

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.

Photoinduced processes



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



Pump-probe experiment

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To obtain 2D maps:

Measure signal of ω_{probe} Scan t_{delay} and ω_{pump} Stack obtained spectra

Features:

Dependent time and frequency resolutions



2DES pulse sequence scheme

Perform Fourier transform over t_1

Features:



Independent time and frequency resolutions

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

pump



Dynamics of the system



If t₂=0 — Pump-probe spectroscopy

Perform Fourier transform over t_1

Features:

Independent time and frequency resolutions

How can theoretical tools help to explain better the system?

2DES pulse sequence scheme

pump

Detector

Experiment

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

Theoretical study

 affords to separate the system into the components

Define **structural parameters** responsible for the features of the spectrum (nature the 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.



Simplified diagram of Huang-Rhys factors and Reorganization energy calculations



- Condon approximation
- Independent harmonic modes
- Parallel Harmonic approximation $\{\mu_r\}=\{\mu_{r'}\}, \{\omega_{\mu r}\}=\{\omega_{\mu r'}\}$



Simplified diagram of Huang-Rhys factors and Reorganization energy calculations



What can we get knowing HR factors?



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General features of the porphyrin

Bare porphyrin



A) Representation of the four Gouterman orbitals in porphyrins.

B) Energy levels of the four Gouterman orbitals

Absorption spectrum of the monomer



DFT 6-311 (d,p)/CAM-B3LYP/PBE0 Solvent: THF (PCM)



Absorption spectrum with the vibronic structure



What can we get knowing HR factors?



IC rate constant calculation

ER between $S_3(B \text{ band})$ and $S_2(Q \text{ band})$ In the basis set of S_1 (Q band) state



What can we get knowing HR factors?



Per mode Reorganization energies (RE) for S_0 -> S_n transitions



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, S₁, Q band)



Scan of PES along the active mode (1514 cm⁻¹, S₁, Q band)



Molecular orbitals involved in the electronic excitations





Is it enough the Gouterman model?

A) Representation of the four Gouterman orbitals in porphyrins.

B) Energy levels of the four Gouterman orbitals

Molecular orbitals involved in the electronic excitations (optimized S₁ geometry)







HOMO-4 Orbital characteristic for the dark state of the bare porphyrin

номо-з ____ Lumo

Orbitals particular for the porphyrin derivative dark state localized on the substituent

HOMO-1 HOMO LUMO LUMO+1 Orbitals of the Gouterman model

Transition energies along the 1514 cm⁻¹ (active) mode (S_1 basis)



Transition energies along the 1514 cm⁻¹ (active) mode (S_1 basis)



"Crossing" inside the Q band along the 1514 cm⁻¹



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

Axes according to bare porphyrin classification

Comparison with the experiment

Pump Probe Spectrum in the Q band range



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



- 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.

Sliding Window Fourier Transform (SWFT) at 685nm for 250 fs gaussian with the steps of 10 fs RE(grey) of S₁->S₂ (opt S₁) VS Integrated FFT for the Excited State coherences at 680-700 nm (black)



RE a weighted by the time of presenting in SWFT

Analysis of RE showing the crucial role of 1514 cm⁻¹ mode in the process and also defines the group of modes (and corresponding vibratons) that are participating at the beginning of the process.

The connecting point between the experiment and the theory?



*States S₁, S₂ correspond to the Q band

How to find "X" mode of S_2 ?

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*States S₁, S₂ correspond to the Q band

How to find "X" mode of S_2 ?

PES energies along the 1514 cm⁻¹ mode (active) and others high ER modes (tuning)

PES near possible crossing of the S₁ and S₂ terms



What can we get knowing HR factors?



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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