Stepwise solvation of polycyclic aromatic hydrocarbons by helium: curvature and dynamical effects

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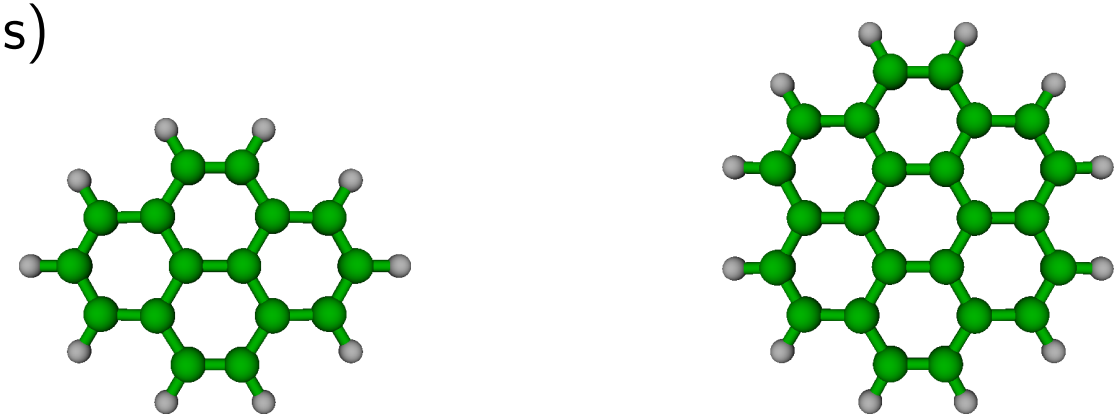
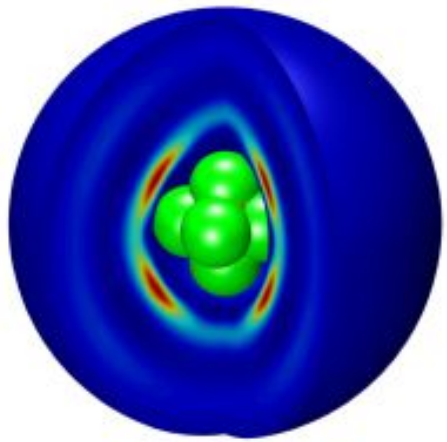
Background: PAHs and helium nanodroplets

Polycyclic aromatic hydrocarbons are plausible candidates to explain some spectroscopic features observed in interstellar media (AIBs, DIBs)



Laboratory studies under the cryogenic environment of helium droplets offer a way to address conditions not too far from astrophysical ones

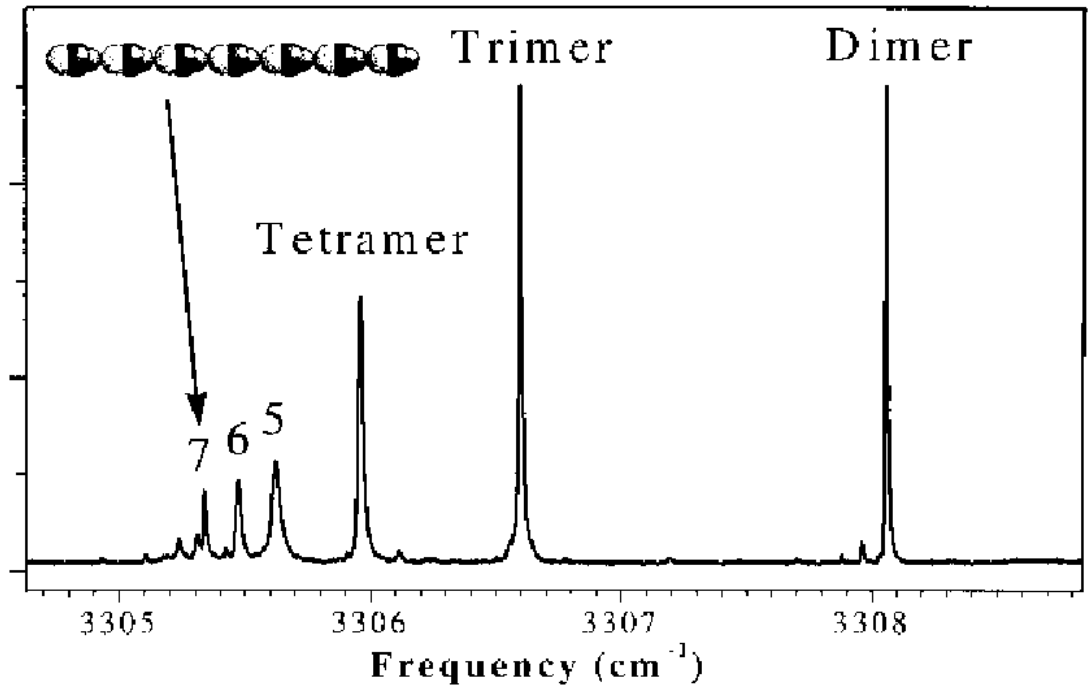


Novel physics from helium droplets

Stabilization of metastable conformations: $(HCN)_n$

Characterization by IR spectroscopy (HC mode)

Nauta & Miller 1999



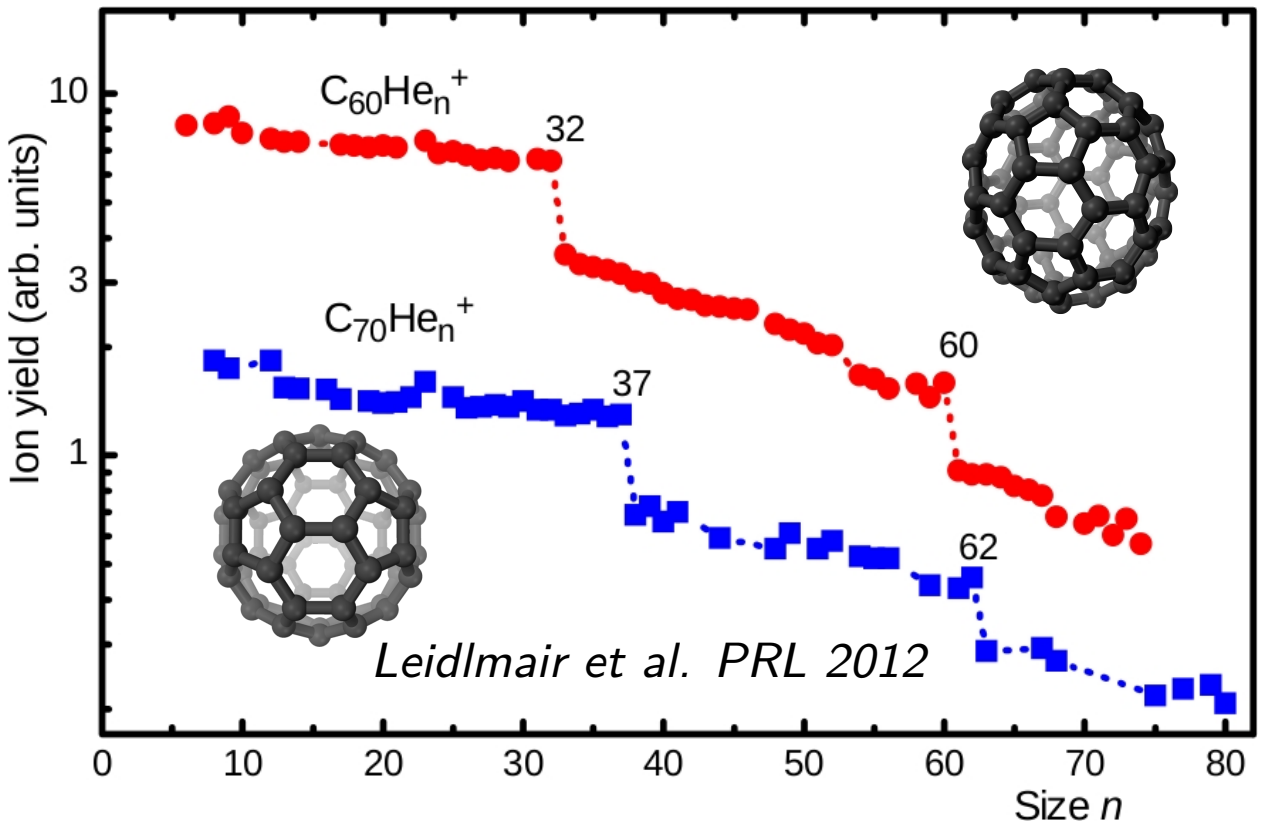
Evidence for formation of linear chains up to heptamer

$\Longrightarrow$freezing of oligomer into high-entropy configurations

$\Longrightarrow$suggests some possible role of kinetics during pick-up

Previously: Fullerene-doped nanodroplets

Case of $C_{60}He_N^+$ *and* $C_{70}He_N^+$



Special stabilities at 32 and 60 reflects particular coating patterns of C_{60}^+ by helium

$\Longrightarrow$simulations indicate suppression of delocalization below $N = 32$ for C_{60}^+, *similar to Atkins' snowballs*

Stepwise solvation of PAHs with helium

PAHs are highly anisotropic molecules, their solvation patterns are also anisotropic

[Earlier theoretical works on benzene, naphthalene, anthracene, tetracene from the Bačić, Whaley, Jortner groups]

1. How does this anisotropy explain special stabilities in mass spectra?
2. What if the molecules are not planar?
3. How could oligomers of PAHs behave under helium droplets?

