Structure and fragmentation properties of small carbon clusters and fullerenes

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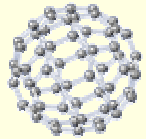
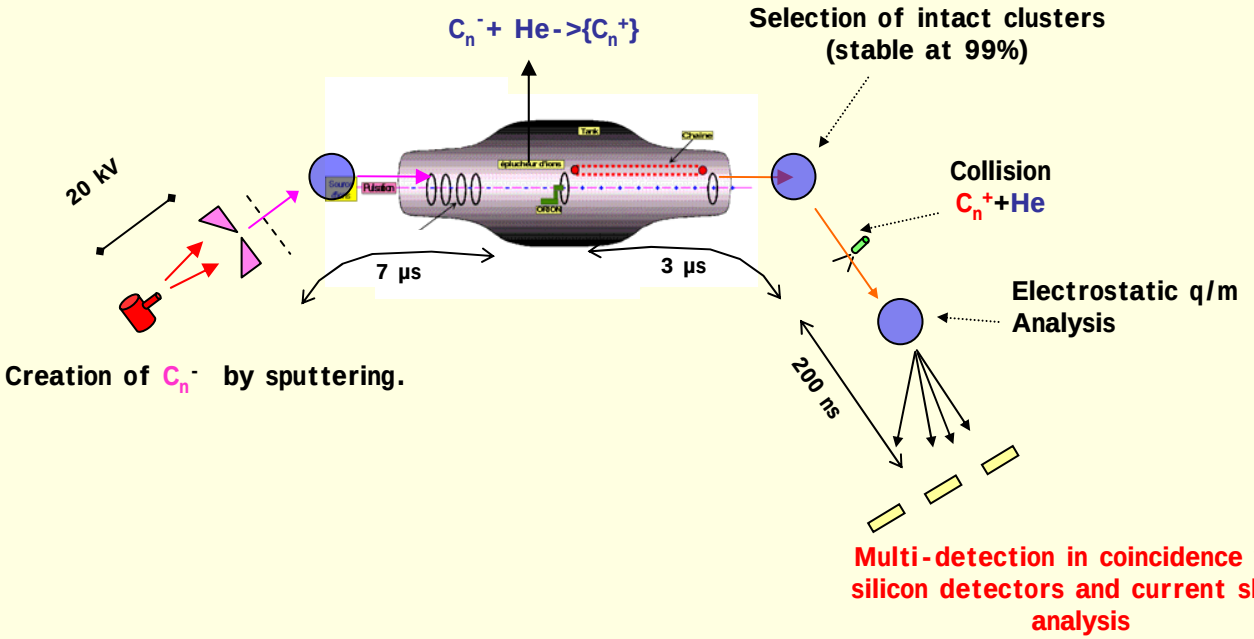


Small carbon clusters: Structure and fragmentation

Experiments in Tandem (Orsay)



Typical collision process $C_7^+ + He$

Neutralization C_7

Excitation / fragmentation $C_7^+ / C_5 + C_2^+$

Ionization / fragmentation $C_7^{+2} / C_4 + C_2^+ + C^+$

Fragmentation

$C_7 \rightarrow C_4 + C_3$

$C_5 \rightarrow C_4 + C$

C_4

Fragmentation models

Weisskopf method

Time dependent description of the fragmentation process.

Rate constants of fragmentation: microcanonical statistical theory of Weisskopf

Metropolis MonteCarlo method

Microscopic data from electronic structure calculations

Obtain the maximum entropy region of a phase space.

Evaluation of the statistical weights.

Microcanonical ensemble: Constant energy.

Thermodynamic equilibrium (not information on the time dependence).

S. Diaz-Tendero et al. Phys. Rev. A 71, 033202 (2005)

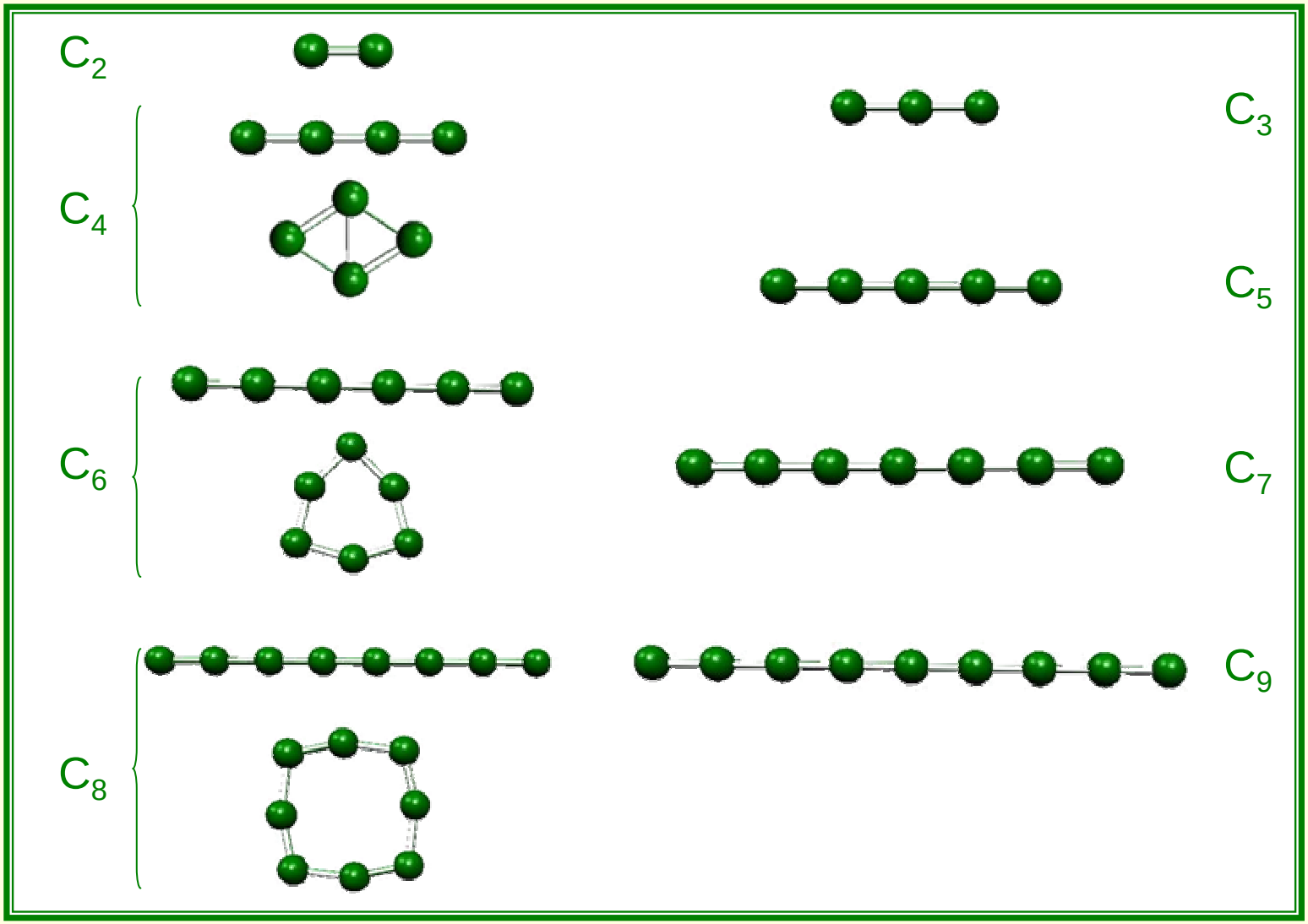
Electronic Structure Calculations

Method: Density Functional Theory

- Geometry optimization.
- Stability and spin contamination analysis.
- Harmonic frequencies and Zero Point Energy correction.
- Moments of inertia.
- Electronic energies:

  CCSD(T) // DFT

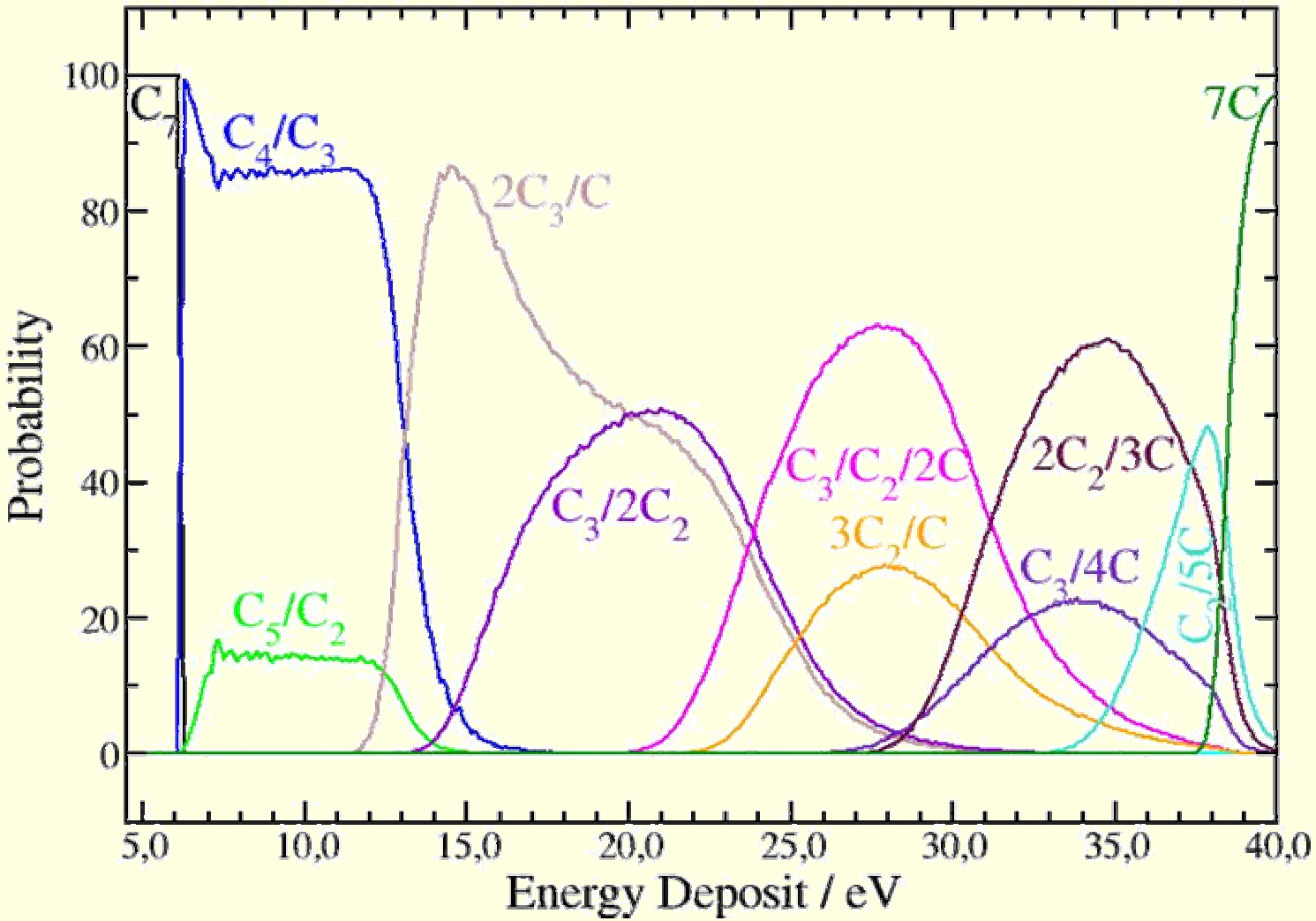
Geometries



S. Diaz-Tendero et al. J. Phys. Chem. A 106, 10782 (2002)
S. Diaz-Tendero et al. Phys. Rev. A 71, 033202 (2005)

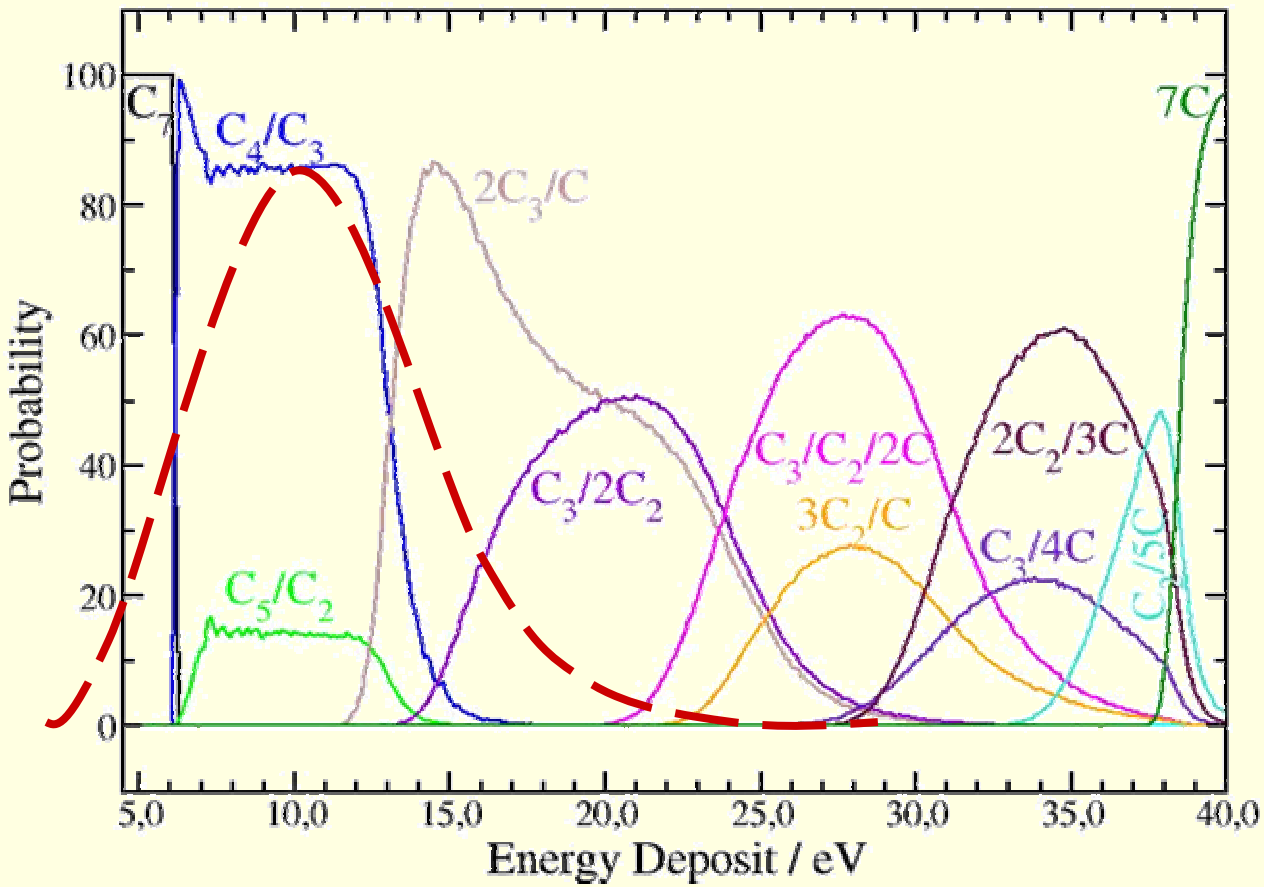
Fragmentation: energy dependence

C_7 fragmentation



Fragmentation: energy distribution

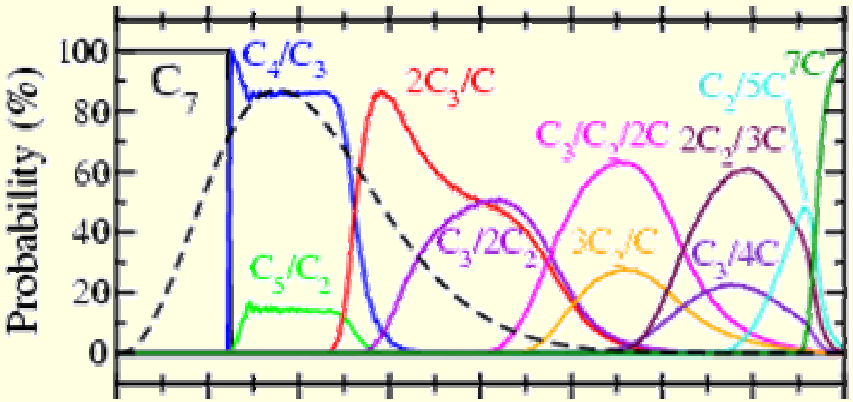
C_7 fragmentation

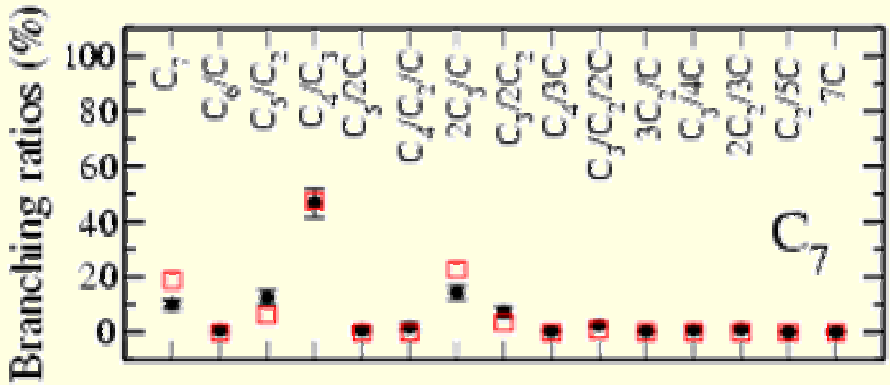


Fragm. Channels (14)	Exp. BR
C_7	10.2 ± 2.0
C_6/C	0.7 ± 0.8
C_5/C_2	12.6 ± 2.5
C_4/C_3	46.7 ± 5.1
$C_5/C/C$	0.75± 0.6
$C_4/C_2/C$	1.8 ± 1.1
$C_3/C_3/C$	14.4 ± 2.5
$C_3/2C_2$	7.3 ± 2.0
$C_4/3C$	0.5 ± 0.4
$C_3/C_2/2C$	2.6 ± 0.8
$2C_2/3C$	0.5 ± 0.5
$2C_2/3C$	1.1 ± 0.8
$C_2/5C$	0.1 ± 0.1
7C	0.1 ± 0.1

G. Martinet, S. Diaz-Tendero et al. Phys. Rev. Lett 93, 063401 (2004)

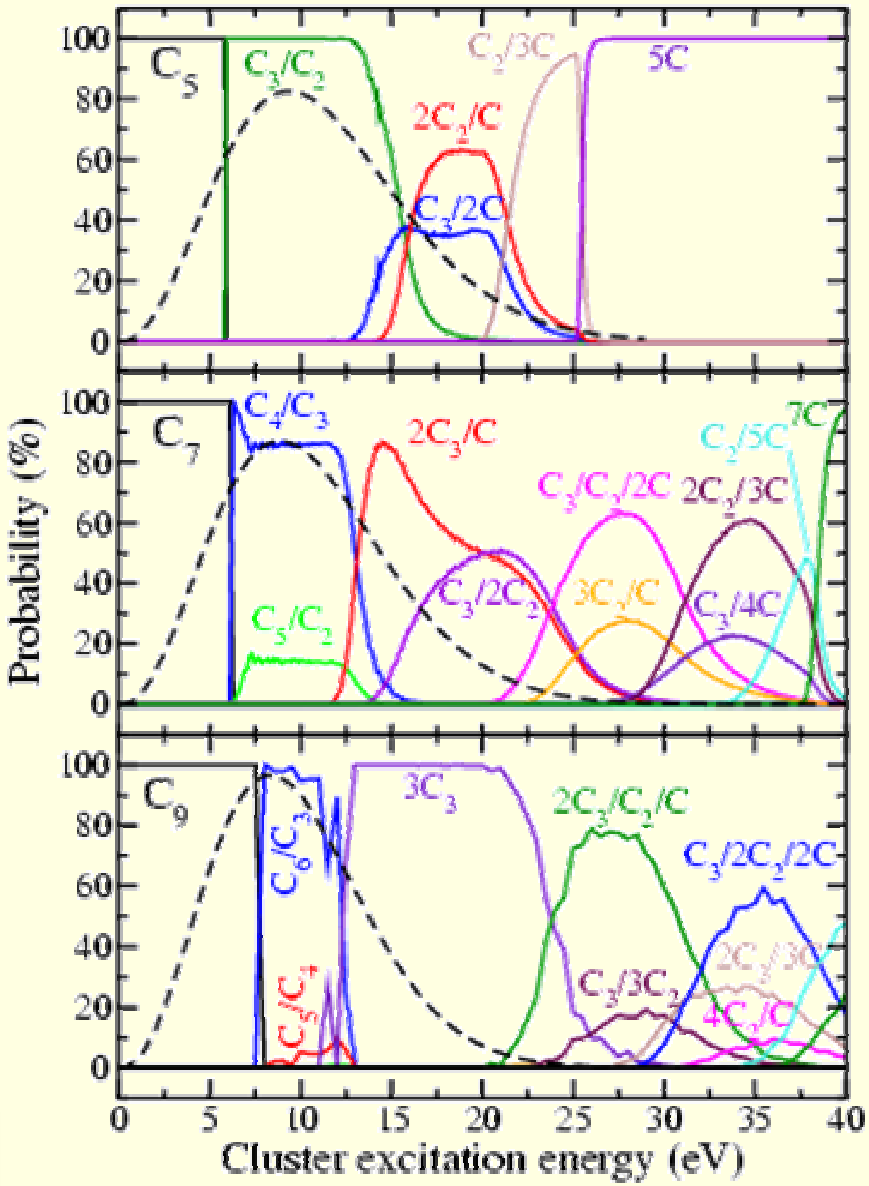
Comparison with experiment

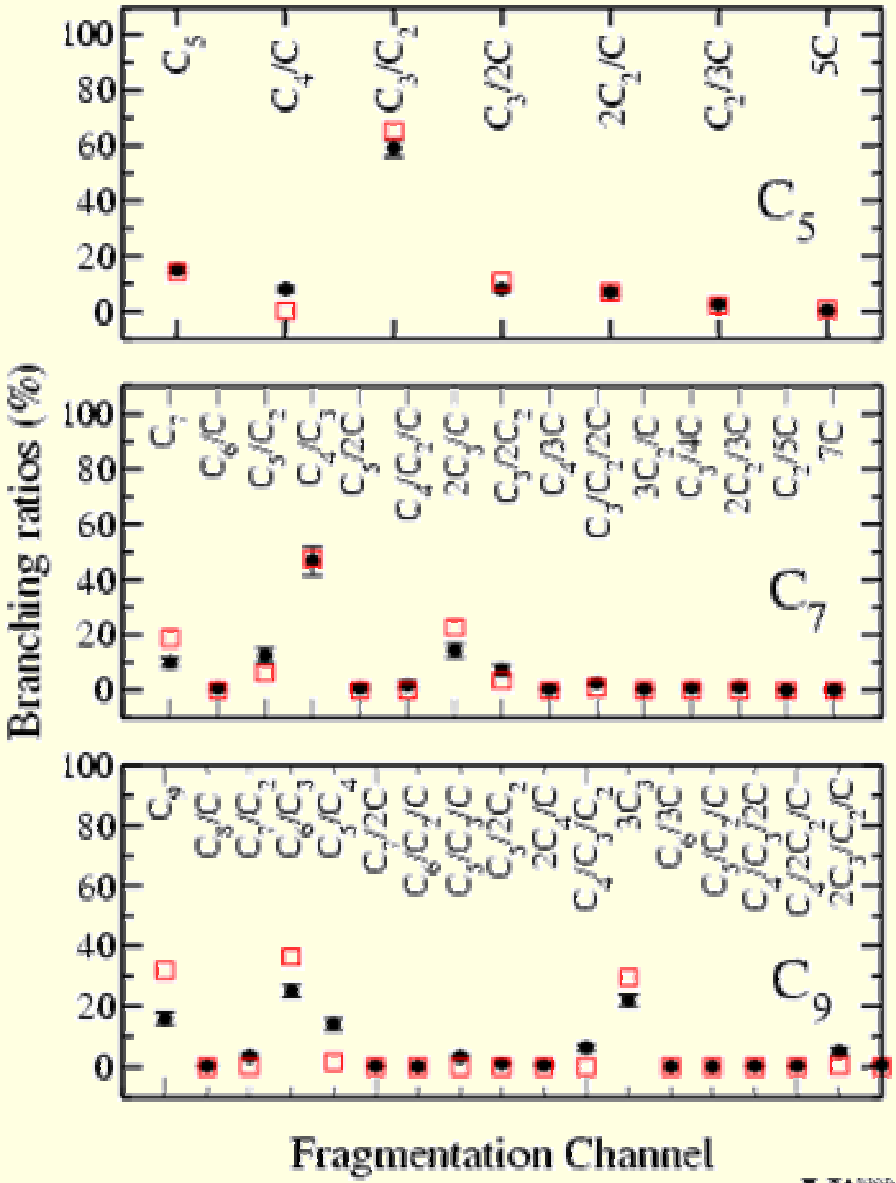




G. Martinet, S. Diaz-Tendero et al. Phys. Rev. Lett 93, 063401 (2004)

Comparison with experiment





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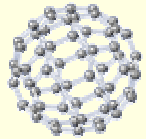
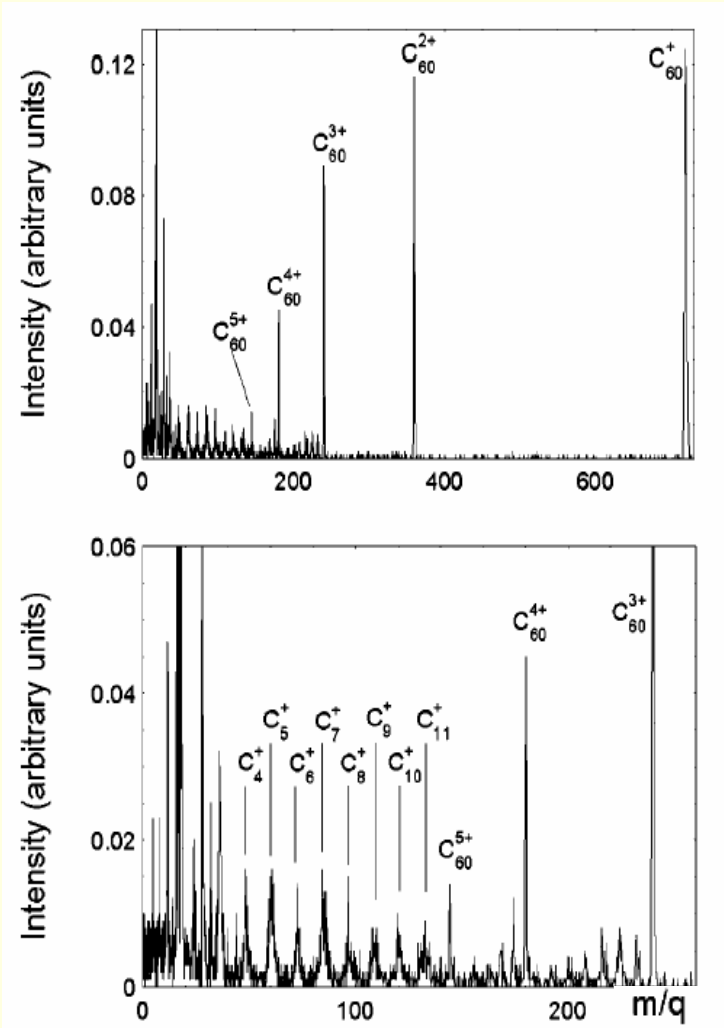


Fullerenes: Structure and fragmentation

Experiments

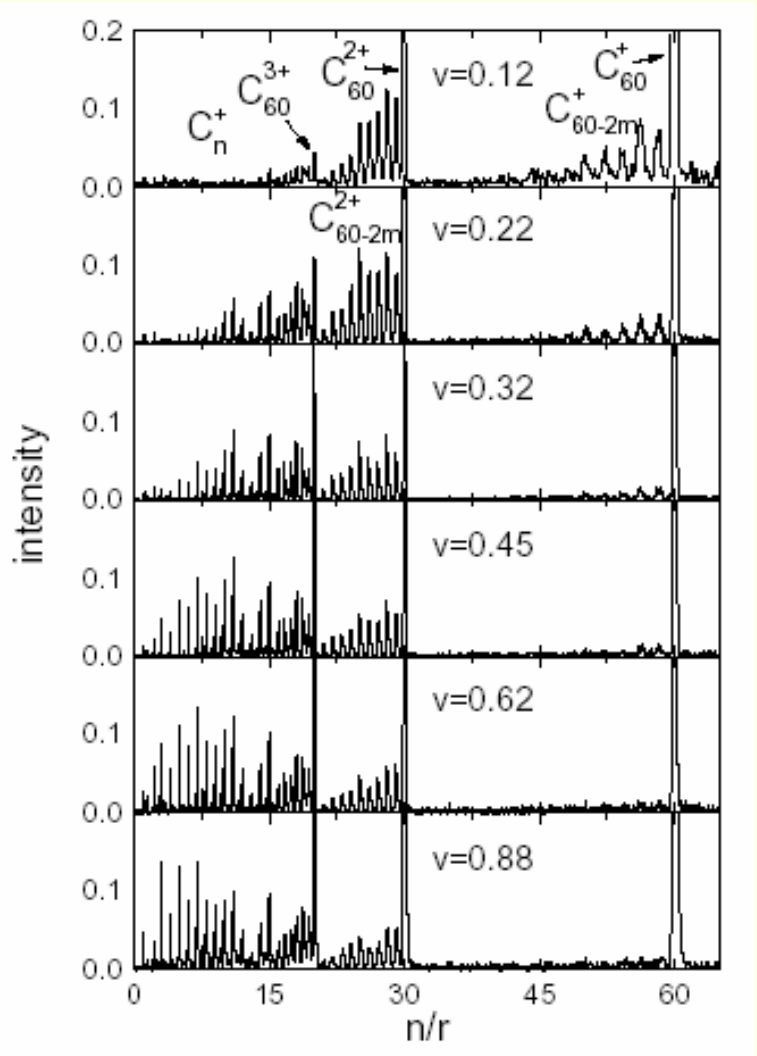
H. Cederquist et al. Phys. Rev. A **61**, 022712 (2000)

