Multiple ionization of atoms and molecules by impact of light charged ions at the intermediate energy range

W. Wolff
H Luna
E C Montenegro

Instituto de Física
Universidade Federal do Rio de Janeiro

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Heavy Ion Fusion & Ion-Collision Research: request + requirements

Request:
Assemble an experimental database of various
PAIRS of projectile ions and target atoms and molecules

FOR
stringent tests between experimental results
+
between exp. and theoretical calculations of

absolute total and partial cross sections +
total ion production +

evaluating the ionization degree of atoms and molecules induced by the effective charge state of projectiles for the pure ionization, S and D capture channels

Requirement:
validation of experiments and theory +
rely on atomic and molecular codes +
search simple and /or scaling laws

- Motivation:
  Answer the question: Why it is relevant to measure absolute cross sections of MI of atoms and molecules by impact of low Z projectile- ions at the intermediate energy range?

- experiment setup + procedure aplied at the lab- IF-UFRJ

- experimental results
  - on multiple ionization of atoms and molecules
    induced by low charged bare and dressed projectiles A^{q+}
    q=2+ and 3+
    selected as benchmark targets: Ne and H_2O

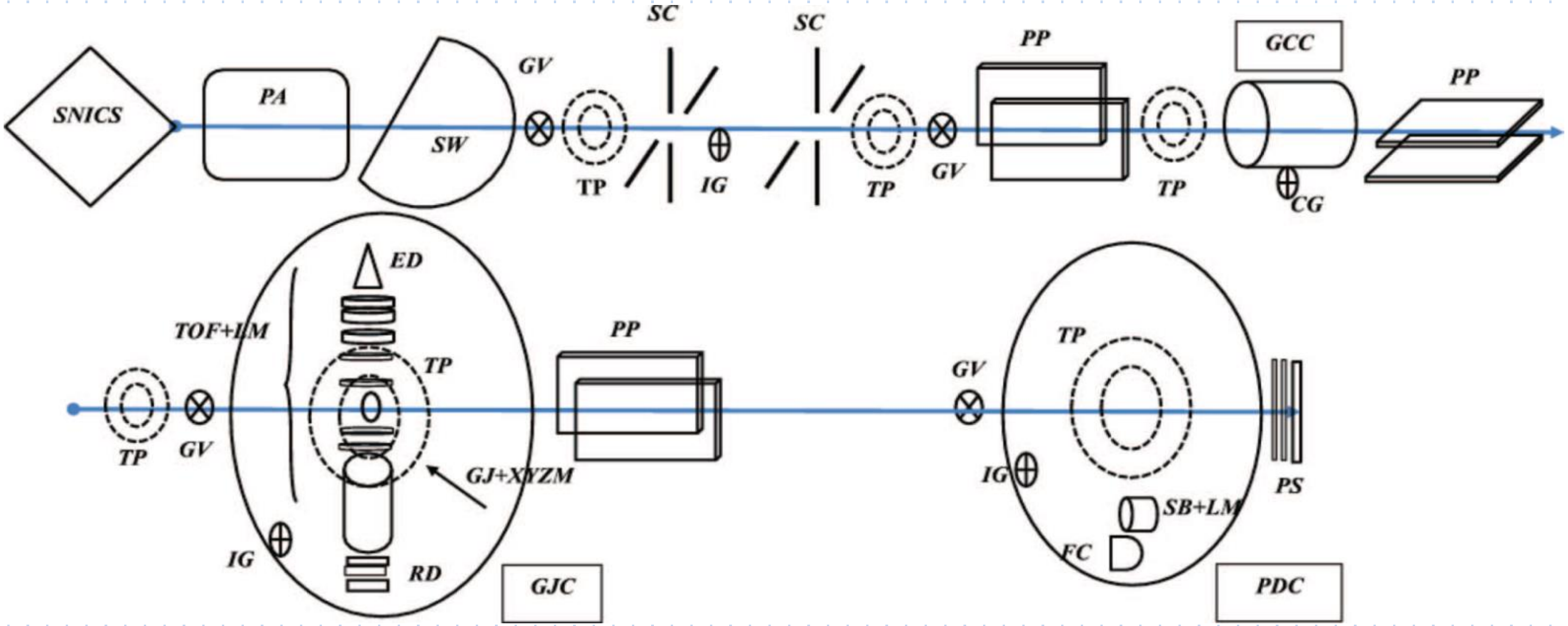
    + compare with
  - theoretical approaches developed for cross section evaluation

- focus of discussion on agreements between
  experiments and theory + limitations
  +
  Contribution of processes on double ionization

Extra topic: stability of complex molecules

Experiment

Experiments on Tandem Pelletron accelerator facility of the Physics Institute at the Rio de Janeiro Federal University



SNICS negative ion source
Double stage pelletron accelerator, terminal voltage up to 1,7 MV
Ion collision beam line is composed by 3 sections:
first chamber based on a gas cell - applied for total cross sections
second based on an effusive gas jet - used for partial cross sections
third for collecting projectiles - discriminates the channels

Experiment

Experiments on Tandem Pelletron accelerator facility of the Physics Institute at the Rio de Janeiro Federal University

total CS : growth rate method

+

partial CS : coincidence experiments

TOF technique

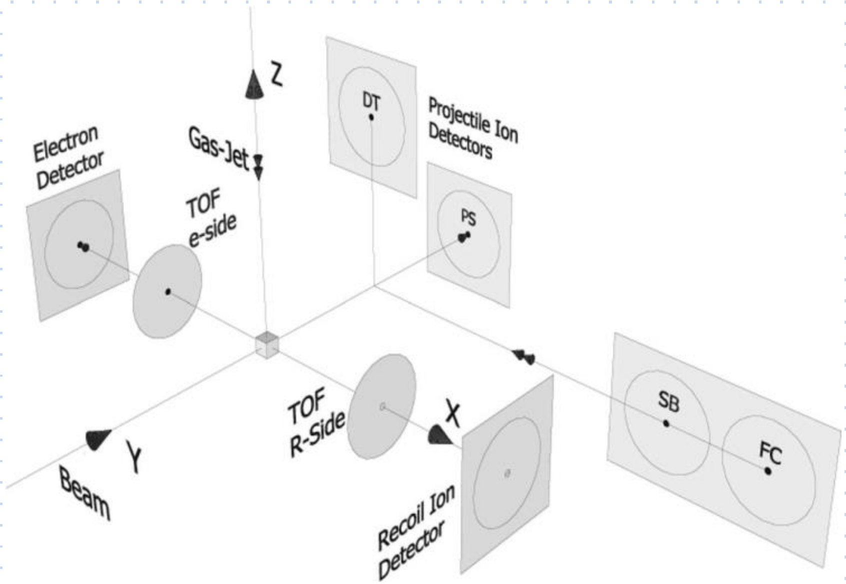
record

single spectra and
ions-pairs (molecules)

collect at he same time
electrons – target ions (recoils/fragments)
+
outgoing projectile-ions –target-ions

for pure ionization and capture channels

scheme of detection setup



Metodology

Experiments on Tandem Pelletron accelerator facility of the Physics Institute at the Rio de Janeiro Federal University

(*i*) for electron capture (EC), the electron-recoil ion trum gives

$$(n \times l_{eff}) \times I_0 \times \varepsilon^r = \left(\frac{\sum_q N_q^e}{\sum_q \varepsilon_q^e \sigma_q^e} \right)$$

and the recoil-projectile spectrum gives

$$(n \times l_{eff}) \times I_0 \times \varepsilon^r = \left(\frac{\sum_q N_q^{EC}}{\sum_q \sigma_q^{EC}} \right).$$

growth rate method

$$\sum_q \sigma_q^{EC} = \sigma^{TEC}$$

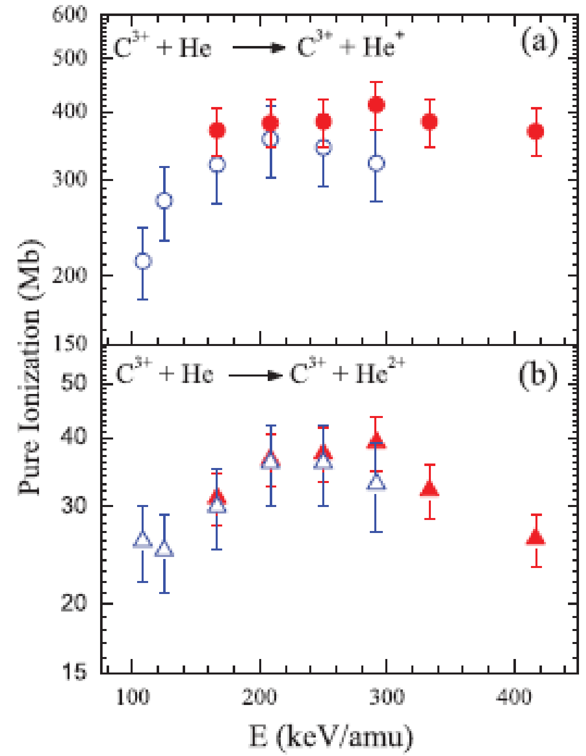
(*ii*) For pure ionization (*PI*), the electron-recoil ion trum gives

$$(n \times l_{eff})' \times I_0' \times \varepsilon^r = \left(\frac{\sum_q M_q^e}{\sum_q \varepsilon_q^e \sigma_q^e} \right)$$

and the recoil ion-projectile spectrum gives

$$(n \times l_{eff})' \times I_0' \times \varepsilon^r = \left(\frac{\sum_q M_q^{PI}}{\sum_q \sigma_q^{PI}} \right).$$

$$\sigma^{TPI} = \sum_q \sigma_q^{PI} = \sigma^{TEC} \times \frac{\sum_q M_q^{PI}}{\sum_q N_q^{EC}} \times \frac{\sum_q N_q^e}{\sum_q M_q^e}$$



Absolute partial cross sections for single electron capture and pure ionization. Open circles and triangles circles: dos Santos et al 2010 ; full circles and triangles : data to validate method

