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Symposium in honor of Prof. A. Laganà

VIRTUAL ENVIRONMENTS AND DETAILED SIMULATION OF MOLECULAR PROCESSES

Experimental and computational studies on Ion-molecule reactive collisions

Symposium in honor of Prof. A. Laganà, 4-5th November 2015, Bettona (Italy)

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Experimental and computational studies on Ion-molecule reactive collisions

Barcelona (RDG) ⟷ Perugia (RDG)

1980, Cortona , NATO advanced summer school…

1982, *first research stay* (experimental Profs. F. Vecchiocattivi & B. Brunetti)

1980'…

end of 1980' *collaboration in theory* Prof. A. Laganà

1991 Li + HCl RIOSA cross section calculations on parallel computers, *Theoretica Chimica Acta,* A. Laganà *et al.*

1990'… *1993-1993* Prof. V. Aquilanti *'hyperquantization algorithm"*

beginning of 2000' Molecular Dynamics studies A. Laganà …

2015 ….

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Congratulations to Antonio Laganà

from ....

GDRQs' members

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Experimental and computational studies on Ion-molecule reactive collisions

Outline

- Experimental *ion-molecule* reactions in the eV energy range
  radiofrequency guided ion beam (RF-GIB) *technique* *(most recent results)*

- Complementary *ab initio* quantum chemistry structure studies
  (*direct quasiclassical trajectory* calculations)

- *Improvements in the RF-GIB setup and future perspectives*

Coauthors:
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Estefanía López *PhD student*
Margarita Albertí
D. Bassi, D. Ascenzi, P. Tosi *(University of Trento (Italy)*
J.M. Bofill *(University of Barcelona, Organic Chemistry Department)*

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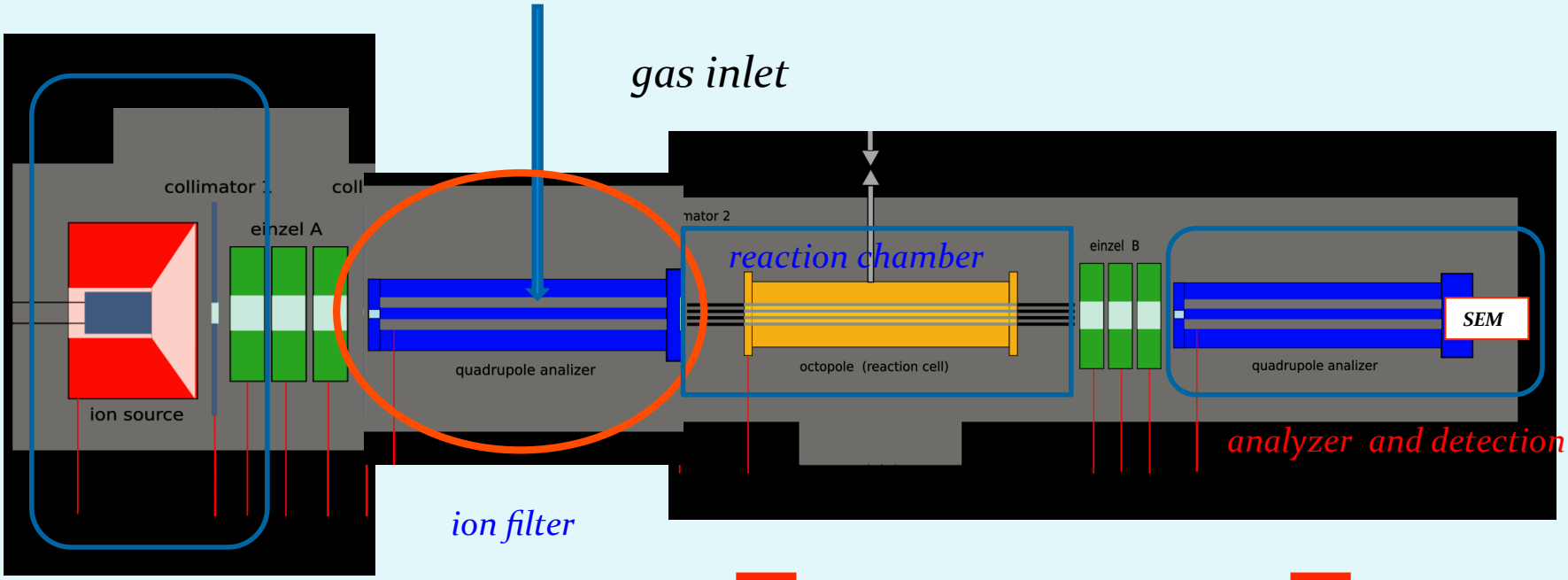
ion-molecule reactions in the eV energy range

radiofrequency guided ion beam (**RF-GIB**) apparatus



alkali ions source

turbo pumps (background pressure ~ 10^{-7} -10^{-6} mbar)
(reaction cell pressure ~ 10^{-6} -10^{-5} mbar)

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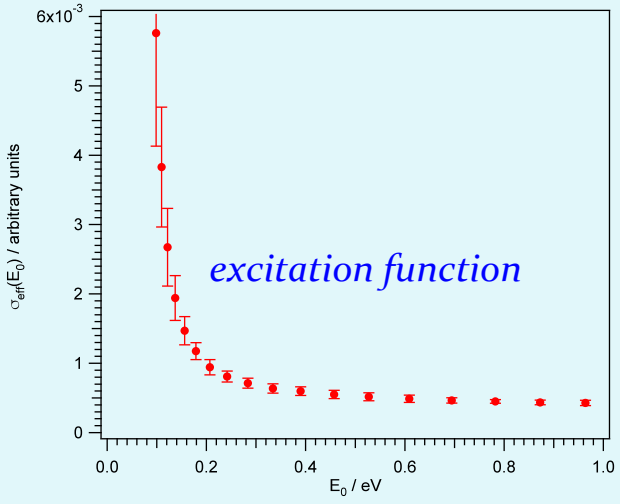
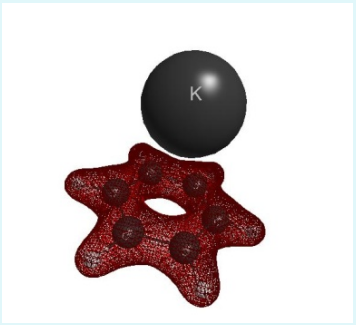
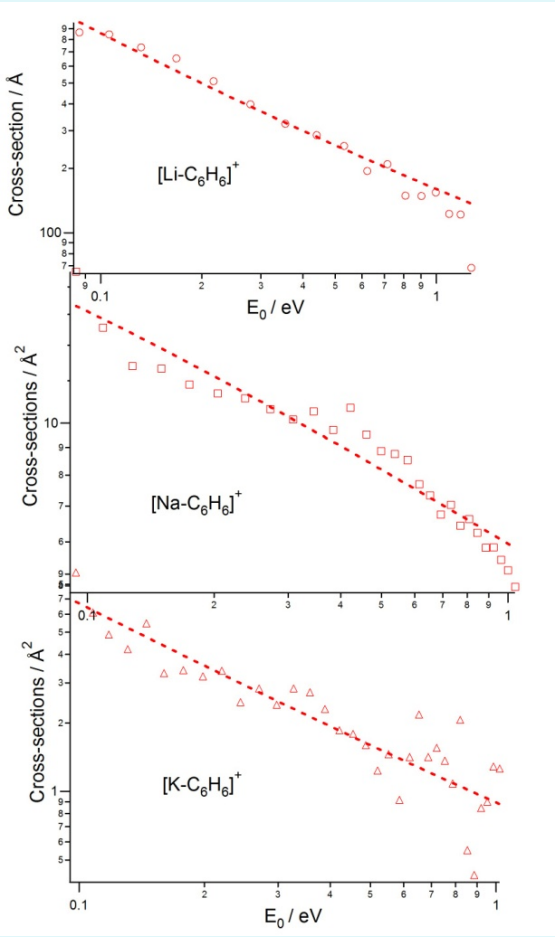
Universitat de Barcelona

