#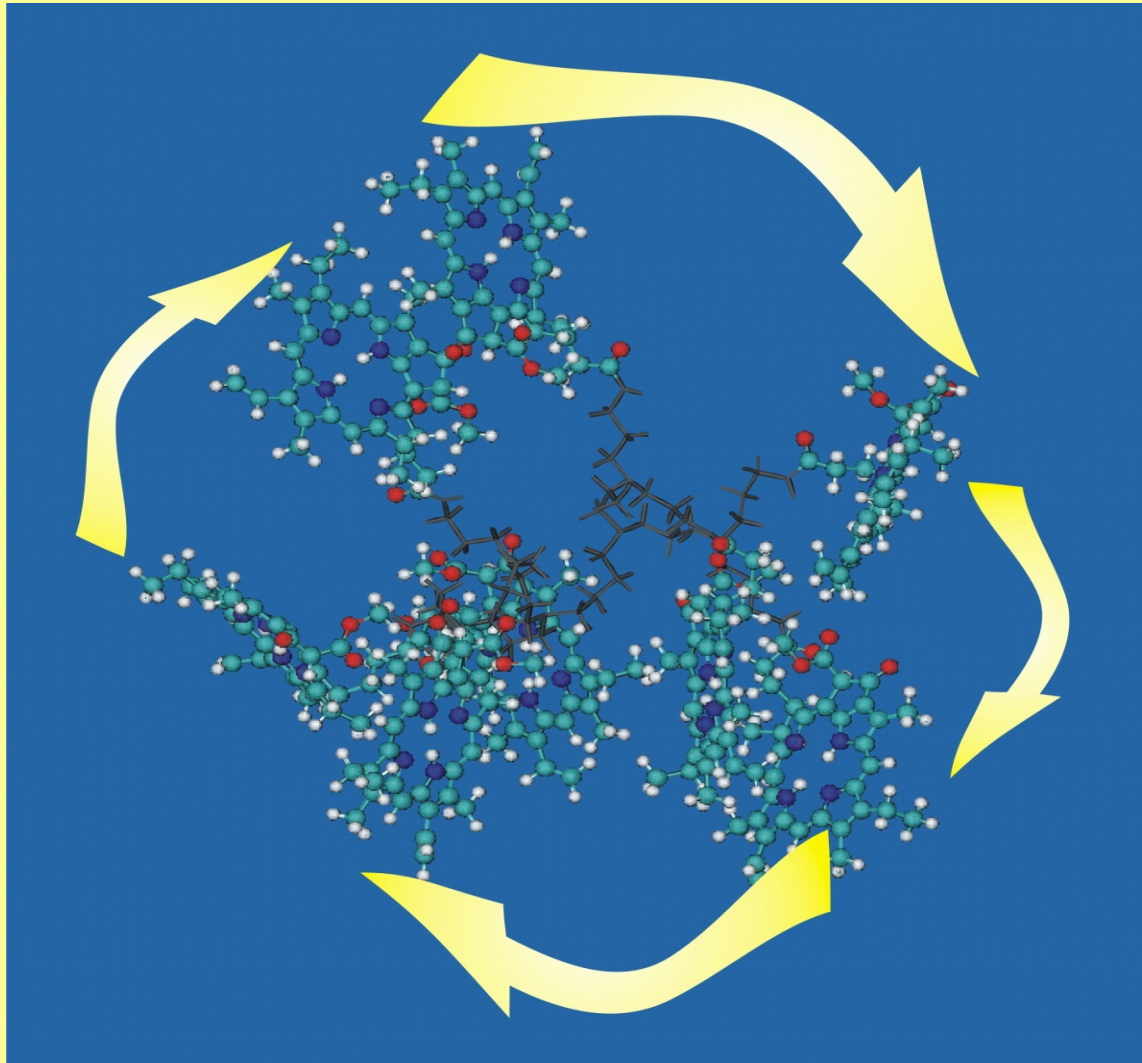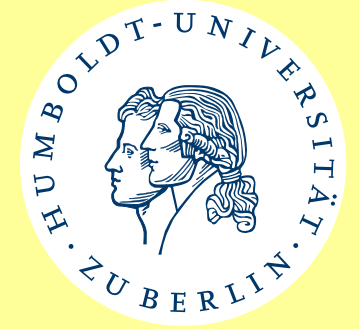 Mixed Quantum-Classical Simulations of Exciton Dynamics and Related Optical Properties: Pheophorbide-a DAB Dendrimers in Solution

Volkhard May
Institute of Physics
Humboldt-University
at Berlin

mixed quantum classical
description:
linear absorbance
excitation energy transfer
time-resolved luminescence

-> excitation energy transfer on a fluctuating structure

-> parameters of the exciton Hamiltonian become time-dependent: $E_m(t)$, $J_{mn}(t)$

-> relation to Haken-Strobl-Reineker model

-> mixed quantum classical description

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

R. D. Gorbunov, P. H. Nguyen, M. Kobus, G. Stock, J. Chem. Phys. 126, 054509 (2007).

**from NGF-theory
of Bloch-electrons**

$$G(\mathbf{k}_1 \tau_1, \mathbf{k}_2 \tau_2) = \frac{1}{i\hbar} \frac{\operatorname{tr}\{\hat{W}_{\mathrm{eq}} \hat{T}_{\mathcal{C}} S_{\mathcal{C}} a_{\mathbf{k}_1}(\tau_1) a_{\mathbf{k}_2}^+(\tau_2)\}}{\operatorname{tr}\{\hat{W}_{\mathrm{eq}} S_{\mathcal{C}}\}}$$

**to density matrix theory of
excitation energy transfer
in molecular systems**

$$\frac{\partial}{\partial t} \rho_{mn}(t) = -i\omega_{mn}\rho_{mn}(t) - \frac{i}{\hbar} \sum_k \left(J_{mk}\rho_{kn}(t) - \rho_{mk}(t)J_{kn} \right) - \sum_{k,l} R_{mn,kl}\rho_{kl}(t)$$

**-> Excitation Energy Transfer in Photosythetic Antennae**

V. Capek,
Generalized Haken-Strobl-Reineker Model of Exciton Transfer,
Z. Phys. B - Condensed Matter 60, 101 (1985).

V. Capek and V. Szöcs,
Stochastic Liouville Equation Model for Nonperiodic Systems
at Finite Temperatures,
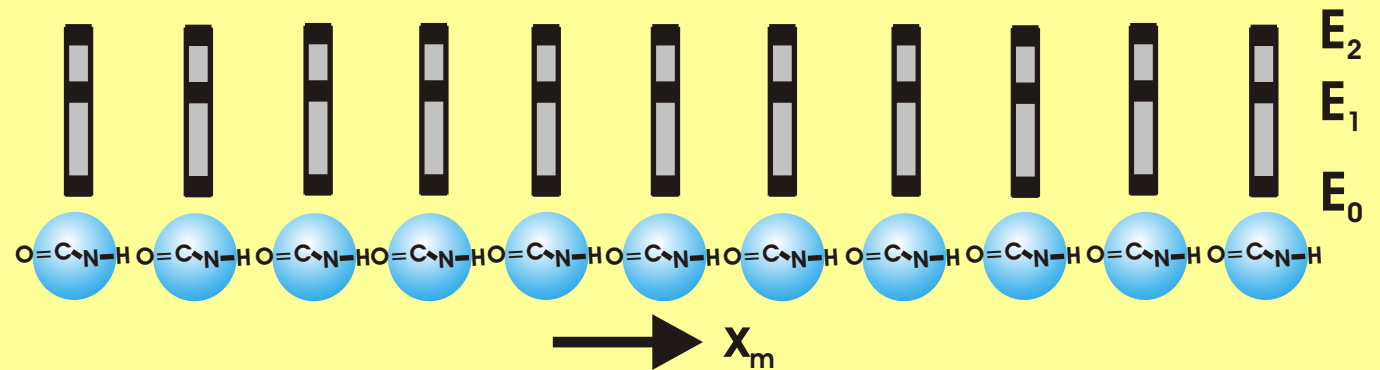phys. stat. sol. (b) 131, 667 (1985).

V. Capek and I. Barvik,
Memory Functions for the Electron-Phonon System,
J. Phys. C: Solid State Phys. 18, 6149 (1985).

V. Capek,
Solitons, Generalised Master Equations and Small-Polaron
Propagation,
J. Phys. C: Solid State Phys. 18, 3201 (1985).

