Theoretical study of internal conversion between excited states in a functionalized porphyrin

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Why should we study porphyrins?

— widely distributed in living tissues where they participate in vital biochemical processes
— serve as the reaction centers in light harvesting systems and can be used as candidates for synthesizing various efficient bioinspired molecular systems by functionalizing peripheral or the core parts of the molecule.

Structural model of Chlorophyll f homodimer based on PsbA of photosystems II. The psbA gene plays an important role in protecting photosystem II (PSII) from oxidative damage in higher plants.
Photoinduced processes

Internal conversion

Vibrational Relaxation

Absorption

Absorption

Internal Conversion

Intersystem Crossing

Fluorescence

Intersystem Crossing

Phosphorescence

Absorption

$S_0$

$S_1$

$S_2$

$T_1$

$T_2$

$T_3$
Pump-probe vs Two-Dimensional Electronic Spectroscopy (2DES)

**Pump-probe experiment**

- **Pump** pulse
- **Probe** pulse
- **Detection** pulse
- Sample
- **Delay time** $t_{\text{delay}}$
- Signal

**2DES pulse sequence scheme**

To obtain 2D maps:

- Measure signal of $\omega_{\text{probe}}$
- Scan $t_{\text{delay}}$ and $\omega_{\text{pump}}$
- Stack obtained spectra

Features:

- Dependent time and frequency resolutions

To obtain 2D maps:

- Measure signal of $\omega_3$
- Scan $t_1$ and $t_2$
- Perform Fourier transform over $t_1$

Features:

- Independent time and frequency resolutions


https://www.femtosecond.fisi.polimi.it
Pump-probe vs Two-Dimensional Electronic Spectroscopy (2DES)

**Dynamics of the system**

2D cube of data \((\omega_1, t_2, \omega_3)\)

- Cut at specific \(t_2\)
- Cut at specific \(\omega_1\)

If \(t_2=0\) — Pump-probe spectroscopy

**2DES pulse sequence scheme**

To obtain 2D maps:
- Measure signal of \(\omega_3\)
- Scan \(t_1\) and \(t_2\)
- Perform Fourier transform over \(t_1\)

**Features:**
- Independent time and frequency resolutions

How can theoretical tools help to explain better the system?

https://www.femtosecond.fisi.polimi.it
Why do we need theoretical study in addition to the experiment?

**Experiment**

- gives the complete picture of the photophysical processes:
  
  a) absorption spectrum  
  b) pump-probe spectrum  
  c) 2D spectrum (showing the dynamics)

- gives exact rates of internal conversion times including the range of important frequency regions

**Theoretical study**

- affords to separate the system into the components

  Define **structural parameters** responsible for the features of the spectrum (nature of the peaks and “shoulders”)

- can define/suggest the channels of radiationless transitions pointing the **structural parts** of molecule that are involved into the process

**What theoretical tool that can be used in both optical and radiationless processes?**
Theoretical tool that can be used in both optical and radiationless processes.

- $r, r'$ — initial and final electronic states
- $m, m'$ — initial and final vibrational states
- $q$ — normal coordinate
- $E_{rm}$ — energy of the vibronic state
- $\varepsilon_r$ — energy of the electronic state
- $\chi_{r'm'}(q)$ — vibronic wavefunction
Input from ab initio calculations:
— optimized geometries of initial/final state
— normal modes (μ) and frequencies (ω_μ) of the initial/final state
— gradients (V_{rm}) on the final/initial state PES

\[ \xi_\mu = \frac{1}{2\hbar} \Delta q_\mu^2 \omega_\mu \] — Huang Rhys (HR) factor

\[ \text{ER}_\mu = \hbar \omega_\mu \xi_\mu \] — per mode reorganization energy (ER)

— Condon approximation
— Independent harmonic modes
— Parallel Harmonic approximation
\[ \{\mu_r\} = \{\mu_r'\}, \{\omega_{ur}\} = \{\omega_{ur}\} \]
Simplified diagram of Huang-Rhys factors and Reorganization energy calculations

- Condon approximation
- Independent harmonic modes
- Parallel Harmonic approximation

