

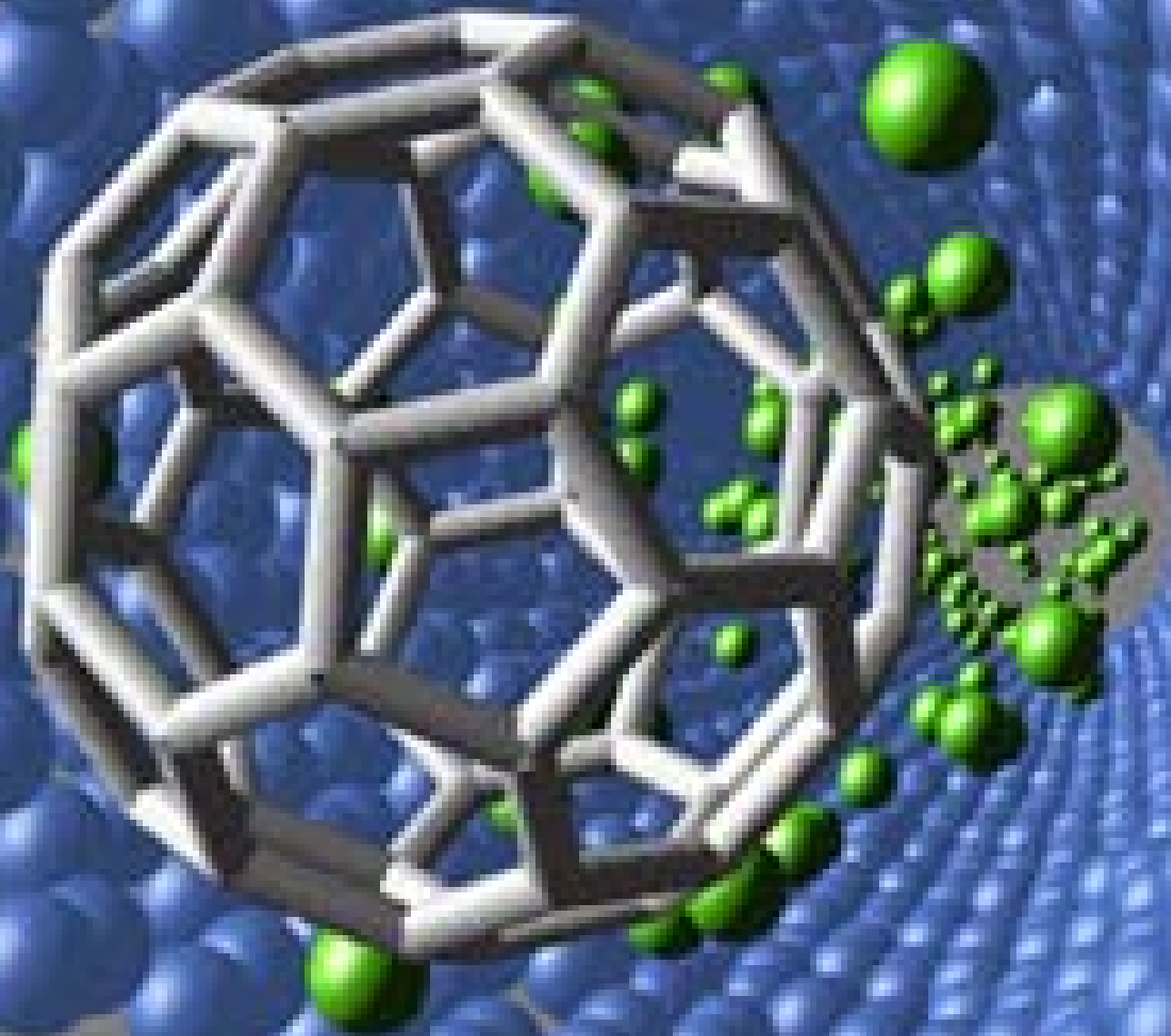
# The nano-science of C<sub>60</sub> molecule



**E.F.Sheka**

Russian Peoples' Friendship  
University, Moscow  
[sheka@icp.ac.ru](mailto:sheka@icp.ac.ru)

# Towards the fullerene $C_{60}$ chemical activity



# The nano-science of C<sub>60</sub> molecule

*E.F.Sheka*

Russian Peoples Friendship University, Moscow

[sheka@icp.ac.ru](mailto:sheka@icp.ac.ru)

One important area of research in nano-science and nano-technology is carbon-based physics in the form of fullerene physics. The paper is stimulated by fascinating medical applications of the fullerene C<sub>60</sub> and its derivatives. A high efficacy of the free-radical-driven biological processes regulation becomes a basis of the molecule action. What is the origin of the phenomenon? Which properties of the molecule can be responsible for the action? The paper presents a new concept on electronic structure of the molecule, which can assist in looking for the answer to the question. That addresses to the problem considering particular features of the molecule odd electron behavior, the number of which is determined by the difference between the numbers related to valence electrons and to atoms bonded with the considered one. A particular chemical activity of the molecule atoms is suggested to be based on the following.

**A particular chemical activity of the molecule atoms is suggested to be based on the following.**

Weakening the interaction between odd electrons of the C<sub>60</sub> molecule (in comparison with that of, say, aromatic molecules) causes a partial excluding of the latter from covalent bonding. Thus released electron density forms  $N_D$  effectively non-paired electrons, which are distributed over the molecule atoms with the relevant partial contribution  $N_{DA}$  of each. The  $N_D$  and  $N_{DA}$  values can be explicitly calculated in the UHF SCF HF approximation [1- 2]. The calculations in the paper have been performed by using semi-empirical AM1 version of the NDDO approximation following the relevant expressions for the above values [2,3]

$$N_{DA} = \sum_{i \in A} \sum_{B=1}^{NAT} \sum_{j \in B} D_{ij}, \quad N_D = \sum_A N_{DA} \quad N_D = \sum_{i,j=1}^{NORBS} D_{ij},$$

where  $D = (P^\alpha - P^\beta)^2$ . Elements of density matrix  $P_{ij}^{\alpha(\beta)}$  are expressed via eigenvectors of the UHF solution as  $P_{ij}^{\alpha(\beta)} = \sum_k^{N^{\alpha(\beta)}} C_{ik}^{\alpha(\beta)} * C_{jk}^{\alpha(\beta)}$ .

Here  $N_\alpha$  and  $N_\beta$  are the numbers of electrons with spin  $\alpha$  and  $\beta$ , respectively.

The availability of non-zero  $N_{DA}$  on the majority of the molecule atoms explains its high sensitivity to reactions with free radicals. Moreover, **the  $N_{DA}$  is considered to be a driving force of addition reactions selecting binding sites for sequential additions by the largest value of the quantity.**

The  $N_{DA}$  related to the singlet state of the molecule opens ordinary addition reactions such as hydrogenation and fluorination of the  $C_{60}$ . However, moderately low value of the ionization potential and high electron affinity of the molecule promote effective donor-acceptor interaction with other molecules. The  $N_{DA}$  provided by odd electrons in the doublet state of the molecular ion  $C_{60}^-$  governs its atoms activity at starting point in this case.

Following the  $N_{DA}$  values at each sequential step of the relevant addition reactions, a *computational synthesis* can be performed. Two examples related to the  $C_{60}F_x$  family as well as to a six-star pyrrolidone- $C_{60}$  DA complex are considered. The obtained data have provided a convincing proof of the suggested approach and show the way how free radicals in a human body can interact with the fullerene molecule.

1. Staroverov V.N., Davidson E.R.// Chem.Phys.Lett. 2000. V.330. P.161..
2. Sheka E.F., Zayets V.A.// Zhurn.Fiz.Khimii (submitted).
3. Zayets V.A. CCLUSTER-Z1: Program of Quantum-Chemical Calculations in  $s,p$ -Basis. Institute of Surface Chemistry, Nat.Ac. of Ukraine, Kiev. 1990.



