Photon-Stimulated Desorption from Cold Molecular Films with Synchrotron Radiation

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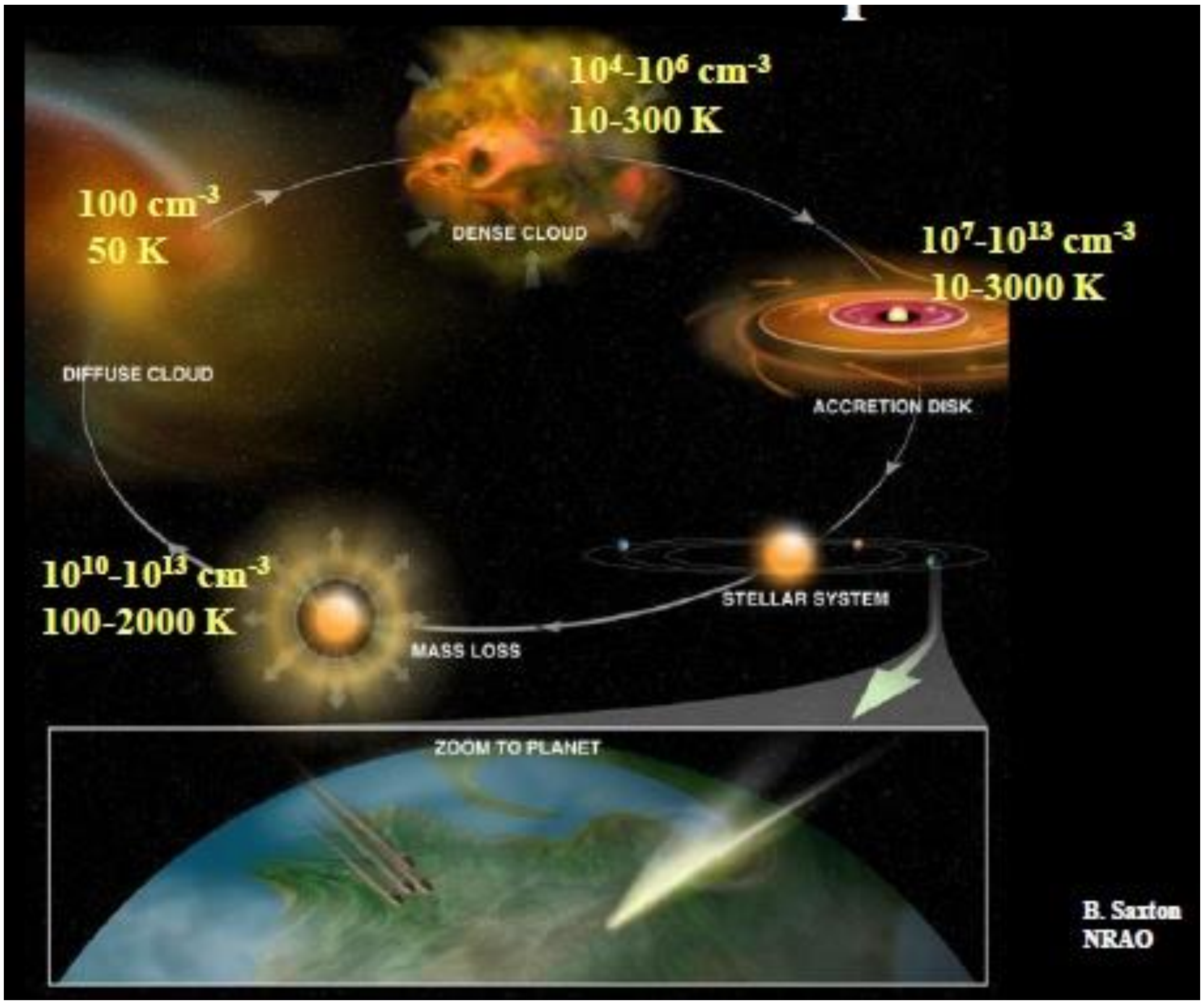
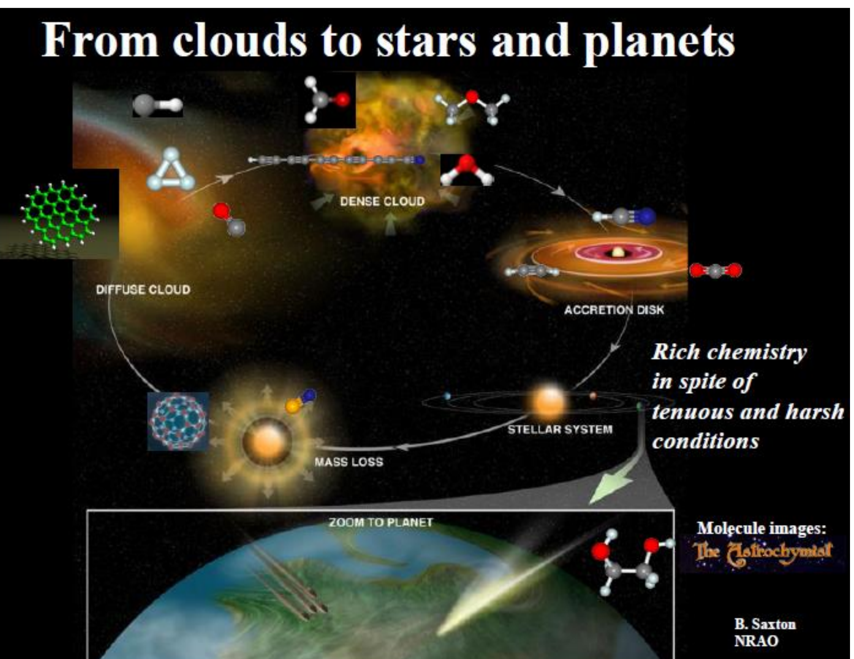
INFN, Frascati 2017

The life Cycle of Interstellar Matter



Molecular Astrophysics

multidiciplanary approach



- Instrumentation for ground-based and space observatories (Herschel, JUICE)

  Observations across the electromagnetic spectrum using world-class space and ground-based facilities (Planck, Herschel, Rosetta, ALMA, NOEMA, SOFIA, VLA, VLT, HST, FUSE…)

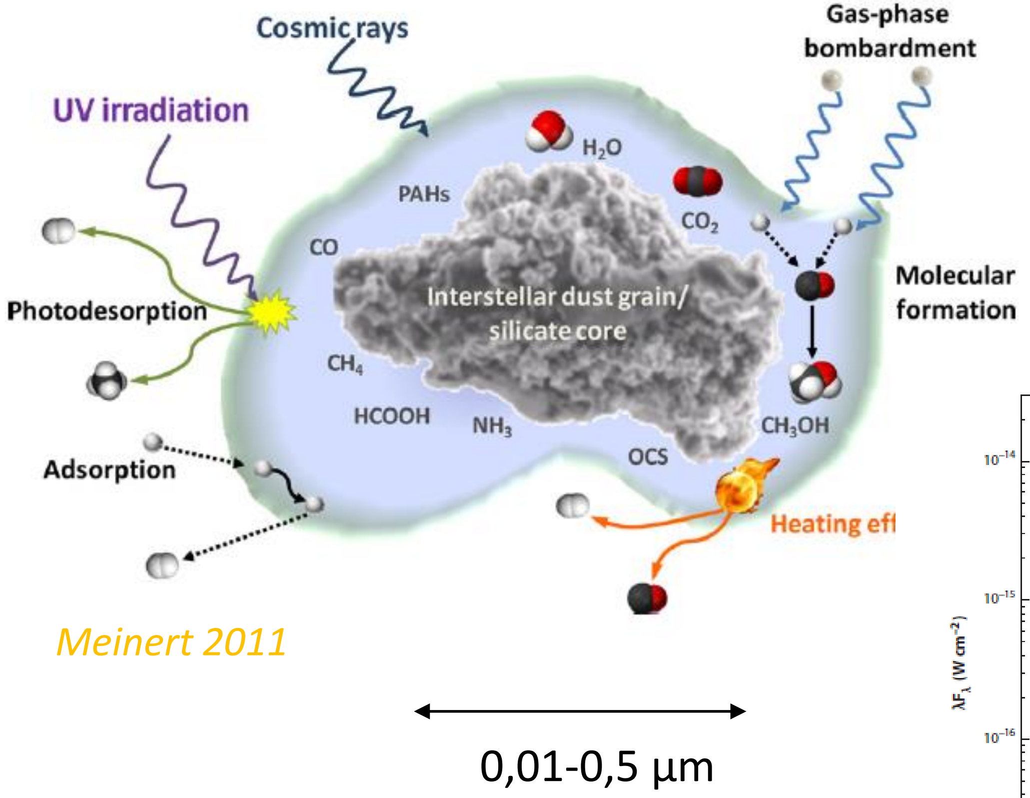
  Theoretical and numerical models of interstellar molecular clouds (PDR, XDR, shocks, turbulence...)

  Understanding of molecular processes through laboratory experiments and computations (collisional rates, chemical reaction rates, interactions between gas phase and grain surfaces…)

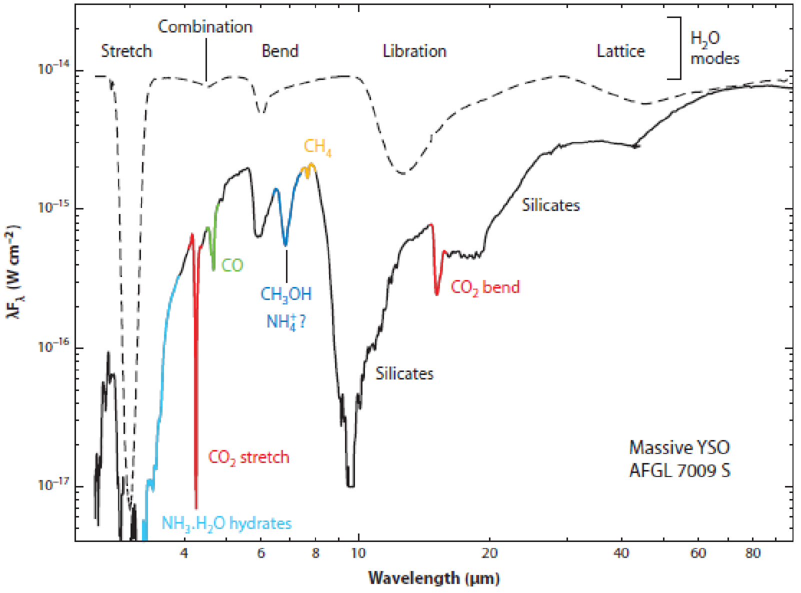
ORION MOLECULAR CLOUD

Credit: Rogelio Bernal Andreo (Deep Sky Colors).

MOLECULAR RESERVOIR IN COLD REGIONS

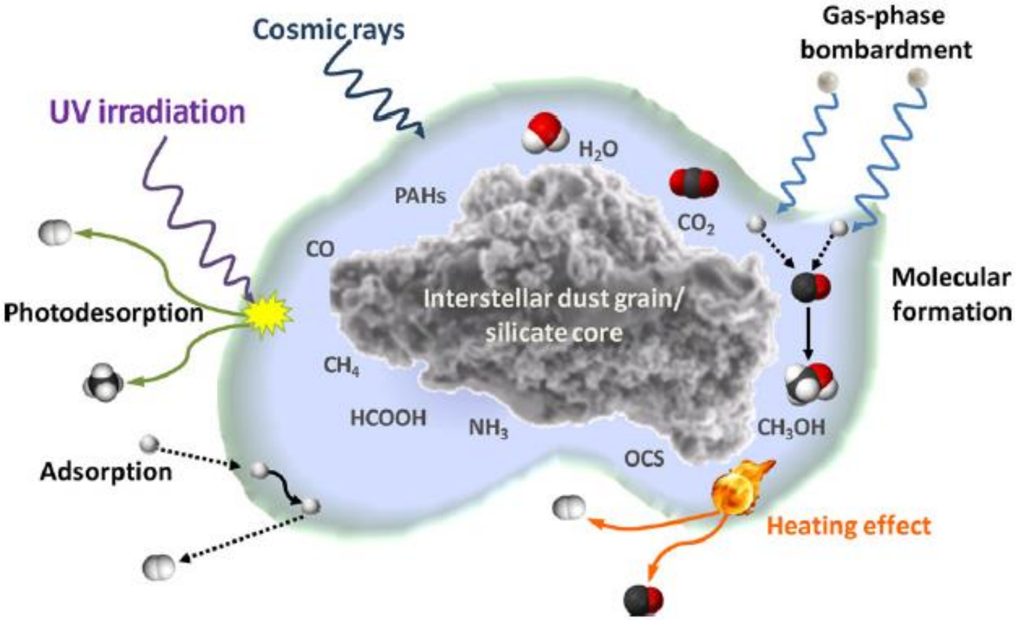


Meinert 2011



Boogert 2015

MOLECULAR RESERVOIR IN COLD REGIONS



Meinert 2011

⟷ 0,01-0,5 µm

The Ice Mantle
a molecular reservoir

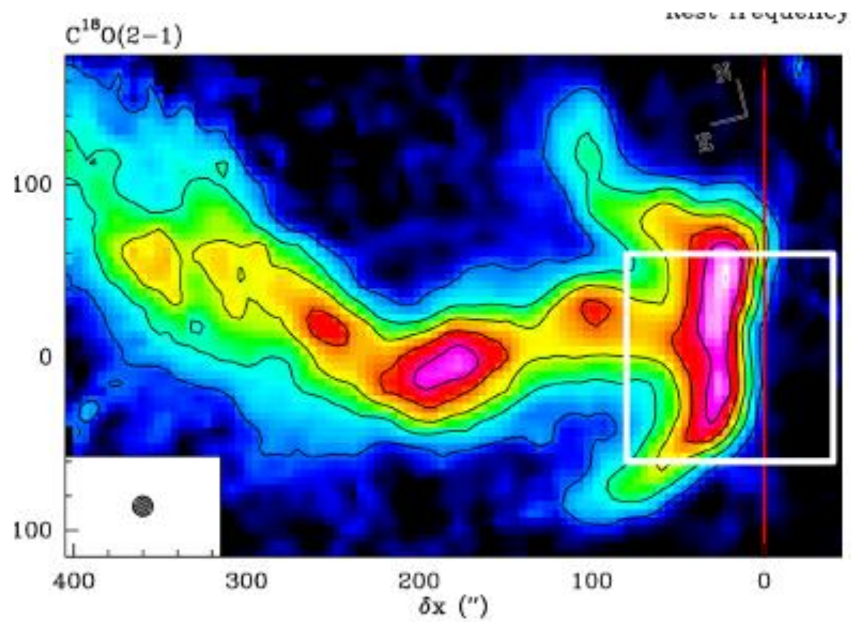
- Mainly H_2O ,
- CO, CO_2 , CH_4
- other organics

Surface chemistry

$$CO \xrightarrow{H} HCO \xrightarrow{H} H_2CO$$

$$\xrightarrow{H} H_3CO \xrightarrow{H} CH_3OH$$

Wideband High-resolution IRAM-30 Survey



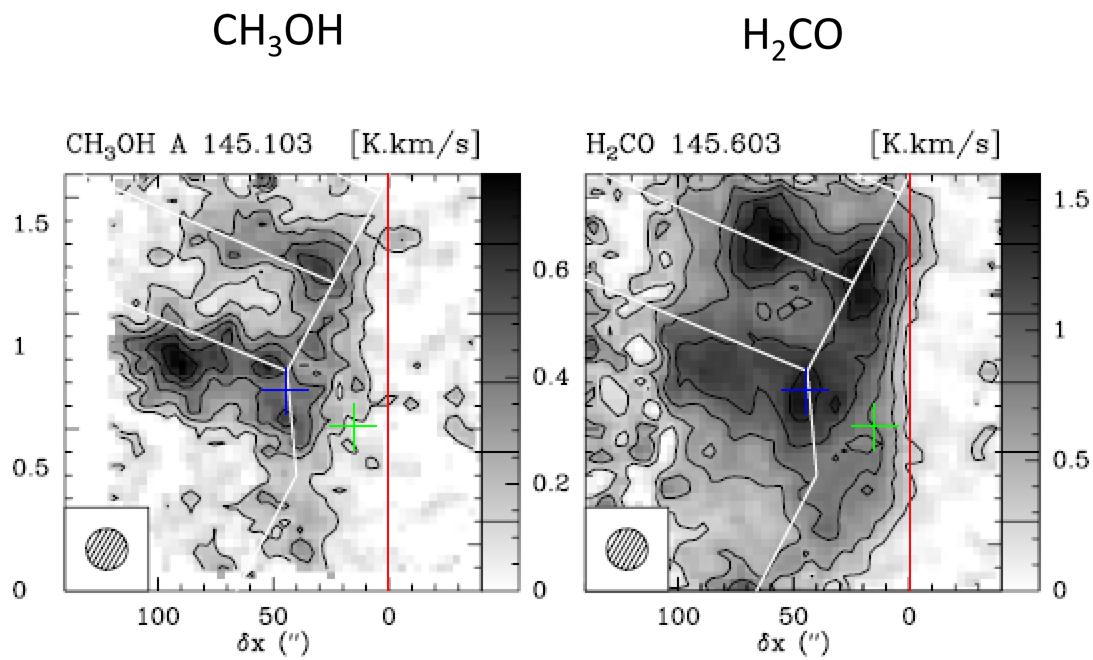
30 meter telescope, Pico Velta, SPAIN

Hily-Blant *et al.* 2005
Pety *et al.* 2005, 2007
Guzman *et al. 2011, 2013*

^{12}CO	$c-C_3H$	$HC^{17}O^+$	CH_3CCH	$HN^{13}C$	NH_2D	HDS
^{13}CO	$l-C_3H$	HOC^+	CN	$H^{15}NC$	N_2D^+	H_2CS
$C^{17}O$	$c-C_3H_2$	H_2CO	^{13}CN	CH_3CN	CS	SO
$C^{18}O$	$l-C_3H_2$	$H_2{}^{13}CO$	$C^{15}N$	CH_3NC	^{13}CS	SO_2
$^{13}C^{18}O$	C_3HD	CH_3OH	HCN	HC_3N	$C^{33}S$	^{34}SO
C_2H	HCO	CH_2CO	HNC	CCO	$C^{34}S$	SO^+
CCD	DCO^+	CH_3CHO	DCN	NO	CCS	NS
^{13}CCH	HCO^+	$HDCO$	DNC	HNO	OCS	SiO
$C^{13}CH$	$H^{13}CO^+$	D_2CO	$H^{13}CN$	$HNCO$	HCS^+	CF^+
C_4H	$HC^{18}O^+$	$HCOOH$	$HC^{15}N$	N_2H^+	$HDCS$	

H_2CO and CH_3OH observed in the Horsehead PDR

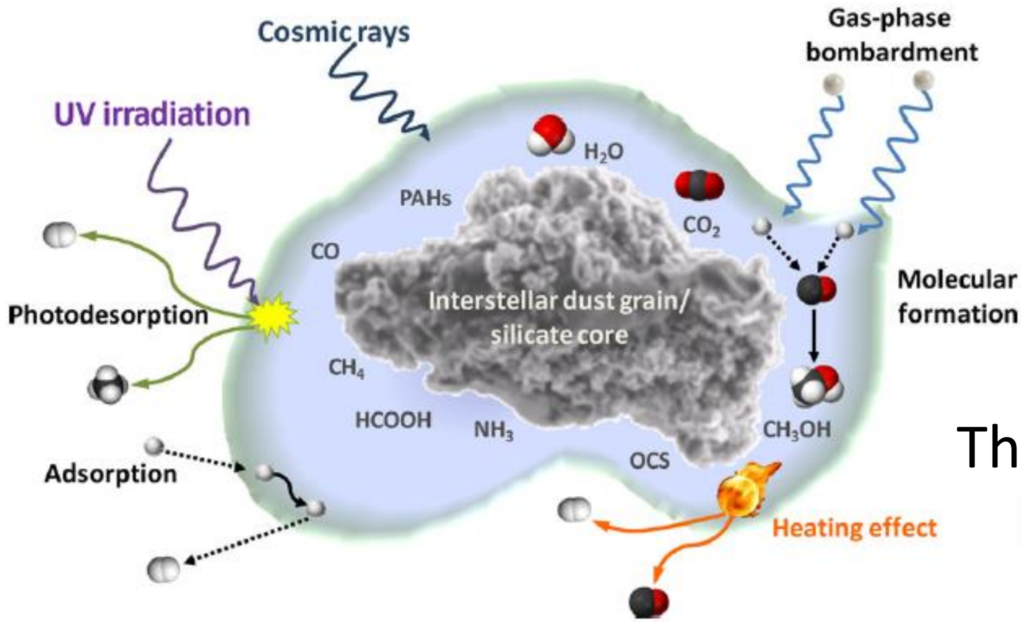
Hily-Blant *et al.* 2005
Pety *et al.* 2005, 2007
Guzman *et al.* 2011, 2013



- At PDR position, non-thermal is needed to explain H2CO and CH3OH abundances

- At the dense core position , on the other hand, non-thermal of ices is needed to explain the observed abundance of CH_3OH, while a pure gas-phase model can reproduce the observed H_2CO abundance.

