united nations educational, scientific and cultural organization
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the **abdus salam** international centre for theoretical physics

ICTP 40th Anniversary

SMR 1564 - 4

SPRING COLLEGE ON SCIENCE AT THE NANOSCALE
(24 May - 11 June 2004)

TDDFT THEORY:

APPLICATIONS TO NANO AND BIO-STRUCTURES

Optical Properties of Nanostructures: Illustration of the physics for nano- and bio structures

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Optical properties of nanostrutures

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http://dipc.ehu.es/arubio   E-mail: arubio@sc.ehu.es

I. Motivation. Basic concepts. Foundations TDDFT.

II. Illustration of the physics for nano- and bio structures

III. Extended systems: problems and new developments



ICTP Spring College on Science at the Nanoscale, Trieste May 24th -June 11th 2004

Optical properties of nanostrutures

II. <u>Illustration of the physics for nano- and bio structures</u>

Seeing bond breaking and formation!!!

Nanostructures: -small metal and semiconductor cluster
-carbon nanotubes: relaxation times

Bio-photoreceptors:
-Green-fluorescent protein
-Isomerisation and device applications of azobencene

*The **octopus project** is aim to the first principle description of the excite state electron-ion dynamics of nanostructres and extended systems within TDDFT*

Implementation:

✔ Numerical description of functions: real space discretization (1D-3D).
✔ Auxiliary use of LCAO/ FFTs. QM/MM for biomolecular structures
✔ Electon-ion coupling: pseudopotentials. Spin-Orbit ....

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

M.A.L. Marques, A. Castro, G. Bertsch, AR Comp.Phys.Comm. (2002)
C. Rozzi, M.A.L. Marques, A. Castro, E.K.U. Gross A. R. (to be published)

Time dependent multicomponent KS theorem

transformation to a body-fixed coordinate frame required

T.Kreibig and E.K.U Gross PRL (2001)

The densities , N of the interacting system can be calculated as densities of a non-interacting (KS) system

$$\rho(\mathbf{r},t) = \sum_j |\varphi_j(\mathbf{r},t)|^2$$

$$N(R,t) = |\chi(R,t)|^2$$

$$i\partial_t \varphi_j(\mathbf{r},t) = \left(\frac{\hbar^2}{2\mu_e} \nabla_r^2 + v_s[\rho,N](\mathbf{r},t) \right) \varphi_j(\mathbf{r},t)$$

$$i\partial_t \chi(R,t) = \left(\frac{\hbar^2}{2\mu_n} \nabla_R^2 + W_s[\rho,N](R,t) \right) \chi(R,t)$$

$$v_s(\mathbf{r},t) = v_{laser}(\mathbf{r},t) + v_{ee}^H(\mathbf{r},t) + v_{en}^H(\mathbf{r},t) + \mathbf{v_{xc}[\rho,N](r,t)}$$

$$W_s(R,t) = W_{laser}(R,t) + \frac{Z_1 Z_2}{R} + W_{en}^H(R,t) + \mathbf{W_{xc}[\rho,N](R,t)}$$

The Electron Localisation Function (ELF) : Seeing Bonds!!! *(what is a bond?)*

Definition:

$$elf_{\sigma} = \frac{1}{1 + \left[\frac{C_{\sigma}(r)}{C_{\sigma}^{uni}(r)} \right]^2}$$

Becke, Edgecombe, JCP92, 5397 (1990)

$$C_{\sigma}^{uni}(r) = \frac{3}{5}(6\pi^2)^{2/3}\rho_{\sigma}^{5/3}(r)$$

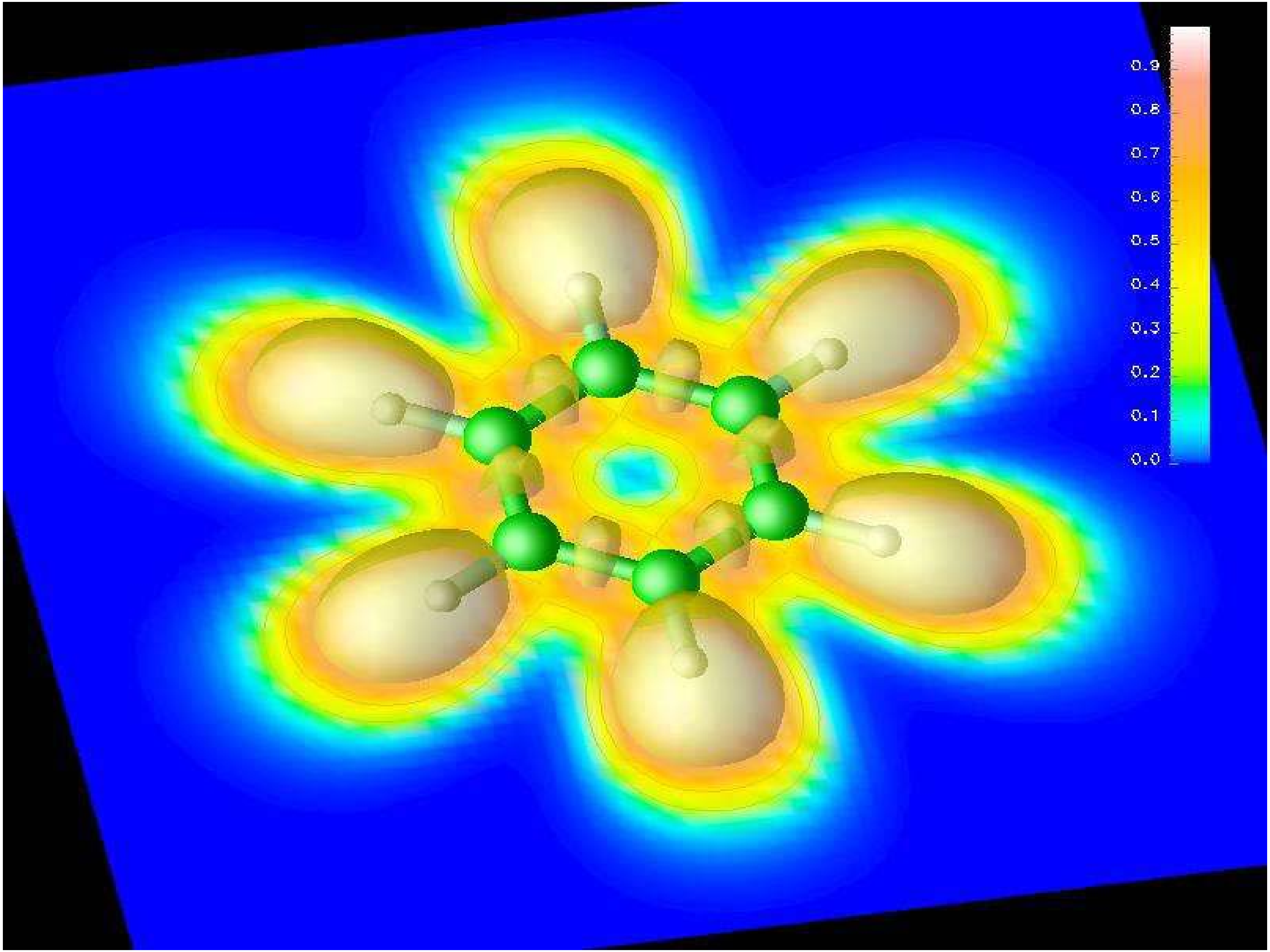
0 < elf < 1

high localisation → $C_{\sigma} \sim 0$ → elf ~ 1

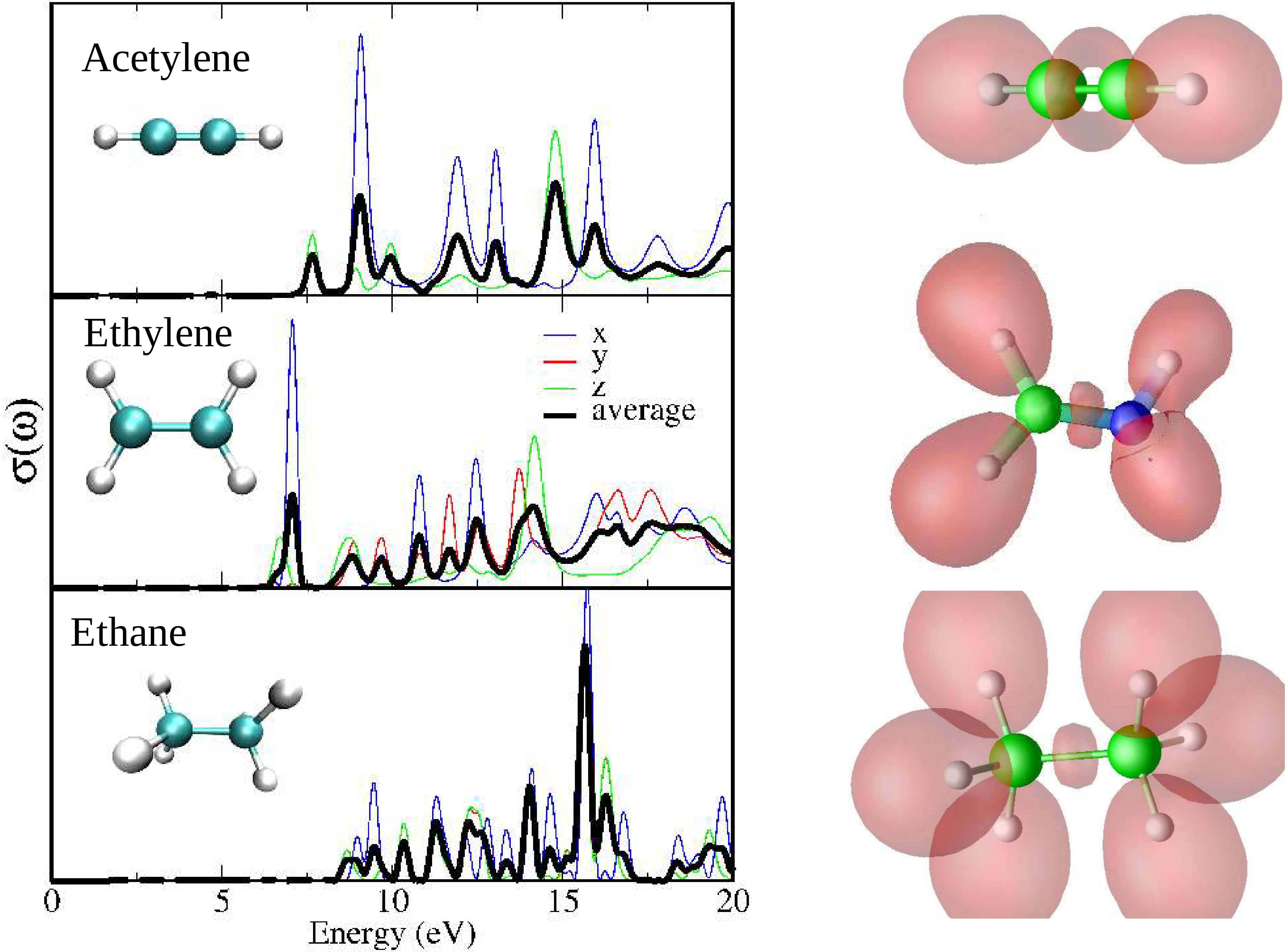
completely delocalised → $C_{\sigma} \sim C_{\sigma}^{uni}$ → elf ~ 1/2

When the wavefunction is a Slater determinant (in the time dependent case)

$$C_{\sigma}^{det}(r,t) = \sum_{i=1}^{N_{\sigma}} |\nabla \varphi_{i\sigma}(r,t)|^2 - \frac{1}{4}\frac{[\nabla \rho_{\sigma}(r,t)]^2}{\rho_{\sigma}(r,t)} - \frac{j\,(r,t)}{(r,t)}$$



0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0

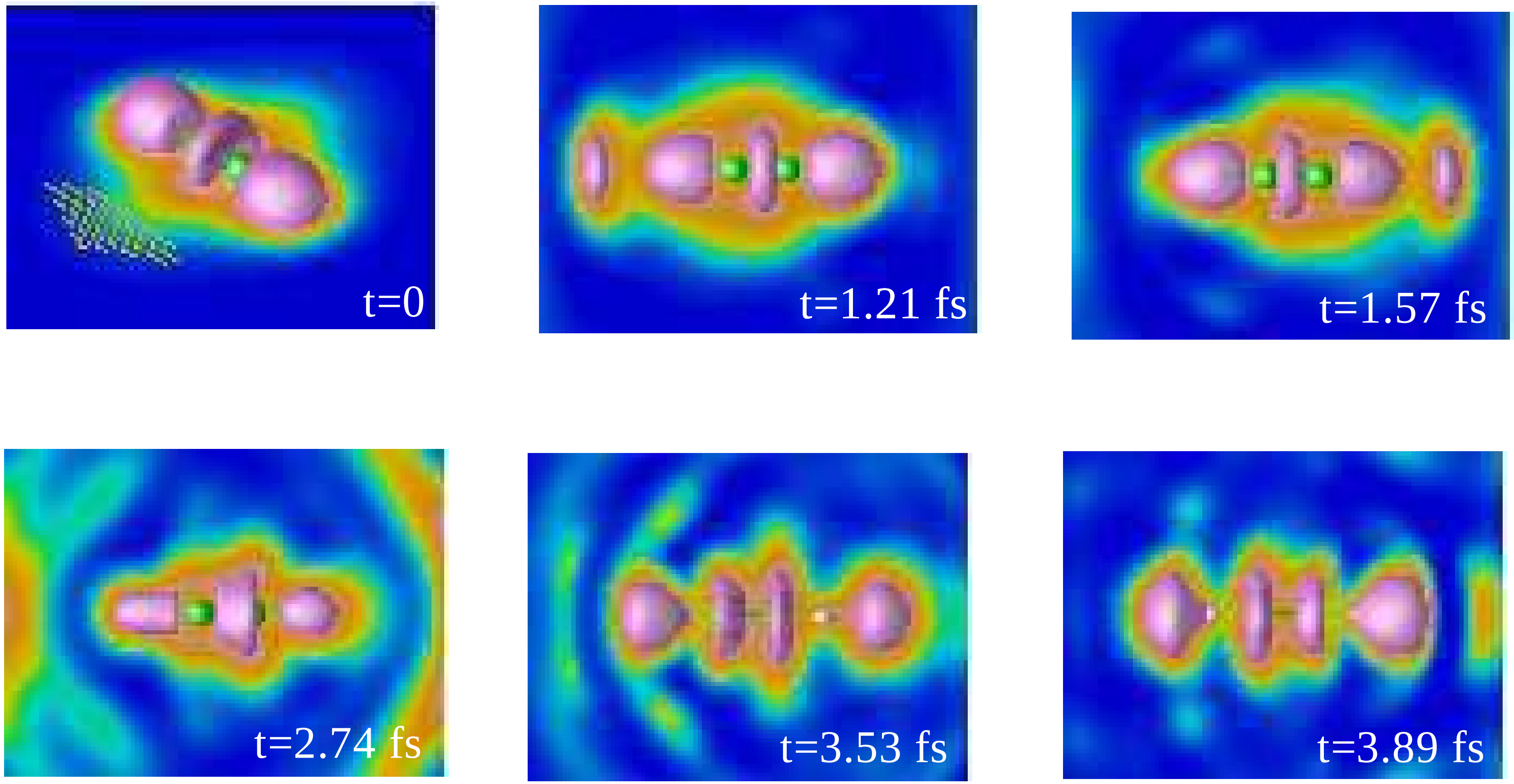


Acetylene
Ethylene
Ethane
x
y
z
average
σ(ω)
0
5
10
15
20
Energy (eV)

