CENTRO DE ASTROBIOLOGÍA

# Photodesorption of ice molecules

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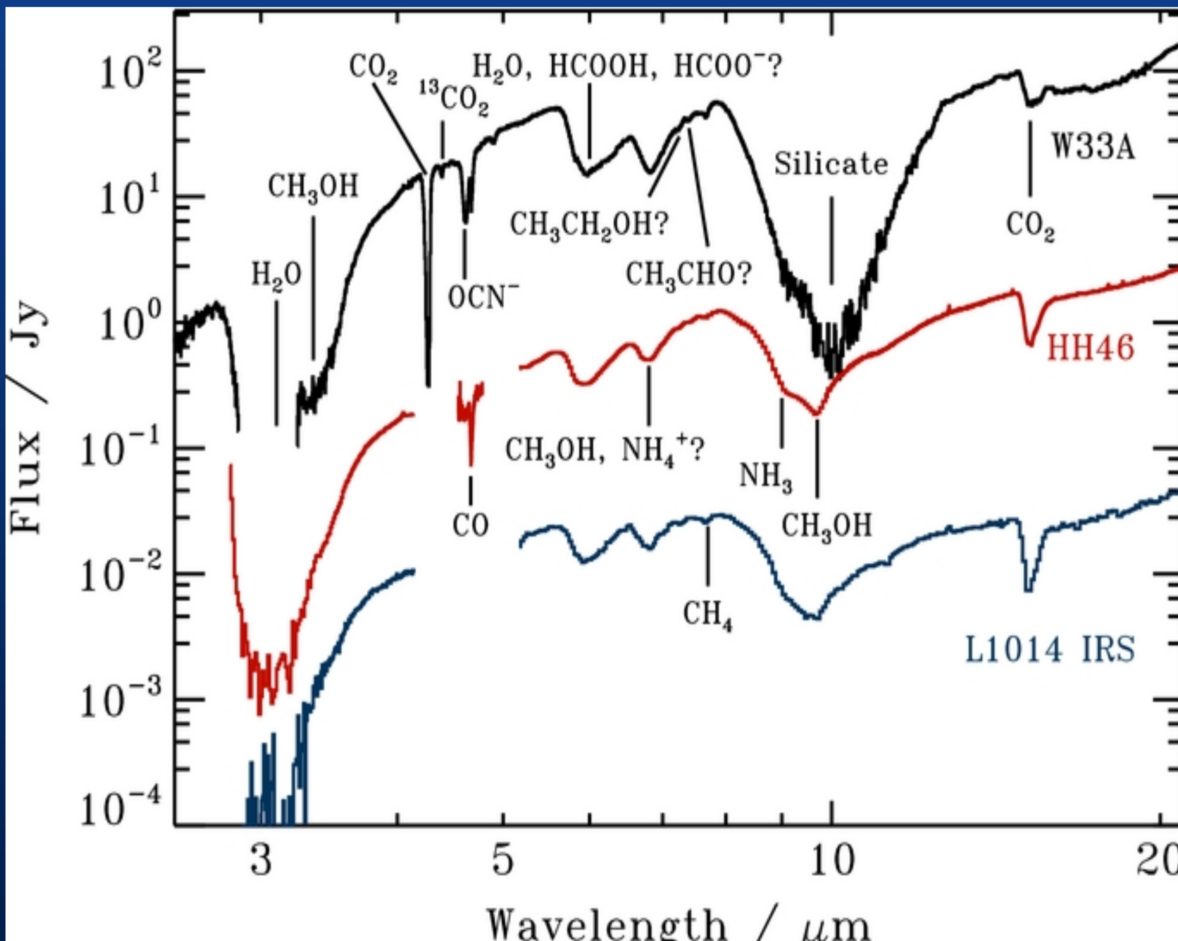
# Outline

1. The astrophysical context: ice mantles

2. Photodissociation, photodesorption, and ¨photochemidesorption¨

3. VUV-spectroscopy of pure ices

# Ice Molecules



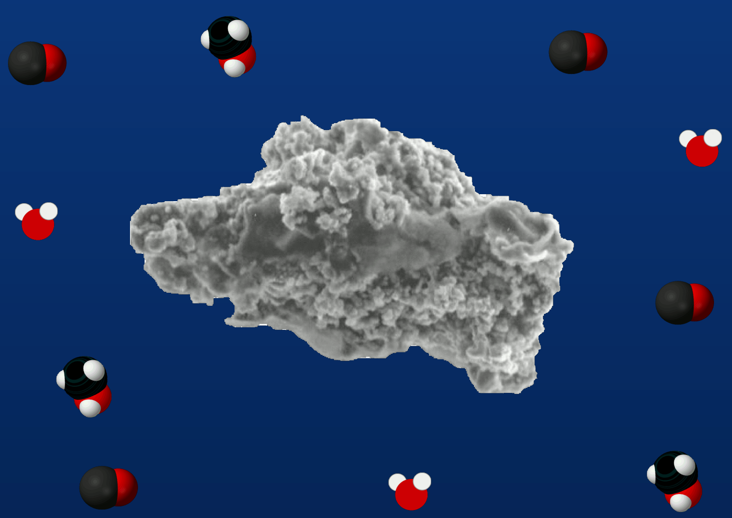

Protostars of $10^5$ $L_\odot$, 12 $L_\odot$ and 0.09 $L_\odot$

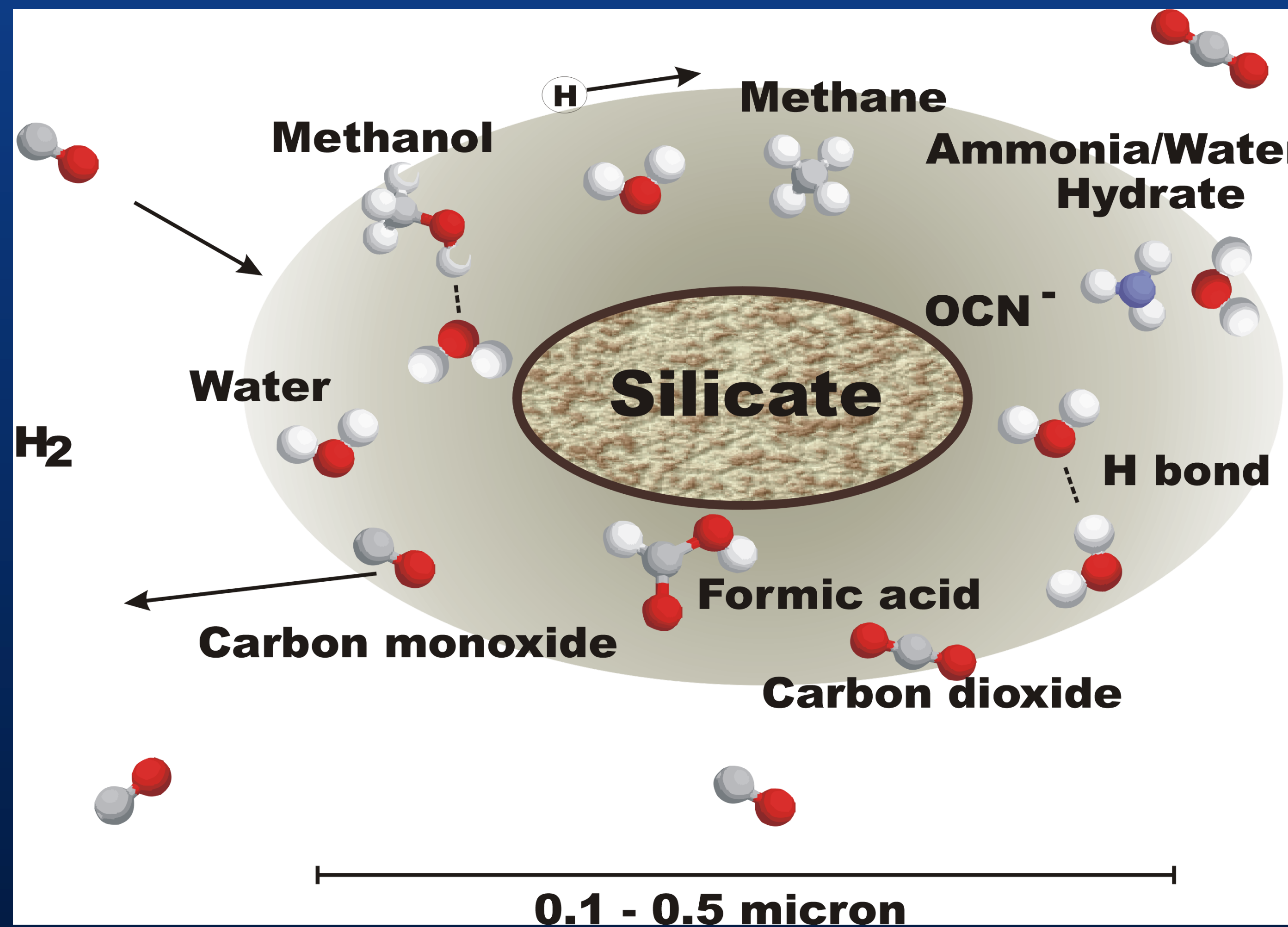
Abundances relative to $H_2O$

| | |
|---|---|
| **CO** | few-50% |
| **$CO_2$** | 15-35% |
| **$CH_4$** | 0.4-8% |
| **$CH_3OH$** | 1-30% |
| **HCOOH** | 1-9% |
| [$NH_3$] | 2-15% |
| $H_2CO$ | 1-6% |
| [HCOO-] | 1-9% |
| OCS | <0.05, 0.2% |
| [$SO_2$] | <=3% |
| [$NH_4$+] | 3-12% |
| [OCN-] | <0.3, 6% |

Öberg et al. 2011

# Model of dust grain with ice mantle

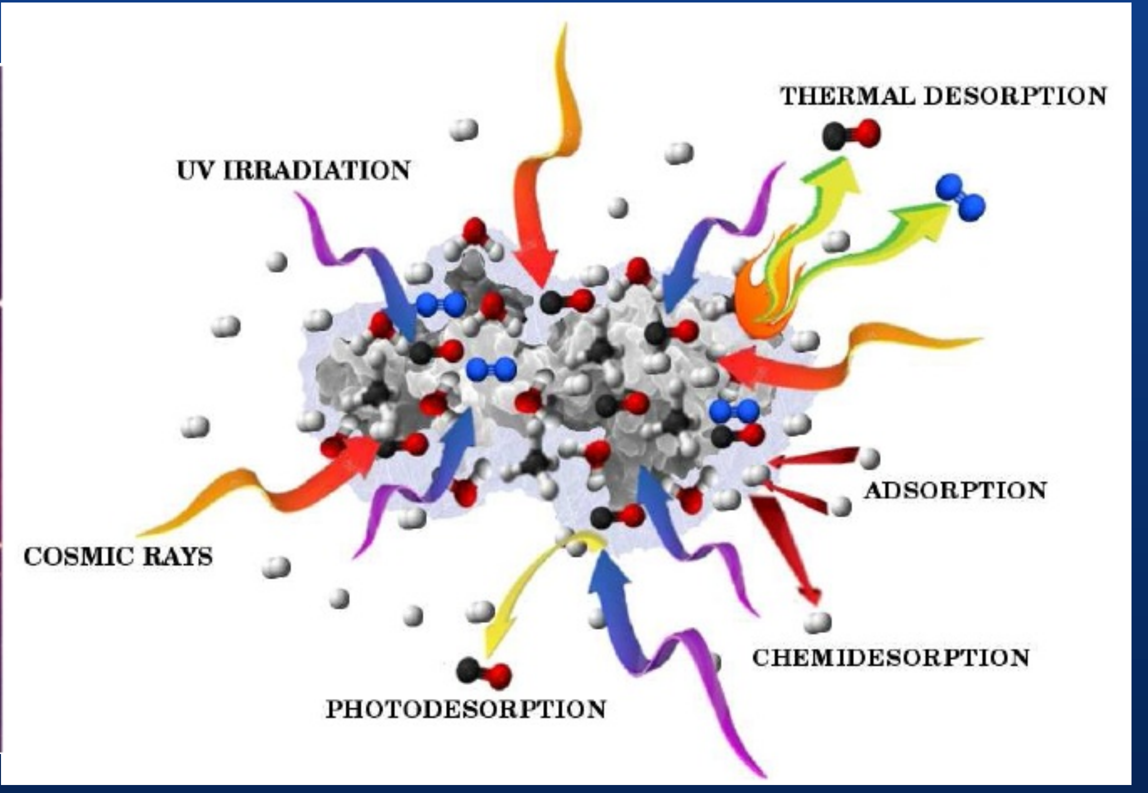







Courtesy of W. F. Thi and A. Jiménez Escobar

# Ice mantle processes

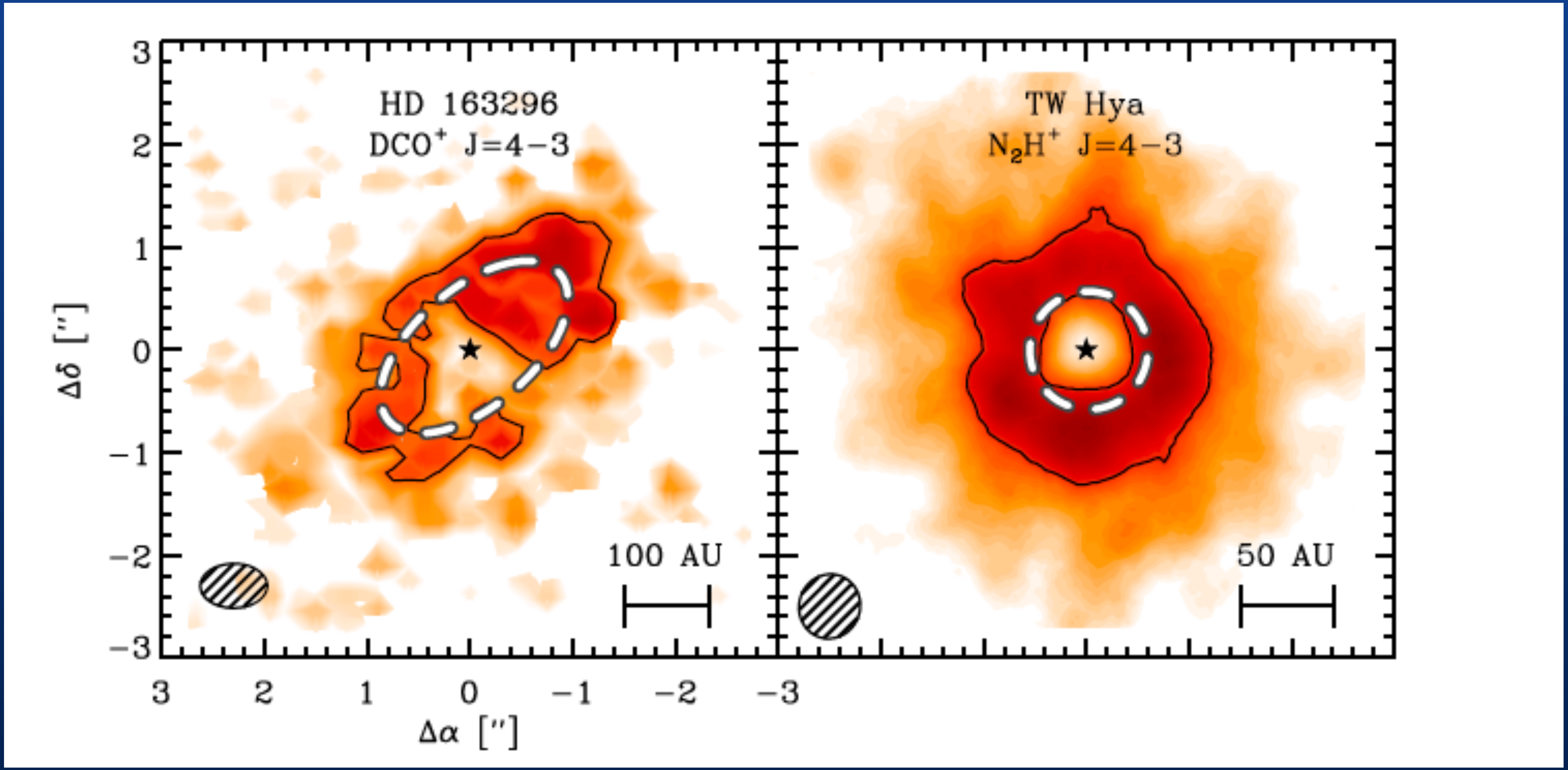



Ice mantles are energetically processed (in **dense cloud interiors**):

- ~~Thermal processing~~
- ~~UV irradiation~~
- Cosmic rays → excitation of $H_2$ → secondary UV-field

Cruz Díaz, PhD thesis (2014)

# The CO snowline




CO snow line observed with ALMA, using tracers of the absence of CO in the gas-phase.
Dashed line is 17 K isotherm where CO freezes out.

