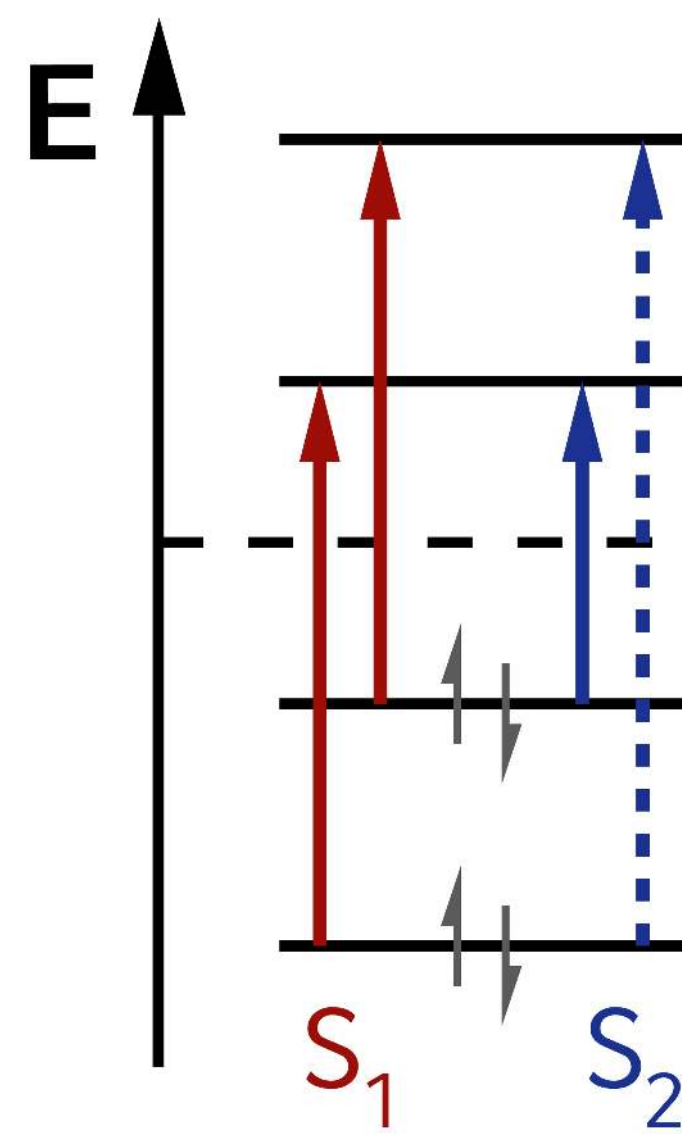
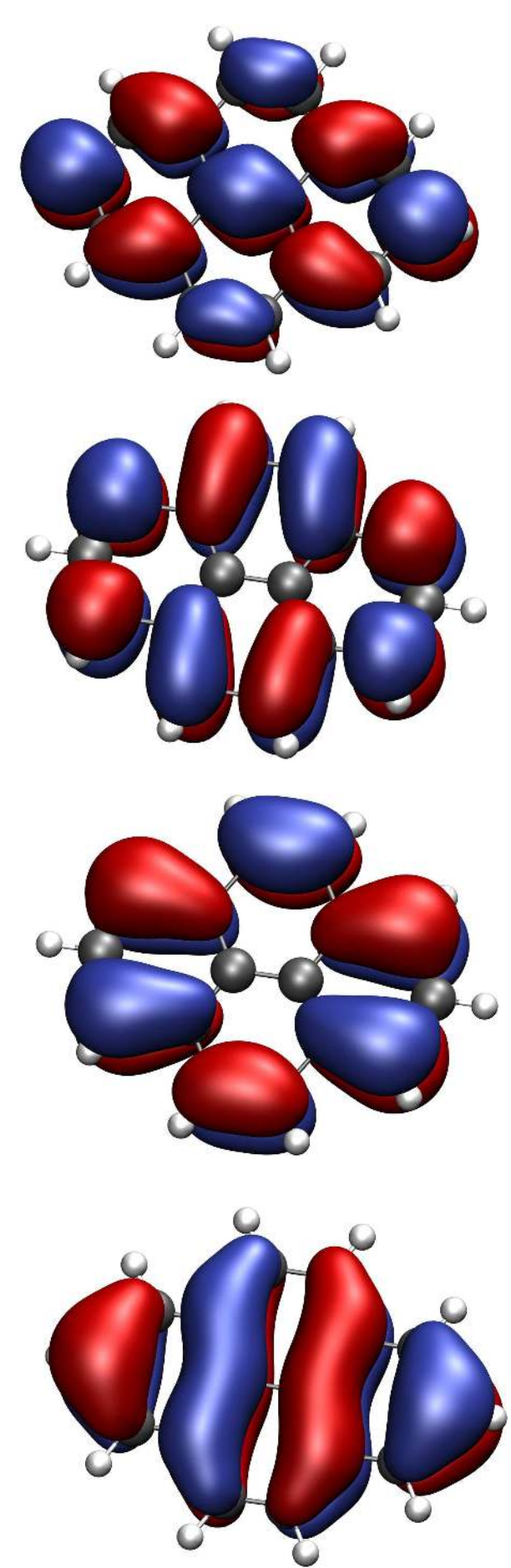


