L1

Photochemistry and Photophysics: Overview

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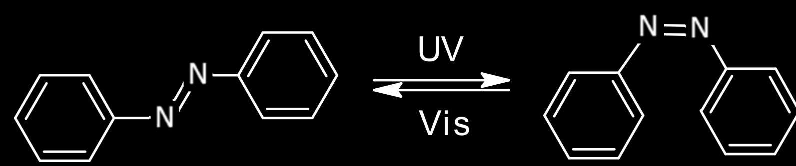
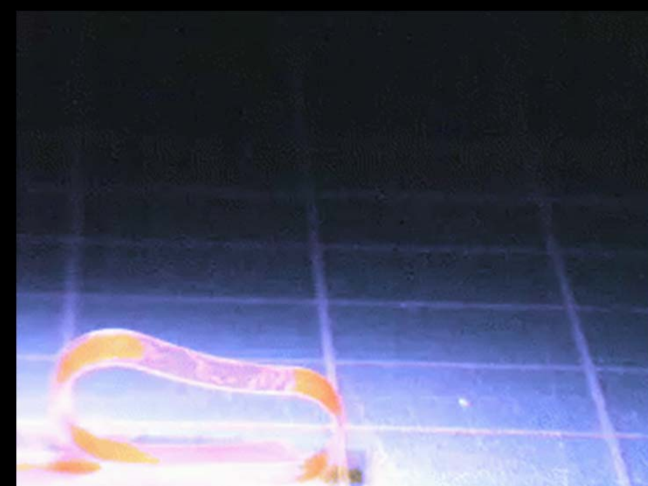
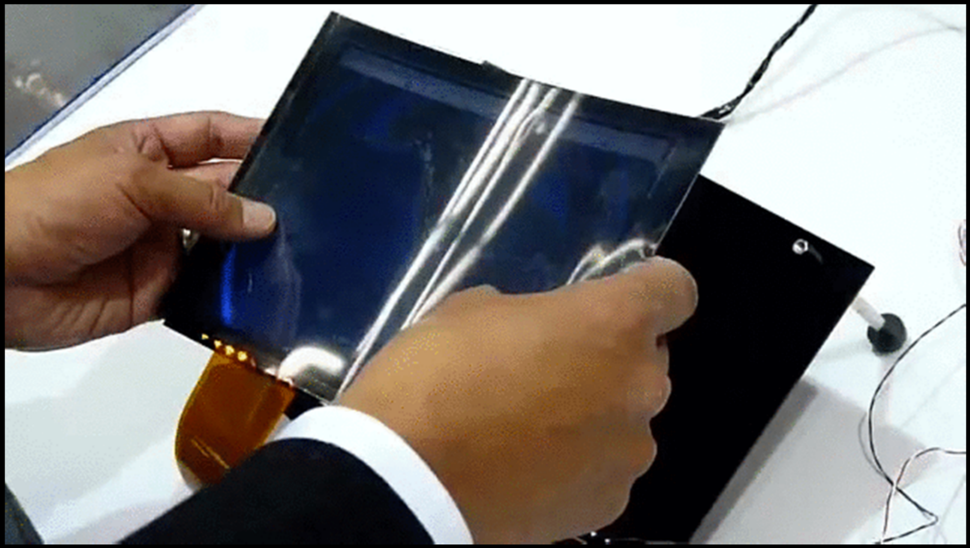
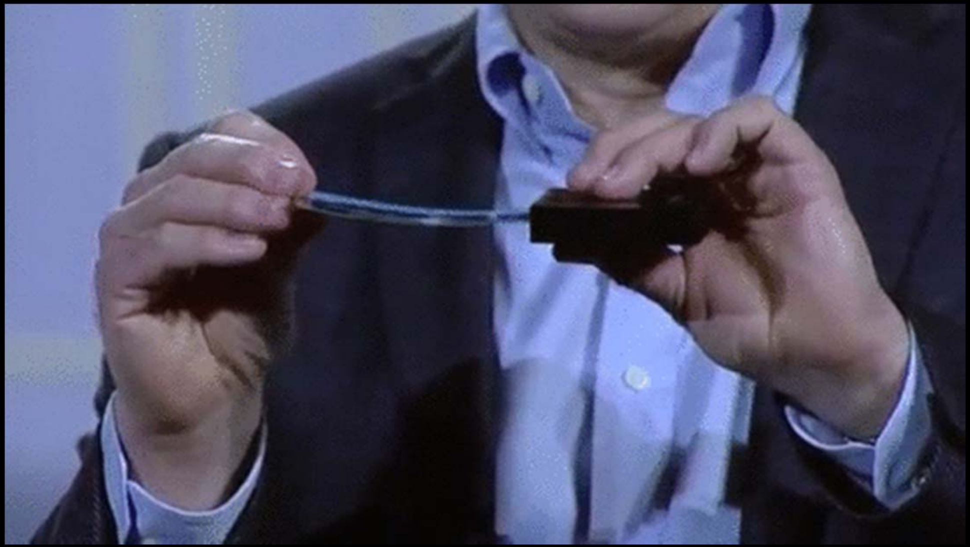




- Yamada et al, J Mater Chem **19**, 60 (2009)



Toshiba, 2011



Samsumg, 2013

Why to study it?

Physical-chemical sciences

- Radiation-matter interaction
- Ultrafast processes
- Interstellar chemistry

Bio-sciences

- Photosynthesis
- Bioluminescence
- Photostability of genetic code
- Vision and light detection

Technology

- Photovoltaics
- OLEDs
- Phototherapy
- Photocatalysis

Pump-probe experiments based on ultra-fast laser pulses have increased the resolution of the chemical measurements to the femtosecond (10^{-15} s) time scale.

The need for Theory

Theory is necessary to map the ground and excited state surfaces and to model the mechanisms taking place upon the photoexcitation.

Theory is indispensable to deconvolute the raw time-resolved experimental information and to reveal the nature of the transition species.

In particular, excited-state dynamics simulations can shed light on time dependent properties such as lifetimes and reaction yields.

Towards industrial applications

Advantages of Organic Electronics:

- Low cost
- Easy processing
- Rich physical chemistry
- Low environmental impact

Drawbacks of Organic Electronics:

- Low photo-efficiency
- Photochemical degradation
- Heuristic approach for synthesis

Main Strategy:

- Tell me what you want and I give you a new material

How can CompChem help in Organic Electronics?

- ☑ Providing insights into physical-chemical phenomena
- ☑ Helping with deconvolution of experimental data
- ☒ Predictig properties before synthesis

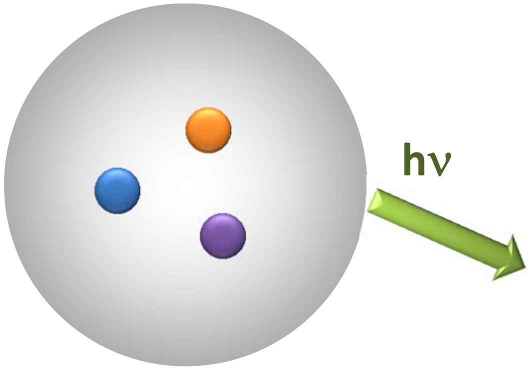
What do we need to achieve these goals?

Settling the bases: photochemistry, excited states, and conical intersections

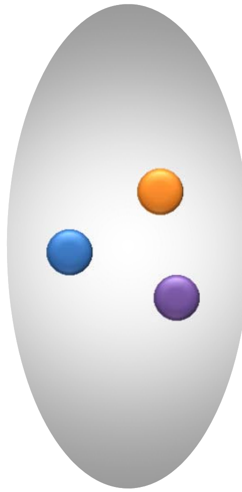
Stating the problem:

- **What does happen to a molecule when it is electronically excited?**
- **How does it relax and get rid of the energy excess?**
- **How long does this process take?**
- **What products are formed?**
- **How does the relaxation affect or is affected by the environment?**
- **Is it possible to interfere and to control the outputs?**

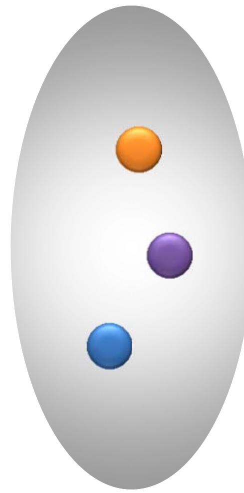
Photoexcitation creates non-equilibrium



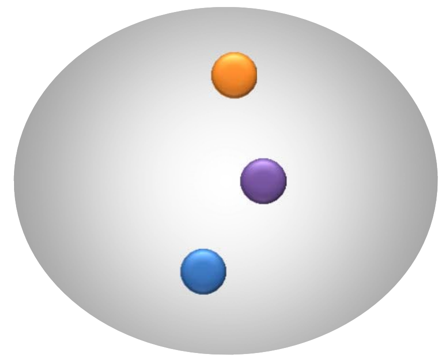
In the ground state, nuclei and electrons are in equilibrium.



A photon changes the electron distribution. Nuclei and electrons are not in equilibrium anymore.

