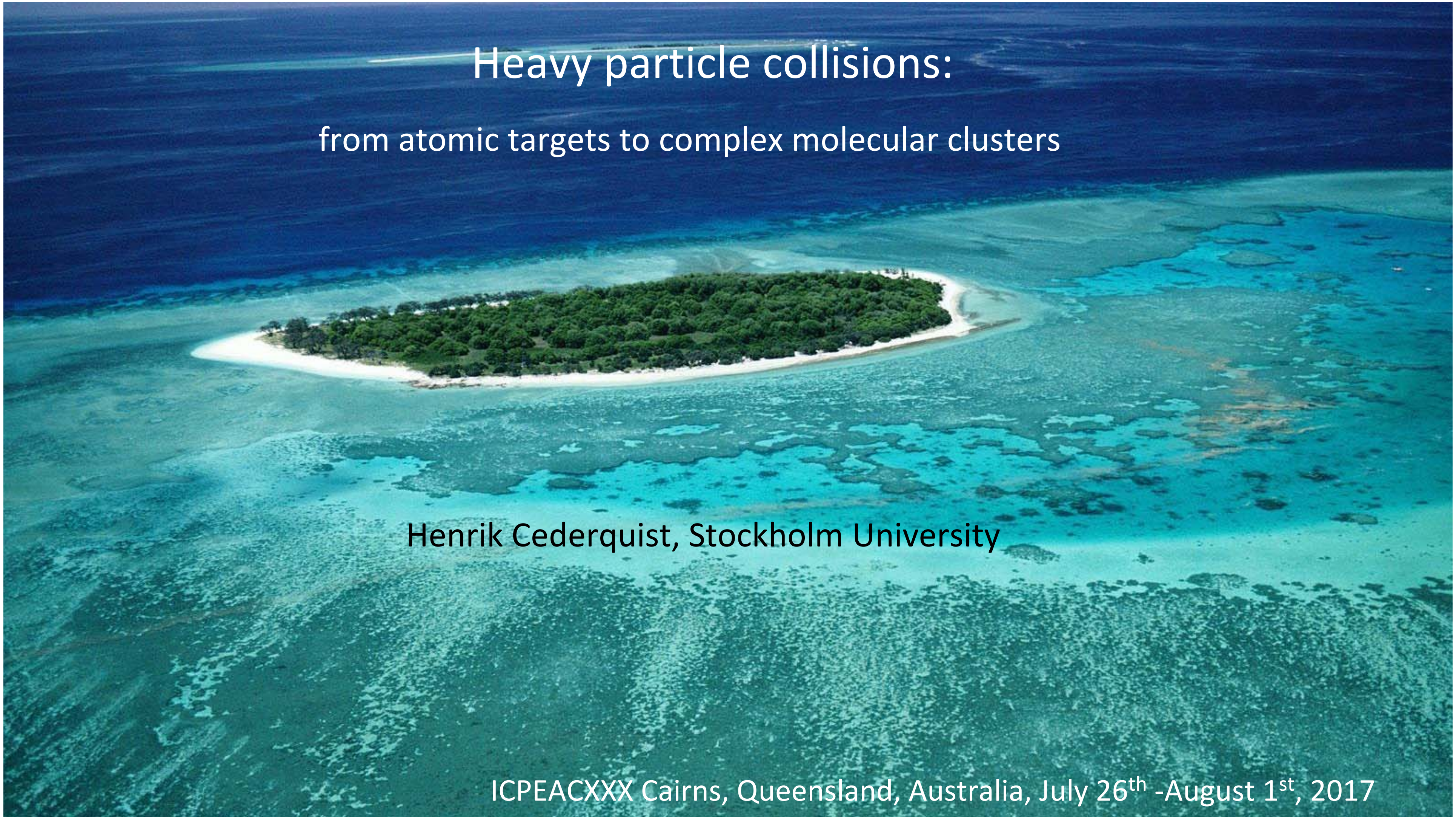


Heavy particle collisions:

from atomic targets to complex molecular clusters

Henrik Cederquist, Stockholm University

ICPEACXXX Cairns, Queensland, Australia, July 26th -August 1st, 2017

Stockholm in winter

…..part of my biking route to work…

I also bike past

Old Town

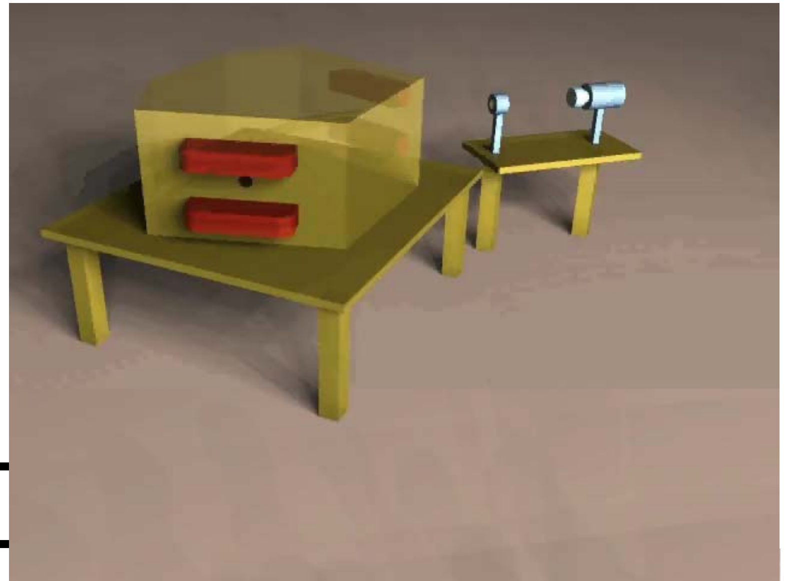
…to reach Stockholm University and the AlbaNova university center

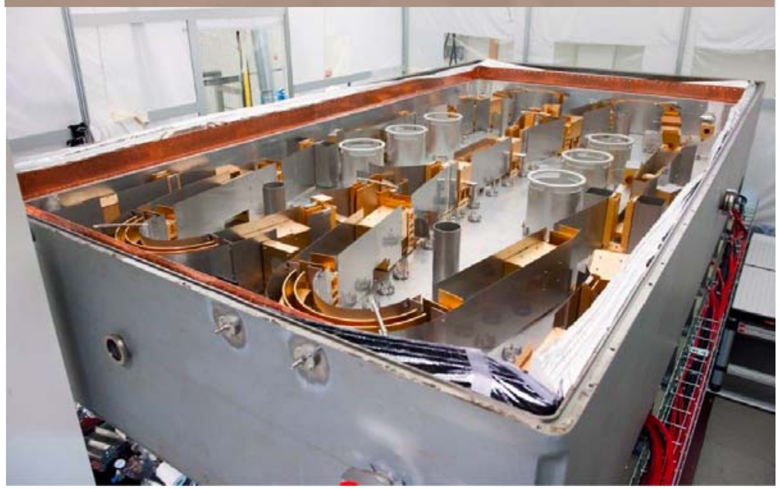
only to meet hard working PhD students

Erik Bäckström

The DESIREE ion-beam storage rings

Erik Bäckström (PhD 2015)





SR on OH^- by Gustav Eklund at 15:30 today !

Selected DESIREE publications:

R.D. Thomas *et al.*, Rev Scientific Instruments **82** 065112 (2011)
H.T. Schmidt *et al.*, Rev Scientific Instruments **84** 055115 (2013)

E. Bäckström *et al.*, *Storing keV negative ions for an hour: the Lifetime of the Metastable $^2P^o_{1/2}$ level in S-*, PRL **114**, 143003 (2015).

H.T. Schmidt *et al.*, *Rotationally cold OH^- in the cryogenic electrostatic ion-beam storage ring DESIREE*, PRL *accepted* (2017).

Poster: Metal clusters cooling in DESIREE, Emma Anderson Mo142

Electrostatic ion-*beam* storage:

-Electrostatic – ions of any mass and charge can be stored for long times

from H^+/H^- to large clusters, bio-molecules, nanoparticles

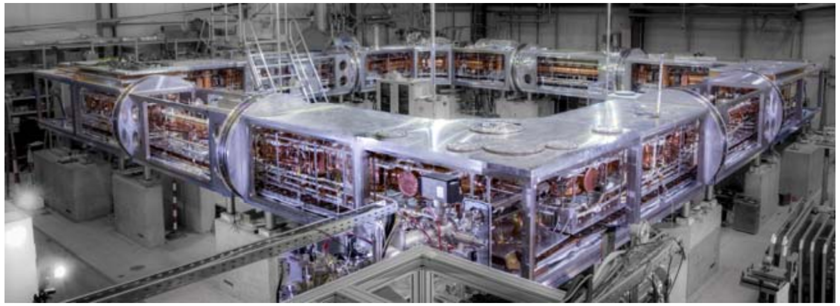
-Efficient collection and detection of reaction products (coincidence experiments)

studies of individual reaction/action events

- Cooling ions - internally and translationally

ions in well defined quantum states

RICE, Tokyo



CSR, MPIK, Heidelberg

DESIREE, Stockholm

…and **ELISA** and **SAPHIRA** in Aarhus, **MINIring** in Lyon, **TMU-ring** at Tokyo Metropolitan University, liner ion-beam traps - **Zajfman traps** - at the Weizmann institute, Israel, ….

Parts of an <u>extended</u> Stockholm group at the conference for Electrostatic Storage Devices

Lyon, France, June 2017

Mark Stockett   Henning Schmidt   Gustav Eklund

Henning Zettergren

"External" members:
Dag Hanstorp, Gothenburg;
Naoko Kuono, TMU, Tokyo

H Cederquist, M Stockett, M Kristiansson, HT Schmidt, N Kuono, D Hanstorp, K Chartakunchand ("KC"), M Wolf, M Kaminska, S Rosén, E Anderson, G Eklund, P Löfgren, RD Thomas, M. Gatchell, H Zettergren

…meanwhile in the lab

L Giacomozzi   N de Ruette

A group photo for a project with astrophysical applications

Paul Barklem, Uppsala University, Sweden

Åsa Larson,
Stockholm
University

with this strong Swedish-Australian connection I am happy to be in Cairns!

Skogens Konung – The King of the Forest

…and the King of Beers

Outline (rest of the talk):

- How are ions and ion collisions important?

  Radiation damage and treatment, astrophysics and –chemistry, stellar and planetary atmospheres

- Collisions with atomic targets – some examples

  Fast and slow collisions, interactions with electron clouds and atomic nuclei, electron capture and highly charged ions

- Atoms, smaller molecules, fullerenes and PAHs (?) in space

  Spectroscopic identifications and predictions

- Collisions with fullerenes, PAHs, and biomolecules

  Statistical and non-statistical fragmentation

- Collisions with clusters of molecules

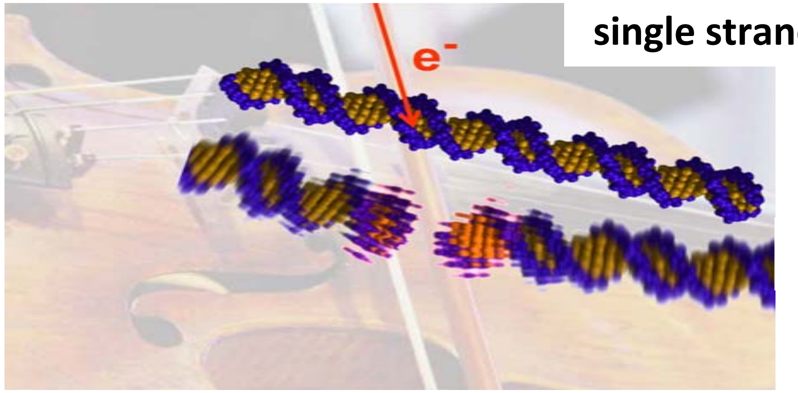
  Ionization, fragmentation, evaporative cooling, and molecular growth

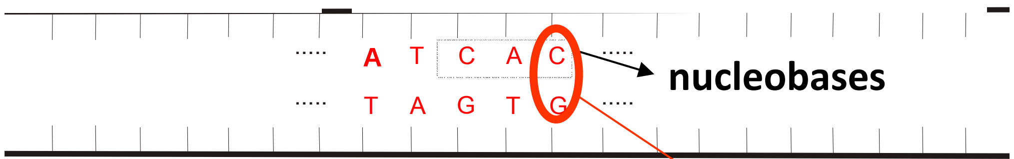
- Final remarks – new prospects for experiments, e.g., with stored ion beams

How are ions and ion collisions important?

Radiation damage and treatment, astrophysics and –chemistry, stellar and planetary atmospheres

Radiation damage of DNA

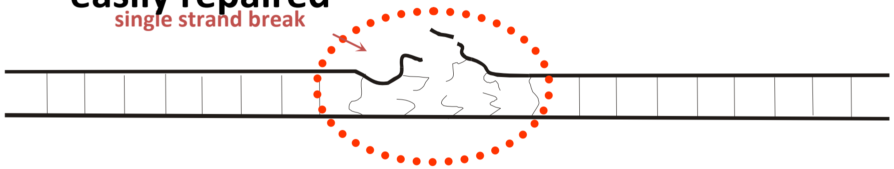




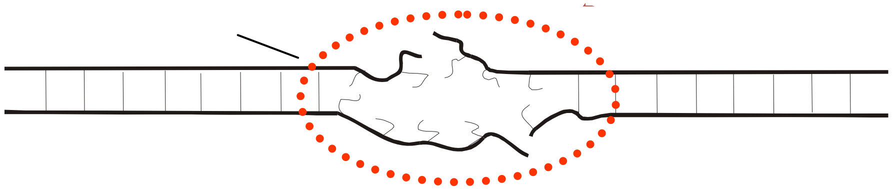
nucleobases:

A: Adenine
T: Thymine
C: Cytosin
G: Guanin

single strand break – easily repaired

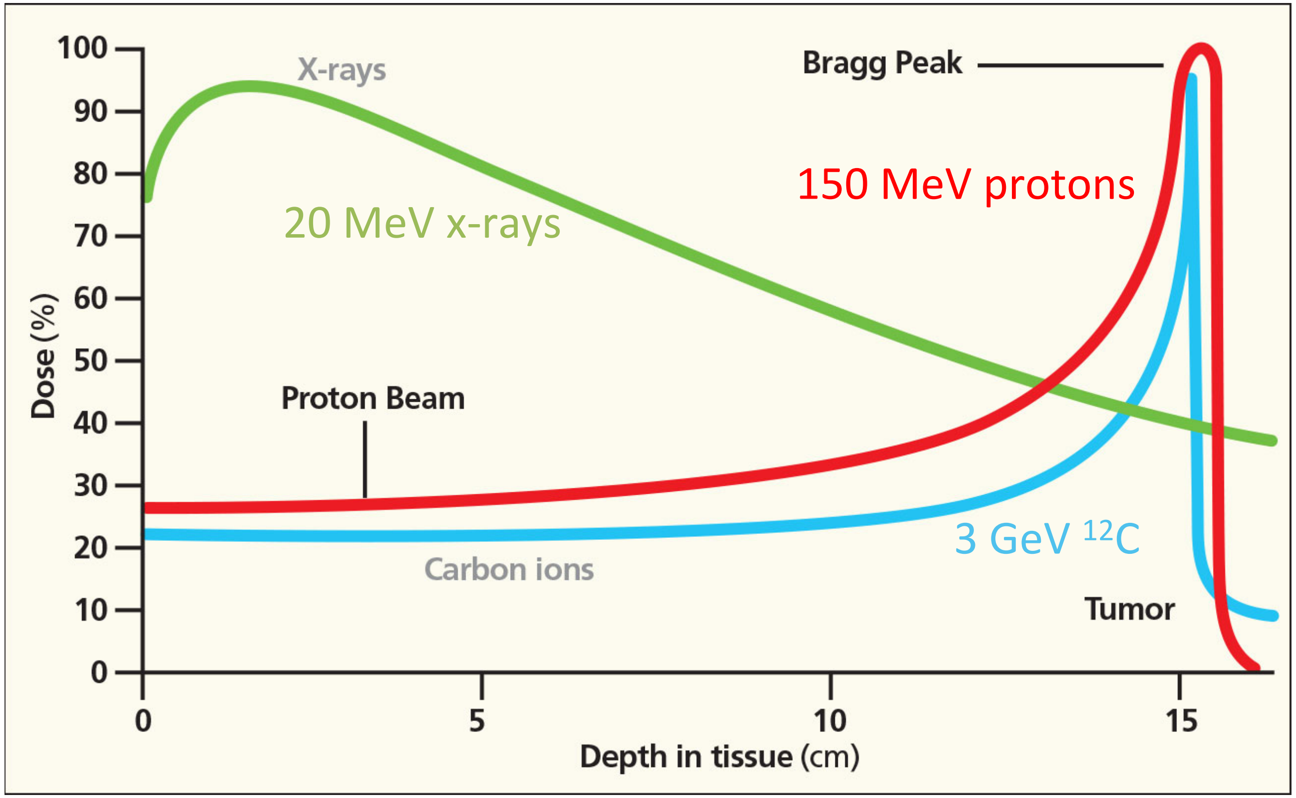


double strand break – not so easily repaired



Radiation damage and radiation treatment

Dose as a function of depth in tissue for 20 MeV x-rays, 150 MeV protons, and 3 GeV carbon



ChemPhysChem **2006**, *7*, 2339 – 2345

Ion-Induced Biomolecular Radiation Damage: From Isolated Nucleobases to Nucleobase Clusters

Thomas Schlathölter,*[a] Fresia … an,[a] Aurelie Lecointre,[a]
Ronnie Hoekstra,[a] Virgil … Manil,[b] Jimmy Rangama,[b] and
Bernd Huber[b]

Evidence for the influence of the cluster environment on radiation damage of the individual molecules!

A large number of studies are … the investigation of the biomolecular ionization and fra…entation dynamics underlying biological radiation damage. Most of these studies have been based on gas-phase collisions with isolated DNA building blocks. The radiobiological significance of these studies is often questioned because of the lack of a chemical environment. To clarify this aspect, we studied interactions of keV ions with isolated nucleobases and with nucleobase clusters by means of coincidence time-of-flight spectrometry. Significant changes already show up in the molecular fragmentation patterns of very small clusters.

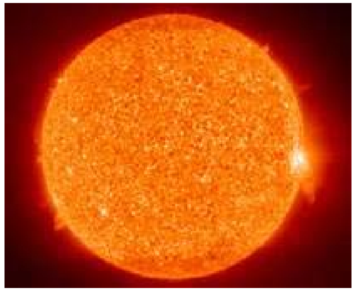
Talk by **Thomas Schlathölter** and Talk by **Paola Bolognesi** on Tuesday afternoon Aug. 1st

How are ions and ion collisions important?

Radiation damage and treatment, astrophysics and –chemistry, stellar and planetary atmospheres

H$^-$ in the atmosphere of the Sun

H^- is present in the Sun's atmosphere



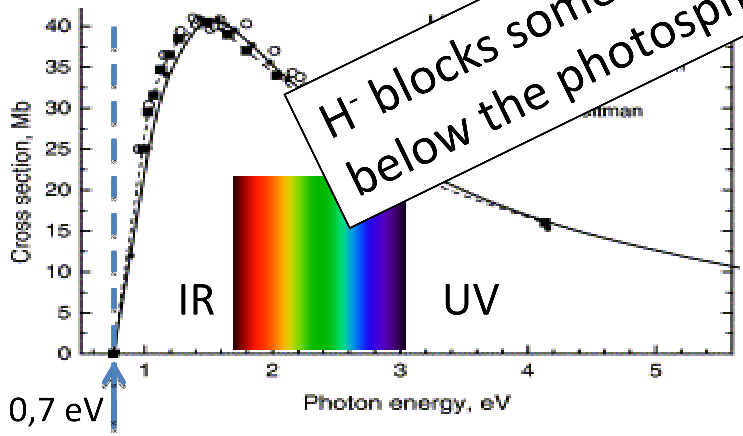
The photosphere

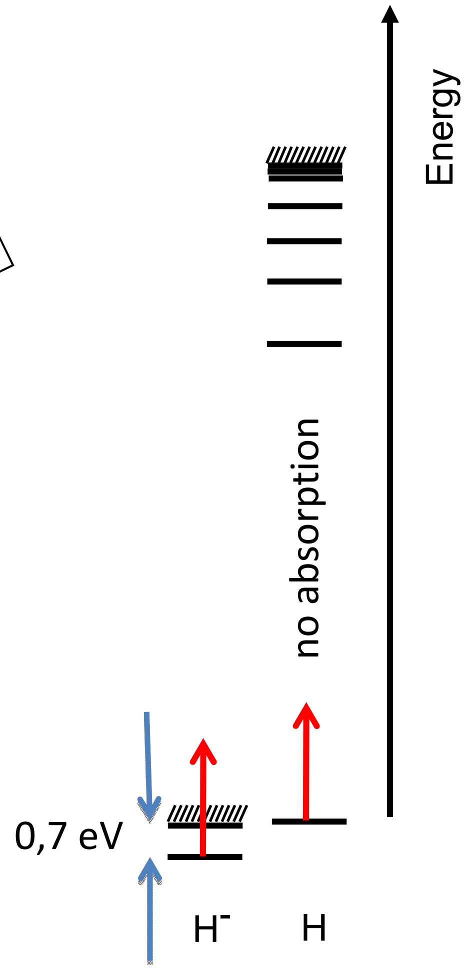
Nuclear fusion processes at 10^8 K
in the interior of the Sun

But we see emission at 57…

H^- blocks some of high energy radiation from below the photosphere of the Sun

H^- Photoabsorption cross section: VK Iv…
PHYSICS AND CHEMISTRY 70 (1-3): 345-37…





How are ions and ion collisions important?

