DSM/IRAMIS

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Centre de Recherche sur les Ions, les Matériaux et la Photonique
Caen, FRANCE

Interdisciplinary research at Ganil: Ion-induced chemistry in molecular clusters

Barrande Project: n° 38079PL

Formation of aerosols by polymerisation of molecular clusters

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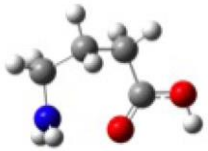
Basic ideas

- Ion collisions with matter are efficient tools to modify and change the structure, bonds and size of finite size systems.
  Large clusters, containing several to several thousands of molecules, are small pieces of solids which can be studied in the gas phase with mass spectrometry.

- → transfer of energy and of charge leads normally to molecular fragmentation (radiation damage, hadrontherapy, molecular shaping and technical applications; see also next talk of P. Nag)



- → when molecular cluster targets are used, also the inverse process, namely molecular growth and polymerisation can occur, leading to the formation of new and larger molecules.

Collision mechanisms

electronic and nuclear stopping power concept

Interaction with target electrons: energy loss due to friction

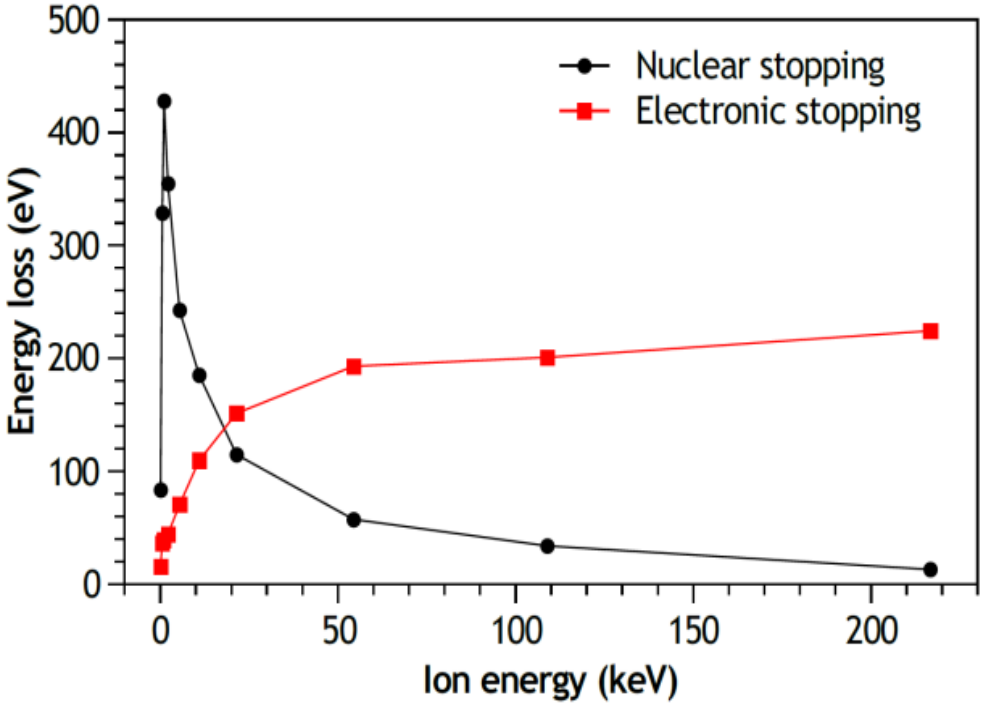
- → individual electronic excitation, plasmon excitation
- → de-excitation by electron-phonon coupling or plasmon decay
- → statistical redistribution of energy leads on longer time scales (> ps) to fragmentation

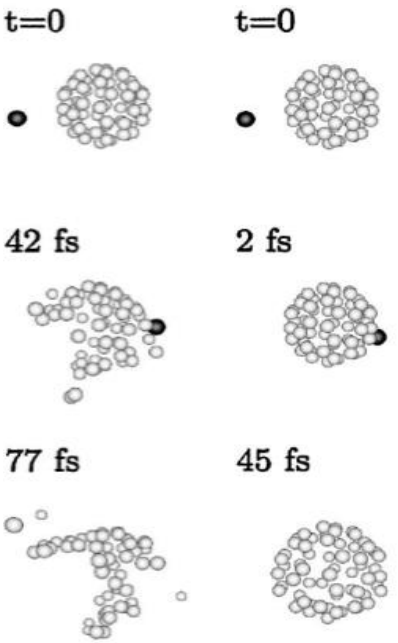
Interaction with atomic nuclei: energy loss due to elastic nucleus-nucleus collisions

- → direct knockout of individual atomic nuclei from the molecule
- → production of highly reactive species
- → due to the high density instantaneous reactions with neighbor molecules (fast reaction: ~10 to 100 fs)

relative importance depends on: projectile mass, velocity and charge.