Pontoppidan et al., Protostars and Planets VI, 2014

# ISAC = InterStellar Astrochemistry Chamber

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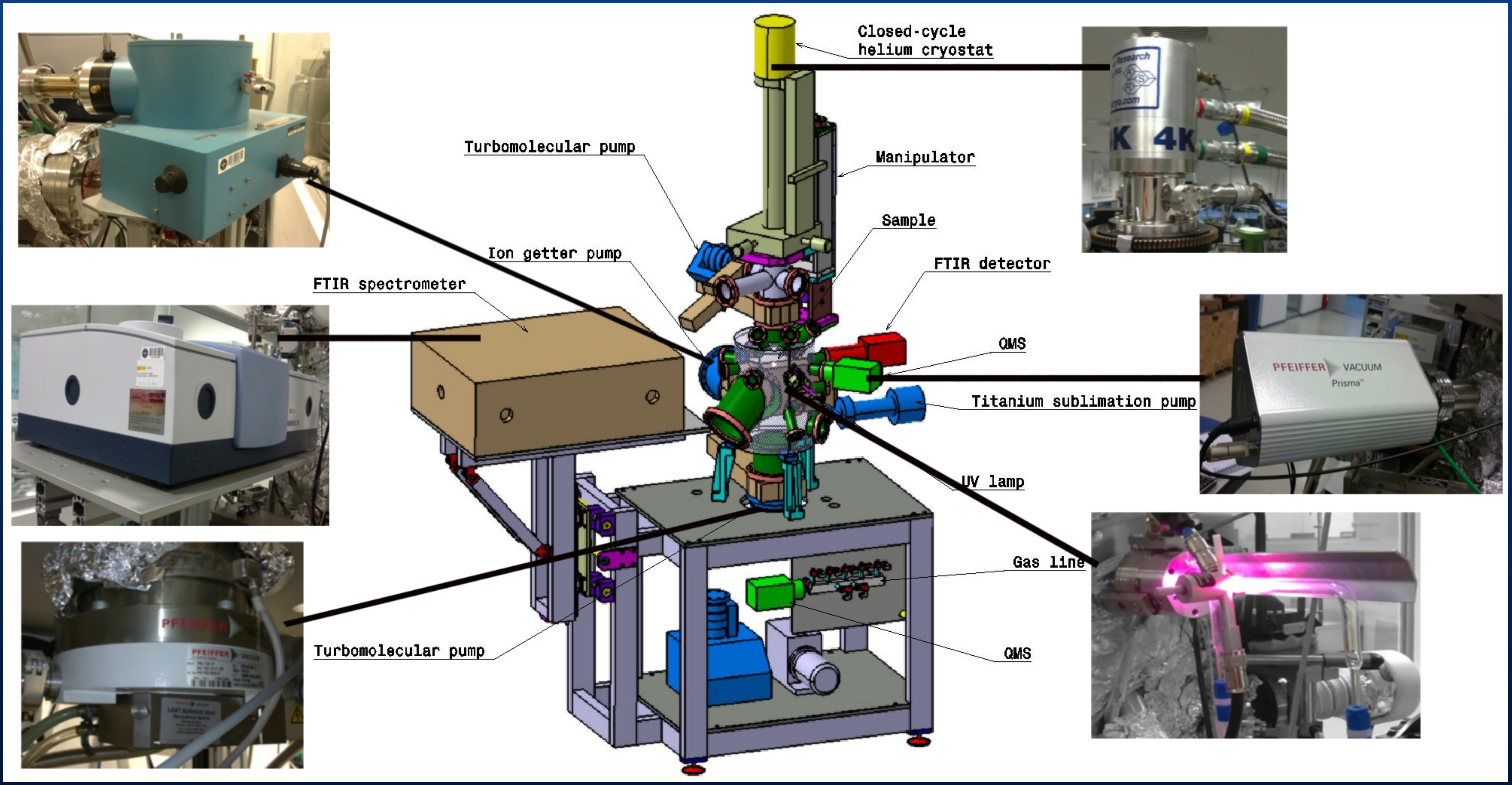
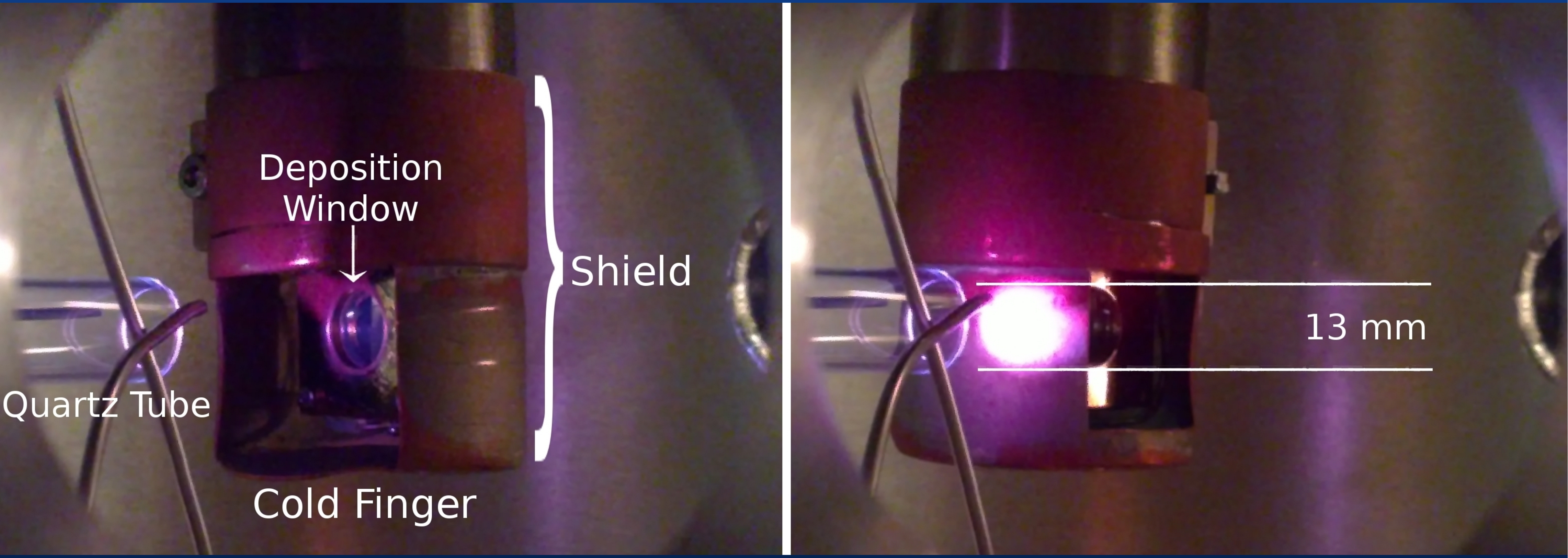
**ISAC** is UHV set-up, P~4 $10^{-11}$ mbar, for ice deposition at 8 K, which can be heated or irradiated.

Solid: IR, Raman, and vacuum-UV spectroscopy
Gas:  QMS



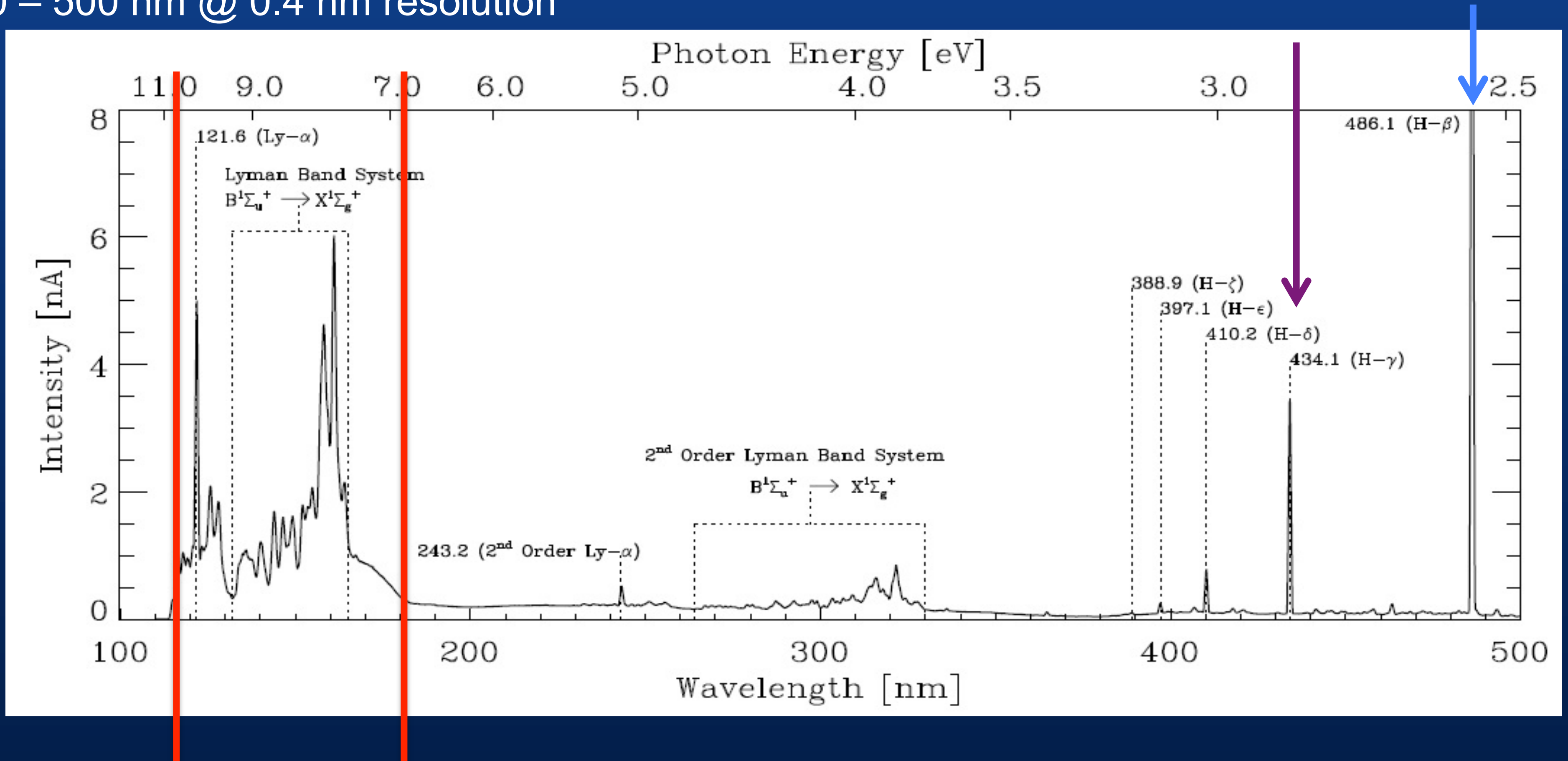
# Sample irradiation with UV



# Photoprocessing of ice analogs

## Vacuum-UV Spectroscopy

- McPherson monochromator + PMT
- 100 – 500 nm @ 0.4 nm resolution




MgF$_2$ cutoff
114 nm / 10.87 eV

Low lamp flux
183 nm / 6.77 eV

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2. Photodissociation, photodesorption, and "photochemidesorption"

3. VUV-spectroscopy of pure ices

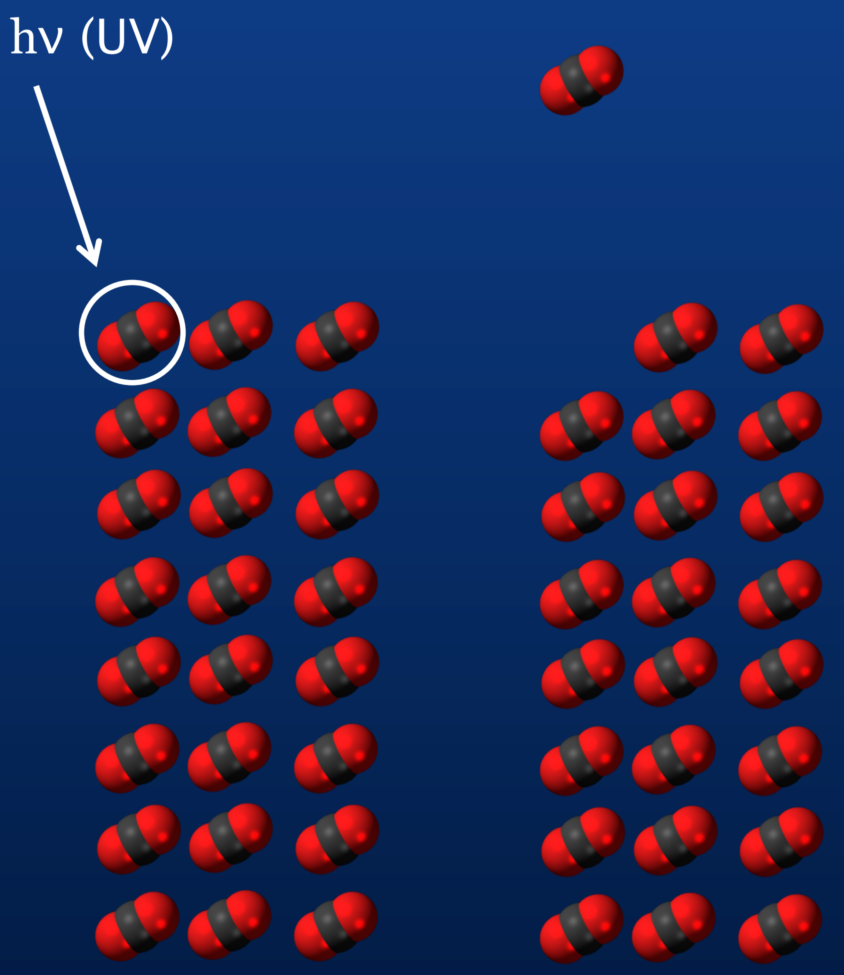
# Ice photodesorption

What is photodesorption?

The absorption of a photon in the ice induces the desorption of a molecule to the gas phase.

Why should we care?

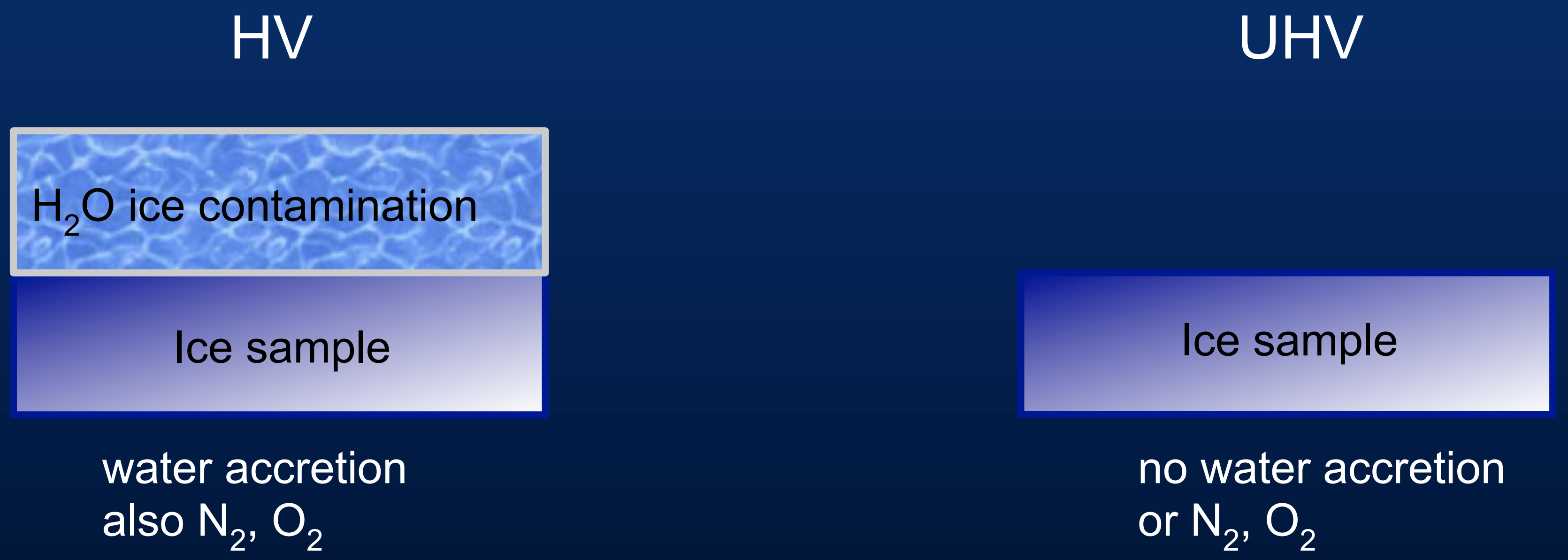
Because we need a non-thermal desorption mechanism to explain the observations of molecules toward very cold regions.



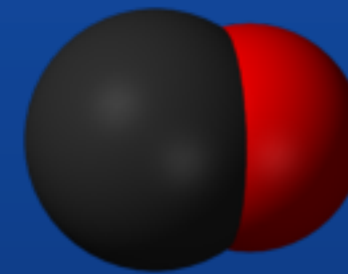
# Photodesorption requires UV irradiation of ice under ultra-high vacuum conditions

Experiments:
Westley+1995; Öberg+2007,2009,2010; Muñoz Caro+2010; Fayolle+ 2011,2013; Bahr&Baragiola2012; Bertin+2012a,b,2013; Yuan&Yates2013,2014; Chen+2014; Fillion+2014; Martín-Doménech+2015, sub.

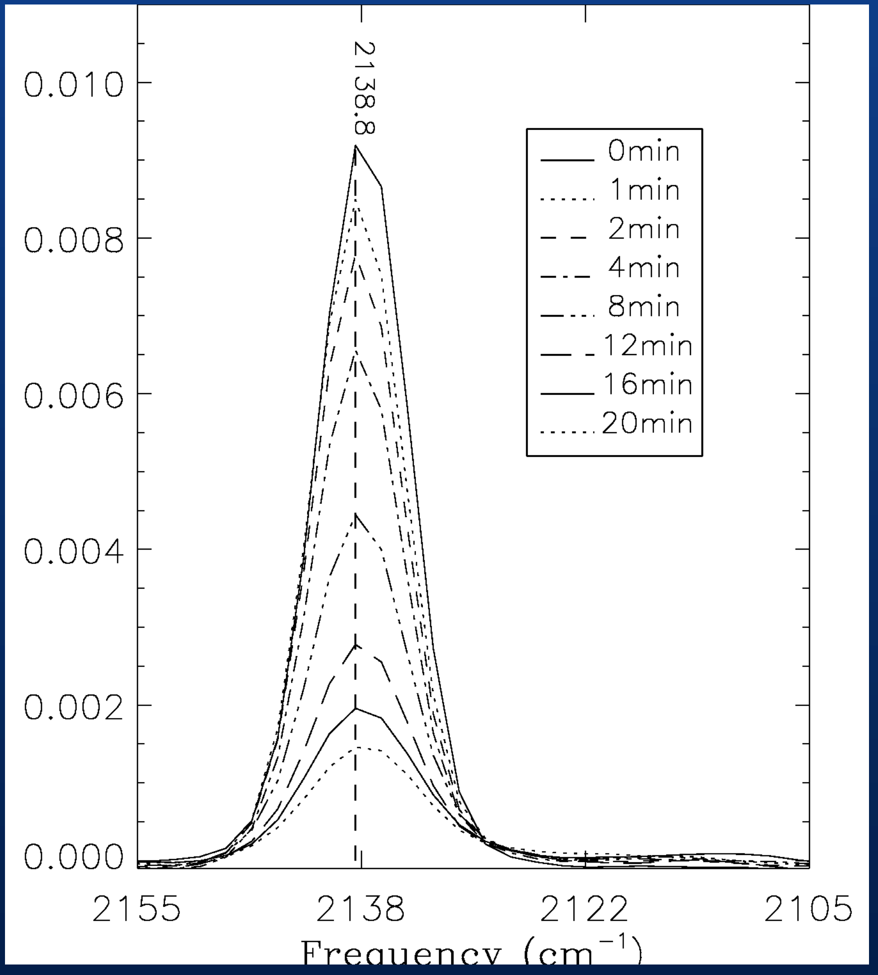
Theory:
Andersson&van Dishoeck2008; Arasa+2013; van Hemert+2015,sub.

