Universität Rostock Traditio et Innovatio

INSTITUT FÜR PHYSIK

Lecture Four: Frenkel Excitons in Natural and Artifical Light-Harvesting

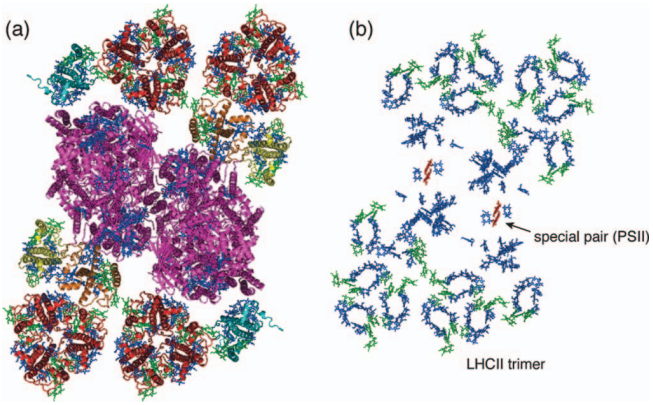
Oliver Kühn

Solar Energy Conversion

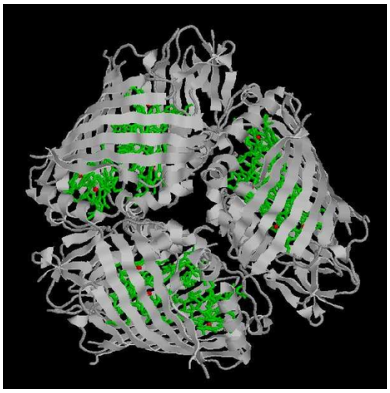
- photon collection and directed energy transfer

Learning From Nature….

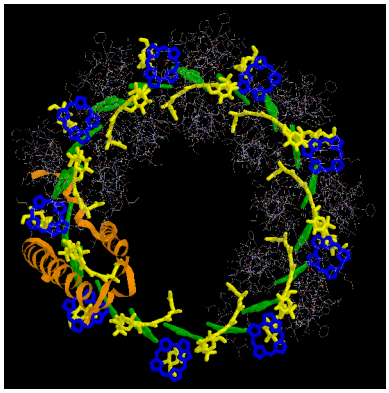
- photosynthetic complexes
- adapted to environment
- high efficiency (95%)



PSII of higher plants, van Amerongen, 2011

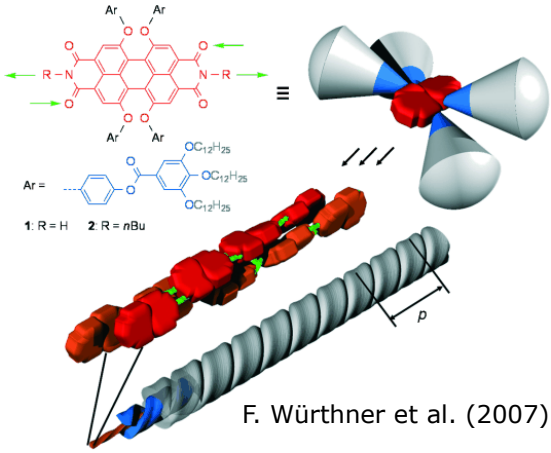


FMO trimer, wikipedia



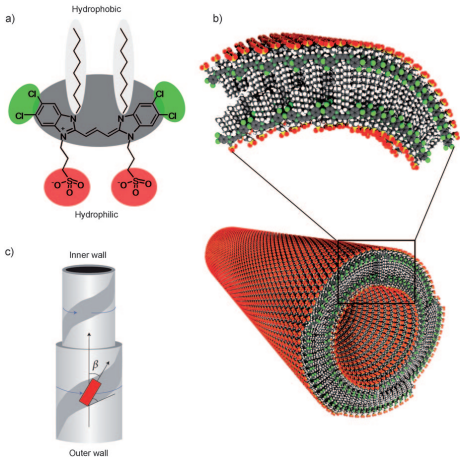
LH2 (Rps. acidophila), T. Pullerits

Molecular Aggregates

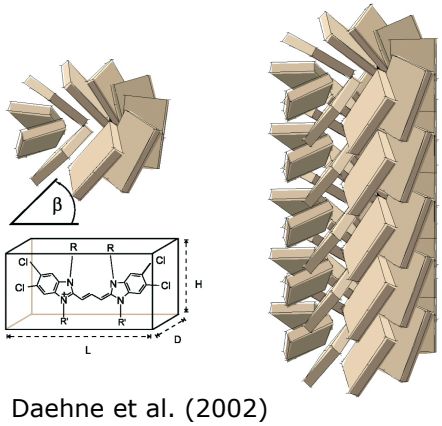


F. Würthner et al. (2007)

- non-covalently bonded dye molecules
- widely tuneable optical properties

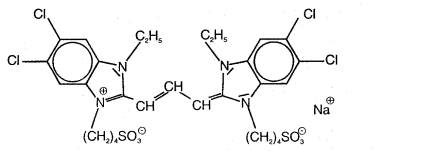


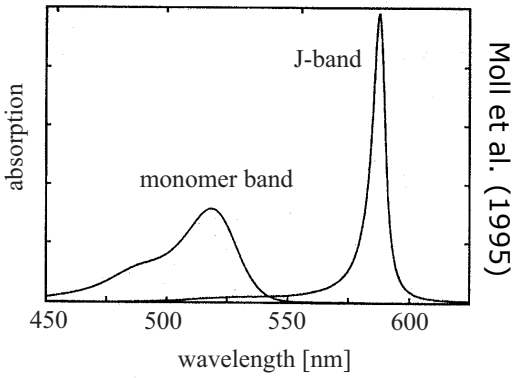
Eisele, D. M., et al. (2009)

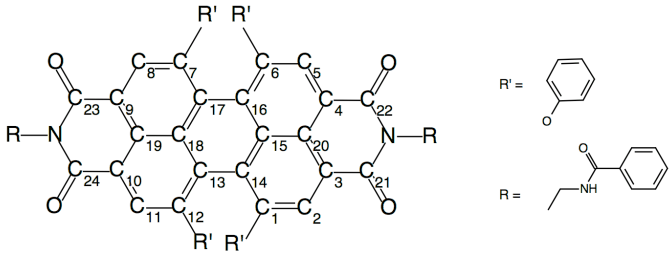


S. Daehne et al. (2002)

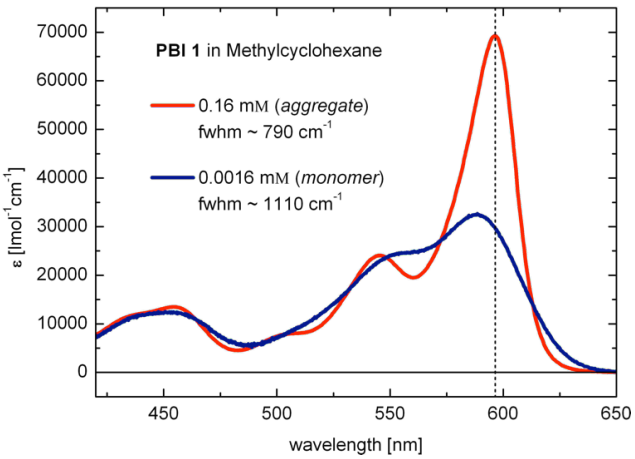
- spectroscopic signatures (Scheibe & Jelley, 1930s)







exp: S. Lochbrunner group



aggregation

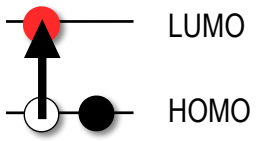
- peak shift
- narrowing of band

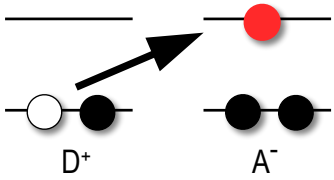
Overview

- Frenkel exciton model
- exciton-vibrational coupling
- from electronic structure to absorption
- coherence in photosynthesis
- beyond a reduced system-bath description

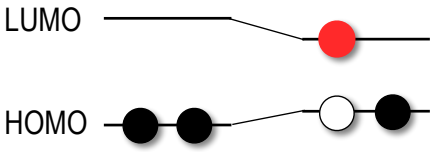
Frenkel Exciton Model

- electron-hole pair
  - Frenkel exciton
  - charge transfer (CT) exciton
  - Wannier-Mott exciton





- monomer: electronic excitation
- aggregate: exciton=delocalized superposition state
- exciton binding energy



Aggregate Hamiltonian

- separation of aggregate into m=1…N_{mol} monomeric building blocks

$$H_{\mathrm{agg}} = \sum_m H_m + \frac{1}{2}\sum_{m,n} V_{mn}$$

monomer Hamiltonian — Coulomb interaction

  - **adiabatic** wave functions & PES

$$H_m^{(\mathrm{el})}(R_m)\varphi_{ma}(r_m;R_m) = V_{ma}(R_m)\varphi_{ma}(r_m;R_m)$$

- aggregate wavefunction (neglecting exchange)

$$\phi_A^{(\mathrm{HP})}(r;R) = \prod_{m=1}^{N_{\mathrm{mol}}} \varphi_{ma_m}(r_m;R_m)$$

- adiabatic state representation of aggregate Hamiltonian

$$H_{\rm agg} = \sum_m \sum_{a,b} H_m(ab)|\varphi_{ma}\rangle\langle\varphi_{mb}| + \frac{1}{2}\sum_{m,n}\sum_{a,b,c,d} J_{mn}(ab,cd)|\varphi_{ma}\varphi_{nb}\rangle\langle\varphi_{nc}\varphi_{md}|$$

  - monomer contribution

$$H_m(ab) = \delta_{a,b}(T_m + V_{ma}) + (1-\delta_{a,b})\Theta_{m,ab}$$

  - Coulomb coupling

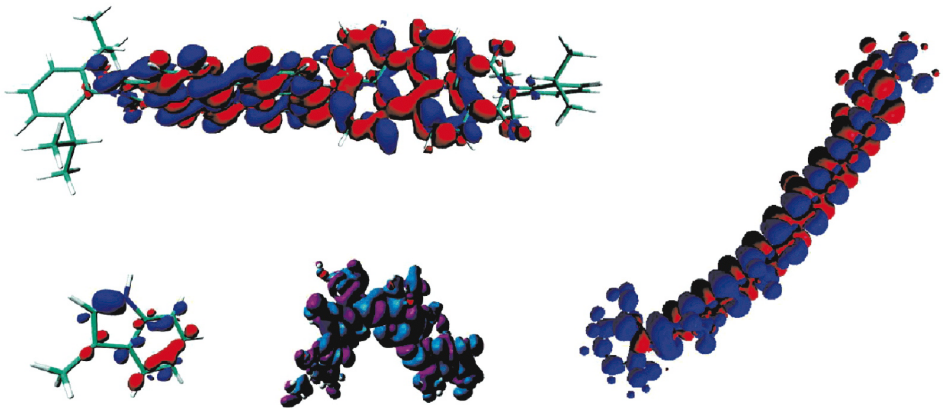
$$\begin{aligned} J_{mn}(ab,cd) \equiv & \int dr_m dr_n\ \varphi^*_{ma}(r_m)\varphi^*_{nb}(r_n)V^{(\rm el-el)}_{mn}(r_m,r_n)\varphi_{nc}(r_n)\varphi_{md}(r_m) \\ + & \ \delta_{b,c}\int dr_m \varphi^*_{ma}(r_m)V^{(\rm el-nuc)}_{mn}(r_m,R_n)\varphi_{md}(r_m) \\ + & \ \delta_{a,d}\int dr_n \varphi^*_{nb}(r_n)V^{(\rm nuc-el)}_{mn}(R_m,r_n)\varphi_{nc}(r_n) + \ \delta_{a,d}\delta_{b,c}V^{(\rm nuc-nuc)}_{mn} \end{aligned}$$