Computationally addressed through

→ A realistic potential energy surface for helium clusters (1–1000 atoms) around neutral or cationic PAHs

→ classical structures and quantum simulations in the path-integral molecular dynamics framework

→ some insight into the dynamics of helium-coated oligomers using ring-polymer molecular dynamics

Polarizable potential

Potential energy surfaces for $(\mathrm{PAH})_k^{(+)}\mathrm{He}_n$ written as

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

with charges from DFT/RESP and polarization treated self-consistently:

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

Dopant molecule usually treated as rigid, except for PAH oligomers: $\begin{cases} \text{intramolecular: tight-binding} \\ \text{intermolecular: LJ+Coulomb} \end{cases}$

Classical perspective: stable structures that minimize $V(R)$

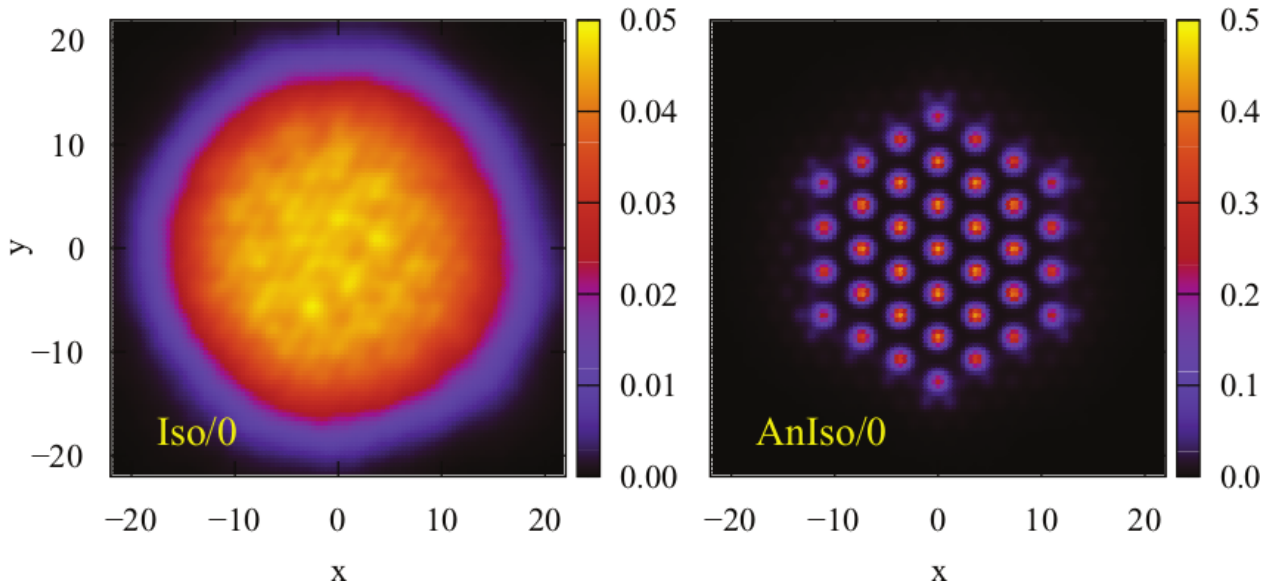
Nuclear quantum effects: harmonic corrections to zero-point energy, and path-integral molecular dynamics simulations

Some insight into the dynamics: ring-polymer MD

Coating of polyaromatics: Importance of corrugation

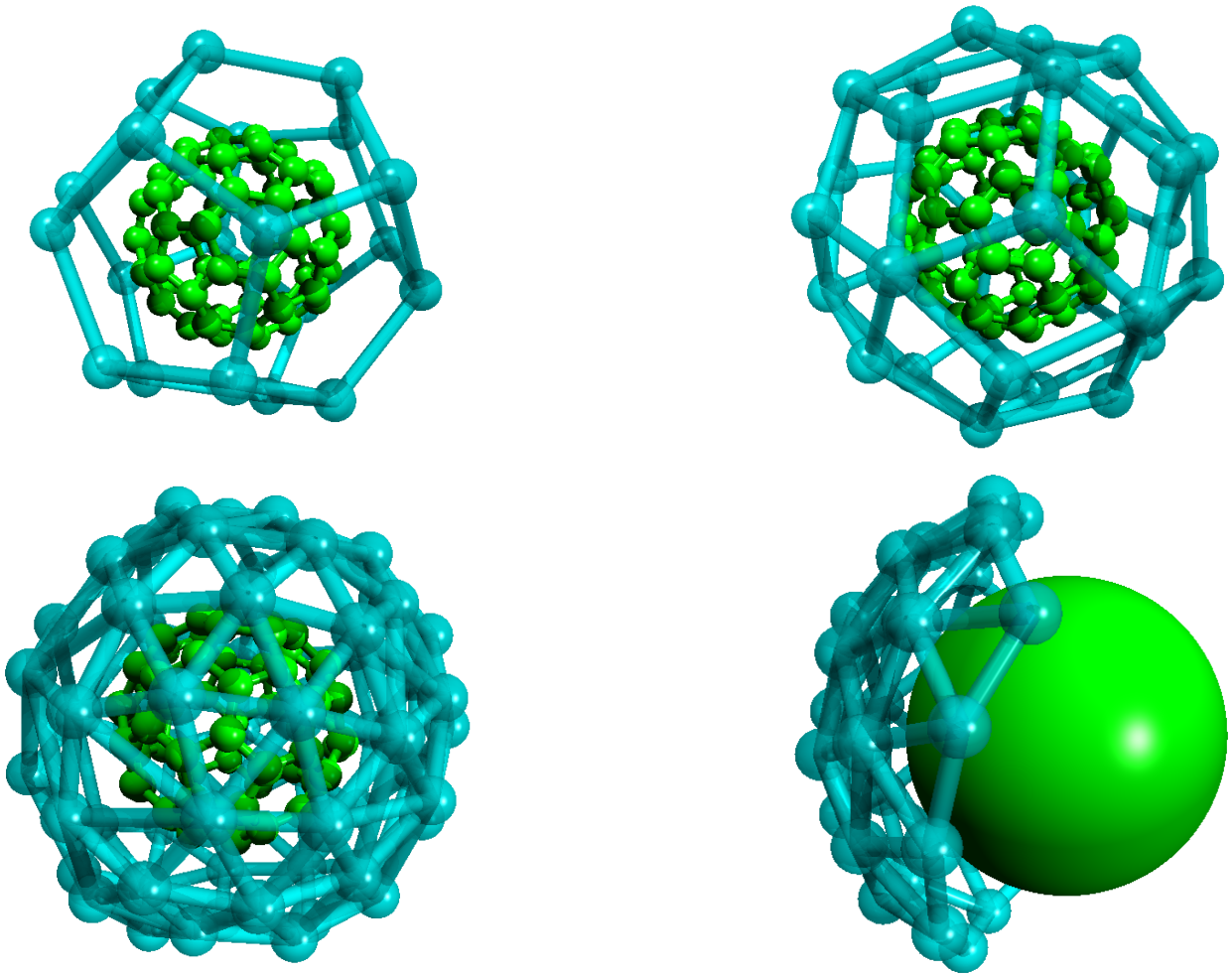
Helium on graphitic substrates shows a rich phenomenology