\{\mu_r\} = \{\mu_{r'}\}, \{\omega_{\mu r}\} = \{\omega_{\mu r'}\}
What can we get knowing HR factors?

\[ \xi_\mu = \frac{1}{2\hbar} \Delta q^2 \omega_\mu \quad \text{Huang-Rhys factor} \]

\[ ER_\mu = \hbar \omega_\mu \xi_\mu \quad \text{Reorganization energy} \]

- Absorption spectrum with the vibronic structure
- Active modes and corresponding vibrations
- IC rate constants
- PES scans along active modes. Search of possible conical intersections/avoided crossings
- Analysis of molecular structure parts that are included in the active modes vibrations. Updating the structure.
What can we get knowing HR factors?

\[ \xi_\mu = \frac{1}{2\hbar} \Delta q^2 \omega_\mu - \text{Huang-Rhys factor} \]

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- PES scans along active modes. Search of possible conical intersections/avoided crossings

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A) Representation of the four Gouterman orbitals in porphyrins.
B) Energy levels of the four Gouterman orbitals

5-Ethoxycarbonyl-10-mesityl-15-carboxymethylbenzene porphyrin
Margherita Maiuri group
IFN-CNR, Politecnico di Milano.
Absorption spectrum of the monomer

DFT 6-311 (d,p)/CAM-B3LYP/PBE0 Solvent: THF (PCM)
Per mode Reorganization energies (ER) for $S_0 \rightarrow S_n$ transitions

$$\text{ER}_\mu = \hbar \omega_\mu \xi_\mu$$

$\xi_\mu$ — Huang Rhys (HR) parameter along the normal mode
$\omega_\mu$ — frequency of the normal mode

* Obtaining the normal modes of $S_2$ and $S_4$ states is complicated due to poor convergence of the optimization procedure.
Absorption spectrum with the vibronic structure

\[ I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} G(t) e^{i\omega t} dt \]

\[ G(t) = \exp \left[ \frac{it(\varepsilon^0_r - \varepsilon^0_{r'})}{\hbar} \right] \prod_{\mu} \exp \left[ -\xi_{\mu} \left( \coth \frac{\hbar \omega_{\mu}}{2kT} (1 - \cos \omega_{\mu} t) - i \sin \omega_{\mu} t \right) \right] D(t) \]

\[ D(t) = e^{-\frac{\Gamma|t|}{\hbar}} \]

\( \varepsilon^0_r - \varepsilon^0_{r'} \) — energy difference between the ground and an excited state

\( \xi_{\mu} \) — Huang Rhys (HR) parameter along the normal mode

\( \omega_{\mu} \) — frequency of the normal mode


\( \Gamma \) — FWHM of low-frequency modes
What can we get knowing HR factors?

\[ \xi_\mu = \frac{1}{2\hbar} \Delta q^2 \omega_\mu - \text{Huang-Rhys factor} \]

\[ ER_\mu = \hbar \omega_\mu \xi_\mu - \text{Reorganization energy} \]

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IC rate constant calculation

\[ k_{rr'm'} = \frac{2\pi}{\hbar} \nu_{el}^2 \sum_{m,m'} F_{rr'm'} \delta_{\gamma}(E_{rm} - E_{r'm'}) \]

\[ F_{rr'm'} = f(\frac{\xi}{\mu}) \text{ Frank-Condon factor} \]

ER between \( S_3 \) (B band) and \( S_2 \) (Q band) in the basis set of \( S_1 \) (Q band) state

\[ \Delta E (B-Q) = 6078 \text{ cm}^{-1} \]

Optimization + energy and gradient calculation: DFT 6-311 (d,p)/CAM-B3LYP
Solvent: THF (PCM)
\( \Delta E \) (B-Q) = 6078 cm\(^{-1}\)
\( u_{el}^2 \) (NACME\(^2\), a.u., CASSCF) = 0.1

Exp \( \sim \) 100 fs

IC time = 260 fs

6 modes (51\% ER)

19 modes (77\% ER)

39 modes (90\% ER)