  - transition density

$$n^{(m)}_{ab}(\mathbf{x}) = \varrho^{(m)}_{ab}(\mathbf{x}) - \delta_{a,b}\sum_{\mu\in m} eZ_\mu\delta(\mathbf{x}-\mathbf{R}_\mu)$$

  - Coulomb matrix elements

$$J_{mn}(ab,cd) = \int d\mathbf{x}d\mathbf{x}'\frac{n^{(m)}_{ad}(\mathbf{x})n^{(n)}_{bc}(\mathbf{x}')}{|\mathbf{x}-\mathbf{x}'|}$$



Beljonne et al., J. Phys. Chem. B 113, 6583 2009)

Dipole Approximation

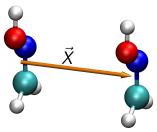
- assume that size of transition densities small w.r.t. intermonomer distance
- dipole moment

$$\mathbf{d}_{mab} = \int d^3\mathbf{x}\, \mathbf{x} n_{ab}^{(m)}(\mathbf{x}) = \int d^3\mathbf{x}\, \mathbf{x} \varrho_{ab}^{(m)}(\mathbf{x}) - \delta_{a,b} \sum_{\mu \in m} eZ_\mu \mathbf{R}_\mu$$

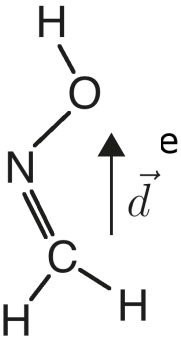
- Coulomb matrix elements

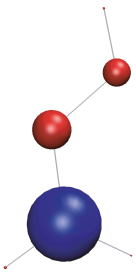
$$J_{mn}(ab,cd) \approx \frac{\mathbf{d}_{mad}\mathbf{d}_{nbc}}{|\mathbf{X}_{mn}|^3} - 3\frac{(\mathbf{X}_{mn}\mathbf{d}_{mad})(\mathbf{X}_{mn}\mathbf{d}_{nbc})}{|\mathbf{X}_{mn}|^5}$$

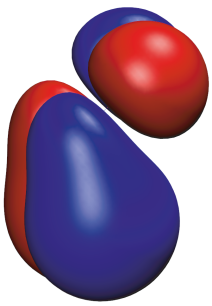
Testing the Dipole Approximation

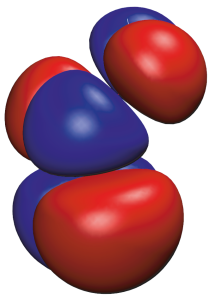


- For the Oxime dimer





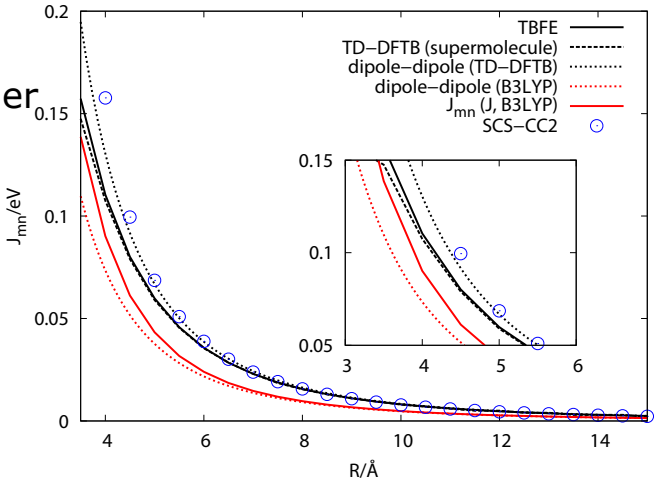




transition charges

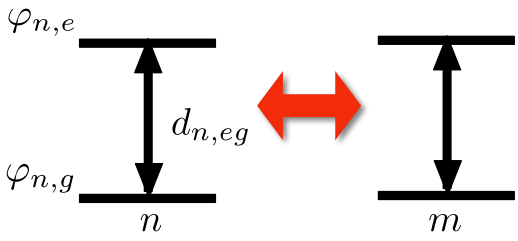
HOMO-1

LUMO



- specification of Coulomb matrix elements for two level model

	Matrix element	Interaction process
(I)	$J_{mn}(gg, gg)$ $J_{mn}(ee, ee)$ $J_{mn}(ge, eg)$ $J_{mn}(eg, ge)$	between charges at molecules m and n
(II)	$J_{mn}(eg, gg)$ $J_{mn}(gg, ge)$ $J_{mn}(ge, ee)$ $J_{mn}(ee, eg)$	between transitions at molecule m with charges at n
(III)	$J_{mn}(eg, eg)$ $J_{mn}(ge, ge)$	between $S_0 \rightarrow S_1$ transition at molecule m and $S_1 \rightarrow S_0$ transition at n (and reverse)
(IV)	$J_{mn}(ee, gg)$ $J_{mn}(gg, ee)$	simultaneous excitation and deexcitation of molecules m and n



- Coulomb coupling for TLS with resonant terms only

$$J_{mn}(eg, eg) \equiv J_{mn} = \int d^3\mathbf{x} d^3\mathbf{x}' \, \frac{\varrho_{eg}^{(m)}(\mathbf{x}) \varrho_{ge}^{(n)}(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|}$$

  - dipole approximation

$$J_{mn} \approx \kappa_{mn} \frac{|\mathbf{d}_m||\mathbf{d}_n^*|}{|\mathbf{X}_{mn}|^3}$$

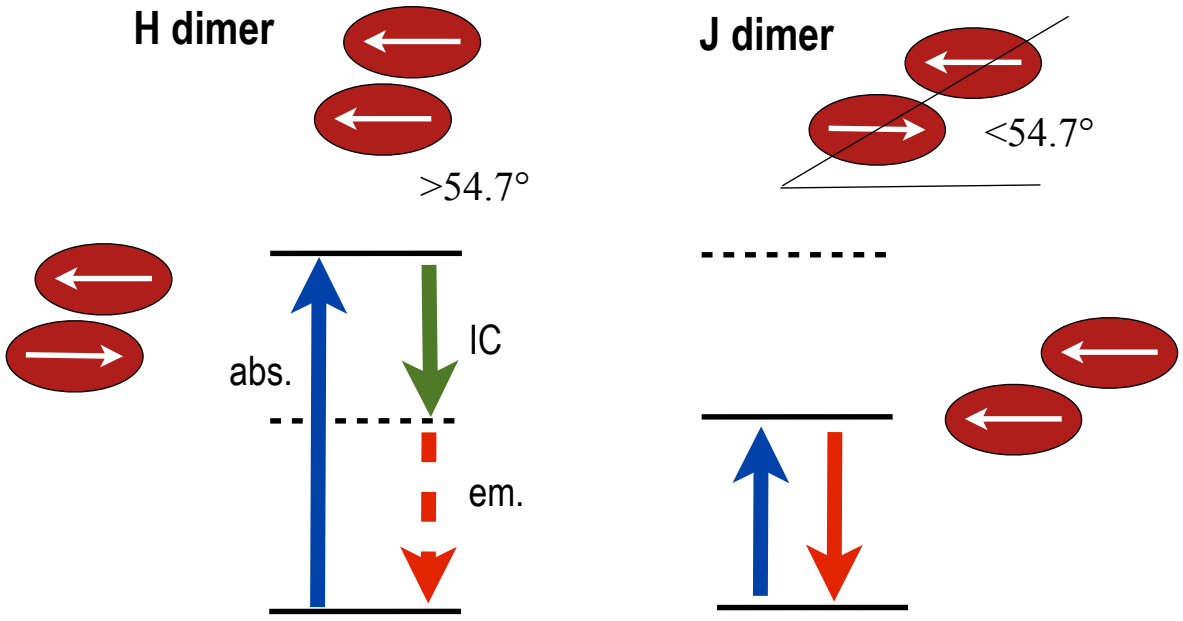
  - orientation factor

$$\kappa_{mn} = \mathbf{n}_m \, \mathbf{n}_n - 3(\mathbf{e}_{mn} \, \mathbf{n}_m)(\mathbf{e}_{mn} \, \mathbf{n}_n)$$

  - absorption of electronic homodimer

$$E_{\alpha_1 = \pm} = \frac{\hbar\omega_{eg}}{2} \pm J \qquad |\alpha_1 = \pm\rangle = \frac{1}{\sqrt{2}}(|1\rangle \pm e^{-i\arg(J)}|2\rangle)$$

J- vs. H-Aggregates



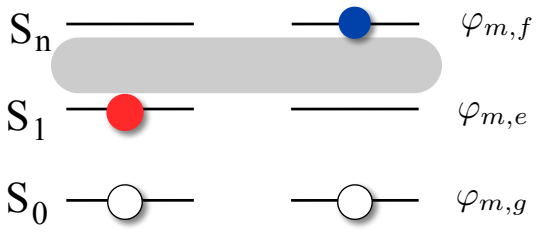
- for applications that require strong fluorescence J-aggregates preferable

Three-State Approximation

- organic dyes will have more than one excited state
- important whenever more than two photons are absorbed
- for **two-photon processes** one should take into account states where

$$E_e - E_g \approx E_f - E_e$$

- minimal effective model should include three levels



N-Excitation States

- classification of aggregate's electronic state acoording to number of excitations

$$\sum_A |\phi_A^{(\mathrm{HP})}\rangle\langle\phi_A^{(\mathrm{HP})}| = |0\rangle\langle 0| + \sum_m |m\rangle\langle m| + \sum_{m,n\geq m} |mn\rangle\langle mn| + \ldots$$

  - zero excitation

$$|0\rangle = \prod_m |\varphi_{mg}\rangle$$

  - single excitation

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

  - double (**local and nonlocal**) excitation

$$|mn\rangle = (1-\delta_{mn})|\varphi_{me}\rangle|\varphi_{ne}\rangle \prod_{k\neq m,n} |\varphi_{kg}\rangle + \delta_{mn}|\varphi_{mf}\rangle \prod_{k\neq m} |\varphi_{kg}\rangle$$