Ar^{8+}-C_{60} (16 keV)



T. Schlathölter et al. Phys. Rev. Lett. **82**, 73 (1999)

He^{+}-C_{60}



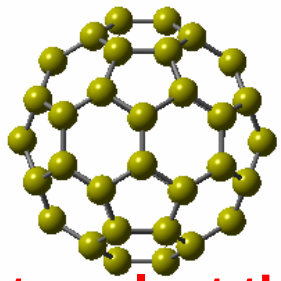
Fullerene structure

Classical fullerenes

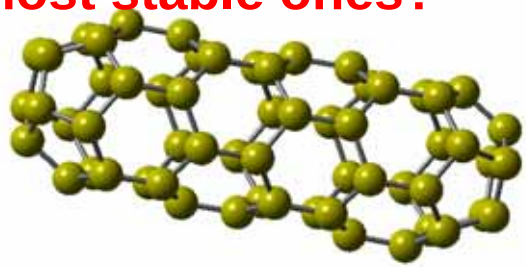
- Cage exclusively formed by hexagons and pentagons
- 12 pentagons are needed (Euler)

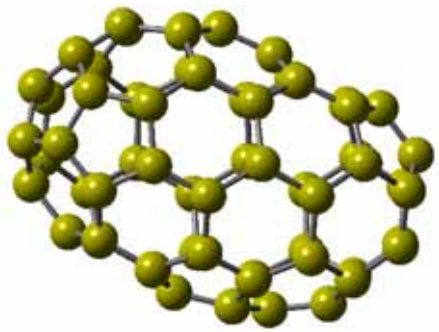
How many possibilities are there?

C_n	Isomers
C_{60}	1812
C_{58}	1205
C_{56}	924
C_{54}	580
C_{52}	437
C_{50}	271



How to select the most stable ones?





Fullerene structure

Adjacent pentagons introduce strain

Isolated Pentagon Rule (IPR)

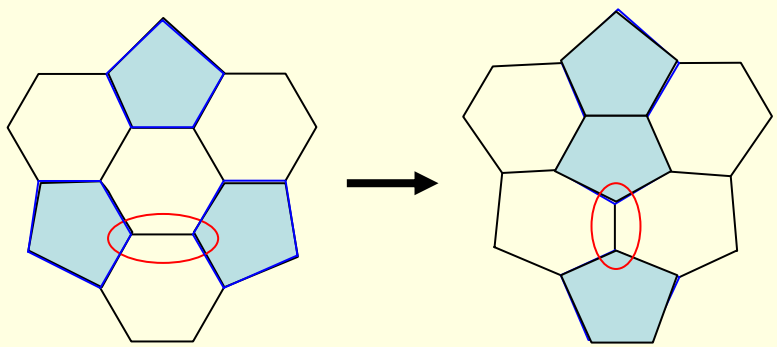
The most stable and abundant fullerenes only present isolated pentagons: C_{60} and C_{70}

Pentagon Adjacency Penalty Rule (PAPR)

If pentagons cannot be isolated, the fewer pentagon adjacencies the better.

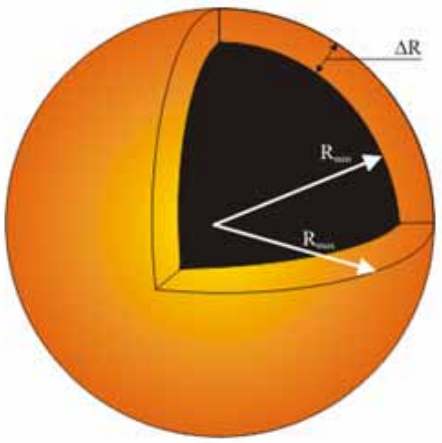
Stone-Wales transformations

A mechanism to generate adjacent pentagons.



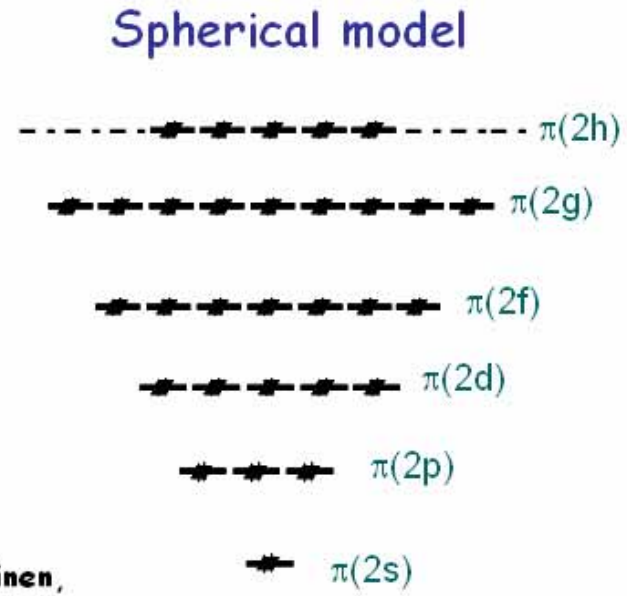
Fullerene structure

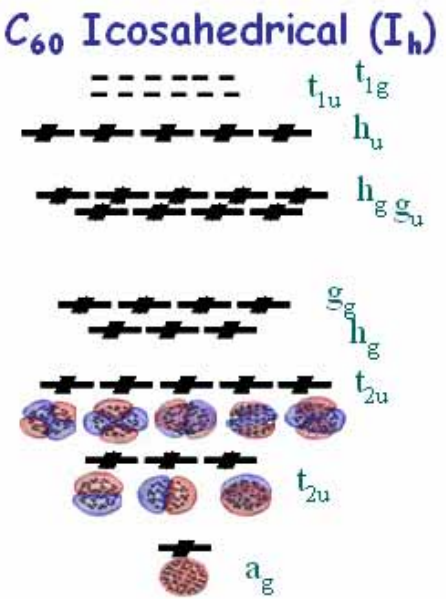
Hollow sphere model for π electrons



$$\Psi \approx R_{nl}(r) Y_{lm}(\vartheta, \varphi)$$

M. J. Puska and R. M. Nieminen,
Phys. Rev. A 47, 1181 (1993)



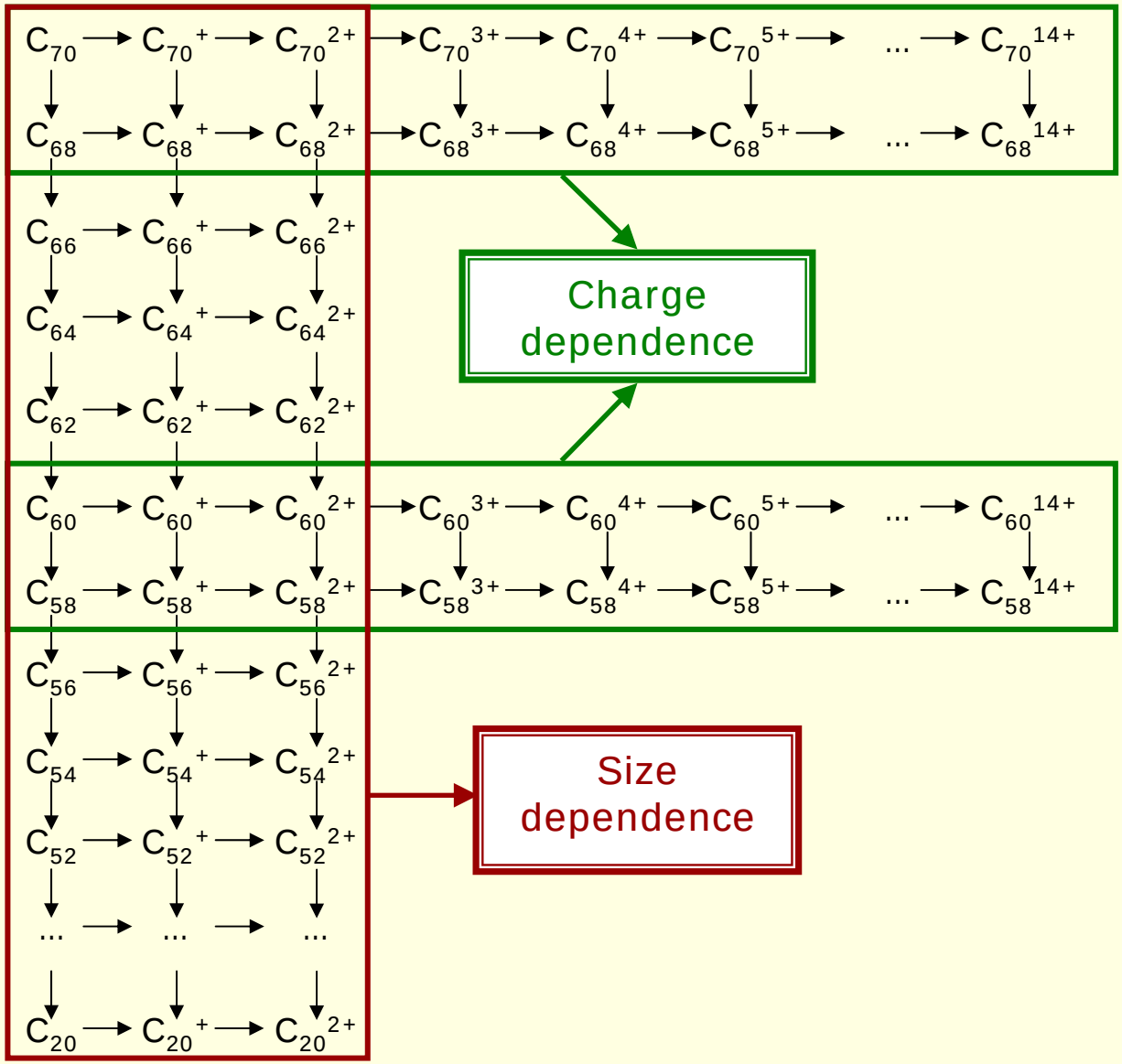


Closed shells have additional stability

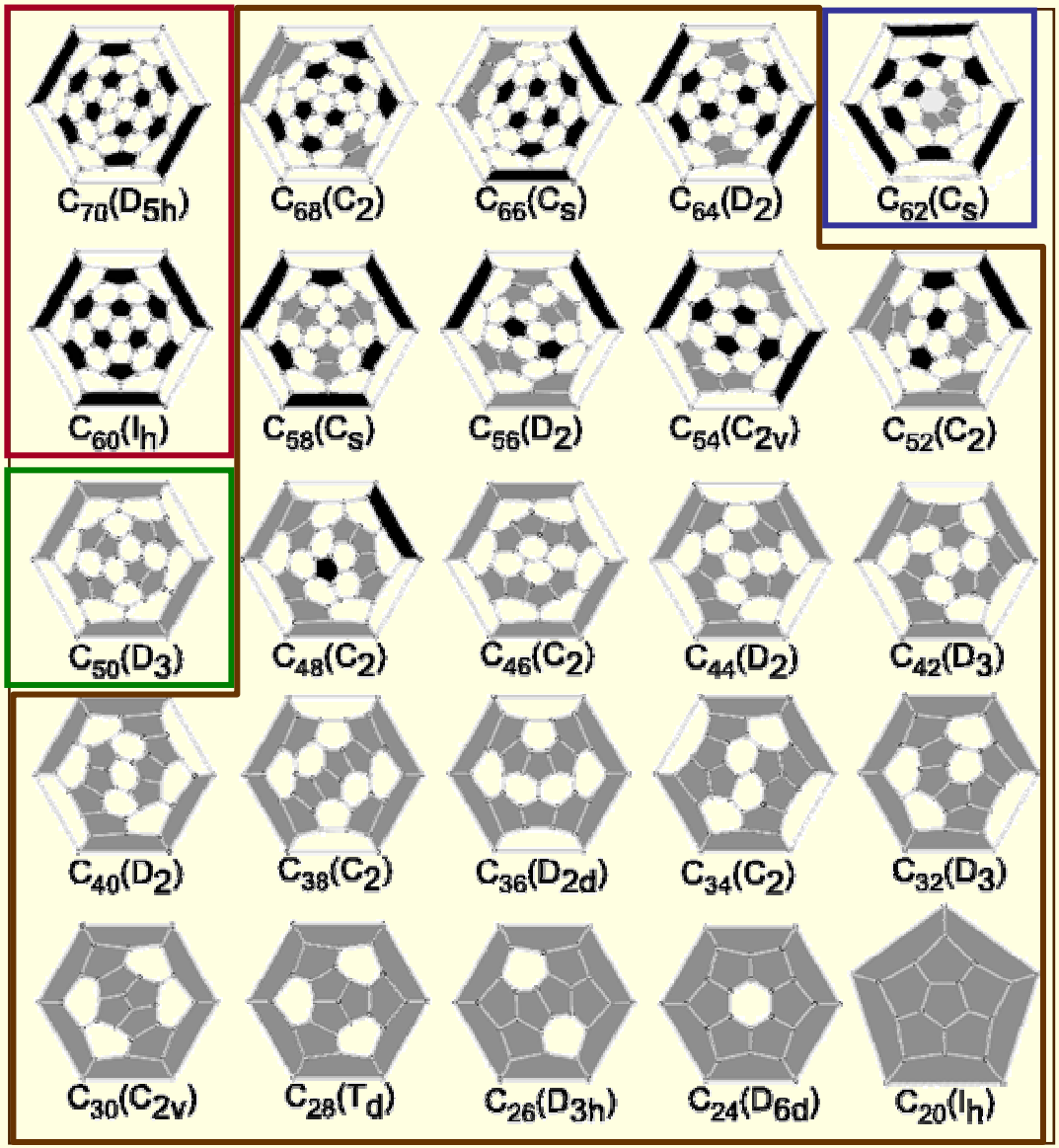
Number of π electrons (atoms) 2, 8, 18, 32, 50, 72 …

