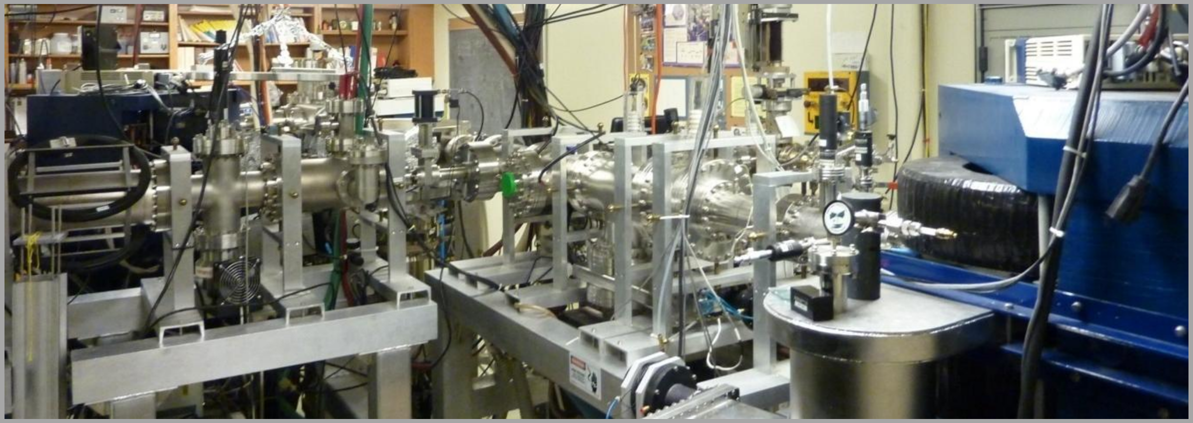
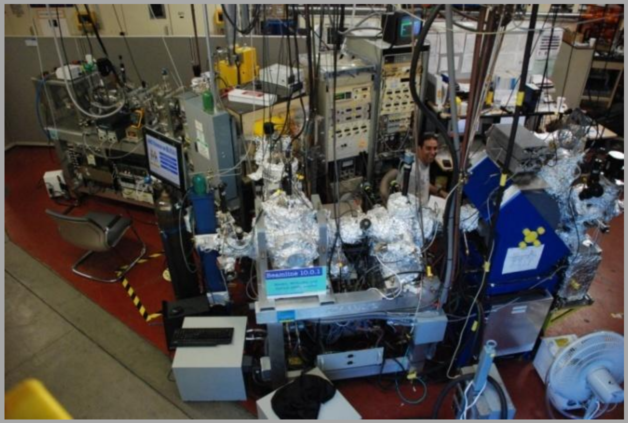
Cross-Section Measurements with Interacting Beams:





Search for Confinement Resonances in Photoionization of Caged Atoms

Ron Phaneuf
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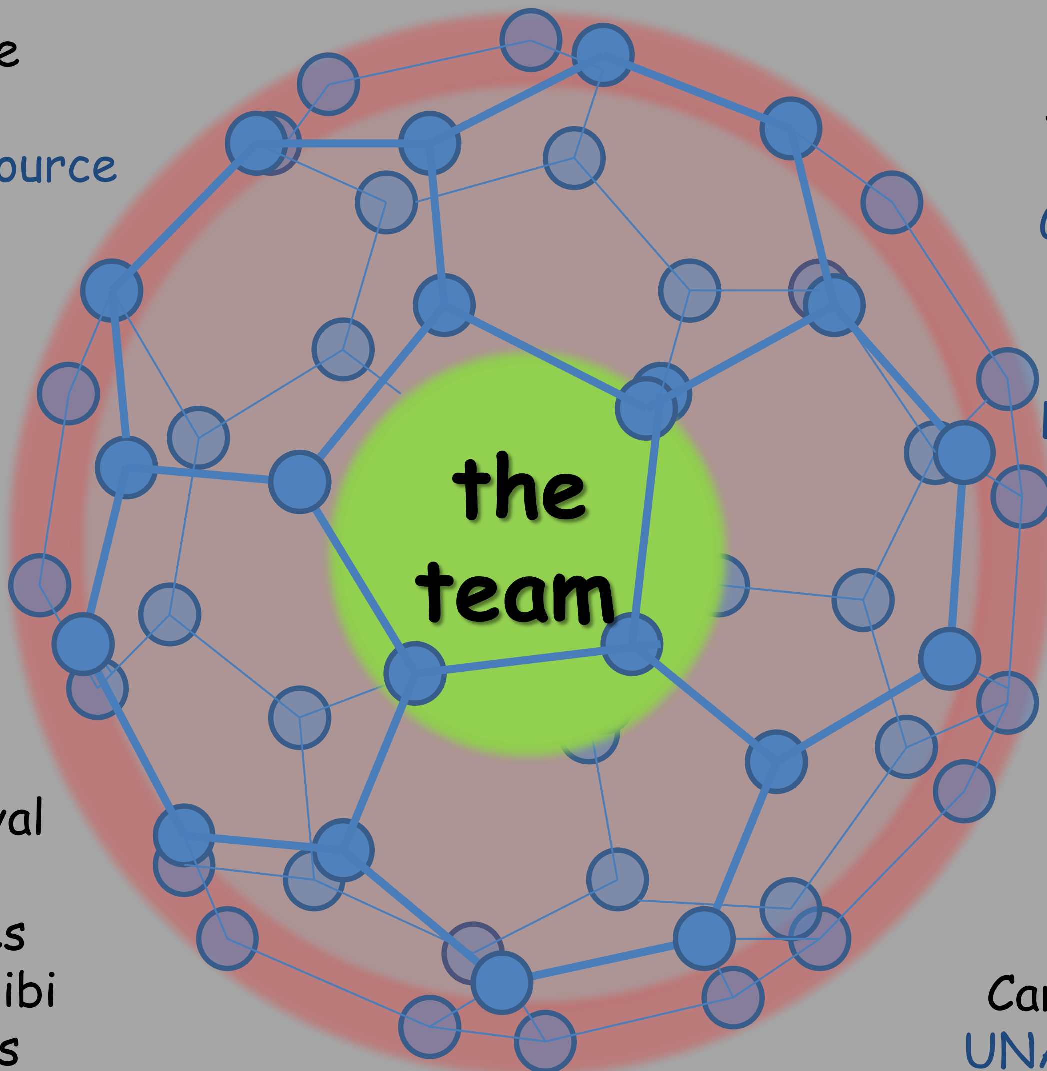
ICAMDATA 2012

ALS
ADVANCED LIGHT SOURCE

David Kilcoyne
Alex Aguilar
Advanced Light Source



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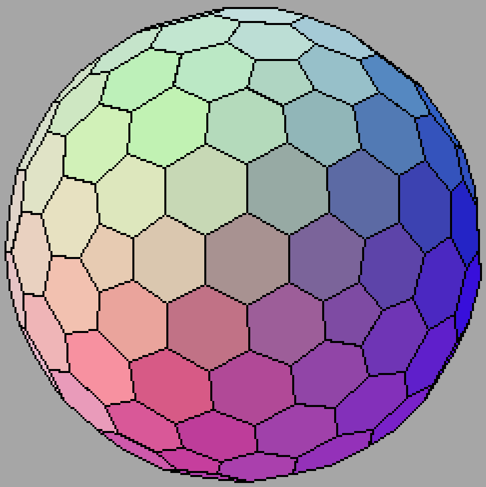
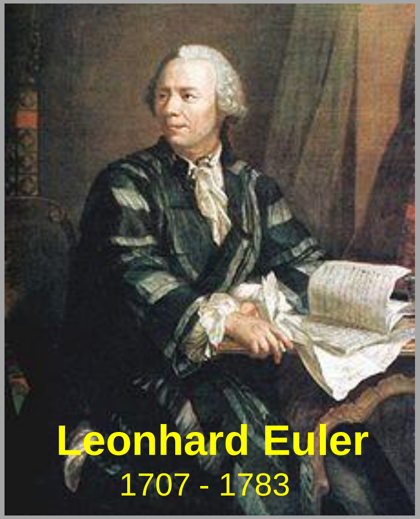
Outline

- Fullerene (Buckyball) molecules
- Endofullerenes: atoms in a molecular cage
- Giant resonances in photoionization
- Confinement resonances in endofullerenes.
- Merged-beams experiments with EUV photons and ions
- Photoionization with fragmentation of
  - Ce^{q+}, C_{82}^{+}, $Ce@C_{82}^{+}$
  - Xe, C_{60}^{+}, $Xe@C_{60}^{+}$

Closed Carbon Polyhedrons (C_n)



Geometrical Criterion:
A closed C_n polyhedron composed of a carbon atom at each intersection point may be constructed from 12 pentagons and $n/2 - 10$ hexagons ($n \geq 20$).



n	Molecule	Pentagons	Hexagons
20	C_{20}	12	0
60	C_{60}	12	20
70	C_{70}	12	25
76	C_{76}	12	28
84	C_{84}	12	32

smallest n → (row n = 20)

"magic" numbers (rows n = 60, 70, 76, 84)

Fullerene molecules have been observed for even values of n between 20 and 650

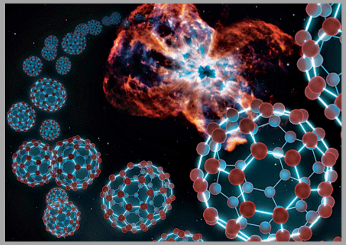
Fullerenes occur naturally in ...

- chimney soot, forest fires

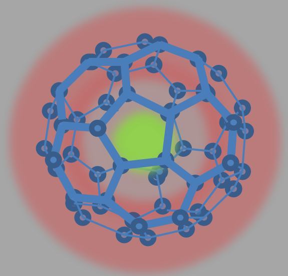
- coal deposits

- meteor impact craters

- planetary nebulae



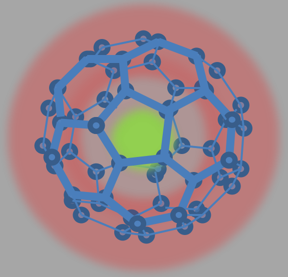
Some fullerenes contain an atom inside the cage



- Shortly after the discovery of C_{60} in 1985 by Kroto, Curl and Smalley, they synthesized fullerenes with an atom inside their spherical molecular cage ($A@C_{60}$).
- These so-called endofullerenes were subsequently discovered in meteor, comet and asteroid impact craters on the Earth.
  - Isotopic analysis of caged noble gas atoms indicates that the endohedral fullerene molecules are of **extra-terrestrial origin**.