Energy loss in ion/fullerene collisions (Ar^+ + C_{60})





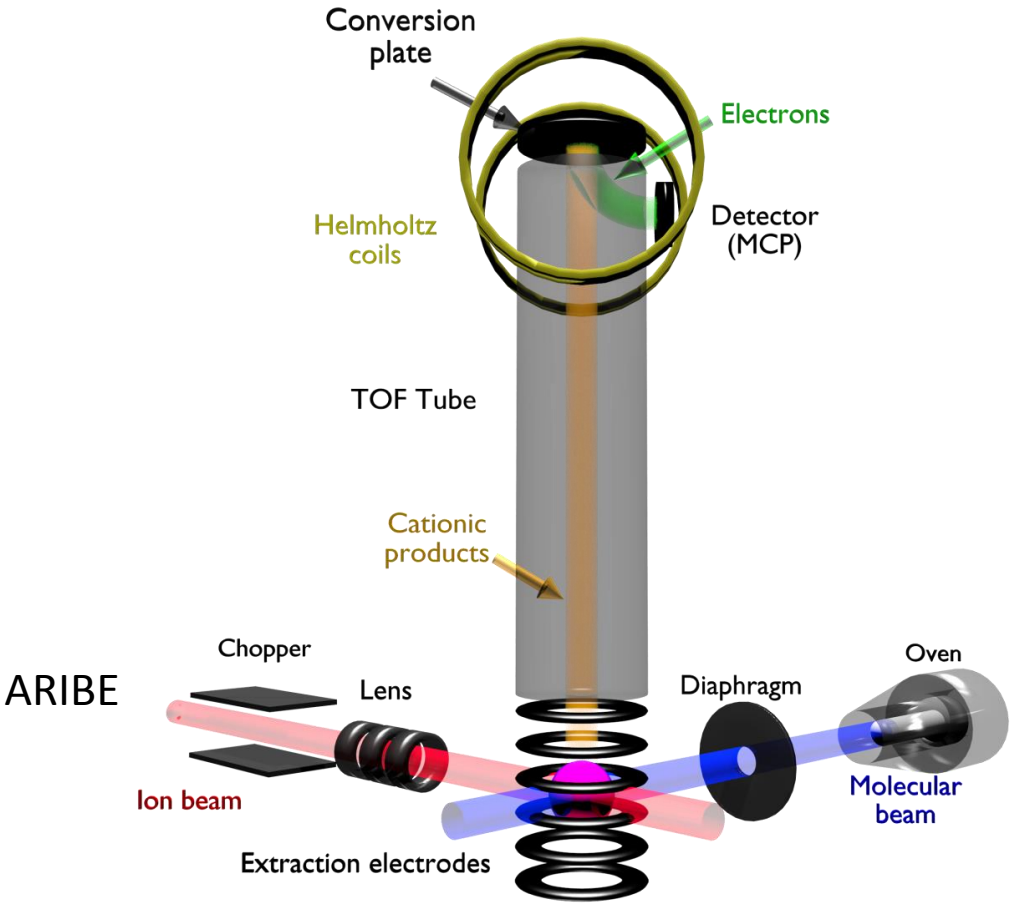
Nuclear energy loss is dominant at very low energies.

Electronic energy loss dominates at high velocities.

Theoretical results from non-adiabatic QMD calculations, impact parameter: 0,2 a.u.; Th Kunert and R. Schmidt, Phys. Rev. Lett. 86, 5258 (2001)

E_k = 0,4 keV 200 keV

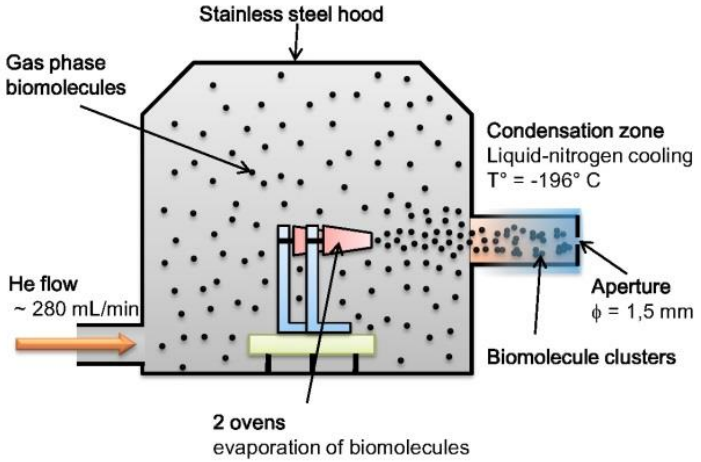
Experimental set-up and principle



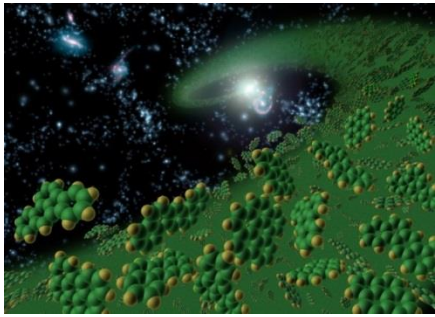
Collision energy: 10 – 500 keV

Analysis:

TOF-mass spectrometry multicoincidence technique **event-by-event registration**



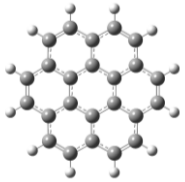
Cluster aggregation source

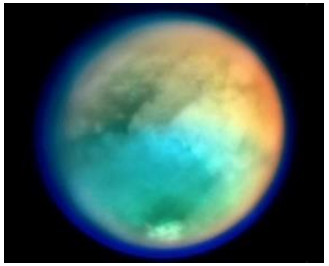


First example:
Molecular growth and dust particles in space and planetary atmospheres

Molecular inventary in space: more than 200 small molecules as well as larger carbon-containing systems like :

Polycyclic aromatic hydrocarbons (PAHs), Fullerenes (C_{60}, C_{70}) or **Dust particles** (containing more than 1000 C-atoms).





