Problems of Modern Physics

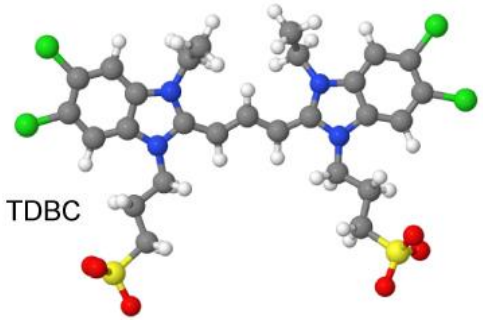
Lecture 6

Semion K. Saikin
Department of Chemistry and Chemical Biology
Harvard University

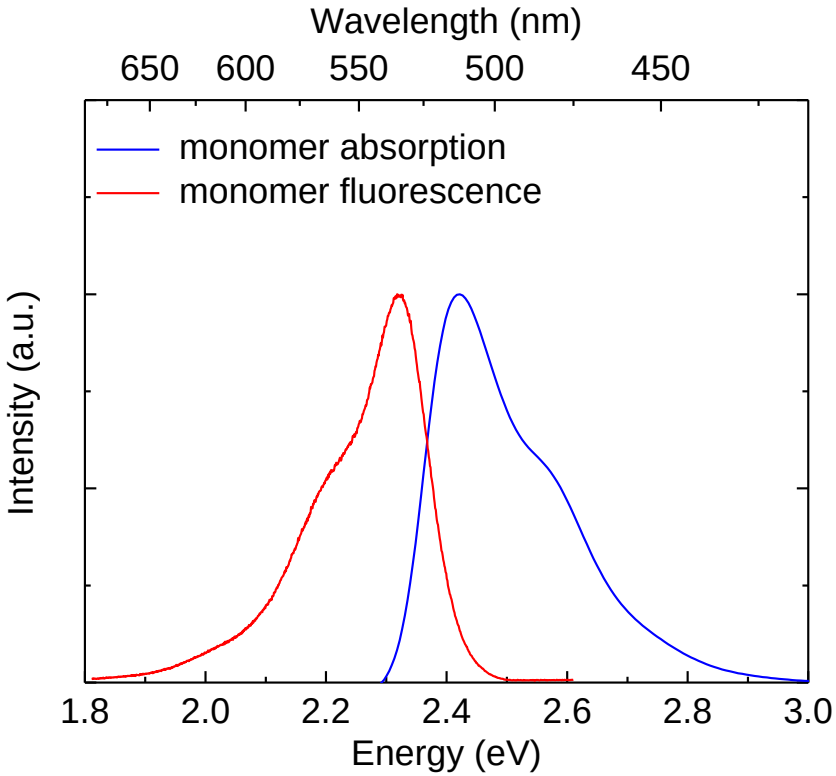
Email: saykin@fas.harvard.edu

Molecular aggregates

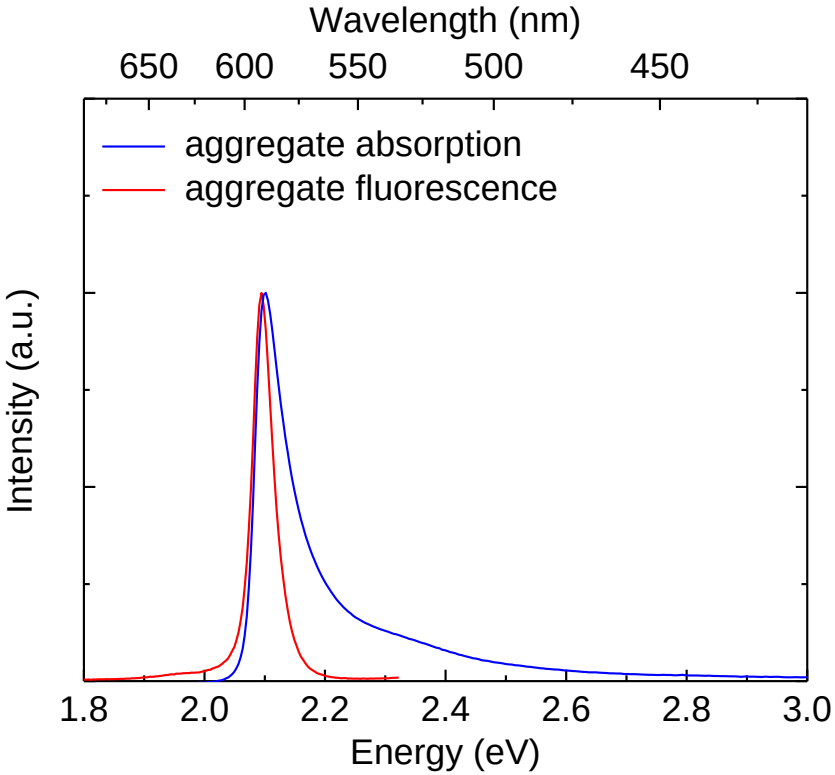
Aggregates of dyes



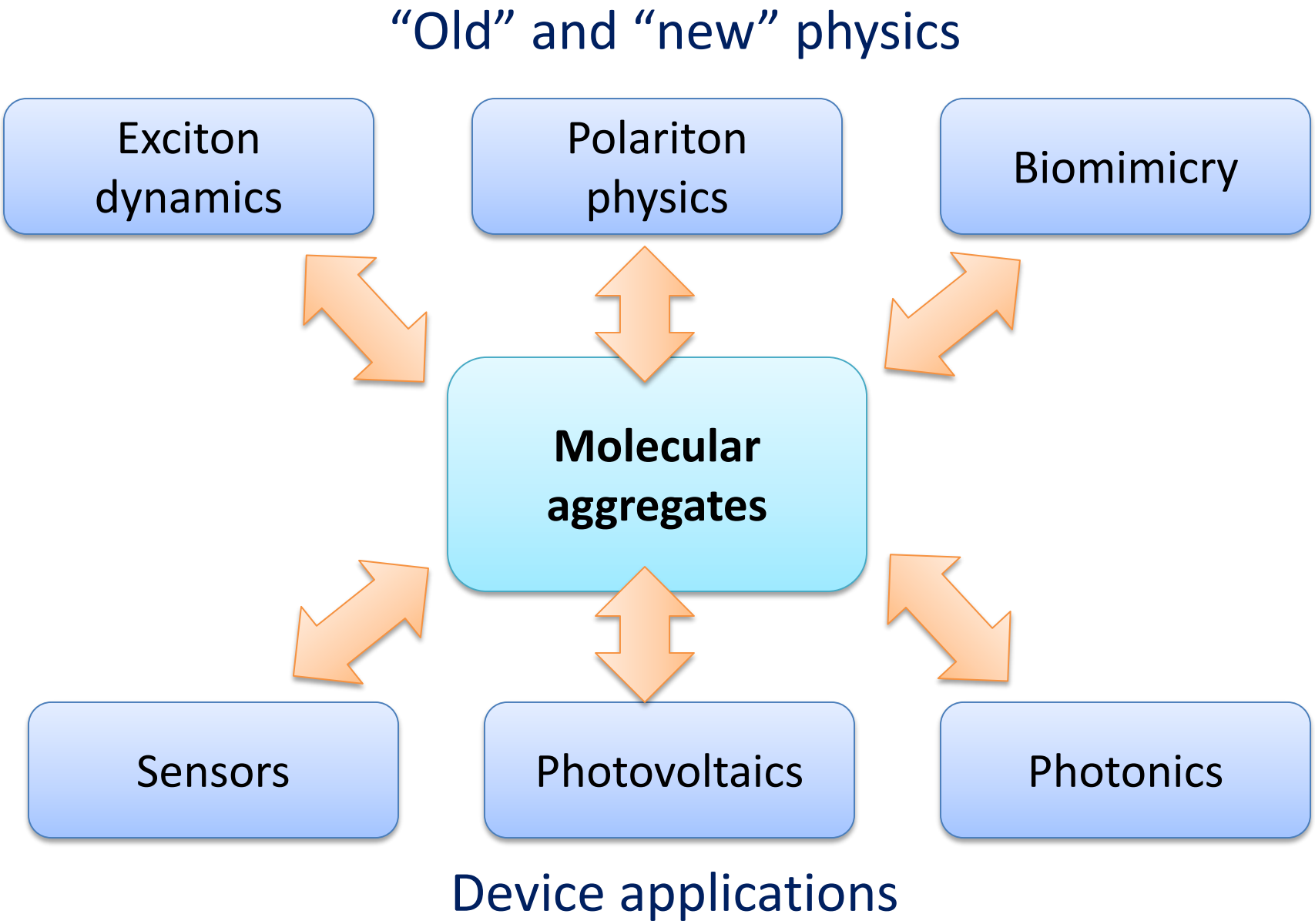
Solution



Aggregate

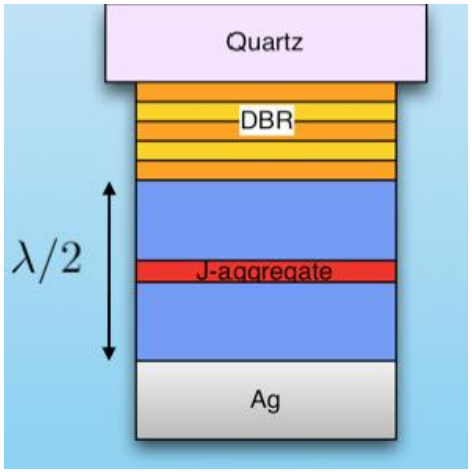


Motivation


"Old" and "new" physics
Exciton dynamics
Polariton physics
Biomimicry
Molecular aggregates
Sensors
Photovoltaics
Photonics
Device applications

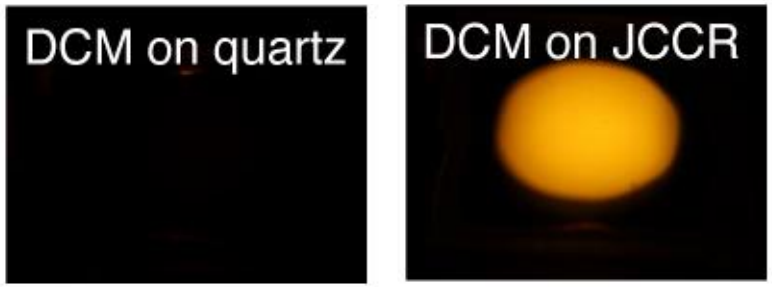
Applications

Photonic devices:



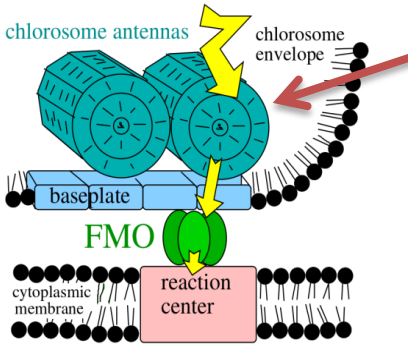
Strong exciton-photon coupling in organic cavities

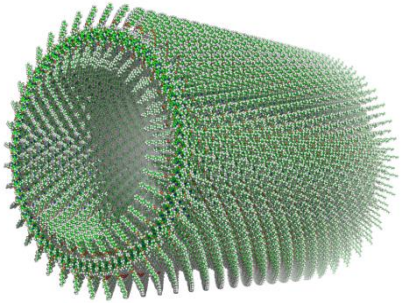
Photosensitization:



Fluorescence enhancement from DCM molecules on a J-aggregate film

Biomimicry:





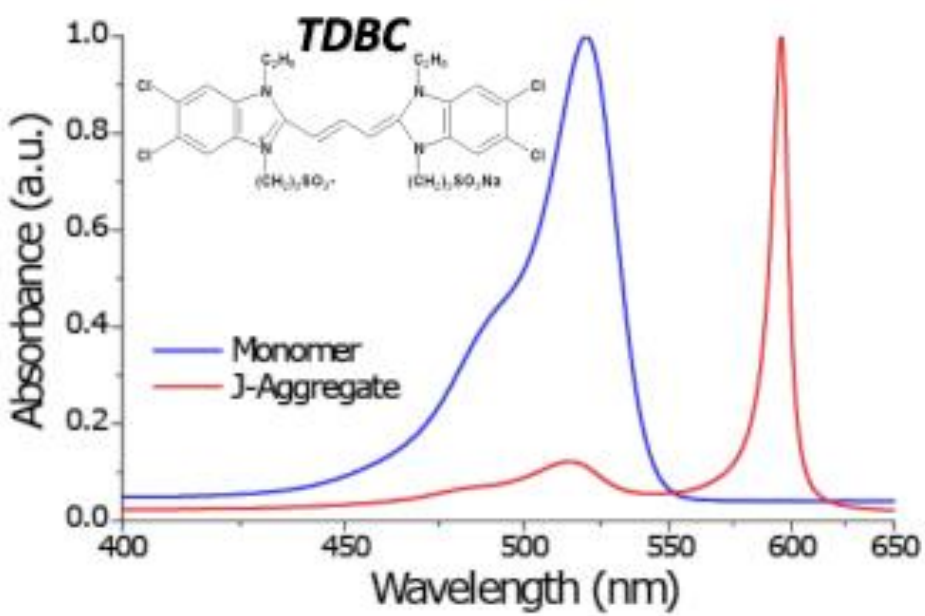
Photosynthesis in green sulfur bacteria

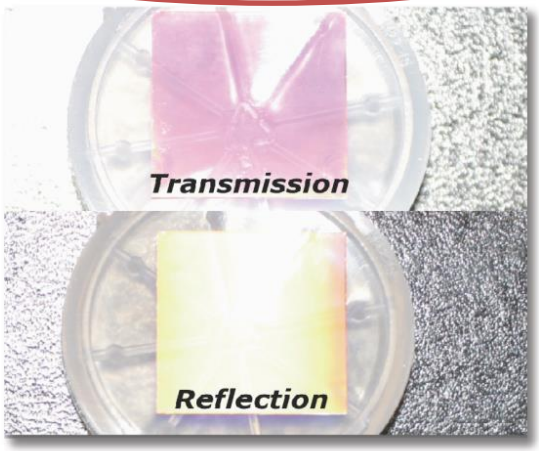
Thin-film aggregates

- Few molecular layers
- Self-assembly
- Room temperature
- Spatial order on the scale of 100 nm

Finished 5 nm film: $\alpha = 10^6\ \mathrm{cm}^{-1}$

40% of light absorbed at 595 nm





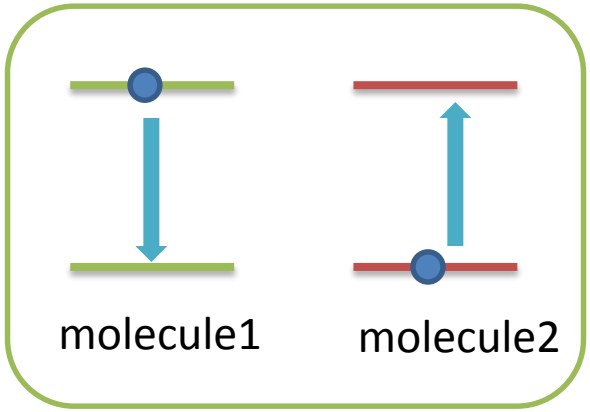
Bulovic group, MIT

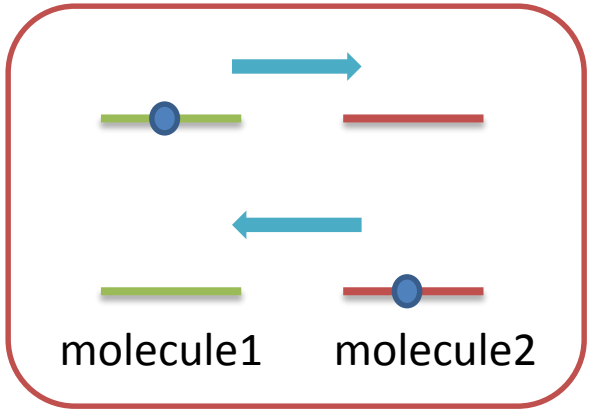
Bradley, M., et. al., *Adv. Mat.*, **17**, 1881 (2005)

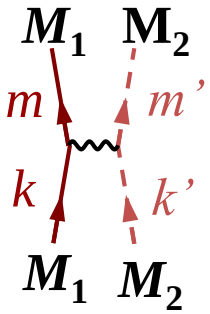
Intermolecular resonance coupling

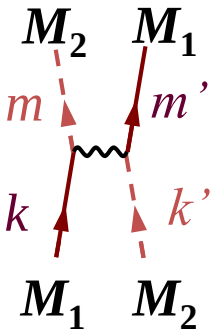
Förster and Dexter interactions

$$H_{\text{Coulomb}} = \frac{1}{2}\frac{1}{4\pi\varepsilon_0}\sum_{ij}\frac{e^2}{|r_i - r_j|}$$



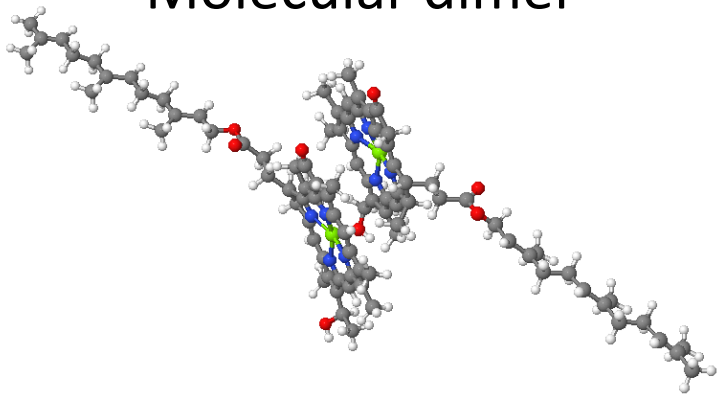


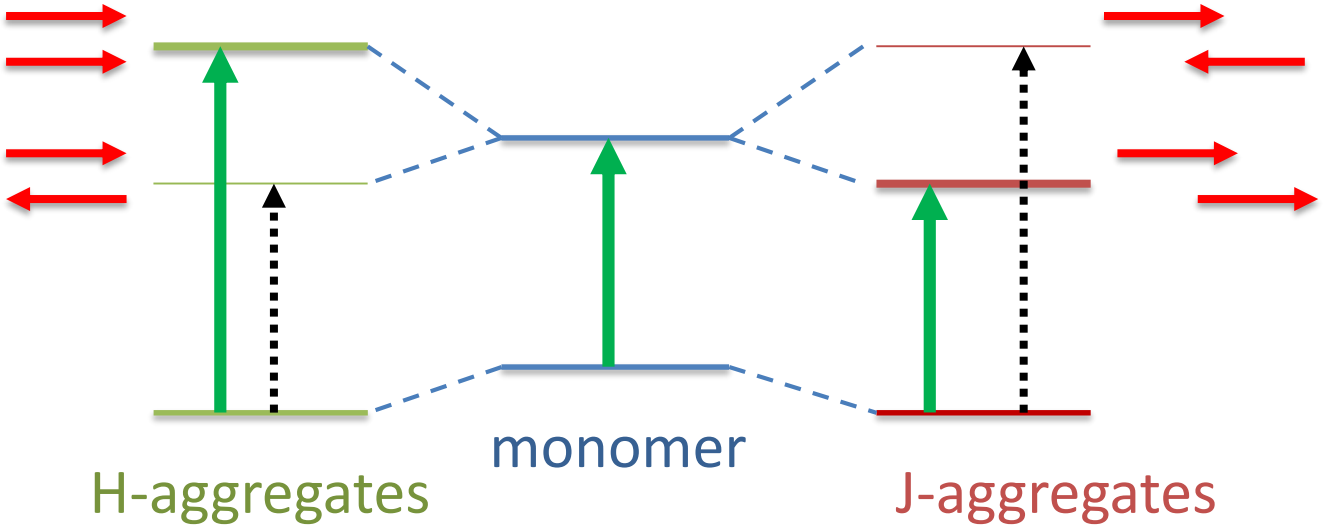




Intermolecular resonance coupling

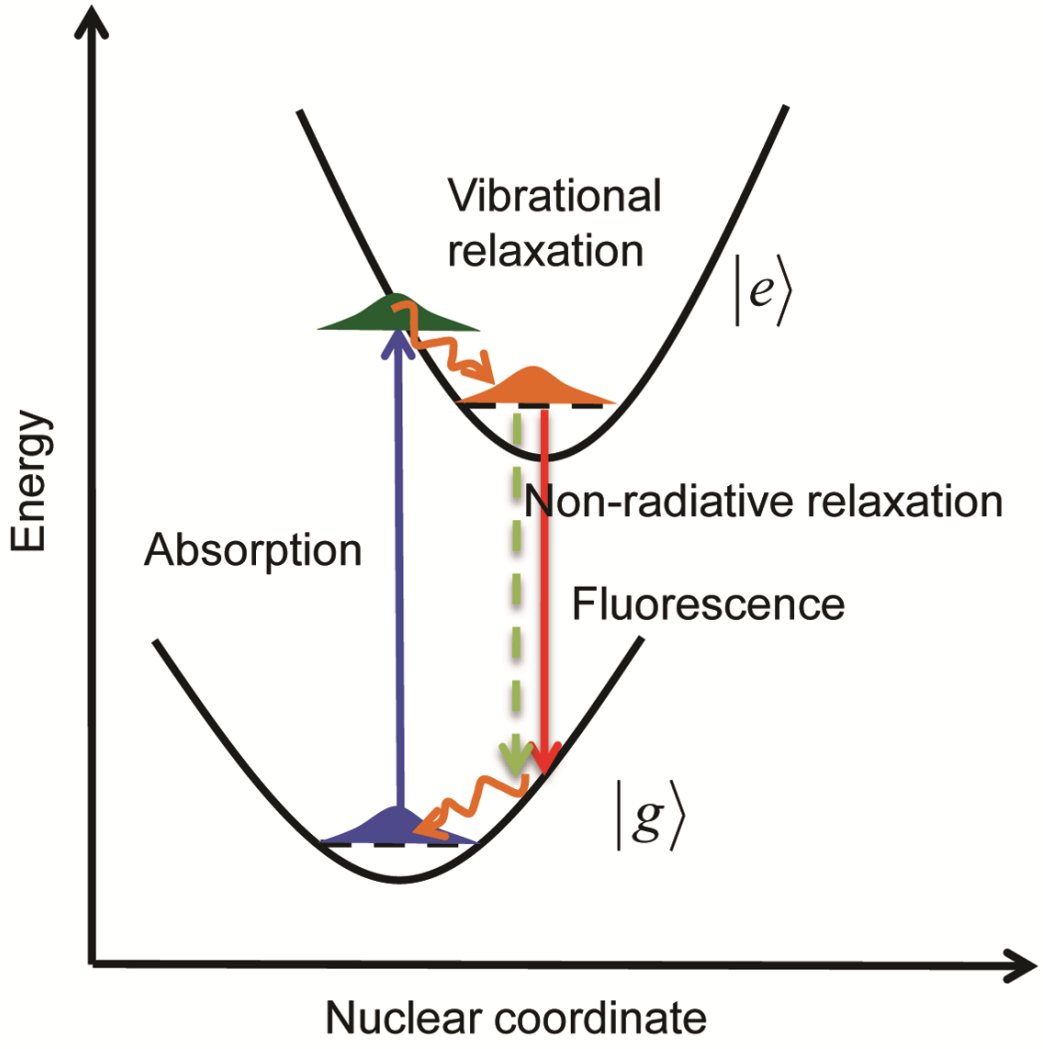
Molecular dimer





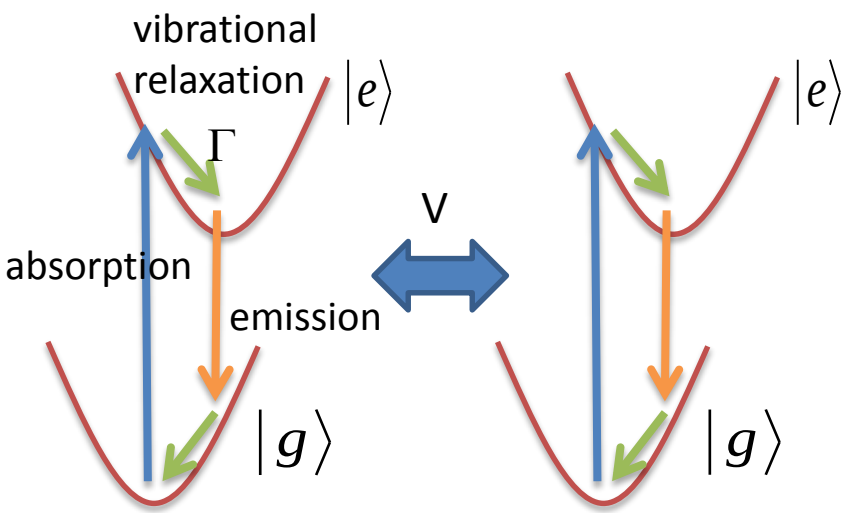
E. E. Jelly, *Nature* **138**, 1009 (1936); G. Scheibe, *Angew. Chem.* **49**, 563 (1936)

