VUV photolysis of molecules in astrophysical media: Branching ratios of photodissociative channels for databases

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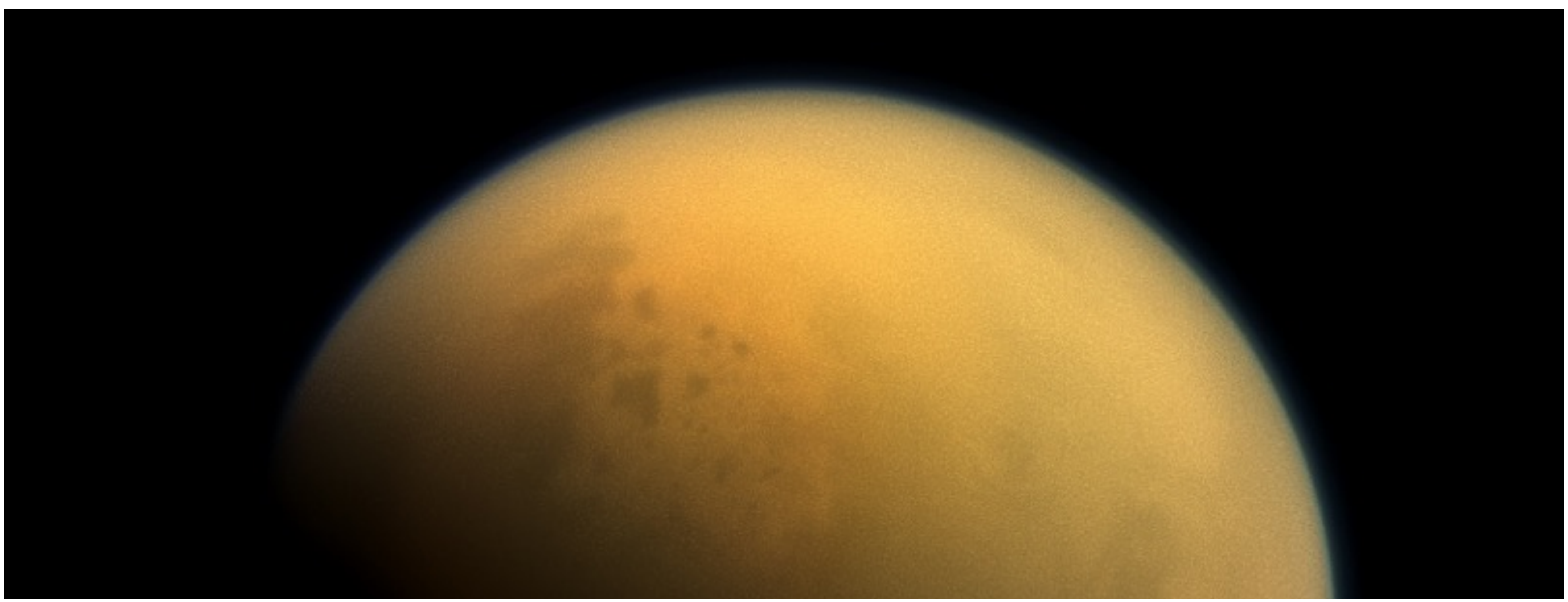
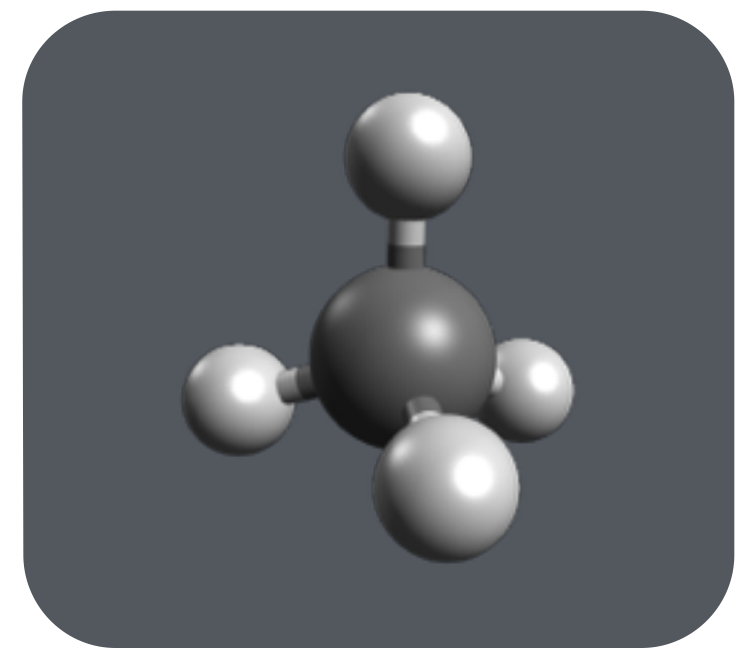


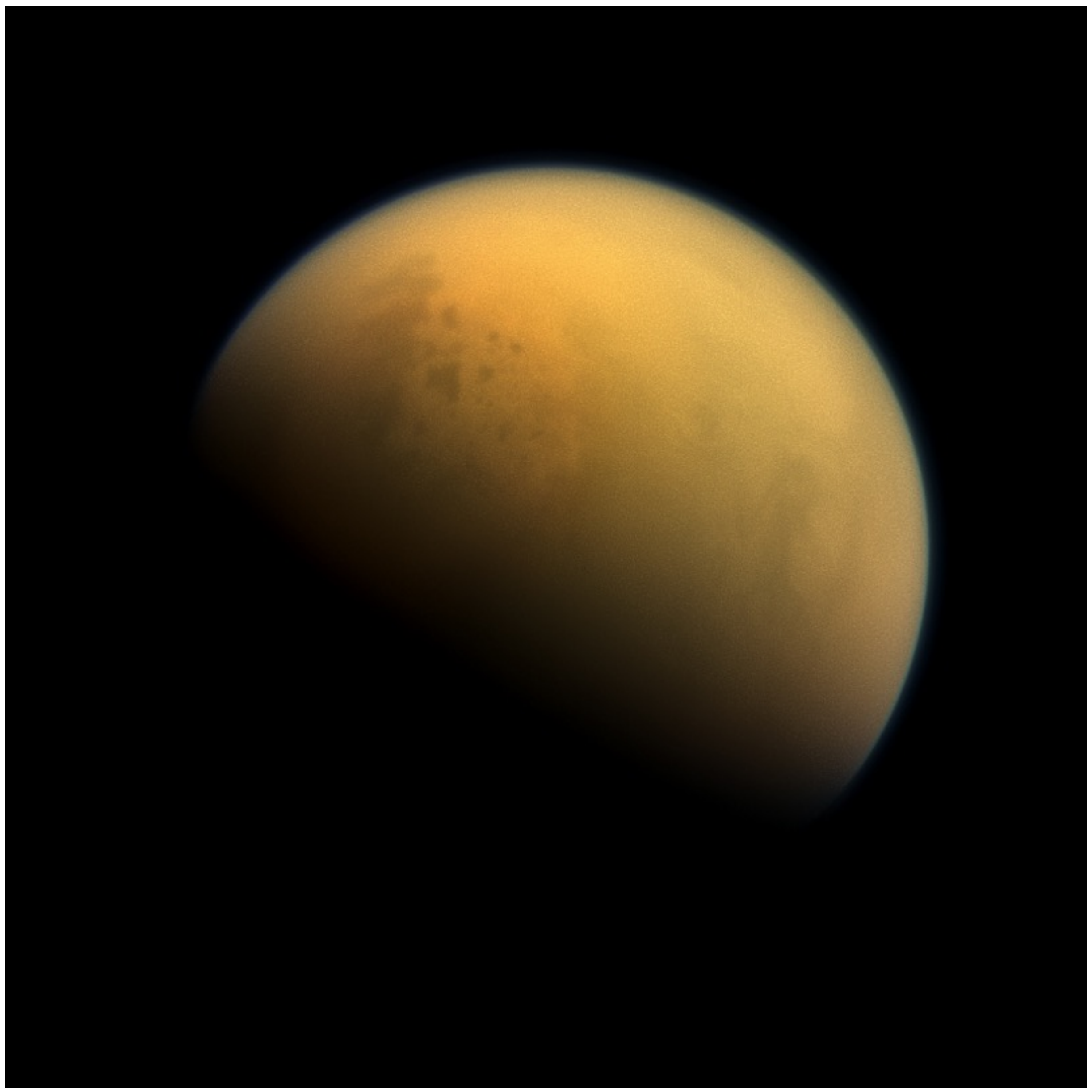
KIDA meeting - 2015

Outline

- Introduction and motivation in the context of Titan
- Example: VUV Photolysis of Methane (CH_4)
  - First step: radical photoionization cross section measurement.
  - Second step: Branching ratio measurement
- Conclusions and perspectives

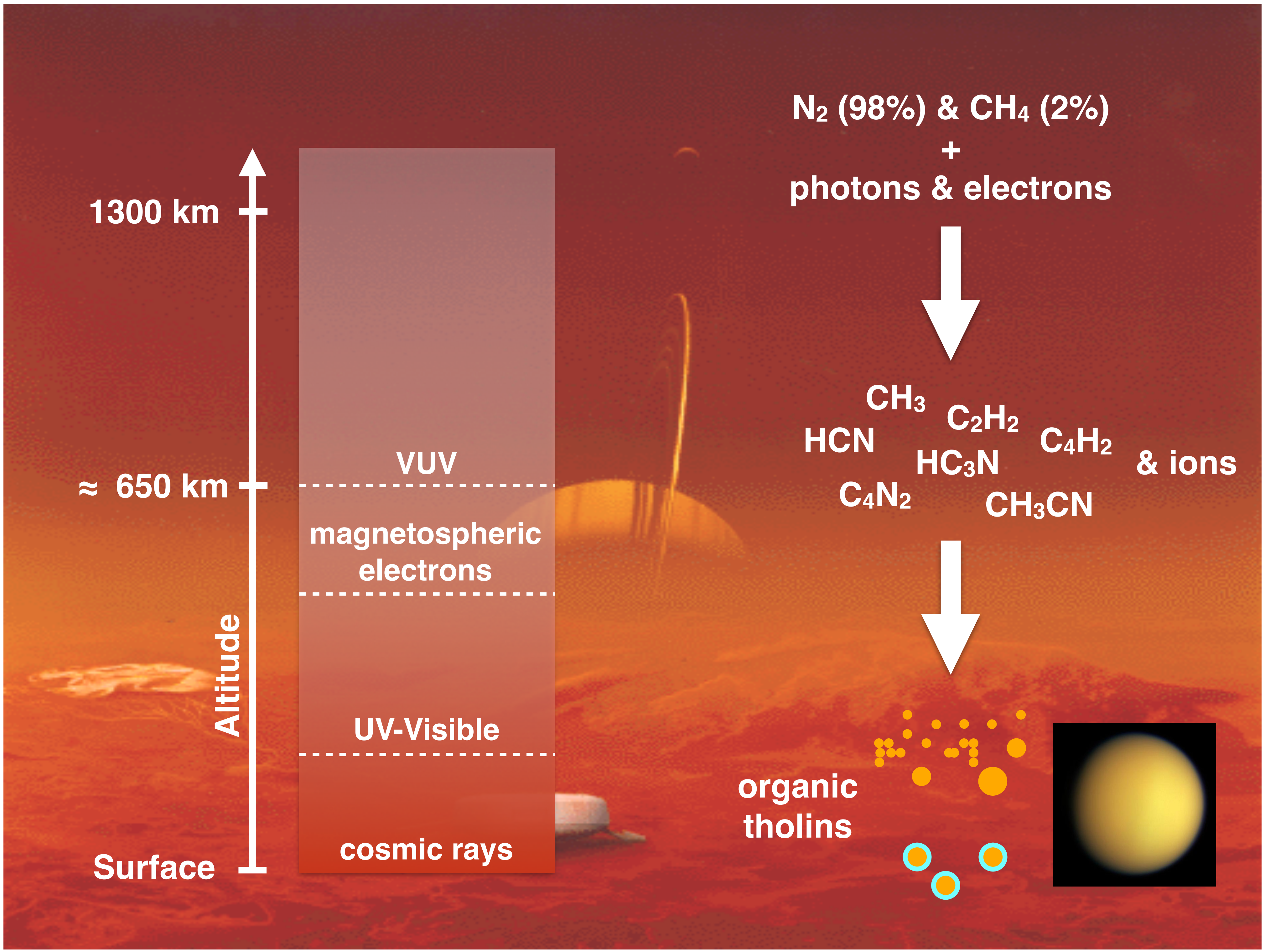


Introduction

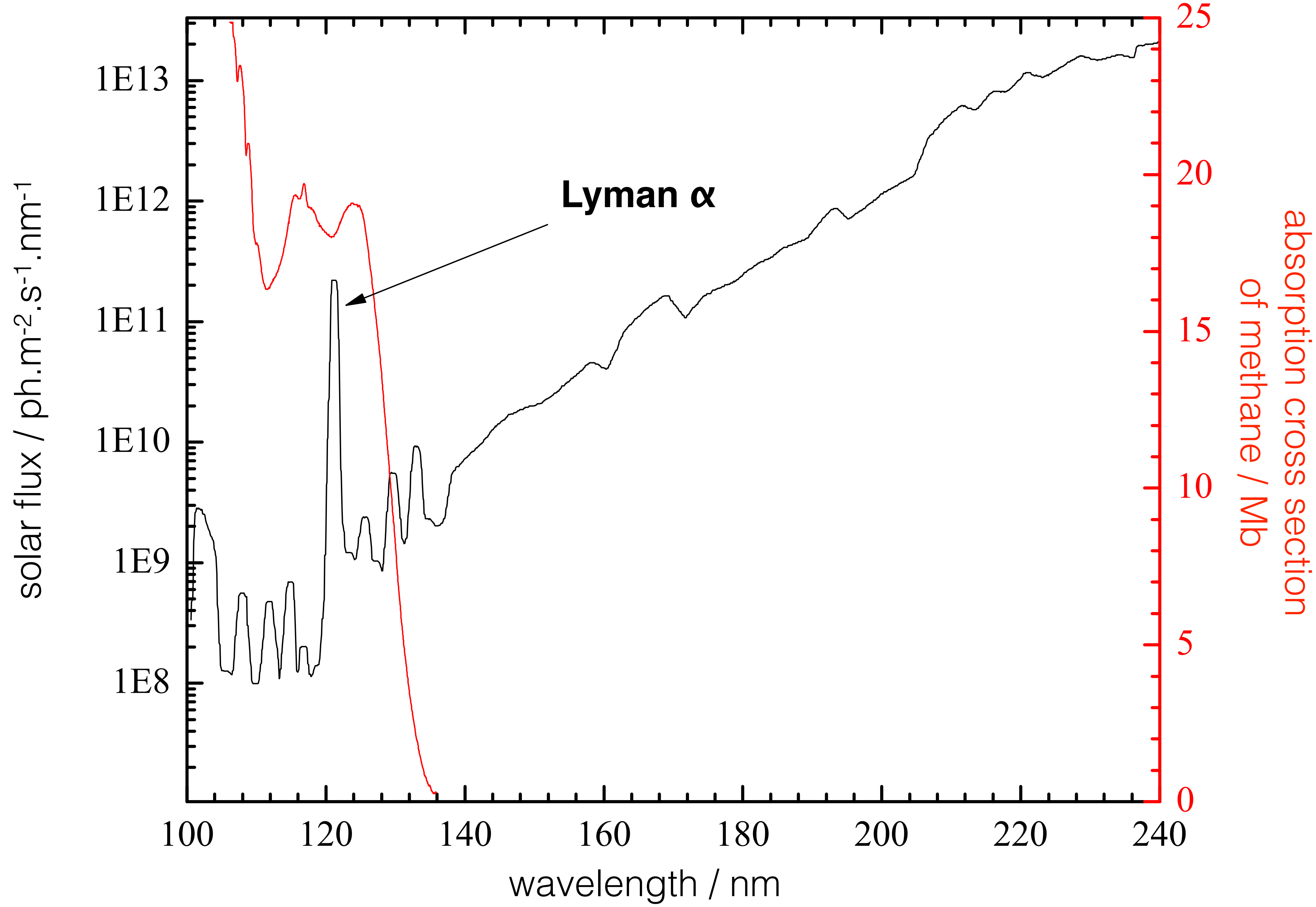


Titan:
- Biggest moon of Saturn
- Dense atmosphere ($P_S \approx$ 1.5 bar)
- $T_S \approx$ 94 K
- Composition:
  - $N_2 \approx$ 98 %
  - $CH_4 \approx$ 1.6 %
  - organic molecules
- Active atmosphere