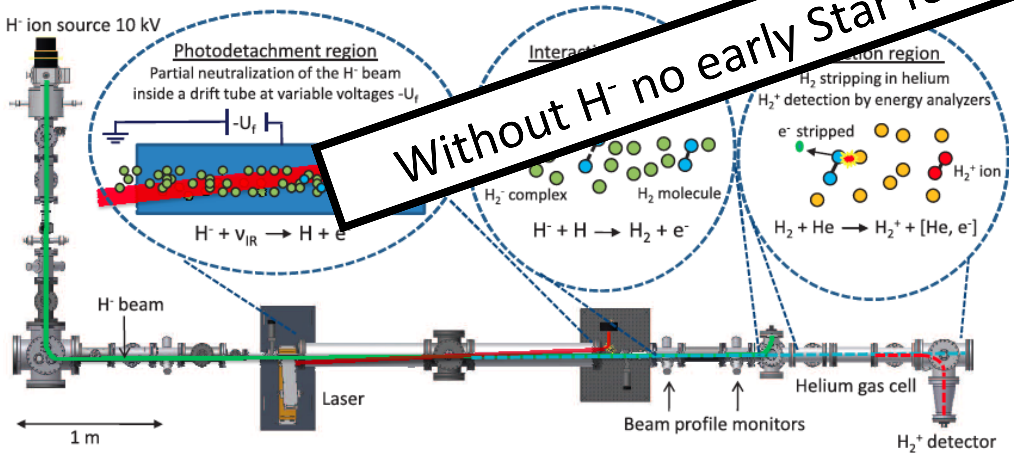
Radiation damage and treatment, astrophysics and –chemistry, stellar and planetary atmospheres

$H^- + H$ associative detachment -> $H_2 + e^-$

Experimental Results for H_2 Formation from H^- and H and Implications for First Star Formation

H. Kreckel,[1*†] H. Bruhns,[1‡] M. Čížek,[2] S. C. O. Glover,[3] K. A. Miller,[1] X. Urbain,[4] D. W. Savin[1]

During the epoch of first star formation, molecular hydrogen (H_2) generated via associative detachment (AD) of H^- and H is believed to have been the main coolant of primordial gas for temperatures below 10^4 kelvin. The uncertainty in the cross section for this reaction has limited our understanding of protogalaxy formation during this epoch and of the characteristic masses and cooling times for the first stars. We report precise energy-resolved measurements of the AD reaction, made with the use…



Without H^- no early Star formation!

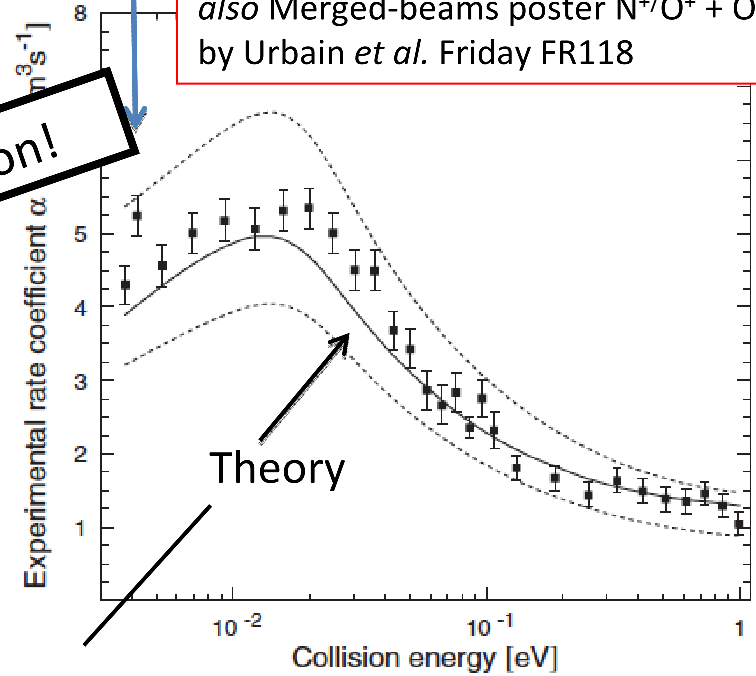
2 JULY 2010 VOL 329 SCIENCE www.sciencemag.org

see also H. Bruhns *et al.* PHYSICAL REVIEW A **82**, 042708 (2010)

Associative Detachment H^-+H → H_2 + e^- rate coefficients

4 meV

also Merged-beams poster N^{+}/O^{+} + O^- by Urbain *et al.* Friday FR118



M. Čížek, J. Horáček, W. Domcke, *J. Phys. B* **31**, 2571 (1998)

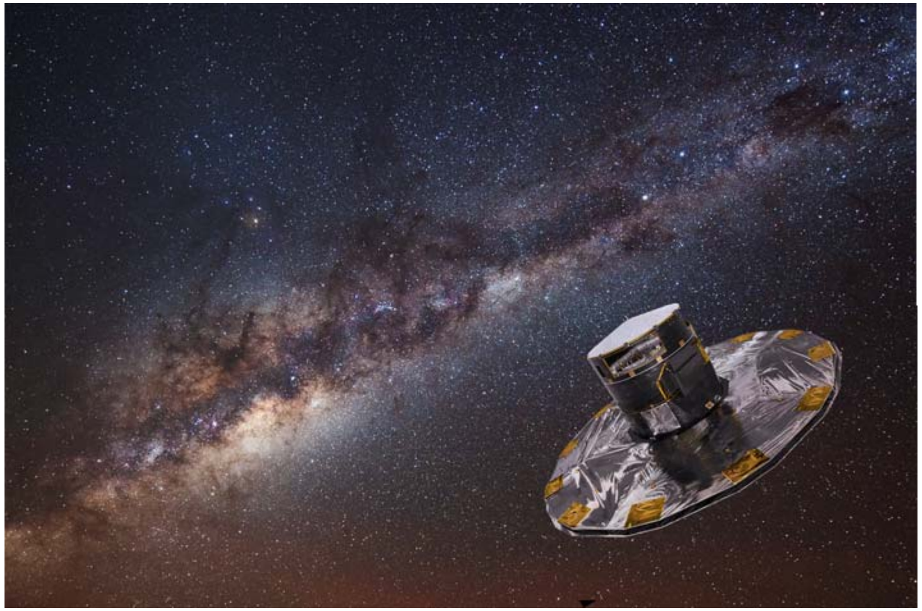
How are ions and ion collisions important?

Radiation damage and treatment, astrophysics and –chemistry, stellar and planetary atmospheres

H^- in stellar atmosphere – for diagnostics

H^-/X^+ reactions in stellar atmospheres for gauging the history and evolution of galaxies

Absolute Mutual Neutralization (MN) and ion-pair formation rates for X^+/H^-, X/H, are needed to determine chemical abundances X=Li, Na, Mg, Fe,….



Gaia - satellite

Gaia (ESA) maps positions and velocities of 10^9 stars in the Milky Way (10^{11} stars).

The 4MOST telescope provides complementary spectral data of a few thousand stars

Astron Astrophys Rev (2016) 24:9
DOI 10.1007/s00159-016-0095-9

REVIEW ARTICLE

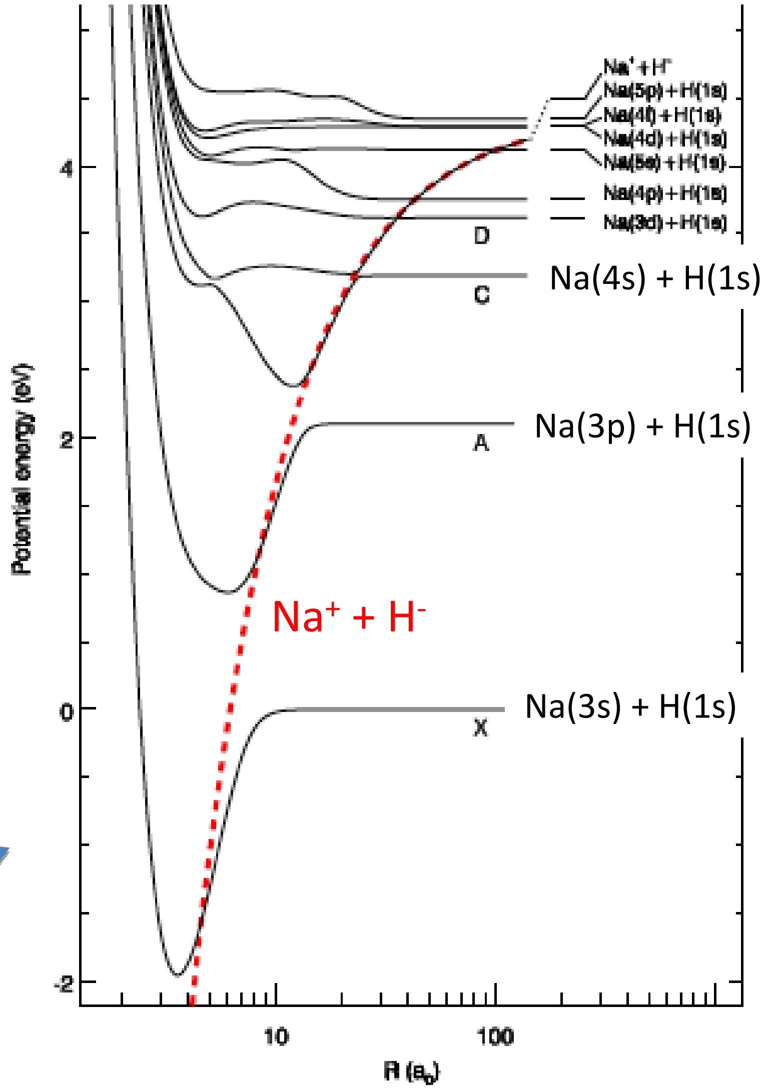
Accurate abundance analysis of late-type stars: advances in atomic physics

Paul S. Barklem[1]

Abstract The measurement of stellar properties such as c… …ons, masses and ages, through stellar spectra, is a fundamenta… …physics. Progress in the understanding, calculation and measure… …perties and processes relevant to the high-accuracy analysis of F… …ellar spectra is reviewed, with particular emphasis on abundanc… …udes fundamental atomic data such as energy levels, wavelengt… …obabilities, as well as processes of photoionisation, collisional … …astic collisions. A recurring theme throughout the review is th… …n theoretical atomic physics, laboratory measurements, and astr… …g, all of which contribute to our understanding of atoms and atom… …well as to modelling stellar spectra.

Reactions with H and H^- for gauging stellar chemical compositions

Potential energy curves NaH system
(from Dickinsson *et al* (1999))



How are ions and ion collisions important?

Radiation damage and treatment, astrophysics and –chemistry, stellar and planetary atmospheres

Northern Light

Green: The solar wind excites N_2, which transfers energy to atomic oxygen, oxygen emits at 557.7 nm.

Northern Light over Stockholm

blue: molecular nitrogen emission at 428 nm

Southern light over Cairns (?)

red: atomic oxygen emitting at 630 nm

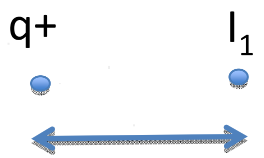
Collisions with atomic targets – some examples

Fast slow and collisions, interactions with electron clouds and atomic nuclei, electron capture and highly charged ions

Fast and slow collisions

PHYSICAL REVIEW A VOLUME 23, NUMBER 2 FEBRUARY 1981

Single-electron-capture cross section for medium- and high-velocity, highly charged ions colliding with atoms



H. Knudsen, H. K. Haugen, and P. Hvelplund
Institute of Physics, University of Aarhus, DK-8000 Aarhus C, Denmark
(Received 6 June 1980)

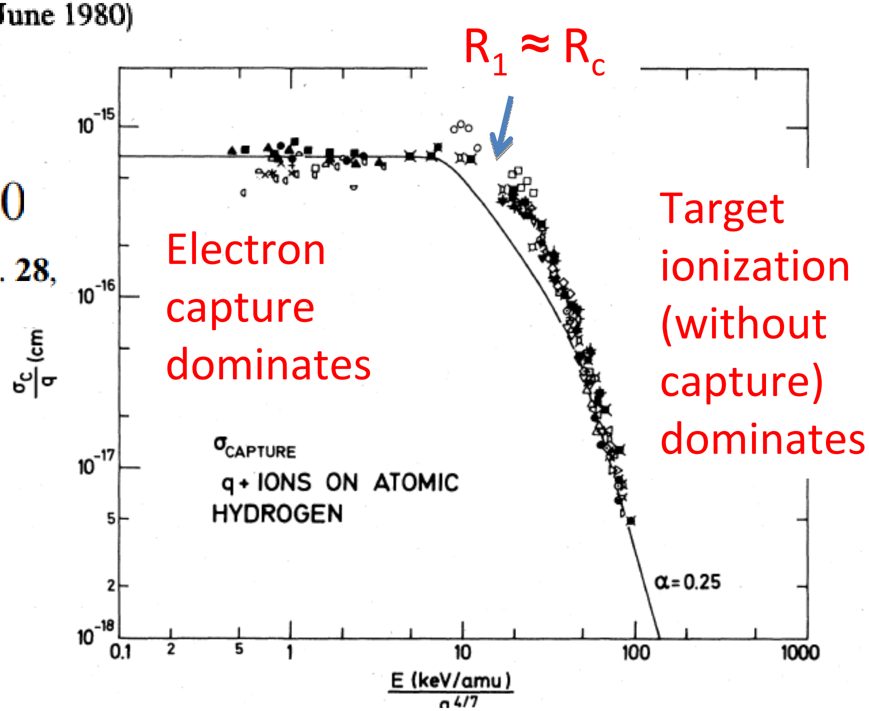
Release distance: $R_1 = (2\sqrt{q} + 1)/I_1$

Capture distance (R_c): $E^{e}_{\mathrm{tot}} = v^2/2 - q/R_c = 0$

Bohr, N. and Lindhard, J., K. Dan.Vidensk. Selsk. Mat. Fys. Medd. **28**, No 7 (1954).

Preben Hvelplund

Helge Knudsen



Collisions with atomic targets – some examples

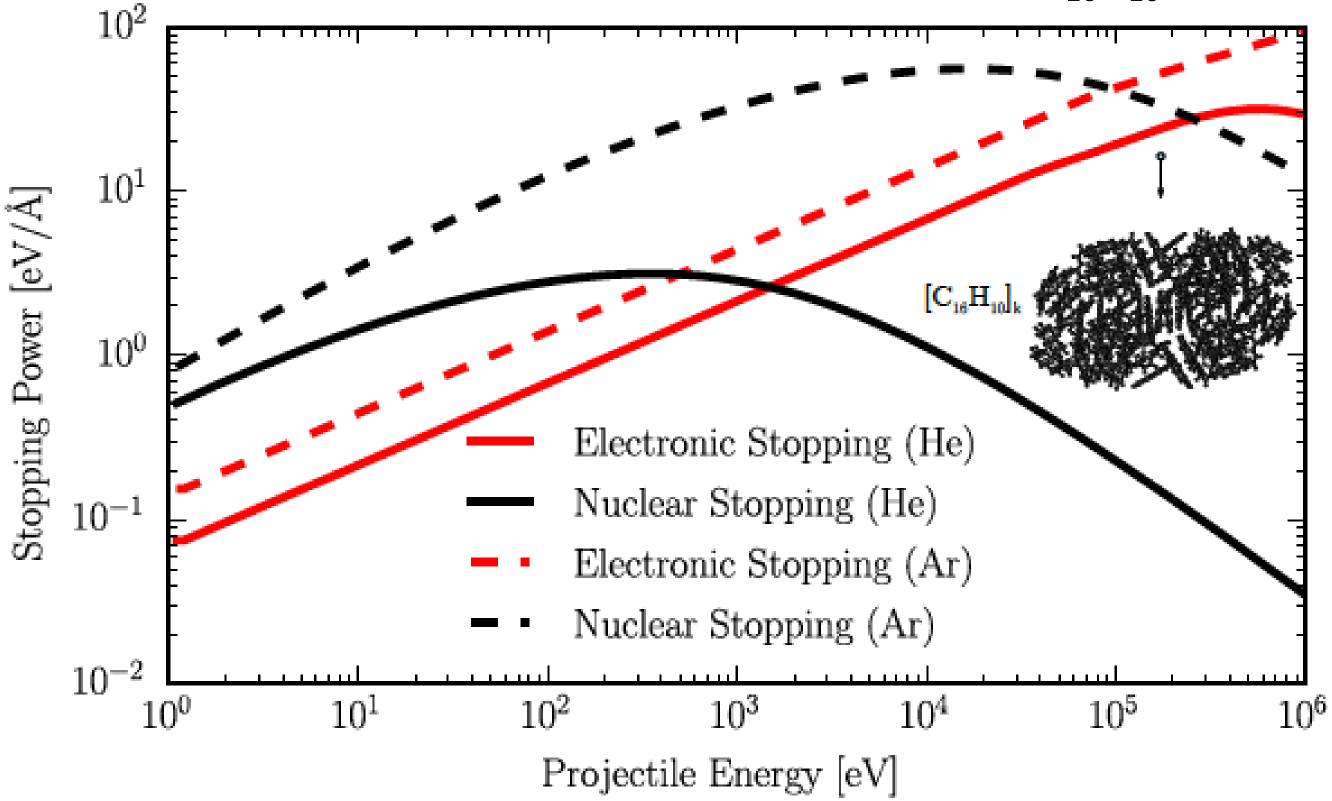
Fast slow and collisions, interactions with electron clouds and atomic nuclei, electron capture and highly charged ions

Electronic and nuclear stopping

From M. Gatchell, PhD thesis, SU

Michael Gatchell

SRIM calculations: He/Ar on a solid pyrene ($C_{16}H_{10}$) target



Collisions with atomic targets – some examples

Fast slow and collisions, interactions with electron clouds and atomic nuclei, electron capture and highly charged ions

Separation of scattering on target electrons and target nuclei is that possible?

yes with COLTRIMS, reaction microscopes….