Abstract

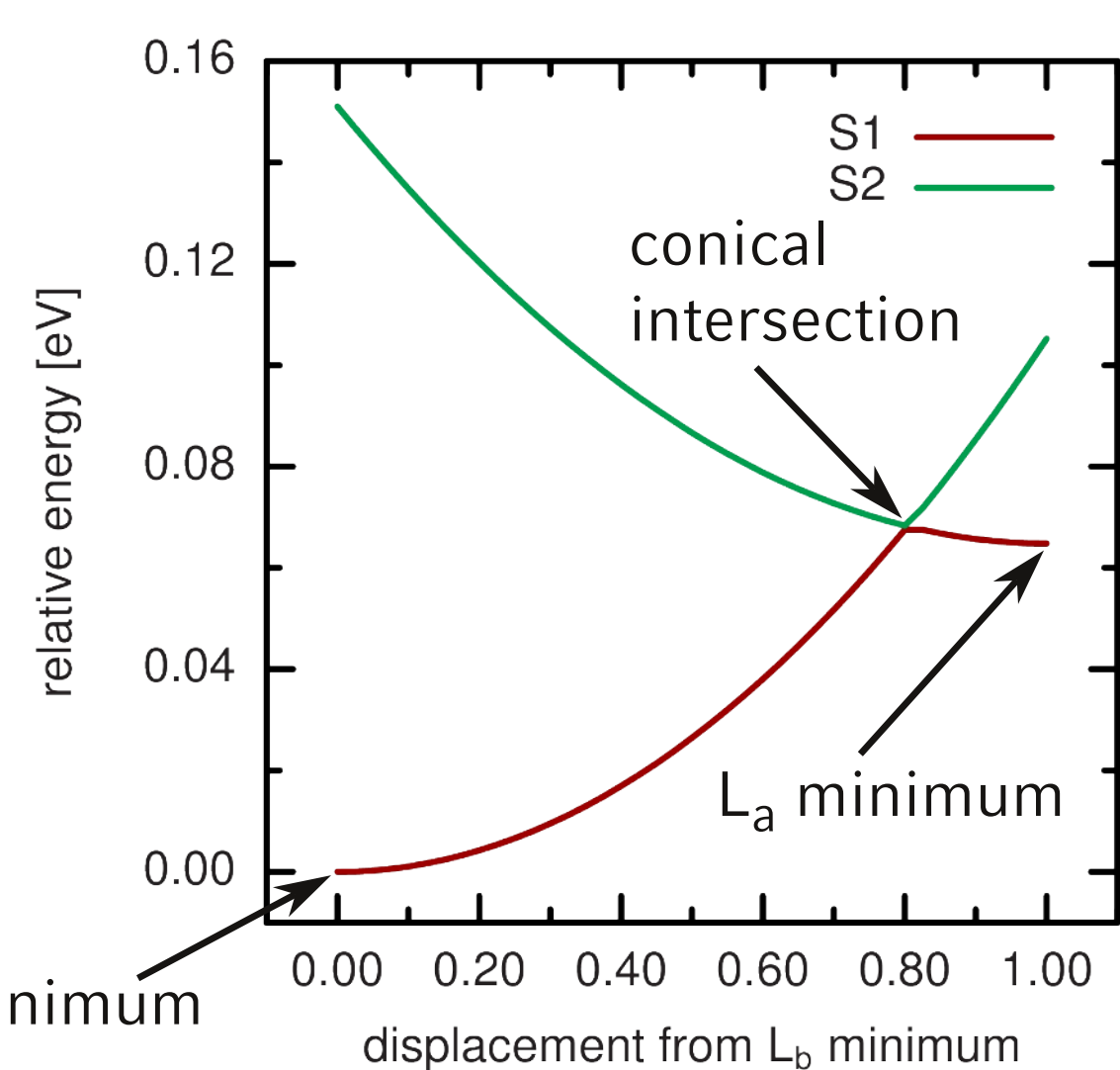
Pyrene is a fluorescent dye, known for its long fluorescence lifespan, high quantum yield and the ability to form dimers that are only stable in an electronically excited state, so called excimers. All these attributes make it ideally suited for applications in photochemical sensors, organic LEDs or the fluorescent tagging of biological preparations. Despite this wide range of applications, some aspects of the pyrene photophysics like ultrafast population transfer are yet to be understood in detail. We focus on CASSCF calculations to describe the excitations in the L_a and L_b state. The active space consists of four electrons in four orbitals. Furthermore, we can show that including further π -orbitals actually worsens the picture. We located a conical intersection connecting both states in question, representing the key element for the population transfer. Using excitation displacement vectors, we are able to span a two-dimensional space for quantum dynamical calculations and observe that the wavepacket passes through the conical intersection and reaches both minima, L_a and L_b . Here, the G-matrix method is used for the kinetic energy operator. In comparison, we simulated the process in full dimensionality via on-the-fly semiclassical methods. Here, the L_b state is reached very efficiently (85 %) and the dynamics is slightly faster than in the experiments.