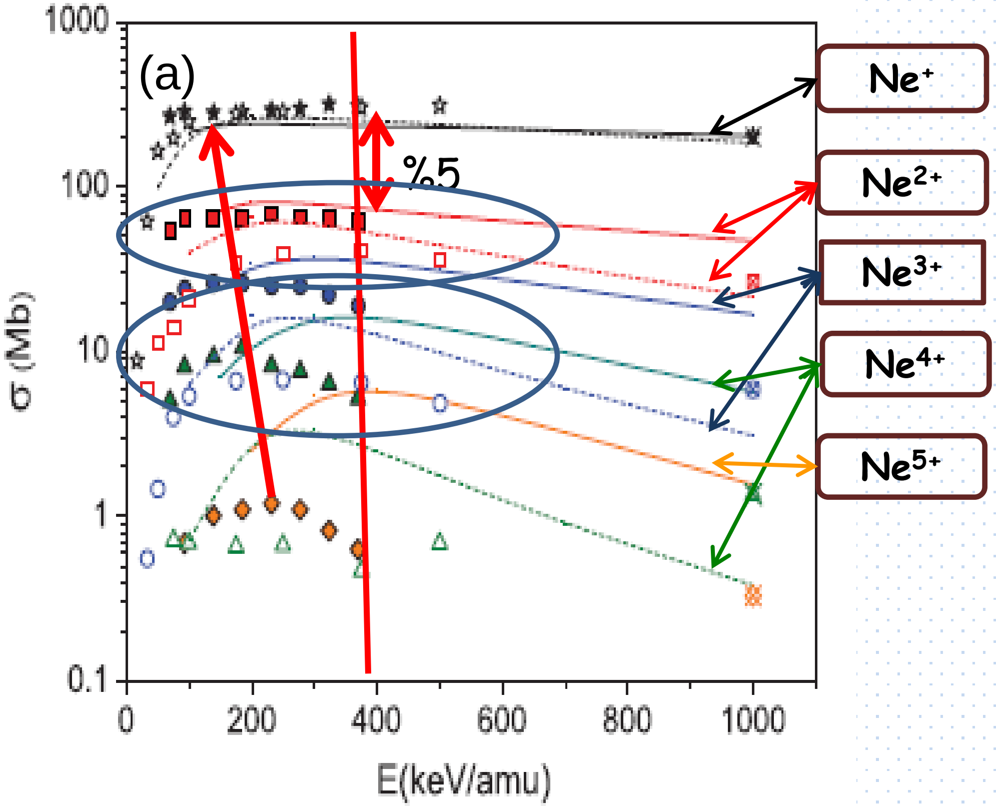
ATOM

Ne Case

Experimental results and theoretical calculations

Multiple ionization in pure ionization channel induced by the He, B, F with q=2+ projectiles

Partial ionization cross sections of Ne

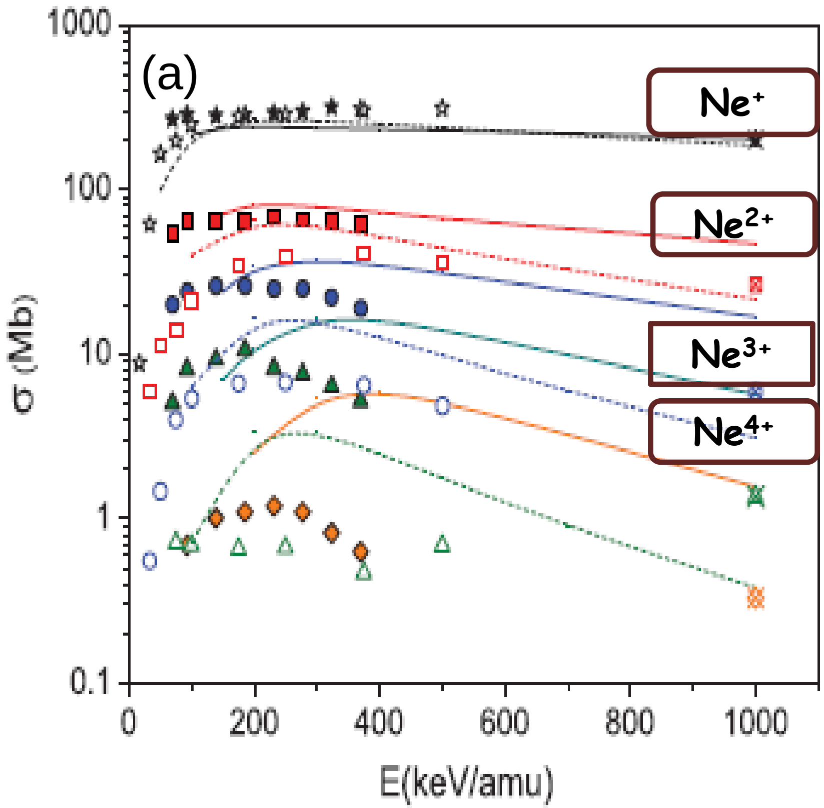


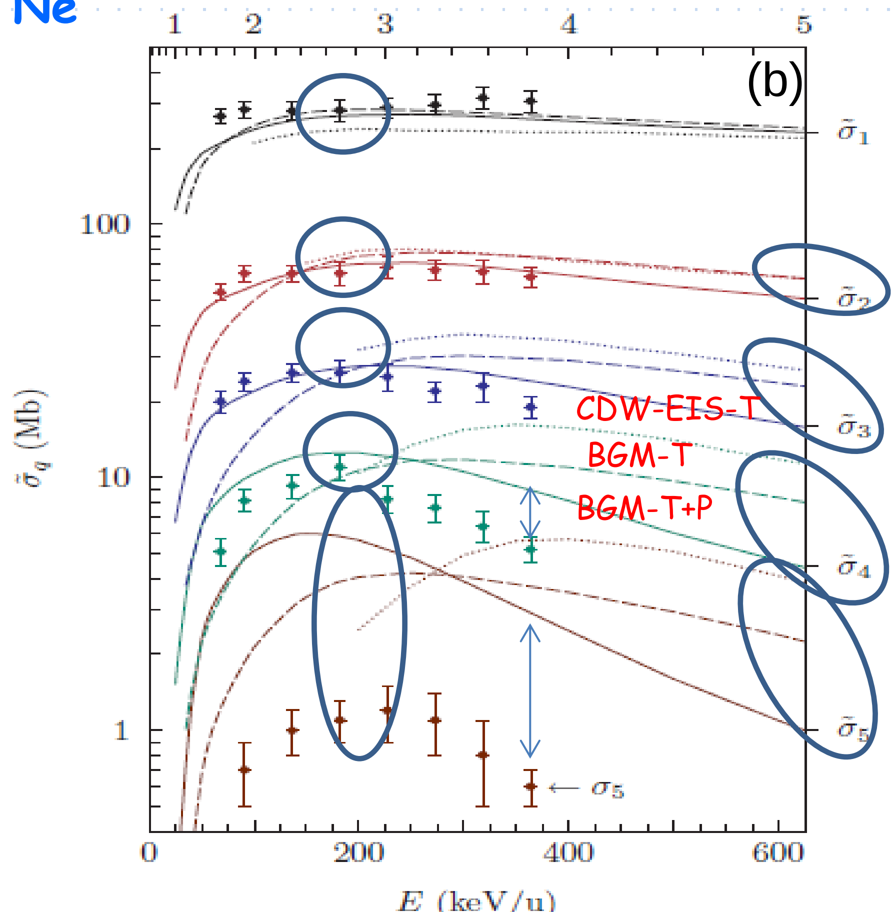
Cross sections for multiple ionization of Ne as a function of the projectile energy/amu. Experiment: stars, Ne+; squares, Ne2+; circles, Ne3+; triangles, Ne4+; lozenges, Ne5+. Closed symbols B2+, open symbols He2+ ; open crossed symbols F2+. (a) Theory: full line, CDW-EIS with Auger for B2+ projectiles (Ne+up to Ne5+); dashed lines, CDW-EIS with Auger for He2+ projectiles (Ne+ up to Ne4+).

CONCLUSION: calculation overestimates CS for He2+ and B2+ for the triple and etc Ne ionization

Multiple ionization in pure ionization channel induced by He, B, F with q=2+ projectiles