Self-Trapping of Excitation Energy
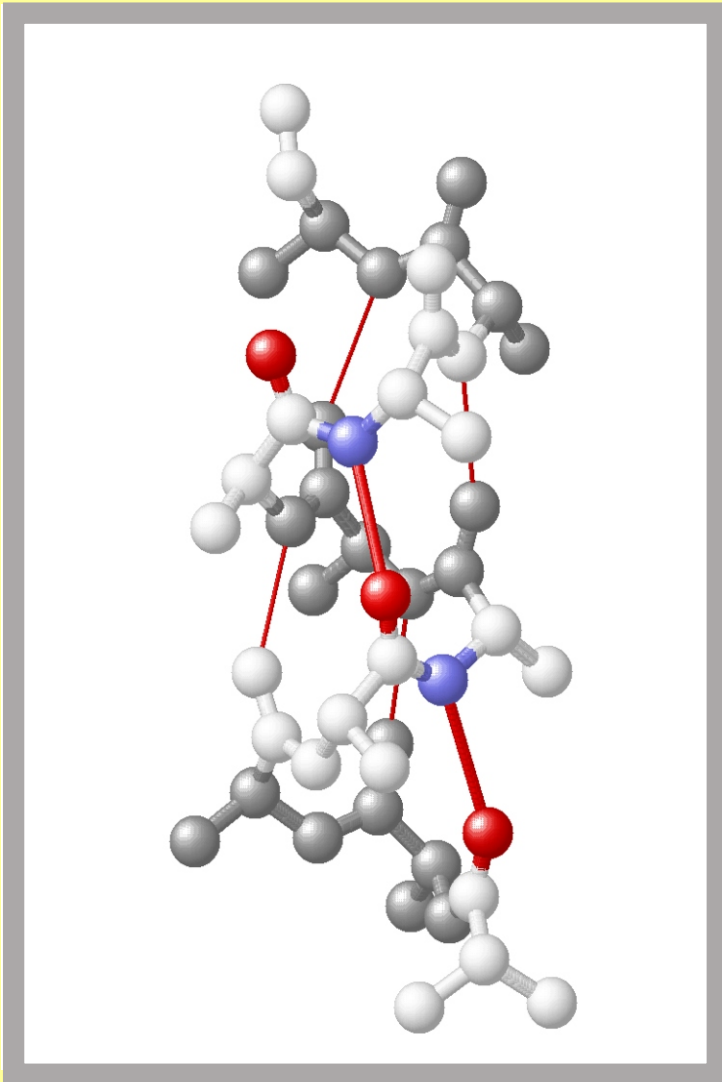
Vibrational Frenkel-Excitons in α-Helices
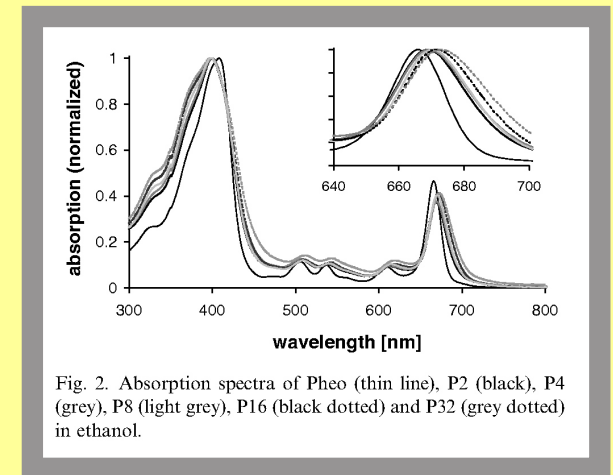

Three-level model of a hydrogen bonded elastic chain

D.V. Tsivlin, H.-D. Meyer, and V. May:
Vibrational Excitons in alpha-Helical Polypeptides: Multiexciton Self-Trapping and Related Infrared Transient Absorption
J. Chem. Phys. 124, 134907 (2006).
D. V. Tsivlin and V. May:
Self-Trapping of the N-H Vibrational Mode in alpha-Helical Polypeptides
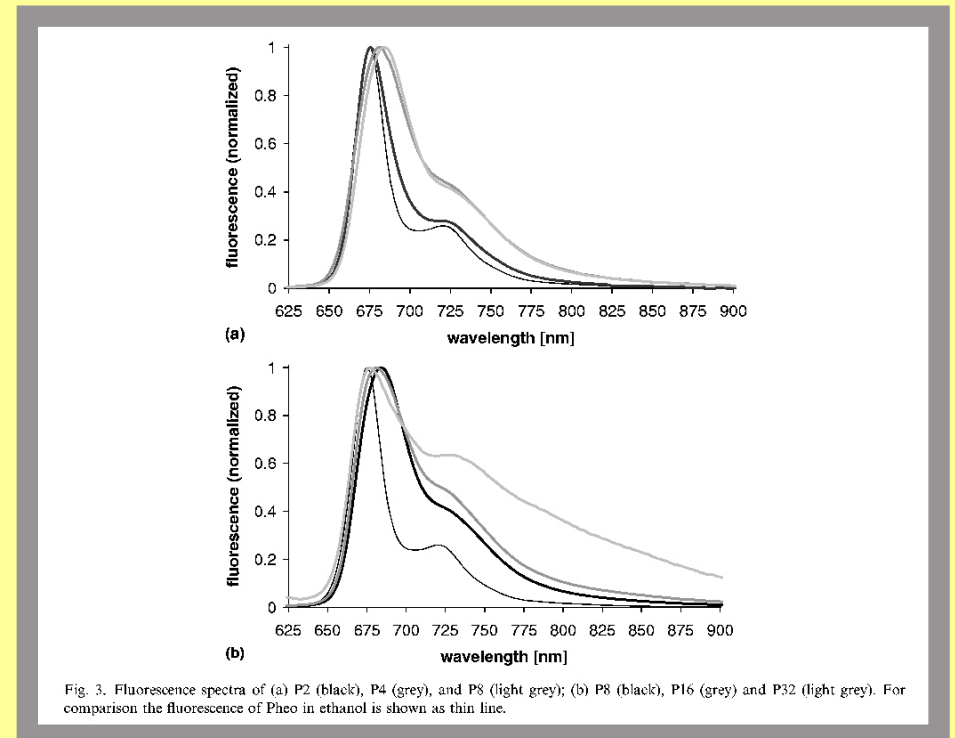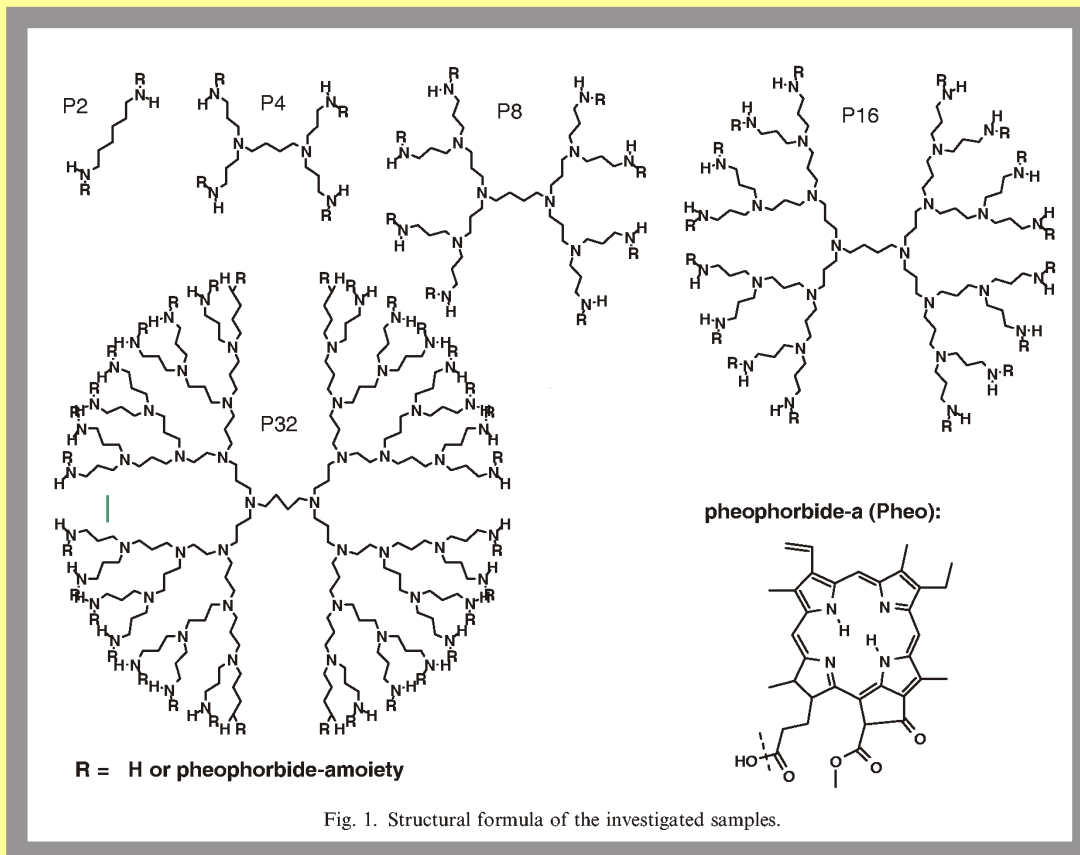J. Chem. Phys. 125, 224902 (2006).
D. Tsivlin and V. May:
Multidimensional Wave Packet Dynamics in Polypeptides: Coupled Amide-Exciton Chain-Vibrational Motion in an alpha-Helix
Chem. Phys. 338, 150 (2007).

