

Abstract

Pyrene is a fluorescent dye, known for its long fluorescence lifespan, high quantum yields and the ability to form dimers that are only stable in an electronically excited state, so called excimers. All these attributes make it ideally suited for applications in photochemical sensors, organic LEDs or the fluorescent tagging of biological preparations. Despite this wide range of applications, some aspects of the pyrene photophysics like excimer formation and ultrafast population transfer are yet to be understood in detail. We focus on TD-DFT calculations to describe excitations and simulate absorption spectra. We found that the very small oscillator strength of L_b is not due to symmetry reasons, but is based on annihilation of contributions from two equally weighted excitations. Calculated potential energy surfaces of S_2 and S_1 allow first insights into the occurring ultrafast dynamics. Using CASSCF, we located a conical intersection connecting both states in question, representing the key element for the population transfer. A second aspect of our work is the search for possible minimum geometries of intermolecular and intramolecular pyrene excimers during which we optimized five and four different structures, respectively, using TDA-DFT-D3. For the first time optimized bridged pyrene excimer structures are presented confirming literature speculations. The stability of these excimers can be explained by bonding orbital interactions in excited states overcompensating the strain in the chair-like formed bridge.

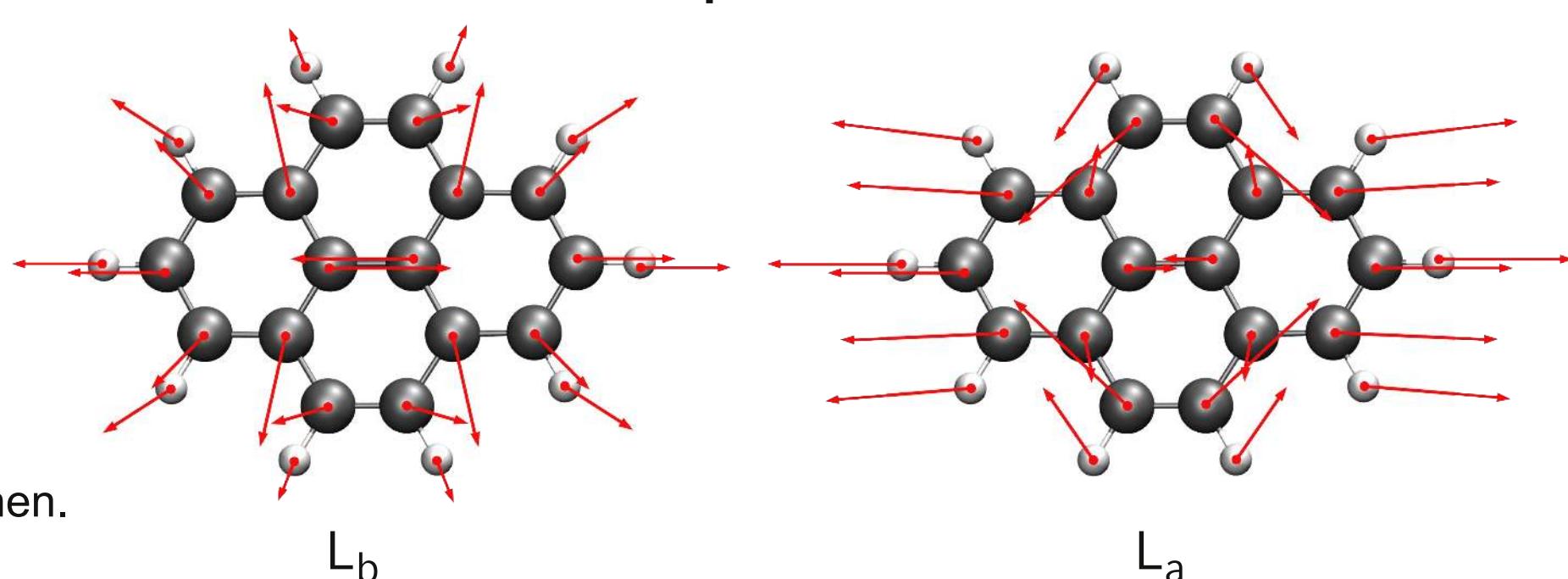
Ultrafast Population Transfer

TD-DFT/CAM-B3LYP/6-31G* & CAS(4,4)