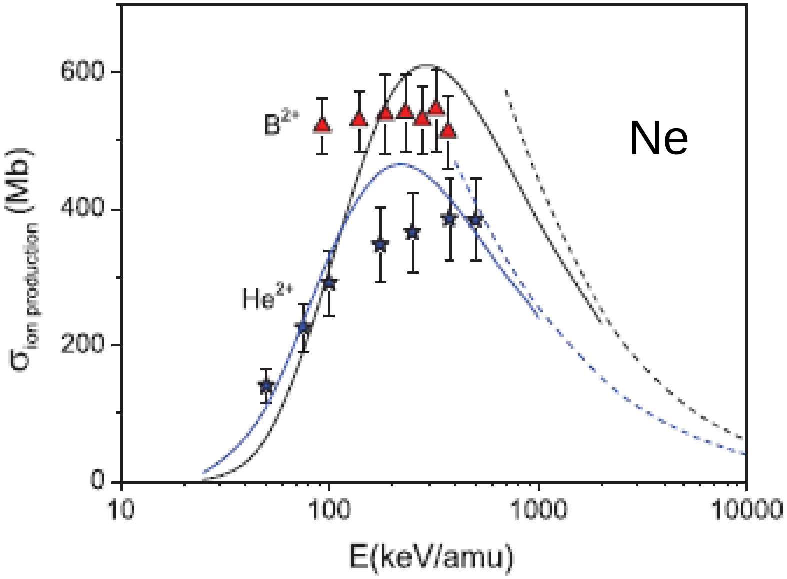
Partial ionization cross sections of Ne

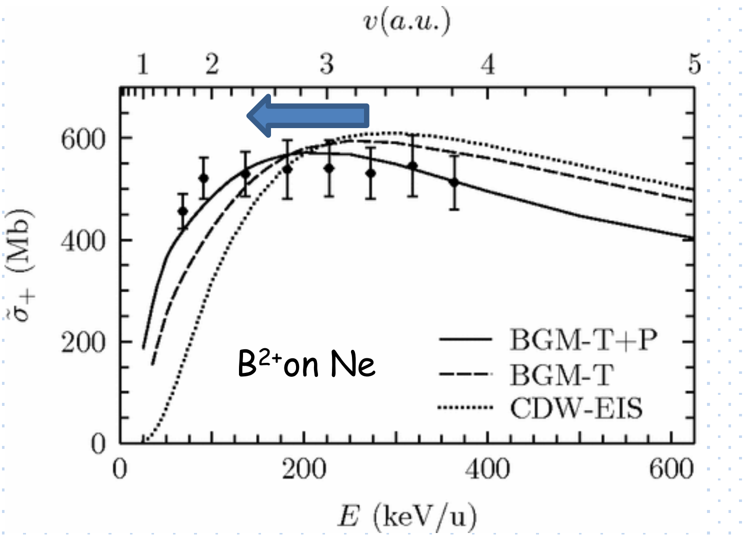




Cross sections for multiple ionization of Ne as a function of the projectile energy/amu.
Experiment: stars, Ne^{+}; squares, Ne^{2+}; circles, Ne^{3+}; triangles, Ne^{4+}; lozenges, Ne^{5+}. Closed symbols B^{+2}, open symbols He^{+2} + ; open crossed symbols F^{+2}. (a) Theory: full line, CDW-EIS with Auger for B2+ projectiles (Ne^{+up} to Ne^{5+}); dashed lines, CDW-EIS with Auger for He2+ projectiles (Ne^{+up} to Ne^{4+}). (b) Theory with final-state analysis that considers active target and projectile electrons BGM-T+P (solid line), and target electrons BGM-T (dashed line). Target-e CDW-EIS [11] (dotted line).

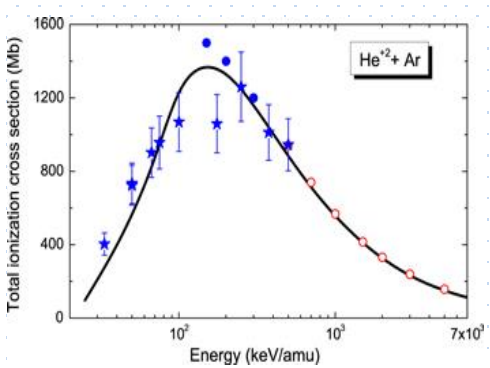
Ion production ionization CS
bare He^{2+} and dressed B^{2+} projectiles – Ne and Ar





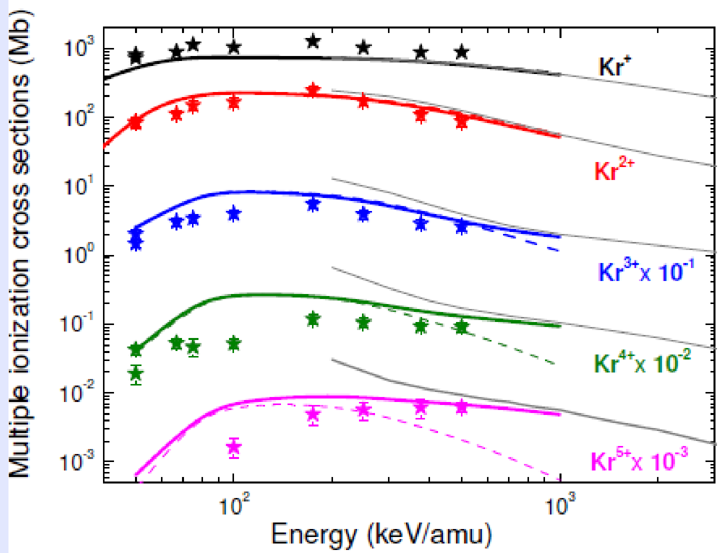
Cross section for positive ion production as a function of the impact energy/amu. Experiment: triangles, B^{+2} +; stars, He^{+2} . Theory: CDW-EIS calculations: full curves; Born approximation: dashed curves.

Total cross section for positive ion production σ_+ Experimental data Wolff *et al.* Theory with final-state analysis considers active Target and Projectile electrons (T+P - solid line), and target electrons T only (dashed line). CDW-EIS-T (dotted line). Figure from Schenk et al Phys. Rev A 2013

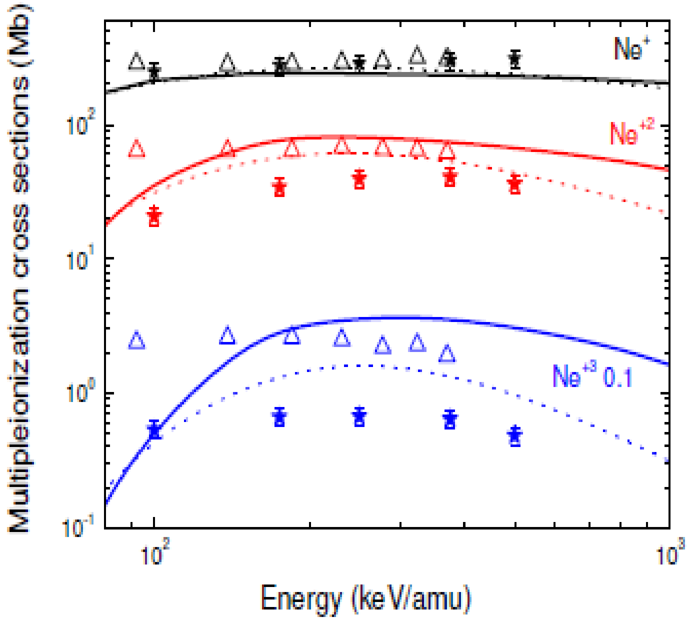


Total ionization cross section of Ar by He^{+2}. Curves: present results for *pure* ionization. Symbols, experimental data: full stars, DuBois ; full circles, Rudd; empty circles, Rudd *et al* for proton impact ×4 J Phys. B 2016.

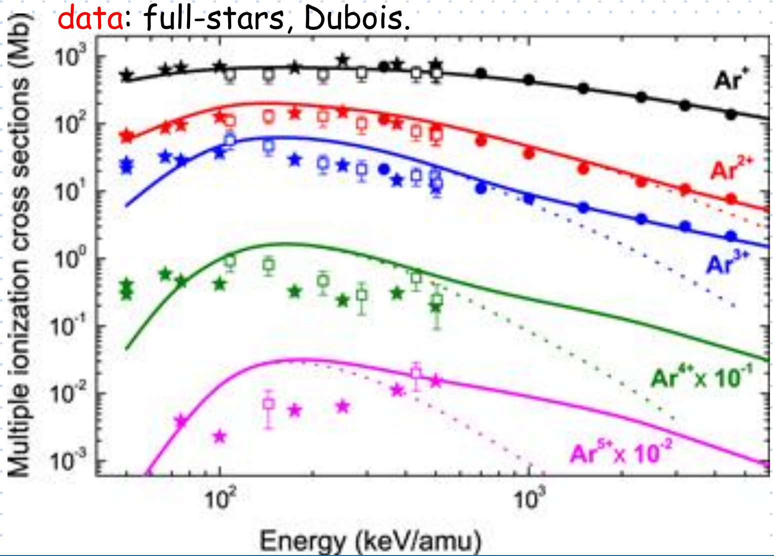
WHY Ne? - Multiple ionization in pure ionization channel of Kr, Ar and Ne by Li and He with q=2+



CDW-EIS with and without Auger Single, double, triple, quadruple ,and quintuple ionization cross sections of Kr by He^{2+} impact. solid and dashed lines, Experimental data: full-stars, Dubois.

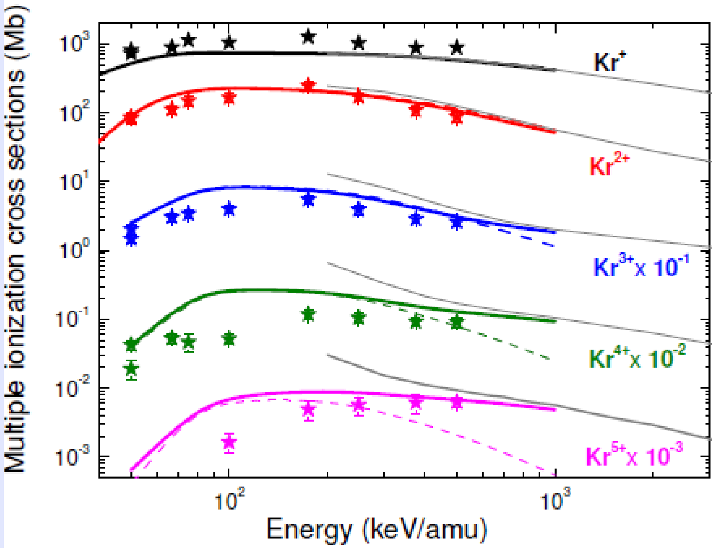


Single, double and triple and ionization cross sections of Ne by B^{2+} and He^{2+} ions, calculated with CDW-EIS including PCI. Experimental data: Wolf *et al* , t: open triangles B^{2+}, full-stars, Dubois et al for He^{2+}.