In the case of *graphene*, calculations indicate near degeneracy between liquid monolayer and $\sqrt{3} \times \sqrt{3}$ commensurate solid



[Vranješ Markić *et al.*, PRB 2013]

Classical coating of C_{60}^{+}

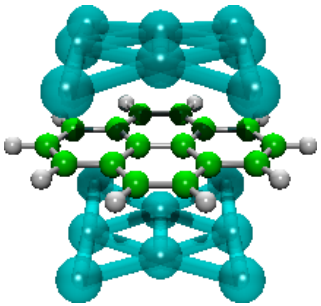


Highly symmetric structures at $n = 20$ and 32... but not 60

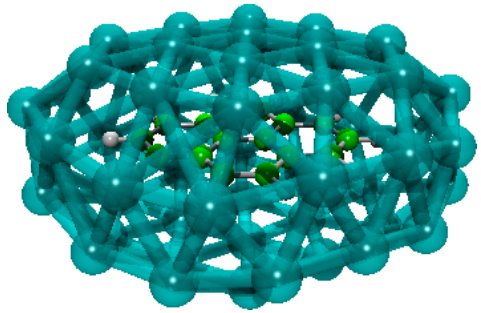
Corrugation is again essential to stabilize isotropic structures

Case of polycylic aromatic hydrocarbons

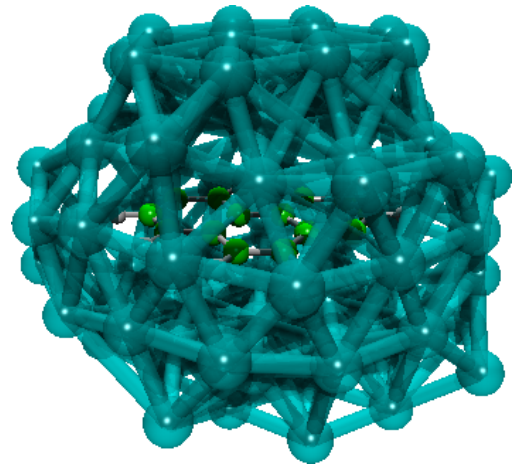
pyrene^{+}He$_{16}$

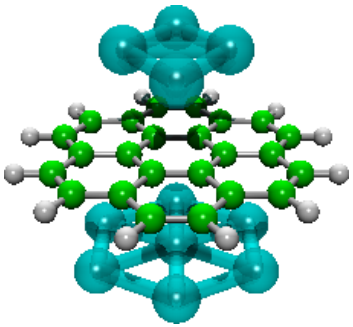


pyrene^{+}He$_{56}$

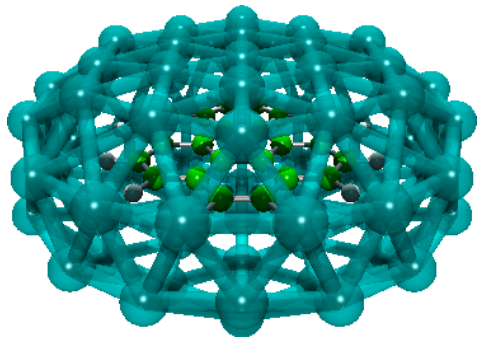


pyrene^{+}He$_{90}$

