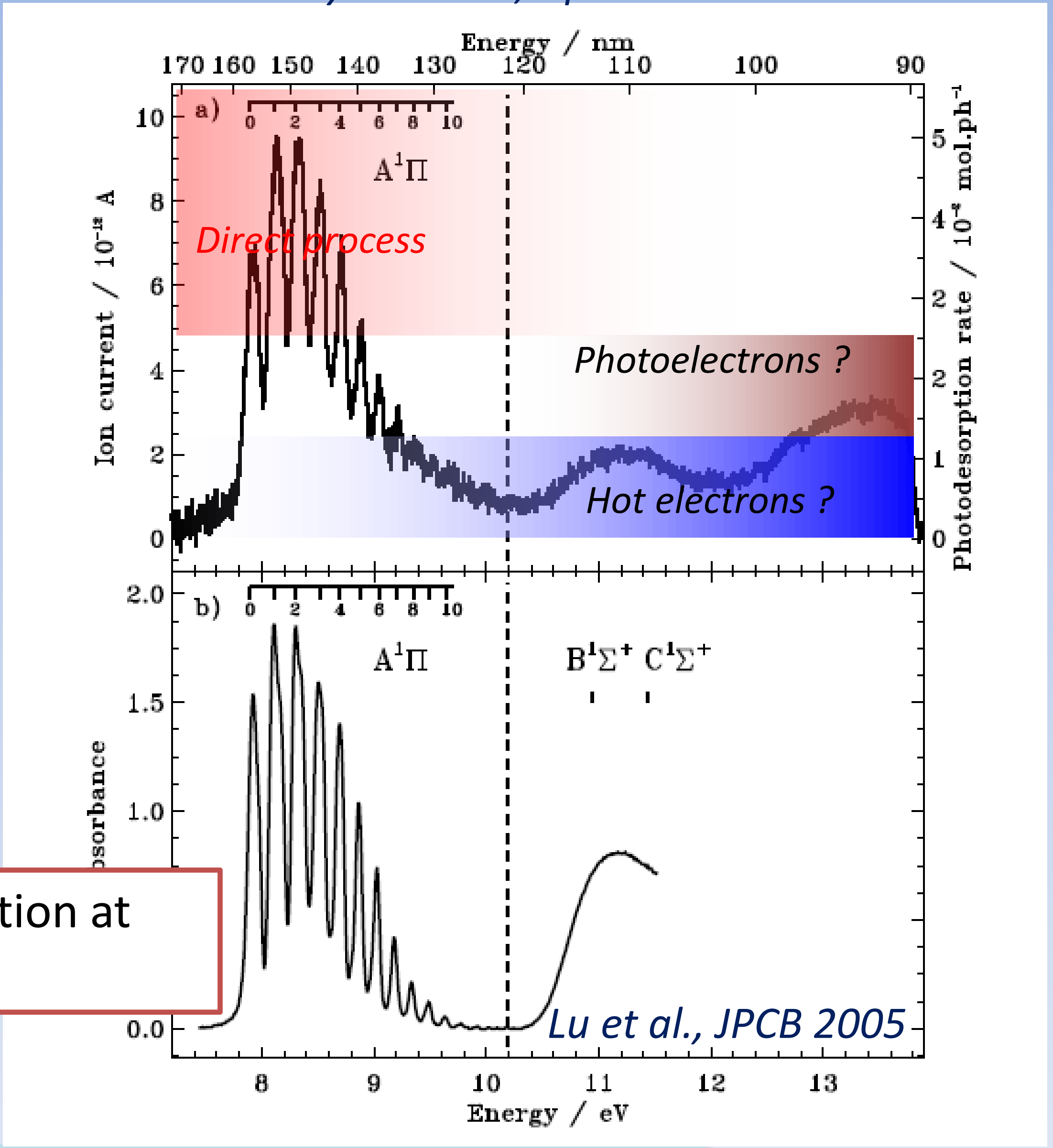
CO

e-

h+

Hot electrons production

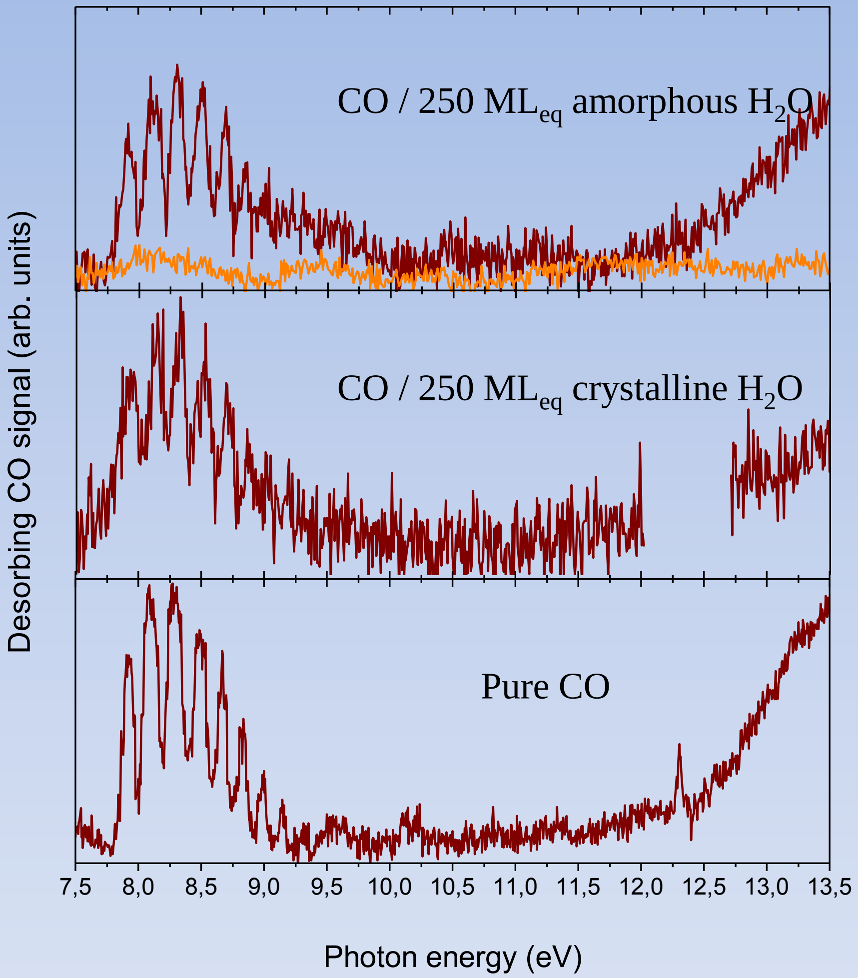
Au, 18 K



Lu et al., JPCB 2005

Hot electrons can trigger