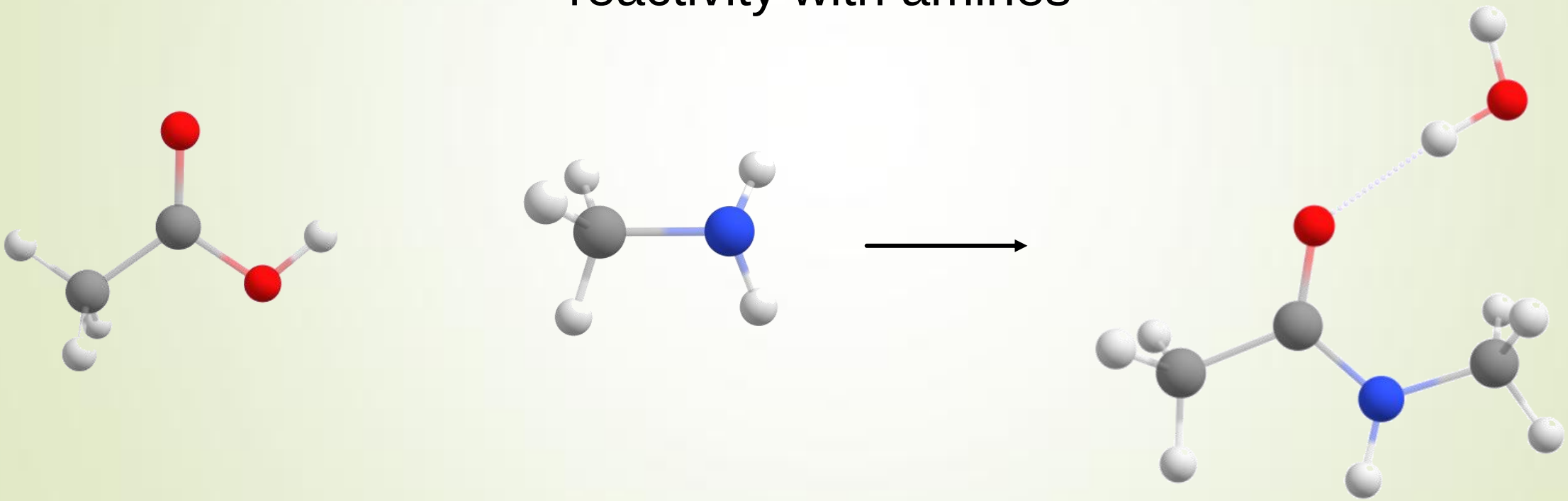
Influence of non-covalent interactions on carbonyl reactivity with amines



E.L. Zins, O. Aroule, N. Solem, C. Romanzin, C. Alcaraz, R. Thissen

Objectives:

- Understand how non-covalent interactions with a third-species can affect reactivity between A and B
  - Bio-chemistry
  - Atmospheric chemistry
  - Astrochemistry

Objectives:

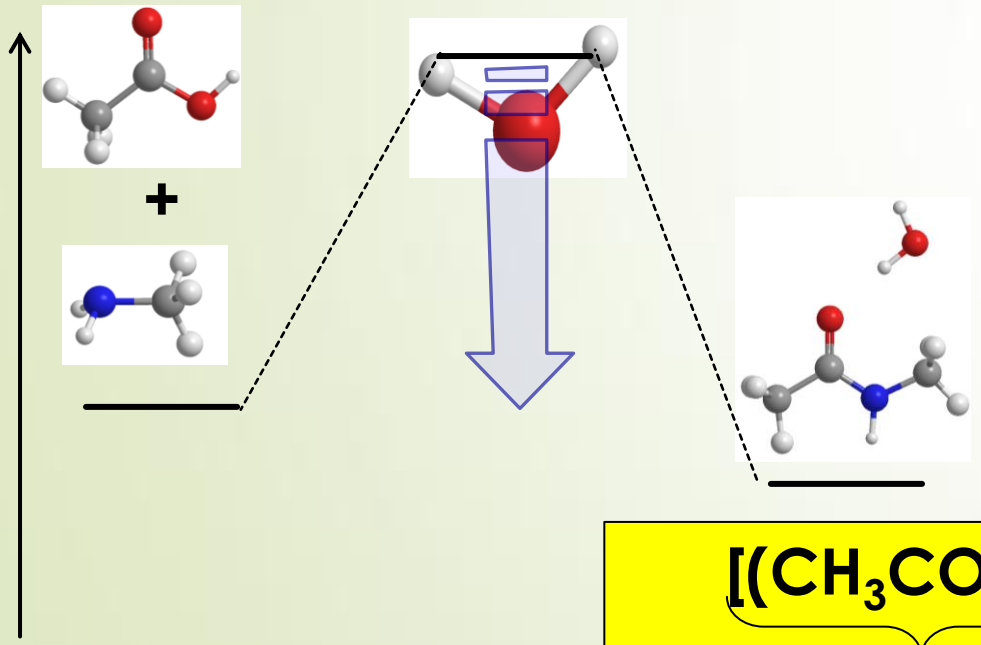
- Understand how non-covalent interactions with a third-species can affect reactivity between A and B

- Compare theoretical data with experimental observations

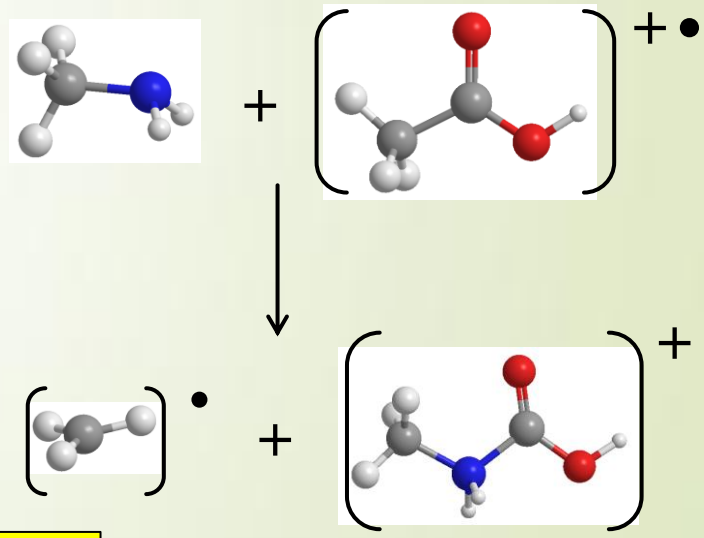
  - Gas phase reactivity
  - LC-ωPBE + GD3-BJ
  - Mass spectrometry+ molecular beam
  - Radicals cations or protonated aggregates

Previous results:

On the relevance of the electron density analysis for the study of micro-hydration and its impact on the formation of a peptide-like bond. Derbali, et al. (2022). *Theor. Chem. Acc., 141*, 34.

