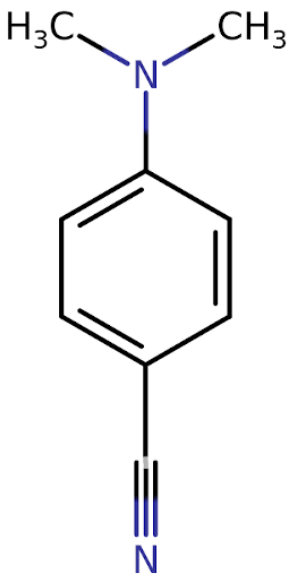
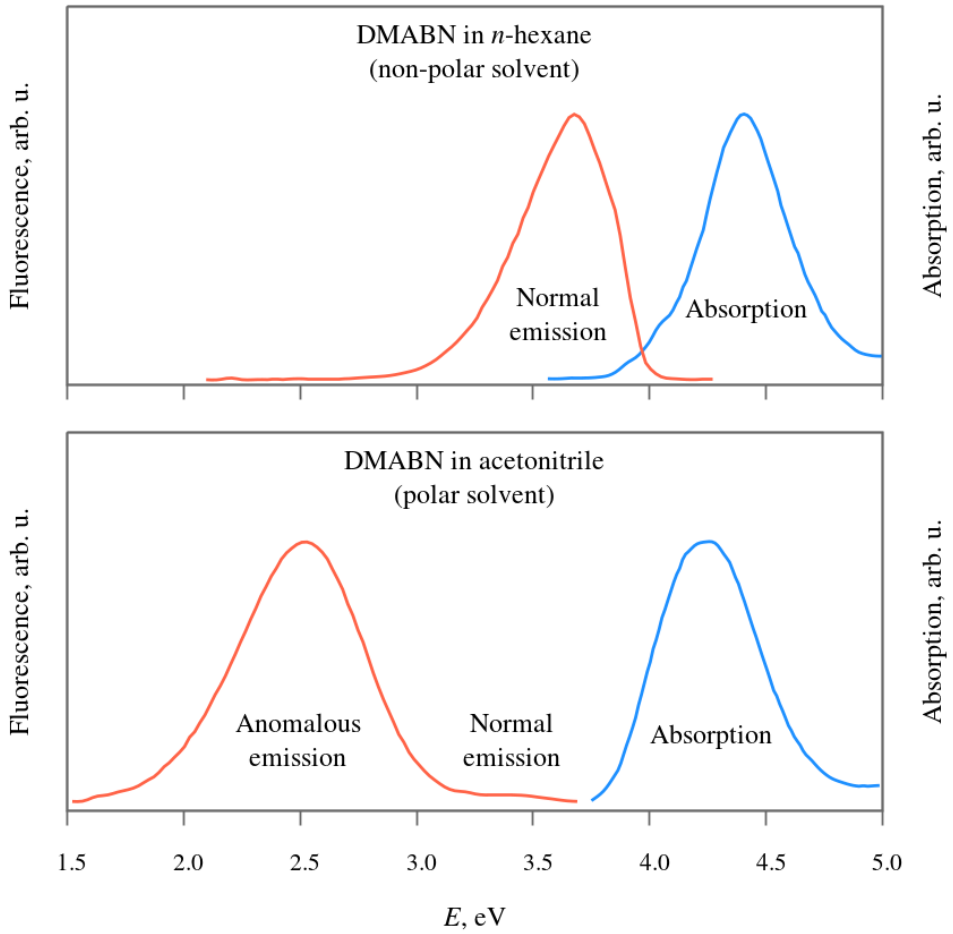
Michał Andrzej Kochman

April 12, 2023

Simulating the photophysics of DMABN: what have we learned, and where do we go from here?

