Photodesorption from interstellar ice analogues: what do we currently know from laboratory experiments

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MONARIS

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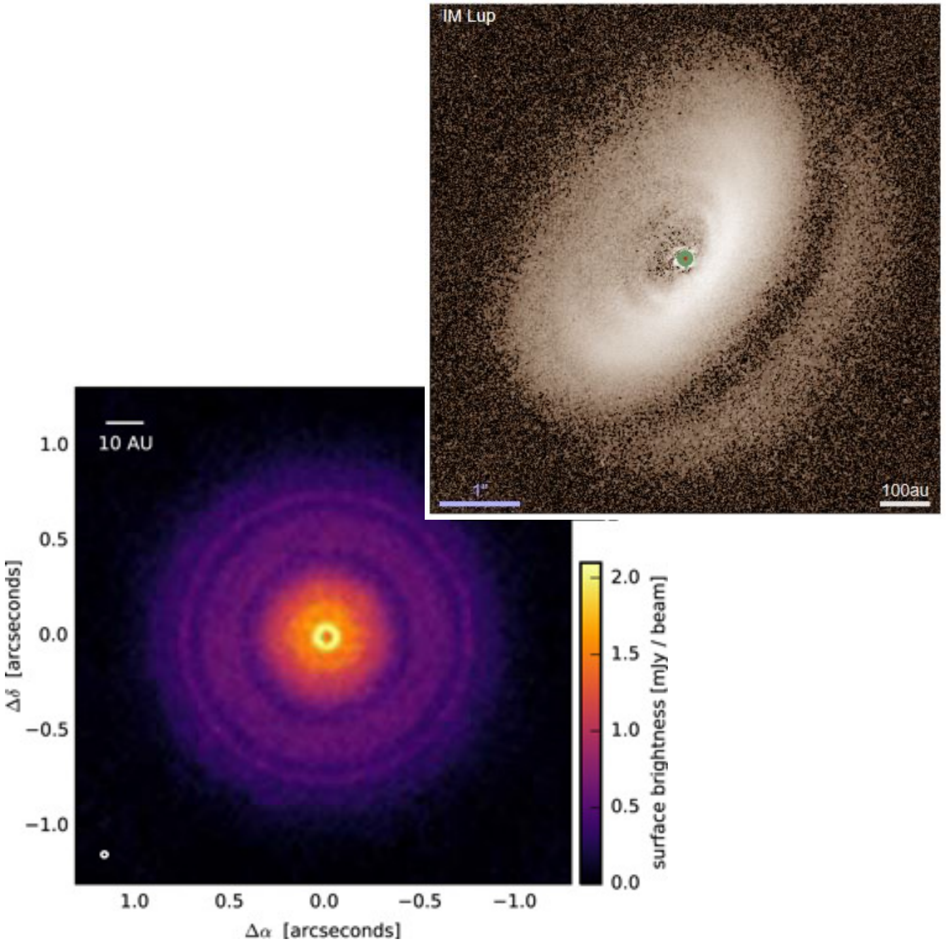
Motivations: non-thermal desorption in the cold ISM

In cold regions

Clouds (inner regions and borders)

T = 10 – 100 K

Density = $10^2 – 10^5$ cm^{-3}



Protoplanetary disks

T = 10 – 300 K

Density = $10^6 – 10^{15}$ cm^{-3}

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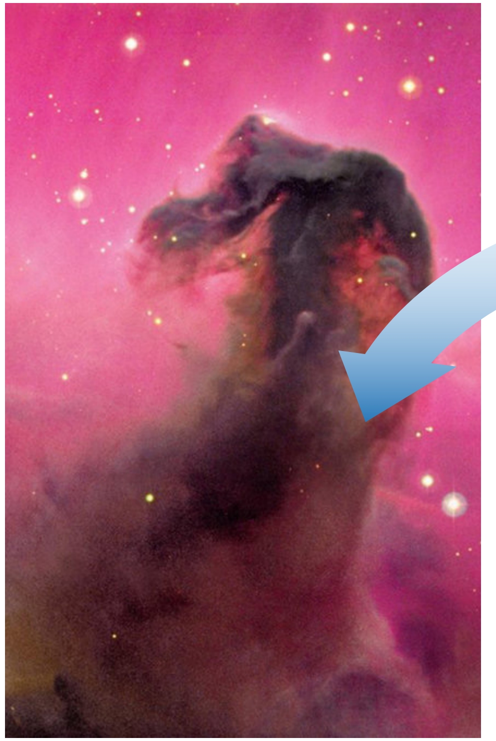
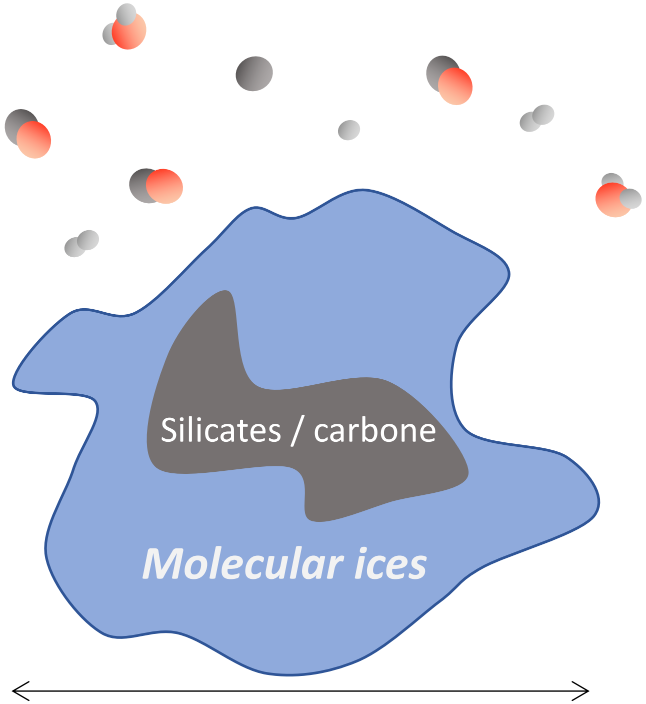
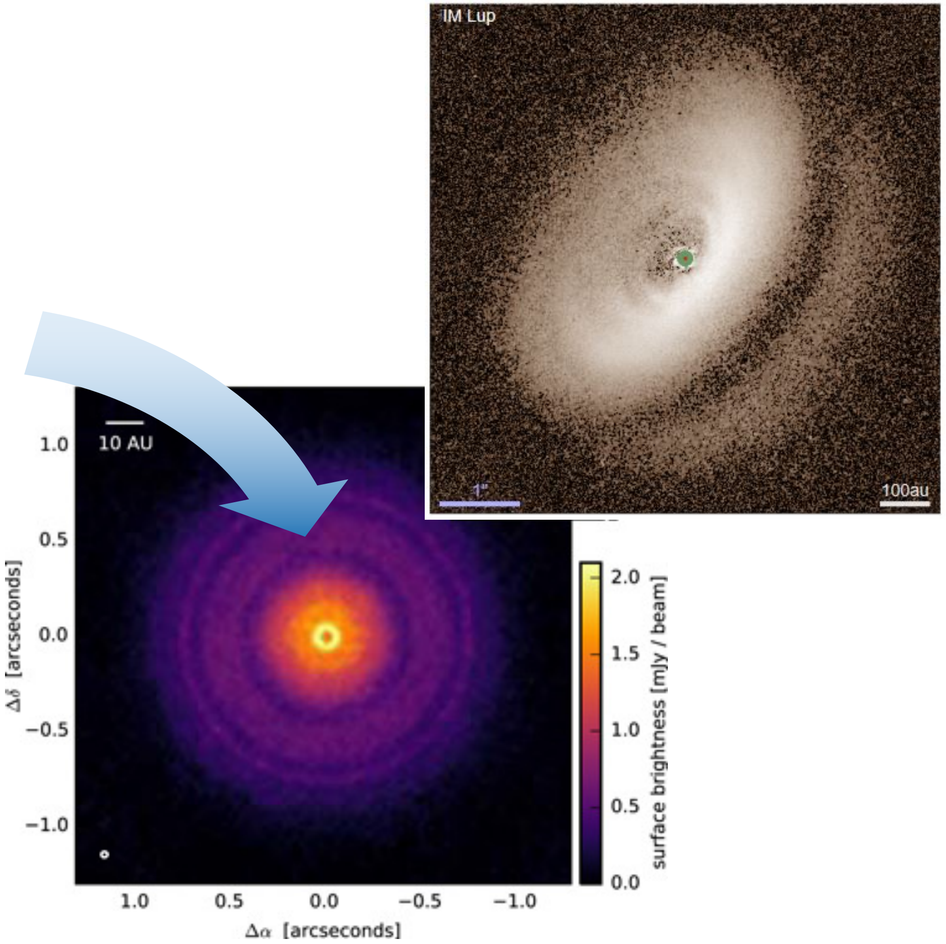
In cold regions





Main reservoir of molecular matter



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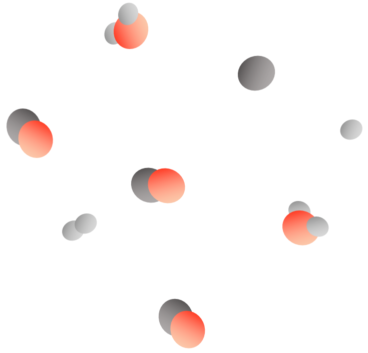


Gas Phase

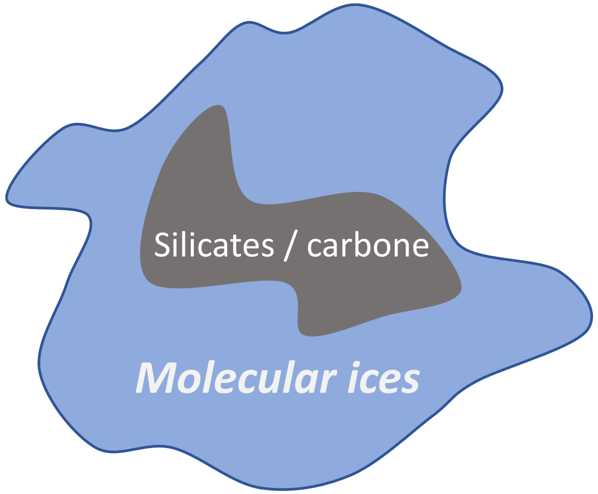
High molecular richness even in cold regions…

In frontier regions (PDR): H_2O, CO, CO_2, CH_3OH, H_2CO, CH_3CN… (Guzman+ 2011, 2013, 2014 ; Gratier+ 2013, Putaud+ 2019…)

In prestellar cores: CH_3OH, CH_3CN, HCOOH, $HCOOCH_3$… (Vastel+ 2014, Bacmann+ 2012, Jimenez-Serra+ 2016…)

In disks: H_2O, CO, CH_3CN in many sources, CH_3OH, HCOOH in TW Hydrae

(Willacy&Langer 2000, Hogerheidje+ 2011, Bergner+2018, Carney+2019, Walsh+2016, Favre+2018, Loomis+2018)



Solid Phase

Main reservoir of molecular matter

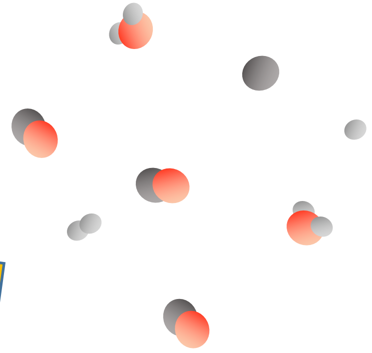
Mostly H_2O, CO, CO_2, CH_3OH, NH_3, CH_4…
Boogert+2015, McClure+2023, Sturm+2023

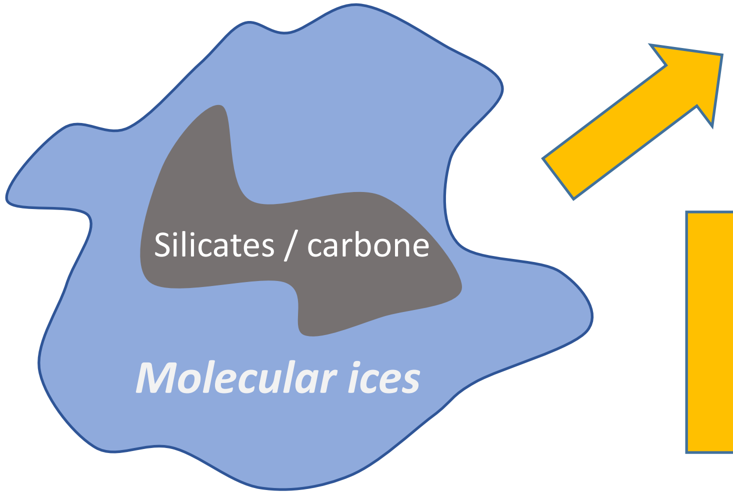
Motivations: non-thermal desorption in the cold ISM

Gas Phase

High molecular richness even in cold regions…

…But should be depleted on grains





Need for **non-thermal desorption processes** to maintain molecular abundances in the gas phase

Yields must be known
Mechanisms must be constrained

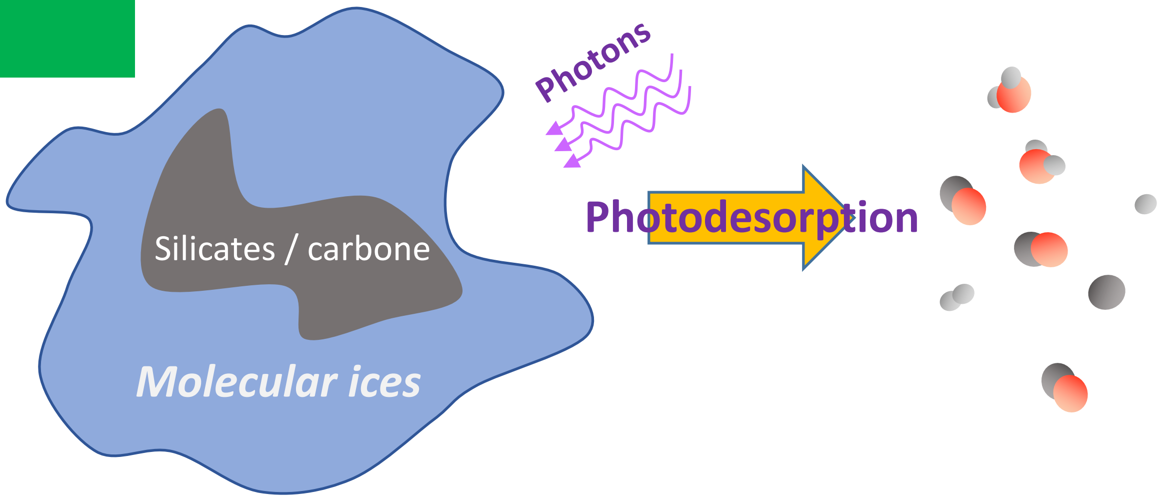
Solid Phase

Main reservoir of molecular matter

Mostly H_2O, CO, CO_2, CH_3OH, NH_3, CH_4…

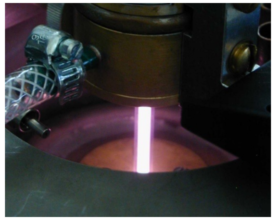
Boogert+2015, McClure+2023, Sturm+2023

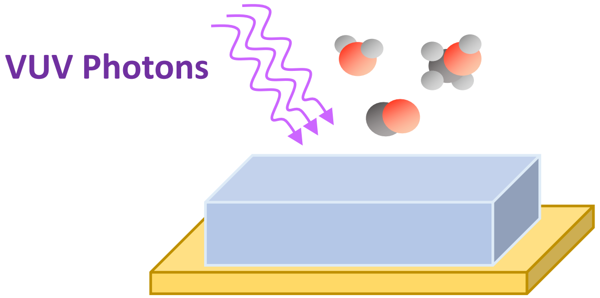
Motivations: experimental study of photodesorption



Considered for a long time as a possible candidate to explain observation of gaseous molecules in cold regions

