Transfer Phenomena in Molecular Nanostructures: From Nanosecond Reactions to Femtosecond Wavepacket Motion

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Electron transfer in donor-acceptor complexes
E. G. Petrov (Kiev)

Charge transmission through molecular wires
E. G. Petrov (Kiev), P. Hänggi (Augsburg)

Ultrafast heterogeneous electron transfer
L. Wang, F. Willig (Berlin)

Exciton transfer in photosynthetic antennae
B. Brüggemann (Berlin), V. Sundström (Lund)
R. van Grondelle (Amsterdam)

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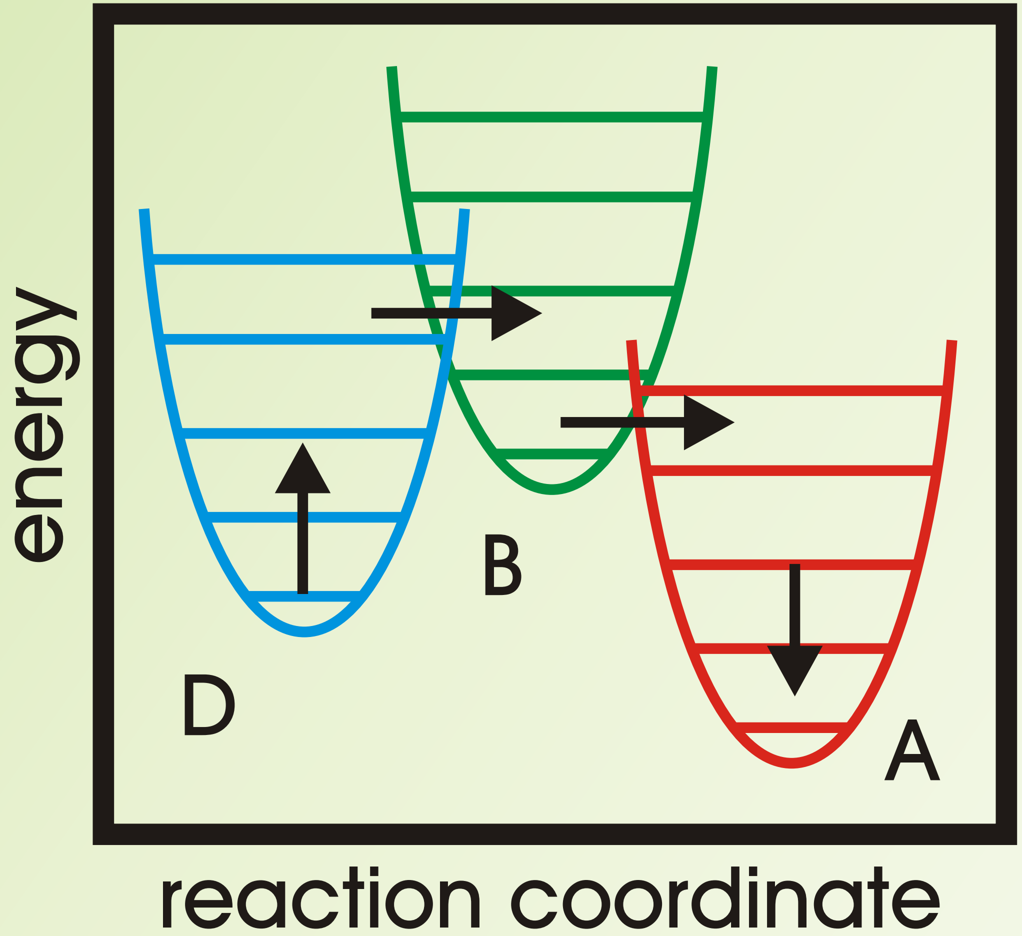
Photoinduced Reactions
VW-Foundation: “Intra and Intermolecular Electron Transfer”

Basic Theoretical Description of Electron Transfer

Energetics



Dynamics

Electron-Vibrational Density Matrix

m{M},n{N}

ET on a fs-timescale

$\tau_{ET} << \tau_{IVR}$

electron and vibrational coherences

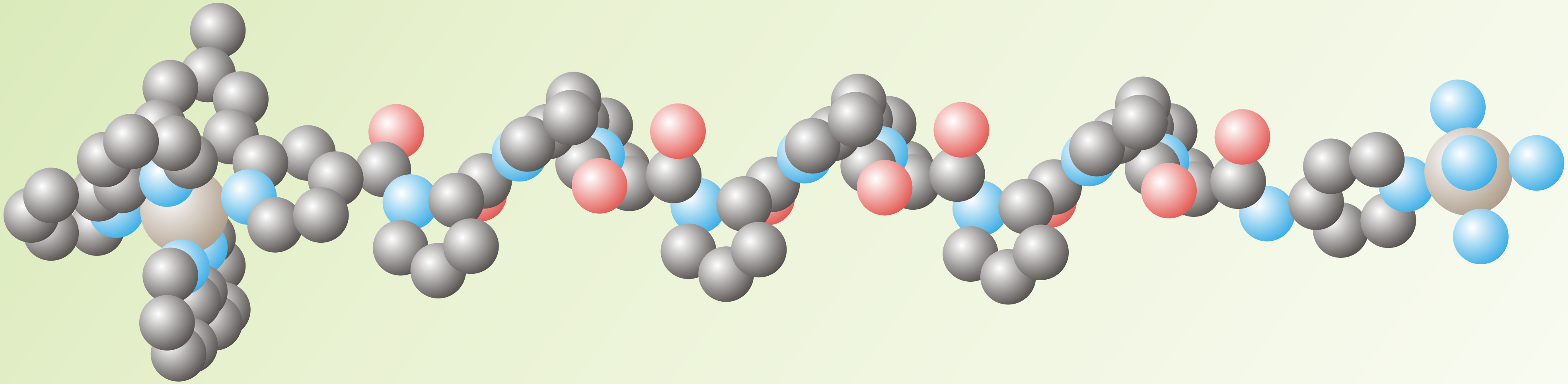
ET on a ns-timescale

$\tau_{ET} >> \tau_{IVR}$

electron populations

Electron Transfer in Donor-Acceptor Complexes

Polyproline Mediated Electron Transfer



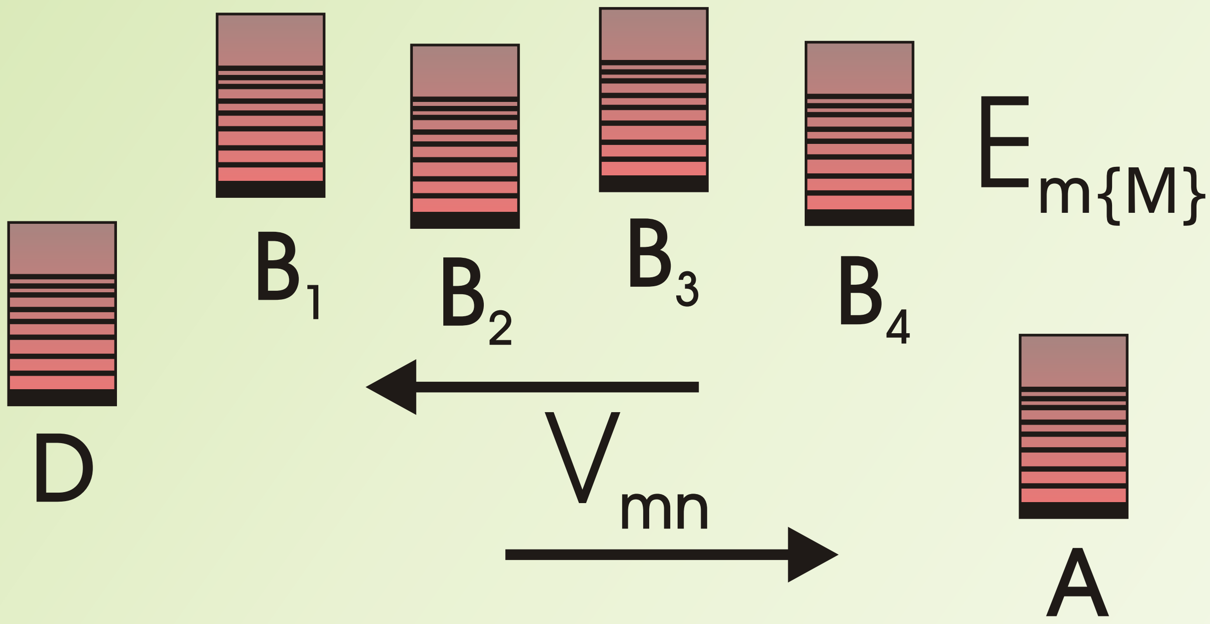
<u>Experiments:</u>

Isied, Ogawa, and Wishart, Chem. Rev. 92, 381 (1992).

<u>Theory:</u>

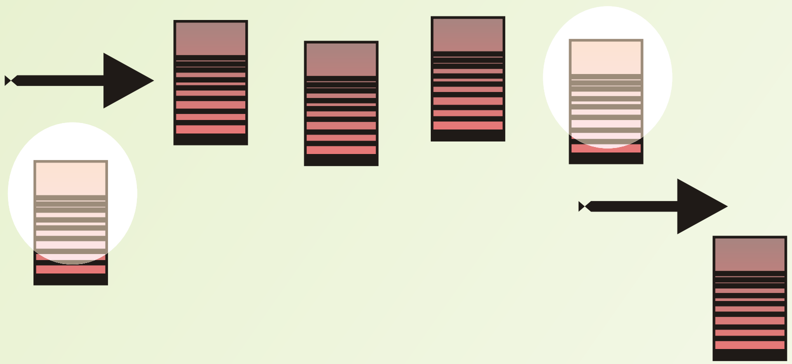
Petrov, Shevchenko, Teslenko, and May, J. Chem. Phys. 115, 7107 (2001).
Petrov and May, J. Phys. Chem. A 105, 10176 (2001).
Petrov, Shevchenko, and May, Chem. Phys. 288, 269 (2003).
Bade, Petrov, and May, Eur. Phys. J D 26, 187 (2003).

