Transient Chemical Structures, March 14th, 2005, Paris

Two-Dimensional Spectroscopy of Electronic Couplings

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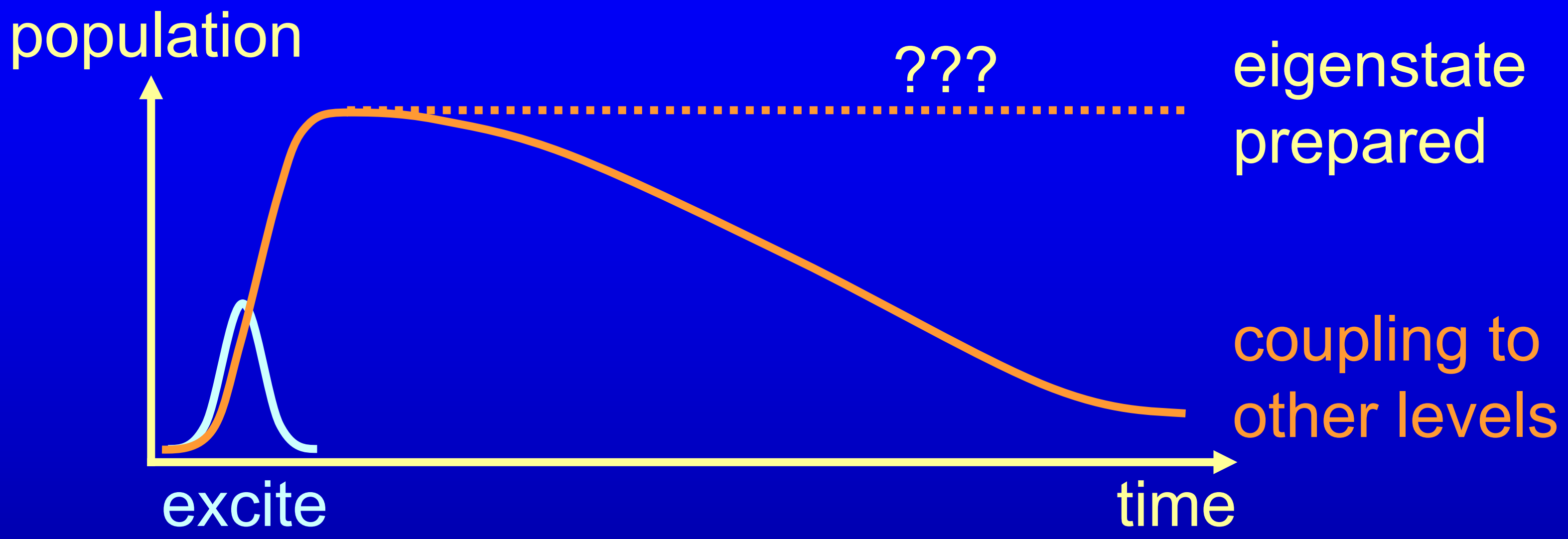
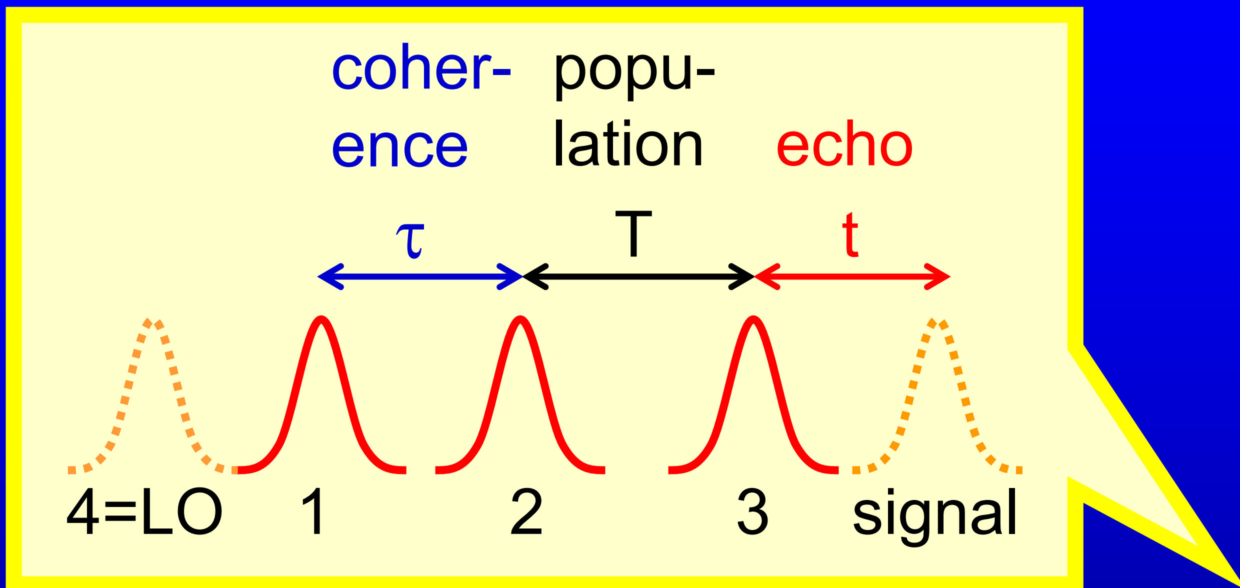
Time for a change

