Modeling Photo-induced dynamical processes in massive parallel architectures

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OUTLINE

Introduction: framing the problem

“theoretical synchrotron: ETSF”

“Modeling new materials properties”

Theoretical background:

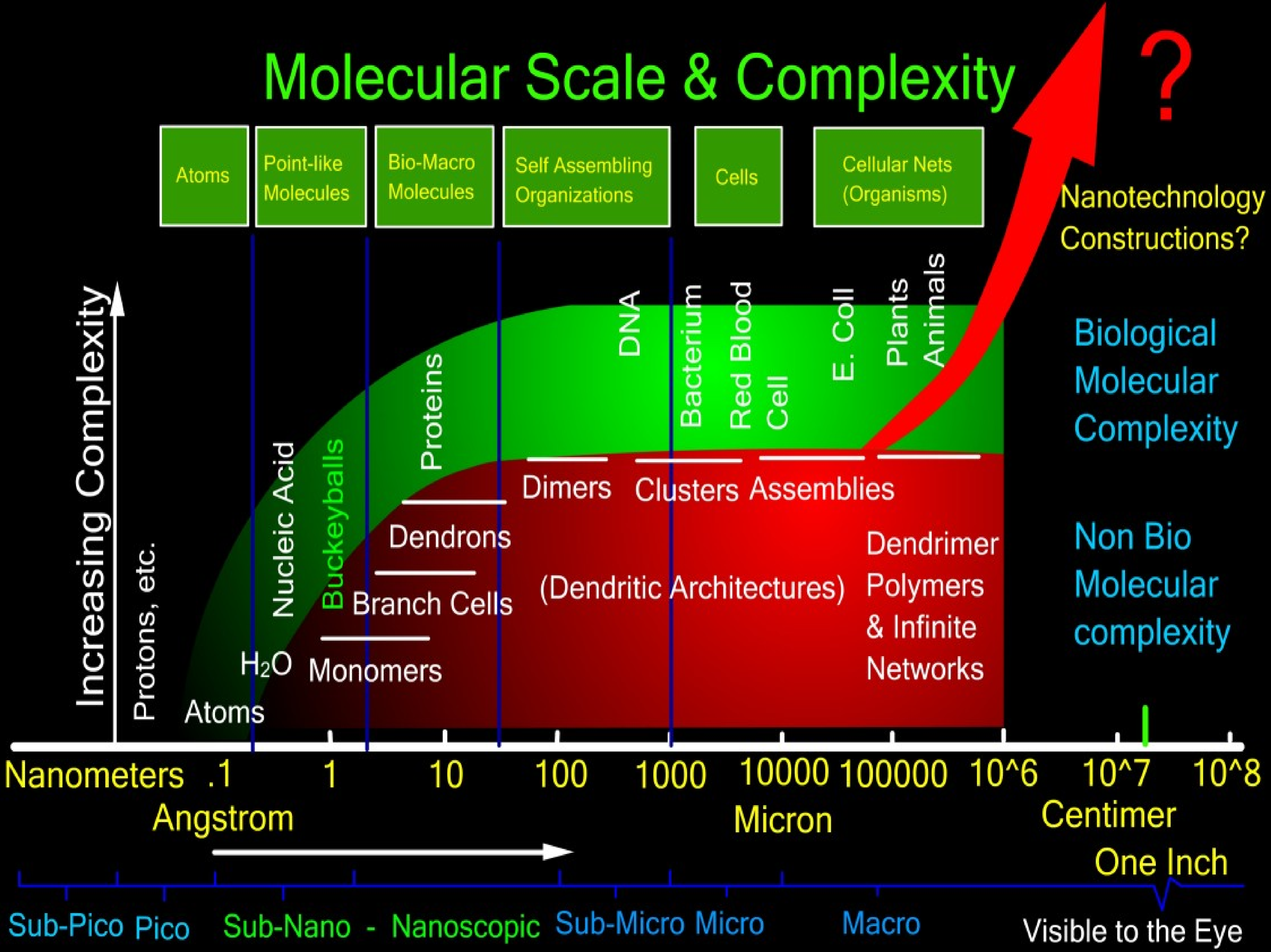
Some Applications:

* (excite state dynamics and energy store/harvesting)
* photo-excitation light-harvesting carotenoid-porphyrin-C60
* Chlorophylls: photosynthesis

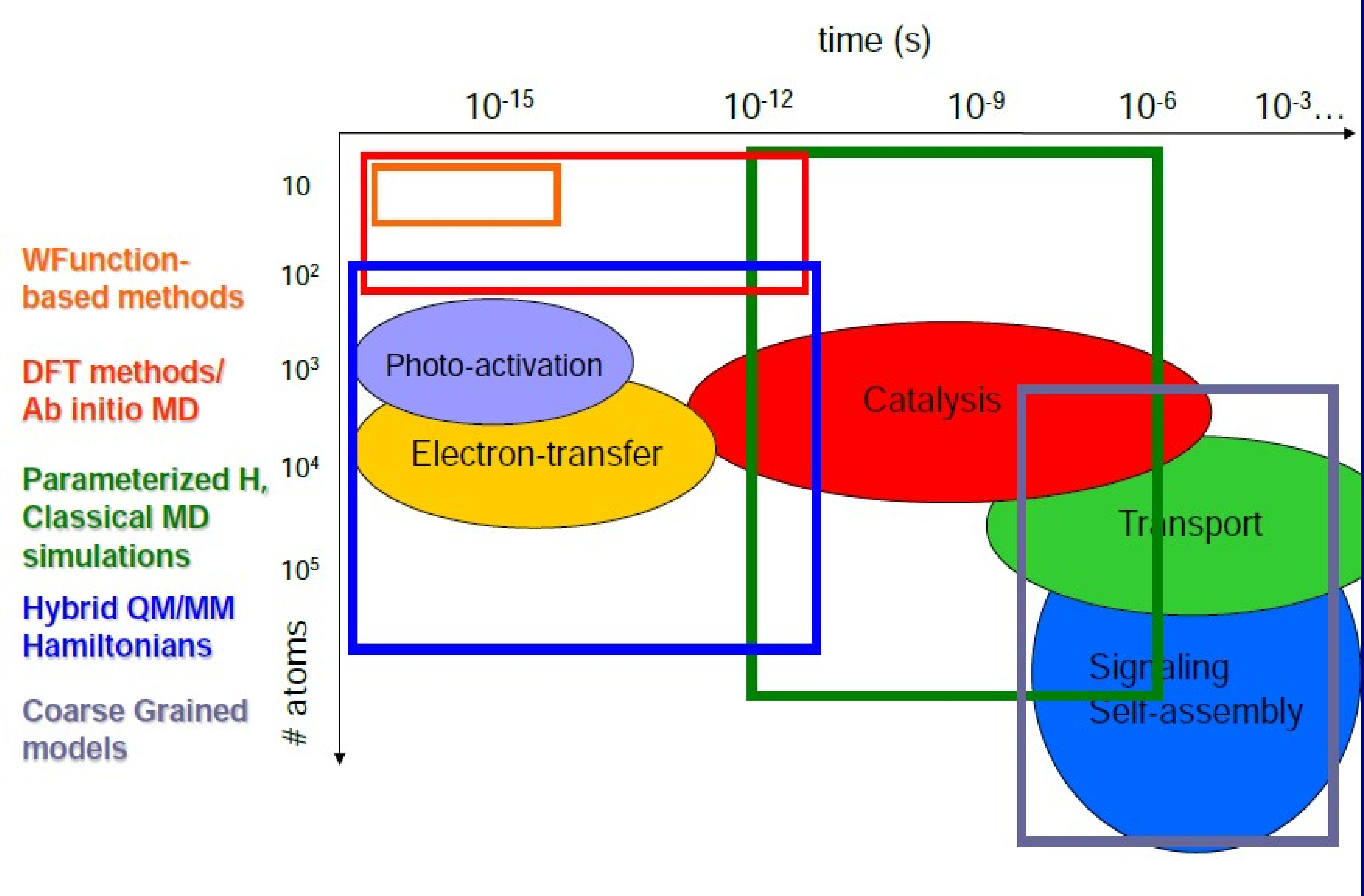
* Optimal control of bond-breaking and
high harmonic generation

Conclusions

Molecular Scale & Complexity

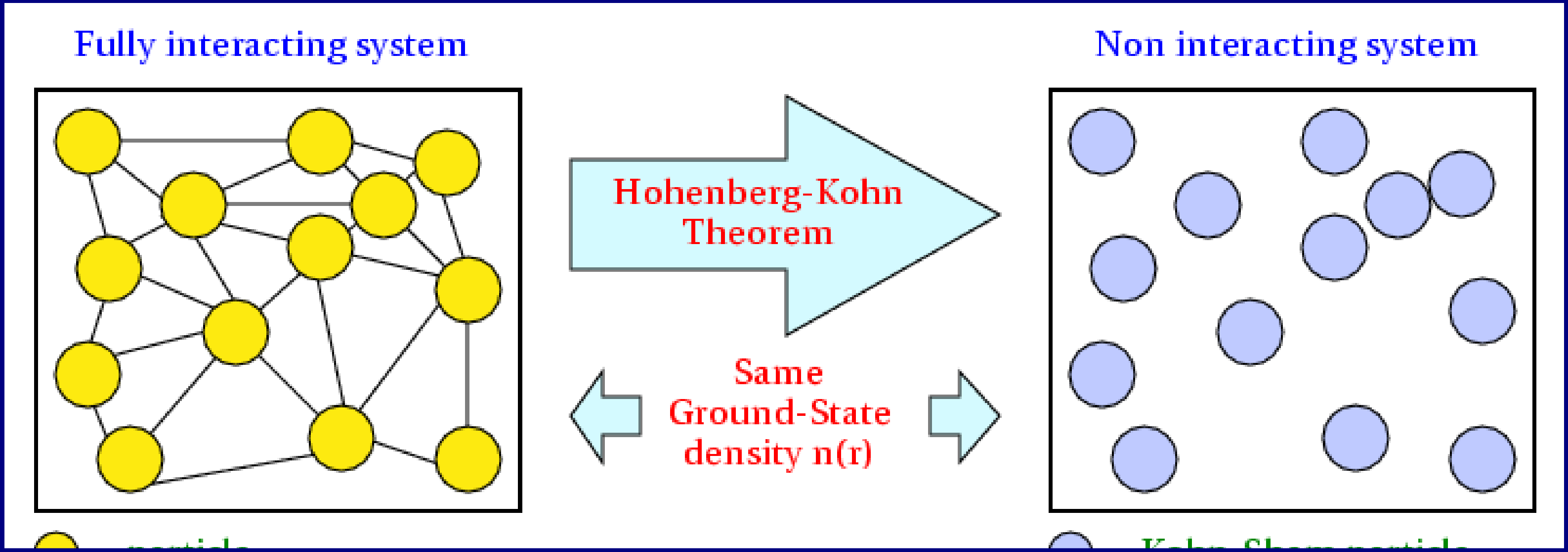


Time and size scales



Theoretical Framework

Density Functional versus Many-body perturbation theory



ground state

What about excited-state properties: electron-ion dynamics, spectroscopies

DFT Success “~chemical accuracy”

EXACT ALTERNATIVE:
Time Dependent Density Functional Theory

All observables are functionals of the TD density

One-to-one correspondence between the time-dependent density and the external potential, v(r,t) <------> ρ(r,t)

$$i\hbar\frac{d}{dt}\Phi=H\Phi \quad \rightarrow \quad i\hbar\frac{d}{dt}\psi_i=H_{KS}\left[\left\{\psi_j\right\}\right]\psi_i, \quad i=1,\cdots N$$

?

$$H_{KS}=\frac{\hbar^2}{2m}\left(i\nabla-\frac{e}{c\hbar}\left(A+A_{xc}\right)\right)^2+V_{external}+V_{hartree}+V_{exchange}+V_{correlation}$$

Linear and non linear phenomena accessible

Octopus Code http://www.tddft.org

Time-Dependent Density Functional Theory, Lecture Notes in Physics, Vol. 706 (Springer, Berlin, 2006)

Universidad del País Vasco Euskal Herriko Unibertsitatea CSIC

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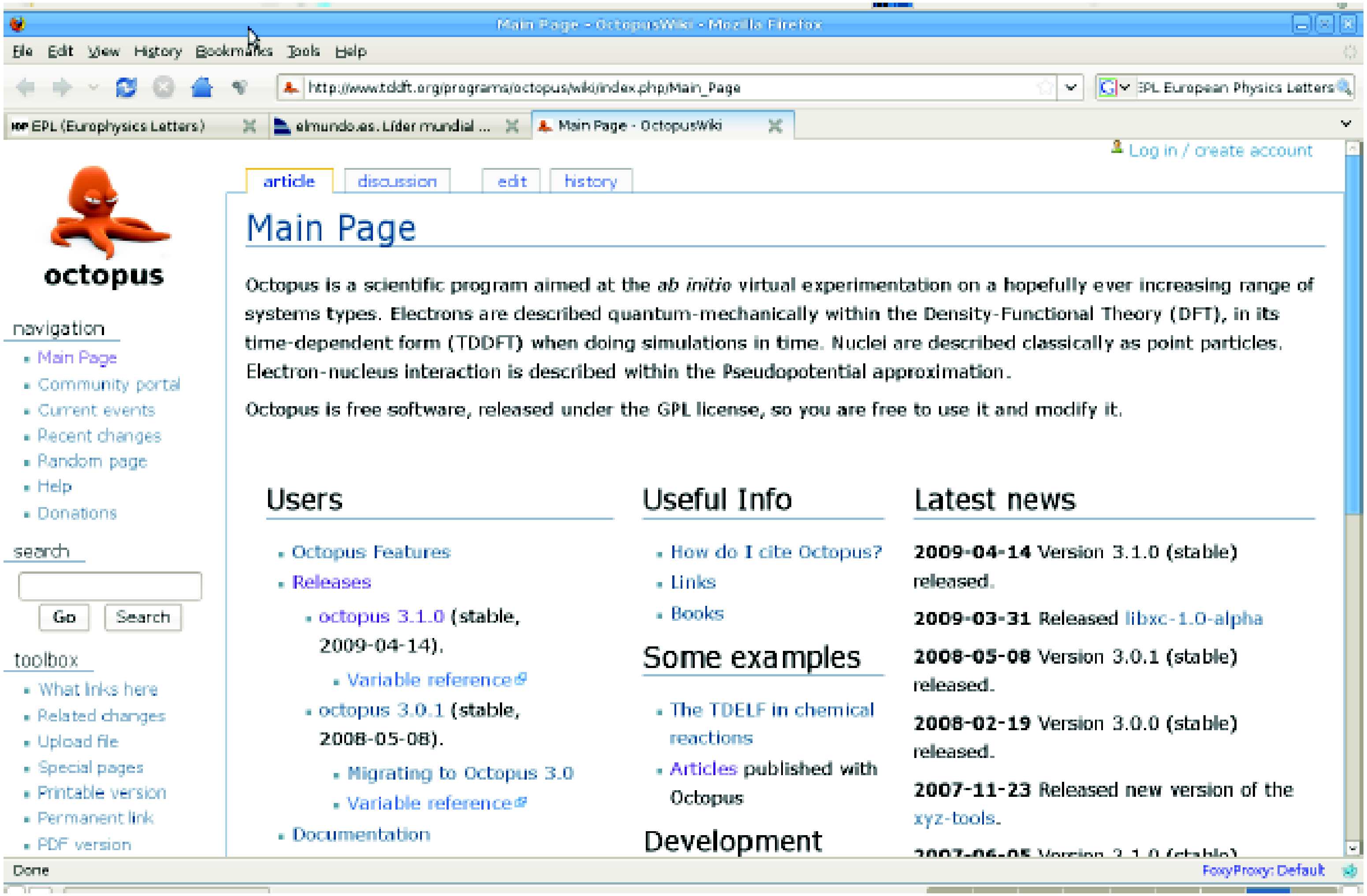
ImagineNano, HPC 2011 (High Performance Computing), Bilbao Exhibition Centre, 14-April 2011

ETSF European Theoretical Spectroscopy Facility

octopus



Main Page

Octopus is a scientific program aimed at the *ab initio* virtual experimentation on a hopefully ever increasing range of systems types. Electrons are described quantum-mechanically within the Density-Functional Theory (DFT), in its time-dependent form (TDDFT) when doing simulations in time. Nuclei are described classically as point particles. Electron-nucleus interaction is described within the Pseudopotential approximation.

