
# VUV-absorption cross sections of ices, photodissociation and photodesorption

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# Outline

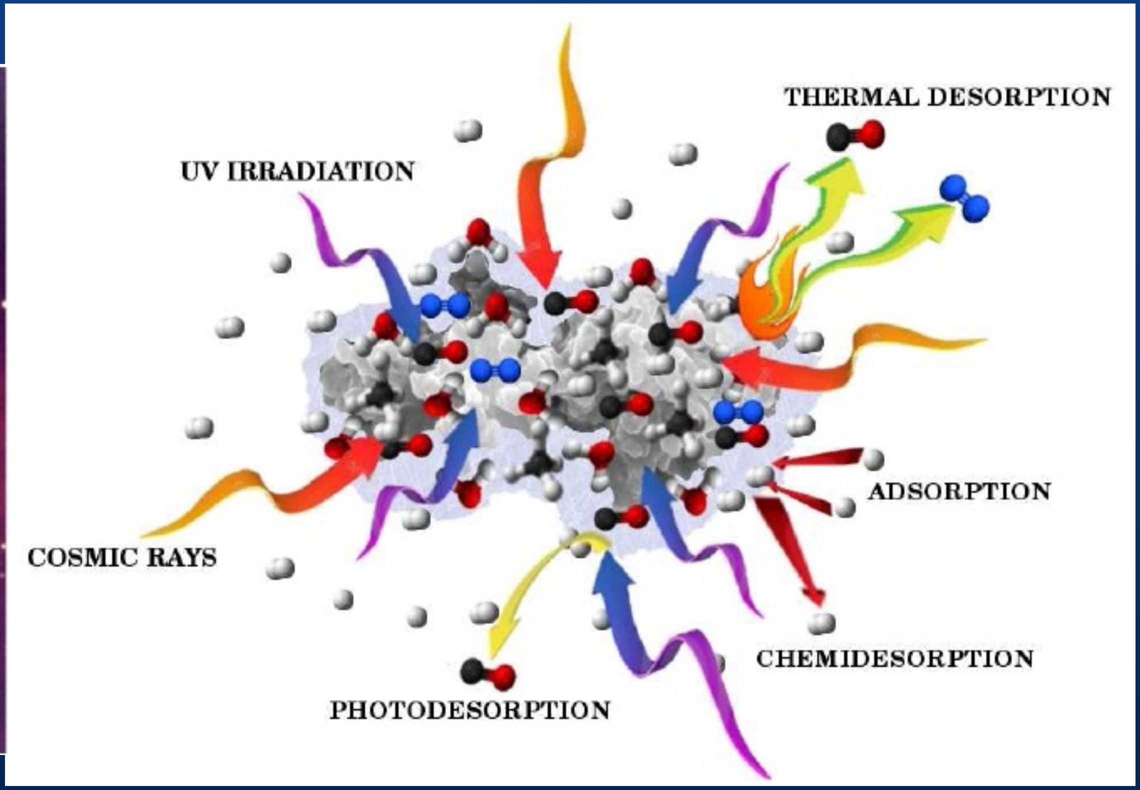
1. The astrophysical context: ice mantles

2. Photodissociation, photodesorption, and ¨photochemidesorption¨

3. VUV-spectroscopy of pure ices

# 1. The astrophysical context: Ice mantles

# Processing of interstellar ice mantles




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

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

# Energetic processing of ice mantles

Photon and ion processing

Photon and ion + thermal processing

INTERSTELLAR

CIRCUMSTELLAR

Dense cloud interiors

Hot cores

Solar System

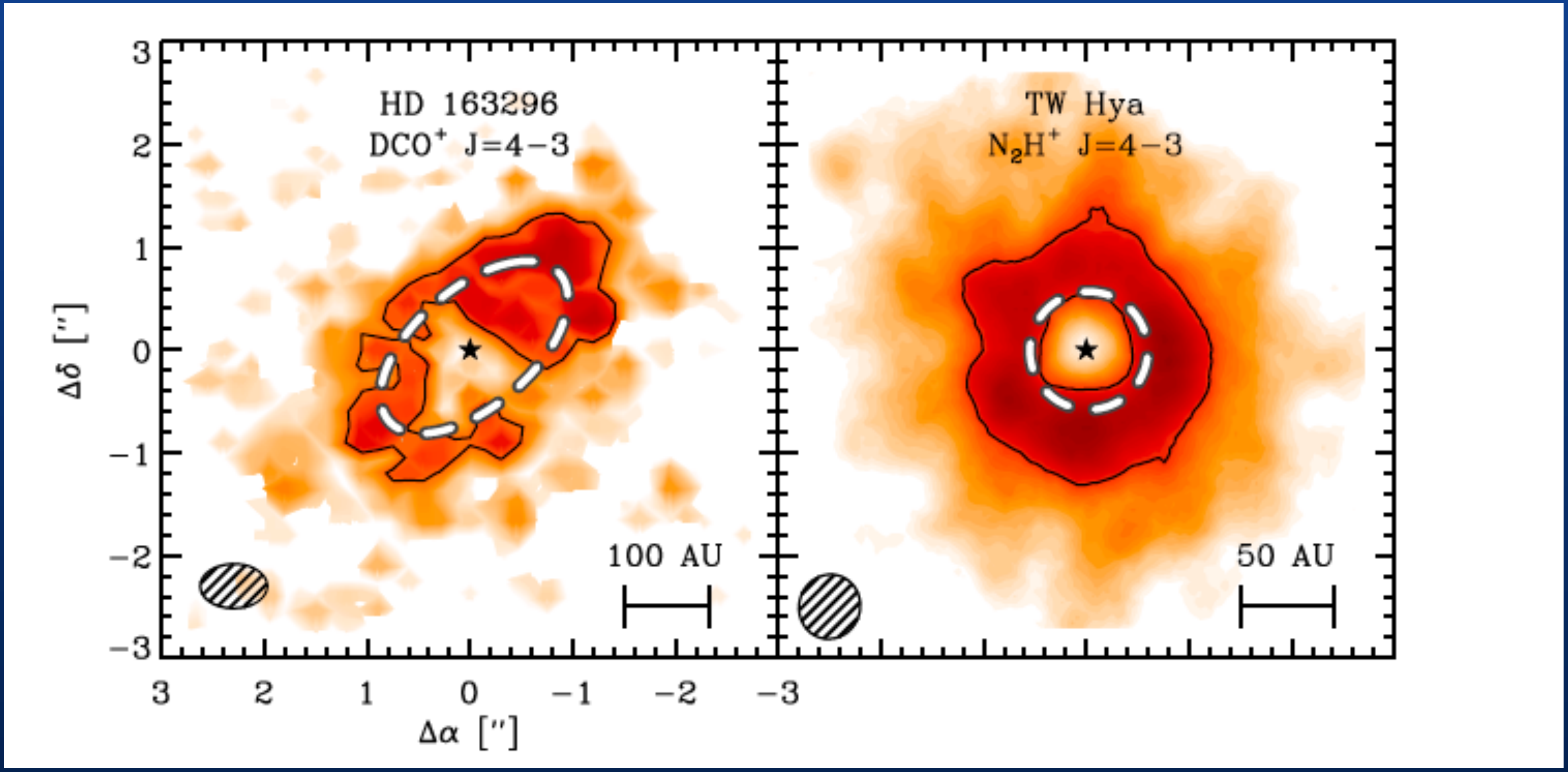
Interstellar ices

Circumstellar ices

Cometary ices

- Thermal desorption
- Structural changes
  - Difussion
  - Phase transition
  - Segregation

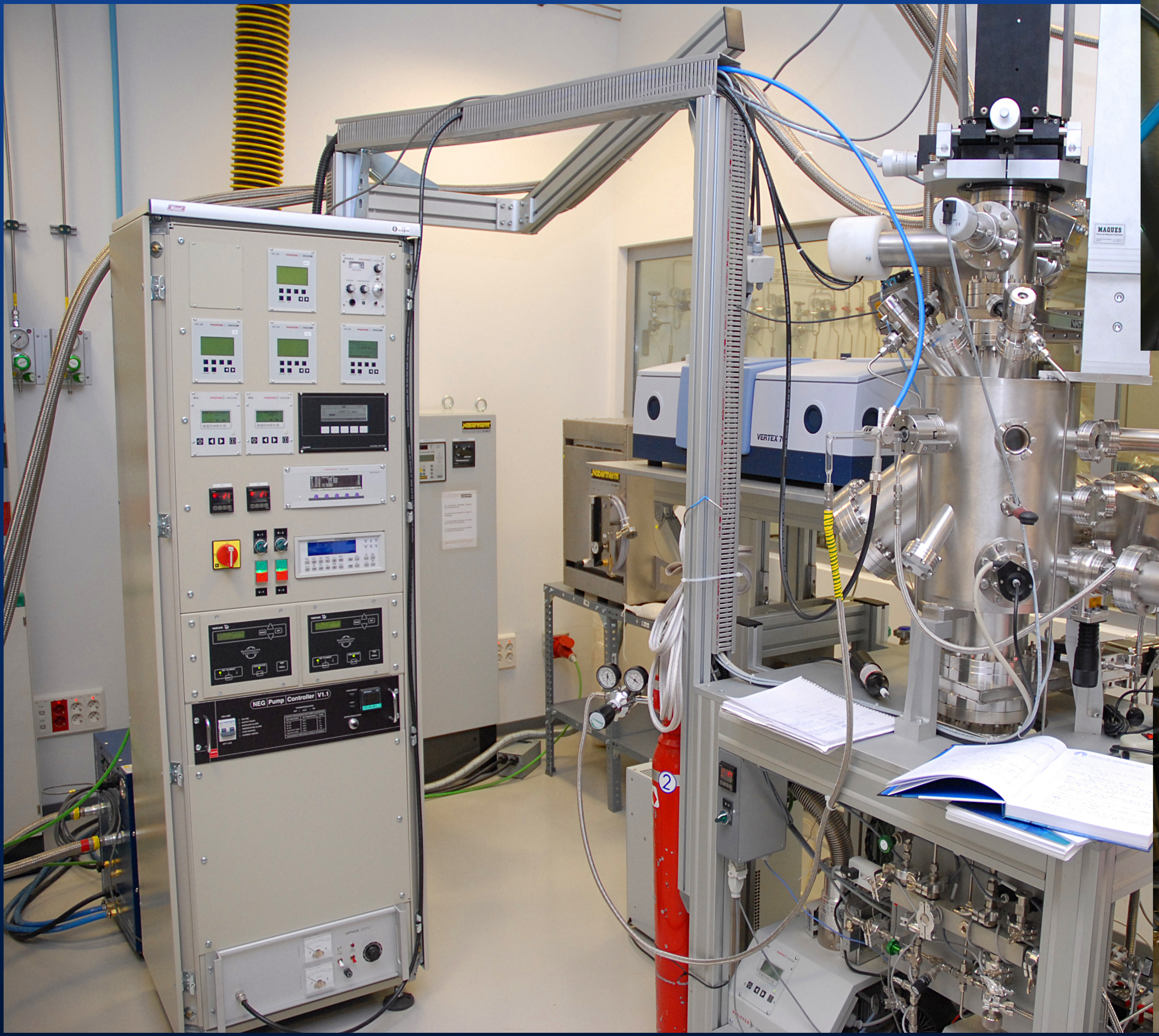
# The CO snowline

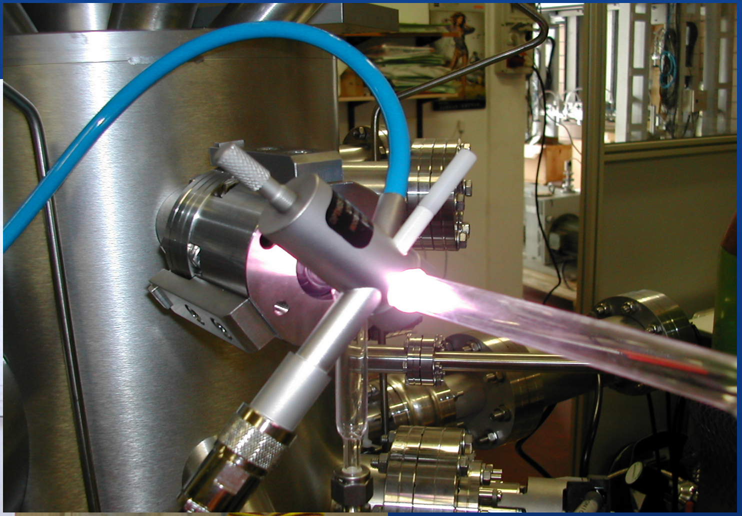


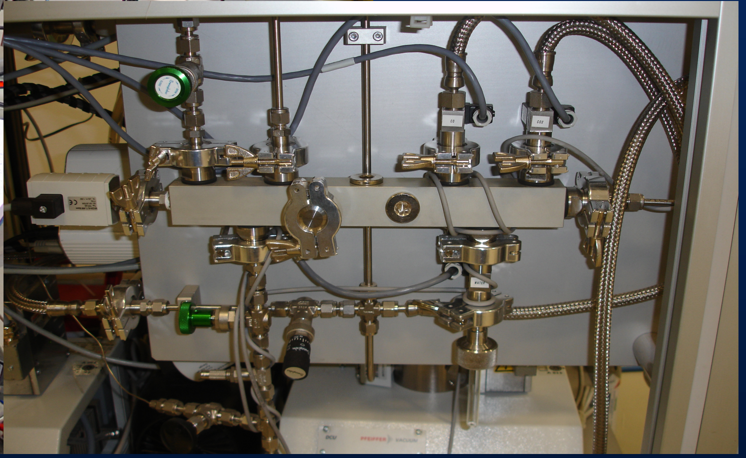

CO snow line observed with ALMA, using tracers of the absence of CO in the gas-phase. Dashed line is 17 K isotherm where CO freezes out.

