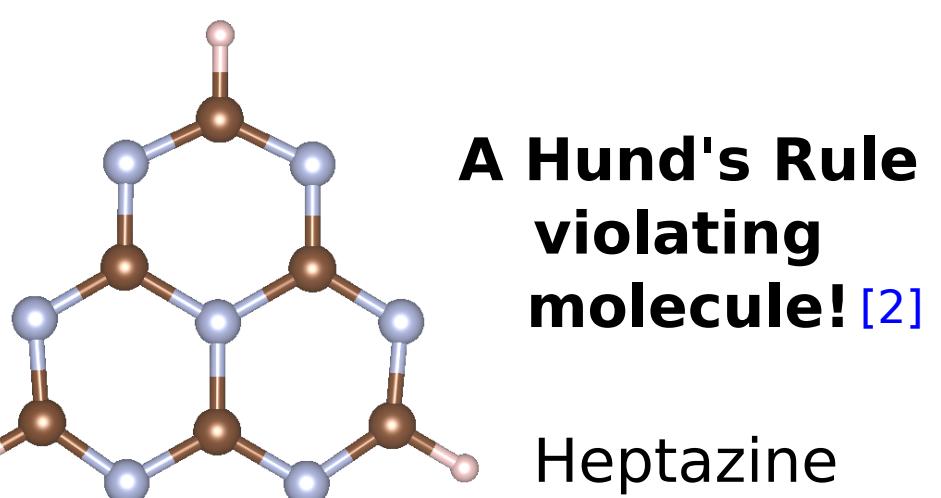
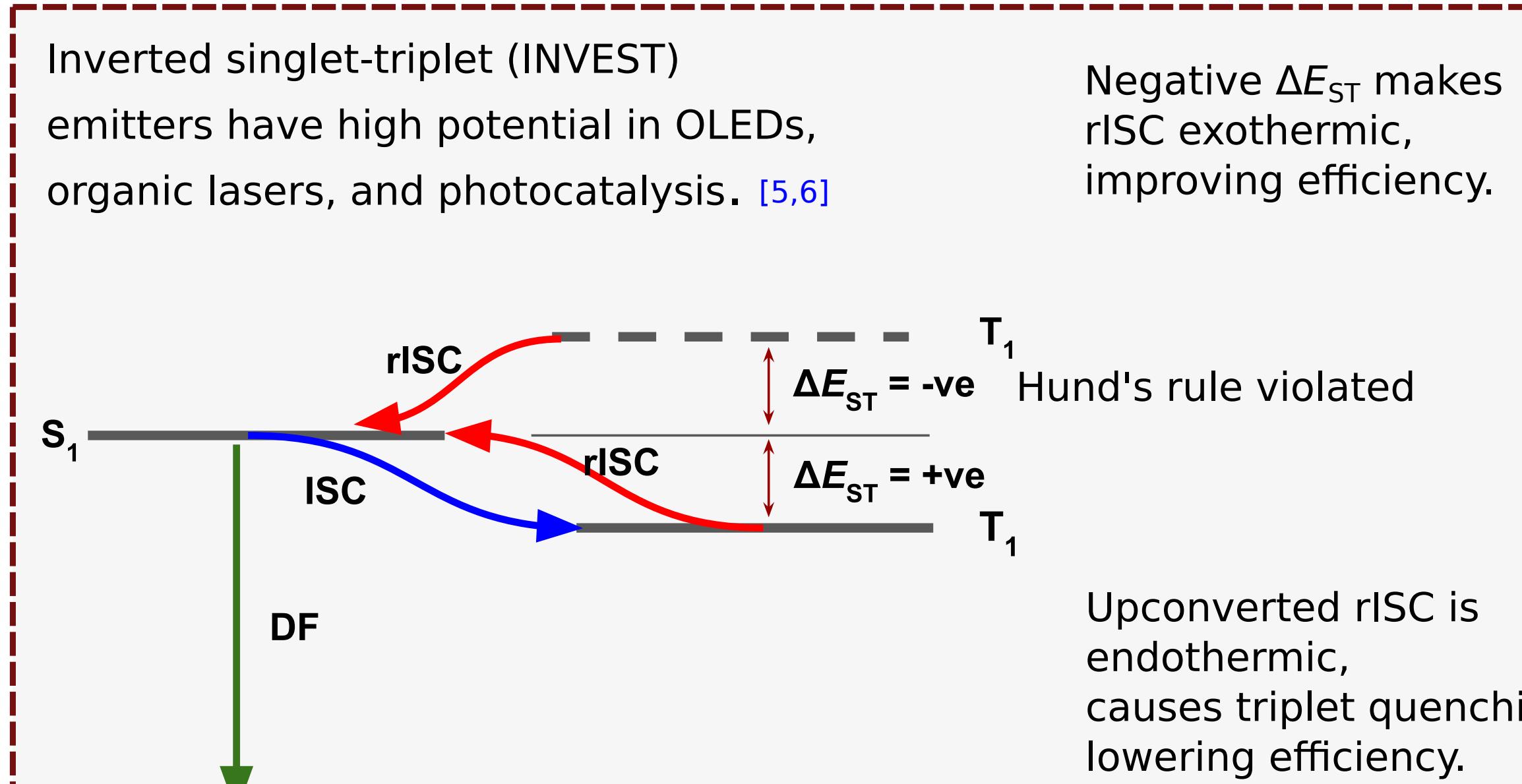