butanediamine dendrimers to which up to 32 pheophorbide-a molecules have been covalently linked
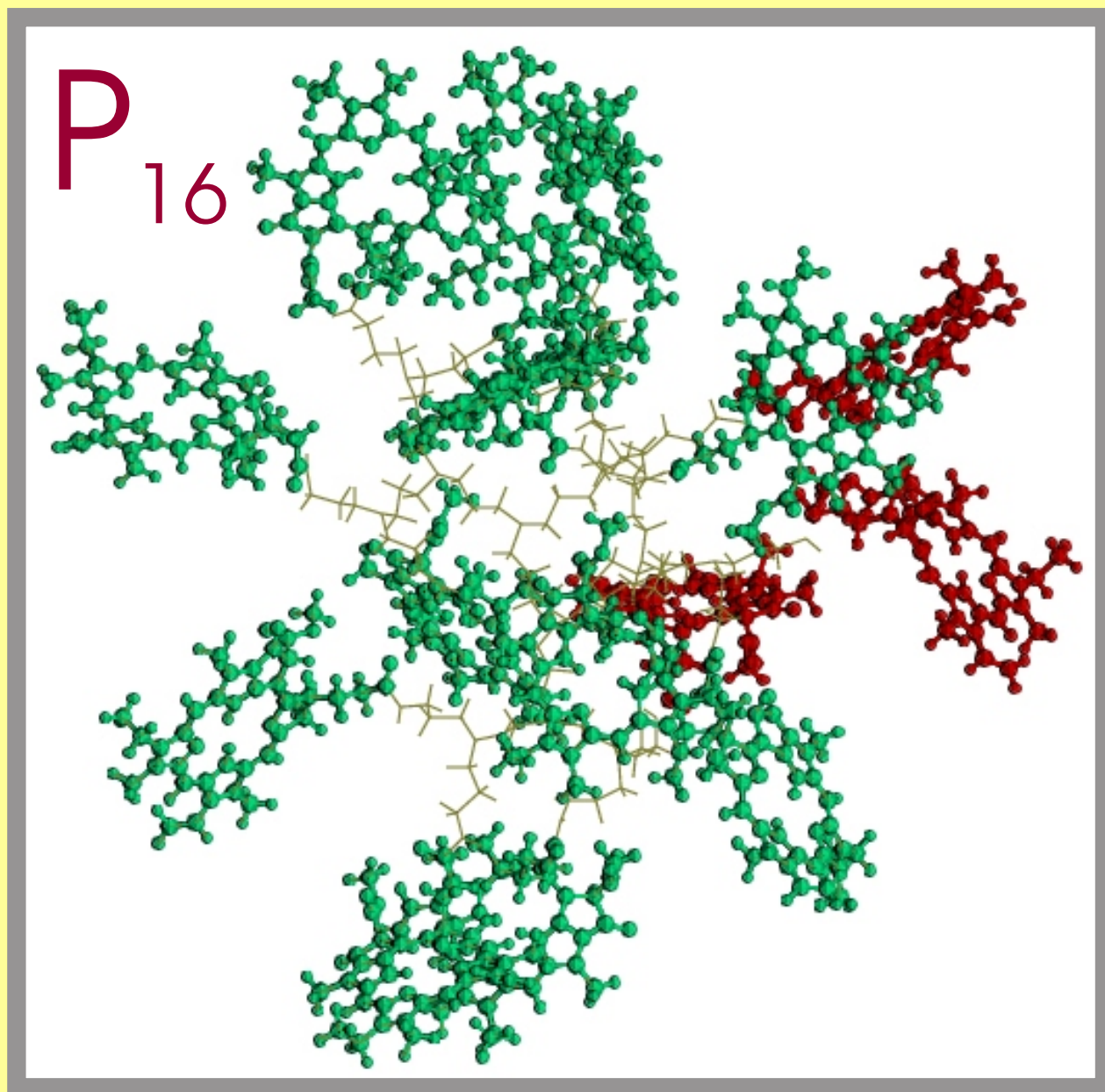
some importance for photodynamic therapy (-> efficiency of singlet oxygen generation)

Fig. 2. Absorption spectra of Pheo (thin line), P2 (black), P4 (grey), P8 (light grey), P16 (black dotted) and P32 (grey dotted) in ethanol.

S. Hackbarth, E. A. Ermilov, and B. Röder, Opt. Comm. 248, 295 (2005).

R = H or pheophorbide-a moiety

Fig. 1. Structural formula of the investigated samples.

pheophorbide-a (Pheo):

Fig. 3. Fluorescence spectra of (a) P2 (black), P4 (grey), and P8 (light grey); (b) P8 (black), P16 (grey) and P32 (light grey). For comparison the fluorescence of Pheo in ethanol is shown as thin line.

NpT-Ensemble Molecular Dynamics Simulation

P$_{16}$

NAMD package
AMBER force field

33256 atoms
- 78 per Pheo
- 310 of the dendremeric
structure
- 3522 ethanol molecules

simulation box
7.3nm x 8.4nm x 7.9nm

cut off radius 1.5nm
equilibration time: 100 ps

Mixed Quantum Classical Dynamics

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

$$M_\nu \frac{\partial^2}{\partial t^2} \mathbf{R}_\nu(t) = -\boldsymbol{\nabla}_\nu \langle \Psi(R(t)) | H_{\mathrm{el}}(R(t)) | \Psi(R(t)) \rangle$$
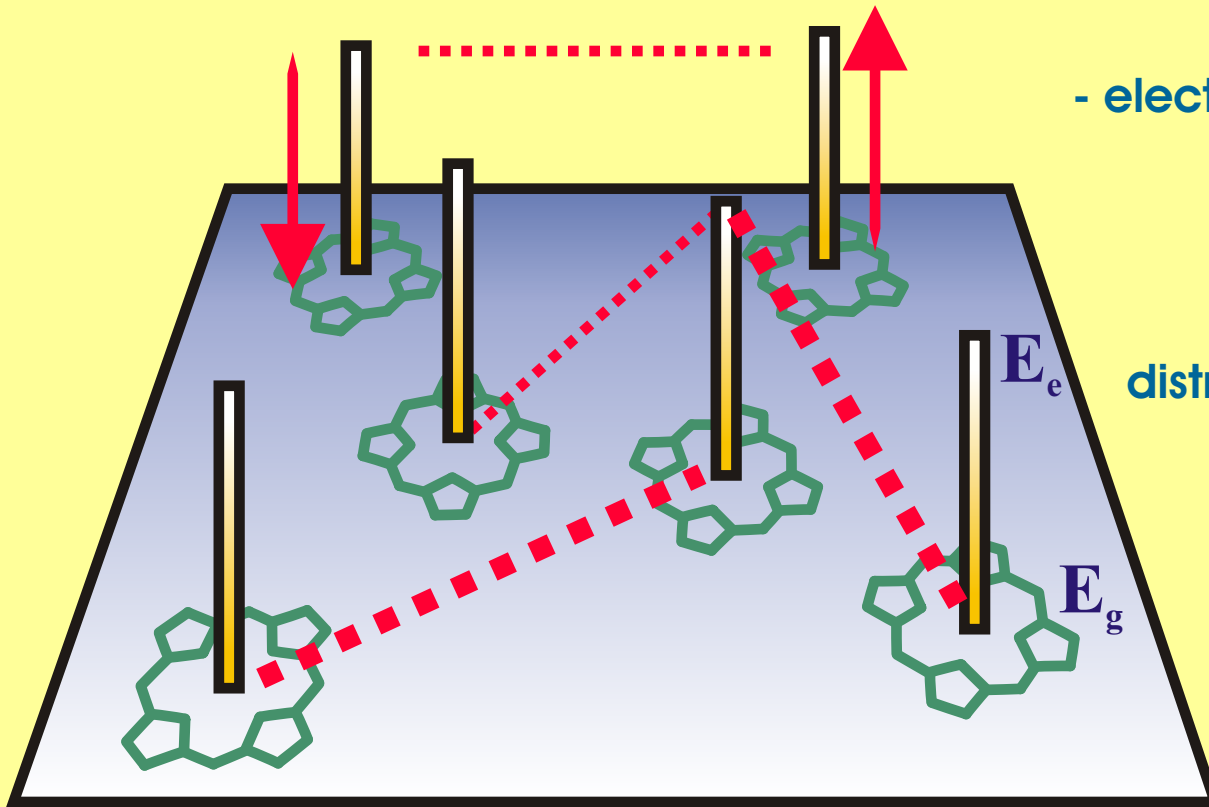
Ehrenfest dynamics
-> surface hopping
-> classical path approximation

Model of Interacting Chromophores

$$H_{\mathrm{CC}} = (T_{\mathrm{nuc}} + \mathcal{U}_0(R))|\phi_0\rangle\langle\phi_0| + \sum_{m,n} (\delta_{m,n} T_{\mathrm{nuc}} + \mathcal{U}_{mn}(R))|\phi_m\rangle\langle\phi_n|$$

