
Tarantula Nebula
NIRCam, JWST

Institut de Chimie Physique

université PARIS-SACLAY

Differential reactivity of the HCO^+/HOC^+ isomers

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Detections of HCO^+ and HOC^+

Interstellar medium:
Photon-Dominated Regions, Dark Clouds

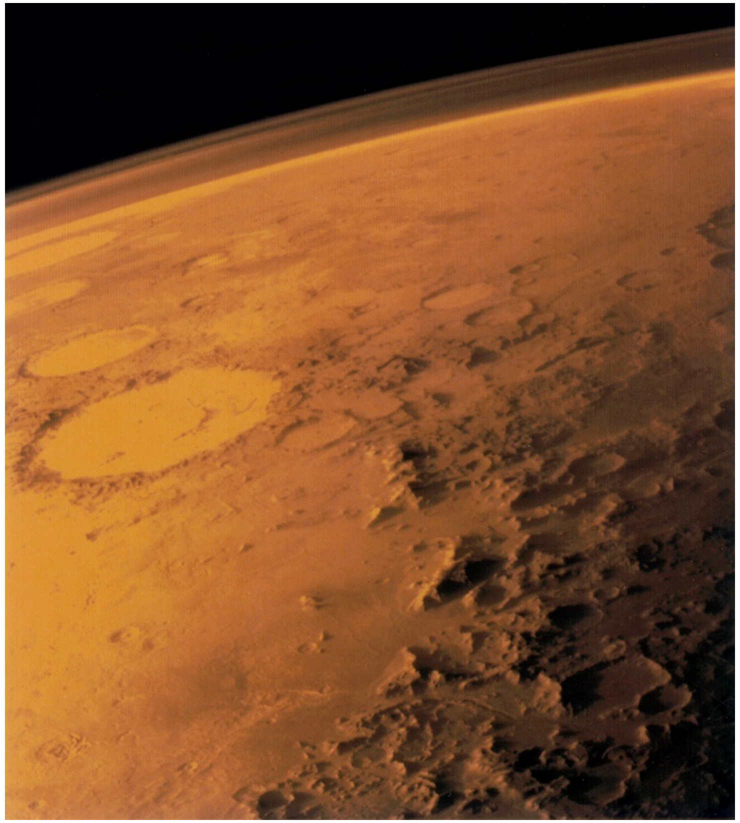
Orion Bar, NIRCam, JWST

L. M. Ziurys, A. J. Apponi, 1995, *ApJ*
H. Liszt et al., 2004, *A&A*

$$CO + {H_3}^+ \rightarrow [CHO]^+ + H_2$$

Abundance HCO^+: 10^{-9}-10^{-10}
$[HCO^+]/[HOC^+] \approx 50$-$120$

Ionospheric medium:
Mars atmosphere

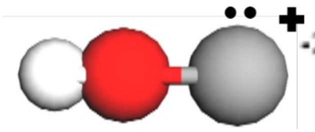


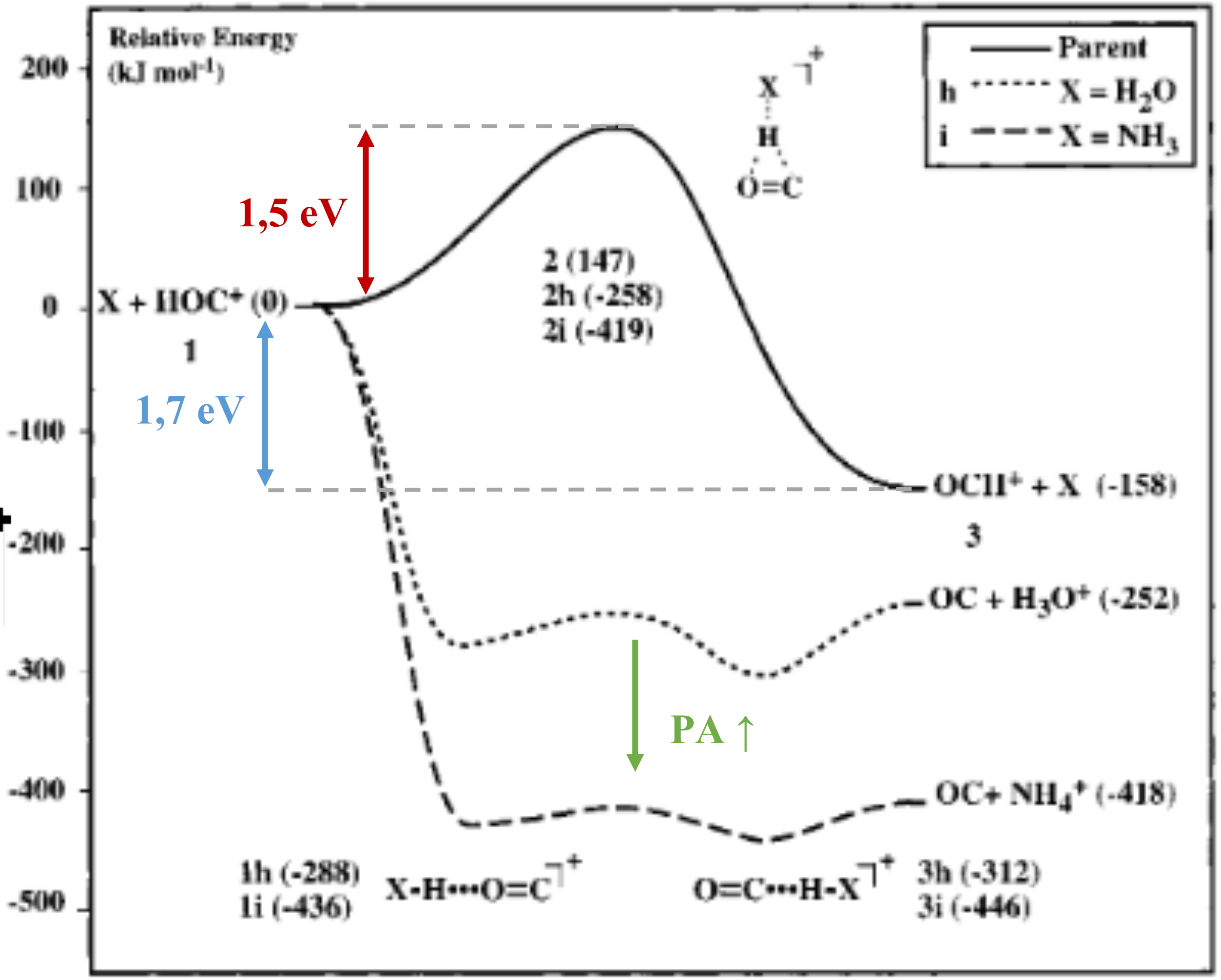
Mars atmosphere, Viking probe

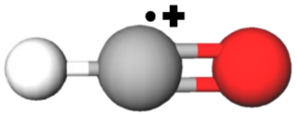
J. Fox, 2015, *Icarus*
M. Matta et al., 2013, *J. Geophys. Res. Space Phys.*

Isomerism between HCO^+ and HOC^+

PA(X) < PA(CO*) < PA(X) < PA(*CO) < PA(X)



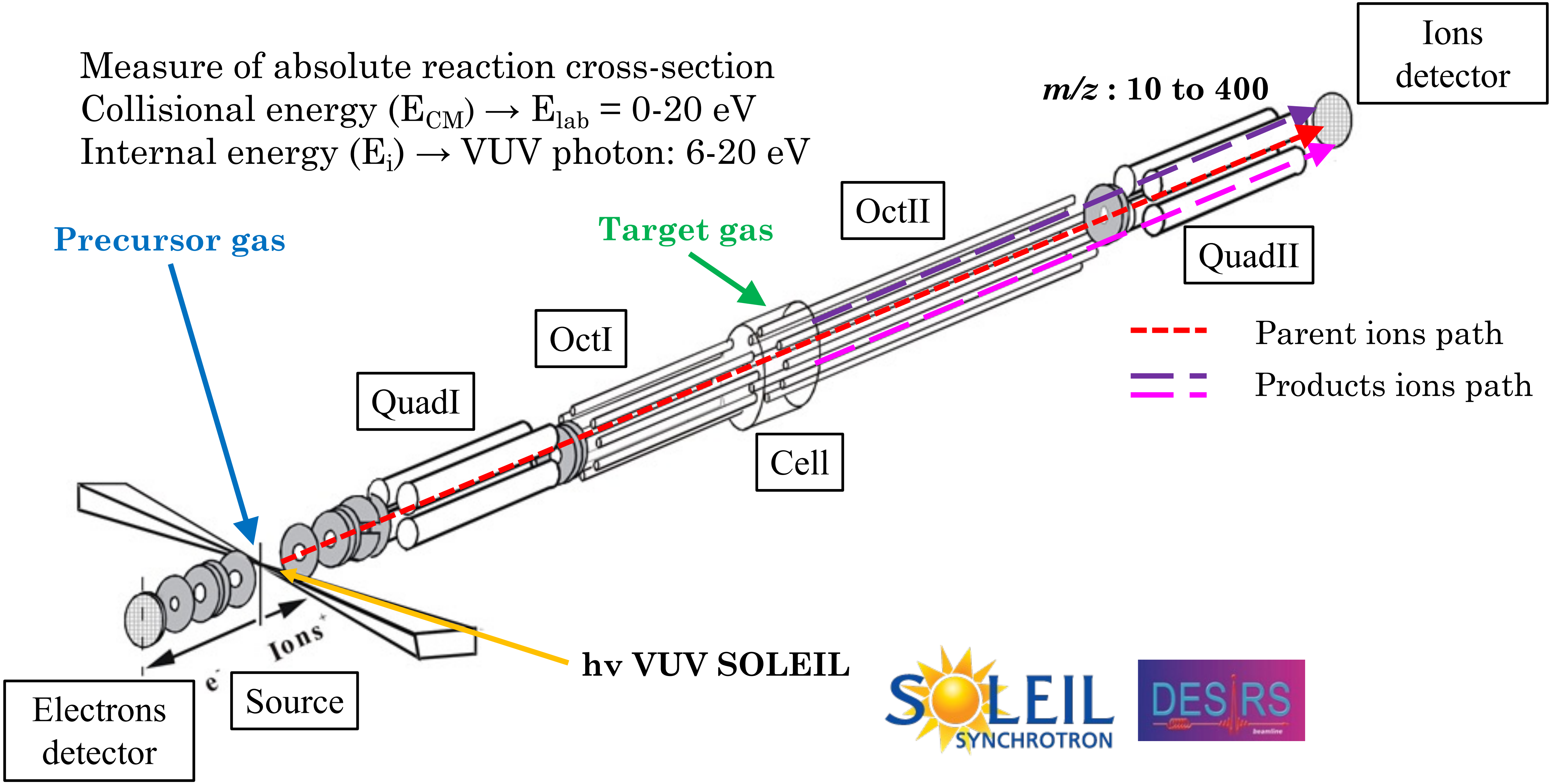




A. Chalk, L. Radom, 1997, *J. Am. Chem. Soc.*

Research instrument: CERISES

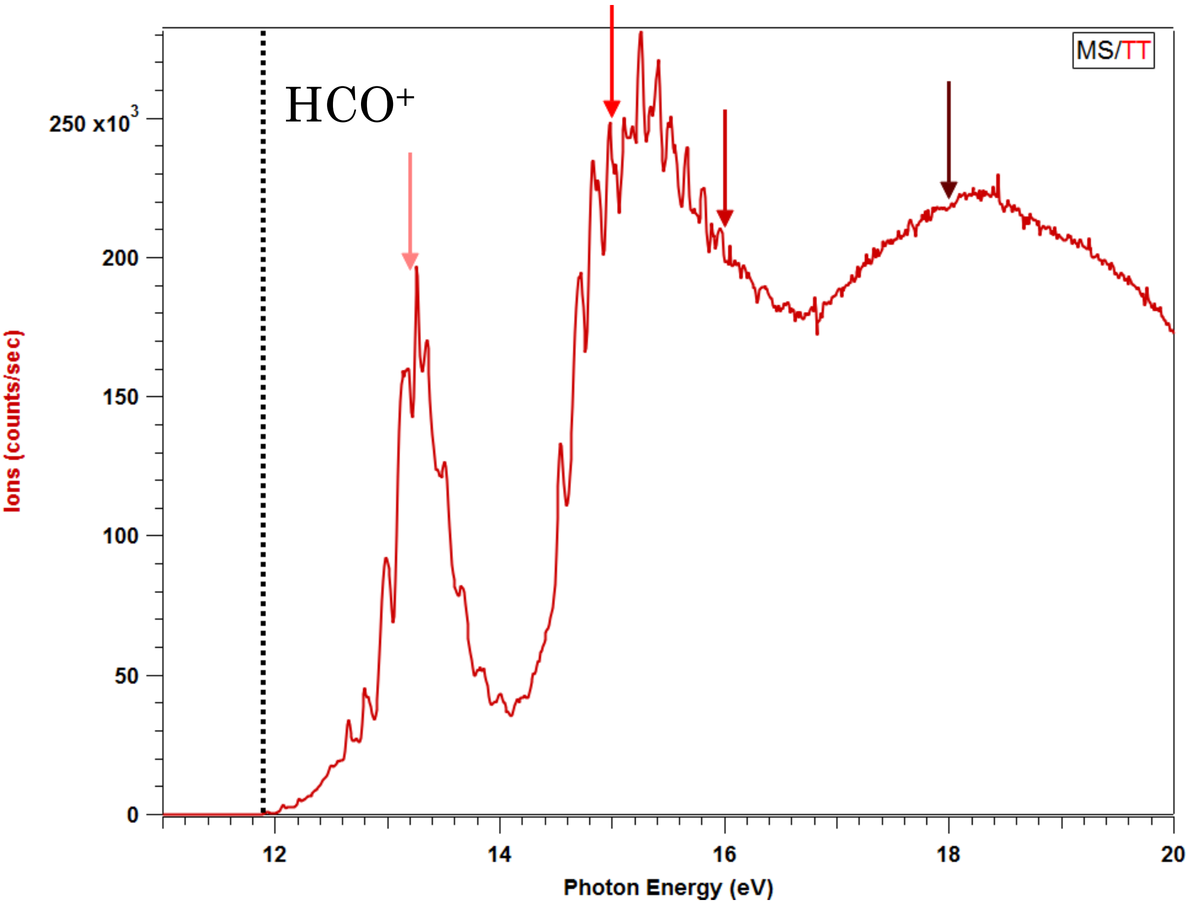
Measure of absolute reaction cross-section
Collisional energy (E_{CM}) → E_{lab} = 0-20 eV
Internal energy (E_i) → VUV photon: 6-20 eV