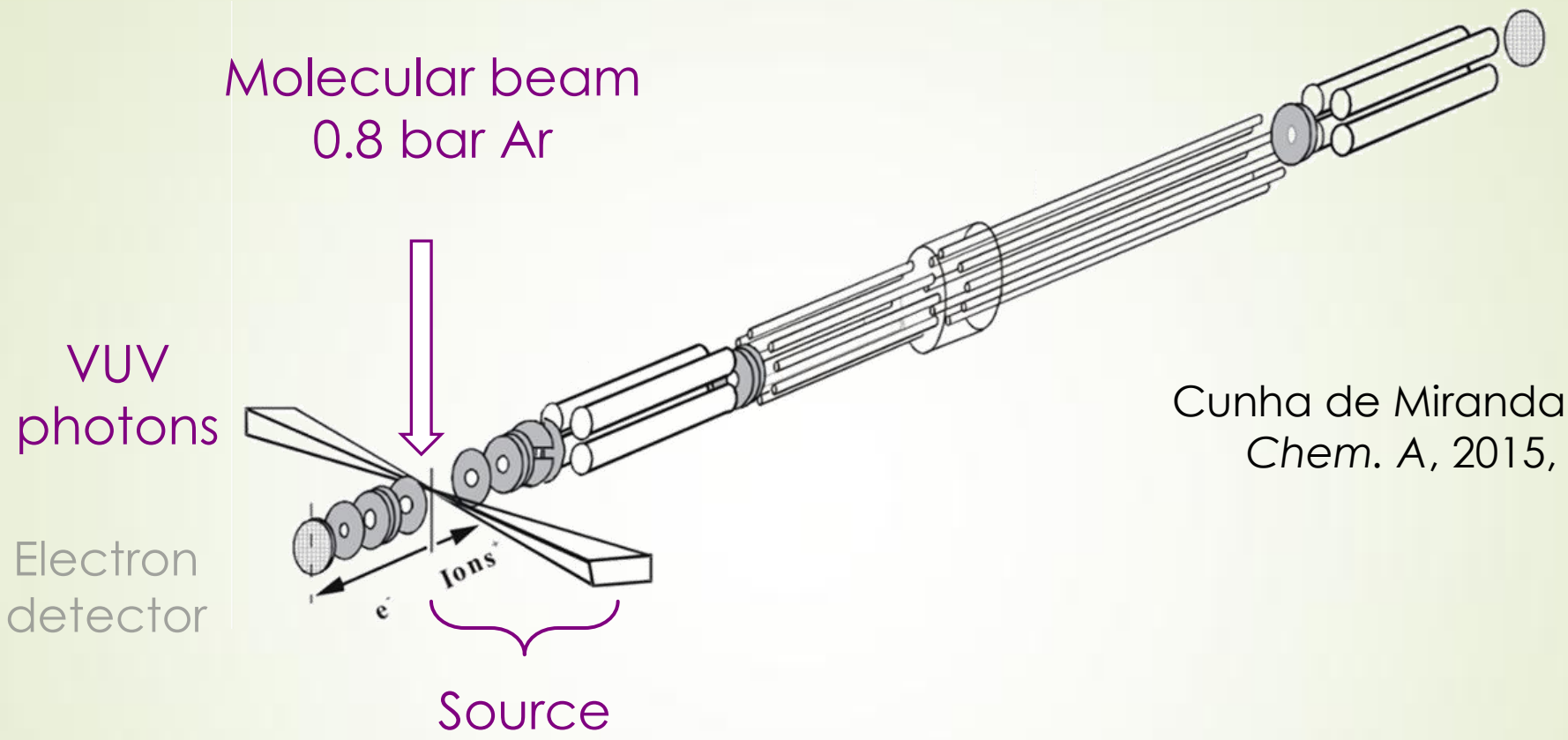


Study of the Reactivity of $CH_3COOH^{+\bullet}$ and $COOH^+$ Ions with CH_3NH_2: Evidence of the Formation of New Peptide-like C(O)–N Bonds. Derbali, et al. (2021). *J. Phys. Chem. A, 125*, 10006



$$\underbrace{[(CH_3COOH)_x}_{Ac}\underbrace{(H_2O)_y}_{W}H]^+ + \underbrace{NH_2CH_3}_{Ma}$$

Ion molecule reactivity experiments



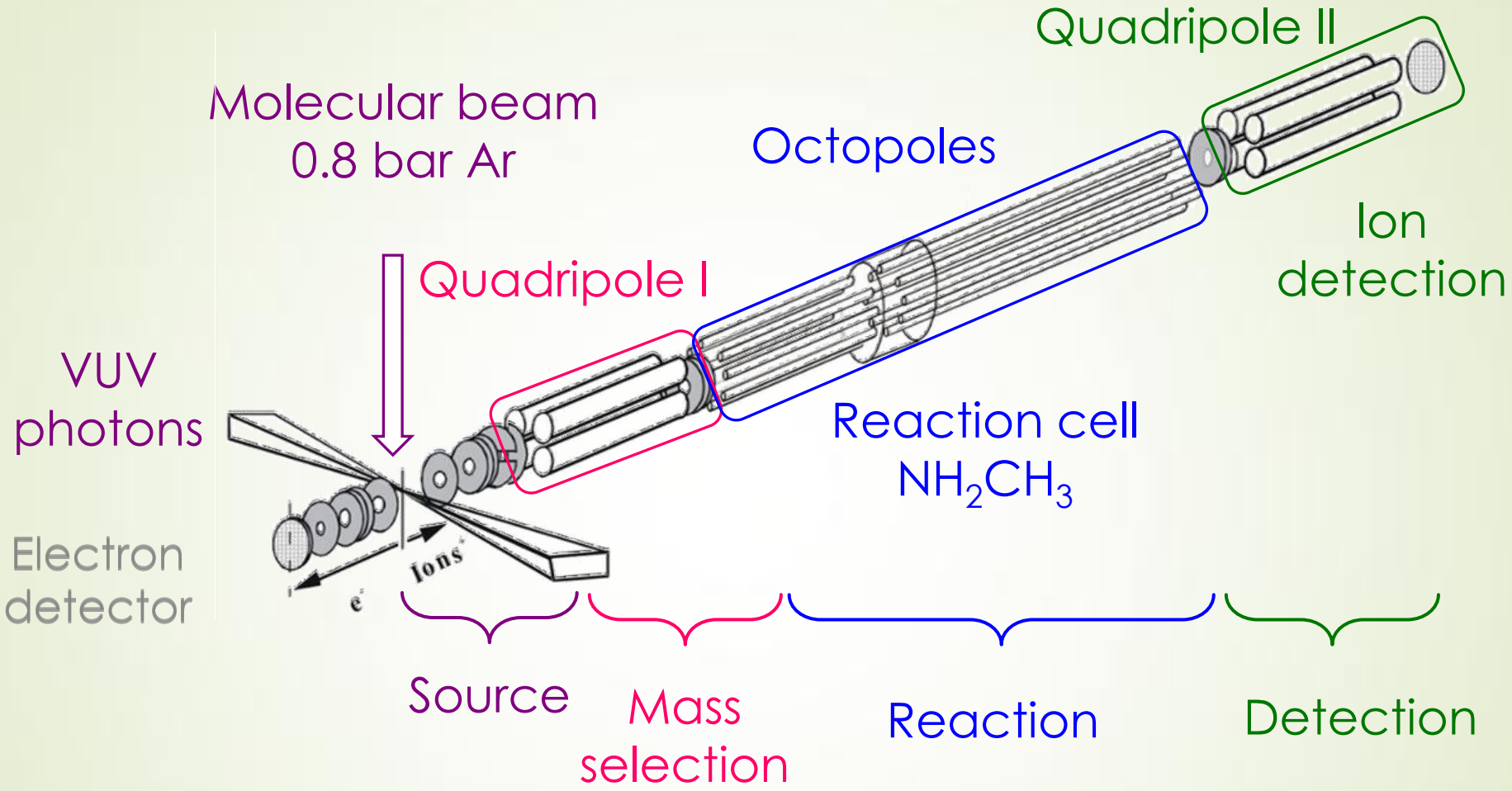
Cunha de Miranda el al., *J. Phys. Chem. A*, 2015, **119**, 6082.