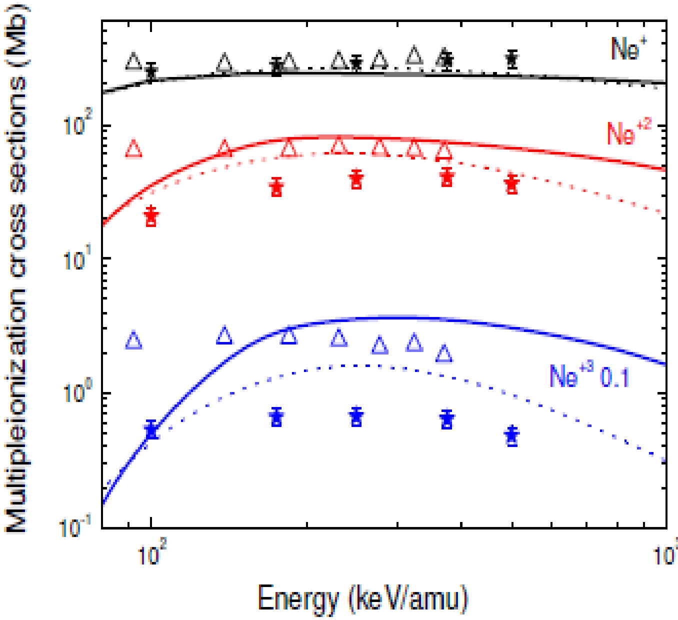


Multiple ionization cross section of Ar by He^{2+}. Curves: solid-lines, present theoretical results including direct ionization and PCI; dotted-lines, present results for direct ionization only. Symbols, experimental data: full circles, Andersen *et al*; full stars, DuBois ; open squares, Li^{2+} impact data Losqui et al

WHY Ne? - Multiple ionization in pure ionization channel of Kr, Ar and Ne by Li and He with q=2+



CDW-EIS with and without Auger Single, double, triple, quadruple ,and quintuple ionization cross sections of Kr by He^{2+} impact. solid and dashed lines, Experimental data: full-stars, Dubois.



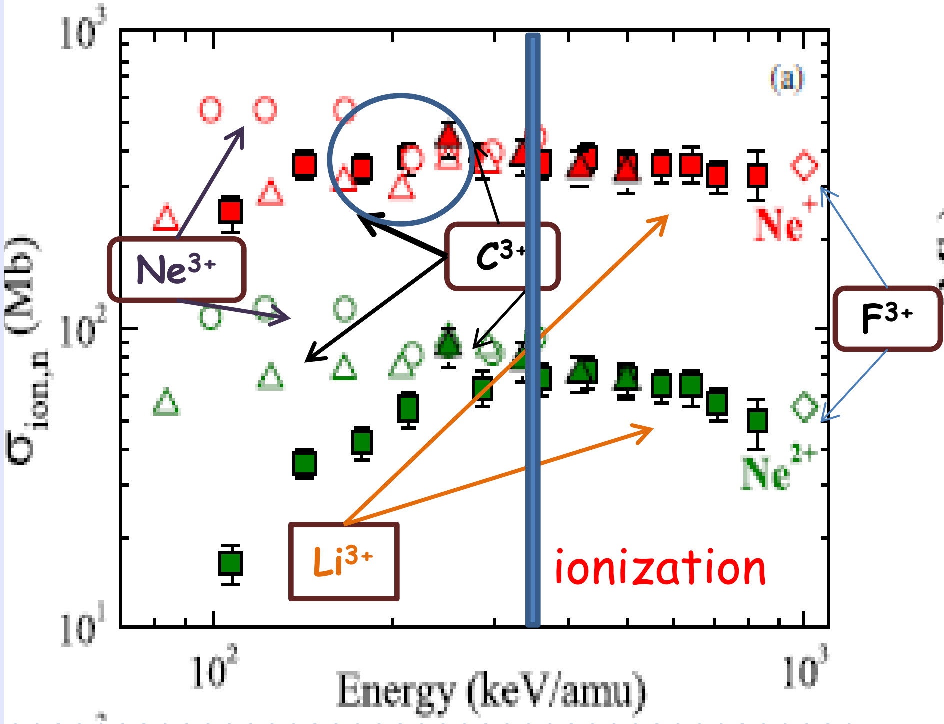
Single, double and triple and ionization cross sections of Ne by B^{+} and He^{2+} ions, calculated with CDW-EIS including PCI. Experimental data: Wolf *et al* , t: open triangles B^{2+}, full-stars, Dubois et al for He^{2+} +.

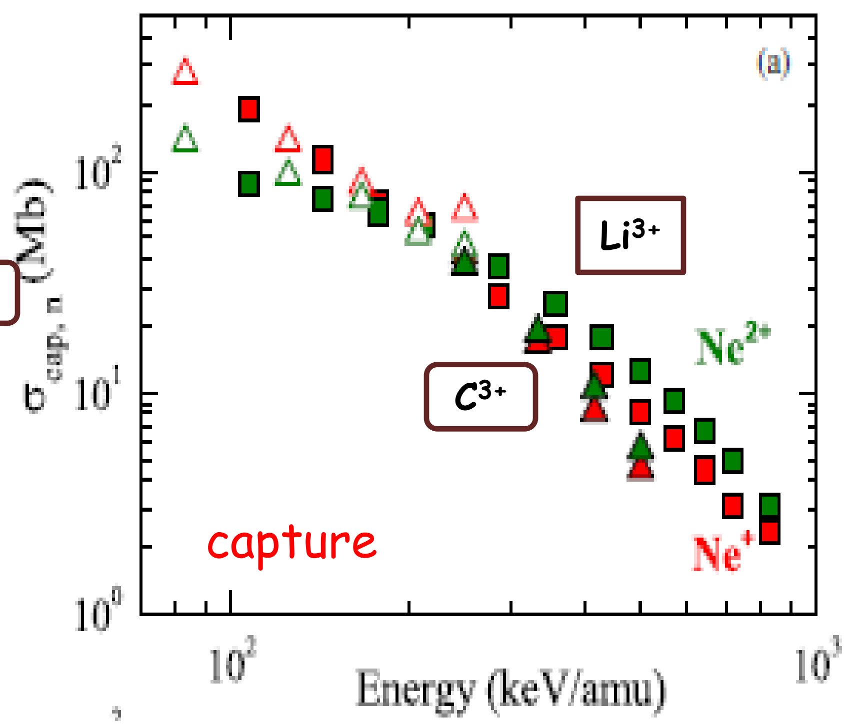
CONCLUSION CDW-EIS :

For Kr target, results are good in agreement with exp. data
For Ne CDW-EIS overestimates CS in the region where pure ionization dominates.
Ne serves as benchmark target
for multiple-ionization research to clear up questions such as validity of multinomial statistics or importance of correlation among electrons, questions that probed to have different answers for Kr and Ne.

Multiple ionization in pure ionization and electron capture of atoms Induced by Li, C, F, Ne with q=3+ projectiles

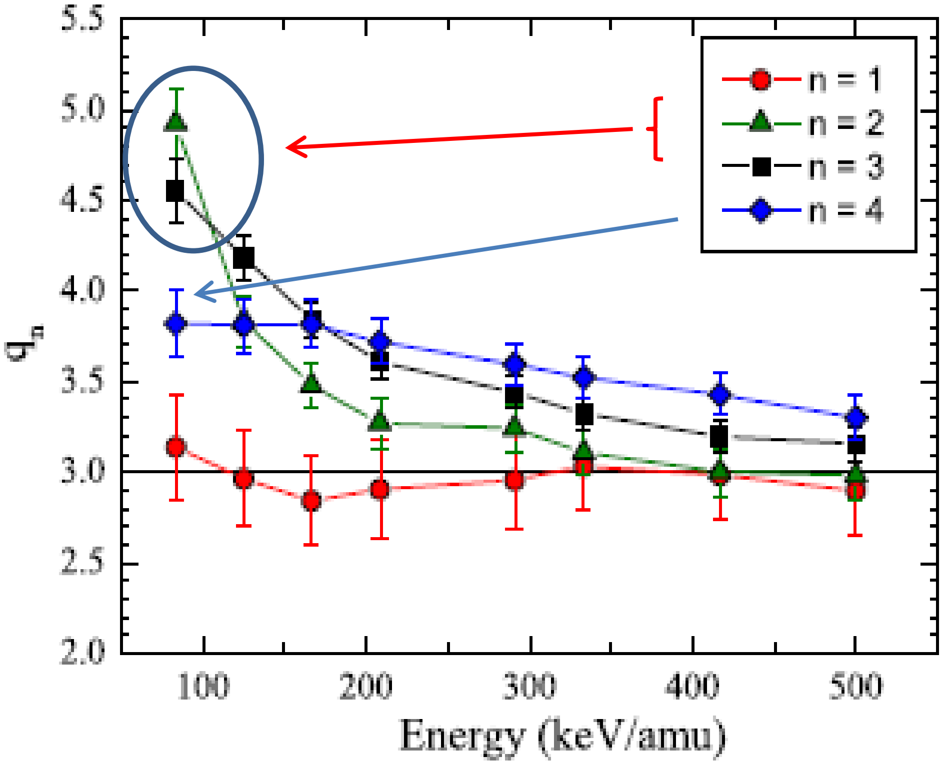
single and multiple ionization of Ne





Cross sections for direct multiple ionization of Ne, as a function of the projectile energy, for the ionization channel. Experiment: closed squares, Li^{3+}; closed triangles, C^{3+}, open circles, Ne^{3+} Ullrich *et al*; open diamonds, F^{3+}+ Heber *et al.* Theory: open triangles, C^{3+} TC-BGM approach Kirchner *et al*

Dependence of the projectile effective charge with the ionization state n of the recoil ion in the case of dressed projectiles
Screening effect - C^{3+} on Ne



Exp. Data give indication of the strength of the screening effect for *n*-fold ionization

Observation:
Inversion of the effective charge q with target ionization degree n (n= 2 and 3) at lower energies,

MOLECULE

H_2O Case

Experimental results and theoretical calculations

+

Focus attention on how some dynamic signatures, such as shape of the cross section for fragment-ion production as a function of the energy of the projectile are related to the production of

primary vacancies in the outer /inner valence shells

Single and double ionization of molecules

Partial cross sections obtained using similar approach as Ne atoms, but there is a major difference:

recoil-ion detection efficiencies are different corrected for molecules

Production of two single ions lead to a scenario where (at least) one of the produced ions H^+ or OH^+ is not detected *double ionization* event measured as single ionization event, producing artificial enhancement of single-ion channels, $H_2O^+ \rightarrow H^+ + OH$.