Bridge Mediated Nonadiabatic Electron Transfer

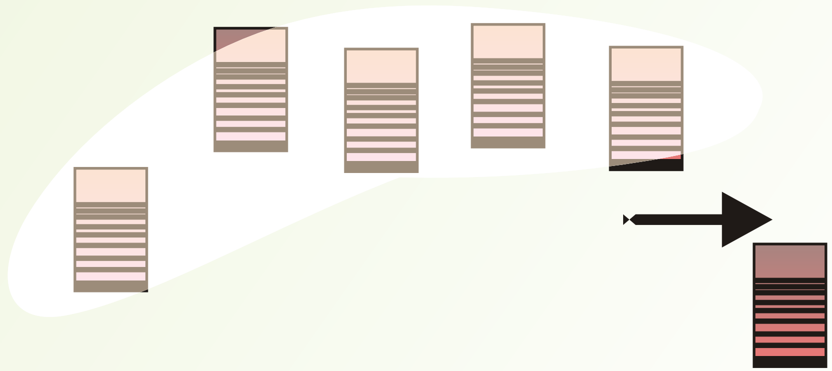


- diabatic electronic states
- electronic interstate coupling
- finite lifetime of vibrational levels

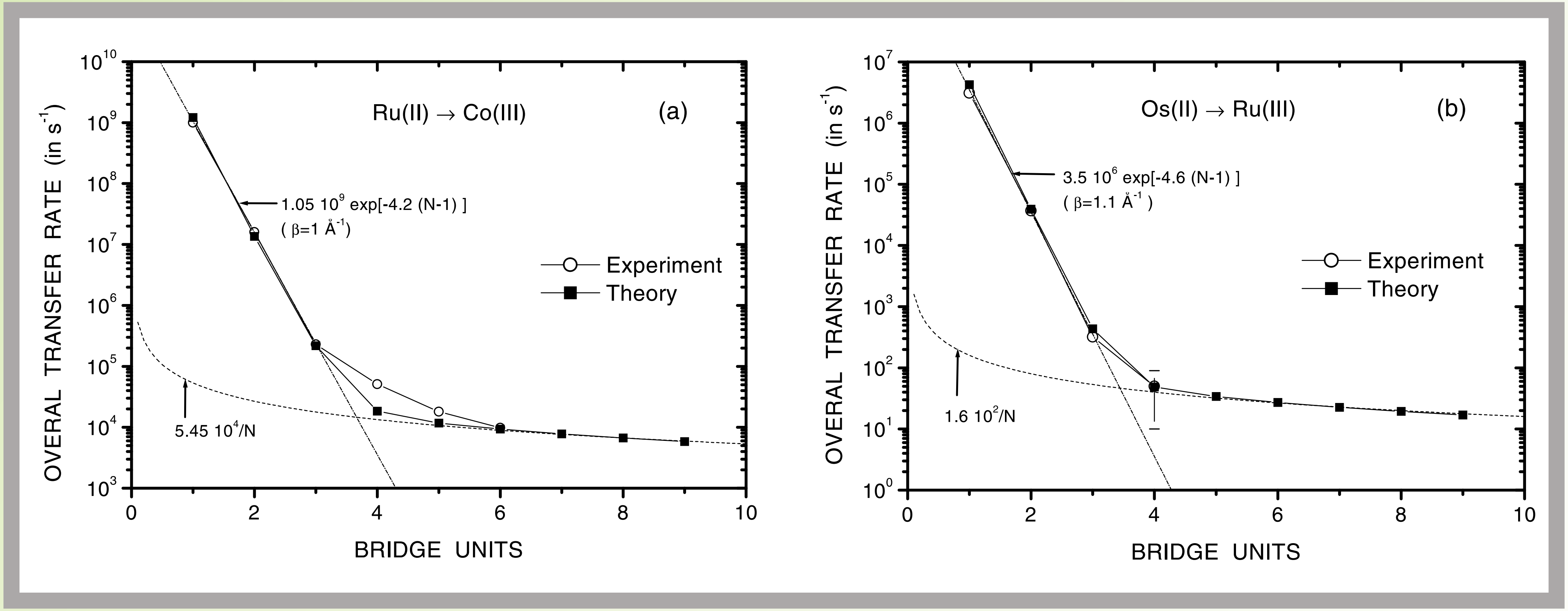
Sequential ET



Superexchange ET

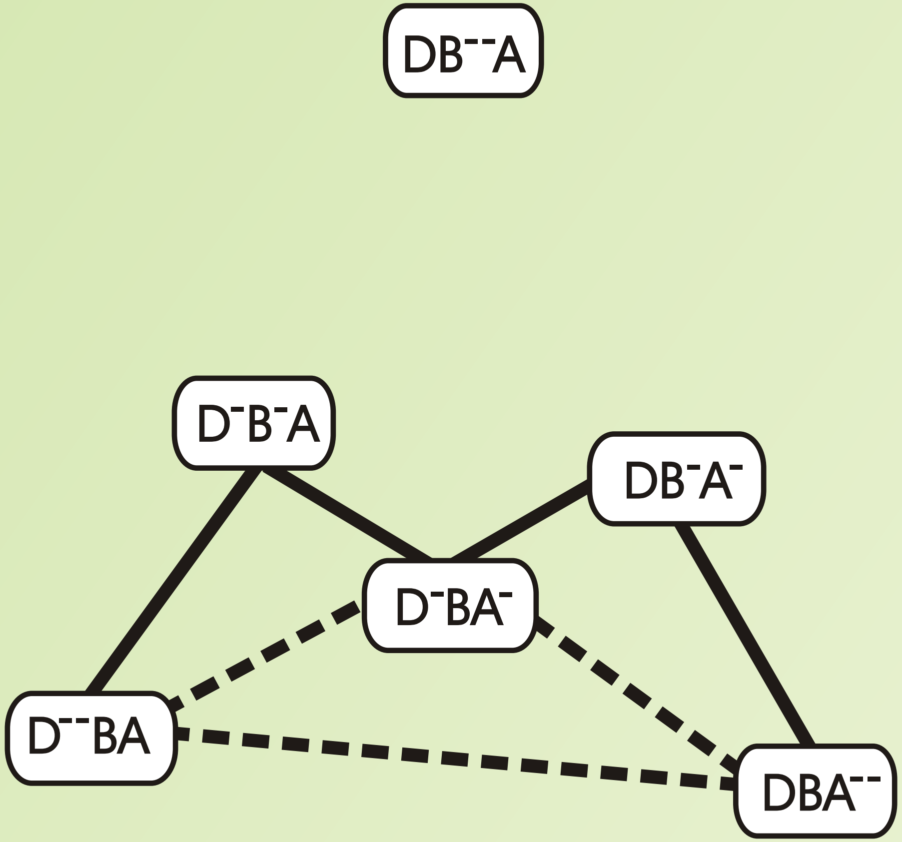


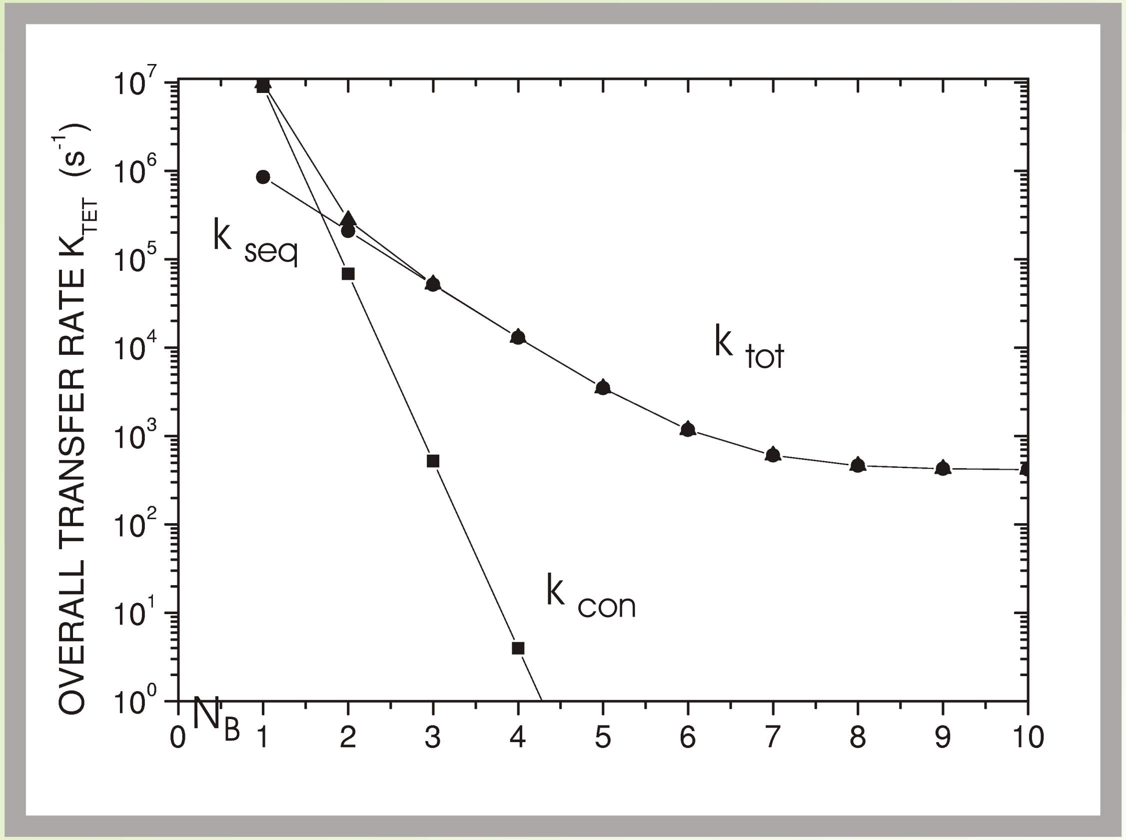
Electron Transfer through Donor-Oligo-Proline-Acceptor Complexes