Excitation displacement vectors:

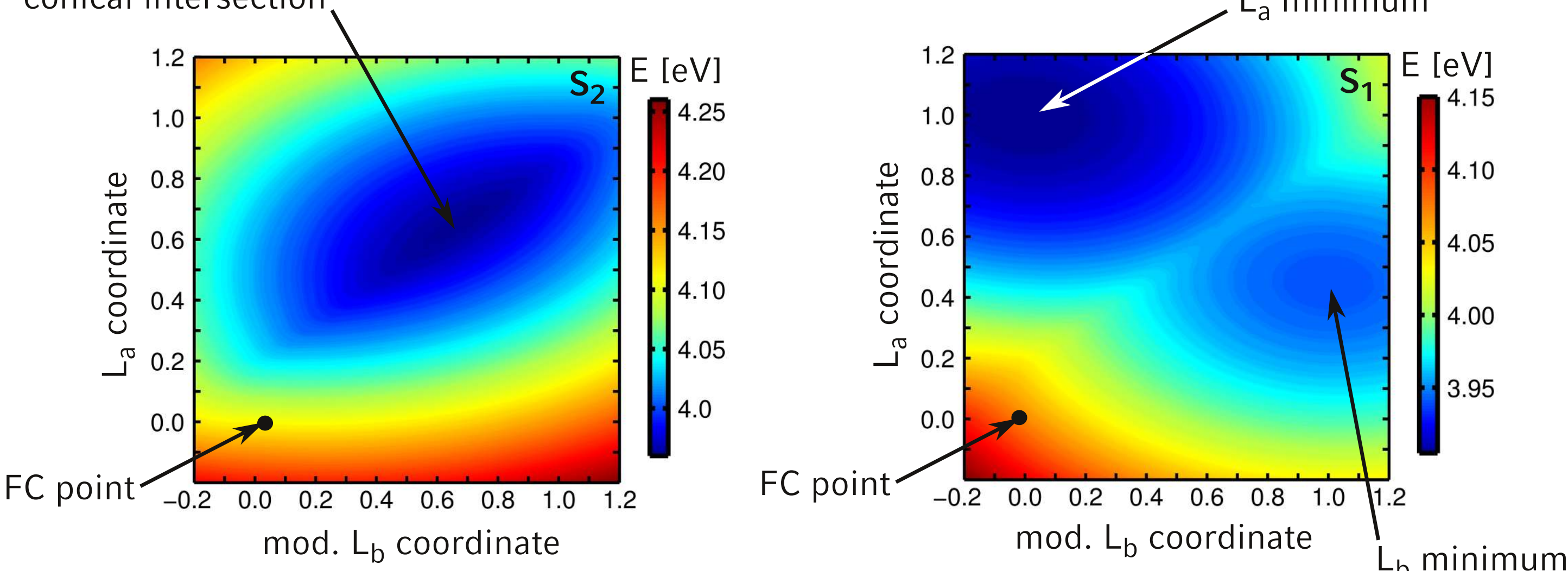
Experiment:

- excitation to L_a
- 85 fs transfer to L_b [1]
- emission from L_b



[1] N. Krebs, *Dissertation 2013*, LMU München.