Photochemistry on Titan



Methane photolysis: a key process for Titan photochemistry



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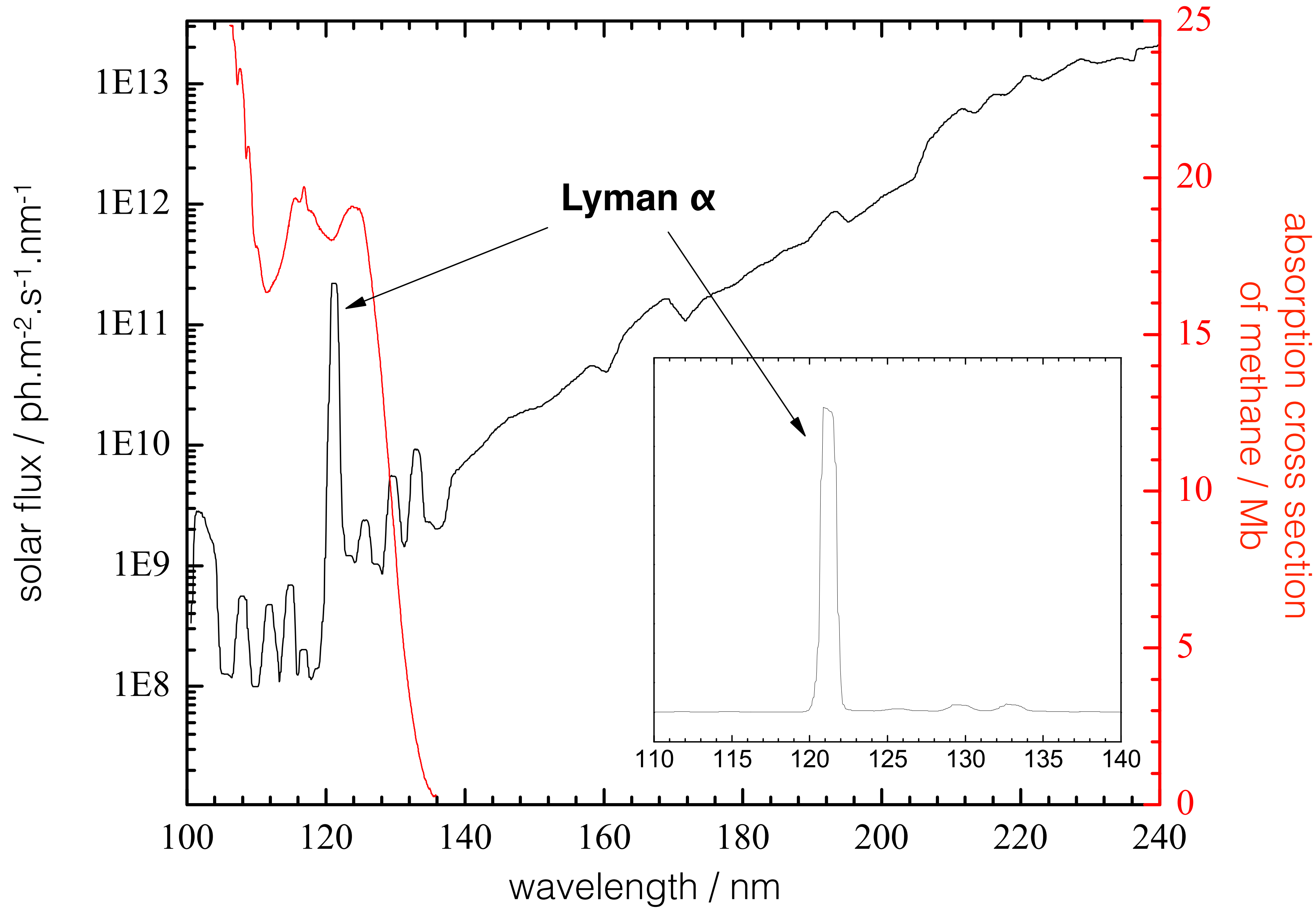

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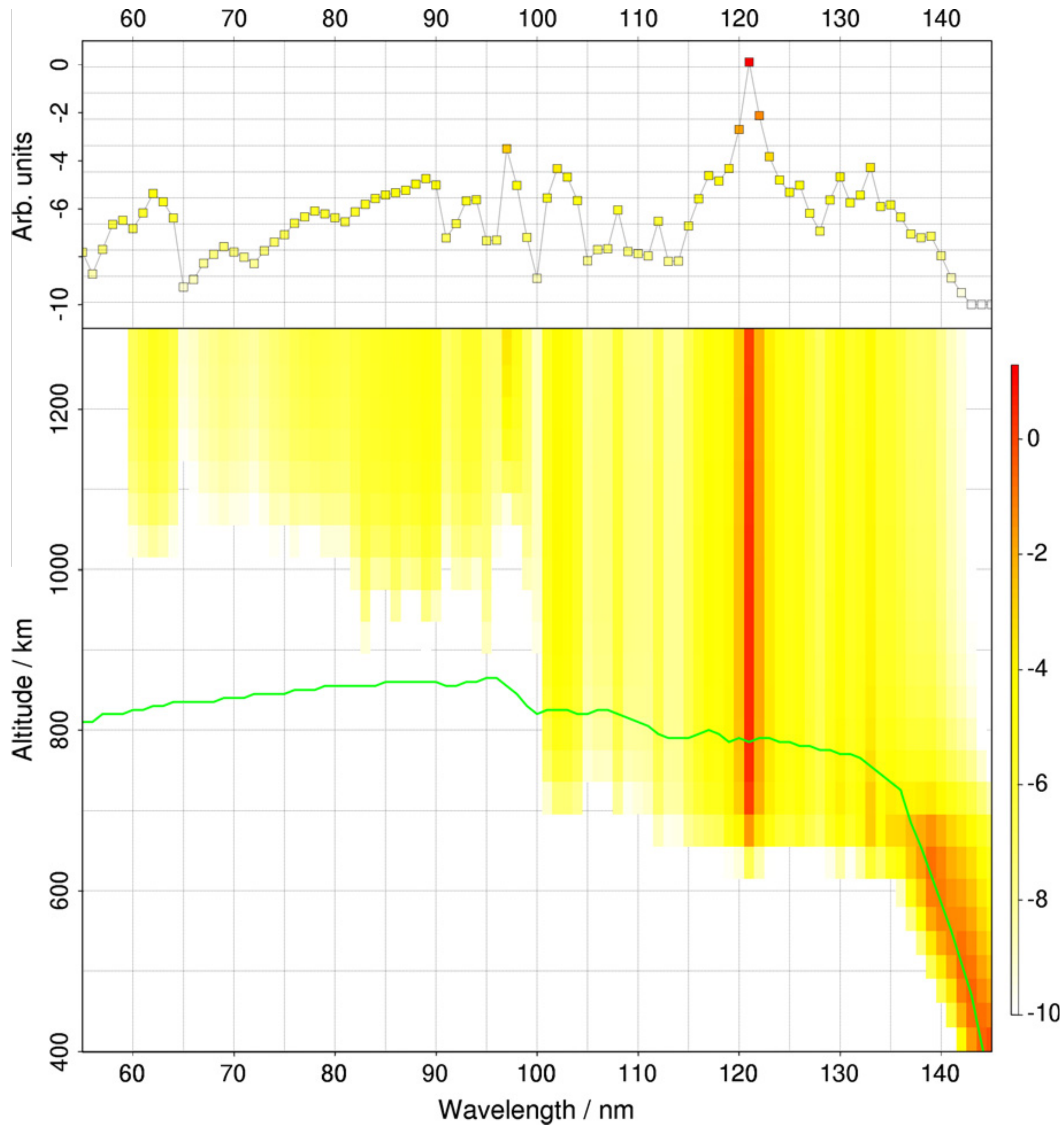

B. Gans, Z. Peng, N. Carrasco, D. Gauyacq, S. Lebonnois, P. Pernot, *Icarus* **223** (2013) 330–343

Previous measurements at Lyman α (121.6 nm)

Dissociative channel	Mordaunt et al. S1 & S2 (1993)		Heck et al. (1995)	Brownsword et al. (1997)	Wang et al. (2000)	Park et al. (2008)
$CH_3(X)+H$	0.51	0.49	0.66	0.38	0.291	0.31
$CH_2(a)+H_2$	0.24	0	0.22	0.52	0.584	0.63
$CH_2(b)+H_2$	/	/	/	/	/	/
$CH_2(X)+2H$	0.05	≈ 0	≈ 0	0.01	/	/
$CH_2(a)+2H$	0.2	≈ 0	≈ 0		0.055	/
$CH(X)+H+H_2$	0	0.51	0.11	0.08	0.07	0.059
$C(^1D)+2H_2$	0	0	0	0	0	0.0004
Φ(H)	1	1	0.77	0.47	0.47	0.31
Φ(H_2)	0.24	0.51	0.33	0.6	0.654	0.69

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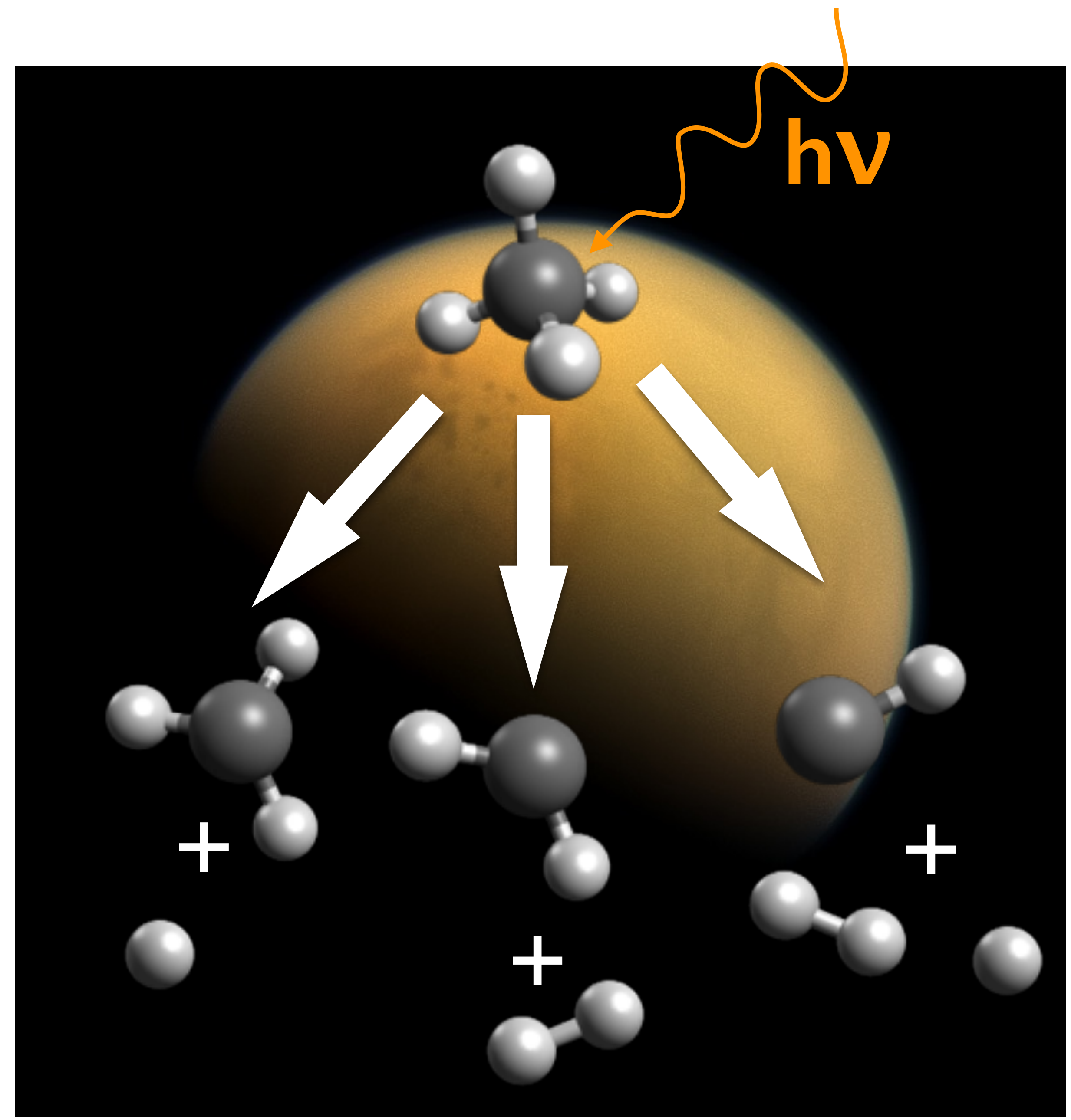
How was methane photolysis implemented in the Titan atmosphere models until recently?

- 3 dissociation pathways:
  - $CH_3 + H$
  - $CH_2 + H_2$
  - $CH + H + H_2$

- Two different energy ranges:
  - at Lyman-α (121.6 nm)
  - Out Lyman-α



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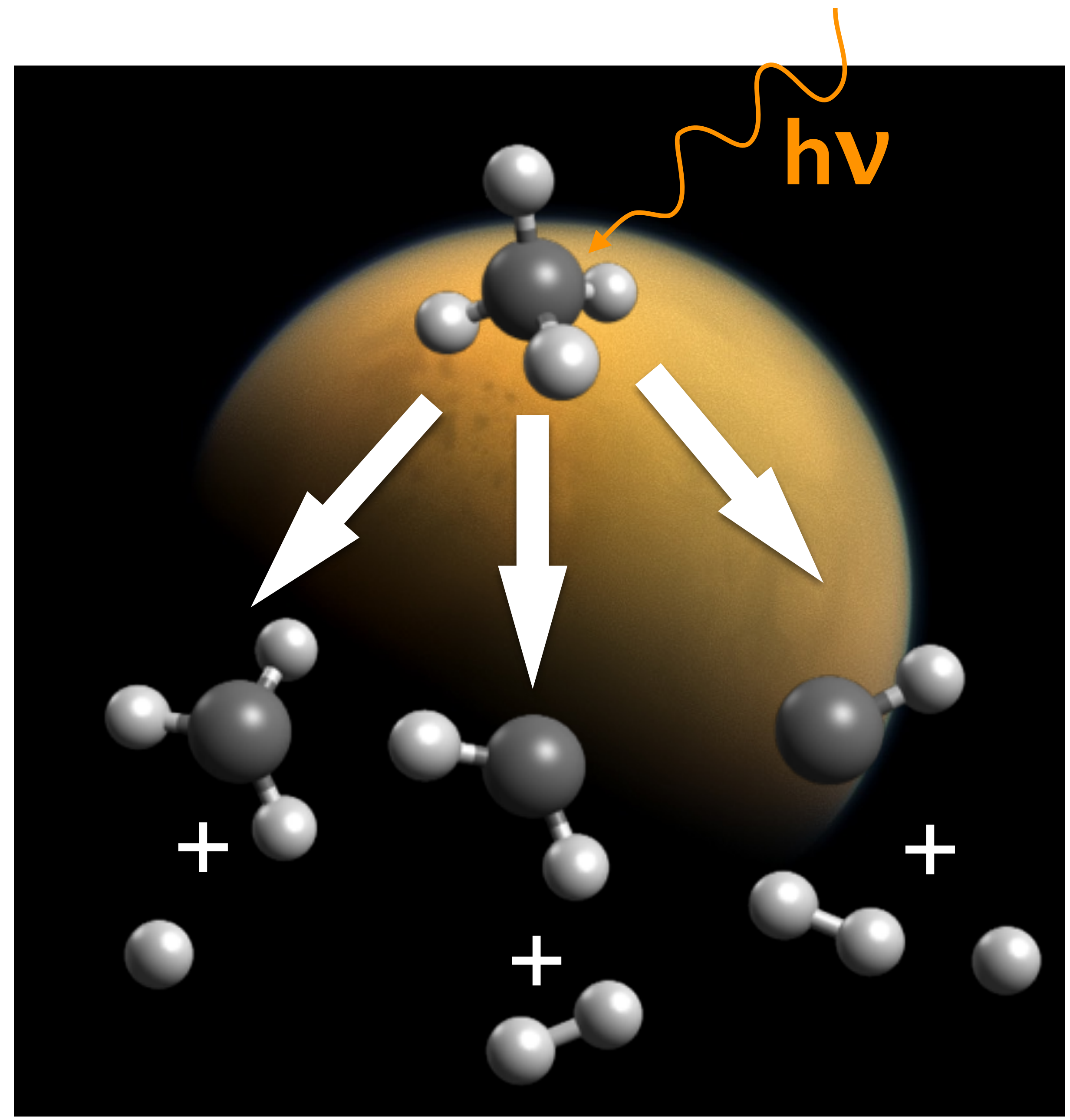

