Unravelling the excited state dynamics in Graphene Quantum Dots: from coronene to circumcoronene.

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September 7, 2023

Introduction

Graphene quantum dots (GQDs):

What is a GQDs?

"nanoparticle or region that exhibits quantum confinement in all three spatial directions."

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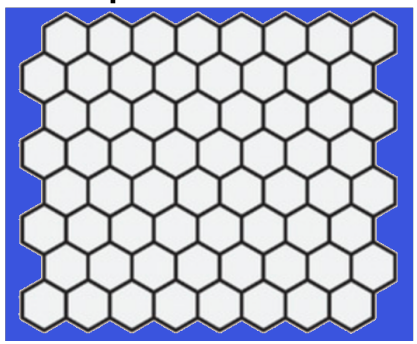

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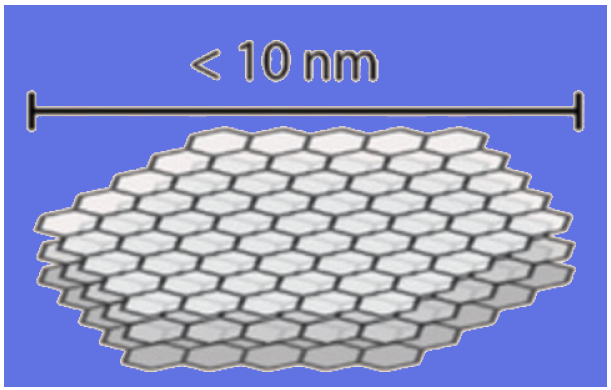

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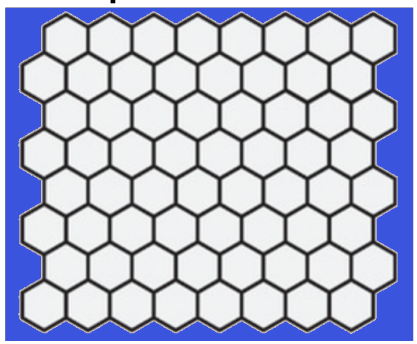

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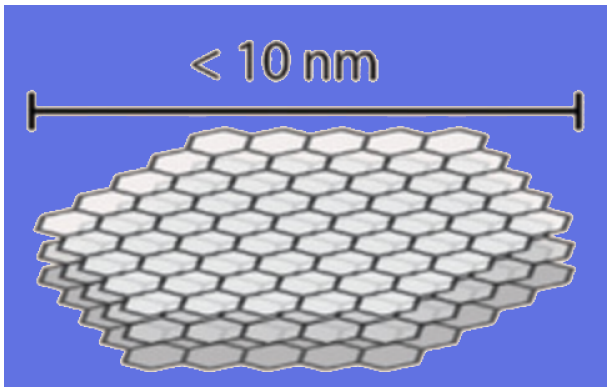

And then...why **QUANTUM**?

"...due to their nanoscale size, quantum effects play a significant part in their light emitting properties"

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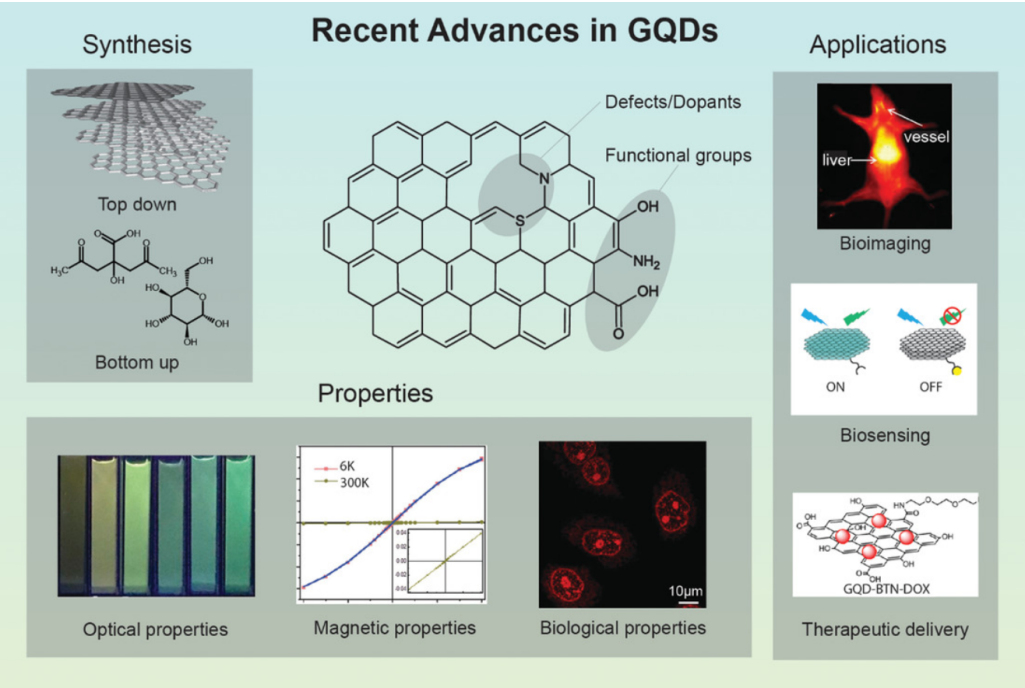

Unique properties for a **wide range of applications:**

- → Tunable electronic structure, magnetic properties, biological properties, photoluminescence (PL),...
- → Bioimaging (via optical/ magnetic modalities), in vitro/in vivo biosensing, drug delivery or gene delivery in therapeutic approaches, photodynamic therapy (PDT),...

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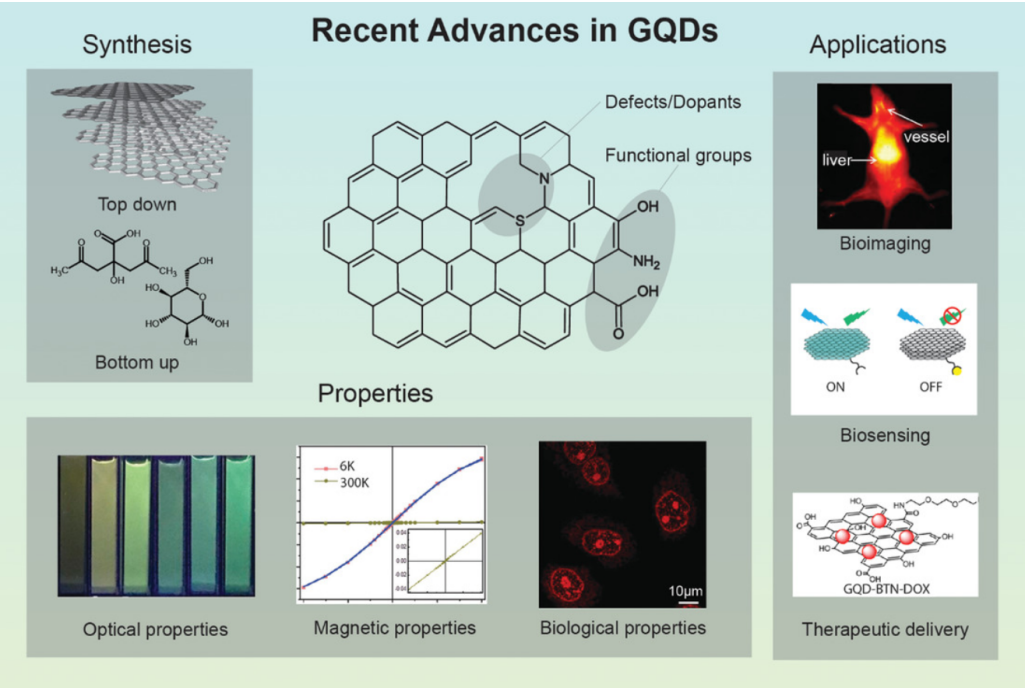

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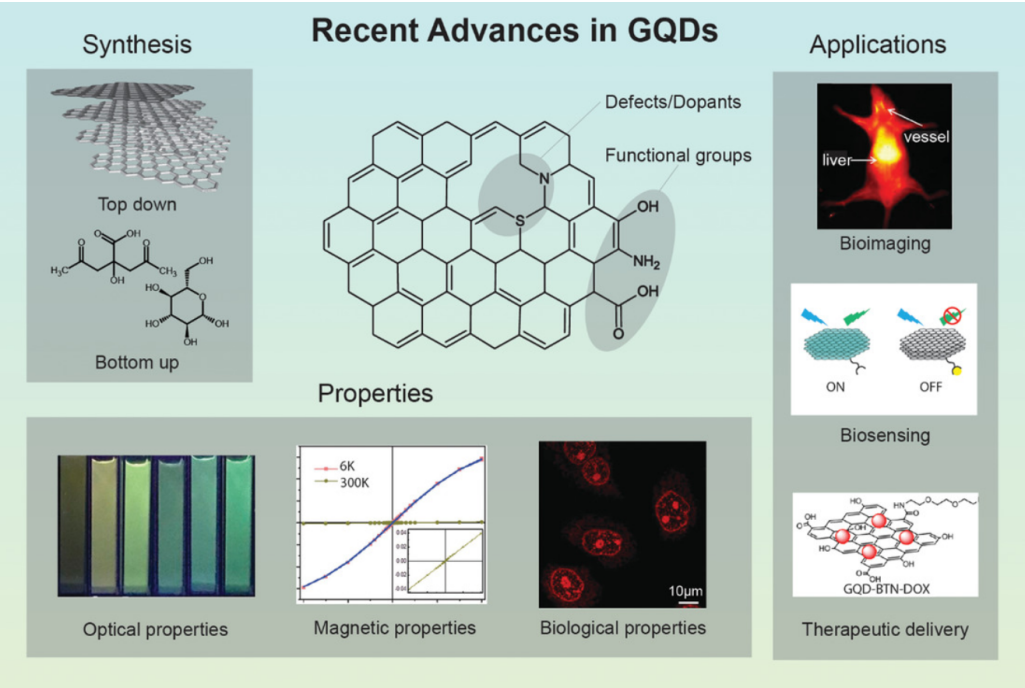

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We are theoreticians, so we need **reduced model** systems

Reduced model system: Coronene

Coronene

Smallest **Polycyclic aromatic hydrocarbons (PAHs)**

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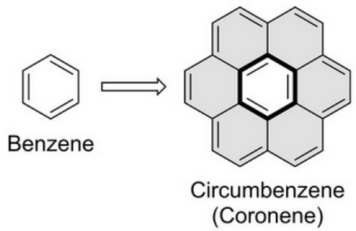

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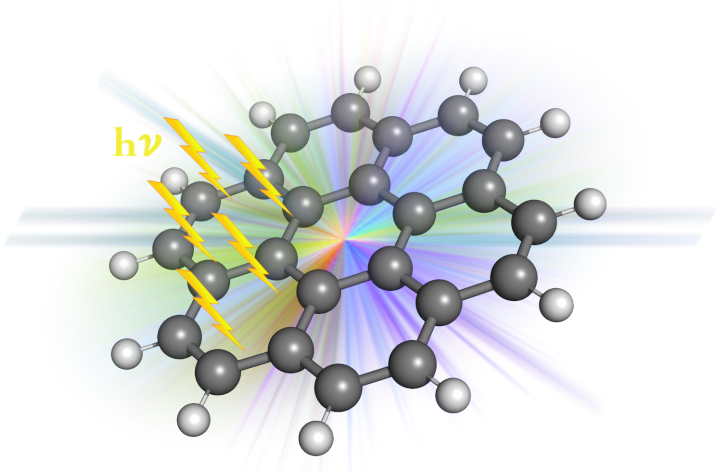

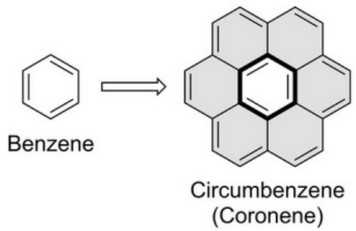

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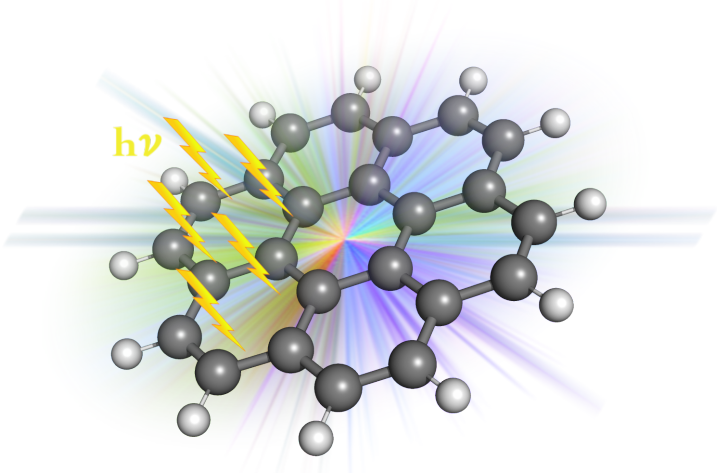

