Nonlinear optical response of excitons in a quantum mechanical bath

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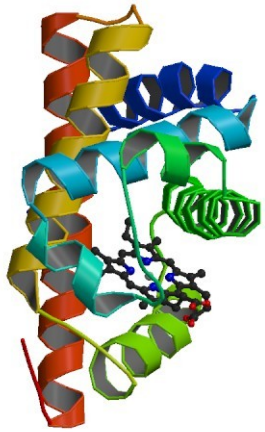
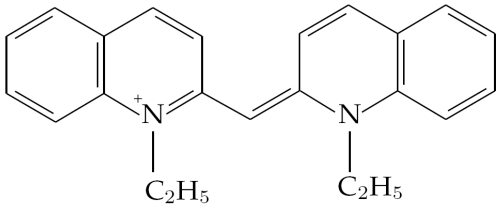
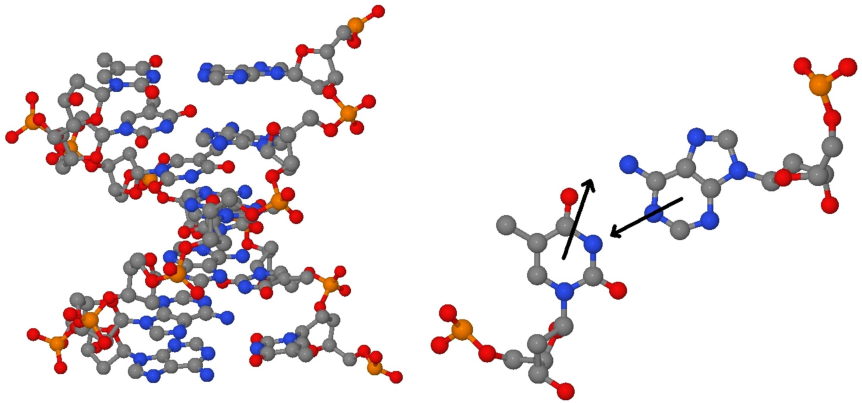
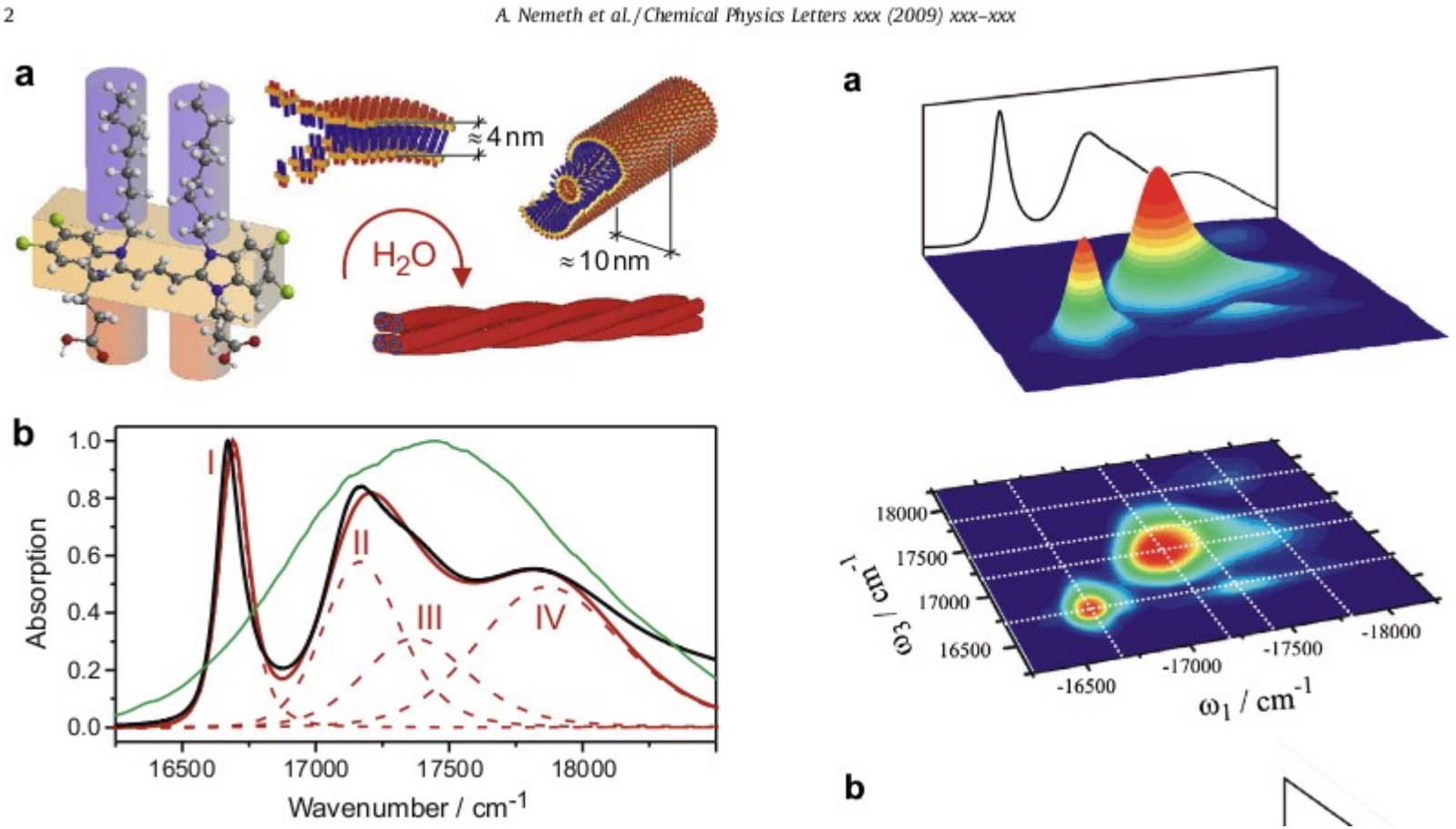