Multi (Two)-Exciton Hamiltonian

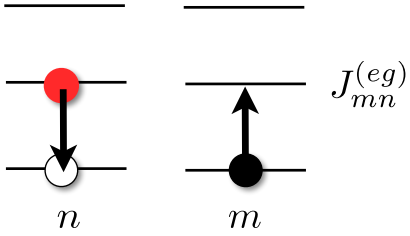
- restrict Hamiltonian to two excitation space

$$H = H^{(0)} + H^{(1)} + H^{(2)} + H^{(1-2)}$$

$$H^{(0)} = \sum_m H_{m,g}|0\rangle\langle 0| \qquad H_{m,a} = T_m + V_{ma}$$

$$H^{(1)} = \sum_{m,n} [\delta_{mn}(H_{m,g} + U_{m,eg}) + J_{mn}^{(eg)}]|m\rangle\langle n|$$

one-exciton motion $|m\rangle \leftrightarrow |n\rangle$



gap coordinate

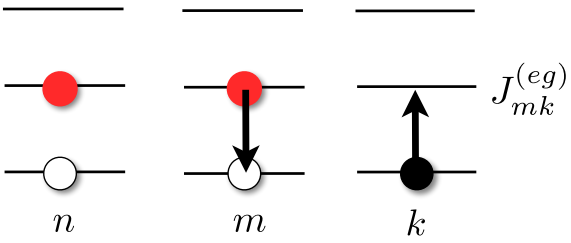
$$U_{m,ab} = V_{m,a} - V_{m,b}$$

$$J_{mn}(eg,eg) = J_{mn}^{(eg)}$$

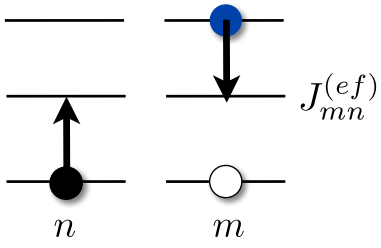
$$
\begin{aligned}
H^{(2)} &= \sum_{l\geq k}\sum_{n\geq m}\{\delta_{mk}\delta_{nl}[(1-\delta_{mn})(H_{m,g}+U_{m,eg}+U_{n,eg})+\delta_{mn}(H_{m,g}+U_{m,fg})] \\
&+ (1-\delta_{mn})(1-\delta_{kl})[J^{(eg)}_{km}\delta_{nl}+J^{(eg)}_{ln}\delta_{mk}+J^{(eg)}_{kn}\delta_{lm}+J^{(eg)}_{lm}\delta_{kn}] \\
&+ (1-\delta_{mn})\delta_{kl}[J^{(fe)}_{km}\delta_{kn}+J^{(fe)}_{kn}\delta_{mk}] \\
&+ \delta_{mn}(1-\delta_{kl})[J^{(fe)}_{km}\delta_{lm}+J^{(fe)}_{lm}\delta_{km}]\}|kl\rangle\langle mn|
\end{aligned}
$$

$$J_{mn}(fg,ee) = J^{(fe)}_{mn}$$

two-exciton motion $|nm\rangle \leftrightarrow |nk\rangle$



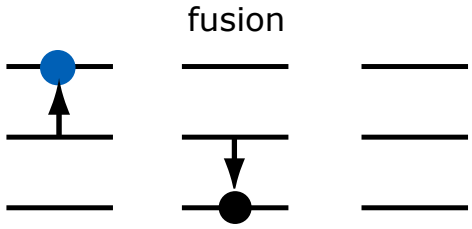
„fusion/fission" $|0m\rangle \leftrightarrow |nm\rangle$



Exciton-Exciton Annihilation

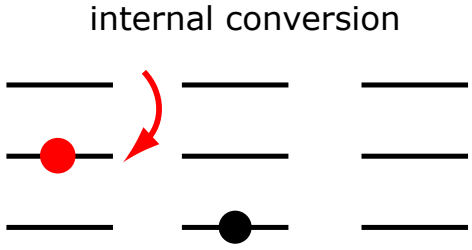
- „interband" (nonadiabatic) transitions

$$H_m(ab) = \delta_{a,b}(T_m + V_{ma}) + (1-\delta_{a,b})\Theta_{m,ab}$$



  - exciton representation

$$H^{(1-2)} = \sum_m \Theta_{m,fe}|mm\rangle\langle m| + \text{h.c.}$$



  - **local** process

$$\Theta_{m,fe} \propto [\int dr_{\text{el}}\, \varphi_{mf}(r_{\text{el}};R_{\text{nuc}})\nabla_{\text{nuc}}\varphi_{me}(r_{\text{el}};R_{\text{nuc}})]\ \nabla_{\text{nuc}}$$

Multi-Exciton Eigenstates

- diagonalization of *N*-exciton Hamiltonian

$$H^{(N)}|\alpha_N\rangle = E_{\alpha_N}|\alpha_N\rangle$$

  - state expansions

$$|\alpha_1\rangle = \sum_n C_n(\alpha_1)|n\rangle$$

$$|\alpha_2\rangle = \sum_{m>n} C_{mn}(\alpha_2)|mn\rangle + \sum_m C_{mm}(\alpha_2)|mm\rangle$$

  - exciton bands

Exciton-Vibrational Coupling

- one-exciton Hamiltonian

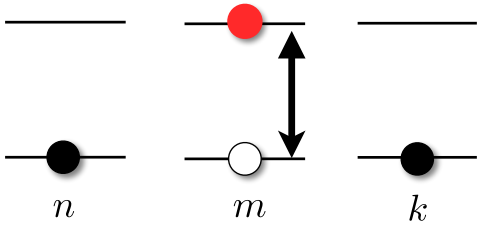
$$H^{(1)} = \sum_{m,n}[\delta_{mn}(H_{m,g} + U_{m,eg}) + J^{(eg)}_{mn}]|m\rangle\langle n|$$

  - ground state vibrations

$$H_{m,g} \equiv H_{m,g}(R_m) = T_m + V_{mg}(R_m)$$

  - gap coordinate for excitation

$$U_{m,eg}(R_m) = V_{m,e}(R_m) - V_{m,g}(R_m)$$



Strategies

- stochastic models (e.g. Haken-Strobel-Reineker)
- harmonic bath models (spectral density):
  - single bath (e.g. intramolecular)
  - multi-mode Brownian oscillator
  - can be used to fit experimental sepectral densities
- atomistic models: molecular dynamics simulations plus electronic structure theory

Huang-Rhys Model

- shifted oscillator model for nuclear DOF

$$U_m(Q_{m,\xi}) = E_m + \sum_\xi \frac{\hbar\omega_\xi}{2}(Q_{m,\xi} - Q^{(0)}_{m,\xi})^2$$

- coupling given by Huang-Rhys factor

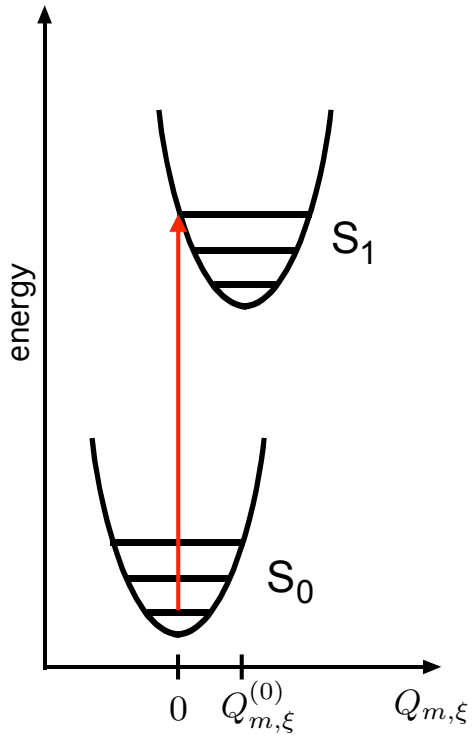
$$S_{m,\xi} = \frac{1}{2} Q^{(0)\,2}_{m,\xi}$$

- correlation function

$$C_m(\omega) = 2\pi\omega^2(1 + n(\omega))[\mathcal{J}_m(\omega) - \mathcal{J}_m(-\omega)]$$

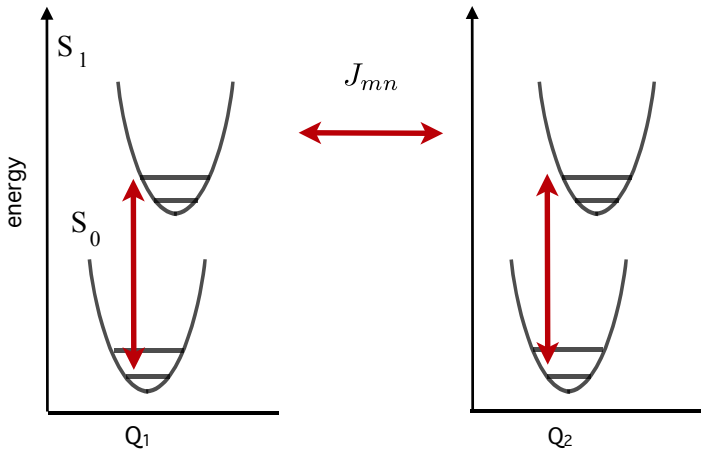
- spectral density

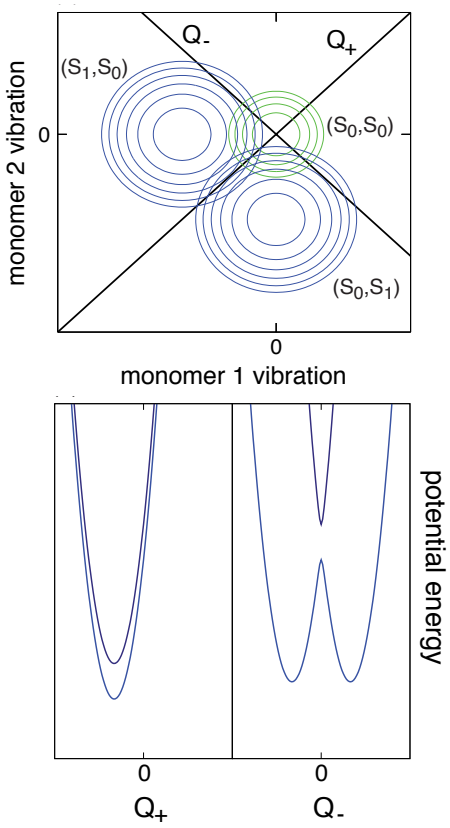
$$\mathcal{J}_m(\omega) = \sum_\xi S_{m,\xi}\delta(\omega - \omega_{m,\xi})$$



Huang-Rhys + Coulomb Coupling

- exciton-vibrational states





  - single excitation states

$$|m, M_{e_m}, M_{g_n}\rangle \quad |n, N_{g_m}, N_{e_n}\rangle$$

  - effective Coulomb coupling

$$J_{mn}\langle M_{e_m}|N_{g_m}\rangle\langle M_{g_n}|N_{e_n}\rangle$$

Absorption Spectrum

- recall correlation function approach

$$J(t) = \mathrm{tr}\Big\{\mu U_0(t)\mu\rho_{\mathrm{eq}}U_0^+(t)\Big\}$$

$$\mu = \sum_\alpha \mu_\alpha|\alpha\rangle\langle 0| + \mathrm{h.c} \qquad U_0(t)|\alpha\rangle = e^{-iE_\alpha t/\hbar}|\alpha\rangle \qquad \rho_{\mathrm{eq}} = |0\rangle\langle 0|$$

$$\rightarrow \quad \chi''(\omega) \propto \sum_\alpha |\mu_\alpha|^2\delta(\hbar\omega - E_\alpha)$$