29% 64% 7%

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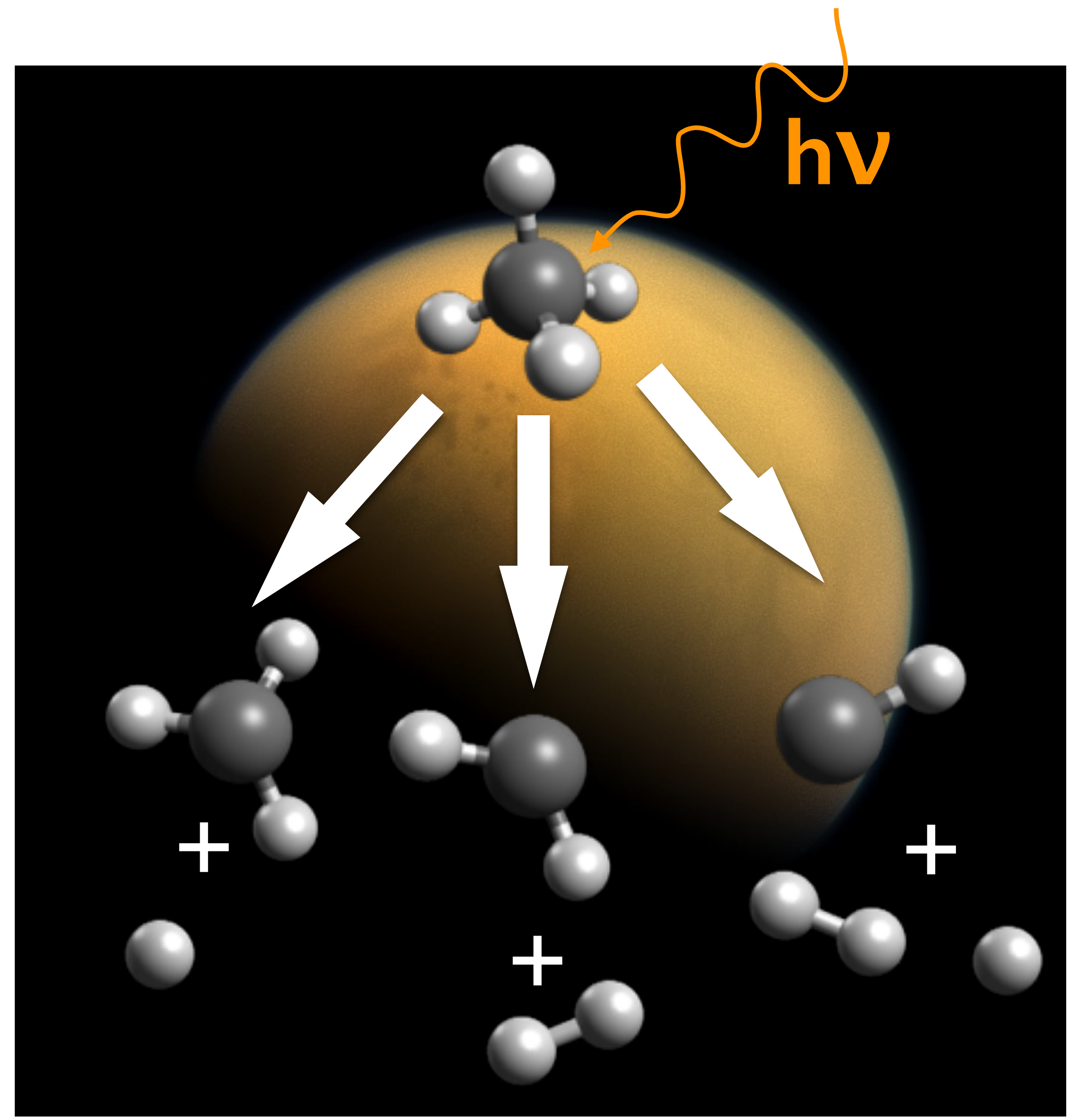

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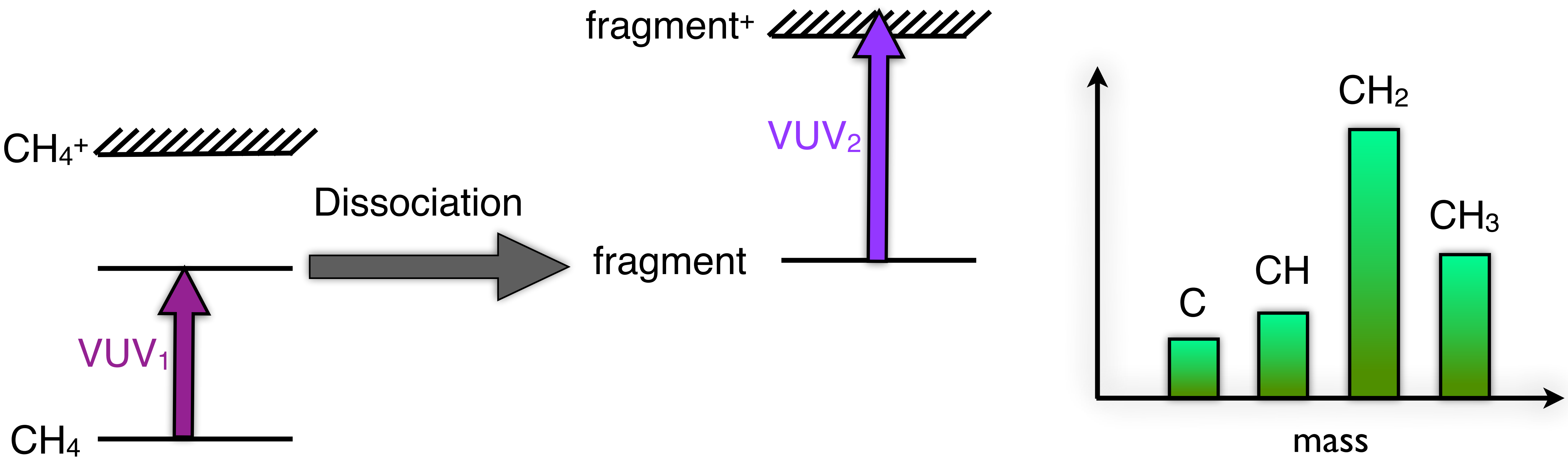
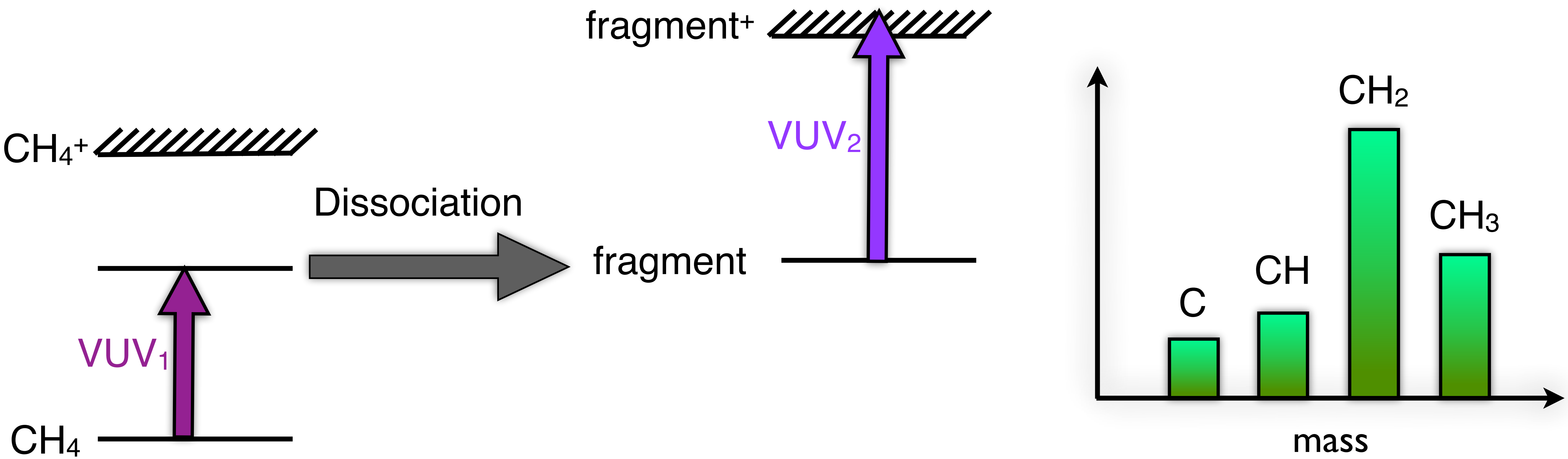
What is important?

- from the simulations:
  - **CH_2** and **CH_3** are the most important products,
  - **Lyman α** is the most influent wavelength, but «out-Lyman α» wavelengths have an effect,
- from the literature:
  - **direct probing of CH_2 and CH_3 fragments is mandatory**

Strategy

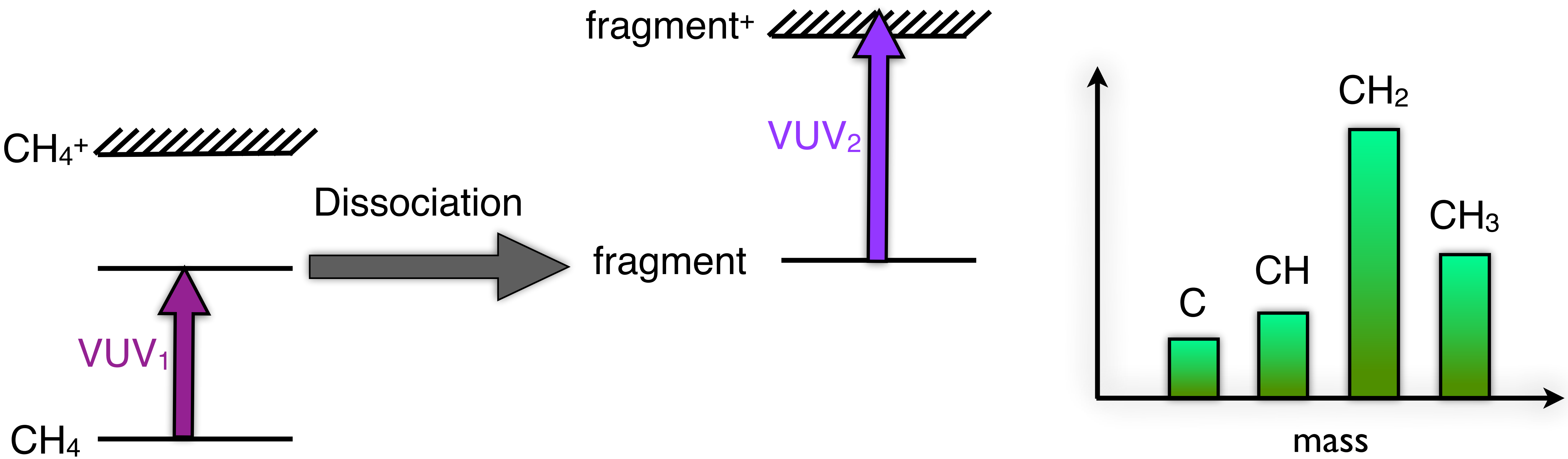

fragment$^+$
VUV$_2$
CH_4^+
Dissociation
fragment
VUV$_1$
CH_4
CH_2
CH_3
CH
C
mass

Strategy



$$S_{\mathrm{CH}_n} \propto \sigma_{\mathrm{CH}_n}^{\mathrm{ion@VUV_2}} \times \phi_{\mathrm{CH}_n}^{\mathrm{VUV_1}} \times \sigma_{\mathrm{CH_4}}^{\mathrm{abs@VUV_1}} \times N_{\mathrm{CH_4}}$$

Strategy



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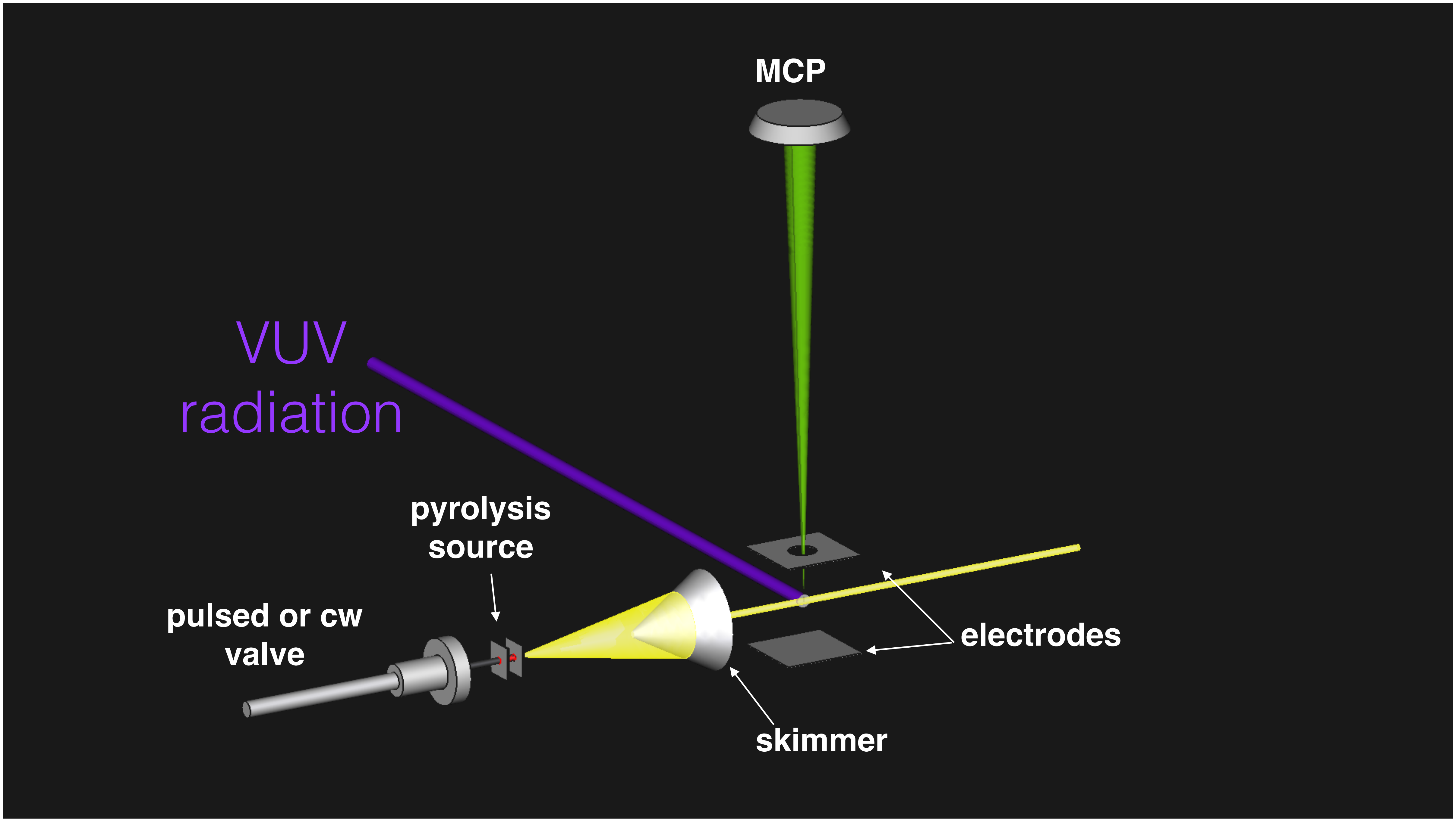
➡ Branching ratios can be extracted from the mass spectrum if the photoionization cross sections of the radical products are known

First step: absolute photoionization cross section measurements of radicals

Experimental setup for radical cross section measurements



VUV sources

In the lab (ISMO)

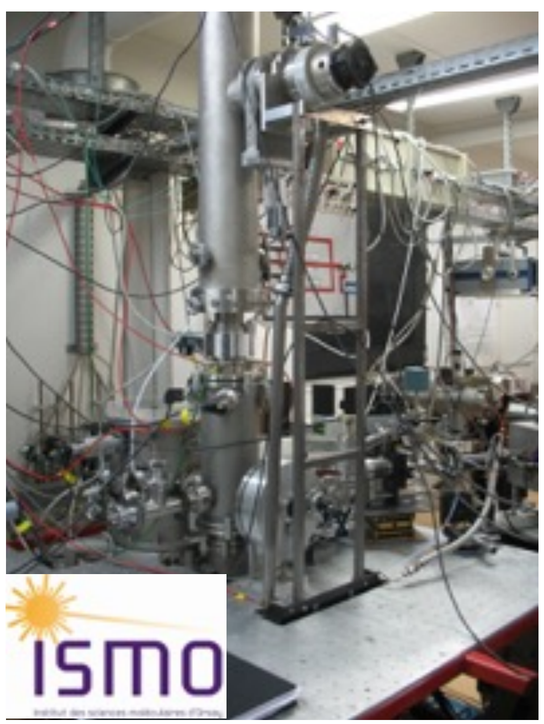
VUV laser at 118.2 nm (3ω)

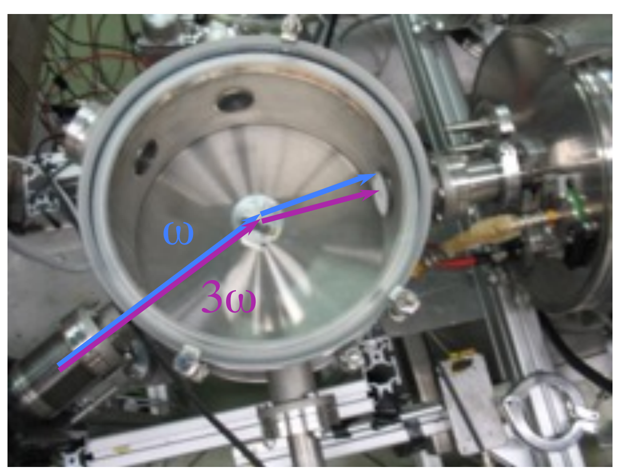
(84602.4 cm-1)

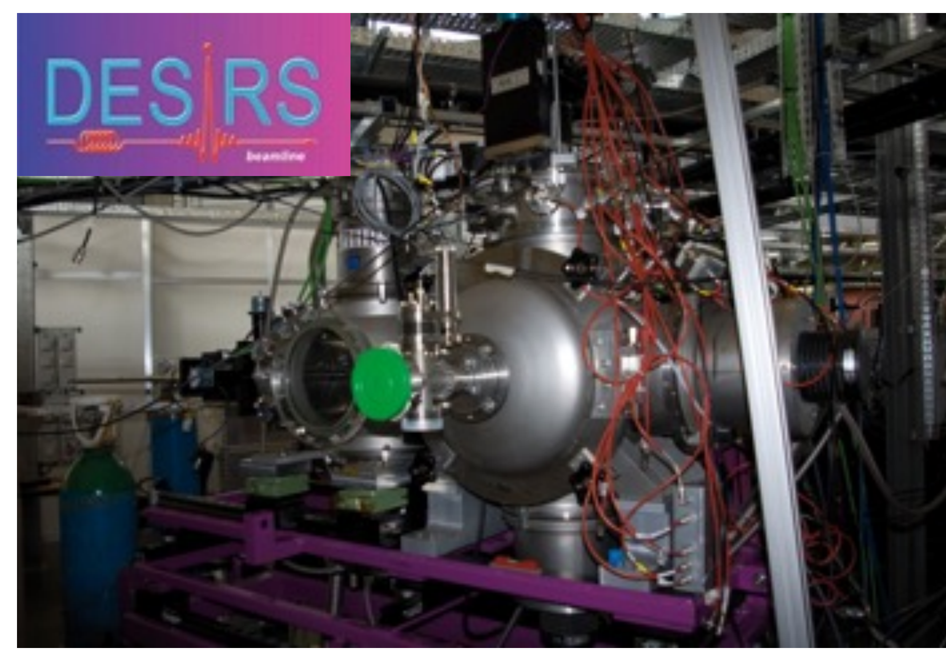
SOLEIL synchrotron

8→12 eV

(64524.4→96786.5 cm^{-1})