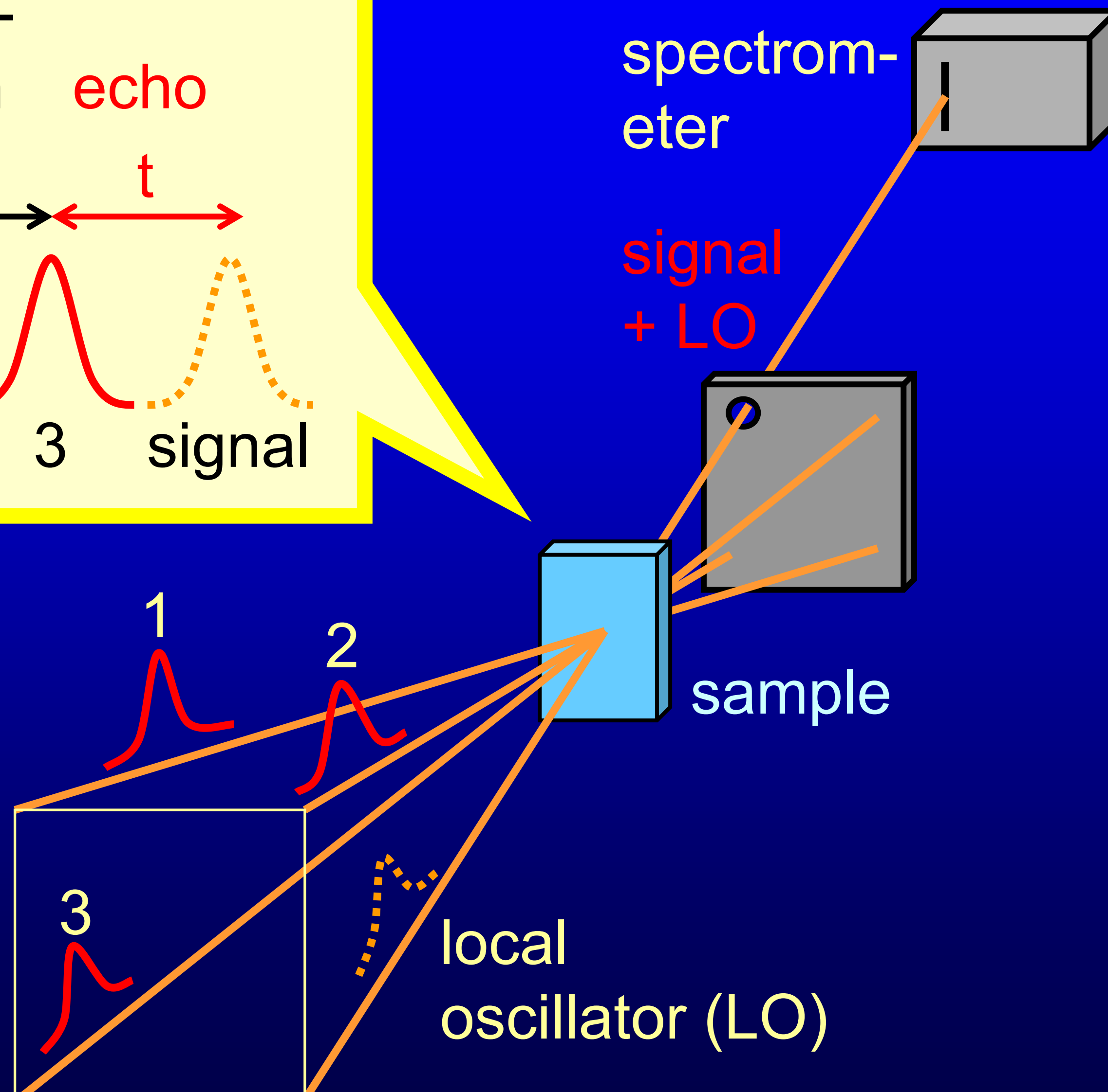


Couplings are the fundamental cause of anything that changes with time

But: Conventional optical spectroscopies in general do not measure couplings

2D Electronic spectroscopy

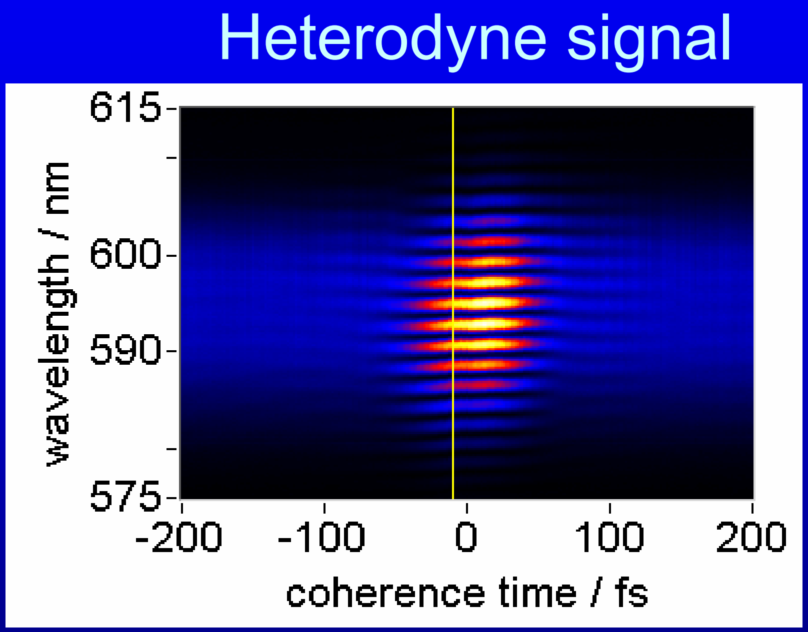


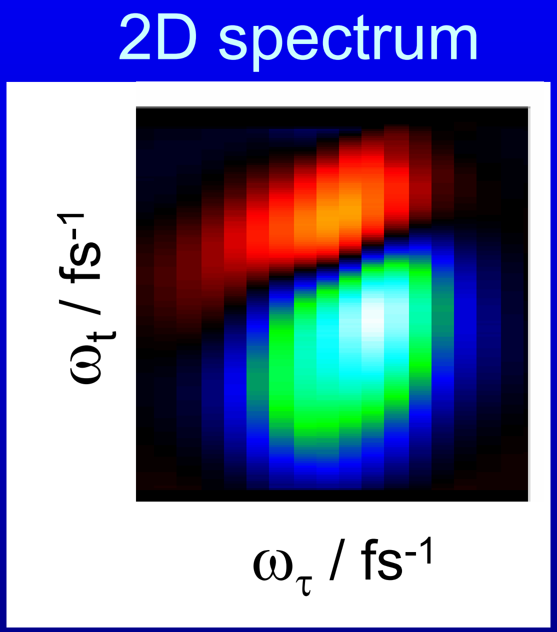


phase-stabilized
frequency-tunable
sensitivity <100 aJ
precision 10 as

Opt. Lett. **29**, 884 (2004)