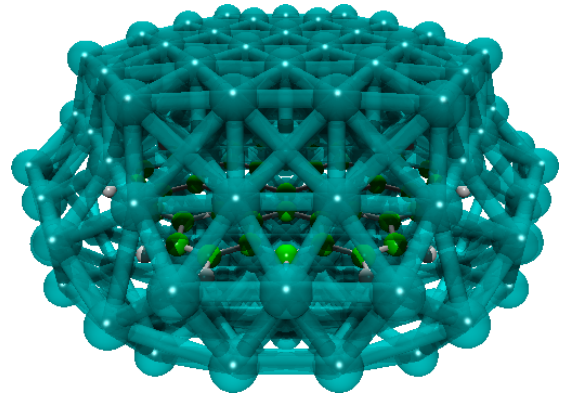




coronene^{+}He$_{11}$

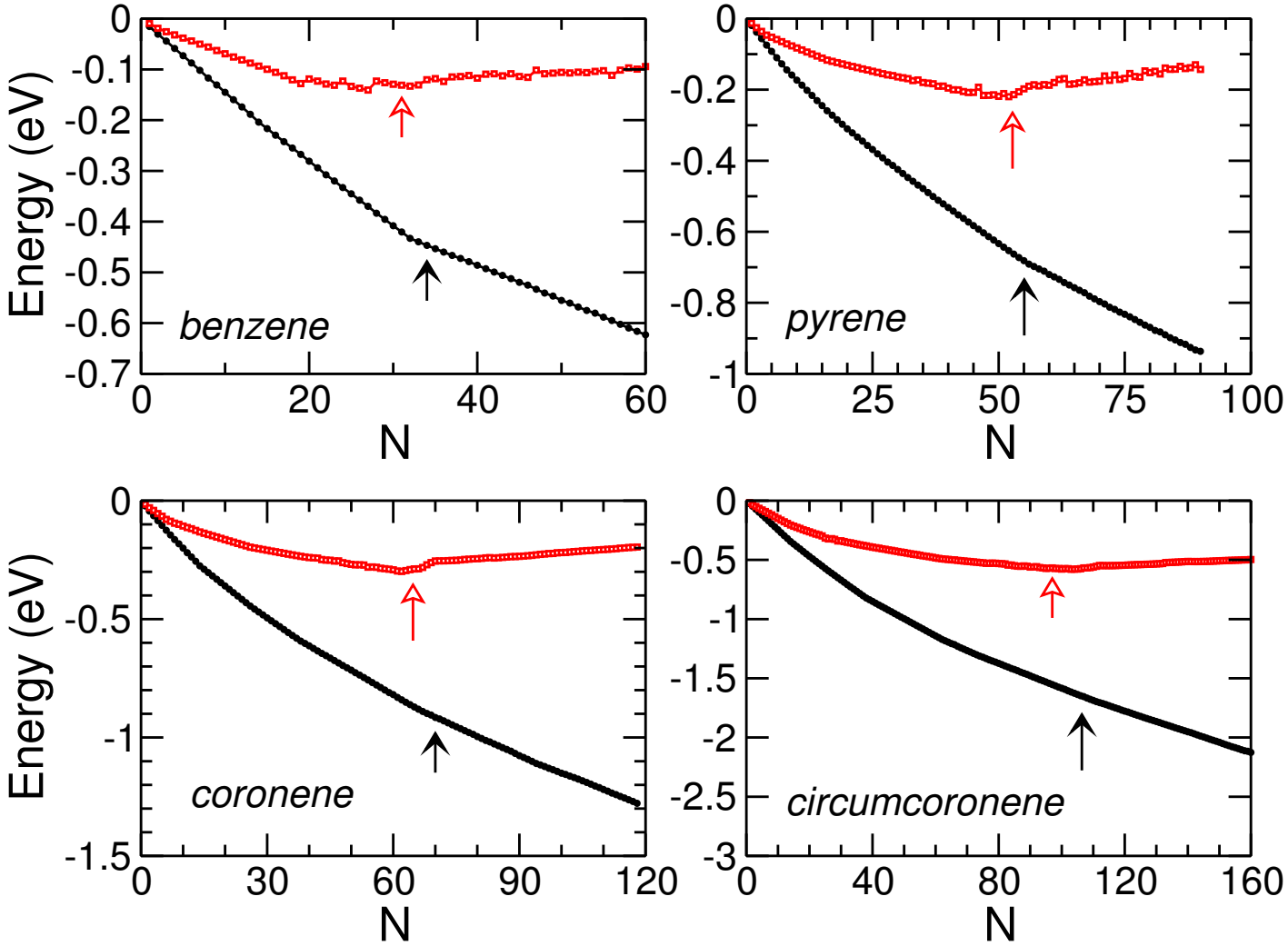


coronene^{+}He$_{70}$



circumcoronene^{+}He$_{160}$

Binding energies and classical snowballs

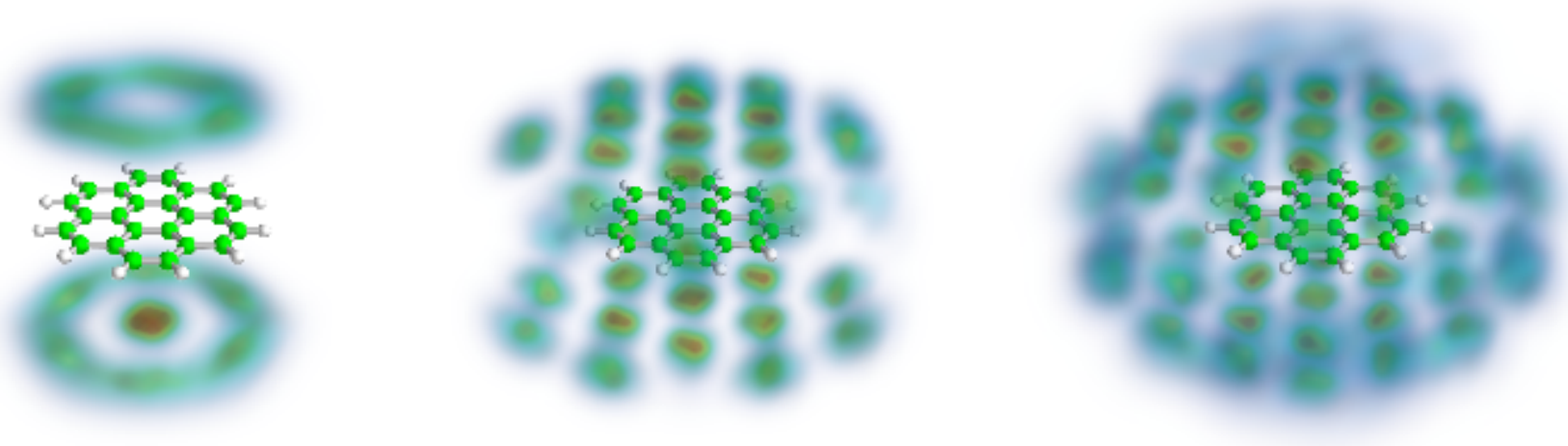


First layer complete at $n_C = 34$, 56, 70, and 112

Nuclear quantum effects lower shell size significantly

Size effects and solvation around coronene cation

$n = 10$ $n = 32$ $n = 70$



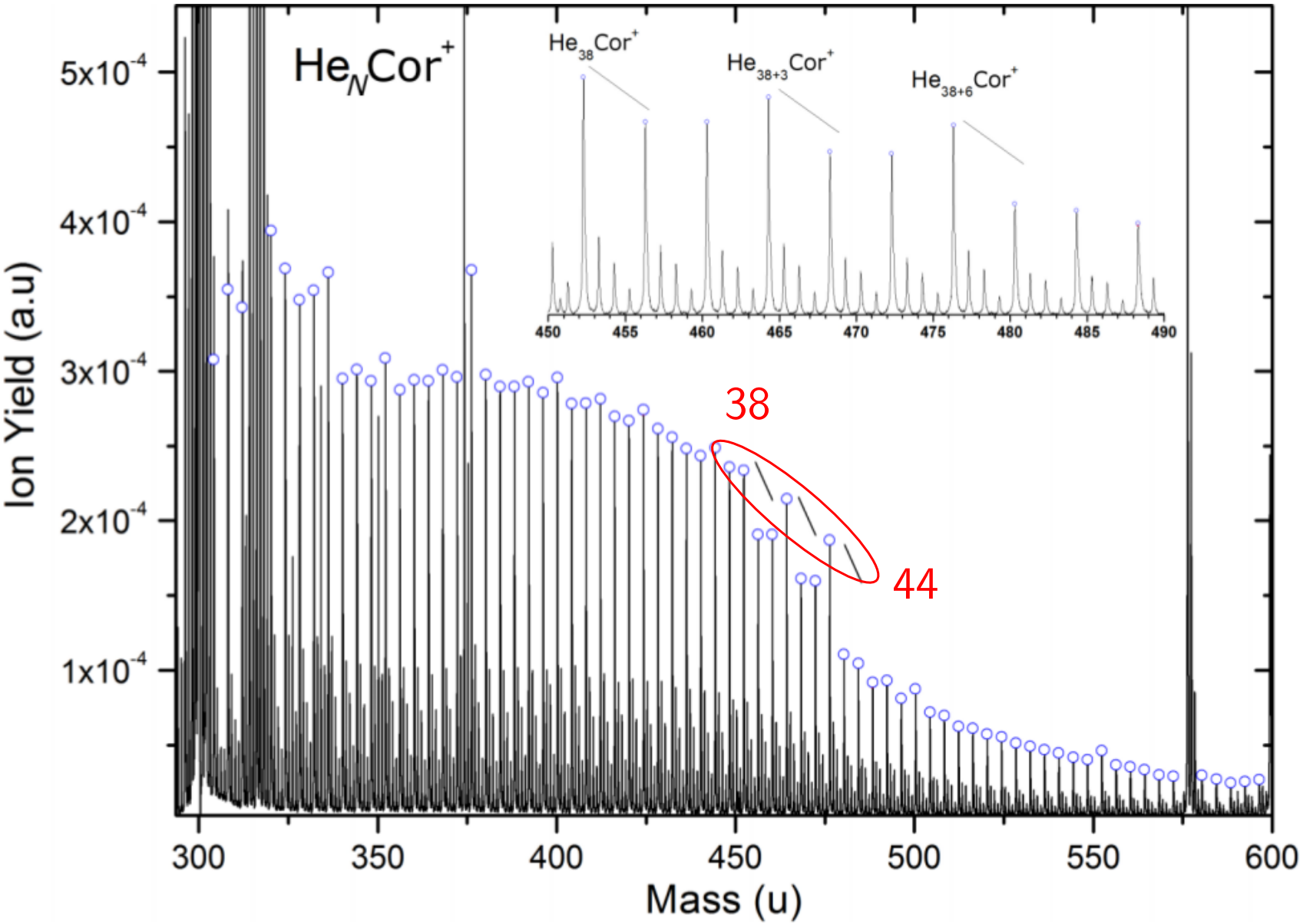
$\Longrightarrow$ completion starts at $n = 38$ on both faces (19+19)

$\Longrightarrow$ completion ends at $n = 44$ around the belt (19+19+6)

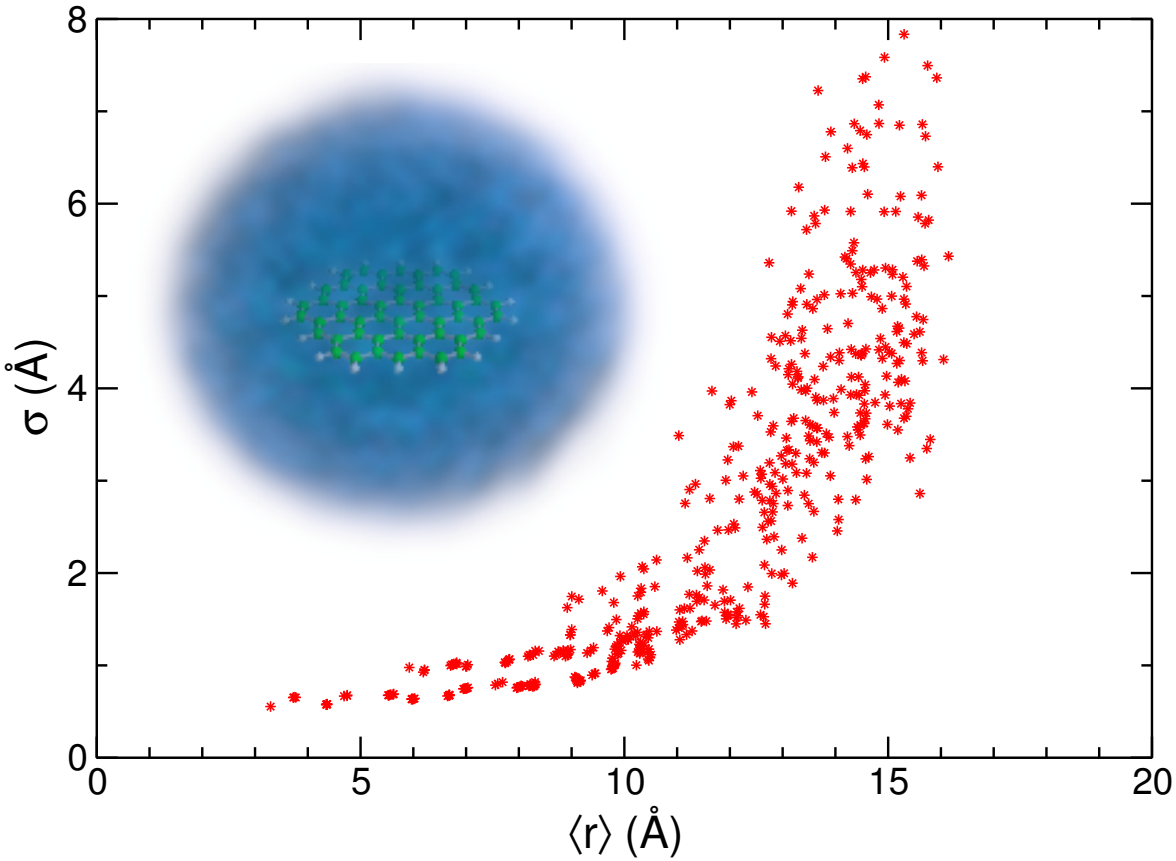
(but not in molecular plane)