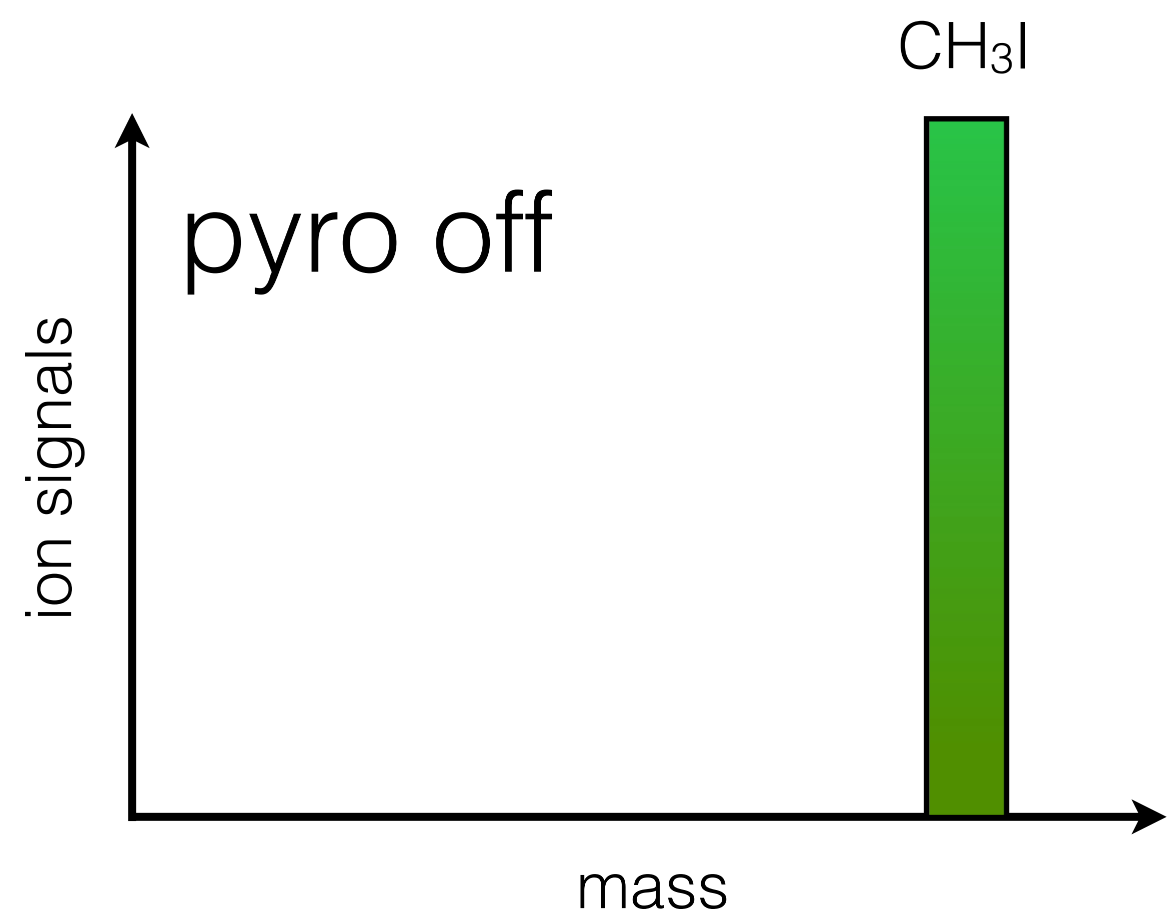




Method for measuring absolute photoionization cross sections

Pyrolysis of CH_3I :

$$\mathrm{CH_3I} \xrightarrow{\Delta} \mathrm{CH_3} + \mathrm{I}$$



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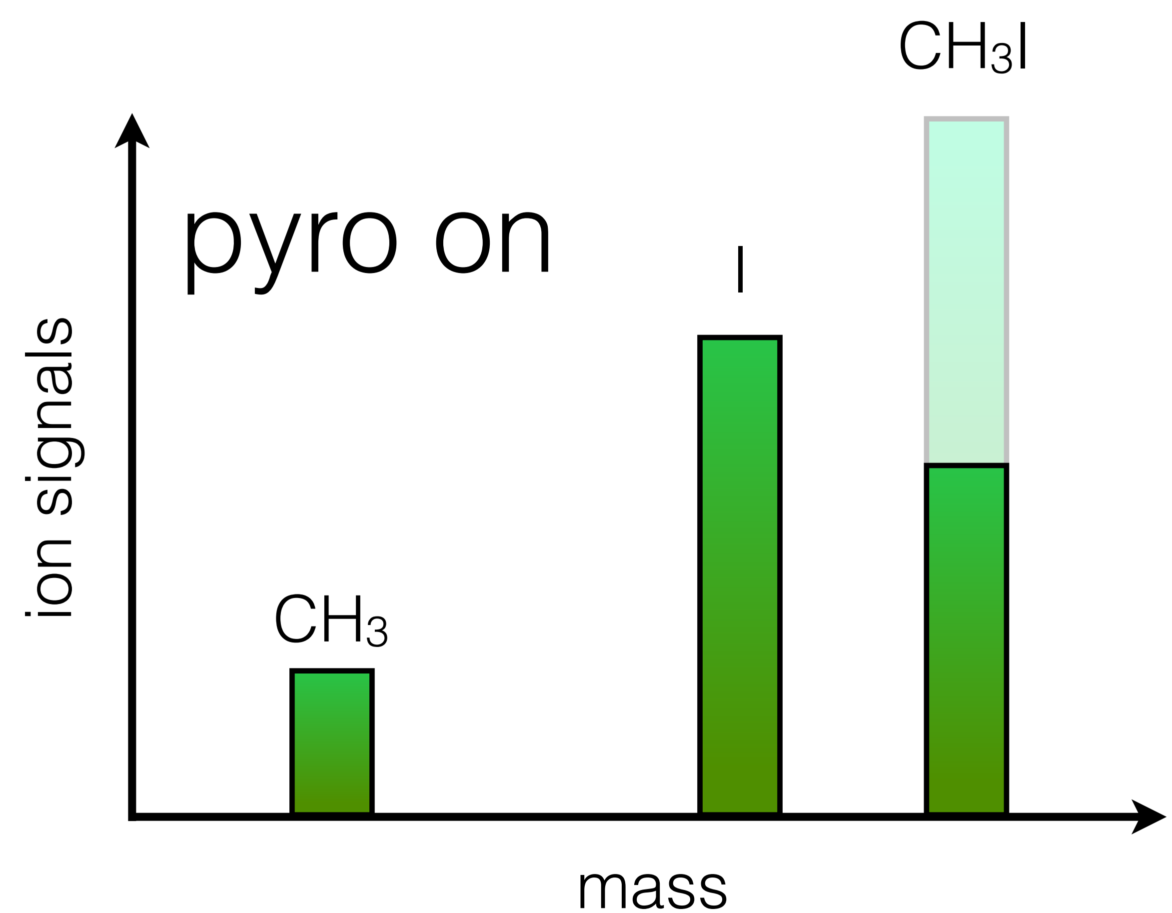

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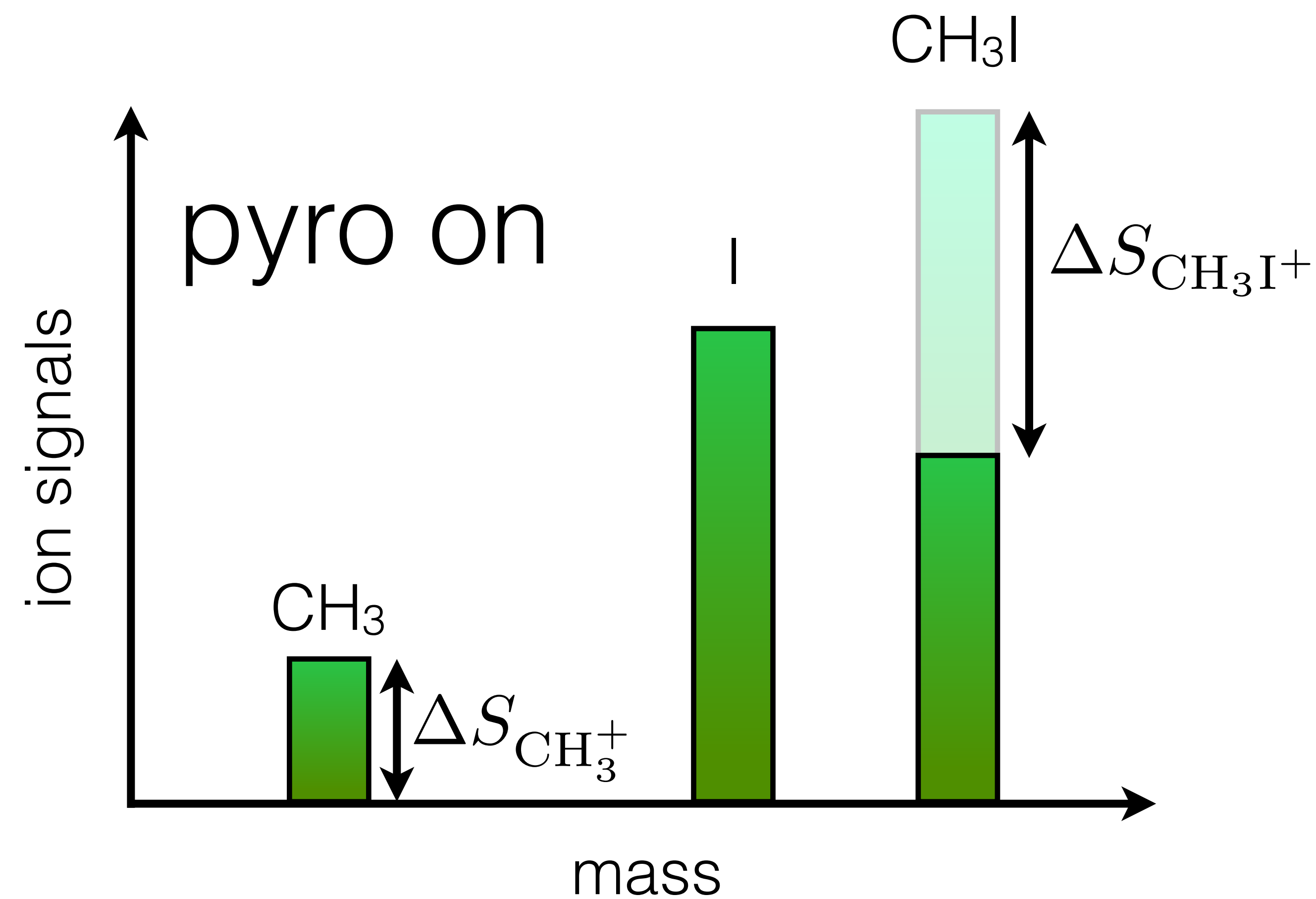

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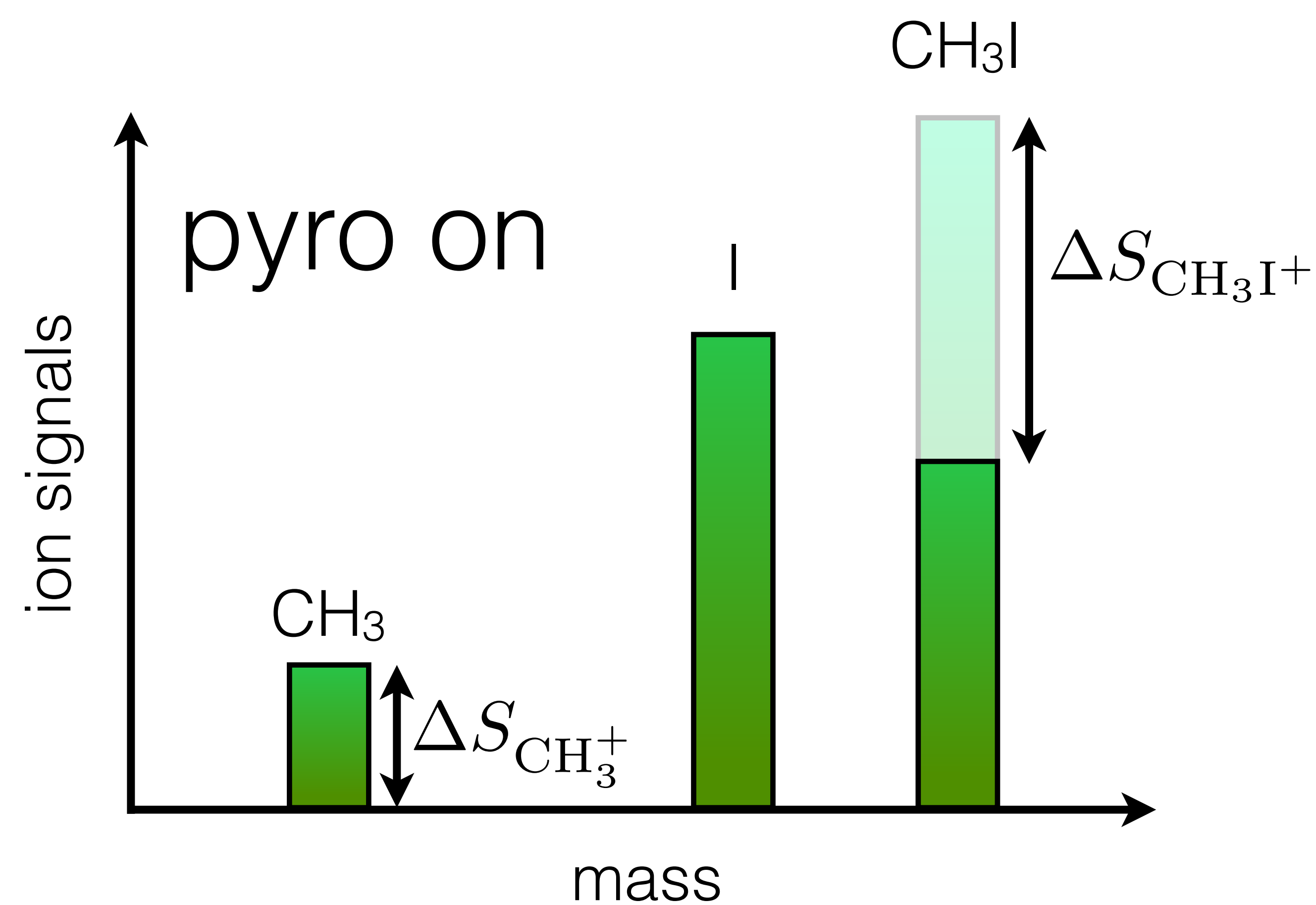

$$\frac{\Delta S_{CH_3^+}}{\Delta S_{CH_3I^+}} \times \frac{F_{CH_3I}}{F_{CH_3}} = \frac{\sigma_{CH_3}^{i@118,2}}{\sigma_{CH_3I}^{i@118,2}}$$