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

Two-Electron Transfer in a Donor-Bridge-Acceptor Complex

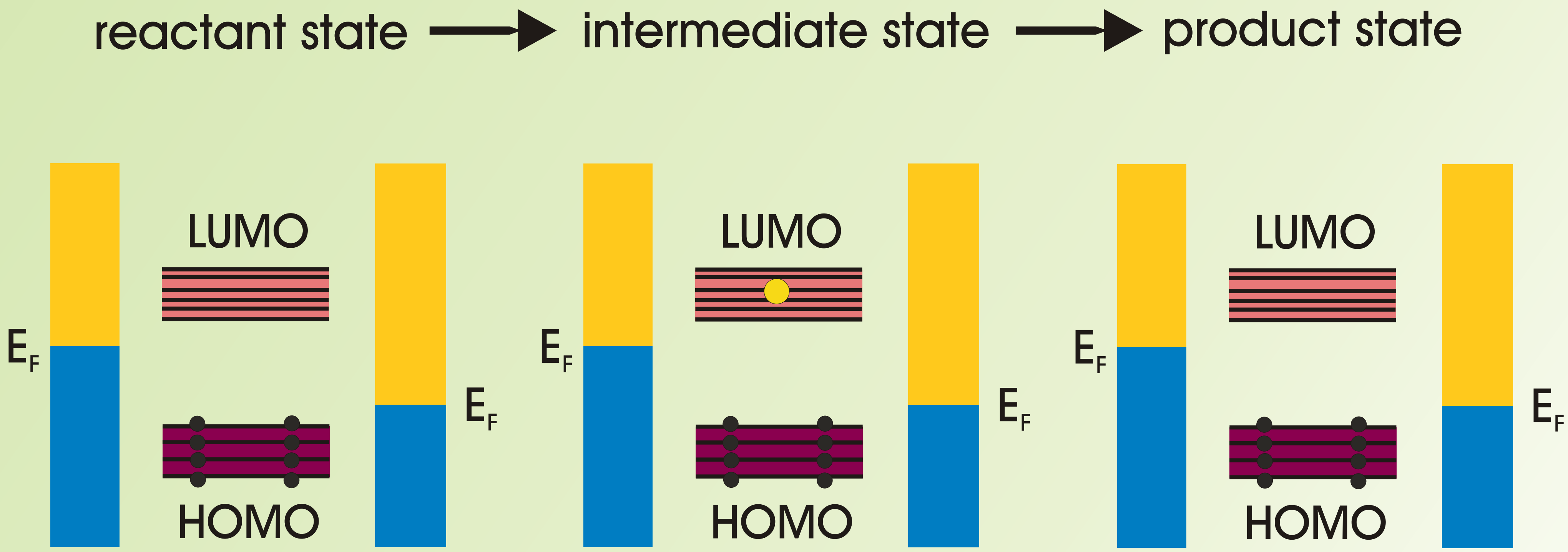




E. G. Petrov and V. May,
J. Chem. Phys. 120, 441 (2004)

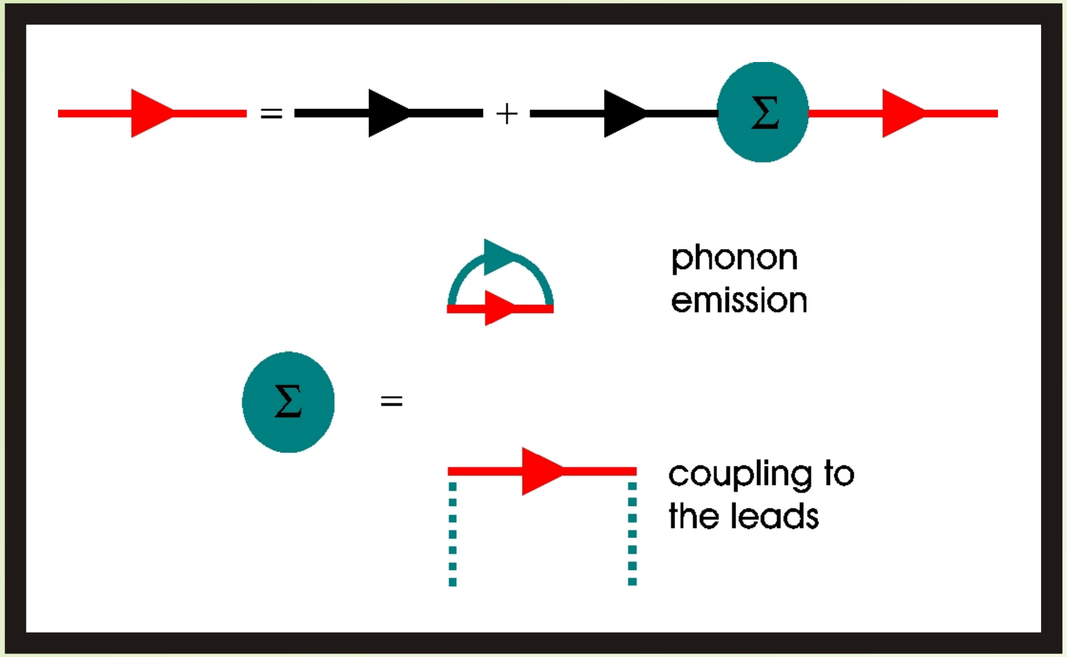
CHARGE TRANSMISSION THROUGH MOLECULAR WIRES

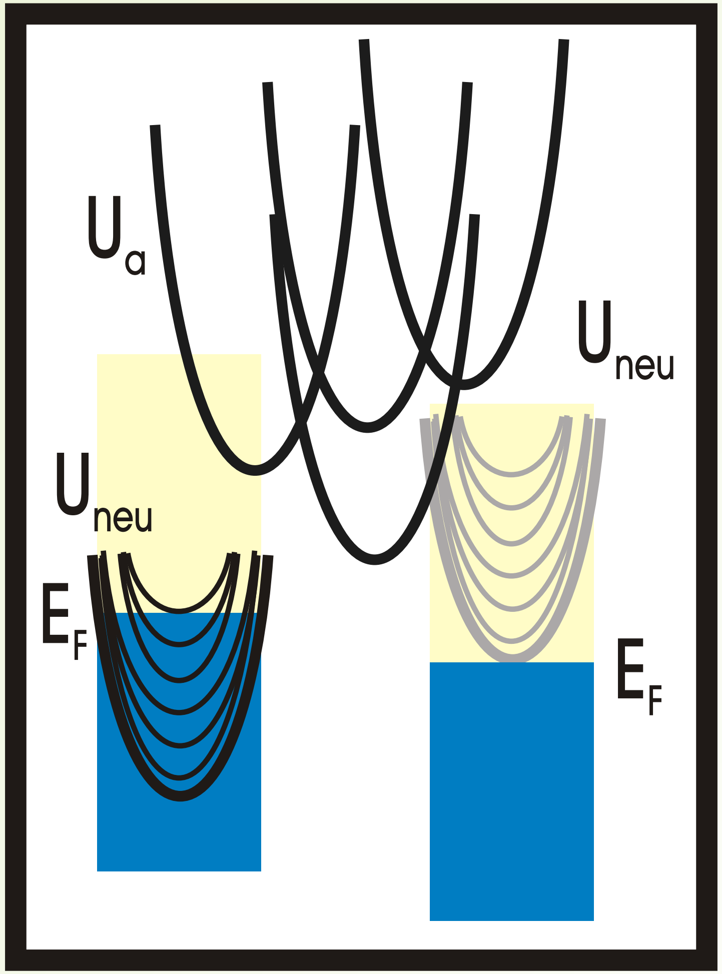
Single Electron Transmission



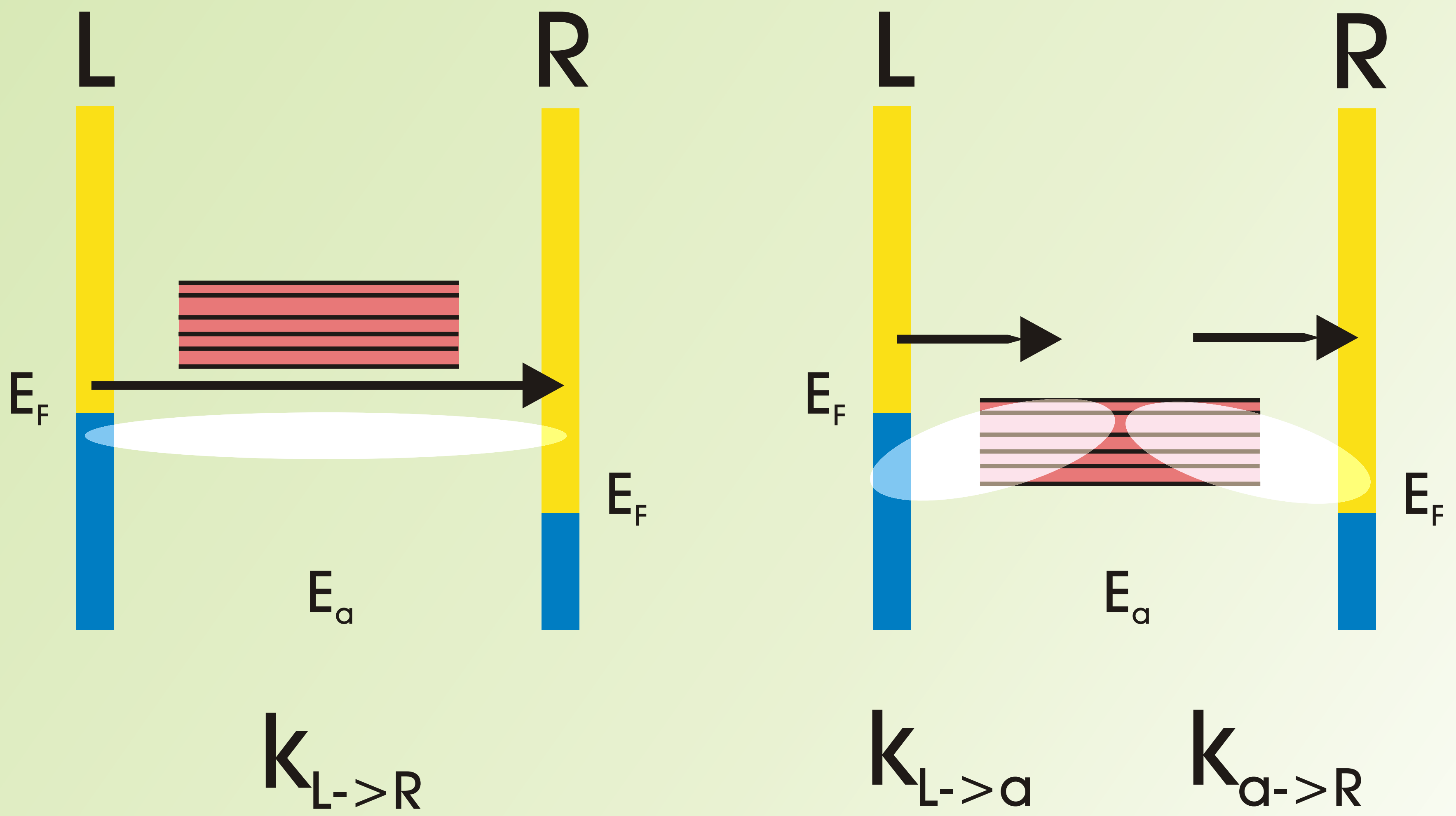
Theoretical Chemical Physics

Many-Particle Theory





Elastic Transfer versus Sequential Transfer

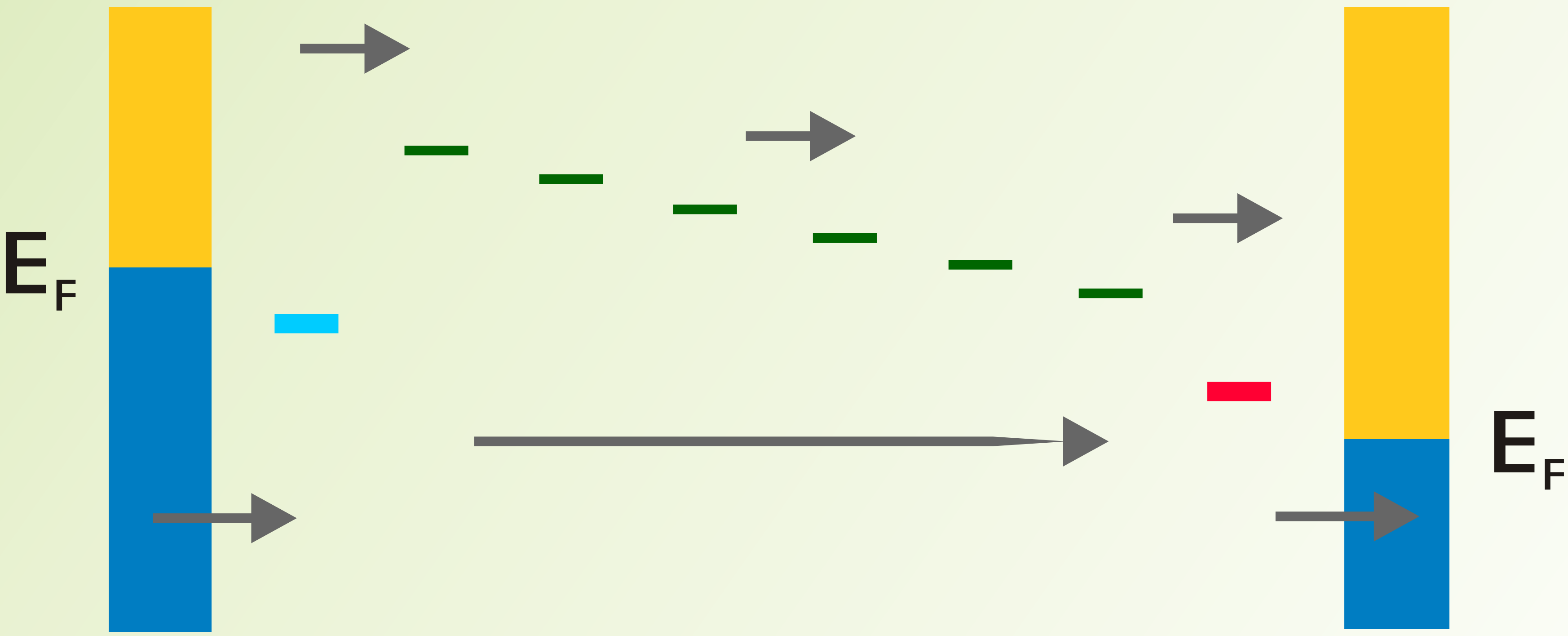