Time-dependet case: acetylene C_2H_2 in a strong laser field

=17eV, T= 8fs, I= 1.2x10^{14} Wcm^{-2}

fast ionisation



to *

T. Burnus, M.A.L.Marques, E.K.U Gross, (2004)

Nano (bio-) structures

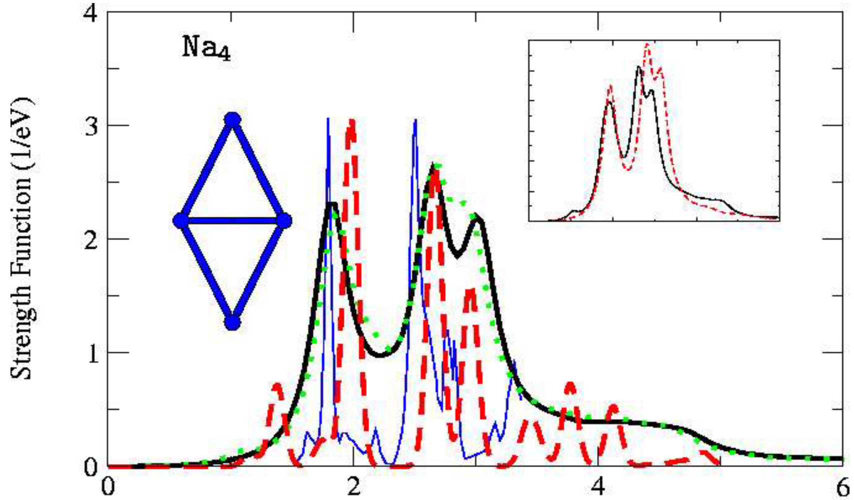
How good is the performance of TDDFT and present DFT XC-functionals?

G. Onida, L. Reining and AR, Rev. Mod. Phys. ***74****, 601 (2002)*

Linear optical response: general aspects

$$\chi(\omega)=\chi_0(\omega)+\chi_0(\omega)(v+f_{xc}(\omega))\chi(\omega)$$

$$\chi_0(r,r',w)=\sum_{ij}(f_j-f_i)\frac{\varphi_i^c(r)\varphi_j(r)\varphi_i(r')\varphi_j^c(r')}{\epsilon_i-\epsilon_j-w}$$



$$[1-(v+f_{xc}(\omega))\chi_0(\omega)]\lambda(\omega)=0$$

Single-pole approximation ⇒

$$\Omega=\left(\varepsilon_{j_0}-\varepsilon_{k_0}\right)+K$$

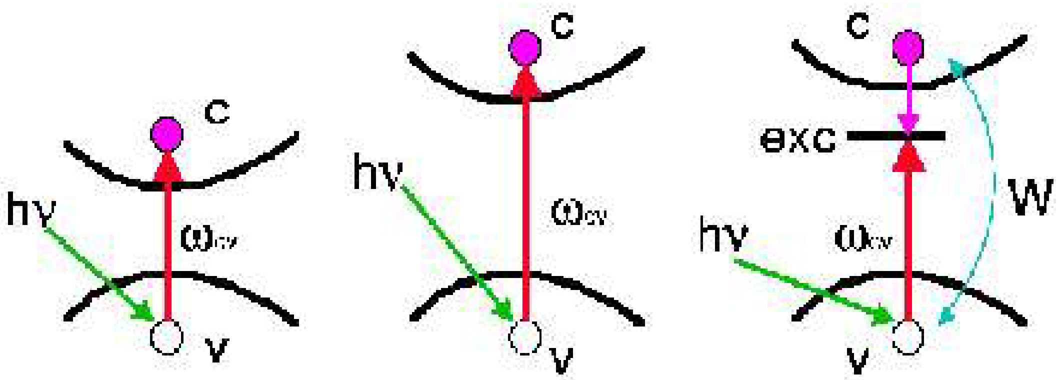
$$K\approx\int d^3r\int d^3r'\varphi_{j_0}(r)\varphi_{j_0}^*(r')\varphi_{k_0}(r')\varphi_{k_0}^*(r)\cdot\left(\frac{1}{|r-r'|}+f_{xc}(r,r')\right)$$

LDA- thick solid line

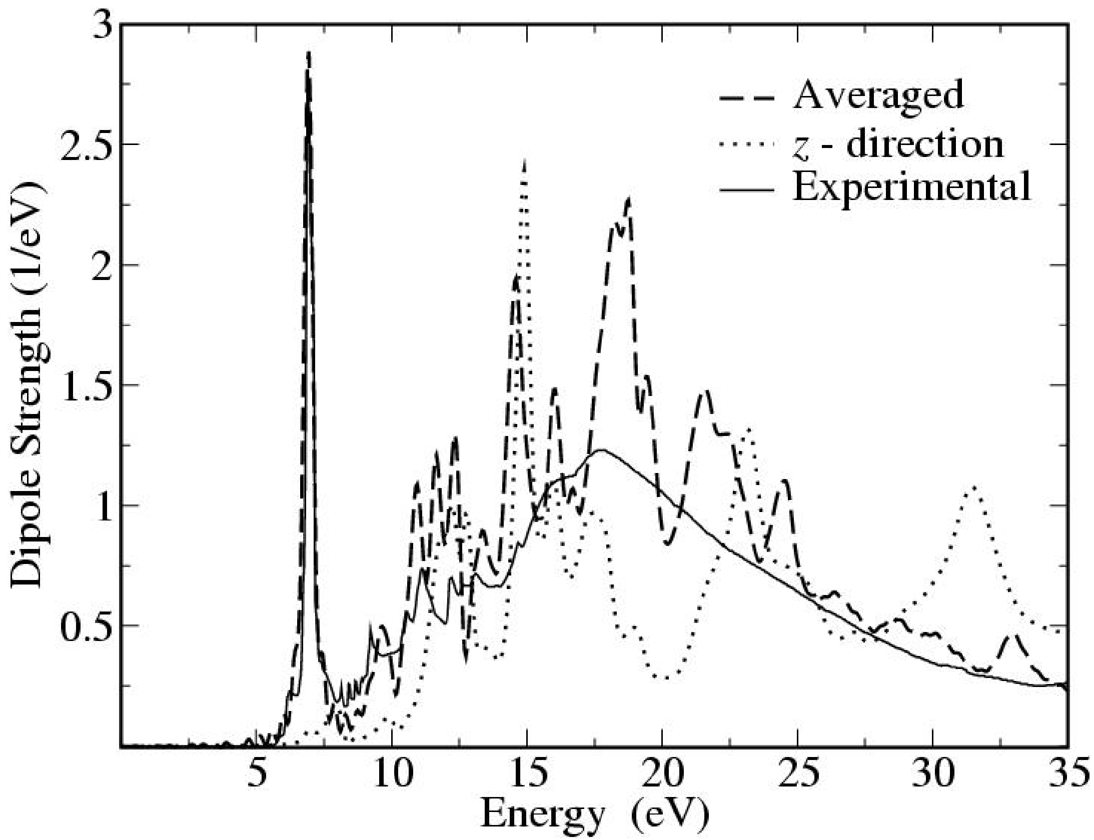
EXX- dotted line

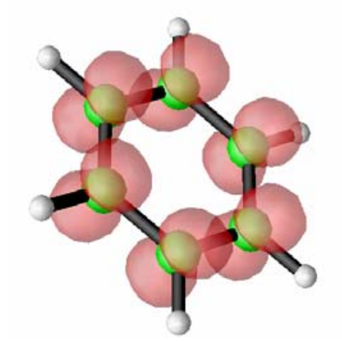
Bethe-Salpeter

Experiments



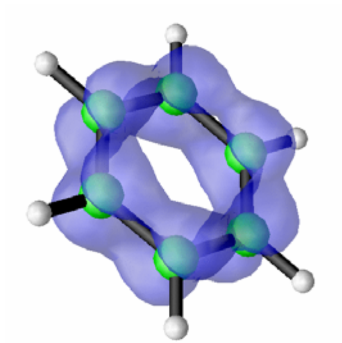
Optical response: (Benzene)





π* (LUMO)

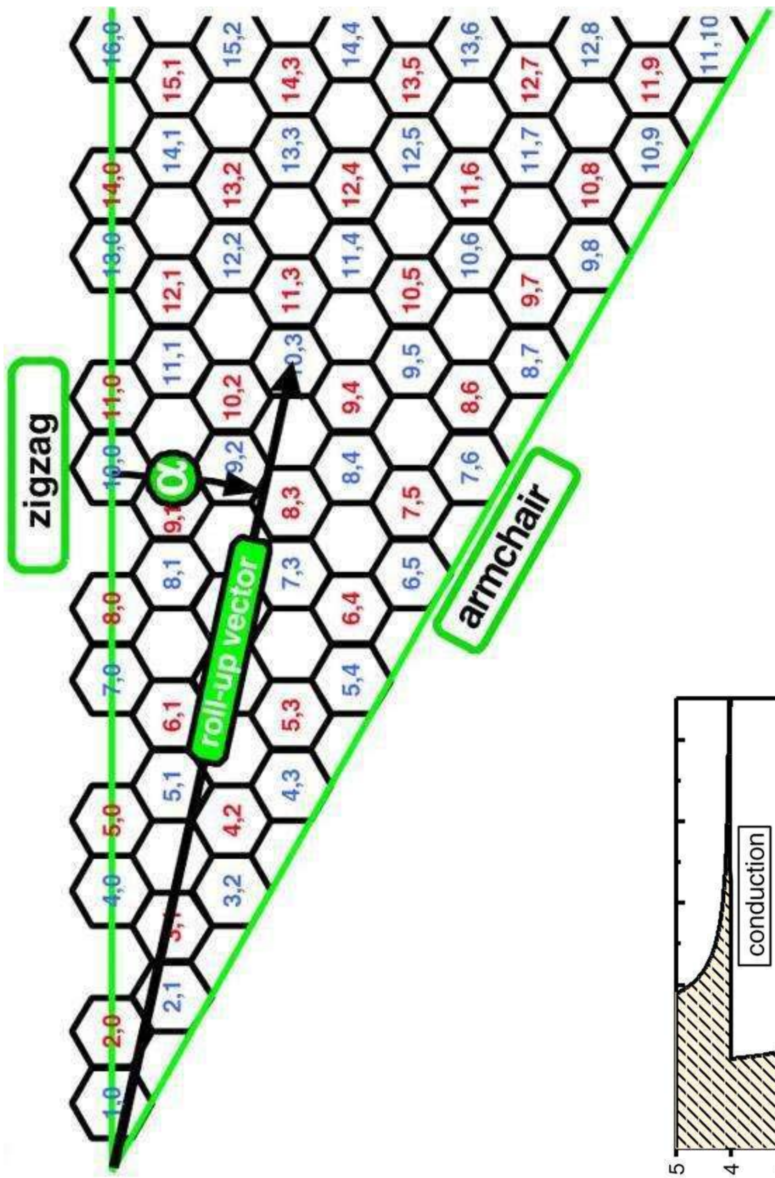
7eV



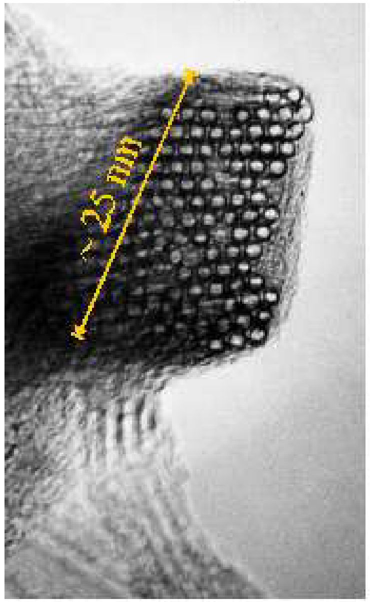
π (HOMO)

M.A.L Marques, A. Castro, G.F. Bertsch and AR, Comp. Phys. Comm. (2002);
K. Yabana and G. F. Bertsch, Int. J. Quantum Chem. 75, 55 (1999)

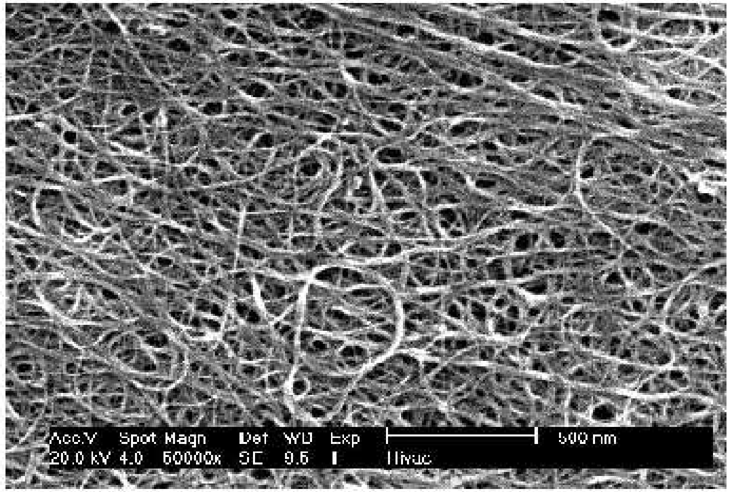
Carbon nanotubes: Iijima (1991)