Excited States & Active Space

CAS(4,4)



Scan between L_a and L_b minimum structures

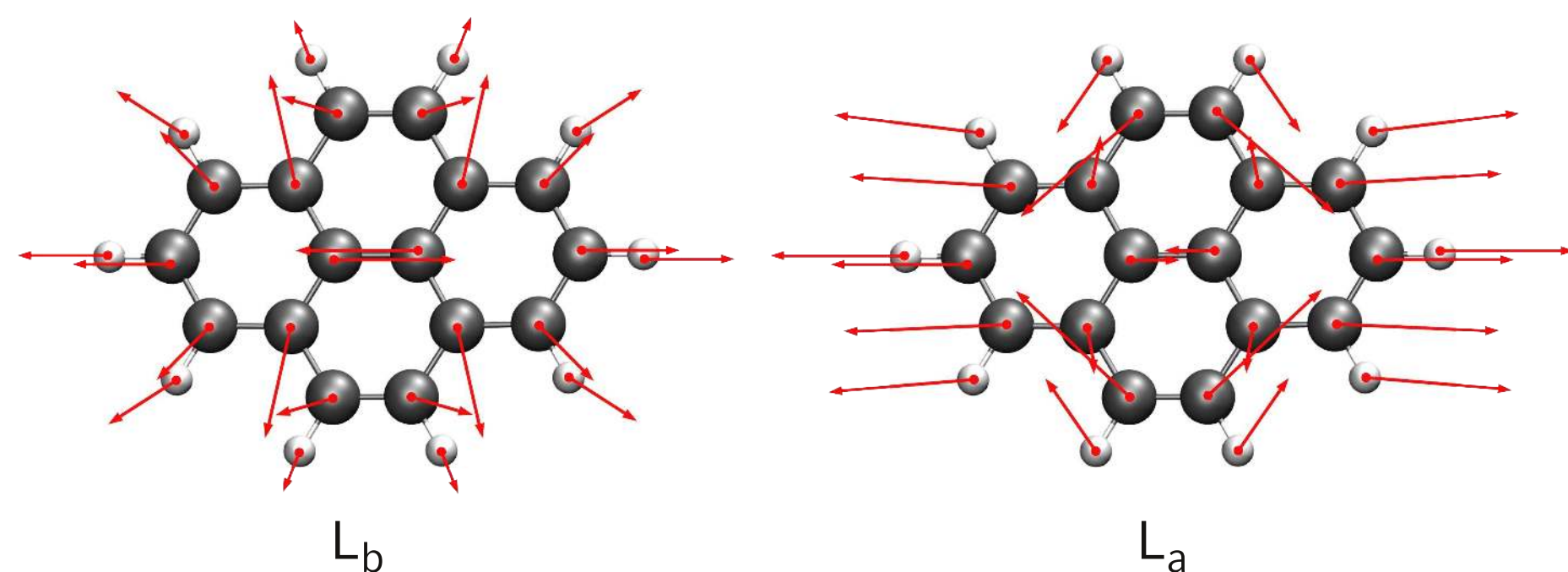


- smallest possible active space to describe L_a and L_b state
- optimization of conical intersection successful

	char.	symm.	E_{vert} [eV]	f	E_{exp} [eV]
S_1 (L_b)	$\pi\pi^*$	$1B_{2u}$	5.44	0.00	3.41
S_2 (L_a)	$\pi\pi^*$	$1B_{1u}$	5.52	0.30	3.85

