Ultrafast Transfer Processes in Molecular Nanostructures

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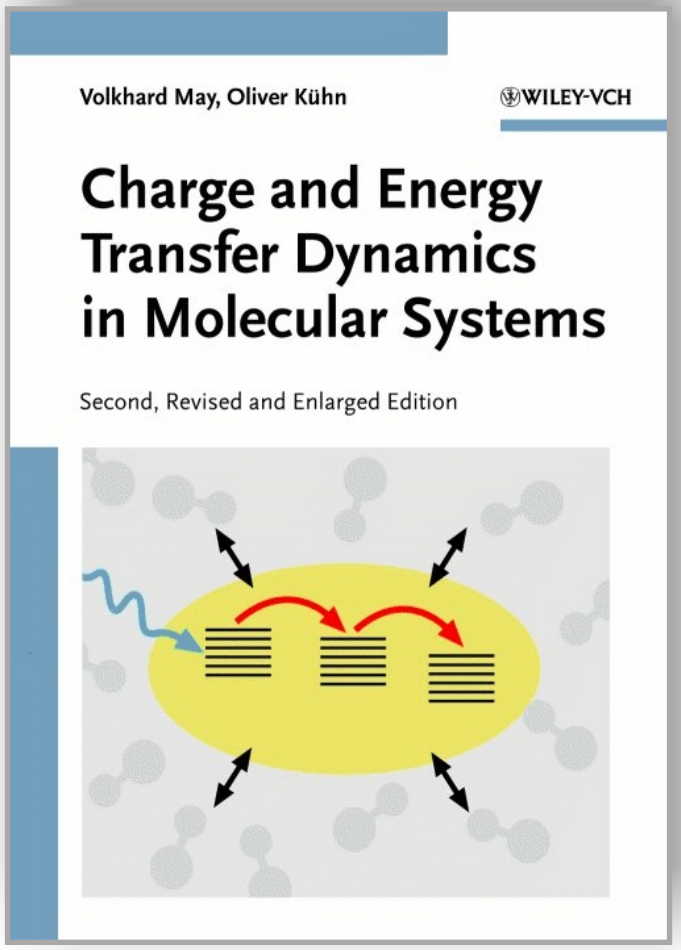
Humboldt-University at Berlin

Chemical Physics
Physical Chemistry
Spectroscopy
Nanotechnology

Quantum Dynamics of Molecular Systems

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Quantum Transport in Molecular Systems

Theory

- photoinduced quantum dynamics in closed and open systems
- wave packet dynamics
- density matrix theory
- computation of optical signals
- mixed quantum-classical description
- electron structure calculations
- MD simulations

Experiment

- relation of transient optical and infrared signals to molecular dynamics
- laser pulse control of molecular dynamics

Systems and Processes to be Discussed

introductory examples
- electron transfer in donor-acceptor systems
- charge transfer through single molecules
- dynamics of Frenkel excitons
- laser pulse control

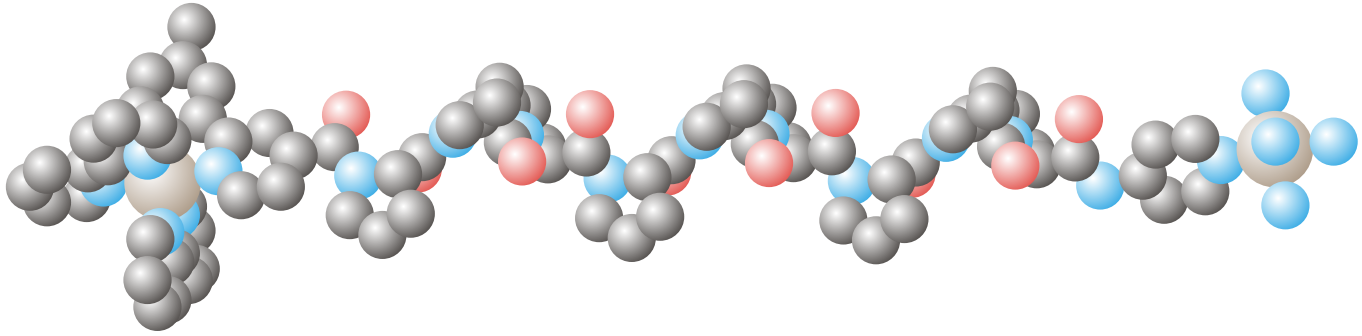
laser pulse control of non-adiabatic transitions

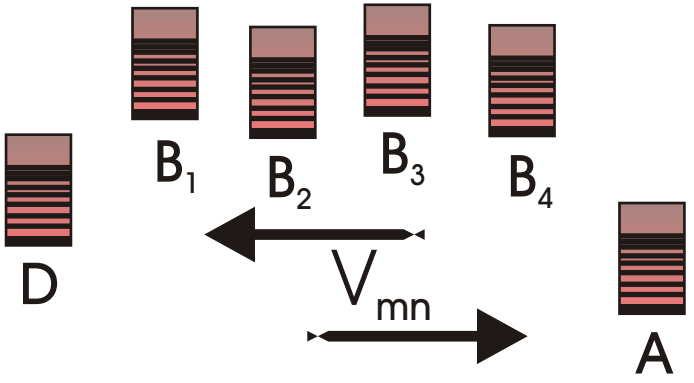
heterogeneous electron transfer

excitation energy transfer in supramolecular complexes

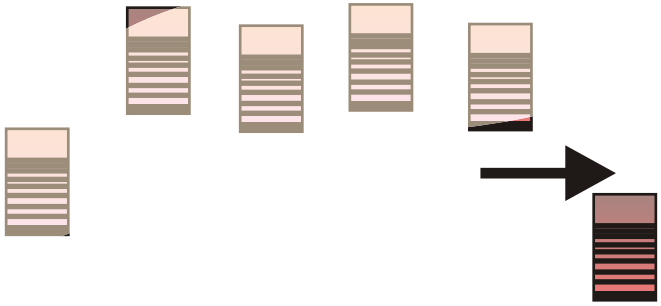
Introductory Examples

Polyproline Mediated Electron Transfer

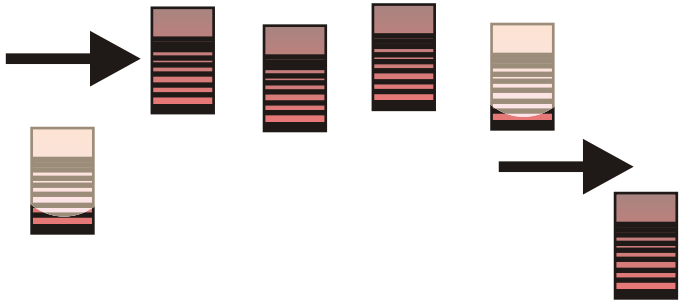


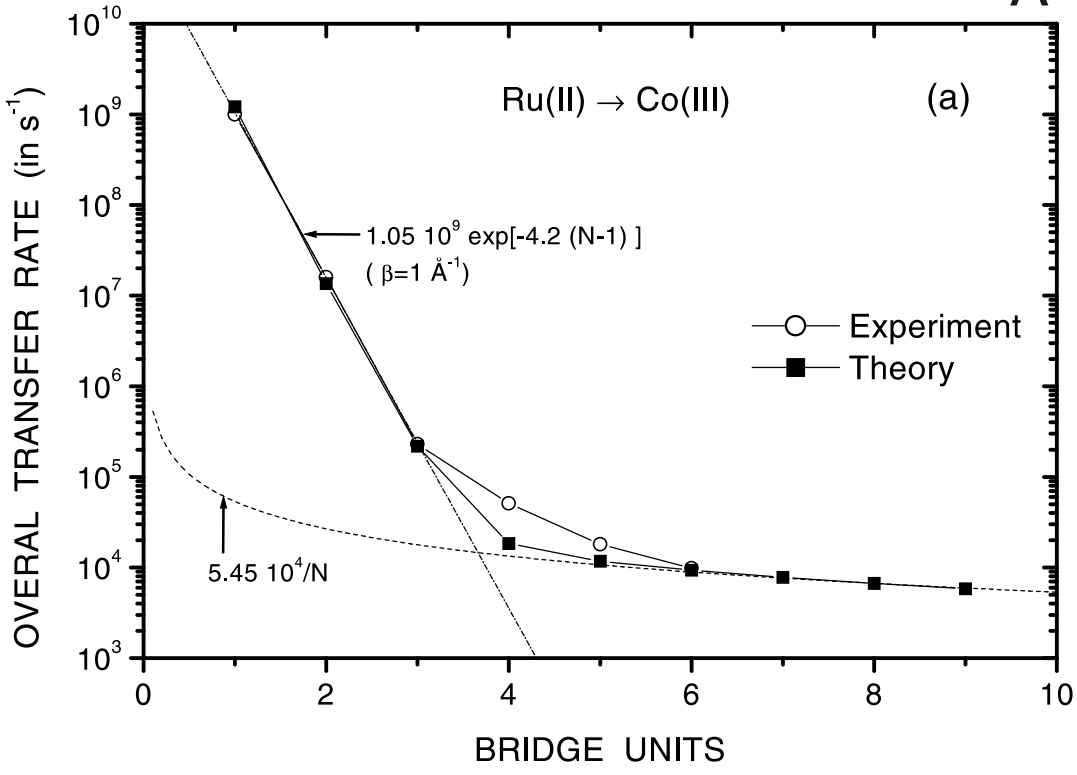


Superexchange ET



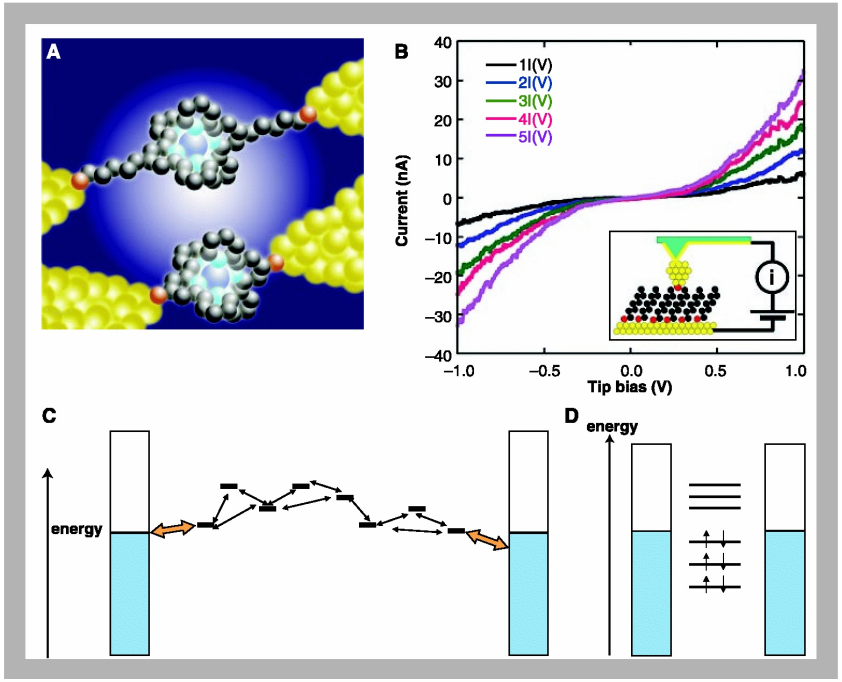
Sequential ET

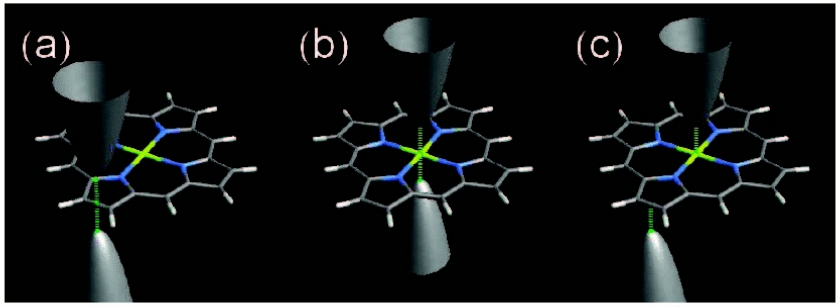




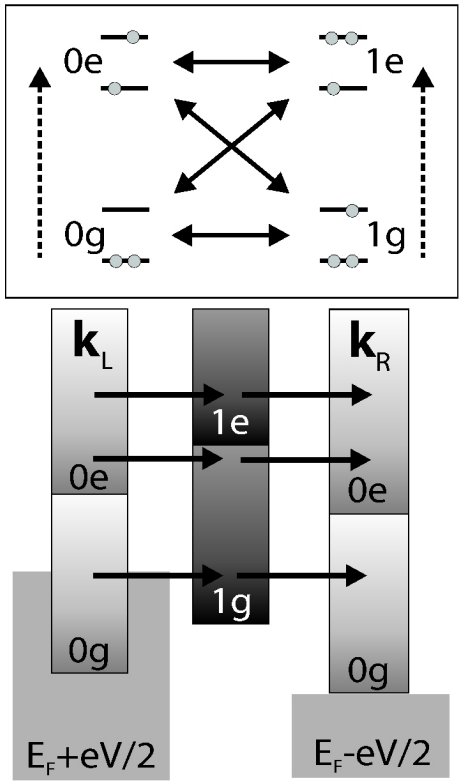
E.G. Petrov and V. May, J. Phys. Chem. A 105, 10176 (2001)