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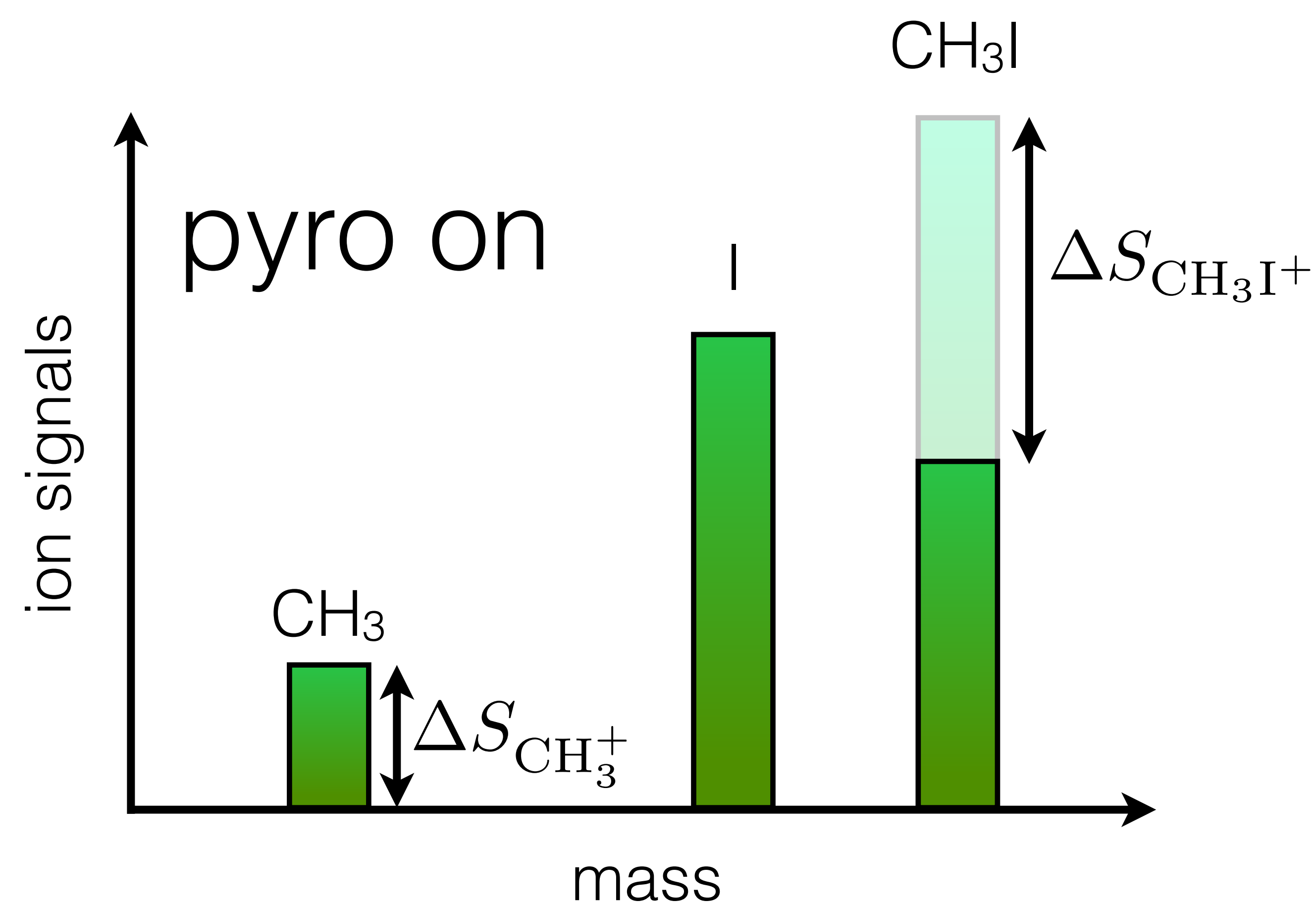

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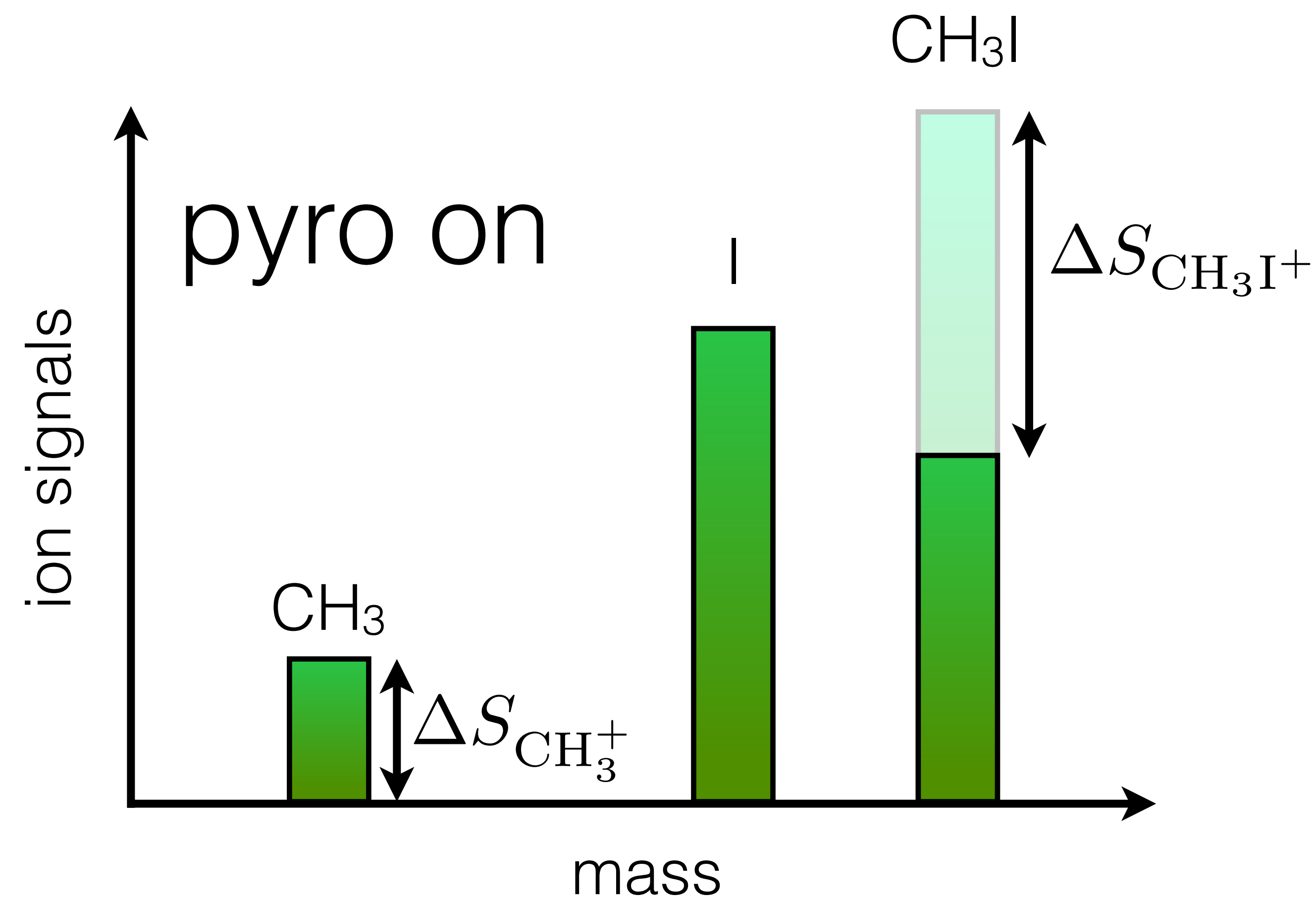

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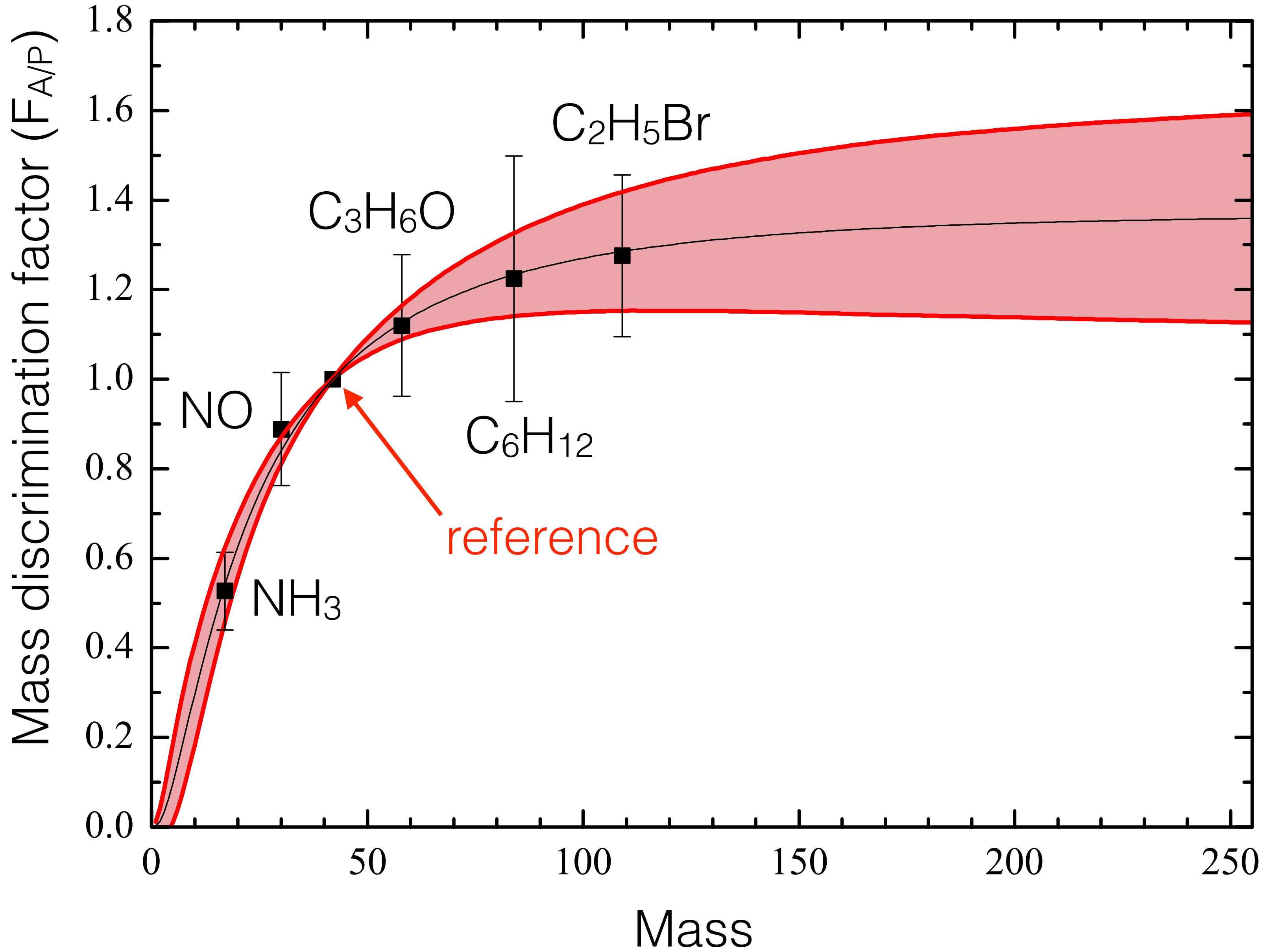
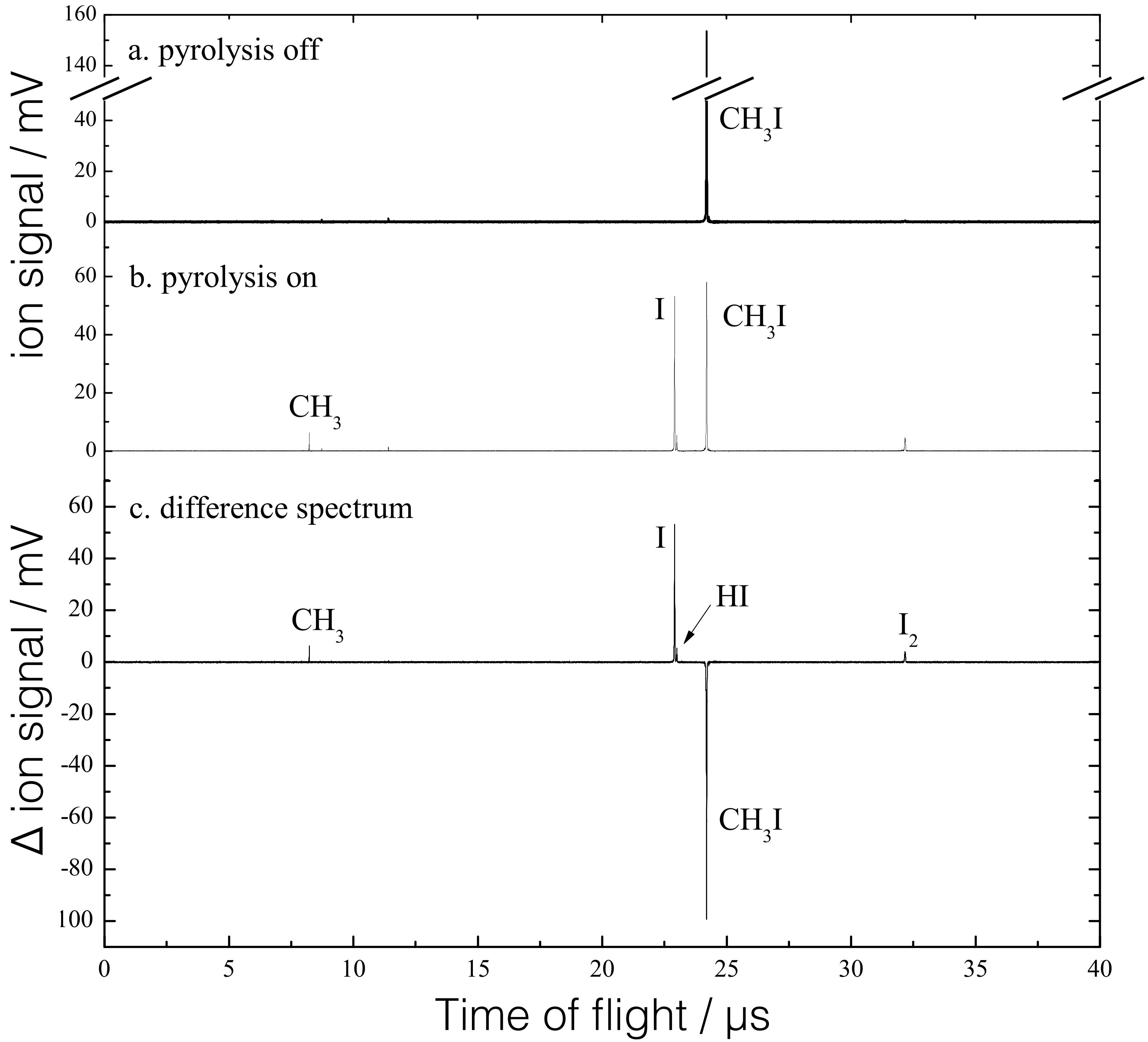
How to measure F mass discrimination factor?

- 6 molecules :
  - NH_3 (Ammonia)
  - NO (Nitric oxide)
  - C_3H_6 (propene, reference)
  - C_3H_6O (acetone)
  - C_6H_{12} (cyclohexane)
  - C_2H_5Br (bromoethane)
- Extrapolation

  (collaboration with P. Pernot, LCP)
  - best fit
  - uncertainty propagation





ion signal / mV
Δ ion signal / mV
Time of flight / μs
a. pyrolysis off
b. pyrolysis on
c. difference spectrum
CH3I
I
CH3
HI
I2
160
140
40
20
0
60
-20
-40
-60
-80
100
5
10
15
25
30
35
40

Use of pyrolysis radical source …under control!

- First requirement: Photoionization cross section independent with temperature (in the pyrolysis temperature range).

- Corrections are needed:

  - Pyrolysis temperature has physical effects on the beam (**expansion facteur**),

  - **Reactivity** has to be controlled.