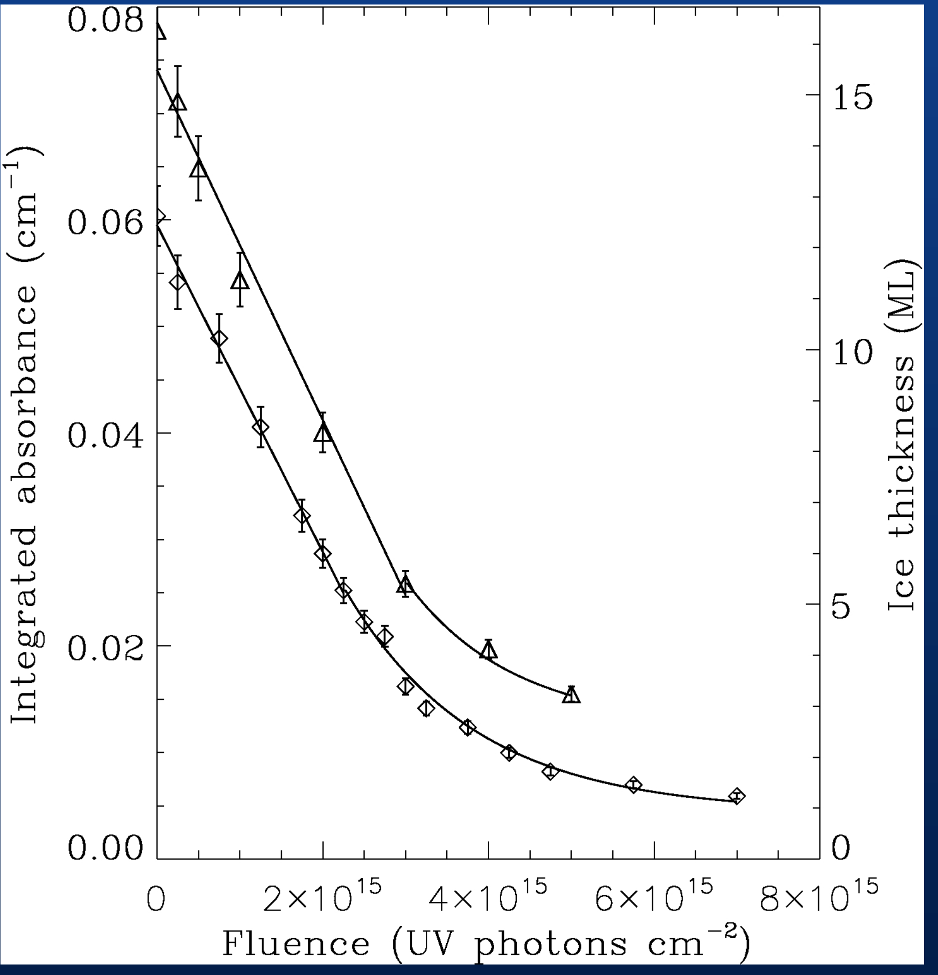


# Photodesorption of CO ice



Solid sample ←→IR spectroscopy



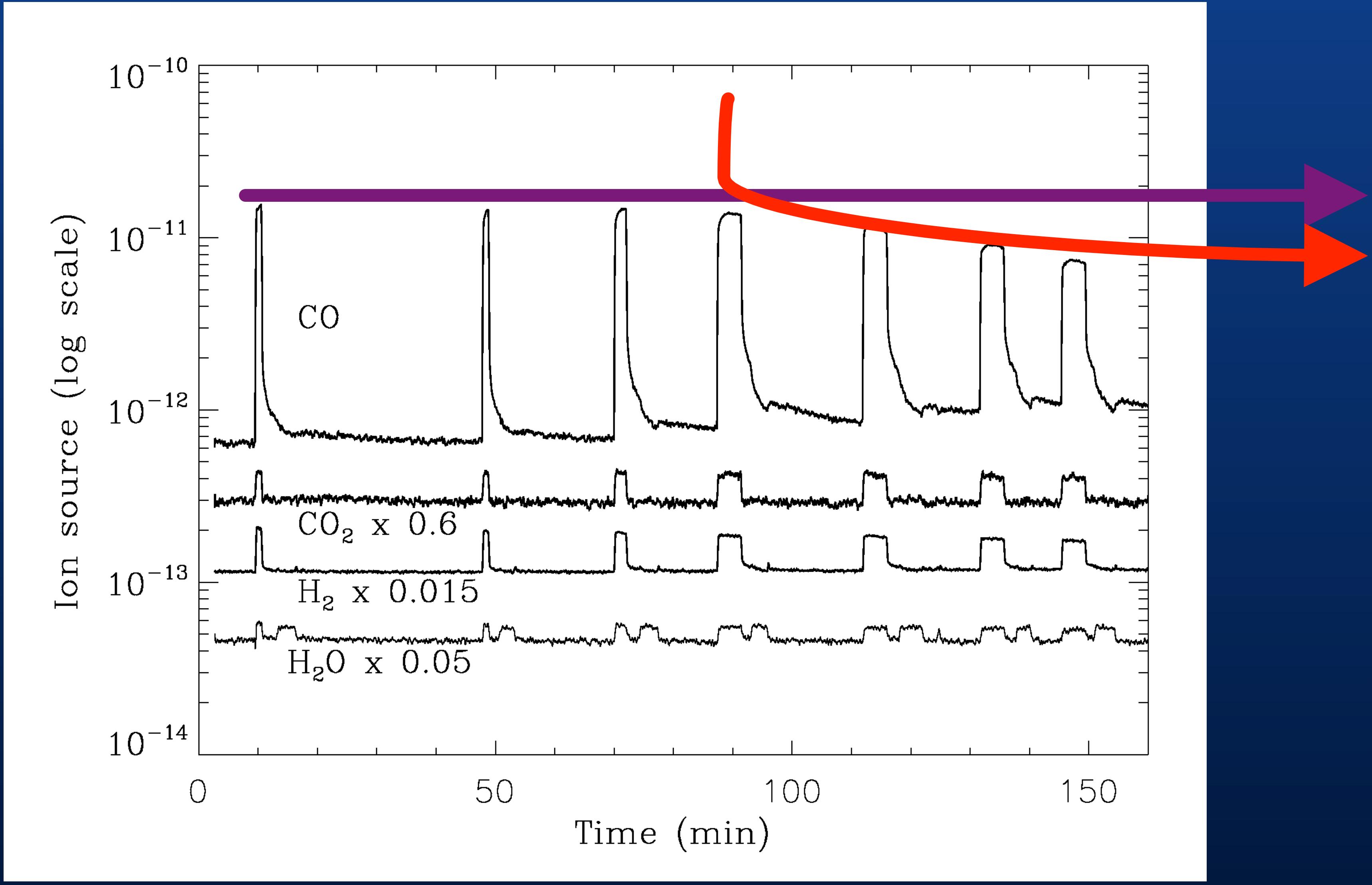




IR bands are integrated to measure decrease in column density during irradiation

Muñoz Caro et al. 2010

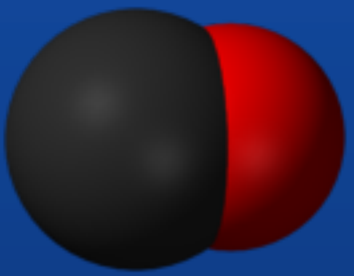
# Photodesorption of CO ice

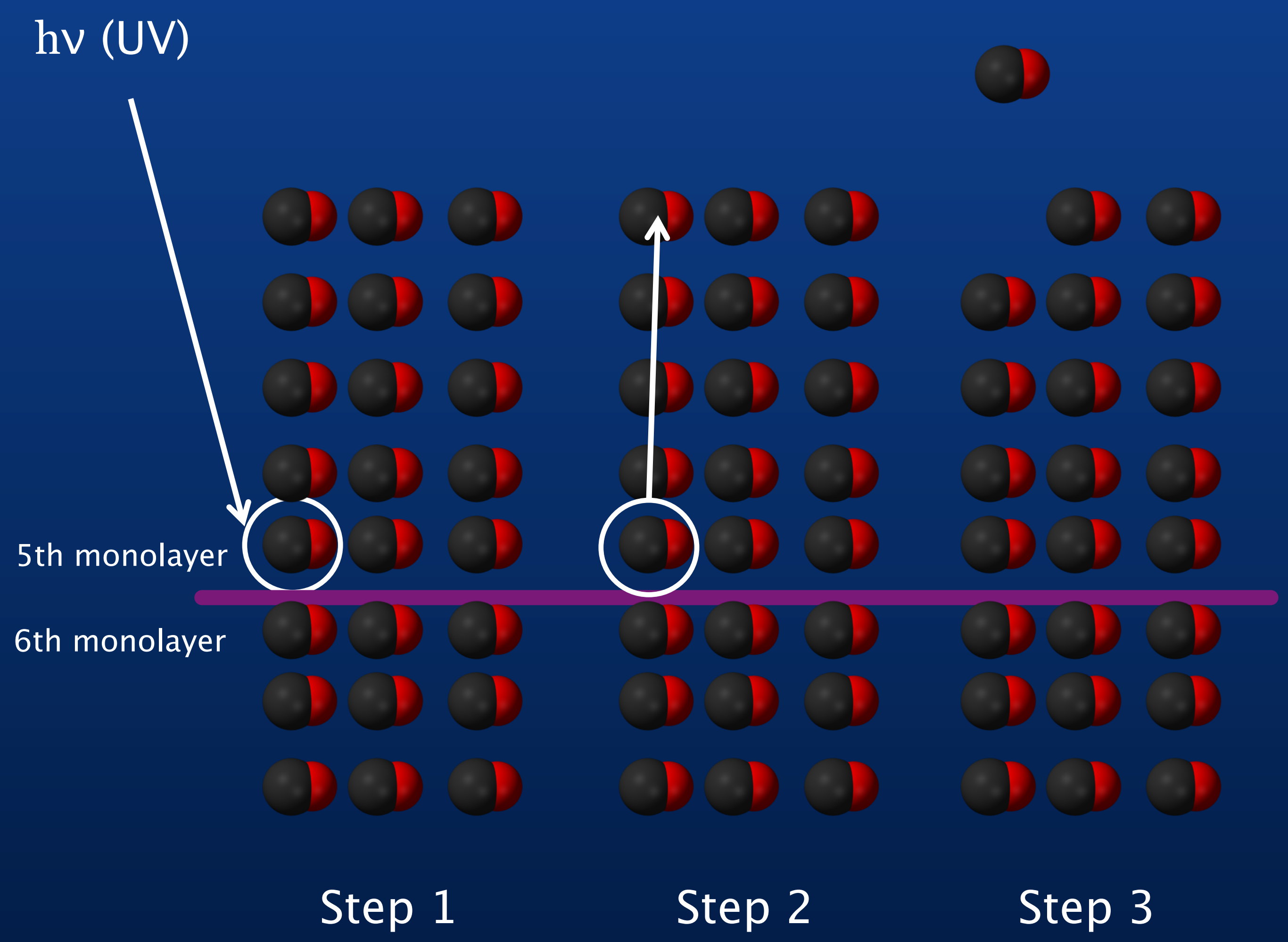
Gas phase ←→ Mass spectrometry




Muñoz Caro et al., A&A, 2010

# Photodesorption of CO ice






Indirect desorption induced by electronic transitions (DIET): Electronic excitation energy is redistributed to neighbors and provides energy to surface molecules breaking intermolecular bonds.

A proper understanding of DIET needs the photodesorption rate *per absorbed photon*

We need to measure the ice UV absorption cross sections!!

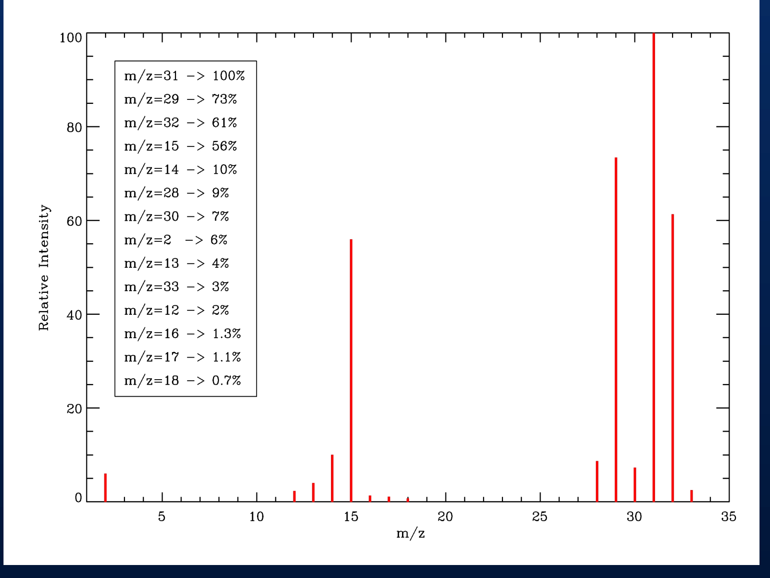
Muñoz Caro et al. 2010, Fayolle et al. 2011, Chen et al. 2014

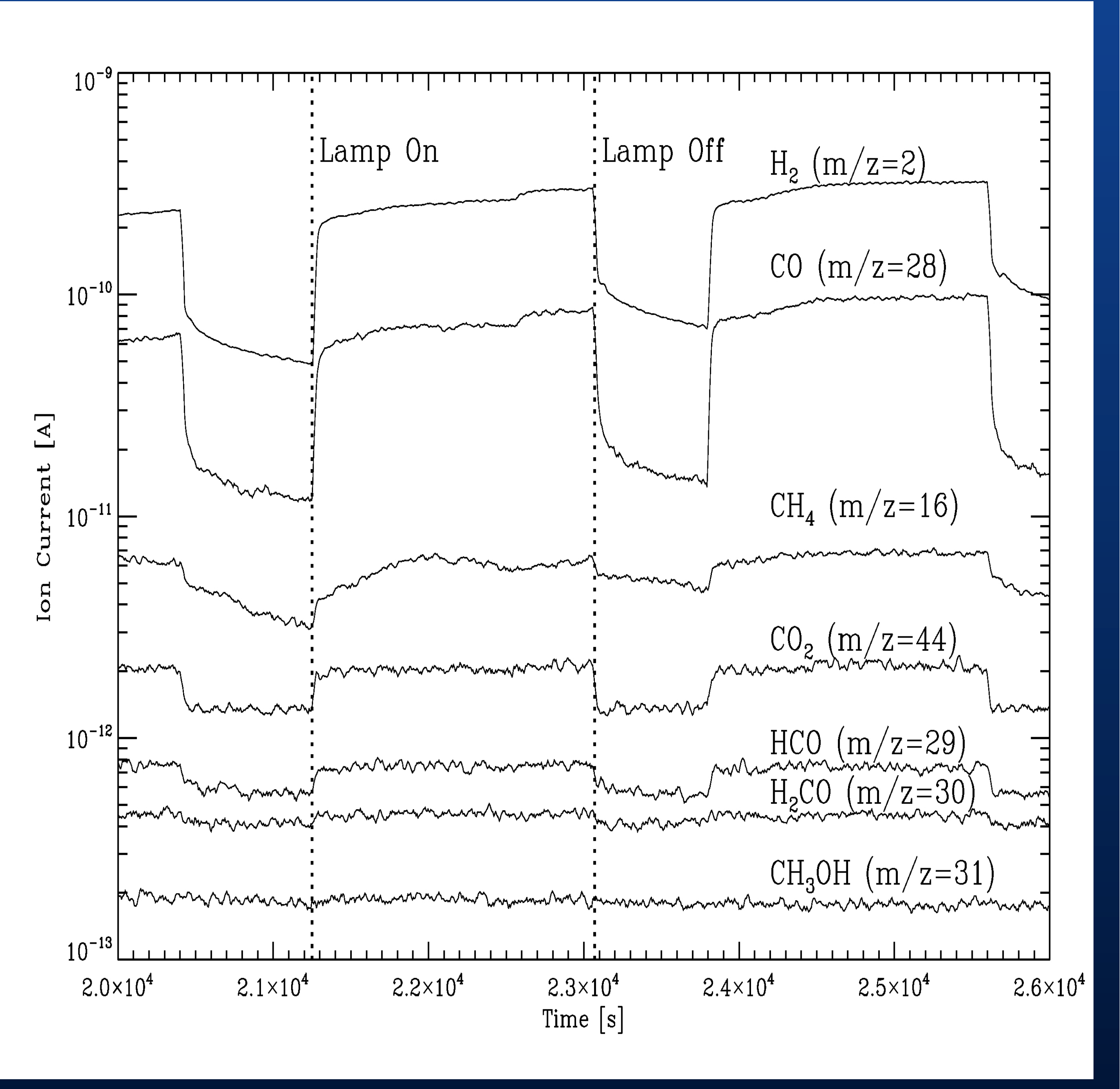
# UV irradiation of pure $CH_3OH$ ice

Non-thermal desorption mechanism of $CH_3OH$ in cold regions is required to explain gas phase abundances.