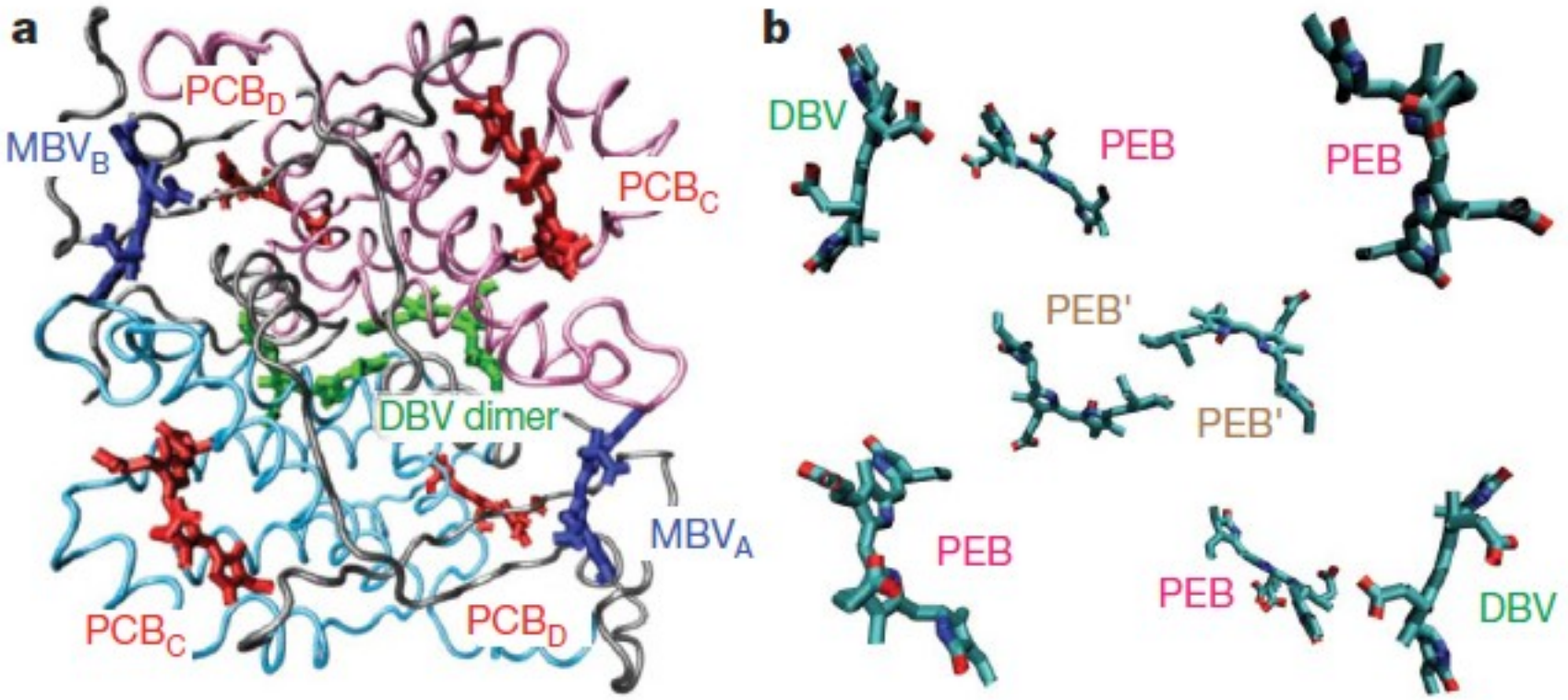
Nonlinear spectroscopy: excitons

double-wall cylinders (Kauffmann)

