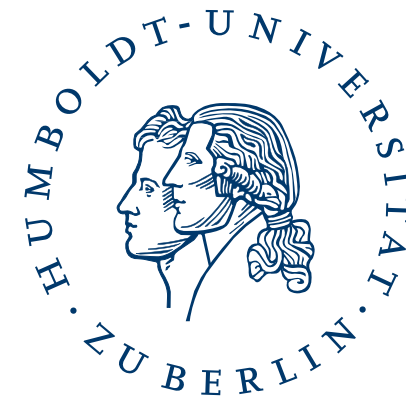# Mixed Quantum-Classical Description of Electronic Excitation Energy Transfer in Supramolecular Complexes
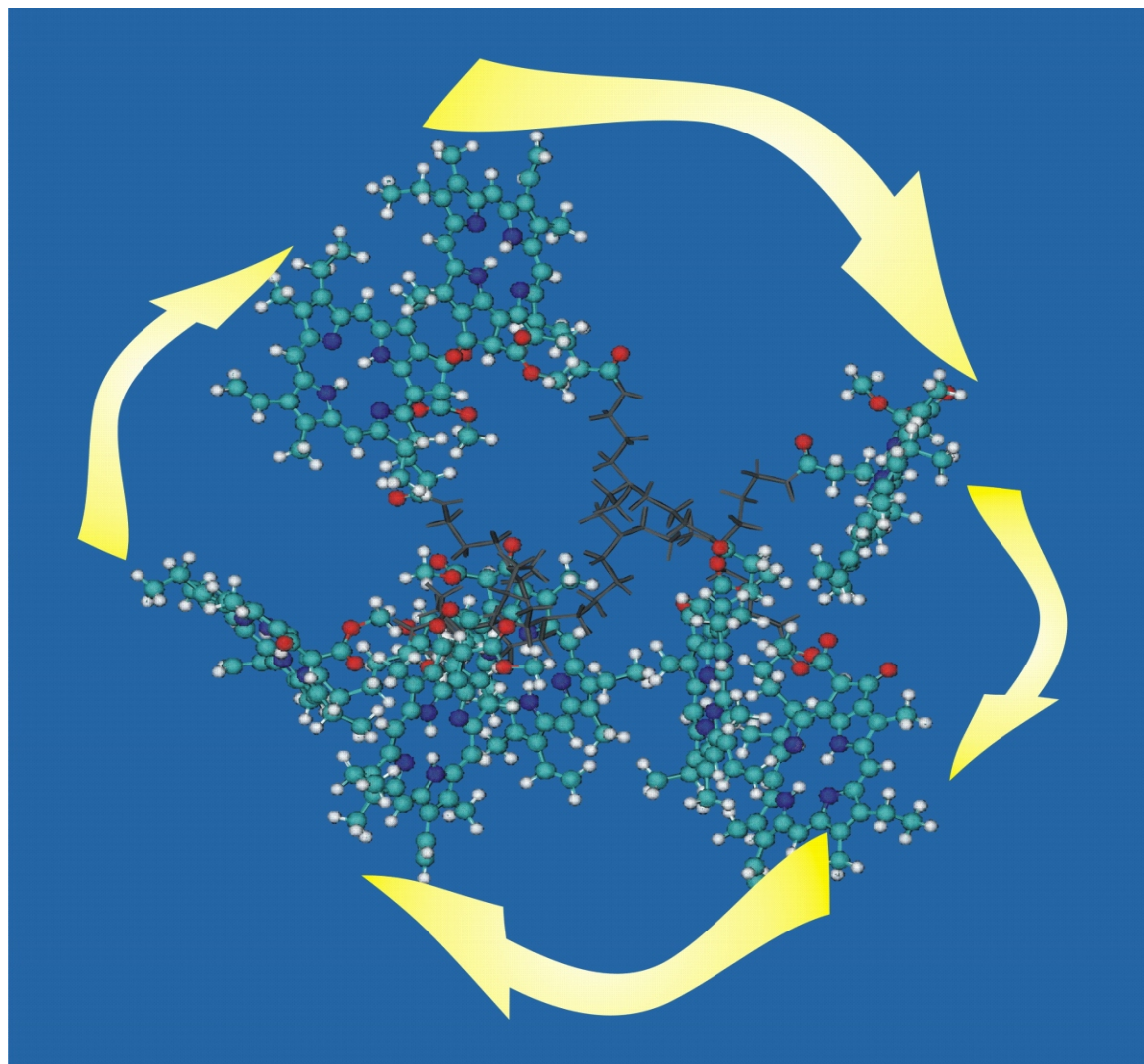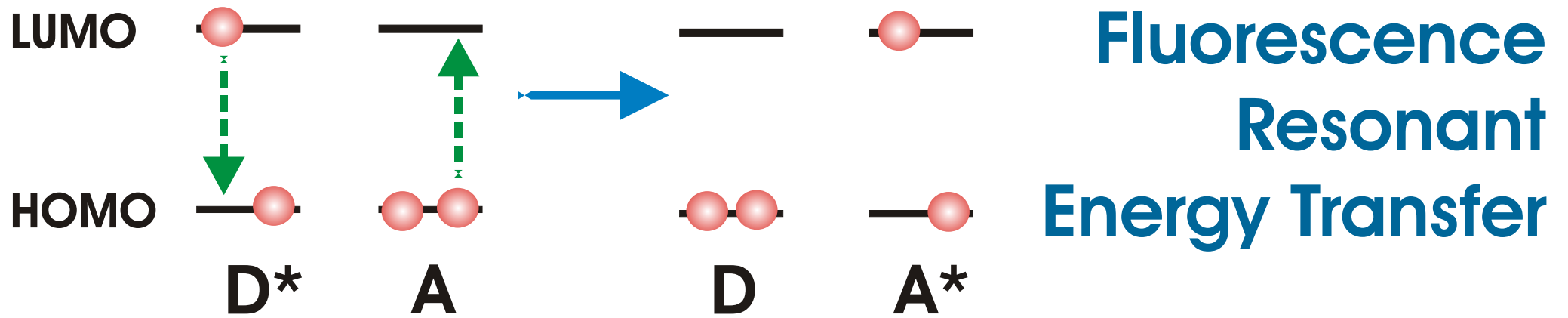

Volkhard May
Institute of Physics
**Humboldt-University at Berlin**

- introduction
- trends in molecular exciton physics
- models of frenkel excitons
- density matrix theory
- rate equation approach
- mixed quantum classical description

LUMO

HOMO

D*   A   D   A*

Fluorescence Resonant Energy Transfer

description of molecular systems requires the use of potential energy surfaces

energy

U_{De}

U_{Ae}
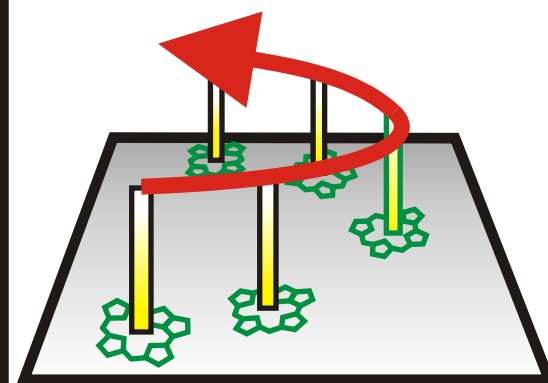
U_{Dg}

U_{Ag}

Q_D Q_A
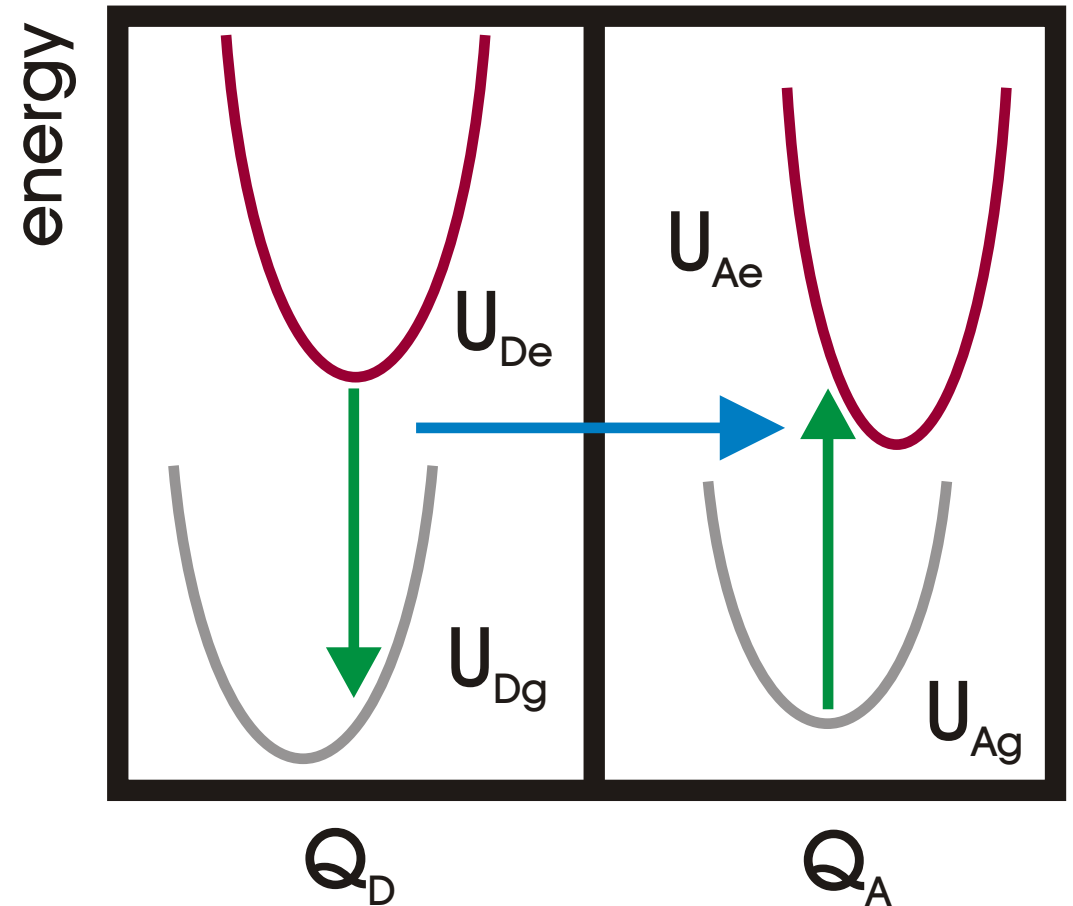
Schemes of Excitation Energy Transfer
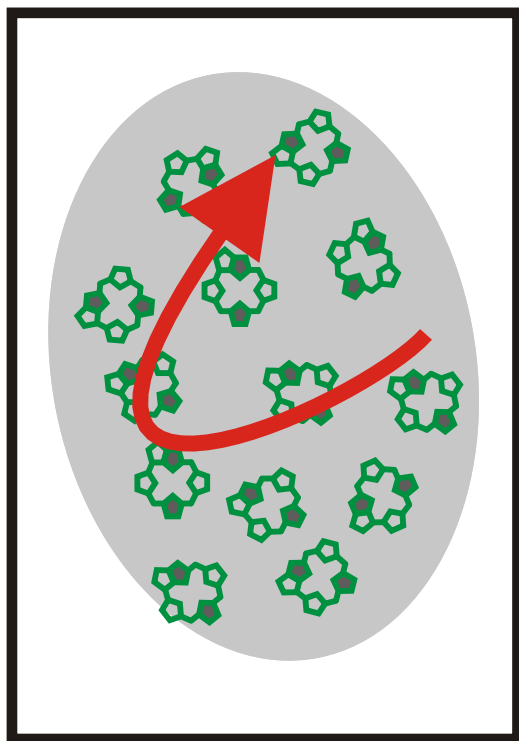
coherent excitation energy motion
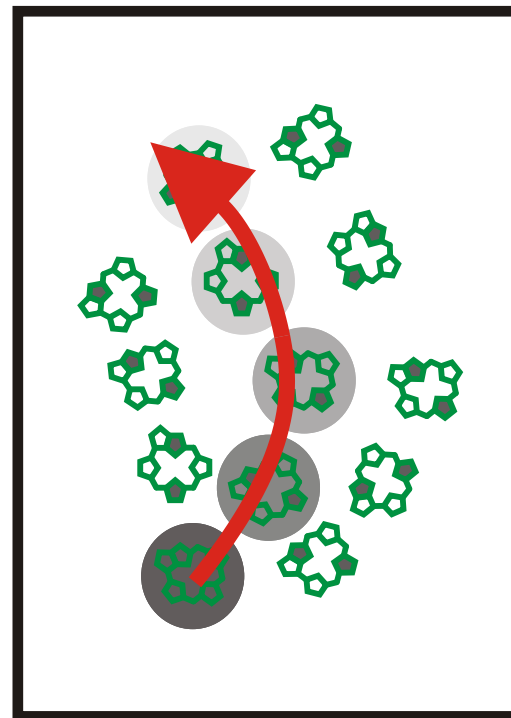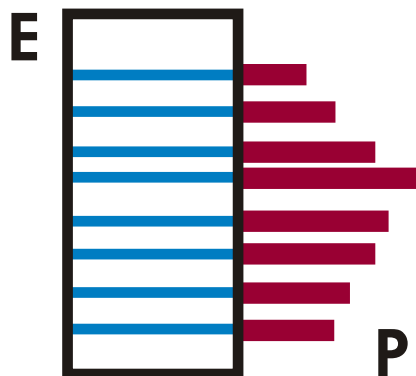
incoherent excitation energy motion