E_e

E_g

- electronic two-level model per chromophore

- excitonic coupling

- electrostatic interaction via charge distributions in the ground and excited state
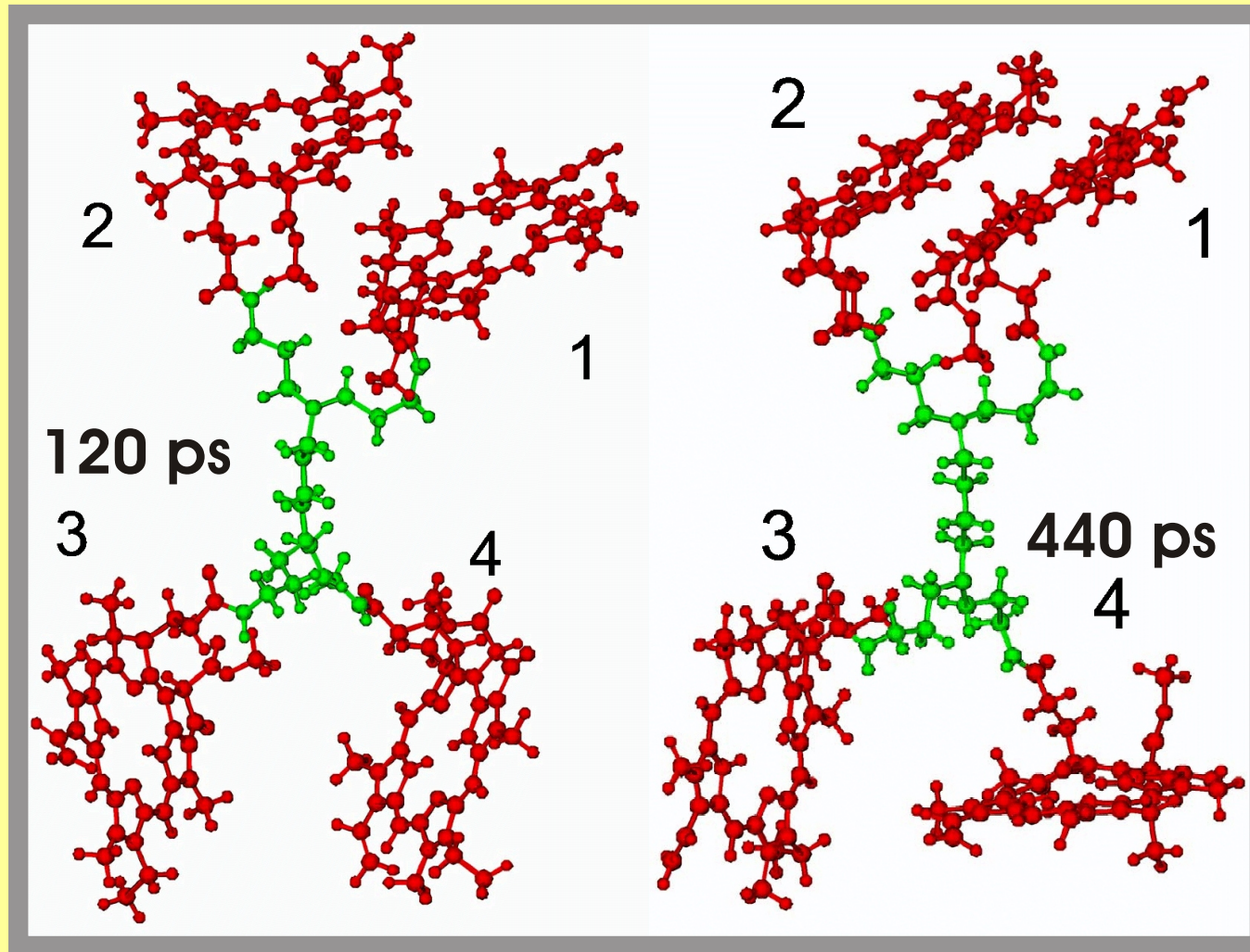
- electrostatic interaction with solvent molecules

atomic centred partial charges

$$J_{mn}(ab, cd) = \langle\varphi_{ma}\varphi_{nb}|V_{mn}|\varphi_{nc}\varphi_{md}\rangle = \int d^3\mathbf{x}\, d^3\mathbf{x}' \frac{n_{ad}^{(m)}(\mathbf{x}) n_{bc}^{(n)}(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|}$$
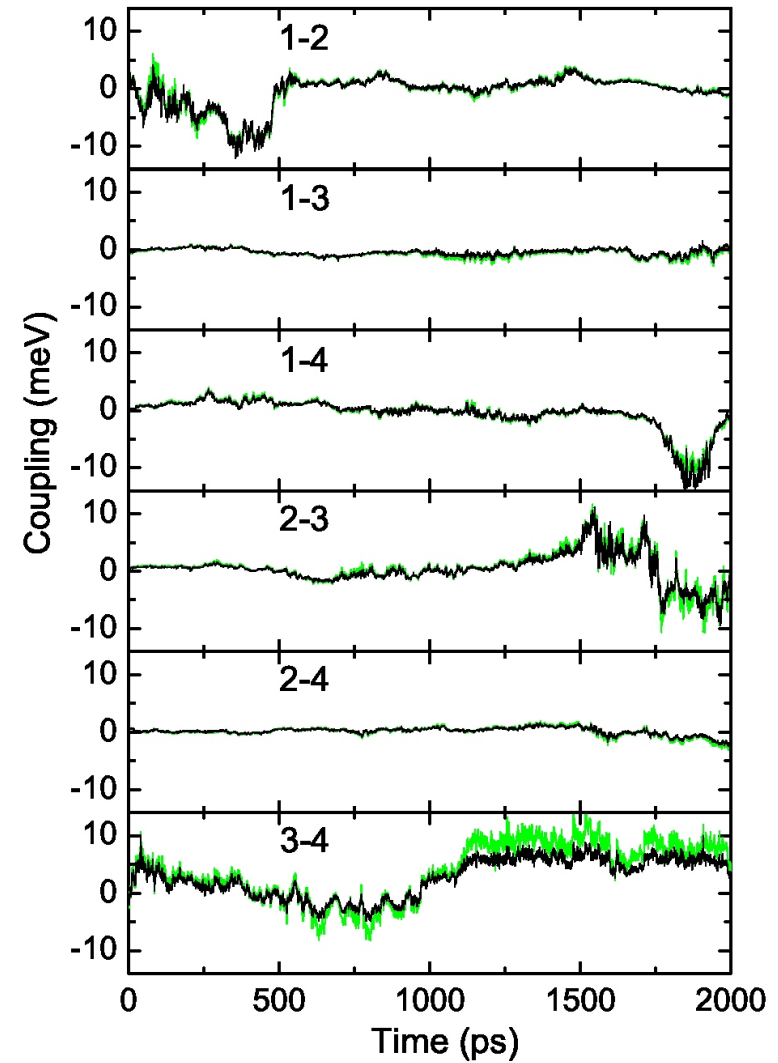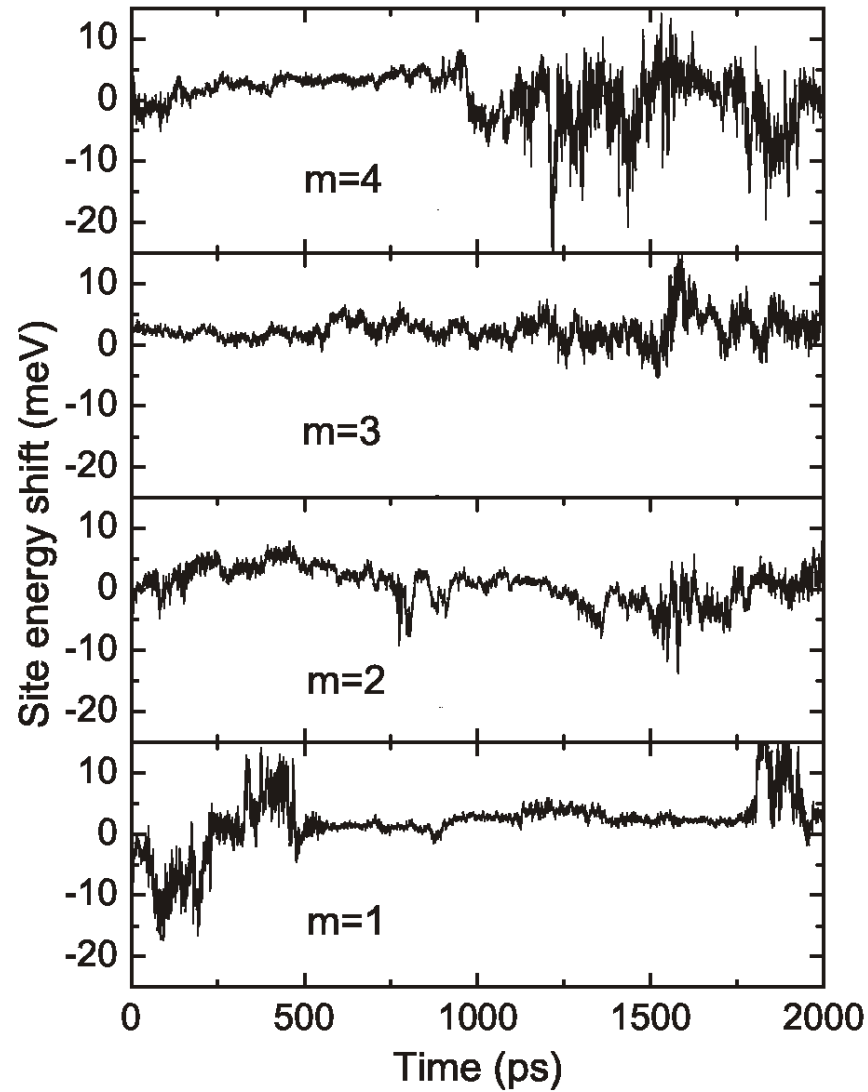
$$J_{mn}(ab, cd) = \sum_{\mu,\nu} \frac{q_{m\mu}(ad) q_{n\nu}(bc)}{|\mathbf{R}_{m\mu} - \mathbf{R}_{n\nu}|}$$