Electronic excitations in single molecules



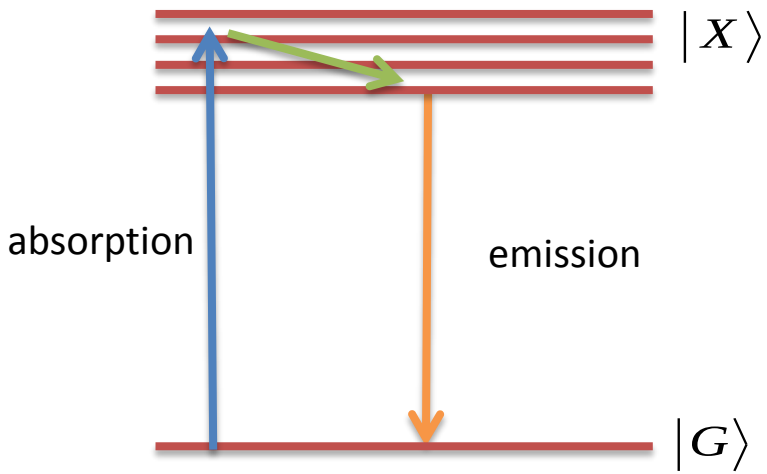
Coupling regimes

Weak: V << Γ



- Excitons jumps incoherently between molecules
- Environment thermalizes excitons on single molecules

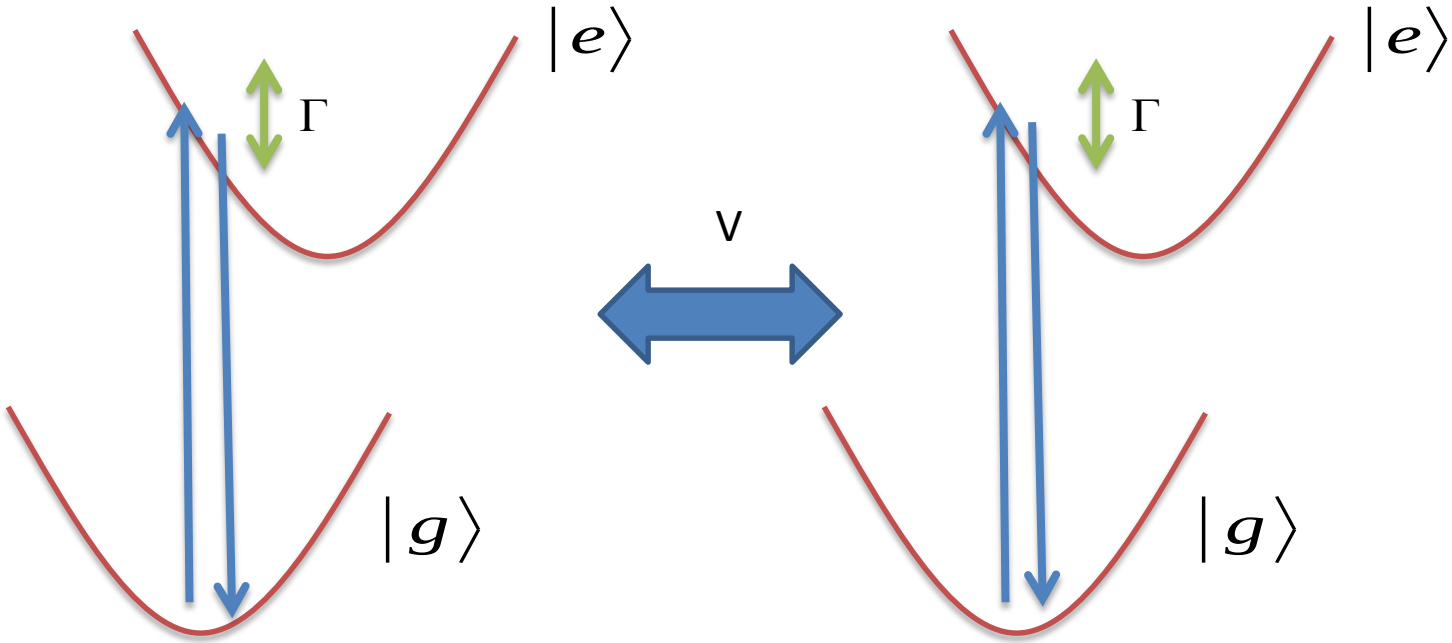
Strong: V >> Γ



- Molecular excitations form bands – coherent coupling between sites
- Coupling to the environment enters as thermalization between bands

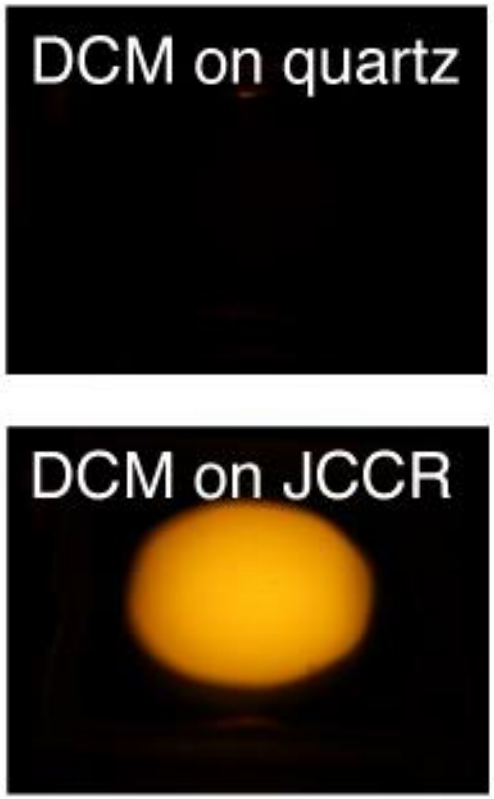
Coupling regimes

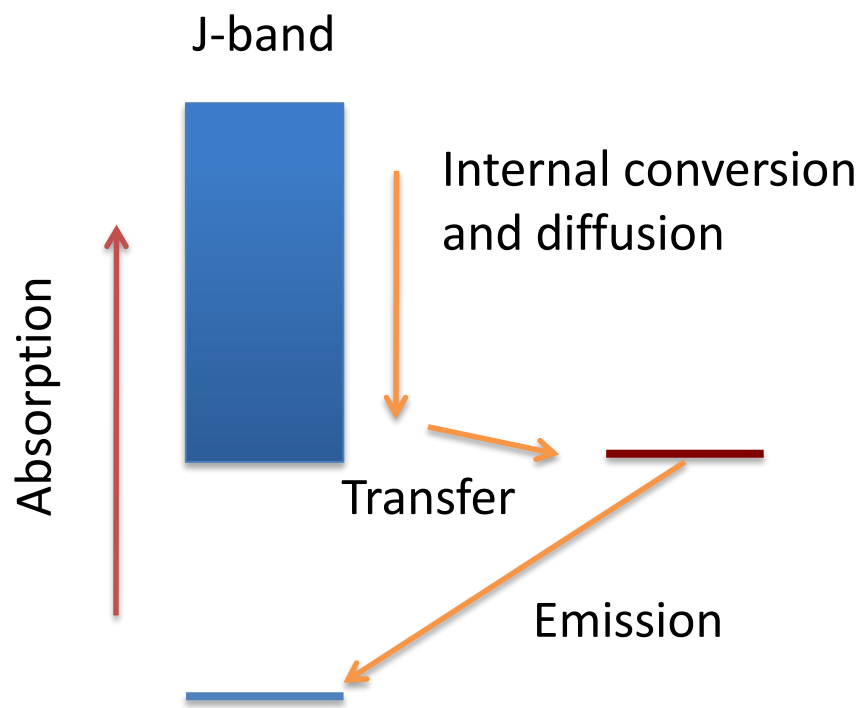
Intermediate coupling, $V \approx \Gamma$



- Molecules are coupled coherently
- Coupling to the environment enters as frequency diffusion
- Excitons are NOT thermalized

Example: fluorescence enhancement





Y. Yonezawa, D. Möbius, H. Kuhn,
J. Appl. Phys. 62, 2016 (1987)

Experimental data: Gleb M. Akselrod
the Bulovic group, MIT

DCM = 4-Dicyanmethylene-2-methyl-6-(p-dimethylaminostyryl)-4H –pyran
JCCR = J-aggregate critically coupled resonator

Excitons in molecular aggregates

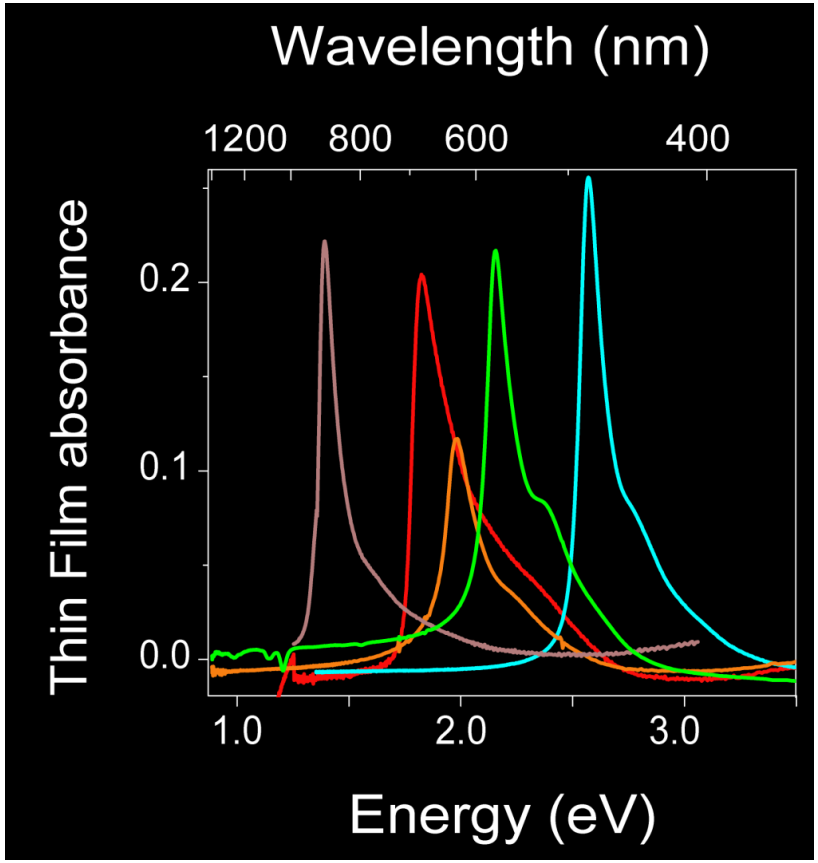
Existing claims:

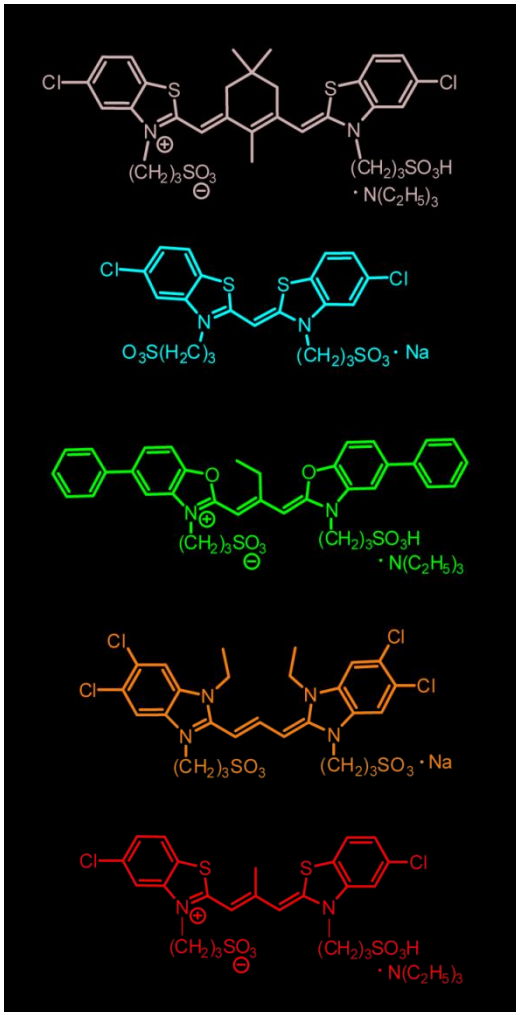
- Excitons are delocalized
- Large diffusion length
- Coherent dynamics

Concerns:

- Structure is not well characterized
- Transport measured indirectly
- Transport is hard to model

Dyes



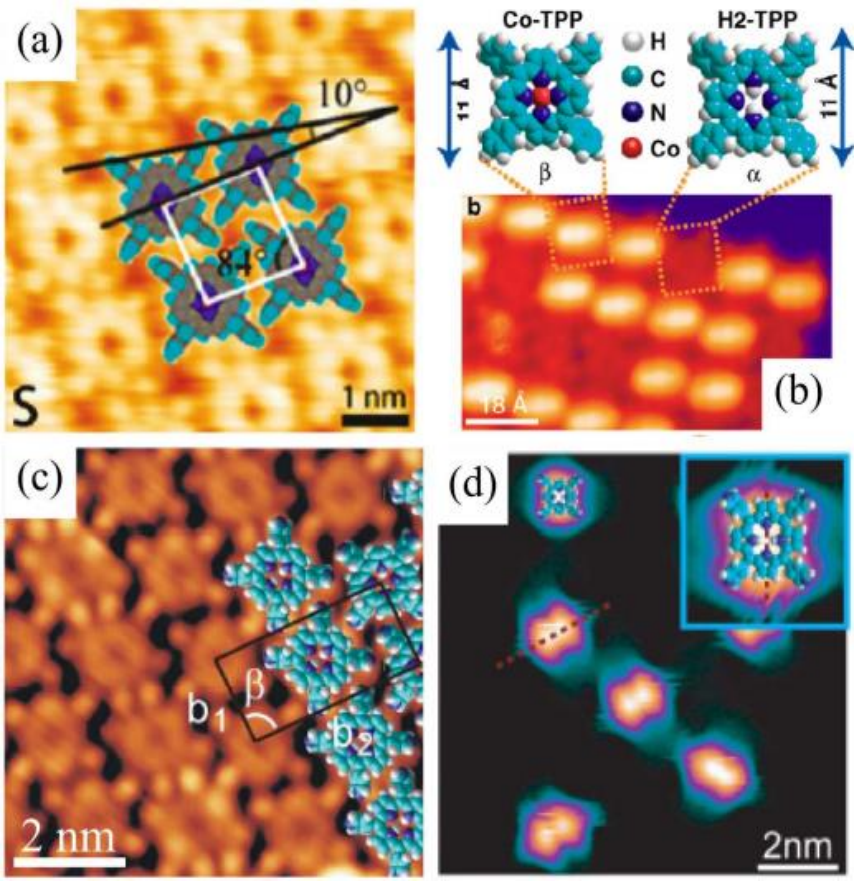


Brian Walker
Bawendi group, MIT

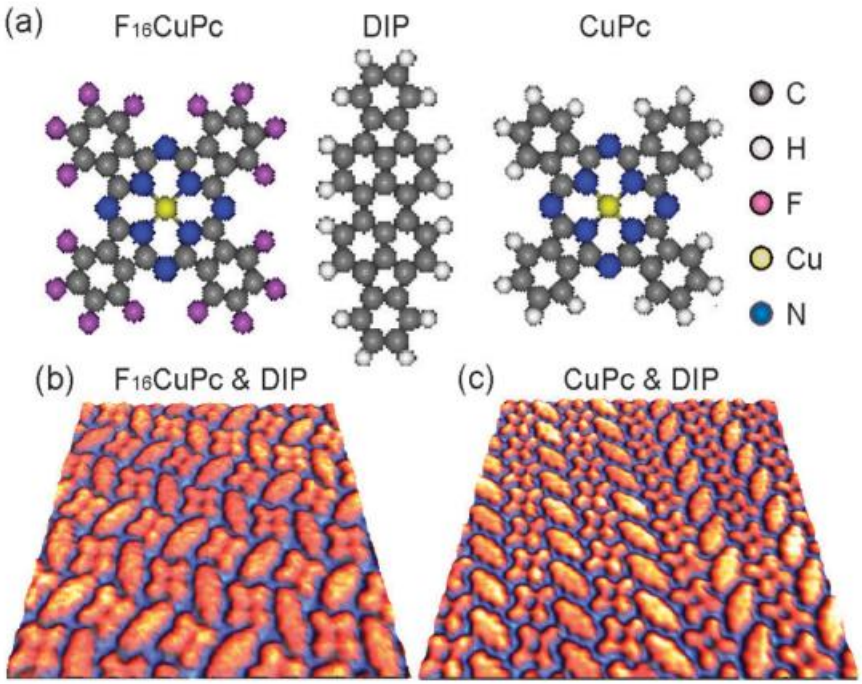
- Spectra can be tuned by changing the dye

More packing structures

2D excitonic materials from self-assembly!

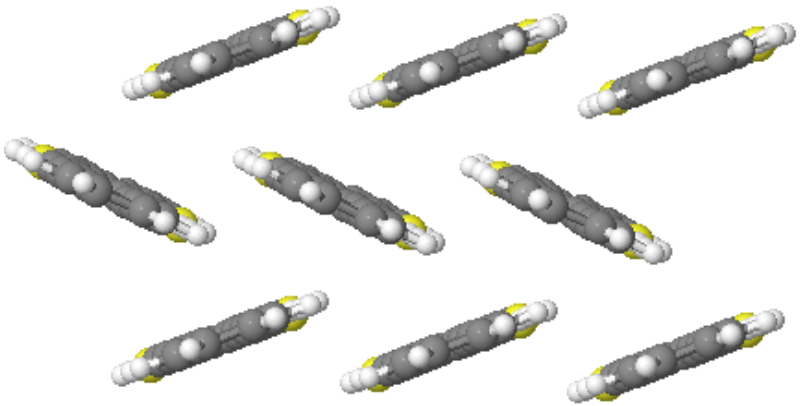


Chen group (Singapore)

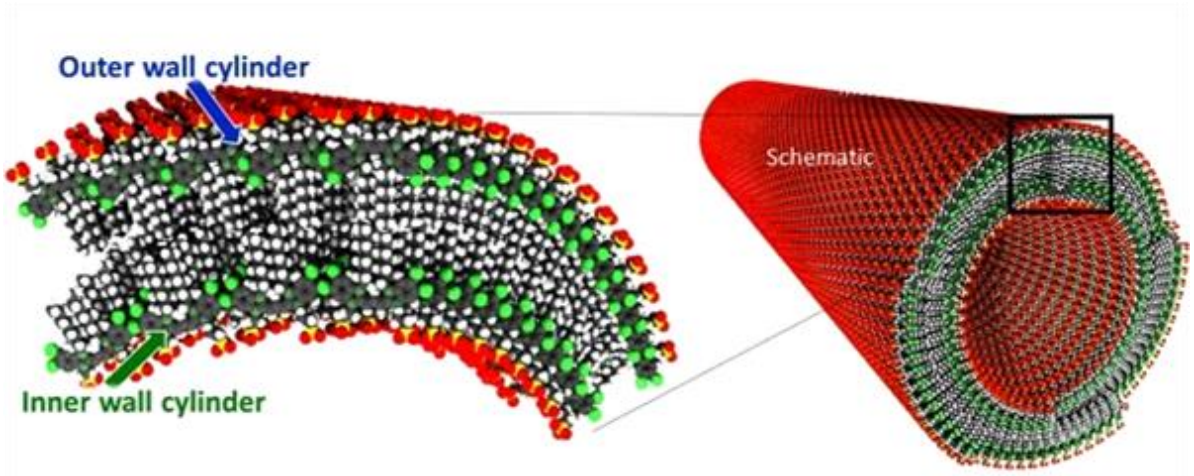


Wakayama group (Tsukuba)

More packing structures



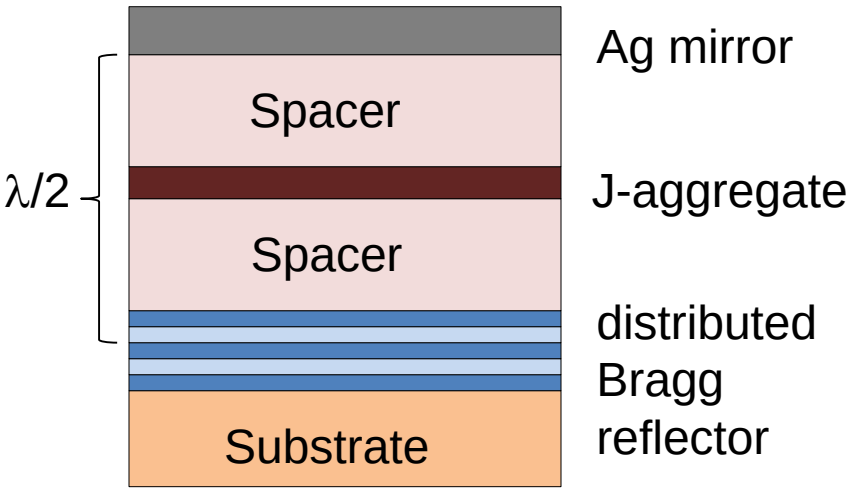
Herringbone 3D packing in DATT molecular crystals