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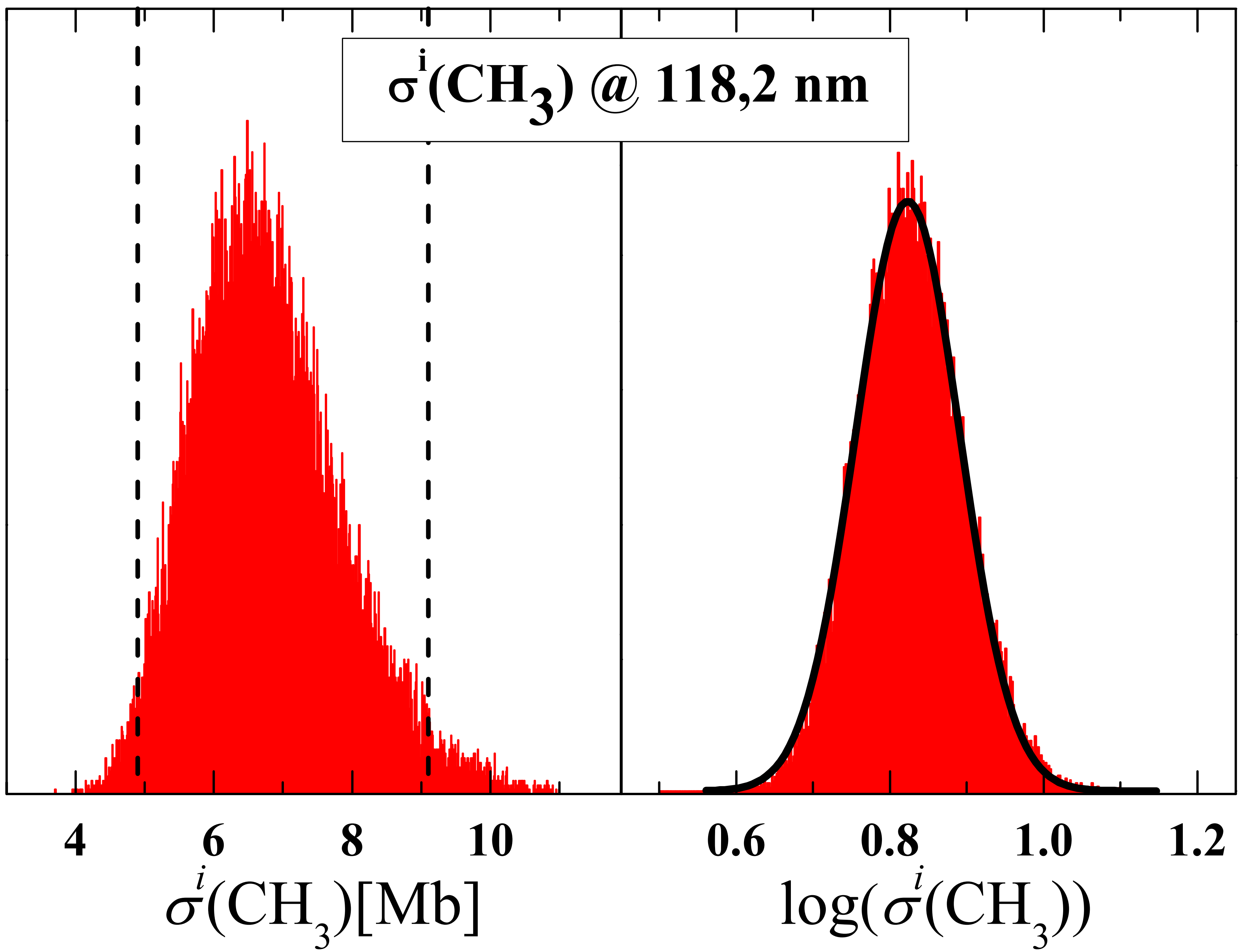
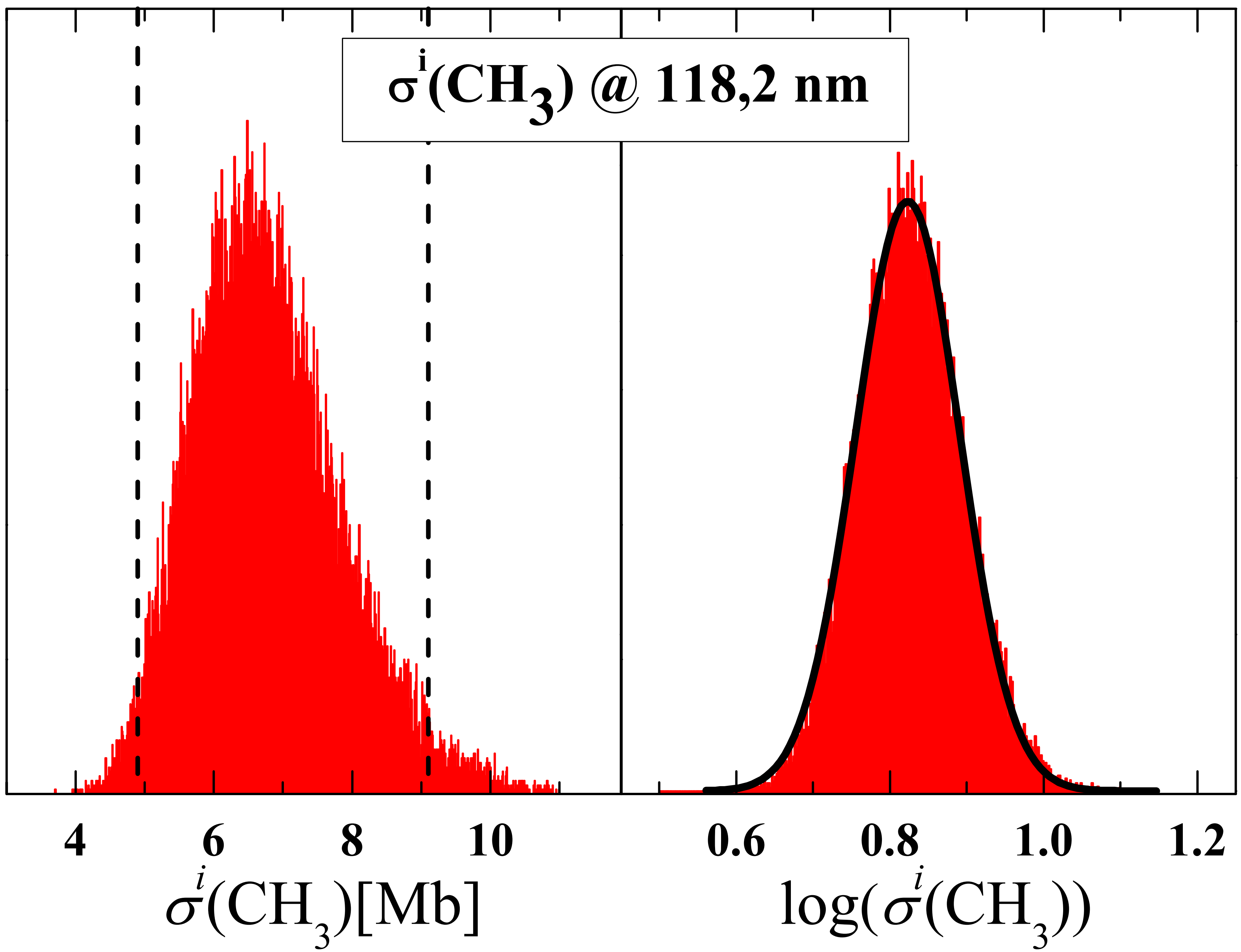
Photoionization cross section of CH_3 at 118.2 nm



$$\sigma_{CH_3}^{i@118,2} = 6,7\,^{+2,4}_{-1,8}\ \text{Mb}$$



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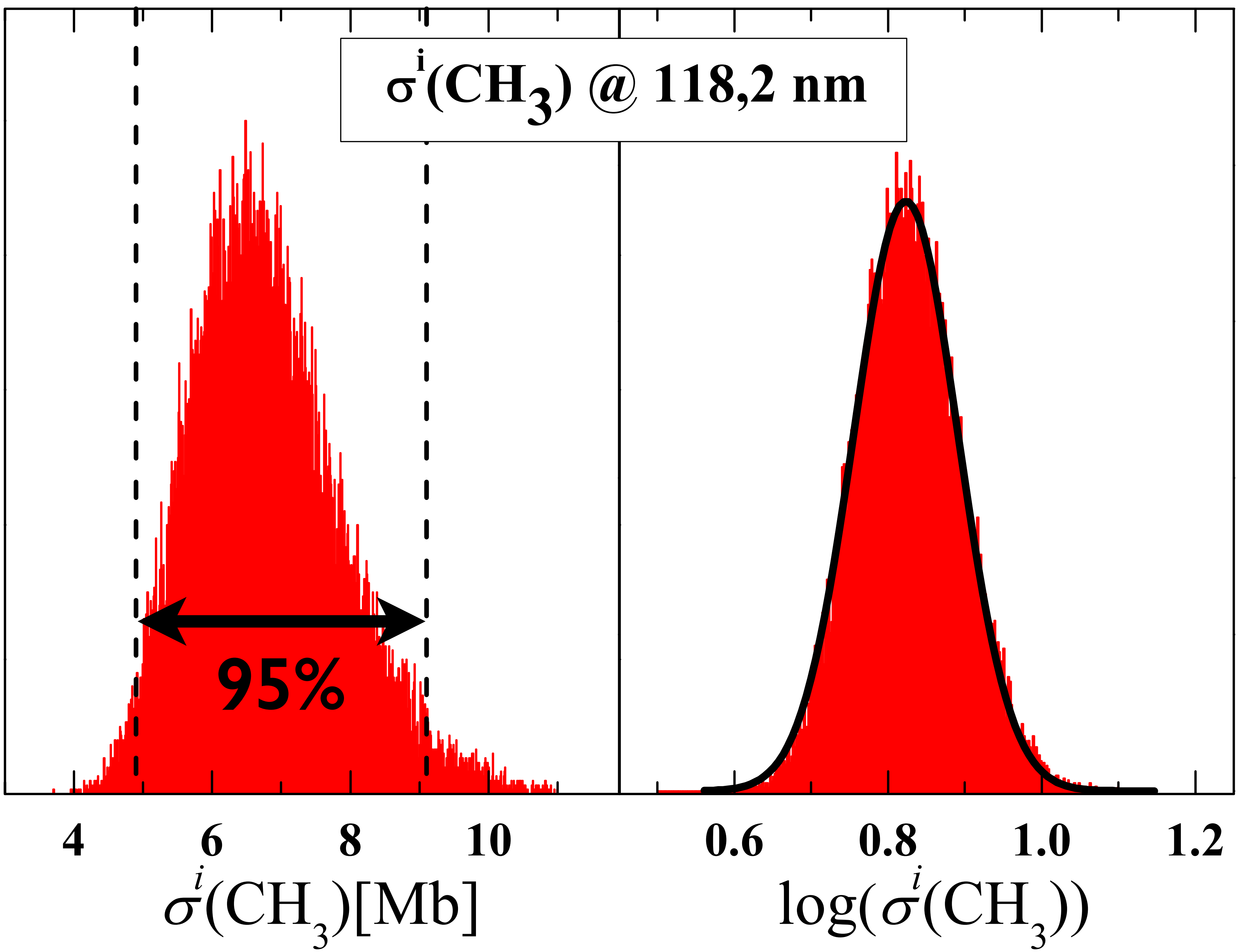
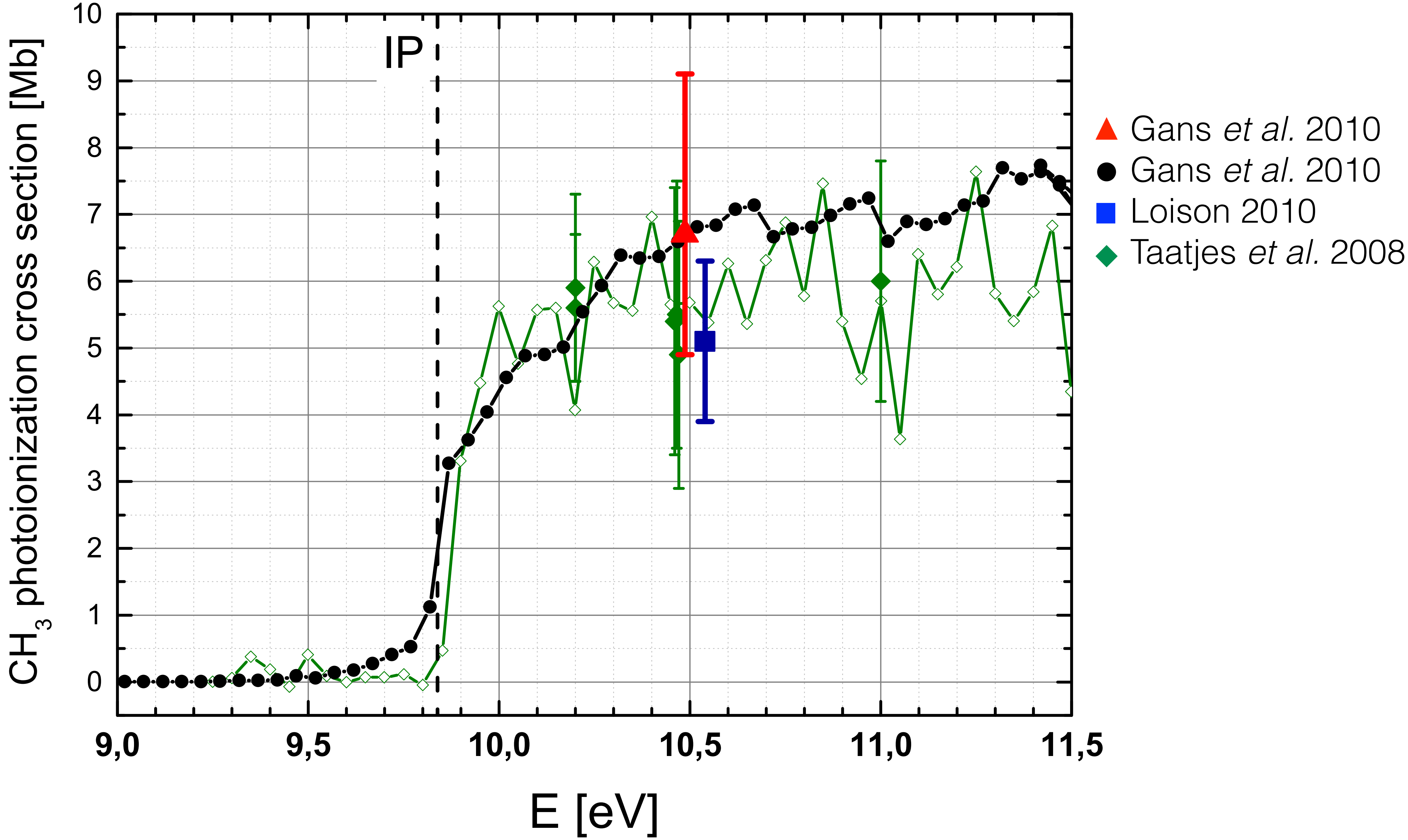


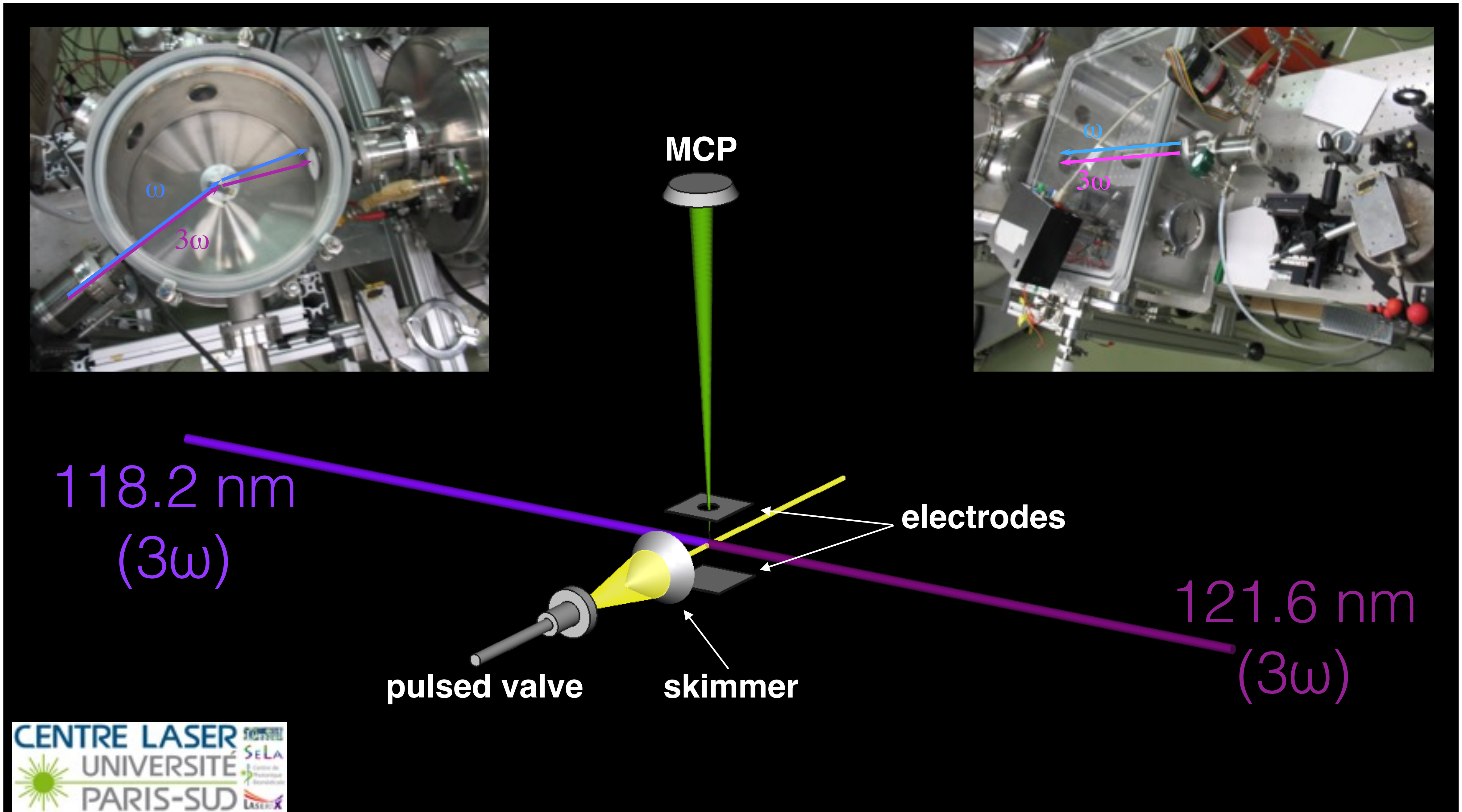
Energy-dependent photoionization cross section: Combination Laser / synchrotron experiments

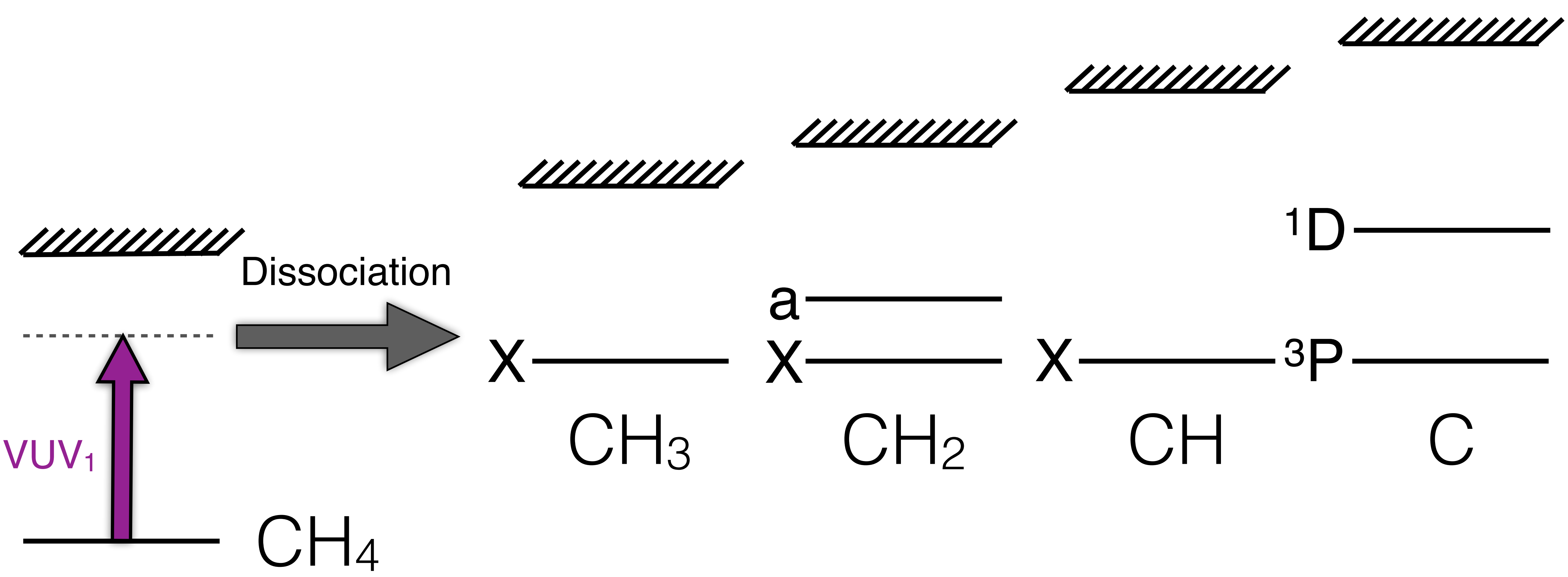


B. Gans, L. A. Vieira Mendes, S. Boyé-Péronne, S. Douin, G. Garcia, H. Soldi-Lose, B. K. Cunha de Miranda, C. Alcaraz, N. Carrasco, P. Pernot and D. Gauyacq, *J. Phys. Chem. A* **114**, 3237–3246 (2010)