desorption at any photon energy

Photodesorption of CO on H_2O ices

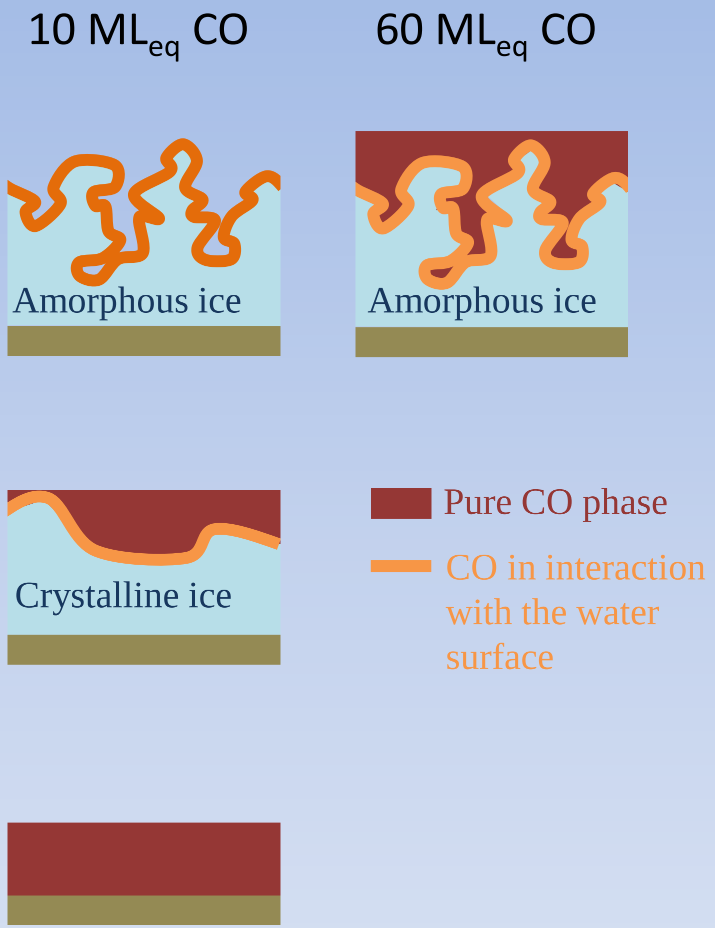


60 ML_{eq} CO / H_2O

10ML_{eq} CO / H_2O

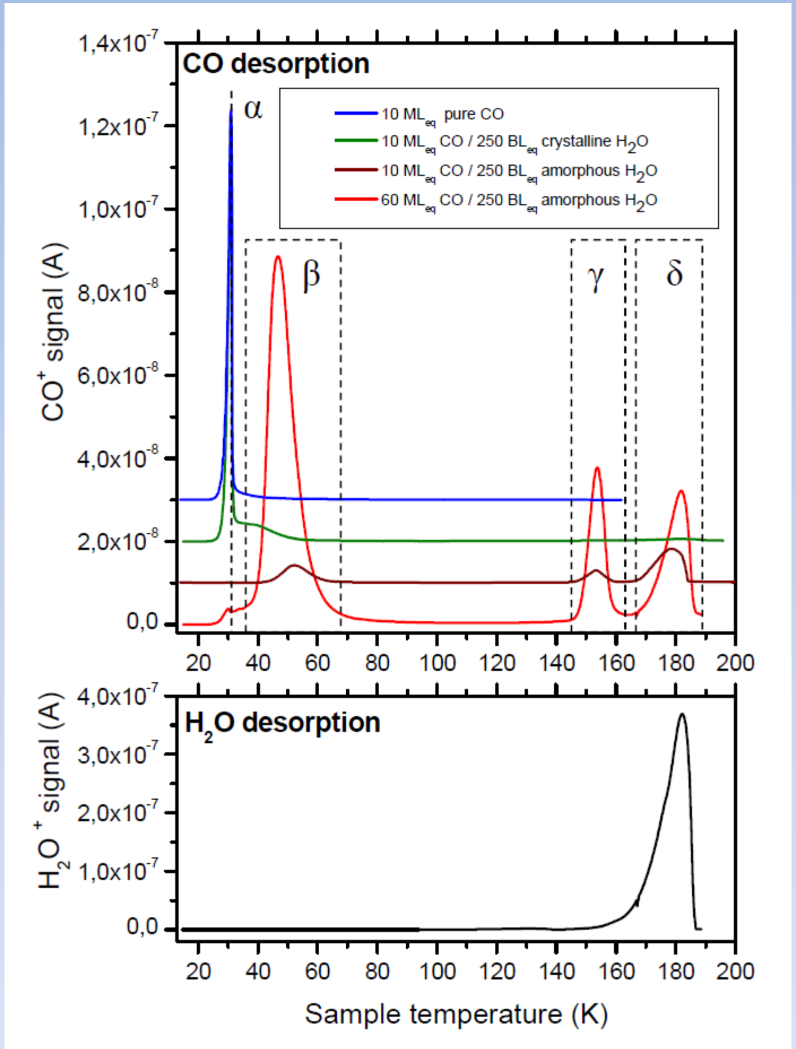