Experimental confirmation

Kurzthaler et al. JCP (2016)

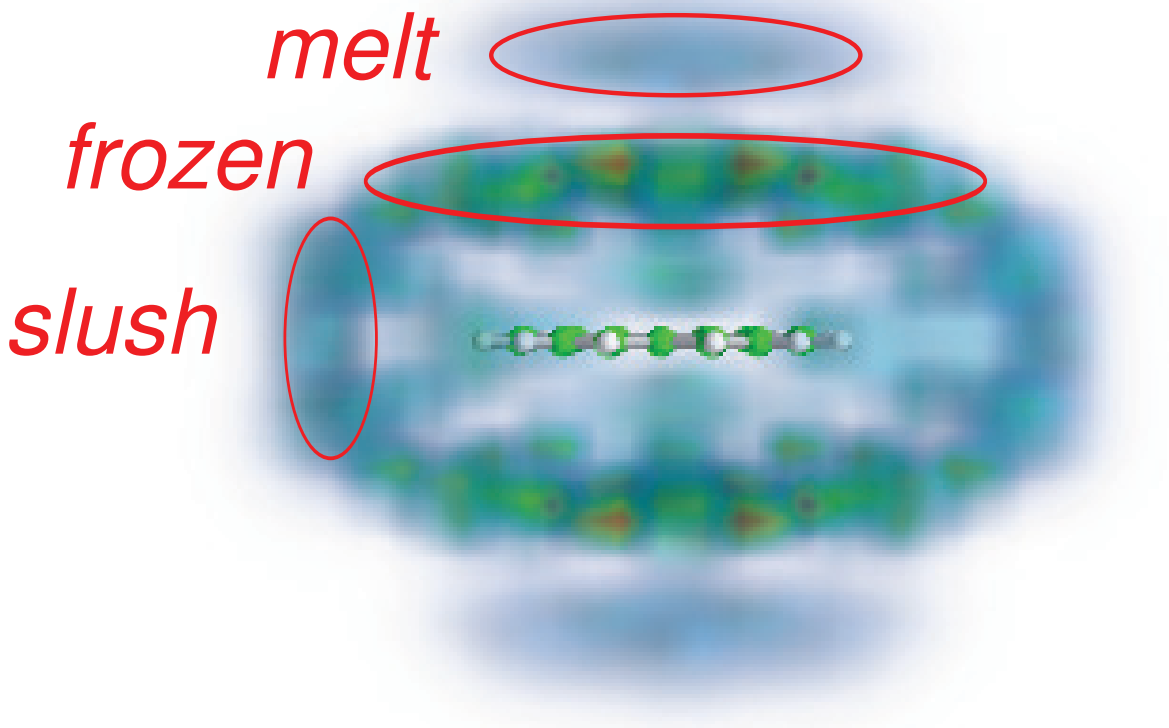


Case of a larger droplet: circumcoronene$^+$He$_{500}$



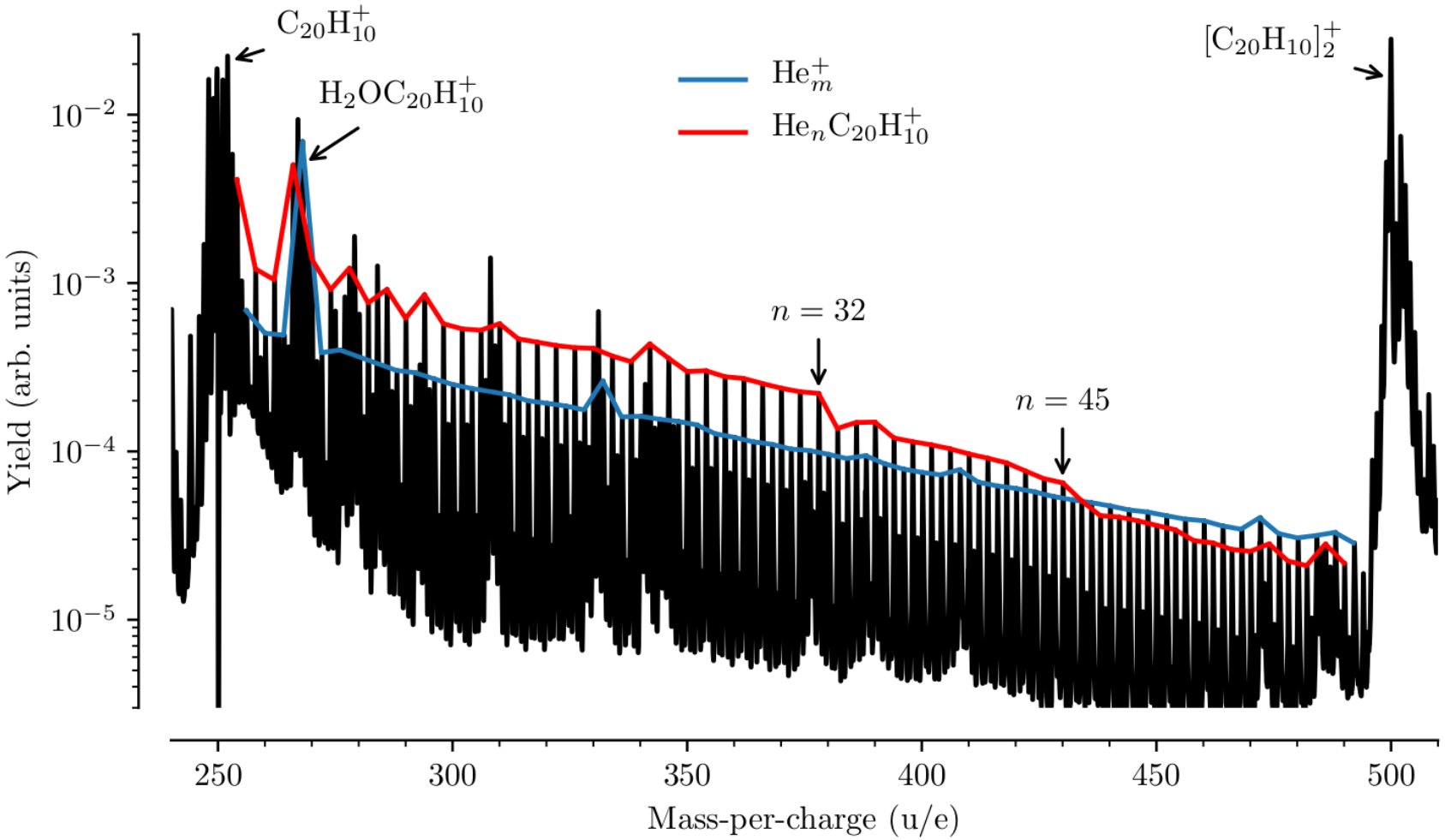
$\Longrightarrow$ Heterogeneous behavior with localized layers on both sides of the PAH layer, liquid far away from it, and intermediate in the peripheral region