Moon Titan and its specific orange haze

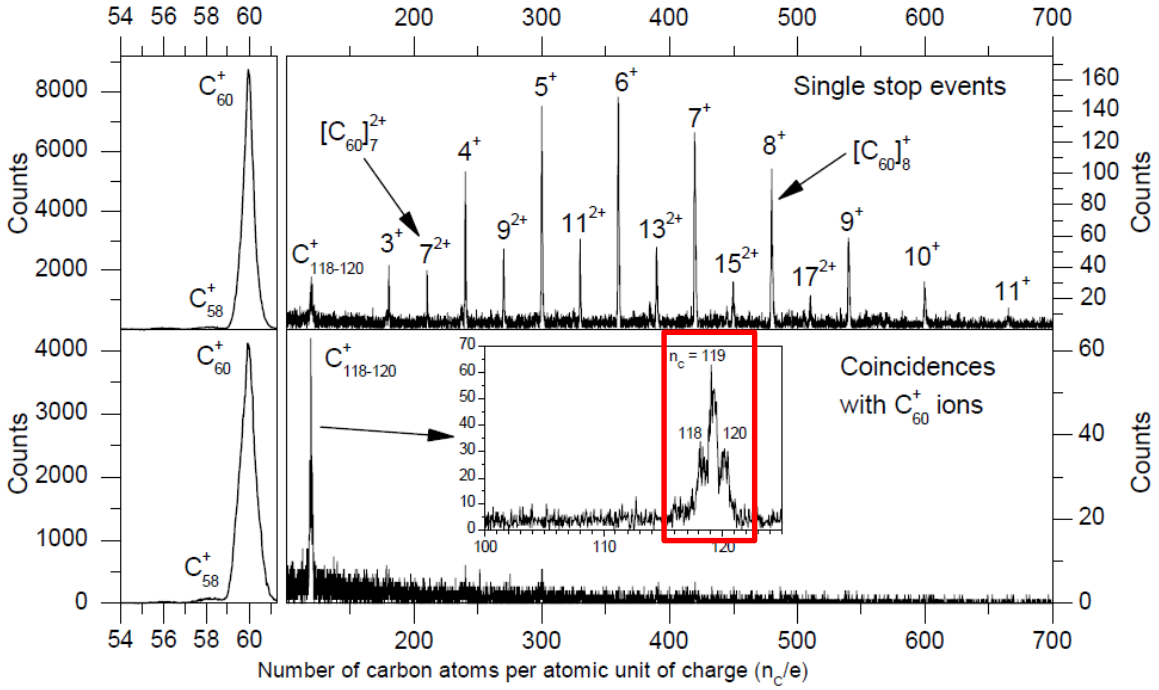
How these particles are formed?

In a **top-down process**, where larger ejecta are emitted from stars which loose during their lifetime a large fraction of mass by evaporation or fragmentation induced by photons or ions?

Or in a **bottom-up process**, where smaller molecules aggregate to larger ensembles?

He^{2+} @ 22.5 keV (solar wind) collisions with $(C_{60})_n$ vdW clusters

Mass/ charge spectrum



$C_{59}^+ + C_{60} \rightarrow C_{119}^+$

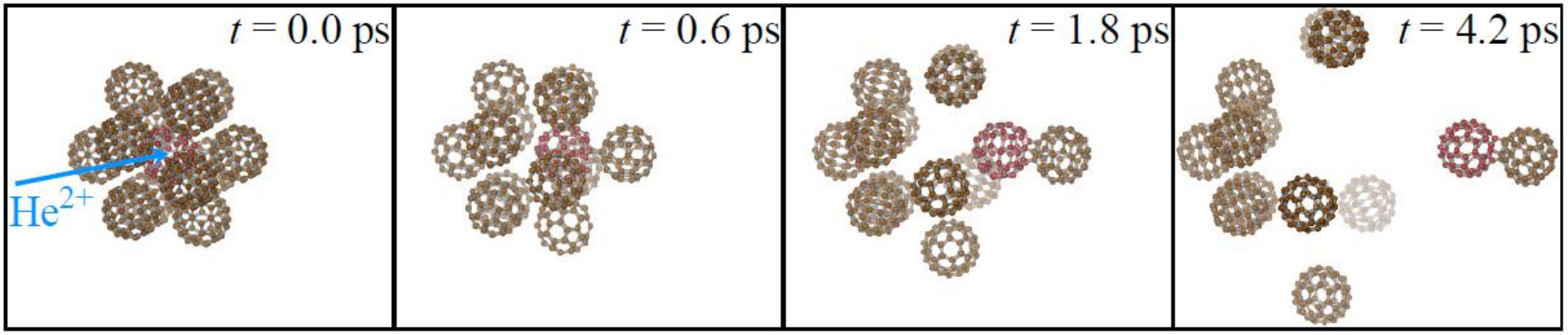
(covalent)

Formation of C_{119}^+ and C_{118}^+:

i) **Knockout of 1 or 2 carbon atoms** from one C_{60} molecule → C_{58}^+, C_{59}^+

ii) Species are **highly reactive** and make **covalent bonds** with neighbor molecule

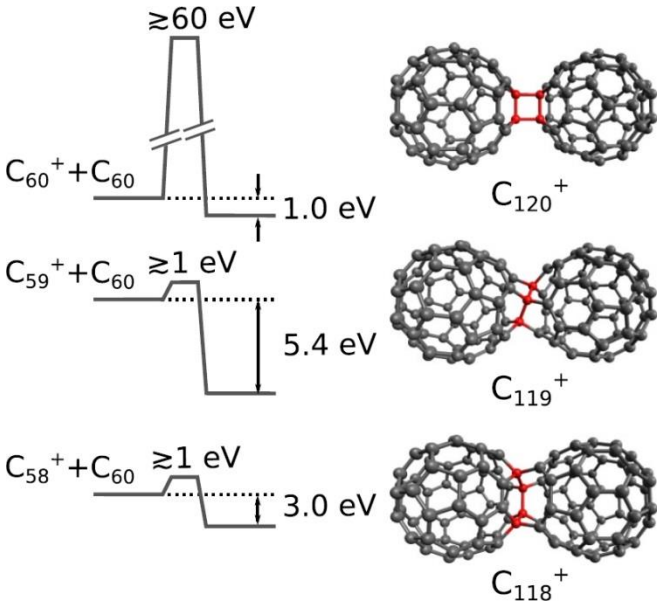
Collision Dynamics (He^{2+} + $(C_{60})_{13}$)