Octopus is free software, released under the GPL license, so you are free to use it and modify it.

Users

- Octopus Features
- Releases
  - octopus 3.1.0 (stable, 2009-04-14).
    - Variable reference
  - octopus 3.0.1 (stable, 2008-05-08).
    - Migrating to Octopus 3.0
    - Variable reference
- Documentation

Useful Info

- How do I cite Octopus?
- Links
- Books

Some examples

- The TDELF in chemical reactions
- Articles published with Octopus

Development

Latest news

2009-04-14 Version 3.1.0 (stable) released.

2009-03-31 Released libxc-1.0-alpha

2008-05-08 Version 3.0.1 (stable) released.

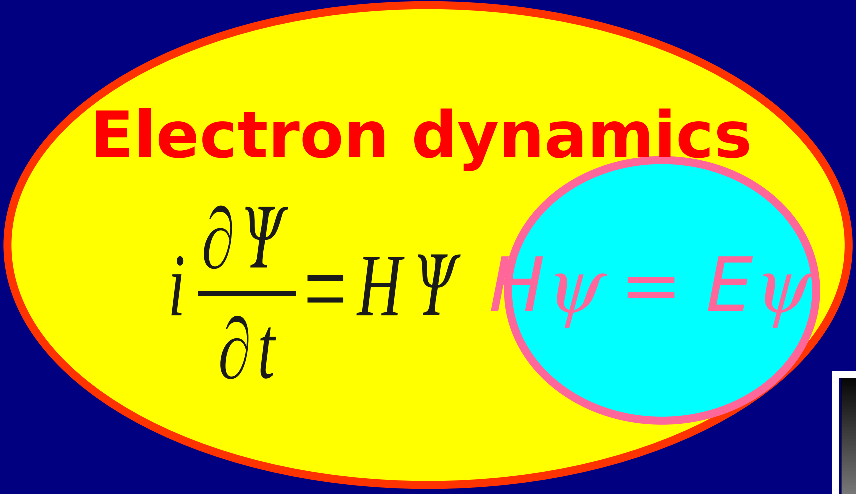
2008-02-19 Version 3.0.0 (stable) released.

2007-11-23 Released new version of the xyz-tools.

2007-06-05 Version 3.1.0 (stable)

http://www.tddft.org/programs/octopus/

Ehrenfest's dynamics (non-adiabatic)

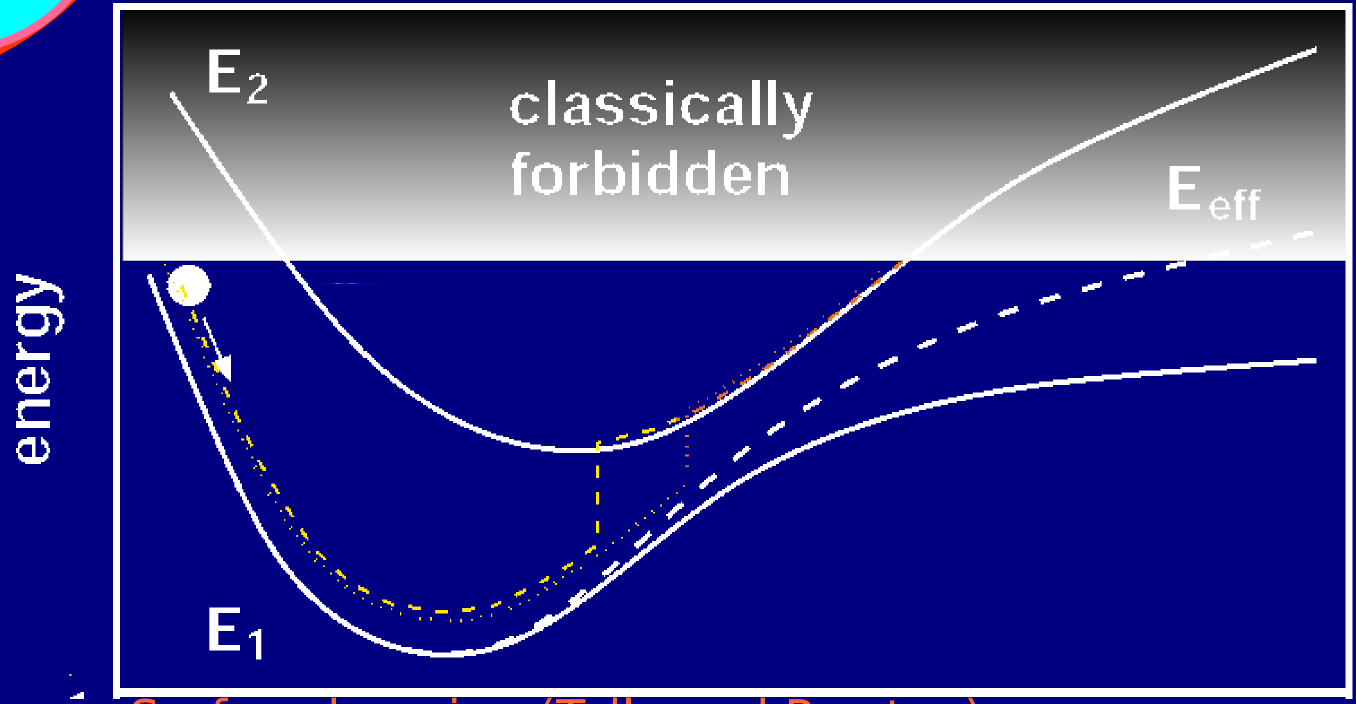


Electron dynamics

$$i\frac{\partial \Psi}{\partial t} = H\Psi \qquad H\psi = E\psi$$

MD $F = m\alpha$

Multicomponent (TD)DFT: work in progress, way to describe the non-adiabatic processes



Surface hopping (Tully and Preston)

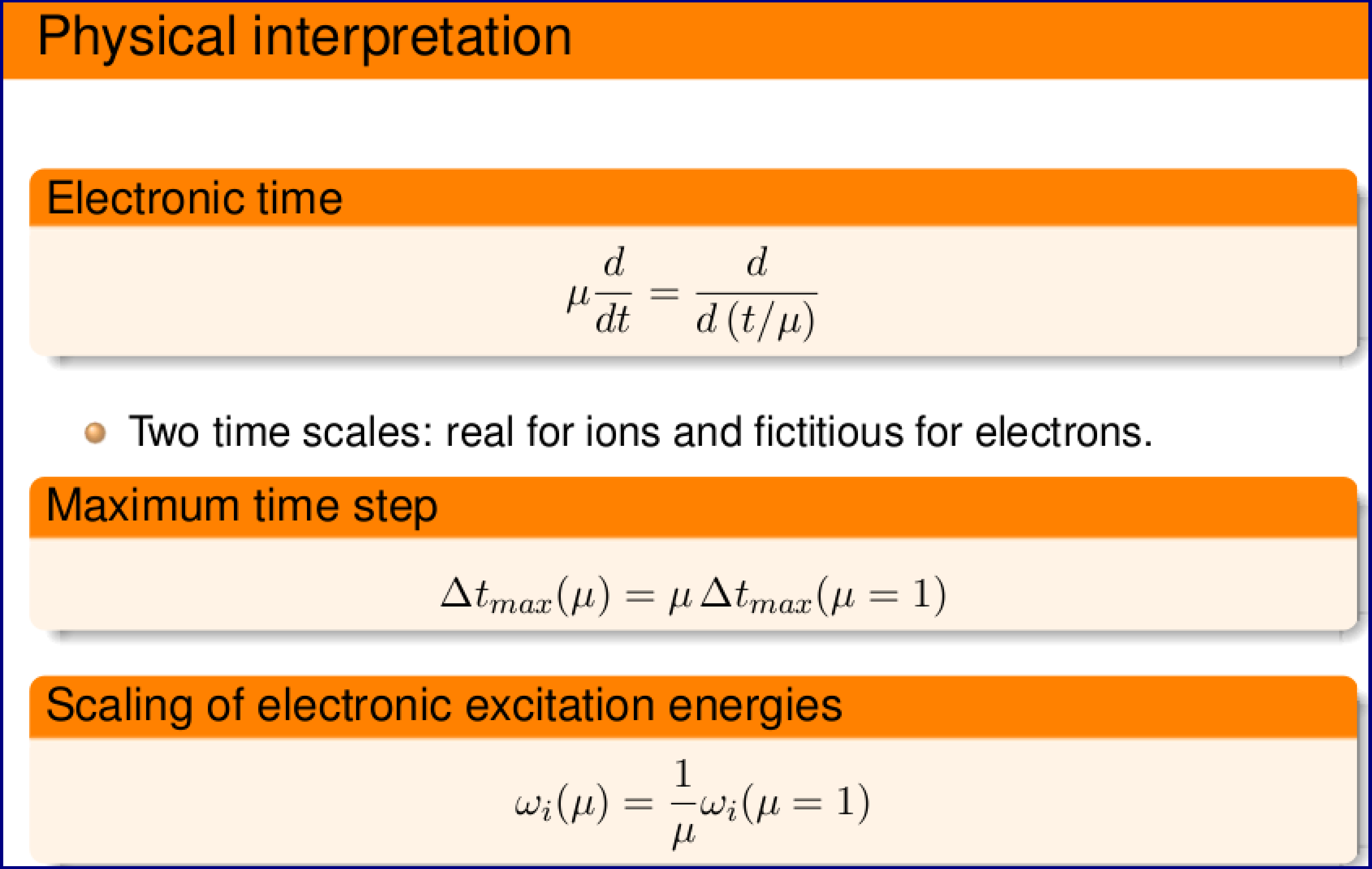
See review by N.L Doltsinis and D. Marx, J.Theo.Comp.Chem 1, 319 (2002)
and the book on TDDFT Springer Lecture Notes in Physics Vol 706 (2006)

TDDFT formulation for BO-MD dynamics: fictitious dynamics as in Car-Parrinello dynamics

The equation of motion without external field for simplicity

$$i\mu \frac{\partial}{\partial t}\psi_i = \left[\frac{-\hbar^2}{2\mathrm{m}}\nabla^2 + V_{ion} + V_H + V_{xc}\right]\psi_i \qquad M_I \ddot{R}_I = -\nabla_I E[\psi, R]$$

J.L. Alonso, X. Andrade, P. Echenique, F. Falceto, D. Prada, AR PRL (2008), JCTC (2009), NJP (2010)



Physical interpretation

Electronic time

$$\mu \frac{d}{dt} = \frac{d}{d\left(t/\mu\right)}$$

- Two time scales: real for ions and fictitious for electrons.

Maximum time step

$$\Delta t_{max}(\mu) = \mu\, \Delta t_{max}(\mu = 1)$$

Scaling of electronic excitation energies

$$\omega_i(\mu) = \frac{1}{\mu}\omega_i(\mu = 1)$$

TDDFT Lagrangian formulation for BO-MD dynamics: fictitious dynamics: performance

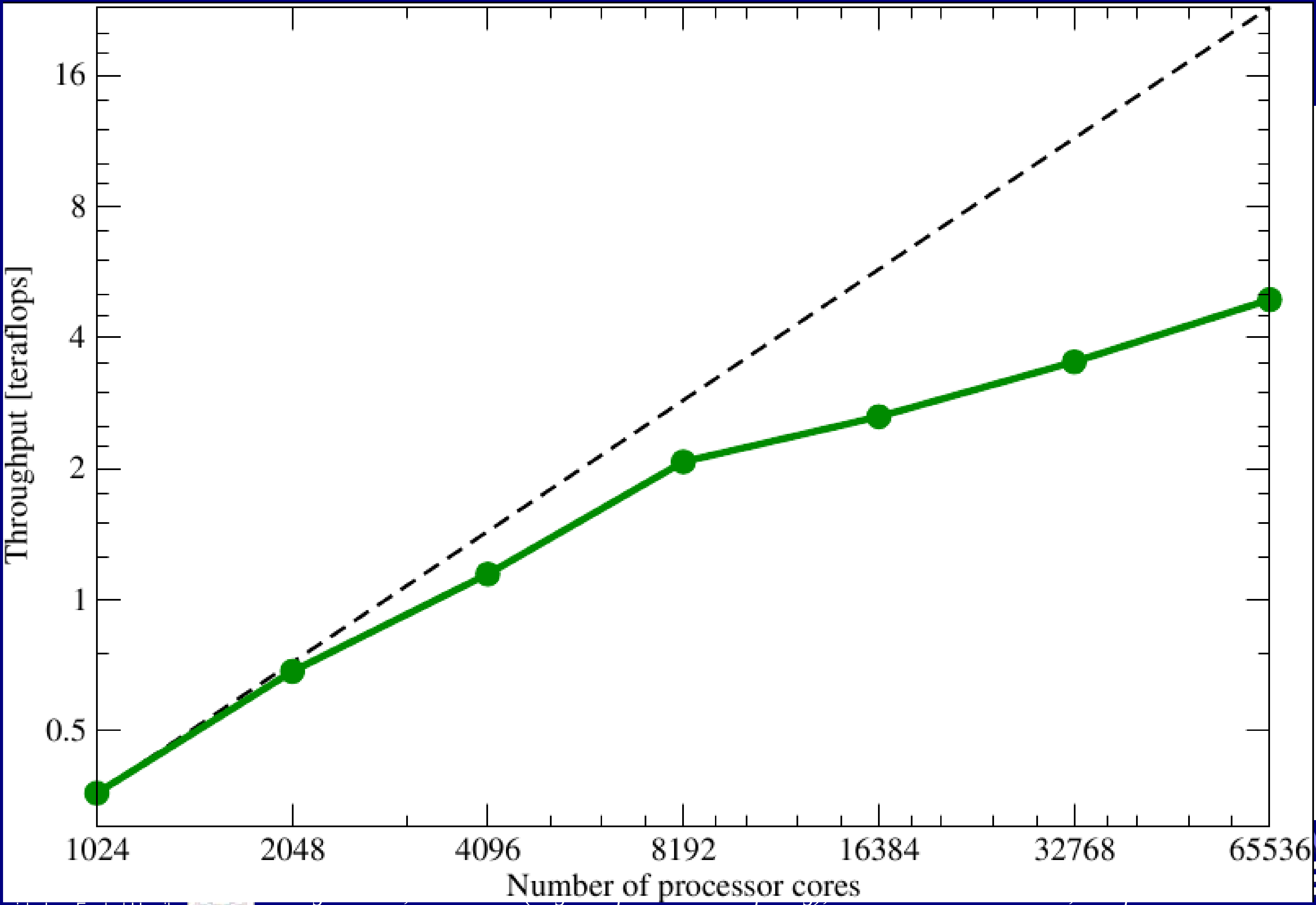


Illustration: Some applications

Optical properties of nanostructures and biomolecules (excite state dynamics and energy store/harvesting)