Becker et al, *Science* **272**, 249 (2001); *Science* **291**, 1530 (2001)

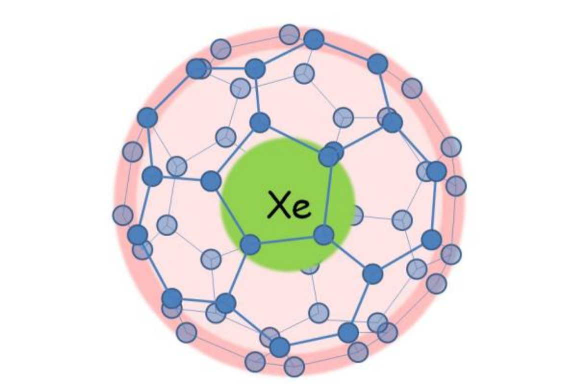
Applications of endofullerenes



- in medicine
  - for treatment of diseases such as cancer
  - for chemical isolation of toxic or reactive species
  - as a delivery medium for pharmaceuticals
- in information technology
  - as gates for quantum computers
- in energy research
  - as a chemical energy storage medium (e.g. for H_2)
  - as nanoscale targets for inertial confinement fusion

Giant 4d resonance in xenon

- Xe has a filled inner 4d subshell (10 electrons) that may be excited by EUV light.
- Strong electron correlation leads to the so-called **giant 4d resonance** in photoionization of Xe.
- What happens when a Xe atom inside a C_{60} molecular cage ($Xe@C_{60}$) is photoionized?



Confinement Resonances

If a caged atom is photo-ionized, the outgoing electron de Broglie wave may

- pass through the cage and escape.
- be reflected by the cage and then escape.

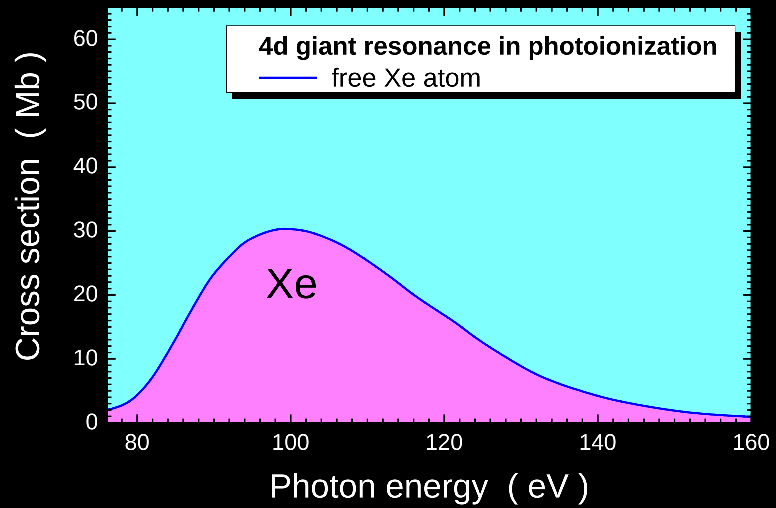
Multi-path interference of outgoing electron waves is predicted to produce

confinement resonances

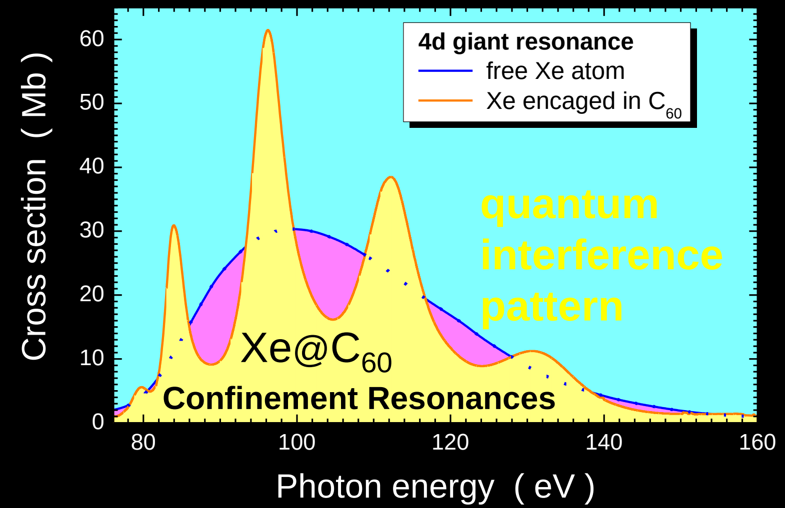
in the photoionization cross section.

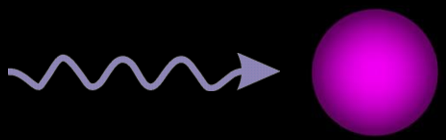
Giant resonance in EUV photoionization of a Xenon atom

theory and experiment

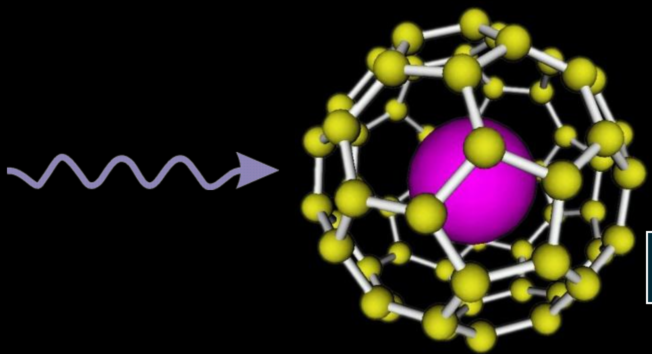


theoretical prediction





Xe atom



$Xe@C_{60}$

Xe in a C_{60} cage

What happens when a Xenon atom is ionized inside a fullerene cage?

M. Ya. Amusia et al., J. Phys. B 38, L169 (2005)

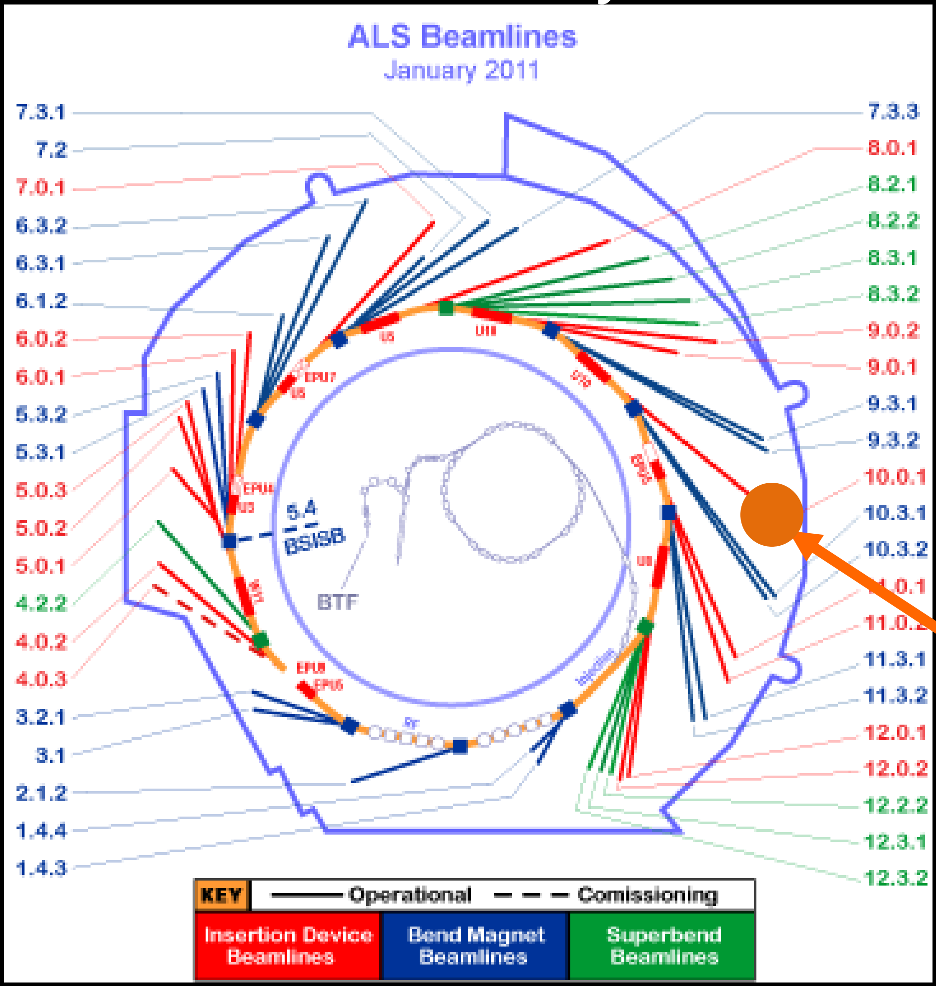
Why search for confinement resonances with ions?

Ions carry a net charge and may be . . .

- accelerated and formed into beams.
- directed with a known velocity.
- selected by charge-to-mass ratio.
- quantified by current density.
- detected individually.