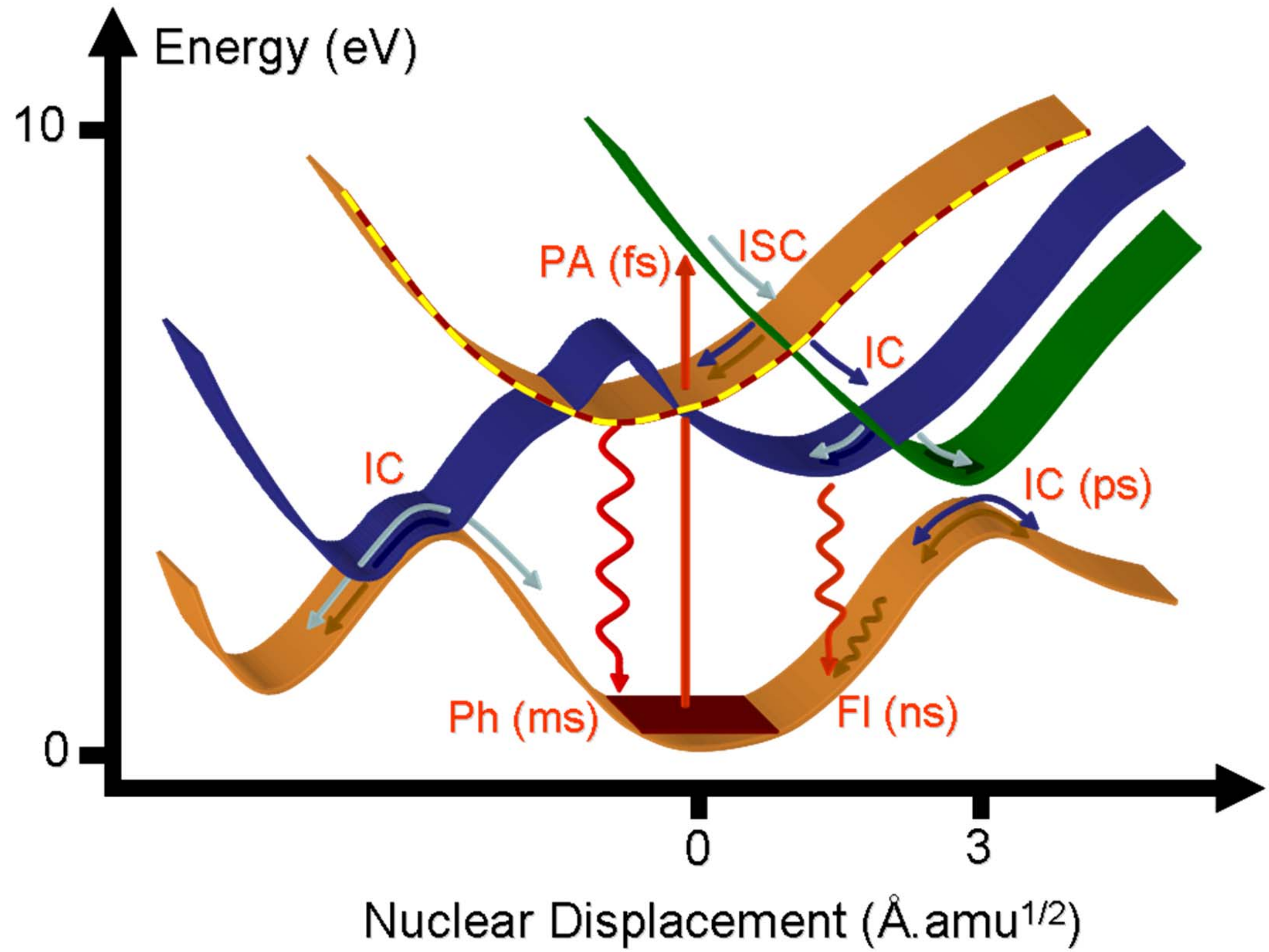


The nuclei move in response to the new electronic forces.

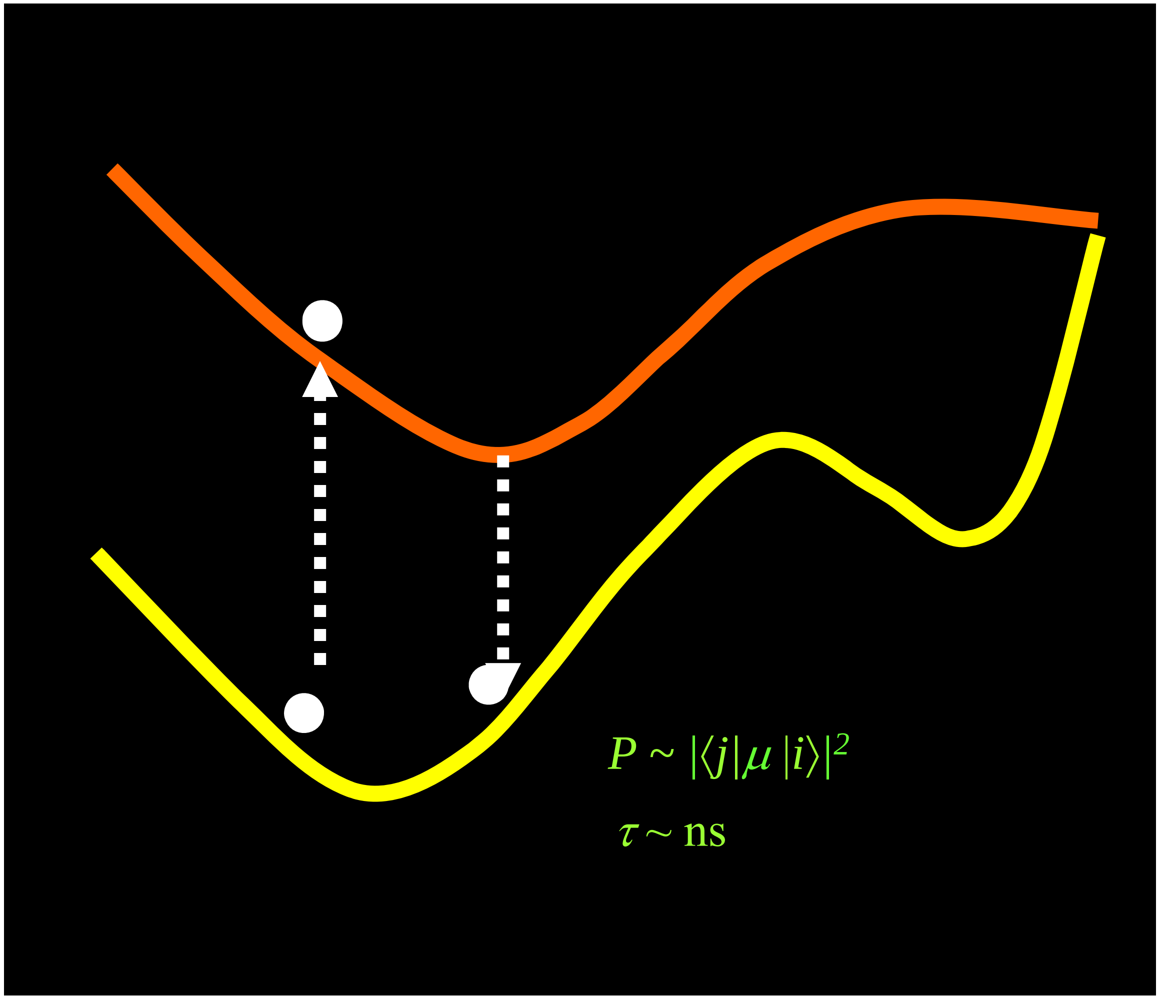


Electronic distribution changes to adjust to the new nuclear positions.

