Energy harvesting and energy transfer in molecular quantum systems

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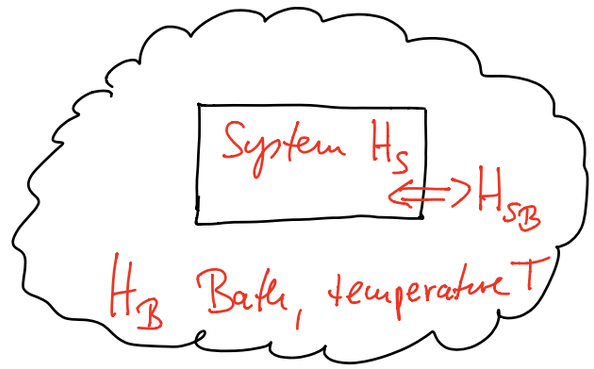
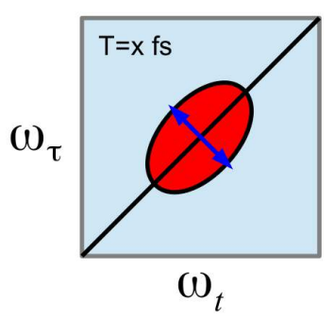
Ubiquitous Quantum Physics:
The New Quantum Revolution
ICTP Workshop & School 18.2. - 1.3. 2019, Trieste

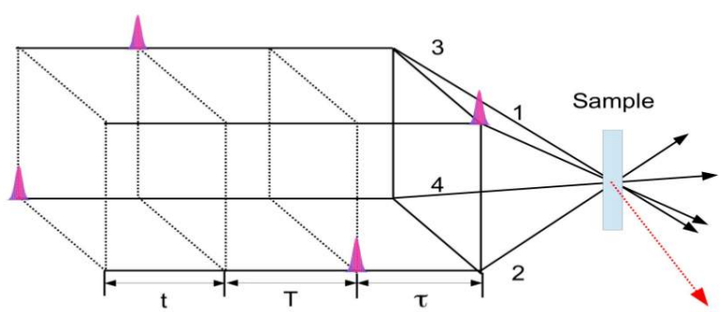
Overview

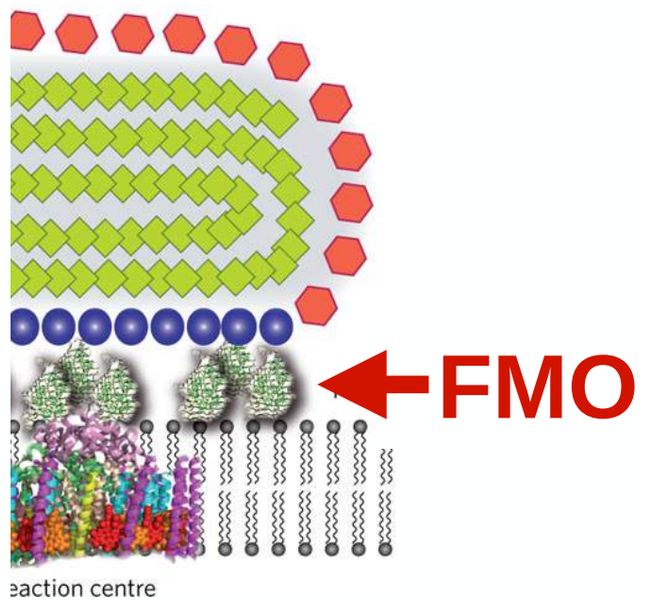
Part I: Light-harvesting & quantum coherence in biomolecular systems



1. Introduction: Excitons, dynamics, environment
2. Open quantum systems: System-Bath-Model
3. Path integral approach: Feynman-Vernon influence functional
4. Numerically exact: Quasiadiabatic Propagator Path Integral (QUAPI)
5. Application: Fenna-Matthews-Olson (FMO) complex
6. Experiment: 2D nonlinear spectroscopy
7. Is exciton transfer quantum coherent?

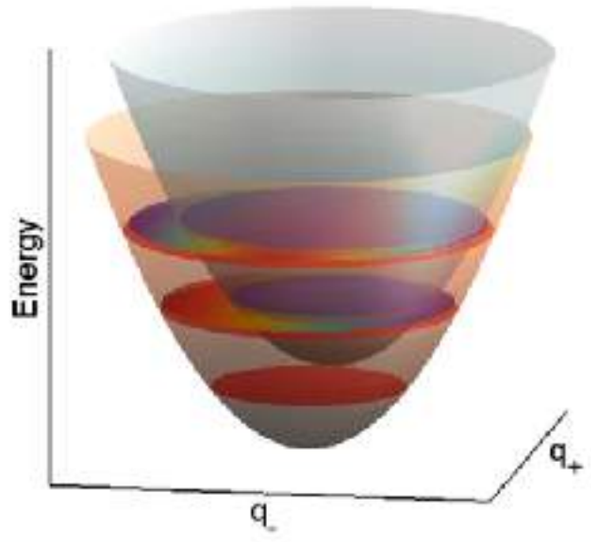




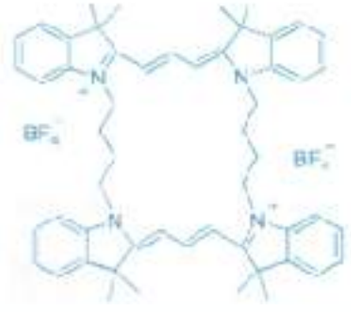


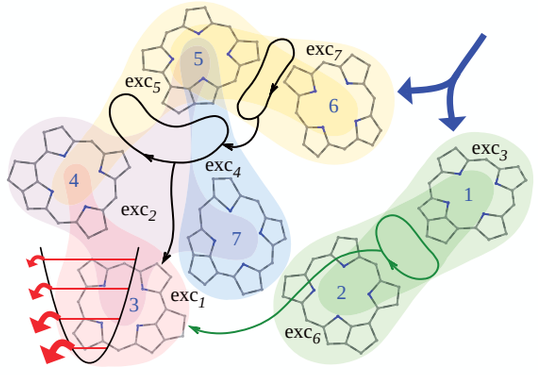
Overview

Part II: Role of vibrational modes & vibronic coupling



1. Small dye molecule: strong coupling to vibrations
2. Electronic vs vibrational vs vibronic coherence
3. Role of coherence on exciton transfer efficiency
4. Can long-live vibrational coherence enhance exciton coherence?
5. Can strong exciton coherence enhance vibrations?
6. Can strong vibronic coupling speed-up exciton transfer?

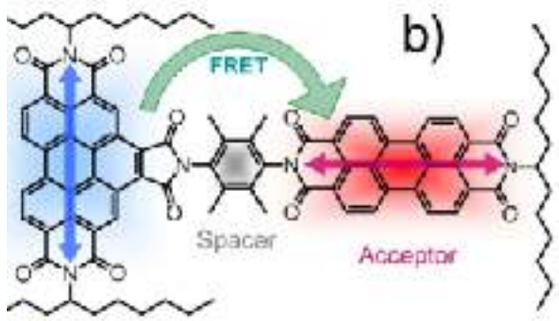




Overview

Part III: Förster transfer in molecules with orthogonal dipole moments

1. Dye molecules with orthogonal dipole moments: no dipole coupling
2. Role of angle fluctuations: induce fast transfer
3. Presence of vibrations of molecular backbone

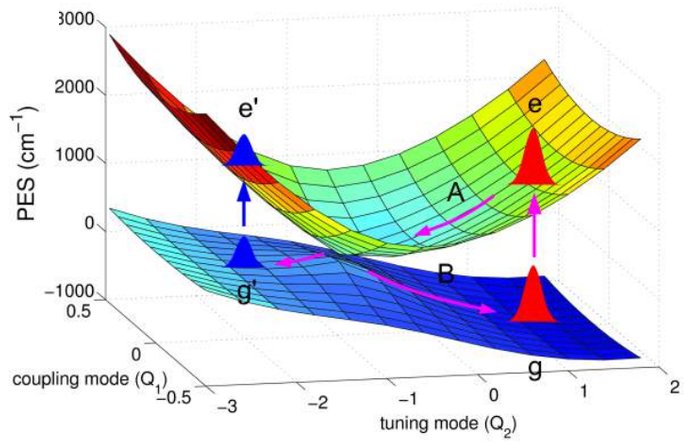


Part IV: Exciton transfer & conical intersections

1. Vibrational coherence at a conical intersection:

   overdamped / underdamped

2. Holstein & Peierls phonon viewed at conical intersection



Literature

Textbooks:

- U. Weiss: Quantum Dissipative Systems (World Scientific)
- A. O. Caldeira: Macroscopic Quantum Phenomena and Quantum Dissipation (Cambridge)
- H.-P. Breuer, F. Petruccione, The Theory of Open Quantum Systems (Oxford)
- T. Dittrich, P. Hänggi, G.-L. Ingold, B. Kramer, G. Schön, and W. Zwerger, Quantum Transport and Dissipation (Wiley-VCH)
- V. May, O. Kühn, Charge and Energy Transfer Dynamics in Molecular Systems (Wiley-VCH)

Original works (incomplete):

- A.O. Caldeira and A.J. Leggett, Influence of Dissipation on Quantum Tunneling in a Macroscopic System, Phys. Rev. Lett. 46, 211 (1981)
- H. Grabert, P. Schramm und G.-L. Ingold, Quantum Brownian Motion: The Functional Integral Approach, Phys. Rep. 168, 115 (1988)
- R.P. Feynman and F.L. Vernon, The theory of a general quantum system interacting with a linear dissipative system, Ann. Phys. 24, 118 (1963)
- N. Makri, Numerical path integral techniques for long time dynamics of quantum dissipative systems, J. Math. Phys. 36, 2430 (1995)
- M. Thorwart, P. Reimann, P. Hänggi, Iterative algorithm versus analytic solutions of the parametrically driven dissipative quantum harmonic oscillator, Phys. Rev. E 62, 5808 (2000)

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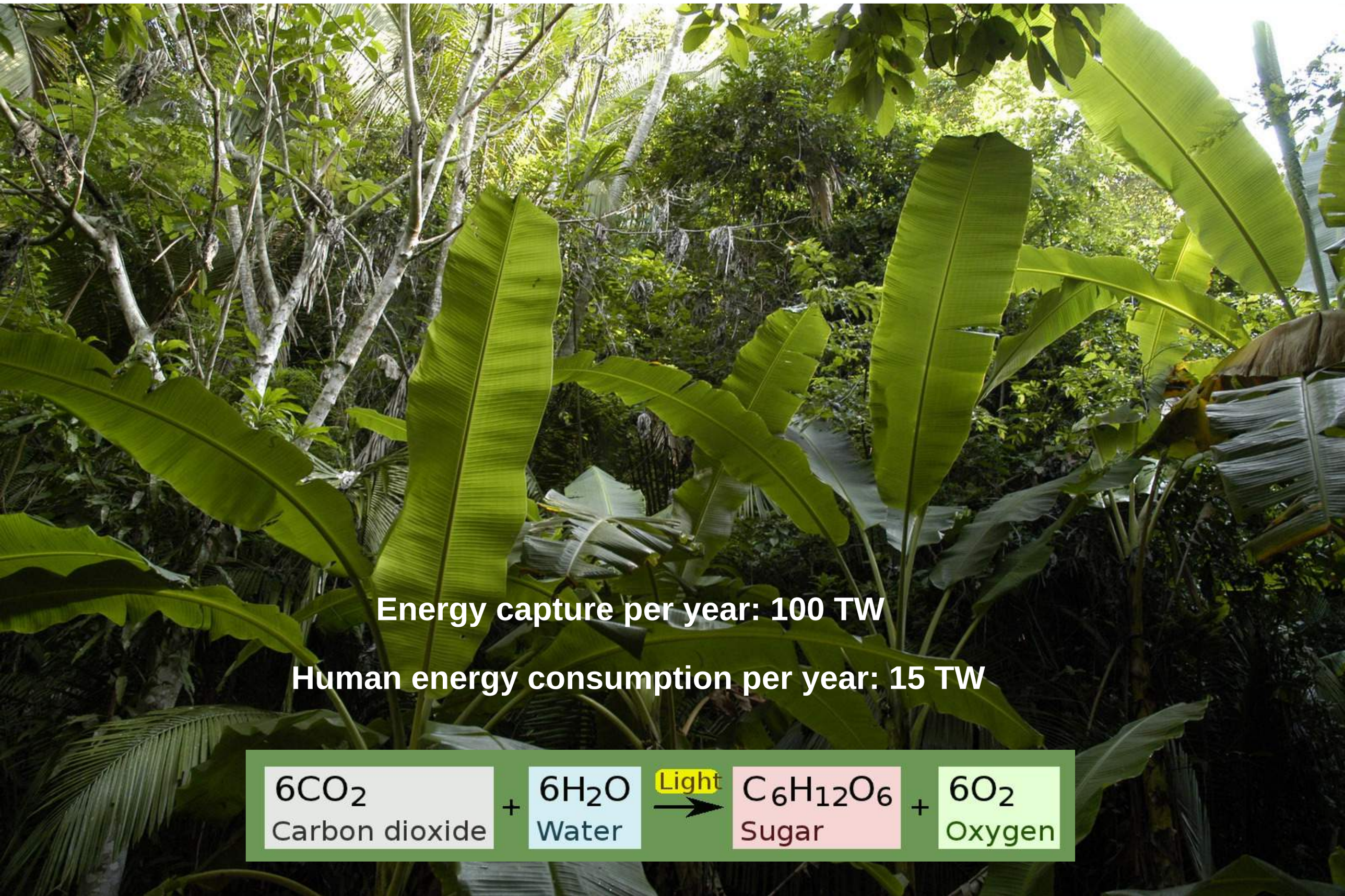
- P. Nalbach, D. Braun, M. Thorwart, Exciton transfer dynamics and quantumness of energy transfer in the Fenna-Matthews-Olson complex, Phys. Rev. E 84, 041926 (2011)
- C. Mujica-Martinez, P. Nalbach, M. Thorwart, Quantification of non-Markovian effects in the Fenna-Matthews-Olson complex, Phys. Rev. E 88, 062719 (2013)
- H.-G. Duan, V. Prokhorenko, R. Cogdell, K. Ashraf, A. Stevens, M. Thorwart, R.J.D. Miller, Nature does not rely on long-lived electronic quantum coherence for photosynthetic energy transfer, Proc. Natl. Acad.Sci. 114, 8493 (2017)
- H.-G. Duan, P. Nalbach, V. Prokhorenko, S. Mukamel, M. Thorwart, On the nature of oscillations in two-dimensional spectra of excitonically-coupled molecular systems, New J. Phys. 17, 072002 (2015)
- H.-G. Duan, A. Stevens, P. Nalbach, M. Thorwart, V. Prokhorenko, R.J.D. Miller, Two-dimensional electronic spectroscopy of Light Harvesting Complex II at ambient temperature: a joint experimental and theoretical study, J. Phys. Chem. B 119, 12017 (2015)
- H.-G. Duan, V. Prokhorenko, E. Wientjes, R. Croce, M. Thorwart, R.J.D. Miller, Primary charge separation in the reaction center revealed by two-dimensional electronic spectroscopy, Sci. Rep. 7, 12347 (2017)
- P. Nalbach, M. Thorwart, The role of discrete molecular modes in the coherent exciton dynamics in FMO, J.Phys. B: At. Mol. Opt. Phys. 45, 154009 (2012)
- P. Nalbach, C. Mujica-Martinez, M. Thorwart, Vibronic speed-up of the excitation energy transfer in the Fenna-Matthews-Olson complex, Phys. Rev. E 91, 022706 (2015)
- P. Nalbach, I. Pugliesi, H. Langhals, M. Thorwart, Noise-induced Förster resonant energy transfer between orthogonal dipoles in photoexcited molecules, Phys. Rev. Lett. 108, 218302 (2012)
- H.-G. Duan, M. Thorwart, Quantum Mechanical Wavepacket Dynamics at a Conical Intersection with Strong Vibrational Dissipation, J. Chem. Phys. Lett. 7, 382 (2016)
- H.-G. Duan, R.J.D. Miller, M. Thorwart, Impact of Vibrational Coherence on the Quantum Yield at a Conical Intersection, J. Chem. Phys. Lett. 7, 3491 (2016)

Photosynthesis

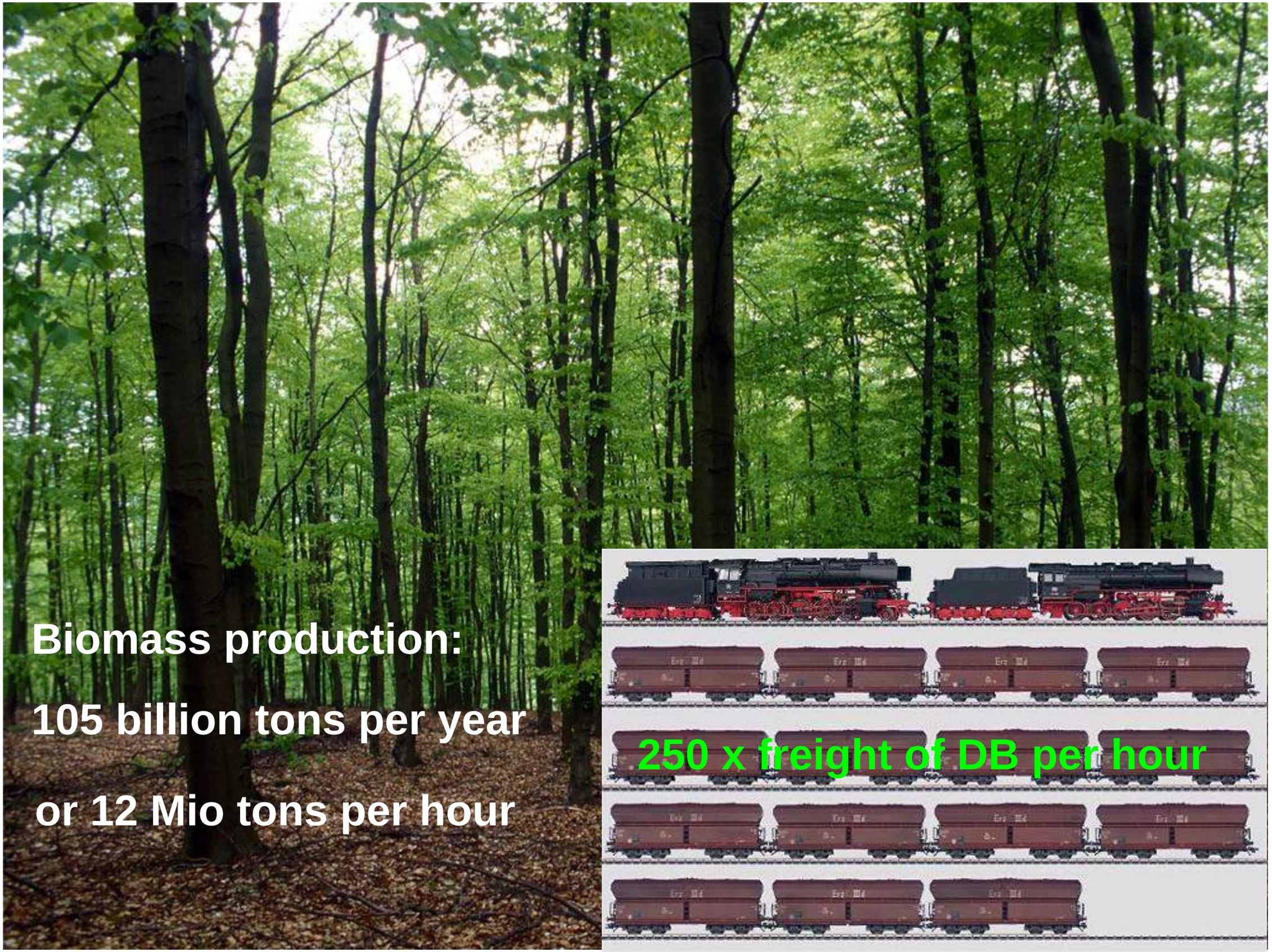


Energy capture per year: 100 TW

Human energy consumption per year: 15 TW

$6CO_2$ Carbon dioxide + $6H_2O$ Water —Light→ $C_6H_{12}O_6$ Sugar + $6O_2$ Oxygen

Photosynthesis

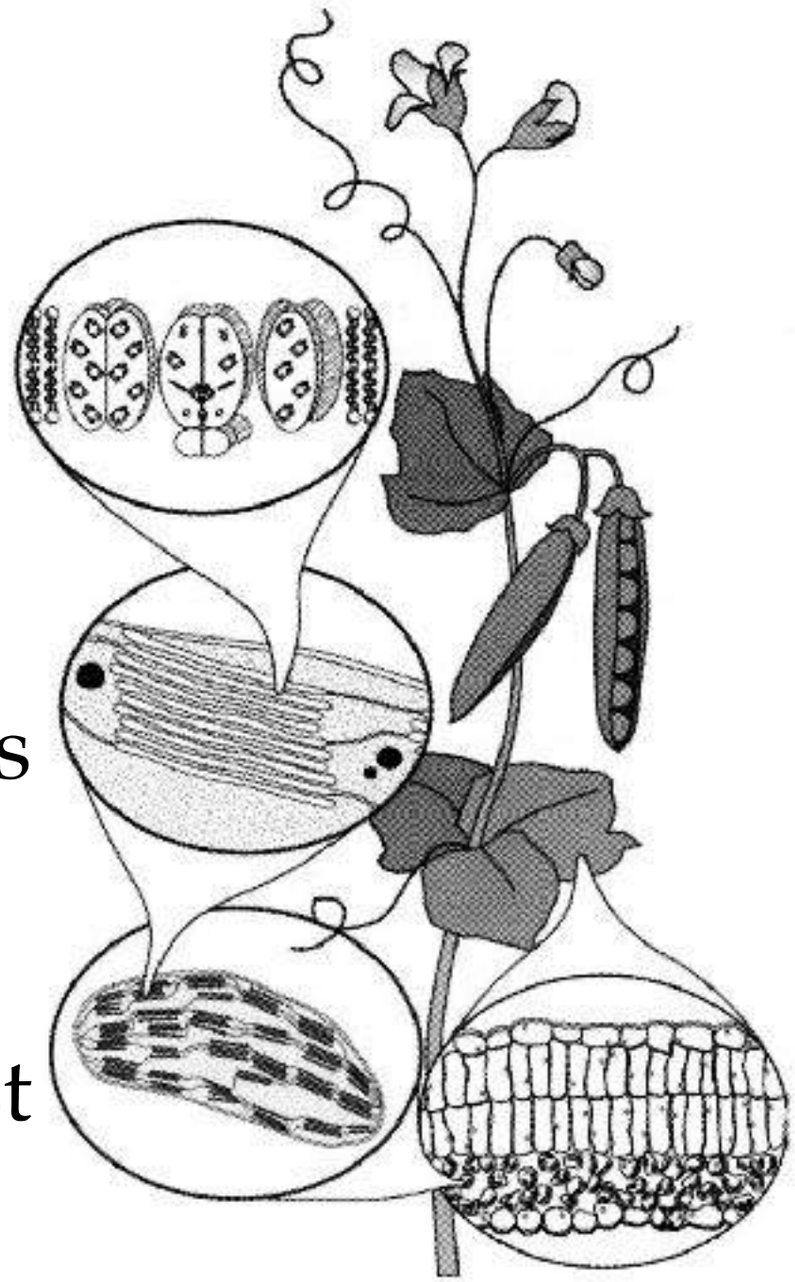


Light-harvesting in plants

molecular structure of membrane

Stack of membranes

Chloroplast



Blankenship, Molecular Mechanisms of Photosynthesis

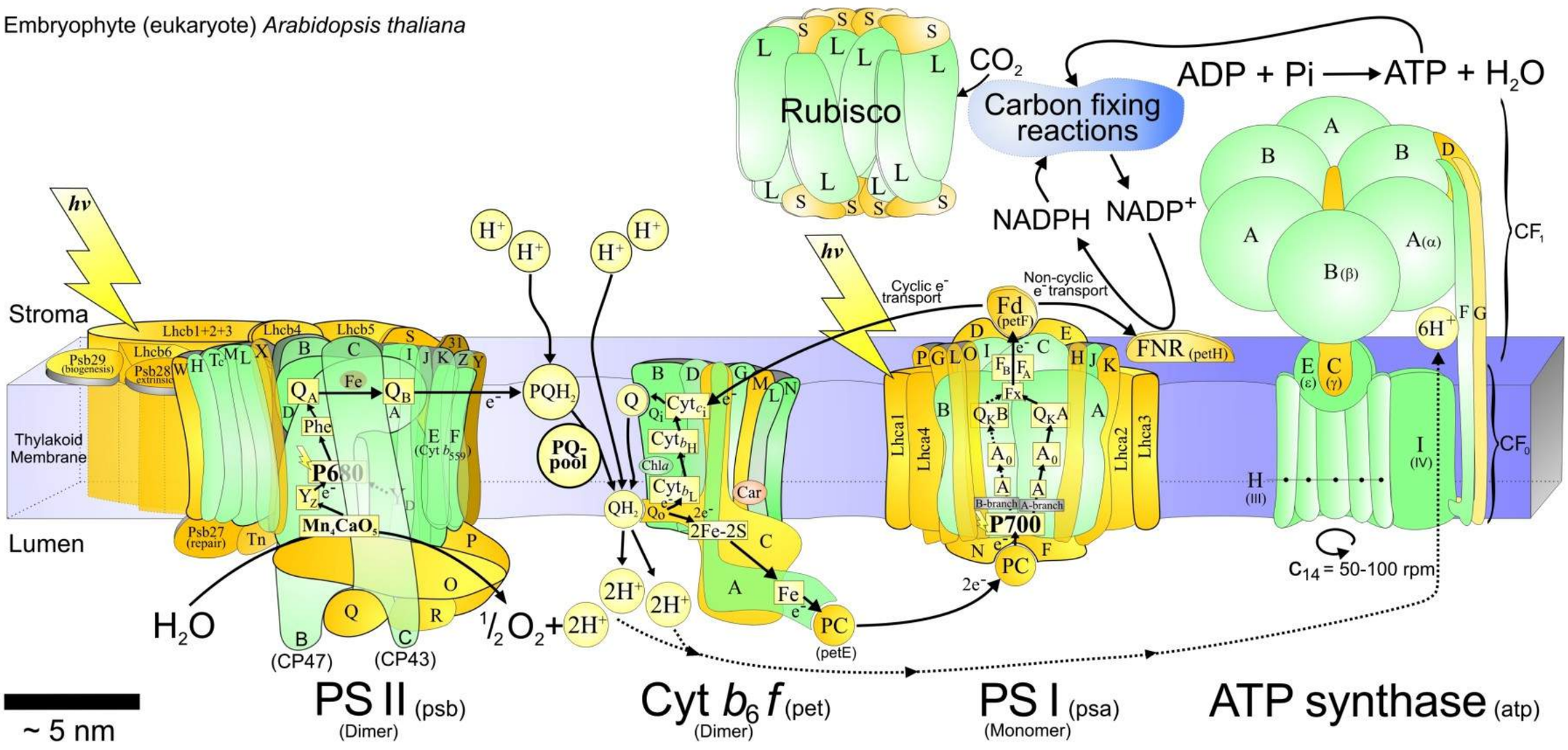
Light-harvesting in plants

A structural phylogenetic map for chloroplast photosynthesis

John F. Allen, Wilson B. M. de Paula, Sujith Puthiyaveetil, Jon Nield
School of Biological and Chemical Sciences, Queen Mary University of London

TRENDS in Plant Science

Embryophyte (eukaryote) *Arabidopsis thaliana*



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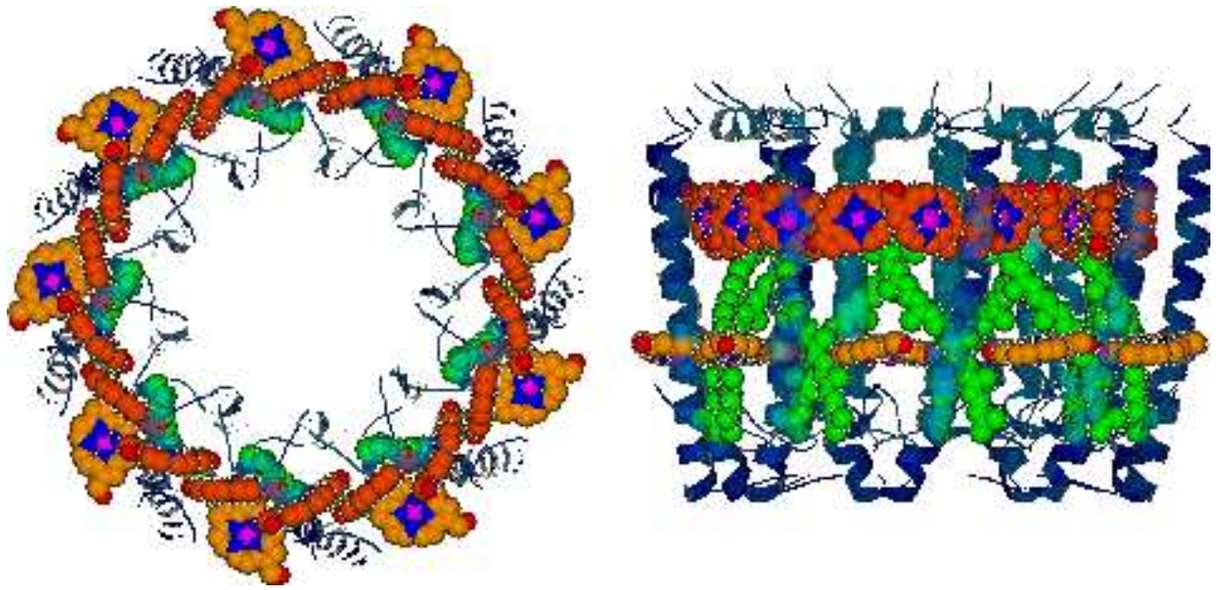
Energy transfer in biomolecules

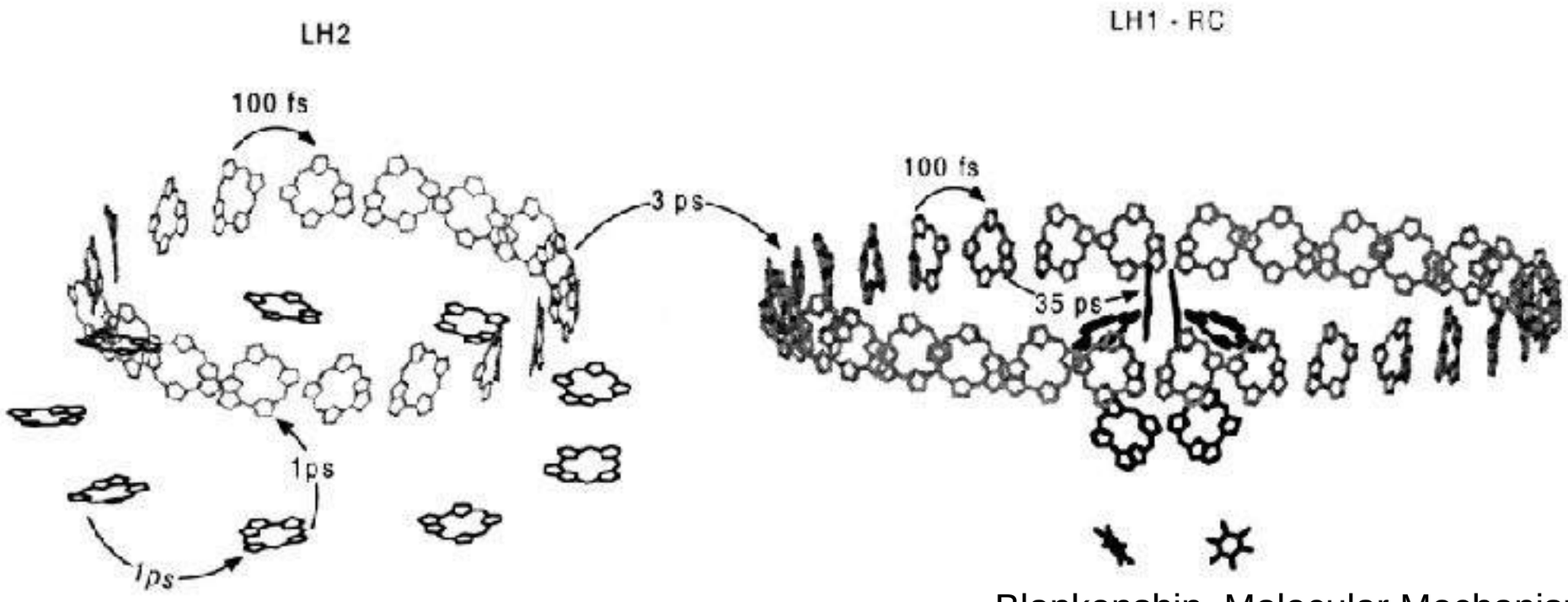


LH-2 antenna complex of Rps. Acidophila

K. Schulten, UIUC

- Molecular structure often ring-shaped
- Photon => Exciton
- Transfer of excitation energy
- Different „hopping“ time scales:

100 fs to few ps

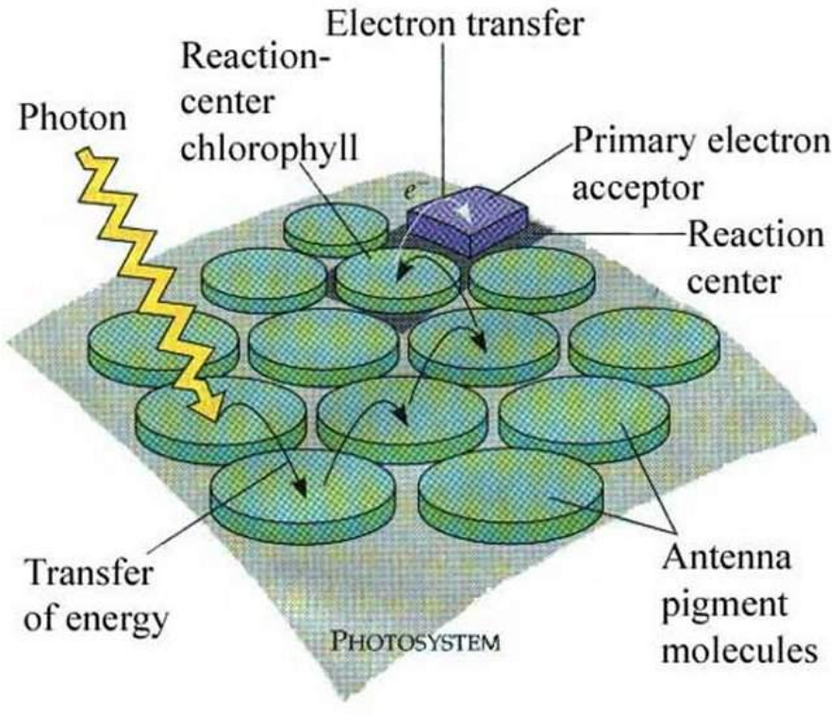


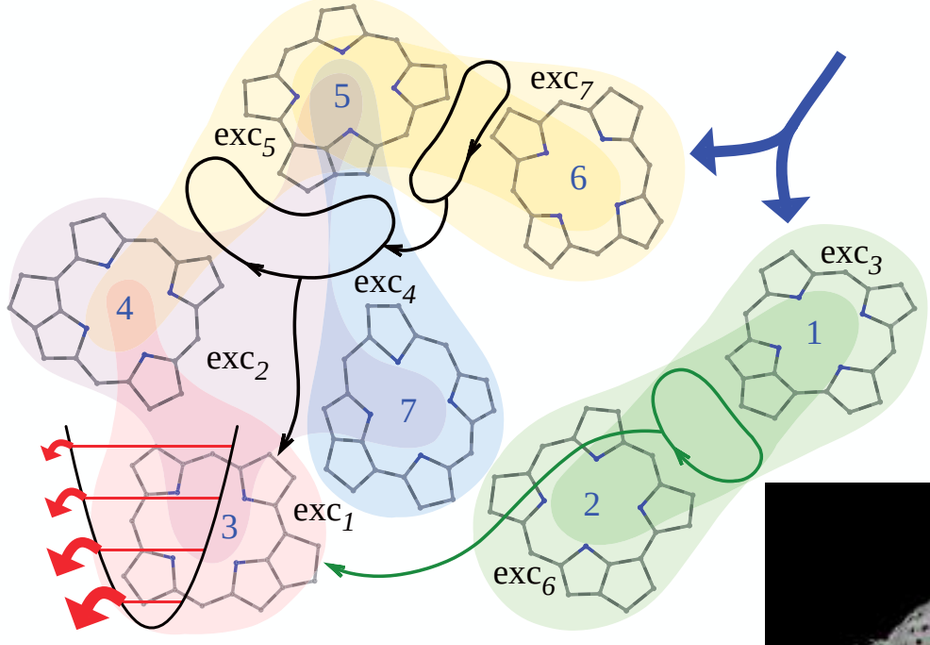
Blankenship, Molecular Mechanisms of Photosynthesis

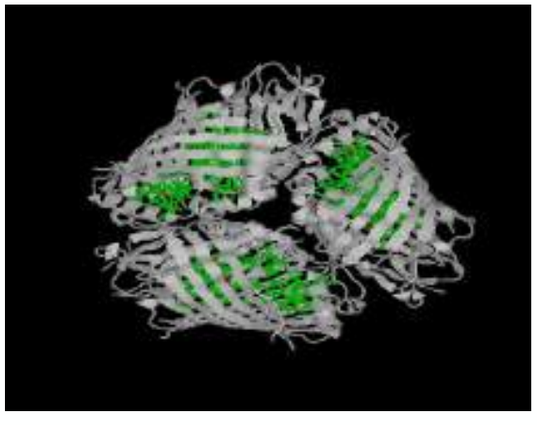
Energy transfer in biomolecules

A physicist's view:

- formation of an exciton (quasiparticle, bound e-h pair)
- radiationless transfer of excitation energy on a network of molecular sites via dipole coupling
- final step: reaction center, energy sink ⇒ electron transfer
- important: polar solvent or vibrational effects ⇒ fluctuations





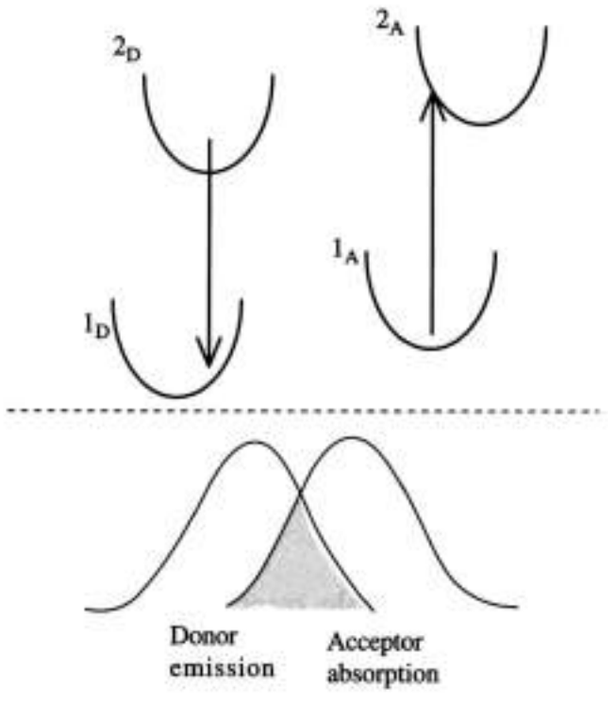


FMO complex

Förster mechanism (1946)

- Exciton wave function unperturbed by coupling
- Born-Oppenheimer approximation:
  nuclei provide static potential energy surfaces for electrons
- Classical occupation probability
- quantum transfer rate in lowest order in coupling:

$$k = \frac{\text{geometr.}}{R^6} \frac{\hbar}{2\pi} \int_{-\infty}^{\infty} dE \; k^A_{2\leftarrow 1} \; k^B_{1\leftarrow 2}(E) \sim \left(\frac{R_0}{R}\right)^6$$



Th. Förster

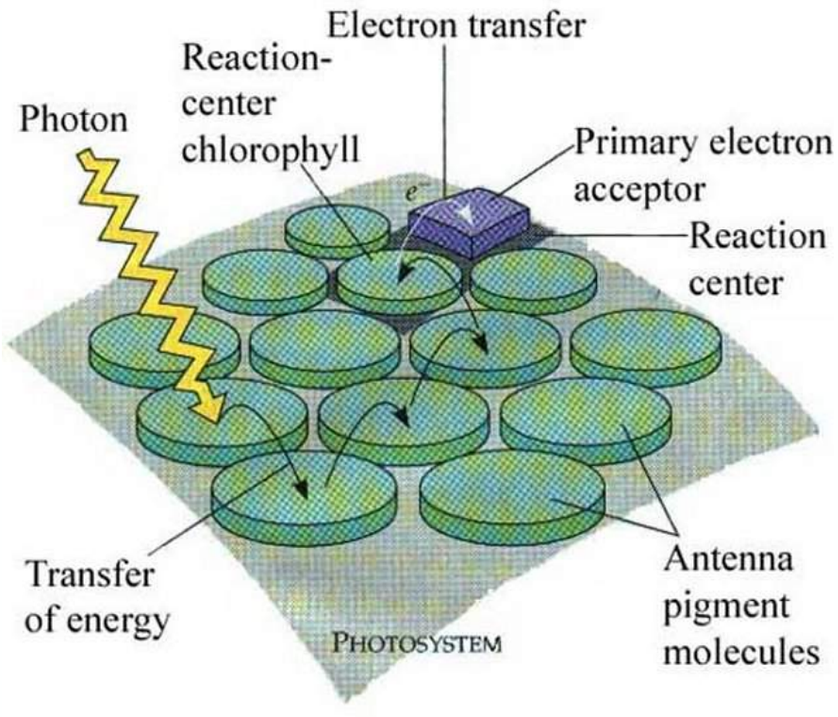
Energy transfer in biomolecules

Are there nontrivial quantum effects in biomolecular energy transfer?

- classical „hopping“, or,
- quantum coherent wave-like energy transfer?

New field of quantum biology?

- fundamental: Role of quantum coherence in energy transfer?



Aharonov, Rohrlich, *Quantum Paradoxes,* Wiley-VCH

Quietschgrüne Quantenwesen

FRANKFURTER ALLGEMEINE SONNTAGSZEITUNG, 30. JULI 2017, NR. 30

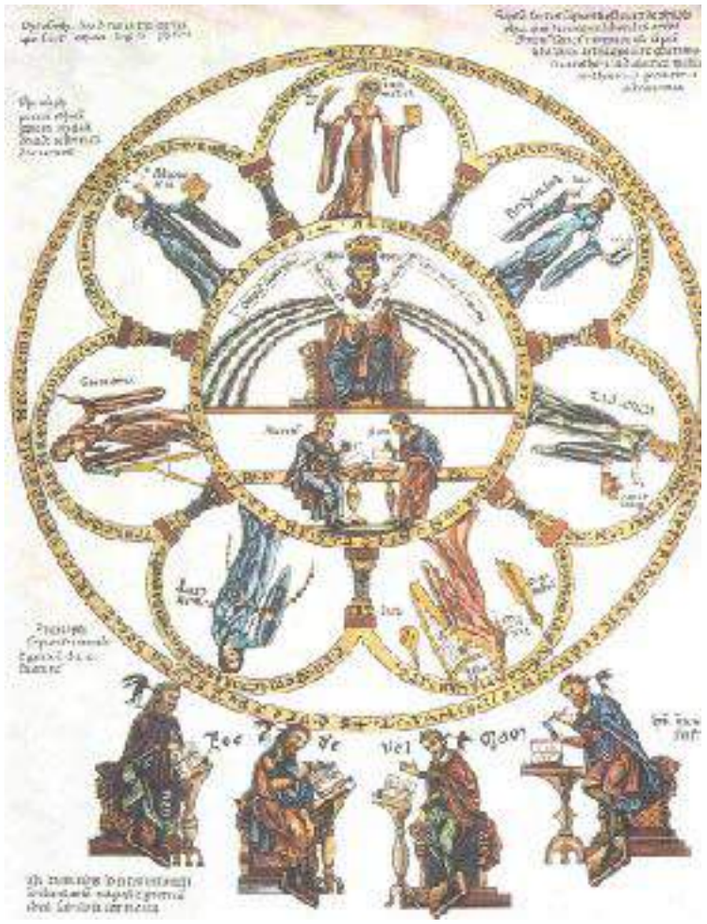
58 WISSENSCHAFT SPEZIAL

Trivial vs. nontrivial

Are there nontrivial quantum effects in biomolecular energy transfer?

Septem Artes Liberales („curriculum proper to a free man“)

- Tri-vium (three-fold way): Grammar, Rhetoric, Dialectic (Logic)
- Quadri-vium (four-fold way): Arithmetic, Geometry, Music, Astronomy



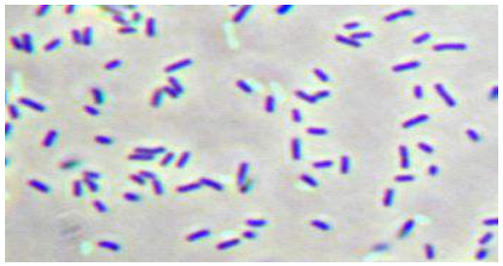
Trivial = Part of the tri-vium

= Basic

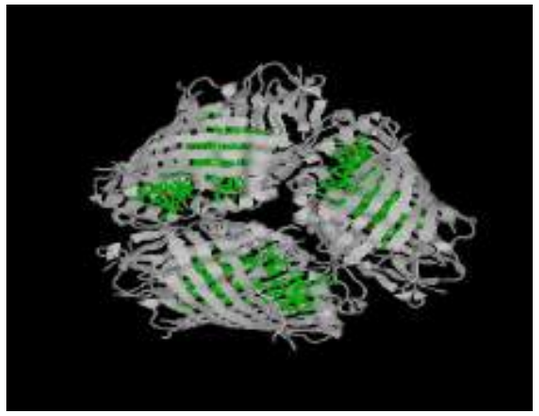
Biomolecular quantum coherence: Experiments

Fenna-Matthews-Olson protein:

„exciton wire“

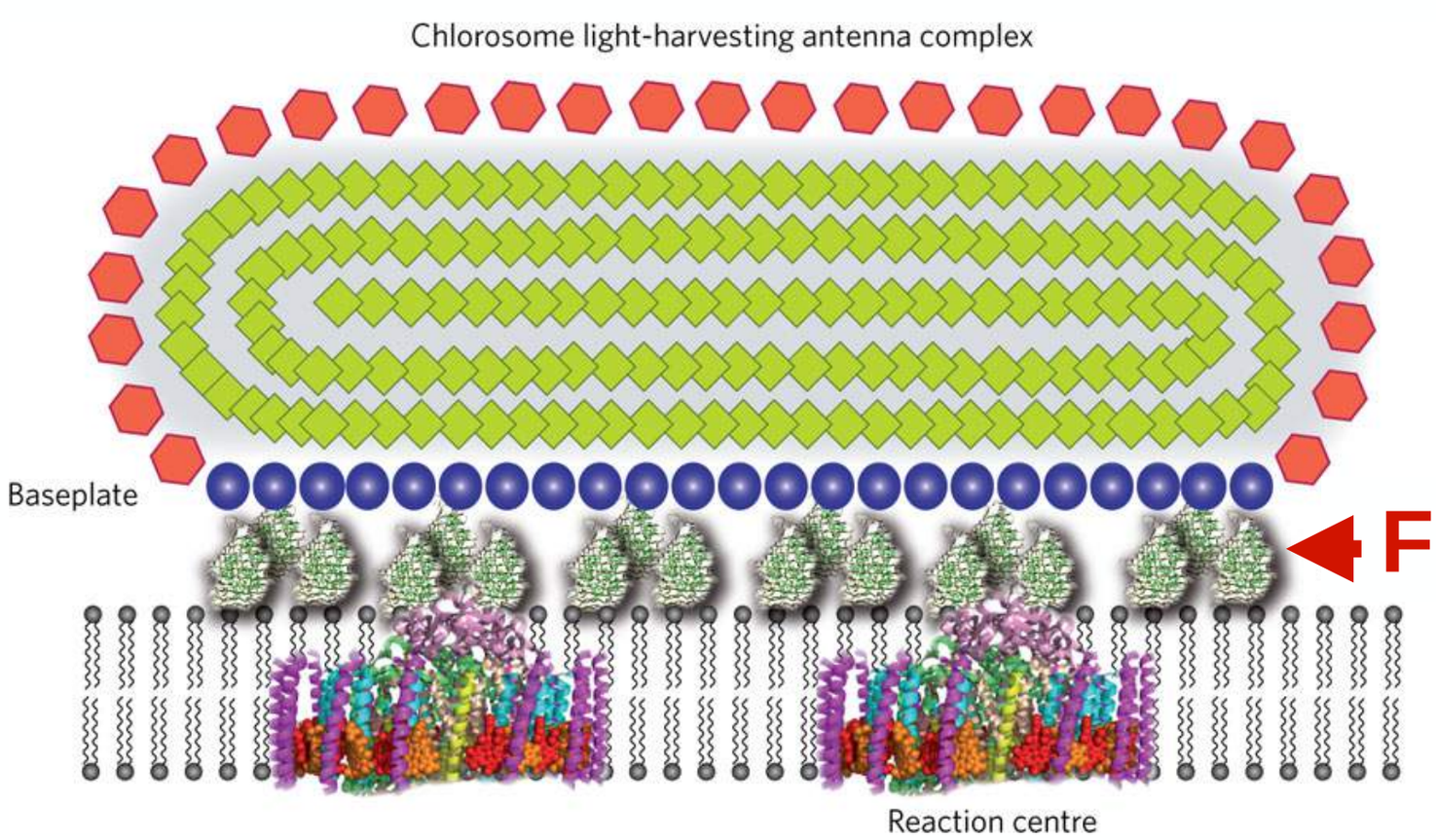


Light micrograph

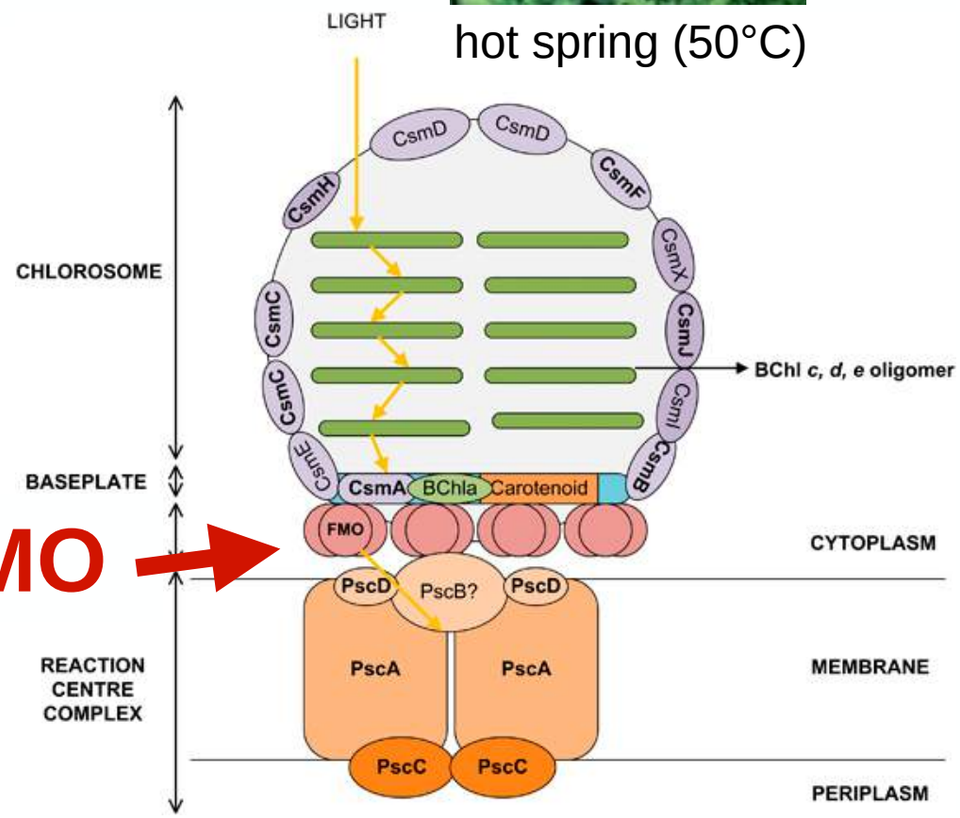


FMO complex

hot spring (50°C)



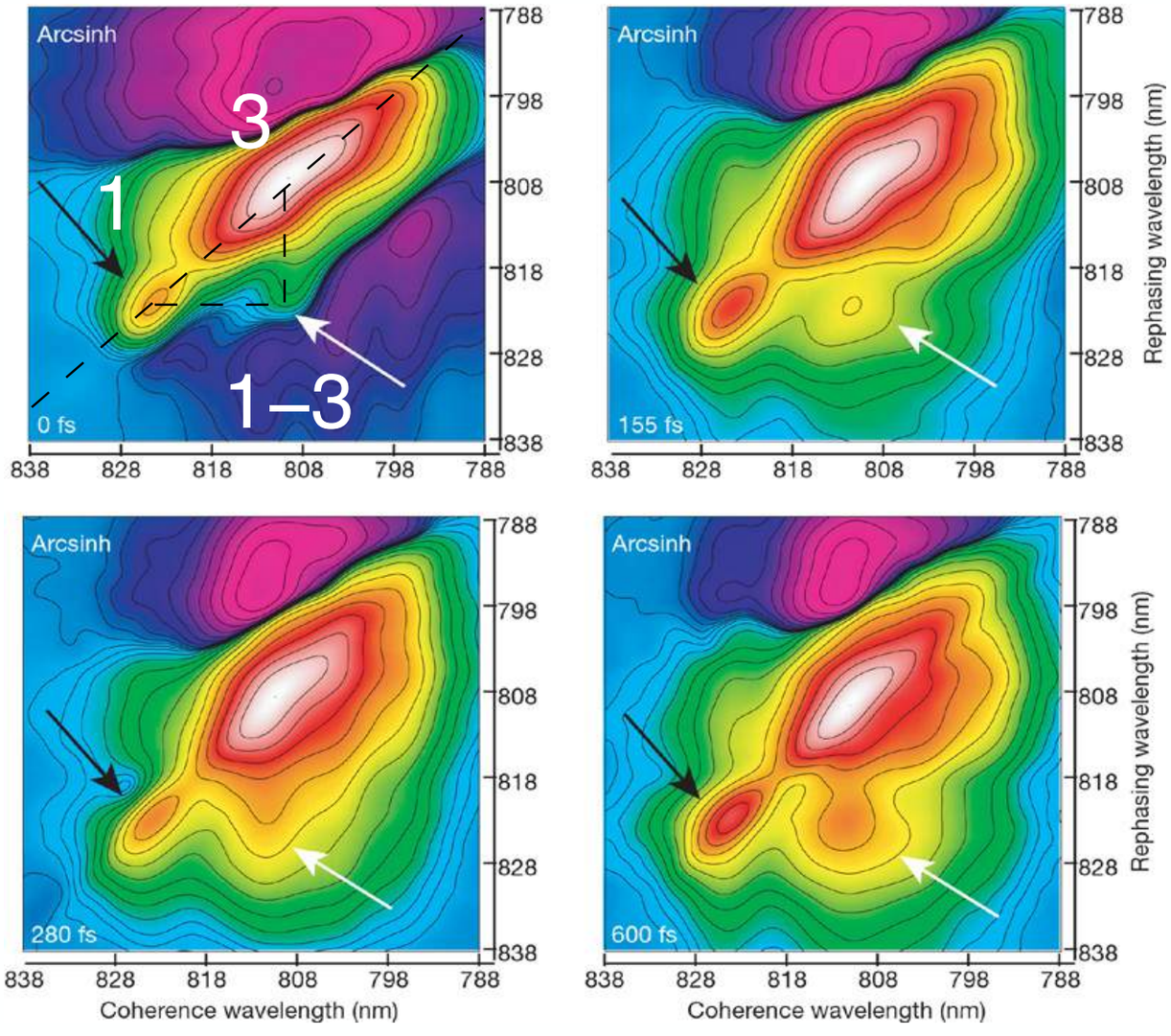
FMO

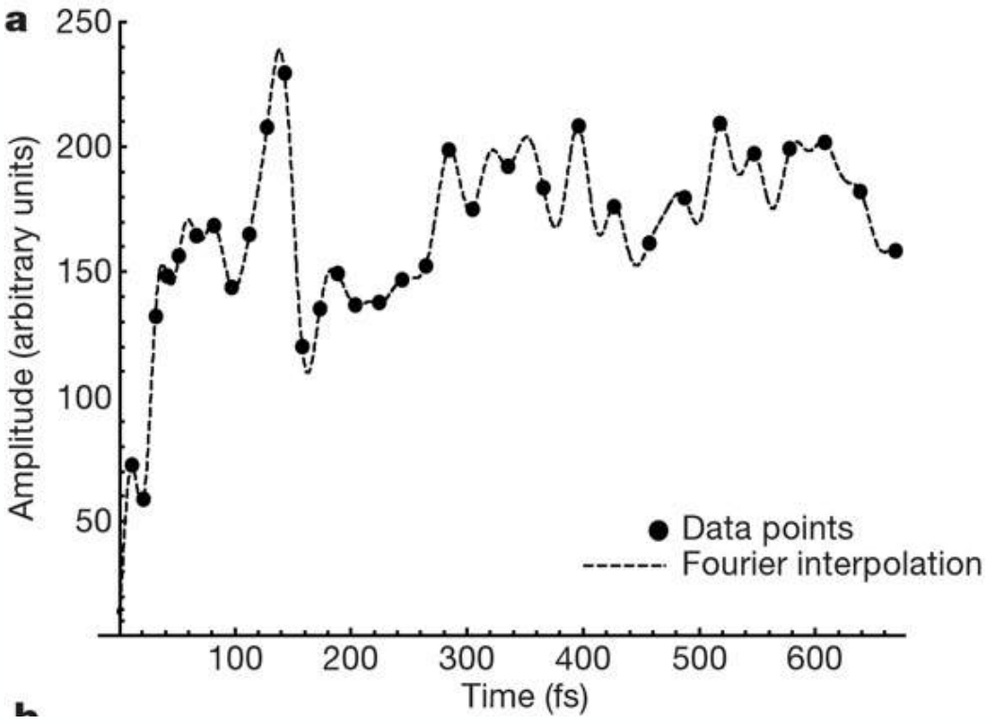


Biomolecular quantum coherence: experiments

G. Engel et al. (Berkeley), Nature **446**, 782 (2007)

- long-lived excitonic quantum coherence
- up to 660 fs (system: 100 fs)
- temperature 77 K





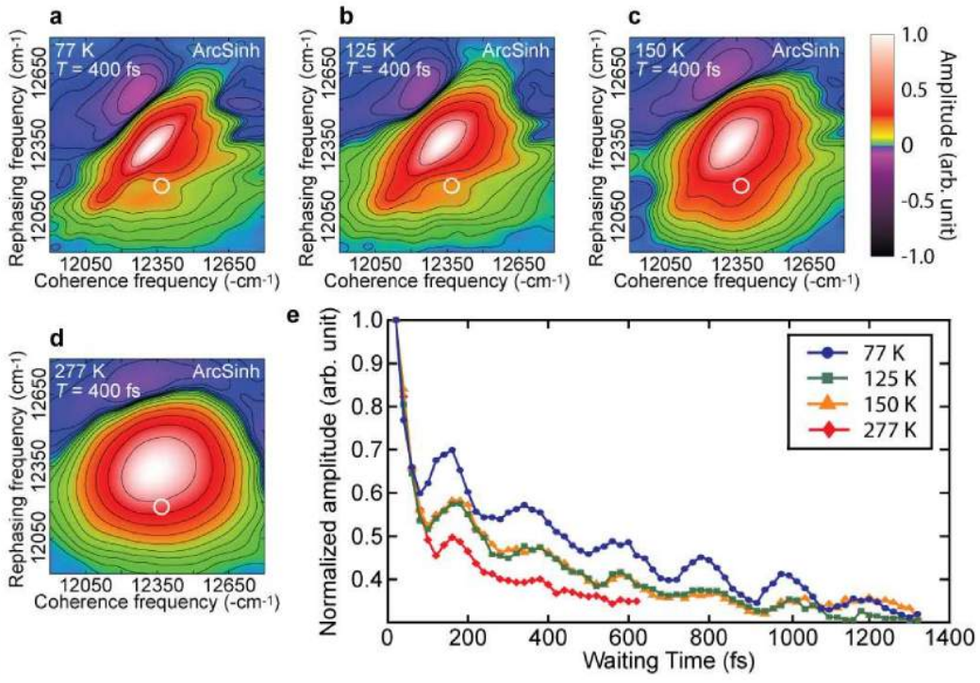
dicted[12,13] and indirectly observed[14]. Here we extend previous two-dimensional electronic spectroscopy investigations of the FMO bacteriochlorophyll complex, and obtain direct evidence for remarkably long-lived electronic quantum coherence playing an important part in energy transfer processes within this system. The quantum coherence manifests itself in characteristic, directly observable quantum beating signals among the excitons within the *Chlorobium tepidum* FMO complex at 77 K. This wavelike characteristic of the energy transfer within the photosynthetic complex can explain its extreme efficiency, in that it allows the complexes to sample vast areas of phase space to find the most efficient path.