$$[(Ac)_x] \xrightarrow{h\nu} [(Ac)_yH]^+ + [(Ac)_z(CH_3COO)]^\bullet + e^-$$

$$[(Ac)_x(W)_{x'}] \xrightarrow{h\nu} [(Ac)_y(W)_{y'}H]^+ + [(Ac)_z(W)_{z'}(CH_3COO)]^\bullet + e^-$$

CERISES setup (Collision Et Réactions d'Ions Sélectionnés par Electrons de Seuil)

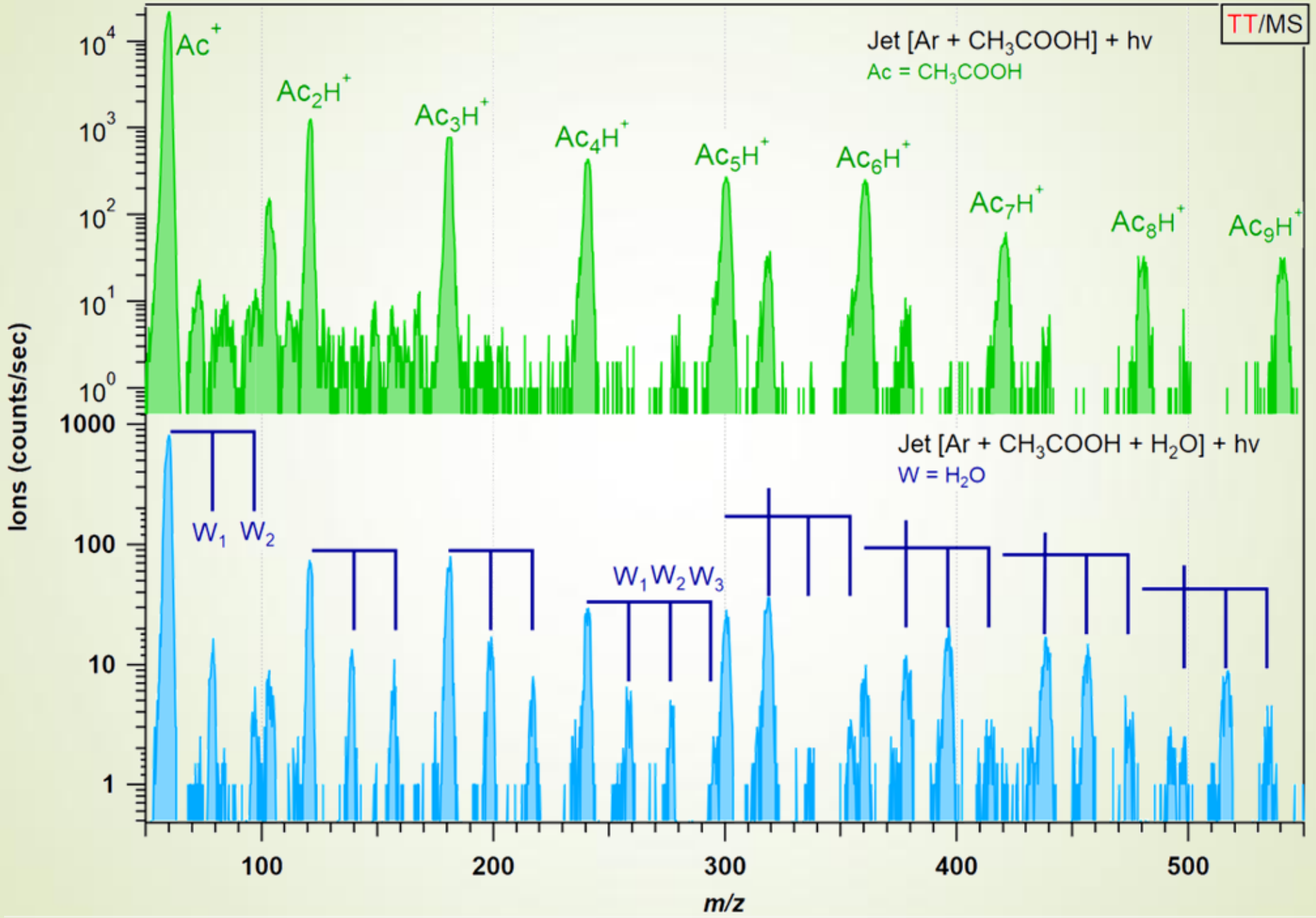