Energetic Characteristics

from Molecular Dynamics simulationss

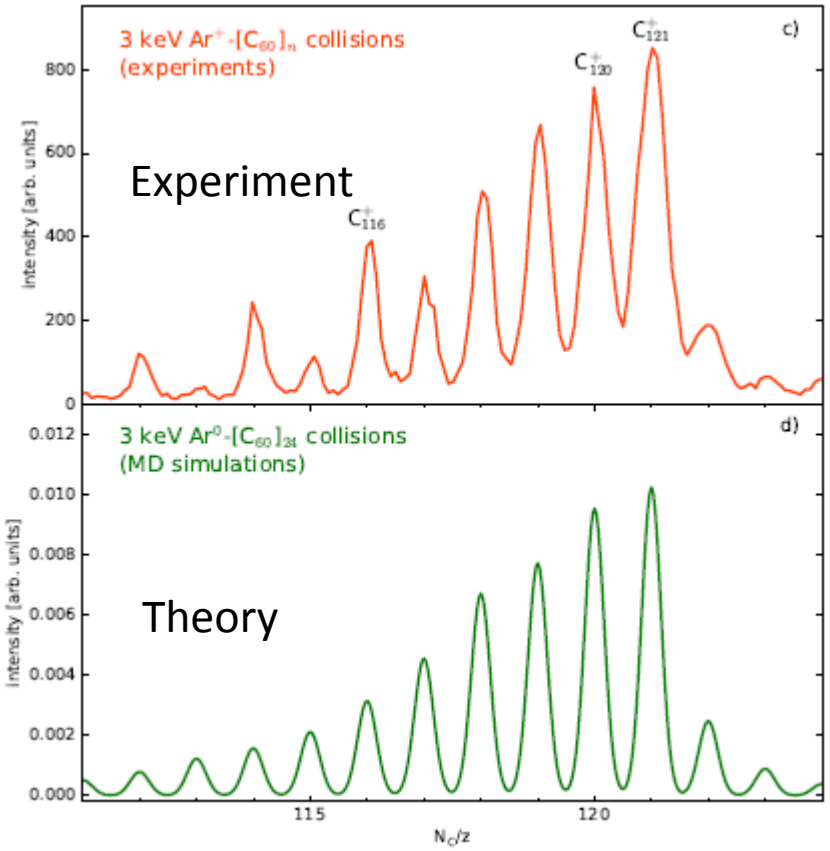
Zettergren et al.,
Phys. Rev. Lett. 110, 185501 (2013)