$[CHO]^+$ formation

Parent ions formation
Precursor H_2CO

$$E_{int}(CHO^+) = h\nu + AE + E_k(e^-) - E_k(CHO^+) - E_k(H) - E_{int}(H)$$



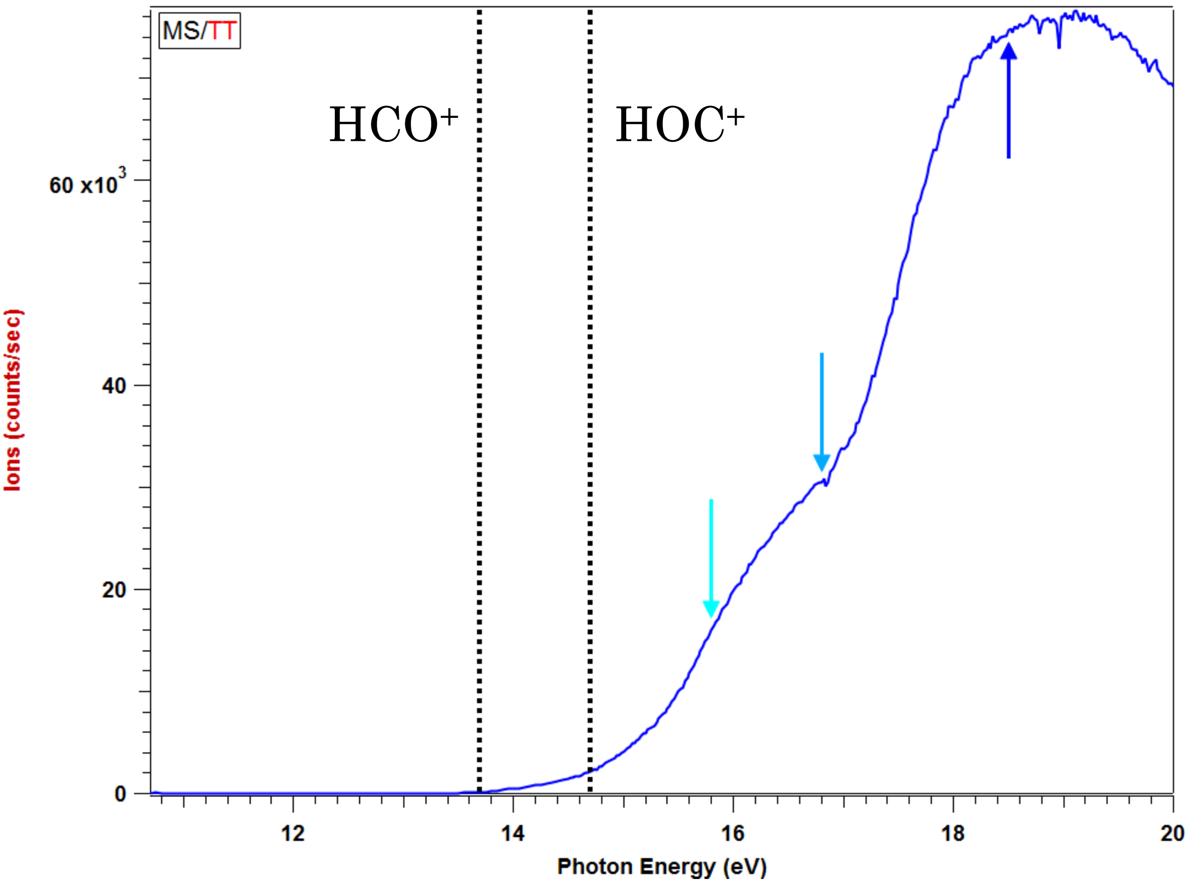
$$H_2CO + h\nu \rightarrow HCO^+ + H + e^-$$

Appearance energy: **11,9 eV**

P.-M. Guyon et al., 1976, *J. Chem. Phys.*, 64, 1419

Parent ions formation
Precursor CD_3OH

$$E_{int}([CHO]^+) = h\nu + AE + E_k(e^-) - E_k([CHO]^+) - E_k(D_2) - E_{int}(D_2) - E_k(D) - E_{int}(D)$$



$$CD_3OH + h\nu \rightarrow [CHO]^+ + D_2 + D + e^-$$

Appearance energy:
HCO^+: 13,7 eV
HOC^+: 14,8 eV (thermodynamic)

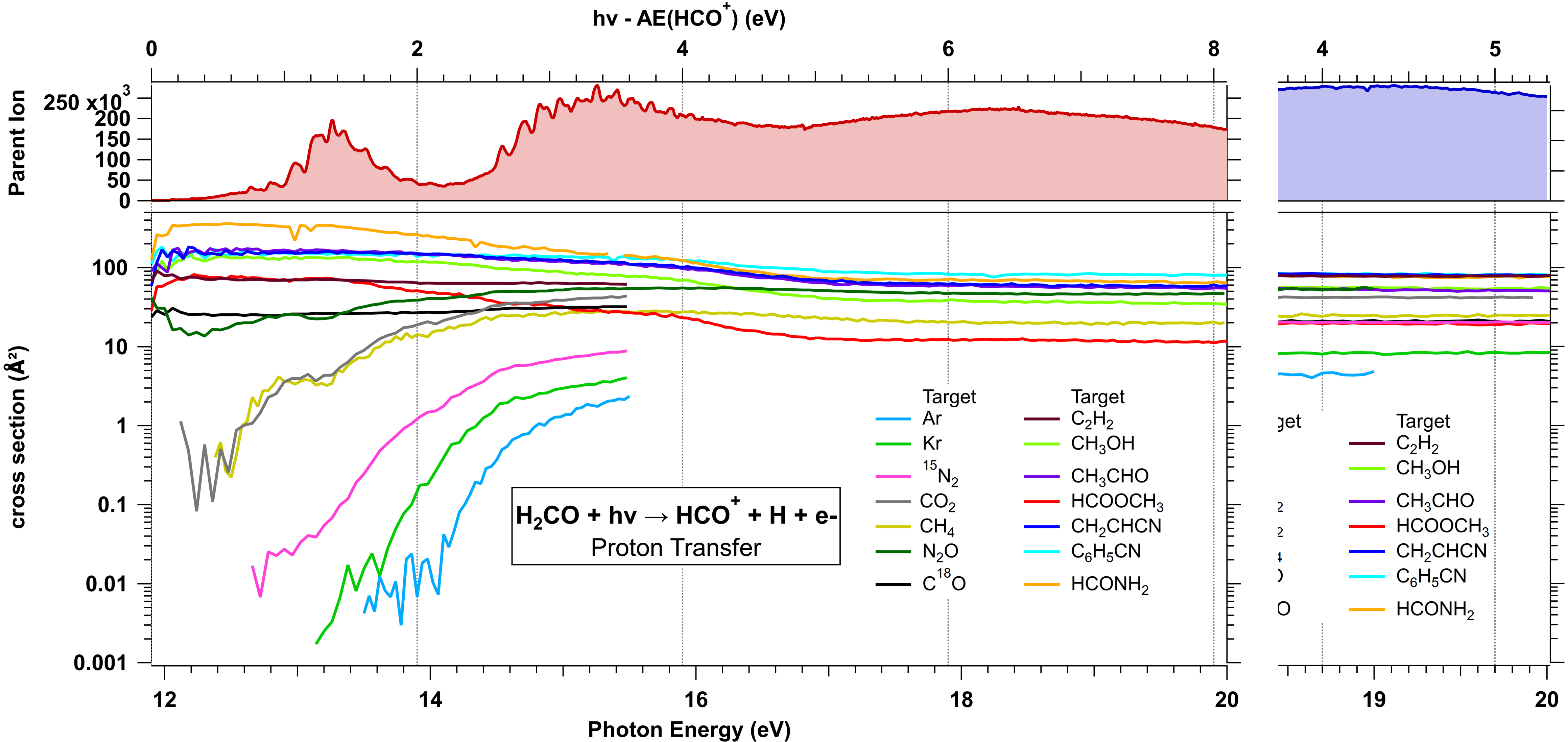
J. Berkowitz et al., 1978, *J. Chem. Phys.*, 69, 3044

Reactivity and characterization

Proton Transfer:

$$[CHO]^{+} + A \rightarrow CO + \boldsymbol{AH}^{+}$$

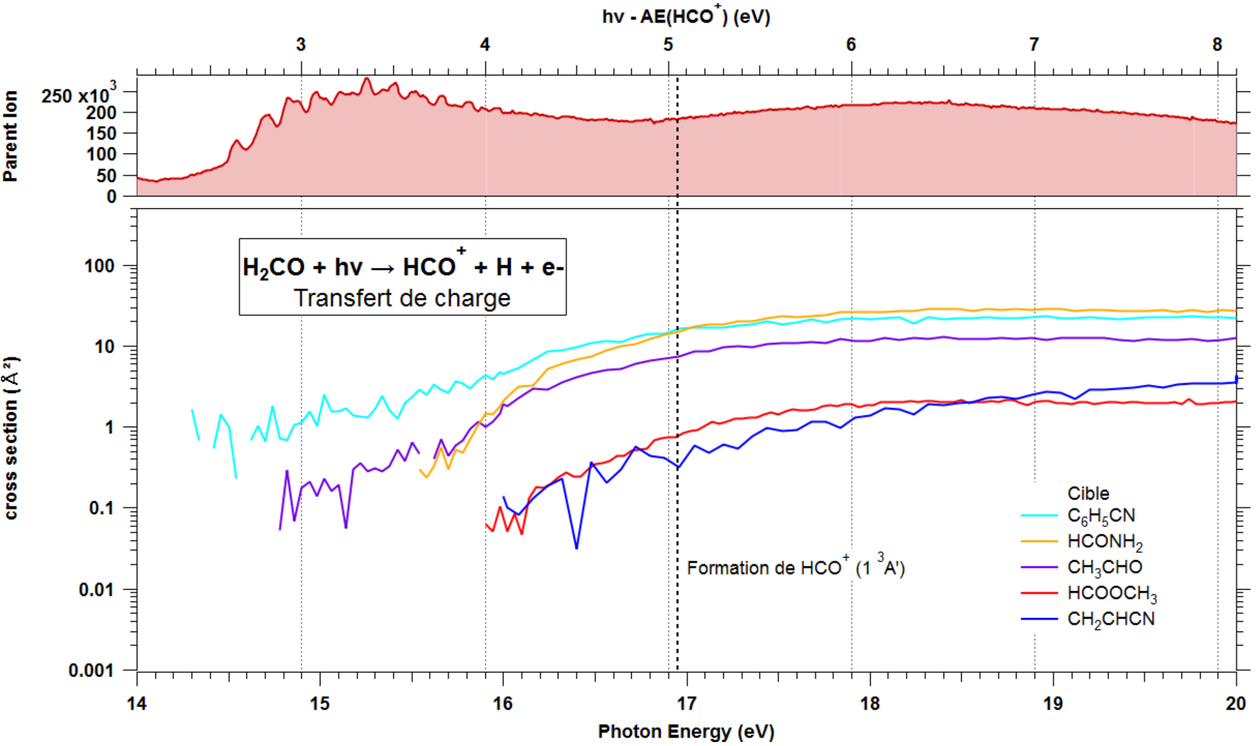
- **Main path**

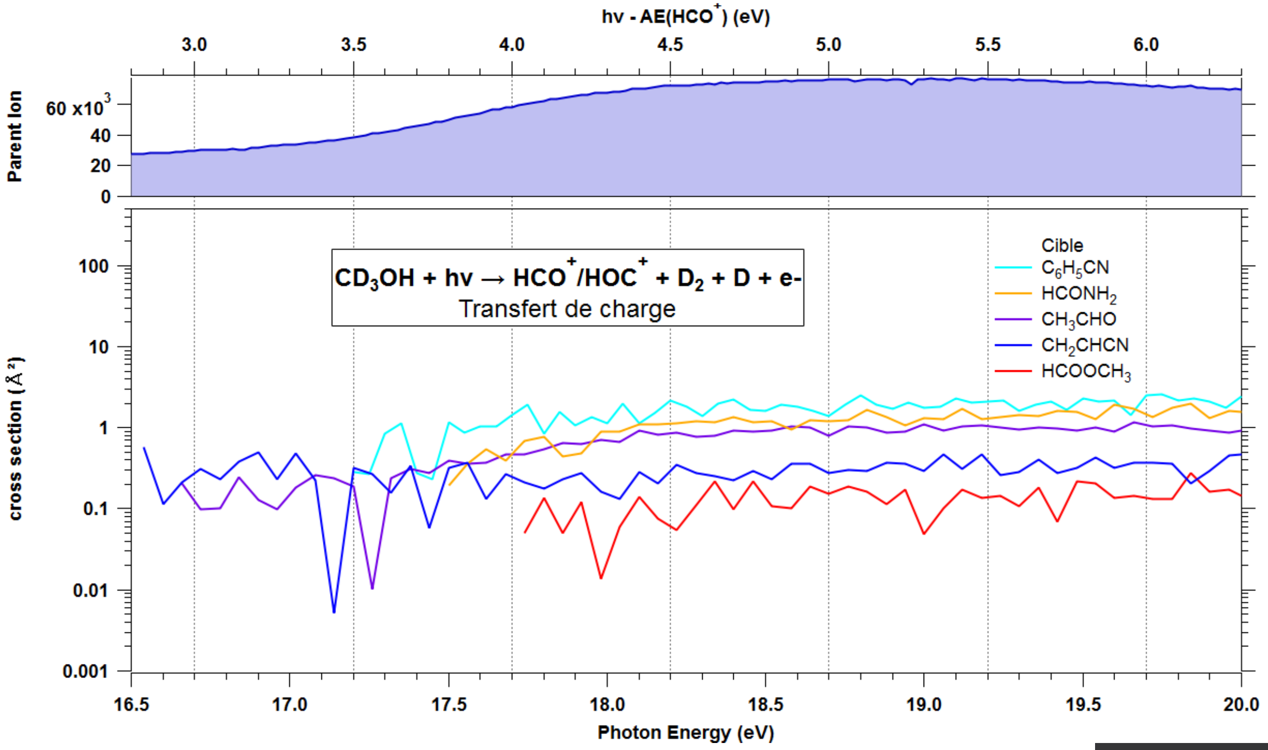


Charge Transfer:

$$[CHO]^{+} + A \rightarrow [CHO] + \boldsymbol{A}^{+}$$

- Little effect of collision energy → **Long distance** interaction
- E_i and E_{CM} thresholds shifted → **Inefficiency of energy**
- Only **HCO^+** reacts : $m/z = 29$ (**CD_3OH**) : **90% of HOC^+**

