Helium microsolvation of polycyclic aromatic hydrocarbon cations

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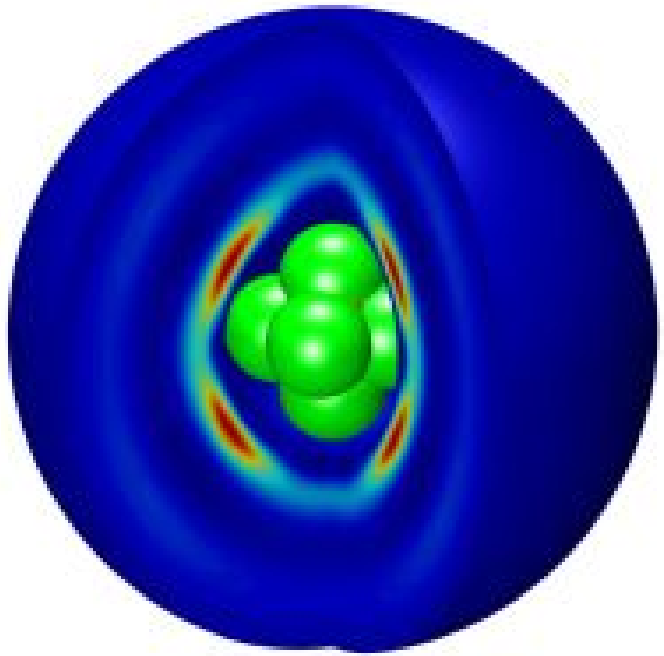
Introduction: helium nanodroplets

Unique cryogenic solvent: chemically inert, can trap exotic molecules and enable high resolution spectroscopy



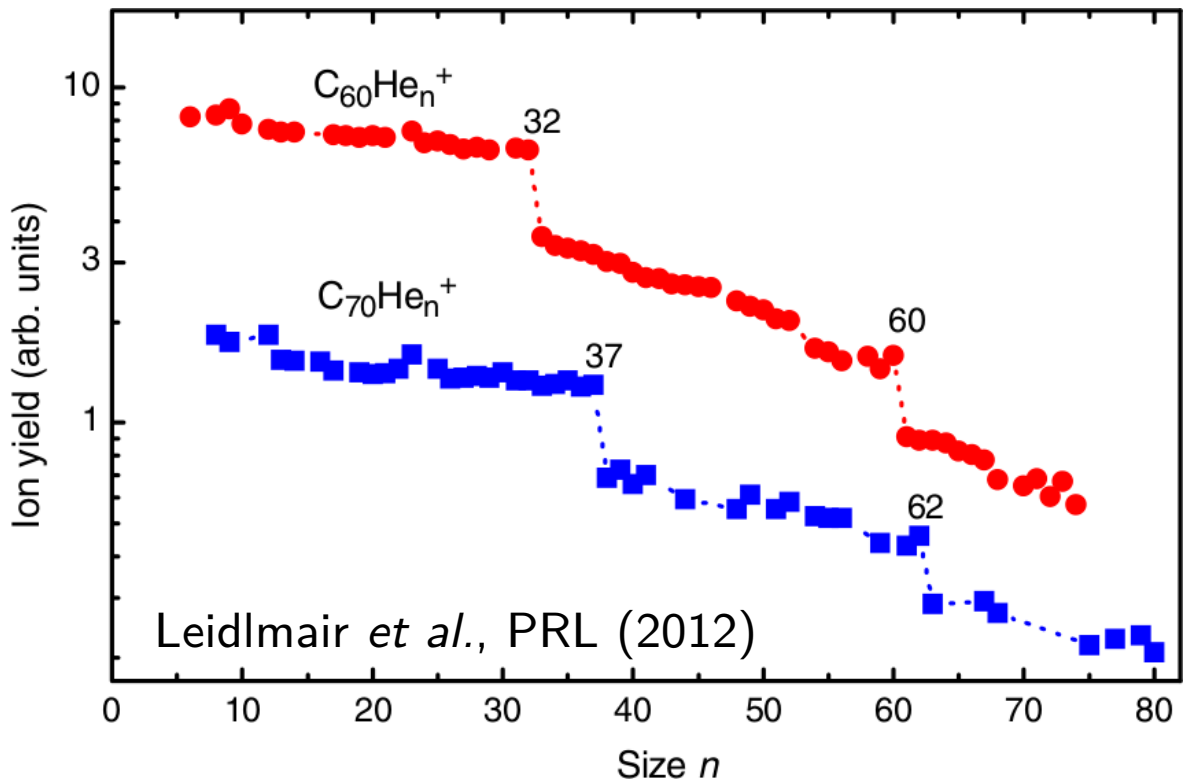
Numerous *atoms, molecules and ions* have been investigated inside (or outside) helium droplets, both experimentally and computationally

Mass spectrometry experiments

Ion abundances of complexes microsolvated by helium give direct insight into their relative stability

$\Longrightarrow$theoretical support needed to provide a more complete picture of microsolvated complex

One important historical step achieved on fullerene ions:



Interpretation of fullerene experiments

Atomistic modeling of cationic complexes $[C]^+He_n$ using

1. *polarizable potential energy surfaces*

$$V(\mathbf{R}) = \underbrace{V_{\mathrm{He-He}}(\mathbf{R})}_{\text{pair potential}} + V_{\mathrm{He-dopant}}(\mathbf{R}) + V_{\mathrm{pol}}(\mathbf{R})$$