Ion molecule reactivity experiments

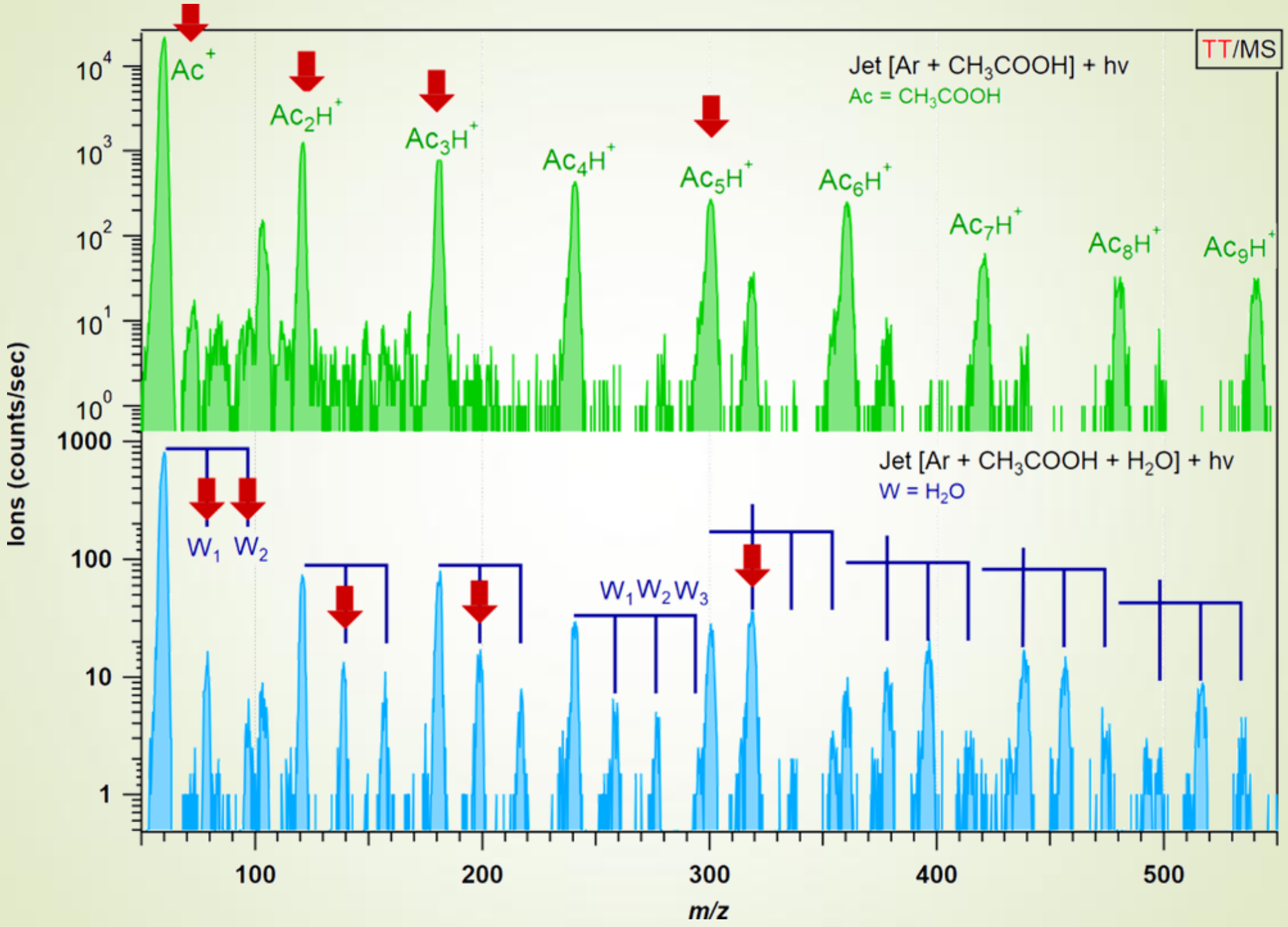


Cunha de Miranda el al., *J. Phys. Chem. A*, 2015, **119**, 6082.

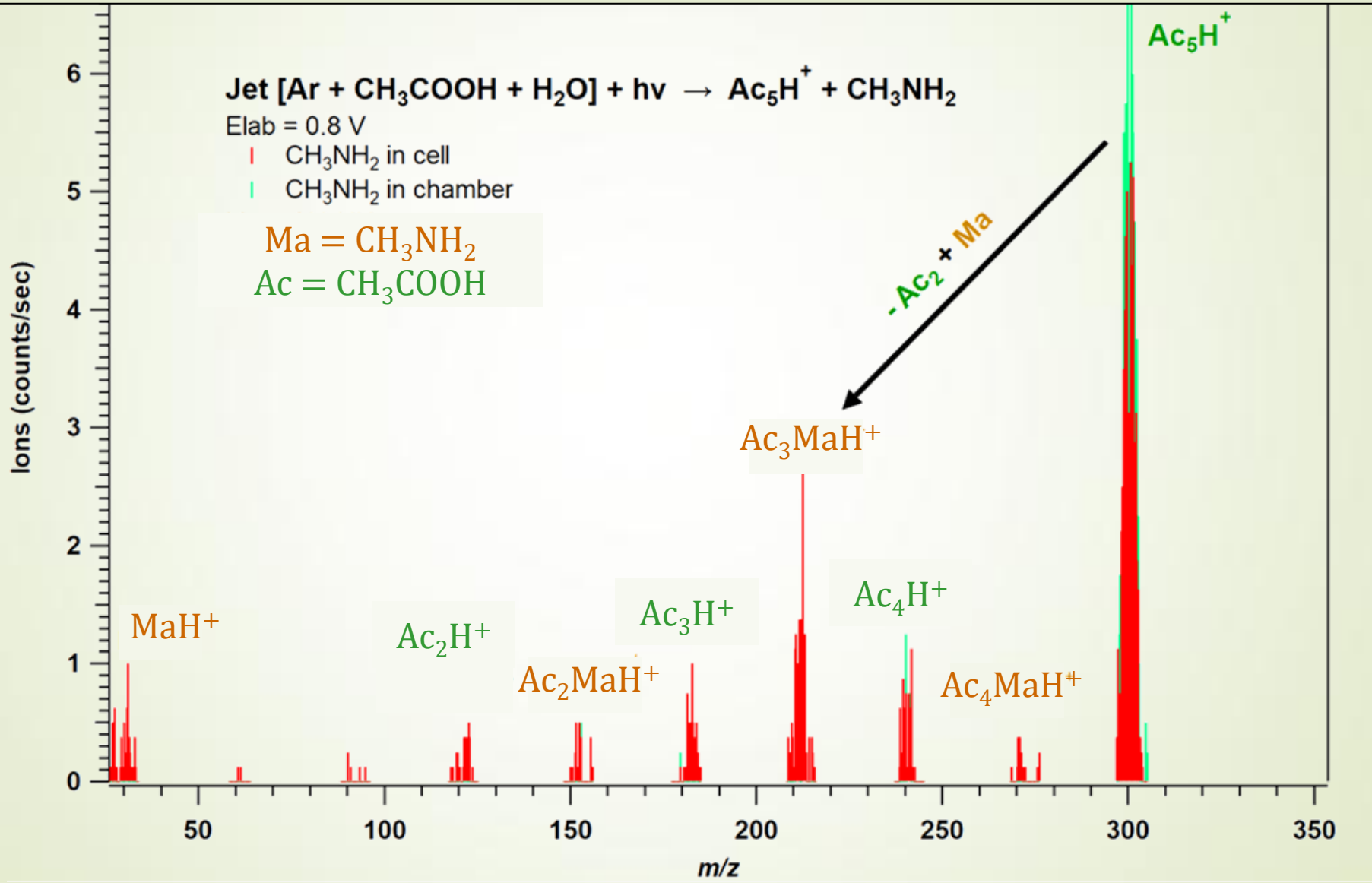
Quadripoles : $10 < m/z < 600$

CERISES setup (Collision Et Réactions d'Ions Sélectionnés par Electrons de Seuil)