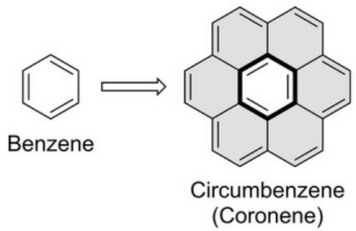

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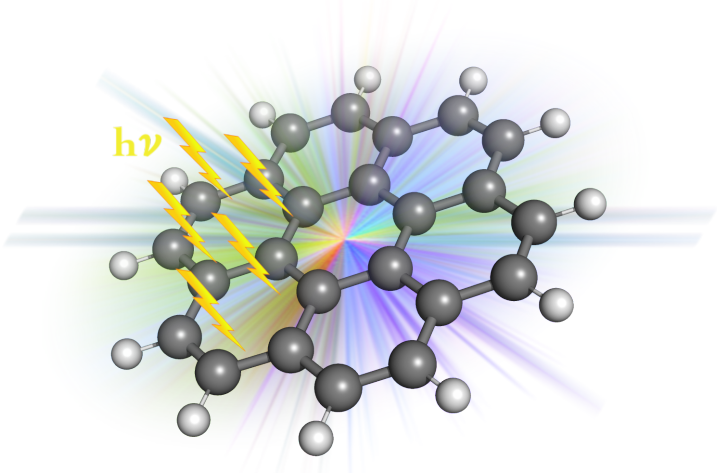

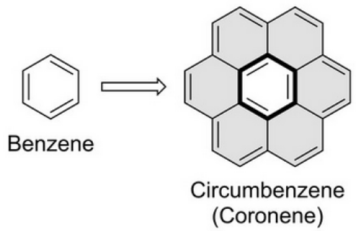

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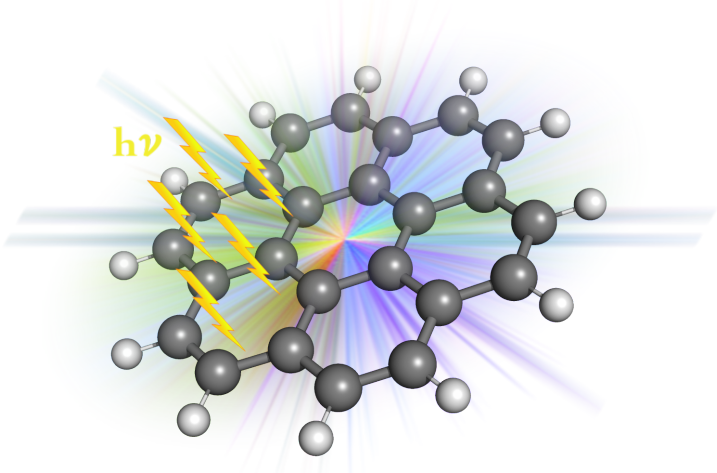

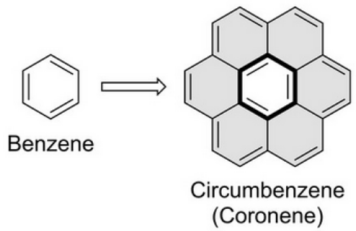

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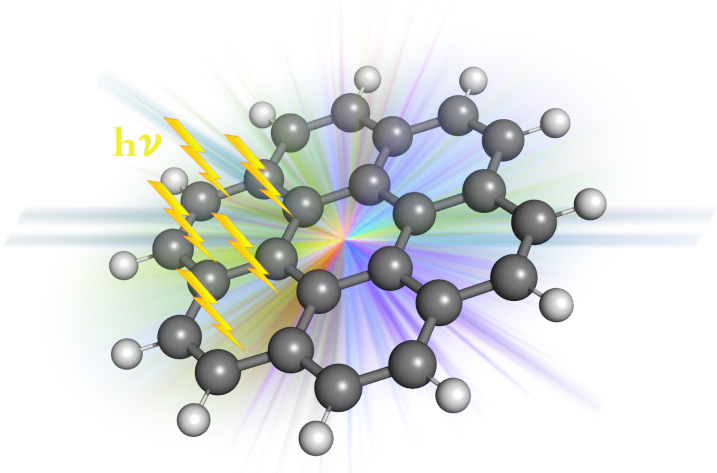

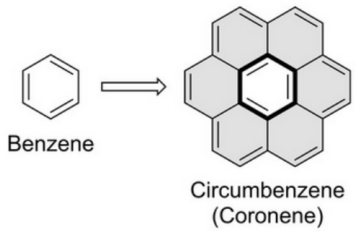

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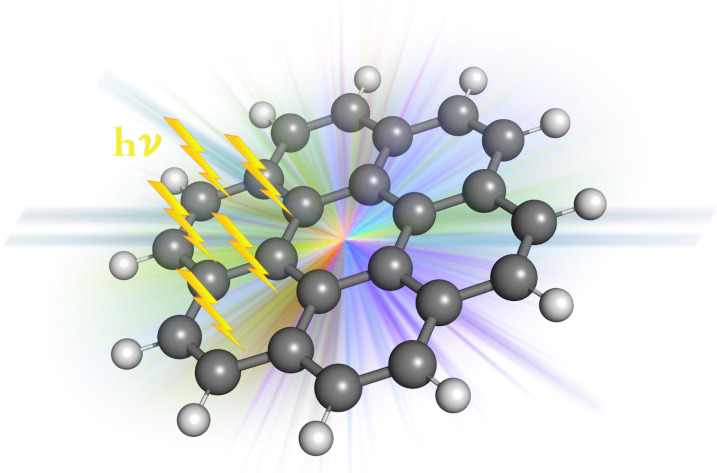

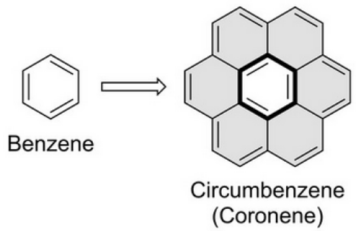

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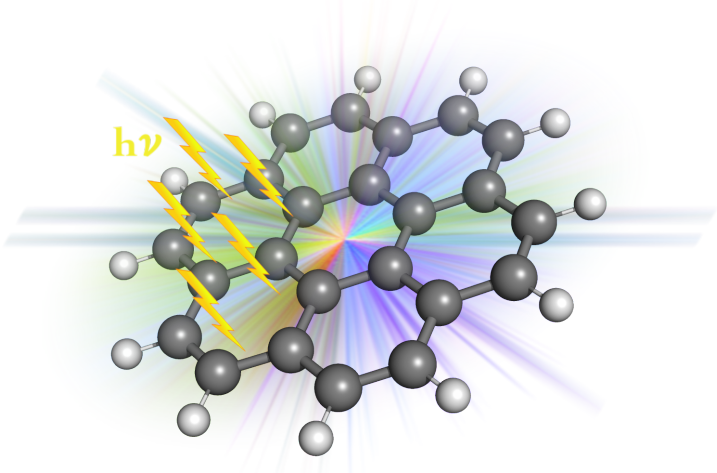

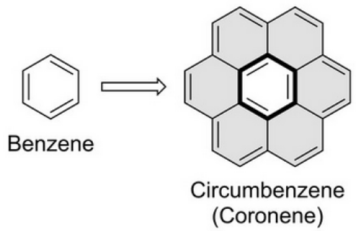

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- → Very high density of states

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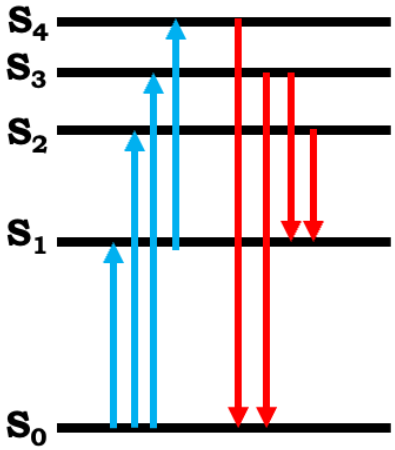
Coronene: Absoption and Emission experiments



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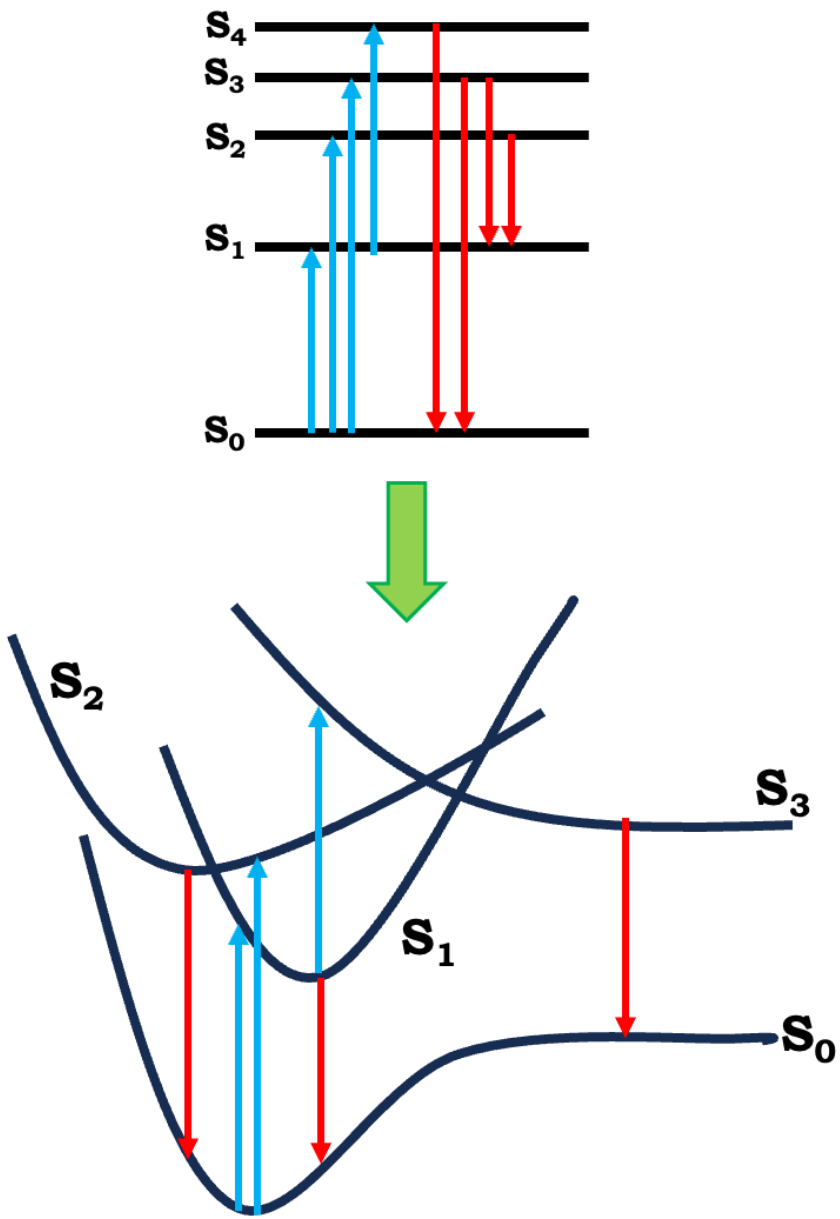

