Our Experience with TD-DFT and TD-DFTB in Biological, Bio-inspired, and Other Photoprocesses

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SITh

UNIVERSITÉ Grenoble Alpes

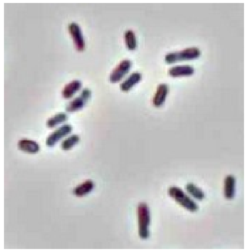
département de chimie moléculaire

cnrs dépasser les frontières

INSTITUT DE CHIMIE MOLECULAIRE DE GRENOBLE
ICMG FR CNRS-UJF 2607

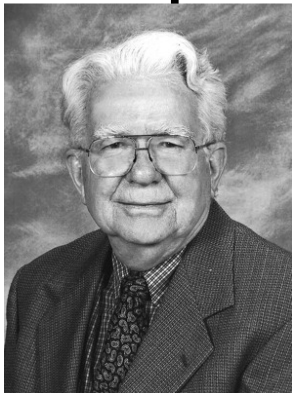
SISSA
Zoom Workshop
Hosted by ICTP, Trieste, Italy
30 minutes

@ Ville de Grenoble - www.ville-grenoble.fr



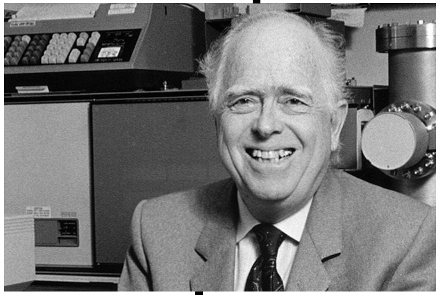
Lester Earl CASIDA
1904–1986
Prof. Univ. Wisconsin, Madison

American Society of Animal Science has named a scholarship for doctoral students in Reproductive Physiology in his honor.



Lester Earl CASIDA Jr.
1928-2017
Prof. Penn. State Univ.

Industrial and soil microbiology
Discovered bacterium:
Ensifer adherens Casida 1982



John Edward CASIDA
1929-2018
Prof. Univ. Calif., Berkeley

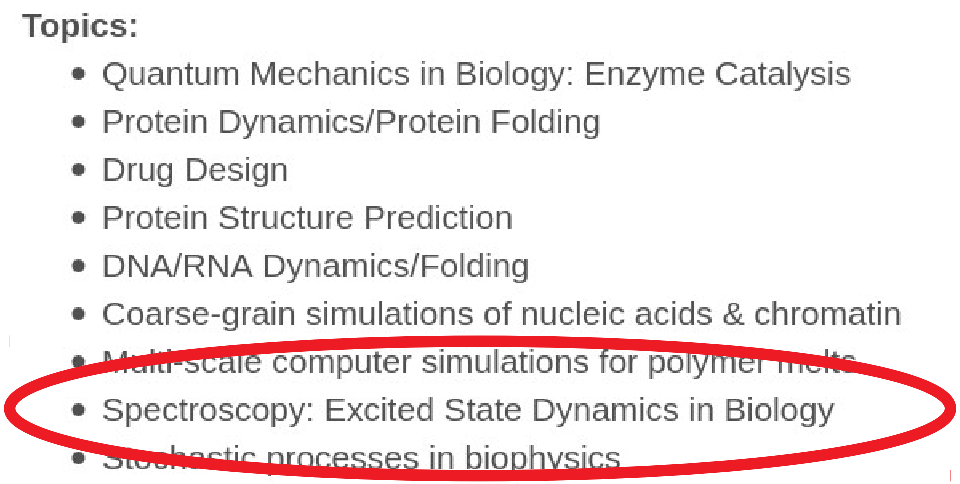
Entomology and toxicology
Very distinguished (member USA NAS, UK Royal Society, Wolf Prize in Agriculture, ...)

Mark Earl CASIDA
1957-?
Prof. Univ. Grenoble Alpes

Theoretical Chemistry
Casida equations for TD-DFT

$$\left[\begin{pmatrix}\mathbf{A} & \mathbf{B}\\ \mathbf{B} & \mathbf{A}\end{pmatrix} - \Omega_n\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}\right]\begin{pmatrix}X_n\\ Y_n\end{pmatrix} = 0$$

ICTP-SISSA-CECAM Workshop on Molecular Dynamics and its Applications to Biological Systems | (smr 3483)



Topics:

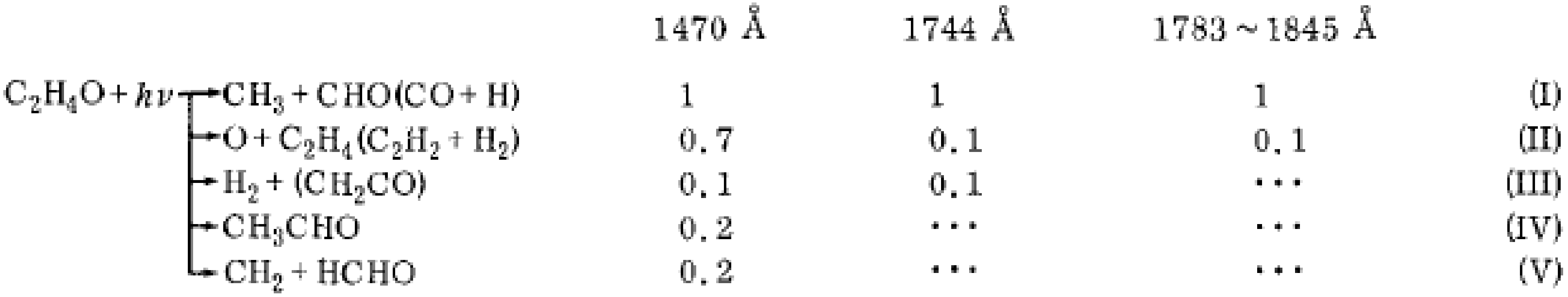
- Quantum Mechanics in Biology: Enzyme Catalysis
- Protein Dynamics/Protein Folding
- Drug Design
- Protein Structure Prediction
- DNA/RNA Dynamics/Folding
- Coarse-grain simulations of nucleic acids & chromatin
- Multi-scale computer simulations for polymer melts
- Spectroscopy: Excited State Dynamics in Biology
- Stochastic processes in biophysics

OUTLINE

I. PHOTOCHEMICAL THINKING
II. ELECTRONIC EXCITED-STATE PROCESSES
III. TD-DFT(B)
IV. STATIC APPLICATIONS
  A. Luminescence indices
  B. Retinal
  C. Excitonic effects
V. TD-DFT(B) FSSH
VI. DYNAMICS APPLICATIONS
  A. Easy case: oxirane
  B. Hard case: pentacene/buckyball
VII. CONCLUSION

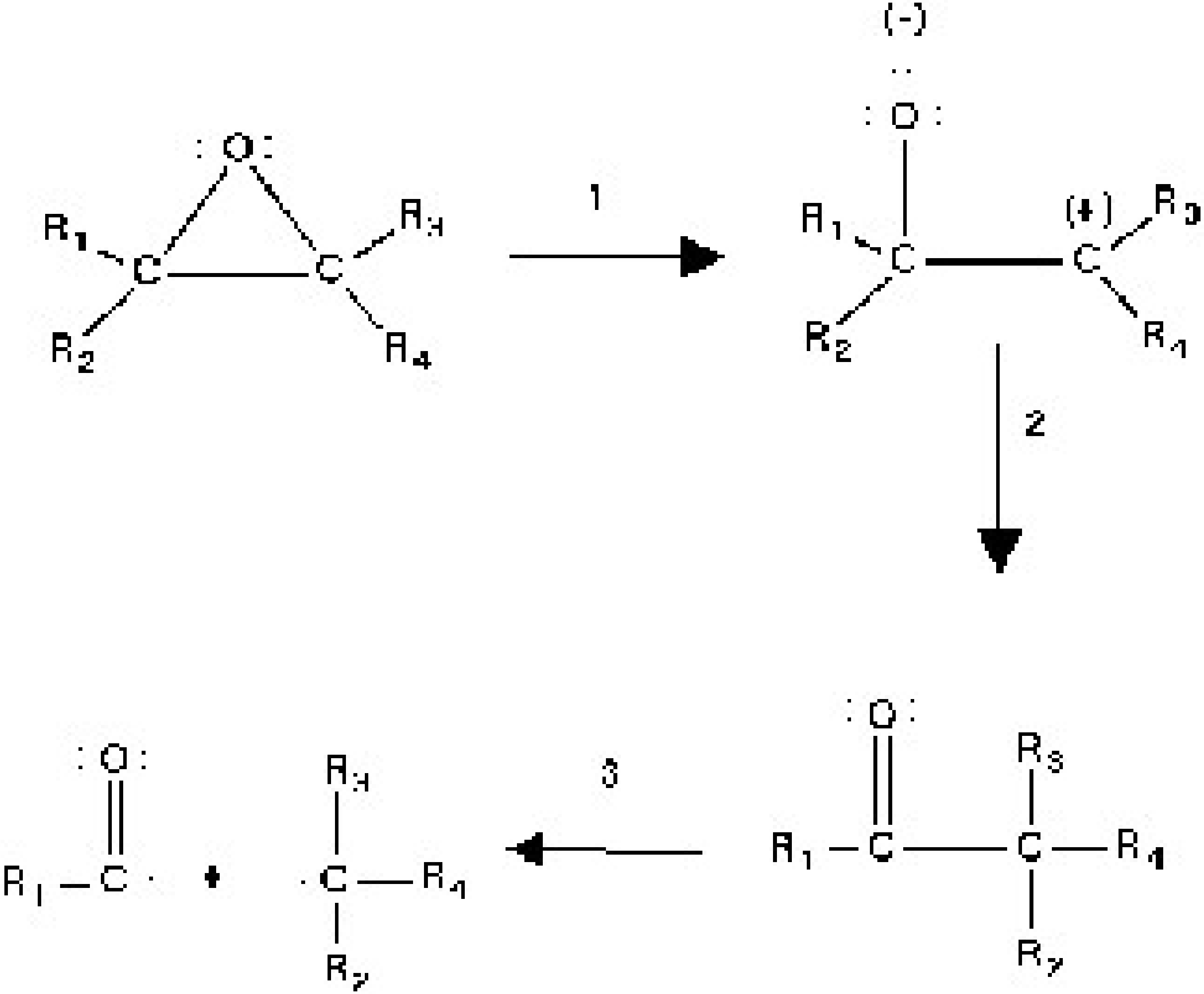
OXIRANE PHOTOCHEMISTRY

T. Ibuki, M. Inasaki et Y. Takesaki, *J. Chem. Phys.* 59, 2076 (1973).



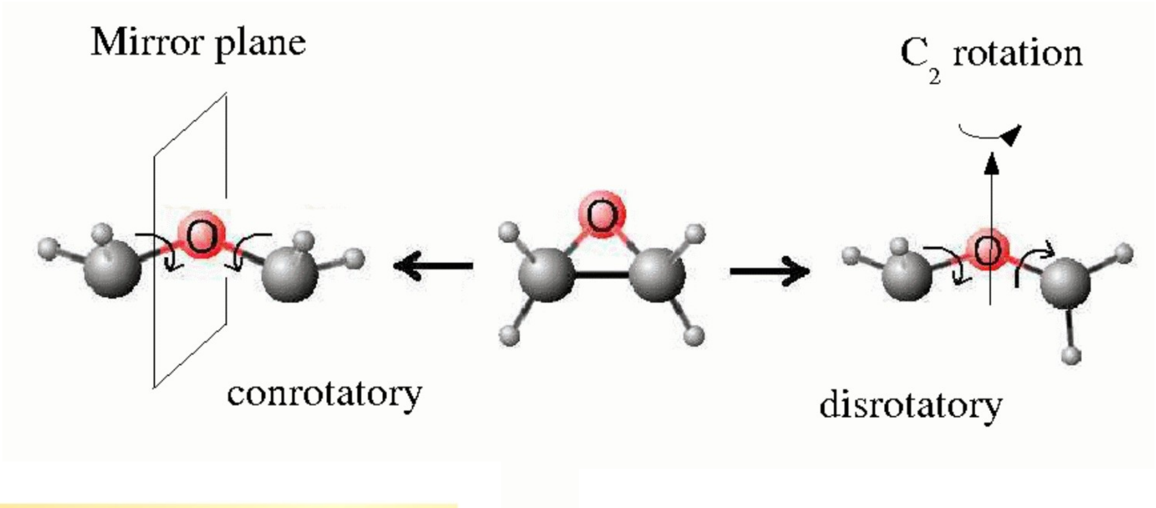
	1470 Å	1744 Å	1783 ~ 1845 Å	
$C_2H_4O + h\nu$ → $CH_3 + CHO(CO + H)$	1	1	1	(I)
→ $O + C_2H_4(C_2H_2 + H_2)$	0.7	0.1	0.1	(II)
→ $H_2 + (CH_2CO)$	0.1	0.1	⋯	(III)
→ CH_3CHO	0.2	⋯	⋯	(IV)
→ $CH_2 + HCHO$	0.2	⋯	⋯	(V)

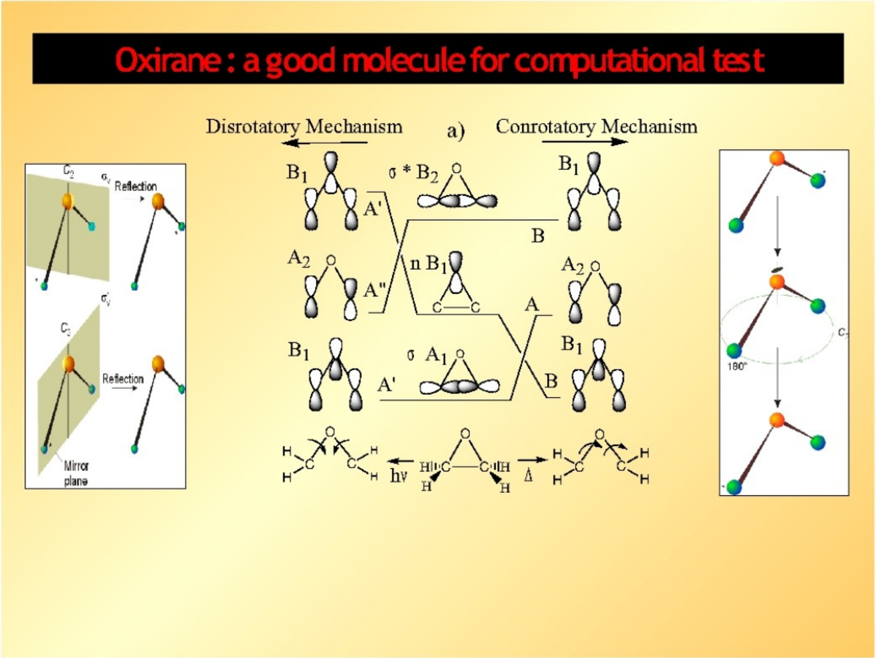
LEWIS STRUCTURES



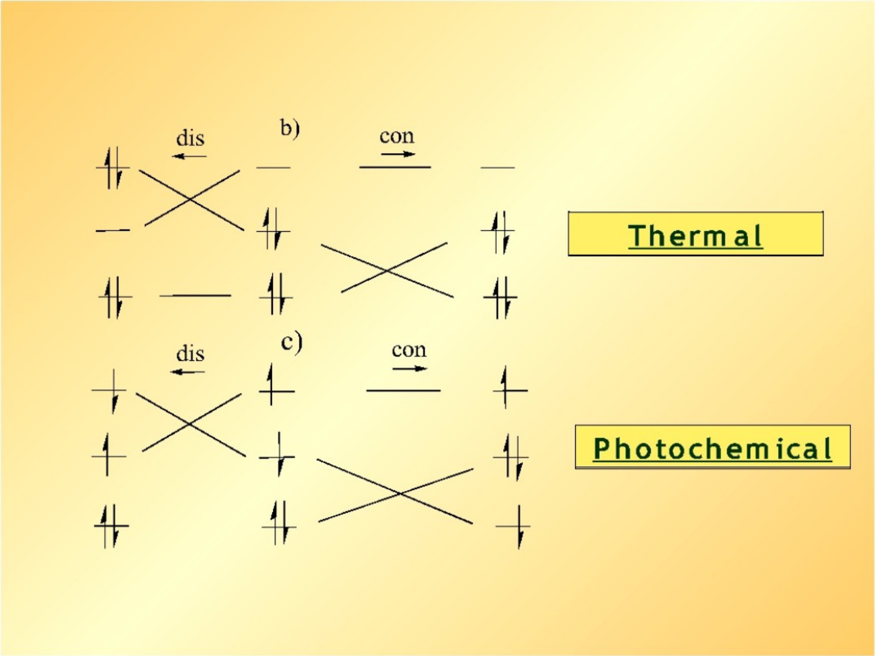
Gomer-Noyes Mechanism [E. Gomer et W.A. Noyes, Jr., J. Am. Chem. Soc. 72, 101 (1950); T. Ibuki, M. Inasaki et Y. Takesaki, J. Chem. Phys. 59, 2076 (1973).]

ORBITAL THINKING: WOODWARD-HOFFMANN RULES





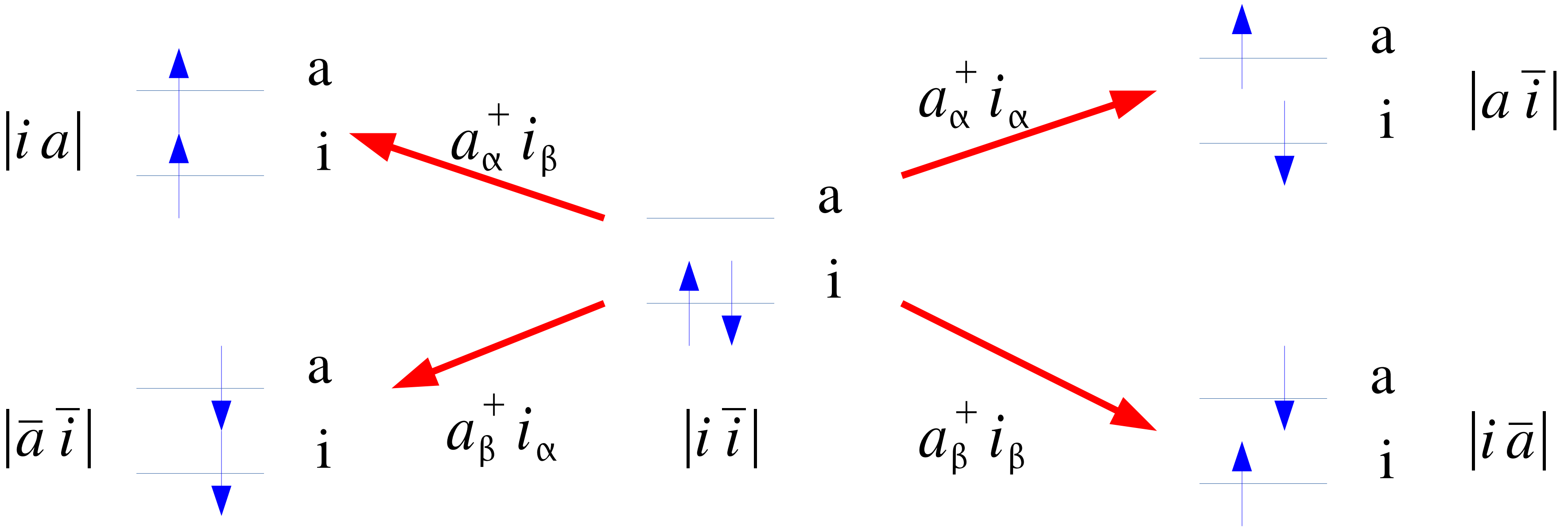
Oxirane : a good molecule for computational test



Thermal

Photochemical

STATES: TWO-ORBITAL TWO-ELECTRON MODEL (TOTEM)



$|i\,a|$ a i $a_\alpha^+ i_\beta$

$a_\alpha^+ i_\alpha$ a i $|a\,\bar{i}|$

a i $|i\,\bar{i}|$

$|\bar{a}\,\bar{i}|$ a i $a_\beta^+ i_\alpha$

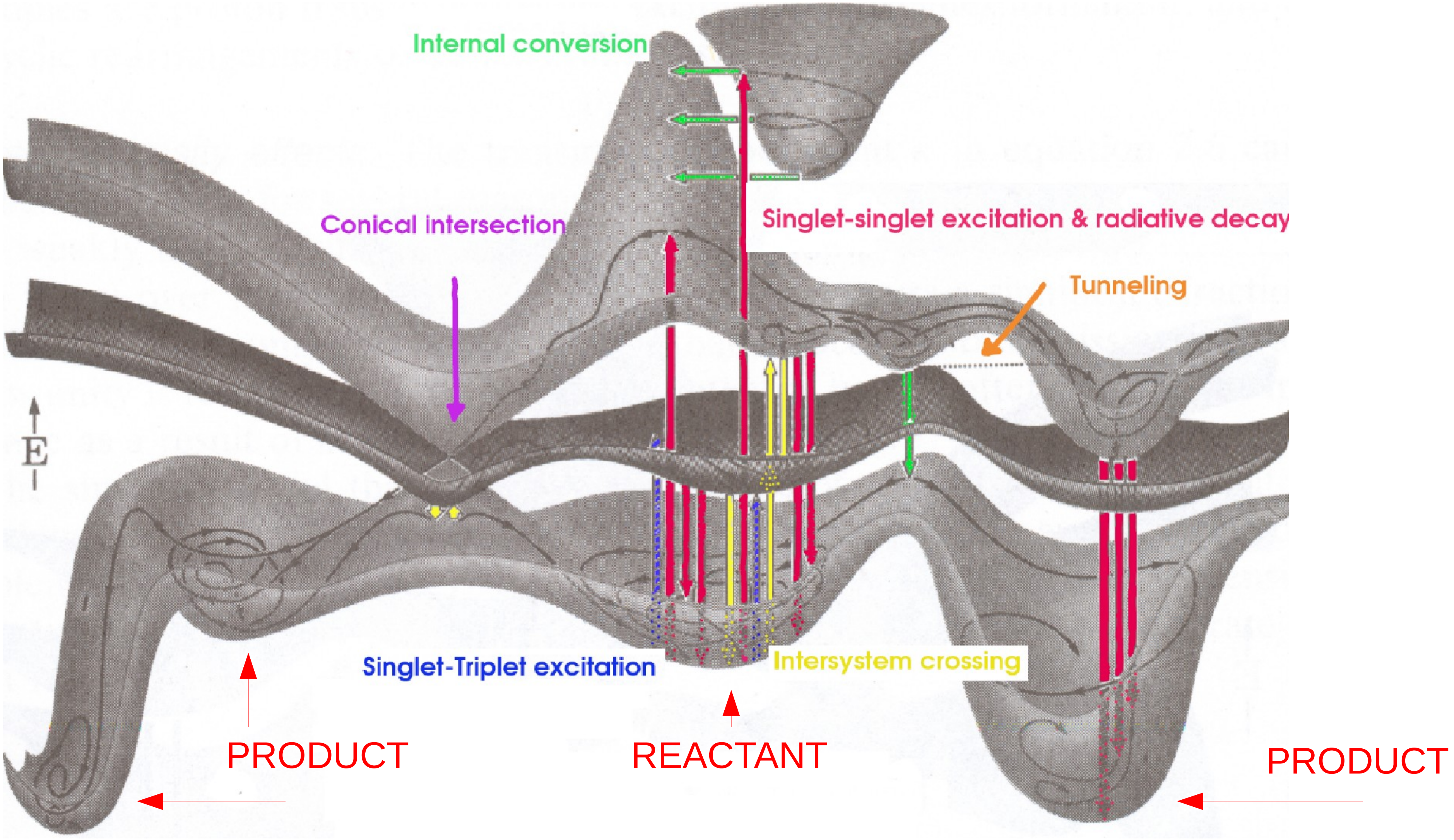
$a_\beta^+ i_\beta$ a i $|i\,\bar{a}|$

	Ψ_{S,M_S}
Singlet	$\Psi_{0,0}=\frac{1}{\sqrt{2}}\left(\lvert a\,\bar{i}\rvert+\lvert i\,\bar{a}\rvert\right)$
Triplets	$\Psi_{1,0}=\lvert i\,a\rvert$ $\Psi_{1,0}=\frac{1}{\sqrt{2}}\left(\lvert a\,\bar{i}\rvert-\lvert i\,\bar{a}\rvert\right)$ $\Psi_{1,-1}=\lvert\bar{a}\,\bar{i}\rvert$

$$\omega_S=\epsilon_a-\epsilon_i+2\left(ai\middle|f_H\middle|ia\right)-\left(aa\middle|f_H\middle|ii\right)$$

$$\omega_T=\epsilon_a-\epsilon_i-\left(aa\middle|f_H\middle|ii\right)$$

POTENTIAL ENERGY SURFACES (PESs)



Original image: J. Michl and V. Bonacic-Koutecky, *Electronic Aspects of Organic Photochemistry* (Wiley: New York, 1990), p. 71. Embellishment: E. Tapvicza.