COLD TARGET RECOIL ION MOMENTUM SPECTROSCOPY: A ‘MOMENTUM MICROSCOPE’ TO VIEW ATOMIC COLLISION DYNAMICS


Horst Schmidt-Böcking

R. DÖRNER[a], V. MERGEL[a], O. JAGUTZKI[a], L. SPIELBERGER[a], J. ULLRICH[b], R. MOSHAMMER[b], H. SCHMIDT-BÖCKING[a]

[a] *Insitut für Kernphysik, Universität Frankfurt, August Euler Str. 6, D60486 Frankfurt, Germany*
[b] *Fakultät für Physik, Universität Freiburg, Hermann-Herder-Str. 3, D79104 Freiburg, Germany*

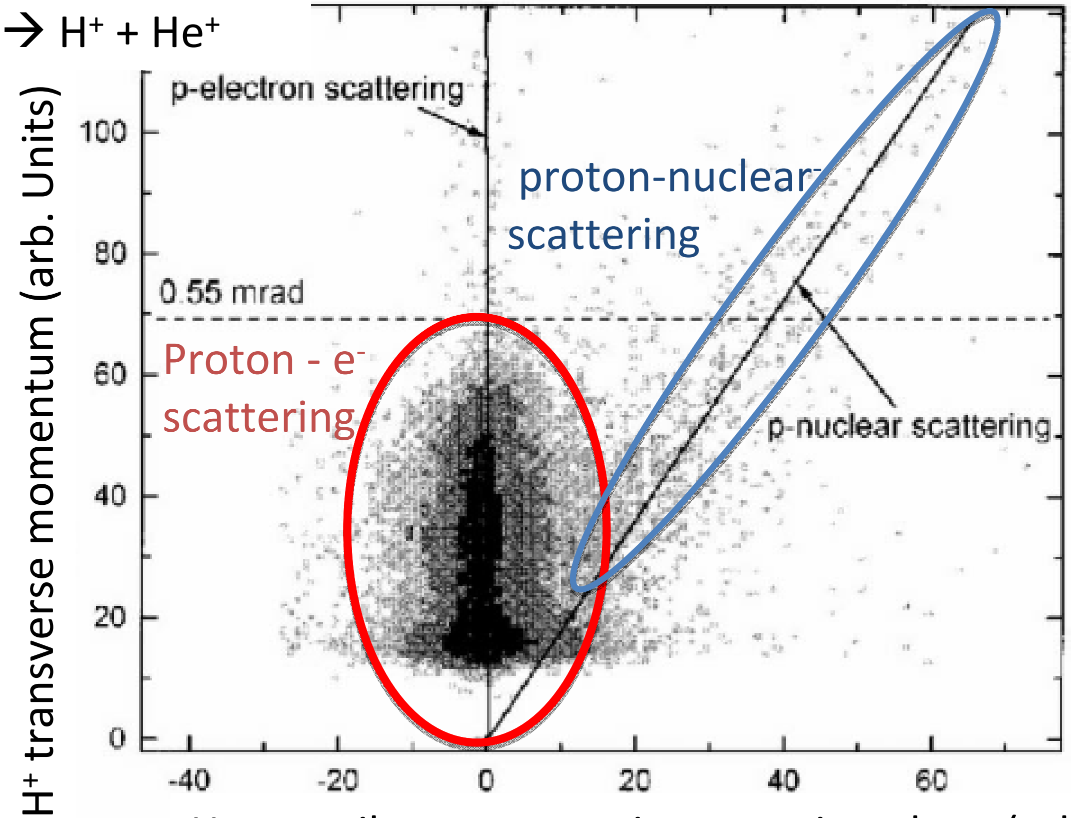
Physics Reports 330, p. 95 (2000)

In this Physics Report a COLTRIMS study from Kansas State University is discussed

R. Dörner et al. / Physics Reports 330 (2000) 95–192

Exp. from Kansas State Univ: DeHaven *et al.*, PRA **57** (1998)

6 MeV $H^+ + He \rightarrow H^+ + He^+$



He⁺ recoil momentum in scattering plane (arb. units)

Lew Cocke, KSU

Collisions with atomic targets – some examples

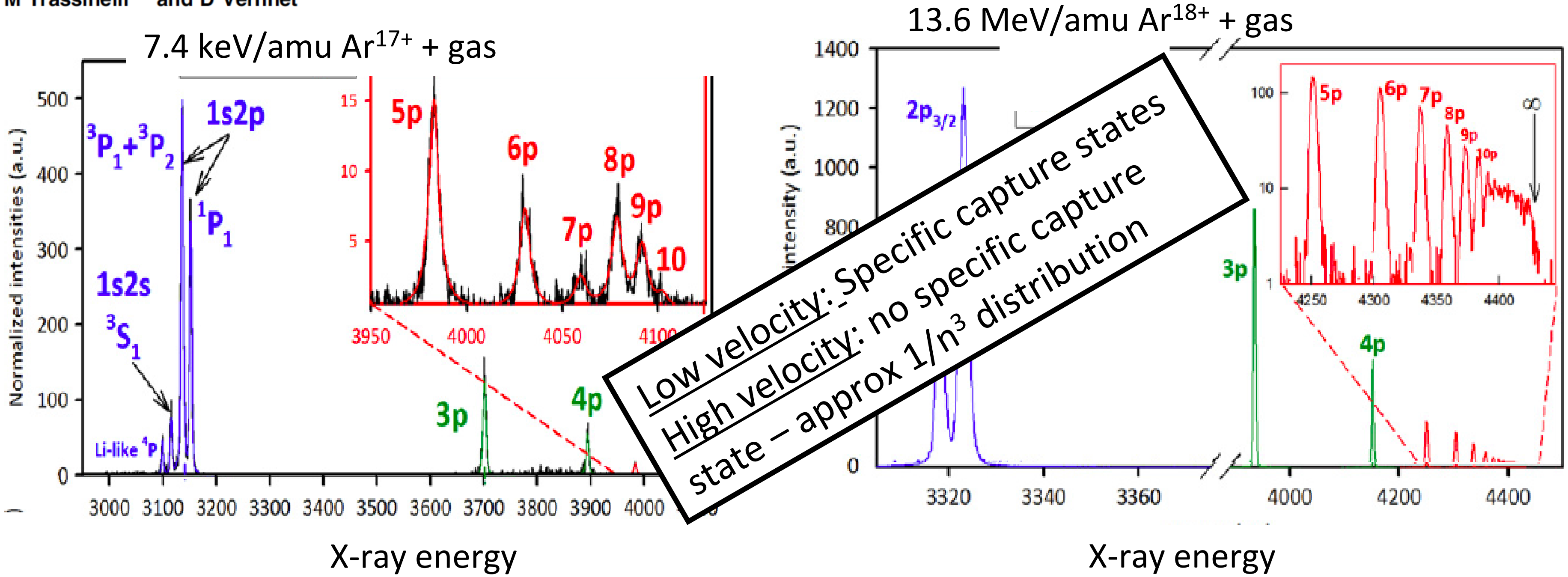
Fast slow and collisions, interactions with electron clouds and atomic nuclei, electron capture and highly charged ions

IOP Publishing | Journal of Physics B: Atomic, Molecular and Optical Physics

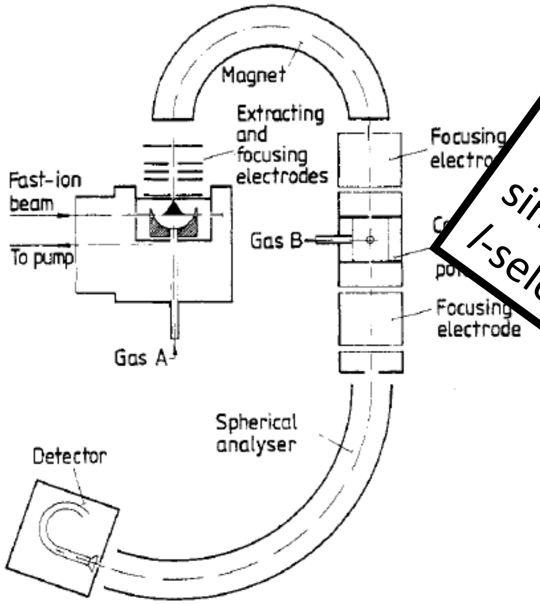
J. Phys. B: At. Mol. Opt. Phys. **48** (2015) 144016 (9pp) | doi:10.1088/0953-4075/48/14/144016

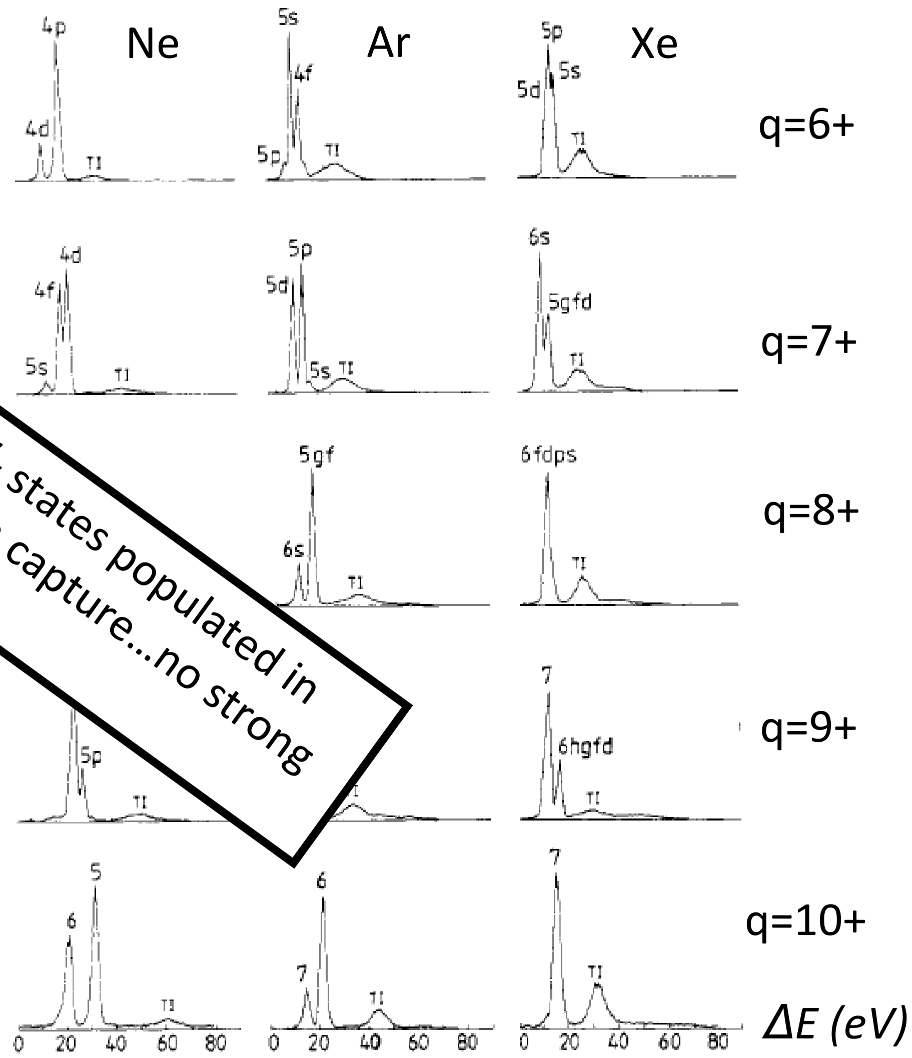
High-resolution x-ray spectroscopy to probe quantum dynamics in collisions of $Ar^{17+,18+}$ ions with atoms and solids, towards clusters

E Lamour[1,2], C Prigent[1,2], J-M Ramillon[3], J-P Rozet[1,2], S Steydli[1,2], M Trassinelli[1,2] and D Vernhet[1,2]



1 keV Ar^{q+} + Ne, Ar, Xe → $Ar^{(q-1)+}$ + ….. collisions





only few *nl*- states populated in single-electron capture…no strong *l*-selectivity

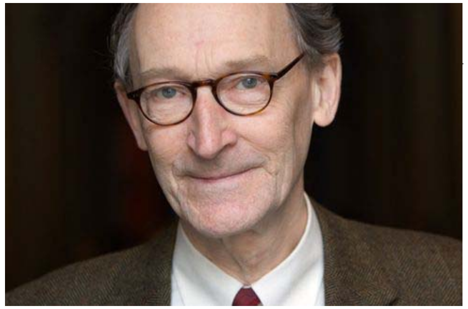
Measurements of the Q-values of the reactions $Q \approx \Delta E$ *(eV)*

E.H. Nielsen *et al.*,

J. Phys. B: At. Mol. Phys. **18** (1985) 1789–1808.

Nuclear Instruments and Methods in Physics Research B9 (1985) 397–399
North-Holland, Amsterdam

Anders Bárány



ABSOLUTE CROSS SECTIONS FOR MULTI-ELECTRON PROCESSES IN LOW ENERGY Ar^{q+}–Ar COLLISIONS: COMPARISON WITH THEORY

A. BÁRÁNY [1)], G. ASTNER [2)], H. CEDERQUIST [2)], H. DANARED [2)], S. HULDT [3)],
P. HVELPLUND [4)], A. JOHNSON [2)], H. KNUDSEN [4)], L. LILJEBY [2)] and K.-G. RENSFELT [2)]

$$R_m = \left[2(q-m+1)^{1/2} m^{1/2} + m\right] / I_m$$

I_m: m:th ionization potentials

first capture state $n \approx q^{3/4}/I_1^{1/2}$

$$\sigma_1 = \pi\left(R_1^2 - R_2^2\right),$$
$$\sigma_2 = \pi\left(R_2^2 - R_3^2\right),$$
$$\ldots$$
$$\sigma_N = \pi R_N^2.$$

See also Niehaus, A., J. Phys. B **19**, 2925 (1986)

Over-the-barrier electron transfer models for different collision scenarios

Projectile-sphere radius	Target-sphere radius	Static OBM model for:
Finite	Finite	Cluster-cluster H. Zettergren *et al.*, (2002) Physical Review A **66**, 032710
$\rightarrow 0$	Finite	Ion-cluster Bárány and Setterlind NIMB (1995) Cederquist *et al*. PRA (2000)
$\rightarrow 0$	$\rightarrow 0$	Ion-atom Bárány *et al* NIMB (1985). Niehaus J Phys B (1986).
$\rightarrow 0$	$\rightarrow \infty$	Ion-surface Burgdörfer, J., Lerner, P. and Meyer, F. W., Phys. Rev. A **5674** (1991)
Finite	$\rightarrow \infty$	Cluster-surface H. Zettergren *et al.*, (2002) Physical Review A **66**, 032710

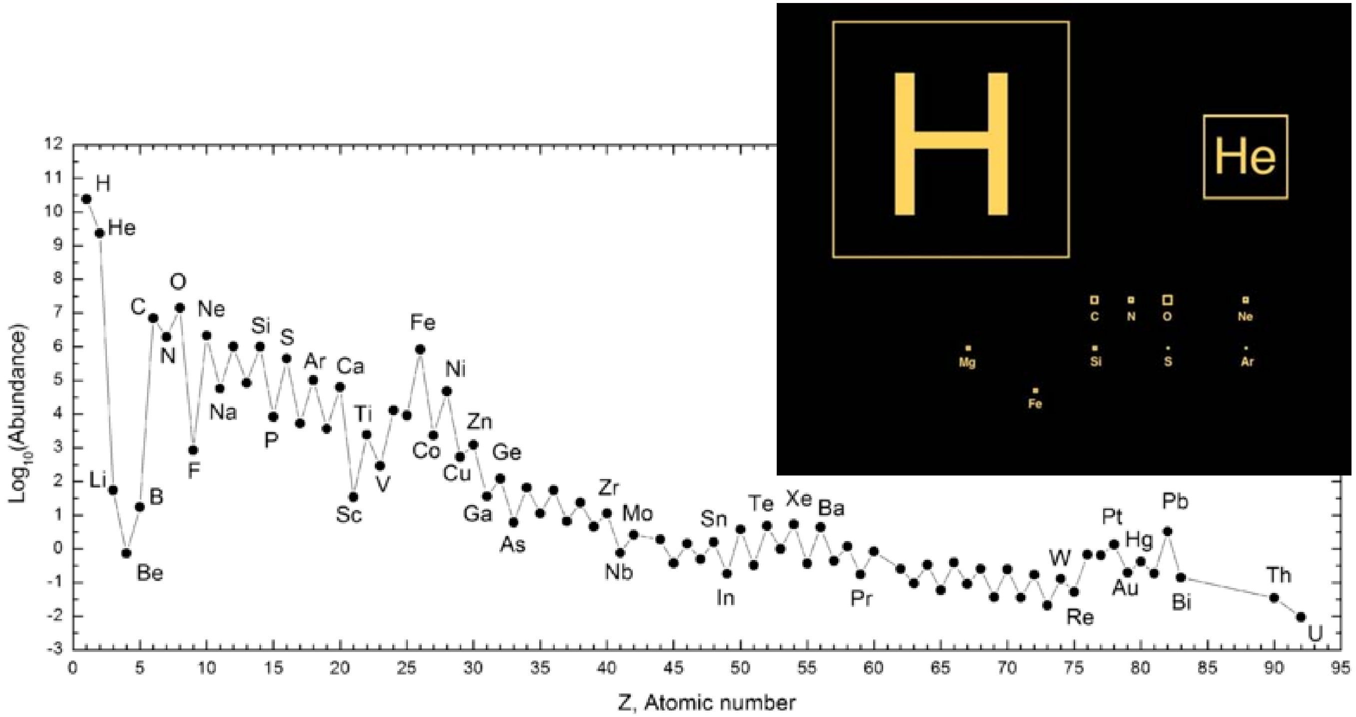
NEW! Electron transfer between dielectric spheres, Lindén *et al.*, JCP **145**, 194307 (2016)

Ion- metal disc (PAH-molecule), B. Forsberg et al., JCP **138**, 054306 (2013)

Atoms, smaller molecules, fullerenes and PAHs (?) in space

Spectroscopic identifications and predictions

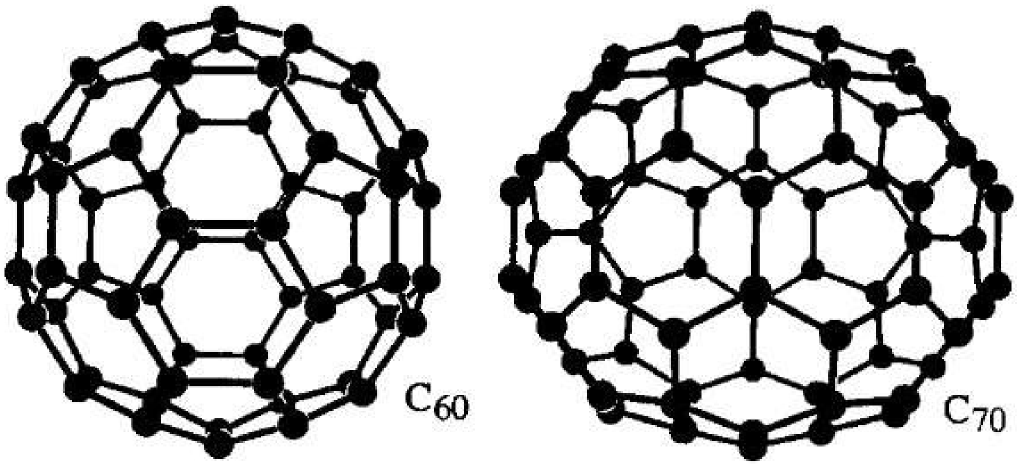
Abundances of elements in the universe



Elemental abundance in the interstellar medium, B.J. McCall, PhD thesis, University of Chicago 2001.

Molecules in the universe (as of 2013)

since then for examples



and C_{60}^+

Table from A.G.G.M. Tielens, "The Molecular Universe", Reviews of Modern Physics **85**, 1022 (2013).

See http://www.astrochymist.org/ or https://www.astro.uni-koeln.de/cdms/ for updates

TABLE I. Identified interstellar and circumstellar molecules. [Most molecules have been detected at radio and millimeter wavelengths, unless otherwise indicated (IR, VIS, or UV). Species labeled with a question mark await confirmation.]