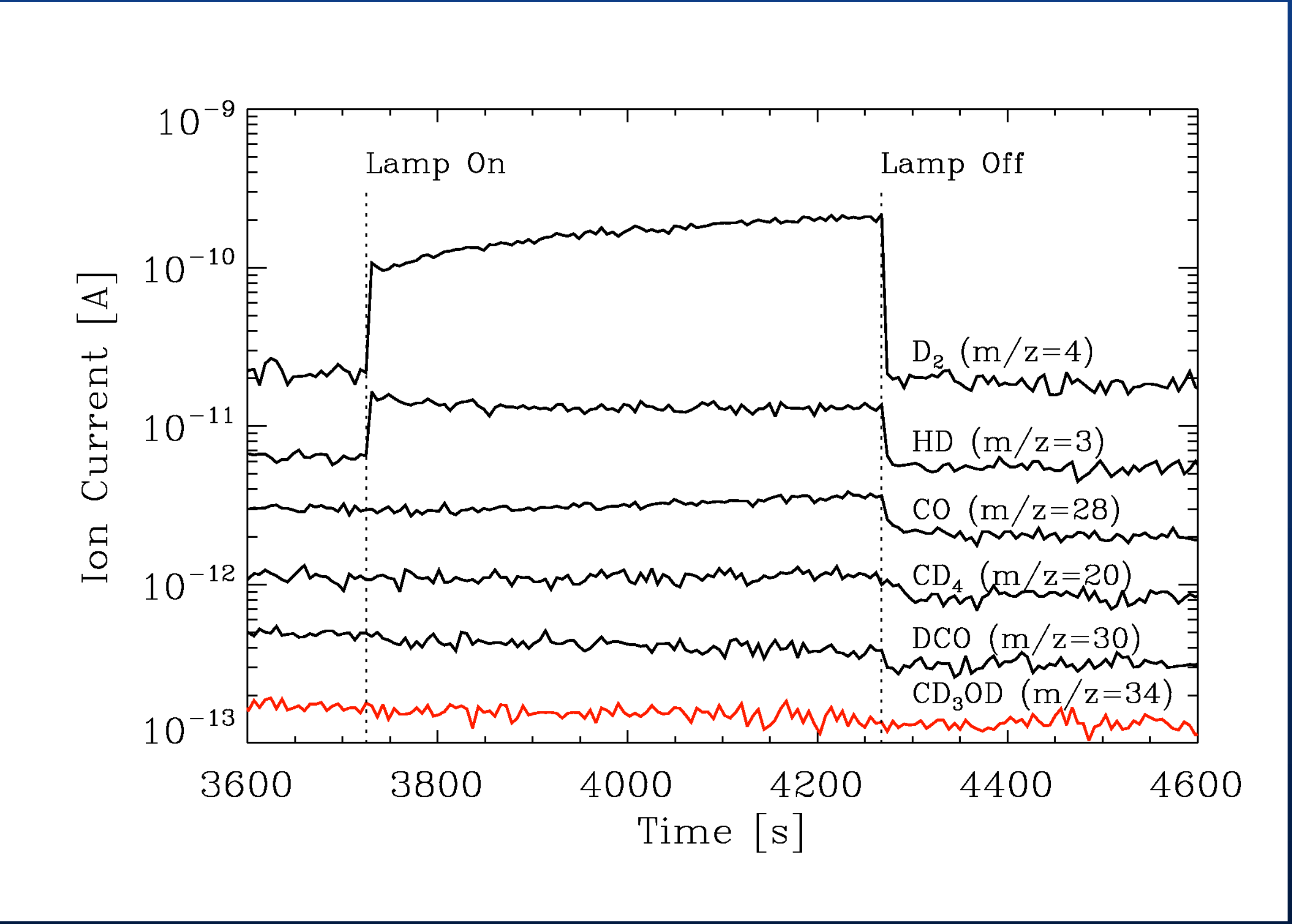
We see **photodesorption** of
m/z = 2 (H2), 28 (CO), 16 (CH4), 29 (HCO), 30 (H2CO), 32 (O2),
but no m/z = 31...
no methanol photodesorption!!!
Rate <3 $10^{-4}$ molecules/photon

m/z 31



# UV irradiation of pure $CD_3OD$ ice

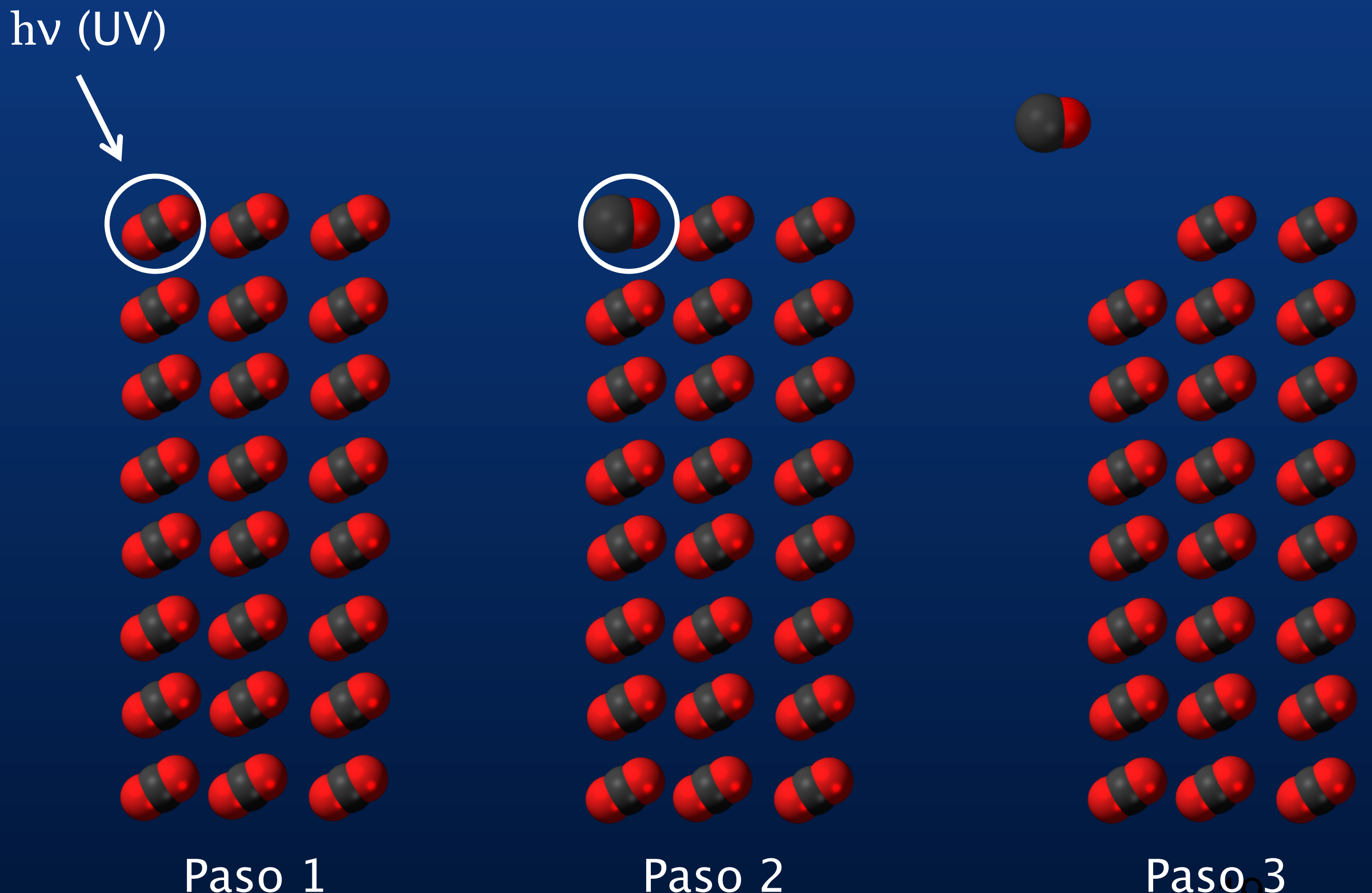



Cruz Diaz et al. 2015, A&A, sub.

# "New" process: Photochemidesorption

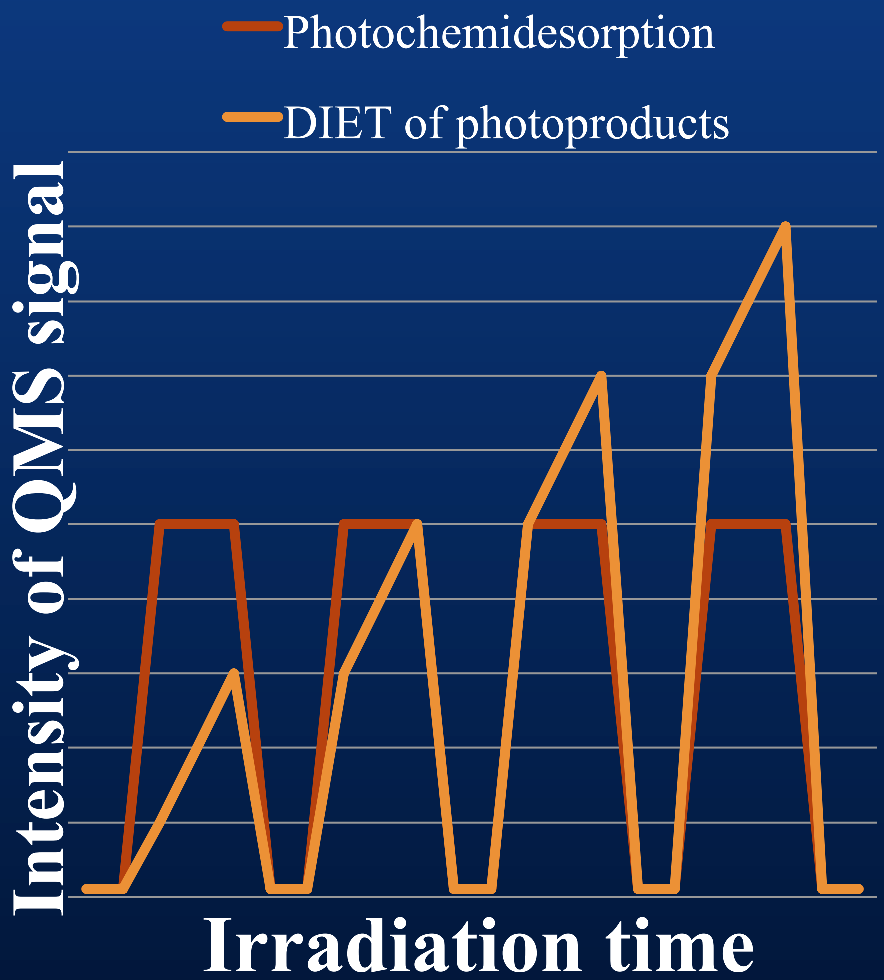
Photochemidesorption: a new molecule forms on the surface and directly desorbs when the kinetic energy overcomes intermolecular binding energy.

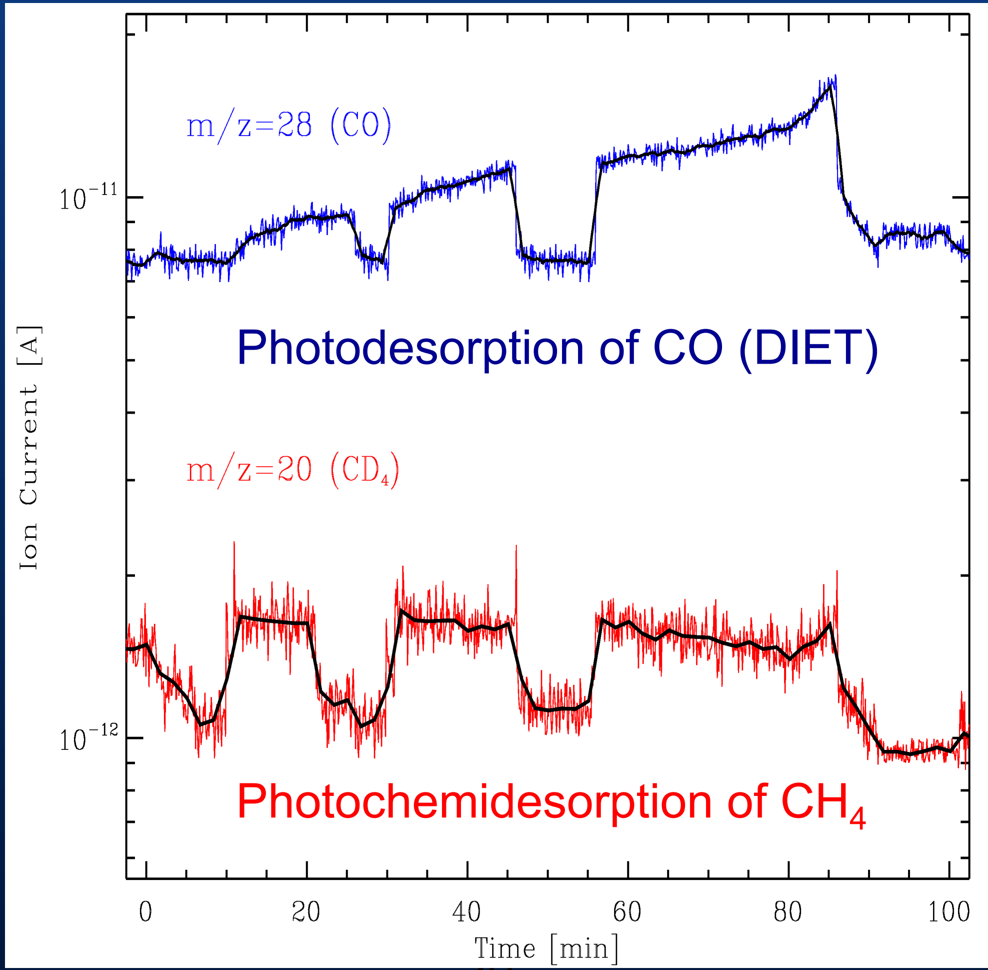
Example: Pure $CH_4$ ice does not photodesorb significantly, but photochemidesorption of $CH_4$ occurs during $CH_3OH$ ice irradiation.



# Photochemidesorption versus DIET

Photoproducts formed in the ice bulk can desorb later via the DIET mechanism, after the ice monolayers on top are removed during irradiation (2 photons involved).






Cruz Díaz et al. 2015, A&A; Martín-Doménech et al. 2015, A&A

# Calibration of QMS for photodesorption (I)

$$A(m/z) = k_{QMS}\ \sigma(X)\ N(X)\ I_f(X)\ F_f(X)\ S(m/z)$$

A(m/z) is integrated area of QMS signal during photodesorption

$k_{QMS}$ is a proportionality constant

σ(mol) is ionization cross section of species X for electron energy of MS

N(X) is total number of desorbed molecules per $cm^{-2}$

$I_f$ is fraction of molecules ionized z times in MS

$F_f(X)$ is fraction of molecules ionized leading to a fragment of mass *m* in MS

S(m/z) is sensitivity of QMS to the mass fragment *m/z*

**Note: $k_{QMS}$ and S(m/z) must be calibrated for every MS. Pumping speed of the molecules also plays a role.**

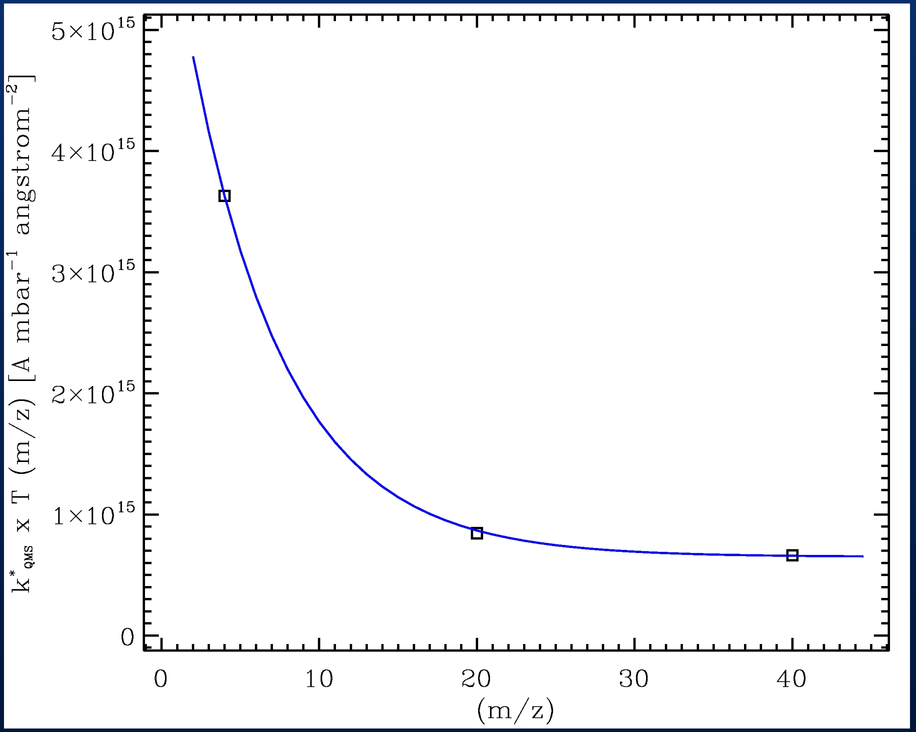
# Calibration of QMS for photodesorption (II)

$A(m/z) = k_{CO} \times (\sigma(X)/\sigma(CO)) \times N(X) \times (I_f(X)/I_f(CO)) \times F_f(X)/F_f(CO) \times (S(m/z)/S(28))$