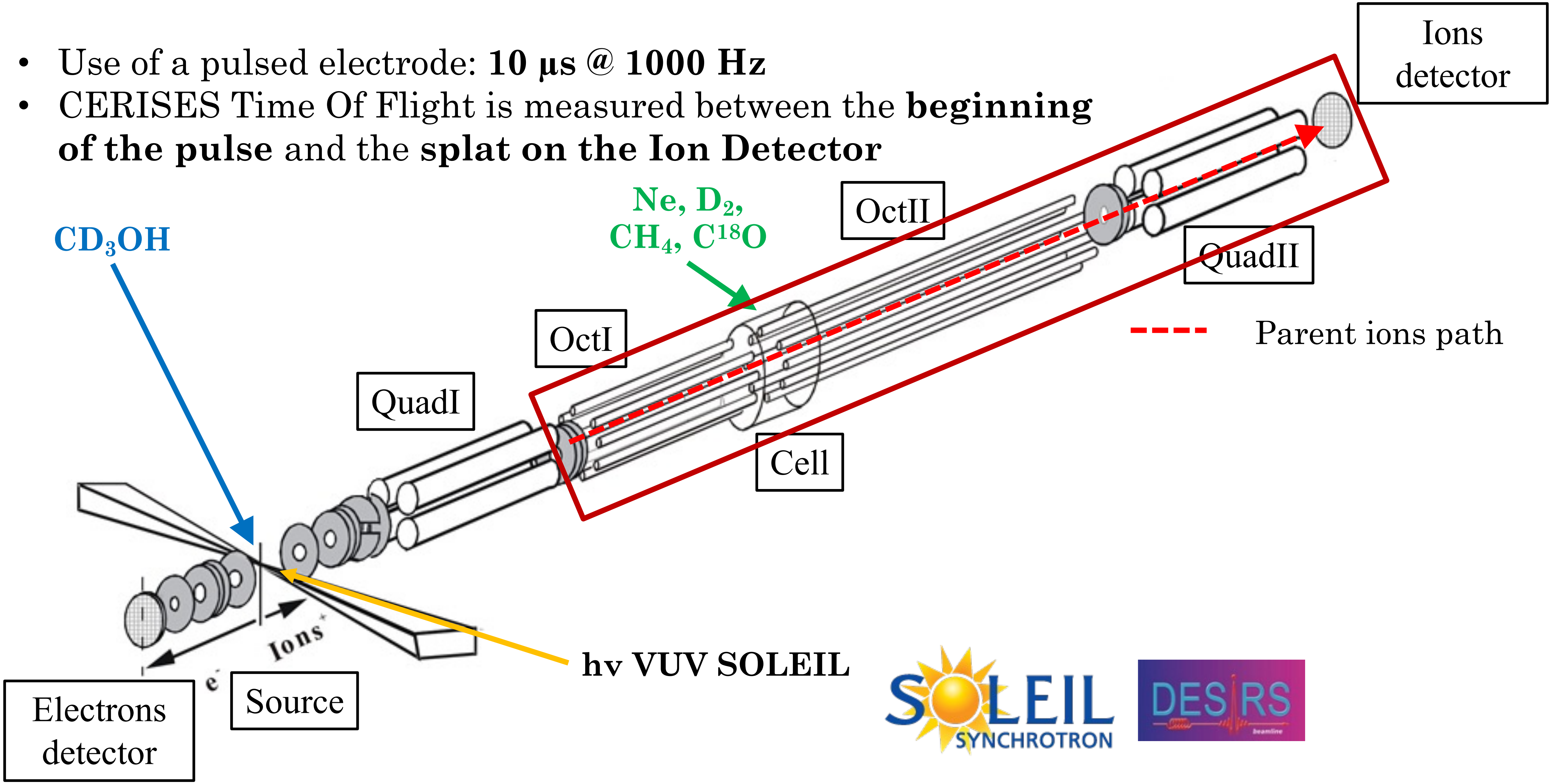




Catalytic isomerization of HOC^+

Time Of Flight setup on CERISES

- Use of a pulsed electrode: **10 µs @ 1000 Hz**
- CERISES Time Of Flight is measured between the **beginning of the pulse** and the **splat on the Ion Detector**



Isomerism between HCO^+ and HOC^+

PA(X) < PA(CO*) < PA(*CO)

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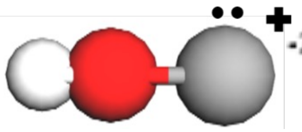
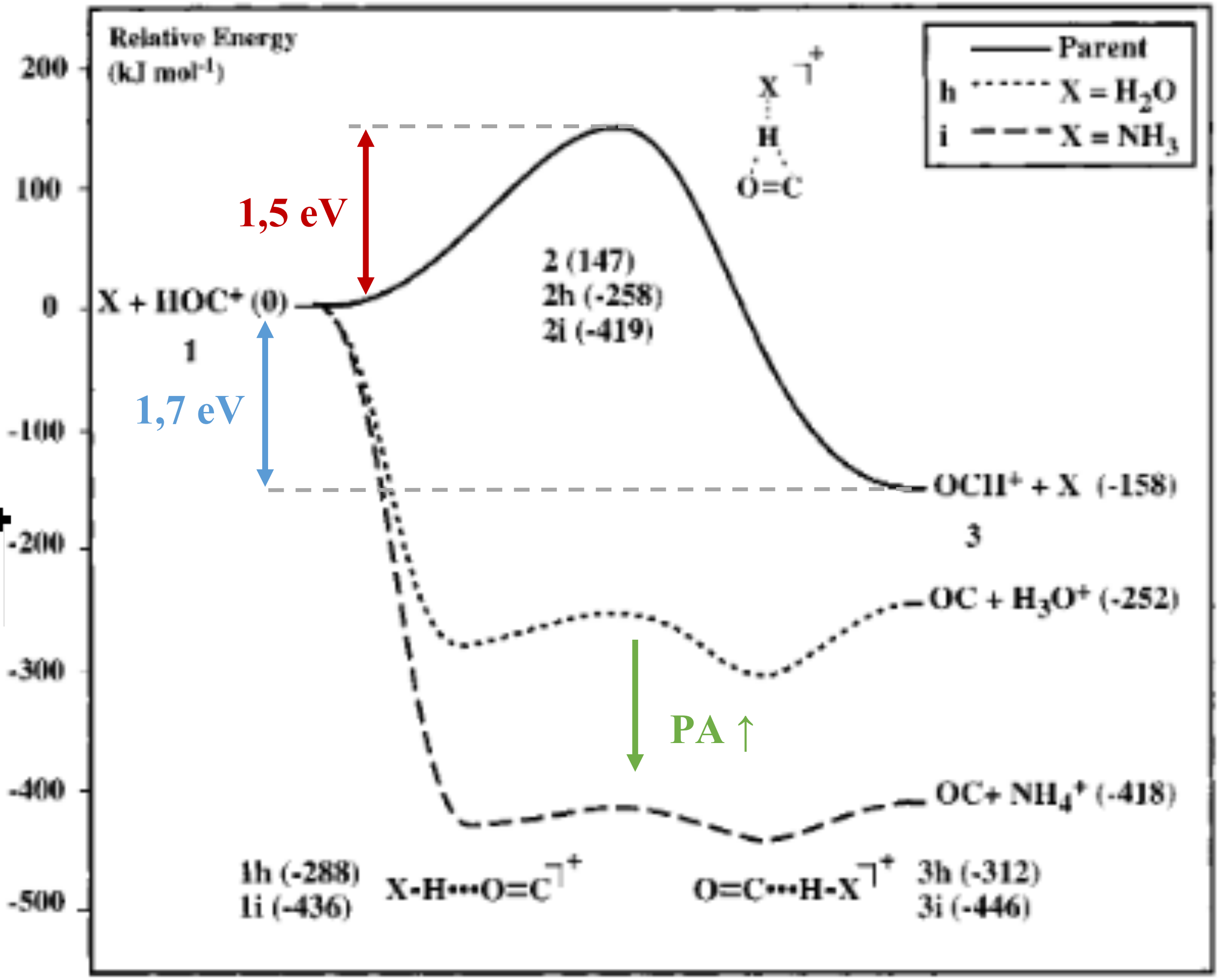
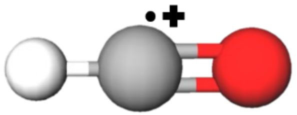




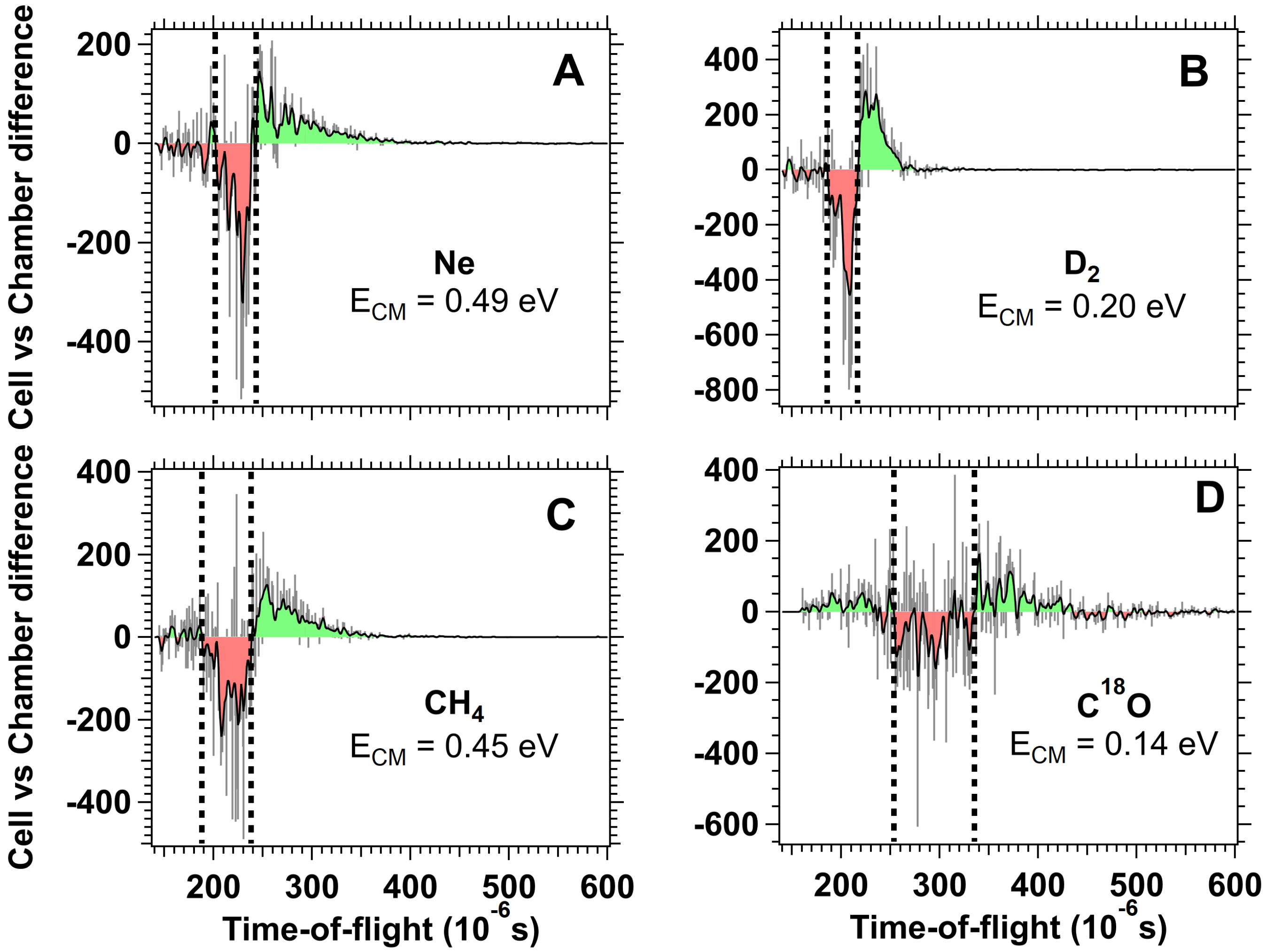


A. Chalk, L. Radom, 1997, *J. Am. Chem. Soc.*

Experimental TOF Differences

Barrier = 131 kJ.mol^{-1}

Barrier = -2,9 kJ.mol^{-1}



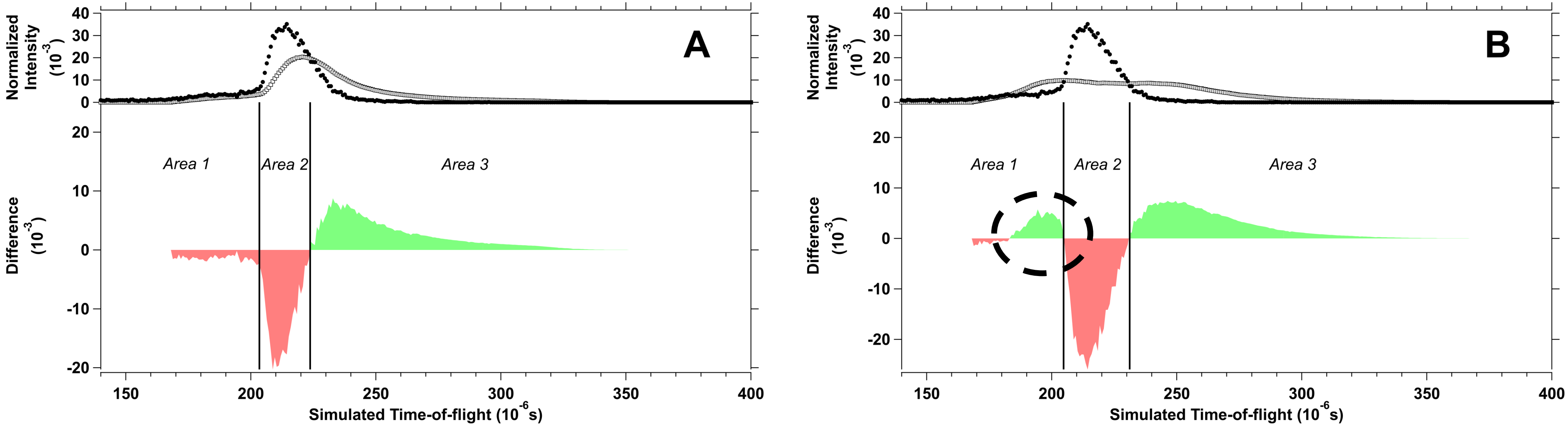
Barrier = -106 kJ.mol^{-1}

Barrier = -163 / -10 kJ.mol^{-1}

$$Diff = Cell\left(\frac{\int peak_{Chamber}}{\int peak_{Cell}}\right) - Chamber$$