Pontoppidan et al., Protostars and Planets VI, 2014

# ISAC = InterStellar Astrochemistry Chamber



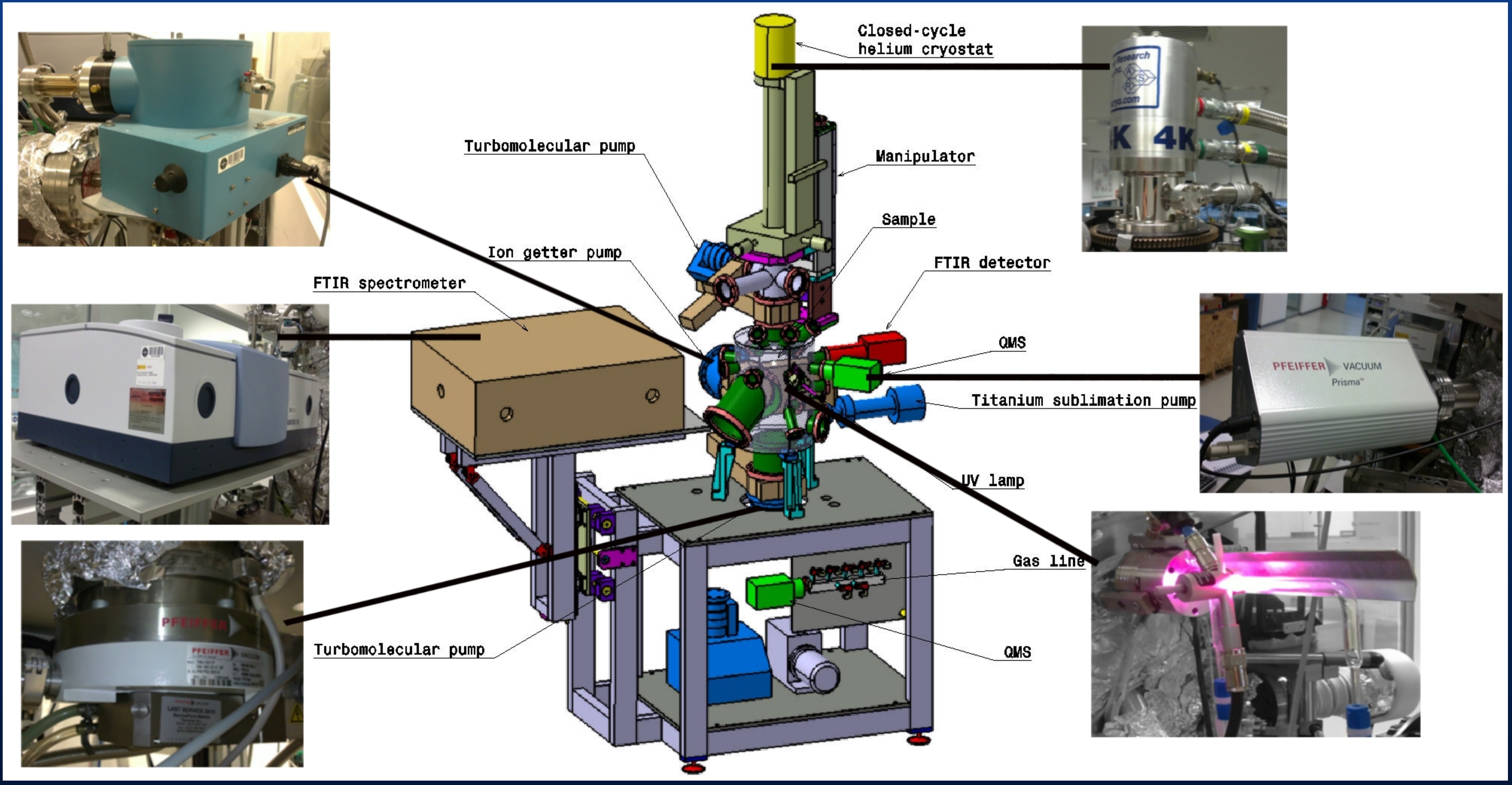





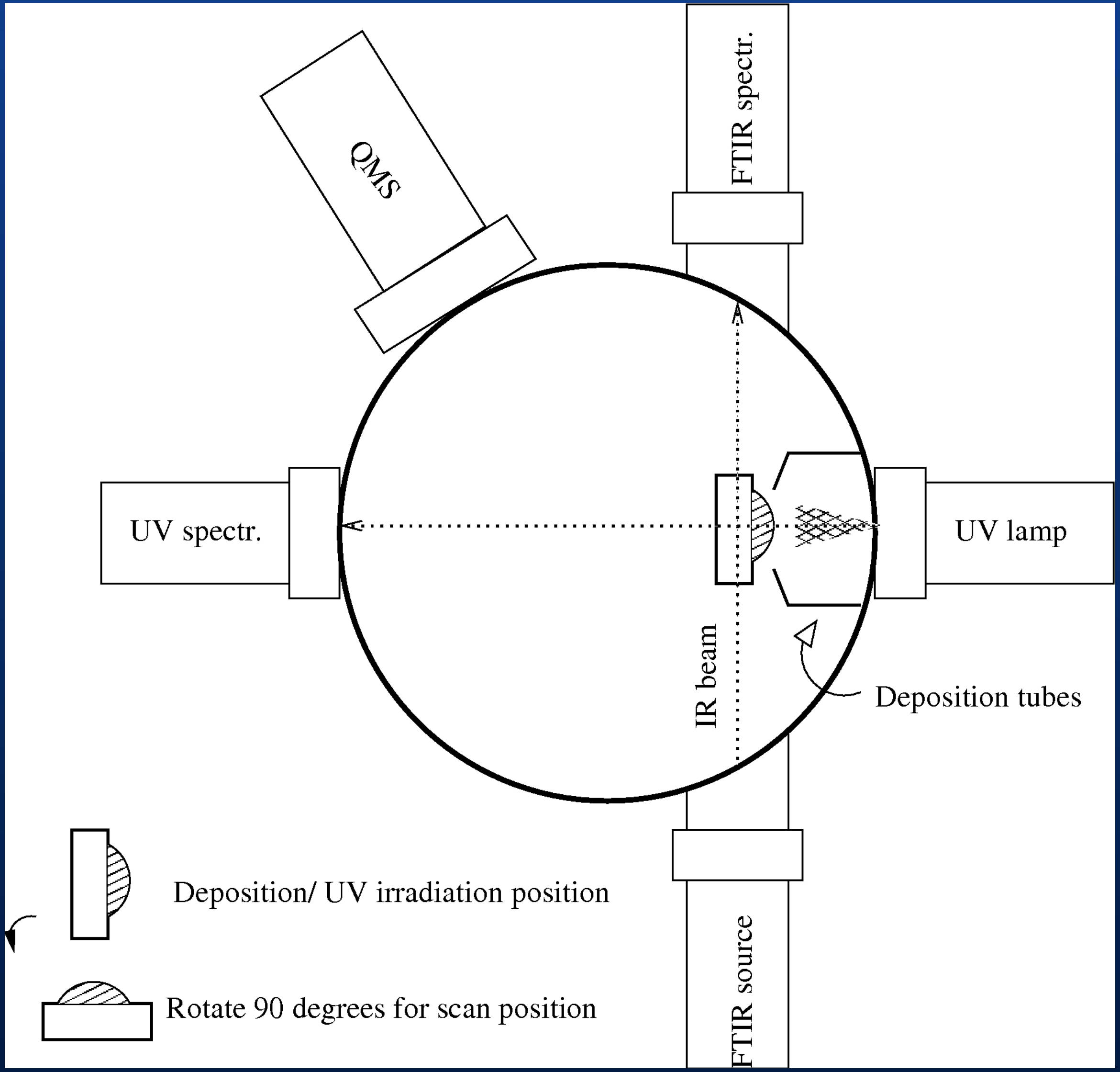
# ISAC = InterStellar Astrochemistry Chamber

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

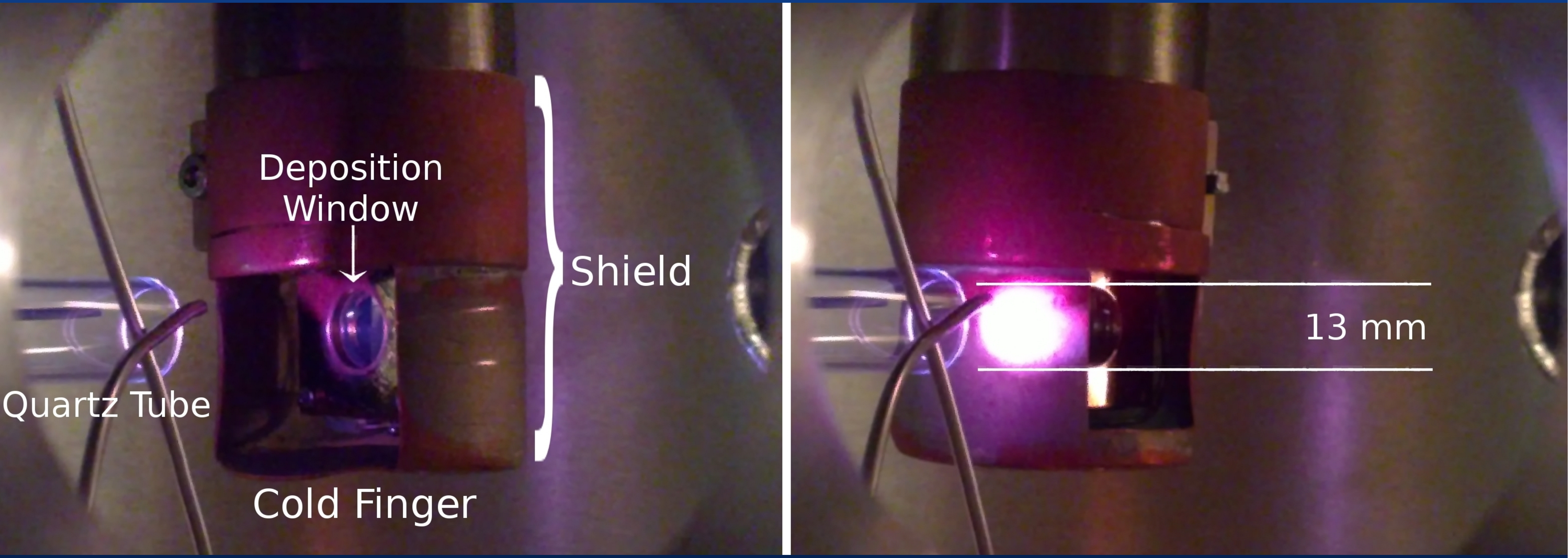
Solid: IR, Raman, and vacuum-UV spectroscopy
Gas: QMS



# ISAC = InterStellar Astrochemistry Chamber



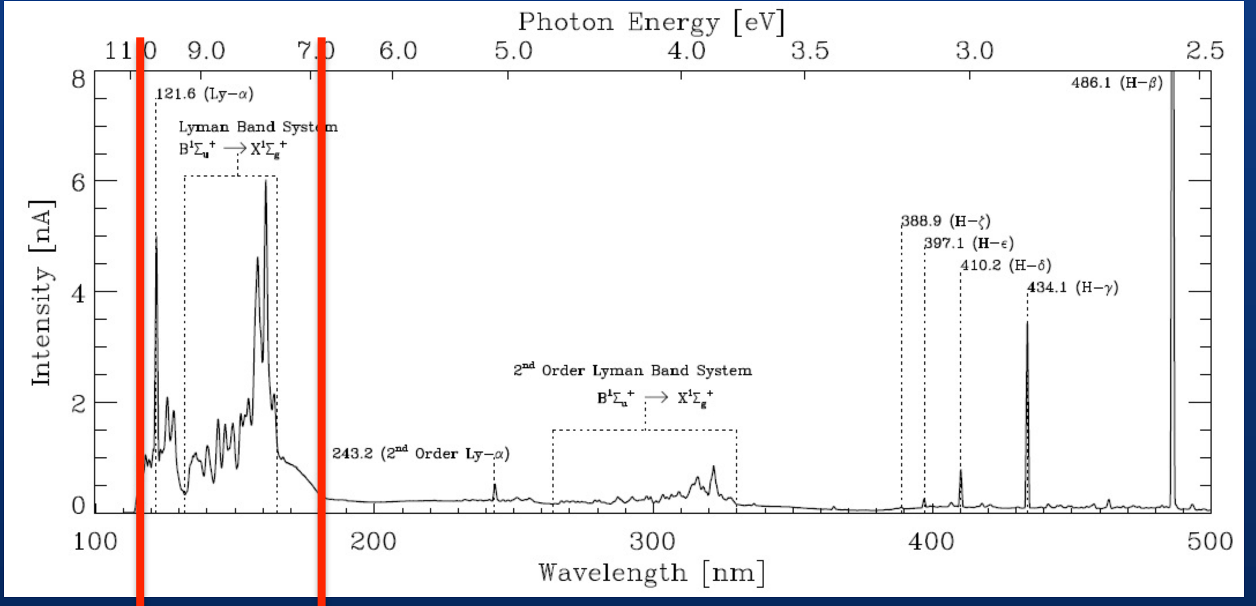
# Sample irradiation with UV



# Photoprocessing of ice analogs

## Vacuum-UV Spectroscopy

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



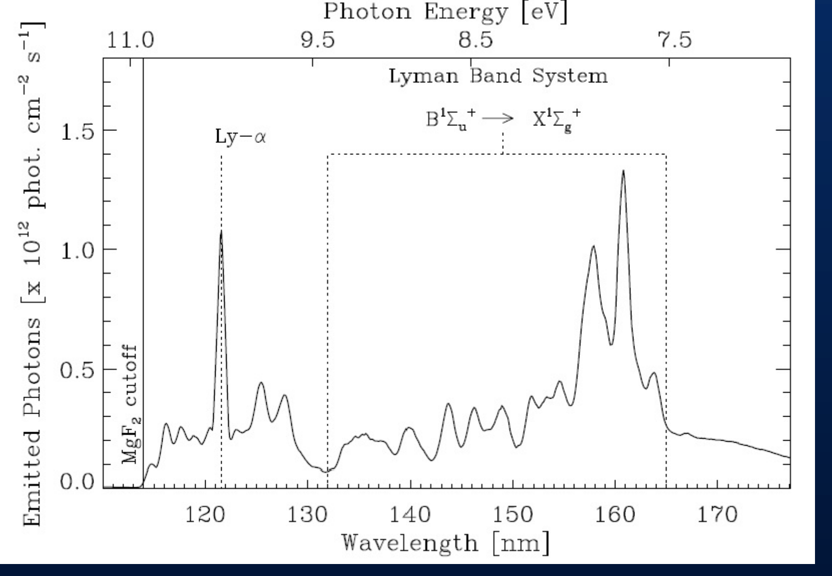

MgF$_2$ cutoff
114 nm / 10.87 eV

Low lamp flux
183 nm / 6.77 eV

Limitation for VUV- spectroscopy

Effective UV-radiation of the ice analog

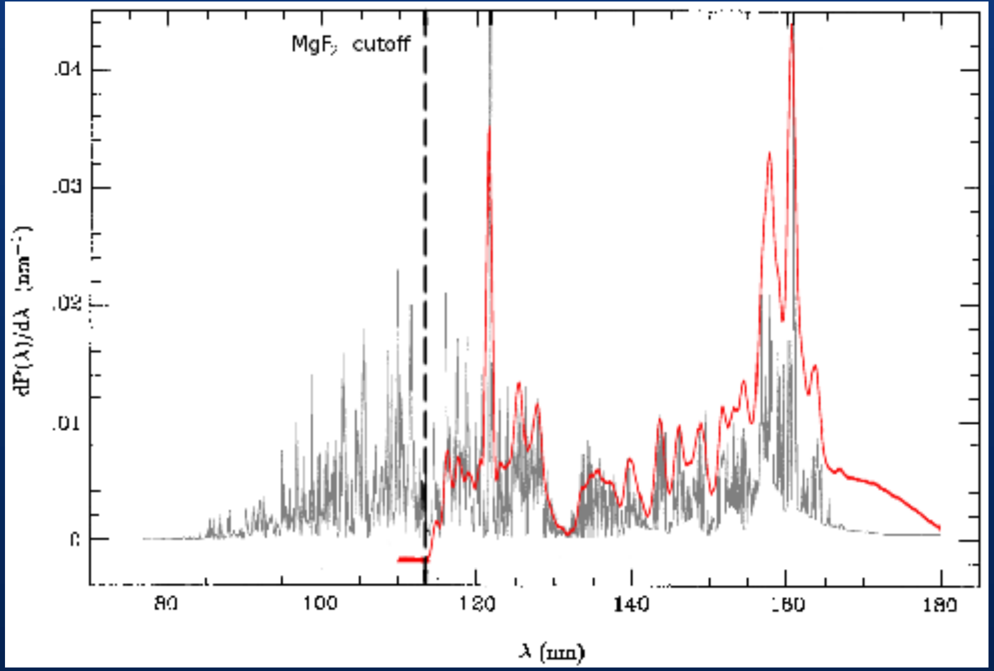
- $E_{photon}$ = 8.6 eV
- Main features:
  - Ly-α @ 121.6 nm (10.20 eV)
  - H$_2$ bands @
    - 157.8 nm (7.85 eV)
    - 160.8 nm (7.71 eV)