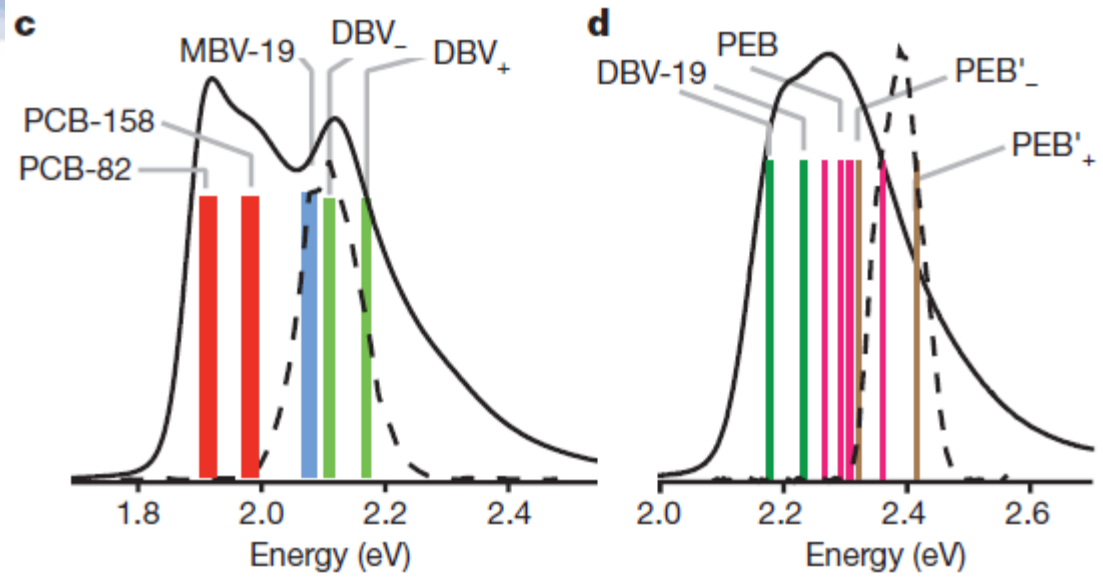


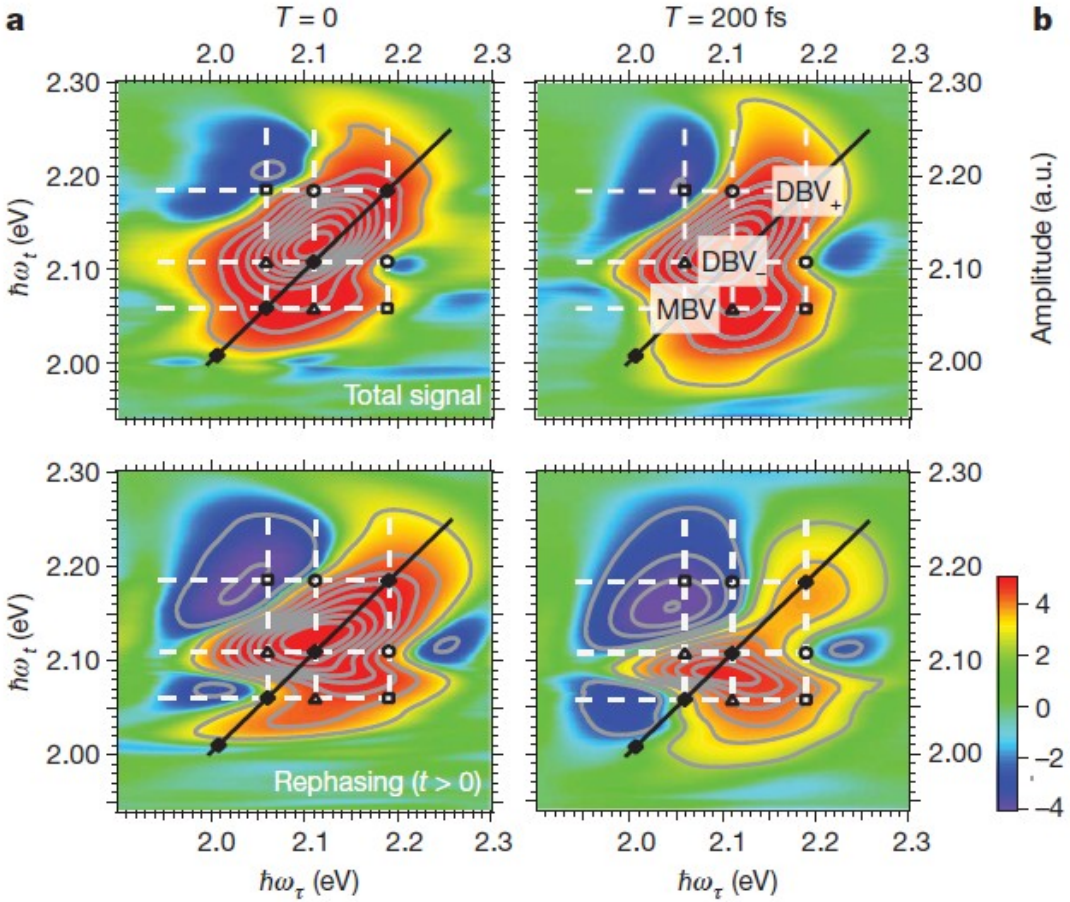
PC645

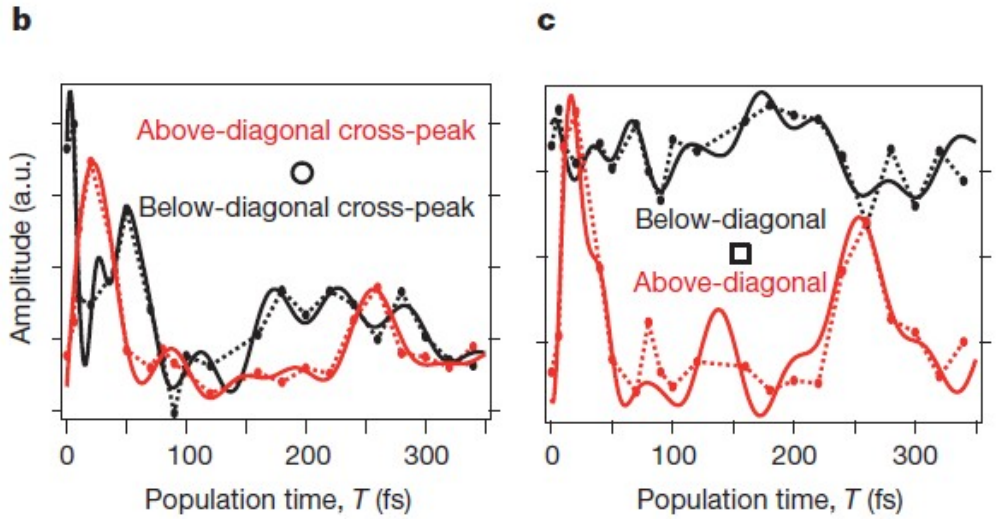
PE545



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

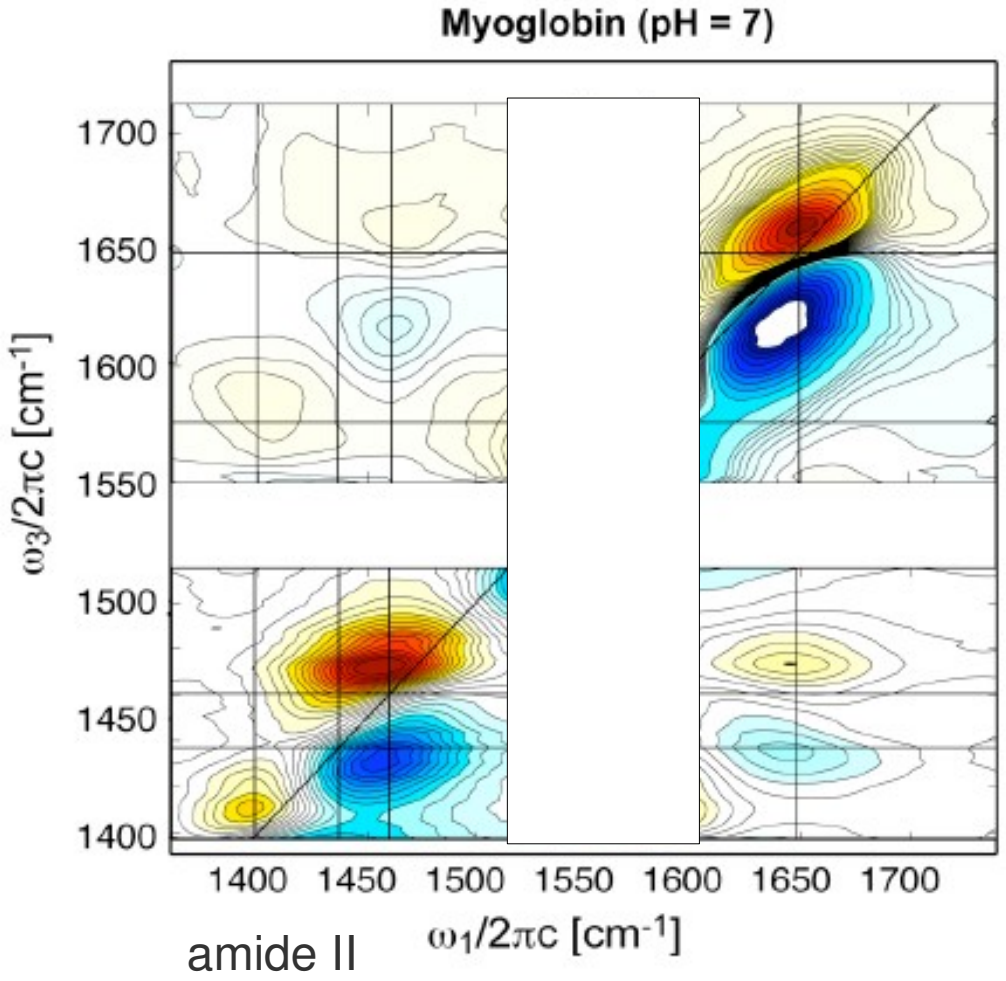


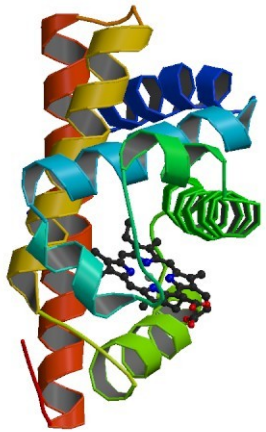




E. Collini et al. Nature 463, 644 (2010)