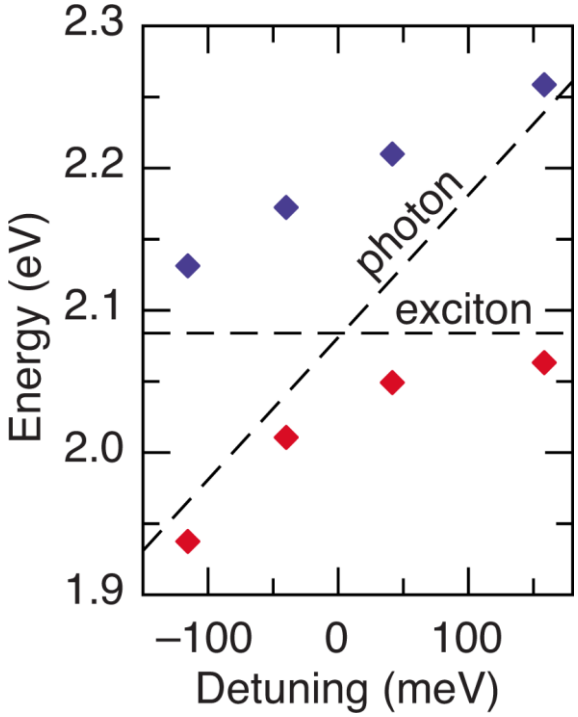
Tubular aggregates of cyanine dyes

J-aggregates in a cavity

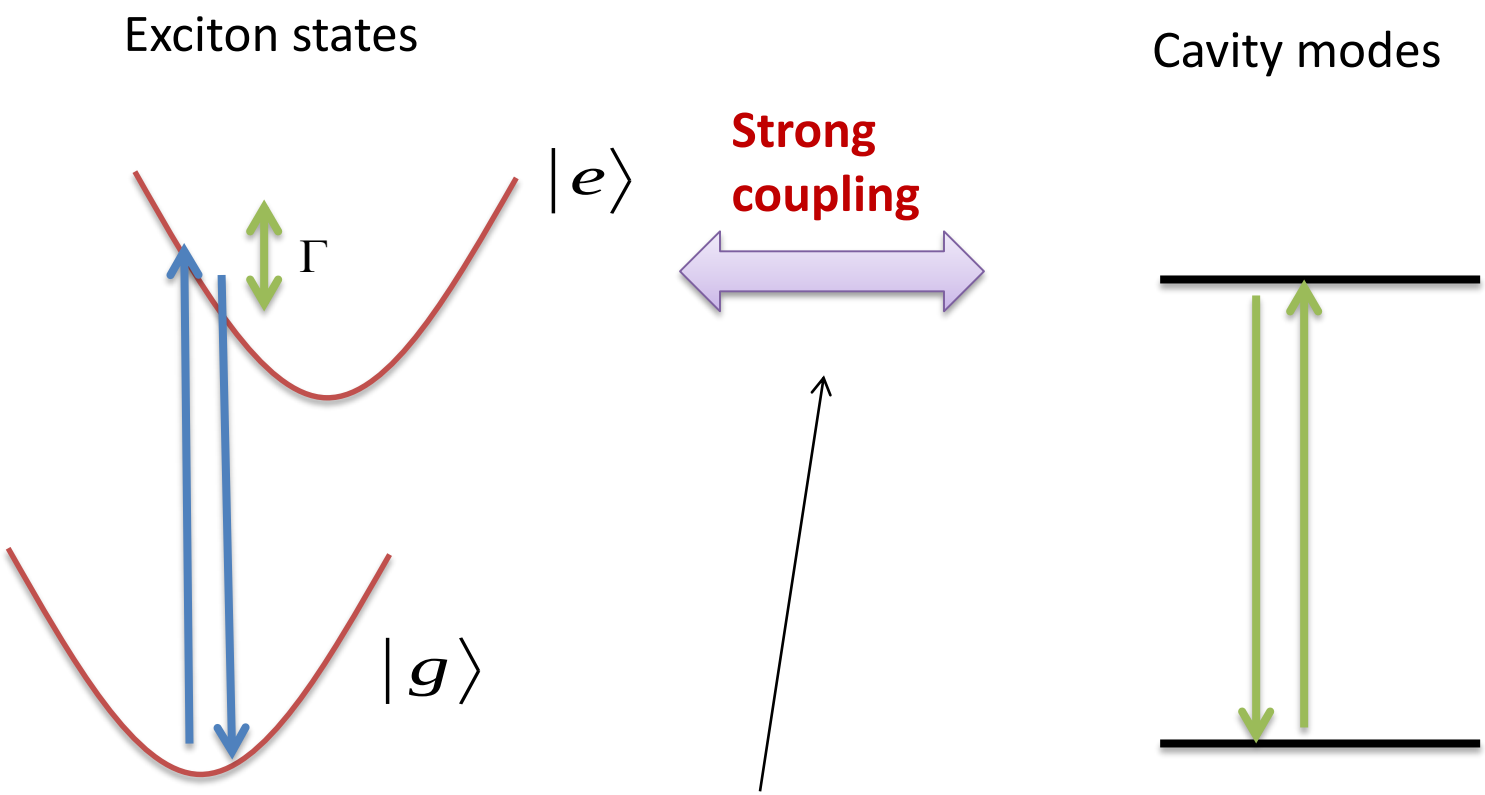
Schematic structure



Dispersion curve



J-aggregates in a cavity



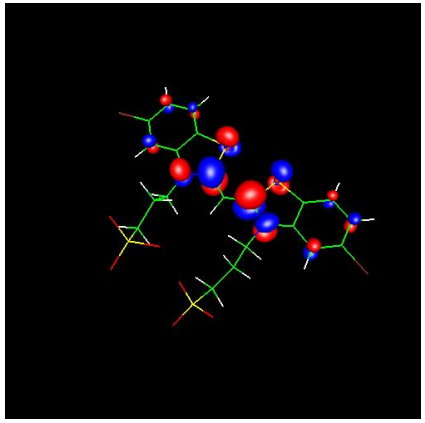
Photon emission/absorption is faster than excited state relaxation