# UHF SCF HF approach



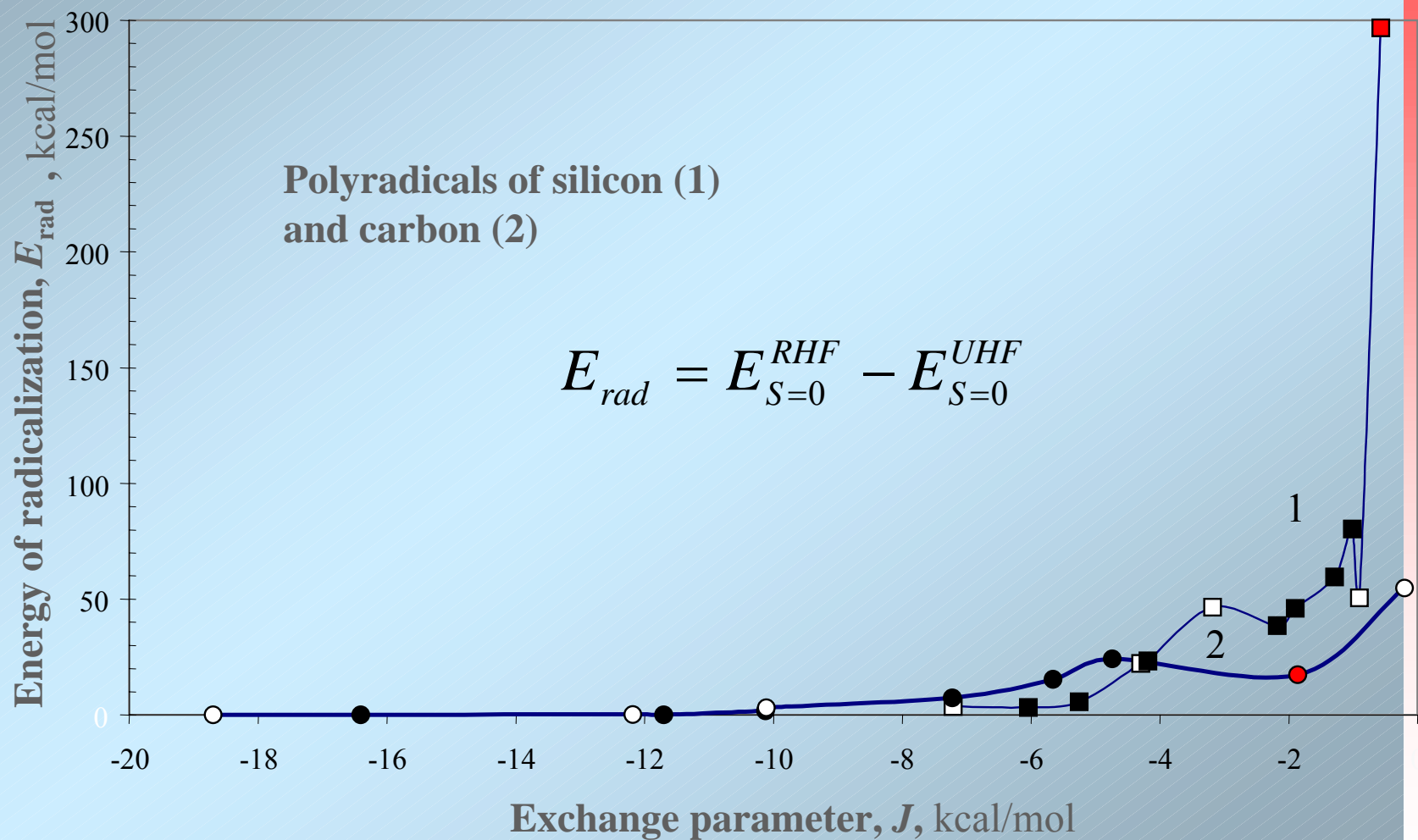
## Characteristics of the molecule radicalization:

- non-zero energy of radicalization  $E_{rad} = E_{S=0}^{RHF} - E_{S=0}^{UHF}$
- non-zero  $\langle S^2 \rangle^{UHF} = 1/4(N_\alpha - N_\beta)^2 + 1/2|N_\alpha - N_\beta| - Sp(P^\alpha S P^\beta S)$
- non-zero spin density on the molecule atoms  $D_{sp,A} = \sum_{i \in A} P_{ii}^\alpha - P_{ii}^\beta$
- small exchange integral  $J = \frac{E_{AF}^{UHF} - E_F^{UHF}}{S_{\max}^2}$
- effectively non-paired electrons  $N_D = \sum_{i,j=1}^{NORBS} D_{ij},$
- partial contribution of effectively non-paired electrons on atom

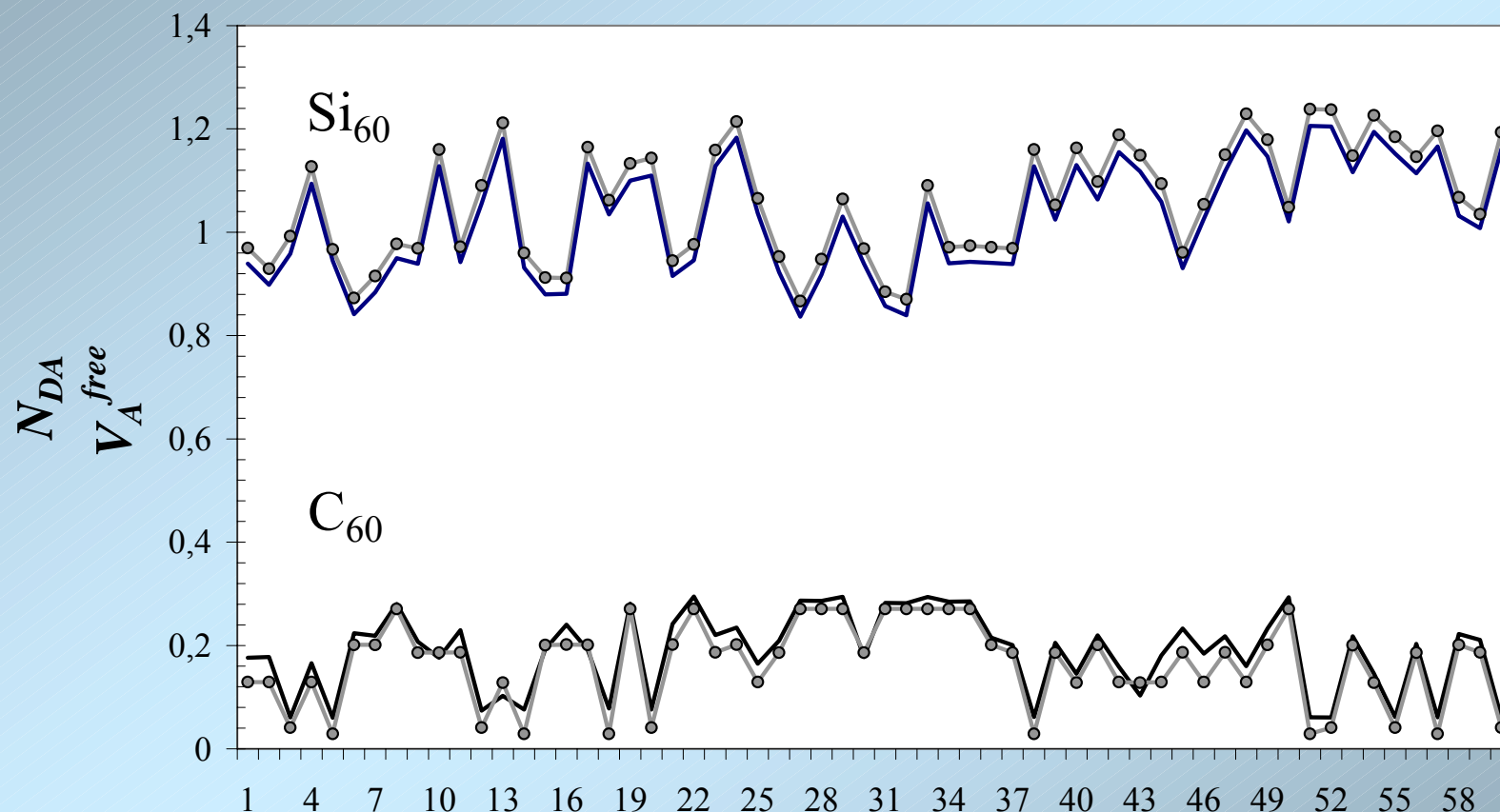
$$N_{DA} = \sum_{i \in A} \sum_{B=1}^{NAT} \sum_{j \in B} D_{ij},$$

Sheka E.F.// CEJP, 2004. V. 2. P.160.

Sheka E.F.//Int.Journ.Quant.Chem. 2004. V.100, No.4. P.375.