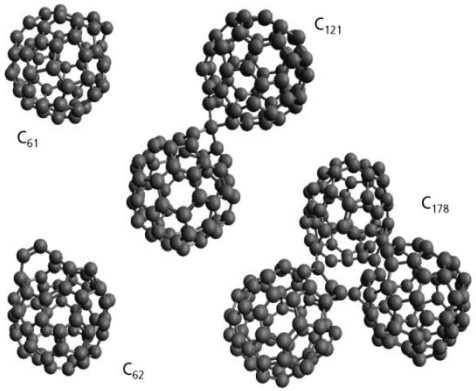


Ar^+ @ 3 keV colliding with $(C_{60})_n$ clusters

(higher projectile mass and lower velocity → Knockout more likely

Mass spectrum in the dimer region





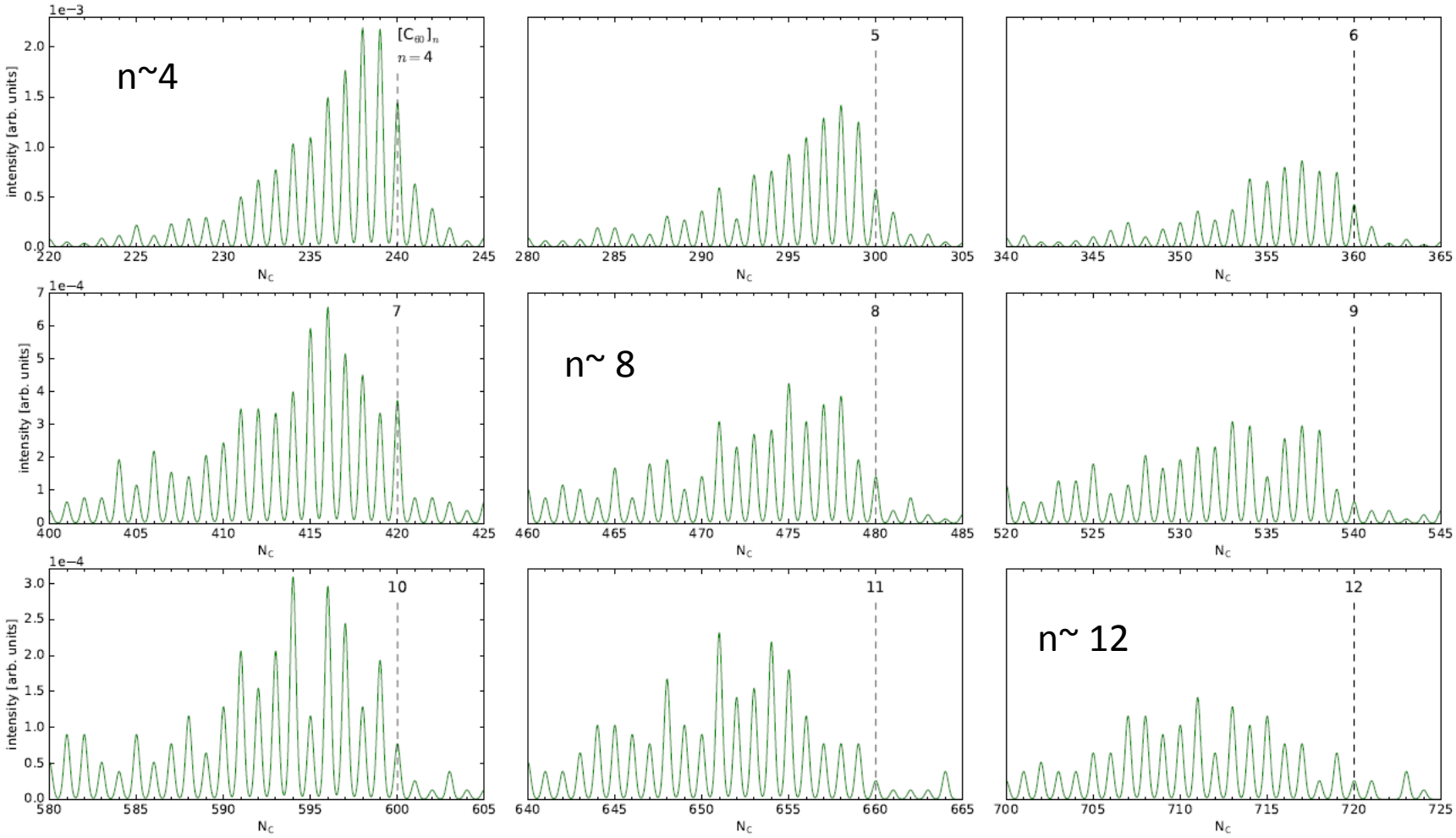
Structure calculation

→ **Large covalently bound molecular systems** can be formed in low energy ion collisions

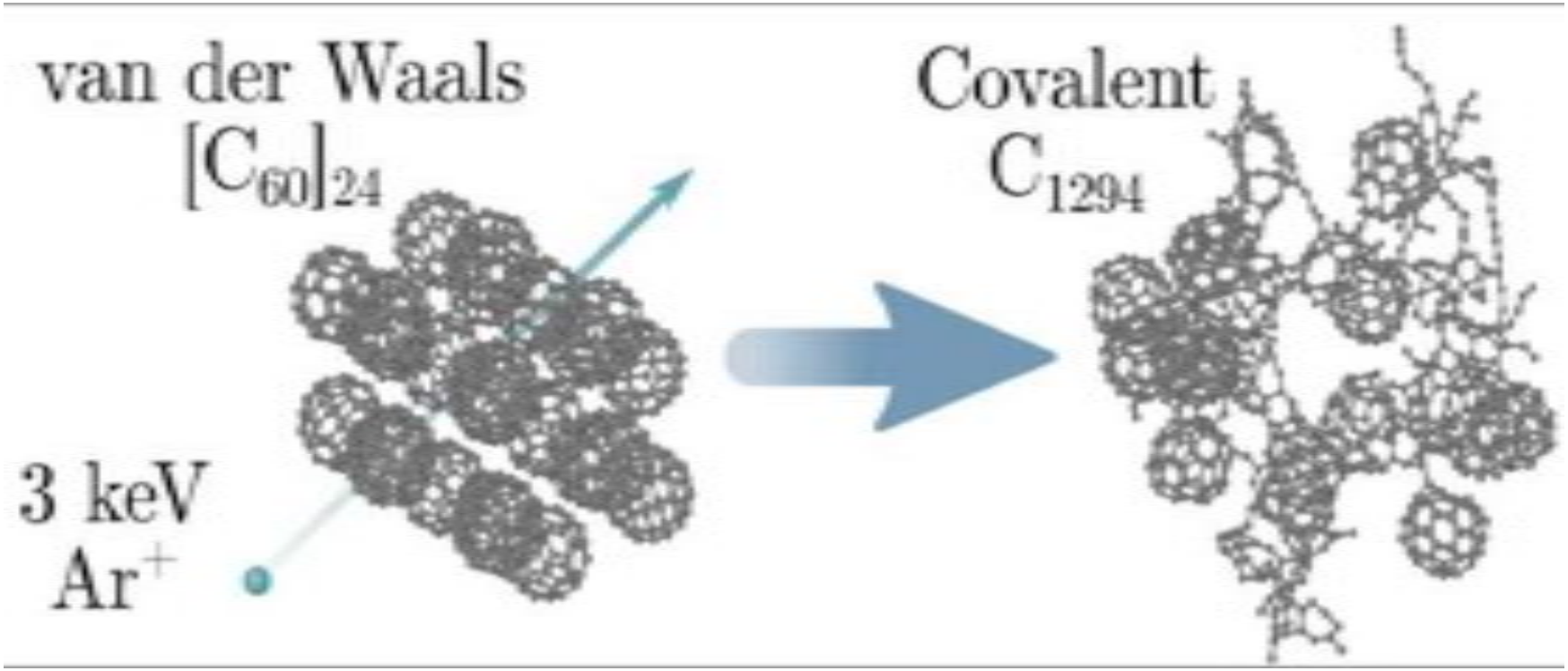
→ **Very good agreement between experiment and theory** based on knockout collisions