The ALS is one of the world's brightest tuneable extreme ultraviolet light sources

1.9 GeV Electron Synchrotron

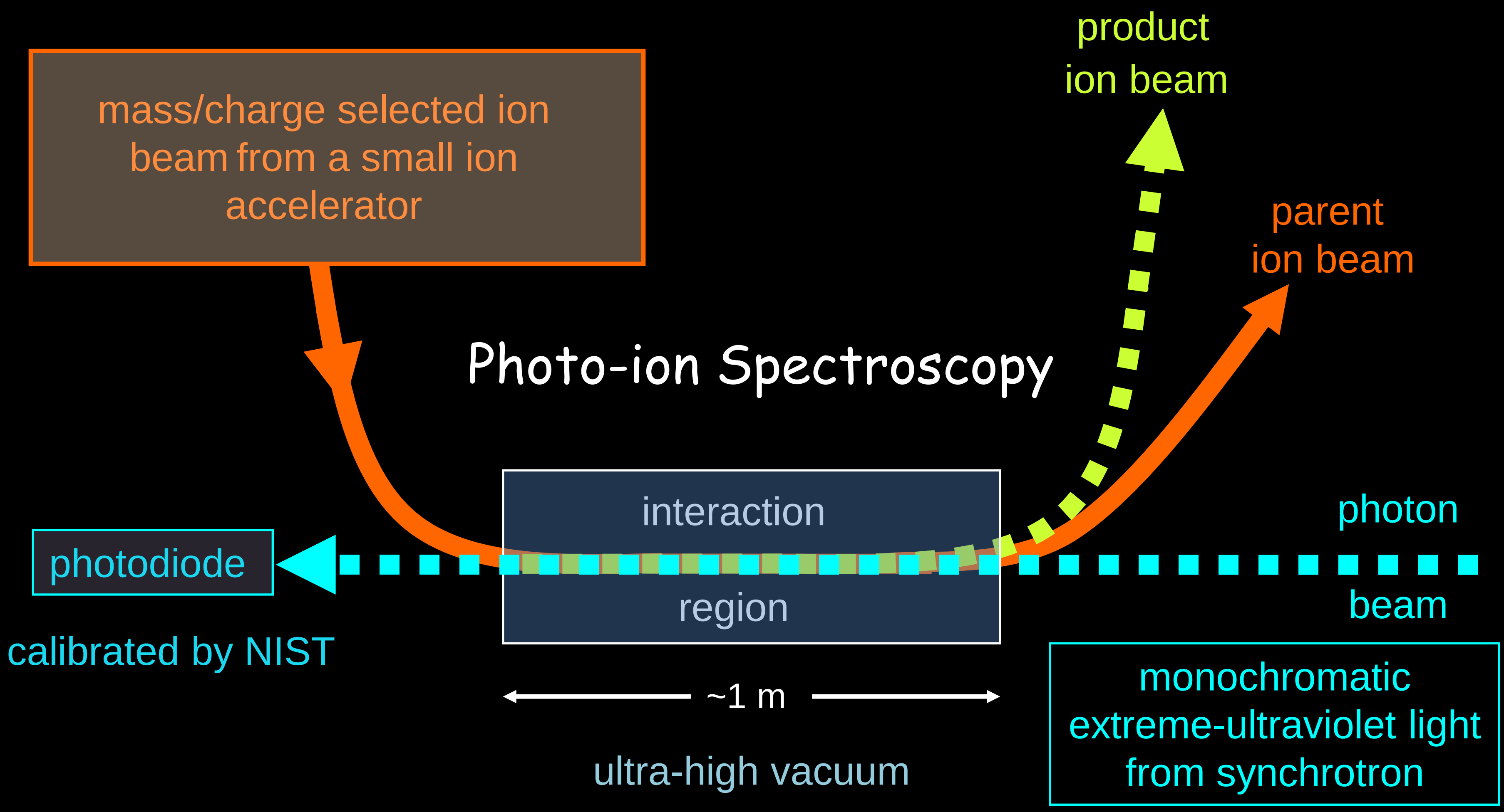


Lawrence Berkeley National Laboratory

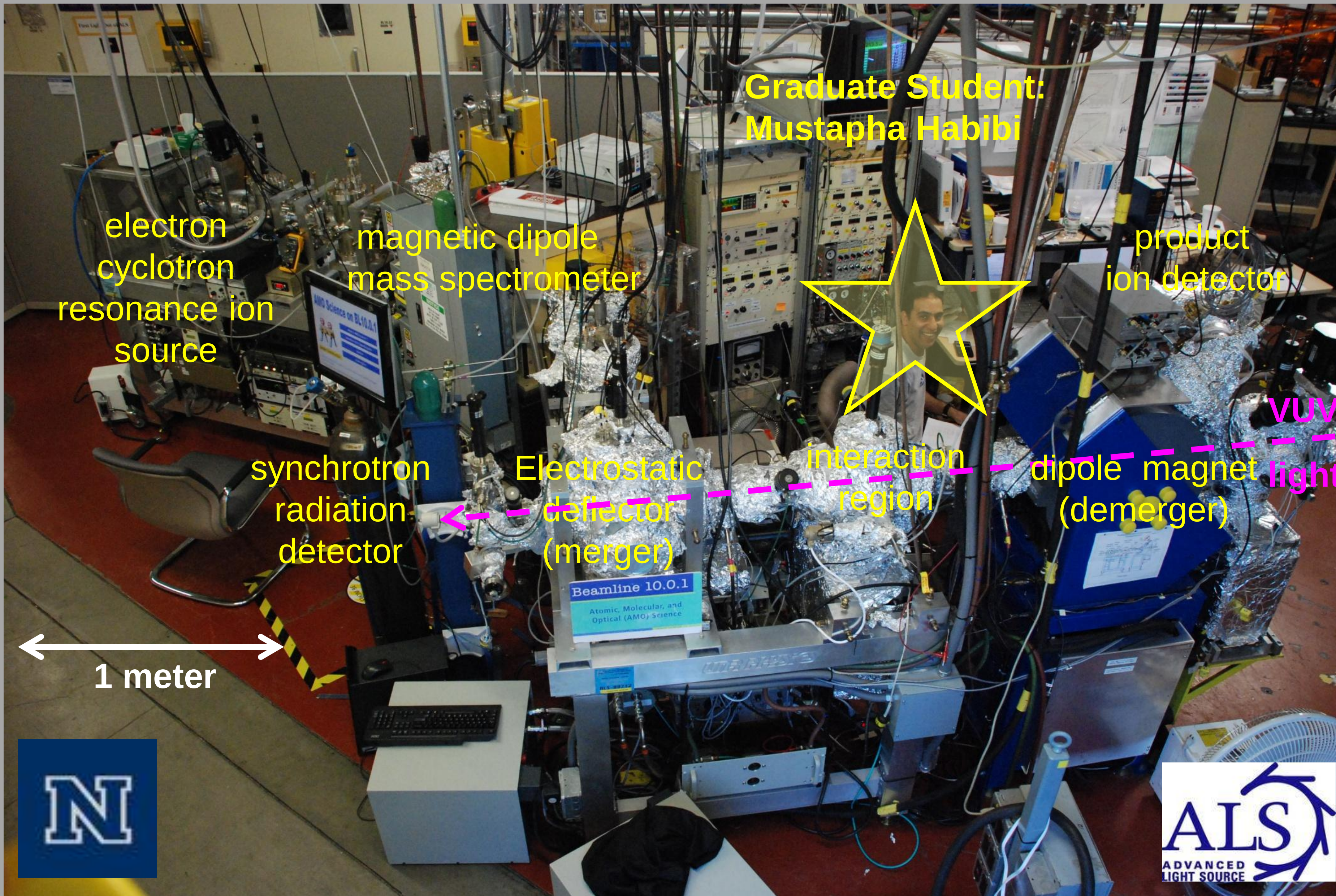
The Advanced Light Source

Ion-Photon-Beam (IPB)
Merged-Beams
Research Endstation
Undulator Beamline 10.0

Merged photon and ion beams: using synchrotron radiation to study EUV photoionization of ions at ALS



ALS Ion-Photon-Beam Endstation



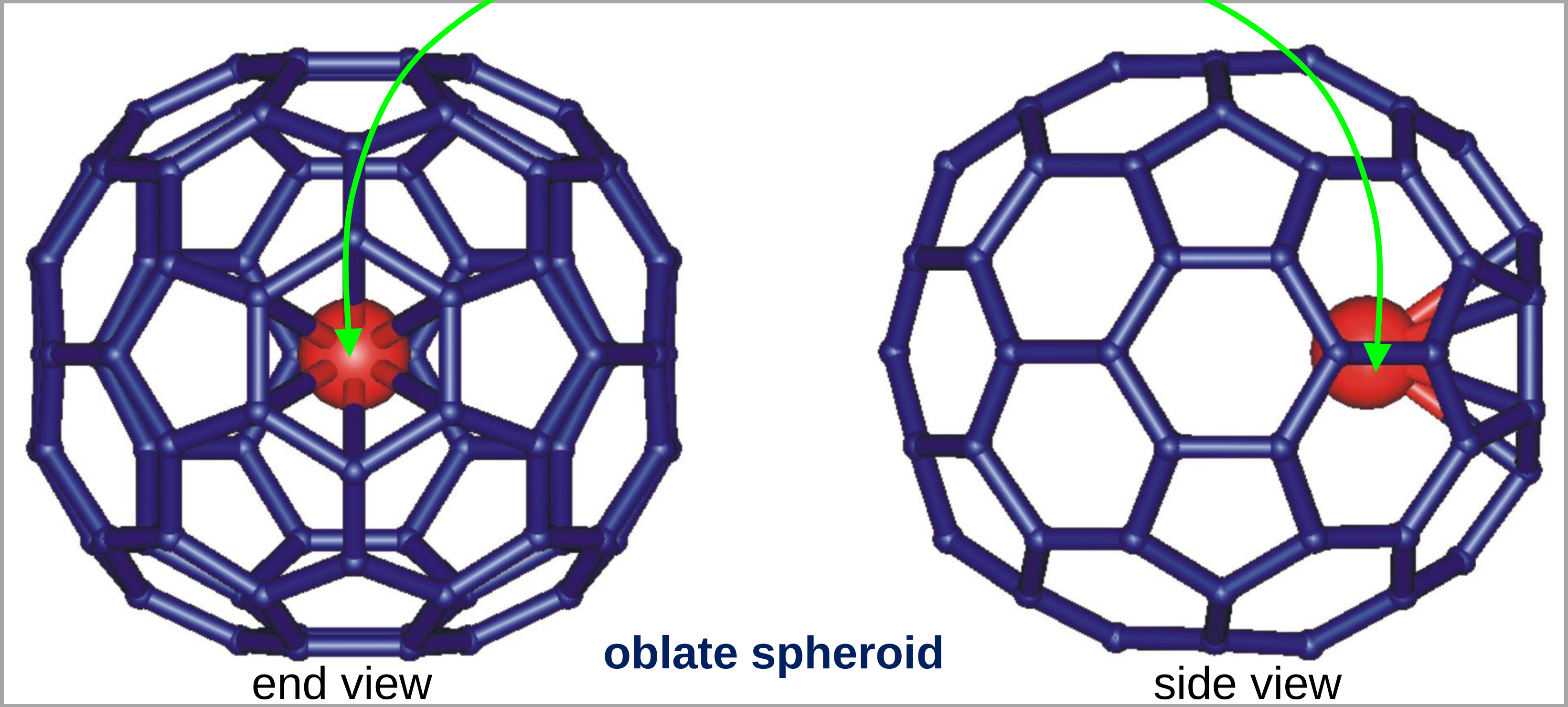
Experimental search for confinement resonances

- $Xe@C_{60}$ was unavailable in sufficient quantity for an experiment.
- Like xenon, cerium (a lanthanide) has a filled 4d inner subshell and exhibits a giant 4d resonance in photoionization.
- The group of Lothar Dunsch at the Leibnitz Institute in Dresden was successful in synthesizing the $Ce@C_{82}$ endofullerene.
- Available quantities of $Ce@C_{82}$ (several grams) were sufficient to conduct an experiment.