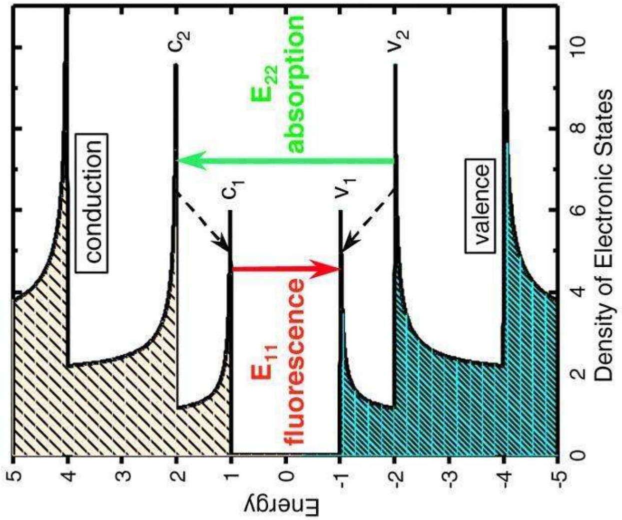


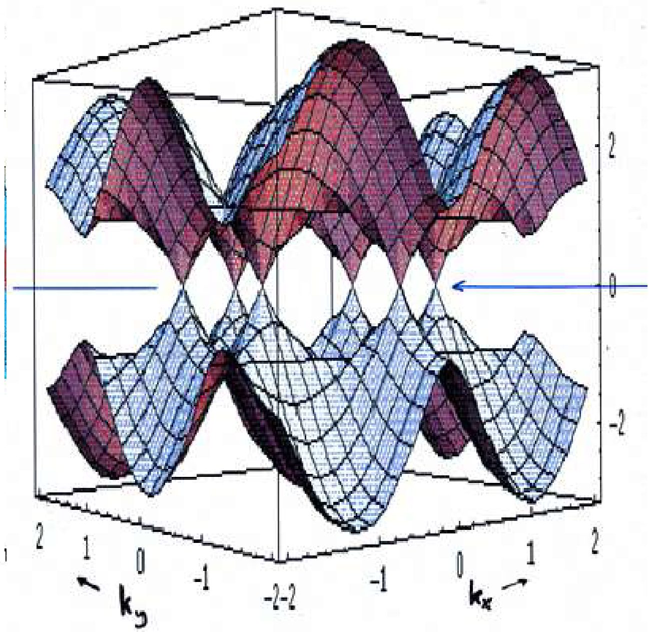
TEM of Rope



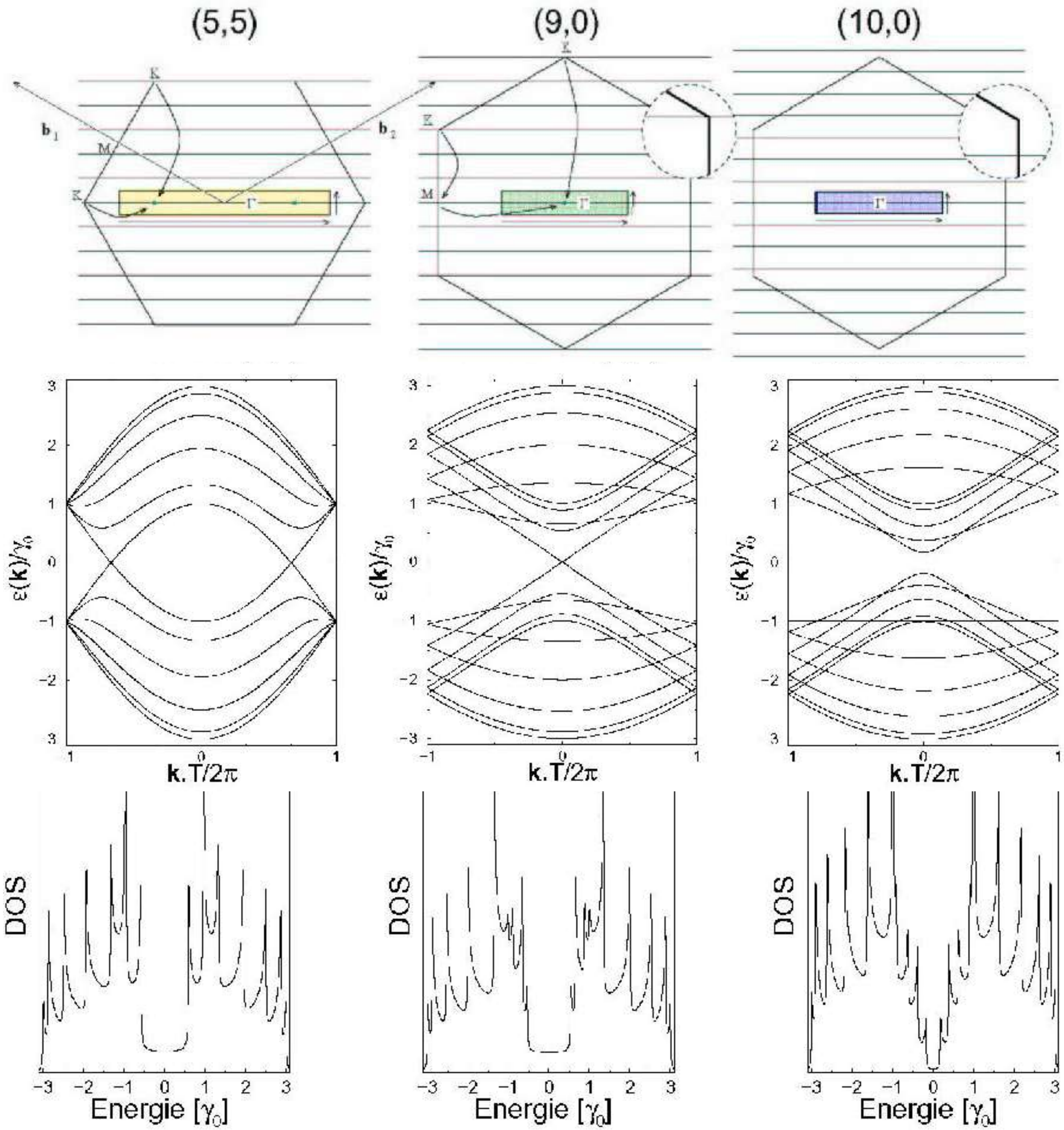
SEM: 'bucky-paper'

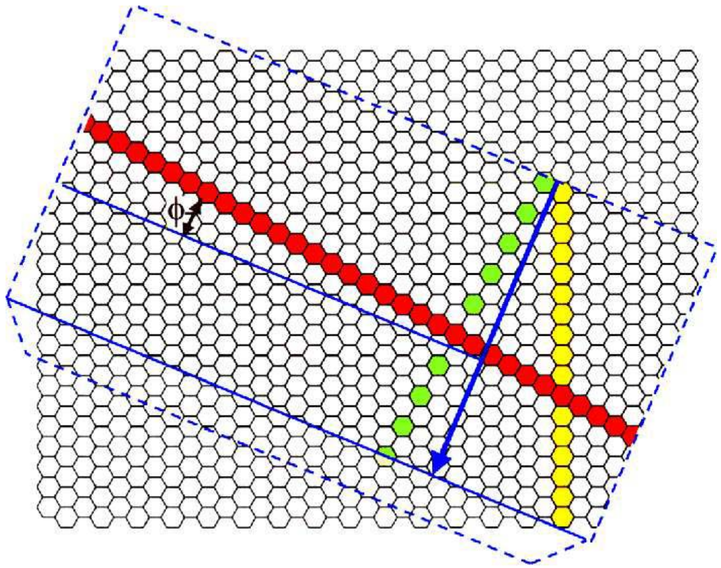


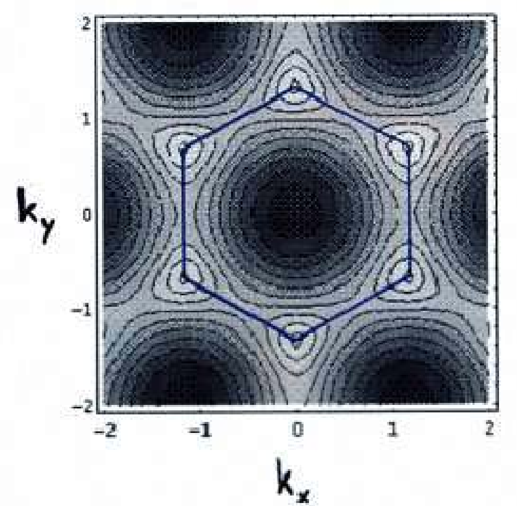




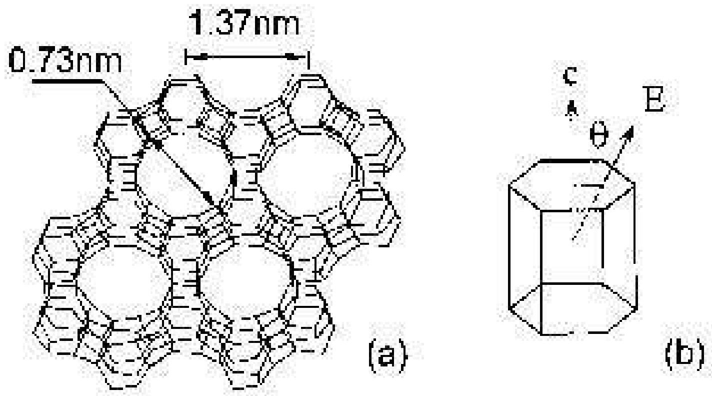
Simple model for the electronic structure: TB of C-tubes



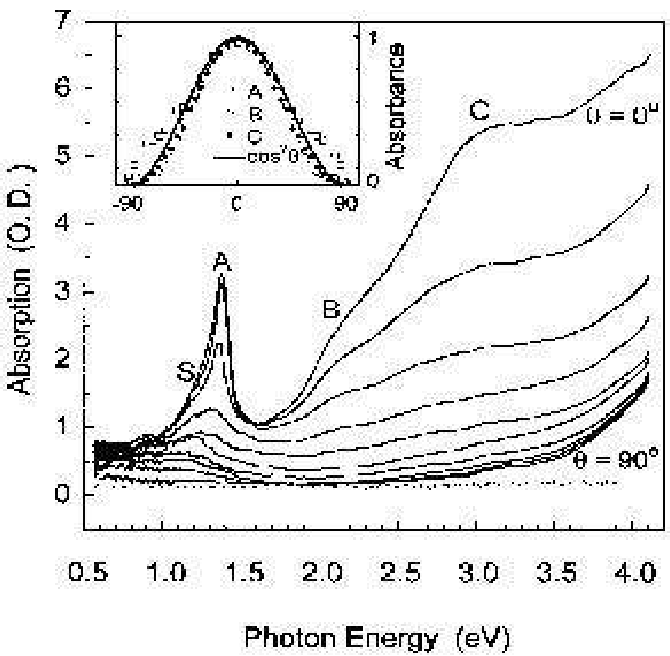




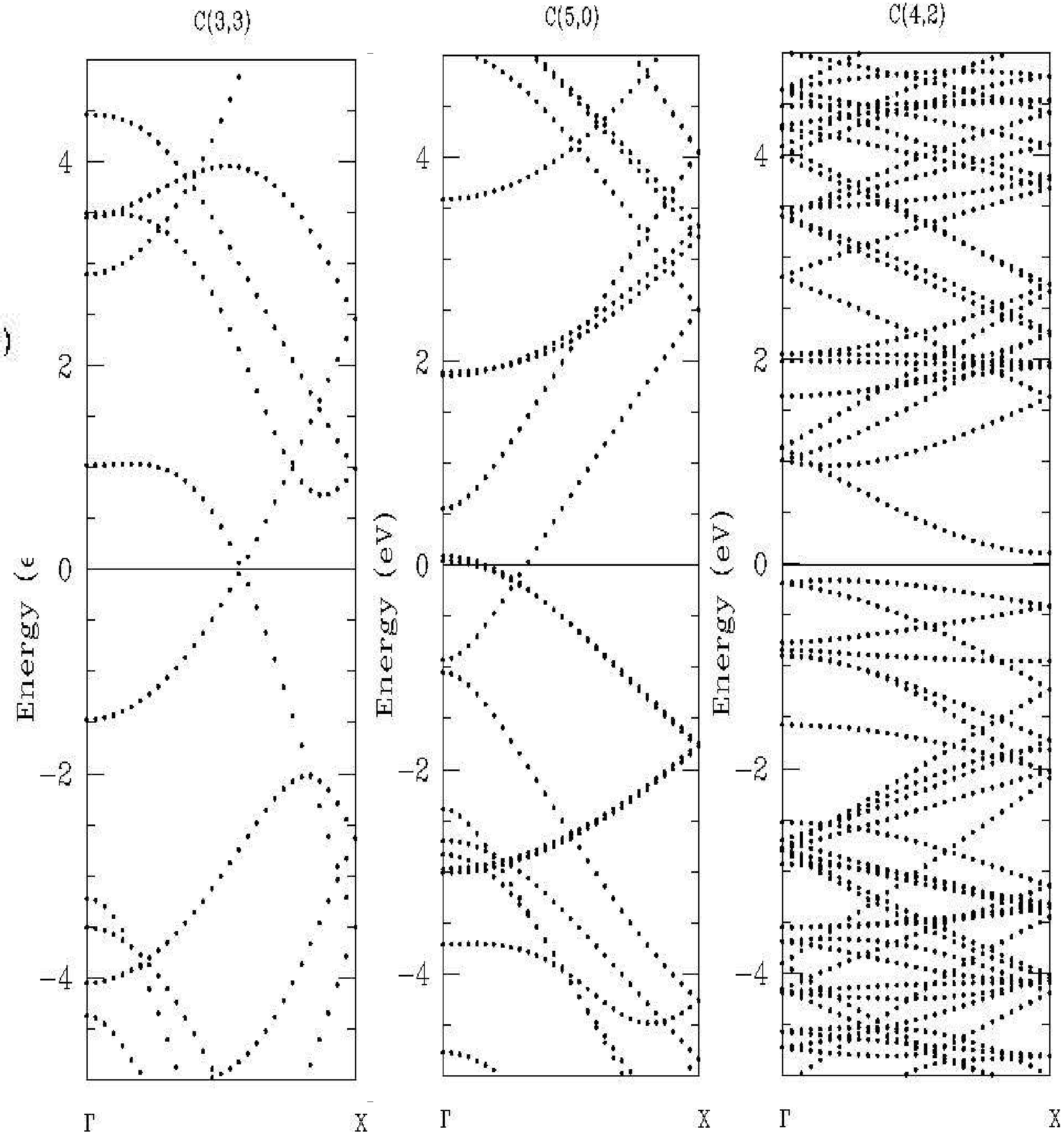
Optical Properties of C-Tubes: A way to elucidate tube-chirality