Trends in Molecular Exciton Physics

excitons in DNA

E. Emanuele, K. Zakrzewska, D. Markovitsi,
R. Lavery, and P. Millie,
J. Phys. Chem. B 109, 16109 (2005).
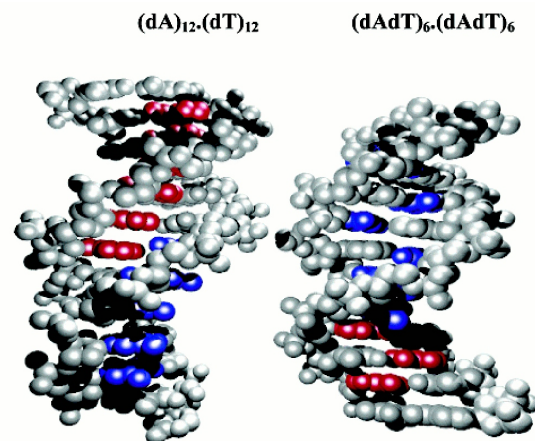
excitation energy transfer in complex artificial structures

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).

$(dA)_{12}.(dT)_{12}$ $(dAdT)_6.(dAdT)_6$

(b)

(a)
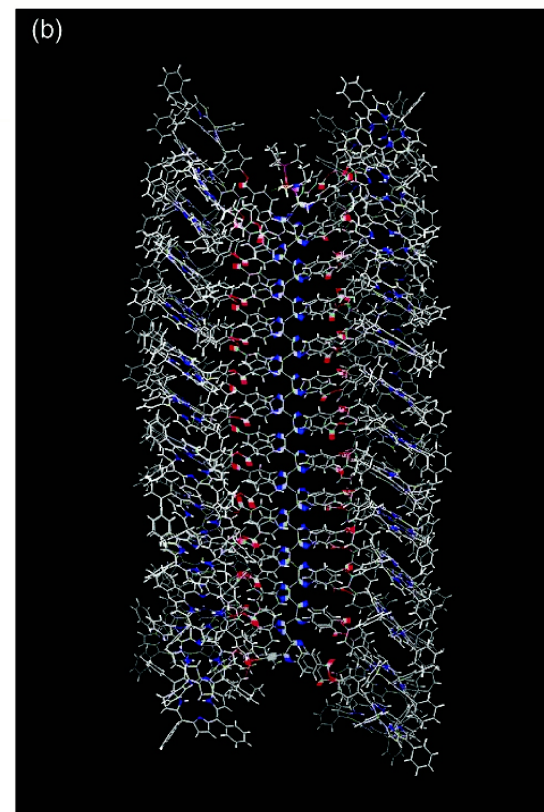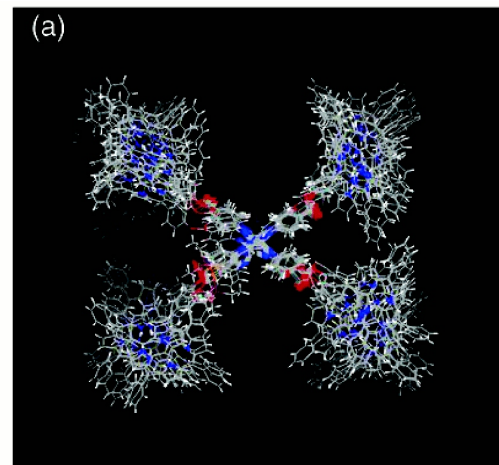
Y.-Z. Ma, R. A. Miller, G. R. Fleming, and M. B. Francis, Energy Transfer Dynamics in Light-Harvesting Assemblies Templated by Tobacco Mosaic Virus Coat Protein, J. Phys. Chem. B 112, 6887 (2008).
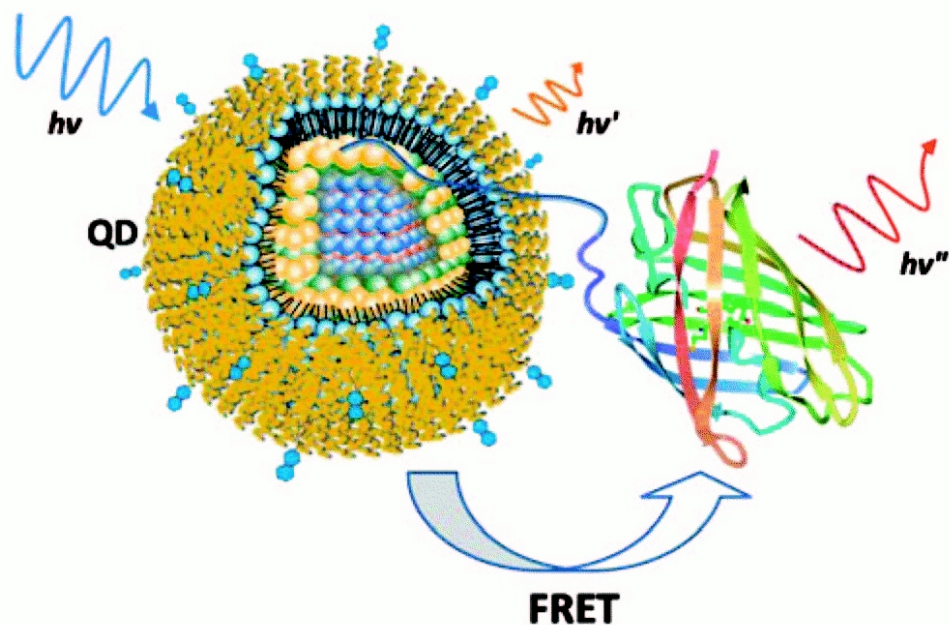
A. M. Dennis and G. Bao, Quantum Dot-Fluorescent Protein Pairs as Novel Fluorescence Resonance Energy Transfer Probes, NanoLett. 8, 1439 (2008).
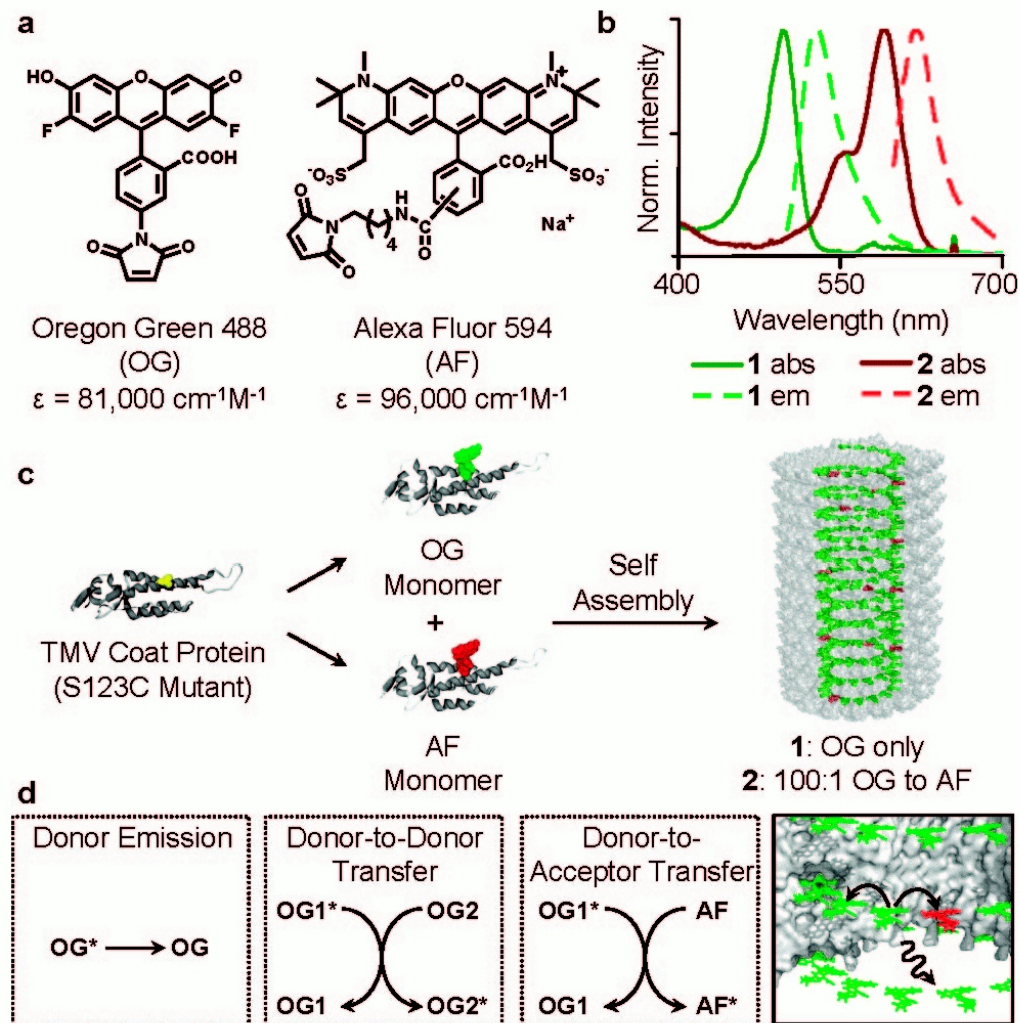
bridge mediated excitation energy transfer single molecule spectroscopy

D*   IS   A   →(EET)→   D   IS   A*
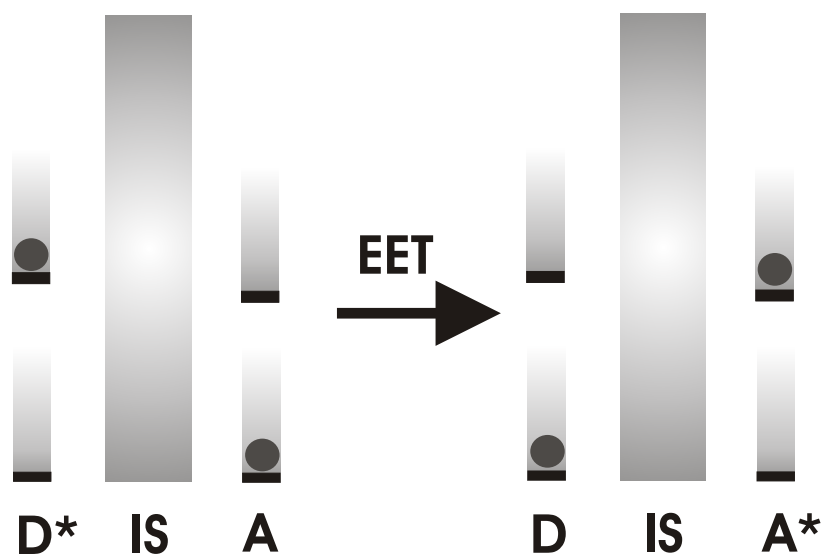
SCHEME 1:   Molecular Structure of 1

164⁰

136⁰

4.1 nm

D

A

(a) Probability density — TDI acceptors, PDI donors — 0-0 electronic transitions (cm⁻¹)