Probability of detecting only OH^+ takes into account detection of single OH^+ constrained to lack of detection of the transmitted fast H^+

$OH^+ + H$ channel, corrected yields

$$Y^{\mathrm{corr}}(\mathrm{OH}^+ + \mathrm{H}) = \frac{Y^{\mathrm{meas}}(\mathrm{OH}^+ + \mathrm{H})}{\bar{\epsilon}} - \frac{\bar{\epsilon}(1-\bar{\epsilon})}{\bar{\epsilon}} Y^{\mathrm{corr}}(\mathrm{H}^+ + \mathrm{OH}^+), \quad (1)$$

where $Y^{\mathrm{corr}}(\mathrm{H}^+ + \mathrm{OH}^+)$ is the corrected yield for $\mathrm{H}^+ + \mathrm{OH}^+$ production,

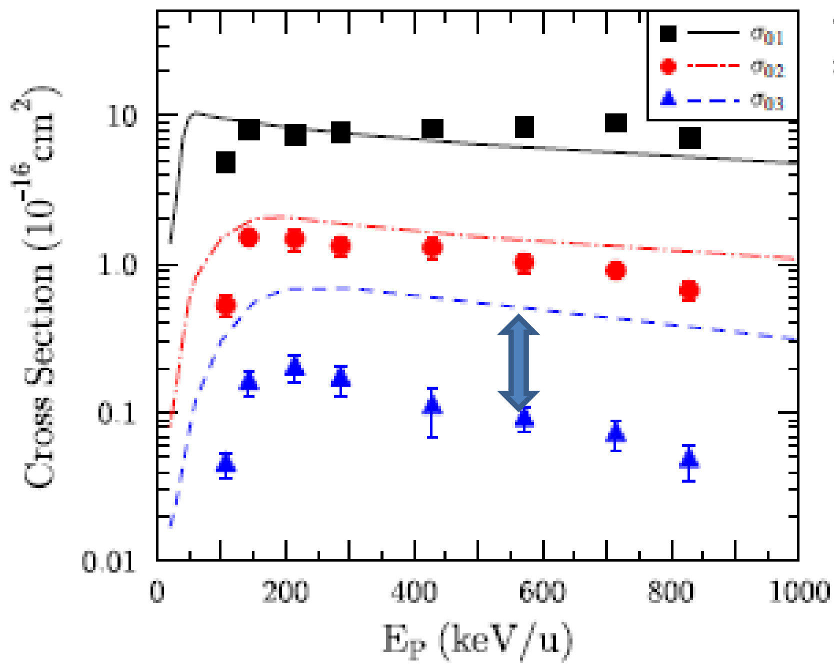
$$Y^{\mathrm{corr}}(\mathrm{H}^+ + \mathrm{OH}^+) = \frac{Y^{\mathrm{meas}}(\mathrm{H}^+ + \mathrm{OH}^+)}{\bar{\epsilon}^2}. \quad (2)$$

$$Y^{\mathrm{corr}}(\mathrm{H_2O}^+) = \frac{Y^{\mathrm{meas}}(\mathrm{H_2O}^+)}{\bar{\epsilon}} \quad (3)$$

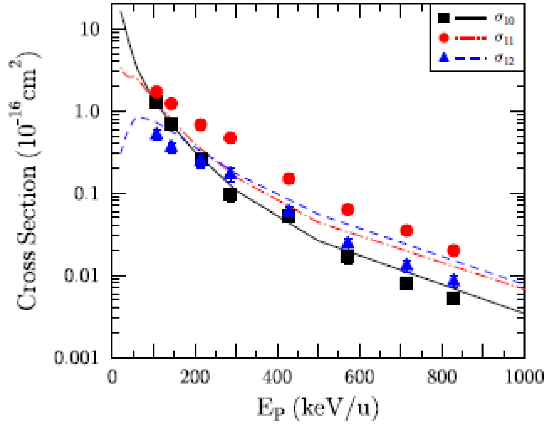
and

$$Y^{\mathrm{corr}}(\mathrm{H}^+) = \left[\frac{Y^{\mathrm{meas}}(\mathrm{H}^+)}{\bar{\epsilon}}\right] - \left[\frac{\bar{\epsilon}(1-\bar{\epsilon})}{\bar{\epsilon}^3}\right] \times \left[Y^{\mathrm{meas}}(\mathrm{H}^+ + \mathrm{OH}^+) + \sum_q Y_q^{\mathrm{meas}}(\mathrm{H}^+ + \mathrm{O}^{q+})\right]. \quad (4)$$

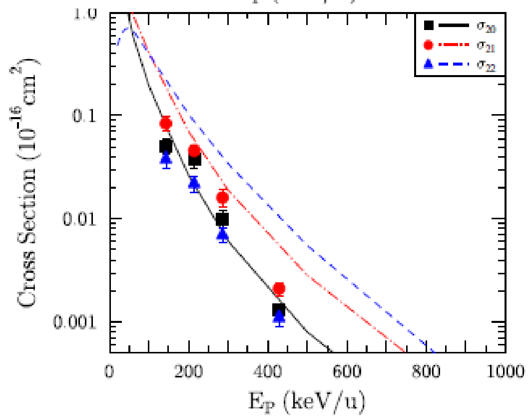
Impact of Li^{3+} on H_2O
Channels + Removal of electrons of water molecule



Pure-ionization cross sections σ_{01}, σ_{02}, and σ_{03} as functions of impact energy



Single capture cross sections σ_{10}, σ_{11}, and σ_{12} as functions of impact energy



Double-capture cross sections σ_{20}, σ_{21}, and σ_{22} as functions of impact energy

Symbol: experimental results and lines calculations (including Auger- electron emission).

Good agreement between theory and experiment for total single capture and for pure single and double ionization.

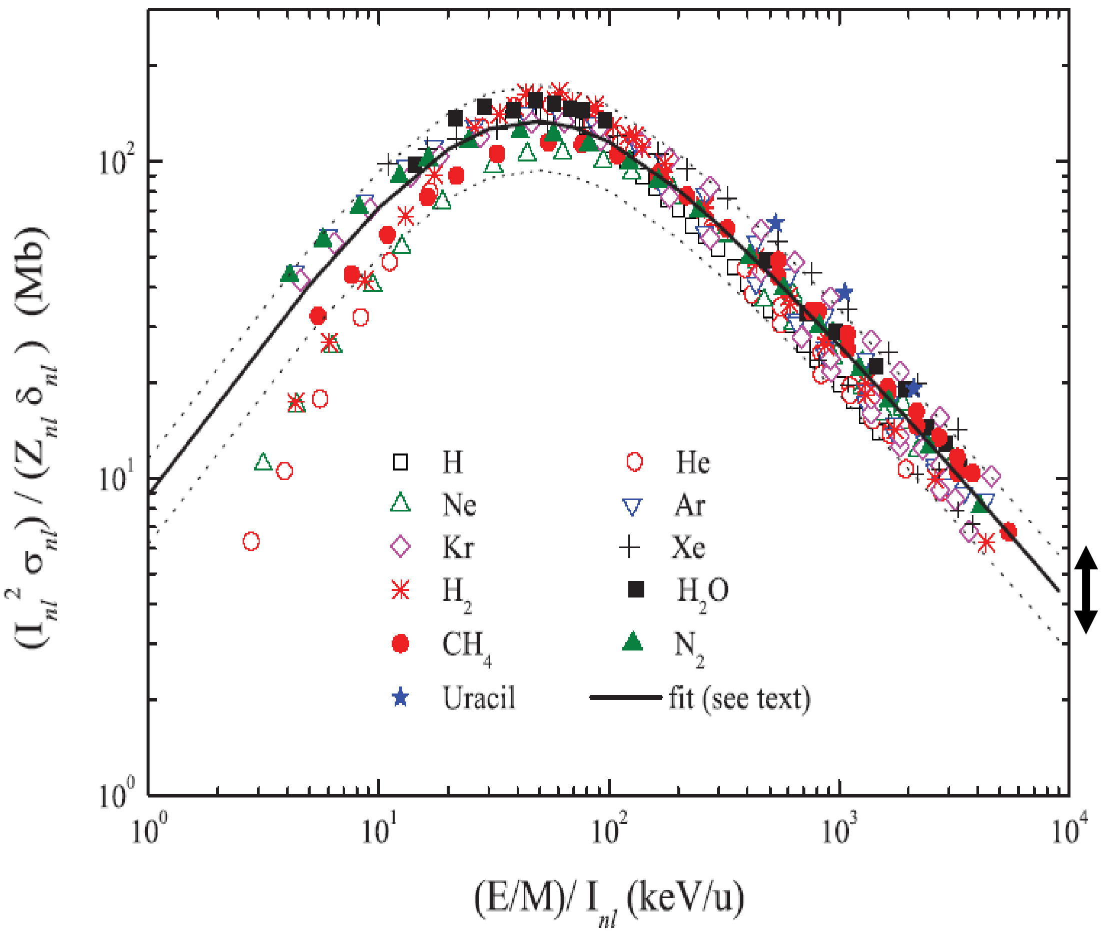
Cross sections for higher degrees of ionization overestimated by calculations.