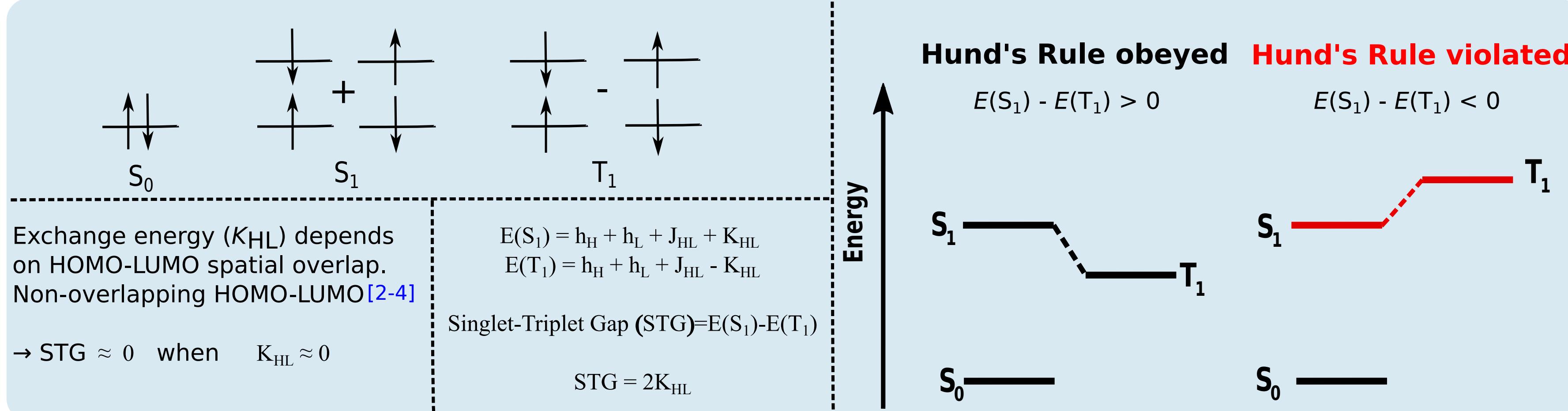