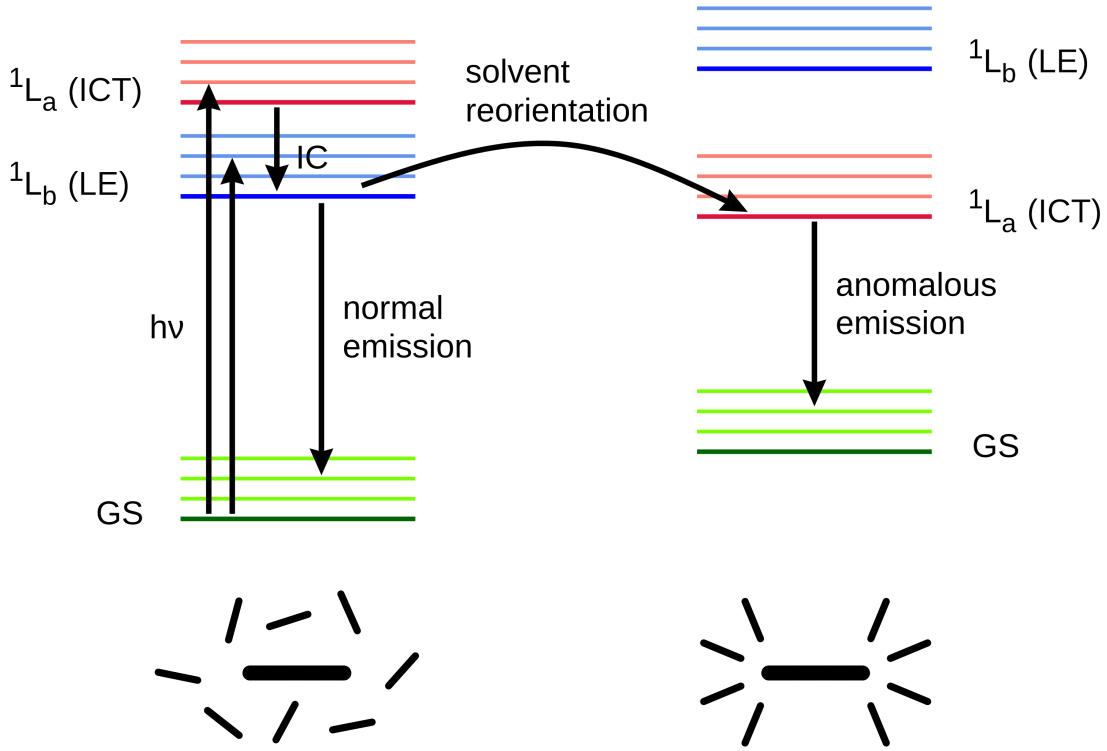
Dual Fluorescence of DMABN





Molecular structure and dual fluorescence of 4-(*N*,*N*-dimethylamino)benzonitrile (DMABN).

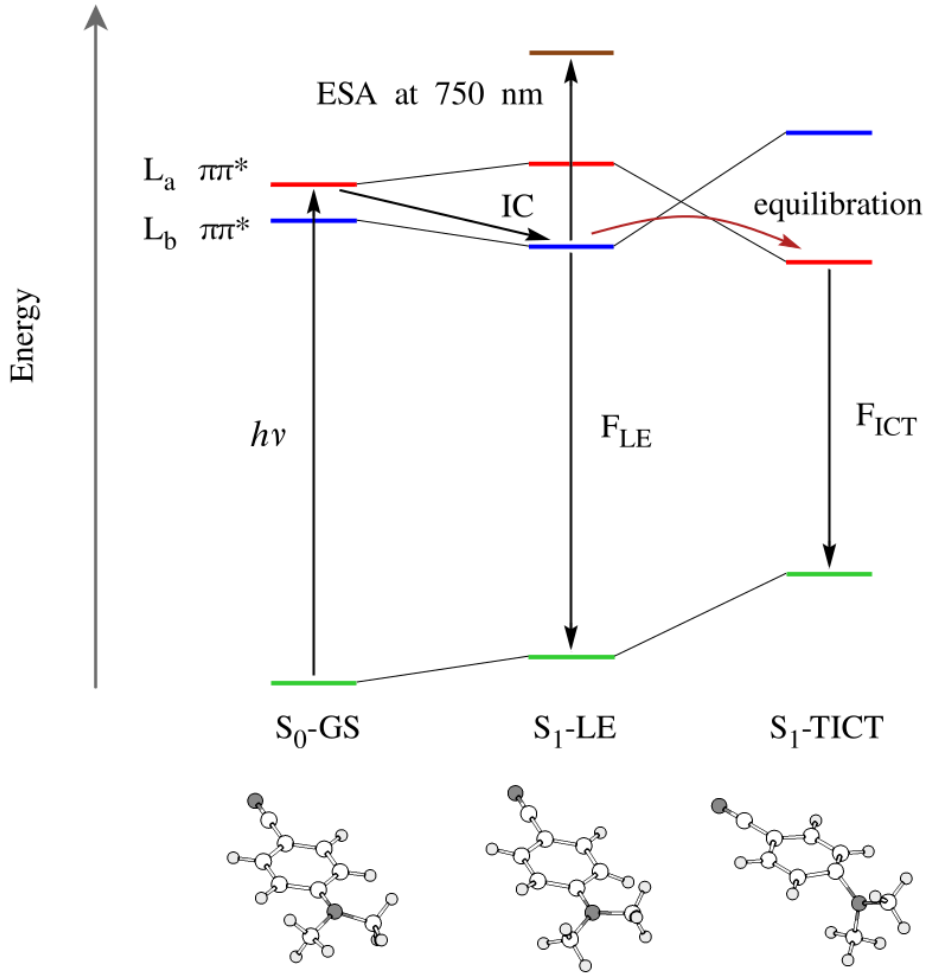
State Reversal Model



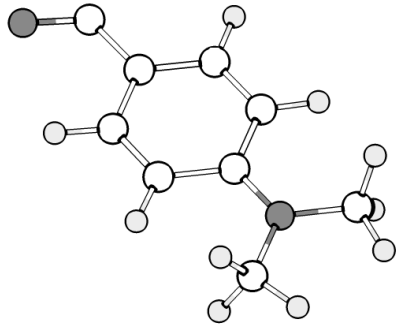
The state reversal model, proposed by Lippert et al. in 1962.

^1L_a state – intramolecular charge transfer (ICT) state

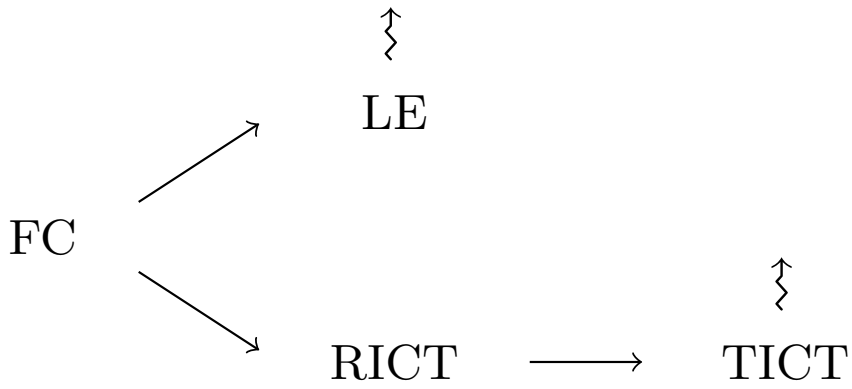
^1L_b state – locally excited (LE) state

