Ultrafast Exciton Dynamics in Molecular Systems

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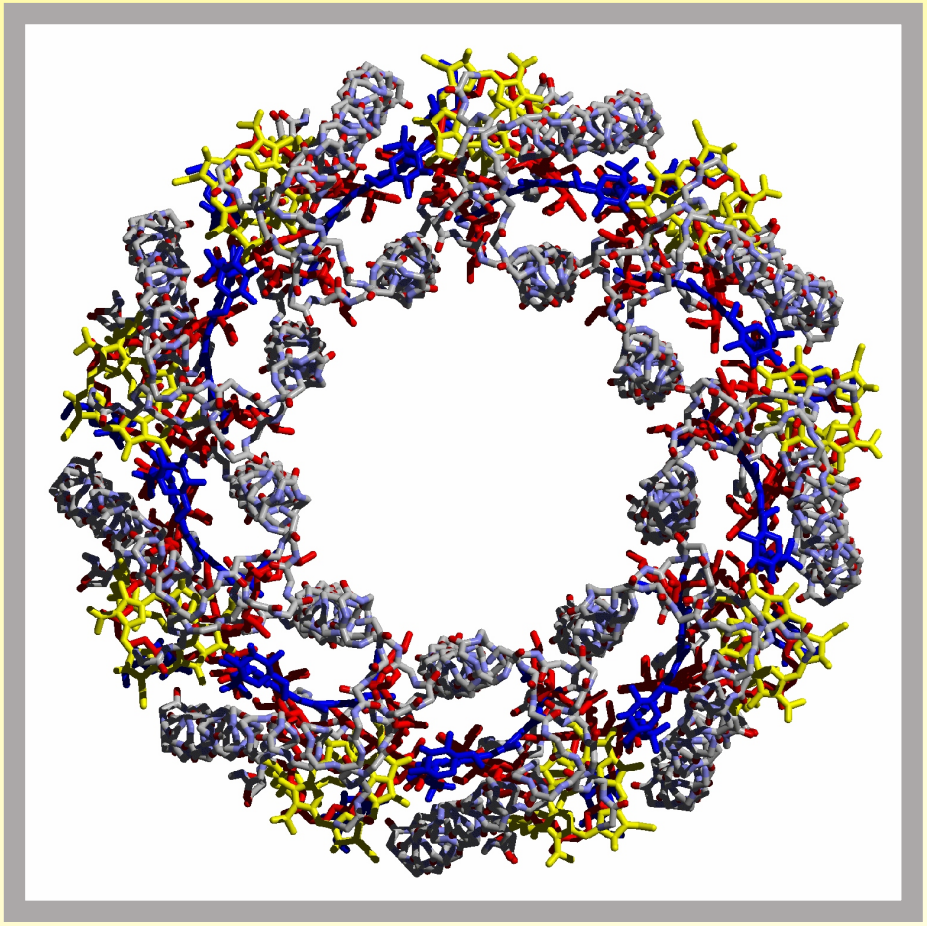
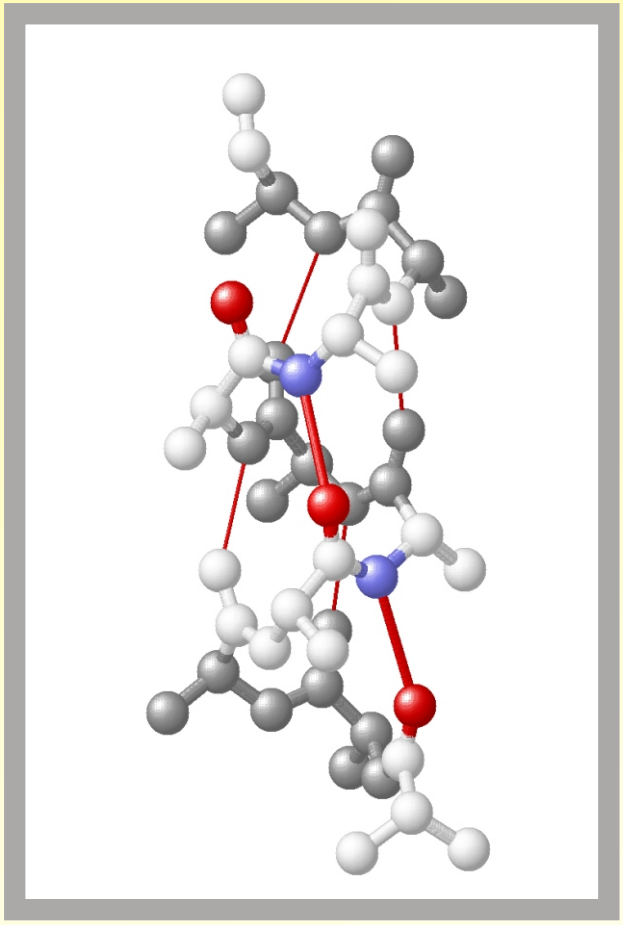
electronic Frenkel-excitons in photosynthetic antenna systems



vibrational Frenkel-excitons in -helical polypeptides



-> simulation of femtosecond spectroscopic data

-> stepwise improved description of exciton-vibrational coupling

Electronic Frenkel-Excitons

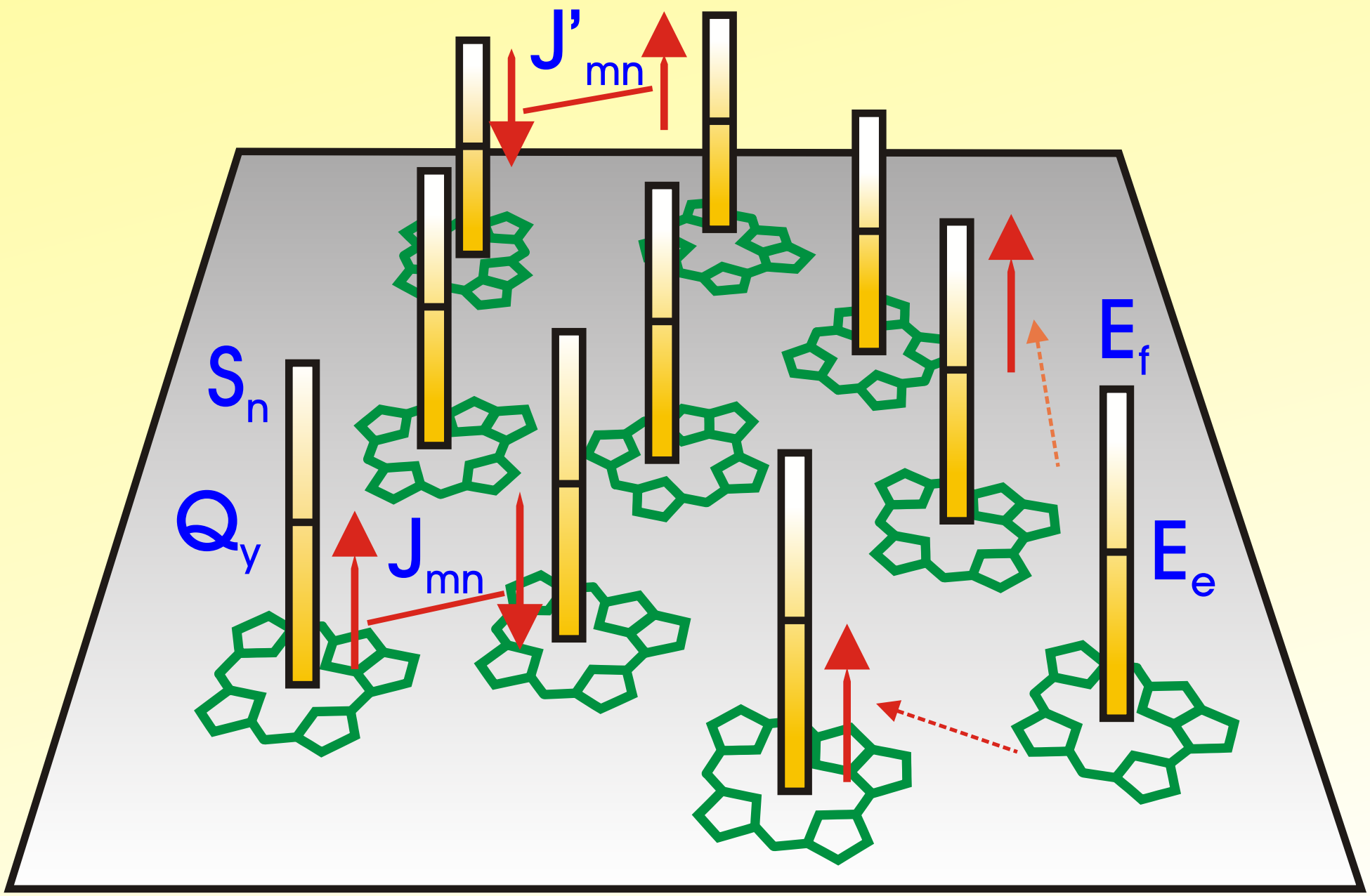
Excitation Energy Motion in Photosynthetic Antennae

Understanding femtosecond spectra
related to excitons in chromophore complexes:
-> formation of single- and two-exciton states
-> electronic excitation energy dissipation
-> presence of static disorder

ab initio description of the single-exciton states possible (Schulten, 1998, ...)