Data analysis





D. M. Jonas: *Annu. Rev. Phys. Chem.* **54**, 425 (2003)
Brixner et al.: *J. Chem. Phys.* **121**, 4221 (2004)

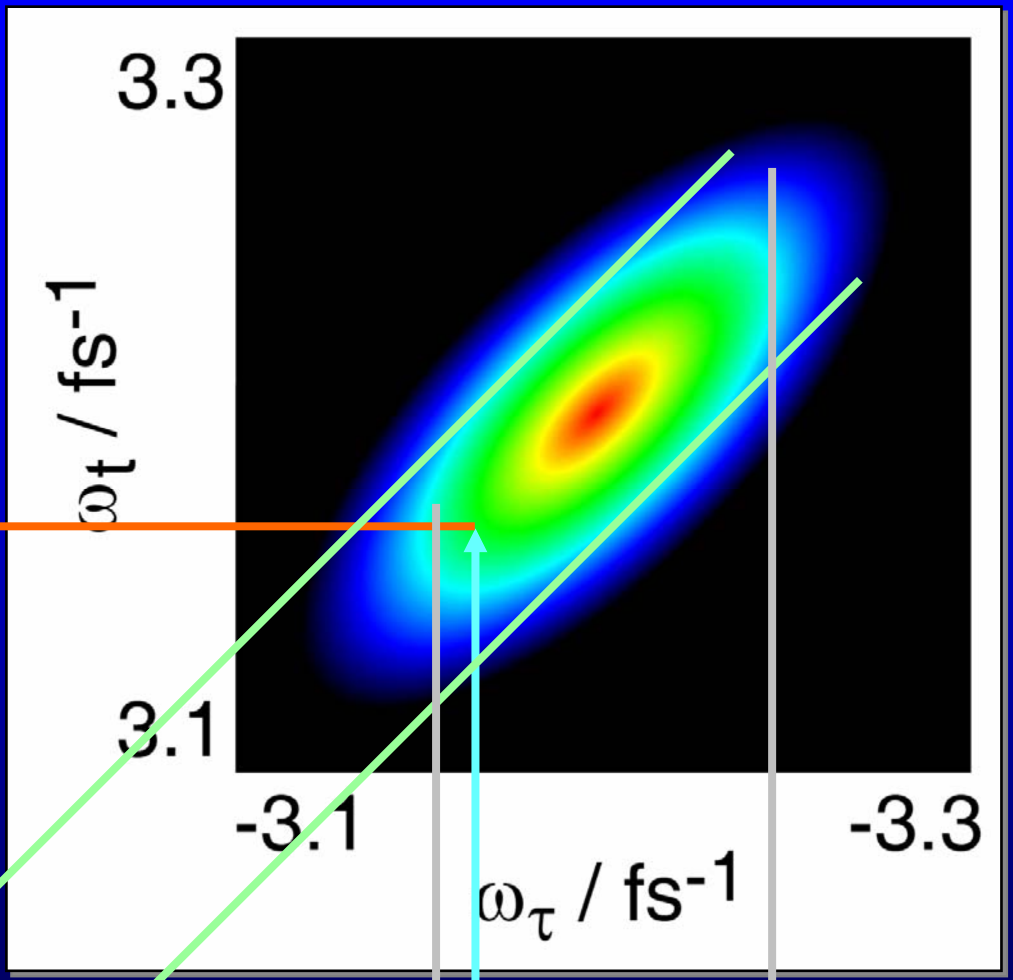
2D Spectrum

"probability distribution"
Re $\{S_2(\omega_\tau, T, \omega_t)\}$

2: wait for population time T

3: emit or bleach at frequency ω_t

here: inhomogeneous system "remembers" excitation after time T



"homogeneous" linewidth

1: excite at frequency ω_τ

"inhom." linewidth

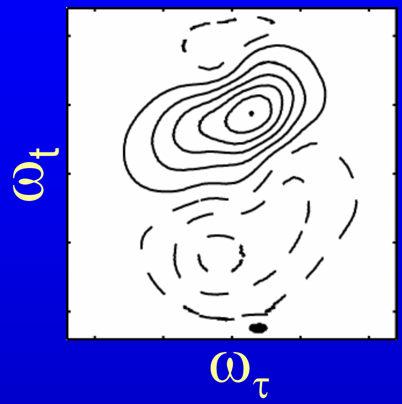
Limiting examples

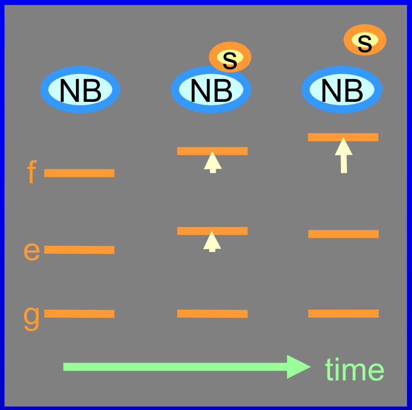
No electronic coupling

Nile Blue monomer:

- three electronic states
- electronic correlations

Opt. Lett. **29**, 884 (2004)
J. Chem. Phys. **121**, 4221 (2004)