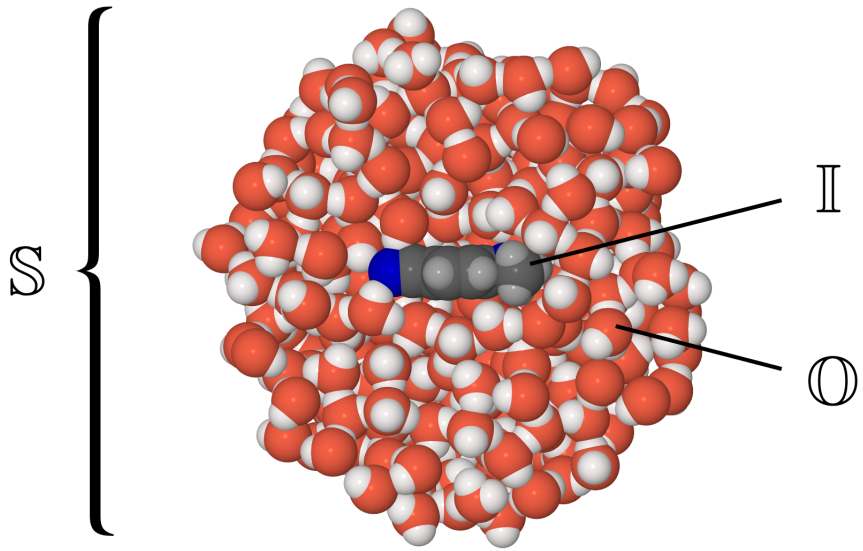


Quasi-equilibrium between the LE and the twisted ICT (TICT) structures. The latter was first proposed to exist by Rotkiewicz et al. in 1973.



Is the rehybridized ICT (RICT, with a bent nitrile group) structure involved in the dual fluorescence mechanism?
The sequence of events according to Fujiwara et al.:





- The PESs are generated with the additive QM/MM method:

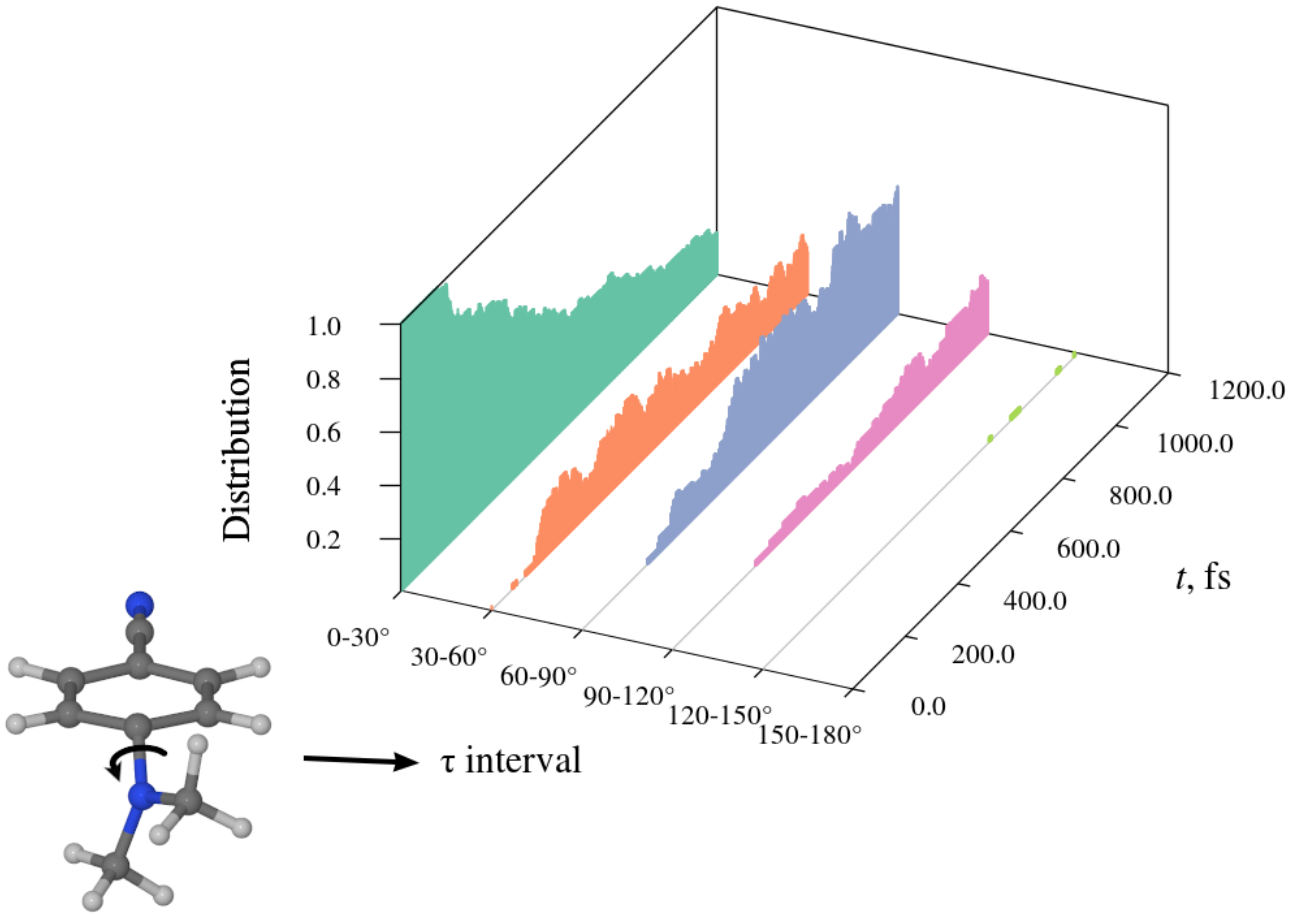
$$E_{\mathrm{QM/MM}}(\mathbb{S}) = E_{\mathrm{QM}}(\mathbb{I}) + E_{\mathrm{MM}}(\mathbb{O}) + E_{\mathrm{QM\text{-}MM}}(\mathbb{I}, \mathbb{O})$$