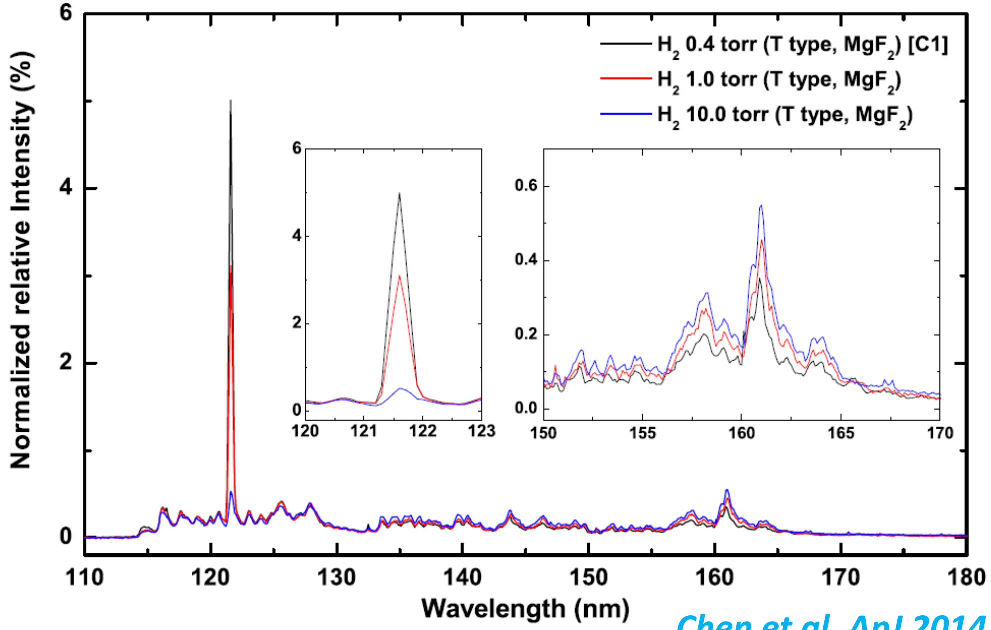
→ Has motivated many experimental works





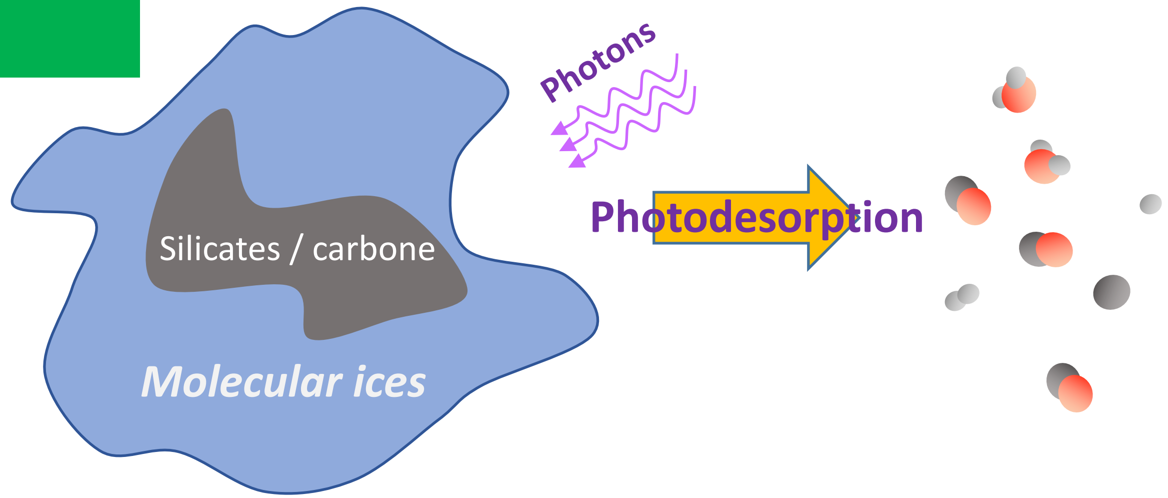
Cold substrate (10 < T < 100 K)

- ***Broadband Hydrogen mw-discharge lamp***
  « Tabletop » source
  Broad spectrum with a strong contribution at the Ly-α
  No control on the photon energy, Cut-Off above 10.5 eV
  Flux high



Chen et al. ApJ 2014

Motivations: experimental study of photodesorption



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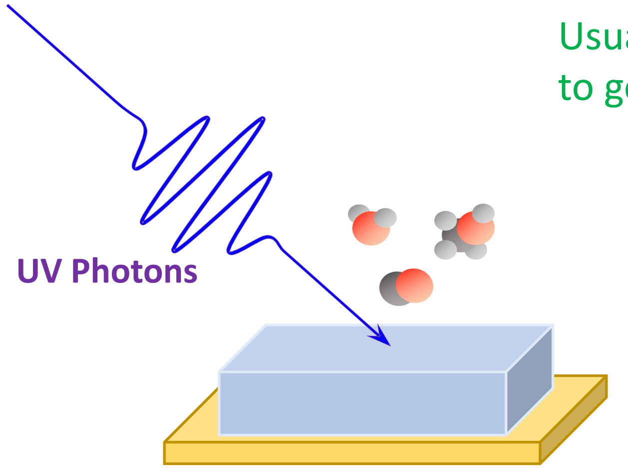


Cold substrate (10 < T < 100 K)

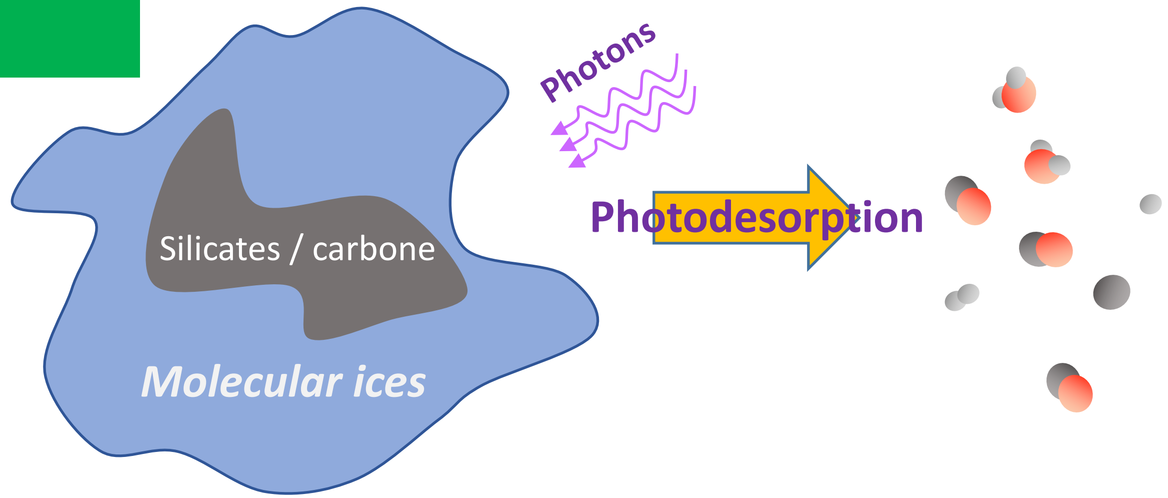
- ***Monochromatic laser sources***

  Usually limited to some wavelength, and difficult to go to high energies

  Allows time-resolved measurements

  Very difficult to make quantitative measurements

Motivations: experimental study of photodesorption



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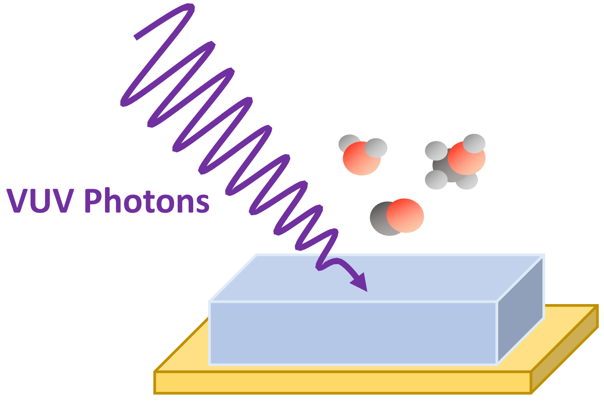
→ Has motivated many experimental works

- *Synchrotron monochromatic and tunable VUV Ouput*

Energy easy to tune over very wide range

Not limited to the V-UV domain and unlocks the possibility to study X-ray photodesorption

Not tabletop at all !!!



State of the experimental studies of UV photodesorption: simple species and yields

« Simple » molecules

Probably not exhaustive

Molecule	Ice	Desorbed species	ref
CO	Pure & with N_2	CO	Fayolle+2011; Munoz-Caro+2010, 2016, Oberg+2009, Bertin+2013, Paardekooper+2016…
H_2O & D_2O	pure (in different morphologies)	H_2O, OH, O_2, H_2	Westley+1995, Oberg+2009, Cruz-Diaz+2018, Bulak+2022, Fillion+2022
CO_2	Pure	CO_2, CO, O_2, CO_3	Oberg+2009, Fillion+2014, Martin-Domenech+2015, Sie+2019
N_2	Pure & with CO & with CO_2	N_2	Fayolle+2013, Bertin+2013, Carrascosa+2019
NH_3	Pure	NH_3, N_2	Martin-Domenech+2018, Torres-Diaz+2024
CH_4	Pure & with CO & with H_2O	CH_4, CO, H_2CO	Martin-Domenech+2016, Dupuy+2017, Bulak+2020
O_2	Pure	O_2	Fayolle+2013, Zheng+2014
NO	Pure	NO	Dupuy+2017
H_2CO	Pure & with CO	H_2CO, H_2, CO	Féraud+2019

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CH_4	Pure & with CO & with H_2O	CH_4, CO, H_2CO	Martin-Domenech+2016, Dupuy+2017, Bulak+2020
O_2	Pure	O_2	Fayolle+2013, Zheng+2014
NO	Pure	NO	Dupuy+2017
H_2CO	Pure & with CO	H_2CO, H_2, CO	Féraud+2019

- Yields mostly extracted from pure ices

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NO	Pure	NO	Dupuy+2017
H_2CO	Pure & with CO	H_2CO, H_2, CO	Féraud+2019

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- Photochemistry coupled to the desorption

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H_2CO	Pure & with CO	H_2CO, H_2, CO	Féraud+2019

- Yields mostly extracted from pure ices
- Photochemistry coupled to the desorption

- Different experimental conditions: Broadband UV lamp / Tunable Monochromatic light + photon fluxes between 10^{13} – 10^{16} ph/s/cm²

State of the experimental studies of UV photodesorption: simple species and yields

« Simple » molecules

- Yields vary from molecules to molecules

Averaged yield for secondary photons *(Gredel+1989)*

Pure CO : $\Gamma_{CO} \sim 10^{-2} - 10^{-3}$

Pure CH_4 : $\Gamma_{CH_4} \sim 10^{-3}$

Pure H_2O : $\Gamma_{H_2O} \sim 5.10^{-4}$

Pure H_2CO : $\Gamma_{H_2CO} \sim 10^{-4}$

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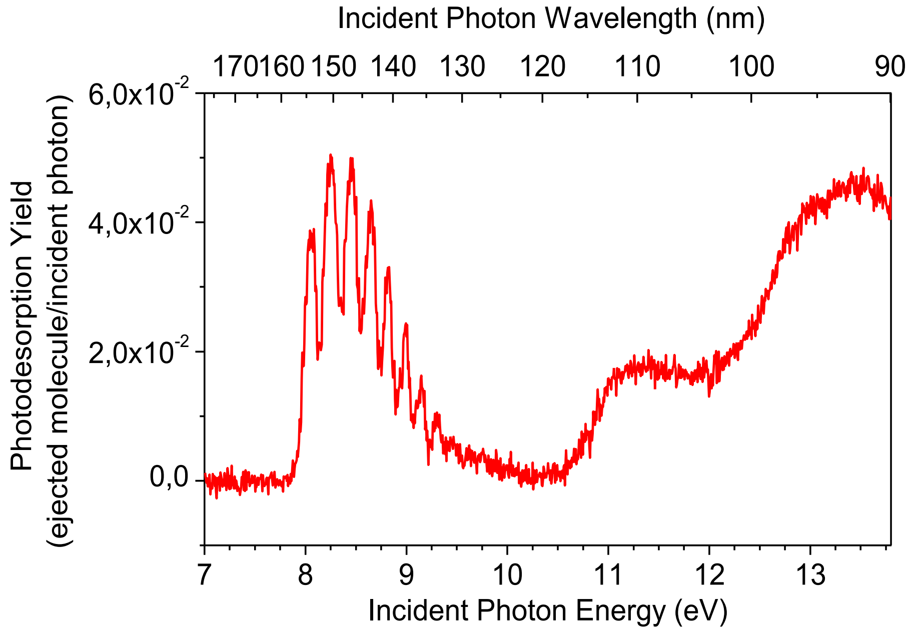
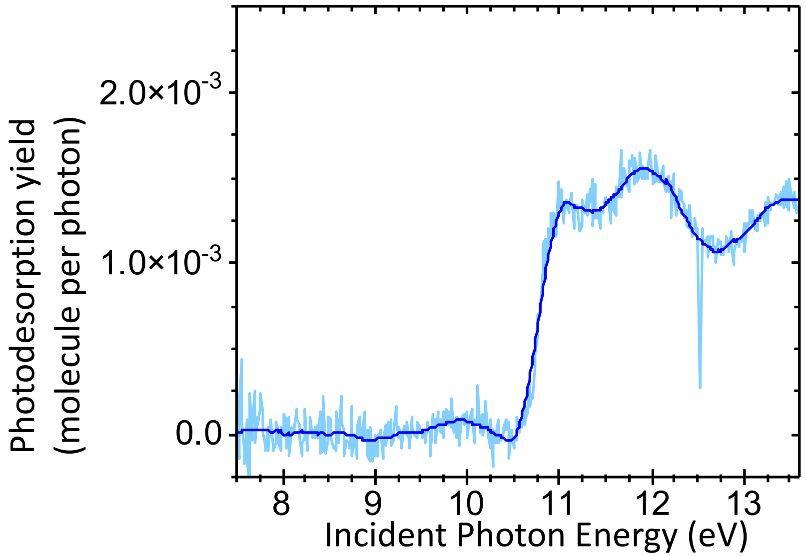
- Yields are wavelength-dependent



Pure CO photodesorption yields

Fayolle+2011



CO_2 photodesorption yields from pure CO_2

Fillion+2014

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(Gredel+1989)

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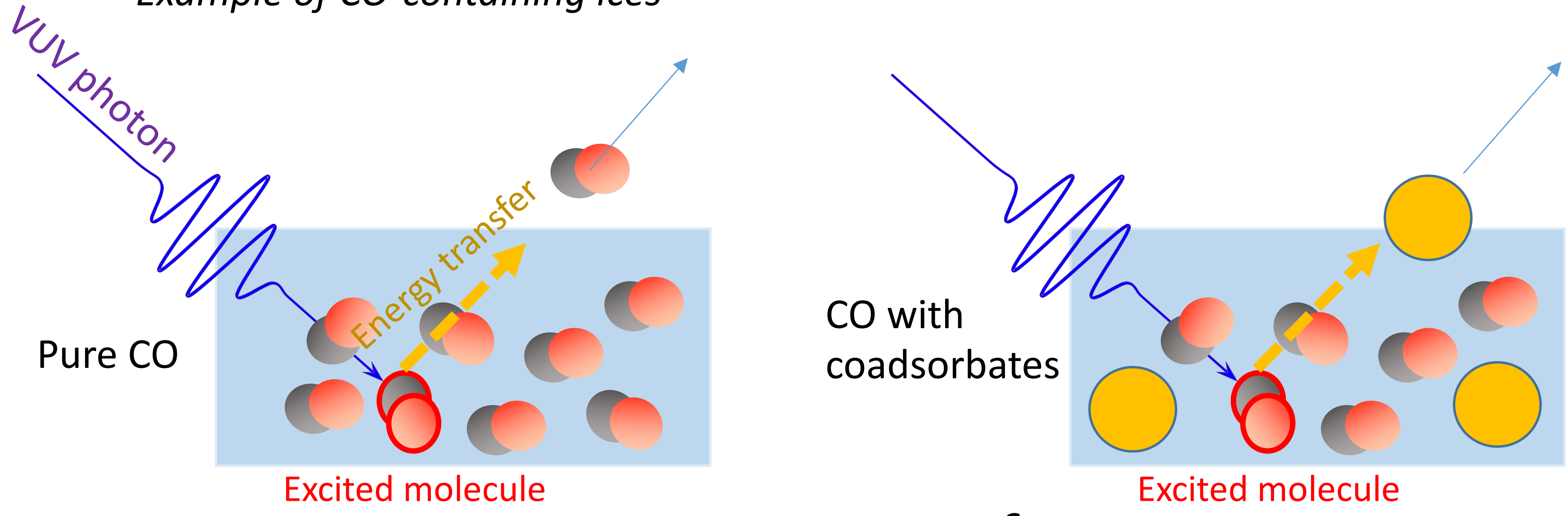
- Yields are wavelength-dependent

- Yields depend on the composition of the ice via indirect processes

Example of CO-containing ices



Efficient for N_2, CH_4, CO_2, rare gas…

But it is not very clear why, and if it always work that way with any coadsorbed species!

