Controlling Structure and Energy Transfer in Liposome Ordered Porphyrin Dimers Studied by Fluorescence-Detected 2D Electronic Spectroscopy

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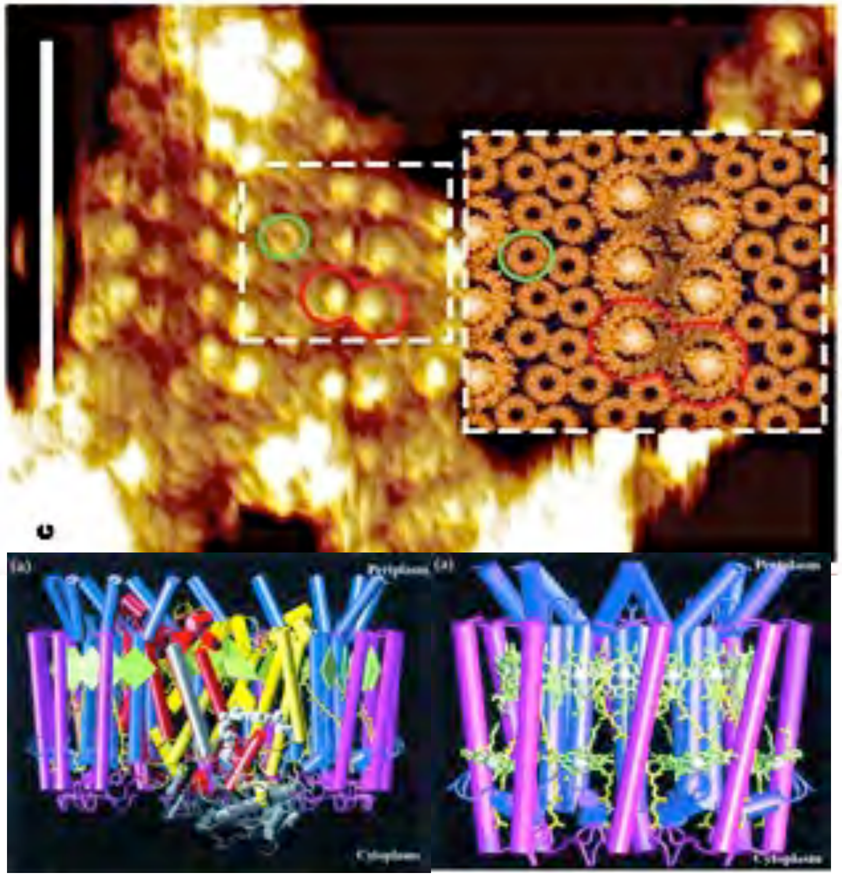
Workshop on Evolution and Control of Complexity:
Key Elements Using Sources of Hard X-Rays
October 11 - 13, Advanced Photon Source, Argonne National Lab