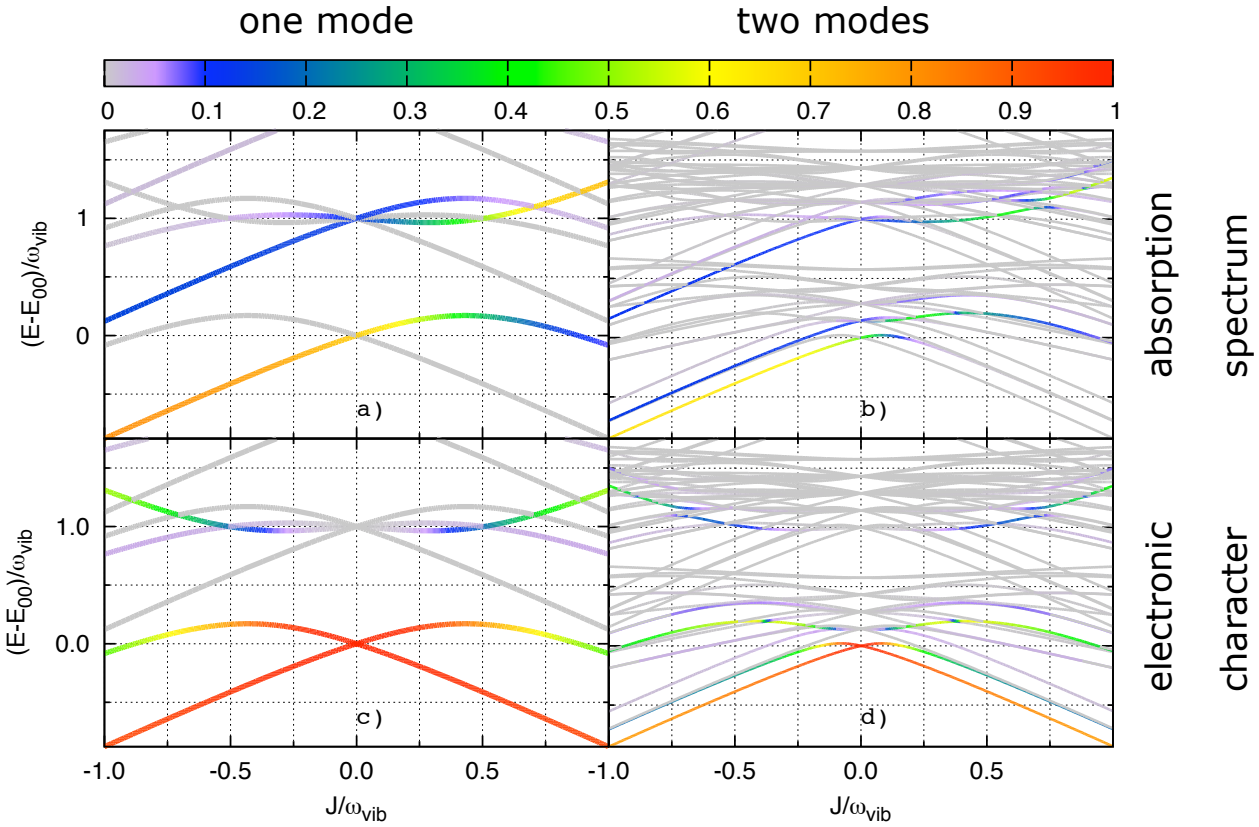
- basis set expansion for exciton-vibrational states

$$|\alpha\rangle = \sum_{M_{e_1},M_{g_2}} C_\alpha(2, M_{e_1}, M_{g_2})|1, M_{e_1}, M_{g_2}\rangle + \sum_{M_{e_1},M_{g_2}} C_\alpha(2, M_{g_1}, M_{e_2})|2, M_{g_1}, M_{e_2}\rangle$$

- electronic character of certain state

$$C_{\mathrm{el}} = \langle\alpha| \sum_{m=1,2} |m, 0, 0\rangle\langle 0, 0, m| \ |\alpha\rangle$$

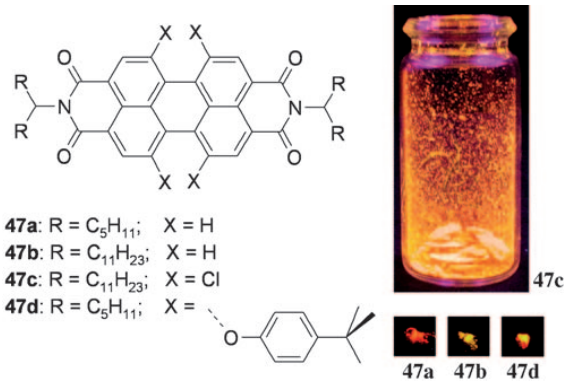
- exciton-vibrational states (by matrix diagonalization)



M. Schröter et al., Phys. Rep. 567, 1 (2015)

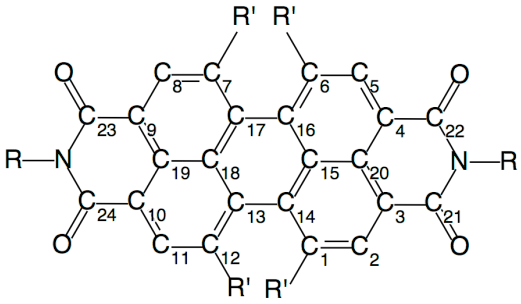
Perylene Bisimides

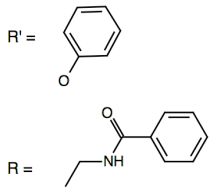
- high performance color pigments
- fluorescence quantum yield up to unity in solution, drops in solid state
- optical properties shaped by bay substituents
- type of arrangement in aggregate depends on imide substituents



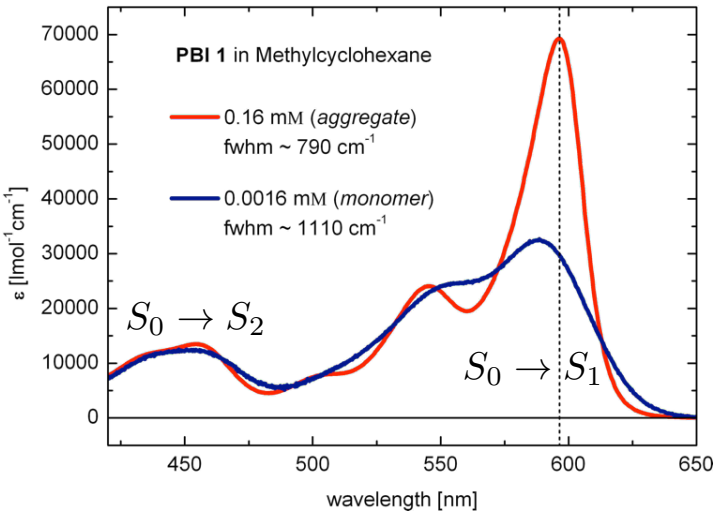
Würthner et al., Angew. Chem. Int. Ed. 50, 3376 (2011)

Perylene Bisimide Aggregates





exp: S. Lochbrunner group



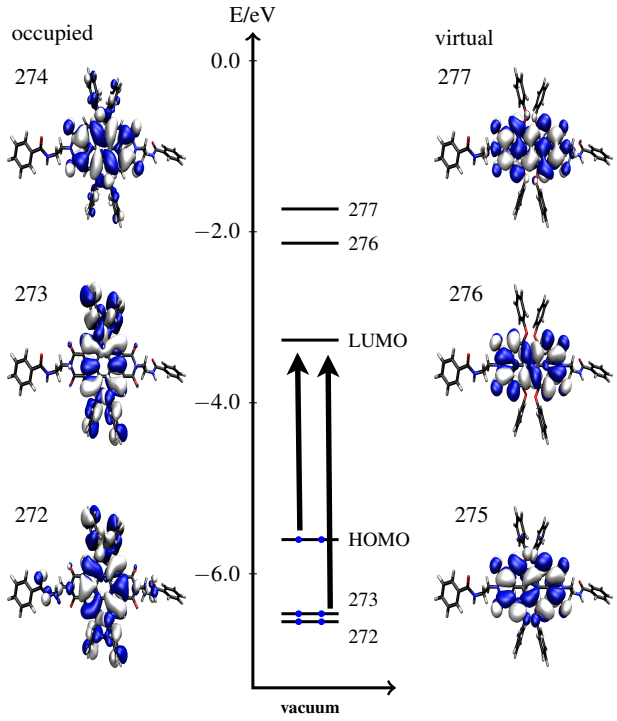
- rare J-aggregate perylene derivative
- 1D diffusion (~100nm)
- delocalization length ~2

H. Marciniak et al., J. Phys. Chem. A 115, 648 (2011)

Vertical S_0-S_n Excitation Spectrum

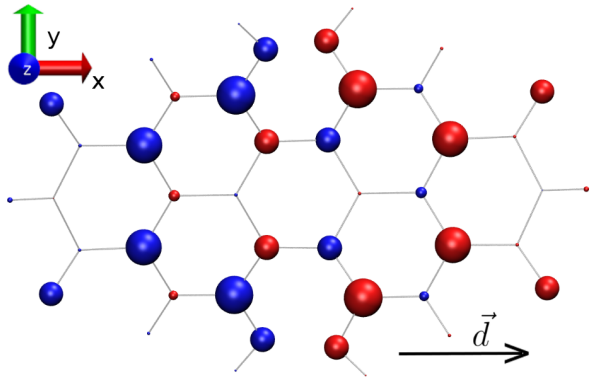
- TDDFT/B3LYP (6-311G*)
  - response function formalism
  - based on ground state KS density

E / eV	f	excitation	one-electron excitation	λ/nm
2.13	0.59	$\pi_{pbi} \rightarrow \pi^*_{pbi}$	$^1S_1$(274-275)	582.2
2.74	0.22	$\pi_{per+bay} \rightarrow \pi^*_{pbi}$	$^1S_2$(273-275)	453.2
4.22	0.28	$\pi_{pbi} \rightarrow \pi^*_{pbi}$	$^1S_{34}$(274-281)	293.8
4.25	0.05	$\pi_{pbi=o} \rightarrow \pi^*_{pbi}$	^{1}CT (250-275)	292.0
4.25	0.16	$\pi_{per+bay} \rightarrow \pi^*_{pbi}$	$^1S_{36}$(272-277)	291.6
4.48	0.07	$\pi_{pbi} \rightarrow \pi^*_{bay}$	^{1}CT (274-283)	278.2
4.67	0.05	$\pi_{bay} \rightarrow \pi^*_{pbi}$	^{1}CT (262-276)	265.7
4.70	0.05	$\pi_{pbi=o} \rightarrow \pi^*_{pbi}$	^{1}CT (256-276)	263.8



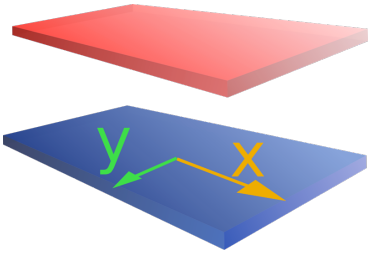
D. Ambrosek et al., PCCP 13, 17649 (2011)