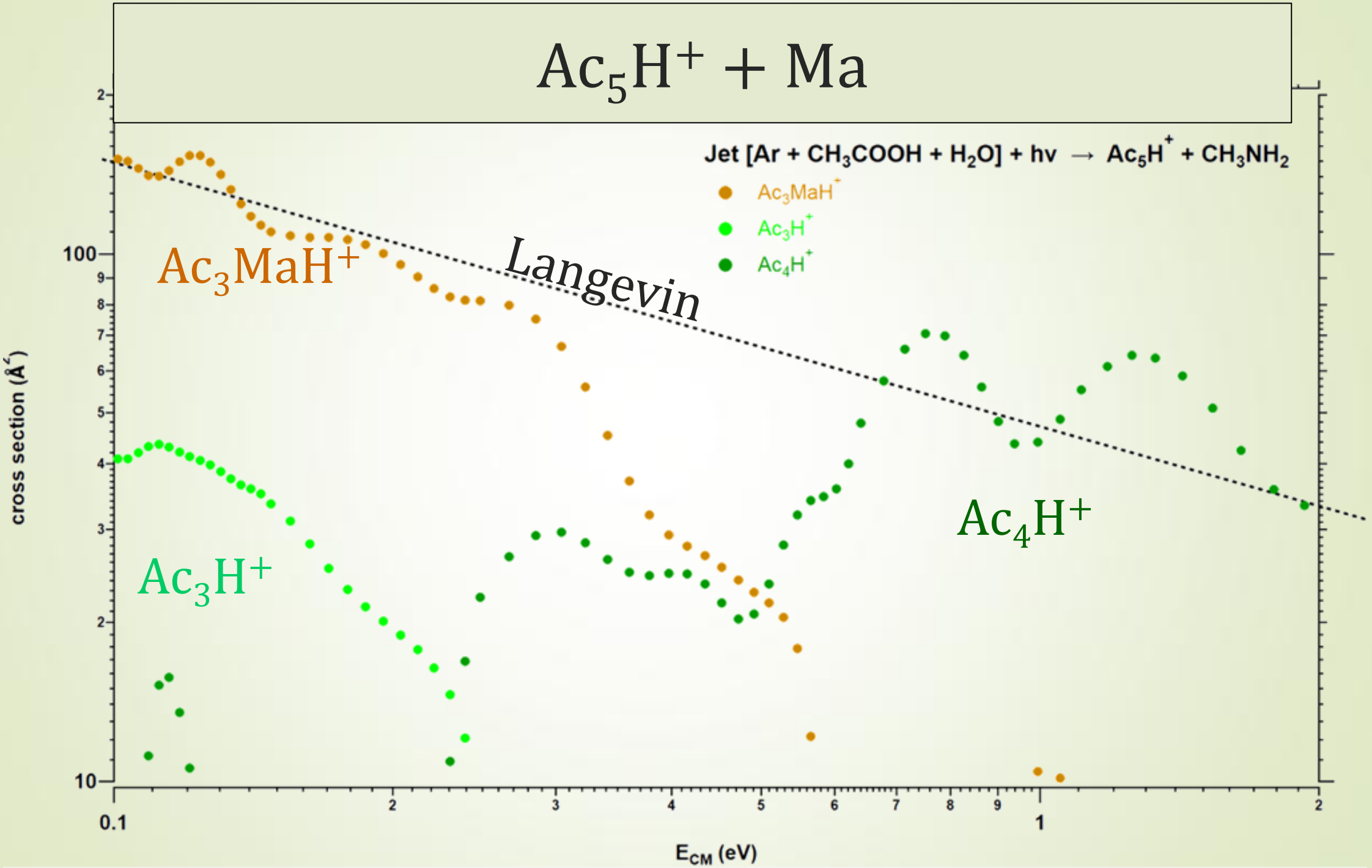

TT/MS
Jet [Ar + CH3COOH] + hv
Ac = CH3COOH
Ac+
Ac2H+
Ac3H+
Ac4H+
Ac5H+
Ac6H+
Ac7H+
Ac8H+
Ac9H+
Jet [Ar + CH3COOH + H2O] + hv
W = H2O
W1 W2
W1W2W3
Ions (counts/sec)
m/z
10^4
10^3
10^2
10^1
10^0
1000
100
10
1
100
200
300
400
500


TT/MS
Jet [Ar + CH3COOH] + hv
Ac = CH3COOH
Ac+
Ac2H+
Ac3H+
Ac4H+
Ac5H+
Ac6H+
Ac7H+
Ac8H+
Ac9H+
Jet [Ar + CH3COOH + H2O] + hv
W = H2O
W1 W2
W1W2W3
Ions (counts/sec)
m/z
100
200
300
400
500
1
10
100
1000
10^0
10^1
10^2
10^3
10^4

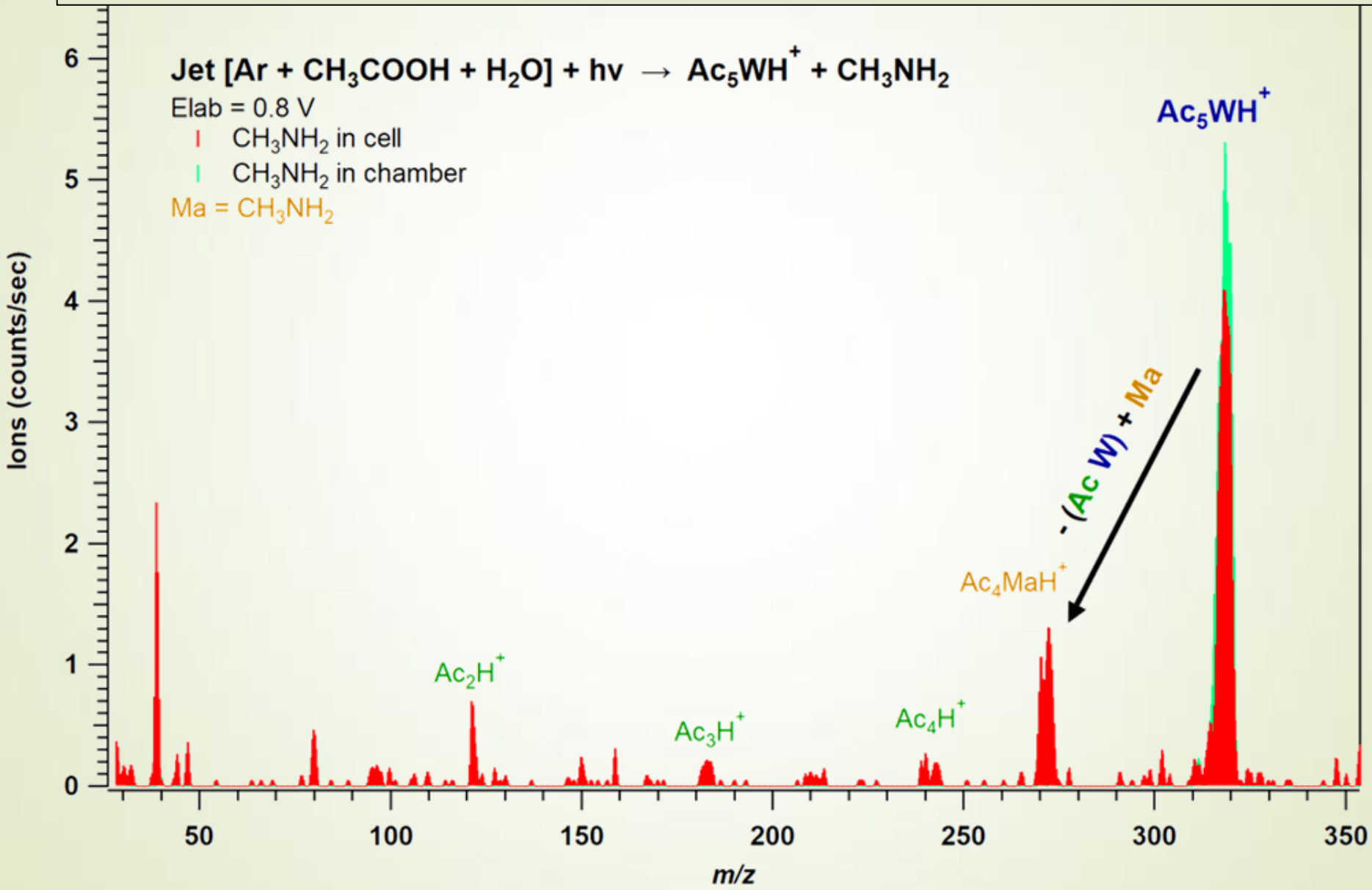
$Ac_5H^+ + Ma$


Jet [Ar + CH3COOH + H2O] + hv → Ac5H+ + CH3NH2
Elab = 0.8 V
CH3NH2 in cell
CH3NH2 in chamber
Ma = CH3NH2
Ac = CH3COOH
Ac5H+
-Ac2 + Ma
Ac3MaH+
Ac4H+
Ac3H+
Ac2H+
Ac4MaH+
Ac2MaH+
MaH+
Ions (counts/sec)
m/z
0
1
2
3
4
5
6
50
100
150
200
250
300
350

$Ac_5H^+ + Ma$


Jet [Ar + CH3COOH + H2O] + hv → Ac5H+ + CH3NH2
Ac3MaH+
Ac3H+
Ac4H+
Langevin
Ac3MaH+
Ac3H+
Ac4H+
cross section (Å2)
100
10
2
0.1
1
ECM (eV)