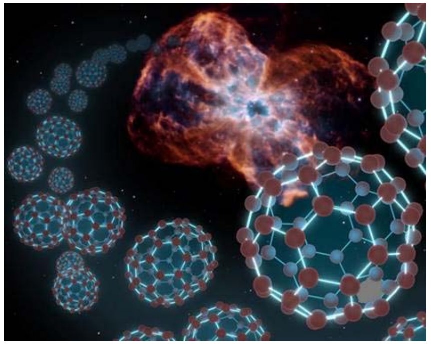
		Simple hydrides, oxides, sulfides, halogens		
H_2 (IR, UV)	CO	NH_3	CS	HCl
O_2	H_2O_2	PO	CO_2 (IR)	$NaCl$[a]
H_2O	SO_2	OCS	H_2S	KCl[a]
PN	SiO	SiH_4[a] (IR)	SiS	$AlCl$[a]
N_2O	CH_4 (IR)	$HSCN$	HF	AlF[a]
$HONC$	$HNCO$	$AlOH$		
		Nitriles and acetylene derivatives		
C_2 (IR)	HCN	CH_3CN	HNC	C_2H_4[a] (IR)
C_3 (IR,UV)	HC_3N	CH_3C_3N	$HNCO$	C_2H_2 (IR)
C_5[a] (IR)	HC_5N	CH_3C_5N	$HNCS$	C_6H_2 (IR)
C_3O	HC_7N	CH_3C_2H	$HNCCC$	C_3H_6
C_3S	HC_9N	CH_3C_4H	CH_3NC	C_3H_7CN
C_4Si[a]	$HC_{11}N$	CH_3C_6H	$HCCNC$	
H_2C_4	HC_2CHO	CH_2CHCN	CH_2CCHCN	
		Aldehydes, alcohols, ethers, ketones, amides		
H_2CO	CH_3OH	$HCOOH$	$HCOCN$	CH_3CH_2CN
CH_3CHO	CH_3CH_2OH	$HCOOCH_3$	CH_3NH_2	NH_2CH_2CN
CH_3CH_2CHO	CH_2CCHOH	CH_3COOH	CH_3CONH_2	NH_2CN
NH_2CHO	$(CH_2OH)_2$	$(CH_3)_2O$	H_2CCO	CH_2CHCN
CH_2OHCHO	$(CH_3)_2CO$	H_2CS		
C_2H_5OCHO		CH_3SH		
		Cyclic molecules		
C_3H_2	SiC_2	c-C_3H	CH_2OCH_2	C_6H_6 (IR) ?
c-SiC_3	H_2C_3O	C_2H_4O		
		Molecular cations		
CH^+	CO^+	$HCNH^+$	OH^+	HN_2^+
CH_3^+	HCO^+	HC_3NH^+	H_2O^+	H_3^+ (IR)
HS^+	HOC^+	H_2COH^+	H_3O^+	SO^+
HCS^+	$HOCO^+$	CF^+	HCl^+	H_2Cl^+
		Molecular antions		
C_4H^-	C_6H^-	C_8H^-		
CN^-	C_3N^-	C_5N^-		
		Radicals		
OH	C_2H	CN	C_2O	C_2S
CH	C_3H	C_3N	NO	NS
CH_2	C_4H	$HCCN$[a]	SO	SiC[a]
NH (UV)	C_5H	CH_2CN	HCO	SiN[a]
NH_2	C_6H	CH_2N	C_5N[a]	CP[a]
SH	C_7H	$NaCN$	KCN	$MgCN$
C_3H_2	C_8H	$MgNC$	$FeCN$	
C_4H_2	HNO	H_2CN	HNC_3	HO_2
C_6H_2	$AlNC$	$SiNC$	C_4Si	$SiCN$
HCP	CCP	AlO		
		Fullerenes		
C_{60} (IR)	C_{70}[a] (IR)	C_{60}^+ (VIS) ?		

[a]These species have been detected only in the circumstellar envelope of carbon-rich stars.

Detection of C_{60} and C_{70} in a Young Planetary Nebula

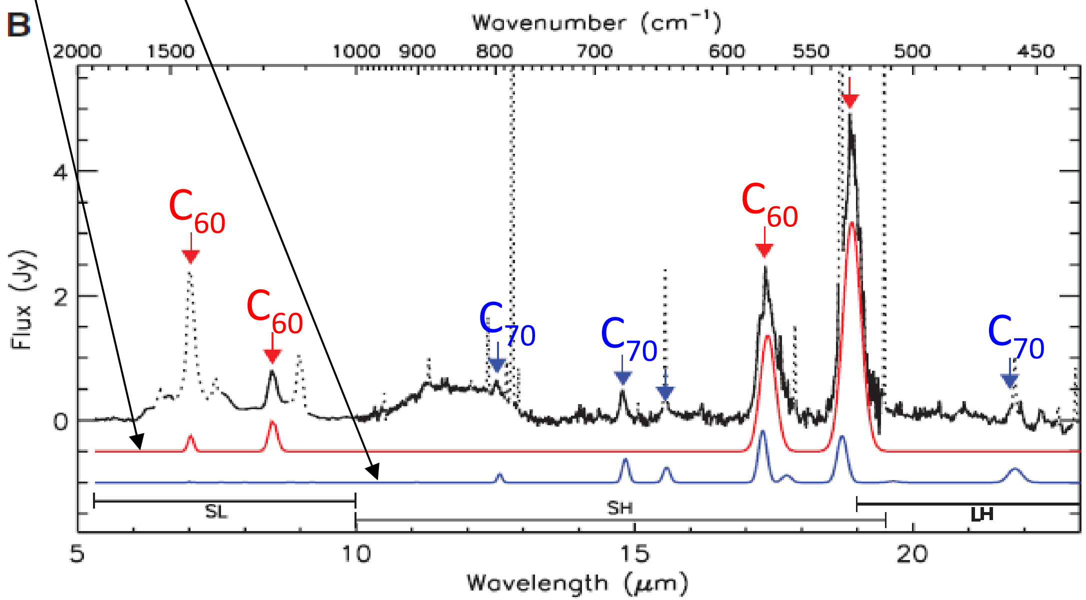
Jan Cami,[1,2]* Jeronimo Bernard-Salas,[3,4] Els Peeters,[1,2] Sarah Elizabeth Malek[1]

3 SEPTEMBER 2010 VOL 329 SCIENCE www.sciencemag.org



5-20 km/s outflow from a carbon-rich AGB star

Red and **blue** lines: IR-emission spectra of C_{60} and C_{70}



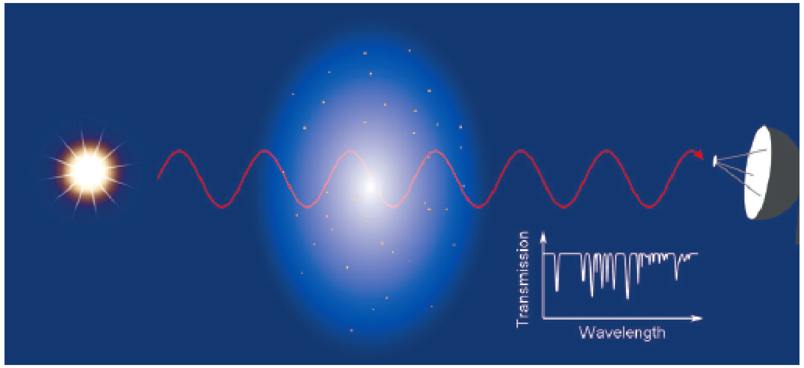
C_{60}: 330 K

C_{70}: 170 K

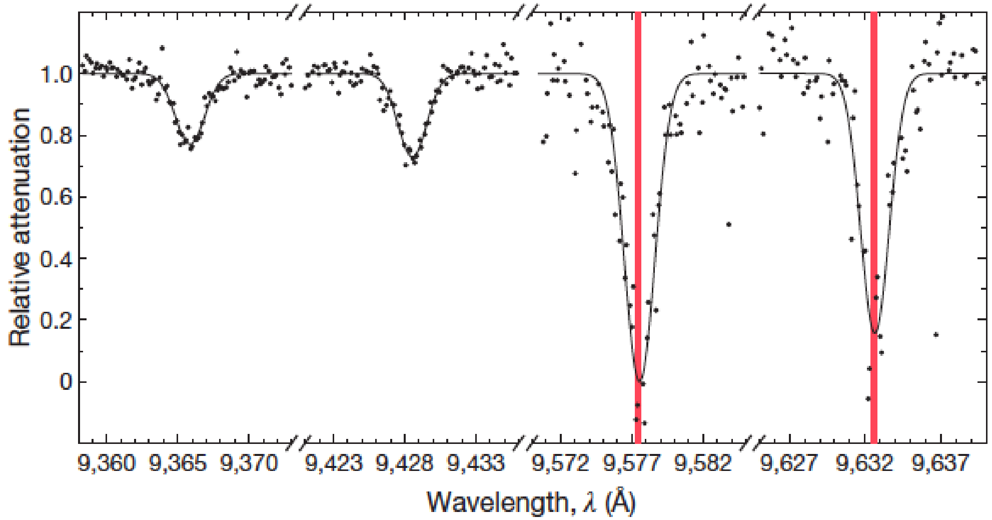
LETTER 322 | NATURE | VOL 523 | 16 JULY 2015 doi:10.1038/nature14566

Laboratory confirmation of C_{60}^+ as the carrier of two diffuse interstellar bands

E. K. Campbell[1], M. Holz[1], D. Gerlich[2] & J. P. Maier[1]



Diffuse interstellar Bands – illustration from J.P. Maier and E.K. Campbell, Angew Chem Int Ed 56, 4920 (2017)).

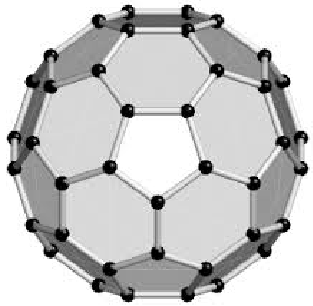


ARTICLE

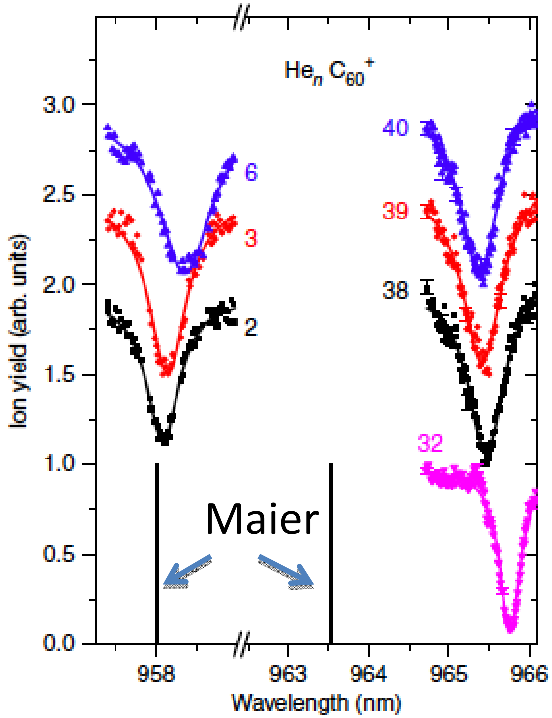
Received 17 Jun 2016 | Accepted 13 Oct 2016 | Published 22 Nov 2016 DOI: 10.1038/ncomms13550 OPEN

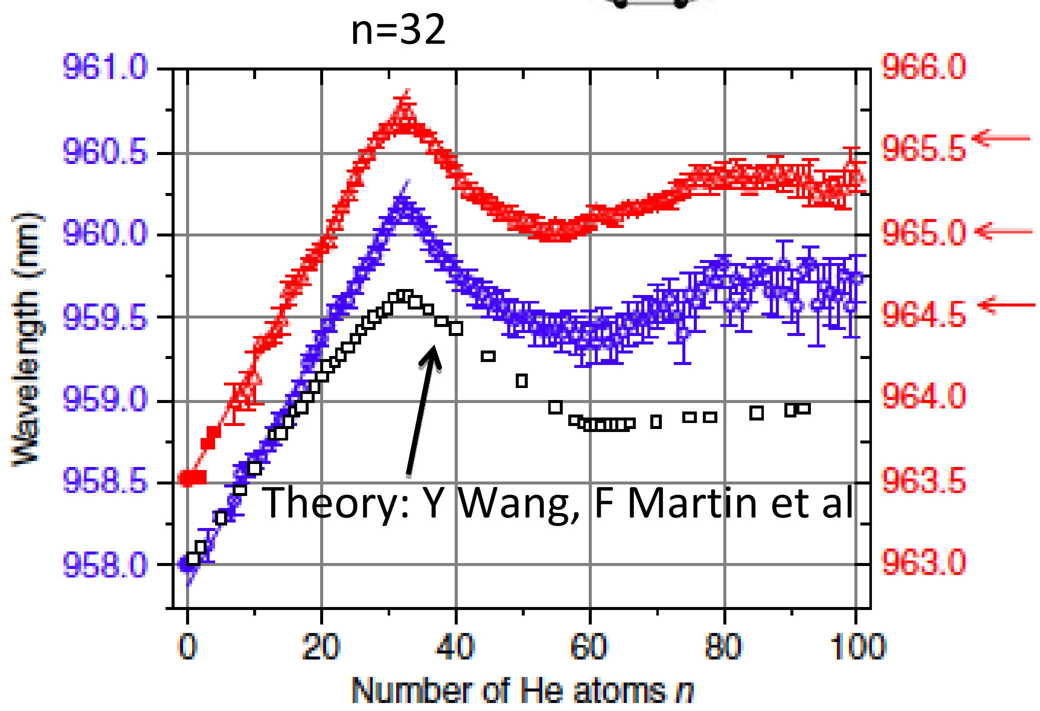
Atomically resolved phase transition of fullerene cations solvated in helium droplets

M. Kuhn[1], M. Renzler[1], J. Postler[1], S. Ralser[1], S. Spieler[1], M. Simpson[1], H. Linnartz[2], A.G.G.M. Tielens[2], J. Cami[3,4], A. Mauracher[1], Y. Wang[5,6,7], M. Alcamí[5,6,7], F. Martín[5,6,8], M.K. Beyer[1], R. Wester[1], A. Lindinger[9] & P. Scheier[1]



12+20=32



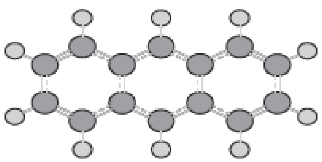


Atoms, smaller molecules, fullerenes and PAHs (?) in space

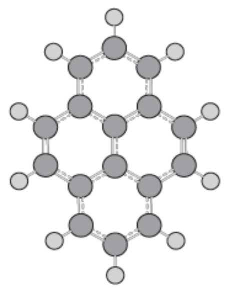
Spectroscopic identifications and predictions

How are fullerenes made? Are they made from PAHs?

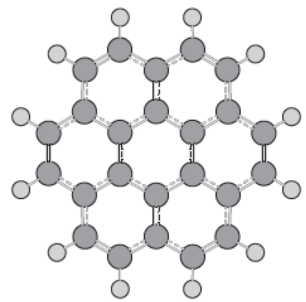
PAH: Polycyclic Aromatic Hydrocarbons



Anthracene
$C_{14}H_{10}$



Pyrene
$C_{16}H_{10}$



Coronene
$C_{24}H_{12}$

Formation of buckminsterfullerene (C_{60}) in interstellar space

Olivier Berné[1] and A. G. G. M. Tielens

Leiden Observatory, Leiden University, P.O. Box 9513, NL- 2300 RA Leiden, The Netherlands

<u>Suggested route:</u>

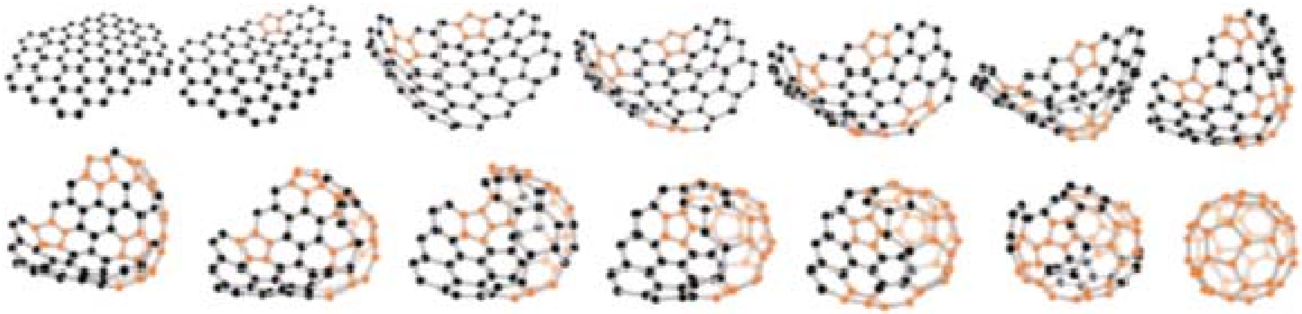
PAHs + UV photons →

Hydrogen emission →

Small pieces of graphene →

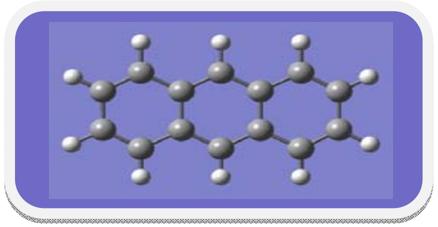
Carbon emission →

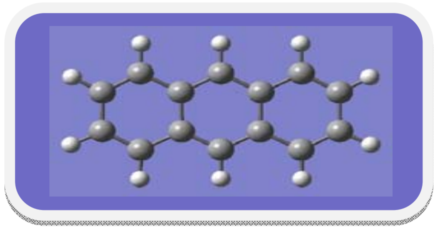
Pentagons (curvature) → Fullerenes

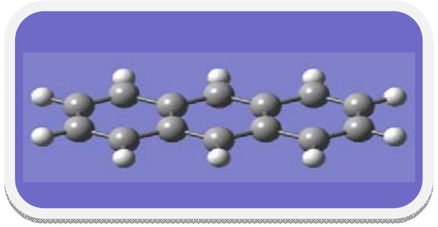


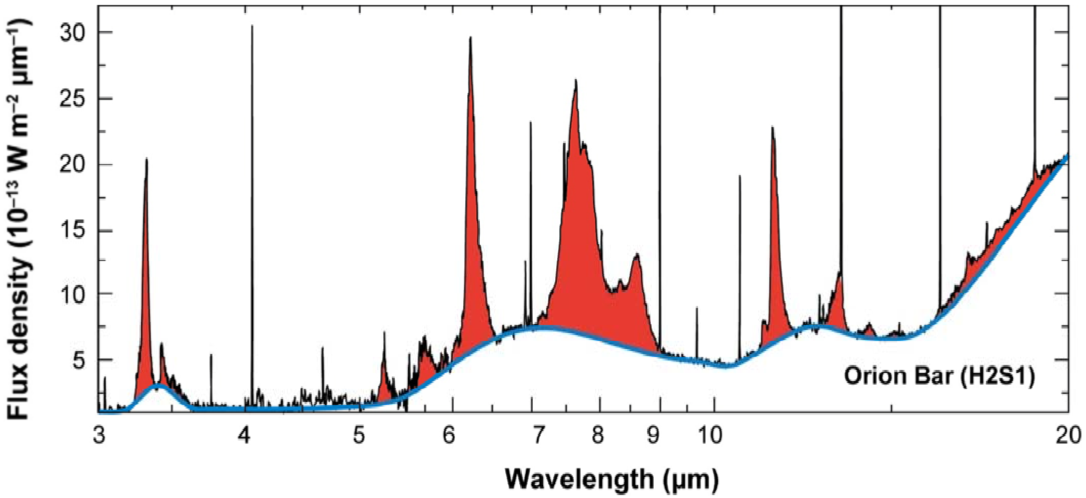
Unidentified Infrared Emission

The PAH hypothesis – no identification of a specific PAH so far









Tielens (2008), *Annu. Rev. Astro. Astrophys.* **46**, 289.