description of all other effects requires the introduction of certain models

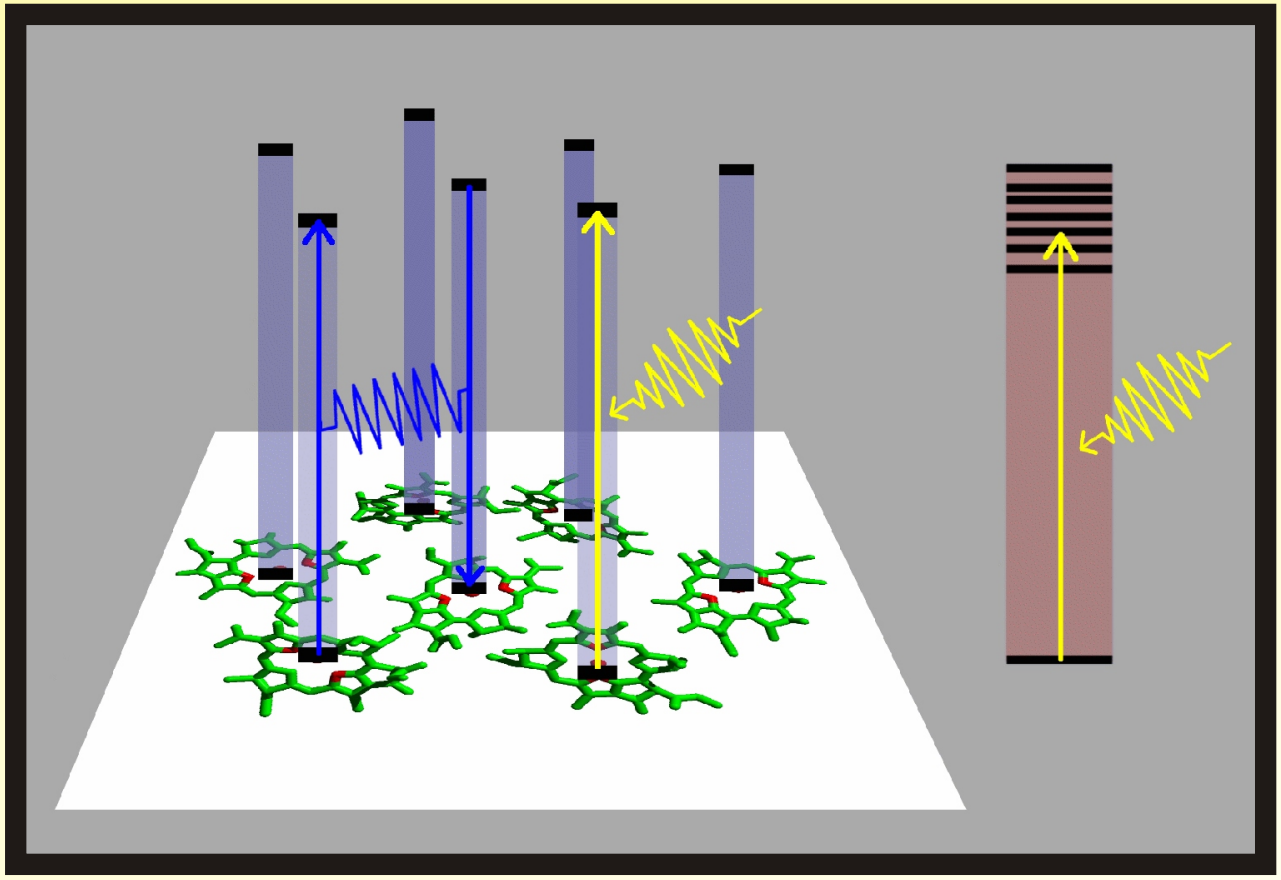
Electronic Level Scheme

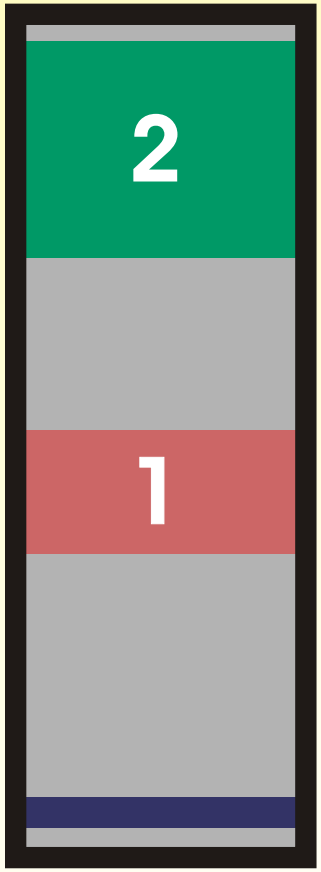


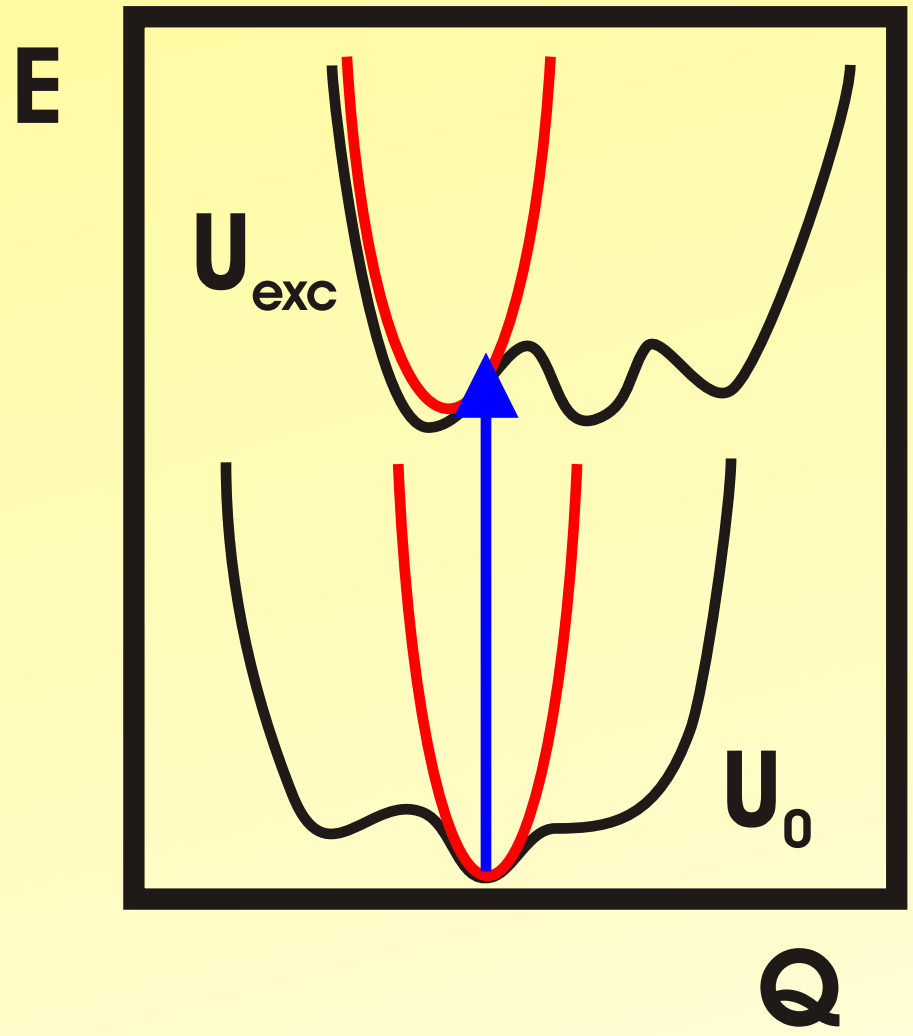
Introduction of Delocalized Exciton States

$$|\alpha\rangle = \sum_m C_\alpha^{(1)}(m)|\phi_{m\,e}\rangle$$

$$|\tilde{\alpha}\rangle = \sum_m C_{\tilde{\alpha}}^{(2)}(m)|\phi_{m\,f}\rangle + \sum_{m,n} C_{\tilde{\alpha}}^{(2)}(m\,n)|\phi_{m\,e,n\,e}\rangle$$







Harmonic approximation for the vibrational motion

$$H_{\mathrm{ex-vib}} \approx \sum_{\alpha,\beta} \sum_{\xi} \hbar\omega_{\xi} g_{\alpha,\beta}(\xi) Q_{\xi} |\alpha\rangle\langle\beta|$$

Multiexciton Density Matrix Theory

second-order perturbation theory with respect to the exciton-vibrational coupling

J >

Projection superoperator

$$\mathcal{P}\ldots = \hat{r}_0^{(\mathrm{eq})}\mathrm{tr}_{\mathrm{vib}}\{\ldots\}$$

$$\hat{\rho}(t) = \mathrm{tr}_{\mathrm{vib}}\{\hat{W}(t)\}$$

Multiexciton density operator

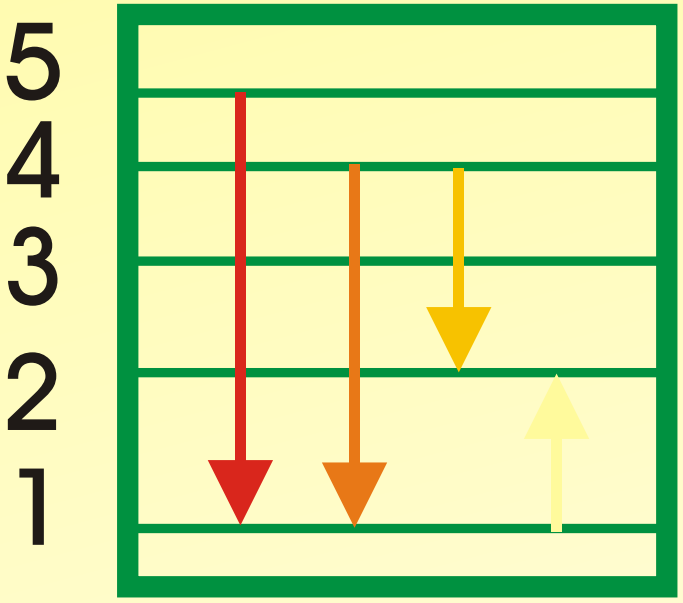
Single-exciton density matrix equations

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

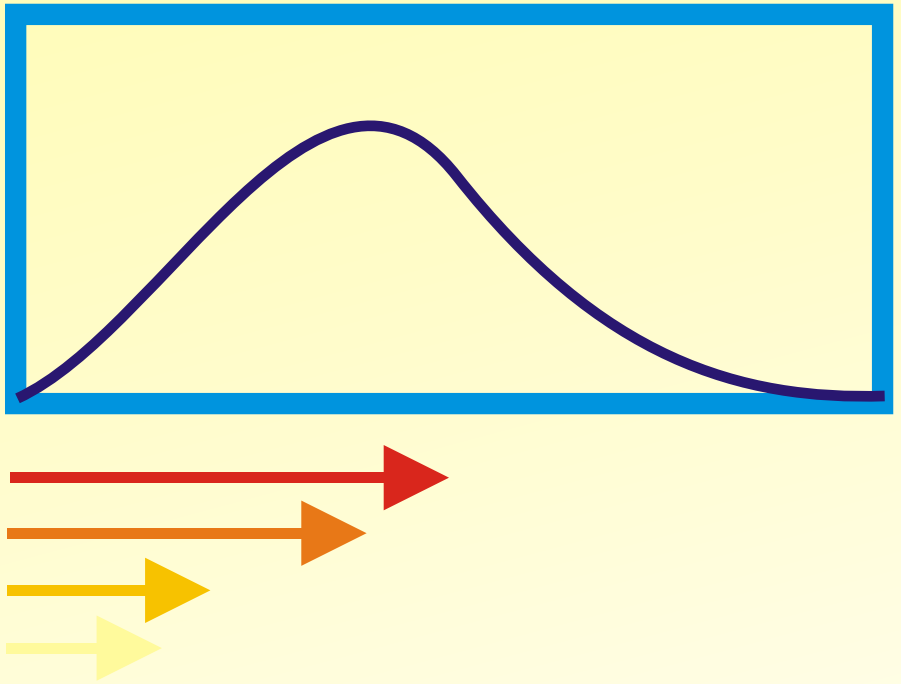
$$-(1-\delta_{\alpha\beta})(\Gamma_\alpha + \Gamma_\beta)\rho_{\alpha\beta} + \frac{i}{\hbar}E(t)(d_\alpha\rho_{0\beta} - d^*_\beta\rho_{\alpha 0})$$