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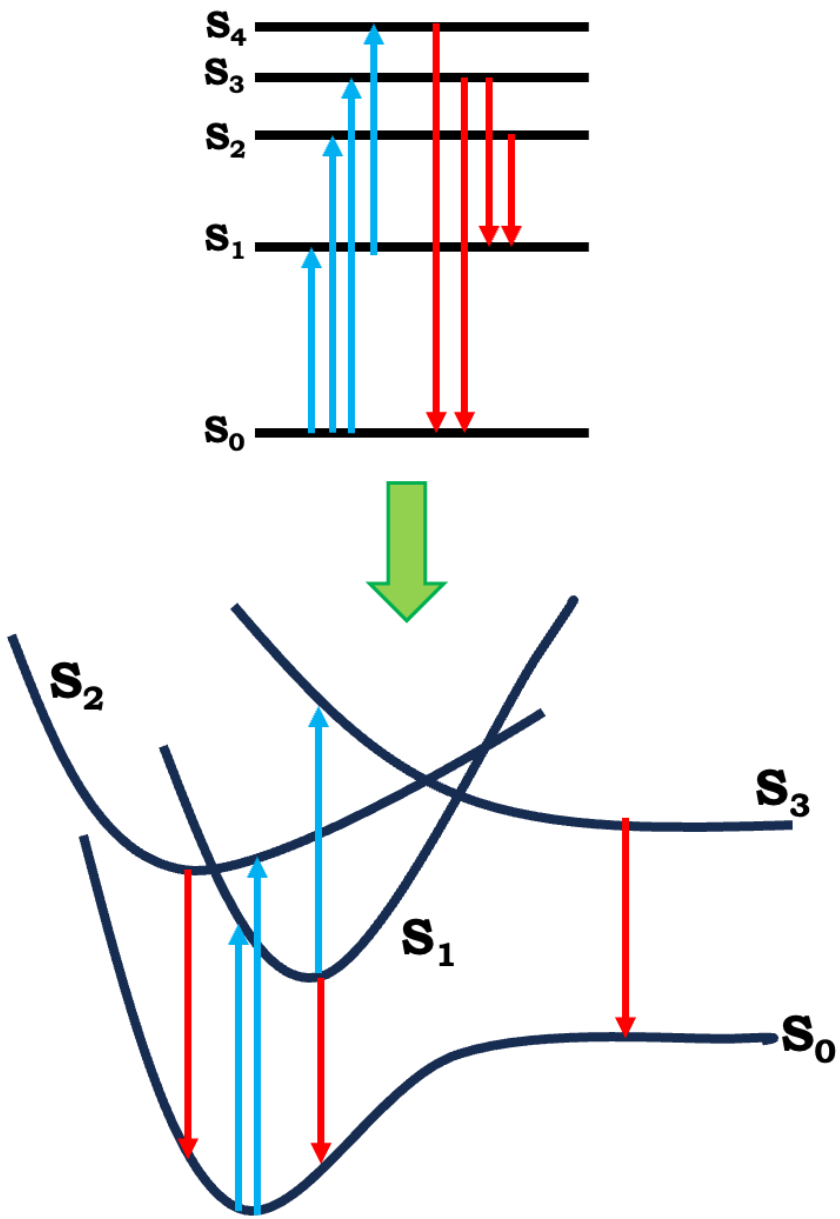

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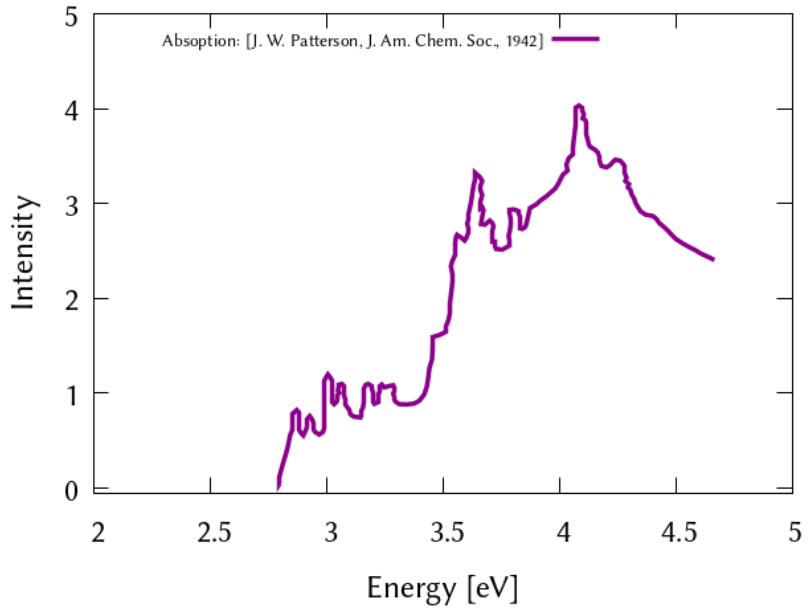

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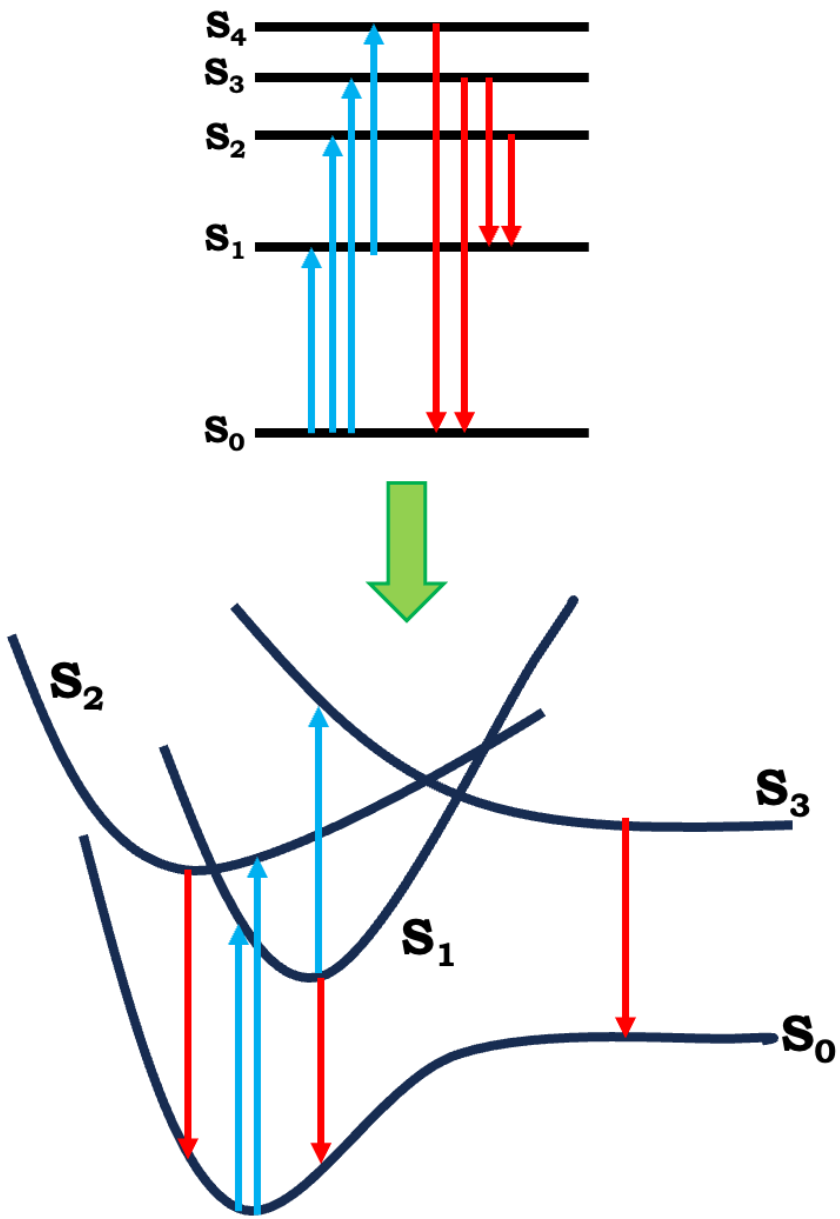

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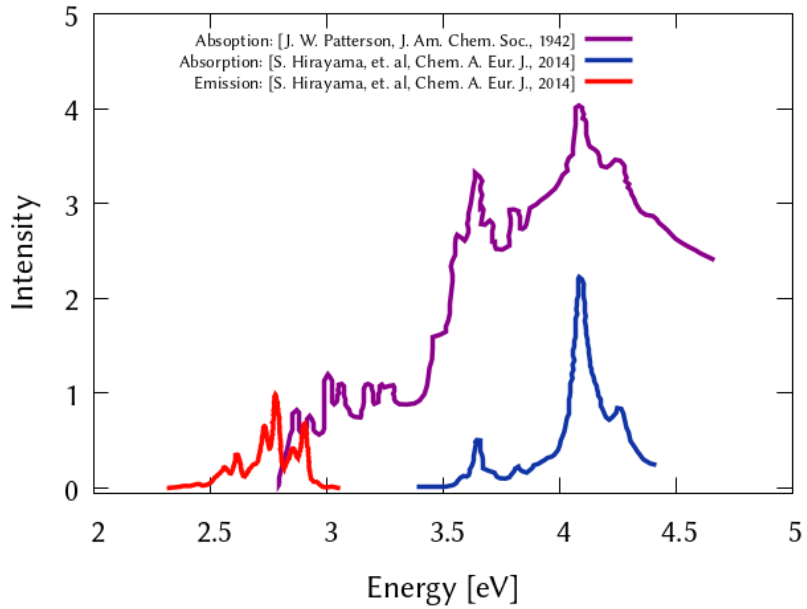
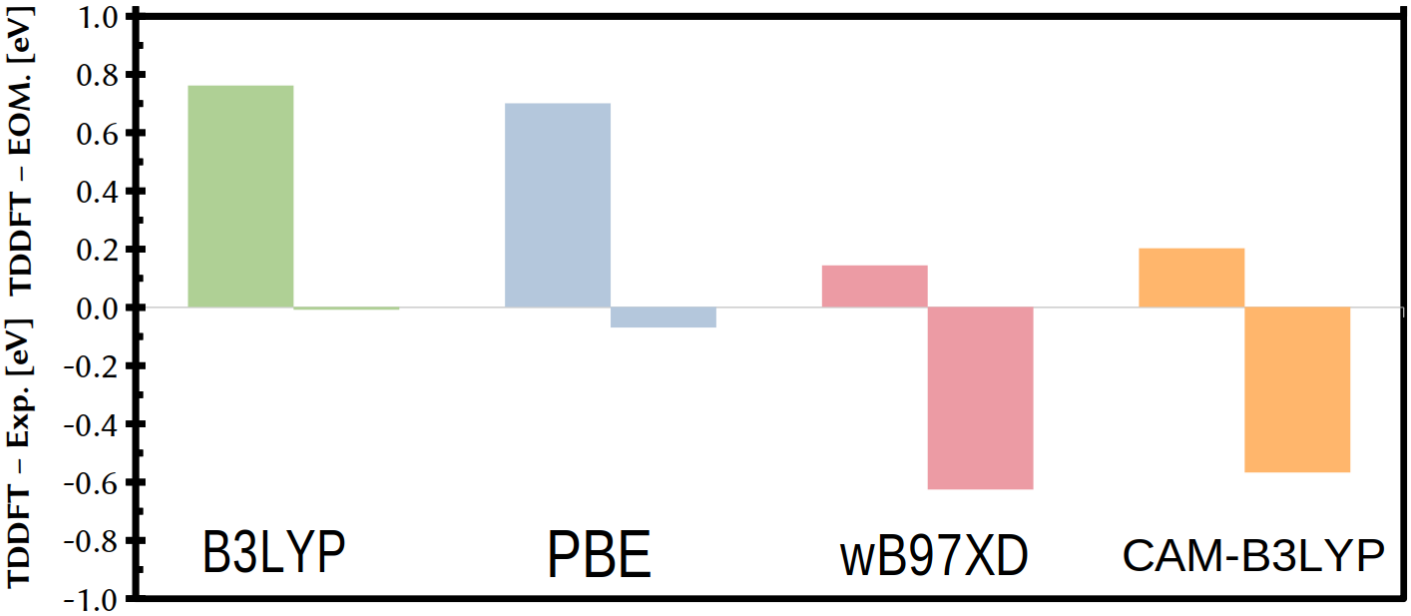


1st absorption band at 3.65 eV
2nd absorption band at 4.13 eV
Emission (exciting to the 1st band)
2.4-2.8 eV (phosphorescence?)

Coronene: Quantum chemistry benchmark

Energy deviations of the bright state with respect to experiment and EOM-CCSD.