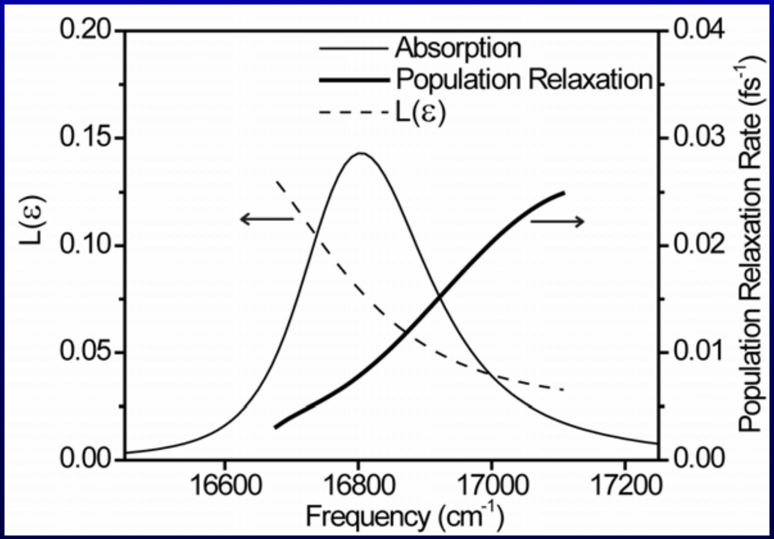


Strong electronic coupling

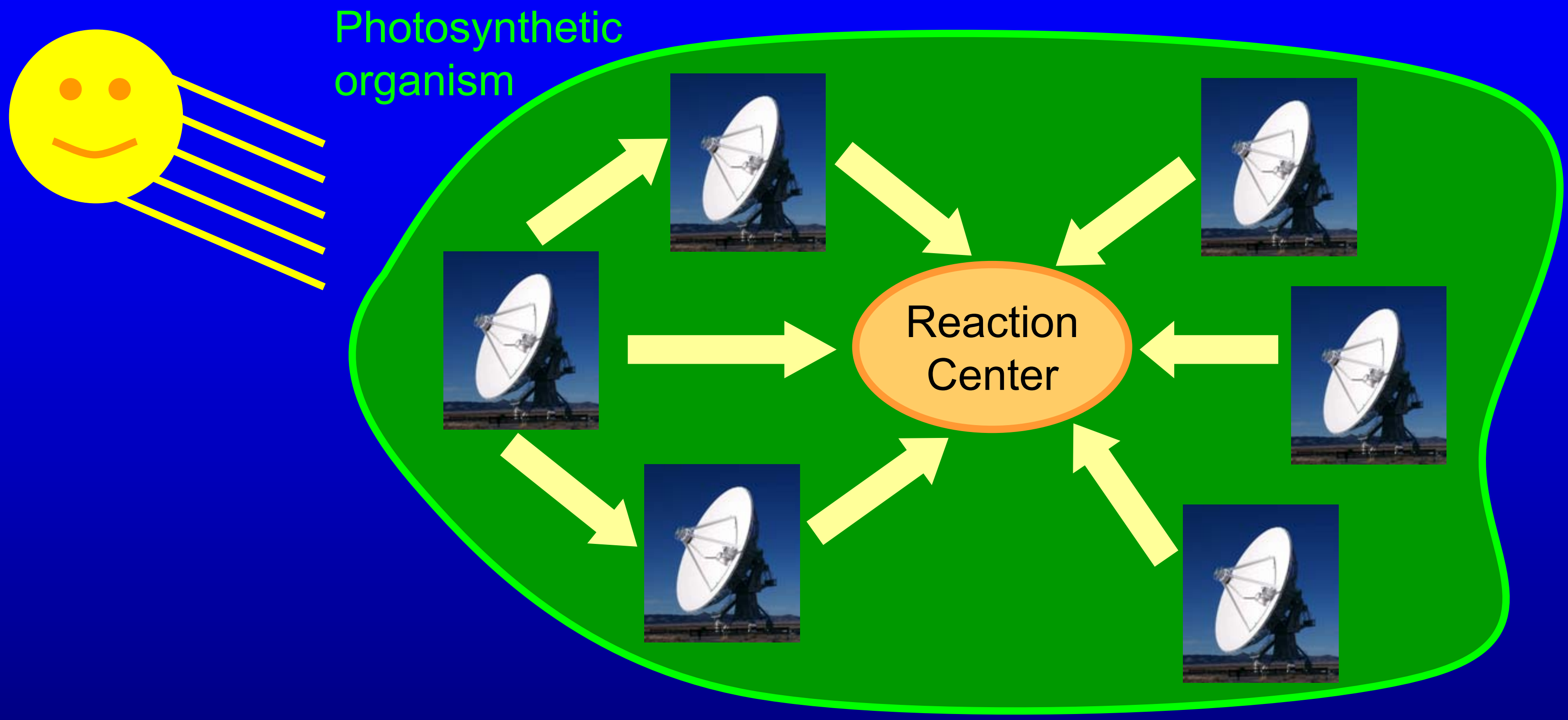
BIC J-Aggregates:

- static/dynamic inhomogeneity
- frequency-dependent relaxation

Ultrafast Phenomena XIV, in press (2005)