$Ac_5WH^+ + Ma$


Jet [Ar + CH3COOH + H2O] + hv → Ac5WH+ + CH3NH2
Elab = 0.8 V
CH3NH2 in cell
CH3NH2 in chamber
Ma = CH3NH2
Ac5WH+
- (Ac W) + Ma
Ac4MaH+
Ac2H+
Ac3H+
Ac4H+
Ions (counts/sec)
m/z
0
1
2
3
4
5
6
50
100
150
200
250
300
350

Theoretical study

- Theory/experience comparison
  - Determine the enthalpy of reaction formation:
  - Search for the structures of the reagents and the products

    LC-ωPBE + GD3-BJ
- How?
  - MESP (Molecular Electrostatic Potential)
  - CREST (Conformer Rotamer Ensemble Sampling Tool), Density-functional based tight binding (DFTB)

Pracht, P., Bohle, F., & Grimme, S. (2020). Automated exploration of the low-energy chemical space with fast quantum chemical methods. *Physical Chemistry Chemical Physics*, *22*(14), 7169-7192.

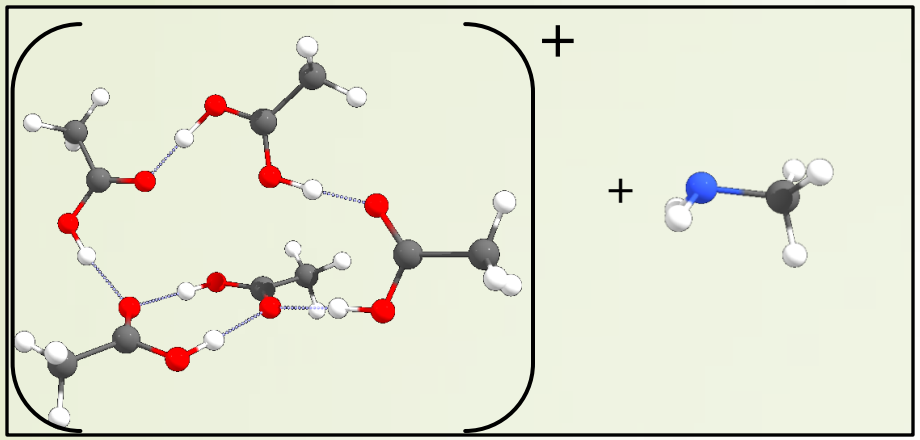
$Ac_5H^+ + Ma$

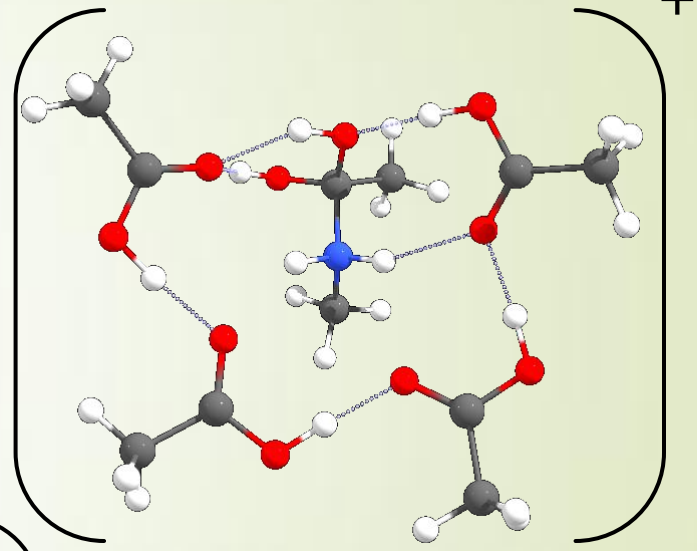
ΔE(eV)

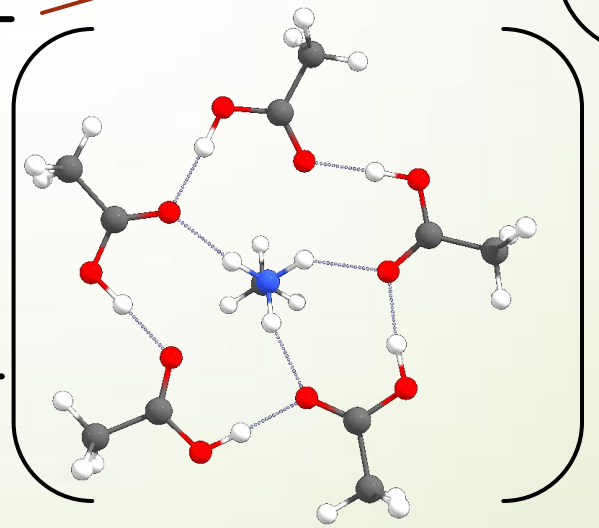
0

-0.91

-1.74

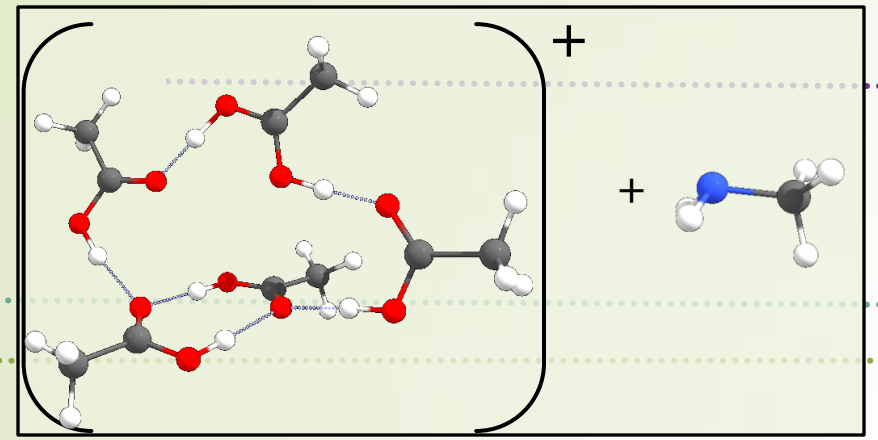






ΔE(eV)