Dos Campus d'Excel·lència Internacional: BKC Barcelona Knowledge Campus HUBc Health Universitat de Barcelona Campus

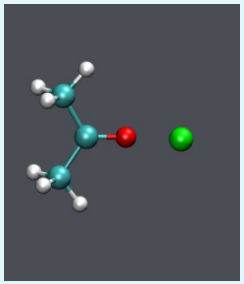
association ion-molecule reactions (*adducts*)







$C_6H_6 + K^+ \rightarrow [K\text{--}C_6H_6]^+$



non-covalent interactions
... ab initio calculations,
dynamics models ,semi empirical
PES and MD simulations

$CH_3\text{-}CO\text{-}CH_3 + Li^+ \rightarrow [Li\text{--}\ CH_3\text{-}CO\text{-}CH_3]^+$

J. Allison and D.P. Ridge (1976)

- ...*dehydrohalogenation* of halogenated hydrocarbons and *dehydration* of alcohols induced by *alkali ions* (M^+)...

$$C_nH_{2n+1}X \rightarrow C_nH_{2n} + HX \qquad X\text{: halide, OH ;} \quad H\text{-}X\text{: hydrogen}$$

(hydrogen halide or H2O)

two reactions channels,

$$C_nH_{2n+1}X + M^+ \rightarrow [M\text{--}C_nH_{2n}]^+ + HX \qquad \text{channel (1)}$$

$$\rightarrow \; C_nH_{2n} + [M\text{—}HX]^+ \qquad \text{channel (2)}$$

observed channels 1 and 2 depend on the nature of both reactants and normally only one product channel was detected in the Allison & Ridge list ...
or both reaction channels were not observed

moreover, we observed the decompositions reactions

$$C_nH_{2n+1}X + M^+ \rightarrow [C_nH_{2n}]^+ + HX \qquad \text{channel (3)}$$

$$[C_nH_{2n}]^+ \rightarrow \textit{decomposition products} \qquad \text{channel (4)}$$

at moderately higher energies

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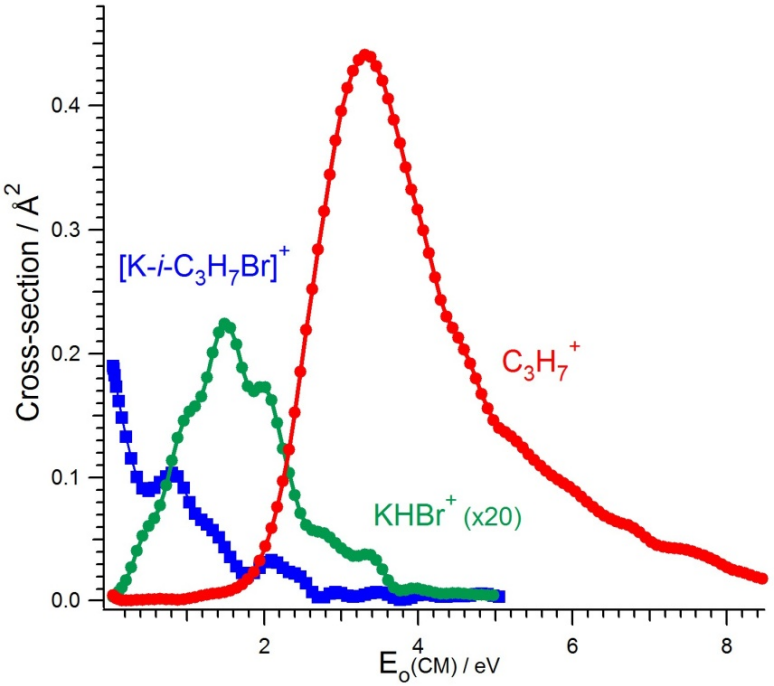
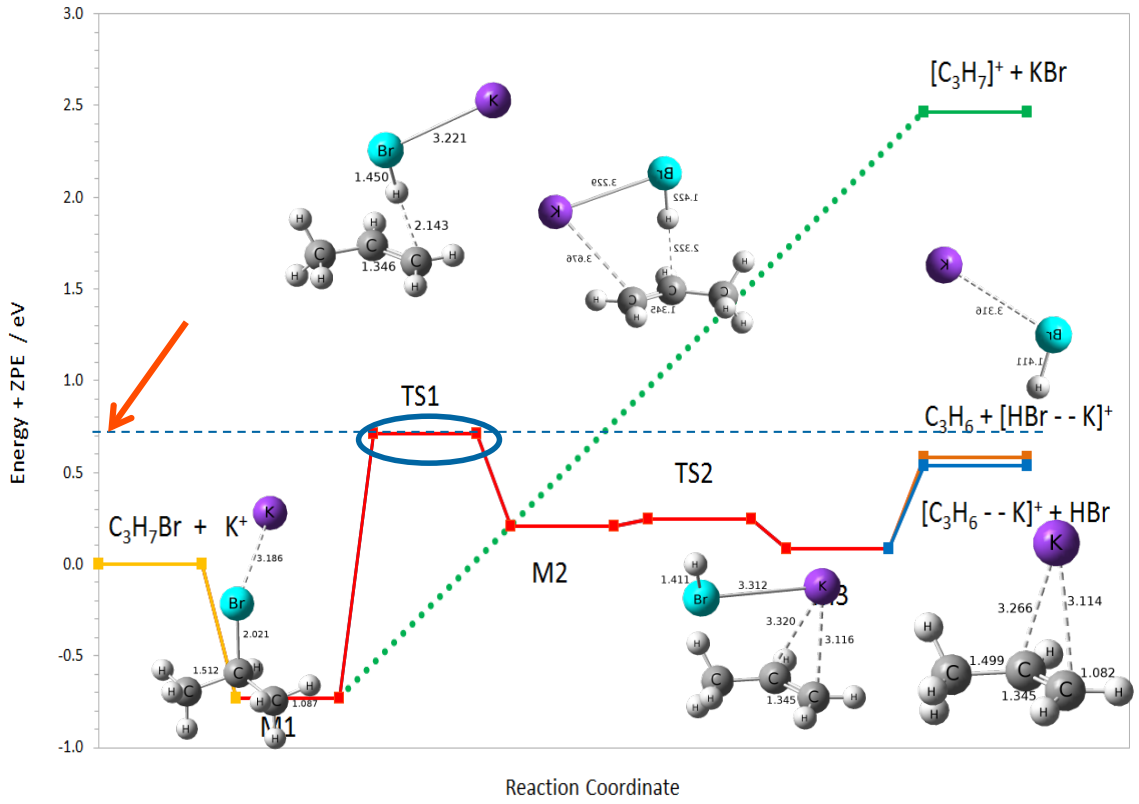
Measured *excitation functions* and *ab initio potential energy surface* profile *along the reaction coordinate* for the different reactive channels observed in $K^+ + i\text{-}C_3H_7Br$ collisions