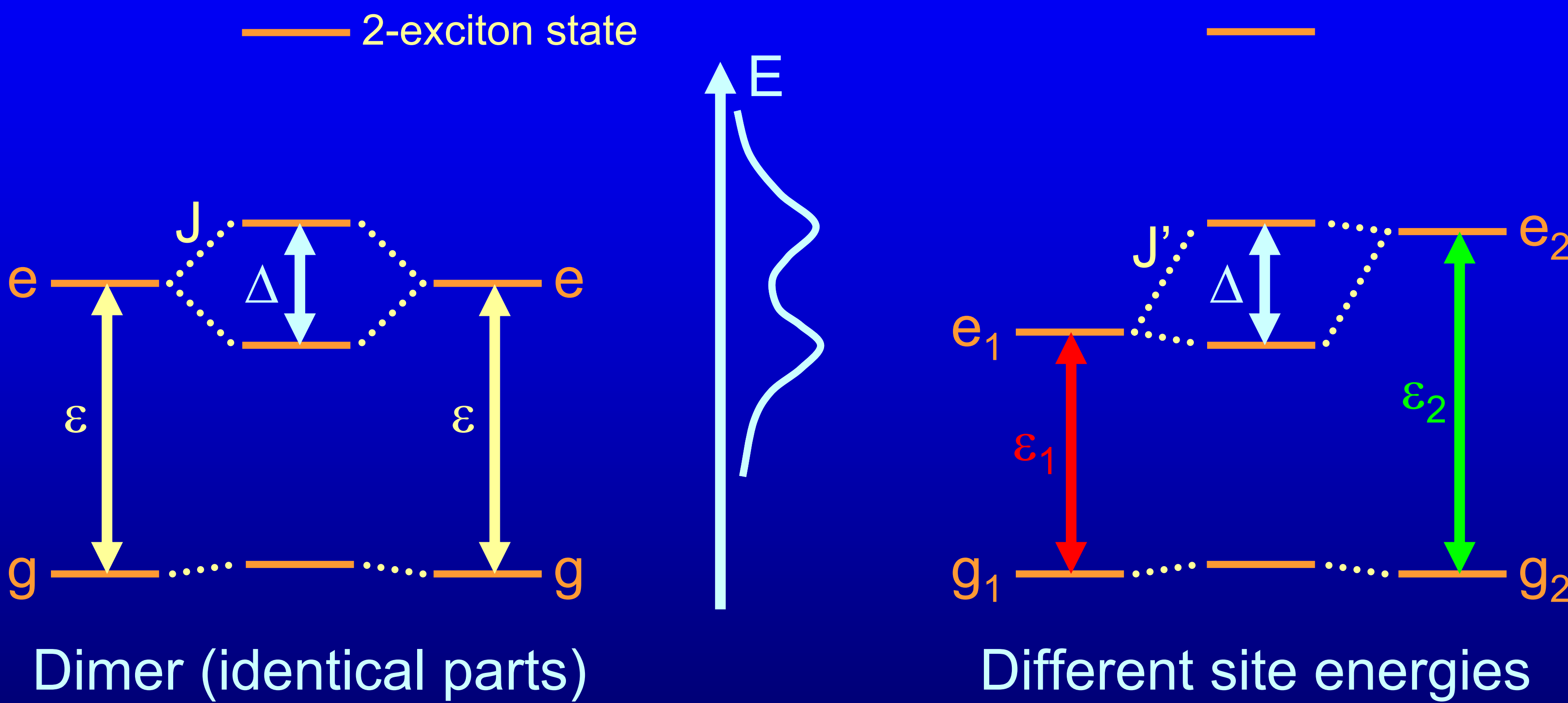
Light-harvesting antennas



Efficiency of energy transport to RC: 100%

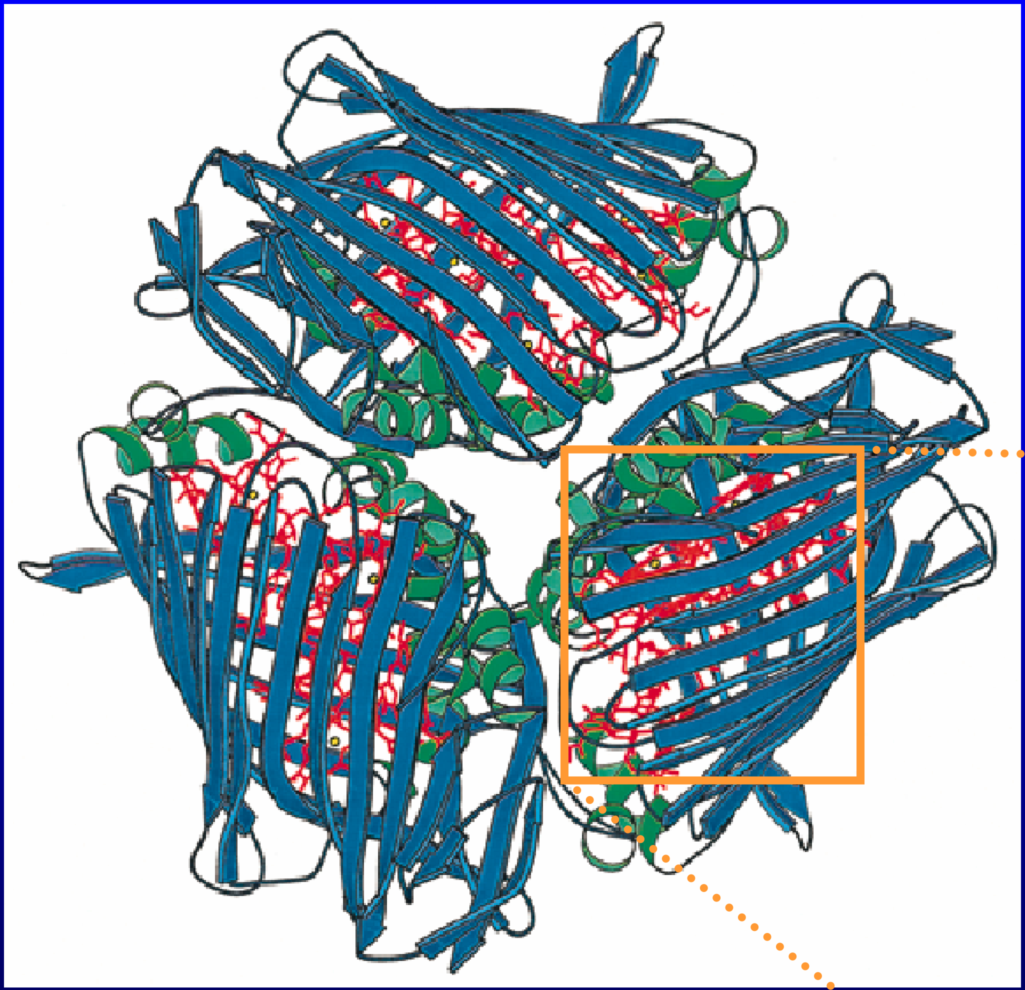
Why?