Energy transfer in light-harvesting units

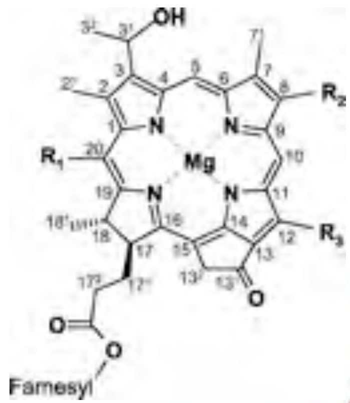


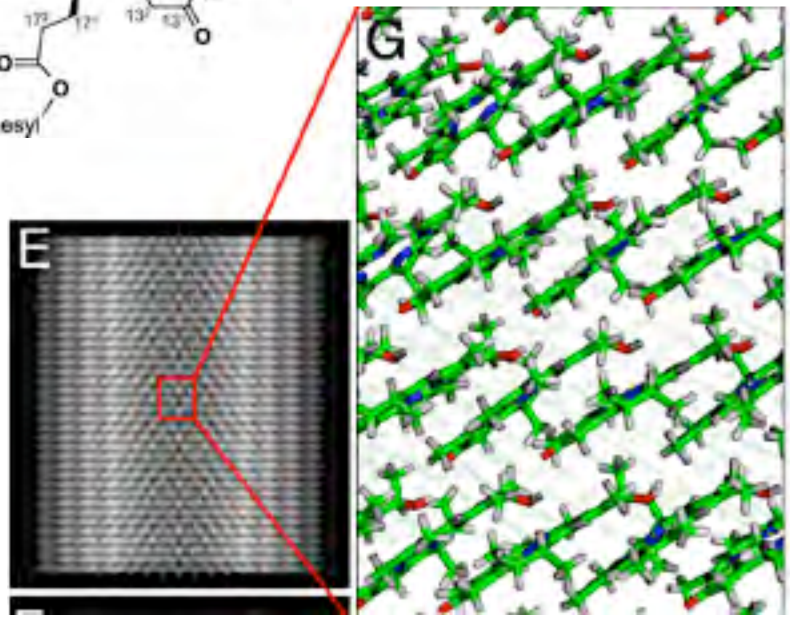
AFM images (top) of LH1 and LH2 (bottom) in *purple bacteria*

Svetlana Bahatyrova, et al. *Nature* 2004; **430**, 1058-1062

Hu X et al. PNAS 1998; 95:5935-5941

BChlls in chlorosome of green sulfur bacteria mutant.





Ganapathy S et al. PNAS 2009;106:8525-8530

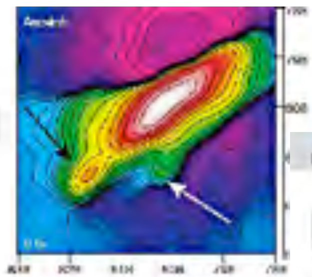
2D electronic spectroscopy for energy transfer dynamics

Engel et al.,
Nature, 446, 782 (2007).

nature

LETTERS

Evidence for wavelike energy transfer through quantum coherence in photosynthetic systems

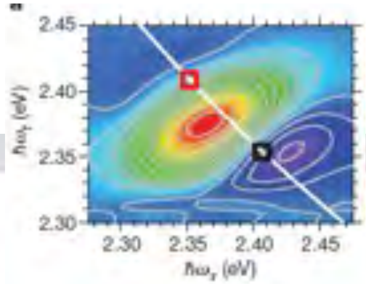


Collini et al.,
Nature, 463, 644 (2010).

nature

LETTERS

Coherently wired light-harvesting in photosynthetic marine algae at ambient temperature



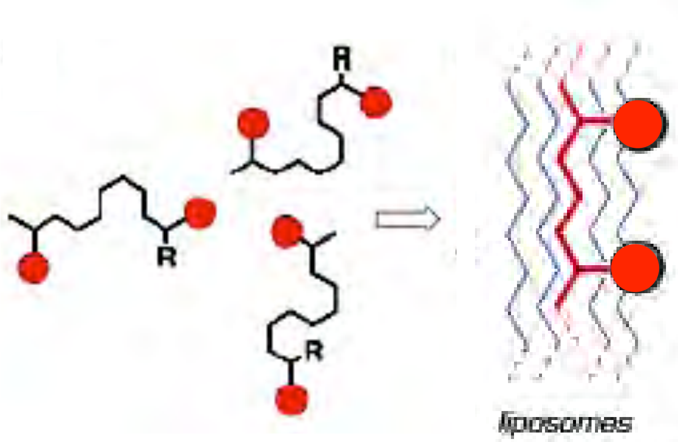
- **Role of protein environment**
- **Coherent vs Incoherent EET?**
- **Relation between transfer mechanism and known structure**

2D ES as an approach to solve supramolecular structure?