# Distribution of $N_{DA}$ (points) and free valence $V_A^{free}$ over atoms of the $C_{60}$ and $Si_{60}$ molecules

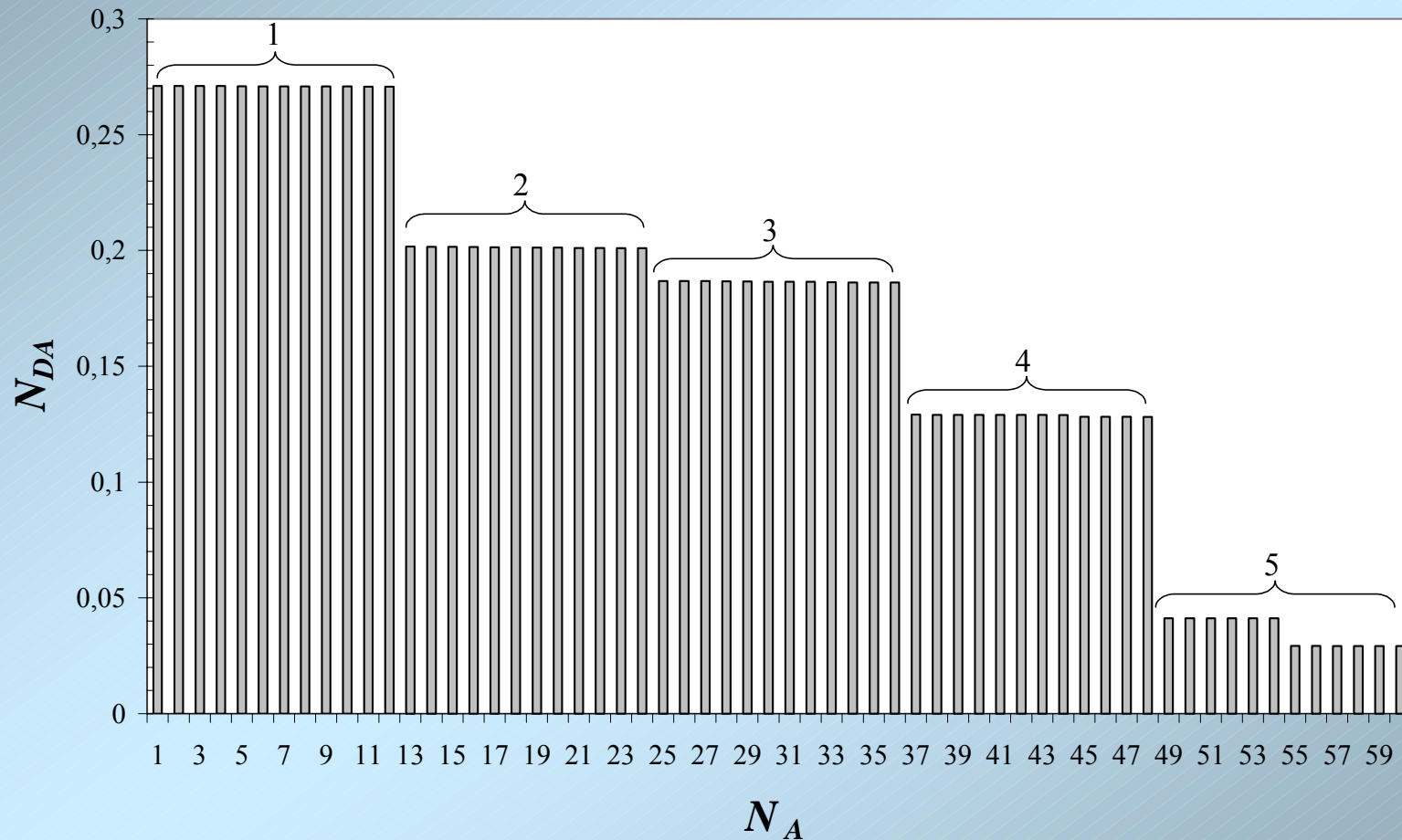


$$V_A^{free} = N_A^{val} - \sum_{B \neq A} K_{AB} N_A$$

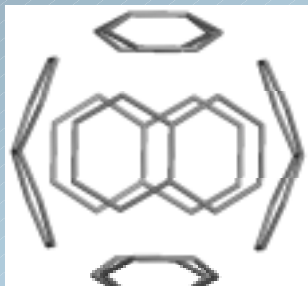
$K_{AB}$  are generalized Wiberg's coefficients



Ordered  $N_{DA}$  distribution over atoms of the  $C_{60}$  molecules:  
there are five groups of equivalent atoms

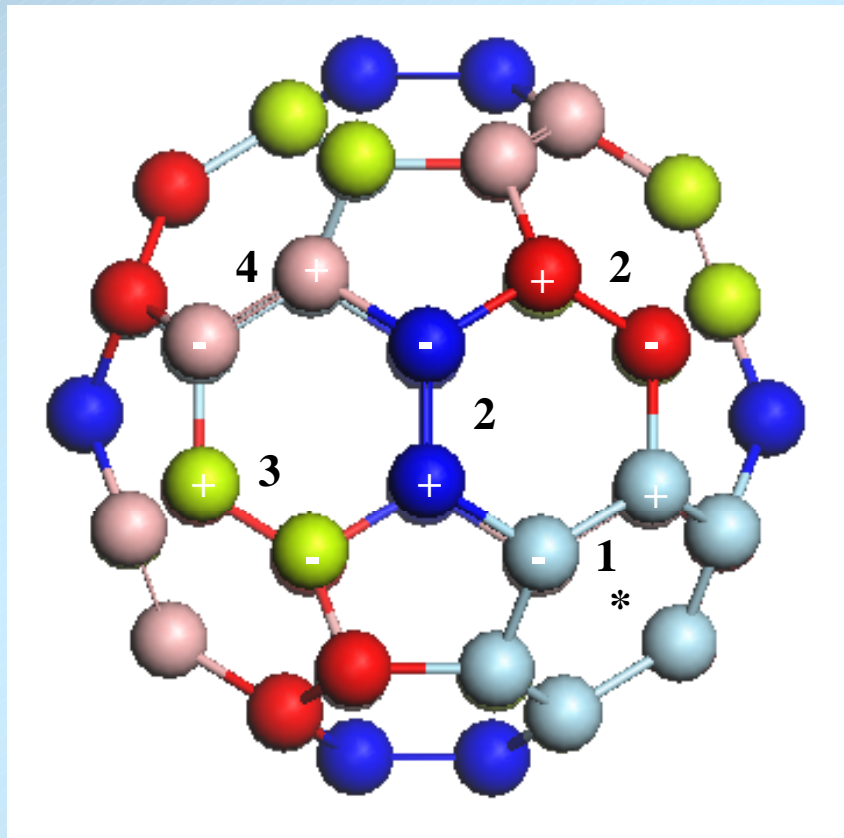
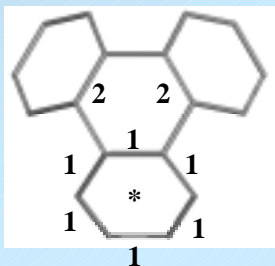


# “Chemical” portrait of the $C_{60}$ fullerene



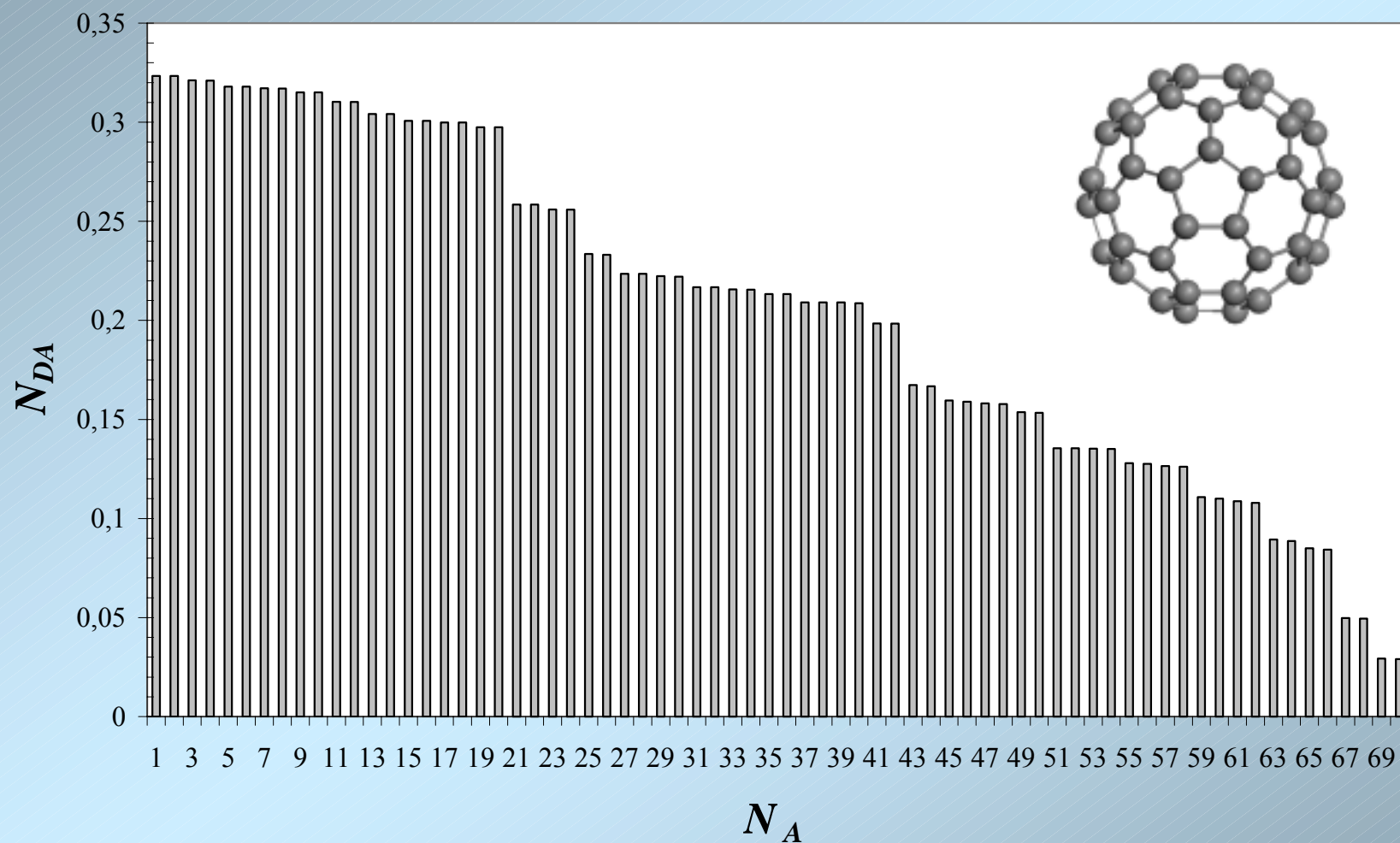
**6\* C<sub>10</sub> model**

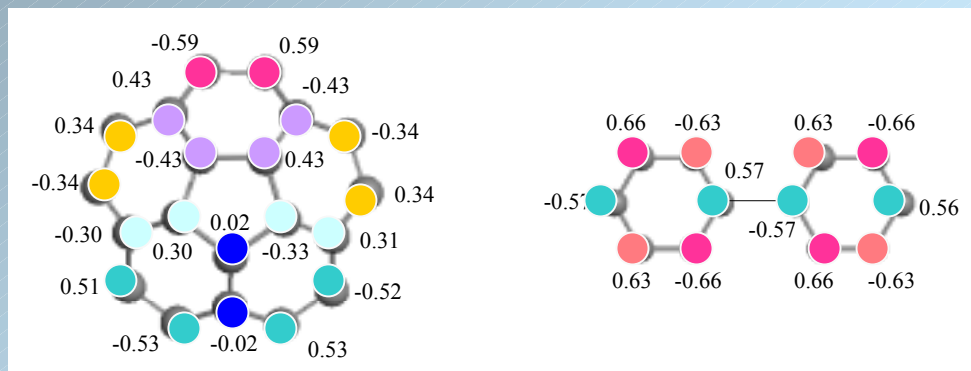
Bulychev@Udod, 1995



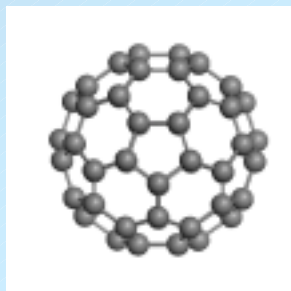
10 effectively non-paired electrons in total