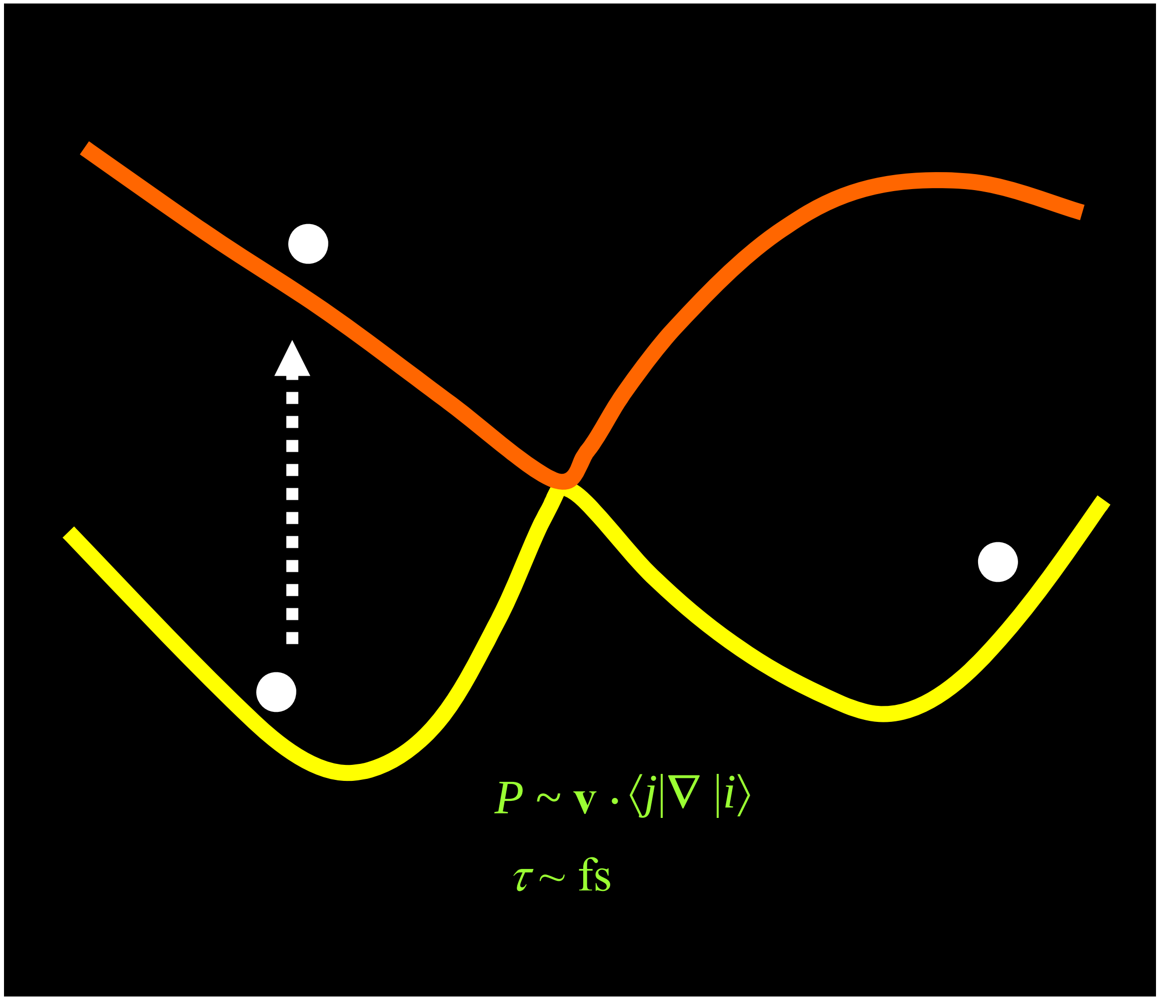
Photochemistry and photophysics



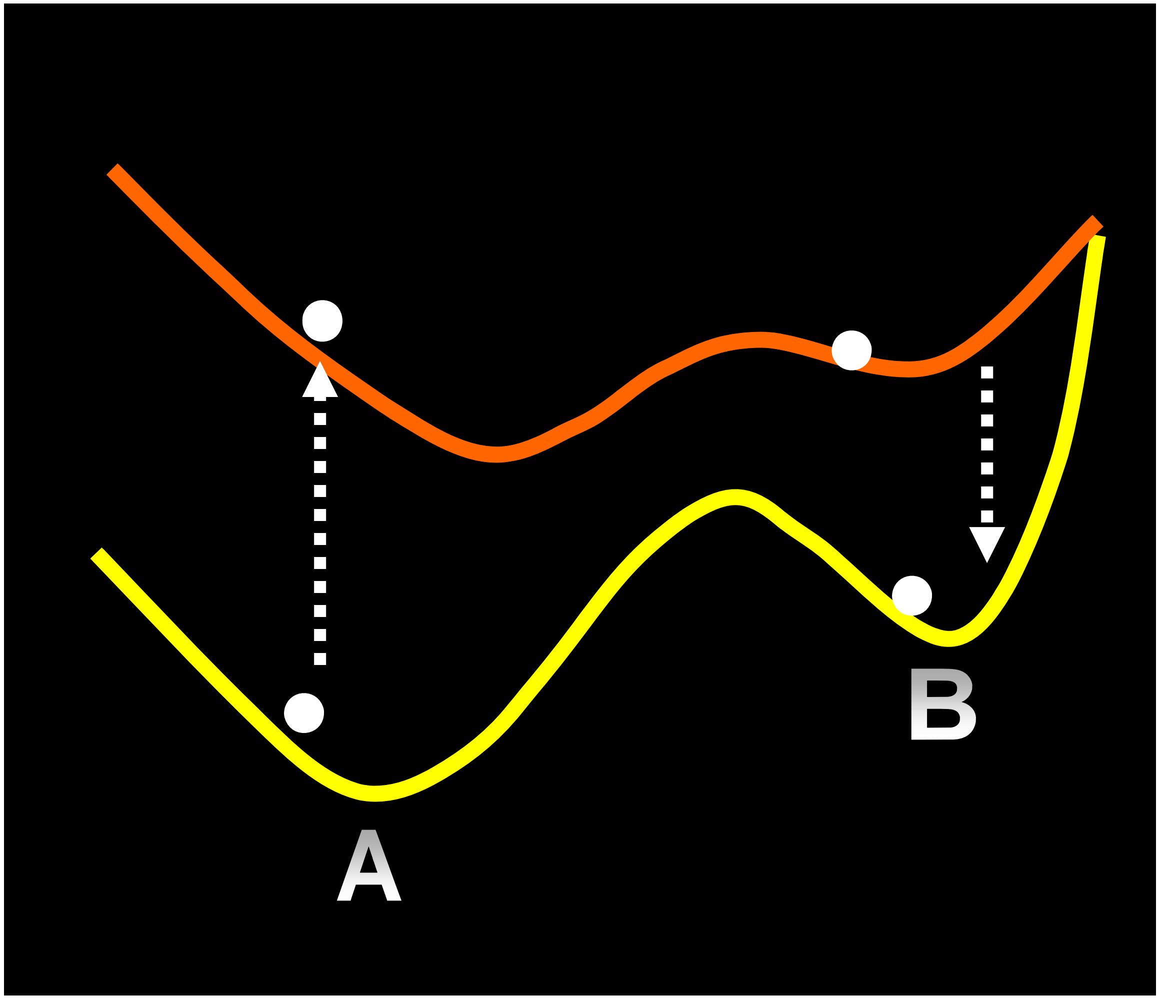
Basic process I: Radiative decay (fluorescence)