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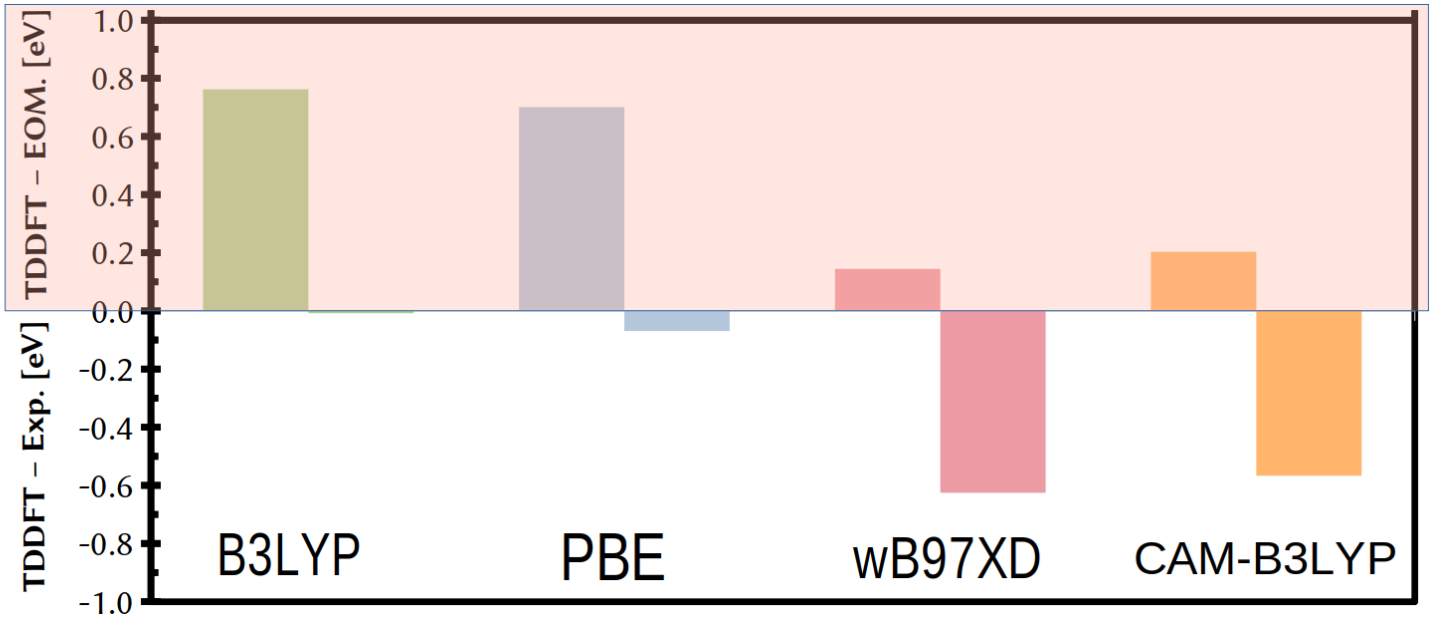

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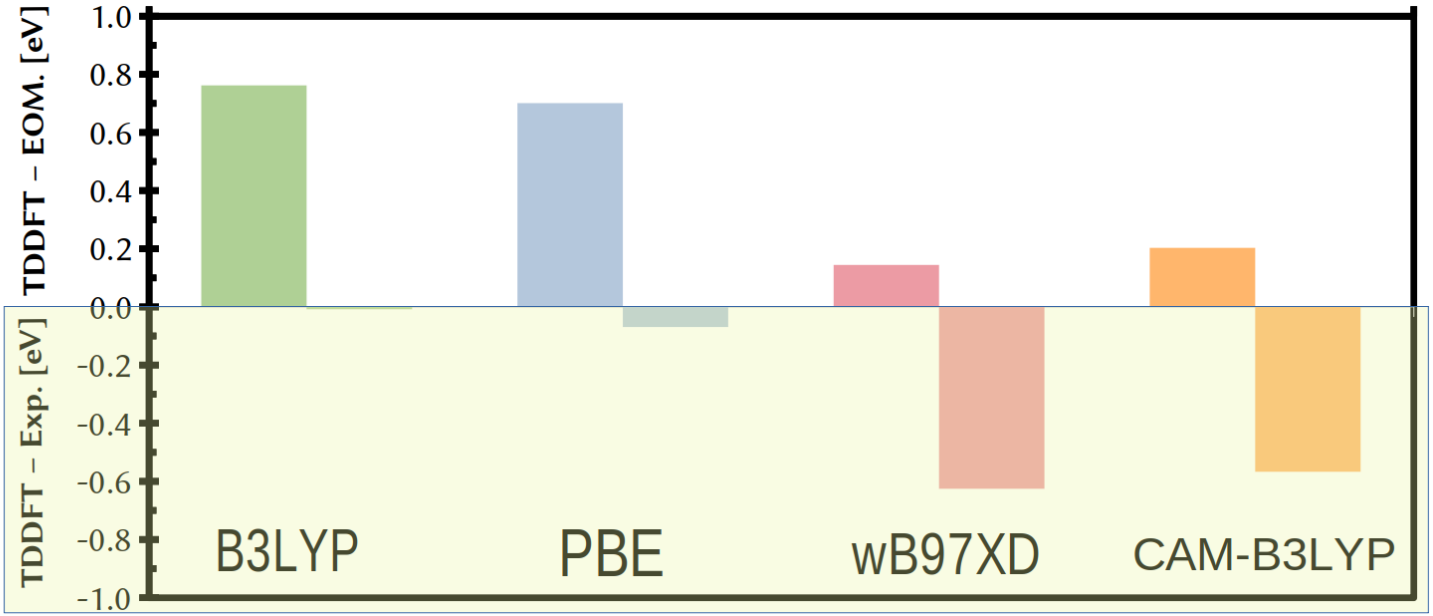
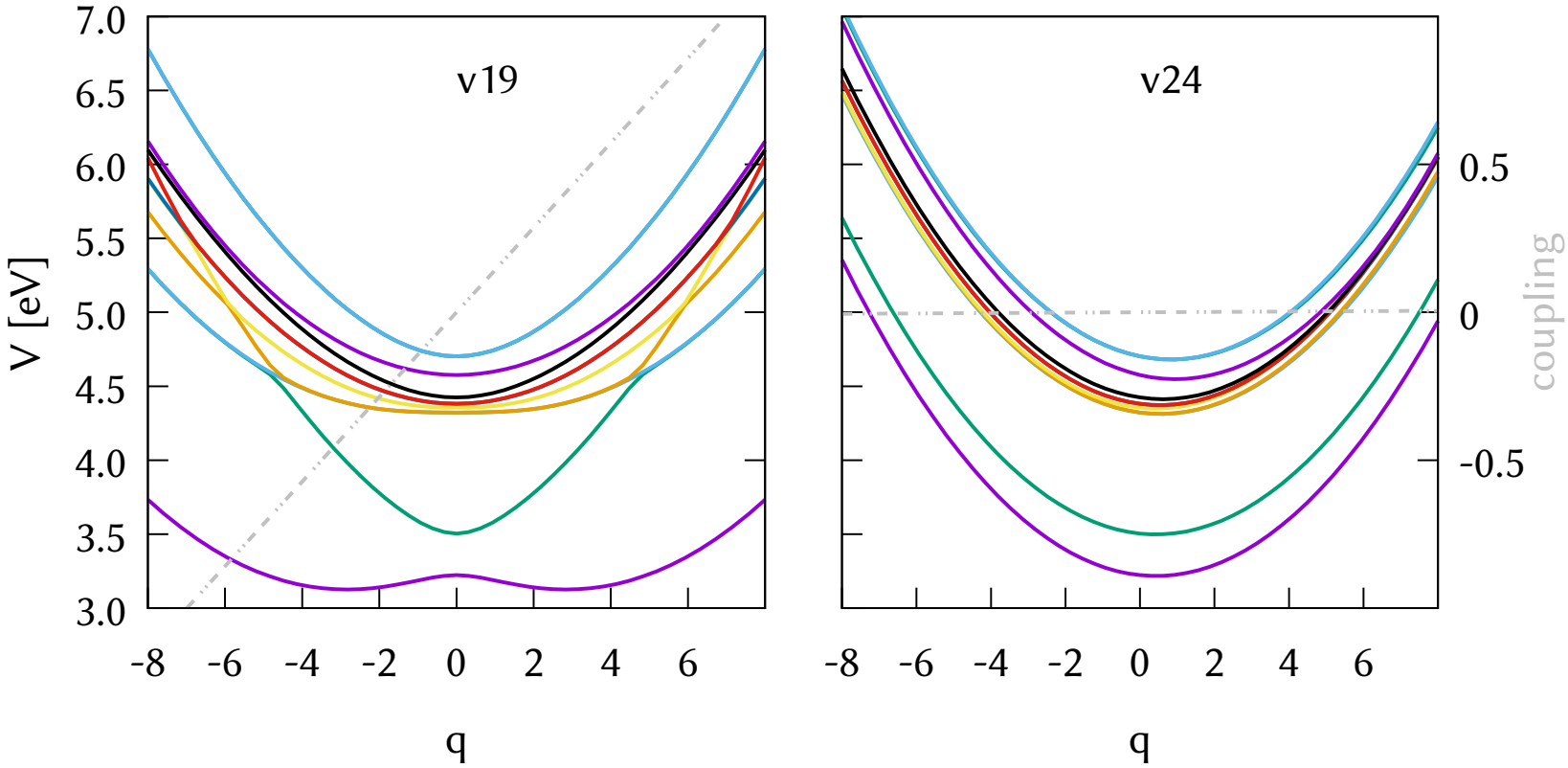


Based on experiments: We choose B3LYP/6-31G**+.

Let's start computing the absorption spectrum!
What about dynamic effects?

Coming back to coronene

First step: Construction of the LVC potentials



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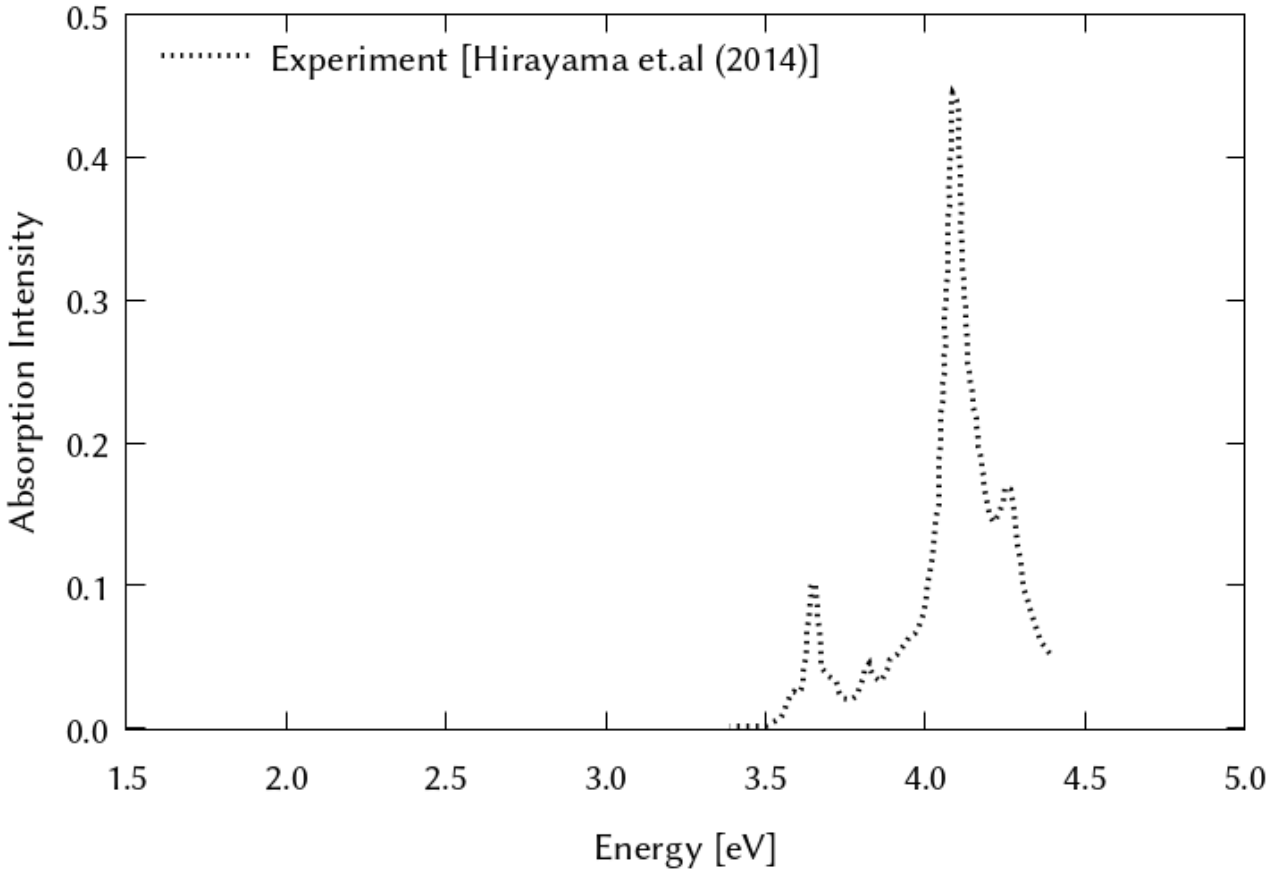
Second step: Validate the approximated Hamiltonian