Current through Single Molecules

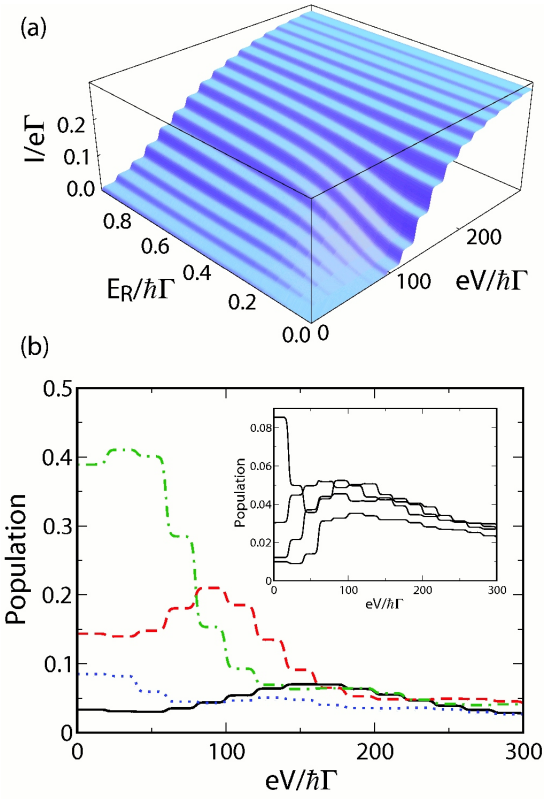




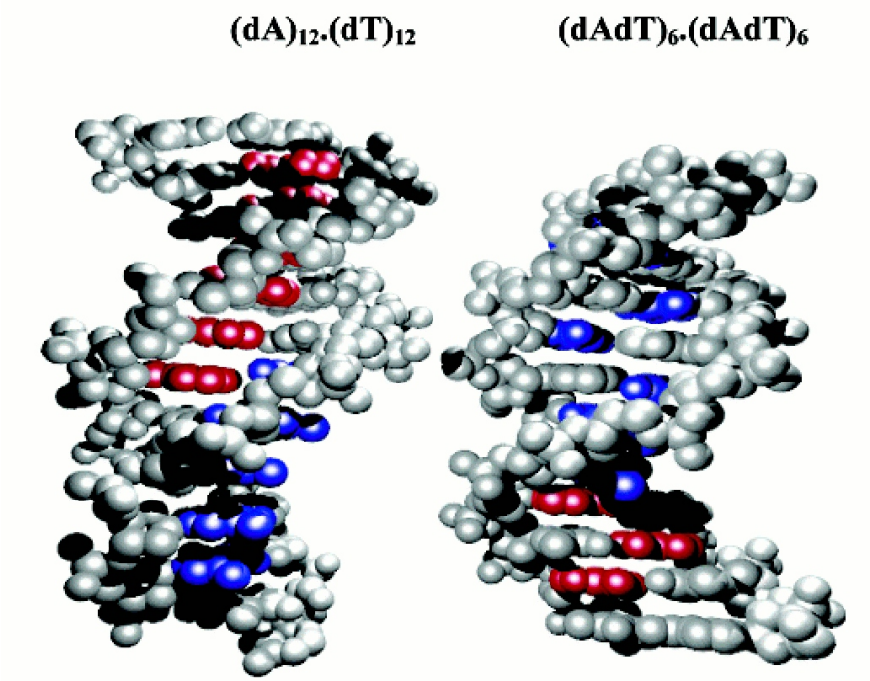
V. May and O. Kühn:
Photoinduced Removal of the Franck-Condon Blockade in Single Electron Inelastic Charge Transmission
Nano Lett. 8, 1095 (2008).



Schematic view of possible charge transfer (solid arrows) and photoinduced (dashed arrows) transitions.



(a) Total current versus applied voltage and external field--strength (b) Stationary vibrational populations in the electronic ground state of the neutral molecule



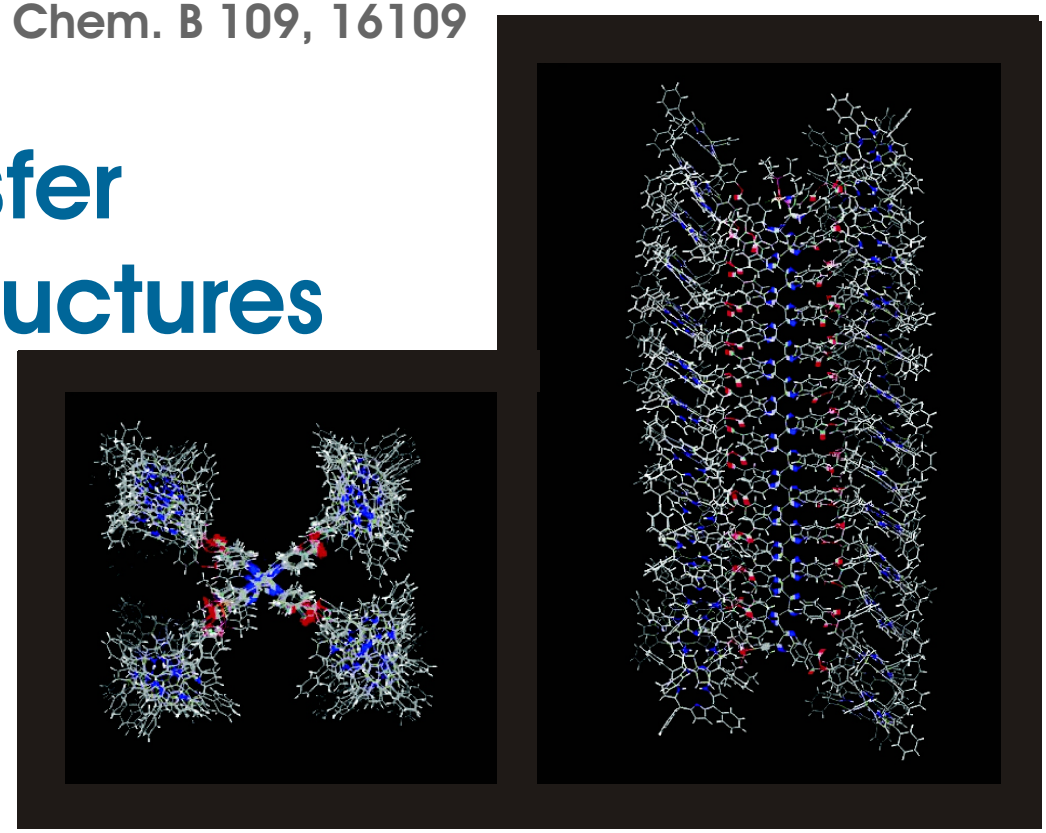
Frenkel Excitons in Molecular Systems

excitons in DNA

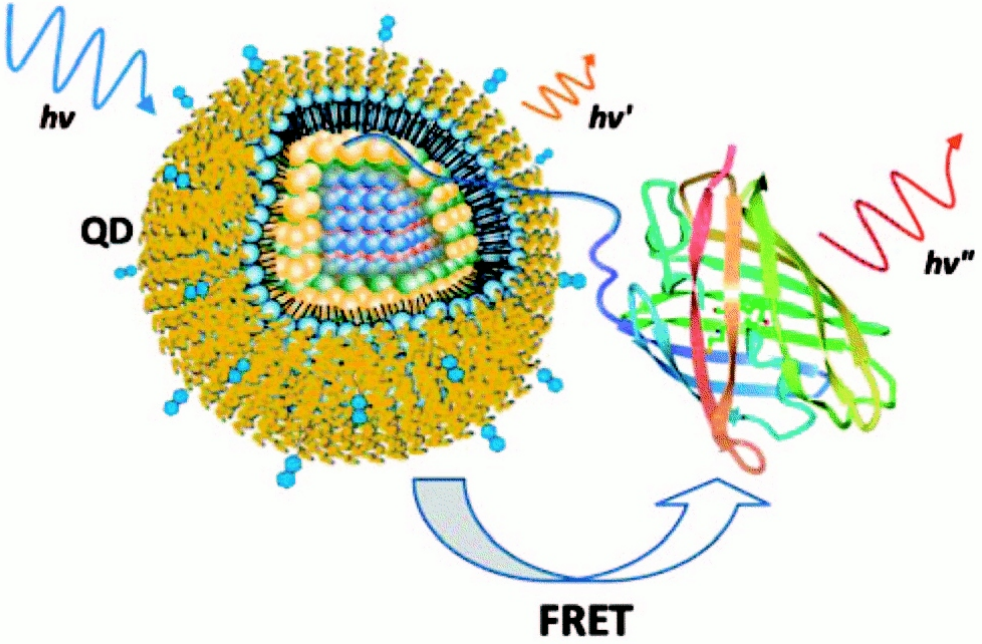
E. Emanuele, K. Zakrzewska, D. Markovitsi, R. Lavery, and P. Millie, J. Phys. Chem. B 109, 16109 (2005).

excitation energy transfer in complex artificial structures

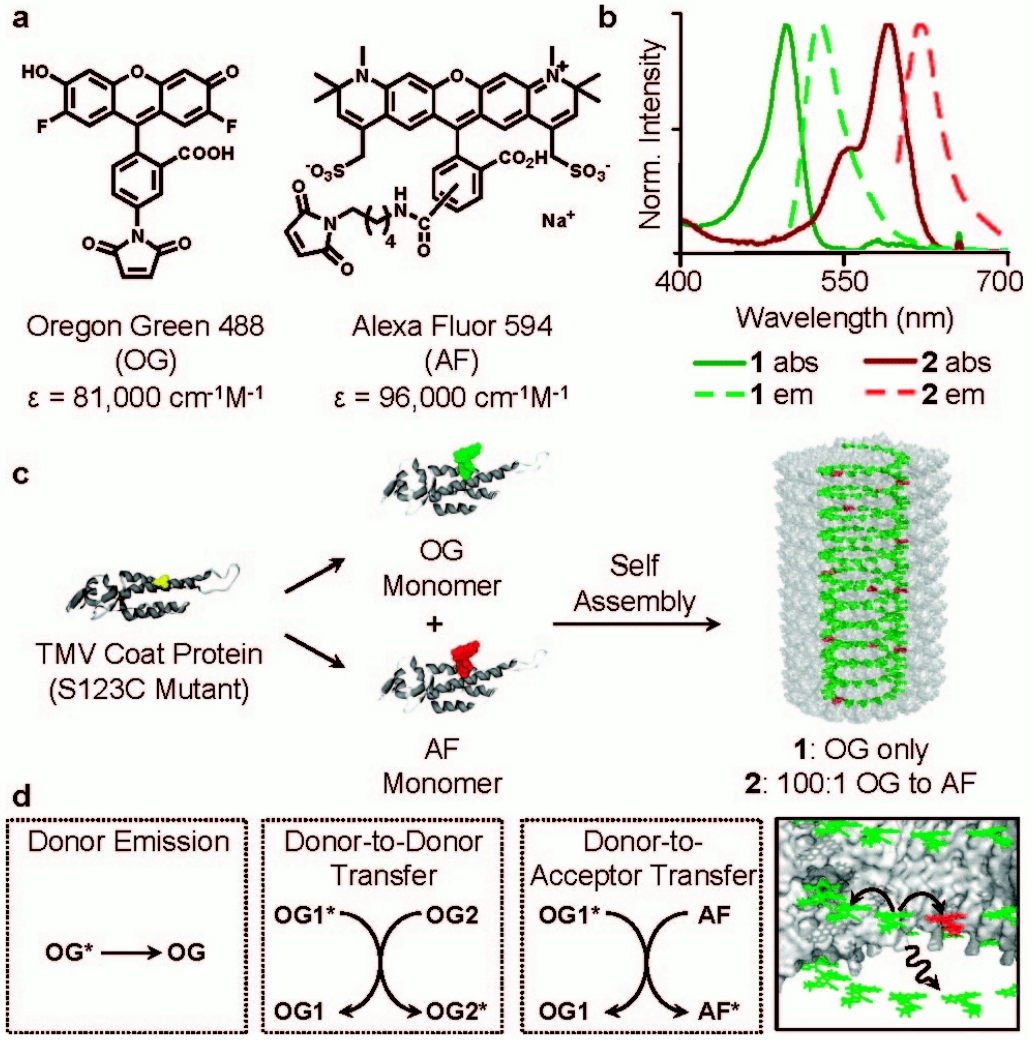
H. Zhu, M. Fujitsuka, A. Okada, S. Tojo, F. Takei, K. Onitsuka, S. Takahashi, and T. Majima, Rapid Exciton Migration and Fluorescent Energy Transfer in Helical Polyisocyanides with Regularly Arranged Porphyrin Pendants, J. Phys. Chem. B 108, 11935 (2004).



Y.-Z. Ma, R. A. Miller, G. R. Fleming, and M. B. Francis,
Energy Transfer Dynamics in Light-Harvesting Assemblies Templated by Tobacco Mosaic Virus Coat Protein,
J. Phys. Chem. B 112, 6887 (2008).



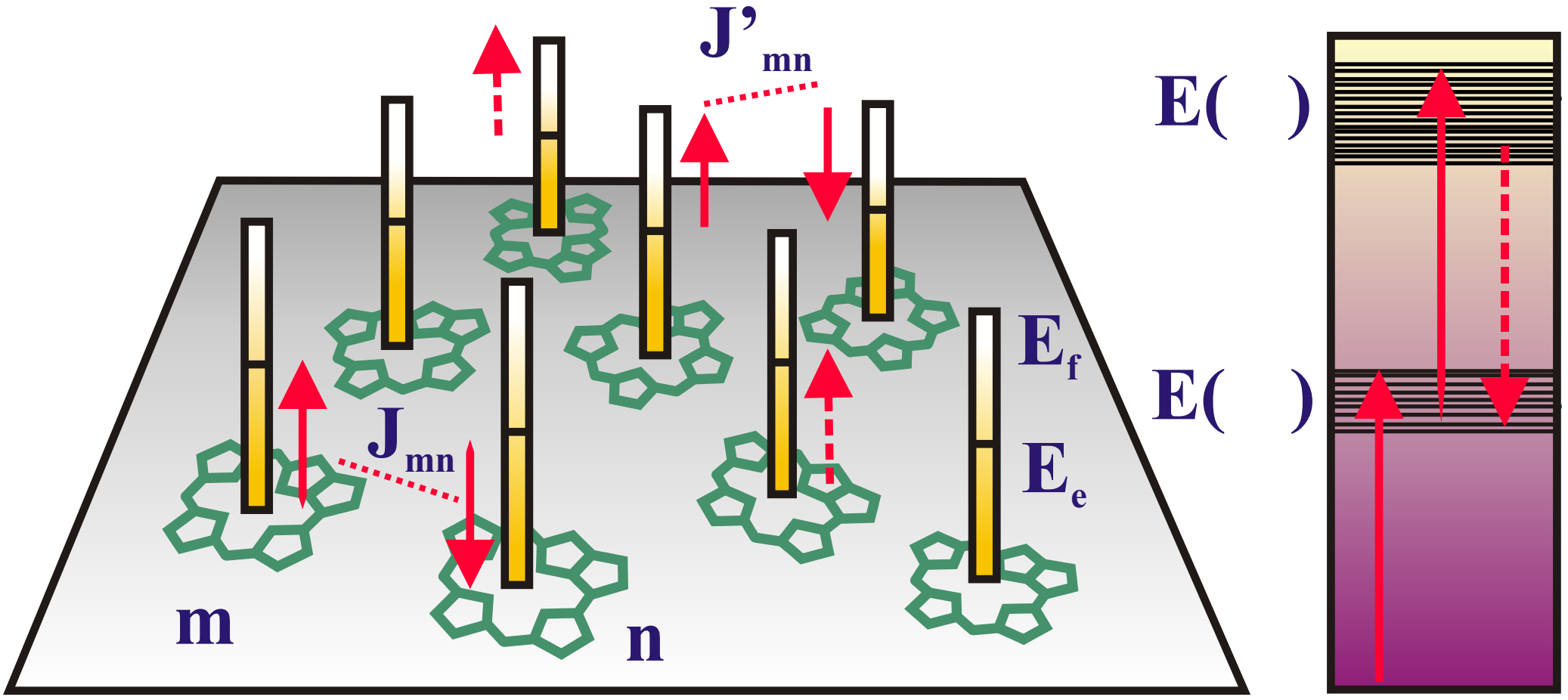
A. M. Dennis and G. Bao, **Quantum Dot-Fluorescent Protein Pairs as Novel Fluorescence Resonance Energy Transfer Probes,**
NanoLett. 8, 1439 (2008).