(b) Absorption (A.U.) / Fluorescence (A.U.) — TDI acceptor, PDI donor — B, C, A — Wave number (cm⁻¹)
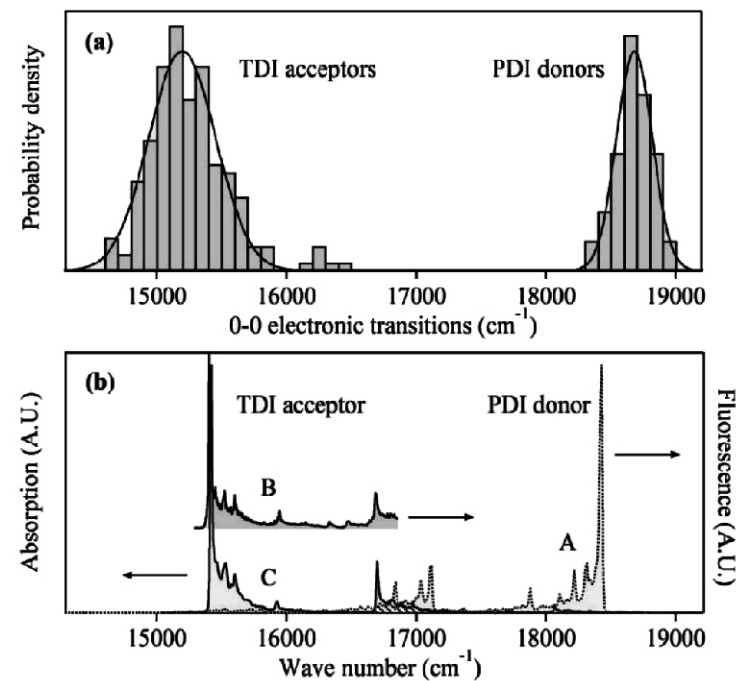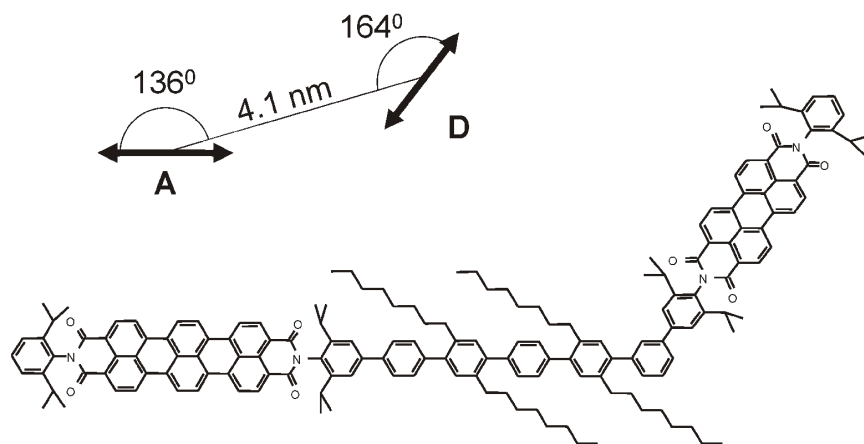
laser pulse control

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.
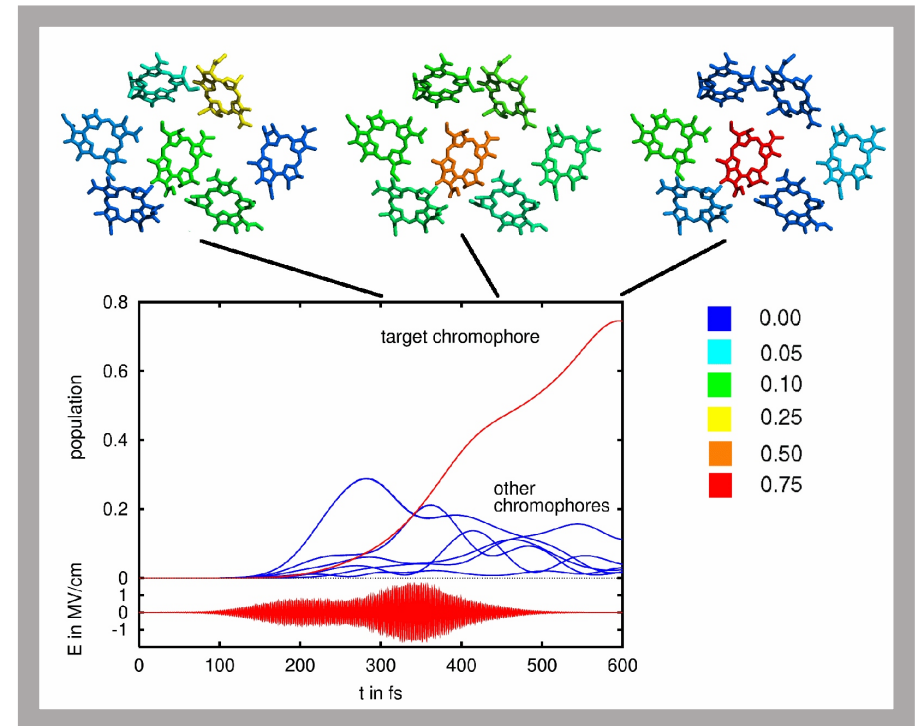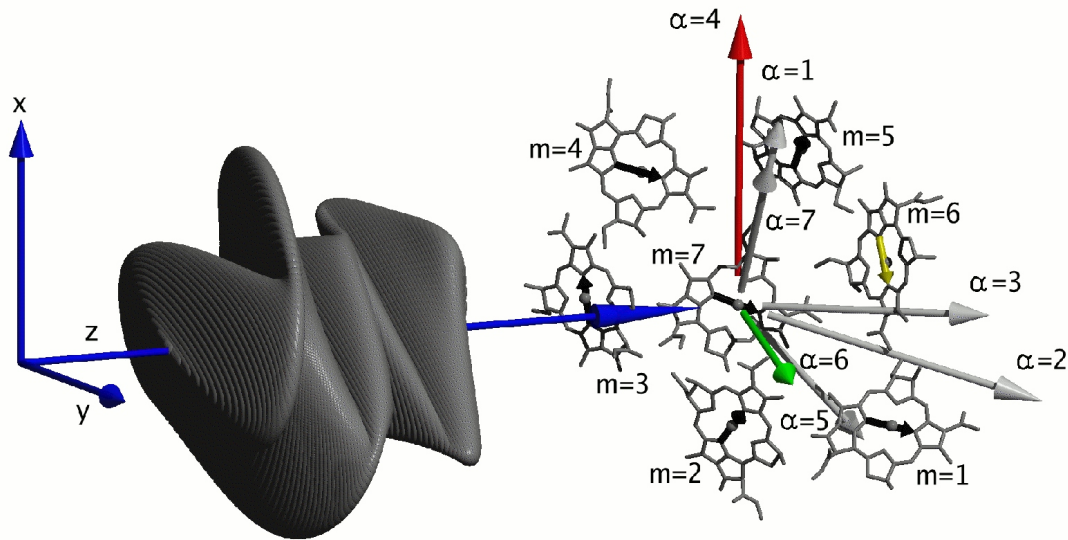
local field enhancement effects

T. Brixner, F. J. Garcia de Abajo, J. Schneider, C. Spindler, and W. Pfeiffer,
Ultrafats Adaptive Optical Near-Field Control, Phys. Rev. A 79, 125437 (2006).

Trends in the Theory of Molecular Excitons

- **quantum chemical foundation of exciton models**
- **mixed quantum classical description**
  - infrared spectroscopy of oligopeptides (Cho, Mukamel, Knoester, Stock, 2003 - 2008)
  - excitation energy transfer dynamics in DNA strands (Markovitsi, 2003 - 2006)
  - hybrid systems (Prezhdo, 2007)

Gorbunov et al., JCP 126, 054509 (2007)

FIG. 1. Scheme and atom labeling of trialanine cation A_3^+.

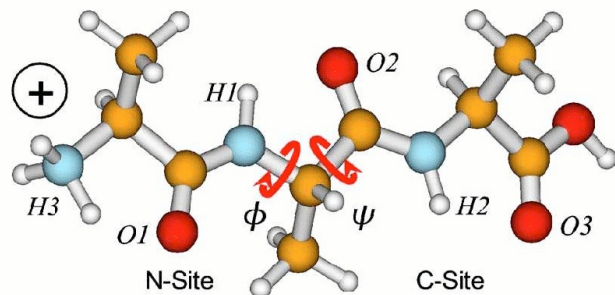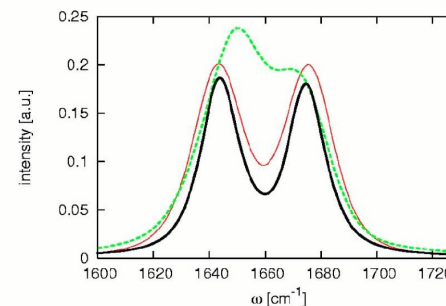FIG. 9. Comparison of experimental (Ref. 39, green dashed line) and calculated amide I absorption spectra of trialanine. The latter were obtained directly from semiclassical line-shape theory [via Eq. (5), thick black line] and by invoking adiabatic and cumulant approximations [via Eq. (8), thin red line].

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

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

electronic density matrix $\rightarrow$ density matrix equations

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

state population $\rightarrow$ master equations

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

mixed quantum classical dynamics
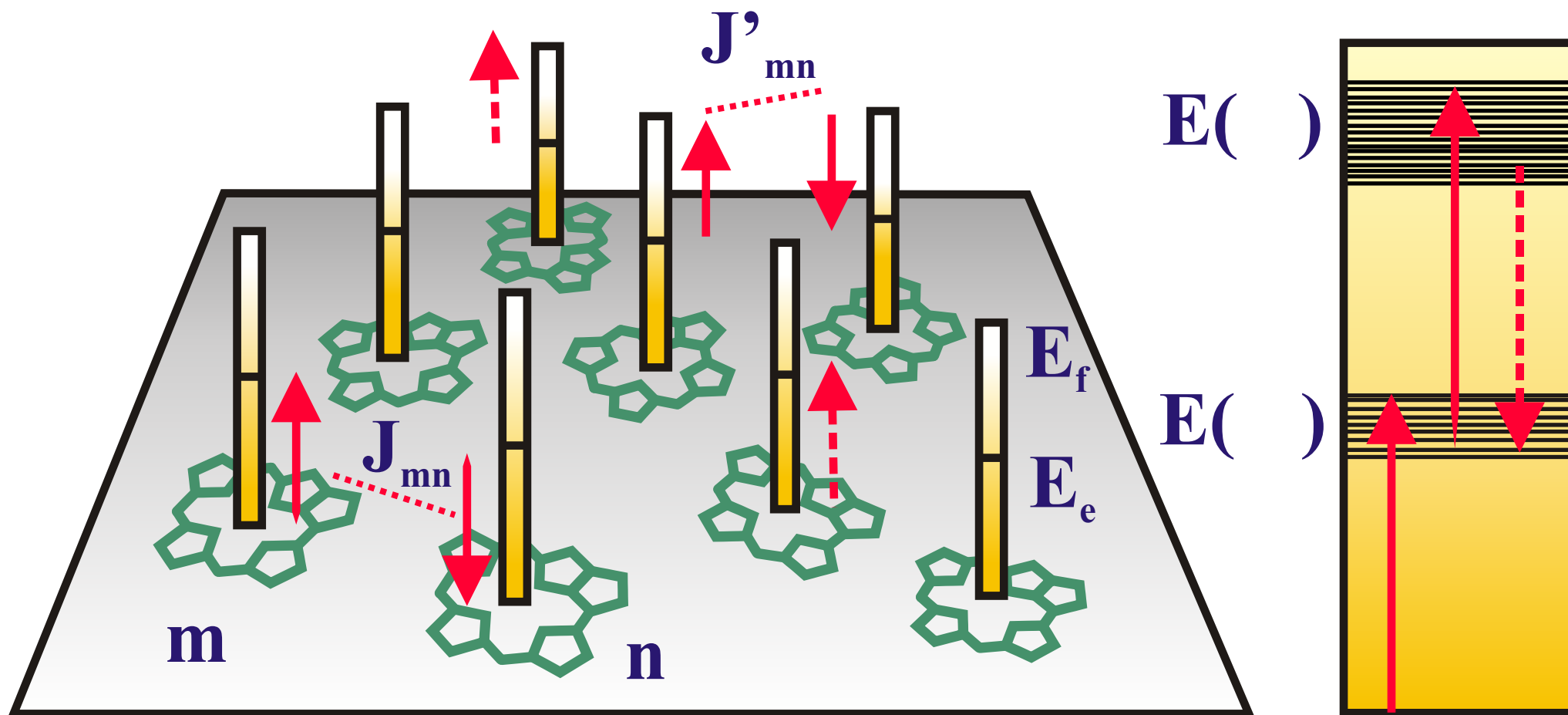quantum mechanical description of the electrons $\rightarrow$ $\varphi_a(r; R)$
classical description of the nuclei $\rightarrow$ $R(t)$

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

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

Frenkel Exciton Model

Standard Exciton Model

ordering with respect to the excitation manifolds

$$H_{\mathrm{ex}} = H_{\mathrm{ex}}^{(0)} + H_{\mathrm{ex}}^{(01)} + H_{\mathrm{ex}}^{(1)} + H_{\mathrm{ex}}^{(2)} + ...$$

site representation: $|\phi_m\rangle = |\varphi_{me}\rangle \, \Pi_{n \neq m} \, |\varphi_{ng}\rangle$