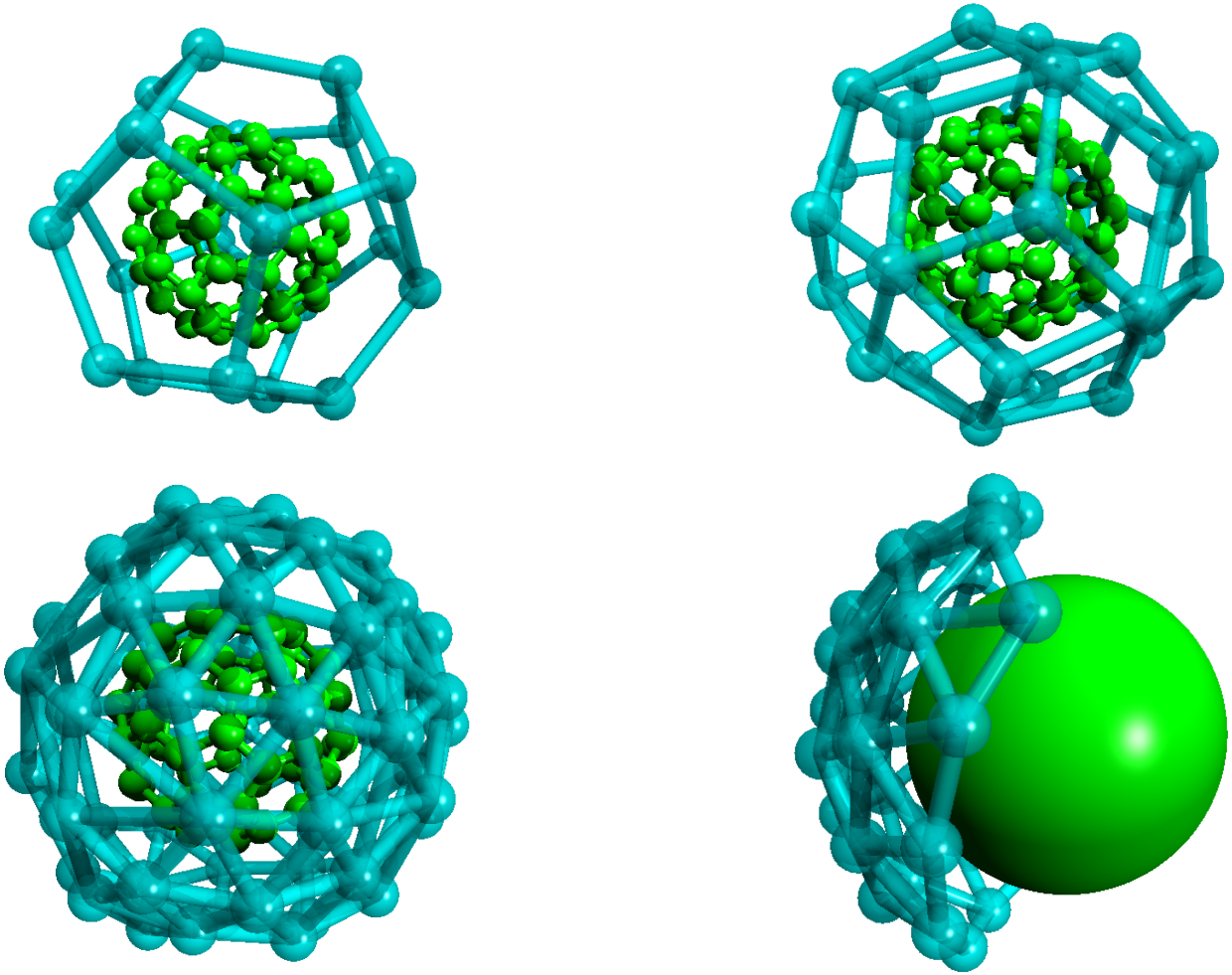
with polarization treated self-consistently:

$$V_{\mathrm{pol}}(\mathbf{R}) = -\sum_{i \in \mathrm{He}} \frac{\alpha_{\mathrm{He}}}{2} \underbrace{\vec{E}_i}_{\text{total field}} \cdot \underbrace{\vec{E}_i^0}_{\text{bare field}}$$

parametrized based on quantum chemical calculations

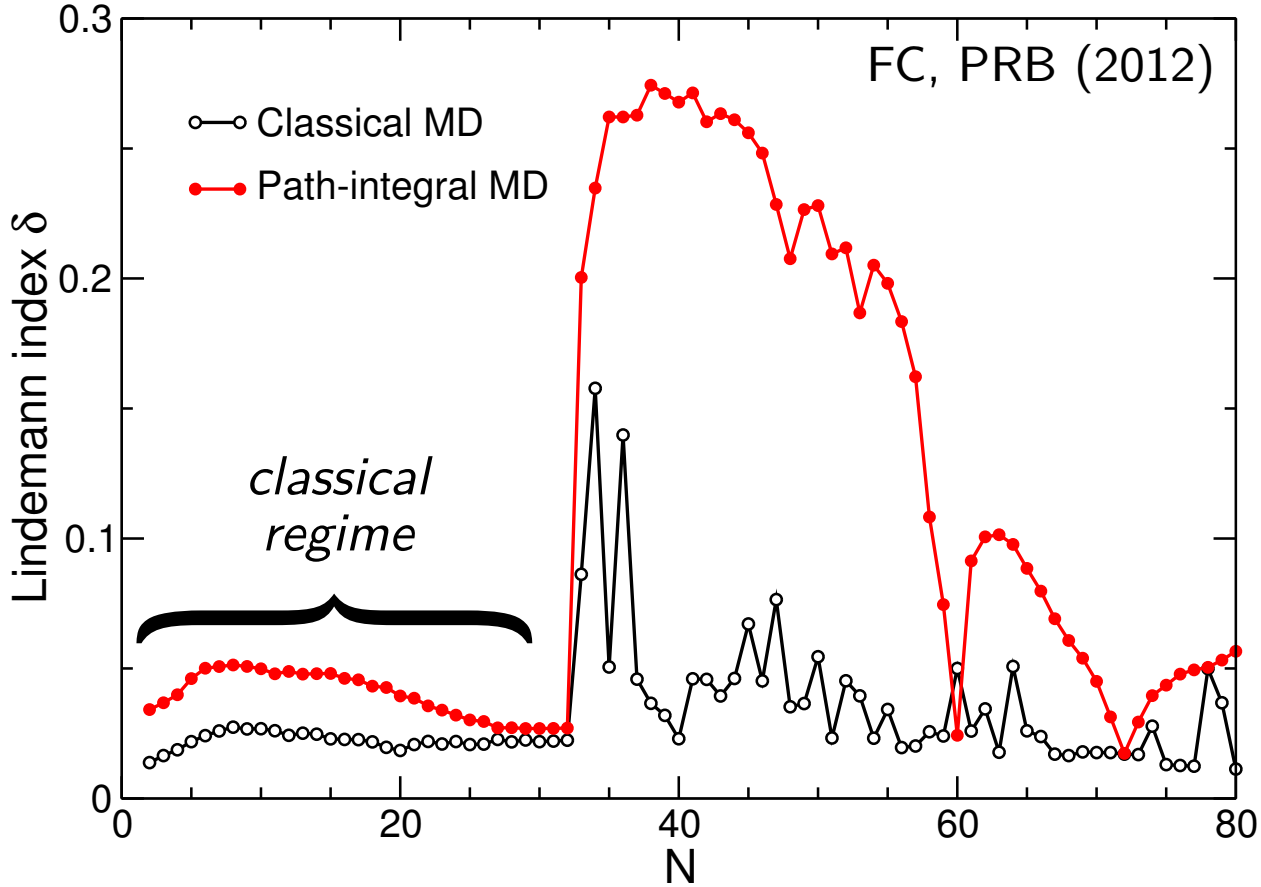
2. A rigid approximation for the *dopant molecular cation* (DFT geometry)
3. A classical survey of the stable structures
4. A more realistic incorporation of *nuclear quantum effects* using path-integral molecular dynamics