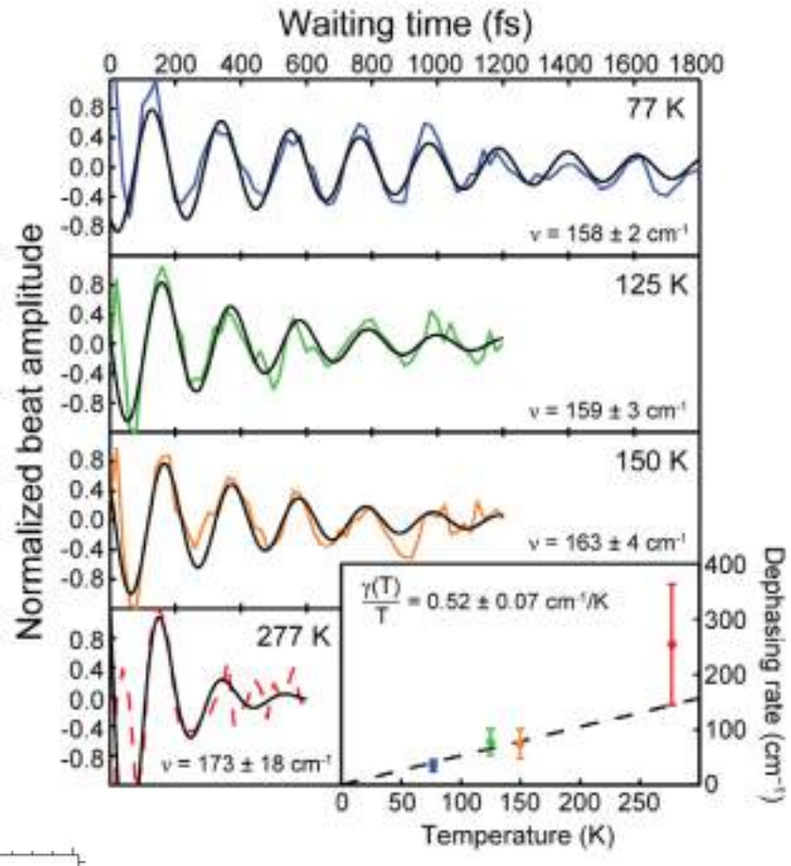
Biomolecular quantum coherence: experiments

- FMO @ room temperature:

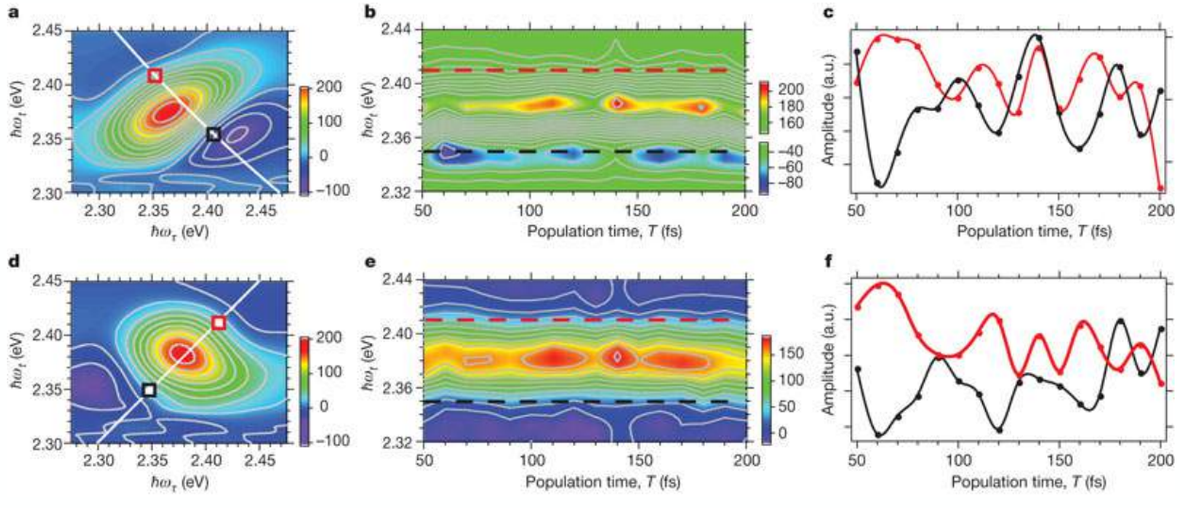
G. Panitchayangkoon et al. (G. Engel)
PNAS **107**, 12766 (2010)

coherence time 300 fs





- Marine cryptophyte algae

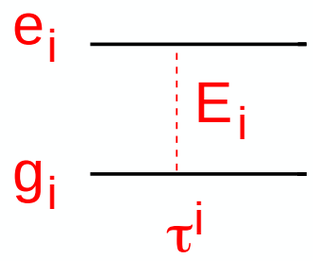


E. Collini et al. (G. Scholes),
Nature **463**, 644 (2010)

Quantum transfer of excitation energy: exciton model

Dimer formed by two monomers:

- A single chromophore at site i: $|g_i\rangle \quad |e_i\rangle$



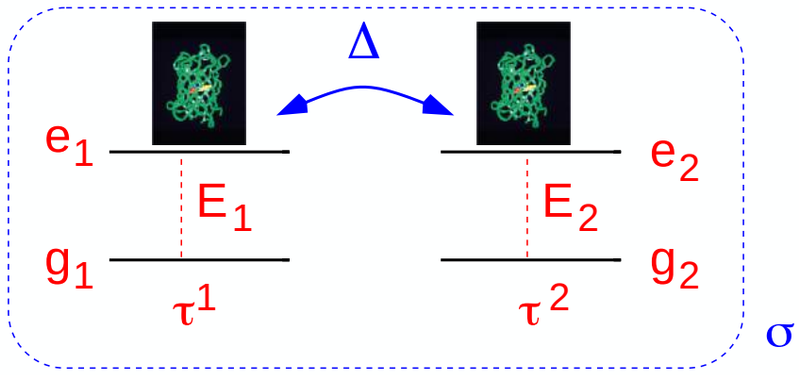
$$H_i = \frac{E_i}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

- Pair of chromophores with dipole coupling:

$$H = \frac{E_1}{2}\tau_z^1 + \frac{E_2}{2}\tau_z^2 + \Delta(\tau_x^1\tau_x^2 + \tau_y^1\tau_y^2) \qquad \Delta = \frac{\kappa\mu_1\mu_2}{R^3}$$

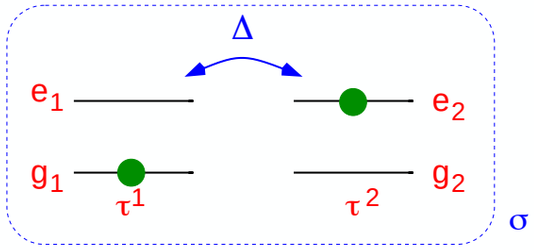
(neglect doubly excited state, high energy!)

$$H_S = \frac{\hbar\epsilon}{2}\sigma_z + \frac{\hbar\Delta}{2}\sigma_x, \qquad \epsilon = E_1 - E_2$$

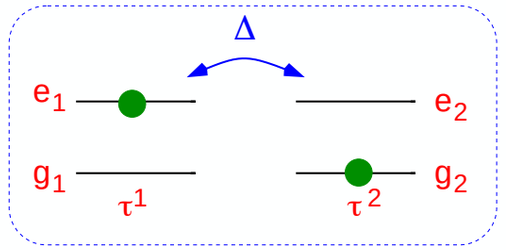


- Two quantum states:

$$|\uparrow\rangle = |$$



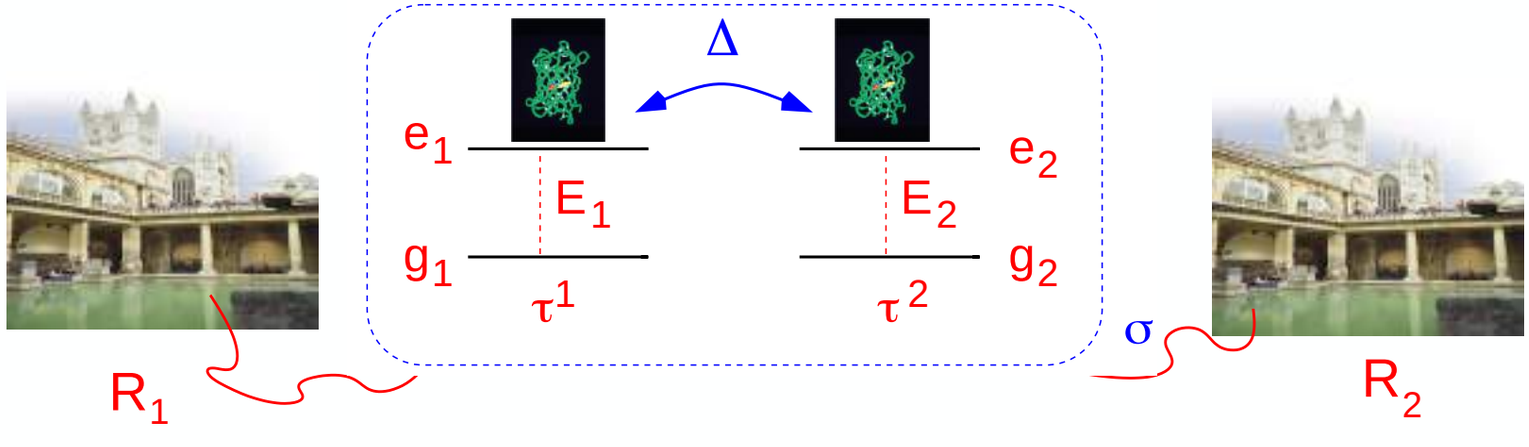
$$\rangle \qquad |\downarrow\rangle = |$$



$$\rangle$$

Quantum transfer of excitation energy: exciton model

Dimer in an environment:



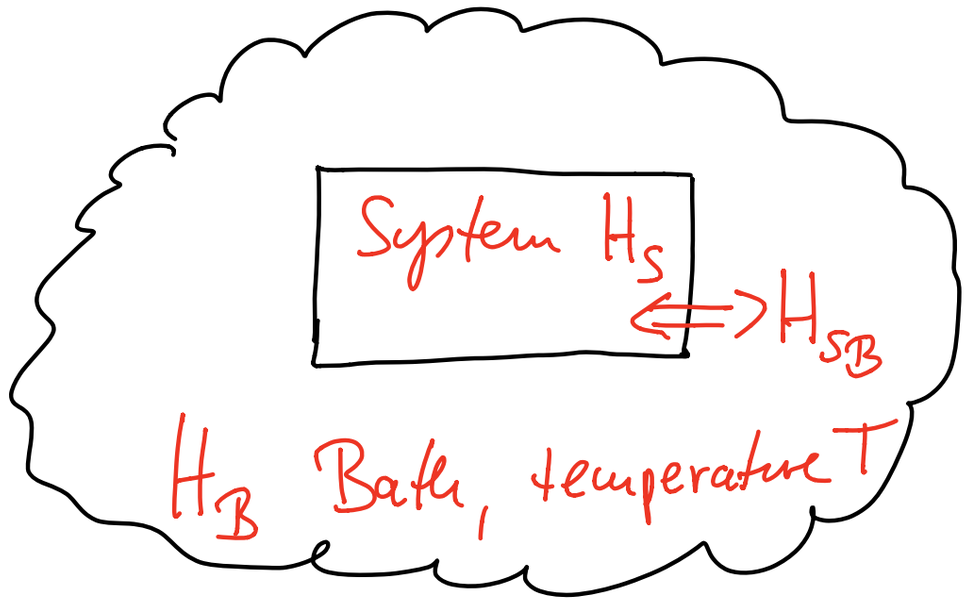
$$H_{\rm tot} = H_{\rm dimer} + \hbar\sigma_z \underbrace{\sum_\kappa \lambda_\kappa (b_\kappa^\dagger + b_\kappa)}_{\text{fluctuating force} \sim \xi(t)} + \sum_\kappa \hbar\omega_\kappa b_\kappa^\dagger b_\kappa$$

- Protein-solvent environment:
  - Polar solvent = dielectric continuum
  - Protein host = discrete vibrational modes

- System-bath model

System-bath model

$$H_{\rm tot} = H_S(t) + H_B + H_{SB}$$



System: (for example)

$$\mathbf{H}_{\rm S}(t) = \frac{\mathbf{p}^2}{2\mathcal{M}} + V(\mathbf{q},t)$$

Bath + interaction:

$$\mathbf{H}_{\rm B} = \sum_{j=1}^{\mathcal{N}} \mathbf{H}_j(\mathbf{q}) = \sum_{j=1}^{\mathcal{N}} \frac{1}{2}\left[\frac{\mathbf{p}_j^2}{m_j} + m_j\omega_j^2\left(\mathbf{x}_j - \frac{c_j}{m_j\omega_j^2}\mathbf{q}\right)^2\right]$$

- set of uncoupled harmonic oscillators
- bilinear coupling to the system
- effect of bath can be strong since (infinitely) many oscillators couple to system

Initial condition:

$$\mathbf{W}(t_0) = \rho_{\rm S}(t_0) \otimes \rho_{\rm B}^0$$

- required for dynamics
- uncoupled at t=0
- instantaneous switching on at $t=0^+$

$$\rho_{\rm B}^0 = Z_{\rm B}^{-1} \exp\left(-\beta \mathbf{H}_{\rm B}^0\right)$$

Quantum Langevin equation

Heisenberg equations of motion:

System: $$\mathcal{M}\ddot{\mathbf{q}}(t) + V'(\mathbf{q},t) + \mathbf{q}(t)\sum_{j=1}^{\mathcal{N}} \frac{c_j^2}{m_j\omega_j^2} = \sum_{j=1}^{\mathcal{N}} c_j \mathbf{x}_j(t)$$

insert here

Bath: $$m_j\ddot{\mathbf{x}}_j(t) + m_j\omega_j^2\mathbf{x}_j(t) = c_j\mathbf{q}(t)\,, \qquad j = 1,...,\mathcal{N}$$

harmonic oscillator driven by the system displacement, solution:

$$\mathbf{x}_j(t) = \mathbf{x}_j(t_0)\cos\omega_j(t-t_0) + \frac{\mathbf{p}_j(t_0)}{m_j\omega_j}\sin\omega_j(t-t_0) + \frac{c_j}{m_j\omega_j}\int_{t_0}^{t} ds \sin\left[\omega_j(t-s)\right]\mathbf{q}(s)$$

$$= \left[\mathbf{x}_j(t_0) - \frac{c_j}{m_j\omega_j^2}\mathbf{q}(t_0)\right]\cos\omega_j(t-t_0) + \frac{\mathbf{p}_j(t_0)}{m_j\omega_j}\sin\omega_j(t-t_0)$$

$$- \frac{c_j}{m_j\omega_j^2}\int_{t_0}^{t} ds \cos\left[\omega_j(t-s)\right]\dot{\mathbf{q}}(s) + \frac{c_j}{m_j\omega_j^2}\mathbf{q}(t)$$

Result:

$$\mathcal{M}\ddot{\mathbf{q}}(t) + \int_{t_0}^{t} ds \underbrace{\left[\sum_{j=1}^{\mathcal{N}} \frac{c_j^2}{m_j\omega_j^2}\cos\omega_j(t-s)\right]}_{=\mathcal{M}\gamma(t-s)}\dot{\mathbf{q}}(s) + V'(\mathbf{q},t) = \underbrace{\sum_{j=1}^{\mathcal{N}} c_j\left[\mathbf{x}_j(t_0)\cos\omega_j(t-t_0) + \frac{\mathbf{p}_j(t_0)}{m_j\omega_j}\sin\omega_j(t-t_0)\right]}_{=\Gamma(t)}$$

Quantum Langevin equation

Heisenberg equations of motion:

System: $$\mathcal{M}\ddot{\mathbf{q}}(t) + V'(\mathbf{q},t) + \mathbf{q}(t)\sum_{j=1}^{\mathcal{N}} \frac{c_j^2}{m_j\omega_j^2} = \sum_{j=1}^{\mathcal{N}} c_j \mathbf{x}_j(t)$$

insert here

Bath: $$m_j\ddot{\mathbf{x}}_j(t) + m_j\omega_j^2\mathbf{x}_j(t) = c_j\mathbf{q}(t)\,, \qquad j = 1,...,\mathcal{N}$$

harmonic oscillator driven by the system displacement, solution:

$$\mathbf{x}_j(t) = \mathbf{x}_j(t_0)\cos\omega_j(t-t_0) + \frac{\mathbf{p}_j(t_0)}{m_j\omega_j}\sin\omega_j(t-t_0) + \frac{c_j}{m_j\omega_j}\int_{t_0}^{t} ds\,\sin\left[\omega_j(t-s)\right]\mathbf{q}(s)$$

$$= \left[\mathbf{x}_j(t_0) - \frac{c_j}{m_j\omega_j^2}\mathbf{q}(t_0)\right]\cos\omega_j(t-t_0) + \frac{\mathbf{p}_j(t_0)}{m_j\omega_j}\sin\omega_j(t-t_0)$$

$$- \frac{c_j}{m_j\omega_j^2}\int_{t_0}^{t} ds\,\cos\left[\omega_j(t-s)\right]\dot{\mathbf{q}}(s) + \frac{c_j}{m_j\omega_j^2}\mathbf{q}(t)$$

Result: Quantum Langevin equation

$$\mathcal{M}\ddot{\mathbf{q}}(t) + \mathcal{M}\int_{t_0}^{t} ds\,\gamma(t-s)\dot{\mathbf{q}}(s) + V'(\mathbf{q},t) = \mathbf{\Gamma}(t) - \mathcal{M}\gamma(t-t_0)\mathbf{q}(t_0)$$

Quantum Langevin equation

$$\mathcal{M}\ddot{\mathbf{q}}(t) + \mathcal{M}\int_{t_0}^{t} ds\,\gamma(t-s)\dot{\mathbf{q}}(s) + V'(\mathbf{q},t) = \mathbf{\Gamma}(t) - \mathcal{M}\gamma(t-t_0)\mathbf{q}(t_0)$$

Operator-valued stochastic force, since drawn from thermal ensemble:

$$\mathbf{\Gamma}(t) = \sum_{j=1}^{\mathcal{N}} c_j \left[\mathbf{x}_j(t_0)\cos\omega_j(t-t_0) + \frac{\mathbf{p}_j(t_0)}{m_j\omega_j}\sin\omega_j(t-t_0)\right]$$

Gaussian statistics:

1. Mean: $\langle\mathbf{\Gamma}(t)\rangle_{\mathrm{B}} = 0$

2. Variance: Bath autocorrelation function:

$$\begin{aligned} m_j\omega_j\langle\mathbf{x}_j(t_0)\mathbf{x}_k(t_0)\rangle_{\mathrm{B}} &= \frac{1}{m_j\omega_j}\langle\mathbf{p}_j(t_0)\mathbf{p}_k(t_0)\rangle_{\mathrm{B}} = \delta_{jk}\frac{\hbar}{2}\coth\frac{\hbar\omega_j\beta}{2} \\ \langle\mathbf{x}_j(t_0)\mathbf{p}_k(t_0)\rangle_{\mathrm{B}} &= -\langle\mathbf{p}_j(t_0)\mathbf{x}_k(t_0)\rangle_{\mathrm{B}} = i\,\delta_{jk}\frac{\hbar}{2} \end{aligned}$$

$$\langle\mathbf{\Gamma}(t-s+t_0)\mathbf{\Gamma}(t_0)\rangle_{\mathrm{B}} = \hbar\sum_{j=1}^{\mathcal{N}}\frac{c_j^2}{2m_j\omega_j}\left[\coth\frac{\hbar\omega_j\beta}{2}\cos\omega_j(t-s) - i\sin\omega_j(t-s)\right]$$

Bath spectral density

All bath parameters come in a specific combination: Bath spectral density:

$$J(\omega) = \frac{\pi}{2} \sum_{j=1}^{\mathcal{N}} \frac{c_j^2}{m_j \omega_j} \delta(\omega - \omega_j)$$

Continuum limit: $\langle \mathbf{\Gamma}(t)\mathbf{\Gamma}(s)\rangle_{\mathrm{B}} = \hbar L(t-s) = \frac{1}{\pi}\int_0^\infty d\omega\, J(\omega) \left[\coth\frac{\hbar\omega\beta}{2}\cos\omega t - i\sin\omega t\right]$

due to non-commuting position & momentum

weight function

thermal Green's function of a single harm. oscillator

Damping kernel: $\gamma(t) = \frac{2}{\pi\mathcal{M}}\int_0^\infty d\omega \frac{J(\omega)}{\omega}\cos\omega t$

Damping becomes Markovian: $\gamma(t-s) = 2\gamma\delta(t-s)$

Simplest case: Ohmic bath: $J(\omega) = \mathcal{M}\gamma\omega\ e^{-\omega/\omega_c}$

Dielectric environment: $J(\omega) \propto (\Delta\mu)^2 \mathrm{Im}\frac{2(\epsilon(\omega)-\epsilon_p)}{2\epsilon(\omega)+\epsilon_p}$

Localized vibration mode: $J(\omega) \propto \delta(\omega - \Omega)$

Quantum Langevin equation is impractical (Heisenberg picture)!

Alternative: Schrödinger picture: Feynman-Vernon influence functional

Path integral approach to open quantum systems

Full density operator of system+bath at time t in coordinate space:

$$\langle q_{\rm f}\boldsymbol{x}_{\rm f}|\mathbf{W}(t)|q'_{\rm f}\boldsymbol{x}'_{\rm f}\rangle = \langle q_{\rm f}\boldsymbol{x}_{\rm f}|\mathbf{U}(t,t_0)\mathbf{W}(t_0)\mathbf{U}^{-1}(t,t_0)|q'_{\rm f}\boldsymbol{x}'_{\rm f}\rangle$$

$$= \int dq_{\rm i}dq'_{\rm i}\prod_{j=1}^{\mathcal{N}}dx_{j,{\rm i}}\prod_{j=1}^{\mathcal{N}}dx'_{j,{\rm i}}U(q_{\rm f},\boldsymbol{x}_{\rm f},t;q_{\rm i},\boldsymbol{x}_{\rm i},t_0)\langle q_{\rm i}\boldsymbol{x}_{\rm i}|\mathbf{W}(t_0)|q'_{\rm i}\boldsymbol{x}'_{\rm i}\rangle U^*(q'_{\rm f},\boldsymbol{x}'_{\rm f},t;q'_{\rm i}\boldsymbol{x}'_{\rm i},t_0)$$

with propagator as path integral:

$$U(q_{\rm f},\boldsymbol{x}_{\rm f},t;q_{\rm i},\boldsymbol{x}_{\rm i},t_0) = \langle q_{\rm f}\boldsymbol{x}_{\rm f}|\mathcal{T}\exp\left[-\frac{i}{\hbar}\int_{t_0}^{t}ds\,\mathbf{H}(s)\right]|q_{\rm i}\boldsymbol{x}_{\rm i}\rangle$$

$$= \int_{q(t_0)=q_{\rm i}}^{q(t)=q_{\rm f}}\mathcal{D}q\prod_{j=1}^{\mathcal{N}}\int_{x_j(t_0)=x_{j,{\rm i}}}^{x_j(t)=x_{j,{\rm f}}}\mathcal{D}x_j\exp\left\{\frac{i}{\hbar}\left[S_{\rm S}[q]+\sum_{j=1}^{\mathcal{N}}S_{\rm B}[q,x_j]\right]\right\}$$

with the classical actions:

$$S_{\rm S}[q] = \int_{t_0}^{t}ds\left\{\frac{\mathcal{M}}{2}\dot{q}^2(s)-V(q(s),t)\right\}$$

$$S_{\rm B}[q,x_j] = \int_{t_0}^{t}ds\left\{\frac{m_j}{2}\dot{x}_j^2(s)-\frac{m_j}{2}\omega_j^2[x_j(s)-\frac{c_j}{m_j\omega_j^2}q(s)]^2\right\}$$

Path integral approach to open quantum systems

Bath d.o.f. not under control & not of interest: average over them:

Reduced density operator in system Hilbert space: $\rho(t) \equiv \mathrm{tr_B}\mathbf{W}(\mathrm{t})$

possible, since action quadratic: Gaussian integral

$$\rho(q_\mathrm{f}, q'_\mathrm{f}, t) = \prod_{j=1}^{\mathcal{N}} \int dx_{j,\mathrm{f}} \, \langle q_\mathrm{f} \boldsymbol{x}_\mathrm{f} | \mathbf{W}(t) | q'_\mathrm{f} \boldsymbol{x}_\mathrm{f} \rangle$$

$$= \int dq_\mathrm{i} \int dq'_\mathrm{i} \, \mathcal{G}(q_\mathrm{f}, q'_\mathrm{f}, t; q_\mathrm{i}, q'_\mathrm{i}, t_0) \rho_\mathrm{S}(q_\mathrm{i}, q'_\mathrm{i}, t_0)$$

$$\mathcal{G}(q_\mathrm{f}, q'_\mathrm{f}, t; q_\mathrm{i}, q'_\mathrm{i}, t_0) = \int_{q(t_0)=q_\mathrm{i}}^{q(t)=q_\mathrm{f}} \mathcal{D}q \int_{q'(t_0)=q'_\mathrm{i}}^{q'(t)=q'_\mathrm{f}} \mathcal{D}q' \exp\left\{ \frac{i}{\hbar} \left(S_\mathrm{S}[q] - S_\mathrm{S}[q'] \right) \right\} \mathcal{F}_\mathrm{FV}[q, q']$$

Feynman-Vernon influence functional:

$$\mathcal{F}_\mathrm{FV}[q, q'] = e^{-\frac{1}{\hbar}\phi_\mathrm{FV}[q,q']}$$

Feynman-Vernon influence functional

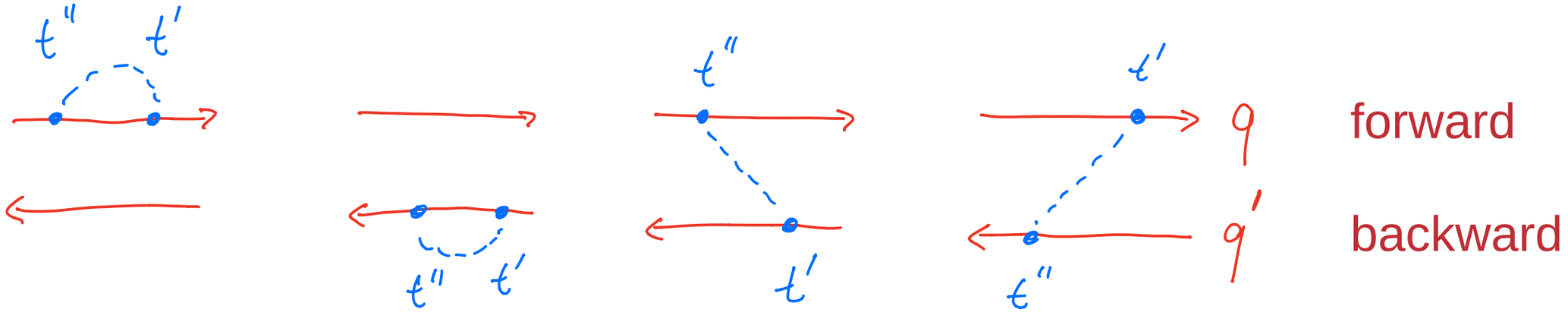
$$\mathcal{F}_{\mathrm{FV}}[q,q'] = e^{-\frac{1}{\hbar}\phi_{\mathrm{FV}}[q,q']}$$

with

$$\phi_{\mathrm{FV}}[q,q'] = \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' \{q(t') - q'(t')\}\{\eta(t'-t'')q(t'') - \eta^*(t'-t'')q'(t'')\}$$

with integral kernel

$$\eta(t) = L(t) + i\delta(t)\frac{2}{\pi}\int_0^\infty d\omega \frac{J(\omega)}{\omega}$$



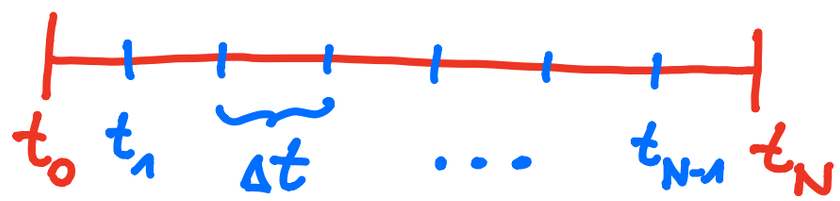
Consequences of bath fluctuations:

- time correlations between paths of system dynamics
- complex correlation function

Quasiadiabatic propagator path-integral

N. Makri, J. Math. Phys. **36**, 2430 (1995)

Time discretization (as usual)



QUAPI in 3 steps:

$$\mathbf{H}(t) = \mathbf{H}_{\mathrm{S}}(t) + \mathbf{H}_{\mathrm{B}}$$

contains $\mathbf{H}_{\mathrm{B}} + \mathbf{H}_{\mathrm{SB}}$

1. Step: Symmetric Trotter splitting of short-time propagator:

$$\mathbf{U}(t_{k+1}, t_k) \approx \exp(-i\mathbf{H}_{\mathrm{B}}\Delta t/2\hbar)\mathbf{U}_{\mathrm{S}}(t_{k+1}, t_k)\exp(-i\mathbf{H}_{\mathrm{B}}\Delta t/2\hbar)$$

General time-ordered system propagator

$$\mathbf{U}_{\mathrm{S}}(t_{k+1}, t_k) = \mathcal{T}\exp\left\{-\frac{i}{\hbar}\int_{t_k}^{t_{k+1}} dt'\,\mathbf{H}_{\mathrm{S}}(t')\right\}$$

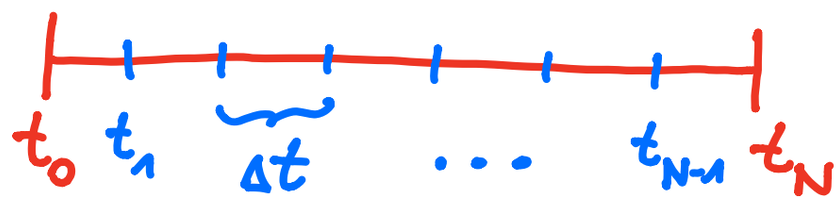
Trotter error:

$$\sim \mathcal{O}([\mathbf{H}_{\mathrm{B}}, [\mathbf{H}_{\mathrm{S}}, \mathbf{H}_{\mathrm{B}}]]\Delta t^3)$$

Quasiadiabatic propagator path-integral

N. Makri, J. Math. Phys. **36**, 2430 (1995)

Time discretization (as usual)



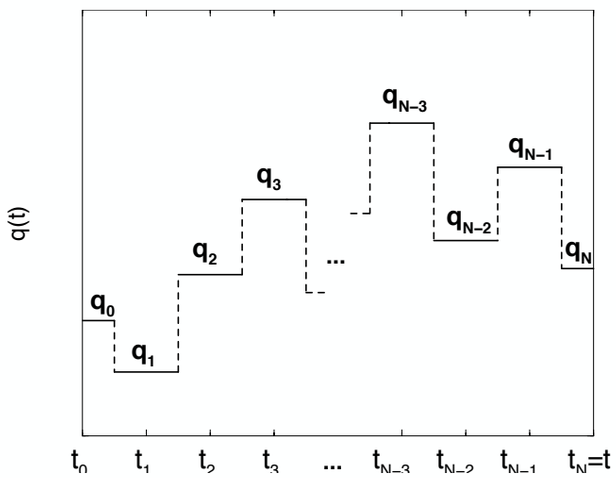
$$\mathbf{H}(t) = \mathbf{H}_{\mathrm{S}}(t) + \mathbf{H}_{\mathrm{B}}$$

contains $\mathbf{H}_{\mathrm{B}} + \mathbf{H}_{\mathrm{SB}}$

1. Step: Symmetric Trotter splitting of short-time propagator:

Short-time propagator factorizes:

$$\langle q\,\Pi_j x_j|\mathbf{U}(t_{k+1},t_k)|q'\,\Pi_j x'_j\rangle \approx \langle q|\mathbf{U}_{\mathrm{S}}(t_{k+1},t_k)|q'\rangle \prod_{j=1}^{\mathcal{N}} \langle x_j|e^{-i\mathbf{H}_j(q)\Delta t/2\hbar} e^{-i\mathbf{H}_j(q')\Delta t/2\hbar}|x'_j\rangle$$



System coordinate treated quasi-adiabatically
-> QUAPI

Quasiadiabatic propagator path-integral

N. Makri, J. Math. Phys. **36**, 2430 (1995)

Combine to full propagator from initial to final time (use completeness…)
& carry out integration over bath d.o.f. (partial trace):

Reduced density operator at time t:

$$\rho(q_{\rm f},q'_{\rm f};t)=\int dq_0\ldots\int dq_N\int dq'_0\ldots\int dq'_N\,\delta(q'_{\rm f}-q'_N)\,\delta(q_{\rm f}-q_N)$$
$$\times\langle q_N|\mathbf{U}_{\rm S}(t,t-\Delta t)|q_{N-1}\rangle\ldots\langle q_1|\mathbf{U}_{\rm S}(t_0+\Delta t,t_0)|q_0\rangle$$
$$\times\langle q_0|\rho_{\rm S}(t_0)|q'_0\rangle\langle q'_0|\mathbf{U}_{\rm S}^{-1}(t_0+\Delta t,t_0)|q'_1\rangle\ldots\langle q'_{N-1}|\mathbf{U}_{\rm S}^{-1}(t,t-\Delta t)|q'_N\rangle$$
$$\times\mathcal{F}_{FV}^{(N)}(q_0,q'_0,\ldots,q_N,q'_N)$$

discrete Feynman-Vernon influence functional:

$$\mathcal{F}_{FV}^{(N)}(q_0,\ldots,q'_N)=\exp\left\{-\frac{1}{\hbar}\sum_{k=0}^{N}\sum_{k'=0}^{k}[q_k-q'_k][\eta_{kk'}q_{k'}-\eta^*_{kk'}q'_{k'}]\right\}\ .$$

$$\eta_{kk'}=\eta(t_k-t'_k)$$

Remember:

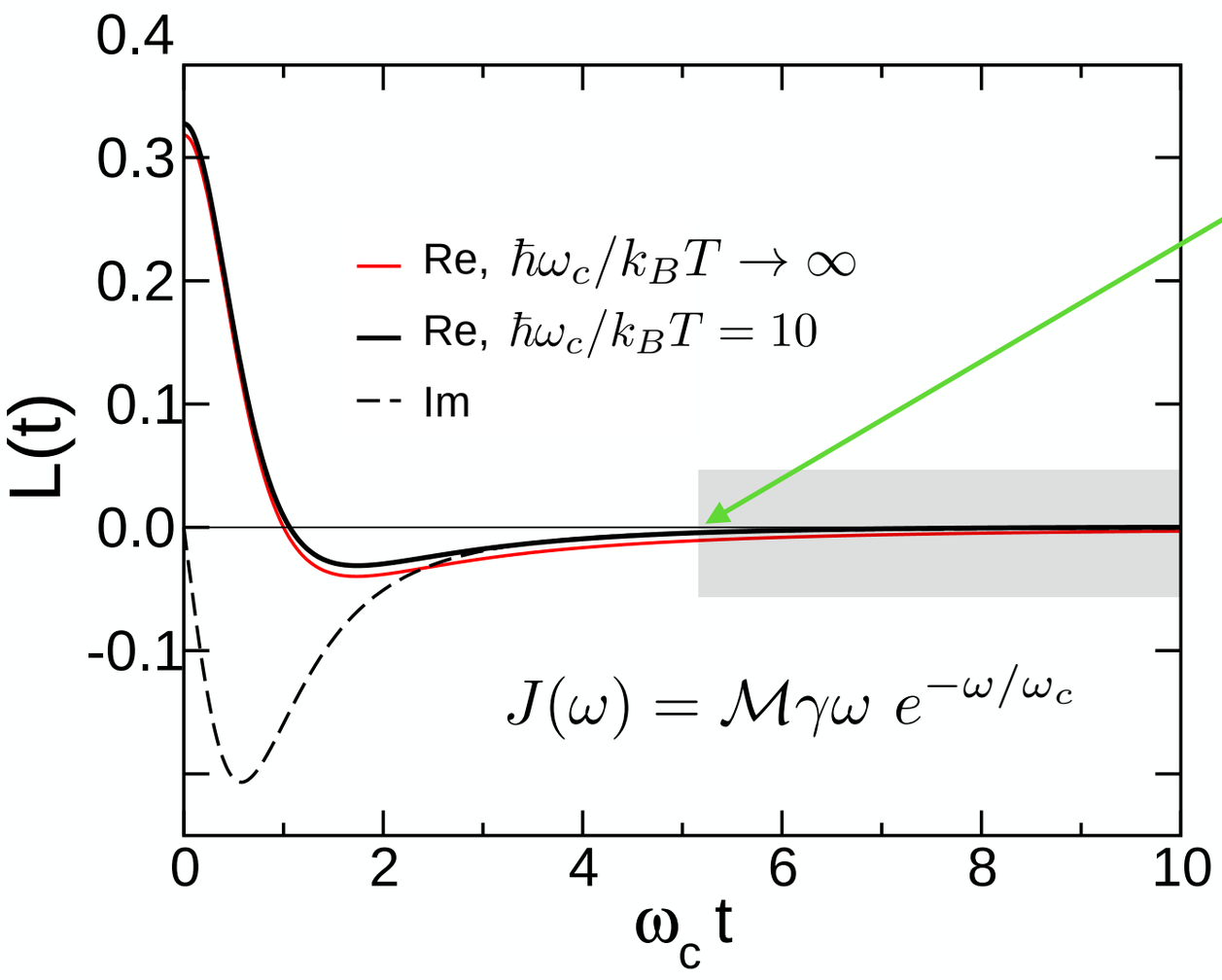
$$\eta(t)=L(t)+i\delta(t)\frac{2}{\pi}\int_0^\infty d\omega\frac{J(\omega)}{\omega}$$

Quasiadiabatic propagator path-integral

N. Makri, J. Math. Phys. **36**, 2430 (1995)

2. Step: Cut memory when it is negligible:

For any finite temperature: memory decays exponentially, i.e., there exists a memory time scale!



$$\tau_{\rm mem} = K\Delta t$$

Idea: neglect memory when it is small enough for convergence!

Remember:

$$L(t) = \frac{1}{\pi}\int_0^\infty d\omega\, J(\omega)\left[\coth\frac{\hbar\omega\beta}{2}\cos\omega t - i\sin\omega t\right]$$

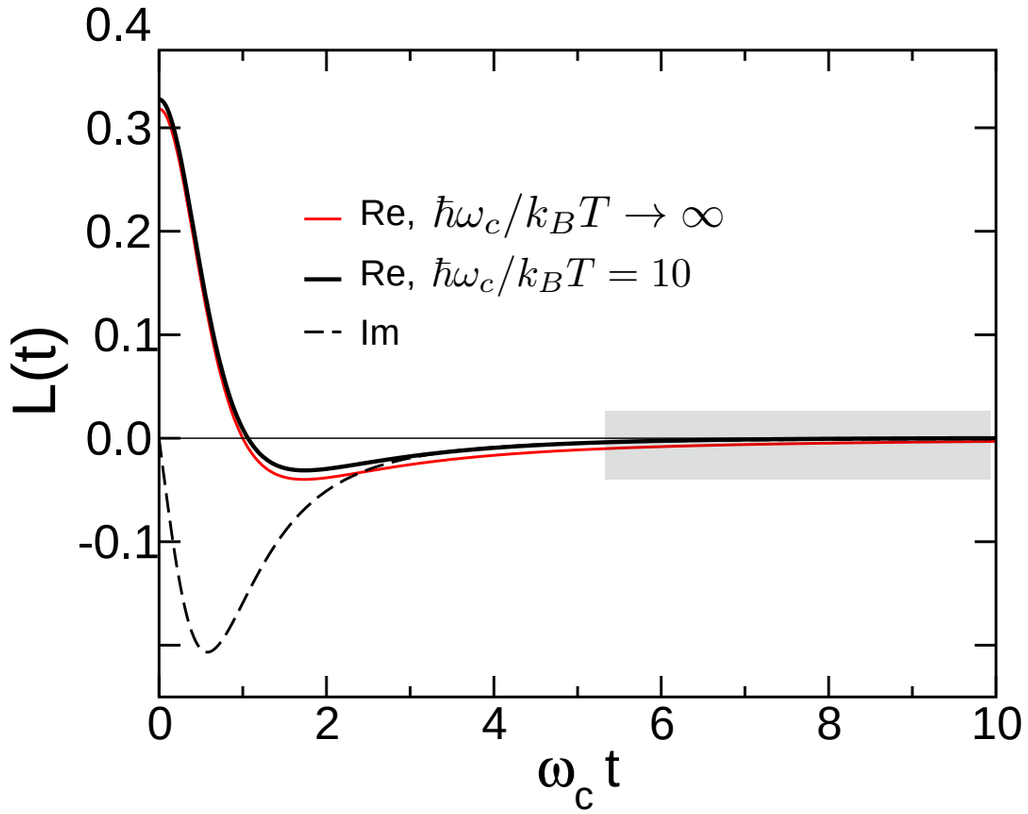
Quasiadiabatic propagator path-integral

N. Makri, J. Math. Phys. **36**, 2430 (1995)

2. Step: Cut memory when it is negligible:

$$\tau_{\rm mem} = K\Delta t$$

$$\mathcal{F}_{FV}^{(N)}(q_0,...,q'_N) \approx \prod_{k=0}^{N} \prod_{k'=0}^{\min\{N,K\}} \exp\left\{-\frac{1}{\hbar}[q_k - q'_k][\eta_{kk'}q_{k'} - \eta^*_{kk'}q'_{k'}]\right\}$$



in practice: increase K until numerical convergence is established

Remember:

$$\mathcal{F}_{FV}^{(N)}(q_0,...,q'_N) = \exp\left\{-\frac{1}{\hbar}\sum_{k=0}^{N}\sum_{k'=0}^{k}[q_k - q'_k][\eta_{kk'}q_{k'} - \eta^*_{kk'}q'_{k'}]\right\} .$$

Quasiadiabatic propagator path-integral

N. Makri, J. Math. Phys. **36**, 2430 (1995)

Iterative tensor multiplication scheme:

$$\rho(q, q', t) \equiv \rho_k(q_k, q'_k) \quad \Rightarrow \quad A_k(q_k, ..., q'_{k+K-1})$$

reduced density matrix (local in time) → reduced density tensor (depends on memory)

propagate numerically: iteration:

$$A_{k+1}(q_{k+1}, ..., q'_{k+K}) = \int dq_k \int dq_{k'} \Lambda_k(q_k, ..., q'_{k+K})\, A_k(q_k, ..., q'_{k+K-1})$$

with propagating tensor:

$$\Lambda_k(q_k, ..., q'_{k+K}) = \langle q_{k+1}|\mathbf{U}_{\mathrm{S}}(t_{k+1}, t_k)|q_k\rangle\langle q'_k|\mathbf{U}_{\mathrm{S}}^{-1}(t_{k+1}, t_k)|q'_{k+1}\rangle \prod_{k'=0}^{K} \exp\left\{-\frac{1}{\hbar}[q_k - q'_k][\eta_{kk'}q_{k'} - \eta^*_{kk'}q'_{k'}]\right\}$$

At final time: $\rho(q_f, q'_f, t) = A_N(q_f, q'_f, \hat{q}, ..., \hat{q})\, \exp\left\{-\frac{1}{\hbar}[q_f - q'_f][\eta_{NN}q_f - \eta^*_{NN}q'_f]\right\}$

Quasiadiabatic propagator path-integral

N. Makri, J. Math. Phys. **36**, 2430 (1995)

3. Step: Discrete variable representation

$$\int dq_k \int dq_{k'} \ldots \quad \Rightarrow \quad \sum_{m_k=1}^{M} \sum_{m'_k=1}^{M} \ldots$$

dimension of system Hilbert space

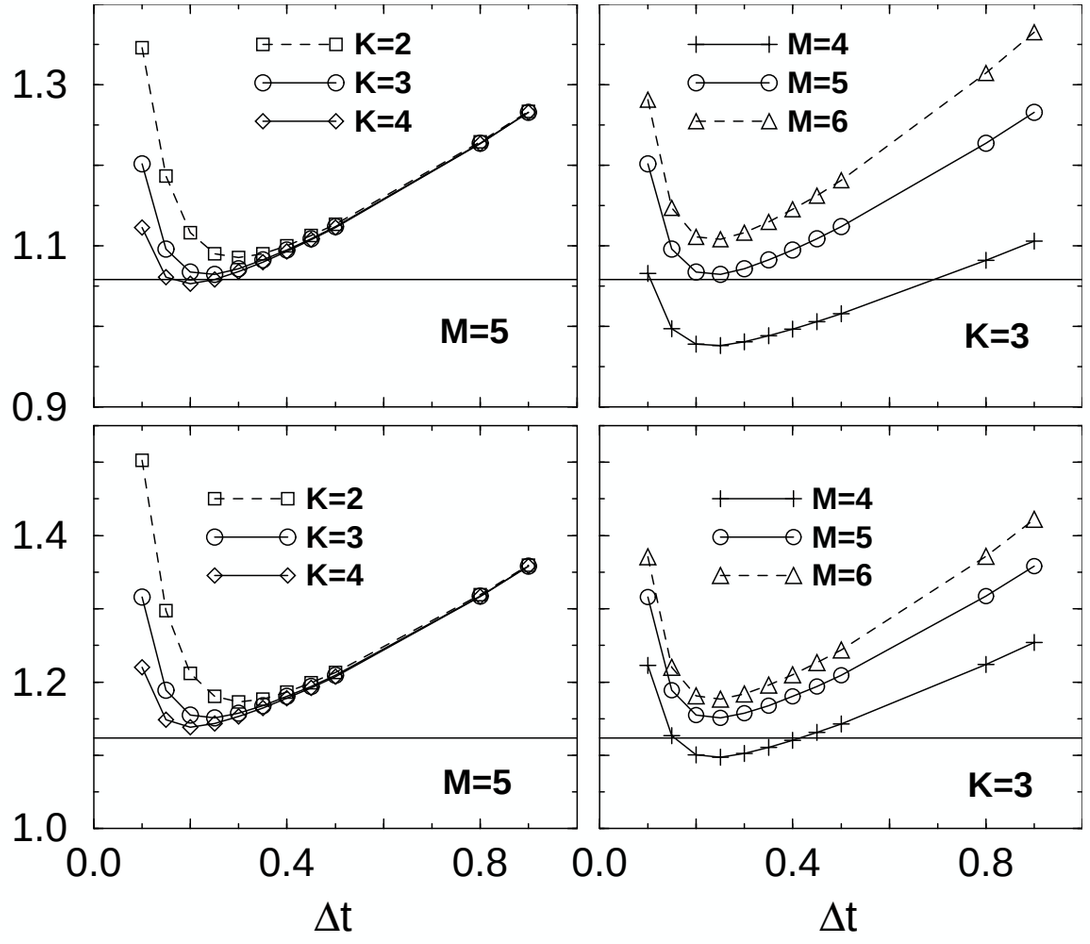
continuous integration in coordinate space

discrete summation in eigenspace of system-bath coupling operator

Careful check for convergence:

- Trotter increment as small as possible
- memory time as large as possible
- optimum in between

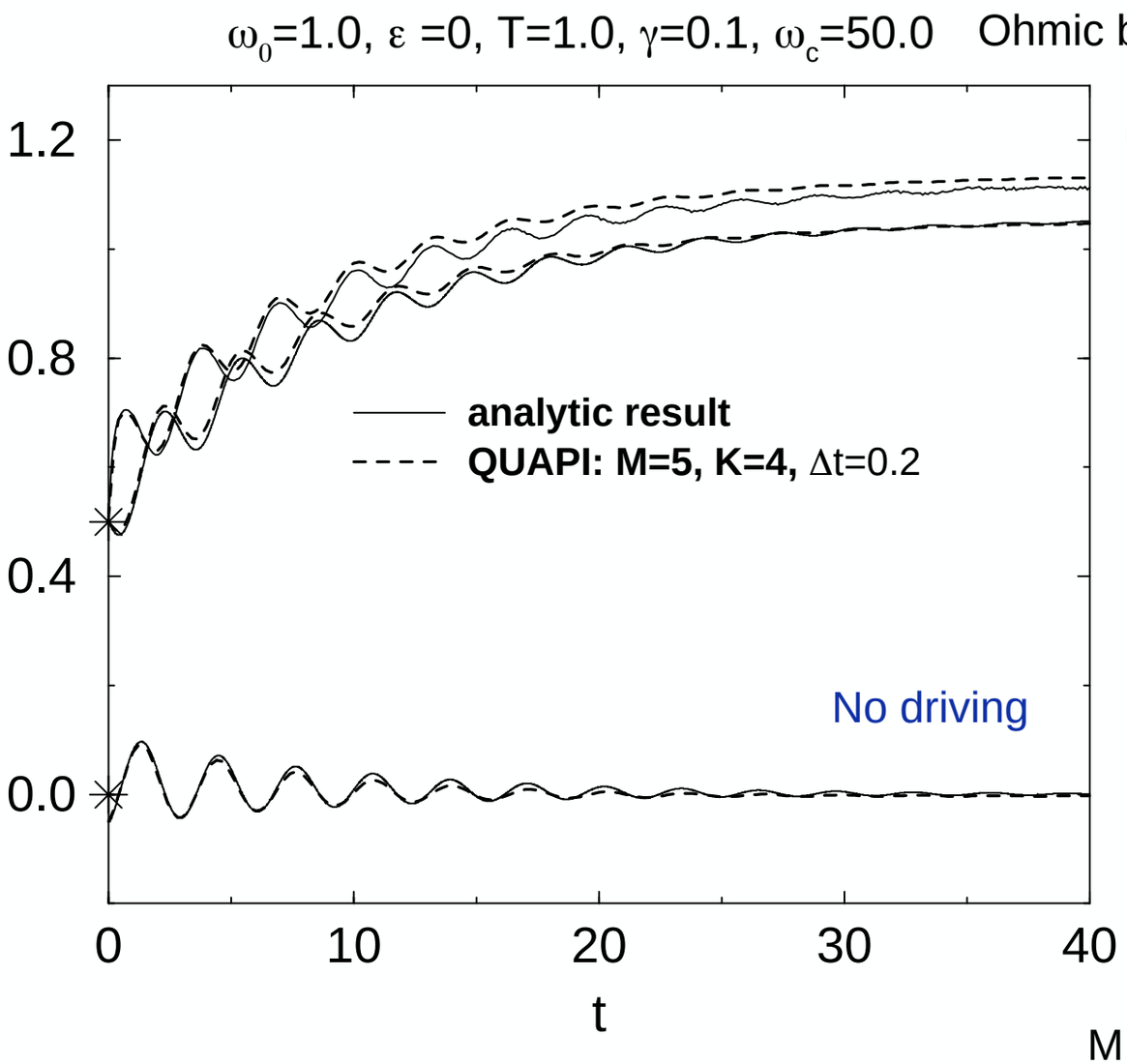
M. Thorwart, P. Reimann, P. Hänggi, Rev. E **62**, 5808 (2000)