Quantum Dynamical Simulations

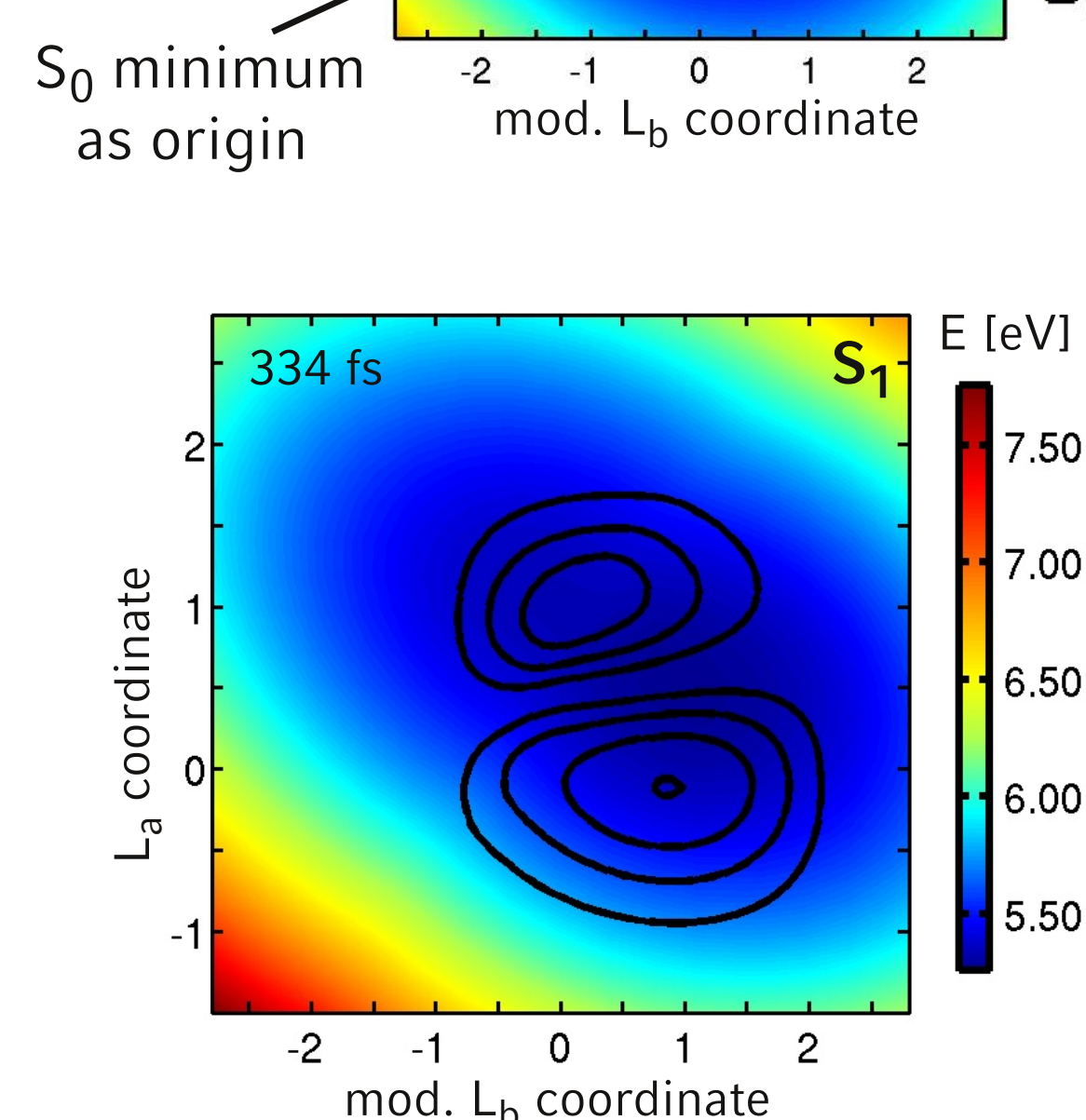
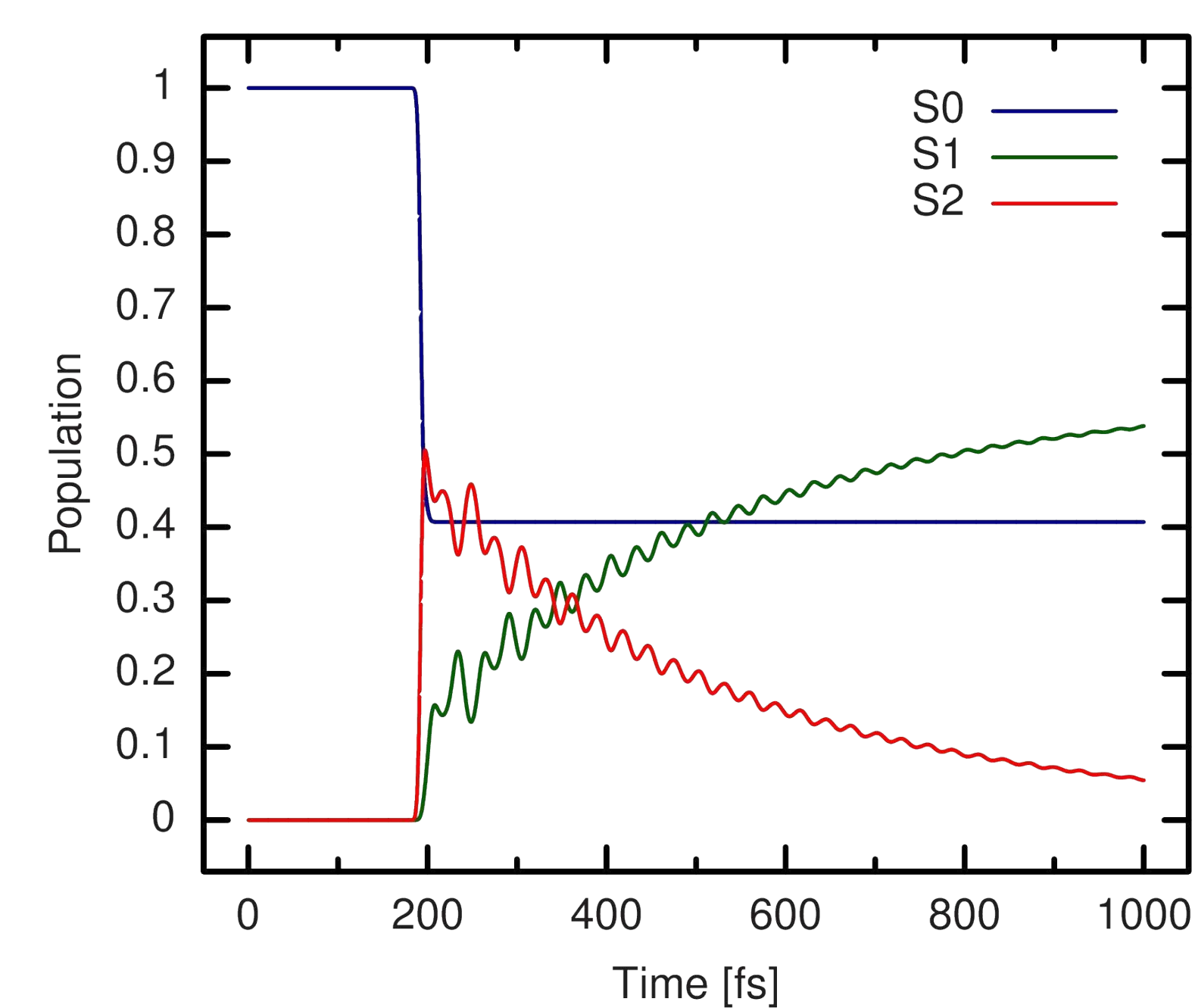