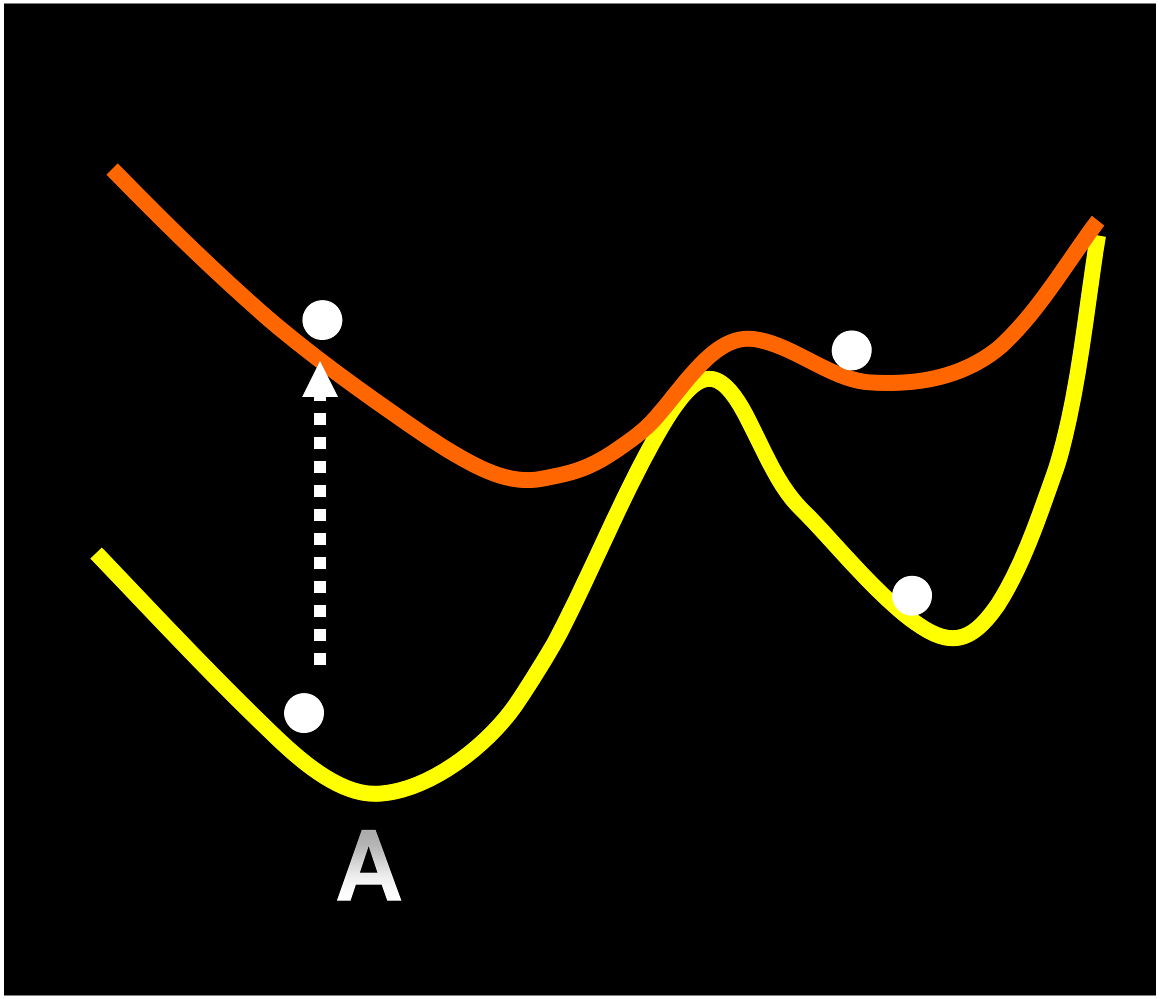
Basic process II: Non-radiative decay



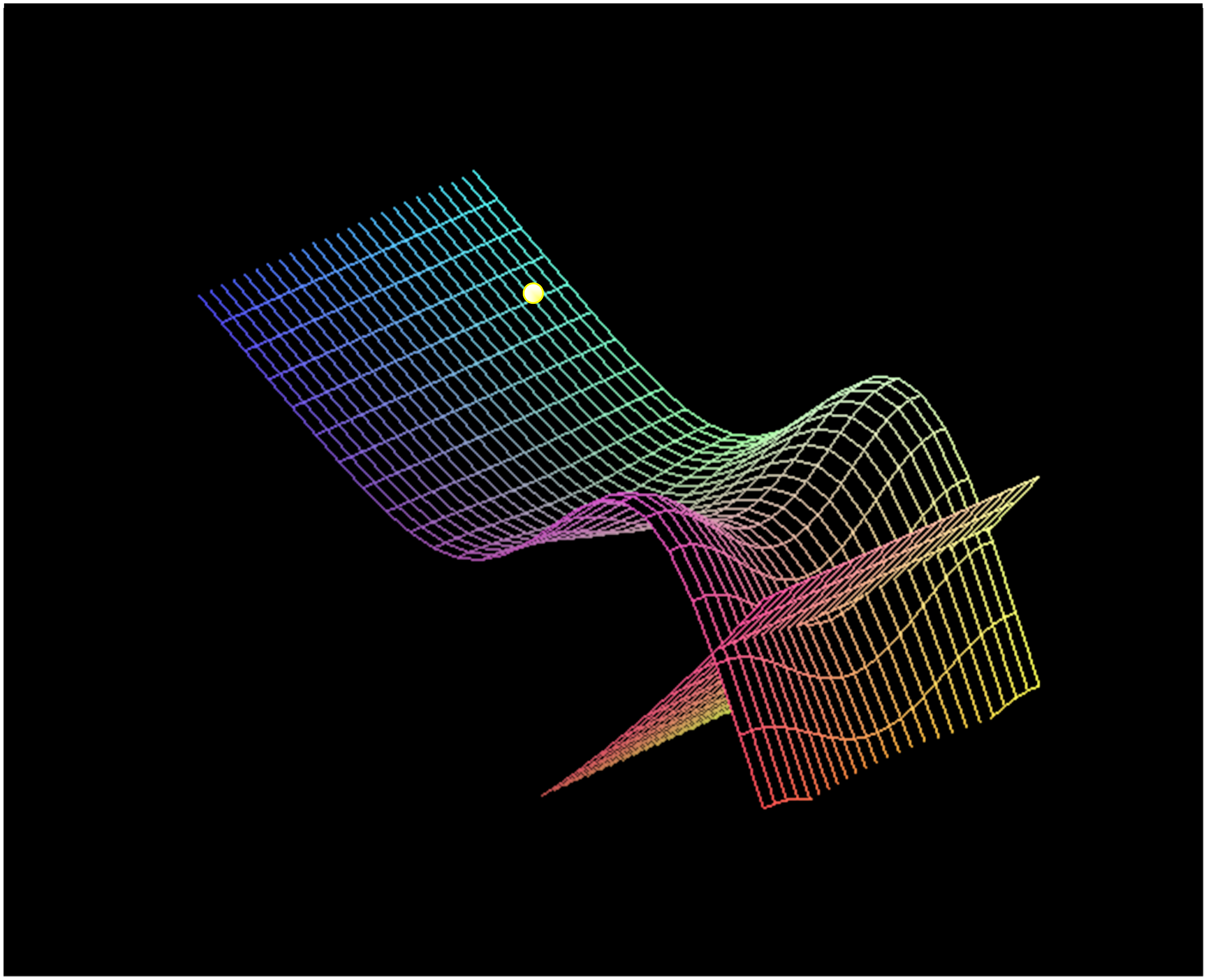
Photochemical process



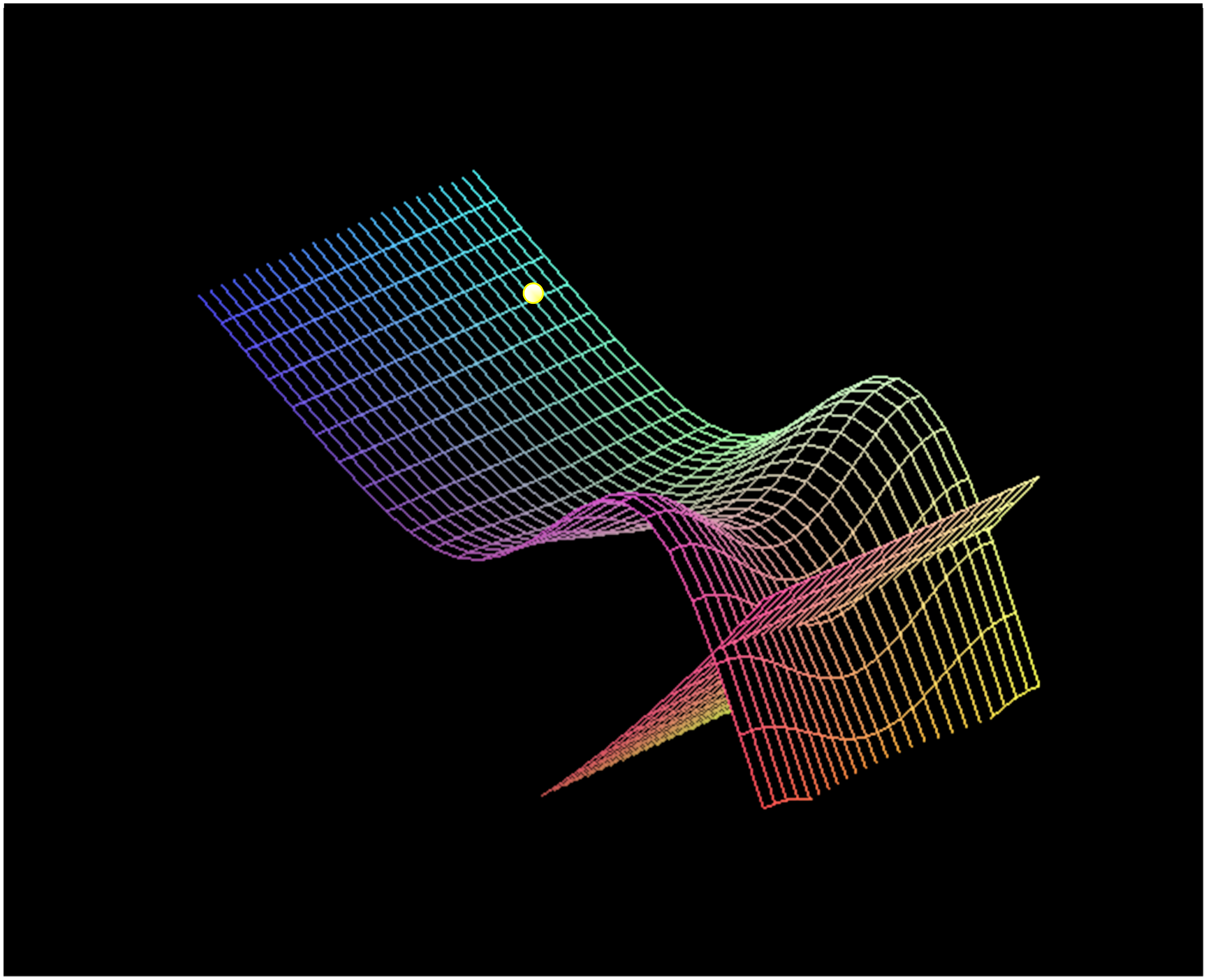
Photophysical process

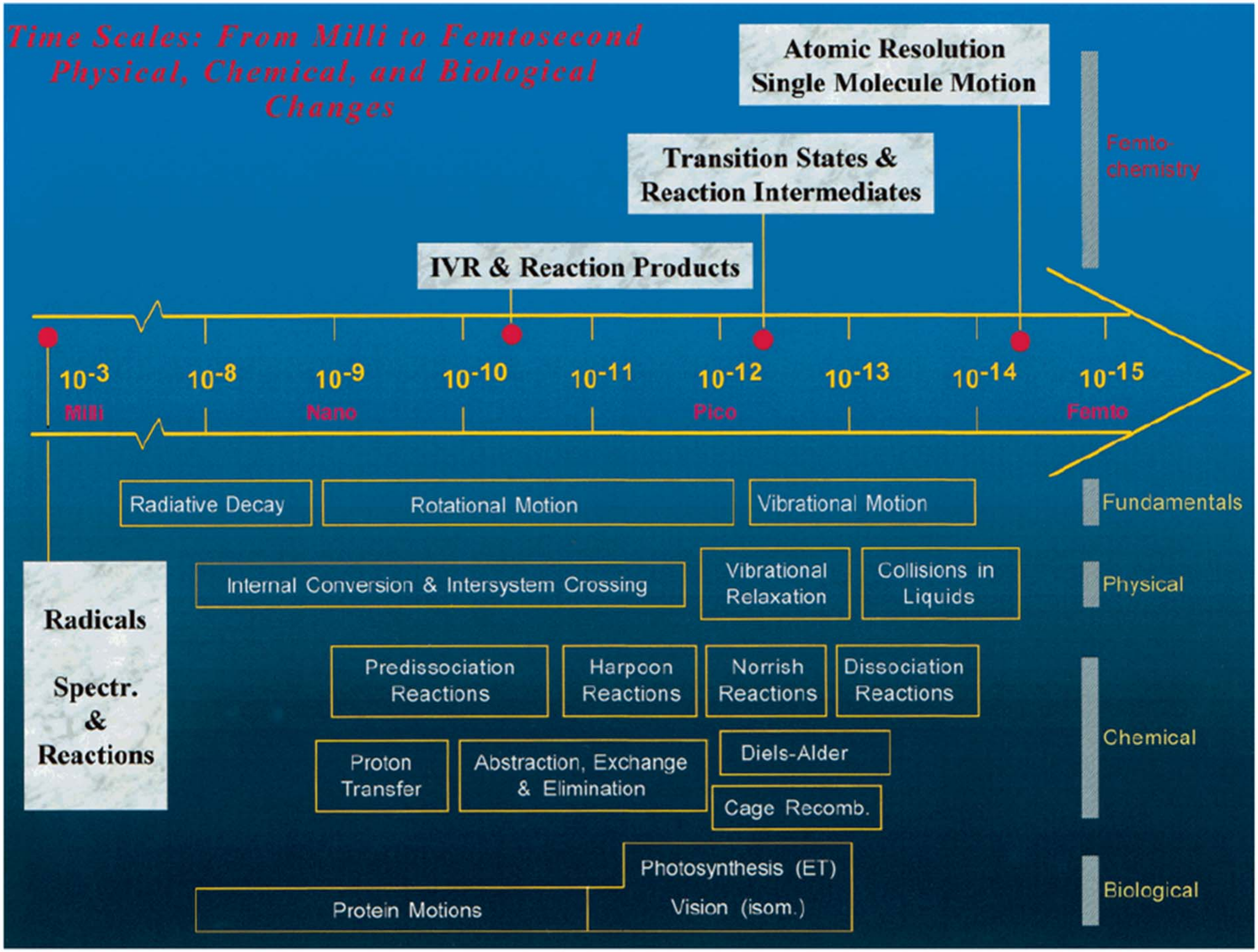


Beyond the simple picture



Beyond the simple picture





- Zewail, J Phys Chem A 104, 5660 (2000)

The Static Problem

1. How are the excited state surfaces?

2. For which geometries does the molecule have conical intersections?

3. Can the molecule reach them?

The Dynamics Problem

At a certain excitation energy:

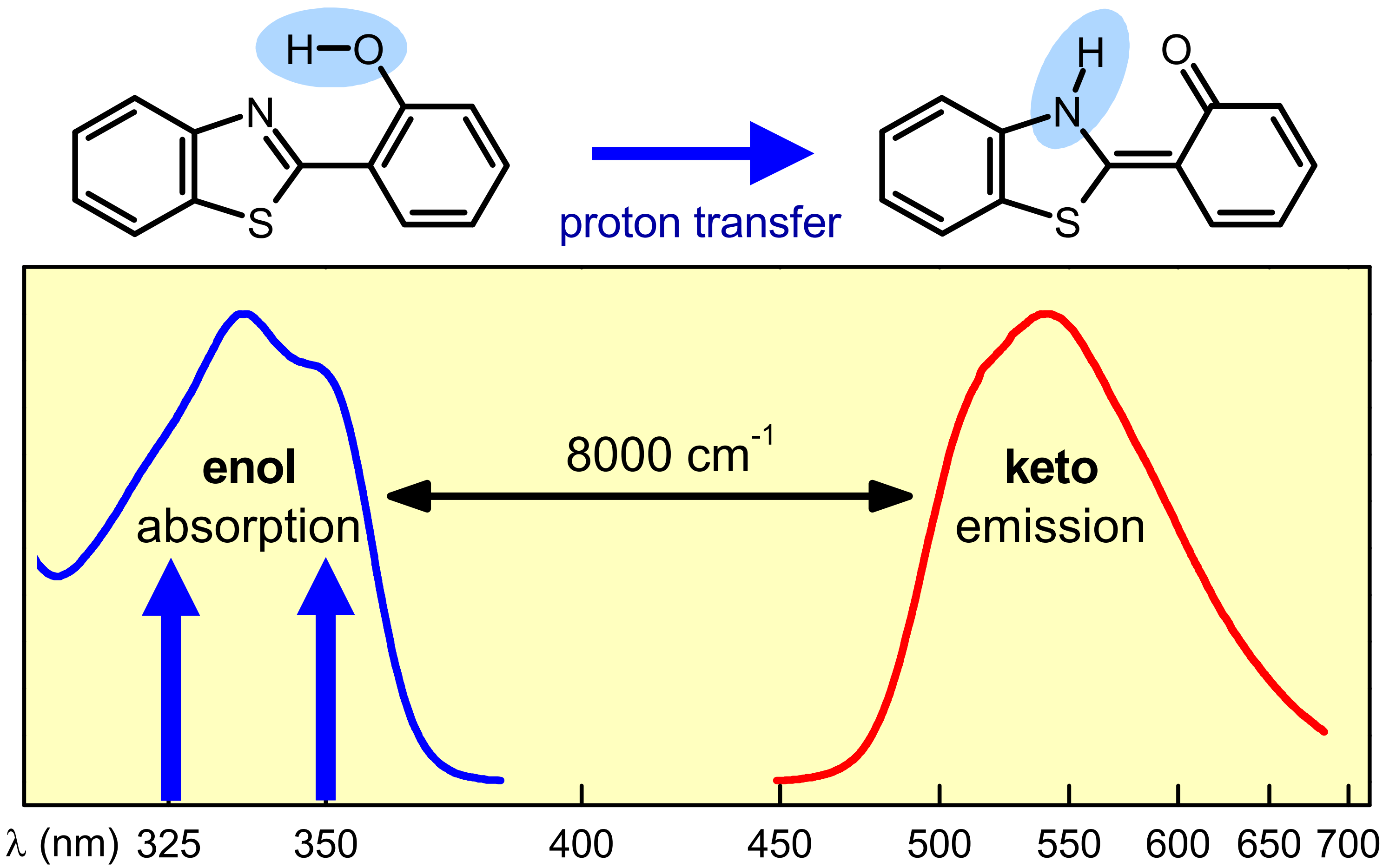
1. Which reaction path is the most important for the excited-state relaxation?