$$I = e \int d\omega \; \mathrm{tr}_{\mathrm{wire}} \{ \; \hat{\Gamma}^{(L)}(\omega) \; \hat{G}^{(\mathrm{ret})}(\omega) \; \hat{\Gamma}^{(R)}(\omega) \; \hat{G}^{(\mathrm{adv})}(\omega) \}$$
$$\times \; \{ f_{\mathrm{Fermi}}(\hbar\omega - \mu_L) + f_{\mathrm{Fermi}}(\hbar\omega - \mu_R) \}$$

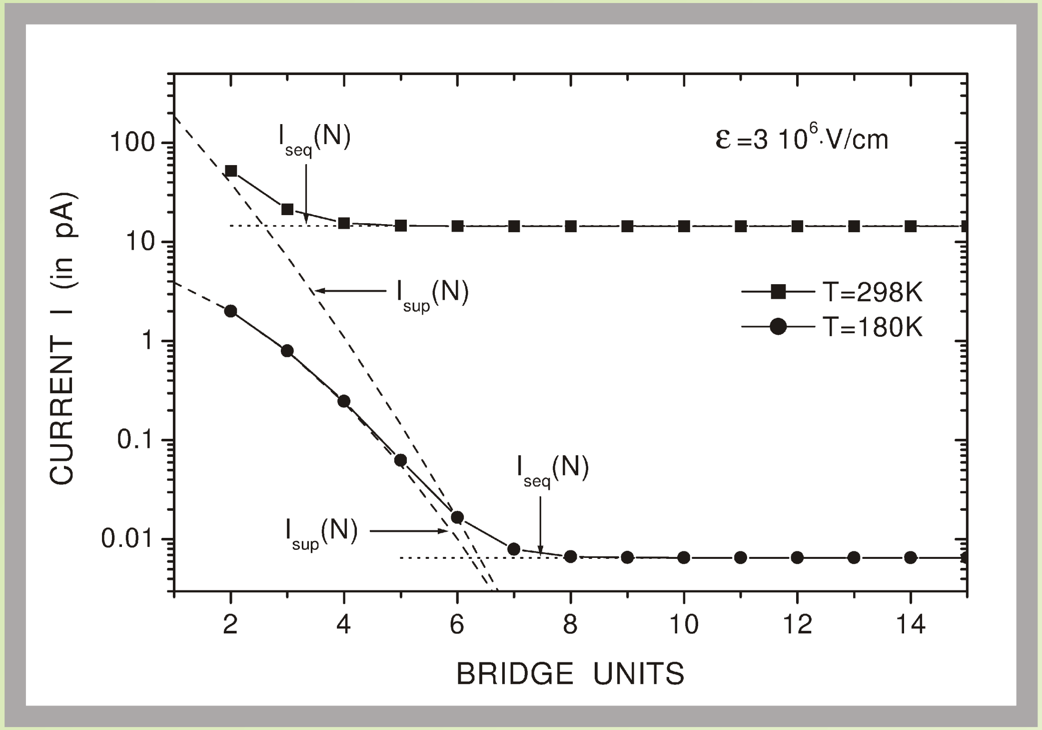
Elastic Transfer versus Sequential Transfer

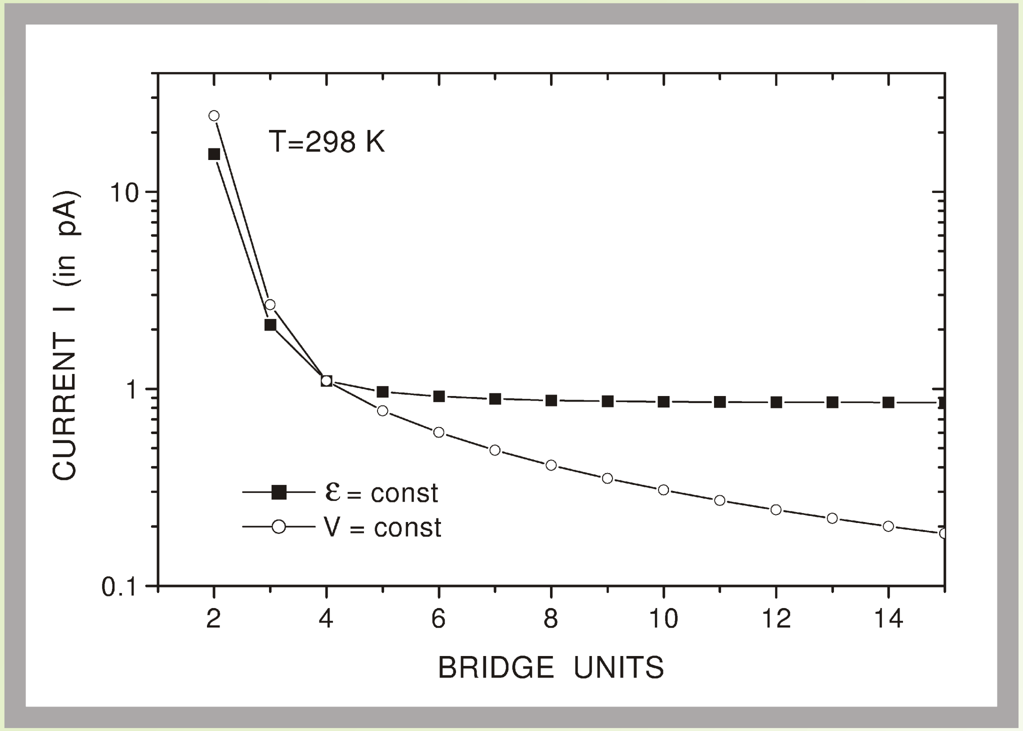
$$I = e \sum_a \frac{k_{L\to a} k_{a\to R} - k_{R\to a} k_{a\to L}}{k_{a\to L} + k_{a\to R}}$$