Inclusion of Auger effect improves agreement with experimental data, for capture channels σ_{10},σ_{20},σ_{21},

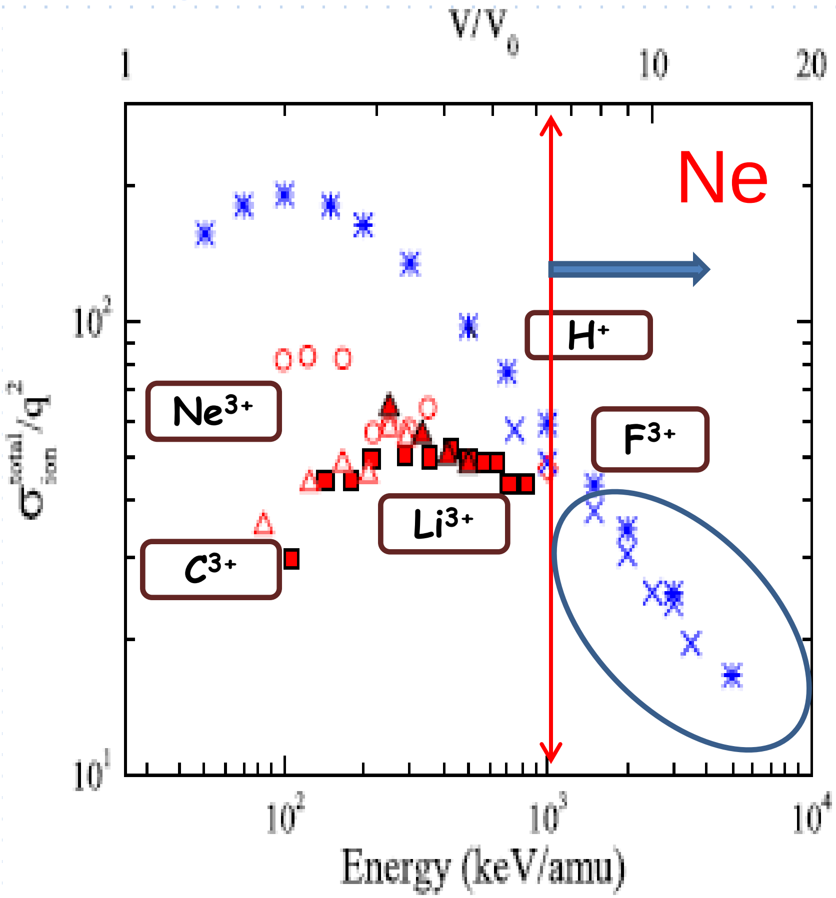
but factor of 2–3 discrepancies observed for transfer-ionization channel σ_{11}.

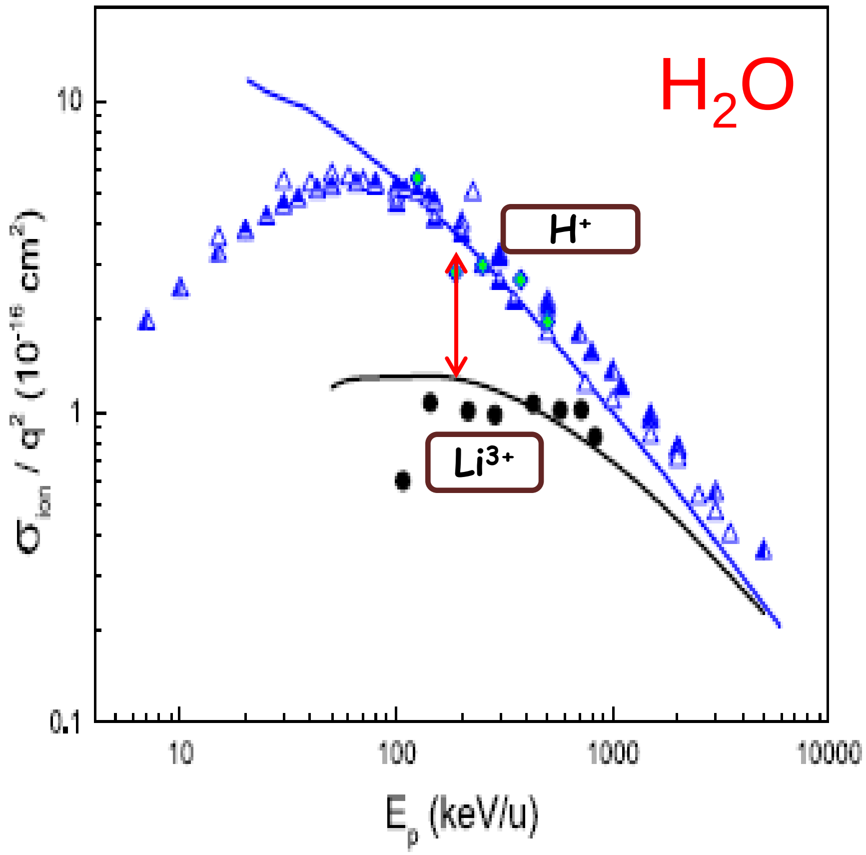
Scaling law of the total ionization cross section of atoms and molecules by proton impact

Exp. data scattered ±30% around a function



Scaling the total ionization cross section - dressed and bare heavy ions





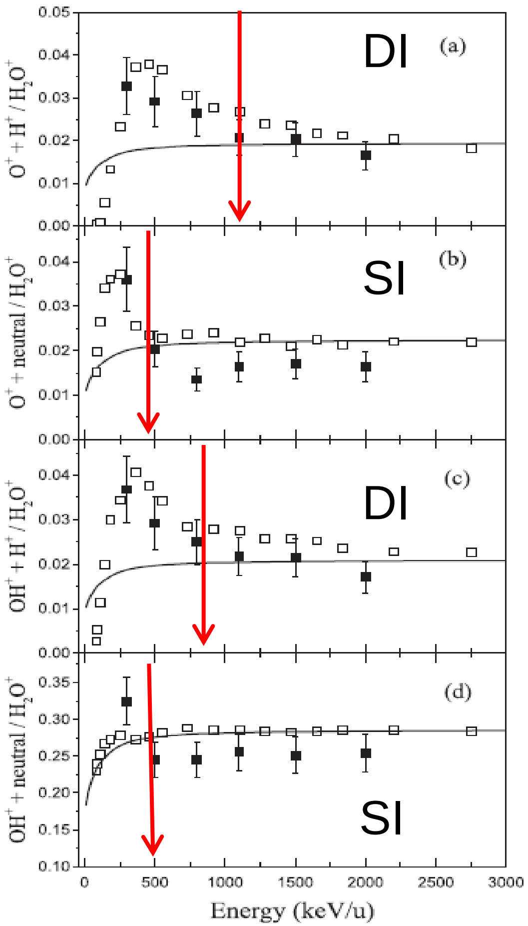
Tendency toward charge independent scaling law at high energies similar for neon and water targets ionization induced by the same projectiles in the same energy range, q^2 scaling rule seems fulfilled at energies above 1000 keV/u.

On the other hand, at lower velocities, the difference from the q^2 scaling reaches factor of ~ 5.

CONCLUSION: Simple first-order theories cannot be used and more sophisticated theoretical approaches such as CDW-EIS and TC-BGM (T+P) must be applied.

Double ionization of water

Inflexion point



Ratios with respect to the H_2O^+ production for double ionization and single ionization channel

closed symbols; proton impact
open symbols; electron impact and
calculation for proton impact, solid line.

Branching ratios (BRs) agree in magnitude for electron and proton projectiles

In asymptotic limit of higher velocities BRs constant for single-and double-ionization ratios

Both processes prompted by single vacancy, not PDI

For proton impact, the mechanism for ionization occurring from a single-vacancy process should have an energy dependence of

$\sim \ln(E)/E$

and
for ionization occurring from sequential double vacancies

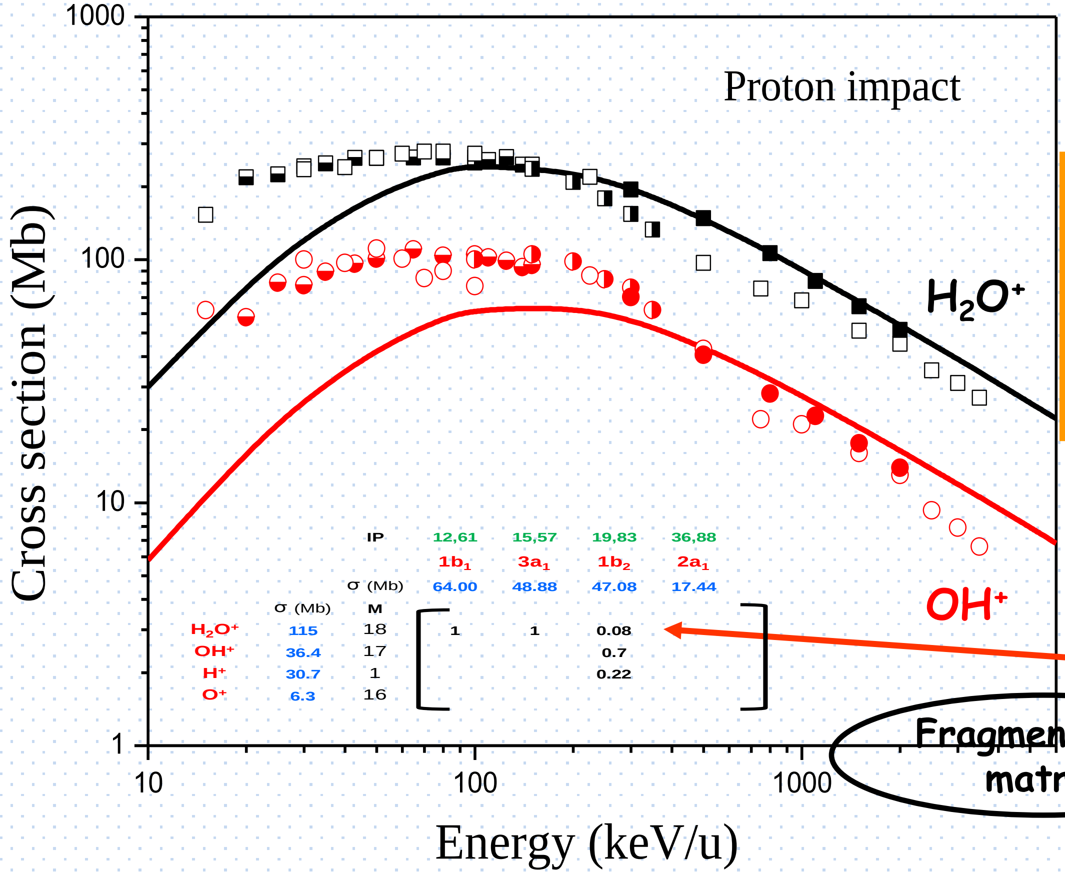
$\sim 1/E2$

Auger - prompted by single vacancy

Question: Inflexion points change with targets + with dissociative channels?