Bertin+2012, Bertin+2013

State of the experimental studies of UV photodesorption: simple species and yields

« Simple » molecules

- Yields vary from molecules to molecules

Averaged yield for secondary photons *(Gredel+1989)*

Pure CO : $\Gamma_{CO} \sim 10^{-2} - 10^{-3}$

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Pure H_2CO : $\Gamma_{H_2CO} \sim 10^{-4}$

- Yields are wavelength-dependent
- Yields depend on the composition of the ice via indirect processes

How to model this? On what parameters will the process depend?

→ **Need to understand the desorption mechanisms on a microscopic scale**

UV photodesorption of organics: status before 2022

« Complex » Organic Molecules

Molecule	Ice	Desorbed species	ref
CH_3OH	Pure & with CO	CH_3OH, CH_3O, H_2CO, CH_3, OH, CO	Oberg+2009, Bertin+2016, Cruz-Diaz+2016

- Data are scarce: only methanol was quantitatively measured for a long time

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- Data are scarce: only methanol was quantitatively measured for a long time
  - Desorption is dominated by the ejection of fragments
    - Desorption yields for the intact molecule is comparatively lower than for simpler species

CH_3OH mixed in CO : $\Gamma_{CH_3OH} < 5.10^{-6}$

But, do all the organics behave like methanol?

Outline

Photodesorption mechanisms from « simple » species: the case of CO ice

Photodesorption of organics: $HCOOH$, $HCOOCH_3$ & CH_3CN

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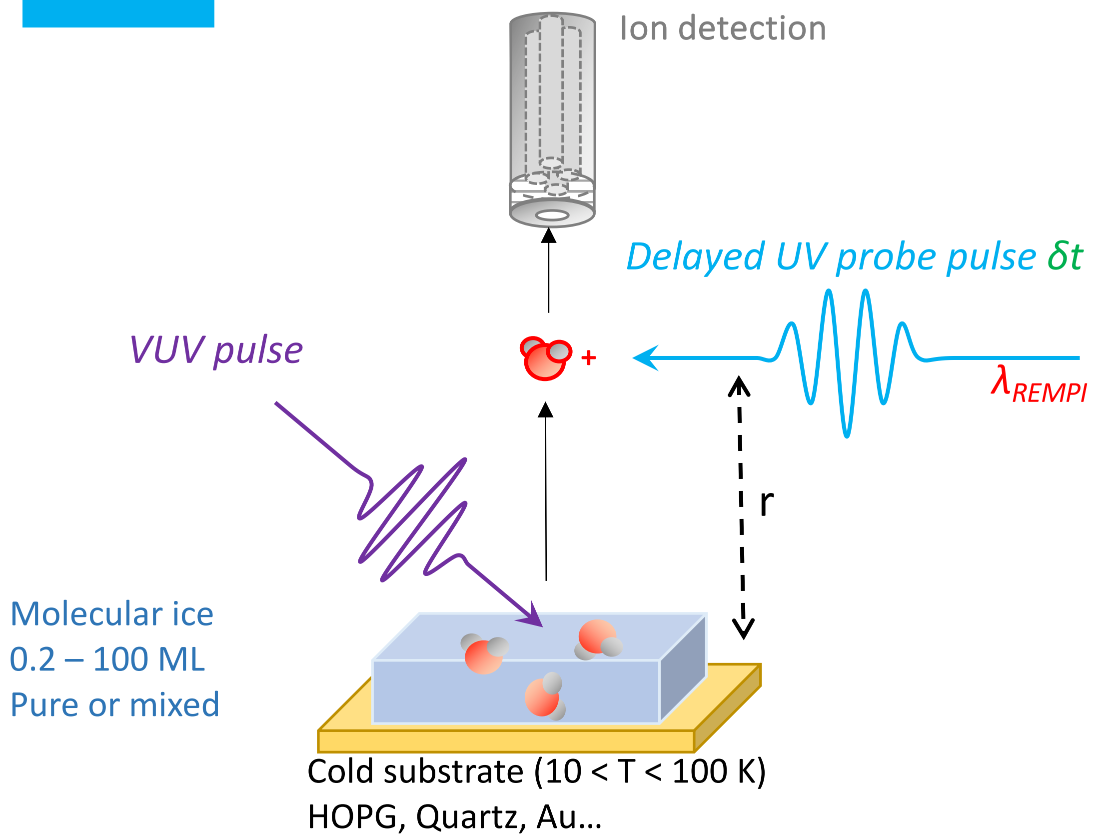
Photodesorption mechanisms from « simple » species: the case of CO ice

Photodesorption of organics: HCOOH, $HCOOCH_3$ & CH_3CN

Photodesorption mechanisms from « simple » species: the case of CO ice

Pulsed method for the study of photodesorption mechanisms



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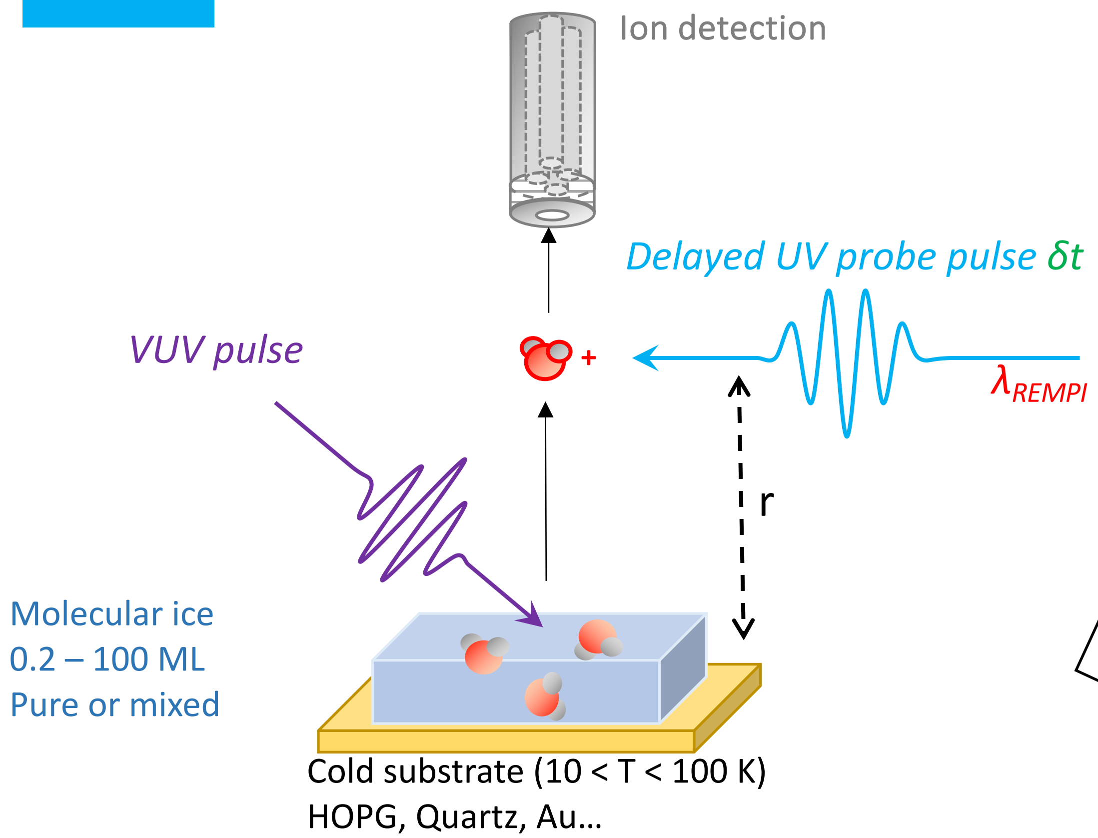

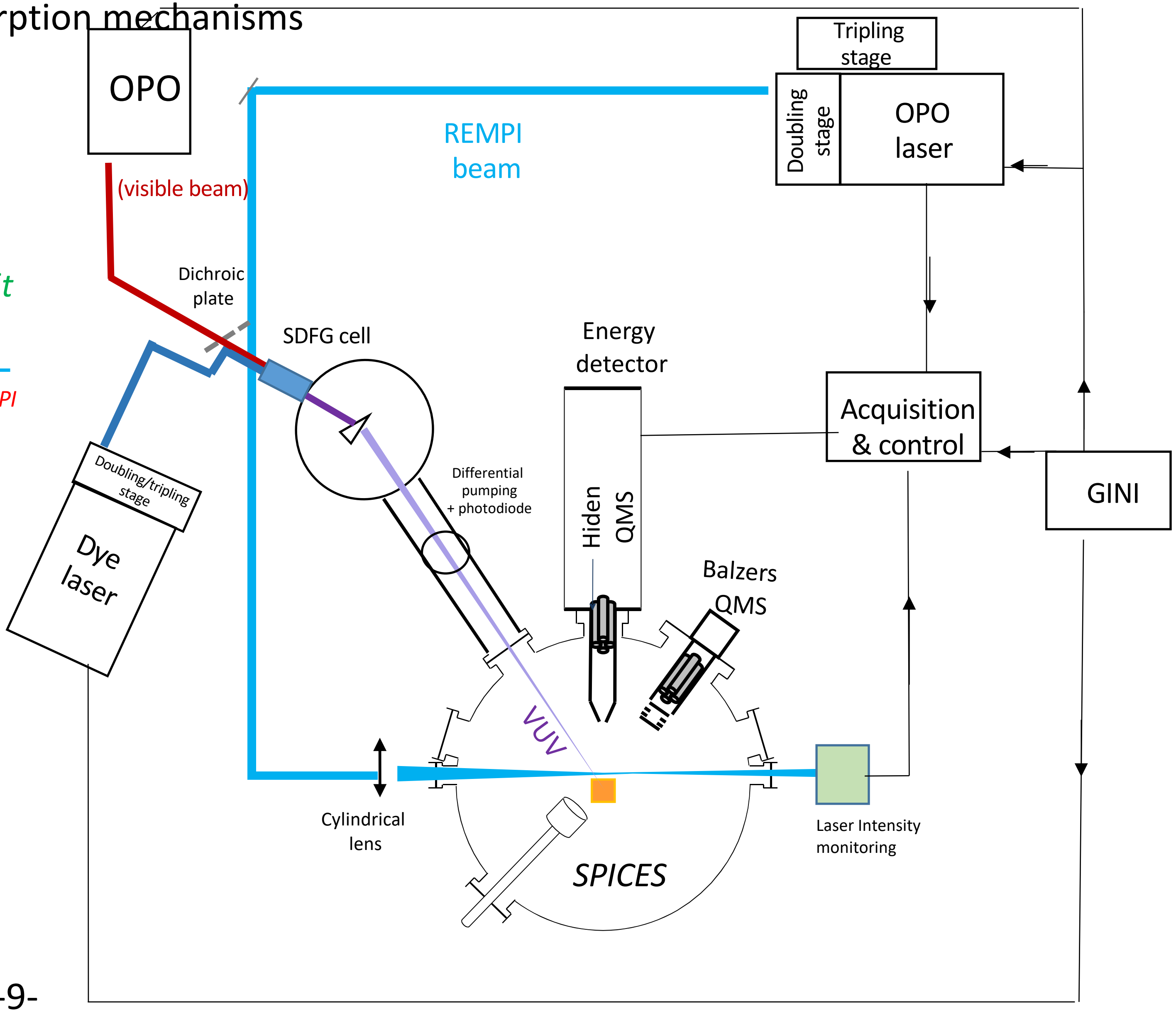

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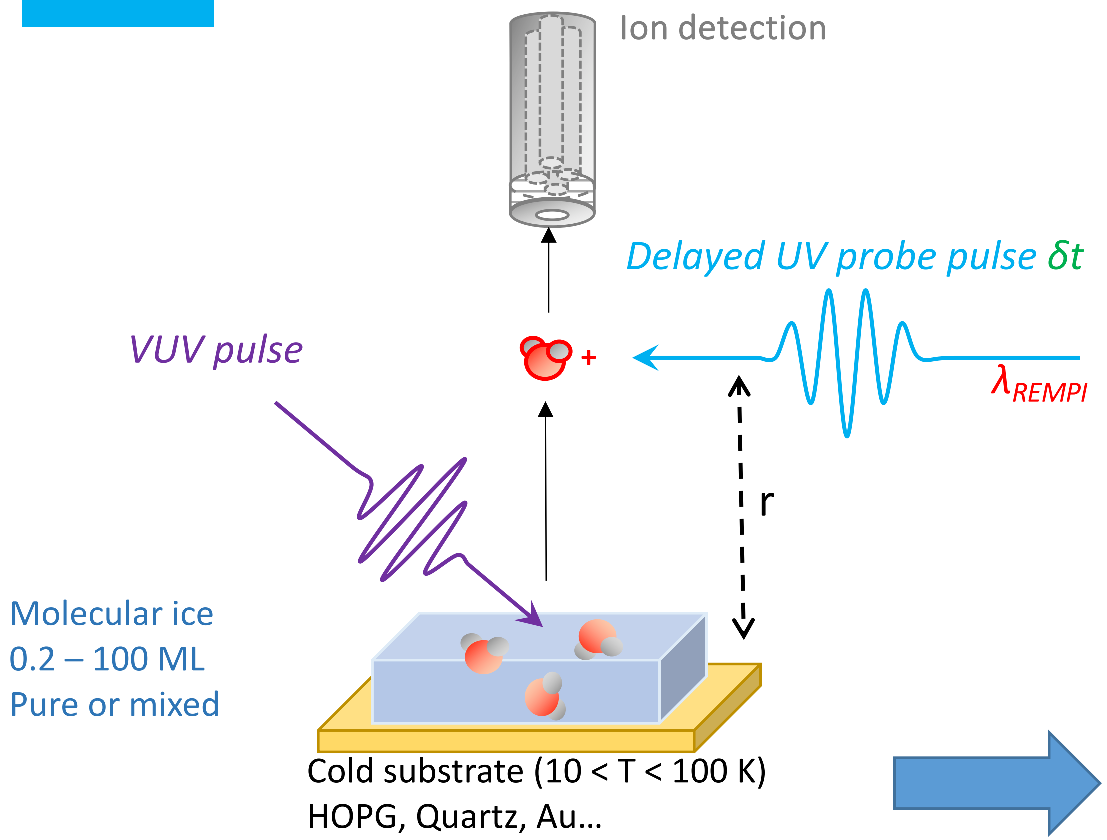


Internal energy distribution of ejected molecules

- By varying λ_{REMPI} and selective resonant ionization REMPI
- Vibrational & rotational population of desorbed species

Kinetic energy distribution of ejected molecules

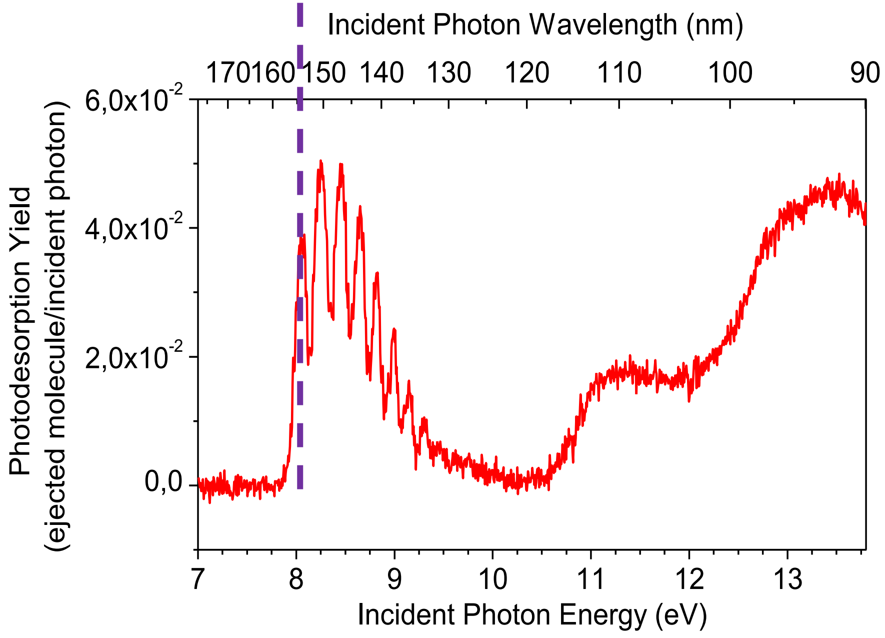
- By varying δt at fixed ionizing wavelength
- Access to normal speed distribution by Time-of-Flight measurement over the distance r