10ML_{eq} CO / H_2O

10ML_{eq} CO

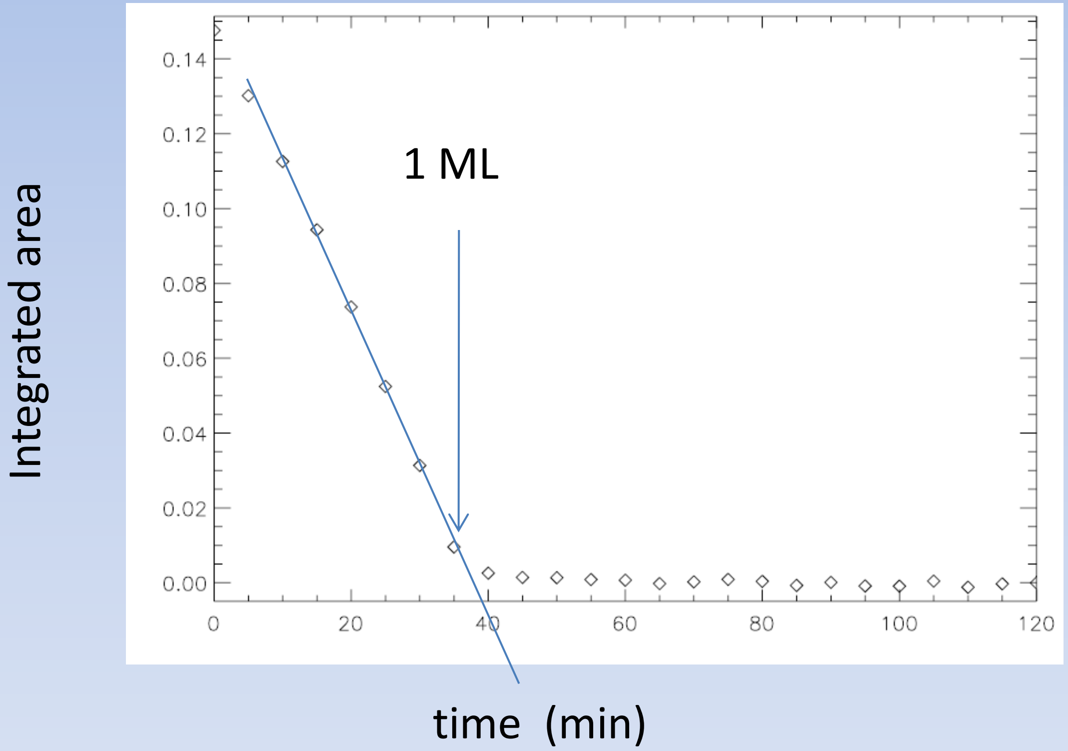


Interactions of CO-H_2O quench the photodesorption process by *at least* a factor of **15**