2. How long does this relaxation take?

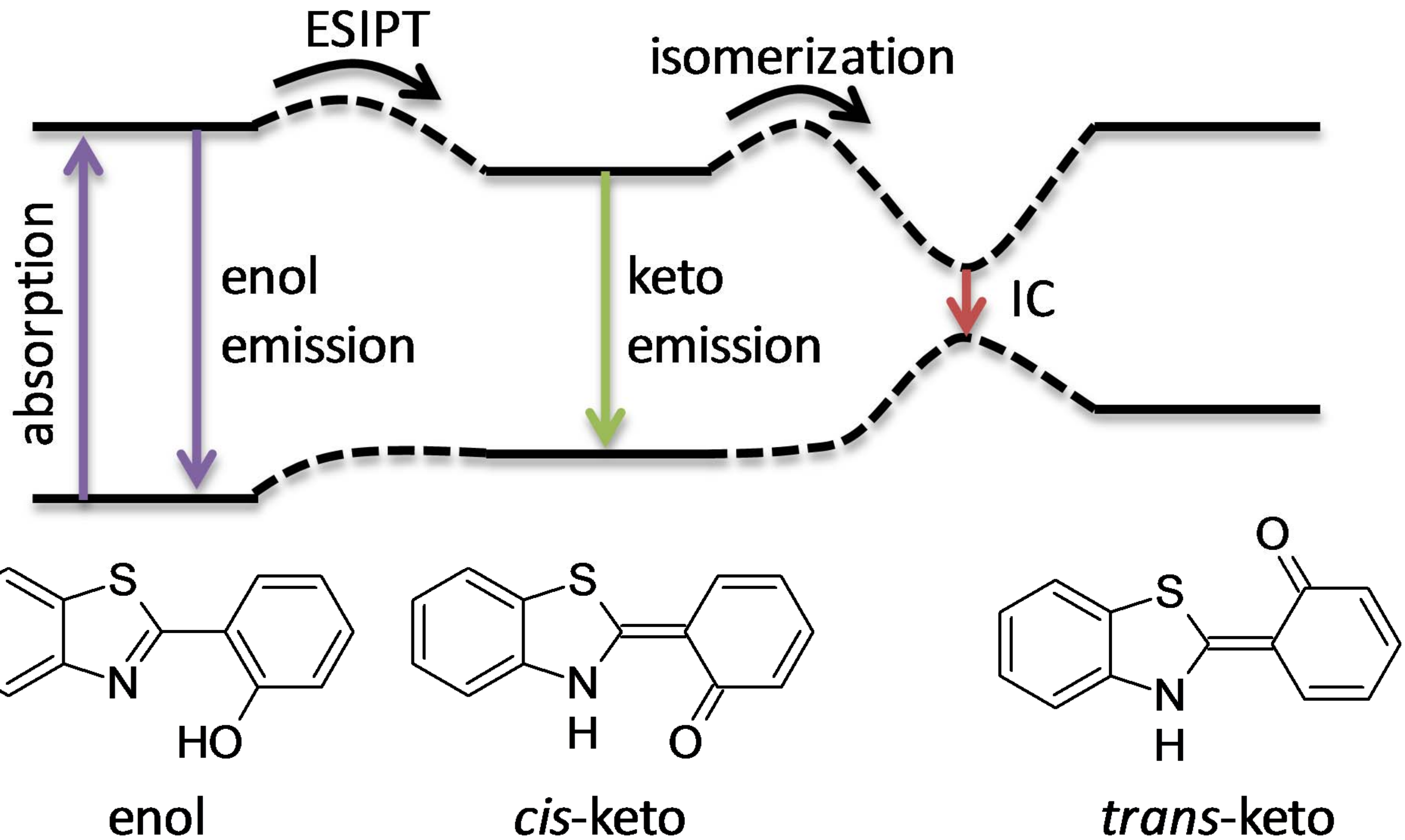
case study

Excited-state intramolecular proton transfer (ESIPT)

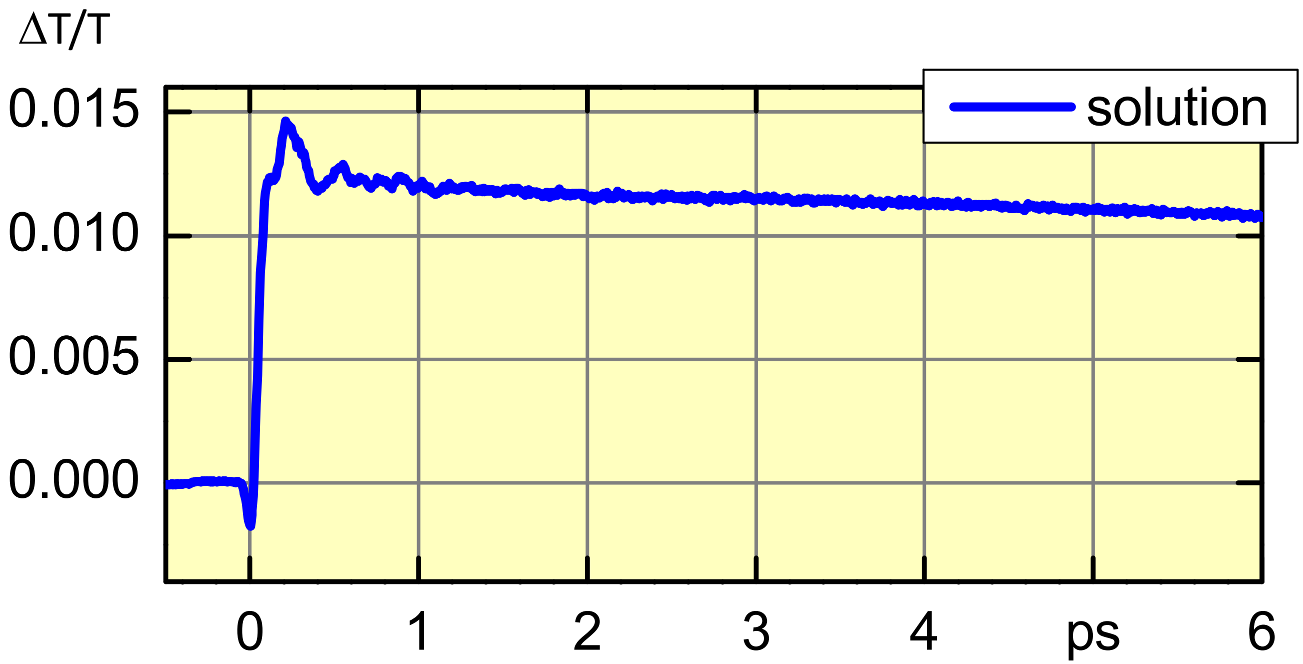
Hydroxyphenyl-benzothiazole (HBT)



Elsaesser and Kaiser, Chem. Phys. Lett. **128**, 231 (1986)

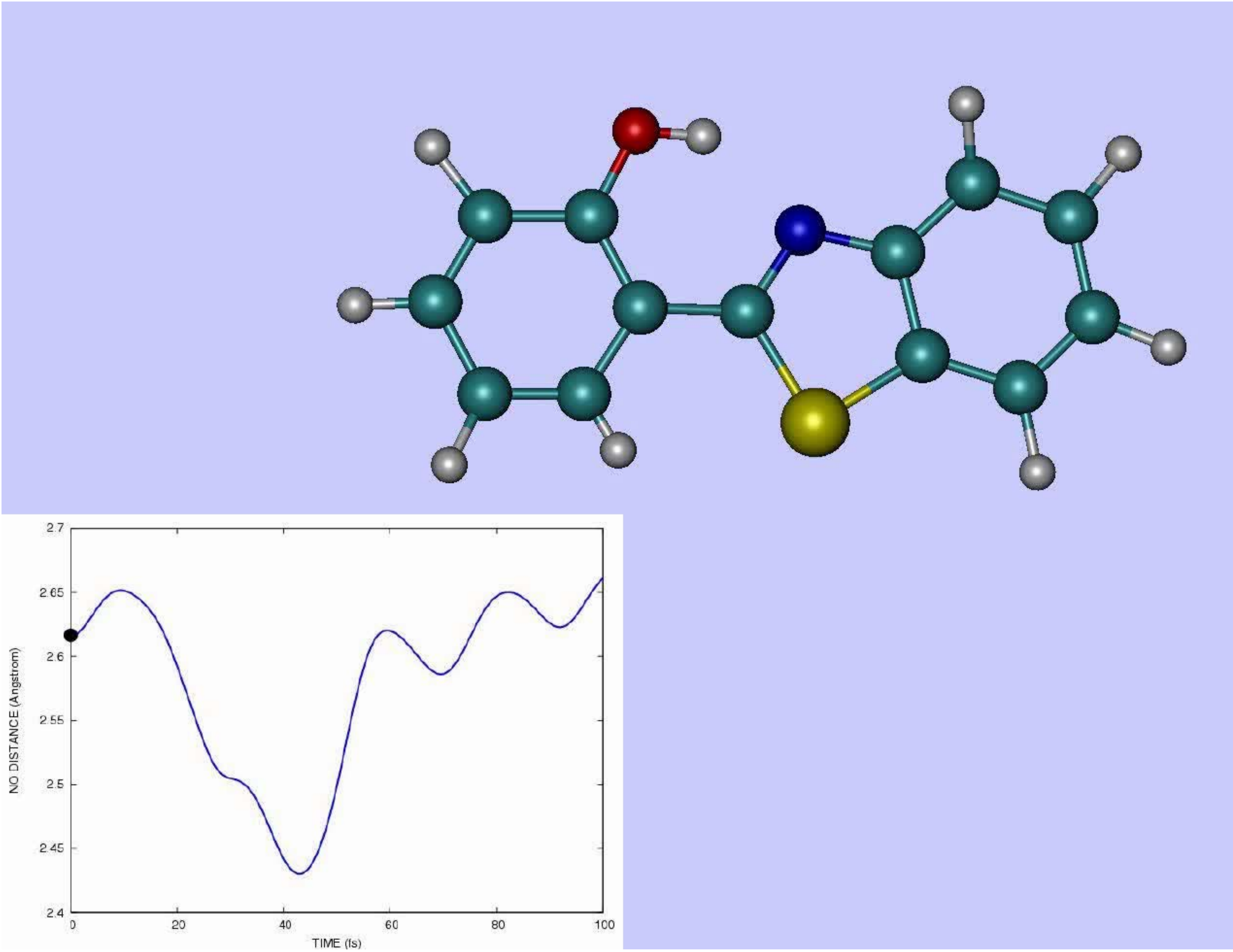

ESIPT
isomerization
absorption
enol
emission
keto
emission
IC
S
N
HO
S
N
H
O
S
N
H
O
enol
cis-keto
trans-keto