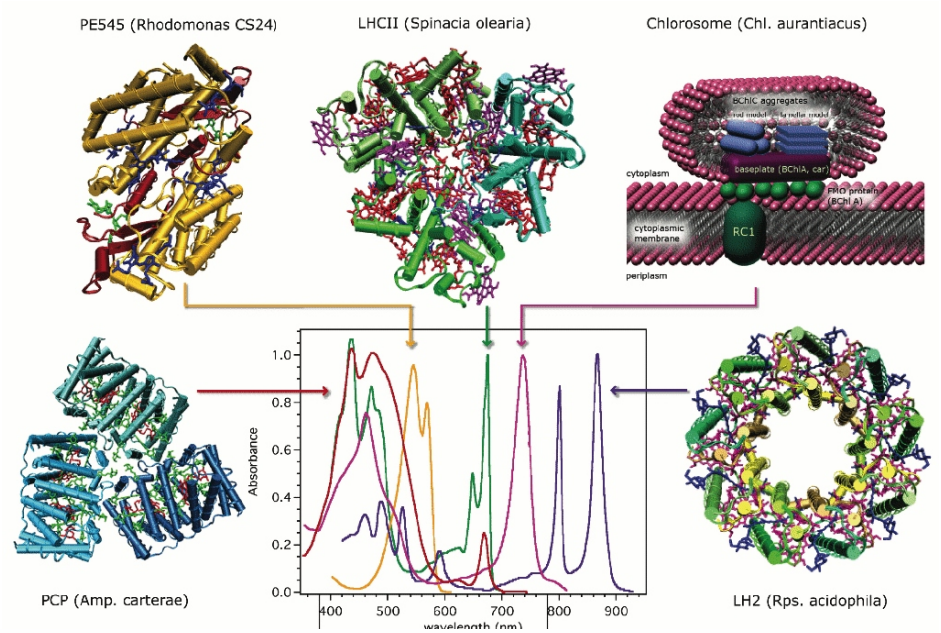


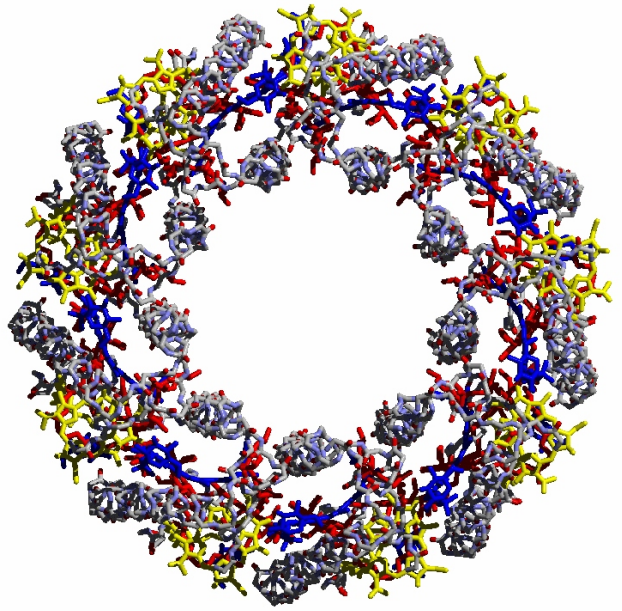
The Standard Frenkel-Exciton Model

delocalized state representation

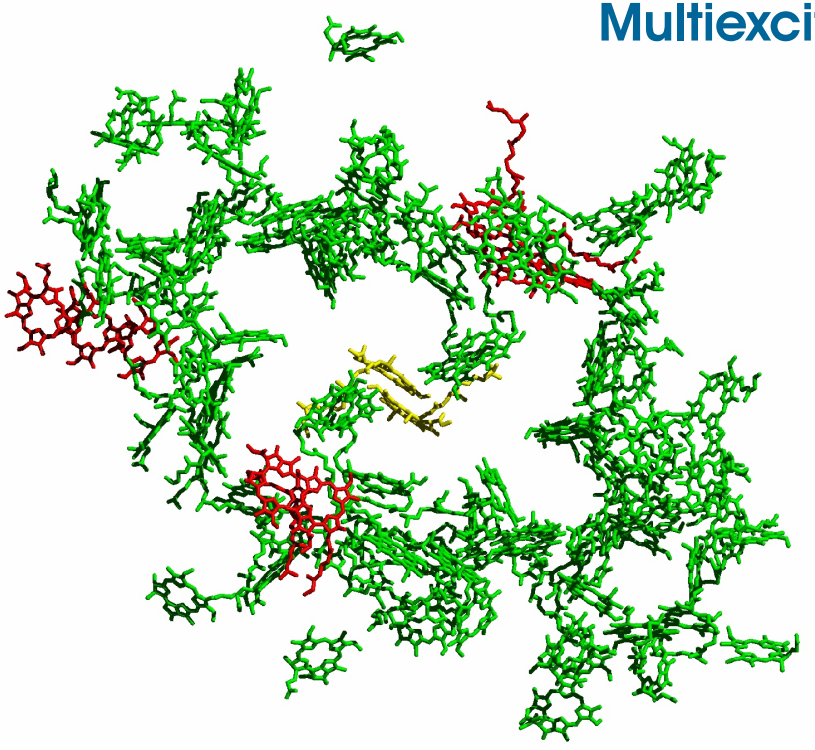
localized state representation

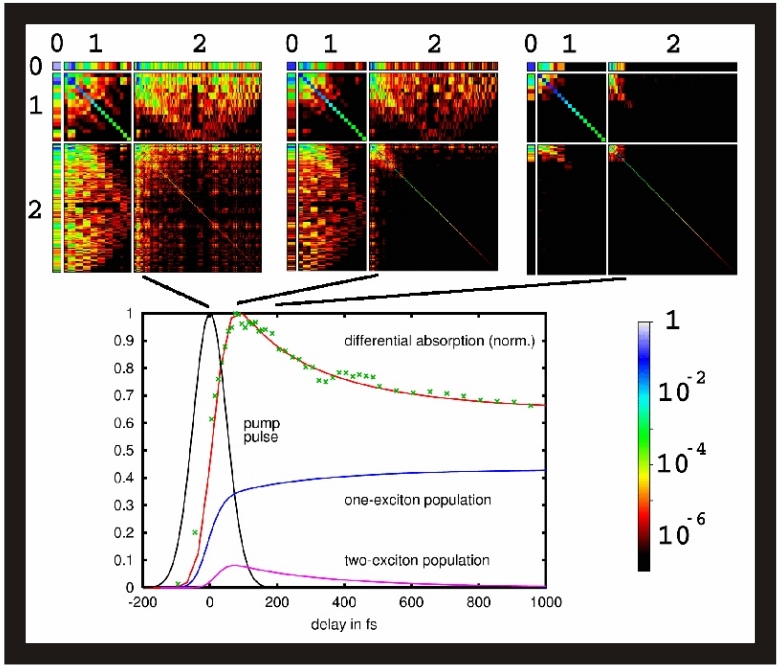


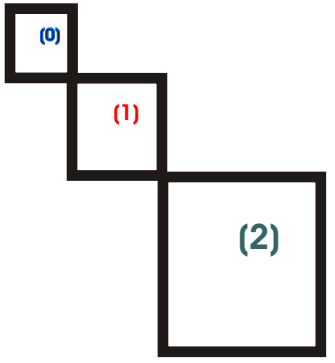




Multiexciton Dynamics and Transient Absorption of the LH2







B. Brüggemann and V. M., JCP 120, 2325 (2004)

Condensed Phase Molecular Dynamics

Electron Nuclei Dynamics in Molecular Systems

molecular Hamiltonian $H_{\mathrm{mol}} = T_{\mathrm{nuc}} + H_{\mathrm{el}}(R)$

adiabatic electronic states $H_{\mathrm{el}}(R)\varphi_a(r;R) = U_a(R)\varphi_a(r;R)$

expansion of the molecular wave function $\Psi(r,R;t) = \sum_a \chi_a(R,t)\varphi_a(r;R)$

time–dependent Schrödinger equation of the nuclear motion

$$i\hbar\frac{\partial}{\partial t}\chi_a(R,t) = (T_{\mathrm{nuc}} + U_a(R))\chi_a(R,t) + \sum_b \hat{\Theta}_{ab}\chi_b(R,t)$$

problems:

$\longrightarrow$ huge number of coordinates

$\longrightarrow$ study of thermal ensembles

$\longrightarrow$ coupling to a solvent or other types of condensed phase environment

reduced quantum dynamics

reduced density operator

$$\hat{\rho}(t) = \int dR \, \langle R|\hat{W}(t)|R\rangle \equiv \mathrm{tr}_{\mathrm{nuc}}\{\hat{W}(t)\}$$

electronic density matrix $\longrightarrow$ density matrix equations

$$\rho_{ab}(t) = \langle\varphi_a|\hat{\rho}(t)|\varphi_b\rangle$$

state population $\longrightarrow$ master equations

$$P_a(t) = \rho_{aa}(t)$$

mixed quantum classical dynamics

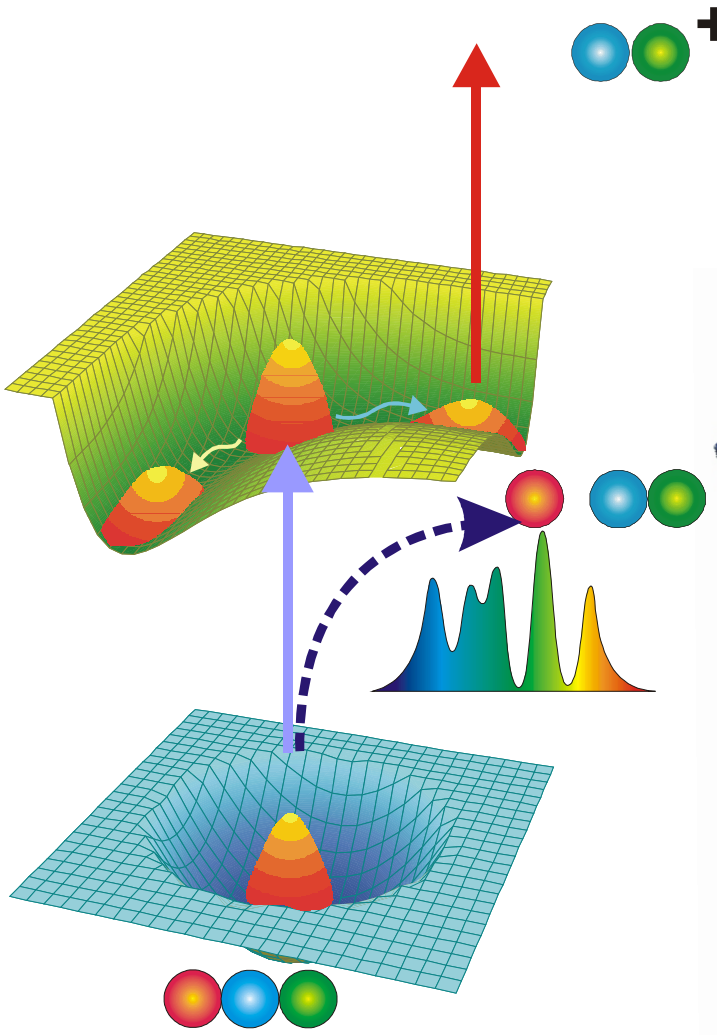
quantum mechanical description of the electrons $\longrightarrow \varphi_a(r;R)$

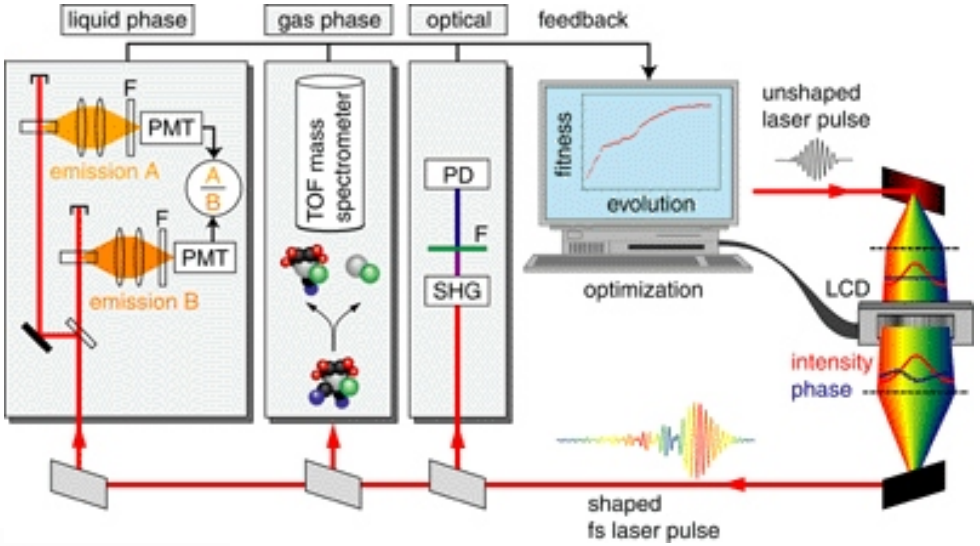
classical description of the nuclei $\longrightarrow R(t)$