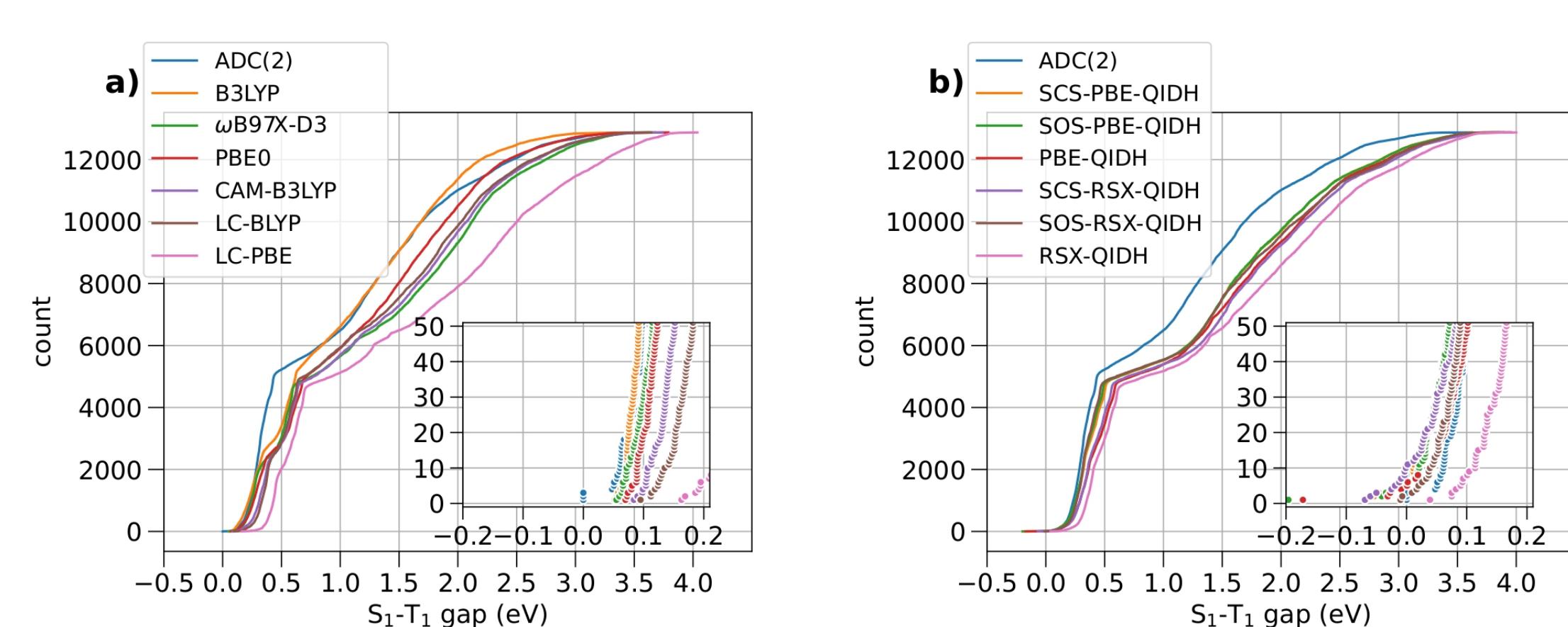
# In Pursuit of Hund's-rule Violating Organic Molecules