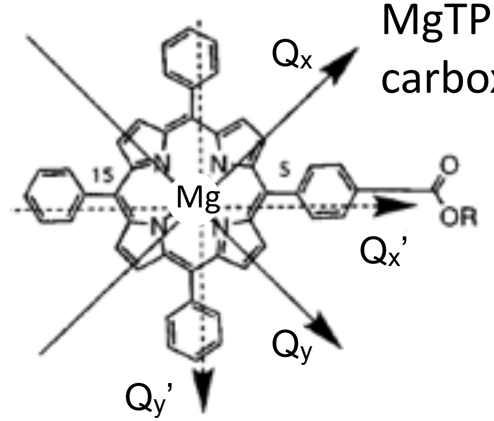
Hard to extract electronic couplings directly from 2D experiments because:

- Line shapes are usually broad due to disorder, and couplings are weak
- Heterogeneity of biological systems lead to spectral dispersion and congestion
- Samples easily photo-degrade

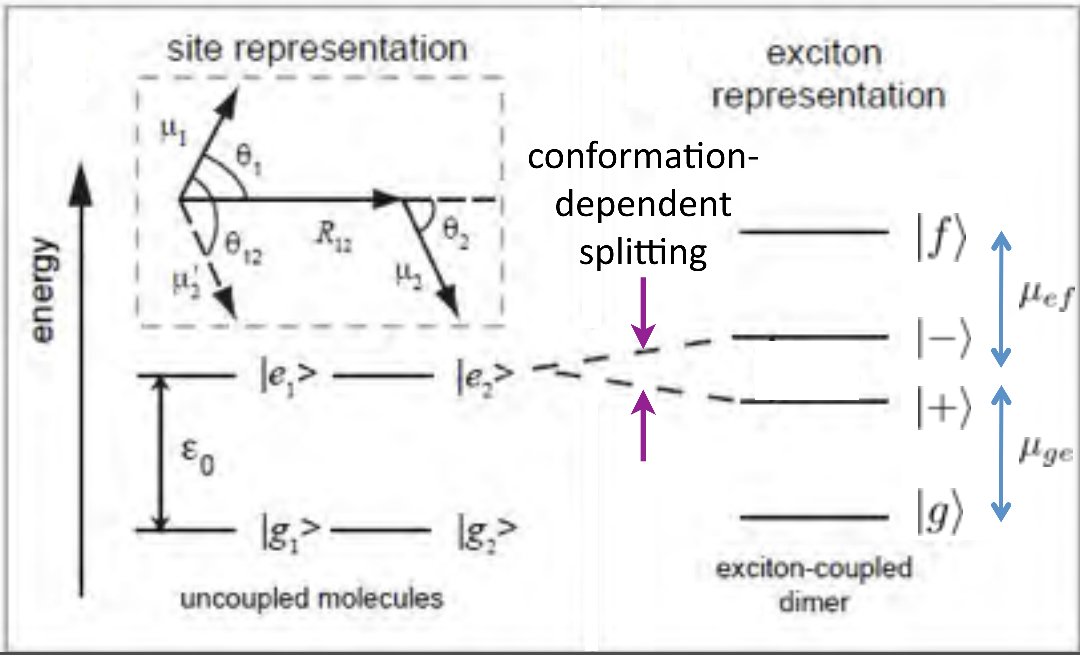
Conformation of exciton-coupled molecular dimers in liposome vesicles



● =



Coupled oscillator model (Kasha): side-to-side ↑↑ blue-shift; end-to-end →→ red-shift



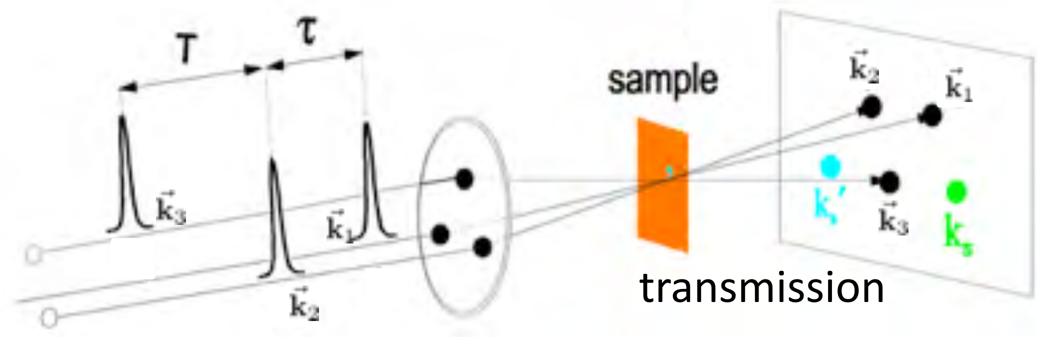
$$I_{\pm} = |\mu|^2 \left(1 \pm \cos\theta_{12}\right)$$