Charge of Ce inside Ce@C_{82}

neutral Ce@C_{82}

charge state +3



K. Muthukumar and J. A. Larsson, J. Phys. Chem. A 112, 1071 (2008)

(prediction based on density-functional theory)

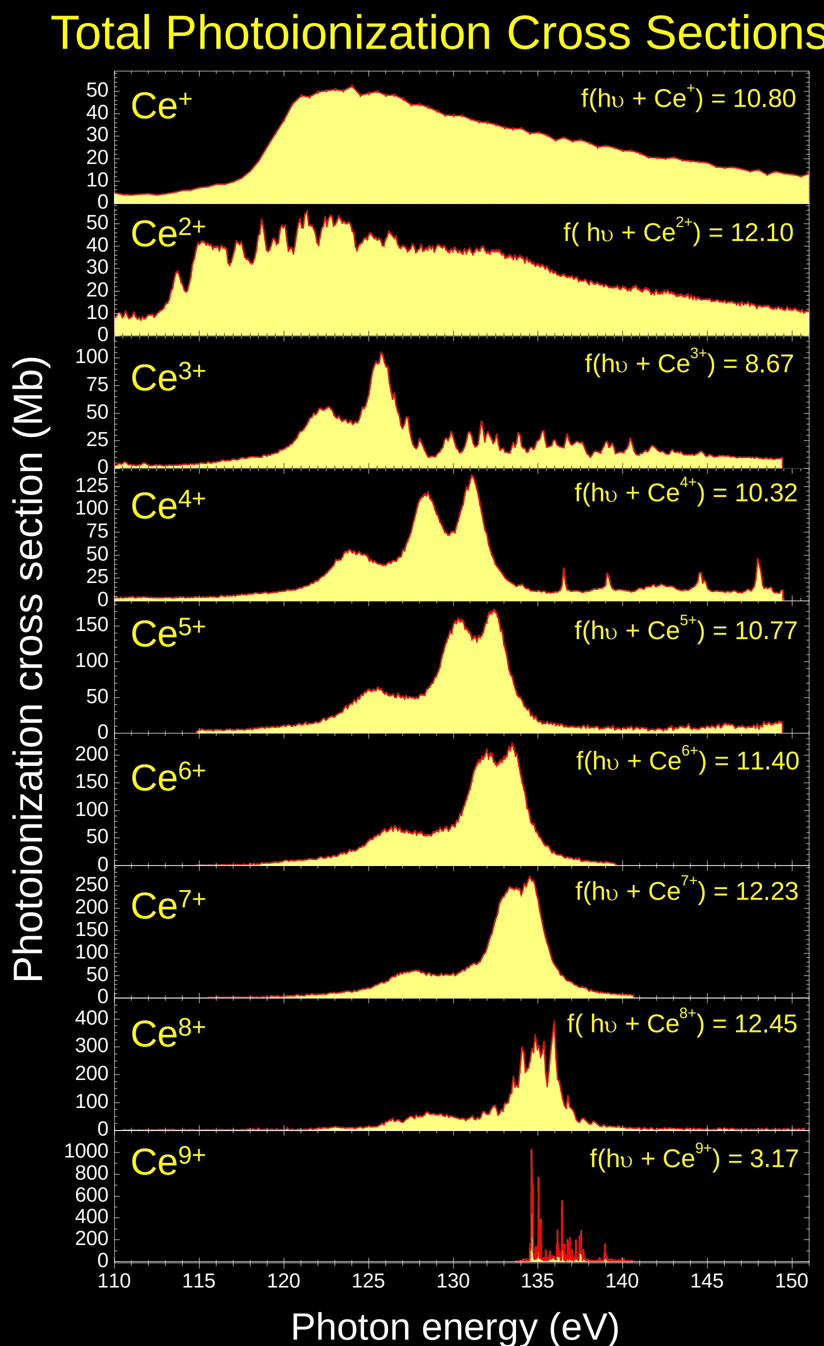
- Strong hybridization between Ce 4d orbitals and π orbitals of the cage
- Ce contributes 3 electrons and is not centered within the carbon cage

Reference EUV photoionization measurements for free cerium ions

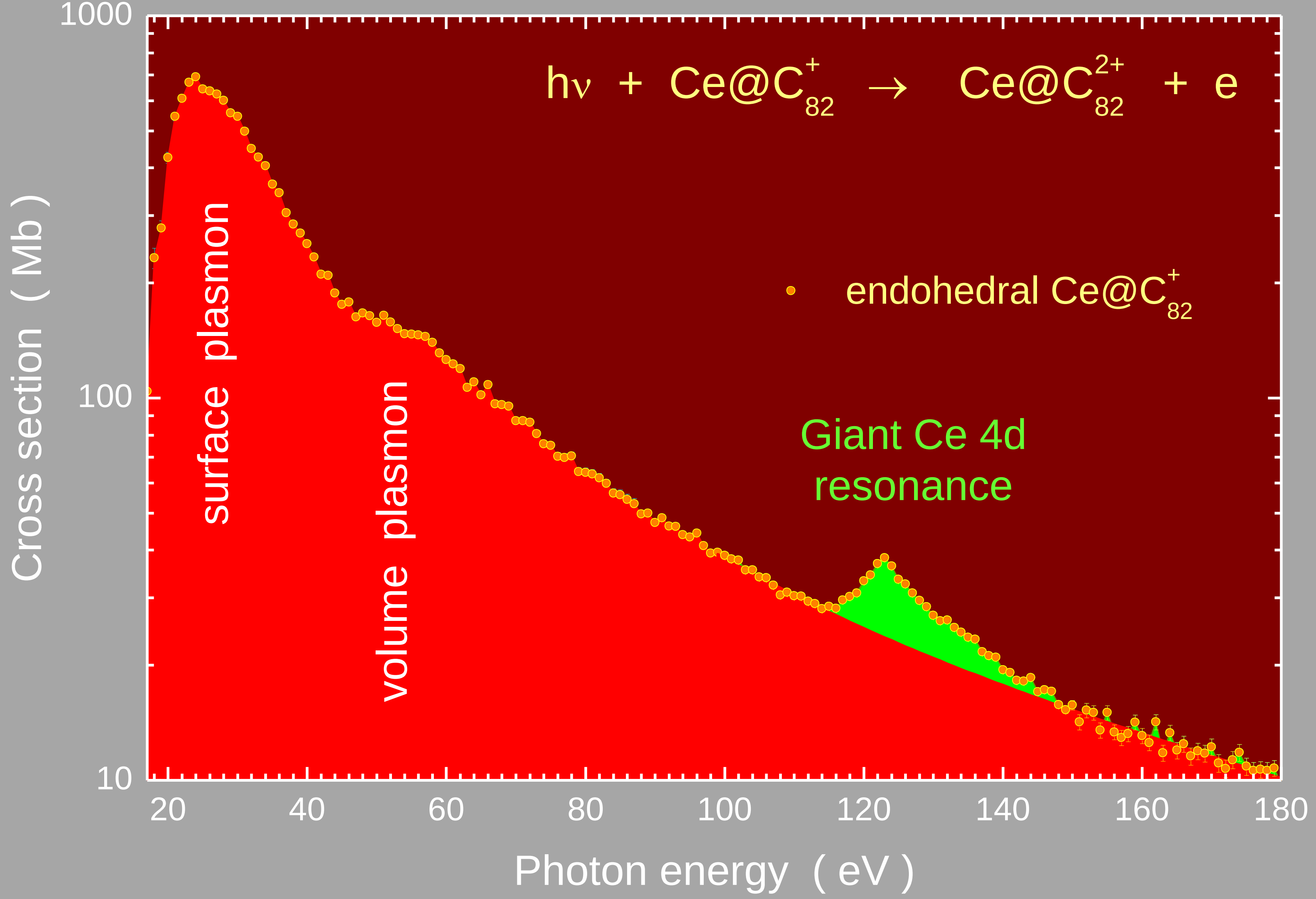
Photoionization of cerium ions in the 110 – 150 eV photon energy range is dominated by the giant resonance due to excitation of inner 4d electrons (as in xenon).

M. Habibi, Ph.D. thesis (2009)

Habibi et al., Phys. Rev. A 80, 033407 (2009)