Consideration of P$_4$

Two different structures of P$_4$ formed in a single MD run. (solvent molecules are not shown, point of view has been slightly changed for optimal presentation).

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

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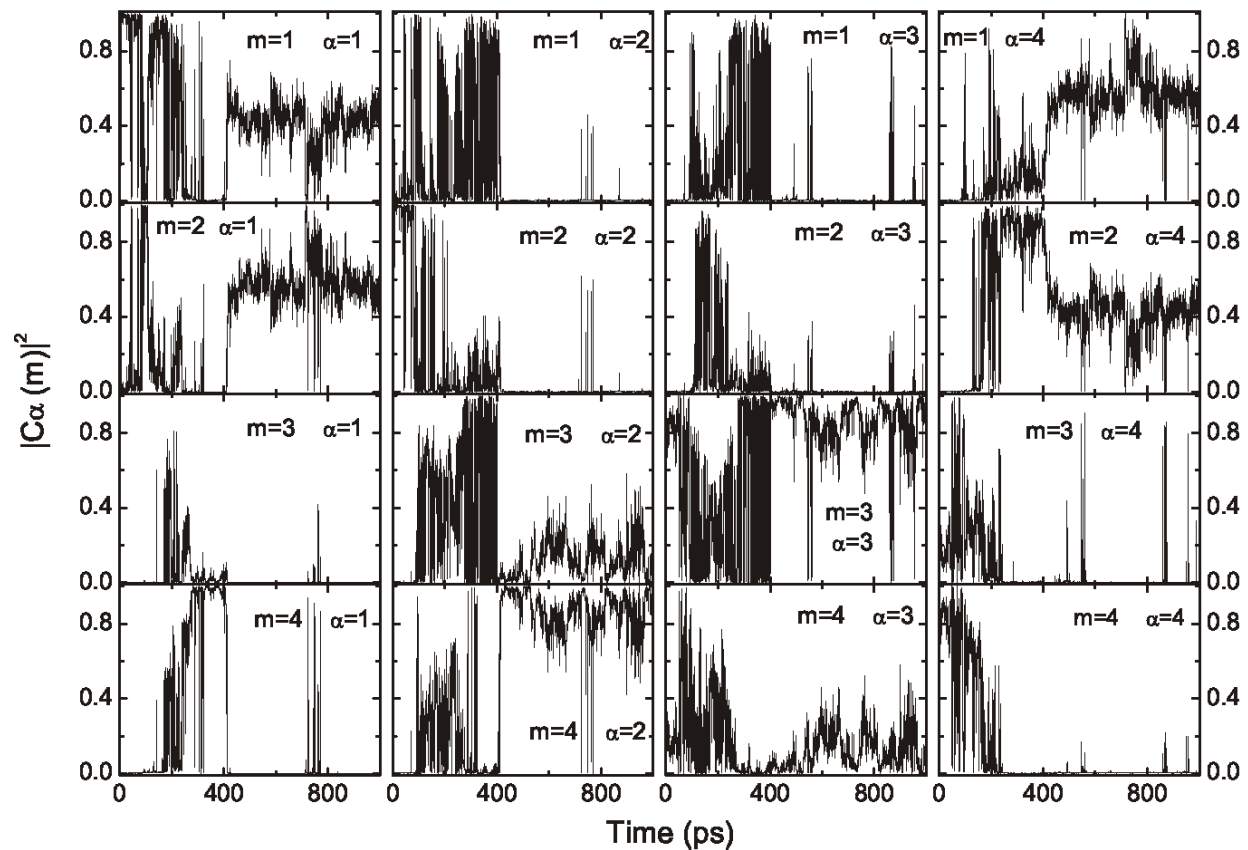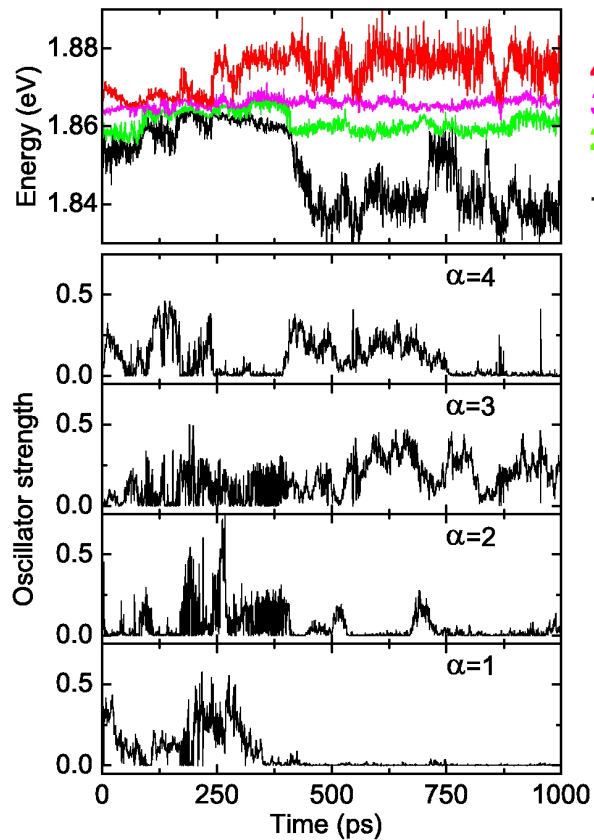
Adiabatic exciton energies and oscillator strengths (data have been computed every 0.5 ps and follow from a single 1 ns MD run).

Square of adiabatic exciton expansion coefficients taken every 0.5 ps .