Example of C_{60}^{+}: role of corrugation



Highly symmetric (I_h group) structures at $n = 20$ and 32...
but not 60
Corrugation is essential to stabilize wetted structures

Path-integral MD simulations at 1 K: rigidity

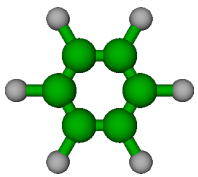


Behavior much more liquidlike in the quantum description;
Vacancy-mediated disorder also in classical case above $n = 32$

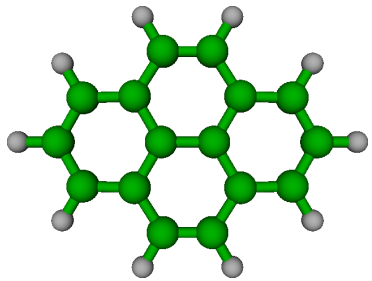
$\Longrightarrow$reentrant freezing at $n = 60$ concomitant with single shell size compatible with rigid body rotation

Polycyclic aromatic hydrocarbon dopants

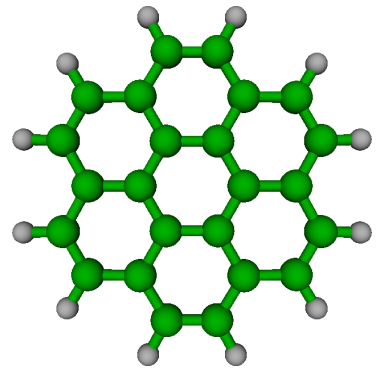
PAHs relevant as combustion products (soot precursors) and indentified in interstellar media



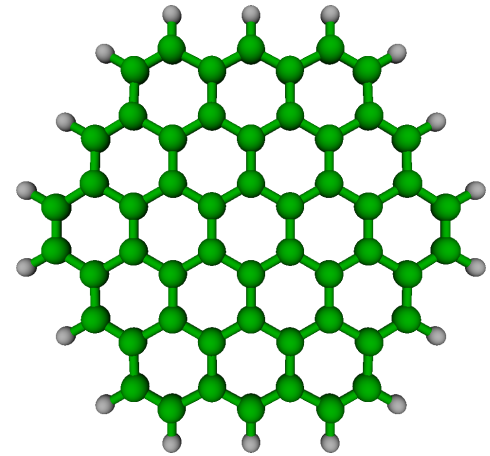
benzene
$C_6H_6^+$



pyrene
$C_{16}H_{10}^+$



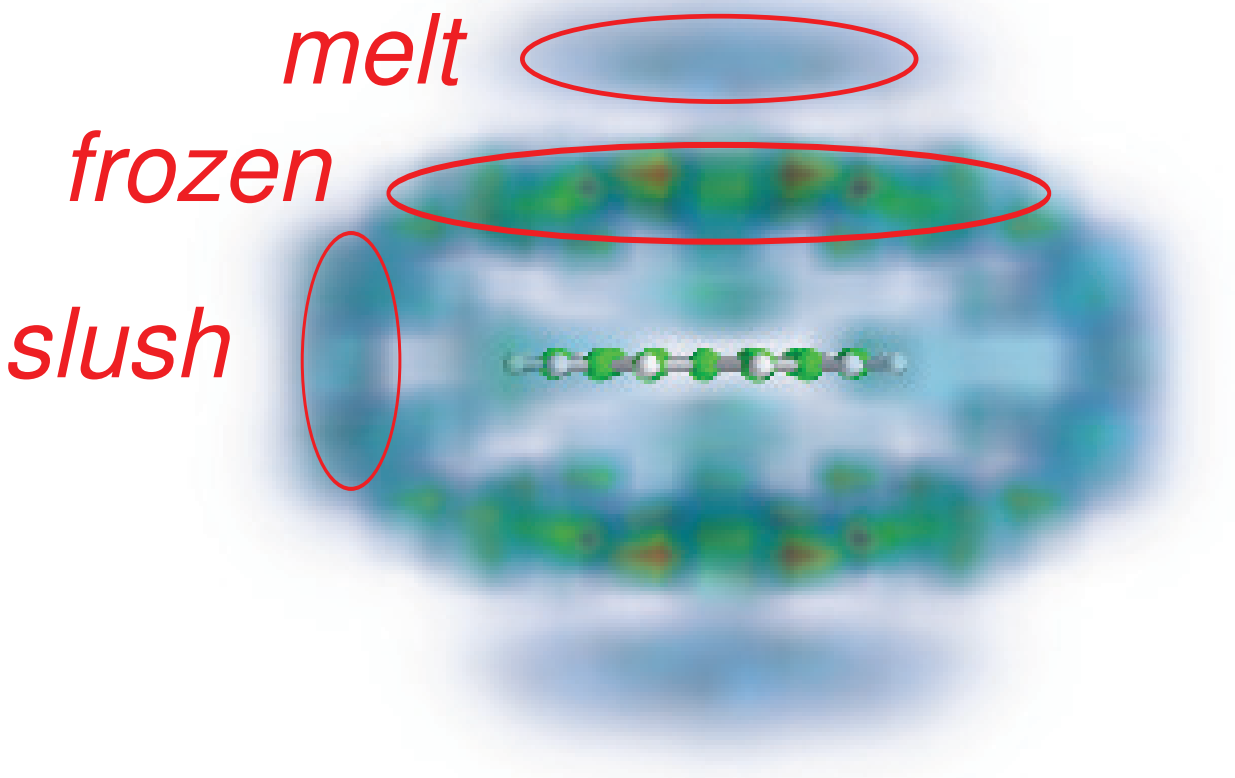
coronene
$C_{24}H_{12}^+$



circumcoronene
$C_{54}H_{18}^+$

Computational exploration of $[PAH]^+He_n$

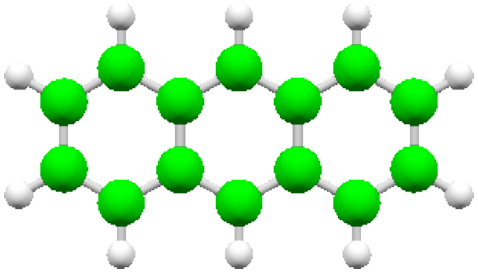
The highly anisotropic nature of the PAH cations reflects on the microsolvation features:



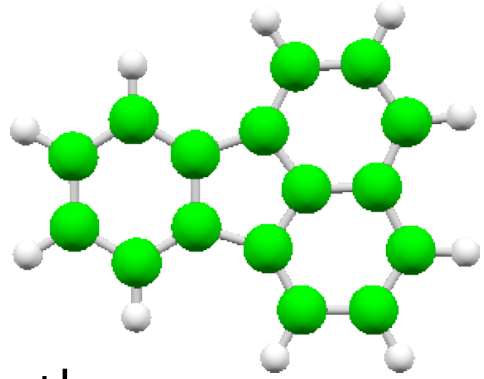
FC, JPCA (2015)

The present?