QUAPI: Verification & tests

Parametrically driven quantum dissipative harmonic oscillator

$$\mathbf{H}_{\mathrm{S}}(t) = \frac{\mathbf{p}^2}{2\mathcal{M}} + \frac{\mathcal{M}}{2}[\omega_0^2 + \epsilon\cos\Omega t]\mathbf{q}^2$$



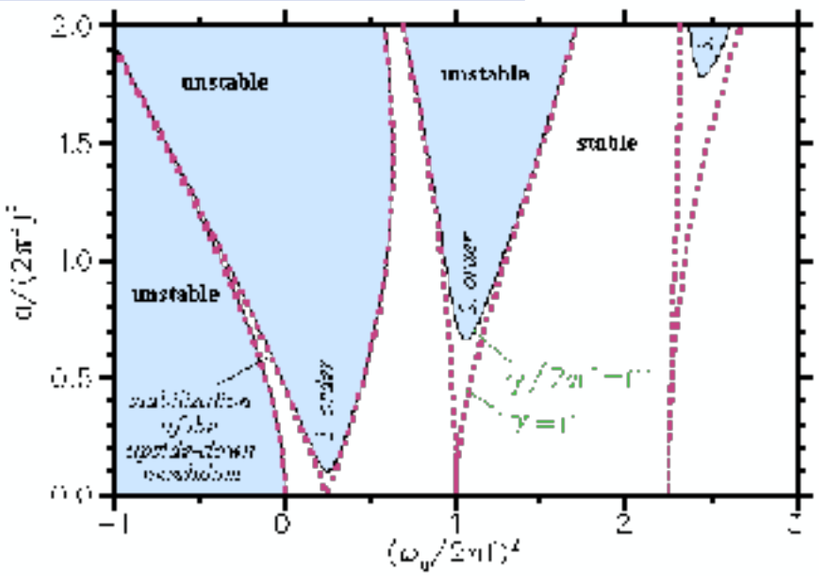
$$\sigma_{qq}(t) \equiv \langle \mathbf{q}^2(t)\rangle - \langle \mathbf{q}(t)\rangle^2$$
$$\sigma_{qp}(t) \equiv \frac{1}{2}\langle \mathbf{q}(t)\mathbf{p}(t) + \mathbf{p}(t)\mathbf{q}(t)\rangle - \langle \mathbf{q}(t)\rangle\langle \mathbf{p}(t)\rangle$$
$$\sigma_{pp}(t) \equiv \langle \mathbf{p}^2(t)\rangle - \langle \mathbf{p}(t)\rangle^2$$

M. Thorwart, P. Reimann, P. Hänggi, Rev. E **62**, 5808 (2000)

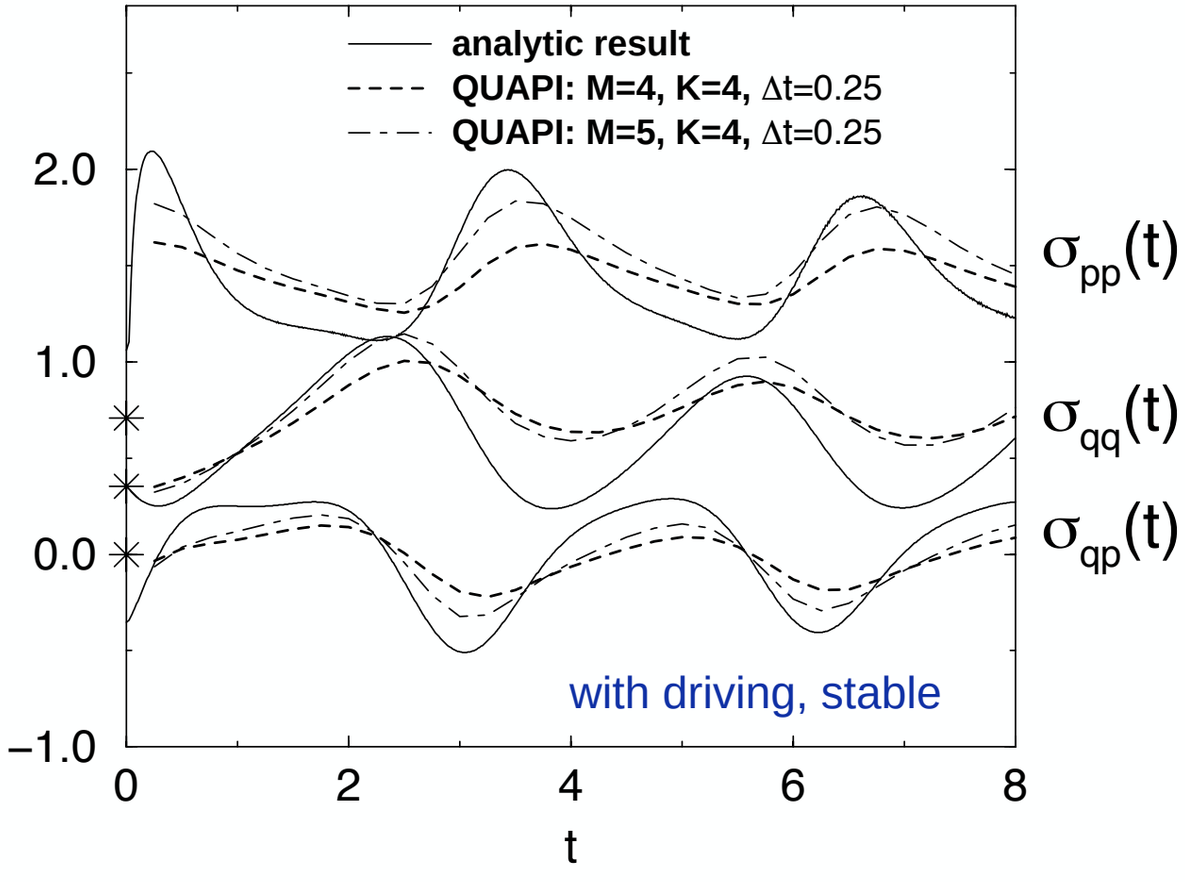
QUAPI: Verification & tests

Parametrically driven quantum dissipative harmonic oscillator

$$\mathbf{H}_{\mathrm{S}}(t) = \frac{\mathbf{p}^2}{2\mathcal{M}} + \frac{\mathcal{M}}{2}[\omega_0^2 + \epsilon\cos\Omega t]\mathbf{q}^2$$



ω_0=1.0, ε =0.5, T=0.1, γ=1.0, ω_c=50.0 Ohmic bath



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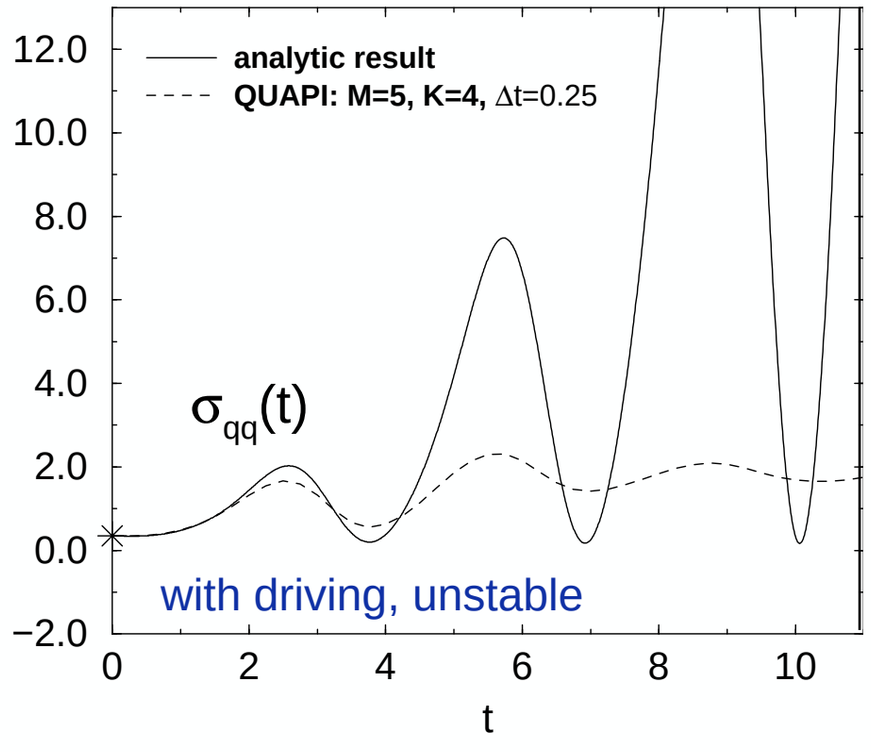
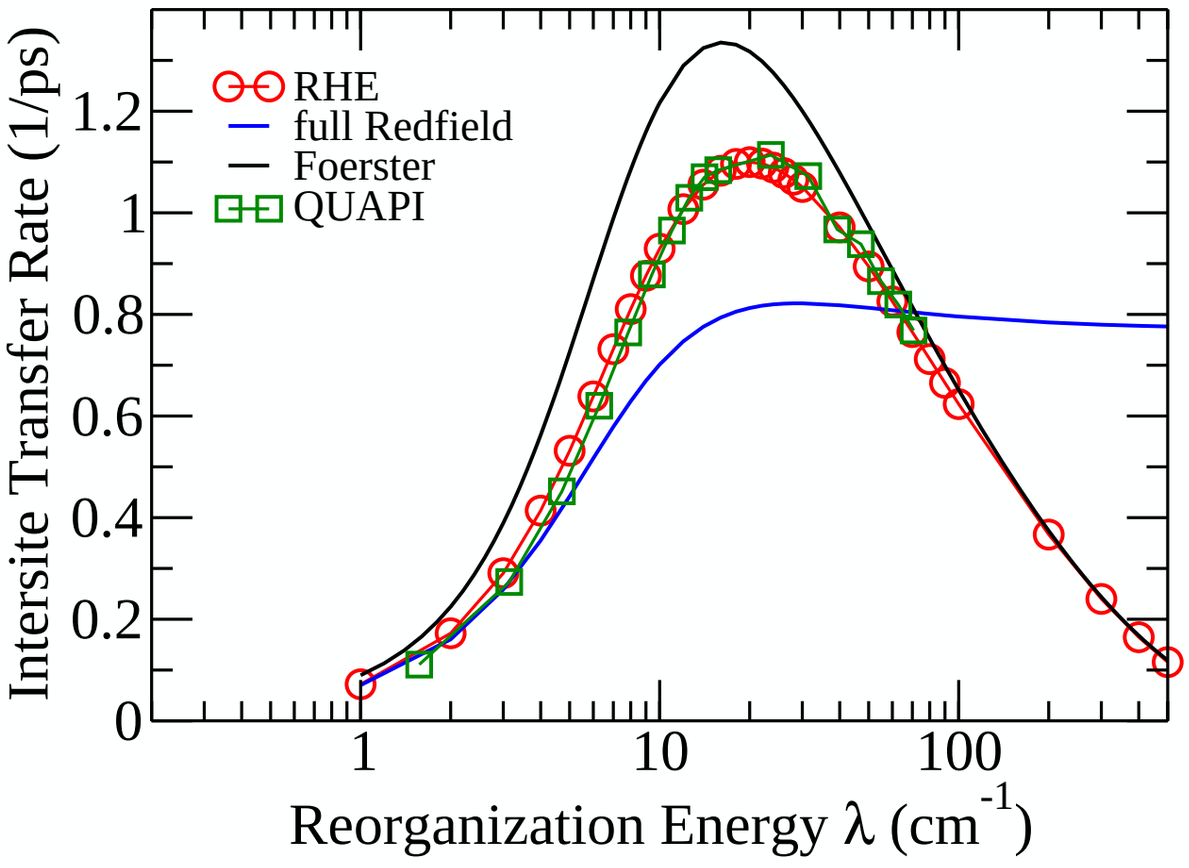


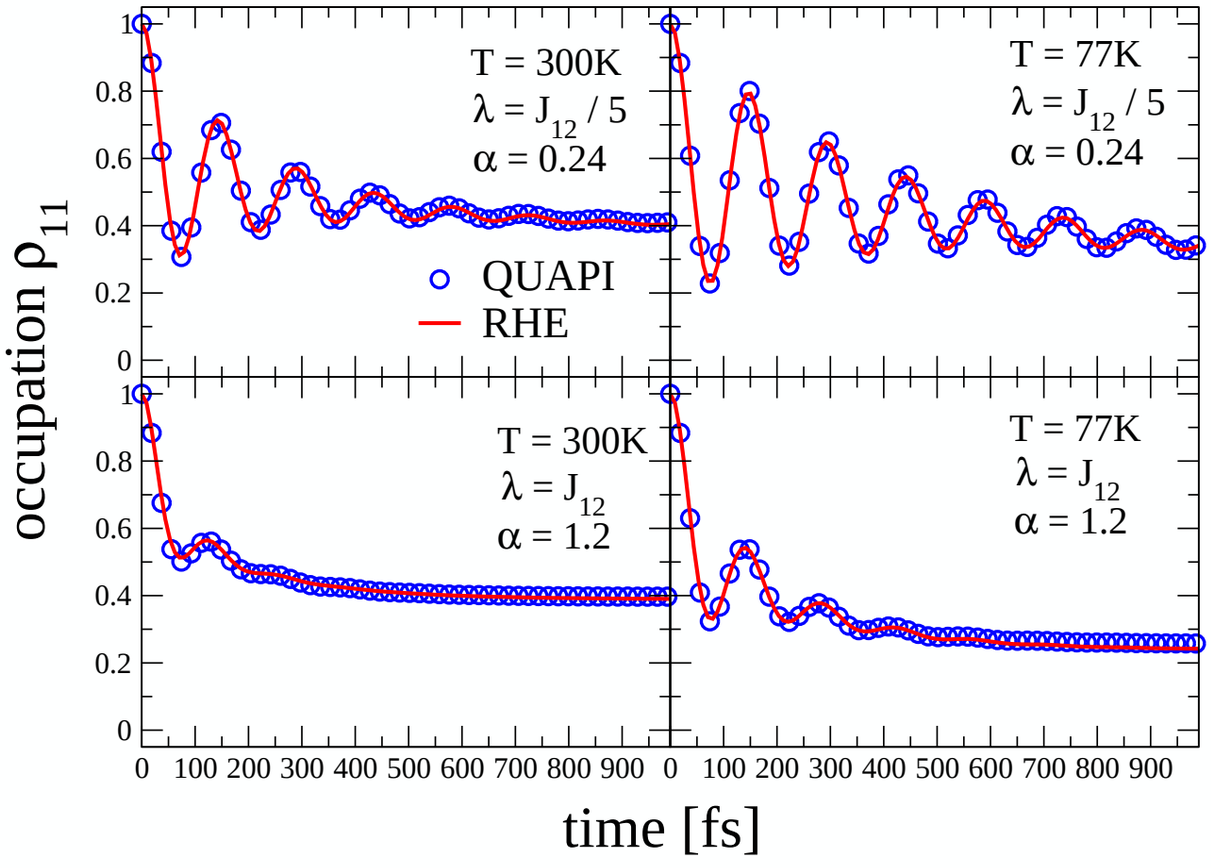
M. Thorwart, P. Reimann, P. Hänggi, Rev. E **62**, 5808 (2000)

QUAPI vs. Hierarchy equation of motion

P. Nalbach, A. Ishizaki, G.R. Fleming, M. Thorwart, New J. Phys. (2011)

- Dimer in an Ohmic bath:





$$\varepsilon = 2.5\Delta, \omega_c = 1.3\Delta, T = 5.2\Delta, \Delta = 40\mathrm{cm}^{-1}$$

$$\omega_c = 53.1\mathrm{cm}^{-1}, J_{12} = 100\mathrm{cm}^{-1} = \Delta/2$$

$$J(\omega) = \frac{\lambda}{\omega_c}\omega e^{-\omega/\omega_c}$$

$$\lambda = 35\mathrm{cm}^{-1}$$

Other techniques (personal selection)

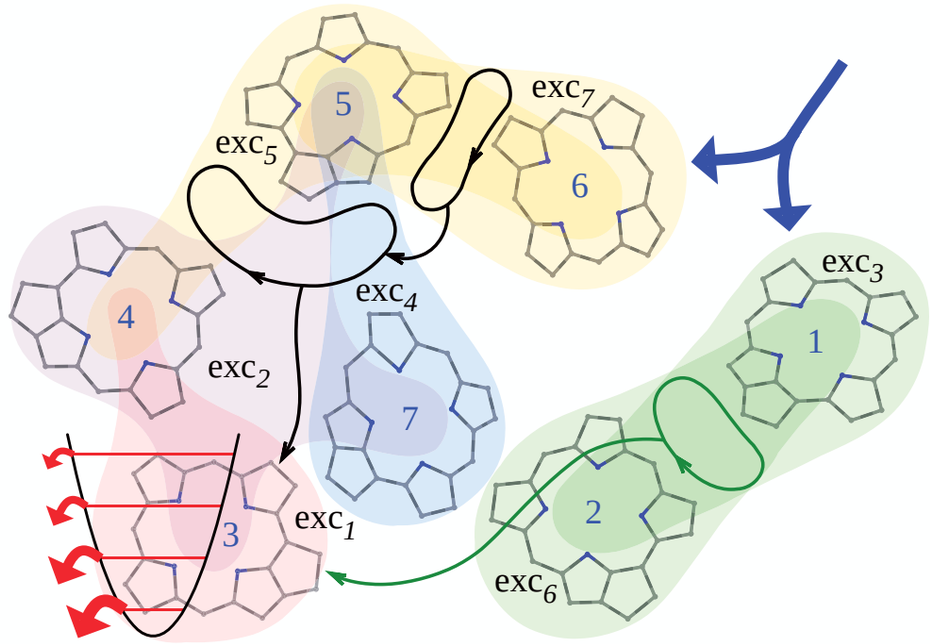
- Quantum Monte Carlo: stochastic sampling of path integral — Egger, Mak, …
  (+: very general, numerically exact, -: sign problem in real time)
- Stochastic Schrödinger Equation & HOPS — Djosi, Strunz, Eisfeld
  (+: very general, very efficient, numerically exact)
- Hierarchy Equation of Motion — Tanimura
  (+: very general, numerically exact)
- Renormalization Groups: DMRG, NRG, fRG, … — Plenio, Burghardt, …

- Flow Equation — Kehrein
  (+: numerical exact, -: limited to smaller systems)
- Time-Nonlocal Quantum Master Equations — Meir, Tannor, …
  (+: very efficient, -: approximative, weak coupling)
- Redfield Equation (Born-Markov master equation) — Redfield, Bloch, …
  (+: very efficient, -: approximative, weak coupling)
- Analytical: NIBA, generalized master equation — Leggett, Weiss, Grabert, Grifoni, Hänggi,…
  (+: analytical, -: approximative/perturbative)

FMO protein complex: Calculations

Nalbach, Braun, Thorwart, Phys. Rev. E (2011)

- Quantum dissipative exciton dynamics
- Monomer: 7 chromophore / sites
- Numerically exact path-integrals QUAPI
- Hamiltonian:



$$H = \begin{pmatrix} 240 & -87.7 & 5.5 & -5.9 & 6.7 & -13.7 & -9.9 \\ & 315 & 30.8 & 8.2 & 0.7 & 11.8 & 4.3 \\ & & 0 & -53.5 & -2.2 & -9.6 & 6.0 \\ & & & 130 & -70.7 & -17.0 & -63.3 \\ & & & & 285 & 81.1 & -1.3 \\ & & & & & 435 & 39.7 \\ & & & & & & 245 \end{pmatrix} \mathrm{cm}^{-1}$$

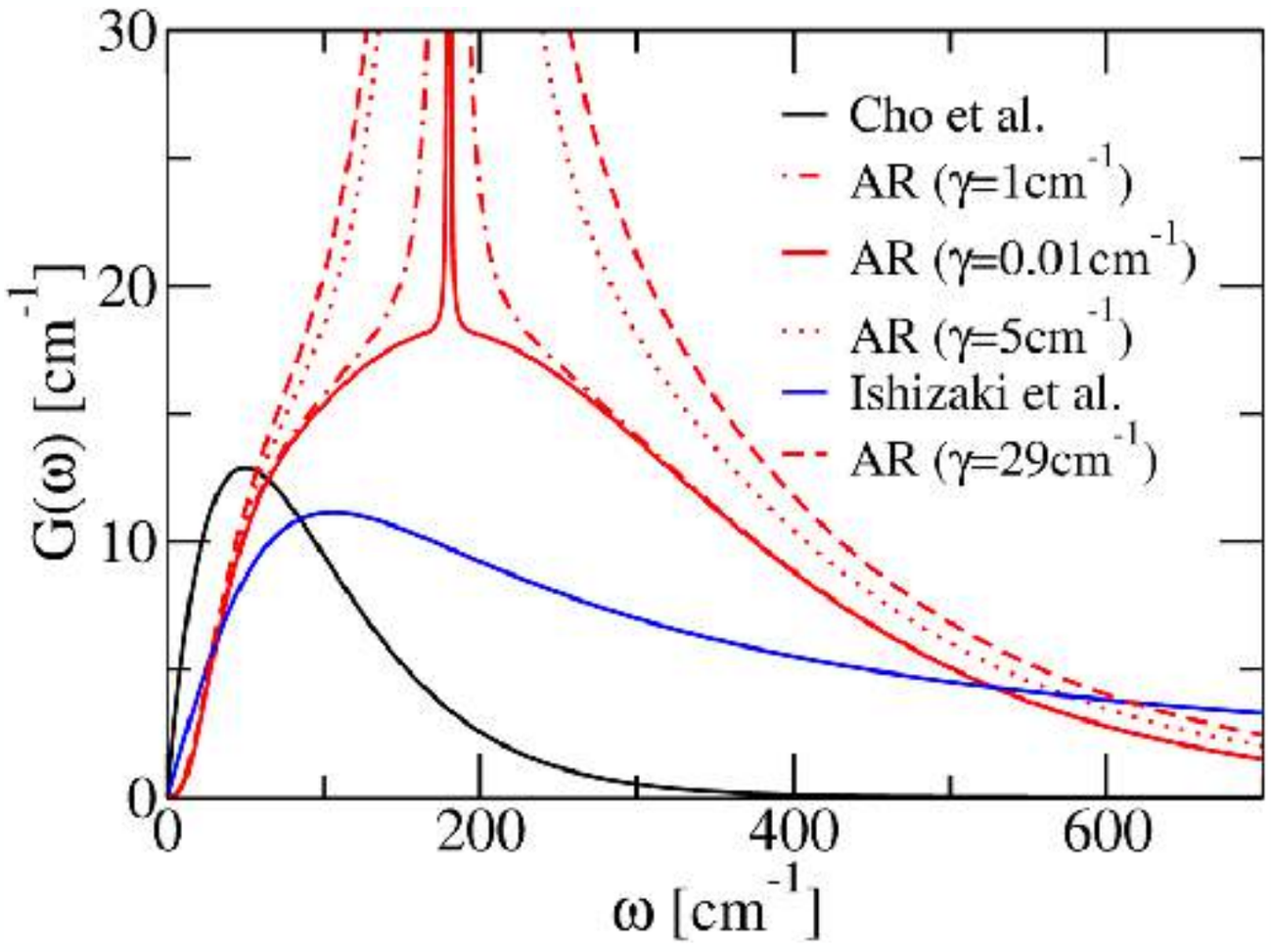
Wendling et al. J. Phys. Chem. B (2000), Adolphs, Renger, Biophys. J. (2006), Renger, Marcus, J. Chem. Phys. (2002)

FMO protein complex: Calculations

Nalbach, Braun, Thorwart, Phys. Rev. E (2011)

- Bath spectral density (from expts. & calcs):

$$J(\omega) = 0.5 \left(c_1 \frac{\omega^5}{\omega_1^4} e^{-\sqrt{\omega/\omega_1}} + c_2 \frac{\omega^5}{\omega_2^4} e^{-\sqrt{\omega/\omega_2}} \right) + 0.22\, \omega^2 \delta \left(\omega - 180\mathrm{cm}^{-1} \right)$$



Total „amount“ of damping: reorganization energy

$$\lambda = \int_0^\infty d\omega J(\omega)$$

- only background:

$$\lambda = 35\mathrm{cm}^{-1}$$

- with broadened vib. mode:

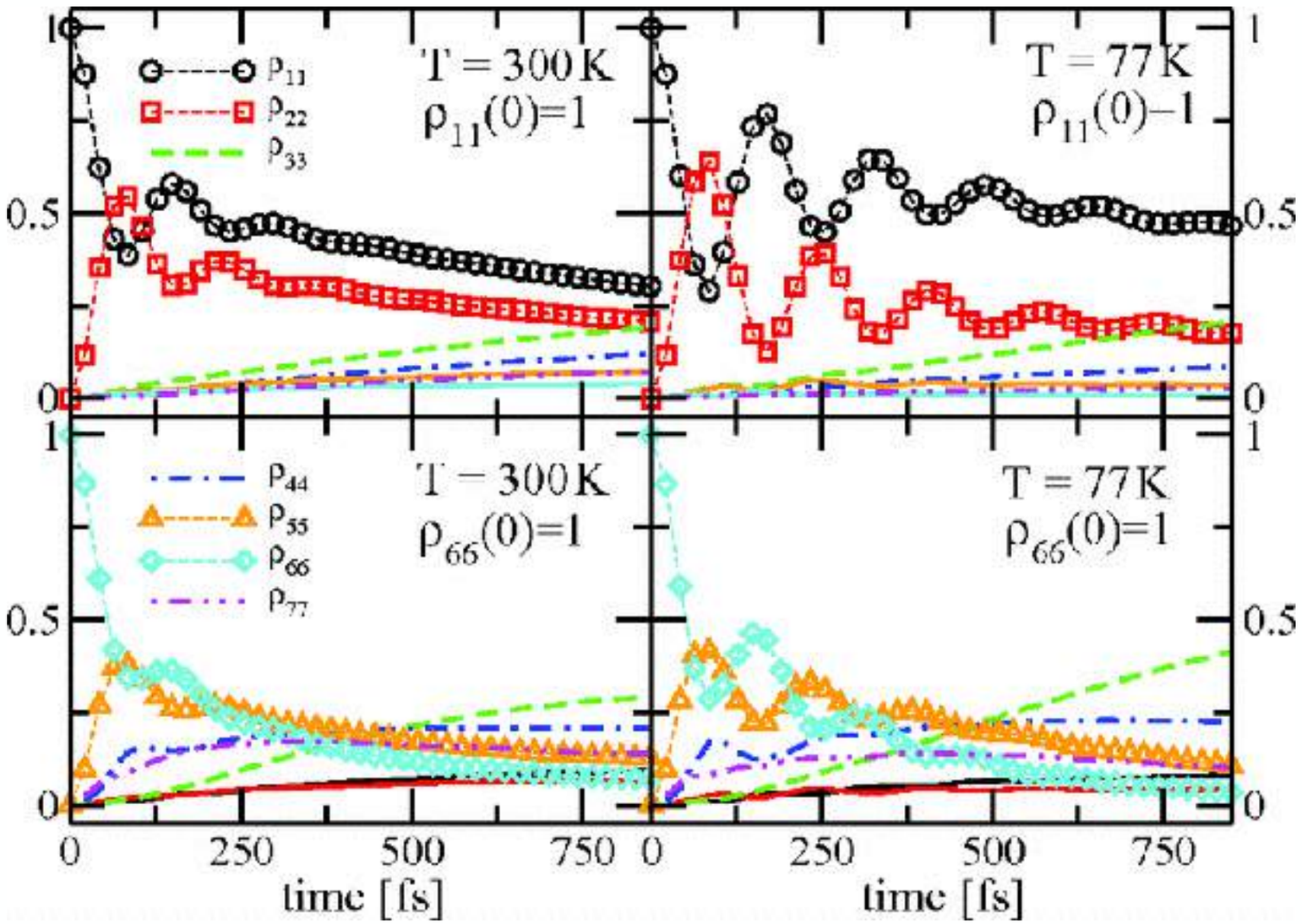
$$\lambda = 100\mathrm{cm}^{-1}$$

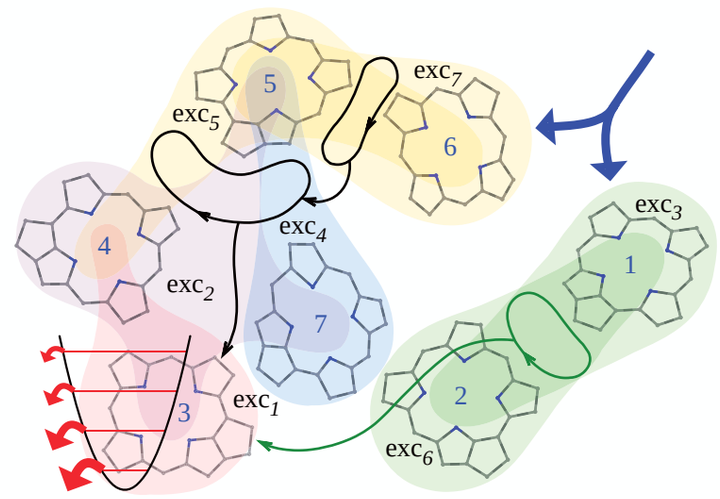
Wendling et al. J. Phys. Chem. B (2000), Adolphs, Renger, Biophys. J. (2006), Renger, Marcus, J. Chem. Phys. (2002)

Dynamics of FMO site populations

Nalbach, Braun, Thorwart, Phys. Rev. E (2011)

- Phenomenological Ohmic bath spectrum (Ishizaki & Fleming)





$$J(\omega) = \frac{\lambda}{\omega_c}\omega e^{-\omega/\omega_c}$$

$$\lambda = 35\mathrm{cm}^{-1}, \omega_c = 50\mathrm{cm}^{-1}$$

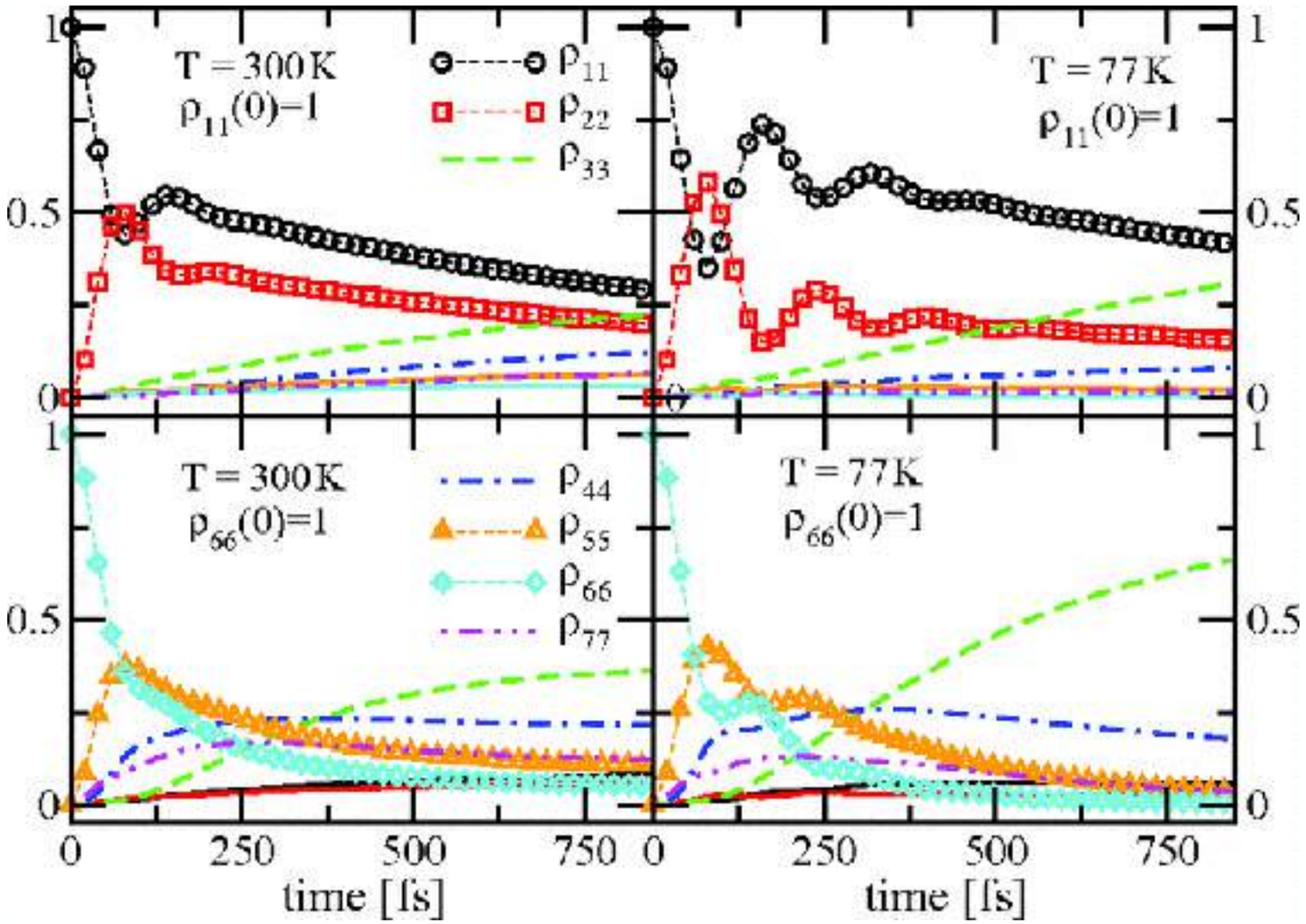
300 K: 350 fs 77 K: 700 fs

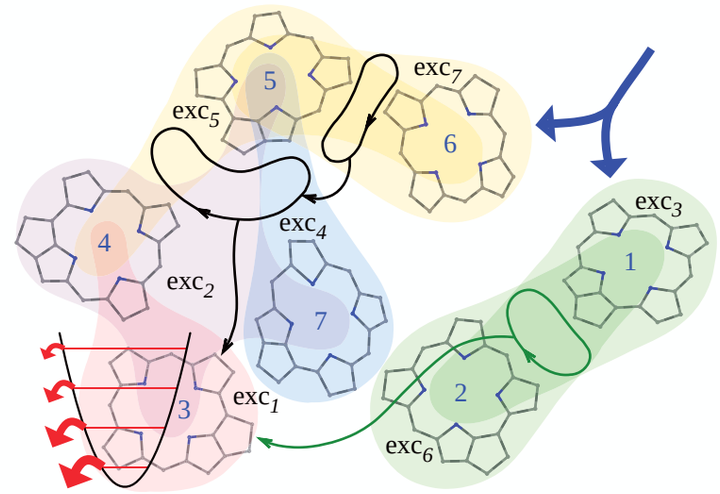
Ishizaki, Fleming, PNAS **106**, 17255 (2009)

FMO protein complex: Calculations

Nalbach, Braun, Thorwart, Phys. Rev. E (2011)

- Measured / parametrized bath spectrum (Adolphs & Renger)





	$\rho_{11}(0)=1$	$\rho_{66}(0)=1$
T= 77 K	500 fs	250 fs
T=300 K	200 fs	none

- No exceptionally long-lived coherence
- Electronic coherence times as expected!

How „quantum“ is the FMO exciton?

- Energy current:

  Nalbach, Braun, Thorwart, Phys. Rev. E (2011)

  Define qm energy current operator $\hat{j}$ via continuity equation

$$\frac{\partial}{\partial t} H(\mathbf{x}, t) + \operatorname{div} \hat{j}(\mathbf{x}, t) = 0$$

- Decompose Hamiltonian $H = \sum_{i=1}^{N} h_i \qquad h_i = \frac{1}{2} \sum_{k=1}^{N} h_{ik} |i\rangle\langle k| + \text{H.c.}$

- Current at site i

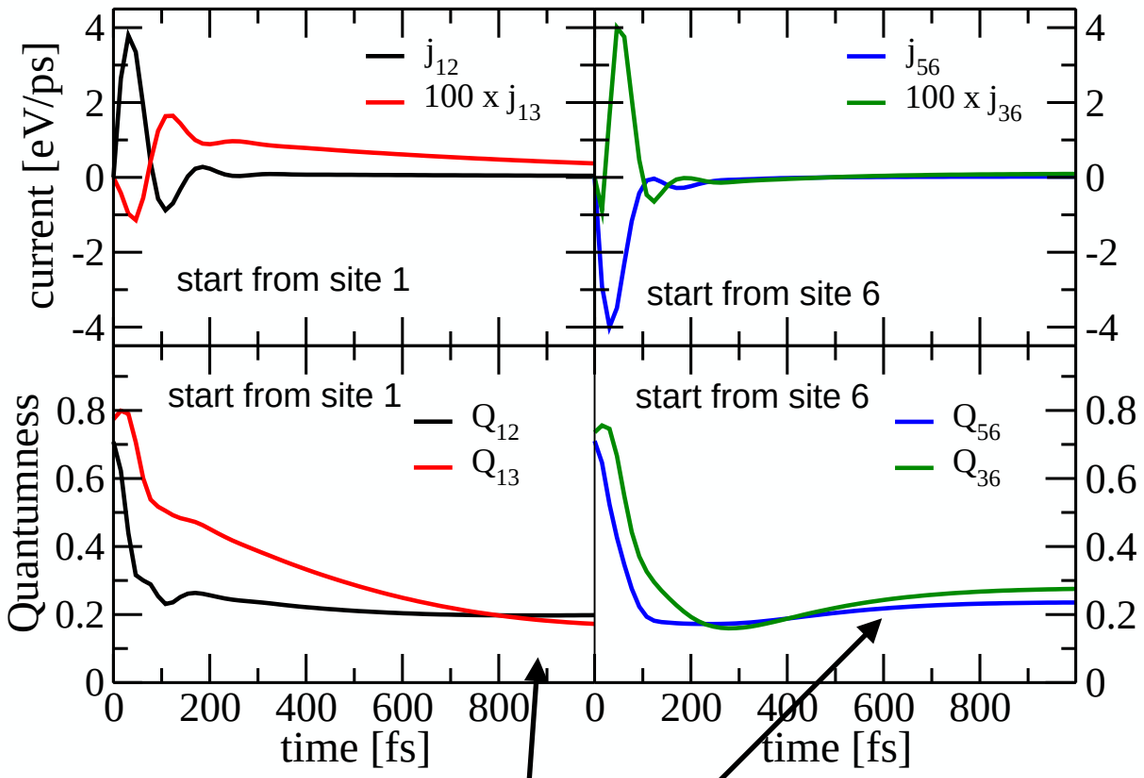
$$\frac{\partial}{\partial t} h_i = \frac{1}{2} \sum_{k \neq i} (s_{k \to i} - s_{i \to k}) \qquad s_{i \to k} = \frac{i}{2\hbar} \sum_{l} (h_{ik} h_{kl} |i\rangle\langle l| + \text{H.c.})$$

- eigenvectors of $\hat{j}$ are pointer states, classical
- Define Quantumness $\mathcal{Q}[\rho]$ = minimal Hilbert-Schmidt distance of a state ρ to the pointer state
- $\mathcal{Q}[\rho] = 0$ for a classical state

How „quantum“ is the FMO exciton?

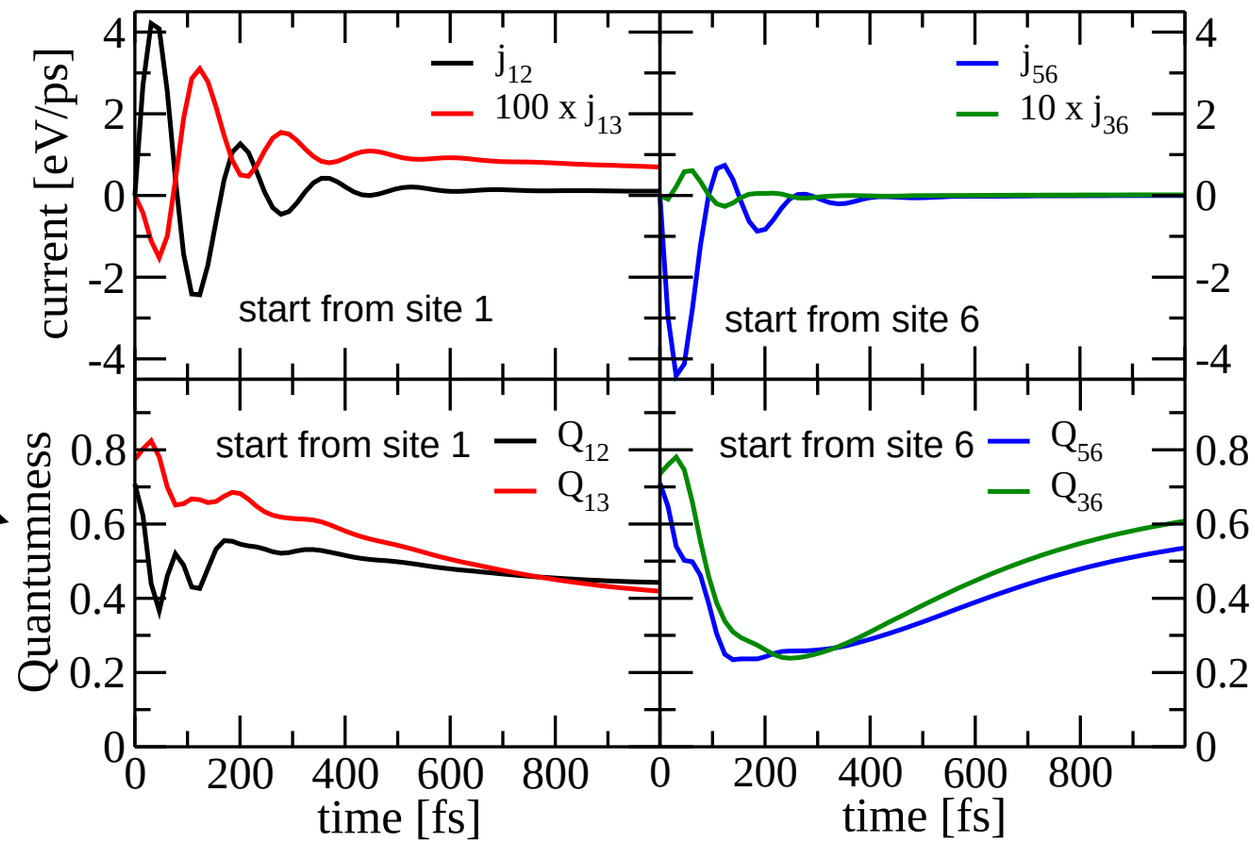
Nalbach, Braun, Thorwart, Phys. Rev. E (2011)

$$T = 77\mathrm{K}$$



Excitons are delocalized !

$$T = 300\mathrm{K}$$



Is the FMO exciton dynamics non-Markovian?

Mujica-Martinez, Nalbach, Thorwart, Phys. Rev. E (2013)

- Non-Ohmic spectral density: Exciton dynamics could be non-Markovian
- Quantify this by non-Markovianity measure Breuer *et al.,* PRL 2009
- based on trace distance between two mixed states:

$$D\left(\rho_1,\rho_2\right)=\frac{1}{2}\mathrm{tr}\left|\rho_1-\rho_2\right| \quad \text{with} \quad \left|O\right|=\sqrt{O^\dagger O}$$

- measures distinguishability of quantum states
- $0 \leq D \leq 1$
- Markovian dynamics: any two different initial states become less distinguishable with time and approach to the steady state, i.e., information flows from system to environment
- non-Markovian dynamics: states may also evolve away from each other, i.e., information backflow from bath to system, i.e, D increases with time

Is the FMO exciton dynamics non-Markovian?

- non-Markovianity measure:

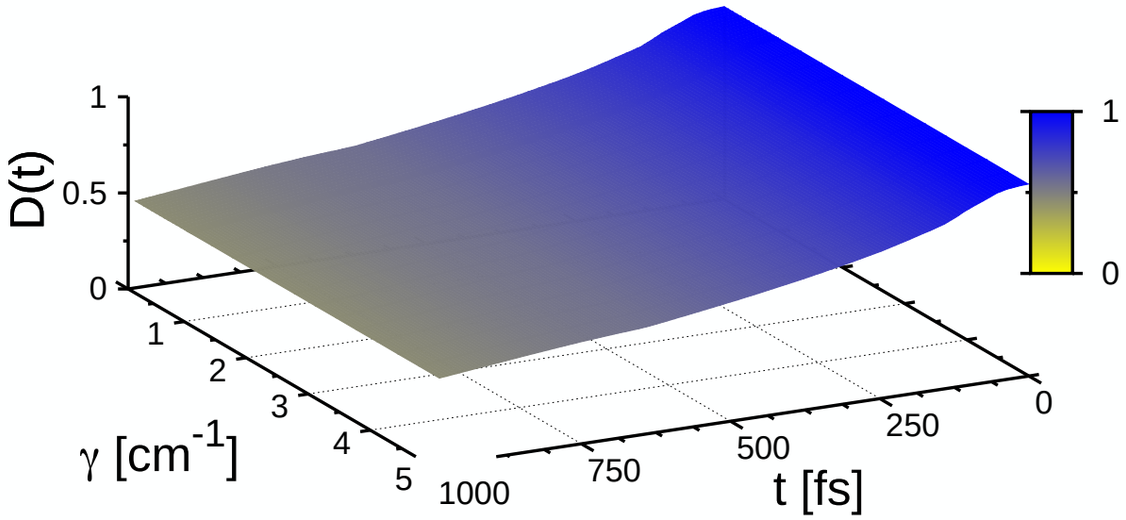
Mujica-Martinez, Nalbach, Thorwart, Phys. Rev. E (2013)

$$\mathcal{N}(\Phi) = \sum_i \left[D\left(\rho_1(b_i), \rho_2(b_i)\right) - D\left(\rho_1(a_i), \rho_2(a_i)\right) \right]$$

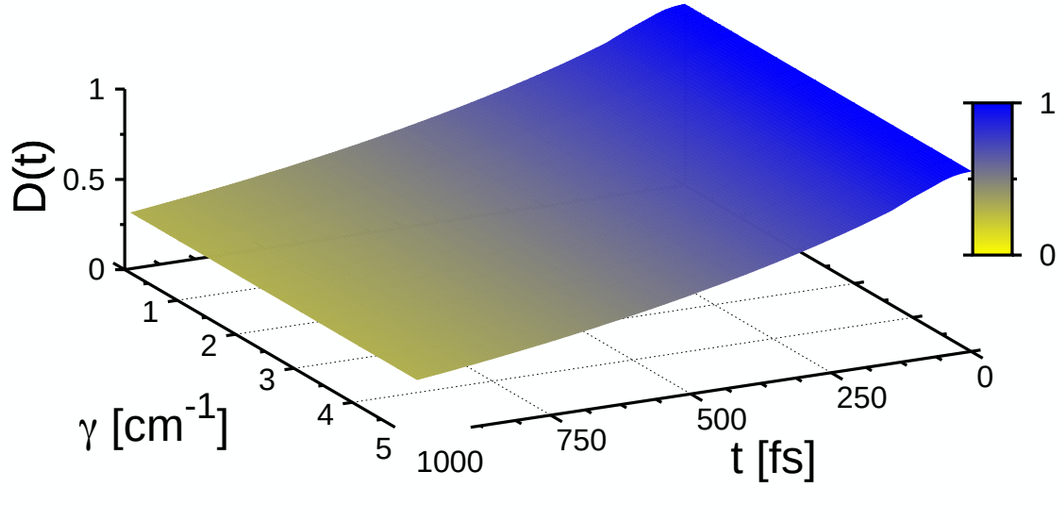
with sum over those time intervals (a_i, b_i), over which D increases

- Result: non-Markovianity is zero at low and room temperature:

$T = 77\mathrm{K}$



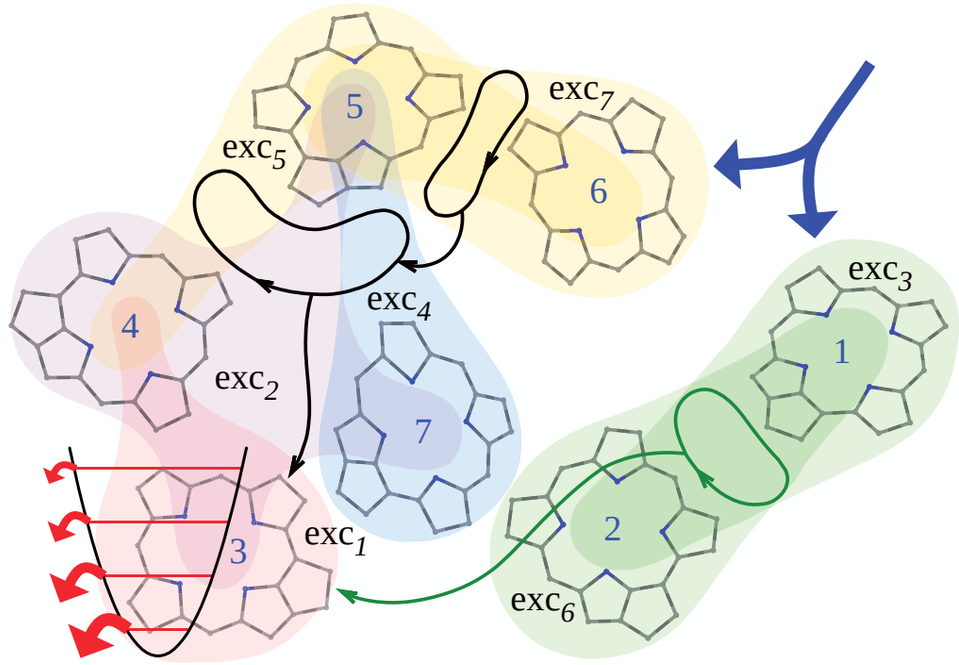
$T = 300\mathrm{K}$



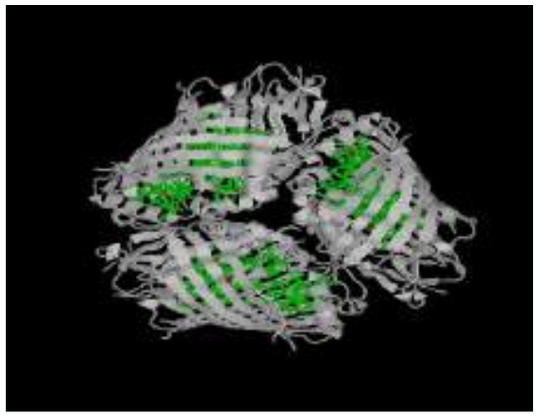
- same when vibrational mode is artificially set in resonance with exciton transitions

Summary up to this point

- Theoretical calculations:
  - no exceptionally long coherence (certainly not at room temperature)
  - Excitons delocalized over a few sites at low and room temperatures
  - Exciton dynamics fully Markovian



- BUT: experiment predicts long-lived quantum coherence
- So: Let us repeat the experiment!