IC time = 60 fs

IC time = 38 fs
What can we get knowing HR factors?

\[ \xi_\mu = \frac{1}{2\hbar} \Delta q^2 \omega_\mu - \text{Huang-Rhys factor} \]

\[ ER_\mu = \hbar \omega_\mu \xi_\mu - \text{Reorganization energy} \]

Absorption spectrum with the vibronic structure

Active modes and corresponding vibrations

IC rate constants

PES scans along active modes. Search of possible conical intersections/avoided crossings

Analysis of molecular structure parts that are included in the active modes vibrations. Updating the structure.
Per mode Reorganization energies (RE) for $S_0 \rightarrow S_n$ transitions

![Graph showing reorganization energies](image)

High frequency modes with the highest per mode Reorganization energies of the Q band: a),b) for $S_0 \rightarrow S_1$; c),d) for $S_0 \rightarrow S_2$ transition. Front view is on the upper panel and lateral one — on the lower.
Scan of PES along the active mode (1514 cm\(^{-1}\), \(S_1\), Q band)

Vibrations along 1514 cm\(^{-1}\)
Normal mode

\[
G_\mu [a, x] = G_{S_0} [a, x] + \text{shift}_\mu [a, x]
\]

\[
\text{shift}_\mu [a, x] = A \cdot l_\mu [a, x] \cdot \sin(\omega_\mu t)
\]

"a" — atom  \(x\) — \(x, y, z\)

*States \(S_1\), \(S_2\) correspond to the Q band
\(S_3\), \(S_4\) to the B band

\(G_\mu [a, x]\) — Geometry along the mode
\(l_\mu [a, x]\) — component of the normal modes matrix
Scan of PES along the active mode (1514 cm\(^{-1}\), \(S_1\), Q band)

Vibrations along 1514 cm\(^{-1}\)
Normal mode

\[ G_\mu[a,x] = G_{S_0}[a,x] + shift_\mu[a,x] \]
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"a" — atom  \(x\) — \(x,y,z\)

\(G_\mu[a,x]\) — Geometry along the mode
\(l_\mu[a,x]\) — component of the normal modes matrix

*States \(S_1, S_2\) correspond to the Q band
\(S_3, S_4\) to the B band
Molecular orbitals involved in the electronic excitations

A) Representation of the four Gouterman orbitals in porphyrins.
B) Energy levels of the four Gouterman orbitals

Is it enough the Gouterman model?
Molecular orbitals involved in the electronic excitations (optimized $S_1$ geometry)

Orbital characteristic for the dark state of the bare porphyrin:
- HOMO-4 $\rightarrow$ LUMO

Orbitals particular for the porphyrin derivative dark state localized on the substituent:
- HOMO-3 $\rightarrow$ LUMO
- HOMO-2 $\rightarrow$ LUMO

Orbitals of the Gouterman model:
- HOMO-1 $\leftrightarrow$ LUMO
- HOMO $\leftrightarrow$ LUMO+1
Transition energies along the 1514 cm$^{-1}$ (active) mode ($S_1$ basis)

Vertical Transition Energies $S_0 \rightarrow S_n$

HOMO-4 $\rightarrow$ LUMO
Orbital characteristic for the dark state of the bare porphyrin

HOMO-3 $\rightarrow$ LUMO
Orbitals particular for the porphyrin derivative dark state localized on the substituent

HOMO-2 $\rightarrow$ LUMO
HOMO $\rightarrow$ LUMO+1
Orbitals of the Gouterman model

orbital composition colormap
oscillator strength (thickness) of $S_0 \rightarrow S_n$
Transition energies along the 1514 cm\(^{-1}\) (active) mode (S\(_1\) basis)

Vertical Transition Energies S\(_0\)->S\(_n\)

Vertical Transition Energies S\(_0\)->S\(_n\) (S\(_0\)=0 eV)

B band

Q band
“Crossing” inside the Q band along the 1514 cm\(^{-1}\)

Vibrations along 1514 cm\(^{-1}\)
Normal mode

\[ E_r(q) = \varepsilon_r(q) + \frac{1}{2} \sum M_{\mu} \omega_{\mu\tau}^2 (q_{\mu\tau} - q_{\mu\tau}^0)^2 \]

\[ E_{r\mu}(q) = \varepsilon_r(q) + \frac{1}{2} M_{\mu} \omega_{\mu\tau}^2 (q_{\mu\tau} - q_{\mu\tau}^0)^2 \]
Transition dipole moment as a tool to define conical intersection?