Peeters et al. (2002) Astron. Astrophys. **390,** 1089

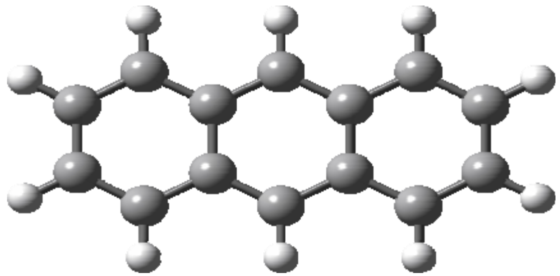
Orion star forming region:
red 8 μm image

Collisions with fullerenes, PAHs, and biomolecules

Statistical and non-statistical fragmentation

Some properties: Typical statistical PAH-fragmentation processes

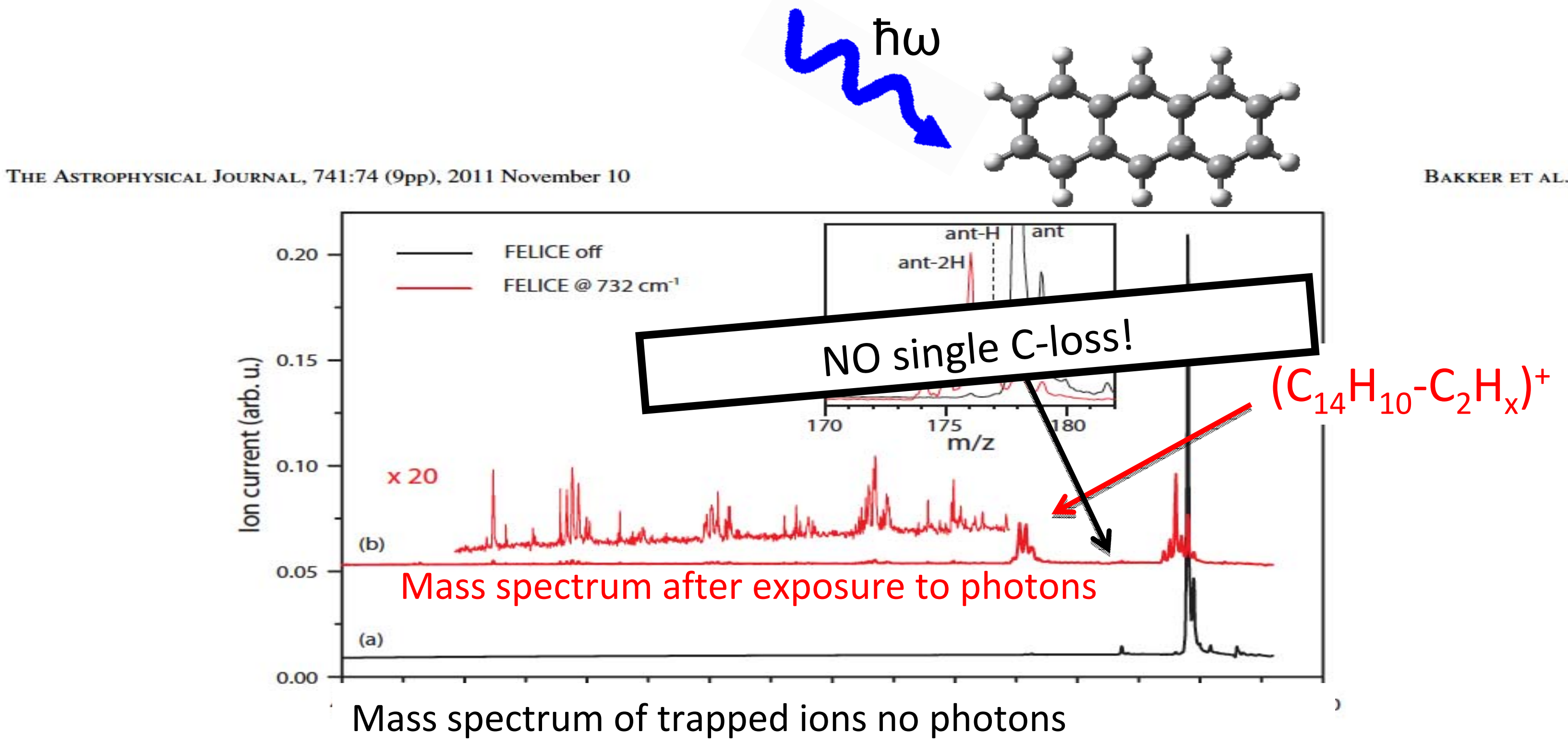
PAH: Anthracene $C_{16}H_{10}$



H- and C_2H_2-loss

Dissociation energies about 5 eV

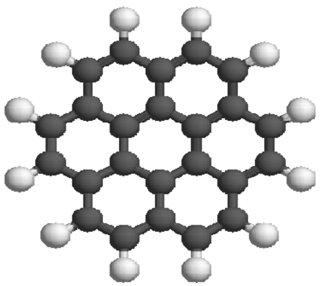
Multiphotoabsorption of IR-photons in trapped anthracene cations, $C_{14}H_{10}^+$



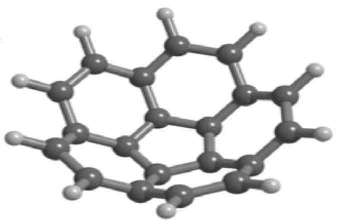
Experiment at the Free Electron Laser FELICE in Nijmegen, the Netherlands

Collisions with 100 eV e^-:

100 eV e^- + Coronene $C_{24}H_{12}$

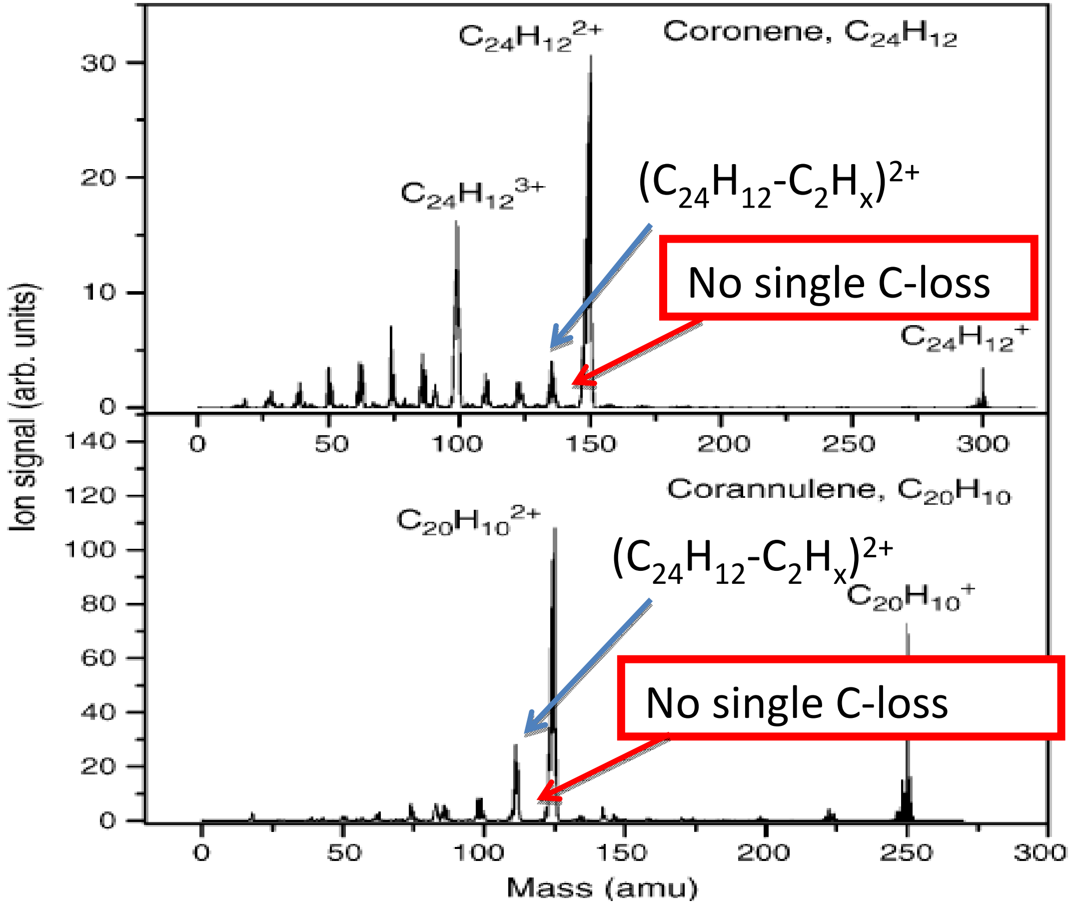


100 eV e^- + Coranule



Bowl shaped!
Has one pentagon!

S. Denifl et al , Int J Mass Spectrom 249-250, 343 (2006)



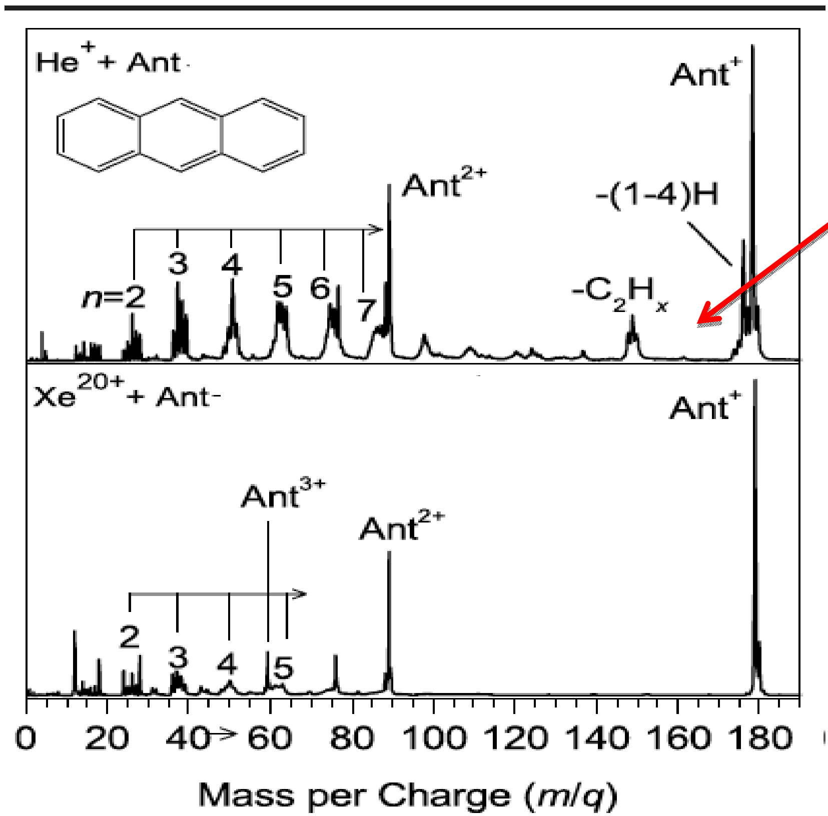
PAHs excited and ionized in **collisions with keV ions**:

10 keV He^+

Low charge:
close collisions
needed to ionize
the PAH

200 keV Xe^{20+}

High charge:
ionization at
large distances



No C-loss

Exp. in Caen with
Patrick Rousseau,
Alicija Domaracka,
Bernd Huber,…

Anne Holm

A I S Holm *et al.*, Phys Rev Lett **105**, 213401 (2010)

Some additional ion-PAH collision studies at keV and MeV energies

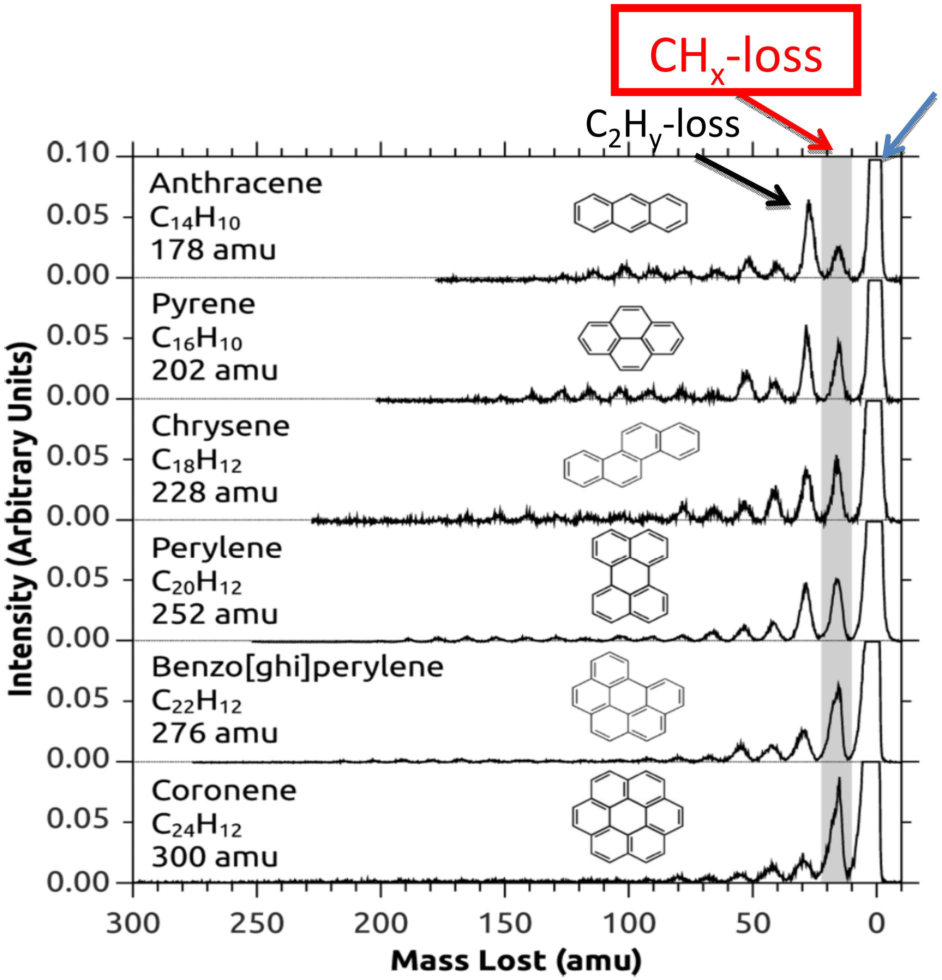
S. Martin *et al* Phys. Rev. A **85** 052715 (2012)
G. Reitsma, *et al* J. Phys. B: At. Mol. Opt. Phys. **45** 215201 (2012)
P. M. Mishra *et al* Phys. Rev. A **88** 052707 (2013)
G Reitsma *et al* J. Phys. B: At. Mol. Opt. Phys. **46** 245201 (2013)
P. M. Mishra *et a*l J. Phys. B: At. Mol. Opt. Phys. **47** 085202 (2014)
S. Biswas and L.C. Tribedi, Phys. Rev. A 92, 060701 R (2015)

…Lyon, Groningen, Mumbai (Tata Institute), Caen, Stockholm,…

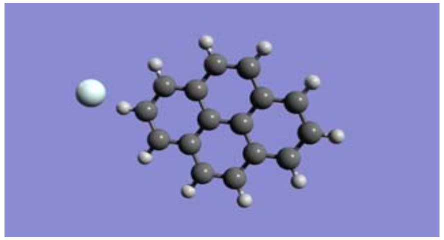
Atom collisions with PAHs at 100 eV. **This is DIFFERENT from keV collisions!**

M.H. Stockett *et al.*, Phys Rev A **89**, 032701 (2014)

Exp. in Stockholm



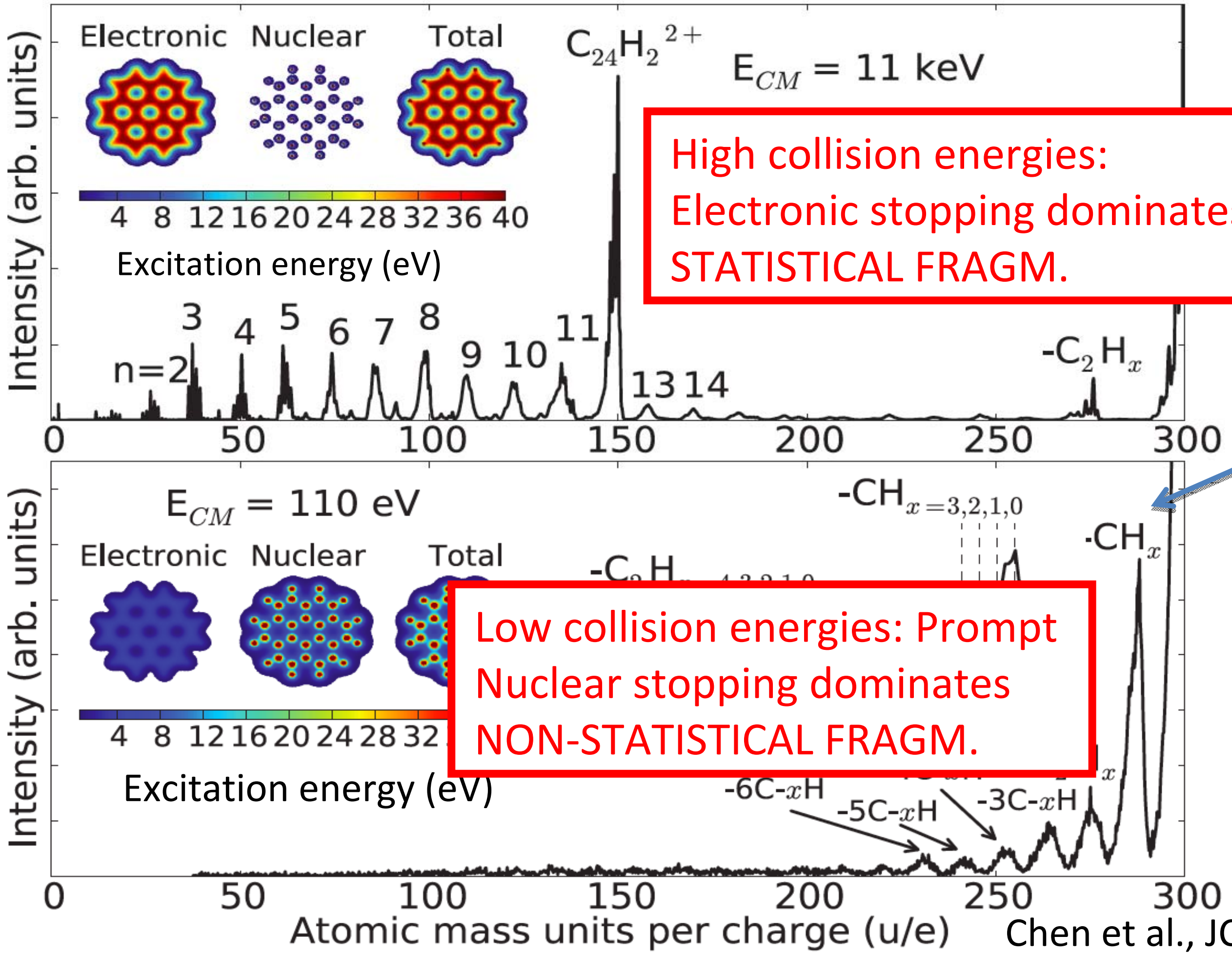
100 eV He on C$_{16}$H$_{10}$



MD-simulation

Why is it DIFFERENT?