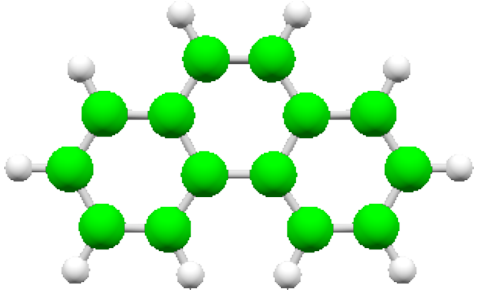
Atom-resolved mass spectrometry experiments on specific PAH cations:



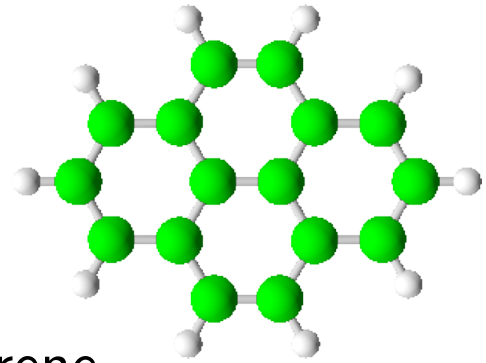
Anthracene



Fluoranthene



Phenanthrene

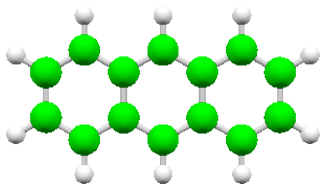


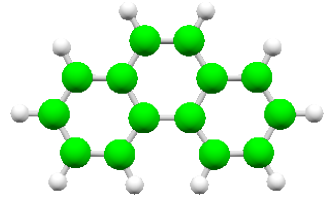
Pyrene

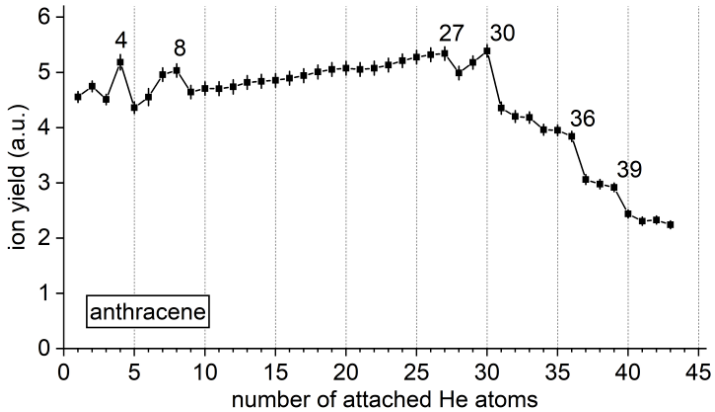
$C_{14}H_{10}^{+}$

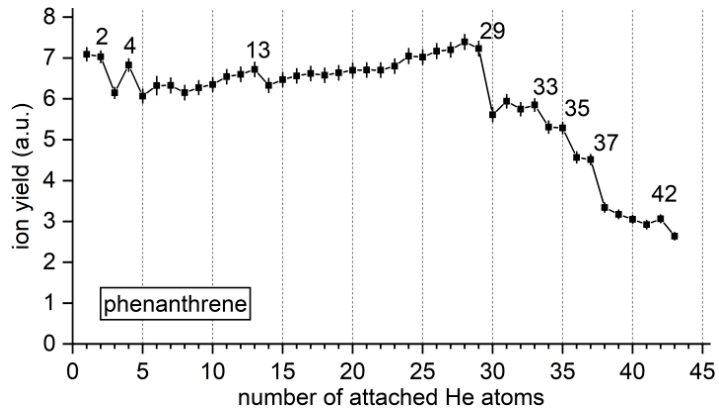
$C_{16}H_{10}^{+}$

Anthracene versus Phenanthrene





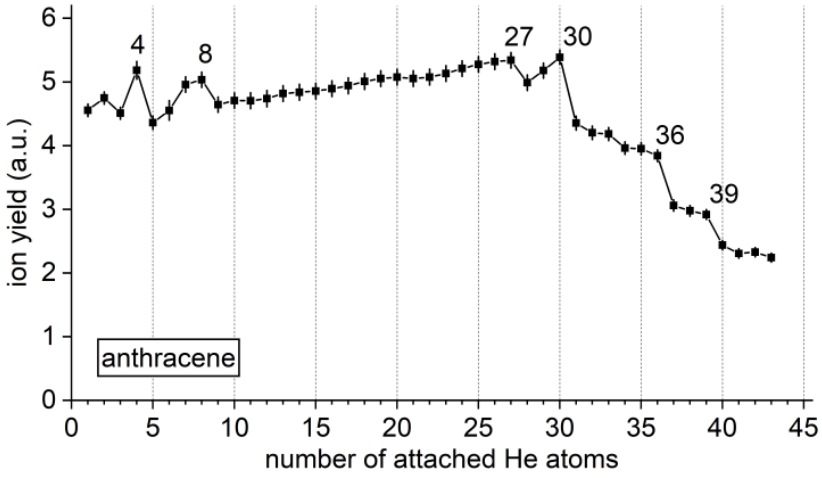


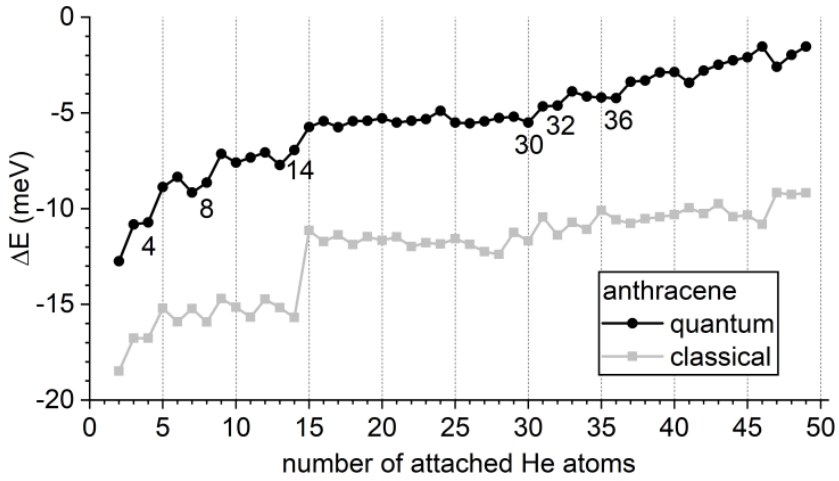


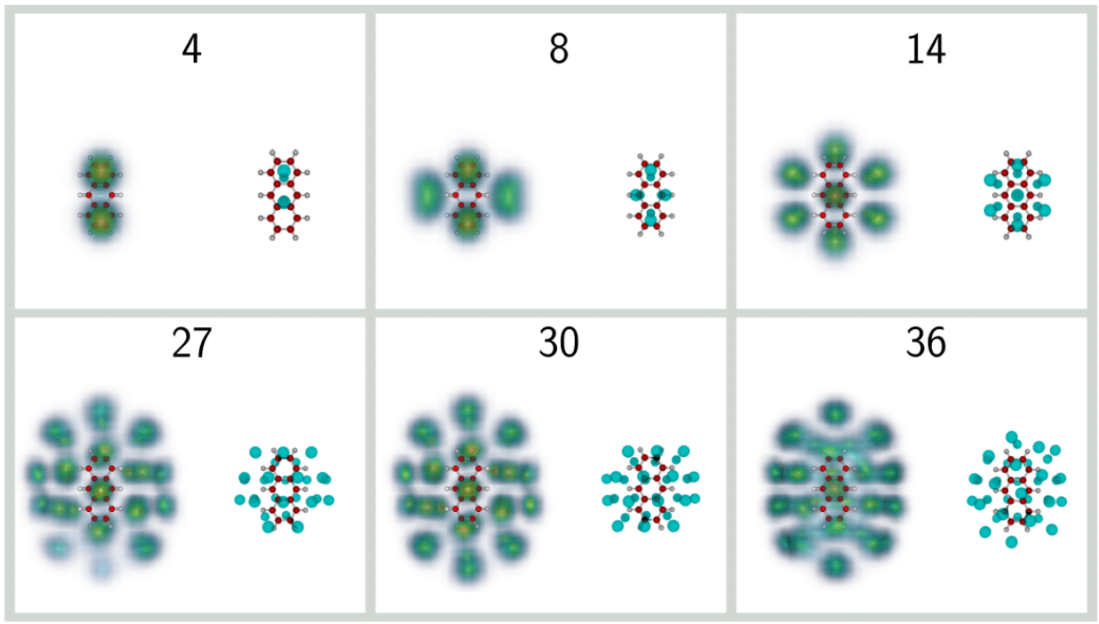
$\Longrightarrow$Different "magic numbers" between the two isomers:

- Extra stabilities at sizes 4, 8, 30, 36 for anthracene cation
- Extra stabilities at sizes 4, 13, 29, 37 for phenanthrene cation