Comparison with theoretical MD simulations

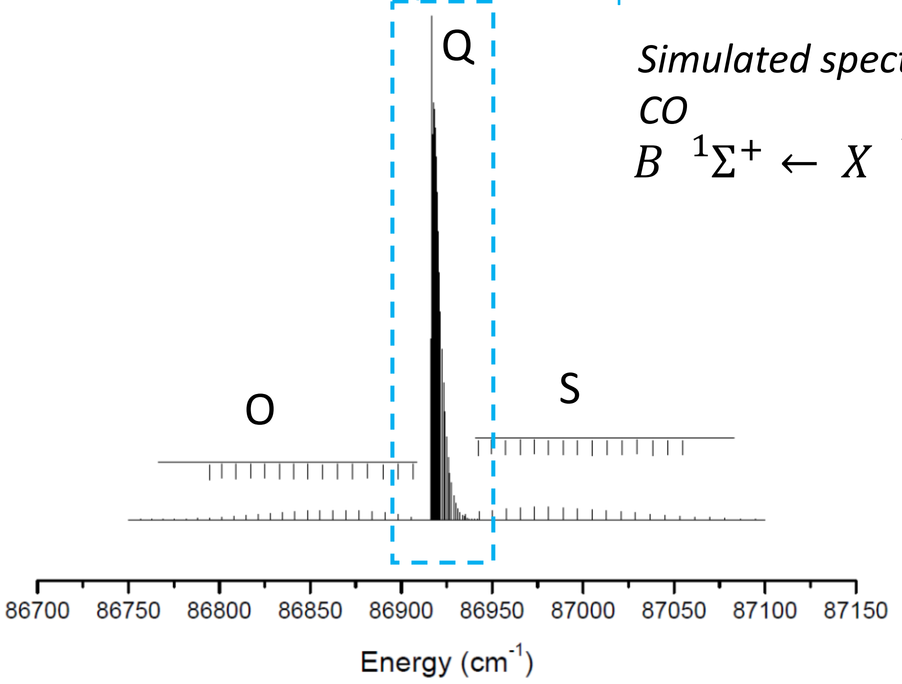
- Ab Initio MD simulations made in PhLAM
- Access to the mechanism at the molecular scale

Photodesorption mechanisms from « simple » species: the case of CO ice

Desorbing pulse: λ_{VUV}



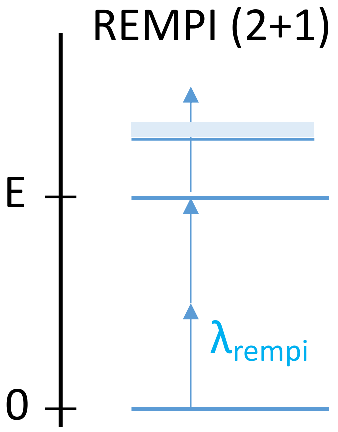
Probe REMPI pulse: λ_{rempi}



Simulated spectrum, T = 300 K

CO

$$B\ ^1\Sigma^+ \leftarrow X\ ^1\Sigma^+\ (0-0)$$

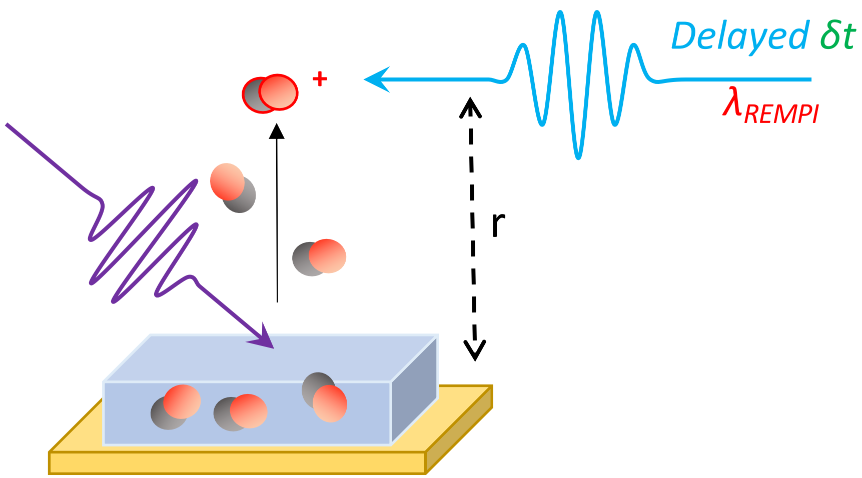


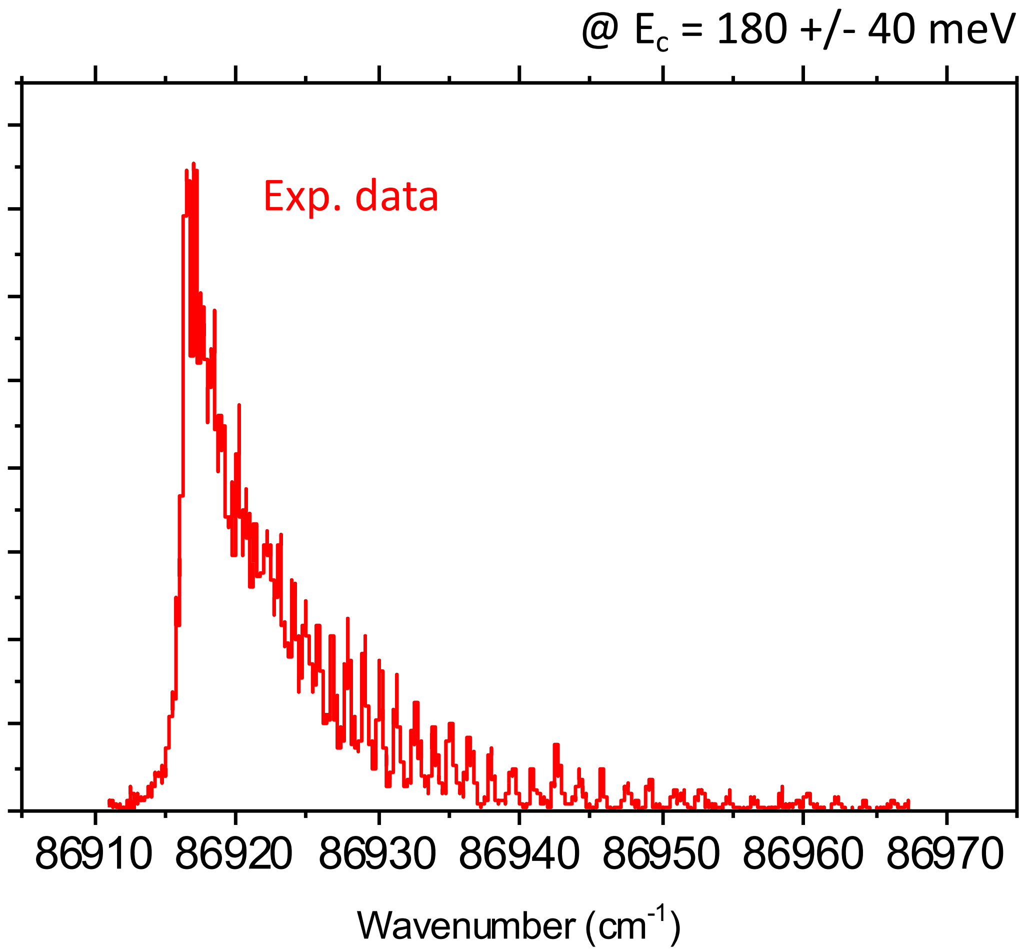
R. Basalgète
PhD 2022

A. Hacquard

Del Fré+ PRL 2023
Hacquard+JCP 2024

Internal energy distribution:





Photodesorption mechanisms from « simple » species: the case of CO ice

Del Fré+ PRL 2023
Hacquard+JCP 2024

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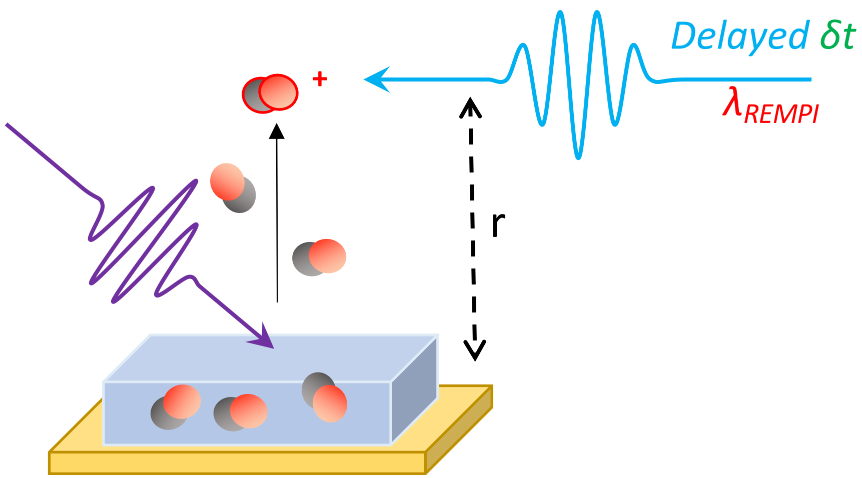

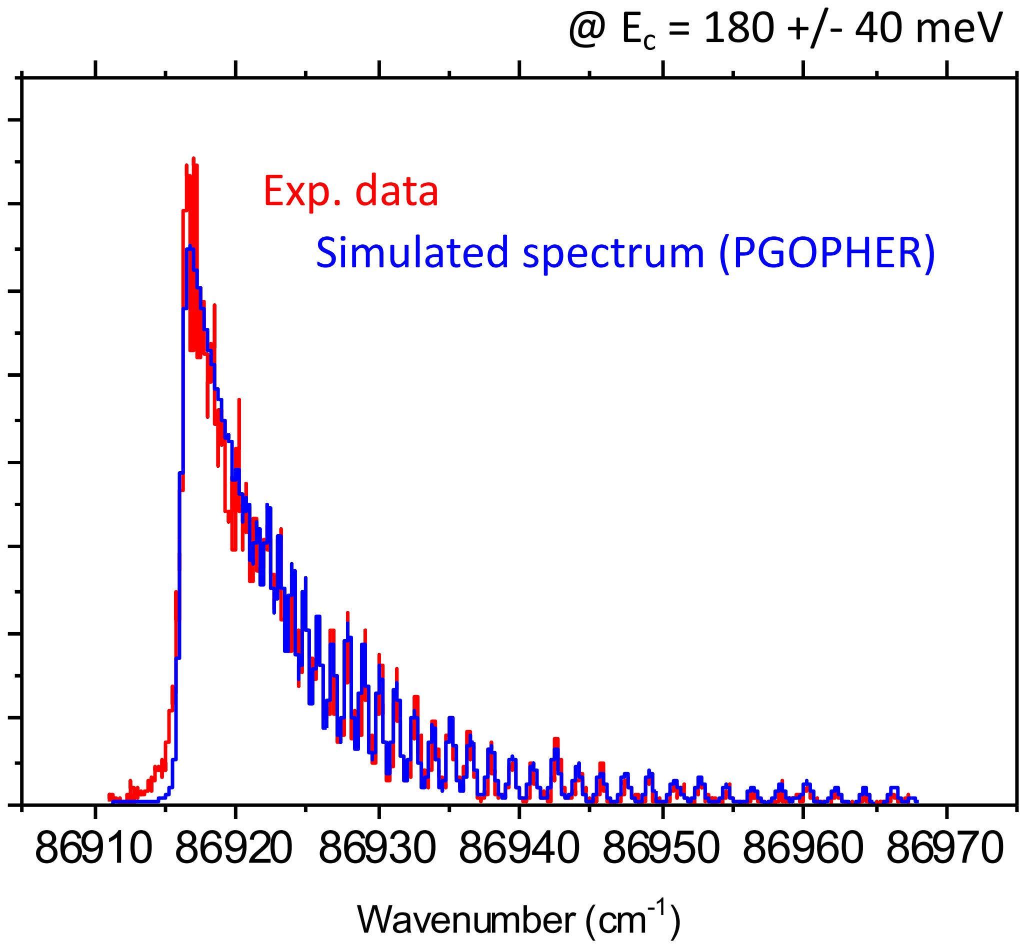

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Del Fré+ PRL 2023
Hacquard+JCP 2024

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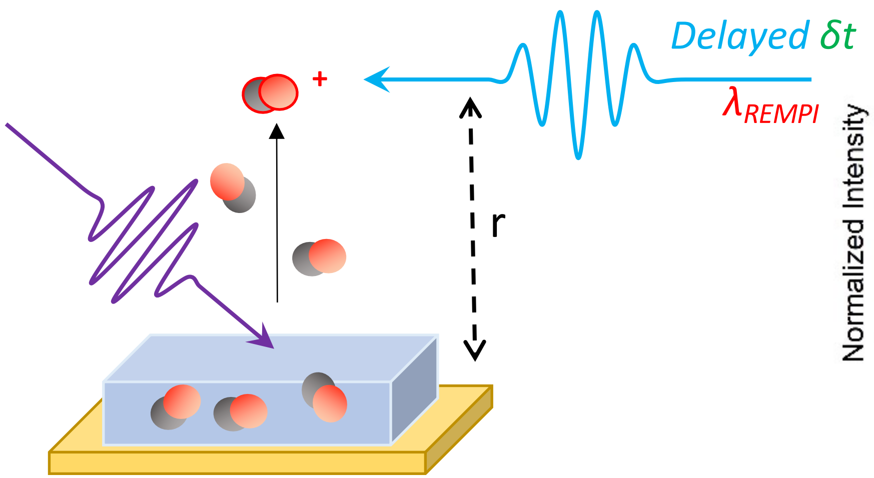
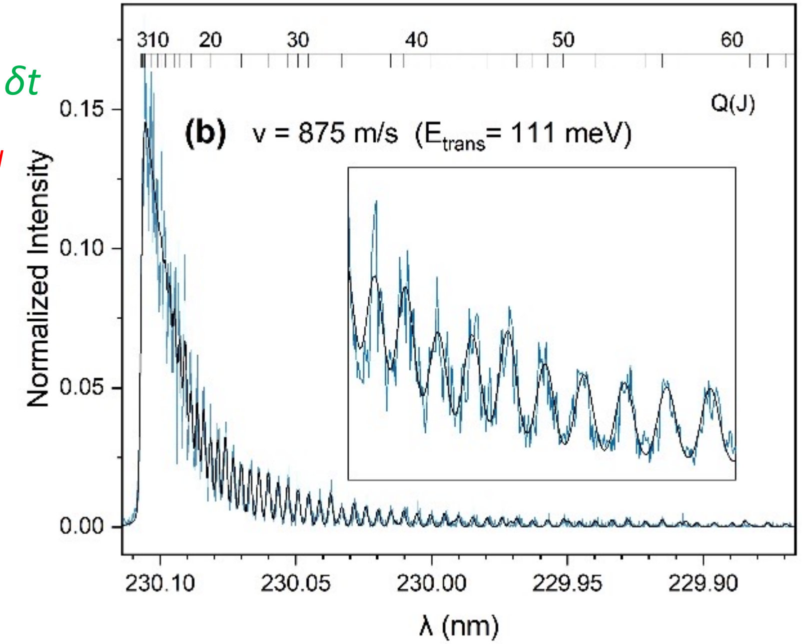
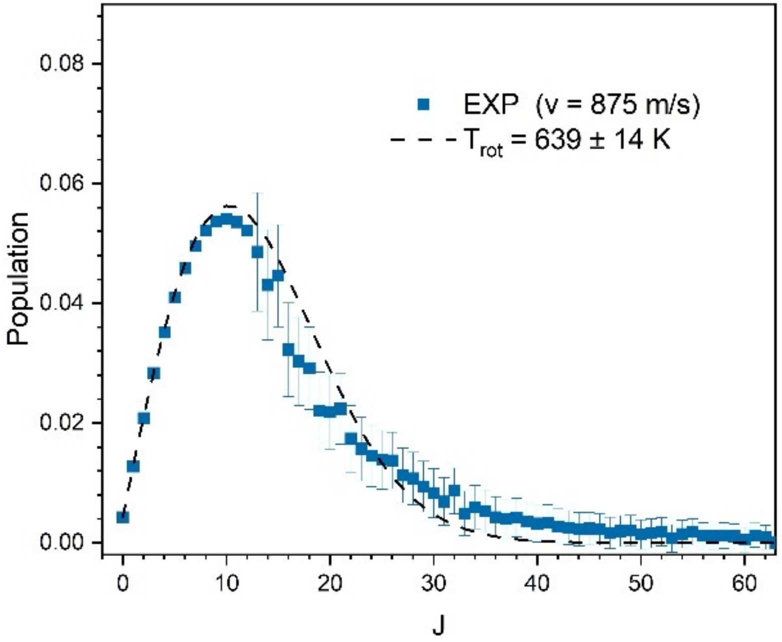