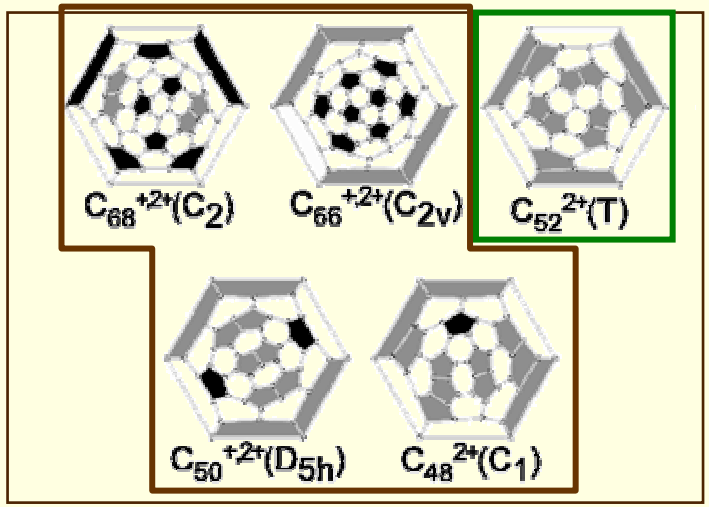
Rule $2(N+1)^2$ – Spherical Aromaticity

Fullerenes studied



C_n^{q+} structures





IPR (C_{70}, C_{60})

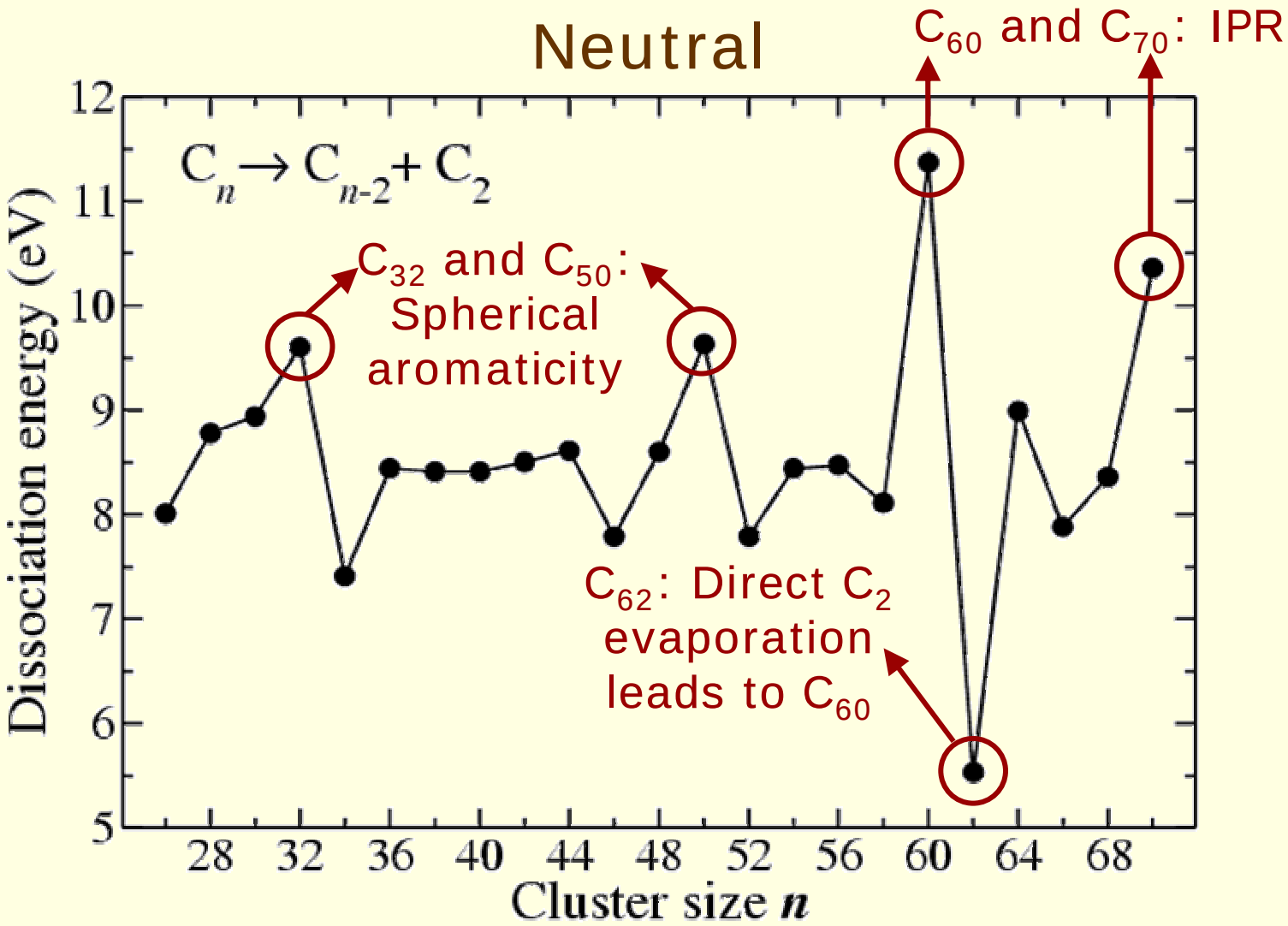
PAPR (others)

Sphericity Rule (C_{50}, C_{52}^{2+})

Non classical fullerenes (C_{62})

S. Díaz-Tendero *et al.*, *J. Chem. Phys*, **119**, 5545 (2003)
G. Sánchez *et al.*, *Chem. Phys. Lett.*, **416**, 14 (2005)
S. Díaz-Tendero *et al.*, *Int. J. Mass Spect.*, **252** 126 (2006)

Dissociation energies



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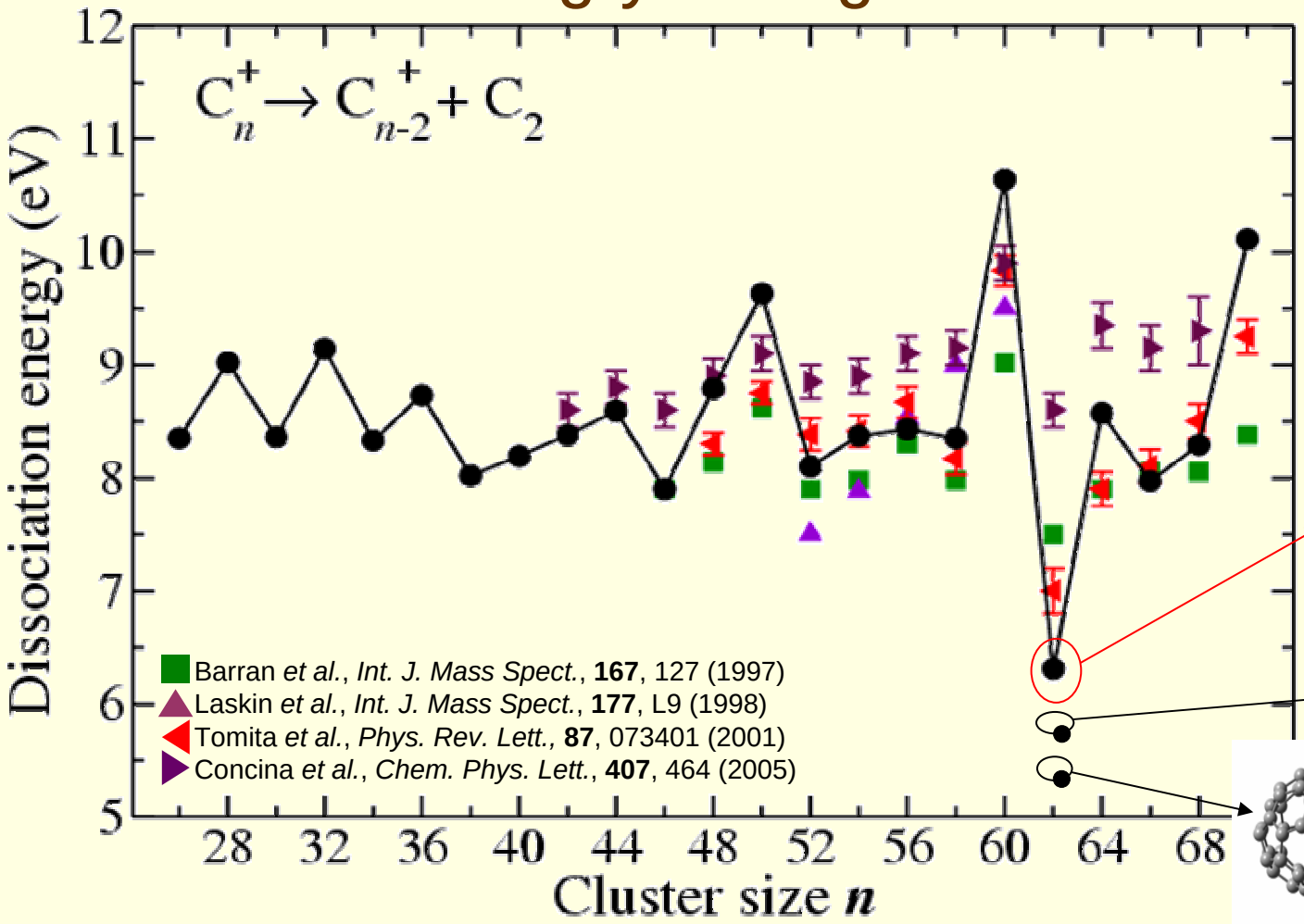
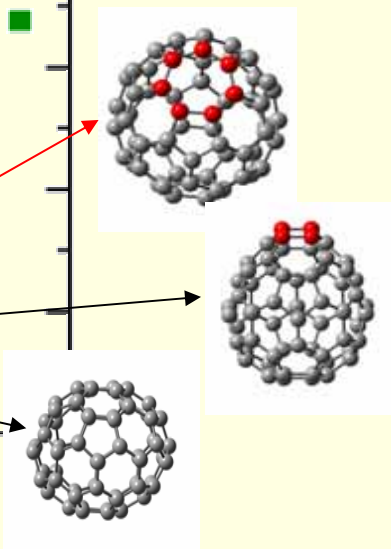
Dissociation energies

Singly charged





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G. Sánchez *et al.*, *Chem. Phys. Lett.*, **416**, 14 (2005)
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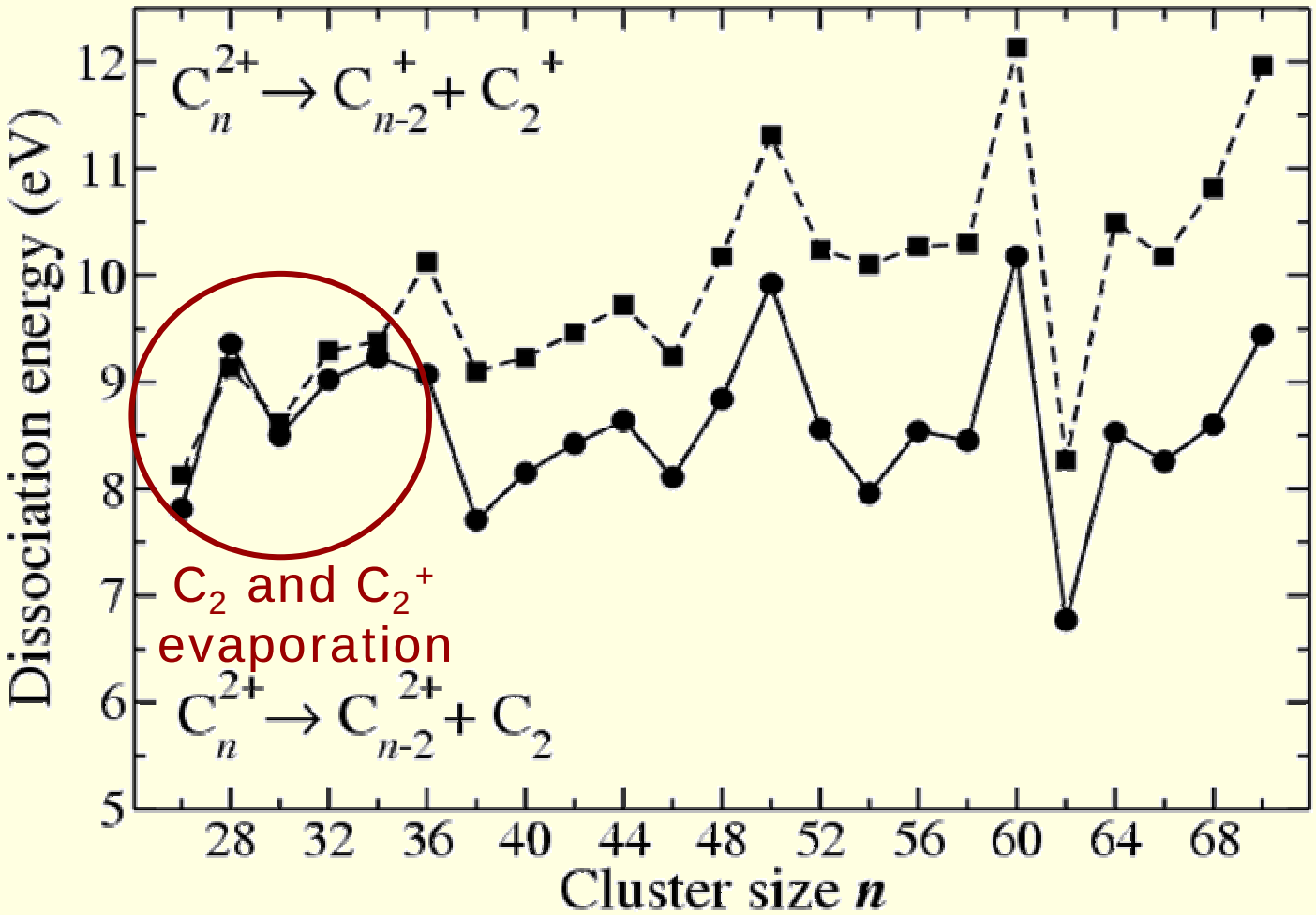
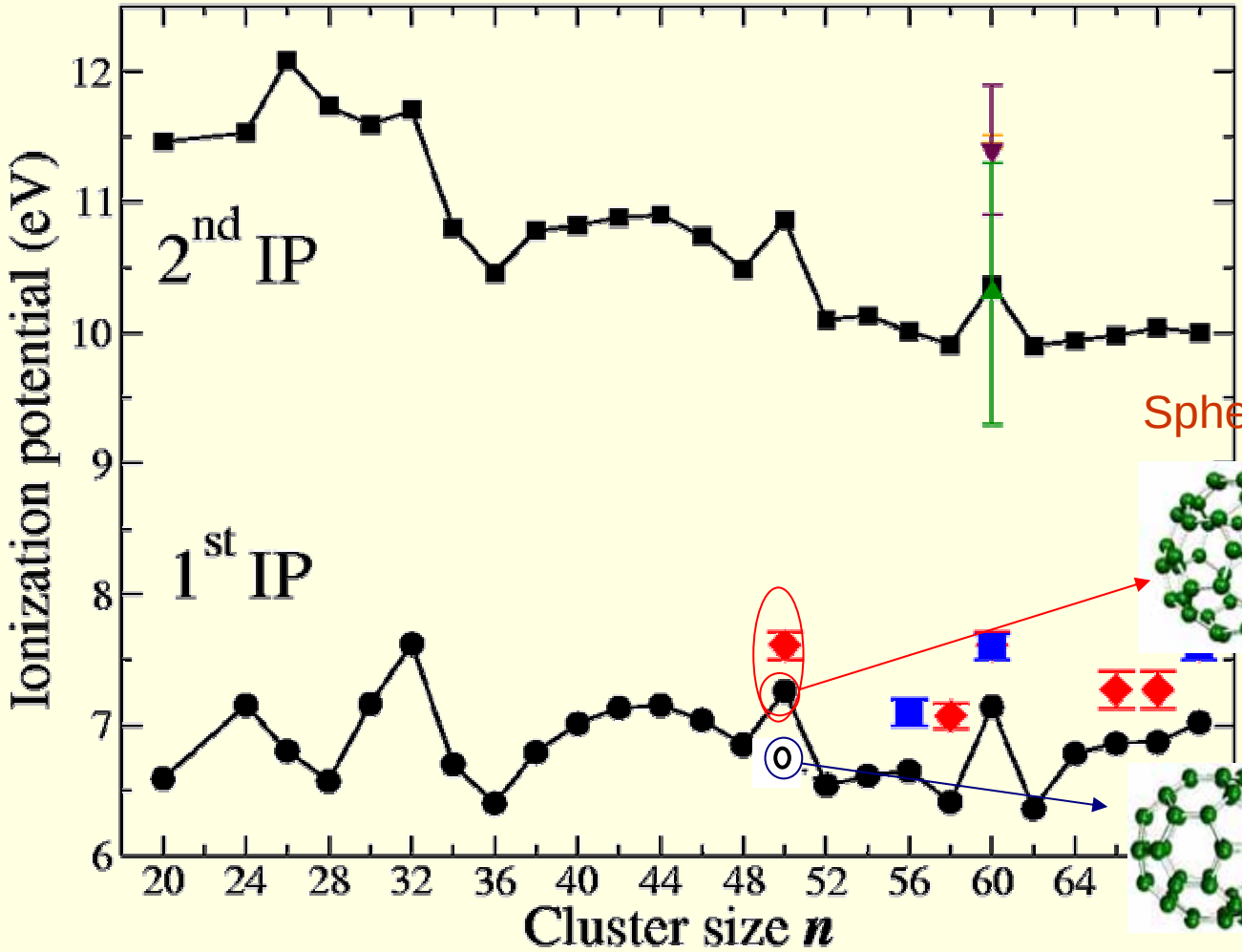
Dissociation energies