TOF simulation differences

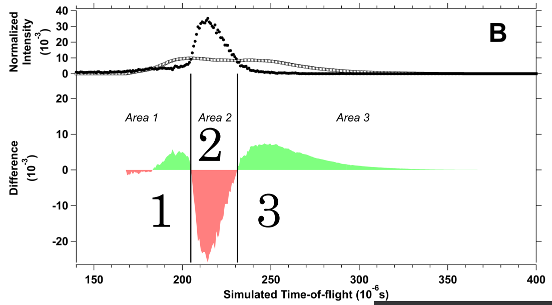
- **SIMION®** simulation with **homemade script**
- A **signature appears** on the differences with isomerization

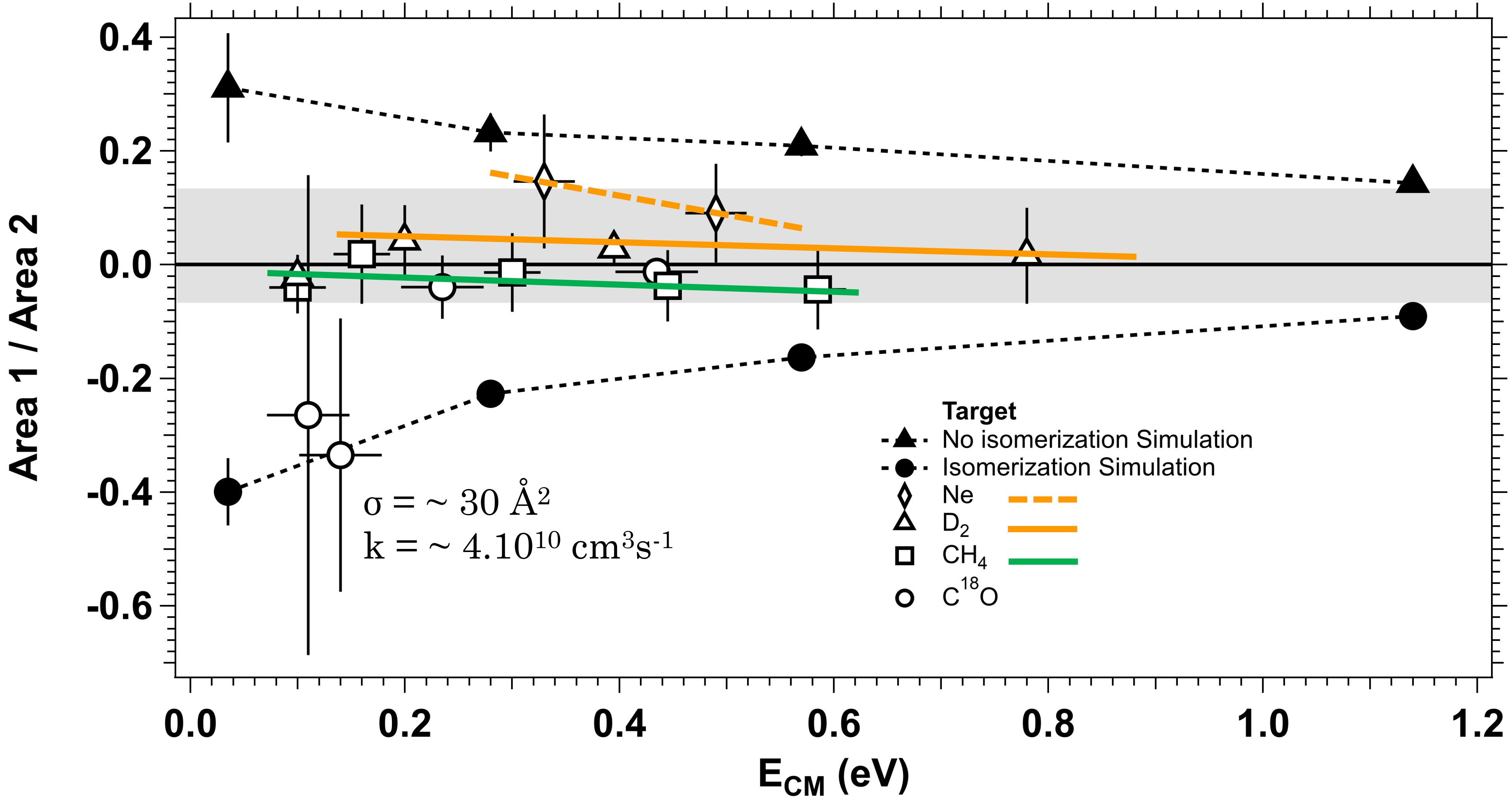


Simulation without isomerization

Simulation with isomerization

Area 1 / Area 2 ratio



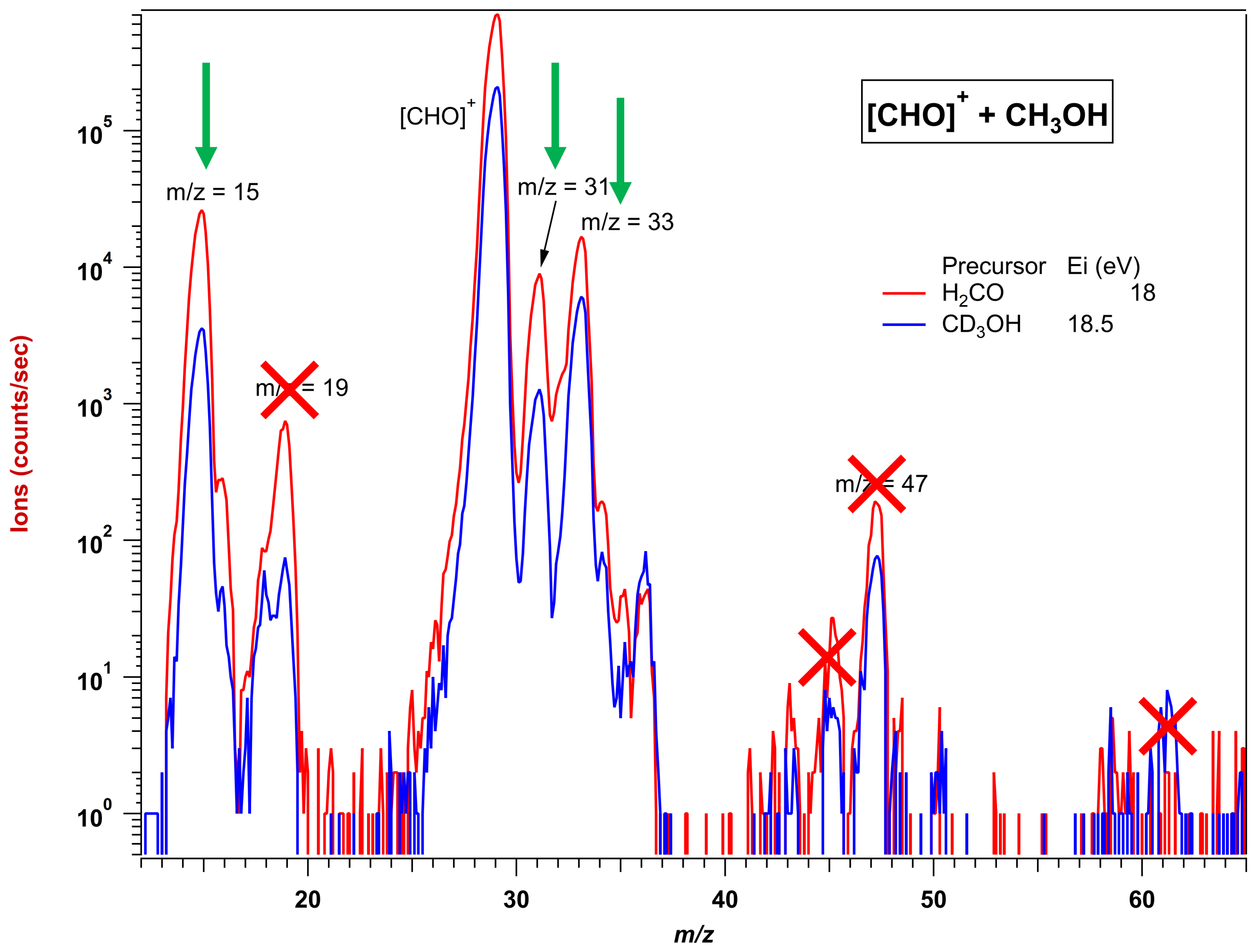


Freeman, C.G. et al., 1987, *Int. J. Mass Spectrom.*
Smith, M.A. et al., 2002, *ApJ*

N. Solem *et al.*, 2024, *J. Mass Spectrom.*, DOI : 10.1002/jms.5066

Complex reactivity with methanol

Methanol, CH_3OH
Products studied



Three products studied

- $m/z = 33$: Proton Transfer

ΔrH°(HCO⁺) (eV)	ΔrH°(HOC⁺) (eV)
-1.684	-3.347

$$CH_3OH + [CHO]^+ \rightarrow \boldsymbol{CH_3OH.H^+} + CO$$

- $m/z = 15$: Dissociative Proton Transfer

ΔrH°(HCO⁺) (eV)	ΔrH°(HOC⁺) (eV)
1.210	-0.453

$$CH_3OH + [CHO]^+ \rightarrow \boldsymbol{CH_3^+} + CO + H_2O$$

- $m/z = 31$: Dissociative Proton Transfer with barrier

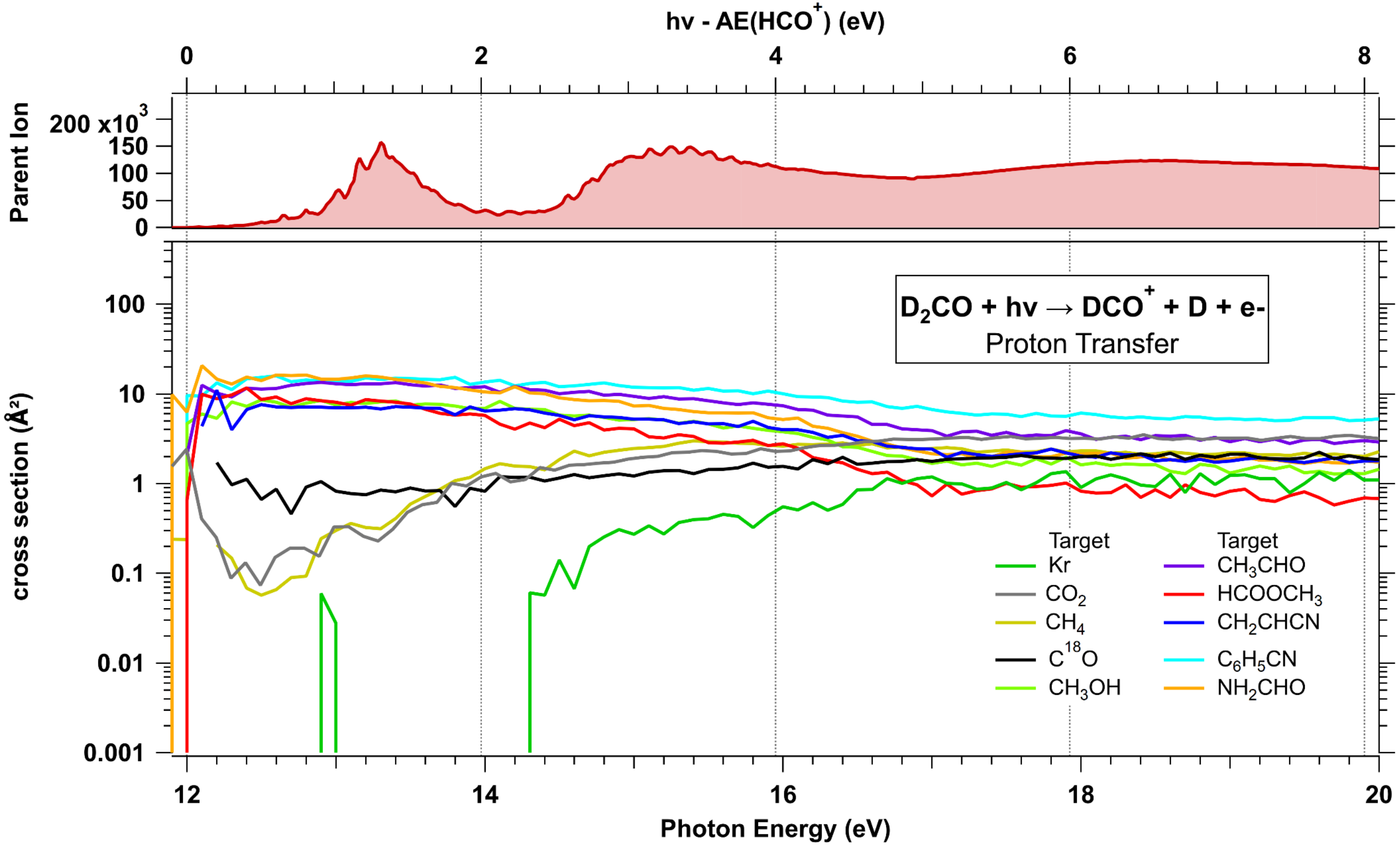
ΔrH°(HCO⁺) (eV)	ΔrH°(HOC⁺) (eV)
-0.280	-1.944