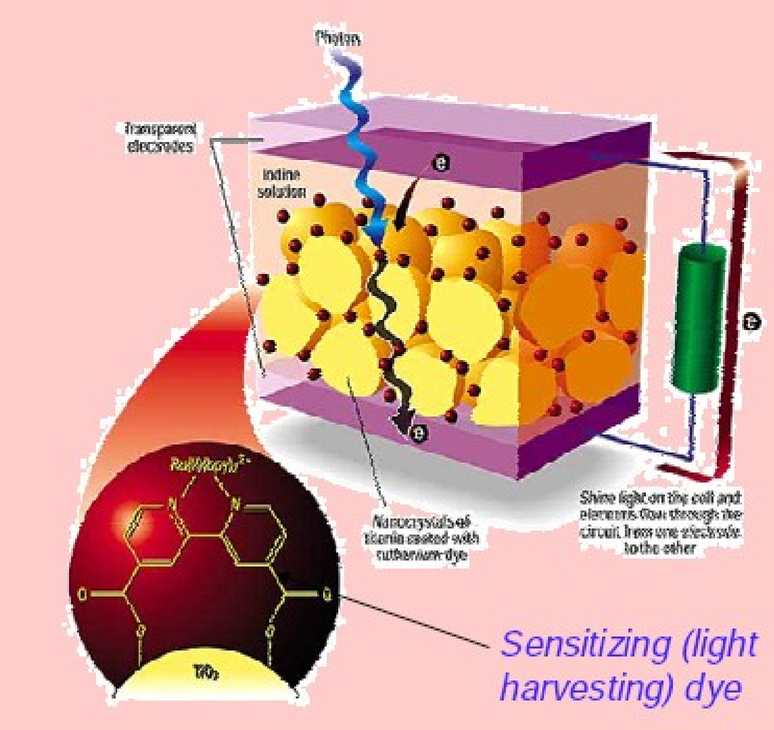
Molecular level alignment

Optimal control theory: High-harmonic generation

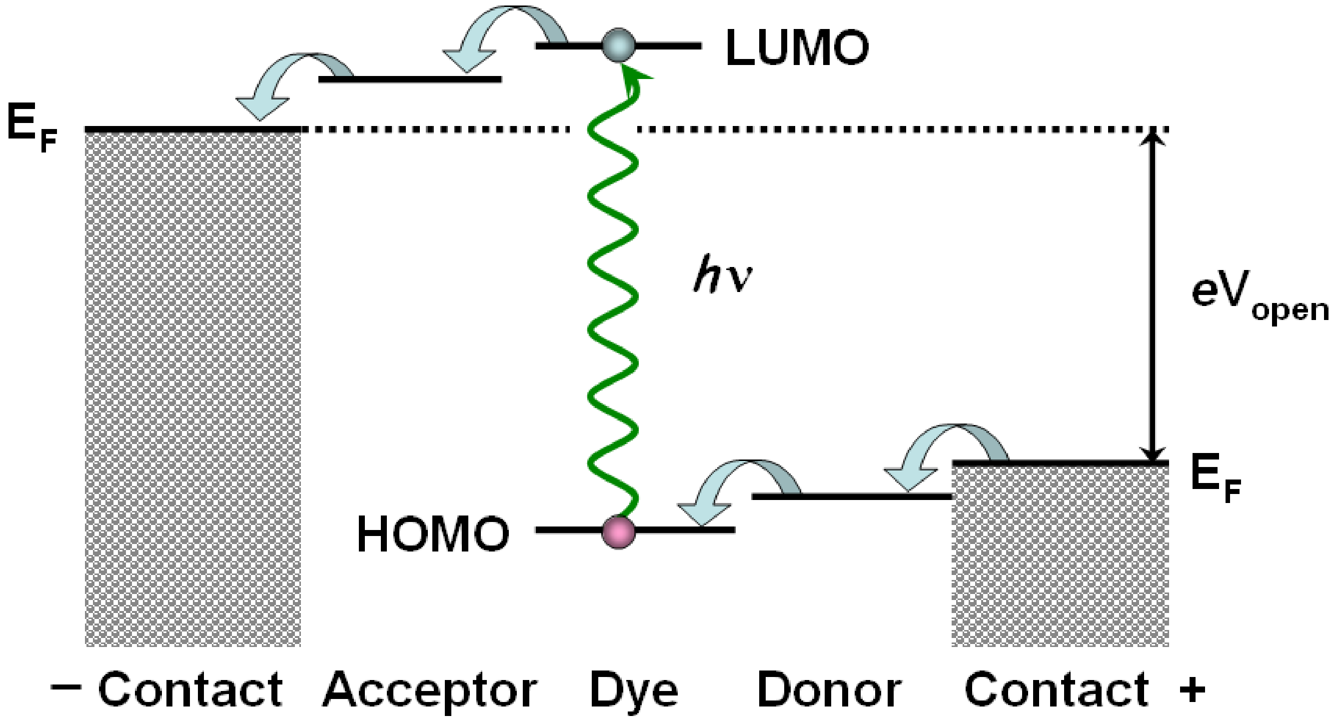
Nanosolvation????

Charge Transfer excitations

Photovoltaic Hybrids: Grätzell cells

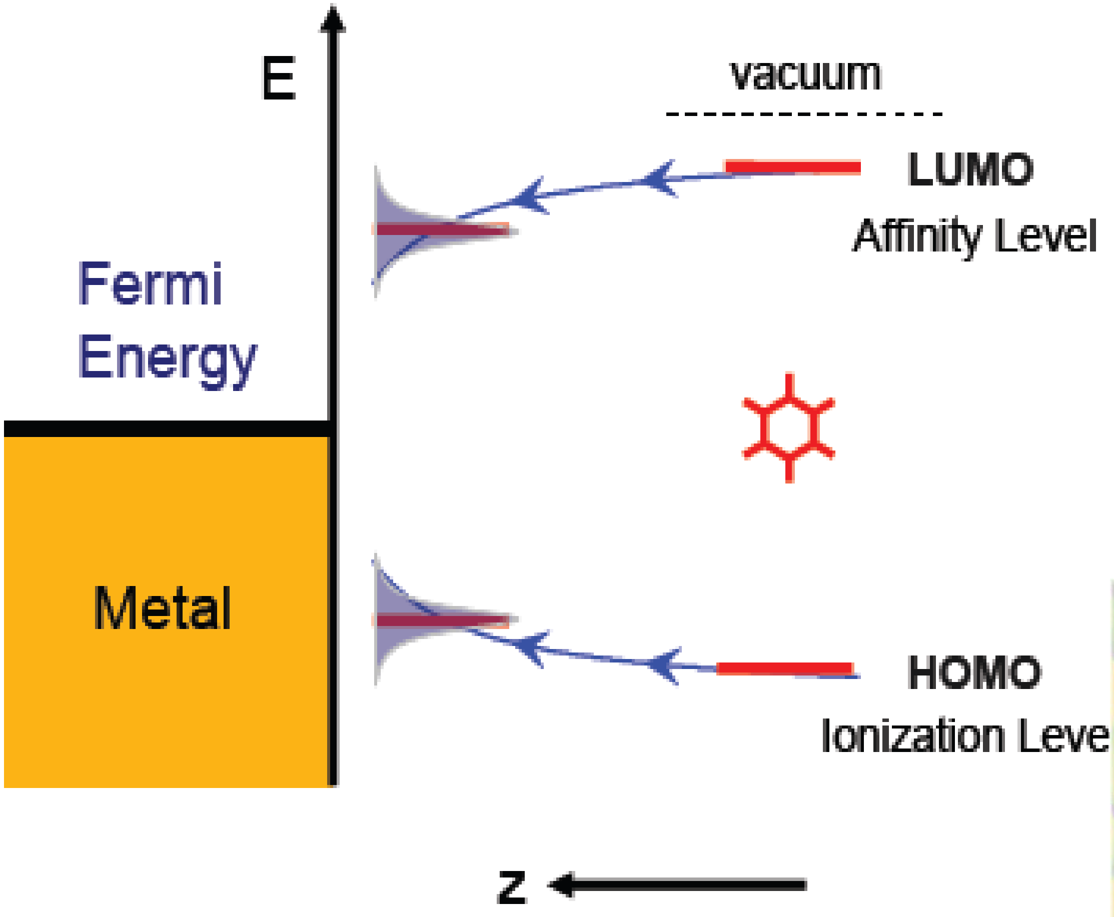


Sensitizing (light harvesting) dye

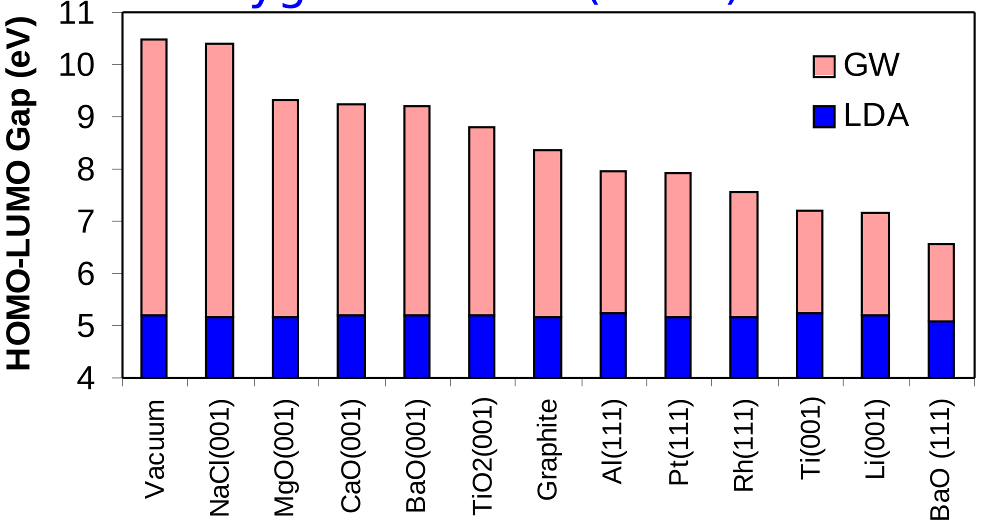


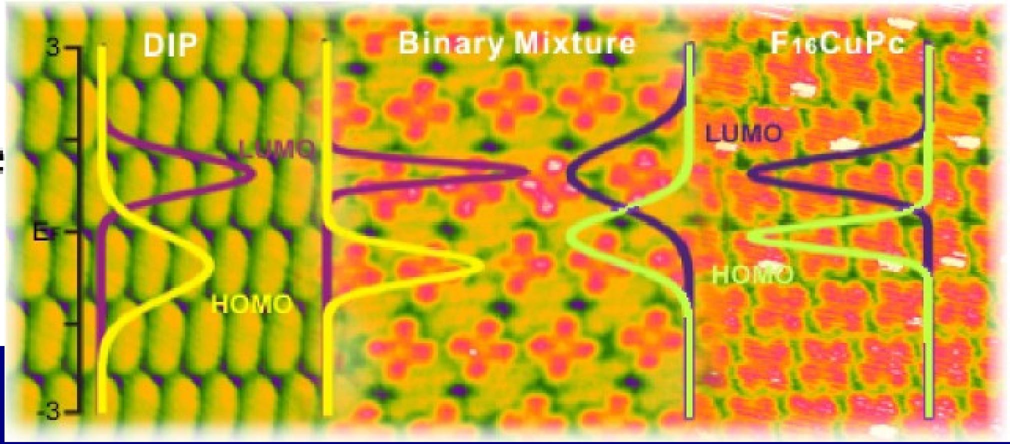
Road to Improving Efficiency: Controlling position of the frontier orbitals

LEVEL ALIGNMENT, Dispersion forces VdW



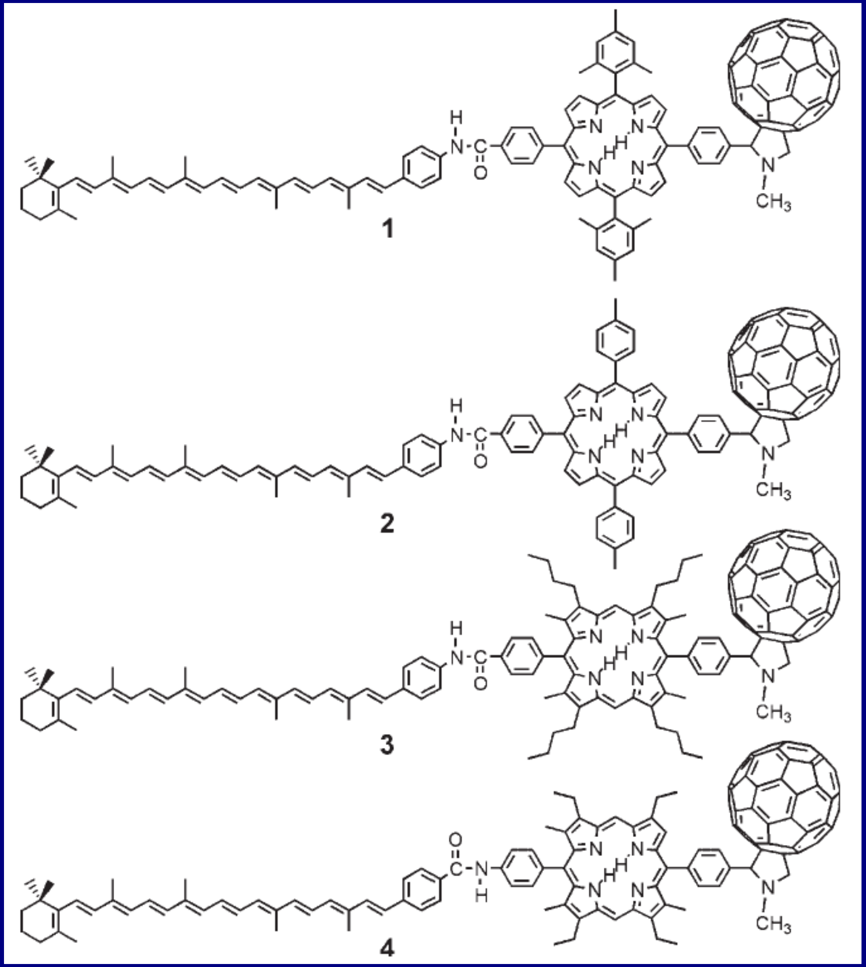
Thygessen et al (2009)





Supramolecular chemistry, Biophysics , Molecular Transport…..