  $\mathbb{S}$ – entire system

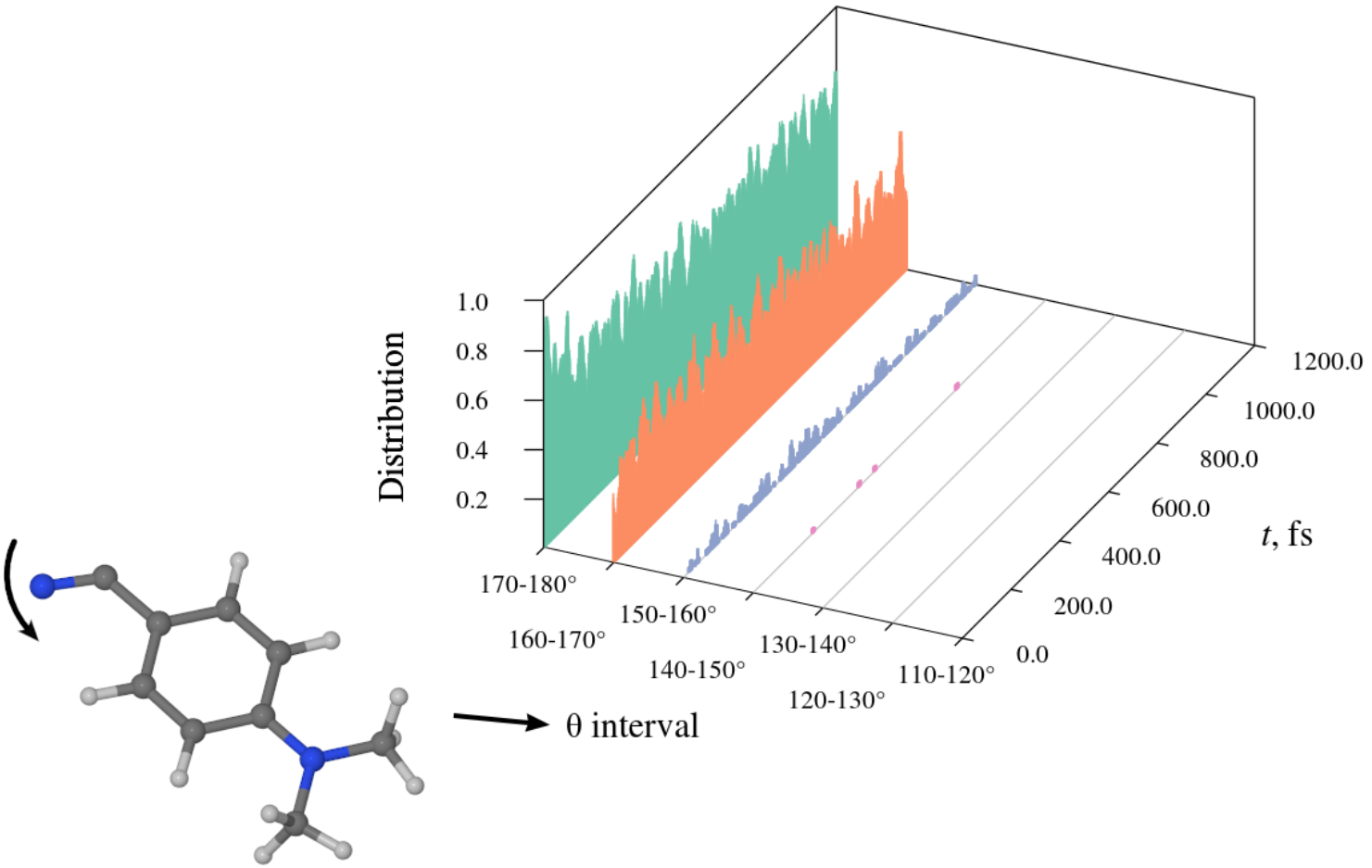
  $\mathbb{I}$ – inner (QM) subsystem

  $\mathbb{O}$ – outer (MM) subsystem

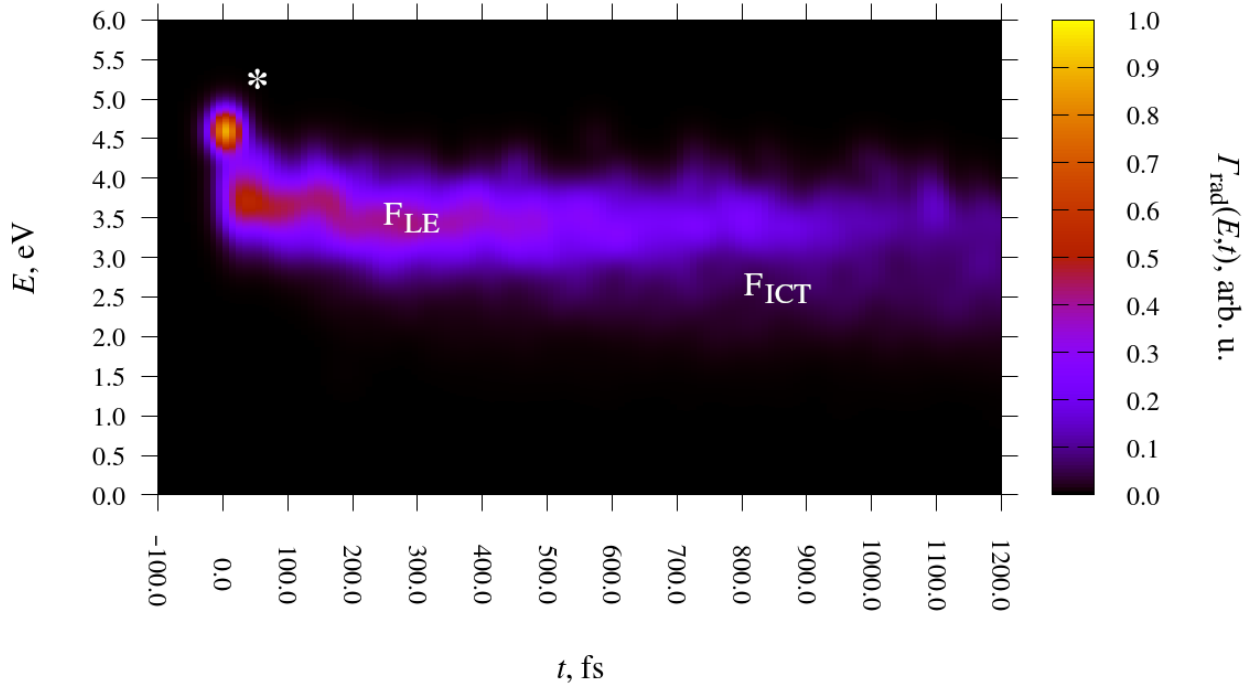
- The QM subsystem is treated with SOS-ADC(2).
- The dynamics of the system is propagated with the surface hopping method.