Nonlinear spectroscopy: vibrons





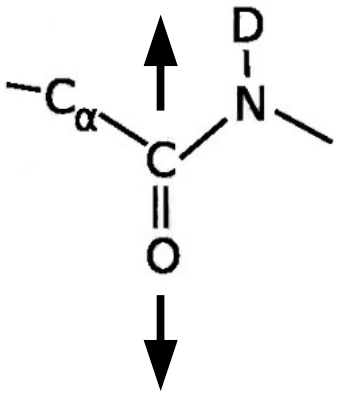
Two vibrational modes in Myoglobin (DeFlores and Tokmakoff)

Outline

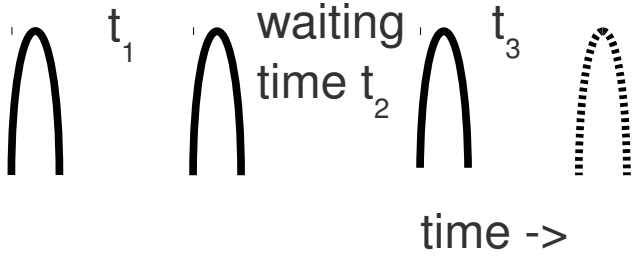
- Classical bath: vibrations in peptides
- Quantum mechanical bath: aggregates
  - Slow bath
  - Fast bath
- Quantum mechanical bath: DNA
  - Time scale of the bath