# Ordered $N_{DA}$ distribution over atoms of the $C_{70}$ molecules

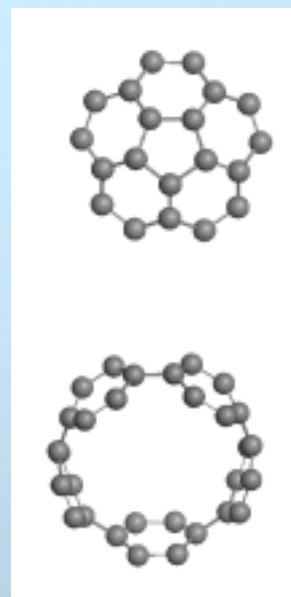




**“Chemical” mapping divides the fullerene C<sub>70</sub> into three five-hexagon-member fragments**



14 effectively non-paired electrons in total



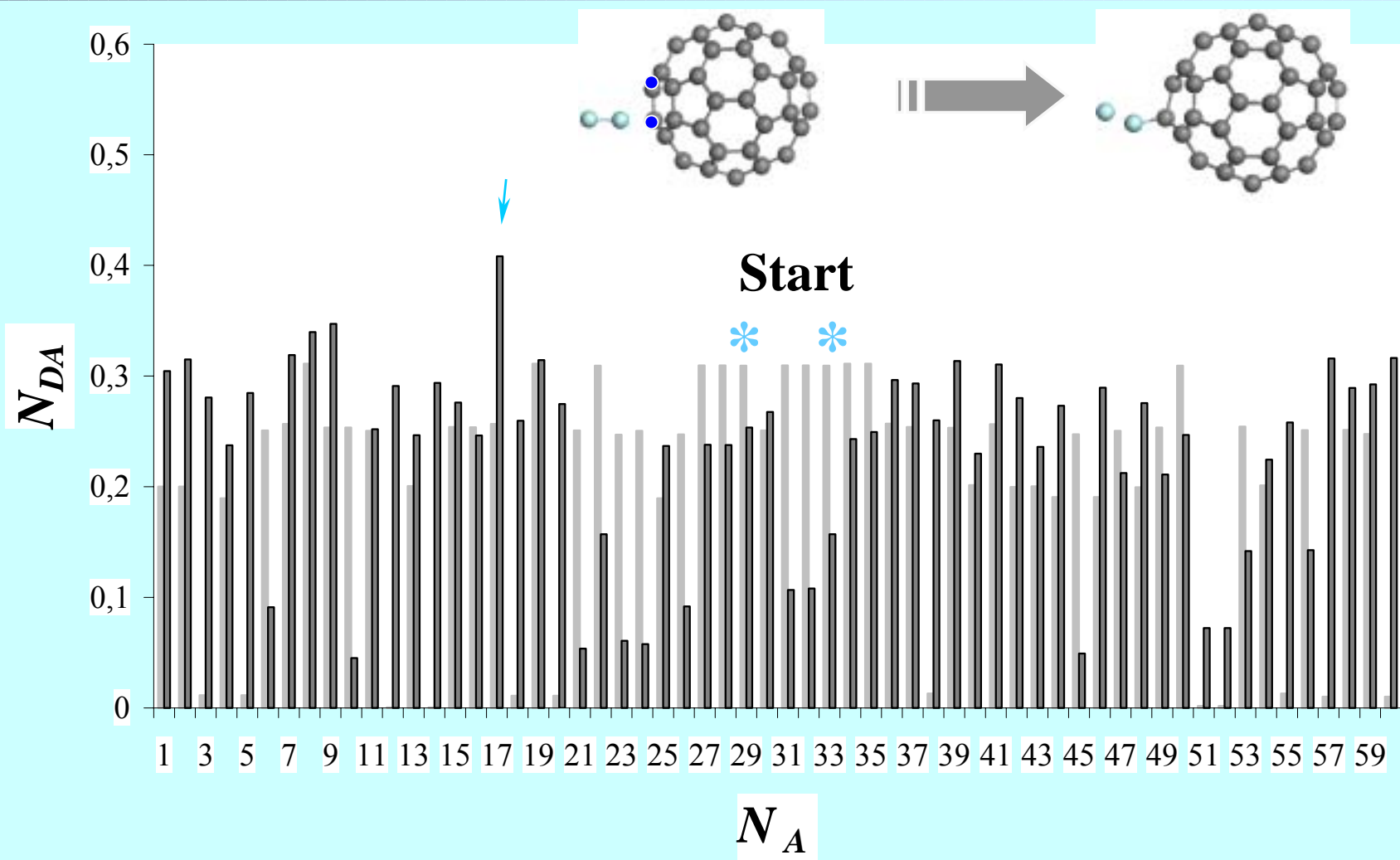
2 fragments of 5 conjugated hexagons

1 fragment of 5 disconjugated hexagons

# Controlled quantum-chemical synthesis

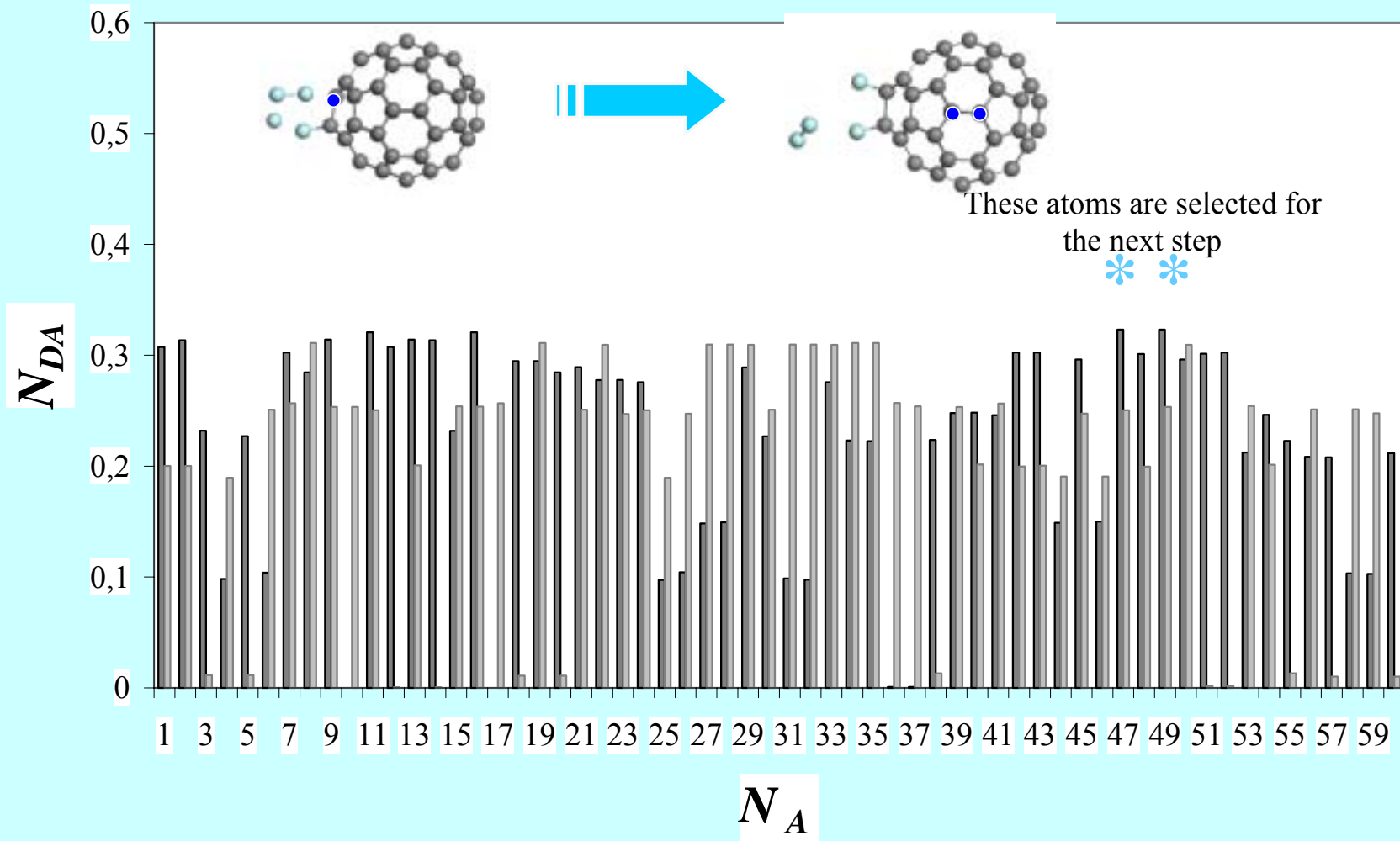
- fluorination @ hydrogenation
- amine derivatization
- polymeric stars formation