SOLID-GAS INTERACTIONS



Meinert 2011

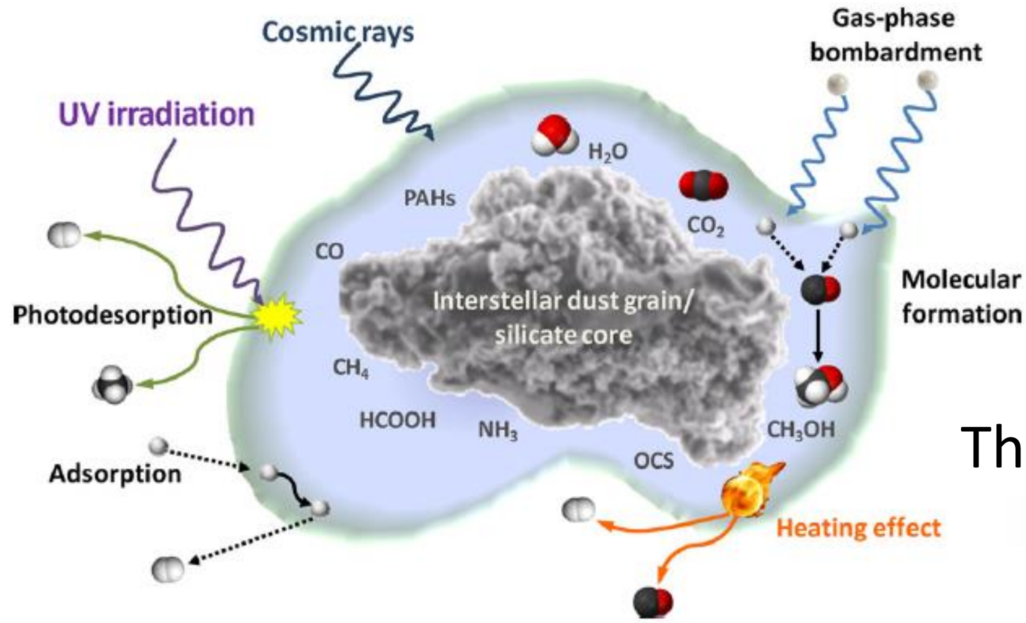
Thermal desorption

GAS

0,01-0,5 µm

ICE MANTLE

- a molecular reservoir
- Mainly H_2O ,
- CO, CO_2 , CH_3OH
- other organics



Meinert 2011

0,01-0,5 µm

Thermal desorption

In cold regions

Non-thermal desorption

- Cosmic Rays sputtering
- Heterogeneous Chemistry
- Sputtering in shocks
- UV and X-ray photodesorption

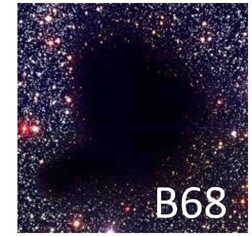
ICE MANTLE

- a molecular reservoir
- Mainly H_2O ,
- CO, CO_2 , CH_3OH
- other organics

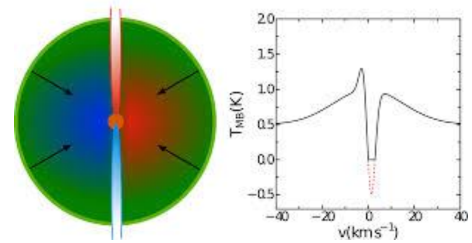
UV-X Photodesorption in the universe

Inner and outer regions of molecular clouds (Hollenbach 2009)

Prestellar cores (Caselli 2012)
cosmic-ray-induced FUV field



Outer parts of protostellar enveloppes (Mottram 2012)



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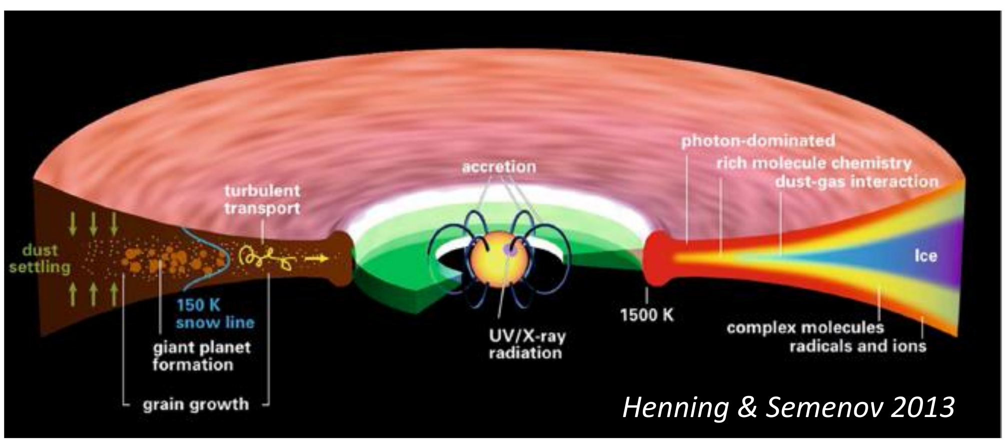
Protoplanetary disks (Dominik 2005, Bergin 2014



UV and X-ray photons

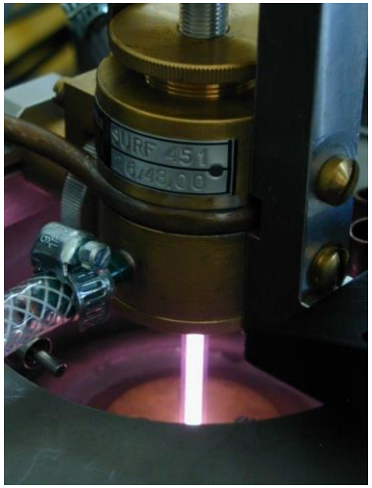
Atmospheres of Icy satellites in the outer solar system

UV Photons : H Ly-α

Credit :Nasa/Johns Hopkins University

UV-Photodesorption in the Laboratory

Microwave-Discharge Hydrogen-Flow Lamp **(Lyα)**



Westley 1995, Öberg 2007, 2009a, 2009b,,
Bahr & Baragiola 2012, Yan & Yates 2013
Muñoz Caro 2010, 2014, 2015, 2016a, 2016b

(Lyα) 10.2 eV + broad band
Absolute Yields

Pulsed-laser induced desorption

Yabushita 2007, 2008a, 2008b, 2008c, 2009
Hama 2010, 2011, 2016

(193 nm) 6.42 eV
(157 nm)7.89 eV

mechanisms

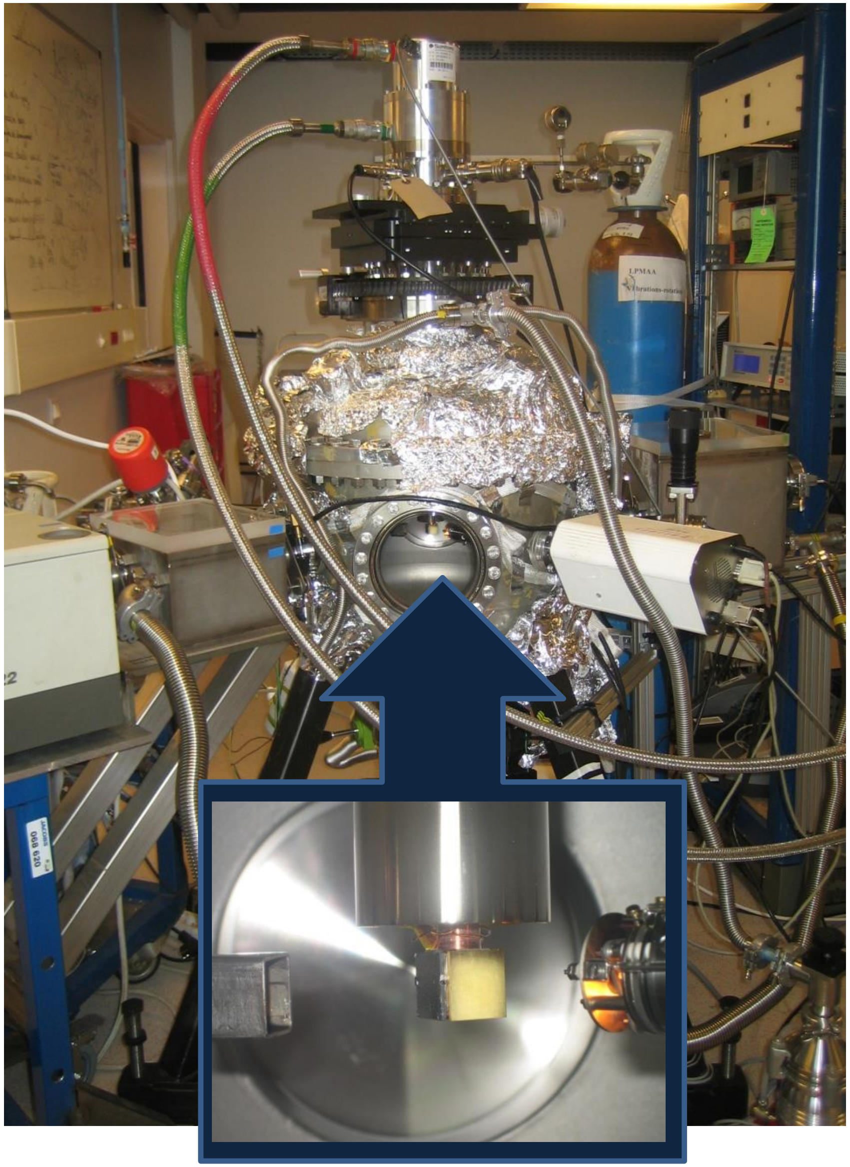
Synchrotron radiation

Fayolle , Bertin, Fillion et al.
2011,2012,2013,2014, 2016

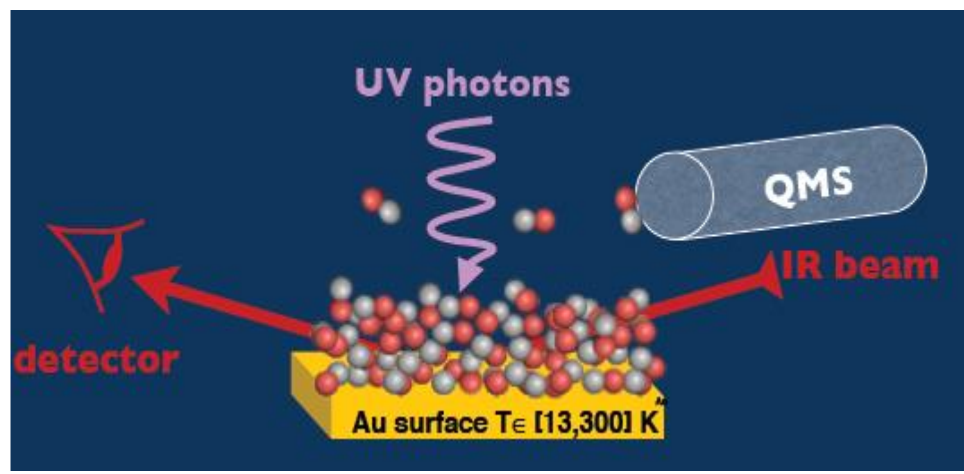
Monchromatic excitation 7-20 eV

Differential absolute Yields + mechanisms

« SPICES » set-up : Surface Processes and ICES



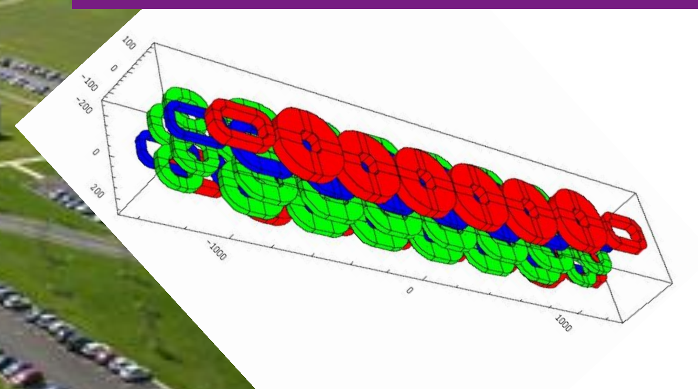
- ❑ UHV - 8-200 K
- ❑ Gas Phase
  Mass spectrometry
- ❑ Surface
  Reflexion Absorption Infrared Spectroscopy



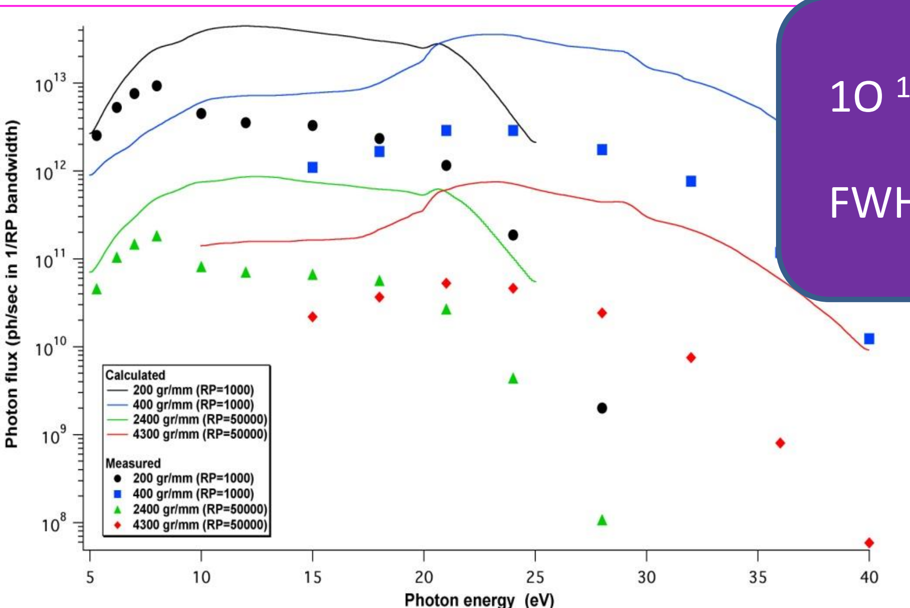
DESIRS BEAMLINE

Fully tailored polarization

Undulator : 4.5 – 40 eV



« SPICES » @ SOLEIL (DESIRS beamline)



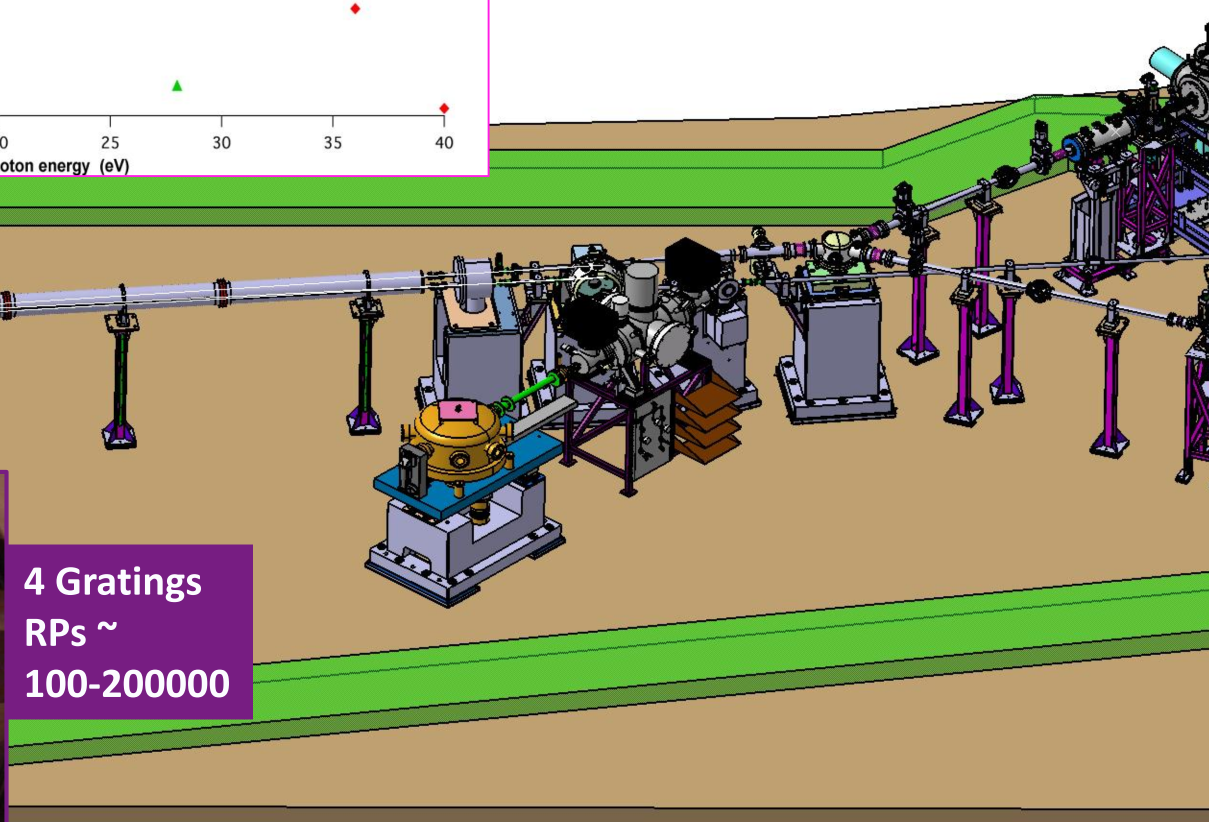
$10^{12\text{-}13}$ photons/s

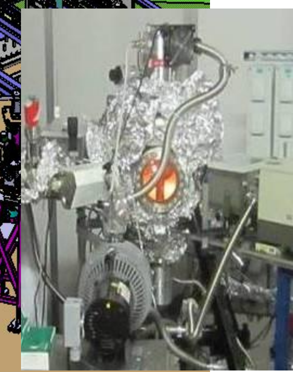
FWHM : 20-40 meV

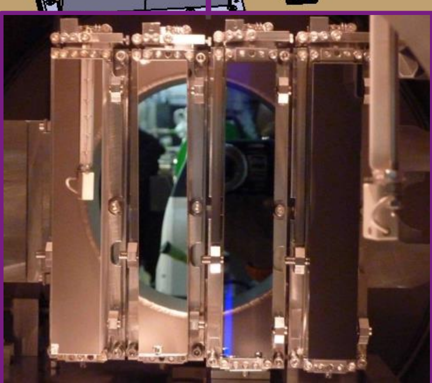
Mass spectrometer

QMS = f(E)

Photon- Stimulated Desorption (PSD) « spectra »

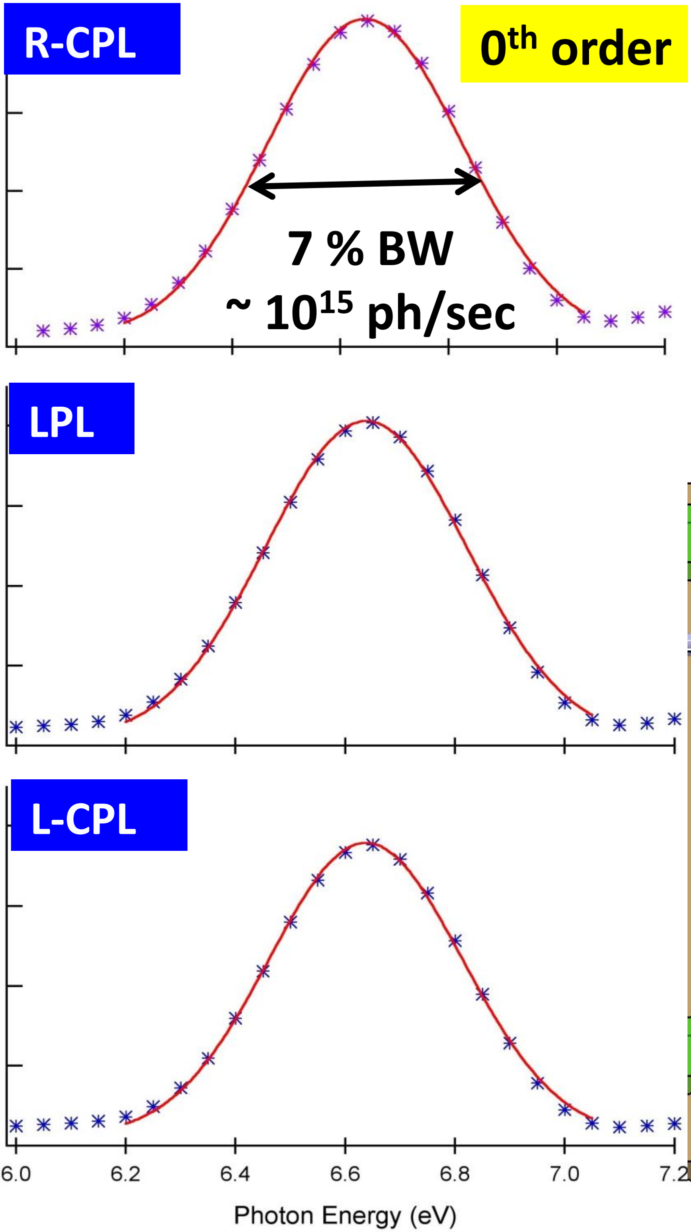




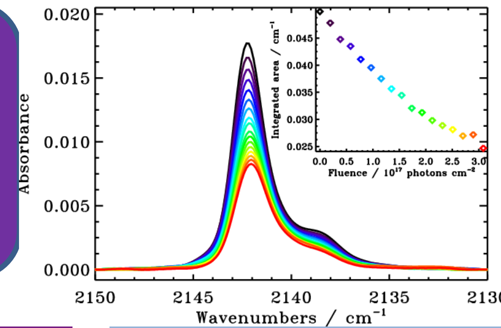


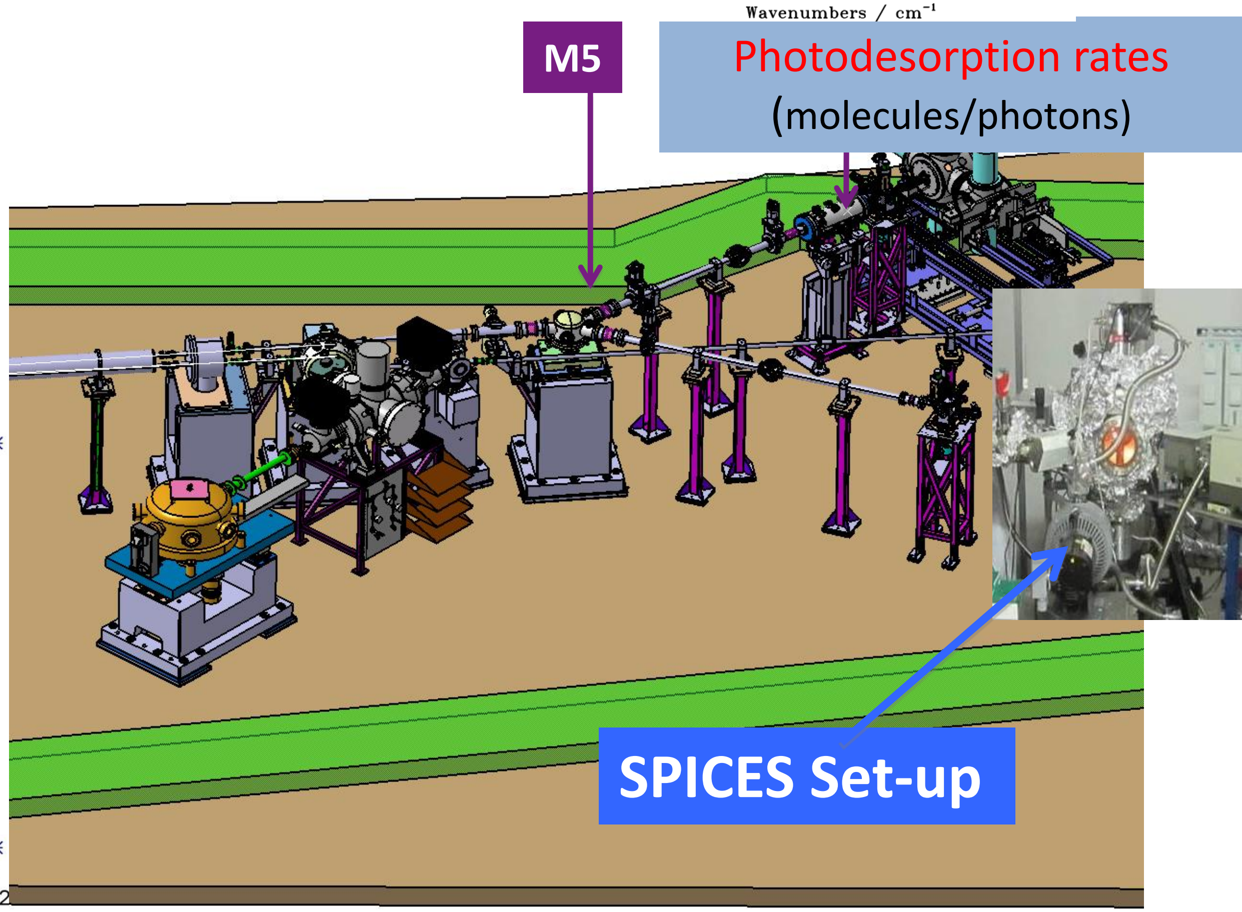
4 Gratings
RPs ~ 100-200000

« SPICES » @ SOLEIL (DESIRS beamline)