WAYS WE TRY TO UNDERSTAND PHOTOCHEMICAL MECHANISMS

- Lewis structures
- Orbital models
- Potential energy surfaces*
  - Pathway approach
    - Minimum energy pathways
    - Funnels
  - Dynamics
    - Ehrenfest
    - Surface hopping

(Star Trek 3D chess)

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* J. Michl and V. Bonacic-Koutecky, *Electronic Aspects of Organic Photochemistry* (Wiley: New York, 1990)

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SOME EXAMPLES OF EXCITED-STATE PROCESSES IN BIOLOGY

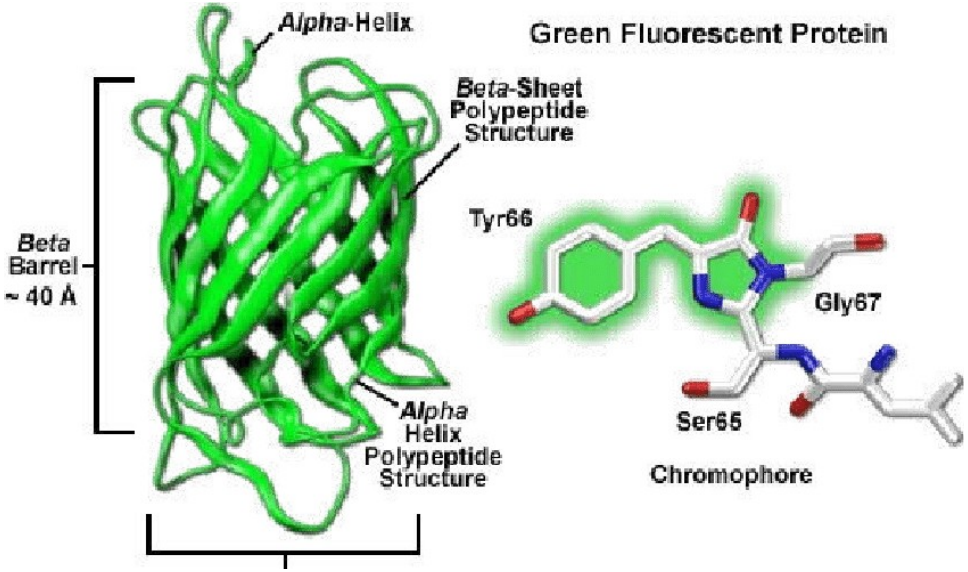
(all fall under a generalized notion of “photochemistry”)

PHOTOPHYSICS:

$$A + h\nu \rightarrow A^* \rightarrow A$$

- Radiationless relaxation
- Luminescence
  - Fluoresence
  - Phosphorescence

Example: green fluorescent protein

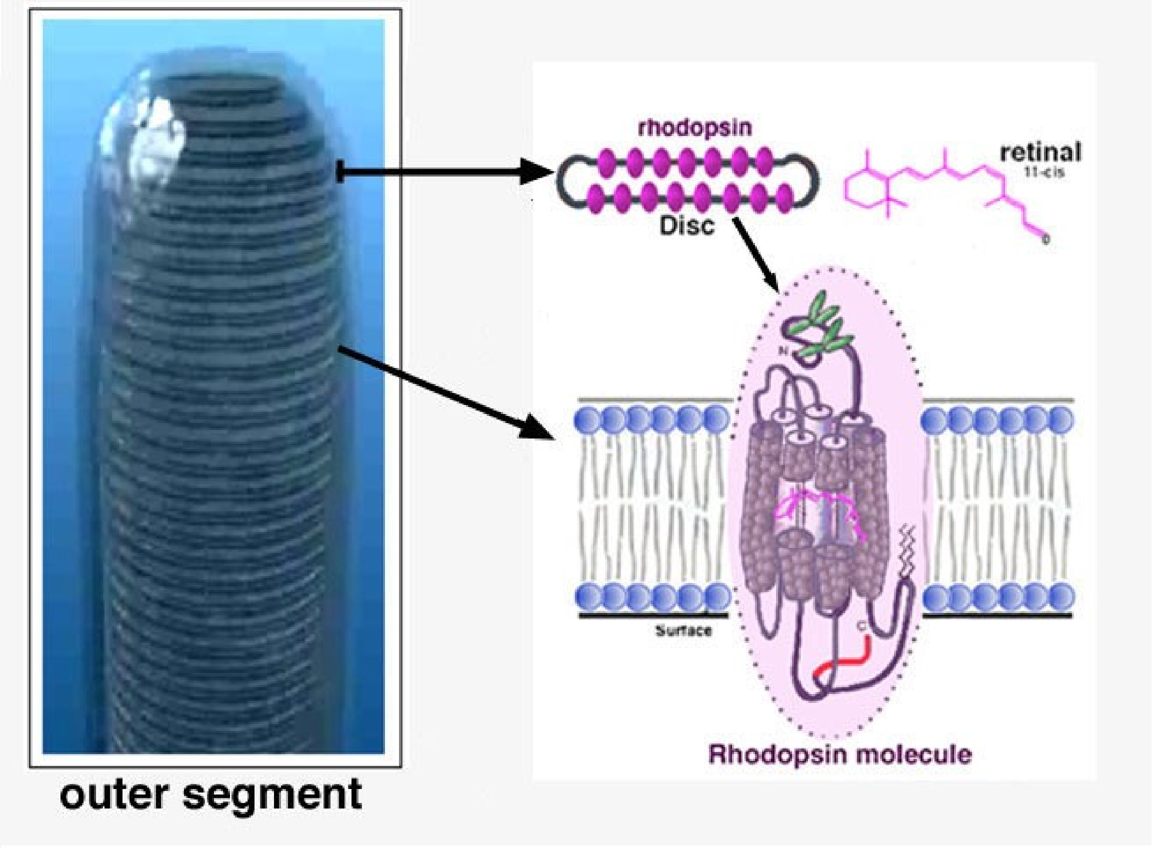


http://zeiss-campus.magnet.fsu.edu/print/probes/fpintroduction-print.html

PHOTOCHEMISTRY

$$A + h\nu \rightarrow A^* \rightarrow B + C$$

Example: vision (rhodopsin)

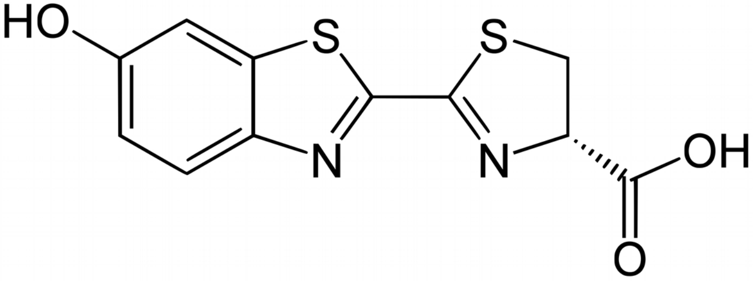


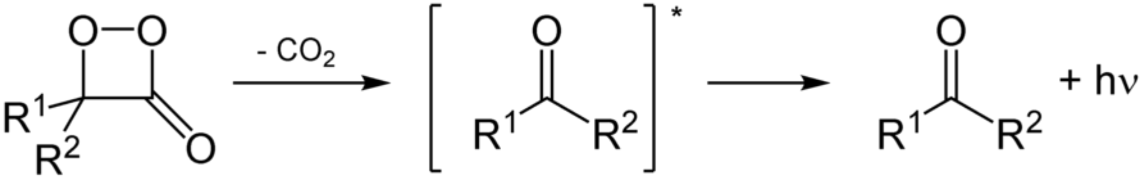
https://www.ncbi.nlm.nih.gov/books/NBK52768/

CHEMILUMINESCENCE

$$B+C \rightarrow A^{*} \rightarrow A+h\nu$$

Example: firefly luciferon

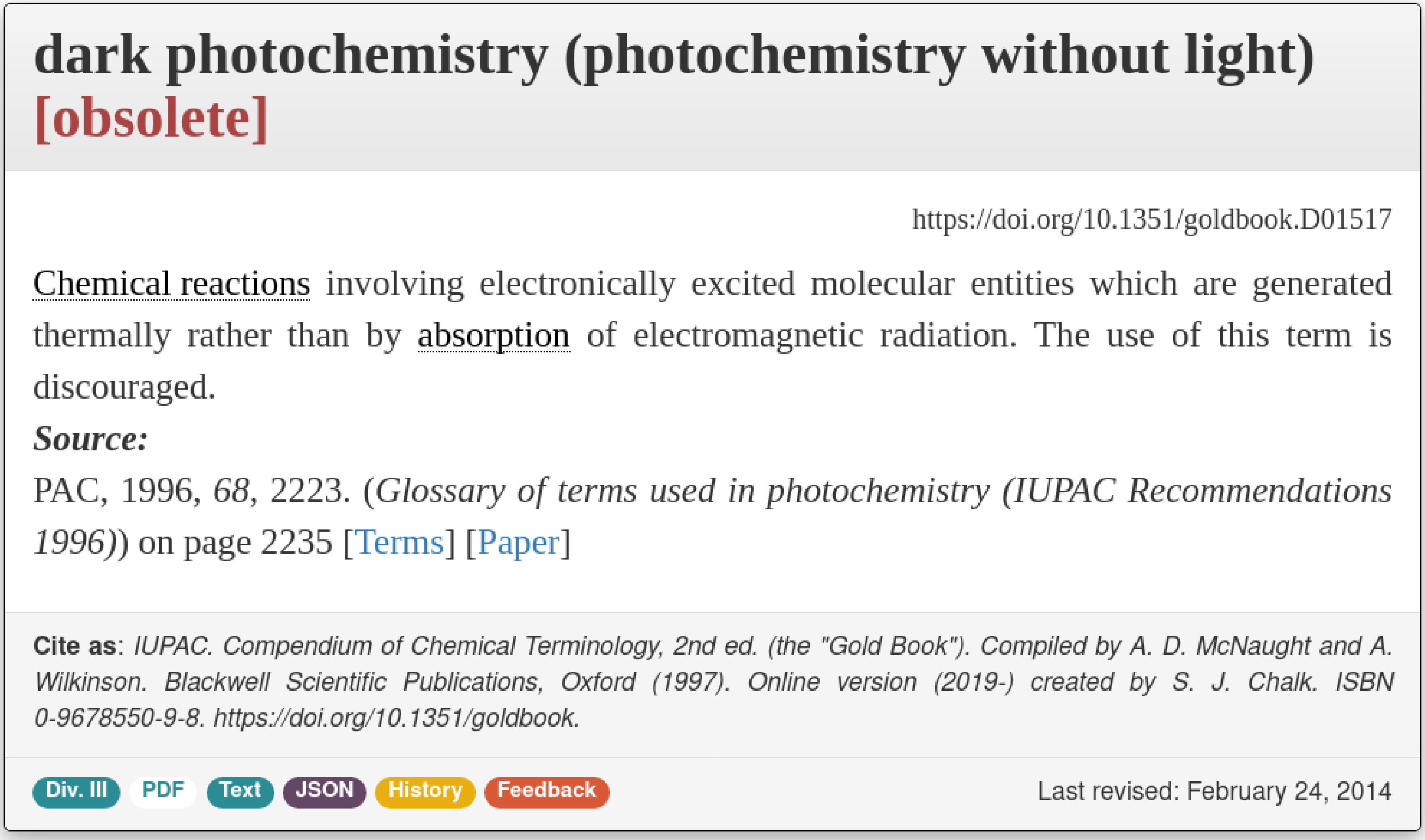




$$A + h\nu \rightarrow A^{*} \rightarrow B + C$$

$$A + \Delta \rightarrow A^{*} \rightarrow B + C$$

E.H. White, J. Wiecko, and D.F. Roswell, “Photochemistry without light”, *J. Am. Chem. Soc.* **91**, 5194 (1969).



dark photochemistry (photochemistry without light) [obsolete]

https://doi.org/10.1351/goldbook.D01517

Chemical reactions involving electronically excited molecular entities which are generated thermally rather than by absorption of electromagnetic radiation. The use of this term is discouraged.

Source:

PAC, 1996, *68*, 2223. (*Glossary of terms used in photochemistry (IUPAC Recommendations 1996)*) on page 2235 [Terms] [Paper]

Cite as: *IUPAC. Compendium of Chemical Terminology, 2nd ed. (the "Gold Book"). Compiled by A. D. McNaught and A. Wilkinson. Blackwell Scientific Publications, Oxford (1997). Online version (2019-) created by S. J. Chalk. ISBN 0-9678550-9-8. https://doi.org/10.1351/goldbook.*

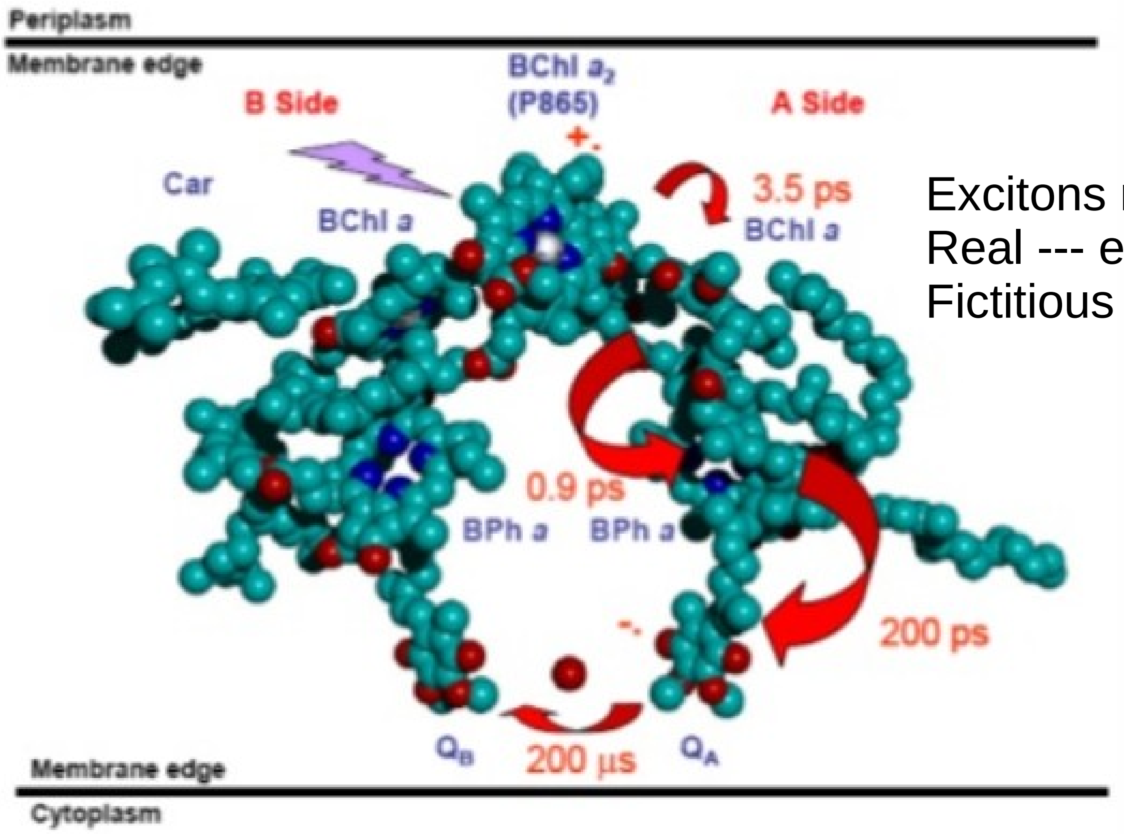
Last revised: February 24, 2014

EXCITONS

$$A^* + B \rightarrow A + B^*$$

$$A^+ + B^- \rightarrow A^- + B^+$$

Example: photosynthesis



Excitons may be:
Real --- energy and charge transfer
Fictitious --- needed to understand complex systems

From a presentation by Neil Greenham

https://www.slideshare.net/cdtpv/thursday-42325335

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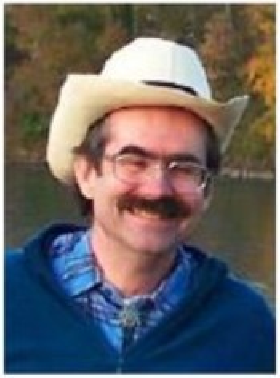
1995

Cartoon given to me by Jean-Paul Malrieu

TDDFT

Prof. Dr. E.K.U. Gross



Prof. Dr. Mark Casida

Presentation uploaded by Deddy Tedjo
https://slideplayer.com/slide/17033333/

TIME-DEPENDENT DENSITY-FUNCTIONAL THEORY (TDDFT)
[E. Runge and E.K.U. Gross, *Phys. Rev. Lett.* 52, 997 (1984)]

For a system, intially in its ground state, exposed to time-dependent perturbation :

Runge-Gross Theorem: $v_{ext}(rt)$ is determined by $\rho(rt)$ up to an additive function of time

Corollary: $\rho(\vec{r}t) \rightarrow N, v_{ext}(\vec{r}\,t) + C(t) \rightarrow \hat{H}(t) + C(t) \rightarrow \Psi(t)\, e^{-i\int_{t_0}^{t} C(t')\,dt'}$

(RG1 assumes functions with Taylor series.)

TIME-DEPENDENT KOHN-SHAM EQUATION

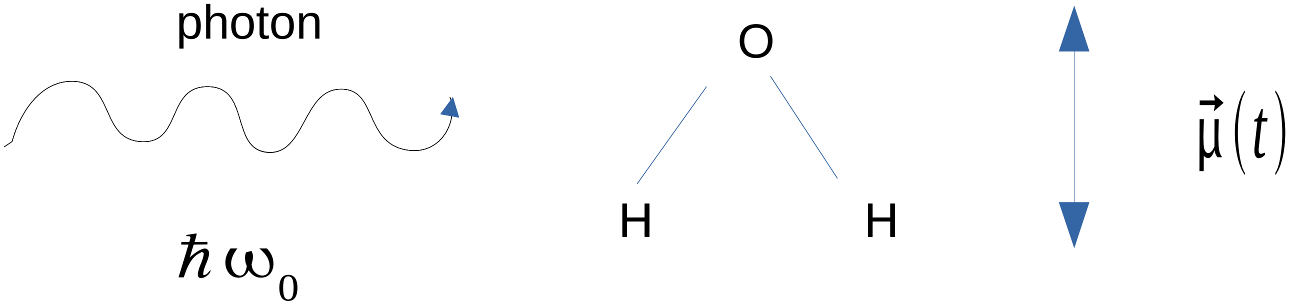
[E. Runge and E. K. U. Gross, *Phys. Rev. Lett.* **52**, 997 (1984)]

$$\left[-\frac{1}{2}\nabla^2+v_{ext}(\vec{r}\,t)+\int\frac{\rho(\vec{r}\,'t)}{|\vec{r}-\vec{r}\,'|}d\vec{r}\,'+v_{xc}(\vec{r}\,t)\right]\psi_i(\vec{r}\,t)=i\frac{\partial}{\partial t}\psi_i(\vec{r}\,t) \qquad (1)$$

where $\rho(\vec{r}\,t)=\sum_{i\sigma}n_{i\sigma}|\psi_{i\sigma}(\vec{r}\,t)|^2$ (2)

and $$v_{xc}(\vec{r}\,t)=\frac{\delta A_{xc}[\rho]}{\delta\rho(\vec{r}\,t)} \qquad (3)$$

Electric-Field Induced Electronic Polarization



Classical model of a photon

$$\vec{\varepsilon}(t)=\vec{\varepsilon}\cos\omega_0 t$$

$$v(\vec{r}\,t)=e\vec{\varepsilon}(t)\cdot\vec{r}$$

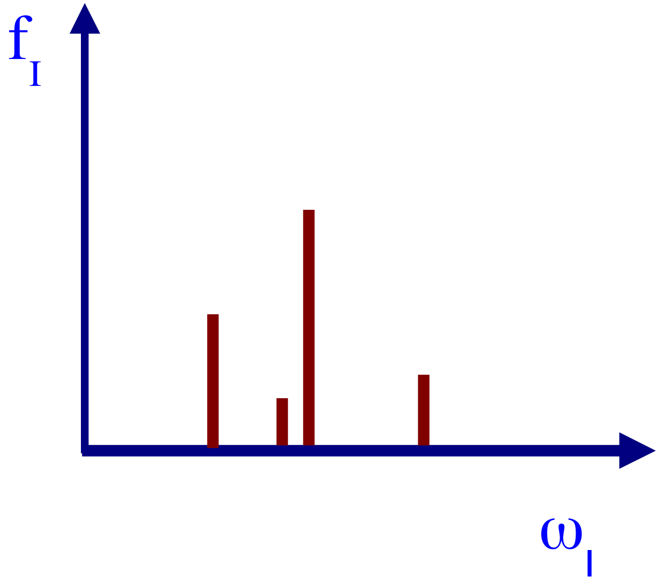
Induced dipole moment

$$\delta\vec{\mu}(t)=-e(<\Psi_0|\vec{r}|\delta\Psi_0(t)>+<\delta\Psi_0(t)|\vec{r}|\Psi_0>)$$

THE DYNAMIC POLARIZABILITY

$$\mu_i(t) = \mu_i + \sum_j \alpha_{i,j}(\omega)\,\varepsilon_j \cos\omega t + \cdots$$

$$\alpha_{r_i,r_j}(\omega) = \sum_{I\neq 0} \frac{2\,\omega_I <\Psi_0|r_i|\Psi_I><\Psi_I|r_j|\Psi_0>}{\omega_I^2 - \omega^2}$$



Sum-over-states (SOS) theorem

$$\alpha(\omega) = \sum_{I\neq 0} \frac{f_I}{\omega_I^2 - \omega^2}$$

$$f_I = \frac{2}{3}\omega_I\left(|<\Psi_0|x|\Psi_I>|^2 + |<\Psi_0|y|\Psi_I>|^2 + |<\Psi_0|z|\Psi_I>|^2\right)$$

How to make computationally convenient?

COMPUTATIONALLY CONVENIENT FORMULATION

Mark E. Casida in *Recent Advances in Density Functional Methods, Part I,*
edited by D.P. Chong (Singapore, World Scientific, 1995), p. 155.
"Time-dependent density-functional response theory for molecules"

“RPA” equation

$$\begin{bmatrix} A(\omega_I) & B(\omega_I) \\ B(\omega_I) & A(\omega_I) \end{bmatrix} \begin{pmatrix} \vec{X}_I \\ \vec{Y}_I \end{pmatrix} = \omega_I \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{pmatrix} \vec{X}_I \\ \vec{Y}_I \end{pmatrix} \tag{1}$$

where

$$A_{ij\sigma,kl\tau}(\omega) = \delta_{\sigma,\tau}\delta_{i,k}\delta_{j,l}(\varepsilon_{j\sigma} - \varepsilon_{j\sigma}) + K_{ij\sigma,kl\tau}(\omega) \tag{2}$$

$$B_{ij\sigma,kl\tau}(\omega) = K_{ij\sigma,lk\tau}(\omega) \tag{3}$$

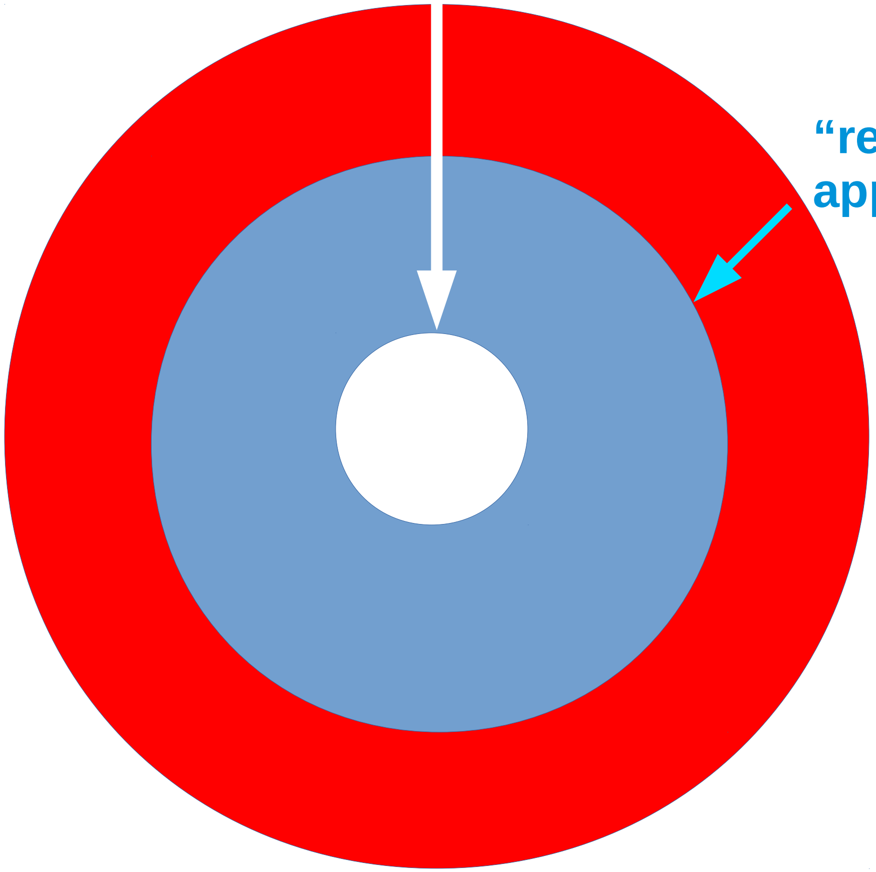
Coupling matrix

$$K_{ij\sigma,kl\tau} = \int\int \psi*_{i\sigma}(\vec{r})\psi_{j\sigma}(\vec{r}) f_{Hxc}^{\sigma,\tau}(\vec{r},\vec{r}\,';\omega)\psi_{k\tau}(\vec{r}\,')\psi*_{l\tau}(\vec{r}\,')\,d\vec{r}\,d\vec{r}\,' \tag{4}$$

Where Conventional TD-DFT Works Best

When the un-symmetry-broken ground-state DFT answer is good
Low energy excitations of dominant single excitation character
Not too much "charge-transfer" (really density relaxation) character
Reasonably localized excitations

"safe place"



"reasonable risk" : where most applications are actually done

"danger zone" : what I would like to do and where we are most "in danger" of learning something interesting

Despite its simplicity, people really like TD-DFT because it allows them to treat problems that they could not treat with other methods!