Doubly charged

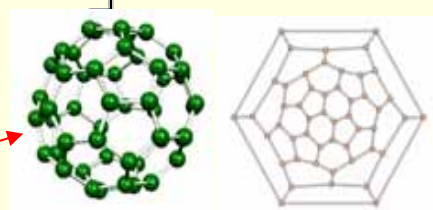


S. Díaz-Tendero *et al.*, *J. Chem. Phys*, **119**, 5545 (2003)
G. Sánchez *et al.*, *Chem. Phys. Lett.*, **416**, 14 (2005)
S. Díaz-Tendero *et al.*, *Int. J. Mass Spect.*, **252** 126 (2006)

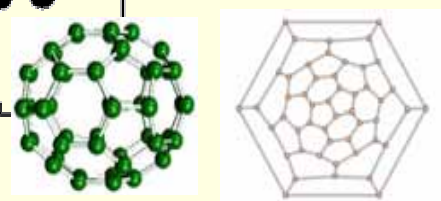
Ionization Potentials



$2(N+1)^2$ e-
Spherical aromaticity



D_3



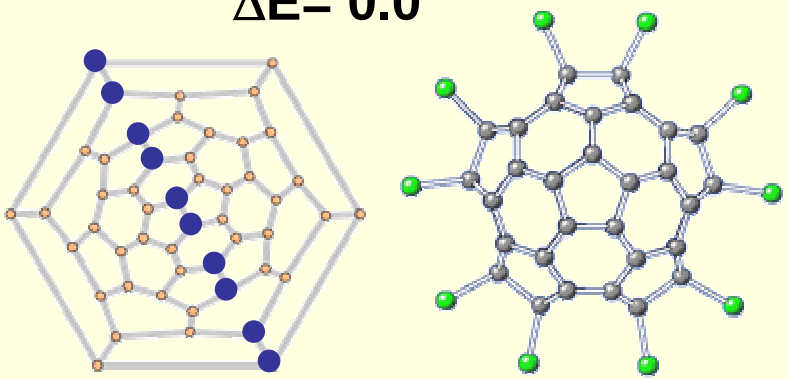
D_{5h}

S. Díaz-Tendero *et al.*, *J. Chem. Phys*, **119**, 5545 (2003)
G. Sánchez *et al.*, *Chem. Phys. Lett.*, **416**, 14 (2005)
S. Díaz-Tendero *et al.*, *Int. J. Mass Spect.*, **252** 126 (2006)

◆ Zimmerman *et al.*, J. Chem. Phys. 94 (1991) 3556.
■ McElvany *et al.*, Proc. of the 39th ASMS Conf. on Mass Spect. 39 (1991) 422.
▲ Baba *et al.*, Int. J. Mass Spectrom. Ion Proc. 114 (1992) R1.
▼ Muigg *et al.*, J. Phys. B 29 (1996) 5193.
X Steger *et al.*, Chem. Phys. Lett. 194 (1992) 452.

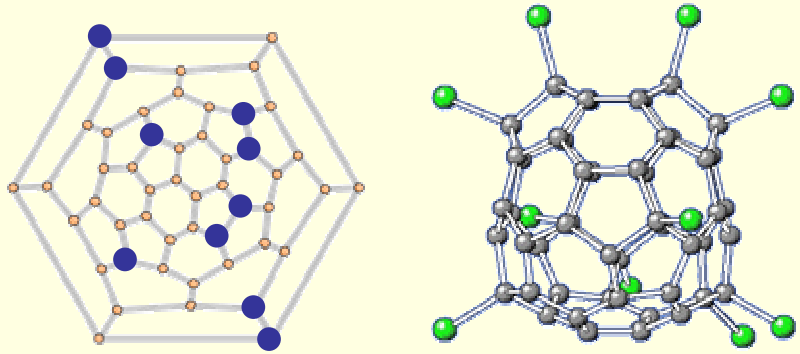
Fullerene derivatives

$C_{50}Cl_{10}$ (D_{5h}) – 5AP
ΔE= 0.0



SP = 4.6

$C_{50}Cl_{10}$ (D_3) – 6AP
ΔE= 76.0

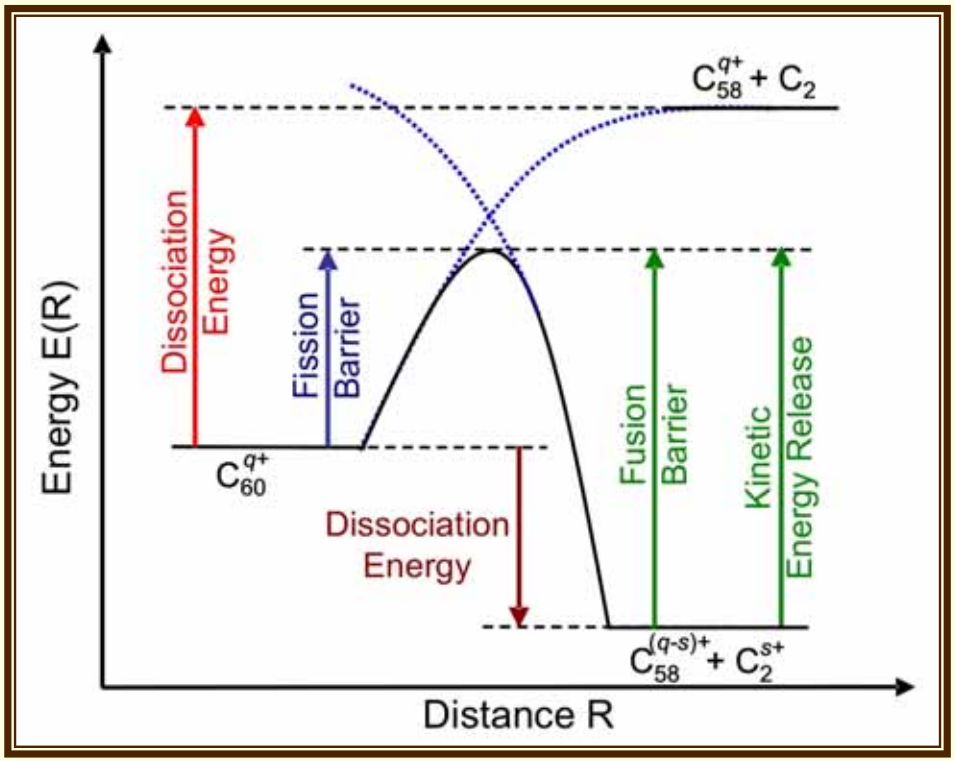


SP = 16.6

Endohedral derivatives x@C_{50}

X	q	D_{5h} 5AP / SP=1.7	D_3 6AP / SP=0.6
Li	-0.8	**0.0**	7.6
Li^+	0.2	0.9	**0.0**
He	0.0	2.2	**0.0**
He^+	1.0	**0.0**	9.1