# Starting point of the $C_{60}$ fluorination



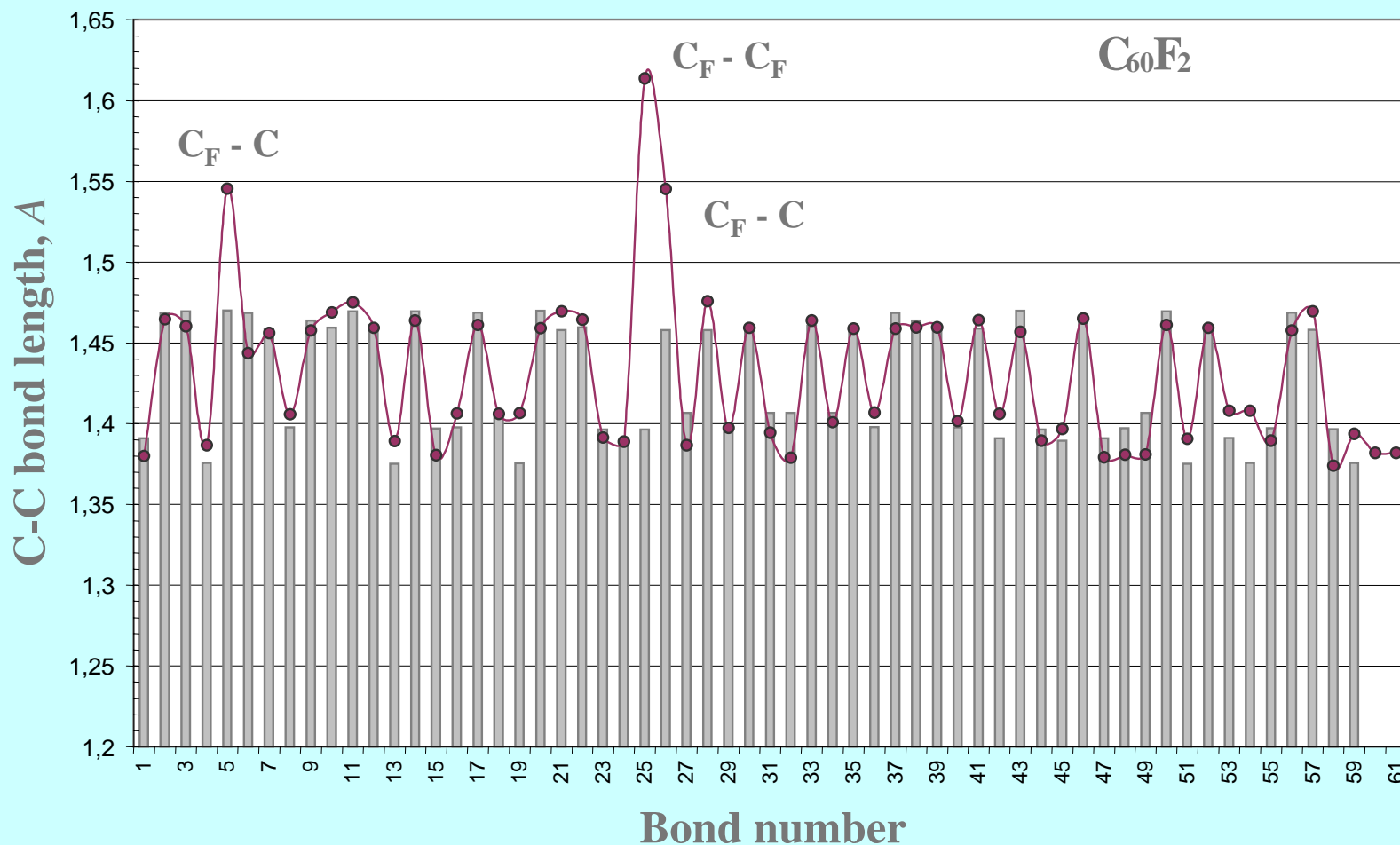


# Starting point of the C<sub>60</sub> fluorination

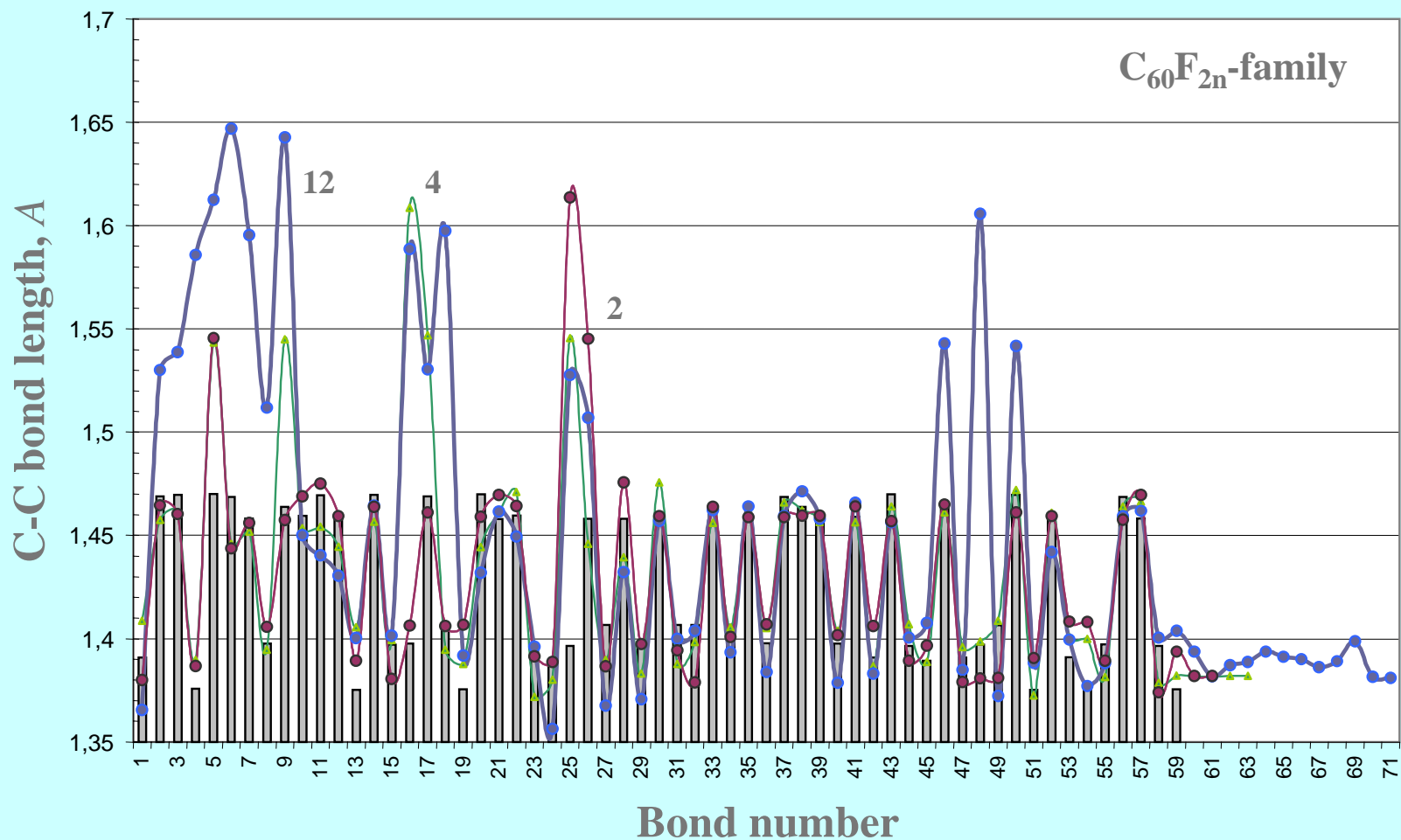


Dark-blue-marked atoms either are or must be attacked

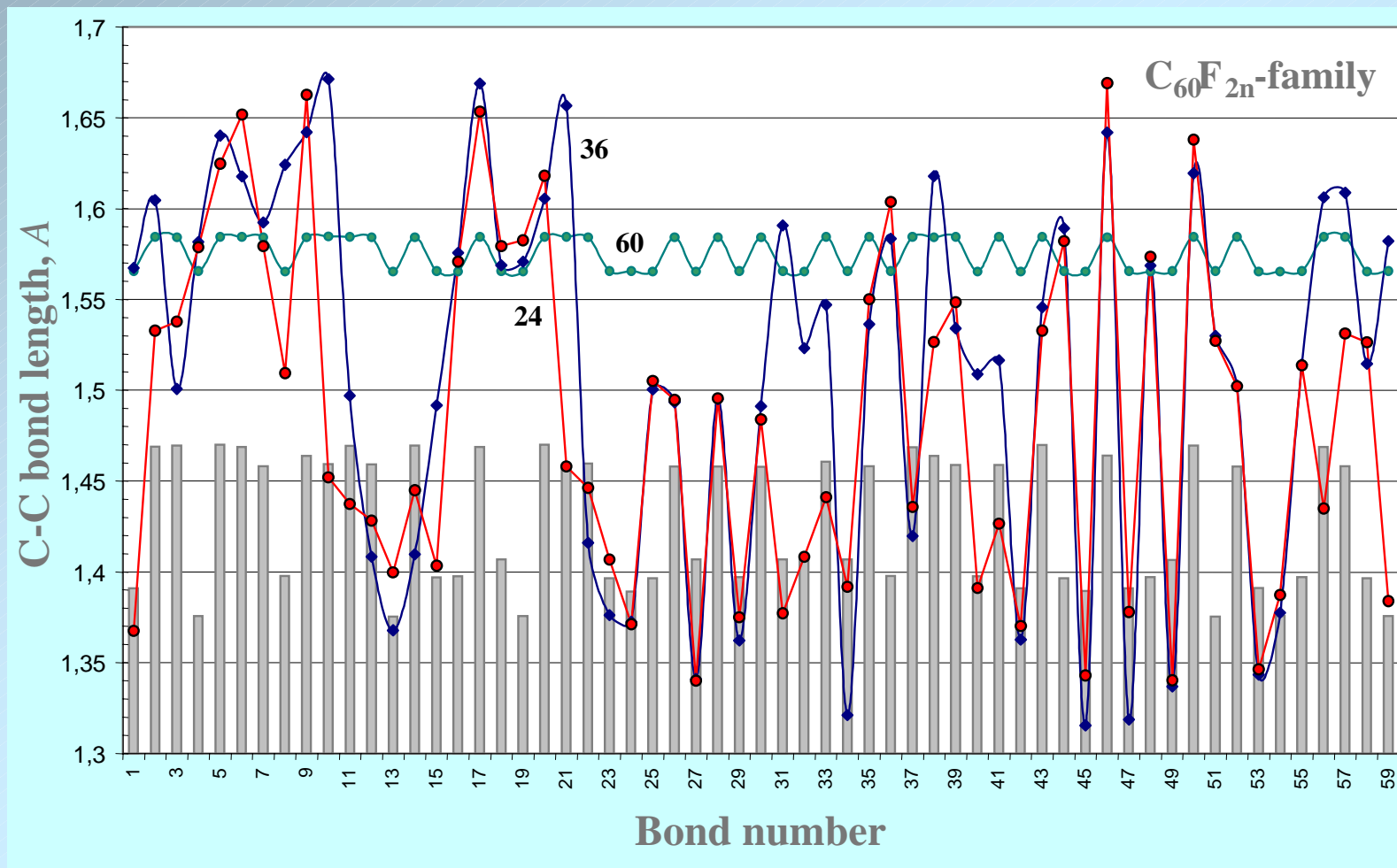