The chicken & egg problem

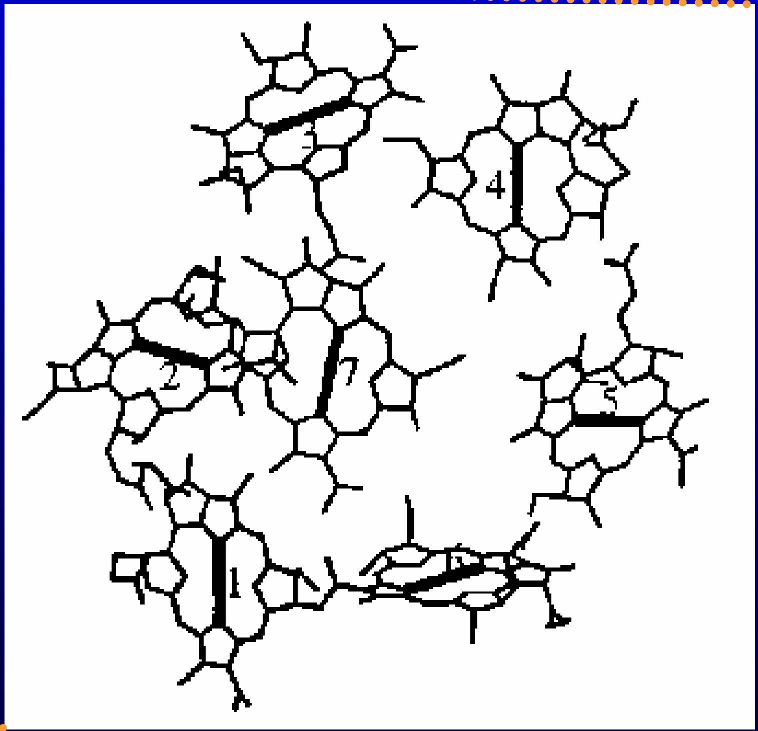


Cannot decide situation / retrieve coupling
just from absorption spectrum

Fenna-Matthews-Olson (FMO)



Light-harvesting complex from green sulfur bacteria *Chlorobium tepidum* containing seven molecules bacteriochlorophyll *a*

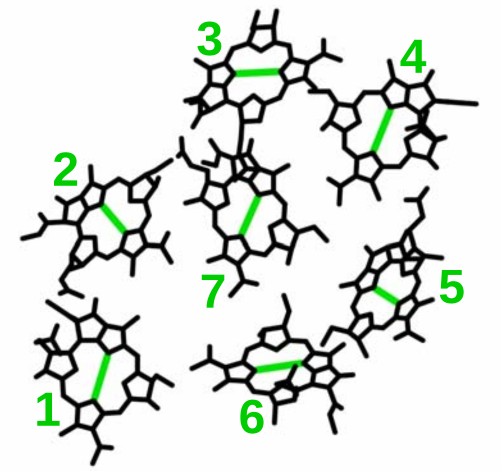


Structure: R. E. Blankenship et al. (Arizona State University)
J. Mol. Biol. **271**, 456 (1997), *Photosynth. Res.* **75**, 49 (2003)

FMO Hamiltonian

BChl	1	2	3	4	5	6	7
1	280	-106	8	-5	6	-8	-4
2	-106	420	28	6	2	13	1
3	8	28	0	-62	-1	-9	17
4	-5	6	-62	175	-70	-19	-57
5	6	2	-1	-70	320	40	-2
6	-8	13	-9	-19	40	360	32
7	-4	1	17	-57	-2	32	260

modified from Aartsma et al.: *J. Phys. Chem. B* **102**, 9577 (1998), in cm^{-1}