Comparison: Fragmentation at low and high He collision energies



$He^+ + C_{24}H_{12} \rightarrow$ ...
E_{CM} = 11 keV

Single-atom knockout

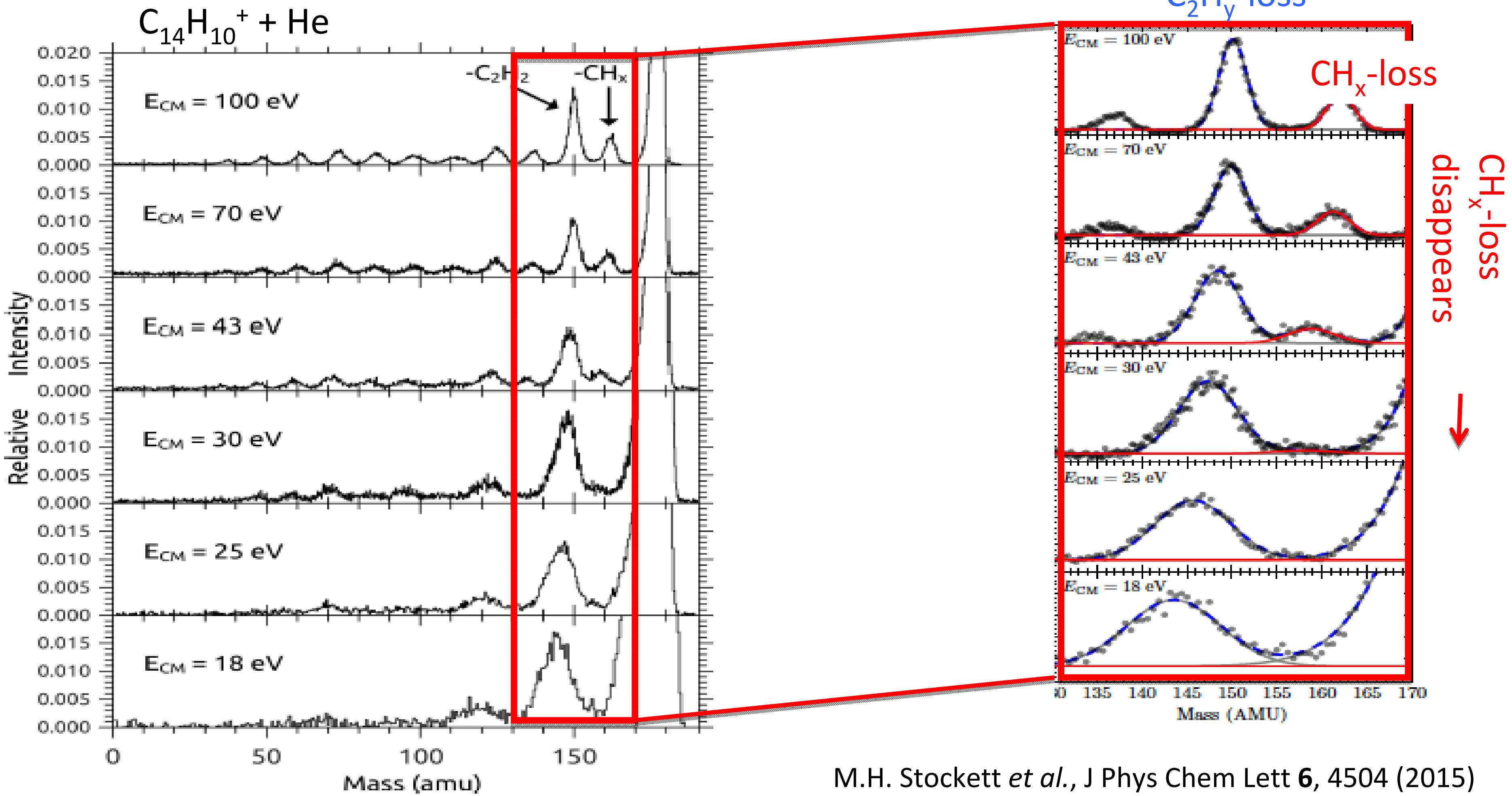
$He + C_{24}H_{12}^+ \rightarrow$ ...
E_{CM} = 110 eV

Chen et al., JCP **140**, 224306 (2014)

Threshold energies for NON-STATISTICAL fragmentation of PAHs

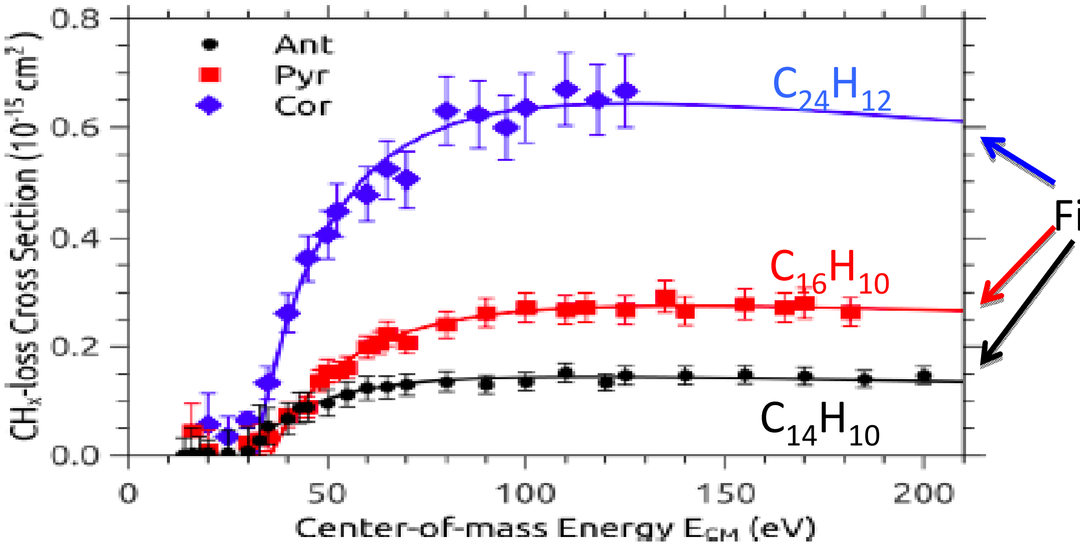
Exp/calc. in Stockholm partly inspired by work of the
Groningen group, e.g., Postma *et al.*, The Astrophysical Journal, 708:435–444, 2010

Threshold energies for CH_x-loss (*Non-statistical fragmentation*)

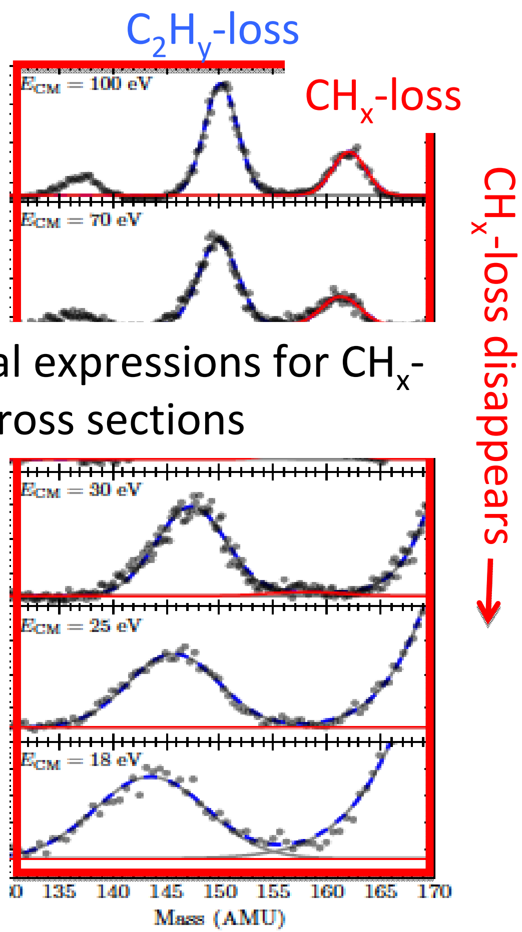


M.H. Stockett *et al.*, J Phys Chem Lett **6**, 4504 (2015)

Thresholds for CH_x-loss (*Non-statistical fragmentation*): The energy dependence of the cross section



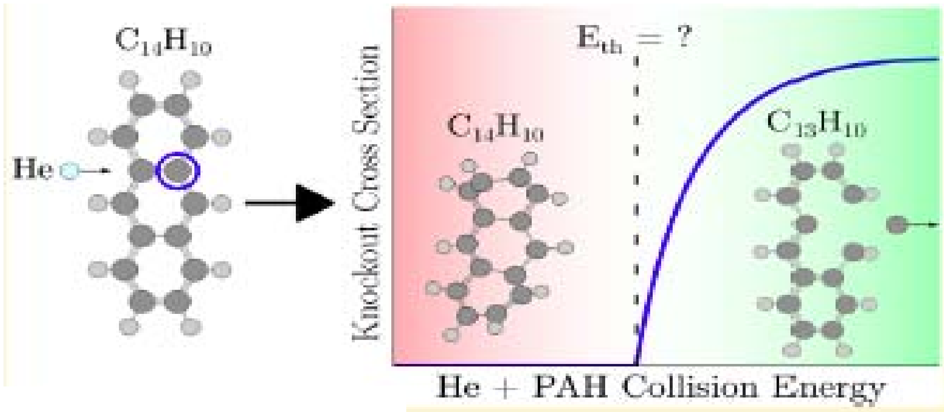
Fitted analytical expressions for CH_x-loss cross sections



M.H. Stockett *et al.*, J Phys Chem Lett **6**, 4504 (2015)

NON-STATISTICAL fragmentation: carbon KnockOut (KO) cross section (analytical expression):

Mark Stockett



$$\sigma_{KO} = \frac{A/E_{CM}}{\pi^2 \arccos^{-2}(\sqrt{E_{th}/E_{CM}}) - 4}$$

E_{CM}: center-of-mass collision energy

E_{th}: threshold energy in the center-of-mass system

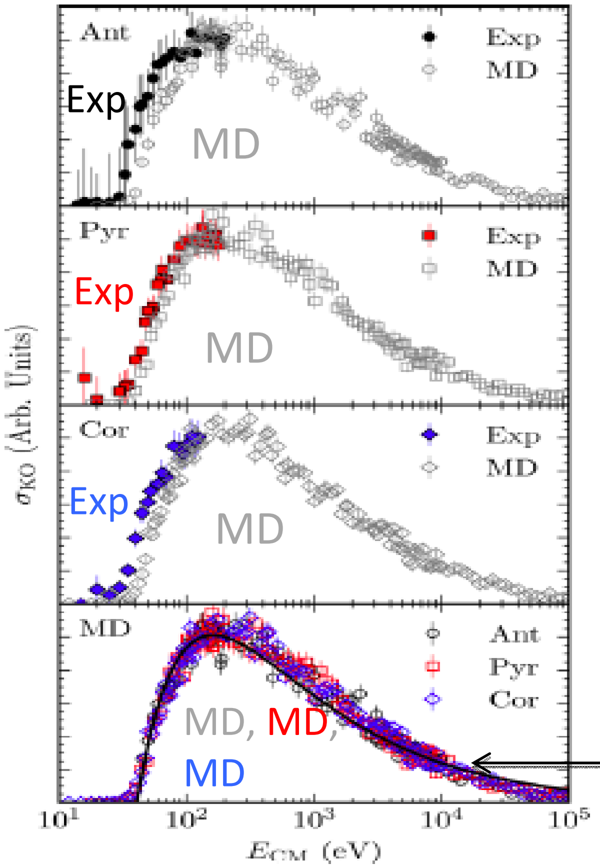
$$A = \frac{4}{3} 0.736 N \frac{2\pi a_0 Z_{He} Z_C}{\sqrt{Z_{He}^{2/3} + Z_C^{2/3}}} \frac{4\pi\epsilon_0}{e^2}$$

N: number of carbon atoms in the PAH

Z_{He} *and* Z_C: nuclear charges

M.H. Stockett *et al.*, J Phys Chem Lett **6**, 4504 (2015)

Comparing the fitted analytical expressions with Classical MD simulations and experimental data (relative cross section scales):



Classical MD-simulations:

-C-C and C-H bonds and their breaking described by Tersoff potentials

-ZBL potential to describe He-C and He-H interactions

-Mutual interactions between all C-, H, and He- atoms during the simulation

-Multiple angular scattering and knockout; secondary knockout

-No electronic excitations

$$\sigma_{KO} = \frac{A/E_{CM}}{\pi^2 \arccos^{-2}(\sqrt{E_{th}/E_{CM}}) - 4}$$

E_{th}: fitting parameter

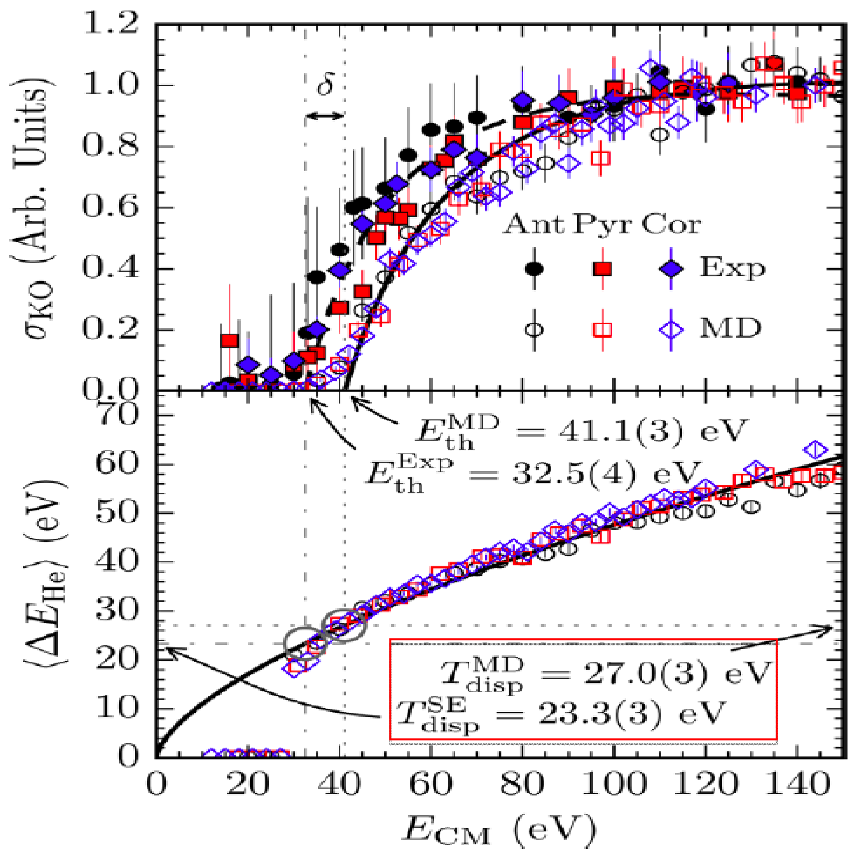
M.H. Stockett *et al.*, J Phys Chem Lett **6**, 4504 (2015)

Semi-Empirical (SE) and MD carbon-displacement energies:

<u>The displacement energy:</u> The energy loss of the projectile (here He), which is equal to the energy transfer to the PAH-system, at the KO threshold.

T_{disp}^{SE} = 23.3±0.3 eV (isolated PAHs)
M.H. Stockett *et al.*, J Phys Chem Lett **6**, 4504 (2015)

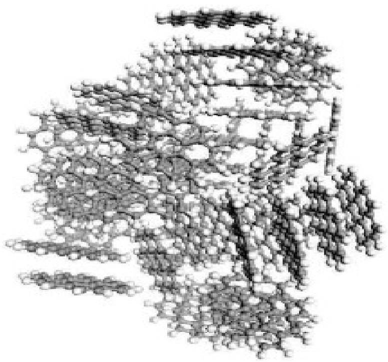
$T_{disp}^{graphene}$ = 23.6 eV (electron bombardment on graphene)
J.C. Meyer *et al.*, Phys Rev Lett **110**, 239902 (2013)



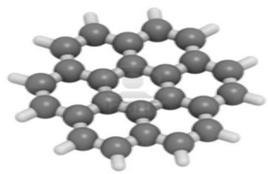
Collisions with clusters of molecules

Ionization, fragmentation, evaporative cooling, and molecular growth

Some further properties – binding energies between molecules in clusters and dissociation energies of molecular building blocks

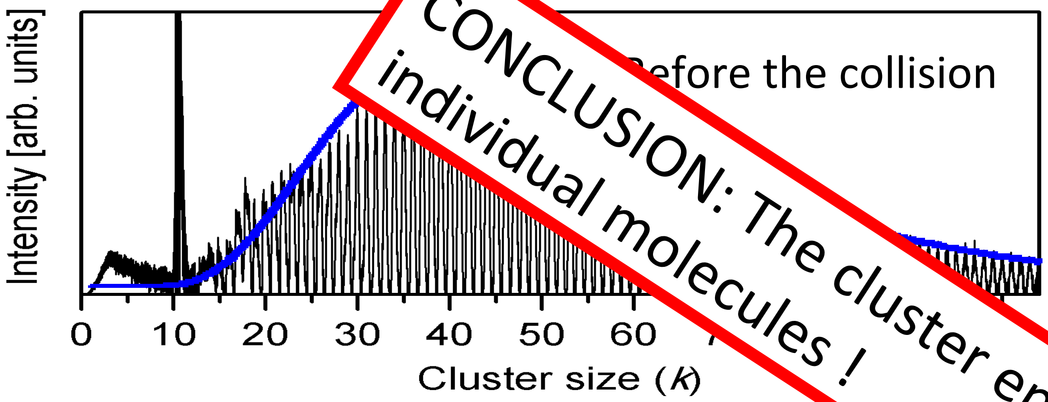


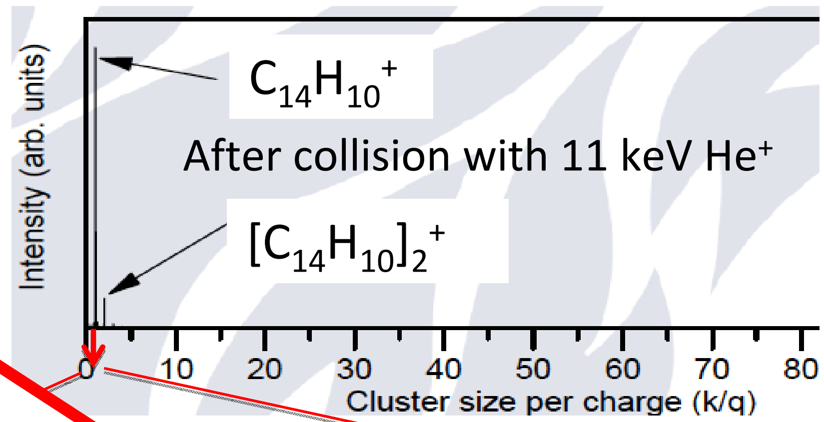
PAH-PAH binding energies
1 eV (for coronene $C_{24}H_{12}$)



Lowest Dissociation
Energy about 5 eV

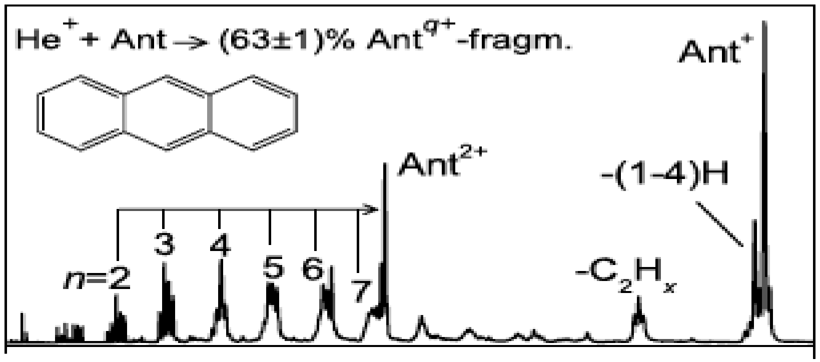
Fragmentation of clusters of PAHs – collisions with He+





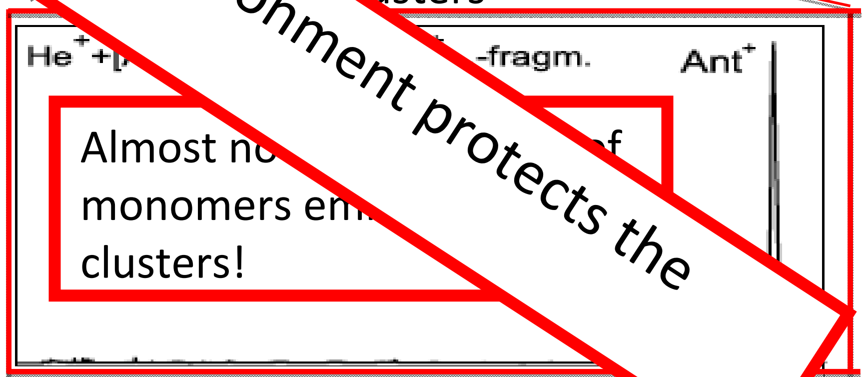
CONCLUSION: The cluster environment protects the individual molecules !