Adiabatic potential energy surfaces:



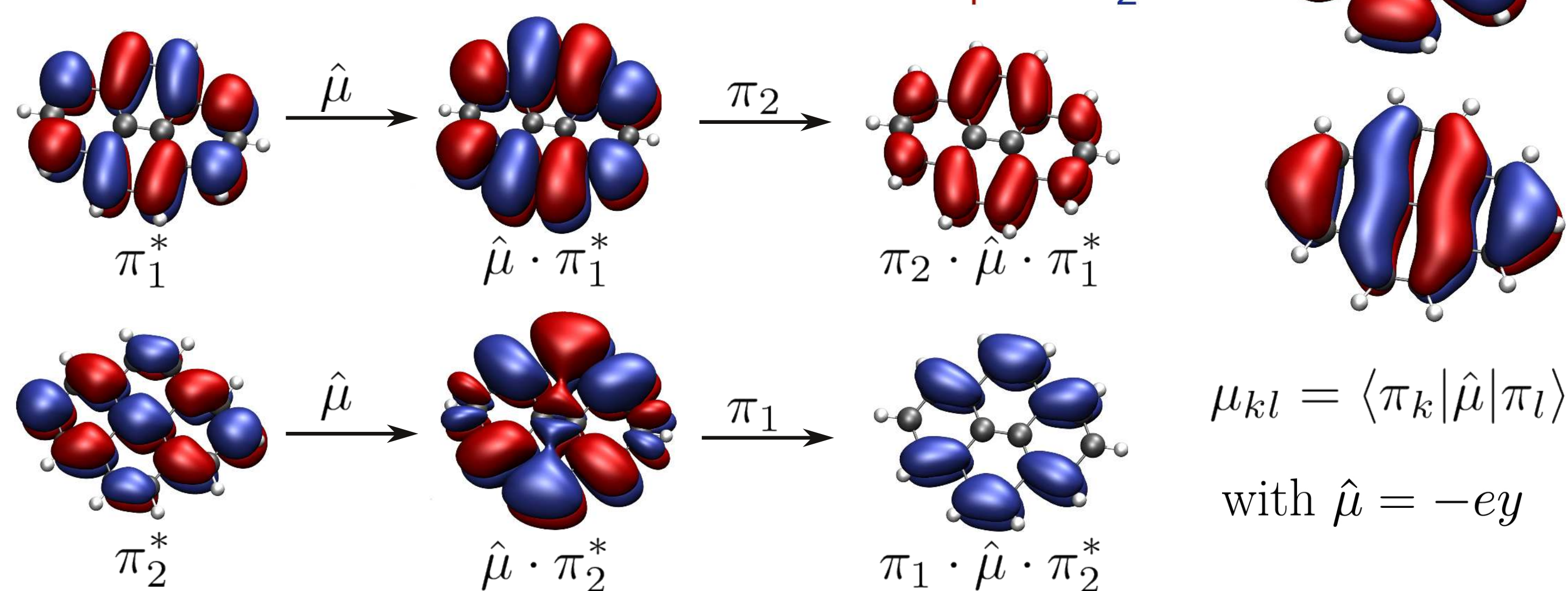
Excited States & Weakly Dipole-Allowed S_1

TD-DFT/CAM-B3LYP/6-31G*

- completely delocalised π -system
- different combinations of transitions for L_a and L_b
- both states dipole allowed, but L_b very weak

→ annihilation of contributions from two equally weighted transitions

	symm.	E_{vert} [eV]	f
$S_1 (L_b)$	$1B_{2u}$	4.07	0.00
$S_2 (L_a)$	$1B_{1u}$	4.11	0.32