# Photoprocessing of ice analogs

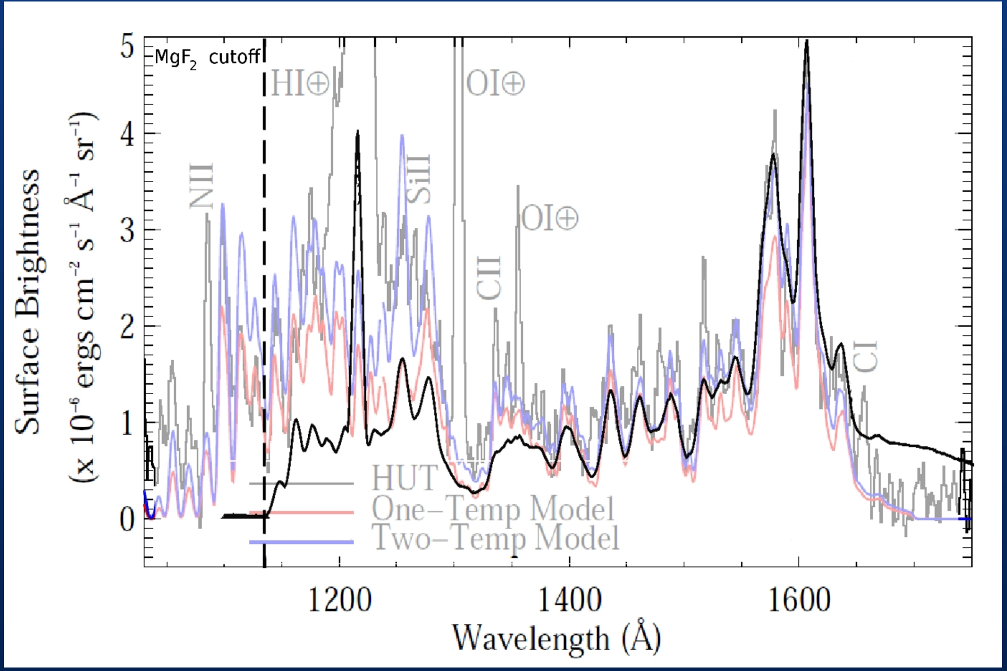
## UV spectrum of lamp vs. radiation field

Calculated secondary UV-field




Gredel et al. 1989

Spectrum of IC63 (emission nebula near Be star)




France et al. 2005

# 2. Photodissociation, photodesorption, and "photochemidesorption"

# Photo-desorption experiments

HV

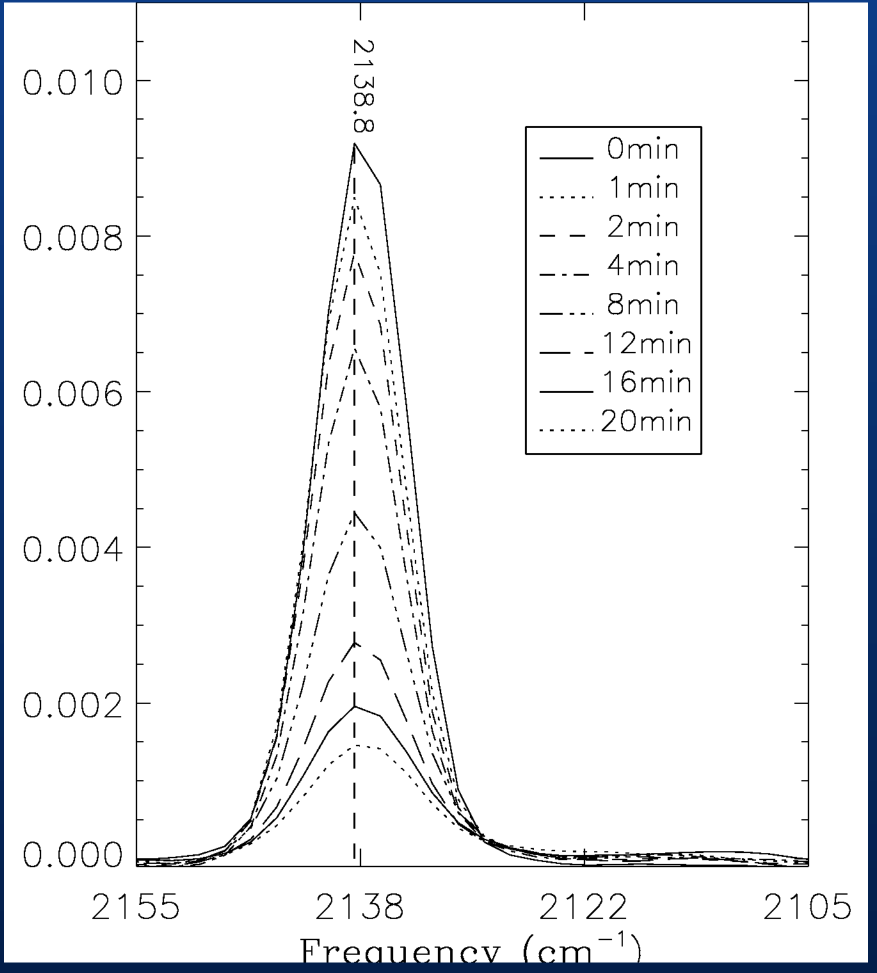

water accretion
also $N_2$, $O_2$

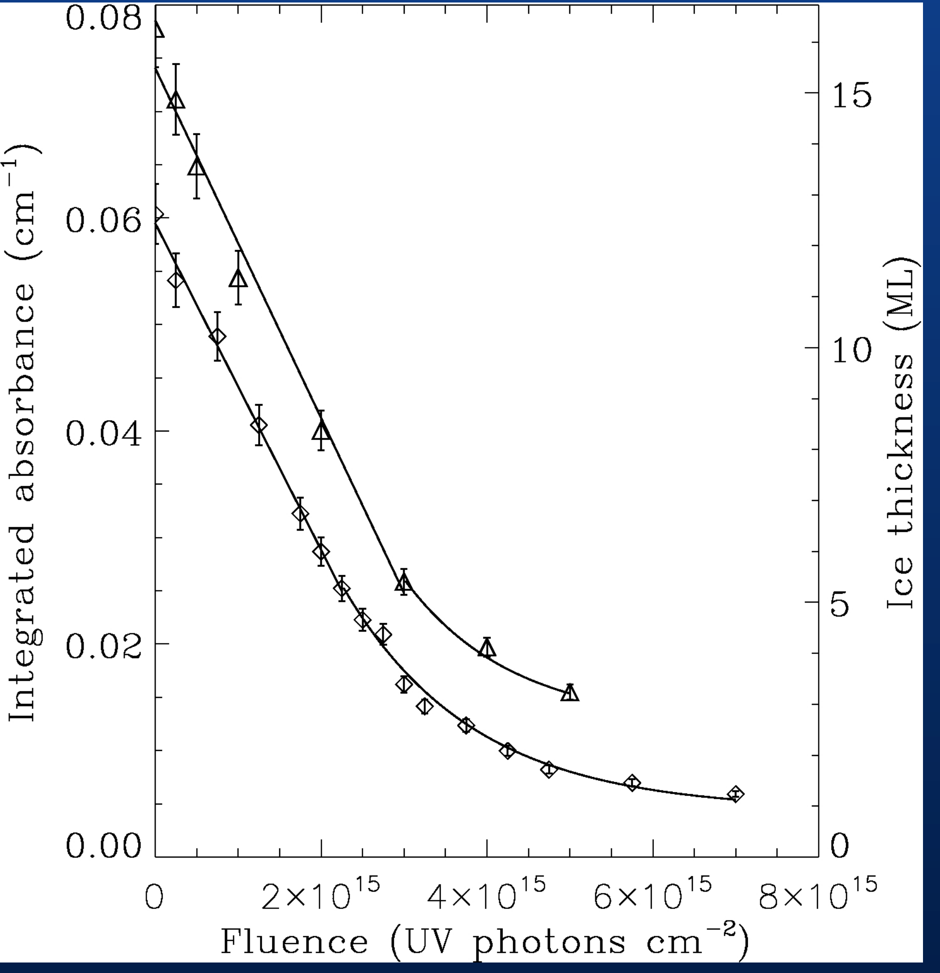
UHV


no water accretion
or $N_2$, $O_2$

# Photodesorption of CO ice

Solid sample ←→ IR spectroscopy



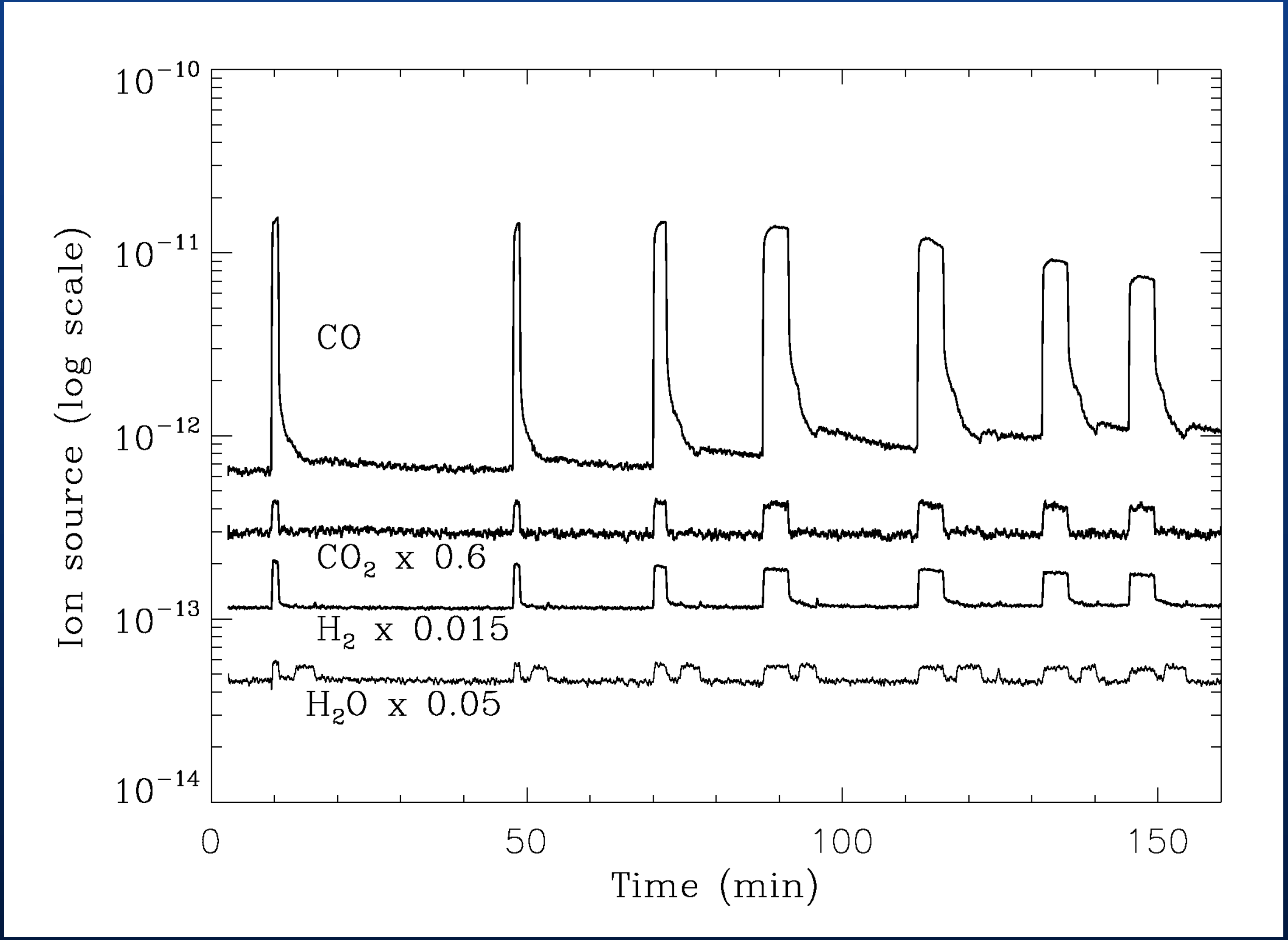




IR bands are integrated to measure decrease in column density during irradiation

Muñoz Caro et al. 2010

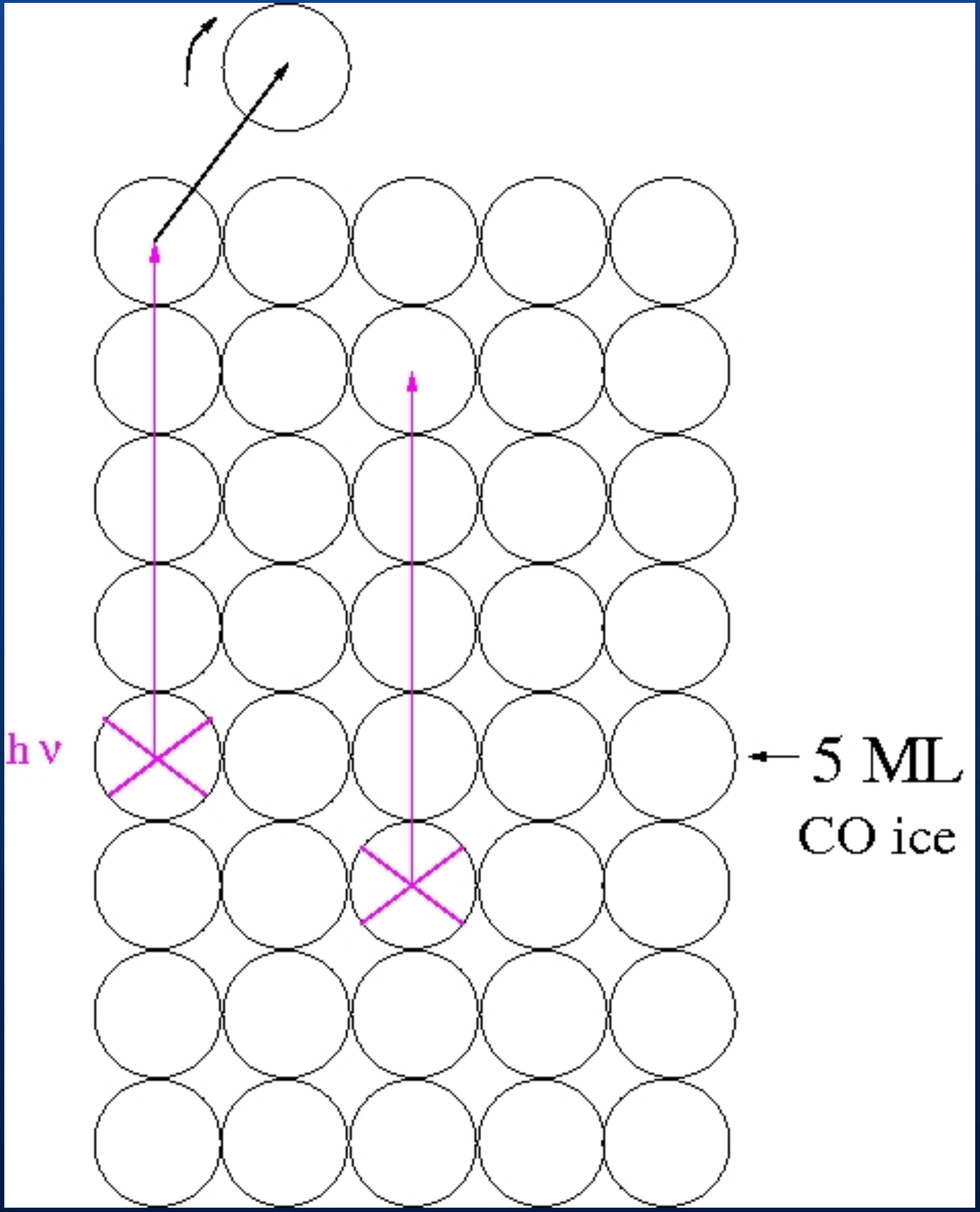
# Photodesorption of CO ice

Gas phase ←→Mass spectrometry




Muñoz Caro et al. 2010

# Photodesorption of CO ice




Why is photodesorption rate independent of ice thickness if there are more than ~ 5 ML?