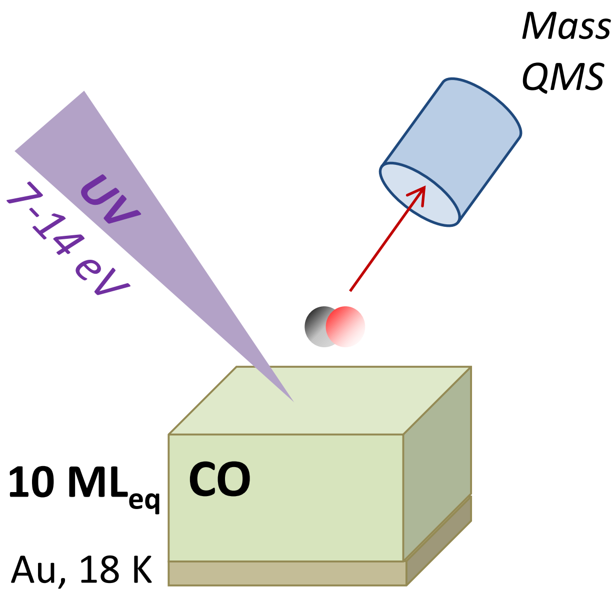


10 ^{15} photons/s
@ E between 5-40 eV
FWHM : 1 eV

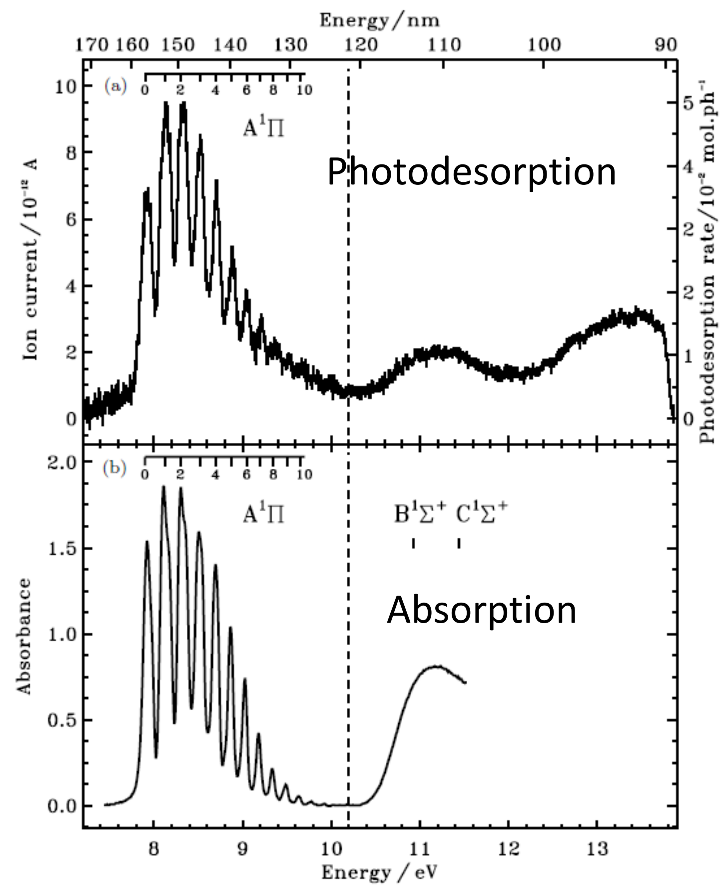




PHOTON STIMULATED DESORPTION of PURE CO ICES



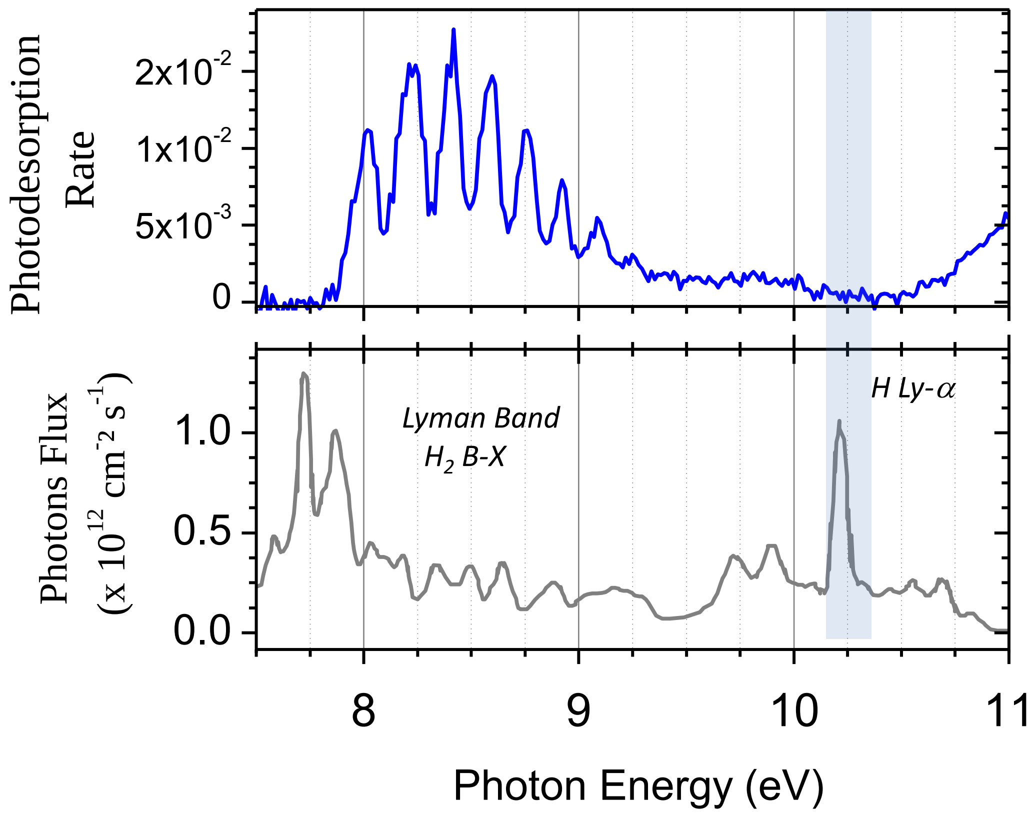
A$^1\Pi$ (v') ← X$^1\Sigma^+$(v=0)



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

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

Importance of Energy dependent Study



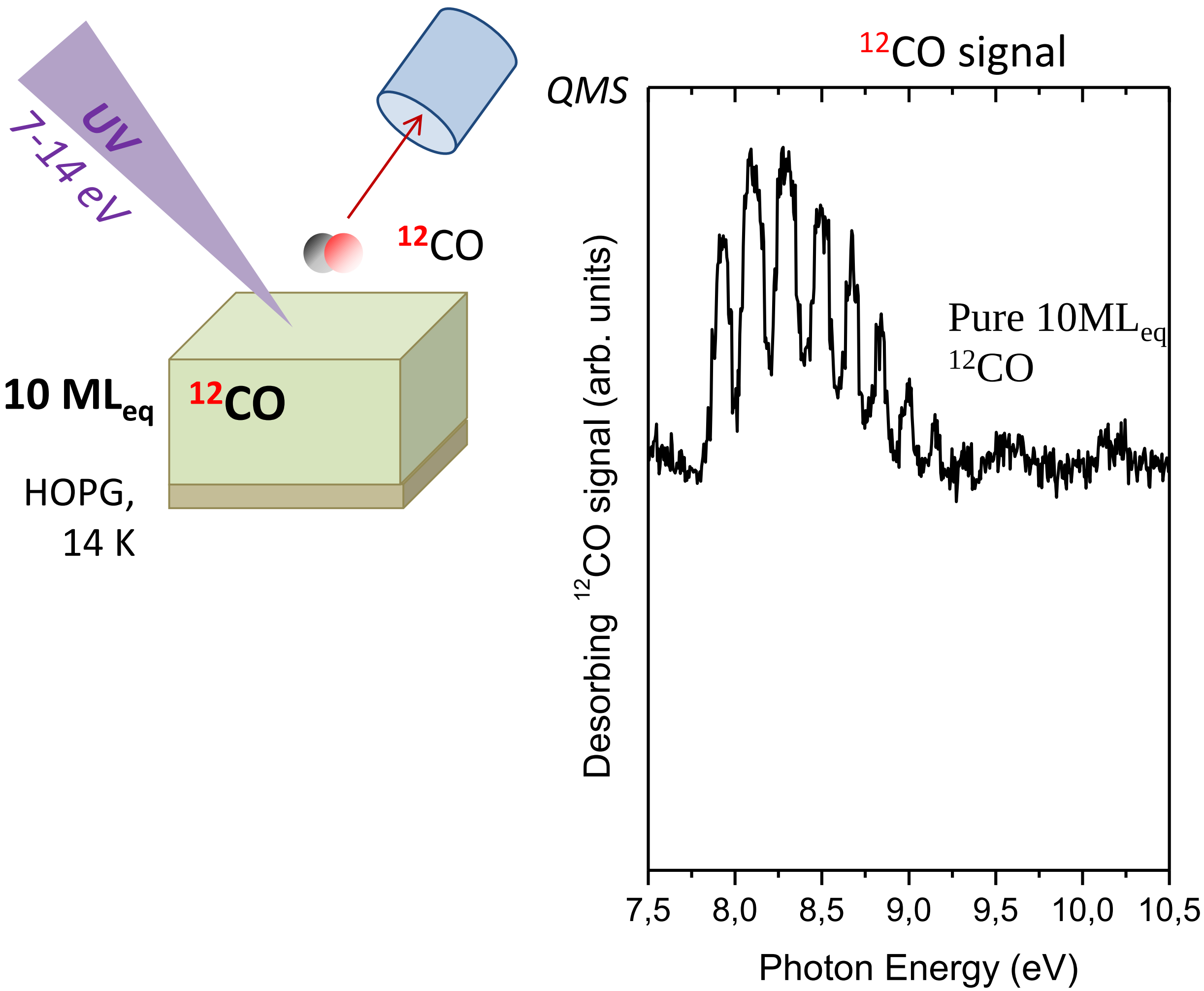
SOLEIL

Discharge Lamp Spectrum*

* From Munoz Caro

CO photodesorption: molecular mechanism

Bertin et al., Phys Chem Chem Phys 2012



CO photodesorption: molecular mechanism

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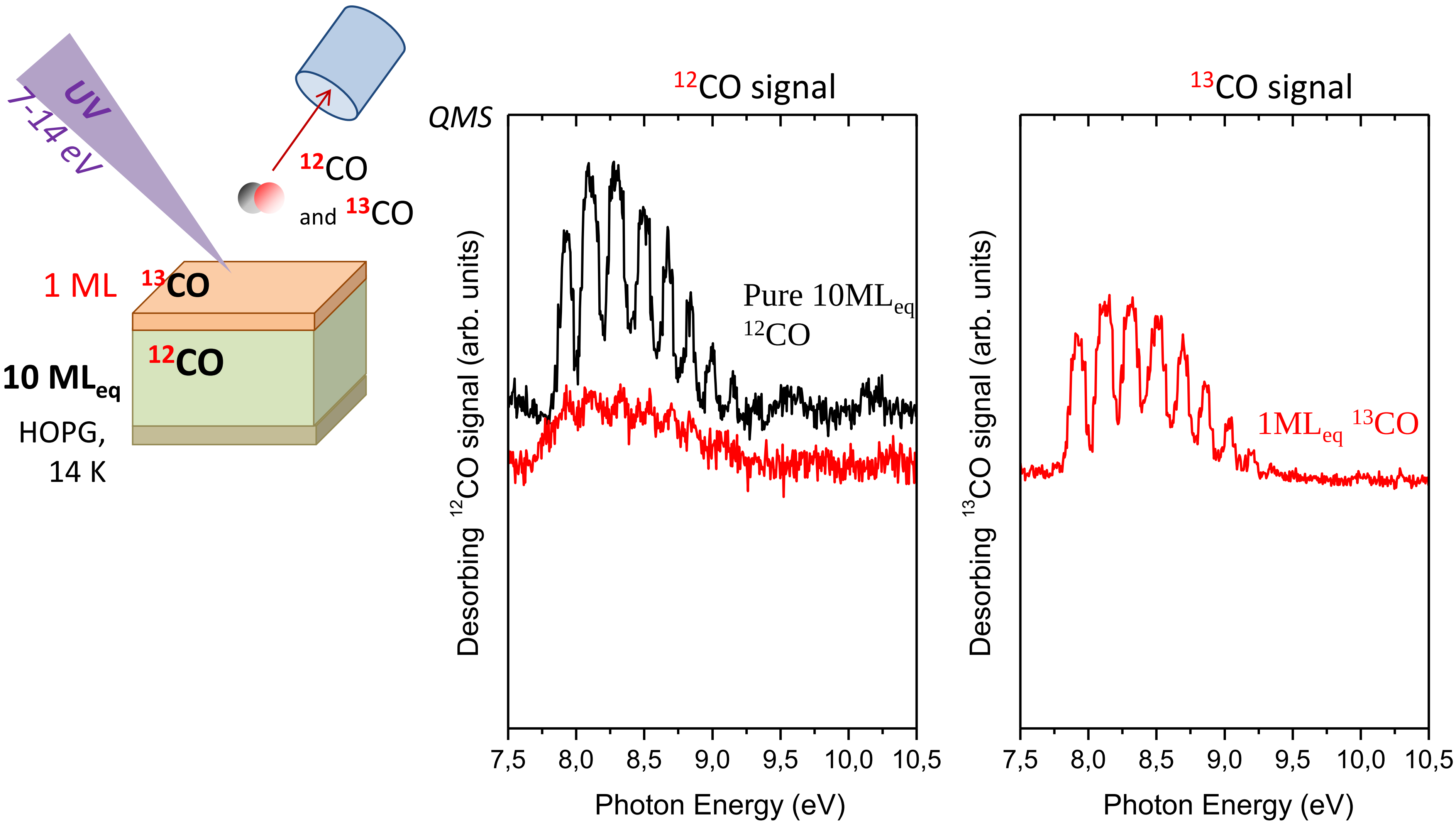
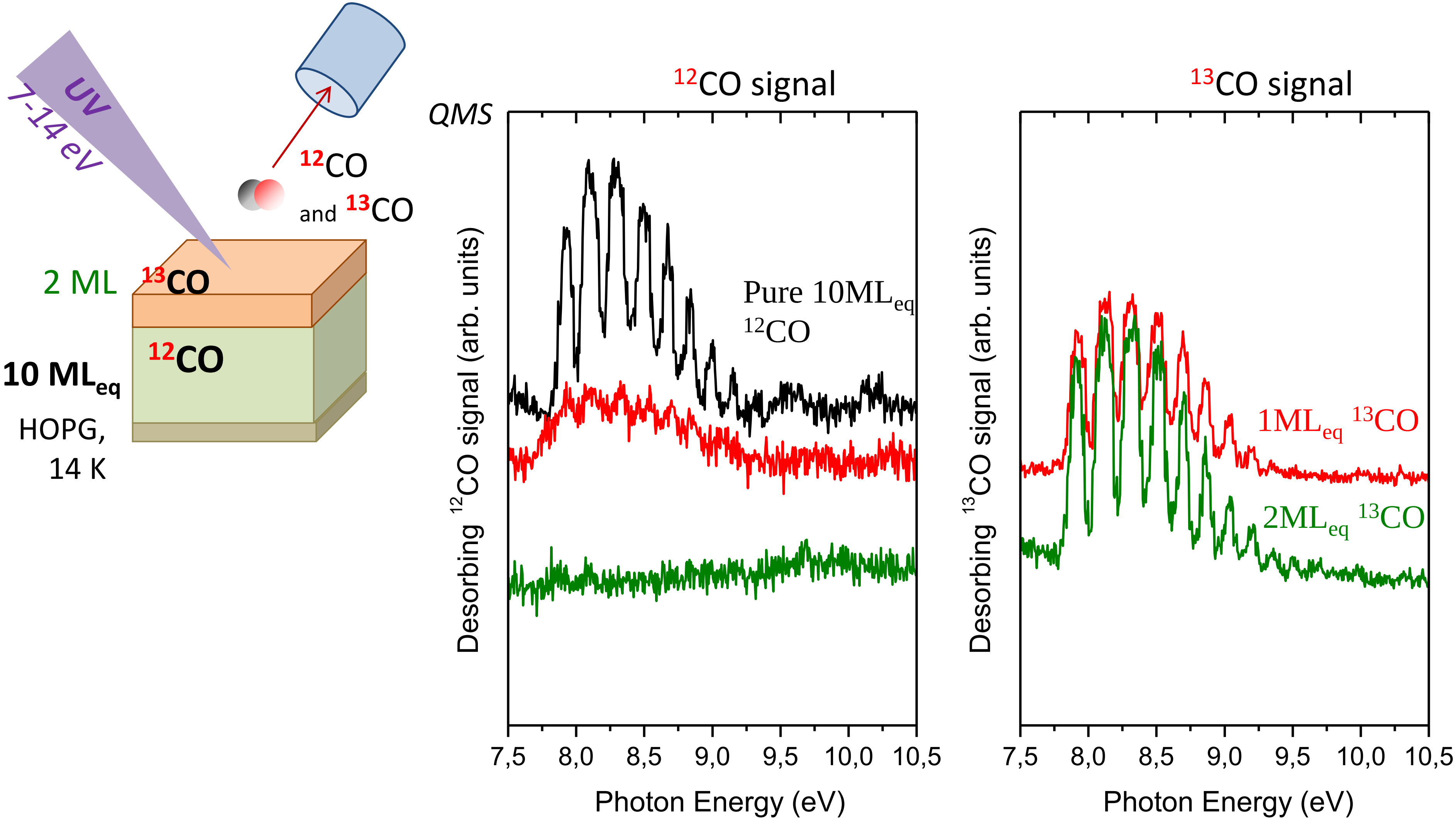