→ Systems may contain **more than 1000 C-atoms**

Peak structures of different clusters sizes starting from $(C_{60})_{24}$



Molecular growth towards dust particles by single ion impact provoking knockout processes

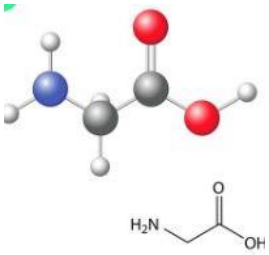


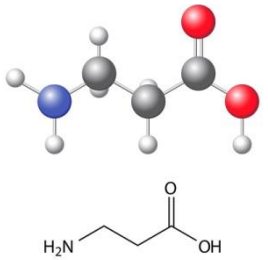
R. Delaunay et al., CARBON **129**, 766-774 (2018)

Second example: Polypeptide formation

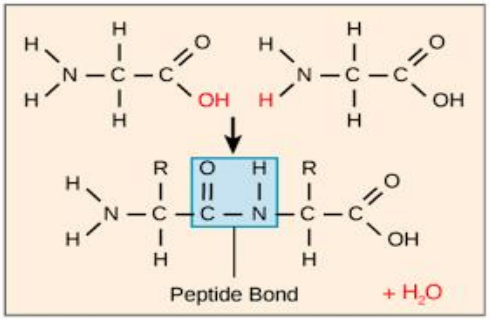
- **Origin of life**

Amino acids like glycine, α- and β-alanine and others are expected in space.

glycine 

β-alanine 

Peptide bond formation by water loss reaction:

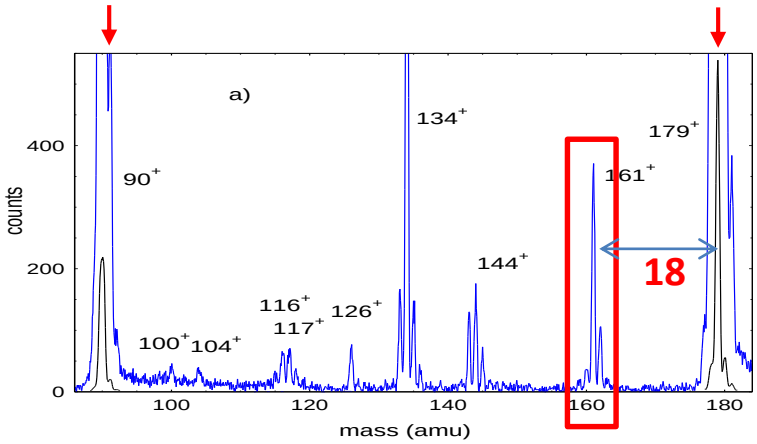


Carboxyl group and amino group of 2 molecules react with each other forming the amide bond C-N and emitting a water molecule.

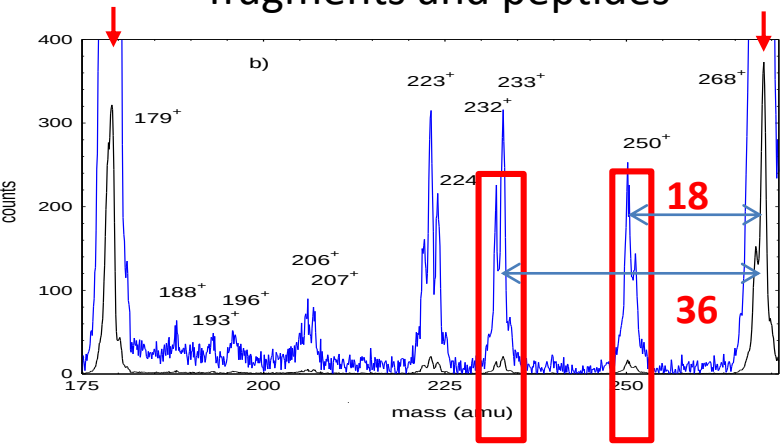
Can this process be induced by ion collisions??

Collisions of He^{2+} @ 35 keV with $(\beta\text{-ala})_n$ clusters

Mass spectra



fragments and peptides



When clusters are charged

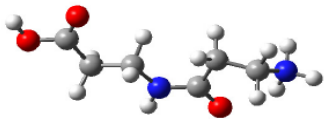
→ **protonation** occurs at the amino group of the molecule

(result of MD calculations → NH_3^+)

monomer: mass 89 au → mass 90 au
dimer: mass 178 au → mass 179 au
trimer: mass 267 au → mass 268 au

Dipeptide is formed at mass 179-18 = 161
Dipeptide + 1 molecule at mass 268 – 18 = 250
Tripeptide at mass 268 – 2x18 = 232