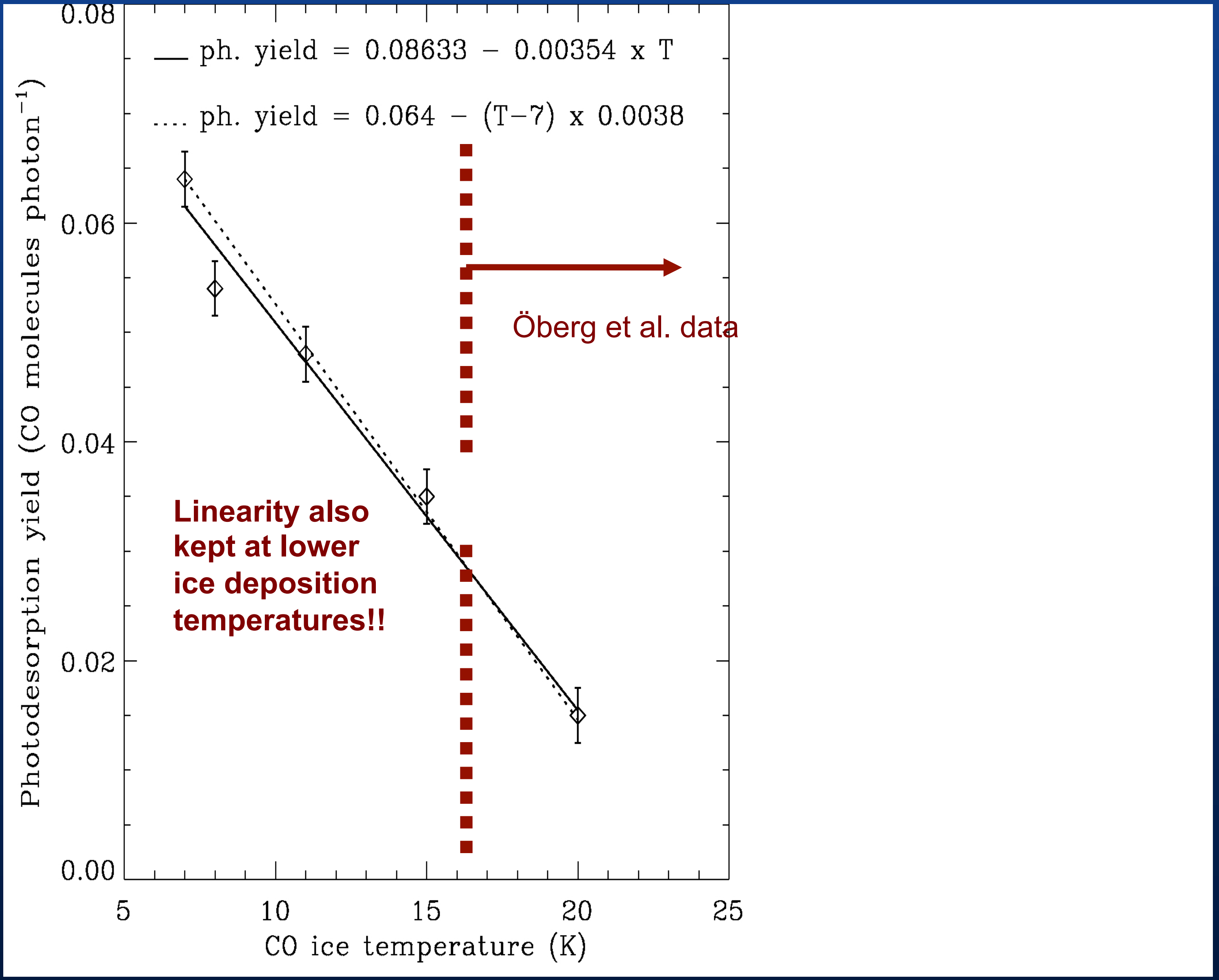
Indirect desorption induced by electronic transitions (DIET): Electronic excitation energy redistributed to neighbors provides energy to surface molecules to break intermolecular bonds.

For a better understanding of this process it is important to measure photodesorption rate *per absorbed photon*

UV absorption cross sections of ice analogs are required

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

# Photodesorption yield vs. ice deposition temperature



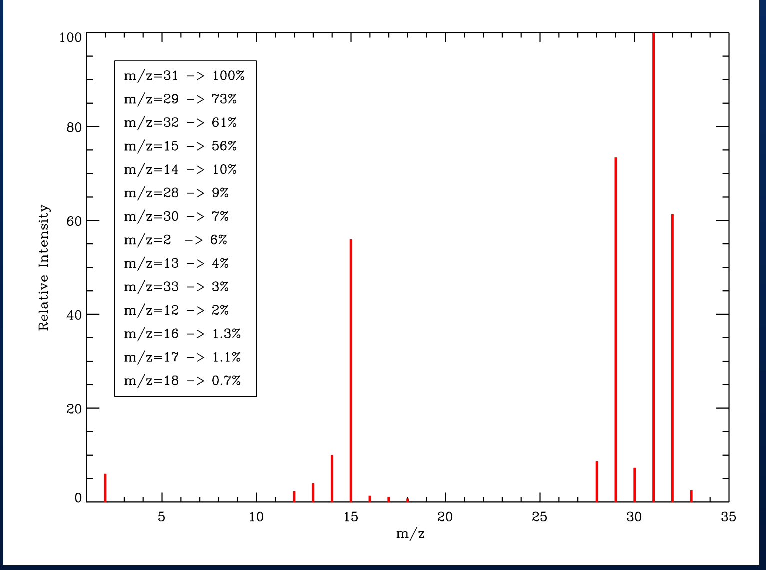

Muñoz Caro et al., in prep.

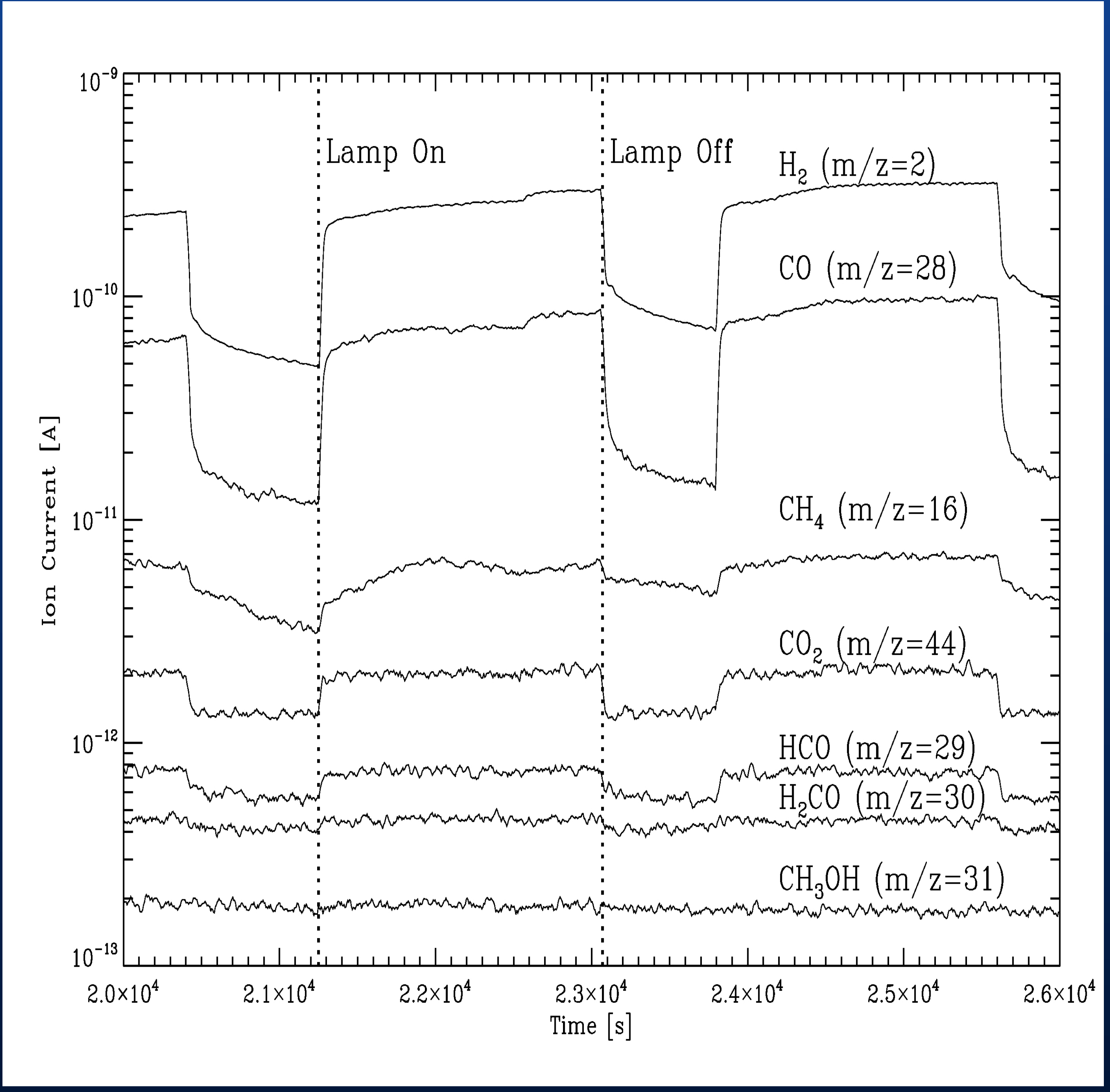
# UV irradiation of pure $CH_3OH$ ice

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



# "Photochemidesorption"

Photochemidesorption is an abbreviation for a photochemical process that leads to the formation of a photoproduct, which can

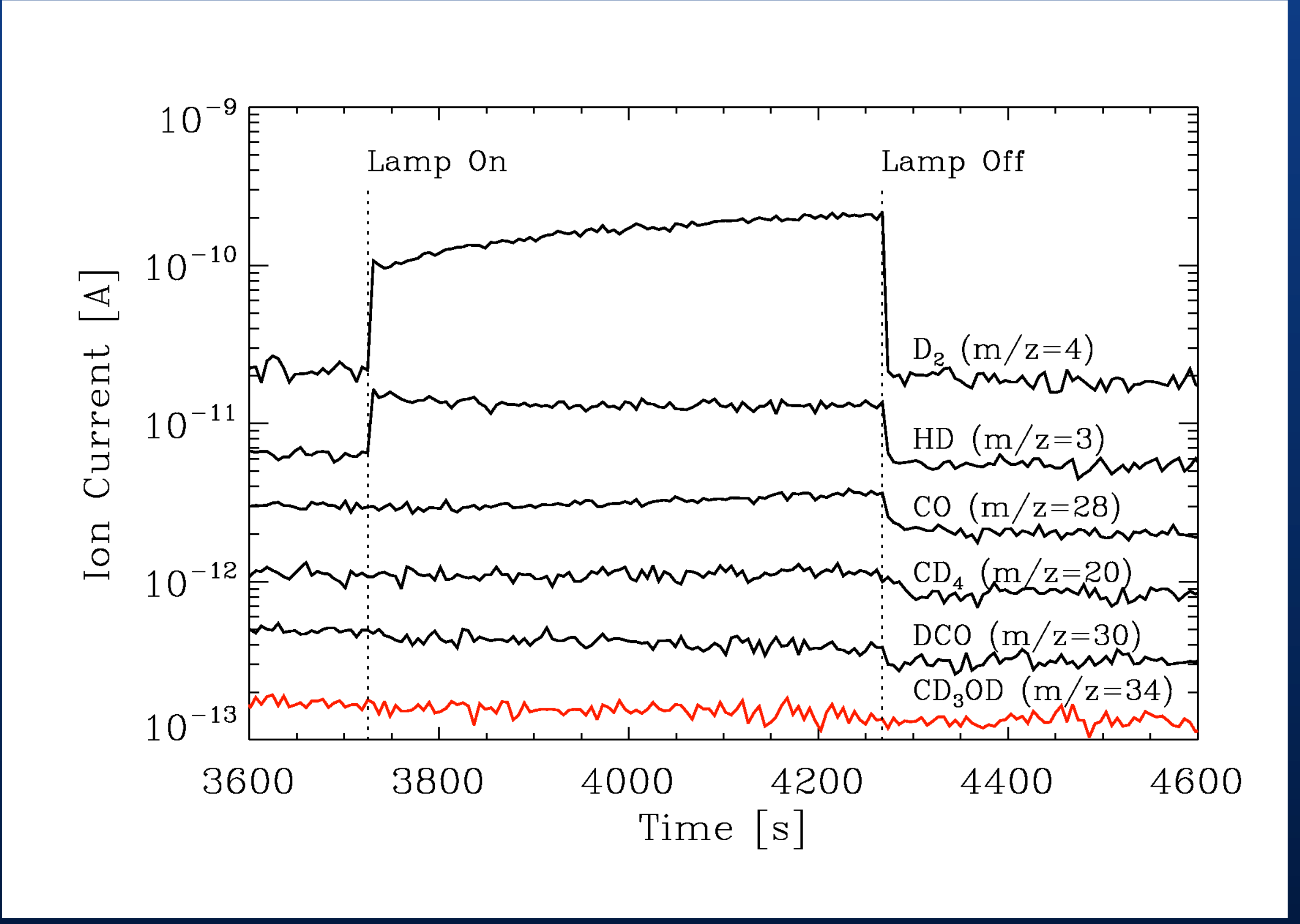
i) directly desorb when formed on the ice surface, or

ii) be formed in the ice bulk and desorb later via the DIET mechanism, after the ice monolayers on top were removed upon continued irradiation.

The first route (i), direct desorption, would lead to a direct rise of the QMS signal at the very beginning of irradiation, but in practice it is difficult to detect with the current sensibility of the QMS.

The second route (ii) will lead to an observable photochemidesorption when a sufficient amount of the photoproduct is accumulated in the ice bulk. An example is the observed photochemidesorption of $CH_4$ in the pure $CH_3OH$ ice irradiation experiment. This mechanism is interesting since it allows the desorption of certain molecules, like $CH_4$, which photodesorption is negligible when pure $CH_4$ ice is irradiated.