$$CH_3OH + [CHO]^+ \rightarrow \boldsymbol{CH_2OH^+} + CO + H_2$$

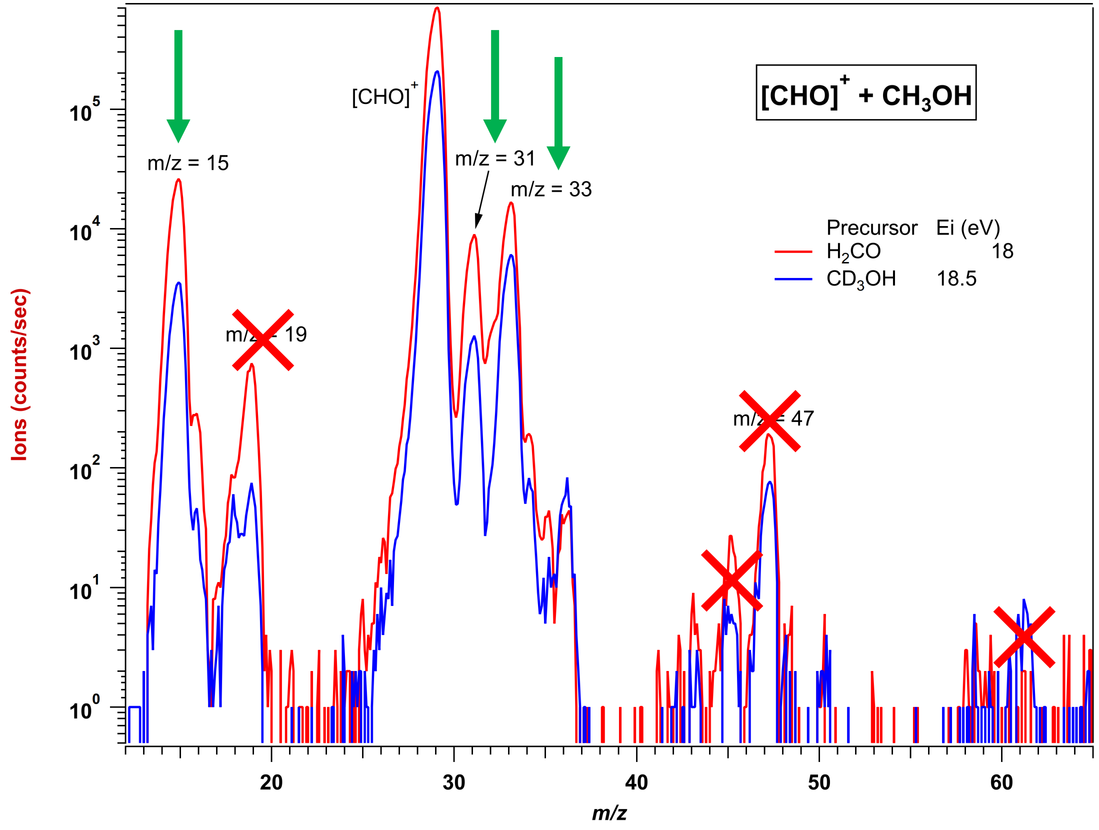
Isotopic effect

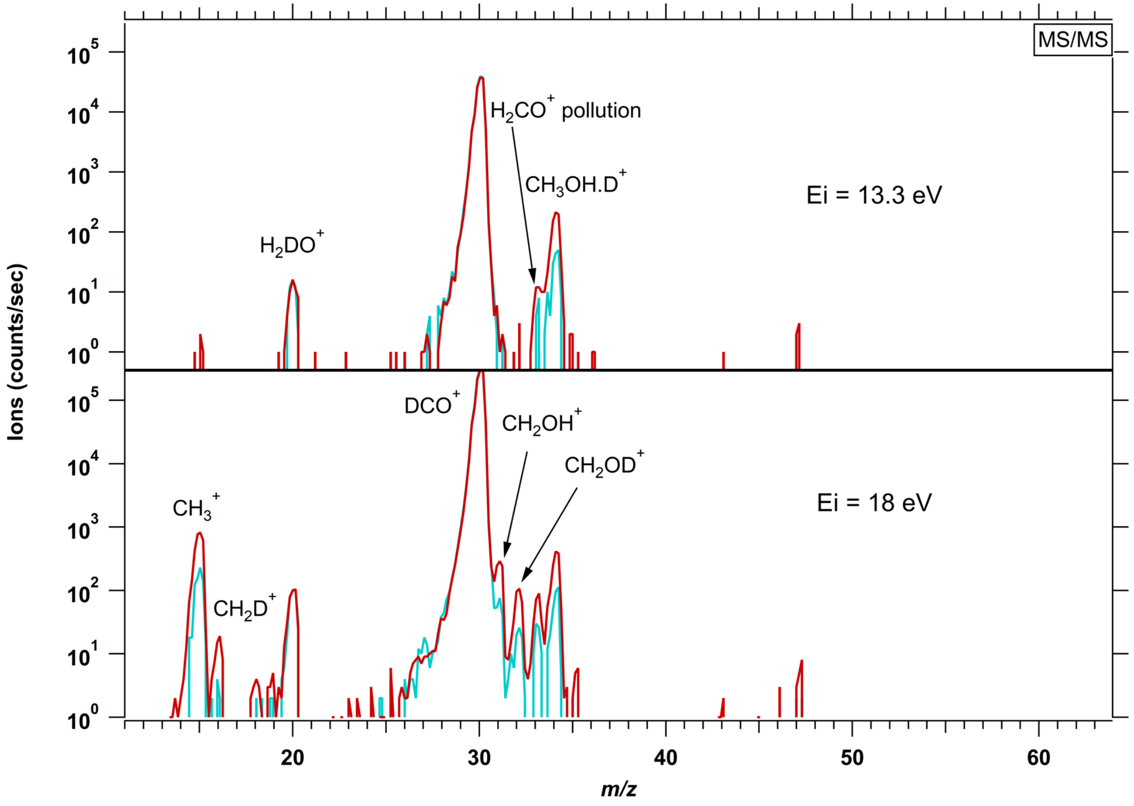
D+ Transfer

$$DCO^+ + A \rightarrow CO + \boldsymbol{AD}^+$$



Methanol, CH_3OH
Products studied





Conclusions

- Ions formed with maximum internal energy from two precursors:
  - **H_2CO/D_2CO** → pure HCO^+/DCO^+
  - **CD_3OH** → 90% of HOC^+

- Main reaction: Proton Transfer
  - 14 targets studied (photon and collisional energy effects)
  - Can be dissociative
  - No Deuterium effect

- Successful evidence of catalytic isomerization of HOC^+ with $C^{18}O$
  - N. Solem *et al.*, 2024, *J. Mass Spectrom.*, DOI : 10.1002/jms.5066

Thank you for your attention

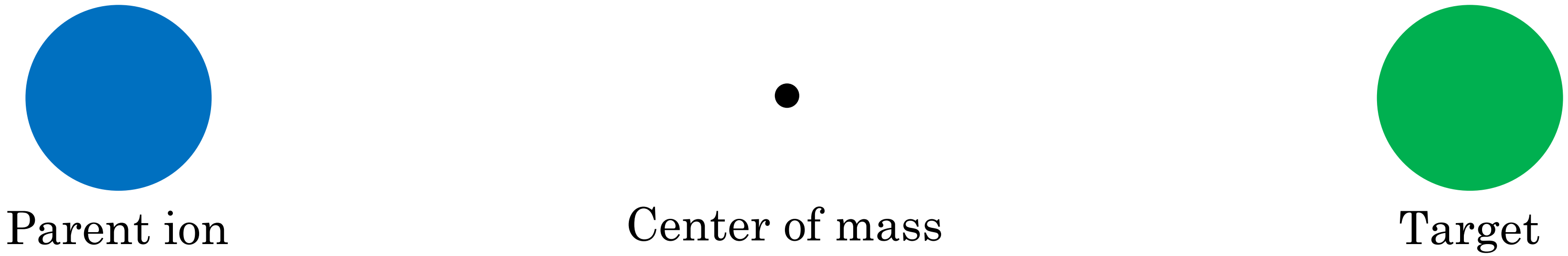
Sunset at Mars' Gusev Crater (Spirit, 2005)

NASA/JPL/Texas A&M/Cornell

Collisional energy

Laboratory frame of reference

$$E_{lab} = \frac{1}{2} m_{\text{parent}} v_{parent}^2$$



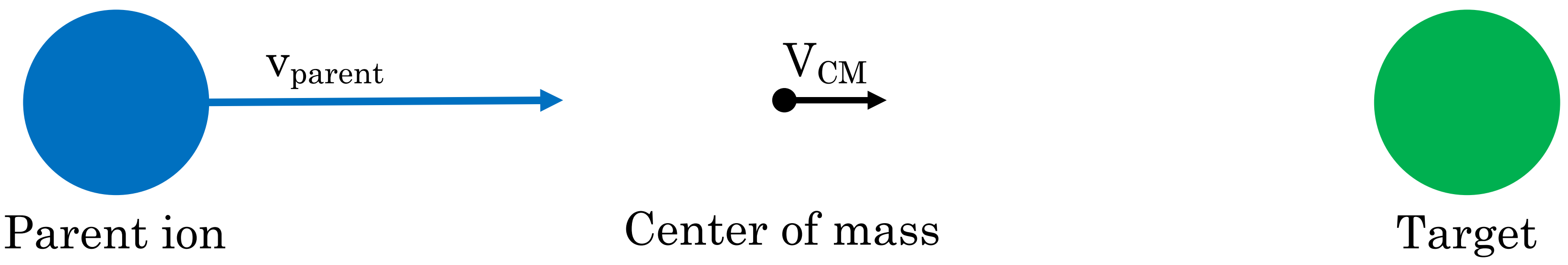
Center of mass frame of reference

$$E_{CM} = E_{lab} \frac{m_{target}}{m_{target} + m_{parent}}$$

Collisional energy

Laboratory frame of reference

$$E_{lab} = \frac{1}{2} m_{\mathrm{parent}} v_{parent}^2$$

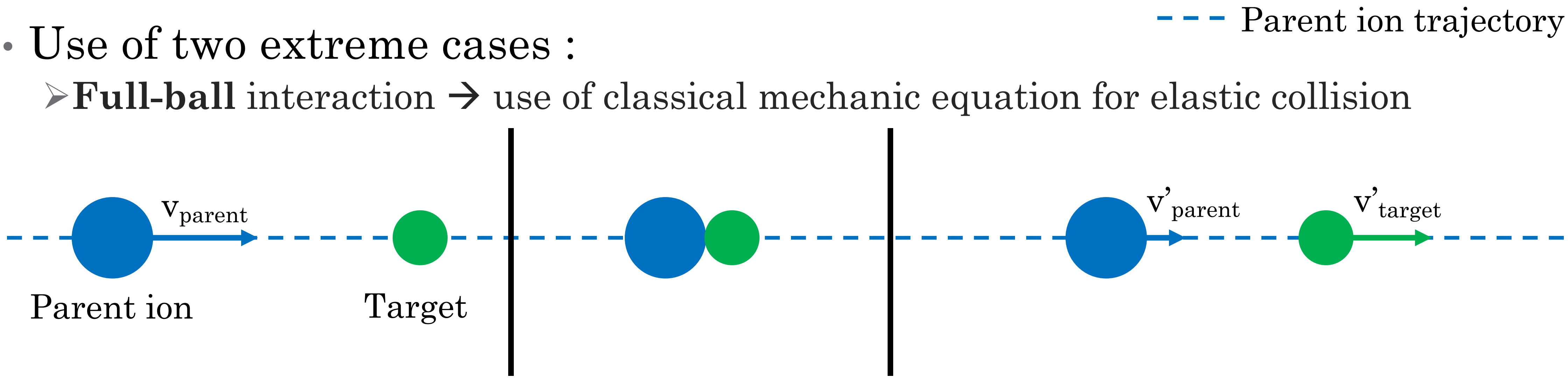


Center of mass frame of reference

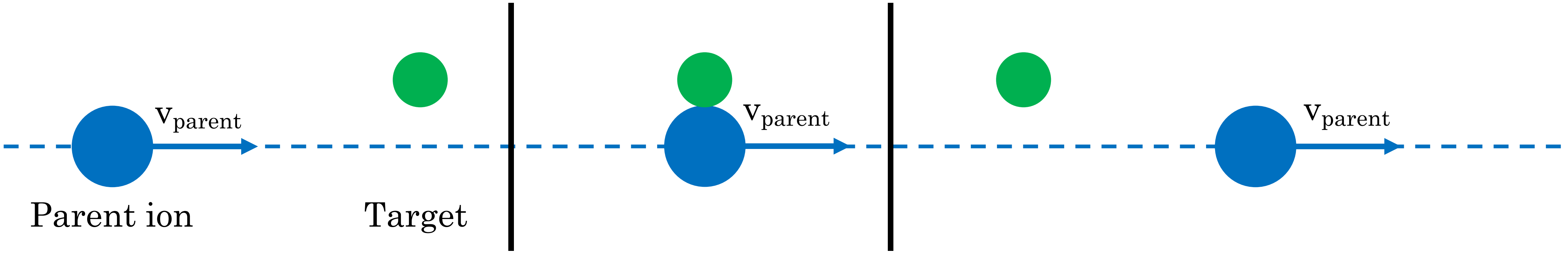
$$E_{CM} = E_{lab} \frac{m_{target}}{m_{target} + m_{parent}}$$