H. Zhu, V. May, B. Röder, M. El-Amine Madjet, and Th. Renger, Chem. Phys. Lett. 444, 118 (2007).
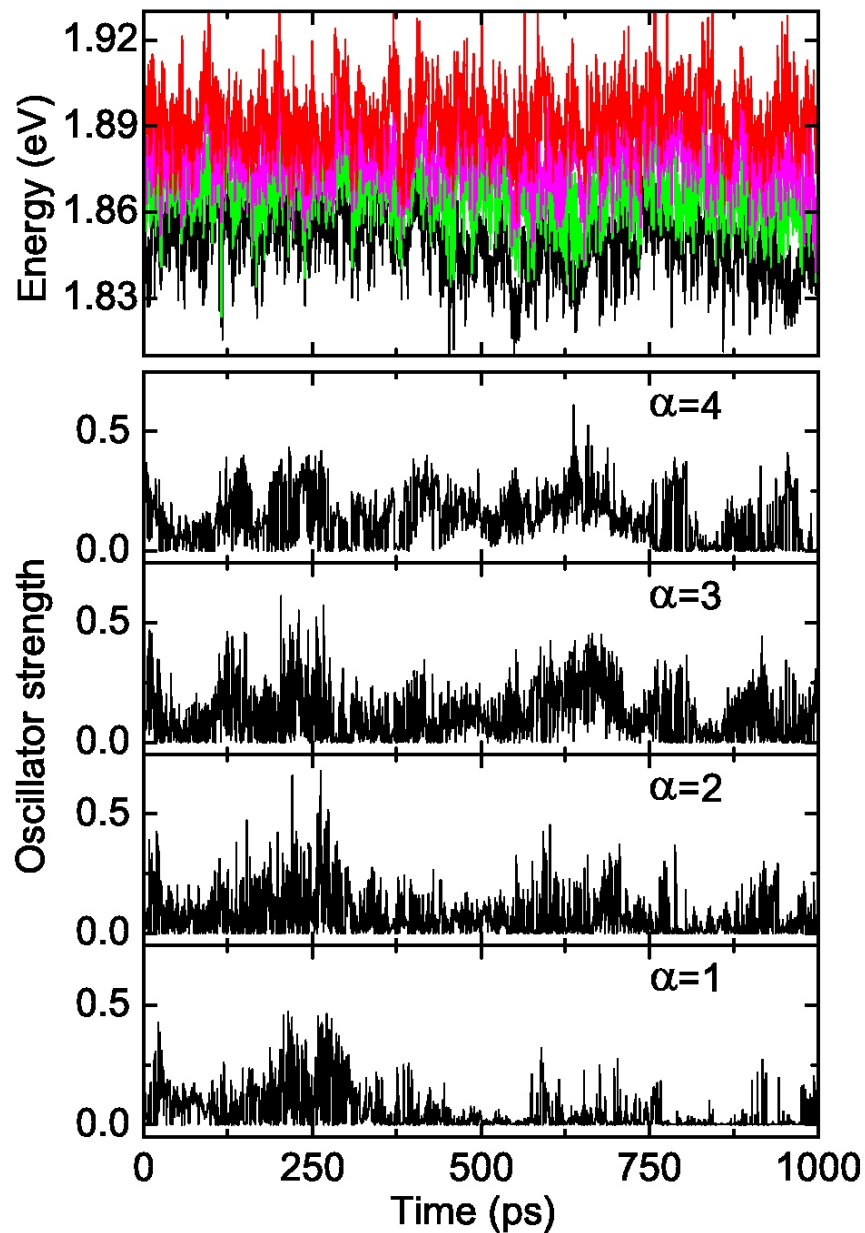
Adiabatic exciton energies and oscillator strengths (data have been computed every 0.5 ps and follow from a single 1 ns MD run).
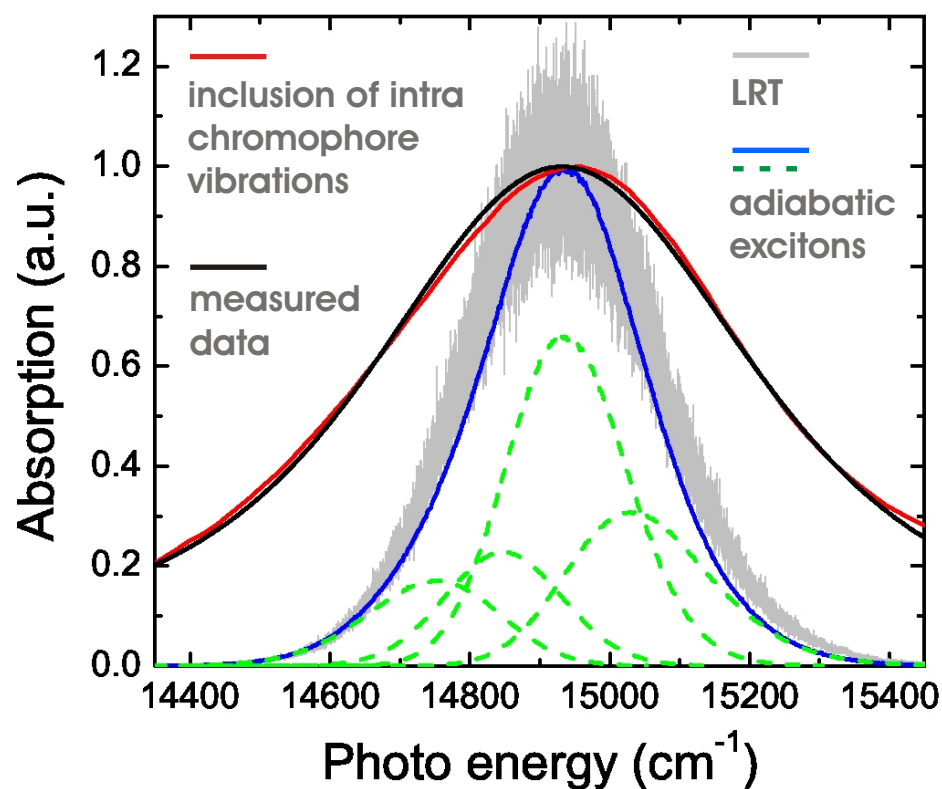
Solvent induced modulations of the single chromophore excitation included.

Room temperature steady state absorption of P$_4$ dissolved in ethanol using different approximations.
(averaging with respect to 40 different 1 ns MD runs, spectra have been normalized to their maxima)
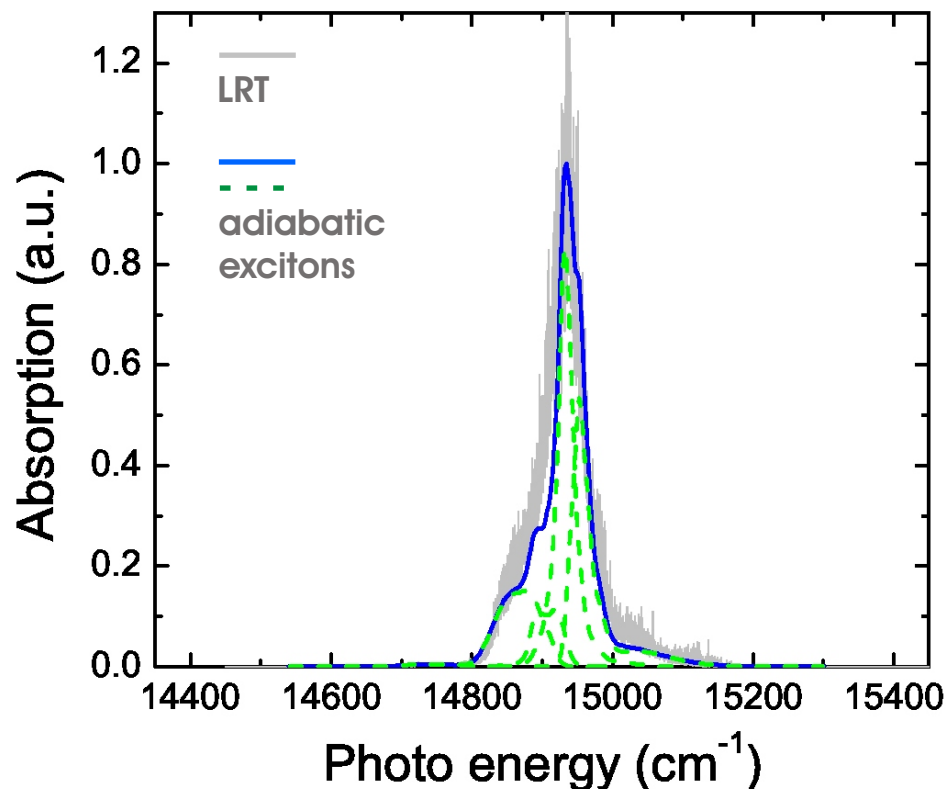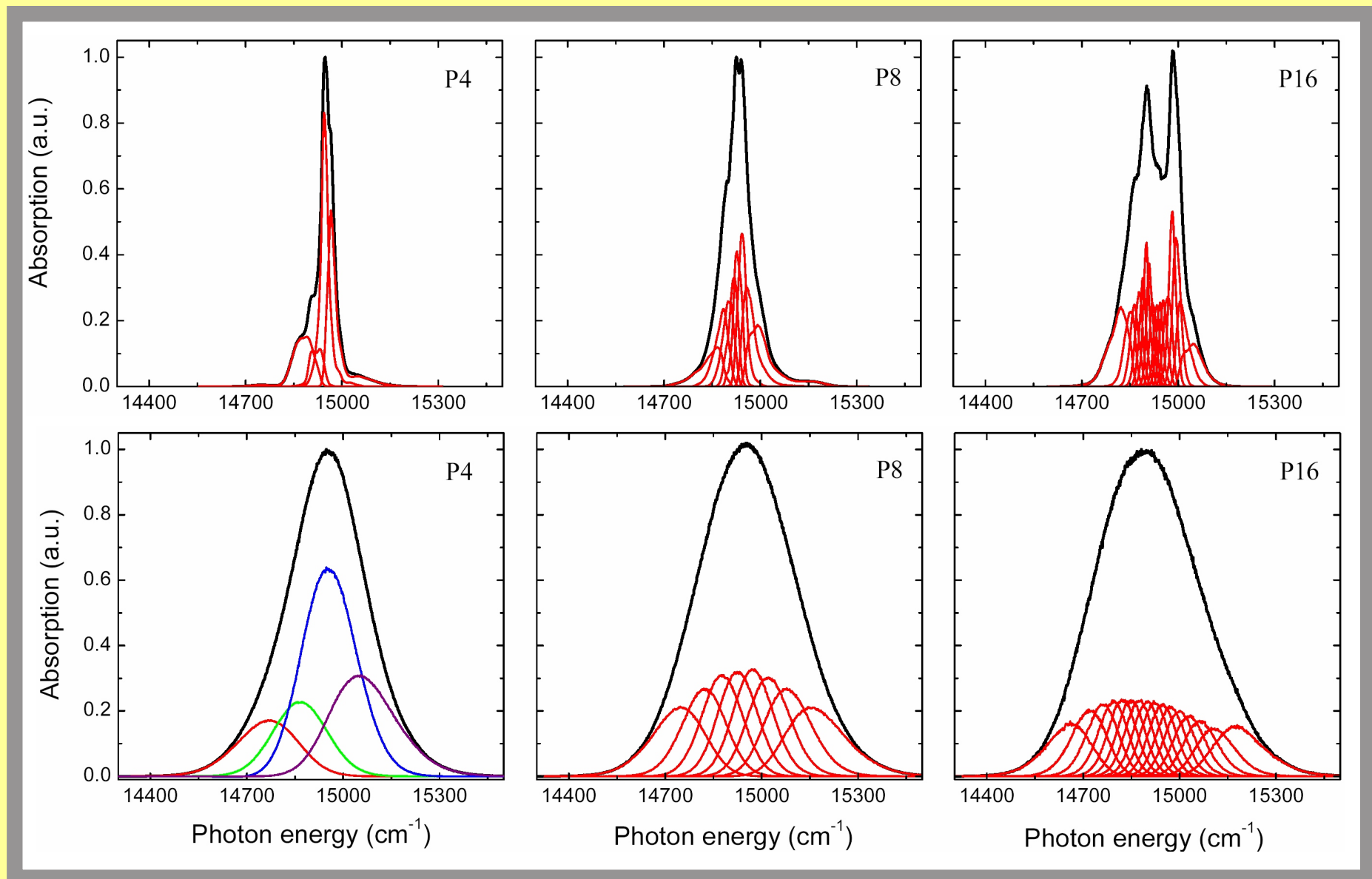