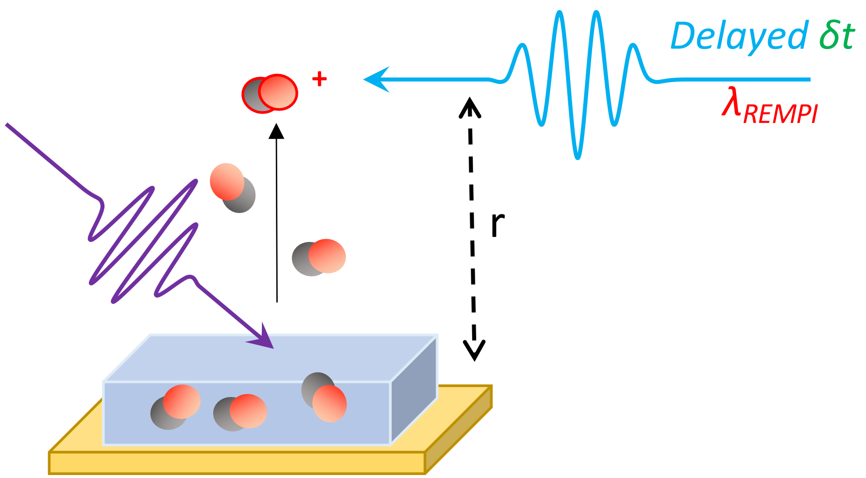


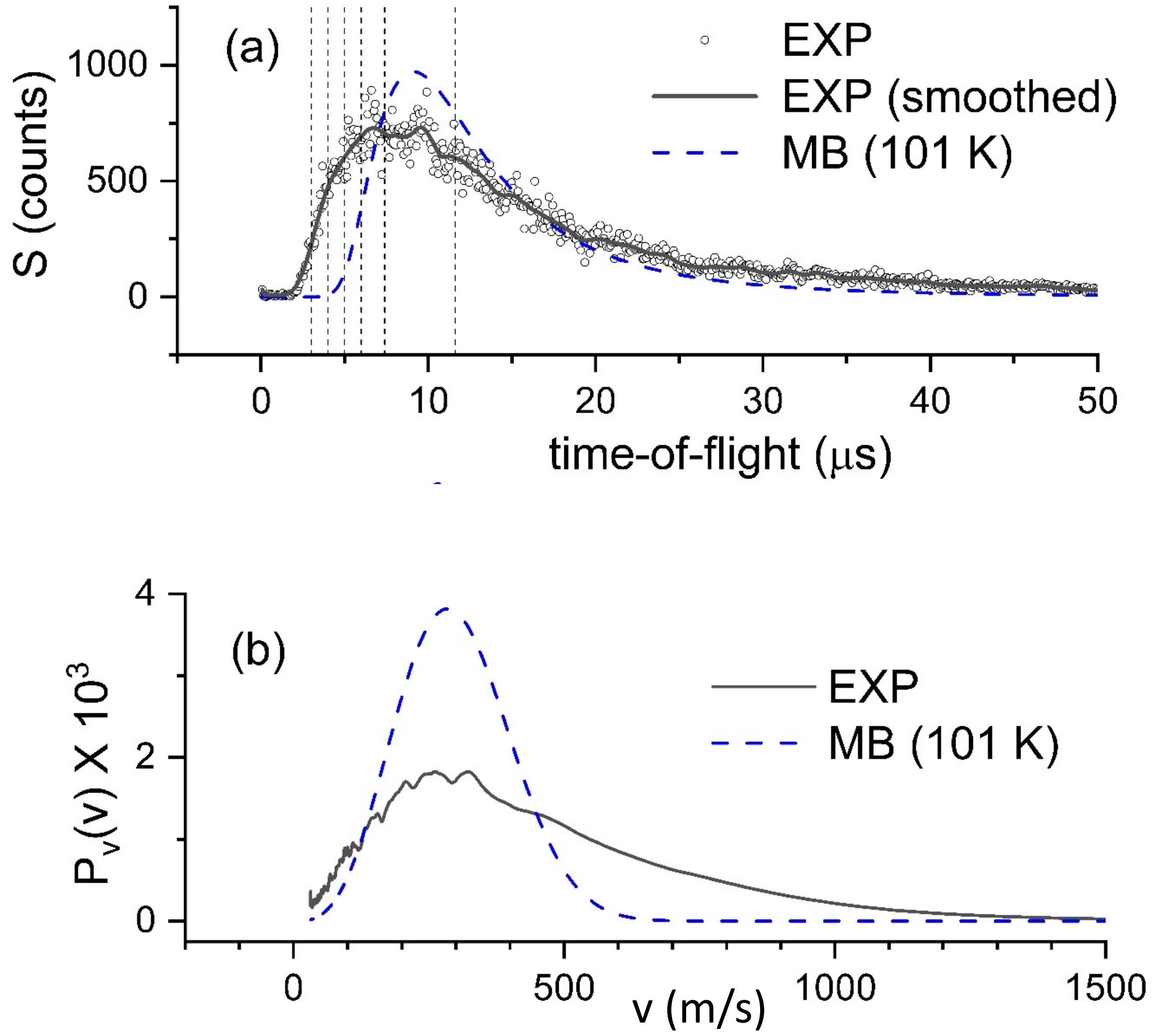
- Rotational distributions can be measured for several velocities
    - And mostly molecules in the v = 0 vibrational state

Photodesorption mechanisms from « simple » species: the case of CO ice

Del Fré+ PRL 2023
Hacquard+JCP 2024

Kinetic energy distribution:





J=0-2

Photodesorption mechanisms from « simple » species: the case of CO ice

Del Fré+ PRL 2023
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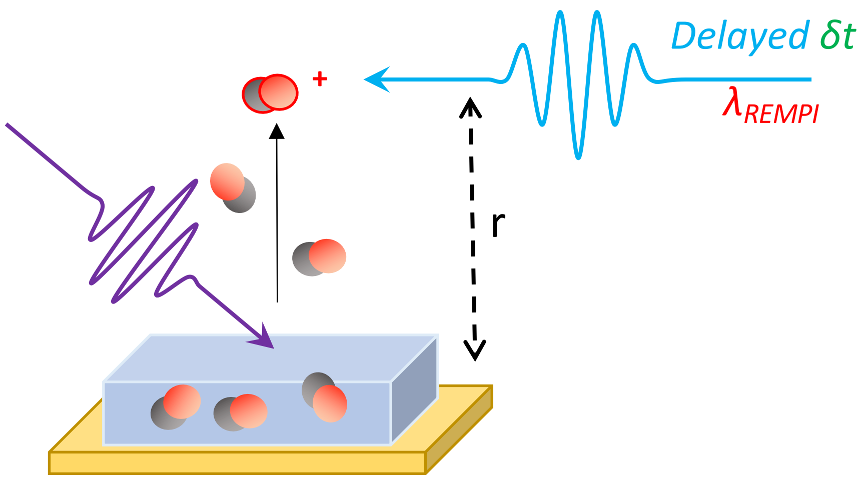
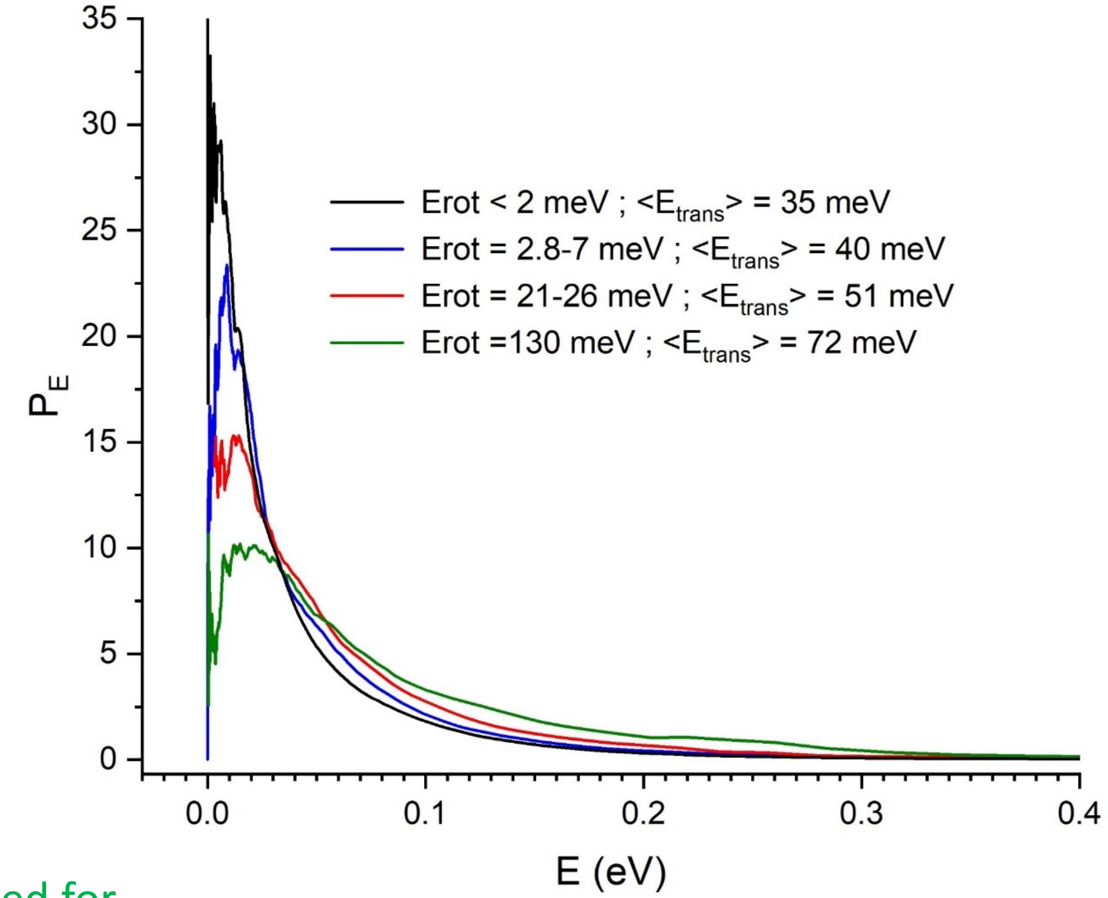
Kinetic energy distribution:





- Kinetic energy distribution can be obtained for given class of internal energies

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Del Fré+ PRL 2023
Hacquard+JCP 2024

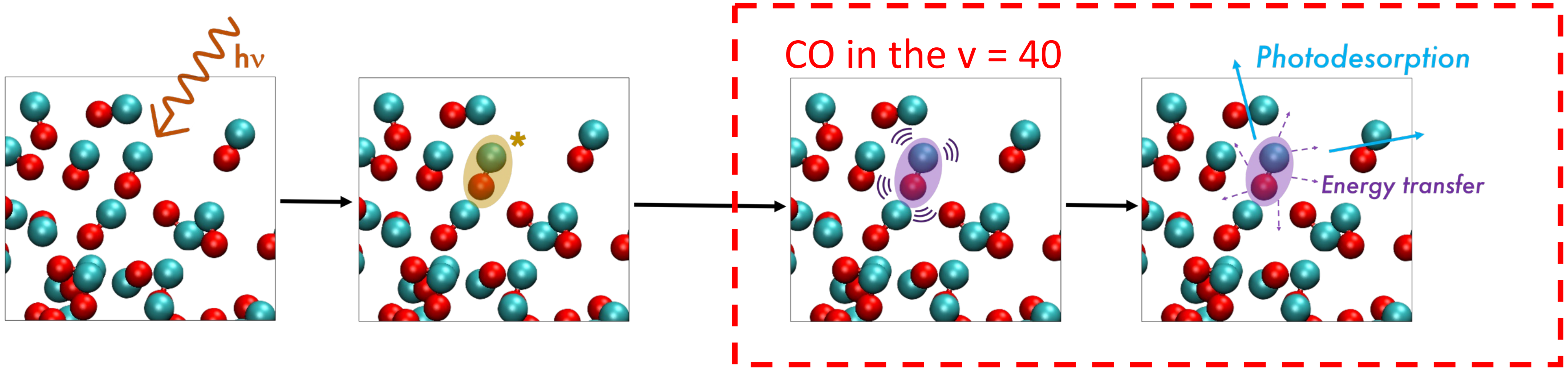
Comparison with theoretical simulations:

PhLAM
Physique des Lasers Atomes et Molécules

S. Del Fré, A. Rivero Santamaria, D. Duflot, M. Monnerville

S. Del Fré

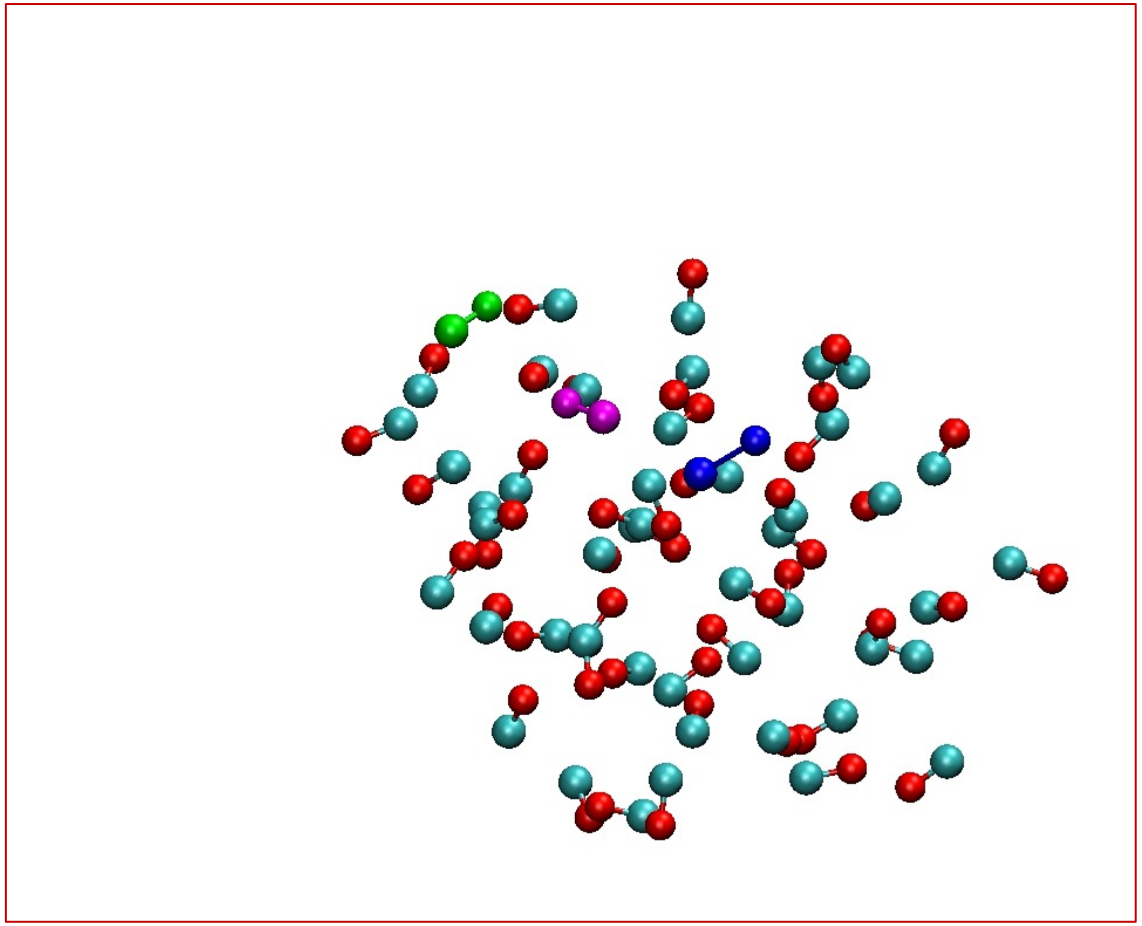
Cluster of 50 CO molecules



Dynamics with Microcanonical Ab Initio-MD (5 ps)