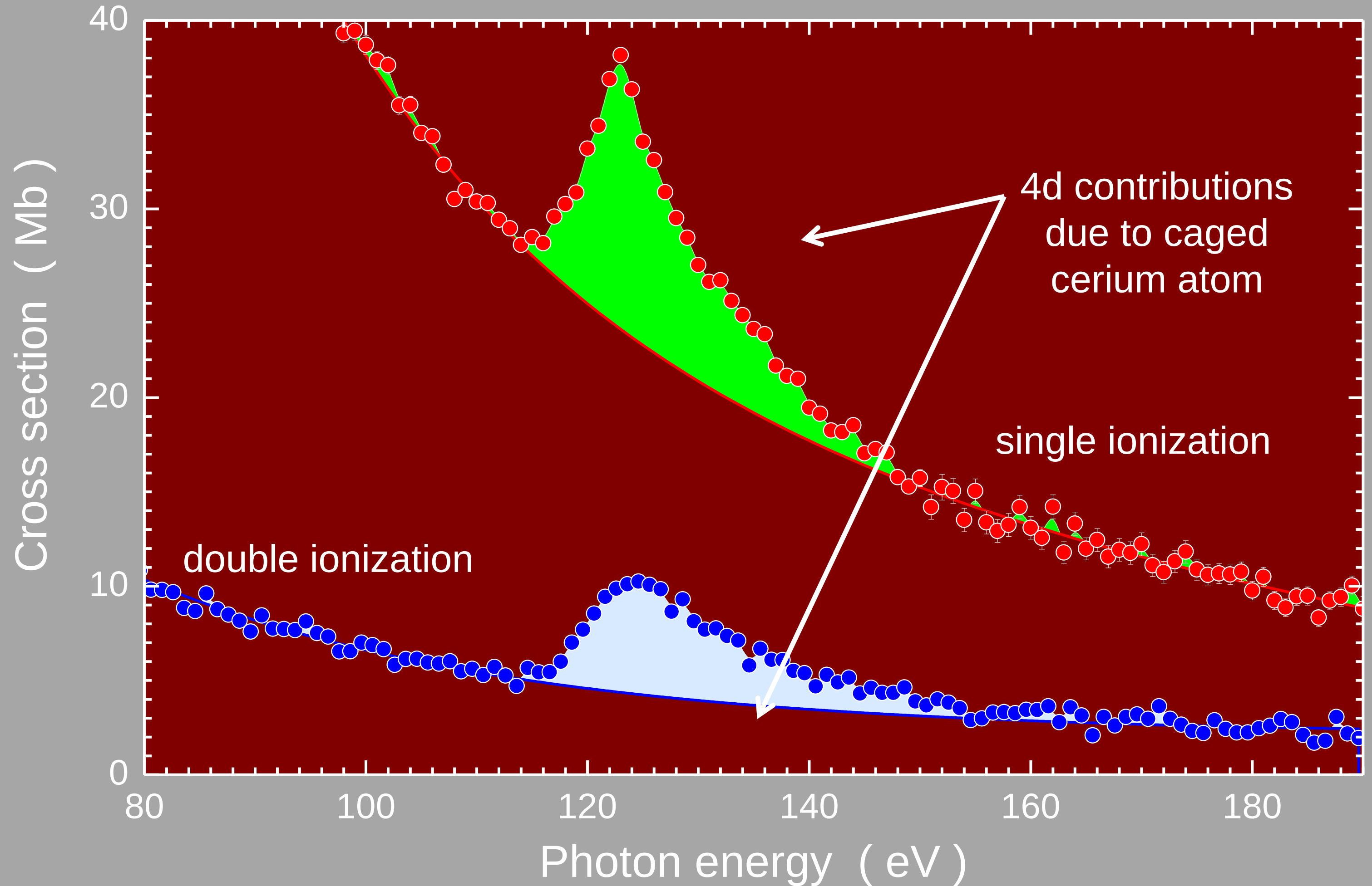


Photoionization of $Ce@C_{82}^{+}$



Müller et al., Phys. Rev. Lett. 101, 133001 (2008)

Photoionization of $Ce@C_{82}^{+}$ near Ce 4d resonance



No evidence of substructure due to confinement resonances !

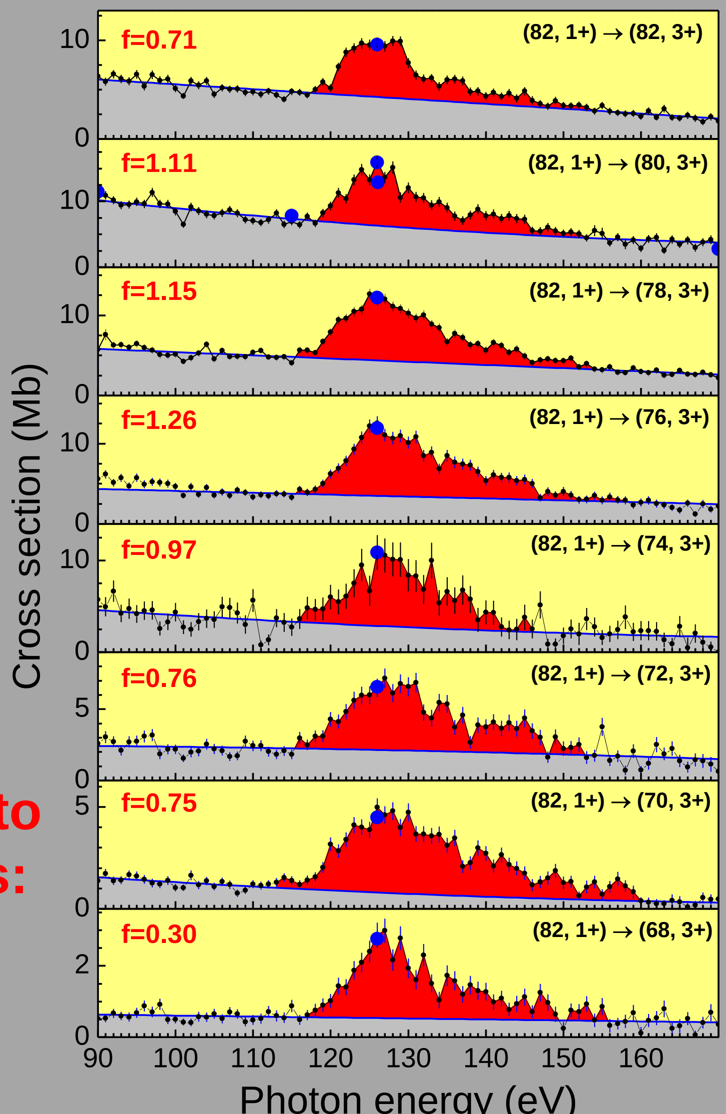
Energy position of Ce 4d resonance verified theoretical prediction that Ce has a charge of +3 in the C_{82} cage.

Müller et al., Phys. Rev. Lett. 101, 133001 (2008)

Confinement resonances do not occur in photoionization of $Ce@C_{82}^{+}$ because

- Ce is not centered within the fullerene cage (destroys interference)
- Ce atomic orbitals hybridized due to ionic bonding (broadens Ce 4d feature)

Ce 4d contributions to double photoionization $Ce@C_{82}^{+}$ accompanied by loss of n C atoms



Sum of Ce 4d contributions to cross sections: ∑ f = 7.0 (total of 10)

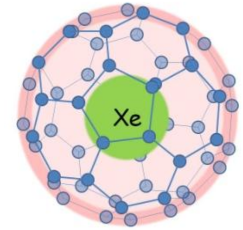
n (C atoms lost)

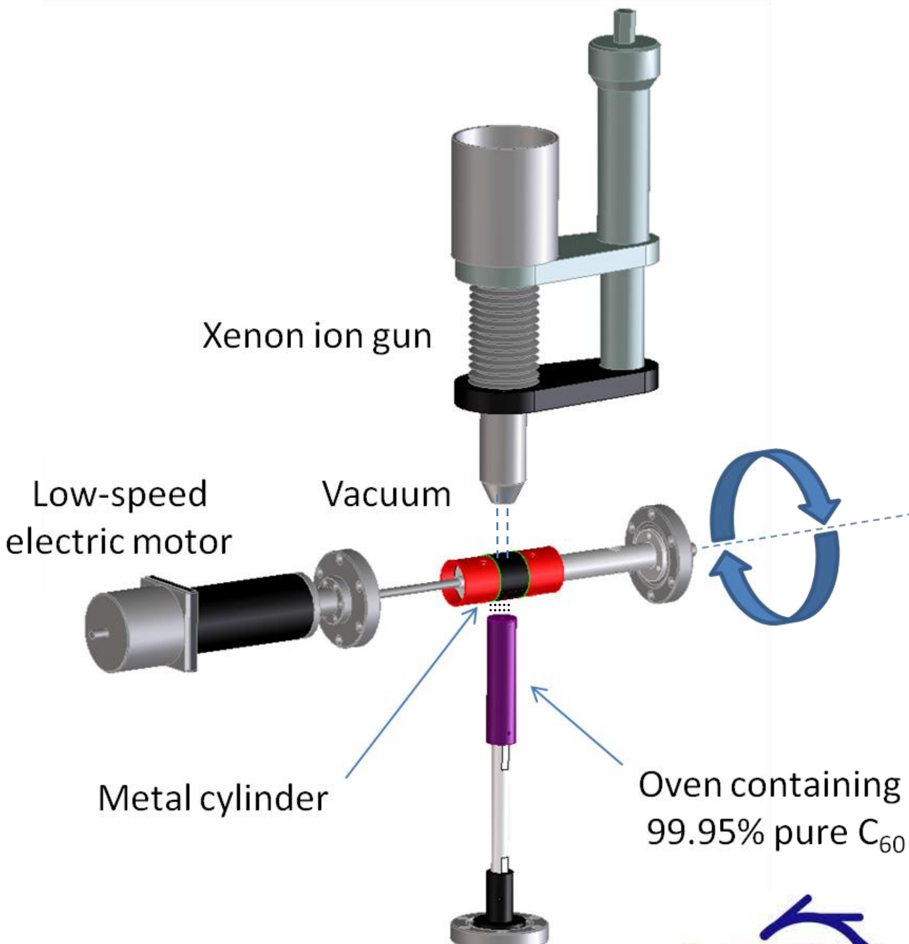
0
2
4
6
8
10
12
14

Fragmentation releases carbon atoms in pairs, because the product fullerene molecule must contain an even number of C atoms.

Ce 4d photoabsorption leads to double ionization product channels for which fragmentation of the C_{60} cage is significant.