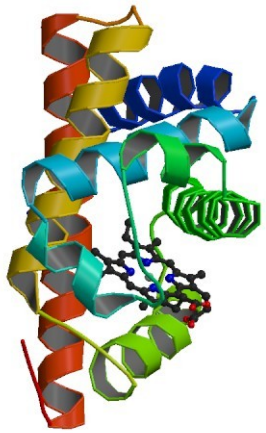
2DIR spectra of proteins

Amide I



- popular in nonlinear IR experiments (large dipole)
- sensitive to the environment
- sensitive to secondary structure (Miyazawa, 1960)
- lifetime 0.5 – 1 ps

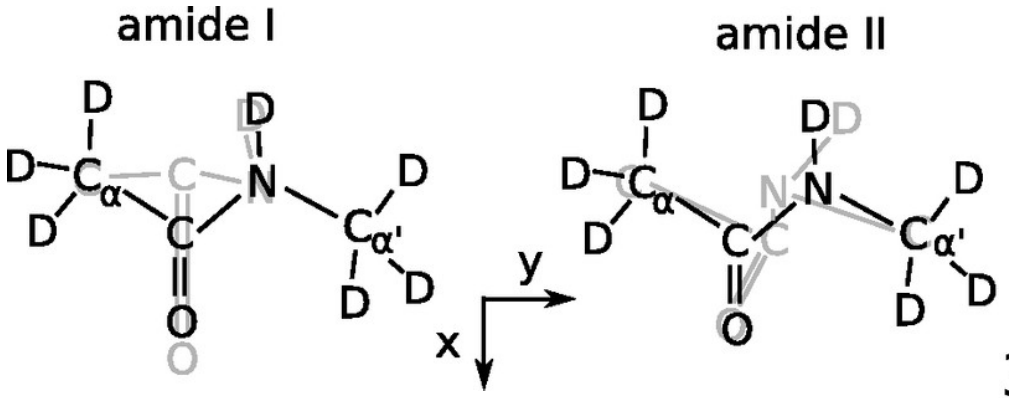




Model system: NMA
single amide I vibration

(correlation spectrum)