Supplementary information

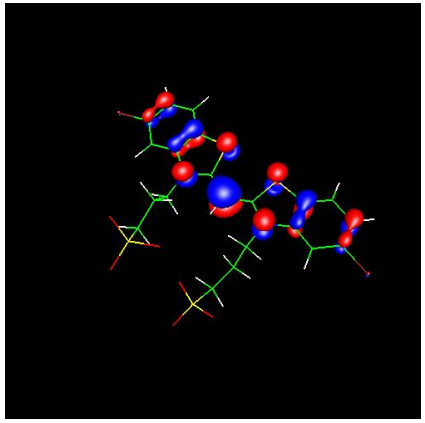
Modeling molecular aggregates

Intramolecular excitations

LUMO

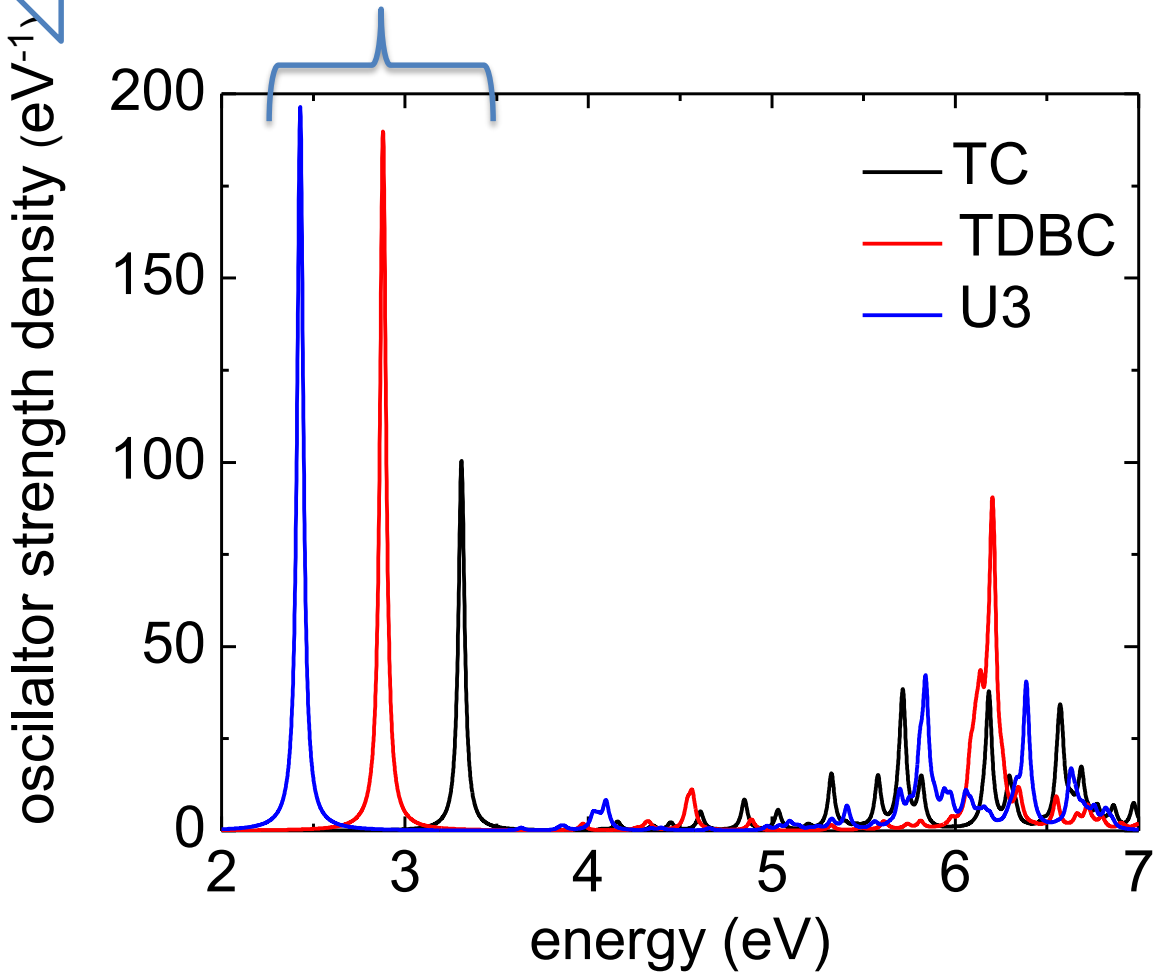


HOMO



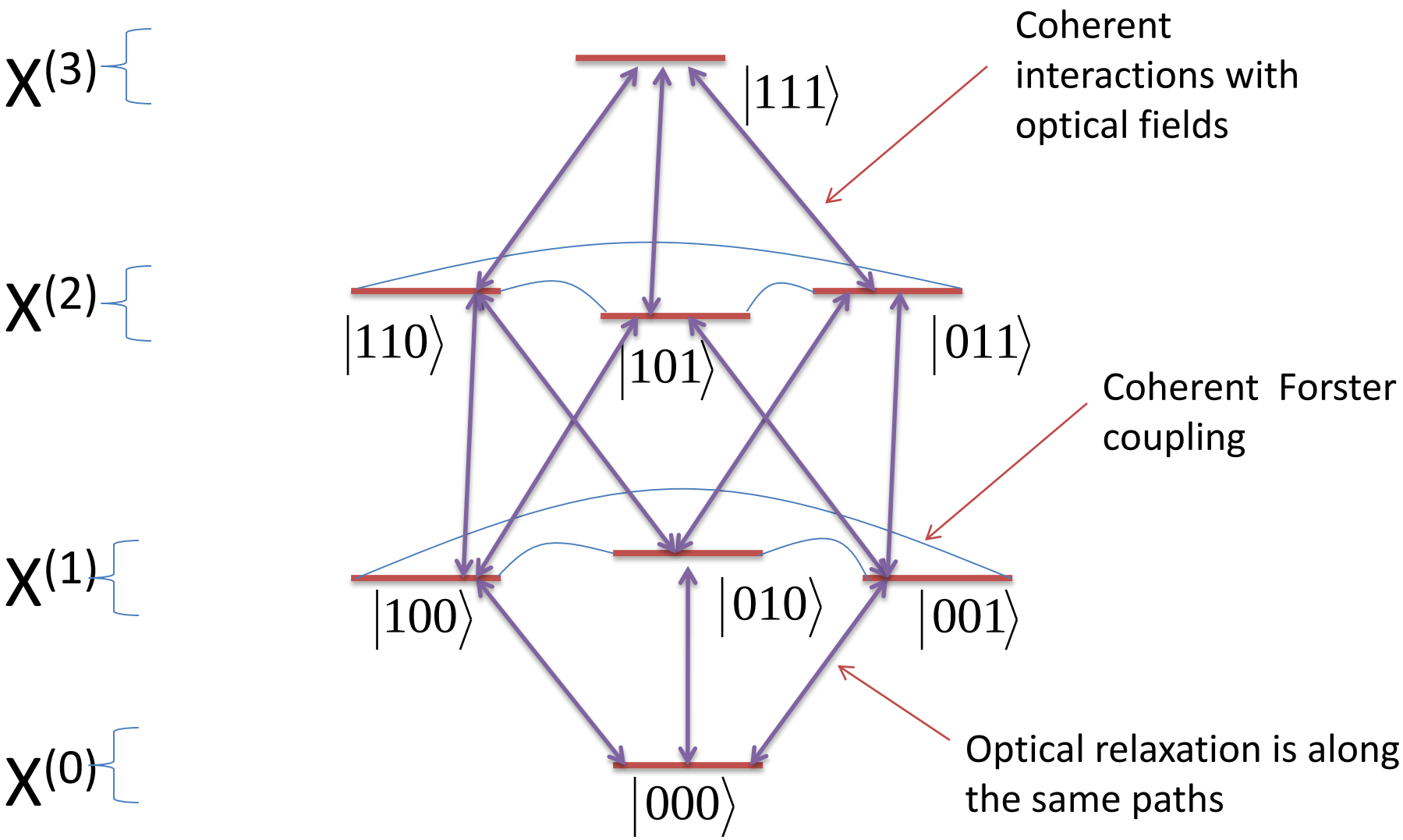
> 98% HOMO → LUMO

- Hybrid functional PBE0
- Triple-ζ basis set
- Polarizable environment - COSMO

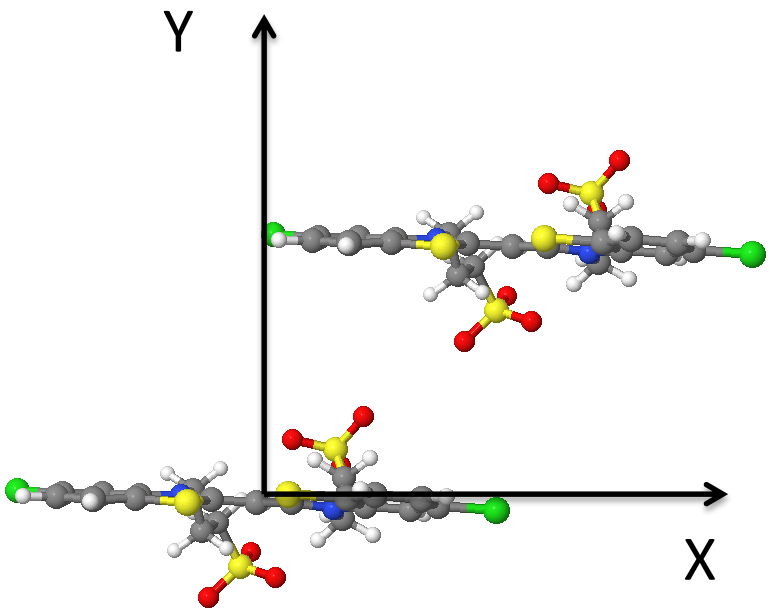


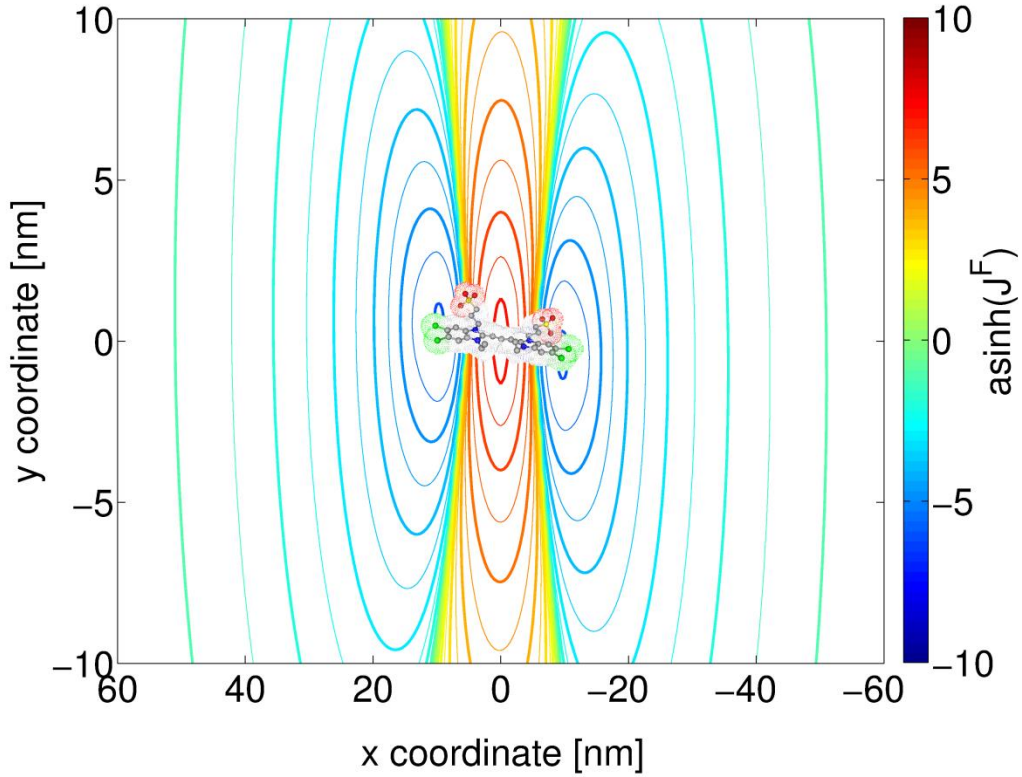
Exciton states

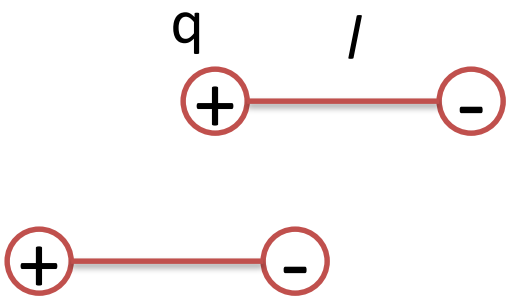
Three 2-level molecules, site basis



Intermolecular couplings







- 2D map of the Forster interaction computed *ab-inito* and fitted with an extended dipole model

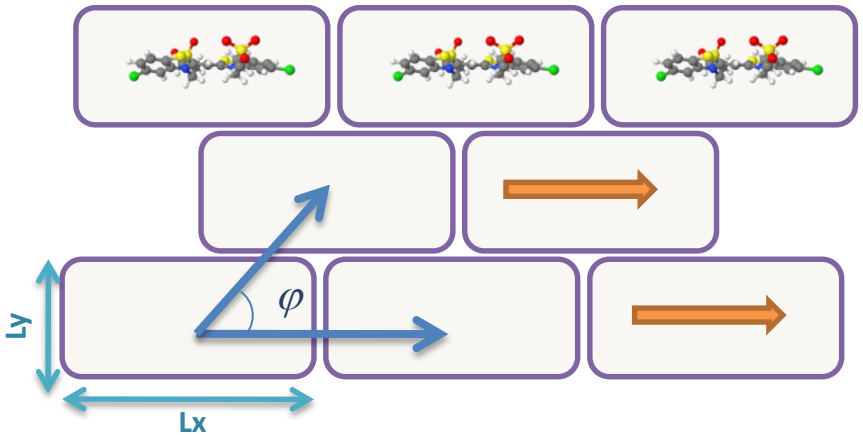
V. Czikklely, H. D. Forsterling, H. Kuhn, Chem. Phys. Lett. **6** , 207, (1970)

Molecular monolayer

Fitting lattice structure to J-band shift

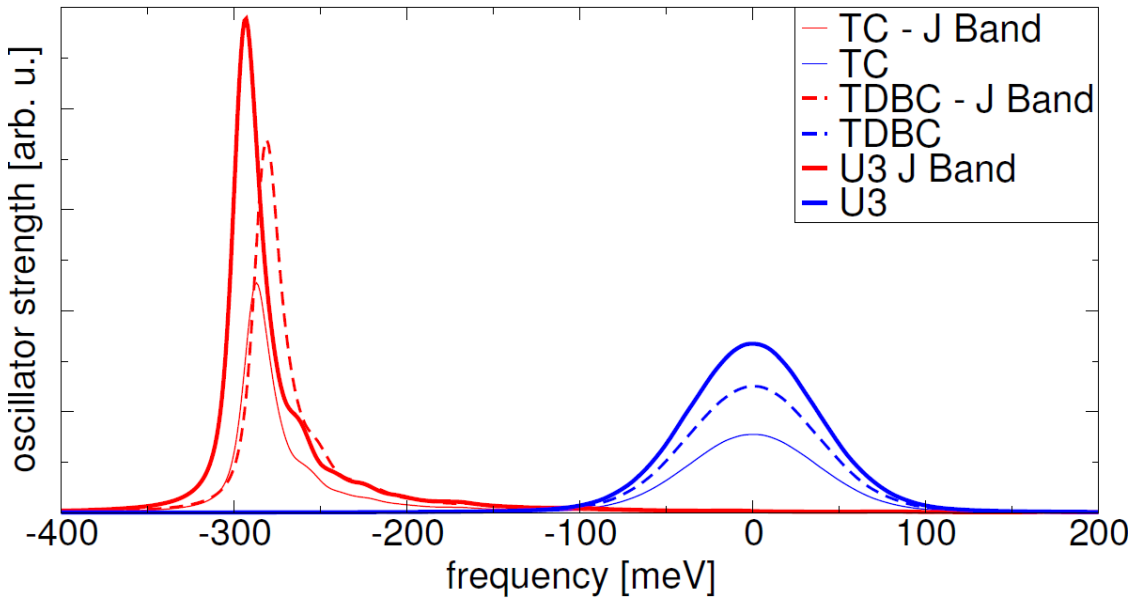
- Ly is varied
- Lx is fixed = length of the molecule + 2*VdW radii

Brickstone model

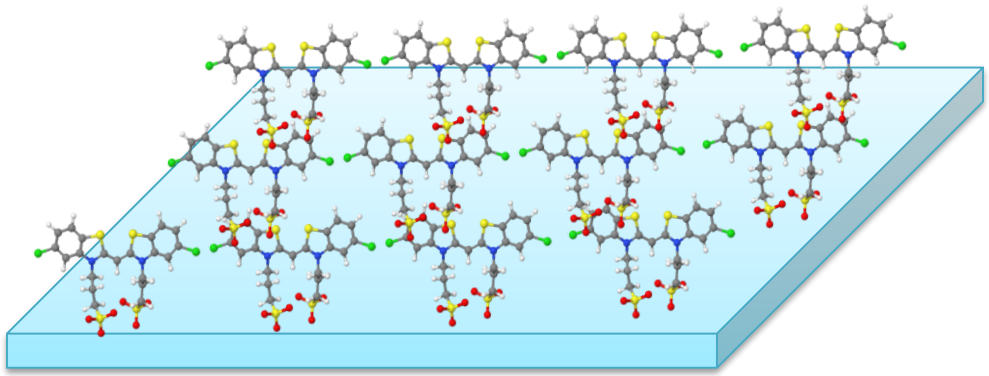


D. Möbius and H. Kuhn, J. Appl. Phys. **64**, 5138 (1988)

J-band shift



Dynamic and static disorder



Fluctuations of molecular transition frequencies and transition dipoles

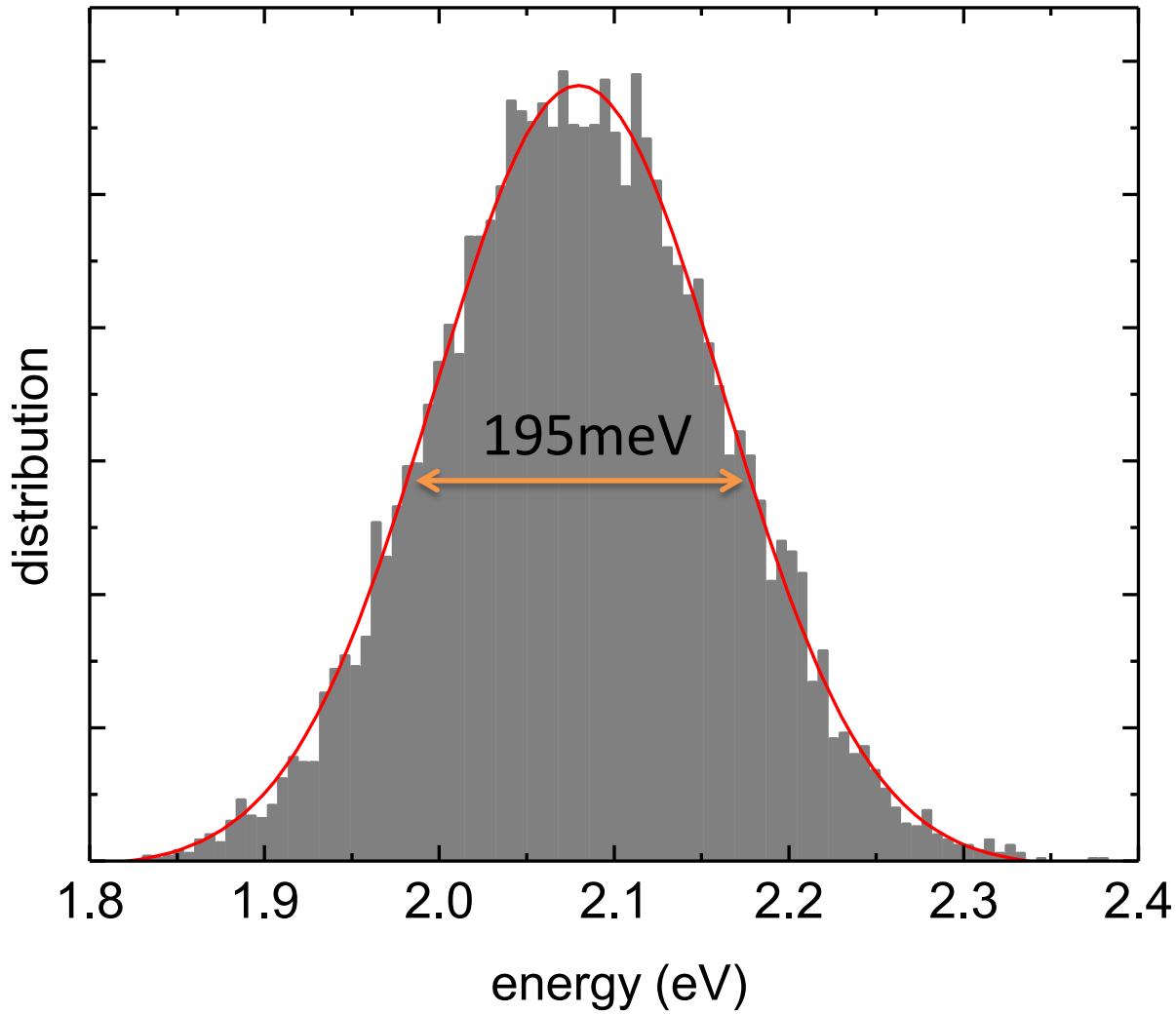
$$\Omega_k(t) \quad \boldsymbol{\mu}_k(t)$$