$\implies$ perturbation theory with respect to the excitonic coupling

$$H_{\mathrm{ex}}^{(1)} = \sum_{mn} (\delta_{m,n}[T_{\mathrm{nuc}} + U_m(R)] + [1 - \delta_{m,n}]J_{mn}(R)) |\phi_m\rangle\langle\phi_n|$$
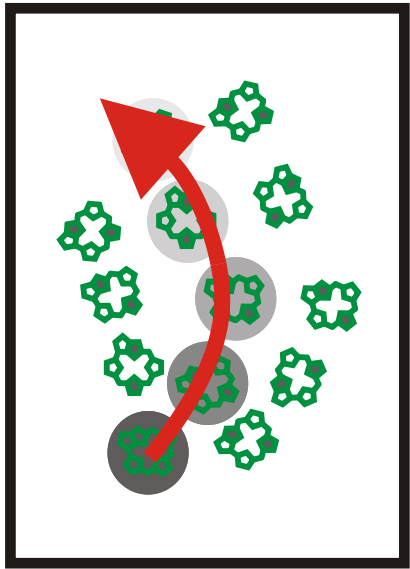
harmonic model for all vibrational coordinates

$$H_{\mathrm{ex}}^{(1)} = \sum_{m,n} (\delta_{mn} E_m + [1 - \delta_{m,n}]J_{mn}^{(0)}) |\phi_m\rangle\langle\phi_n| + \sum_{\xi} \hbar\omega_\xi C_\xi^+ C_\xi \sum_m |\phi_m\rangle\langle\phi_m|$$

$$+ \sum_{mn} \sum_{\xi} \hbar\omega_\xi g_{mn}(\xi)(C_\xi + C_\xi^+) |\phi_m\rangle\langle\phi_n|$$

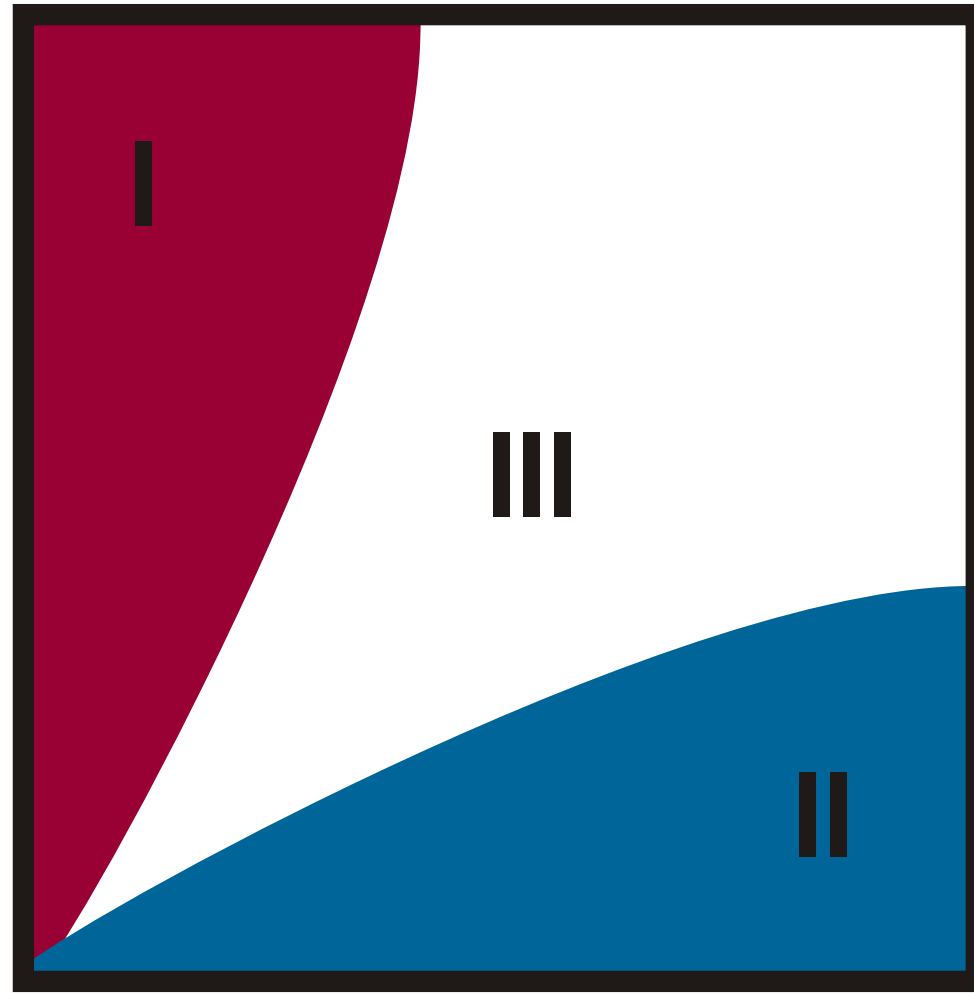exciton representation $|\alpha\rangle = \Sigma_m C_\alpha(m)|\phi_m\rangle$

$\implies$ perturbation theory with respect to the exciton–vibrational coupling

$$H_{\mathrm{ex}}^{(1)} = \sum_{\alpha} (\mathcal{E}_\alpha + \sum_{\xi} \hbar\omega_\xi C_\xi^+ C_\xi) |\alpha\rangle\langle\alpha| + \sum_{\alpha,\beta} \sum_{\xi} \hbar\omega_\xi g_{\alpha\beta}(\xi)(C_\xi + C_\xi^+) |\alpha\rangle\langle\beta|$$
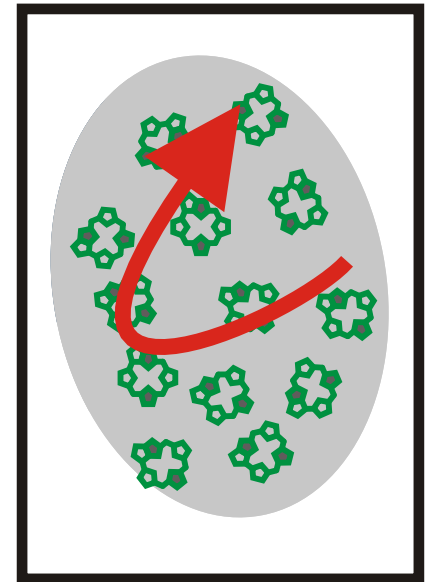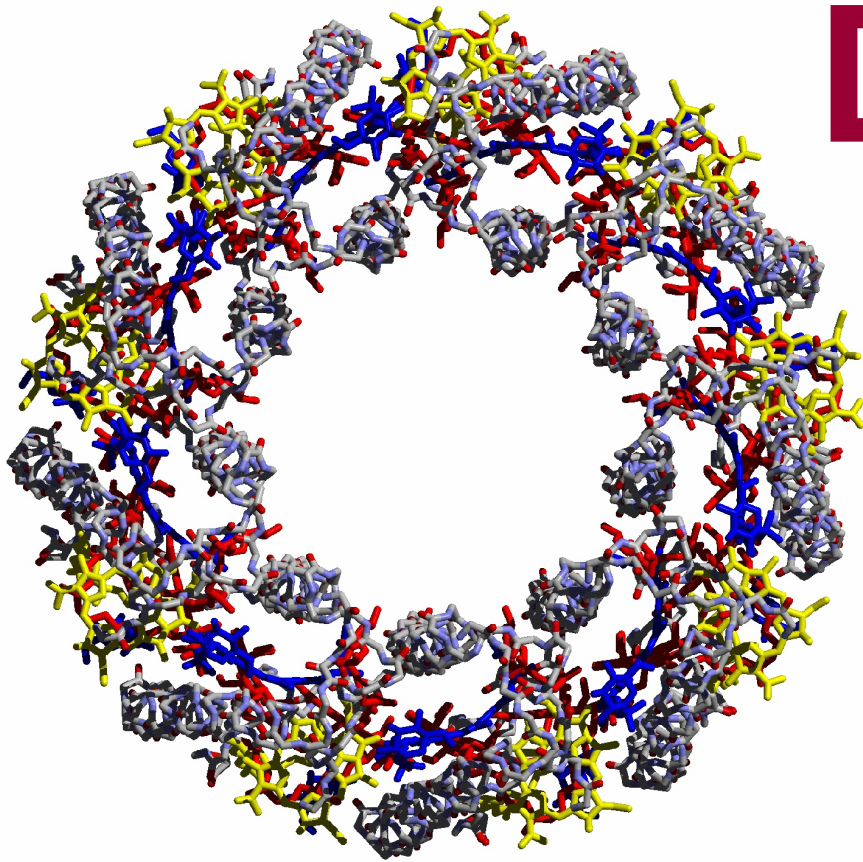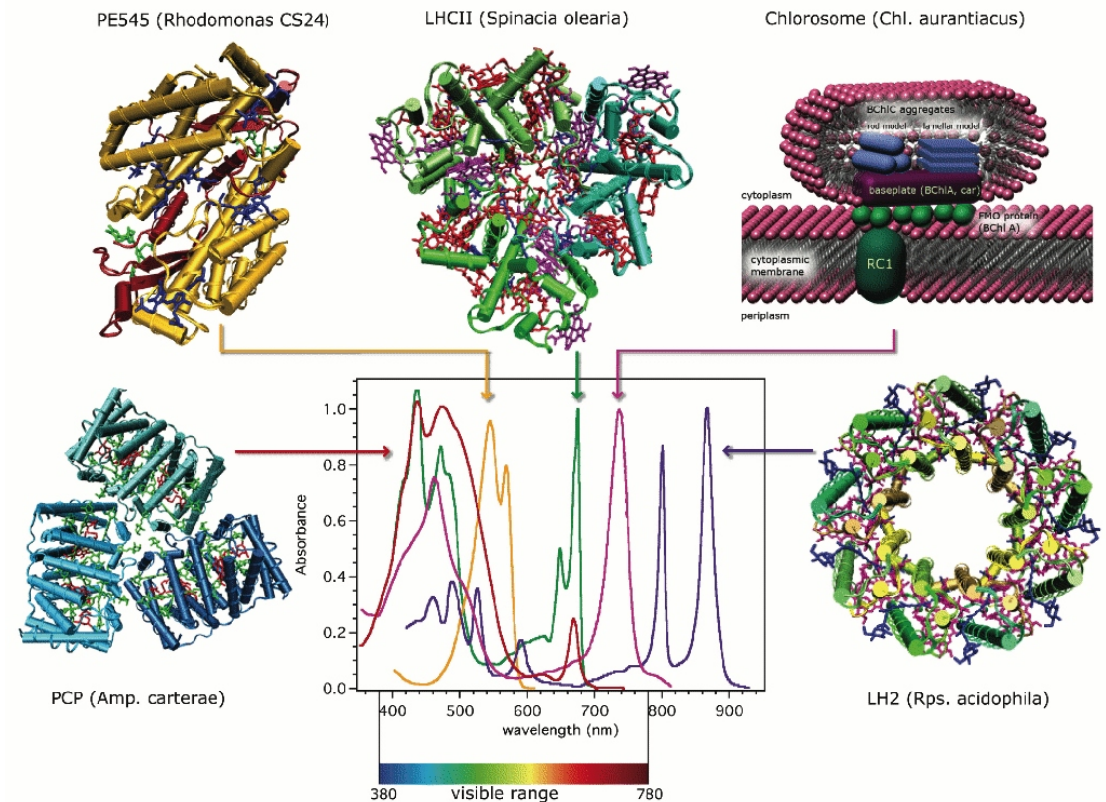
Transfer Regimes

intramol. interaction

intermol. interaction

I

II

III

Density Matrix Theory

- two-exciton manifold
- exciton state populations, coherences,
- appropriate to compute ultrafast optical spectra
- account for static disorder
- consideration of weak exciton vibrational coupling only

Density Matrix Theory of Excitons

$\Longrightarrow$ perturbation theory with respect to the exciton–vibrational coupling
most appropriate when optical excitation is explicitly accounted for

exciton density matrix (dissipative part in secular approximation, Lindblad-form)

$$\rho_{\alpha\beta}(t) = \langle\alpha|\mathrm{tr}_{\mathrm{vib}}\{\hat{W}(t)\}|\beta\rangle$$