Photo-excitation of the light-harvesting carotenoid-porphyrin-C60

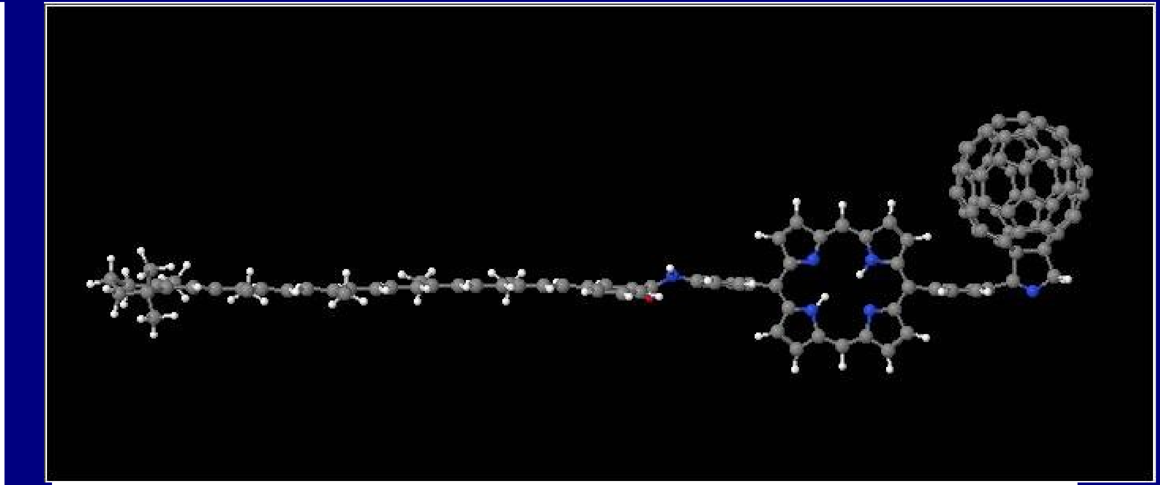


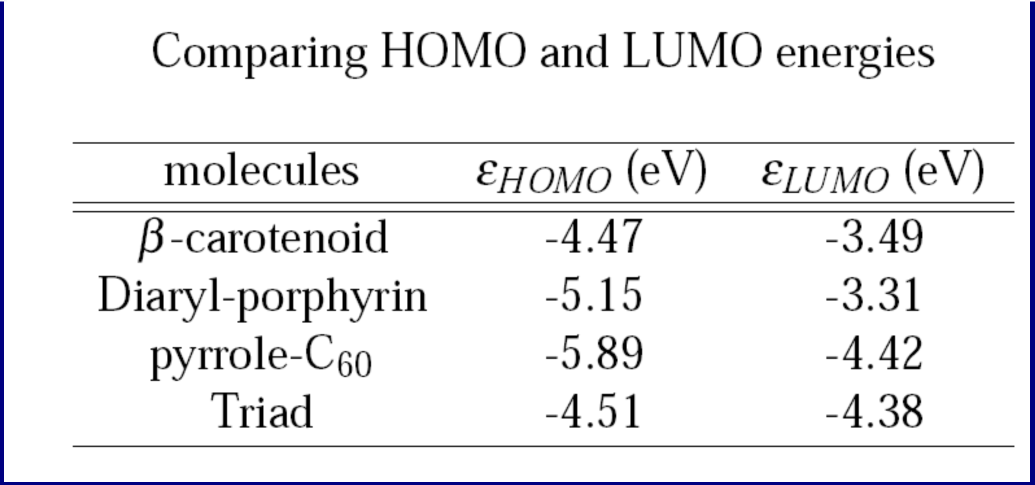
1

2

3

4





Comparing HOMO and LUMO energies

molecules	ε_{HOMO} (eV)	ε_{LUMO} (eV)
β-carotenoid	-4.47	-3.49
Diaryl-porphyrin	-5.15	-3.31
pyrrole-C_{60}	-5.89	-4.42
Triad	-4.51	-4.38

Photo-excitation of the light-harvesting carotenoid-porphyrin-C60

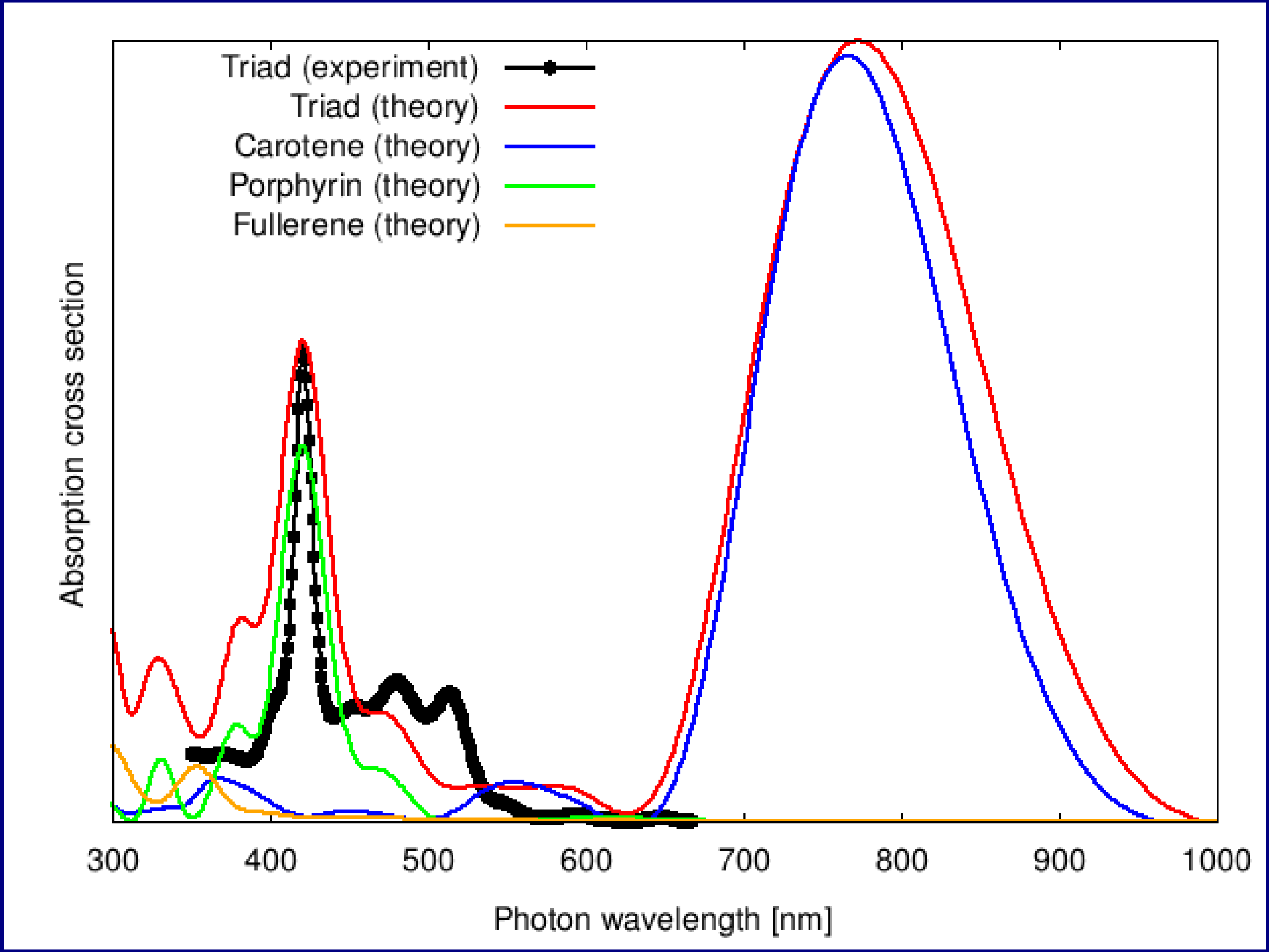
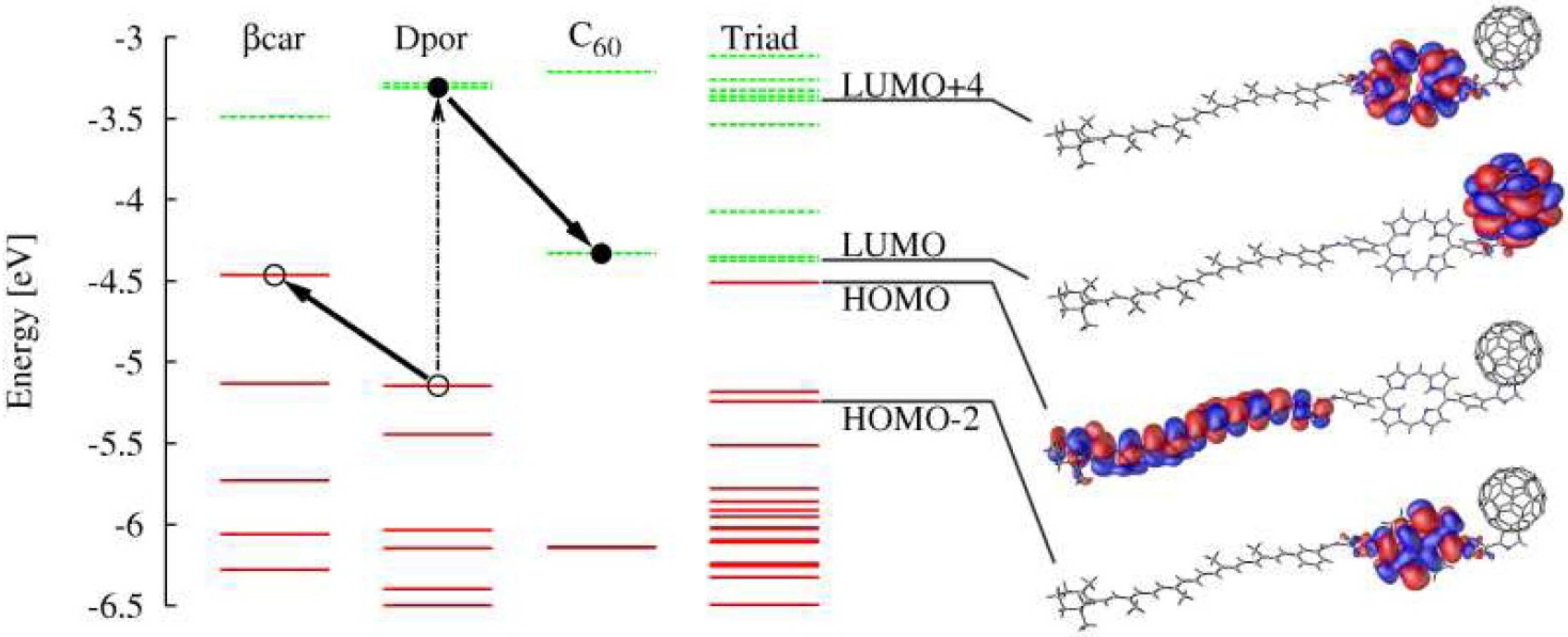


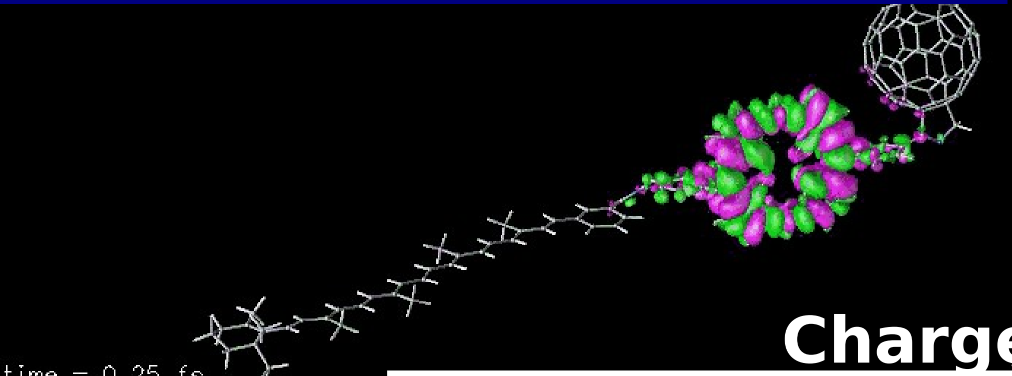
Photo-excitation of the light-harvesting carotenoid-porphyrin-C60

$$\text{C-P-C}_{60} + h\nu \rightarrow \text{C-P}^{*}\text{-C}_{60}^{*}$$

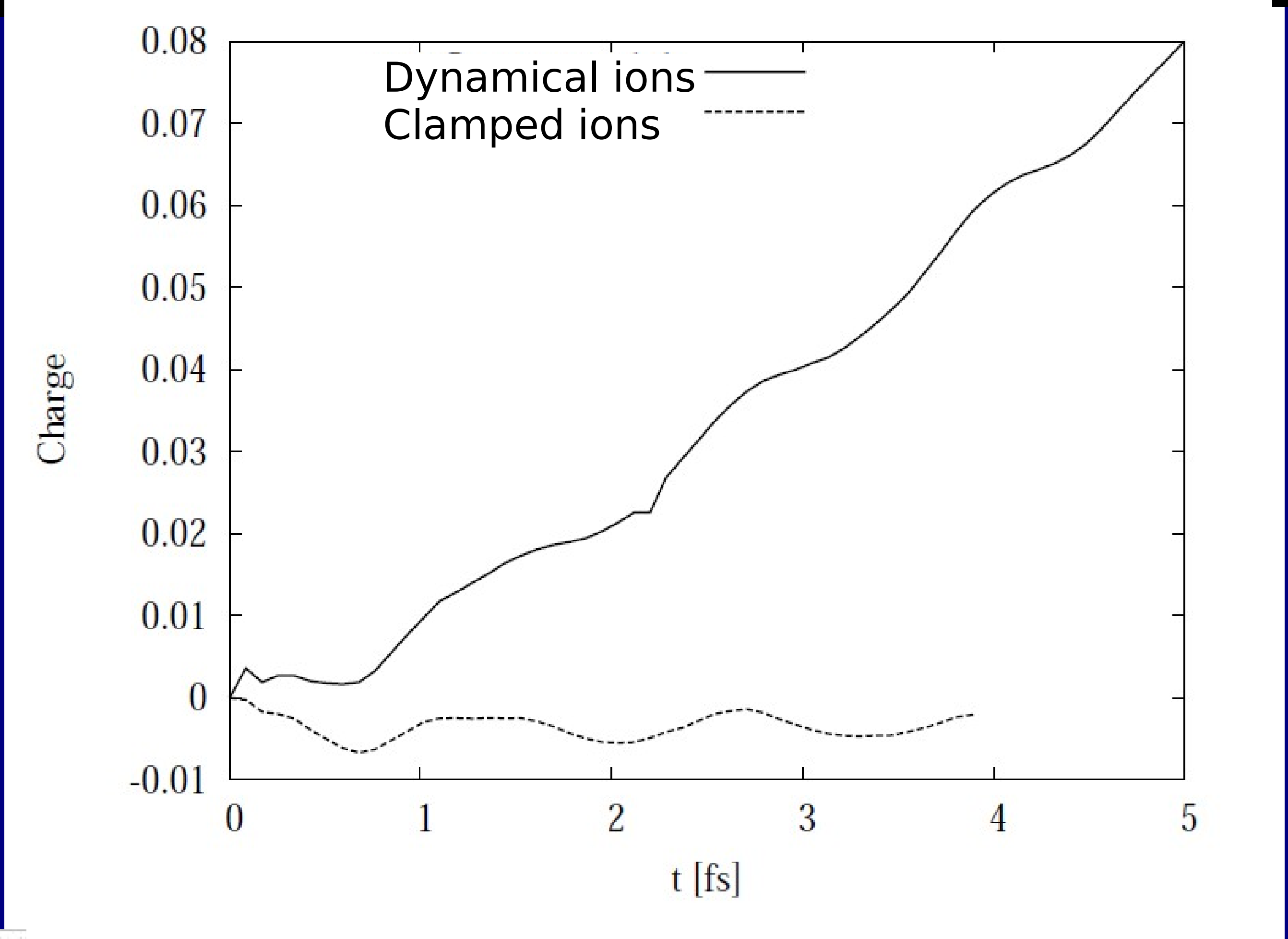
$$\text{C-P}^{*}\text{-C}_{60}^{*} \rightarrow \text{C-P}^{+}\text{-C}_{60}^{*-} \rightarrow \text{C}^{+}\text{-P-C}_{60}^{-}$$