excitation functions in $K^+ + i\text{-}C_3H_7Br$ collisions





Reaction channel $K^+ + i\text{-}C_3H_7Br \rightarrow [KC_3H_6]^+ + HBr$ was not observed with enough confidence...

Potential Energy Surface → *Gaussian 2013 code, MP2 level, 6-31 G(p-d)*

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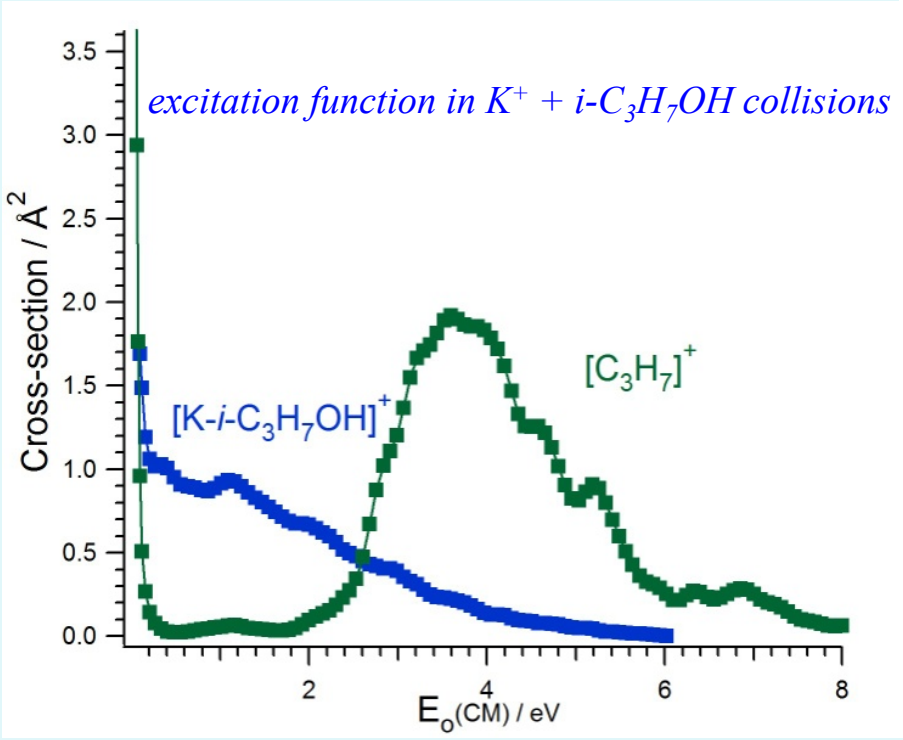
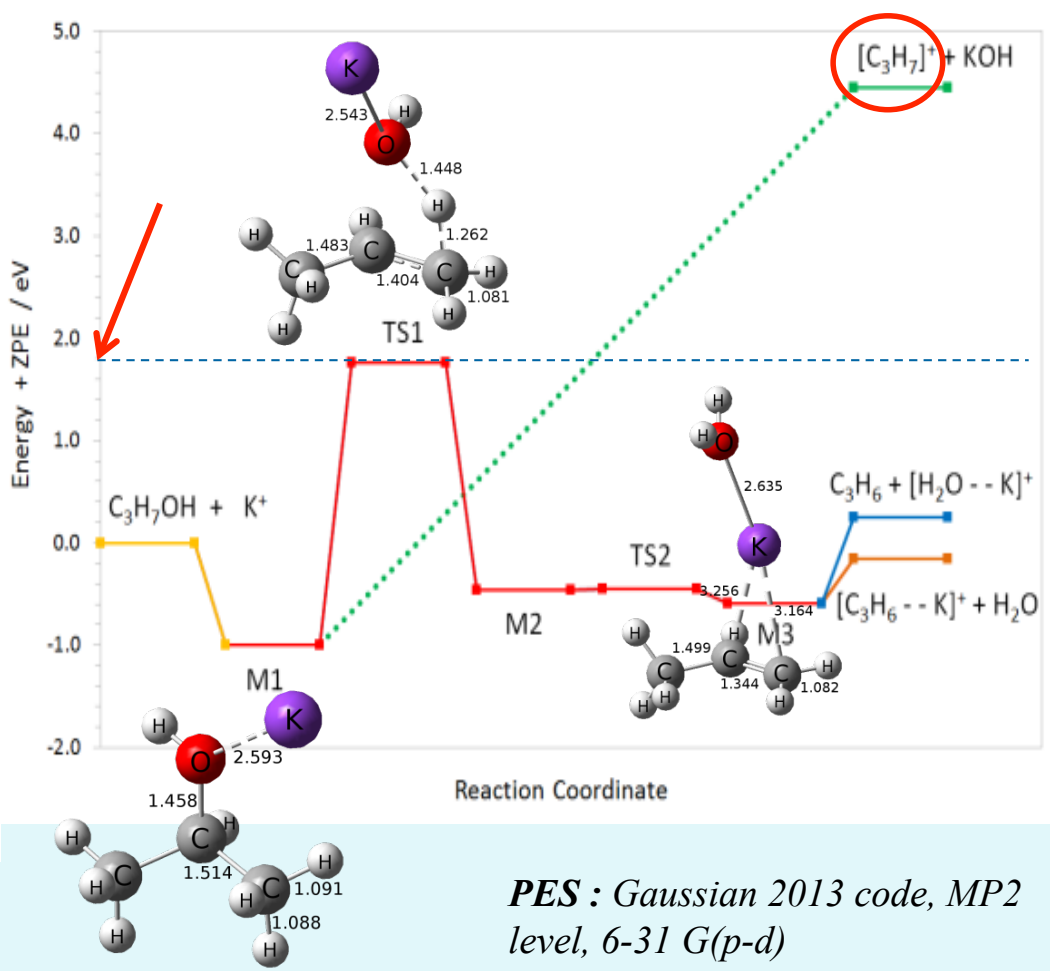
Measured *excitation functions* and *ab initio potential energy surface* profile along the reaction coordinate for the different reactive channels observed in $K^+ + i\text{-}C_3H_7OH$ collisions