# UV irradiation of pure $CD_3OD$ ice




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

# 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.

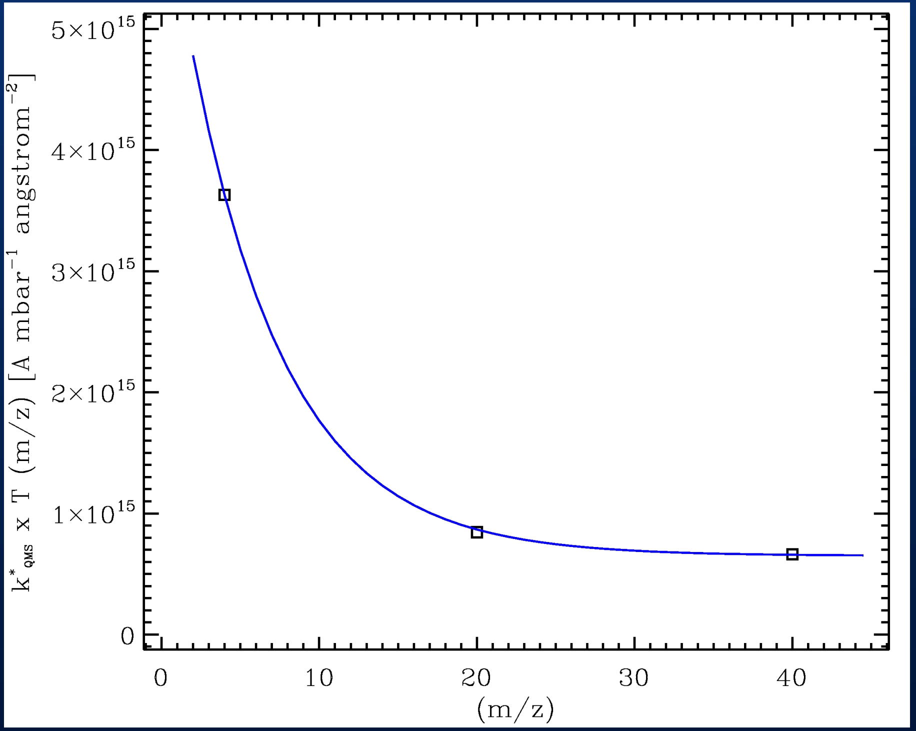
# Calibration of QMS for photodesorption (II)

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

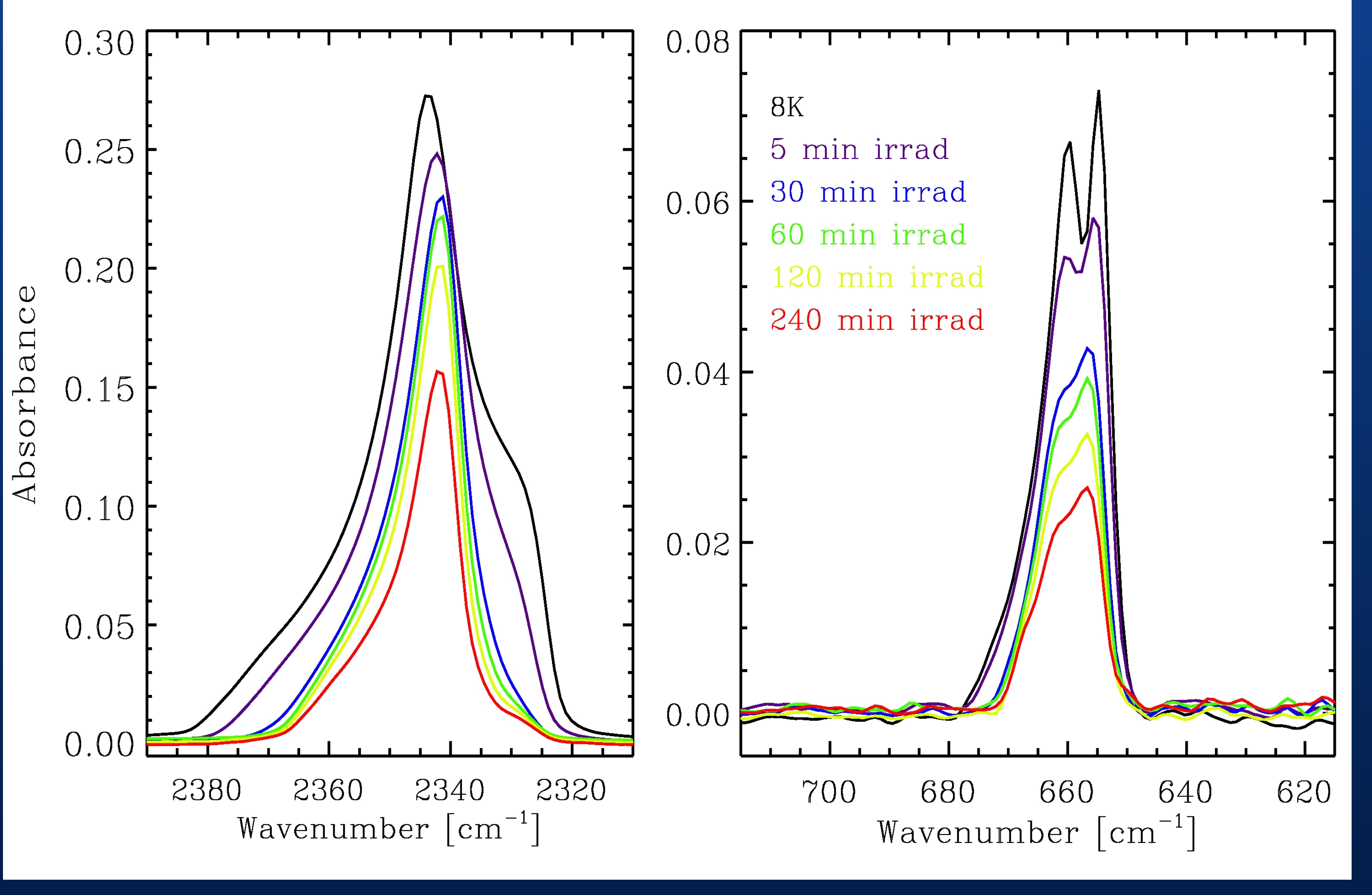
where $k_{CO} = A(28)/N(CO)$

**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:**

$k_{CO} \times S(m/z) = 6.5 \times 10^{14} + 5.73 \times 10^{15} \exp(-(m/z)/6.11)$



# Quantification of $CO_2$ + UV exp.




Infrared $CO_2$ ice bands decrease during irradiation

**Reactions:**

$CO_2$ + hv -> CO + O

$CO_2$ + O -> $CO_3$

O + O -> $O_2$

$O_2$ + O -> $O_3$

**Back reactions:**

CO + O -> $CO_2$

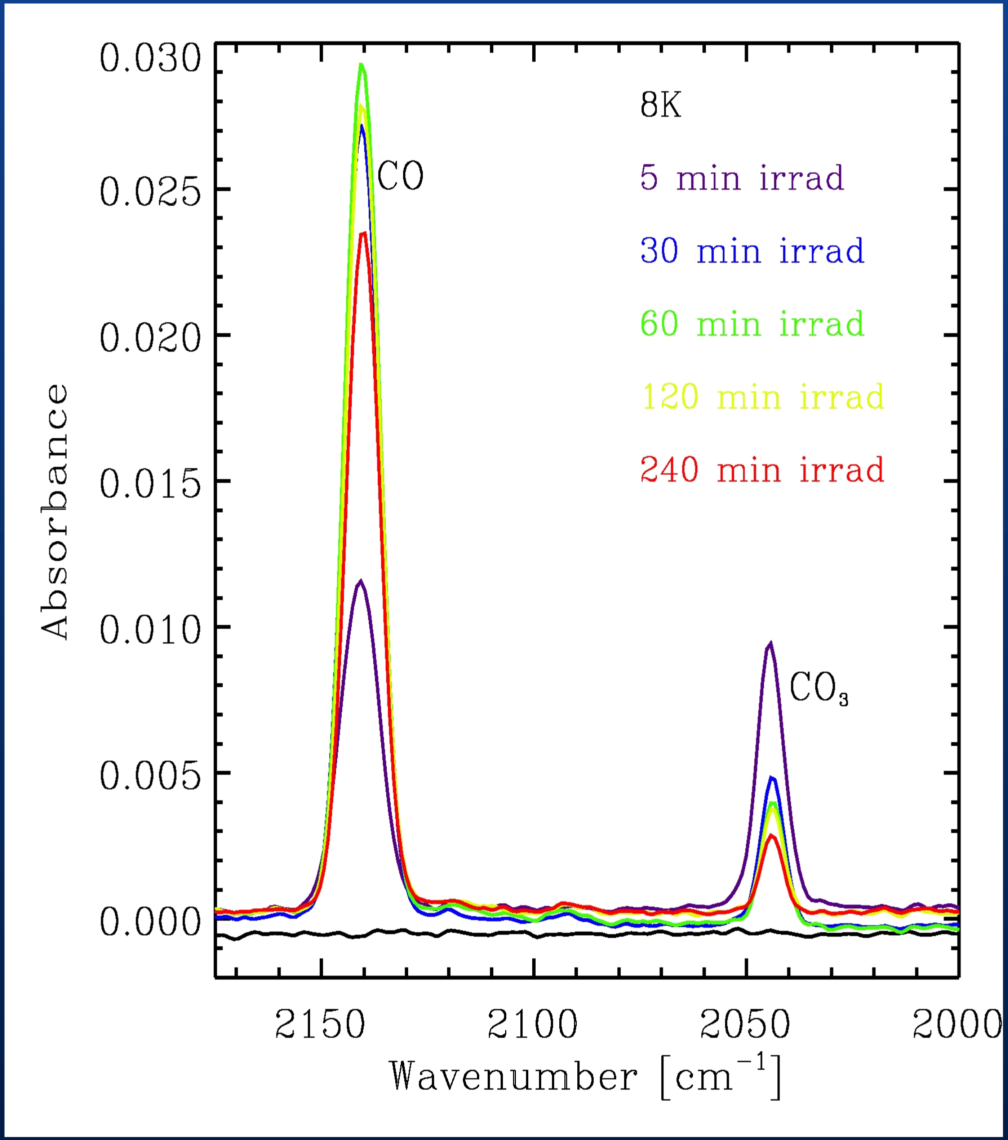
$CO_3$ + hv -> $CO_2$ + O

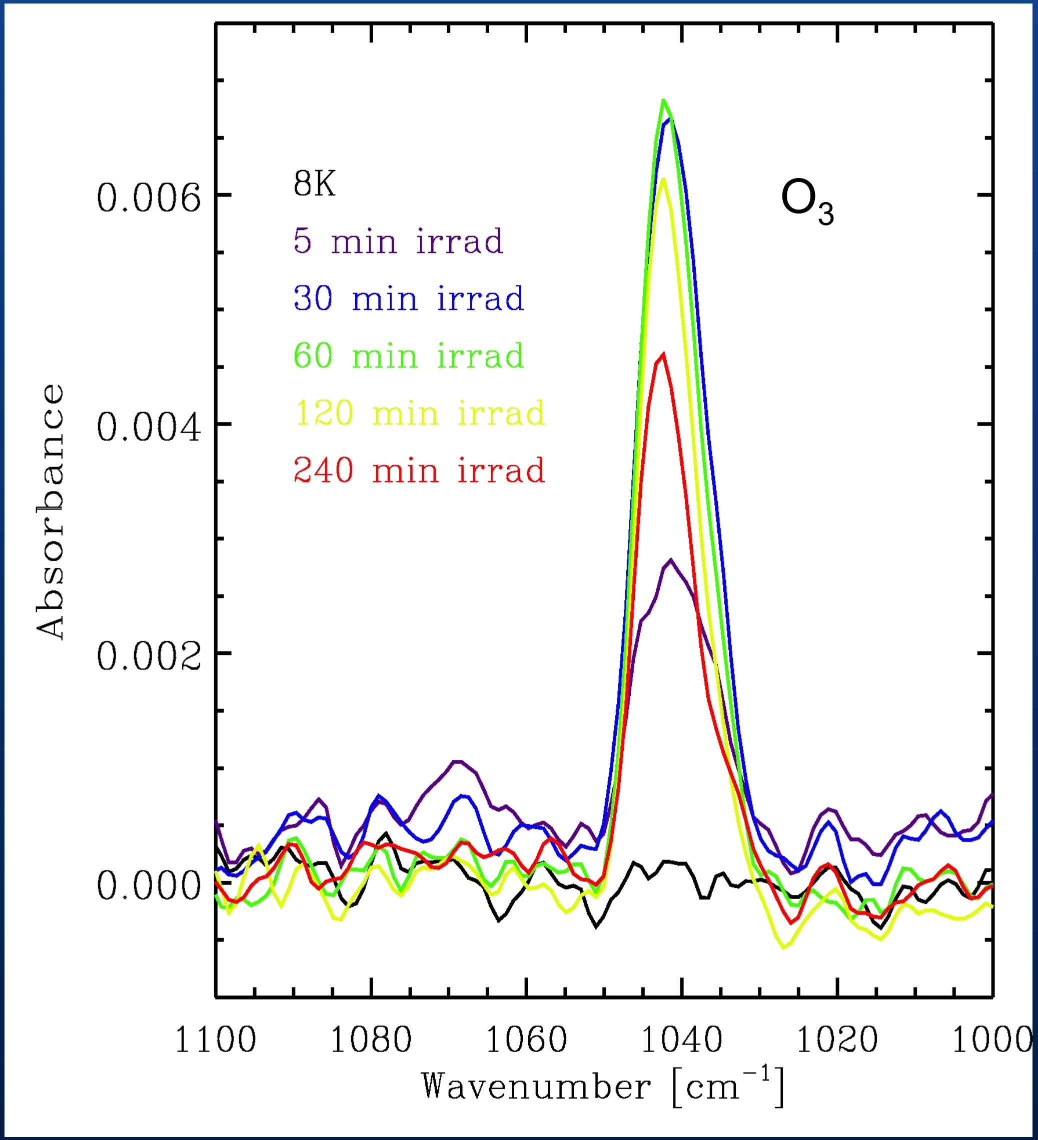
$O_2$ + hv -> O + O

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

Martín-Doménech et al. 2015, submitted

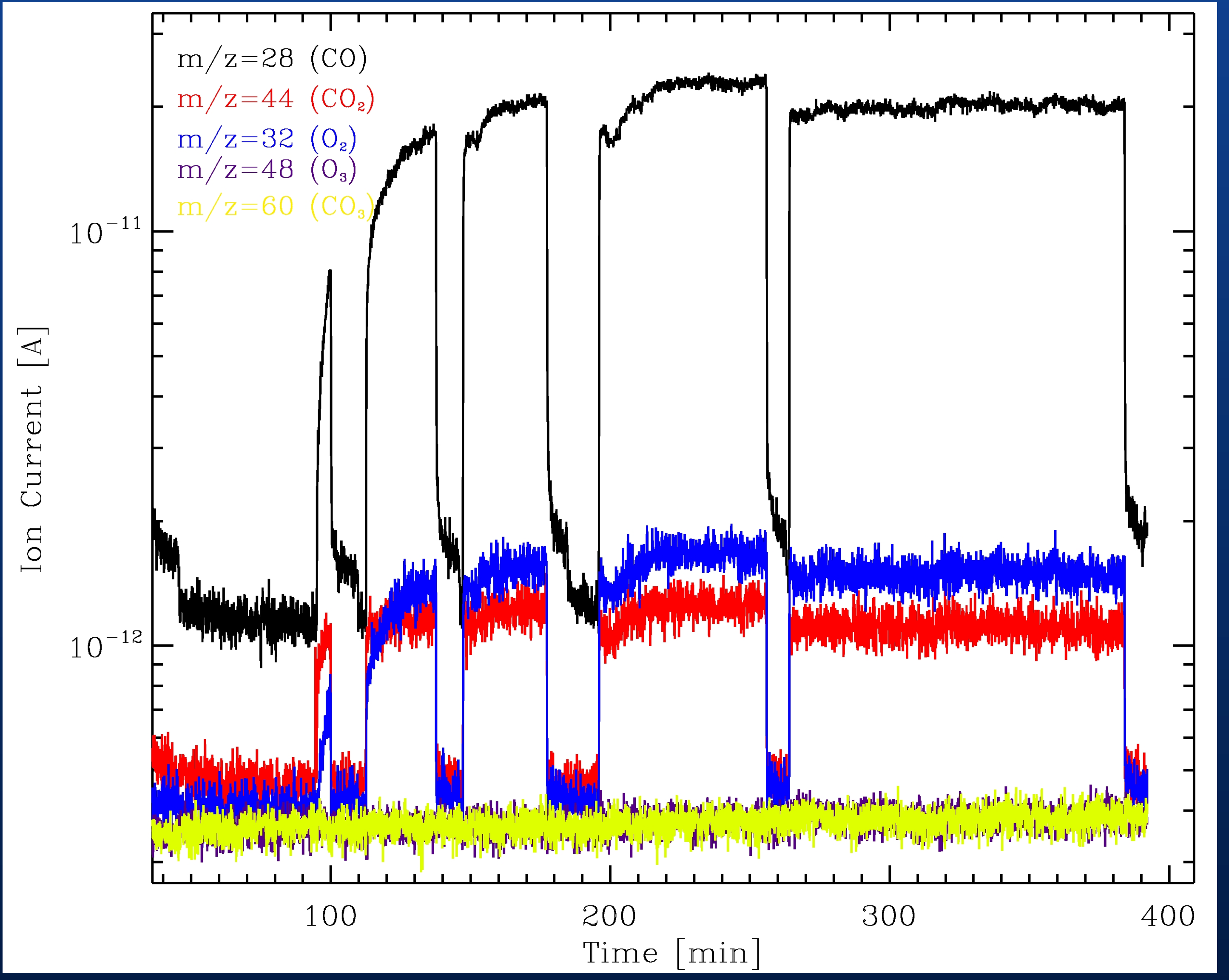
# Quantification of $CO_2$ + UV exp.