DENSITY-FUNCTIONAL TIGHT BINDING (DFTB)

- Resembles DFT
- Minimal basis set
- Monopole expansion of ERIs (γ integrals)
- Only 2-center integrals thanks to the potential or density superposition approximation
- Expansion of repulsion potential in terms of atomic pair potentials
- Self-consistent (response) correction
- Extended to TD-DFTB

I will never do semi-empirical theory!

Sure you will!

(A historic conversation
From Montreal days)

Thomas HEINE,
Technische Universität Dresden

Murphy's Law: “If anything can possibly go wrong, it will.”

(A good law for air craft engineers* and developers of theoretical methods.)

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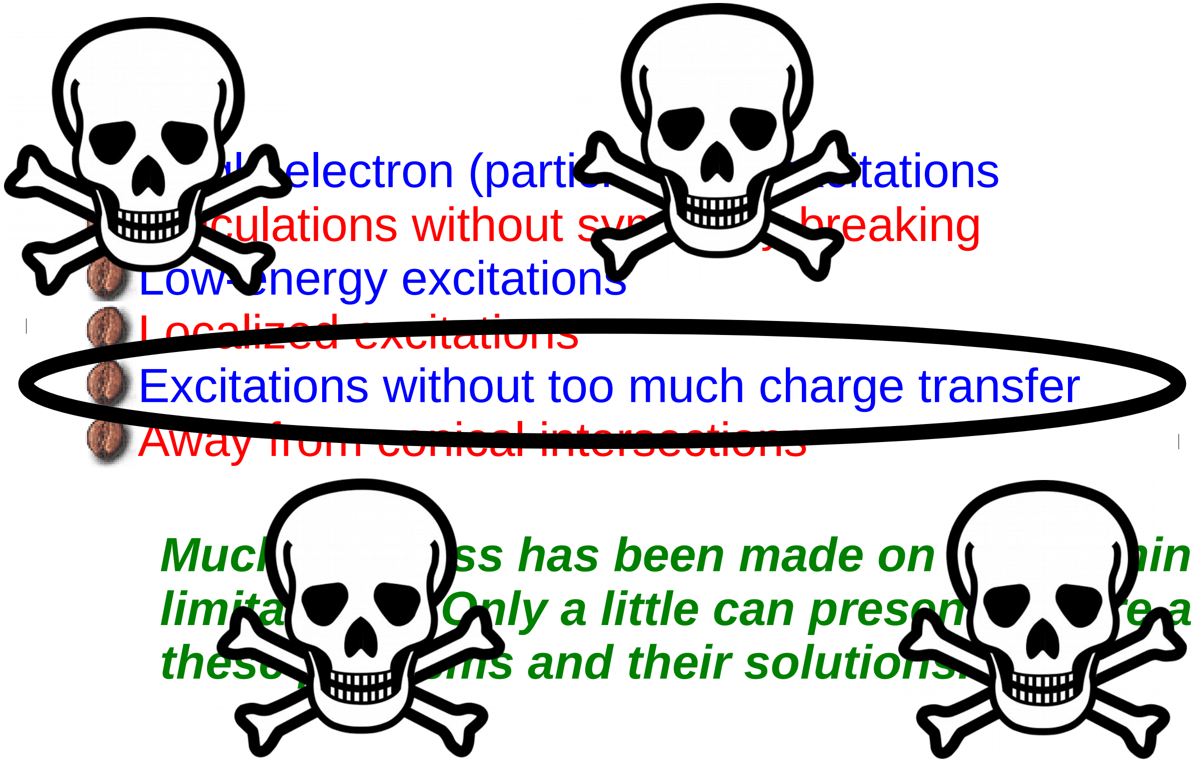
* Edward Murphy was an aeronautics engineer. The original meaning of the “law” was that you need to be ultracareful when you want to design something safe and reliable.

WHERE TD-DFT WORKS BEST:



- [illegible]l electron (parti[illegible] [illegible]itations
- [illegible]culations without sy[illegible] [illegible] breaking
- Low-energy excitations
- Localized excitations
- Excitations without too much charge transfer
- Away from conical intersections

Muc[illegible] [illegible]ss has been made on [illegible]ing thes limita[illegible] Only a little can presen[illegible] [illegible]e about these [illegible]ms and their solutions.

And if you want to look at charge transfer excitations?

RELATED PROBLEM: UNDERESTIMATED CHARGE TRANSFER EXCITATIONS

$$\omega_T = \epsilon_a - \epsilon_i + \left(ia \middle| f_{xc}^{\alpha,\alpha} - f_{xc}^{\alpha,\beta} \middle| ai \right) \quad (1)$$

$$\omega_S = \epsilon_a - \epsilon_i + \left(ai \middle| 2 f_H + f_{xc}^{\alpha,\alpha} + f_{xc}^{\alpha,\beta} \middle| ia \right) \quad (2)$$

Long-range charge transfer =>

$$\omega_{CT} = \epsilon_a - \epsilon_i < EA - IP \quad (3)$$

Should have

$$\omega_{CT} = EA - IP - \frac{1}{R} \quad (4)$$

A. Dreuw, J.L. Weisman, and M. Head-Gordon, “Long-range charge-transfer excited-states in time-dependent density-functional theory require non-local exchange”, *J. Chem. Phys.* **119**, 2943 (2003).

Λ-Criterion*

$$\Lambda = \frac{\sum_{i,a} \kappa_{ia}^2 O_{ia}}{\sum_{i,a} \kappa_{ia}^2} \qquad (1)$$

$$\kappa_{ia} = X_{ia} + Y_{ia} \qquad (2)$$

$$O_{ia} = \int |\psi_i(\vec{r})||\psi_a(\vec{r})| d\vec{r} \qquad (3)$$

Small values (< 0.3) of Λ indicate a high likelihood of a “charge-transfer” underestimation.

---

* M.J.G. Peach, P. Benfield, T. Helgaker, and D.J. Tozer, *J. Chem. Phys.* **128**, 044118 (2008). “Excitation energies in density functional theory: An evaluation and a diagnostic test”

RANGE-SEPARATED HYBRIDS (RSH)

$$\frac{1}{r_{12}} = \underbrace{\frac{erfc(\gamma r_{12})}{r_{12}}}_{SHORT\ RANGE} + \underbrace{\frac{erf(\gamma r_{12})}{r_{12}}}_{LONG\ RANGE}$$

Molecules:
SR <-> DFT
LR <-> WF (e.g. HF)

Solids:
SR <-> WF
LR <-> DFT

Applications in TDDFT:
Y. Tawada, T. Tsuneda, S. Yanagisawa, T. Yanai, and K. Hirao, *J. Chem. Phys.* **120**, 8425 (2004).
S. Tokura, T. Tsuneda, and K. Hirao, *J. Theoretical and Computational Chem.* **5**, 925 (2006).
O.A. Vydrov and G.E. Scuseria, *J. Chem. Phys.* **125**, 234109 (2006).
M.J.G. Peach, E.I. Tellgrent, P. Salek, T. Helgaker, and D.J. Tozer, *J. Phys. Chem. A* **111**, 11930 (2007).
E. Livshits and R. Baer, *Phys. Chem. Chem. Phys.* **9**, 2932 (2007).

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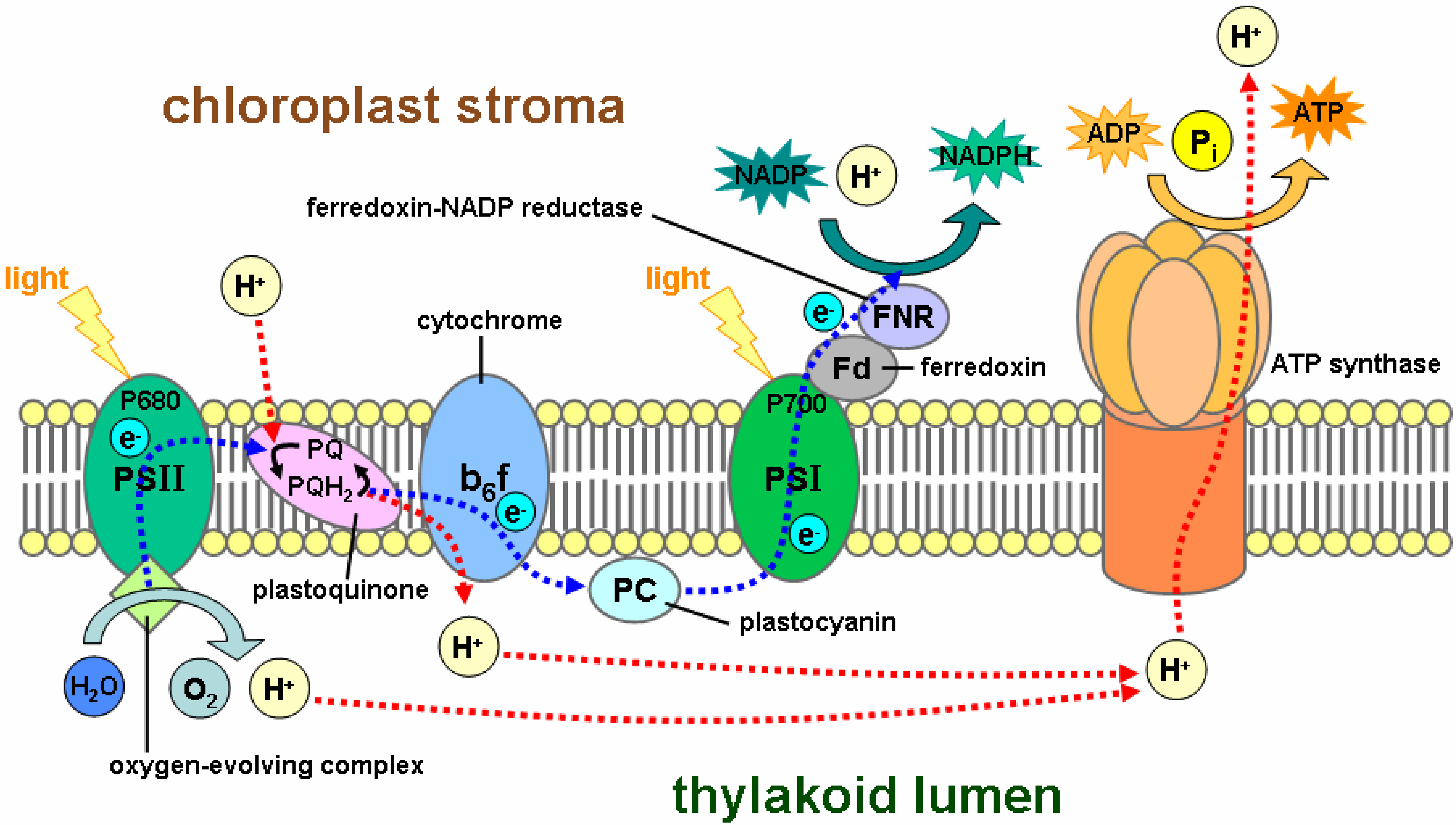
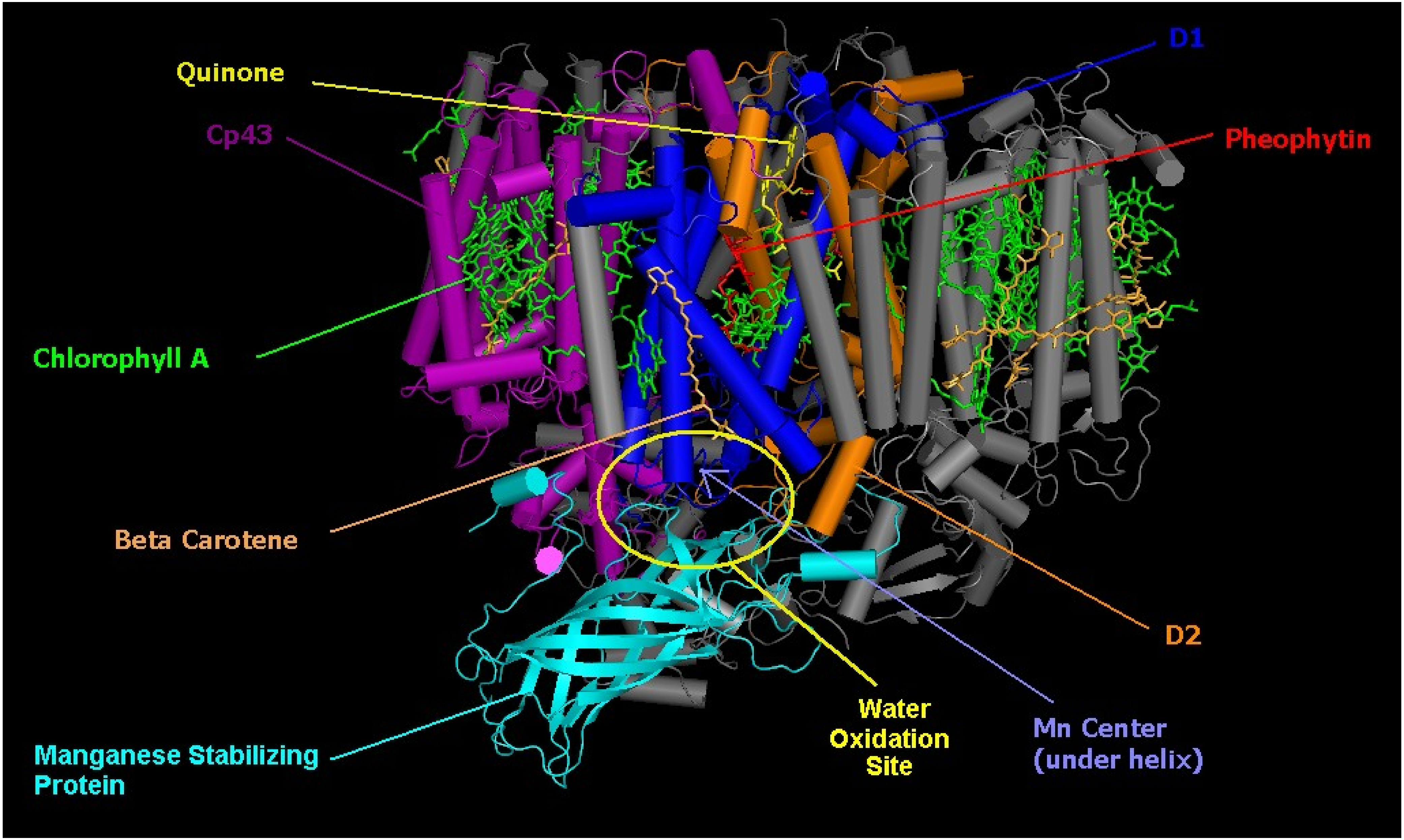
PHOTOSYSTEM II (GREEN PLANTS)



Creates H^+ gradient which is used in the process of making ATP.

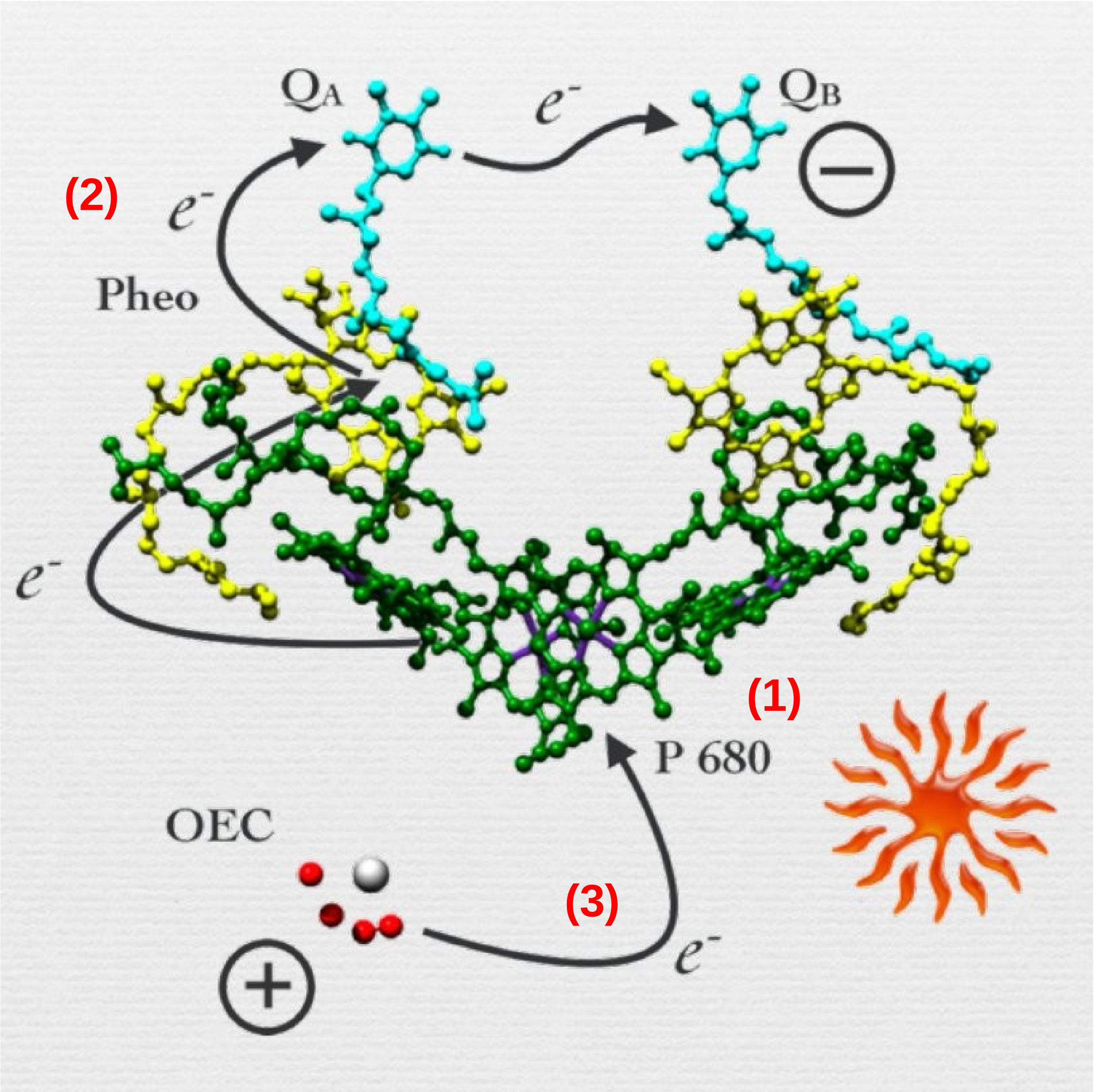
From http://en.wikipedia.org/wiki/Photosystem_II

PHOTOSYSTEM II: Cyanobacteria photosystem II, Monomer, PDB 2AXT.



From http://en.wikipedia.org/wiki/Photosystem_II

PHOTOSYSTEM II (GREEN PLANTS)



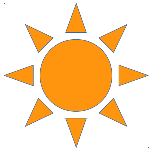
OEC =
oxygen
evolving
complex

Image from Sébastien Liatard's oral defense.

BIO-INSPIRED CHEMISTRY

Donner – **P**igment – **A**cceptor

1) Excitation

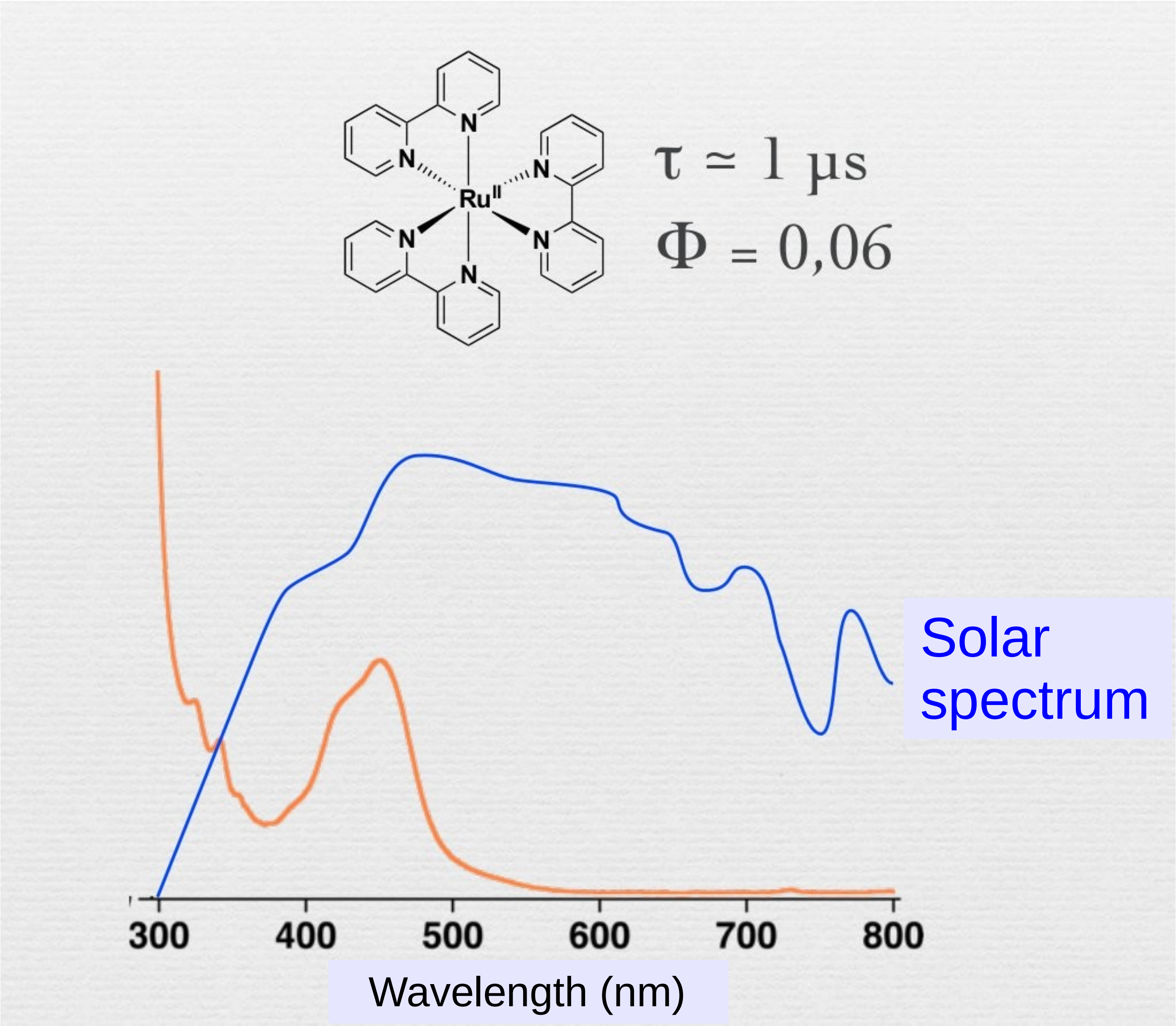


D-P*-A

2) Charge separation

D^{+}-P-A^{-}

MAGIC OF $[Ru(bpy)_3]^{2+}$

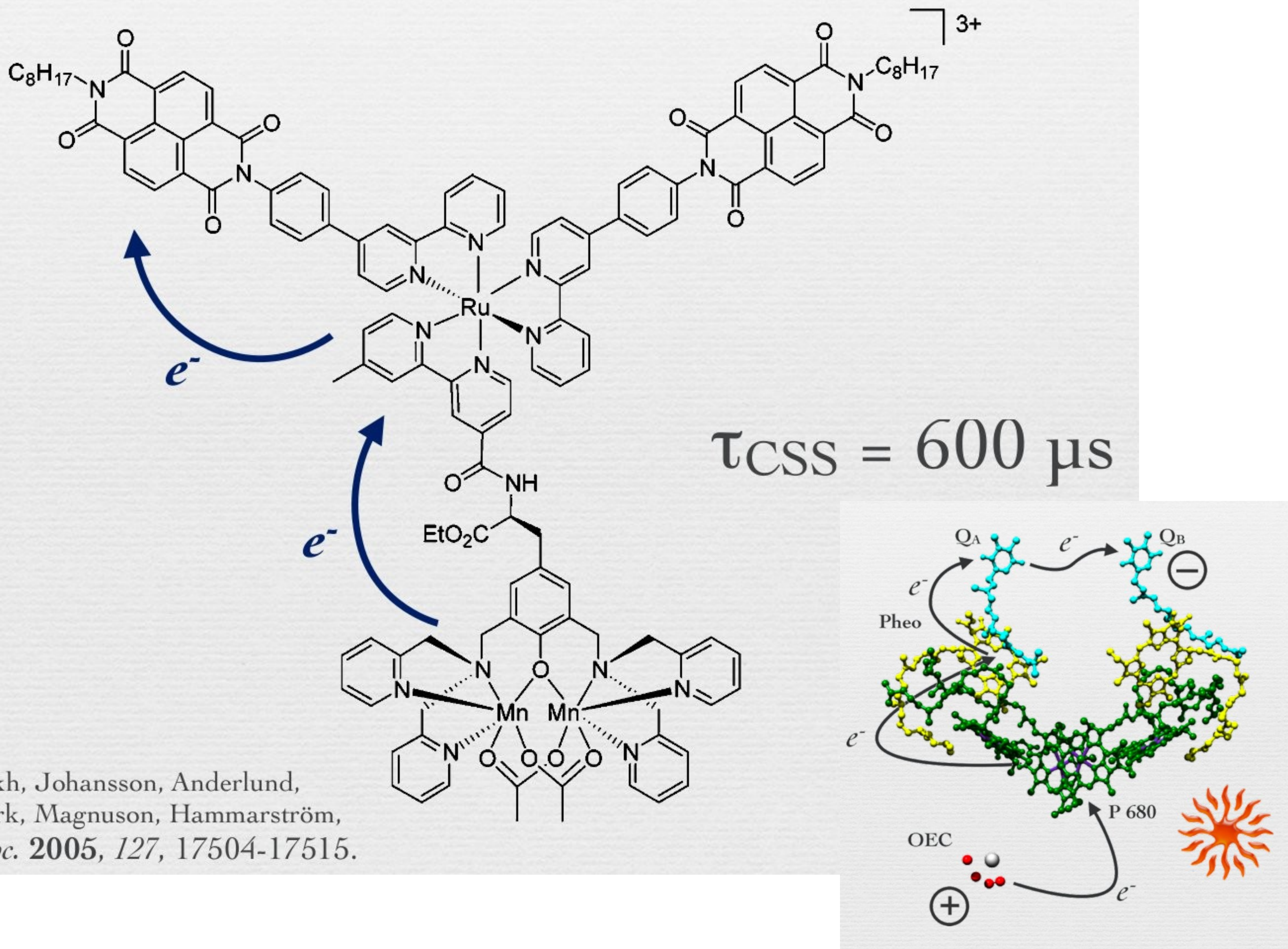


<u>Long-lived excited state</u>

- Phosphorescence
- Easy charge transfer

Image from Sébastien Liatard's oral defense.