# Starting point of the $C_{60}$ fluorination: initial step of the molecule deformation



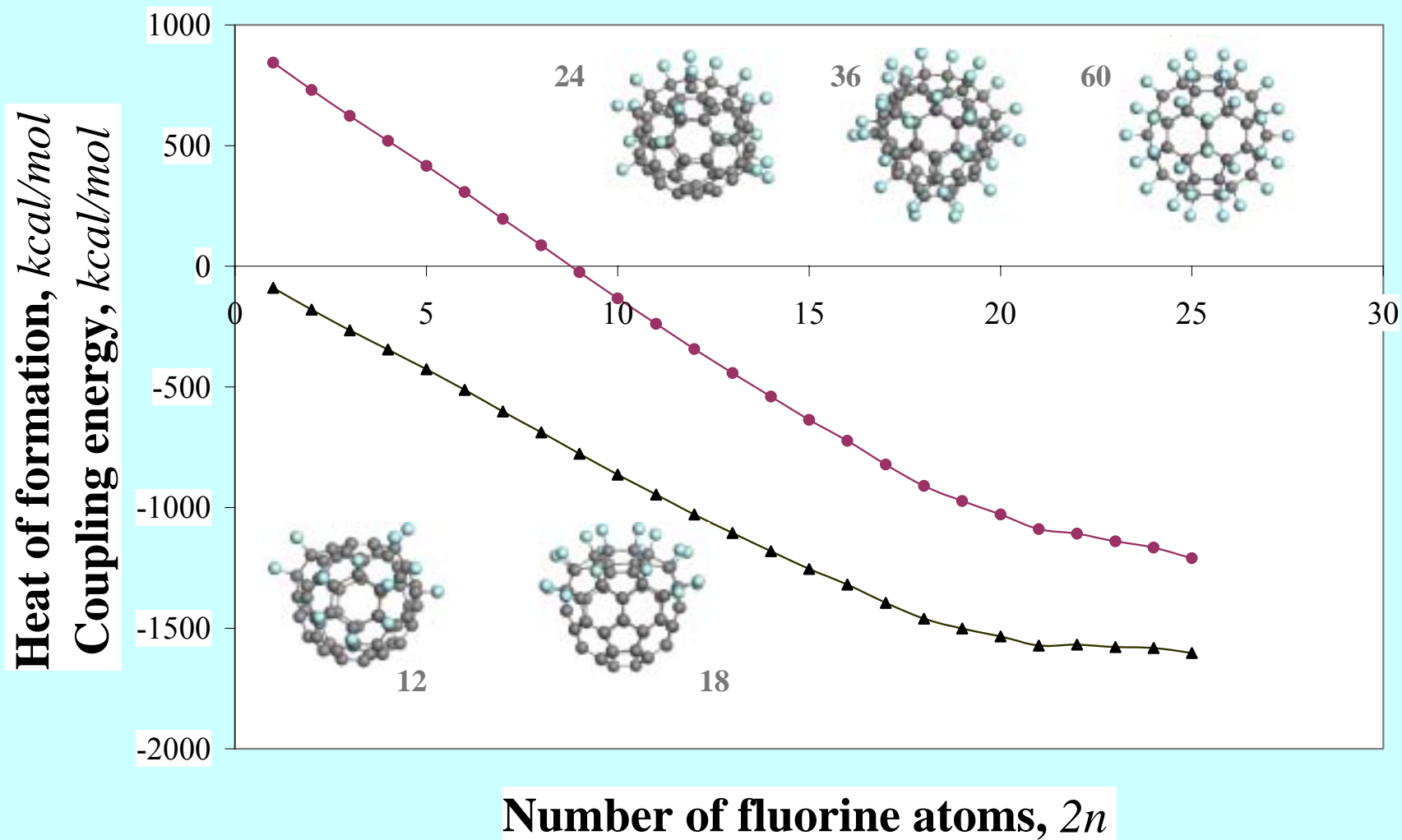
# Additive deformation of the molecule under fluorination



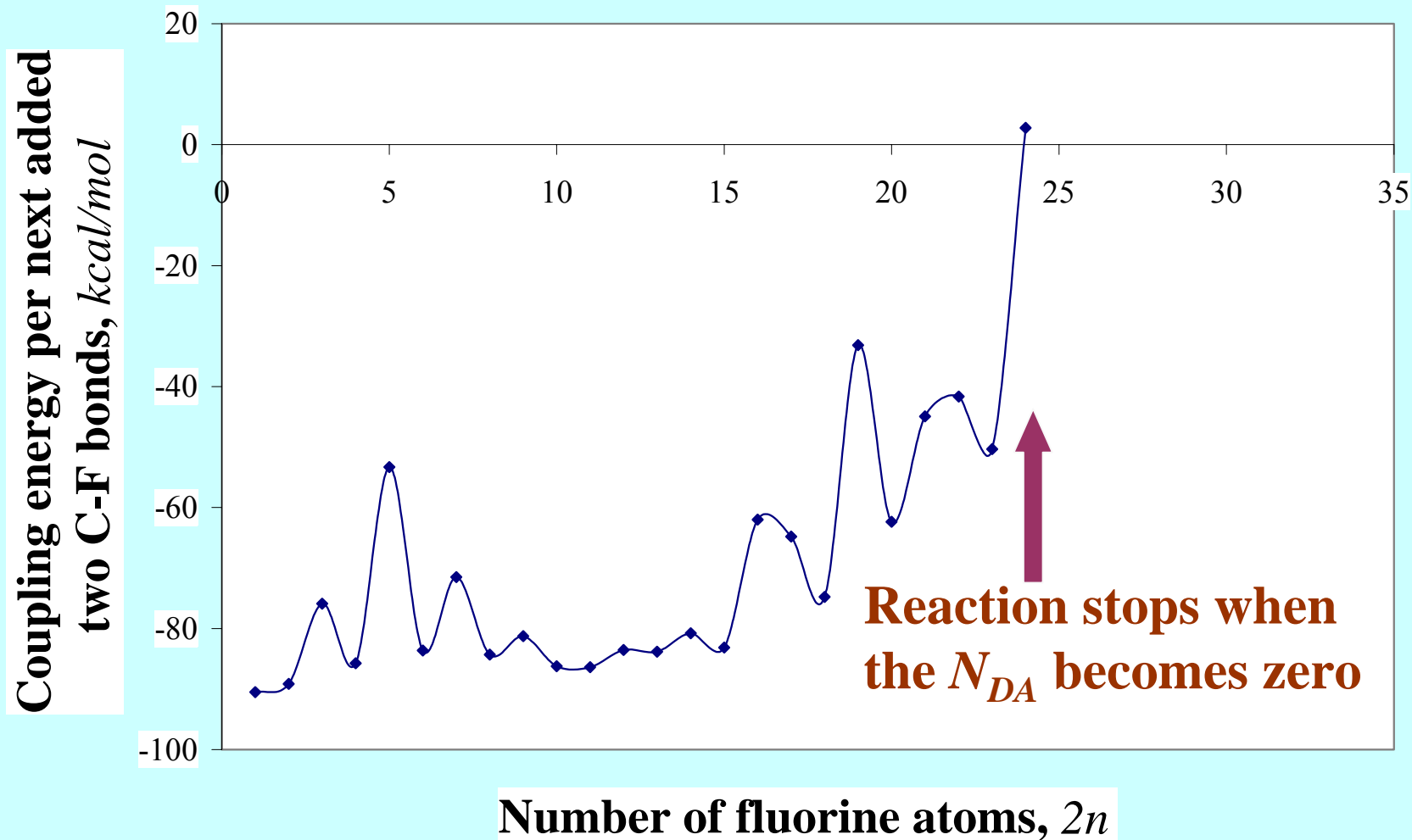
# Final stage of the molecule deformation under fluorination