CO photodesorption: molecular mechanism

Bertin et al., Phys Chem Chem Phys 2012



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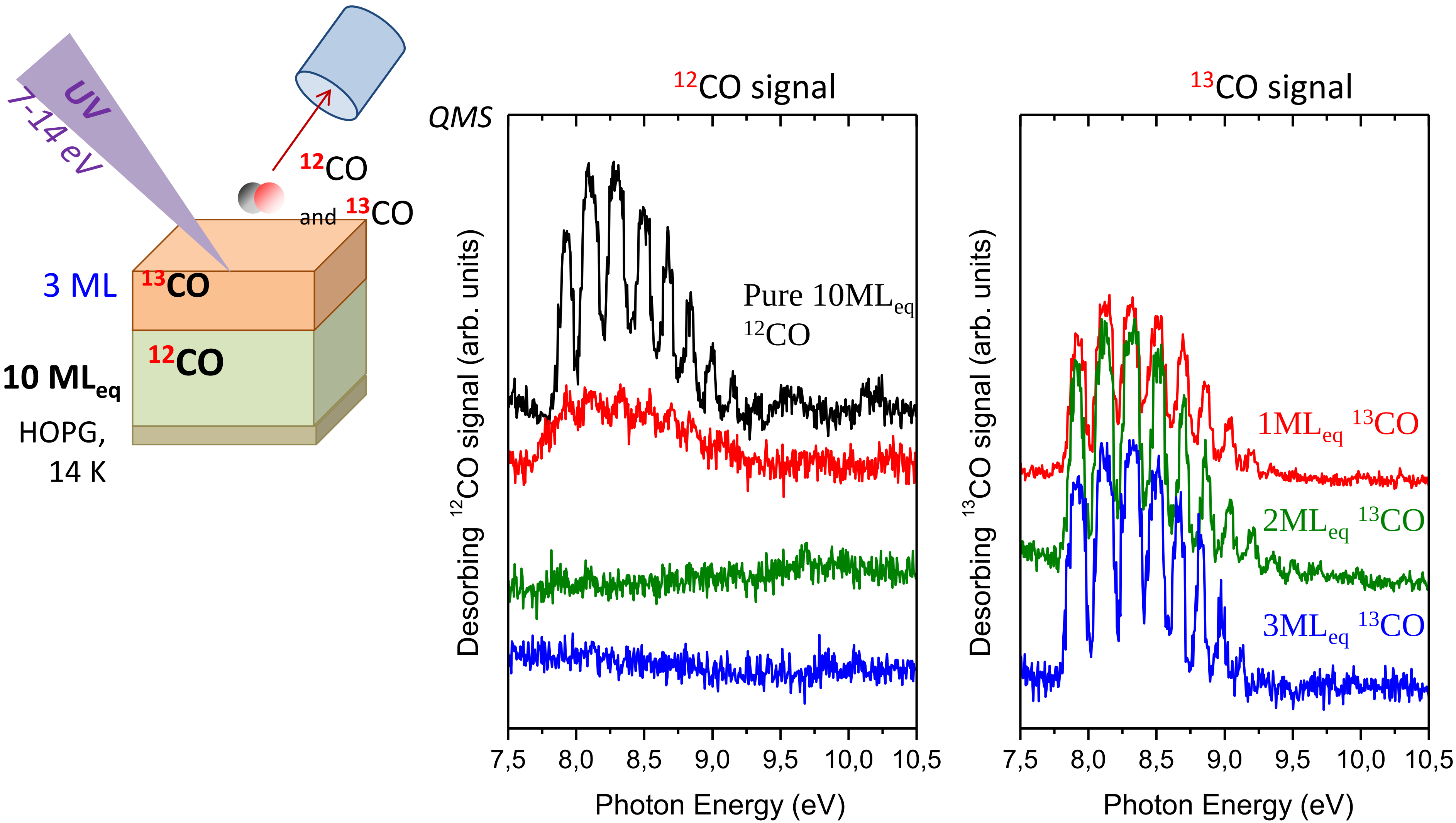
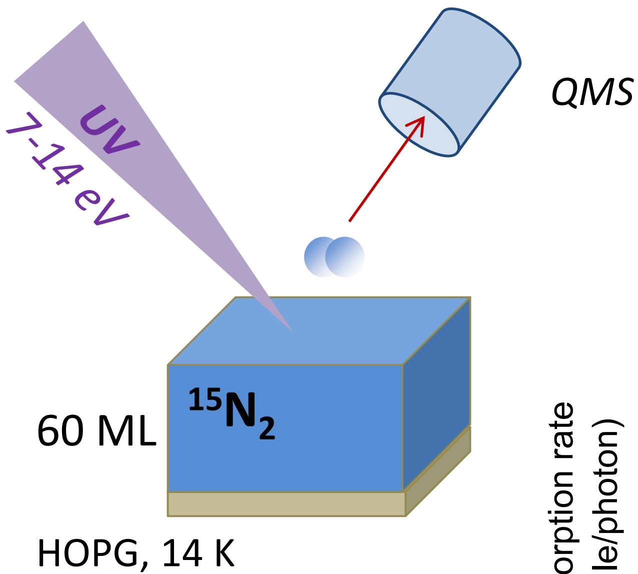
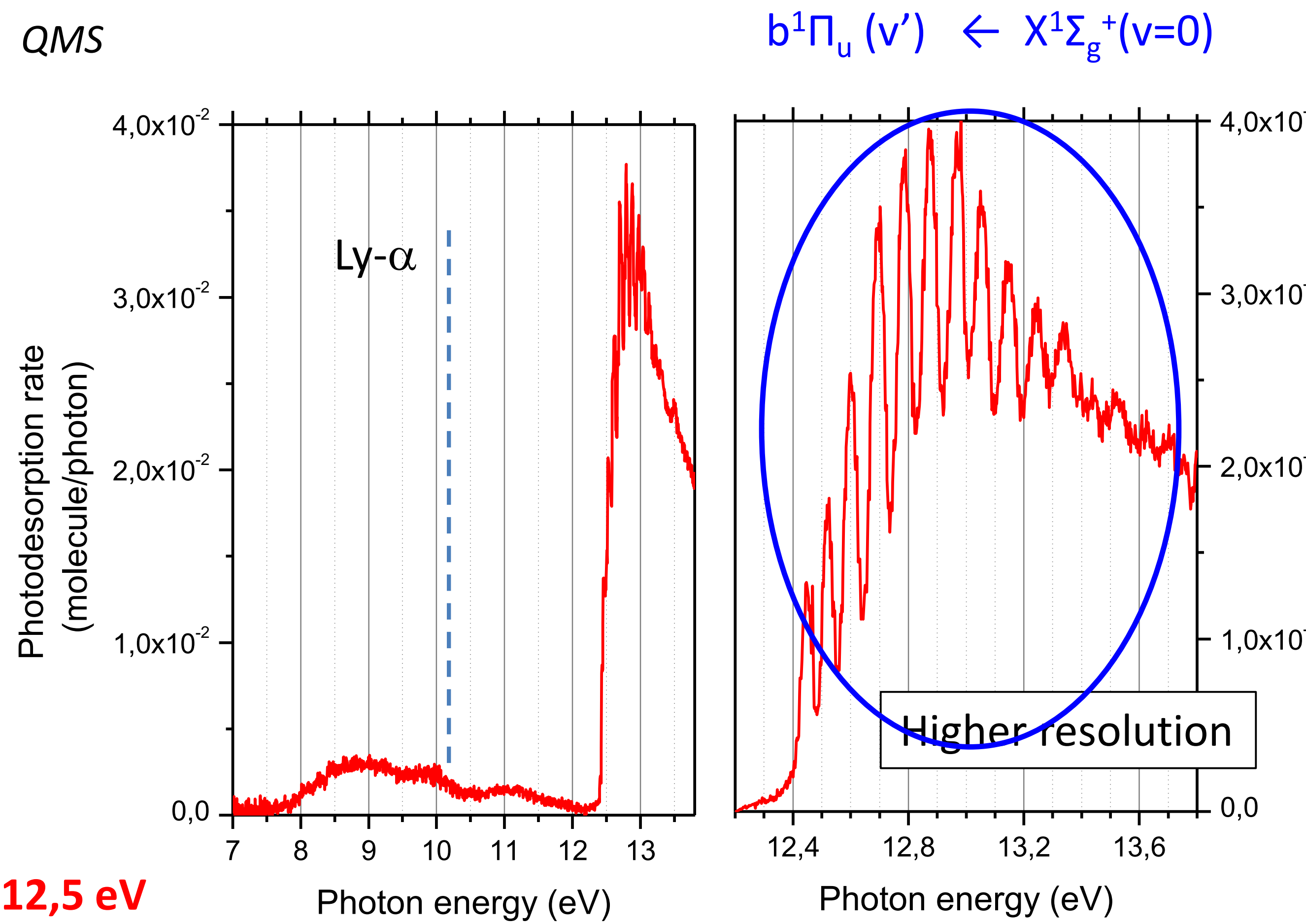


A surface process: only the topmost molecules are desorbing

Only the upper 1-2 layers are affected with photodesorption

Pure N_2 photodesorption

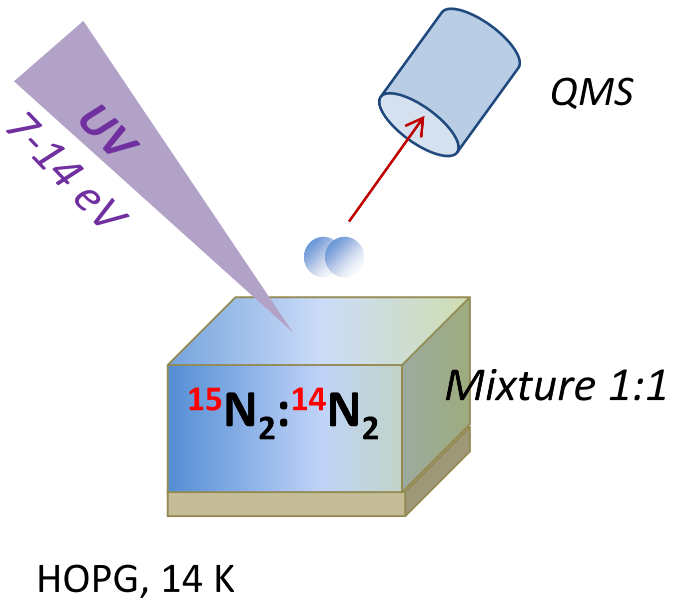


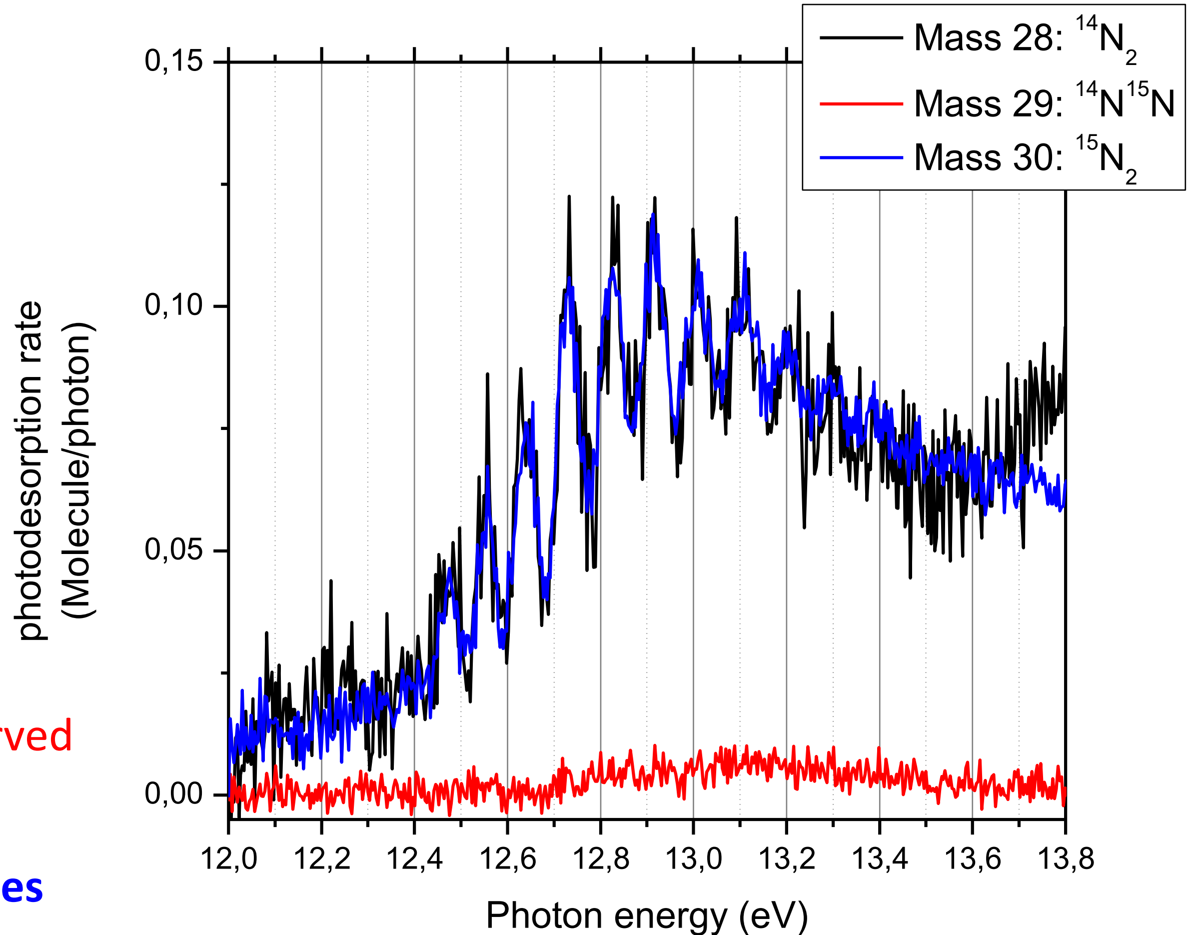


Very high efficiency above 12,5 eV

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

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





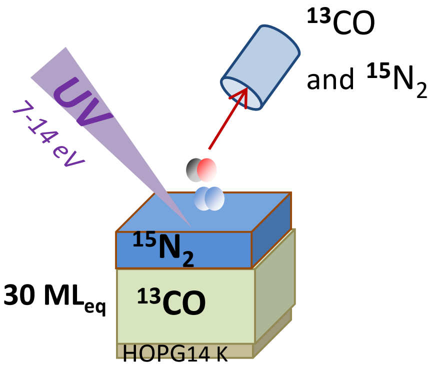
Desorption of $^{14}N_2$ and $^{15}N_2$ is observed

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

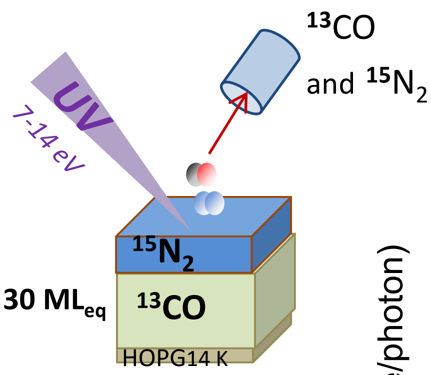
⇨ **Recombination of N_2 does not seem to be operative for the photodesorption**

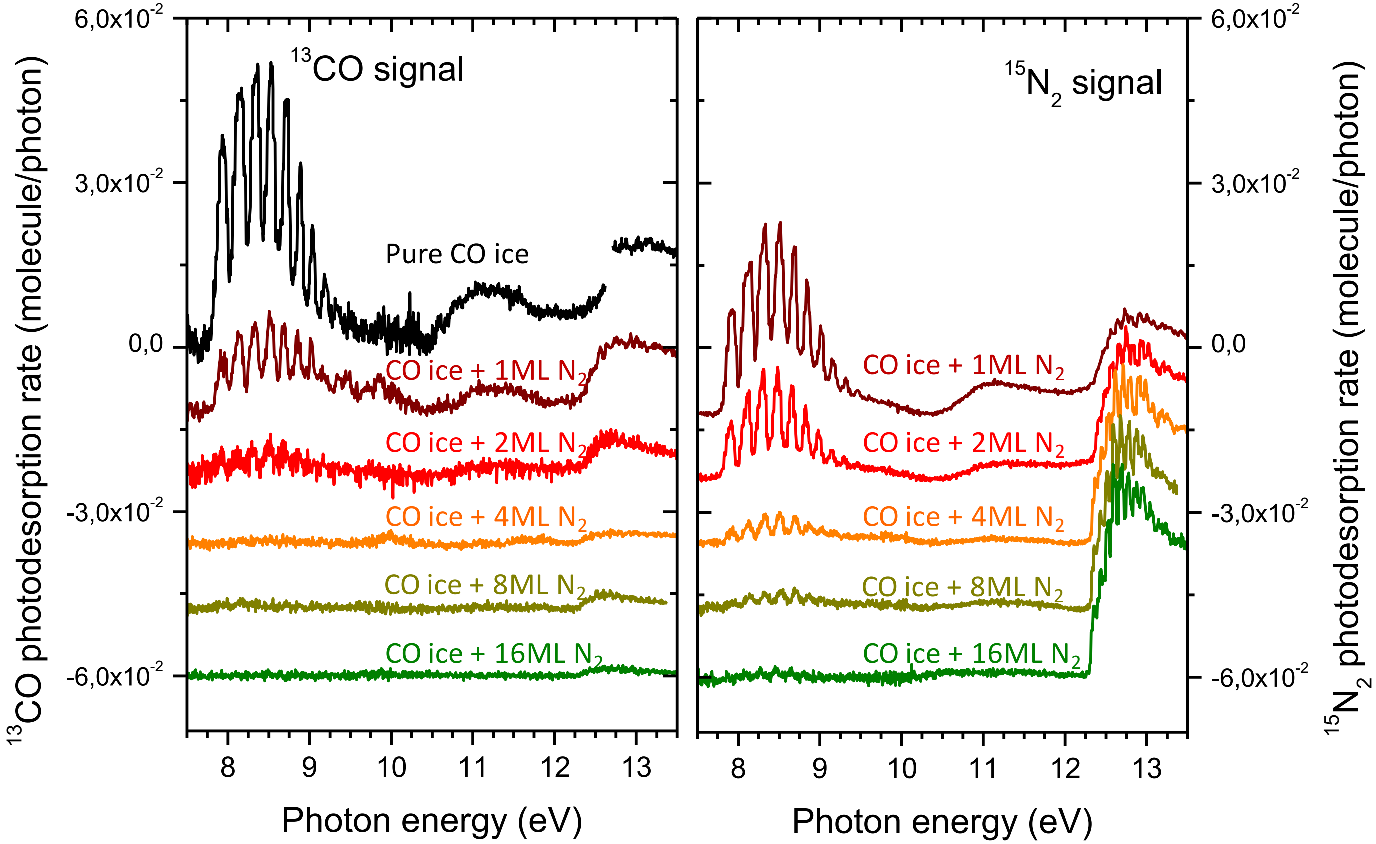
Fayolle et al., A&A. 2013

Mixed ices CO-N_2



Mixed ices CO-N_2





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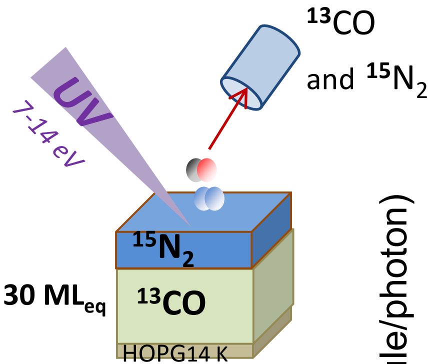
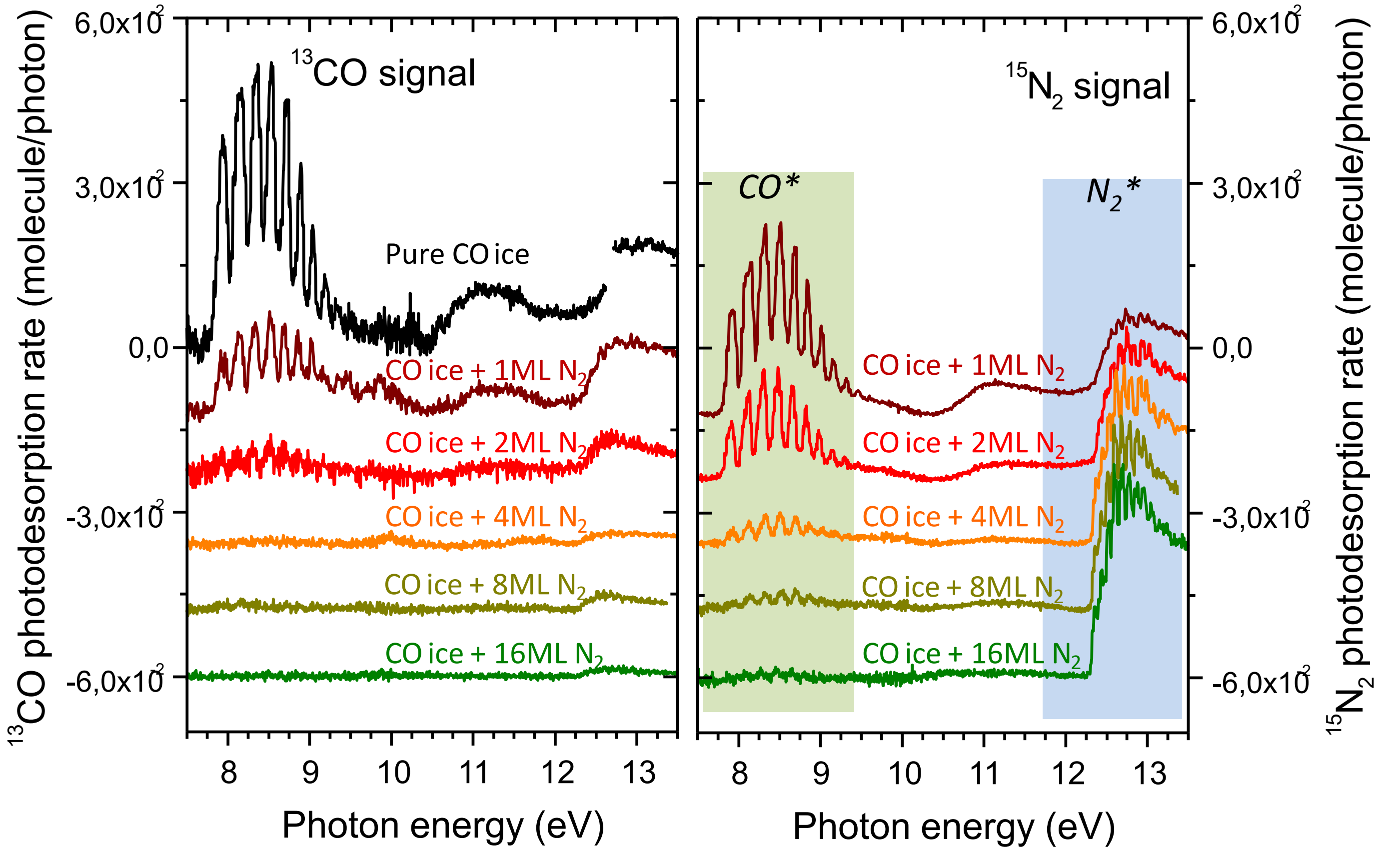
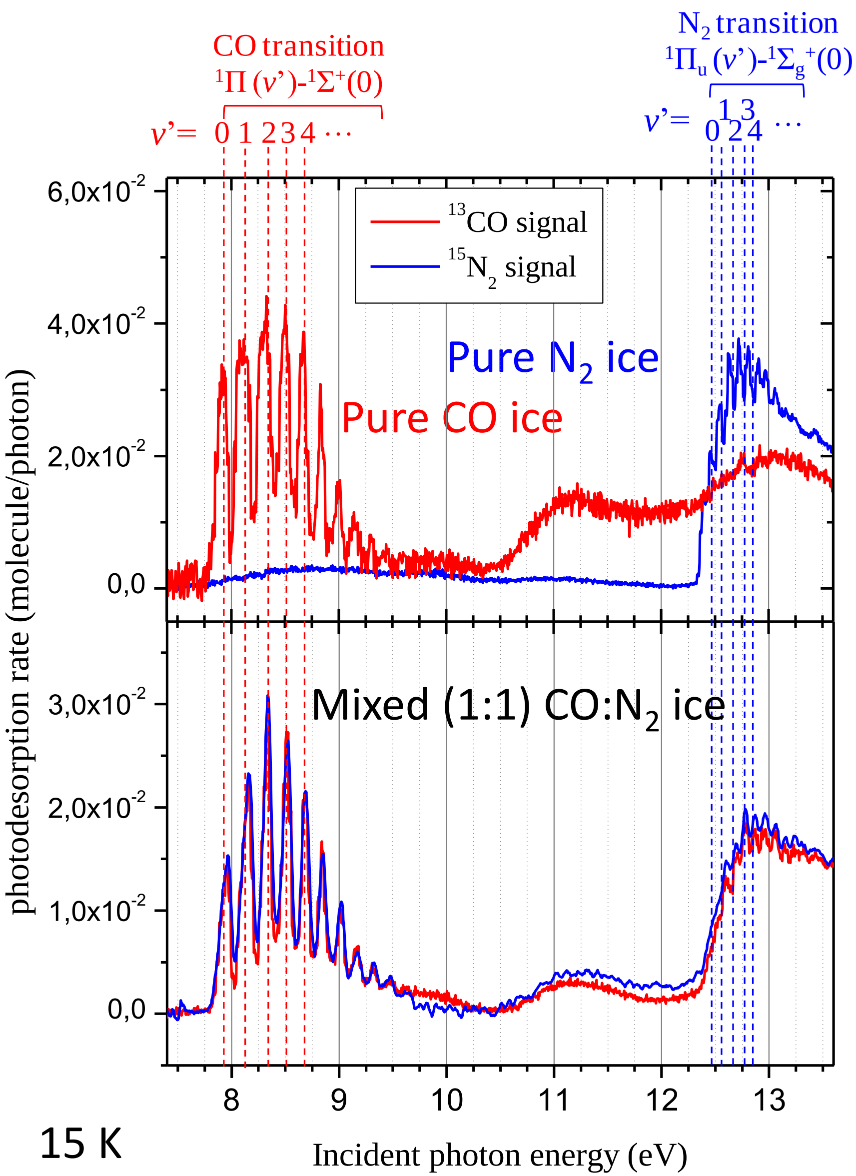
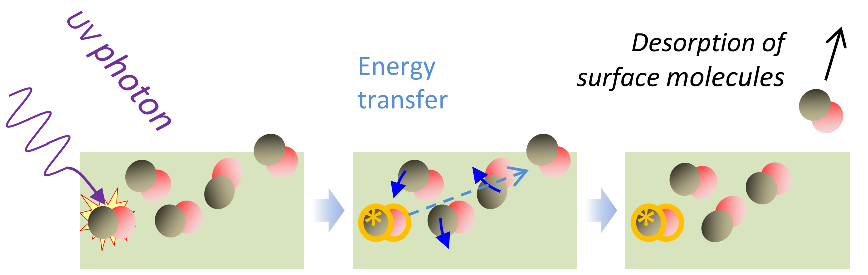