Hopping versus Superexchange Transfer



Wire-Length Dependence of the Current





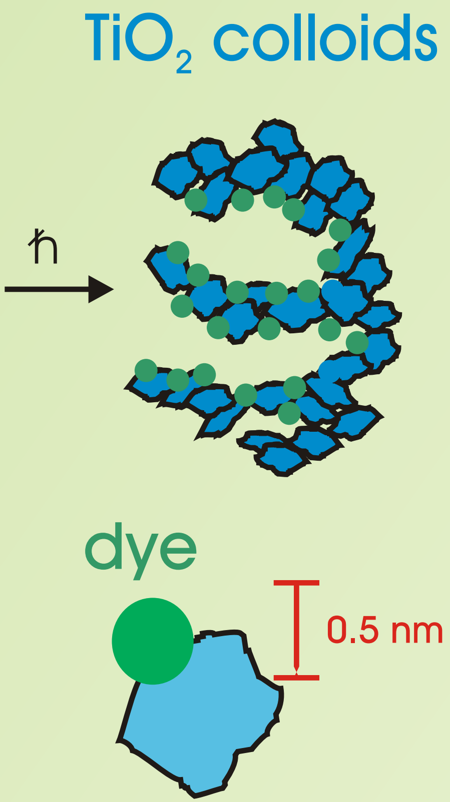
$E = V/d = 3 \times 10^6$ V/cm

$E = V/d = 4.35 \times 10^5$ V/cm

$V = 0.9$ V

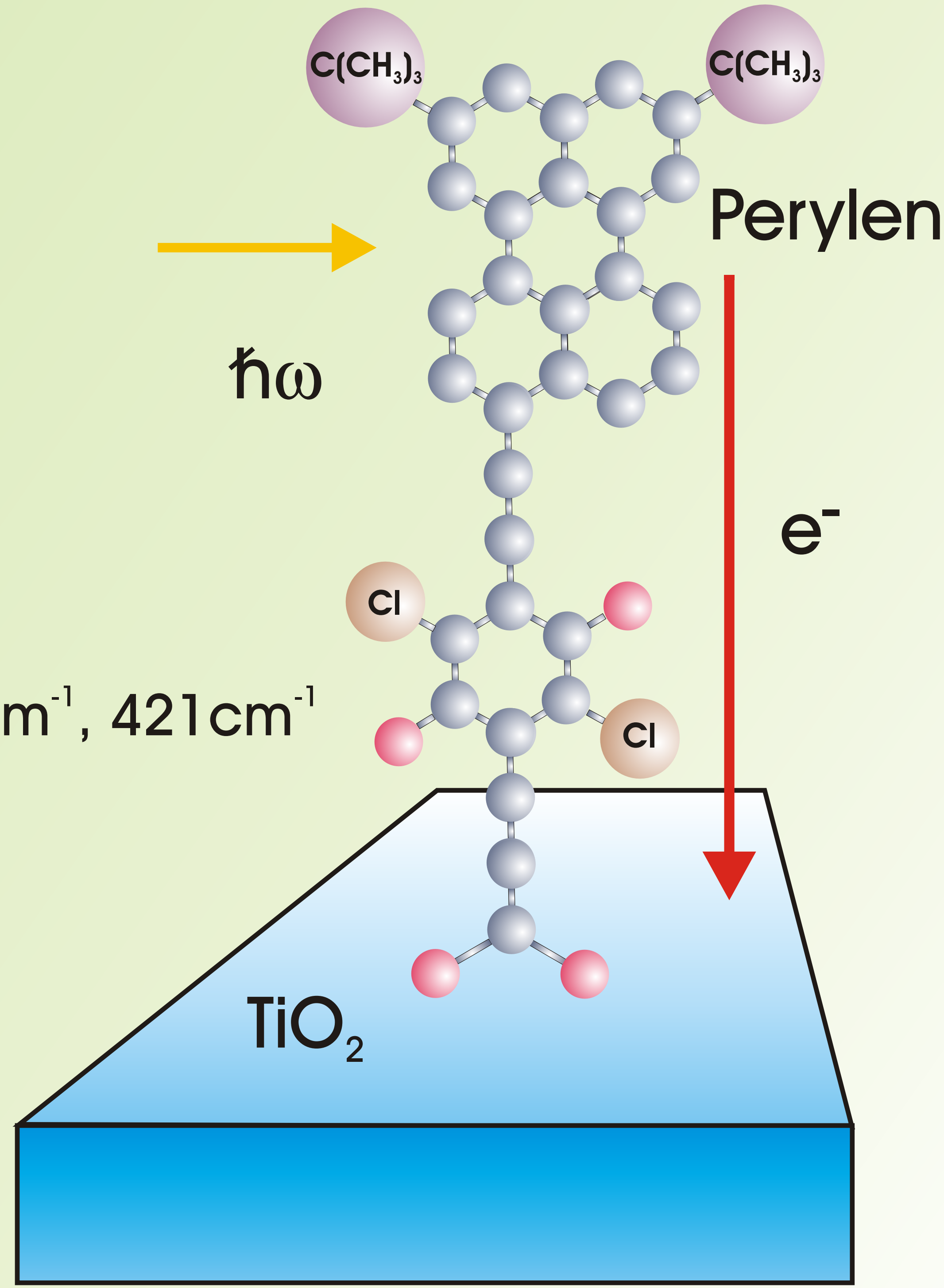
ULTRAFAST HETEROGENEOUS ELECTRON TRANSFER

Perylene on TiO_2

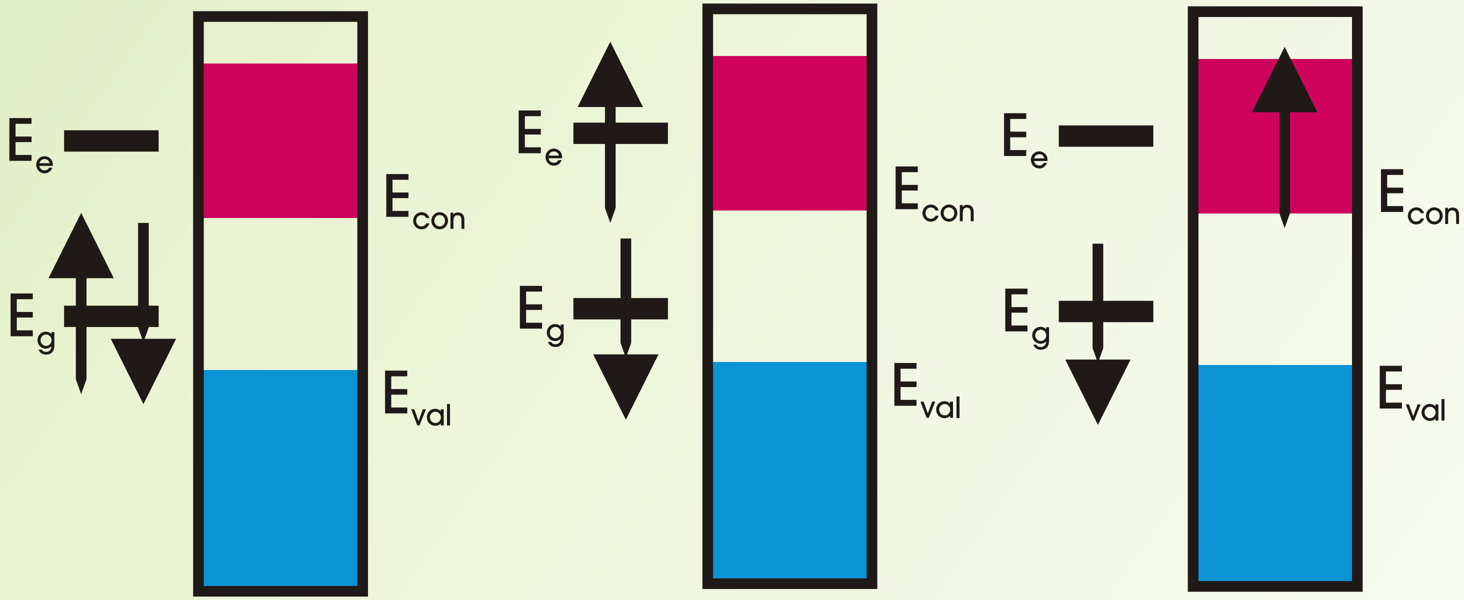


t_{ET} = 75fs

$_{vib}$ = 357cm^{-1}, 421cm^{-1}



Energy level scheme and PES (perylene / TiO_2)



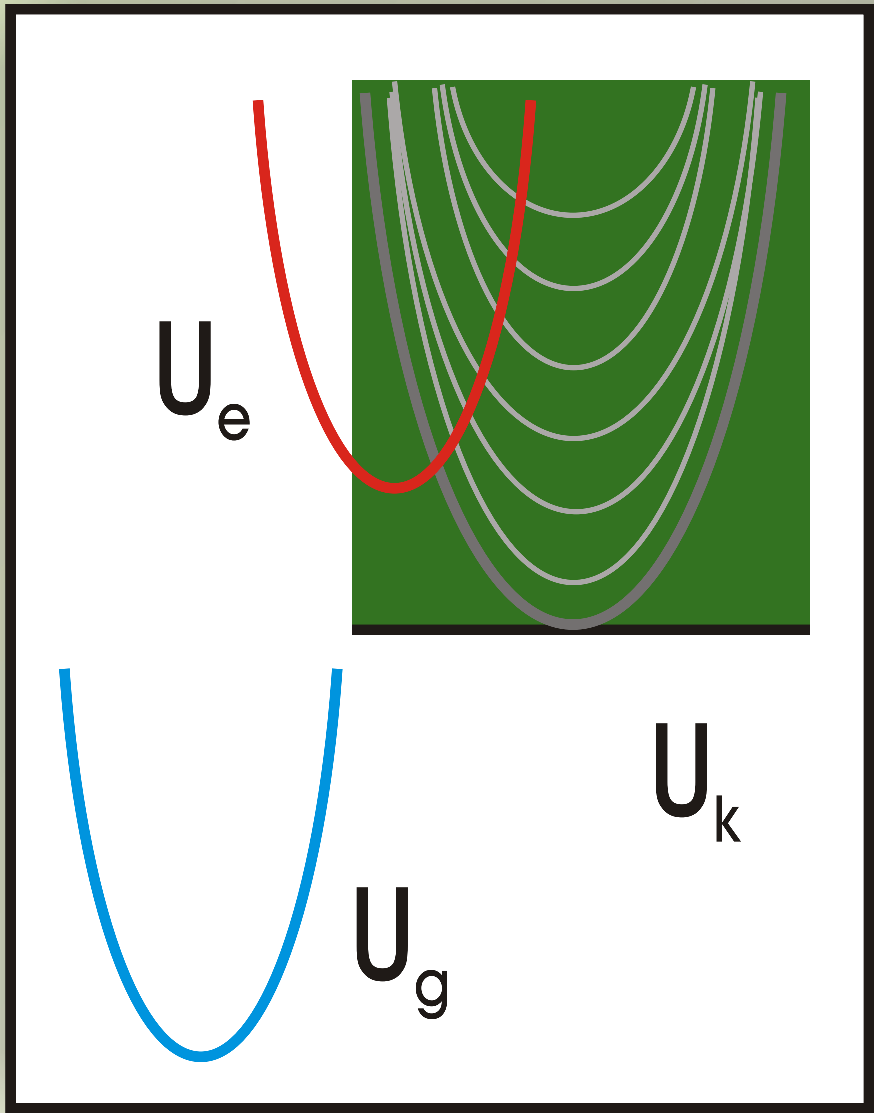
diabatic states

$|D>|A>$ $|D^*>|A>$ $|D^+>|A^->$

$\hbar\omega = 0.17\,\mathrm{eV}$

$\lambda = 0.1 - 0.3\,\mathrm{eV}$

$\tau_{ET} = 75\,\mathrm{fs}$



3.79eV

2.79eV

1.79eV

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

Linear Absorption Coefficient and Combined Density of States

$$\alpha(\omega) = \frac{4\pi\omega n_{\mathrm{mol}}}{\hbar c}\mathrm{Re}\int_0^\infty dt\, e^{i\omega t} < \mathrm{tr}\{\hat{W}_{\mathrm{eq}}\ [\hat{\mu}(t), \hat{\mu}]_-\} >_{\mathrm{disorder}}$$

$$\equiv \frac{4\pi^2\omega n_{\mathrm{mol}}}{3c} \mid d_{eg} \mid^2 \mathcal{D}_{\mathrm{abs}}(\omega - \omega_{eg})$$

$$\mathcal{D}_{\mathrm{abs}}(\omega - \omega_{eg}) = \frac{1}{\pi\hbar}\mathrm{Re}\int_0^\infty dt\, e^{i(\omega-\omega_{eg})t} \langle\chi_{g0}|e^{i\omega_{e0}t}U_{\mathrm{vib}}^{(\mathrm{eff})}(t)|\chi_{g0}\rangle$$

$$U_{\mathrm{vib}}^{(\mathrm{eff})}(t) = \langle\varphi_e|U_{\mathrm{mol-sem}}(t)|\varphi_e\rangle$$