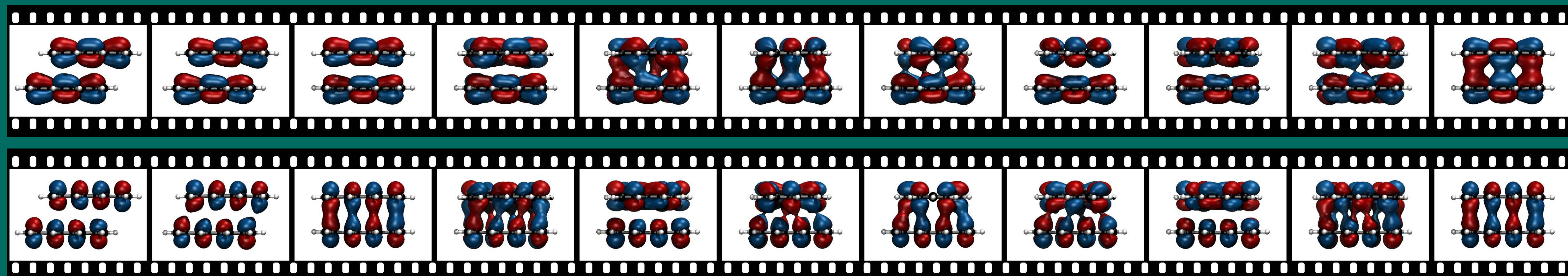
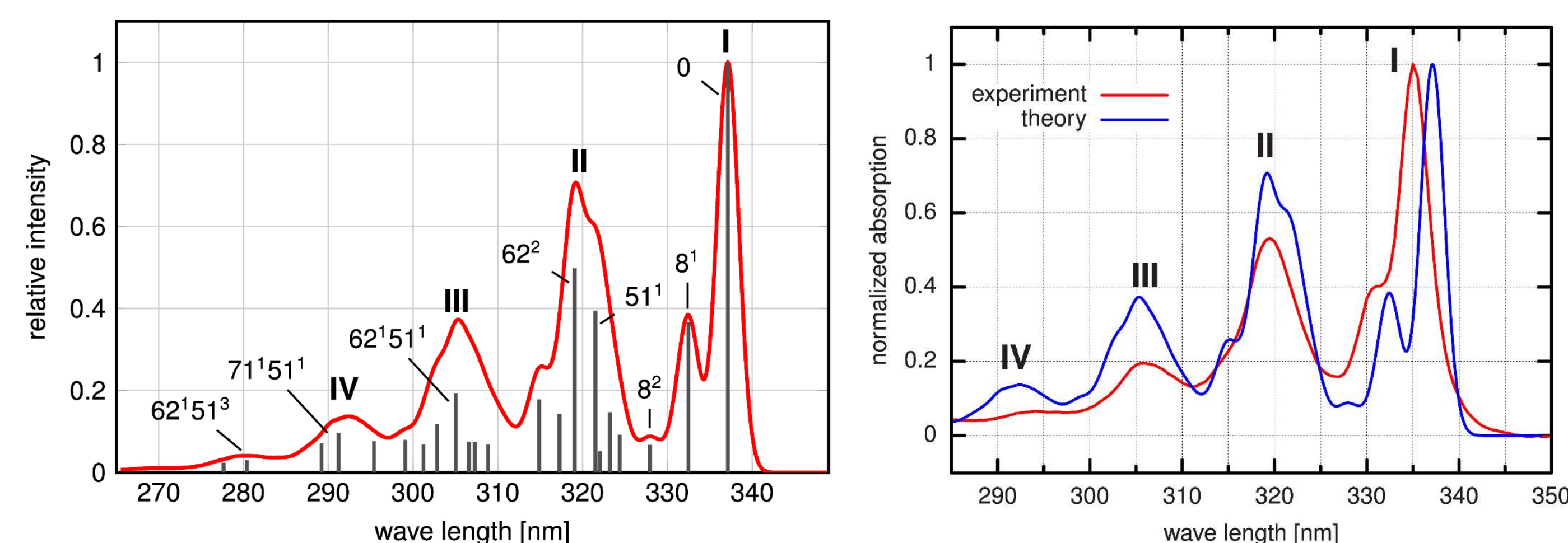