Time evolution of molecular geometry.



Time evolution of molecular geometry.



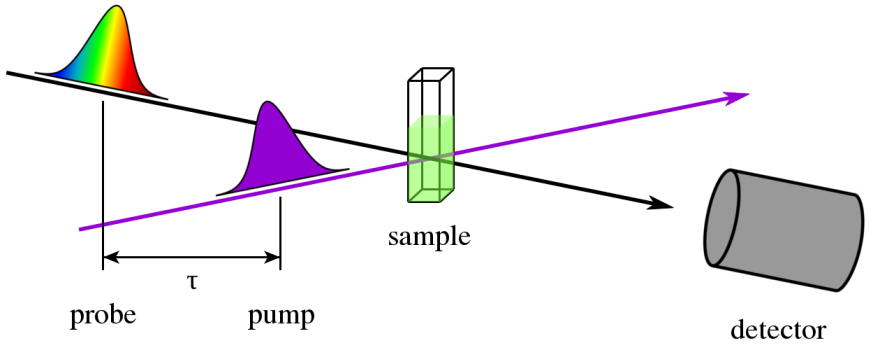
Simulated time-resolved fluorescence spectrum of DMABN in water.

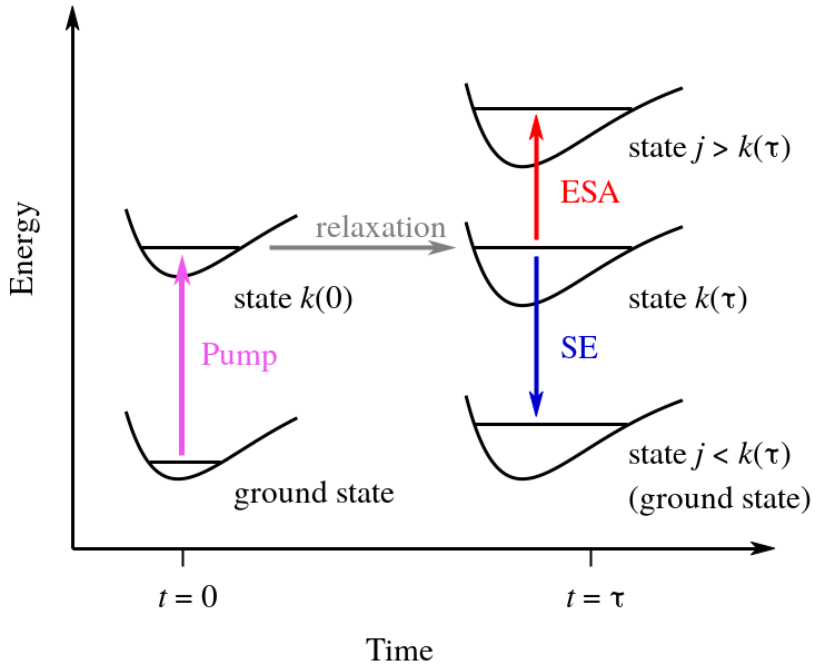
$*$ – short-lived emission from the S_2 state