Elimination reactions leading to $[KC_3H_6]^+$ and KOH^+ *were not observed to occur significantly*

$[K\text{-}i\text{-}C_3H_7OH]^+$ *adduct formation*





PES : *Gaussian 2013 code, MP2 level, 6-31 G(p-d)*

Decomposition reaction:
$K^+ + i\text{-}C_3H_7OH \rightarrow C_3H_7^+ + KOH$

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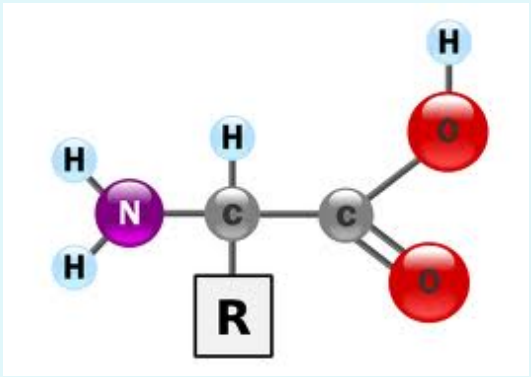
Estefanía López (PhD student) in the LAMP at the University of Trento

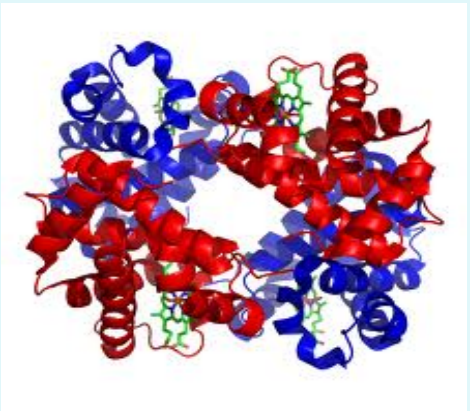
… *another ion-molecule reactions studies involve the cyanide group, … nitriles organic compounds with the* **–C≡N** *functional group*

interstellar clouds, comets & Titan's atmosphere

Intermediates of important organic acids



Amino Acids



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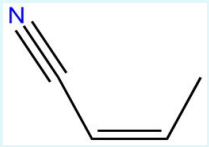
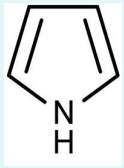
$C_4H_5NH^+$

5 isomers of the $C_4H_5NH^+$ ion (m/q=68) in Titan's atmosphere

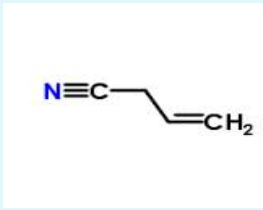
CROTONITRILE



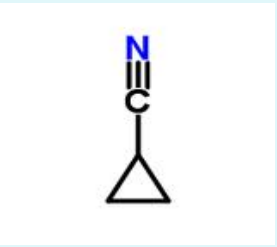
PYRROLE



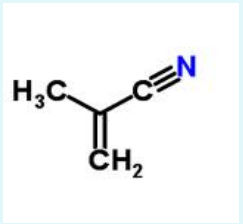
ALLYL CYANIDE



CYCLOPROPIL CYANIDE



METHACRYLONITRILE



… as molecules of *potential prebiotical interest*…

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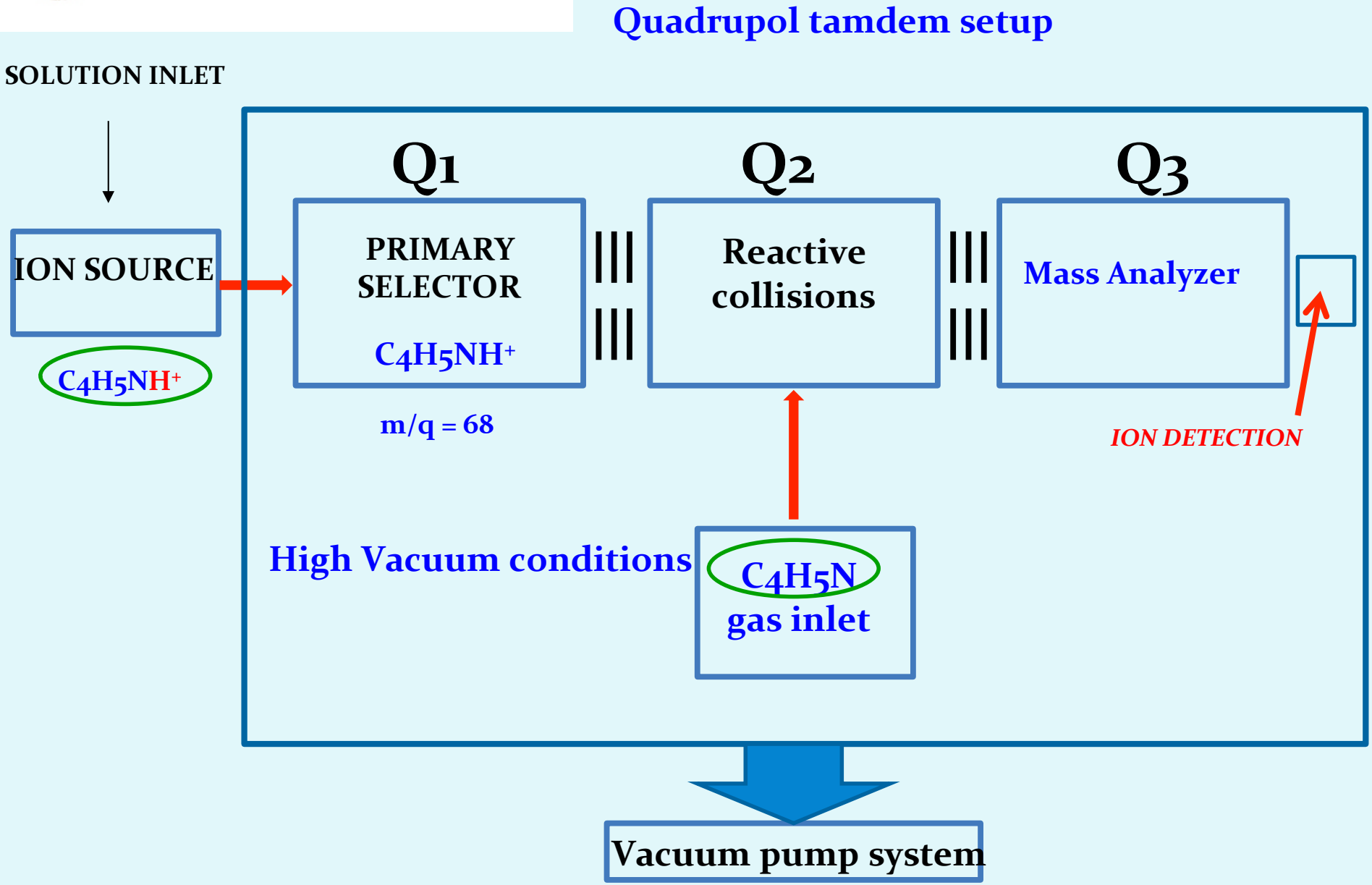
Quadrupol tamdem setup