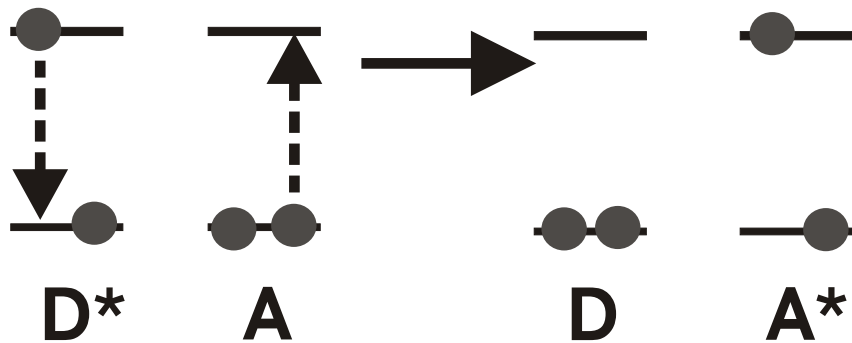## equations of motion

$$\frac{\partial}{\partial t}\rho_{\alpha\beta} = -i\Omega_{\alpha\beta}\rho_{\alpha\beta} - \delta_{\alpha\beta}\sum_{\gamma}(k_{\alpha\to\gamma}\rho_{\alpha\alpha} - k_{\gamma\to\alpha}\rho_{\gamma\gamma})$$

$$-(1 - \delta_{\alpha\beta})\gamma_{\alpha\beta}\rho_{\alpha\beta} + \frac{i}{\hbar}\mathbf{E}(t)(\mathbf{d}_\alpha\rho_{0\beta} - \mathbf{d}^*_\beta\rho_{\alpha 0})$$

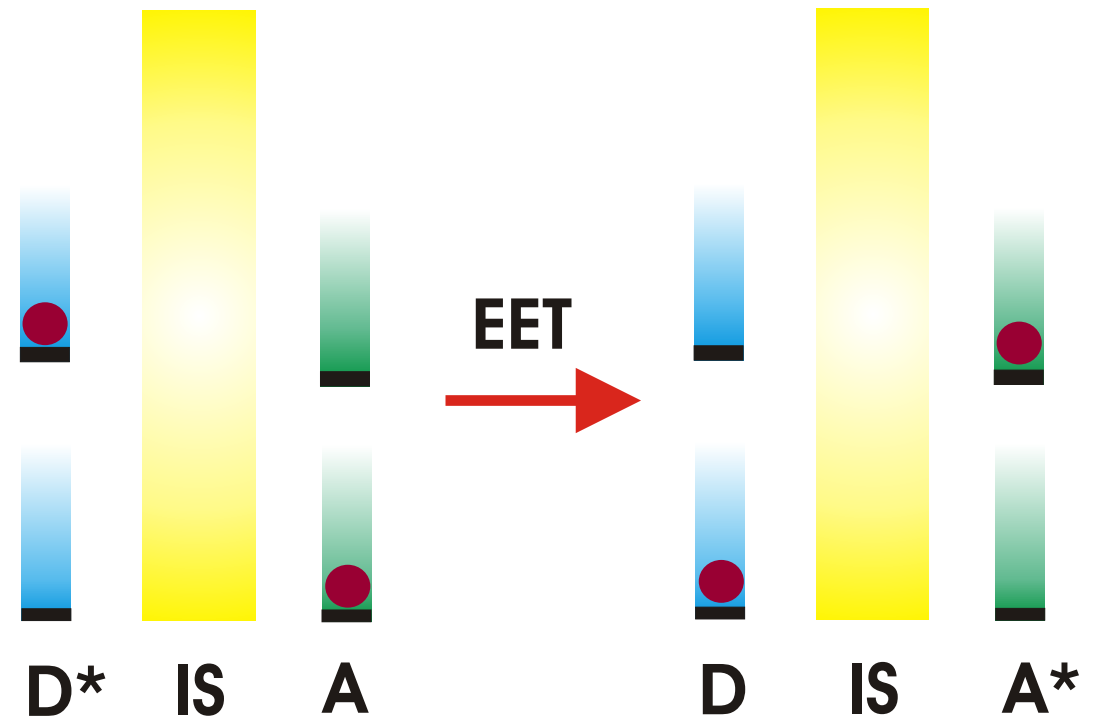## transition rates

$$k_{\alpha\to\beta} = 2\pi\Omega^2_{\alpha\beta}(1 + n(\Omega_{\alpha\beta}))\sum_{m}|C_\alpha(m)C_\beta(m)|^2[J_m(\Omega_{\alpha\beta}) - J_m(-\Omega_{\alpha\beta})]$$

Rate Equation Approach (Förster theory)

- focus on state populations
- inappropriate to compute ultrafast optical spectra
- higher-order perturbation theory with respect to other couplings
- consideration of strong exciton-vibrational coupling

Rate Theory of Excitation Energy Transfer

exciton representation $\Longleftrightarrow$ site representation

site representation $\Longrightarrow$ perturbation theory with respect to the excitonic coupling

second–order rates: Förster–transfer

higher–order rates: intermediate state mediated excitation energy transfer (photon mediated transfer, bridge molecule mediated transfer, Dexter transfer as two electron exchange)
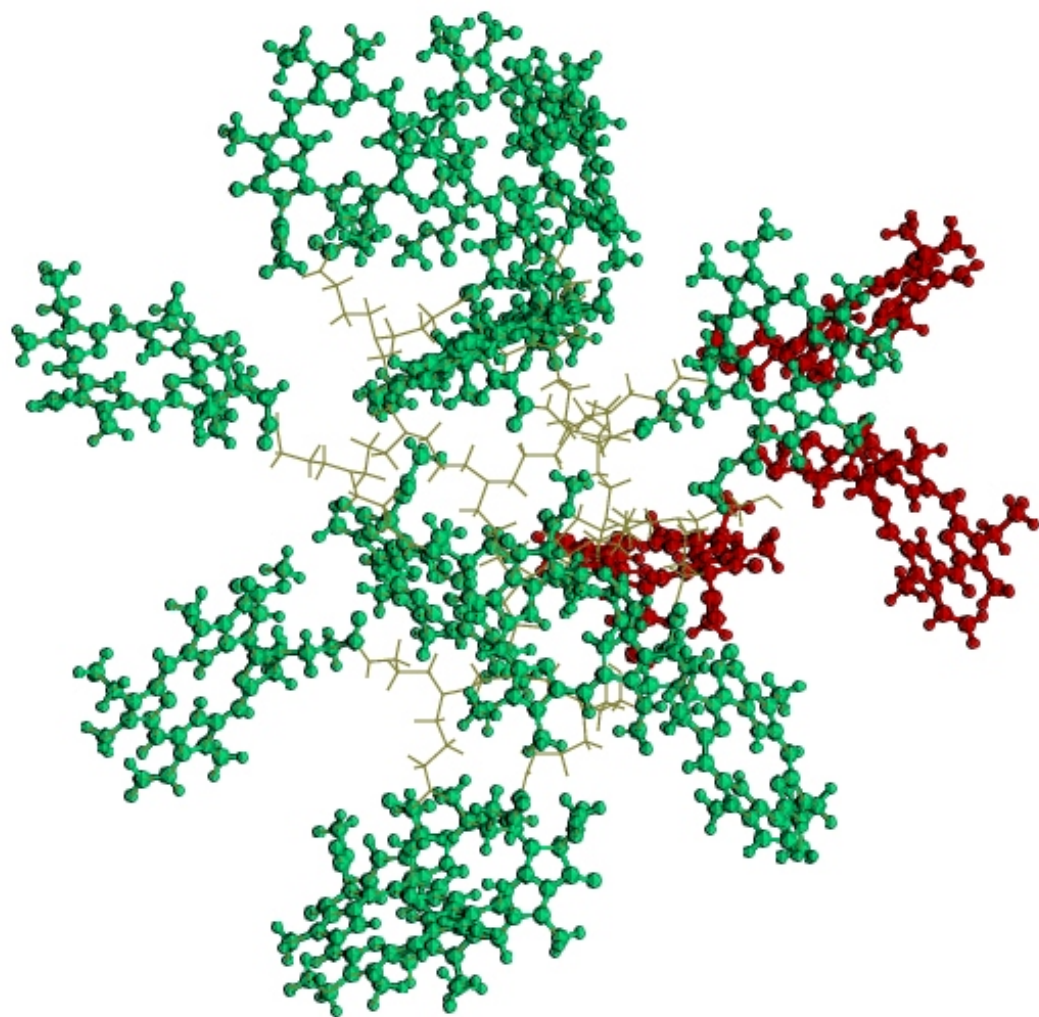
molecular excited state population

$$P_m(t) = \langle \phi_m | \mathrm{tr}\{\hat{W}(t)\} | \phi_m \rangle$$

generalized master equation

$$\frac{\partial}{\partial t} P_m(t) = - \sum_{m \neq n} \int d\bar{t} (K_{m \to n}(\bar{t}) P_m(t - \bar{t}) - K_{n \to m}(\bar{t}) P_n(t - \bar{t}))$$
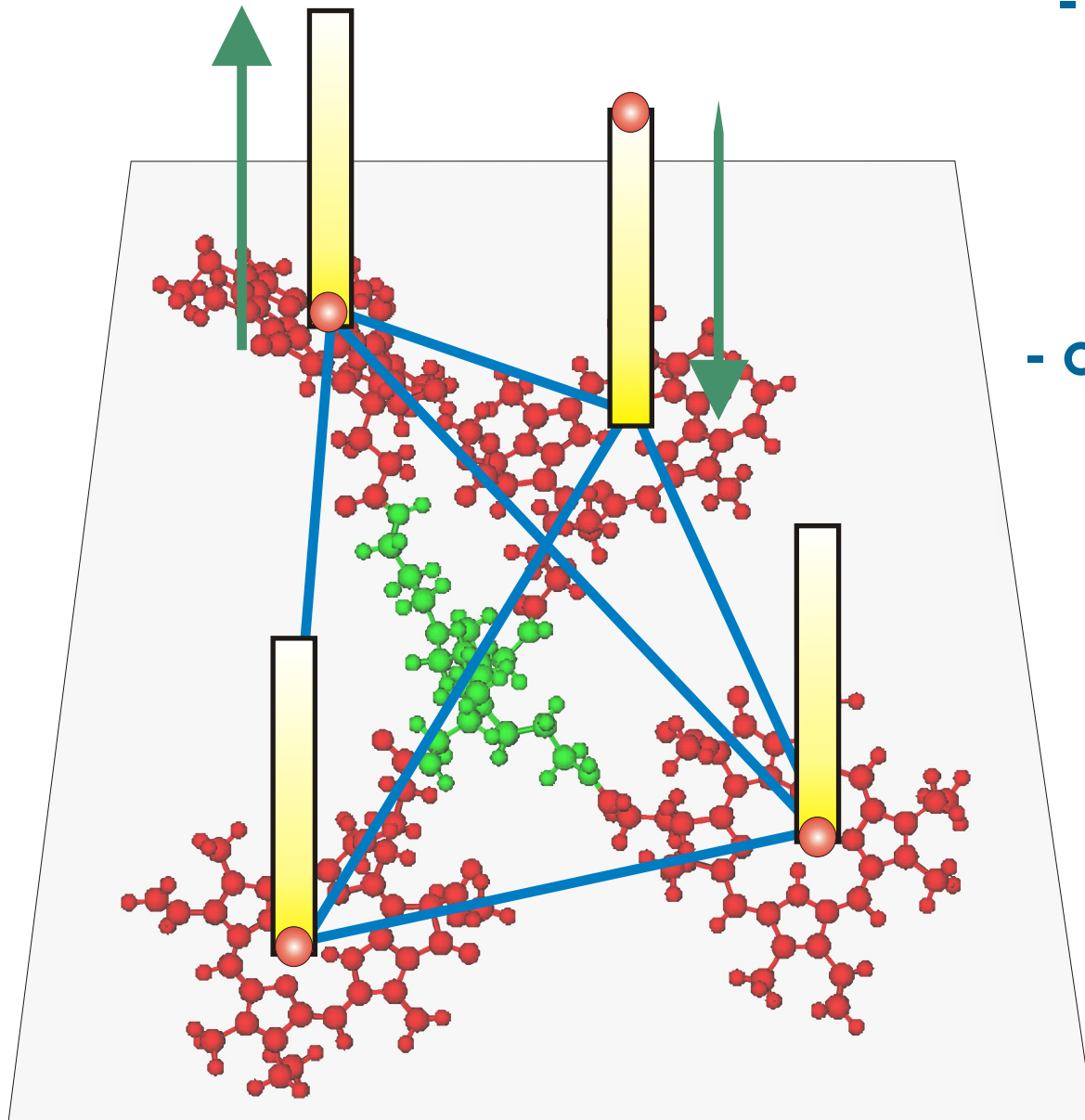
Mixed Quantum Classical Description

16 pheophorbide-a molecules covalently linked to a butanediamine dendrimer in methanol

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

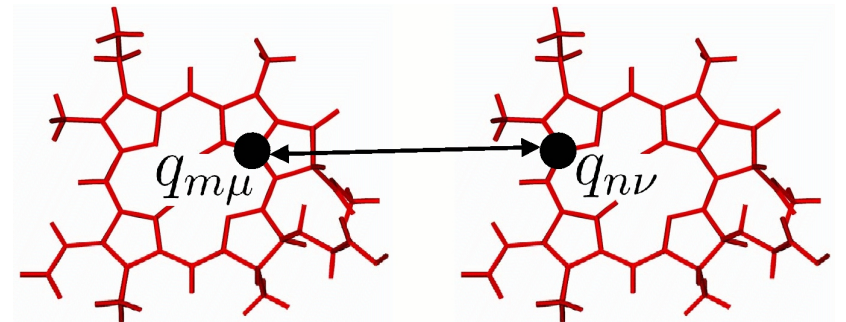H. Zhu, V. May, and B. Röder,
Chem. Phys. 351, 117 (2008).