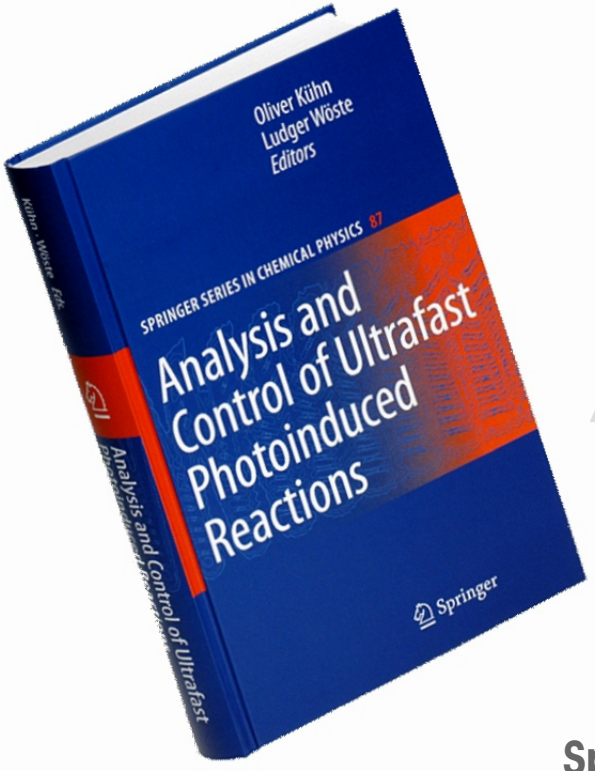
$$i\hbar\frac{\partial}{\partial t}\phi(r,R(t);t) = H_{\mathrm{el}}(R(t))\phi(r,R(t);t)$$

$$M_\nu\frac{\partial^2}{\partial t^2}\mathbf{R}_\nu(t) = -\nabla\langle\phi(R(t);t)|H_{\mathrm{el}}|\phi(R(t);t)\rangle$$

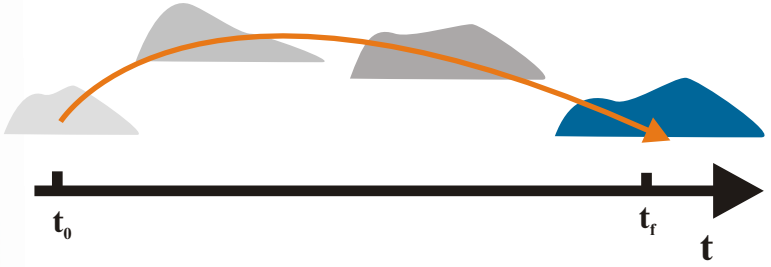
Laser Pulse Control of Molecular Dynamics





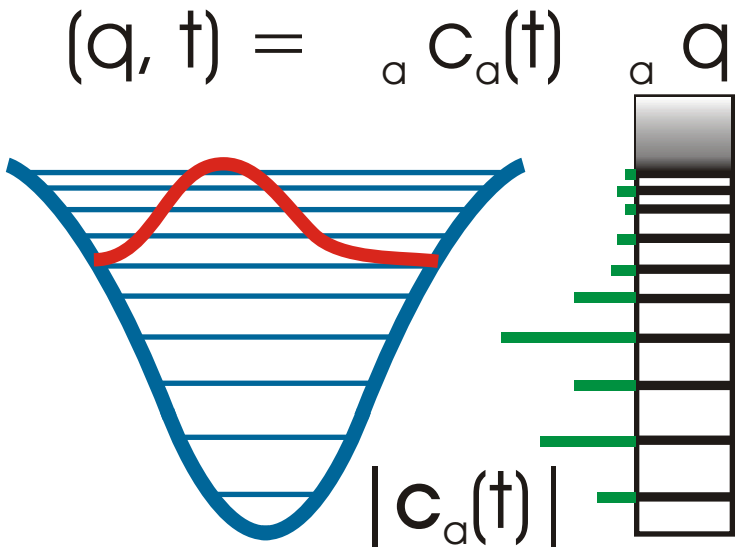


Adaptive Femtosecond Quantum Control



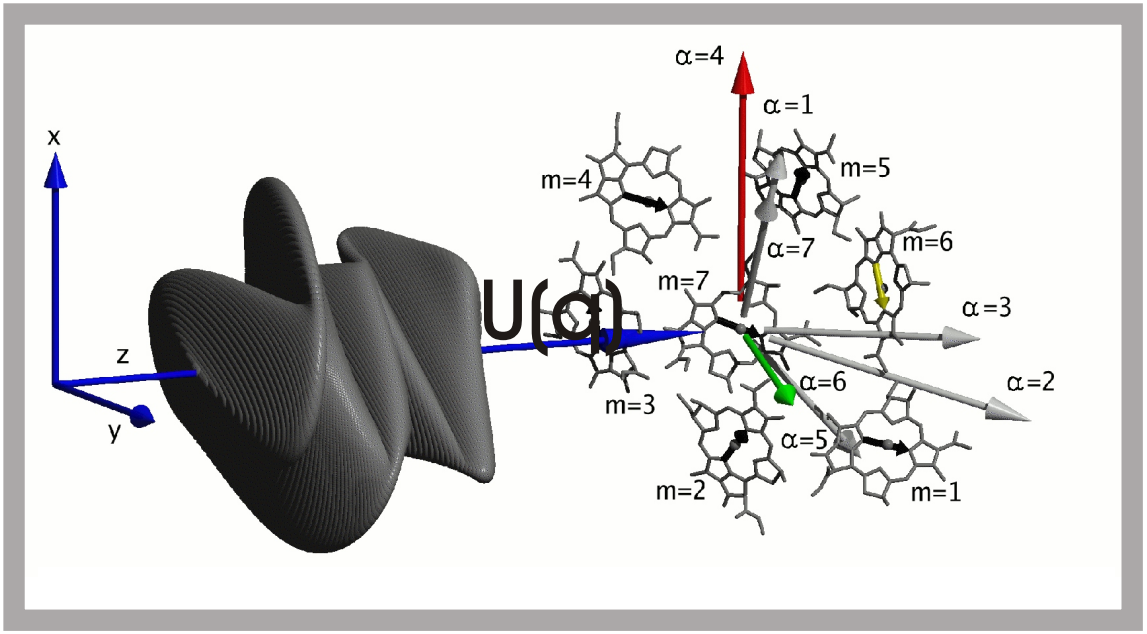
"Analysis and Control of Ultrafast Photoinduced Reactions"
O. Kühn and L. Wöste (eds.)
Springer Series in Chemical Physics, Vol. 87 (Springer-Verlag, 2007)

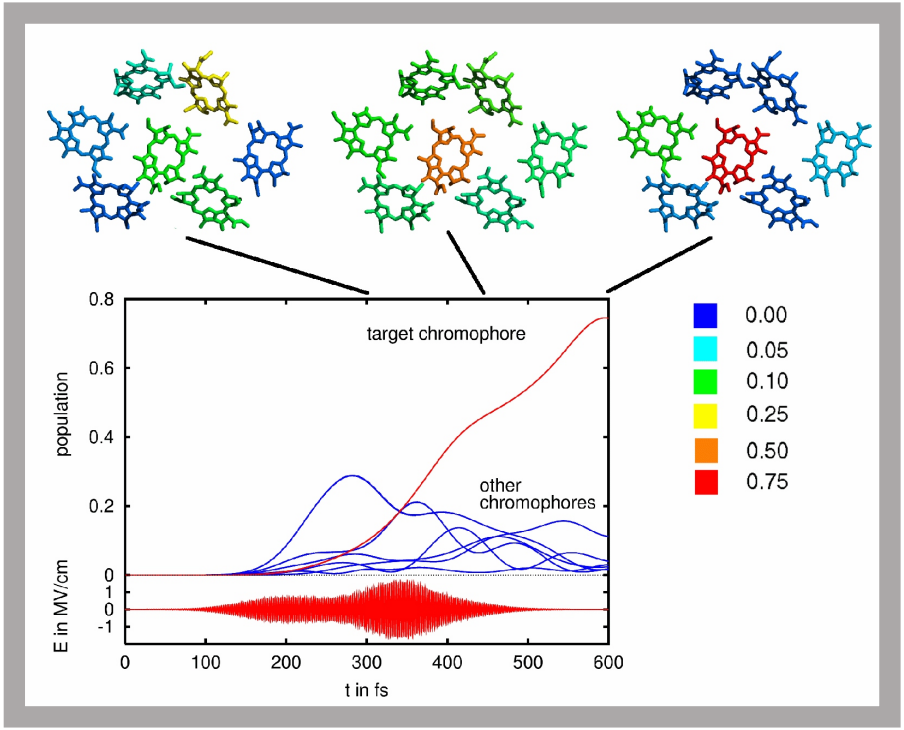
laser pulse control of excitation energy transfer



B. Brüggemann, T. Pullerits, and V. May
J. Photochem. Photobio. A 190, 372 (2007).

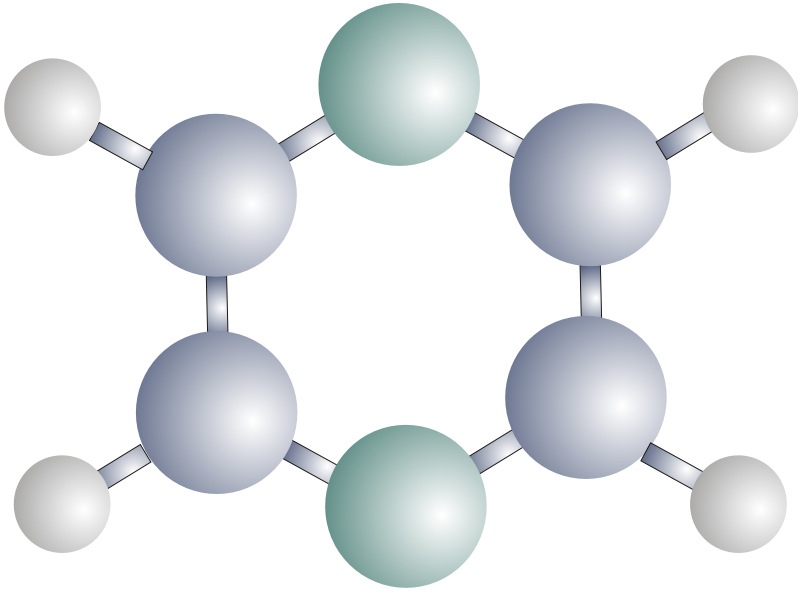
B. Brüggemann and V. May
in "Analysis and Control of Ultrafast Photoinduced Reactions",O. Kühn and L. Wöste (eds.), Springer Series in Chemical Physics Vol. 87 (Springer-Verlag, 2007), p. 774.

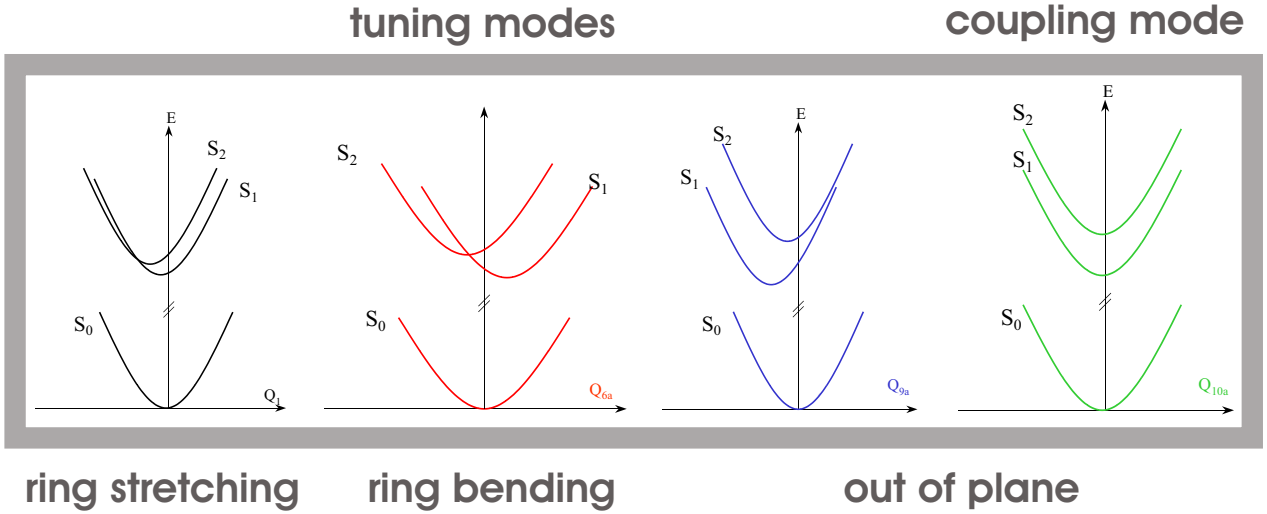




Laser Pulse Control of Nonadiabatic Transitions

4-Mode Model of Pyrazine (vibronic coupling model)





Multiconfiguration Time-Dependent Hartree Method

$$\chi_a(Q_1,\ldots,Q_N;t) = \sum_{\kappa_1=1}^{M_1} \cdots \sum_{\kappa_N=1}^{M_N} A^{(a)}_{\kappa_1\ldots\kappa_N}(t) \prod_{j=1}^{N} \zeta^{(a)}_{\kappa_j}(Q_j,t)$$

$$\mathcal{O}[\mathbf{E}_c] = \mathrm{trs}\{\hat{O}\hat{\rho}(t_f)\}$$

$$\mathcal{O}[\mathbf{E}_c] = \int_{t_0}^{\infty} dt_f \int dp\ \mathrm{trs}\{\hat{O}(t_f;p)\hat{\rho}(t_f;p)\}$$