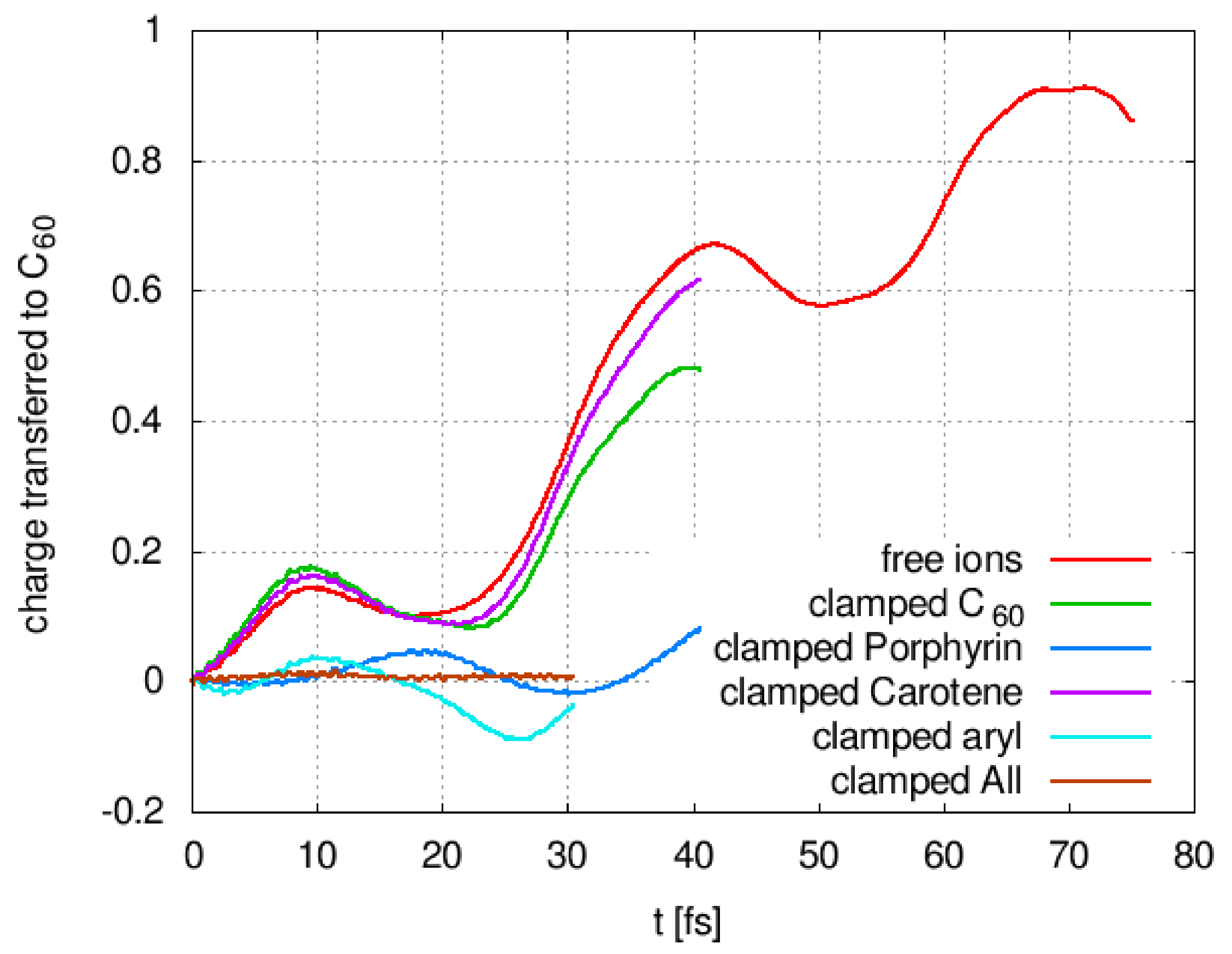


Carotenoid-porphyrin-C60 photodynamics

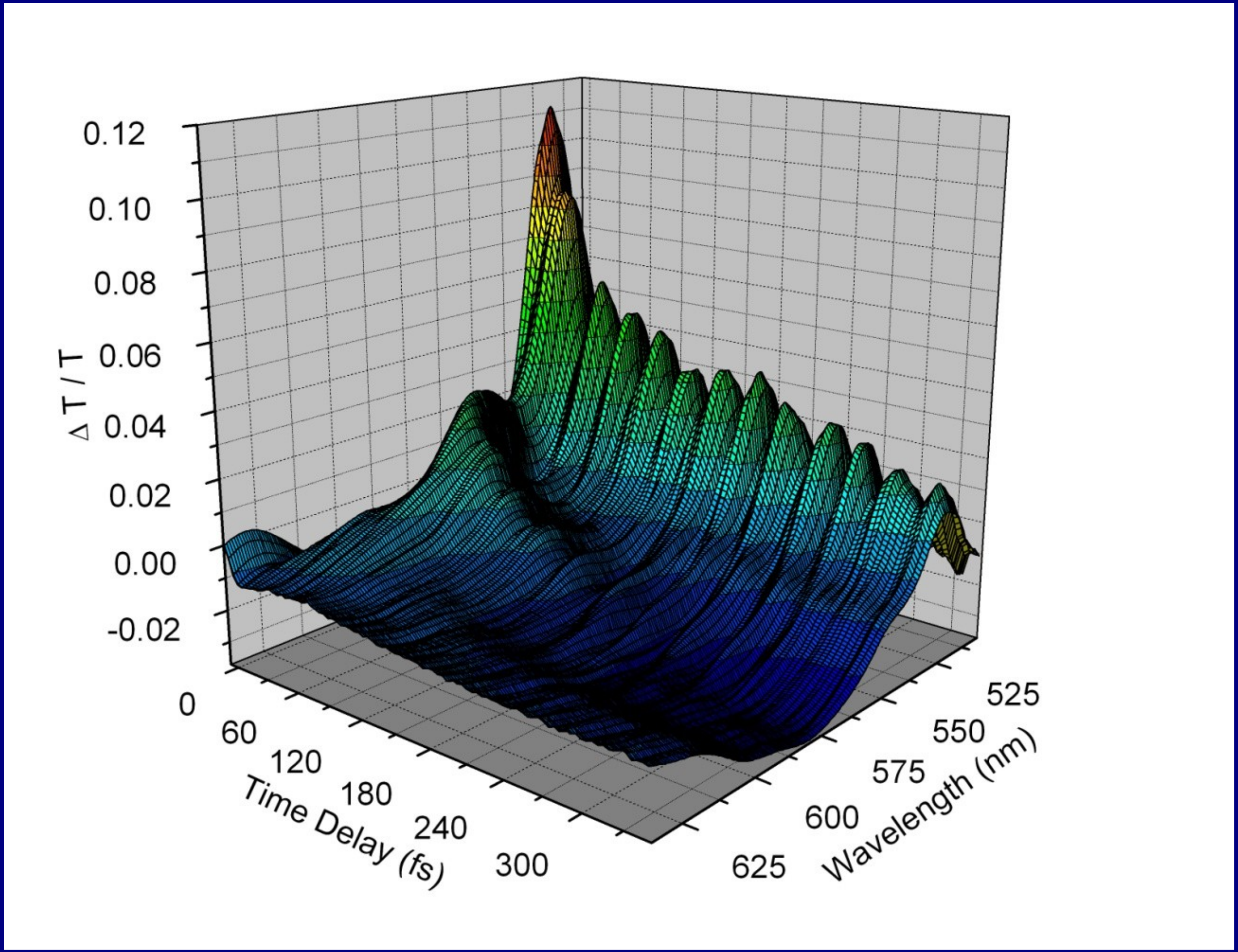


Charge on the C60




charge transferred to C_{60}
1
0.8
0.6
0.4
0.2
0
-0.2
0
10
20
30
40
50
60
70
80
t [fs]
free ions
clamped C_{60}
clamped Porphyrin
clamped Carotene
clamped aryl
clamped All

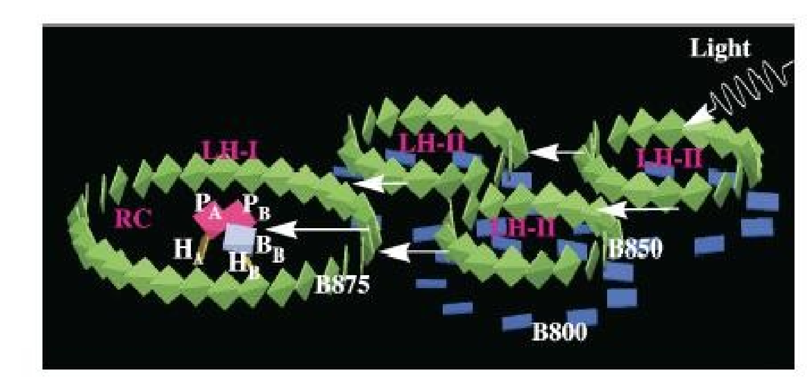
Simulation of the Time resolved spectra

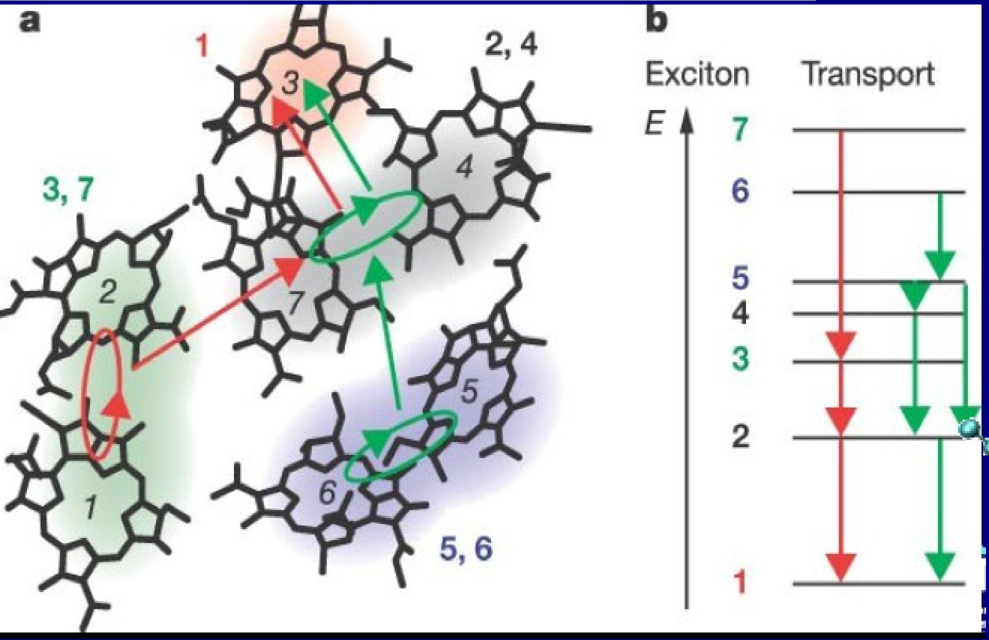


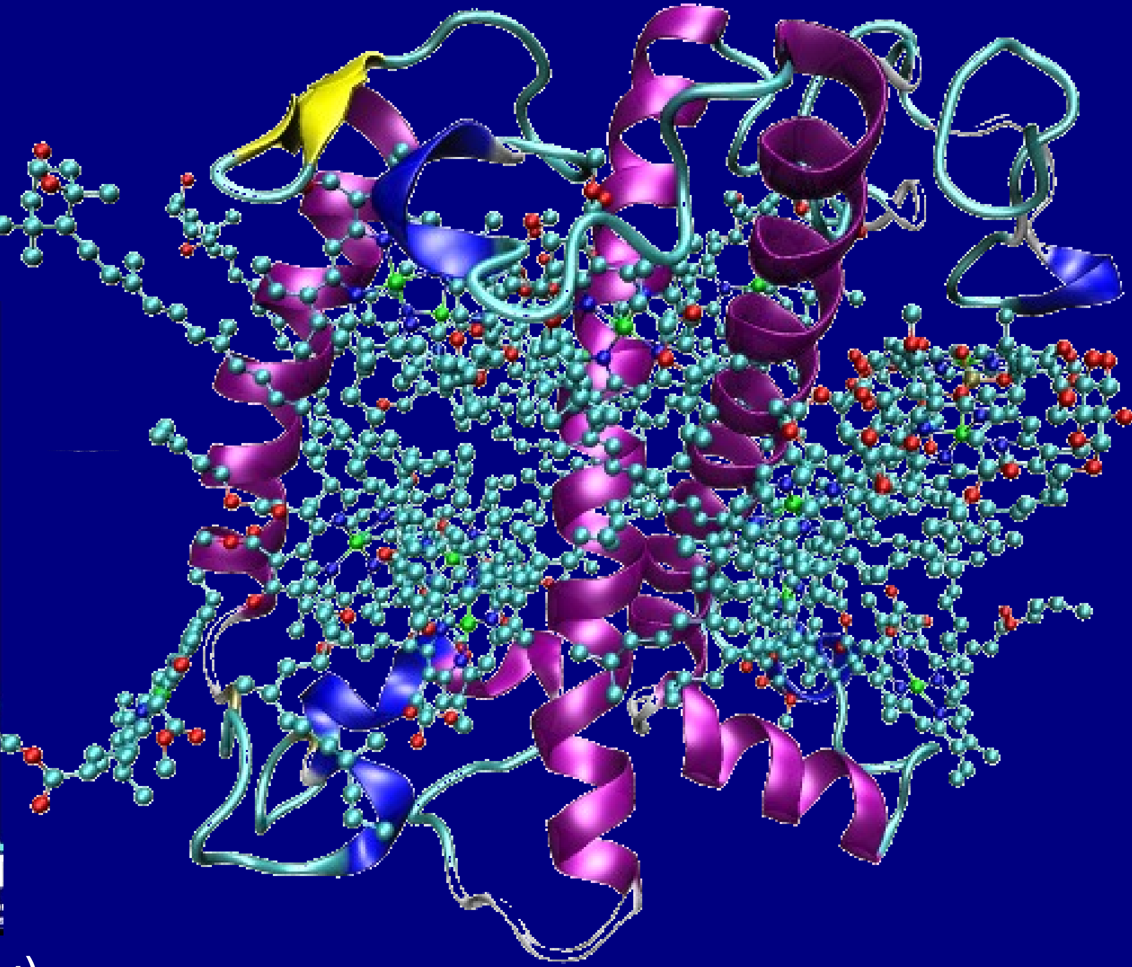
The carotene feature around 523 nm oscillates both in intensity and energy, the porphyrin feature red-shifts from about 540 nm to 573 nm and decays almost completely within the first 100 fs after phtoexcitation