Vibrationally-Resolved Absorption Spectrum for L_a

TD-DFT/CAM-B3LYP/6-31G*

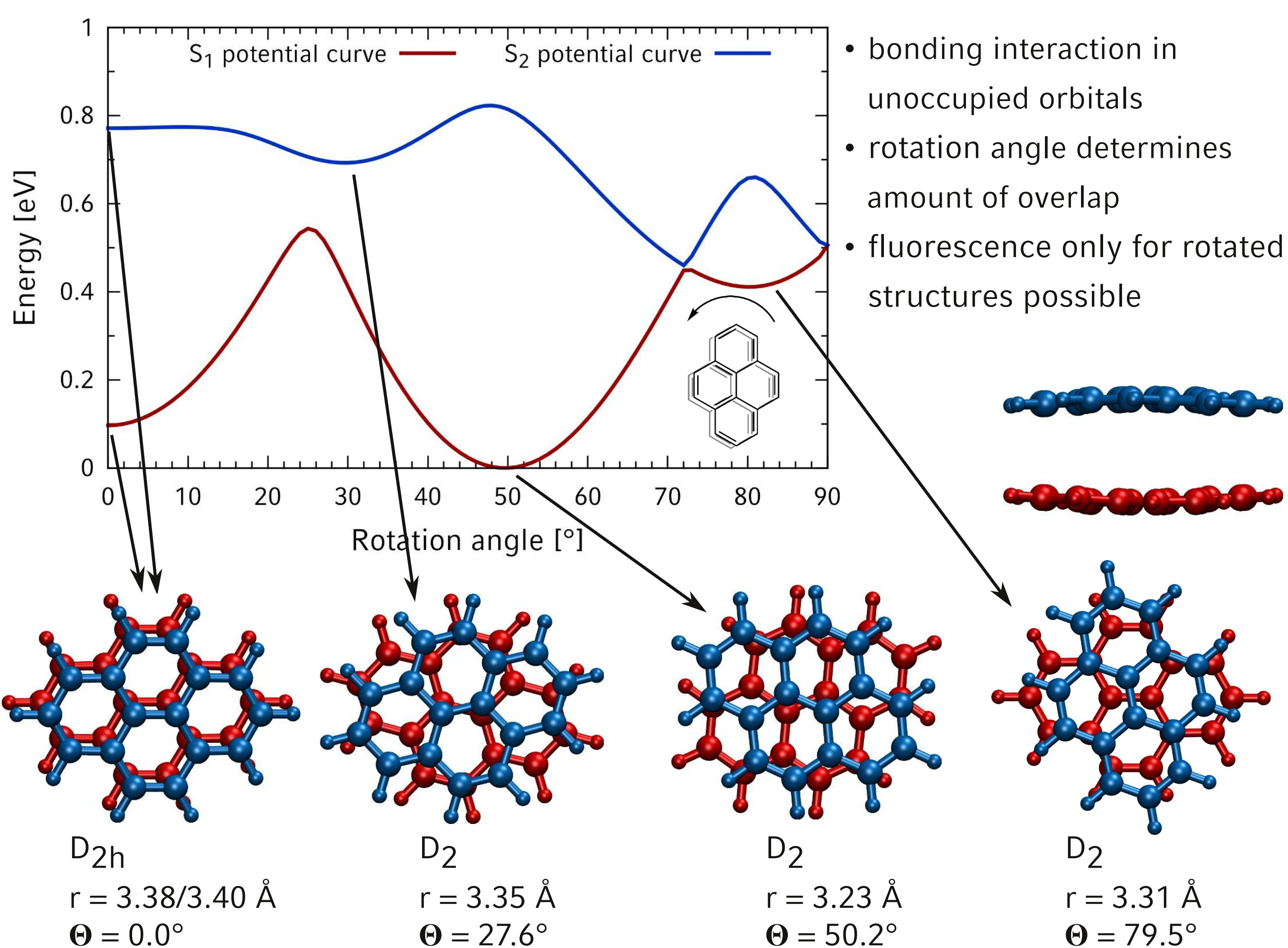
simulation via Franck-Condon theory

shift theory to experiment: 3 nm
all peaks present in theory



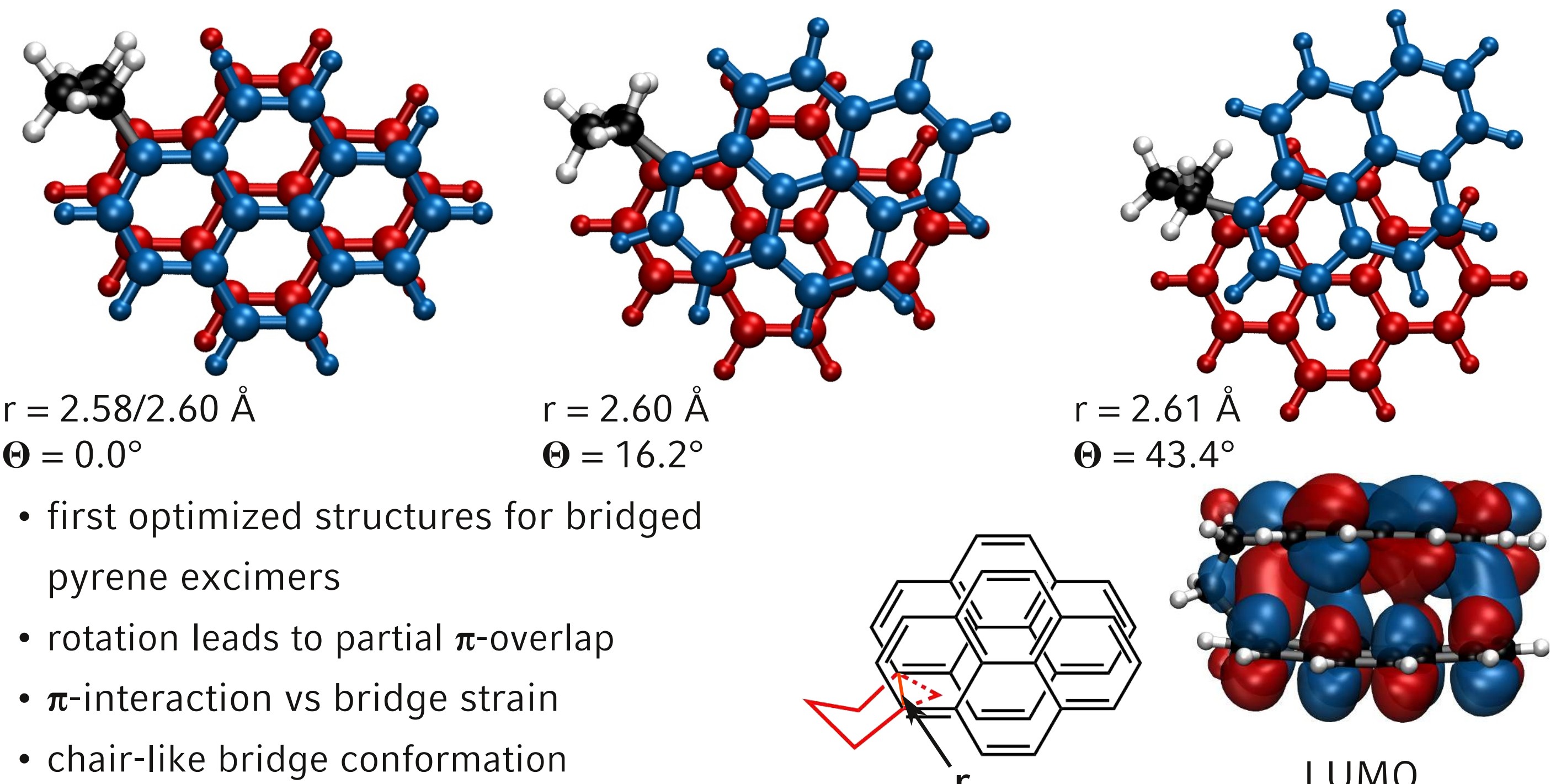
Potential Energy Surface Scans & Pyrene Excimers

TD-DFT/CAM-B3LYP/6-31G*



Propyl Bridged Pyrene Excimers

TDA-DFT-D3/CAM-B3LYP/6-31G*



Outlook

- calculations with CASSCF & CASPT2
- better excitation energies
- NAC at conical intersection
- quantum dynamical calculations
- emission spectra
- triplet states