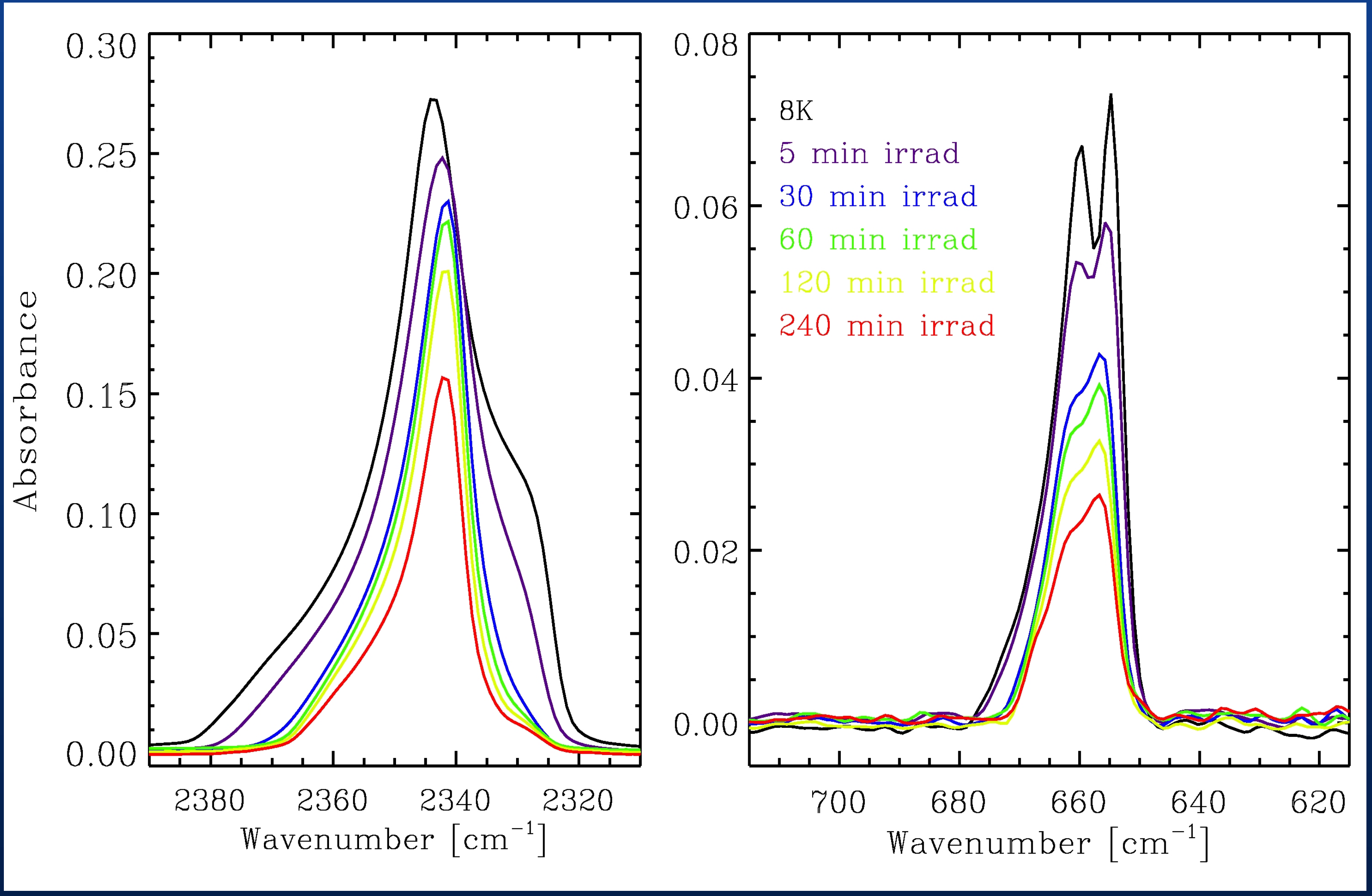
where $k_{CO} = A(28)/N(CO)$

**In addition we consider the mass dependence of QMS sensitivity, by fitting a sensitivity curve for He (m/z 4), Ne (m/z 20), Ar (m/z 40) measurements:**