Exciton Relaxation and the Spectral Density

energy

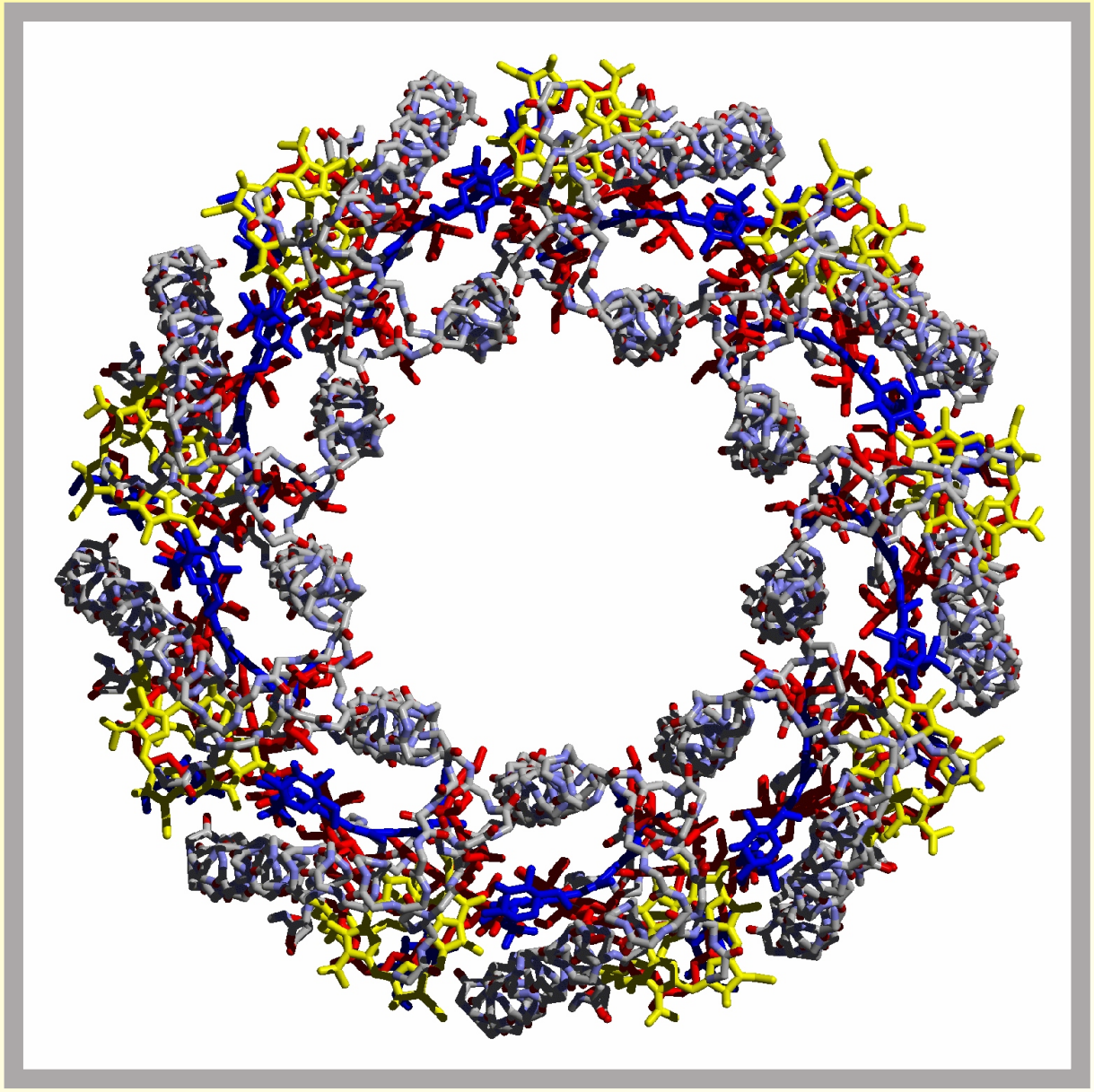


spectral density

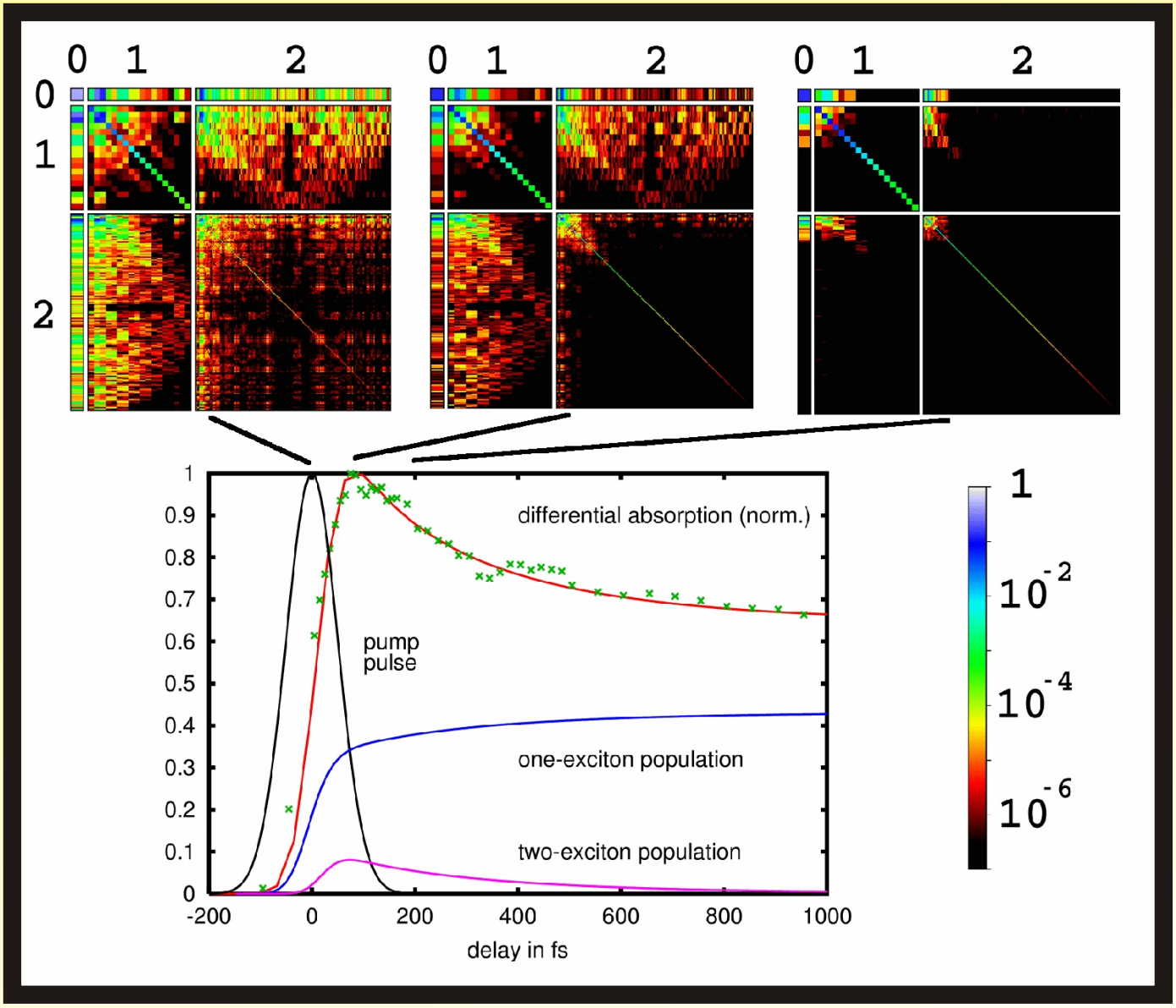


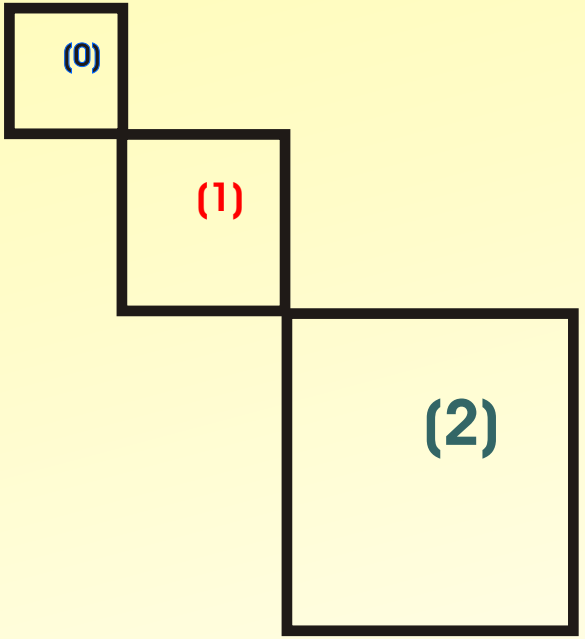
$$k_{\alpha\to\beta} = 2\pi\Omega_{\alpha\beta}^2(1+n(\Omega_{\alpha\beta}))\sum_m |C_\alpha(m)C_\beta(m)|^2[J_m(\Omega_{\alpha\beta}) - J_m(-\Omega_{\alpha\beta})]$$