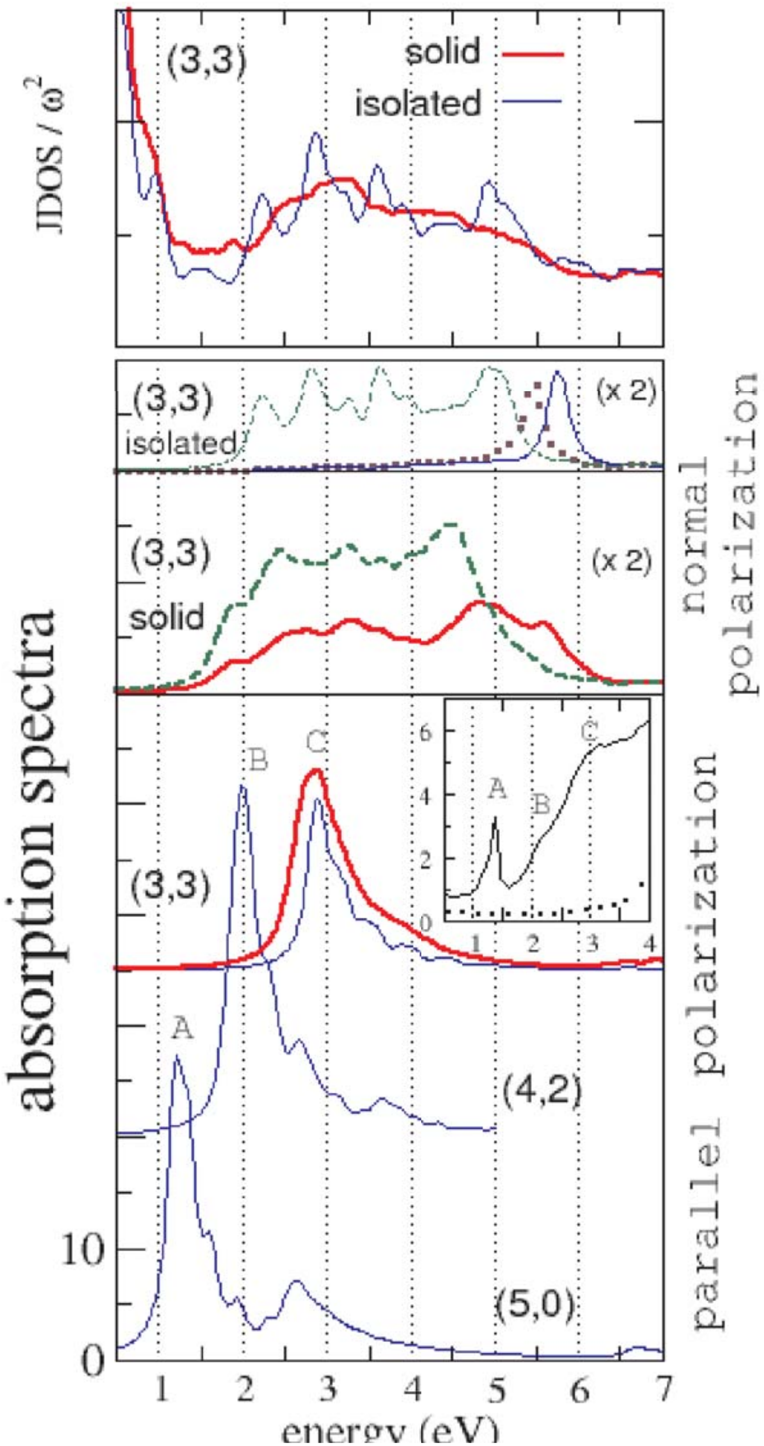
Zeolite type $AlPo_4$-5



Z.M..Lie et al, PRL (2001)



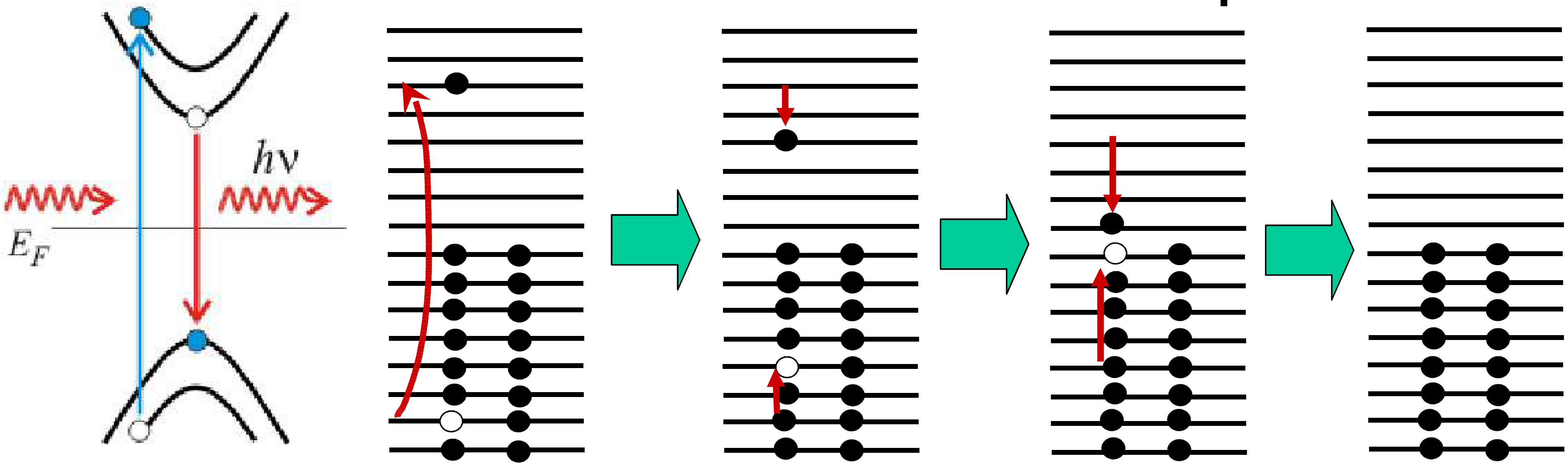
A.G. Marinopoulus, L. Reining, A.R. PRL (2003)



("*depolarization effects*")

Hot carrier relaxation in nanotube

Relaxation of hole and electron after photo-excitation



TDDFT-MD is parameter free and treats

* Time evolution of wave function with ionic motion: **electron phonon coupling**
*Time evolution of charge density: **electron-electron coupling** within DFT
* excitonic effects!!!!!!

Y. Miyamoto, D. Tomanek, AR (unpublished)

Ichida, et al., Physica B 323, 237 (2002)

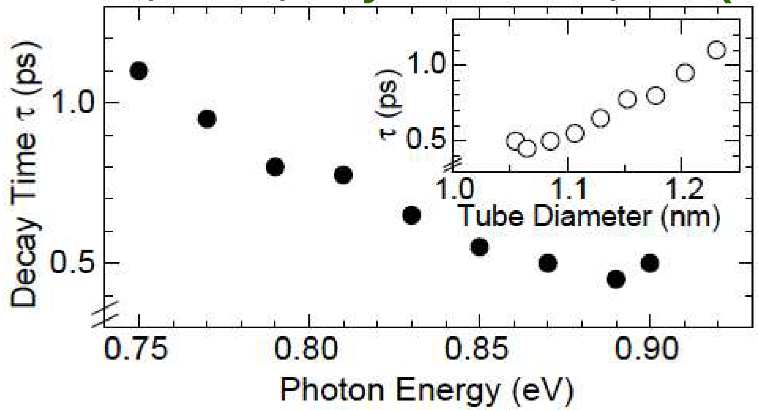
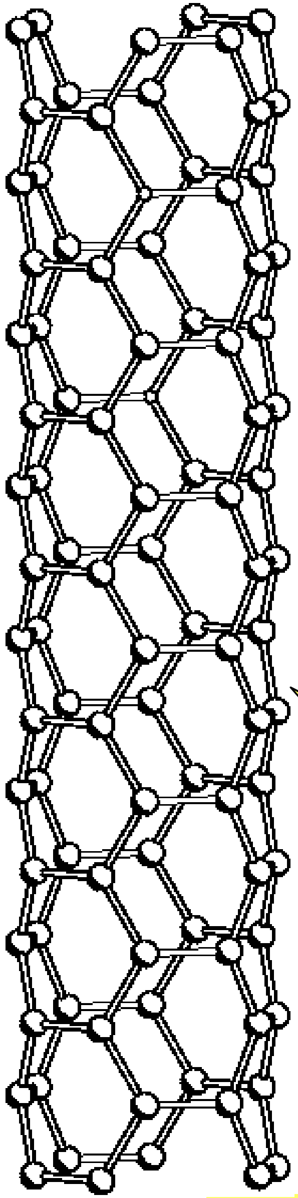


Fig. 2. Observed fast decay time as a function of probe photon energy. Inset: Tube diameter dependence of decay time.

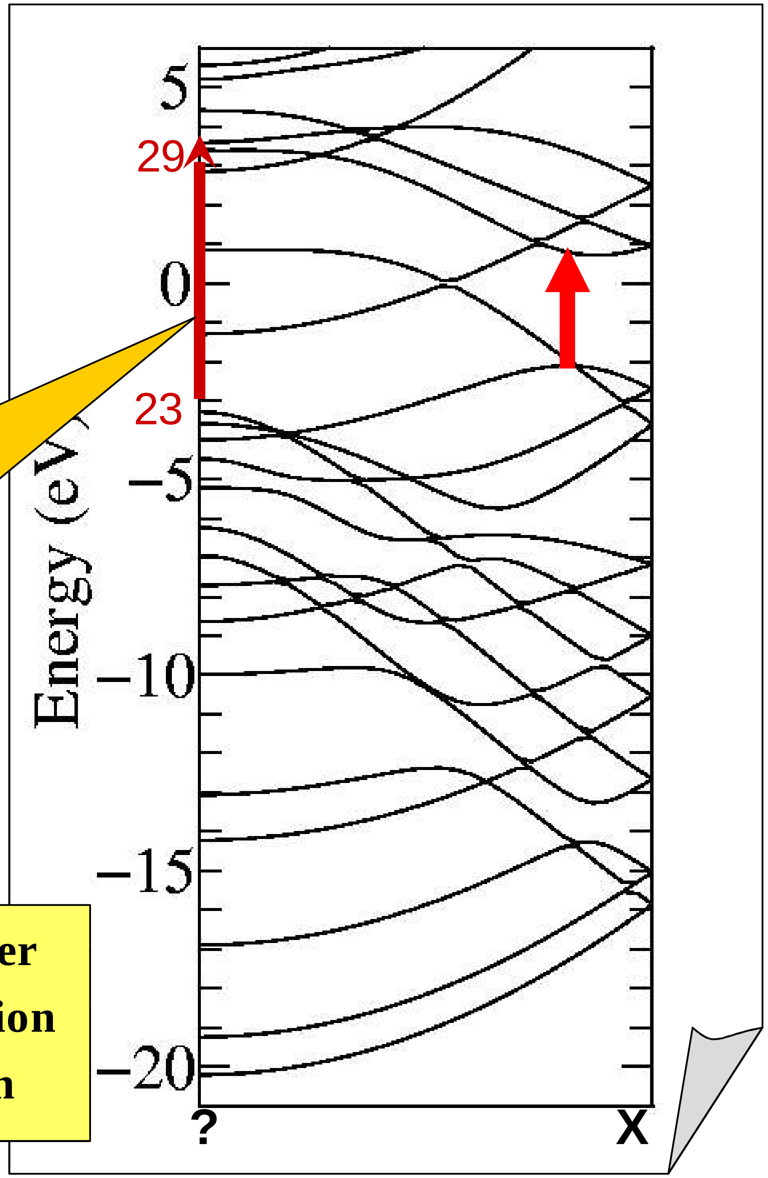
Present case: (3,3) nanotube



Assigned excitation with experimental data

[Z. M. Li et al, Phys. Rev. Lett. 87, 127401 (2001).]

Transition considered: Optically allowed, with E// (tube axis), but *not observed experimentally*!!