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$C_4H_5NH^+ + C_4H_5N \longrightarrow (C_4H_5N)_2H^+$

m/z = 68

m/z = 135

- HCN

m/z = 108

$C_7H_9NH^+$

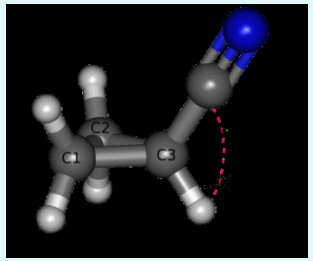
other products...

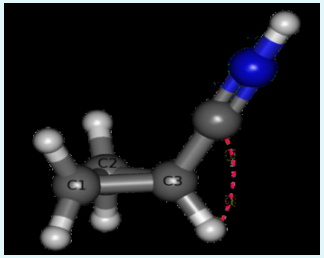
measured signals at m/z = 68 and 135

$C_4H_5N + C_4H_5NH^+ \rightarrow C_8H_{10}N_2H^+$

neutral and protonated *cyclopropyl cyanide*

both in their electronic singlet ground state





Equilibrium geometries
singlet ground state
Gamess 2013, *ab initio* RHF *and* MP2
/ 6-31 G (p,d)

The study of the ground singlet PES of the $C_8H_{10}N_2H^+$ system did not show any relevant information in addition to the expected presence of the ion-molecule adduct at different levels of theory considering singlet closed shell reference configurations but we must consider too...

... the potentially biradical character of the *cyclopropyl cyanide...*
... the possible singlet open shell reference configurations

... the inability of the protonated cyclopropyl cyanide to open the 3-carbon ring...
... that we are exploring the ground singlet PES of the system at the CASCI level using some (x e^-, y m.o.) active space & the IRC method...

... that Ψ_{CASCI} *electronic wave functions could be able to clearly show important contributions from open shell electronic configurations if these are really involved...*

... work is in progress in this direction.

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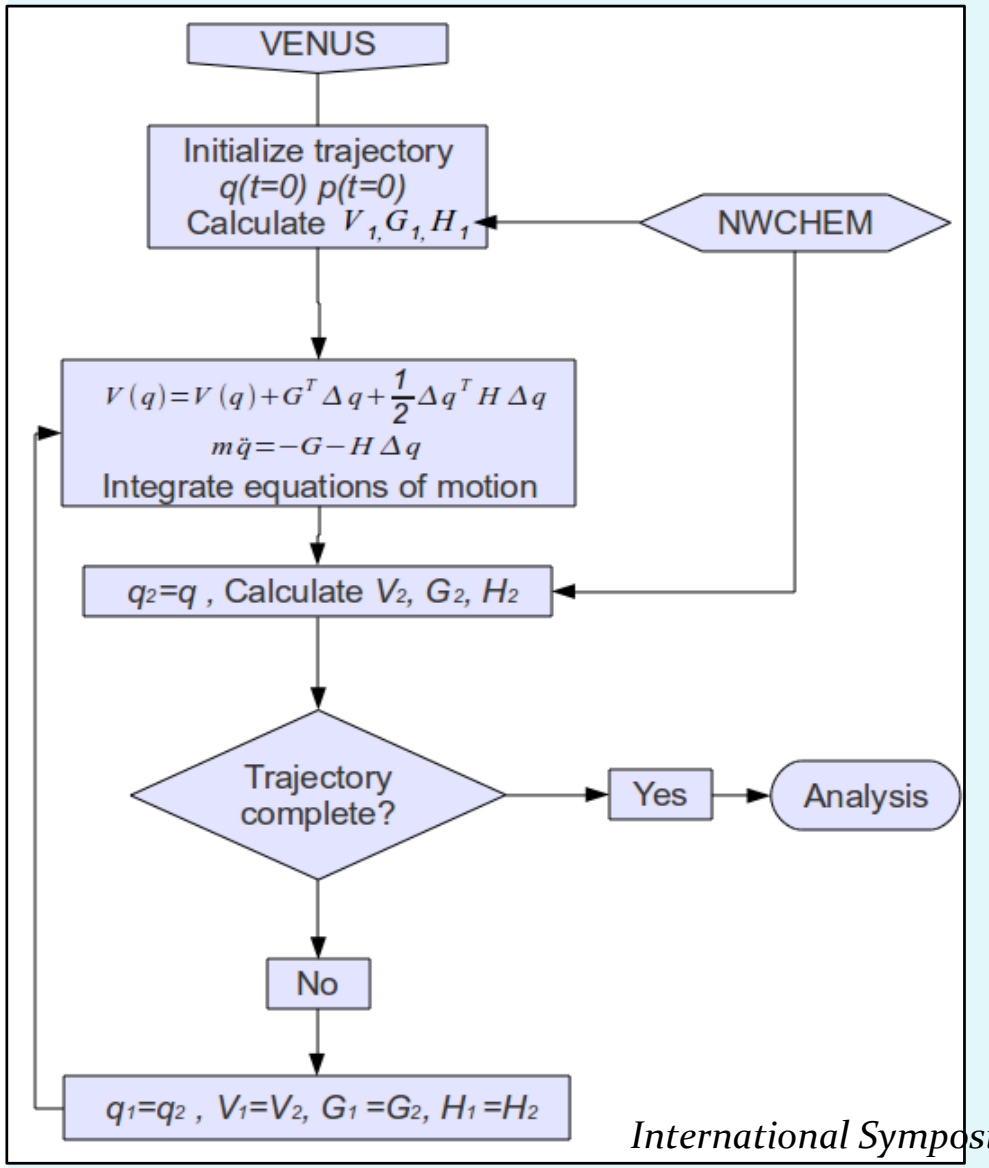
how trajectories are done?