Highly charged C_{60}^{q+}

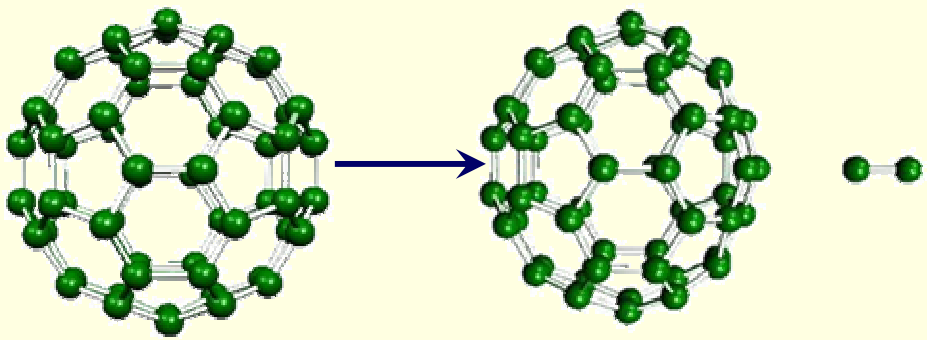


Structure C_{60}^{q+} and C_{58}^{q+}

Ionization potentials

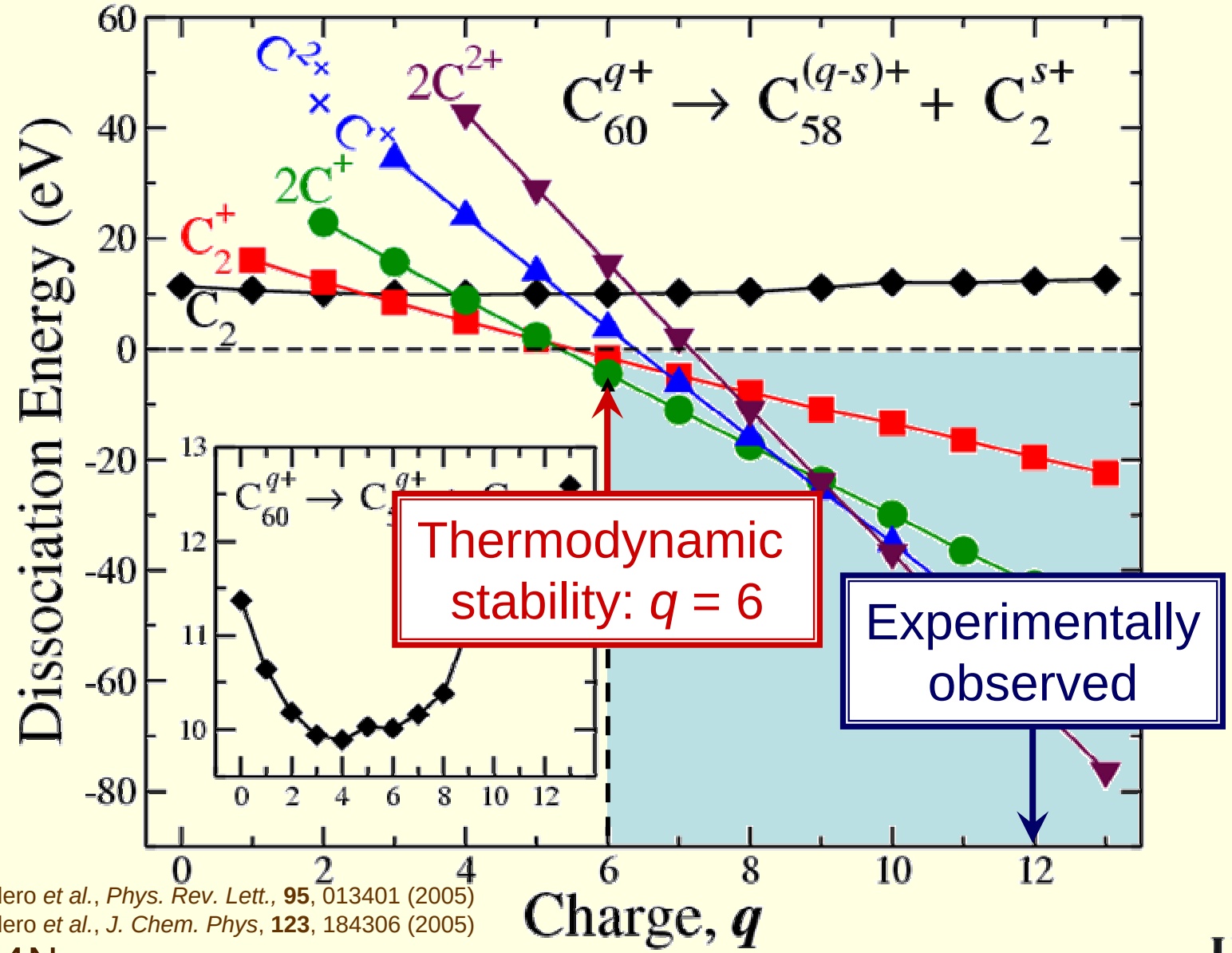
Dissociation energies

Fission Barriers



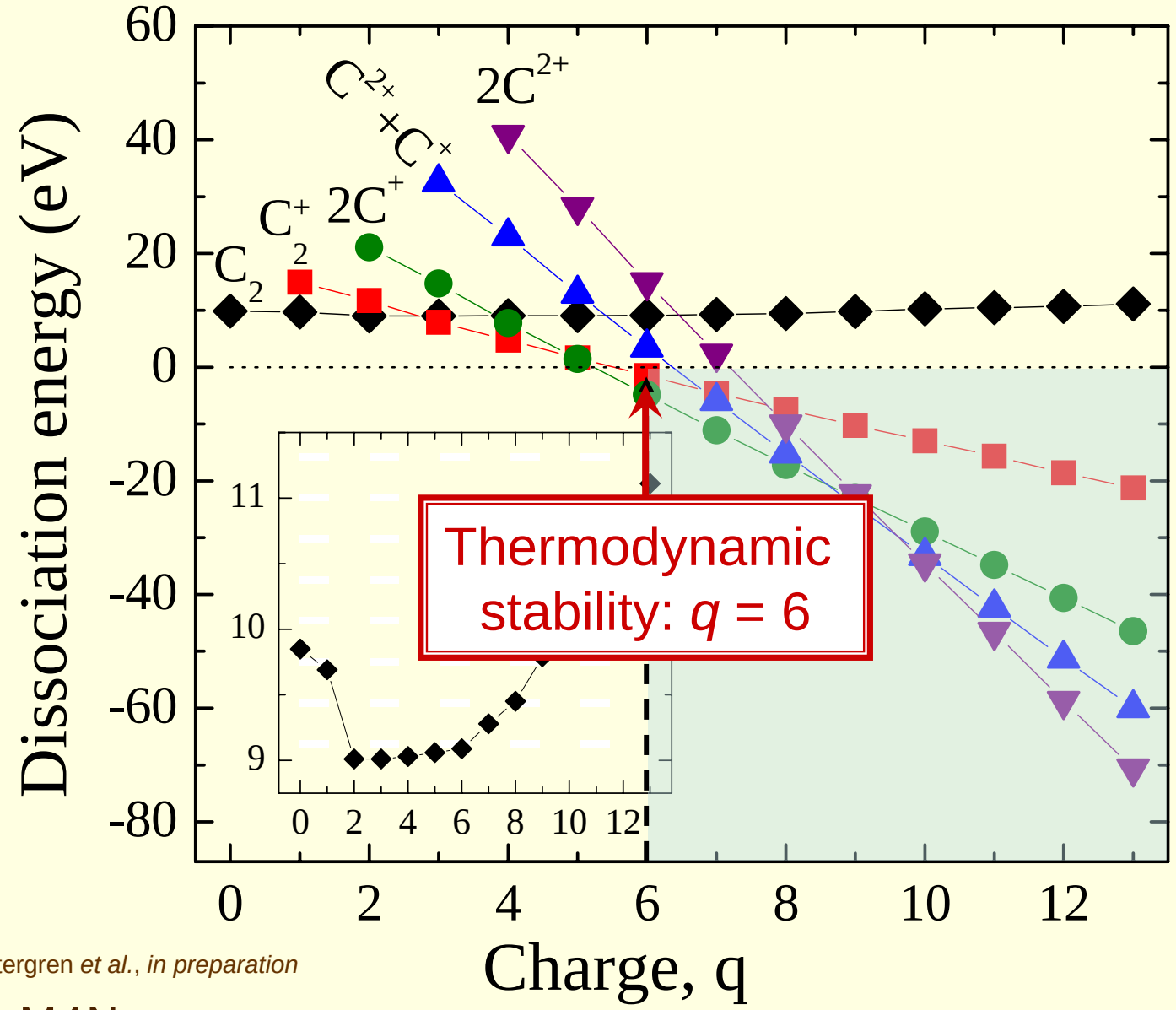
$$C_{60}^{q+} \rightarrow C_{58}^{(q-s)+} + C_2^{s+}$$

Dissociation energies



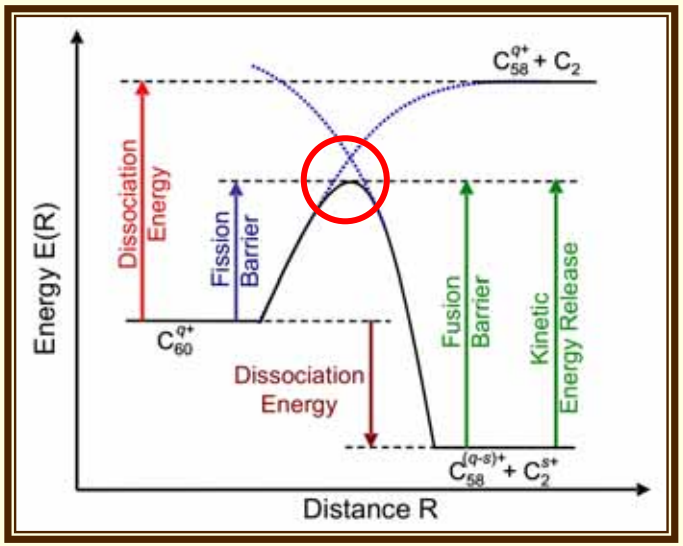
S. Díaz-Tendero *et al.*, *Phys. Rev. Lett.*, **95**, 013401 (2005)
S. Díaz-Tendero *et al.*, *J. Chem. Phys*, **123**, 184306 (2005)

Dissociation energies

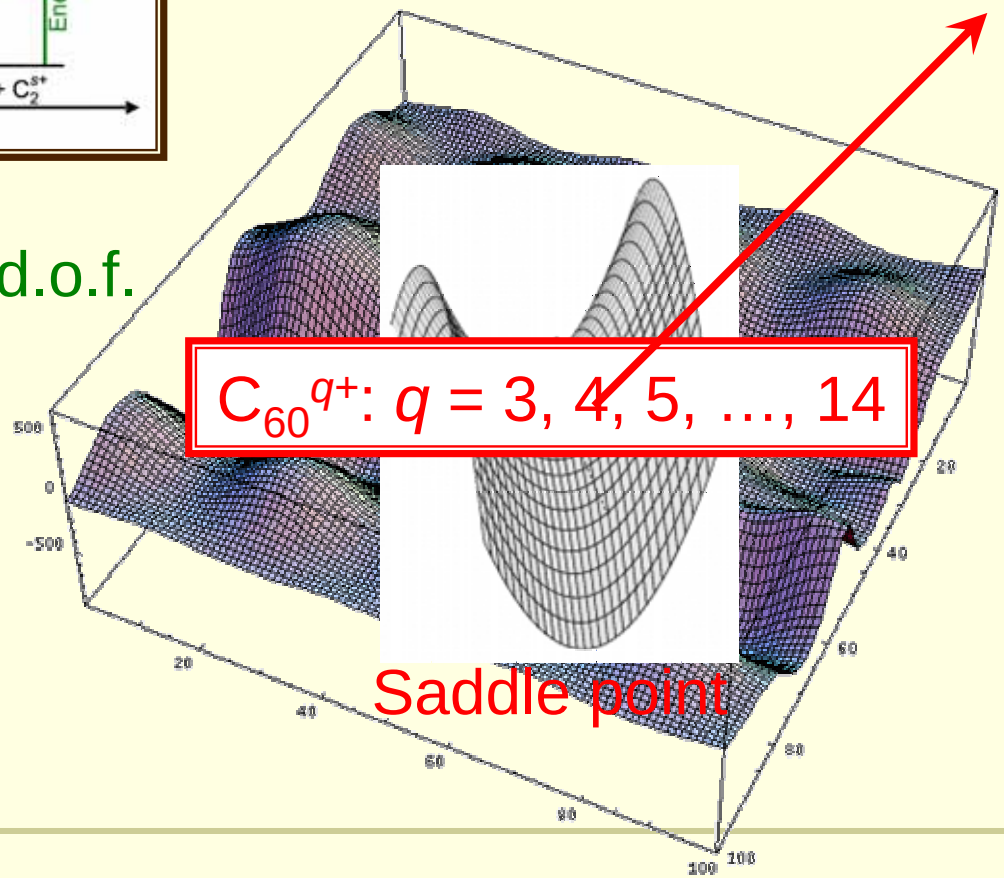


H. Zettergren *et al.*, *in preparation*

Fission barriers: PES



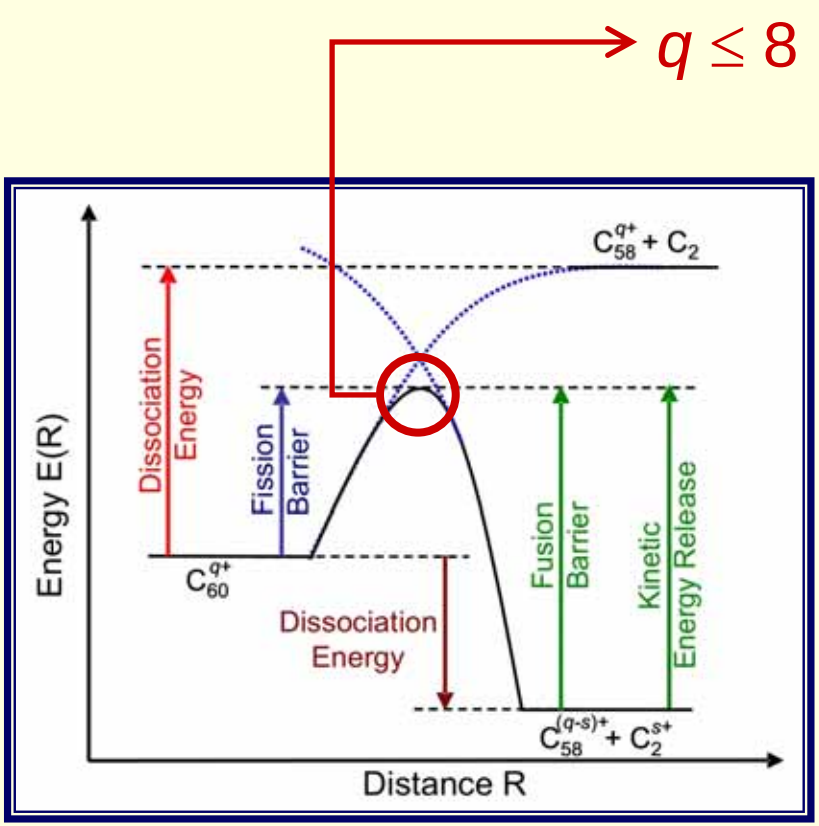
PES: 174 nuclear d.o.f.

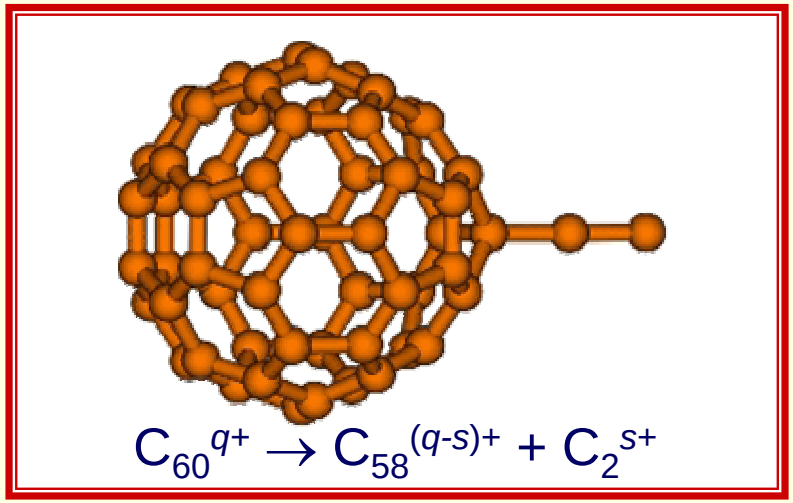


C_{60}^{q+}: q = 3, 4, 5, …, 14

Saddle point

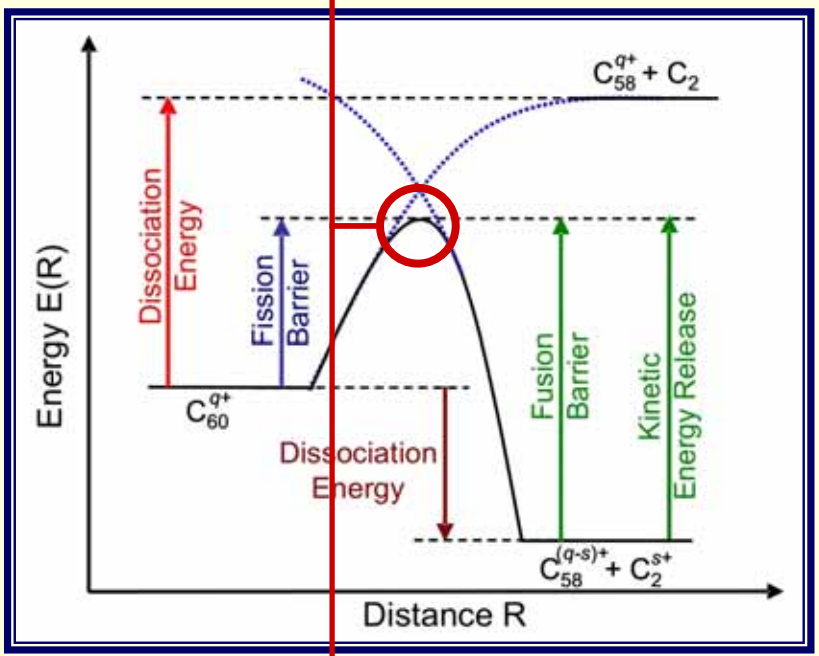
Fission barriers: Transition states

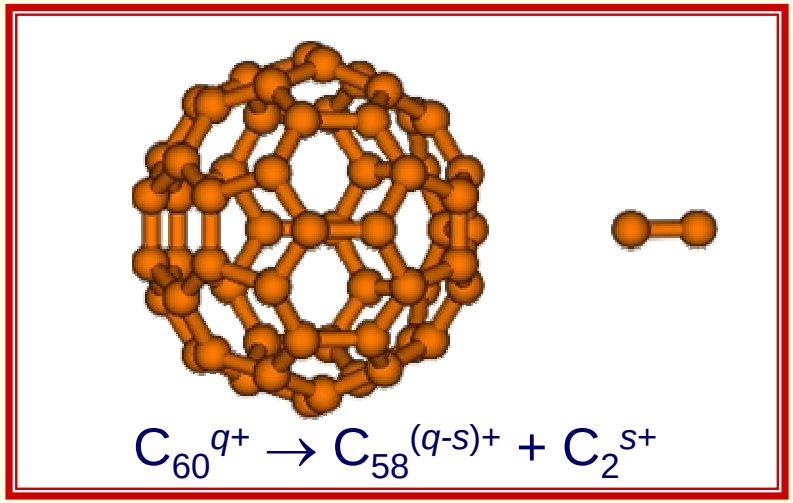


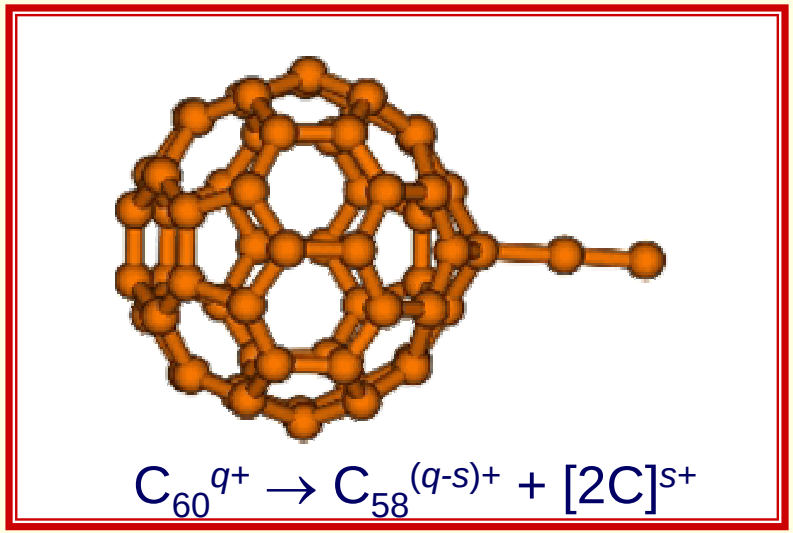


S. Díaz-Tendero *et al.*, *Phys. Rev. Lett.*, **95**, 013401 (2005)
S. Díaz-Tendero *et al.*, *J. Chem. Phys*, **123**, 184306 (2005)