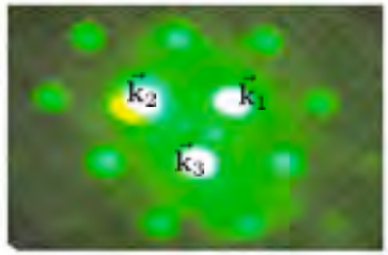
"Imposing order upon random coiled, long chain 1,n-diol TPP carboxylate esters by chain alignment within liposomes,"
MacMillan & Molinski, *Angew. Chem. Int. Ed.* **2004**, 43, 5946.
Matile et al., *JACS*, **1996**, 118, 5198.

2D spectroscopy experimental setups

http://www.cchem.berkeley.edu/grfgrp/research/index.html

Four-wave mixing (FWM)





Fleming group

$$\vec{k}_S^{RP} = -\vec{k}_1 + \vec{k}_2 + \vec{k}_3$$

Photon echo signal

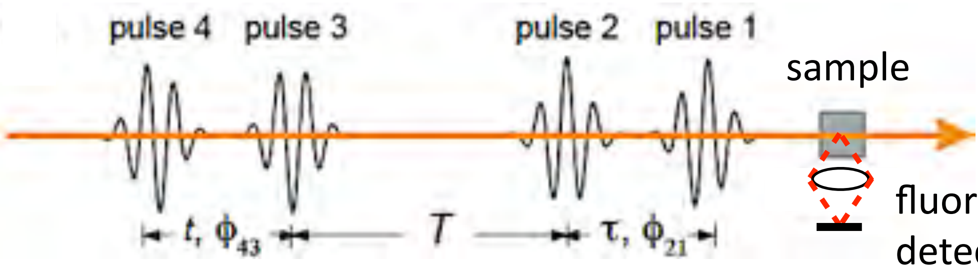
$$\vec{k}_S^{NRP} = \vec{k}_1 - \vec{k}_2 + \vec{k}_3$$

'Virtual echo' signal

Third-order polarization: $\mathbf{P}(t) = \langle \hat{\mu}(t) \rangle \quad \mathbf{P}^{(3)}(t) = \langle \mu(t)\rho^{(3)}(t) \rangle$

Phase-Modulation Electronic Coherence Spectroscopy (PM-ECS)

Collinear geometry:



P. F. Tekavec, G. A. Lott, A. H. Marcus, *J. Chem. Phys.* **2007**, *127*, 214307-1-21.

$$S_S^{RP} \sim e^{-i(\phi_{43} - \phi_{21})}$$

$$S_S^{NRP} \sim e^{-i(\phi_{43} + \phi_{21})}$$

Fourth-order excited state population: $A(t) = \langle \hat{A}(t) \rangle \quad \langle \hat{A}^{(4)}(t) \rangle = \langle \hat{A}(t)\rho^{(4)}(t) \rangle \quad A = \sum_e |e\rangle \langle e|$

Advantages of fluorescence-detected 2D PM-ECS

- Detection of fluorescence provides a route to high sensitivity; resonant signals are easily separated from non-resonant background and scattered excitation.

- Phase modulation of excitation pulses, combined with lock-in detection, amplifies weak fluorescence outside of the bandwidth of laboratory noise. This provides a high S/N approach to fully characterize phase-coherent 2D optical spectra.

- Most important: fluorescence allows for the selective detection of nonlinear optical coherence pathways that result in excited population on specific states. This significantly reduces spectral congestion and enhanced resolution, conferring more accurate structural and dynamical characterization of exciton-coupled systems.