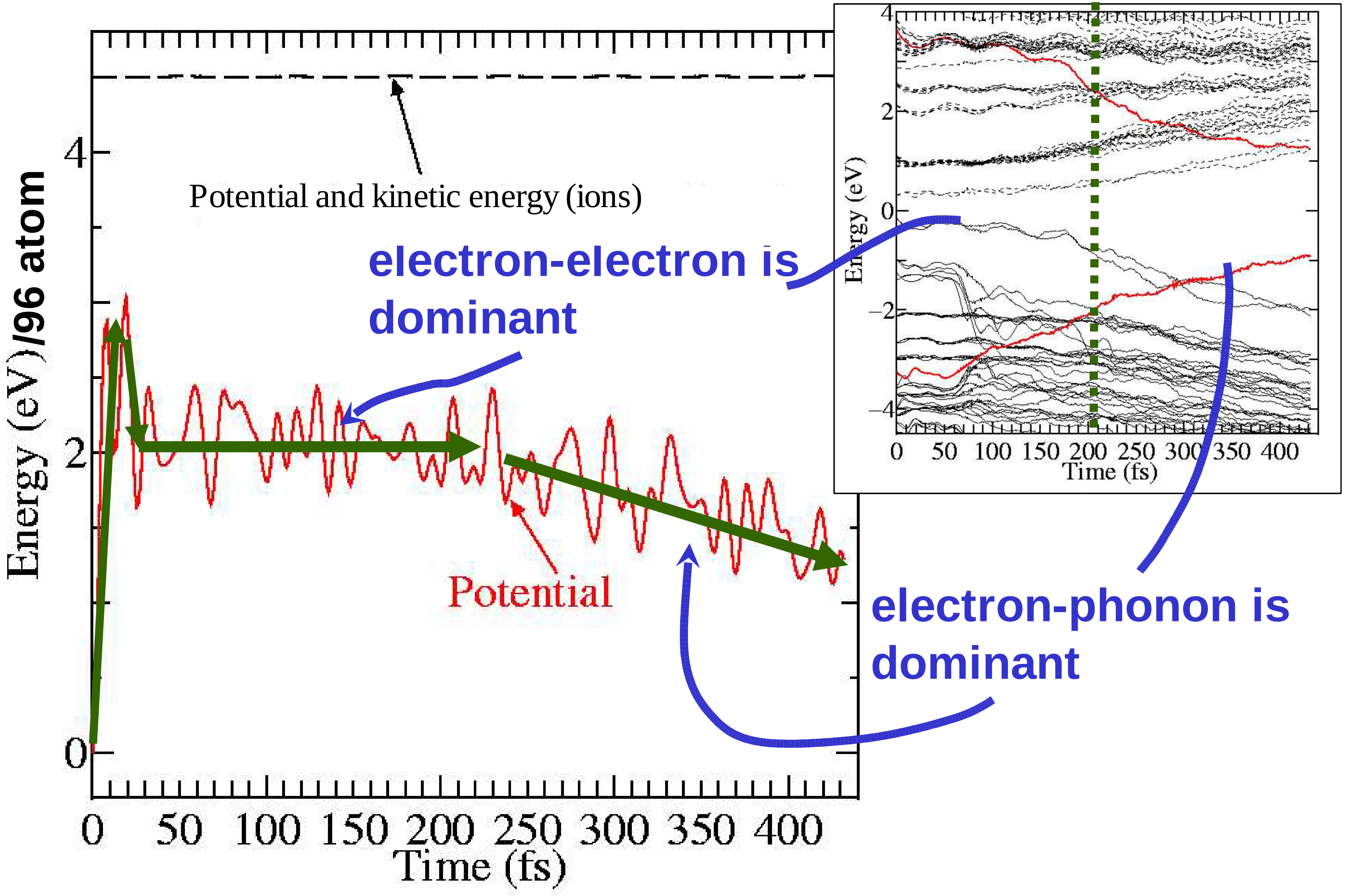
Randomized ionic velocities under the Maxwell-Boltzmann distribution with 300K as an initial condition

Computational conditions: TDLDA (with adiabatic xc potential)

Time step: 0.08 a.u. (=0.0019 fs)

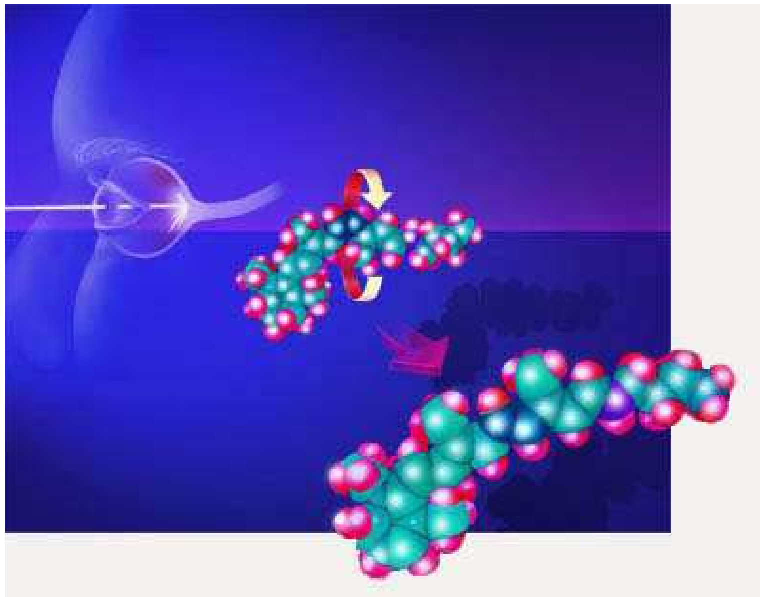
Energy transfer with longer time-scale

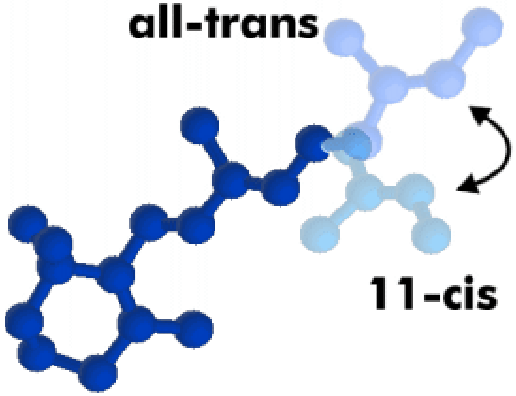
electron-electron vs. electron-phonon interaction on real-time axis

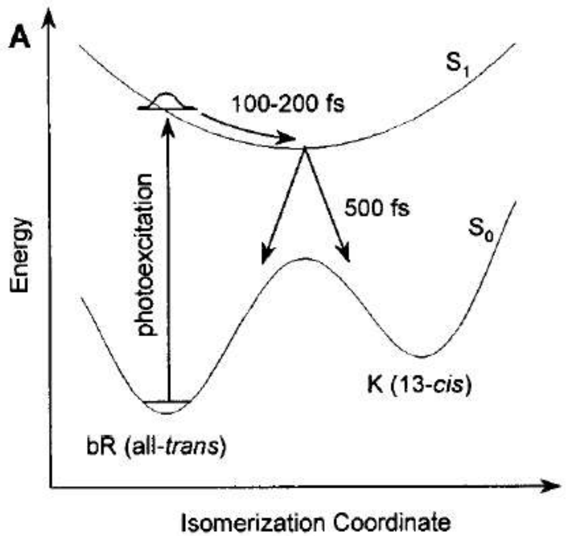


<u>Biological molecules: photoreceptors</u>

QM/MM + TDDFT   approach







F. Gai et al. Science <u>279</u>, 1886 (1998)

M.A.L Marques, X. Lopez, D. Varsano, A. Castro, and A. R. Phys. Rev. Lett. ***90****, 158101 (2003)*

Time Scales:

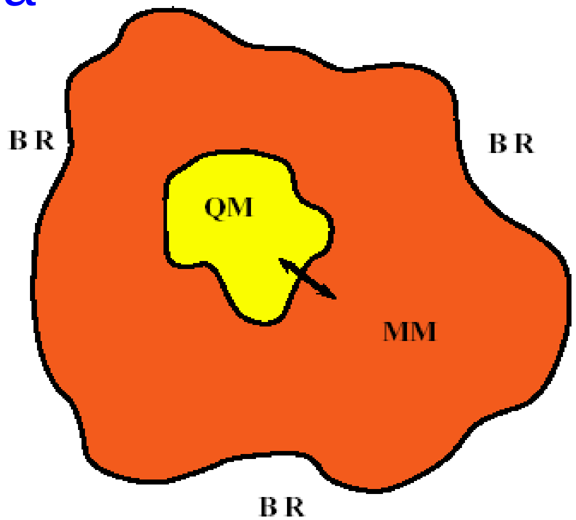
- Local Motions (0.01 to 5 Å, 10^{-15} to 10^{-1} s)
  - Atomic fluctuations
  - Sidechain Motions
  - Loop Motions
- Rigid Body Motions (1 to 10Å, 10^{-9} to 1s)
  - Helix Motions
  - Domain Motions (hinge bending)
  - Subunit motions
- Large-Scale Motions (> 5Å, 10^{-7} to 10^{4} s)
  - Helix coil transitions
  - Dissociation/Association
  - Folding and Unfolding

QM/MM Hamiltonian

For Local Phenomena

$$\widehat{H} = \widehat{H}_{QM} + \widehat{H}_{QM/MM} + \widehat{H}_{MM} + \widehat{H}_{boundary} + \widehat{H}_{restraints}$$

$$\widehat{H}_{QM/MM} = \widehat{H}^{elec}_{QM/MM} + \widehat{H}^{vdW}_{QM/MM} + \widehat{H}^{bonded}_{QM/MM}$$



1. Warshel , A.; Levitt, M. J. Mol. Biol., **1976**, *103*, 227

2. Field, M.J.; Bash, P.A.; Karplus, M. J. Comp. Chem., **1990**, *11*, 700

QM/MM Electrostatics

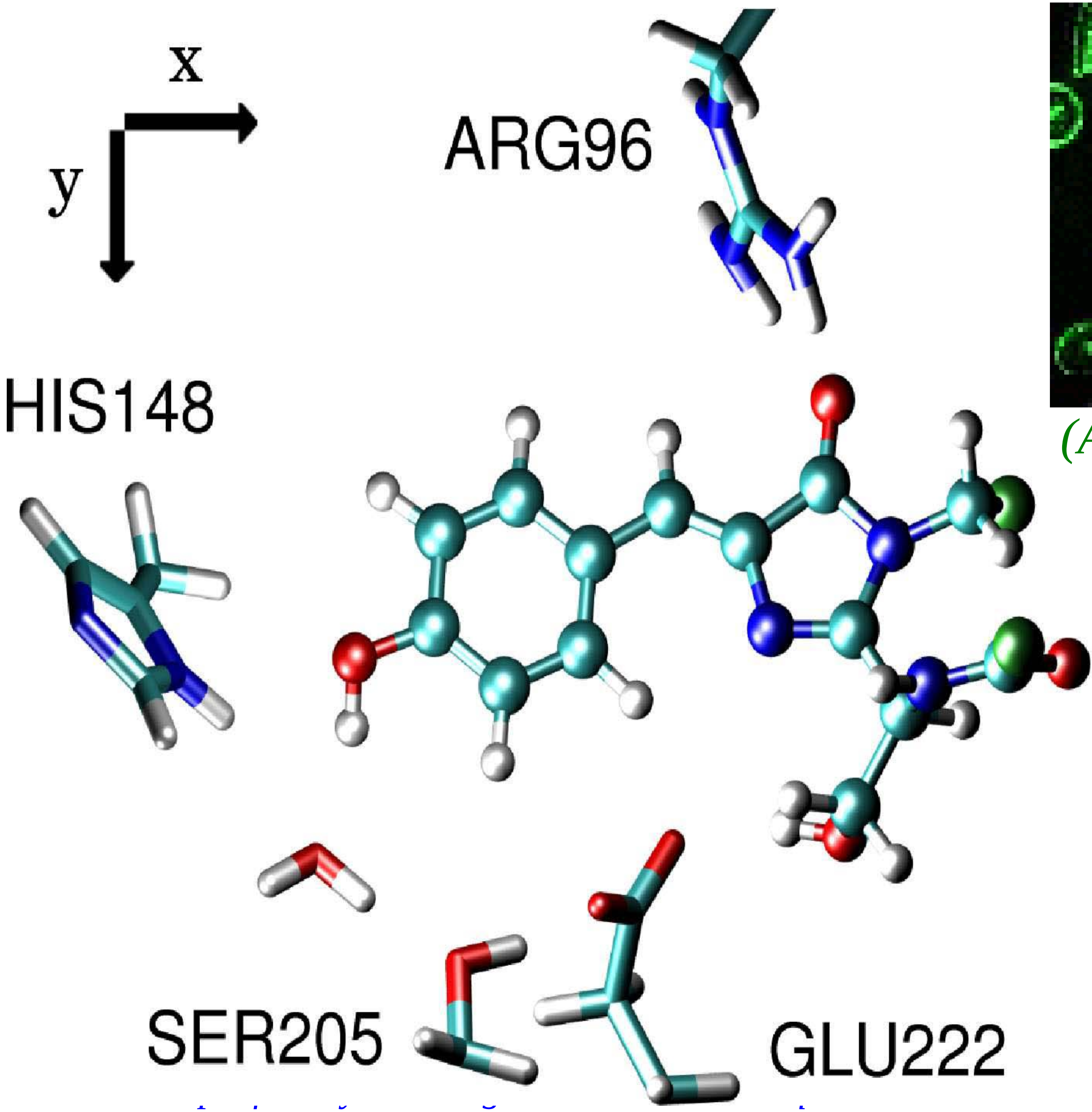
$$\widehat{H}^{elec.}_{QM/MM} = -\sum_{i,M} \frac{q_M}{r_{iM}} + \sum_{\alpha,M} \frac{Z_\alpha q_M}{R_{\alpha M}}$$

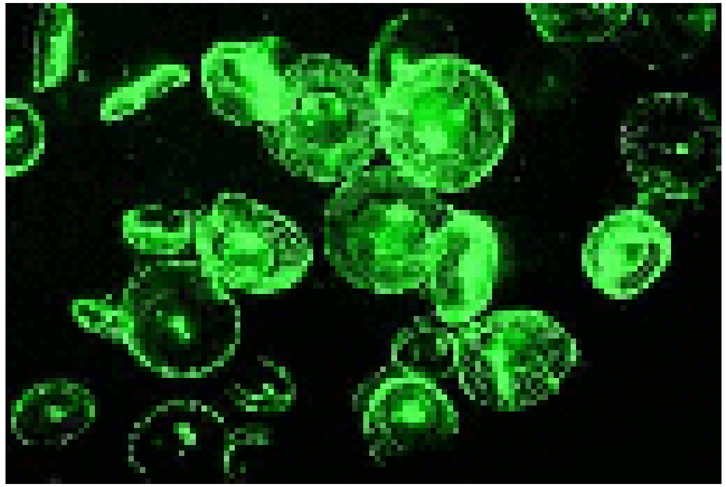
Van der Waals Interactions

$$\widehat{H}^{v.d.Waals}_{QM/MM} = \sum_{\alpha,M} \left[\frac{A_{\alpha M}}{R^{12}_{\alpha M}} - \frac{B_{\alpha M}}{R^{6}_{\alpha M}} \right]$$