Lh2 of Purple Bacteria



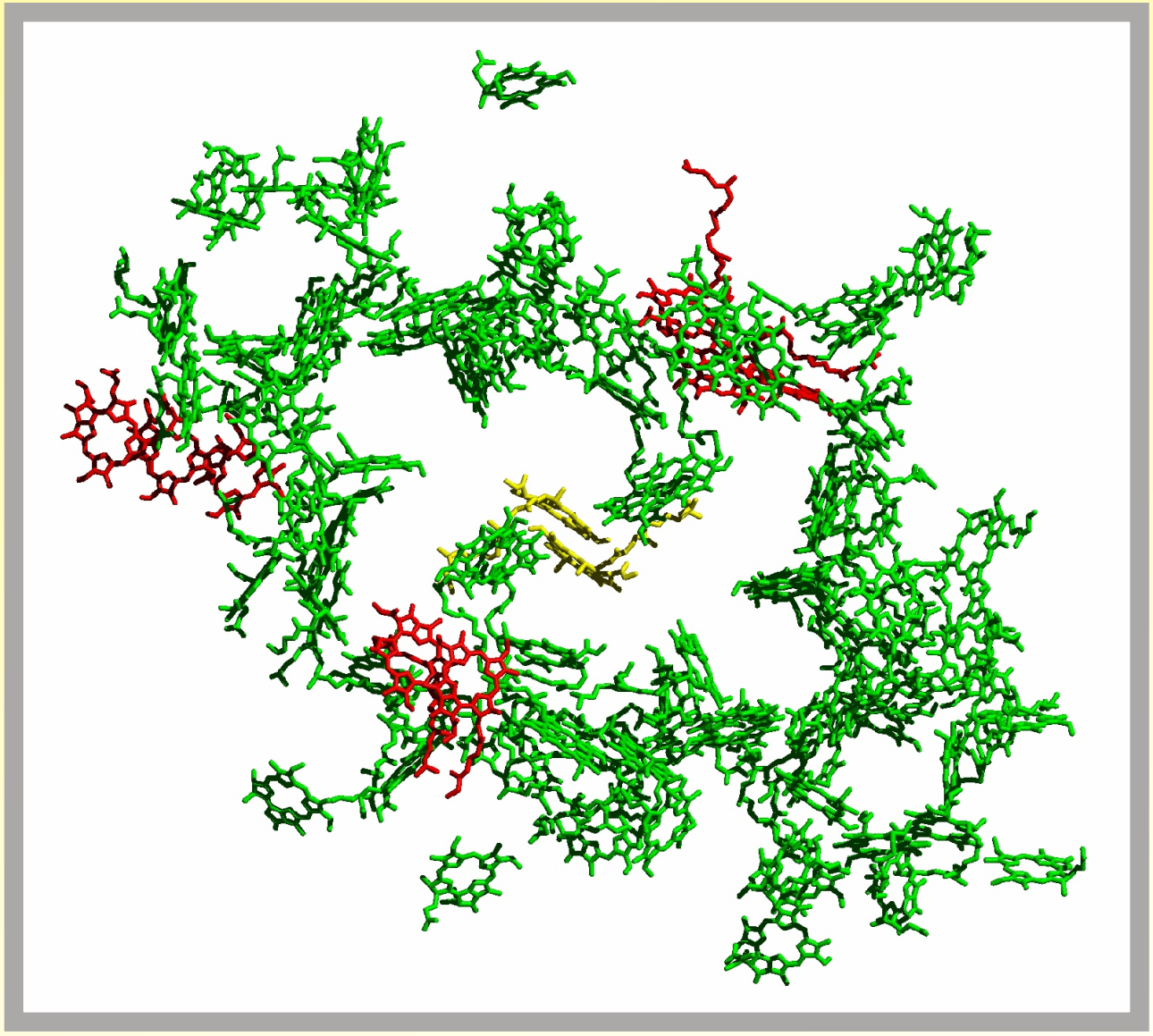
Multiexciton Dynamics and Transient Absorption of the Lh2





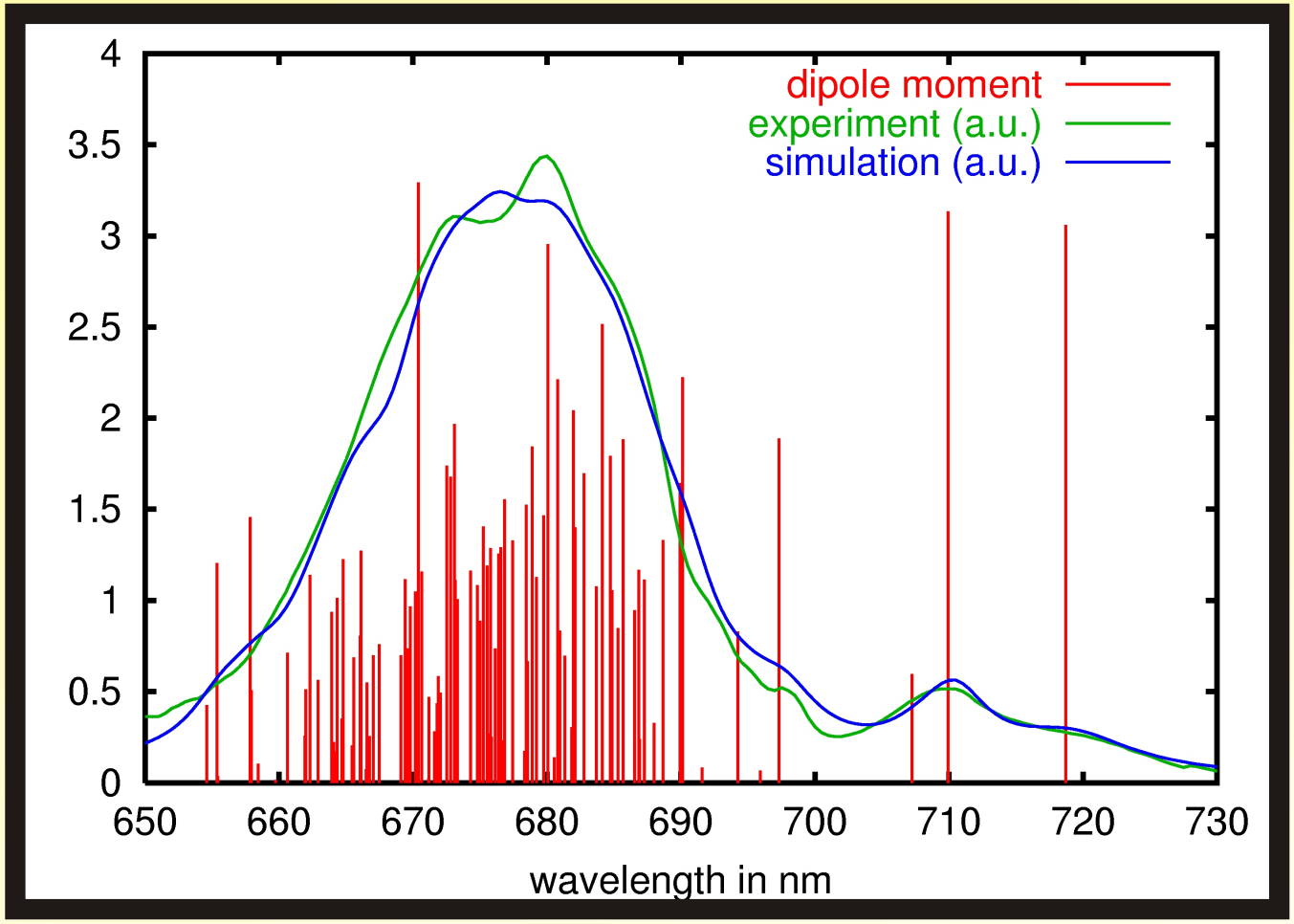
B. Brüggemann and V. M., JCP 120, 2325 (2004)

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



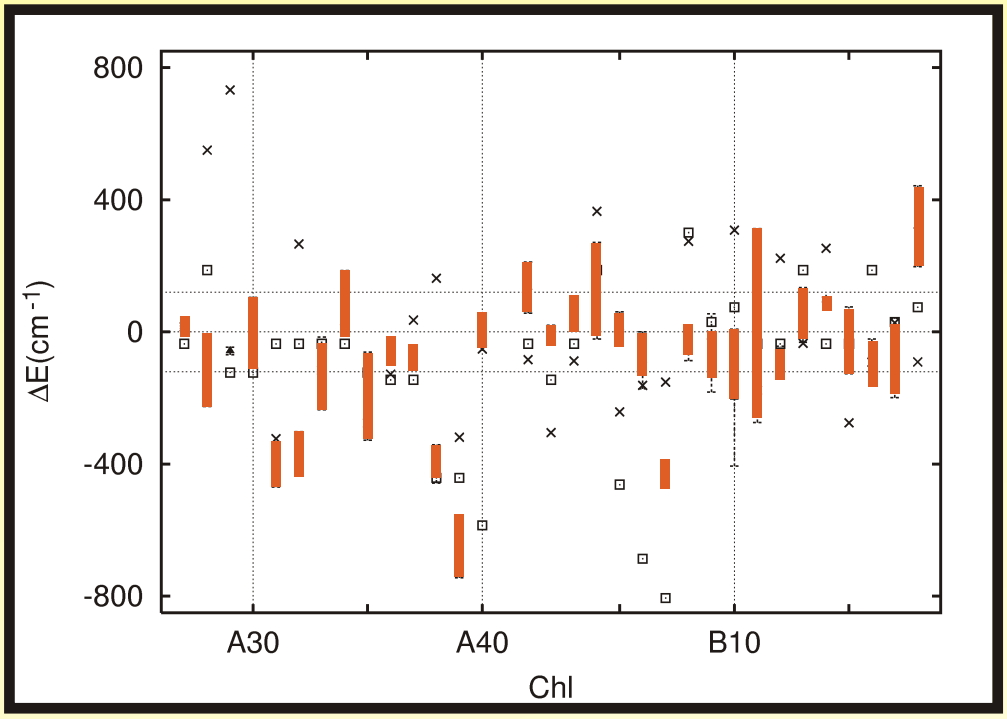
Linear Absorption of the Ps1 Complex

$$A(\omega) \sim \sum_{\alpha} |d_{\alpha}|^2 \frac{\Gamma_{\alpha}}{(\omega - \Omega_{\alpha})^2 + \Gamma_{\alpha}^2}$$