Slushy phases



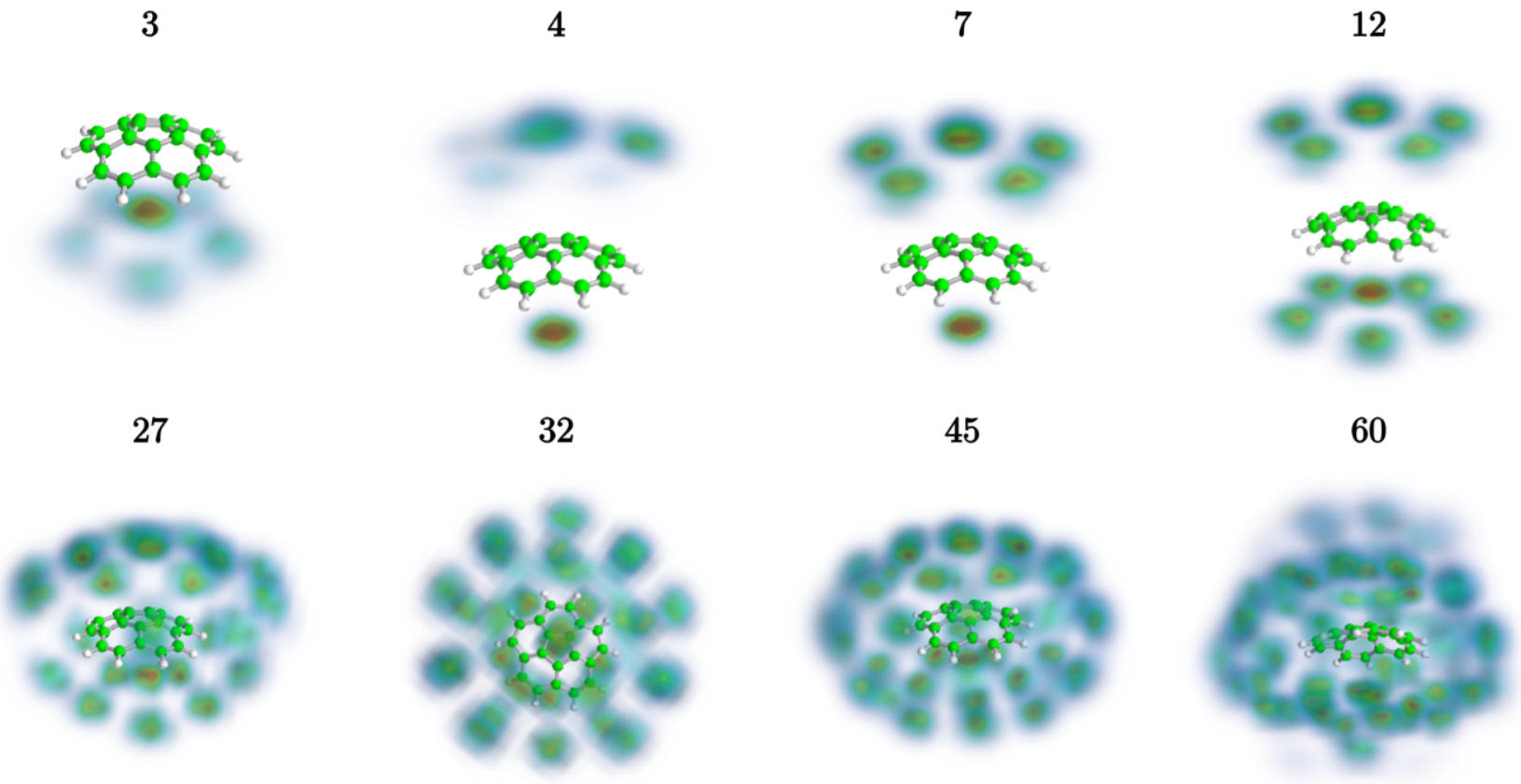
Curvature effects: case of corannulene $C_{20}H_{10}^+$

[Gatchell *et al.*, Faraday Discussions (2019)]



→range of shell filling between 32 and 45 helium atoms?

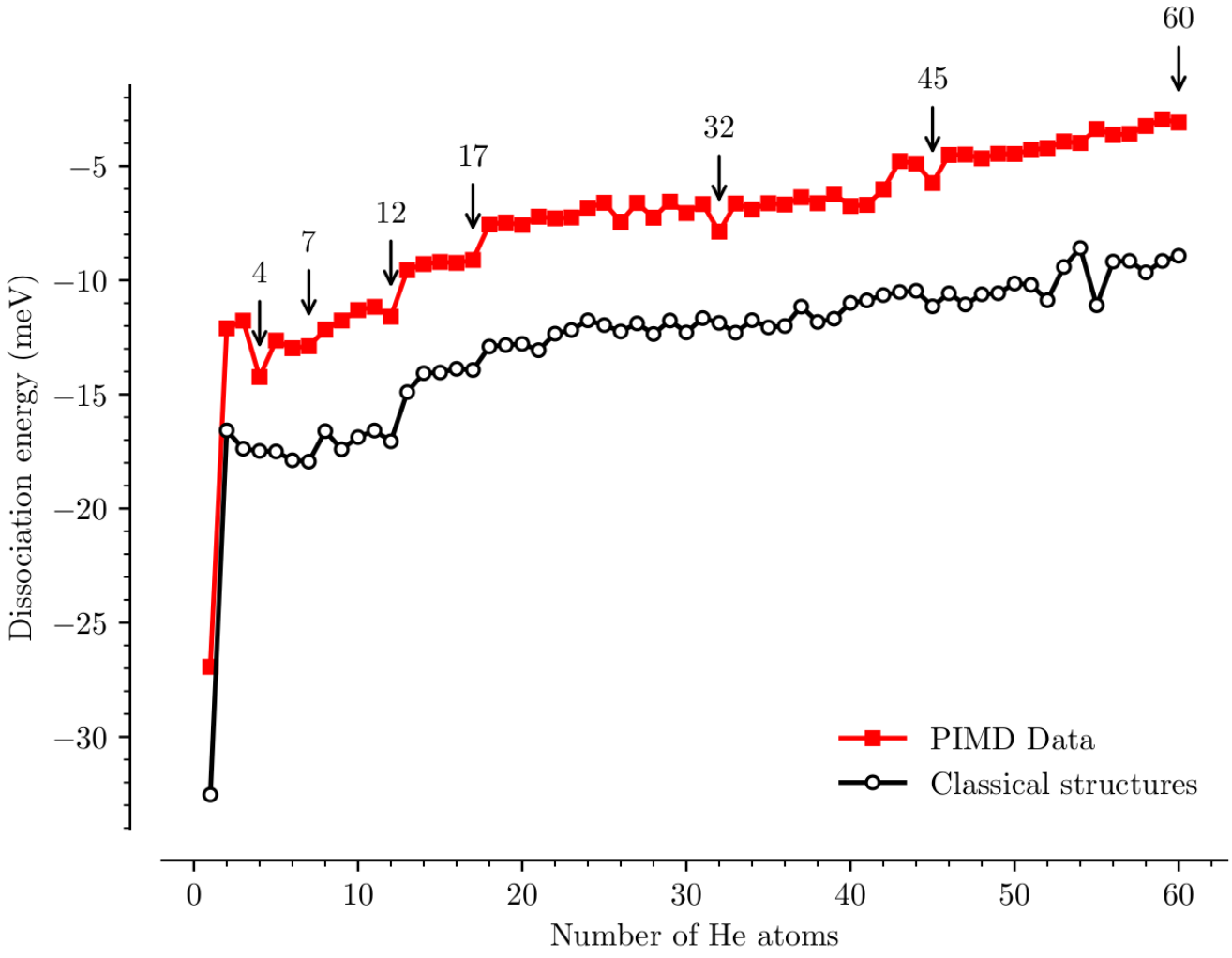
Stable structures for corannulene$^+$@He$_n$



$\Longrightarrow$coating becomes asymmetric, binding varies from 32 meV inside to 15 meV outside