UV Photodesorption: *case of simple molecules* Bertin et al., ApJ 2013



15 K



- Surface process : top few ML

$E_{des} < 100$ meV

@ 8.2 eV

- Yields ~ X 10^{-2} molecules/ photons
- Decrease with ice deposition Temp
- σ_{abs} ~ 1.5 10^{-17} cm^2

Quantum Yield

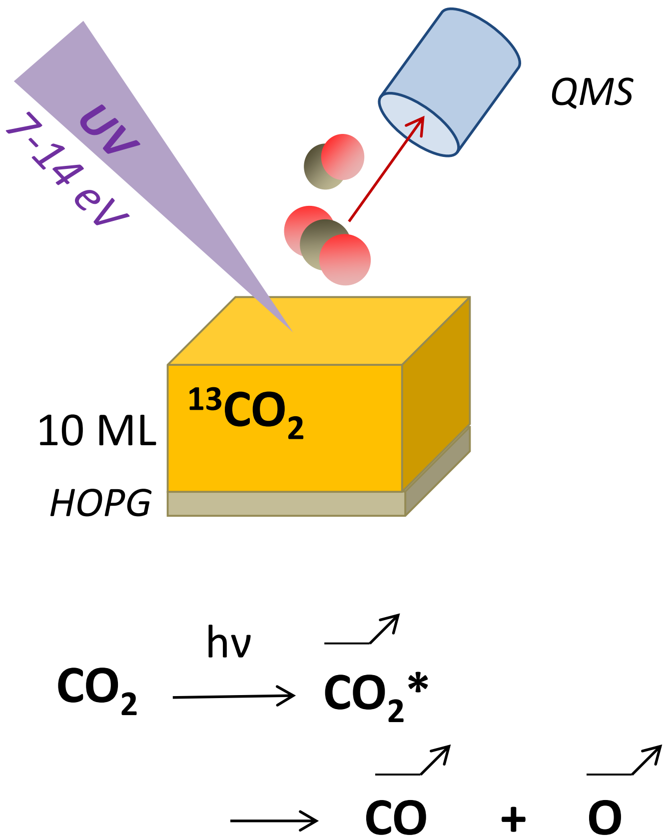
~ 1 molecule /absorbed photon

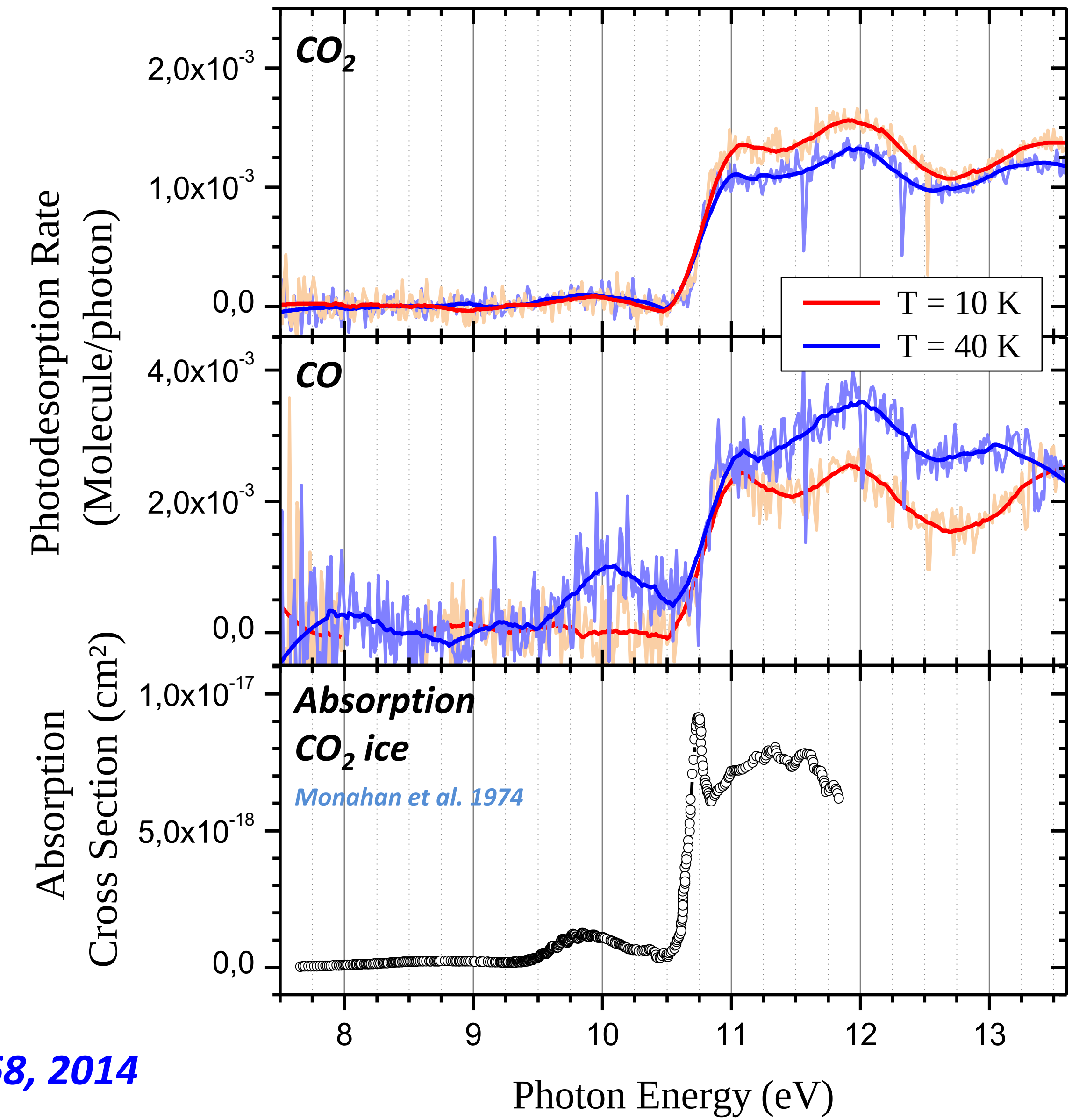
in top 3 ML (10-20 K)

Photodesorption and photochemistry
The CO_2 case

The role of Photochemistry : the CO_2 case

Fillion et al., Faraday Discus. 2014

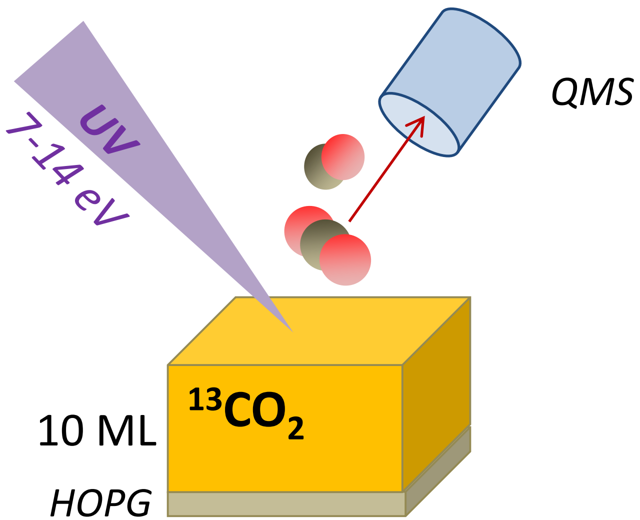




Fillion et al., Faraday Discus. 168, 2014

The role of Photochemistry : the CO_2 case

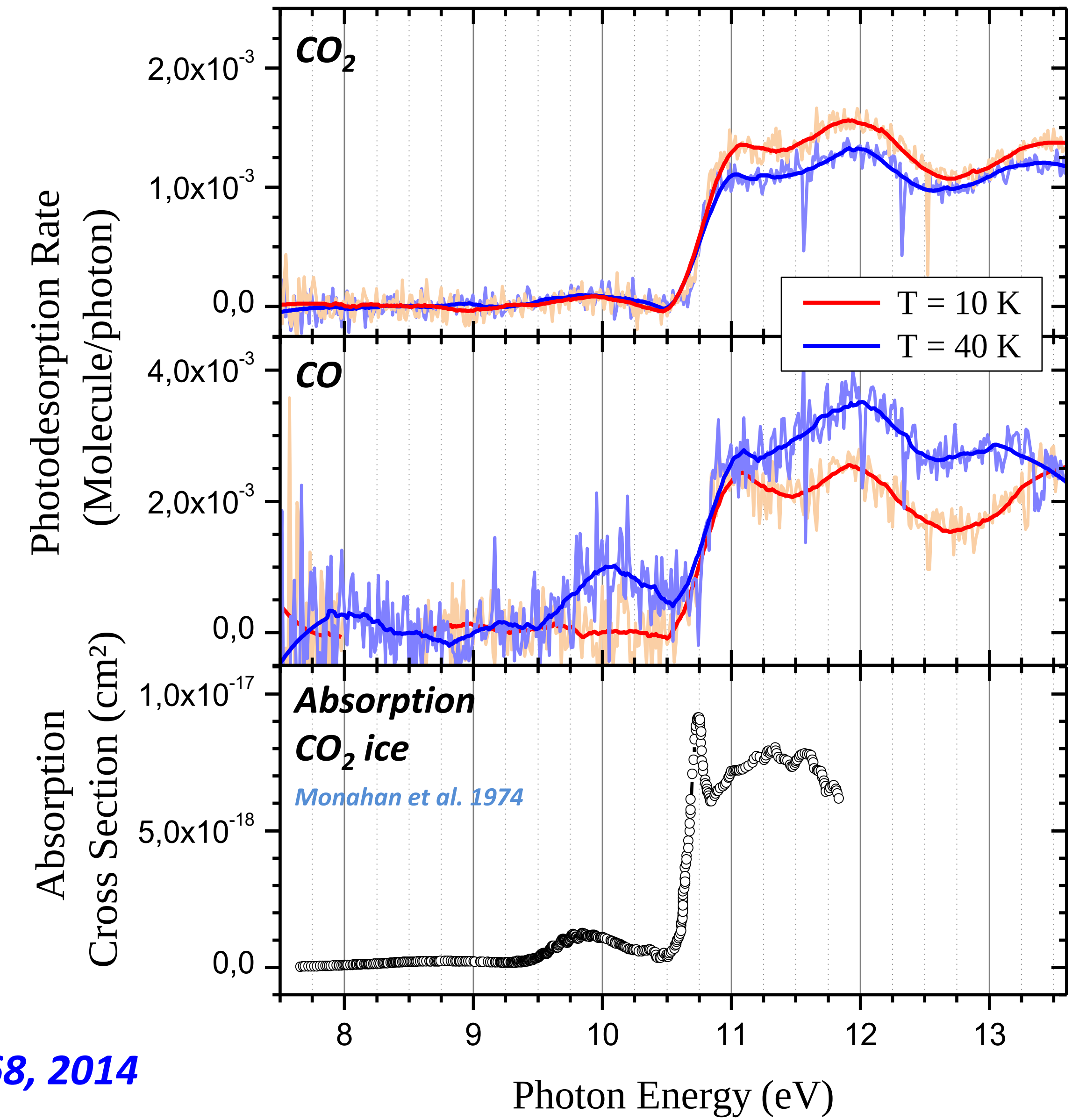
Fillion et al., Faraday Discus. 2014



$$CO_2 \xrightarrow{h\nu} CO_2^{*}\nearrow$$

$$\longrightarrow CO\nearrow + O\nearrow$$

$$CO + O \longrightarrow CO_2\nearrow$$

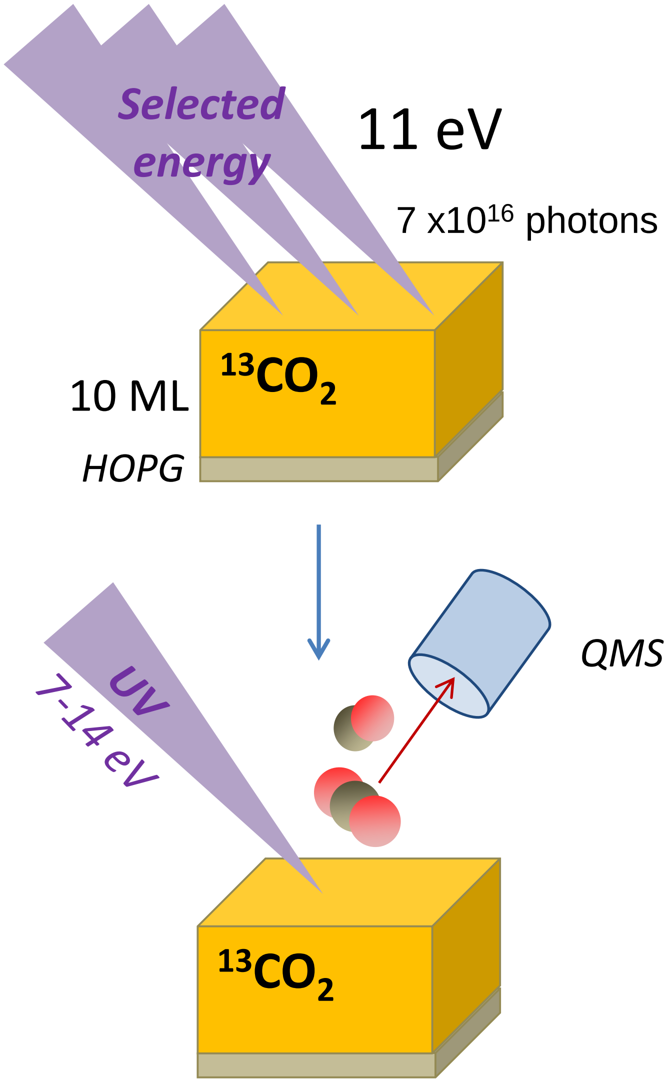


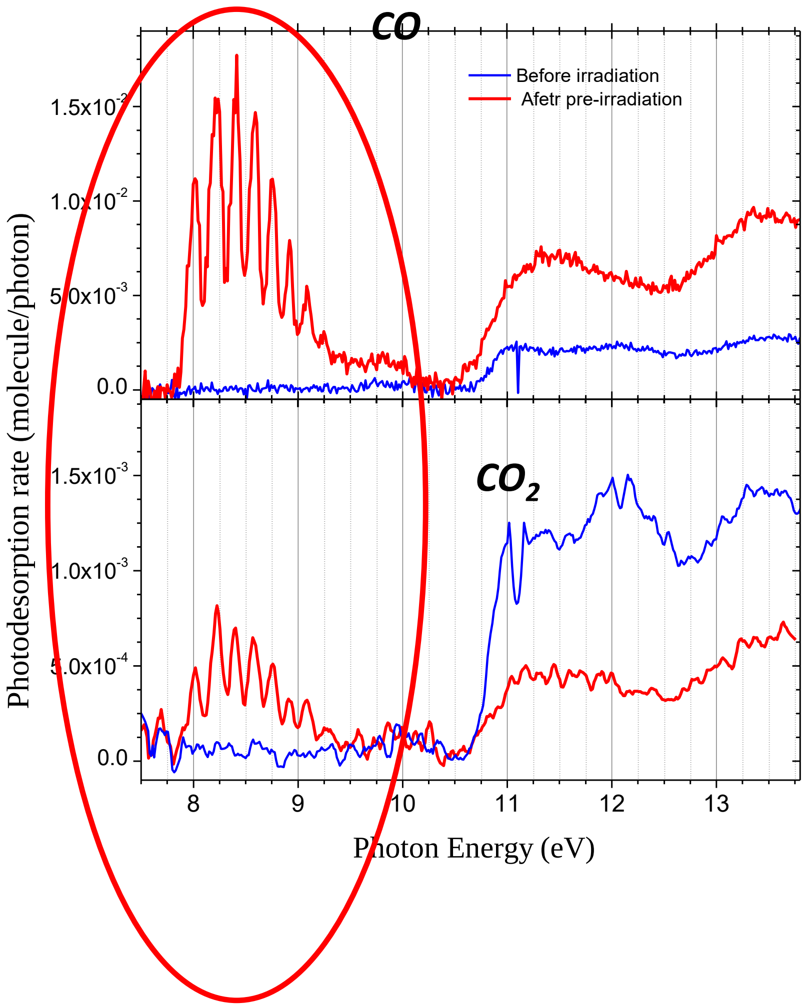
Fillion et al., Faraday Discus. 168, 2014

The role of Photochemistry : the CO_2 case

Fillion et al., Faraday Discus. 2014

$A^1\Pi$ (v') ← $X^1\Sigma^+$(v=0)





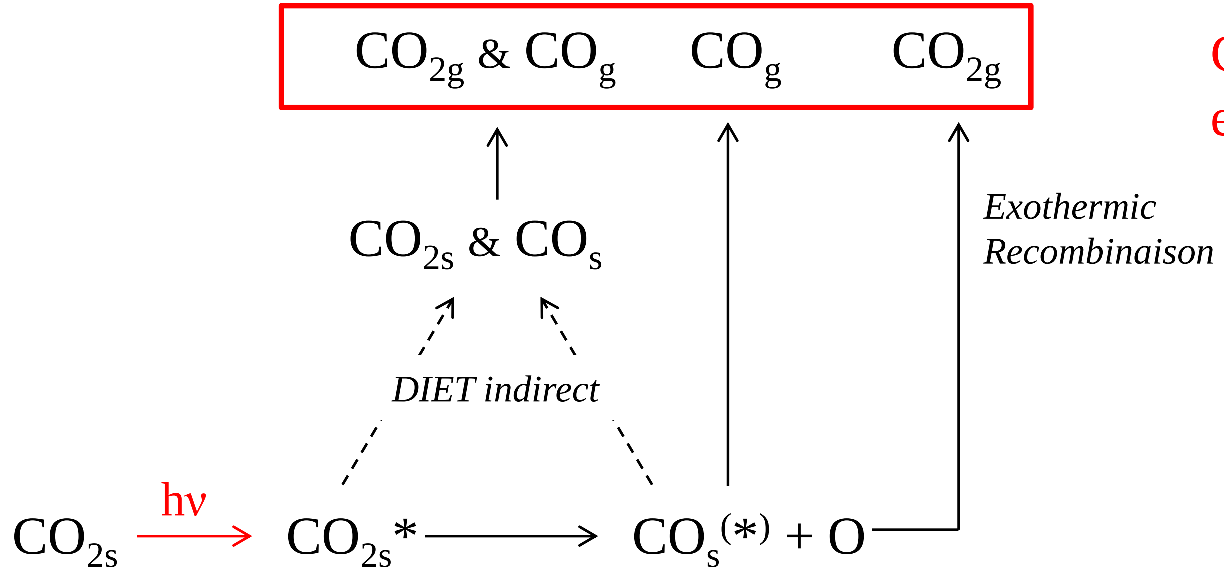
The role of Photochemistry : the CO_2 case