Emission signal at the keto wave number appears after only 30 fs



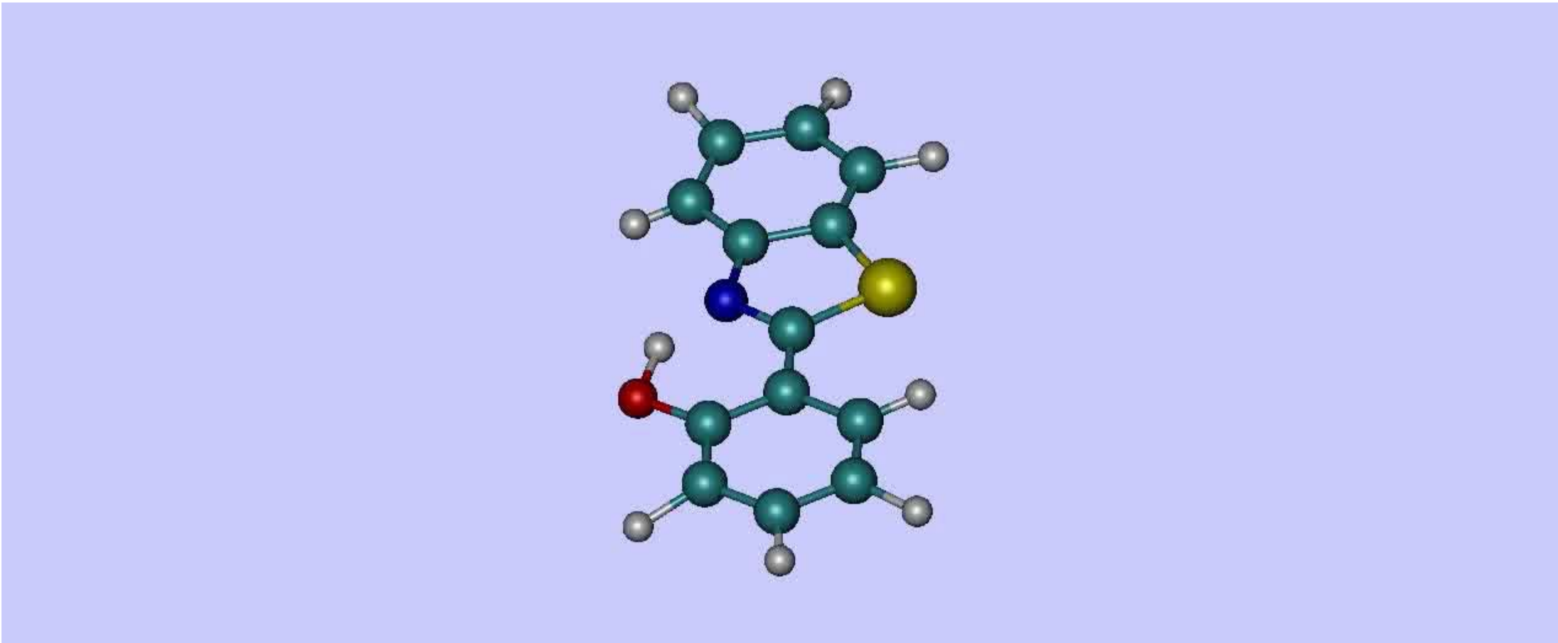
Lochbrunner, Wurzer, Riedle, J. Phys. Chem. A **107** 10580 (2003)

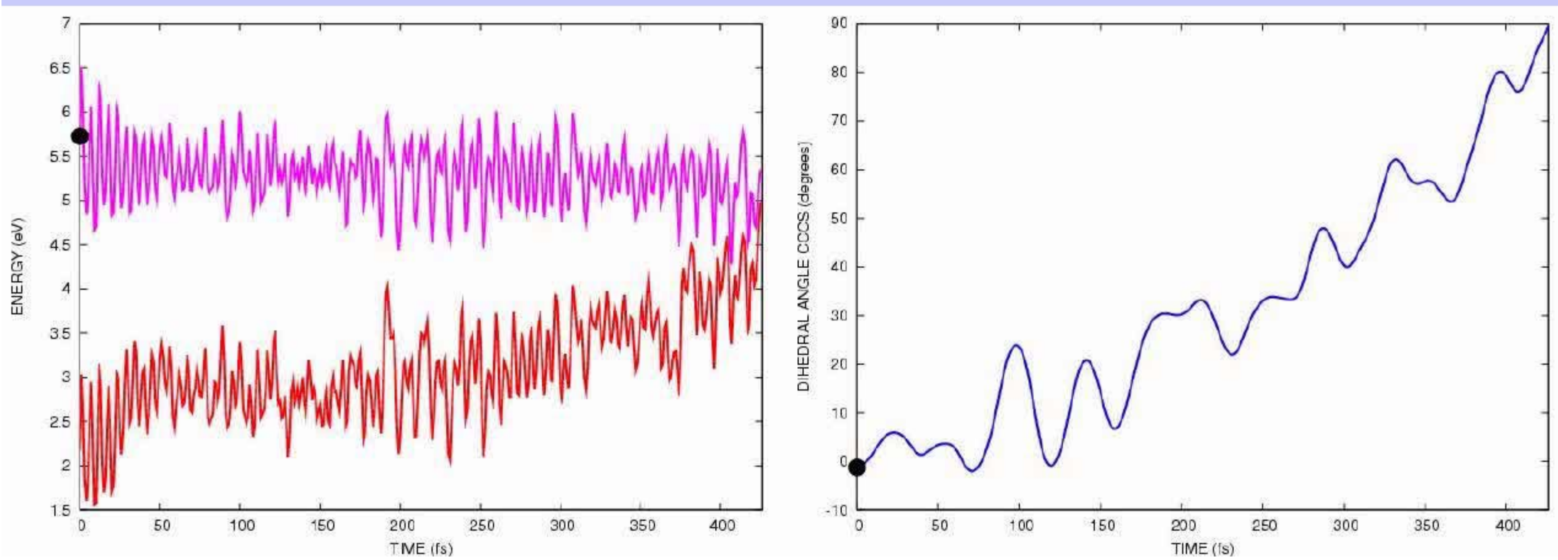
A N D
J L E S



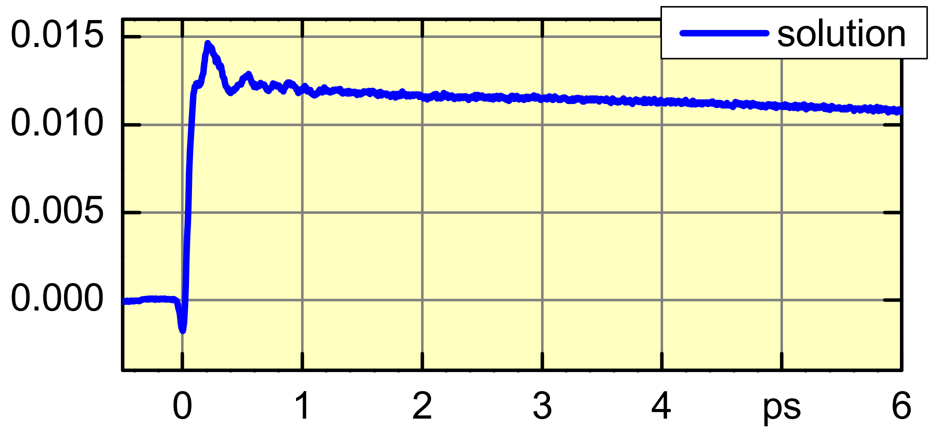
NO DISTANCE (Angstrom)
TIME (fs)
2.7
2.65
2.6
2.55
2.5
2.45
2.4
0
20
40
60
80
100