Compare: He^{+} + PAH-monomers



ion mass-to-charge ratio

…lusters



ion mass-to-charge ratio

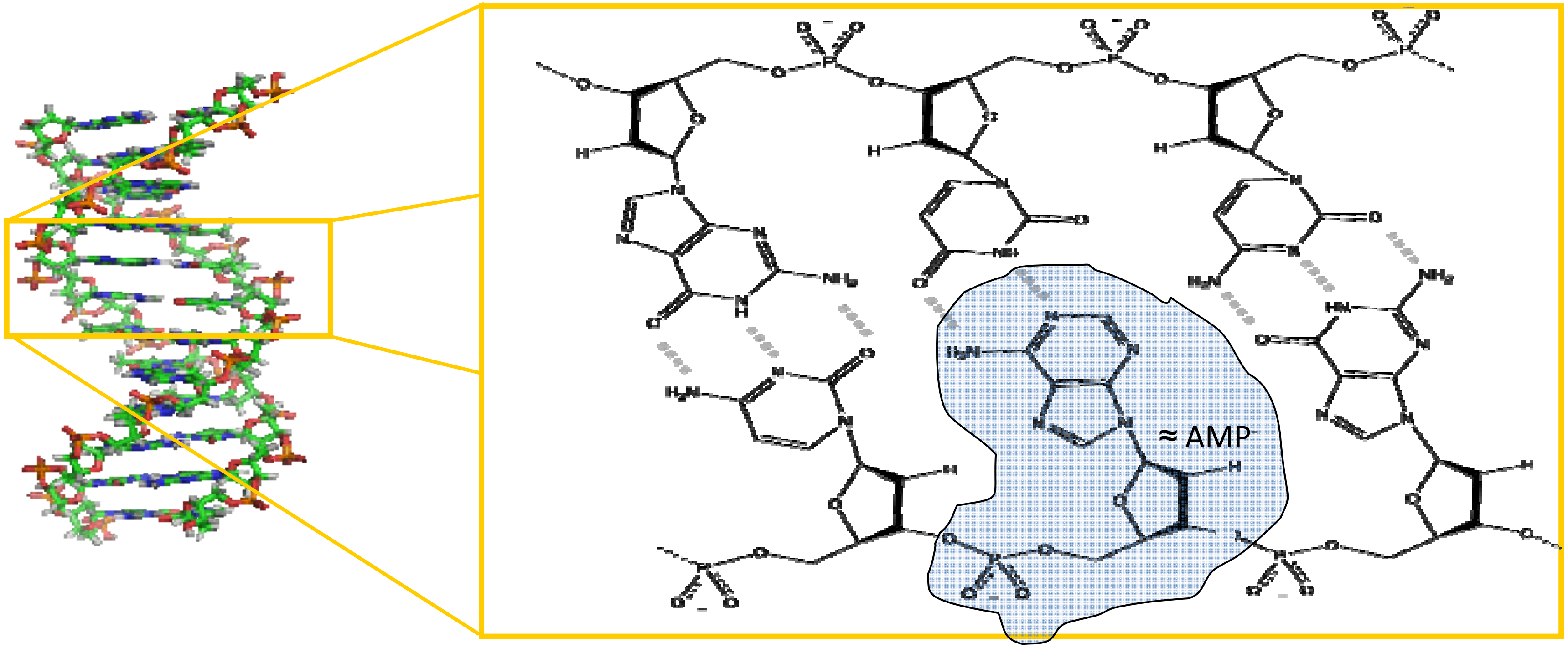
A.I. S. Holm *et al*, *Phys. Rev. Lett.*, **105**, 213401 (2010)

Collisions with clusters of molecules

Ionization, fragmentation, evaporative cooling, and molecular growth

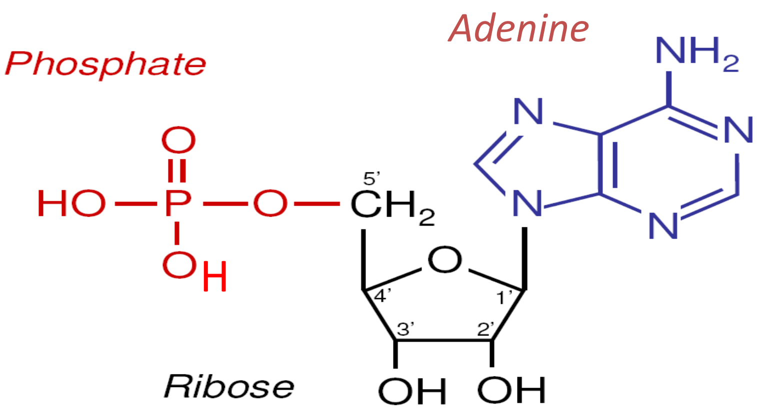
Biomolecules imbedded in water

Selecting a small piece of DNA for the experiment



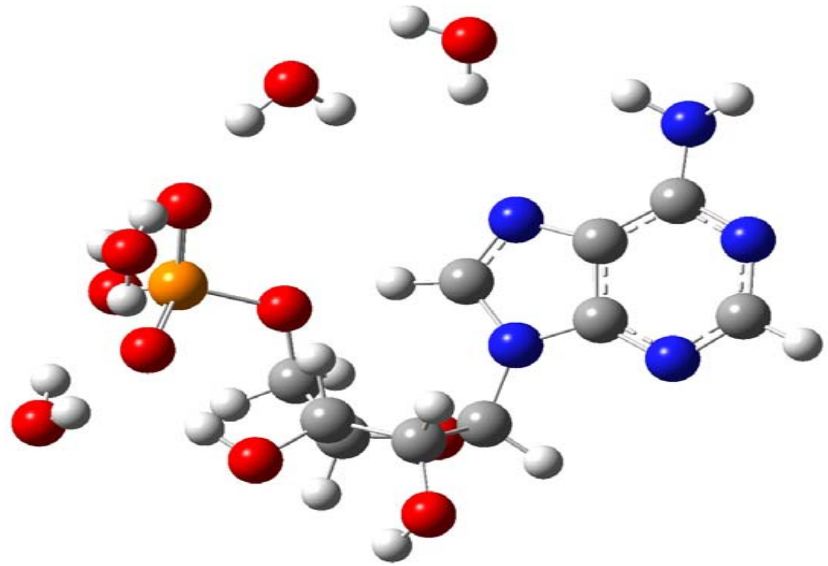
[1] Liu et al. (2006) *Phys. Rev. Lett.* **97**, 133401
[2] Liu et al. (2008). *J. Phys. Chem.* **128**, 075102.
[3] Haag et al. (2009). *J. Phys.: Conf. Ser.* **194**, 012053.

Selecting adenosine 5’-monophosphate (AMP)



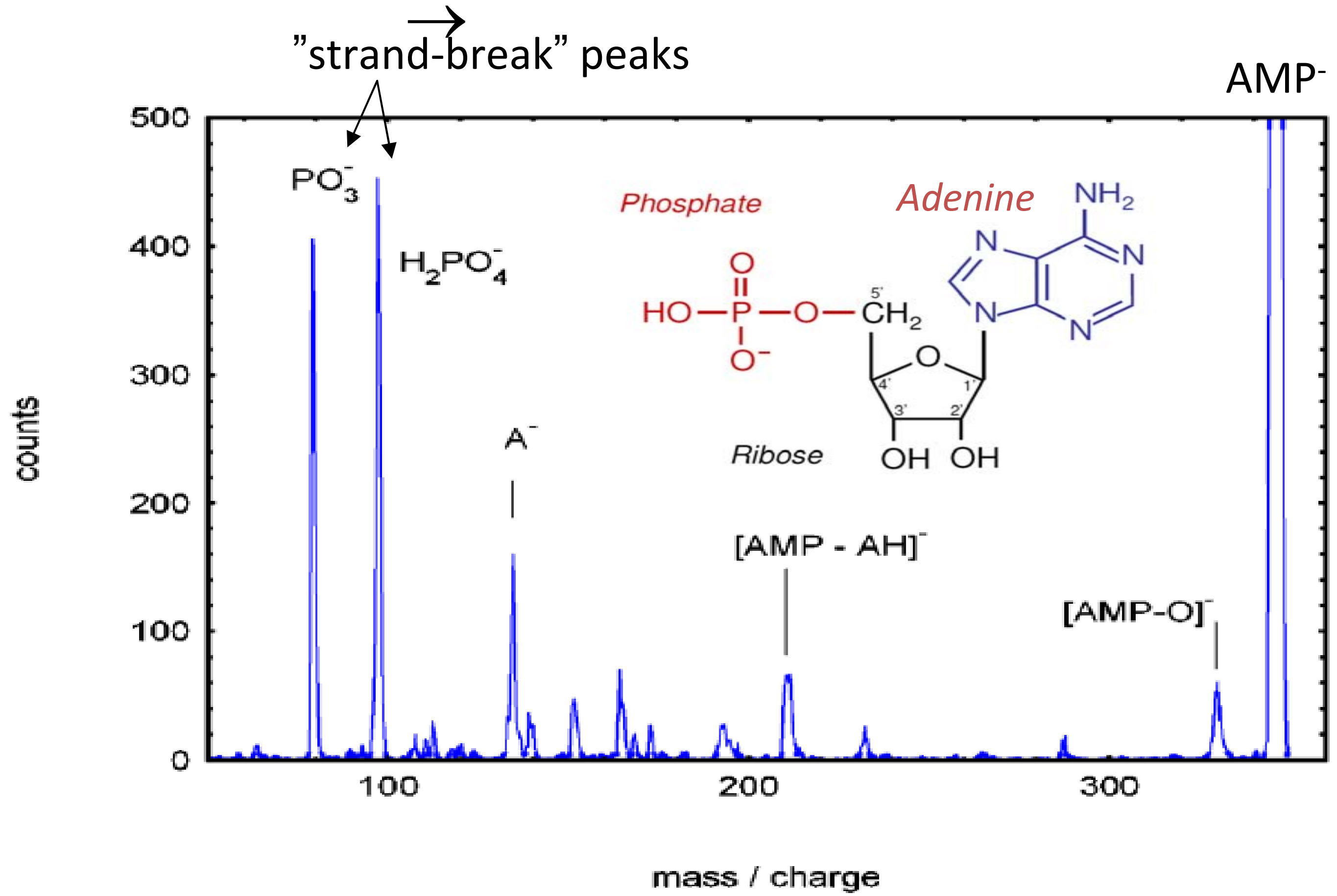
$C_{10}H_{14}N_5O_7P$ (AMP^-)

Dress it with H_2O

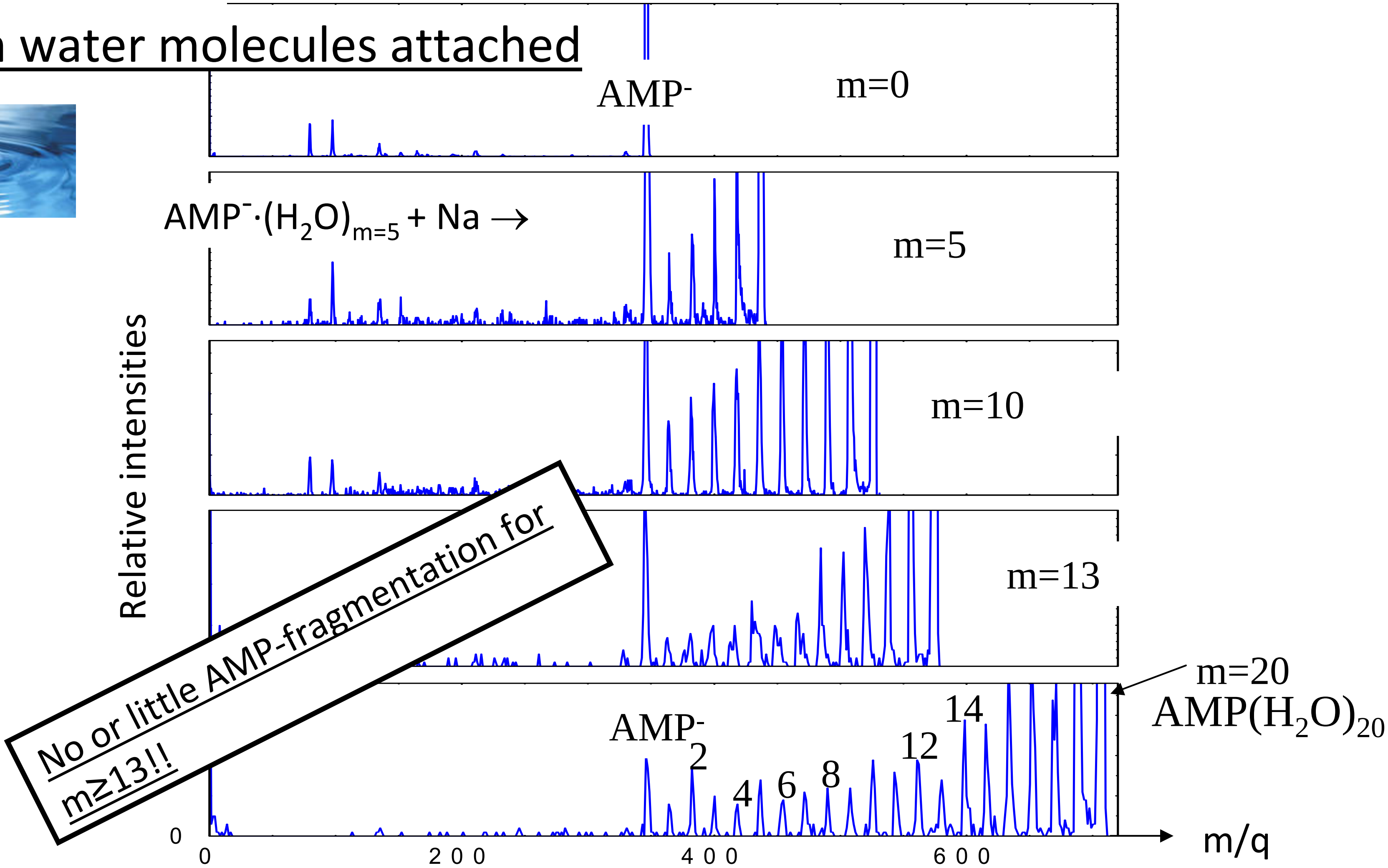


$AMP^- \cdot (H_2O)_4$

Without water attached: 50 keV AMP⁻ + Na



With m water molecules attached



Collisions with clusters of molecules

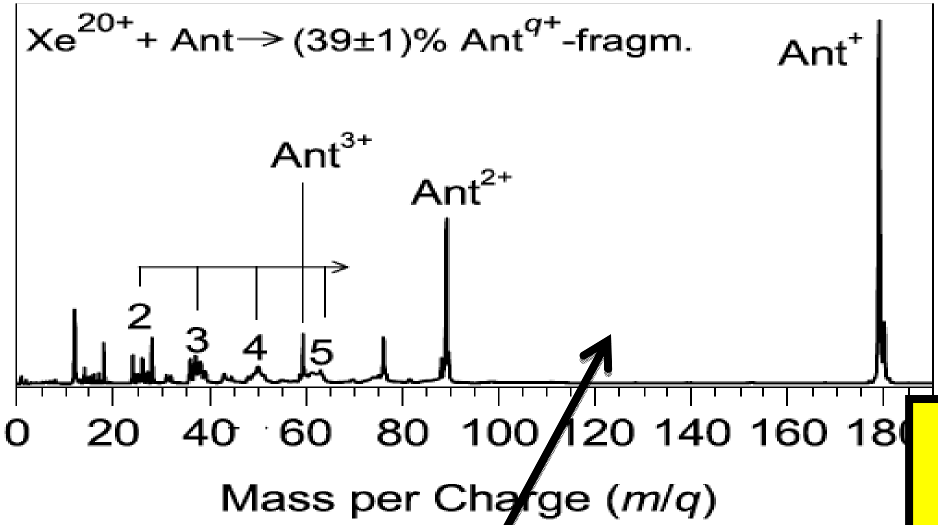
Ionization, fragmentation, evaporative cooling, and molecular growth

Also charge is distributed over molecular clusters before they disintegrate!

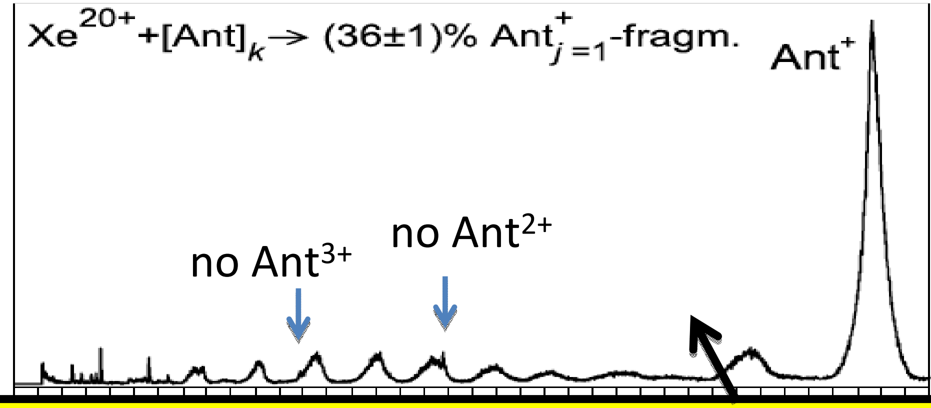
Charge mobility within PAH-clusters: ***Charge them high to see the effect!***

360 keV Xe^{20+} collisions on monomer and cluster targets:

Xe^{20+} + Monomer target



Xe^{20+} + Cluster target



Charge is induced locally but redistributed ***over the cluster*** before fragmentation!

Highly charged ions on anthracene monomers. Narrow peaks correspond to intact singly and multiply ionized single anthracene molecules!

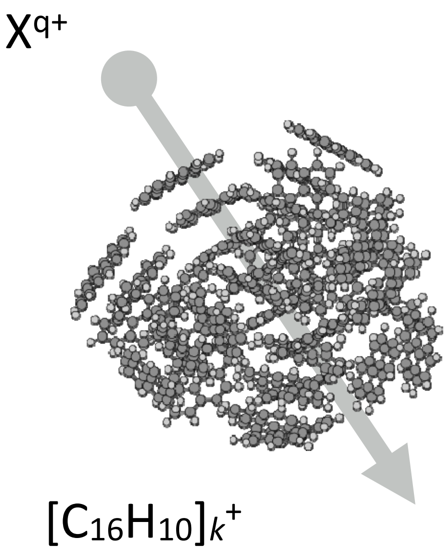
A.I. S. Holm *et al*, *Phys. Rev. Lett.*, **105**, 213401 (2010)

Collisions with clusters of molecules

Ionization, fragmentation, evaporative cooling, and molecular growth

Close collisions with molecular clusters

Molecular Growth in collisions with clusters of PAH molecules



THE JOURNAL OF PHYSICAL CHEMISTRY Letters

Letter

pubs.acs.org/JPCL

Molecular Growth Inside of Polycyclic Aromatic Hydrocarbon Clusters Induced by Ion Collisions

Rudy Delaunay,[†,‡] Michael Gatchell,[*,¶] Patrick Rousseau,[*,†,‡] Alicja Domaracka,[†] Sylvain Maclot,[†,‡] Yang Wang,[§,∥] Mark H. Stockett,[¶] Tao Chen,[¶] Lamri Adoui,[†,‡] Manuel Alcamí,[§,∥] Fernando Martín,[§,∥,⊥] Henning Zettergren,[¶] Henrik Cederquist,[¶] and Bernd A. Huber[†]

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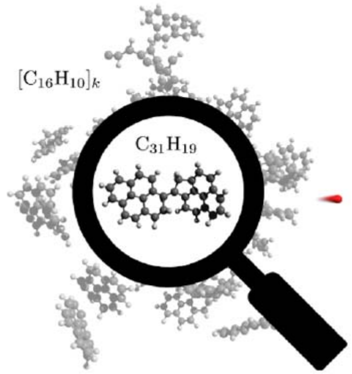
[‡]Université de Caen Basse-Normandie, Esplanade de la Paix, CS 14032, 14032 Caen cedex 5, France

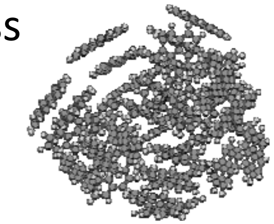
[¶]Department of Physics, Stockholm University, AlbaNova University Center, S-10691 Stockholm, Sweden