PM-ECS vs FWM response functions

FWM: $\mathbf{P}^{(3)}(t) = \langle \mu(t)\rho^{(3)}(t)\rangle$

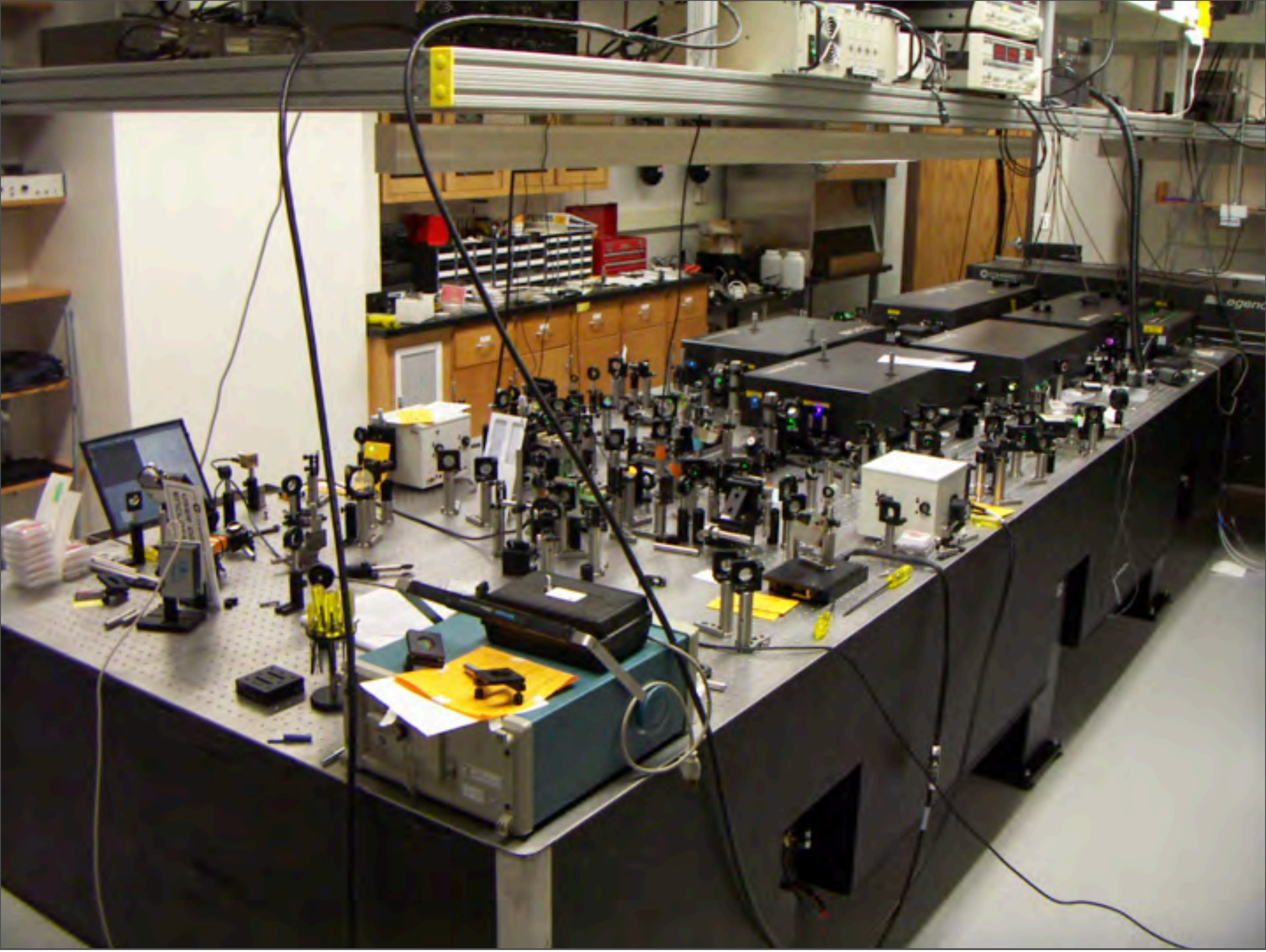
$$S^{(3)}(t_3,t_2,t_1) \equiv \left(\frac{i}{\hbar}\right)^3 \langle \hat{\mu}(t_3+t_2+t_1+t_0)[\hat{\mu}(t_2+t_1+t_0),[\hat{\mu}(t_1+t_0),[\hat{\mu},\hat{\rho}(t_0)]]]\rangle$$