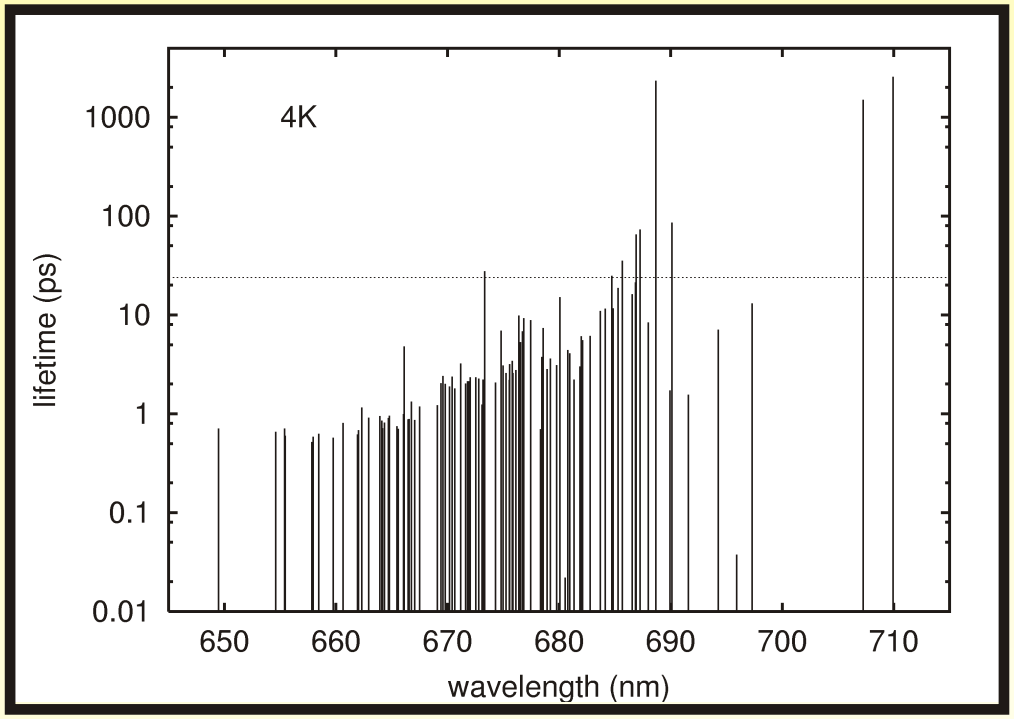


B. Brüggemann, K. Sznee, V. Novoderezhkin, R. van Grondelle, and V. M., JPC B 108, 13563 (2004)

Distribution of site-energies (local Q_y Chl excitations)



Inverse exciton dephasing rates (life times) versus wavelength

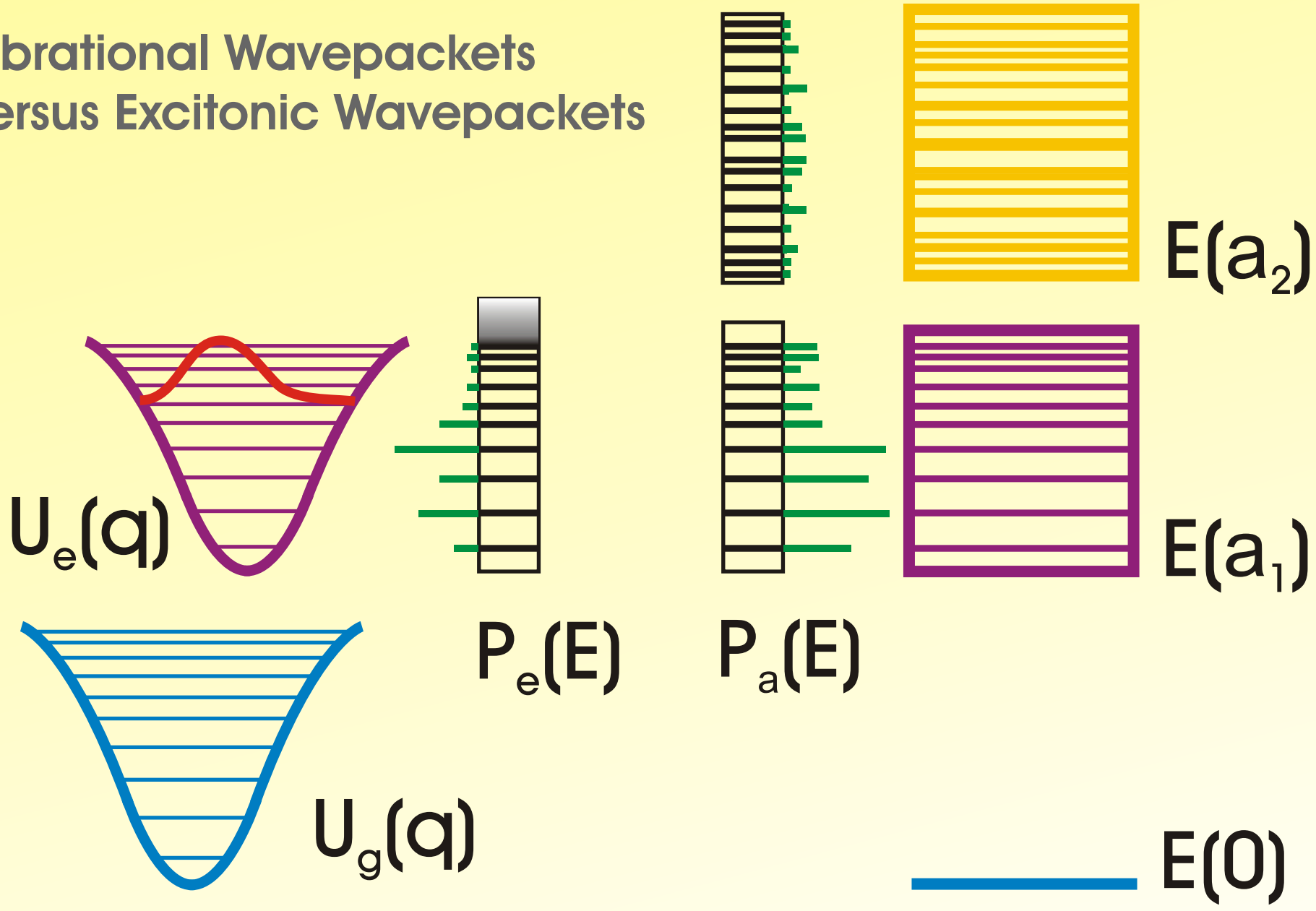


error bars: this work
squares: Byrdin et al. (2002)
crosses: Damjanovich et al. (2002)

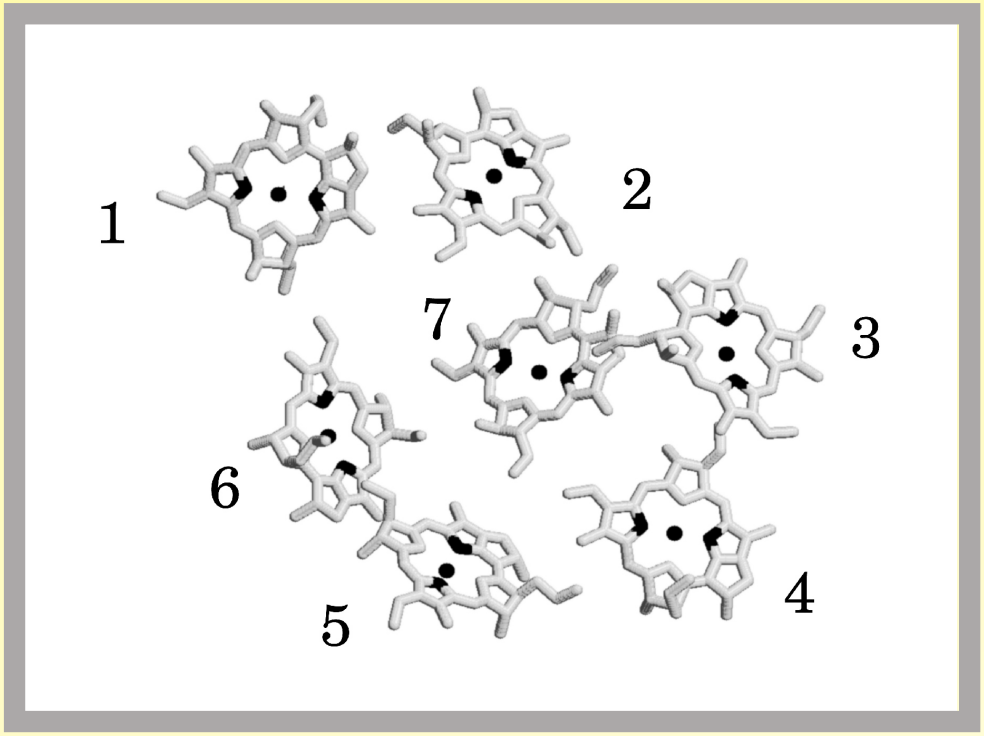
Fs-Laser Pulse Control of Exciton Dynamics

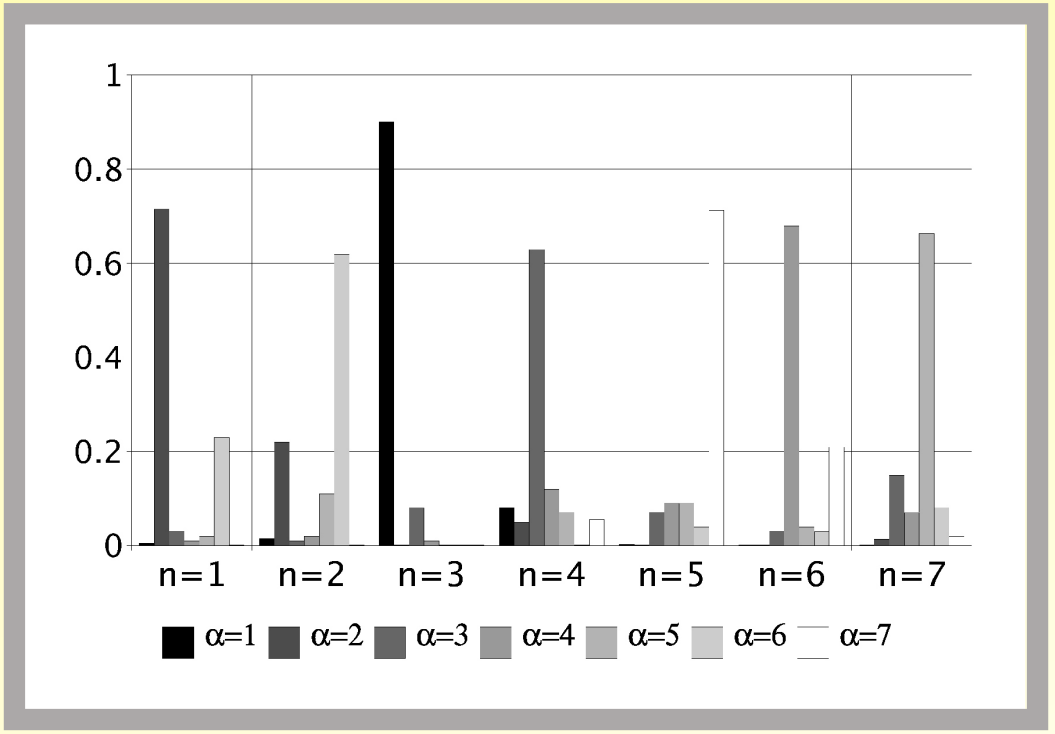
-> spatial localization of excitation energy
-> study of different relaxation pathways