# Energetics of the C<sub>60</sub> fluorination



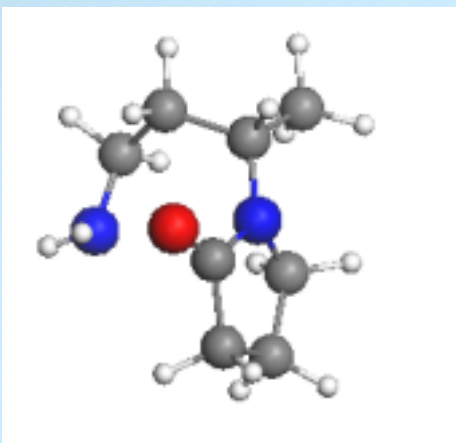
# Energetics of the C<sub>60</sub> fluorination





# Computational Synthesis of the Fullerene C<sub>60</sub> Star-Like Adducts with Primary Amines

- C<sub>60</sub> with poly (N-vinyl-pyrrolidone)
  - effective material for non-linear optics
  - consolidant of the long-term memory disturbance



The primary amine head of poly (N-vinyl-pyrrolidone)

# Formation of the $C_{60} - I_1$ adduct

Energy,  
kcal/mol

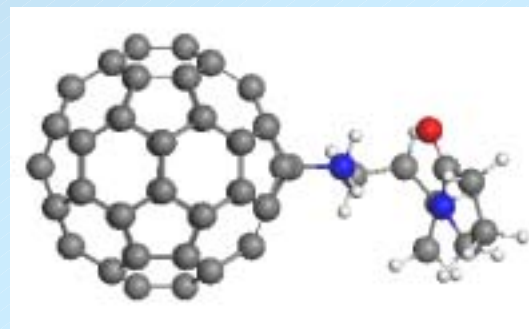
$E_{inf}(A+B^-)$

1013.05

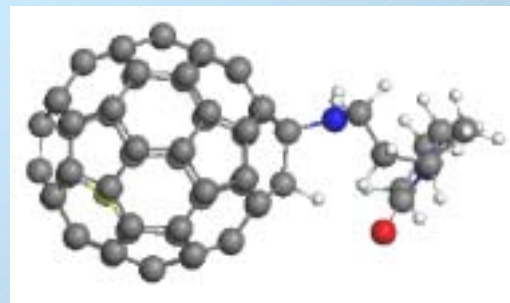
897.27

$n=1$

880.55

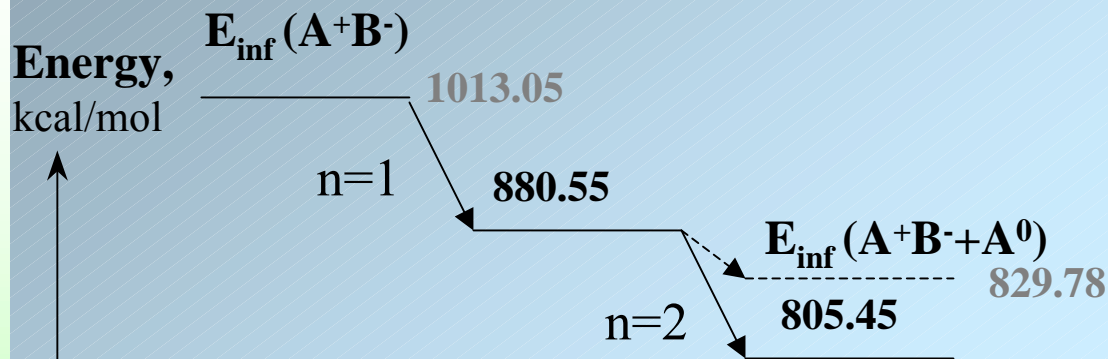


$$E_{coupl} = -115.78$$



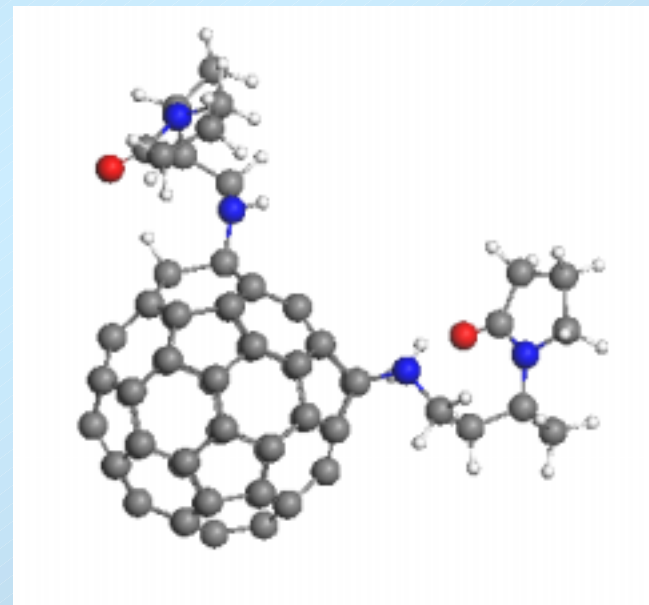
$$E_{coupl} = -132.50$$

# Formation of the $C_{60} - I_2$ adduct



**Formation of the  $C_{60} - I_2$  adduct is by 24.33 kcal/mol preferable over the  $C_{60} - I_1$  one.**

Binding sites are selected according to the RED diagram of the  $C_{60} - I_1$  adduct



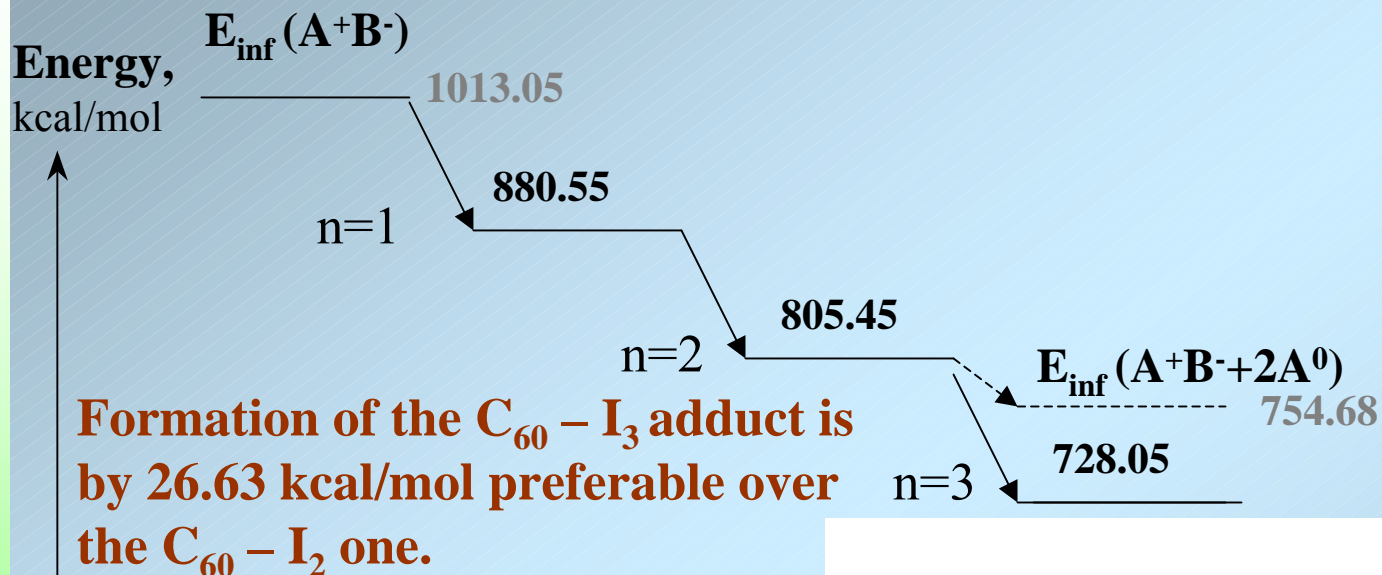
Preset numbers:

$$N_m - C_f \leq 1.40A$$

$$H_m - C_f \sim 1.08A$$

$$E_{coupl} = -156.83$$

# Formation of the $C_{60} - I_3$ adduct



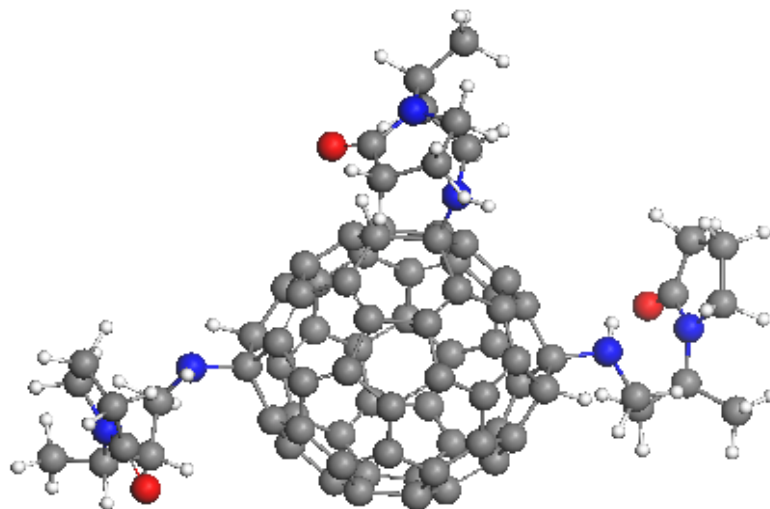
Binding sites are selected according to the RED diagram of the  $C_{60} - I_2$  adduct