... VENUS-NwChem package as provided by Prof. W. L. Hase

VENUS (for QCT calculations):

Selection of initial conditions:

... collision energy

... impact parameter

... thermal rotational energy content

... thermal vibrational energy content or selecting specific vibrational states

... random molecule-molecule orientation

... Set of coordinates (q) and momenta (p) for t=0

NwChem (for quantum chemistry calculations, semiempirical, *ab initio* or DFT)

... Some conditions are given for ending trajectories

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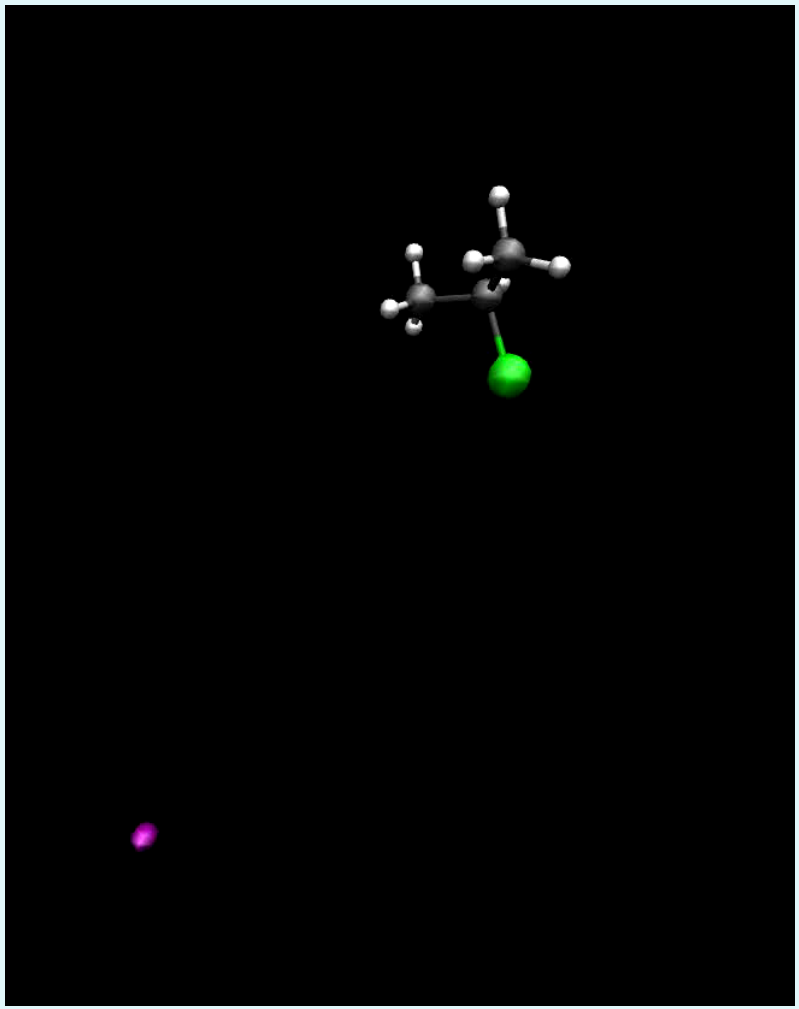

RC_1

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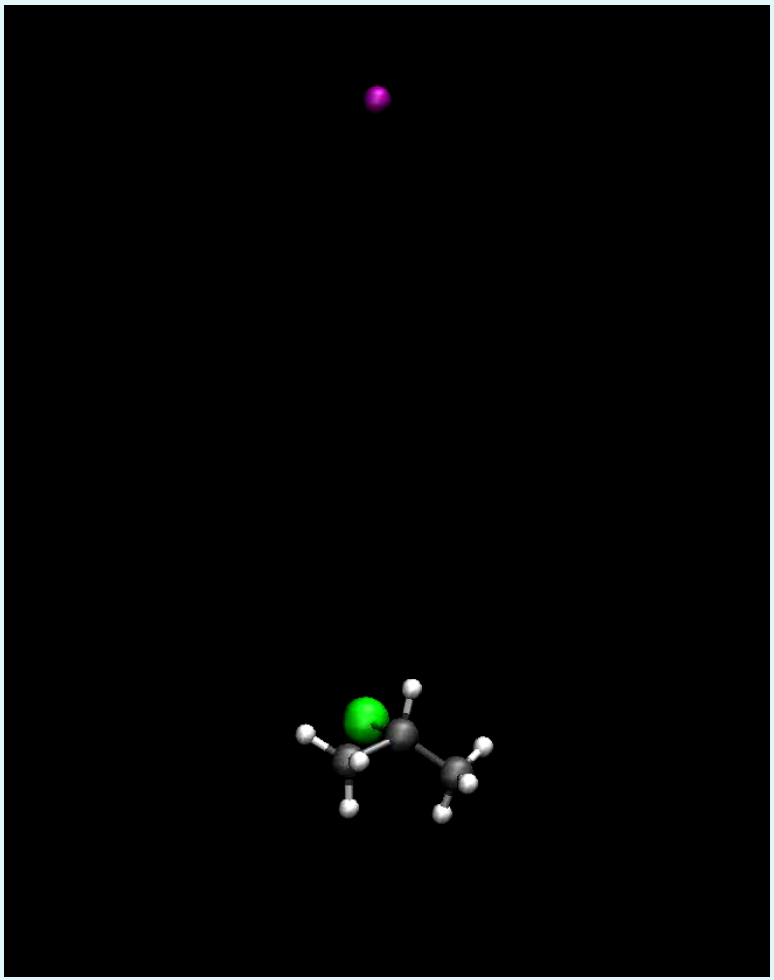

RC_2

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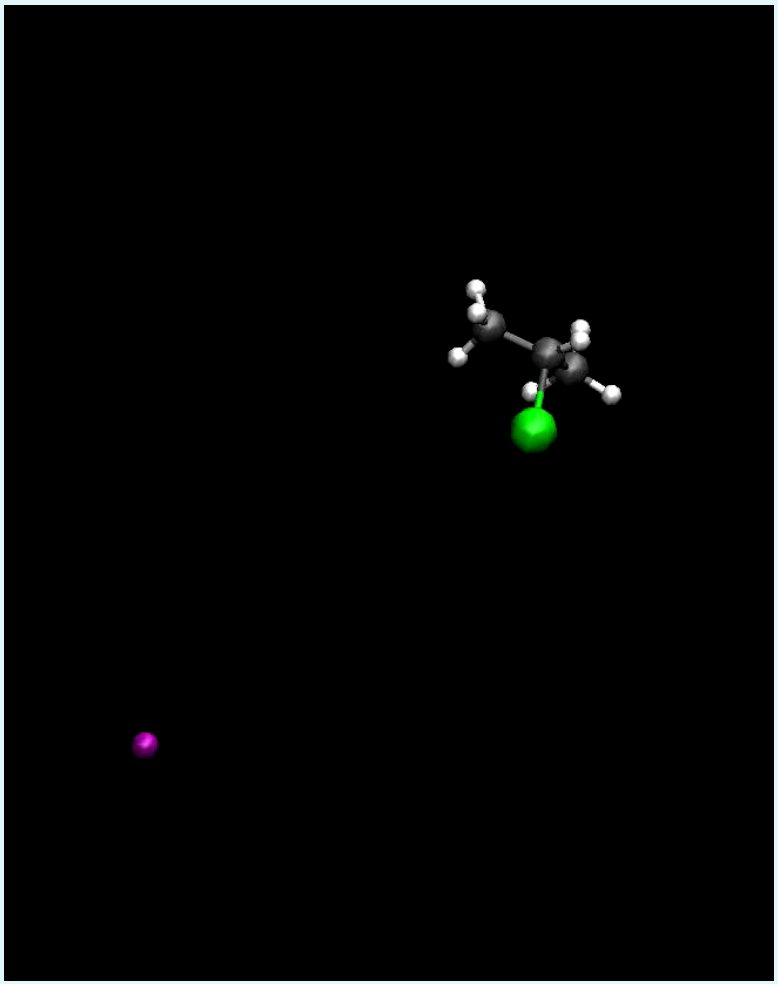