$k_{CO} \times S(m/z) = 6.5\times10^{14} + 5.73\times10^{15} \exp(-(m/z)/6.11)$



# Quantification of $CO_2$ ice + UV




**Reactions:**

$CO_2$ + hv -> CO + O

$CO_2$ + O -> $CO_3$

O + O -> $O_2$

$O_2$ + O -> $O_3$

**Back reactions:**

CO + O -> $CO_2$

$CO_3$ + hv -> $CO_2$ + O

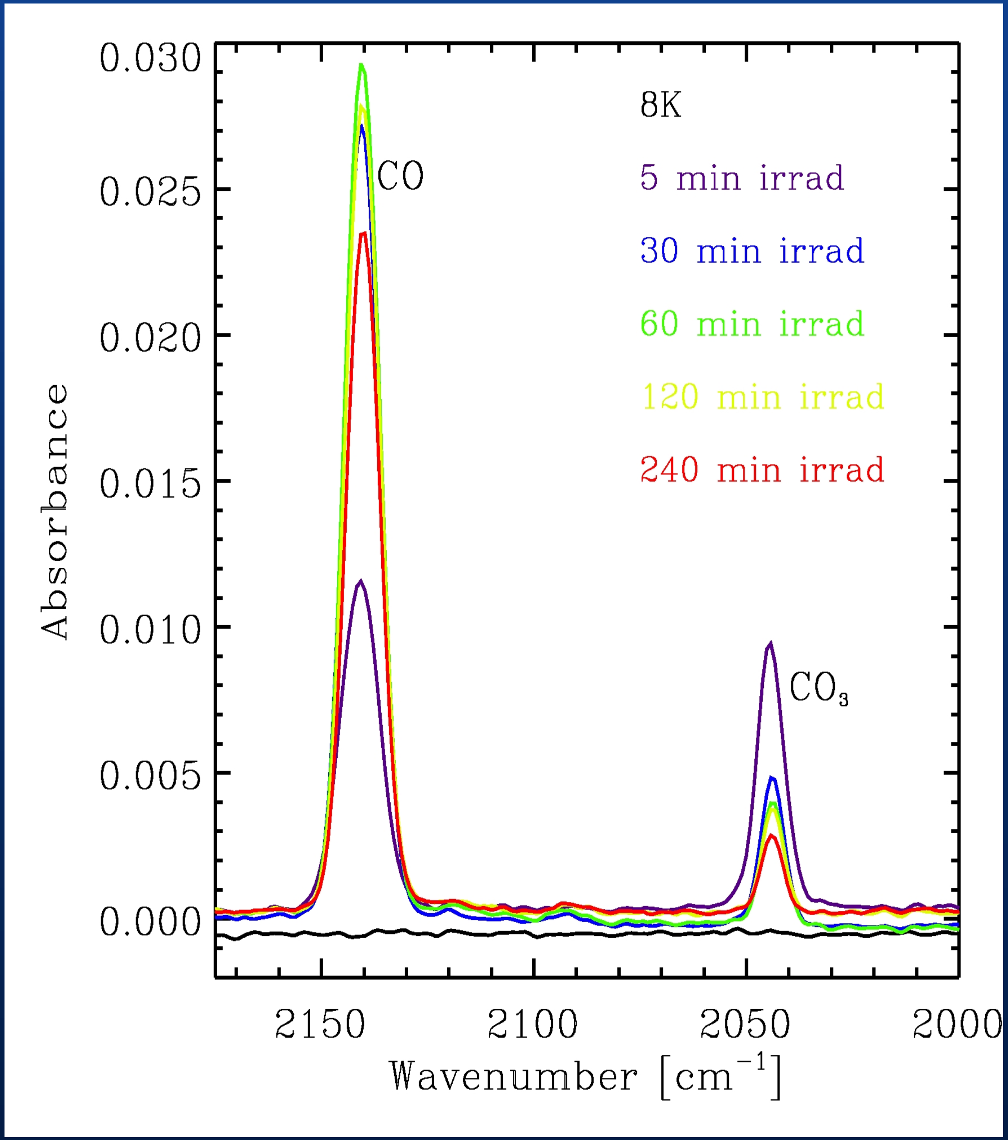
$O_2$ + hv -> O + O

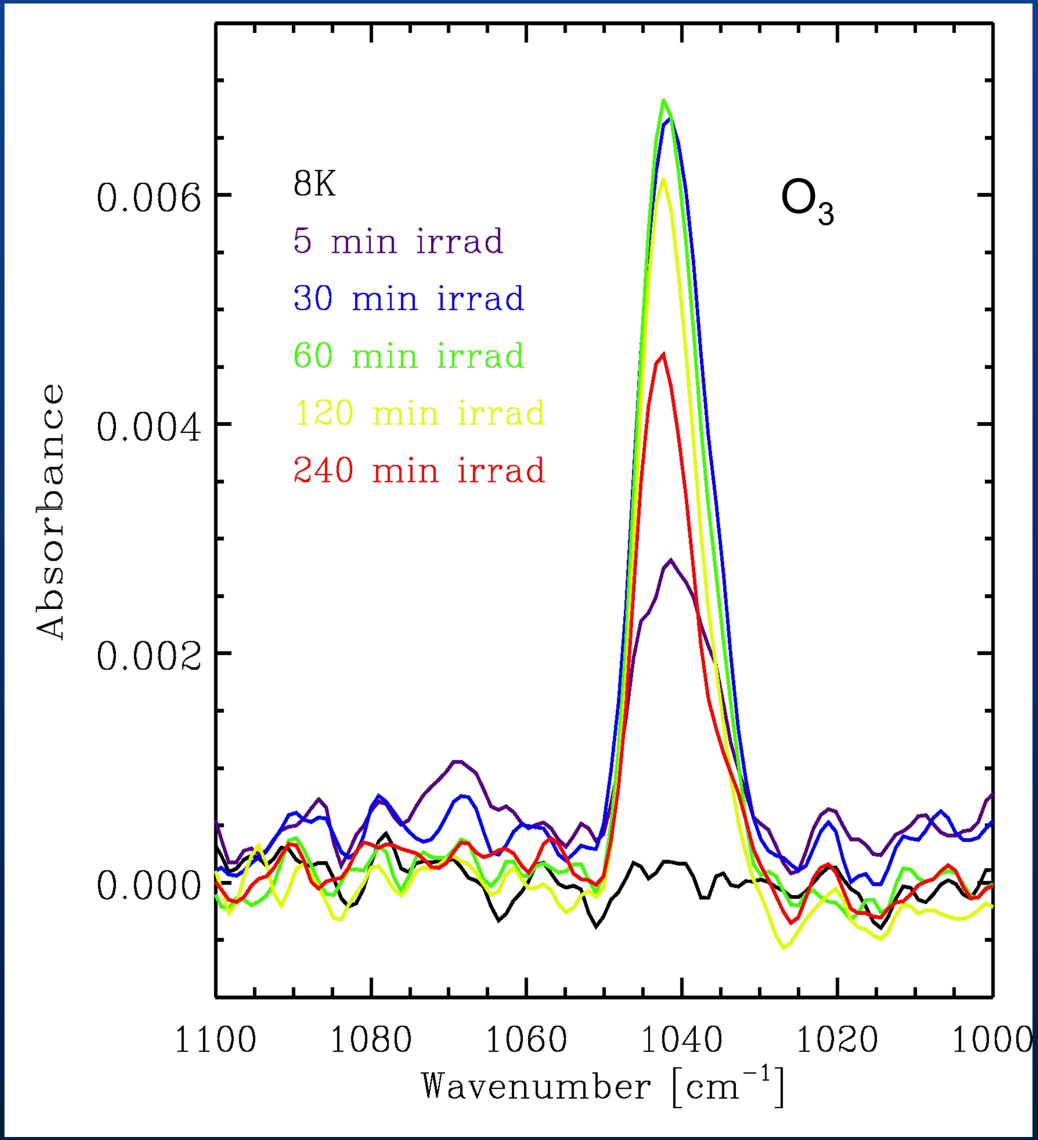
$O_3$ + hv -> $O_2$ + O

**Infrared $CO_2$ ice bands decrease during irradiation**

Martín-Doménech et al. 2015, submitted

# Quantification of $CO_2$ ice + UV

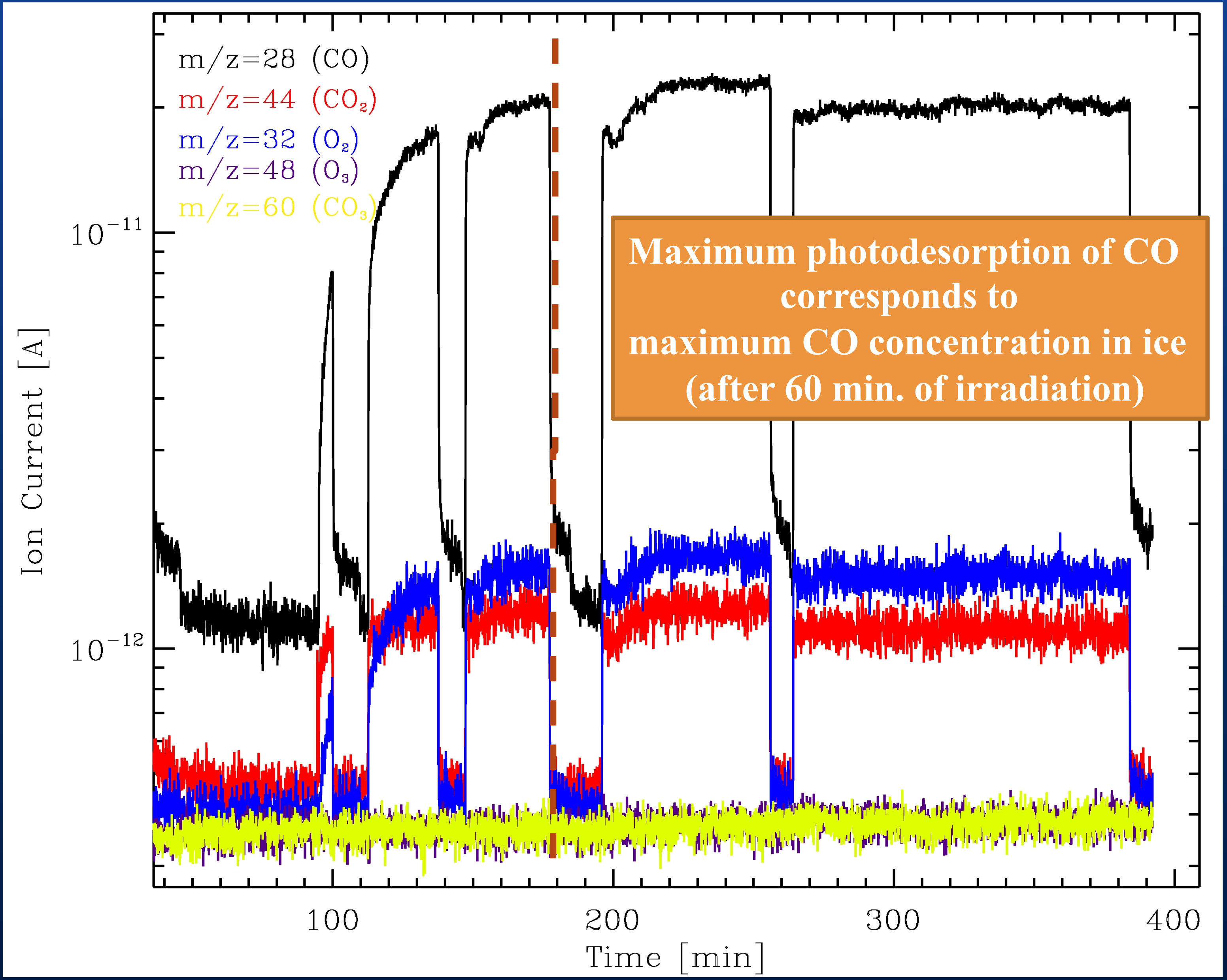



**Formation of photoproducts observed in infrared during irradiation**

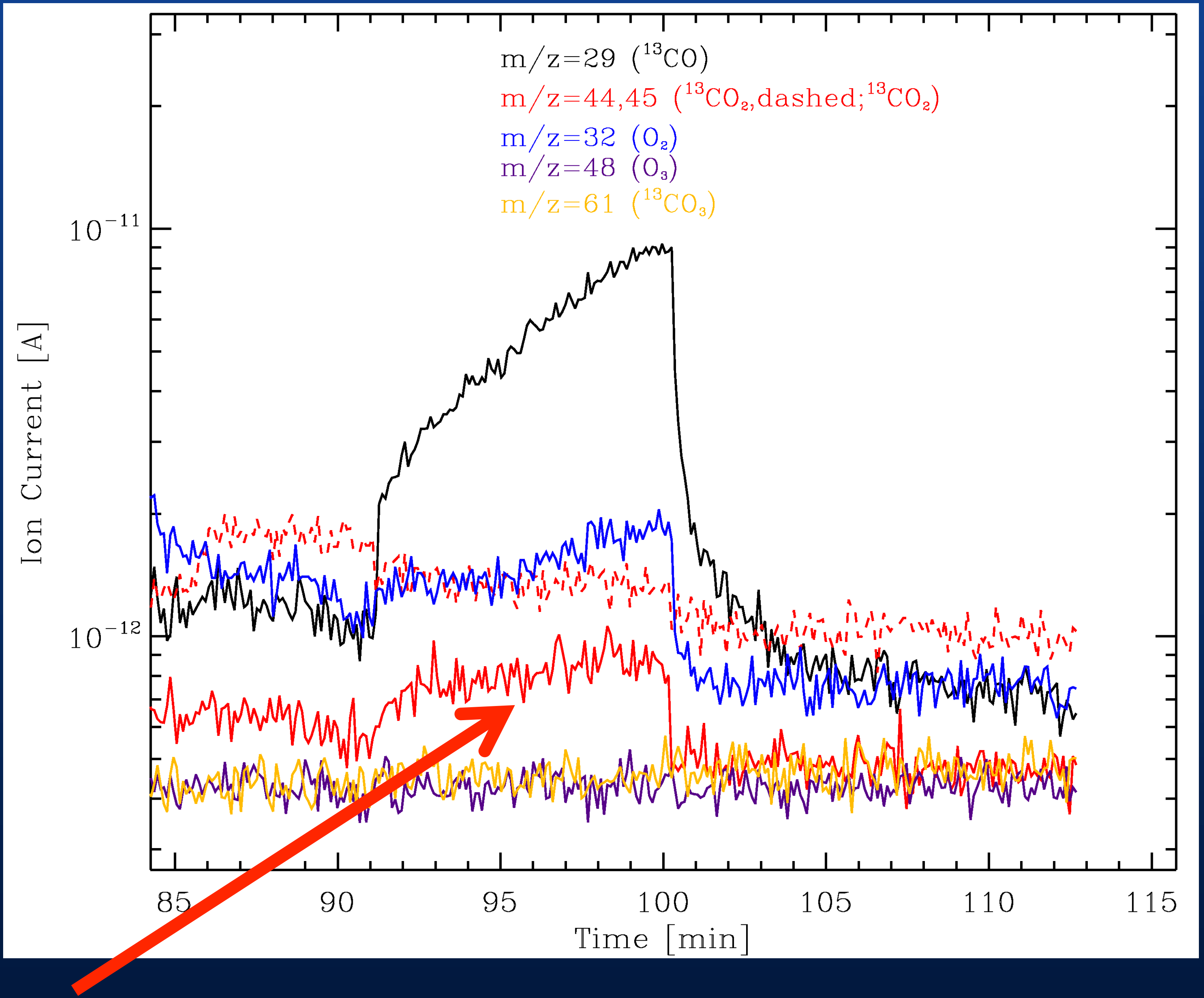
Martín-Doménech et al. 2015, submitted

# Quantification of $CO_2$ ice + UV



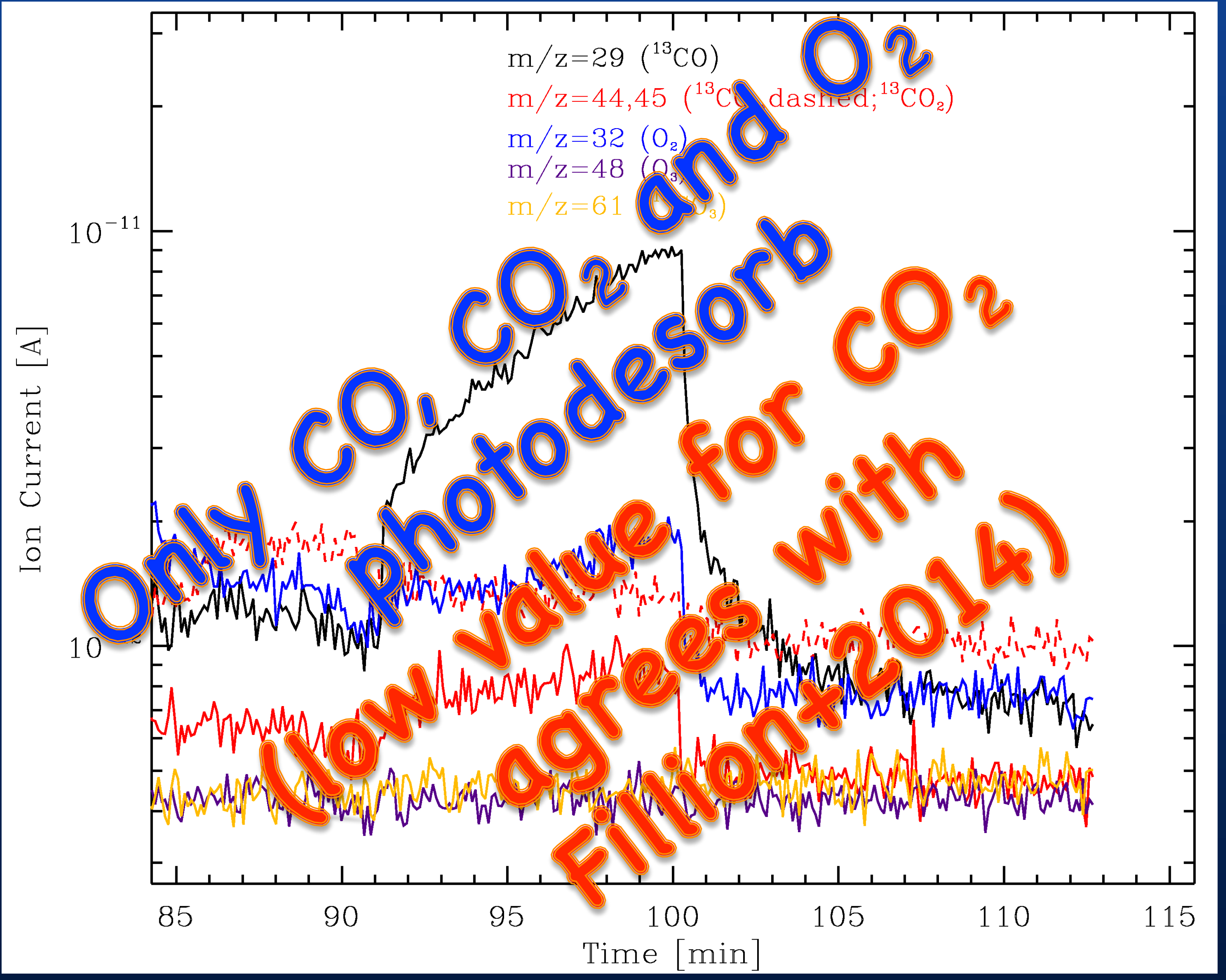

**Photodesorption of CO and $O_2$ observed by QMS**

# Quantification of $^{13}CO_2$ ice + UV



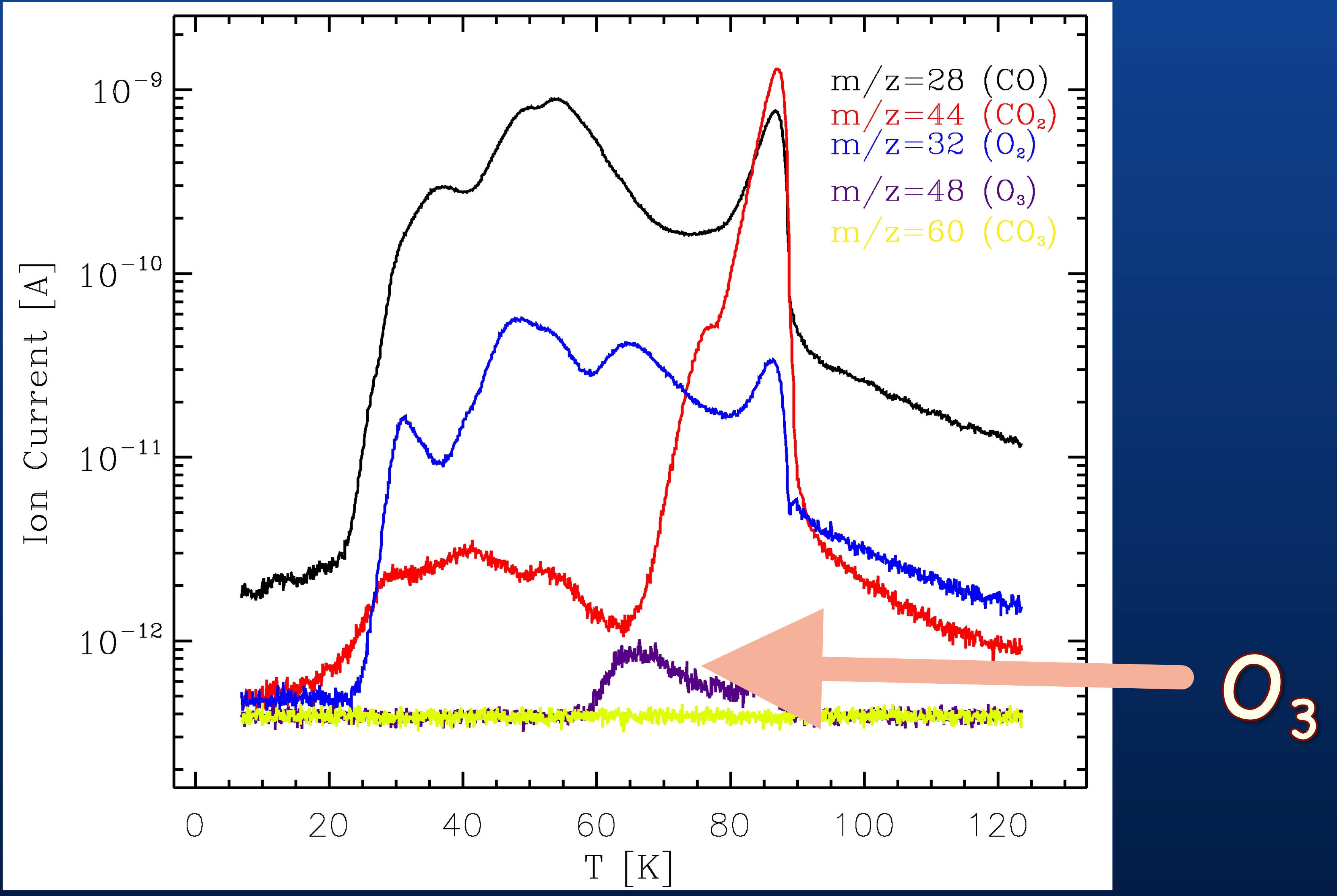

**$^{13}CO_2$ ice photodesorption observed with rate 1.1 $10^{-4}$ molecules/photon**

# Quantification of $^{13}CO_2$ ice + UV




**$^{13}CO_2$ ice photodesorption observed with rate 1.1e-4 molecules/photon**

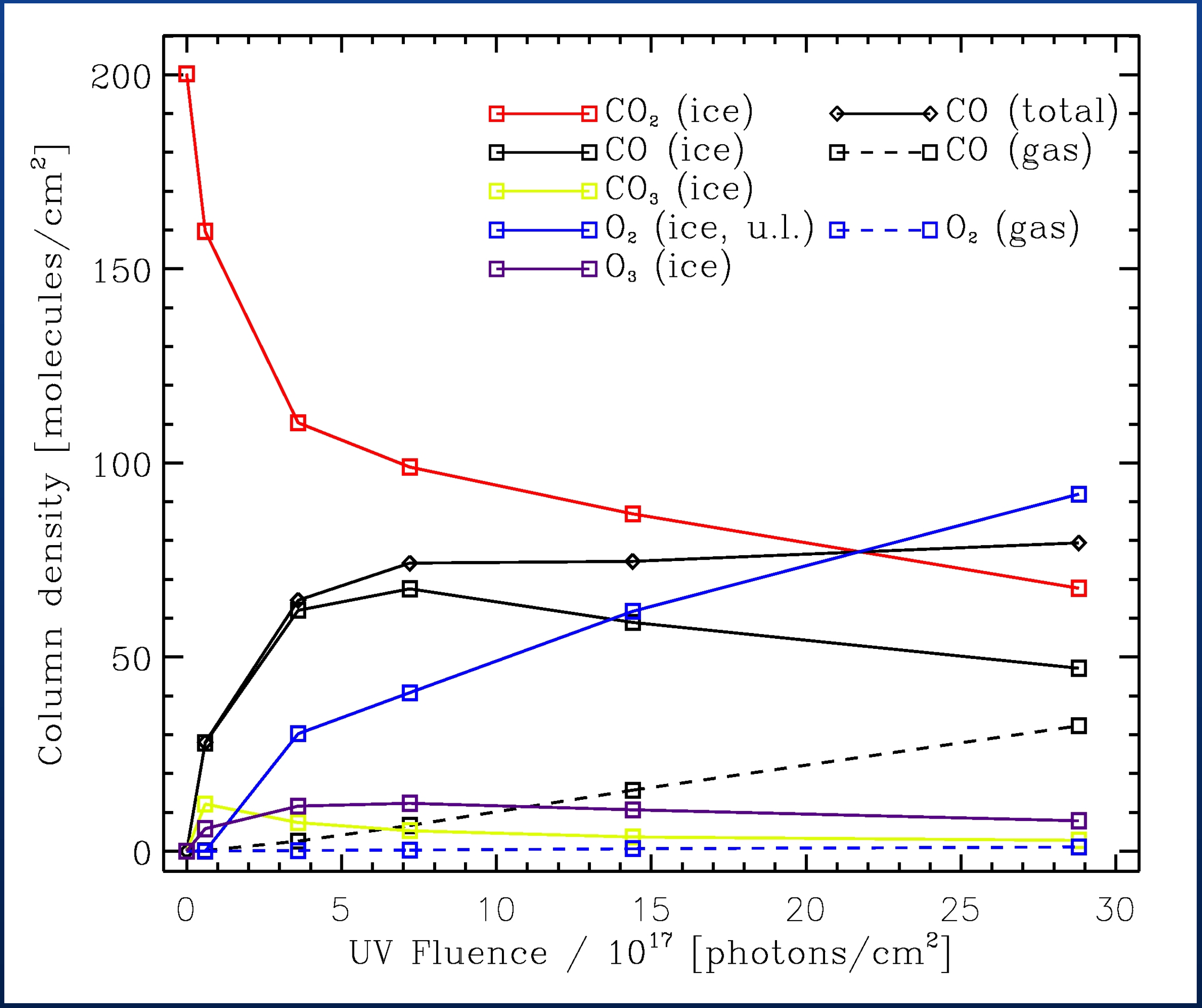
# Quantification of $CO_2$ ice + UV




**Thermal desorption of irradiated $CO_2$ ice showing photoproducts**

Martín-Doménech et al. 2015, submitted

# Quantification of $CO_2$ ice + UV




Photoproducts of $CO_2$ ice en as a function of UV fluence

**For UV fluence in dense cloud interior (3 x $10^{17}$ photons $cm^{-2}$), relative to the initial $CO_2$ ice:**

| | |
|---|---|
| **CO** | **32%** |
| **$CO_3$** | **4%** |
| **$O_3$** | **6%** |
| **$O_2$** | **15%** |

**Photodesorption rates of CO, $O_2$, and $CO_2$ are 1.2 $10^{-2}$, 9.3 $10^{-4}$, and 1.1 $10^{-4}$ molecules / photon (only 4% of CO formed does photodesorb, and a bit of $O_2$ and $CO_2$).**

Martín-Doménech et al. 2015, submitted

VUV-spectroscopy of ice needed to understand photodesorption!!

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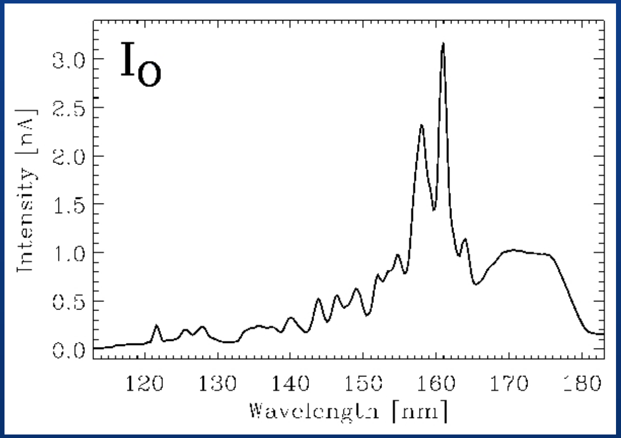
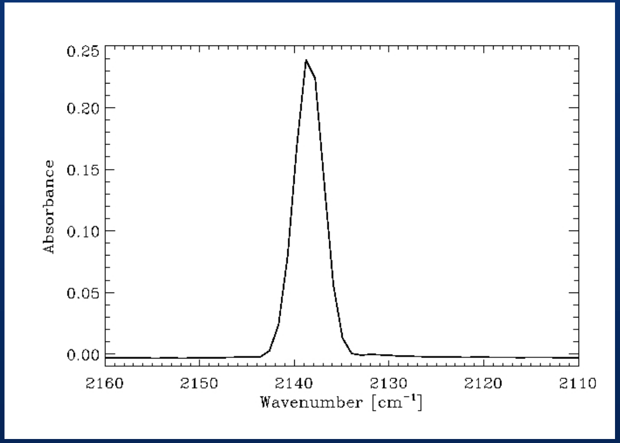
# Vacuum-UV Spectroscopy