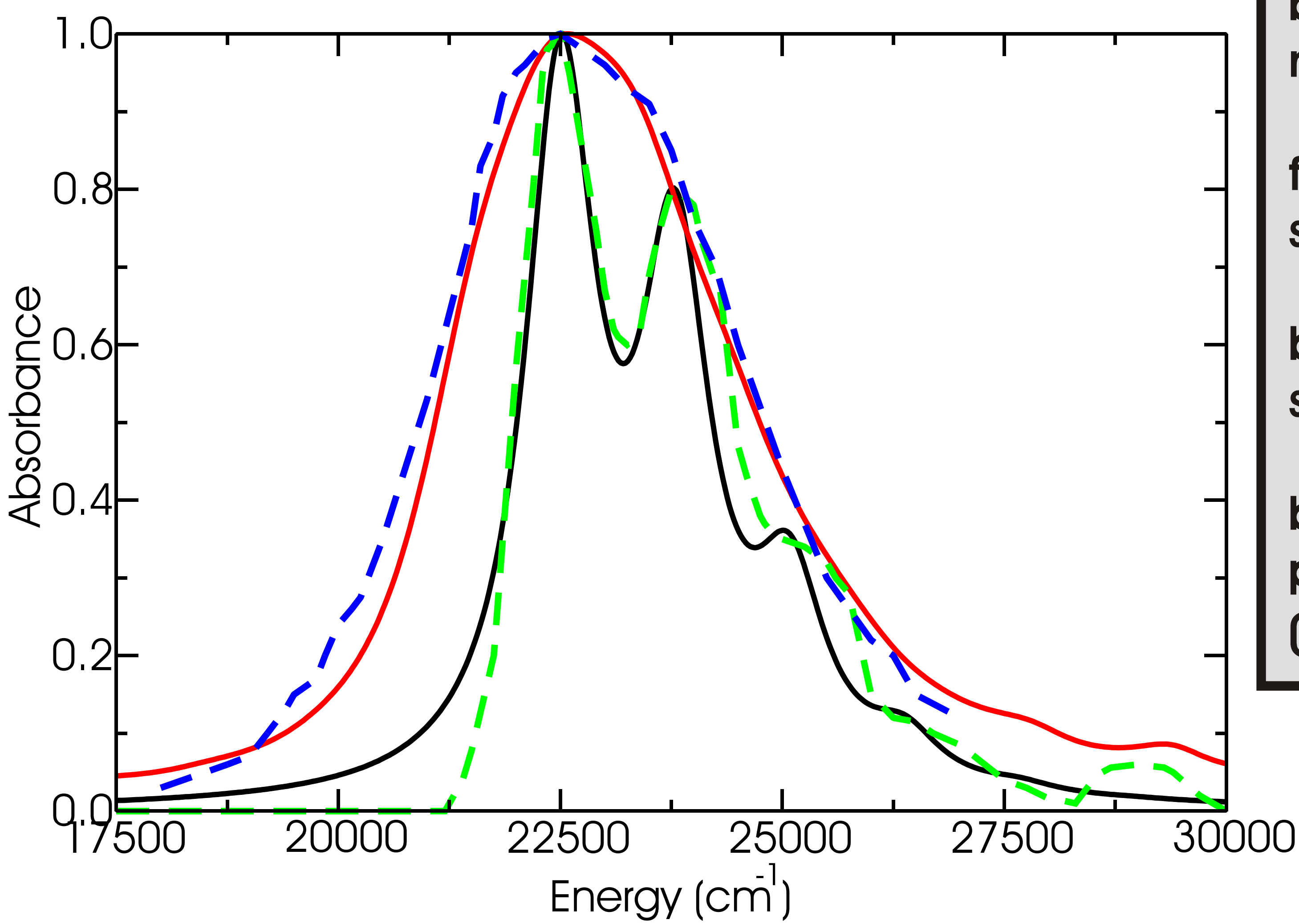
Expansion of the Wavefunction: Basis Set Expansion versus TDMCH-Approach

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

$$|\Psi(t)\rangle = \sum_a \chi_a(q_1, ..., q_f; t)\ |\varphi_a\rangle = \sum_a \sum_{j_1=1}^{n_1} \cdots \sum_{j_f=1}^{n_f} A^{(a)}_{j_1,...,j_f}(t) \prod_{\kappa=1}^{f} \phi^{(a\kappa)}_{j_\kappa}(q_\kappa, t)\ |\varphi_a\rangle$$

$$\mathcal{D}_{\rm abs}(\omega - \omega_{eg}) = \frac{1}{\pi\hbar}{\rm Re}\int_0^\infty dt\, e^{i(\omega-\omega_{eg})t} \sum_M e^{i\omega_{e0}t}\langle\chi_{g0}|\chi_{eM}\rangle C_{eM}(t)$$

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)

Effect of the Conduction Band Continuum

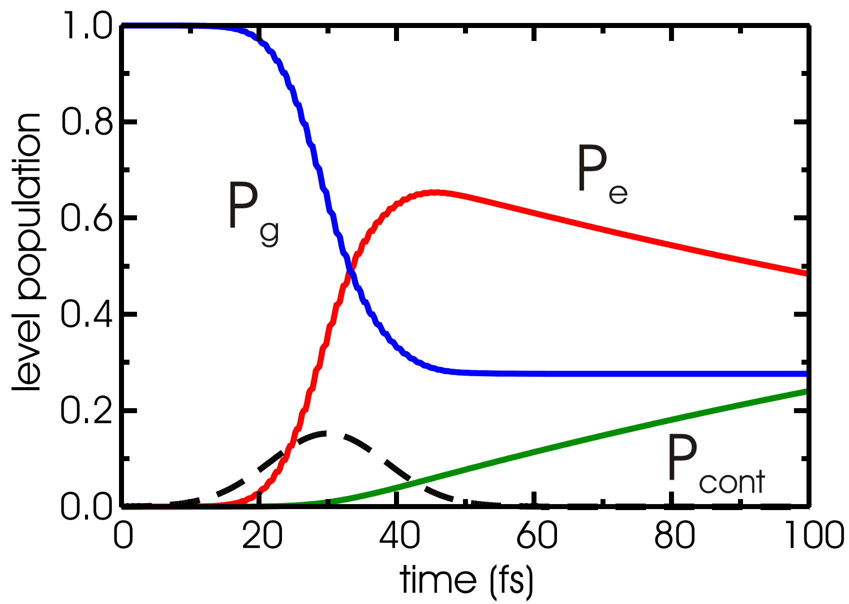
$$\mathcal{D}_{\mathrm{abs}}(\omega-\omega_{eg}) = -\frac{1}{2\pi^2\hbar}\sum_{M,N} f(\hbar\omega_{gN})\left|\langle\chi_{gN}|\chi_{eM}\rangle\right|^2$$

$$\times \mathrm{Re}\int d\bar{\omega}\,\frac{1}{\omega-\omega_{eM,gN}-\bar{\omega}+i\epsilon}\,\frac{1}{\bar{\omega}-\Sigma(\bar{\omega})+i\epsilon}$$

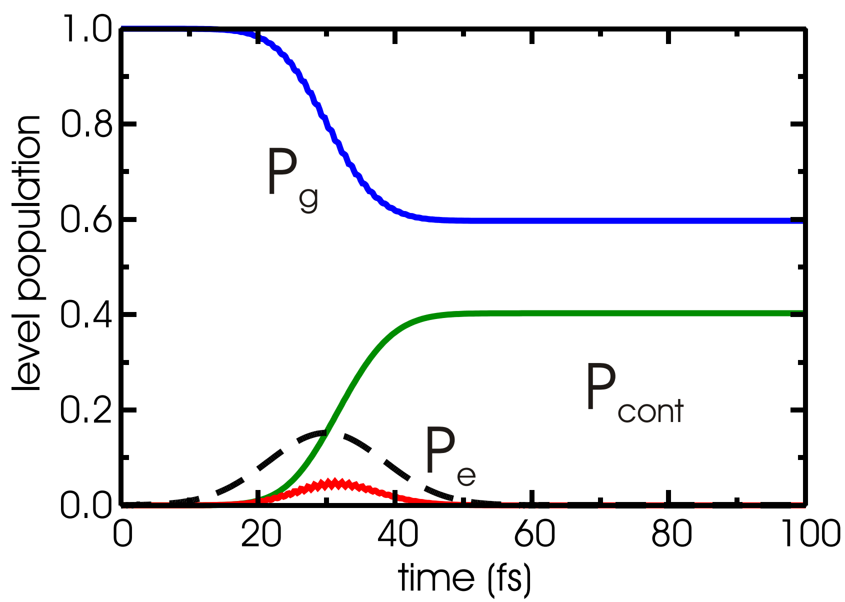
$$\Sigma(\omega) = \frac{1}{\hbar^2}\int d\Omega\,\frac{\mathcal{N}(\Omega)|V_e(\Omega)|^2}{\omega-[\Omega-\omega_e]+i\epsilon}$$