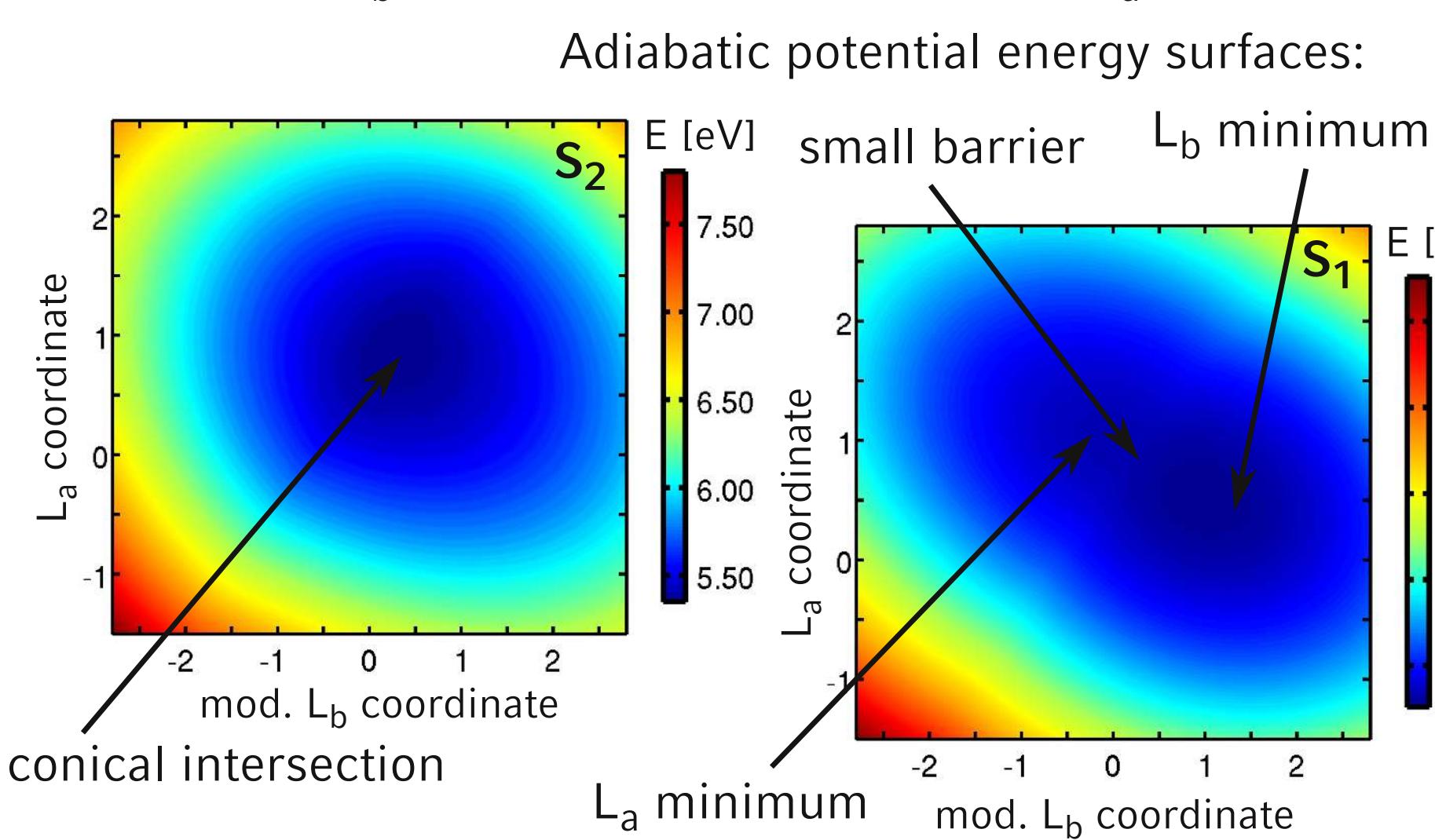
Excitation displacement vectors:



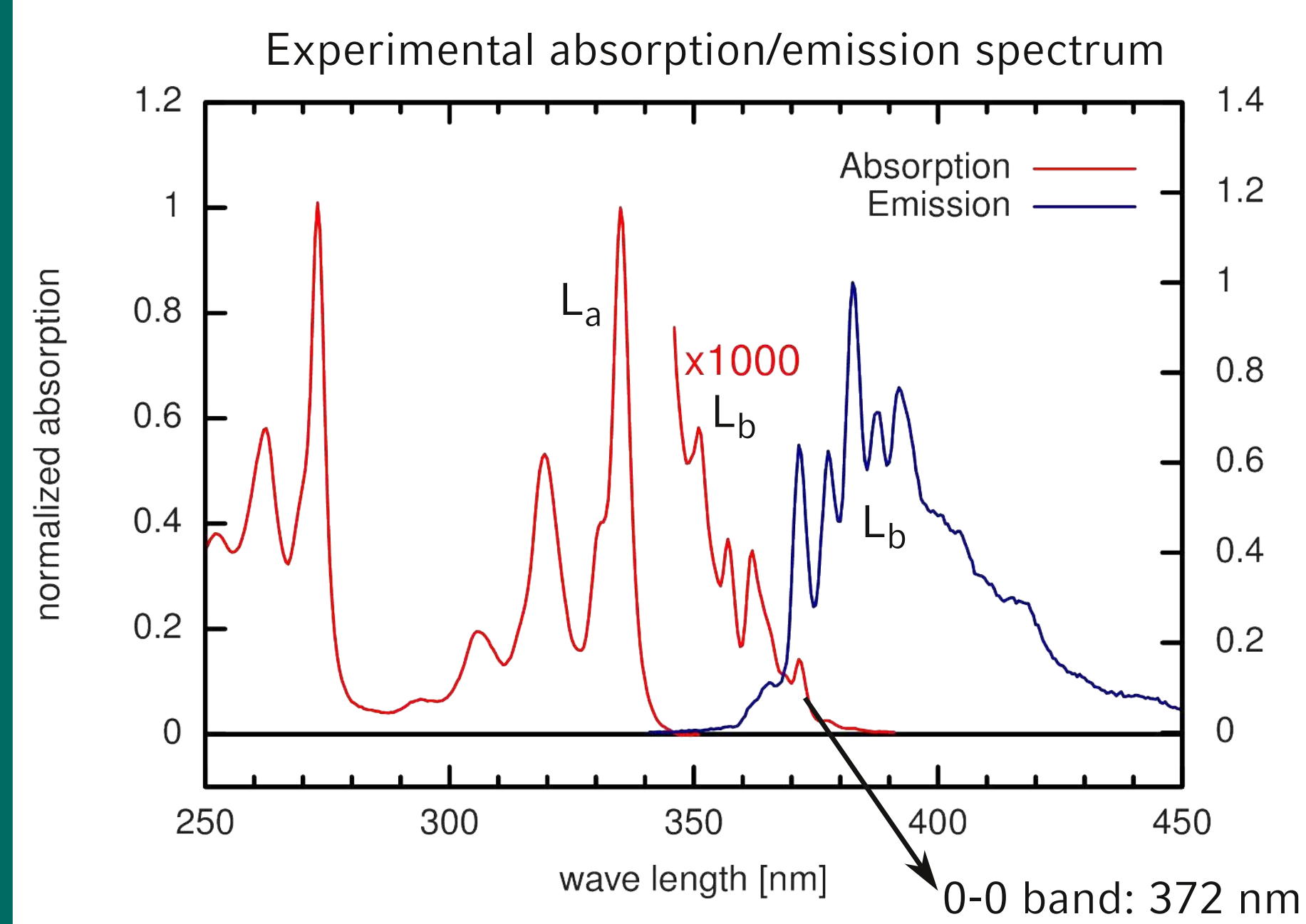
- orthogonalized displacement vectors between minima as coordinates
- G-matrix method for kinetic energy operator [3,4]:

$$G_{rs} = \sum_{i=1}^{3N} \frac{1}{m_i} \frac{\partial q_r}{\partial x_i} \frac{\partial q_s}{\partial x_i}$$

constant G-matrix without off-diagonal terms



Introduction

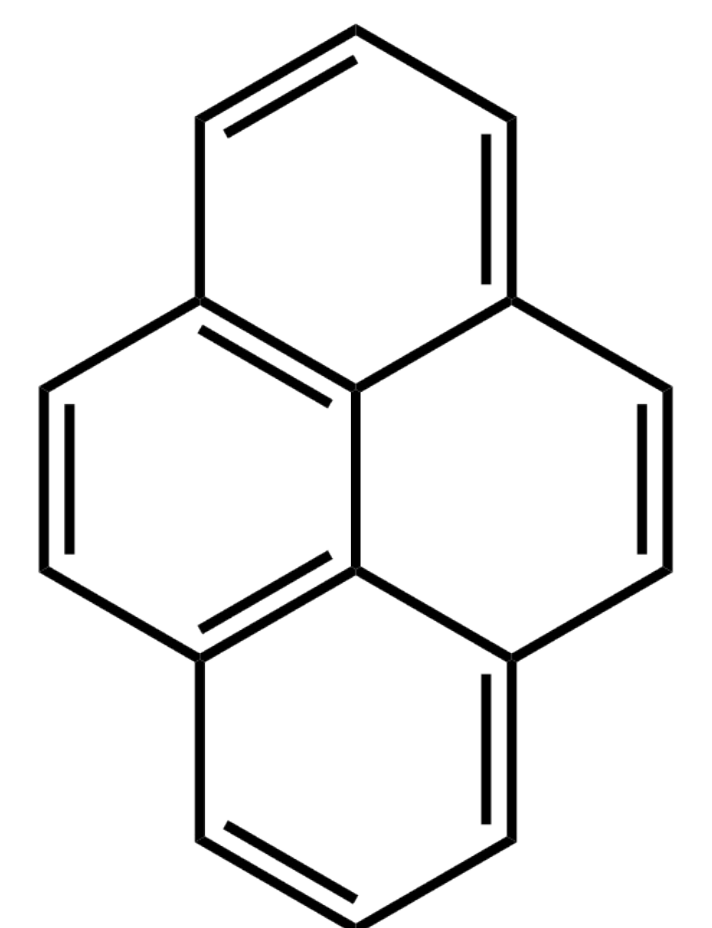


TD-DFT/CAM-B3LYP/6-31G*

	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

ultrafast population transfer 85 fs [2]

- planar aromatic molecule
- completely delocalised π -system
- point group D_{2h}

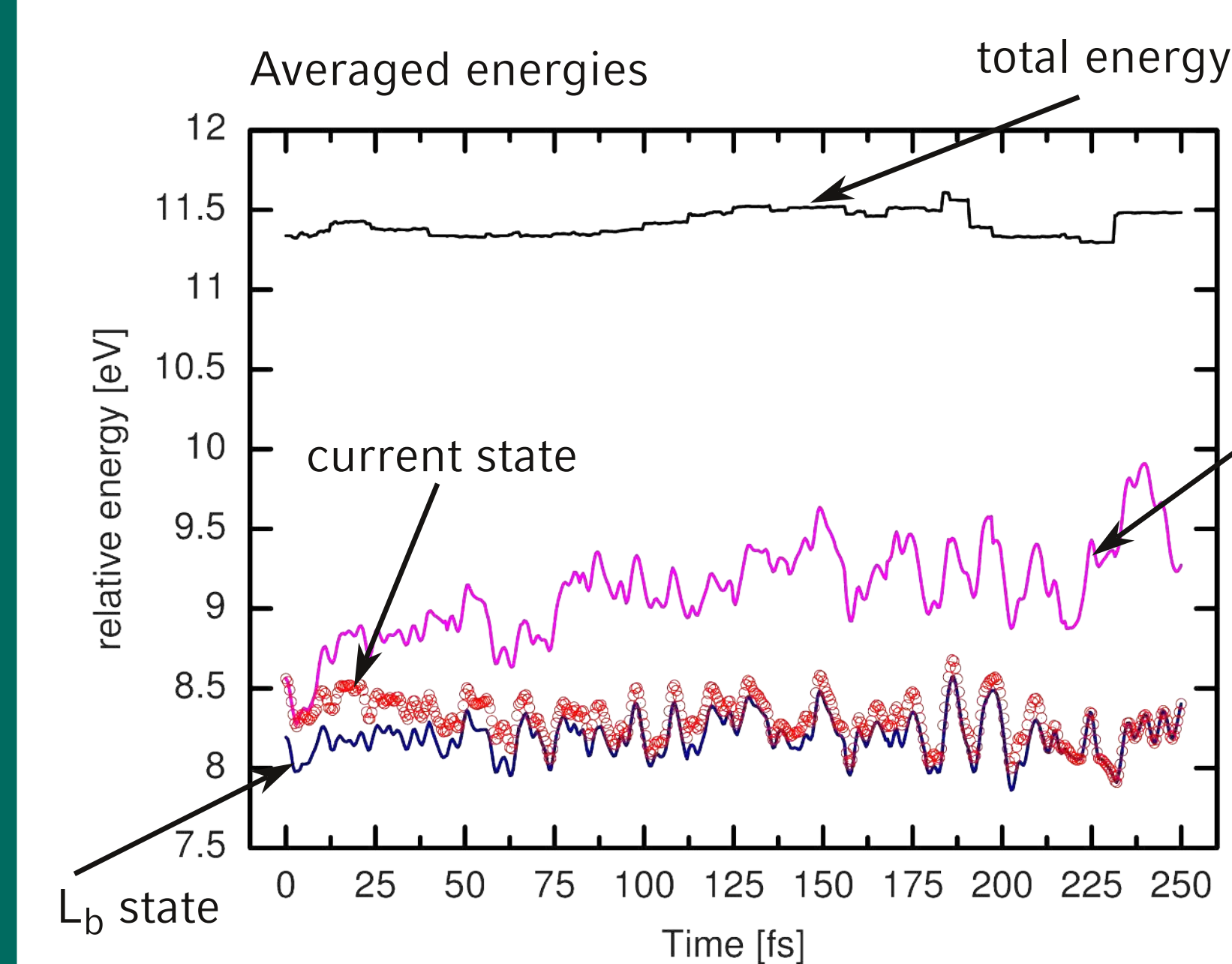


- strong absorption for L_a
- emission only from L_b
- no significant overlap between absorption and emission
- long lifetime for L_b : 339 ns [1]
- high quantum yield: 0.75 [1]

How not to choose active space!