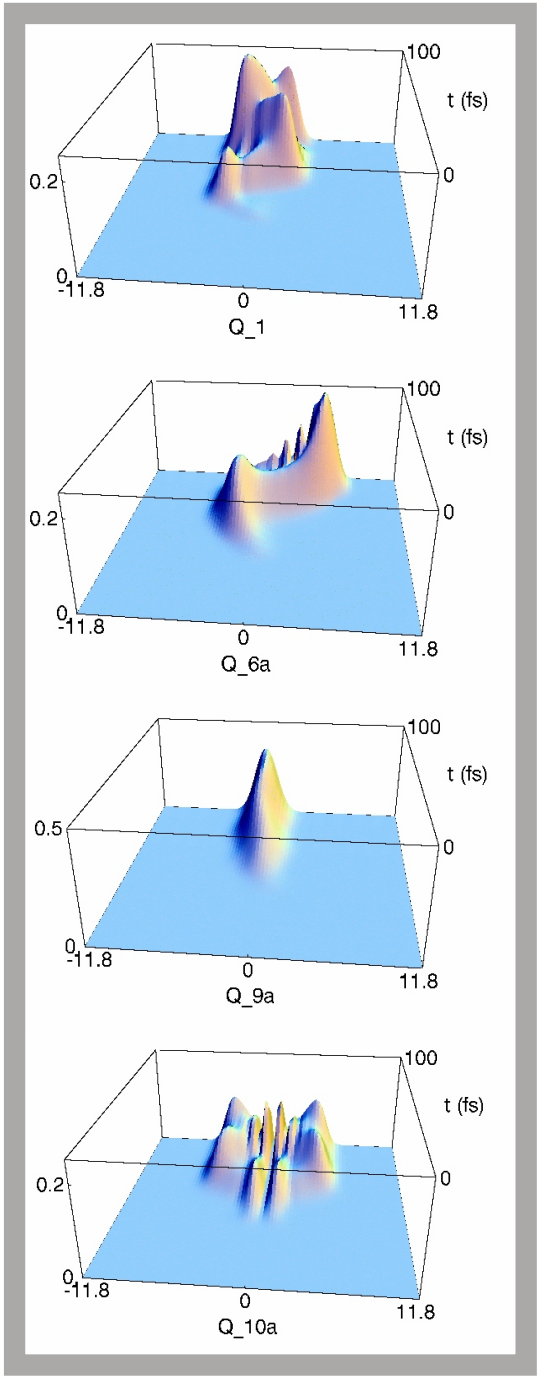
optimization of an observable at a finite time or in a time and parameter space interval

control functional to be optimized -> Optimal Control Theory

$$J[\mathbf{E_c}] = \mathcal{O}[\mathbf{E_c}] - \lambda(\frac{1}{2}\int_{t_0}^{t_f} dt\ \mathbf{E}_c^2(t) - I_0)$$

functional equation determining the optimal pulse

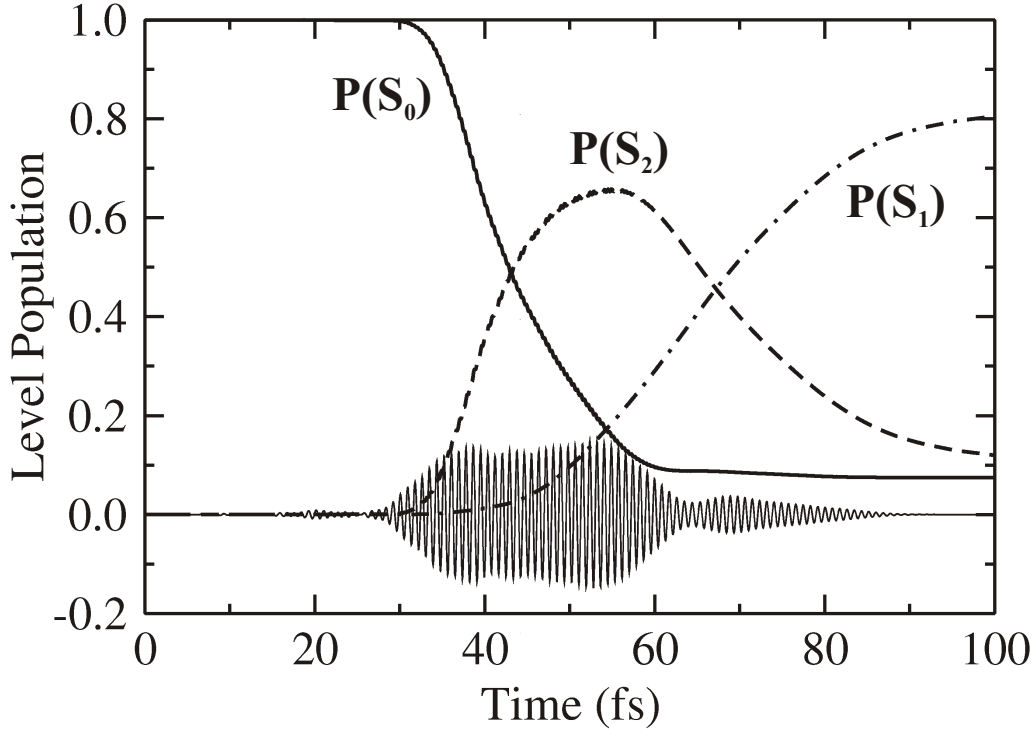
$$\mathbf{E}_c(t) = \frac{i}{\hbar\lambda}\int dp\ \mathrm{trs}\{\hat{O}(t;p)\mathcal{U}(t_f,t;p;\mathbf{E}_c)[\hat{\mu},\hat{\rho}(t;p)]\}$$



Reduced probability distribution of the four modes

L. Wang, H.-D. Meyer, and V. May:
Femtosecond Laser Pulse Control of Multidimensional Vibrational Dynamics:Computational Studies on the Pyrazine Molecule
J. Chem. Phys. 125, 014102 (2006).

Optimization of the overall S_1-population



$$P_{S_1}(Q_j, t) = \int dQ' \, |\chi_{S_1}(Q_1, Q_{6a}, Q_{9a}, Q_{10a}, t)|^2$$

Heterogeneous Electron Transfer

L. Wang, V. M., et al.:

Laser Pulse Control of Bridge Mediated Heterogeneous Electron Transfer
Chem. Phys. (in press).

Ultrafast Photoinduced Electron Transfer from Anchored Molecules into Semiconductors
in "Analysis and Control of Ultrafast Photoinduced Reactions",
O. Kühn and L. Wöste (eds.),Springer Series in Chemical Physics Vol. 87
(Springer-Verlag, 2007), p. 437.

Theory of Ultrafast Heterogeneous Electron Transfer:
Contributions of Direct Charge Transfer Excitations to the Absorbance
J. Chem. Phys.126, 134110 (2007).

Theory of Ultrafast Heterogeneous Electron Transfer
Molecular Simulation (special issue on electron transfer) 32, 765 (2006).

Heterogeneous Electron Transfer Reactions:
Comparative Theoretical Studies in the Time and Frequency Domain
J. Chem. Phys. 124, 014712 (2006).

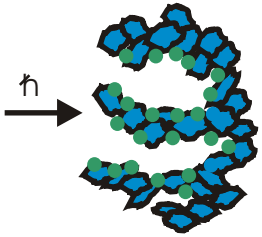
Absorption Spectra Related to Heterogeneous Electron Transfer Reactions:
The Perylene-TiO2 System
J. Phys. Chem. B 109, 9589 (2005).

Laser Pulse Control of Ultrafast Heterogeneous Electron Transfer: A Computational Study
J. Chem. Phys. 121, 8039 (2004).

Molecule Semiconductor-Surface System

Perylene on TiO_2

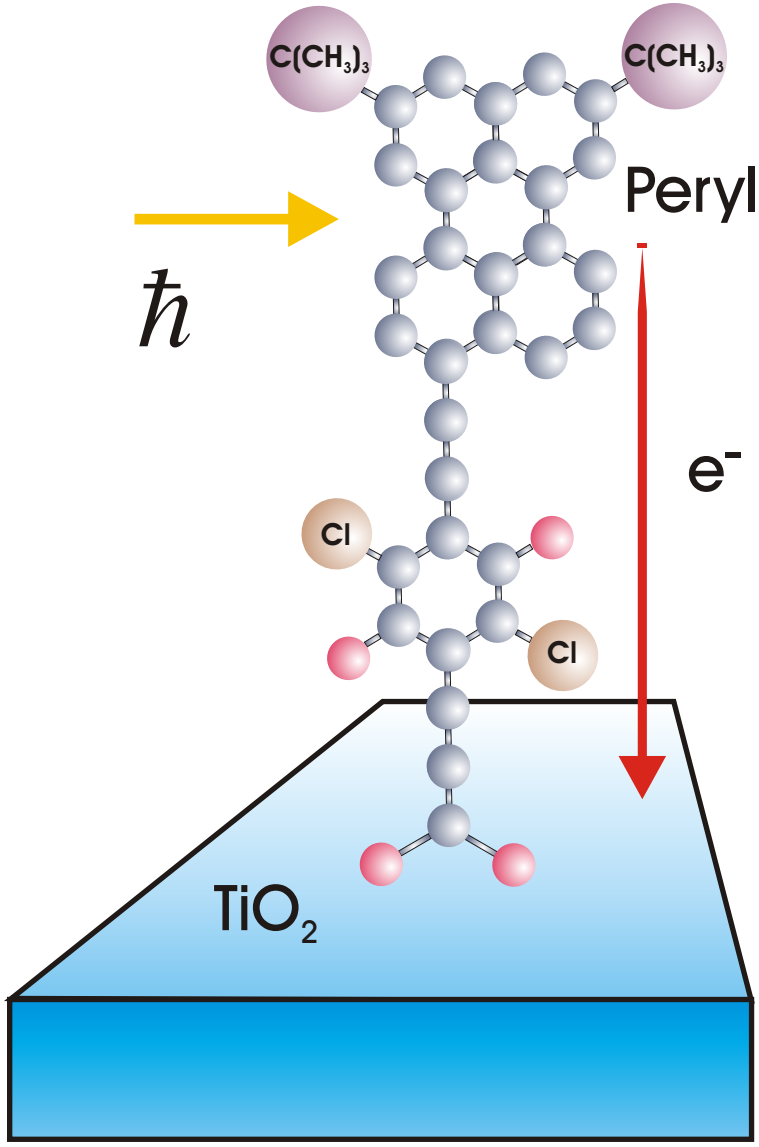
TiO_2 nanoparticles

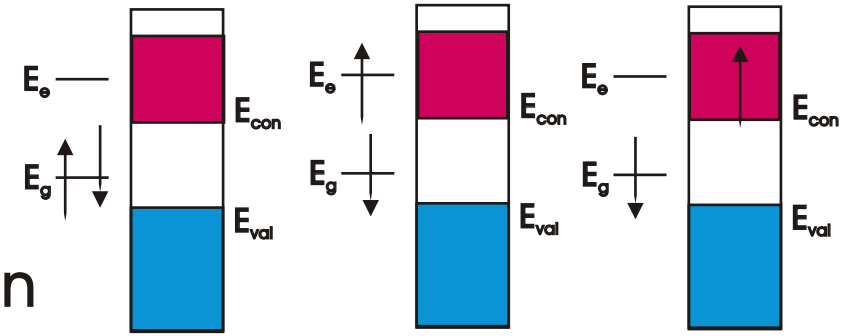


dye

τ_{HET} = 10 ... 57 fs

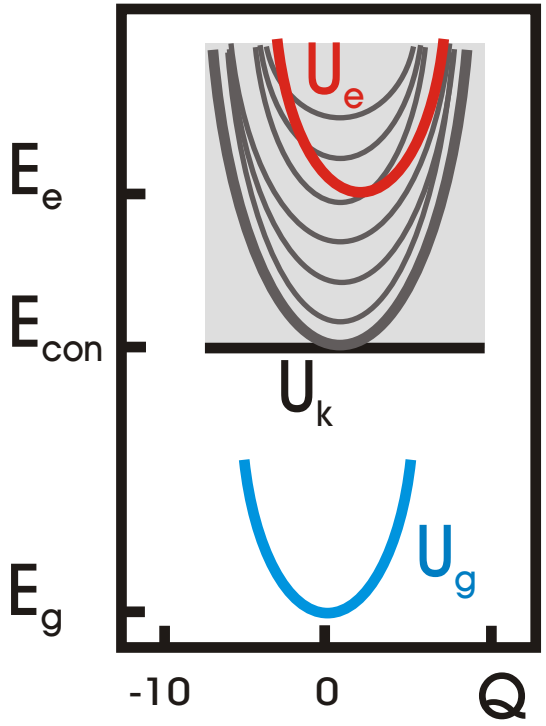
τ_{vib} = 1370 cm^{-1}



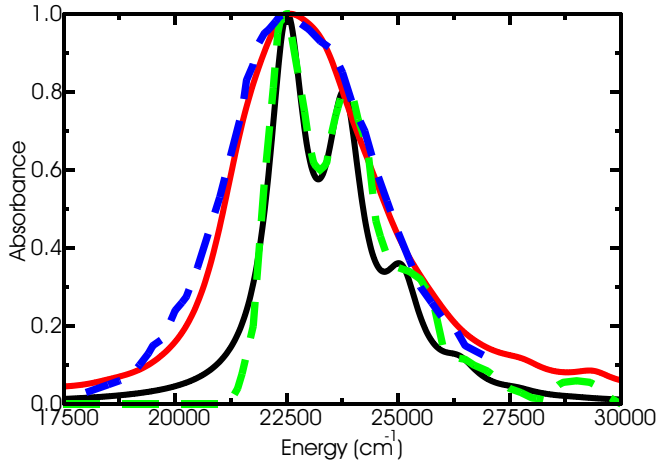


diabatic states

|D> |A> |D*> |A> |D+> |A->



Linear Absorption of Perylene



broken lines: measured data

full lines: simulations

black and green: solvent case

blue and red: perylene on TiO_2 (DTB-Pe-COOH)

Model Hamiltonian

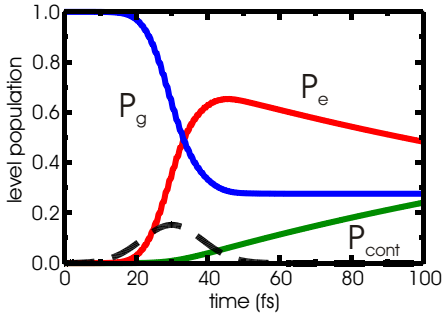
$$H_{\mathrm{mol-sem}} = \sum_{a=g,e,\mathbf{k}} (E_a + H_a)|\varphi_a\rangle\langle\varphi_a| + \sum_{\mathbf{k}} (V_{\mathbf{k}e}|\varphi_{\mathbf{k}}\rangle\langle\varphi_e| + V_{e\mathbf{k}}|\varphi_e\rangle\langle\varphi_{\mathbf{k}}|)$$