Photodesorption mechanisms from « simple » species: the case of CO ice

Del Fré+ PRL 2023
Hacquard+JCP 2024



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Simulation time ≈ **3 ps**

“kick” mechanism

T = 10 K, t_{step} = 0.5 fs

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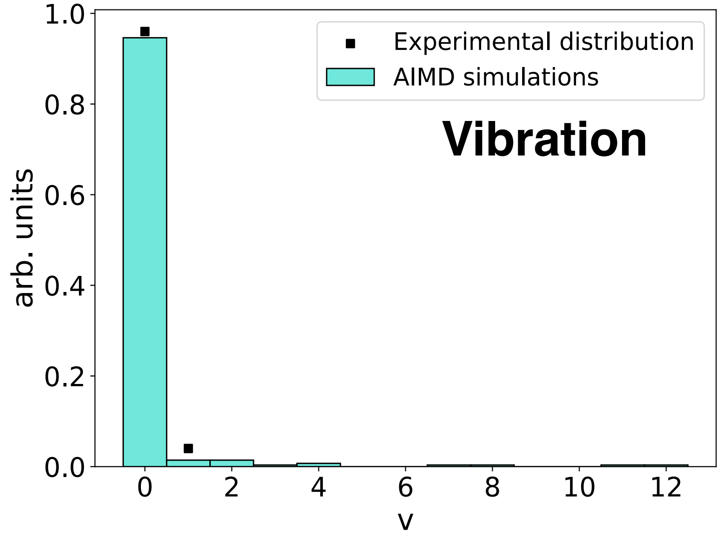
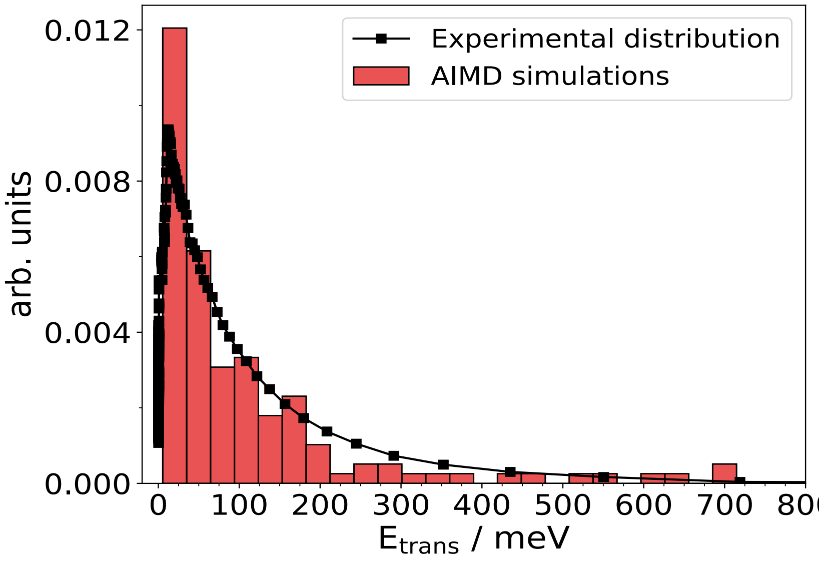
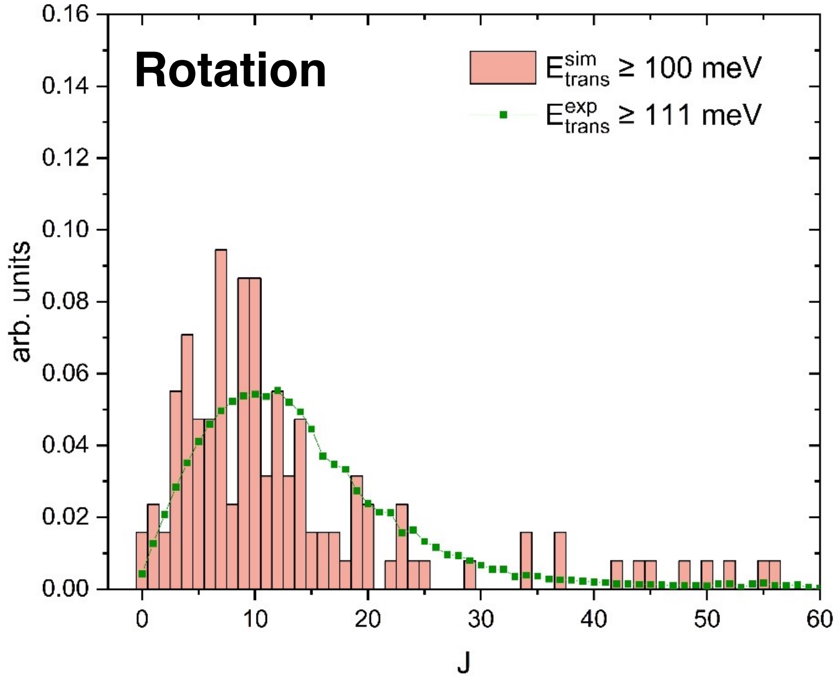
Comparison with theoretical simulations

Translation (v = 0 and j < 7 states)







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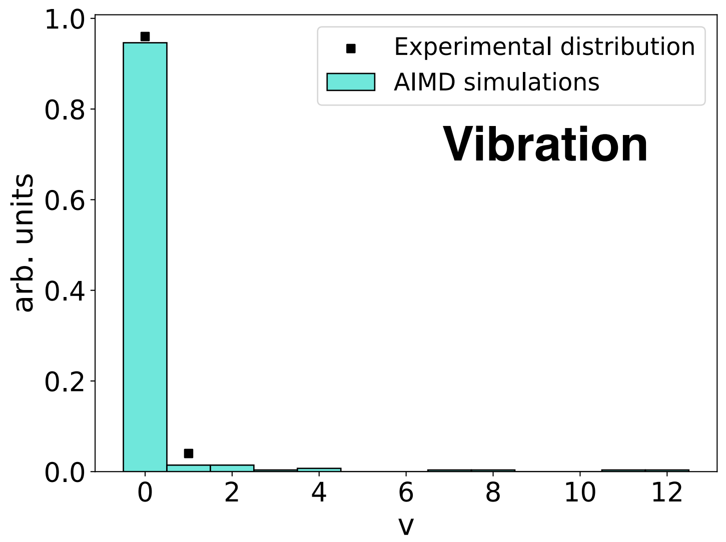

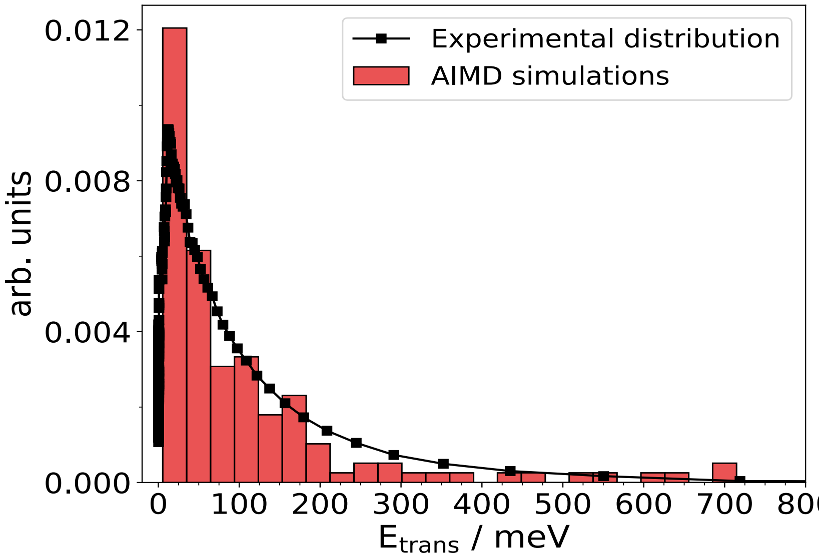

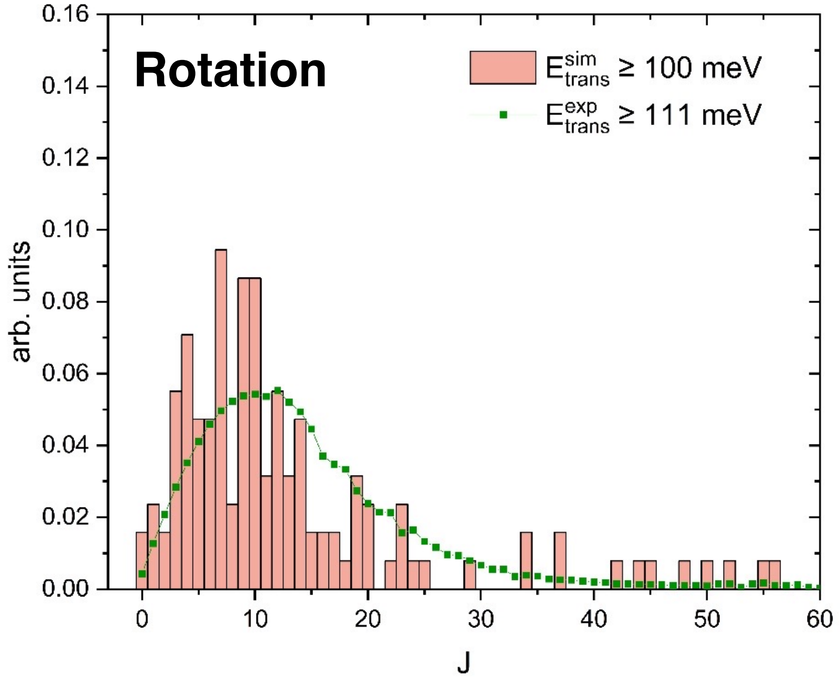

Very good agreement with experimental distributions validates the mechanism

Conclusions

- **Powerful concerted approach theory/experiments for determining microscopic steps of the photodesorption**

The question of the indirect mechanims in pure CO was left open from 2012…

- **Going progressively toward mixed systems**

Theoretical studies of coadsorbates in CO clusters, from simple model systems (N_2, NO) to more complex (and astrophysically-relevent) (H_2CO, CH_3OH)

Laser-based experimental studies from mixed ices of the same molecules

➡ On what parameters will the indirect process depend on?

Outline

Photodesorption mechanisms from « simple » species: the case of CO ice

Photodesorption of organics: HCOOH, $HCOOCH_3$ & CH_3CN

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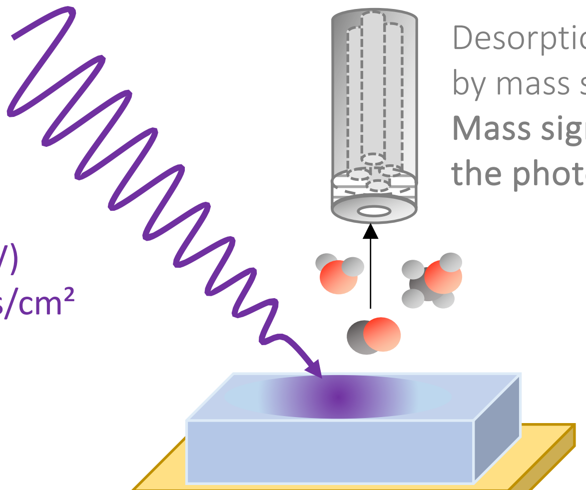
Methods for photodesorption yields measurements

VUV photons (7 – 16 eV)
ΔE = 1 eV 10^{15} ph/s/cm²



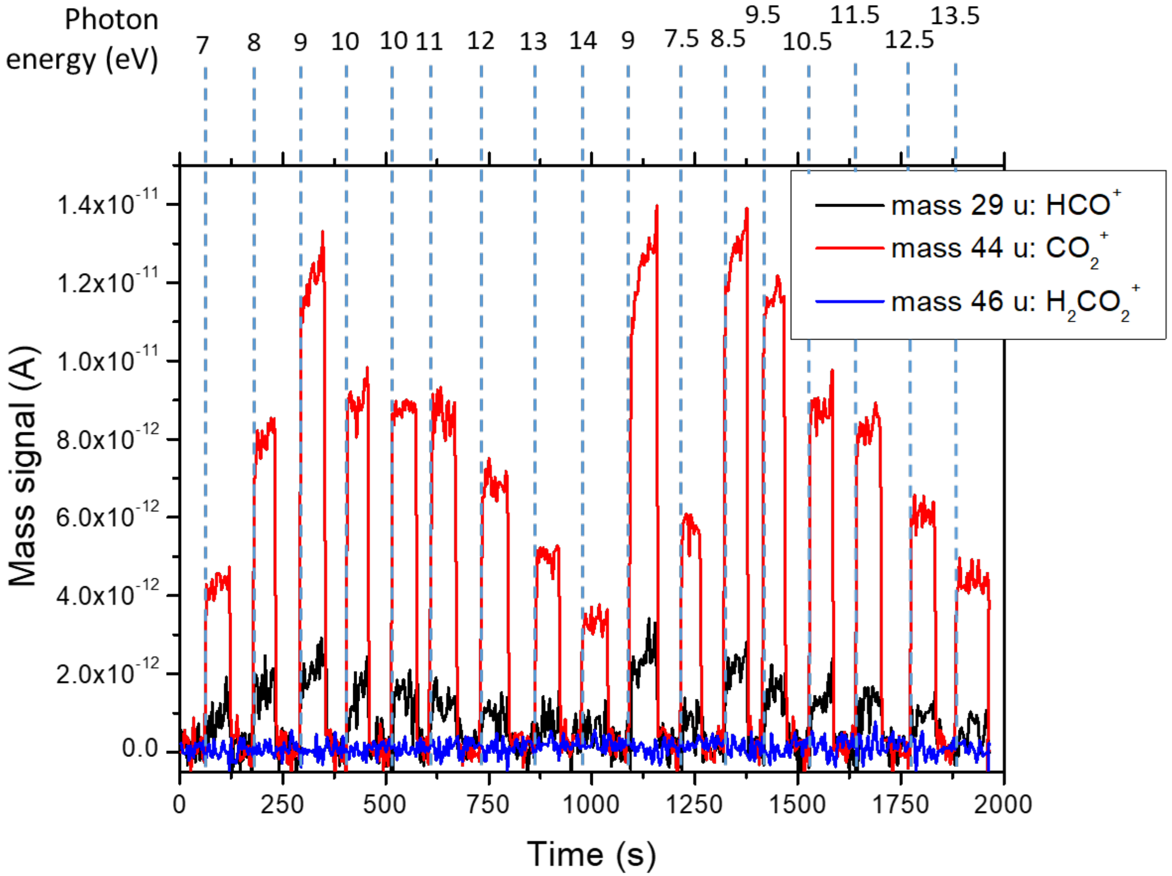
Desorption flux monitored by mass spectrometry
Mass signal as a function of the photon energy

Photodesorption Yields as a function of the photon energy

Cold substrate (10 < T < 100 K)
HOPG, Quartz, Au…

Molecular ice
60 ML

- Pure Organics
- 1ML Organics on top of H_2O or CO ice
- Mixed H_2O:organics and CO:organics