$\Longrightarrow$ both sides coated at $n = 32$, belt filled near $n = 45$

Dissociation energies



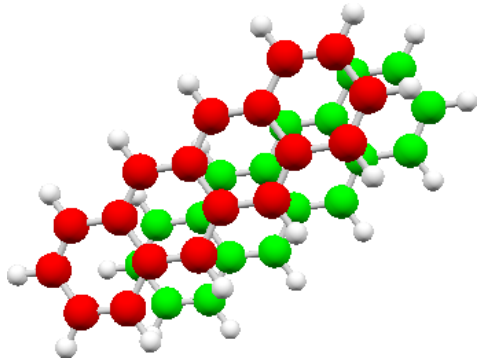
$\Longrightarrow$confirmation of the experimental range of solvation shell closure

PAH oligomers and pick-up experiments

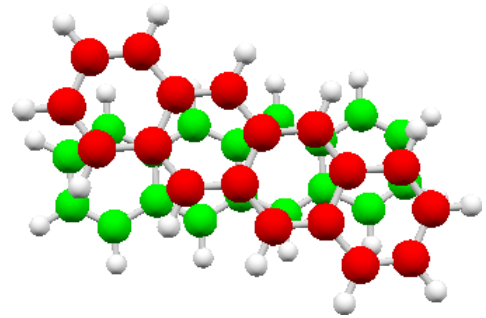
In the gas phase PAHs usually form stacked clusters owing to relatively strong dispersion forces

Precise arrangement is non trivial due to a variety of factors, mainly competition between dispersion and multipolar forces

Case of tetracene dimer



parallel displaced



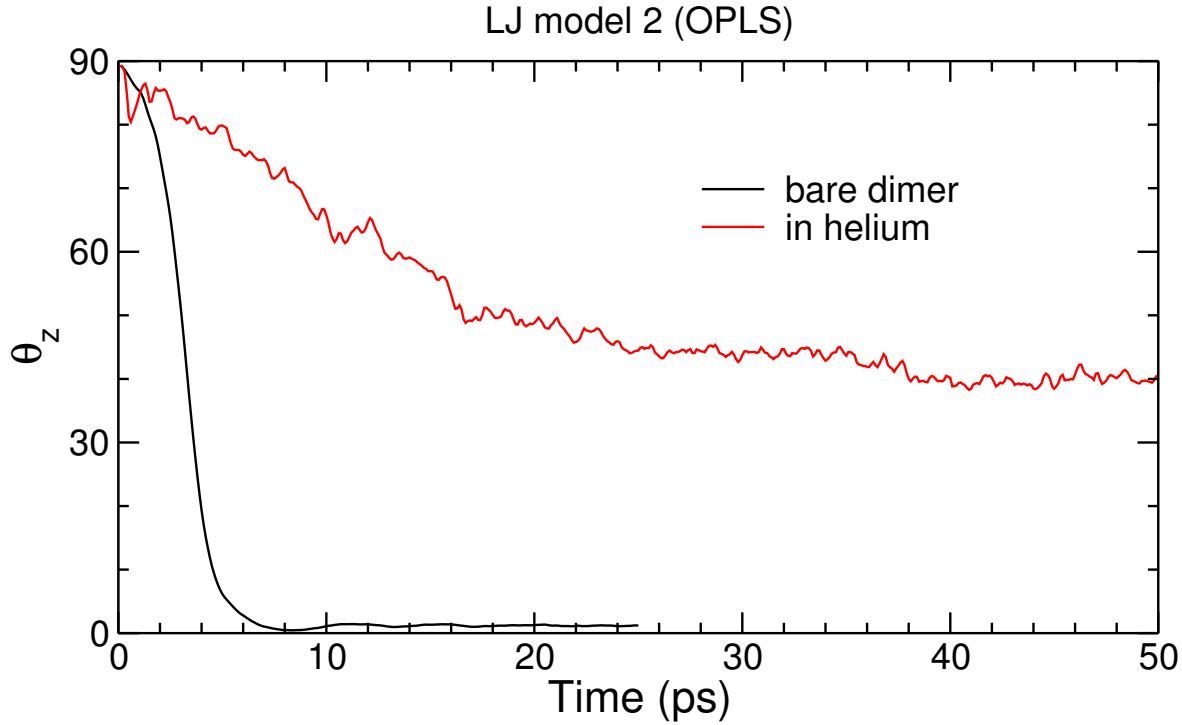
rotated

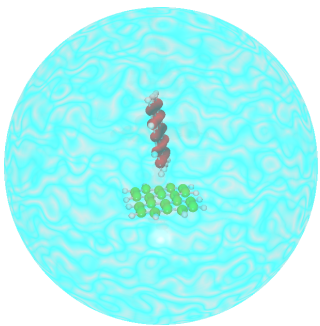
$\rightarrow$Relative energies in vacuum vary from -100 meV to +800 meV depending on QC level

In helium environment, individual molecules may drag some helium atoms in the vicinity of aromatic planes

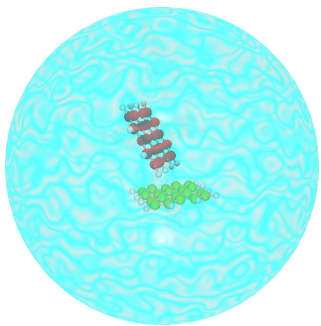
Simulating pick-up experiments: perylene dimer

Successive pick-up of perylene molecules: case of metastable "T-shape" configuration