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

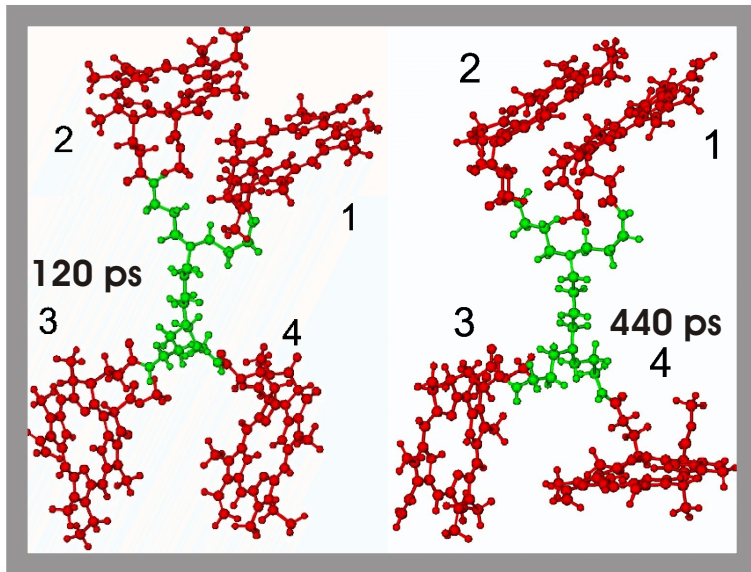single chromophore excitation energies and excitonic couplings
(coupling to solvent molecules neglected)

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).
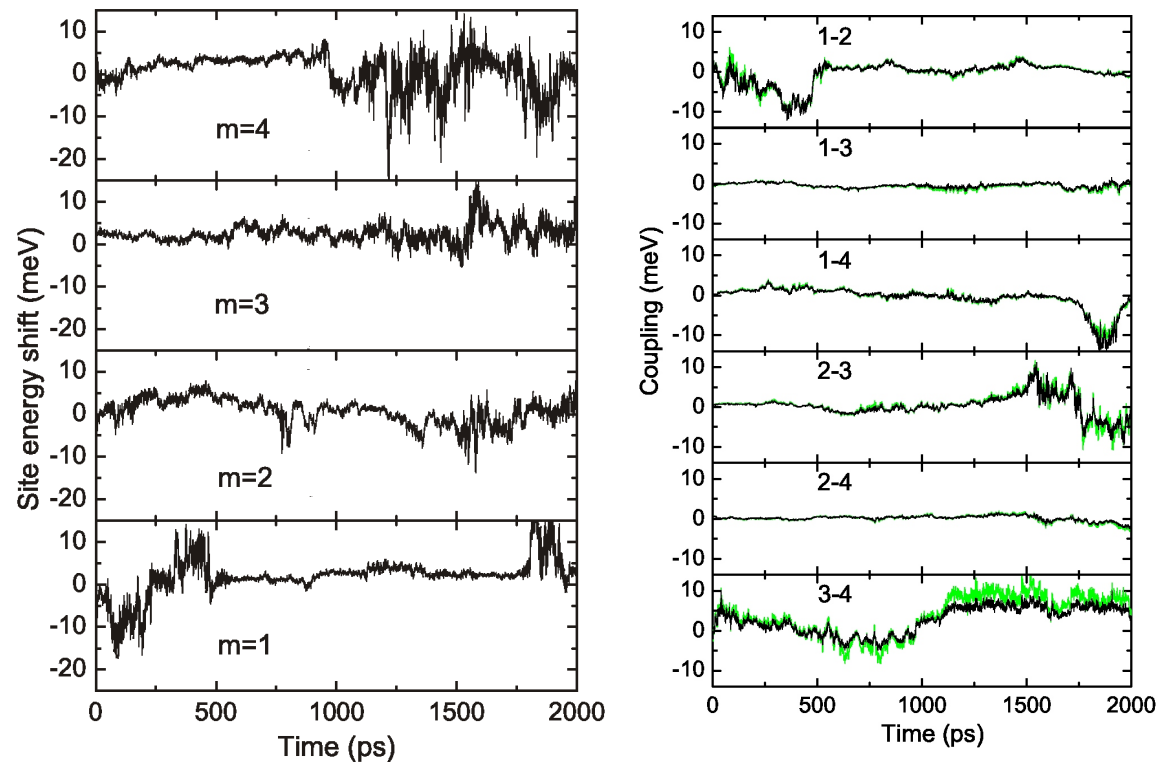
adiabatic (instantaneous) excitons

energies, oscillator strengths, and expansion coefficients
(coupling to solvent molecules has been neglected)
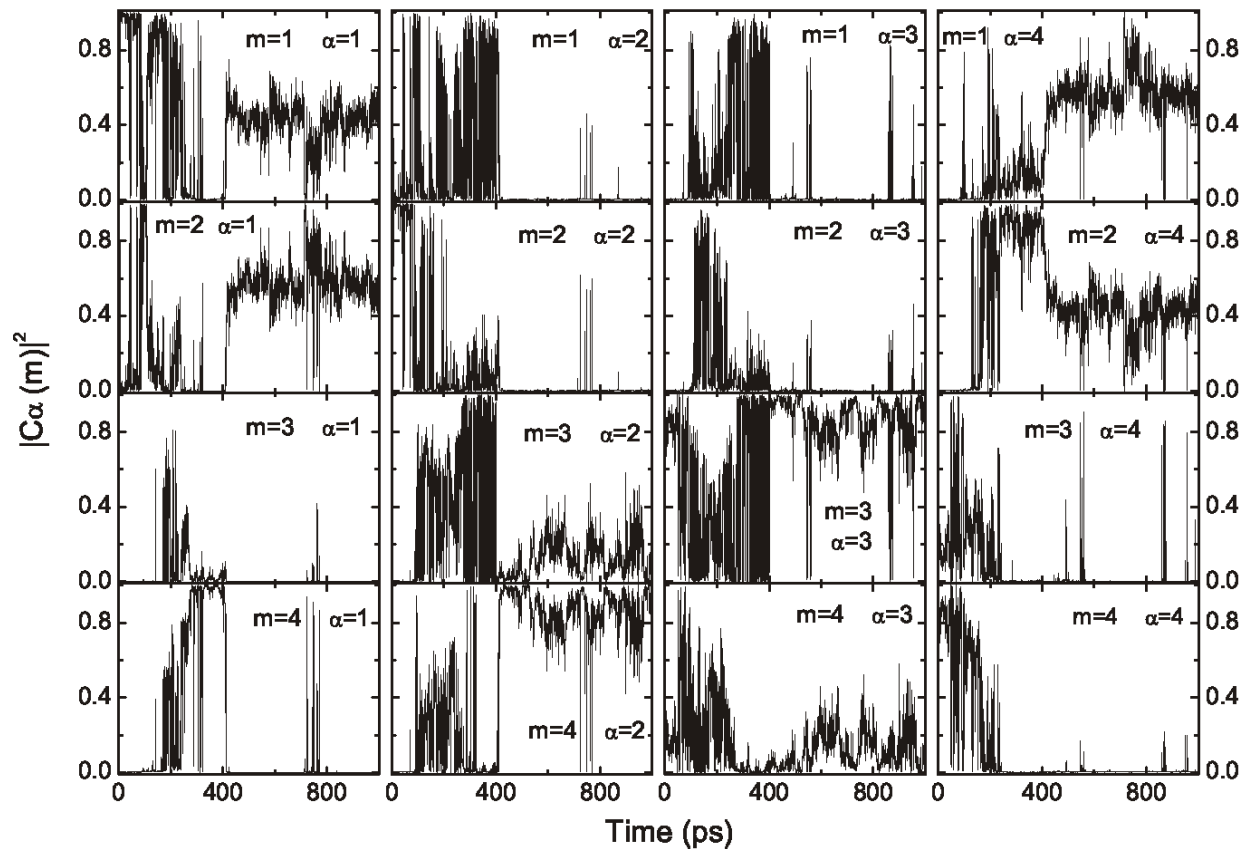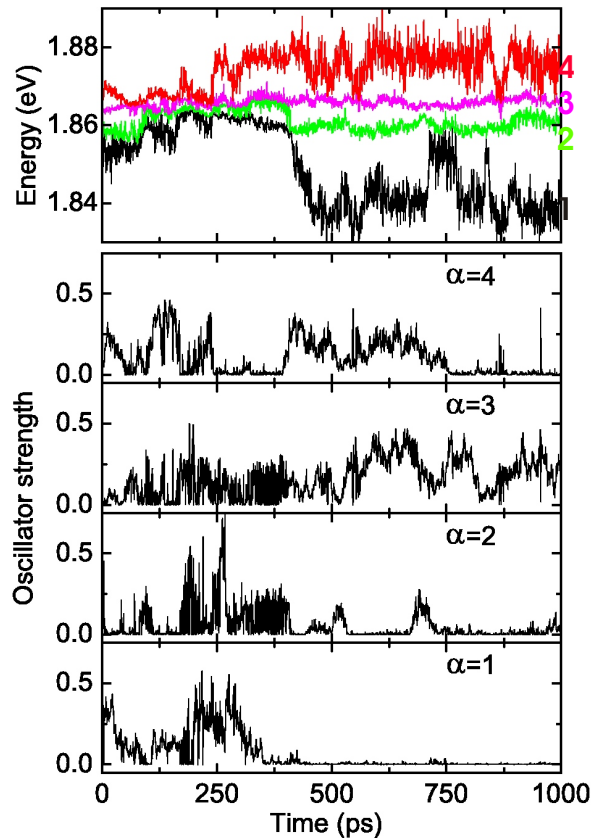
Adiabatic exciton energies and oscillator strengths (data have been computed every 0.5 ps within a single 1 ns MD run)

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

Mixed Quantum Classical Theory of Excitation Energy Transfer

Wigner representation of the density matrix for excitation energy transfer: $\rho_{mn}(R, P; t)$

Ehrenfest dynamics

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

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

- exact account for excitonic coupling and exciton vibrational interaction
- back reaction of the electron dynamics on the nuclear motion due to a mean force
- excitation energy motion at fluctuating exciton parameters

expansion of the wave function with respect to locally excited states

$$\Phi(r, R(t); t) = A_0(t)\phi_0(r, R(t)) + \sum_m A_m(t)\phi_m(r, R(t))$$

$$A_0(t) = \langle \phi_0 | U_{\text{ex}}^{(0)}(t, t_0) | \Phi(t_0) \rangle \qquad A_m(t) = \langle \phi_m | U_{\text{ex}}^{(1)}(t, t_0) | \Phi(t_0) \rangle$$

equations of motion for the expansion coefficients

$$i\hbar \frac{\partial}{\partial t} A_0(t) = \mathcal{U}_0(R(t)) A_0(t) - \sum_m \mathbf{d}_m^*(t) \mathbf{E}(t) A_m(t)$$

$$i\hbar \frac{\partial}{\partial t} A_m(t) = \sum_n \mathcal{U}_{mn}(R(t)) A_n(t) - \mathbf{d}_m(t) \mathbf{E}(t) A_0(t)$$

Newtons's equations for the nuclear coordinates

$$M_\nu \frac{\partial^2}{\partial t^2} \mathbf{R}_\nu(t) = -|A_0(t)|^2 \nabla_\nu \mathcal{U}_0(R(t)) - \sum_{m,n} A_m^*(t) A_n(t) \nabla_\nu \mathcal{U}_{mn}(R(t))$$

- ground–state classical path approximation can be taken
- excitation energy transfer can be characterized the probability to have the chromophore m in the excited state $P_m(t) = <|A_m(t)|^2>$