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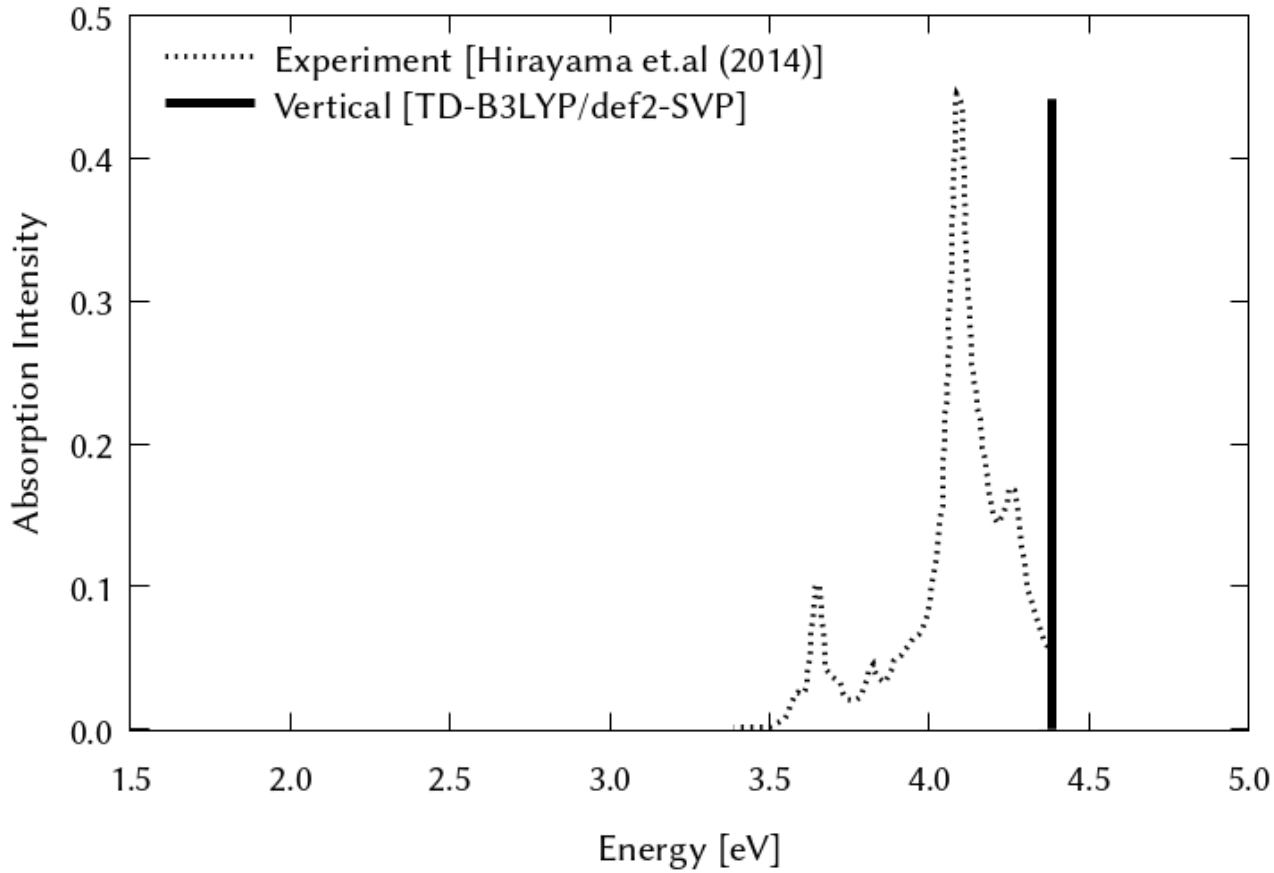

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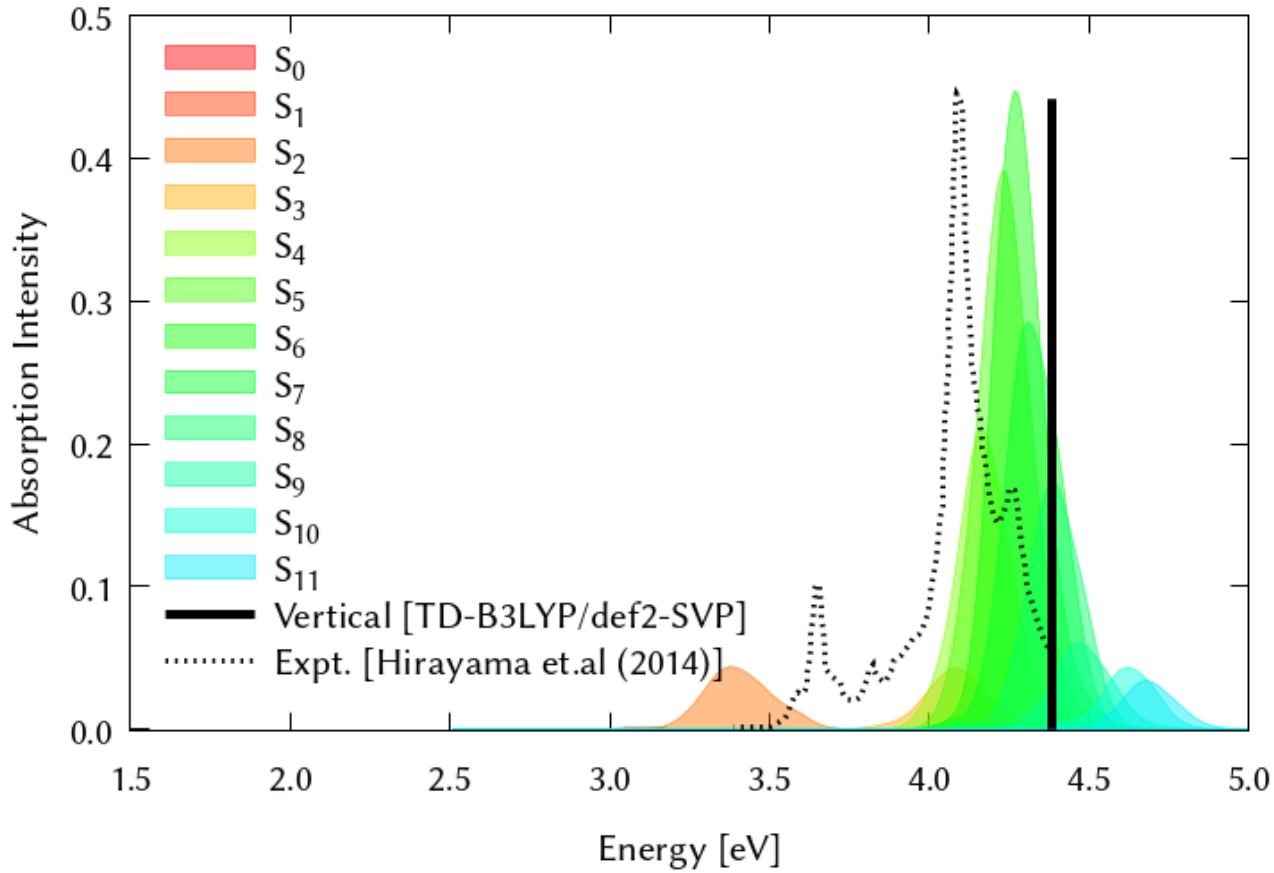
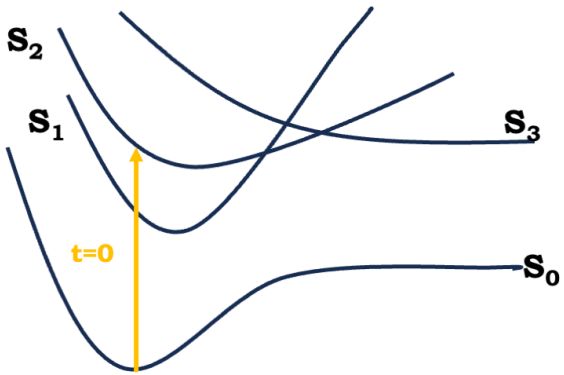


Excited state quantum dynamics from the $1B_{3u}$ (S_2)



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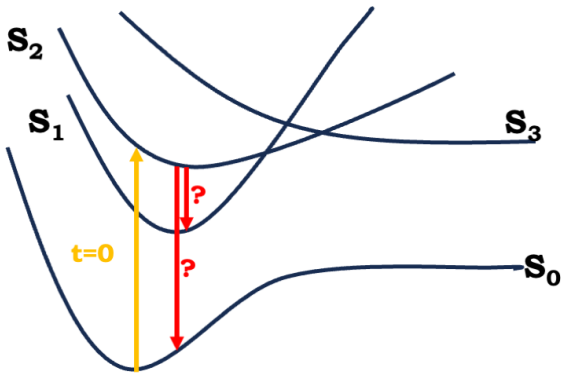

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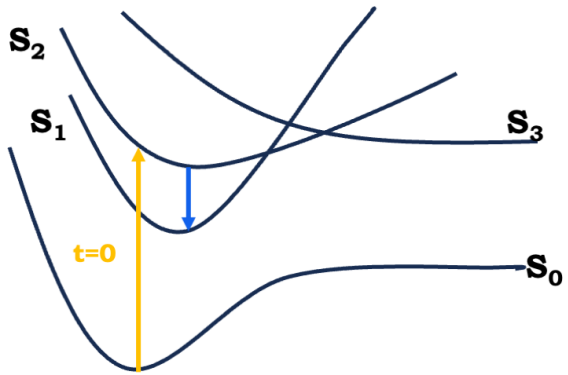

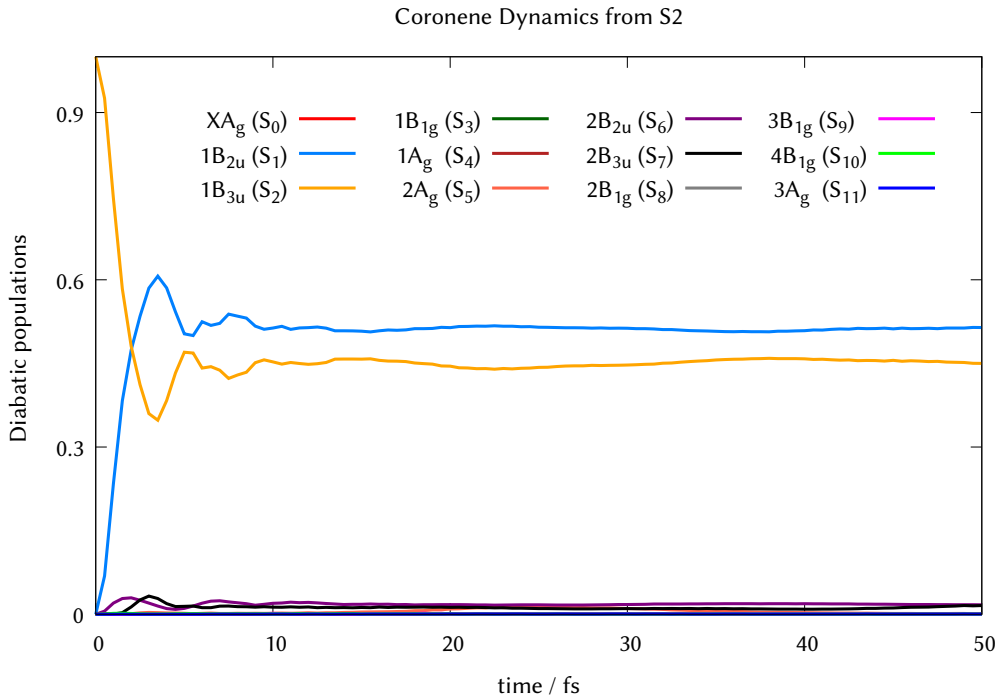

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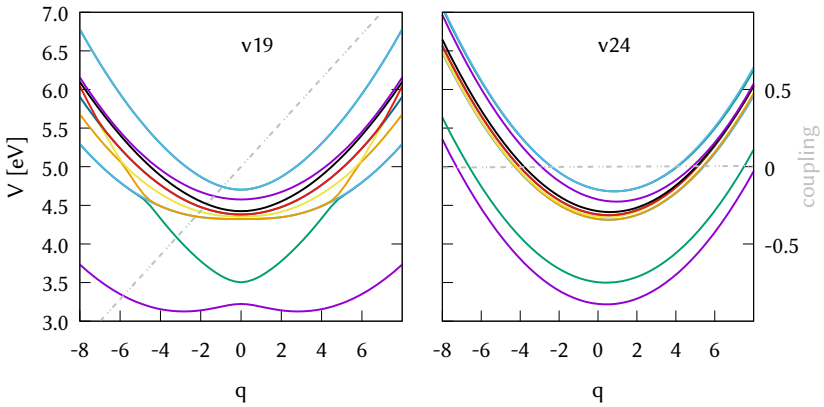