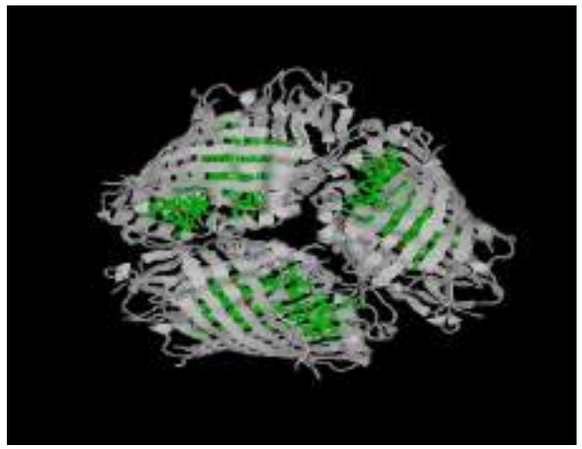


FMO complex

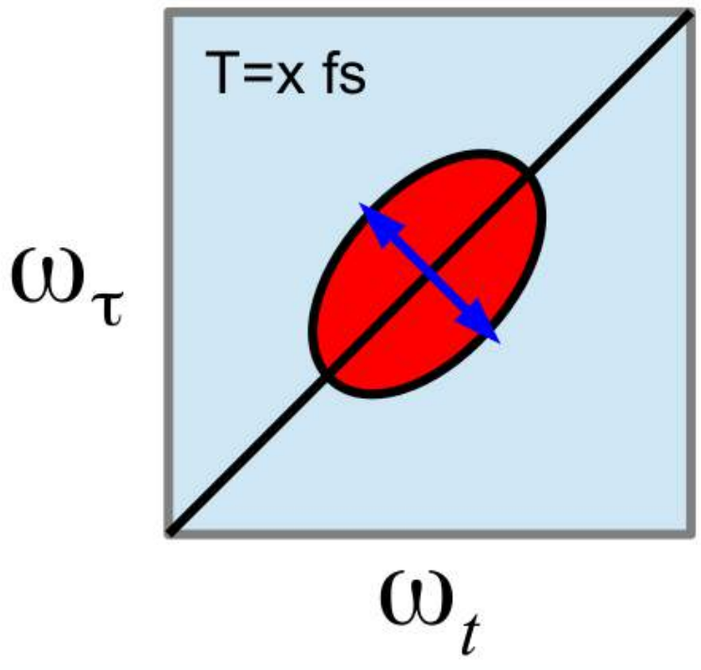
FMO: Experiment Nonlinear 2D Spectroscopy

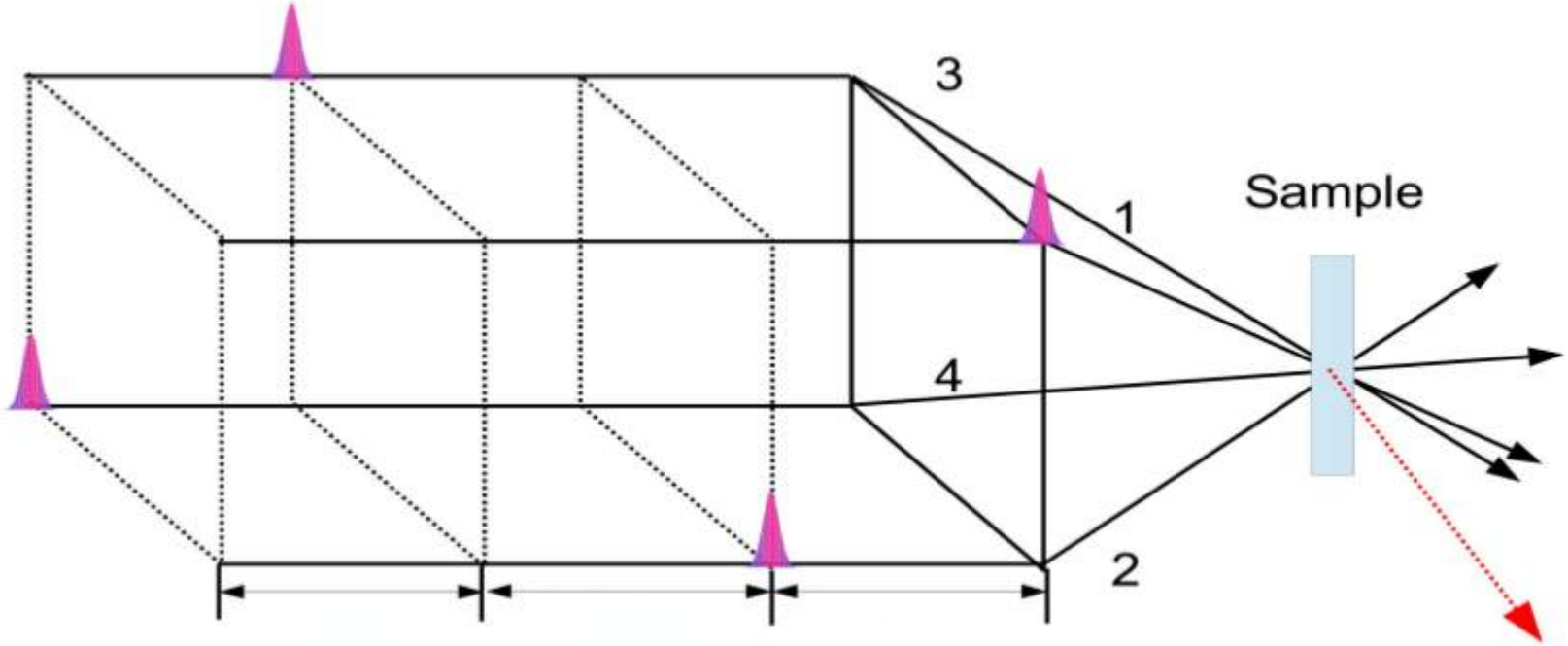
- ☆ Experiment repeated at room temperature
- ☆ 2D ultrafast optical spectroscopy
- ☆ compared with theoretical model
- ☆ 2D: phase-matching approach

Gelin, Egorova, Domcke, J. Chem. Phys (2005)



FMO complex

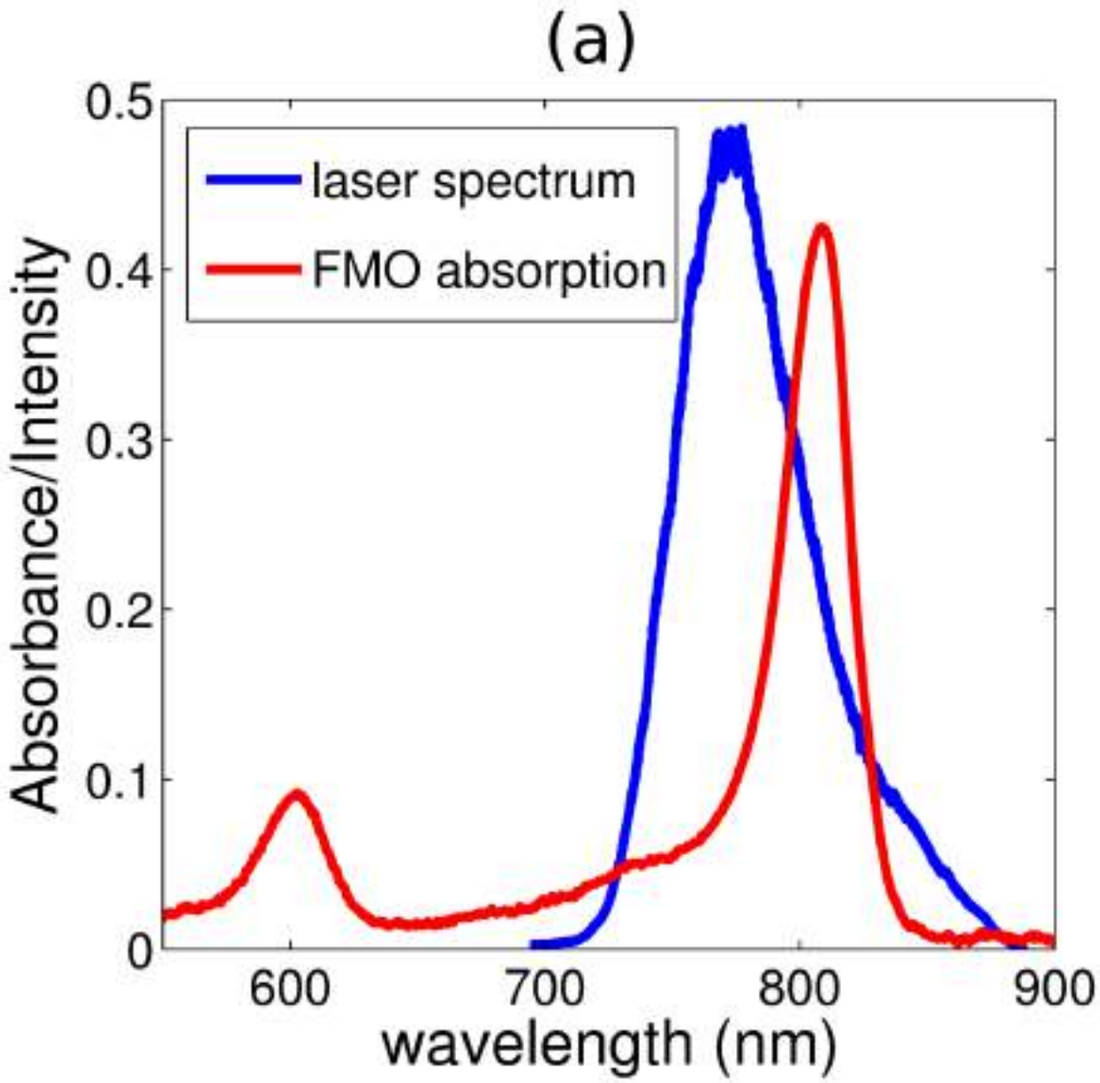


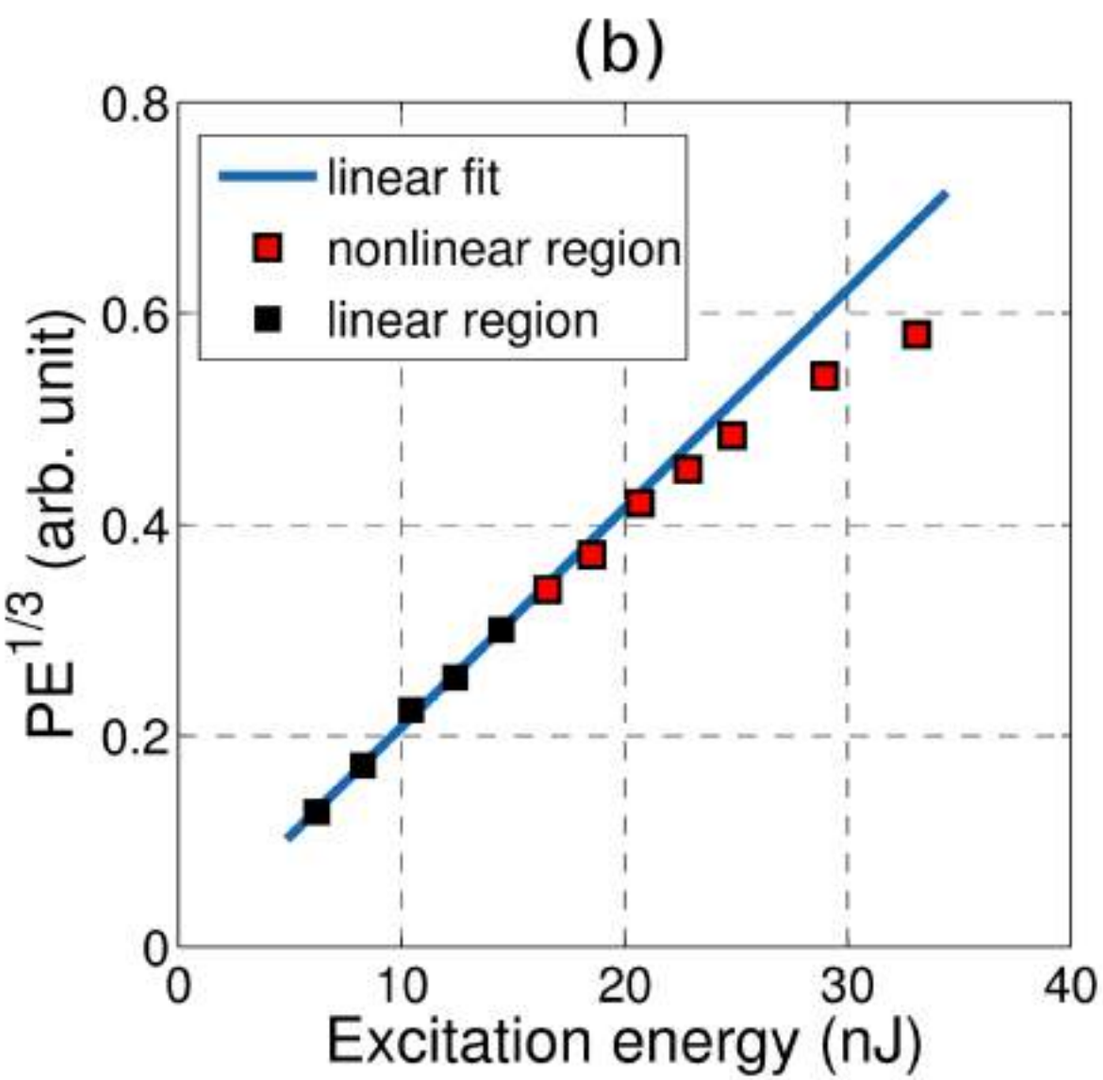


Duan, Prokhorenko, Cogdell, Ashraf, Stevens, Thorwart, Miller, PNAS **114**, 8493 (2017)

FMO: Experiment Nonlinear 2D Spectroscopy

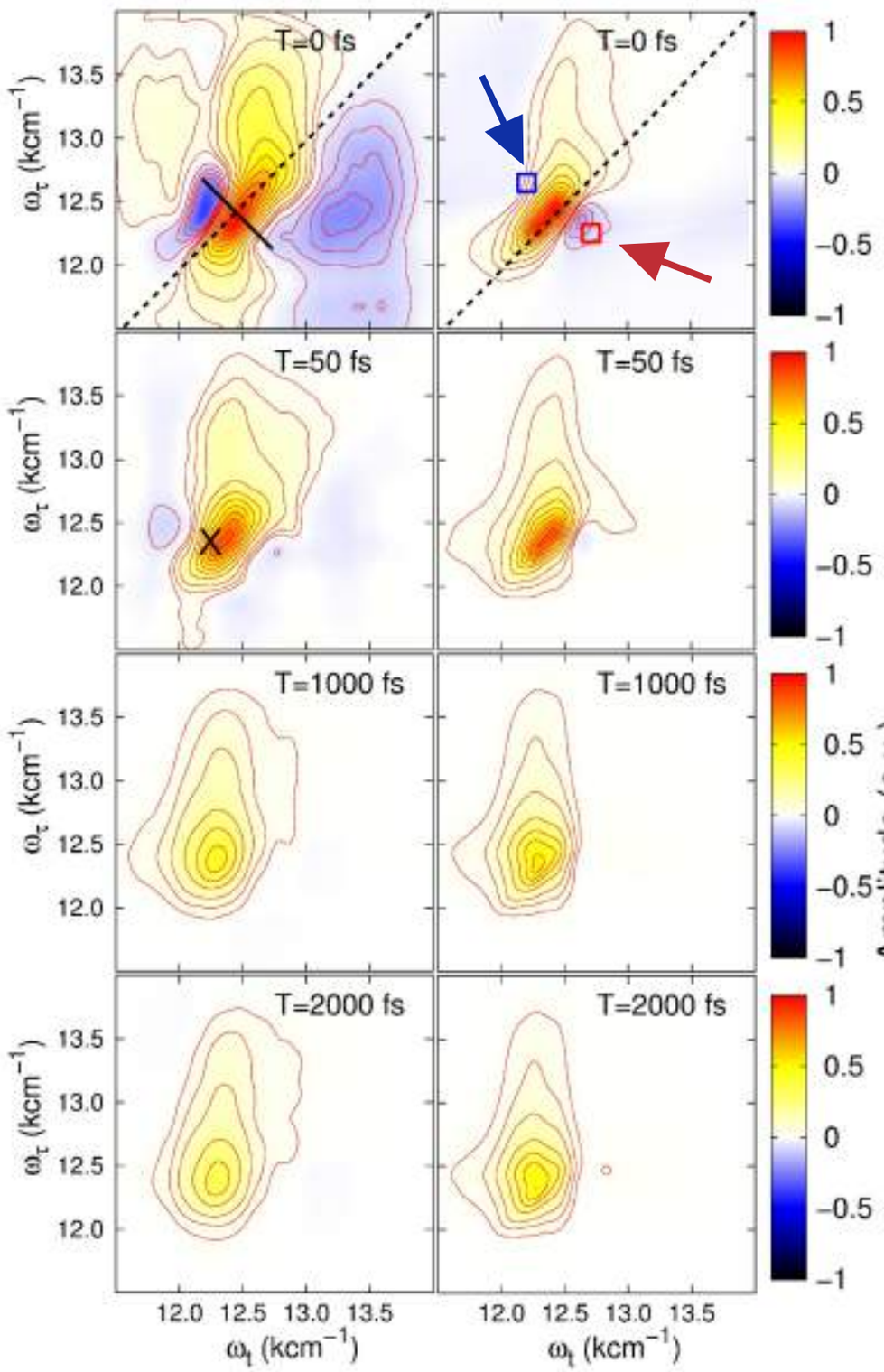
- Laser excitation strength low enough

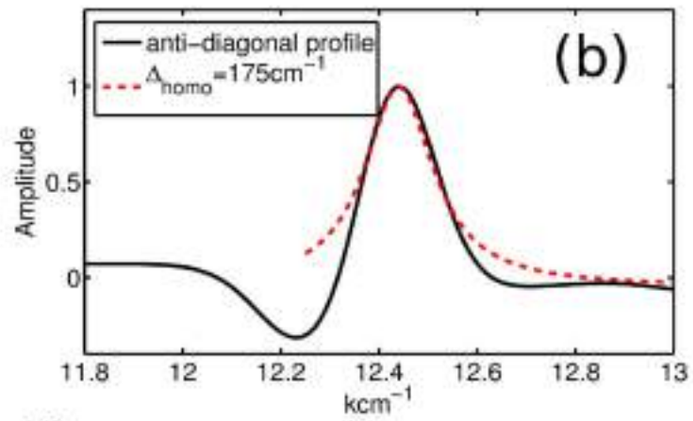




Duan, Prokhorenko, Cogdell, Ashraf, Stevens, Thorwart, Miller, PNAS **114**, 8493 (2017)

FMO: Experiment Nonlinear 2D Spectroscopy

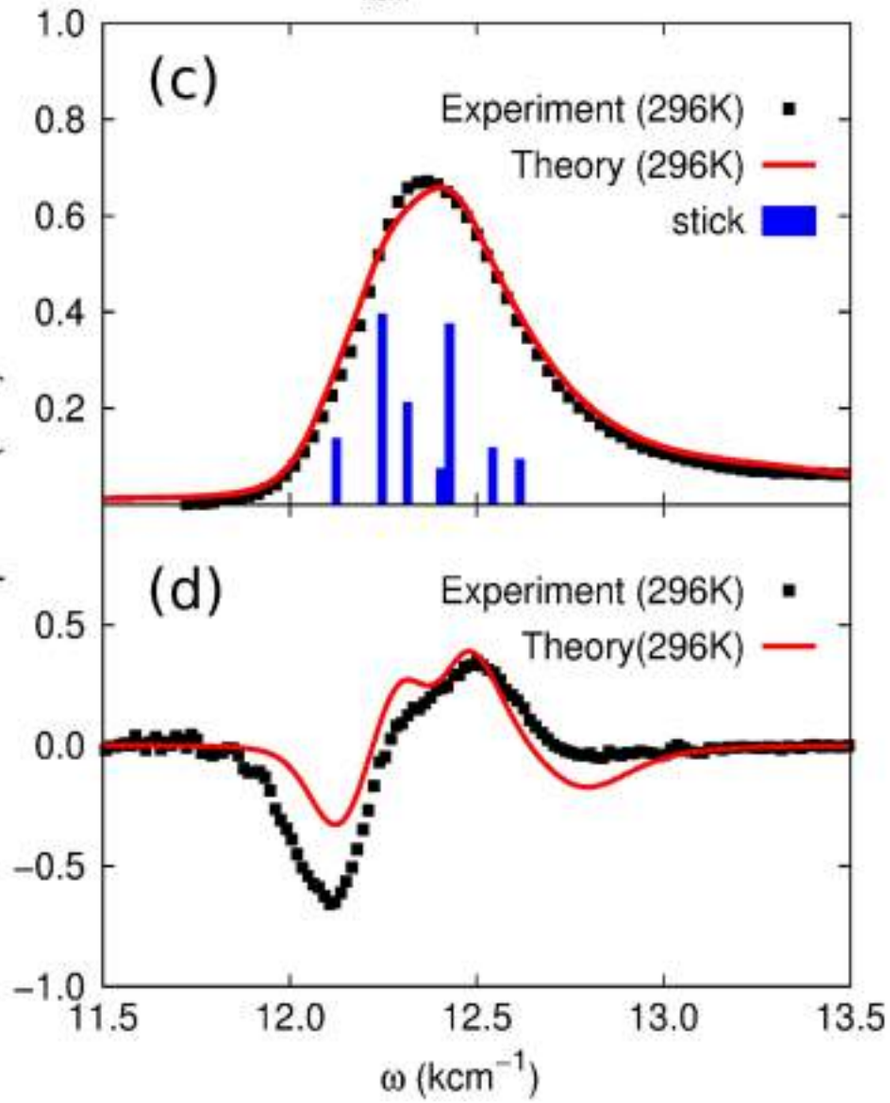




Antidiagonal cut

=

dephasing



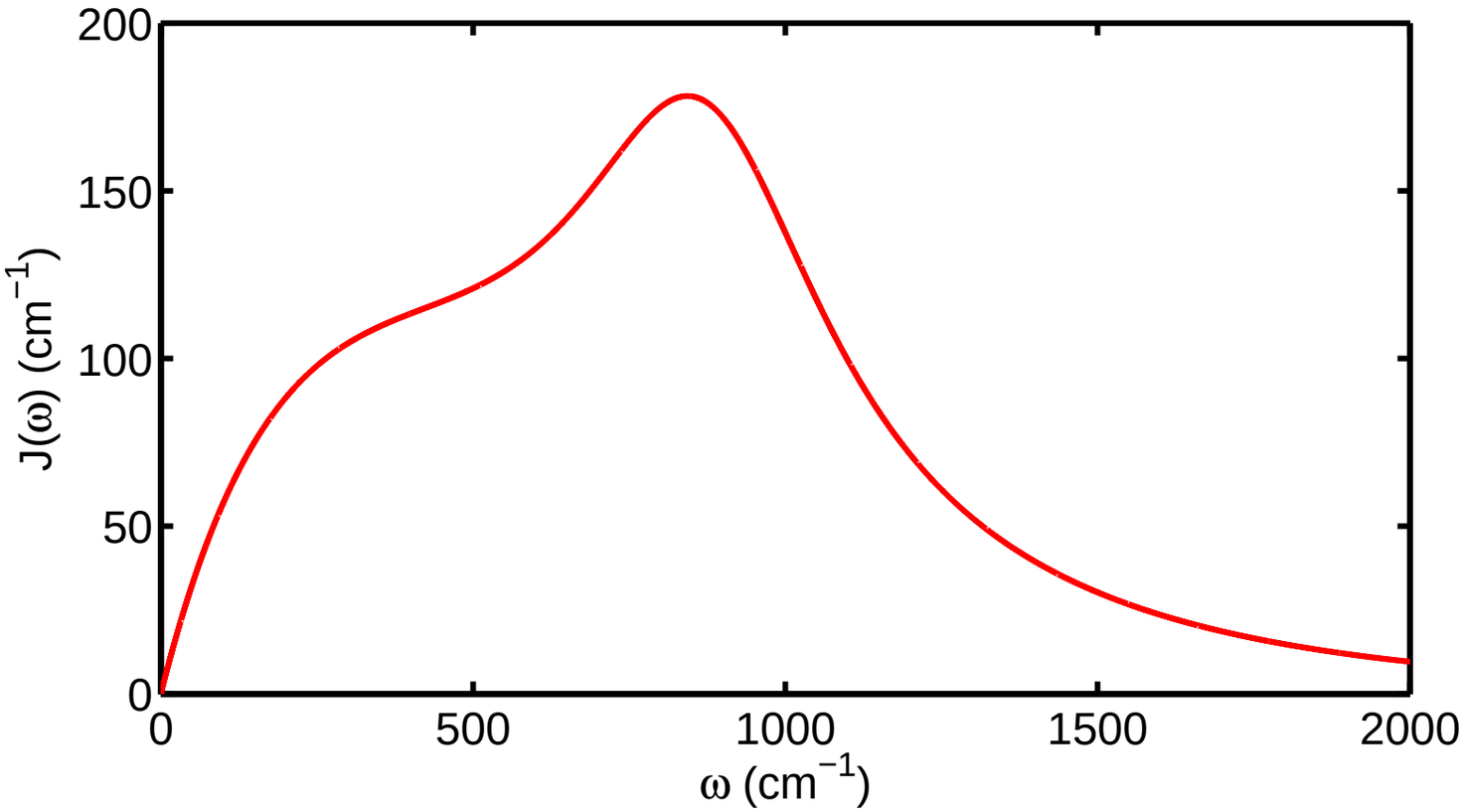
Linear photoabsorption

CD spectrum

Duan, Prokhorenko, Cogdell, Ashraf, Stevens, Thorwart, Miller, PNAS **114**, 8493 (2017)

FMO: Theory: Spectral density

$$J(\omega) = \gamma\omega e^{-\omega/\omega_c} + \frac{2}{\pi} S\Omega^3 \frac{\omega\Gamma}{(\Omega^2 - \omega^2)^2 + \omega^2\Gamma^2}$$



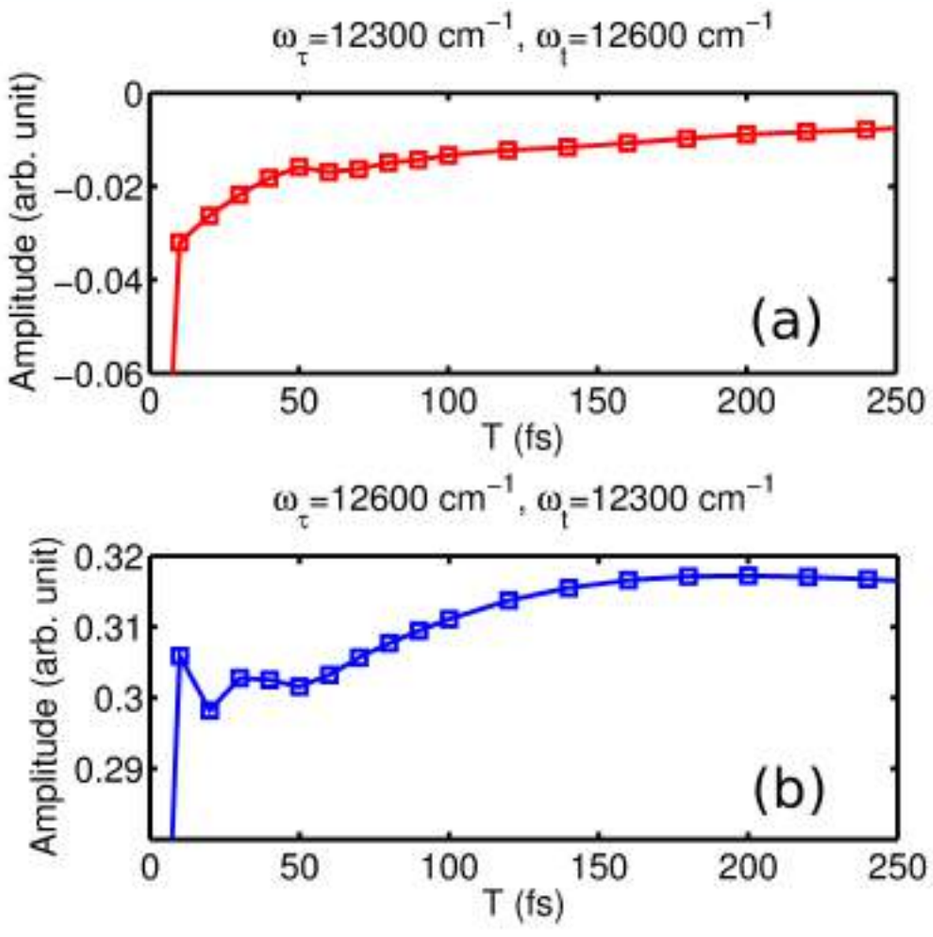
$$\gamma = 0.7, \omega_c = 350\mathrm{cm}^{-1}, S = 0.12, \Omega = 900\mathrm{cm}^{-1}, \Gamma = 700\mathrm{cm}^{-1}$$

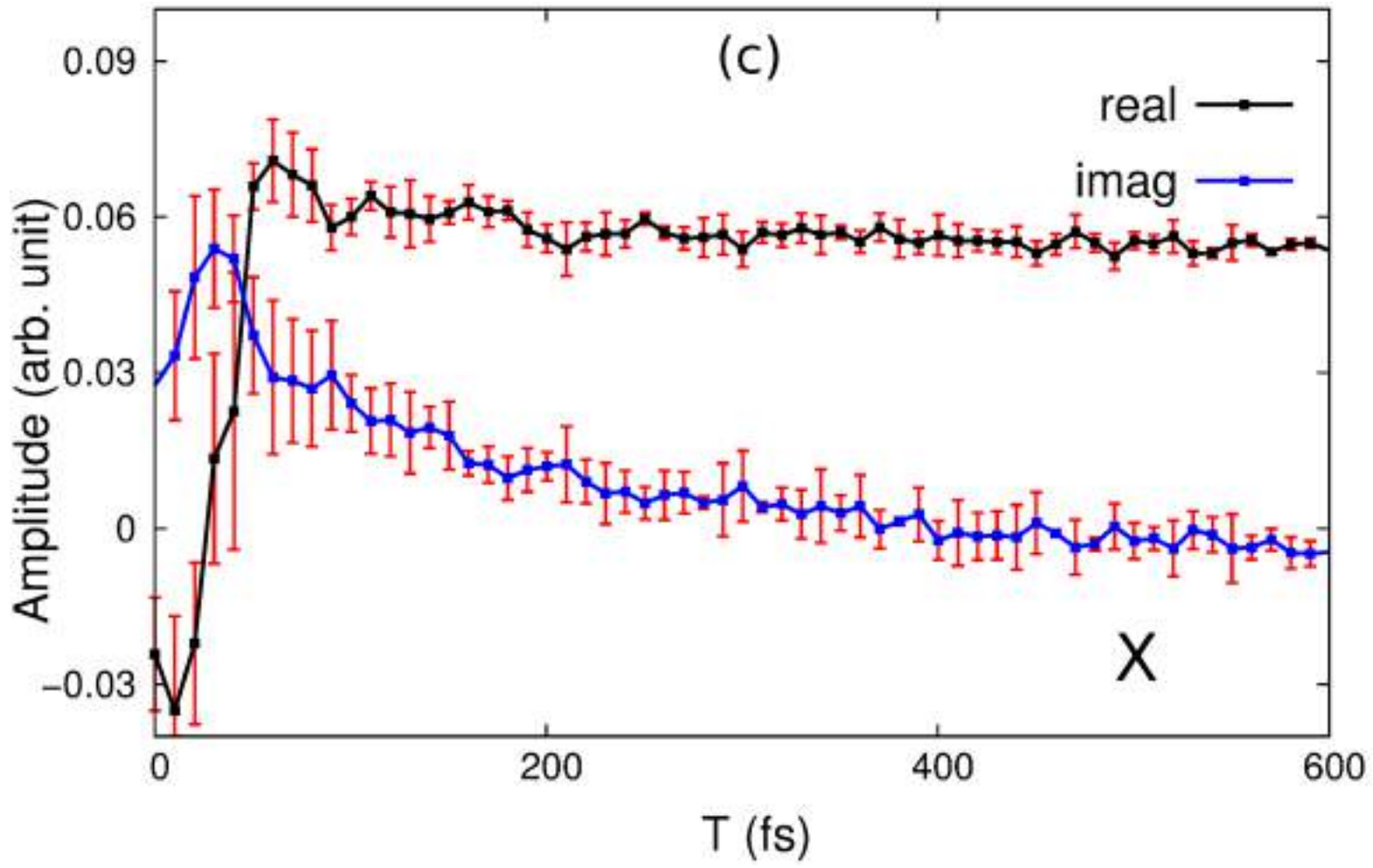
$$\lambda = 190\mathrm{cm}^{-1}$$

Duan, Prokhorenko, Cogdell, Ashraf, Stevens, Thorwart, Miller, PNAS **114**, 8493 (2017)

FMO: Experiment Nonlinear 2D Spectroscopy

Time evolution of coherence signal: **electronic dephasing time ~ 60 fs**





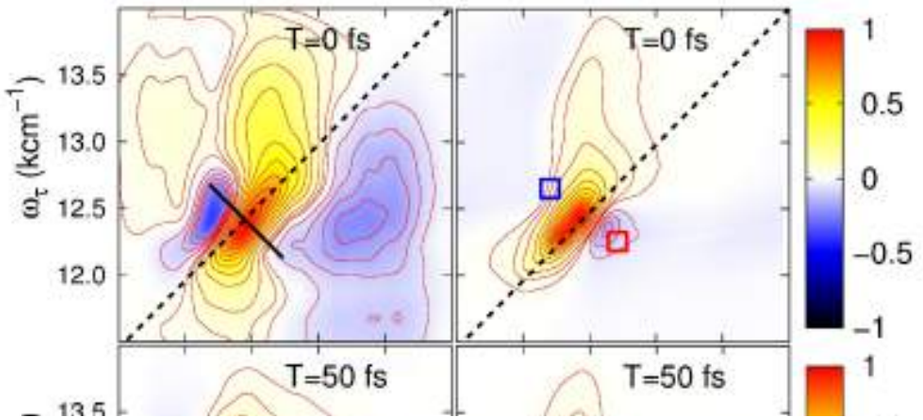
Duan, Prokhorenko, Cogdell, Ashraf, Stevens, Thorwart, Miller, PNAS **114**, 8493 (2017)

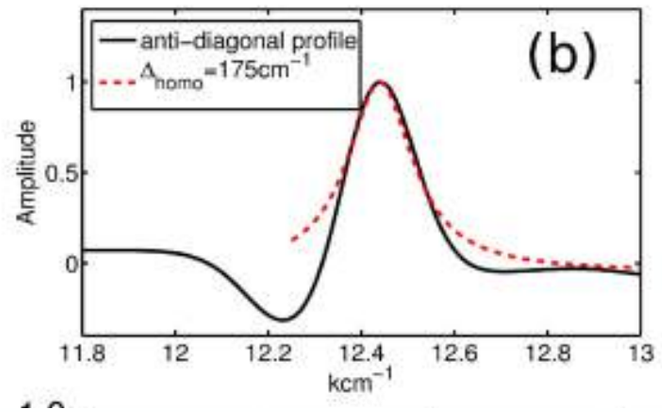
FMO: Experiment Nonlinear 2D Spectroscopy

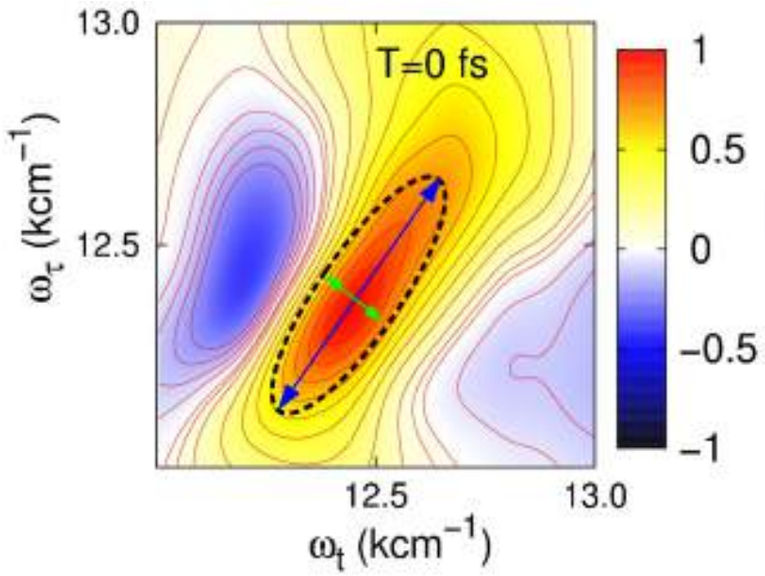
Duan, Prokhorenko, Cogdell, Ashraf, Stevens, Thorwart, Miller, PNAS **114**, 8493 (2017)

Self-consistence check:

Anti-diagonal width = **electronic dephasing time ~ 60 fs**

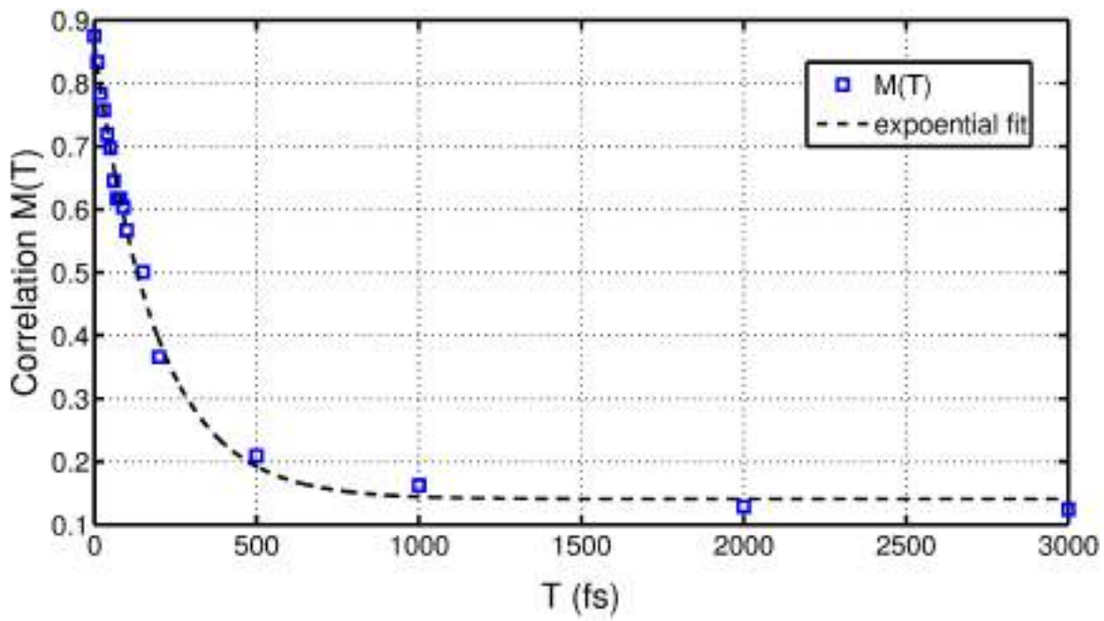






Fast modulation limit: exponential decay of correlation

$$M(T) = \frac{(a^2 - b^2)}{(a^2 + b^2)}$$



Hamm, Zanni, Concepts of 2D IR spectroscopy (CUP, 2011)

Consistent with Mujica-Martinez,

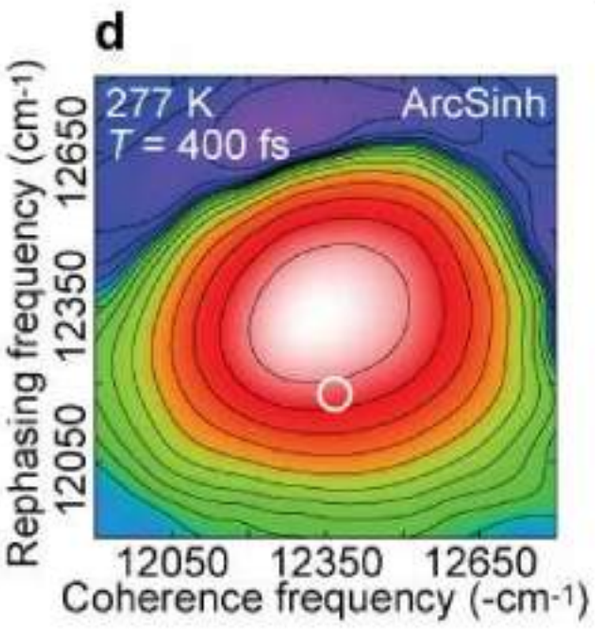
Nalbach, Thorwart, Phys. Rev. E 2013:

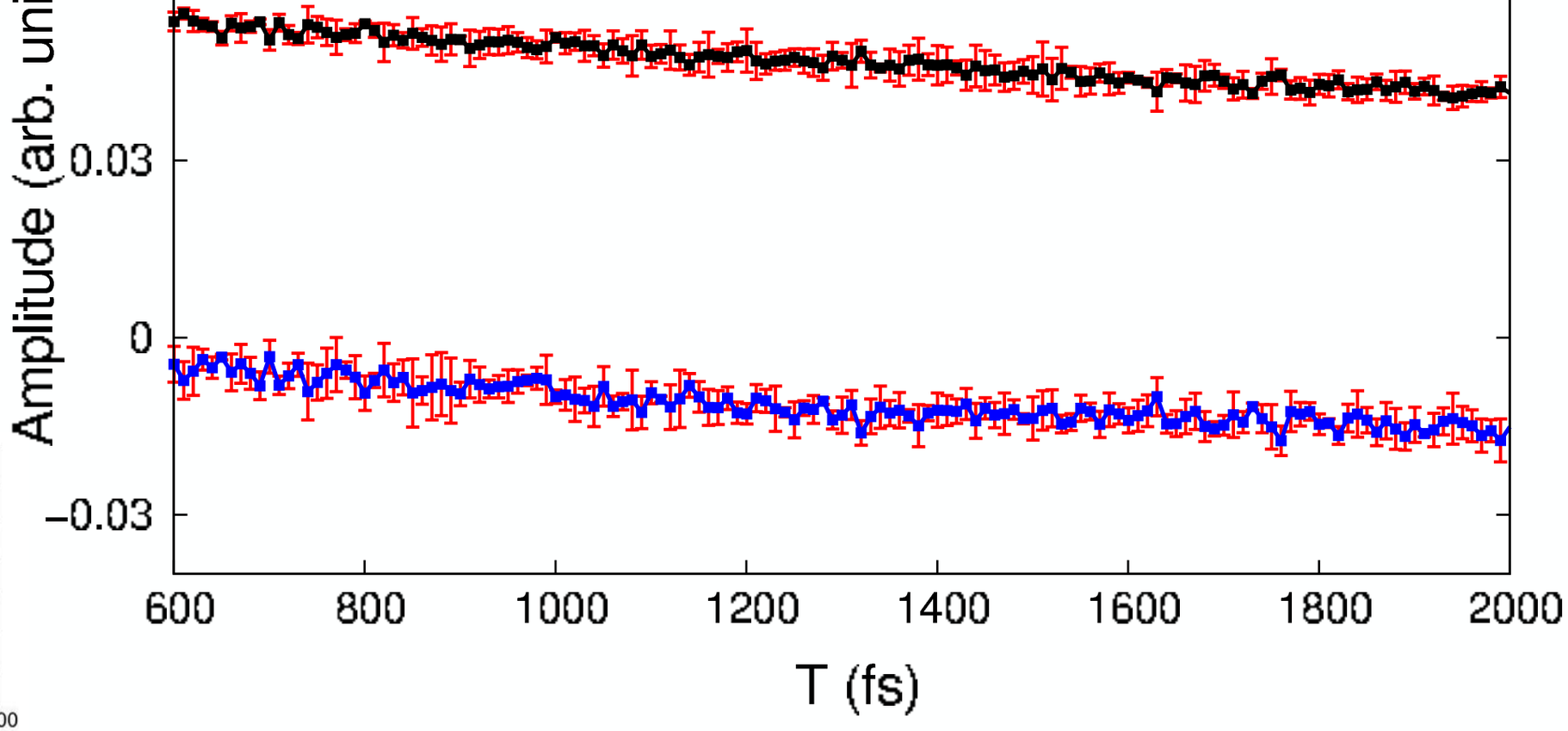
Dynamics is fully Markovian

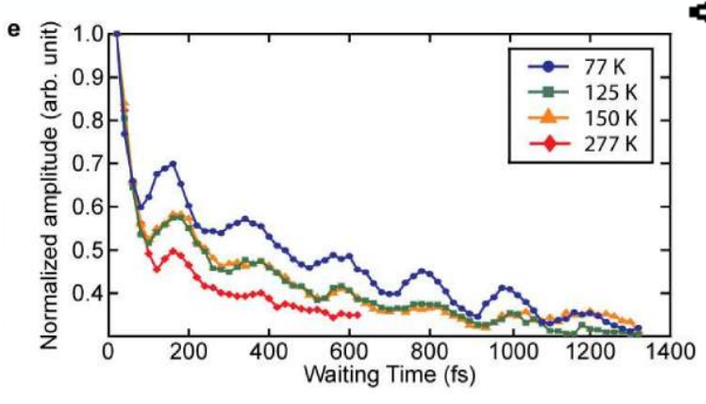
FMO: Experiment Nonlinear 2D Spectroscopy

Duan, Prokhorenko, Cogdell, Ashraf, Stevens, Thorwart, Miller, PNAS **114**, 8493 (2017)

Cross peak at spectral position of Ref. [1]:





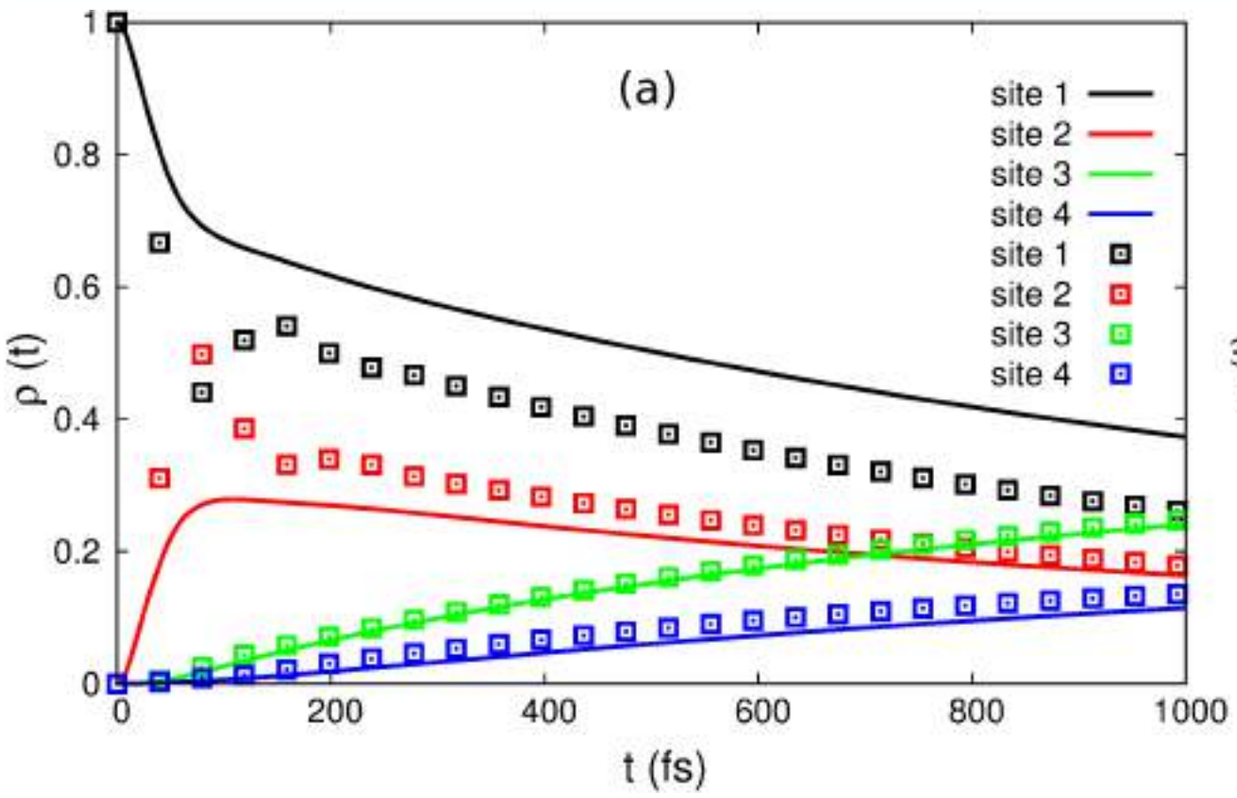


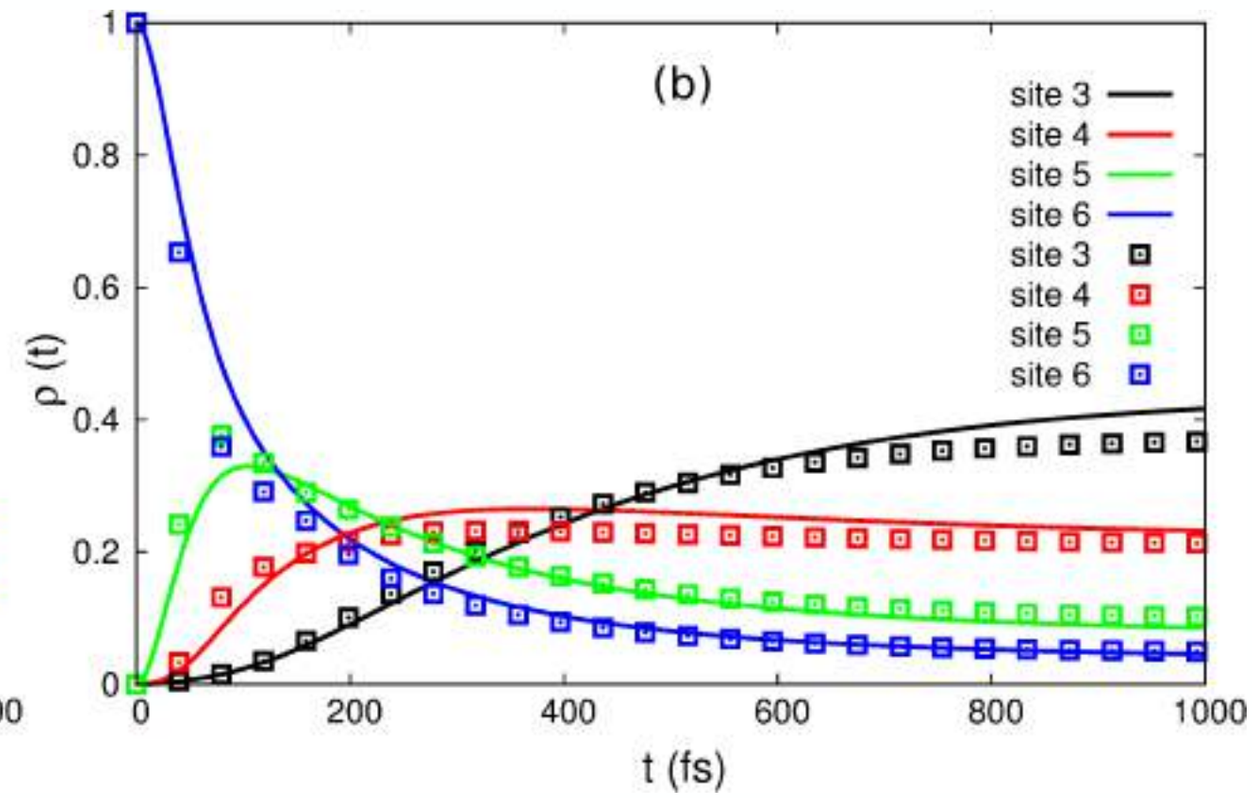
[1] G. Panitchayangkoon et al. (G. Engel), PNAS **107**, 12766 (2010)

FMO: Experiment Nonlinear 2D Spectroscopy

Duan, Prokhorenko, Cogdell, Ashraf, Stevens, Thorwart, Miller, PNAS **114**, 8493 (2017)

Comparison with independent previous exact calculation of Ref. [2]





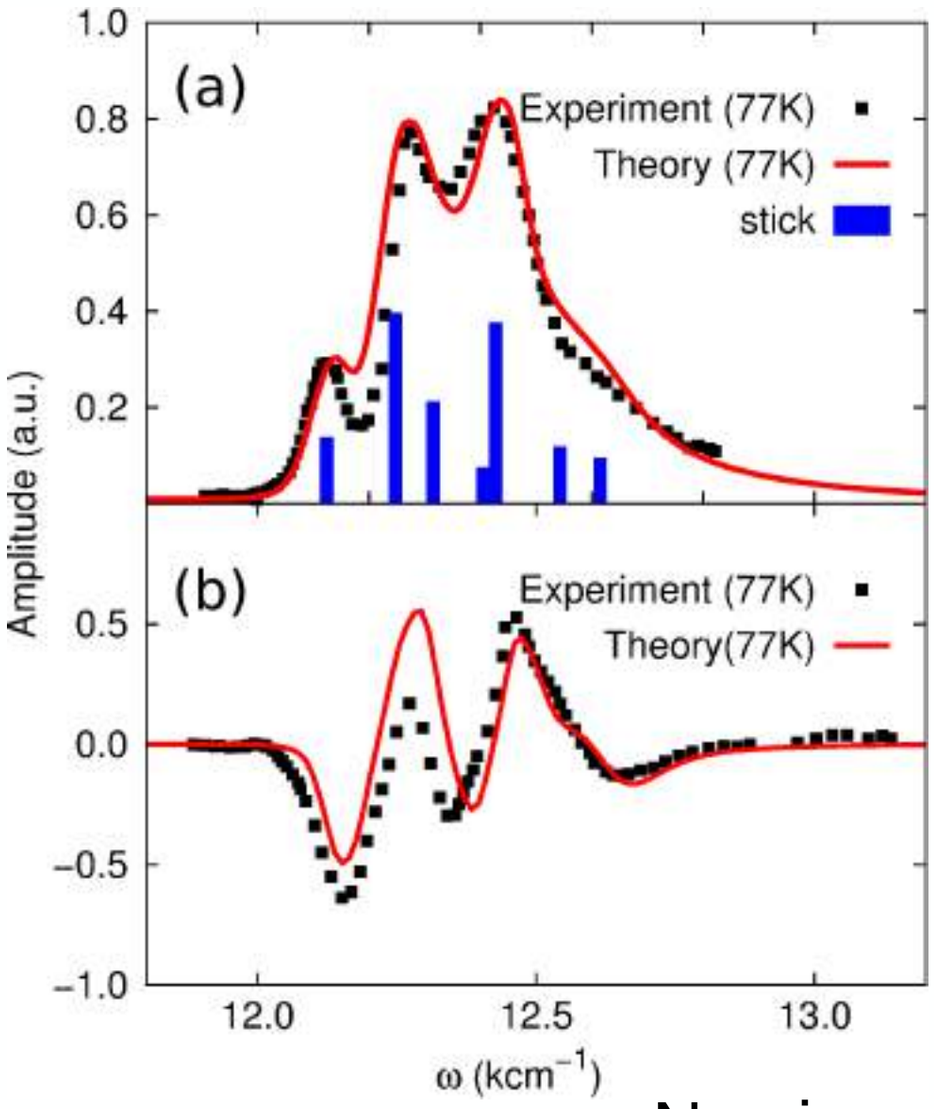
No signatures of long-lived coherence

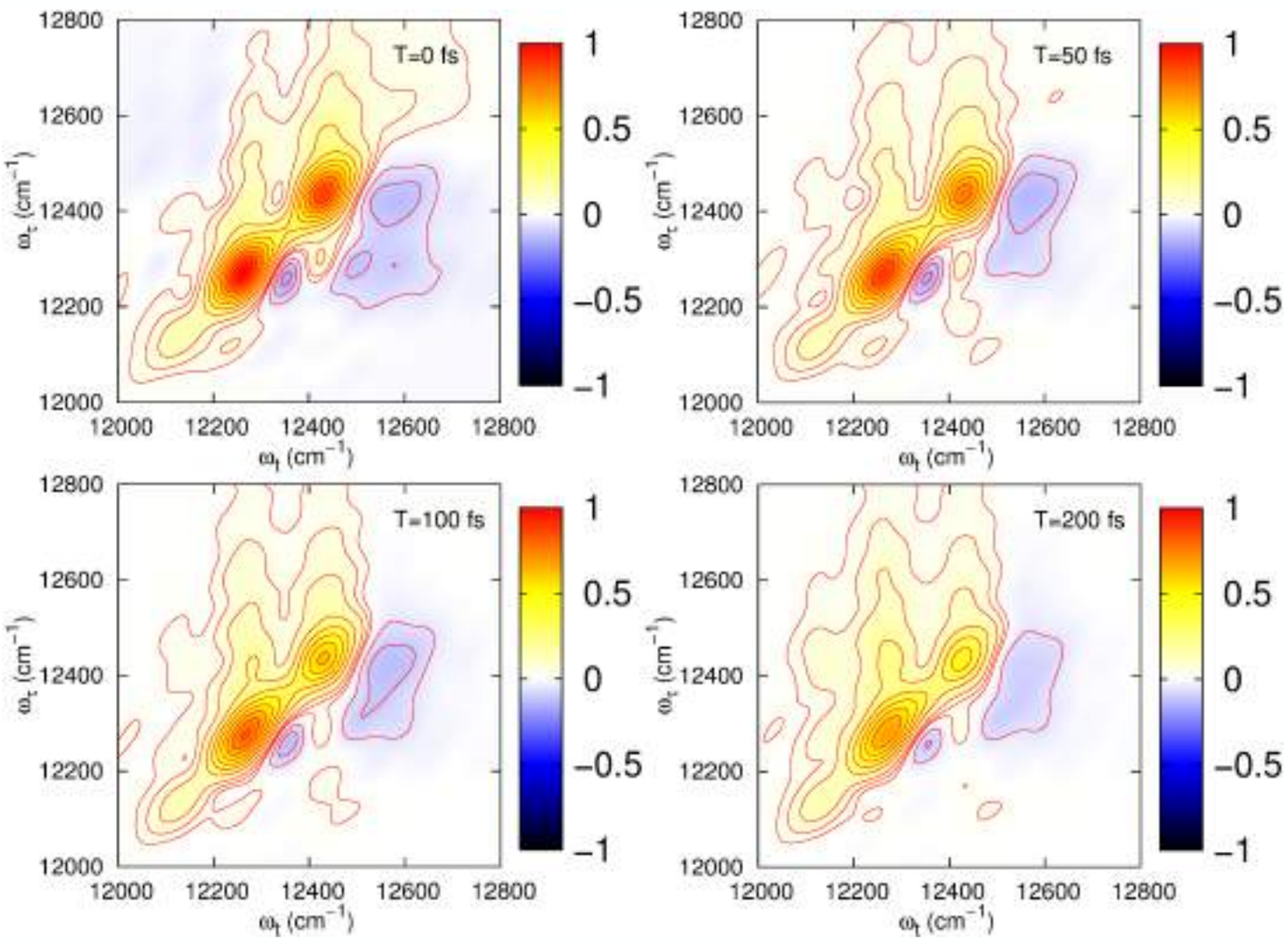
[2] Nalbach, Braun, Thorwart, Phys. Rev. E (2011)

FMO: Experiment Nonlinear 2D Spectroscopy

Duan, Prokhorenko, Cogdell, Ashraf, Stevens, Thorwart, Miller, PNAS **114**, 8493 (2017)

Calculate low temperature T=77 K and compare to exp. of Ref. [3]