Vibrational Wavepackets versus Excitonic Wavepackets



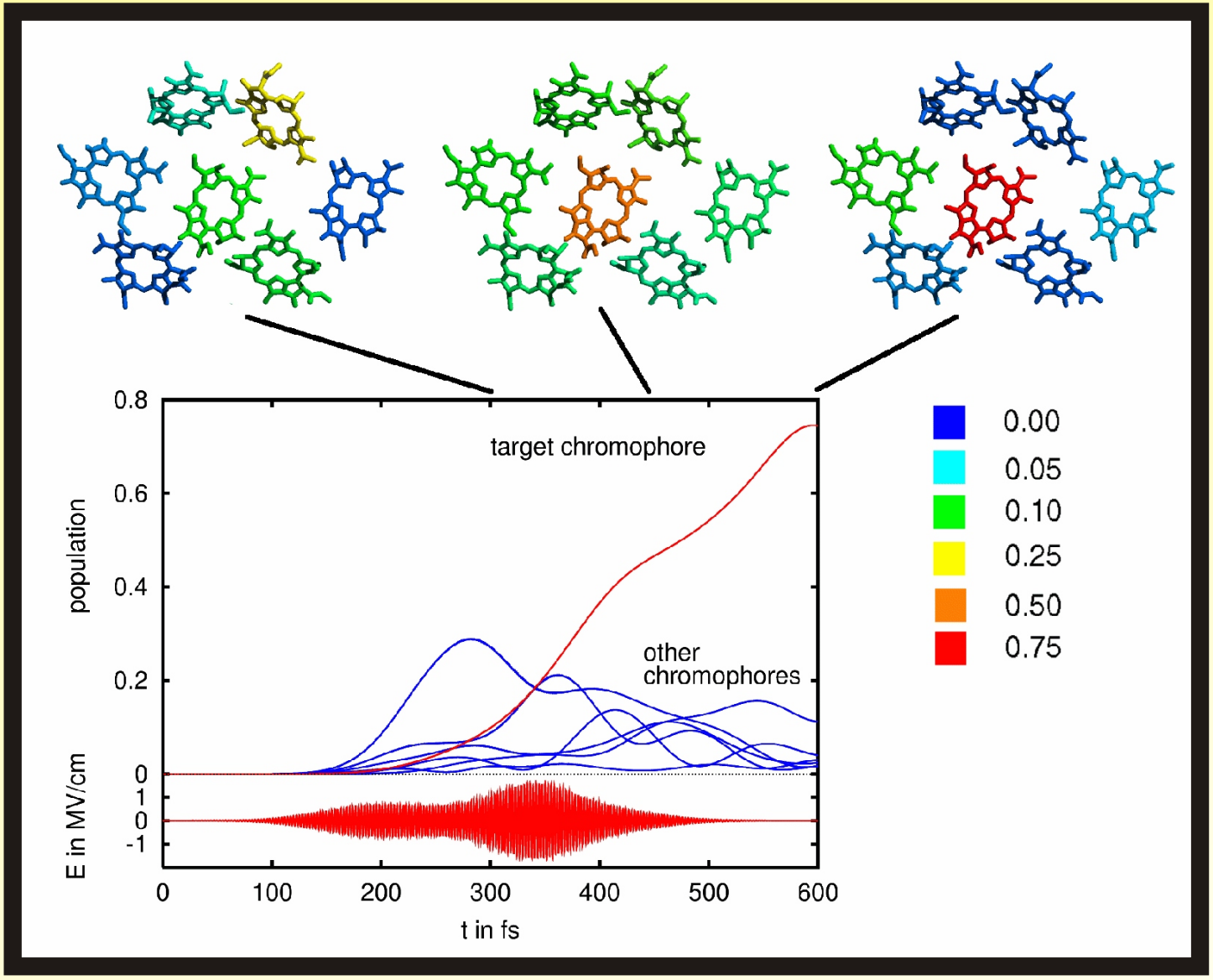
Monomeric Structure of the FMO Complex and Distribution of Exciton Expansion Coefficients





$$|\phi_{me}\rangle = \sum_{\alpha} C_{\alpha}^{(1)*}(m)|\alpha\rangle$$

Laser Pulse Excitation Energy Localization in the FMO-Complex



Optimal Control Theory

$$J(t_f;\mathbf{E}) = \mathrm{tr}_{\mathrm{mx}}\{\hat{\rho}(t_f;\mathbf{E})\hat{\Pi}_{\mathrm{tar}}\} - \frac{\lambda}{2}\int_{t_0}^{t_f} dt\ \mathbf{E}^2(t)$$

B. Brüggemann, and V. M., JPC B 108, 10529 (2004)

Beyond Weak Exciton-Vibrational Coupling

Exciton Polaron States -> Timpmann, Rätsep, Hunter and Freiberg, JPC B 108, 10581 (2004)

Perturbation theory with respect to the electronic inter-chromophore coupling

$$\mathcal{P}\ldots = \sum_m \hat{r}_m^{(\mathrm{eq})} \hat{\Pi}_m \mathrm{tr}\{\hat{\Pi}_m \ldots\} \qquad \hat{\Pi}_m = |\phi_{m\,e}\rangle\langle\phi_{m\,e}|$$

Projection superoperator

Generalized rate equations

$$\frac{\partial}{\partial t} P_m(t) = \sum_n \int d\tau \; K_{mn}(\tau) P_n(t-\tau) \qquad K_{mn}(t) = -\Theta(t)\mathrm{tr}\{\hat{\Pi}_m \, \mathcal{J}\, \tilde{\mathcal{U}}(t)\, \mathcal{J}\, \hat{r}_n^{(\mathrm{eq})} \hat{\Pi}_n\}$$

second-order rates -> Förster theory

$$k_{m\to n} = \frac{|J_{mn}|^2}{\hbar^2} \int dt \; \mathrm{tr}_{\mathrm{vib}}\{\hat{r}_m^{(\mathrm{eq})} e^{iH_m t/\hbar} e^{-iH_n t/\hbar}\}$$

fourth-order rates -> Kakitani, Kimura, Sumi, JPC B 103, 3720 (1999)

Introduction of Excitonic Potential Energy Surfaces

$$U_\alpha(Q) = \hbar\Omega_\alpha - \sum_\xi \hbar\omega_\xi g^2_{\alpha\alpha}(\xi) + \sum_\xi \frac{\hbar\omega_\xi}{4}(Q_\xi + 2g_{\alpha\alpha}(\xi))^2$$

$$\mathcal{H}_1 = \sum_{\alpha,\beta} (\delta_{\alpha,\beta}(T_{\text{vib}} + U_\alpha) + (1-\delta_{\alpha,\beta}) \sum_\xi \hbar\omega_\xi g_{\alpha\beta}(\xi) Q_\xi) |\alpha\rangle\langle\beta|$$

Perturbation theory with respect to the off-diagonal exciton-vibrational coupling

Linear Absorption

$$A(\omega) \sim \sum_{\alpha} |d_\alpha|^2 e^{-G_\alpha(0)} \int dt\; e^{i(\omega-\Omega_\alpha-\lambda_\alpha)+G_\alpha(t)}$$

$$G_\alpha(t) = \sum_{\xi} g^2_{\alpha\alpha}(\xi)([1+n(\omega_\xi)]e^{-i\omega_\xi t} + n(\omega_\xi)e^{i\omega_\xi t})$$

$$\lambda_\alpha = \sum_{\xi} \omega_\xi g^2_{\alpha\alpha}(\xi)$$

description of pump-probe spectra

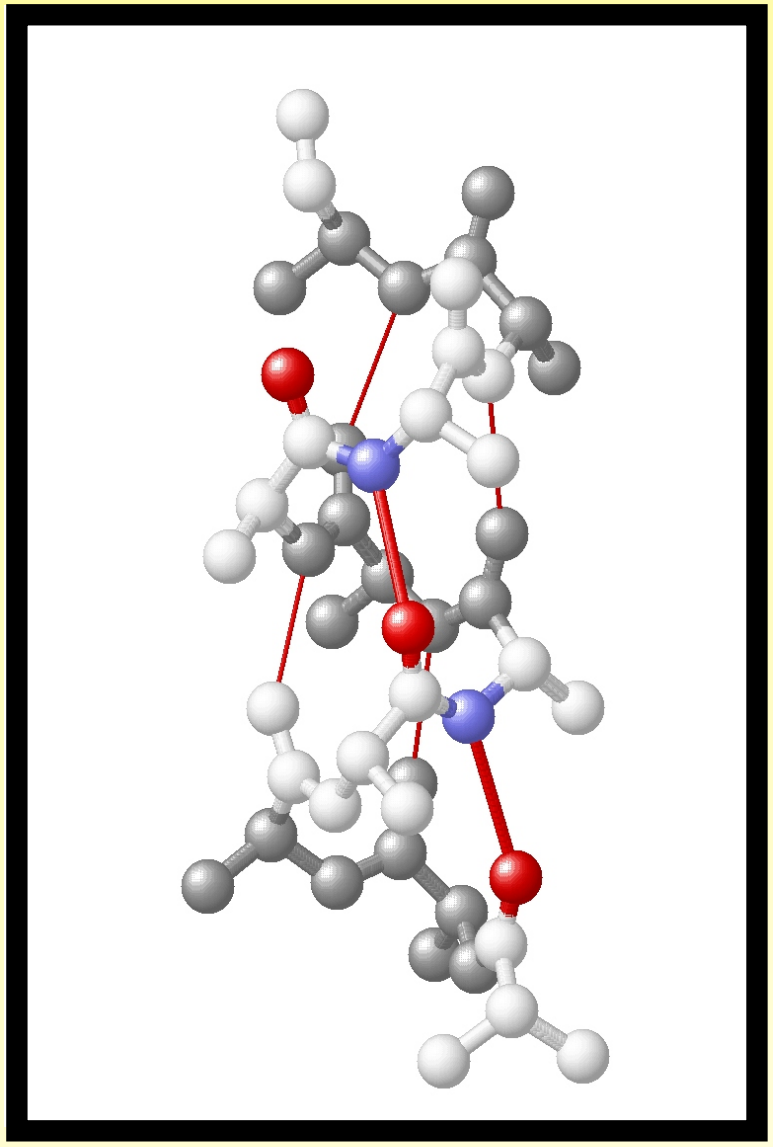
-> Zhang, Meier, Chernyak, Mukamel, JCP 108, 7763 (1998)