CAN WE ADD “WIRES”? CAN WE MAKE IT LOOK MORE LIKE PS II?

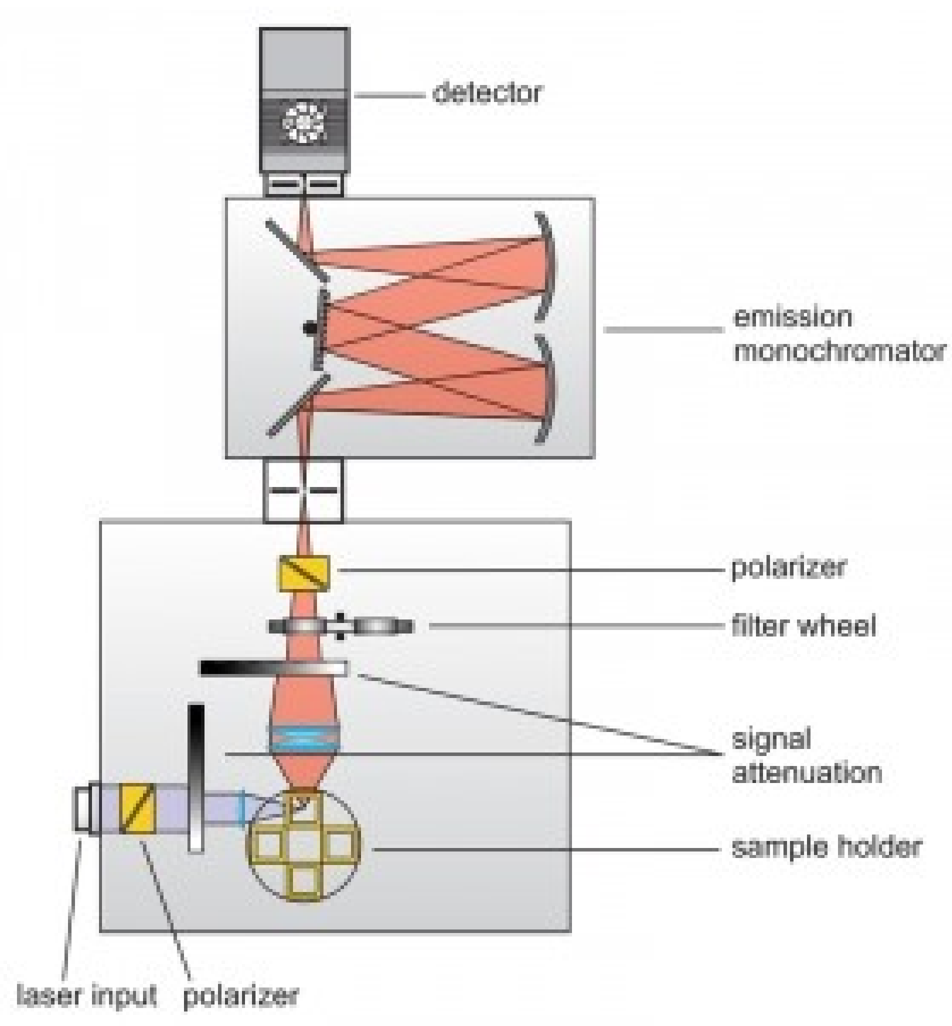


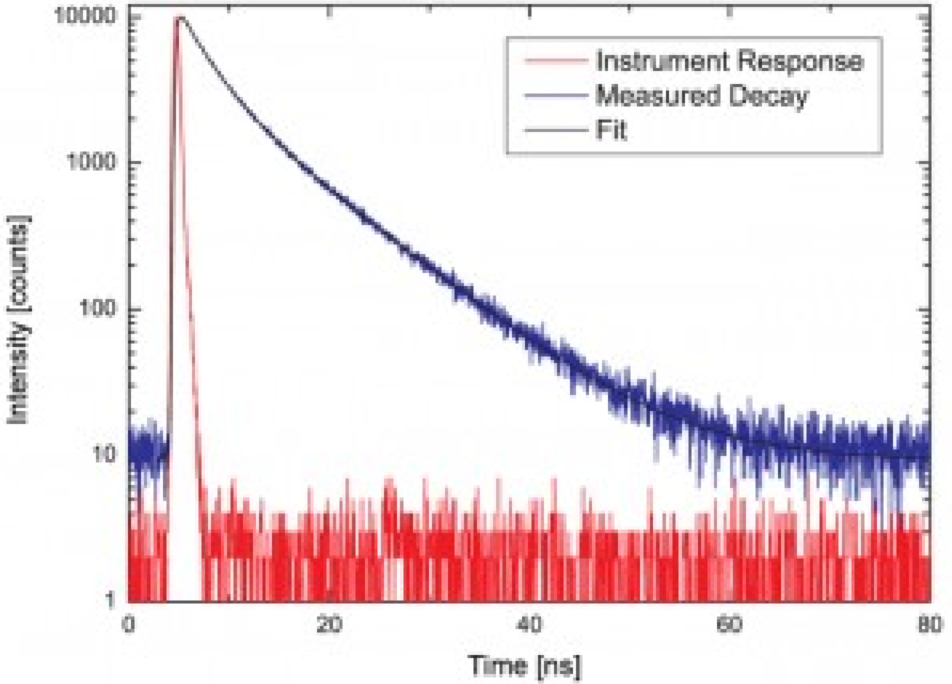
$\tau_{CSS} = 600\ \mu s$

Borgström, Shaikh, Johansson, Anderlund, Styring, Akermark, Magnuson, Hammarström, *J. Am.Chem. Soc.* **2005**, *127*, 17504-17515.

Image from Sébastien Liatard's oral defense.

TIME RESOLVED PHOTOLUMINESCENCE

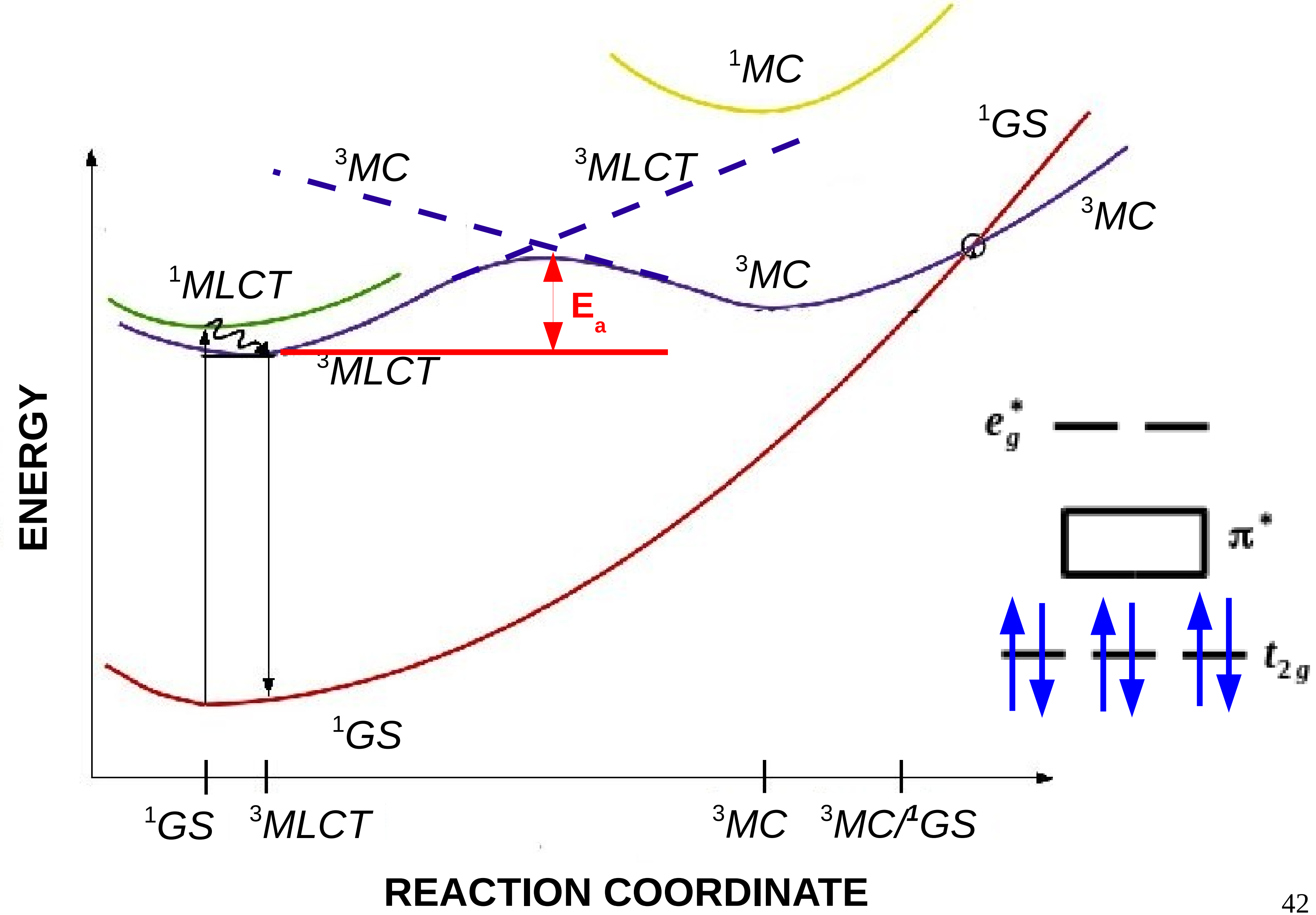




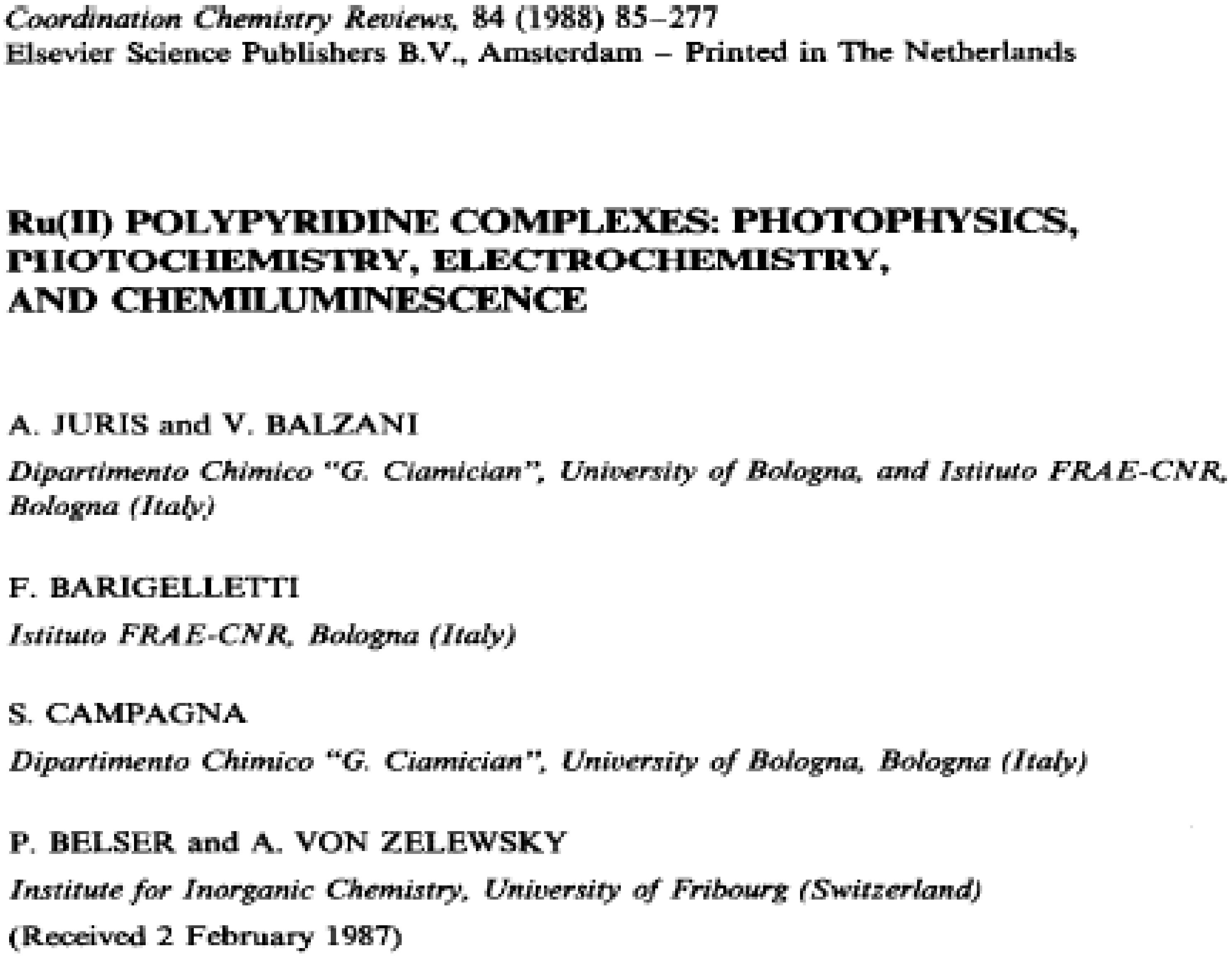
The experiment measures the rate of disappearance of the excited state, either by luminescence *or by other mechanisms such as radiationless relaxation.*

https://www.picoquant.com/applications/category/life-science/time-resolved-fluorescence

LUMINESCENCE LIFETIME DEPENDS UPON THE HEIGHT OF A BARRIER



Section “E. Collection of spectroscopic, redox, photochemical, and photophysical data” pp. 145-243 is a gold mine of data on many different Ru(II) polypyridine complexes!!



Coordination Chemistry Reviews, 84 (1988) 85–277
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Ru(II) POLYPYRIDINE COMPLEXES: PHOTOPHYSICS, PHOTOCHEMISTRY, ELECTROCHEMISTRY, AND CHEMILUMINESCENCE

A. JURIS and V. BALZANI

Dipartimento Chimico "G. Ciamician", University of Bologna, and Istituto FRAE-CNR, Bologna (Italy)

F. BARIGELLETTI

Istituto FRAE-CNR, Bologna (Italy)

S. CAMPAGNA

Dipartimento Chimico "G. Ciamician", University of Bologna, Bologna (Italy)

P. BELSER and A. VON ZELEWSKY

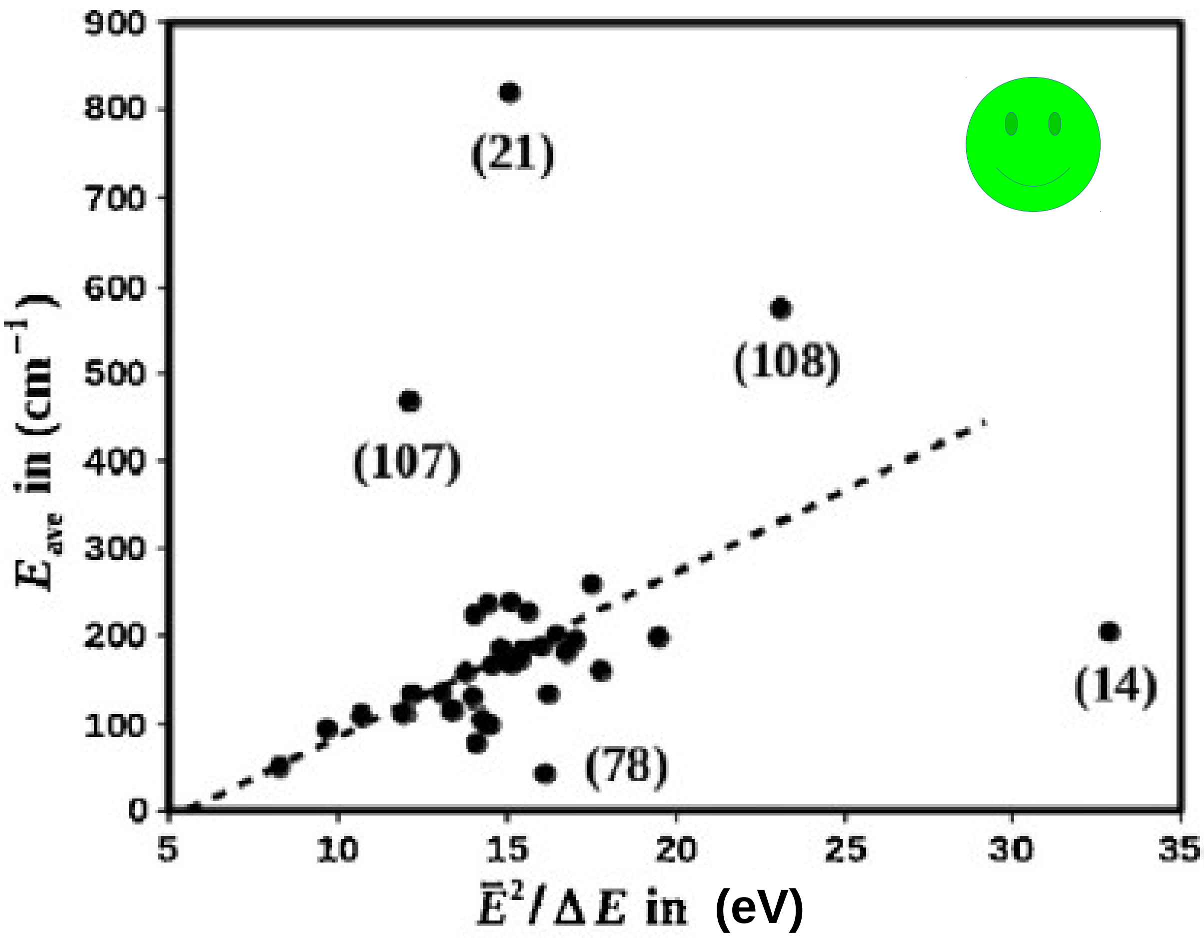
Institute for Inorganic Chemistry, University of Fribourg (Switzerland)

(Received 2 February 1987)

Allows us to extract an empirical barrier height: E_{ave}

FINAL LUMINESCENCE INDEX?

[MCA+17] Denis Magero, Mark E. Casida, George Amolo, Nicholas Makau, and Lusweti Kituyi, *J. Photochem. Photobiol. A* **348**, 305 (2017). Preprint: https://arxiv.org/abs/1707.03665
"Partial Density of States Ligand Field Theory (PDOS-LFT): Recovering a LFT-Like Picture and Application to Photoproperties of Ruthenium(II) Polypyridine Complexes"

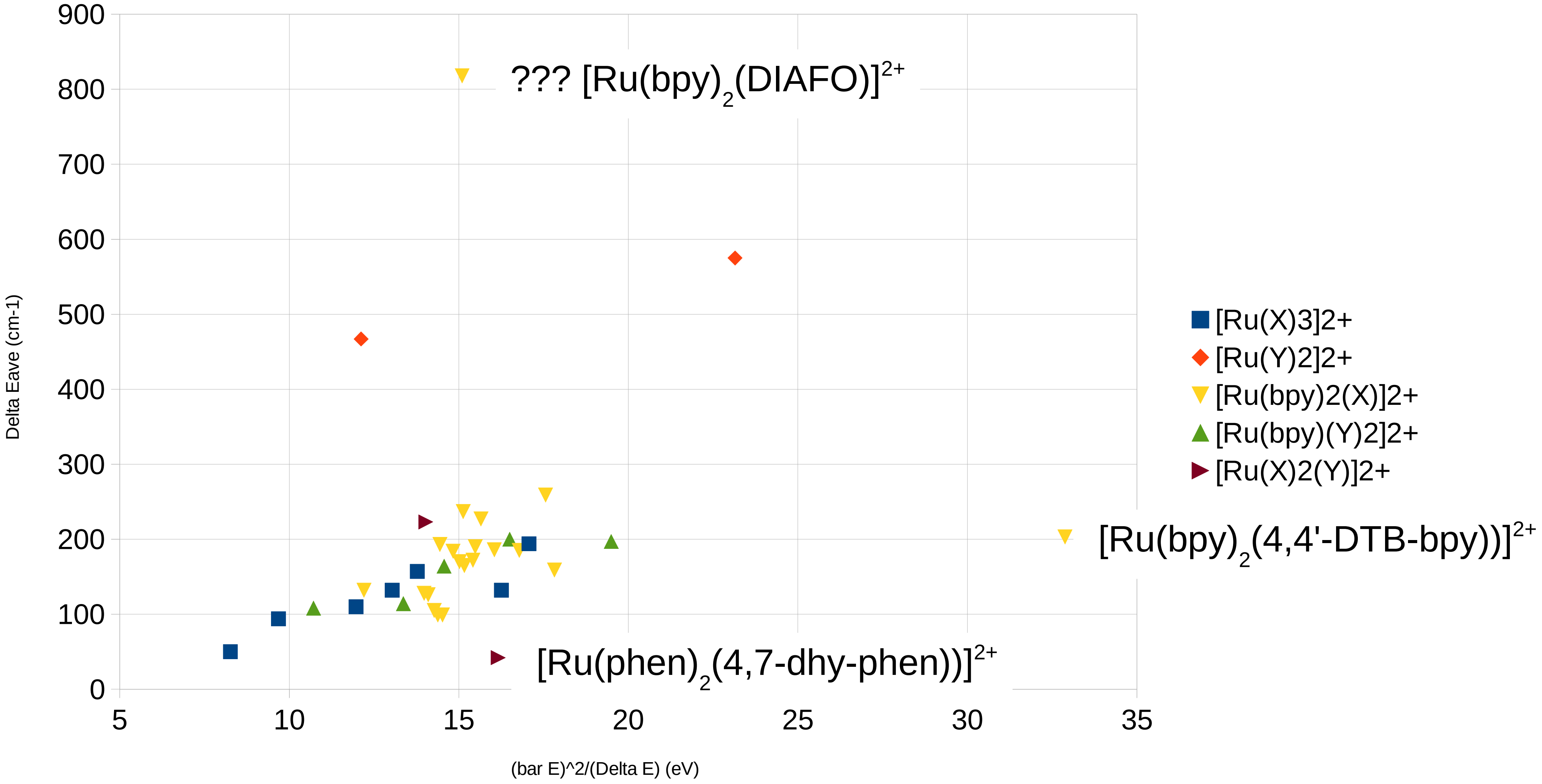


Not perfect, but very good considering all the approximations made!