Exploring the Coulomb Coupling

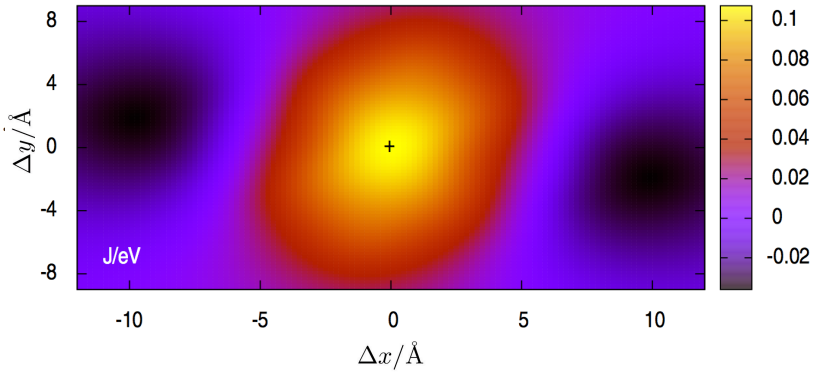


DFTB Mulliken transition charges of PBI

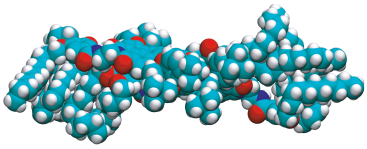
- $S_0 \rightarrow S_1$ transition
- remove side groups
- lateral displacement



Coupling of the dimer shifted along x- and y-direction

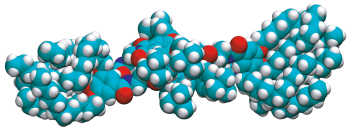


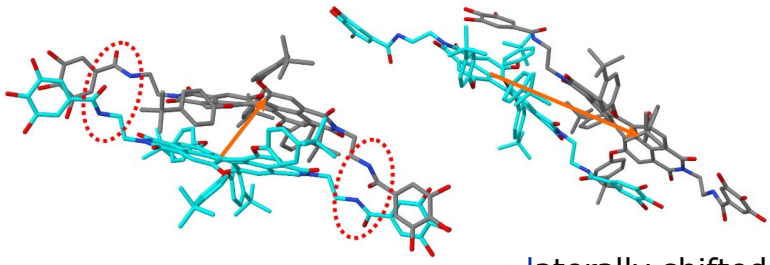
- dimer structures (DFTB simulated annealing)



H-dimer

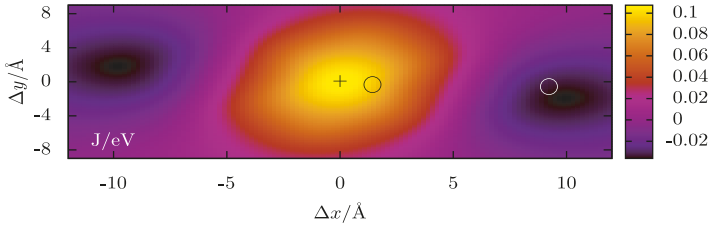
J-dimer





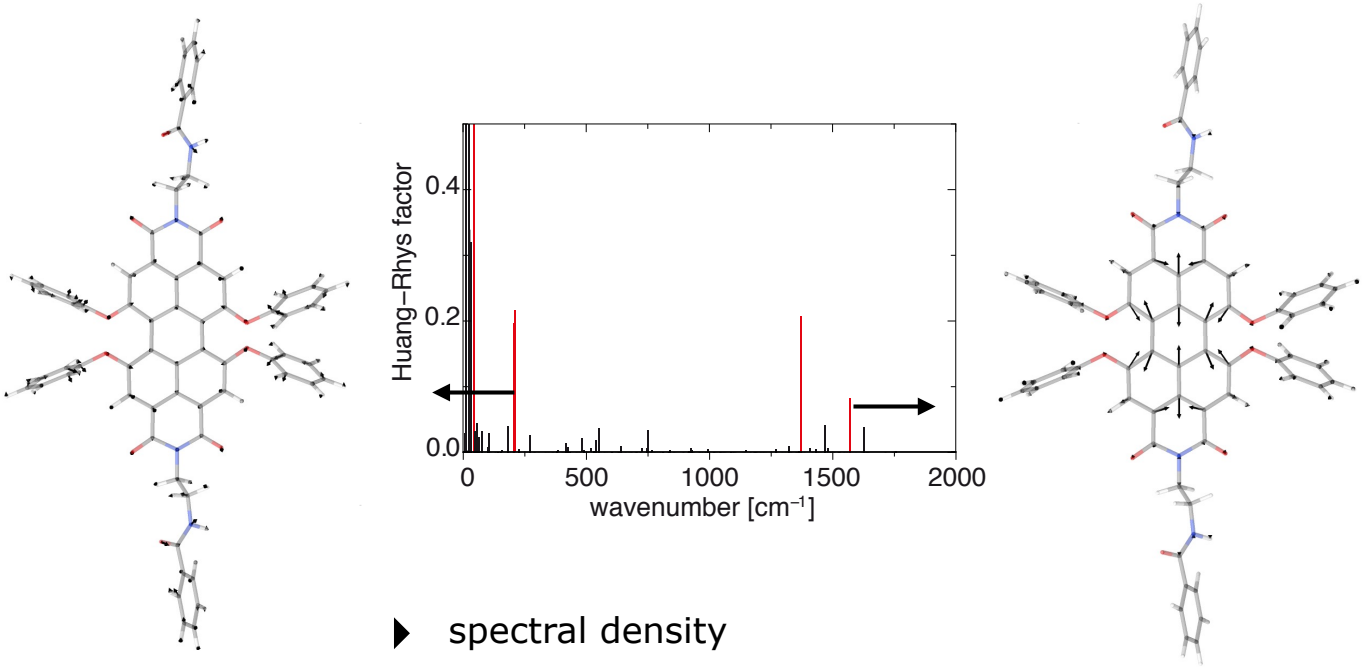
- sandwich geometry
- cannot be elongated
- H-bonded

- laterally shifted
- nucleus for longer aggregates
- weaker π–stacking



Configuration	J_{mn}/eV (TBFE)	J_{mn}/eV (DFT)
H	0.091	0.103
H + 1 Å	0.068	0.076
J	− 0.030	− 0.034
J + 1 Å	− 0.019	− 0.021

- Franck-Condon active modes (TDDFT, B3LYP, 6-311G*)

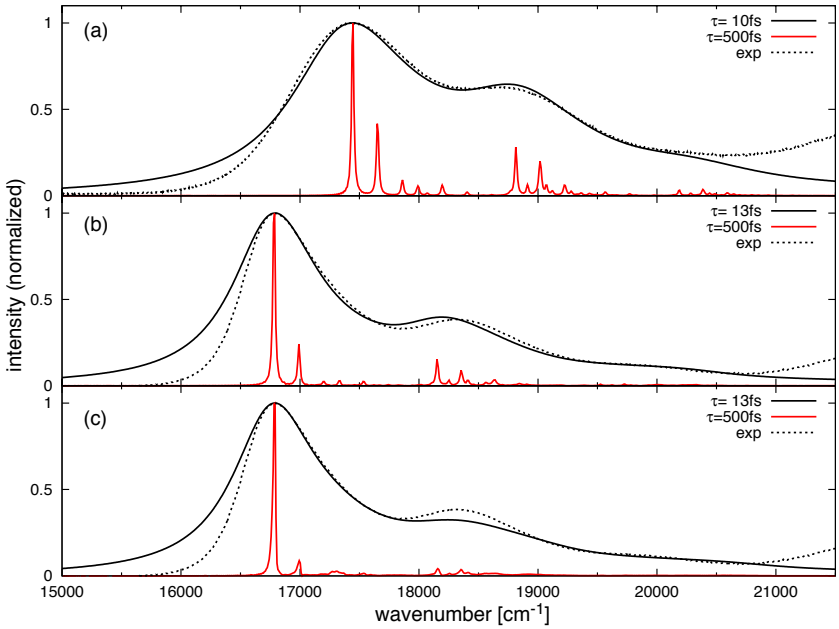


- spectral density

$$\mathcal{J}_m(\omega) = \sum_{\xi} S_{m,\xi}\delta(\omega - \omega_{m,\xi})$$

Linear Absorption

- 10 mode model (200-1600 cm^{-1}, J_{mn}=-500 cm^{-1})



exp: S. Lochbrunner et al.

$N_{\mathrm{agg}} = 1$

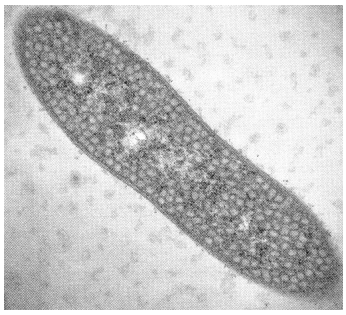
$N_{\mathrm{agg}} = 2$

$N_{\mathrm{agg}} = 6$

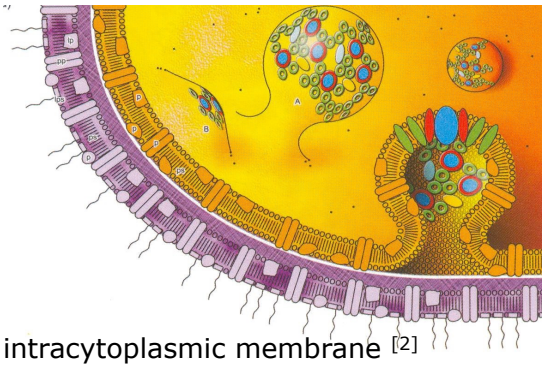
- dilution of FC progression upon increasing aggregate size

D. Ambrosek et al., JPC A 116, 12451 (2012)

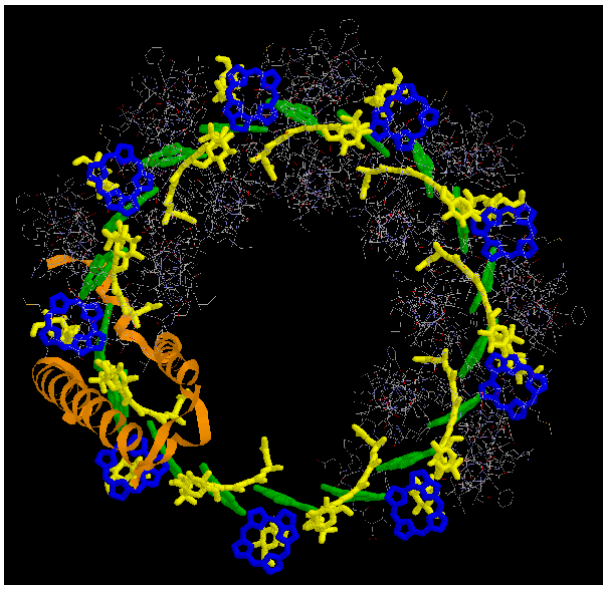
LH2: Photosynthetic Antenna



Rb. capsulatus [1]



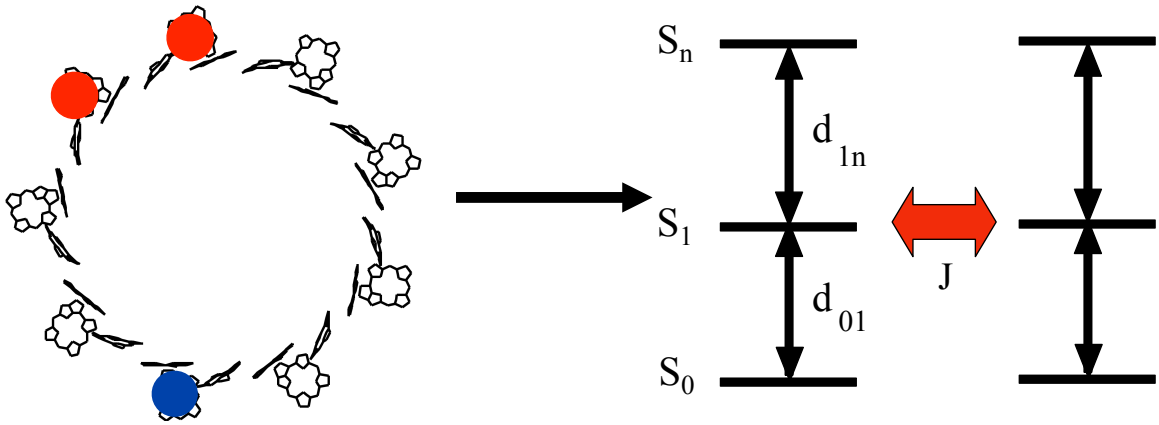
intracytoplasmic membrane [2]