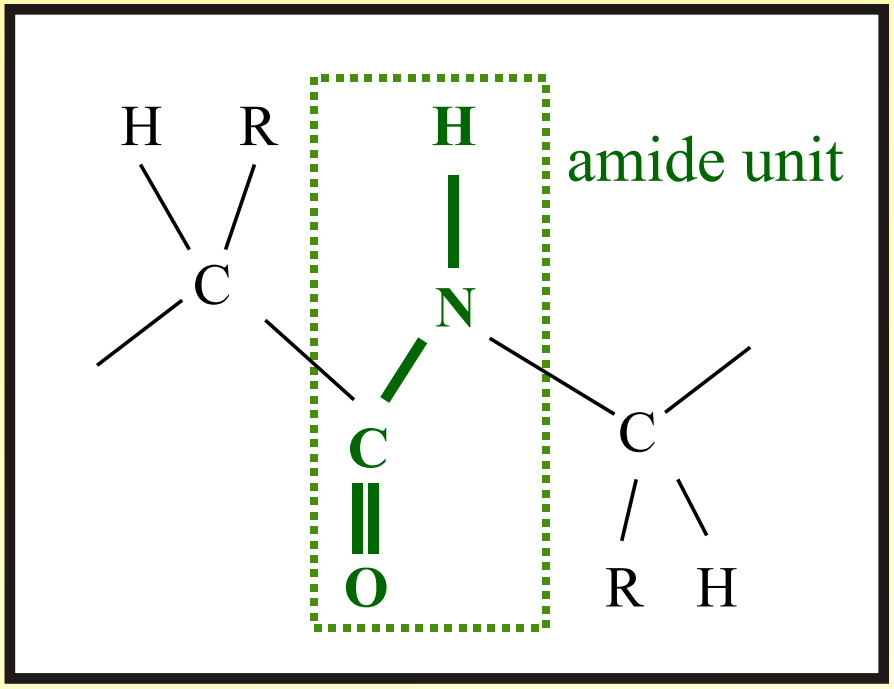
-> Novoderezhkin, Palacios, van Amerongen, van Grondelle JPC B 108, 10363 (2004)

Vibrational Frenkel-Excitons

Self-Trapping of Excitation Energy in -Helices

exact description of the
exciton-vibrational quantum dynamics

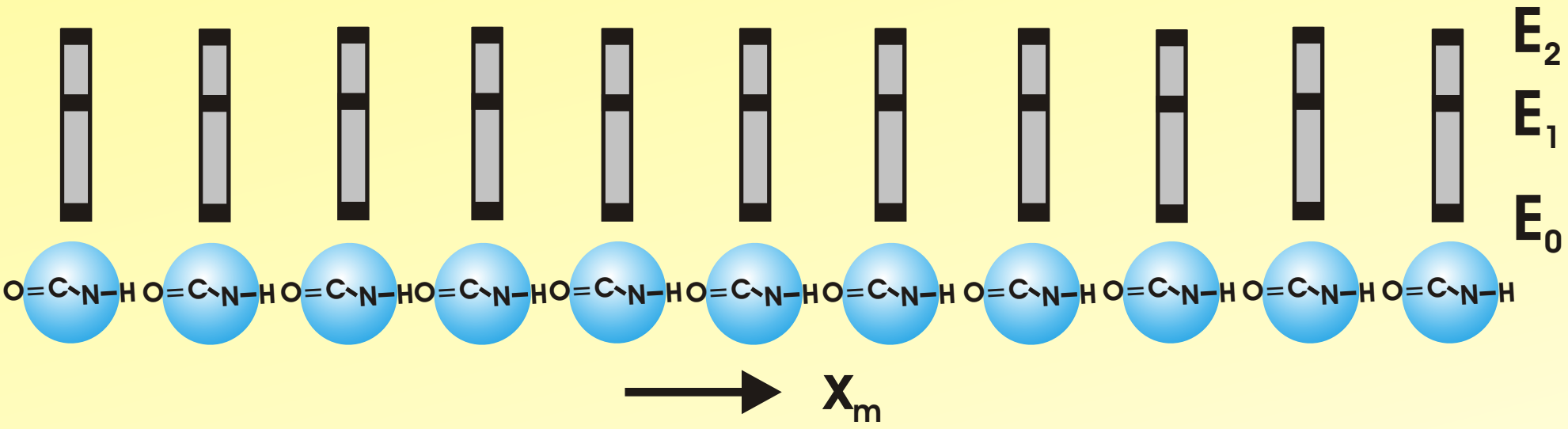




recent experiments on
poly- -benzyl-L-glutamate helices:
Edler, Pfister, Pouthier, Falvo and Hamm,
PRL 93, 106405 (2004)

recent theory on two-vibron
self-trapping:
Pouthier, Phys. Rev. E 68, 021909 (2003)

Three-level model of a hydrogen bonded elastic chain

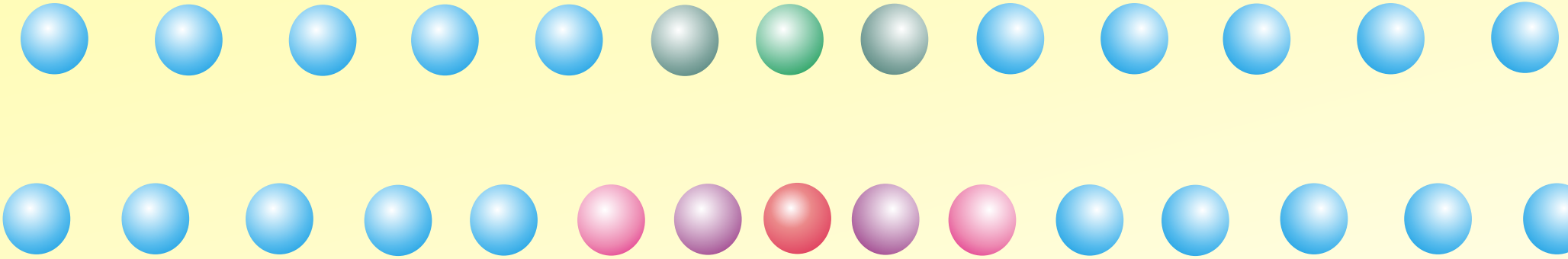


-> local high-frequency peptide group oscillations
-> first and second excited local oscillator states
-> coupling J of different chain units via transition dipoles
-> modulation of local oscillator energies by chain vibrations

$$H_{\mathrm{ex-vib}} = \frac{1}{2}\chi \sum_m q_m^2 (x_{m+1} - x_{m-1})$$

Chain ground-state

Self-trapped single- and double-excited states

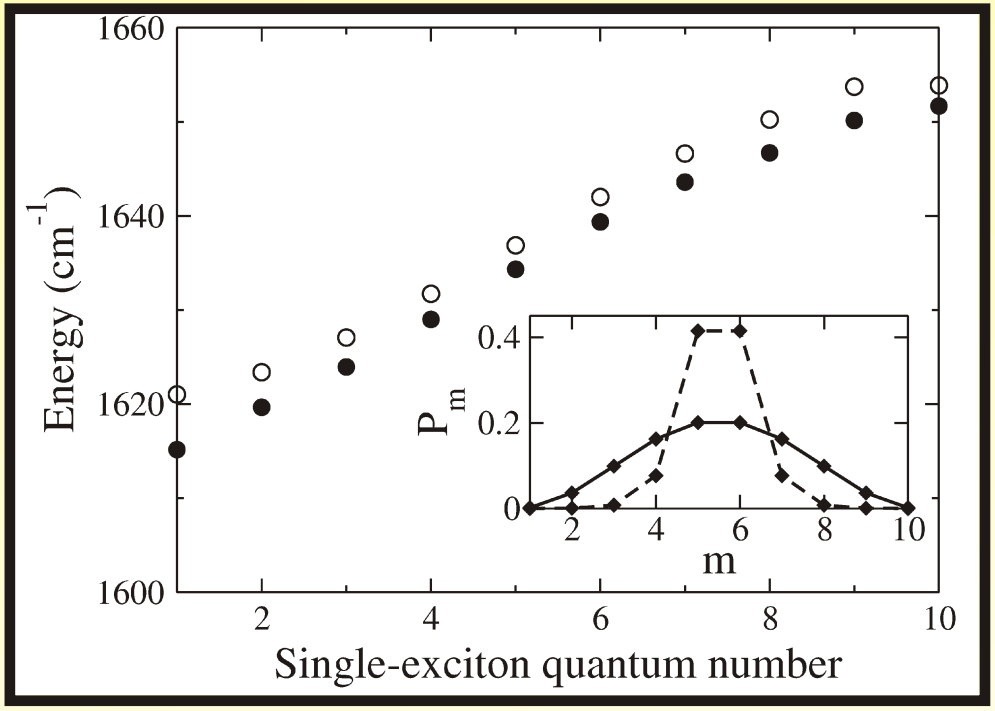


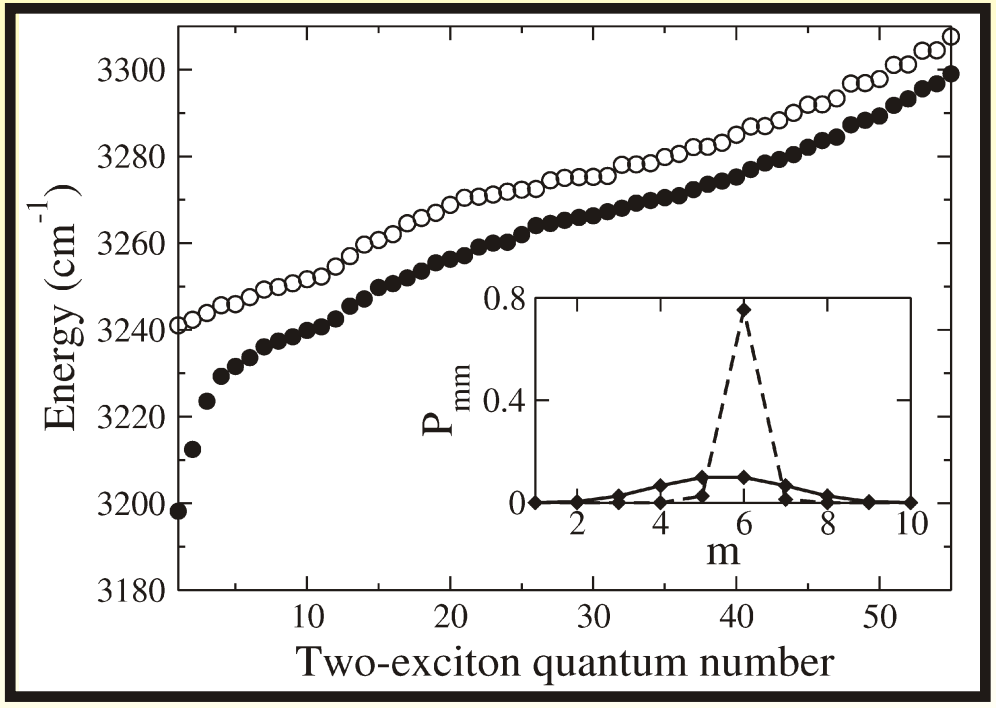
Introduction of quantum mechanical superposition states