$$\bar{E} = \frac{\epsilon_{e_g^*} + \epsilon_{\pi^*}}{2}$$

$$\Delta E = \epsilon_{e_g^*} - \epsilon_{\pi^*}$$

BREAKDOWN BY LIGAND FAMILIES

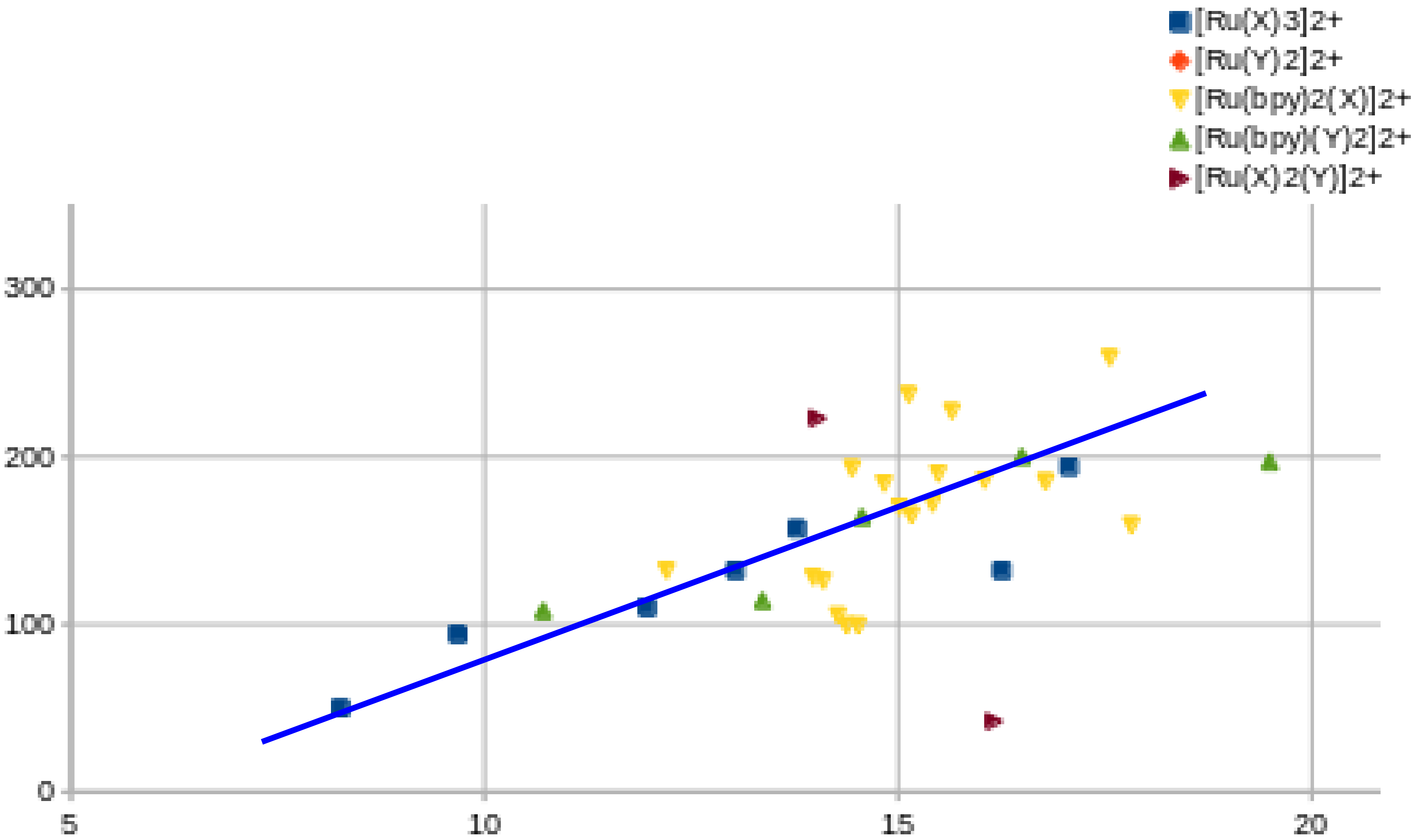


??? $[Ru(bpy)_2(DIAFO)]^{2+}$

$[Ru(bpy)_2(4,4'\text{-DTB-bpy})]^{2+}$

$[Ru(phen)_2(4,7\text{-dhy-phen})]^{2+}$

BREAKDOWN BY LIGAND FAMILIES



OUTLINE

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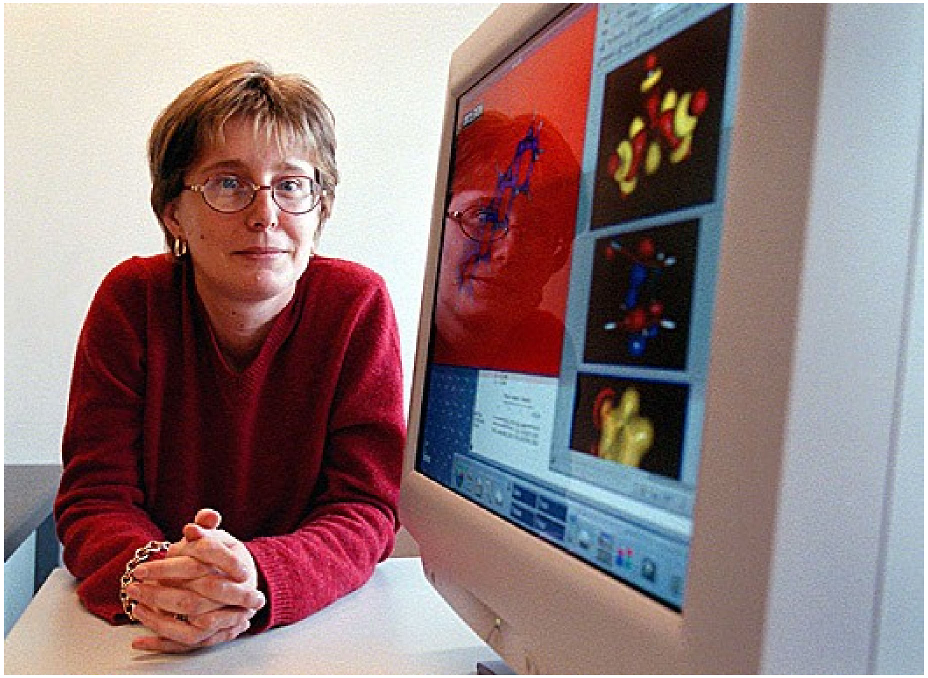
II. ELECTRONIC EXCITED-STATE PROCESSES
III. TD-DFT(B)
IV. STATIC APPLICATIONS
  A. Luminescence indices
  B. Retinal
  C. Excitonic effects
V. TD-DFT(B) FSSH
VI. DYNAMICS APPLICATIONS
  A. Easy case: oxirane
  B. Hard case: pentacene/buckyball
VII. CONCLUSION

O. Valsson, C. Filippi, and M.E. Casida, *J. Chem. Phys.* **142**, 144104 (2015)

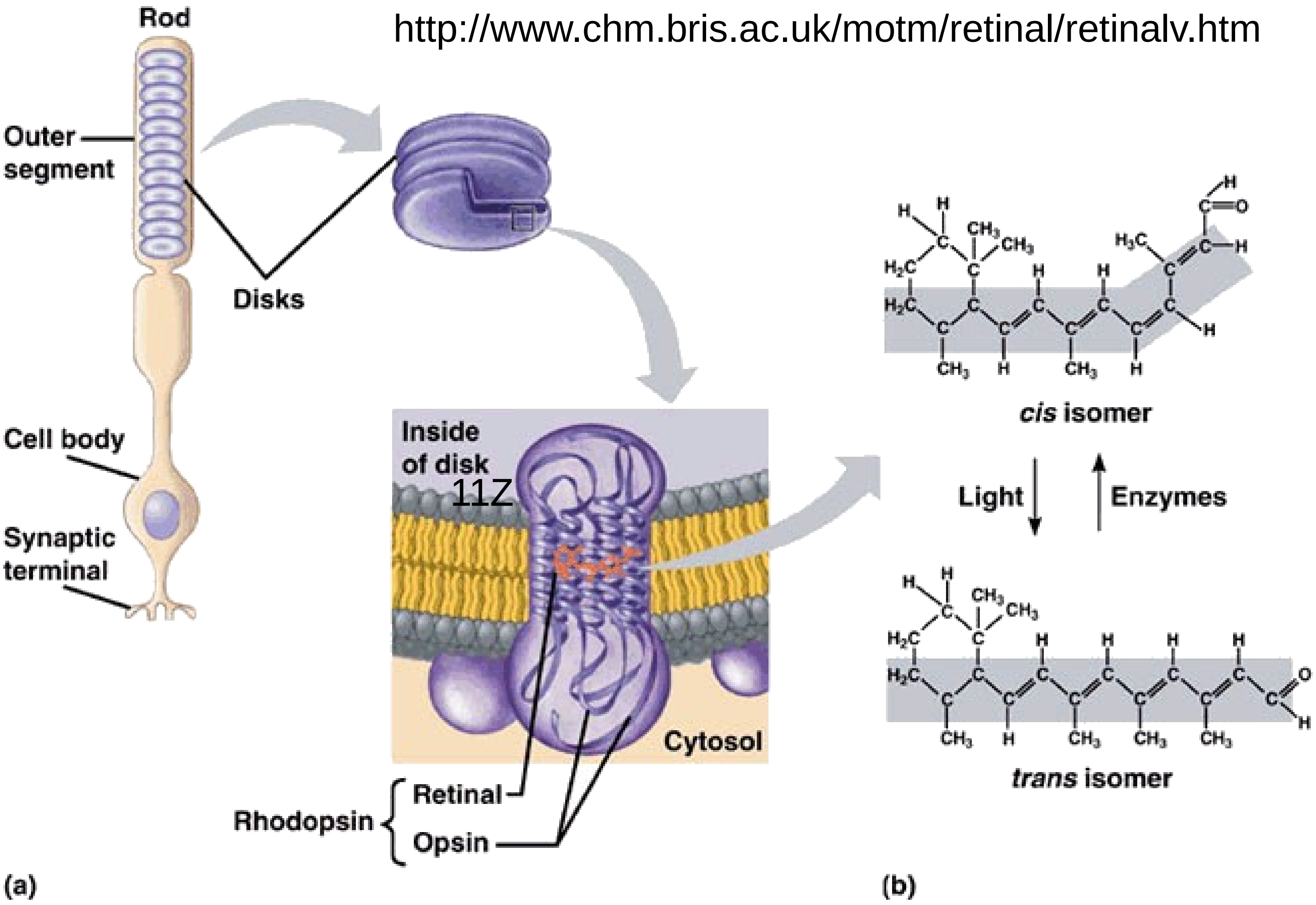
Regarding the use and misuse of retinal protonated Schiff base photochemistry as a test case for time-dependent density-functional theory



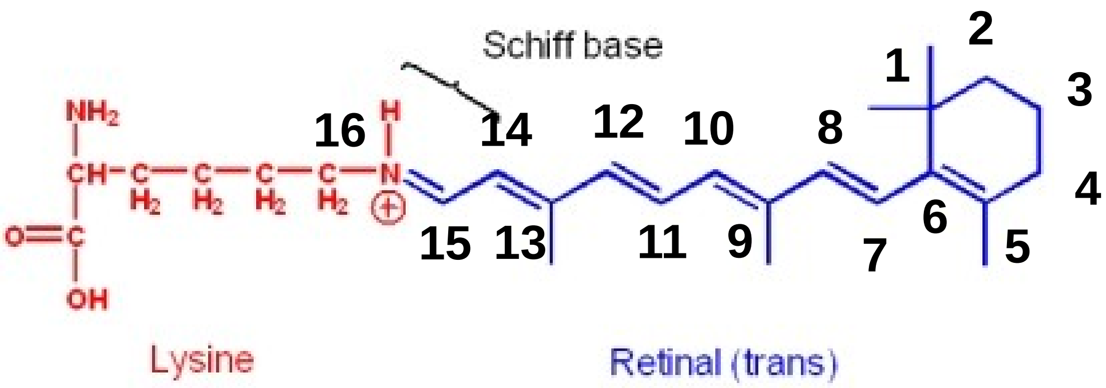
SOME BIOCHEMISTRY

Elizabeth Taylor

http://www.chm.bris.ac.uk/motm/retinal/retinalv.htm



RETINAL PROTONATED SCHIFF BASE (PSB)



$$11Z \xrightarrow{h\nu} 11E$$

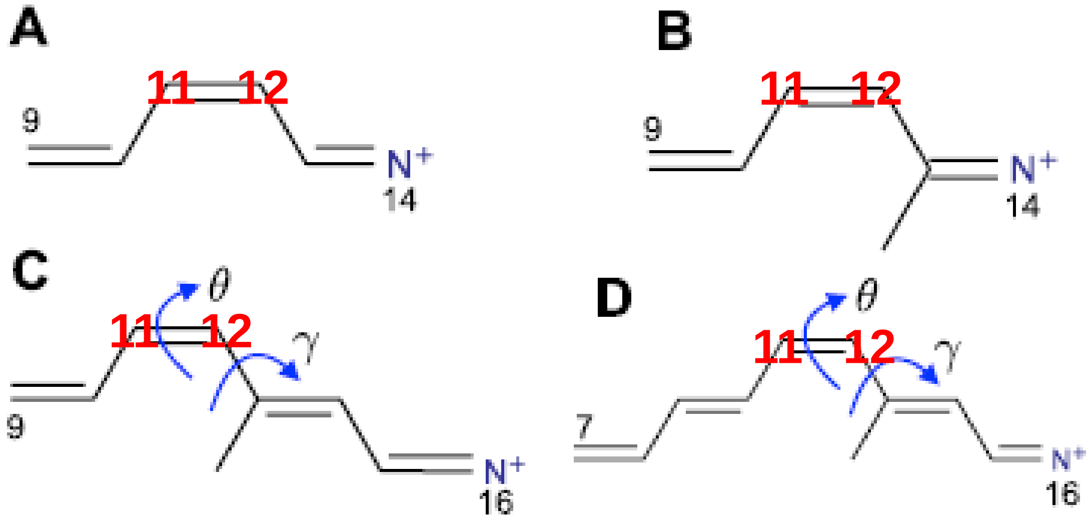


FIG. 2. Model retinal chromophores: **A** PSB3(0), **B** PSB3(1), **C** PSB4(1), and **D** PSB5(1). The naming PSBx(y) denotes the number of double bonds and methyl groups, x and y, respectively. The atom numbering for the full 11-*cis* retinal chromophore is used for all models (see Fig. S3 in the supplementary material[12]), so the *cis* bond is always between C_{11} and C_{12}. The torsional angles are defined as $\theta = \mathrm{Dih}(C_{10}–C_{11}–C_{12}–C_{13})$ and $\gamma = 180^\circ - \mathrm{Dih}(C_{11}–C_{12}–C_{13}–C_{14})$.

d = double bond in ground state

CASSCF

$\theta = 93^o$

$\gamma = 0^o$

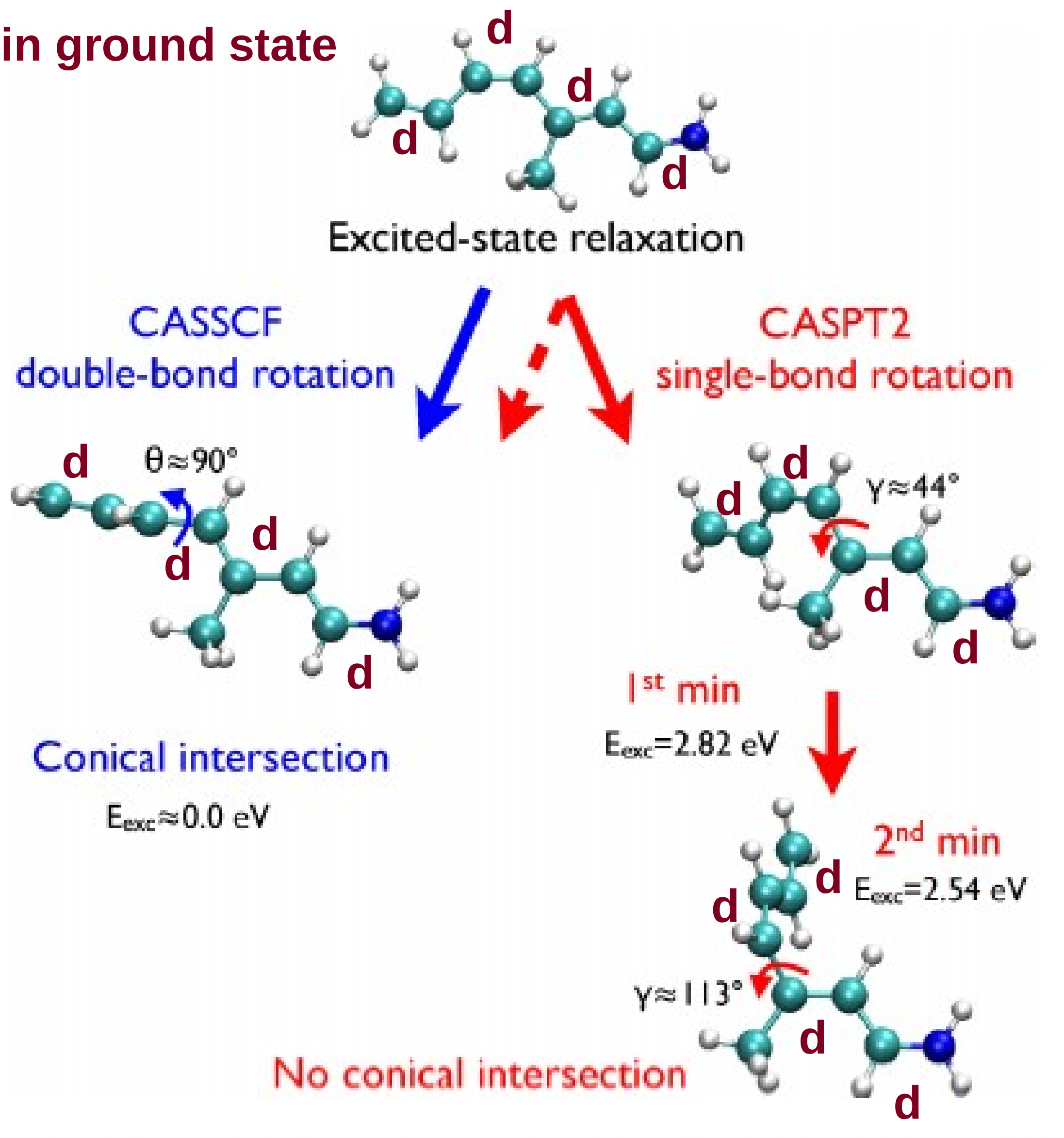


FIG. 1. The excited-state out-of-plane minima obtained with CASSCF and CASPT2. The solid arrows indicate MEPs while the dashed (red) arrow indicates the presence of a transition state on the S_1 surface.

CASPT2

$\theta = -10^o$

$\gamma = 43.6^o$

B3LYP	**CAM-B3LYP**
---	---

LC-BLYP

$\theta = -27.4^o$

$\gamma = 17.7^o$

CASPT2

$\theta = 8.1^o$

$\gamma = 112.7^o$

B3LYP	**CAM-B3LYP**
$\theta = -2.4^o$	$\theta = -1.2^o$
$\gamma = 85.4^o$	$\gamma = 85.2^o$

LC-BLYP

$\theta = -0.2^o$

$\gamma = 86.8^o$

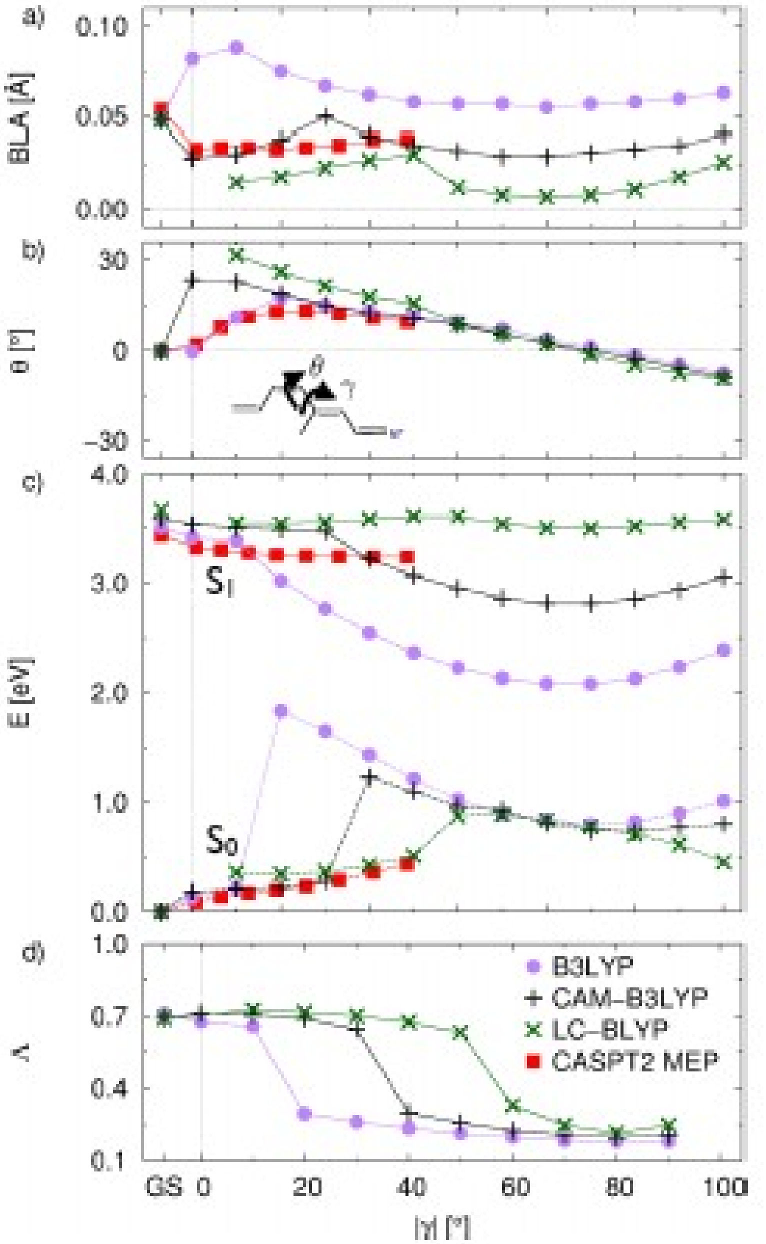


FIG. 6. Constrained geometrical excited-state optimization of the PSB4(1) model (C) for fixed torsional angle γ (formal single-bond rotation) obtained within TD-DFT. The CASPT2 MEP as a function of the torsional angle γ is also shown. We plot the BLA (panel (a)), the torsional angles θ for double-bond rotations (panel (b)), and the ground- and excited-state energies along the paths (panel (c)), and the Λ values along the TD-DFT paths (panel (d)).

Scan around single bond

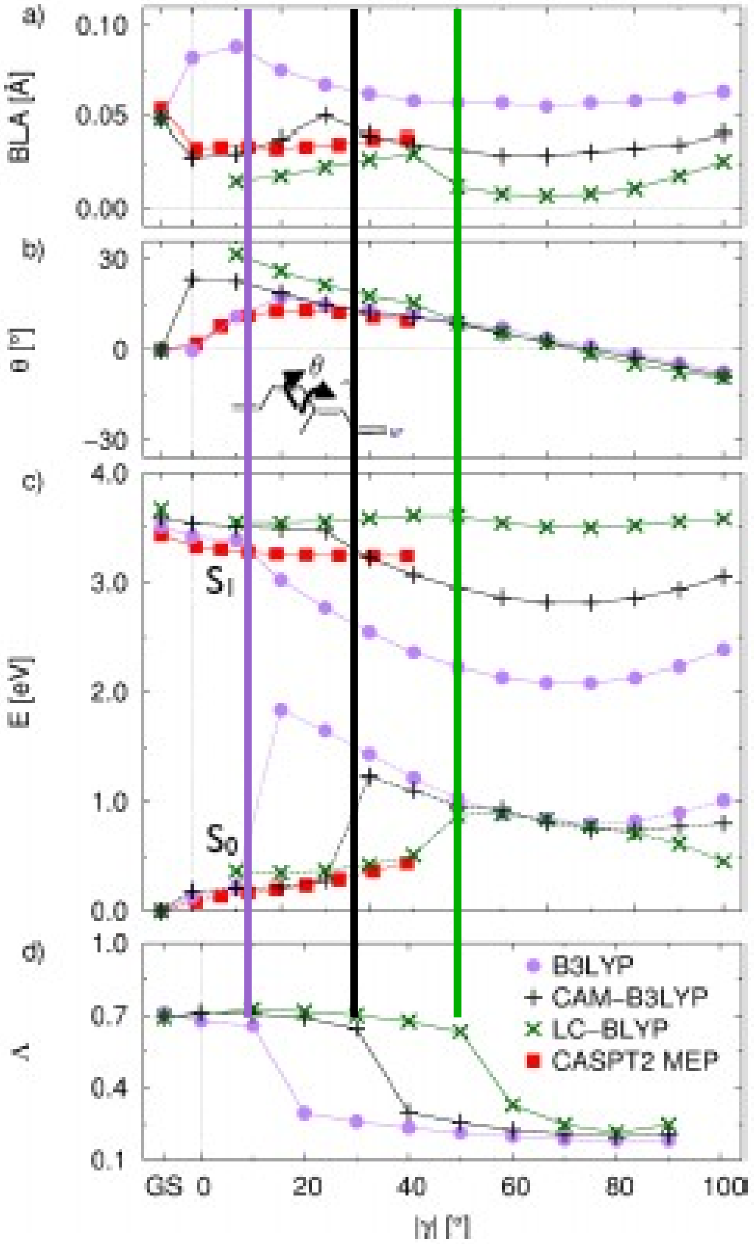


FIG. 6. Constrained geometrical excited-state optimization of the PSB4(1) model (C) for fixed torsional angle γ (formal single-bond rotation) obtained within TD-DFT. The CASPT2 MEP as a function of the torsional angle γ is also shown. We plot the BLA (panel (a)), the torsional angles θ for double-bond rotations (panel (b)), and the ground- and excited-state energies along the paths (panel (c)), and the Λ values along the TD-DFT paths (panel (d)).

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A.A.M.H.M. Darghouth, G.C. Correa, S. Juillard, M.E. Casida, A. Humeniuk, and R. Mitrić, "Davydov-Type Excitonic Effects on the Absorption Spectra of Parallel-Stacked and Herringbone Aggregates of Pentacene: Time-Dependent Density-Functional Theory and Time-Dependent Density-Functional Tight Binding", *J. Chem. Phys.* **149**, 134111 (2018)

Spectral effects seen in dye aggregates:

J-aggregates (Jelly/Scheibe) spectrum shifts to lower energies and new narrow peaks appear.

H-aggregates (hypsochromic) spectrum shifts to higher energies.