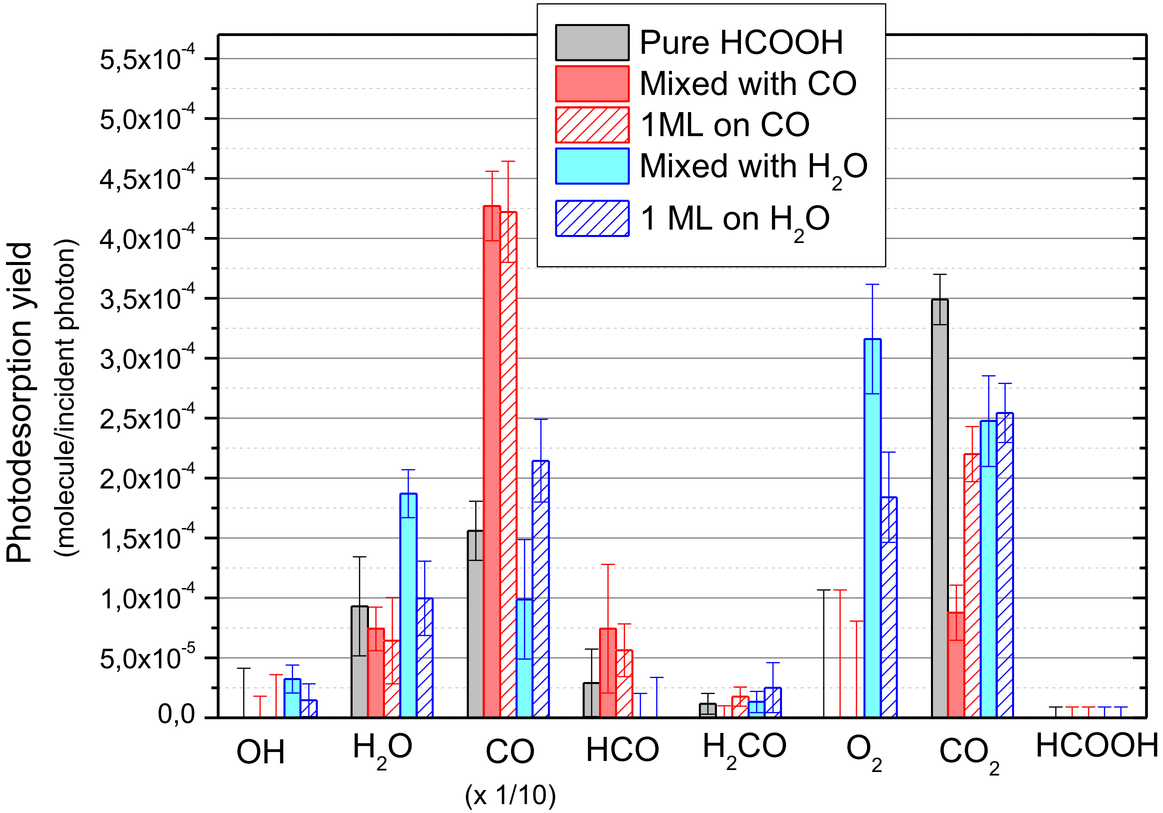


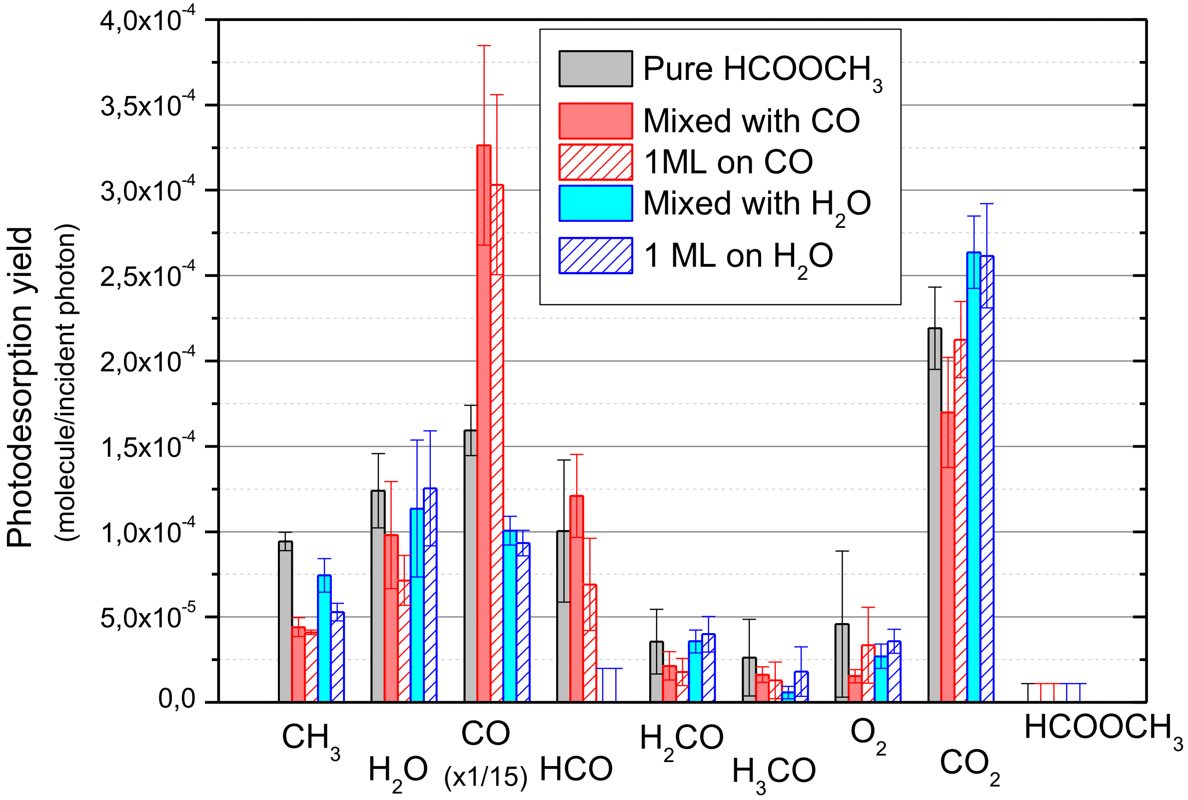
Photodesorption of organics: HCOOH, $HCOOCH_3$ & CH_3CN

Bertin+ Faraday Discuss. 2023

Cases of $HCOOCH_3$ and HCOOH

Photodesorption yields @ 10.5 ± 0.5 eV





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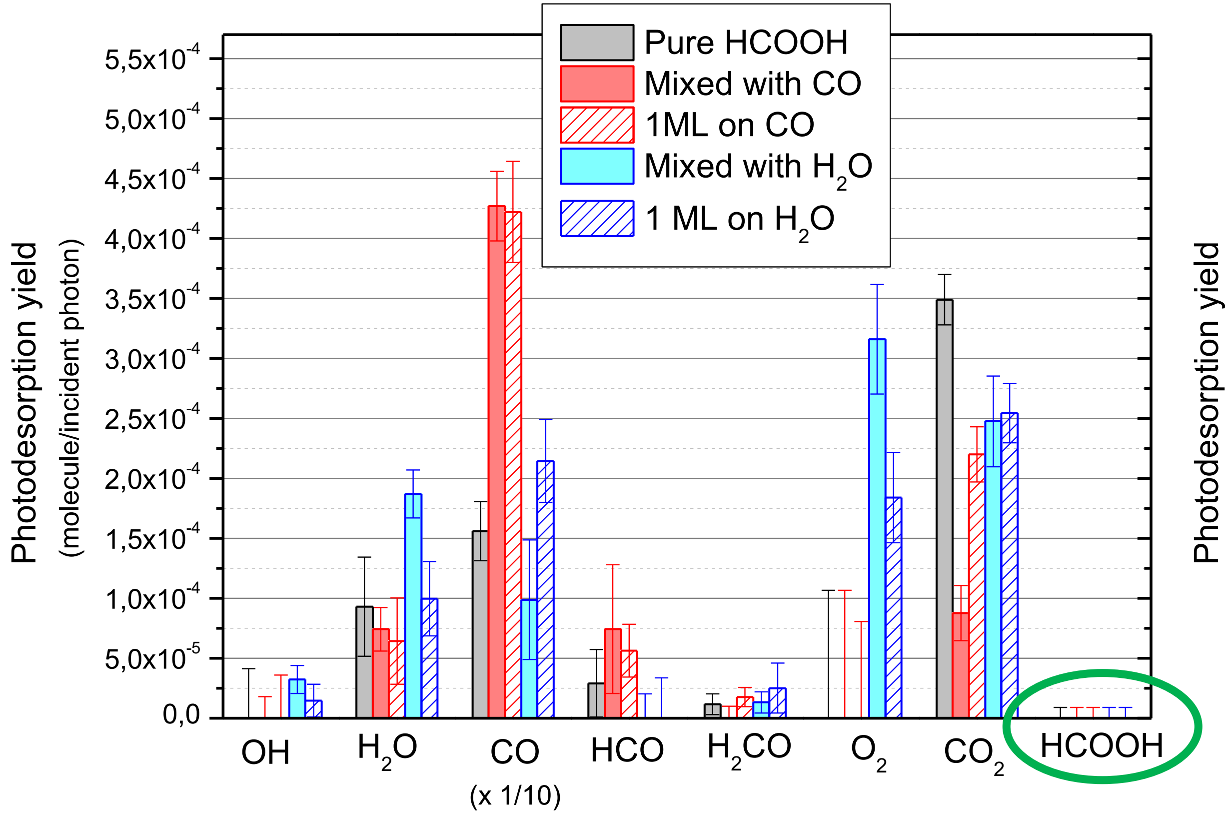

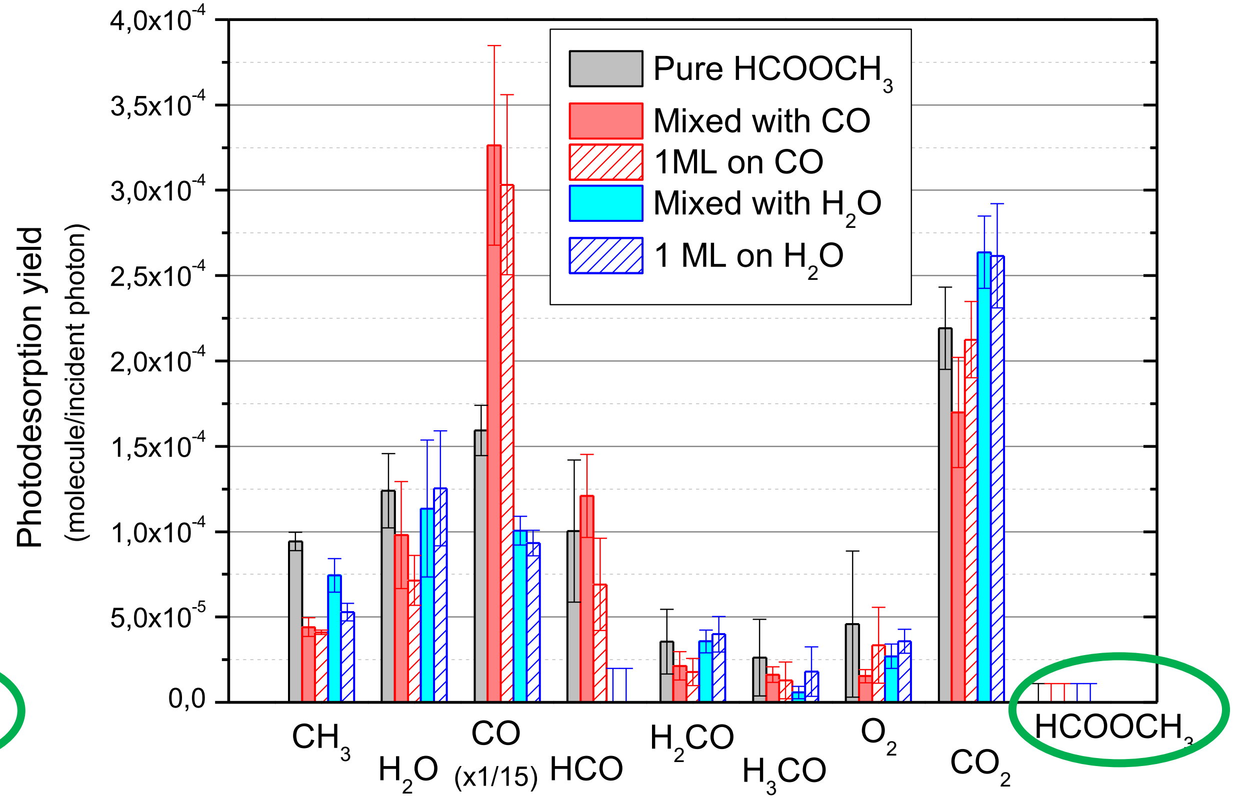

- **Desorption of the intact molecule could not be detected - < 10^{-5} molecules/photon**
- **Desorption is dominated by the primary photofragments**
- **No dependence on the ice composition,** no efficient indirect process or photochemistry to explain desorption

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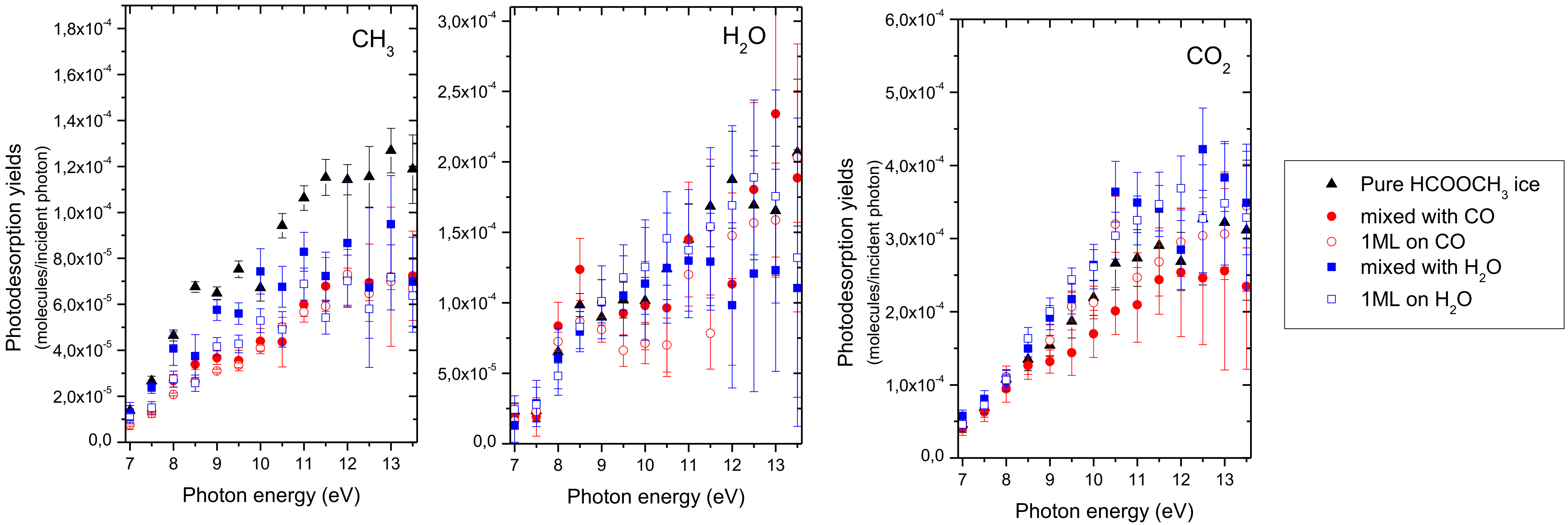