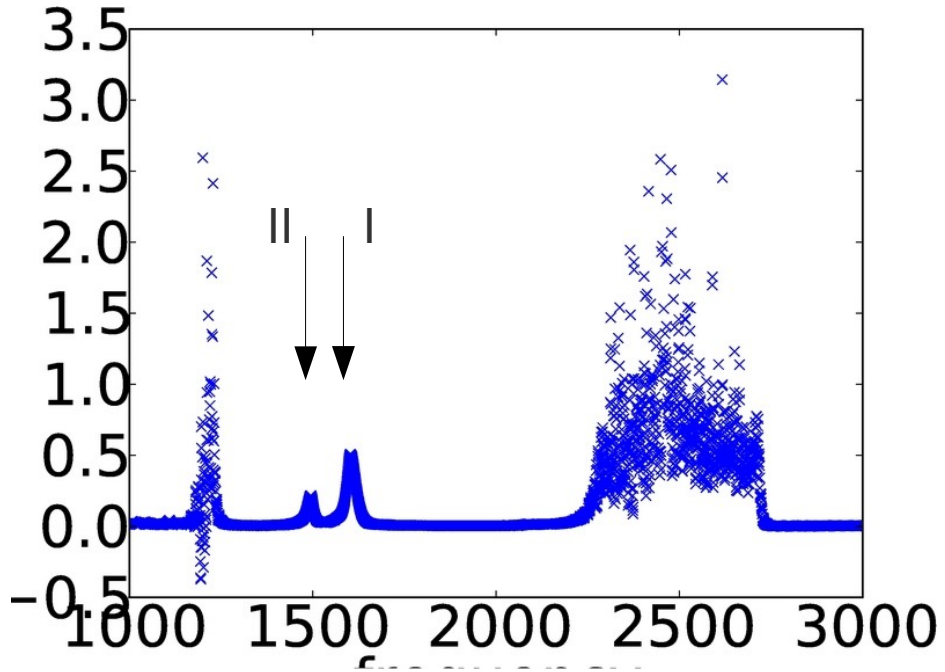
Amide I and II modes



~ 1600 cm^{-1}
lifetime 0.5 – 1 ps

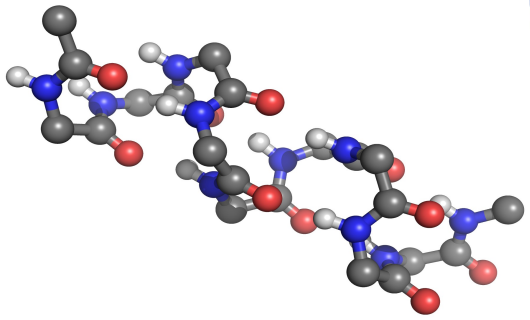
~ 1500 cm^{-1}

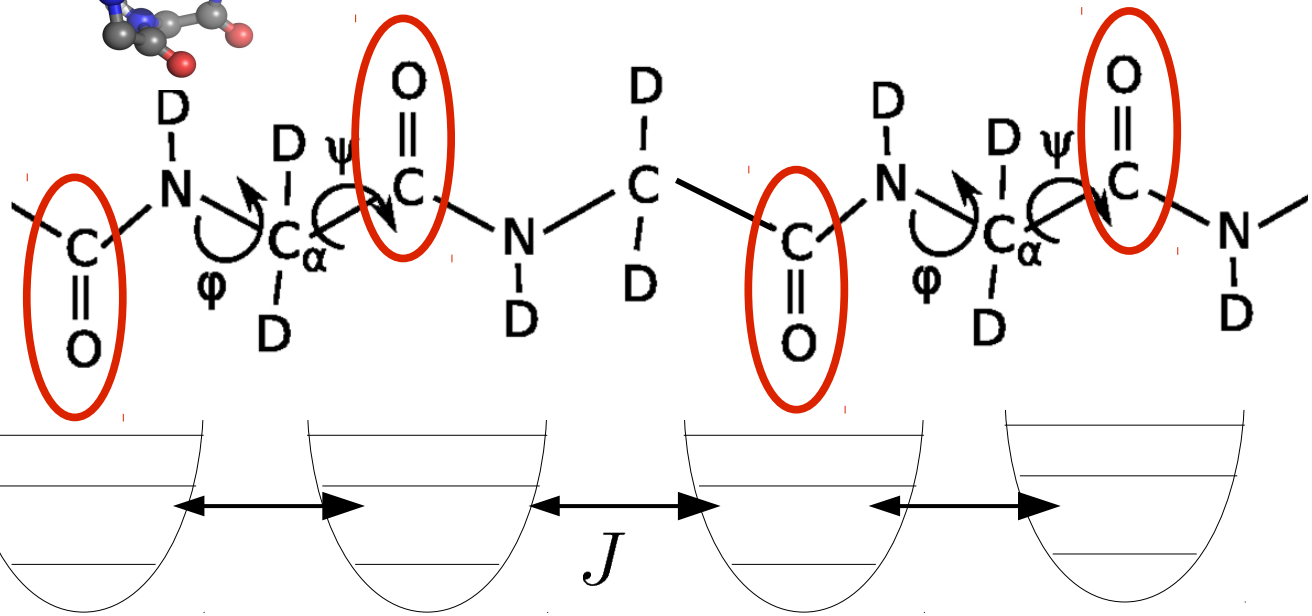
NMA-d7
Amide I, II: independent?