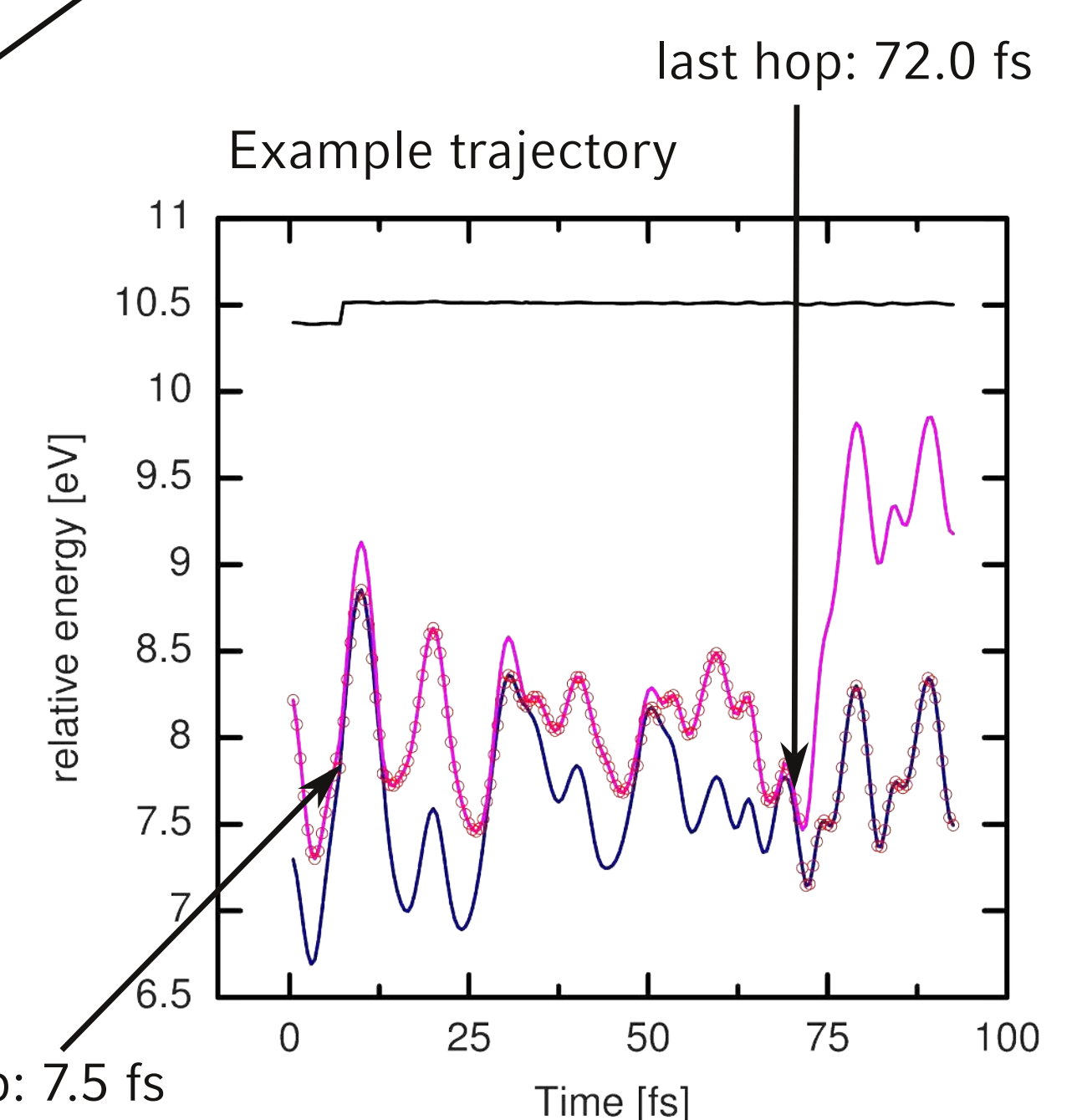
	Experiment	CAS(4,4)	CAS(10,10)	CAS(12,12)	CAS(16,16)
HOMO	N/A				
HOMO-1	N/A				
$\Delta\Delta E$ [eV]	0.44	0.09	1.15	0.80	2.07
conical intersection?	yes	yes	no	no	no

Semiclassical Dynamical Simulations



- 100 trajectories starting from an uncorrelated Wigner distribution
- Tully's fewest switches surface hopping with NewtonX/Molpro

- efficient population transfer: 85 % L_b
- L_a and L_b stay close: 3.24 hops/traject.
- maximum hops in 1 traject.: 14
- average last hop: 53 fs



Citations

- [1] D.S. Karpovich, and G.J. Blanchard, *J. Phys. Chem.* **99** (1995), 3951.
- [2] N. Krebs, PhD thesis, LMU München, 2013.
- [3] L.J. Schaad, and J. Hu, *J. Mol. Struct.: THEOCHEM* **185** (1989), 203.
- [4] S. Thallmair, M.K. Roos, and R. de Vivie-Riedle, *J. Chem. Phys.* **144** (2016), 234104.