## SCIENTIFIC BACKGROUND

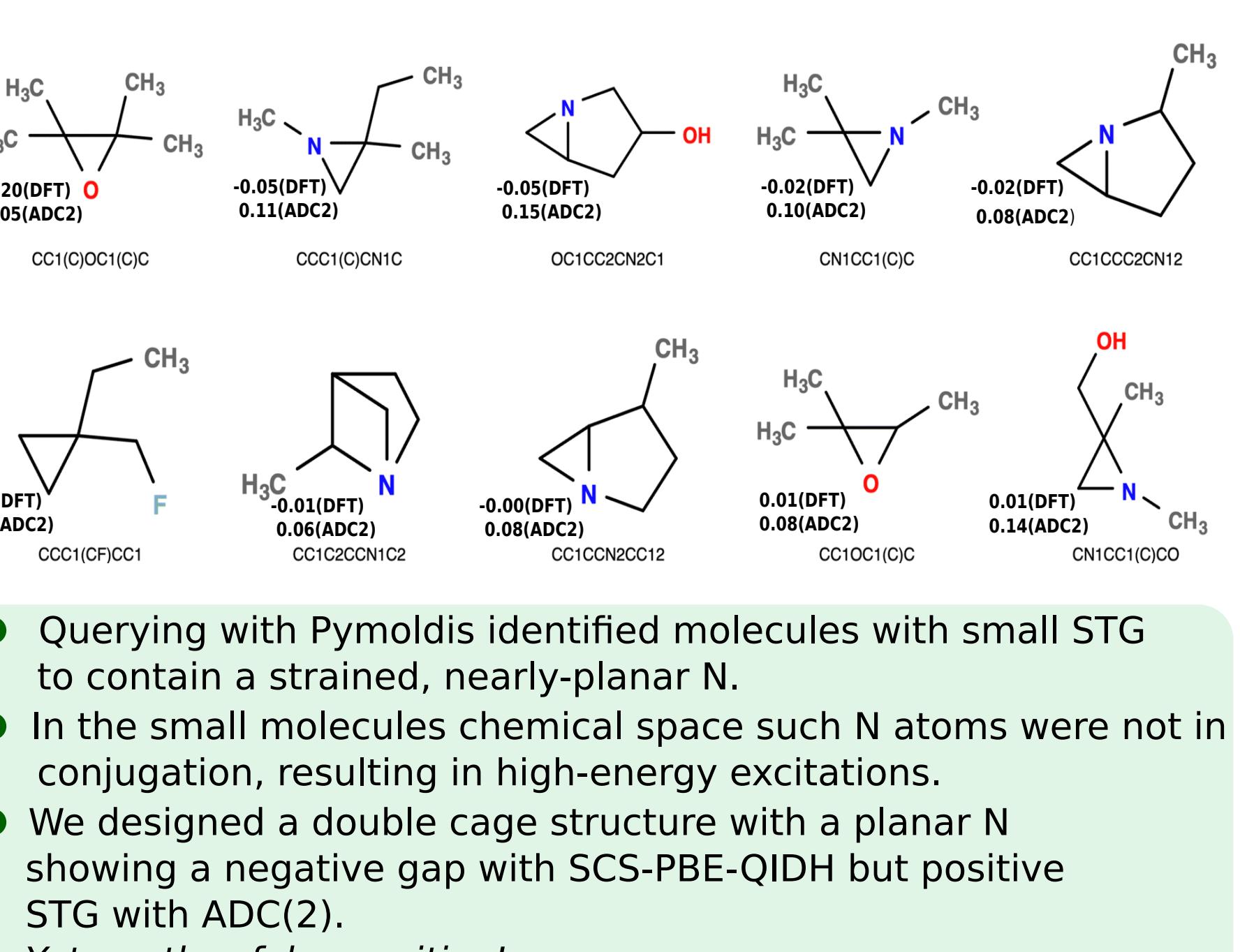
Hund's Rule: For a given electronic configuration, the term with maximum multiplicity has the lowest energy. [1]  
Energy of a triplet state (spin = 1) < Energy of a singlet state (spin = 0)



## CHEMICAL SPACE ANALYSIS



- At the ADC(2) level, none of the 12,880 molecules show a negative STG.
- Upon SCS/SOS corrections in DFT, preferentially lower S1, hence predict negative STG.



### Conclusion:

- Structural features that lower the STG can be found in the chemical space.
- No evidence of Hund's rule violation.

## ONGOING WORK

- Complete enumeration of unique APs.
- Basis set polation scheme to generate accurate geometries in lesser computational cost.
- Classifying them as systems undergoing distortion and systems retaining symmetry.
- Investigating the excited state energies and STG of all the systems with most accurate methods.

electron rich center replacing C by N is charge stabilizing

electron deficient center replacing C by N is charge destabilizing

Distribution of 104 azaphenalenenes

e- rich center (15) e- deficient center (3) mixed (85)

$C_{2v}$  6 2 20 63

$CS$  7 0 2 7

$D_{3h}$  1 1 1 1

$C_{3h}$  1 0 1 1

## OUTLOOK AND OPEN QUESTIONS

- Hund's rule prevails across thousands of organic molecules with systematically varying structures covering almost all prototypical small organic molecules.
- The chemical space of small molecules lacks features responsible for the negative STG as in molecules such as heptazine showing a downhill rISC mechanism.
- Symmetry lowering in 1AP is confirmed, with the true minimum ( $C_{3h}$ ) showing a positive STG ( $\sim 0.04$  eV), aligning with experiments.
- APs (5AP, 7AP) with N at electron-rich sites retain symmetry and violate Hund's rule, while those with N at electron-deficient sites exhibit stronger symmetry-lowering tendencies, while adhering to Hund's rule.
- Higher-level methods are needed to validate energy differences and ensure accurate modeling.
- How critical are the oscillator strengths of Hund's rule violating molecules for designing efficient emitters?
- What are the quantum chemical reasons for post MP2 treatment of azaphenalenenes?
- What are the insilico design principles for new INVEST molecules?