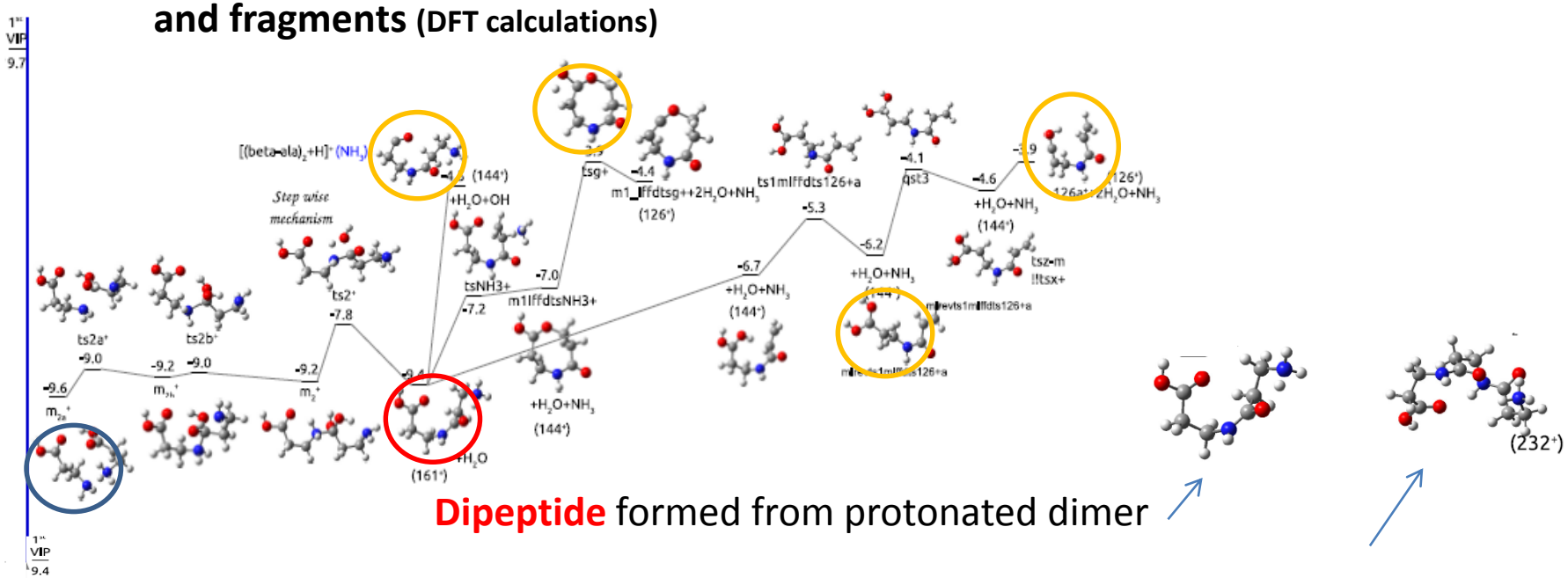
dipeptide



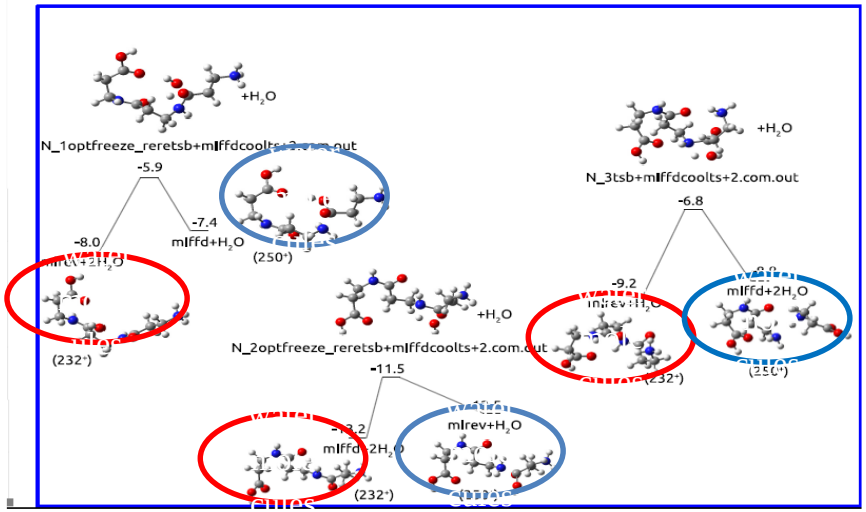
Also **quadropeptides** are observed in larger systems.

→ **Ions are an efficient tool for inducing peptide bonds**
→ **Possible polypeptide formation in space and planetary atmospheres**

Potential energy surfaces explaining most of the observed polypeptides and fragments (DFT calculations)



Dipeptide formed from protonated dimer



Tripeptides formed from protonated trimer

The formation **does not require knockout**, but only transfer of low energy.

Photon collisions allow also for dipeptide formation, **ion collisions** allow due to trajectory effects for the formation of **polypeptides**

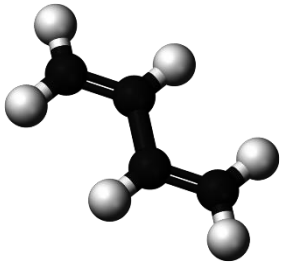
Third example: Growth of small hydrocarbon chains

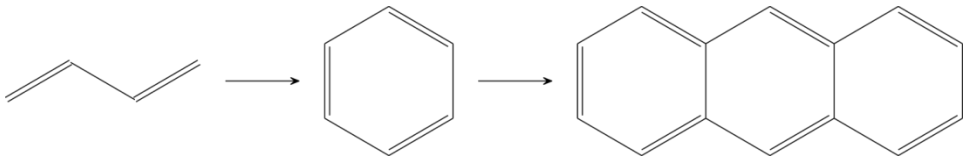
Objectives:

Production of aromatic molecules from small linear hydrocarbon chains in clusters