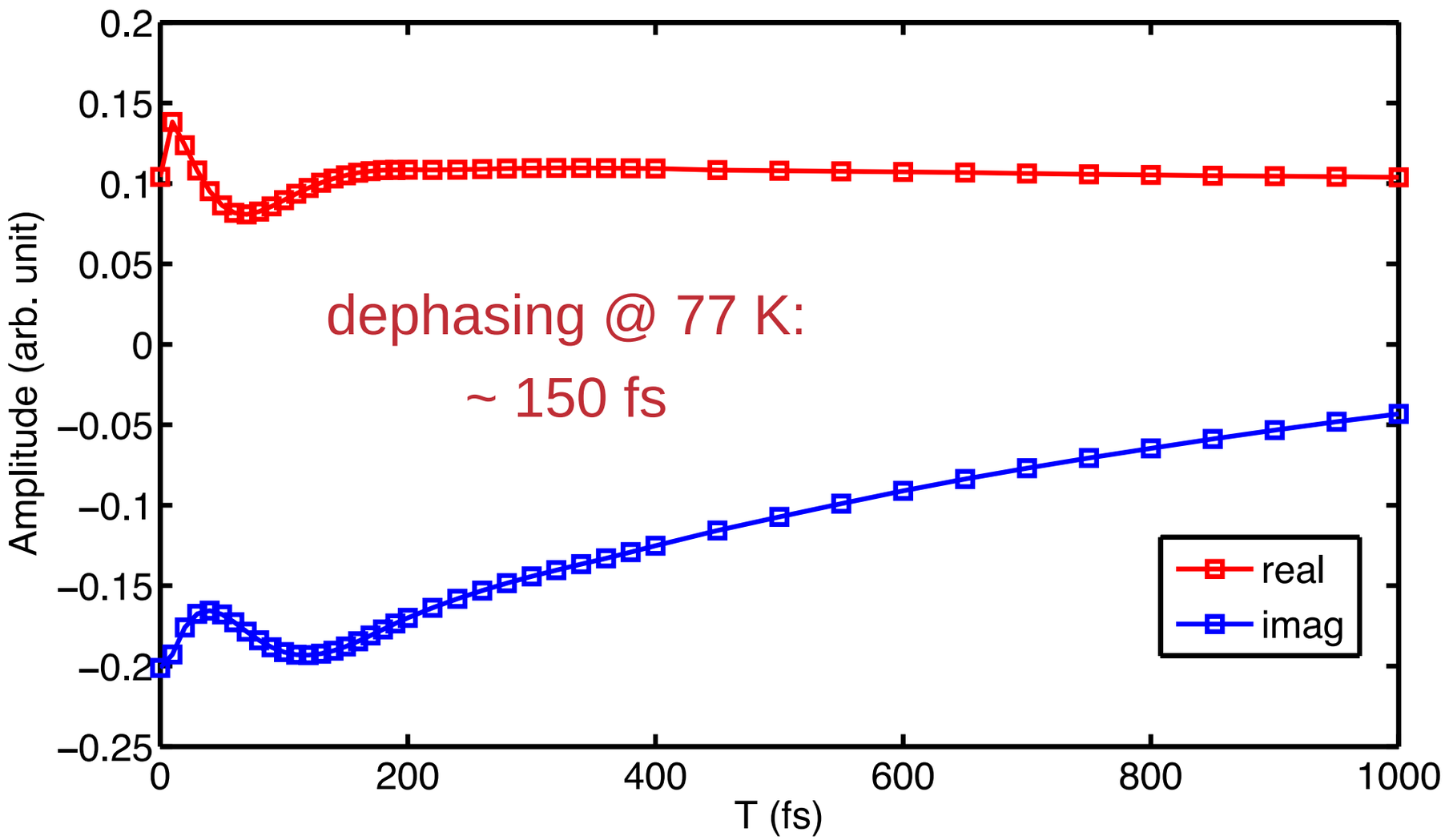
No signatures of long-lived coherence

[3] Zigmantas et al., J. Chem. Phys. Lett. (2016)

FMO: Experiment Nonlinear 2D Spectroscopy

Duan, Prokhorenko, Cogdell, Ashraf, Stevens, Thorwart, Miller, PNAS **114**, 8493 (2017)

Calculate low temperature T=77 K and compare to exp. of Ref. [3]



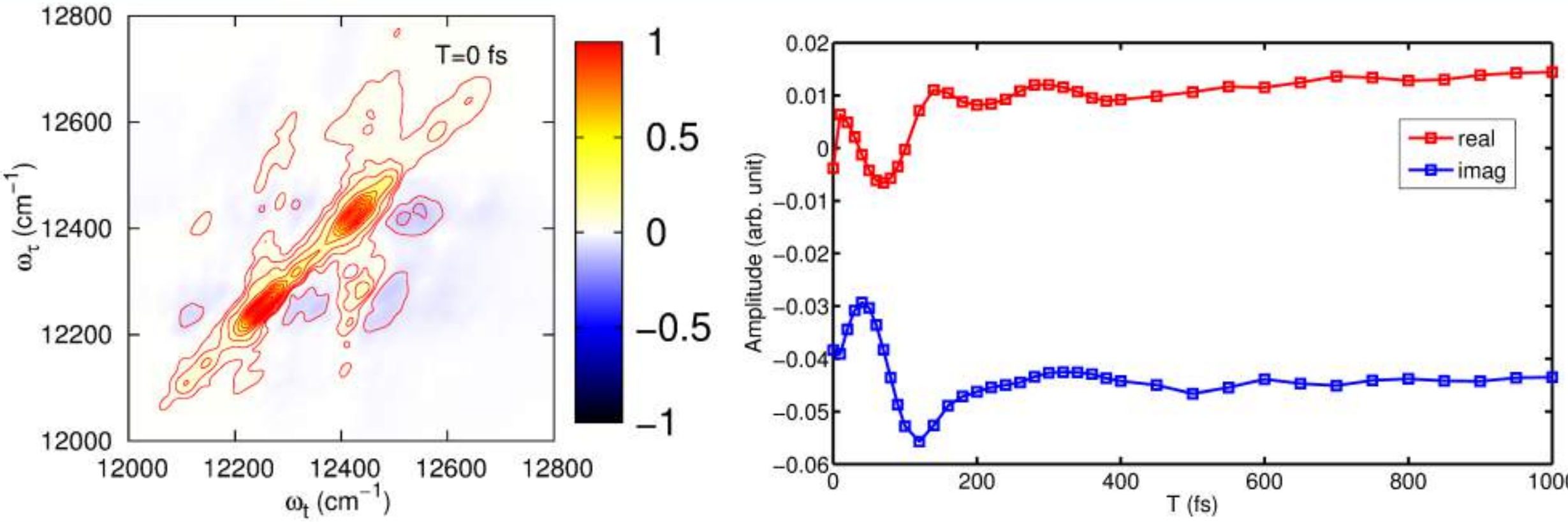
Agreement: No signatures of long-lived coherence even at 77 K

[3] Zigmantas et al., J. Chem. Phys. Lett. (2016)

FMO: Experiment Nonlinear 2D Spectroscopy

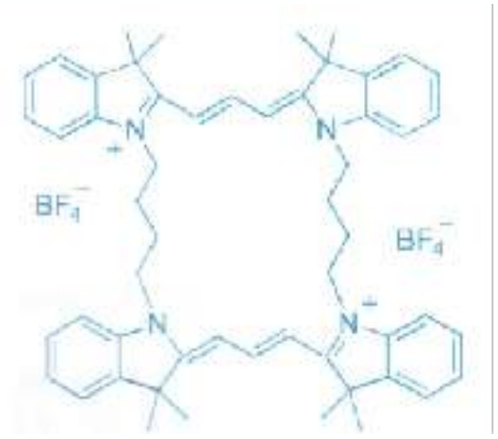
Duan, Prokhorenko, Cogdell, Ashraf, Stevens, Thorwart, Miller, PNAS **114**, 8493 (2017)

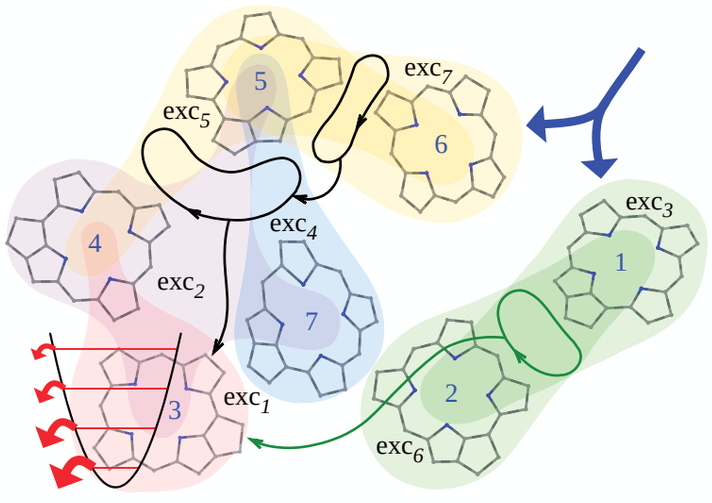
Simulate long-lived electronic coherence:
choose weak damping by hand

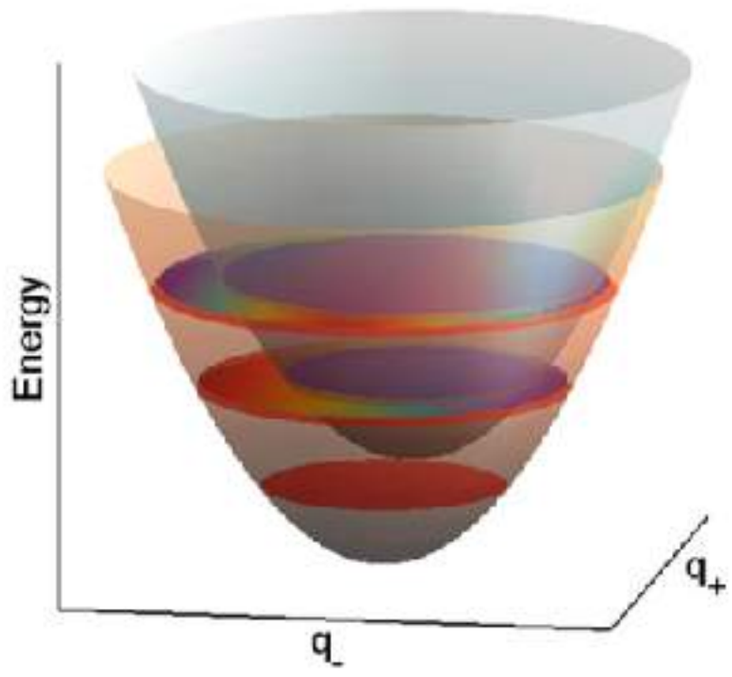


Unrealistically small anti-diagonal width, sharp ridge in 2D spectrum
(clear difference to experiment)

2) Role of vibrations & Vibronic coherence



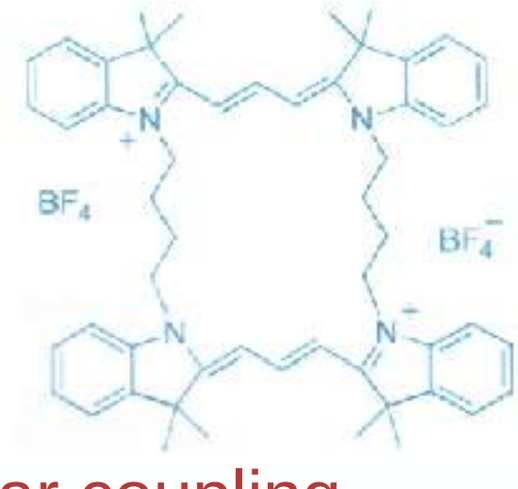




Vibrational effects on exciton transfer

Duan, Nalbach, Prokhorenko, Mukamel, Thorwart, NJP **17**, 072002 (2015)

monomer



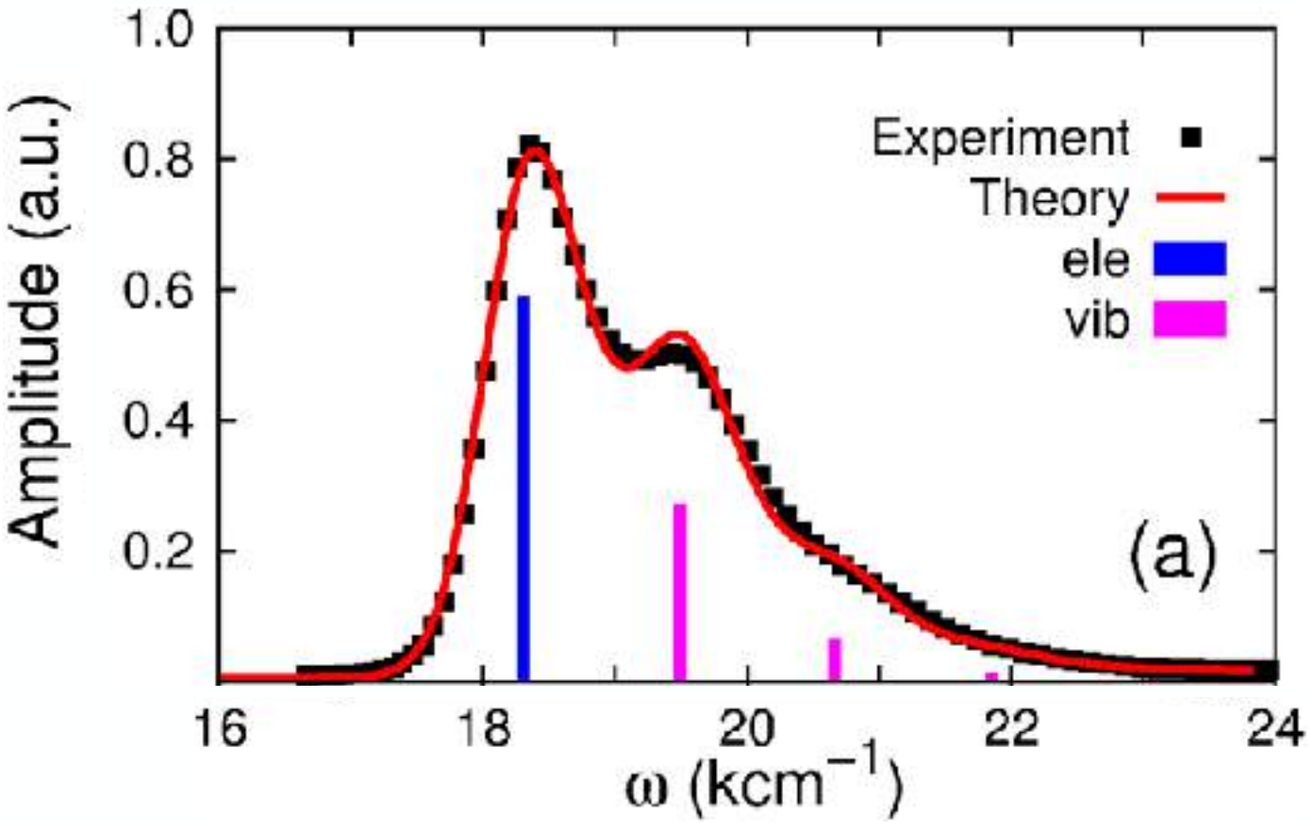
dimer

Other molecular complexes:

- Cyanine dye:
- much smaller (dimer), strong electron-nuclear coupling
- no protein environment
- no conformational statistics
- no long-lived electronic coherence
- vibronic coherence lasts longer

Vibrational effects on exciton transfer

Duan, Nalbach, Prokhorenko, Mukamel, Thorwart, NJP **17**, 072002 (2015)



monomer

Absorption spectrum

$$I(\omega) \propto \int_{-\infty}^{+\infty} dt\, e^{i\omega t} \langle \mu(t)\mu(0) \rangle_g$$

Time-nonlocal master equation

Meir, Tannor, J. Chem. Phys. (1999)

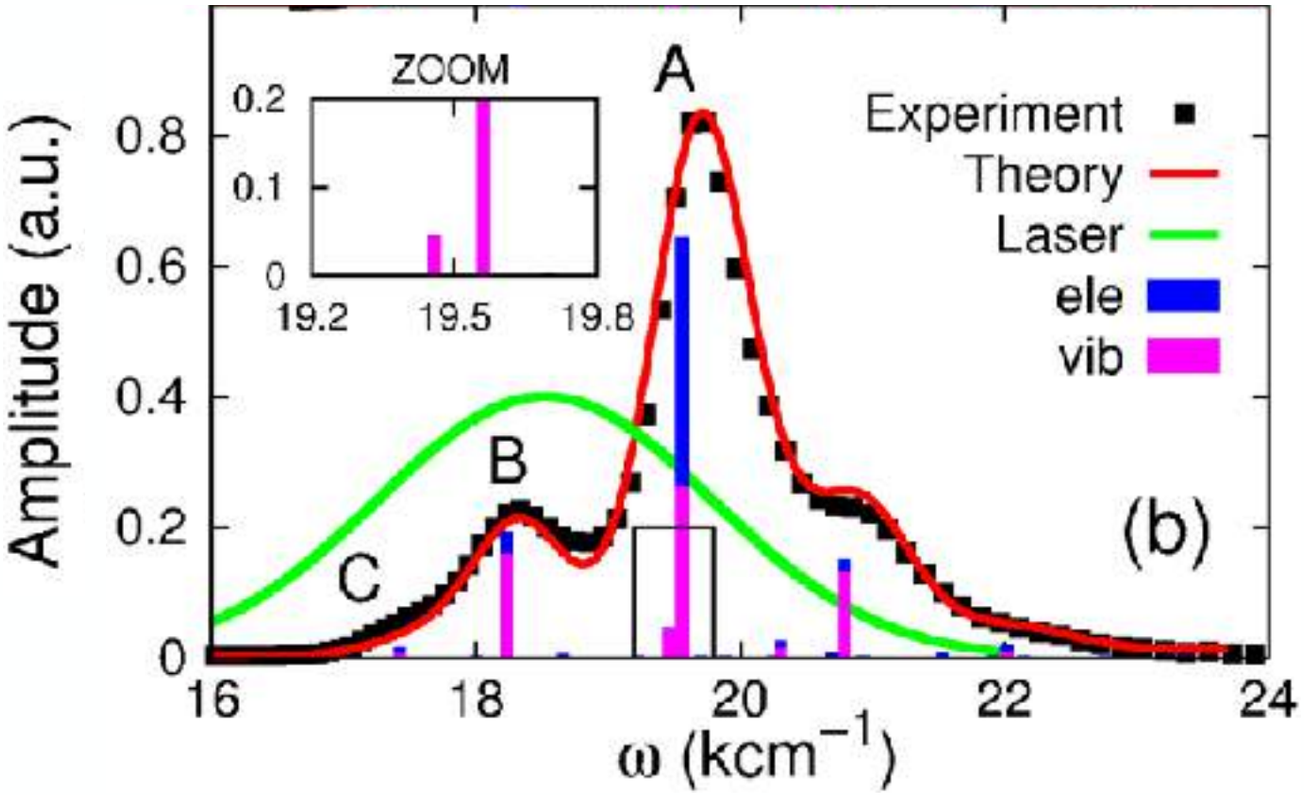
$$H_{\text{mono}} = H_g + H_e = |g\rangle h_g \langle g| + |e\rangle \left(h_e + E\right) \langle e|$$

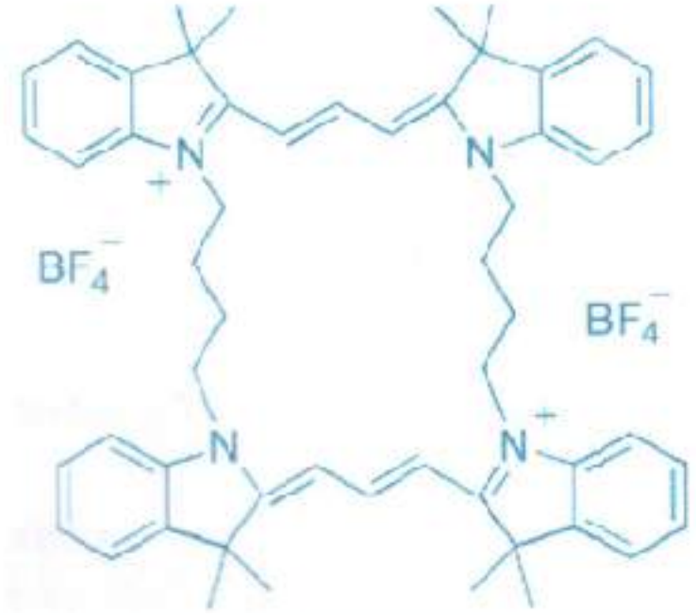
$$h_g = \Omega \left(b^+ b + 1/2\right) \qquad h_e = \Omega \left(b^+ b + 1/2\right) + g(b^+ + b)$$

$$H_{SB} = |e\rangle\langle e|\xi_{\text{el}}(t) + (b^+ + b)\xi_{\text{vib}}(t)$$

Vibrational effects on exciton transfer

Duan, Nalbach, Prokhorenko, Mukamel, Thorwart, NJP **17**, 072002 (2015)





dimer

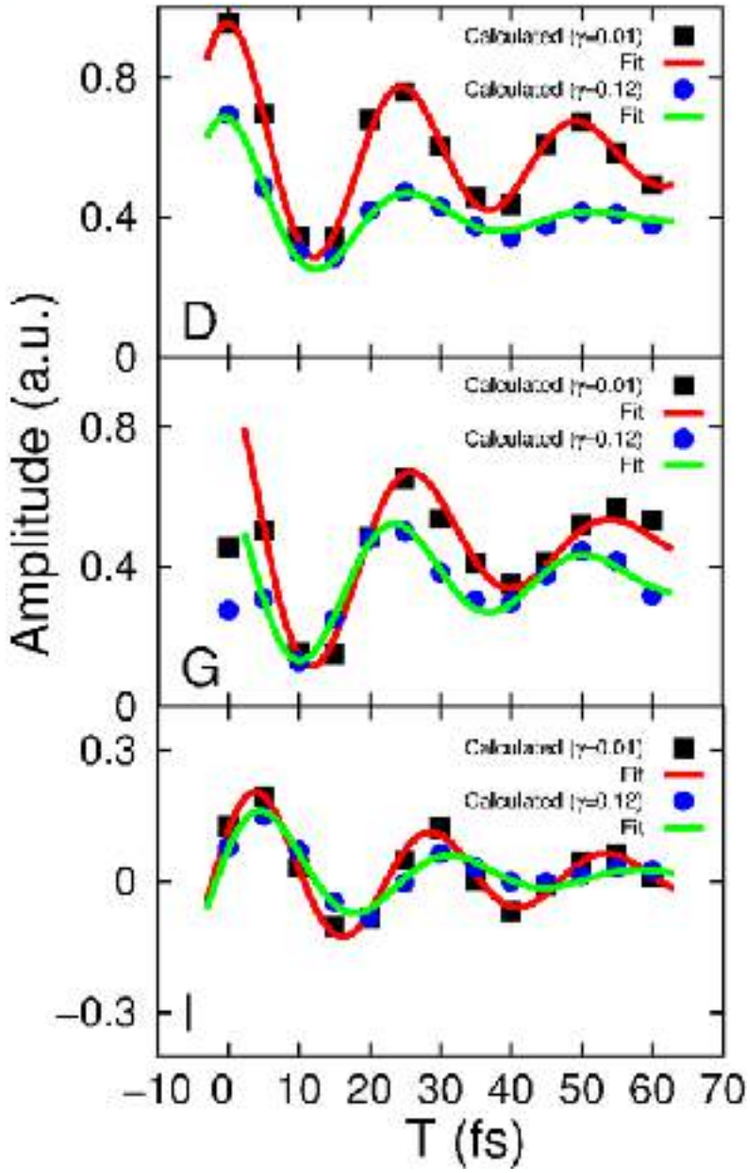
$$H_{\rm dim} = \sum_{\alpha,\beta=g,e} |\alpha\beta\rangle(h_\alpha^A + h_\beta^B)\langle\alpha\beta| + |ge\rangle U\langle eg| + |eg\rangle U\langle ge|$$

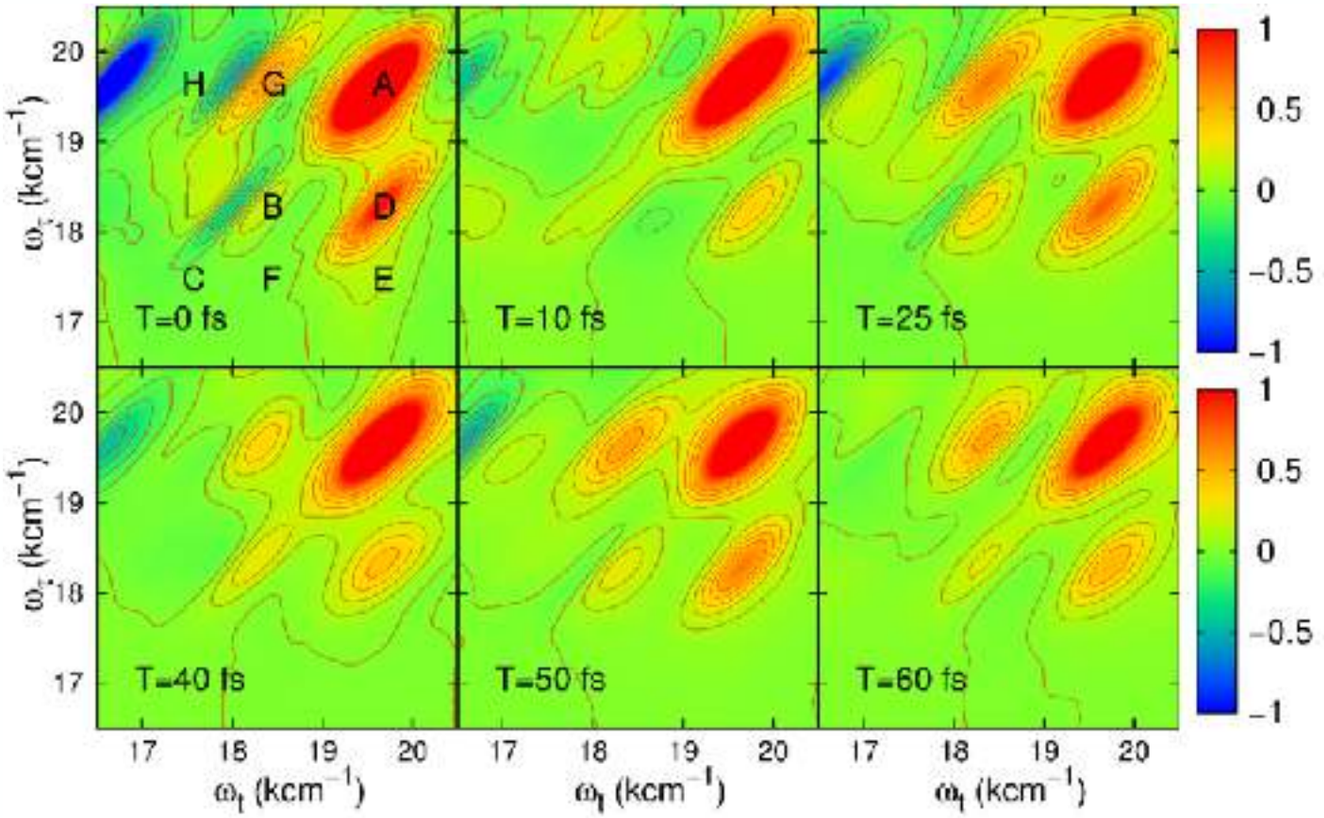
$$h_g^{A/B} = \Omega\left(b_{A/B}^+ b_{A/B} + 1/2\right)$$

$$h_e^{A/B} = E + \Omega\left(b_{A/B}^+ b_{A/B} + 1/2\right) + g\left(b_{A/B}^+ + b_{A/B}\right)$$

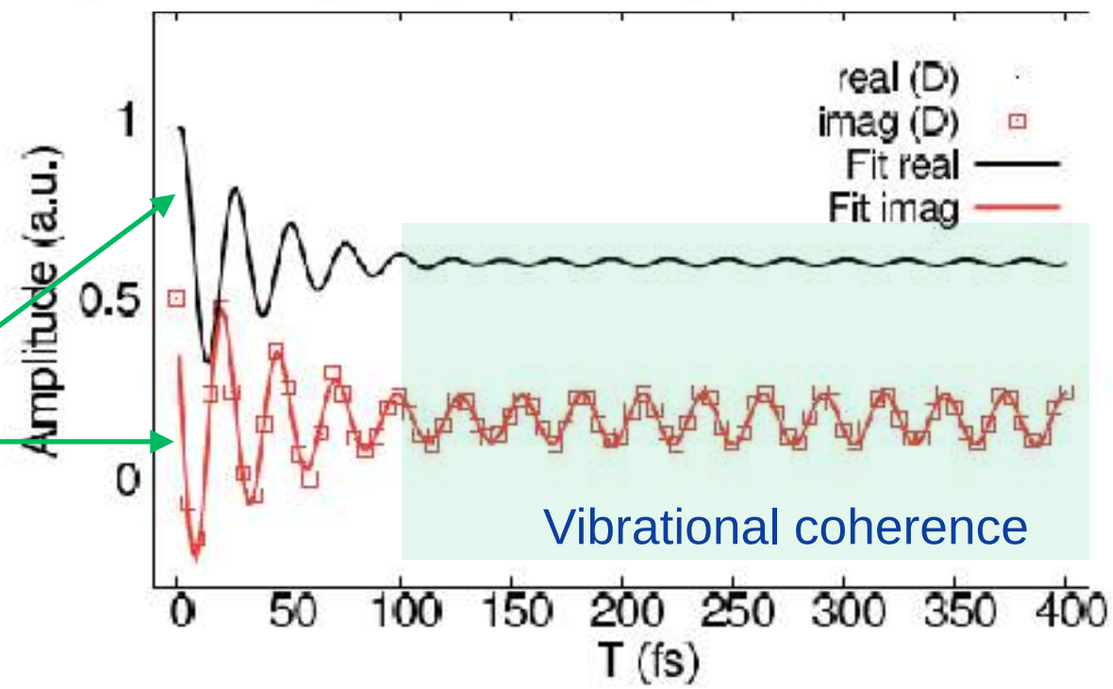
Vibrational effects on exciton transfer

Duan, Nalbach, Prokhorenko, Mukamel, Thorwart, NJP **17**, 072002 (2015)





Electronic coherence
(short lived)



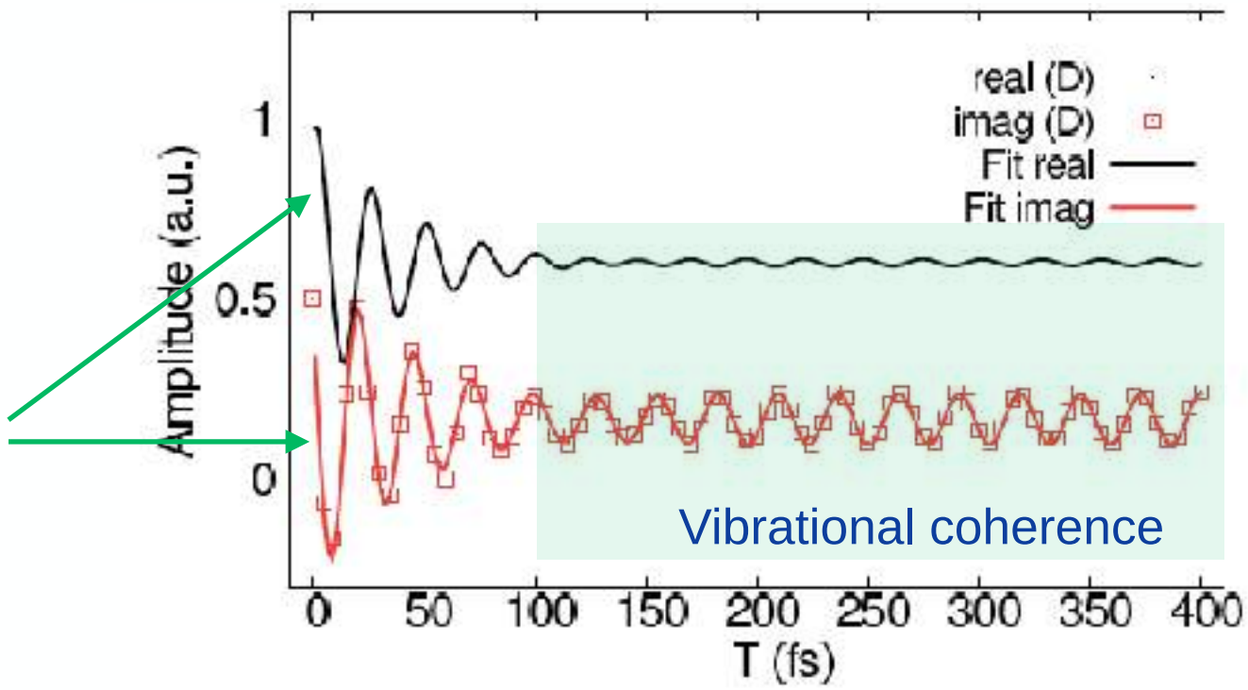
Vibrational effects on exciton transfer

Duan, Nalbach, Prokhorenko, Mukamel, Thorwart, NJP **17**, 072002 (2015)

Generic picture (= orthodox picture):

- **Electronic coherence**
  - short-lived (<100 fs)
  - large amplitudes
  - rapid decay
- **Vibrational coherence**
  - longer lived (few ps)
  - small amplitudes
  - slow decay

Electronic coherence
(short lived)

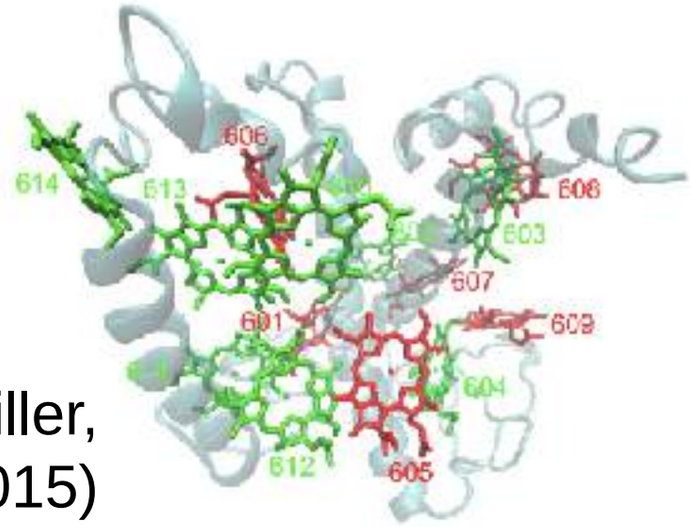


Are these results generic?

Other biomolecular complexes:

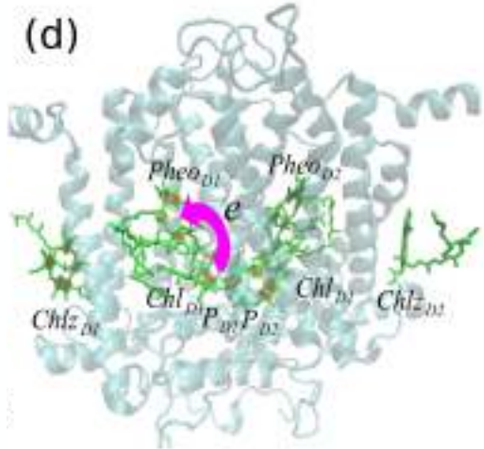
- LHII complex under ambient conditions:
  - no long lived quantum coherence

Duan, Stevens, Nalbach, Thorwart, Prokhorenko, Miller,
J. Phys. Chem. B **119**, 12017 (2015)



- PSII Reaction Center under ambient conditions:
  - no long lived quantum coherence

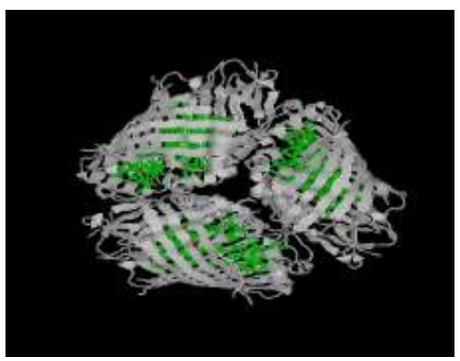
Duan, Prokhorenko, Wientjes, Croce, Thorwart, Miller,
Sci. Rep. **7**, 12347 (2017)



Consistent with very recent experiment with FMO:

- purely vibrational coherence, 240 fs @77 K
- no long lived electronic coherence

Thyrhaug et al. (Zigmantas), Nature Chem. (2018)



FMO complex

Are these results generic?

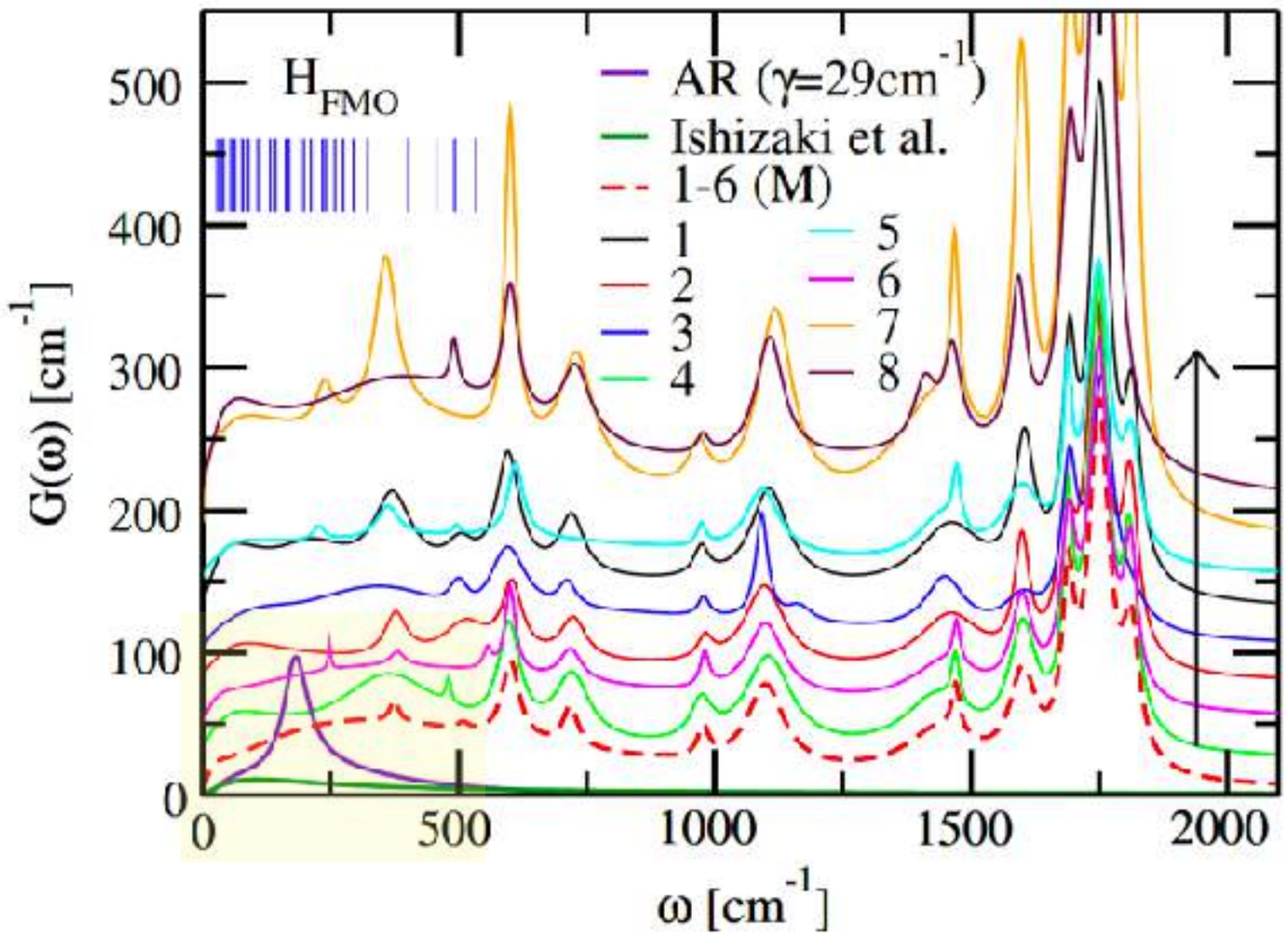
sample	Lifetime (fs)	Reference
LHCII	~65 fs	JPCB **119**, 12017 (2015).
Reaction center	~56 fs	Sci. Rep. **7**, 12347 (2017).
Indocarbocyanine dimer	~50 fs	New J. Phys. **17**, 072002 (2015). Nat. Chem. **6**, 196 (2014).
FMO	~60 fs	PNAS **114**, 8493 (2017).
Perovskite solar cell	~45 fs	ACS Photonics **5**, 852 (2018)

Can long-lived vibrational coherence enhance electronic coherence?

Nalbach, Thorwart, J.Phys. B: At. Mol. Opt. Phys. **45**, 154009 (2012)

Can we use long-lived vibrations to induce long-lived coherence in excitons?
(„vibrational laser“ drive?)

- Again FMO complex, QUAPI plus nontrivial environment (MD simulations)



Olbrich, Kleinekathoefer, Schulten et al., J. Chem. Phys. Lett. (2011)

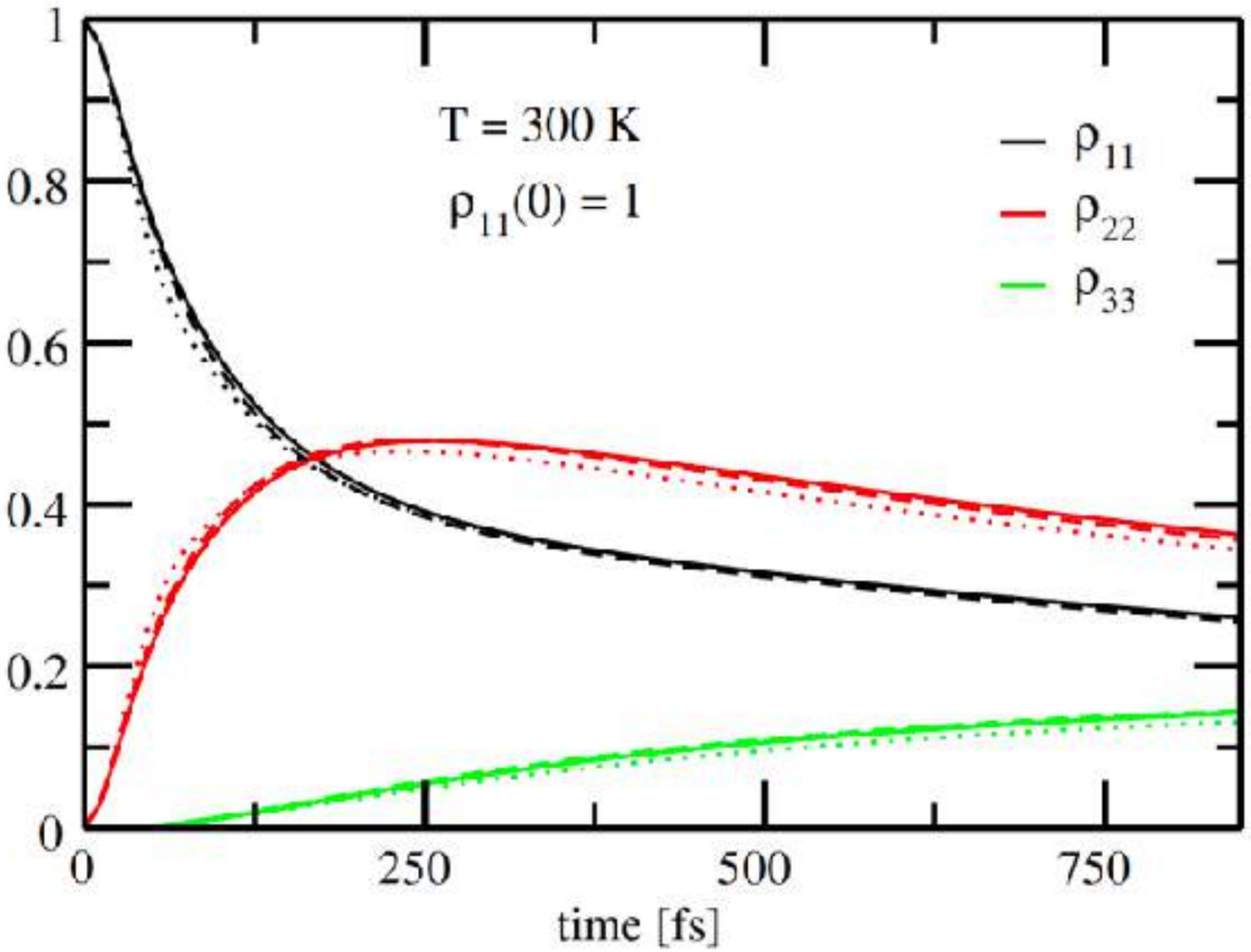
each vertically shifted relative to the next by 25 cm^{-1}

Can long-lived vibrational coherence enhance electronic coherence?

Nalbach, Thorwart, J.Phys. B: At. Mol. Opt. Phys. **45**, 154009 (2012)

Can we use long-lived vibrations to induce long-lived coherence in excitons?
(„vibrational laser“ drive?)

QUAPI



Three cases coincide:

- full spectral density
- vib. modes only up to 750 cm^{-1}
- only continuous backgroun (no vibs)

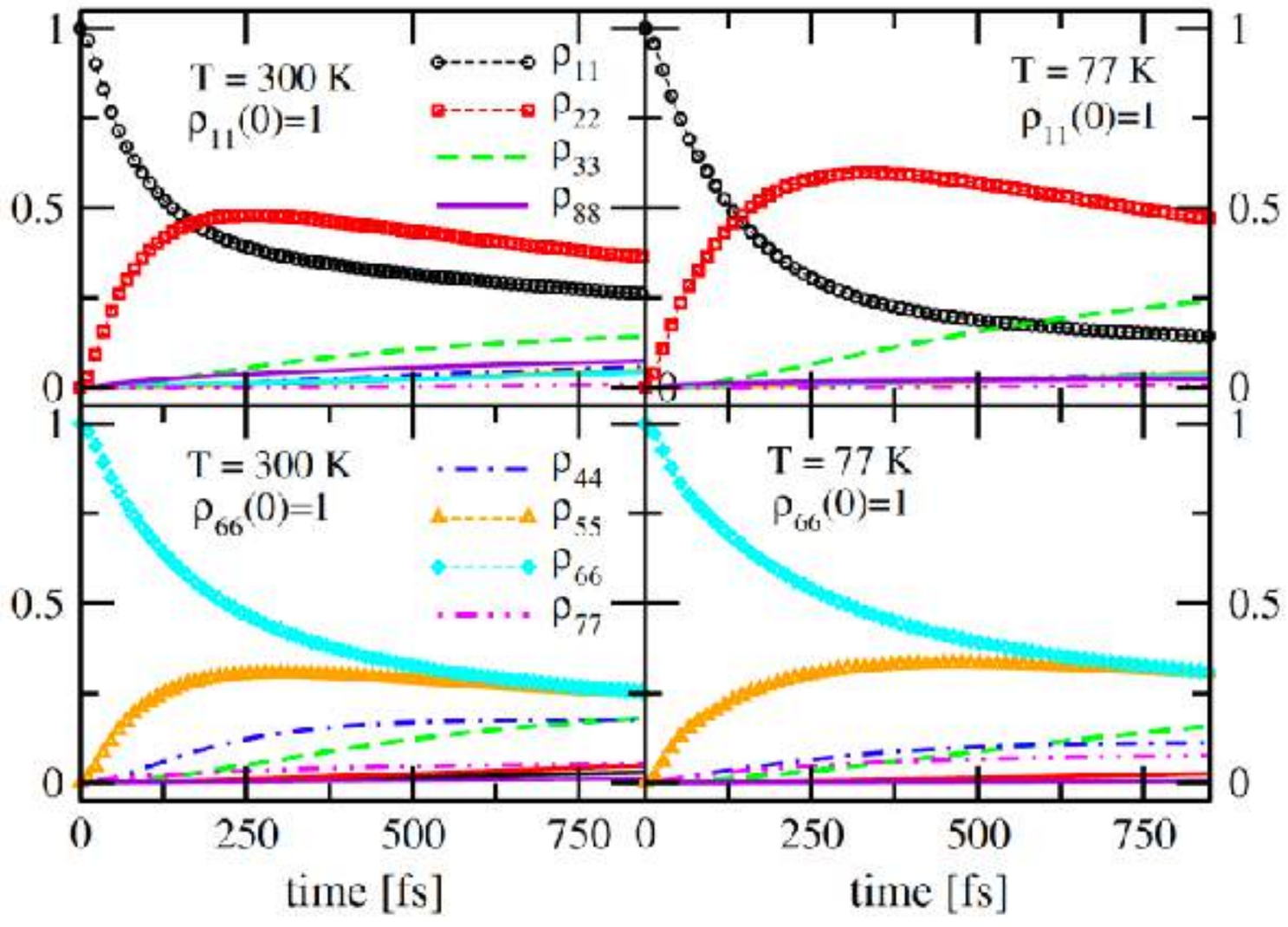
Conclusion: No

Can long-lived vibrational coherence enhance electronic coherence?

Nalbach, Thorwart, J.Phys. B: At. Mol. Opt. Phys. **45**, 154009 (2012)

Can we use long-lived vibrations to induce long-lived coherence in excitons?
(„vibrational laser“ drive?)

QUAPI



All sites:

No coherent oscillations in the populations for full spectral density

Can electronic coherence enhance vibrational coherence?

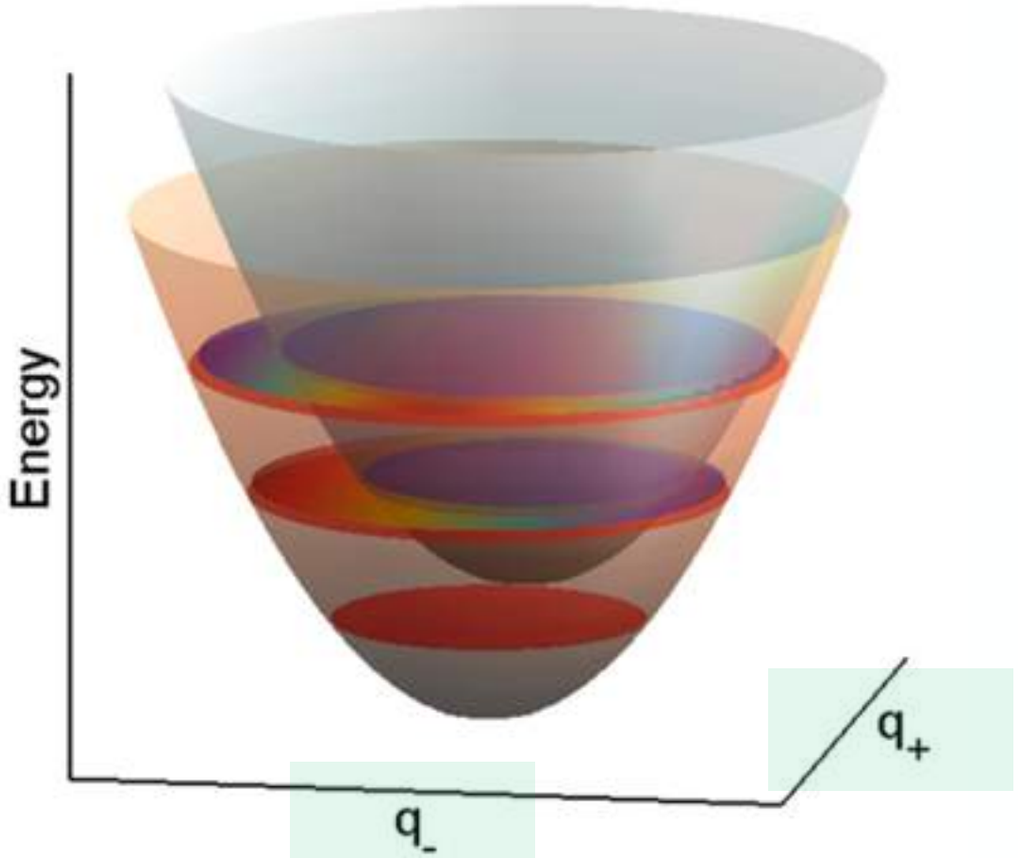
Duan, Thorwart, Miller, in review (2018)

Electronic resonance with anticorrelated pigment vibrations drives photosynthetic energy transfer outside the adiabatic framework

PNAS

Vivek Tiwari, William K. Peters, and David M. Jonas[1]

PNAS | January 22, 2013 | vol. 110 | no. 4 | 1203–1208



Pullerits, Zigmantas, Sundström, PNAS 2013

- Electronic dimer plus vibrational modes
- correlated & anti-correlated mode important

$$q_+ = q_A + q_B \qquad q_- = q_A - q_B$$

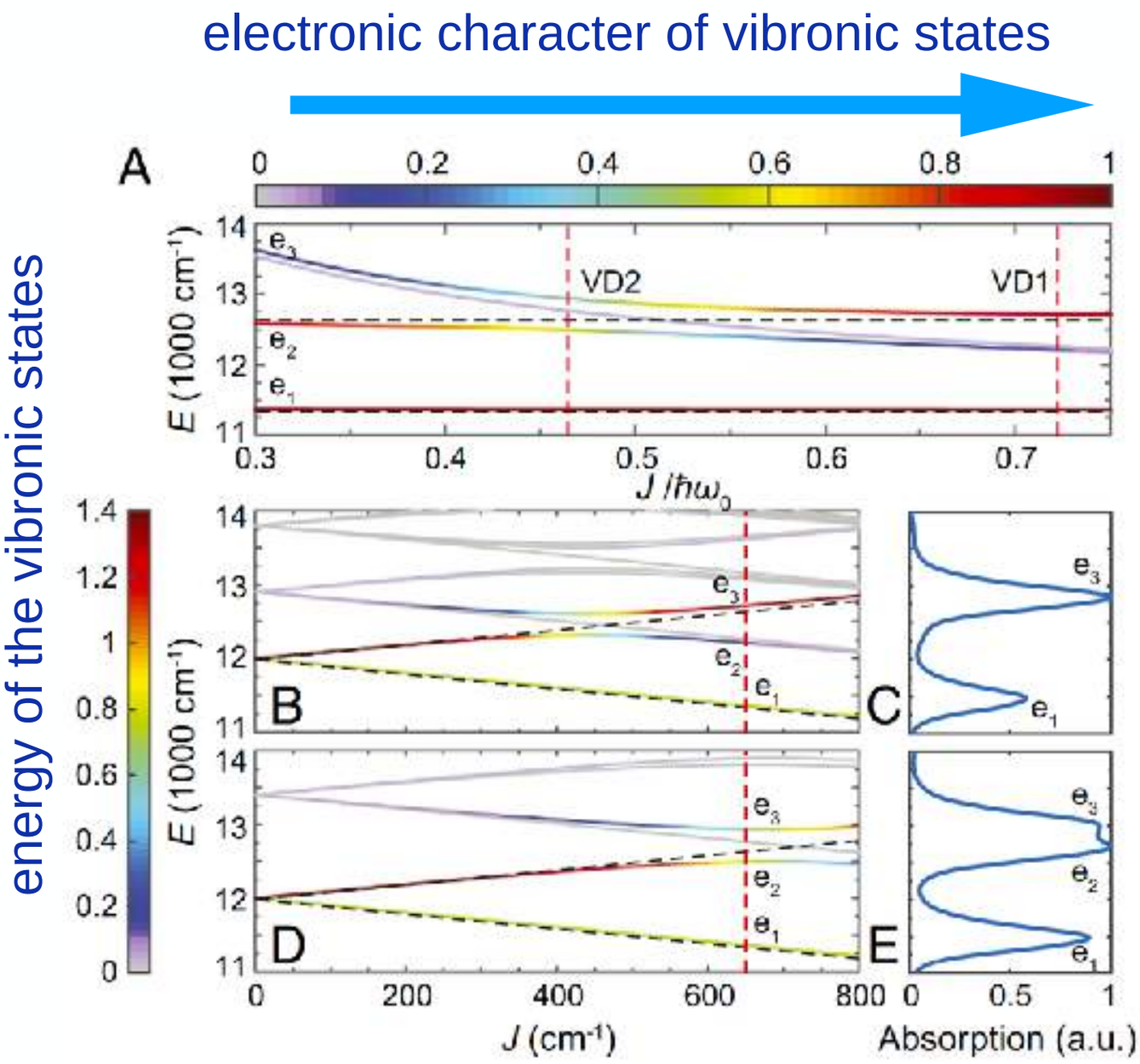
- vibrational levels on different potential energy surfaces are in resonance
- strong non-adiabatic coupling / mixing
- with strong electronic character of the vibronic, exact non-adiabatic levels

↓

strong coherent electronic admixture enhances amplitude of anti-correlated vibrations

Can electronic coherence enhance vibrational coherence?