VUV emission of lamp

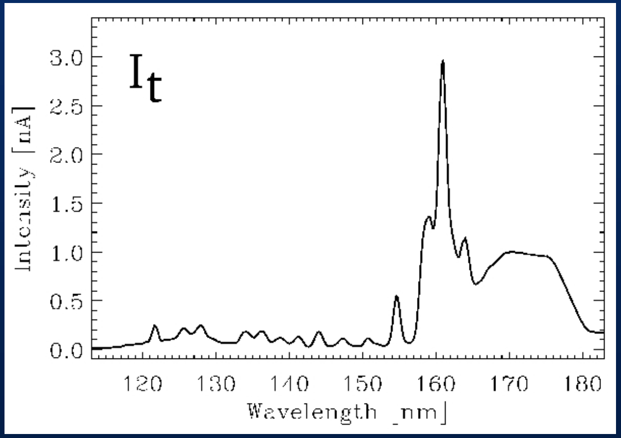



IR for determination of ice column density

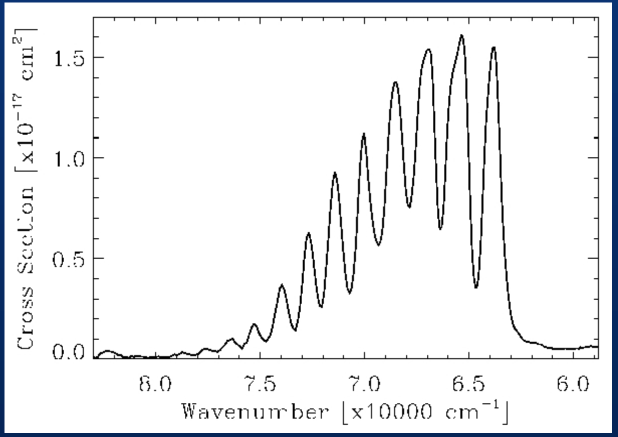



$$N = \frac{1}{A} \int_{band} \tau_\nu d_\nu$$

VUV transmitted by sample



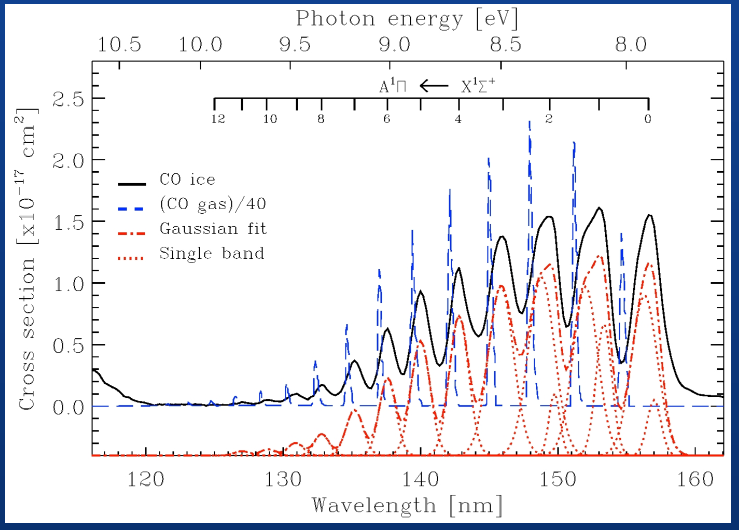

VUV ice absorption cross section



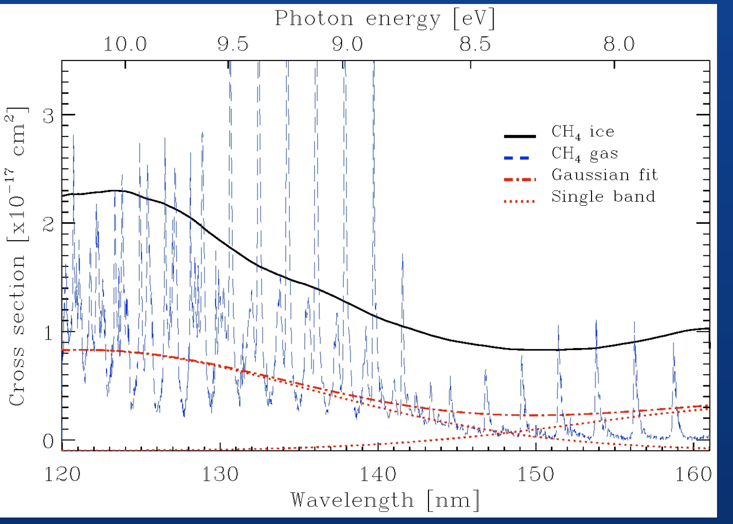

$$\sigma(\lambda) = \frac{1}{N} Ln \frac{I_t(\lambda)}{I_0(\lambda)}$$

$$I_t(\lambda) = I_0(\lambda) e^{-\sigma(\lambda) N}$$

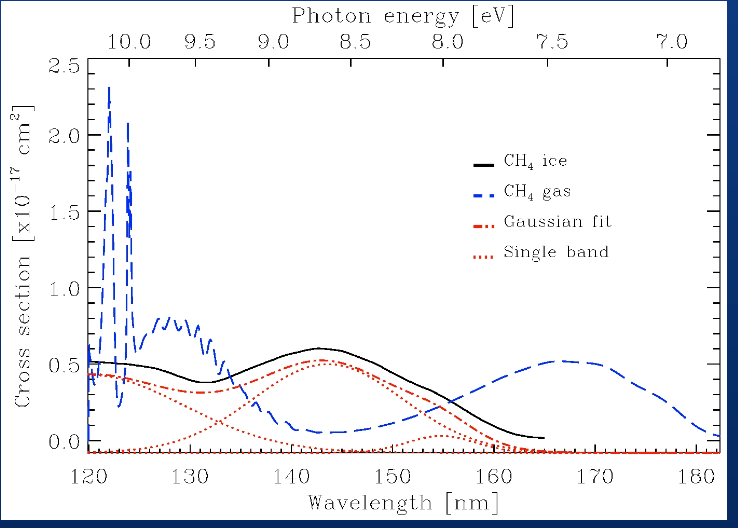
# Polar ices



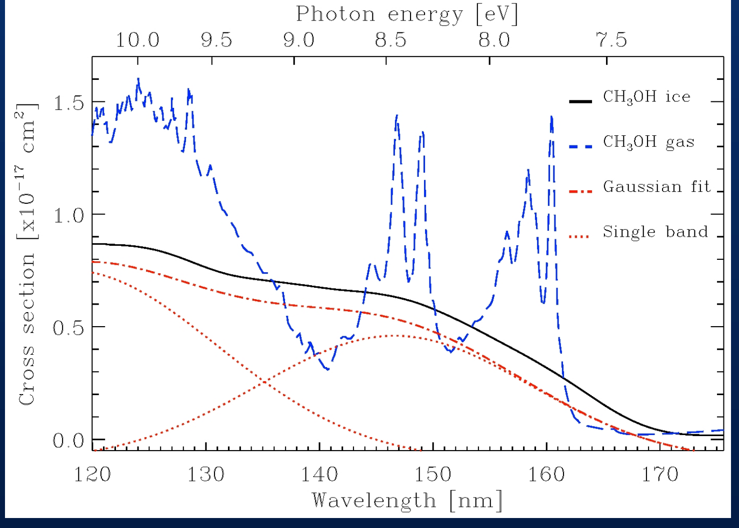

Carbon monoxide



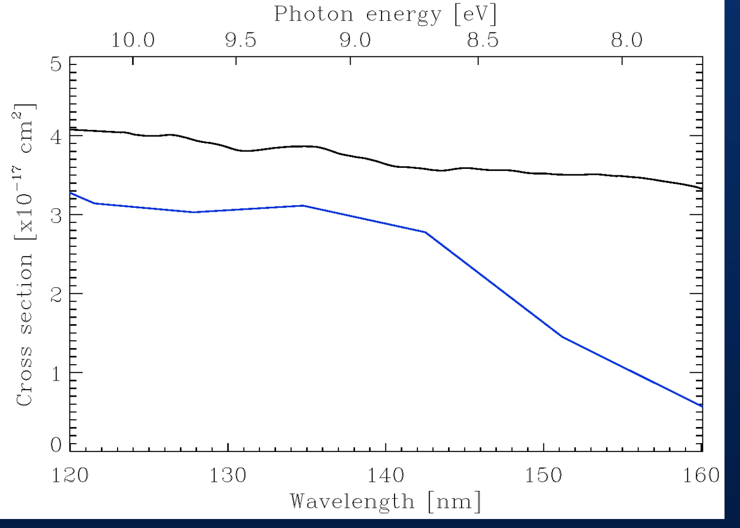

Ammonia




Water



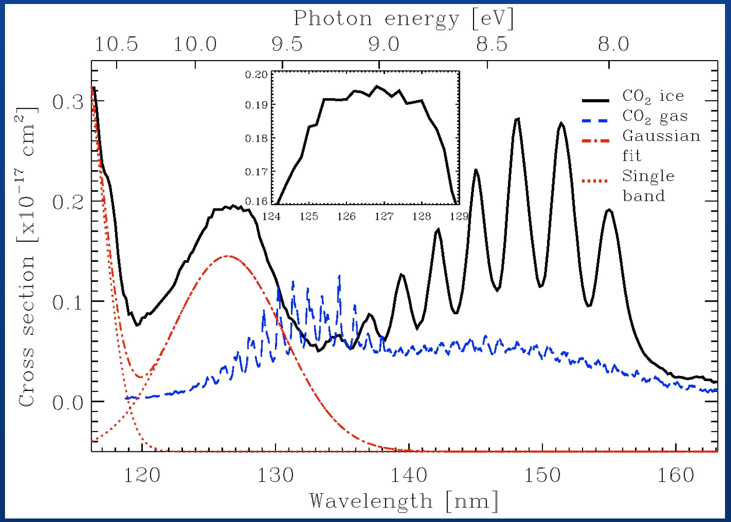

Methanol

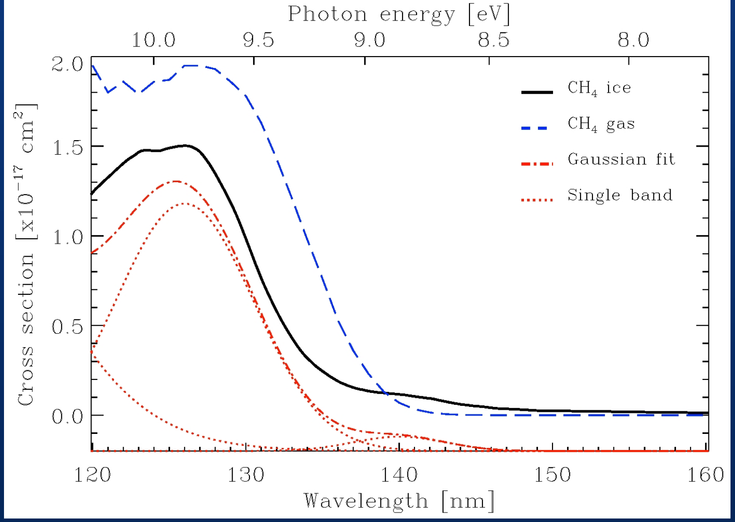



Hydrogen sulfide

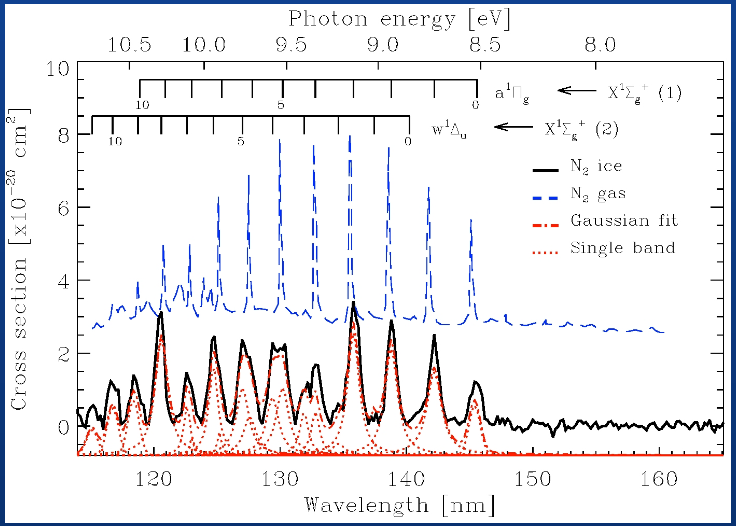
Cruz-Diaz et al., A&A, 2014a

# Apolar ices

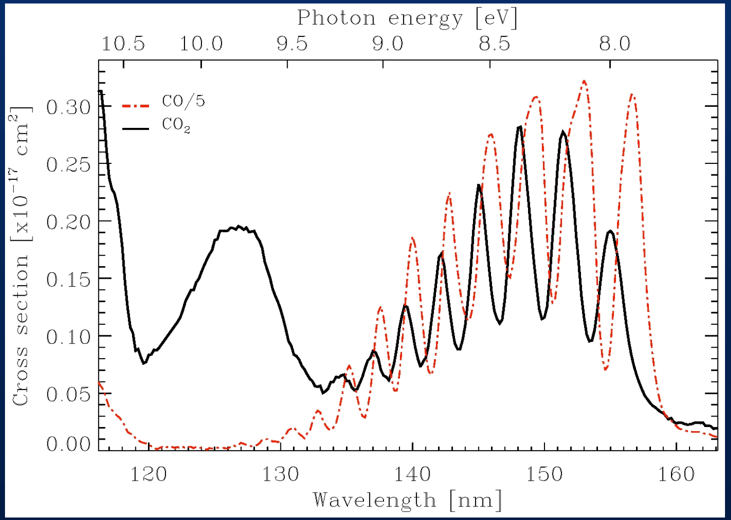


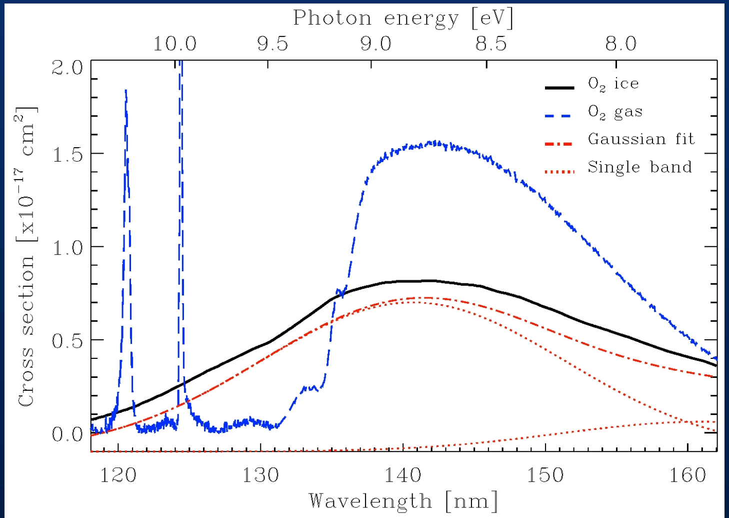

Methane




Nitrogen




Carbon dioxide

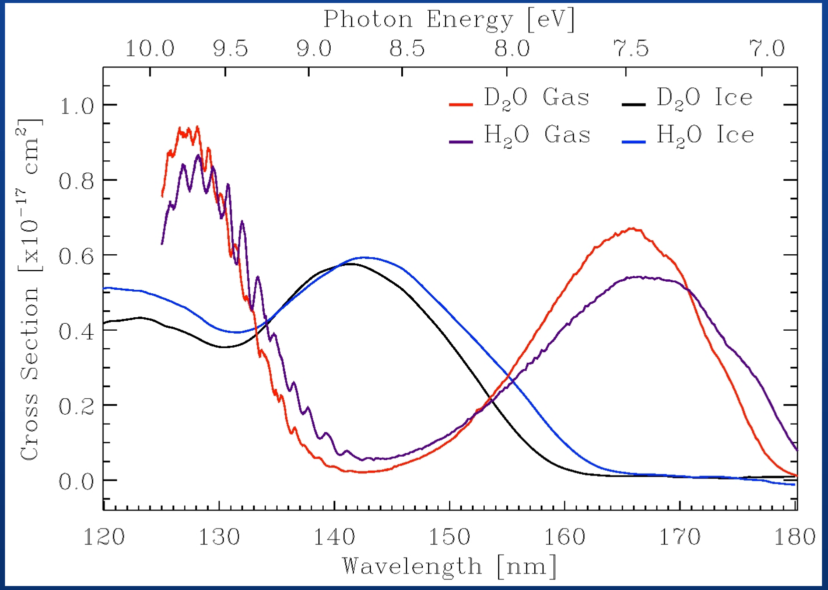



Oxygen

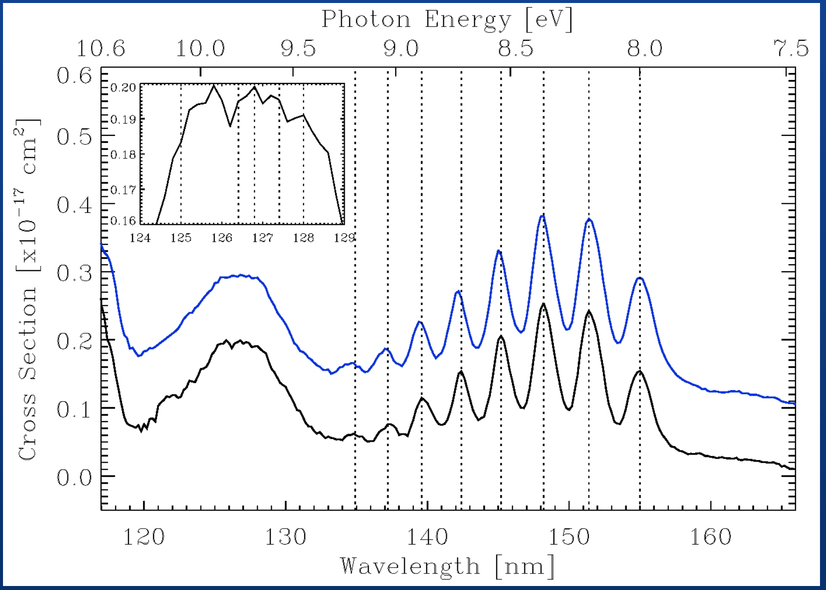
Cruz-Diaz et al., A&A, 2014b

# Isotopic Effects

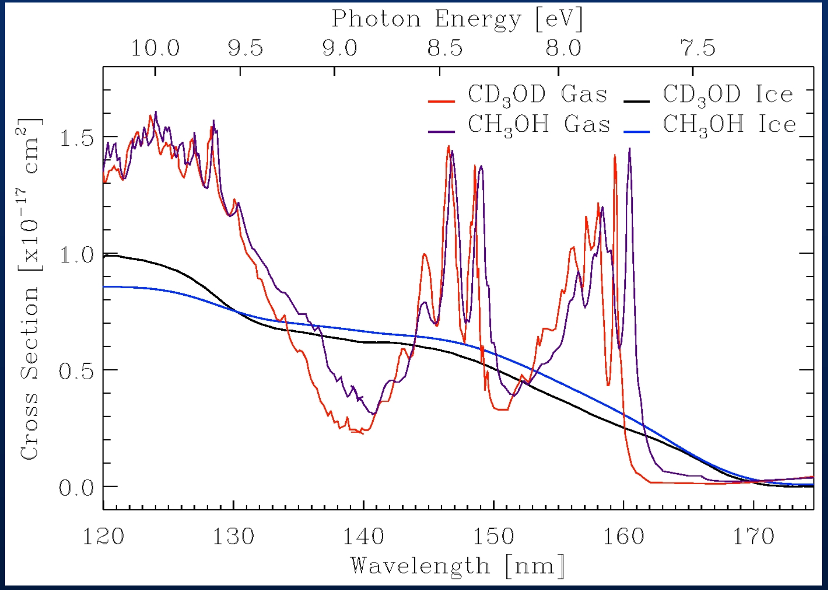
Cruz-Diaz et al., MNRAS, 2014



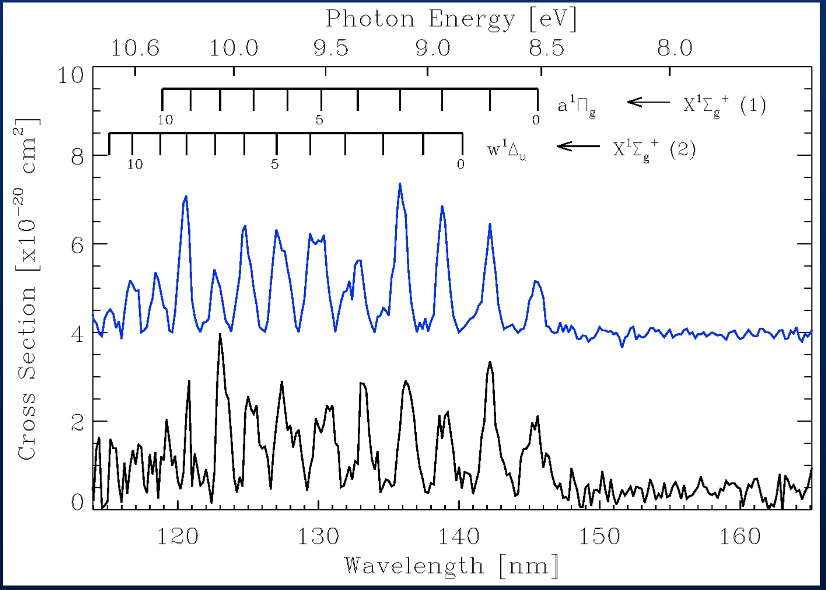

Deuterated water




13-Carbon dioxide




Deuterated methanol




15-Nitrogen

# Astrophysical implications

## VUV penetration depth in ice

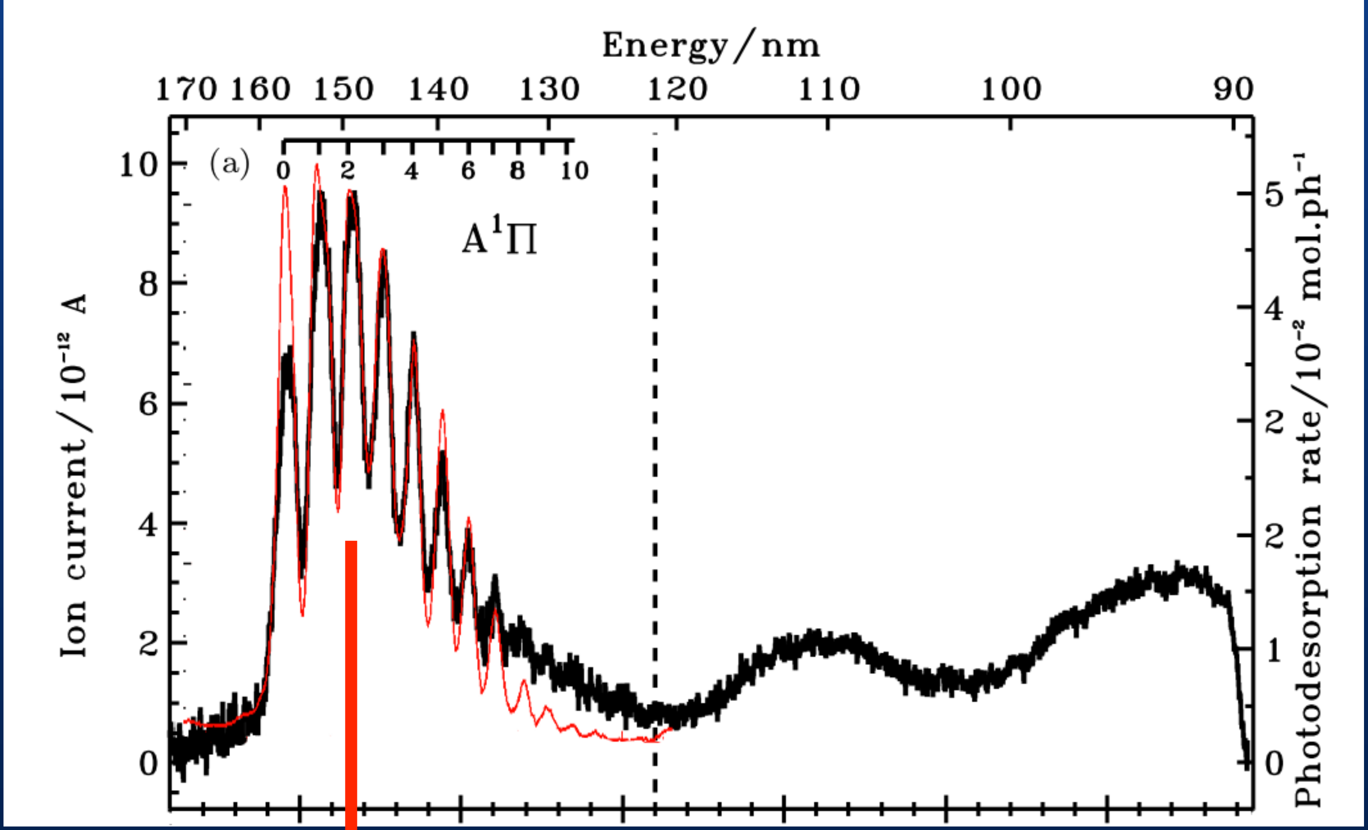
| species | 95% photon absorption Ly-α | Avg. | Max. | 99% photon absorption Ly-α | Avg. | Max. |
|---|---|---|---|---|---|---|
| | ($\times 10^{17}$ molecule cm$^{-2}$) | | | ($\times 10^{17}$ molecule cm$^{-2}$) | | |
| $D_2O$ | 6.8 | 11.1 | 5.3 | 10.5 | 17.1 | 8.1 |
| $CD_3OD$ | 3.1 | 6.5 | 3.1 | 4.7 | 10.0 | 4.7 |
| $^{13}CO_2$ | 27.2 | 43.7 | 12.0 | 41.8 | 67.1 | 18.4 |
| $^{15}N_2$ | 19971 | 3443 | 749 | 30701 | 5293 | 1151 |
| $H_2O$ | 5.8 | 8.3 | 4.9 | 8.9 | 13.0 | 7.7 |
| $CH_3OH$ | 3.5 | 5.7 | 3.4 | 5.4 | 8.7 | 5.3 |
| $CO_2$ | 29.3 | 44.5 | 15.1 | 45.1 | 68.4 | 23.3 |
| $N_2$ | 29957 | 4280 | 881 | 46052 | 6579 | 1354 |

Cruz-Diaz et al., 2014a,b,c

# Astrophysical implications

## CO photodesorption

**VUV – absorption cross section spectrum VS photodesorption rate at different wavelengths**



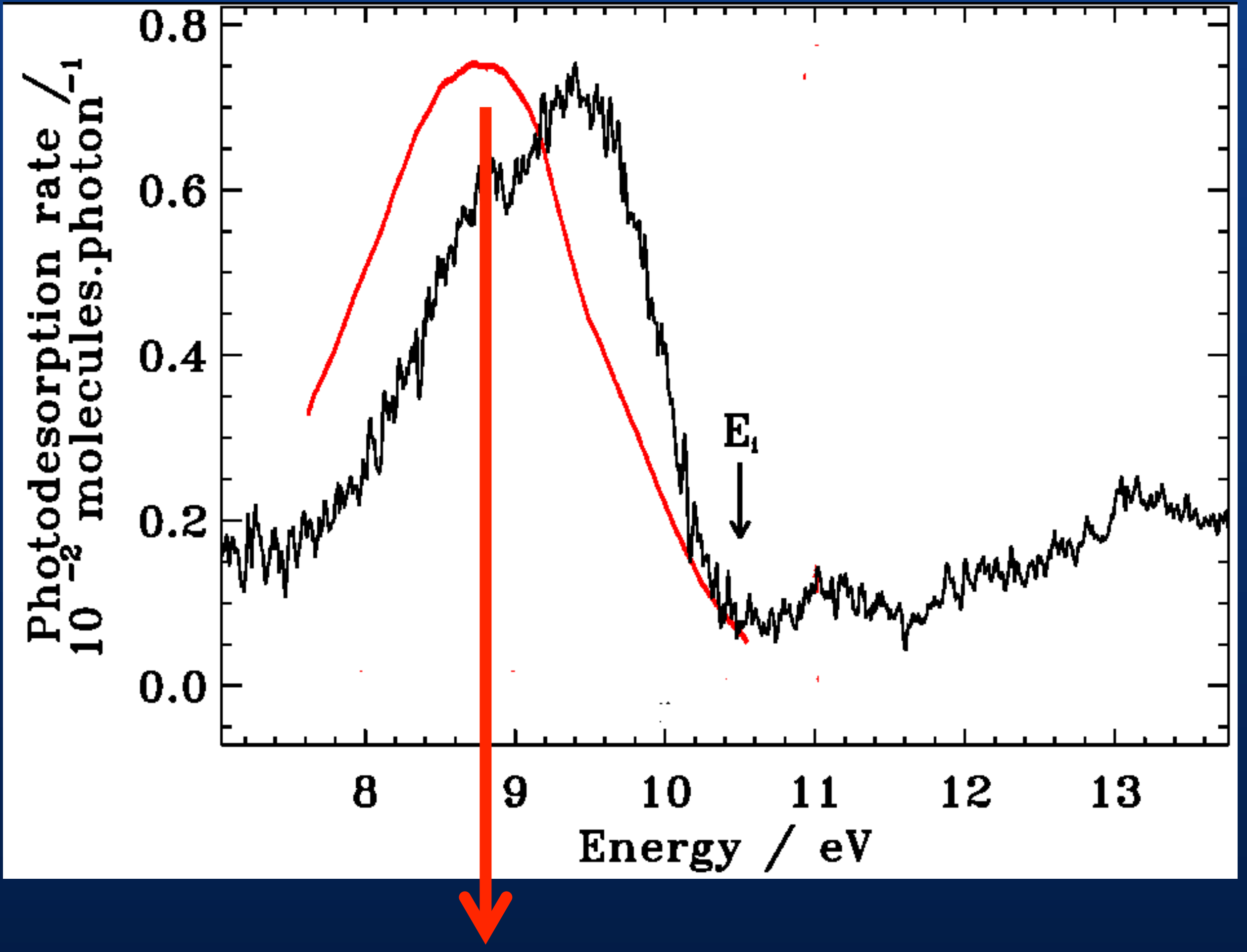

Fayolle et al. 2011
Lu et al. 2005
Cruz-Diaz et al., A&A, 2014a