Setup to synthesize Xe@C_{60}





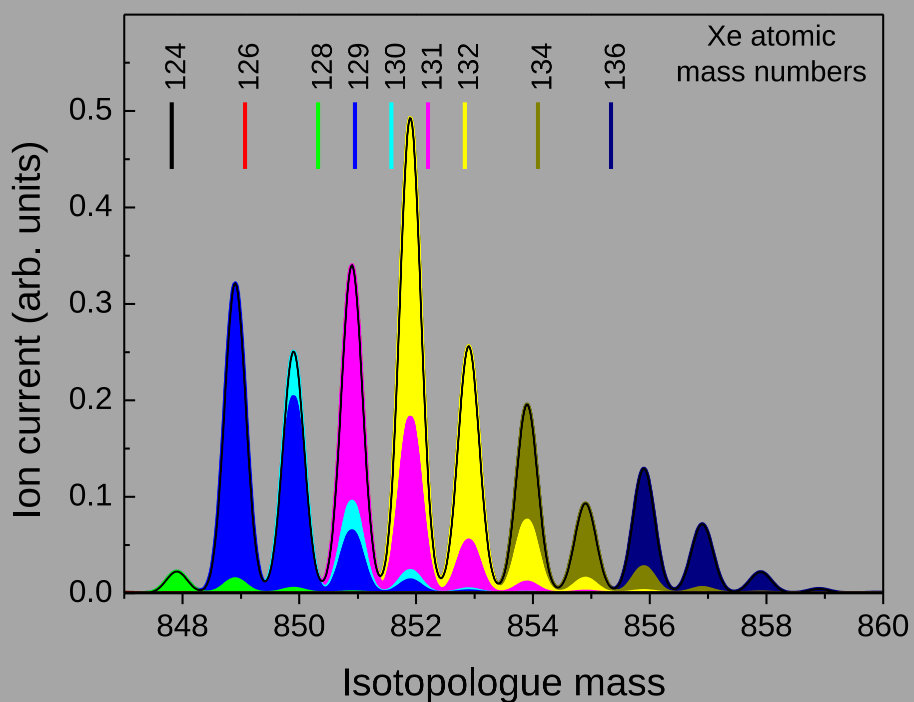
David Kilcoyne

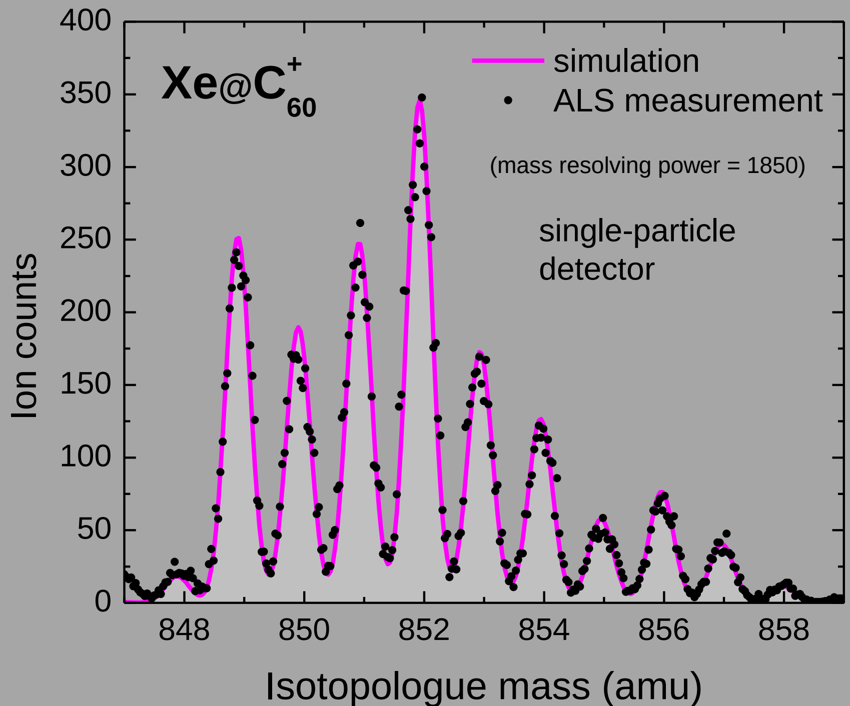
ADVANCED LIGHT SOURCE

Ultra-high-purity commercial C_{60} powder was continuously evaporated and deposited onto a rotating metal cylinder while it was being simultaneously bombarded by 160 eV Xe^{+} ions.

After weeks of operation, the fullerene material deposited on the cylinder was 'harvested' for later re-evaporation into an ECR ion source.

Simulated and Measured High-Resolution Mass Spectrum of $Xe@C_{60}^{+}$



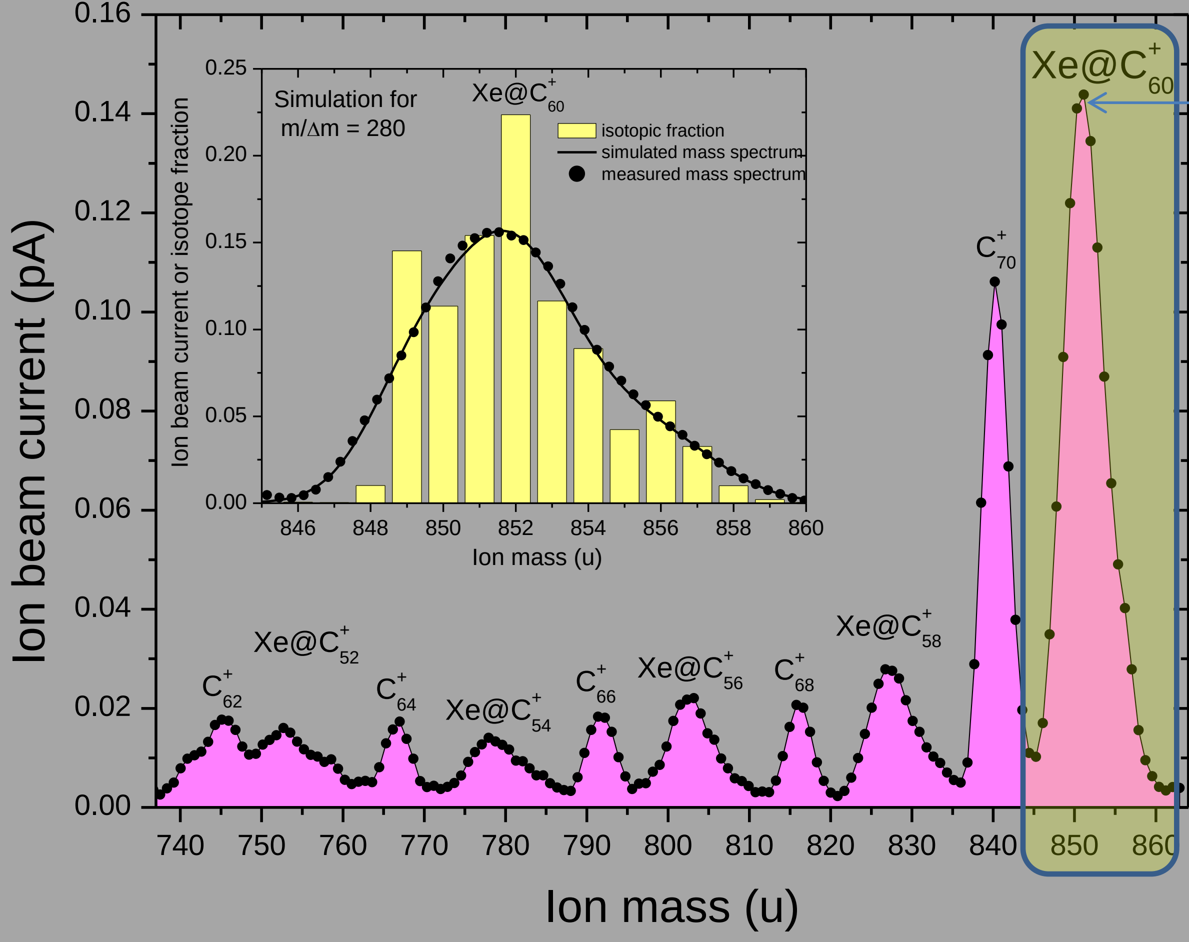


Simulation based on natural isotopic abundances of C and Xe and a binomial distribution for the number of ^{13}C atoms in C_{60}

Measured high-resolution mass spectrum (points) compared with simulation (curve)

A. Müller and S. Schippers - ALS 2010

Mass Spectrum from ECR Ion Source

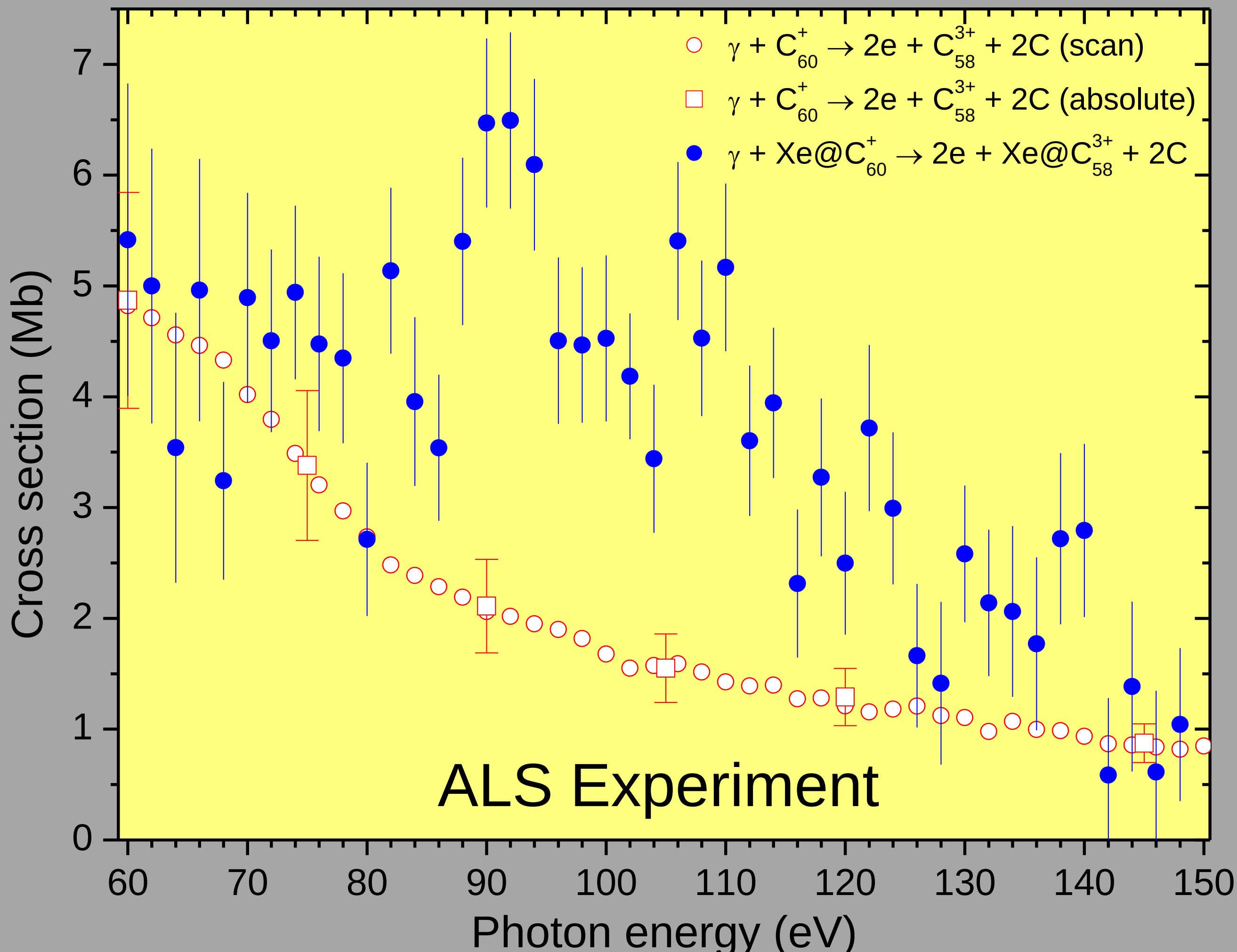


$$\frac{N(Xe@C_{60})}{N(C_{60})} \sim \frac{1}{10^5}$$

The yield of $Xe@C_{60}$ was small but a pure $Xe@C_{60}^+$ ion beam was obtained!

Xenon has 9 stable isotopes and carbon has 2:
(11 possible masses of $Xe@C_{60}$ with abundances > 1%).