$Ac_5H^+ + Ma$



$Ac_5 + MaH^+$ 0.54

0

$Ac_4 + AcMaH^+$ 0.03

$Ac_3 + Ac_2MaH^+$ -0.08

$Ac_2 + Ac_3MaH^+$ -0.52

-0.91

$Ac + Ac_4MaH^+$ -0.78

-1.74

Reactivity of Ac_xH^+ : Theoretical results

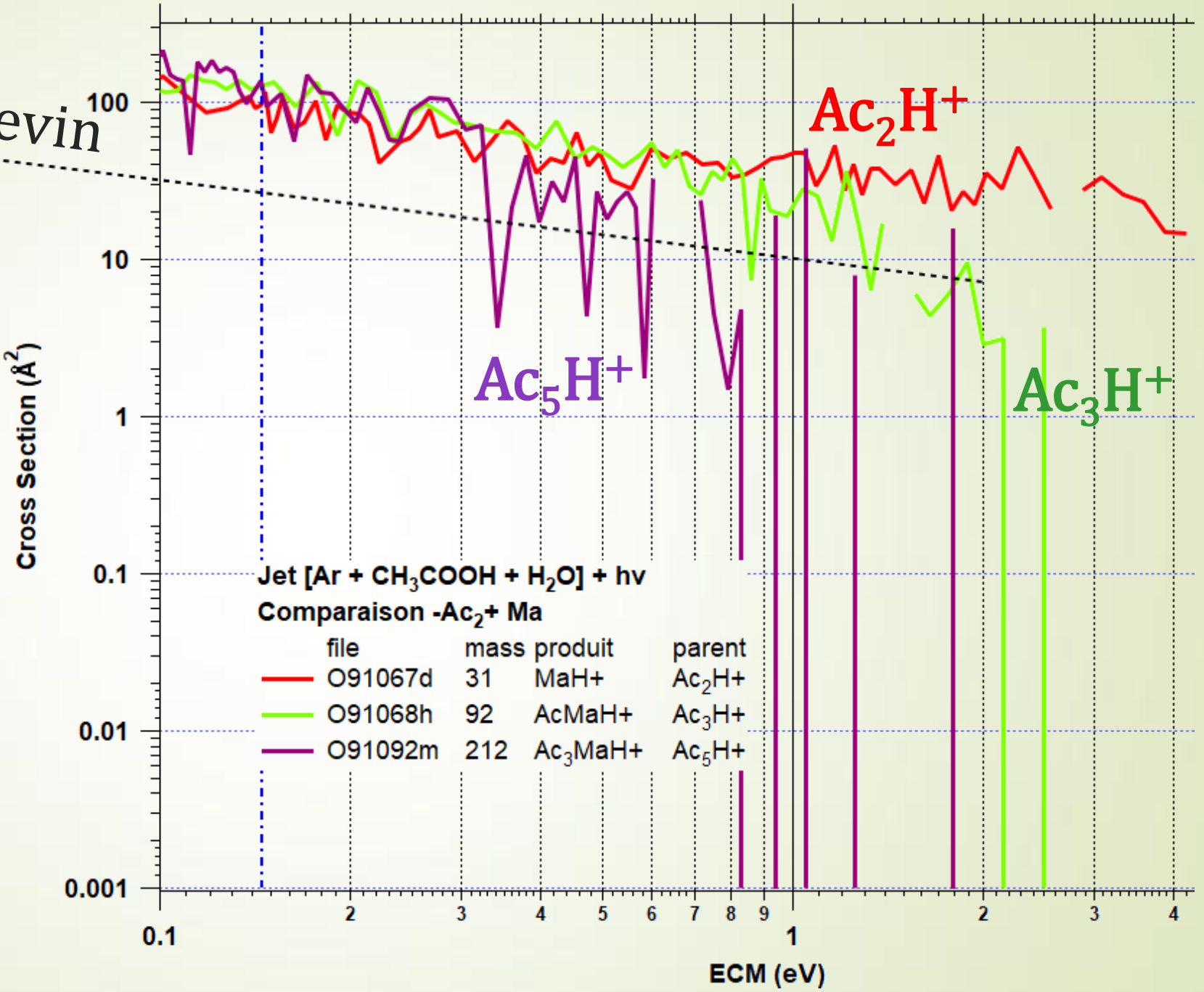
x =	Cov Cplex	Non-cov Cplex	Product formation energy (eV)				
			$Ac_x + MaH^+$	$Ac_{x-1} + AcMaH^+$	$Ac_{x-2} + Ac_2MaH^+$	$Ac_{x-3} + Ac_3MaH^+$	$Ac_{x-4} + Ac_4MaH^+$
1	-1,42	-2,16	-1,19				
2	-1,07	-1,69	-0,63	-0,88			
3	-0,89	-1,54	-0,05	-0,65	-0,73		
5	-0,92	-1,74	0,54	0,03	-0,08	-0,52	-0,79

Conclusions and perspectives

- Possible study of aggregates' reactivity
  - Successful observation of the reaction of $Ac_{1\text{-}5}W_{1\text{-}2}H^+$ aggregates
  - Complementarity of theoretical and experimental approaches
- Similar reactivity regardless the aggregates'size
  - Strong interaction between protonated aggregates and methylamine
  - Non-covalent complexes versus covalent interactions
  - Dissociation of initial complexes formed with methylamine
- Micro-hydrated complexes
  - Preferential loss of water molecules

Thank you for your attention!

$$Ac_xH^+ + Ma \rightarrow Ac_2 + Ac_{x-2}MaH^+$$



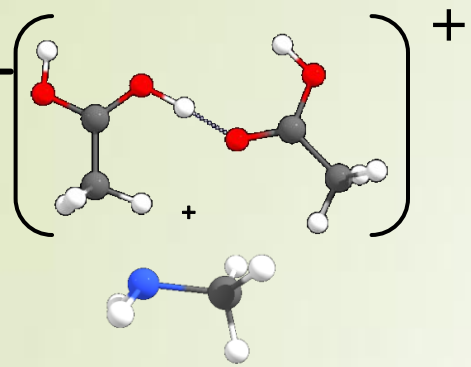
Experimental results

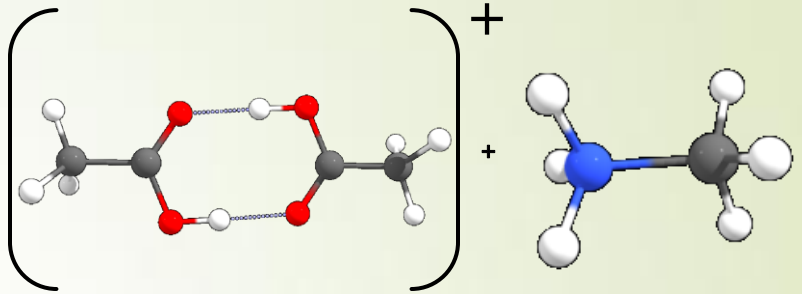
Parent Ac_xH^+	Exothermic/Endothermic		
	$[MaH]^+$	$[AcMaH]^+$	$[(Ac)_2MaH]^+$
2	Exothermic	Exothermic	Exothermic
3	Endothermic	Exothermic	Exothermic
5	Endothermic	Not observed	Exothermic

ΔE (eV)