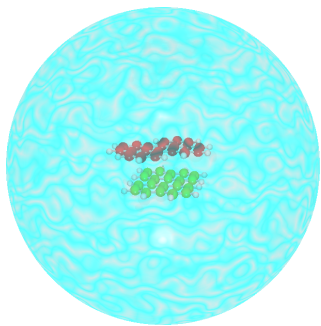




T shape

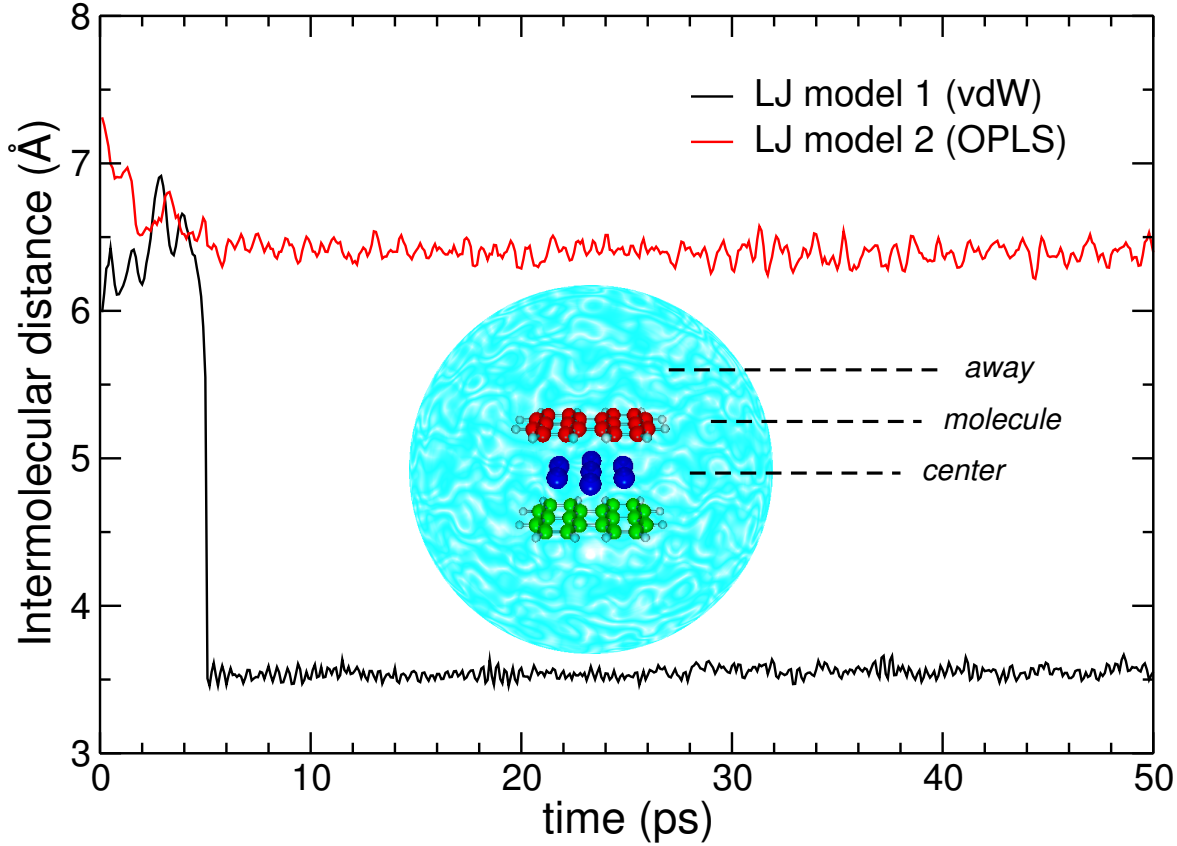


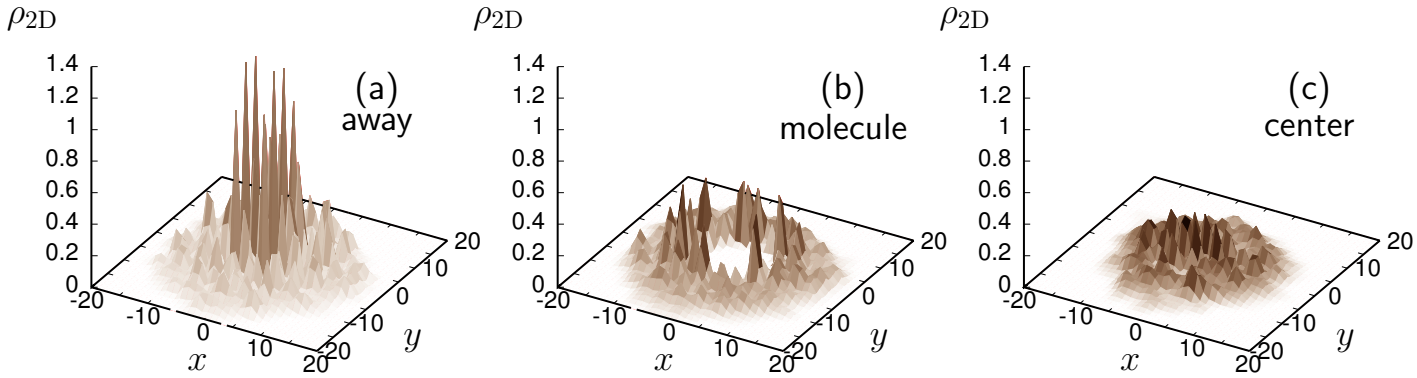
bent



stacked

"Sandwiched" metastable dimer

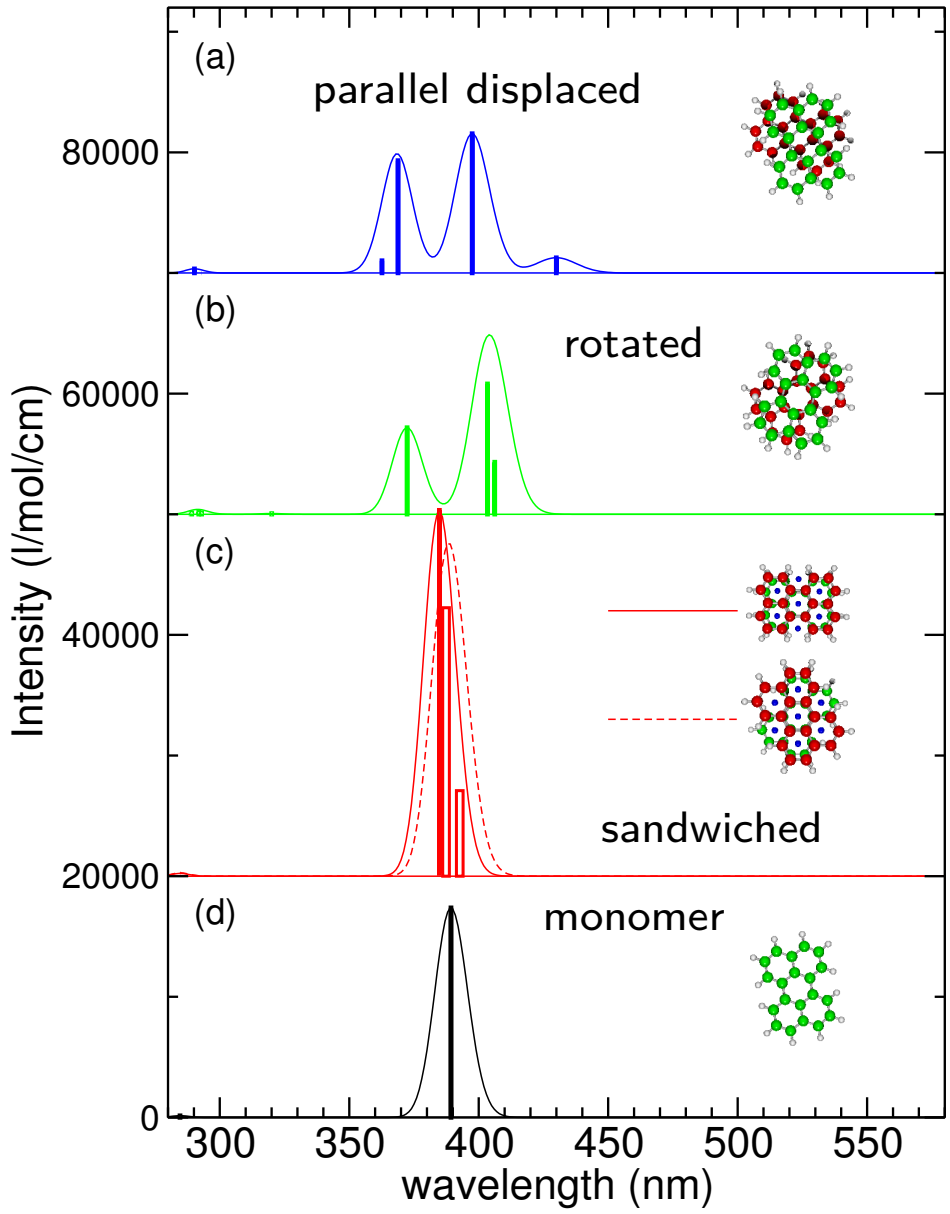




Optical signature?

TD-DFT calculation of optical absorption spectra of the various oligomers

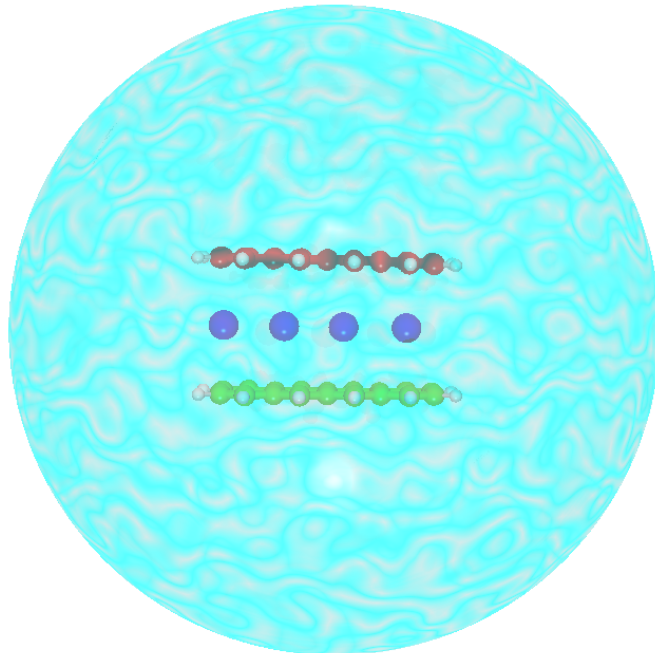
→metastable configurations *not distinguishable*



Metastable tetracene dimers?

Stability of a sandwiched stacked configuration of tetracene dimer

t= 0.5 ps



Conlusions and Outlook

- Solvation of polyaromatics begins with strongly localized helium atoms near hexagonal and pentagonal facets; strong preference for interior of curved flakes
- After being filled, additional atoms occupy peripheral regions but are much less bound and localized
- Subsequent atoms nucleate and grow additional solvation shells, tending to become uniformly distributed
- Extra localization can produce metastable oligomers through the formation of Atkins snowballs; localization is expected to be exacerbated for sandwiched atoms

Open questions

1. Role of exchange statistics?
2. Effective potential between monomers?
3. Explore the kinetics of oligomer formation?

Thank you for your attention!