Towards the color of plants:

e.g. Spinach

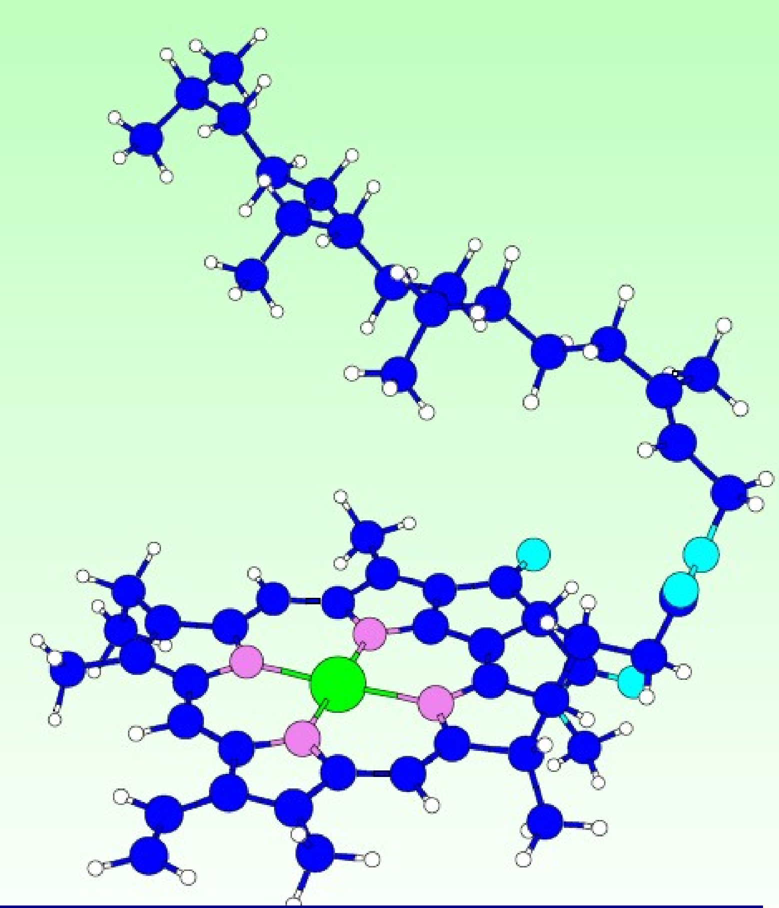


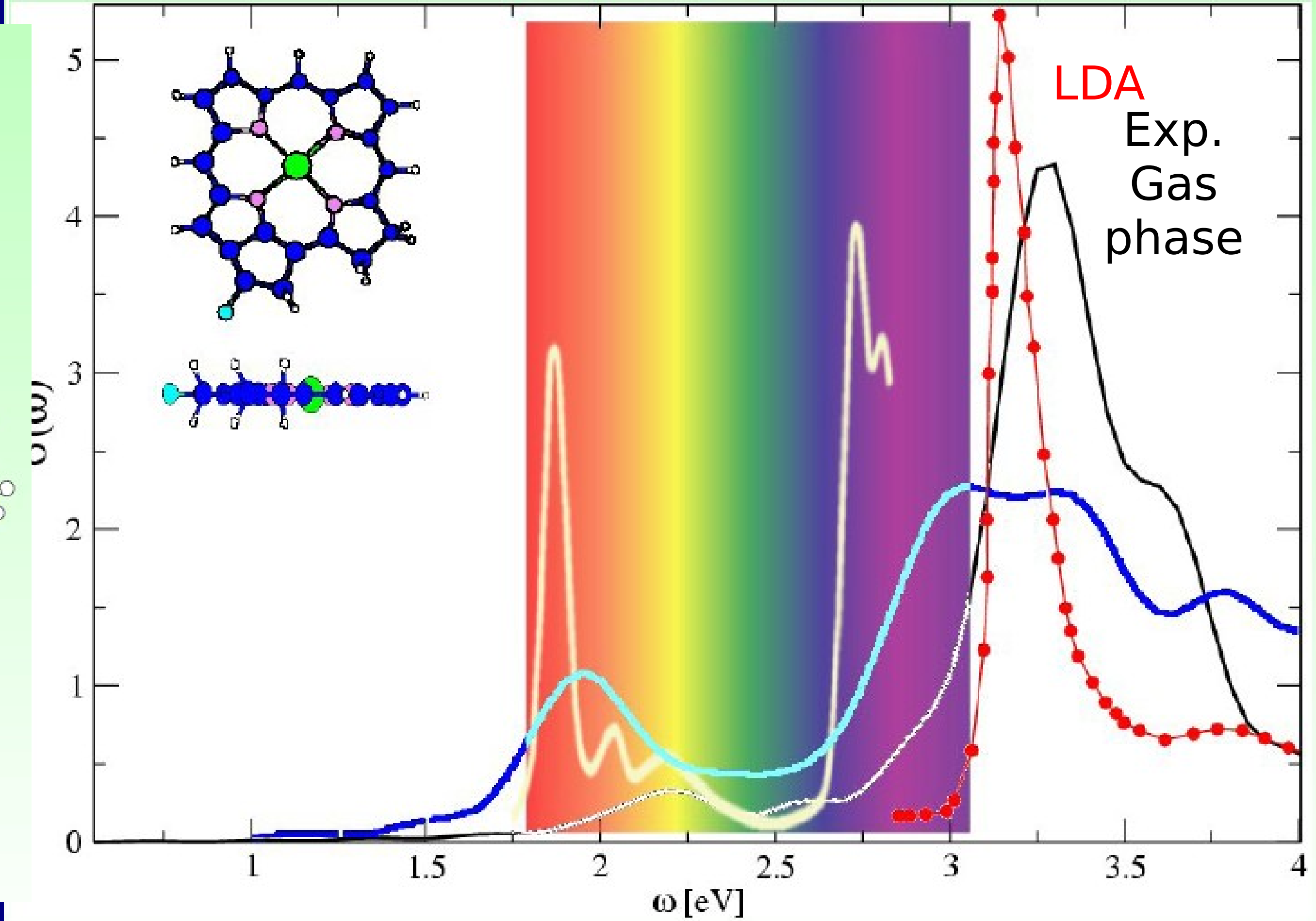




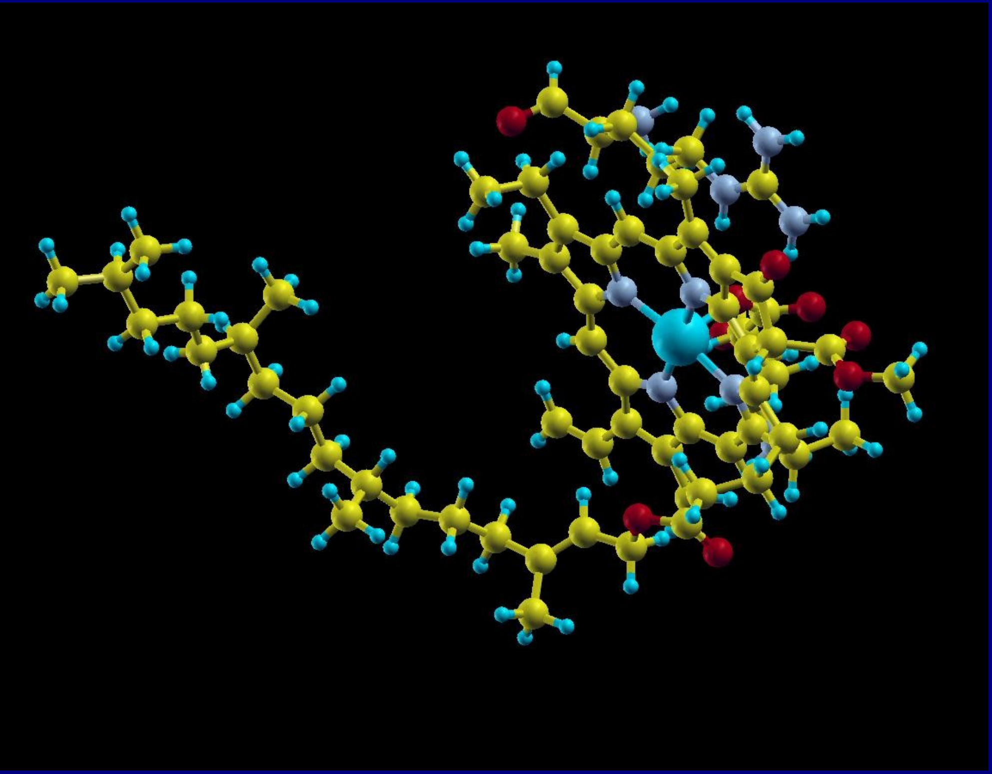
Fleming et al Nature (2005),.... (Berkeley)

Towards the color of plants: The real Chlorophyll molecule

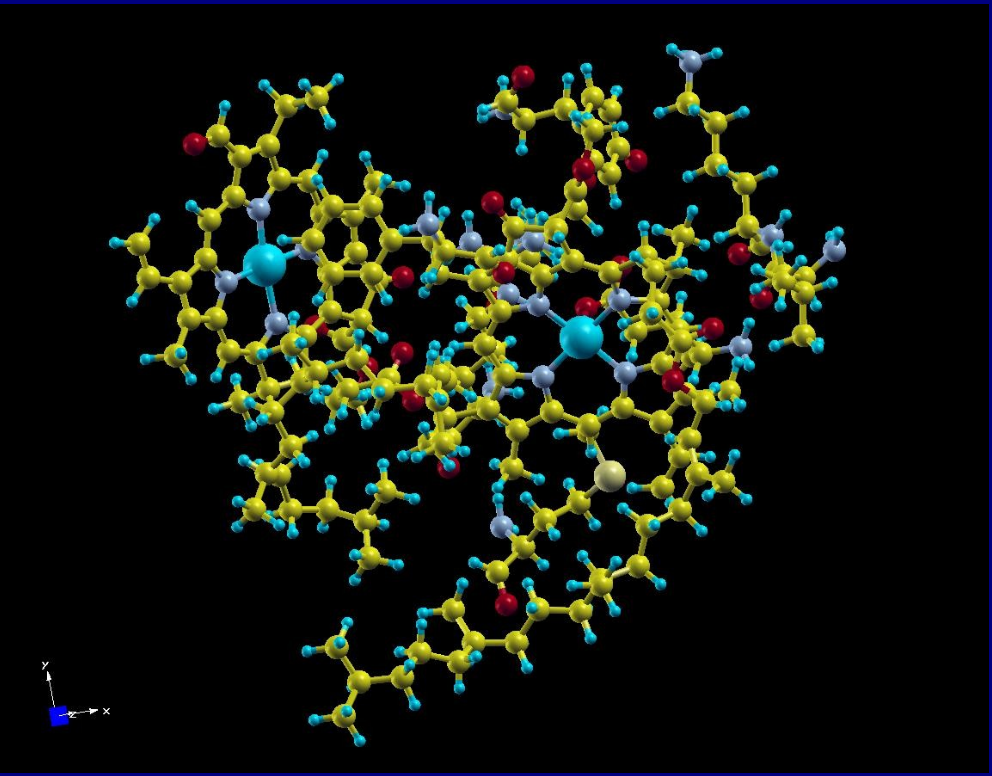




Towards the color of plants:



Towards the color of plants:



?

Challenge: proper treatment of the whole environment, including dissipation for very long simulations from fs to miliseconds and more……

Optimal control theory

Key question: What is the laser pulse that drives the system into a predefined goal?

Procedure: Define a target operator $\hat{O}$ and at the end of the laser interaction (t = T) maximize the functional

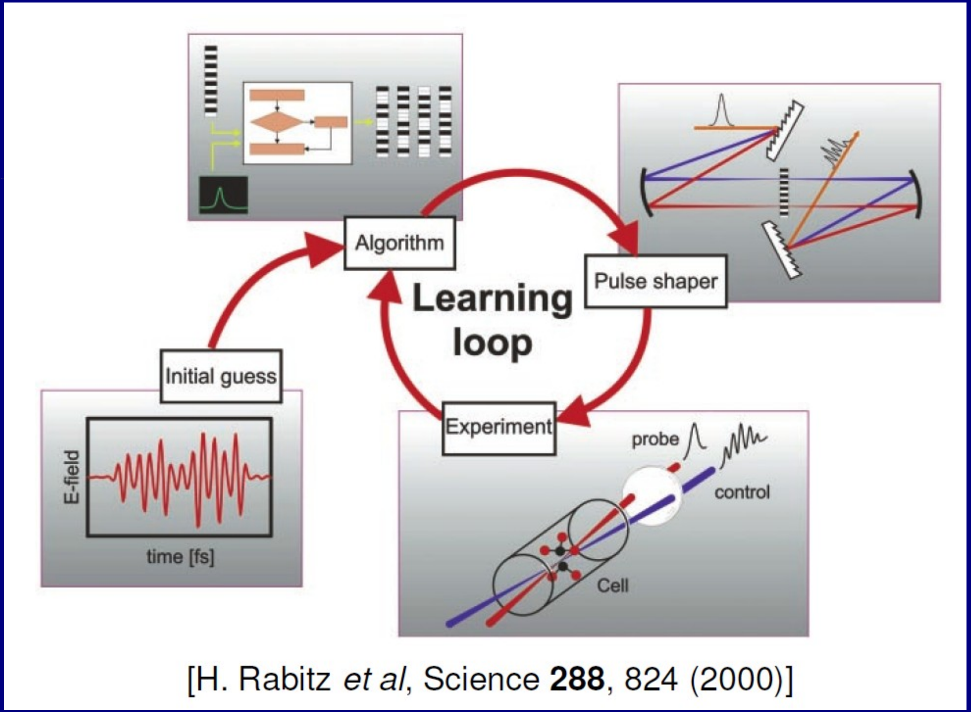
$$J_1[\Psi] = \langle\Psi(T)|\hat{O}|\Psi(T)\rangle = |\langle\Psi(T)|\Phi_\mathrm{F}\rangle|^2$$

$\hat{O} = |\Phi_F><\Phi\,|_F$ target state

W. Zhu, J. Botina, H. Rabitz, JCP 108, 1953 (1998)

What makes experimental "control" possible

- Existence of laser sources, since the 1960's.
- Femto-second laser sources, which allow for fast processes (avoiding decoherence), and extending the band-width.
- High-intensities.
- Laser shapers.
- Learning-loops algorithms.