Proton impact ionization of water

Single vacancy model → description of partial fragmentation cross sections



Experiment: Tavares et al, Luna et al. Gobet et al, Werner et al.

Fragmentation matrix

Semi-Empirical Model based on FBA approximation

Ionization energy

$$\frac{\sigma_{nl} I_{nl}^2}{Z_{nl}\delta_{nl}} = F\left(\frac{E/M}{I_{nl}}\right), \qquad (1)$$

where

$$F(x) = \frac{A\ln(1+Bx)}{x} - \frac{AB}{(1+Cx)^4}, \qquad (2)$$

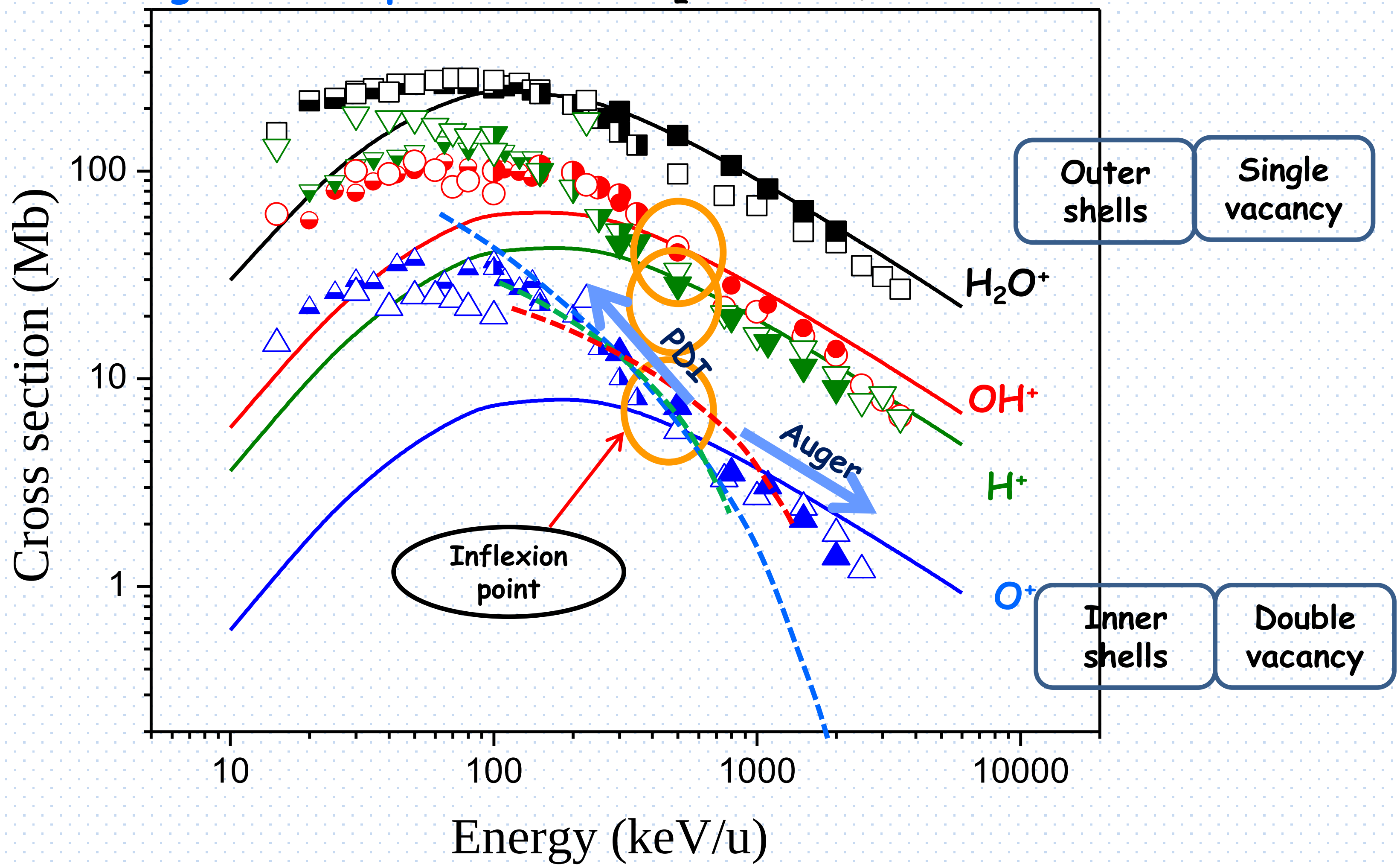
Universal function $x = (E/M)/I_{nl}$

$$\sigma_m = \sum_{nl} f_{m,nl}\sigma_{nl},$$

$$\sum_{nl} f_{m,nl} = 1.$$

Model: Montenegro et al, Wolff et al

Fragment-ion production: H_2O^+, OH^+, H^+ and O^+

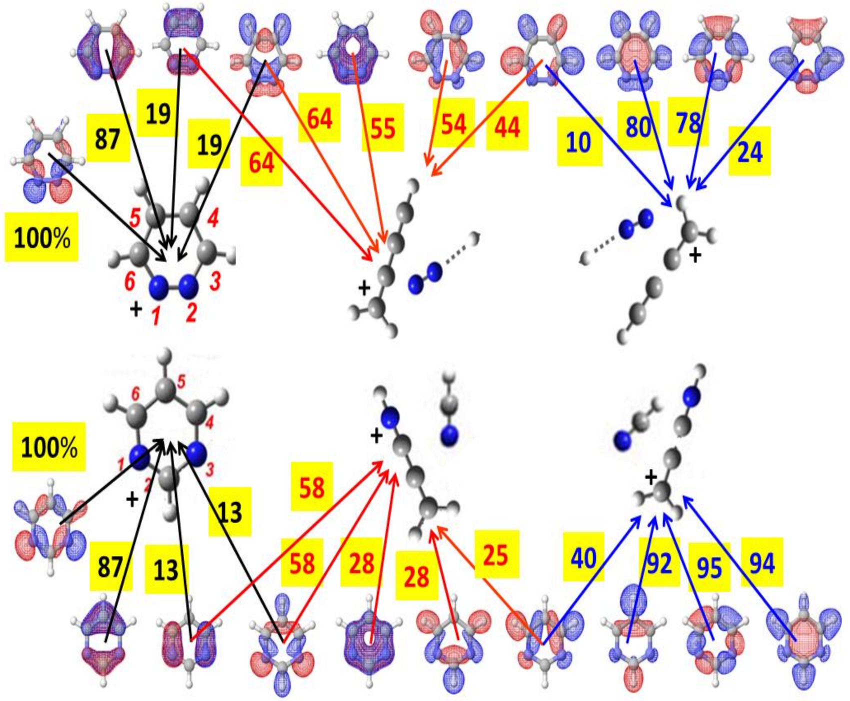


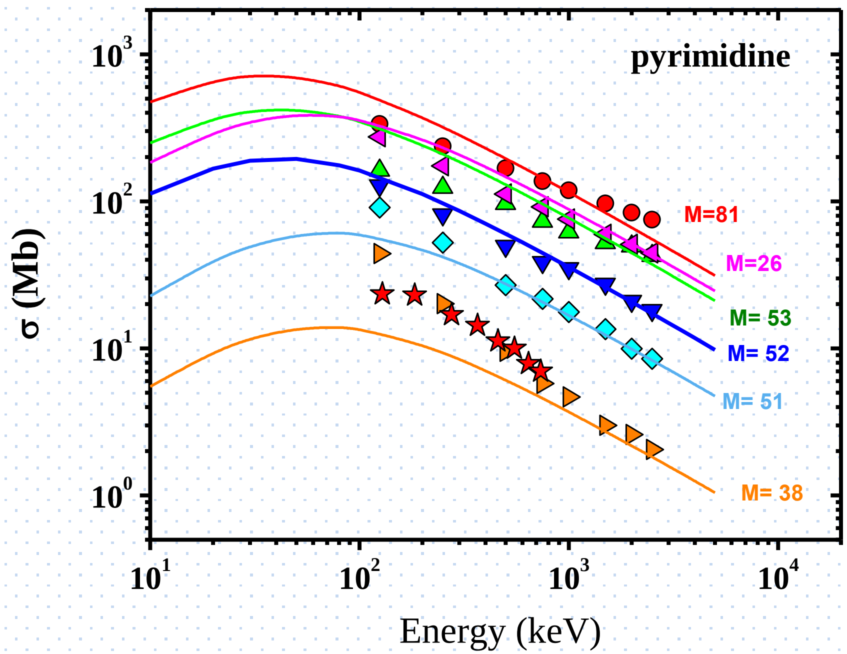
Outer shells: fragment-ion production dominated by single vacancy in broad range of energies with small (negligible) core contribution from double ionization

Inner shells: fragment-ion production divided between single vacancy + double vacancy (Auger + Projectile Double Ionization) production, with significant contribution of PDI at lower energies.

Ionization of molecular orbitals

single vacancy model extended to larger + more complex molecules
isomeric aromatic compounds - pyrimidine and pyridazine



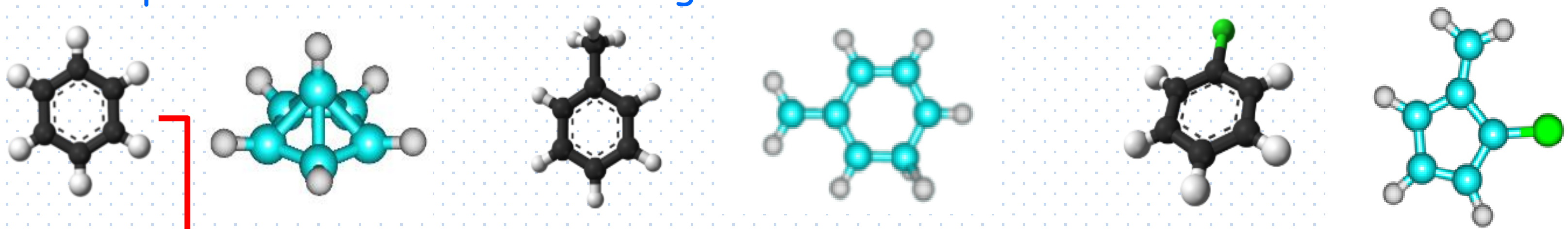


A single molecular orbital generates more than a single fragment species.
A single fragment can be produced by more than a single molecular orbital.