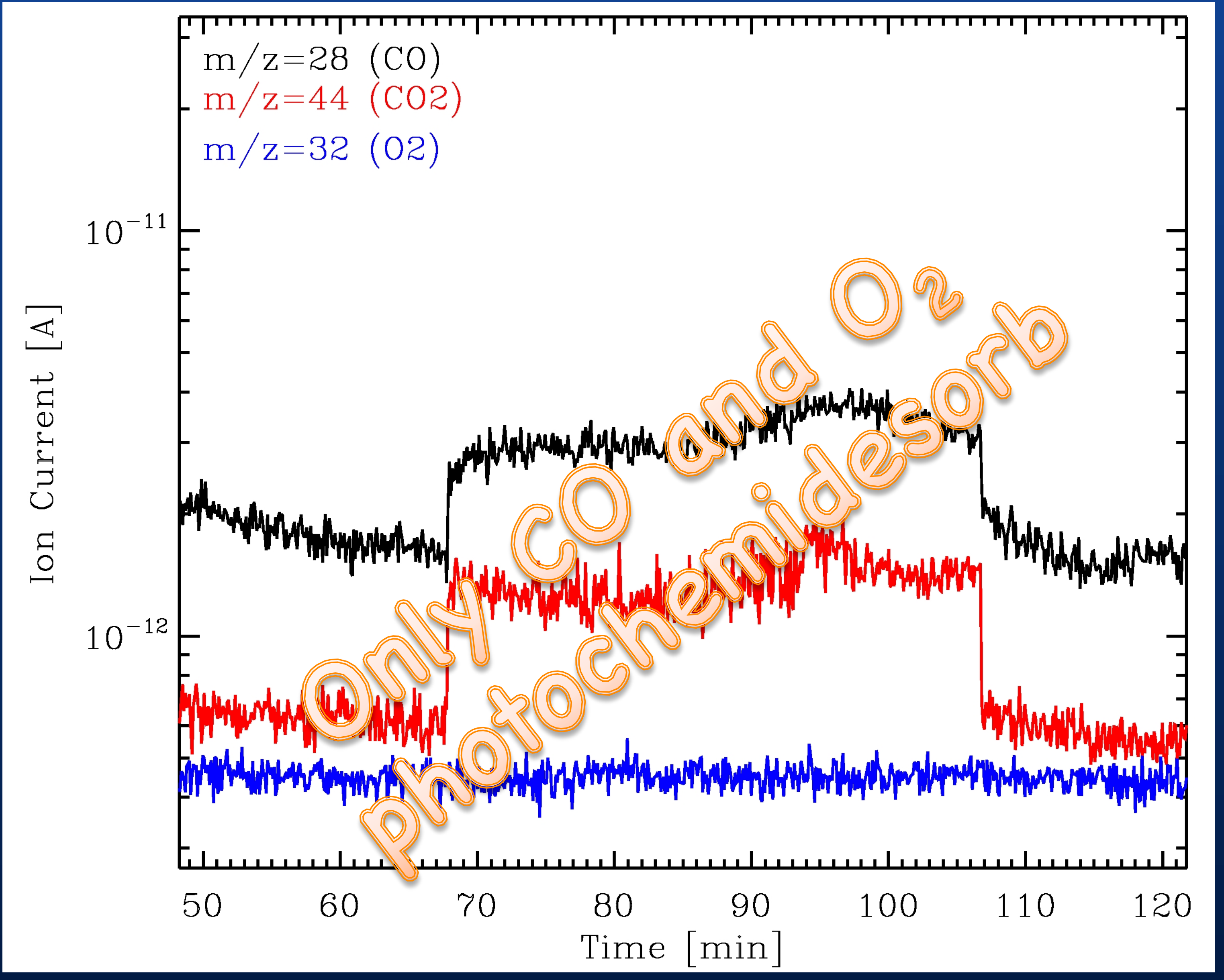

**Formation of photoproducts observed in infrared during irradiation**

# Quantification of $CO_2$ + UV exp.



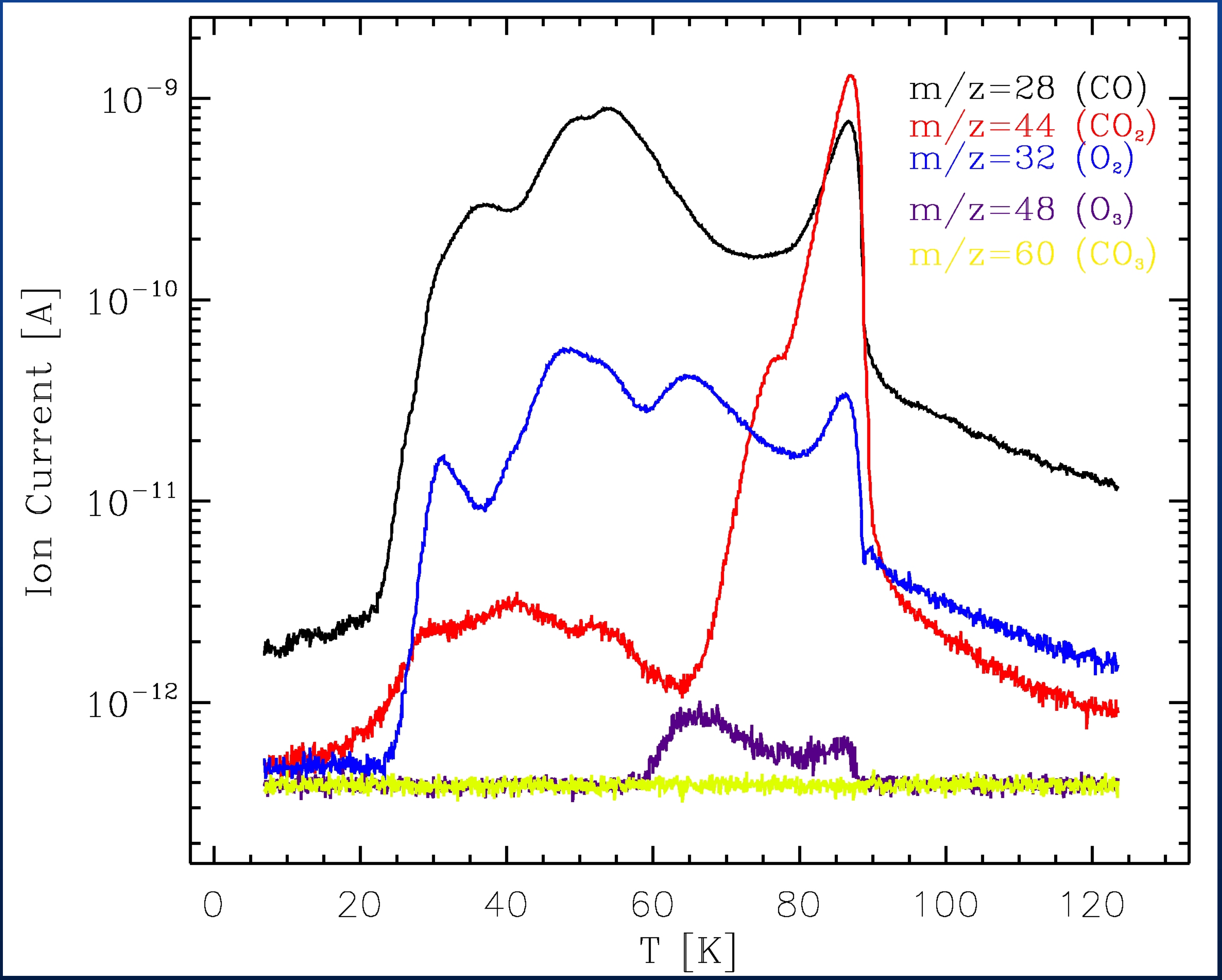

**Photodesorption of CO and $O_2$ observed by QMS**

# Quantification of $CO_2$ + UV exp.



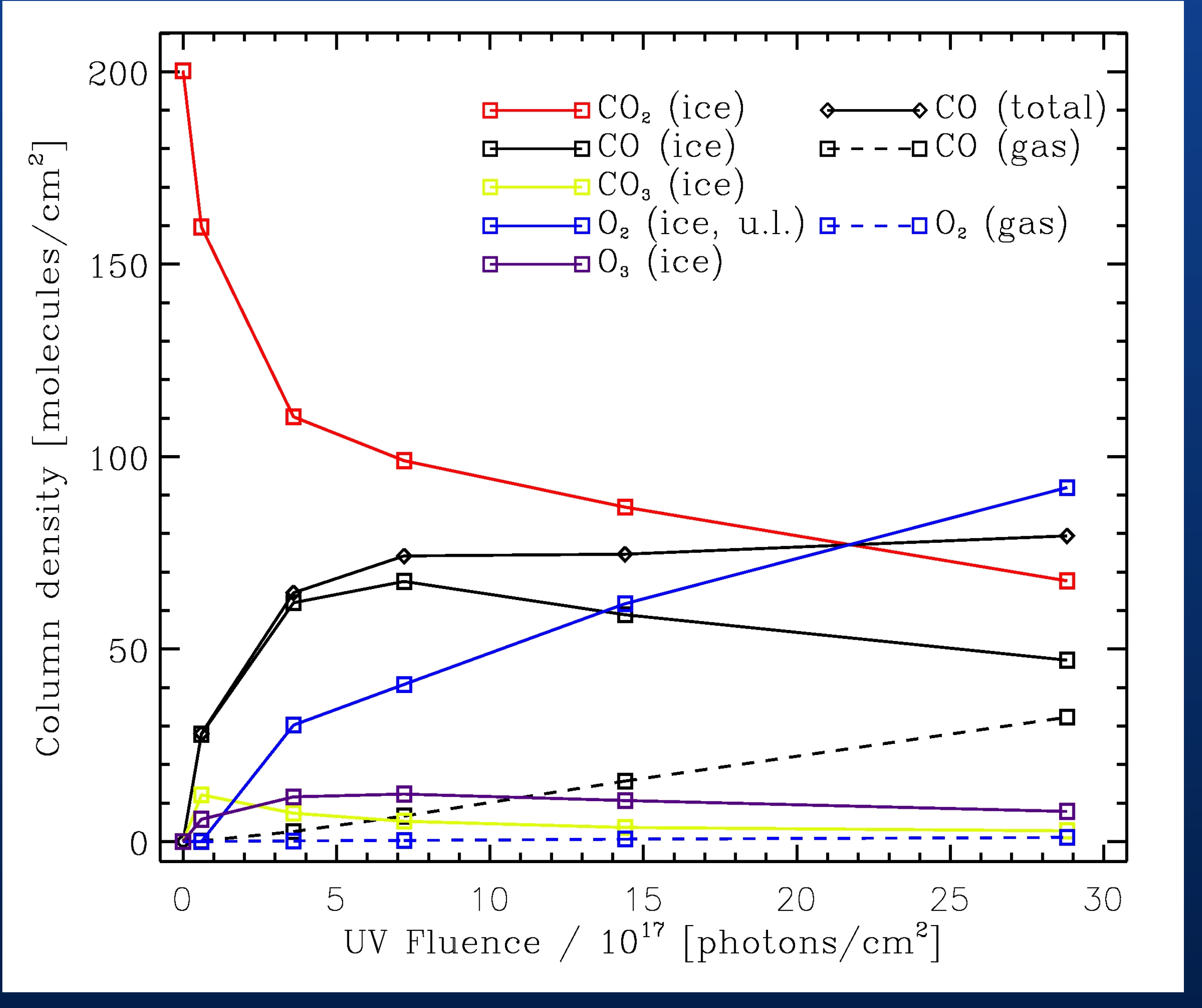

**Background contamination of CO and $CO_2$ (blank with no ice)**

# Quantification of $CO_2$ + UV exp.




**TPD curves of irradiated $CO_2$ ice showing desorption of photoproducts**

# Quantification of $CO_2$ + UV exp.




Photoproducts 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%** |

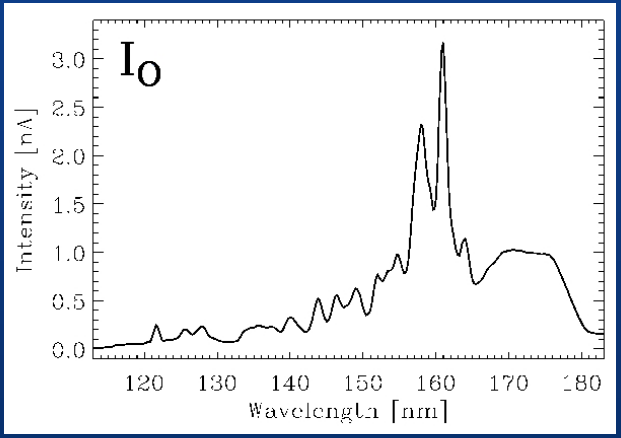
**Only 4% of CO would photochemidesorb and a negligible amount of $O_2$**