## WORKFLOW

### Chemical Space [7,8]

bigQM7ω dataset  
12,880 small organic molecules  
Geometries: ωB97XD/def2-TZVP & ConnGO workflow

Excited state calculations: S1 and T1 energies  
ADC(2)/def2-TZVP

TDA-TDDFT, def2-TZVP

LC-BLYP B3LYP CAM-B3LYP PBE-QIDH RSX-QIDH

LC-PBE PBE0 ωB97X-D3 SCS-PBE-QIDH SOS-RSX-QIDH

SOS-PBE-QIDH SOS-RSX-QIDH

RSX-QIDH

Data mining

import pymoldis

Query S1-T1 gap across chemical space

Hund's rule violation?

### Azaphenalenenes [9]

Six azaphenalenenes for pseudo-Jahn-Teller analysis

- Z-matrix-based symmetry-constrained geometry optimizations
- CCSD(T)/cc-pVTZ geometry optimizations of high-symmetry structures
- Single-point energy calculations
- MP2/cc-pVDZ reaction path scan on a low-dimensional ( $r_1, r_2$ ) PES
- Interpolation using cubic functions
- Single-point energy calculations
- CCSD(T)/cc-pVDZ ground state energy
- ADC(2)/cc-pVDZ excited state energies ( $S_1, T_1, STG$ )
- Identify possible low-symmetry minima ( $r_1 \neq r_2$ , &  $E^{\text{low-sym}} < E^{\text{high-sym}}$ )

### Low-symmetry minima

- CCSD(T)/cc-pVTZ, Z-matrix optimizations of low-symmetry structures starting from the structures identified in the Jahn-Teller-Hund's diagnostics analysis.
- $S_1, T_1, STG$  calculation with ADC(2)/aug-cc-pVTZ

Software:

CCSD(T) optimization: Molpro

DFT/TDDFT: Orca, Gaussian

ORCA

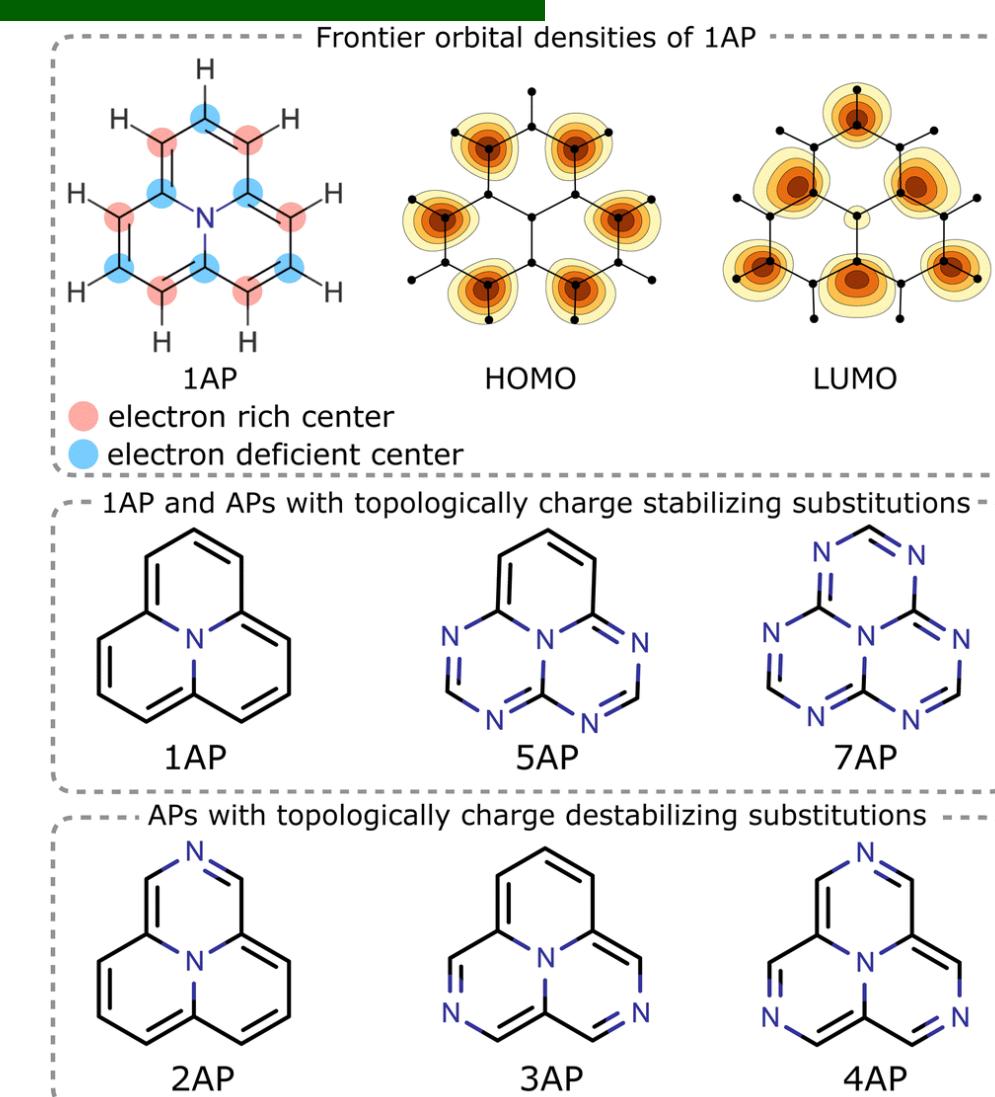
Gaussian, Inc.