Molecule: 1,3-butadiene

C_4H_6

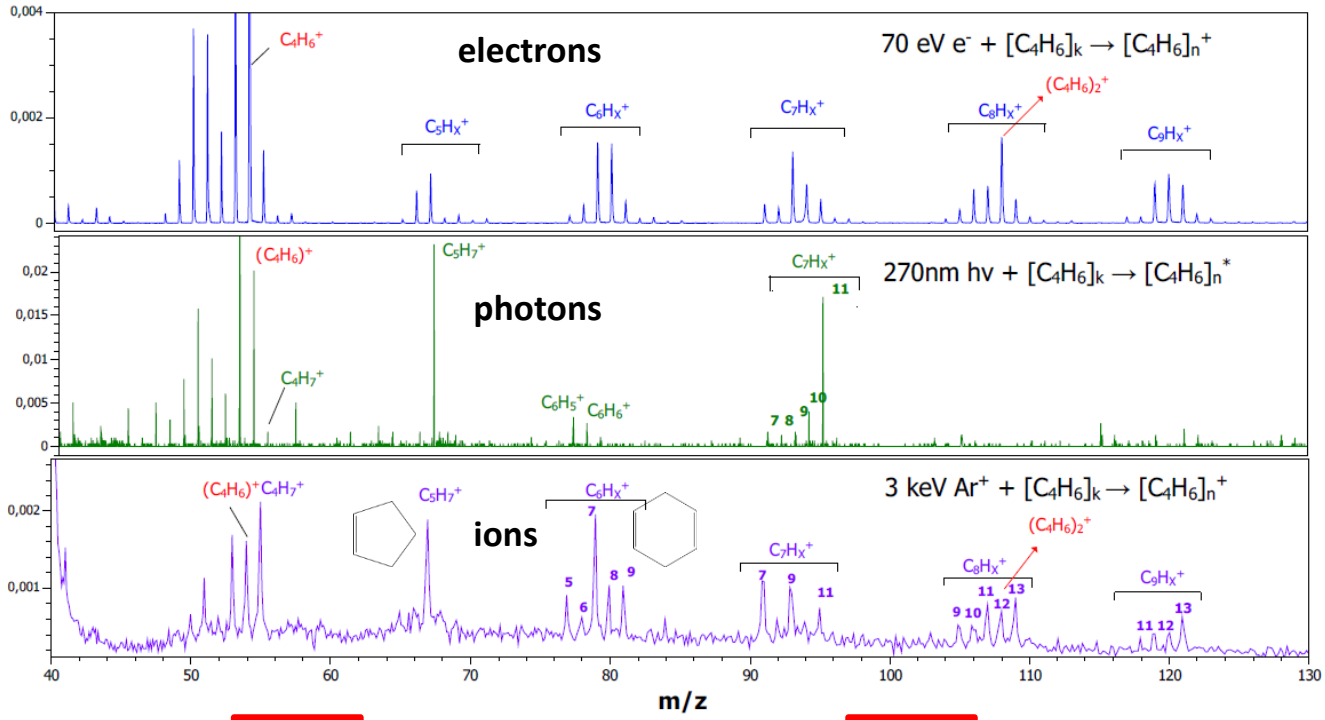


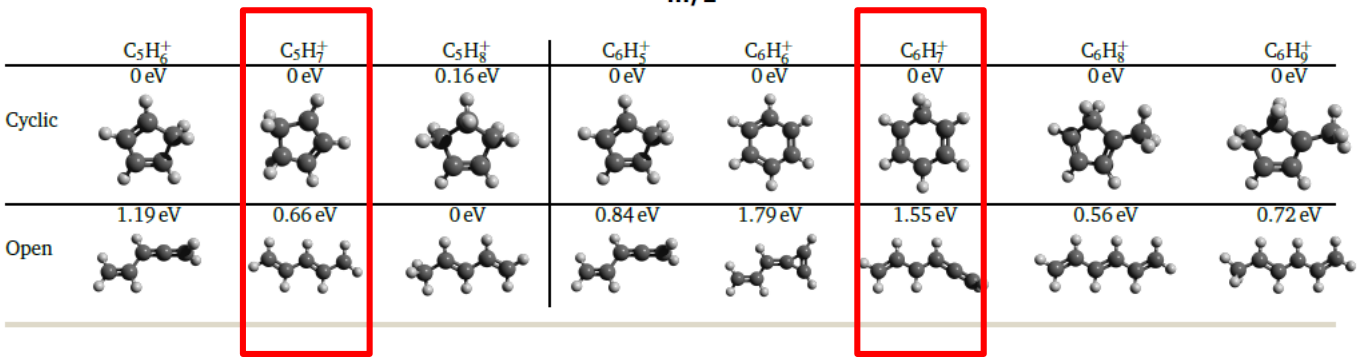


Are cyclisation processes possible?
Which mechanism might be responsible?

Collision studies were performed in the French-Tcheque collaboration **with ions, electrons and photons**.

Mass spectra for different projectiles





Ion spectra: protonated species ($C_4H_7^+$, $C_8H_{13}^+$,...) and growth products

Butadiene polymers ($C_5H_8^+$, C_6H_8+, $C_7H_{10}^+$,...)

"magic" growth products – Cyclic structures

Lower Energies of cyclic Structures compared to linear molecules

Electrons and photons: Show different H-distributions

→ **Summary:**

Mechanism is due to knockout and electronic excitation; Cyckic structures are likely to be formed

Summary

- **Low-energy ion collisions (solar wind, with molecular clusters):**

  → **molecular growth by knockout processes**

  → **polypeptide formation after electronic excitation**

  → **aromatic molecules formed by electronic/nuclear collisions**

Ion collisions with individual molecules

→ **fragmentation (see next talk by P. Nag)**

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