Fillion et al., Faraday Discus. 2014

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

The role of Photochemistry : the CO_2 case

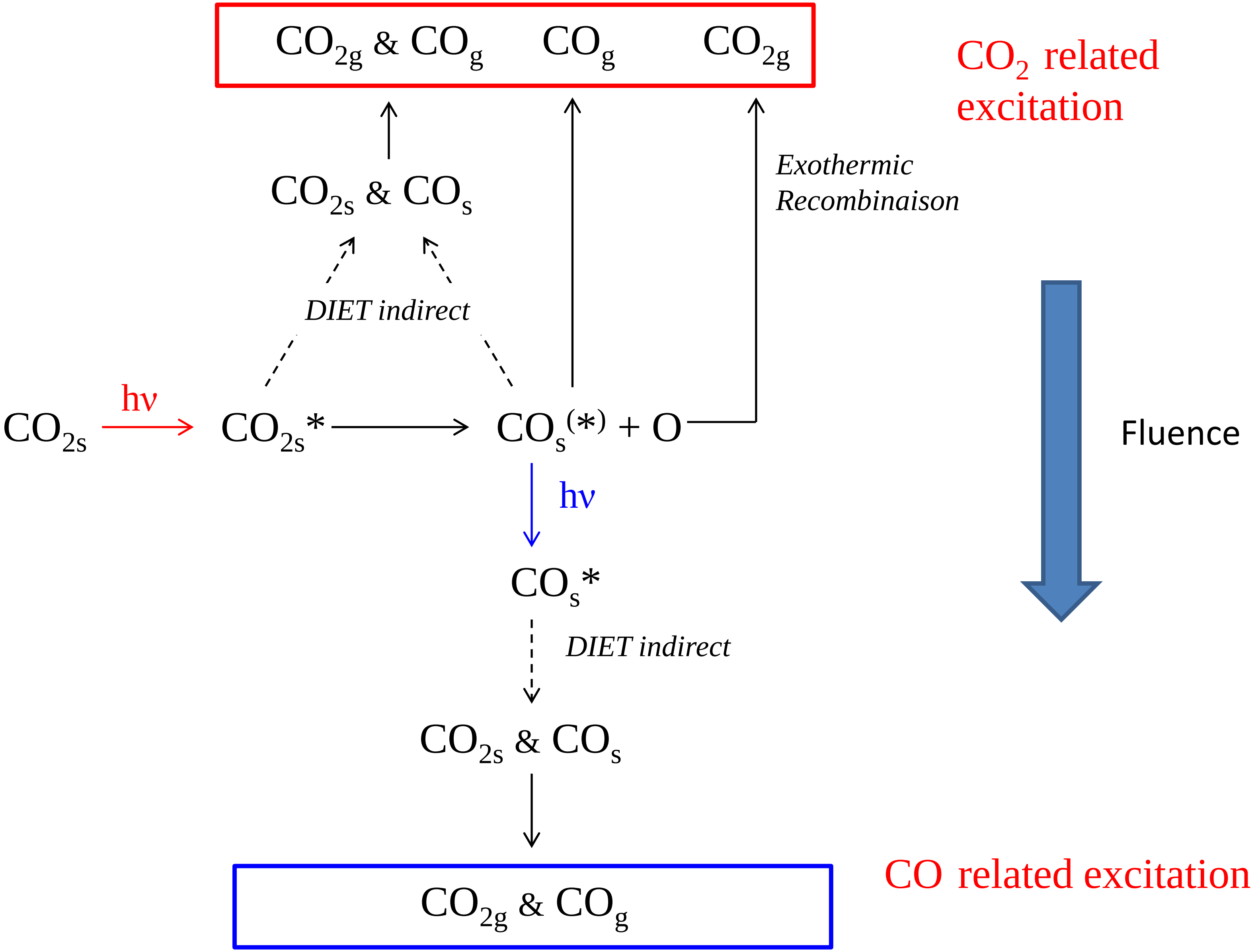
Fillion et al., Faraday Discus. 2014



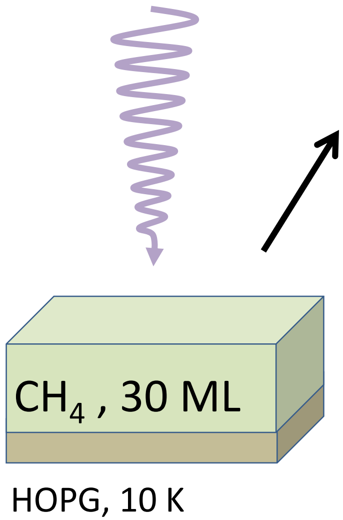
CO_2 related excitation

The role of Photochemistry : the CO_2 case

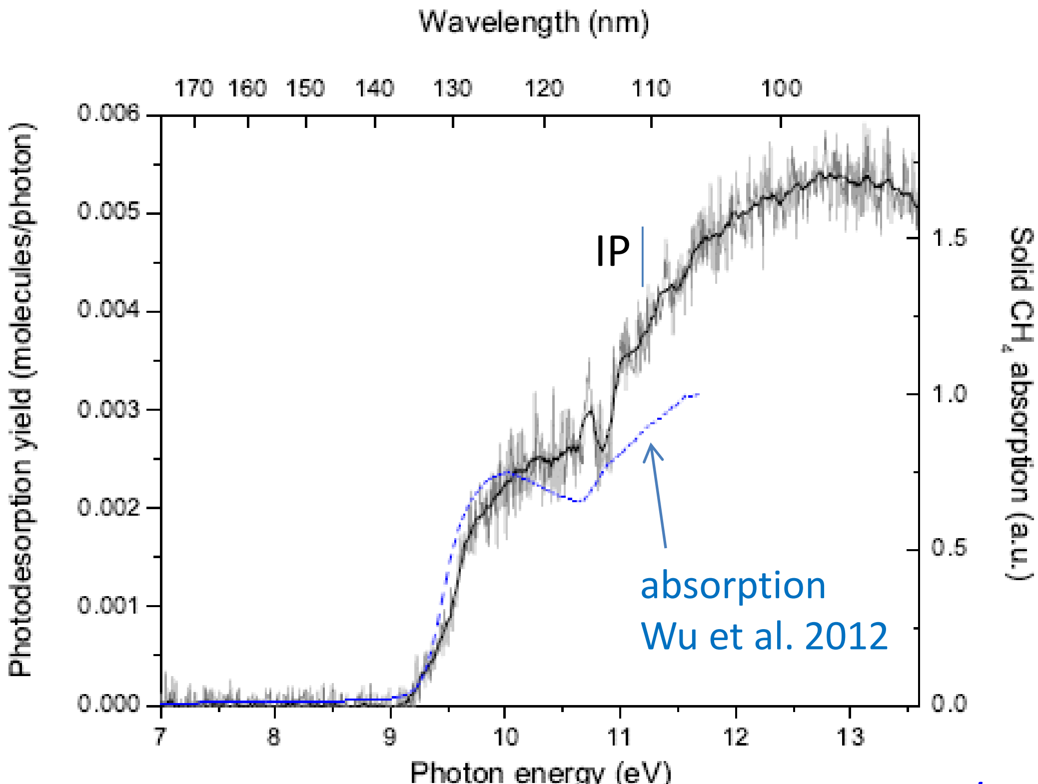
Fillion et al., Faraday Discus. 2014



Photodesorption from condensed CH4



- Only "Fresh ice" results
- Desorption of CH, CH_2, CH_3 not observed

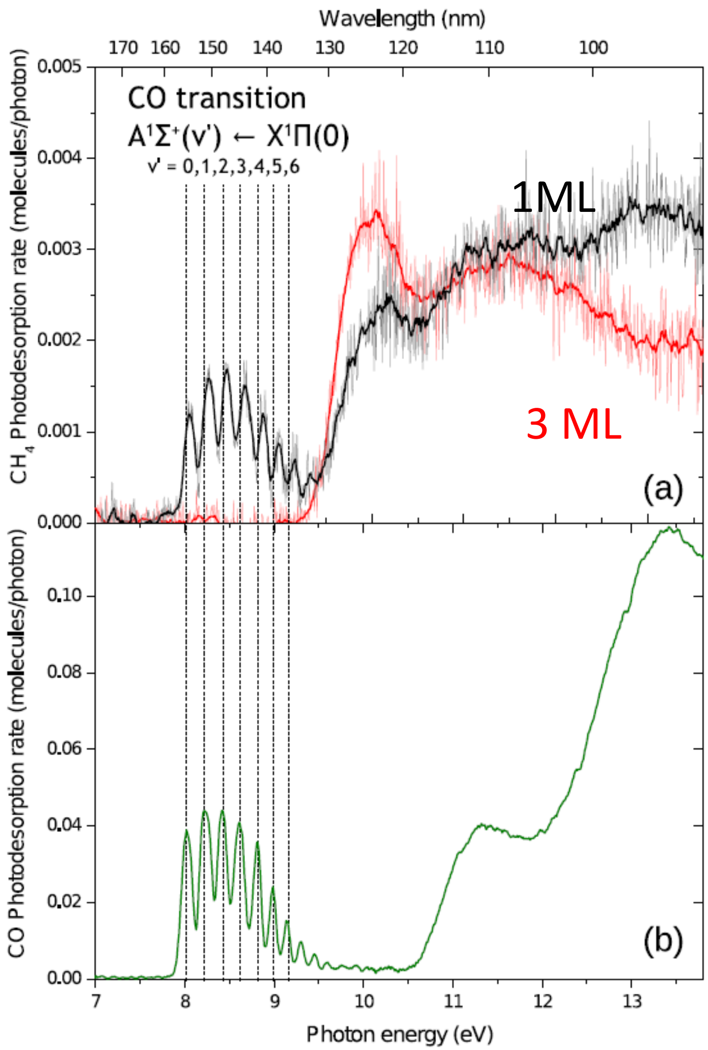


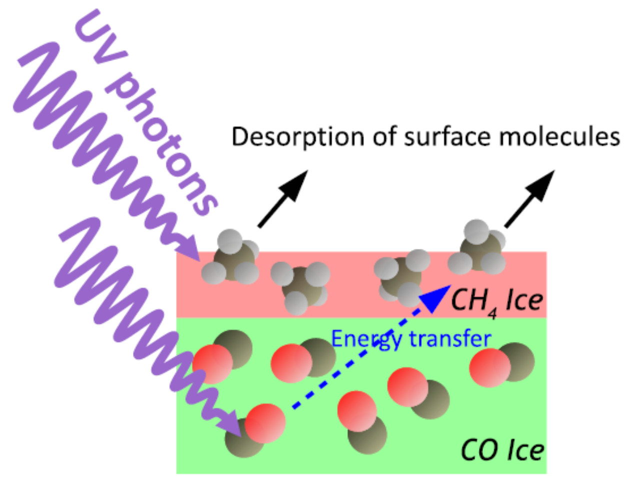
Dupuy et al., A&A 2017

	Dense cores[a]	Protoplanetary disks[b]	ISRF[c]
	($\times 10^{-3}$ molecules/photon)		
Pure CH_4	2.2 ± 1.1	2.2 ± 1.1	2.0 ± 1.0

Notes. UV fields are taken from [a] Gredel et al. (1987); [b] Johns-Krull & Herczeg (2007); and [c] Mathis et al. (1983).

Photodesorption from condensed CH4 on top of CO





10.2 eV @ 10 K (Ly-α)

Photodesorption quantum yield

~ 0.05 molecules /absorbed photon

assuming absorption in top 3 ML of CO

Photodestruction (bulk)

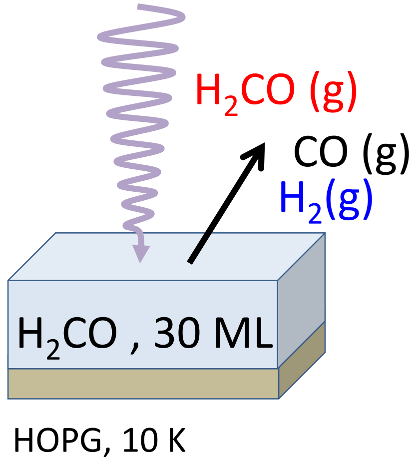
Öberg et al. 2010 $\sigma = 5 \times 10^{-19}$ cm^{-2}

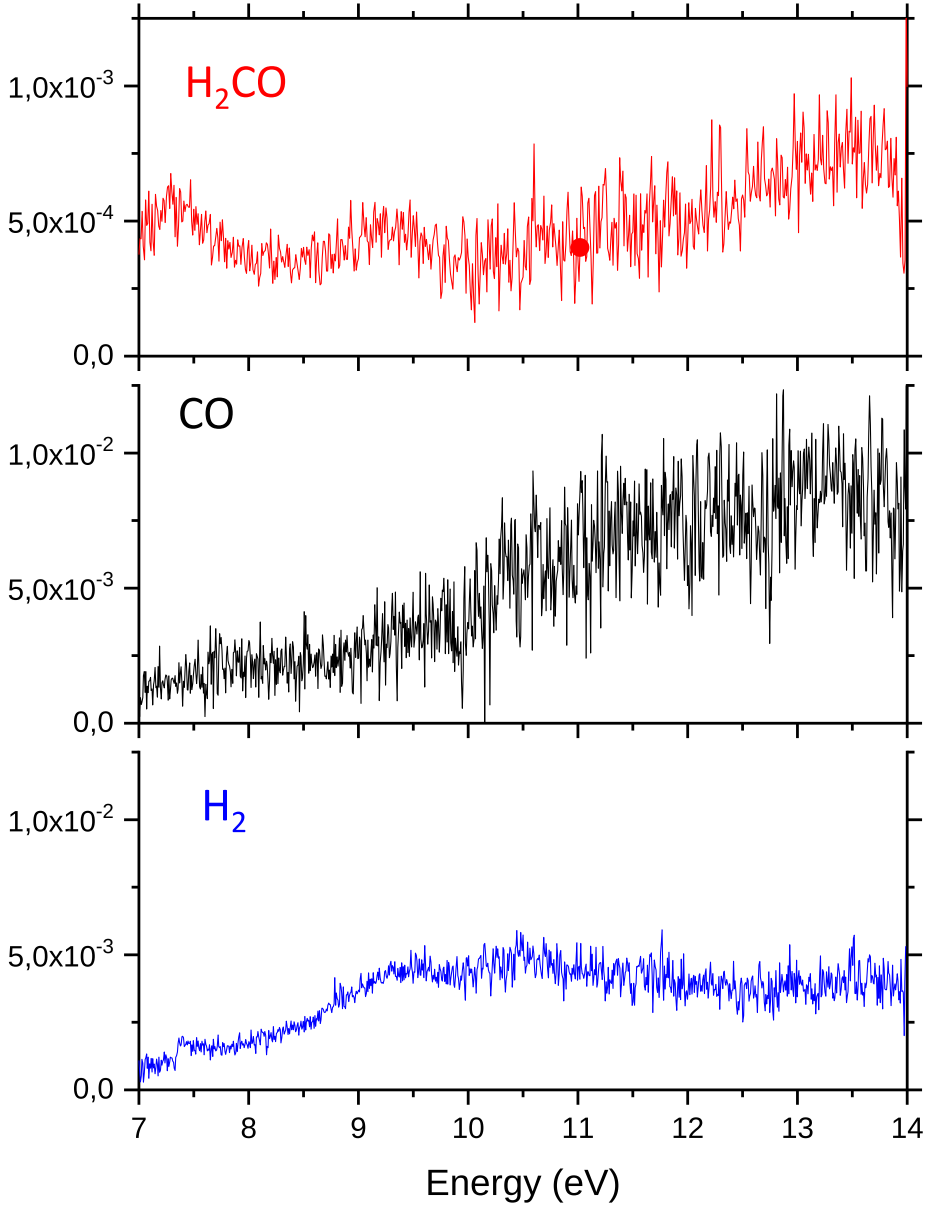
~ 0.033 destroyed molecules per absorbed photons.

Dupuy et al., A&A 2017

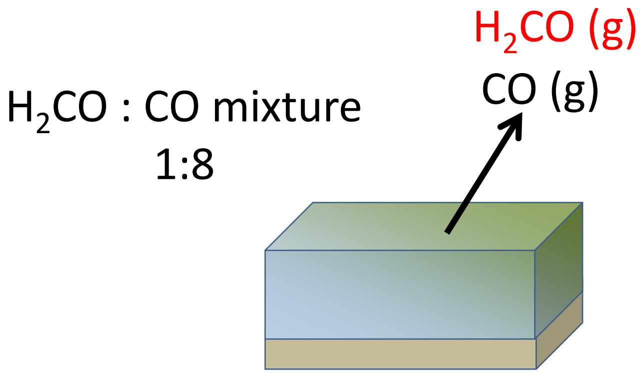
Most of the energy is relaxed away

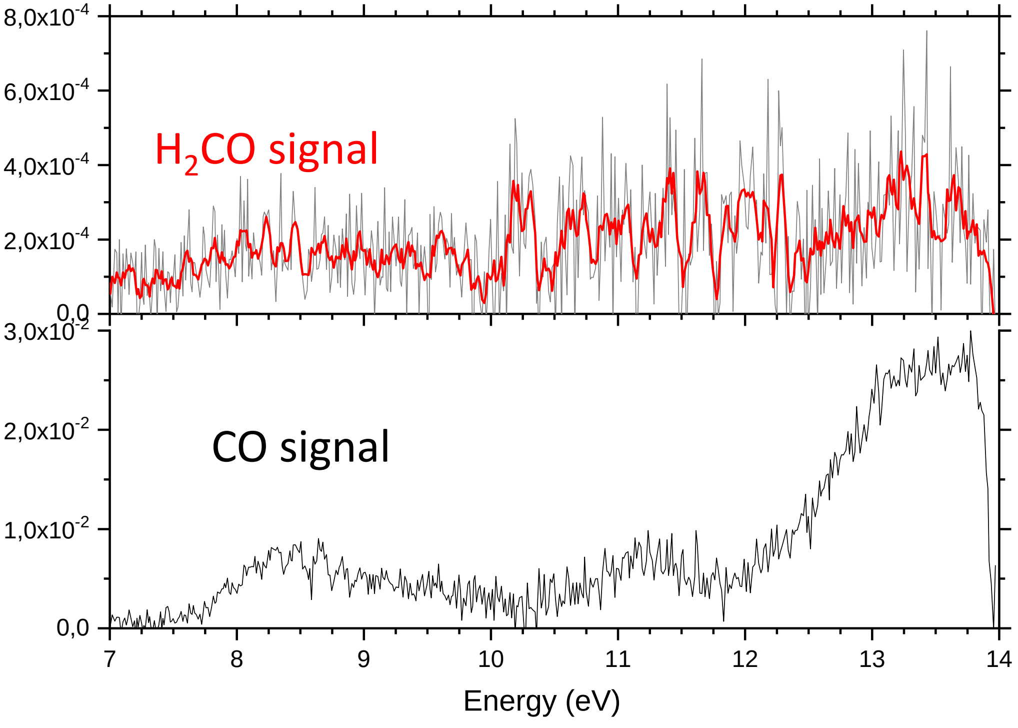
Photodesorption from condensed pure formaldehyde





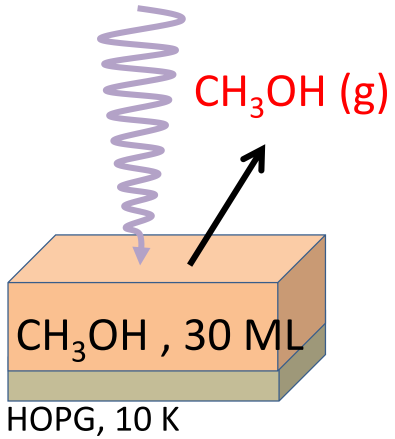
Photodesorption from condensed Mixture of CO and Formaldehyde