LH2 complex (*Rps. acidophila*) [3]

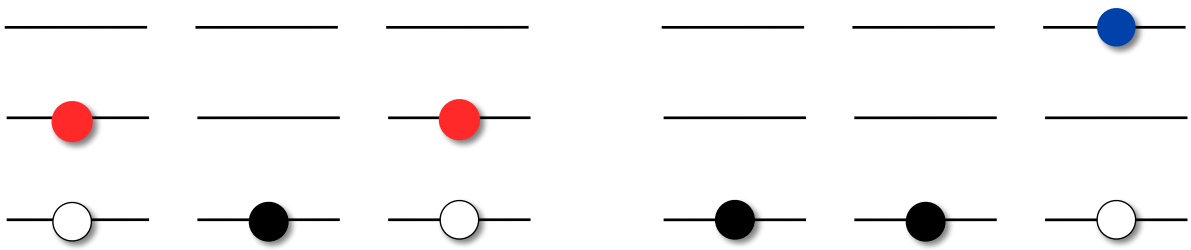
[1] S.J. Schmitt et al.; [2] N. Hunter; [3] T. Pullerits

Multi-Exciton Model



nonlocal two-exciton state

local double excitation state



Quantum Master Equation

- one-exciton reduced density matrix

$$\frac{\partial \rho_{\alpha\beta}}{\partial t} = i(\omega_{\alpha\beta} + \gamma_{\alpha\beta})\rho_{\alpha\beta} - \delta_{\alpha\beta}\sum_{\alpha'}(k_{\alpha'\alpha}\rho_{\alpha'\alpha'} - k_{\alpha\alpha'}\rho_{\alpha\alpha})$$

- Caldeira-Leggett type model (one bath)

$$H_{\mathrm{R}} = \sum_j \frac{\hbar\omega_j}{2}\Big(-\frac{\partial^2}{\partial Q_j^2} + Q_j^2\Big) \qquad H_{\mathrm{S-R}} = \sum_m |m\rangle\langle m| \sum_j \hbar\omega_j g_{m,j} Q_j$$

- relaxation rates

$$k_{ab} = 2\Gamma_{ab,ba}(\omega_{ab}) = \sum_{u,v} K_{ab}^{(u)} K_{ba}^{(v)} C_{uv}(\omega_{ab})$$

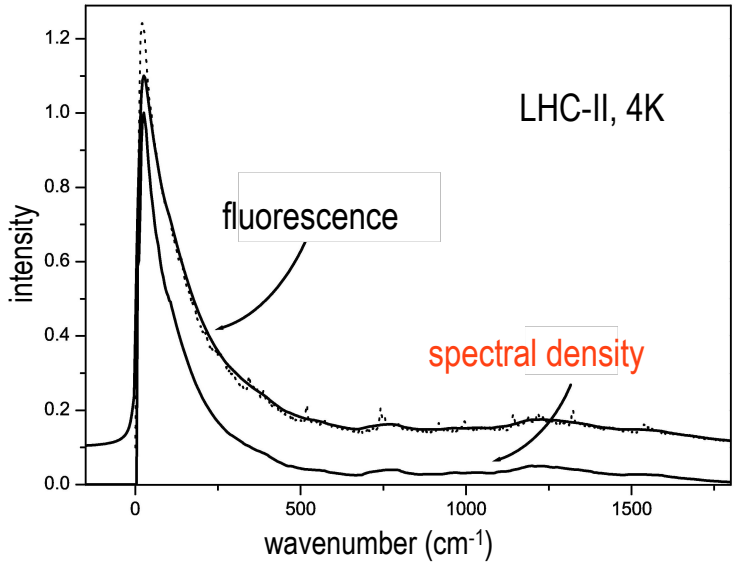
$$\rightarrow \quad k_{\alpha\beta} = 2\pi \sum_m |C_m(\alpha)|^2 |C_m(\beta)|^2 \omega_{\alpha\beta}^2 (1 + n(\omega_{\alpha\beta}))[J_m(\omega_{\alpha\beta}) - J_m(-\omega_{\alpha\beta})]$$

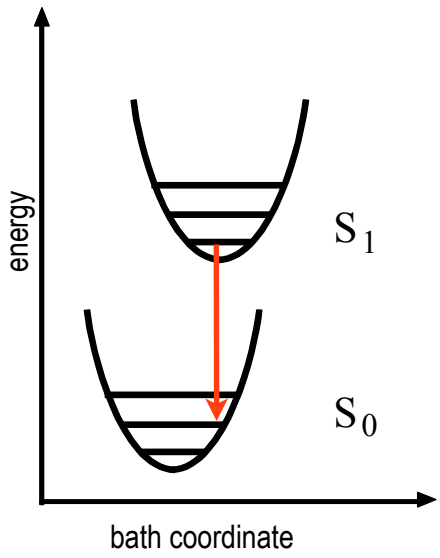
- static disordered via sampling of transition energies

Effective Oscillator Model

$$J(\omega) = \sum_j S_j \delta(\omega - \omega_j)$$

experimental spectral density

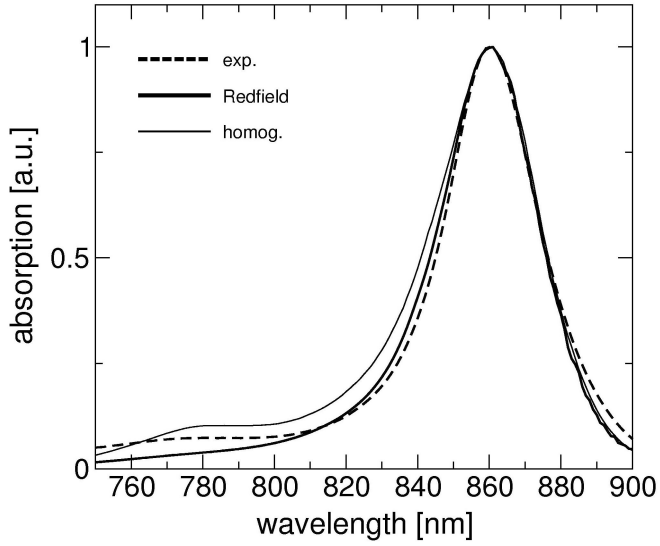




O.K., V. Sundström, T. Pullerits, Chem. Phys. 275, 15 (2002)

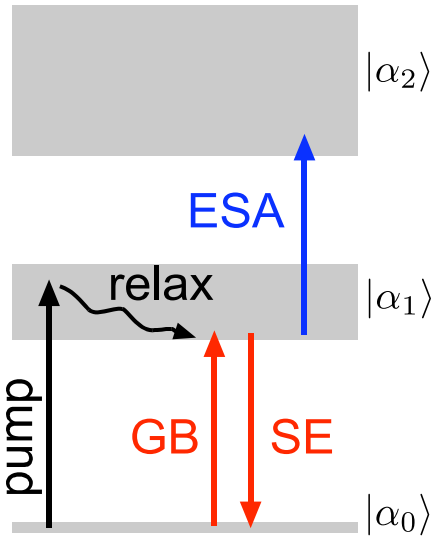
B850 Linear Absorption

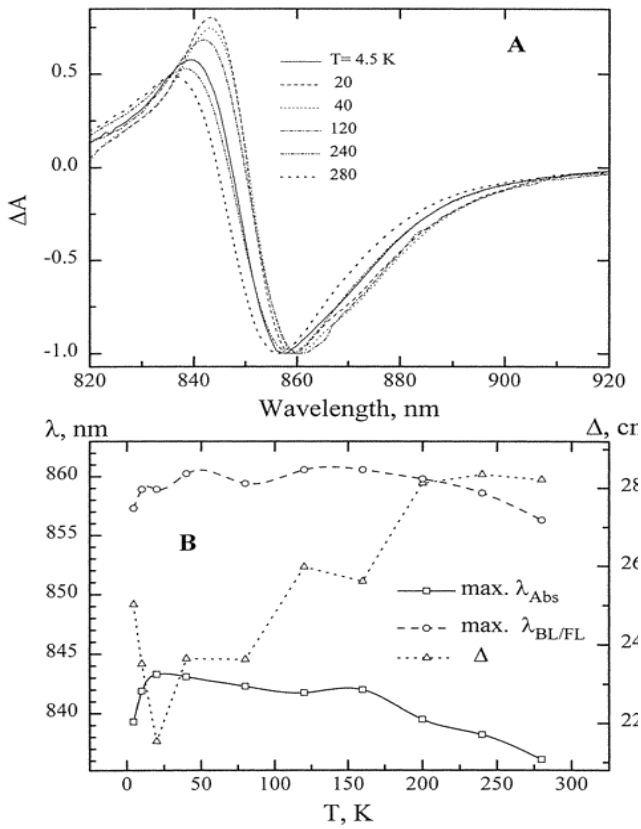
- absorption of LH2 with depleted B800 ring (exp. J. Herek)



$$\sigma = \max(J_{mn}) = 300\,\mathrm{cm}^{-1}$$

B850: Pump-Probe Spectroscopy



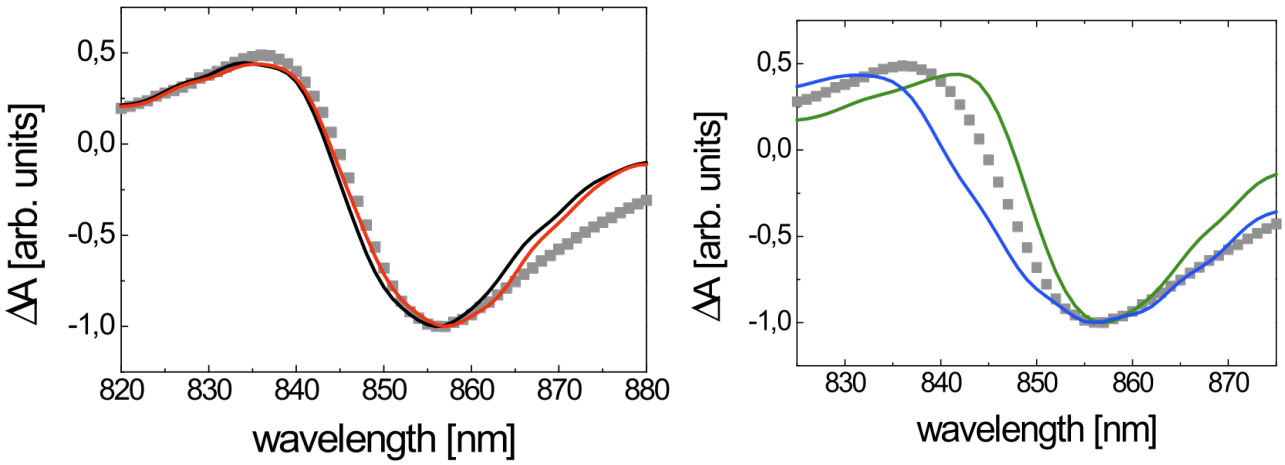


M. Chachisvilis et al., JPC B 101, 7275 (1997)

Quasi-Stationary Spectra

- pump-probe absorption band shape sensitive to disorder strength

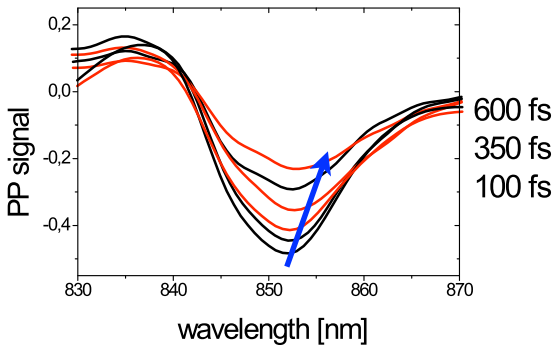
$\sigma = \max(J_{mn}) = 300\,\mathrm{cm}^{-1}$ $\qquad$ $\sigma = 250/350\,\mathrm{cm}^{-1}$