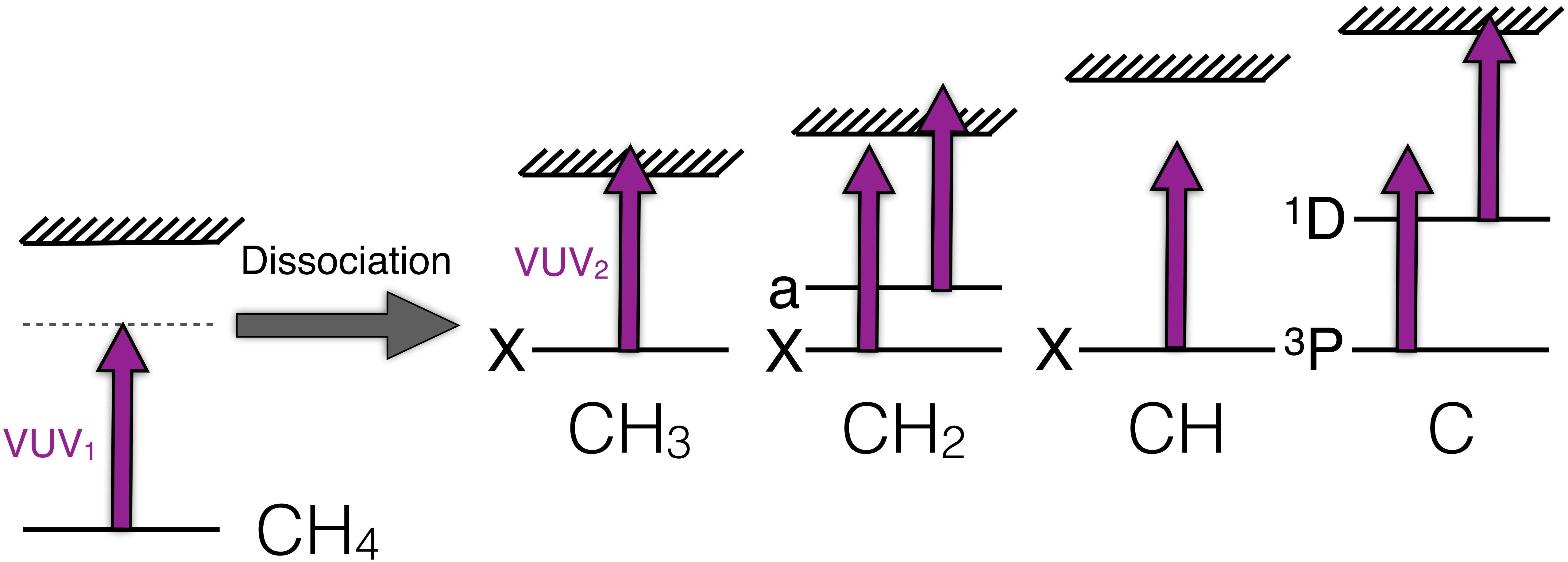
Second step: Methane photolysis experiment

Experimental setup at CLUPS laser center: a VUV pump-VUV probe laser experiment





	$CH_3(X)$	$CH_2(X)$	$CH_2(a)$	$CH(X)$	$C(^1D)$
IP [eV]	9.84	10.40	10.00	10.64	10.02
Ionization at 121.6 nm (10.2 eV)	✔	✘	✔	✘	✔
Ionization at 118.2 nm (10.49 eV)	✔	✔	✔	✘	✔



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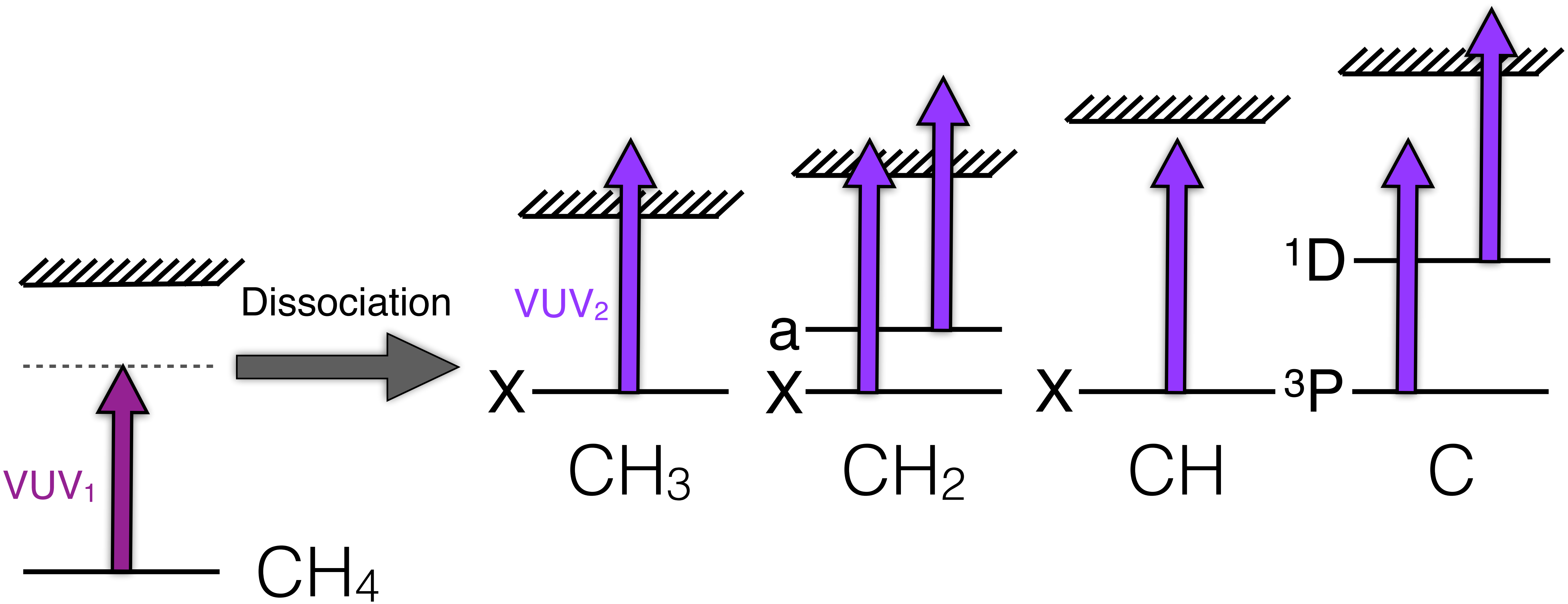

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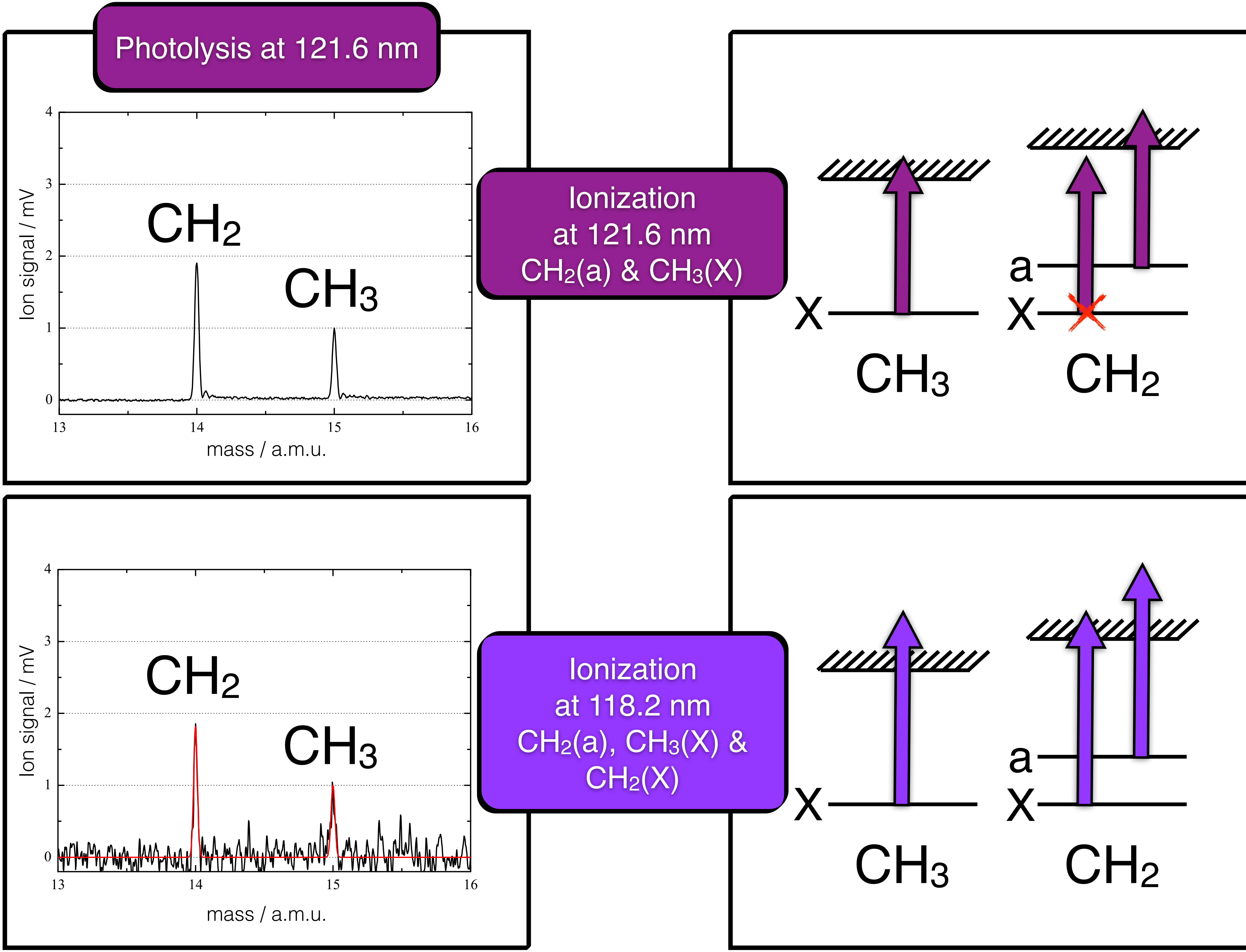
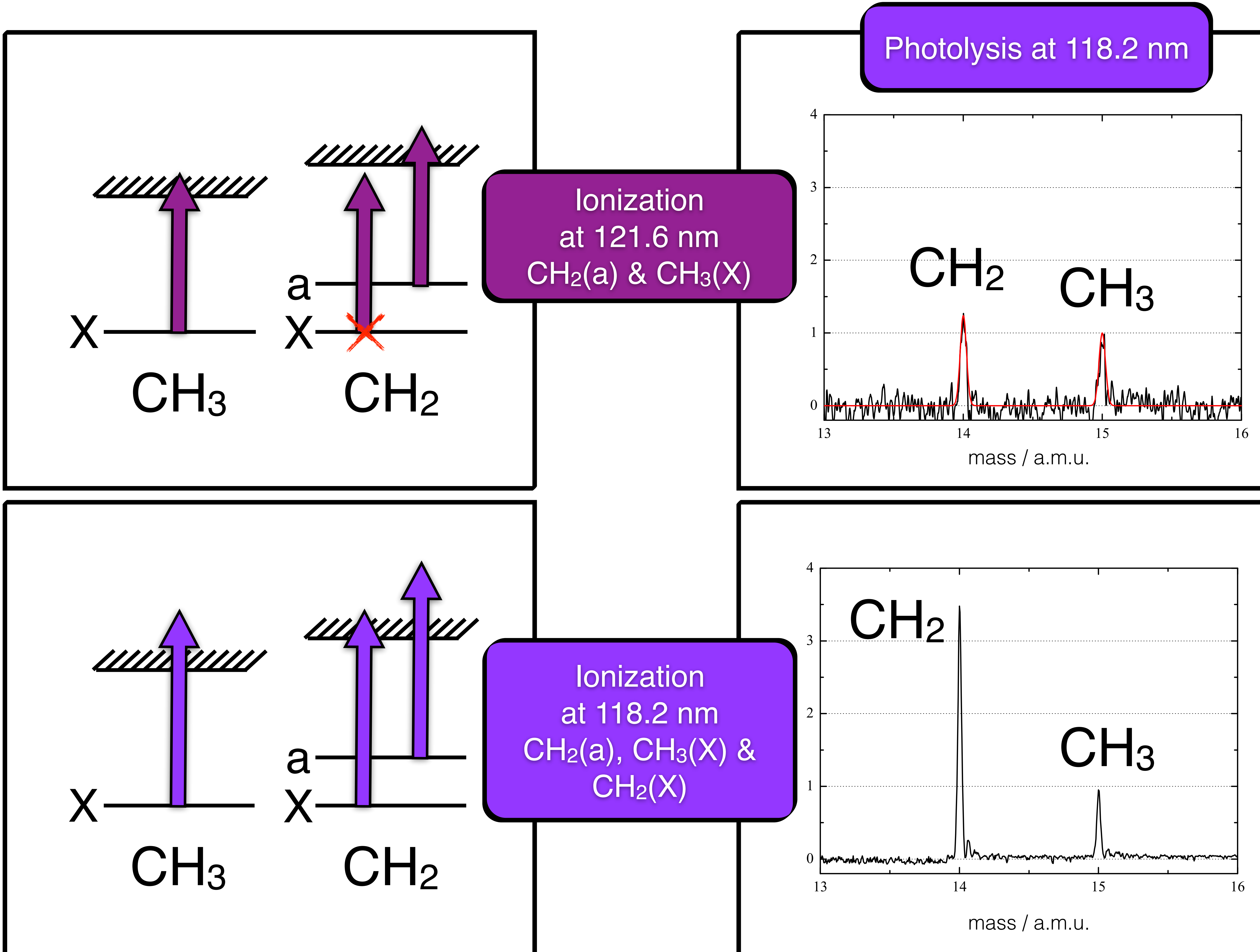
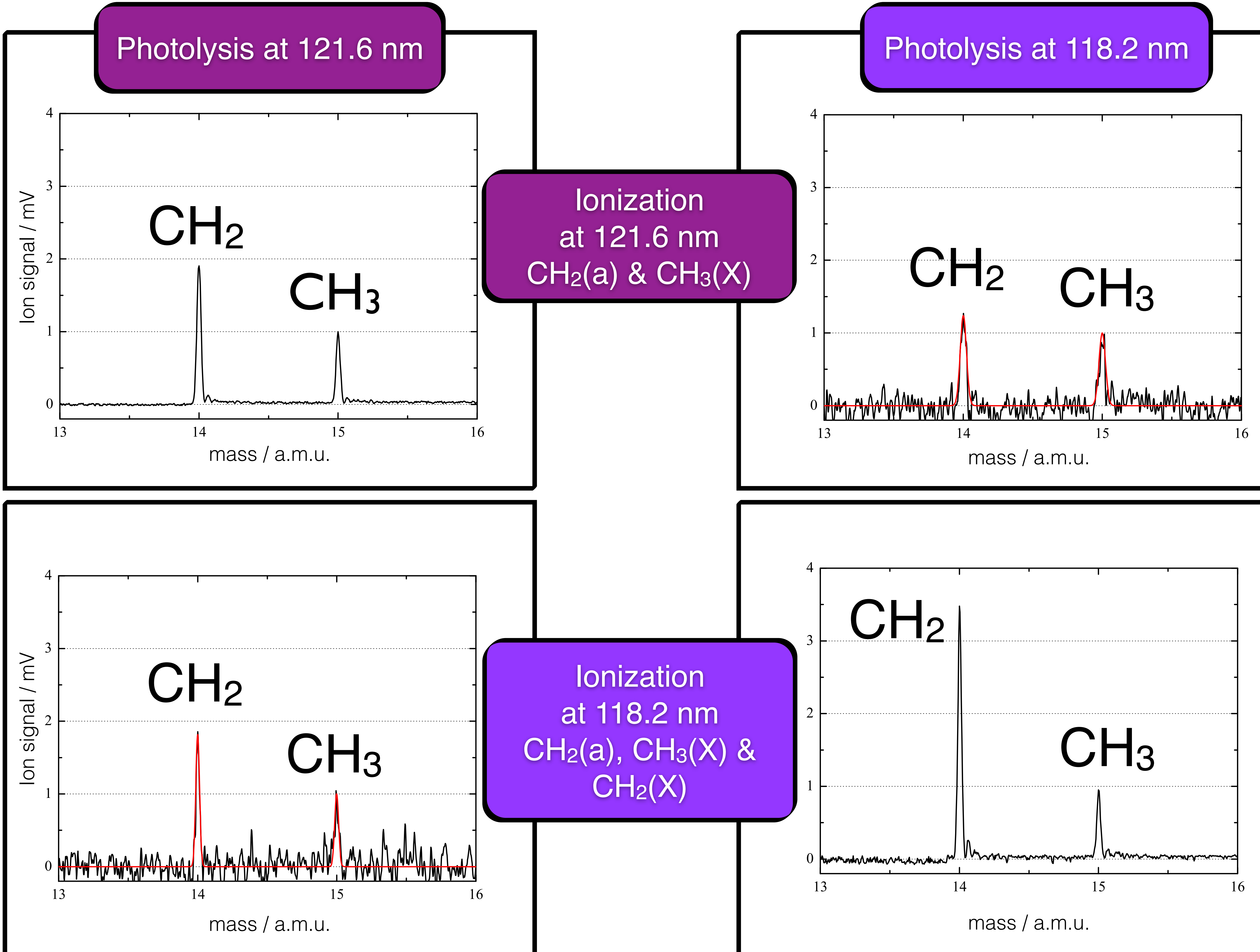