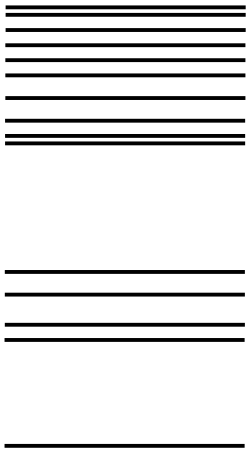


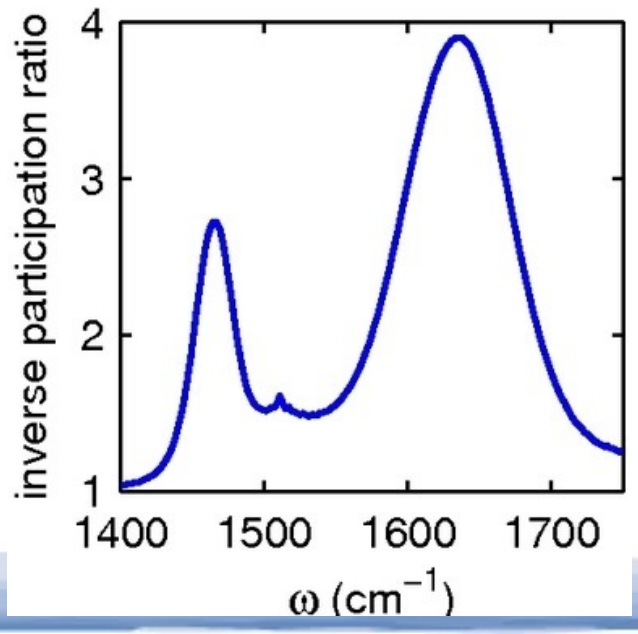
Lot of detail about a small region of the spectrum