RC_3

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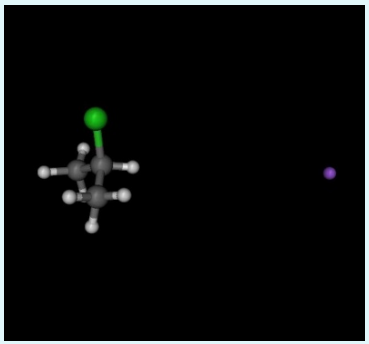
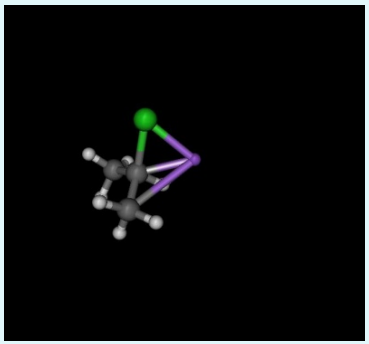
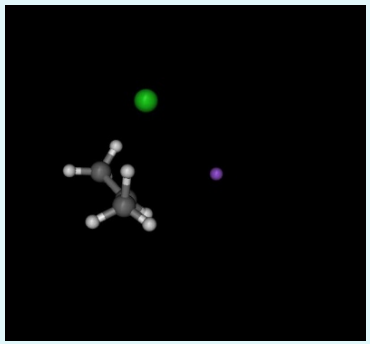
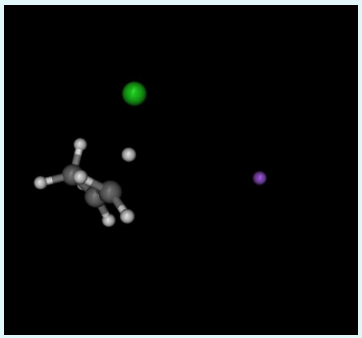
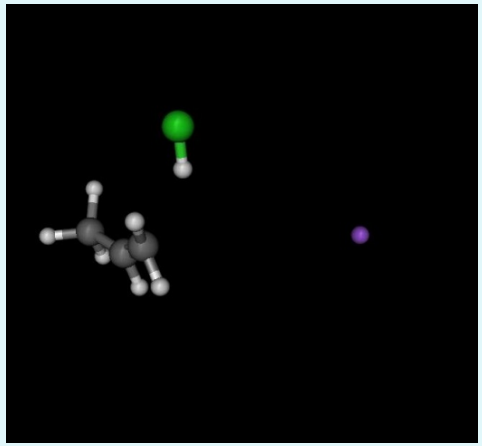
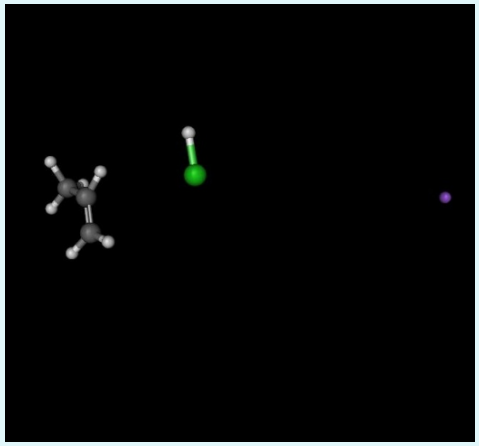

RC or NRC ?