DOS

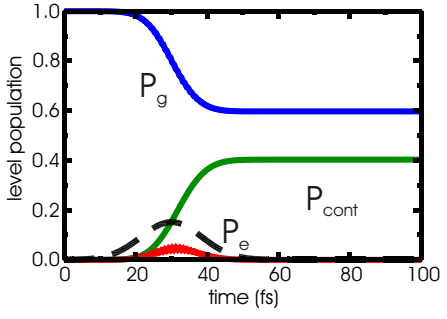
$$\mathcal{N}(\Omega) = \sum_{\mathbf{k}} \delta(\Omega - \omega_{\mathbf{k}})$$

Change of the Injection Time

V = 0.02 eV



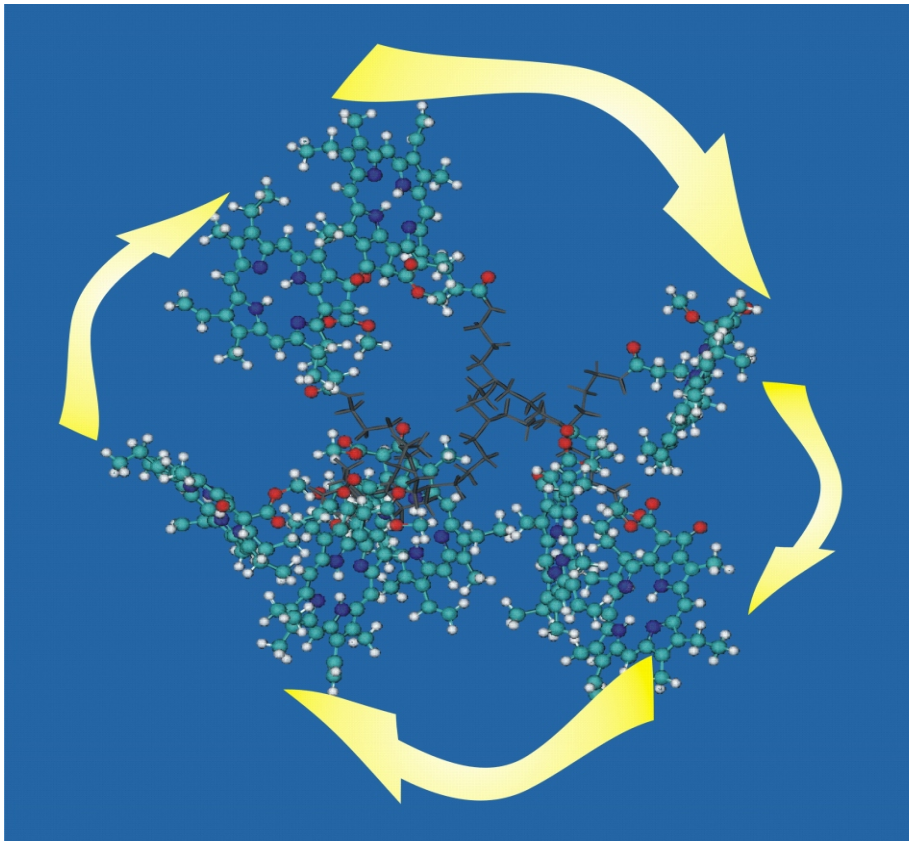
V = 0.2 eV

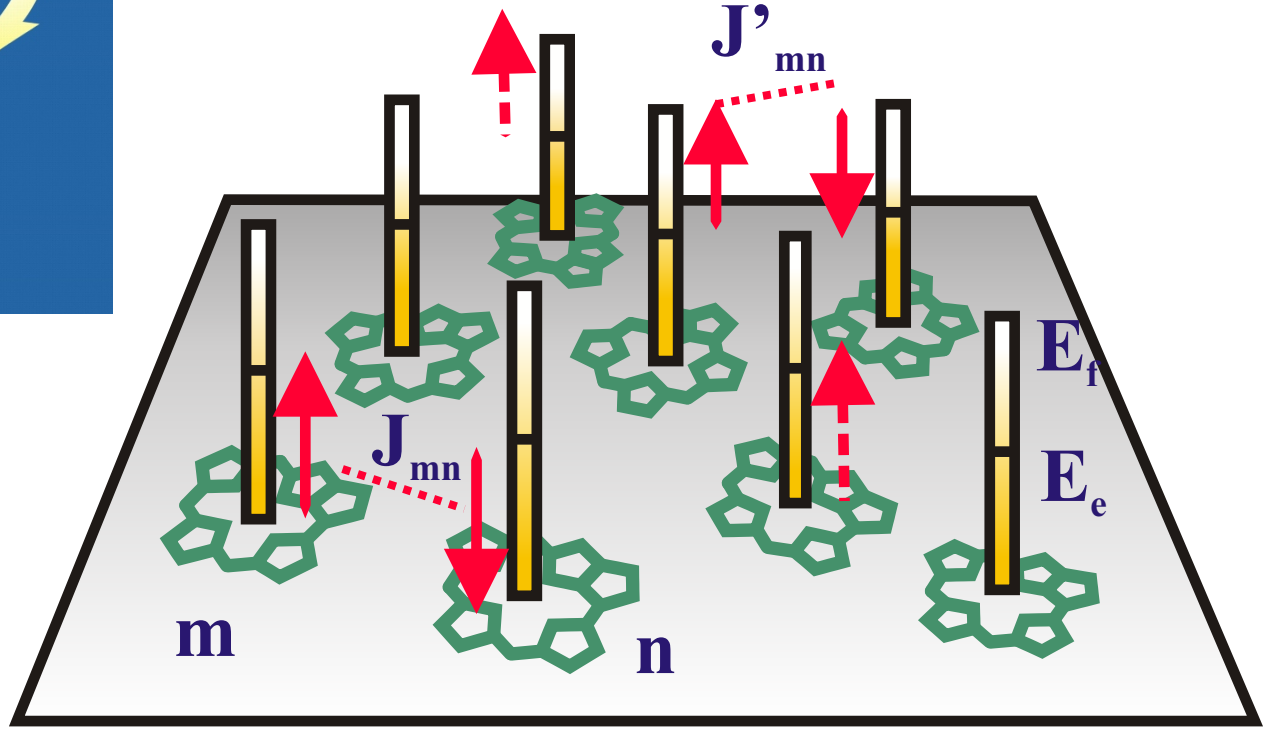


Basis Set Expansion of the Electron-Vibrational State Vector

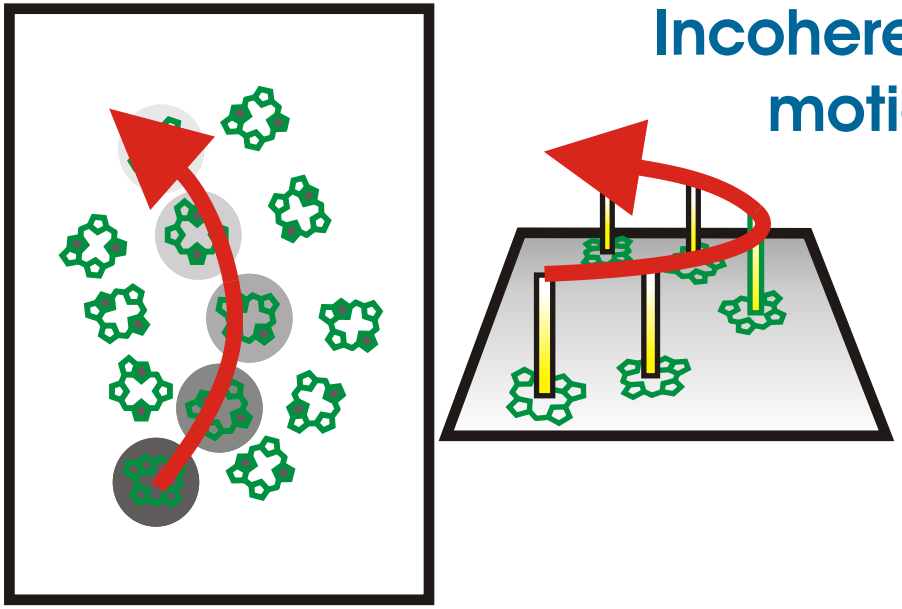
$$|\Psi(t)\rangle = \sum_{a=g,e,\mathbf{k}} \sum_{M} C_{aM}(t)|\chi_{aM}\rangle|\varphi_a\rangle$$

Excitation Energy Transfer in Chromophore Complexes

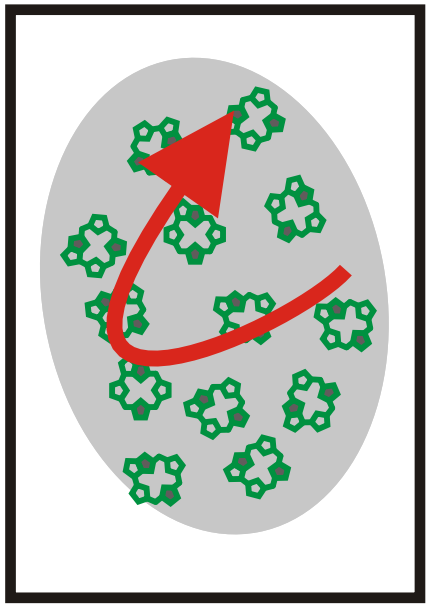




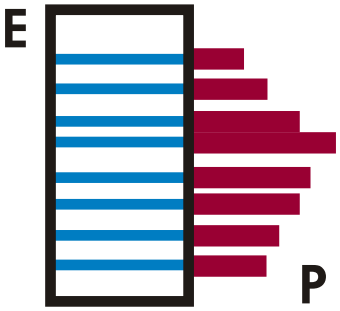
Schemes of Excitation Energy Transfer



Incoherent motion



Coherent motion



$$|\phi_m\rangle = |\varphi_{me}\rangle \prod_{n\neq m} |\varphi_{ng}\rangle$$

site representation

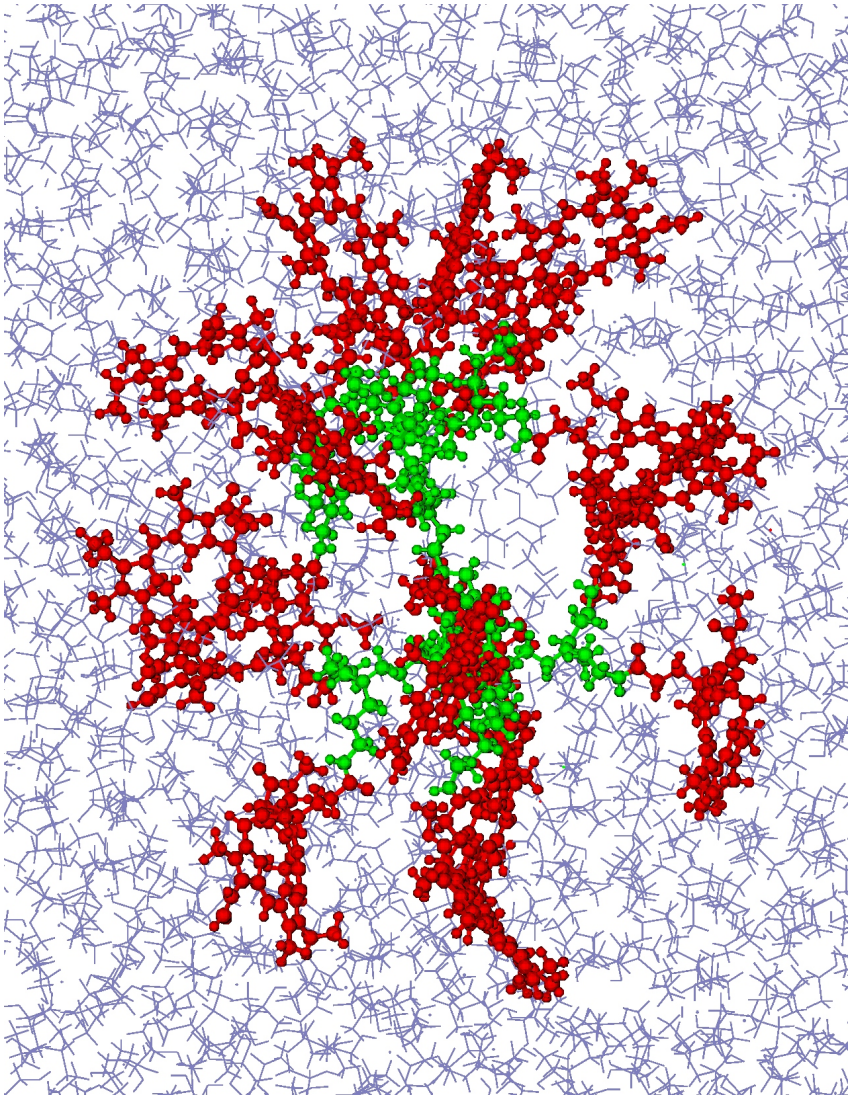
$$H_{\text{ex}} = \sum_{mn} \Big(\delta_{m,n}[T_{\text{nuc}} + U_m(R)] + [1 - \delta_{m,n}] J_{mn}(R) \Big) |\phi_m\rangle\langle\phi_n|$$

$$|\alpha\rangle = \sum_m C_\alpha(m) |\phi_m\rangle$$

exciton representation

$$H_{\text{ex}} = \sum_\alpha \Big(\mathcal{E}_\alpha + \sum_\xi \hbar\omega_\xi C_\xi^+ C_\xi \Big) |\alpha\rangle\langle\alpha| + \sum_{\alpha,\beta} \sum_\xi \hbar\omega_\xi g_{\alpha\beta}(\xi) \Big(C_\xi + C_\xi^+ \Big) |\alpha\rangle\langle\beta|$$

Mixed Quantum Classical Description of Excitation Energy Transfer:



Pheoporbide-a Complexes in Ethanol

V. H. Zhu, V. May, B. Röder, and Th. Renger,
J. Chem. Phys. 128, 154905 (2008).

H. Zhu, V. May, and B. Röder,
Chem. Phys. 351, 117 (2008).

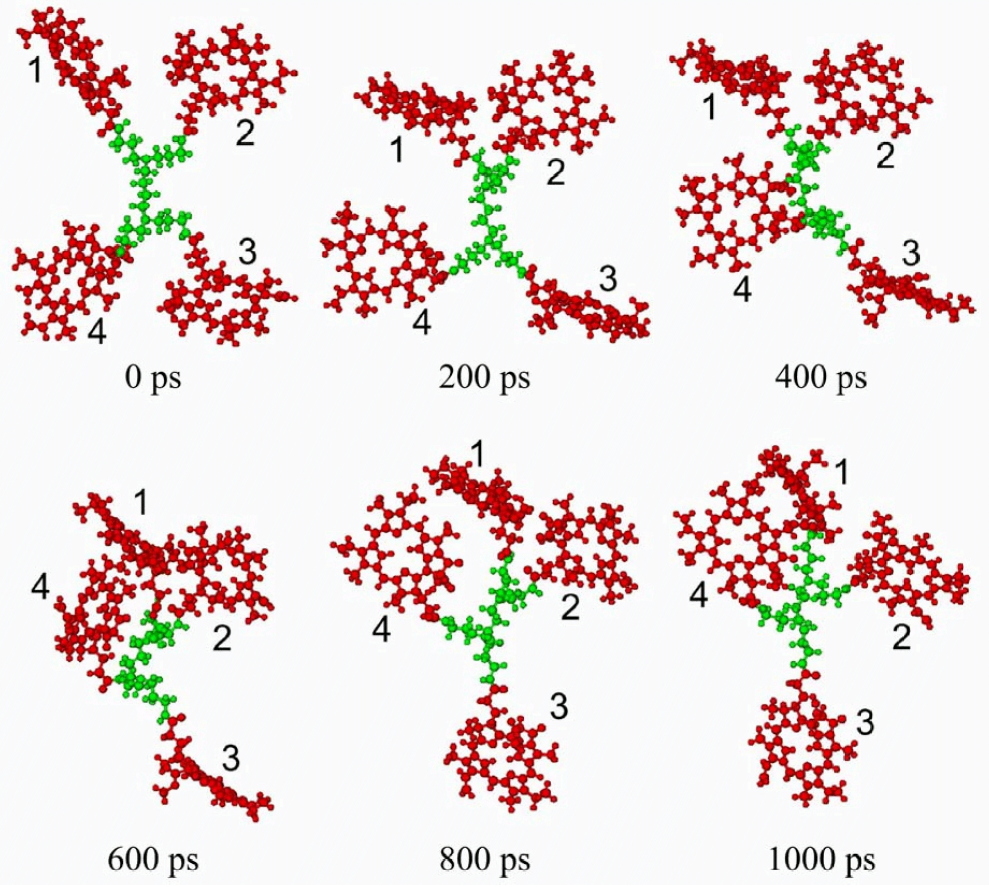
H. Zhu and V. May,
Springer Series in Chemical Physics
(Springer-Verlag, 2009).

$$i\hbar\frac{\partial}{\partial t}\Phi(r,R(t);t) = H_{\rm ex}(R(t))\Phi(r,R(t);t)$$

$$M_\nu\frac{\partial^2}{\partial t^2}\mathbf{R}_\nu(t) = -\nabla_\nu\langle\Phi(R(t);t)|H_{\rm ex}(R(t))|\Phi(R(t);t)\rangle$$

Ehrenfest dynamics

MD simulations of the solvent-solute system



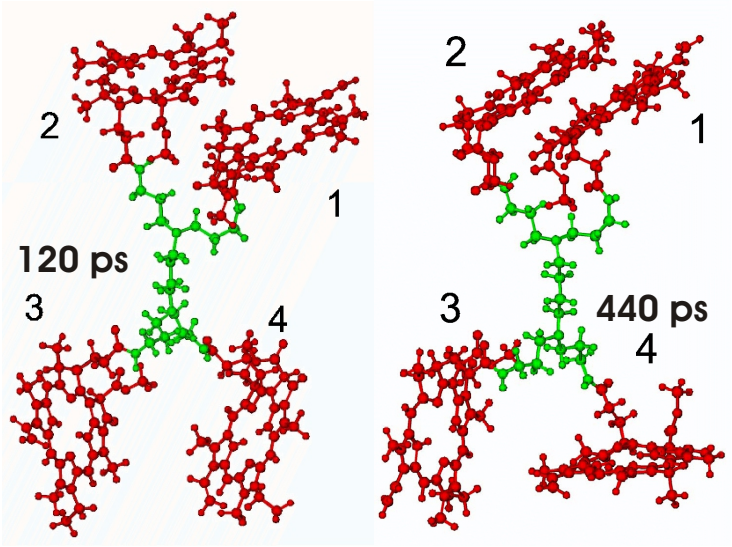
->exact account for exciton vibrational coupling

-> atomic resolution of vibrational dynamics

->back reaction of the electron dynamics on the nuclear motion

-> high-temperature limit

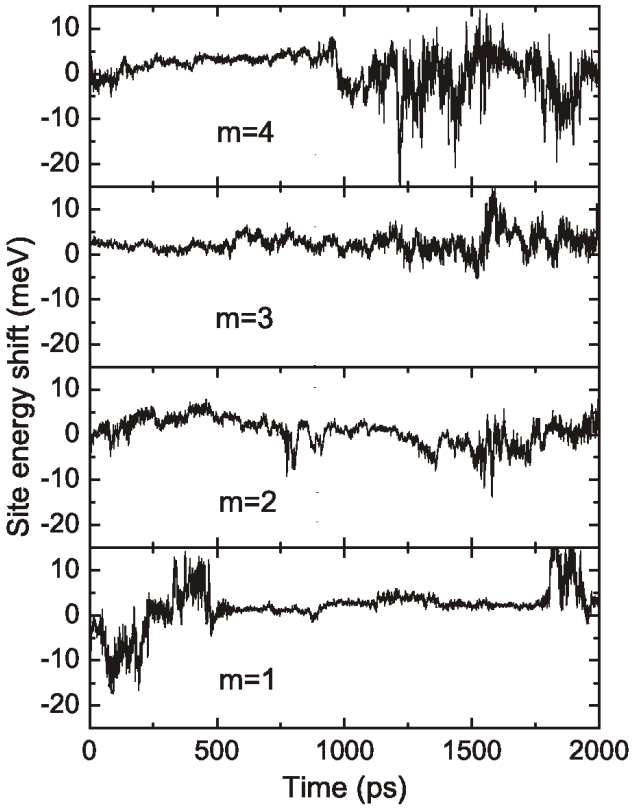
snapshots of P_4 in ethanol along a 1 ns room–temperature MD run

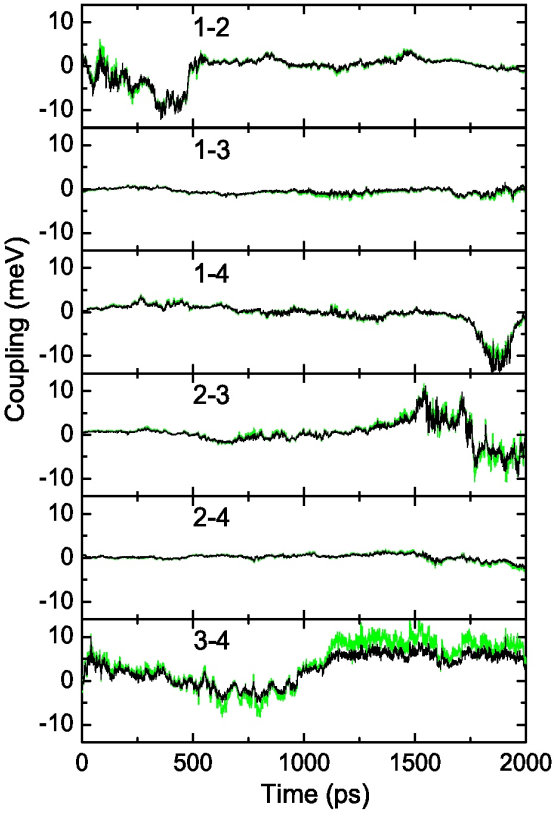


single chromophore excitation energies and excitonic couplings

(coupling to solvent molecules has been neglected)

4 pheophorbide-a molecules covalently linked to a butanediamine dendrimer

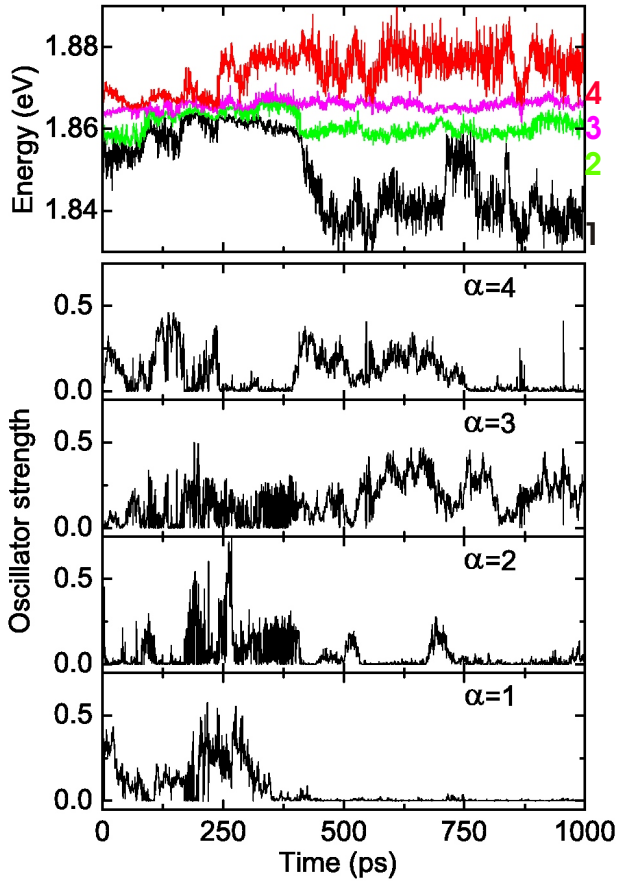




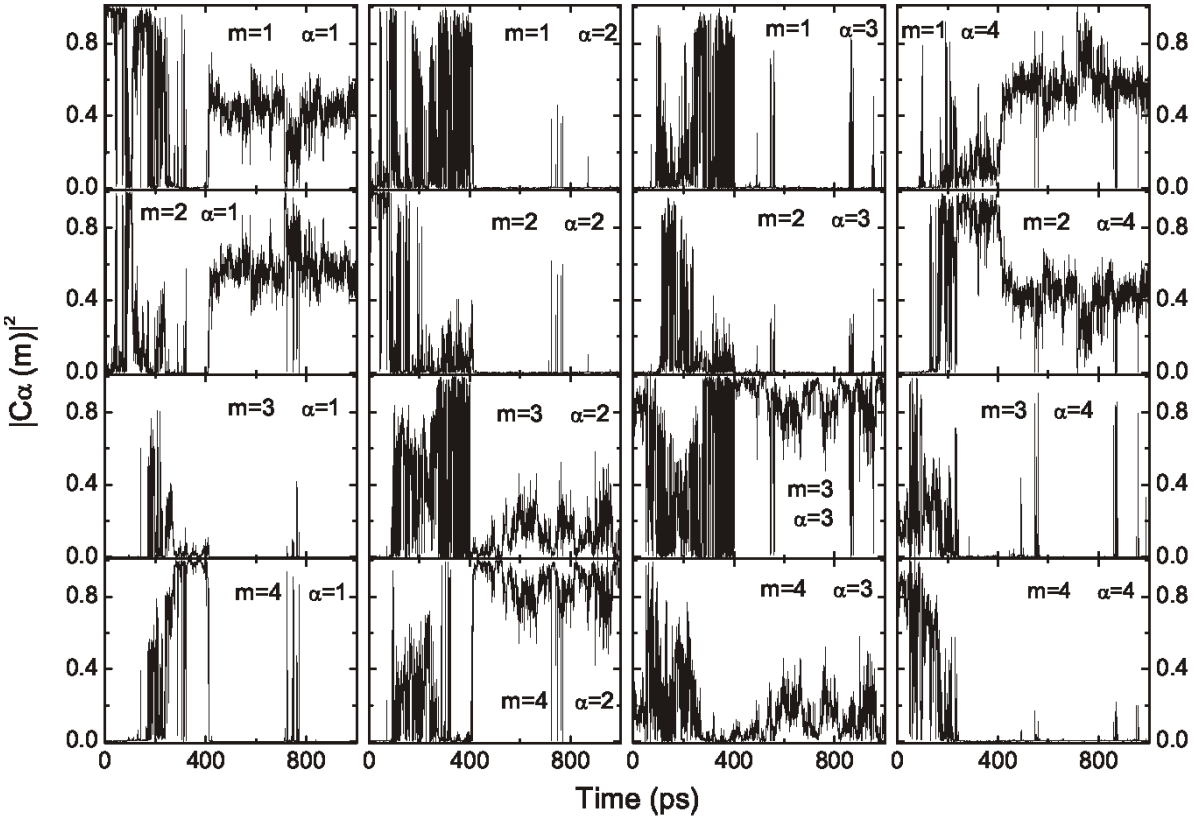
H. Zhu, V. May, B. Röder, M. El-Amine Madjet, and Th. Renger, Chem. Phys. Lett. 444, 118 (2007).