Amide1 adiabatic exciton levels

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

chain of 10 peptide groups





D. Tsivlin and V. M., CPL 408, 360 (2005)

Quantum dynamics of the exciton chain-vibrational motion

$$|\Psi(t)\rangle = \psi_0(x,t)|0\rangle + \sum_m \psi_m(x,t)|\phi_m\rangle + \sum_{m,n} \psi_{mn}(x,t)|\phi_{mn}\rangle$$

multi-excitation expansion of the wavefunction

$$i\hbar\frac{\partial}{\partial t}\psi_0(x,t) = \langle 0|H|0\rangle\psi_0(x,t)$$

$$i\hbar\frac{\partial}{\partial t}\psi_m(x,t) = \sum_n \langle\phi_m|H|\phi_n\rangle\psi_n(x,t)$$

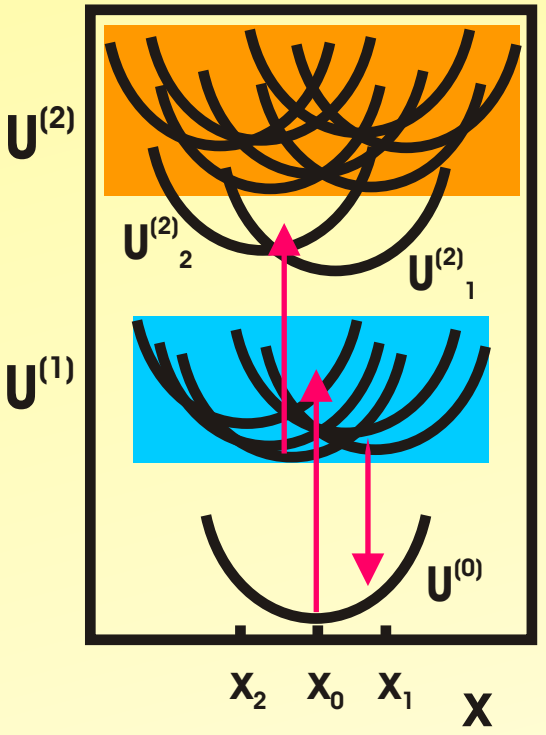
$$i\hbar\frac{\partial}{\partial t}\psi_{mn}(x,t) = \sum_{k,l}\langle\phi_{mn}|H|\phi_{kl}\rangle\psi_{kl}(x,t)$$

set of coupled "diabatic" chain-vibrational wavefunctions

$$\psi_m(x,t) = \sum_{\zeta_1,\ldots,\zeta_f} A^{(m)}(\zeta_1,\ldots,\zeta_f;t)\prod_{j=1}^{f}\psi^{(m)}_{\zeta_j}(x_j,t)$$

wavefunction propagation using the MCTDH-method

Transient absorption signal of a sequential pump-probe experiment

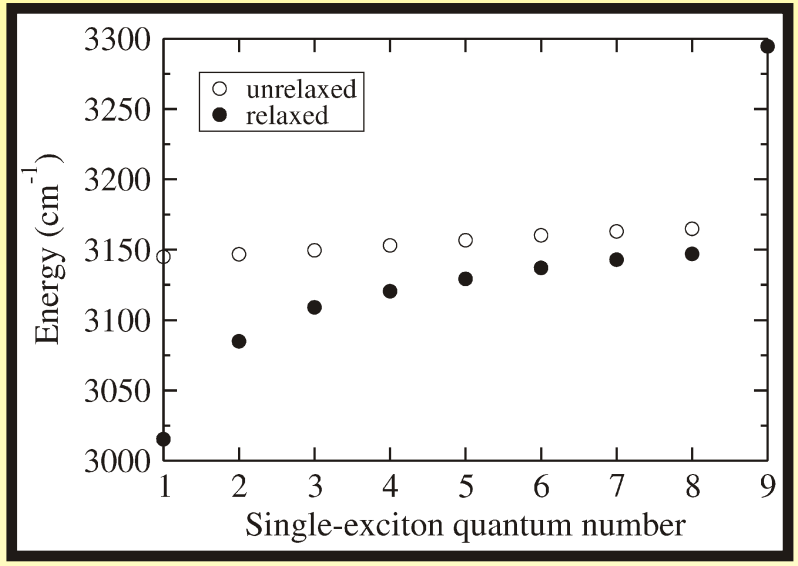


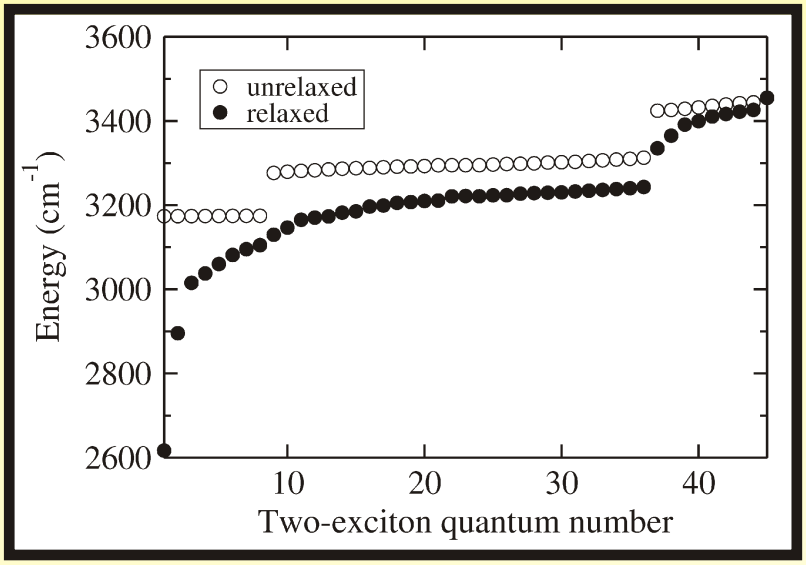
$$\Delta A_{\mathrm{pr}}(\omega) \sim \mathrm{Im}(-R_{\mathrm{pr}}^{(\mathrm{GB})}(\omega) - R_{\mathrm{pr}}^{(\mathrm{SE})}(\omega) + R_{\mathrm{pr}}^{(\mathrm{EA})}(\omega))$$

$$R_{\mathrm{pr}}^{(\mathrm{GB})}(t) \sim \int dx \sum_m d_m^* \psi_0^{(\mathrm{rel})*}(x)\psi_m(x,t) \qquad R_{\mathrm{pr}}^{(\mathrm{SE})}(t) \sim \int dx \sum_m d_m \psi_m^{(\mathrm{rel})*}(x)\psi_0(x,t)$$

$$R_{\mathrm{pr}}^{(\mathrm{EA})}(t) \sim \int dx \sum_m \tilde{d}_m^* \psi_m^{(\mathrm{rel})*}(x)\tilde{\psi}_m(x,t) + \int dx \sum_{m,n} (d_m^* \psi_n^{(\mathrm{rel})*}(x) + d_n^* \psi_m^{(\mathrm{rel})*}(x))\tilde{\psi}_{mn}(x,t)$$

Adiabatic single- and two-exciton levels related to the NH-vibrations in a chain of 9 units and respective spectra of linear and excited-state absorption

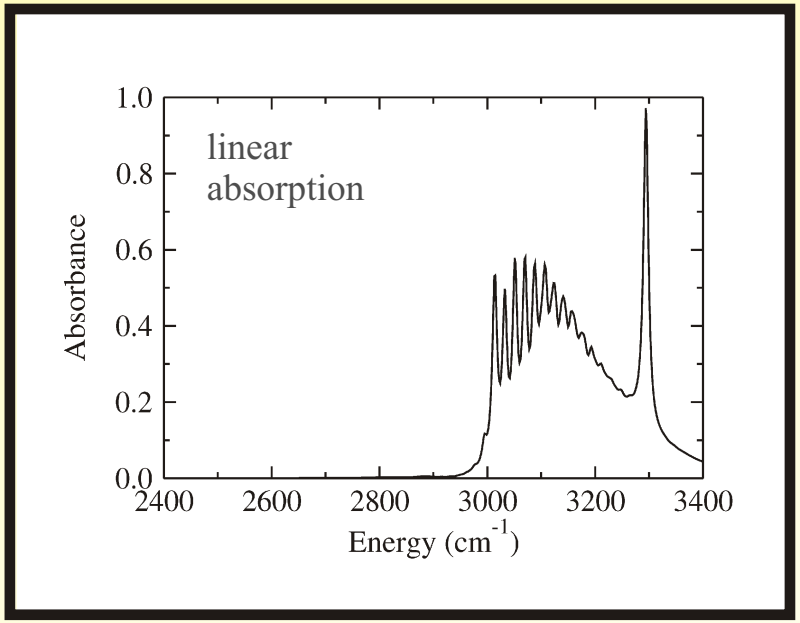


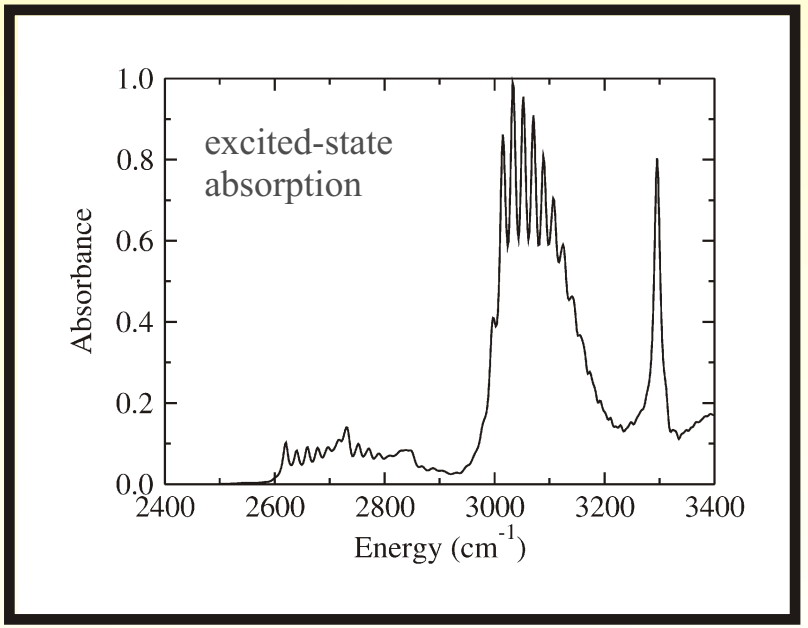


= 300 pN

J = 5 cm^{-1}

= 1 ps





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