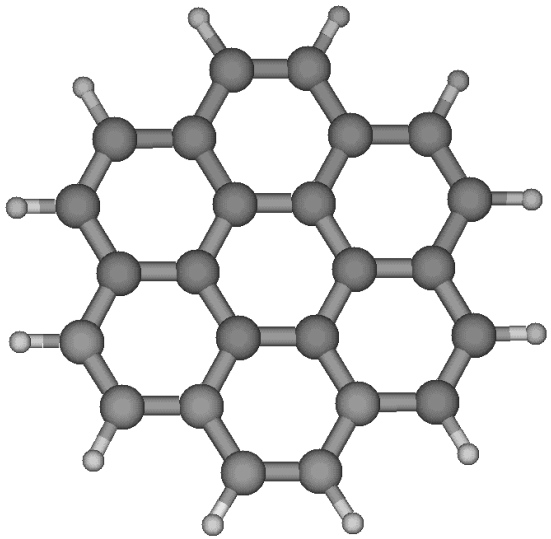

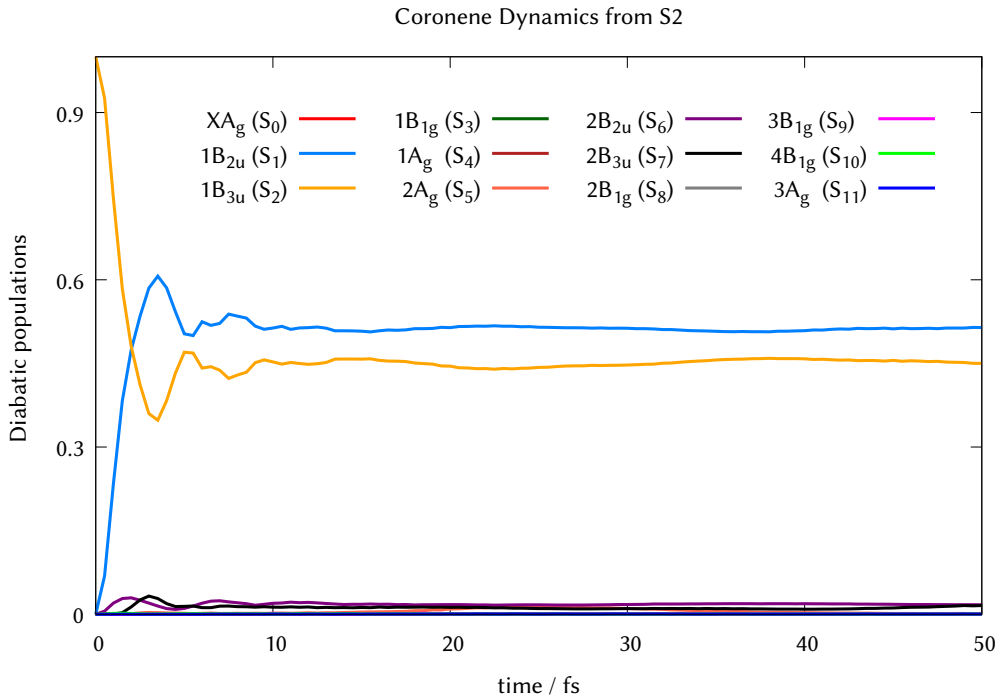

Leading vibrations:

- Breathing: $\nu_{24}, \nu_{60}, \nu_{77}$
- Tilting: $\nu_{19}, \nu_{64}, \nu_{79}, \nu_{88}$
- CH stretching: ν_{108}

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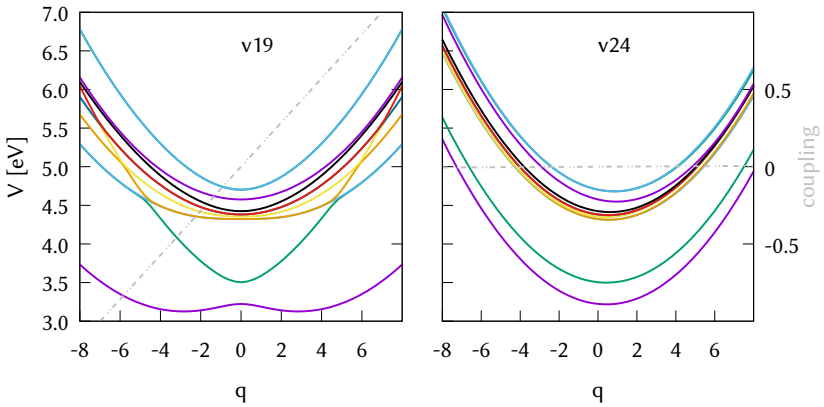

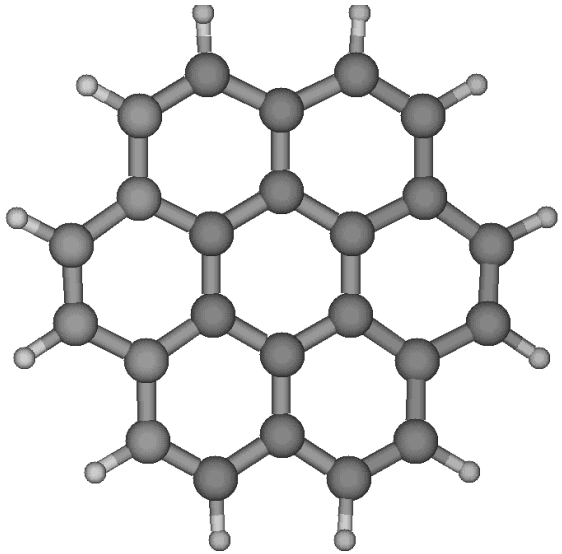

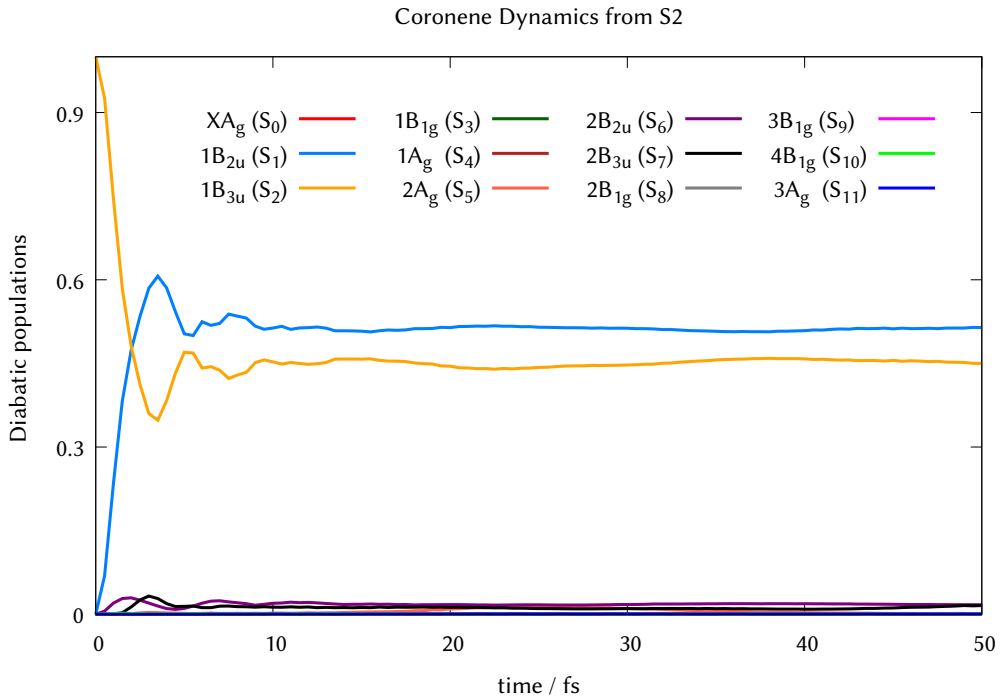

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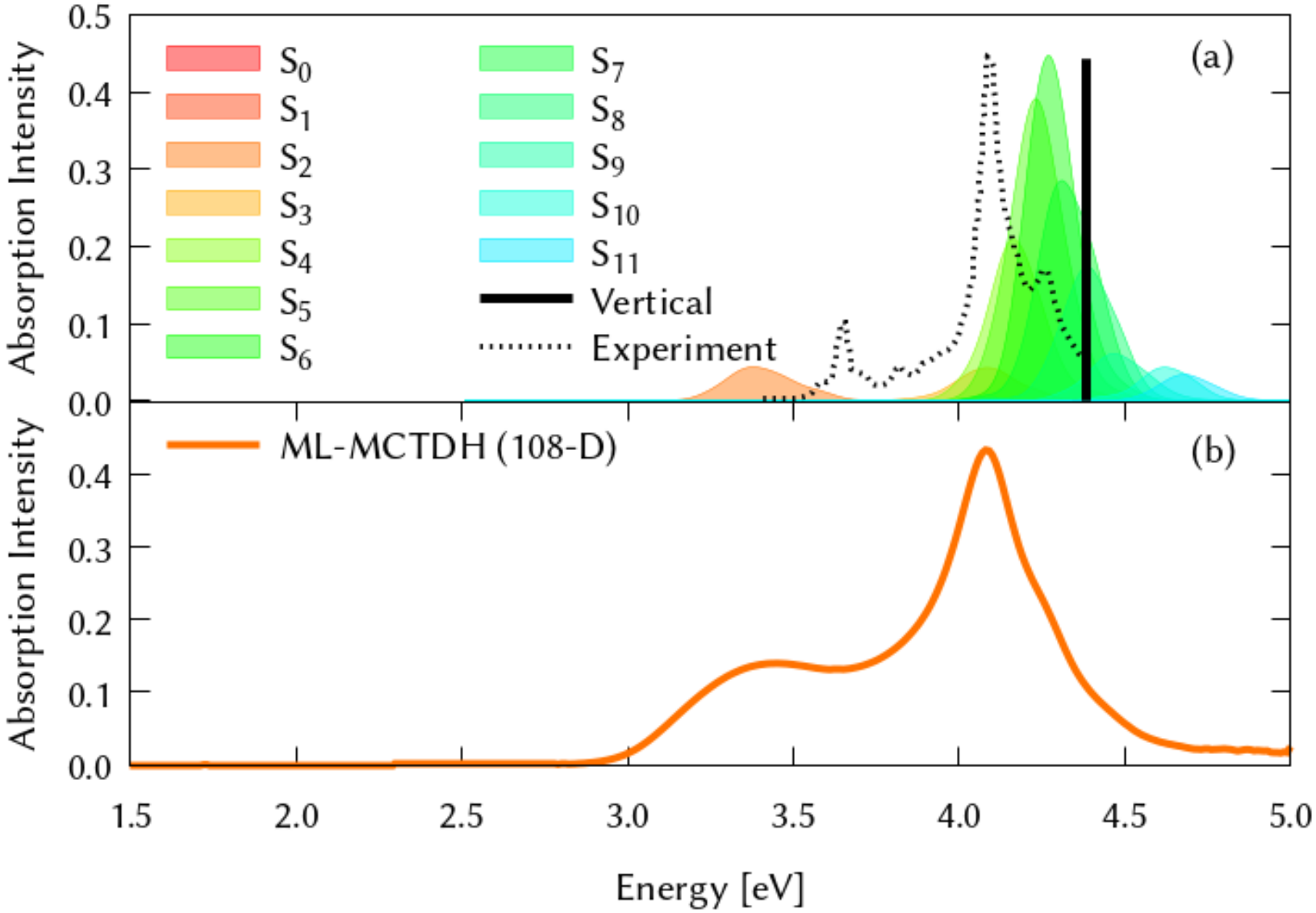
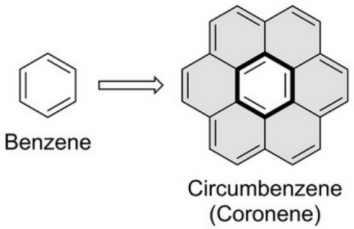
Absorption spectrum of coronene



Towards Graphene: Circumcoronene

Remember we want to study GQDs...