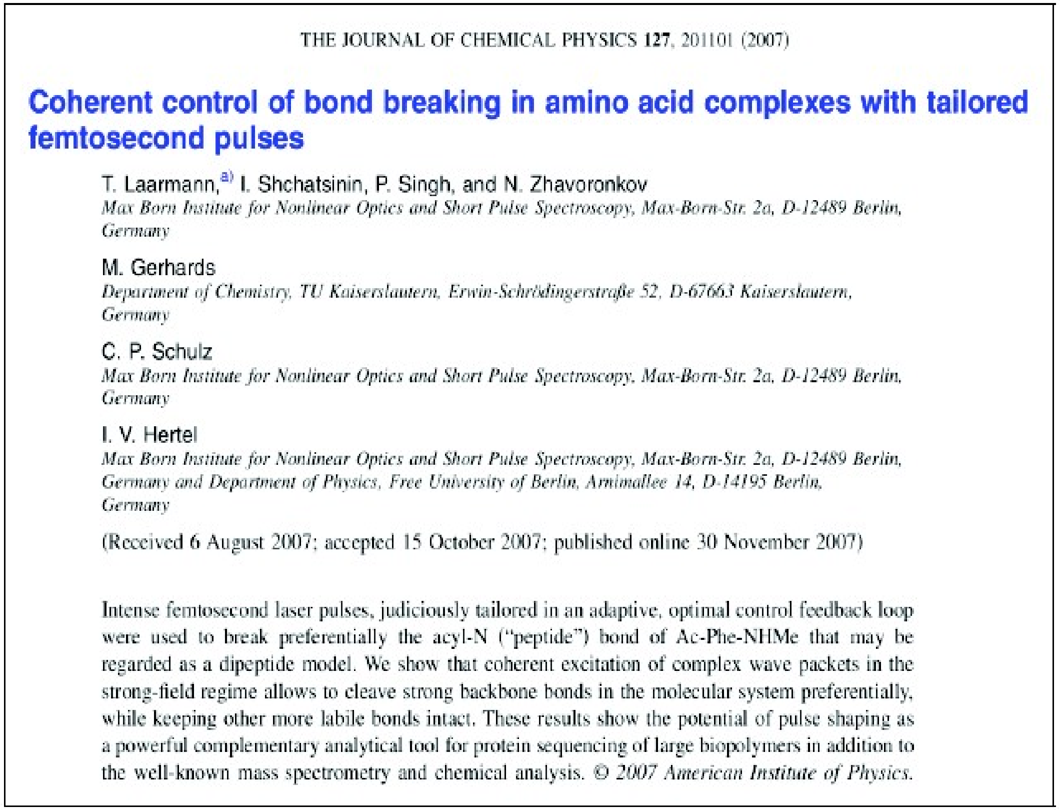


[H. Rabitz *et al*, Science **288**, 824 (2000)]

Applications:

Selective bond-breaking
High-harmonic generations

Design of bond-breaking laser pulses



THE JOURNAL OF CHEMICAL PHYSICS **127**, 201101 (2007)

Coherent control of bond breaking in amino acid complexes with tailored femtosecond pulses

T. Laarmann,[a] I. Shchatsinin, P. Singh, and N. Zhavoronkov
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(Received 6 August 2007; accepted 15 October 2007; published online 30 November 2007)

Intense femtosecond laser pulses, judiciously tailored in an adaptive, optimal control feedback loop were used to break preferentially the acyl-N ("peptide") bond of Ac-Phe-NHMe that may be regarded as a dipeptide model. We show that coherent excitation of complex wave packets in the strong-field regime allows to cleave strong backbone bonds in the molecular system preferentially, while keeping other more labile bonds intact. These results show the potential of pulse shaping as a powerful complementary analytical tool for protein sequencing of large biopolymers in addition to the well-known mass spectrometry and chemical analysis. © *2007 American Institute of Physics.*

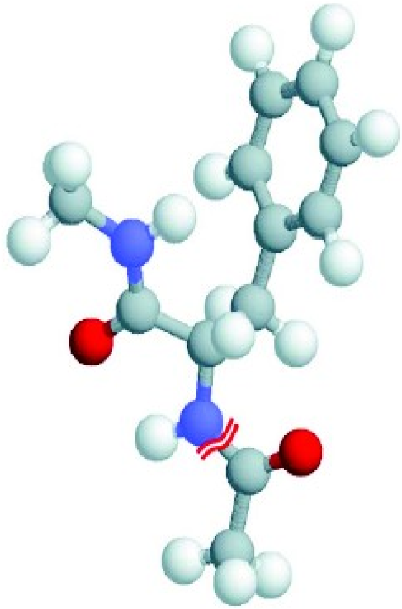
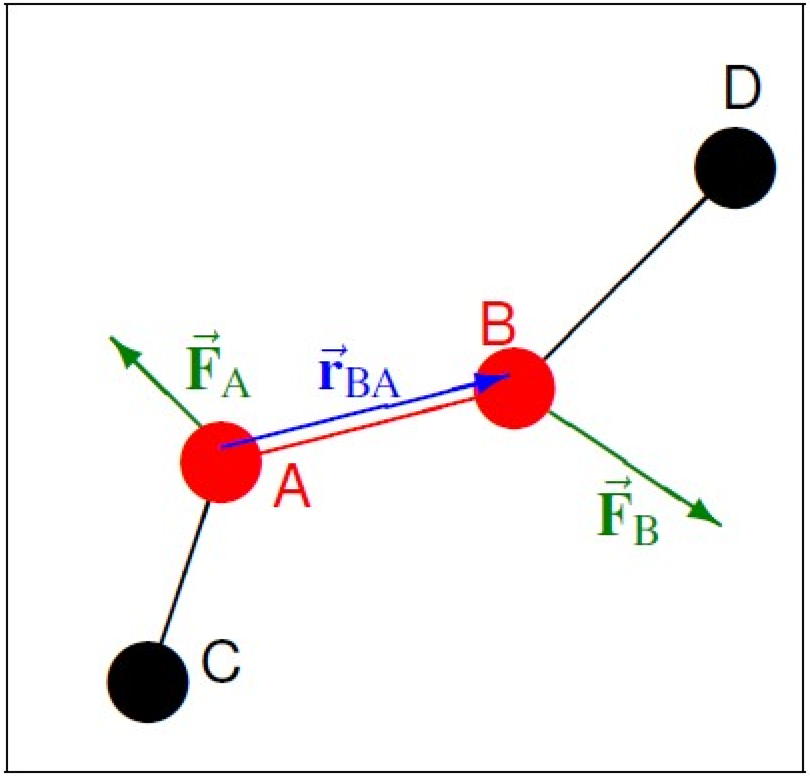


FIG. 1. (Color online) Optimal tailoring of intense femtosecond light can be used to preferentially break peptide bonds, such as the indicated N1–C3 bond in the amino acid complex Ac-Phe-NHMe.

K. Kriger, A. Castro, E.K.U. Gross, (unpublished)

Design of bond-breaking laser pulses (II)



- If the AB bond is breaking,

$$\begin{aligned} \vec{r}_{BA} \cdot \vec{F}_B &> 0 \\ \vec{r}_{BA} \cdot \vec{F}_A &< 0 \end{aligned}$$

$$\Rightarrow$$

$$\begin{aligned} \vec{r}_{BA} \cdot \vec{F}_B - \vec{r}_{BA} \cdot \vec{F}_A &> 0 \Rightarrow \\ \vec{r}_{BA} \cdot \vec{F}_{BA} &> 0 \end{aligned}$$

$$(\vec{F}_{BA} = \vec{F}_B - \vec{F}_A)$$

Design of bond-breaking laser pulses (III)

- Bond-breaking target:

$$J_1[\Psi] = \frac{1}{t_f - t_0}\int_{t_0}^{t_f} \mathrm{d}t\,\langle\Psi(t)|\,|\vec{\mathbf{r}}_{\mathrm{BA}}|\,|\hat{\vec{\mathbf{F}}}_{\mathrm{BA}}(t)|\left(1 + \vec{\mathbf{r}}_{\mathrm{BA}}\cdot\hat{\vec{\mathbf{F}}}_{\mathrm{BA}}(t)\right)|\Psi(t)\rangle\,.$$

- Within TDDFT, $\hat{\vec{\mathbf{F}}}_{\mathrm{A}}$ is a local density operator: the necessary expectation values can be written as simple density integrals.

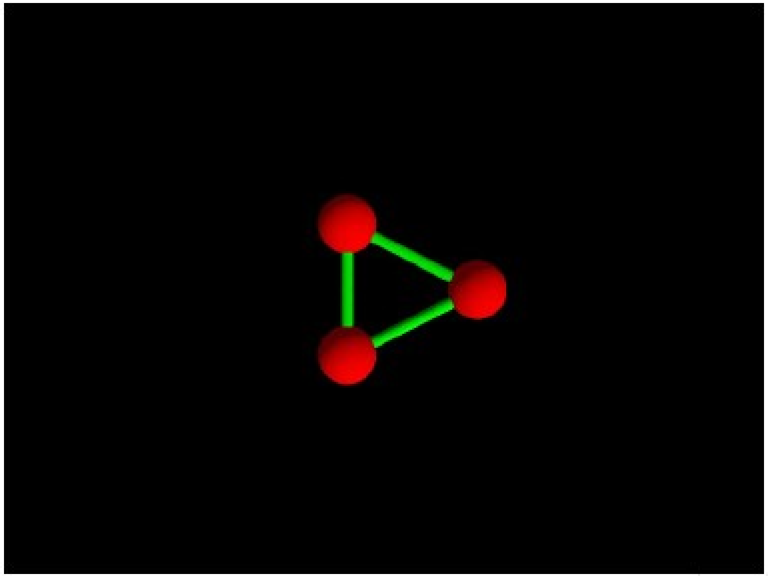
$$\hat{\vec{\mathbf{F}}}_{\mathrm{A}}(t) = \int \mathrm{d}^3r\;\hat{n}(\mathbf{r})\,\nabla_{\vec{\mathbf{r}}_{\mathrm{A}}} v_{\mathrm{KS}}(\mathbf{r},t)\,.$$

- During the time of the pulse, the nuclei are *fixed*. The photo-reaction occurs afterwards, driven by the excited electronic system.

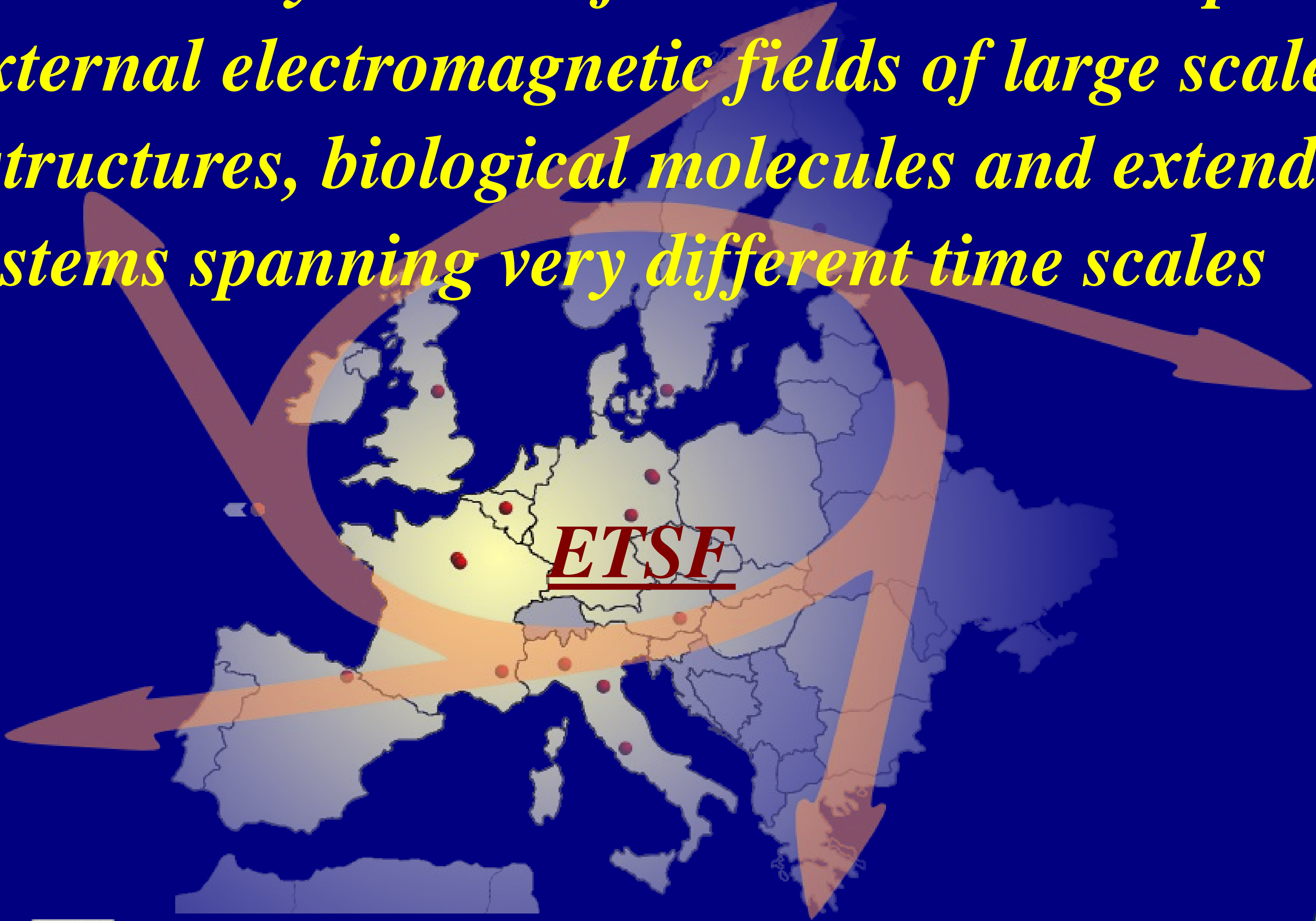
Design of bond-breaking laser pulses (IV)

- Case study: selective photo-dissociation of H_3^+ into H_2 and H^+.
- For this case, we used a gradient-free optimization scheme, which only necessitates forward propagations.
- The field is expanded as a Fourier series:

$$\epsilon(t) = \sum_{n=1}^{N/2} a_n \sqrt{\frac{2}{T}} \cos(\frac{2\pi}{T} nt) + b_n \sqrt{\frac{2}{T}} \sin(\frac{2\pi}{T} nt)$$



TDDFT is a powerful tool to "predictive" describe the combined dynamics of electron/ion in response to external electromagnetic fields of large scale nanostructures, biological molecules and extended systems spanning very different time scales



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ETSF , Department of Material Physics, Centro Mixto CSIC-UPV,
University of the Basque Country, Donostia, Spain

A. Castro, J.A. Alonso,	Zaragoza
E. K. U. Gross	Halle
D. Varsano, C. Rozzi, N. Spallazani	Modena
K. Thygessen	Denmark

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2007 - 2013

EUSKO JAURLARITZA
GOBIERNO VASCO

eman ta zabal zazu

Universidad del País Vasco
Euskal Herriko Unibertsitatea

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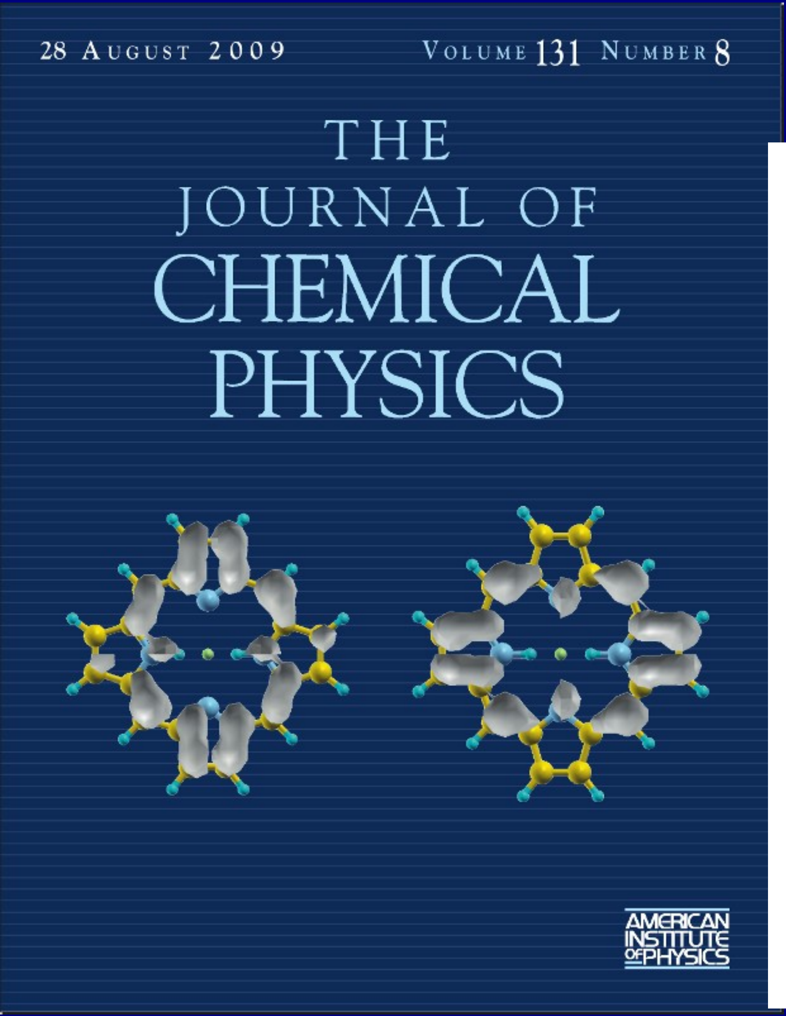
Thank you!!!!