Photodesorption driven by Desorption Induced by Electronic Transitions process (DIET)

# Astrophysical implications

## $O_2$ photodesorption

**VUV – absorption cross section spectrum VS photodesorption rate at different wavelengths**




Fayolle et al.
Cruz-Diaz et al.

DIET? → More photodesorption studies

# Astrophysical implications

## Photodesorption rate per absorbed photon
## VS
## Photodesorption rate per incident photon

photodesortpion rate (e.g. IR spectroscopy)

$$R^{inc}_{ph-des}\left(\text{molec.}/\text{inc.photon}\right) = \frac{\Delta N\left(\text{molec.}/\text{cm}^2\text{s}\right)}{I_0\left(\text{inc.photon}/\text{cm}^2\text{s}\right)}$$

$$R^{abs}_{ph-des}\left(\text{molec.}/\text{abs.photon}\right) = \frac{\Delta N\left(\text{molec.}/\text{cm}^2\text{s}\right)}{I_{abs}\left(\text{abs.photon}/\text{cm}^2\text{s}\right)}$$

photon flux at sample position

- $I_0$ (continuum source)
- $I_0(\lambda)$ (monochromatic source)

$$R^{abs}_{ph-des} = \frac{I_0}{I_{abs}} R^{inc}_{ph-des}$$

where

$$I_{abs} = \sum_{\lambda_i}^{\lambda_f} I_0(\lambda) - I(\lambda) = \sum_{\lambda_i}^{\lambda_f} I_0(\lambda)(1 - e^{-\sigma(\lambda)N})$$

Cruz-Diaz et al., MNRAS, 2014

# Astrophysical implications

## Photodesorption rate per absorbed photon
## VS
## Photodesorption rate per incident photon

N(CO) = 5 ML (Muñoz Caro et al. 2010)

| | Irrad. energy eV | $R^{inc}_{ph-des}$ molec./photon$_{inc}$ | $\sigma$ cm$^2$ | $R^{abs}_{ph-des}$ molec./photon$_{abs}$ |
|---|---|---|---|---|
| Fayolle et al. 2011 | 10.2 | $6.9 \pm 2.4 \times 10^{-3}$ | $1.1 \times 10^{-19}$ | $12.5 \pm 4.4$ |
| | 9.2 | $1.3 \pm 0.91 \times 10^{-2}$ | $2.8 \times 10^{-18}$ | $0.9 \pm 0.6$ |
| | 8.2 | $5 \times 10^{-2}$ | $9.3 \times 10^{-18}$ | 1.1 |
| Cruz-Diaz et al. 2014a | 8.6 | $5.1 \pm 0.2 \times 10^{-2}$ | $4.7 \times 10^{-18}$ | $2.5 \pm 0.1$ |

$$R^{abs}_{ph-des} > 1$$

1 absorbed photon can induce photodesorption of more than 1 molecule!

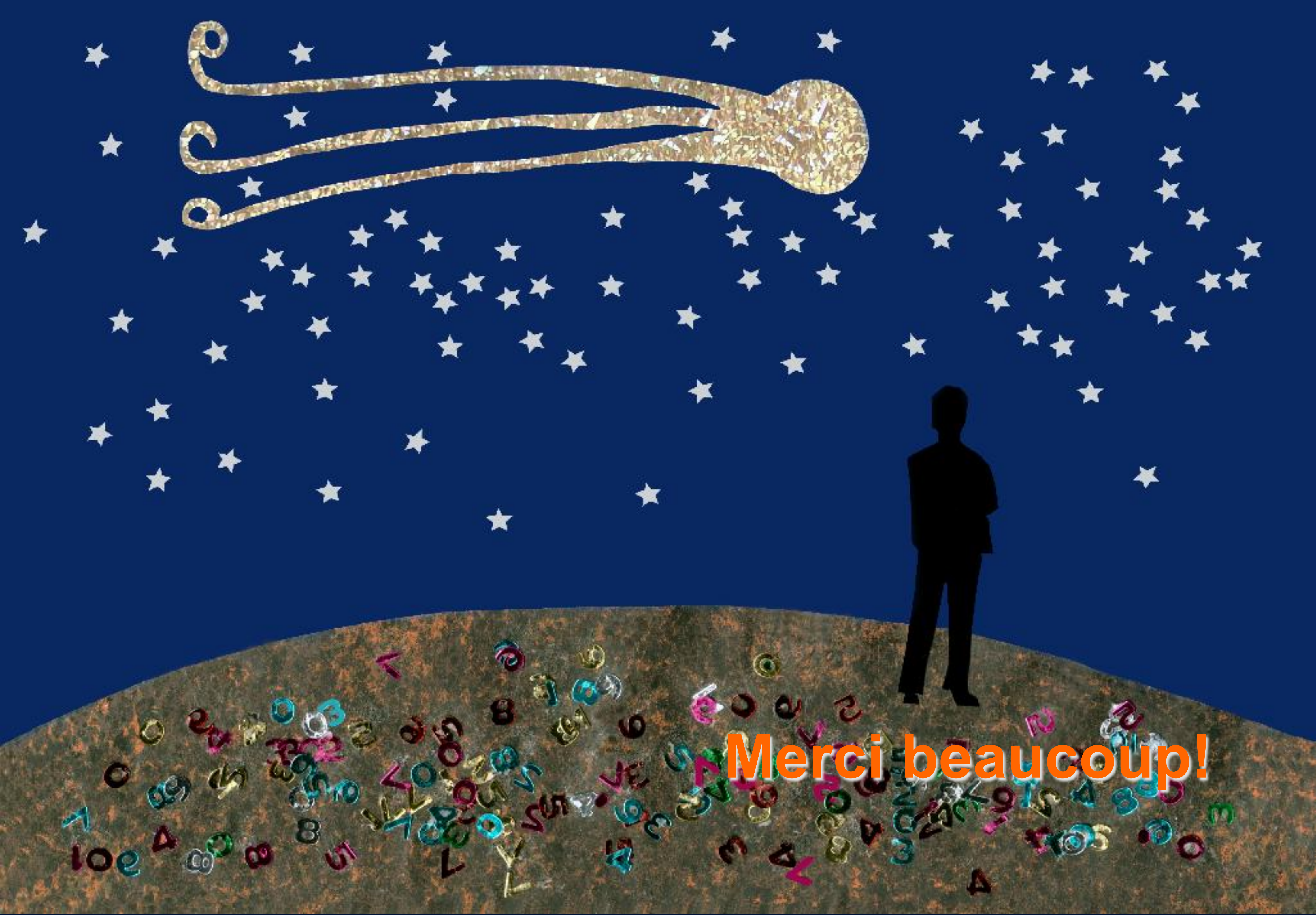
# Acknowledgements

**ISAC:**

**R. Martín Doménech, G.A. Cruz Díaz, J. Manzano, A. Jiménez Escobar, B. M. Giuliano.**

**Colaborators:**

**E. Dartois (IAS), Y. J. Chen (Taiwan), A. Ciaravella & C. Cecchi-Pestellini (O. Palermo), R. Escribano and B. Maté (IEM), J. Cernicharo (ICMM), W.-F. Thi (Garching), S. Cazaux (Groningen), I. Jiménez-Serra (UCL), COSAC-Rosetta team...**


Merci beaucoup!