Adiabatic (instantaneous) excitons

energies, oscillator strengths, and expansion coefficients (coupling to solvent molecules has been neglected)



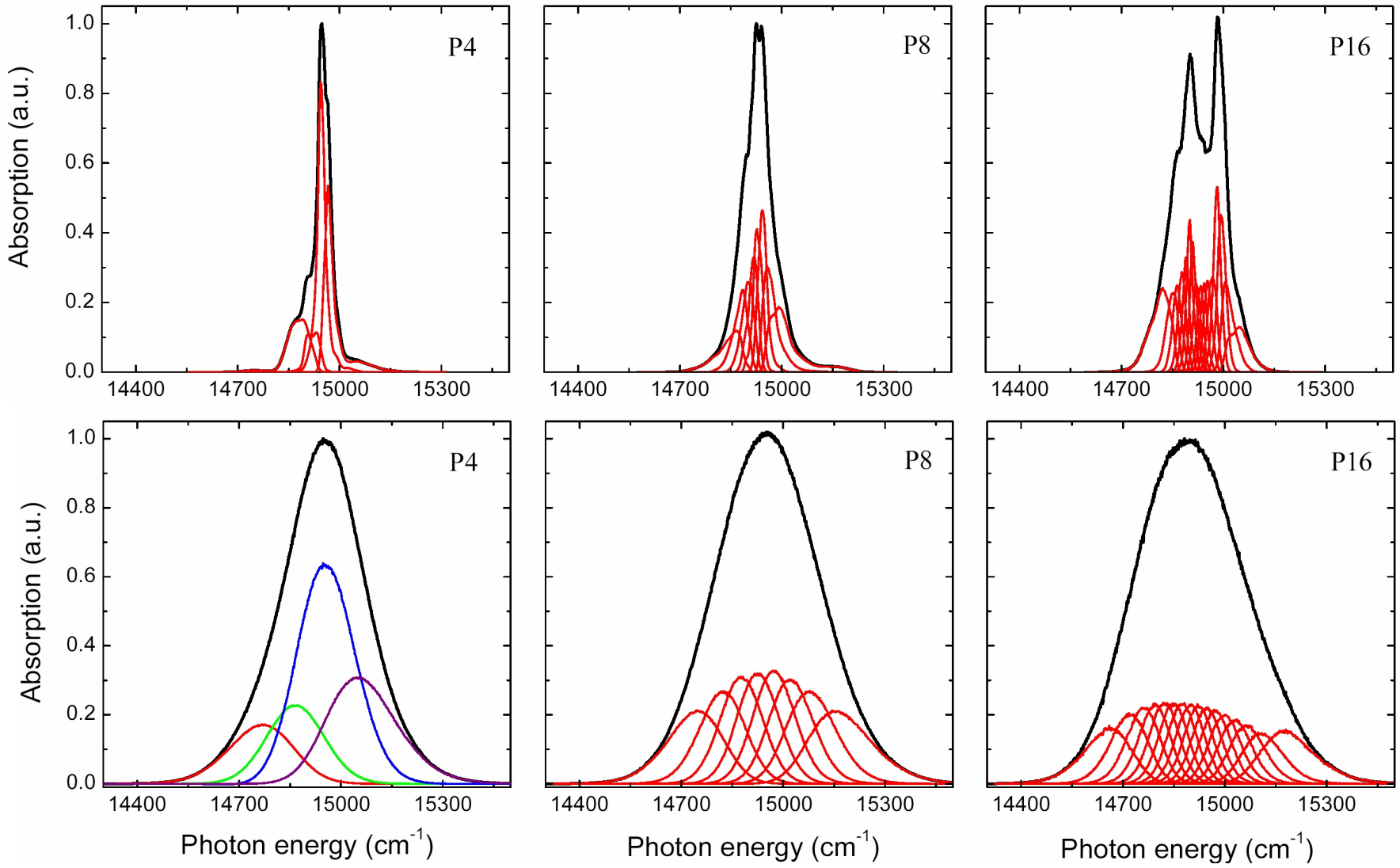
Adiabatic exciton energies and oscillator strengths (data have been computed every 0.5 ps within a single 1 ns MD run)



Square of adiabatic exciton expansion coefficients, taken at every 0.5 ps

Linear Absorption Spectra

The modulation of the single chromophore excitation energy by the solvent molecules is **neglected.**

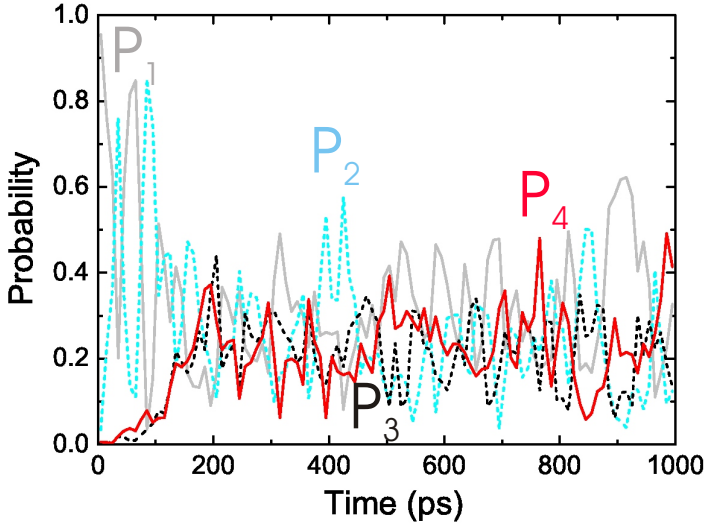


The modulation of the single chromophore excitation energy by the solvent molecules is **included.**

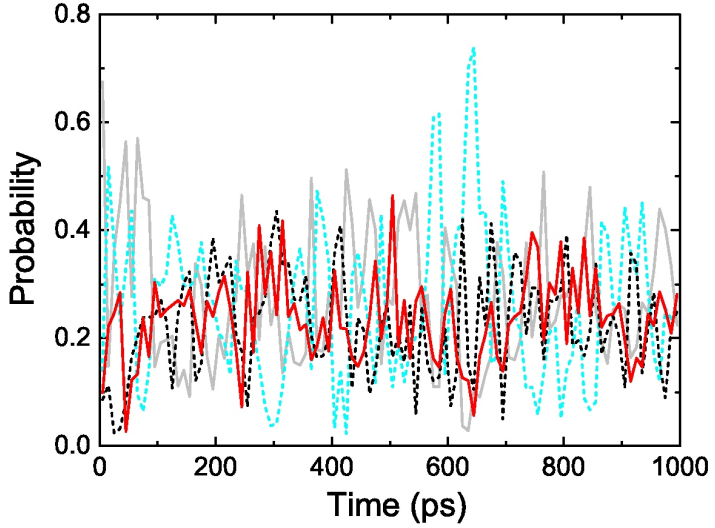
Excitation Energy Transfer Dynamics

averaged with respect to a 10 ps time slice

$$P_m(t) = < |A_m(t)|^2 >_{\mathrm{ens}}$$

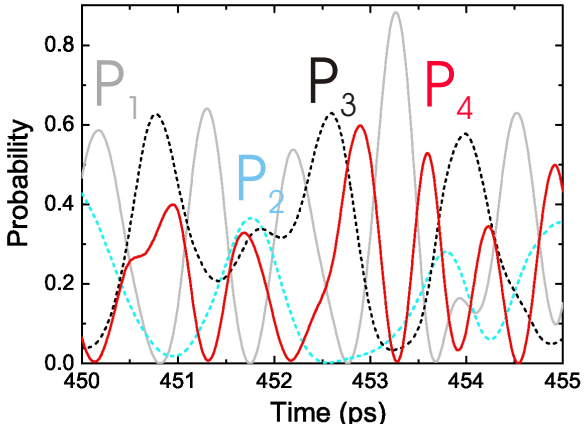


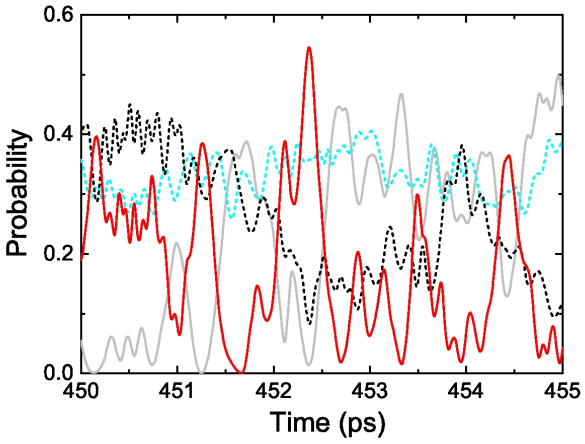
The modulation of the single chromophore excitation energy by the solvent molecules is neglected.

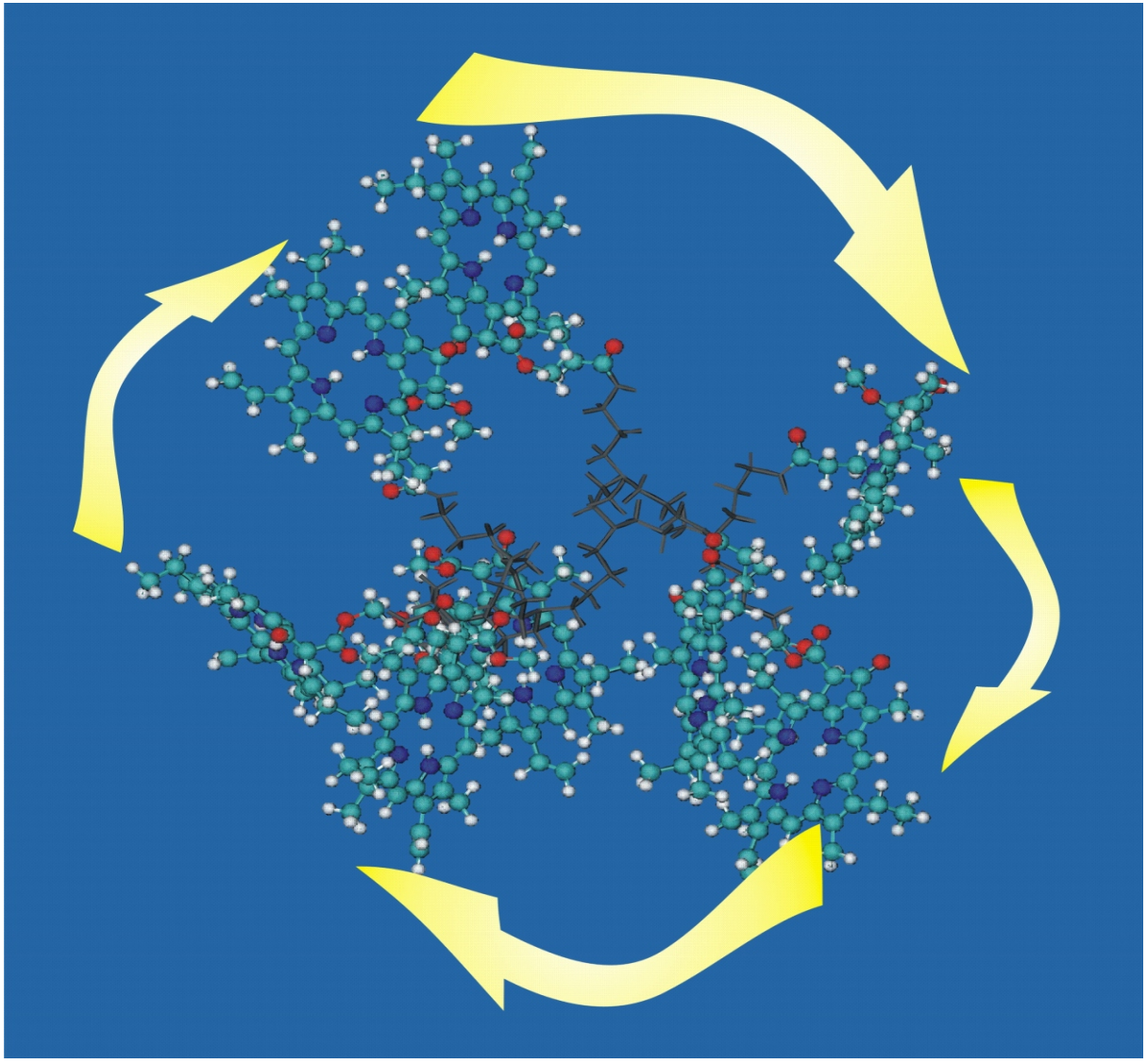


The modulation of the single chromophore excitation energy by the solvent molecules is included.

without time averaging







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Hui Zhu
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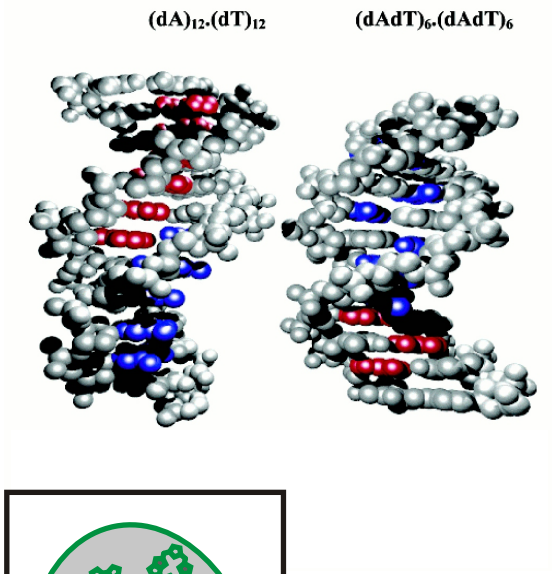

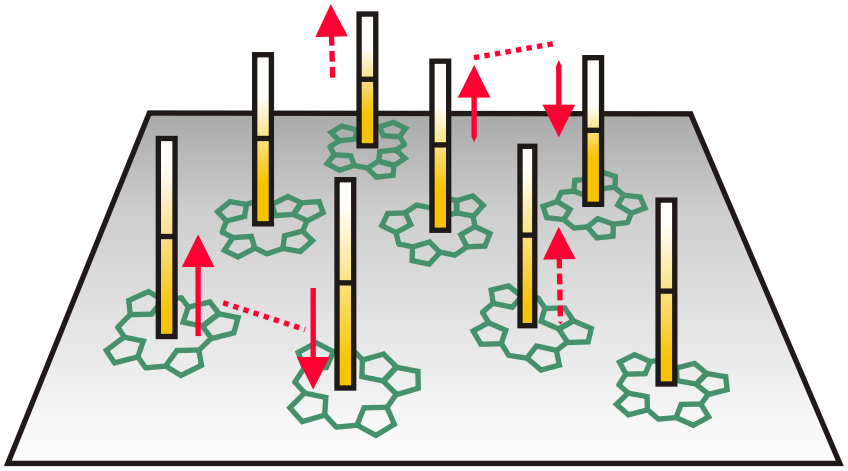

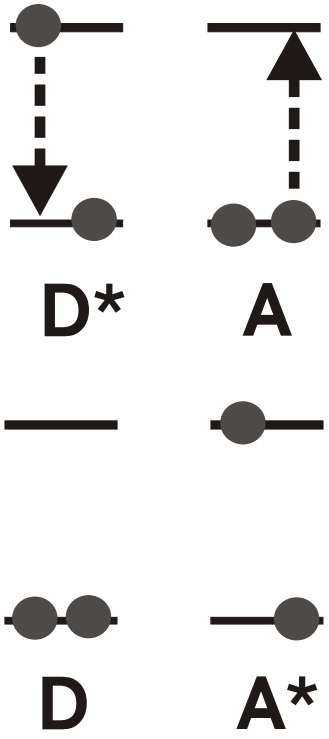

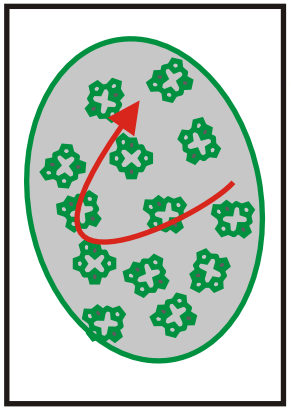

Thanks for your attention