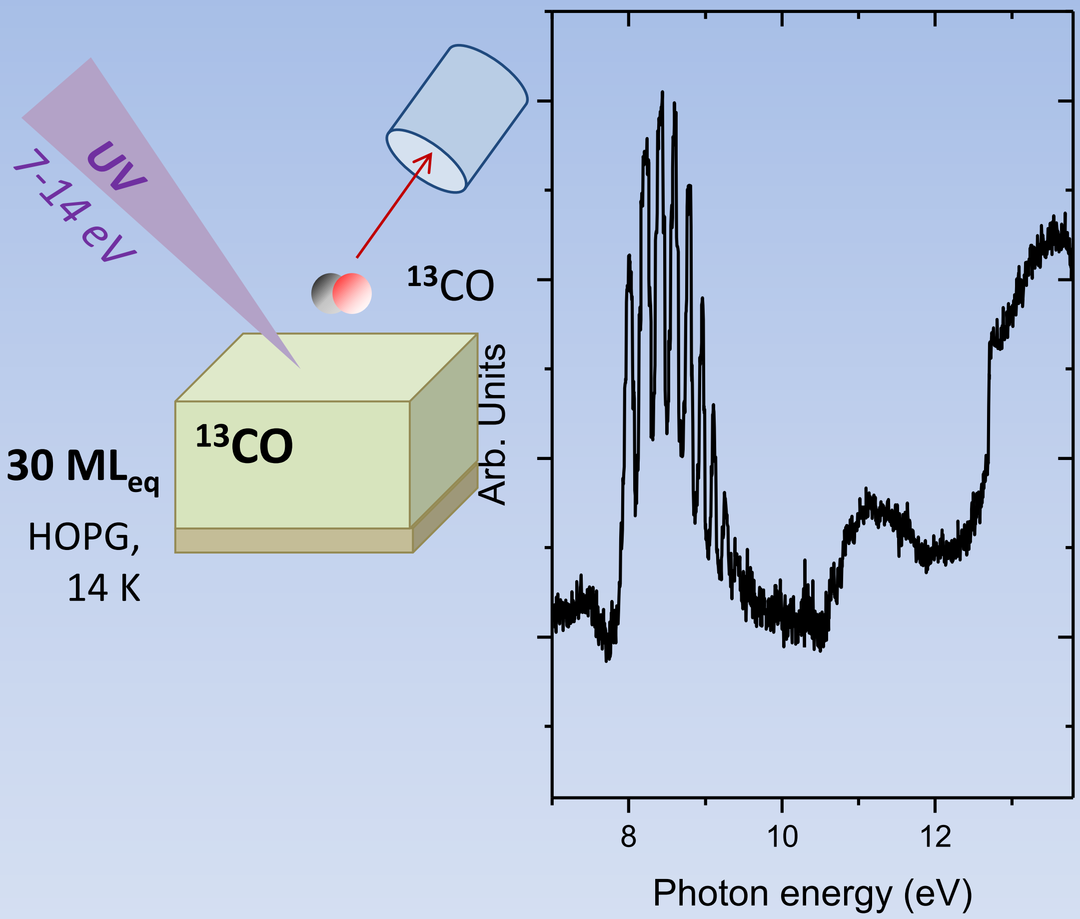
Thermal Desorption Experiments



Isothermal desorption



CO and N2 layered films



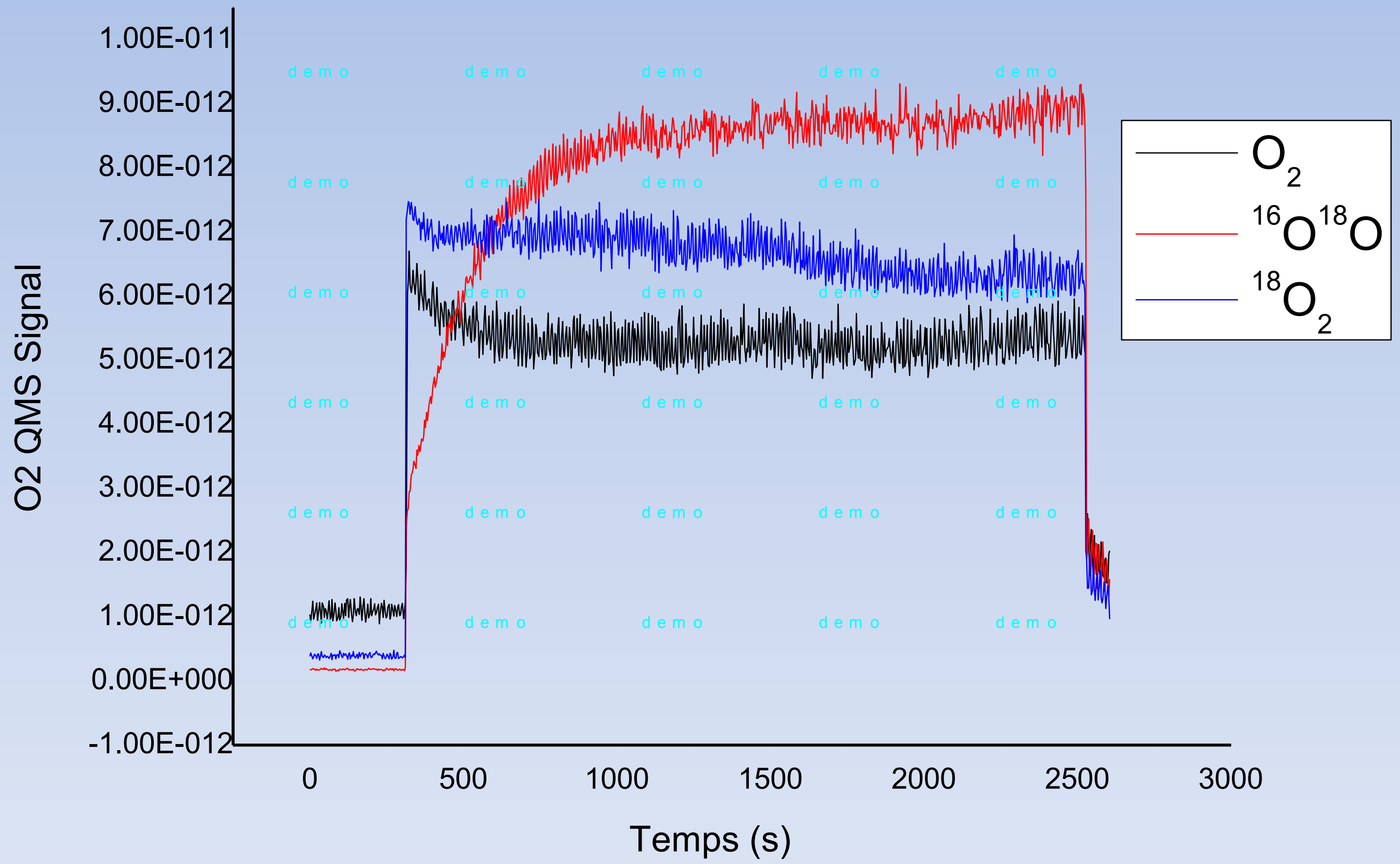
30 ML_{eq}

HOPG,
14 K

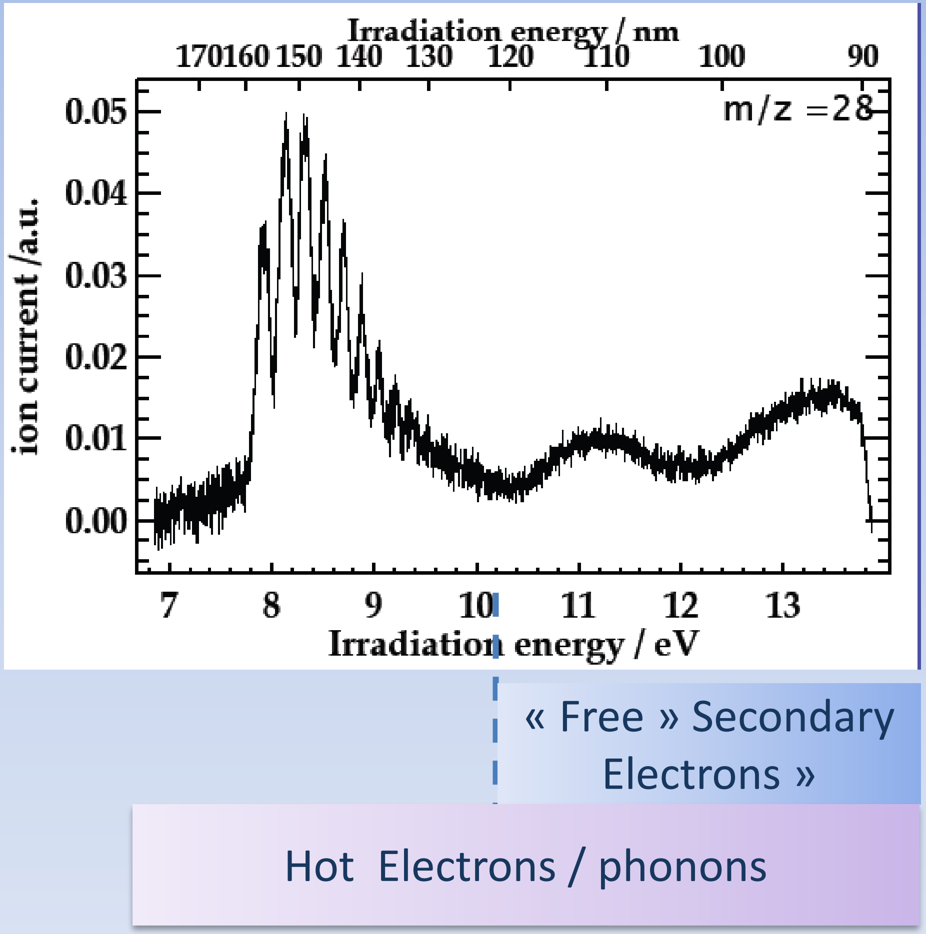
30 ML CO

Photodesorption with time

E = 9,2 eV



Results CO
Secondary processes ?



« Free » Secondary Electrons »

Hot Electrons / phonons

- Metastable / Hot electrons

  Electronic attachment
  Coupling with phonons

- « Free secondary electrons »

  collision induce desorption
  electron energy E > 5,6 eV

  Work function : Φ= 4,42 eV (gold)

Threshold Photon Energy
E ≥10 eV

H_2O Photodesorption

INDIRECT PROCESS

$H_2O \longrightarrow OH + H$

Experiments

Yabushita 2008 (Laser)
Hama 2009,2010 (Laser)

Westley 1995
Öberg 2009

Molecular Dynamics Simulations

Andersson 2005, 2006, 2008
Arasa 2010

H_2O PhotoDesorption

- recombination

$OH + H \longrightarrow H_2O$

- H Kick off H_2O

Total PhotoDesorption

H atoms	$2\ 10^{-2}$ /photon
OH	$3\ 10^{-4}$ /photon
H_2O	$1{,}4\ 10^{-4}$ /photon

Weak Temperature dependence

Photodesorption : H_2O

20 ML ASW H_2O ice on HOPG at 15 K and 100 K