Q_y Transition dipoles

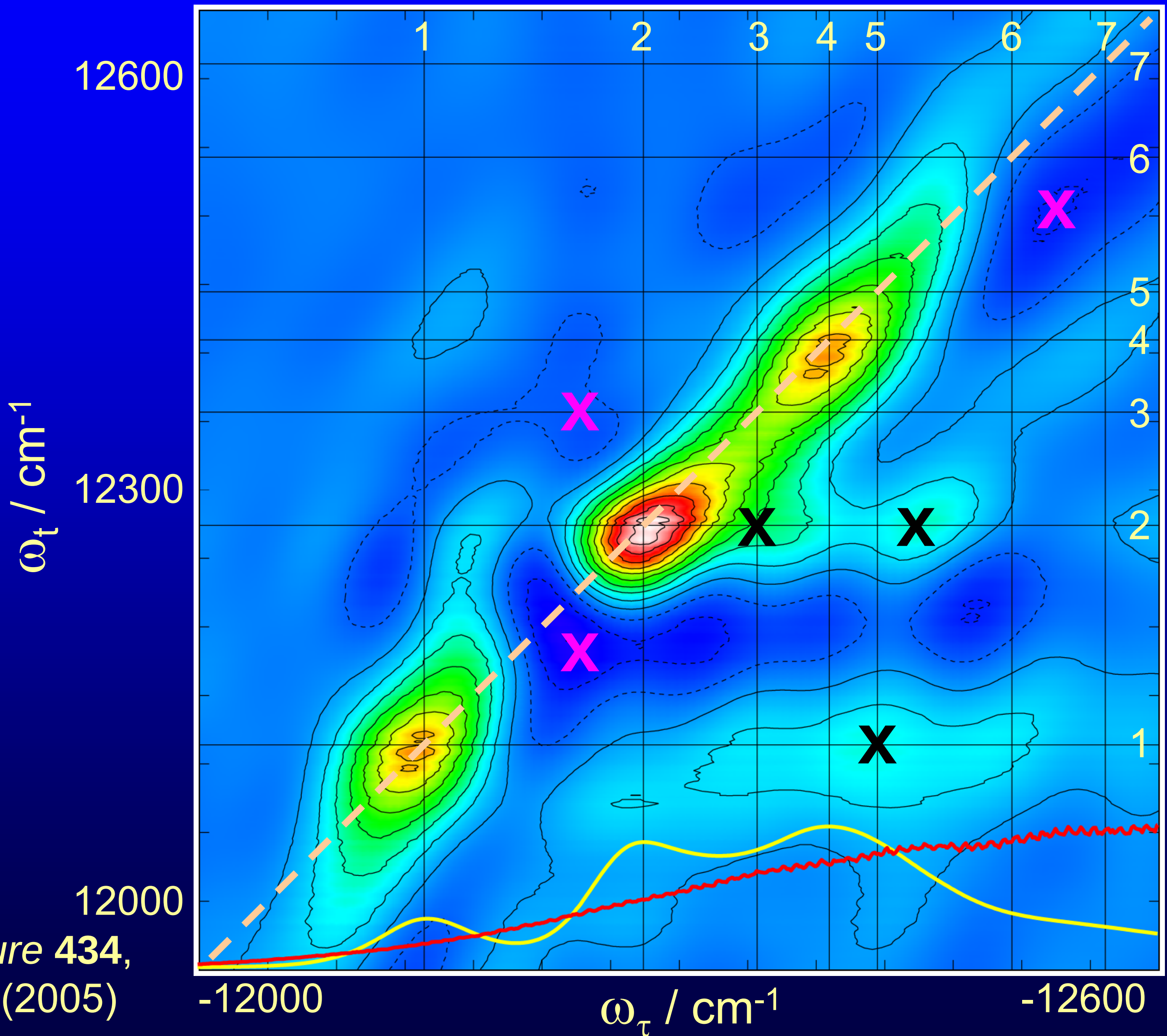
diagonal:
relative site energies

off-diagonal:
dipole–dipole couplings

→ exciton states

2D spectroscopy sensitive to
populations and couplings of exciton states

FMO Electronic coupling



exciton levels

diagonal peaks: absorption and inhomogeneity

cross peaks: couplings

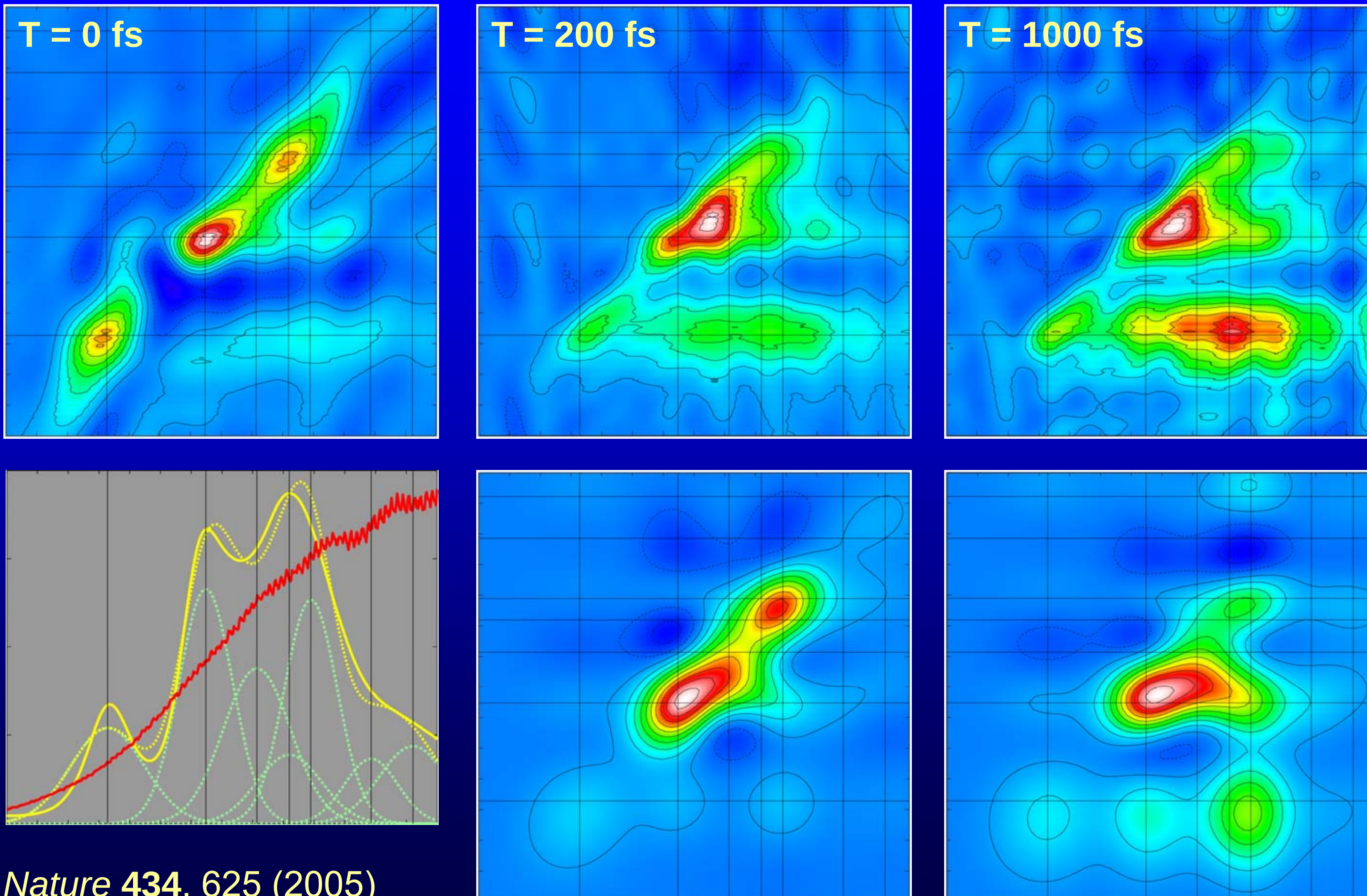
excited-state absorption

laser excitation

FMO absorption

Nature **434**, 625 (2005)

Experiment and simulation



Nature **434**, 625 (2005)