= 8 terms, all contribute

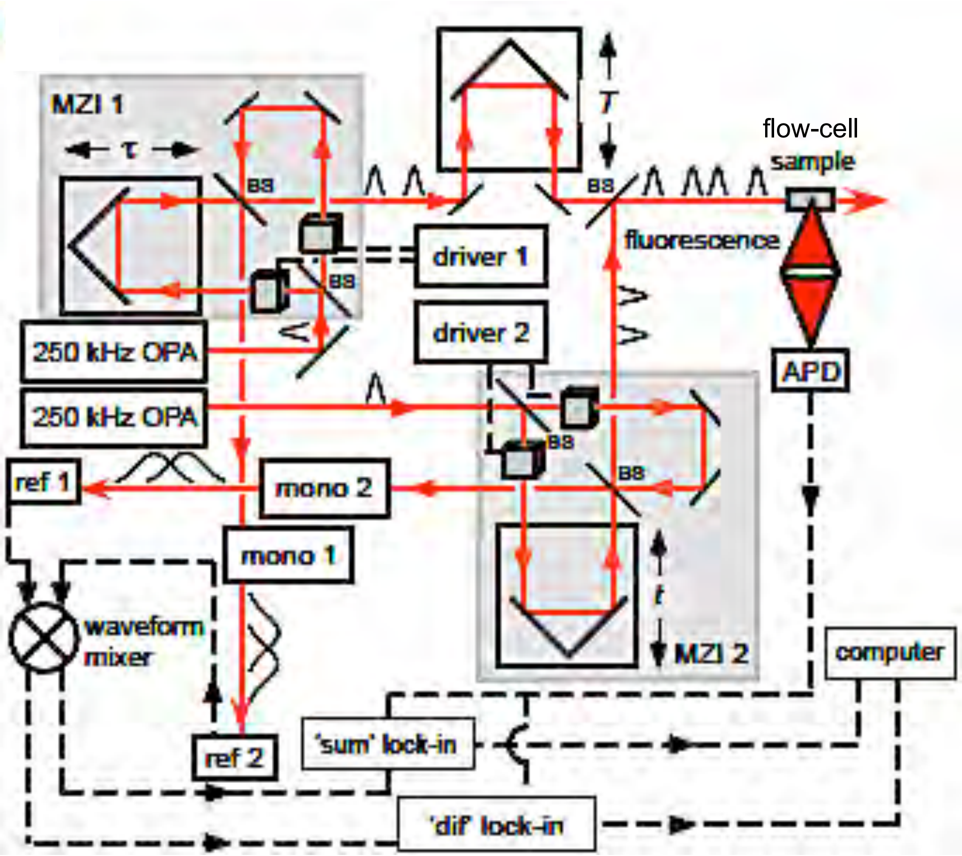
PM-ECS: $\langle \hat{A}^{(4)}(t)\rangle = \langle \hat{A}(t)\rho^{(4)}(t)\rangle$

$$S^{(4)}(t_3,t_2,t_1) \equiv \left(\frac{i}{\hbar}\right)^4 \langle A(t_4+t_3+t_2+t_1+t_0)[\hat{\mu}(t_3+t_2+t_1+t_0),[\hat{\mu}(t_2+t_1+t_0), [\hat{\mu}(t_1+t_0),[\hat{\mu},\hat{\rho}(t_0)]]]]\rangle$$