Preset numbers:

$$N_m - C_f \leq 1.40 \text{ \AA}$$

$$H_m - C_f \sim 1.08 \text{ \AA}$$

$$E_{\text{coupl}} = -183.46$$



# Formation of the $C_{60} - I_4$ adduct

$E_{inf}(A+B^-)$

1013.05

n=1

880.55

n=2

805.45

n=3

728.05

n=4

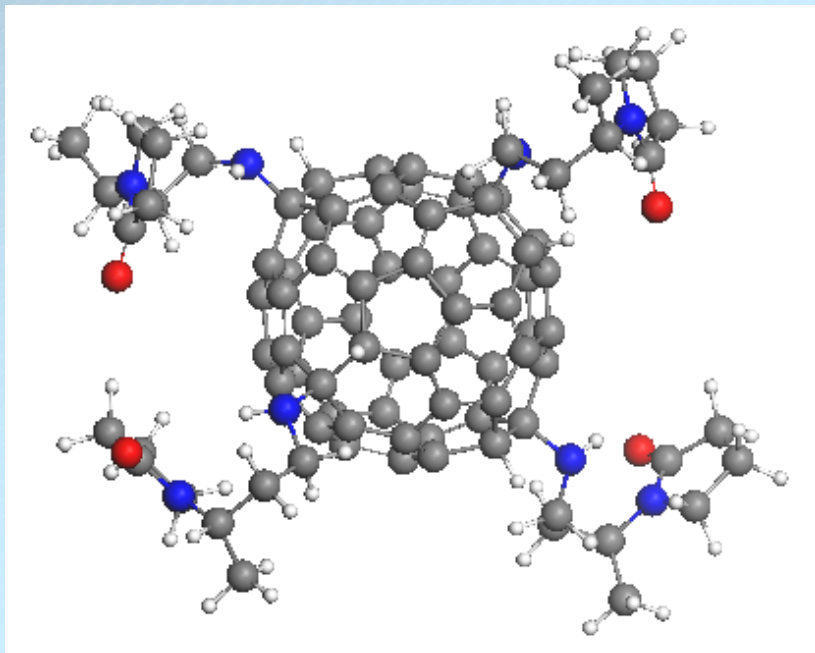
$E_{inf}(A+B^-+3A^0)$

677.28

657.84

Energy,  
kcal/mol

Formation of the  $C_{60} - I_4$  adduct is by 19.44 kcal/mol preferable over the  $C_{60} - I_3$  one.



Binding sites are selected according to the RED diagram of the  $C_{60} - I_3$  adduct

Preset numbers:

$$N_m - C_f \leq 1.40A$$

$$H_m - C_f \sim 1.08A$$

$$E_{coupl} = -203.86$$

# Formation of the $C_{60} - I_5$ adduct

$E_{inf}(A+B^-)$

1013.05

n=1

880.55

n=2

805.45

n=3

728.05

n=4

657.84

n=5

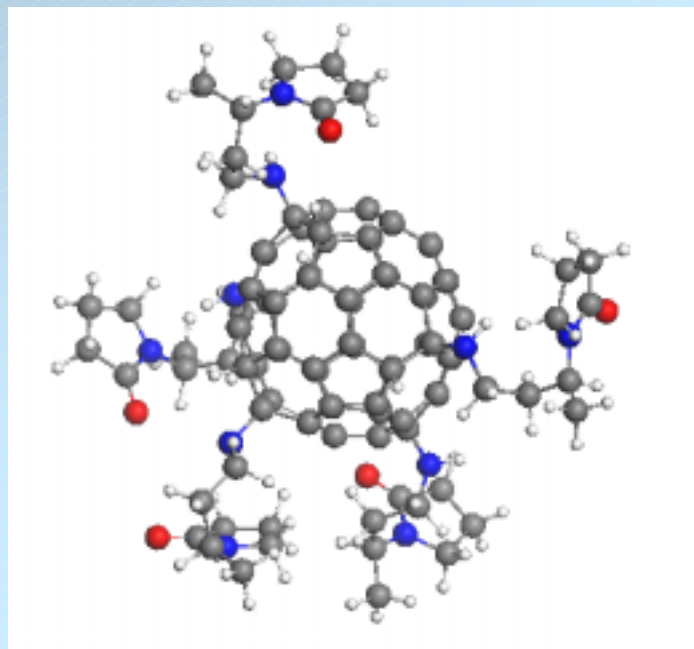
$E_{inf}(A+B^-+4A^0)$

607.07

583.23

Formation of the  $C_{60} - I_5$  adduct is by 23.84 kcal/mol preferable over the  $C_{60} - I_4$  one.

Binding sites are selected according to the RED diagram of the  $C_{60} - I_4$  adduct



Preset numbers:

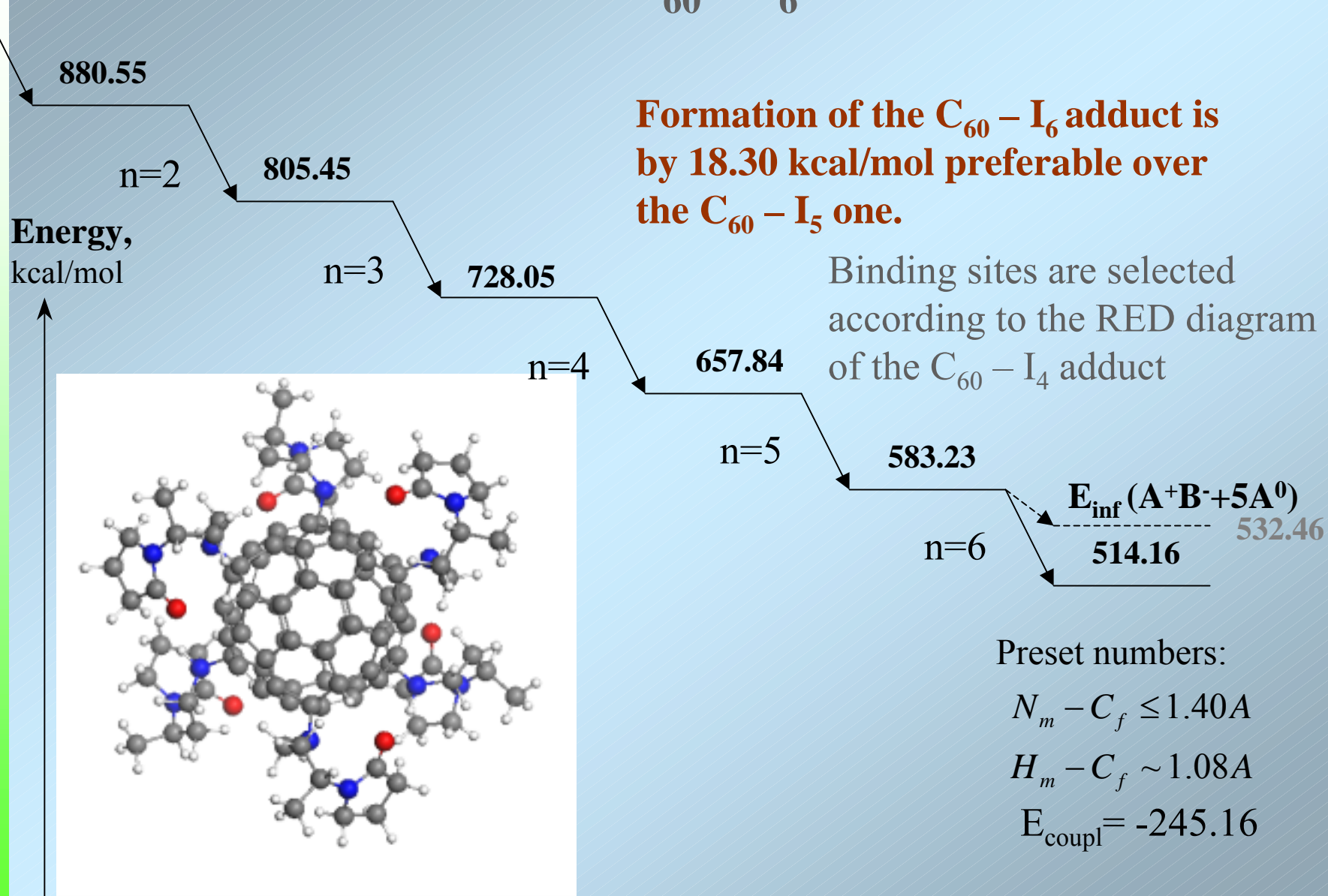
$$N_m - C_f \leq 1.40A$$

$$H_m - C_f \sim 1.08A$$

$$E_{coupl} = -224.86$$



# Formation of the $C_{60} - I_6$ adduct



**Reaction has stopped since the  $N_{DA}$  is zero for the sites that are sterically accessed**

*...Is noted that the more is the degree of fullerene molecule derivatization, the less is its antioxidation ability.*

Scientific report