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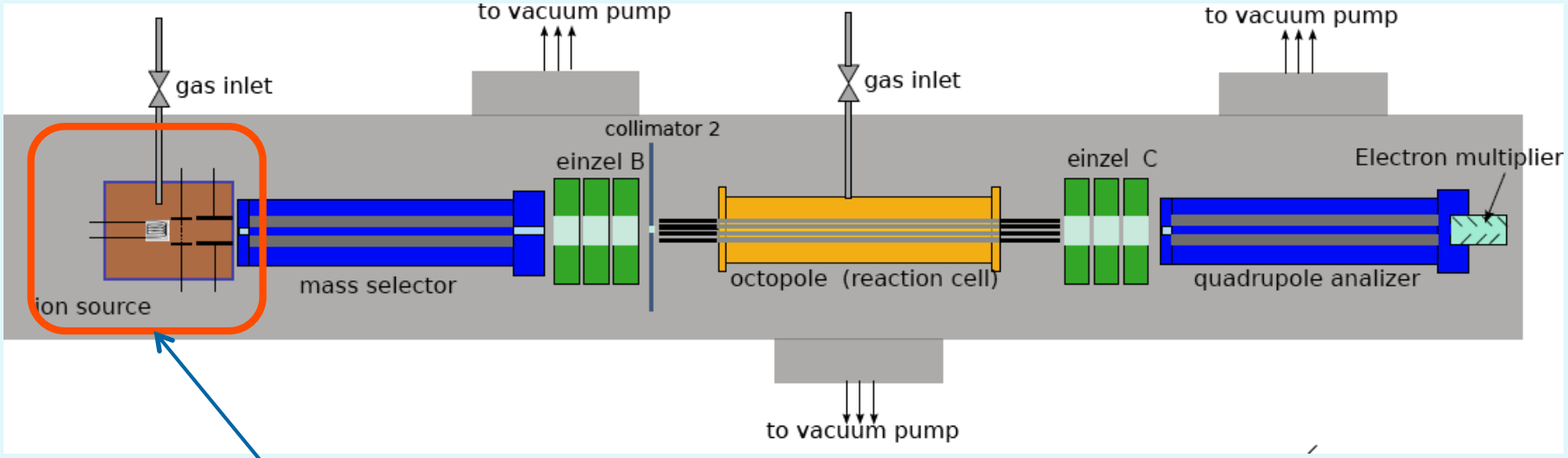
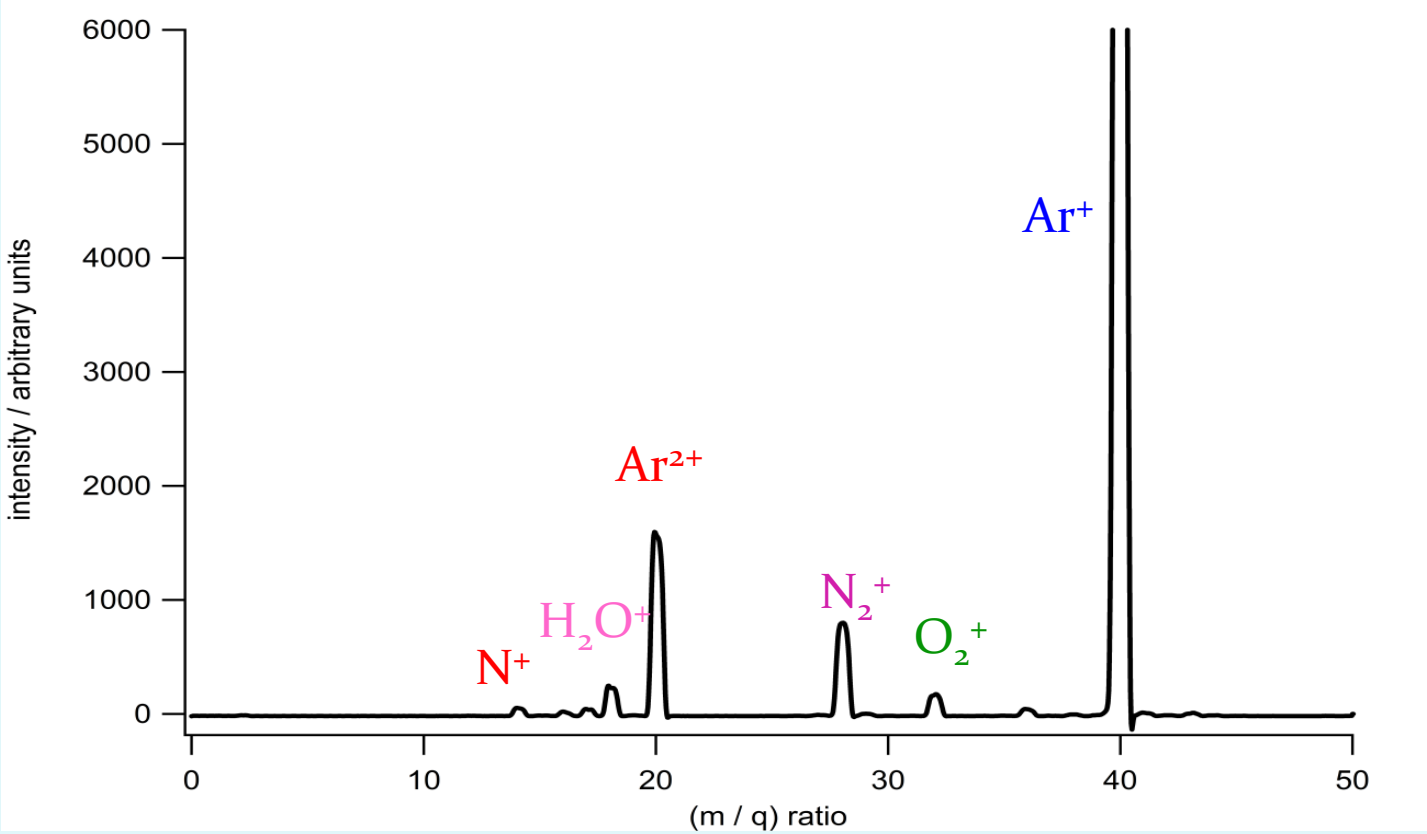
-Improvements in the local **RF-GIB** setup and *future perspectives*

... for the generation of different atomic and molecular ions



- electron impact ionization source / adapted from Pfeiffer Vacuum GmbH

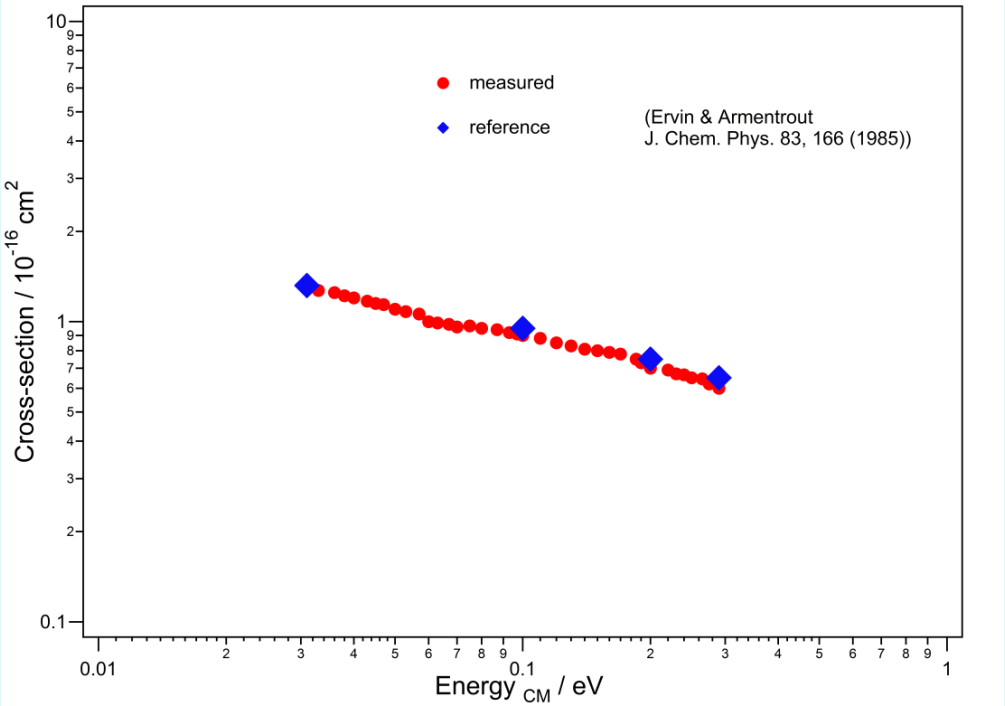
… an argon gas inlet together with some ambient air…



… from the quadrupole mass spectrum…

... calibration reaction with well known cross-section values (Erwin & Armentrout, J. Chem. Phys. 1985, 83, 166-189)

$$Ar^+(^2P) + H_2\,(^1\Sigma^+_g) \rightarrow\ HAr^+(^1\Sigma^+) + H\,(^2S_g)$$



Ar^+, He^+, Ne^+, CO^+, H_2^+, N_2^+, SO^+, SCO^+, N_2O^+, NH_2COH^+,...

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Spanish Ministry of Economía y Competividad (MINECO) Project CTQ2013-41317-P

Catalan Agency for Universities and research / Catalan Research Council

Consorci de Serveis Universitaris de Catalunya (CSUC) for allocating computer time

Thank you for your attention !