It is the coronene a good reduced model to study larger systems?



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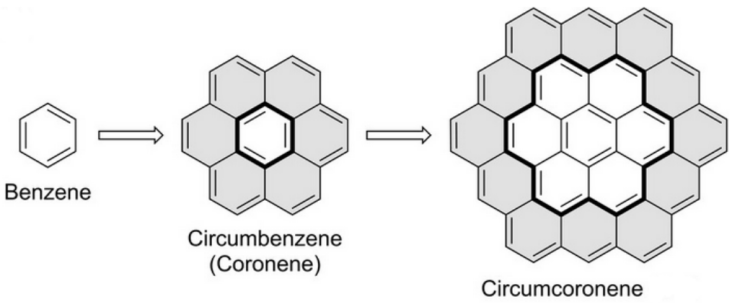
It is the coronene a good reduced model to study larger systems?



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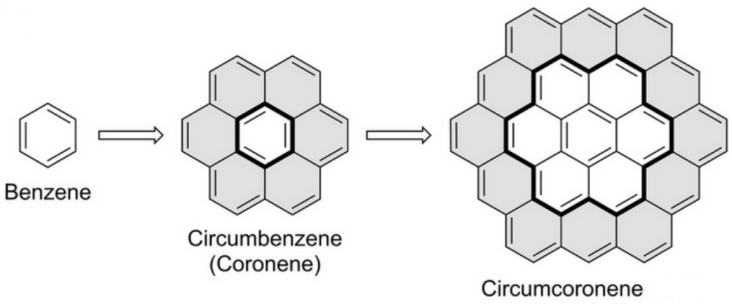
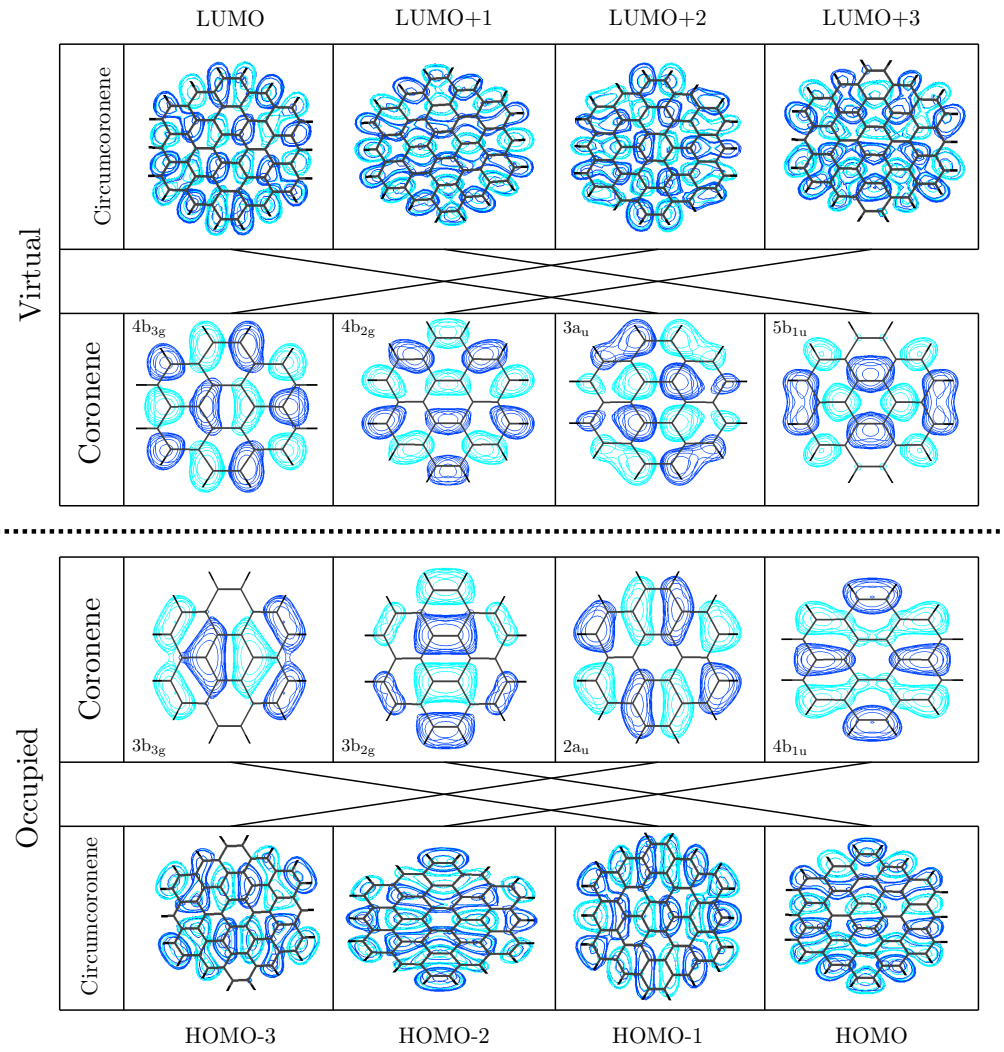


TD-DFT (B3LYP/6-31G**+) $\longrightarrow$

π^* MOs in coronene and circumcoronene:



Towards Graphene: Circumcoronene

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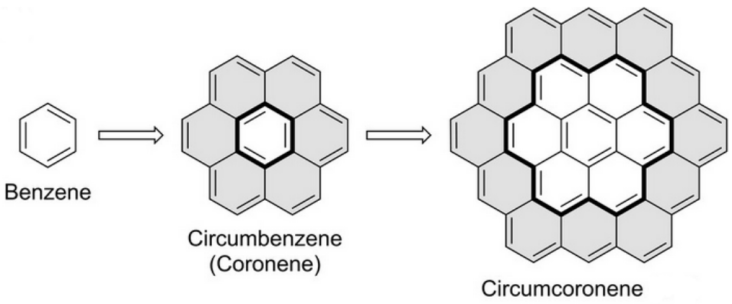
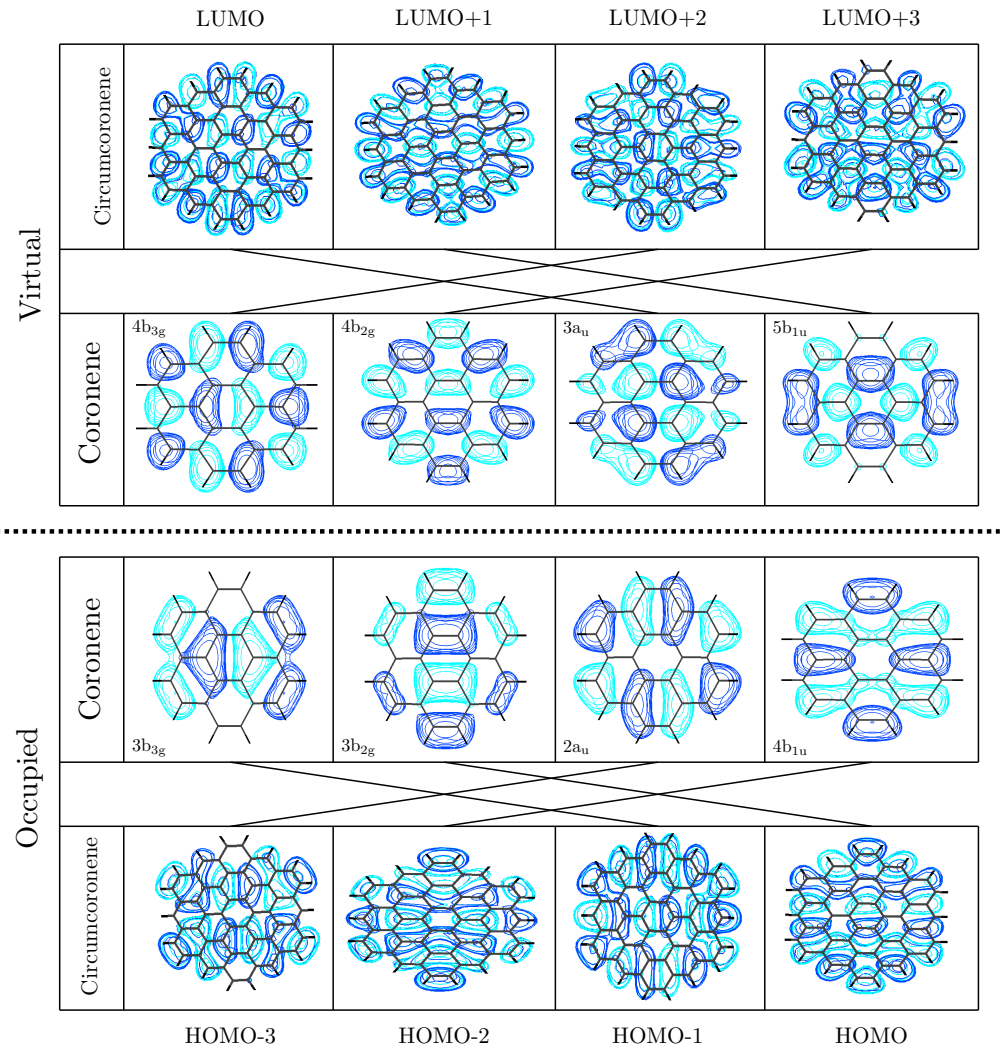


TD-DFT (B3LYP/6-31G**+) $\longrightarrow$

The MOs involved in the bright excited states in coronene:
$2B_{2u}$ (S_6) and $2B_{3u}$ (S_7),

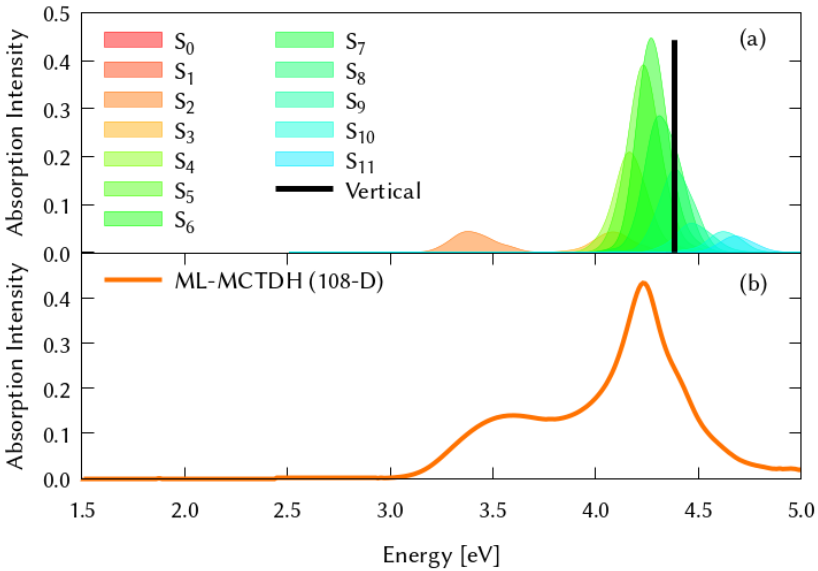
are the same in the bright excited states in circumcoronene:
$2B_{2u}$ (S_3) and $2B_{3u}$ (S_4).