Experimental Results: Photoionization of C_{60}^{+} and $Xe@C_{60}^{+}$

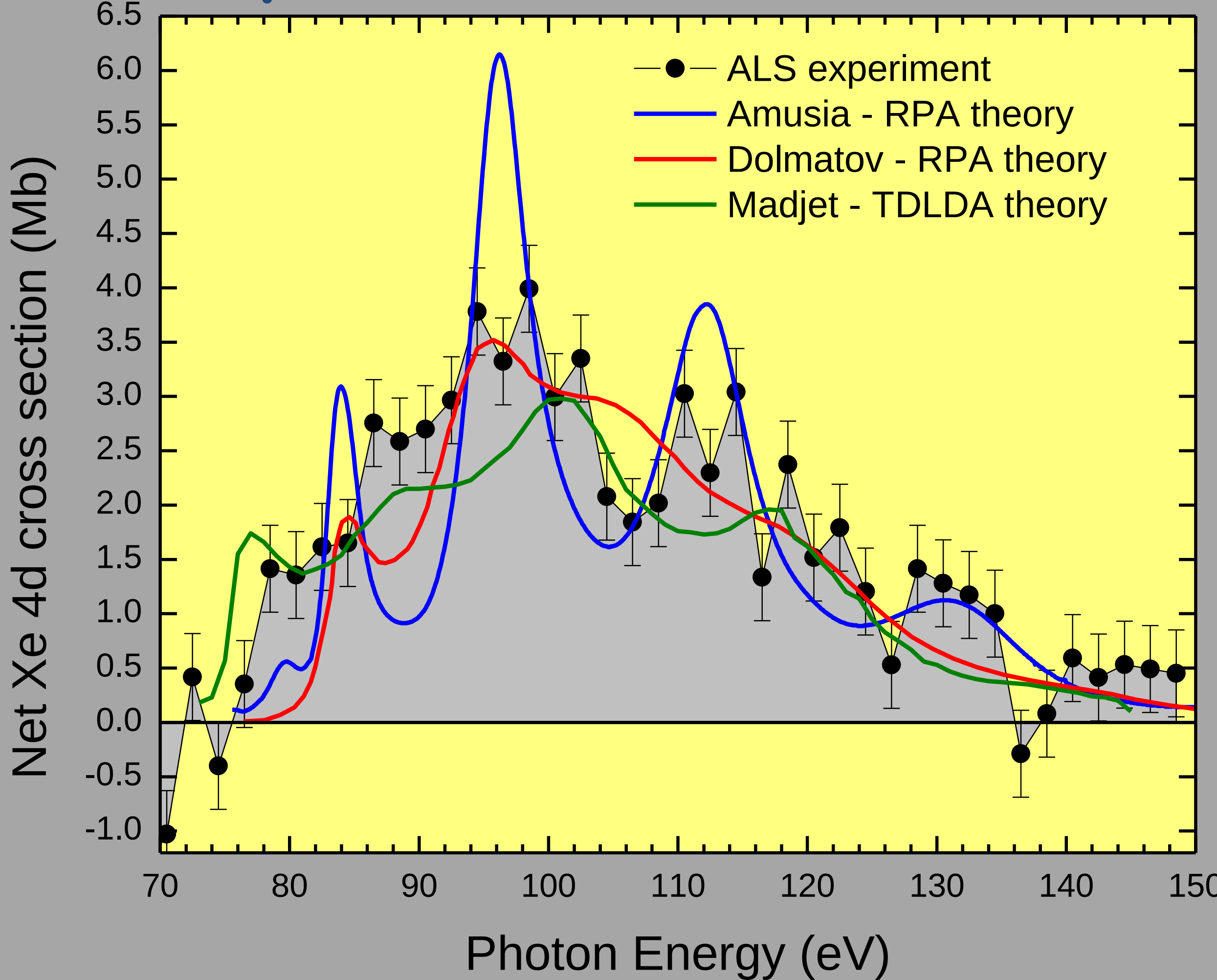


Double photoionization of $Xe@C_{60}^{+}$ with C_2 fragmentation producing $Xe@C_{58}^{+++}$

Reference measurement with empty C_{60}^{+} producing C_{58}^{+++}

Kilcoyne et al., Phys. Rev. Lett. **105**, 213001 (2010)

Excess Xe 4d cross section in photoionization of $Xe@C_{60}^{+}$



Points: experiment
(90% confidence level)

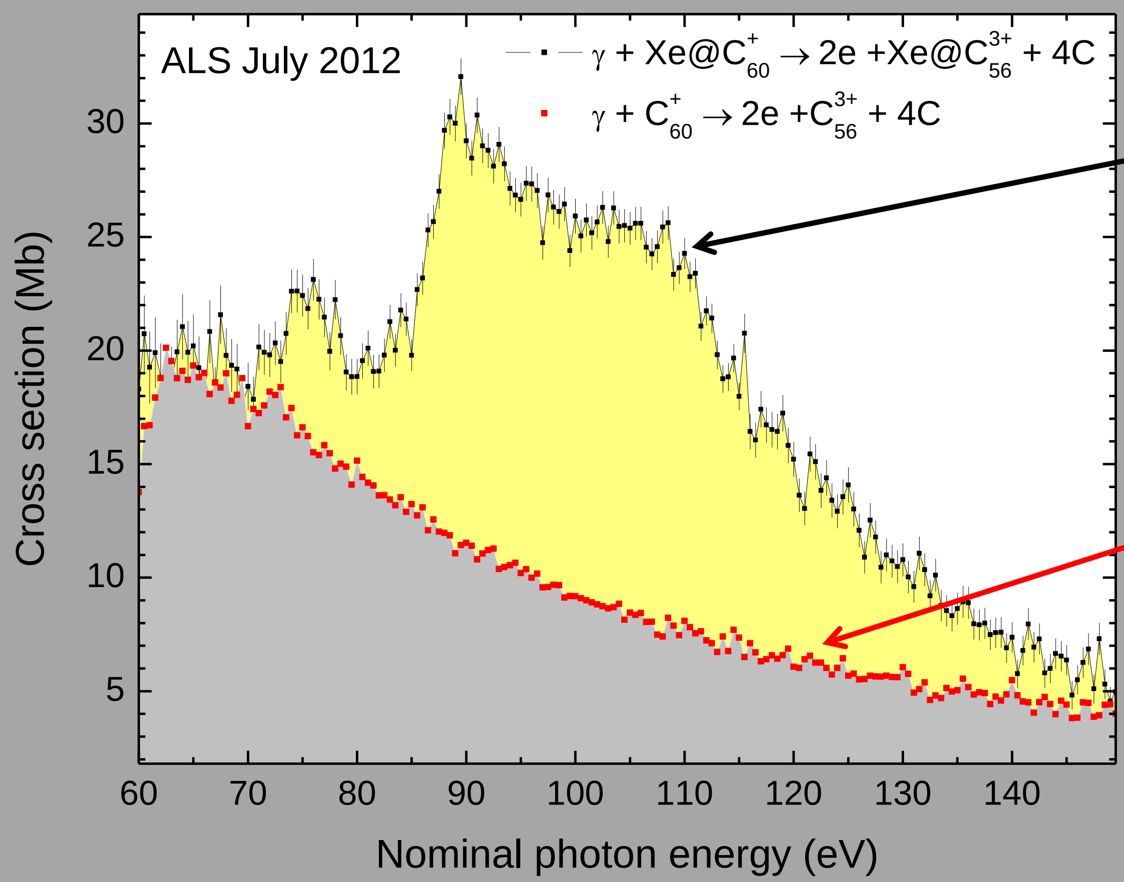
Curves: theory

Measurement suggested interference structure but was inconclusive due to counting statistics.

Strategy: synthesize $Xe@C_{60}$ using a single ^{136}Xe isotope to increase ion beam current.

Kilcoyne et al., Phys. Rev. Lett. **105**, 213001 (2010)

New experimental results for photoionization with fragmentation of C_{60}^+ and $^{136}Xe@C_{60}^+$



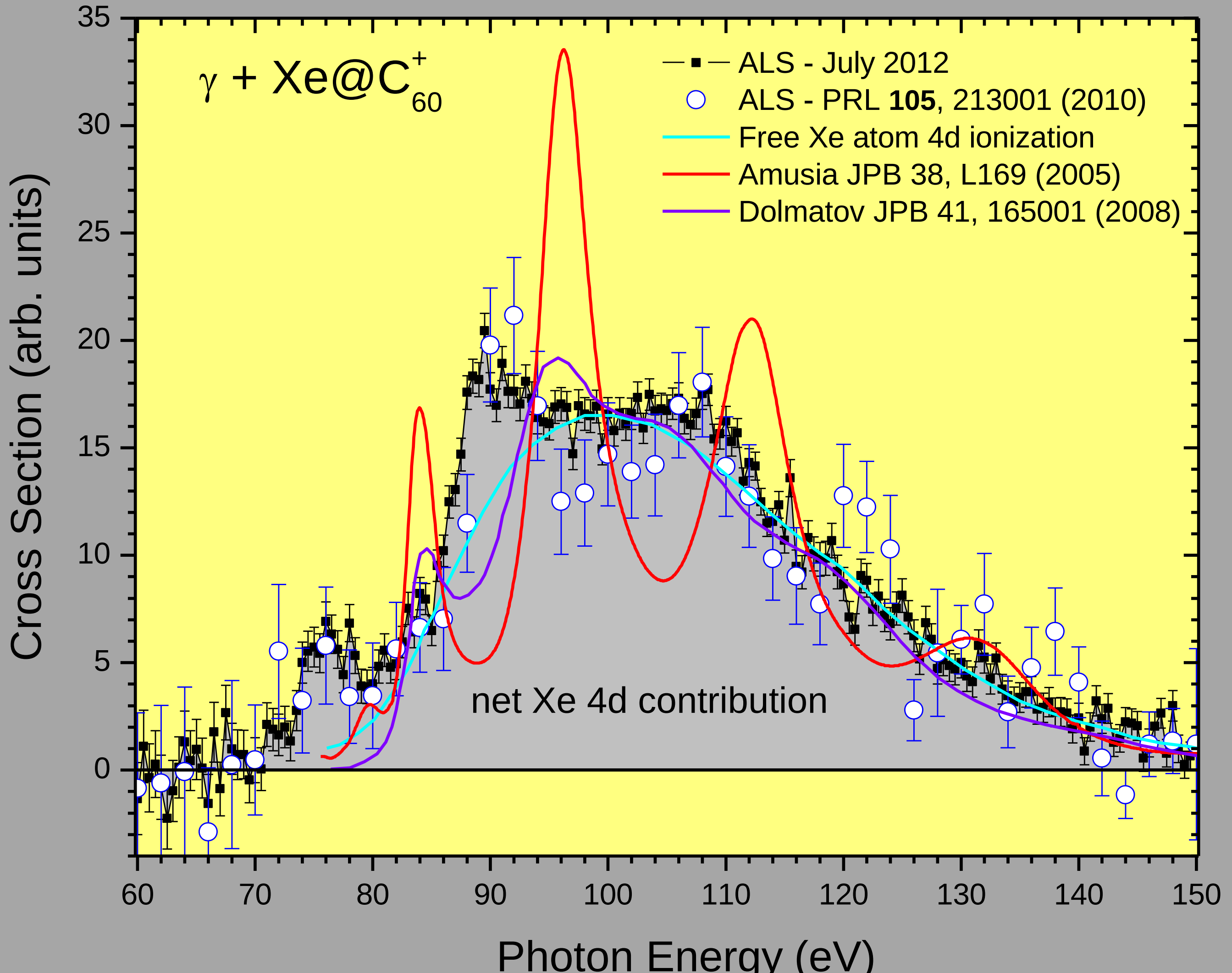
Double photoionization of $^{136}Xe@C_{60}^+$ with double C_2 fragmentation

Corresponding reference measurement with empty C_{60}^+

ALS, July 2012

Optimization of the operating parameters and use of isotopically enriched ^{136}Xe in the synthesis increased the $Xe@C_{60}^+$ ion beam current by more than an order of magnitude!