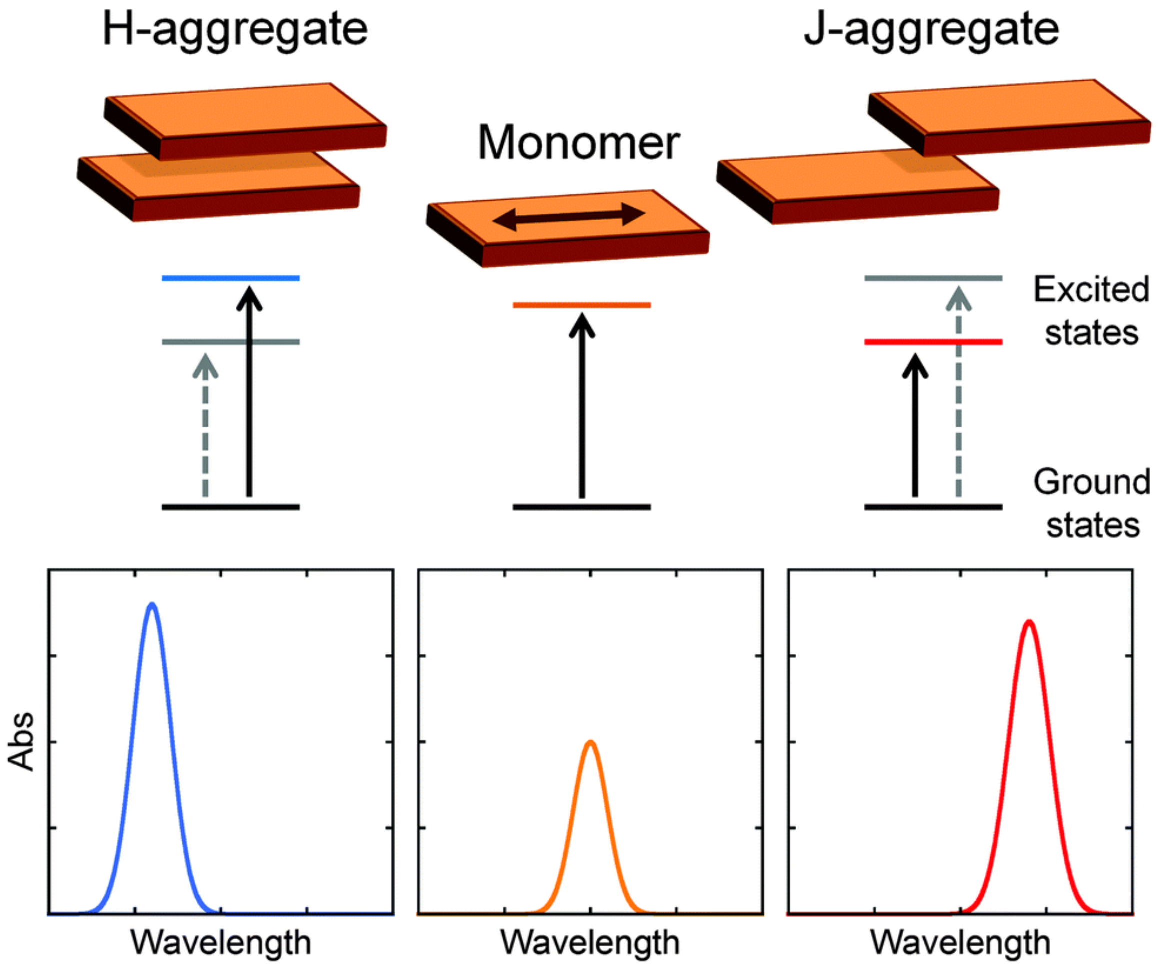
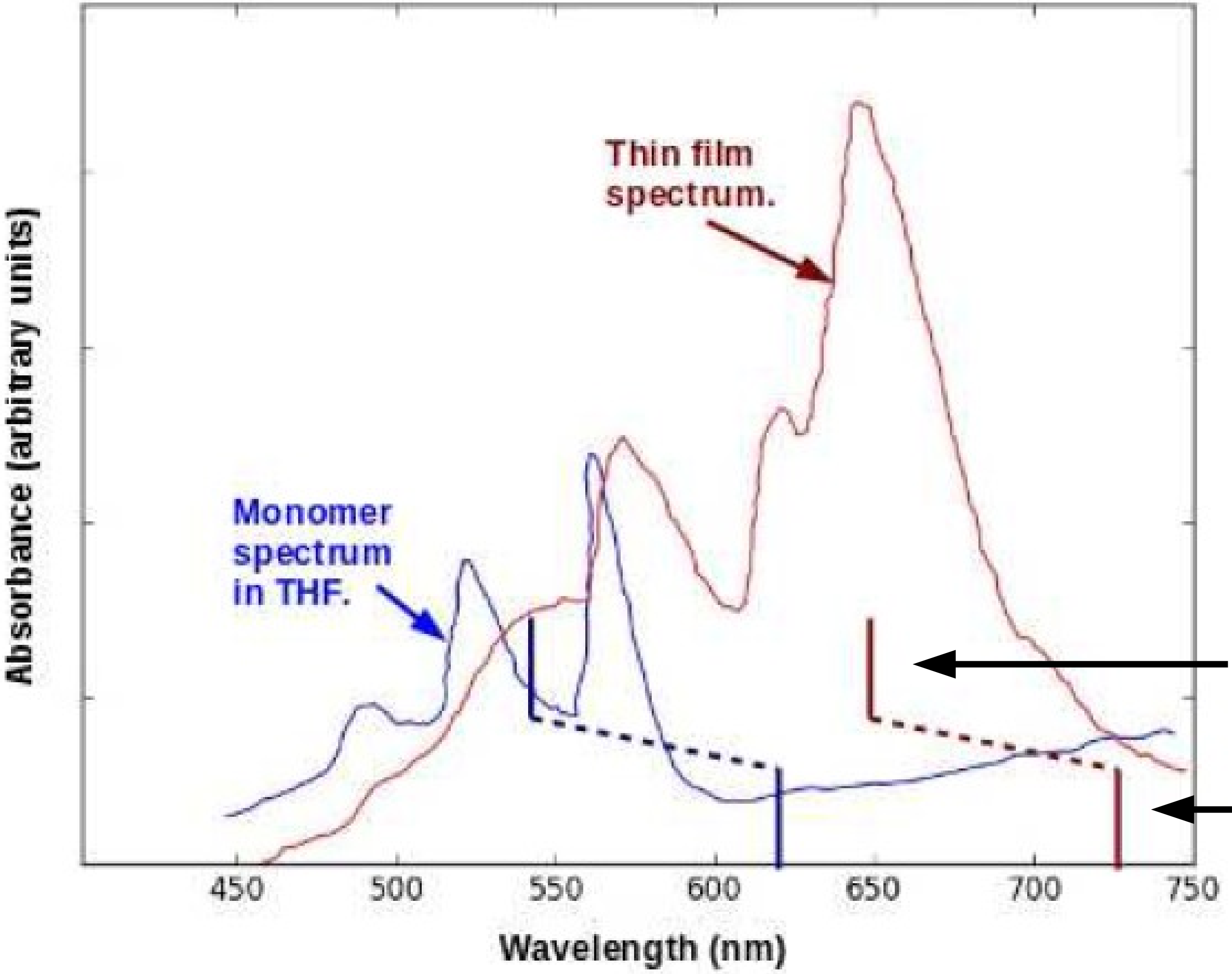


Image from
Chem. Soc. Rev.
43, 5211 (2014)

Davydov Splitting in Pentacene



J-aggregate

Shifted BSE/*GW* results

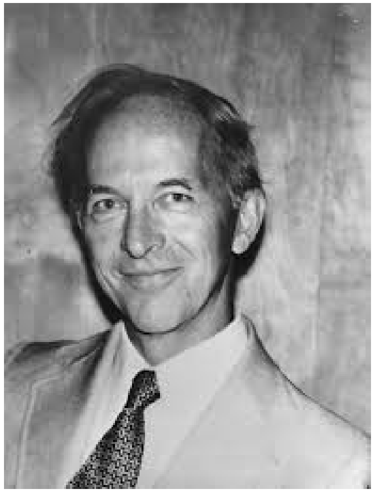
BSE/*GW* results*

---

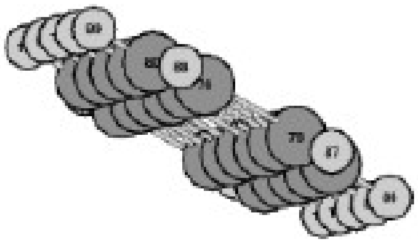
* P. Cudazzo, F. Sottile, A. Rubio, and M. Gatti, “Topical Review: Exciton dispersion in molecular Solids,” *J. Phys. Condens. Matter* **27**, 113204 (2015).

Kasha's Exciton Model*

1. Historical theory (1960s). Necessarily very approximate!
2. Assumes a van der Waals (vdW) dimer.
3. Perturbative. Only zero and first order.
4. Point-dipole point-dipole approximation.

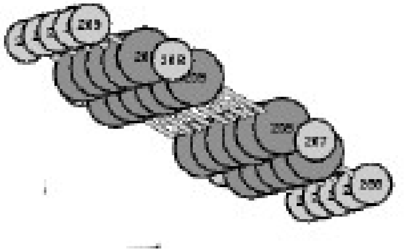


Michael Kasha
(1920-2013)



$$\Psi_1^0 \rightarrow \Psi_1^I \tag{1}$$

$$\omega = E_1^I - E_1^0 \tag{2}$$



$$\Psi_2^0 \rightarrow \Psi_2^I \tag{3}$$

$$\omega = E_1^I - E_1^0 \tag{4}$$

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + \hat{V}_{12} \tag{5}$$

$$\Psi_0 = \Psi_1^0 \Psi_2^0 \tag{6}$$

$$\Psi_I = C_1 \Psi_1^I \Psi_2^0 + C_2 \Psi_1^0 \Psi_2^I \tag{7}$$

---

* **[KRE65]** M. Kasha, H.R. Rawls, and A. El Bayoumi, “The exciton model in molecular Spectroscopy”, *Pure Appl. Chem.* **11**, 371 (1965).

Ground-State Energy

$$E_0 = \langle \Psi_1^0 \Psi_2^0 | \hat{H} | \Psi_1^0 \Psi_2^0 \rangle \qquad \textbf{(1)}$$

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + \hat{V}_{12} \qquad \textbf{(2)}$$

$$E_0 = \langle \Psi_1^0 \Psi_2^0 | \hat{H}_1 | \Psi_1^0 \Psi_2^0 \rangle + \langle \Psi_1^0 \Psi_2^0 | \hat{H}_2 | \Psi_1^0 \Psi_2^0 \rangle + \langle \Psi_1^0 \Psi_2^0 | \hat{V}_{12} | \Psi_1^0 \Psi_2^0 \rangle \qquad \textbf{(3)}$$

$$E_0 = \langle \Psi_1^0 | \hat{H}_1 | \Psi_1^0 \rangle \langle \Psi_2^0 | \Psi_2^0 \rangle + \langle \Psi_1^0 | \Psi_1^0 \rangle \langle \Psi_2^0 | \hat{H}_2 | \Psi_2^0 \rangle + \langle \Psi_1^0 \Psi_2^0 | \hat{V}_{12} | \Psi_1^0 \Psi_2^0 \rangle \qquad \textbf{(4)}$$

$$E_0 = E_1^0 + E_2^0 + \langle \Psi_1^0 \Psi_2^0 | \hat{V}_{12} | \Psi_1^0 \Psi_2^0 \rangle \qquad \textbf{(5)}$$

$$E_0 = E_1^0 + E_2^0 + E_{\mathrm{vdW}}^0 \qquad \textbf{(6)}$$

Excited-State Energy

$$\Psi_I = C_1 \Psi_1^I \Psi_2^0 + C_2 \Psi_1^0 \Psi_2^I$$ **(1)**

$$\begin{bmatrix} A & B \\ B & A \end{bmatrix} \begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = E^I \begin{pmatrix} C_1 \\ C_2 \end{pmatrix}$$ **(2)**

$$A = \langle \Psi_1^I \Psi_2^0 | \hat{H} | \Psi_1^I \Psi_2^0 \rangle = \langle \Psi_1^0 \Psi_2^I | \hat{H} | \Psi_1^0 \Psi_2^I \rangle$$ **(3)**

$$B = \langle \Psi_1^0 \Psi_2^I | \hat{H} | \Psi_1^I \Psi_2^0 \rangle = \langle \Psi_1^I \Psi_2^0 | \hat{H} | \Psi_1^0 \Psi_2^I \rangle$$ **(4)**

$$\Psi_\pm^I = \frac{1}{\sqrt{2}} \left(\Psi_1^I \Psi_2^0 \pm \Psi_1^0 \Psi_2^I \right)$$ **(5)**

$$E_\pm^I = A \pm B$$ **(6)**

Exciton Splitting

$$A=\langle \Psi_1^I \Psi_2^0 | \hat{H} | \Psi_1^I \Psi_2^0 \rangle$$ **(1)**

$$B=\langle \Psi_1^0 \Psi_2^I | \hat{H} | \Psi_1^I \Psi_2^0 \rangle$$ **(2)**

$$\hat{H}=\hat{H}_1+\hat{H}_2+\hat{V}_{12}$$ **(3)**

$$A=E_1^I+E_2^0+\langle \Psi_1^I \Psi_2^0 | \hat{V}_{12} | \Psi_1^I \Psi_2^0 \rangle = E_1^I+E_2^0+E_{\mathrm{vdW}}^I$$ **(4)**

$$B=\langle \Psi_1^0 \Psi_2^I | \hat{V}_{12} | \Psi_1^I \Psi_2^0 \rangle = E_{\mathrm{exciton\ splitting}}$$ **(5)**

$$E_\pm^I=E_1^I+E_2^0+E_{\mathrm{vdW}}^I \pm E_{\mathrm{exciton\ splitting}}$$ **(6)**

$$\omega_\pm^I=E_\pm^I-E^0=\omega_1^0+\left(E_{vdW}^I-E_{vdW}^0\right)\pm E_{\mathrm{exciton\ splitting}}$$ **(7)**

Transition Moments

$$\vec{\mu}^{I0} = \langle \Psi^{I} | \vec{r} | \Psi^{0} \rangle \qquad \textbf{(1)}$$

$$\vec{\mu}^{I0}_{\pm} = \frac{1}{\sqrt{2}} \langle \Psi_1^{I} \Psi_2^{0} \pm \Psi_1^{0} \Psi_2^{I} | \vec{r} | \Psi_1^{0} \Psi_2^{0} \rangle \qquad \textbf{(2)}$$

$$\vec{\mu}^{I0}_{\pm} = \frac{1}{\sqrt{2}} \left(\vec{\mu}_1^{I0} \pm \vec{\mu}_2^{I0} \right) \qquad \textbf{(3)}$$

$$f^{I}_{\pm} = \frac{\omega^{I}_{\pm}}{3} |\vec{\mu}_1^{I0} \pm \vec{\mu}_2^{I0}|^2 \qquad \textbf{(4)}$$

Example: Parallel stacking $\vec{\mu}_{1/2} \perp \vec{r}$ **(5)**

$$f^{I}_{+} = \frac{4}{3} \omega^{I}_{1} |\vec{\mu}_1^{I0}|^2 \qquad \textbf{(6)}$$

$$f^{I}_{-} = 0 \qquad \textbf{(7)}$$

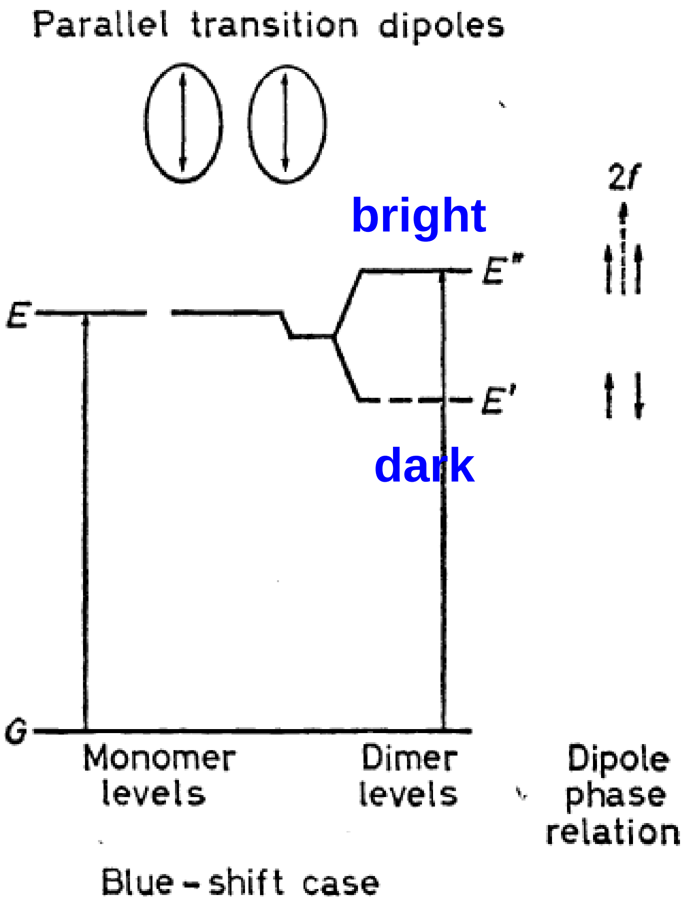
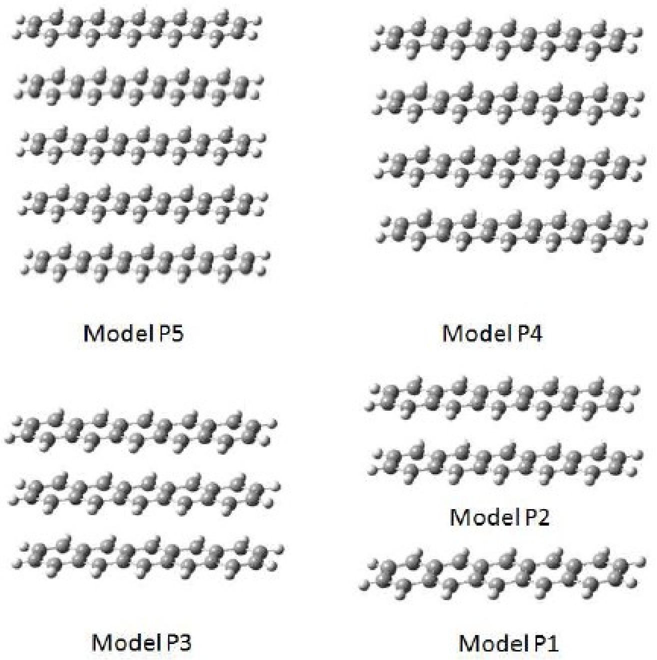
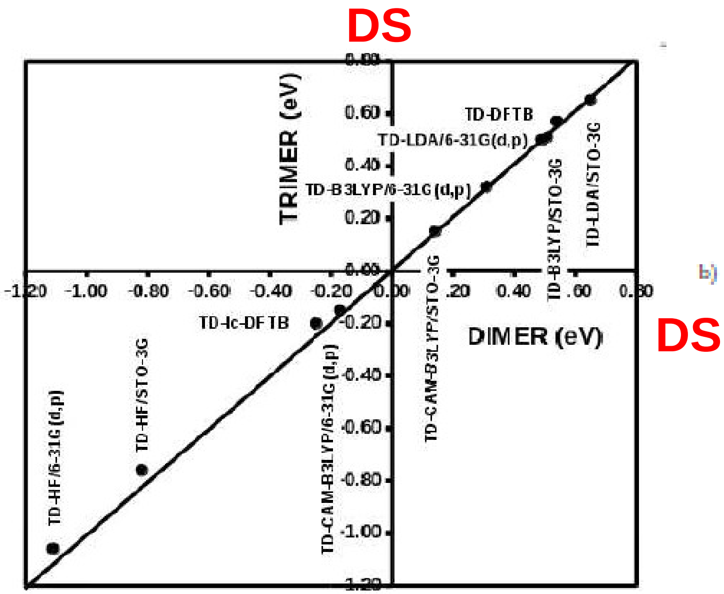
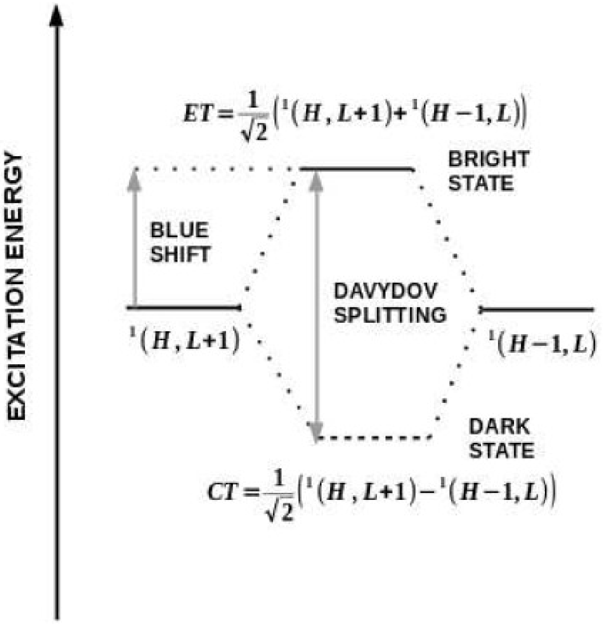


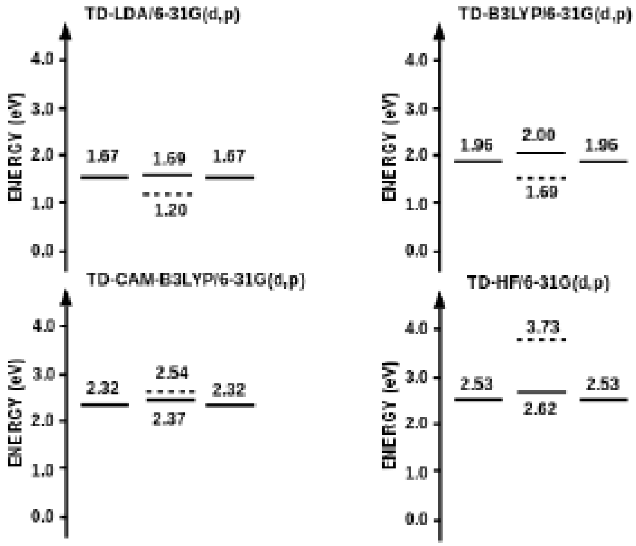
Fig. 1. Ref. **[KRE65]**

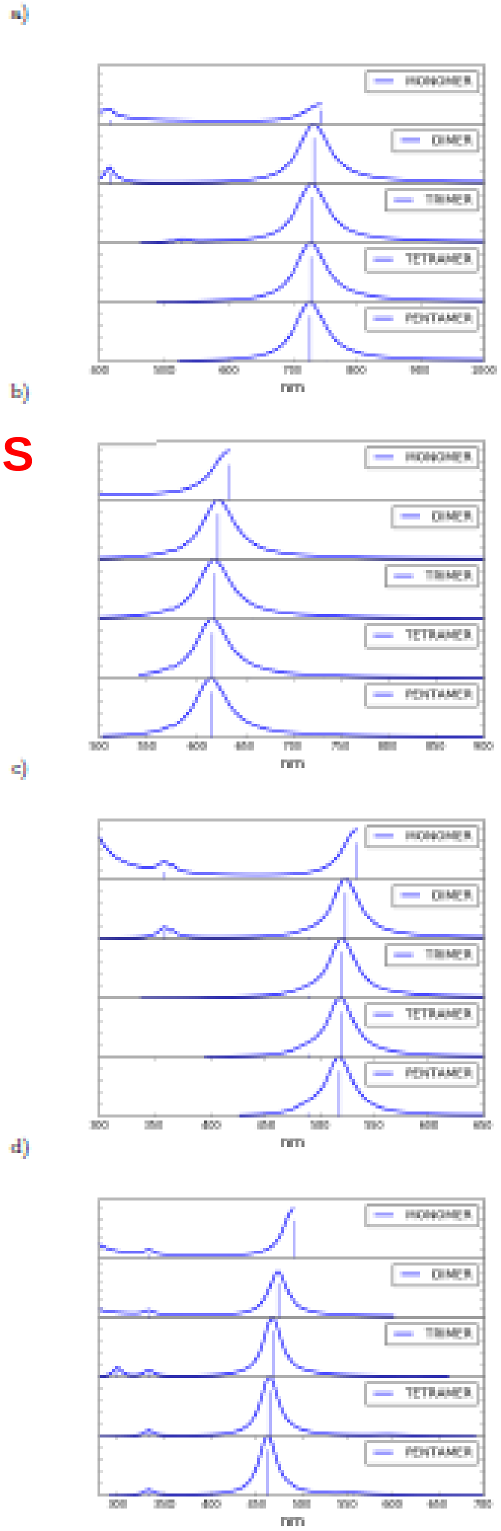
We can apply this to stacked pentacene!!











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MIXED QUANTUM/CLASSICAL DYNAMICS

Electrons treated quantum mechanically.
Nuclei are treated classically.

Electrons :

$$\hat{H}_{elec}(r;R(t))\Psi^{elec}(r,t)=i\hbar\frac{d}{dt}\Psi^{elec}(r,t)$$

Nuclei :

Ehrenfest dynamics: $$M\ddot{R}=-\nabla\langle\Psi^{\mathrm{elec}}(t)|V(R)|\Psi^{\mathrm{elec}}(t)\rangle$$

Surface hopping: $$M\ddot{R}=-\nabla V_m(R)$$

Ehrenfest dynamics moves on an average PES which is physically incorrect and lacks microscopic reversability.

Surface hopping has microscopic reversability and can, in principle, produce relative yields for competing products in a chemical reaction, but is much more difficult to implement and carry out.