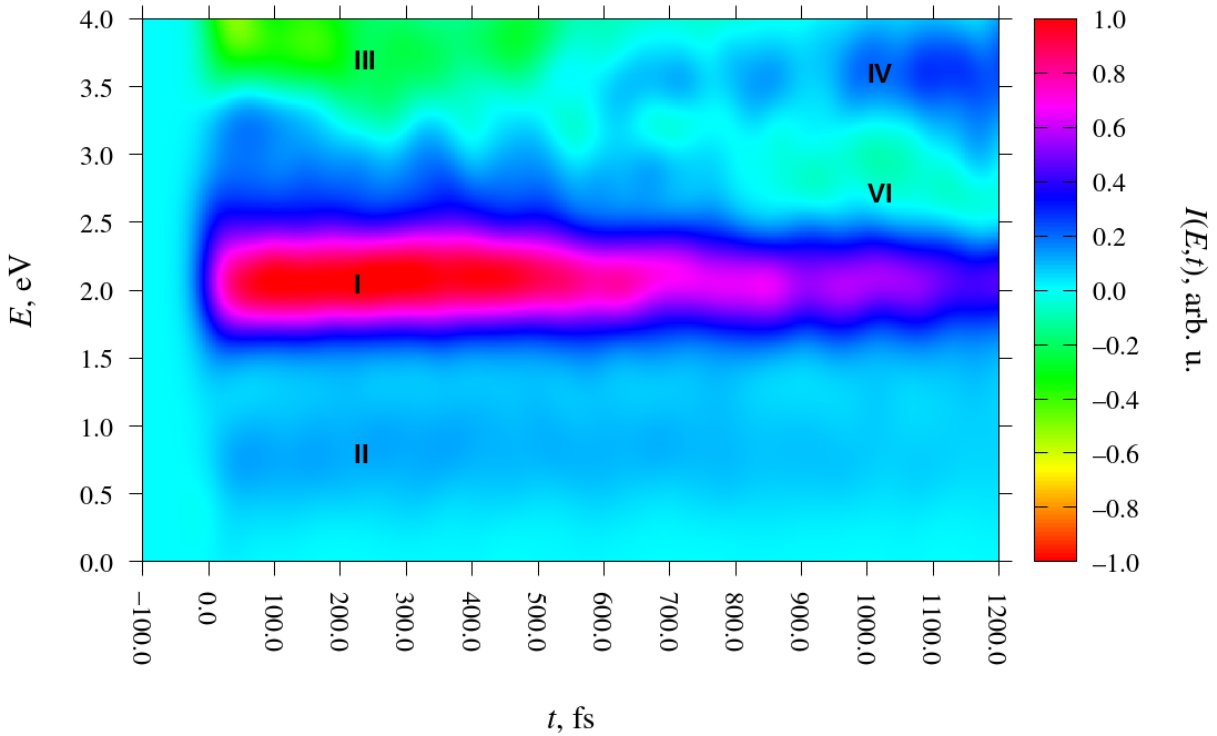
F_{LE} – normal emission

F_{ICT} – anomalous emission

Transient Absorption Spectroscopy





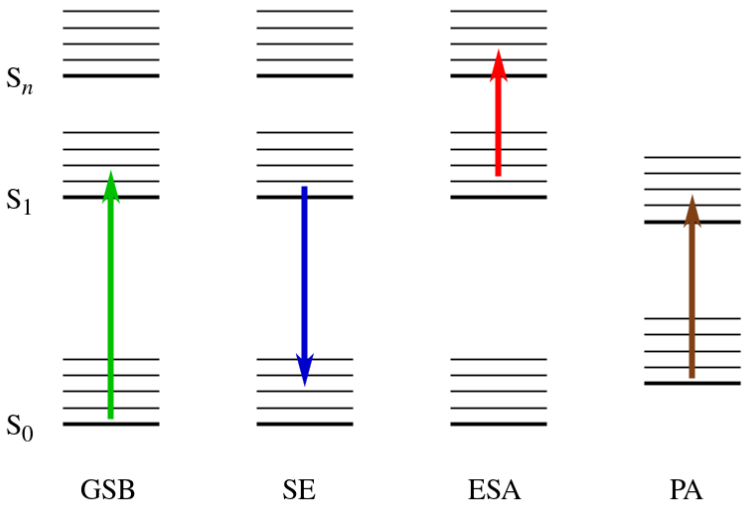


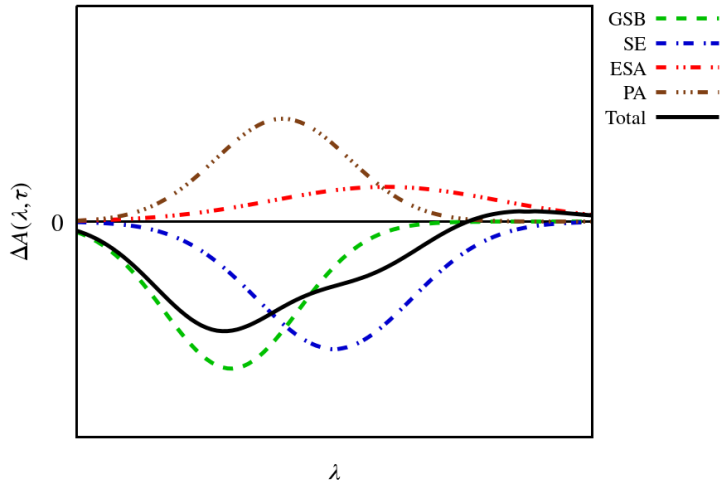
Simulated transient absorption spectrum of DMABN in acetonitrile.