Q-CHEM

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### CASE STUDY ON AZAPHENALENES [9]

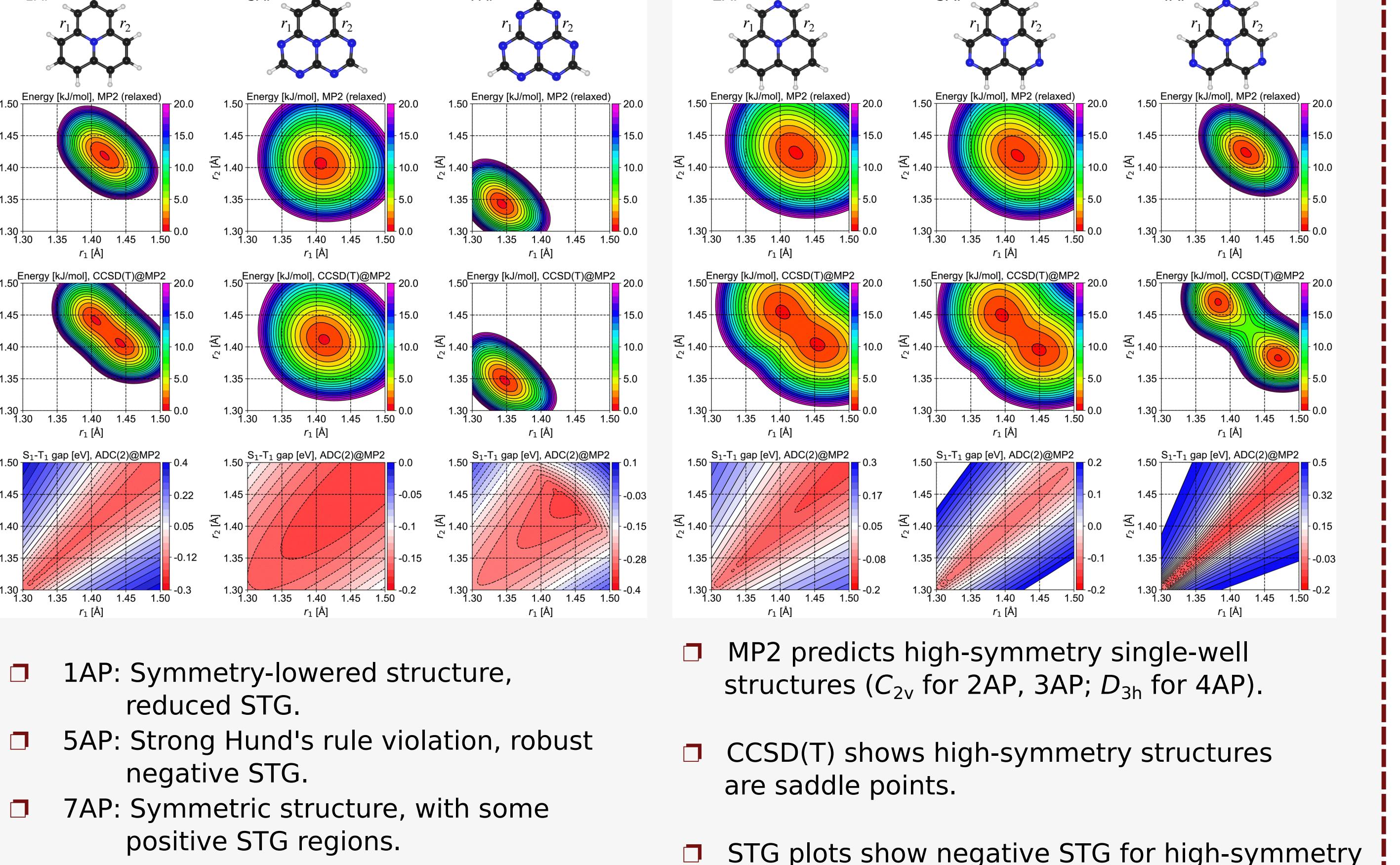
- We focus on 1AP, 5AP, and 7AP, which have already been experimentally studied.
- Additionally we examine 2AP, 3AP, and 4AP, where N is placed at electron-deficient sites of 1AP.
- All six molecules were part of a previous study [10], where TBE predicted negative STG.
- Investigate the potential energy surface at the CCSD(T) level and probe structural distortions and the effect on STG.