SURFACE HOPPING

$$\hat{H}_{elec}(r;R(t))\Psi^{elec}(r,t)=i\hbar\frac{d}{dt}\Psi^{elec}(r,t)$$

Expand the time-dependent wave function in terms of the solutions of the time-independent Schrödinger equation.

$$\hat{H}_{elec}(r;R(t))\Psi_m^{elec}(r;R(t))=E_m(R(t))\Psi_m^{elec}(r;R(t))$$

$$\Psi^{elec}(r,t)=\sum_m \Psi_m^{elec}(r;R(t))C_m(t)$$

1st order equation.

$$\dot{C}_m(t)=-i\,E_m(t)C_m(t)/\hbar-\sum_n \langle m|\frac{dn}{dt}\rangle C_n(t)$$

Probability of finding the system on surface m is

$$P_m(t)=|C_m(t)|^2$$

TULLY'S FEWEST SWITCHES SURFACE HOPPING (FSSH)

Density matrix $$P_{m,n}(t) = C_m(t)\,C_n^*(t)$$

Probability of jumping from surface *m* to surface *n* in the interval (t,t+Δt)

$$g_{m\to n}(t,\Delta t) = \frac{\dot{P}_{m,n}(t)\,\Delta t}{P_{m,m}} = \frac{2\Re(\dot{C}_m(t)\,C_n^*(t))\,\Delta t}{P_{m,m}}$$

Generate a random number ξ in (0,1) and compare

If $\xi < g_{m\to n}(t,\Delta t)$, then jump and set $C_n(t) = 1$

Otherwise continue on surface *m*

J.C. Tully, *J. Chem. Phys.* **93**, 1061 (1990); S. Hammes-Schiffer and J.C. Tully, *J. Chem. Phys.* **101**, 4657 (1994).

DETAILS

The hopping probability is 100% where two surfaces intersect.

After a hop, nuclear kinetic energies need to be readjusted to conserve energy.

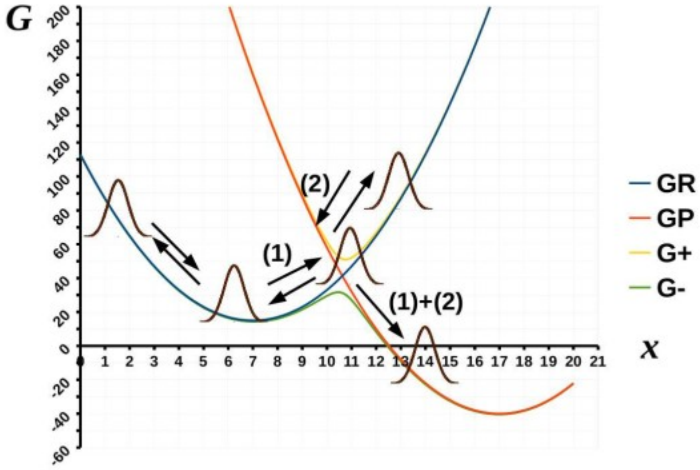
The electronic numerical integration needs to be finer than the numerical integration for the nuclei.

NOT A DETAIL

It is important not to read too much meaning into a single FSSH trajectories. Only *ensemble averages* over swarms of trajectories are physical.

DECOHERENCE CORRECTION

Roughly: The classical part of the calculation should collapse the wave function so that the nuclei are moving on only one PES once we are outside of the crossing region. Otherwise the method is *overcoherent*.



Overcoherence in the Ehrenfest method: the system moves on an *average* PES.

Overcoherence in Tully’s method: the electronic wave function continues *incorrectly* to have components on both surfaces after leaving the crossing region.

Introducing *decoherence corrections* makes the two methods increasingly similar.

OUTLINE

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IV. STATIC APPLICATIONS
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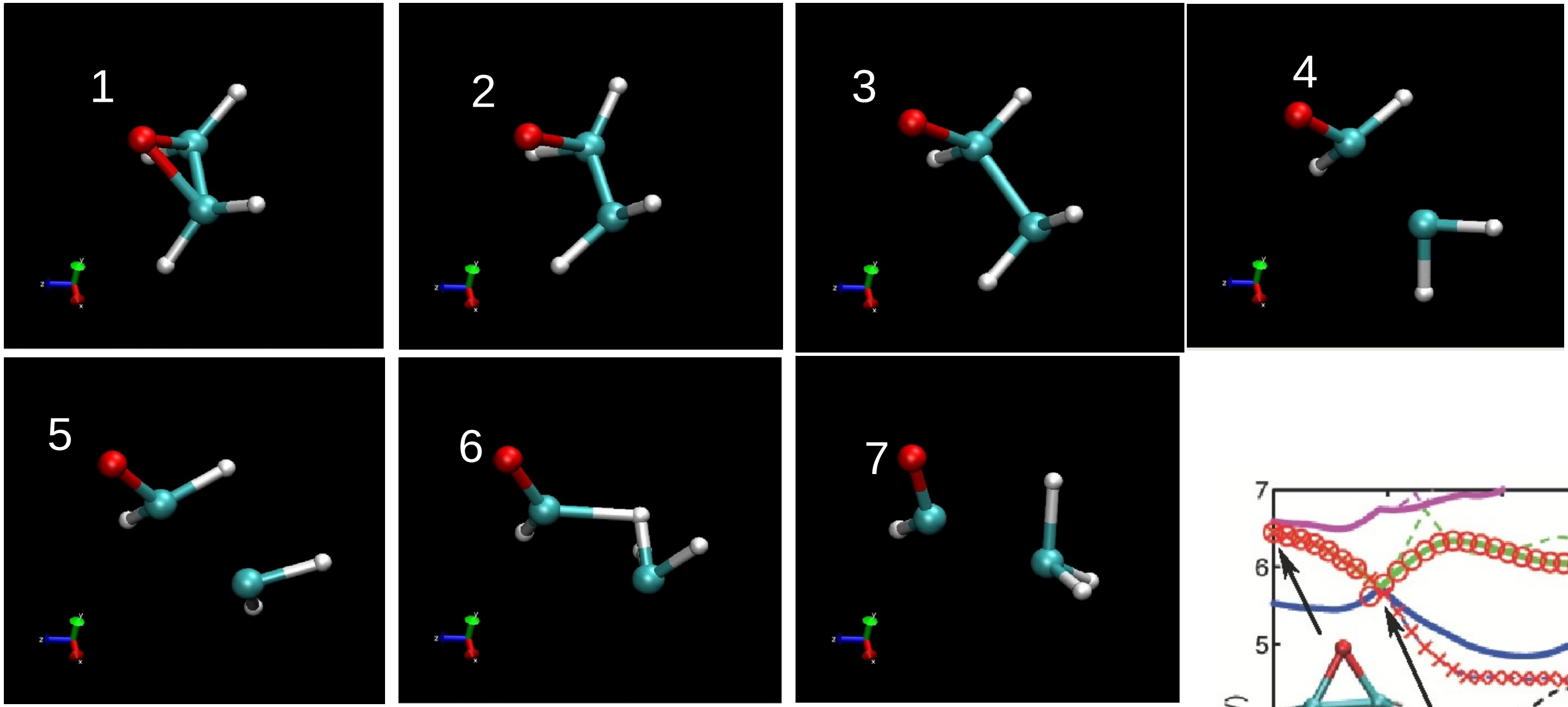
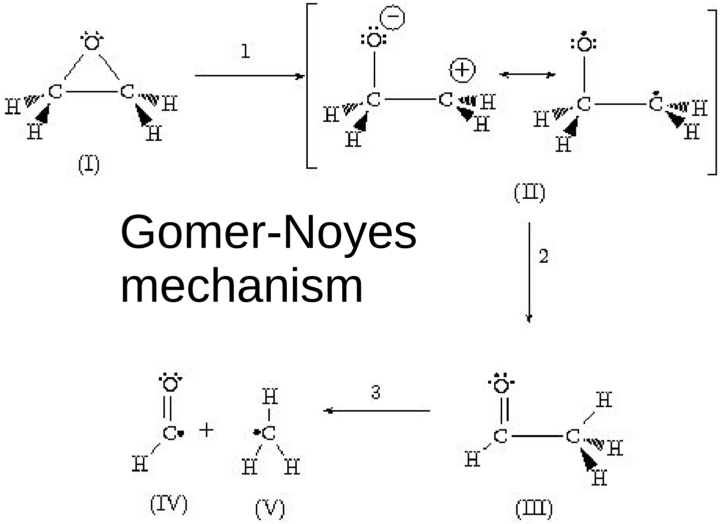
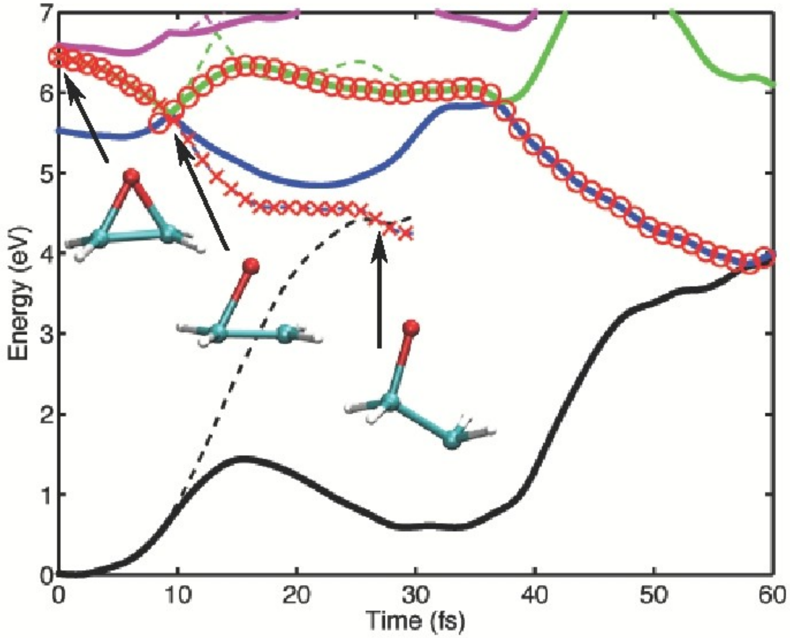
  B. Retinal
  C. Excitonic effects
V. TD-DFT(B) FSSH
VI. DYNAMICS APPLICATIONS
  A. Easy case: oxirane
  B. Hard case: pentacene/buckyball
VII. CONCLUSION

E. Tapavicza, I. Tavernelli, U. Röthlisberger, C. Filippi, and M.E. Casida, “Mixed time-dependent density-functional theory/classical surface hopping study of oxirane photochemistry”, *J. Chem. Phys.* 129, 124108 (2008).





Gomer-Noyes mechanism



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arXiv.org > physics > arXiv:1803.11121

Physics > Chemical Physics

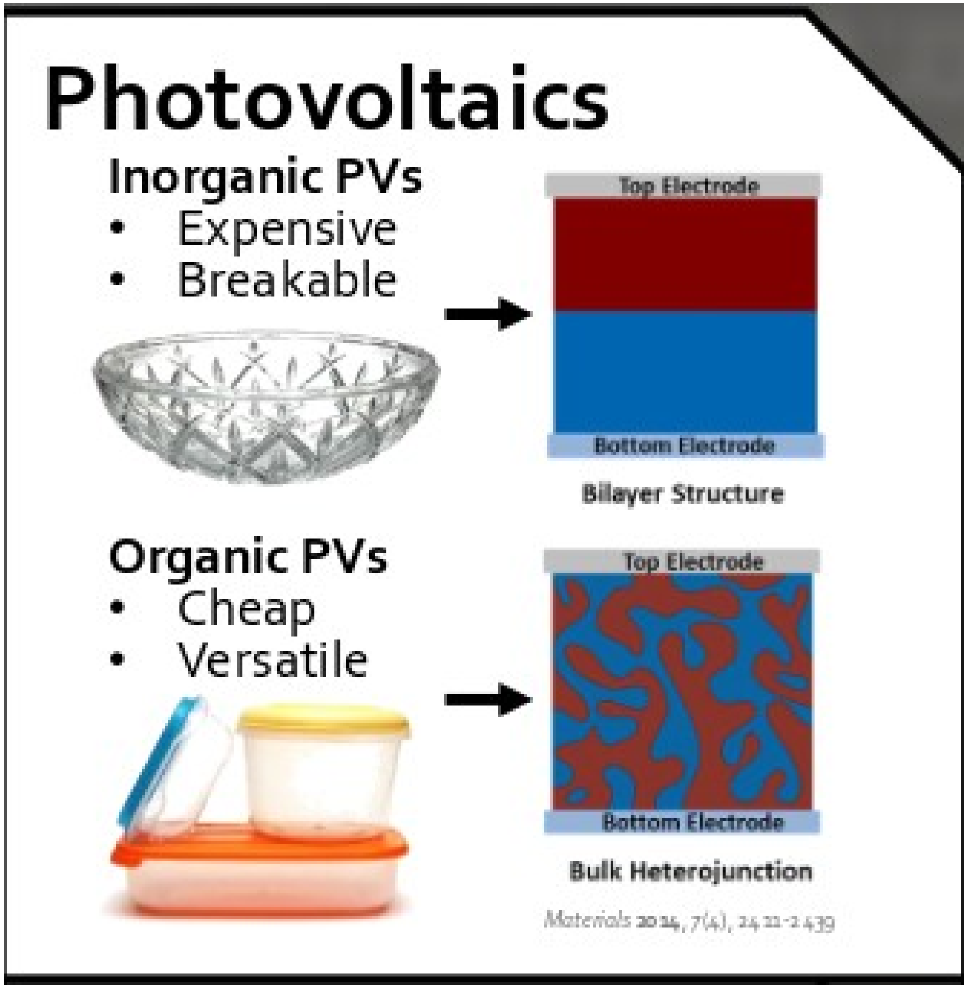
[Submitted on 29 Mar 2018 (v1), last revised 11 Aug 2020 (this version, v3)]

Effect of Varying the TD-lc-DFTB Range-Separation Parameter on Charge and Energy Transfer in a Model Pentacene/Buckminsterfullerene Heterojunction

Ala Aldin M. H. M. Darghouth, Mark E. Casida, Xi Zhu, Bhaarathi Natarajan, Haibin Su, Alexander Humeniuk, Evgenii Titov, Xincheng Miao, Roland Mitric

JCP, *submitted*

ELA*'S TUPPERWARE ANALOGY



Photovoltaics

Inorganic PVs
- Expensive
- Breakable

Top Electrode

Bottom Electrode

Bilayer Structure

Organic PVs
- Cheap
- Versatile

Top Electrode

Bottom Electrode

Bulk Heterojunction

Materials 2014, 7(4), 2411-2439

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* Gabriela Calinao Correa, NSF iREU student with us 17 May – 31 July 2016.

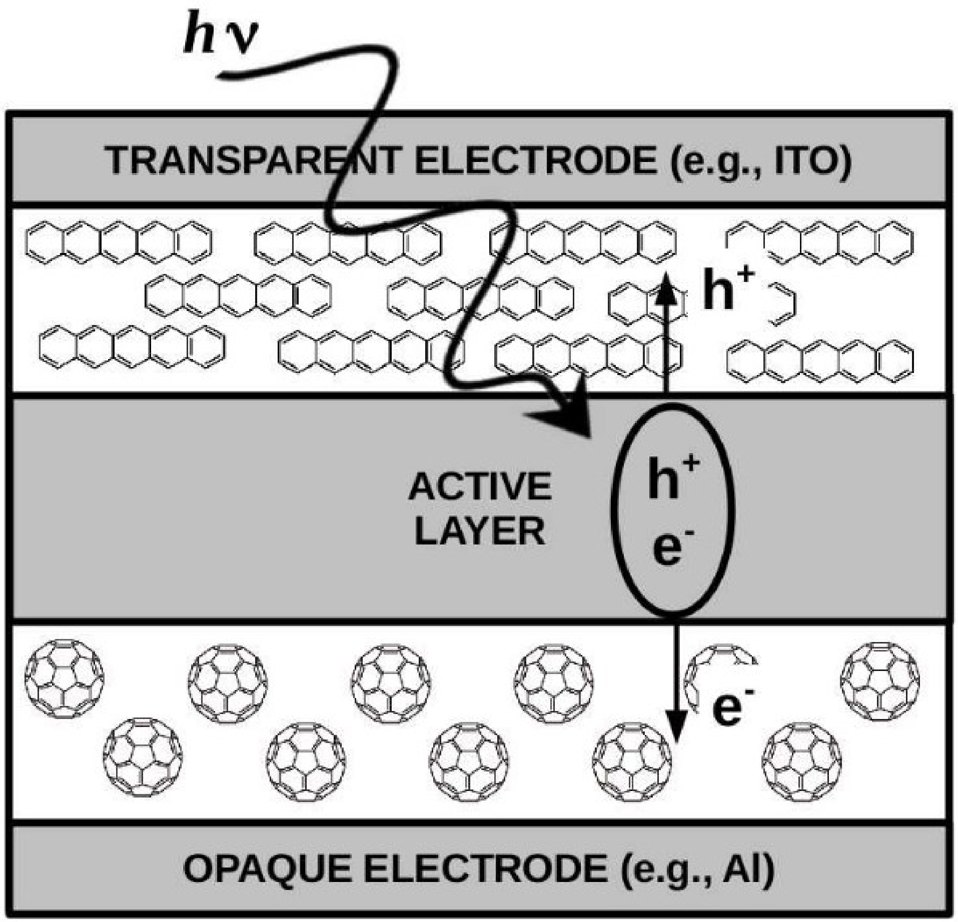
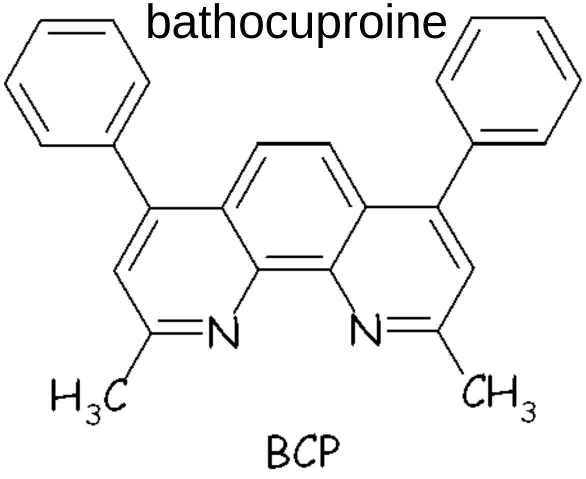


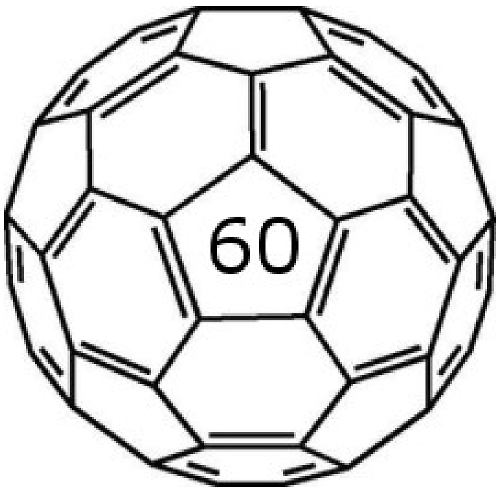
FIG. 2: Cartoon of an idealized Tang-type [25] **P**/**F** solar cell. ITO is a common abbreviation for indium titanium oxide, a transparent conducting oxide. (A realistic working **P**/**F** is described in Ref. [26].)

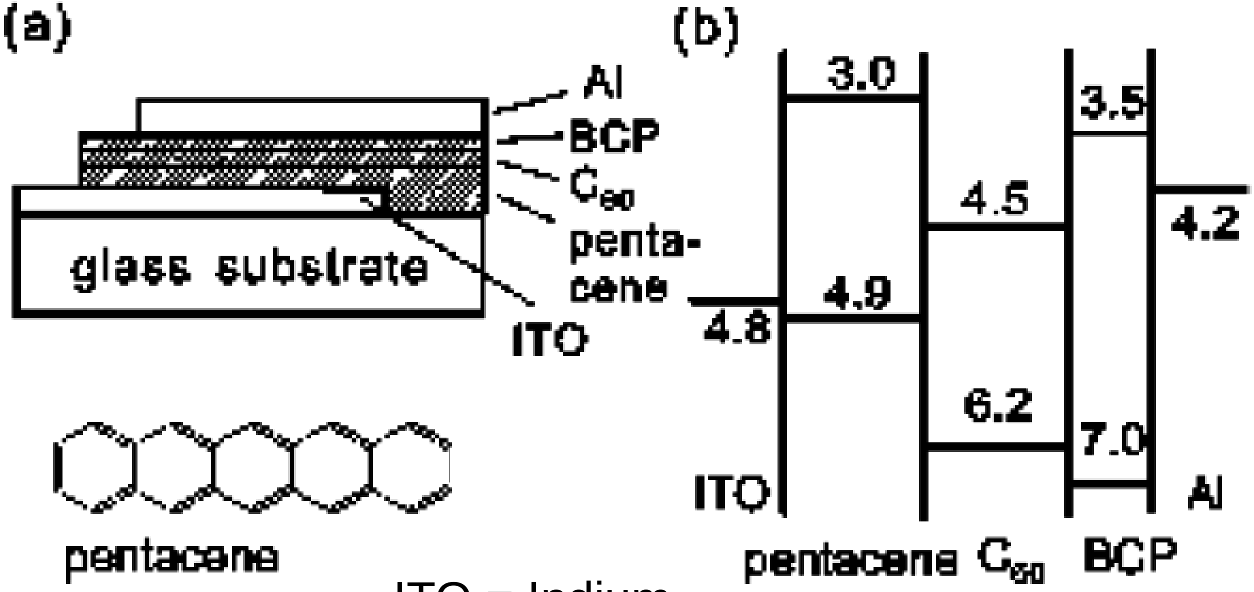
PENTACENE/C$_{60}$ TANG CELL (and spherical cow ☺)

As a first approximation, neglect nuclear motion and just think in terms of electrons.

bathocuproine







ITO = Indium Tin Oxide

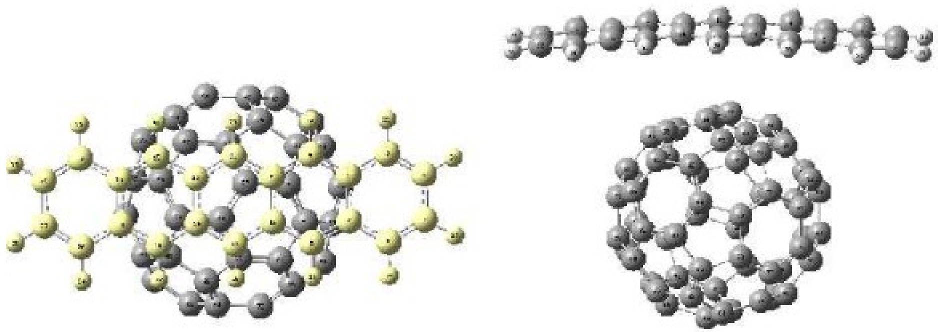
FIG. 1: A Tang-type[10] pentacene/C$_{60}$ solar cell as shown in Fig. 1 of Ref.[8].

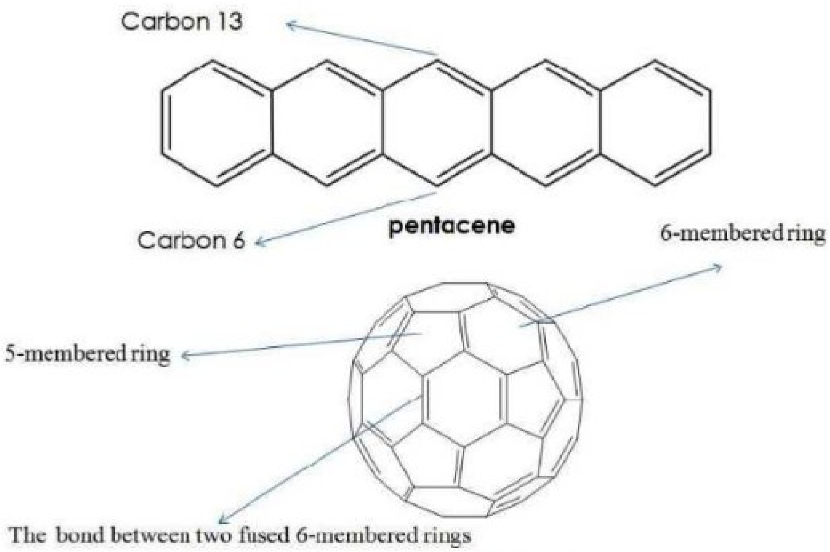
---

[10] C. W. Tang, *Appl. Phys. Lett.* **48** , 183 (1986), Twolayer organic photovoltaic cell .

[8] S. Yoo, B. Domercq, and B. Kippelen, *Appl. Phys. Lett*. **85** , 5427 (2004), Efficient thin-film organic solar cells based on pentacene/C$_{60}$ heterojunctions .