Excitation energy transfer dynamics characterized by the single chromophore populations $P_m(t)$ ($P_m(0) = \delta_{m,1}$) and averaged with respect to a 10 ps time slice
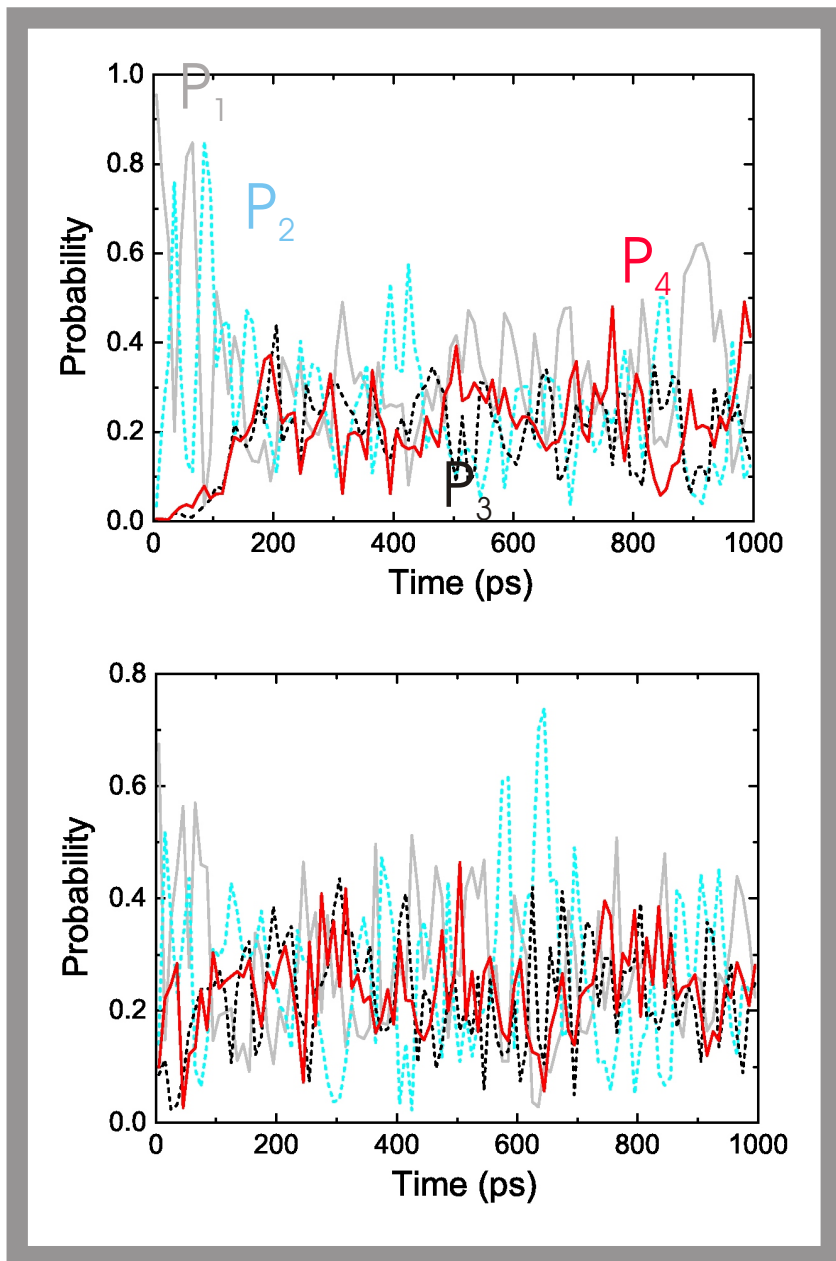
Excitation energy transfer dynamics without time averaging

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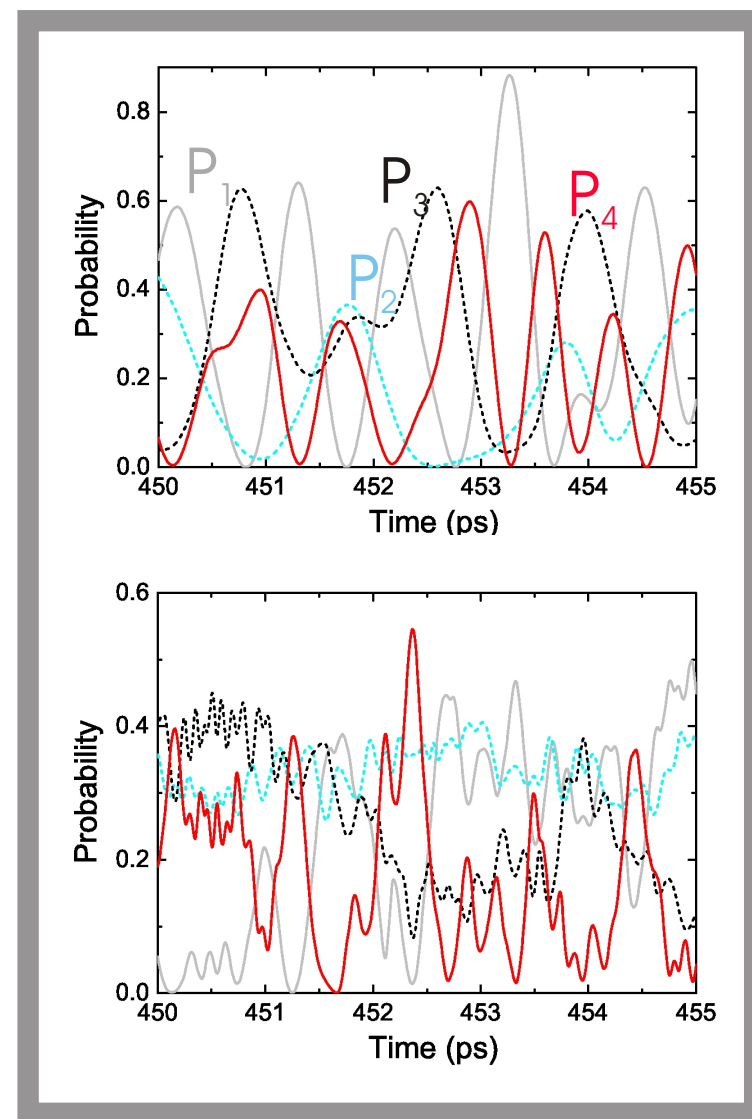
The modulation of the single chromophore excitation energy by the solvent molecules is included.

Relation to the Exciton Density Matrix Theory

mixed quantum classical version of the density matrix (in site representation)

$$\rho_{mn}(t) = \langle \phi_m | \mathrm{tr}_{\mathrm{vib}} \{ \hat{W}(t) \} | \phi_n \rangle$$

$$\Longrightarrow \; < \langle \phi_m(R(t)) | \times | \Phi(R(t); t) \rangle \langle \Phi(R(t); t) | \times | \phi_n(R(t)) \rangle >_{\mathrm{ther}}$$

$$\equiv \sigma_{mn}(t) = < A_m(t) A_n^*(t) >_{\mathrm{ther}}$$

equations of motion (neglecting the coupling to the radiation field)

$$\frac{\partial}{\partial t} \sigma_{mn}(t) = \sum_k < \mathcal{U}_{mk} A_k(t) A_n^*(t) - A_m(t) A_k^*(t) \mathcal{U}_{kn} >_{\mathrm{ther}}$$

$$\equiv \sum_k < \mathcal{U}_{mk} >_{\mathrm{ther}} \sigma_{kn}(t) - \sum_k \sigma_{mk}(t) < \mathcal{U}_{kn} >_{\mathrm{ther}}$$

$$+ \sum_k < \Delta \mathcal{U}_{mk} A_k(t) A_n^*(t) >_{\mathrm{ther}} - \sum_k < A_m(t) A_k^*(t) \Delta \mathcal{U}_{kn} >_{\mathrm{ther}}$$

$$\Delta \mathcal{U}_{mk} = \mathcal{U}_{mk} - < \mathcal{U}_{mk} >_{\mathrm{ther}}$$

Mixed Quantum Classical Theory of Time–Resolved Spontaneous Emission

quantum rate of ideal time and frequency resolved emission

$$F(\omega; t) \sim \text{Re} \int_{t_0}^{t} d\bar{t}\, e^{-i\omega(t-\bar{t})} \sum_{m,n,k}$$

$$\times \text{tr}_{\text{vib}}\{\hat{w}_{mn}(\bar{t}) \langle \phi_n | e^{iH_{\text{ex}}^{(1)}(t-\bar{t})/\hbar} | \phi_k \rangle [\mathbf{d}_k \langle \phi_0 | e^{-iH_{\text{ex}}^{(0)}(t-\bar{t})/\hbar} | \phi_0 \rangle \mathbf{d}_m^+]\}$$

density operator averaged with respect to photon states

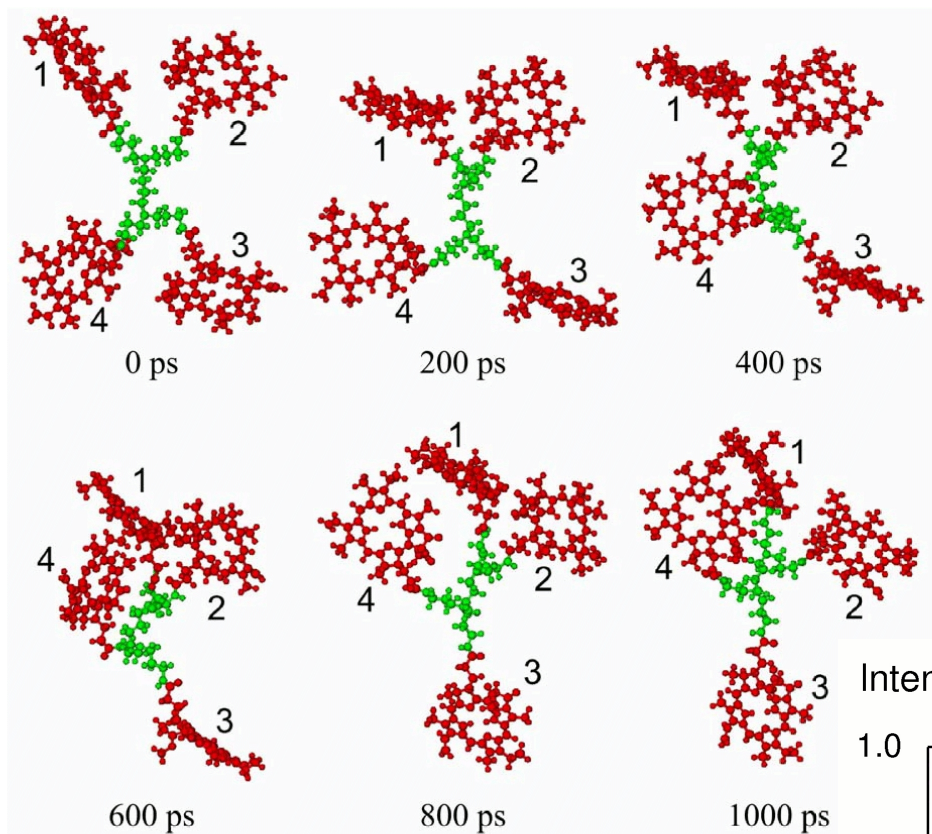$$\hat{w}_{mn}(t) = \langle \phi_m | \text{tr}_{\text{phot}}\{\hat{W}(t)\} | \phi_n \rangle$$

mixed quantum classical version of the rate

$$F(\omega; t) \sim \text{Re} \int_{t_0}^{t} d\bar{t}\, e^{-i\omega(t-\bar{t})} < \sum_{m,n,k} w_{mn}(\bar{t}) \tilde{A}_k^*(t, \bar{t}; n) [\mathbf{d}_k(t) \mathbf{d}_m^*(\bar{t})] >_{\text{ther}}$$

density matrix equations based on the classical path approximation

$$\frac{\partial}{\partial t} w_{mn}(t) = -\frac{i}{\hbar} \sum_k (\mathcal{U}_{mk}\, w_{kn}(t) - w_{mk}\, \mathcal{U}_{kn}) - D_{mn}(t, t_0)$$