The modulation of the single chromophore excitation energy by the solvent molecules is **neglected**.

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

Mixed quantum classical dynamics of excitation energy transfer

$$M_{m\mu}\frac{\partial^2}{\partial t^2}\mathbf{R}_{m\mu} = -\nabla_{m\mu}\mathcal{U}_0(R)$$

MD simulations with the electronic ground-state force field

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

equations of motion for the expansion coefficients including optical excitation

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

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

- solution of the time-dependent Schroedinger equation referring to the time-dependent exciton Hamiltonian

- dynamics known from standard density matrix or rate equation theories have to be expected in the ensemble average

- no formation of thermal equilibrium (infinite temperature limit)

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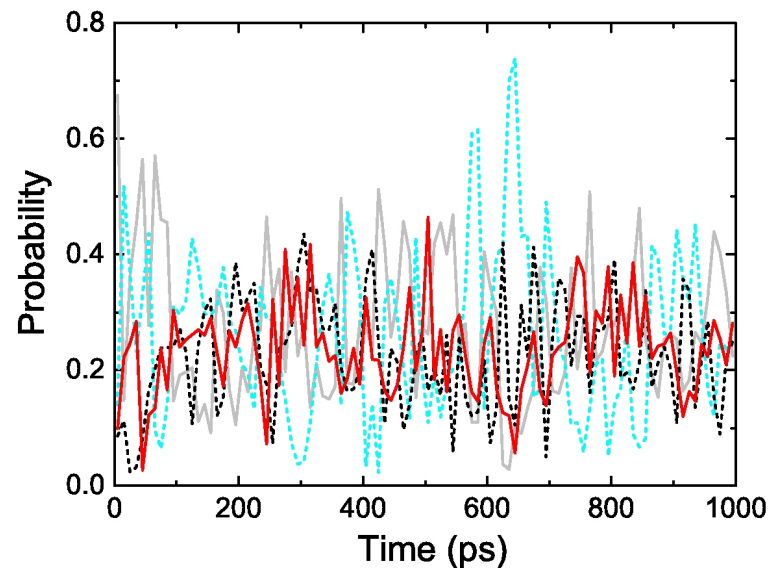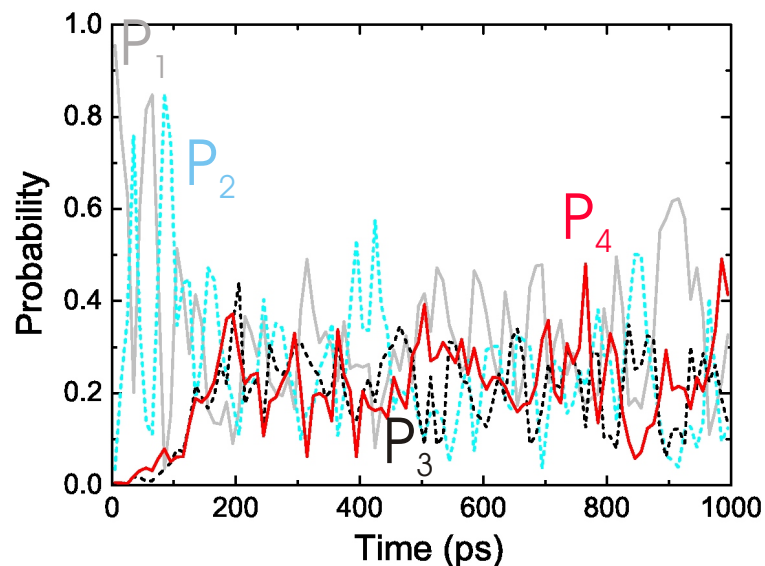
The modulation of the single chromophore excitation energy by the solvent molecules is neglected.

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

Excitation energy transfer dynamics without time averaging
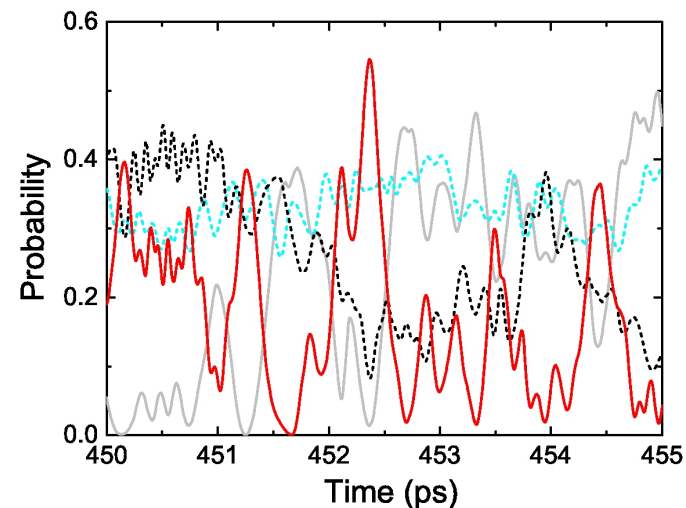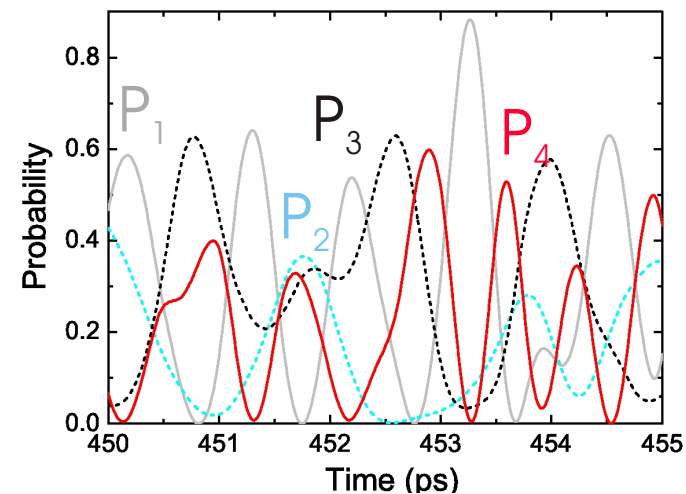
Linear Absorption Spectra

complete quantum formula

$$I(\omega) = \mathrm{Re} \int\limits_{0}^{\infty} dt \, e^{i\omega t} \sum_{m,n} \mathrm{tr}_{\mathrm{vib}}\{\hat{R}_0 \, \langle\phi_0|e^{iH_0 t/\hbar}|\phi_0\rangle \, d_m^+ \, \langle\phi_m|e^{-iH_1 t/\hbar}|\phi_n\rangle \, d_n\}$$

estimate using the Wigner-representation and adiabatic excitons

$$I(\omega) \sim \sum_{\alpha} \int dR \, f_0(R) \, O_\alpha(R) \, \delta(\omega - \mathcal{E}_\alpha(R)/\hbar)$$