Internal conversion should play a role



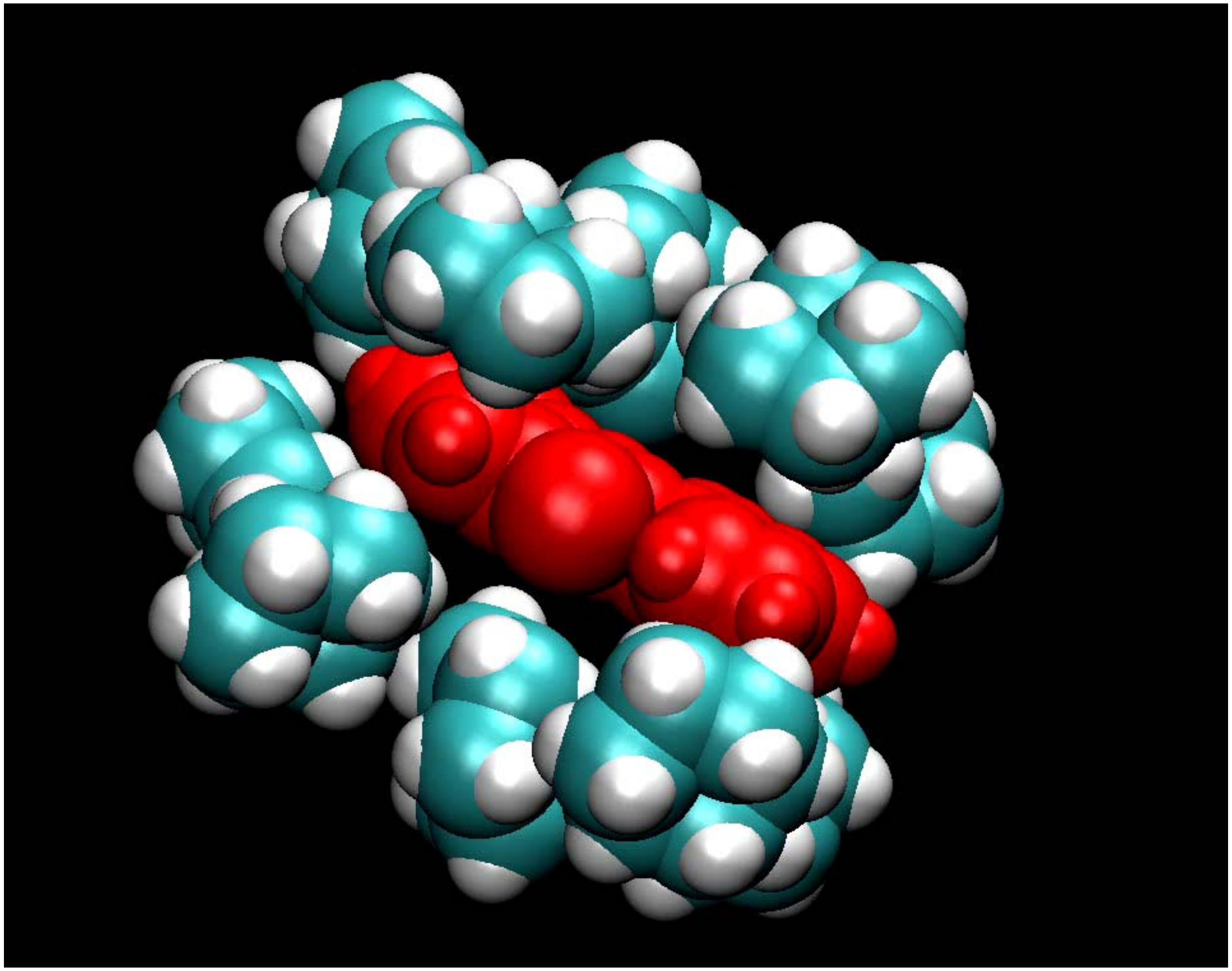


ESIPT: environment effects



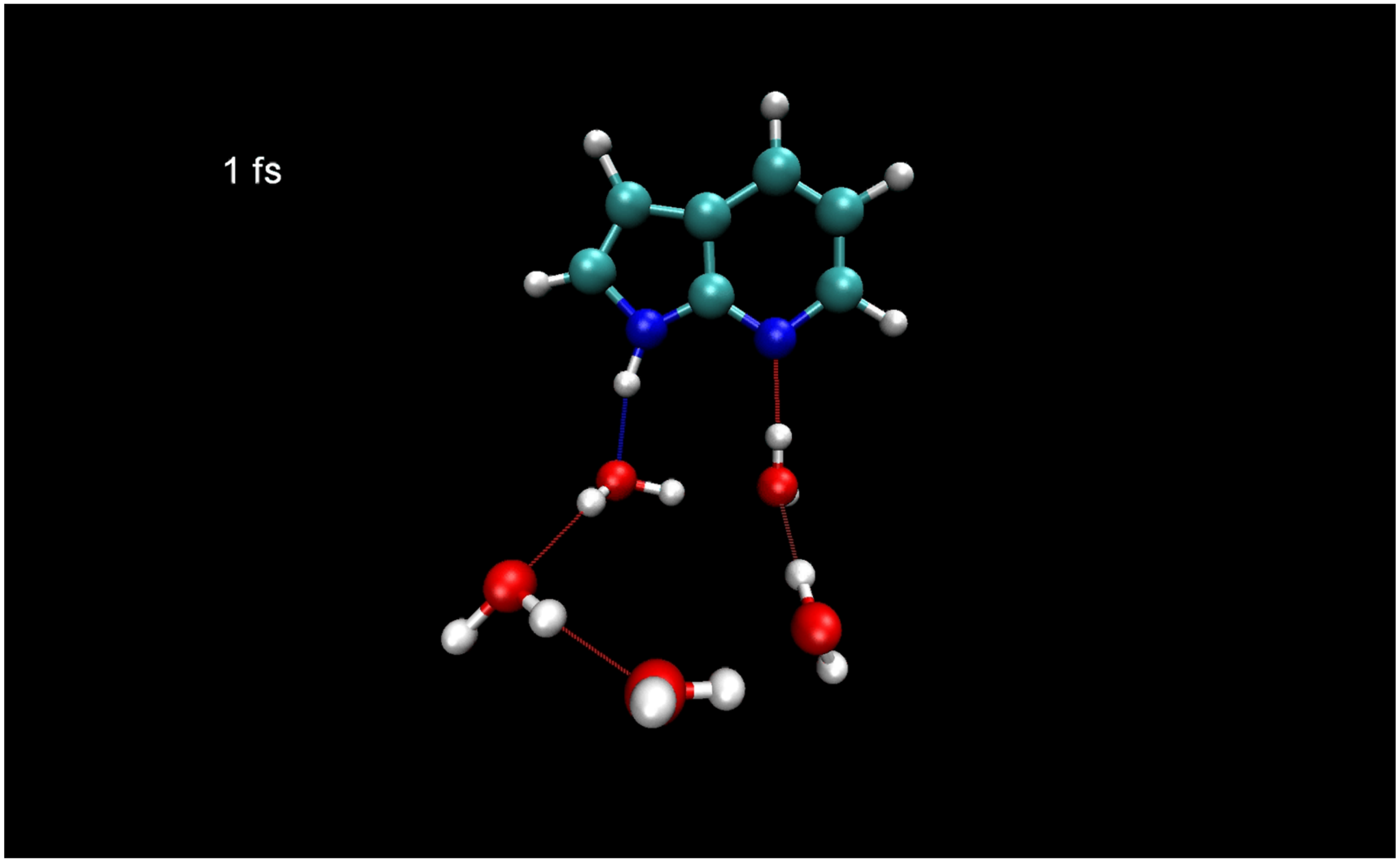
- Barbatti, Aquino, Lischka, Schriever, Lochbrunner, Riedle, PCCP **11**, 1406 (2009)