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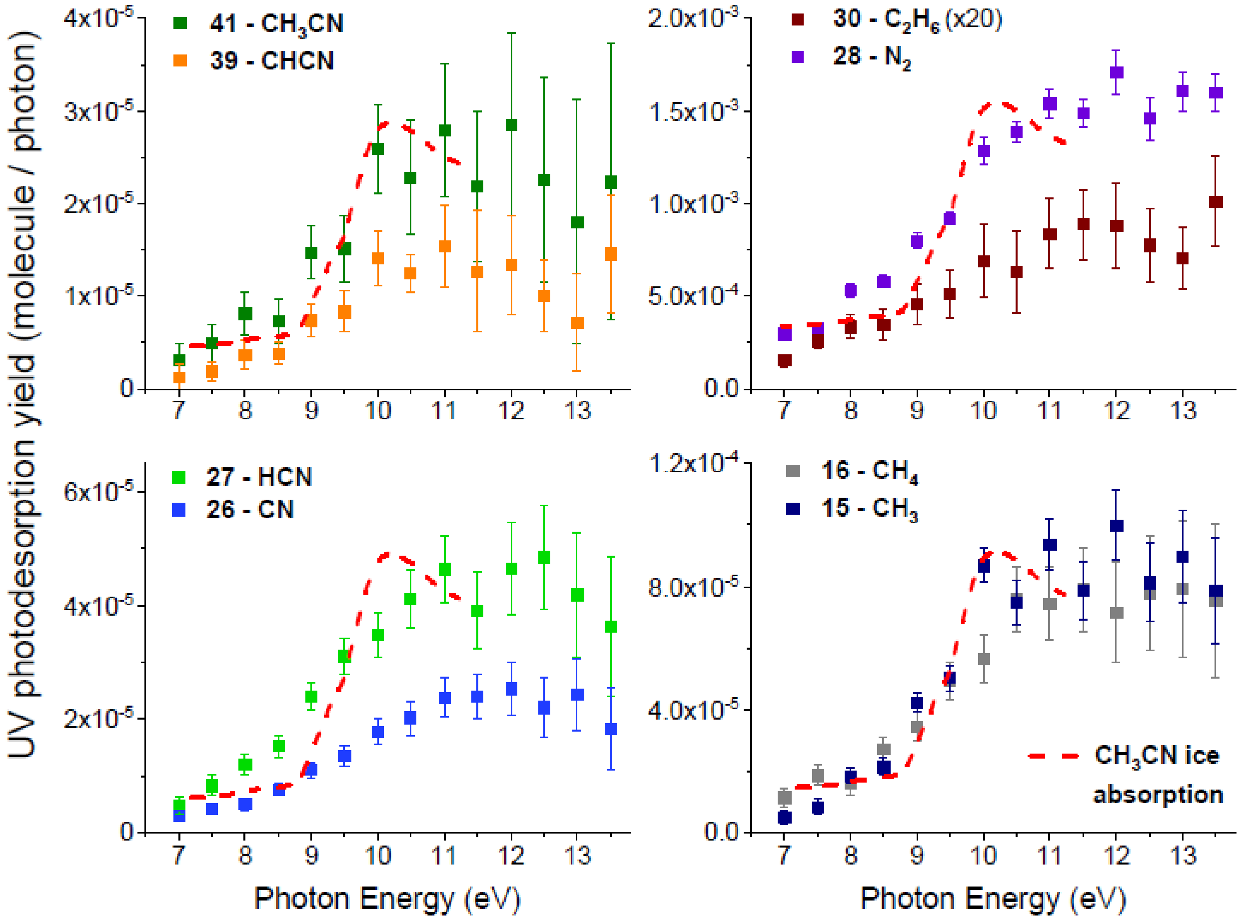
→ **What we mostly see is the organics photodissociation**

Very similar to the CH_3OH case

Photodesorption of organics: HCOOH, $HCOOCH_3$ & CH_3CN

Basalgète+ ApJ 2021

Cases of CH_3CN

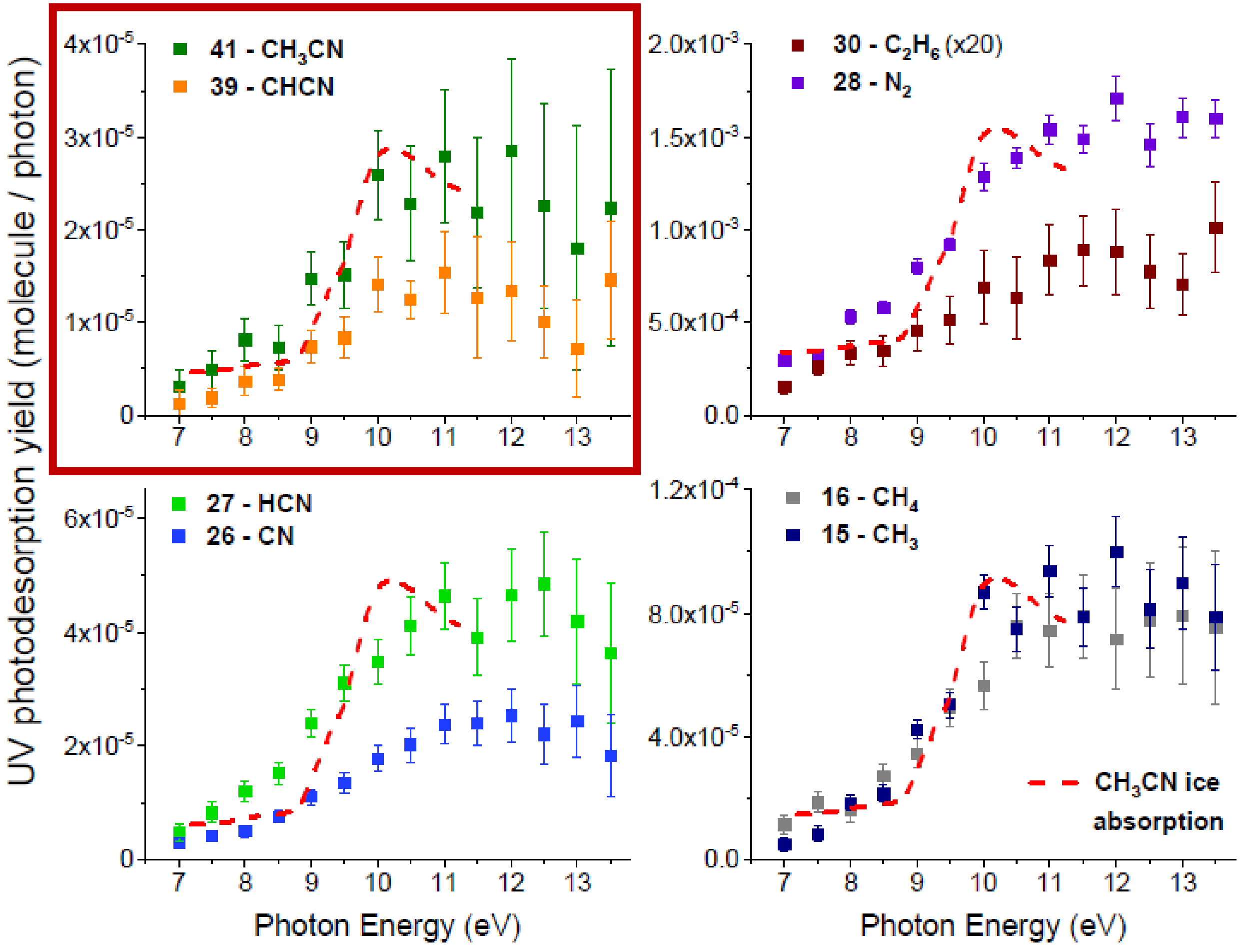


Photodesorption of organics: HCOOH, $HCOOCH_3$ & CH_3CN

Basalgète+ ApJ 2021

Cases of CH_3CN

- Photodesorption of the intact molecule is « efficient » (as compared to that of other COMs)



Photodesorption of organics: HCOOH, $HCOOCH_3$ & CH_3CN

Basalgète+ ApJ 2021

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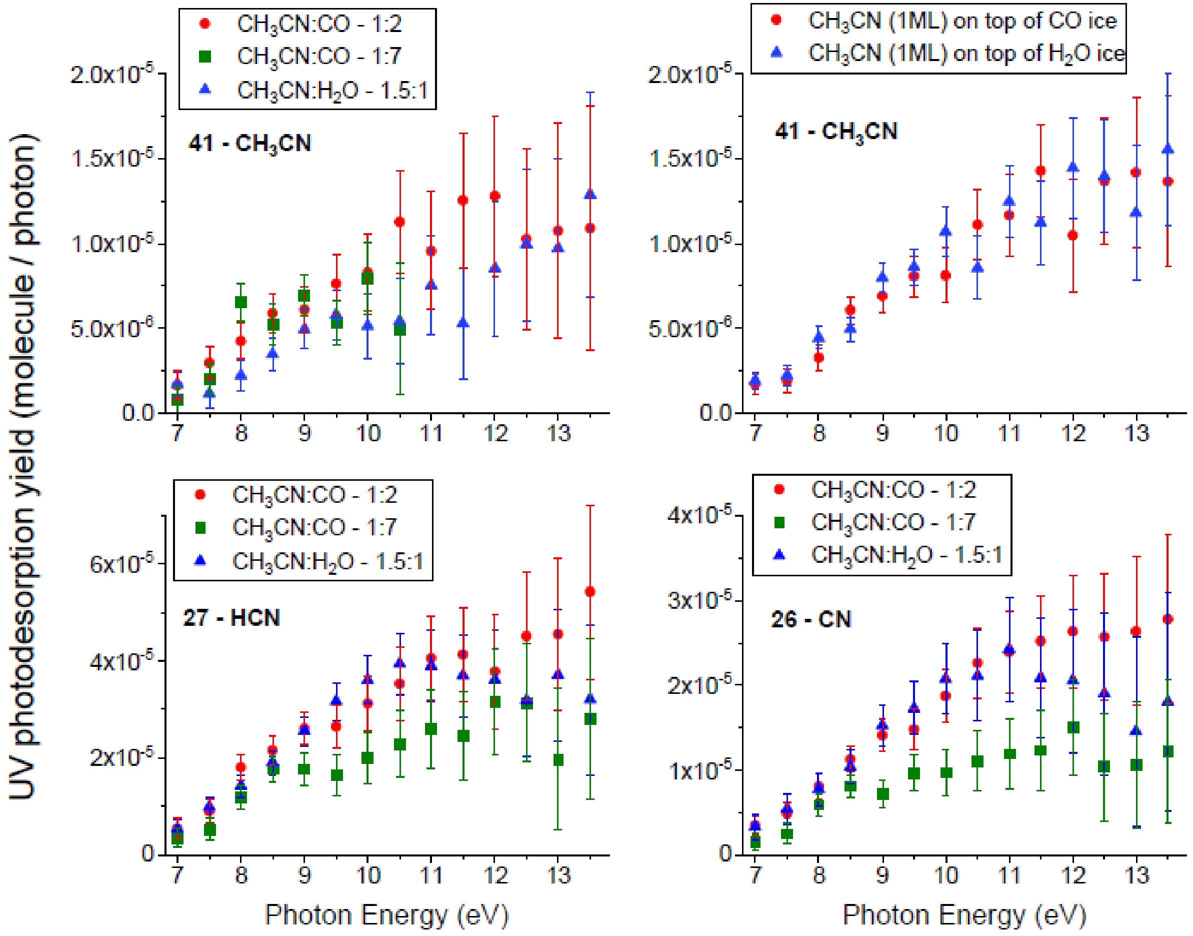
- Yields do not depend on the ice composition



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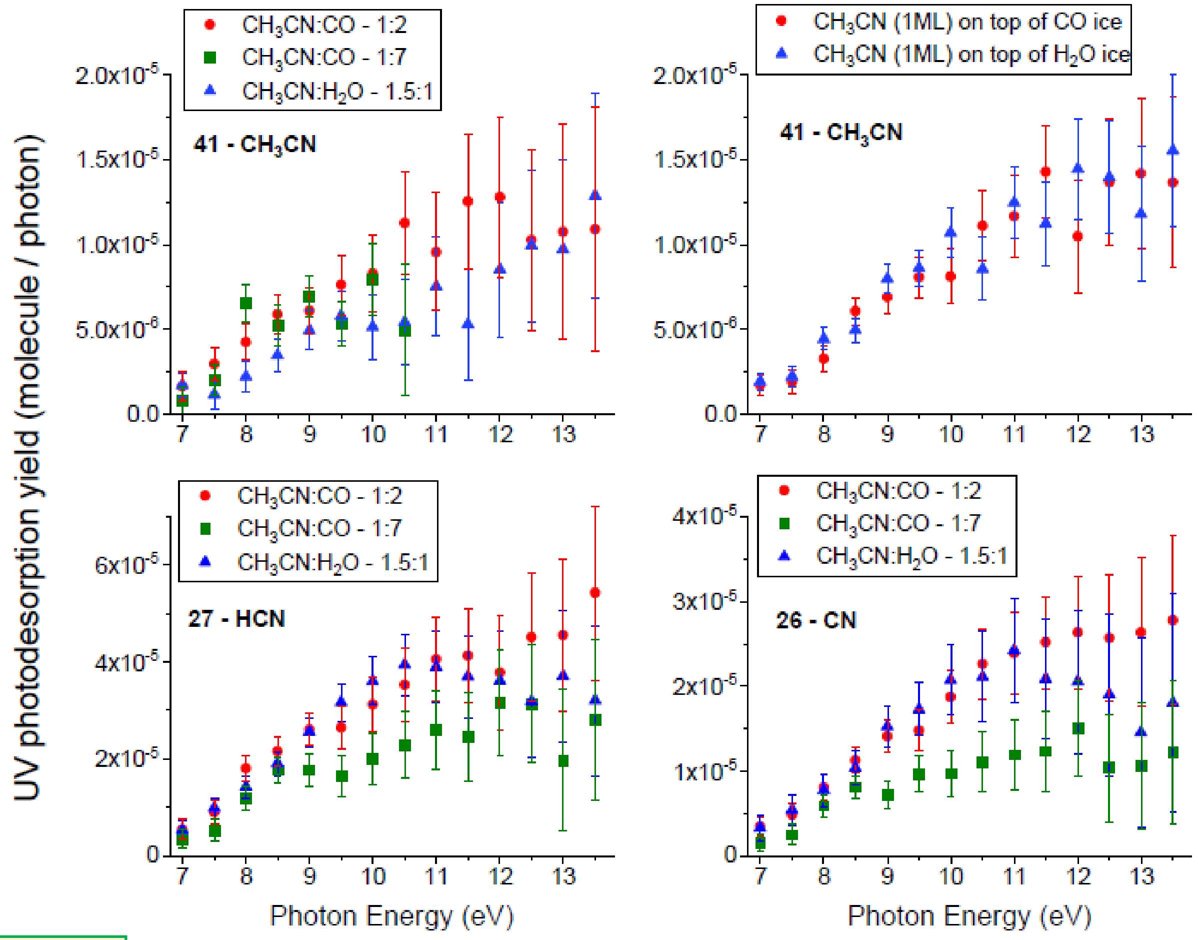

Desorption of the intact species competes with dissociation

NOT similar to the CH_3OH case

Photodesorption of organics: HCOOH, $HCOOCH_3$ & CH_3CN

Conclusions

« Methanol-like » behaviours – CH_3OH, HCOOH, $HCOOCH_3$

- Photodesorption of the intact molecule is « weak » (< 10^{-5} molecules/photon)
- Photodesorption is dominated by the fragmentation of the molecule, with little photochemistry
- **Can it be generalized to any O-bearing molecule? Only to other alcohols, carboxylic acid and esters?**

CH_3CN presents different behaviour

- Desorption of the intact molecule is more efficient, and comparable to photodissociative channels. **Is that true for any nitrile or isonitrile?**
- Difference in UV photodesorption is in agreement with observations in PDR (Horsehead nebulae) or disks. **Can it explain by itself the observed abundances?**

For all studied COMs

- Small impact of the ice composition
- Photodesorption mostly leads to the release of photofragments in the gas, some being radicals
- **Can this effect activate locally gas phase chemistry recreating the COMS in the gas ?**

Photodesorption of organics: $HCOOH$, $HCOOCH_3$ & CH_3CN

Conclusions

Status now

Molecule	Ice	Desorbed species	ref
CH_3OH	Pure & with CO	CH_3OH, CH_3O, H_2CO, CH_3, OH, CO	Oberg+2009, Bertin+2016, Cruz-Diaz+2016
HCOOH	Pure, with CO, with H_2O	HCOOH, H_2CO, HCO, CO_2, CO, H_2O	Bertin+2023
$HCOOCH_3$	Pure, with CO, with H_2O	$HCOOCH_3$, H_3CO, H_2CO, HCO, CH_3, O_2, CO_2, CO, H_2O	Bertin+2023
CH_3CN	Pure, with CO, with H_2O	CH_3CN, HC_2N, HCN, CN, CH_3	Basalgète+2021, Bulak+2021

Upper limits

➡ *There is still work to do…*

Acknowledgments

anr® PIXyES: *Photodesorption Induced by UV-X-rays and Electrons on Surfaces*

Feb. 2020 – Jan. 2025

MONARIS — SCIENCES SORBONNE UNIVERSITÉ

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DESIRS beamline

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Thank you for your attention

… et bon anniversaire
Marie-Aline