**Thermal desorption is required to release the photoproducts to the gas phase**

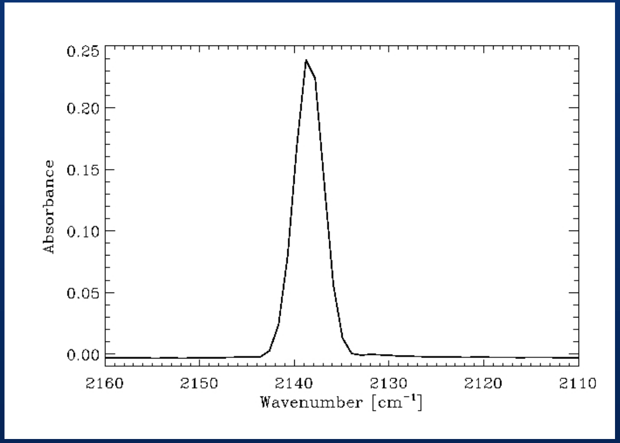
# 3. VUV-spectroscopy of pure ices

# Vacuum-UV Spectroscopy

VUV emission of lamp

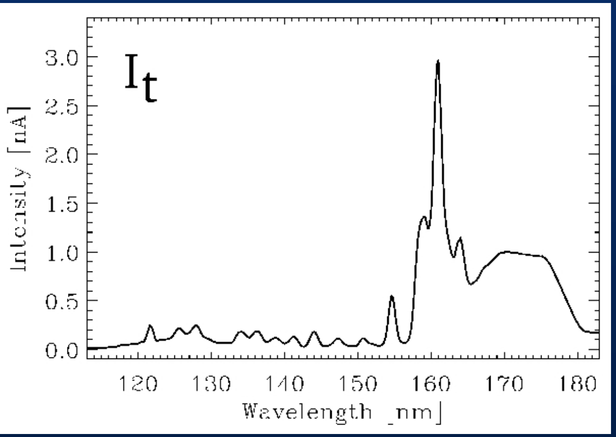



IR for determination of ice column density

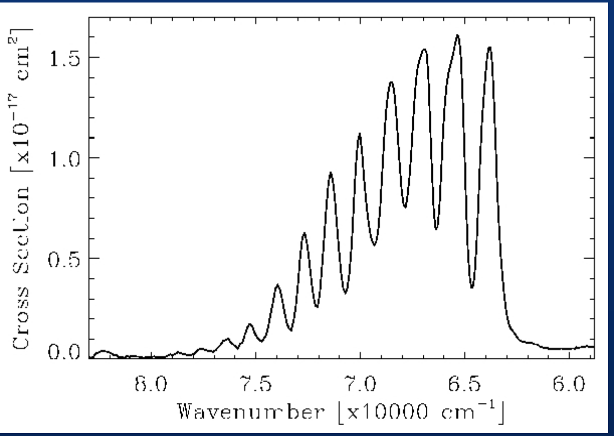



$$N = \frac{1}{A} \int_{band} \tau_\nu d_\nu$$

VUV transmitted by sample



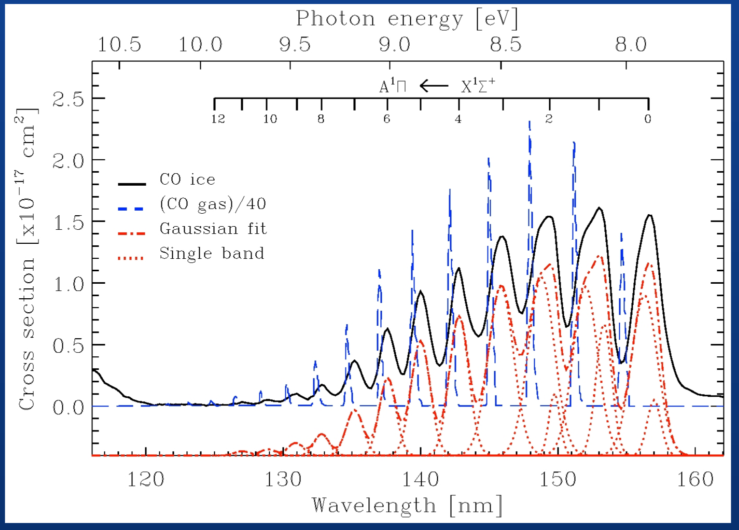

VUV ice absorption cross section



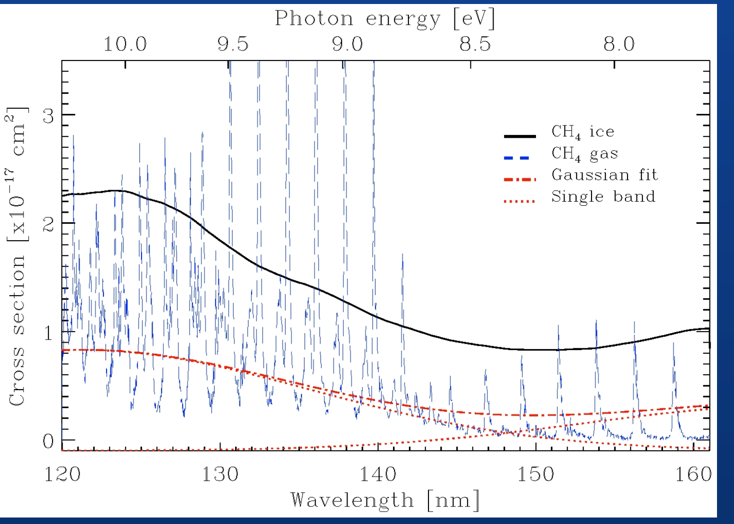

$$\sigma(\lambda) = \frac{1}{N} Ln \frac{I_t(\lambda)}{I_0(\lambda)}$$

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

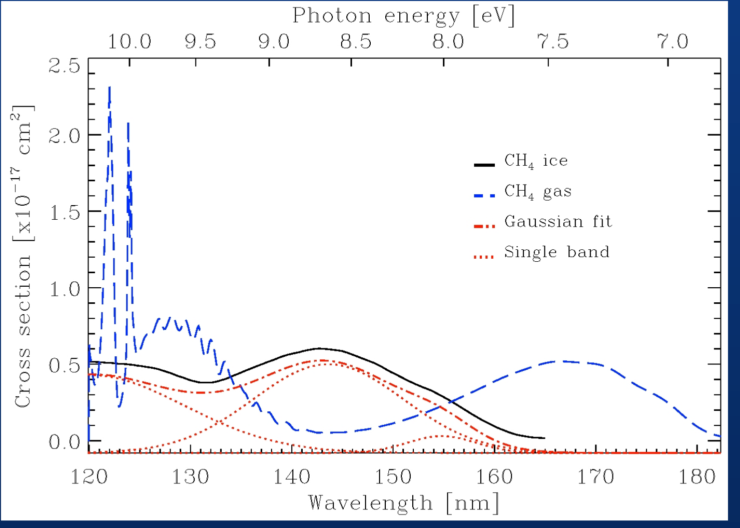
# Polar ices



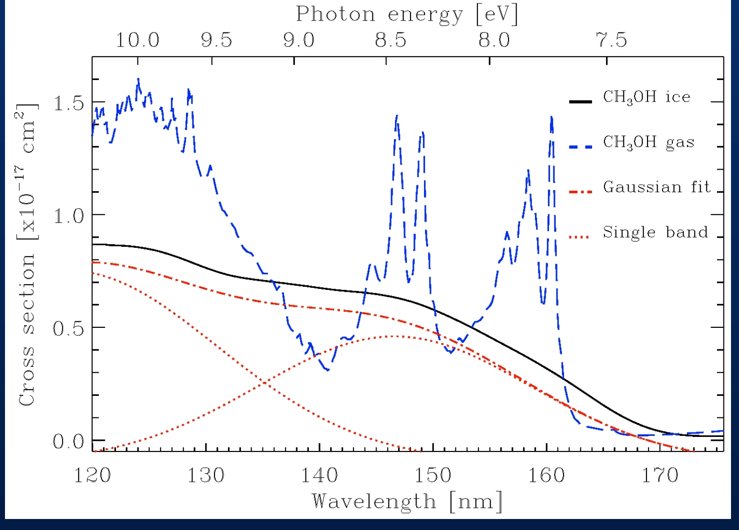

Carbon monoxide



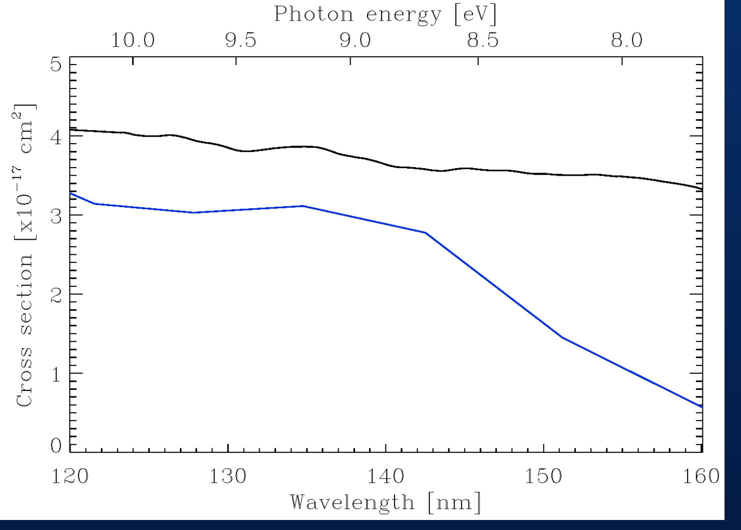

Ammonia




Water



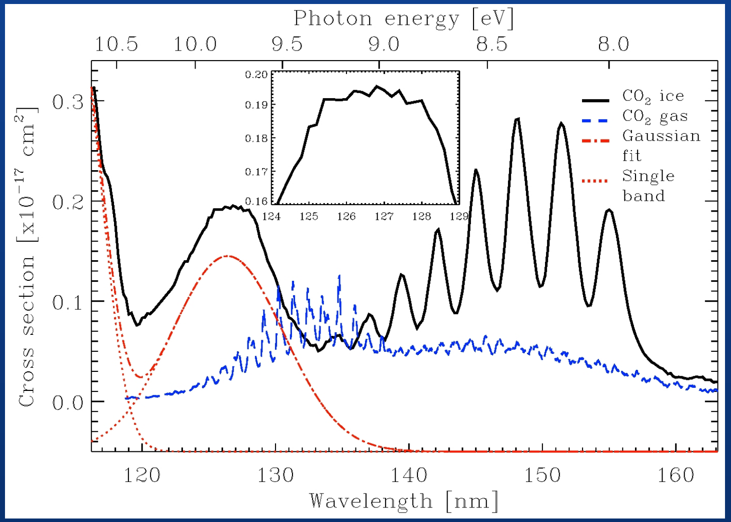

Methanol

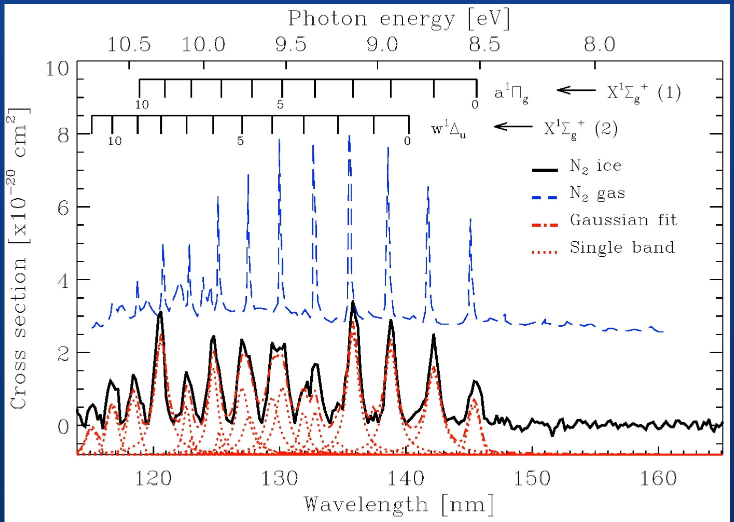



Hydrogen sulfide

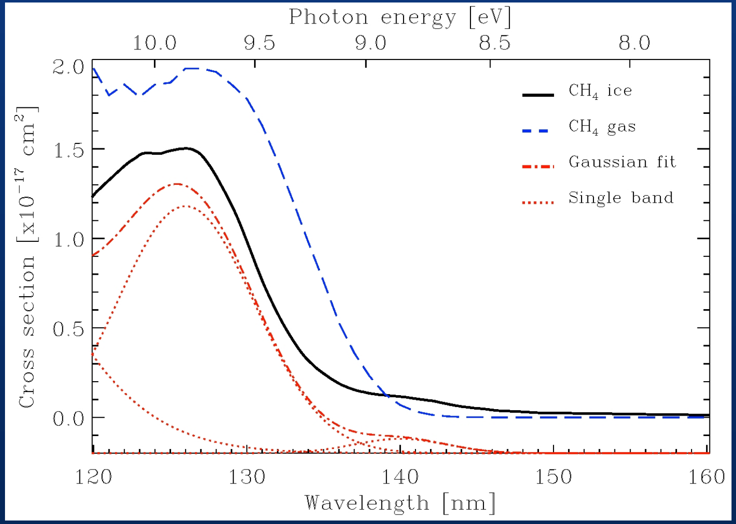
Cruz-Diaz et al., A&A, 2014a

# Apolar ices

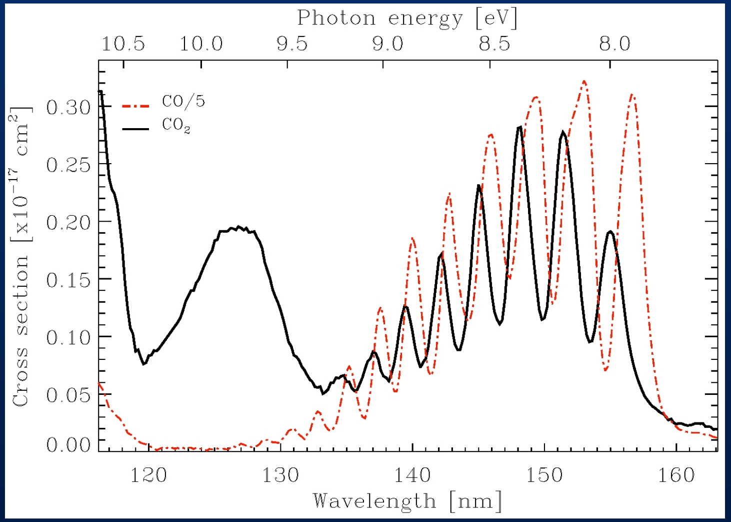


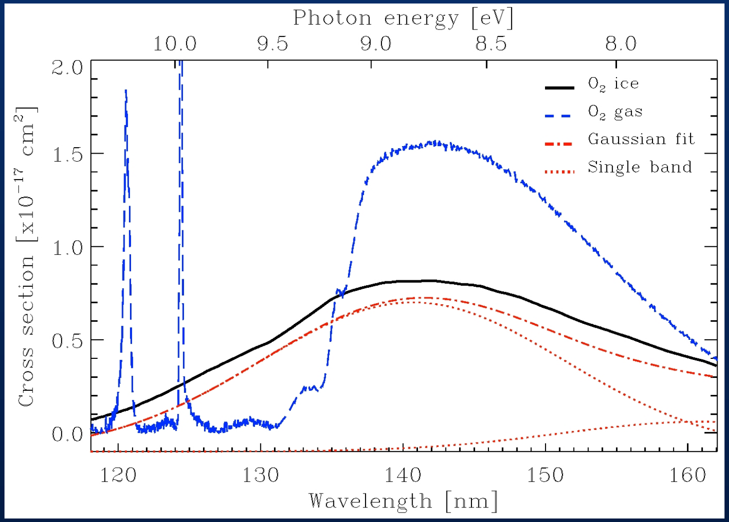




Nitrogen




Methane



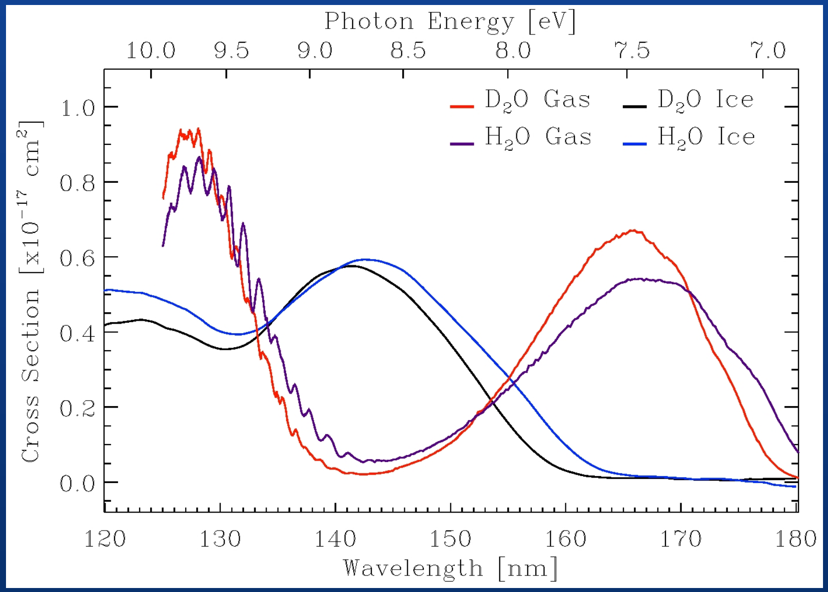

Carbon dioxide

Oxygen

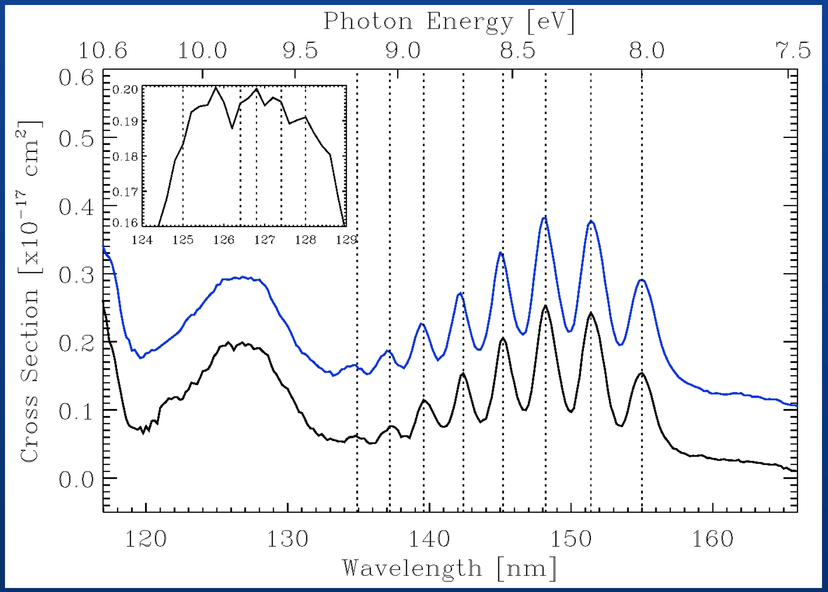