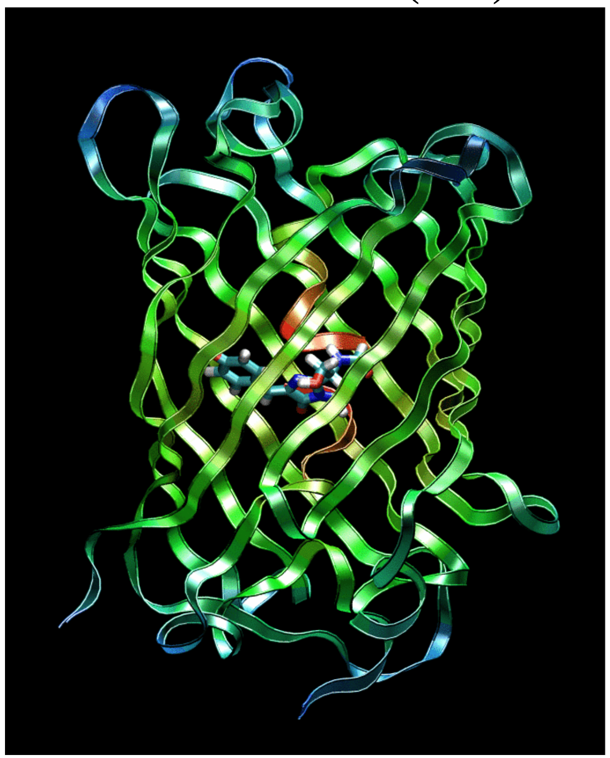
SCF

Towards understanding biomolecule colours



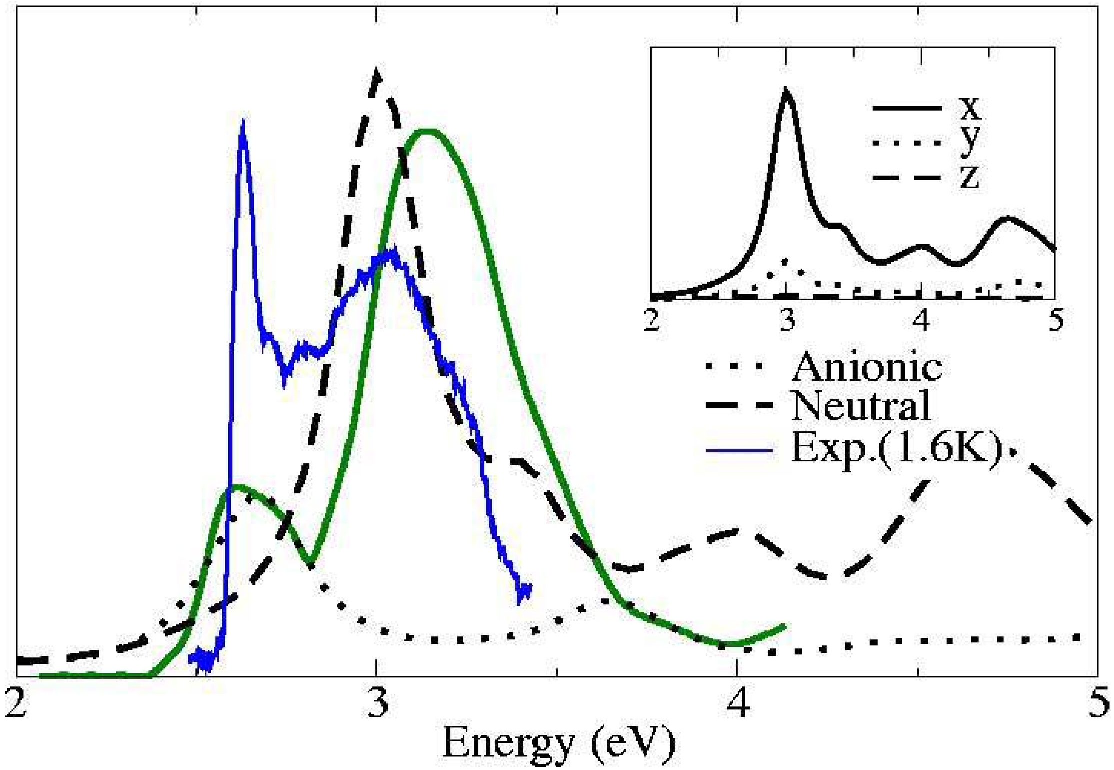


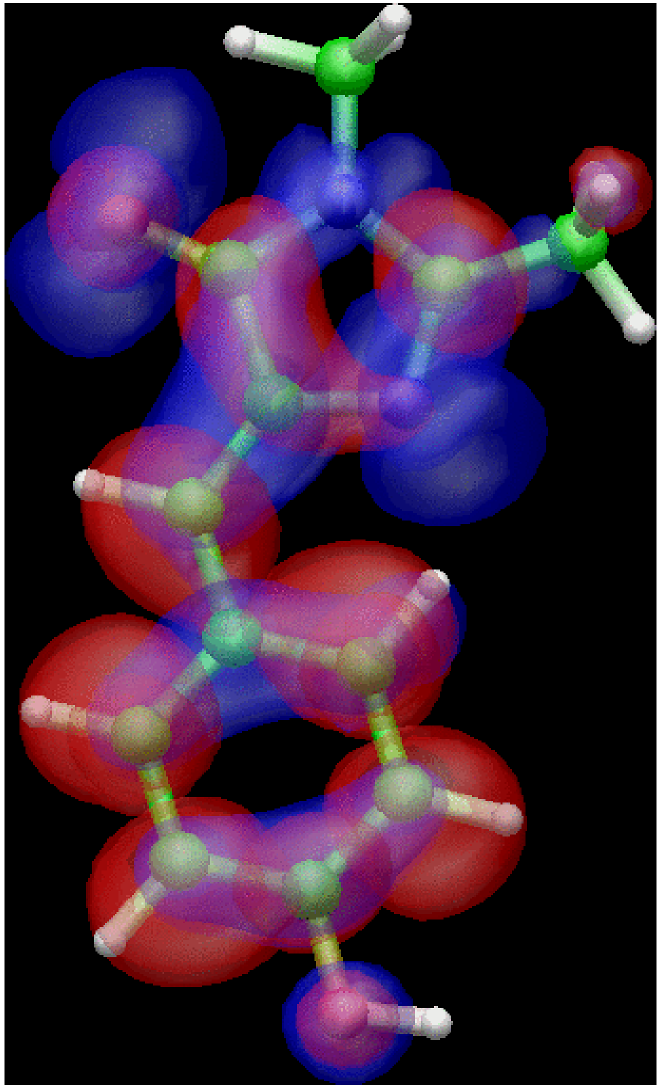
(Aequorea victoria: jellyfish)
Green Fluorescent Protein (GFP).



Towards understanding biomolecular colours: the GFP case

HOMO-LUMO

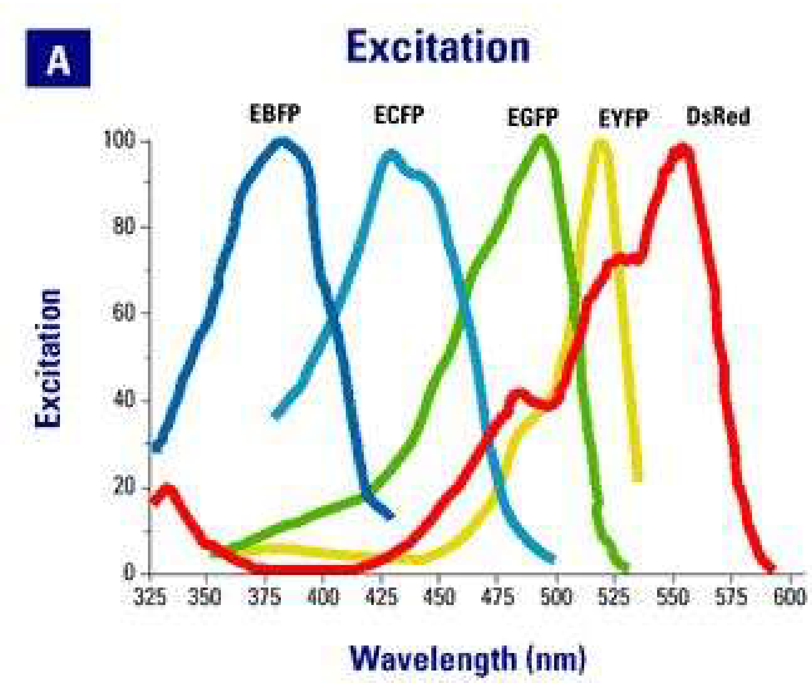


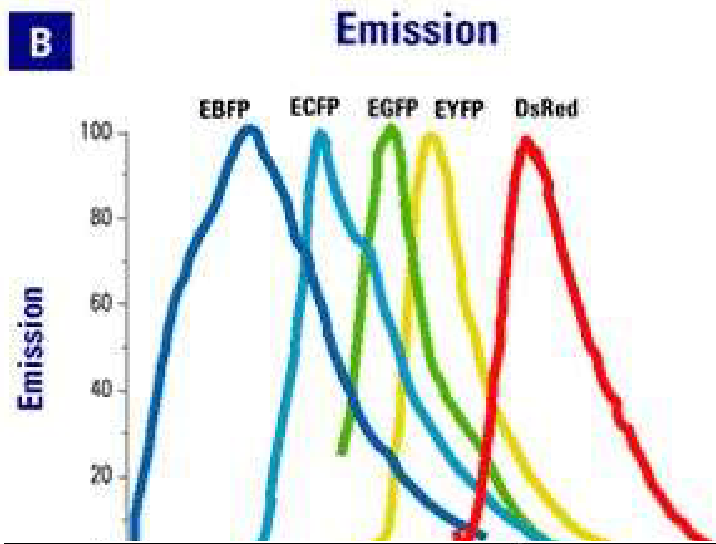


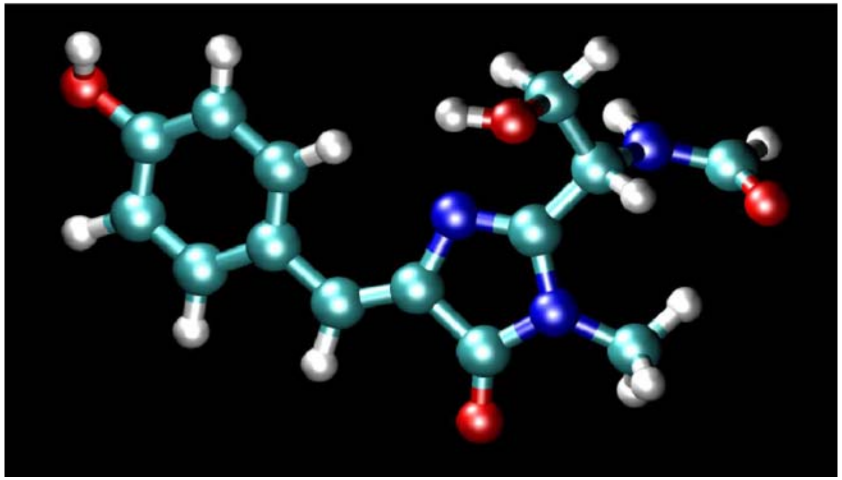
T.M.H. Creemers et al, Proc. Natl. Acad. Sci.. USA (1999)