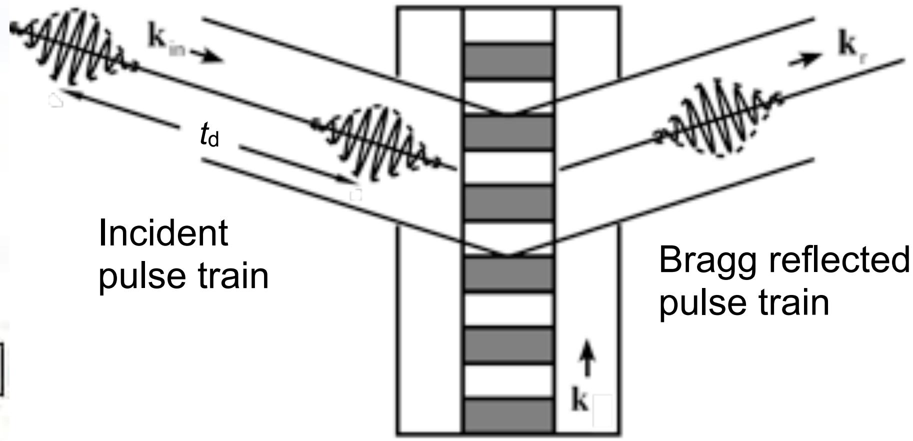
= 16 terms, only 6 contribute



Experimental Apparatus



Bragg cell with continuous acoustic wave



P. F. Tekavec, G. A. Lott, A. H. Marcus, *J. Chem. Phys.* **2007**, *127*, 214307-1-21.

Time-dependence of energy transfer

In the exciton representation, transitions between states are induced by fluctuations of the environment.

-> Energy transfer mechanism will depend on the strength of the electronic coupling, and on the magnitude of the system-bath coupling.

In the membrane system, electronic coupling strength is comparable to $k_B T$ [$E_{split} \sim 5/3\ k_B T$], but it remains to be determined how this compares to the system-bath coupling.

What role do quantum coherences play, and how are they influenced by the bath modes?

In the so-called "intermediate-coupling regime,"

"... excitation moves through space, yet a preferred path can be adopted through wavefunction delocalization and interferences..."

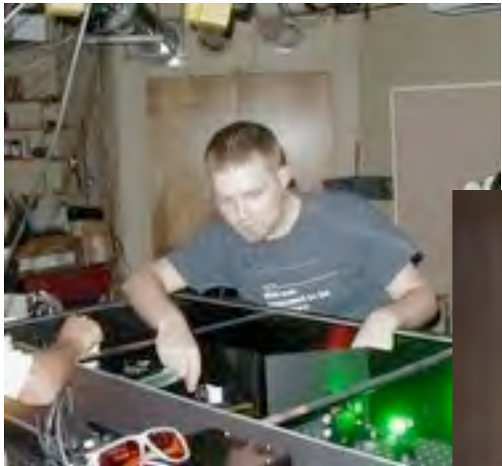
E. Collini and G. D. Scholes, "Coherent intrachain energy migration in a conjugated polymer at room temperature," Science, 323, 369 (2009)

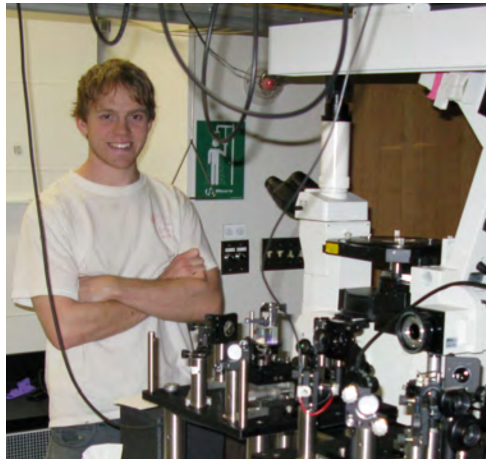
Conclusions

- PM-ECS can resolve exciton splitting and reveal structural information better than linear absorption and FWM -> can distinguish mesoscale structures in membranes.
- Enhanced spectral resolution is due to selective detection of Liouville pathways that generate population on the singly-excited manifold, and exclusion of pathways that lead to population on the doubly-excited state (self-quenching effects of molecular excitons at high densities).
- Short time energy transfer is uphill; quantum effects could be important. Membrane supported chromophore arrays could be a useful platform to examine the influence of of dipole orientation and solvent environment on the mechanisms of energy transport in the intermediate coupling regime.

Acknowledgements

Students and Collaborators:





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