Theoretical interpretation: Anthracene

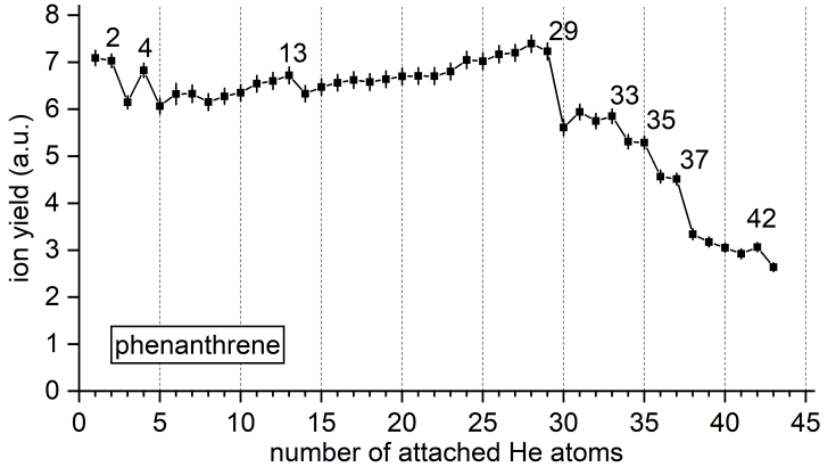


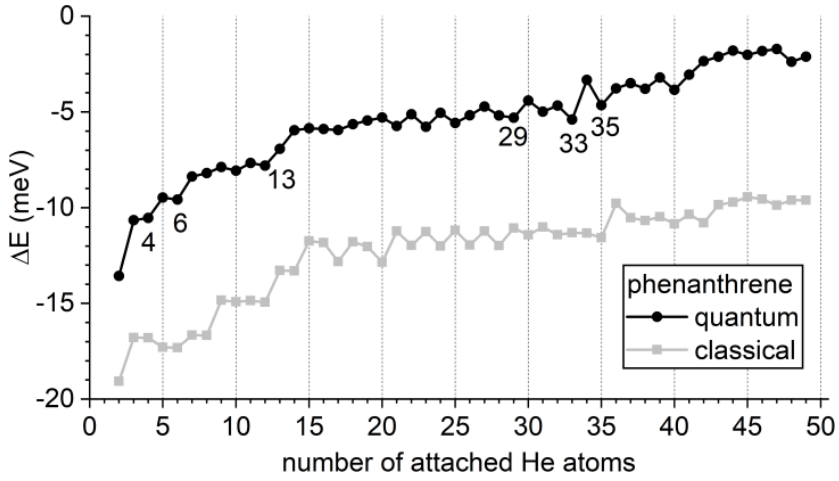


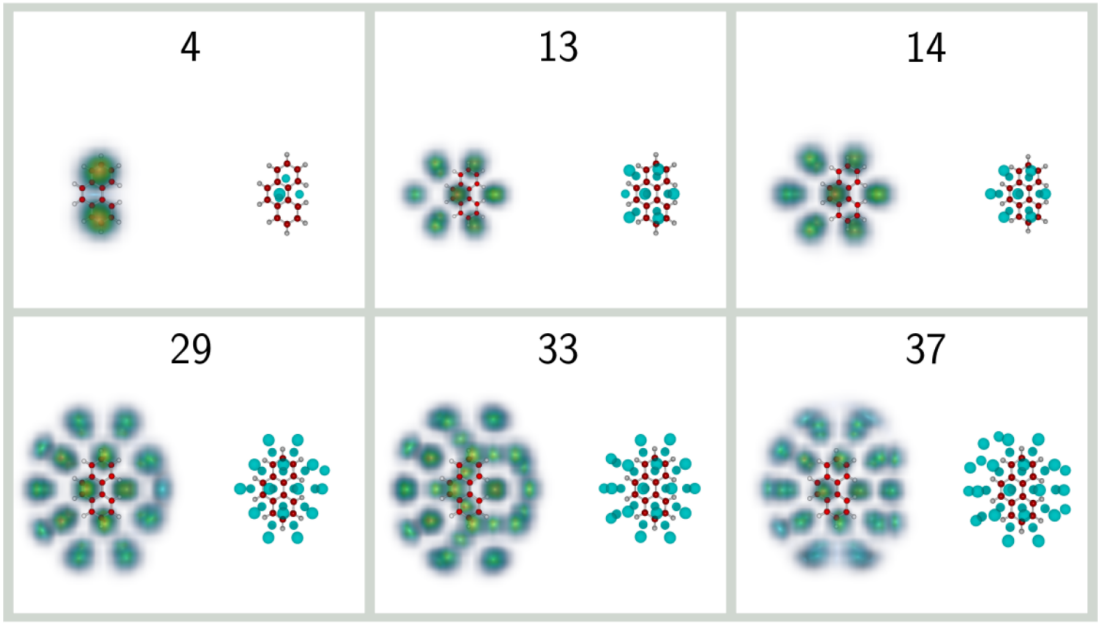


$\Longrightarrow$sizes 8, 30, and 36 associated with geometric shell closures

Theoretical interpretation: Phenanthrene

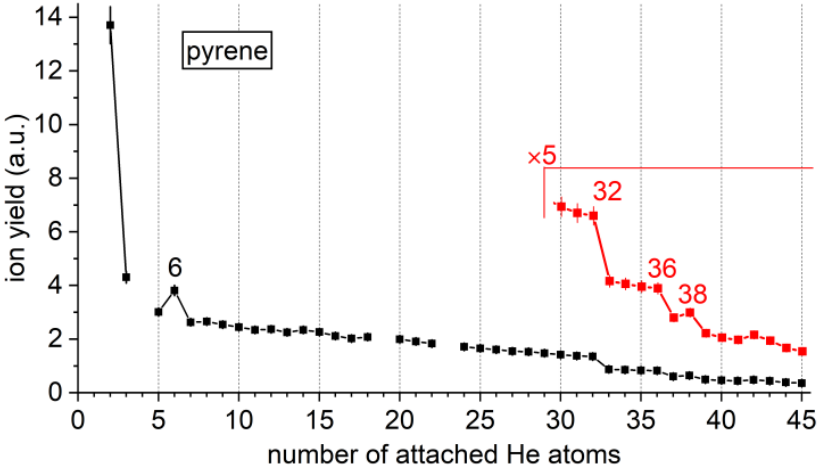


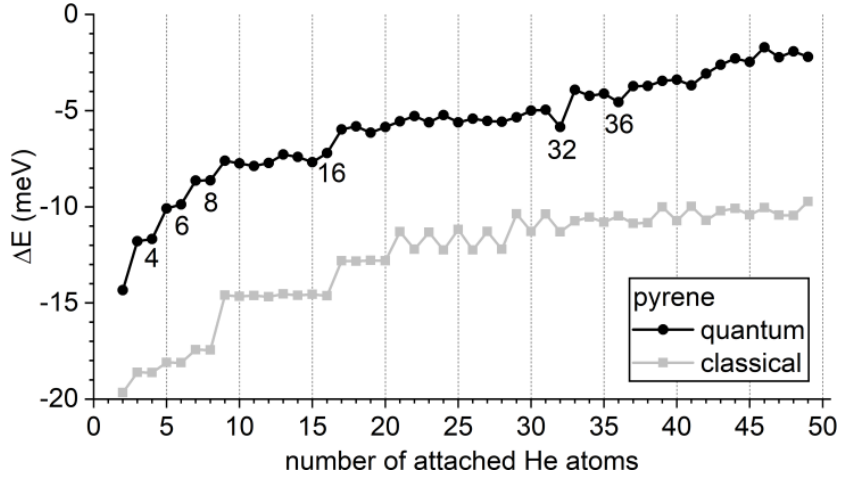


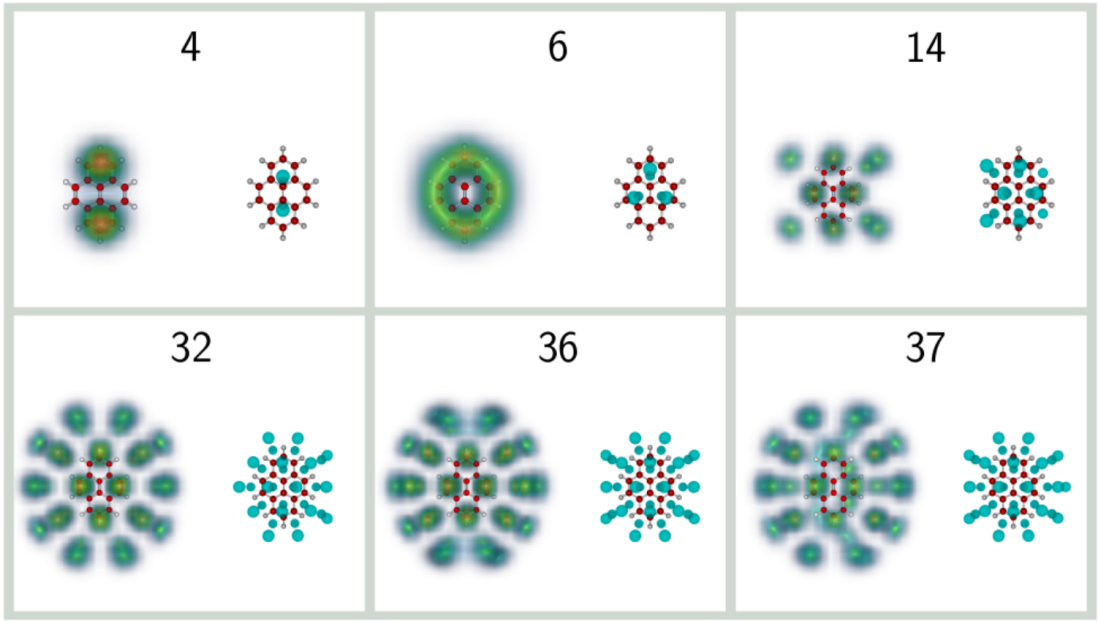


$\Longrightarrow$Only partial agreement (for sizes 30 and 37)