I, **II**, and **III** – signals due to the S_1-LE structure

IV, **VI** – signals due to the S_1-TICT structure

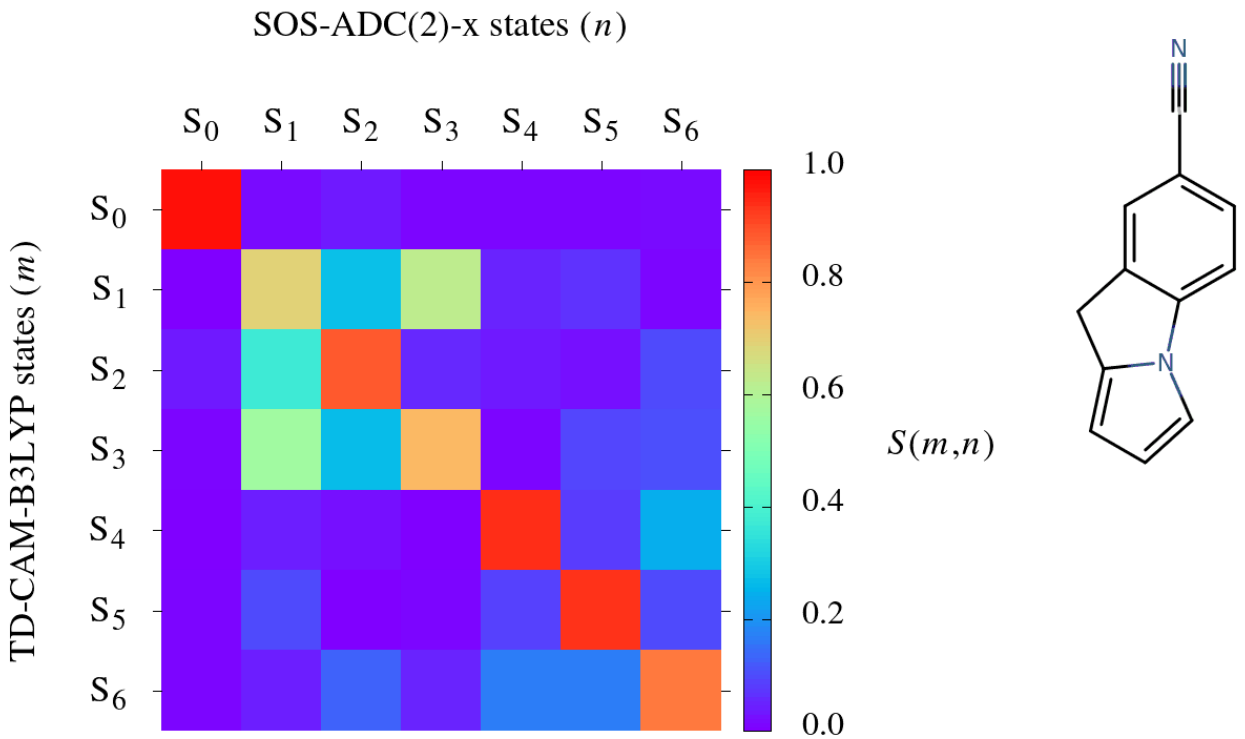
Inclusion of High-Energy Excited States





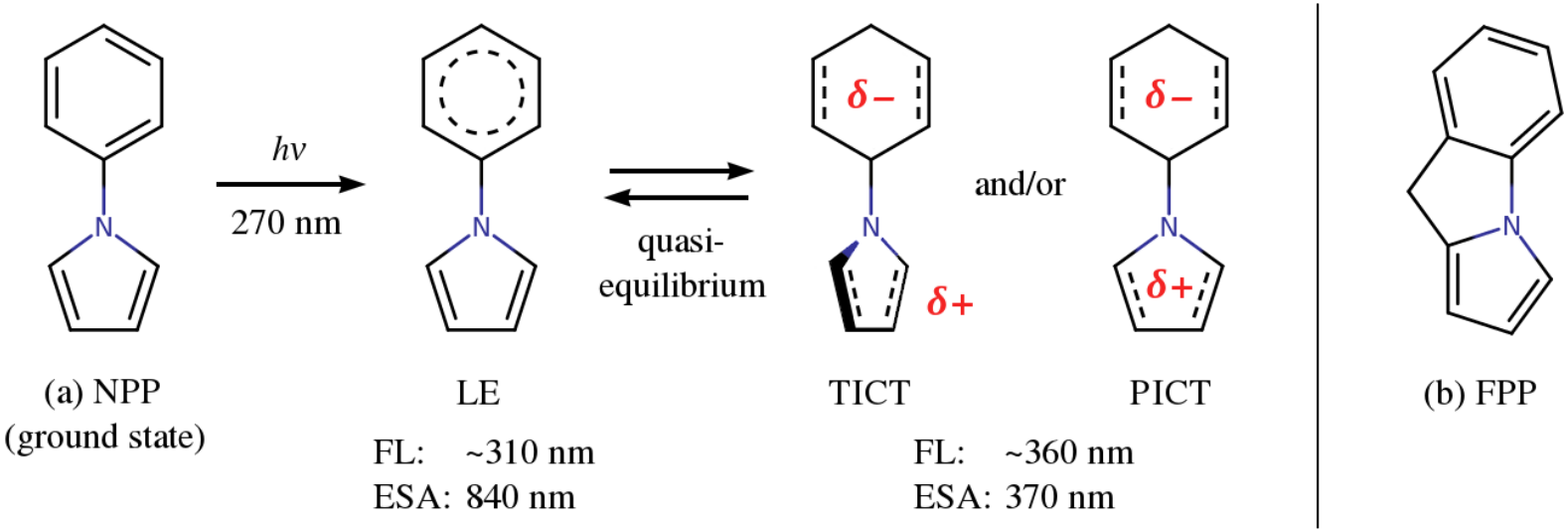
The ESA process involves transitions into high-energy excited states, which may well have doubly excited character.