Kühn et al., J. Chem. Phys. 107, 4154 (1997)

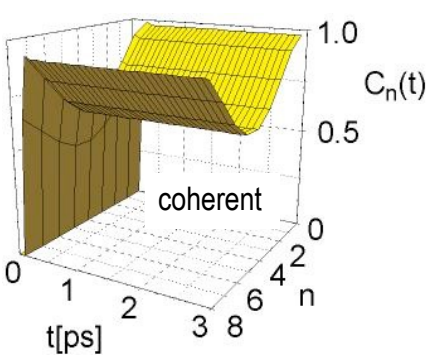
Dynamics & Coherence

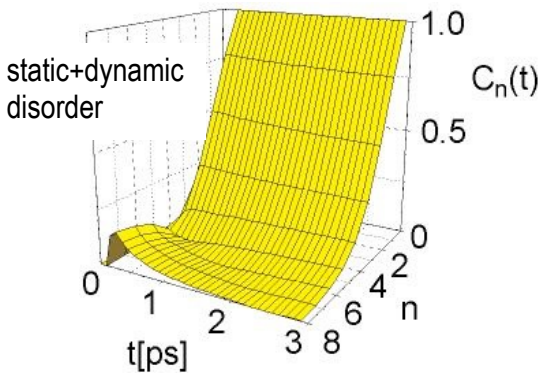
- ultrafast relaxation



- dynamical localization

$$C_n(t) = \sum_m |\langle \rho_{m,m+n}(t) \rangle_{\mathrm{dis}}|$$



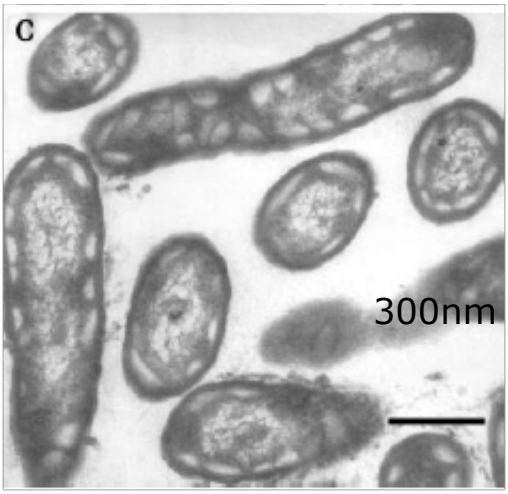


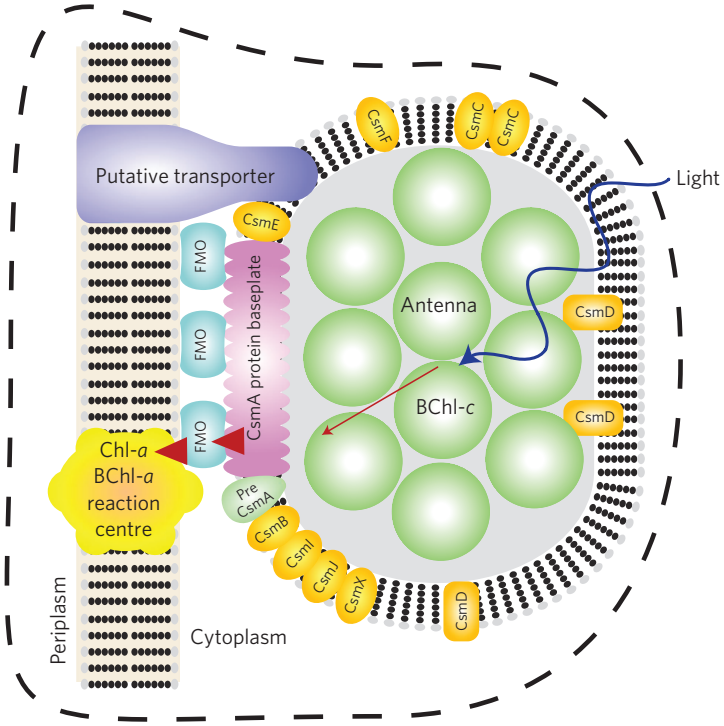
Green Sulfur Bacteria

- inhabit oxygen poor, sulfur rich environments
- adapt to low light conditions

http://universe-review.ca

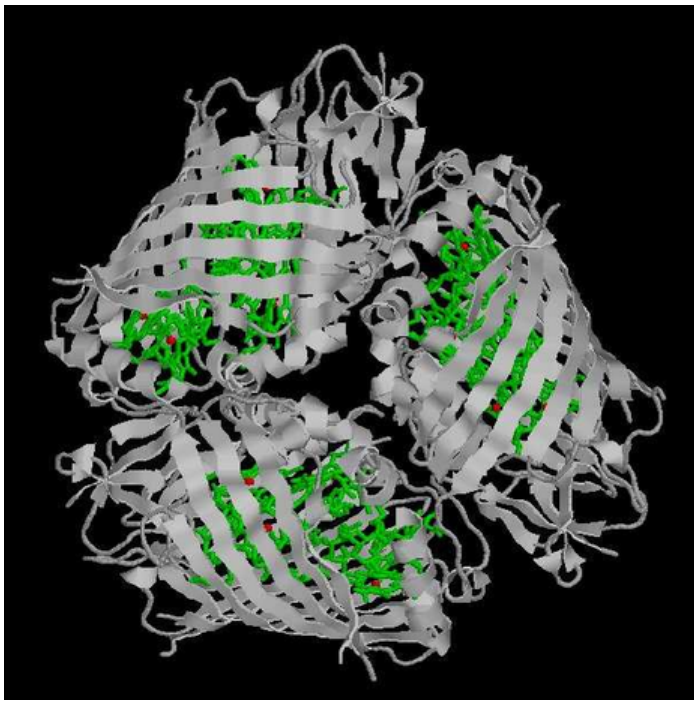
Fenna-Matthews-Olsen (FMO) complex

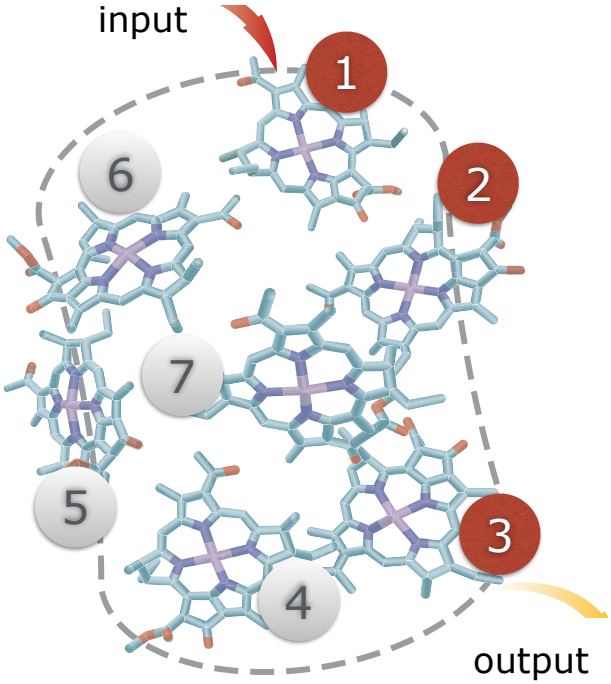




Blankenship et al. (1995); N. Lambert et al. Nat. Phys. 9, 10 (2012)

Fenna-Matthews-Olsen (FMO) Complex

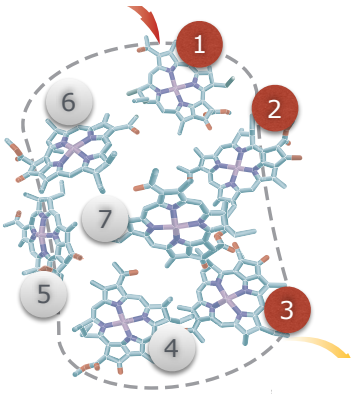


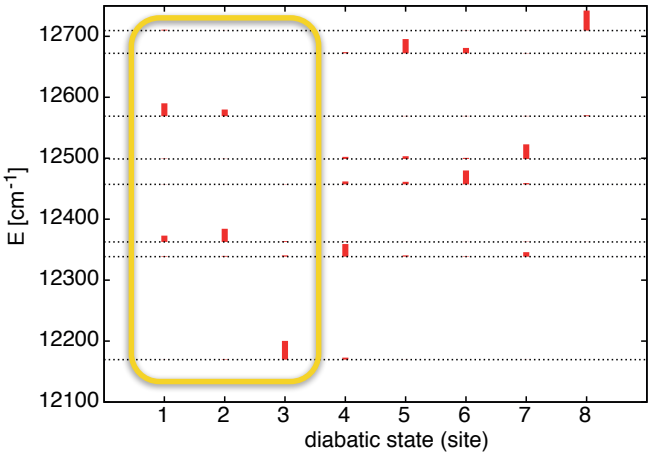


en.wikipedia.org; N. Lambert et al. Nat. Phys. 9, 10 (2012)

Exciton Hamiltonian

$$H_S = \begin{pmatrix} 310 & \mathbf{-97.9} & 5.5 & -5.8 & 6.7 & -12.1 & -10.3 & \mathbf{37.5} \\ \mathbf{-97.9} & 230 & \mathbf{30.1} & 7.3 & 2.0 & 11.5 & 4.8 & 7.9 \\ 5.5 & \mathbf{30.1} & 0 & \mathbf{-58.8} & -1.5 & -9.6 & 4.7 & 1.5 \\ -5.8 & 7.3 & \mathbf{-58.8} & 180 & \mathbf{-64.9} & -17.4 & \mathbf{-64.4} & -1.7 \\ 6.7 & 2.0 & -1.5 & \mathbf{-64.9} & 405 & \mathbf{89.0} & -6.4 & 4.5 \\ -12.1 & 11.5 & -9.6 & -17.4 & \mathbf{89.0} & 320 & \mathbf{31.7} & -9.7 \\ -10.3 & 4.8 & 4.7 & \mathbf{-64.4} & -6.4 & \mathbf{31.7} & 270 & -11.4 \\ \mathbf{37.5} & 7.9 & 1.5 & -1.7 & 4.5 & -9.7 & -11.4 & 505.0 \end{pmatrix}$$