Slower that exciton dynamics = static disorder

Faster that exciton dynamics = dynamic disorder

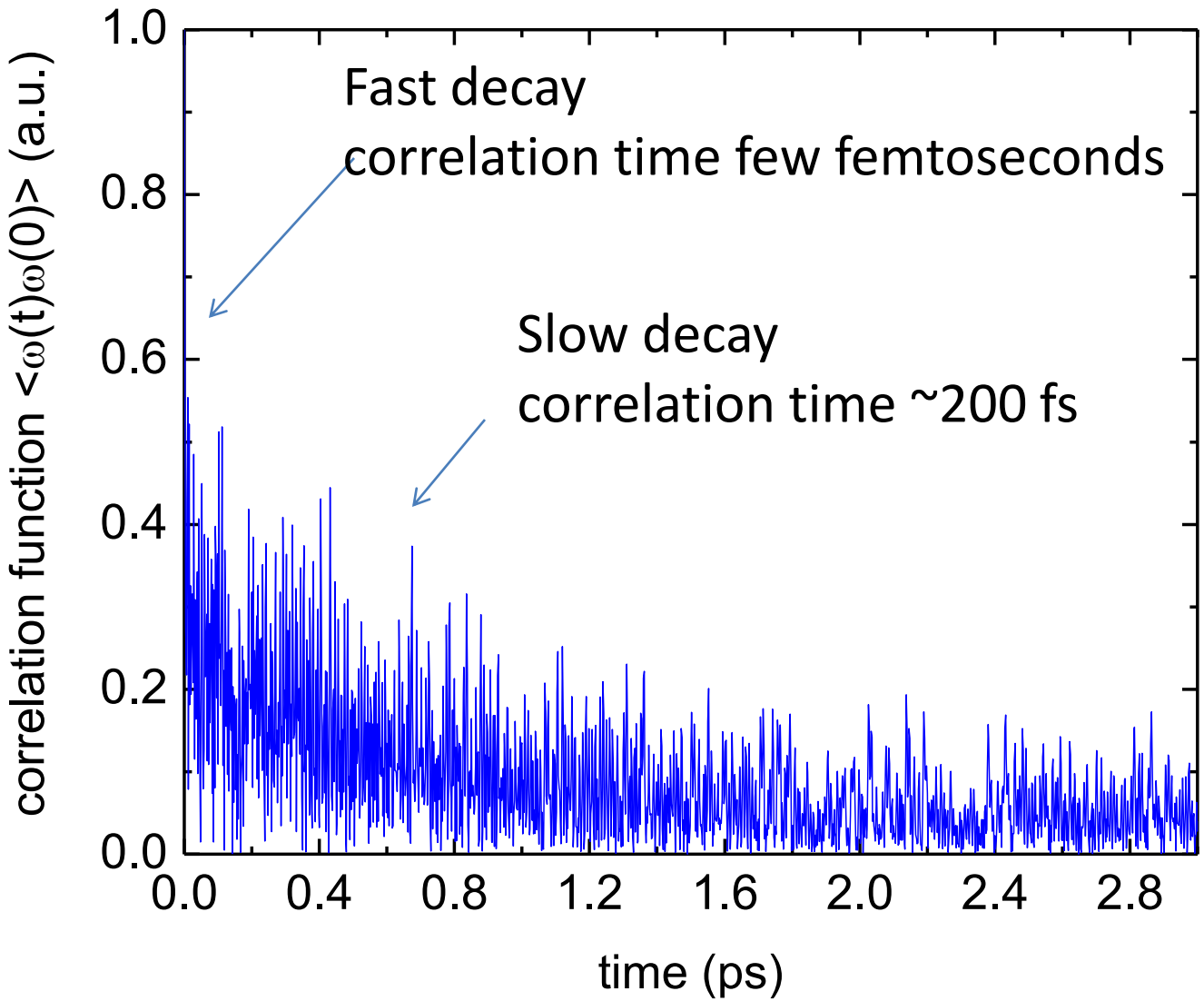
Example: dynamic disorder

Fluctuations of lowest electronic transition in DATT crystal computed with MD/TDDFT



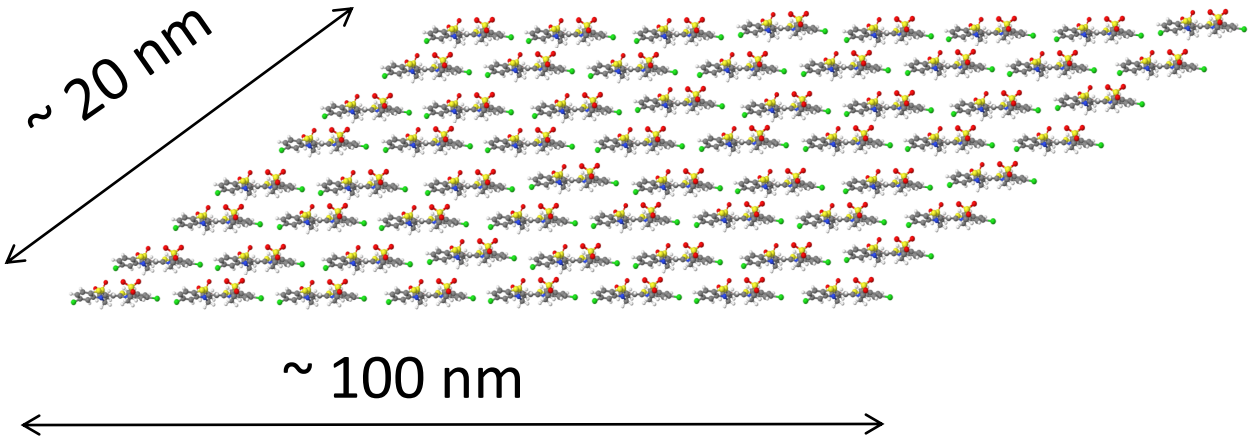
Example: dynamic disorder

Two-times correlation function



Packing structure

About 2000 molecules



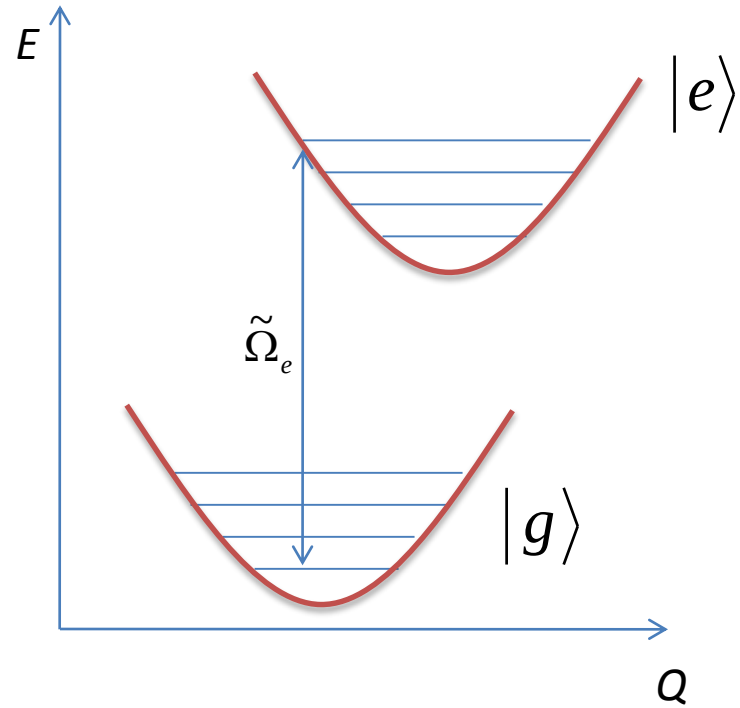
- Monte-Carlo time propagation of exciton wave function on a lattice
- Haken-Reneker-Strobl model for coupling to the environment
- Phenomenological parameters: thermal noise, lattice imperfections

Single molecule Hamiltonian

$$H = \left(0 + \sum_k \omega_k b_{kg}^{+} b_{kg}\right)|g\rangle\langle g| + \left(\Omega_e + \sum_k \omega_k b_{ke}^{+} b_{ke}\right)|e\rangle\langle e|$$

$$b_{ke}^{+} = b_{kg}^{+} + \alpha_k$$

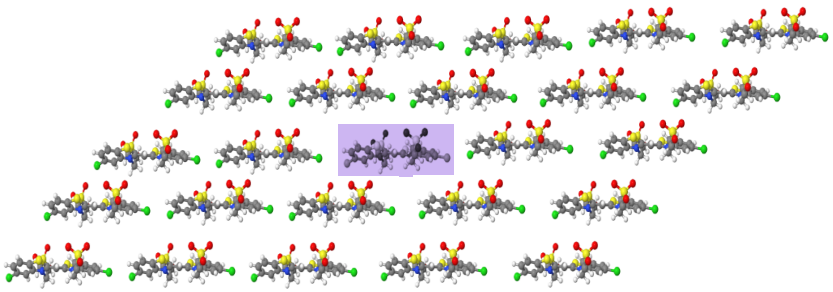
$$H = 0 \cdot |g\rangle\langle g| + \tilde{\Omega}_e |e\rangle\langle e| + \sum_k \omega_k b_{kg}^{+} b_{kg} + \underbrace{\sum_k \lambda_{ke} |e\rangle\langle e| \left(b_{kg}^{+} + b_{kg}\right)}_{\text{noise}}$$