Duan, Thorwart, Miller, in review (2018)



- Idea is in principle correct!
- weight of the electronic component of the vibronic state increases for increasing vibronic coupling

BUT:
Fast electronic dephasing destroys coherent coupling in the electronic sector?

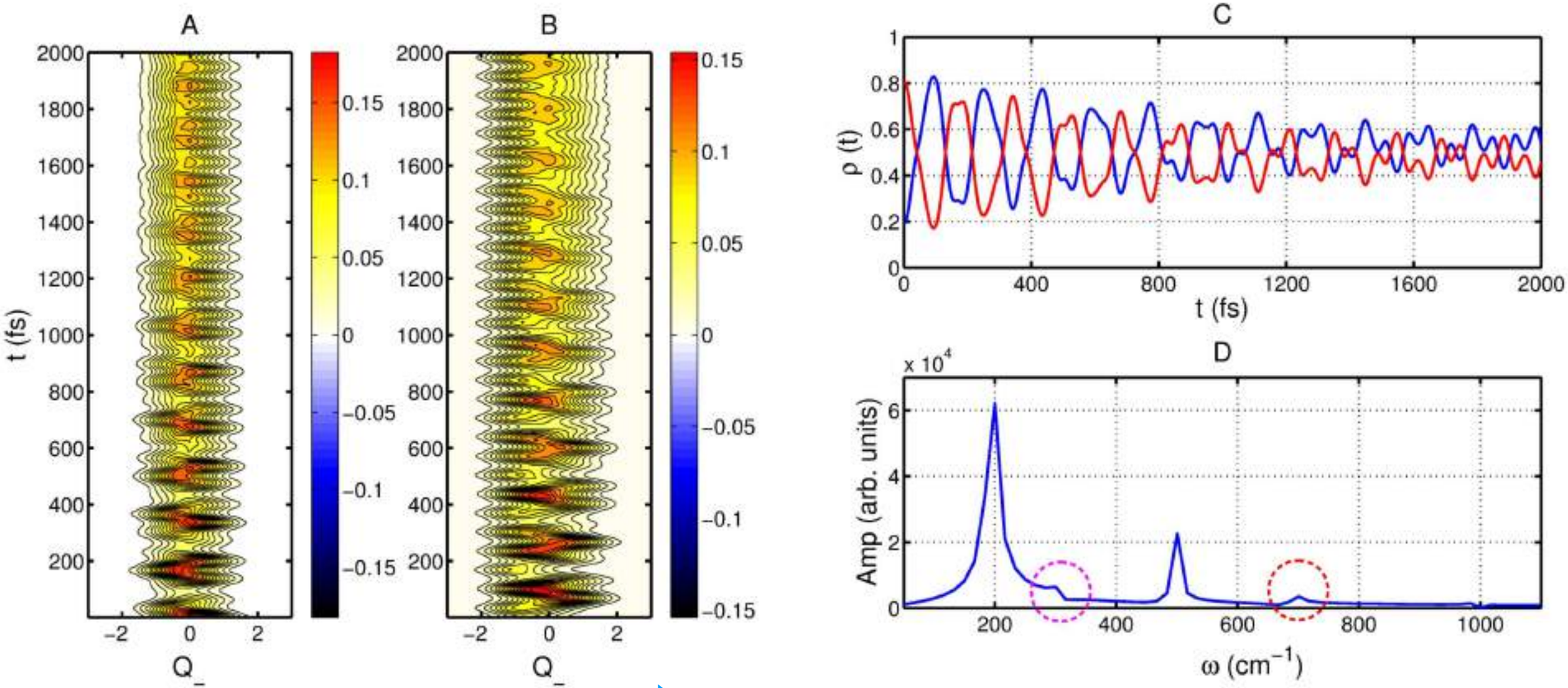
Yeh, Hoehn, Allodi, Engel, Kais, PNAS 2018 Weak electronic dephasing

Can electronic coherence enhance vibrational coherence?

Duan, Thorwart, Miller, in review (2018)

Wave packet tracking on potential energy surfaces

1) Weak electronic dephasing



Indeed: Weak dephasing → large-amplitude vibronic coherent oscillations

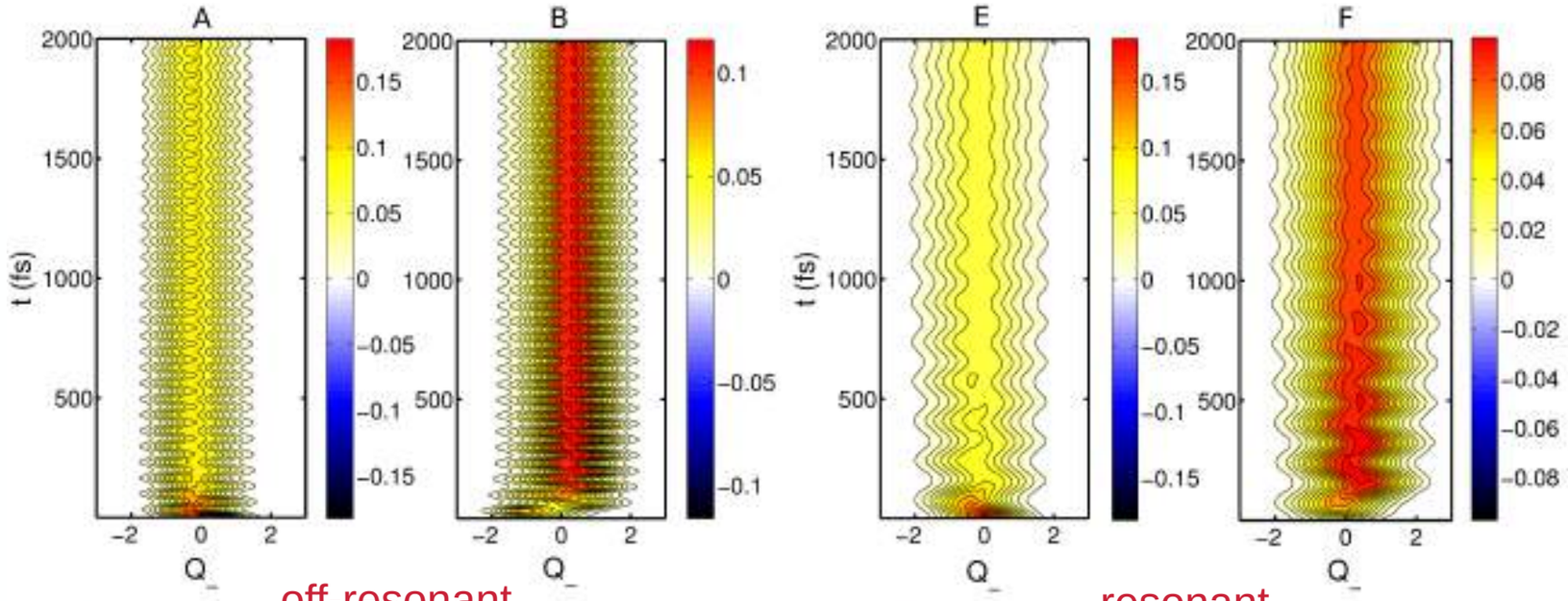
BUT: not realistic values used in Yeh, Hoehn, Allodi, Engel, Kais, PNAS 2018

Can electronic coherence enhance vibrational coherence?

Duan, Thorwart, Miller, in review (2018)

Wave packet tracking on potential energy surfaces

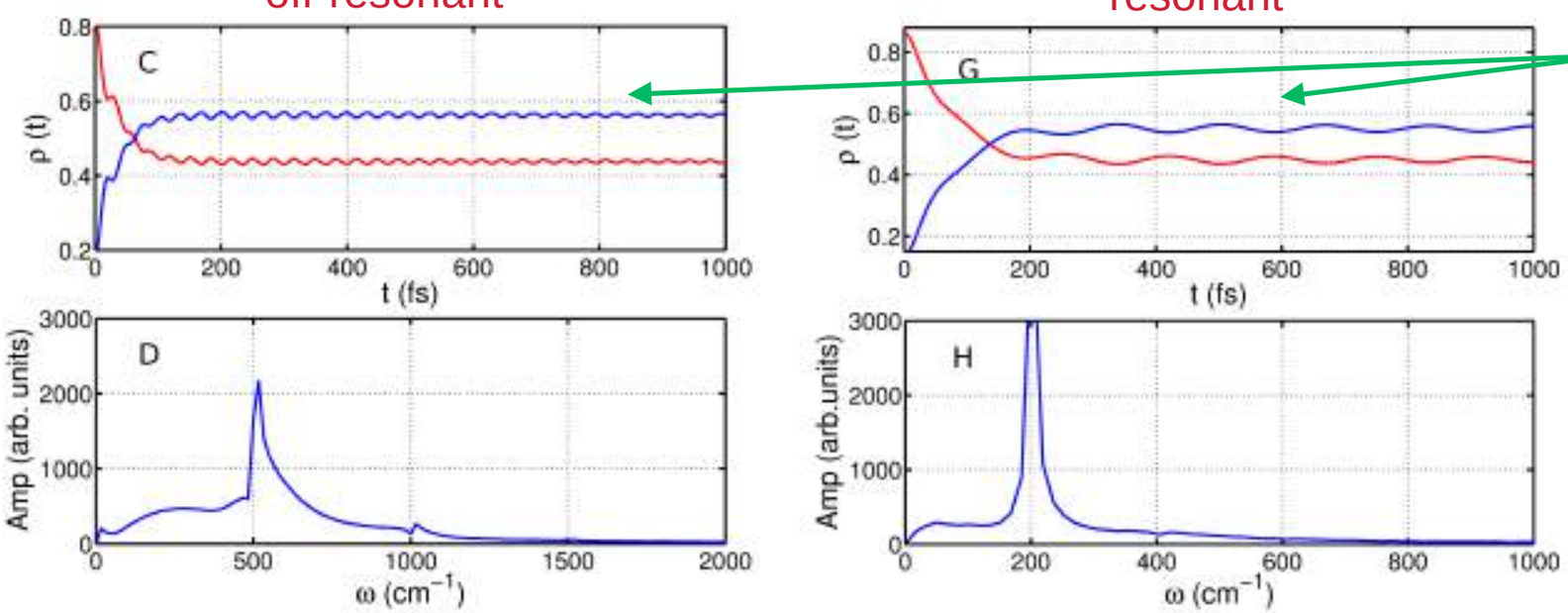
2) Strong (realistic) electronic dephasing from experiment



off-resonant

resonant

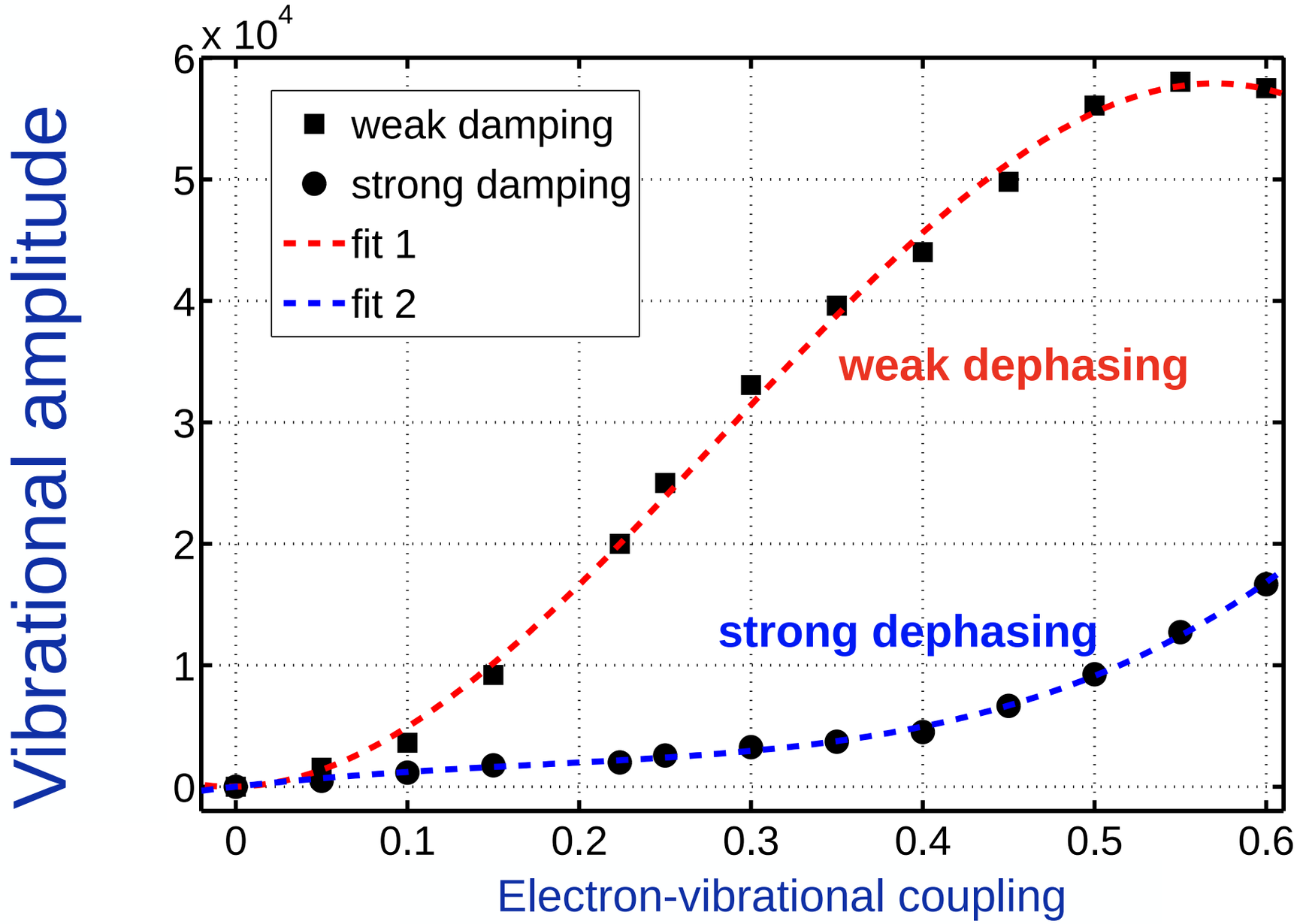
tiny vibrational oscillations



Can electronic coherence enhance vibrational coherence?

Duan, Thorwart, Miller, in review (2018)

Wave packet tracking on potential energy surfaces



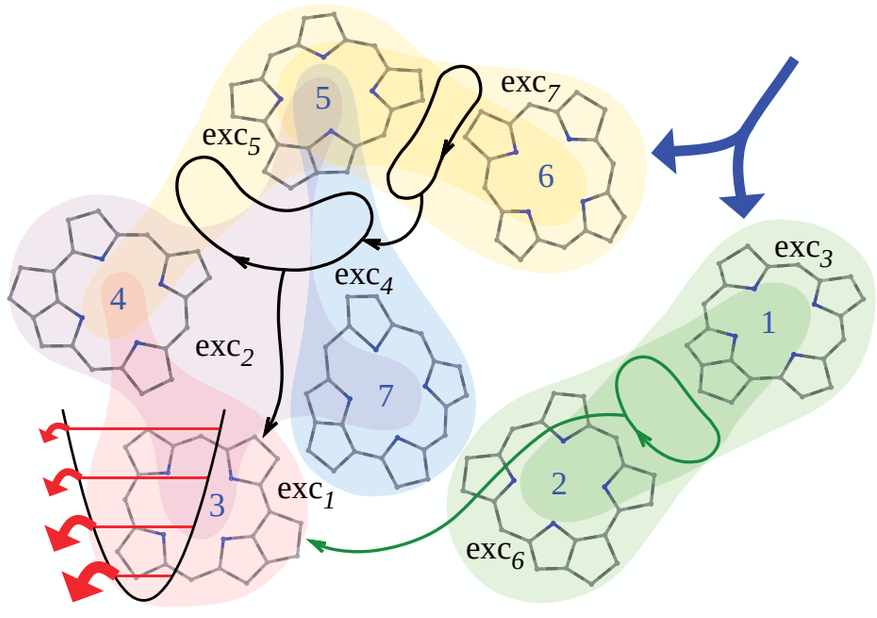
Conclusion: 1) Picture does not apply under realistic conditions of electronic dephasing
2) same for resonant / off-resonant conditions (not shown here)

Can strong vibronic coupling speed-up energy transfer?

Nalbach, Mujica-Martinez, Thorwart, PRE **91**, 022706 (2015)

- **So far:**
  - No enhancement of life time of electronic coherence by long-lived vibrational coherence
  - No enhancement of vibrational amplitude due to large amplitude electronic coherence
  - What about effect on efficiency of energ< transfer?

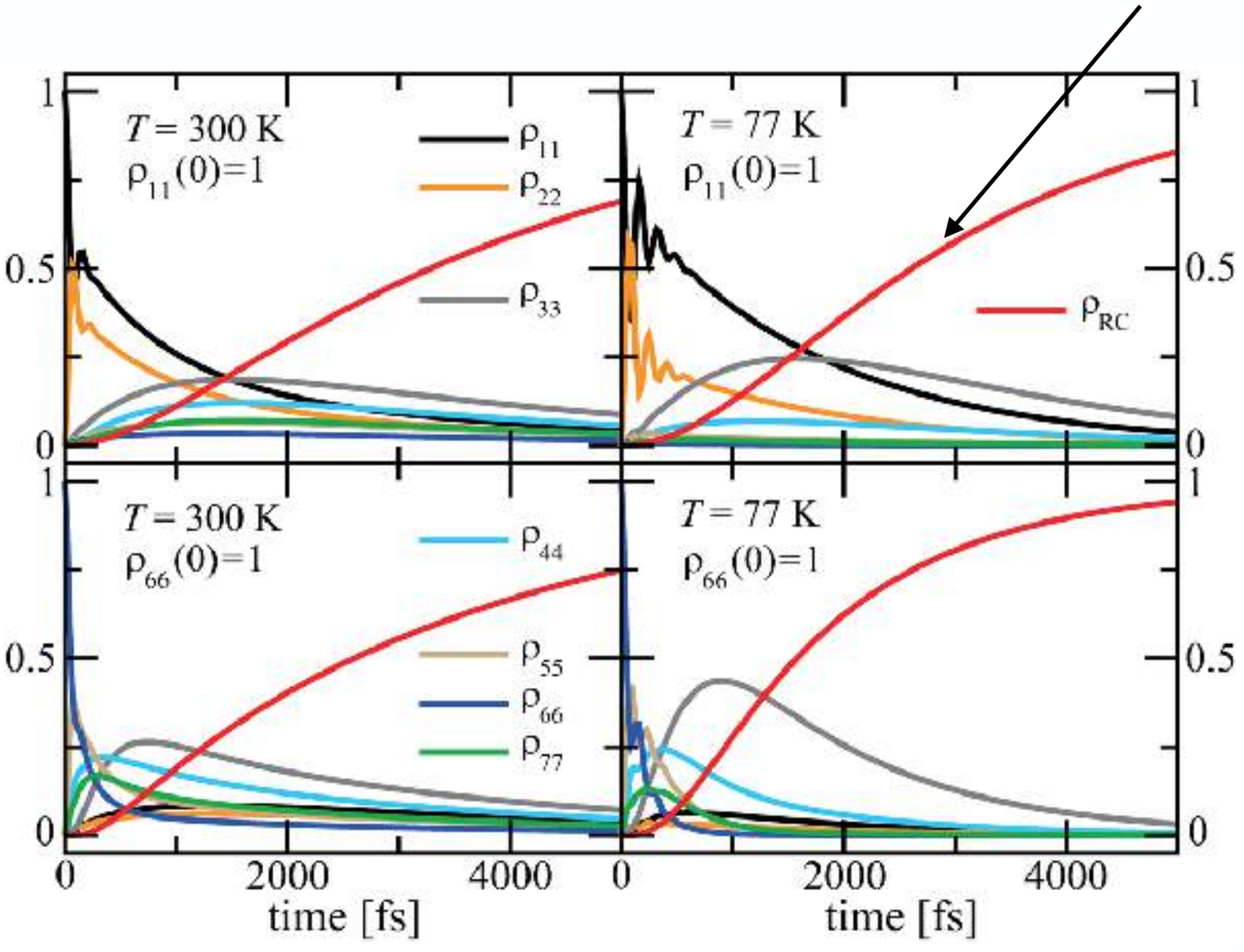
- Non-adiabatic vibration as part of the system (initially not in equilibrium!)
- Cases: Vibrational mode coupled to
  - FMO exit site (= site 3)
  - FMO site 1 (Berkeley experiment)
  - all sites



Can strong vibronic coupling speed-up energy transfer?

Nalbach, Mujica-Martinez, Thorwart, PRE **91**, 022706 (2015)

- Couple an energy sink to exit site 3, no back transfer allowed
- Efficieny of energy transfer given by time constant of its rise kinetics



No vibrational mode:

Transfer times (300K):

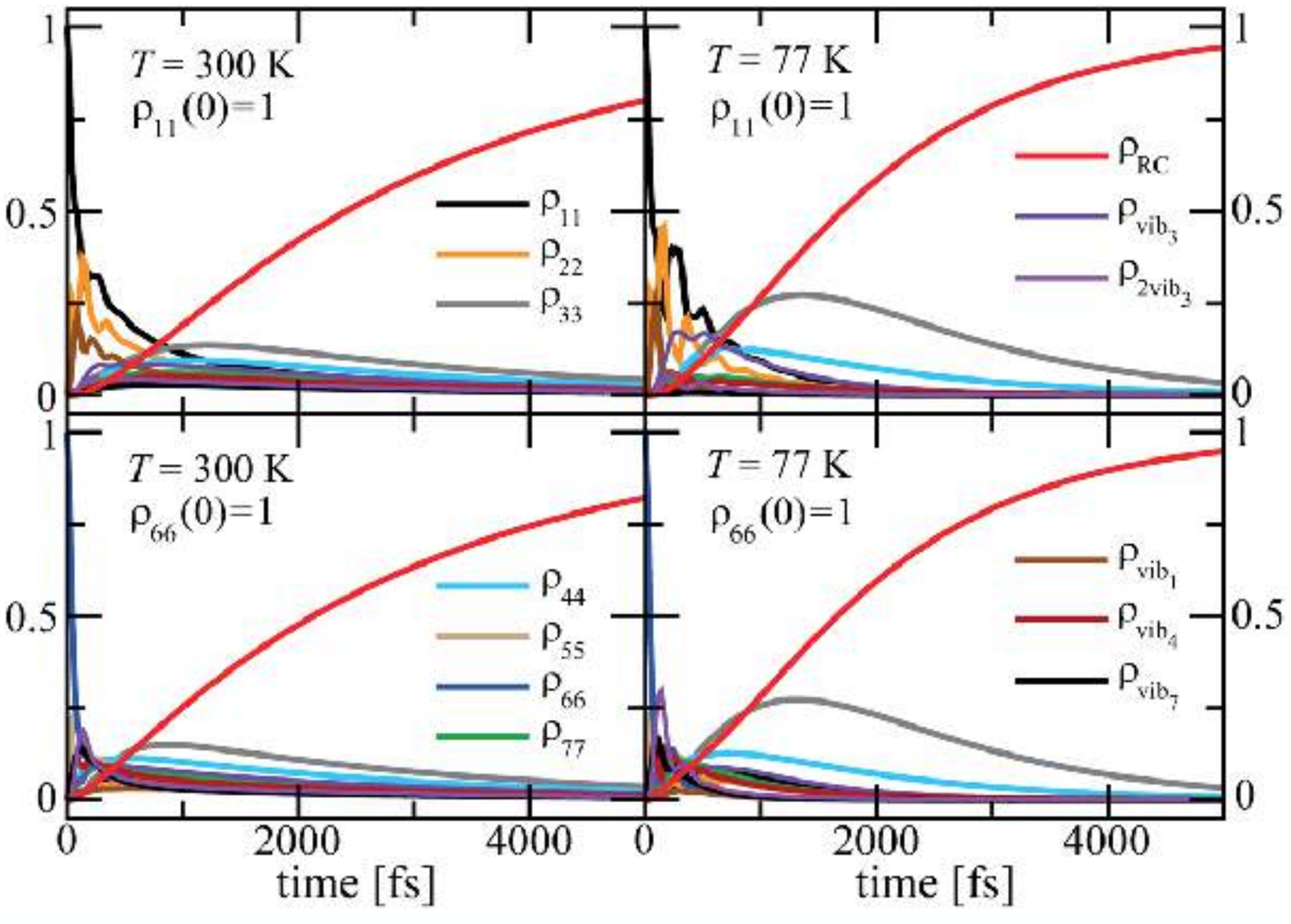
site 1: 3.8 ps

site 6: 3.4 ps

Can strong vibronic coupling speed-up energy transfer?

Nalbach, Mujica-Martinez, Thorwart, PRE **91**, 022706 (2015)

- Underdamped vibrational mode opens up more transfer channels



Vibrational mode at all sites:

- no enhanced coherence
- speed up of transfer!

Transfer times (300K):

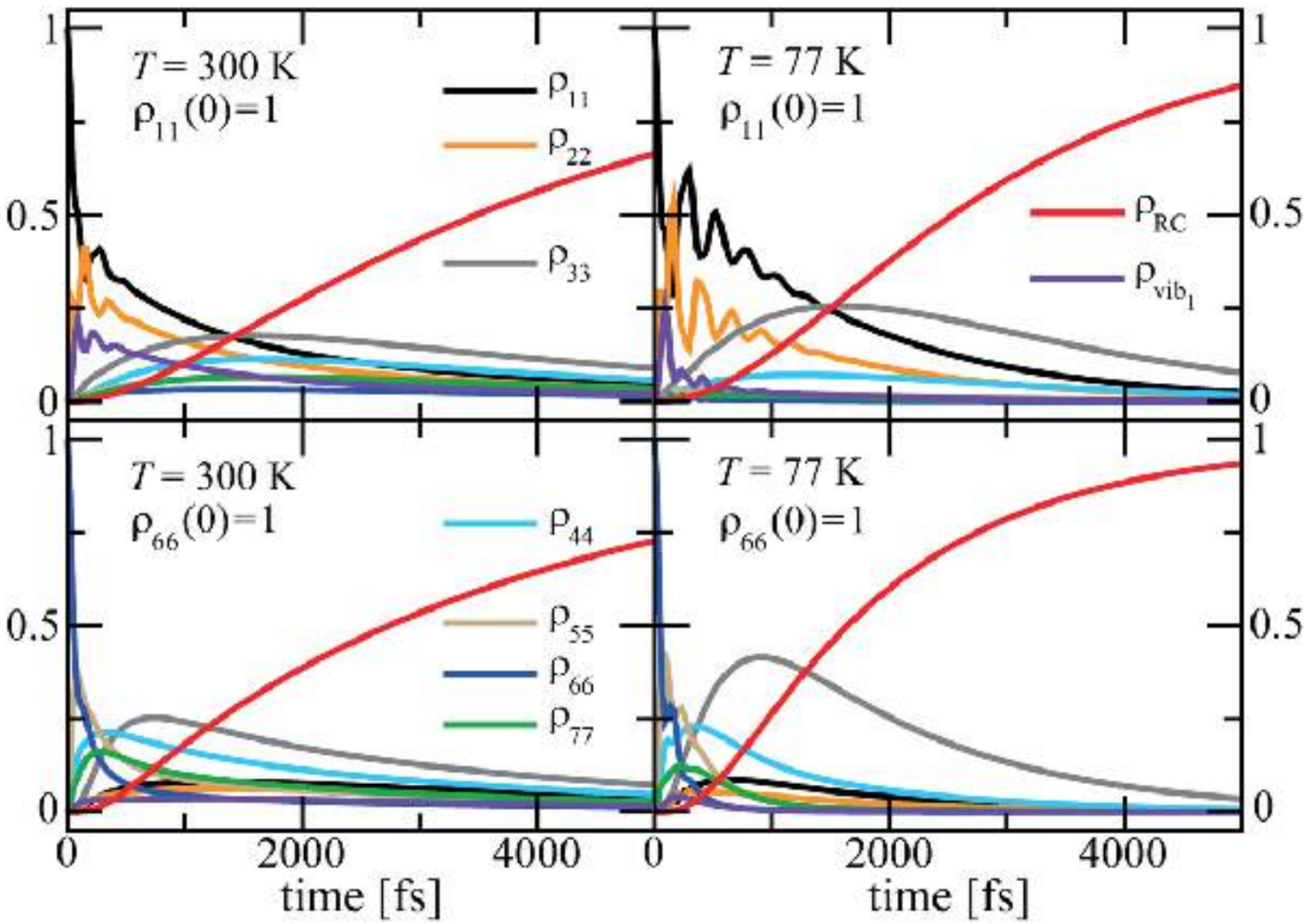
site 1: 2.9 ps (-24%)

site 6: 2.8 ps (-18%)

Can strong vibronic coupling speed-up energy transfer?

Nalbach, Mujica-Martinez, Thorwart, PRE **91**, 022706 (2015)

- Underdamped vibrational mode at entrance: energy is stuck in vibrations!



Vibrational mode at site 1:

- more beatings 1-2
- slow down of transfer!

Transfer times (300K):

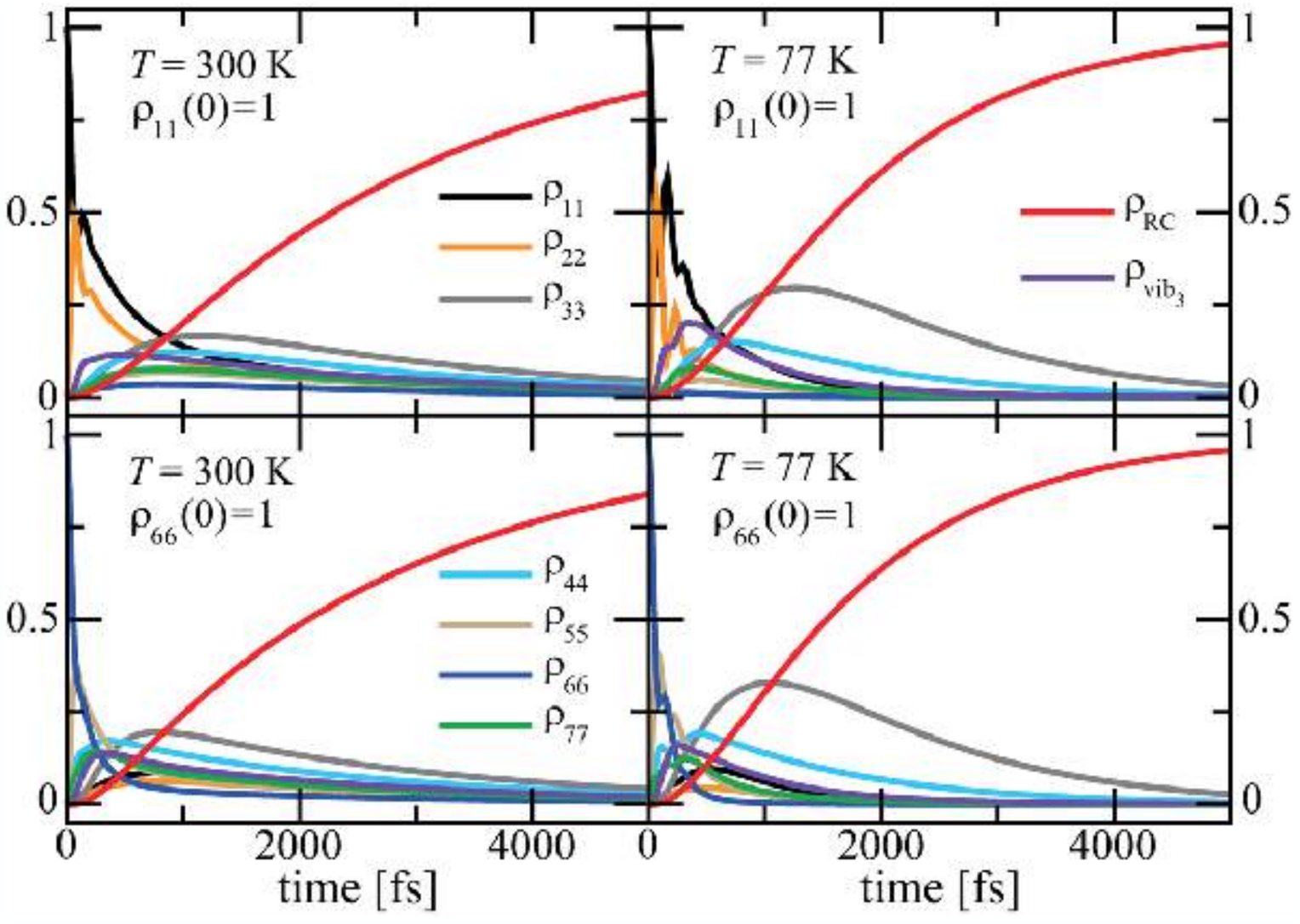
site 1: 4.1 ps (+8%)

site 6: 3.6 ps (+6%)

Can strong vibronic coupling speed-up energy transfer?

Nalbach, Mujica-Martinez, Thorwart, PRE **91**, 022706 (2015)

- Underdamped vibrational mode opens up more exit channels



Vibrational mode at site 3:

- no enhanced coherence
- speed up of transfer!

Transfer times (300K):

site 1: 2.7 ps (-29%)

site 6: 2.6 ps (-24%)

Can strong vibronic coupling speed-up energy transfer?

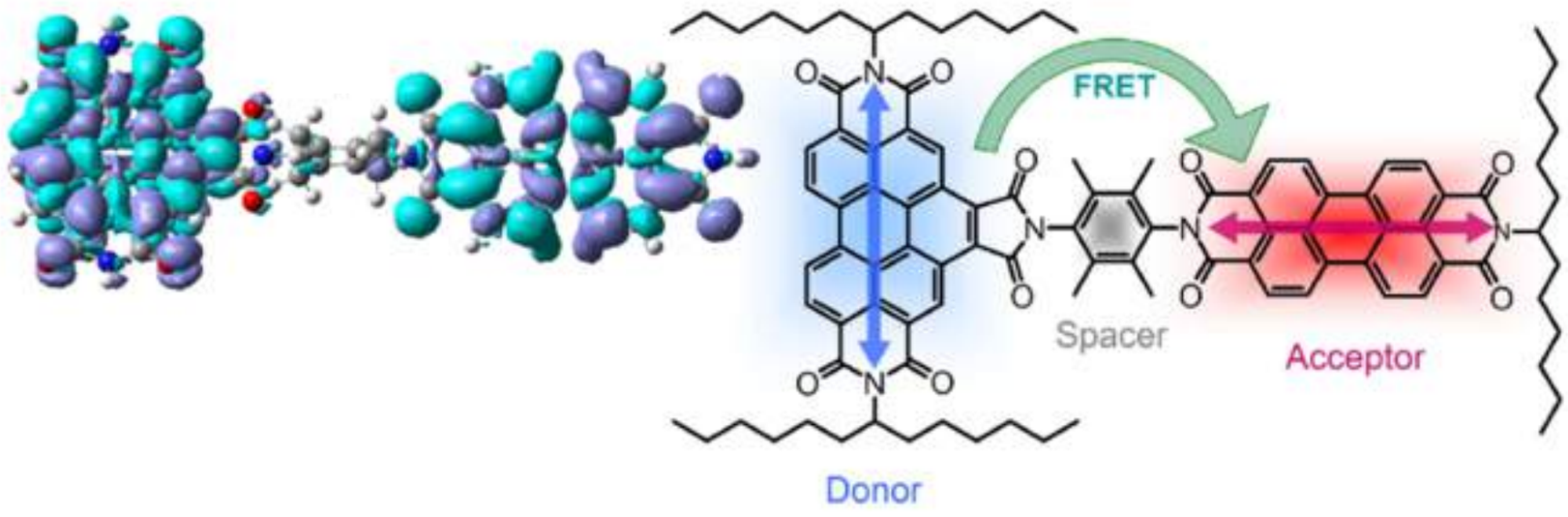
- **YES!**

Nalbach, Mujica-Martinez, Thorwart, PRE **91**, 022706 (2015)

- **More transfer channels open up**

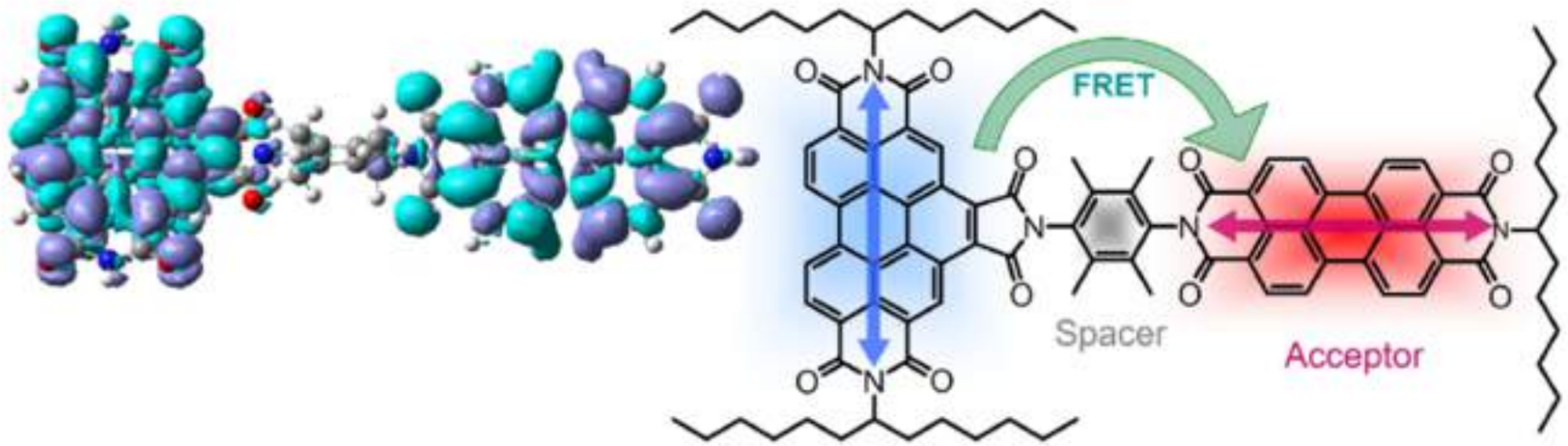
Vibrational mode coupled to	Initial excitation at site	Transfer time (ps)	Change by
NO vibration	1	3.8	–
	6	3.4	–
All sites	1	2.9	−24 %
	6	2.8	−18 %
Site 1	1	4.1	+8 %
	6	3.6	+6 %
Site 3	1	2.7	−29 %
	6	2.6	−24 %

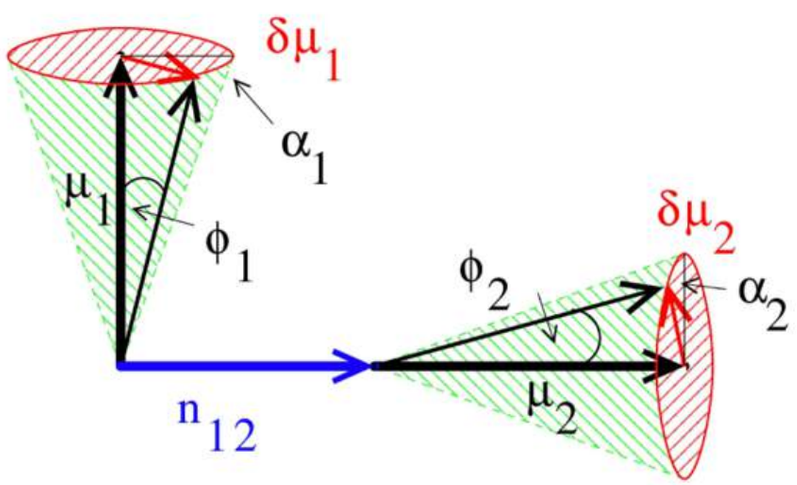
3) FRET in orthogonal dimers



Energy transfer induced by fluctuations

Nalbach, Pugliesi, Langhals, Thorwart, PRL **108**, 218302 (2012)





- Donor: Benzoperylene
- Acceptor: Perylene
- Orthogonally arranged dipole moments
- no FRET in static picture:

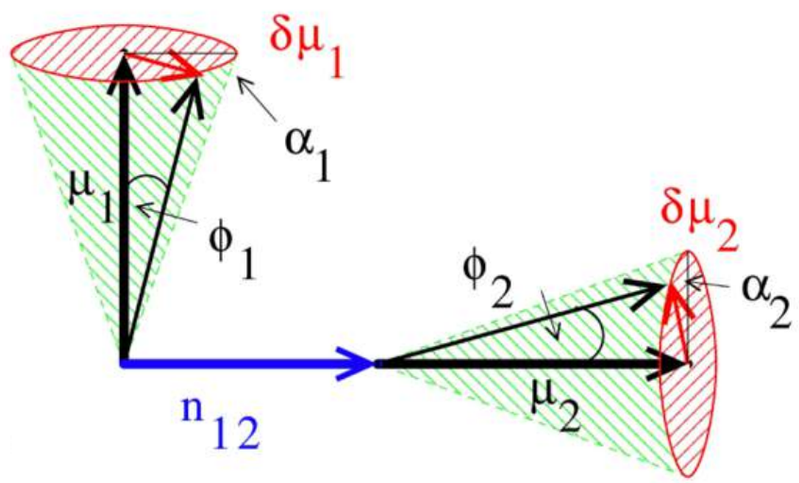
$$V^{(12)}_{\text{dipole}} = \frac{\vec{\boldsymbol{\mu}}_1 \vec{\boldsymbol{\mu}}_2 - 3(\vec{\boldsymbol{\mu}}_1 \vec{\mathbf{n}}_{12})(\vec{\boldsymbol{\mu}}_2 \vec{\mathbf{n}}_{12})}{4\pi\varepsilon_0 R^3_{12}}$$

- **But:** experimentally measured rather fast exciton transfer
- transfer time: 10 ps

Energy transfer induced by fluctuations

Nalbach, Pugliesi, Langhals, Thorwart, PRL **108**, 218302 (2012)

- Idea: Orientational fluctuations of dipole moments in molecule induce coupling
- strength depends on the variance of orientational fluctuations
- effective phenomenological model: angles of rigid dipole moments fluctuate
- How to obtain spectral density of angular fluctuations?



- **dipole coupling:**

$$V = J(\sin\phi_2 \cos\alpha_2 - 2\sin\phi_1 \cos\alpha_1)$$

- We know energy fluctuations δE due to solvent for general arrangements.
- Onsager theory of solvation:

$$G(\omega) = \lambda \frac{2}{\pi} \frac{\omega\omega_c}{\omega^2 + \omega_c^2}$$

- typical values of reorg. energy:
  - in toluene: $\lambda = 245\,\mathrm{cm}^{-1}$
  - in chloroforme: $\lambda = 133\,\mathrm{cm}^{-1}$

Energy transfer induced by fluctuations

Nalbach, Pugliesi, Langhals, Thorwart, PRL **108**, 218302 (2012)

- Scaling argument $\frac{\langle(\delta E)^2\rangle}{W} = \epsilon_{1,2}\frac{\langle(\delta z)^2\rangle}{l^2}$ with typical energy/length scales
- Fluctuations of dipole coupling due to angle fluctuations $\frac{\langle(\delta V)^2\rangle}{W} = J\frac{\langle(\delta z)^2\rangle}{l^2}$
- Corresponding spectral density of angle fluctuations:

$$G_\phi(\omega) = \lambda_\phi \frac{2}{\pi}\frac{\omega\omega_c}{\omega^2+\omega_c^2} \qquad \lambda_\phi = \lambda\frac{J}{\epsilon_{1,2}}$$

- typical values of reorg. energy: $0.5\,\mathrm{cm}^{-1} \lesssim \lambda_\phi \lesssim 5\,\mathrm{cm}^{-1}$

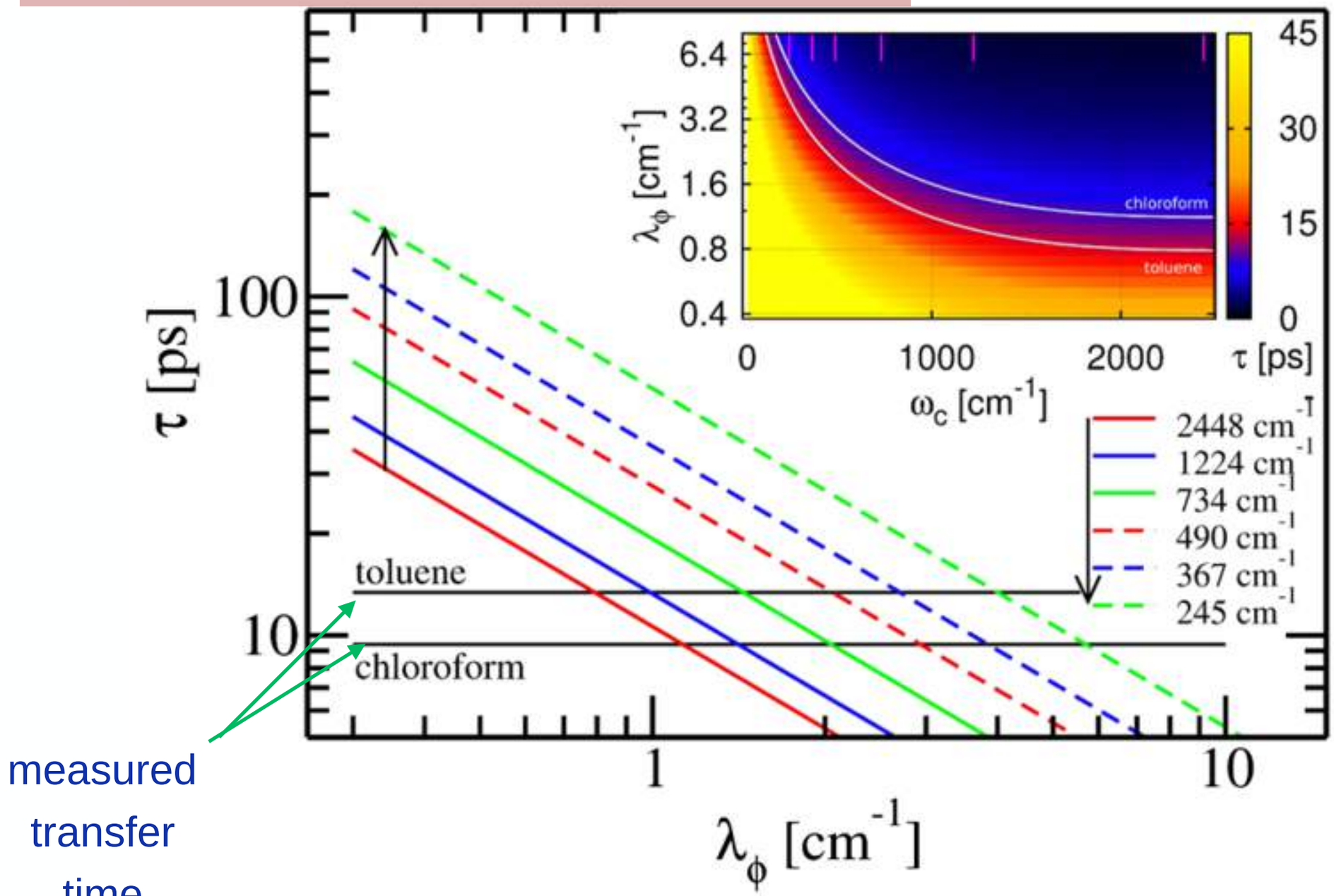
- FRET transfer rate by Fermi's Golden Rule: $\epsilon = 2448\,\mathrm{cm}^{-1}$

$$\tau^{-1} = \frac{\pi}{2}G_\phi(\epsilon)[1+n_B(\epsilon)]$$

Energy transfer induced by fluctuations

Nalbach, Pugliesi, Langhals, Thorwart, PRL **108**, 218302 (2012)

Estimate yields qualitatively correct result



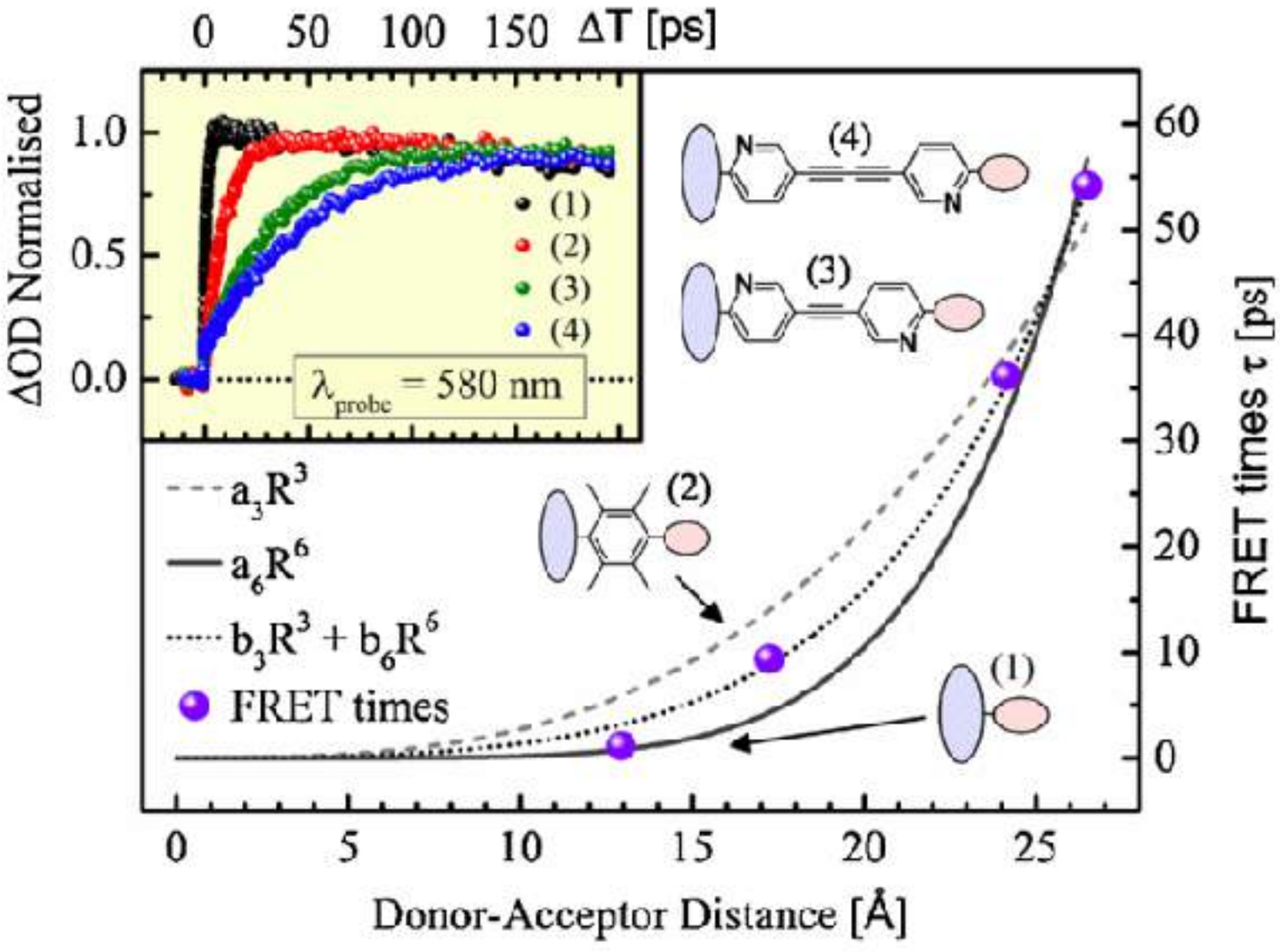
different ω_c

measured transfer time

Distance dependence of transfer time

Nalbach, Pugliesi, Langhals, Thorwart, PRL **108**, 218302 (2012)

Idea: Add spacer molecules between donor & acceptor



- Standard FRET: uncorrelated energy-angle fluctuations

$$\tau \propto R_{\mathrm{DA}}^{6}$$

dominate at large R_{DA}

- Golden Rule for angle fluctuations

$$\tau \propto R_{\mathrm{DA}}^{3}$$

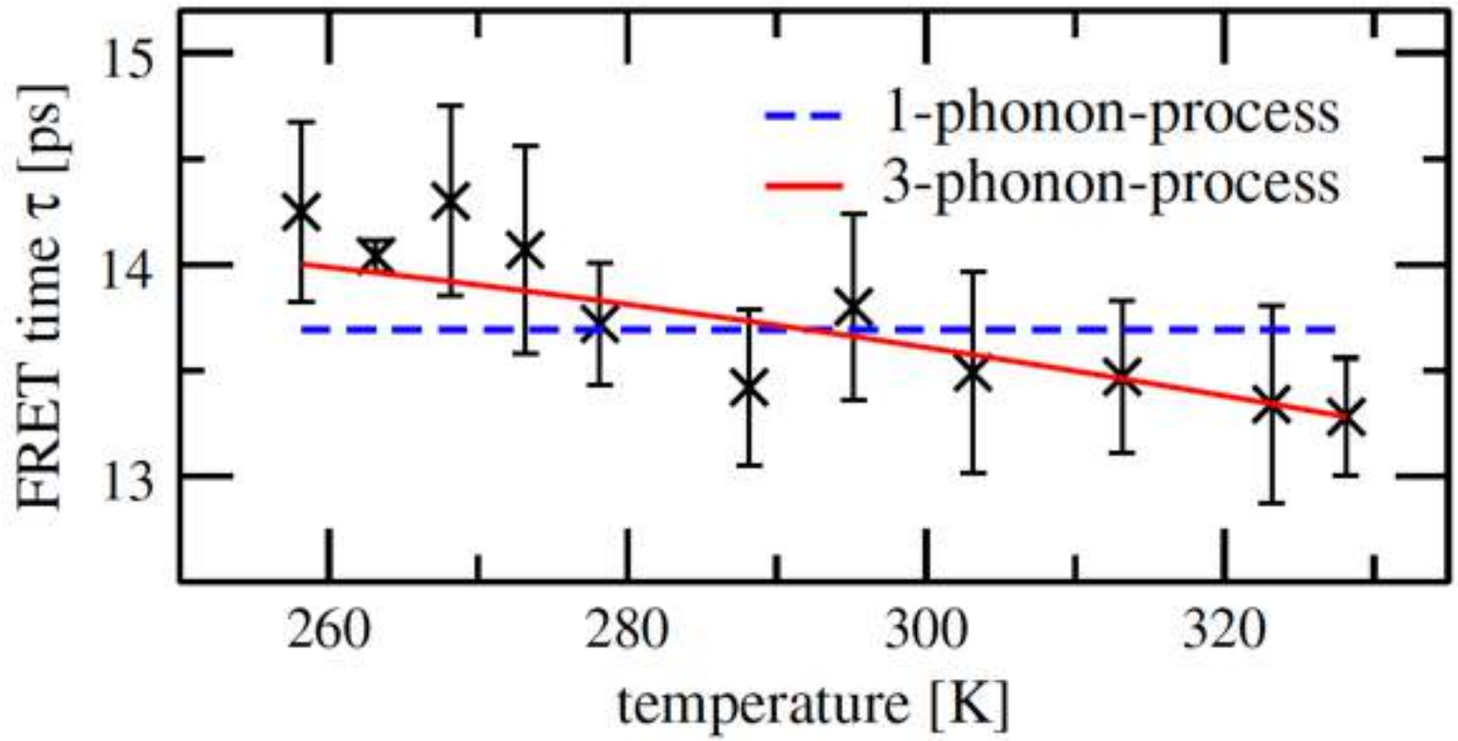
dominate at small R_{DA}

- interpolation fits best: $b_3 R_{\mathrm{DA}}^{3} + b_6 R_{\mathrm{DA}}^{6}$

Temperature dependence

Nalbach, Pugliesi, Langhals, Thorwart, PRL **108**, 218302 (2012)