TOF simulation with ion-target interaction

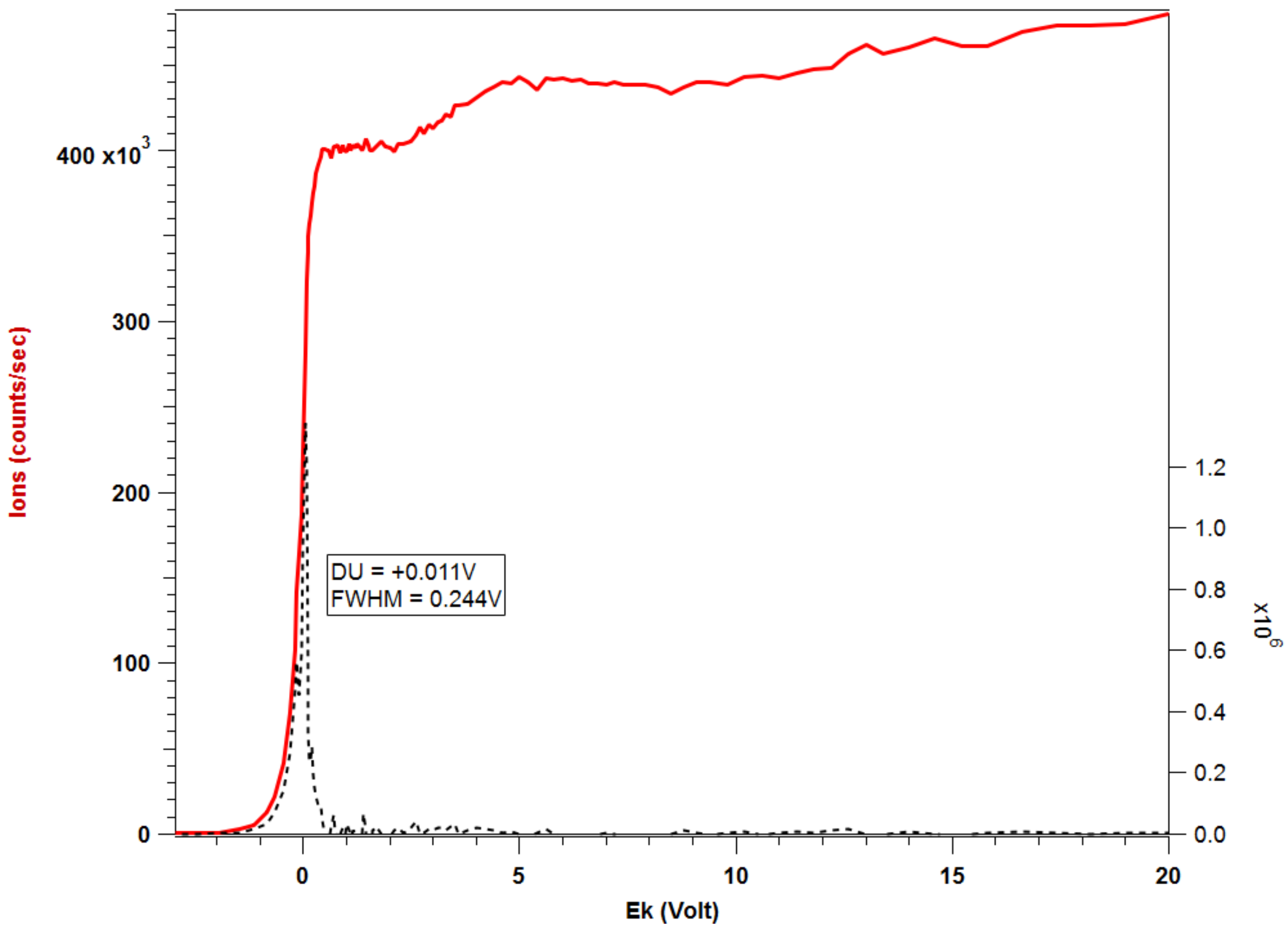
- Use of two extreme cases :
  - **Full-ball** interaction → use of classical mechanic equation for elastic collision



  - **Long distance** interaction → no repartition of the initial ion speed



Collisional energy spectrum



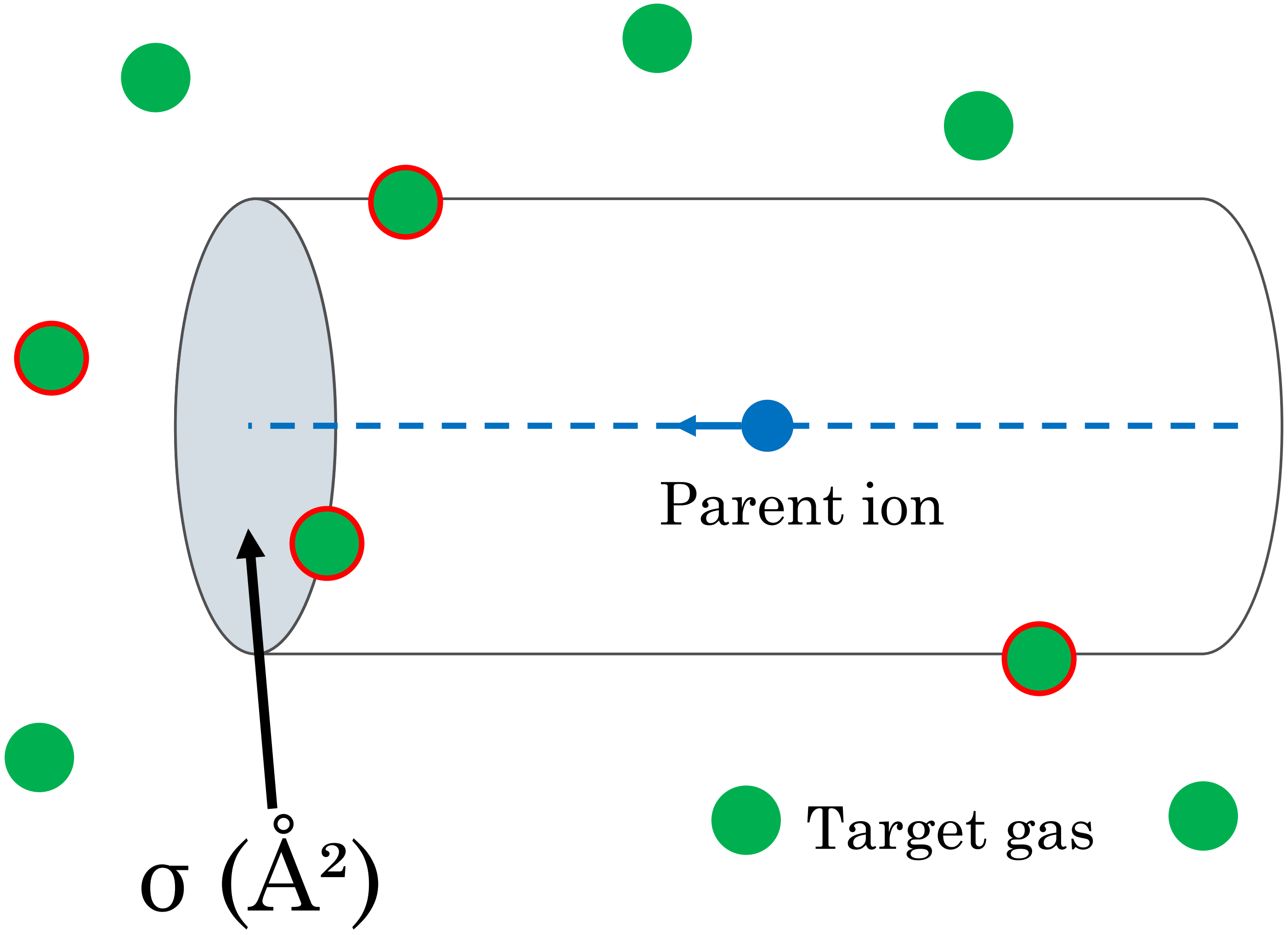
TOF simulation with ion-target interaction

- **Long-lived** complex approximation
  - Exothermicity goes in any direction

Absolute reaction cross-section σ

Related to the reaction probability

$$\sigma_{pro} \propto \frac{1}{P}\frac{N_{pro}}{N_{par}}$$



Head-on collision

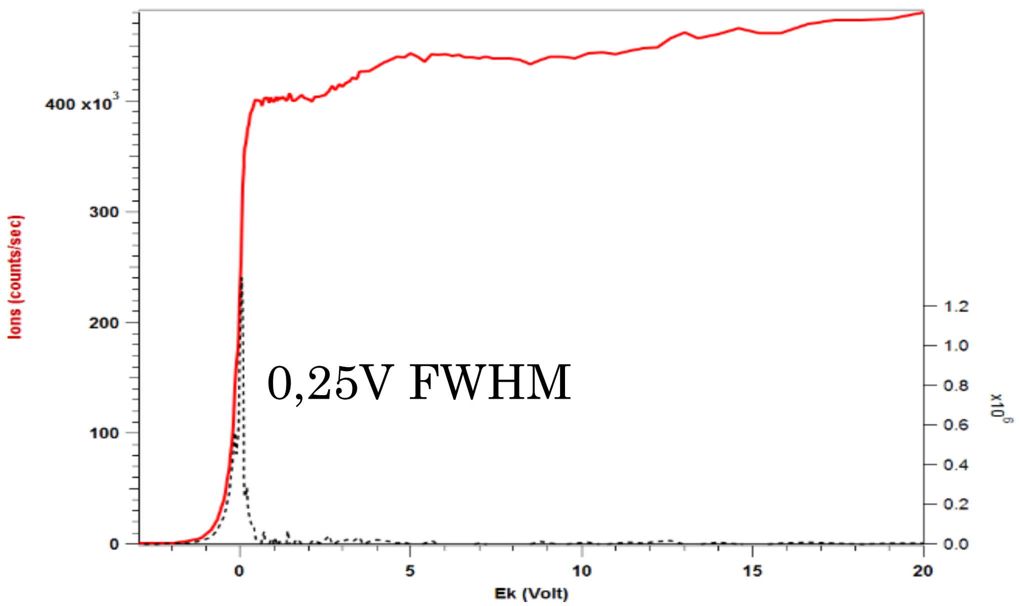
- Use of the **center of mass referential** and **spherical coordinates**

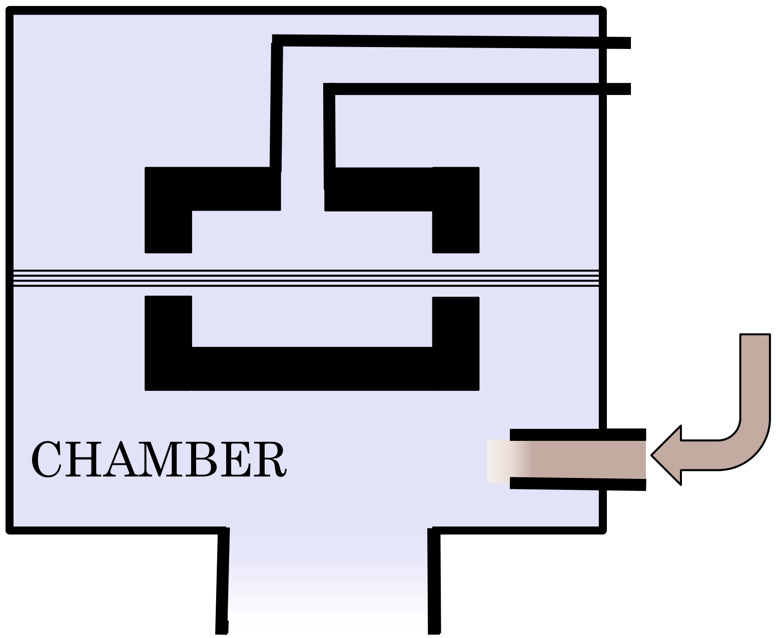
$$u'_1 = -u_1$$

u_1: Velocity in the center of mass referential before collision
u'_1: Velocity in the center of mass referential after collision

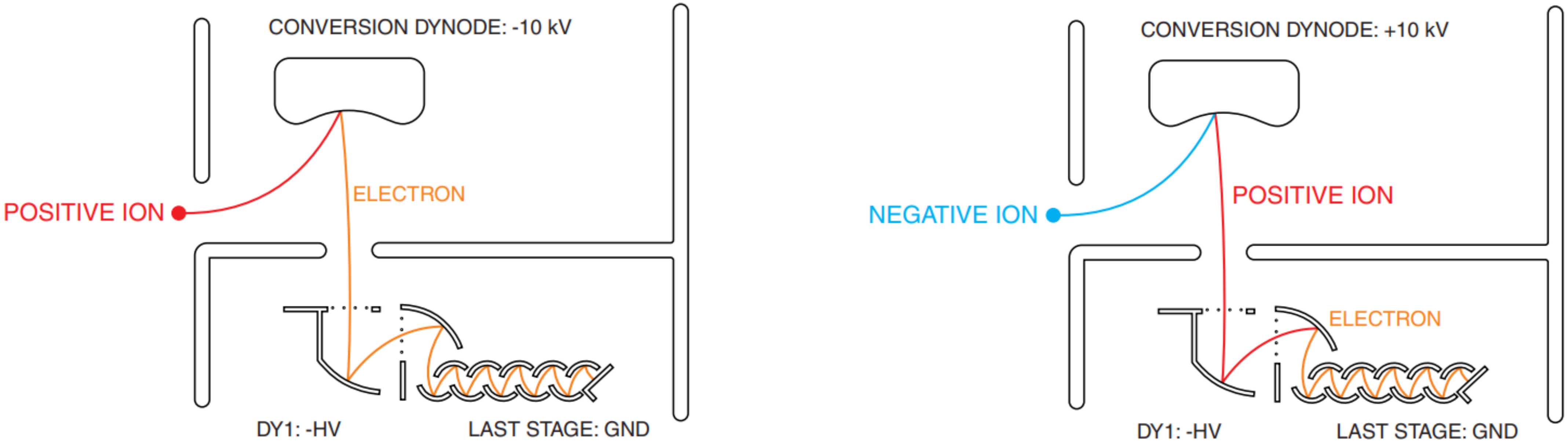
Some specificities

- Single collision regime (integral of products never >10% of parent ion)
- Mass spectra in log scale, very large detection dynamics, small noise
- Systematic measurement with gas in cell and chamber to correct background
- Determination of « zero of kinetic energy » by retarding potential method
- Absolute cross sections derived from simple equation $\sigma_{pro} = \frac{K}{P_{cible}} \frac{N_{pro}}{N_{par}}$