The case of Pyrene



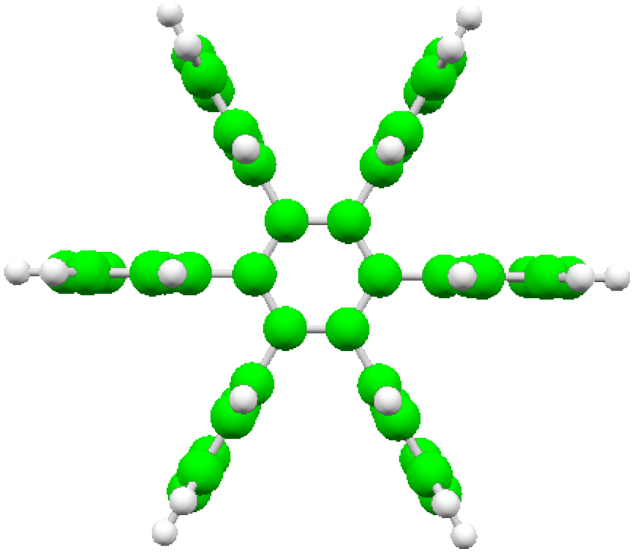




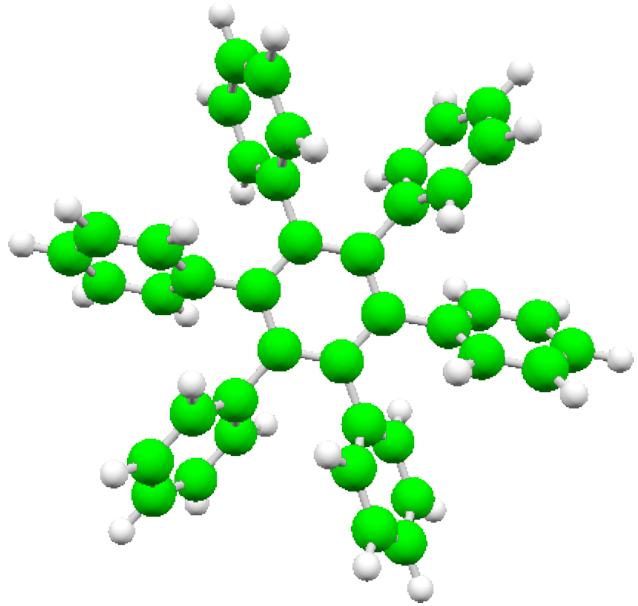
$\Longrightarrow$Shell closures at sizes 32 and 36 reproduced, extreme delocalization at size 6