Excess Xe 4d cross section in photoionization of $^{136}Xe@C_{60}^{+}$



Confinement resonances do exist!

but …

interference pattern is not quite as predicted by theory

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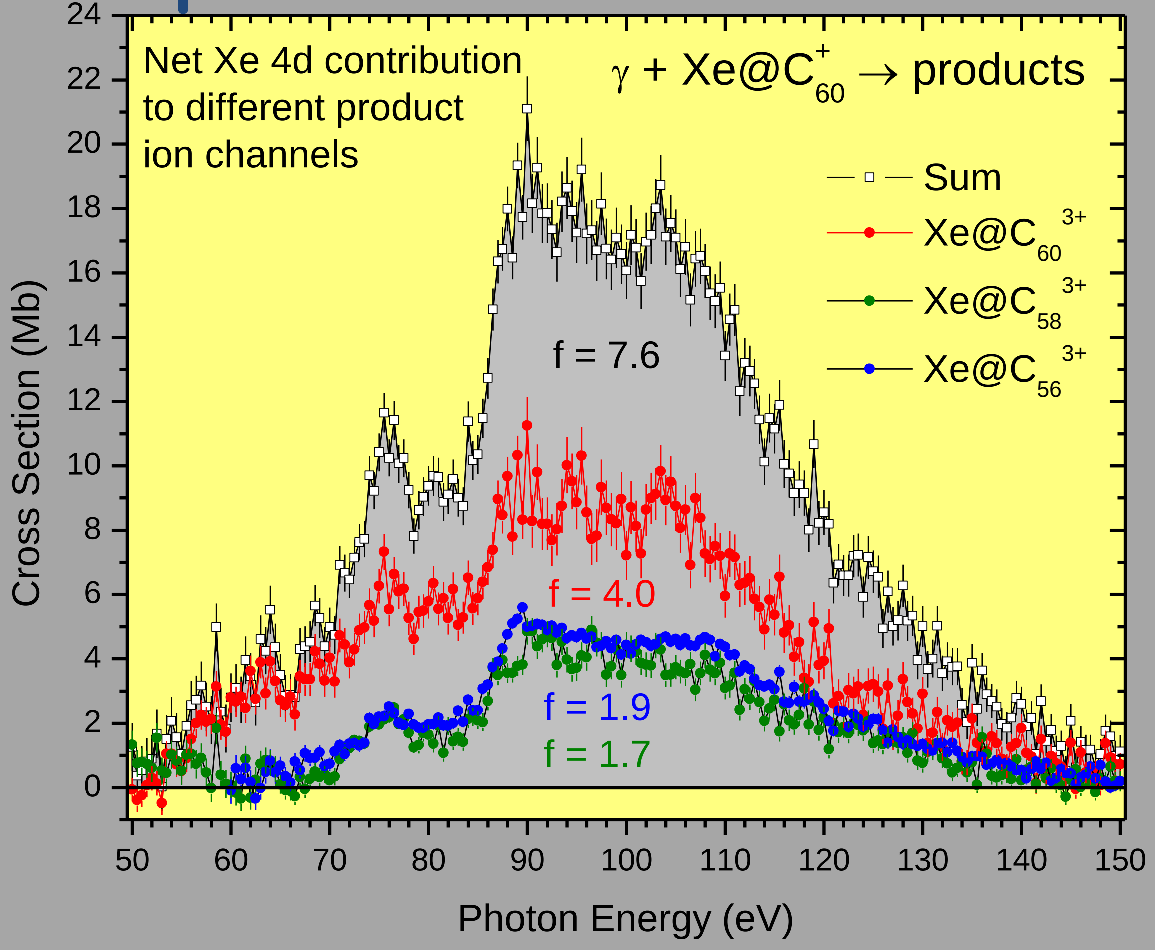
Excess Xe 4d cross section in photoionization of $^{136}Xe@C_{60}^{+}$

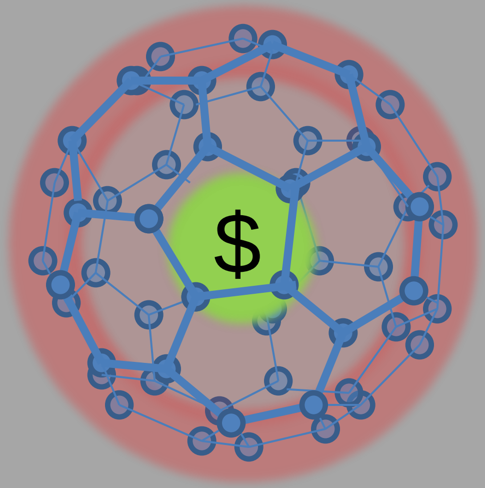


Xe 4d photoabsorption in $Xe@C_{60}^{+}$ leads to double ionization, and is accompanied by fragmentation of the carbon cage about 50% of the time.

These three product channels together account for 3/4 of the total Xe 4d oscillator strength.

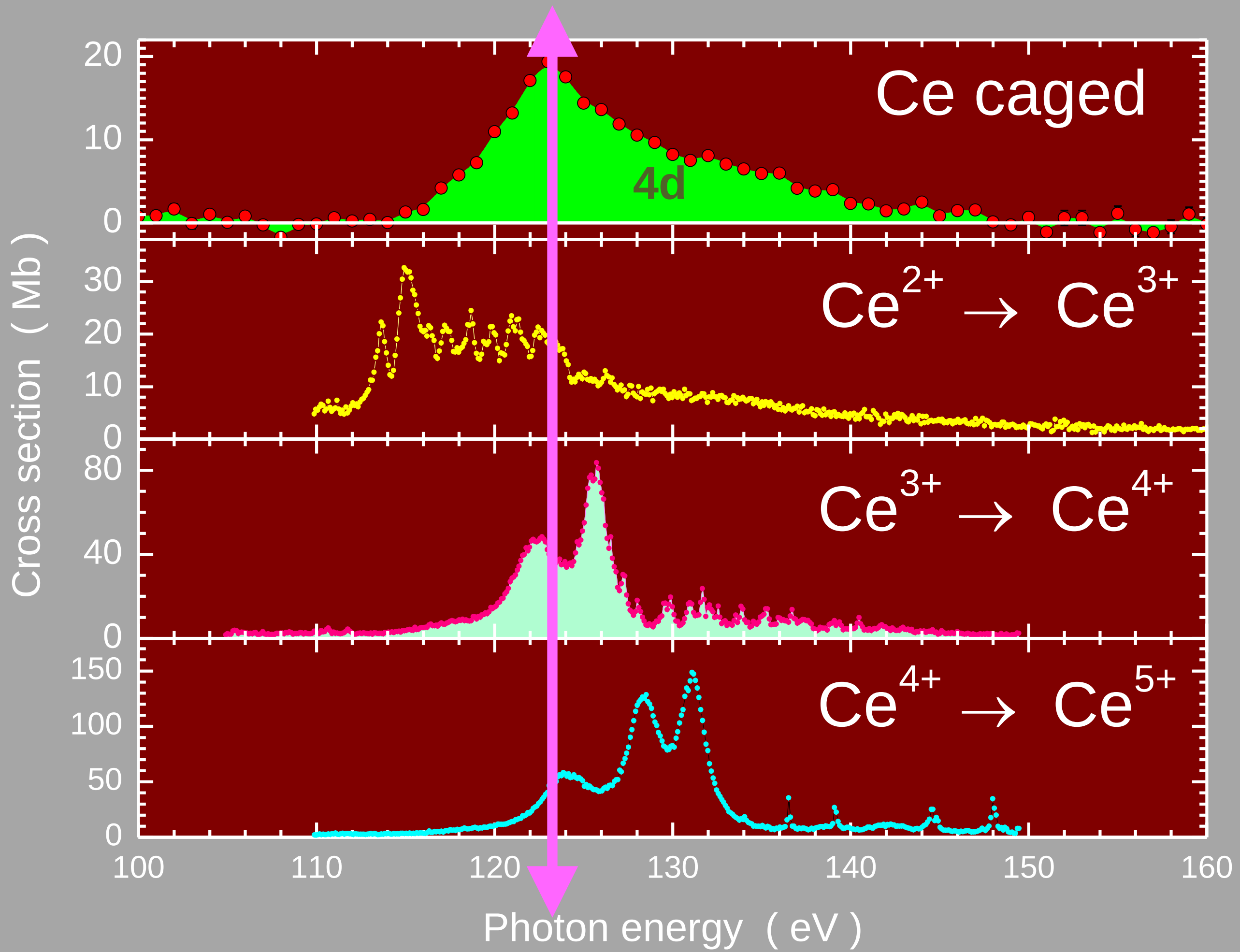
ALS, July 2012

Research Funding



- U.S. Department of Energy, Office of Basic Energy Sciences
  - Division of Chemical Sciences, Geosciences, and Biosciences
- Deutsche Forschungsgemeinschaft, Germany
- CONACyT, Mexico

Photoionization of Ce^{q+} (q=2,3,4) and $Ce@C_{82}^{+}$



As predicted, Ce inside a C_{82}^{+} cage has a valency of +3 but there is no evidence of confinement resonances

Müller et al., Phys. Rev. Lett. 101, 133001 (2008)