dissipative part $D_{mn}(t, t_0) = \frac{1}{2}(k_m + k_n) w_{mn}(t)$

Snapshots of P$_4$ in ethanol along
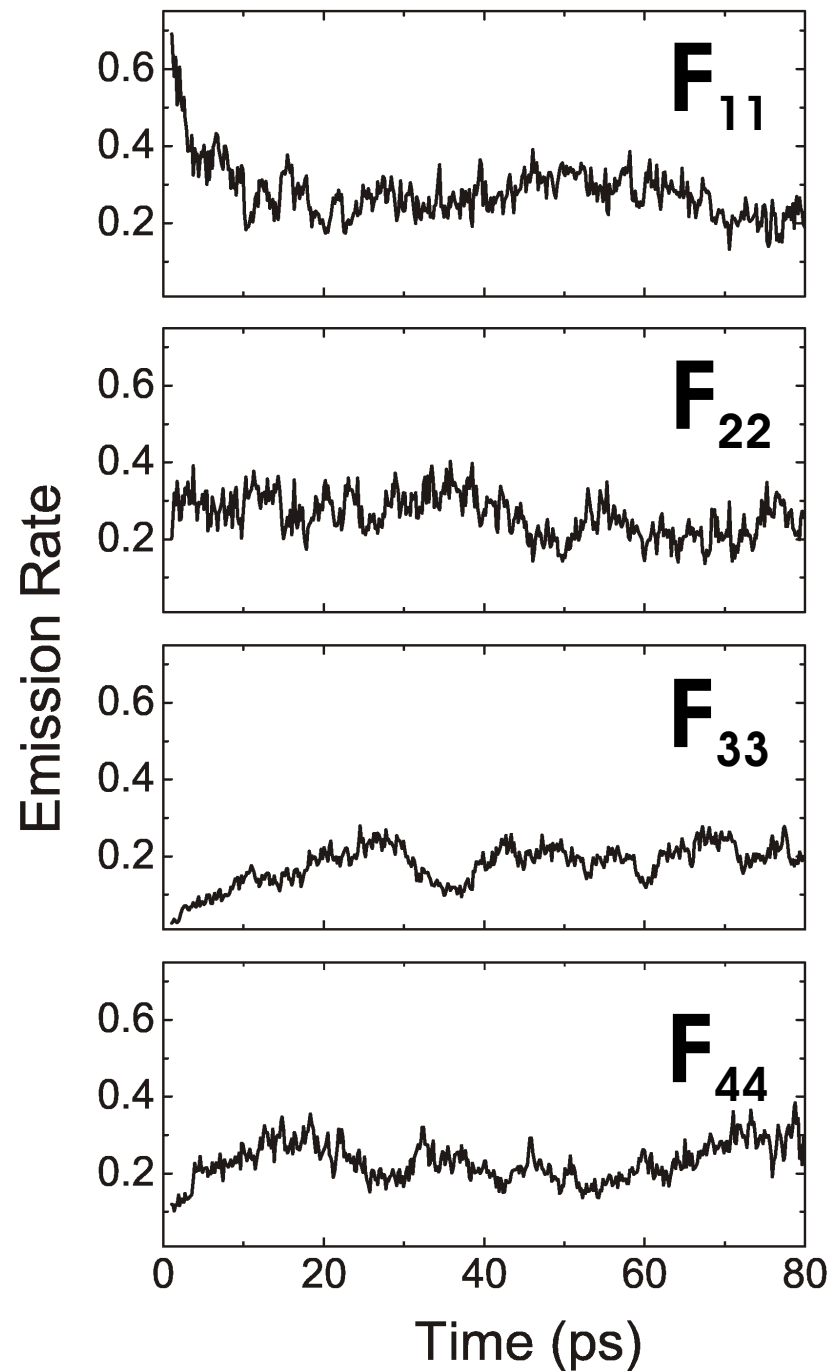a 1 ns room–temperature MD run

Ideal time and frequency resolved
emission spectrum of P$_4$
(normalized by its maximum
and averaged by 10 MD runs
as well as a dephasing time of 20 fs).
The initial excitation corresponds to
an equal distribution of population and the
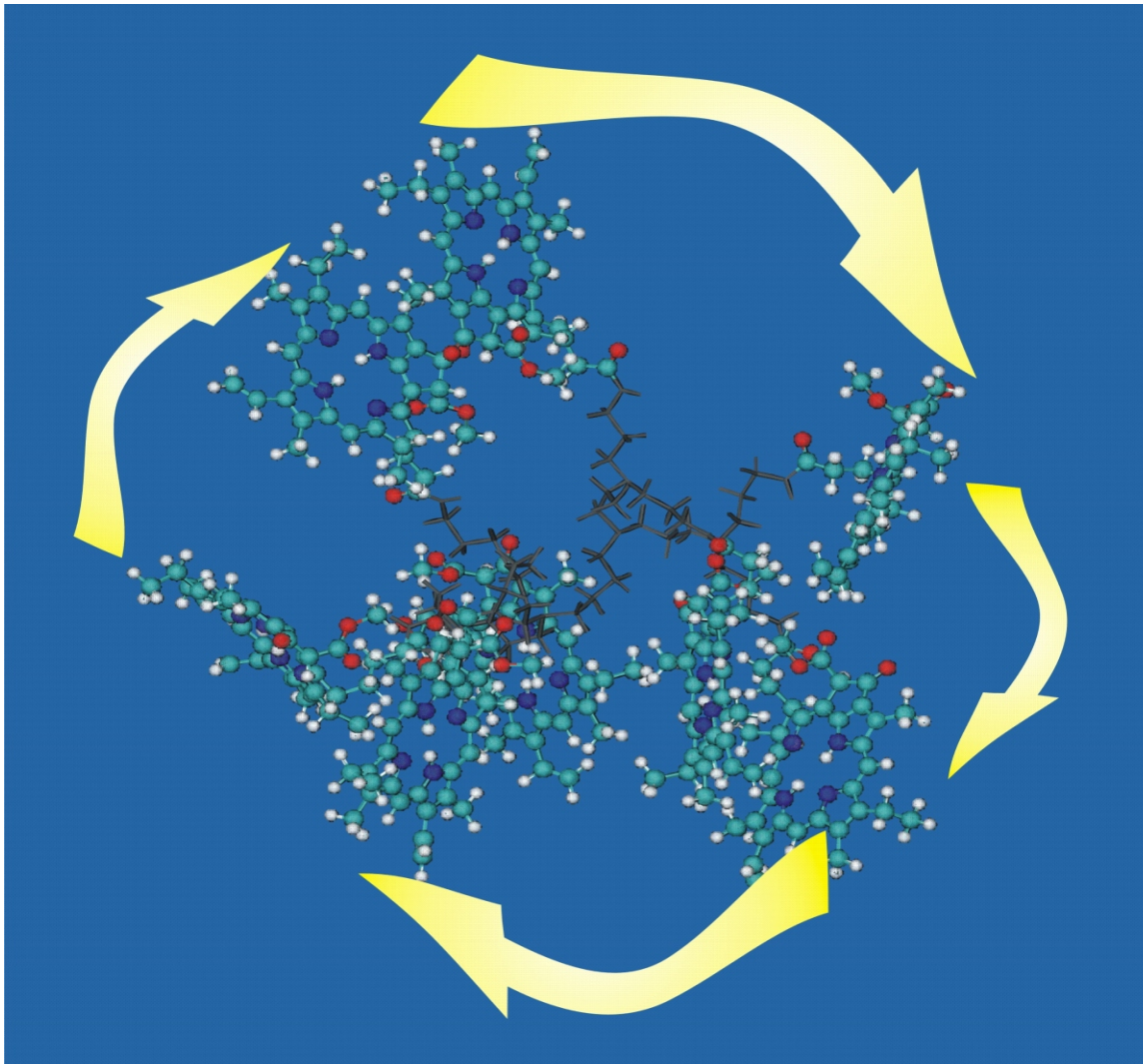absence of inter chromophore correlations.
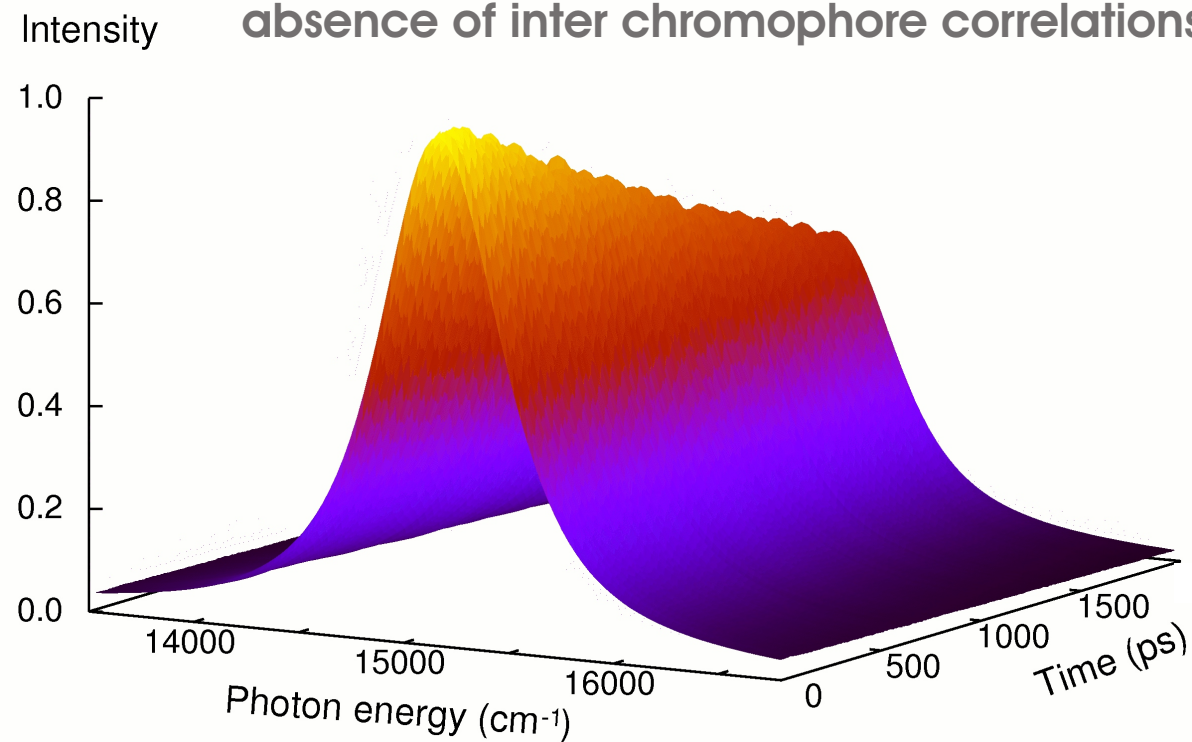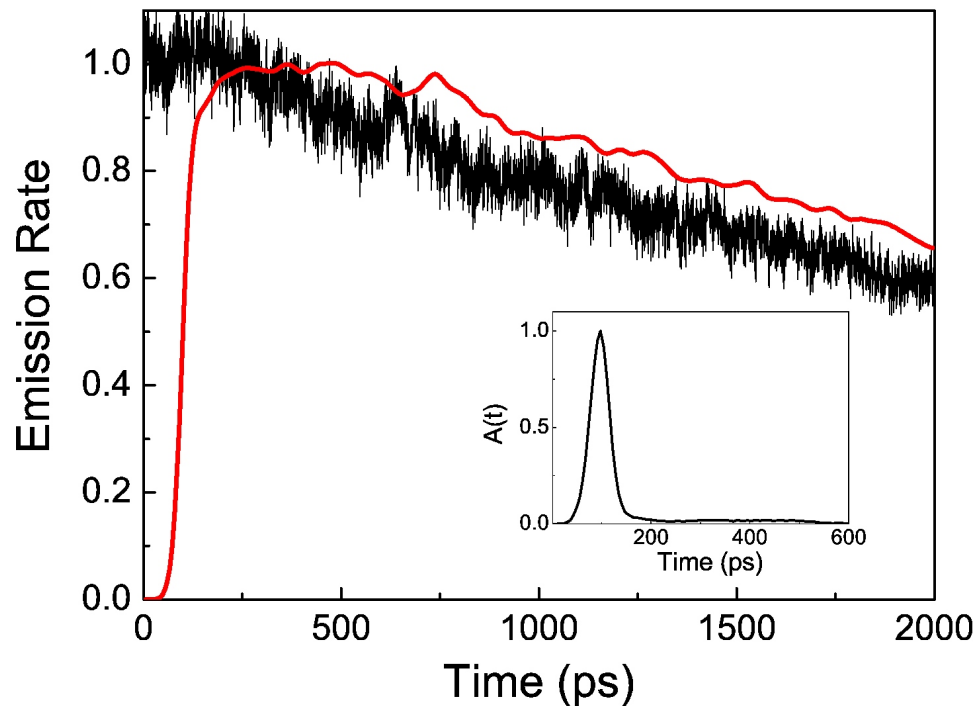
Time resolved emission of P_4 taken at the photon energy of 15015 cm^{-1}.
Red line: emission convoluted with an apparatus function (see insert).

P_4 time resolved emission separated with respect to the different partial spectra F_{mm}

Acknowledgment