### Jahn-Teller-Hund diagnostics:

**1AP, 5AP, 7AP:** Ground state PES (MP2, CCSD(T)) and  $S_1$ - $T_1$  gaps (ADC(2)) shown. Symmetries:  $C_{3h}$  for 1AP/7AP,  $C_s$  for 5AP;  $D_{3h}$  and  $C_{2v}$  along  $r_1 = r_2$ .

**2AP, 3AP, 4AP:** Symmetries:  $C_{3h}$  for 4AP,  $C_s$  for 2AP/3AP;  $D_{3h}$  and  $C_{2v}$  along  $r_1 = r_2$ .



| System       | Nature | Energy barrier (kJ/mol) | STG, Our work [9] (eV) | STG, TBE [10] (eV) | STG, Exp (eV) |
|--------------|--------|-------------------------|------------------------|--------------------|---------------|
| 1AP $D_{3h}$ | TS     | 0.3                     | -0.142                 | -0.131             | +0.04 [11]    |
| 1AP $C_{3h}$ | Min    | -                       | -0.060                 | -                  | -             |
| 2AP $C_{2v}$ | TS     | 2.1                     | -0.102                 | -0.071             | -             |
| 2AP $C_s$    | Min    | -                       | +0.125                 | -                  | -             |
| 3AP $C_{2v}$ | TS     | 5.3                     | -0.079                 | -0.042             | -             |
| 3AP $C_s$    | Min    | -                       | +0.274                 | -                  | -             |
| 4AP $D_{3h}$ | TS     | 11.1                    | -0.073                 | -0.029             | -             |
| 4AP $C_{3h}$ | Min    | -                       | +0.392                 | -                  | -             |
| 5AP $C_{2v}$ | Min    | -                       | -0.147                 | -0.119             | -0.047 [4]    |
| 7AP $D_{3h}$ | Min    | -                       | -0.253                 | -0.219             | < 0 [2]       |

- 1AP: STG is nearly zero ; 5AP, 7AP: True positives
- 2AP, 3AP, 4AP (studied before, TBE): False positives

## REFERENCES

- T. Won et al., *Chem. Phys. Rev.*, 2023, 4, 021310.
- J. Ehrmaier et al., *J. Phys. Chem. A*, 2019, 123, 8099.
- J. C. Sancho-Garcia et al., *J. Chem. Phys.*, 2022, 156, 034105.
- K. D. Wilson et al., *J. Am. Chem. Soc.*, 2024, 146, 15688.
- N. Aizawa et al., *Nature*, 2022, 609, 502.
- P. D. Silva et al., *J. Phys. Chem. Lett.*, 2019, 10, 5674.
- P. Kayastha et al., *Digital Discov.*, 2022, 1, 689.
- A. Majumdar et al., *Phys. Chem. Chem. Phys.*, 2024, 26, 14505.
- A. Majumdar et al., *Phys. Chem. Chem. Phys.*, 2024, 26, 26723.
- P.-F. Loos et al., *J. Phys. Chem. Lett.*, 2023, 14, 11069.
- W. Leupin et al., *J. Am. Chem. Soc.*, 1980, 102, 6068.

## THANK YOU