0

Ac_2H^+ + Ma





Ac_2 + MaH^+

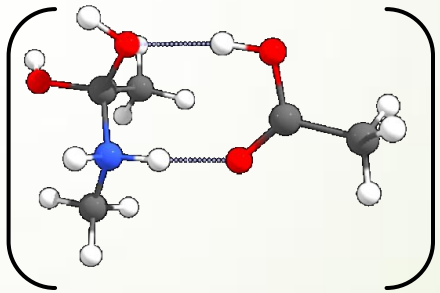
ΔE_{eV} = -0,63

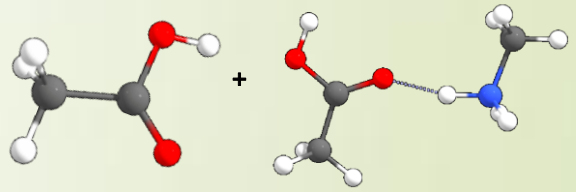
Ac + $AcMaH^+$

ΔE_{eV} = -0,88

Ac_2MaH^+_covalent

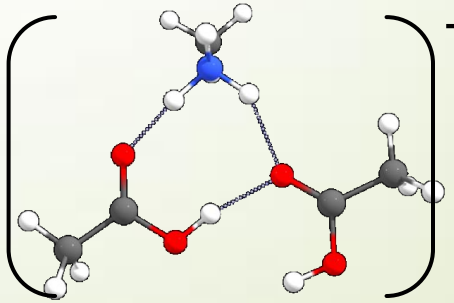
ΔE_{eV} = -1,07



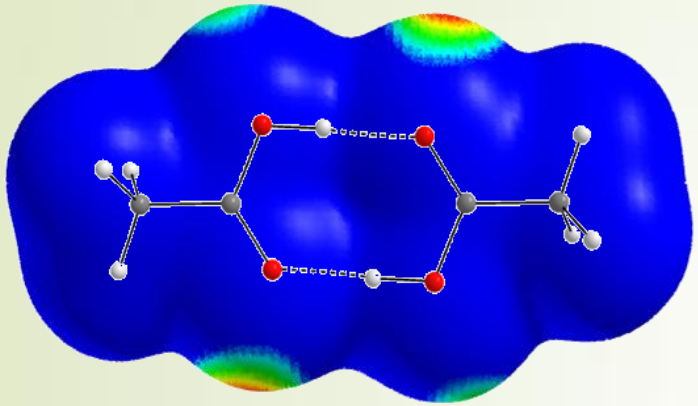


Ac_2MaH^+_noncov

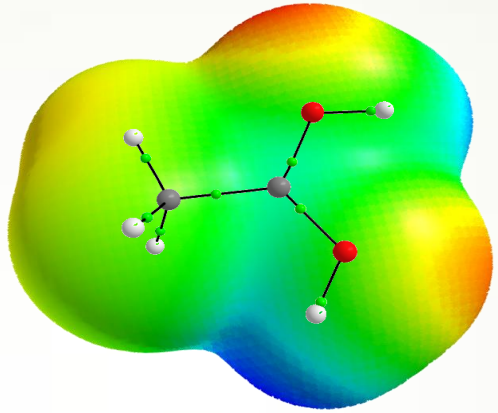
ΔE_{eV} = -1,68



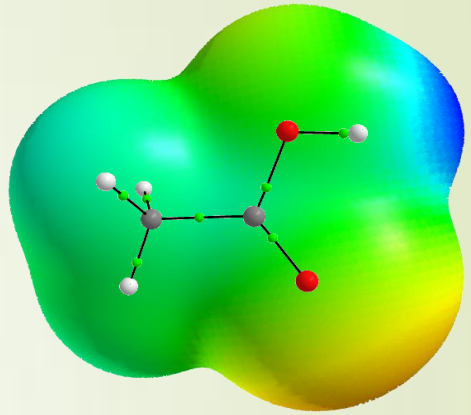
Search for the structure of observed ions



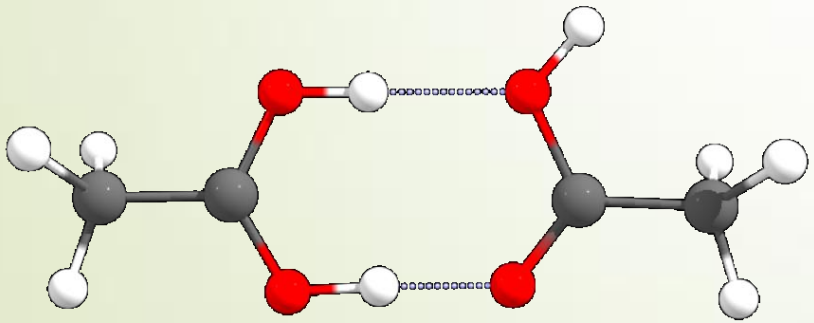
MESP of acetic acid dimer

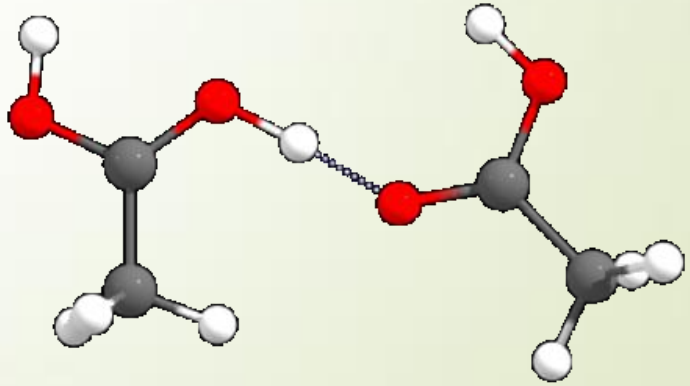


MESP of protonated acetic acid



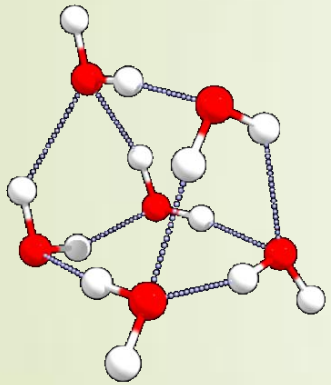
MESP of acetic acid

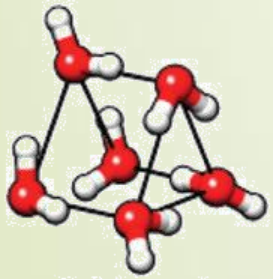




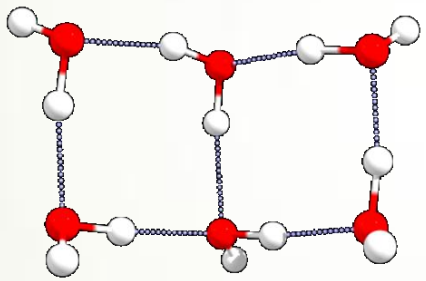
Principle of the CREST study

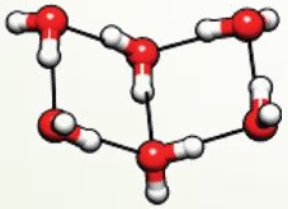
Initial structure → Optimization → CREST → Final structures



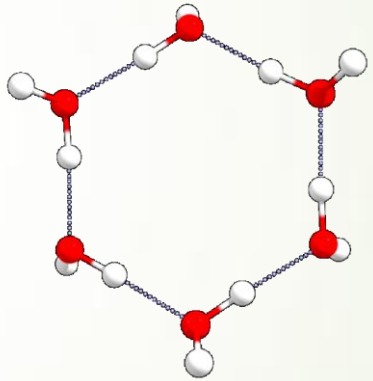


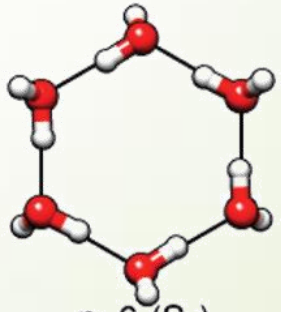
n=6 (Prism)



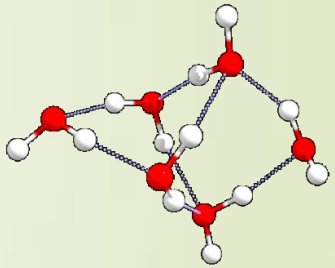


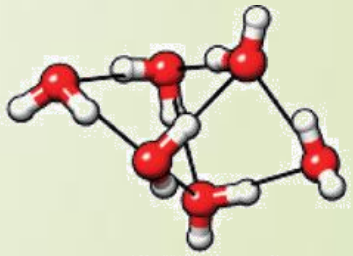
n=6 (Book)





n=6 (S_6)





n=6 (Cage)