Cruz-Diaz et al., A&A, 2014b

# Isotopic Effects

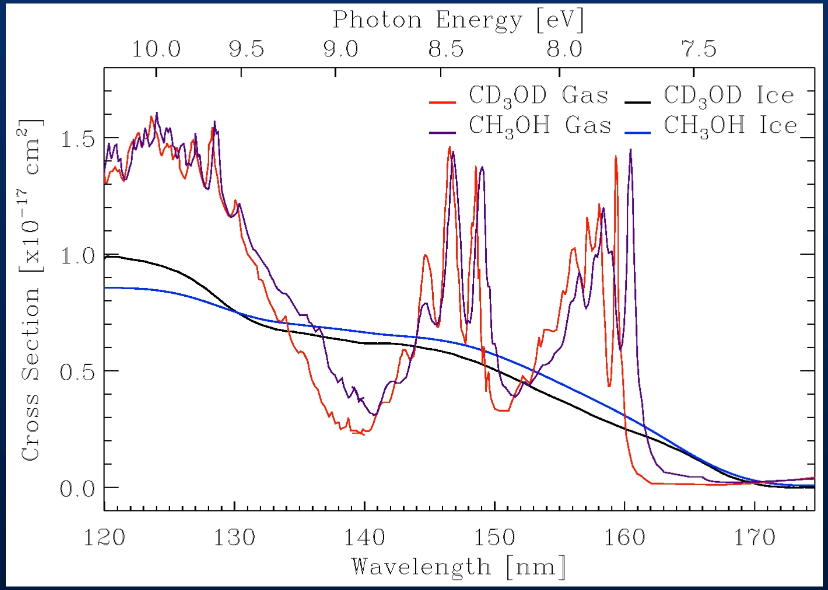
Cruz-Diaz et al., MNRAS, 2014



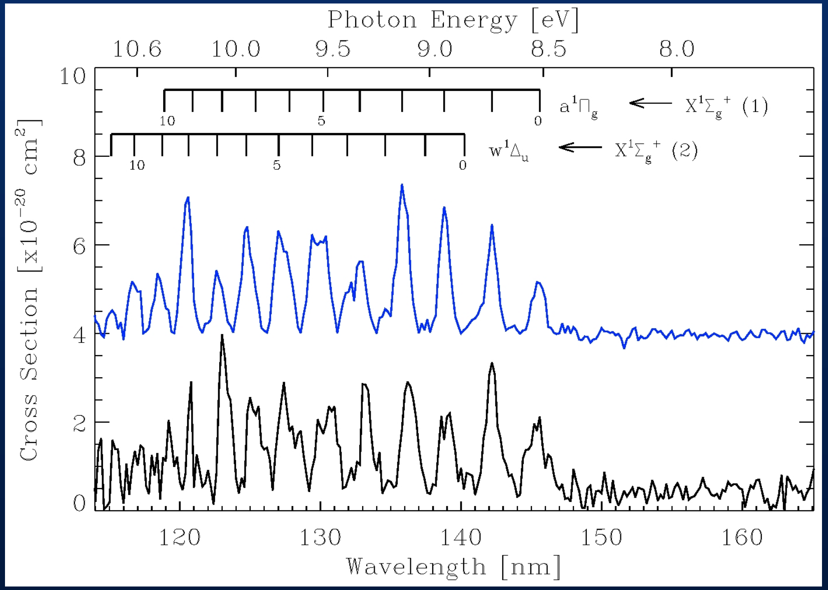

Deuterated water




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

# VUV spectroscopy of $CO_2$ and CO ice

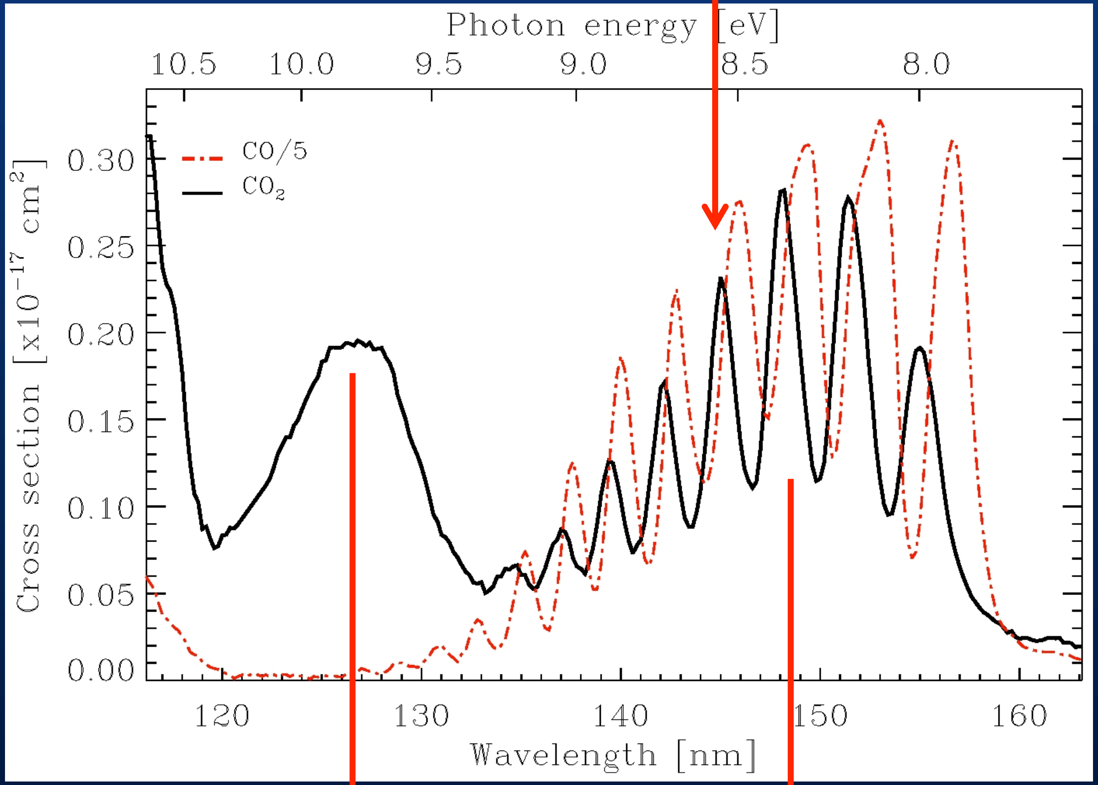
## VUV - absorption cross section of $CO_2$

**PROBLEM**

CO formation by photodissociation of $CO_2$ during irradiation

$N(CO) = 0.22\, N(CO_2)_i$

contribution



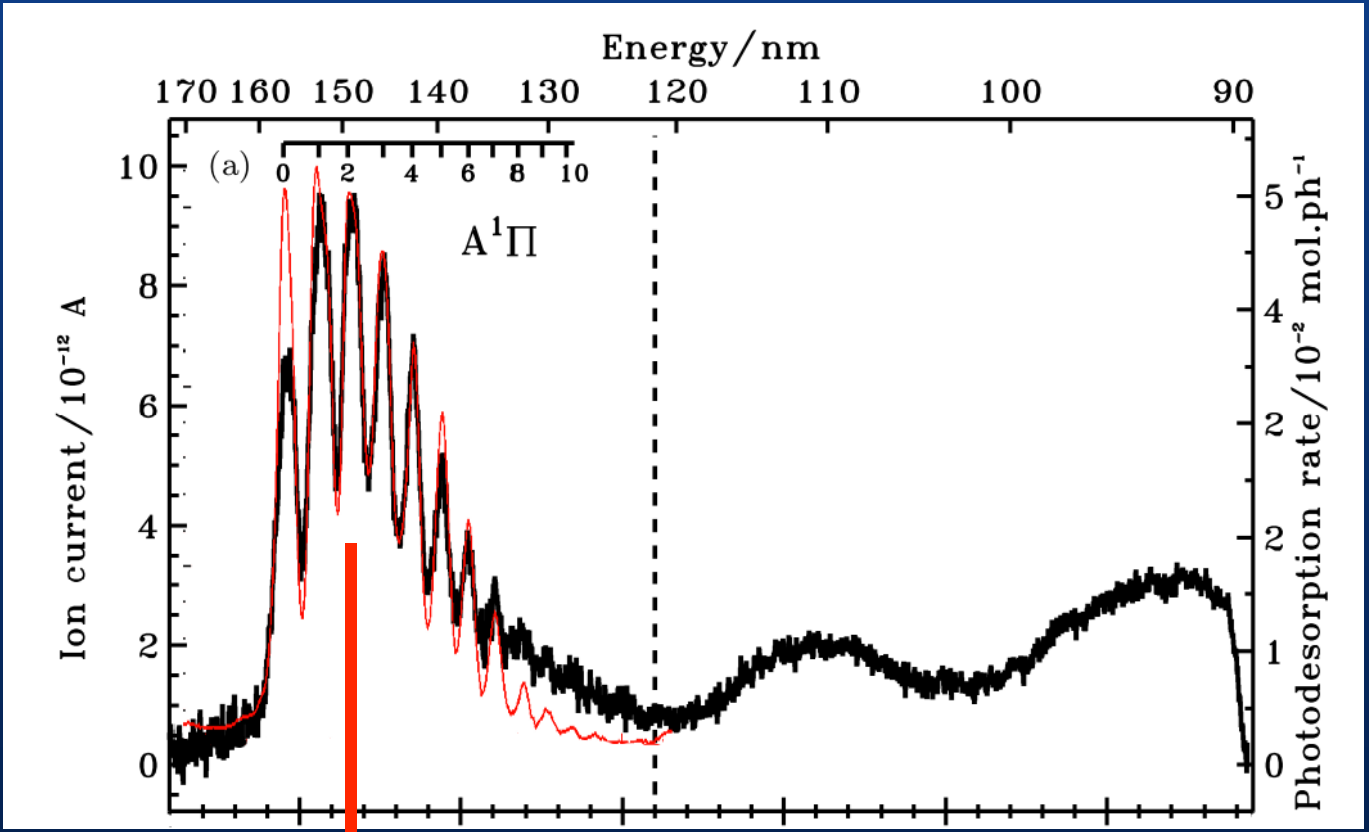

$CO_2$ not affected compared to other works

CO blueshifted compared to pure ice

# Astrophysical implications

## CO photodesorption

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



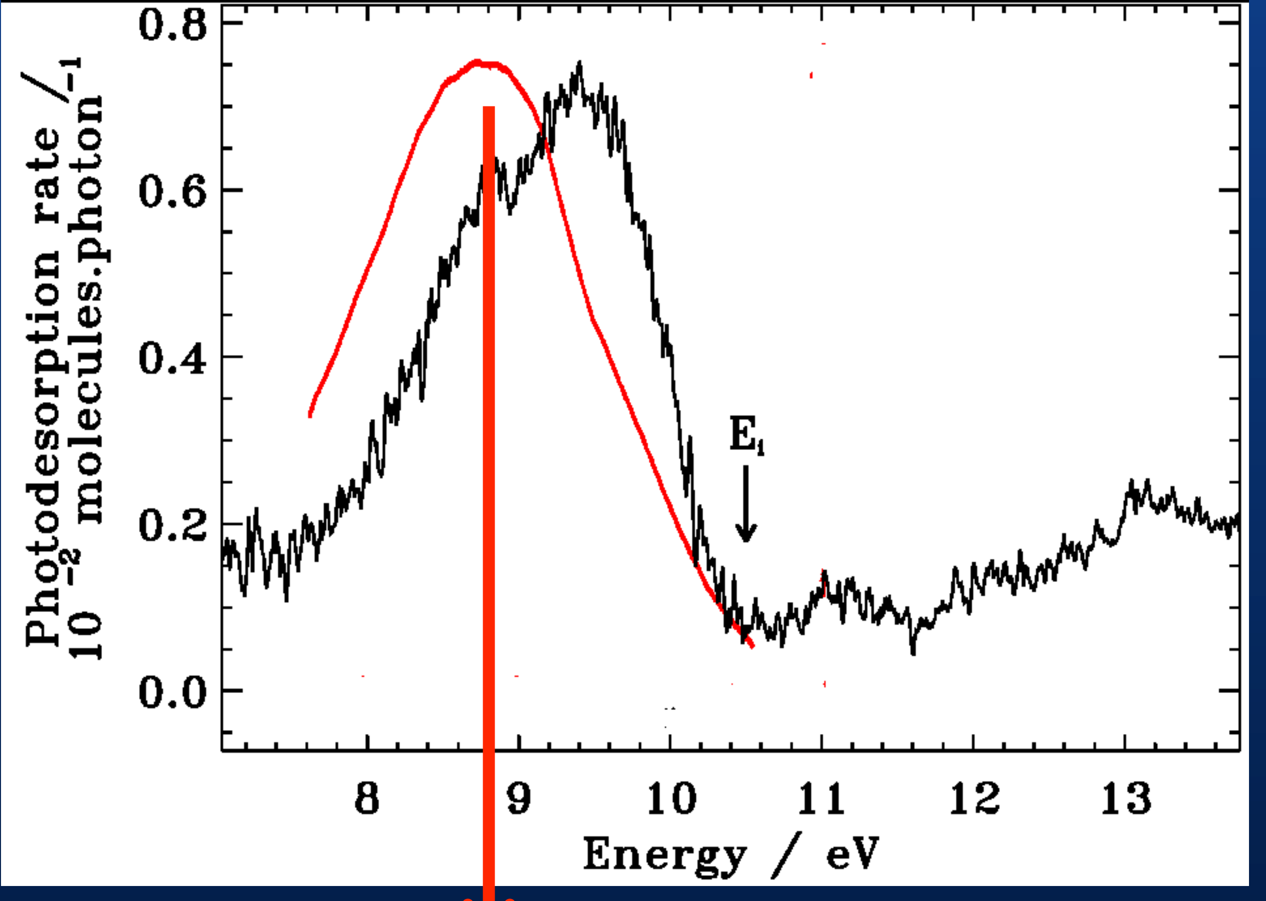

Fayolle et al. 2011
Lu et al. 2005
Cruz-Diaz et al., A&A, 2014a

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$_{abs}$ |
|---|---|---|---|---|
| | 10.2 | $6.9 \pm 2.4 \times 10^{-3}$ | $1.1 \times 10^{-19}$ | $12.5 \pm 4.4$ |
| Fayolle et al. 2011 | 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!

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DO YOU THINK THERE'S INTELLIGENT LIFE OUT THERE?
I HOPE SO, I'D HATE TO THINK WE WERE THE BEST THEY COULD COME UP WITH!
Lynch
¡Muchas gracias!