Fission barriers: Transition states







S. Díaz-Tendero *et al.*, *Phys. Rev. Lett.*, **95**, 013401 (2005)
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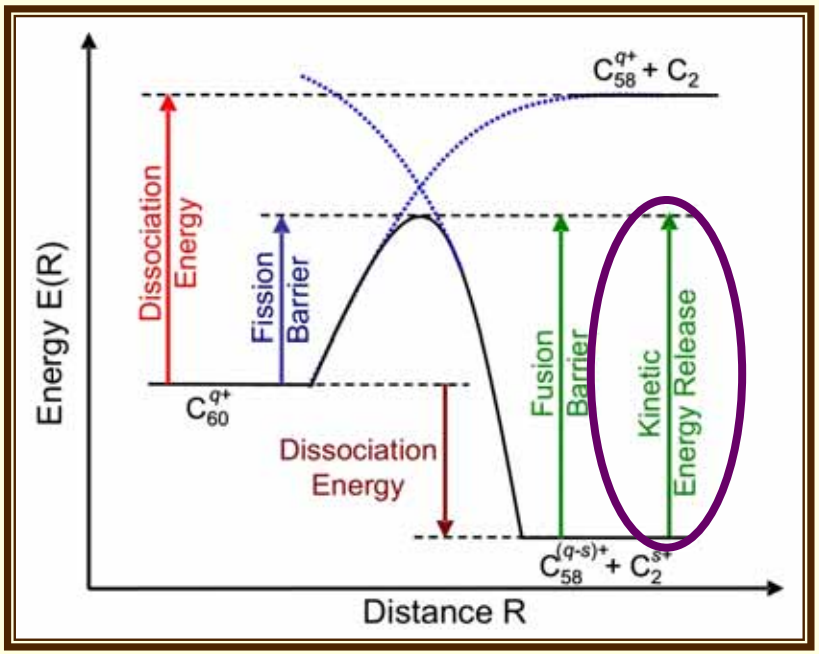
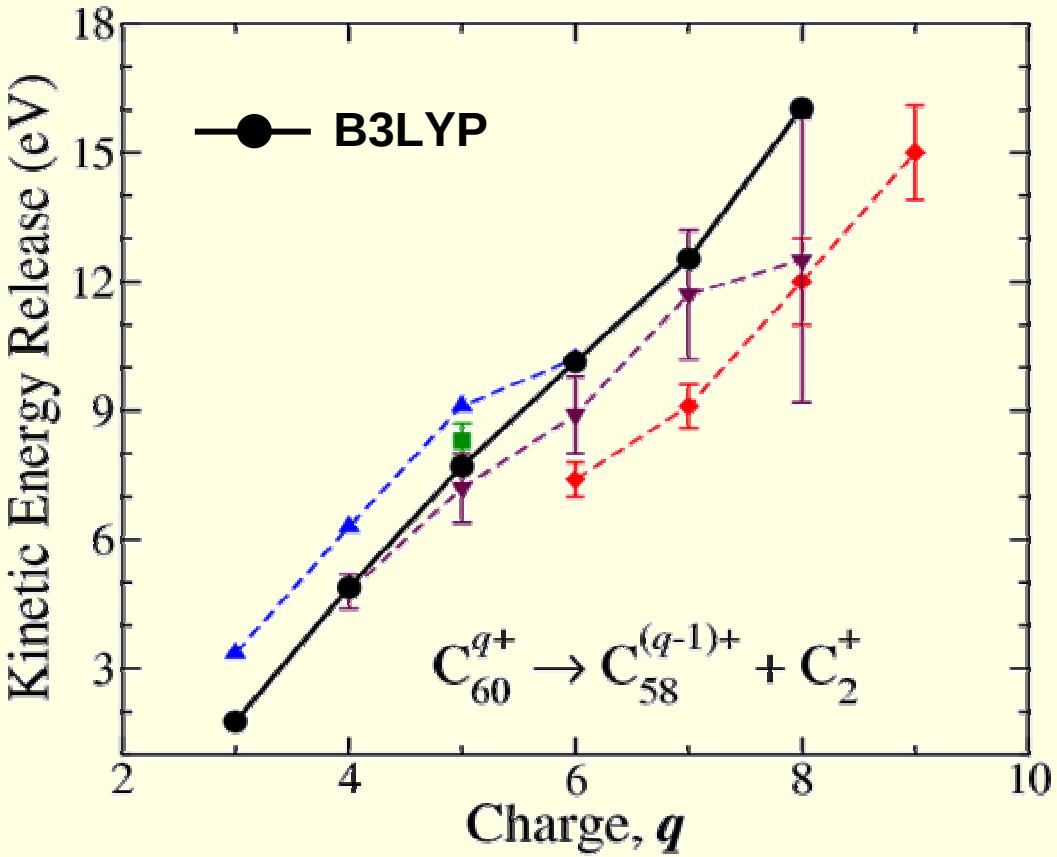
Fission barriers: KER





H. Cederquist et. Al, Phys. Rev. A. **67**, 062719 (2003)

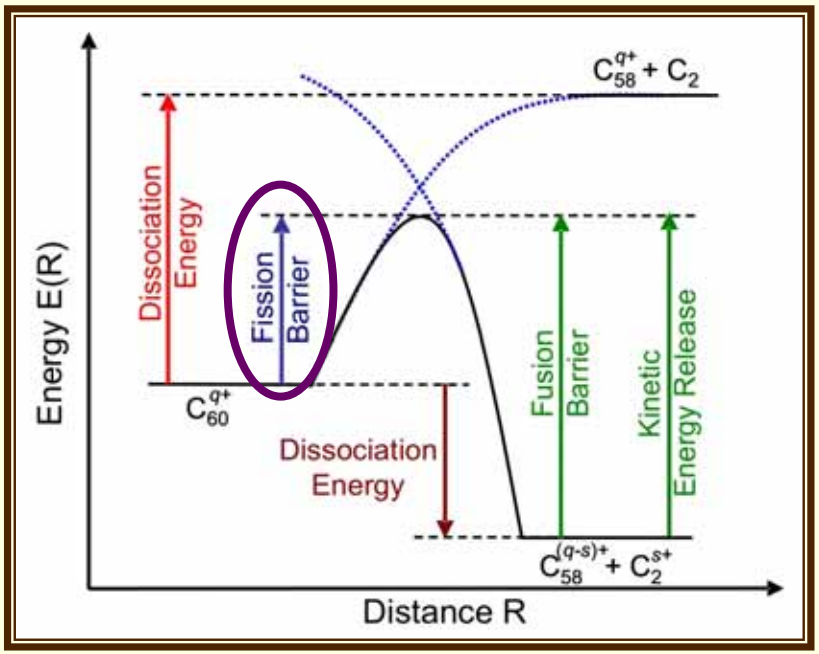
G. Seen *et al.*, J. Chem. Phys. **108**, 990 (1998)

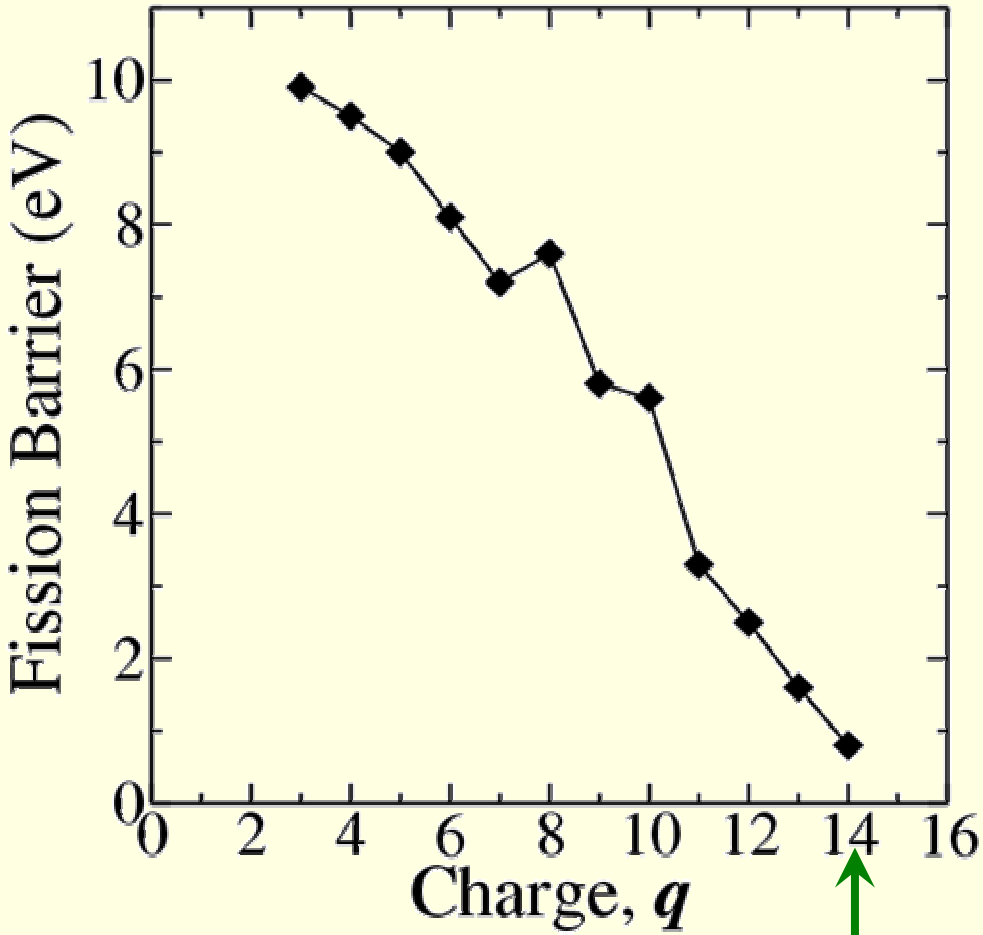
L. Chen *et al.* Phys. Scr. **T92**, 138 (2001)

S. Tomita *et al.*, Phys. Rev. A, **67**, 063204 (2003)

S. Díaz-Tendero *et al.*, *Phys. Rev. Lett.*, **95**, 013401 (2005)
S. Díaz-Tendero *et al.*, *J. Chem. Phys*, **123**, 184306 (2005)

Fission barriers: Coulomb limit



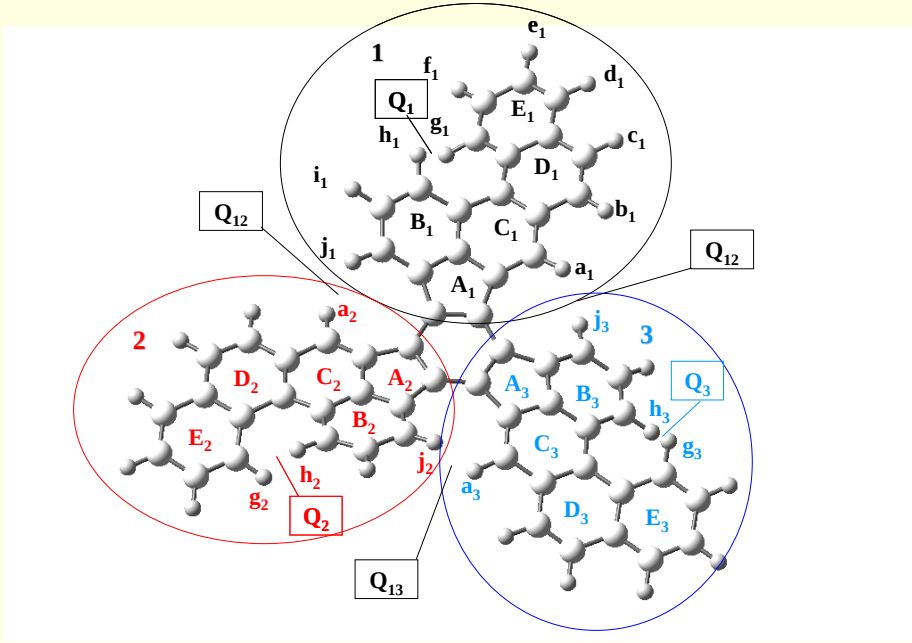


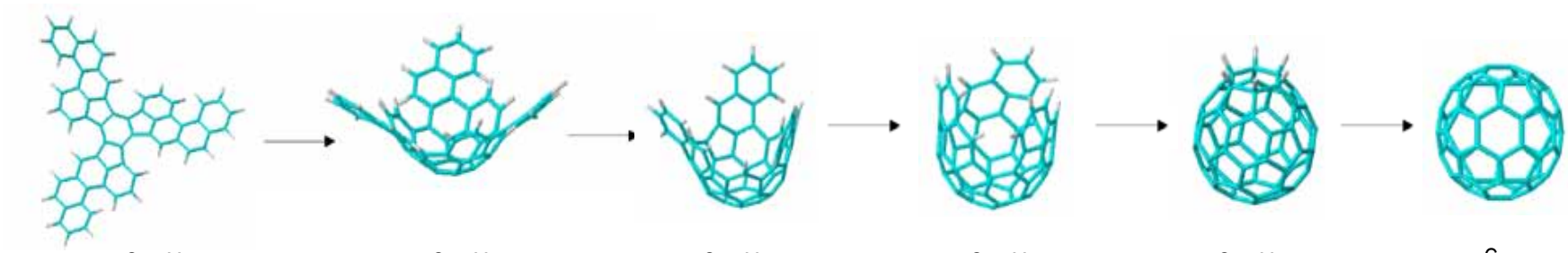
Coulomb stability limit: q =14

S. Díaz-Tendero *et al.*, *Phys. Rev. Lett.*, **95**, 013401 (2005)
S. Díaz-Tendero *et al.*, *J. Chem. Phys*, **123**, 184306 (2005)