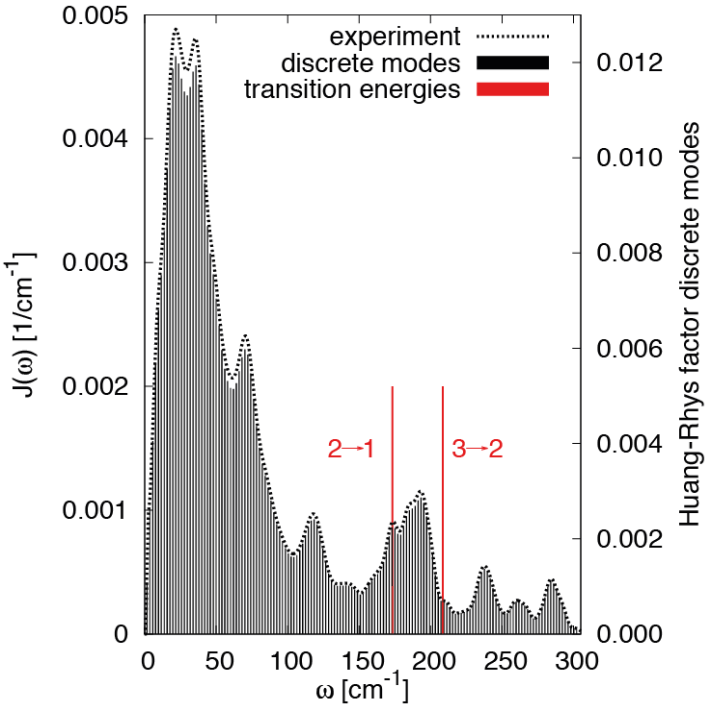




J. Moix et al., J. Phys. Chem. Lett. **2** , 3045 (2011).

BChl *a* Spectral Density

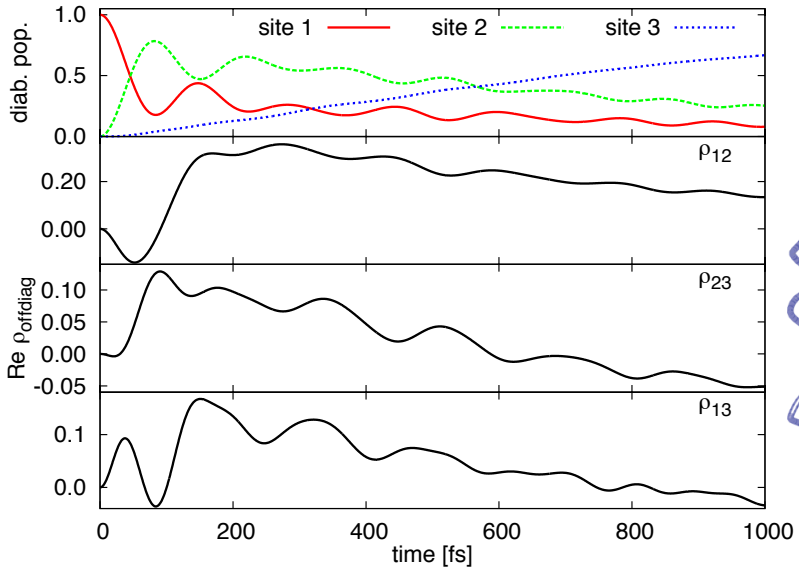
- parametrization of experimental spectral density

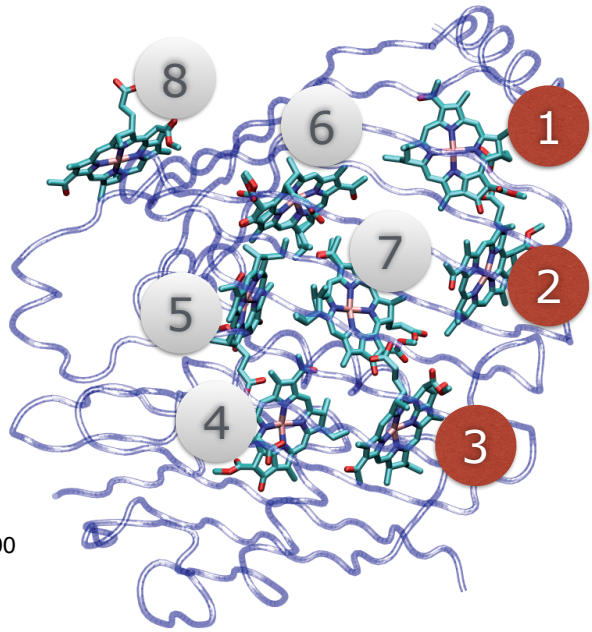


- Quantum Master Equation
  - structured spectral density
  - no info about vibrations
- Schrödinger equation
  - model: 7 electronic states + 74 vibrational modes per site

[1] M. Wendling et al., J. Phys. Chem. B 104, 5825 (2000)

Population and Coherence Dynamics





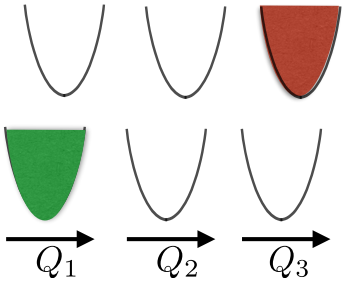
- oscillation frequencies (220, 160 cm^{-1}) differ from bare electronic value (208 cm^{-1})
- dephasing due to high-dimensional vibrational space

J. Schulze, O.K., JPC B **119**, 6211 (2015), J. Schulze, O.K. et al., arXiv:1602.03973 [physics.chem-ph]

Vibrational/Vibronic Dynamics

- vibrational excitation at site *m*

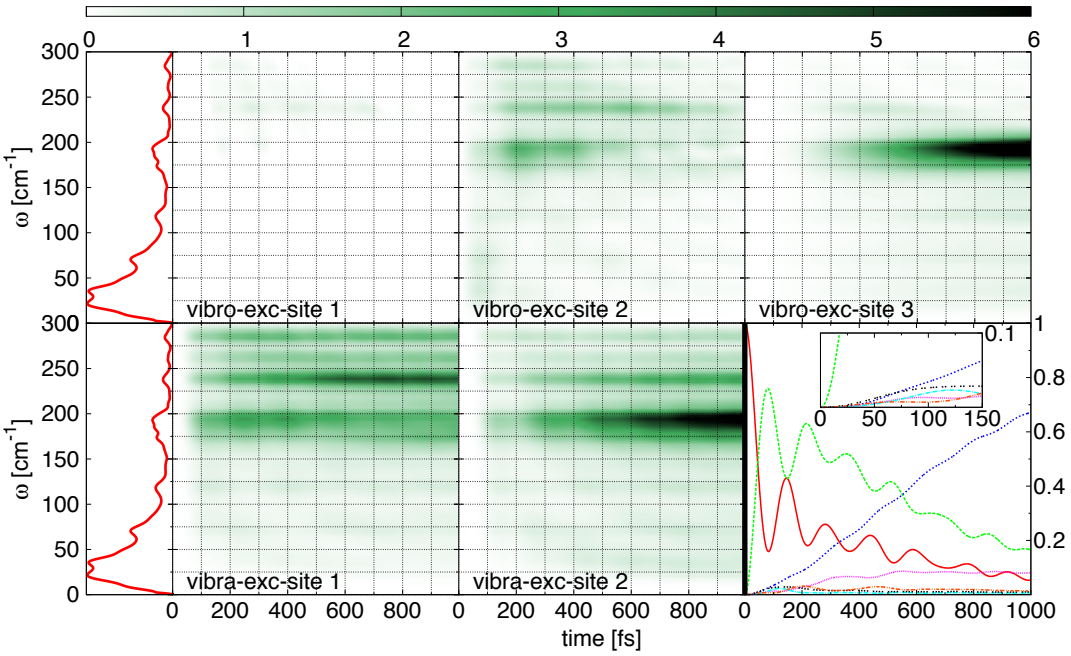
$$H_m^{(\mathrm{vibra})} = \sum_{\xi \in m} \frac{\omega_{m,\xi}}{2} \left(-\frac{\partial^2}{\partial Q_{m,\xi}^2} + Q_{m,\xi}^2 \right) (1 - |m\rangle\langle m|)$$



- vibronic excitation at site *m*

$$H_m^{(\mathrm{vibro})} = \sum_{\xi \in m} \frac{\omega_{m,\xi}}{2} \left(-\frac{\partial^2}{\partial Q_{m,\xi}^2} + Q_{m,\xi}^2 + 2\sqrt{2S_{m,\xi}} Q_{m,\xi} \right) |m\rangle\langle m|$$

Vibrational/Vibronic Excitation



- vibrational excitation at sites 1 and 2 (dynamic picture)
- vibronic excitation at site 3 (resonance picture)

Synopsis

Hamiltonian

Born-Oppenheimer

potential energy surfaces

normal modes QM/MM

Caldeira-Leggett

Dynamics

Schrödinger equation

MCTDH

Quantum Master Equation

spectral density

Spectroscopy

nonlinear polarization

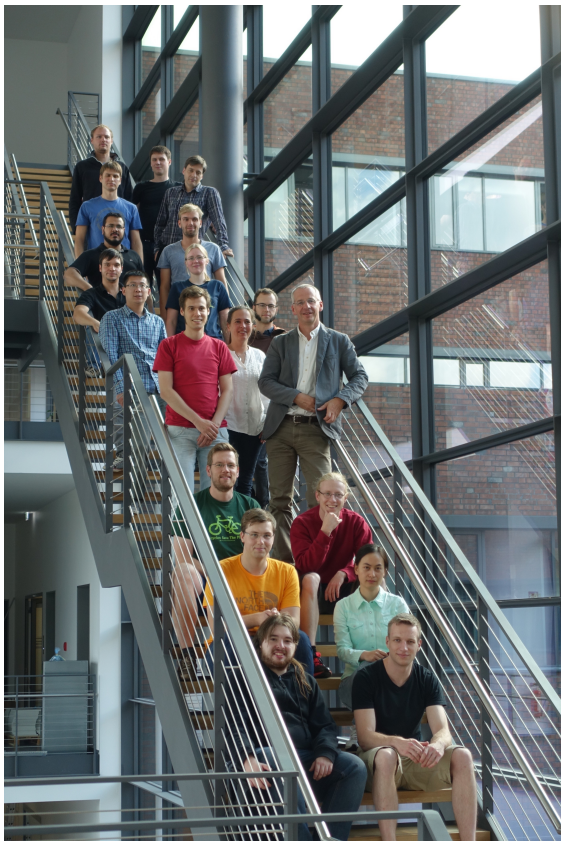
phase matching

response functions

lineshape function

Thanks To

- Rostock
  - Jan Schulze
  - Per-Arno Plötz
  - Marco Schröter
  - Sergey Ivanov
  - Y. Yan
- Berlin
  - V. May
  - H. Naundorf
  - K. Heyne
  - M. Petkovic
  - Y. Yang
  - G. Paramonov
  - G. Krishnan
- Hans-Dieter Meyer (Heidelberg)
- Stefan Lochbrunner and group (Rostock)
- Thomas Niehaus (Lyon)
- T. Pullerits, V. Sundström (Lund)



SFB 652

DFG

Quatar National Research Fund