Ions detector

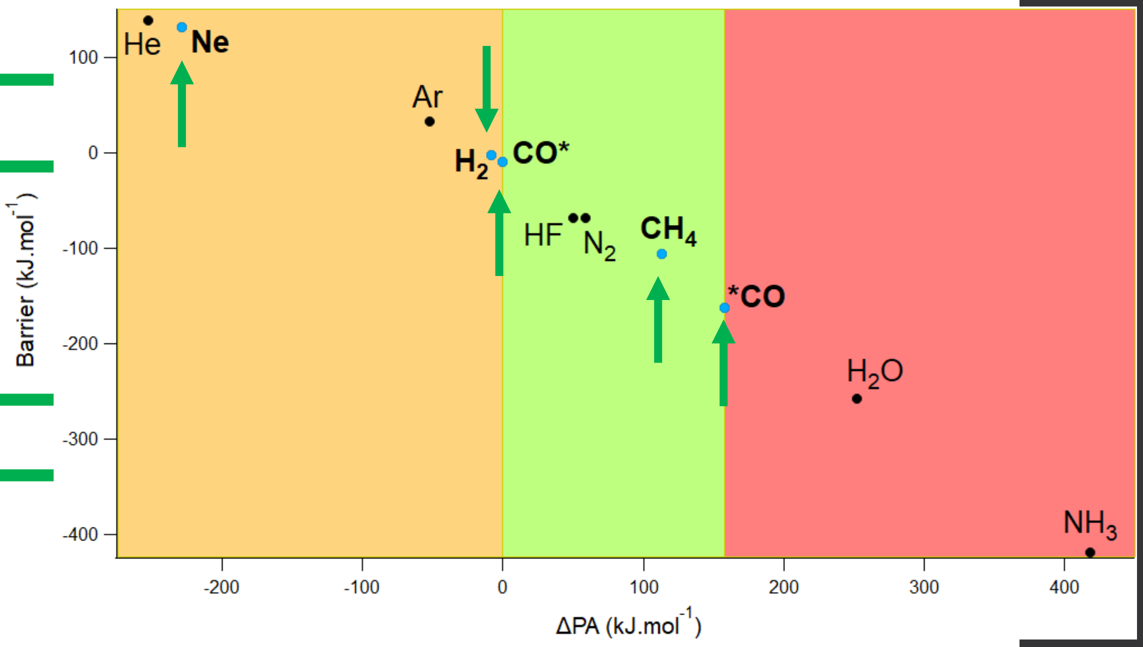


Hamamatsu

Targets choice

Target	ΔPA (kJ.mol^{-1})	Barrier[1] (kJ.mol^{-1})
He	-252,3	138
Ne	**-228,3**	**131**
Ar	-52,3	33
H_2	**-7,8**	**-2.9288[2]**
CO*	**0**	**-10**
HF	50,2	-69
N_2	58,8	-69
CH_4	**113,4**	**-106[3]**
***CO**	**158,1**	**-163**
H_2O	252,2	-258
NH_3	417,8	-419

$$\Delta PA = PA(X) - PA(CO^*)$$



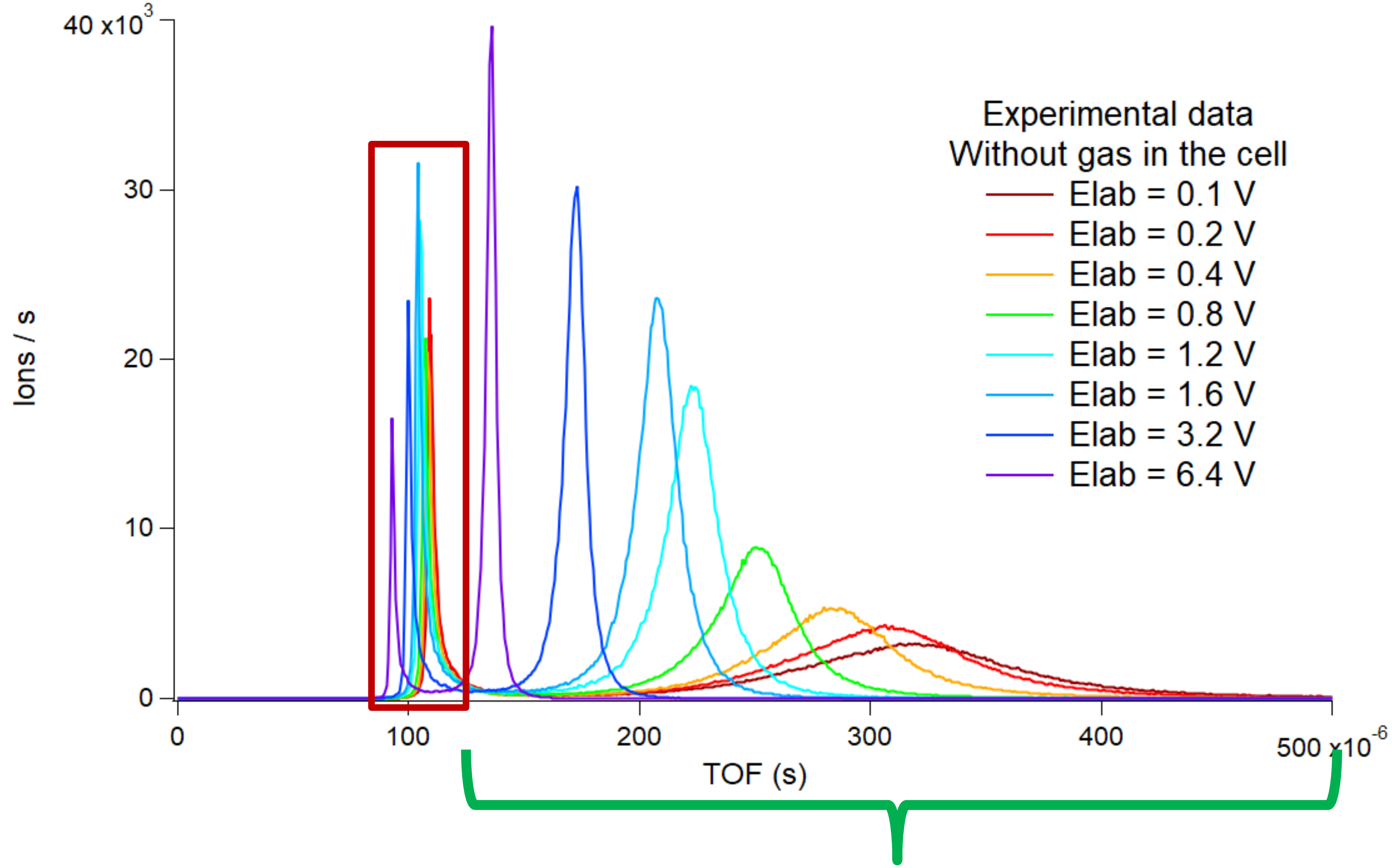
PA: Proton Affinity

(1) A. Chalk, L. Radom, 1997, *J. Am. Chem. Soc.*
(2) E. Herbst and D. Woon, 1996, *Astrophys. J.*
(3) T. D. Fridgen and J. L. Holmes, 2004, *Eur. J. Mass Spectrom.*

Collision energy influence

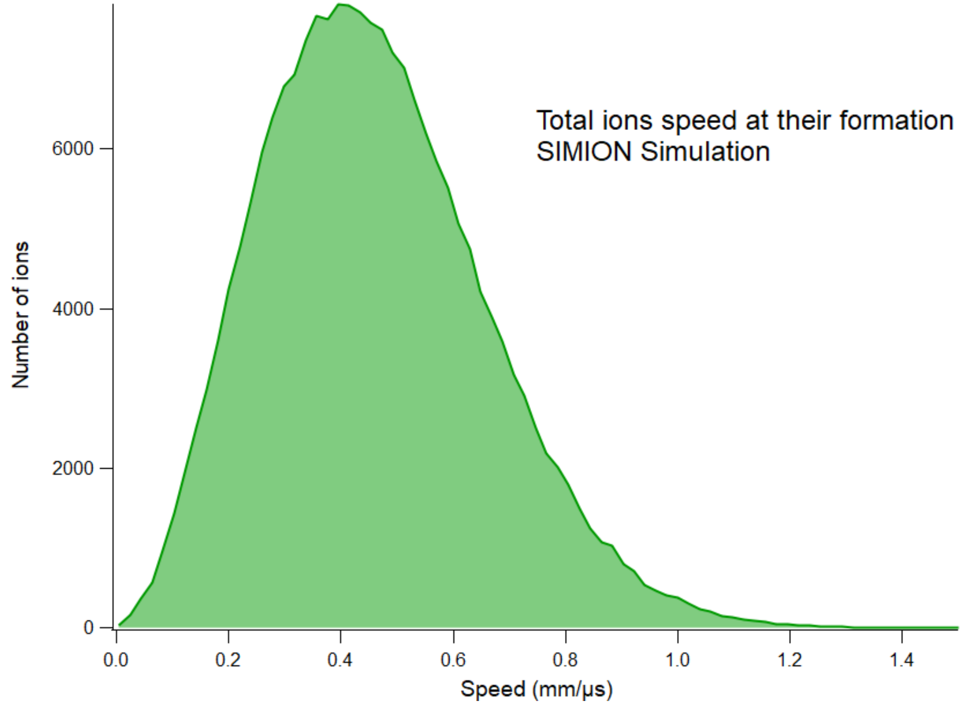
- Experimental Time of Flight of HOC^+ without gas in the cell

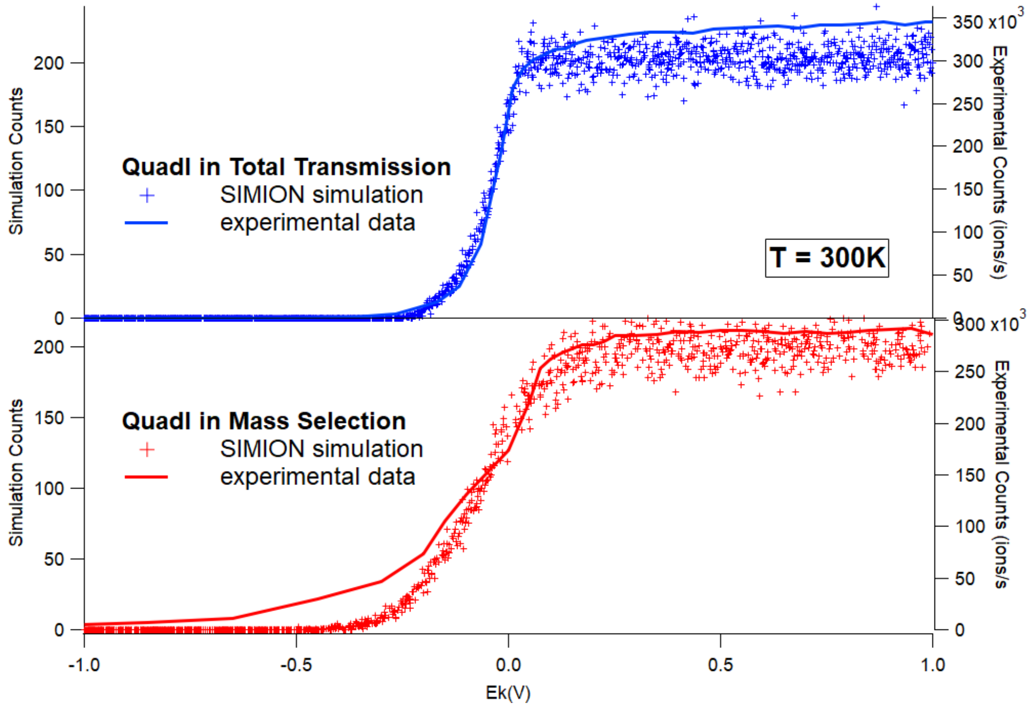
$$E_c = \frac{1}{2} mv^2$$



Construction of the simulation

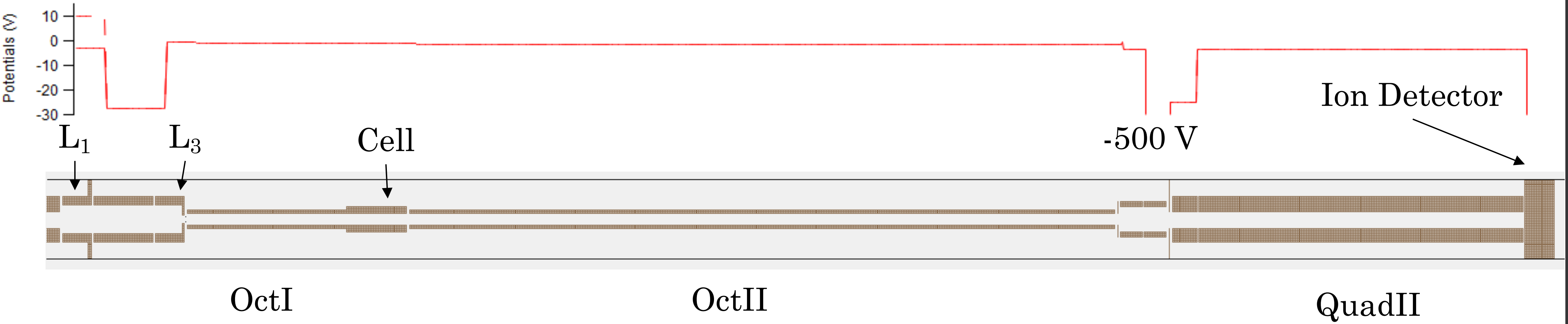
- Use of **SIMION** with our **own code**
- Ion formed with a **Maxwell-Boltzmann** speed distribution (300K)
- Random generation in **position** and **orientation**
- **Comparison** between experimental and simulated data