Rational synthesis of fullerenes

$C_{60}H_{30}$ is a precursor of C_{60}





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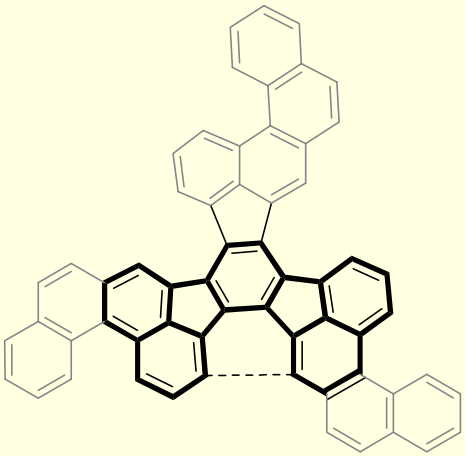
Rational synthesis of fullerenes

Dehydrogenation models



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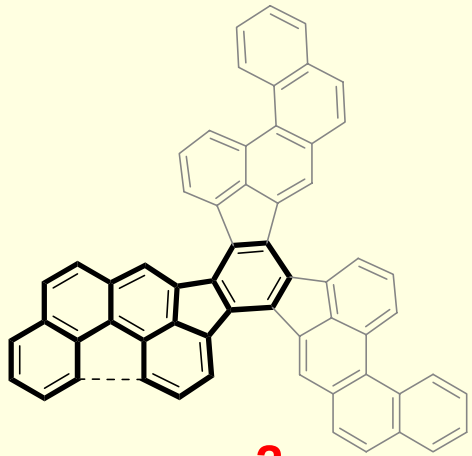

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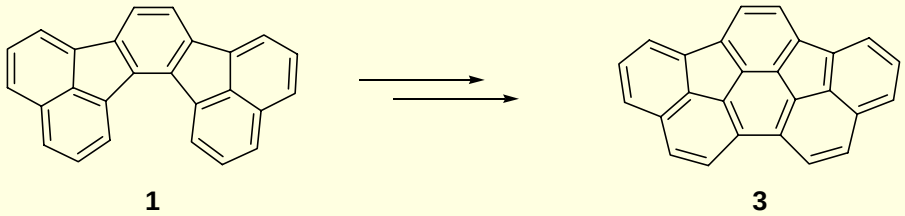
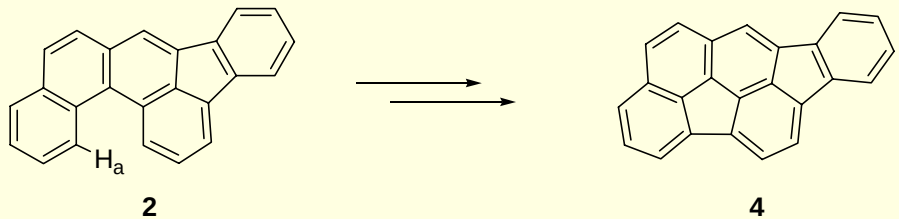
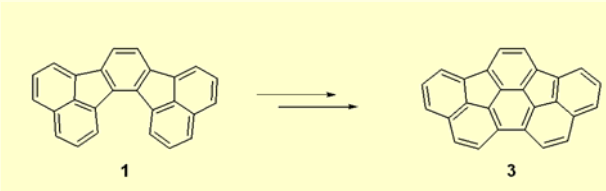
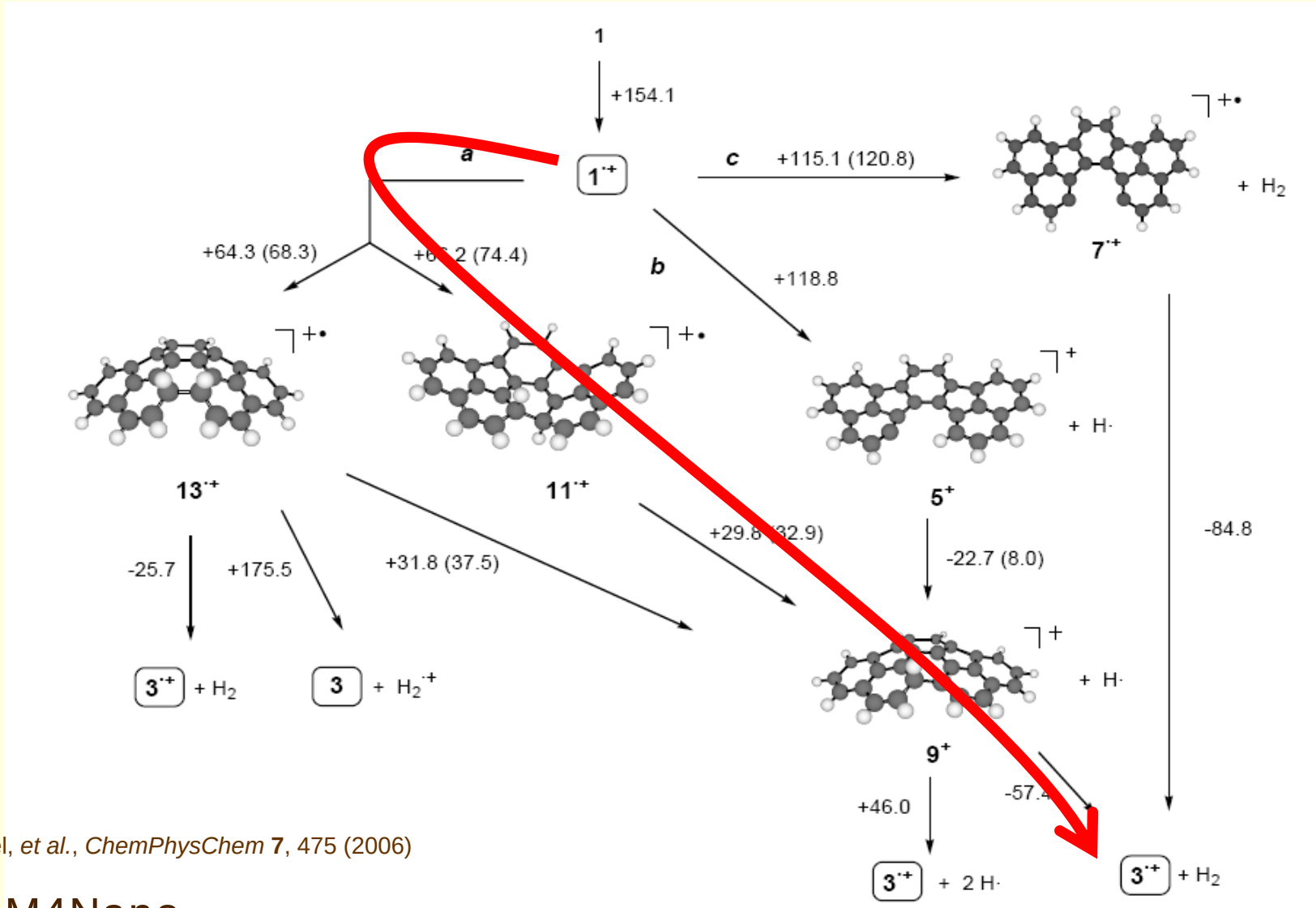
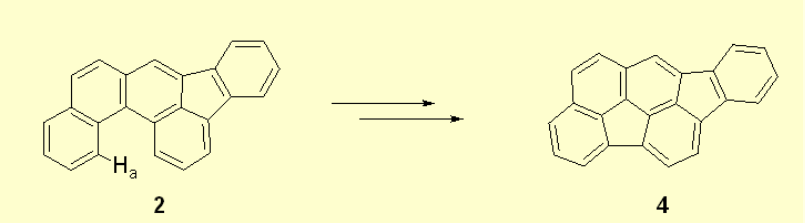


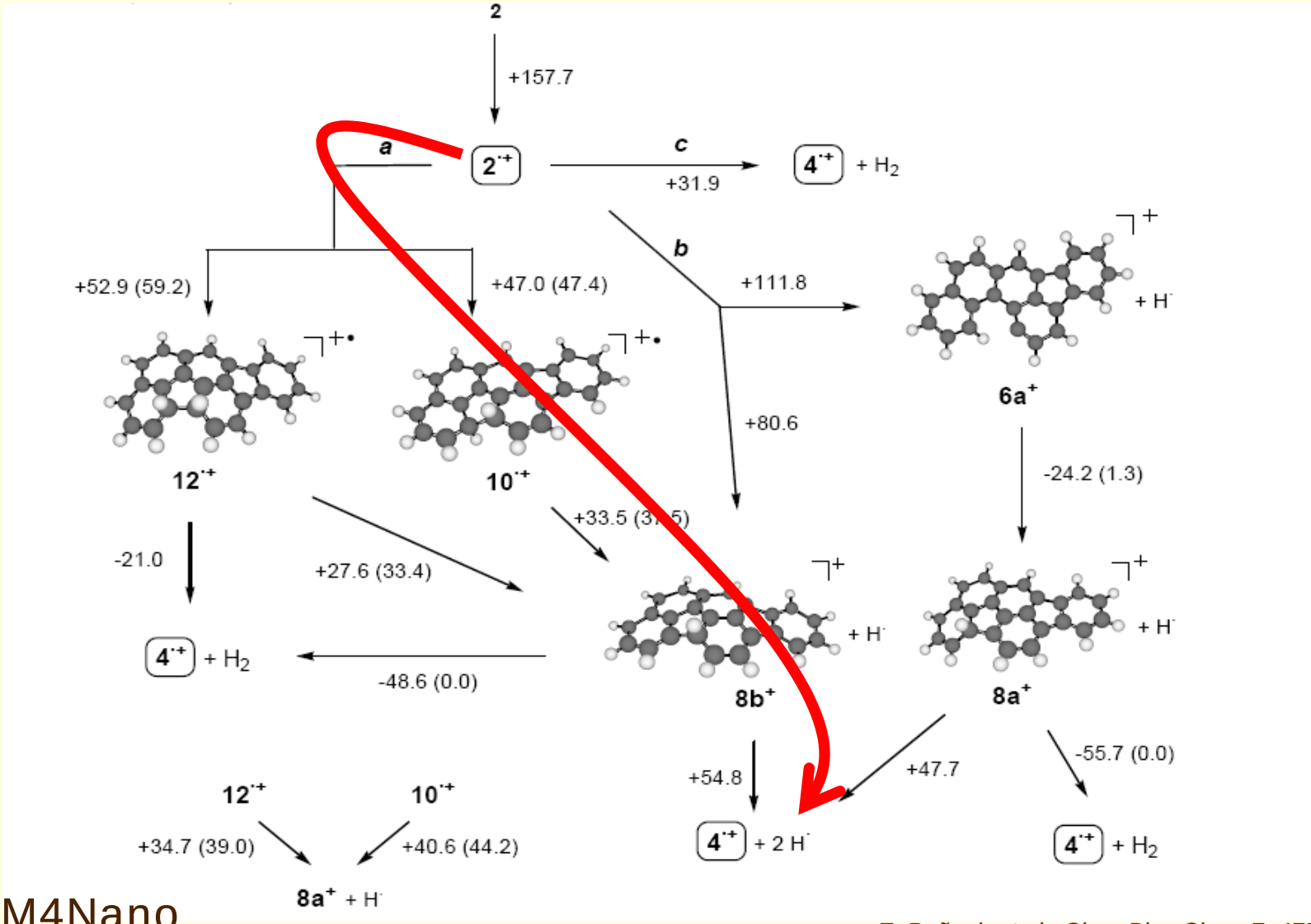






E. Buñuel, *et al.*, *ChemPhysChem* **7**, 475 (2006)





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E. Buñuel, *et al.*, *ChemPhysChem* **7**, 475 (2006)

Work in progress

-Deposition of fullerene derivatives on surfaces

-Structure and fragmentation of C_{70}^{q+} (q = 0,14) and C_{70} derivatives

-Clusters of clusters (fullerenes)

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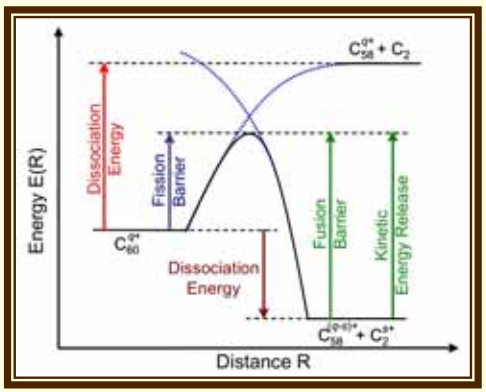
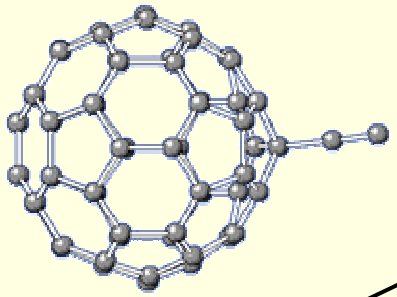
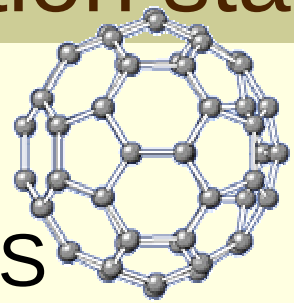
Departamento de Química, C-9

Fission barriers: Transition states





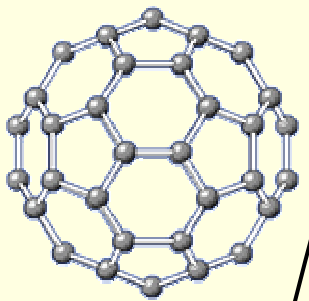


TS

MIN

ΔE_2

$q = 0$ R. L. Murry et al. Nature **366**, 665 (1993)



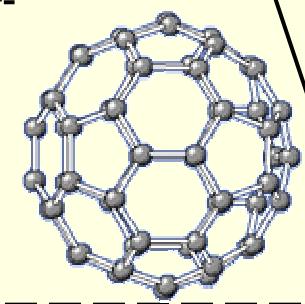
ΔE_1

Fission Barrier

Kinetic Energy Release

C_{60}^{q+}

Dissociation Energy



$C_{58}^{(q-s)+} + C_2^{s+}$

S. Díaz-Tendero *et al.*, *Phys. Rev. Lett.*, **95**, 013401 (2005)
S. Díaz-Tendero *et al.*, *J. Chem. Phys*, (in press)

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