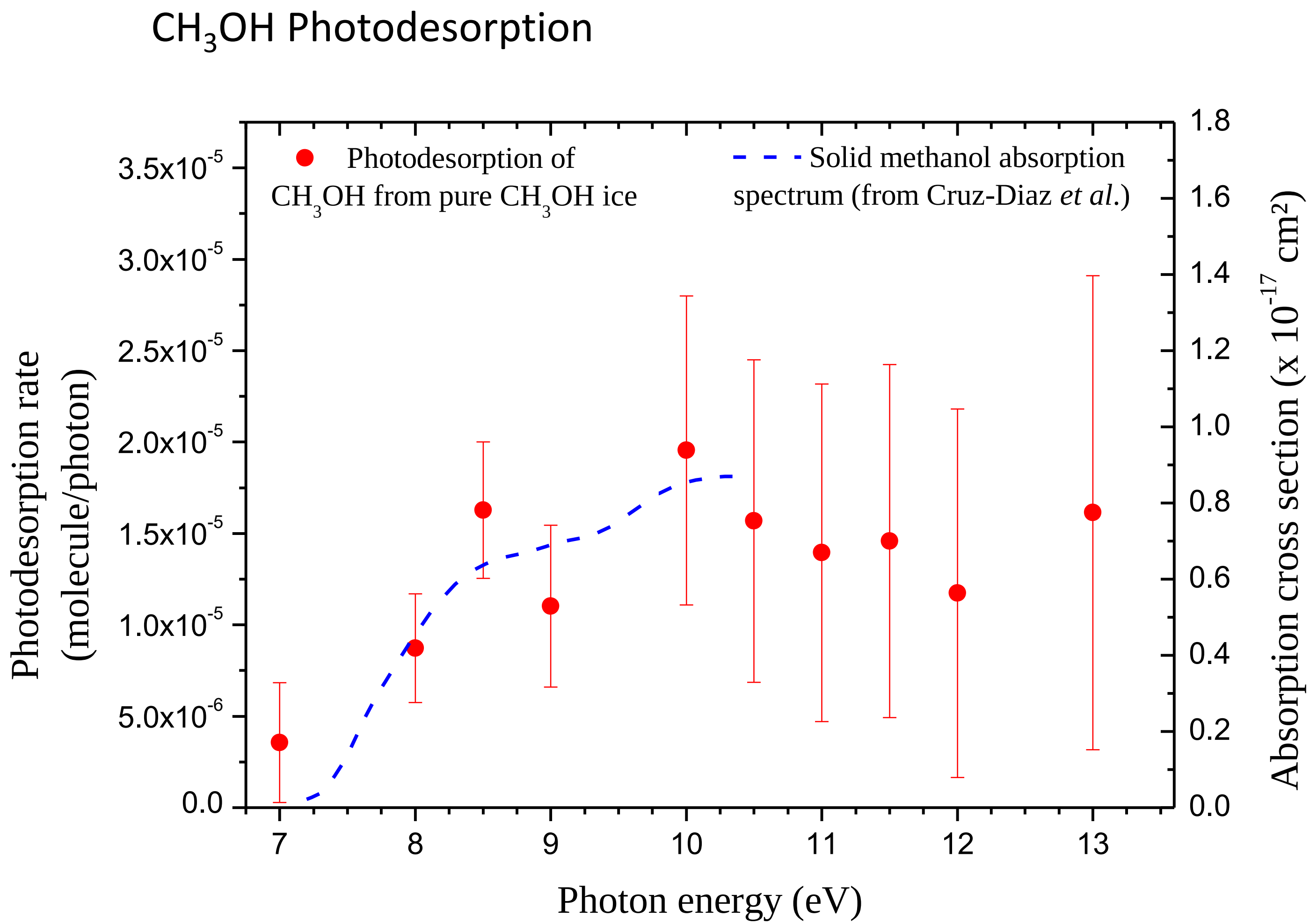




Photodesorption from condensed pure methanol

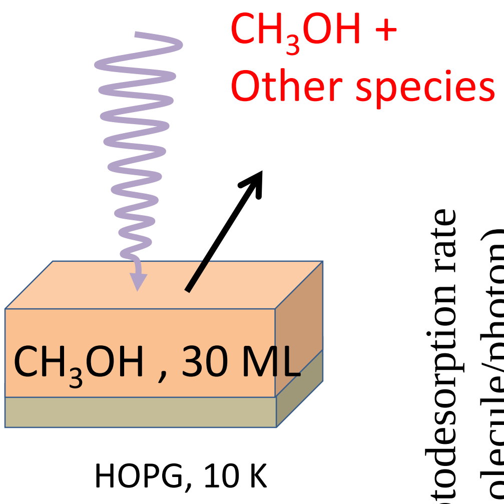
Bertin et al., ApJ Lett 2016

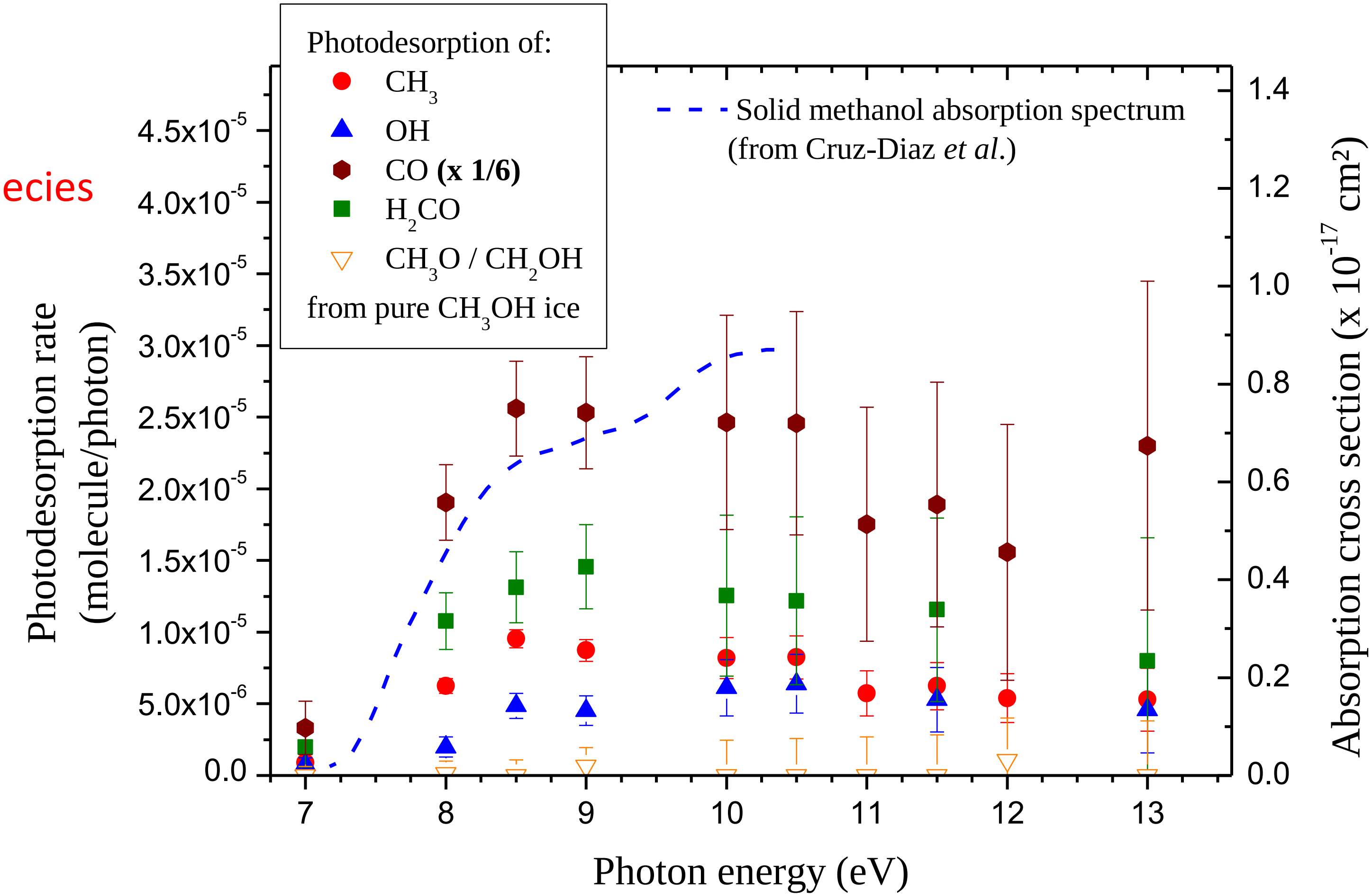




Photodesorption from condensed pure methanol

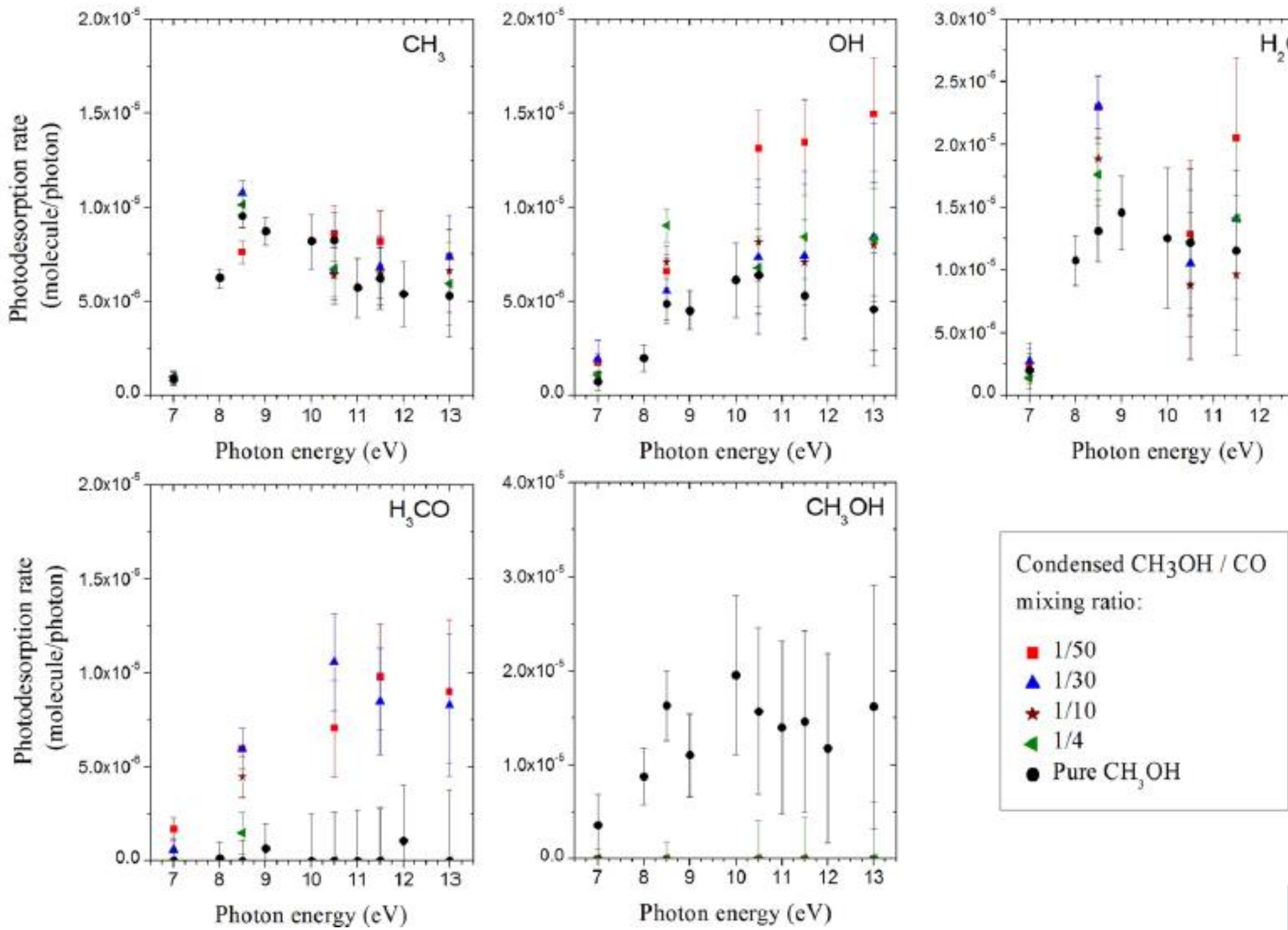
Bertin et al., ApJ Lett 2016

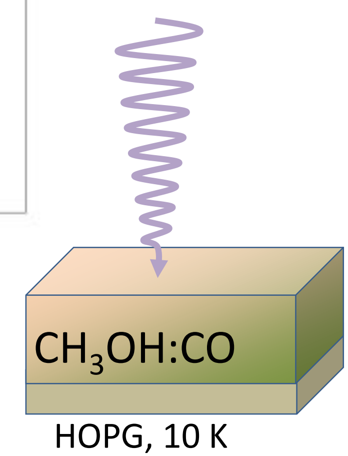




Photodesorption from **Mixture of CO and Methanol**

Bertin et al., ApJ Lett 2016





$$\mathrm{CH_3OH_{solid}} + h\nu \longrightarrow \mathrm{CH_{3gas}} + \mathrm{OH_g}$$

$$\mathrm{CH_3OH_{solid}} + h\nu \longrightarrow \mathrm{H_2CO_{gas}} + \mathrm{H_2}\ (\text{or } 2\mathrm{H})$$

Origin of intact CH_3OH desorption

Exothermic chemical reaction ?

UV and X-ray Photodesorption of water

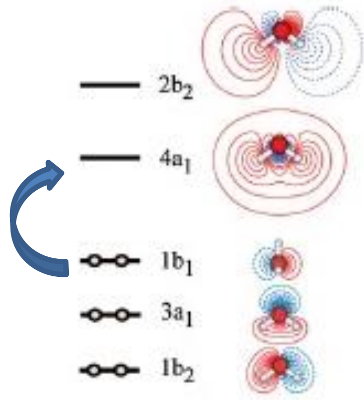
Photon Stimulated Desorption of water with UV photons

Competition dissociation / desorption

Primary processes

- Exciton delocalization and desorption of intact water
- « Kick-out » by fast H-atom produced by photodissociation
- Exothermic recombination

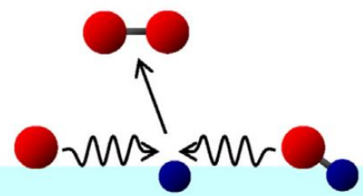
➡ H, OH and H_2O



Secondary processes

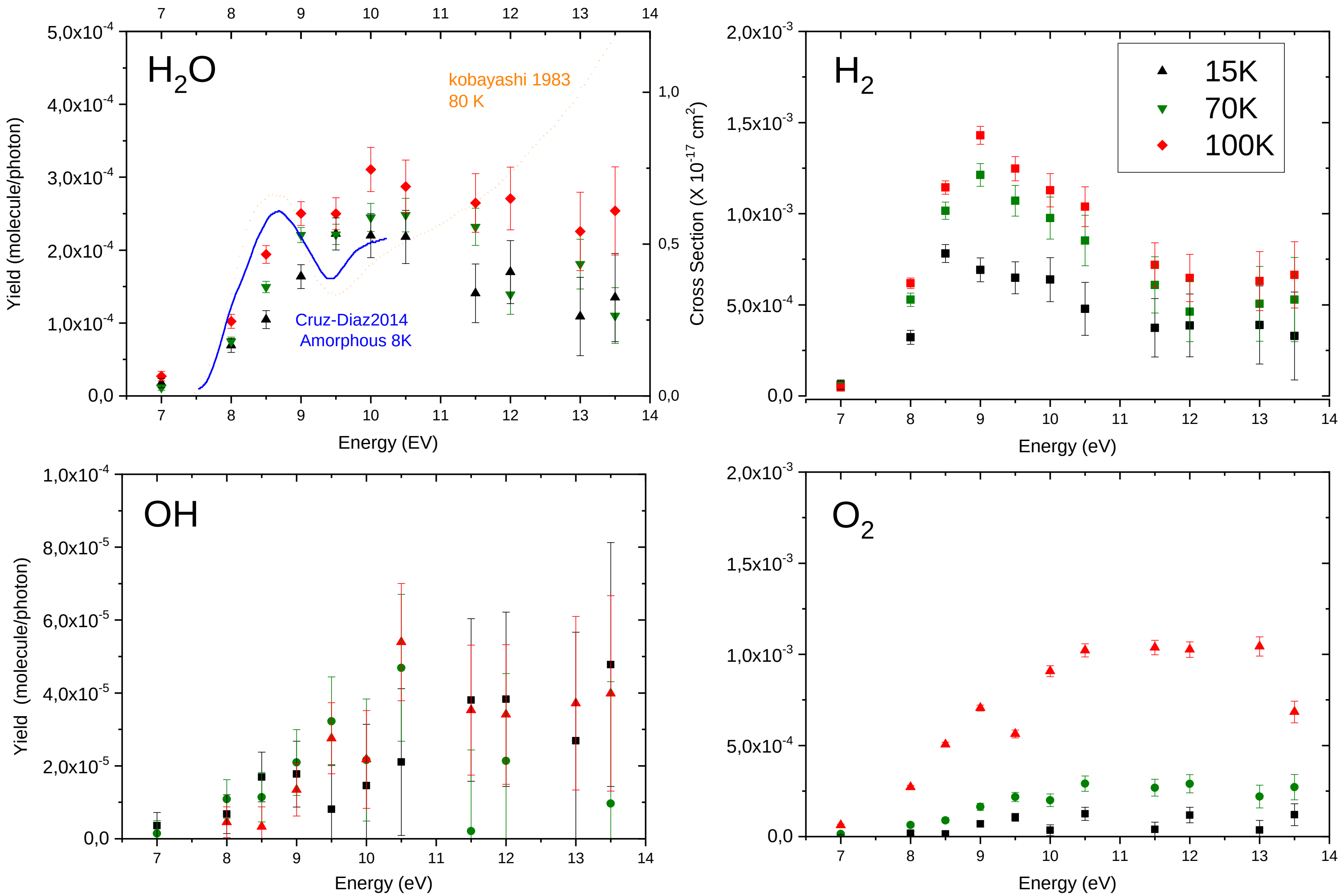
- Photodissociation of water + reactivity of photofragments OH, H and O
- Secondary photolysis and reactivity after prolonged irradiation

➡ O, H_2, O_2, H_2O_2



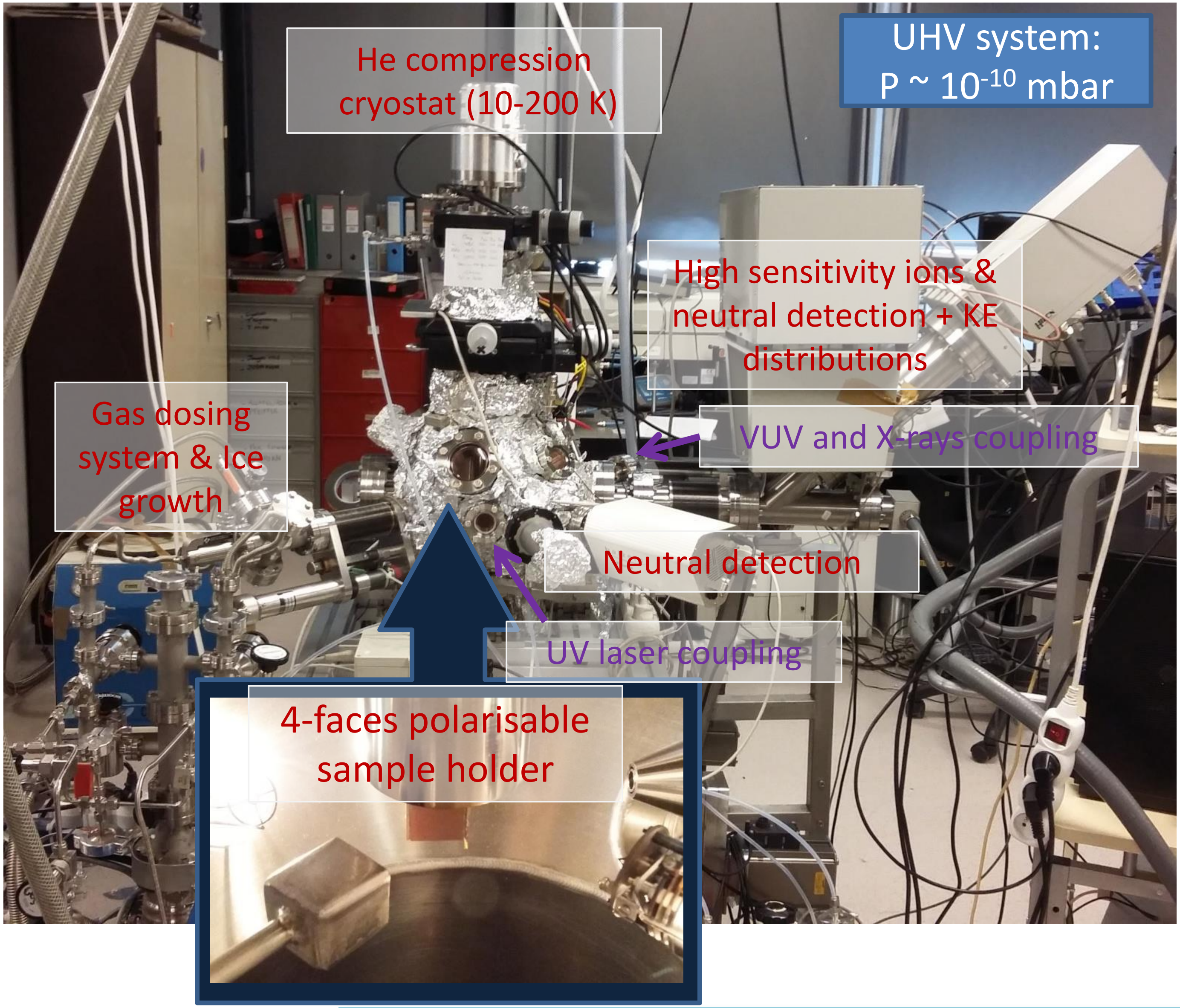
$H_2O + h\nu(157\ \text{nm}) \rightarrow H + OH$
$OH + OH \rightarrow H_2O + O(^3P_J)$
$OH + O(^3P_J) \rightarrow O_2(X^3\Sigma_g^-, v{=}0) + H$

Photon Stimulated Desorption of water with UV photons



Intact water : 2 10^{-4} ph^{-1} at 10 eV → 10^{-3} molecules/ abs photon

« SPICES 2 » set-up : Surface Processes and ICES 2



Higher Sensitivity

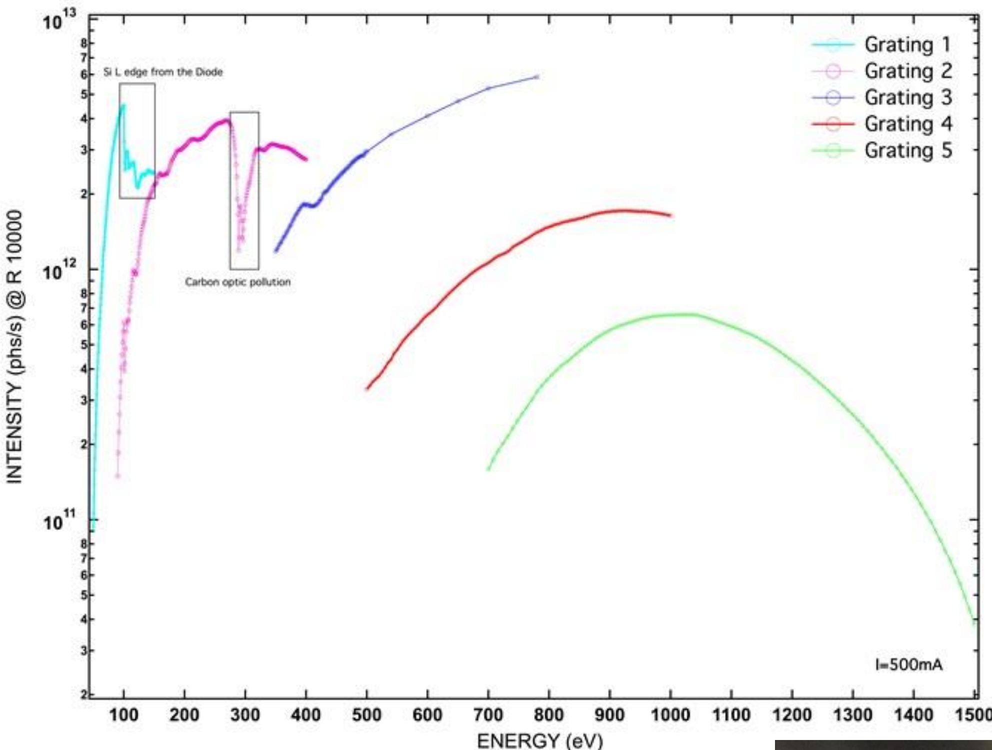
- *Increase vacuum perfomance*
- *New analysis Chamber*
- *New mass spectrometer*

New achievements

- Ion/neutral detection
- Kinetic energy measurement
- Compatible for : continuous (synchrotron) Or pulsed (laser) sources

-> internal energy

« SPICES » @ SOLEIL (SEXTANTS beamline)

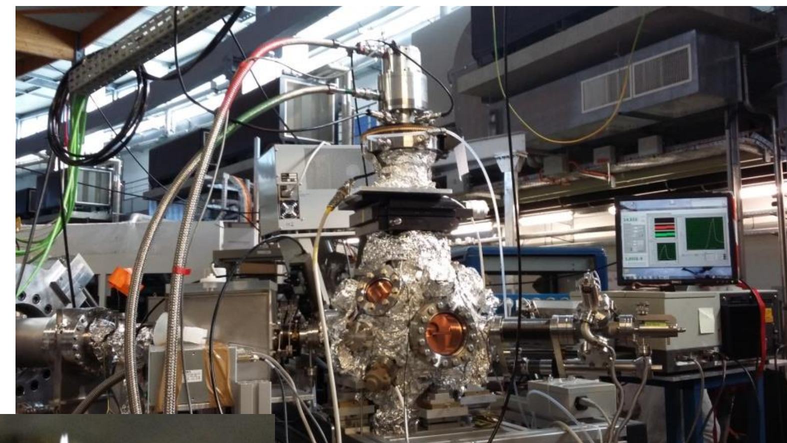


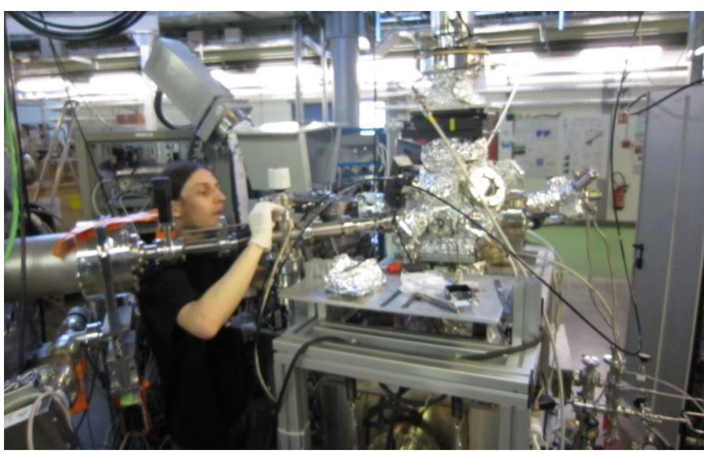
500-600 eV (O K-edge)