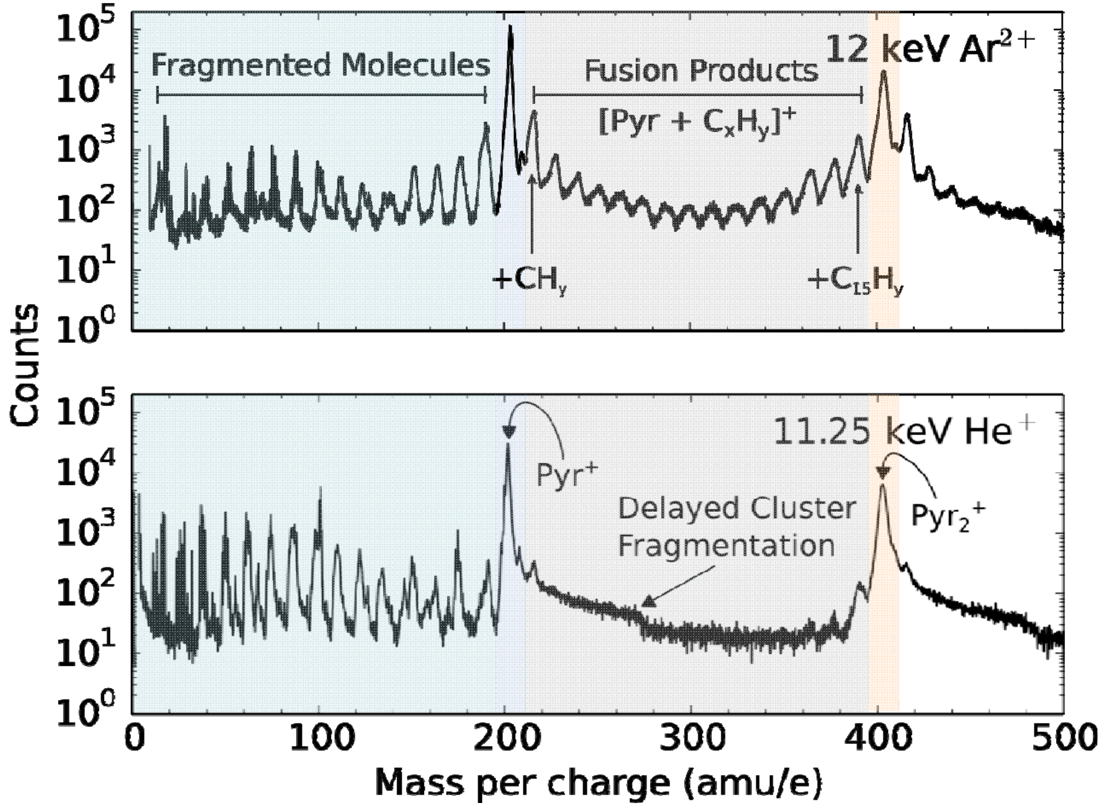
[§]Departamento de Química, Módulo 13 and [⊥]Condensed Matter Physics Center (IFIMAC), Universidad Autónoma de Madrid, 28049 Madrid, Spain

[∥]Instituto Madrileño de Estudios Avanzados en Nanociencias (IMDEA-Nanociencia), Cantoblanco, 28049 Madrid, Spain



Reactions inside the clusters depend on projectile energy and mass



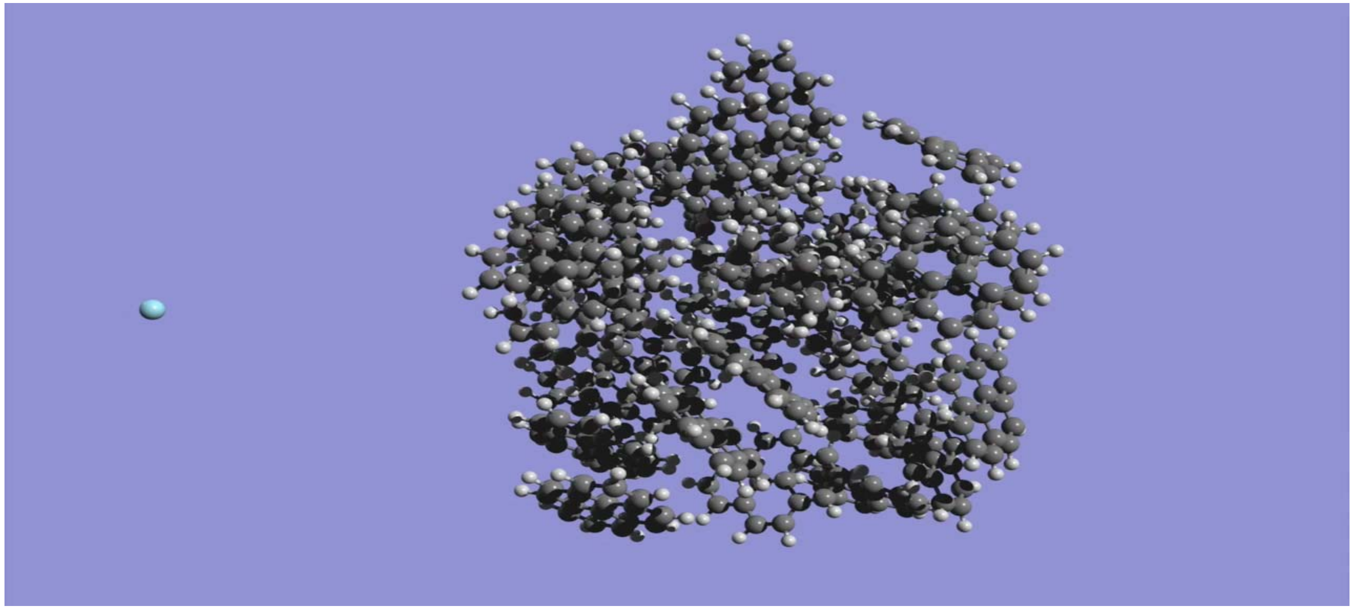


Many new features!

Few new features

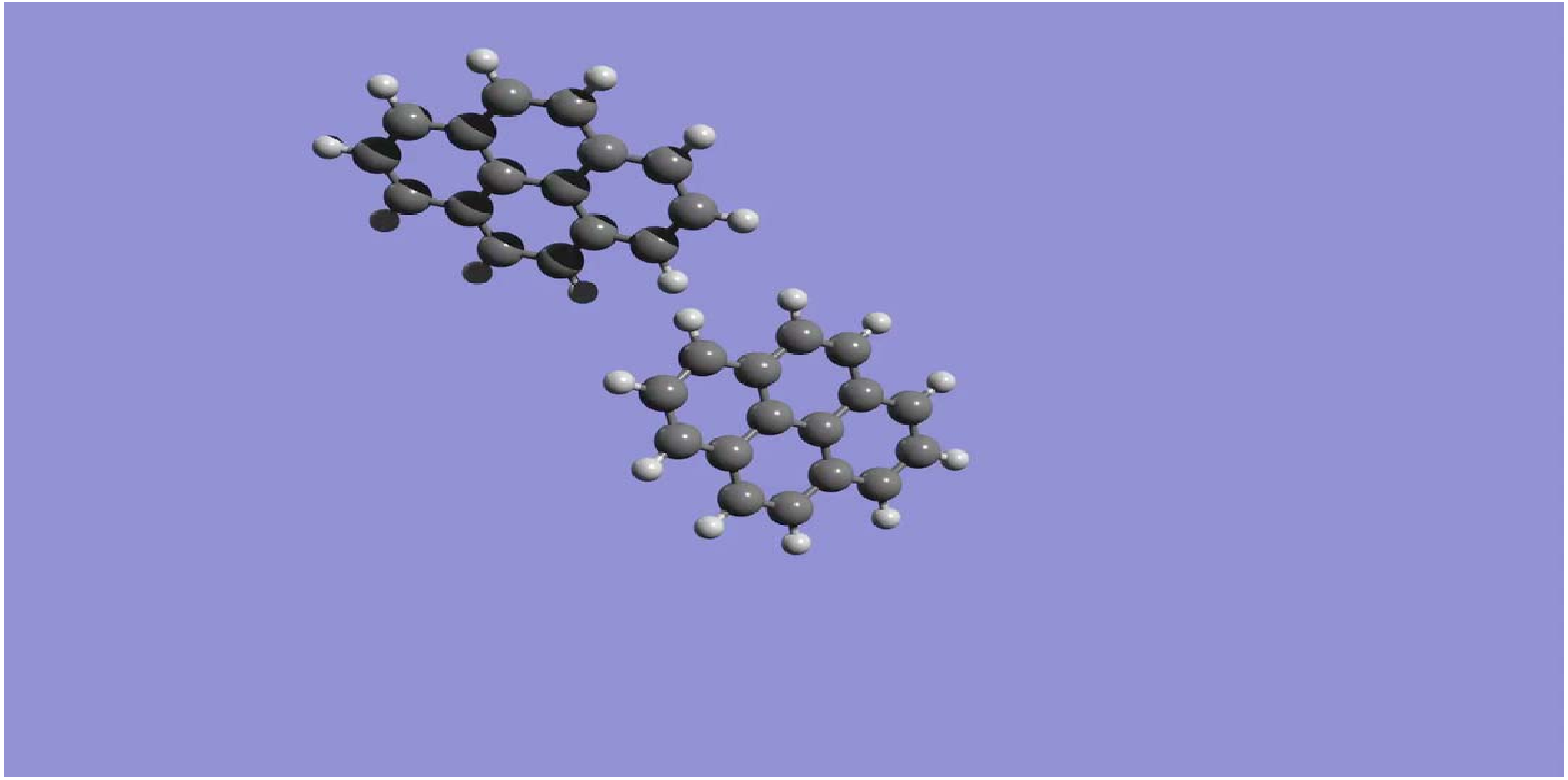
Classical MD-simulations: Ar on $(C_{16}H_{10})_{36}$

Cluster optimized, polarization interaction included (AIREBO force field) , all mutual interactions included, ZBL-potential for Ar-scattering, bonds broken and formed, random orientation of cluster, 10^5 random trajectories, time step 10^{-17} s, simulation time 1 ps, electronic stopping included by assigning an internal temperature (4000 K) before the collision



R Delaunay et al., J Phys Chem Lett **6**, 1536 (2015)

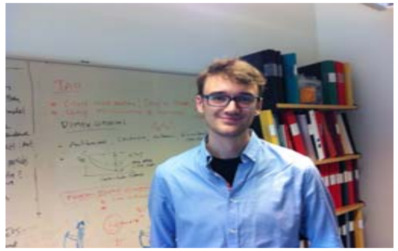
Zoom-in on the two reacting molecules in the cluster for one particular trajectory



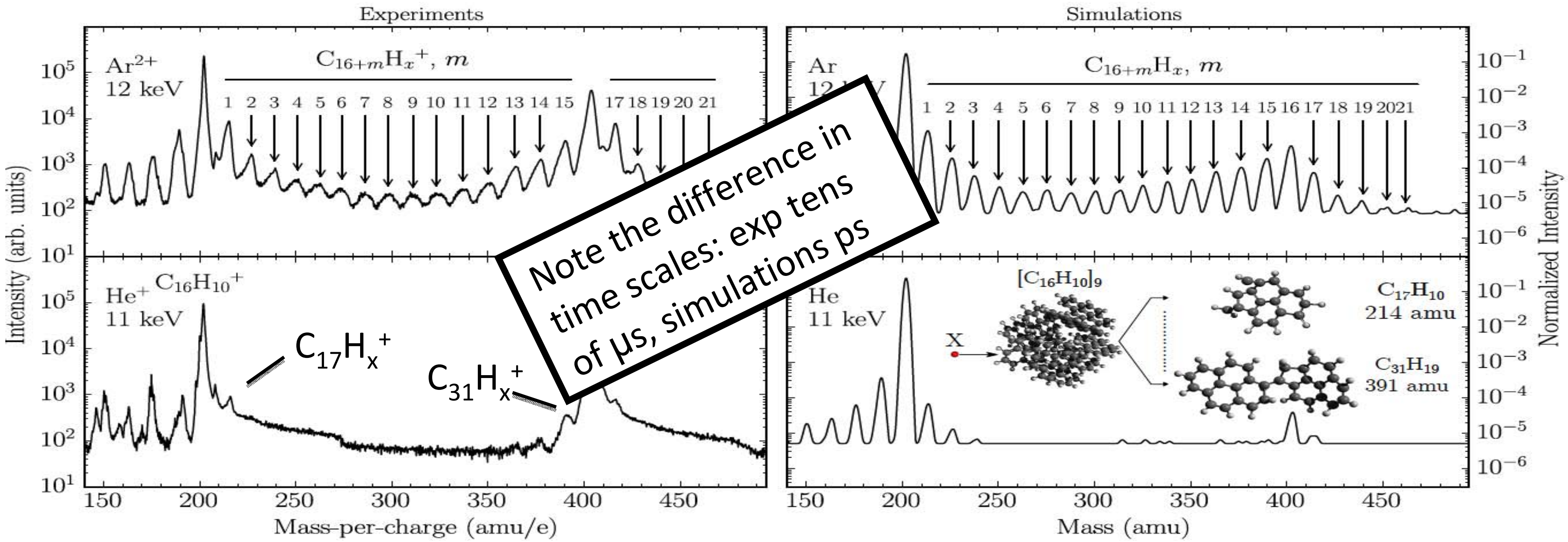
R Delaunay et al., J Phys Chem Lett **6**, 1536 (2015)

Experiment and MD-simulations

Patrick Rousseau, Lamri Adoui *et al.*



Michael Gatchell

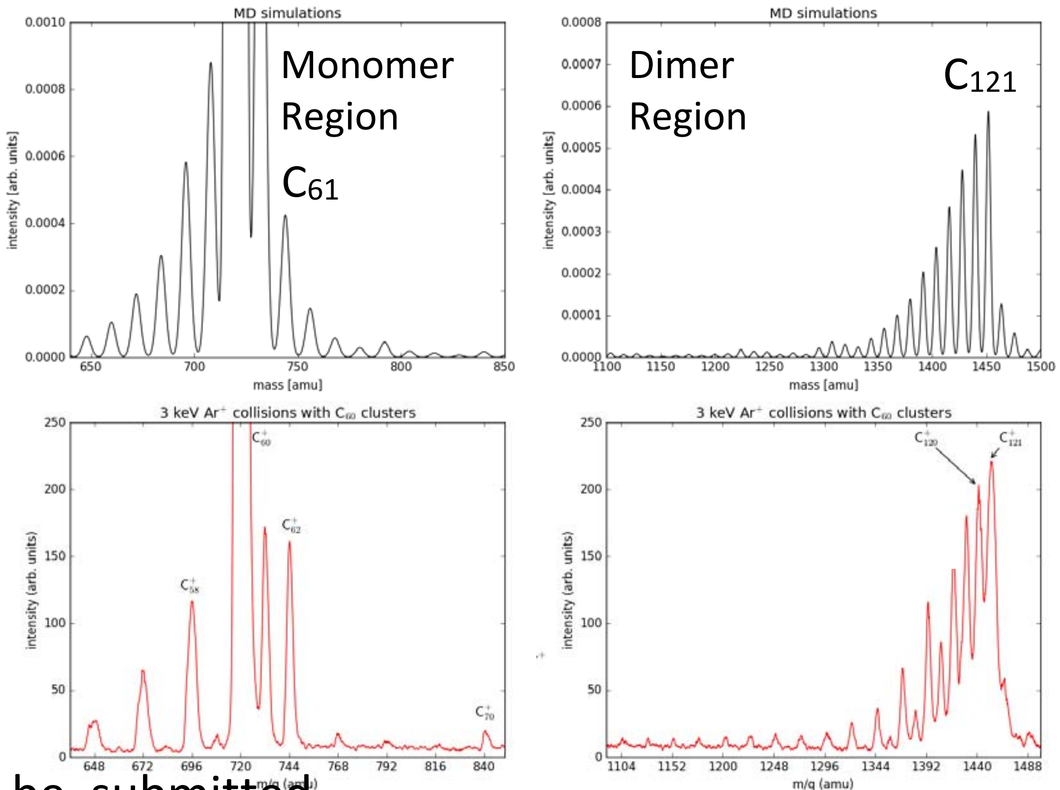


R Delaunay, M. Gatchell et al., J Phys Chem Lett **6**, 1536 (2015)

Reactions in C_{60} clusters

Simulations
3 keV Ar + $[C_{60}]_{24}$

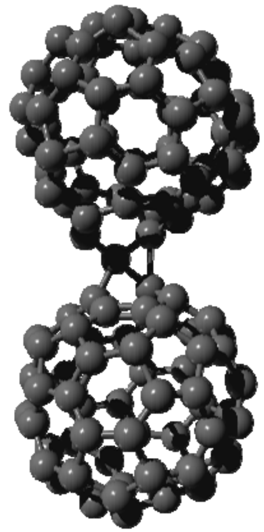
Experiments
3 keV Ar^+ + $[C_{60}]_k$



R. Delaunay *et al.*, to be submitted

C_{61}

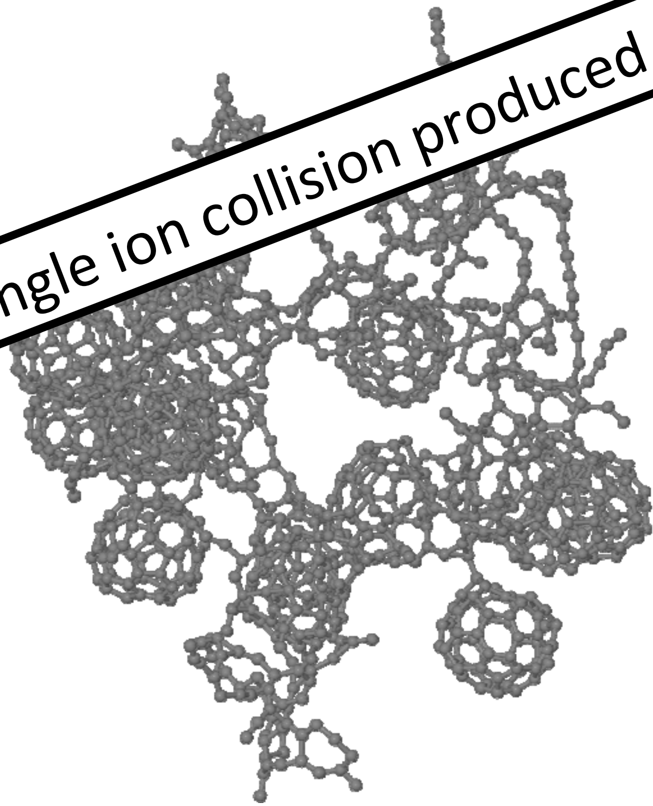
C_{121}



Reactions in C_{60} clusters

Simulations
3 keV Ar + $[C_{60}]_{24}$

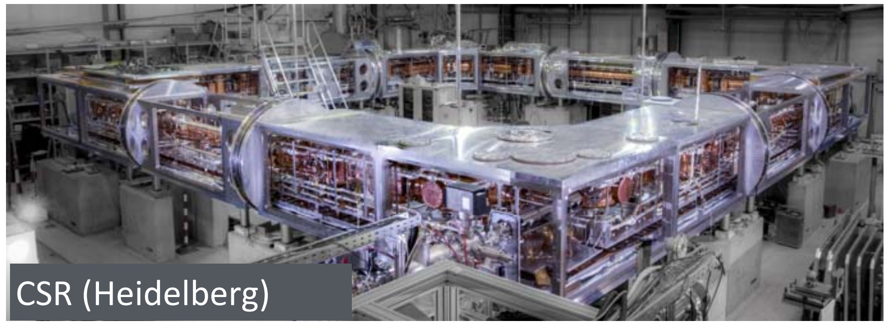
Largest Product Observe
C_{1294} - in the simulations



R. Delaunay *et al.*, to be submitted

Final remarks – points of interest.

- **Non-statistical fragmentation**: a general process for heavy ion collisions on molecules (poster by Linda Giacomozzi *et al*, **Th112**).
- Non-statistical fragmentation leads **to efficient molecular growth**
- **Displacement energies for PAHs measured! For C_{60}** – visit poster by Stockett *et al.* **Th129**
- **How are fullerenes formed in space and elsewhere?** The role of collision induced molecular growth?
- Can aromatic molecules be formed from non-aromatic ones? **Talk by Alicja Domaracka after lunch TODAY!**
- Experiments with **ions in well defined quantum states** – and **conformations** in ion storage rings (**sub-eV** ion-ion and ion-neutral heavy particle collisions). Poster Urbain *et al*. **FR118**.)



CSR-talk: O Novotny at 11 today, Thursday!

Thank you!