What we can see

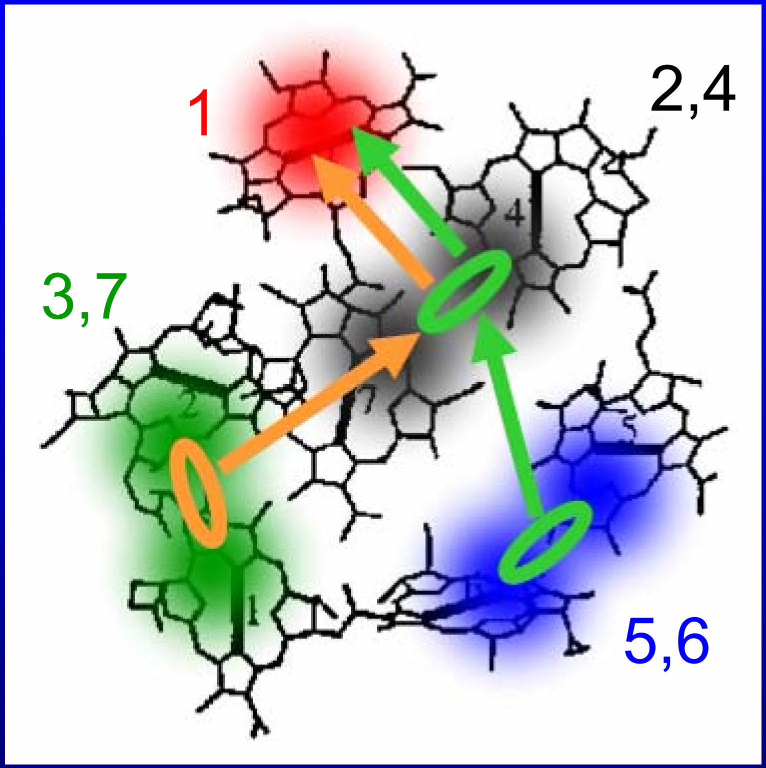
Electronic coupling

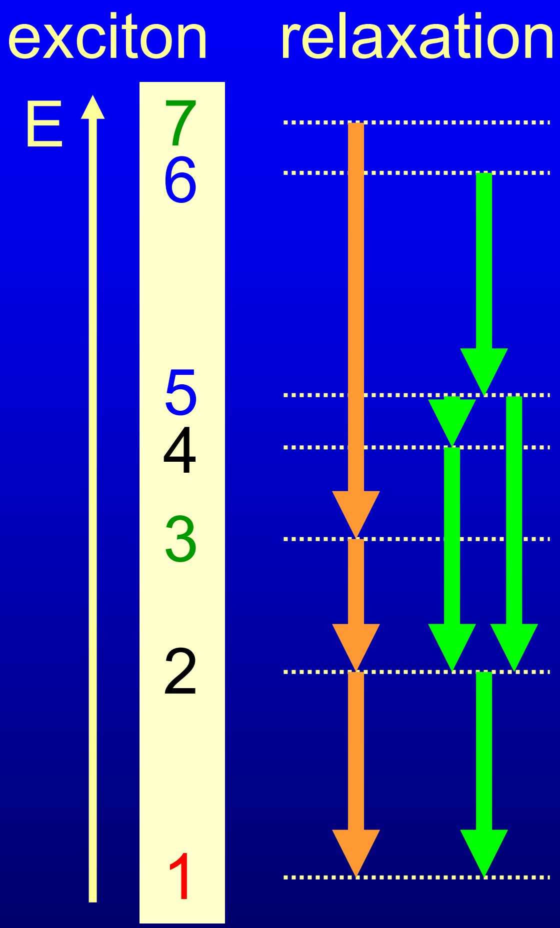
Experiment: cross peaks at $T = 0$
Theory: response function formalism
spatio-energetic position and orientation of chromophores

Energy transfer

Experiment: cross peaks at $T > 0$
Theory: phonon couplings
exciton wavefunction overlap
modified Förster/Redfield theory
one- and two-exciton contributions

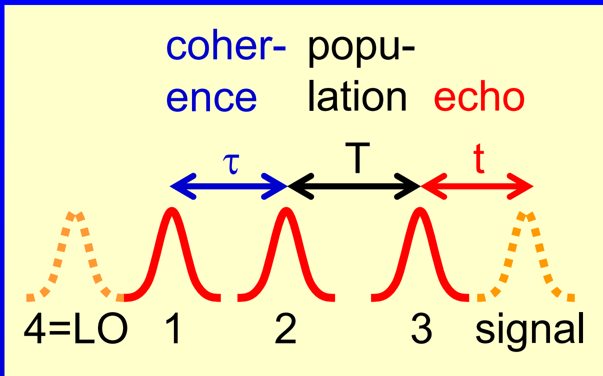
What we can learn



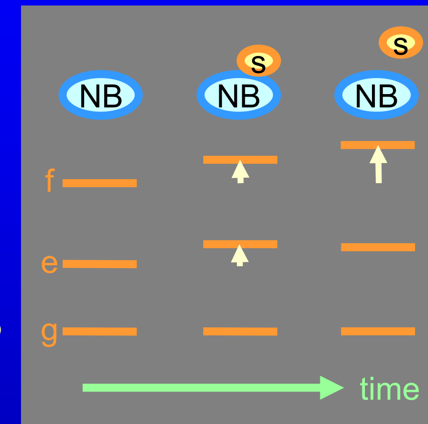


Couplings: exciton delocalization patterns
Dominant energy transport pathways

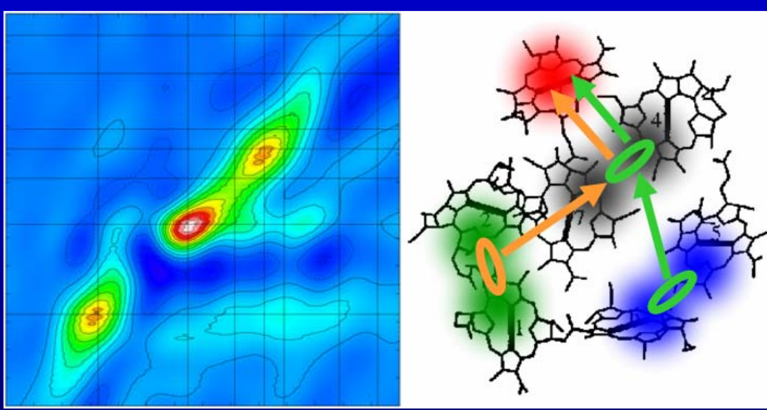
2D Electronic spectroscopy



New technology:
complete response



Monomers and aggregates:
electronic correlations
exciton relaxation



New insights into
natural light harvesting:
electronic couplings
energy transport

Couplings cause dynamics, visible by 2D spectroscopy in any photoactive assembly, macromolecule, or nanostructure

Thanks

Graham R. Fleming

Nile Blue, J-Aggregates: Igor V. Stiopkin, Tomáš Mančal

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