Hexaphenylbenzene: a "rotor" molecule

$C_{42}H_{30}^{+}$: some degree of lateral flexibility



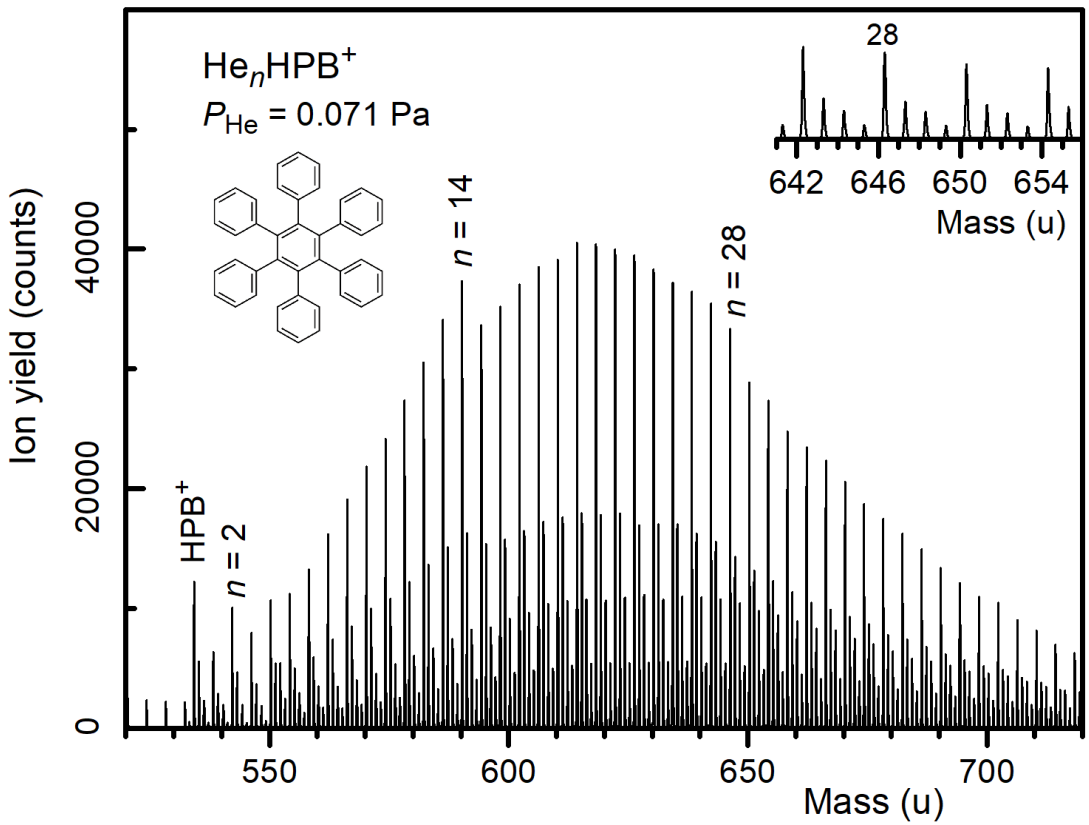
perpendicular



slanted

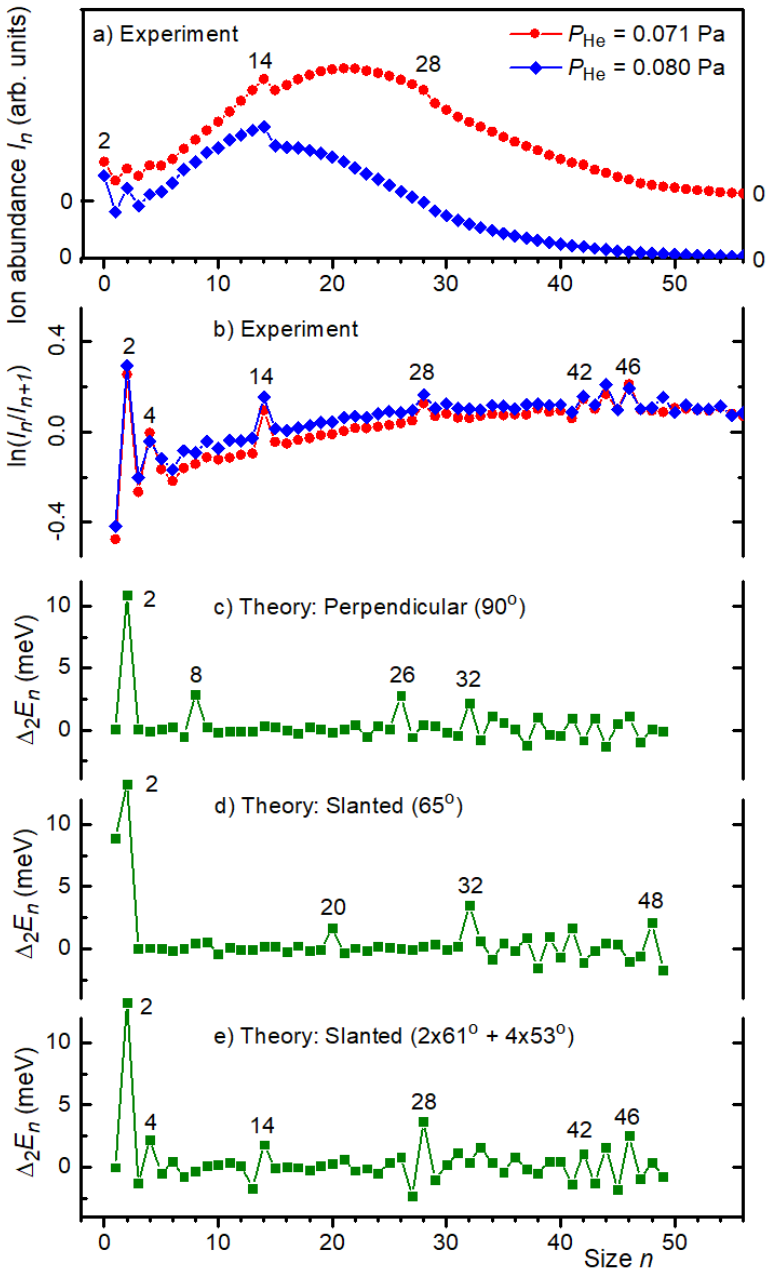
DFT minimization in cationic state breaks the sixfold symmetry, with two phenyl groups rotated by 61° and four groups rotated by 53° ($D_6 \rightarrow D_2$ point group)

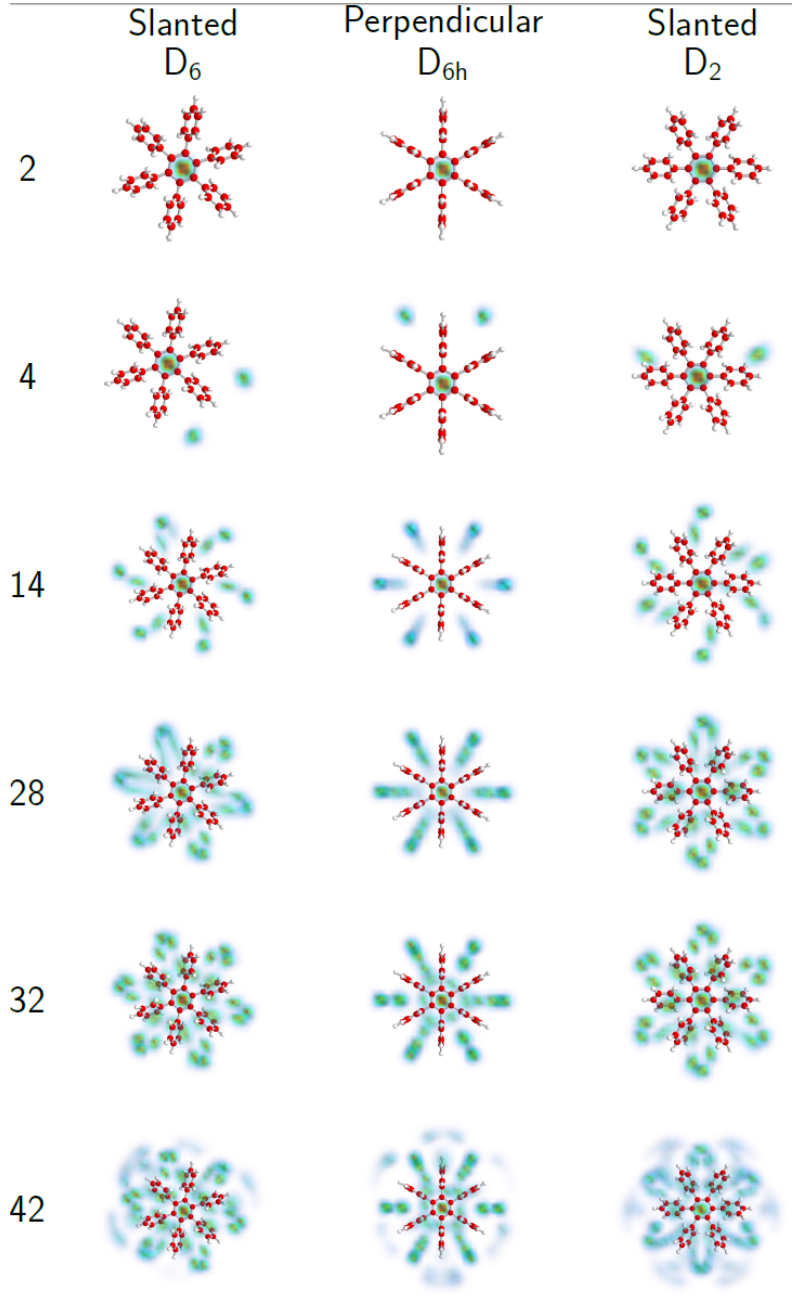
Mass spectrometry abundances on HPB cation



$\Longrightarrow$Special stabilities at sizes 2, 14, and 28

Interpretation of MS experiments





Concluding remarks

1. Theoretical interpretation of mass spectrometry experiments on cationic polyaromatic compounds microsolvated by helium
2. Nuclear delocalization significantly alters the geometrical structure of the microsolvated complexes
3. Special abundances usually associated with shell closures but some residual discrepancies

$\rightarrow$ *high sensitivity* of solvation propensity toward geometrical details of the complex

$\rightarrow$ evidence for *symmetry breaking* in cationic hexaphenylbenzene

Future work

1. Accounting for vibrational structure of the complexes
2. Accounting for superfluidity? ($\rightarrow$QMC)

Thank you for your attention!