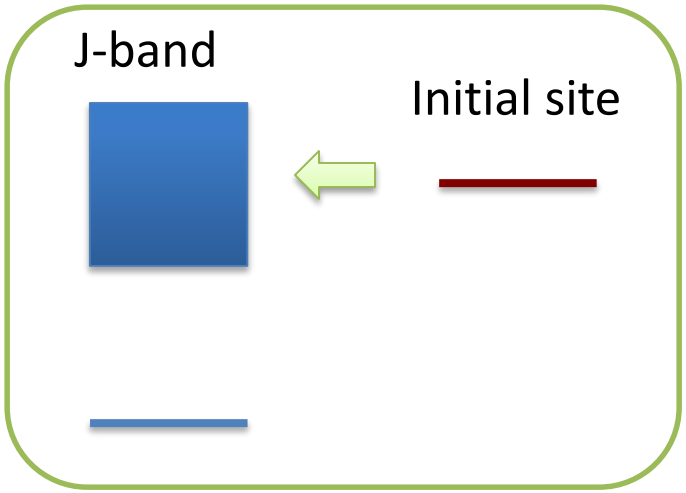


- Two-level system
- Parabolic approximation
- No phonon thermalization

Exciton dynamics

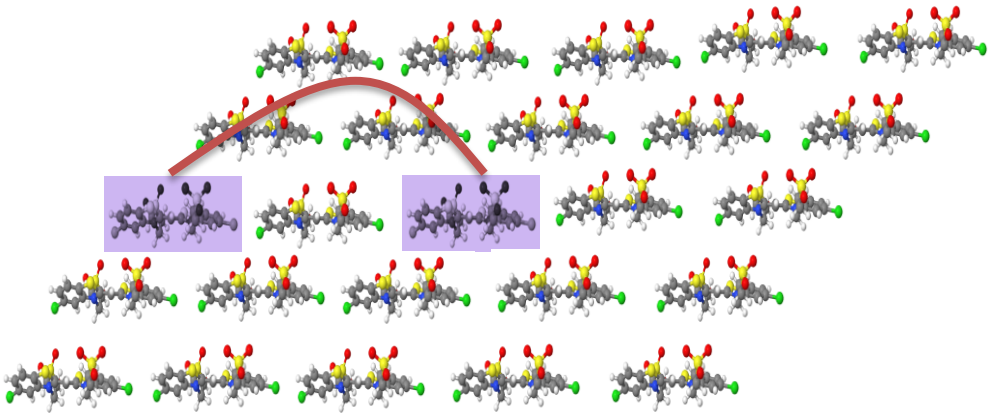
Initial conditions





Exciton dynamics

Coherences



- Coherence = two-sites one-time correlation functions

Exciton dynamics

Coherences

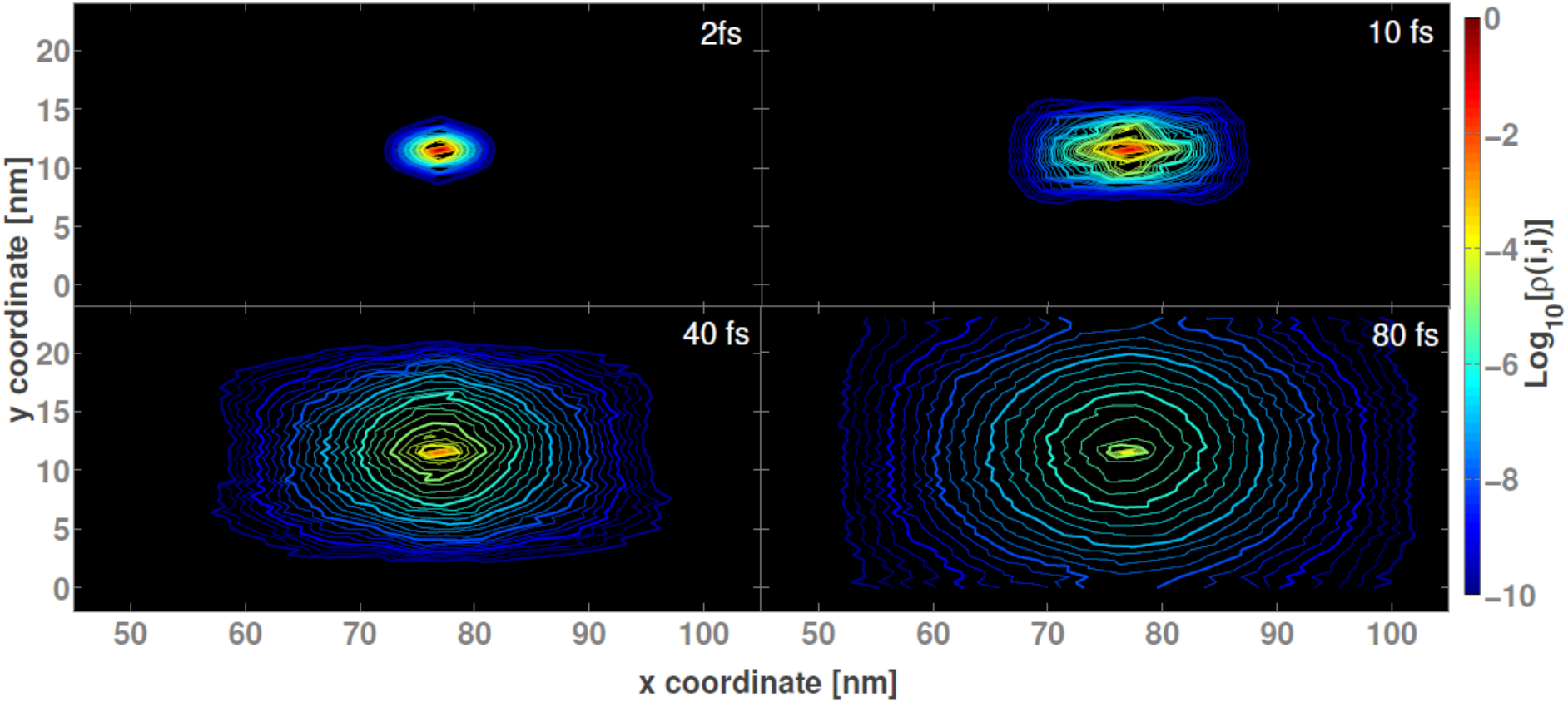
Central site - current site correlations

Central site

$$\rho(t) = \begin{pmatrix} \rho_{00} & \rho_{01} & \rho_{02} & \cdots \\ \cdots & \rho_{11} & \cdots & \\ & & \rho_{22} & \\ & & & \cdots \end{pmatrix}$$

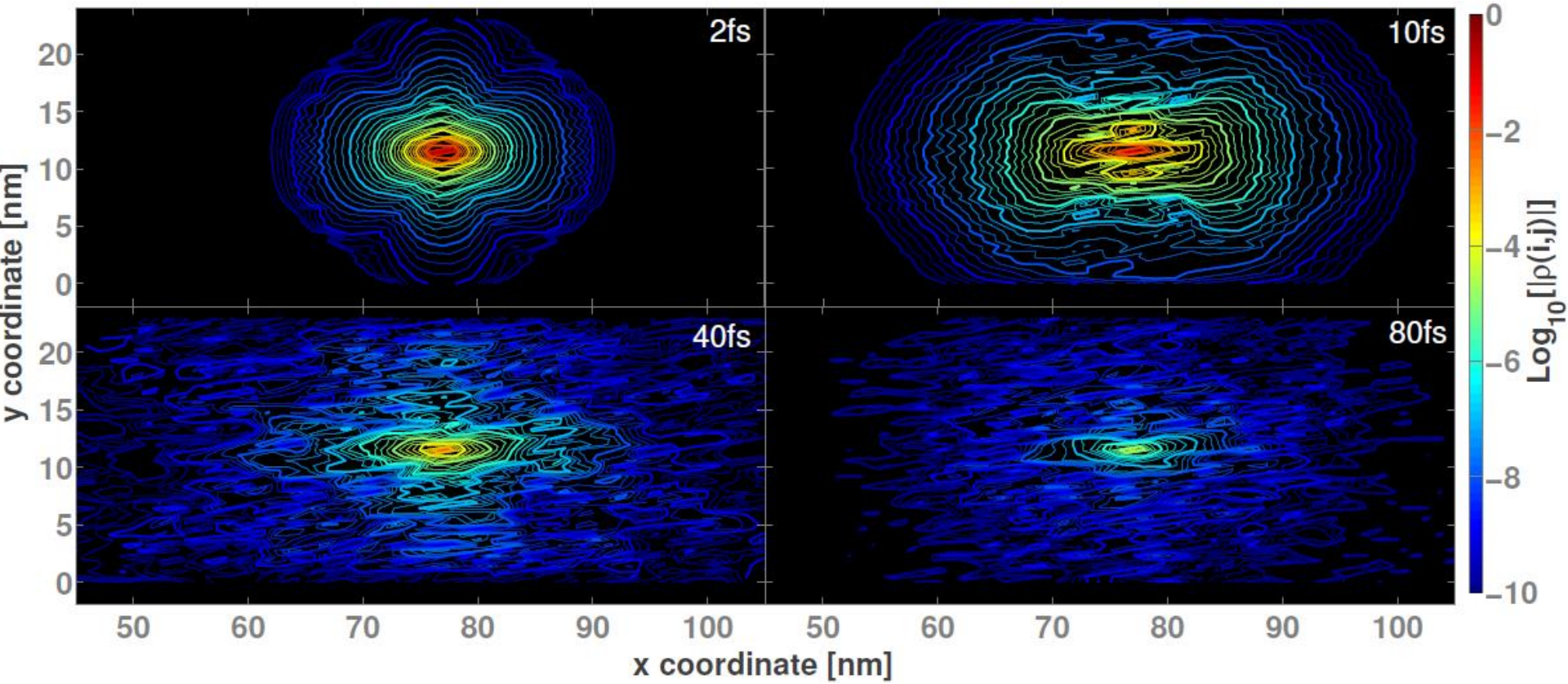
Populations

Exciton population dynamics



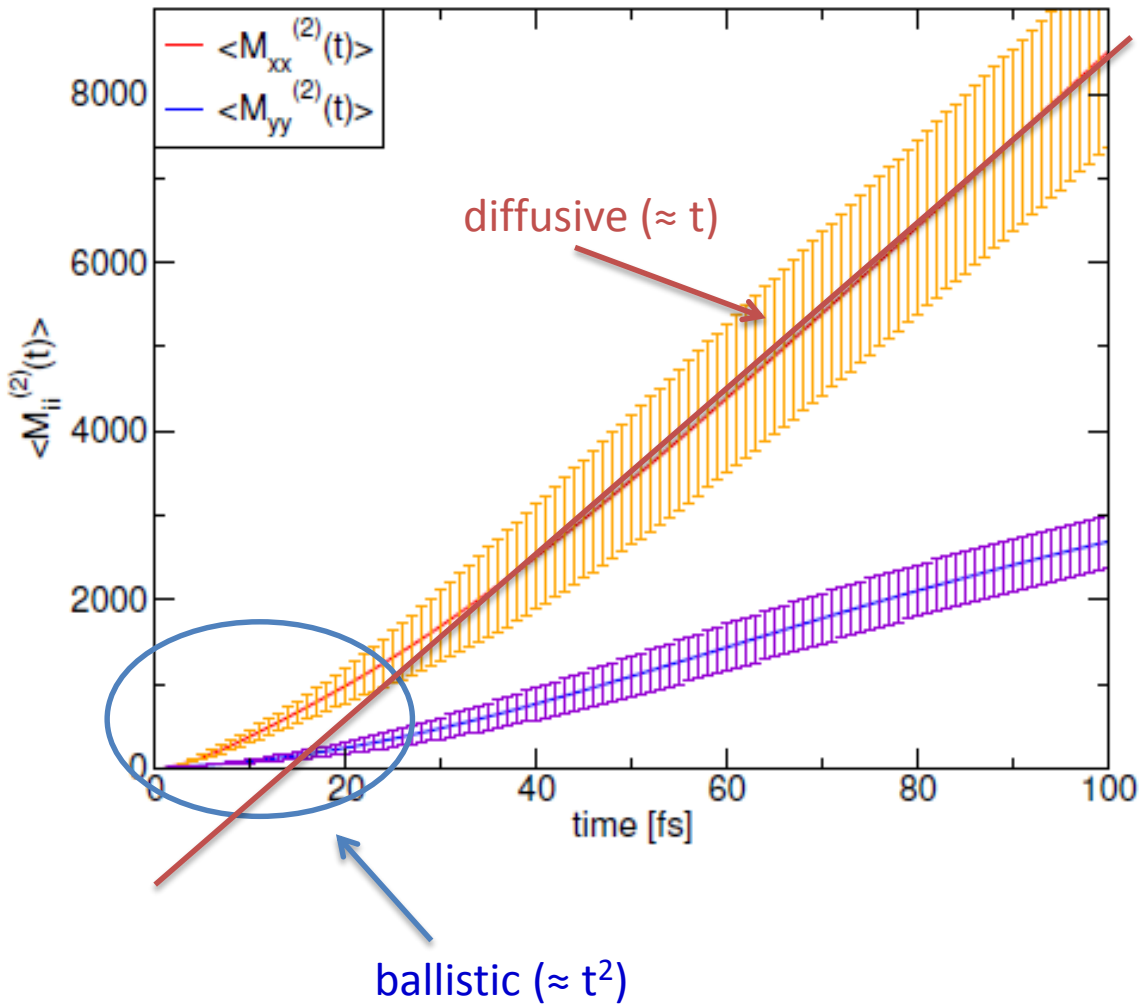
S. Valleau, et. al., *J. Chem. Phys.* 137, 034109 (2012).

Exciton coherence dynamics



S. Valleau, et. al., *J. Chem. Phys.* 137, 034109 (2012).

Ballistic vs. diffusive transport



S. Valleau, et. al., *J. Chem. Phys.* 137, 034109 (2012).