Photolysis at 121.6 nm
Ion signal / mV
mass / a.m.u.
CH2
CH3
Ionization
at 121.6 nm
CH2(a) & CH3(X)
X
a
CH3
CH2
Ionization
at 118.2 nm
CH2(a), CH3(X) &
CH2(X)

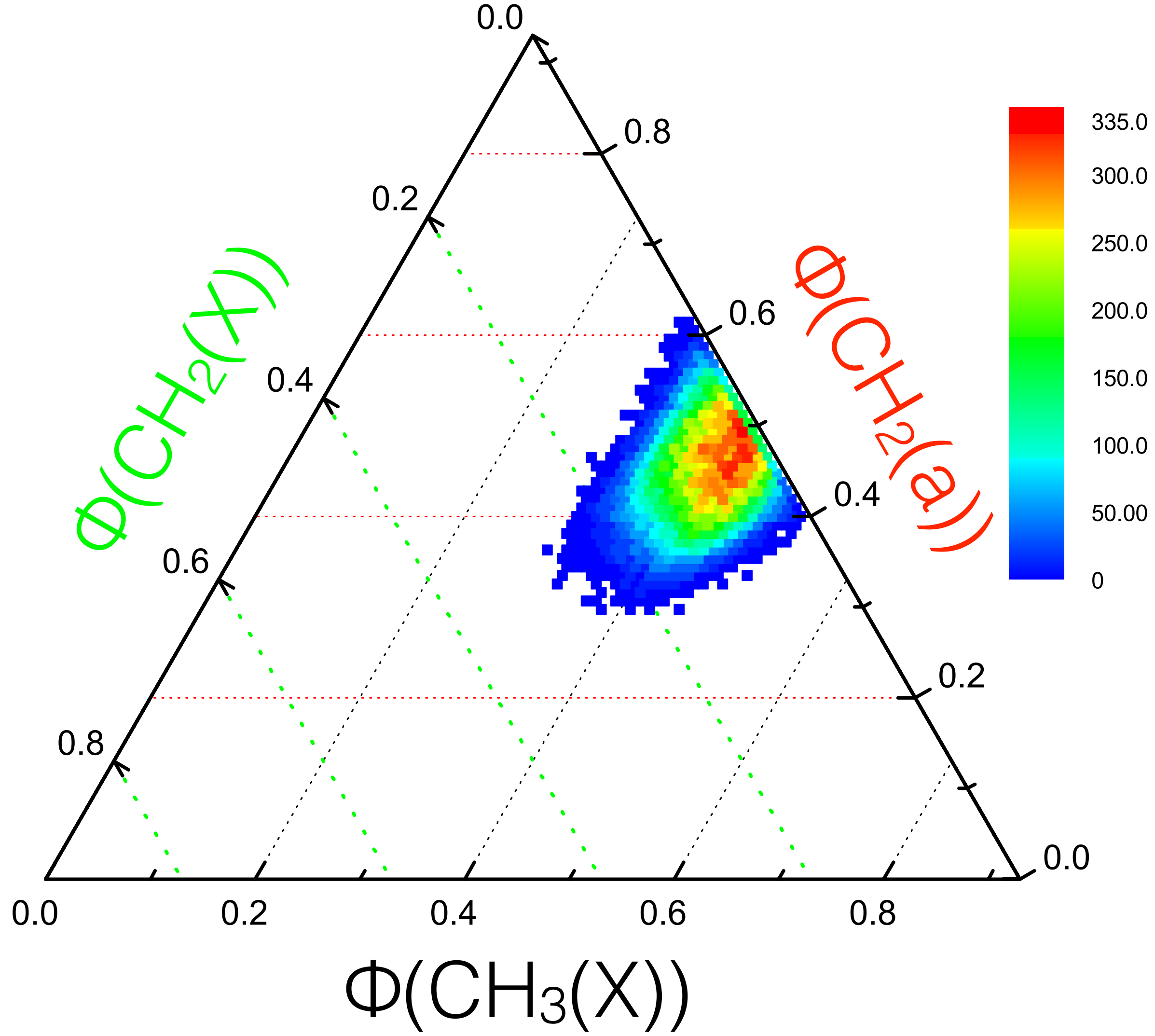


Photolysis at 118.2 nm
Ionization at 121.6 nm CH2(a) & CH3(X)
Ionization at 118.2 nm CH2(a), CH3(X) & CH2(X)
a
X
CH3
CH2
CH2
CH3
mass / a.m.u.
0 1 2 3 4
13 14 15 16

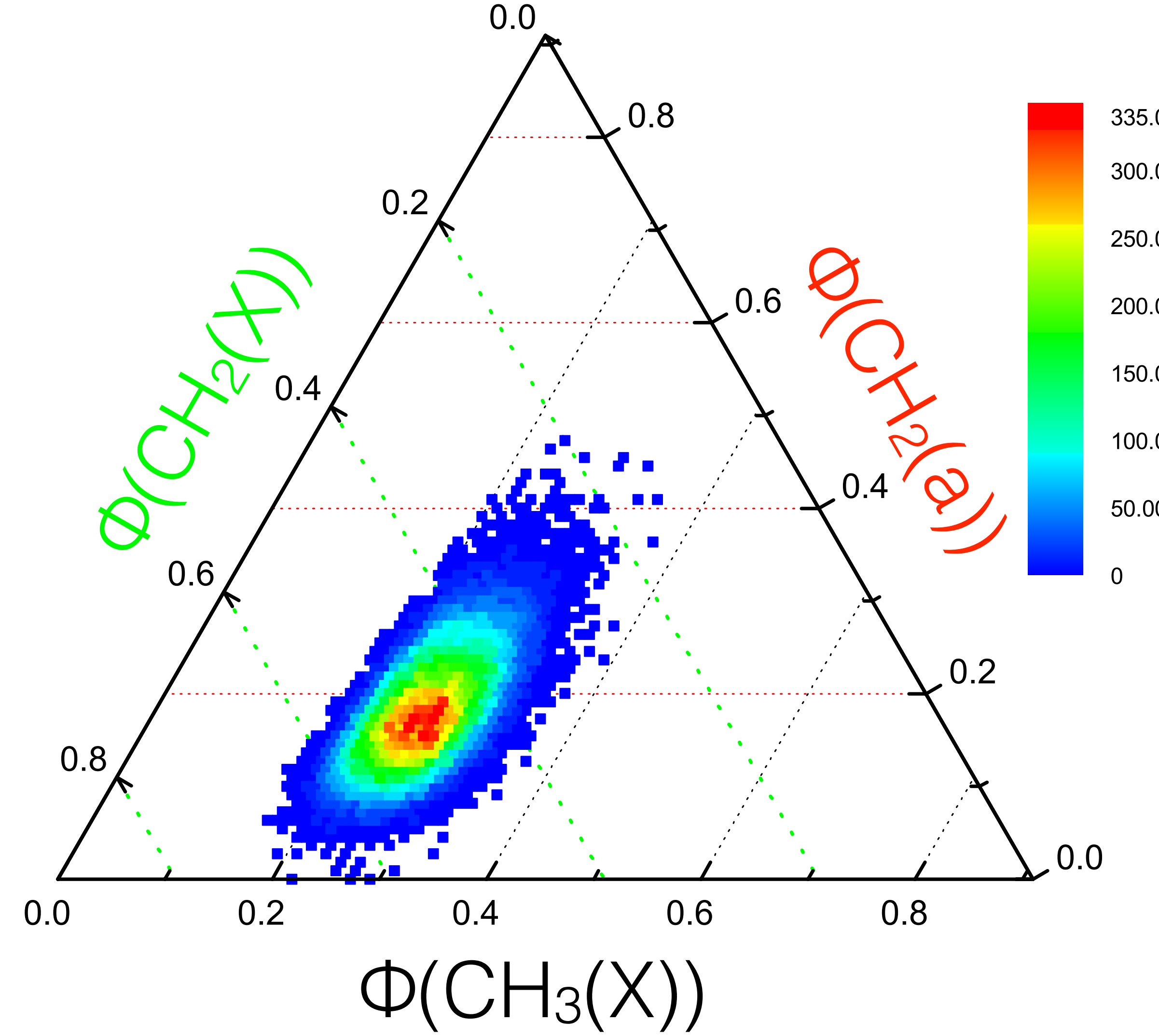

Photolysis at 121.6 nm
Photolysis at 118.2 nm
Ionization
at 121.6 nm
CH2(a) & CH3(X)
Ionization
at 118.2 nm
CH2(a), CH3(X) &
CH2(X)
CH2
CH3
Ion signal / mV
mass / a.m.u.
0
1
2
3
4
13
14
15
16

Results: branching ratios

Photolysis at 121.6 nm



Photolysis at 118.2 nm



$\Phi(CH)=0.07$

$\Phi(CH)=0.09$

■ $CH_3(X)$ ■ $CH_2(X)$ ■ $CH_2(a)$

Comparison with previous studies

Dissociative channel	Mordaunt et al. S1 & S2 1993		Heck et al. (1995)	Brownsword et al. (1997)	Wang et al. (2000)	Park et al. (2008)	This work
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$CH_2(b)+H_2$	/	/	/	/	/	/	≈0
$CH_2(X)+2H$	0.05	≈0	≈0	0.01	/	/	0.03
$CH_2(a)+2H$	0.2	≈0	≈0		0.055	/	≈0
$CH(X)+H+H_2$	0	0.51	0.11	0.08	0.07	0.059	0.07
$C(^1D)+2H_2$	0	0	0	0	0	0.0004	≈0
$\Phi(H)$	1	1	0.77	0.47	0.47	0.31	0.55
$\Phi(H_2)$	0.24	0.51	0.33	0.6	0.654	0.69	0.55

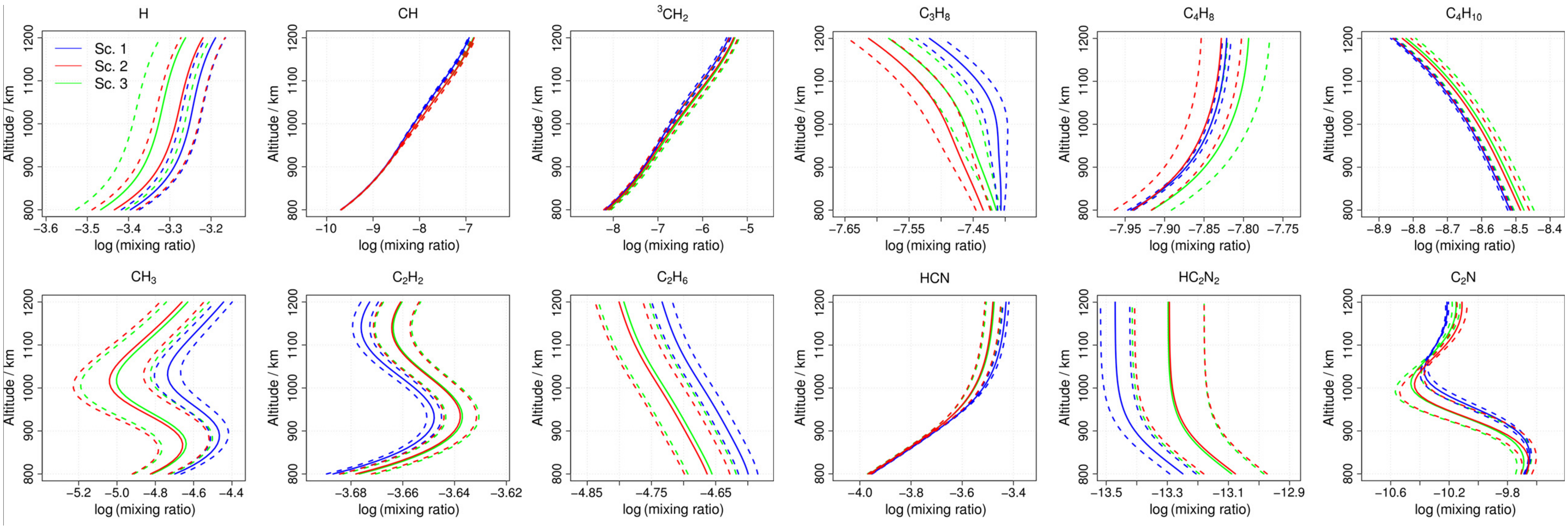
Conclusions

- Pump-probe experiment with 2 VUV beams to study methane photolysis (121.6 nm & 118.2 nm)
- New set of branching ratios at 121.6 nm and first set of BR at 118.2 nm.

    ➡Strong wavelength-dependence of the BR.

- Ready to be implemented in KIDA database !!
- New theoretical studies should be stimulated by these experimental results!

Test with a photochemical model of Titan



B. Gans, Z. Peng, N. Carrasco, D. Gauyacq, S. Lebonnois, P. Pernot, *Icarus* **223** (2013) 330–343

⇒ wavelength dependence of branching ratios should be taken into account.

Actors of the methane photolysis quest

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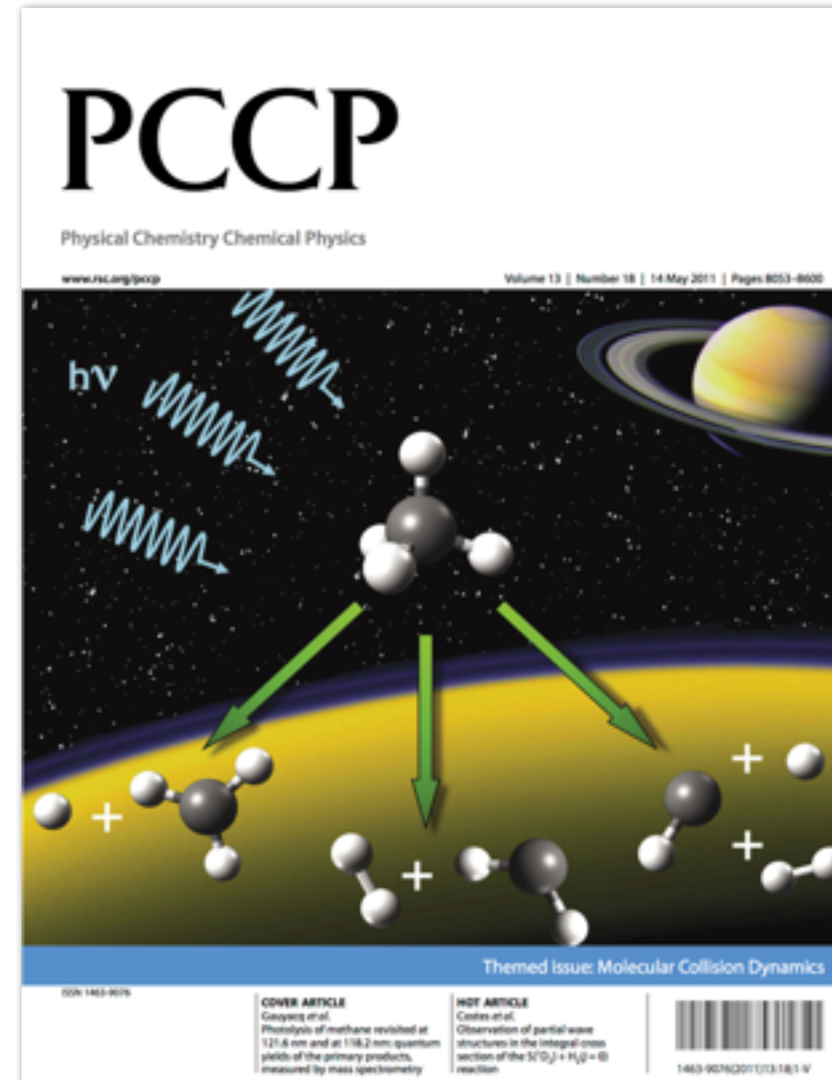

Phys. Chem. Chem. Phys., 2011, **13**, 8140–8152

Perspectives

- Implementation of CH_4 photolysis BR in KIDA database

- Expertise in BR measurements and radical cross sections to be used to study other astrophysically-relevant species:

  - UV and VUV photolysis of NH_3

  - UV and VUV photolysis of cyanopolyynes (HC_3N,…)

  - …

Thank you for your attention!