Change of the Injection Time

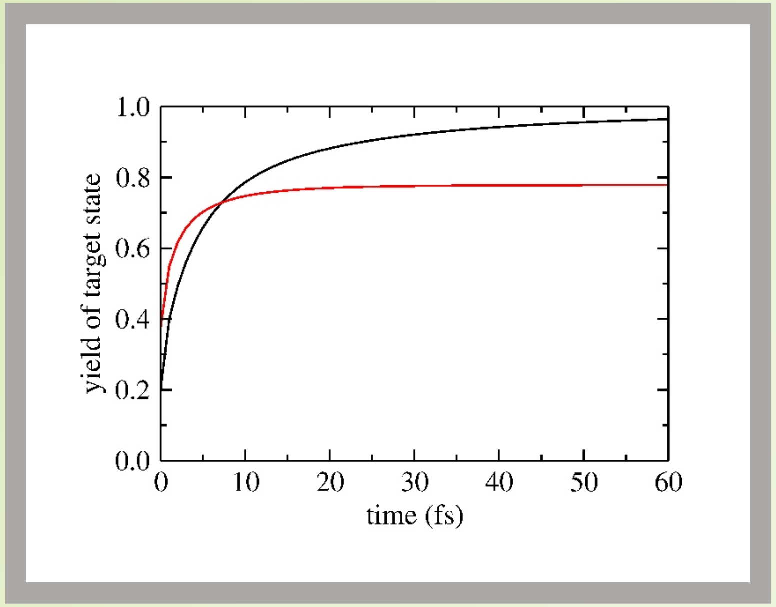
V = 0.02 eV

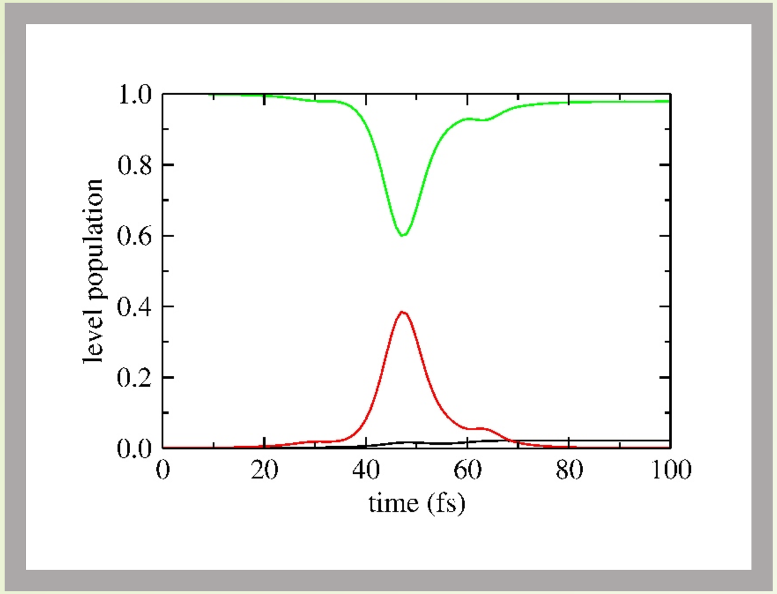


V = 0.2 eV



Laser Pulse Control of the Charge Injection Process



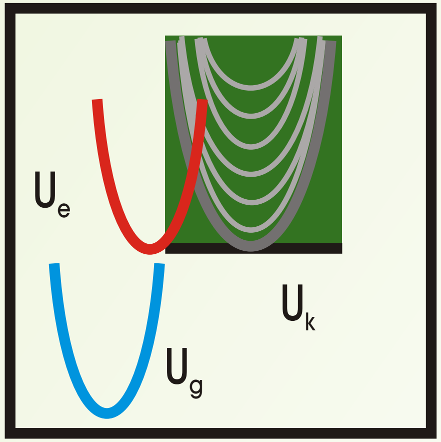


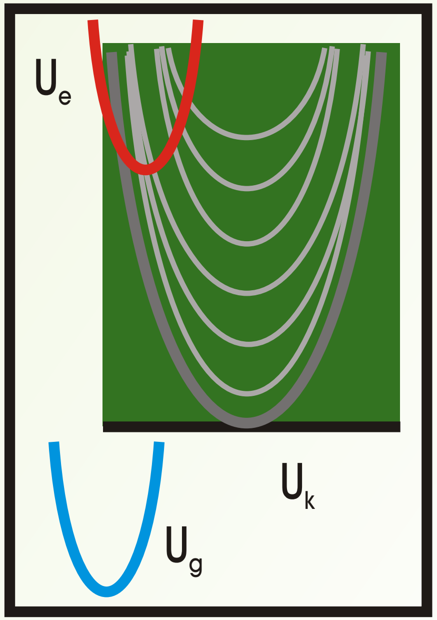
target state:

displaced vibrational ground-state in U_g

length of the control pulse:

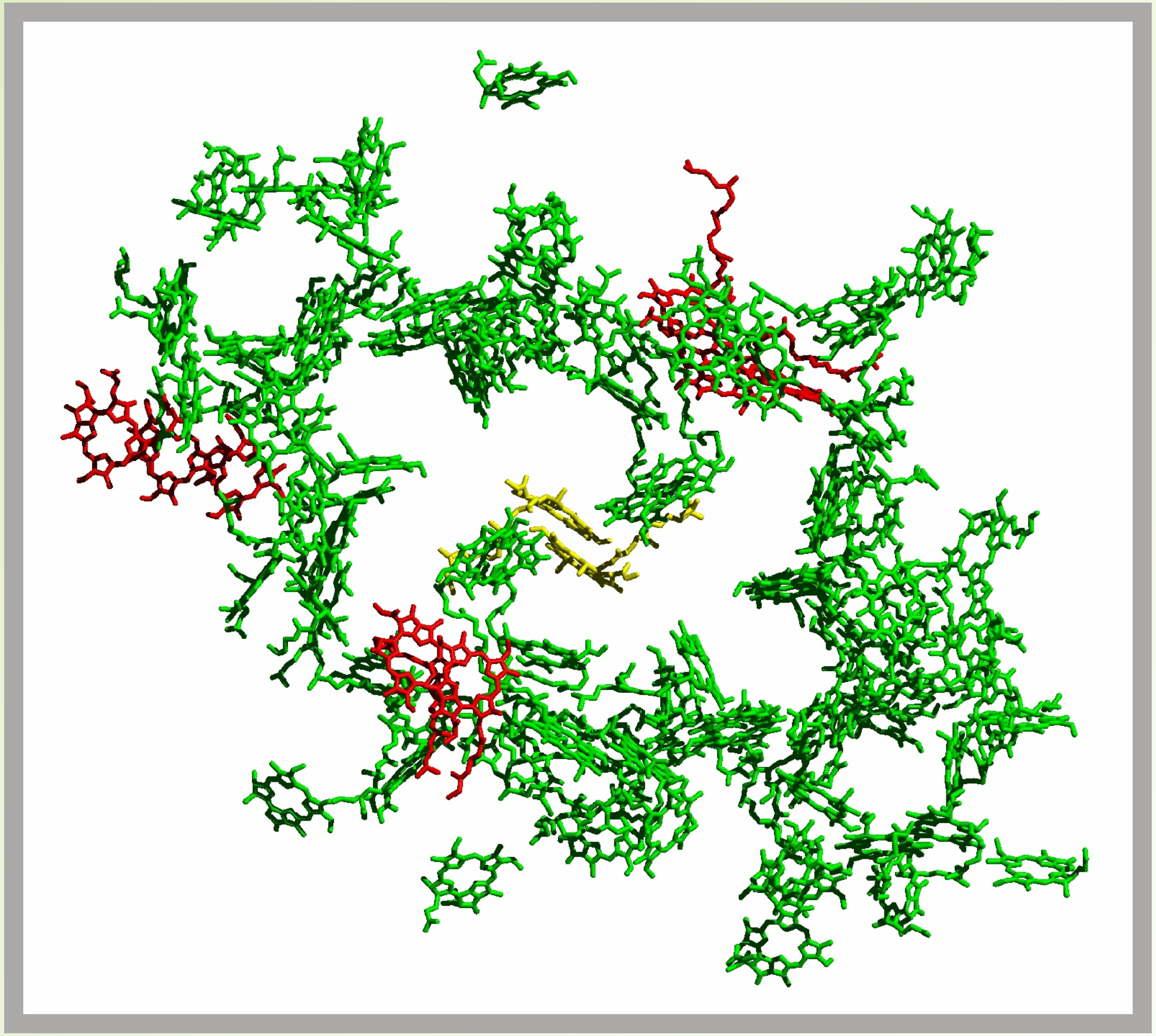
100f



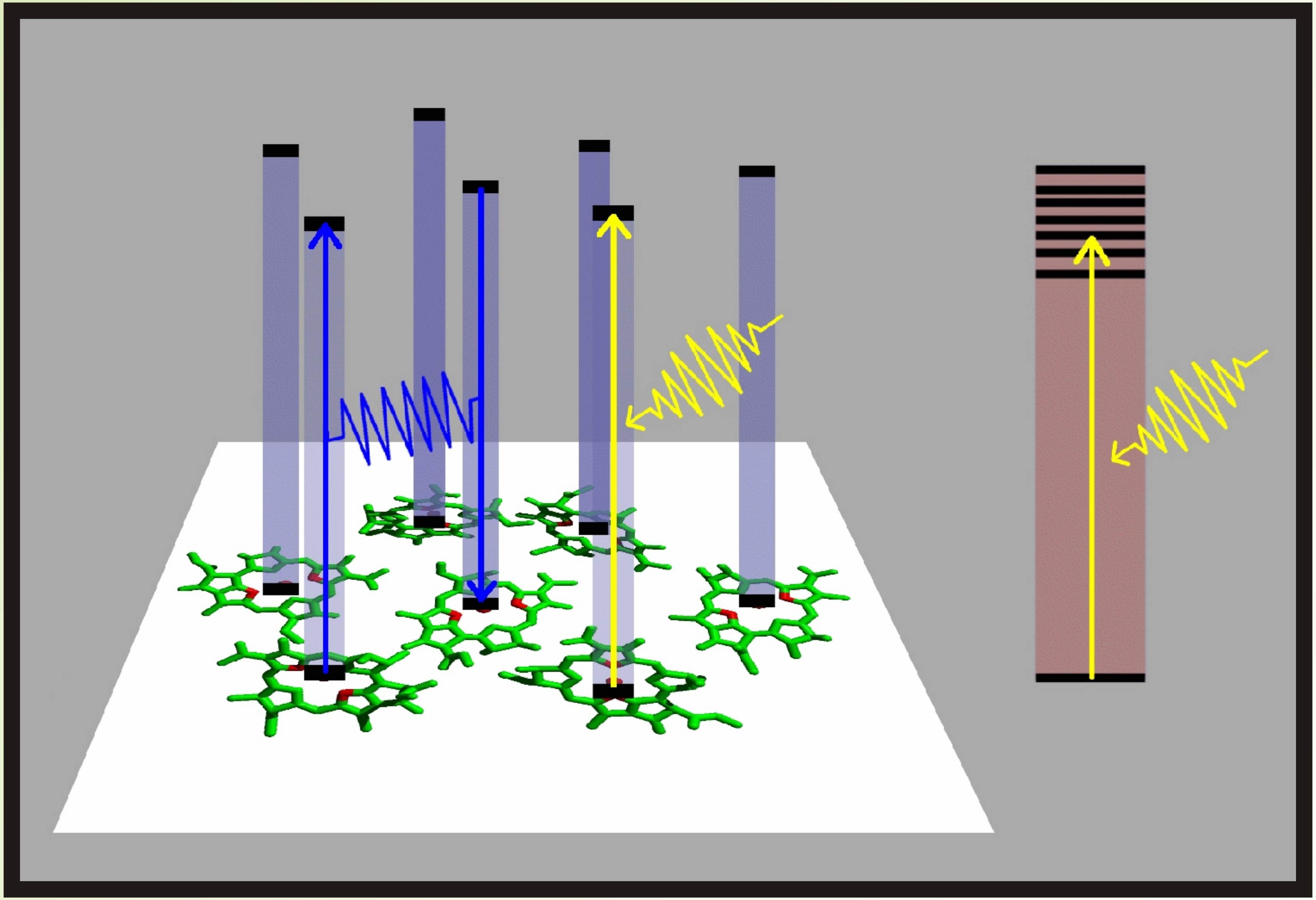


ULTRAFAST EXCITON TRANSFER IN PHOTOSYNTHETIC ANTENNAE

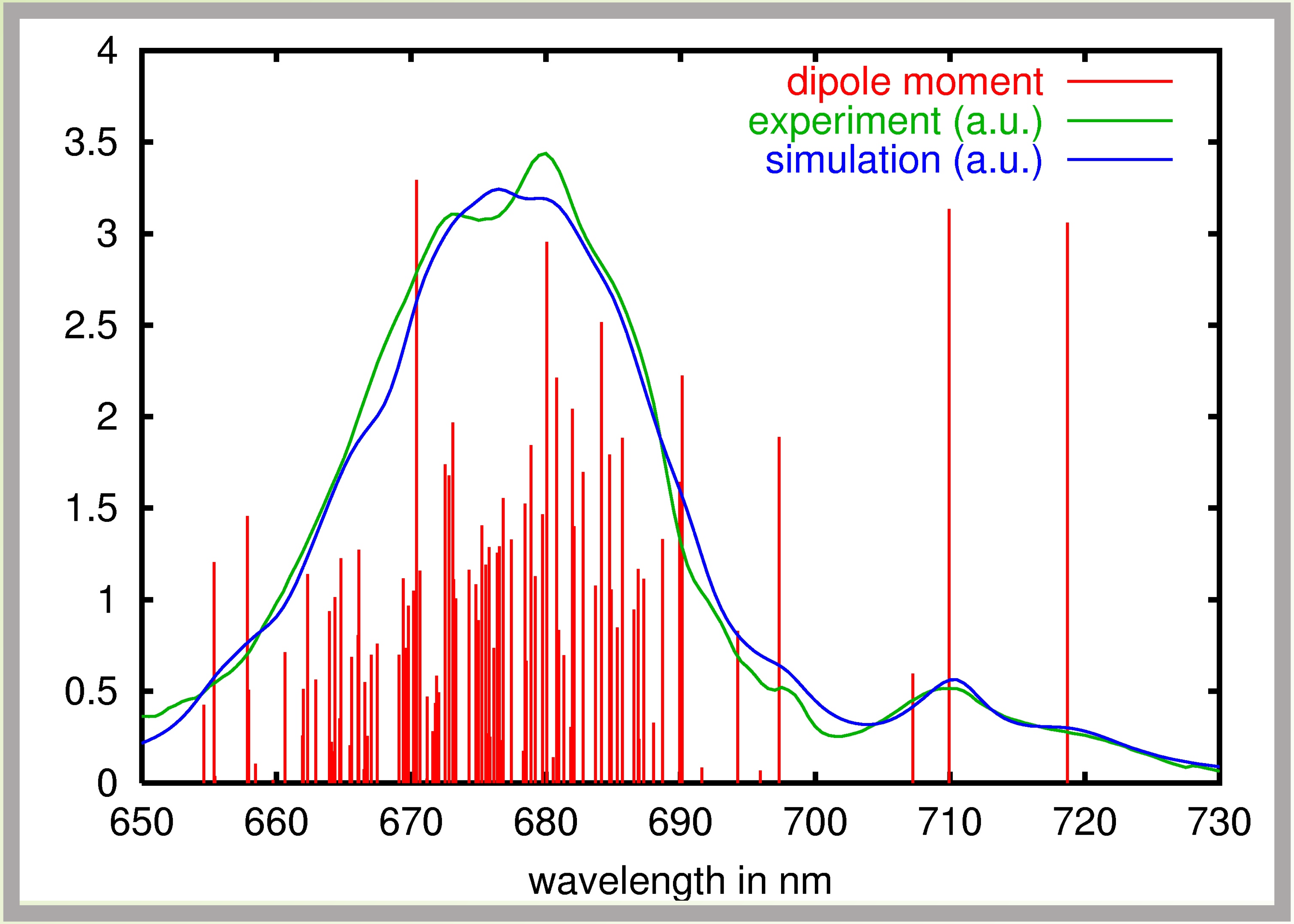
Spatial arrangement of the Chls in the monomeric Ps1 complex of *Synechococcus elongatus*



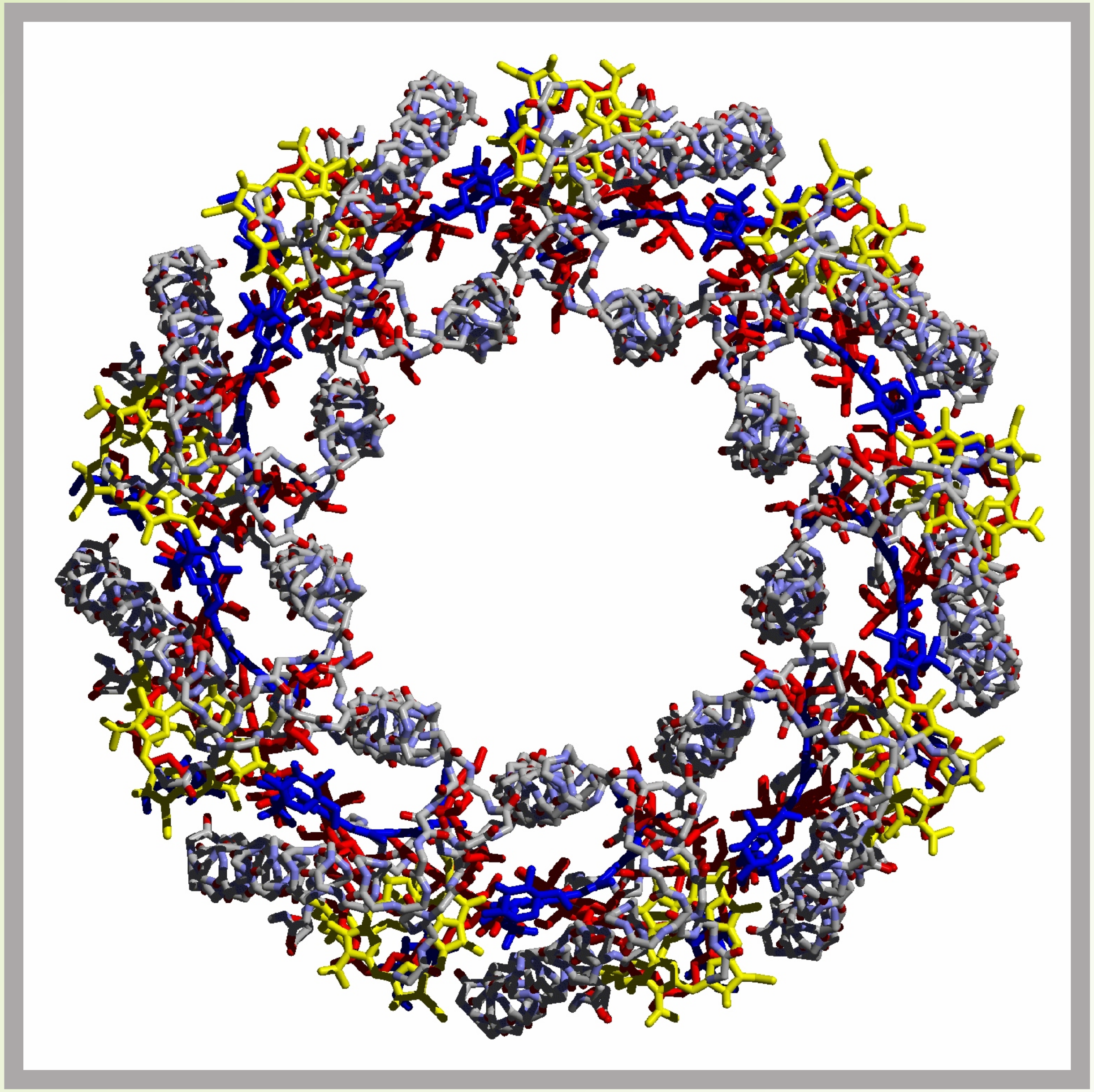
Exciton Model for Photosynthetic Antenna Systems



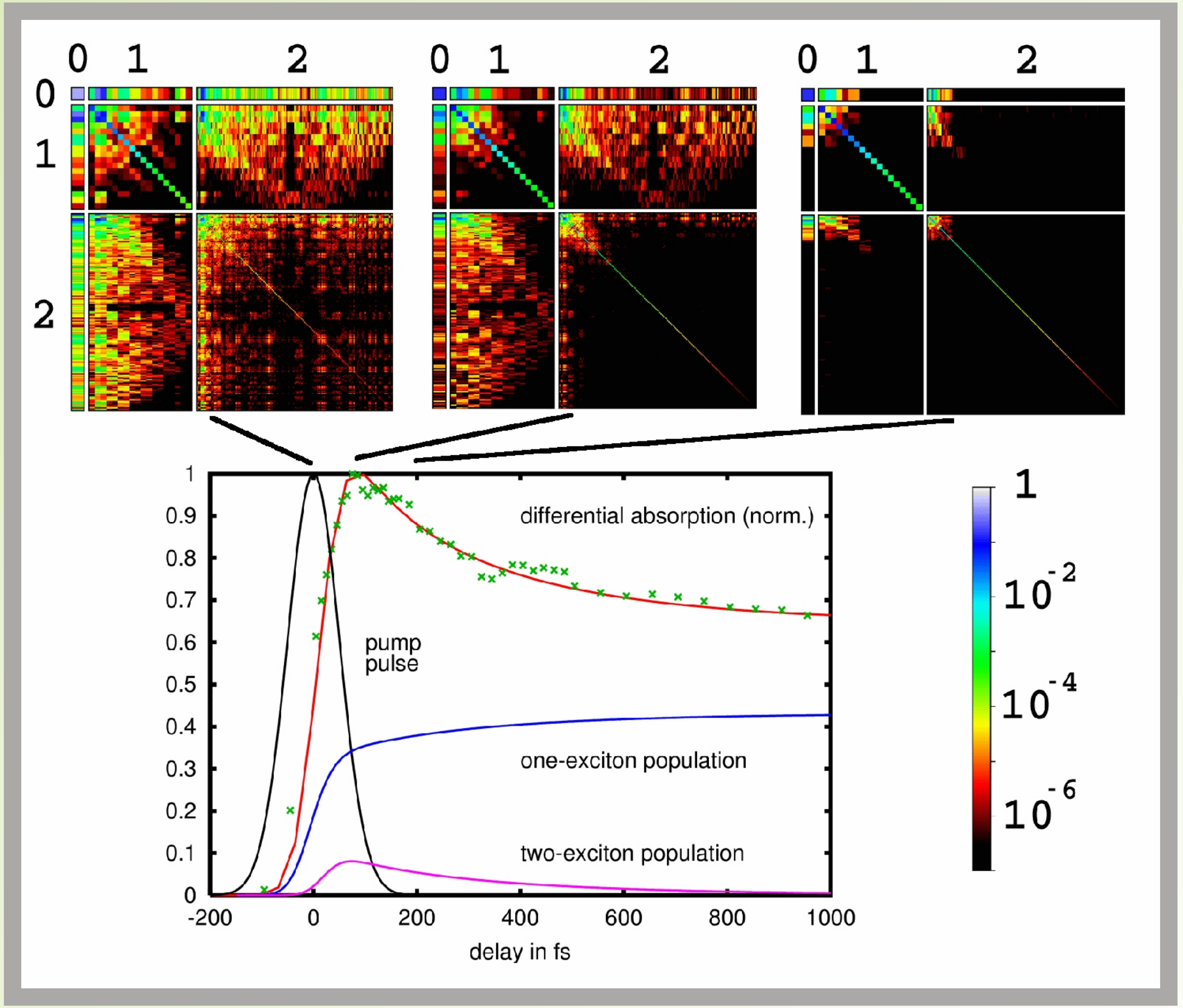
Linear Absorption of the Ps1 Complex



Light Harvesting Complex Lh2 of Purple Bacteria



Transient Absorption of the Lh2



Laser Pulse Control of Excitation Energy Dynamics in the FMO-Complex