QM/MM approach

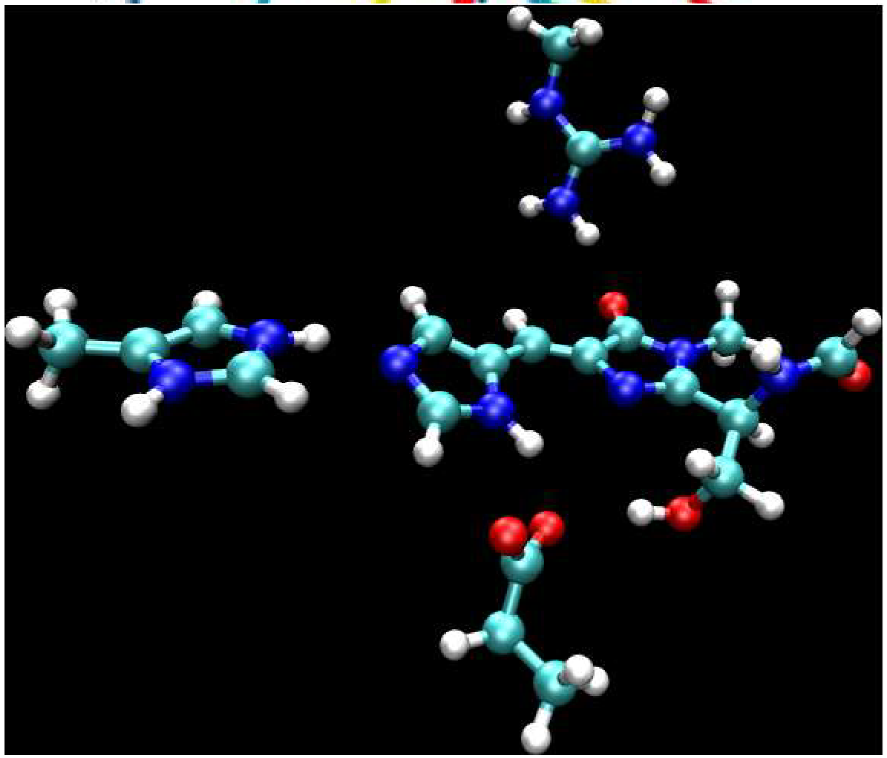
Blue Fluorescent Protein- Mutants

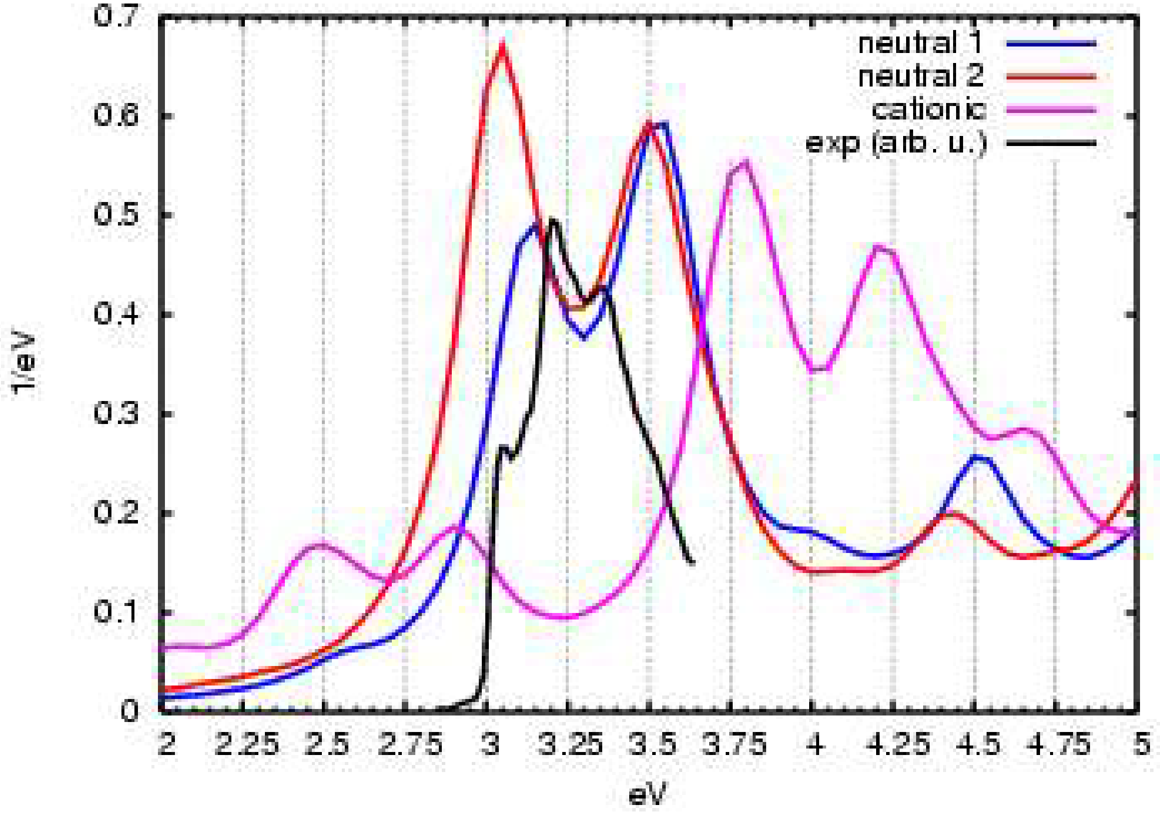


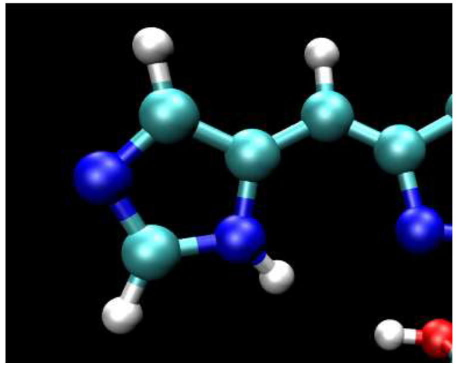




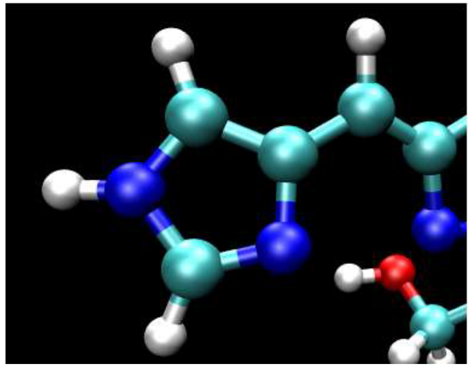
Green



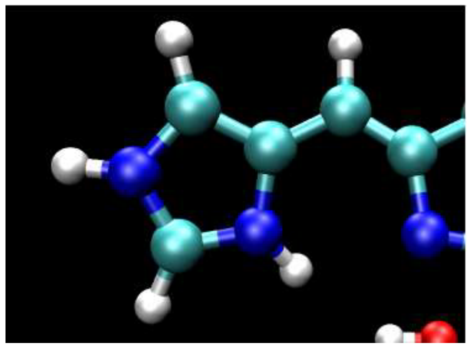




Neutral



Neutral

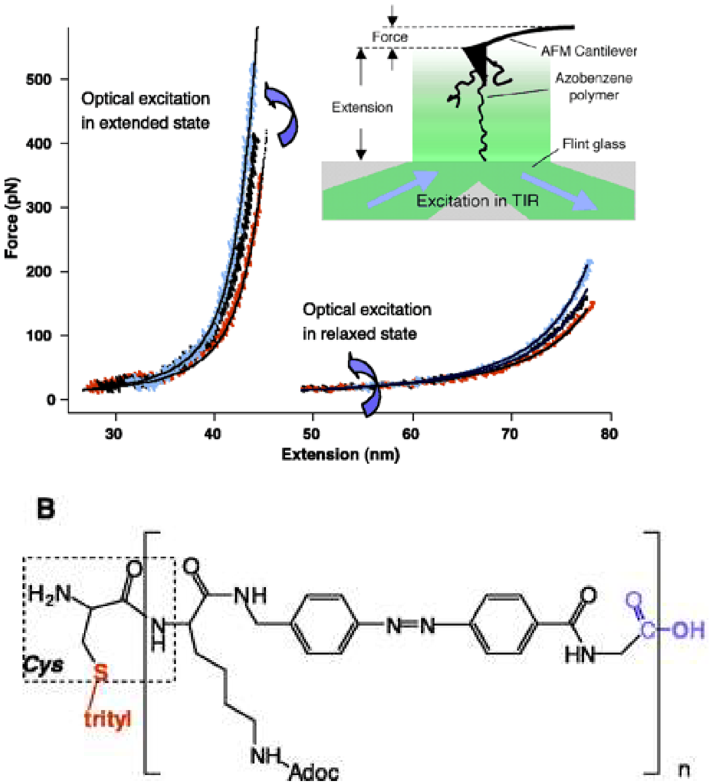


Cationic

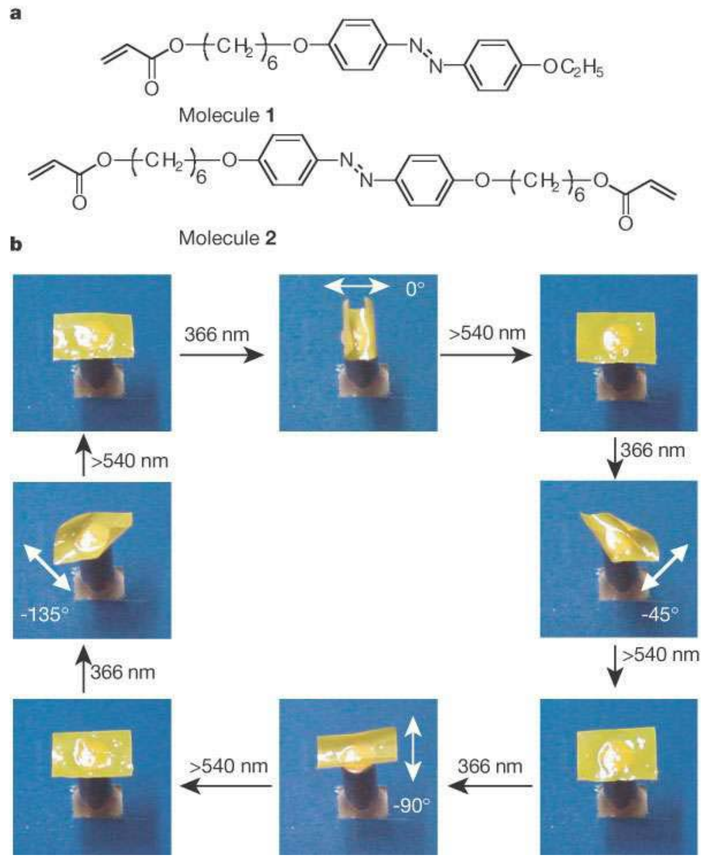
Azobenzene: spectroscopy along femtosecond-laser induced photoisomerization

Azobenzene dyes are known to isomerize at the central N-N bond within fractions of picoseconds at high quantum yield [T. Nägele et al, Chem. Phys. Lett. ***272****, 489 (1997)].*

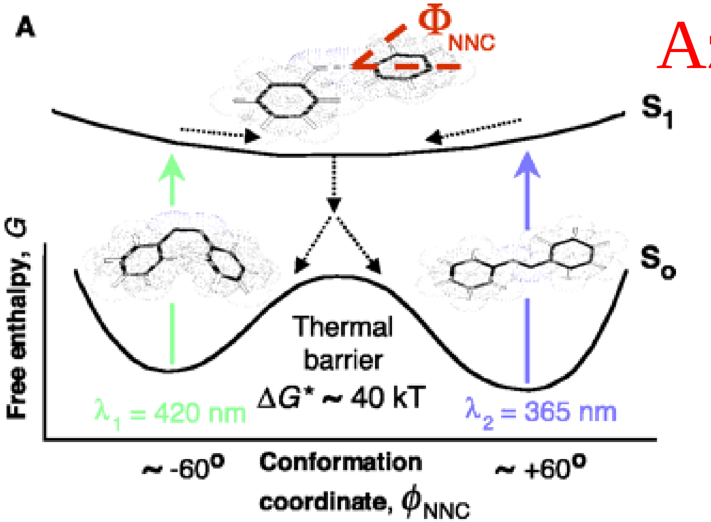
One example is the APB optical trigger: ***Single-Molecule Optomechanical Cycle***



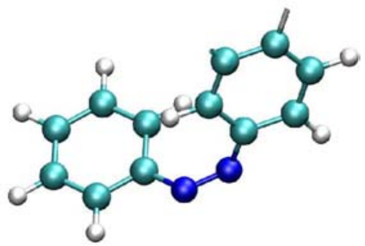
T. Hugel et al, Science, 296, 1103 (2002)

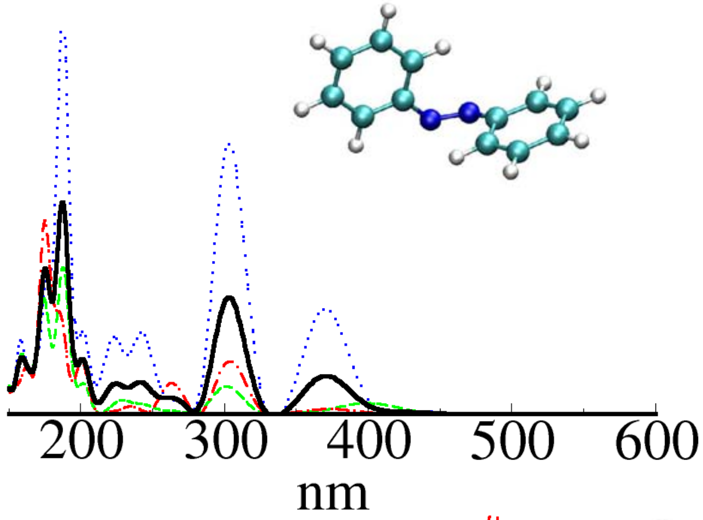


Y. Yu et al, Nature 425, 145 82003)

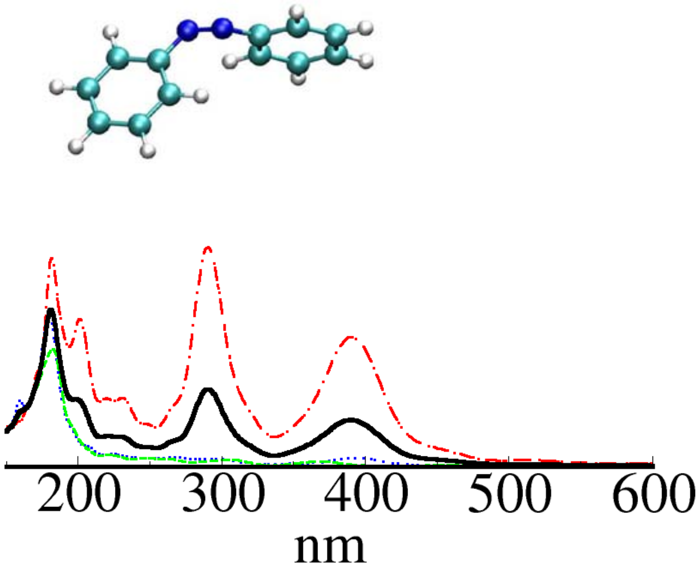


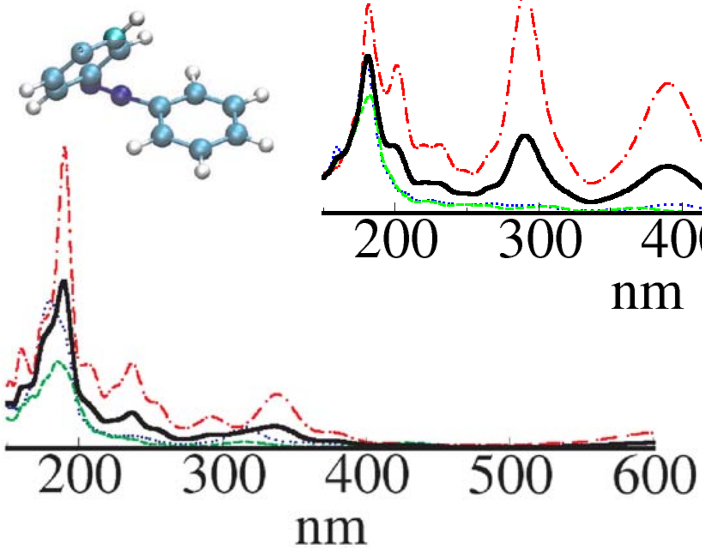
Azobenzene: spectroscopy along femtosecond-laser induced photoisomerization



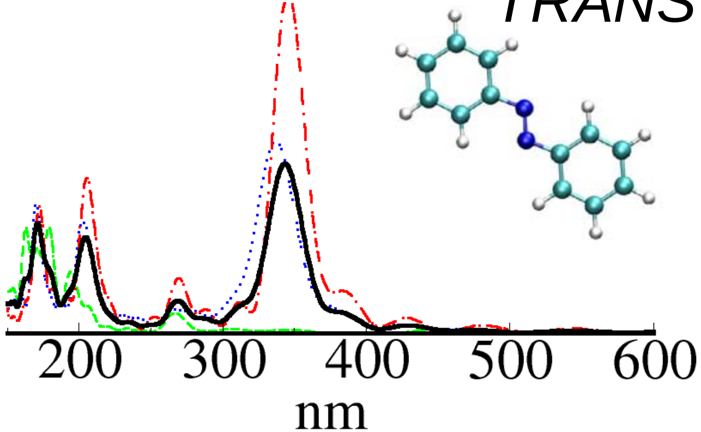


CIS





TRANS



Next step: QM/MM calculation of the chromophore+peptide system

Optical Rotatory Power

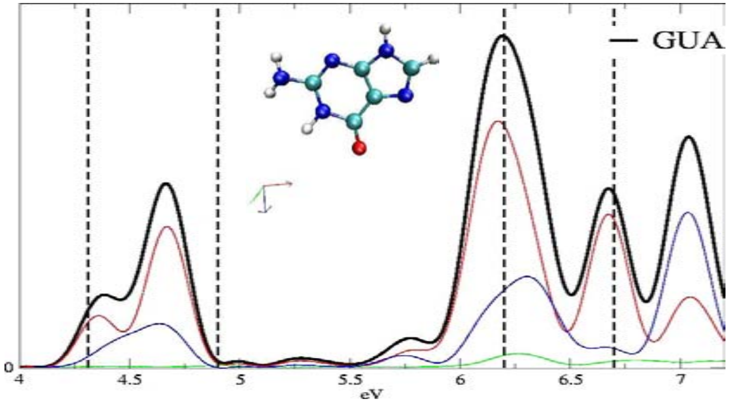
$$\Re_j(E)\propto\int_0^\infty dt\, e^{i(E+i\delta)t} L_j(t) \quad ; \quad \Re(E)=\Re_x+\Re_y+\Re_z$$