1O [11-12] photons/s

FWHM : 150-250 meV

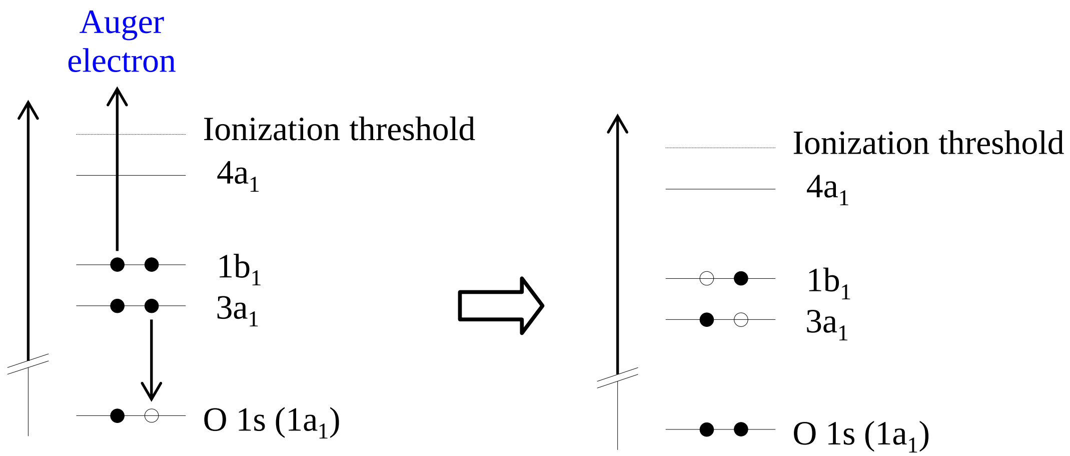
With 5 µm output slits





Desorption mechanisms induced by soft X-ray photons

Auger decay

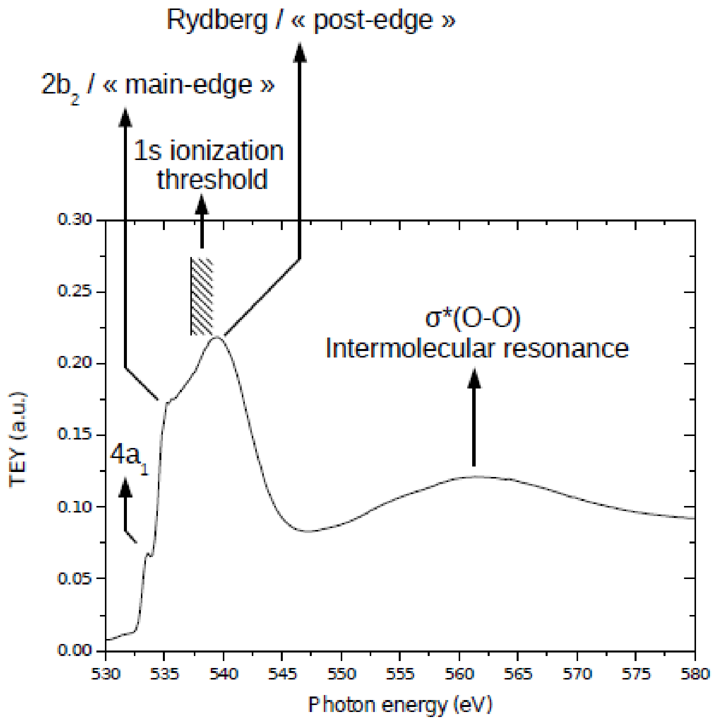


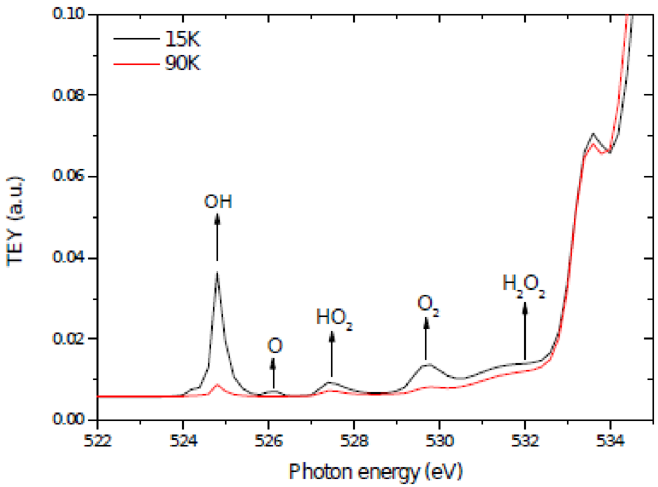
Core hole state → Decay into a final state with holes in the valence bands → Dissociation, repulsive state... → « True » PSD (photon-stimulated desorption)

Core hole state → Ejection of an Auger electron with ~500 eV kinetic energy → Multiple (~25) secondary valence excitation or ionization → « X-ESD » (X-ray induced electron-stimulated desorption)

Near-edge X-ray spectroscopy

Total Electron yield (TEY) ~ Absorption spectrum





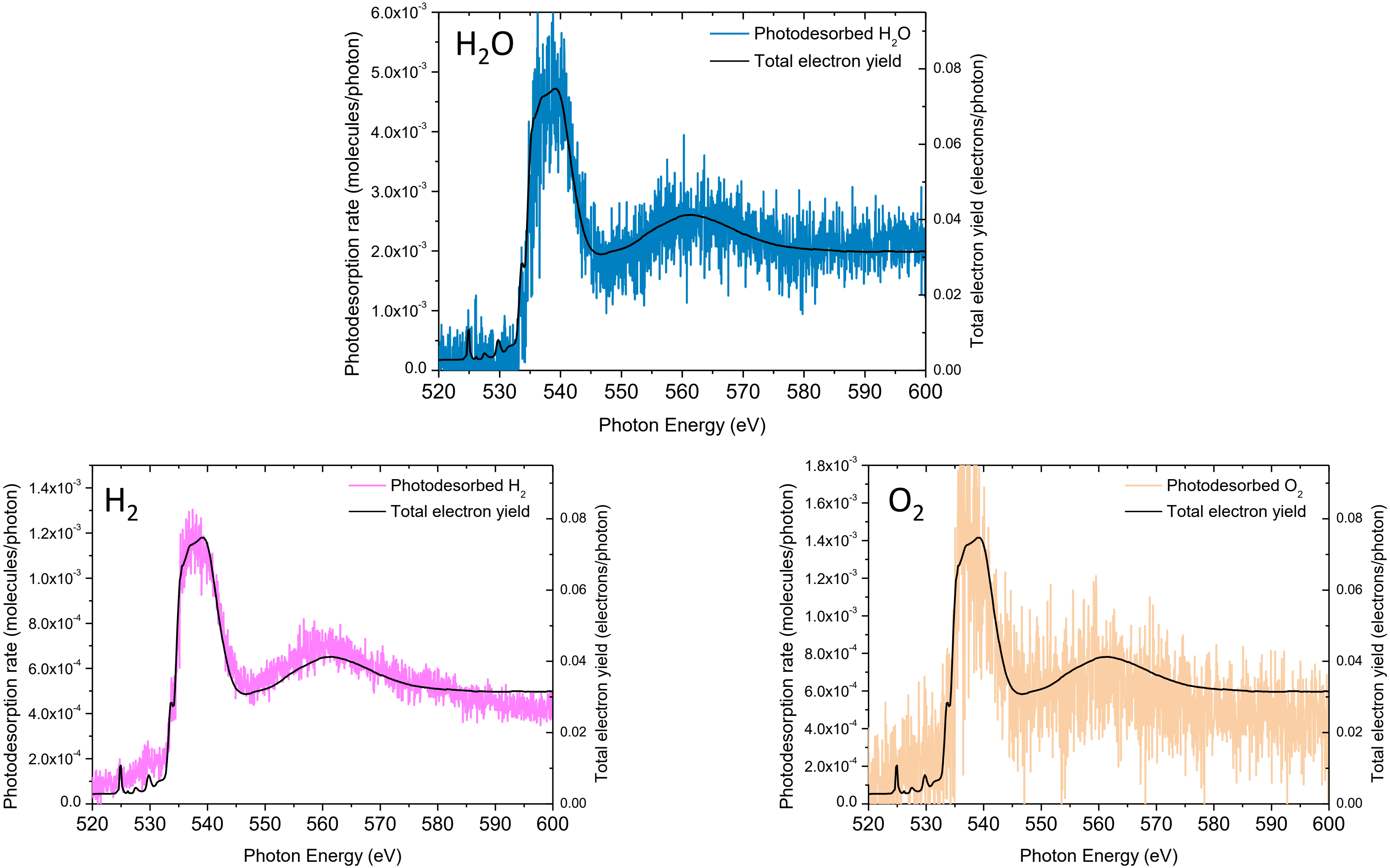
Pre-edge features
Spectroscopic signatures of photo-produced radicals & products

Concentration wrt H_2O : (cf. Laffon et al. 2006)

Species	Concentration/$[H_2O]$	
	15 K	90 K
OH	1×10^{-2}	1×10^{-3}
O	3×10^{-4}	
HO_2	3×10^{-3}	1×10^{-3}
O_2	4×10^{-3}	9×10^{-4}
H_2O_2	1×10^{-2}	6×10^{-3}

Desorption of neutrals from Amorphous Solild Water

X-ray Photodesorption yields from H_2O ices (ASW) @ 15 K



What desorbs

Photodesorption yields @ **540 eV** for ASW at 90K
(molecule or ion per incident photon)

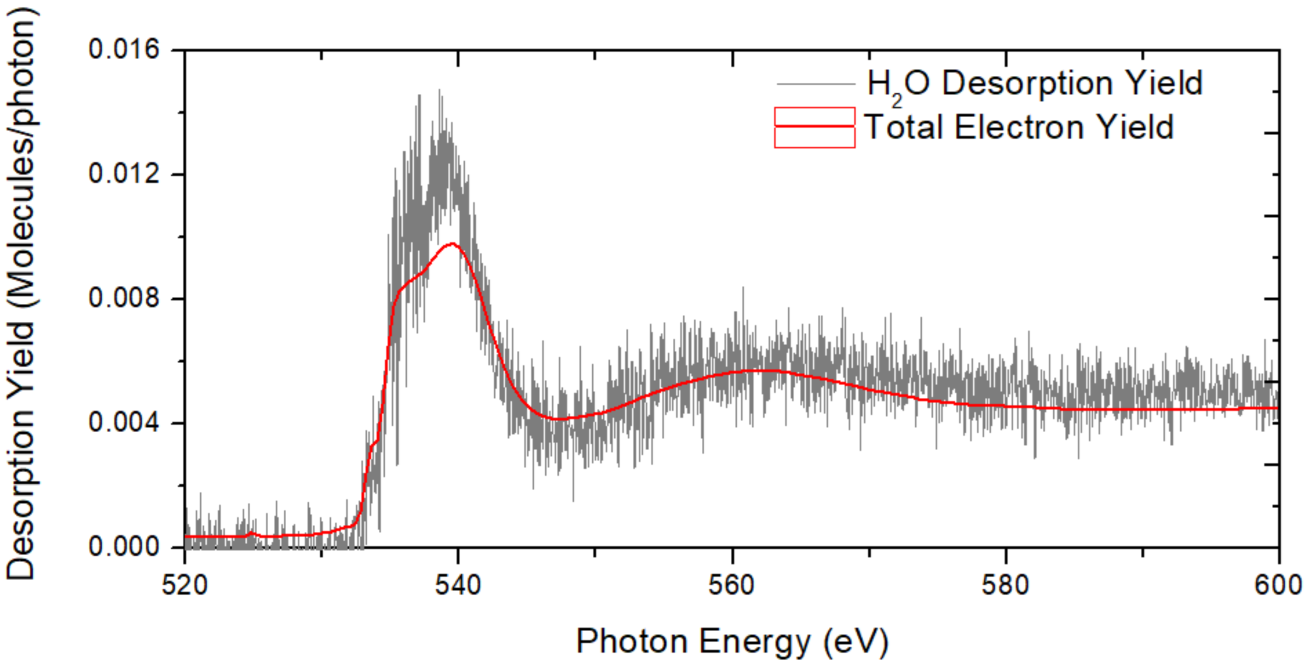
Neutrals		Cations		Anions	
H_2O	1.2×10^{-2}	H^+	1.6×10^{-4}	H^-	1×10^{-5}
H_2	3×10^{-2}	H_2^+	3×10^{-7}	H_2^-	3×10^{-10}
O_2	7×10^{-3}	H_3^+	5×10^{-9}	O^-	7×10^{-8}
OH	$< 1 \times 10^{-3}$	O^+	3×10^{-8}	OH^-	1×10^{-8}
		OH^+	8×10^{-9}	H_2O^-	3×10^{-10}
		H_2O^+	5×10^{-9}	O_2^-	7×10^{-10}
		H_3O^+	2×10^{-8}		
		O_2^+	4×10^{-9}		
		$(H_2O)_2H^+$	6×10^{-8}		

+ $(H_2O)_nH^+$ clusters from n = 3 to 11

➡ Many different species are observed

➡ Desorption of neutral species dominates

Intact H_2O desorption



Desorption spectrum follows TEY

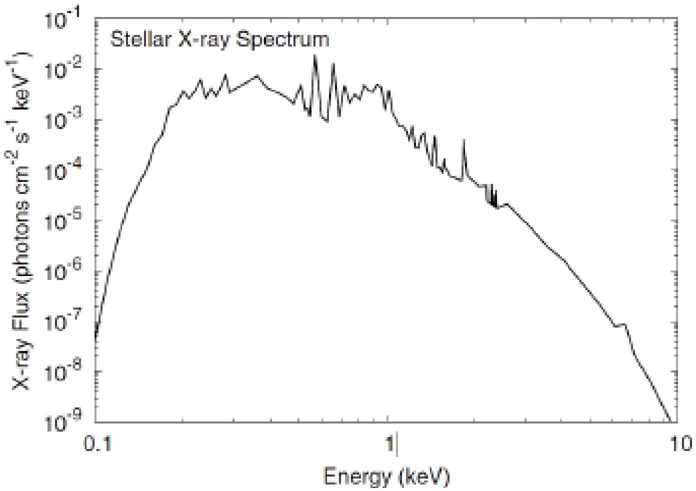
Desorption of H_2O (and other neutral species) is probably dominated by XESD

Taking :
- the absorption cross-section at 540 eV as 1.10^{-18} cm²
- the first 10 ML are involved in desorption (~ mean free path of a 500 eV e- in ice)

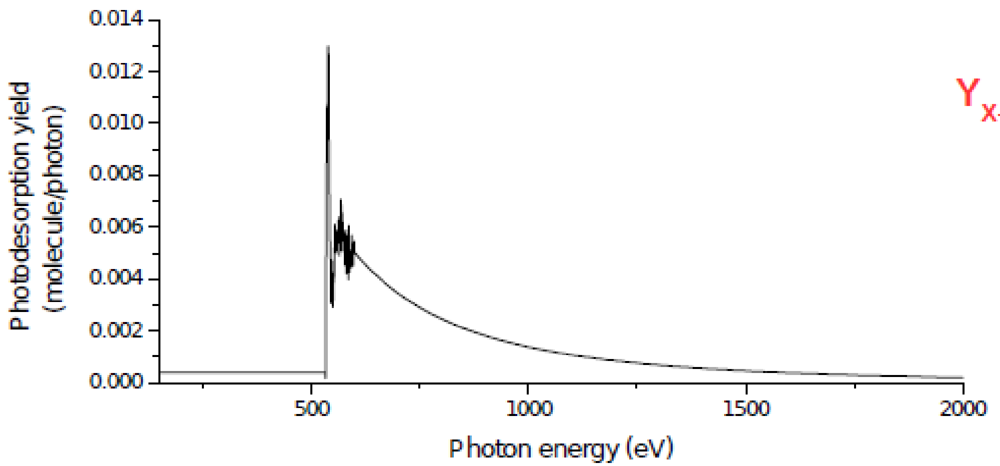
	Y^{inc}	Y^{abs}	
X-Ray (540 eV)	$1,2.10^{-2}$ ph^{-1}	1,2 / absorbed photon	This work
UV (10 eV)	$2.\ 10^{-4}$ ph^{-1}	1.10^{-3} / absorbed photon	This work
Electron (87eV)		0,5 / electron	Kimmel 2005

Astrophysical implication

Astrophysical models integrate from 0,1 to 10 keV.
E.g. spectrum from Walsh et al. 2012
based on TW Hydrae measurements :



Far off-resonance (>600 eV) we can extrapolate our data using the known atomic O 1s absorption cross-section (Berkowitz 2002) :



Multiplied by the above spectrum and averaged :

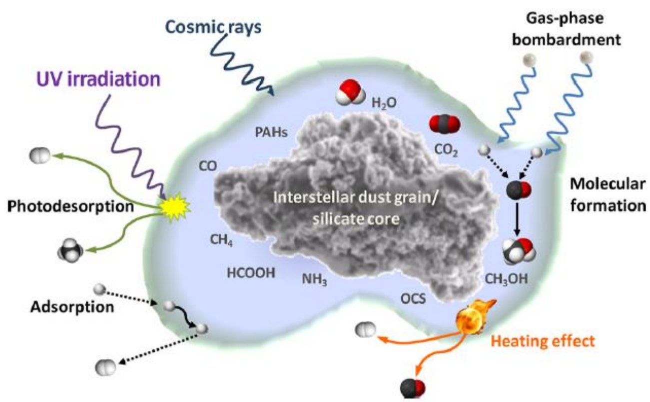
$Y_{X\text{-ray}}$ ~ 2.10-3 molecule/incident photon

➡ **$Y_{X\text{-ray}} > Y_{UV}$ (~3.10^{-4})**

Therefore X-ray photodesorption should dominate in large regions of the disk

Conclusion

SOLID PHASE



GAS PHASE

Non-thermal desorption of intact species

CH_3OH H_2CO $HCOOCH_3$

Dissociation and desorption of fragments

HCO, H_3CO, OH…

?

Gas phase chemistry

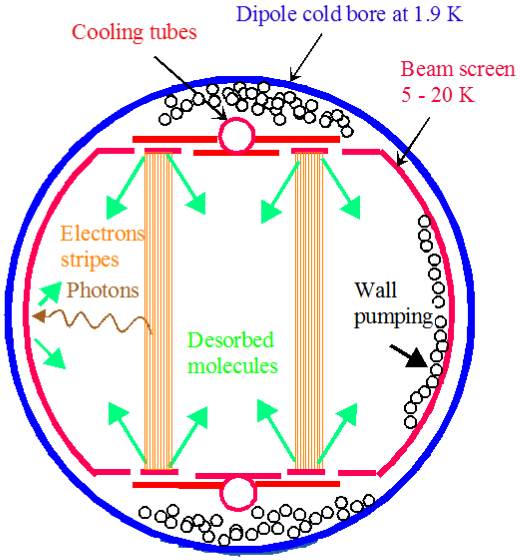
- ❑ CO induced desorption - not the key to explain the desorption of organics
- ❑ *BUT* photodesorption impact *both solid and gas phases chemical networks*
- ❑ Importance to provide accurate Yields
- ❑ Amorphous Solid Water

    New UV and X-rays Yields for neutral H_2O

    Importance of X-rays impact in protoplanetary disks

    Importance to study H_2O-rich ice mixtures

Photon and Electron Stimulated Desorption in particles accelerators

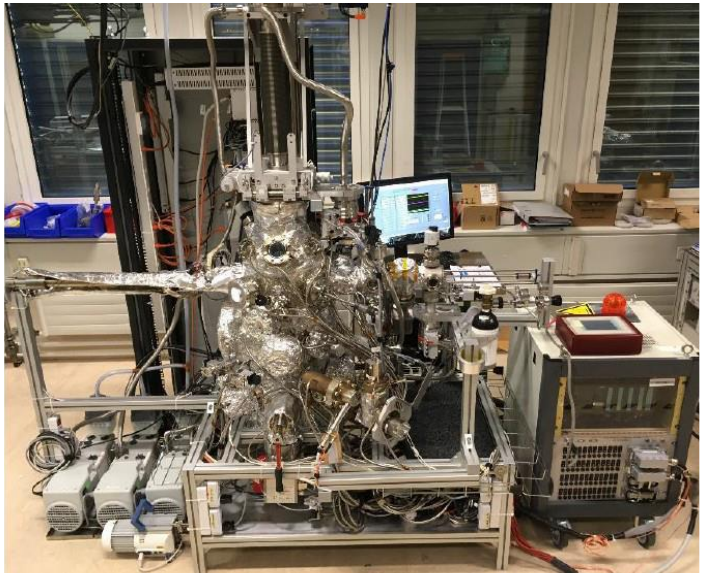


Cut of L H C beam pipe

Cold surfaces
(2 – 20 K)

Residual gases :
H_2, H_2O, CO, CO_2, CH_4…

Set-up at CERN designed by V. Baglin and B. Henrist, installed by M. Haubner and B. Henrist



- Secondary Electron Yields variation with:
  - Electron energy
  - Material, coating
  - Surface treatment
  - Absorbed electron dose (scrubbing)
  - Condensate layers

Acknowledgments

Co-workers

M. Bertin, R. Dupuy, T. Putaud, M. Doronin, G. Feraud, X. Michaut, P. Jeseck, L. Philippe, J.-H. Fillion.

C. Romanzin

collaboration

R. Cimino, V. Baglin

L Nahon
N De Oliveira
G Garcia

Supports

DIM – Astrophysique et Conditions d'Apparition de la Vie