π^* MOs in coronene and circumcoronene:

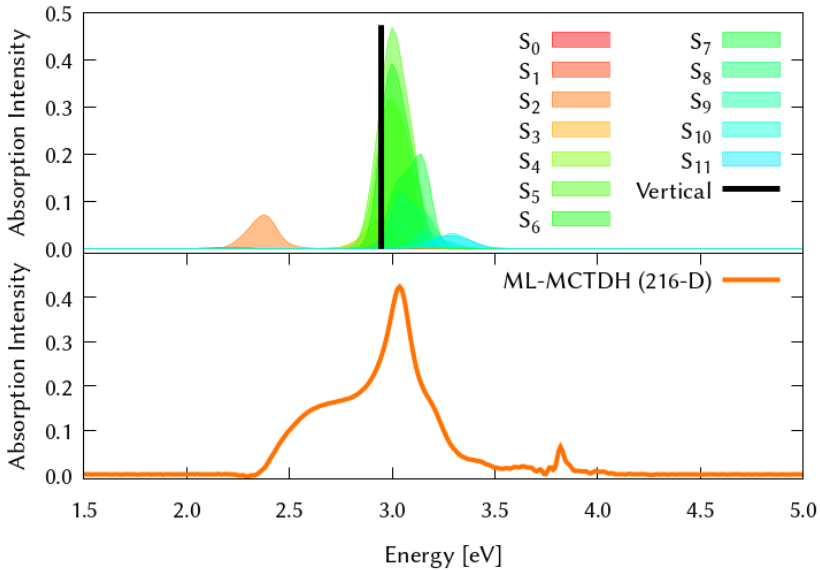


Coronene vs Circumcoronene: Absorption spectra

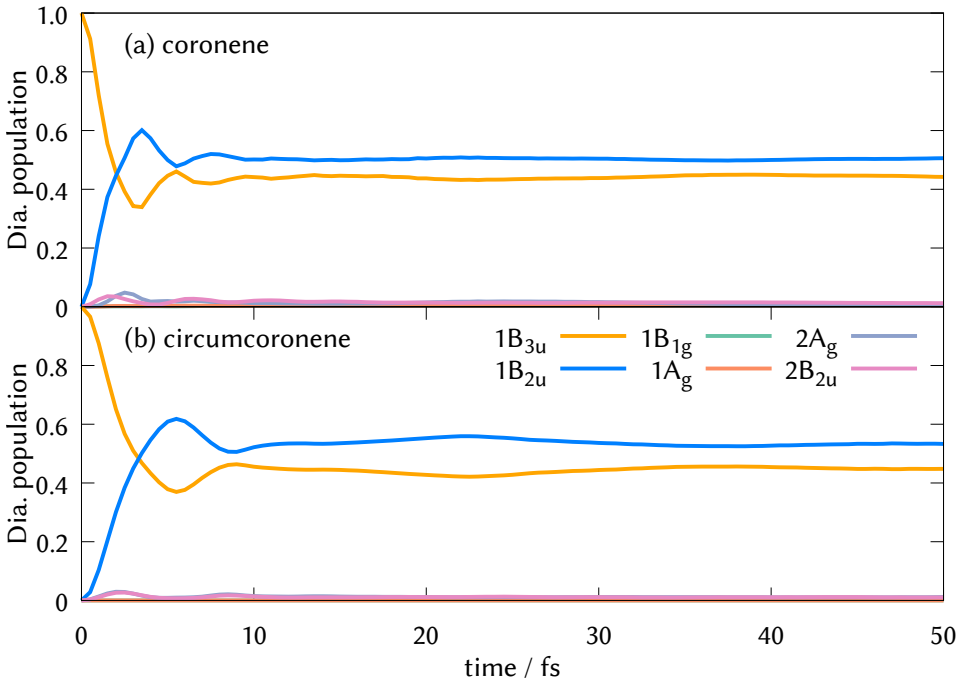
Coronene:



Circumcoronene:



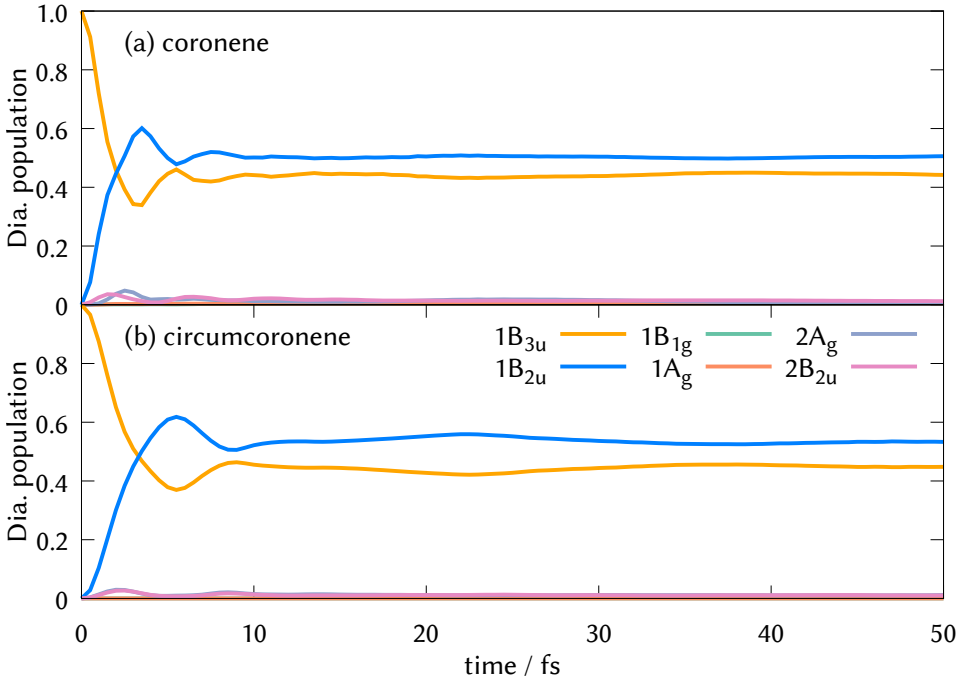
Coronene vs Circumcoronene: Quantum dynamics from S_2



→ Same excited state decay

→ Slower dynamics in circumcoronene

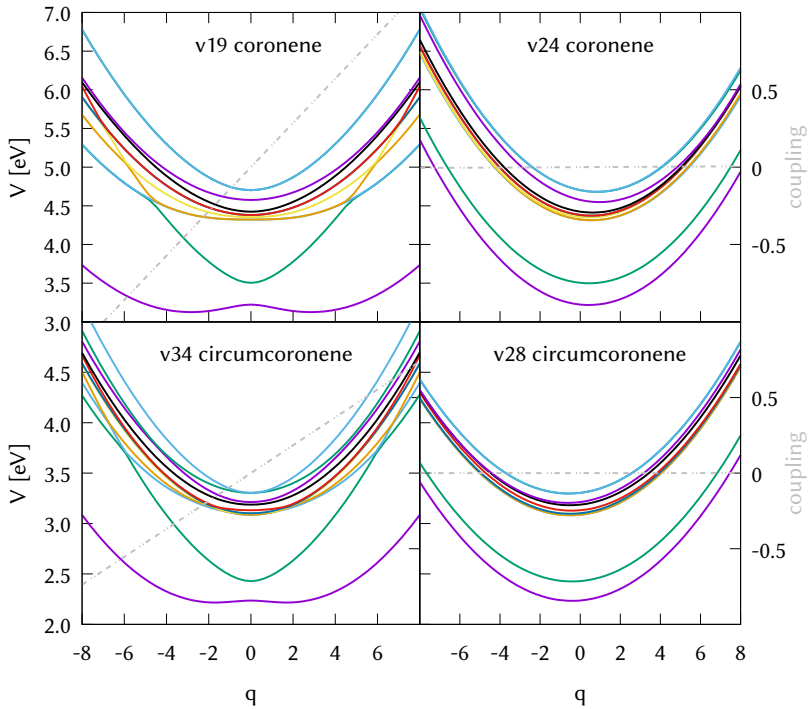
Coronene vs Circumcoronene: Quantum dynamics from S_2



→ Same excited state decay

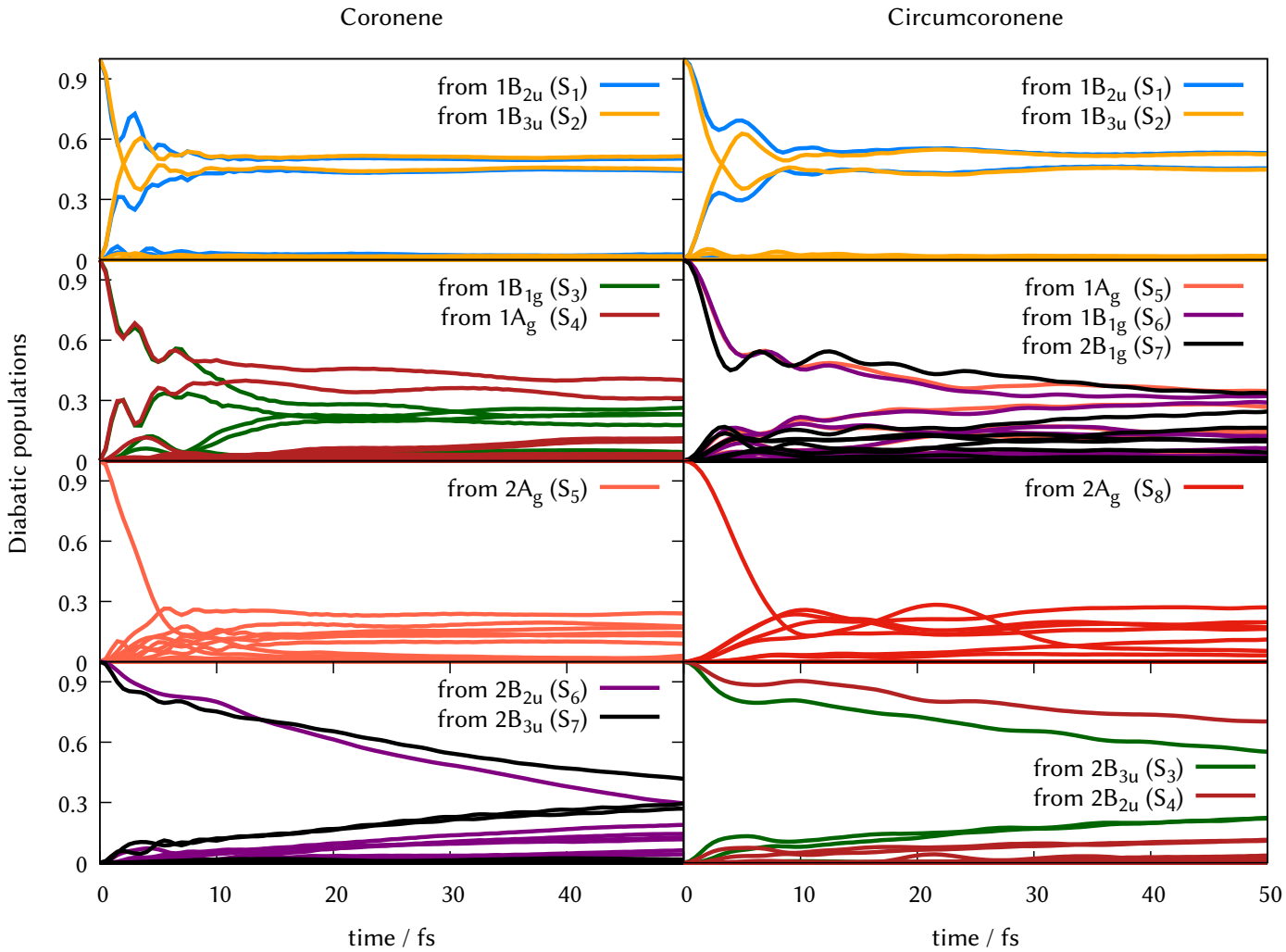
→ Slower dynamics in circumcoronene

→ Same leading modes:



Coronene vs Circumcoronene

Excited state quantum dynamics from every state:



Take home messages

Main conclusions

- Excited state quantum dynamics of coronene:
- Breathing and tilting modes driving the dynamics
- Mixed states in D_{2h}
- Negligible contribution of triplet states

Take home messages

Main conclusions

- Excited state quantum dynamics of coronene:
  - Breathing and tilting modes driving the dynamics
  - Mixed states in D_{2h}
  - Negligible contribution of triplet states
- Excited state quantum dynamics of circumcoronene:
  - Same MOs involve in the bright electronic excited states
  - Same modes responsible of the decay

$\rightarrow$ Coronene is a good model to run ultrafast dynamics in polyaromatic hydrocarbons.

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