Inclusion of High-Energy Excited States



$$S(m,n) = \left| \langle \Psi_m^{\text{TDDFT}} | \Psi_n^{\text{SOS-ADC(2)-x}} \rangle \right|$$

There is *usually* a one-on-one correspondence between excited states obtained with low- and high-level methods.

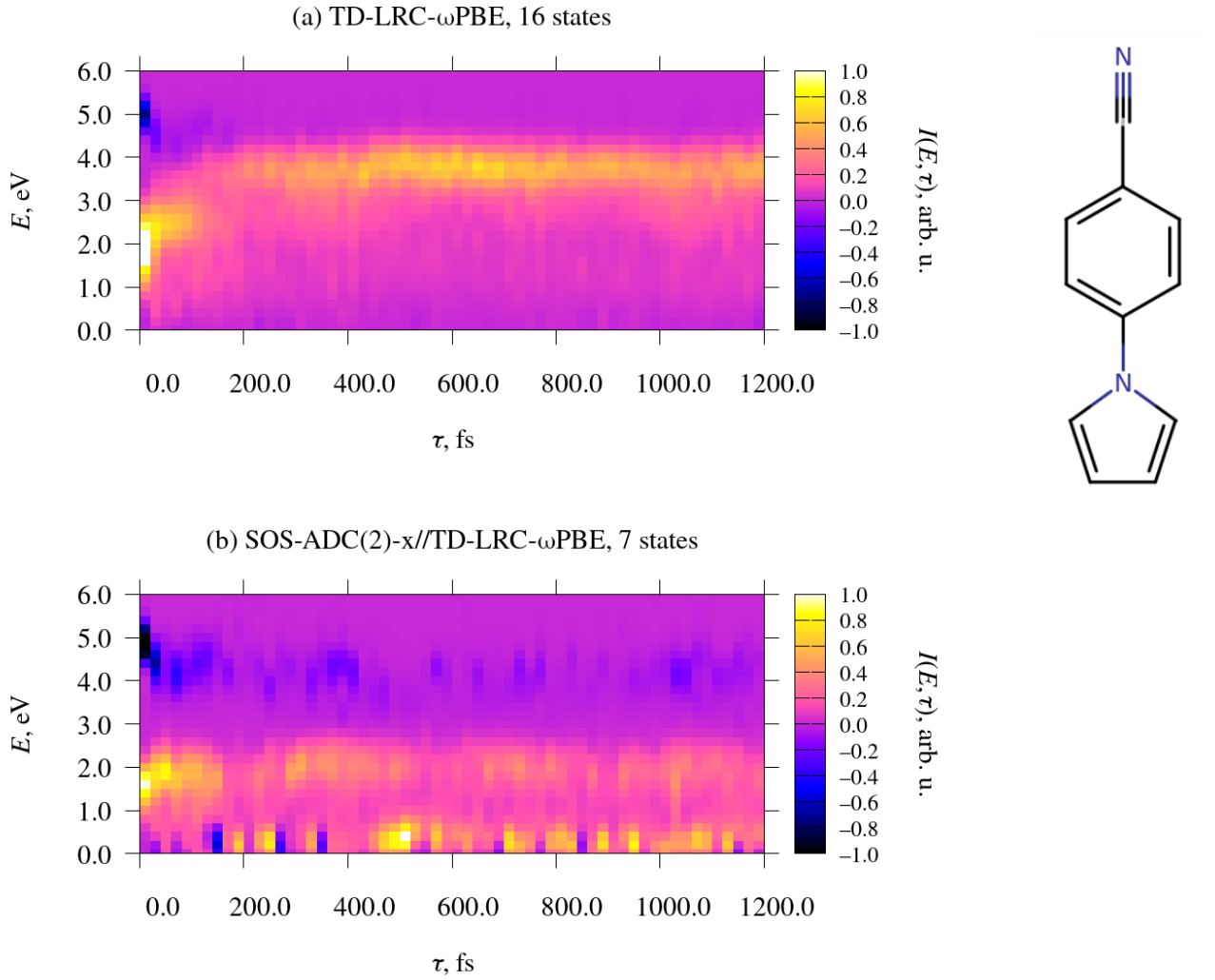


(a) Molecular structure and photophysics of *N*-phenylpyrrole (NPP).

(b) Molecular structure of fluorazene (FPP).

Unlike DMABN, the *N*-phenylpyrroles provide a model of ICT between aromatic moieties.

Simulation Results



Simulated transient absorption spectrum of 4-cyano-*N*-phenylpyrrole in the gas phase.

Acknowledgements

- Funding:
  - From Postdoc to PI: the future leaders of ERA (PD2PI)
  - National Science Centre (NCN), Poland
  - Stiftelsen Olle Engkvist Byggmästare, Sweden
  - Wenner-Gren Stiftelserna, Sweden

- Computing time:
  - Wrocław Centre for Networking and Supercomputing (WCSS)
  - Centre of Informatics of the Tricity Academic Supercomputer and Network (CI TASK)
  - Poznań Supercomputing and Networking Center (PCSS)

- But most importantly:
  - Dr hab. Adam Kubas
  - Prof. Dr Bo Durbeej
  - Prof. Dr R. J. Dwayne Miller
  - Dr Attila Tajti