ESIPT: QM/MM simulations



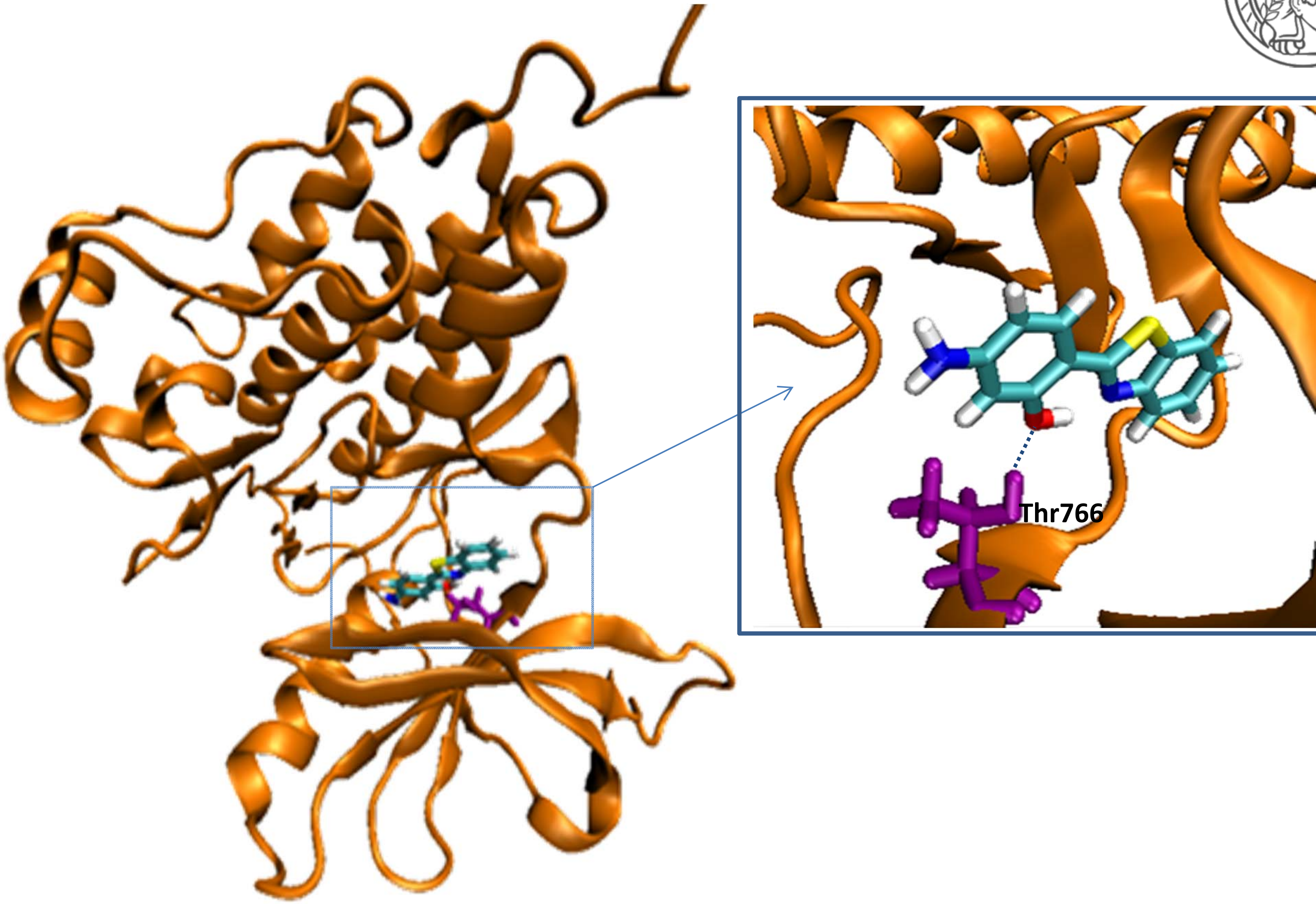
• Ruckenbauer, Barbatti, Lischka, 2014

Protic solvents

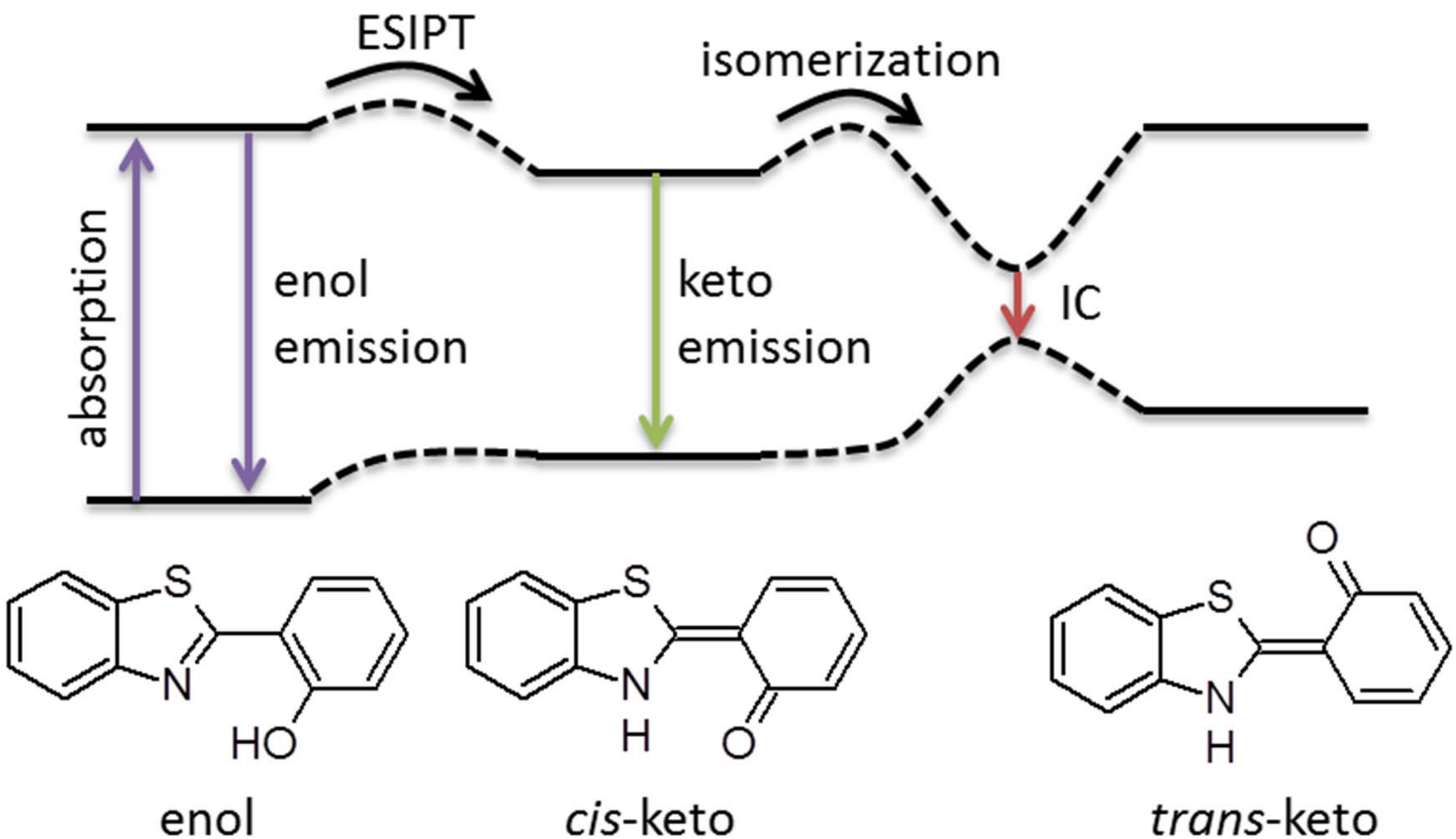


- Kungwan, Kerdpol, Daengngern, Hannongbua, Barbatti, Theor Chem Acc **133**, 1480 (2014)

ESIPT in cancer diagnostic?



Different conformers, different fates



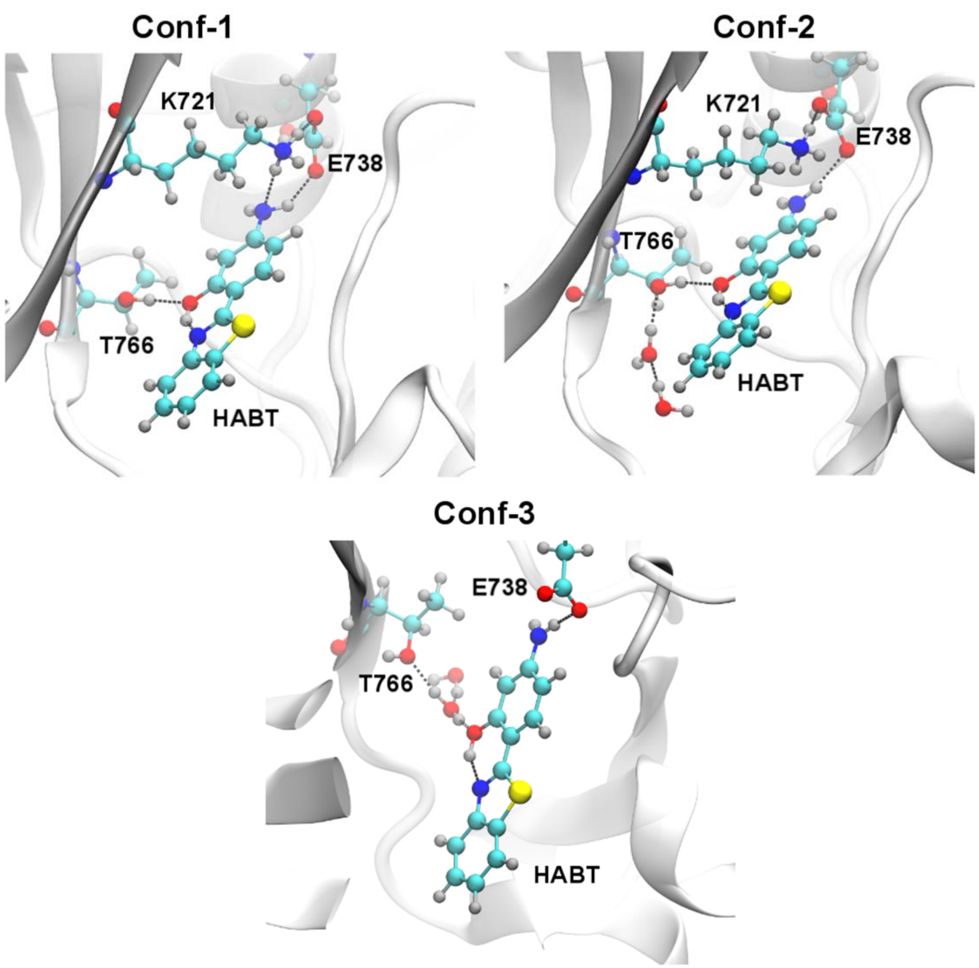
Three facts and one idea

1. Tyrosine kinases (TK) are overexpressed in certain types of cancer
2. Phenylbenzothiazoles (PBTs) have antitumor activity due to docking to TK
3. Enol/Keto conformations of HBTs leads to diverse emission colors

Can we put together the docking activity and the diverse emission colors to monitor tumors?

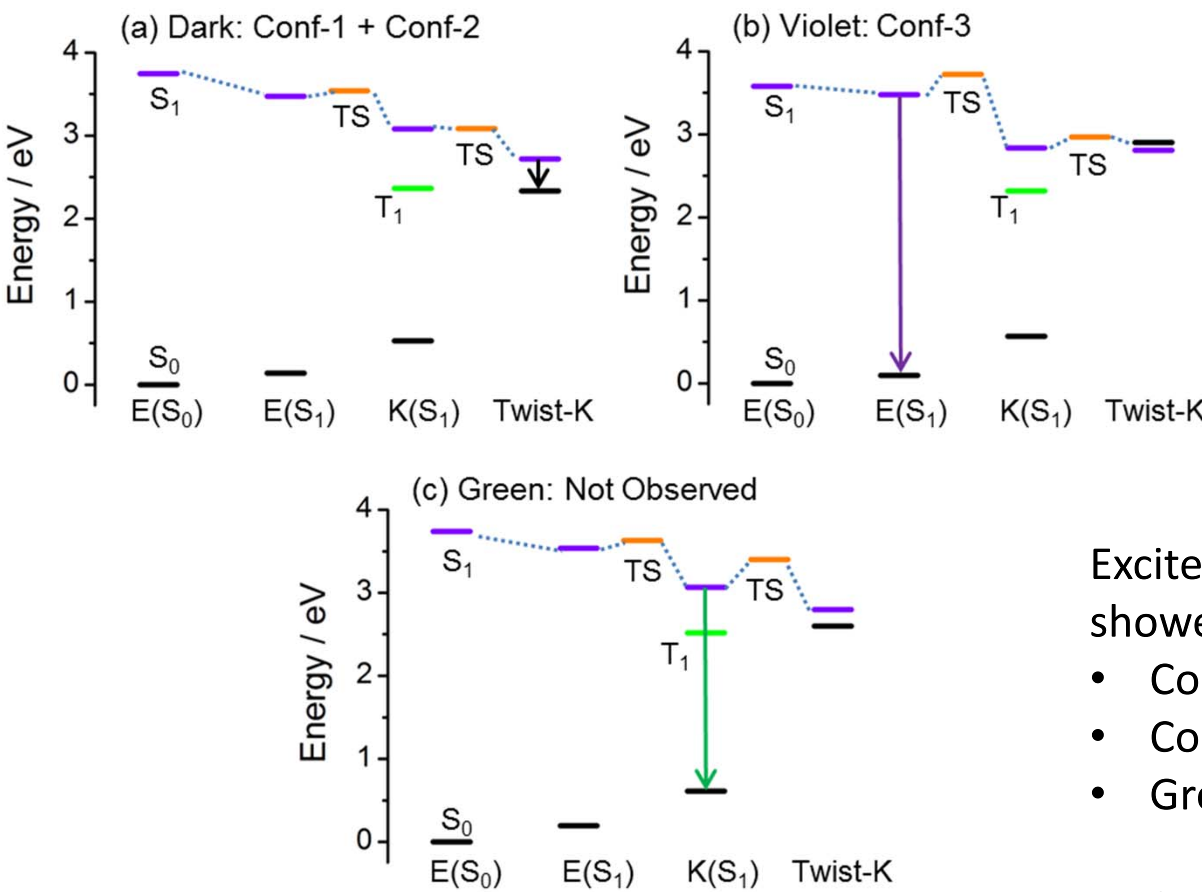
- Mancini, Sen, Barbatti, Thiel, Ramalho, ChemPhysChem **16**, 3444 (2015)

Ground state MD conformations



20 ns of MD run with CHARMM FF revealed three conformations:
Conf-1: 26%
Conf-2: 60%
Conf-3: 14%

Electronic structure with QM/MM



Excited states with TDDFT/MM showed that

- Conf-1 and Conf-2 are dark
- Conf-3 is violet
- Green emission was not found

Each TK will show its ow distribution of dark, green and violet.

A new diagnostic tool

Mutation is a major problem for cancer treatment.
They lead to drug resistance.

The PBT emission signature may tell when mutations occurred.

This might help doctors react faster to the potential development of drug resistance.

Key points

- Excited state phenomena is induced by UV/Vis
- Competition between different deactivation processes
- Close collaboration between theory and experiment is fundamental
- Organic Electronics is becoming very important