-> neglect of non-adiabatic couplings

dynamical classical limit (DCL)

$$I_{\mathrm{DCL}}(\omega) = \mathrm{Re} \int\limits_0^\infty dt \, e^{i\omega t} \sum_{m,n} < d_m^*(t) \, A_m(t;n) \, d_n >$$
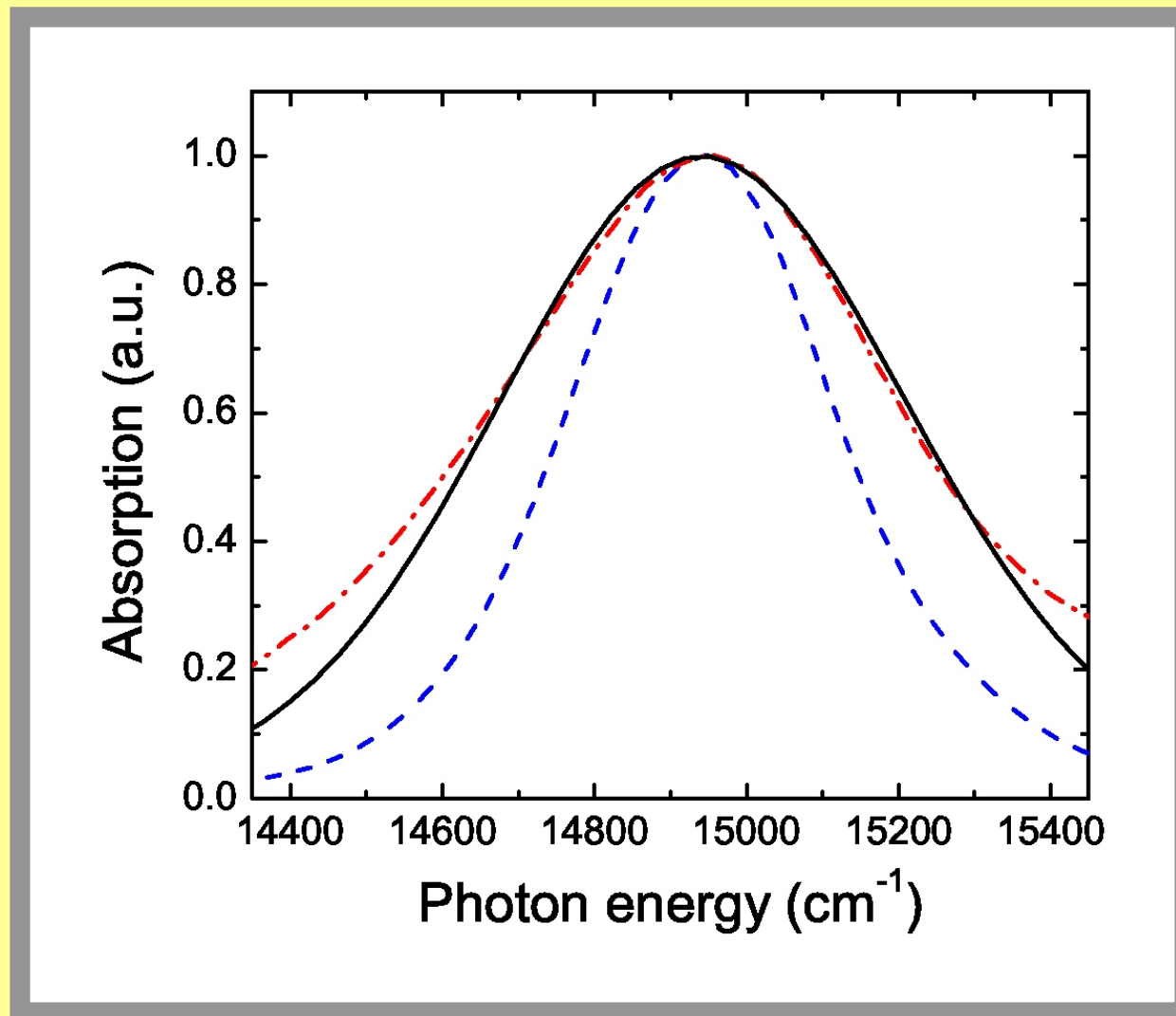
$$A_m(t;n) = \langle \phi_0 | U_0^+(t) | \phi_0 \rangle \langle \phi_m | U_1(t) | \phi_n \rangle$$

absorption signal determined
in linear response theory

$$S_{\mathrm{abs}}(\omega) = 2\omega \mathrm{Im} \int dt \, E^*(t) P(t) = \frac{\omega n_{\mathrm{CC}}}{\hbar} \sum_m < |D(\omega;m)|^2 >$$

$$D(\omega;m) = \int dt \, e^{i\omega t} \sum_n d_{0n}(t) A_n(t;m) E^*(t)$$

Room temperature steady state DCL absorption of P_4 dissolved in ethanol. The modulation of the single chromophore excitation energy by the solvent molecules is incorporated.

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

Computation of time and frequency resolved luminescence

full quantum formula for time and frequency gated spontaneous emission
measured under ideal time and frequency resolution

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

$$\times \sum_{m,n,k} \text{tr}_{\text{vib}} \{ \hat{\rho}_{mk}(\bar{t}) \langle \phi_k | e^{iH_1(t-\bar{t})/\hbar} | \phi_n \rangle \, d_n \, \langle \phi_0 | e^{-iH_0(t-\bar{t})/\hbar} | \phi_0 \rangle \, d_m^+ \}$$

formula for a mixed quantum classical description

$$F(\omega; t) \sim \mathrm{Re} \int_{t_0}^{t} d\bar{t}\, e^{-i\omega(t-\bar{t})} \sum_{m,n,k} < B_m(\bar{t}, t_0) B_k^*(\bar{t}, t_0) A_n^*(t, \bar{t}; k) d_n(t) d_m^* >$$
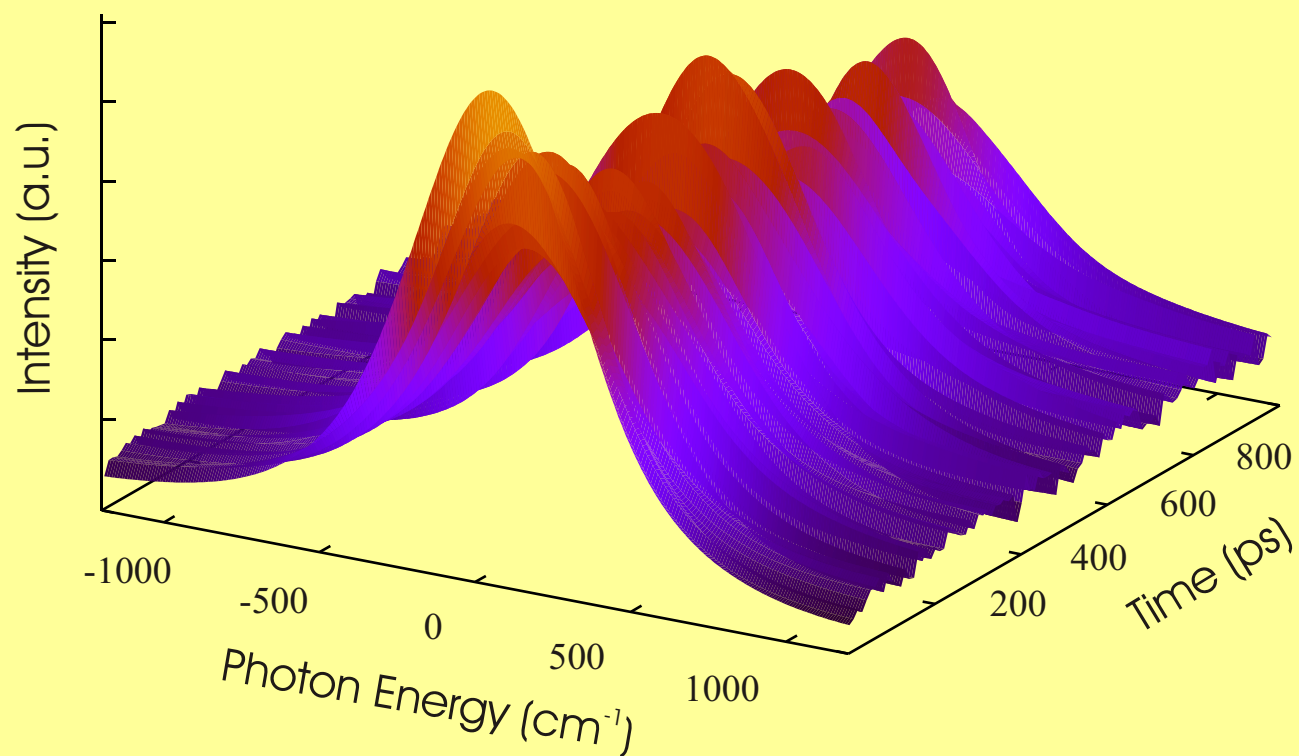
Conclusions

-> mixed quantum classical description of large molecular systems possible

-> exciton vibrational coupling described beyond perturbation theory

-> simultaneous consideration of dynamic and static disorder with atomic resolution

-> extension to ultrafast nonlinear spectra possible

Advertisement of a Vacancy

A PhD position is open at the Humboldt-University at Berlin, Institute of Physics in the field of Theoretical Chemical Physics.

The project is entitled:

Multi-Exciton Description of Amide Group Vibrational Dynamics in Polypeptides and Proteins