For more details see:
http://nano-bio.ehu.es
http://etsf.eu

Free standing porphyrins



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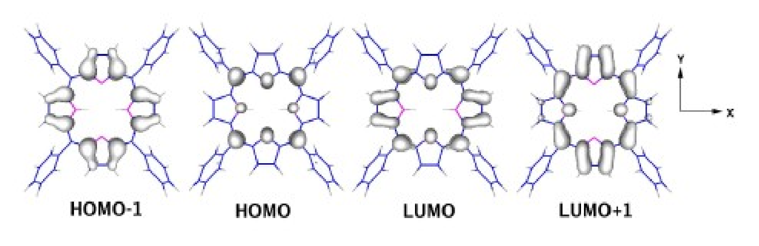
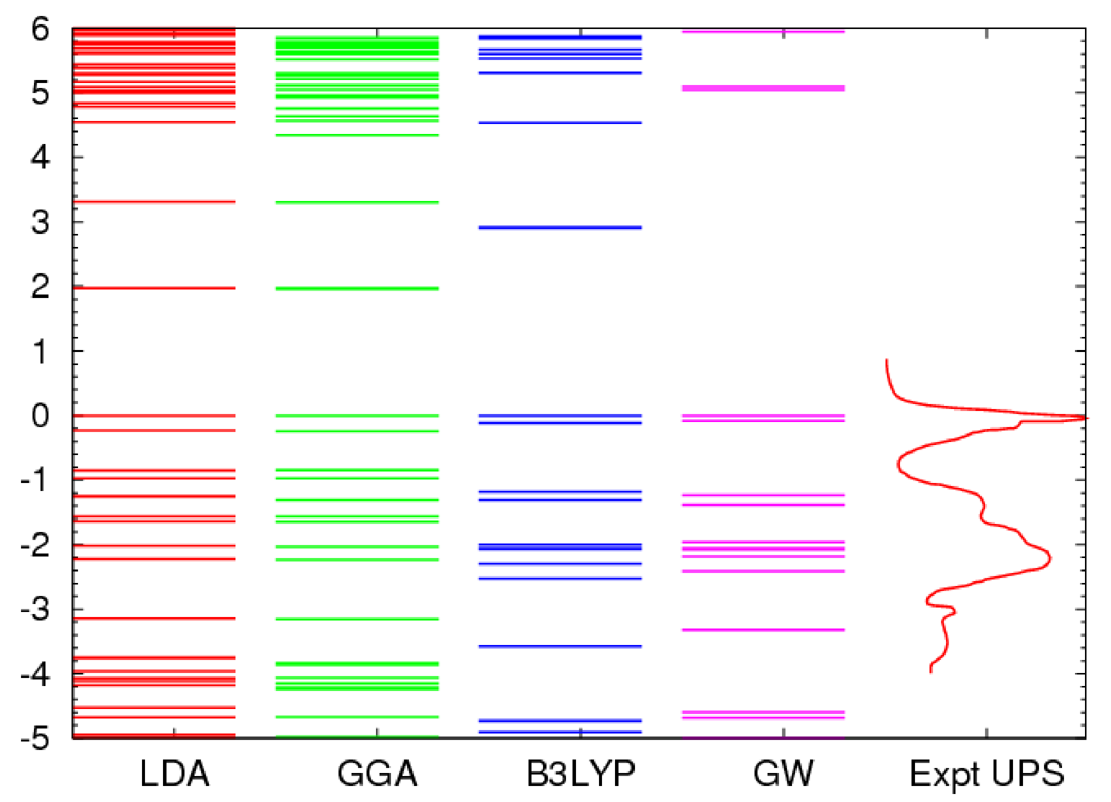




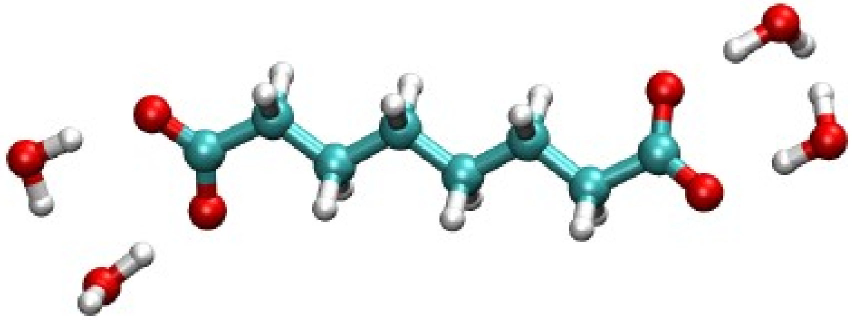
Expt UPS: Ghosh, Theor Chem Acc ***97****, 143 (1997); Dubois, Chem Phys Lett* ***75****, 434 (198*

Journal of Chemical Physics 131, 84101 (2009)

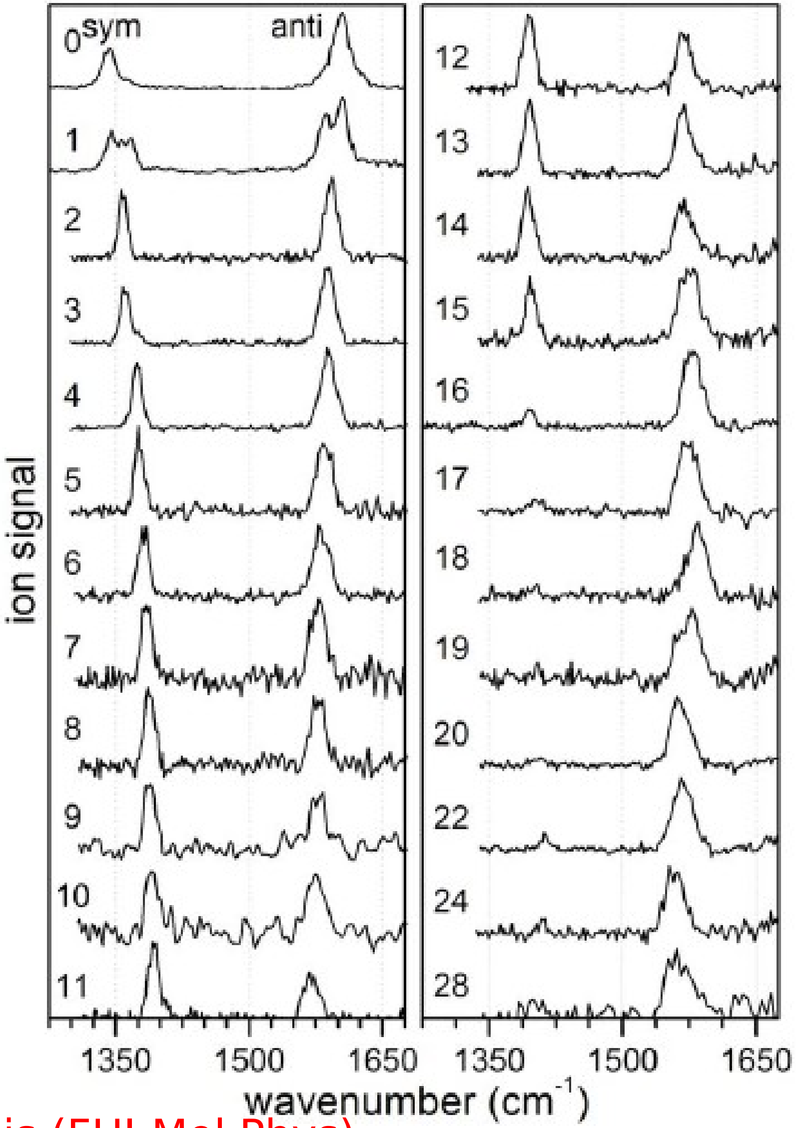
Nano solvation

Spectroscopic Probe for Characterizing Solvent-Mediated Folding in Dicarboxylate Dianions**
Torsten Wende, Marius Wanko, Ling Jiang, Gerard Meijer, Knut R. Asmis and AR (2010)

Microsolvation of the Suberate Dianion



- PE experiments [Yang2004,Wang2008]: SA folds for n≥14…16 water mol.
- IR spectra (PD) at 15 K for clusters of n=0…28 water mol.
- Intensity drop of symmetric C-OO stretching band at n=16

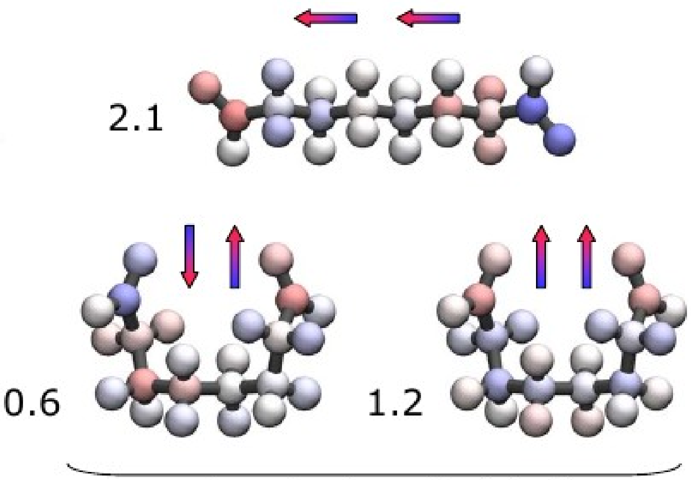


In collaboration with the group of Dr. Knut Asmis (FHI-Mol.Phys)

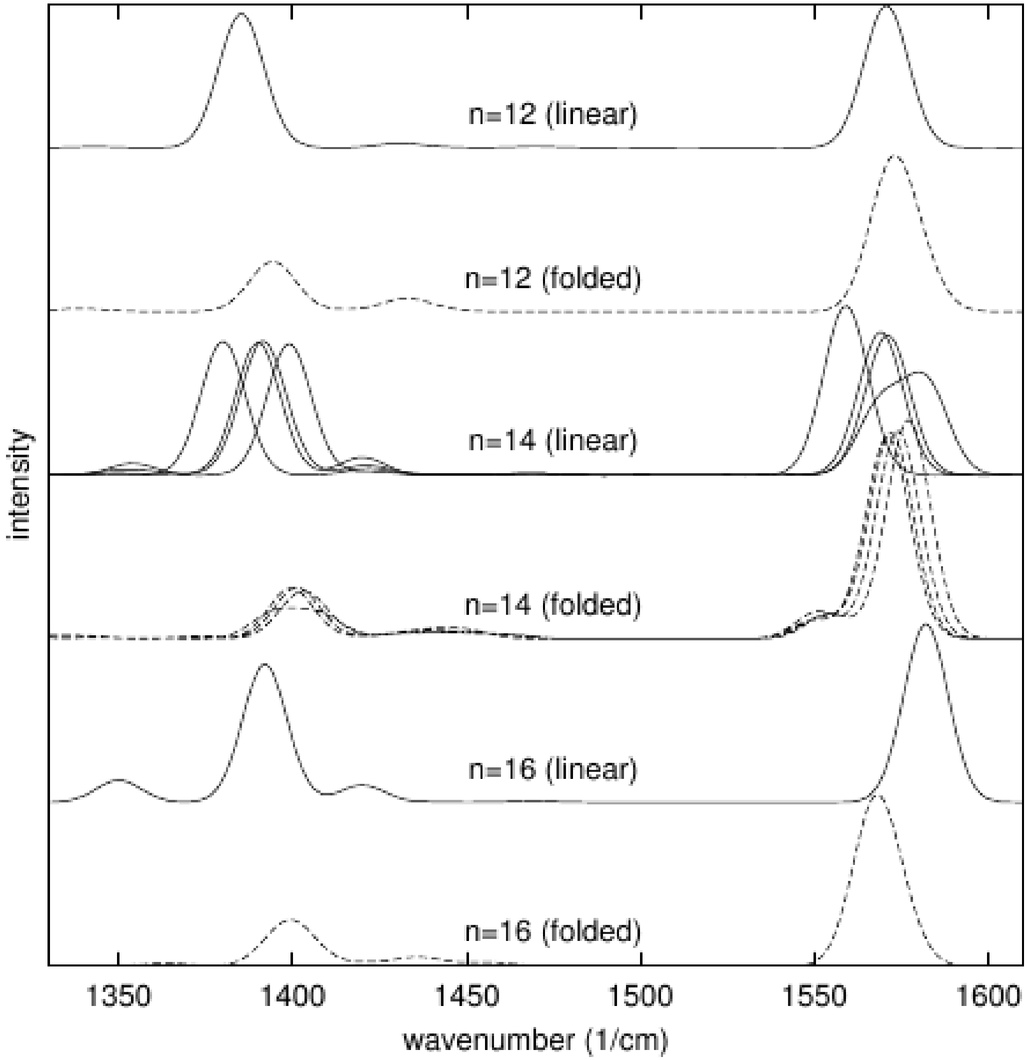
Symmetric Mode: Intensity Drop upon Folding

- intensity drop due to folding is theoretically reproduced
  - for n=12…16
  - for different minimum energy configurations

  ⇒ common feature



color code enhanced by factor 2



Folding Energy