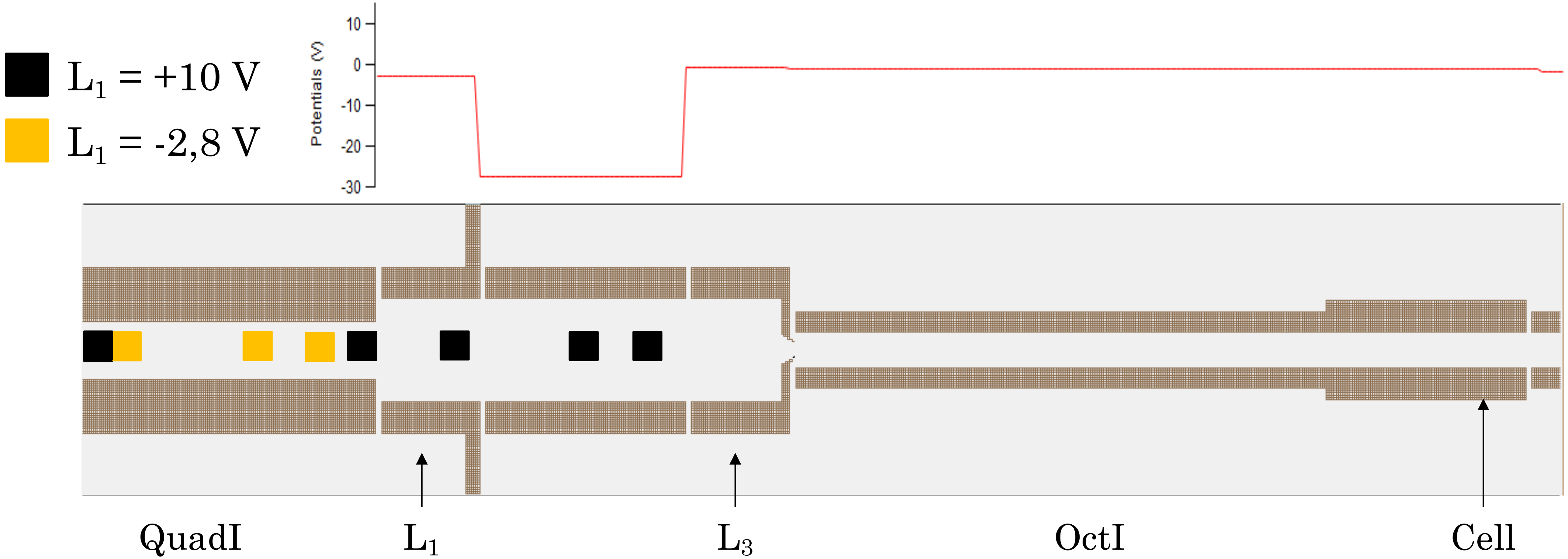
Adding a potential gate to the simulation

- Addition of a potential gate to mimic the experiment
  - L_1 = -2,8 V during the pulse, if not L_1 = +10 V
  - Random gate opening time, between 100 and 120 µs after the ion creation
  - Gate opening duration: 10 µs
  - TOF measurement between the beginning of the opening of the gate and the splat on the detector



Effect of the gate on ions

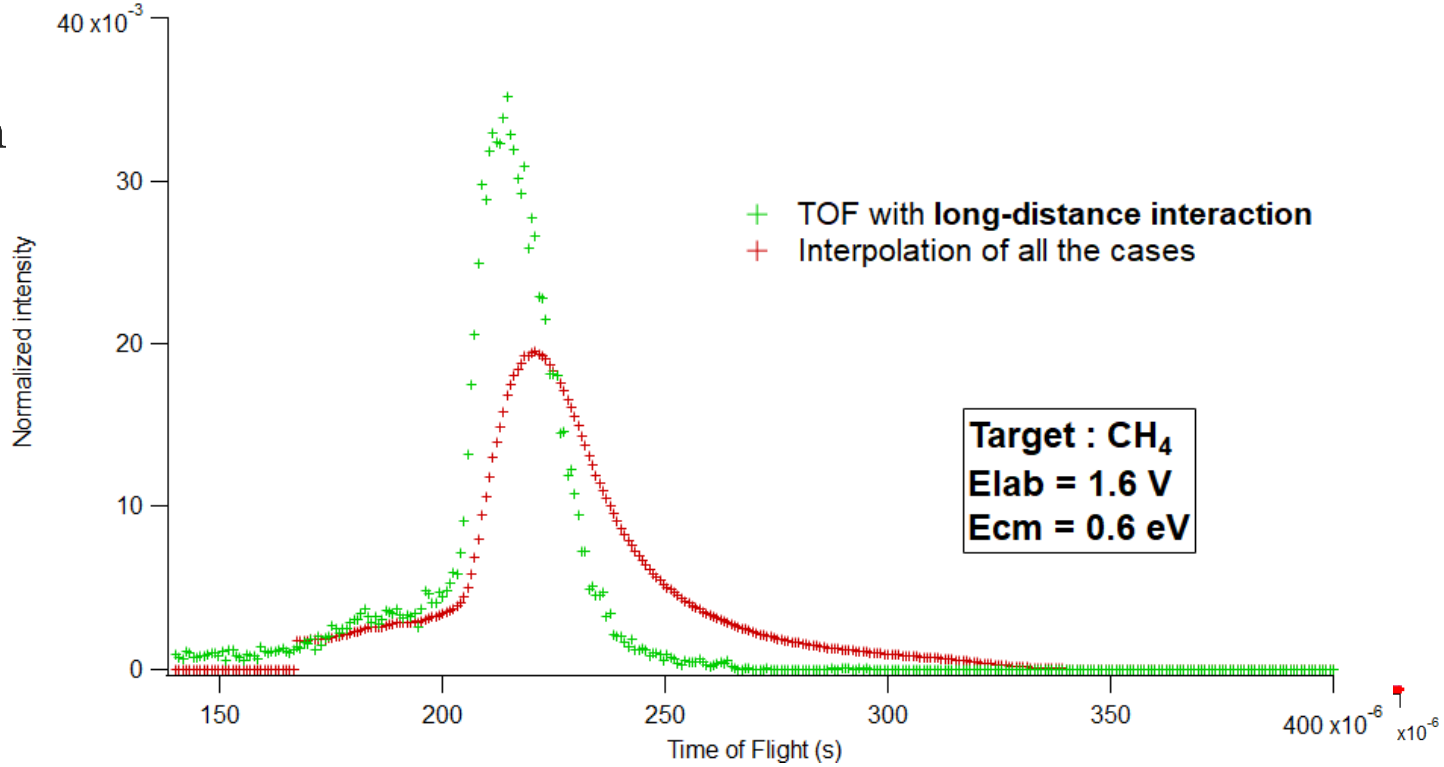
- 4 possible scenarios:
  - No perturbations
  - The ions don't pass L_1
  - The ions are slowed by L_1 pulse → long time peak shape
  - The ions are speeded by L_1 pulse → artefact



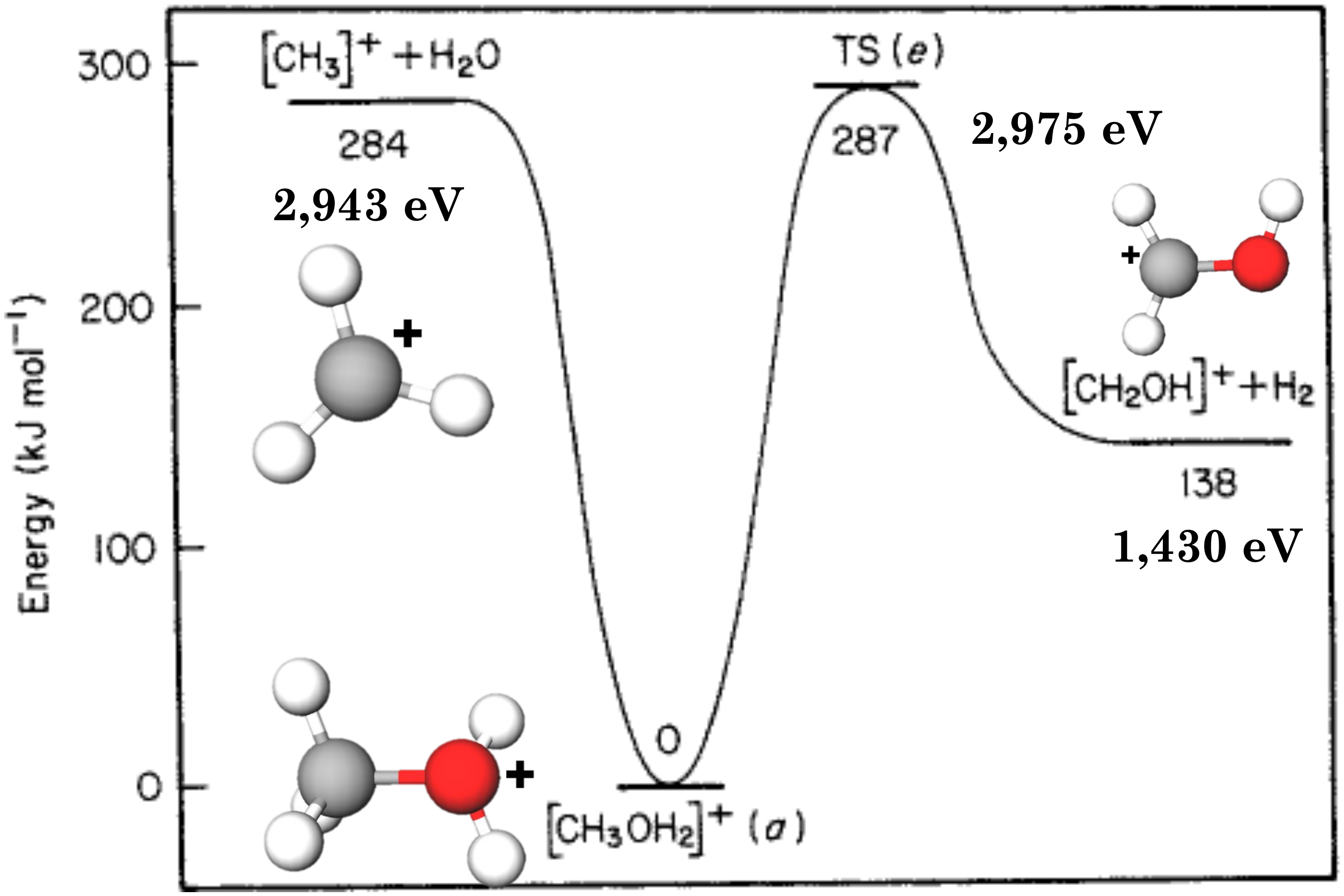
Integration of all the collision parameters

- **Head-on** collision = **Long-distance** interaction **shifted**
  - Possibility of interpolation to obtain all intermediate collisions

- Interpolation
  - **Long-distance** interaction
  - Added at the row n+1
  - **r^2** factor for probability

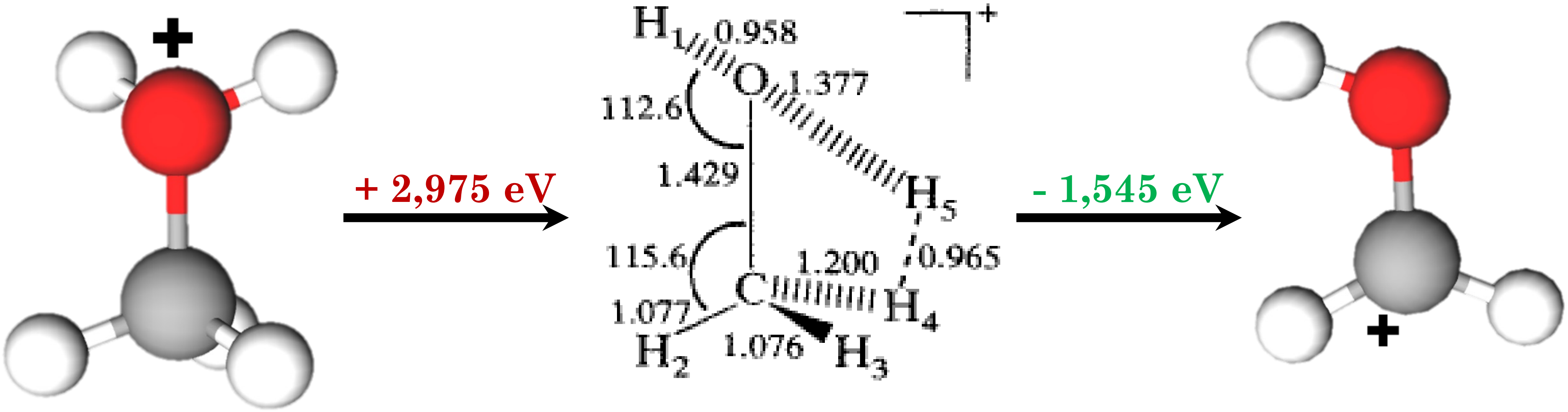


Products of Methanol



R. Nobes, L. Radom, 1982, *Organic Mass Spectrometry*, 17, 340

Etat de transition $m/z = 31$



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