- Standard one-phonon process via Fermi Golden Rule: not optimal fit
- Mimic 3-phonon-process as a guess



Noticeable deviations from one-phonon process

Explicit vibrational effects

Duan, Gerken, Langhals, Miller, Thorwart, unpublished (2019)

- include explicit vibrational effects (same model as before):

$$H_{\mathrm{D}} = E_{\mathrm{D}}|e_{\mathrm{D}}\rangle\langle e_{\mathrm{D}}| + \Omega_{\mathrm{D}} b_{\mathrm{D}}^{\dagger} b_{\mathrm{D}} + \lambda |e_{\mathrm{D}}\rangle\langle e_{\mathrm{D}}| \left(b_{\mathrm{D}}^{\dagger} + b_{\mathrm{D}}\right)$$

$$H_{\mathrm{A}} = E_{\mathrm{A}}|e_{\mathrm{A}}\rangle\langle e_{\mathrm{A}}| + \Omega_{\mathrm{A}} b_{\mathrm{A}}^{\dagger} b_{\mathrm{A}} + \lambda |e_{\mathrm{A}}\rangle\langle e_{\mathrm{A}}| \left(b_{\mathrm{A}}^{\dagger} + b_{\mathrm{A}}\right)$$

$$H_{\mathrm{Dimer}} = H_{\mathrm{D}} + H_{\mathrm{A}} + J\left(|g_{\mathrm{A}} e_{\mathrm{D}}\rangle\langle e_{\mathrm{A}} g_{\mathrm{D}}| + |e_{\mathrm{A}} g_{\mathrm{D}}\rangle\langle g_{\mathrm{A}} e_{\mathrm{D}}|\right)$$

$$J = J_{||} \sin\theta \cos\phi$$

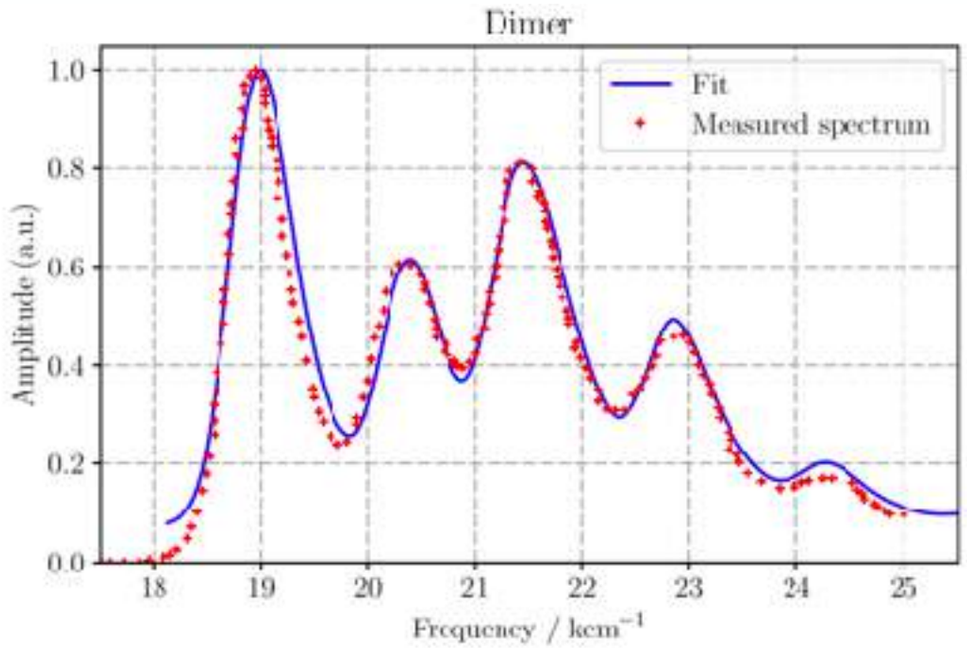
- fluctuating angles: von Mises-Fisher distribution (sphere!):

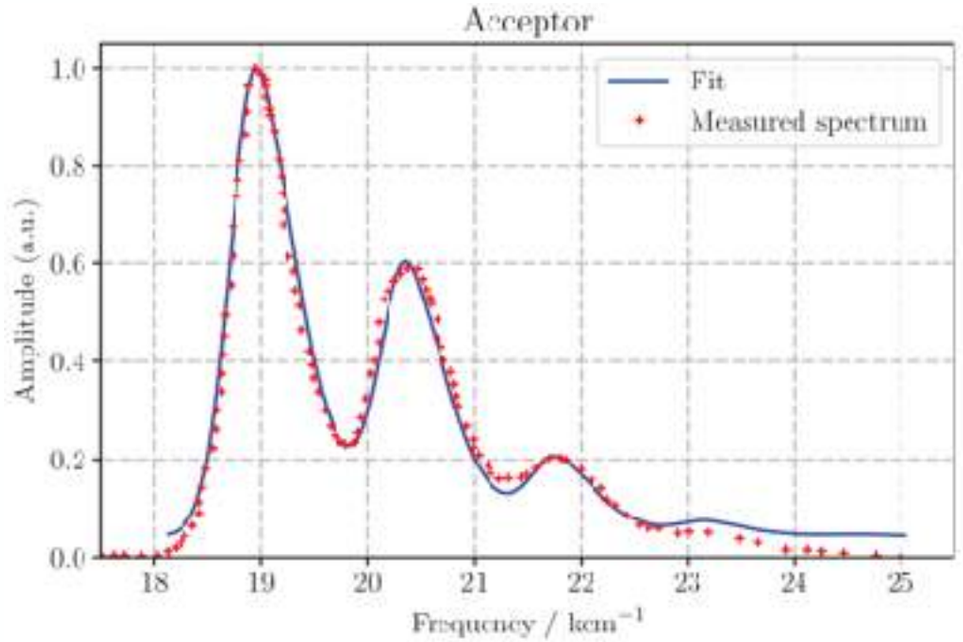
$$f(\theta, \phi) = \frac{\kappa}{4\pi \sinh \kappa} e^{\kappa \cos\theta}$$

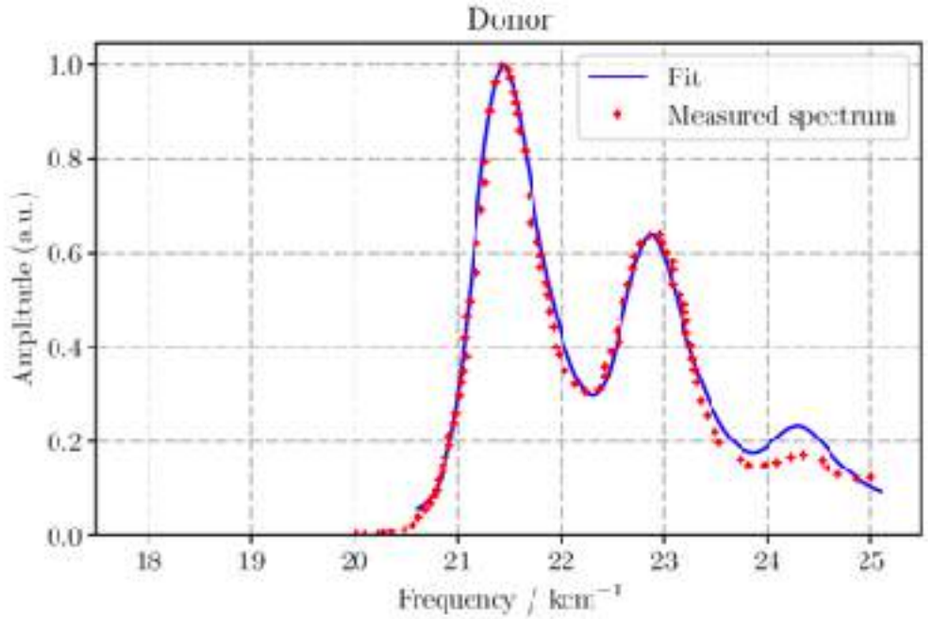
Explicit vibrational effects

Duan, Gerken, Langhals, Miller, Thorwart, unpublished (2019)

- Fit to measured absorption spectra
- strong vibrational progressions







	E/cm^{-1}	Ω/cm^{-1}	λ/cm^{-1}	γ	ω_c/cm^{-1}	σ/cm^{-1}
Acceptor	19730	1410	1050	1.0	600	200
Donor	22200	1450	1080	1.1	800	200

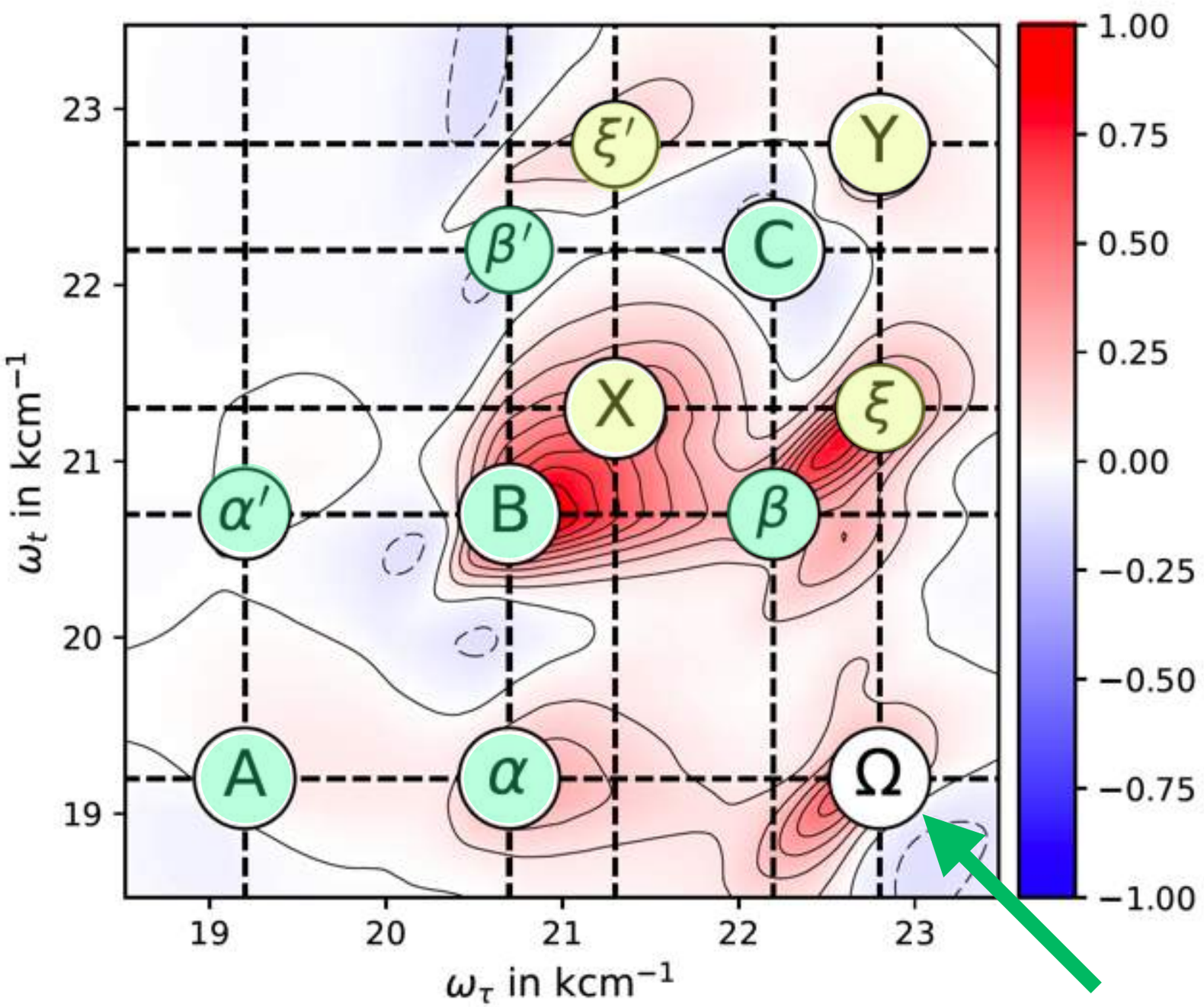
Explicit vibrational effects

Duan, Gerken, Langhals, Miller, Thorwart, unpublished (2019)

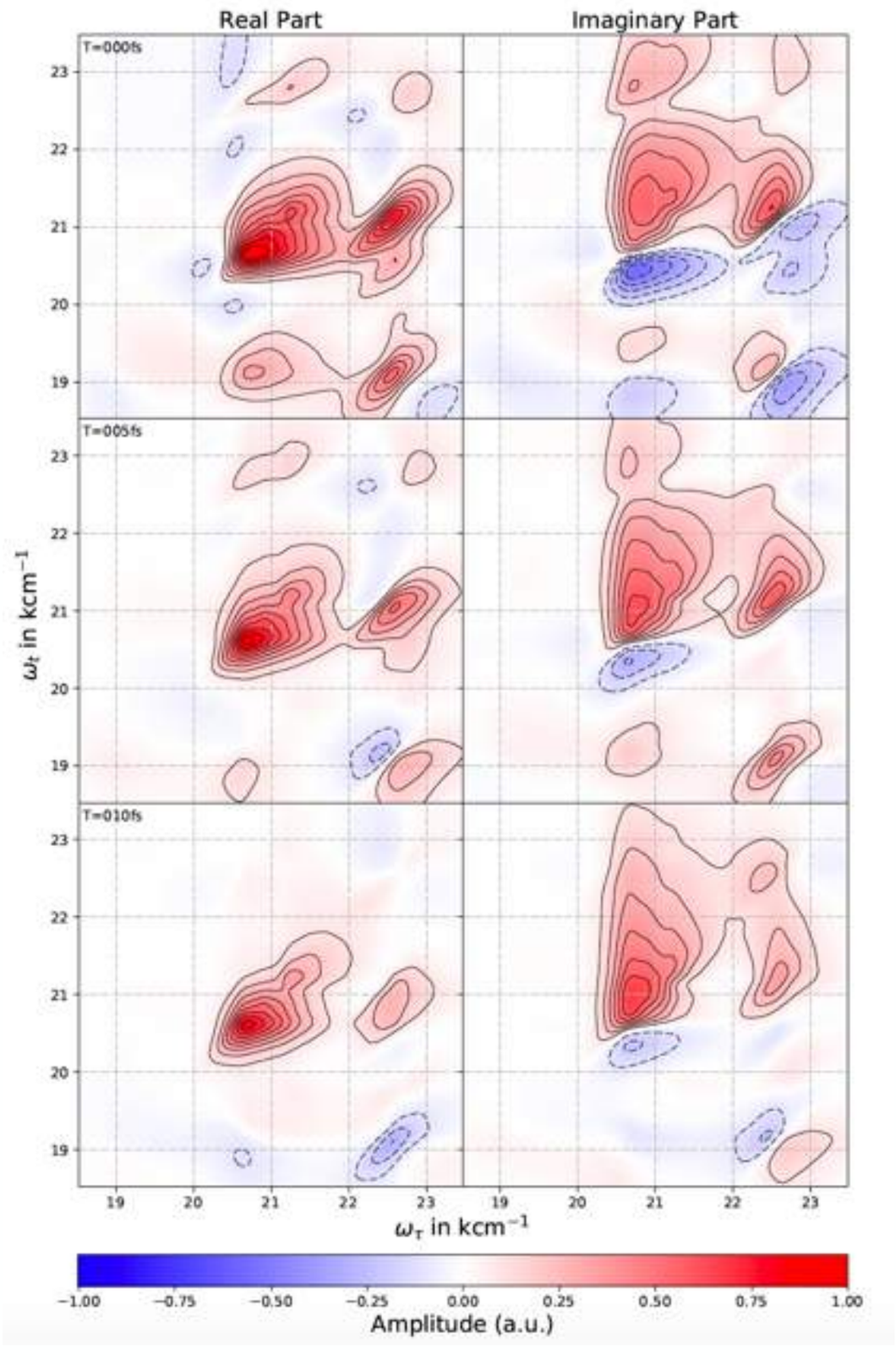
- Calculate with the extracted parameters the 2D spectra:

Donor

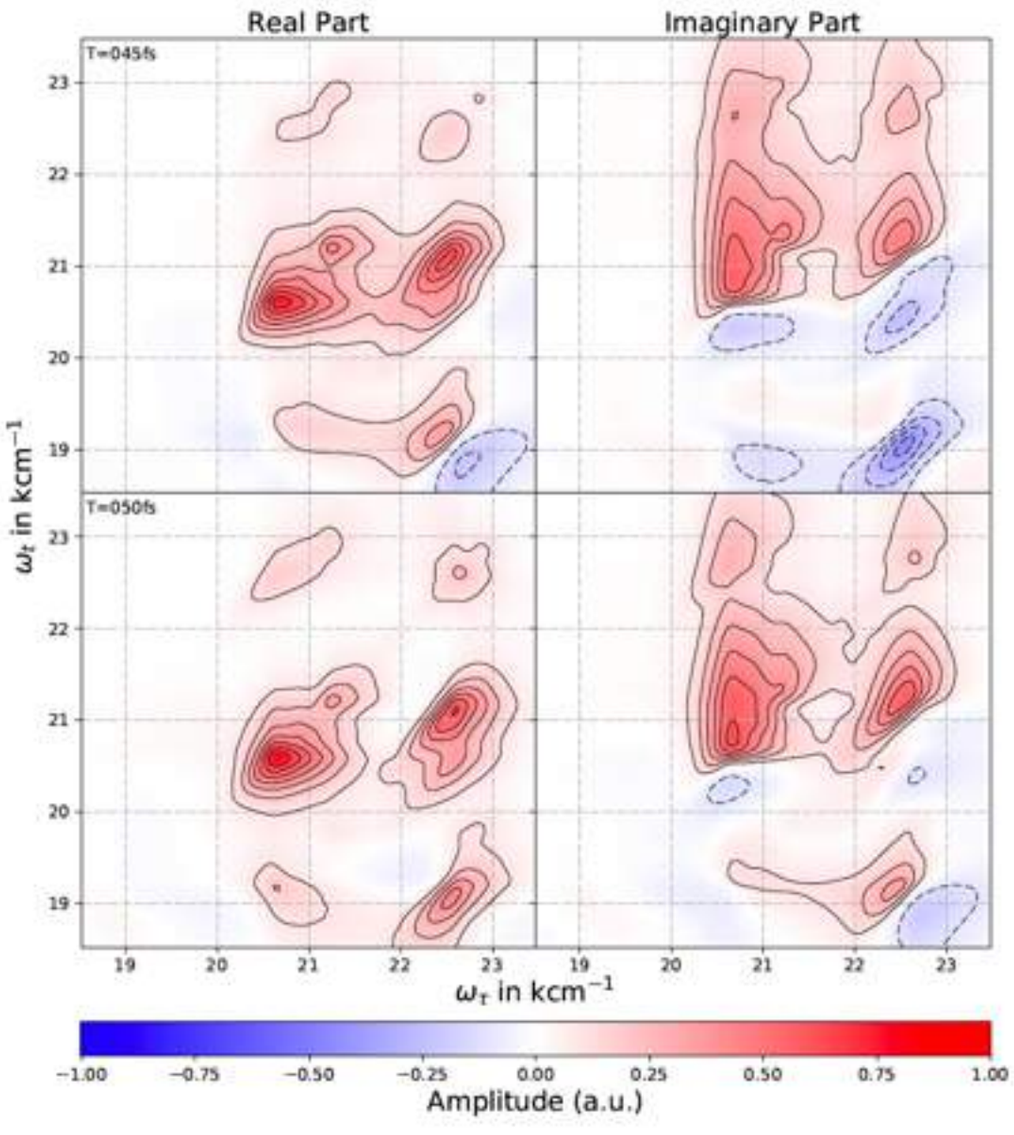
Acc.



Explicit vibrational effects



Duan, Gerken, Langhals, Miller, Thorwart, unpublished (2019)

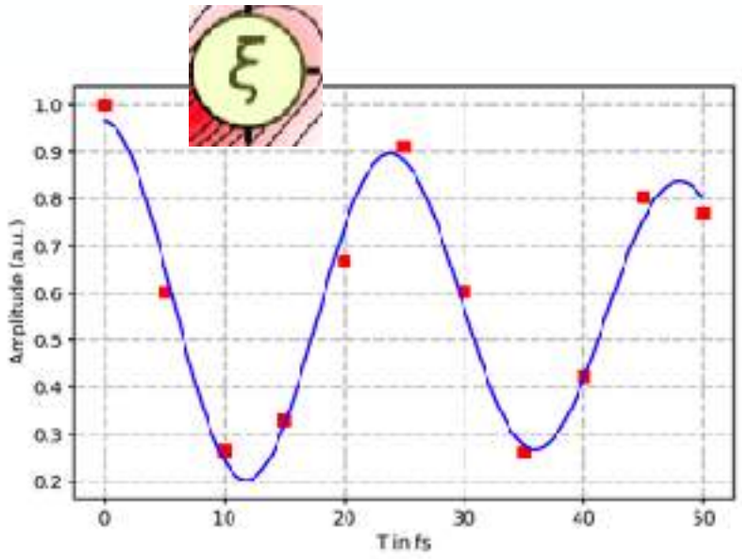


Prediction

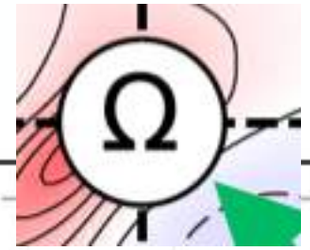
Explicit vibrational effects

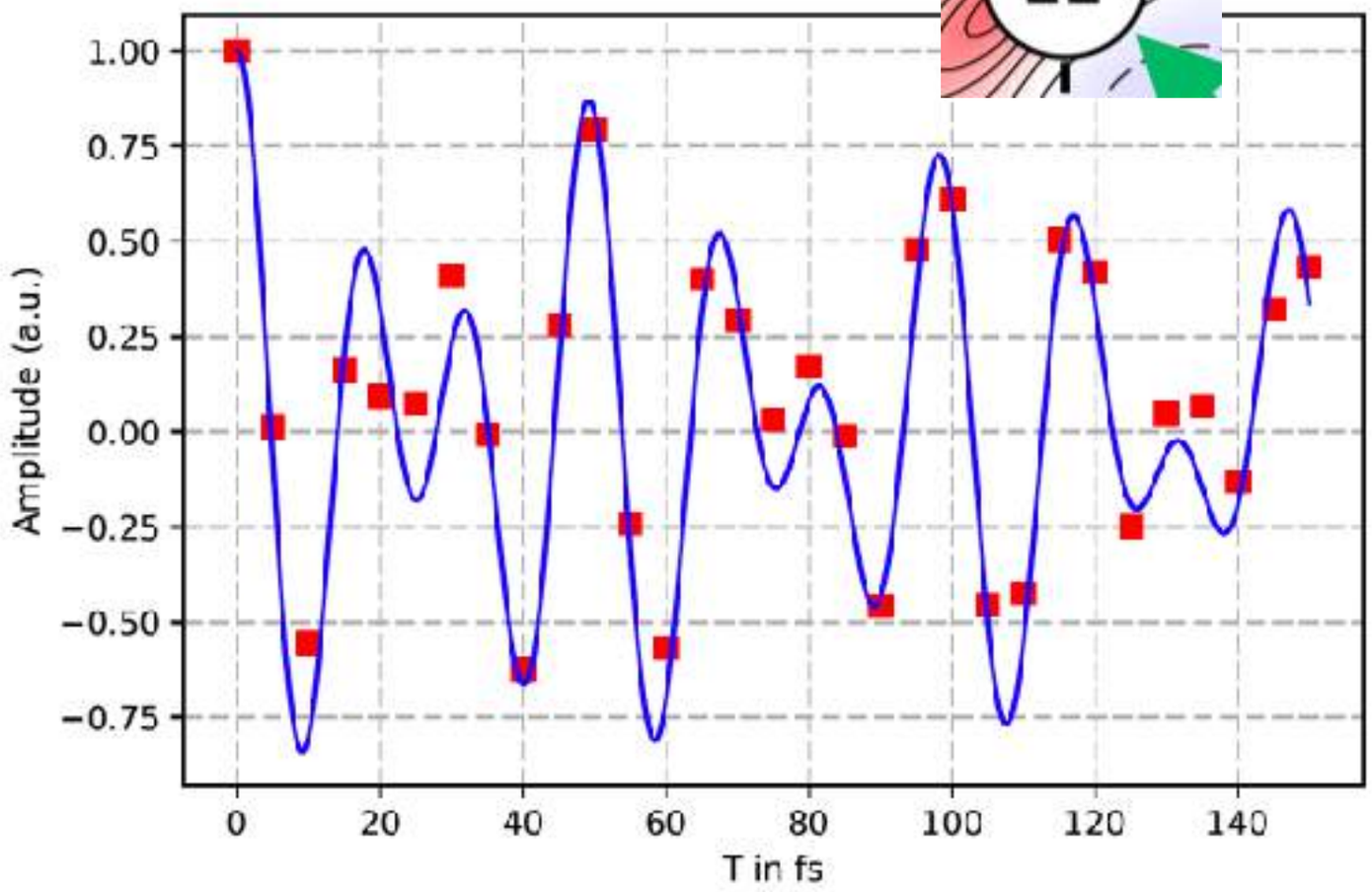
Duan, Gerken, Langhals, Miller, Thorwart, unpublished (2019)

- vibrational cross peak (intra)



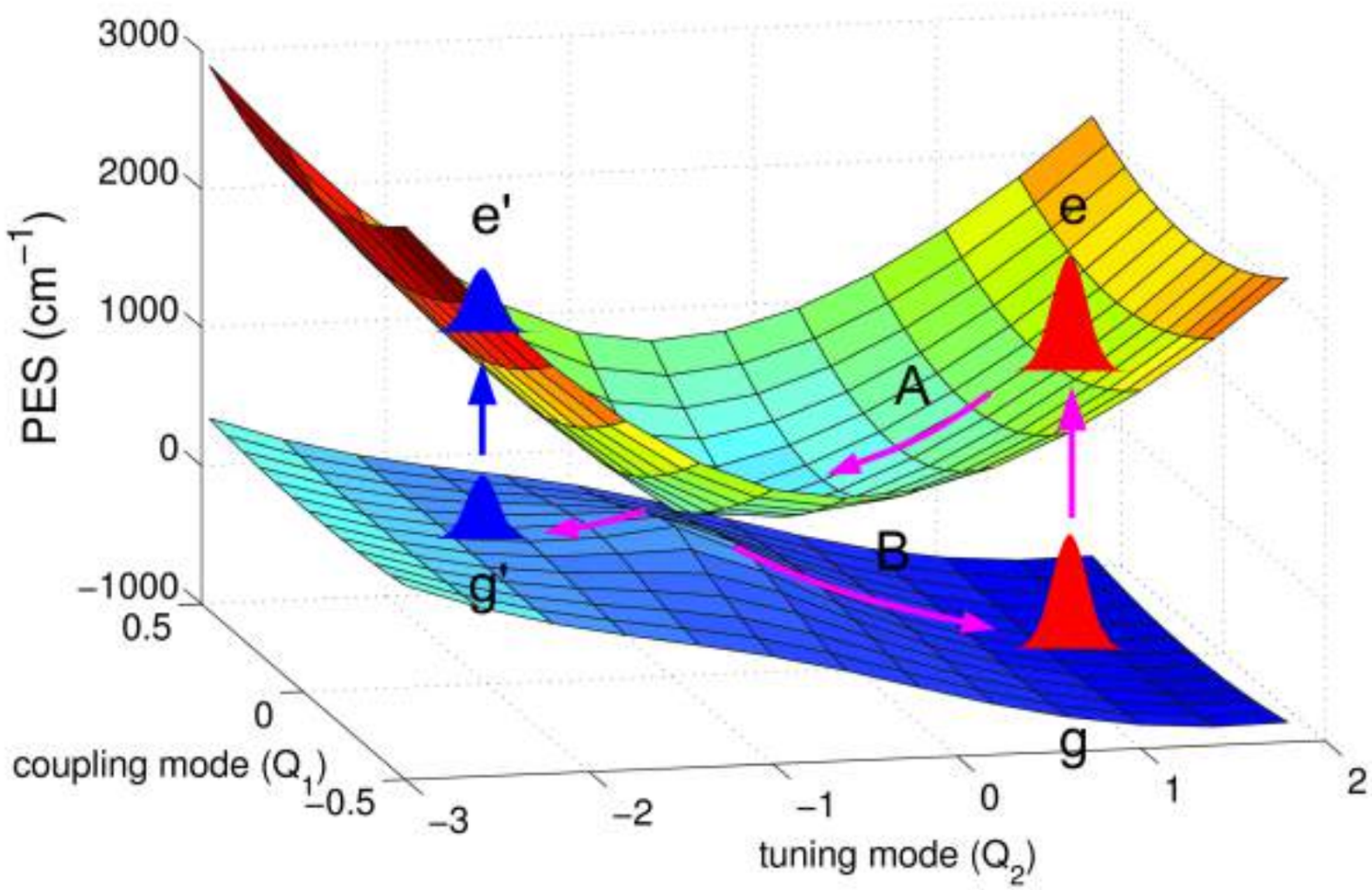
Vibronic cross peak:





Strong vibronic coupling (not only fluctuating angles of dipole moments)!

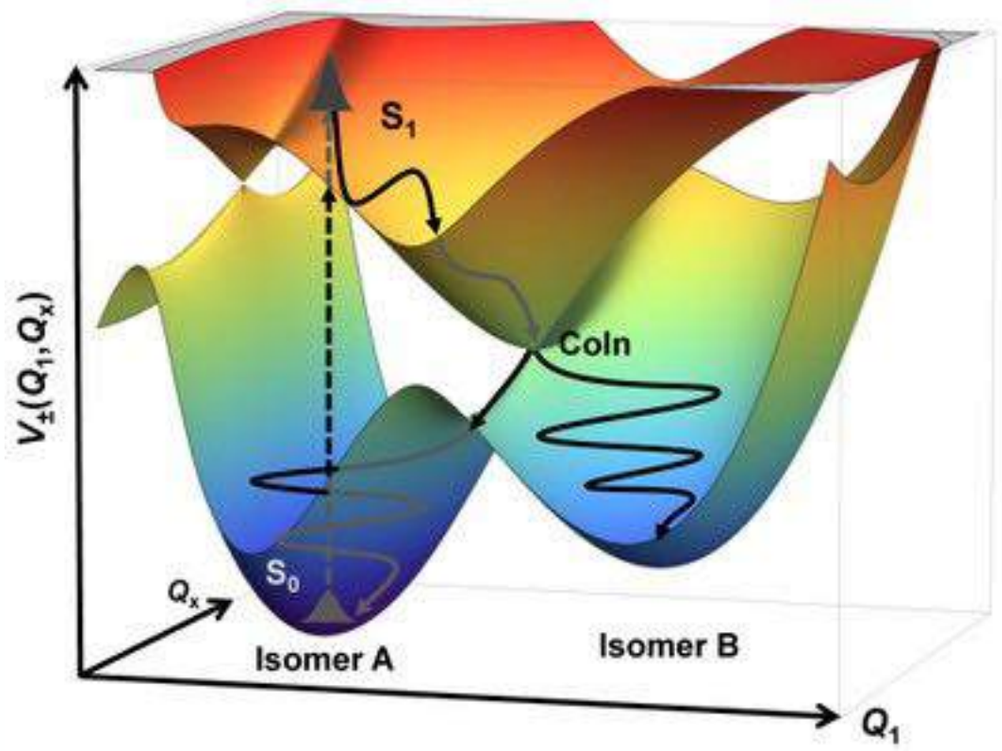
4) Exciton transfer & conical intersections

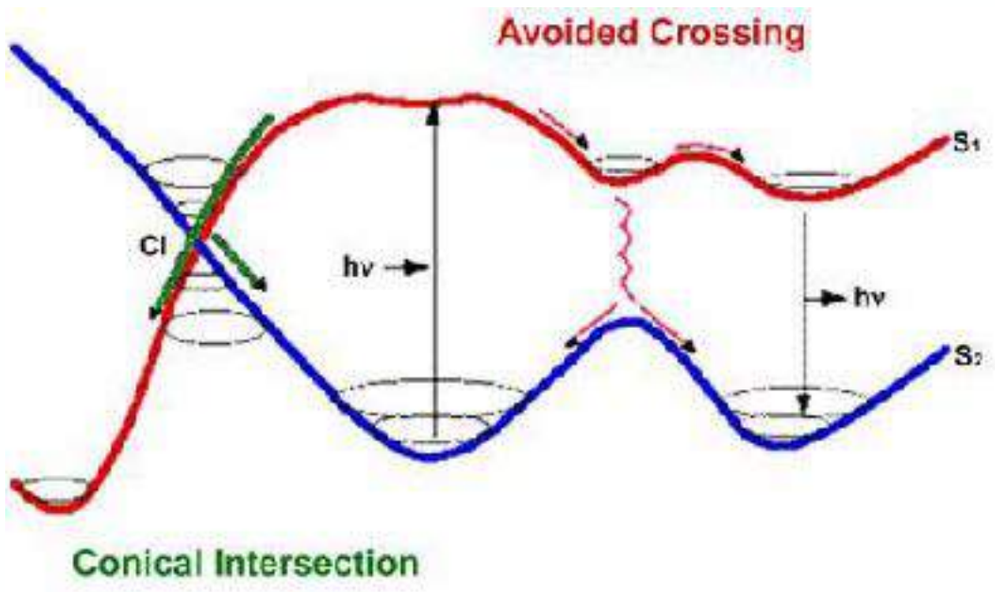


Conical intersection: basics

- Point of degeneracy between two adiabatic potential energy surfaces
- Breakdown of Born-Oppenheimer approximation => Formation of a double cone structure
- explains fast radiationless energy transfer in photoactive molecules
- key: geometric phase of the wavefunction acquired when circulated on a closed loop around the CI (nonadiabatic feature)

F. Temps, Universität Kiel

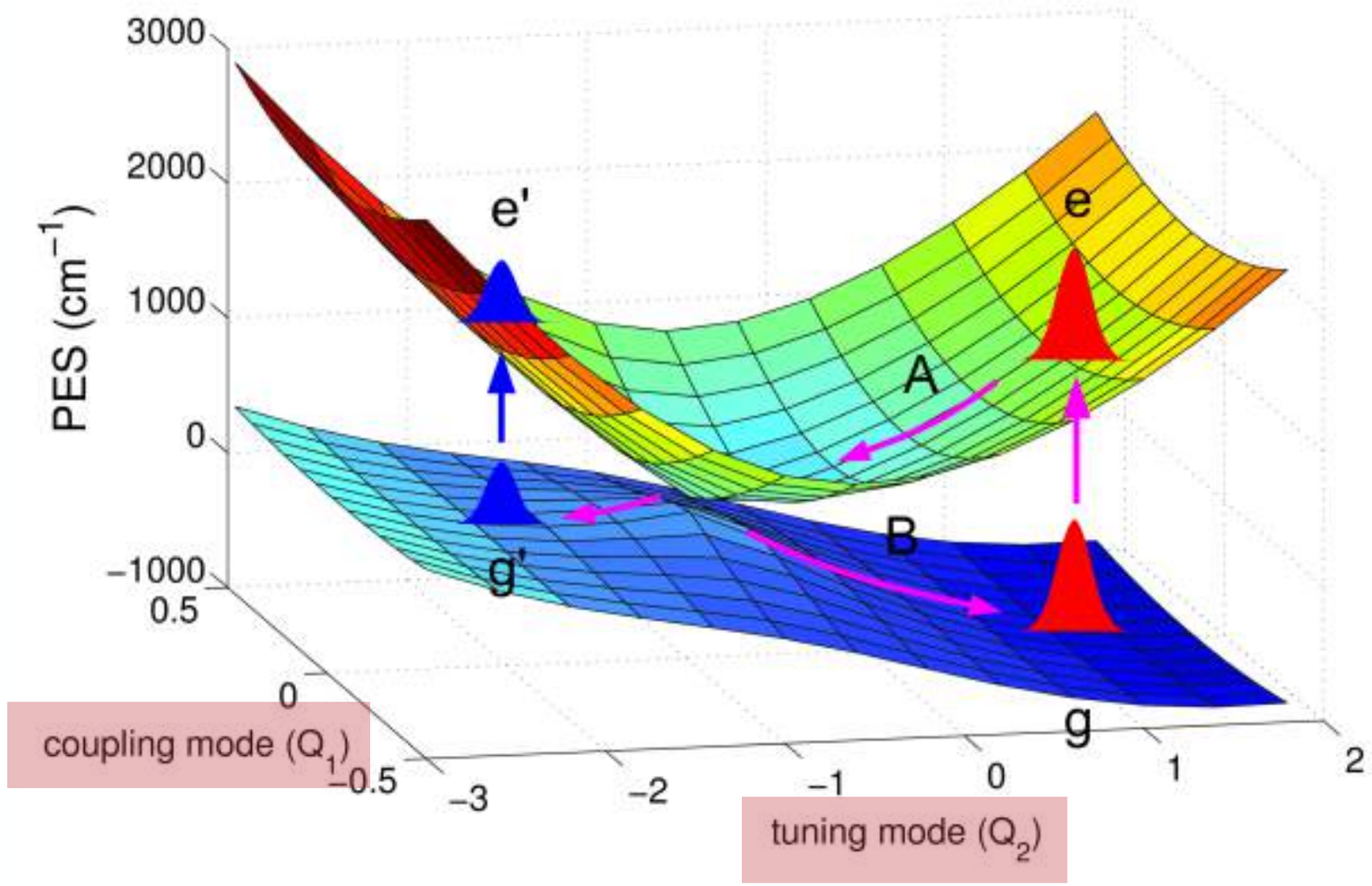




M.A. Robb, *What is a conical intersection,* UC London

Vibrational coherence at conical intersection

Duan, Thorwart, J. Chem. Phys. Lett. **7**, 382 (2016)



Conical intersection of two electronic potential surfaces

Question:
Signatures of CI in presence of strong vibrational dissipation?

$$H_{\rm mol} = H_g + H_e$$

Model: two electronic states plus two harmonic modes:

$$H_g = |g\rangle(h_1 - \epsilon/2)\langle g| \quad \text{and} \quad H_e = |e\rangle(h_2 + \epsilon/2)\langle e| + (|e\rangle V\langle g| + h.c.)$$

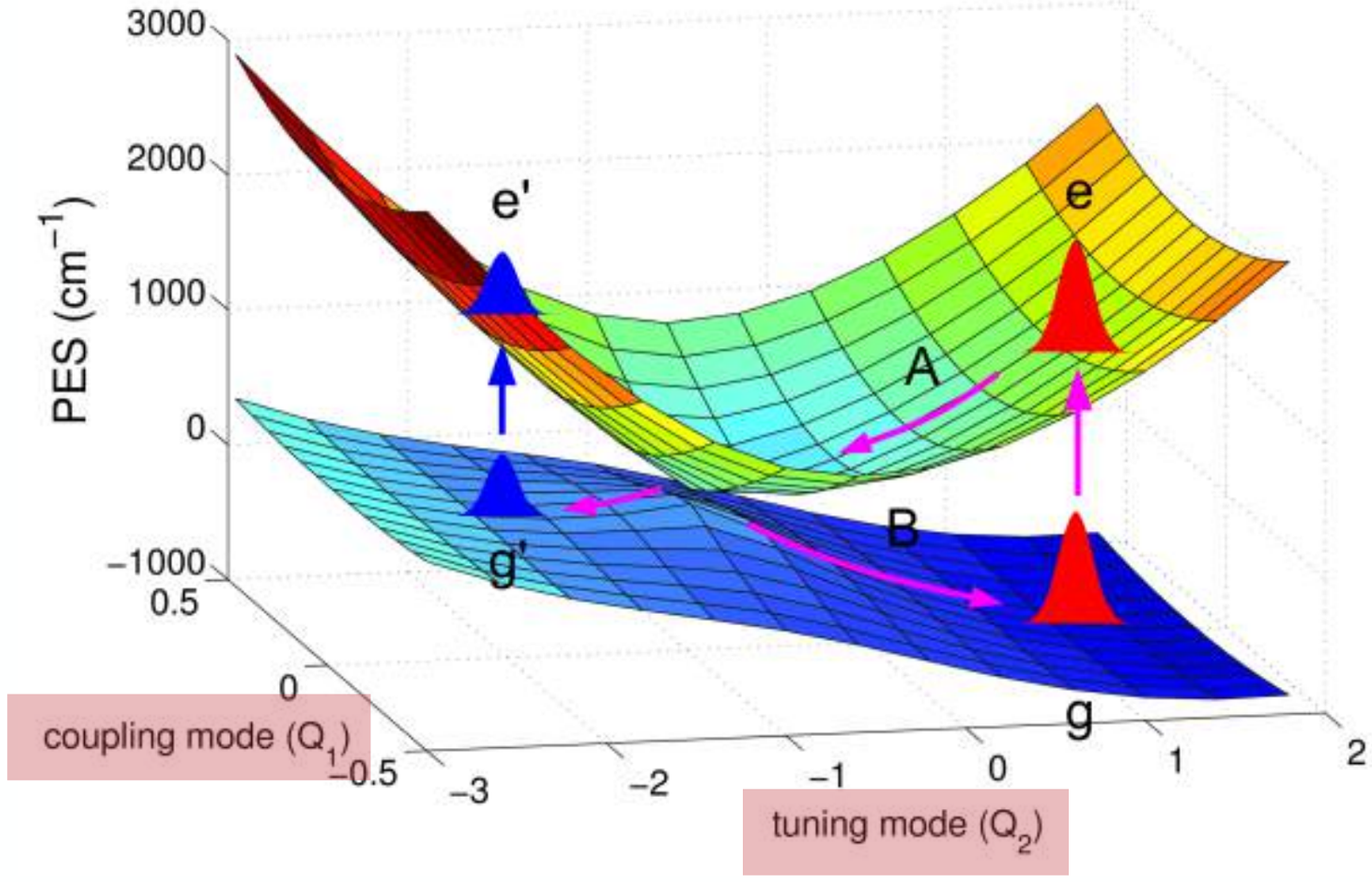
$$h_g = \frac{1}{2}\sum_{i=1,2} \Omega_i (P_i^2 + Q_i^2)$$

$$h_1 = h_g - \kappa Q_2 \quad h_2 = h_g + \kappa Q_2$$

plus two Ohmic vibrational baths

Vibrational coherence at conical intersection

Duan, Thorwart, J. Chem. Phys. Lett. **7**, 382 (2016)



Large Problem:

Dynamics of electronic wave packet on complicated 2D surfaces

$$H_{\mathrm{mol}} = H_g + H_e$$

Model: two electronic states plus two harmonic modes:

$$H_g = |g\rangle(h_1 - \epsilon/2)\langle g| \quad \text{and} \quad H_e = |e\rangle(h_2 + \epsilon/2)\langle e| + (|e\rangle V\langle g| + h.c.)$$

$$h_g = \frac{1}{2}\sum_{i=1,2} \Omega_i(P_i^2 + Q_i^2)$$

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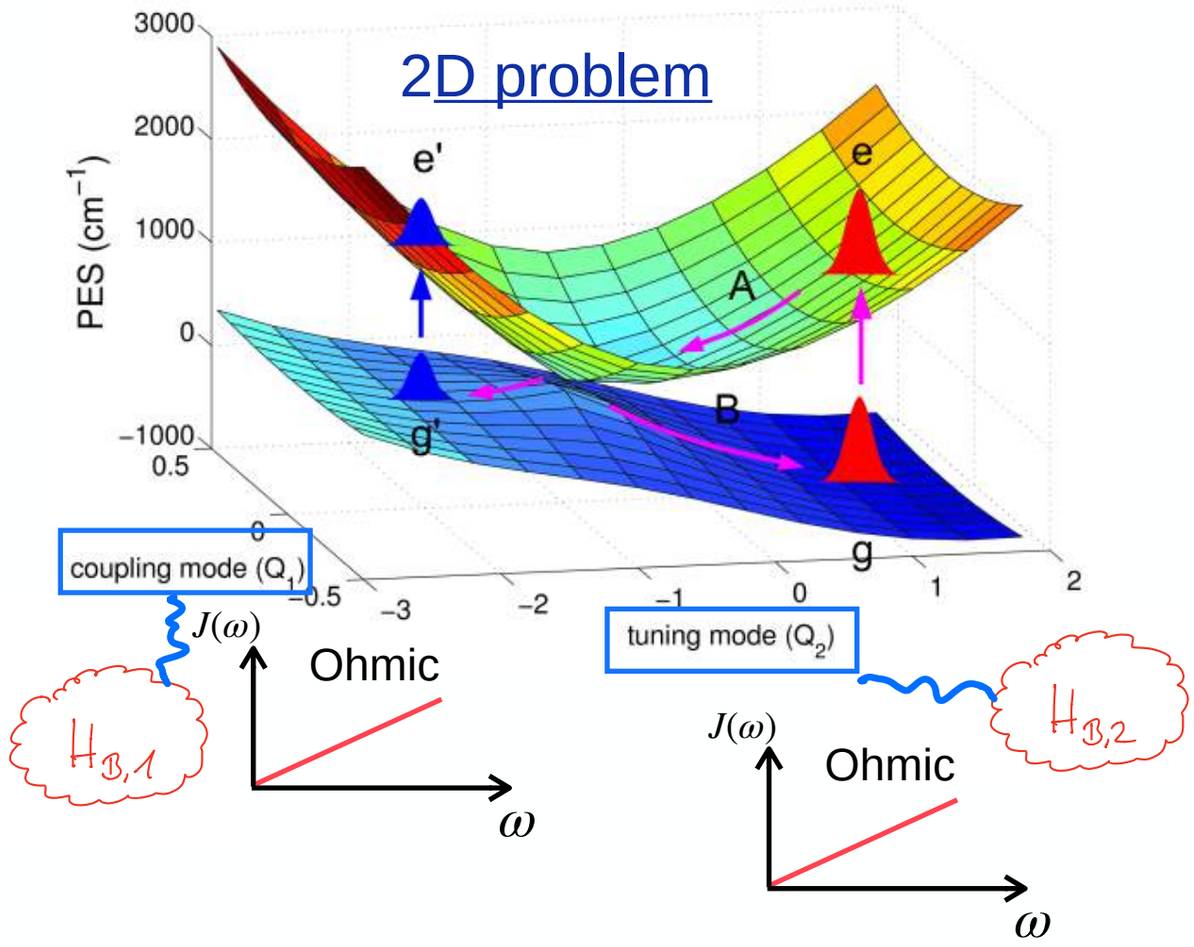
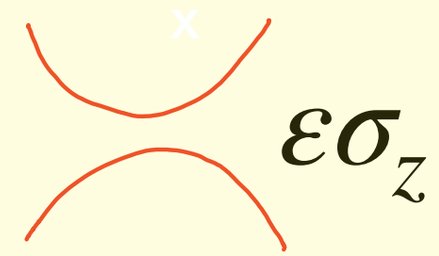


Idea: Put tuning & coupling modes into the bath

unitary equivalent to

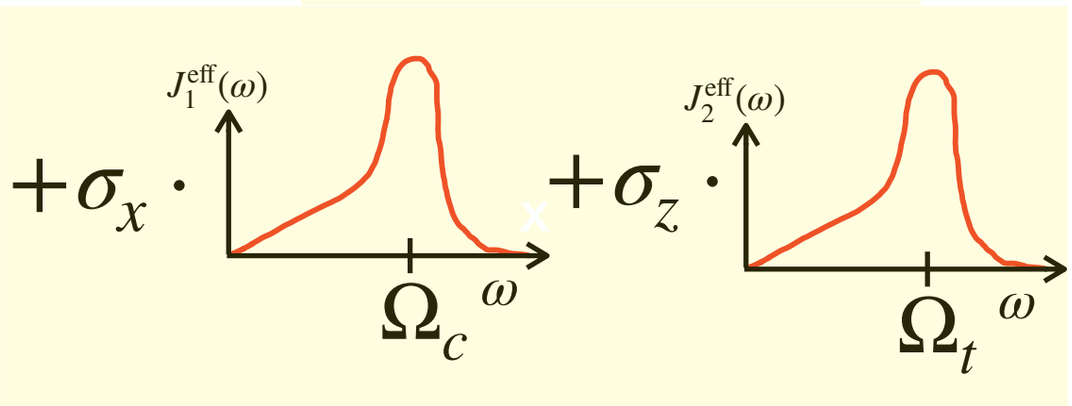
1D problem



with two effective baths:

$$J_{1/2}^{\mathrm{eff}}(\omega) = \lambda_{1/2}\frac{\gamma_{1/2}\Omega_{1/2}^2\omega}{(\Omega_{1/2}^2-\omega^2)^2+\gamma_{1/2}^2\omega^2}$$

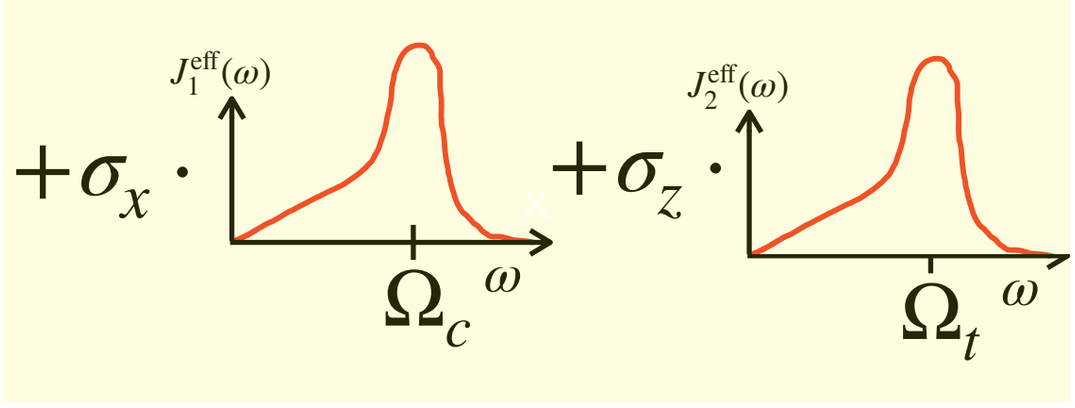
overdamped limit easy: $J_{1/2}^{\mathrm{eff},\infty}(\omega) = \lambda'_{1/2}\frac{\gamma'_{1/2}\omega}{\omega^2+\gamma'^2_{1/2}}$



Vibrational coherence at conical intersection

Duan, Thorwart, J. Chem. Phys. Lett. **7**, 382 (2016)

unitary equivalent to
1D problem



Dissipative quantum two-level system,

BUT…

- highly structured bath spectral densities
- non-Ohmic
- => non-Markovian exciton dyanmics
- require advanced numerical tools (QUAPI, hierarchy equation of motion HEOM)
- but they are available!

with two effective baths:

$$J_{1/2}^{\mathrm{eff}}(\omega) = \lambda_{1/2} \frac{\gamma_{1/2}\Omega_{1/2}^2\omega}{(\Omega_{1/2}^2 - \omega^2)^2 + \gamma_{1/2}^2\omega^2}$$

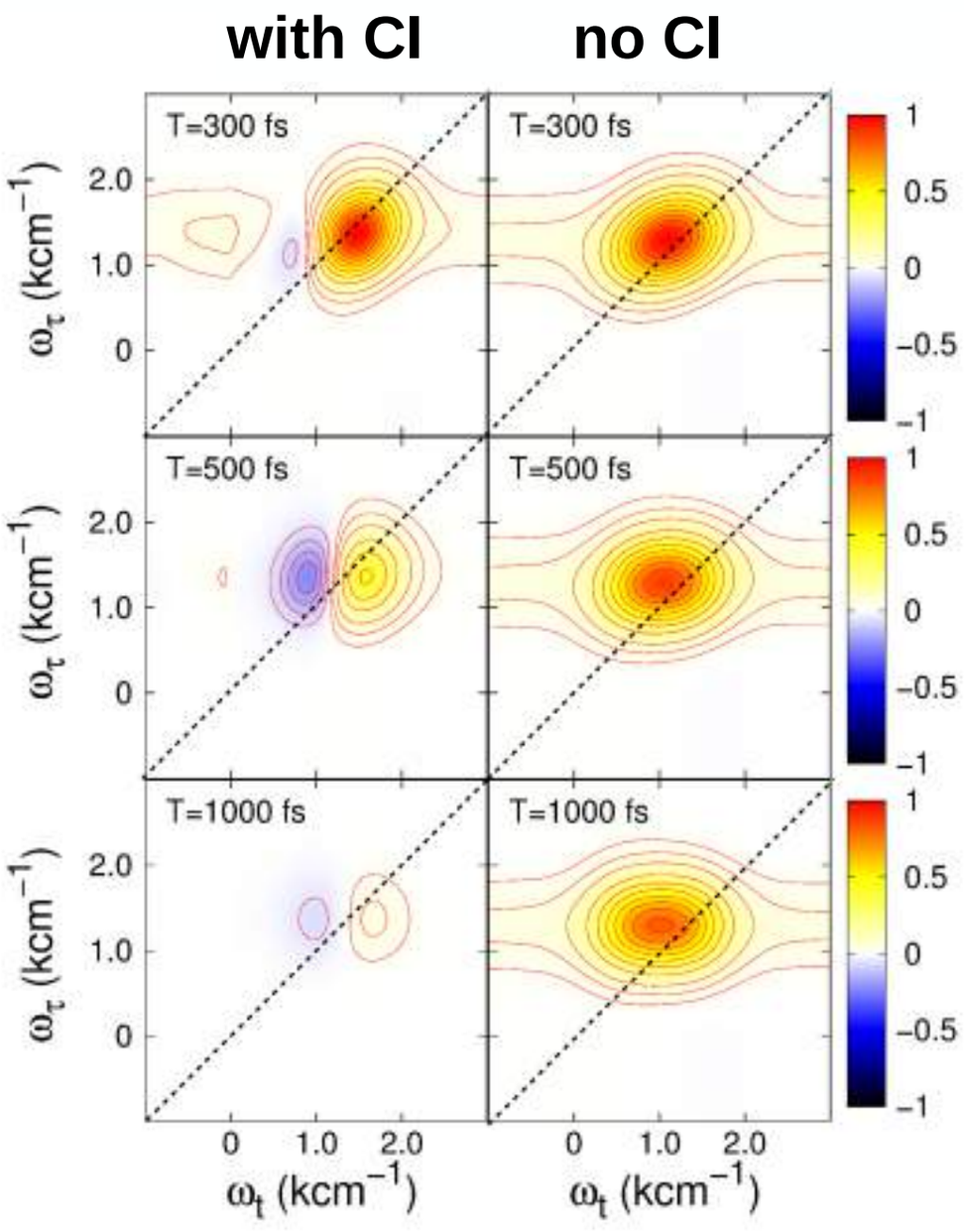
overdamped limit easy: $J_{1/2}^{\mathrm{eff},\infty}(\omega) = \lambda'_{1/2} \frac{\gamma'_{1/2}\omega}{\omega^2 + \gamma'^2_{1/2}}$