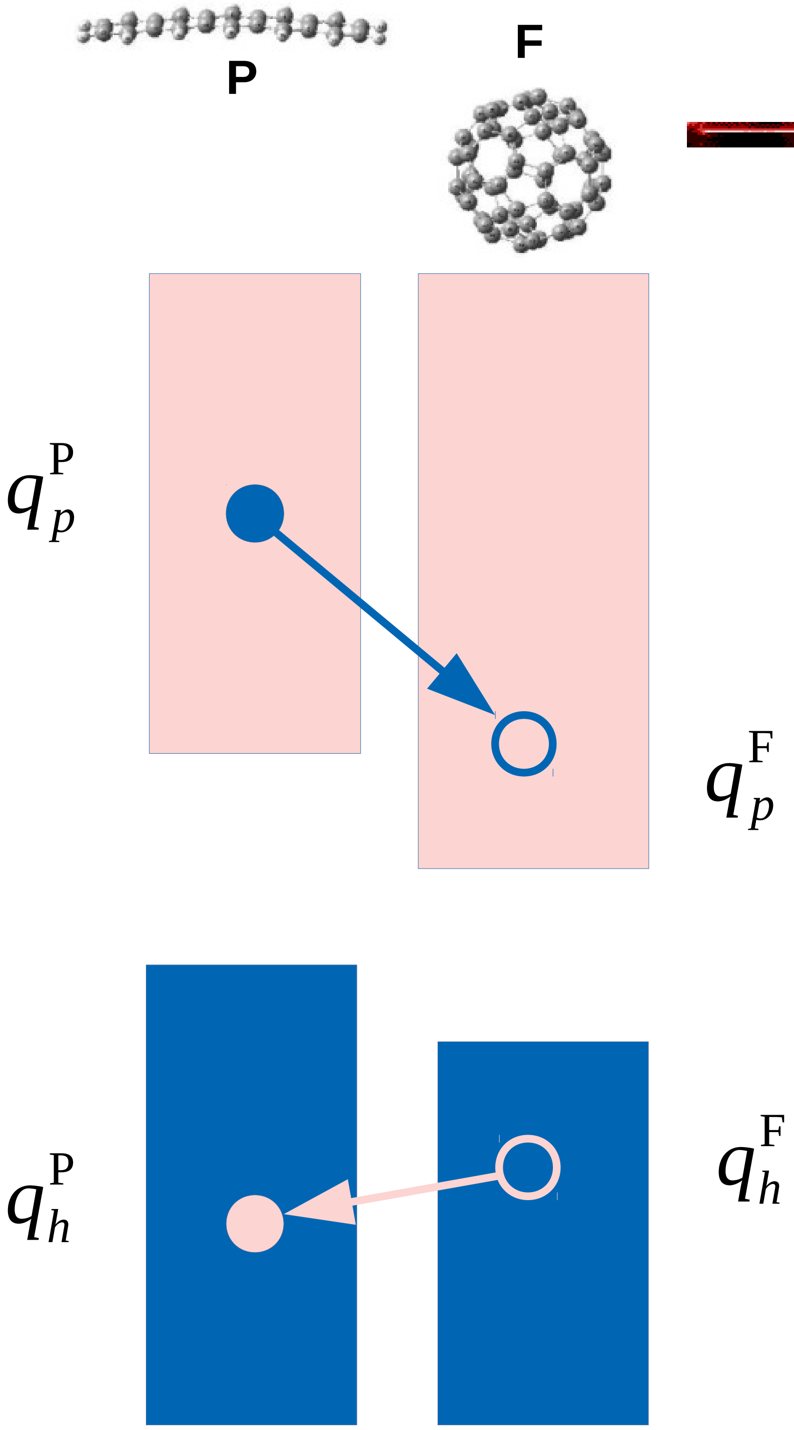
OUR SYSTEM





pentacene

Buckminsterfullerene
C_{60}



OUR OBSERVABLES

Charge transfer (CT) and energy transfer (ET) in terms of particles in the “conduction band” (i.e., empty orbitals) and holes in the “valence band”) (i.e., filled orbitals):

$$\mathrm{CT} = q_h^P - q_p^P = q_p^F - q_h^P$$

$$\mathrm{ET} = 1 - \left(q_p^P + q_h^P\right) = \left(q_h^F + q_p^F\right) - 1$$

This definition is not unique (e.g., Kasha’s exciton model.)

Now, run a swarm of about 100 trajectories and ensemble average!

THE IMPORTANCE OF THE DECOHERENCE CORRECTION

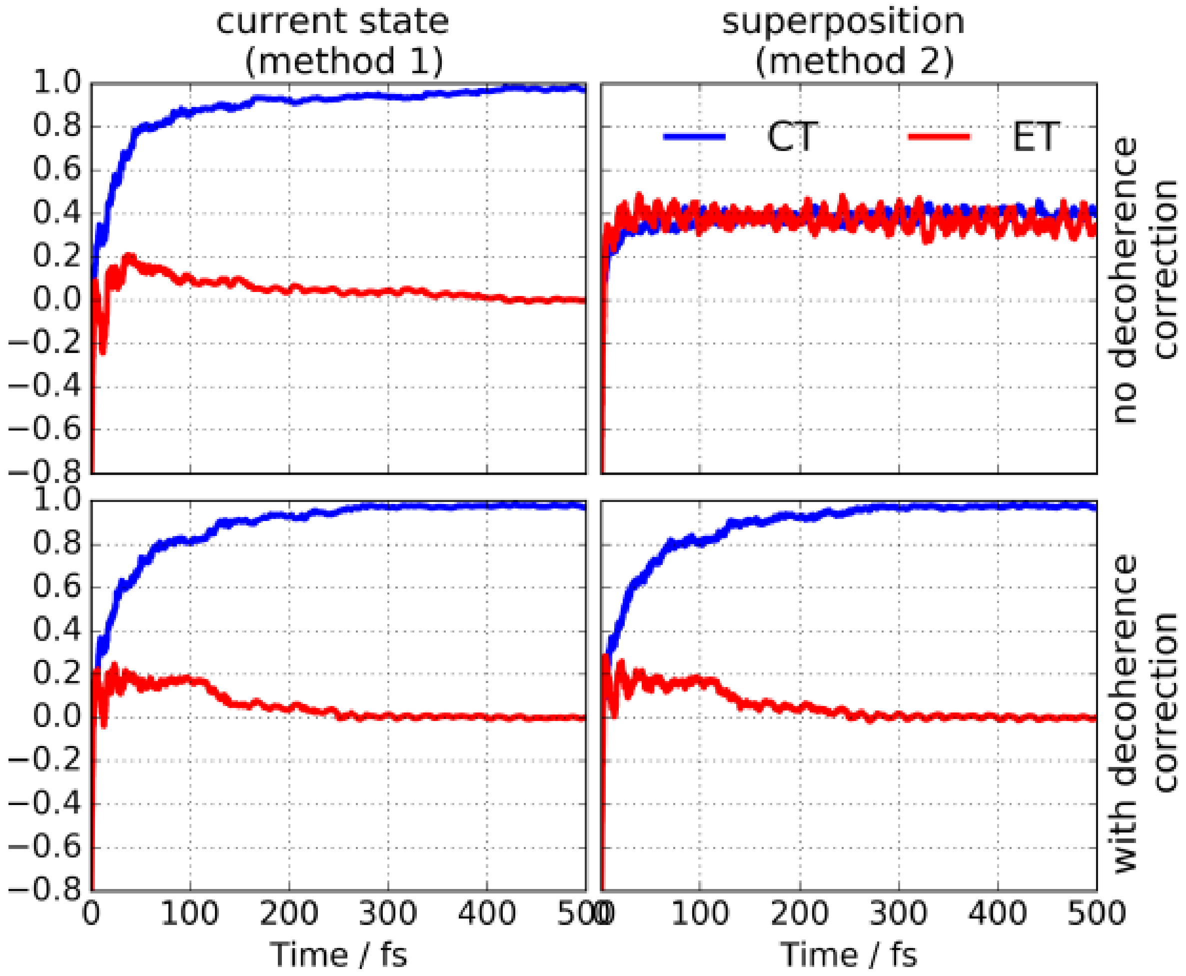
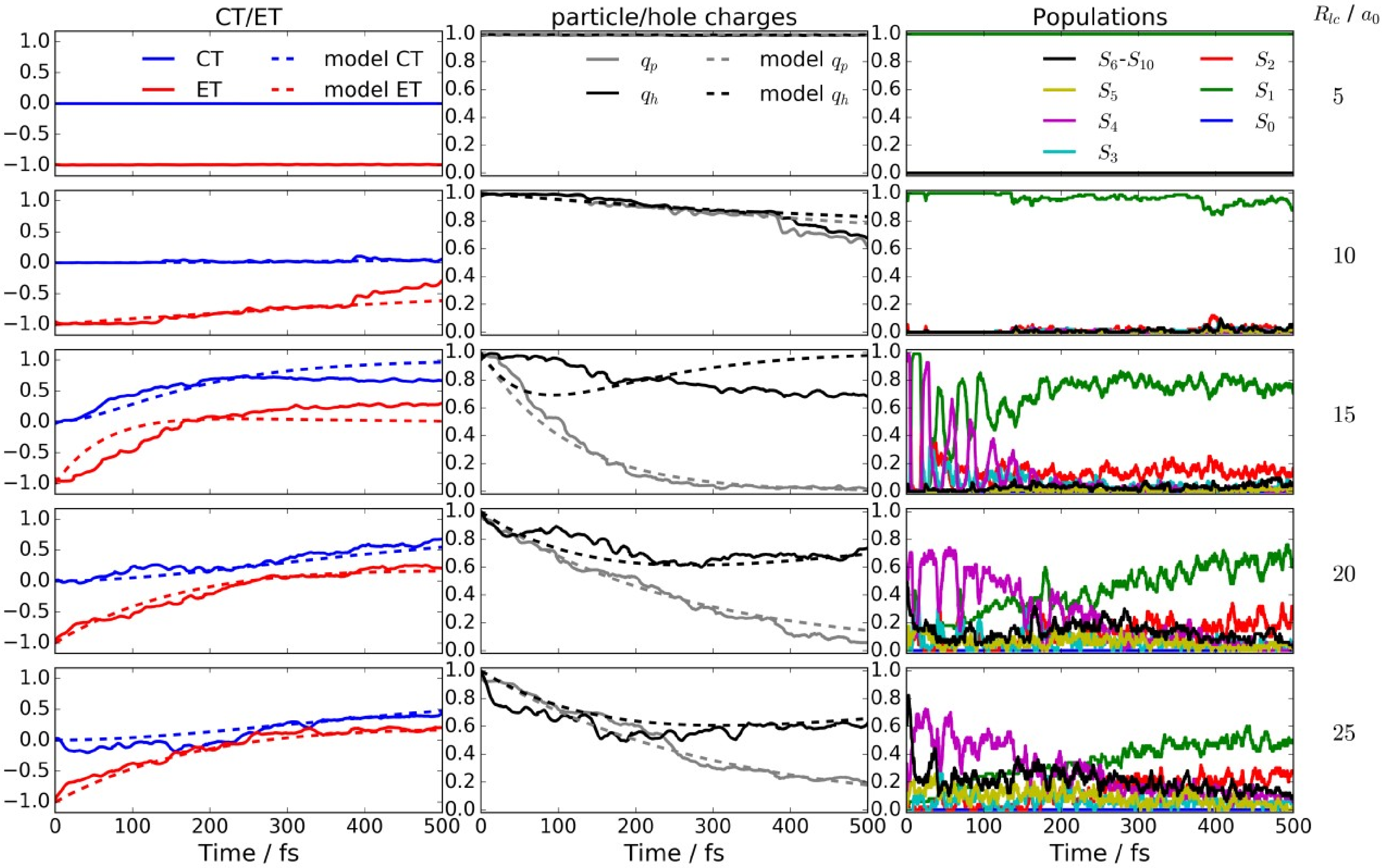
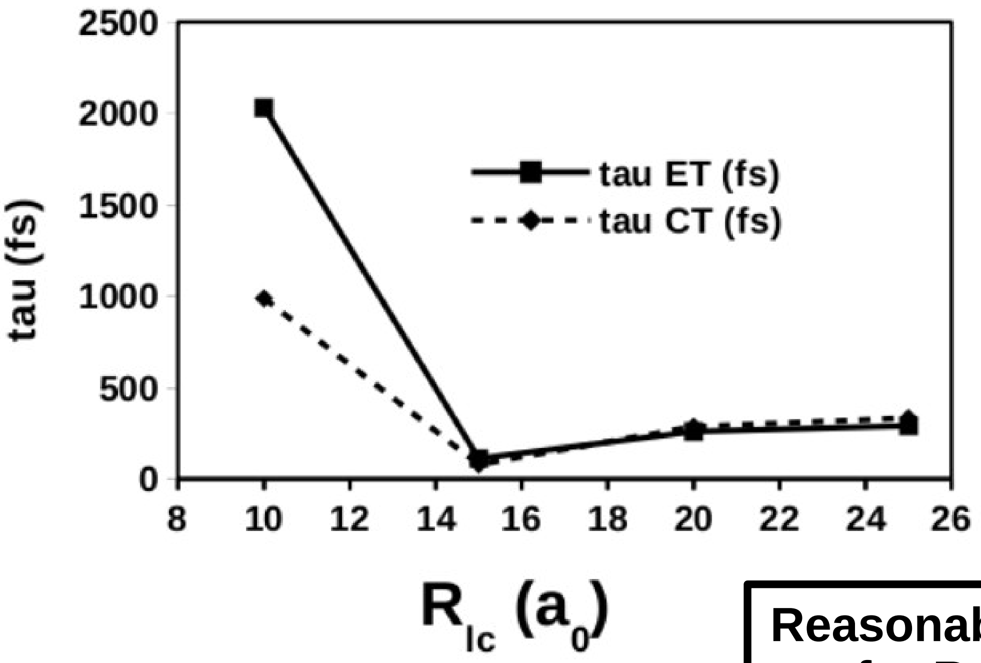


FIG. 5: CIS/AM1 FSSH calculations: “current state” is the same as the surface method; “superposition” is the same as the wavevector method.

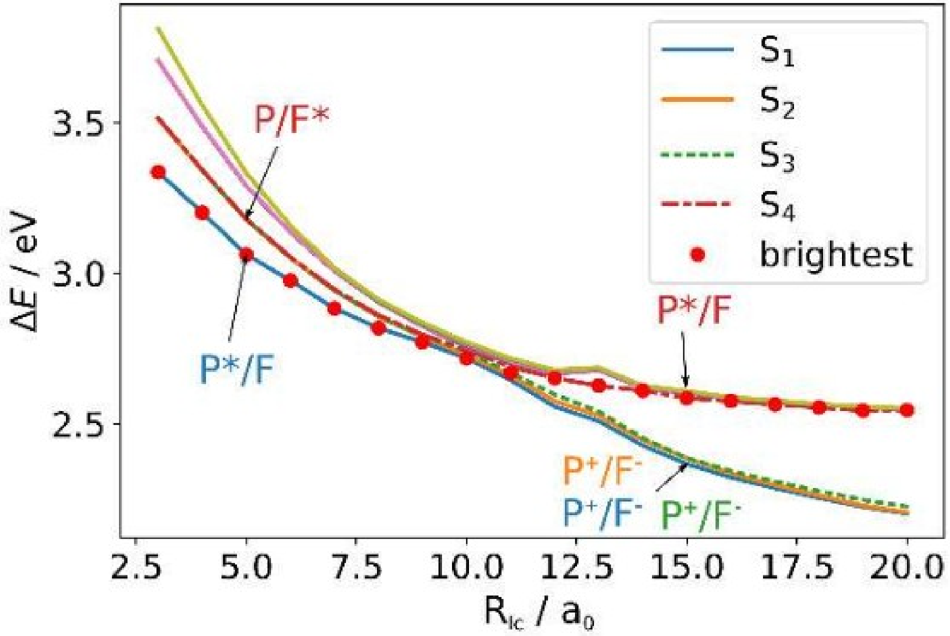
RESULTS AS A FUNCTION OF RANGE SEPARATION PARAMETER



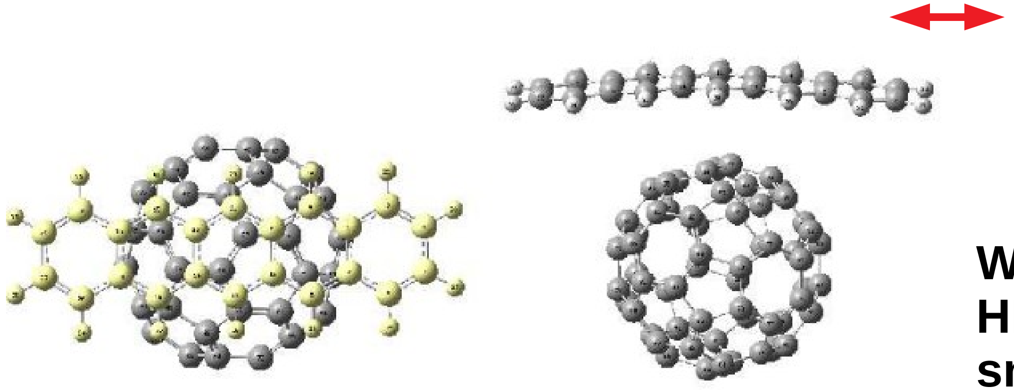
Donor/Acceptor	CT time	Reference
Experiment		
P3HT/PCBM	<100 fs^{a}	[34]
APFO3/PCBM	200 fs^{b}	[35]
MDMO-PPV/PC$_{70}$BM	$\leq$ 100 fs^{c}	[36]
PCPDTBT/PC$_{70}$BM	$\leq$ 100 fs^{c}	[36]
p-DTS(FBTTh$_2$)$_2$/PC$_{71}$BM	82 fs	[31]
P/**F**	110 fs^{d}	[37]
Theory		
4T/**F**	97 fs^{e}	[30]
P/**F**	100 fs^{f}	[38]
P/**F**	714 fs^{g}	[39]
P/**F**	40 fs^{h}	[29]
P/**F**	164 fs^{i}	PW
P/**F**	~300 fs^{j}	PW



Reasonable ET and CT are for R_{lc} > 10 a_0 .

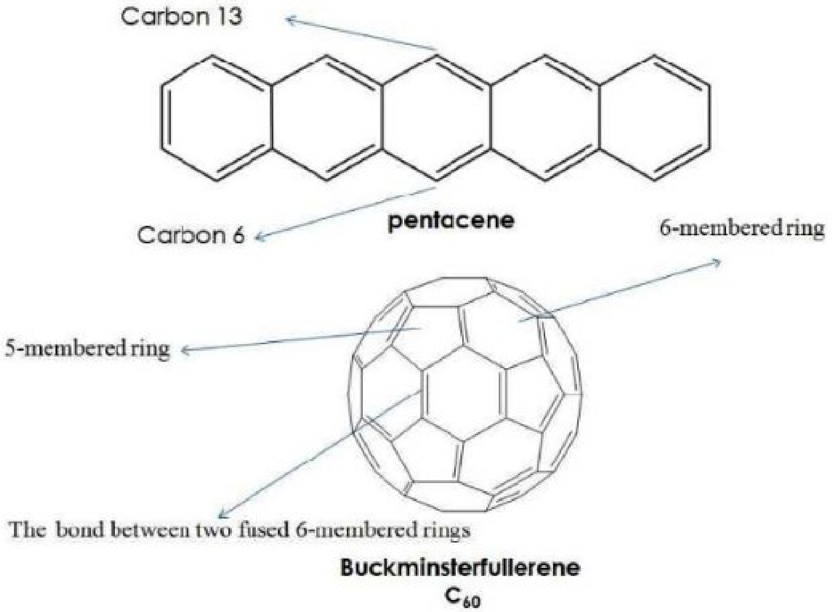


OUR SYSTEM



$$R_{lc} \approx 10\, a_0$$

We should not add HF exchange for smaller distances *in this model*.



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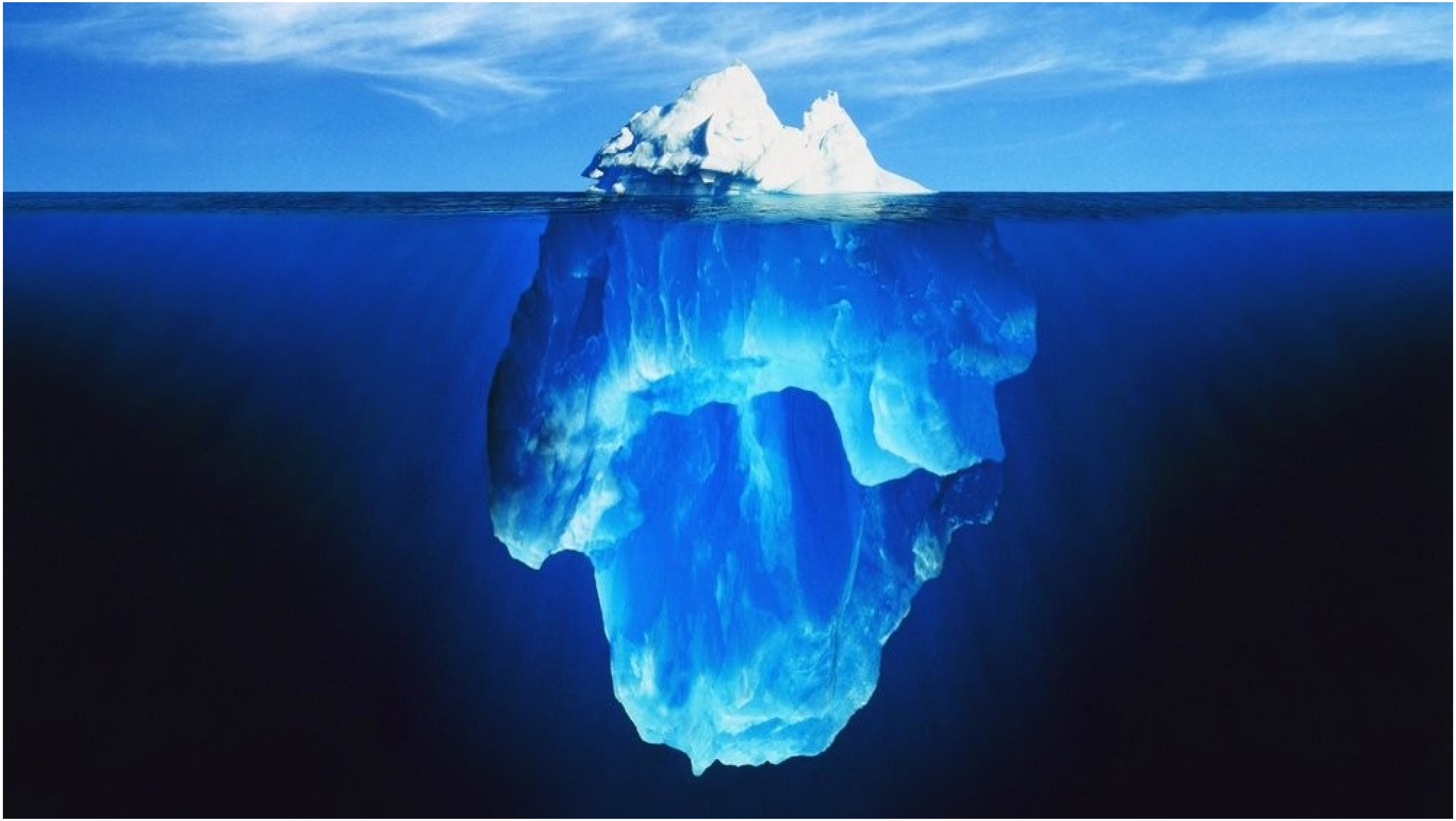
JUST A GLIMPSE … … OF THE TIP OF THE ICEBERG



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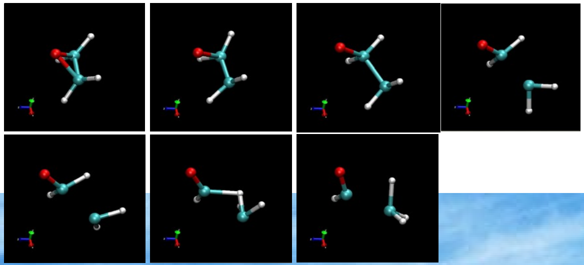
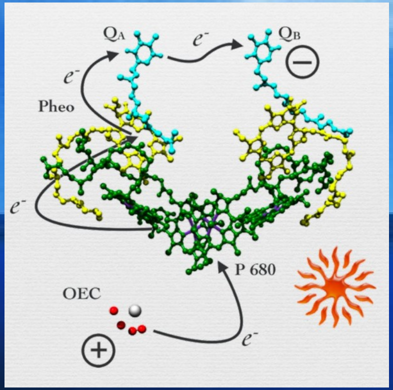
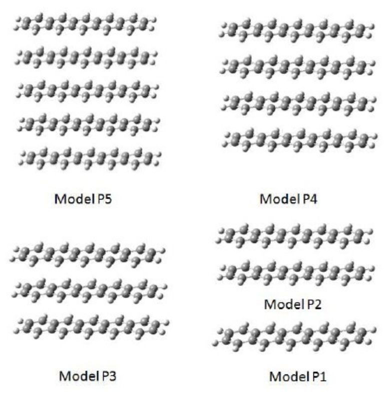






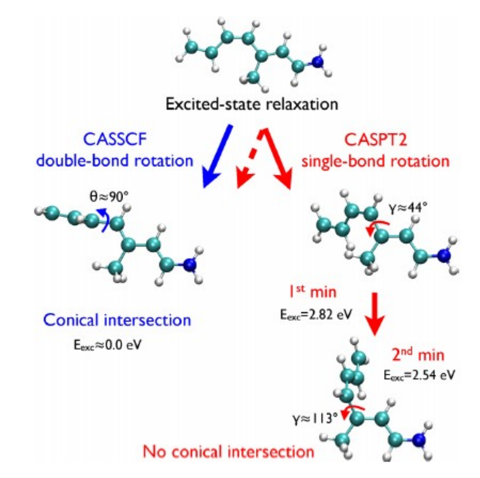
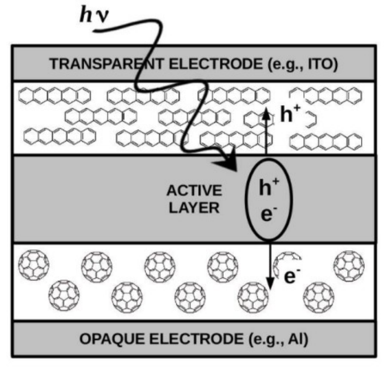


FIG. 1. The excited-state out-of-plane minima obtained with CASSCF and CASPT2. The solid arrows indicate MEPs while the dashed (red) arrow indicates the presence of a transition state on the S_1 surface.



SPECIAL THANKS TO **You !**

and to the organizers !!

https://www.charmingitaly.com/different-types-of-italian-coffee/