Single vacancy model is enough to give broad and good description of the fragment-ions cross sections.

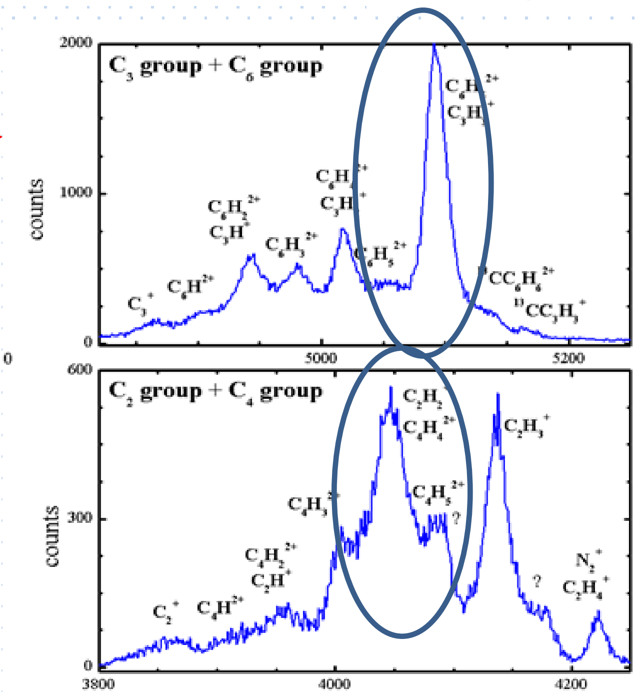
Complex molecules - hydrocarbons
survival of dications

Global minimum structure for the $C_6H_6^{2+}$, $C_6H_5Cl^{2+}$ and $C_7H_8^{2+}$ dications where found, indicating their stability. In all cases occurs loss of structural integrity when compared to their neutral analogues.

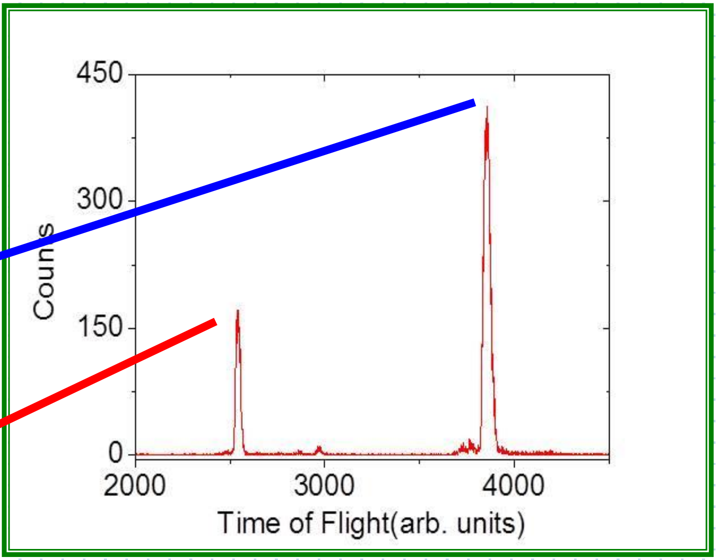


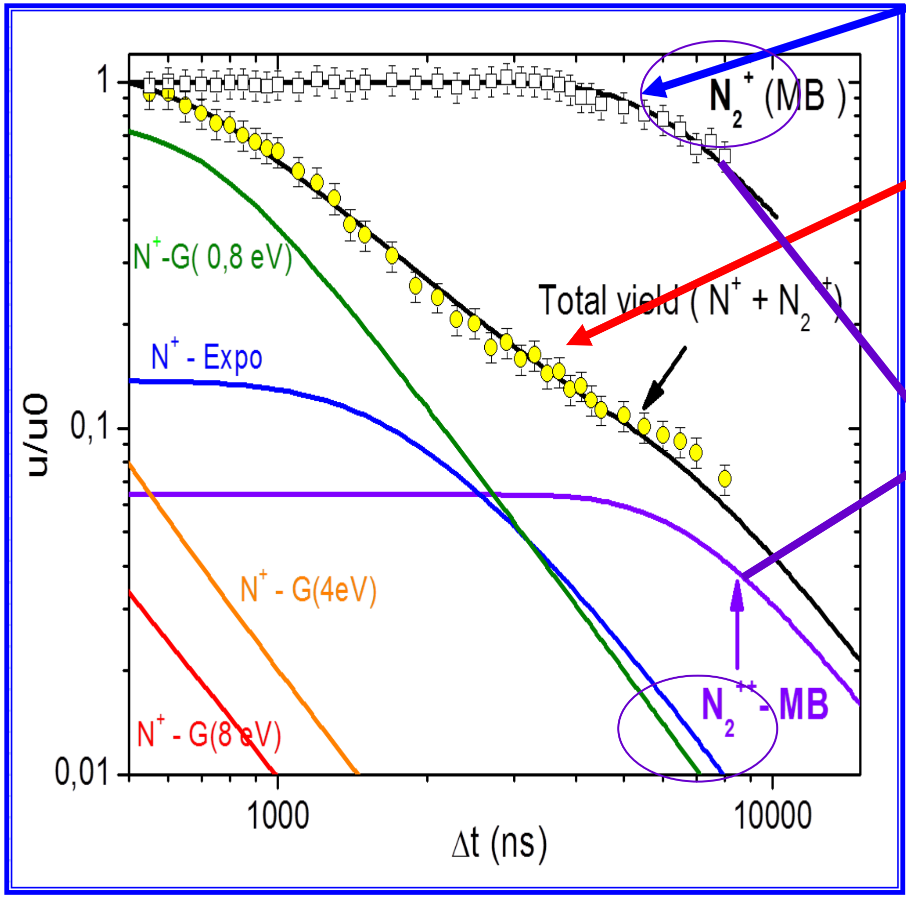
Benzene: metastable and doubly charged ions may be formed
It is not easy to disentangle fragment-ion and dication contributions due to the formation of a fragment-ion with equal dication mass.

Process of separating the contributions by applying the DETOF technique (retarded or delayed time of flight)



DETOF Technique;
sucessfully applied to O_2 and N_2 cases



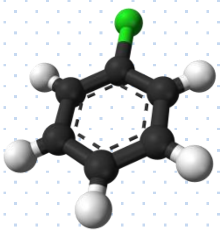


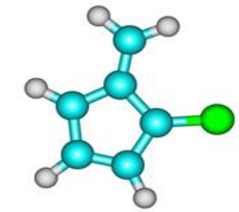
Parent Molecule N_2

Retarded delay time-of-flight mass spectroscopy allows to discriminate the fragment ion, its contribution and kinetic energy

Natalia Ferreira et al., Physical Review A 86, 012702

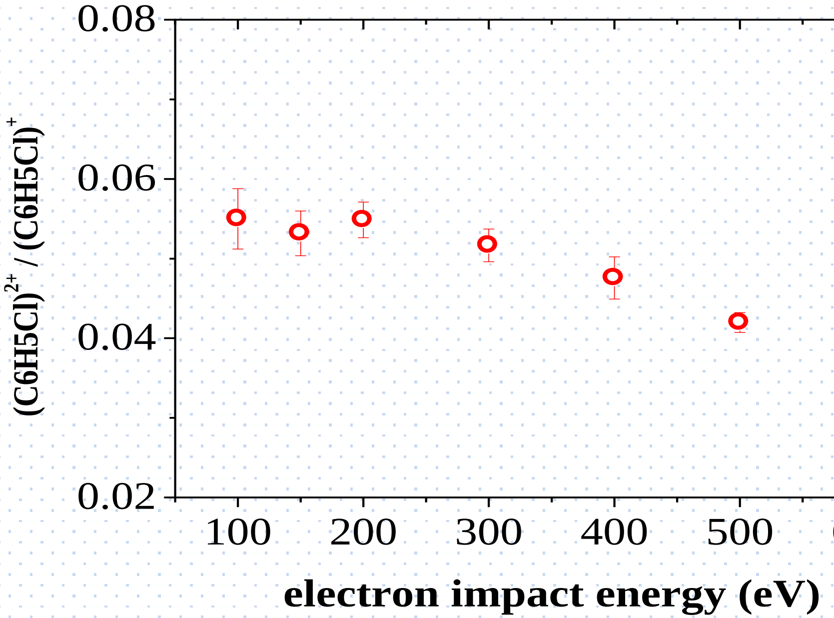
stability of hydrocarbons
survival of dications





$C_6H_5Cl^{2+}$
3-chloro-4-methylene-cyclopentene-3,5-diyl dication

There is no fragment-ion mass possible, stable or metastable frag-ion with equal dication mass in the TOF spectrum, clearly identification



Ratio (parent ion/dication)
$C_6H_5Cl^+ / C_6H_5Cl^{2+}$

Summary

Experimental methods applied to atomic and molecular physics, as the collision ionizing atoms and molecules allows :

- Validation of experimental data : comparison of measurements performed with different setups
- Validation of theories : comparison between measurements and calculations
-
- Differences in the absolute values of CS as function of the energy for bare and dressed projectiles were identified and quantified.
- Single and double ionization of atoms and molecules discriminate the contribution of PDI and Auger by the indication of inflexion points in the CS as function of the energy
- Stable dications points to the "survival" of complex molecules under heavy ion impact