Vibrational coherence at conical intersection

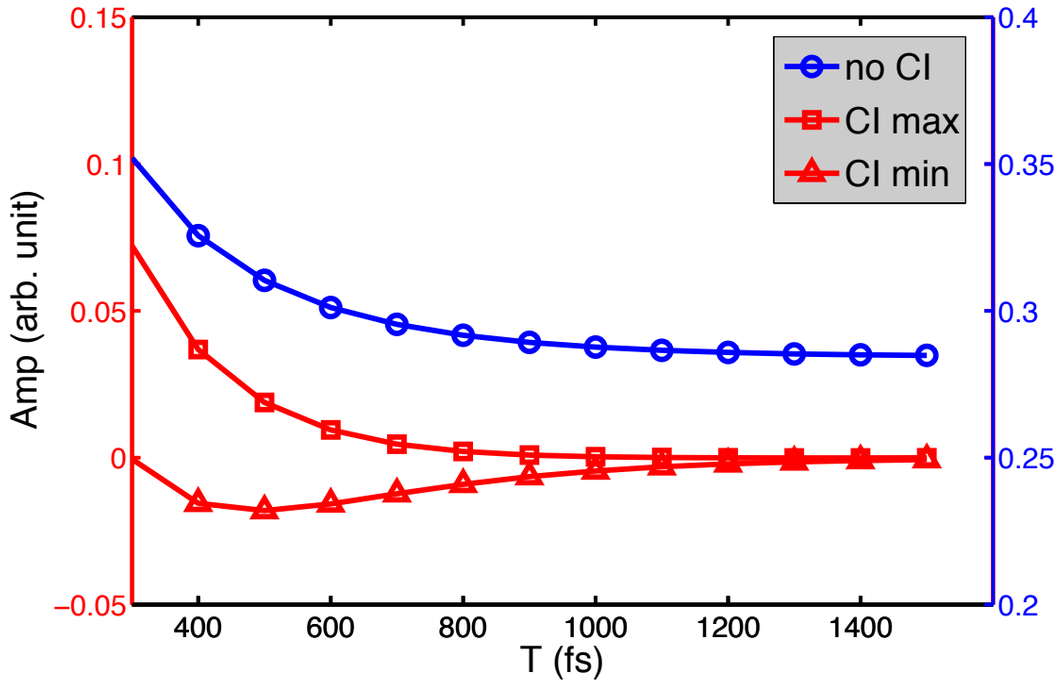
Duan, Thorwart, J. Chem. Phys. Lett. **7**, 382 (2016)

Calculated 2D spectra

Overdamped



Splitting of the diagonal peak as clear signature of CI in a 2D spectrum!



$$\epsilon = 1000\ \mathrm{cm}^{-1},$$

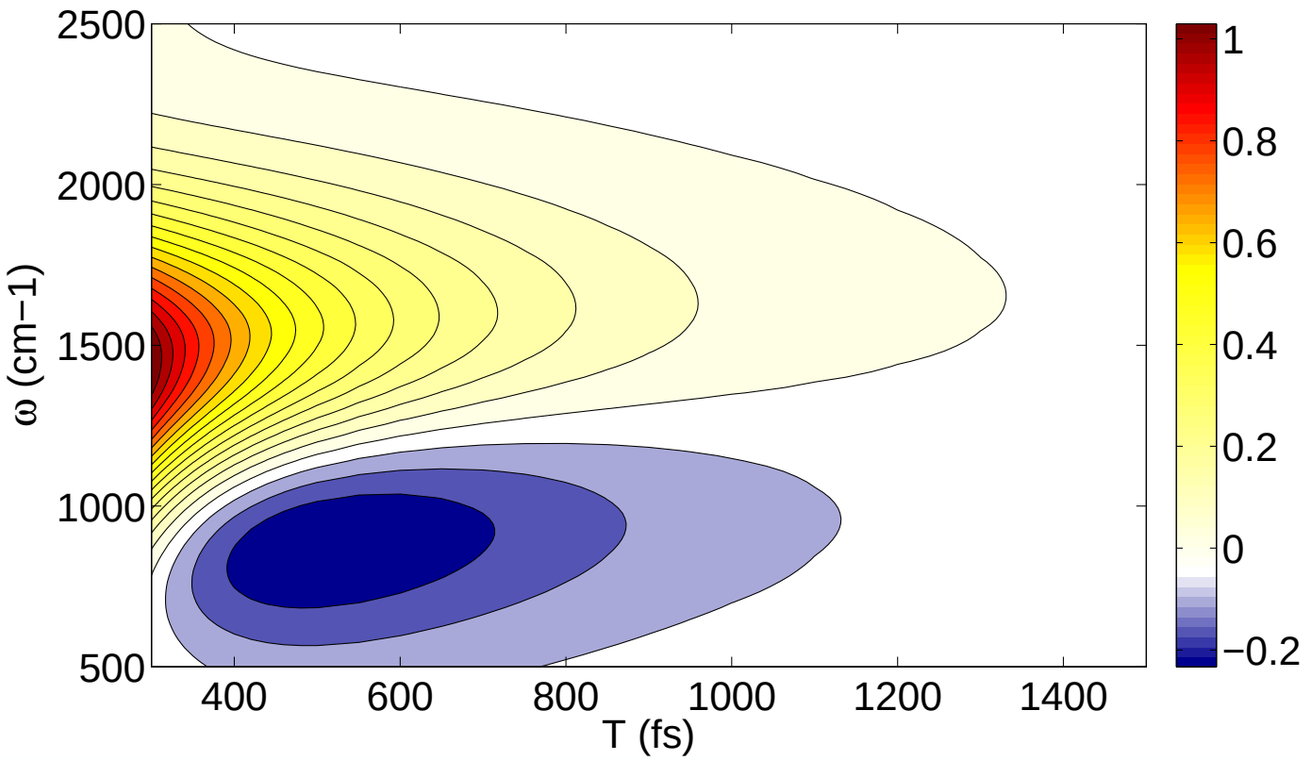
$$\lambda_1' = 150\pi\ \mathrm{cm}^{-1}, \gamma_1' = 150\ \mathrm{cm}^{-1}, \lambda_2' = 150\pi\ \mathrm{cm}^{-1}, \gamma_2' = 20\ \mathrm{cm}^{-1}, \mathcal{T} = 300\ \mathrm{K}$$

Vibrational coherence at conical intersection

Duan, Thorwart, J. Chem. Phys. Lett. **7**, 382 (2016)

Transient absorption spectrum

Overdamped



Two bands with positive & negative amplitude

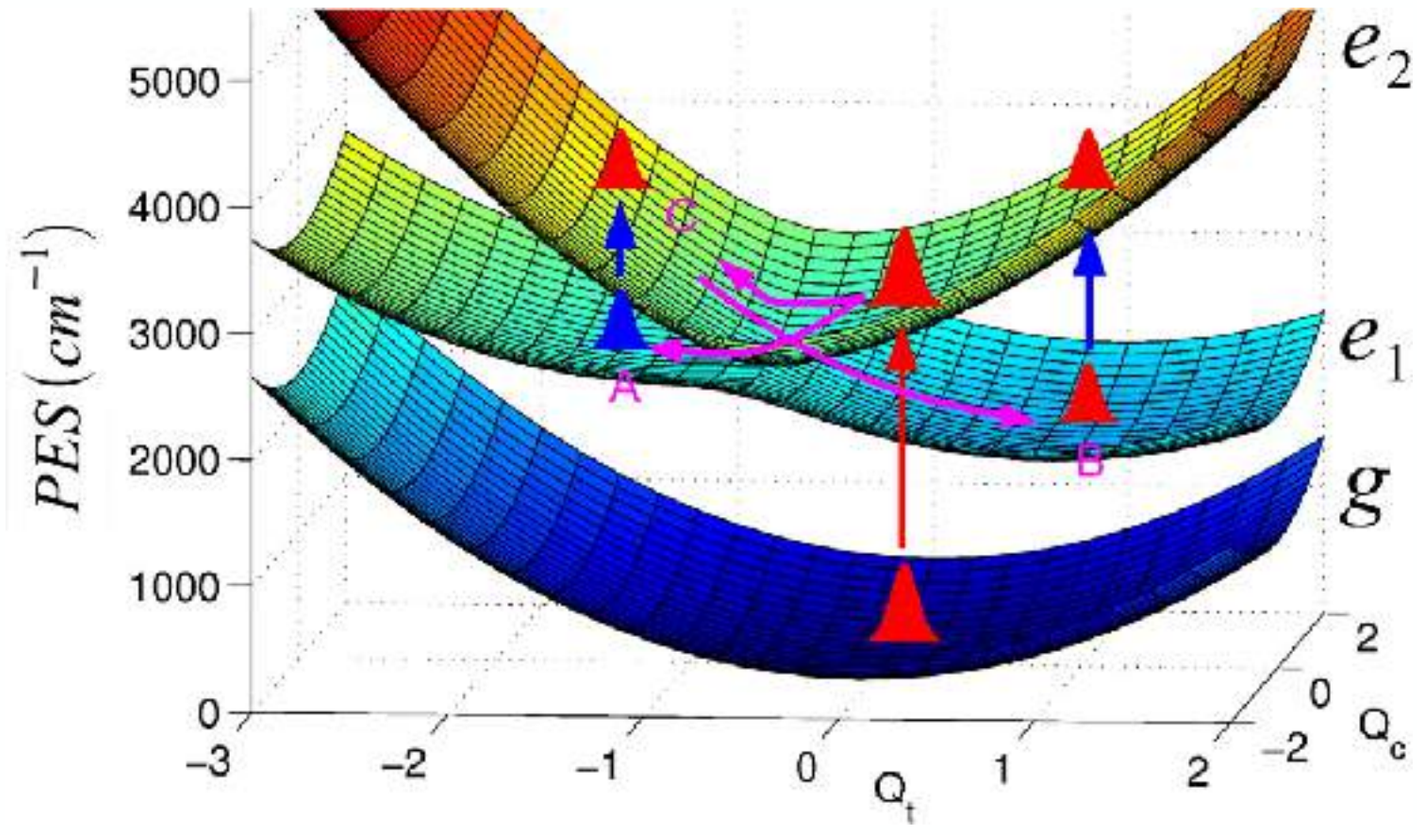
$$\epsilon = 1000\ \mathrm{cm}^{-1},$$

$$\lambda_1' = 150\pi\ \mathrm{cm}^{-1}, \gamma_1' = 150\ \mathrm{cm}^{-1}, \lambda_2' = 150\pi\ \mathrm{cm}^{-1}, \gamma_2' = 20\ \mathrm{cm}^{-1}, \mathcal{T} = 300\ \mathrm{K}$$

Vibrational coherence at conical intersection

Duan, Miller, Thorwart, J. Chem. Phys. Lett. **7**, 3491 (2016)

Underdamped



$$\varepsilon_1 = 2000\text{cm}^{-1}, \varepsilon_2 = 2600\text{cm}^{-1}$$

$$\Omega_t = 500\text{cm}^{-1}, \Omega_c = 200\text{cm}^{-1}$$

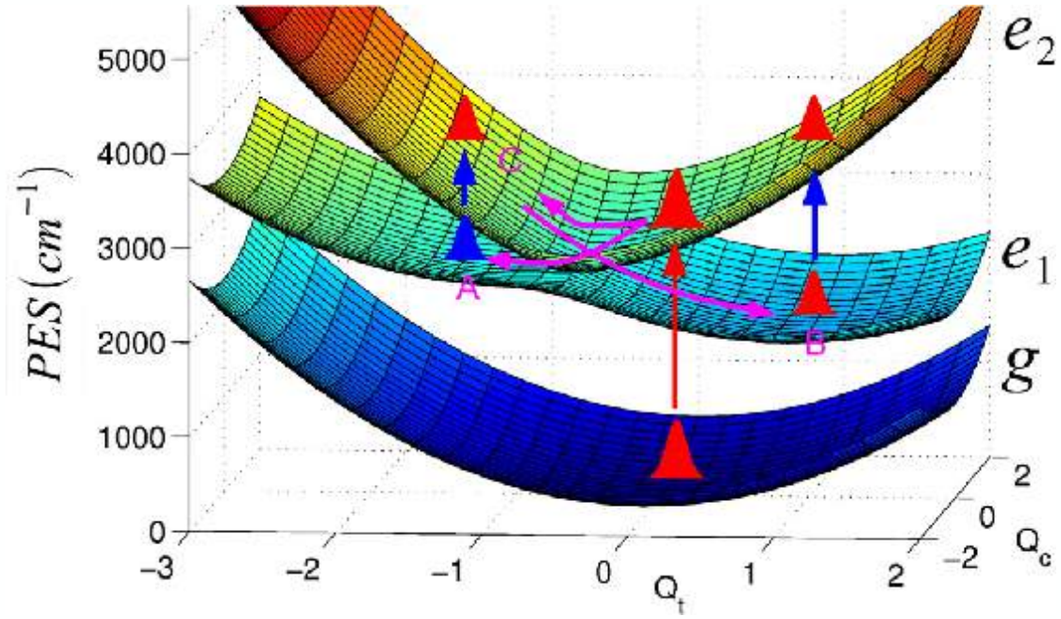
$$\lambda_c = 25\text{cm}^{-1}, \lambda_t = 250\text{cm}^{-1}$$

$$\gamma_{c/t} = 30\text{cm}^{-1}$$

Vibrational coherence at conical intersection

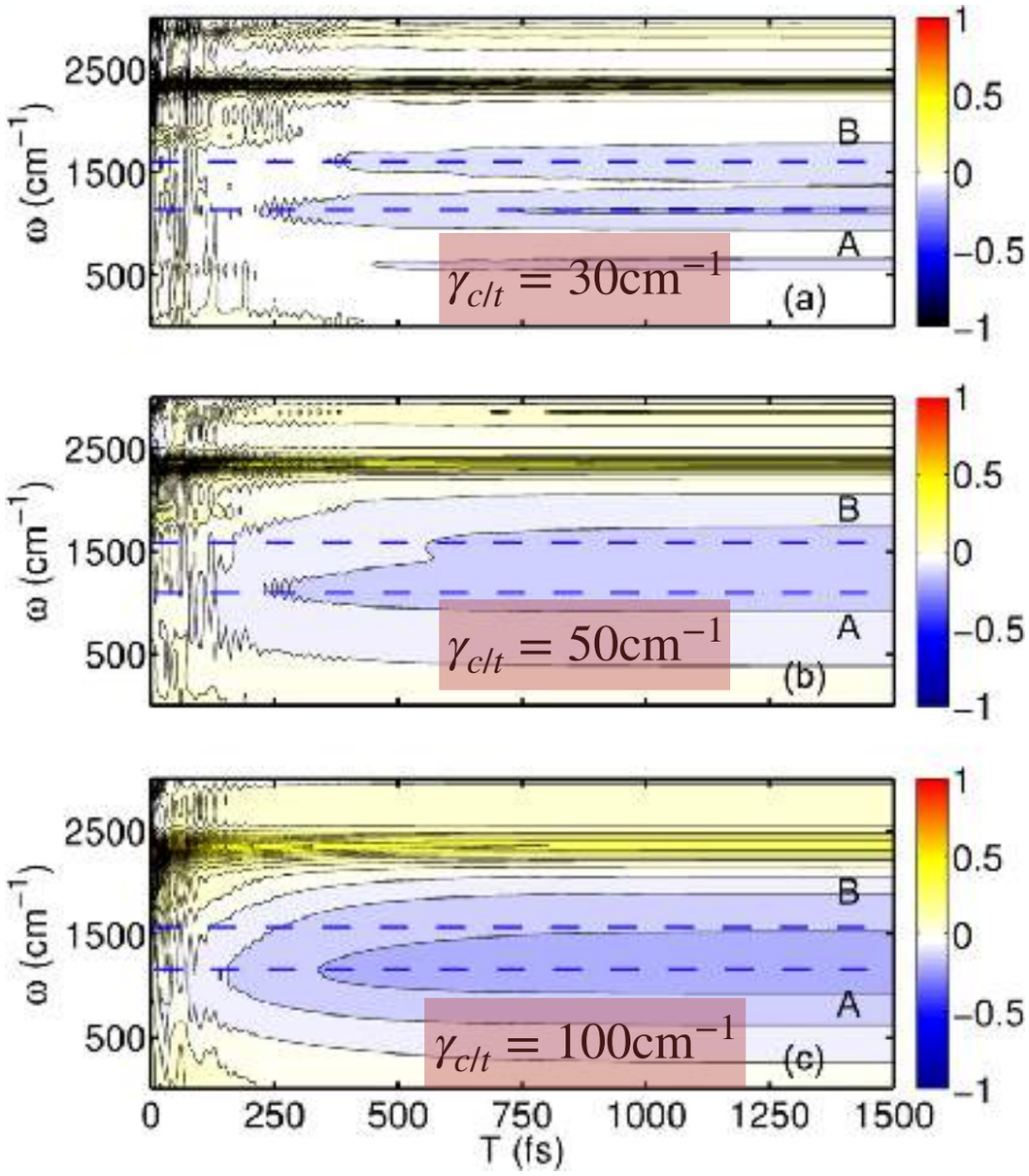
Quantum yield

Duan, Miller, Thorwart, J. Chem. Phys. Lett. **7**, 3491 (2016)

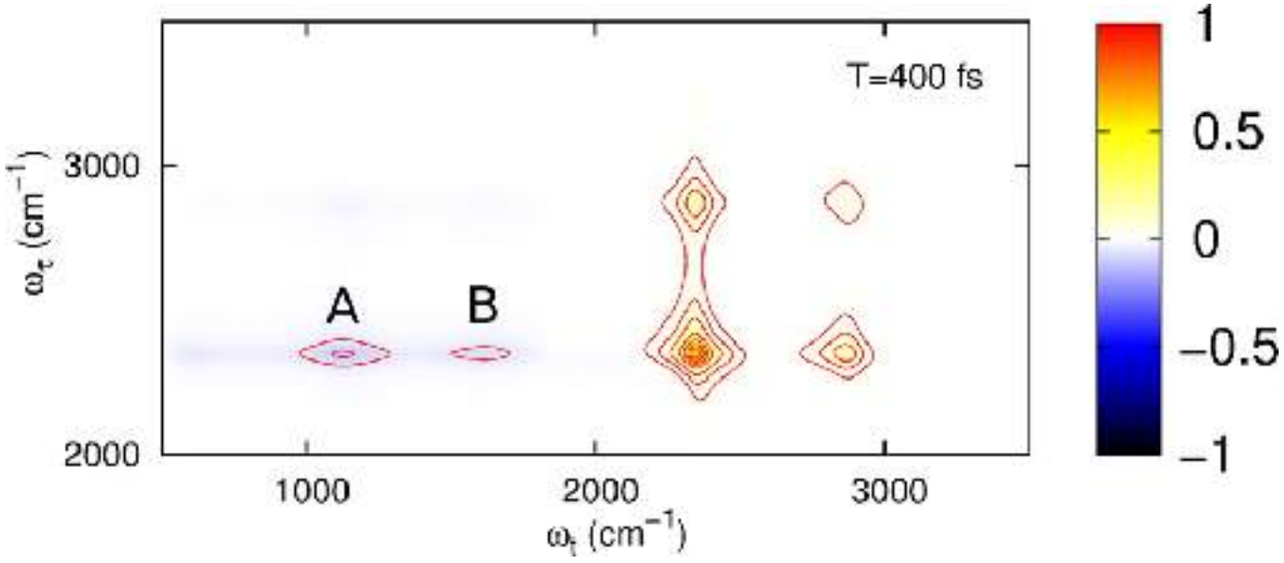


Underdamped

Transient absorption



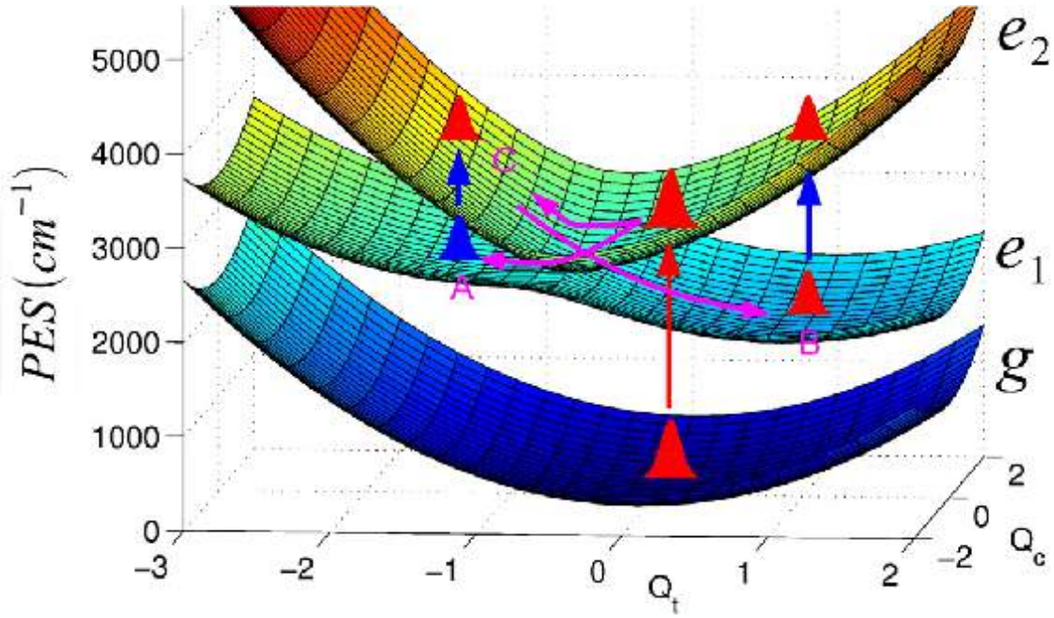
Transition pathways

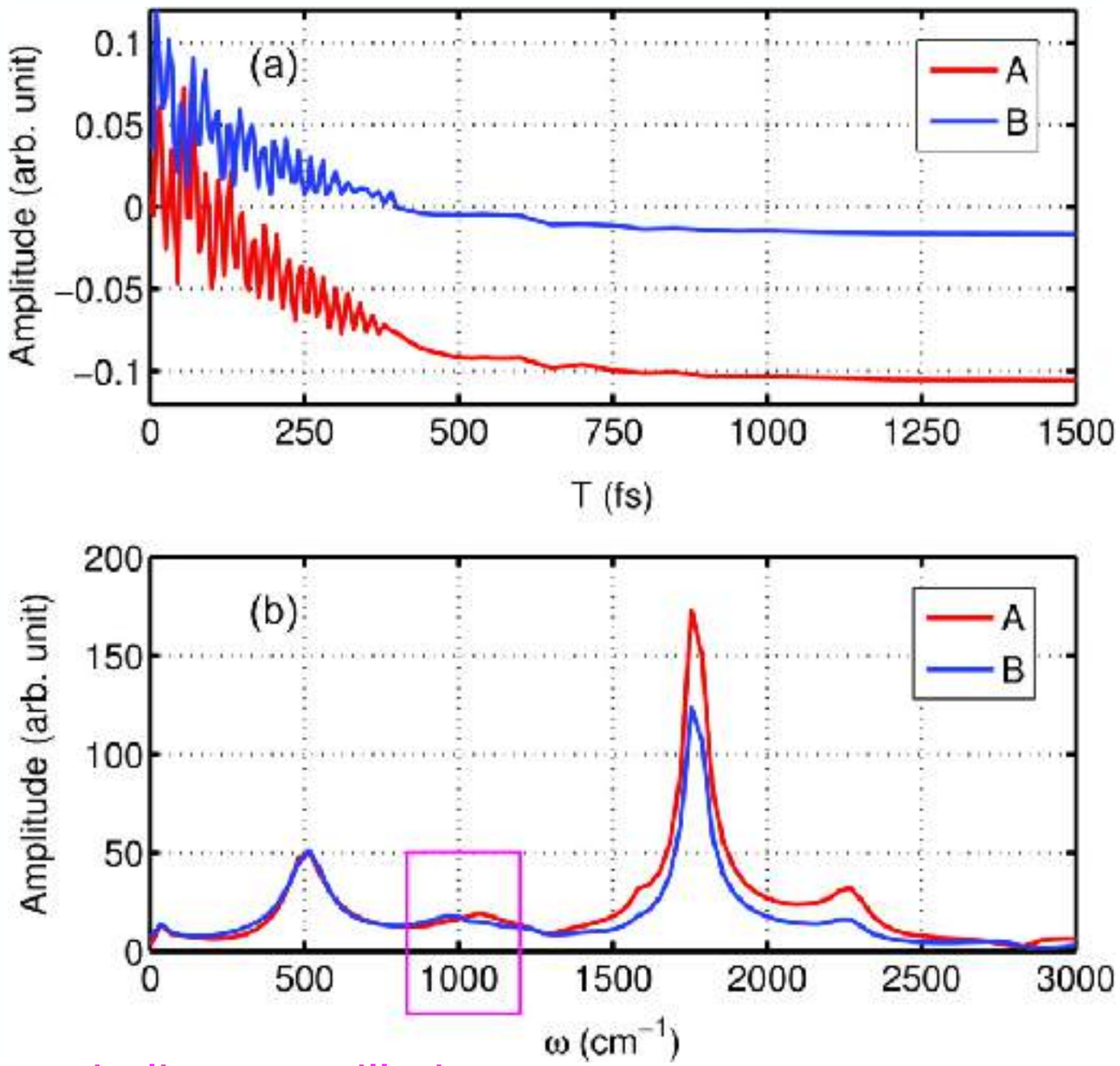


Vibrational coherence at conical intersection

Duan, Miller, Thorwart, J. Chem. Phys. Lett. **7**, 3491 (2016)

Underdamped





$$\varepsilon_1 = 2000\text{cm}^{-1}, \varepsilon_2 = 2600\text{cm}^{-1}$$

$$\Omega_t = 500\text{cm}^{-1}, \Omega_c = 200\text{cm}^{-1}$$

$$\lambda_c = 25\text{cm}^{-1}, \lambda_t = 250\text{cm}^{-1}$$

$$\gamma_{c/t} = 30\text{cm}^{-1}$$

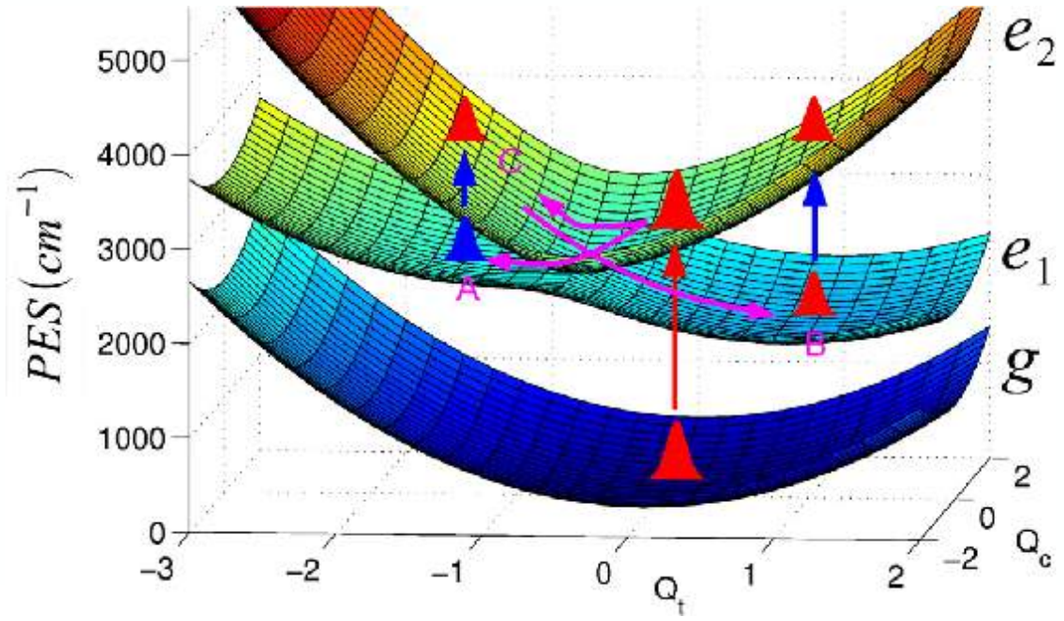
Stueckelberg oscillations

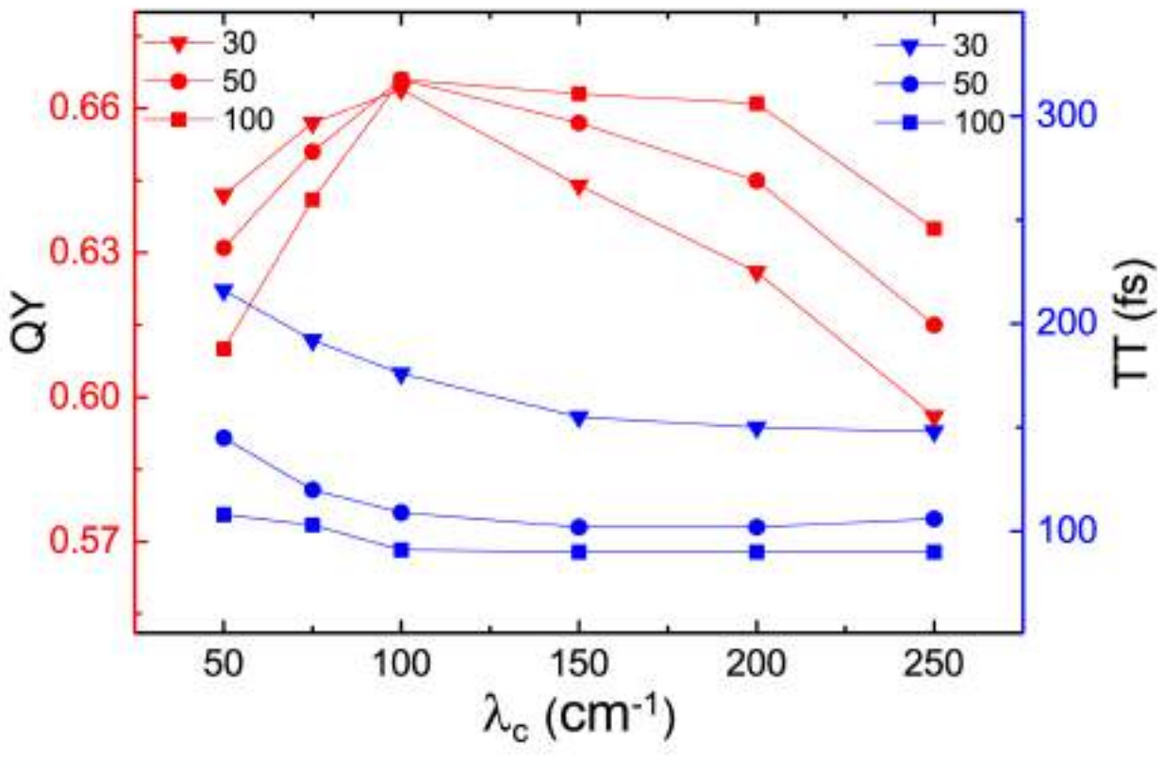
Vibrational coherence at conical intersection

Quantum yield

Duan, Miller, Thorwart, J. Chem. Phys. Lett. **7**, 3491 (2016)

Underdamped





Quantum yield

Table 1. Magnitude for Pathways A (1100 cm^{-1}) and B (1600 cm^{-1}) for Waiting Time T = 5 ps in the Transient Absorption Spectrum with Stable Products A and B[a]

$\gamma_{c/t}$ (cm^{-1})	magnitude A	magnitude B	$A/(A+B)$	Γ_y^{-1} (fs)
30	−0.1001	−0.0630	0.614	285
40	−0.1065	−0.0690	0.607	268
50	−0.1143	−0.0767	0.598	240
100	−0.1601	−0.1206	0.570	200
150	−0.1961	−0.1672	0.540	195

"The ratio $A/(A + B)$ shows that the more coherent wave packet produces a higher quantum yield than the less coherent one. In addition, we show the inverse of the isomerization rate Γ_y.

Peierls vs. Holstein phonons: conical intersection

Duan, Nalbach, Miller, Thorwart, submitted (2018)

Consider usual tight-binding model of an electron:

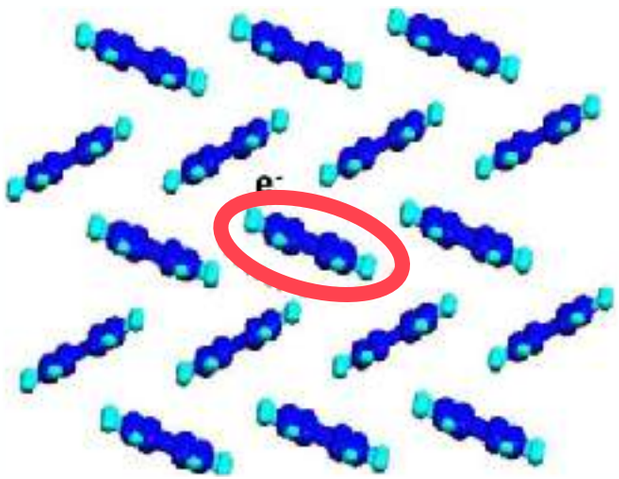
$$H = \sum_m \epsilon_i a_i^\dagger a_i + \sum_{ij} t_{ij} a_i^\dagger a_j$$

Let us include electron-phonon-coupling:

local electron-phonon coupling
(intramolecular phonon)

$$\epsilon_i = \varepsilon_{i,0} + \sum_\alpha \left(\frac{\partial e_i}{\partial Q_\alpha} \right)_0 Q_\alpha + \dots$$

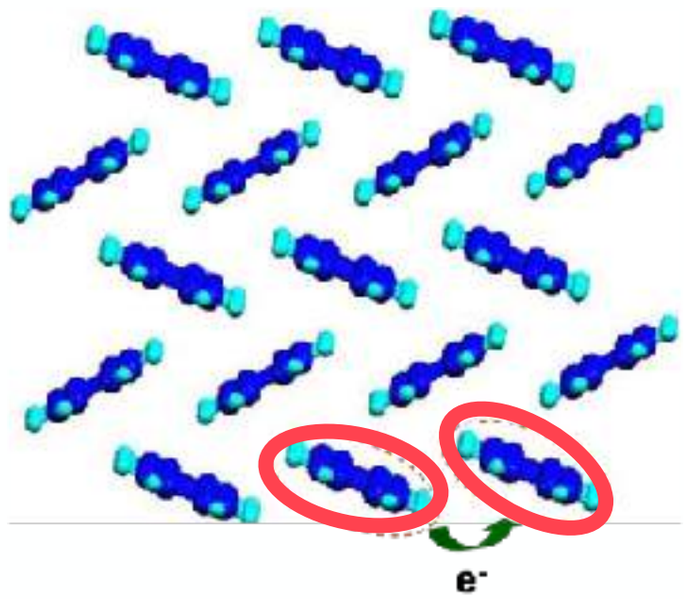
Holstein phonon



nonlocal electron-phonon coupling
(intermolecular phonon)

$$t_{ij} = t_{ij,0} + \sum_\alpha \left(\frac{\partial t_{ij}}{\partial Q_\alpha} \right)_0 Q_\alpha + \dots$$

Peierls phonon



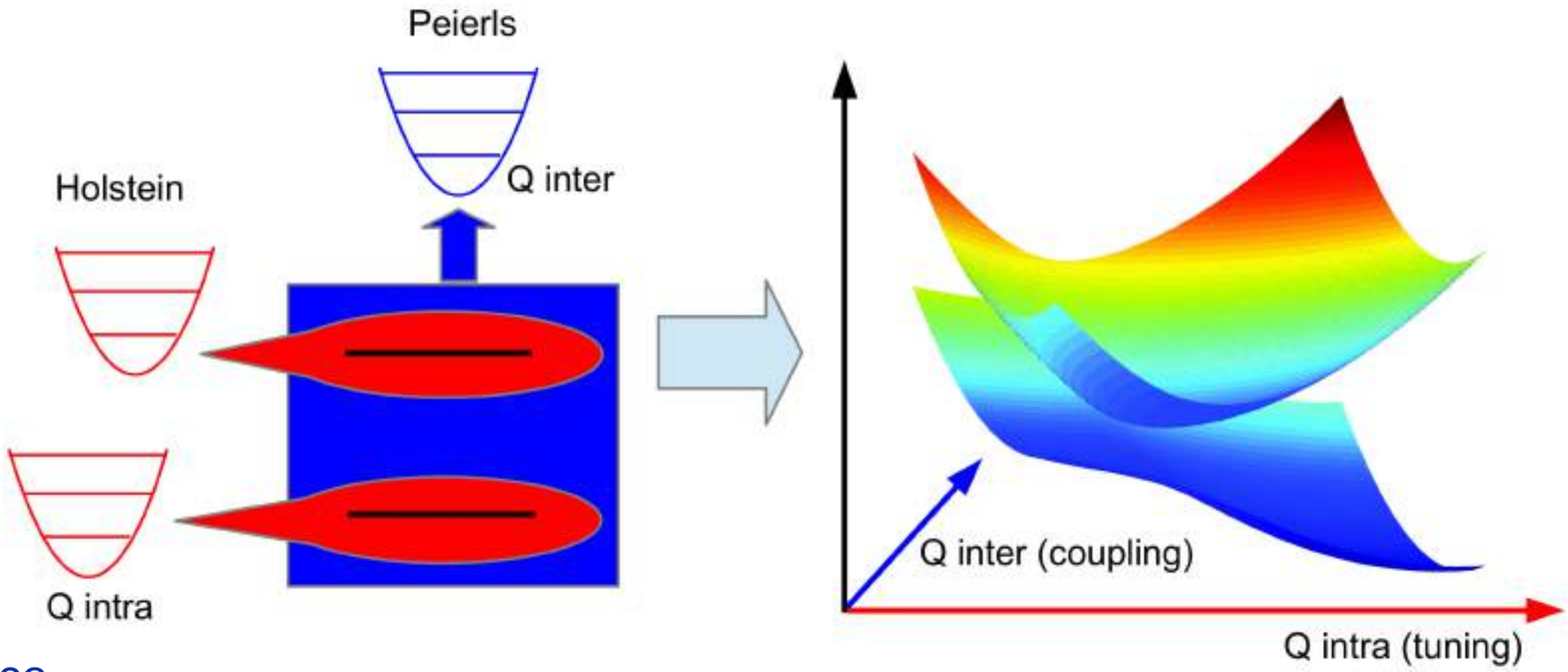
photonicswiki.org

Peierls vs. Holstein phonons: conical intersection

Duan, Nalbach, Miller, Thorwart, submitted (2018)

Idea:

- Understand intramolecular (Holstein) mode as tuning mode in a CI picture
- Understand intermolecular (Peierls) mode as coupling mode in a CI picture



Nice, since

- it explains ultrafast exciton transfer in organic photovoltaics
- experimentally confirmed in singlet fission in a pentacene film (unpublished)

Peierls vs. Holstein phonons: conical intersection

Duan, Nalbach, Miller, Thorwart, submitted (2018)

Model Hamiltonian

$$H_{\rm mol} = |A\rangle h_A \langle A| + |B\rangle h_B \langle B| + (|A\rangle V \langle B| + h.c.)$$

with

$$h_A = \epsilon_A + h_g - \kappa Q_{\rm H}, \qquad h_B = \epsilon_B + h_g + \kappa Q_{\rm H}$$

tuning mode

$$V = V_0 + \Lambda Q_{\rm P}$$

coupling mode

Peierls & Holstein phonons: $h_g = \frac{1}{2} \sum_{i={\rm H,P}} \Omega_i (P_i^2 + Q_i^2)$

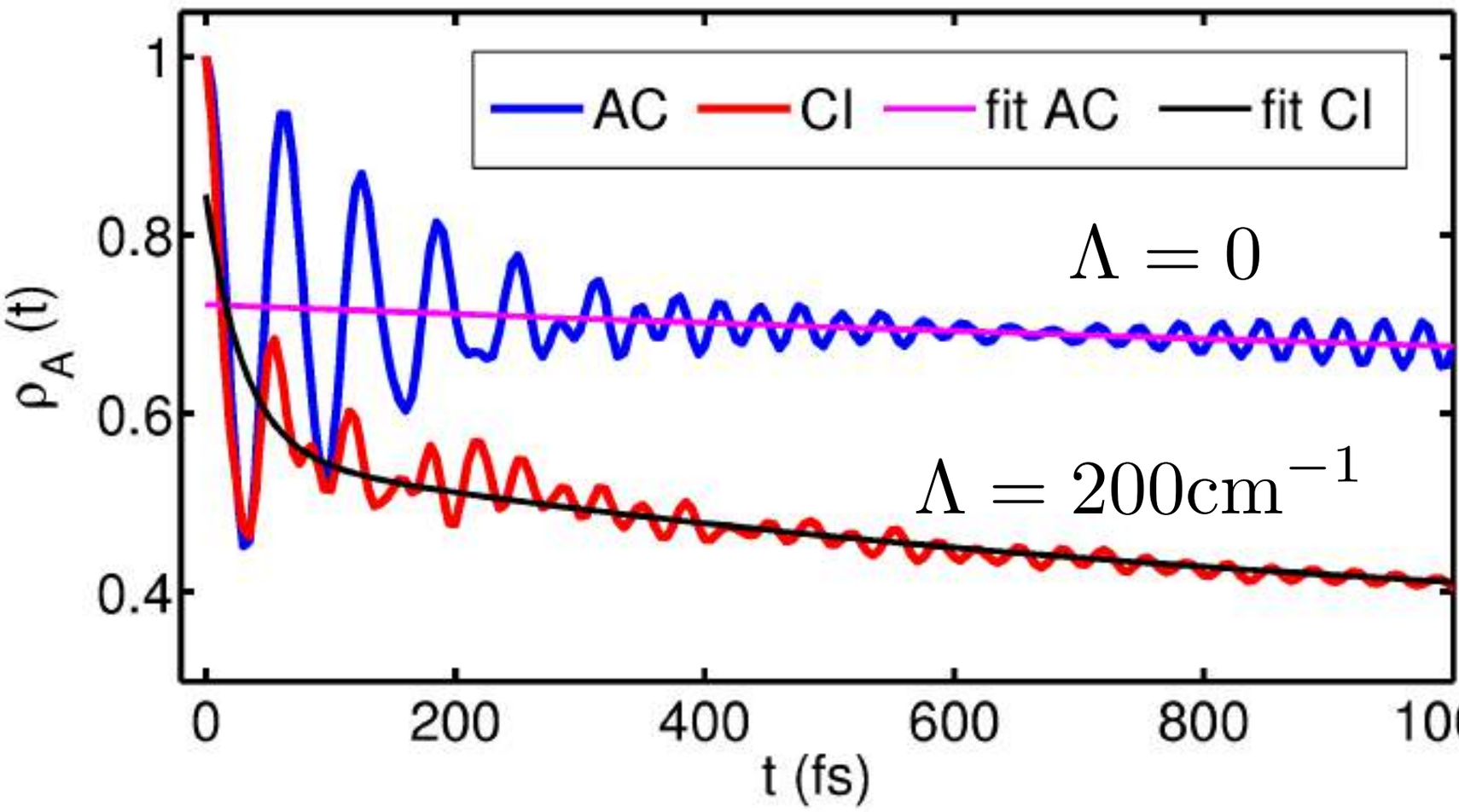
standard Ohmic vibrational baths: $J_{\rm P/H}(\omega) = \eta_{\rm P/H} \omega \exp(-\omega/\omega_c)$

$$H_{\rm env} = \sum_{i={\rm H,P}} \sum_{\alpha} \left[\frac{p_{i,\alpha}^2}{2m_{i,\alpha}} + \frac{m_{i,\alpha}\omega_{i,\alpha}^2}{2} \left(x_{i,\alpha} + \frac{c_{i,\alpha} Q_i}{m_{i,\alpha}\omega_{i,\alpha}^2} \right)^2 \right]$$

Peierls vs. Holstein phonons: conical intersection

Duan, Nalbach, Miller, Thorwart, submitted (2018)

Exciton transfer dynamics (with time-nonlocal quantum master equation):



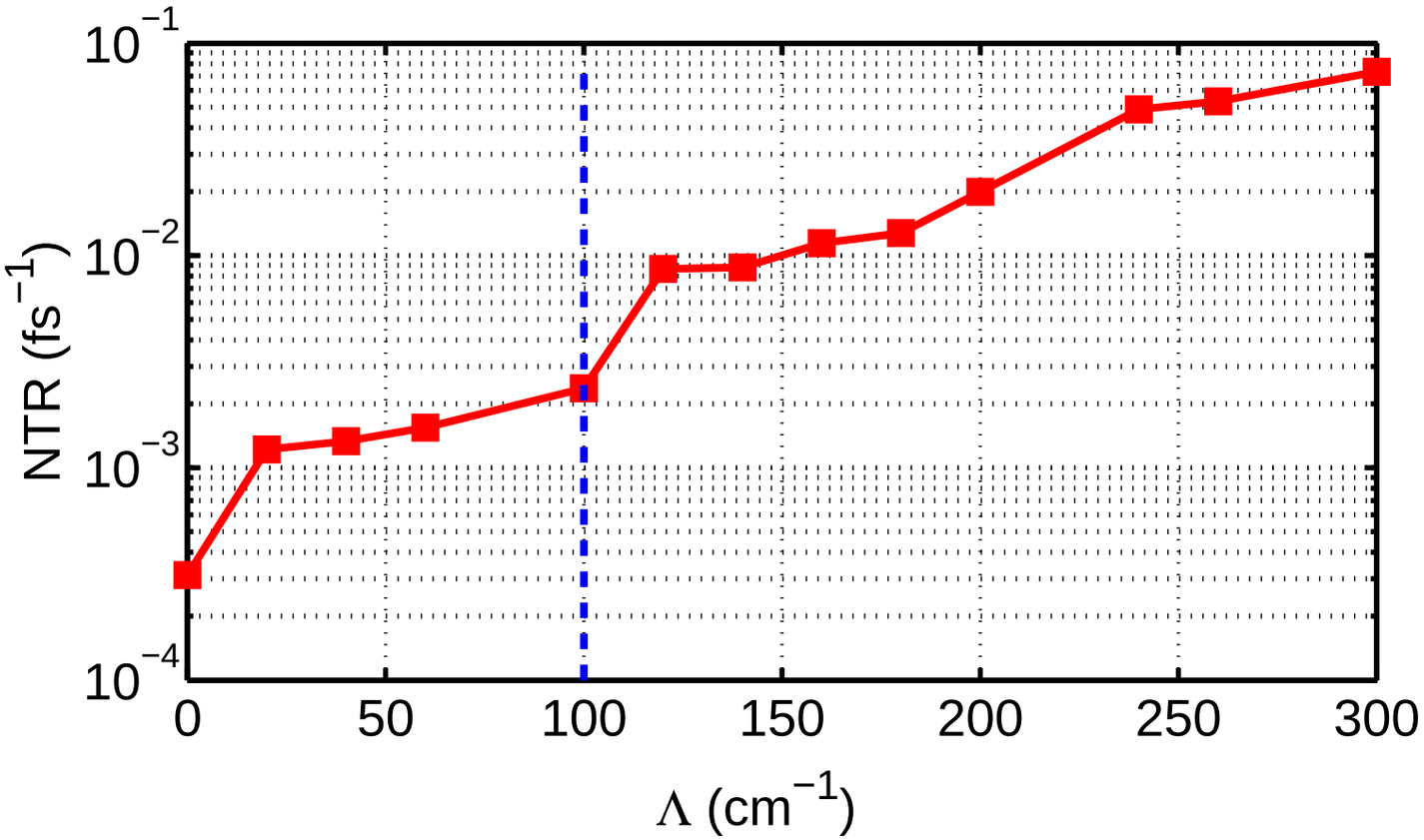
much faster transfer

$$\Omega_{\mathrm{H}} = 1000\mathrm{cm}^{-1}, \quad \Omega_{\mathrm{P}} = 150\mathrm{cm}^{-1}$$
$$\eta_{\mathrm{P/H}} = 0.5, \quad \omega_c = 100\mathrm{cm}^{-1}$$
$$T = 300\mathrm{K} \quad \epsilon = 400\,\mathrm{cm}^{-1}, V_0 = 200\,\mathrm{cm}^{-1}, \kappa = 212\,\mathrm{cm}^{-1}$$

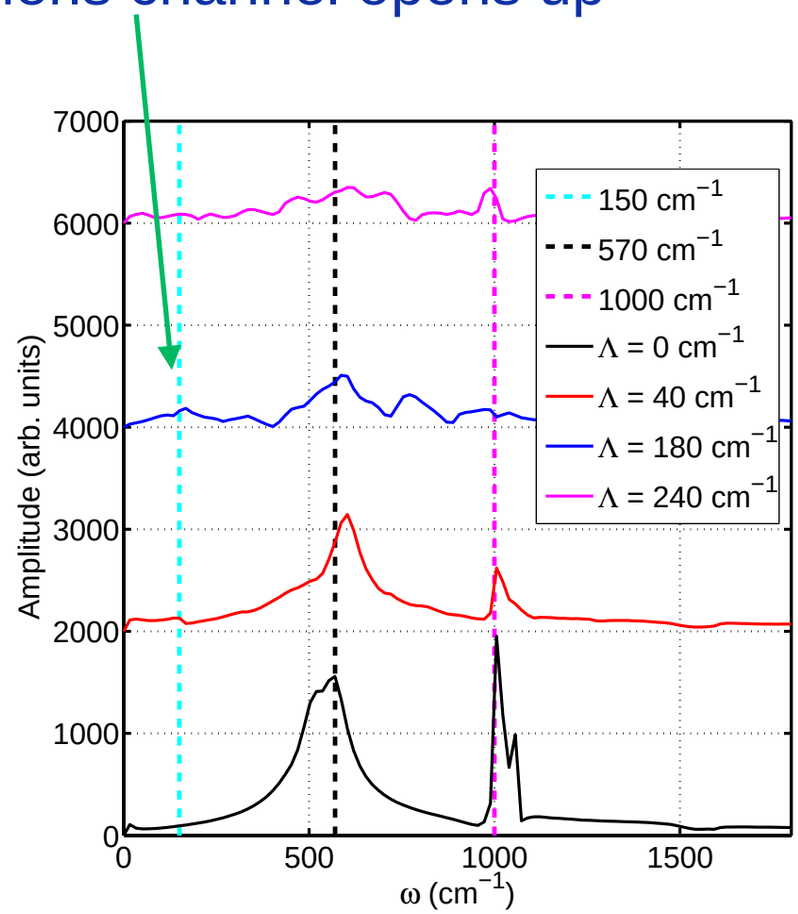
Peierls vs. Holstein phonons: conical intersection

Duan, Nalbach, Miller, Thorwart, submitted (2018)

Normalized transfer rate



Peierls channel opens up

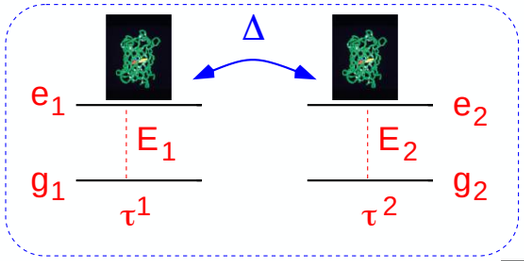


Nice, since

- it helps to understand ultrafast exciton transfer in organic photovoltaics
- experimentally confirmed in singlet fission in a pentacene film (unpublished)

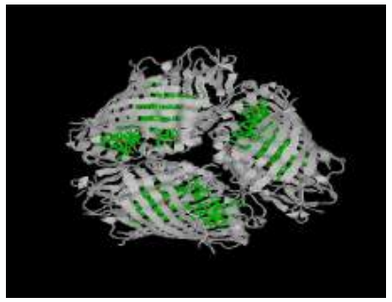
Conclusions

- Quantum transfer of excitation energy / exciton transport
- Simple models

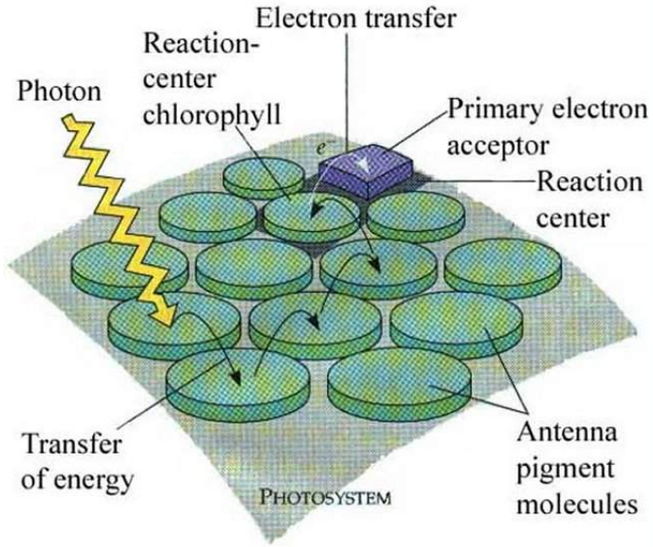


σ

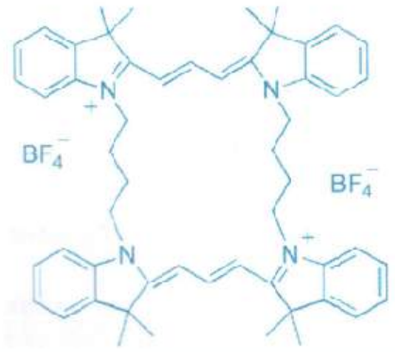
- Fenna-Mathews-Olson complex



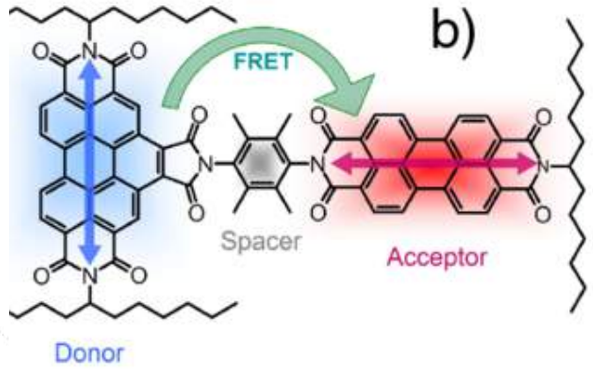
FMO complex



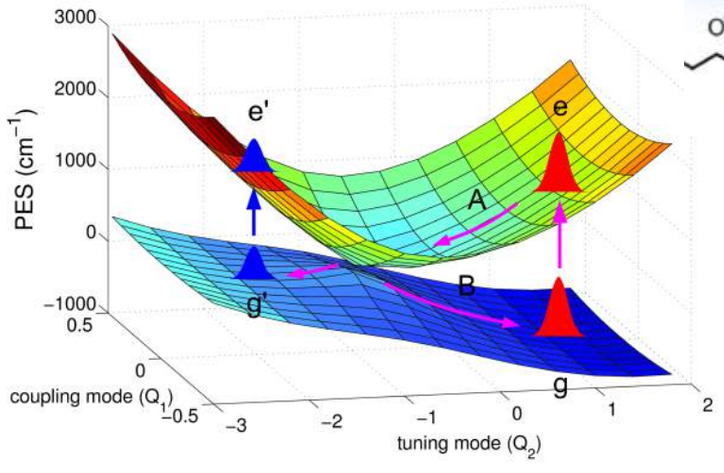
- Vibrational effects



- Orthogonal dipoles



- Conical intersections



Acknowledgements

Nonequilibrium quantum dynamics group:

- Dr. Hong-Guang Duan
- Prof. Peter Nalbach
- Dr. Cesar Mujica-Martinez

MAX-PLANCK-GESELLSCHAFT

Deutsche Forschungsgemeinschaft DFG

Collaborations:

- Prof. R.J.D. Miller (MPI Hamburg)
- Prof. S. Mukamel (UC Irvine)
- Prof. D. Braun (Tübingen)
- Prof. H. Grabert (Freiburg)

JOACHIM HERZ STIFTUNG

PIER

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