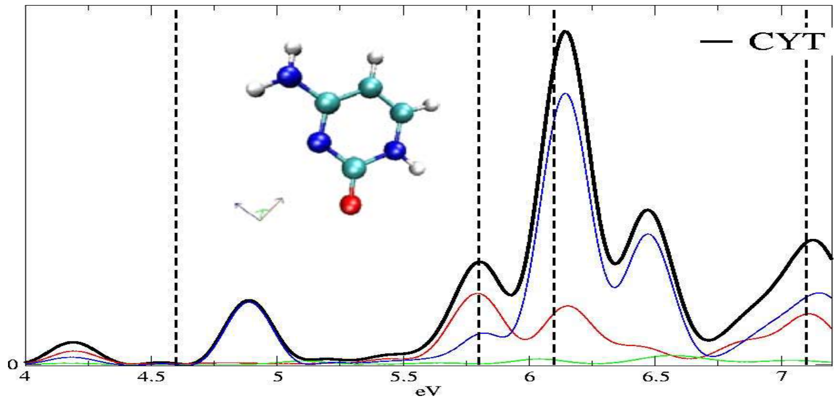
$$R(E)=\Im\frac{\Re(E)}{\pi}$$ rotational strenght function

Guanine

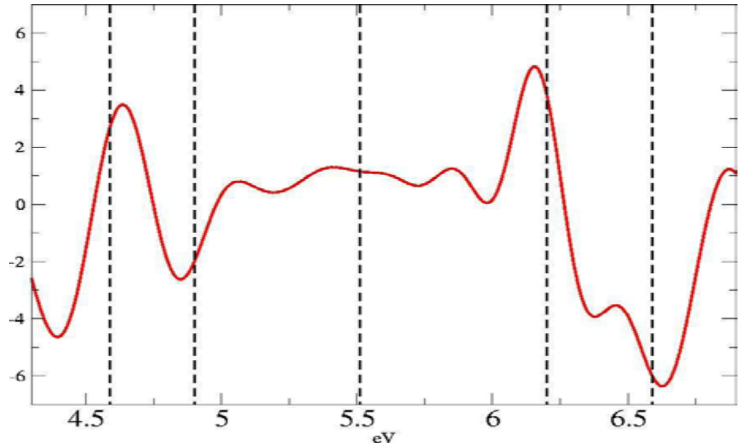
Cytosine

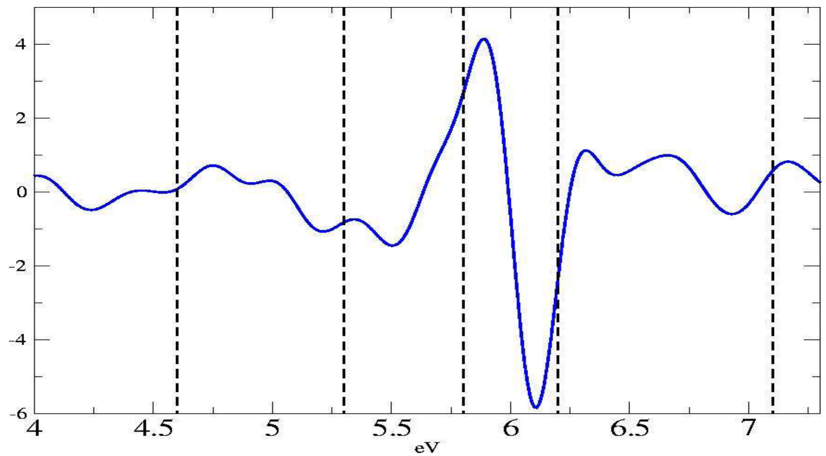
Absorption





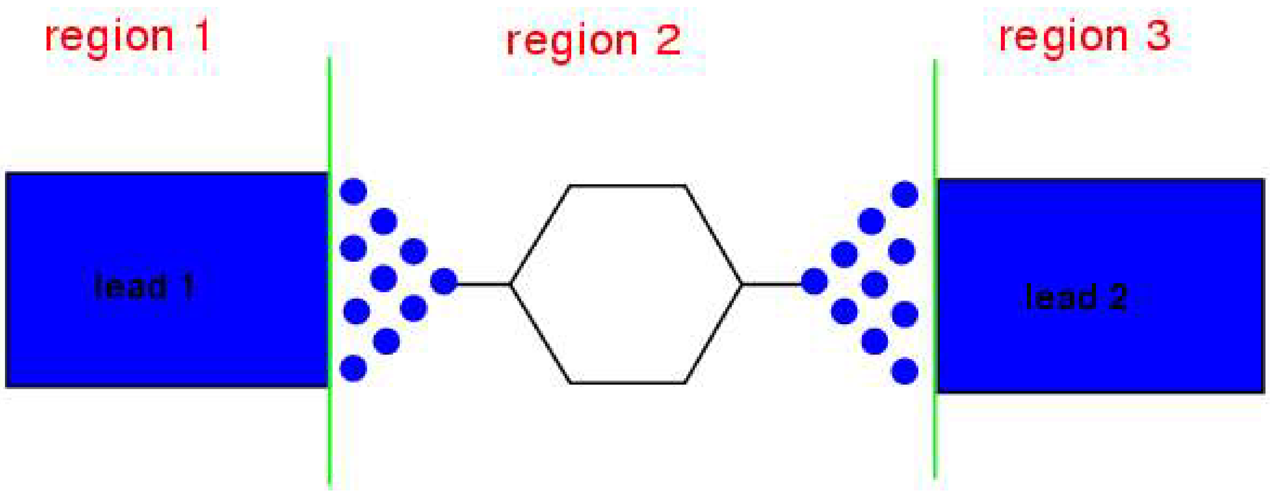
Circular dichroism





First principles description of Molecular transport ??????

In connection with Mark Ratner Lectures!



- (Landauer): Non equilibrium Green's Functions

$$G=\frac{2e^2}{h}Tr[G^R(w)\Gamma_L(w)G^A(w)\Gamma_R(w)]$$

- *TDDFT? -----TD-Current-DFT*

QUESTIONS?

- ✔Ground-state DFT?
  - *J(r,t); virtual exc.*
- ✔Temperature
  - *e-phon coupling?*
- ✔Dissipation??
- ✔Finite bias (resonant)
- ✔AC transport
- ✔Role of contacts
- ✔*MOLECULE*

Friday

III. Extended systems: problems and new developments

Calculation of optical properties

Optical absorption

$$\chi(\omega)=\chi_0(\omega)+\chi_0(\omega)(v+f_{xc}(\omega))\chi(\omega)$$

$$\sigma_{abs}(\omega) \propto Im(\epsilon(\omega))$$

$$EELS \alpha \epsilon^{-1}(\omega)=1+v\chi$$

Dielectric function in Random Phase Approximation (RPA)

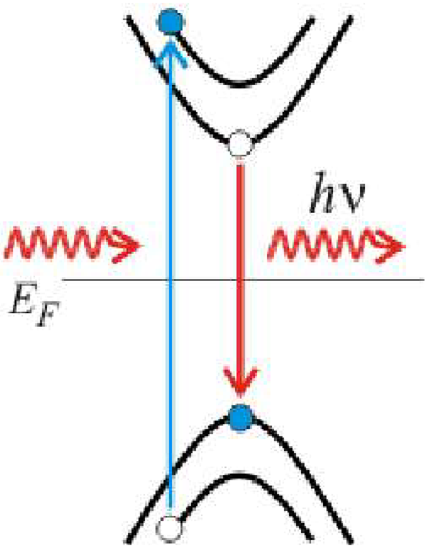
$$\epsilon_{RPA} = 1 - v_c \chi^{(0)}$$

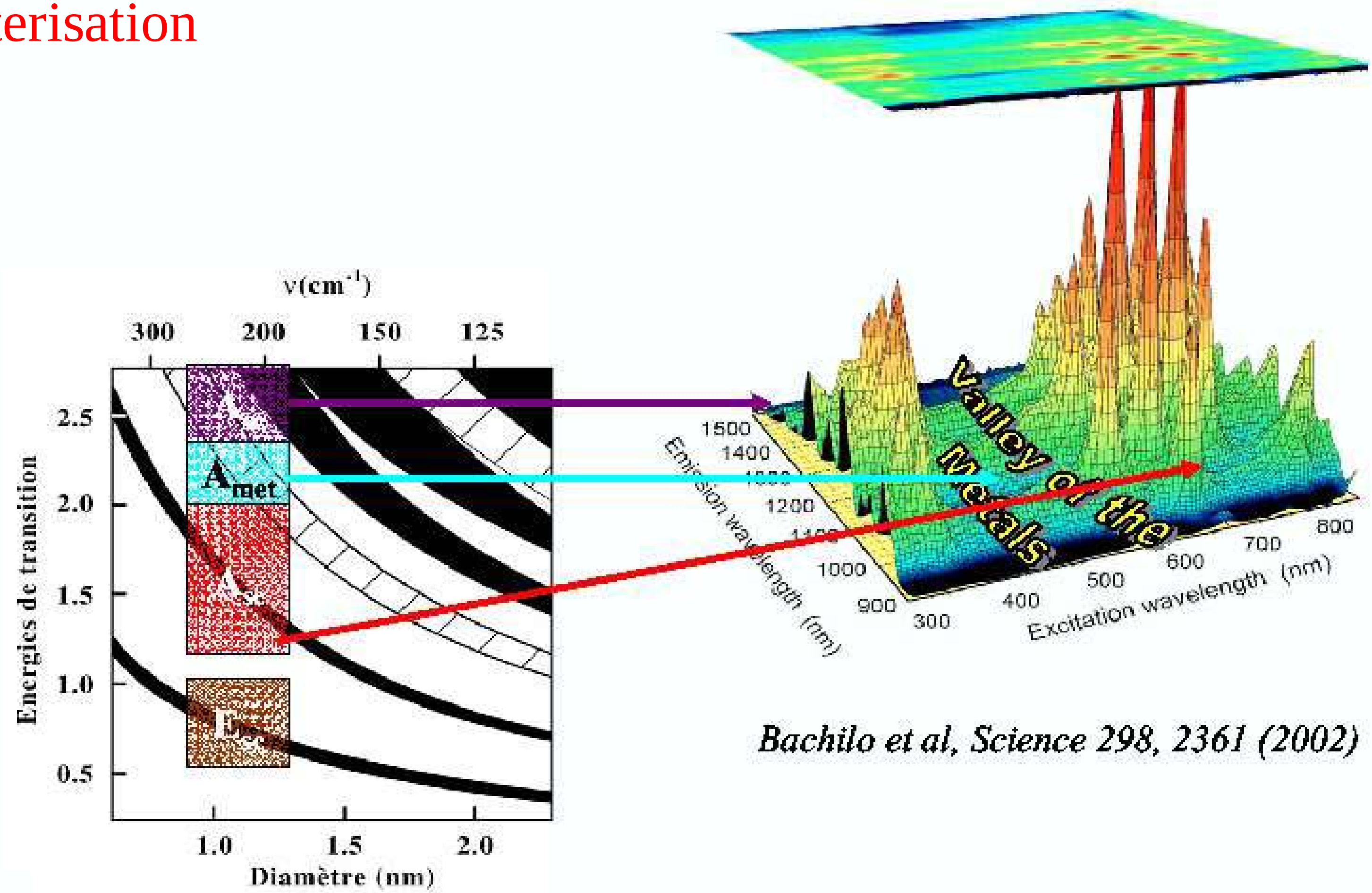
$$\chi^{(0)}(r, r', \omega) = 2 \Sigma_{i \neq j} (f_i - f_j) \frac{\phi_i(r)\phi_j^*(r)\phi_i^*(r')\phi_j(r')}{\epsilon_i - \epsilon_j - \omega - i\eta}$$

Macroscopic ε with local field effects (LFE):

$$\epsilon_M(\omega) = 1/\epsilon^{-1}_{G=G'=0}(q \to 0, \omega)$$

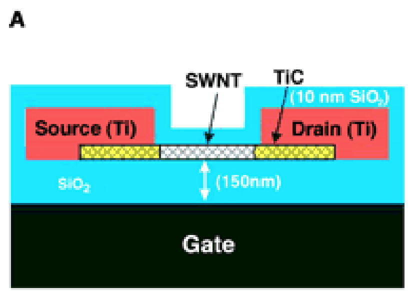
Tube (n,m) characterisation

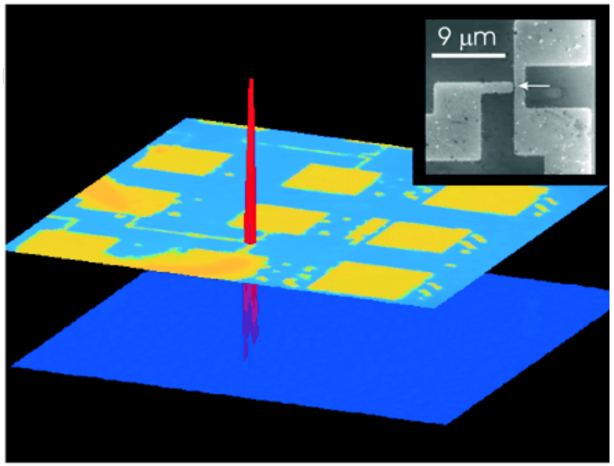




Bachilo et al, Science 298, 2361 (2002)

[Optical FET device!!!!!!]





J. A. Misewich, et al Science 300, 783 (2003)