Transition dipole moment evolution along 1514 cm\(^{-1}\)

Direction of the transition dipole moment.
Color shows which component (X or Y) is prevailing

\(-2.48\) Value of the transition dipole moment along X axis
\(1.38\) Value of the transition dipole moment along Y axis

The nature of the transition dipole moment after “crossing” exchanging between the states inside of the Q band
Comparison with the experiment

Pump Probe Spectrum in the Q band range

Components of the Pump-Probe:
“—” the ground state bleaching (GSB)
“+” excited state absorption (ESA)
“—” stimulated emission (SE)

The 670-700 nm region can have only ESA transition and maybe some SE contribution, but no GSB.
Comparison with the experiment

Sliding Window Fourier Transform (SWFT) at 685nm for 250 fs gaussian with the steps of 10 fs

1. What is the nature of the modes? Ground state or excited state (Q band) ones?
2. Which of the modes are participating in the process?
Reorganization energies of the high frequency modes for the Q band states

Higher values in the $S_1$ (Q band) than in $S_0$ (ground state) basis set confirms that in the Q band modes are playing the main role in the process.
Comparison with the experiment

Sliding Window Fourier Transform (SWFT) at 685 nm for 250 fs gaussian with the steps of 10 fs

RE(grey) of $S_1 \rightarrow S_2$ (opt $S_1$)
VS Integrated FFT for the Excited State coherences at 680-700 nm (black)

Analysis of RE showing the crucial role of 1514 cm$^{-1}$ mode in the process and also defines the group of modes (and corresponding vibrations) that are participating at the beginning of the process.
The connecting point between the experiment and the theory?

Transferring from “X” active mode of $S_2$ to 1514 cm$^{-1}$ of $S_1$

$G_{\mu}[a,x] = G_{S_0}[a,x] + shift_{\mu}[a,x]$

$shift_{\mu}[a,x] = A \cdot l_{\mu}[a,x] \cdot \sin(\omega_{\mu} t)$

$E_{r}(q) = \varepsilon_{r}(q) + \frac{1}{2} M_{\mu} \omega_{\mu}^2 (q_{\mu} - q_{\mu}^0)^2$

*States $S_1$, $S_2$ correspond to the Q band

How to find “X” mode of $S_2$?
The connecting point between the experiment and the theory?

Transferring from "X" active mode of $S_2$ to 1514 cm$^{-1}$ of $S_1$

How to find "X" mode of $S_2$?

*States $S_1$, $S_2$ correspond to the Q band
PES energies along the $1514 \text{ cm}^{-1}$ mode (active) and others high ER modes (tuning)

PES near possible crossing of the $S_1$ and $S_2$ terms

Energy gap between the $S_1$ and $S_2$ terms
What can we get knowing HR factors?

\[ \xi_\mu = \frac{1}{2\hbar} \Delta q_\mu^2 \omega_\mu - \text{Huang-Rhys factor} \]

\[ ER_\mu = \hbar \omega_\mu \xi_\mu - \text{Reorganization energy} \]

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Conclusions

Simple but yet effective approach using HR and ER provides.

1) absorption spectrum including the vibronic structure (band shape)

2) an estimate value of the internal conversion rates and corresponding times of radiationless transitions between excited states

3) The simulations allow us to define active normal modes and corresponding vibrations that contribute to Internal Conversion due to vibrational relaxation. — Thus it is possible to explain experimental data from the the point “Where” the processes are happening and which structural parts of the molecule are involved — Knowing the active modes it is possible to update the molecular structure to enhance or reduce specific features
THANK YOU FOR YOUR ATTENTION!

Theory

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Experiment

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