Collective vibrations







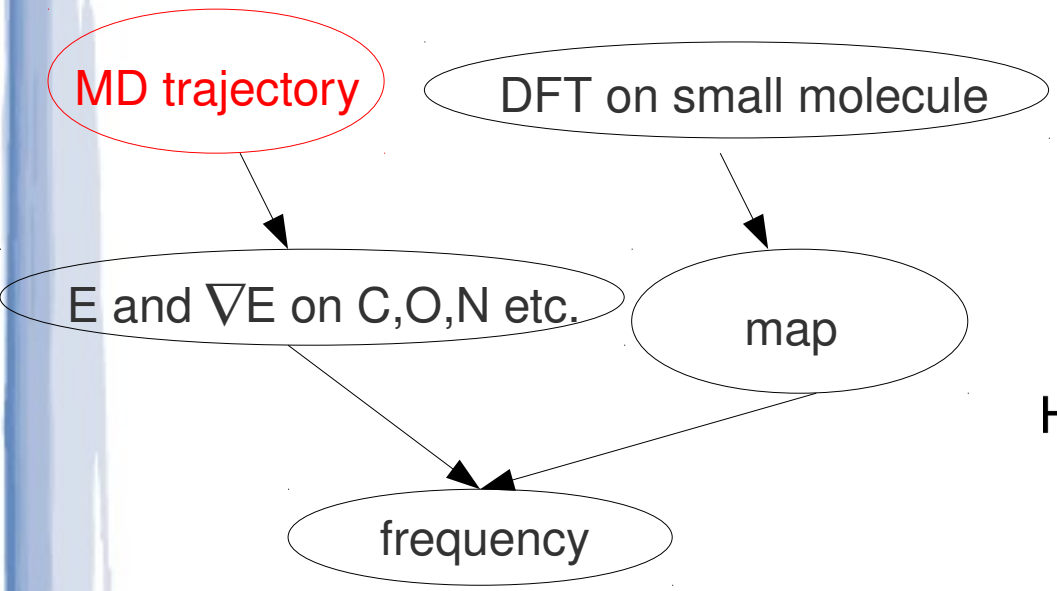


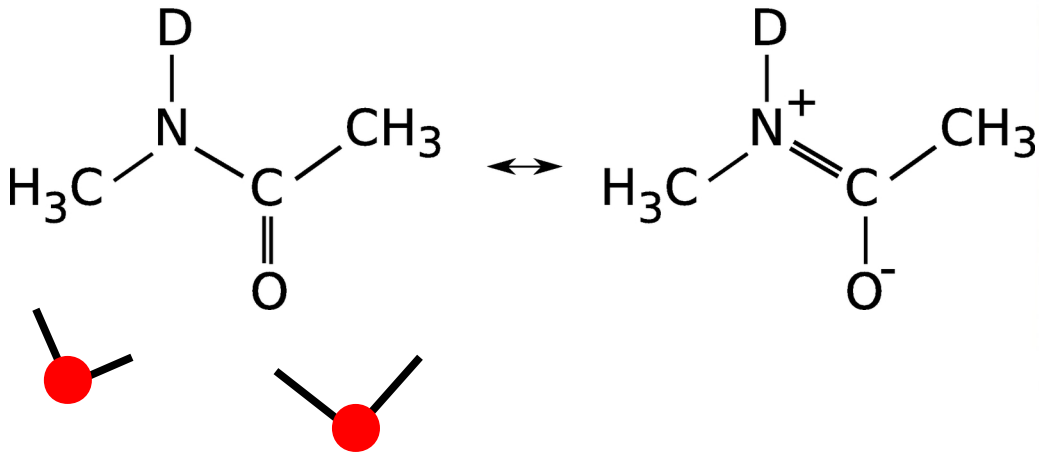
Competition:
coupling → collective states
interaction with environment → localized states

→ ~ **4 amide I local modes vibrate collectively**

Modeling the environment

Stark shift: frequency depends on electric fields caused by the environment
(main effect: hydrogen-bonding)





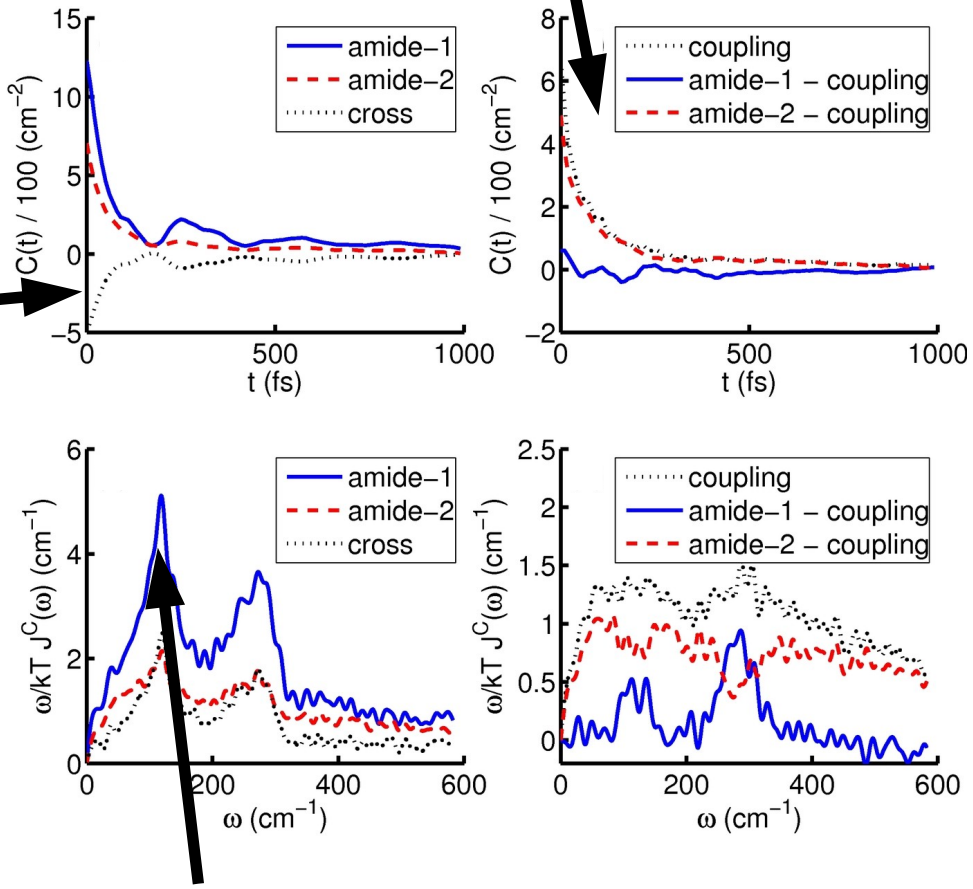
Time-dependent frequencies and amide I-II coupling

Correlation functions (NMA-d_7)

- 2 coupled modes
- water -> fluctuating frequencies
- electrostatic DFT map
- MD trajectories

fluctuating coupling

anti-correlation



Resonance near 100 cm^{-1}
(H-bond)

NISE

$$\frac{\hbar}{i}\frac{\mathrm{d}}{\mathrm{d}t}\psi(t) = H(t)\psi(t)$$

Time-dependent Hamiltonian

$$H(t) = \sum_n \epsilon_n(t) b_n^\dagger b_n + \sum_{nm} J_{nm}(t) b_n^\dagger b_m - \sum_n \frac{A_n}{2} b_n^\dagger b_n^\dagger b_n b_n$$

Fluctuations in site energies as well as couplings

$$\psi(t+\Delta t) = e^{-iH(t)\Delta t}\psi(t) \longrightarrow$$

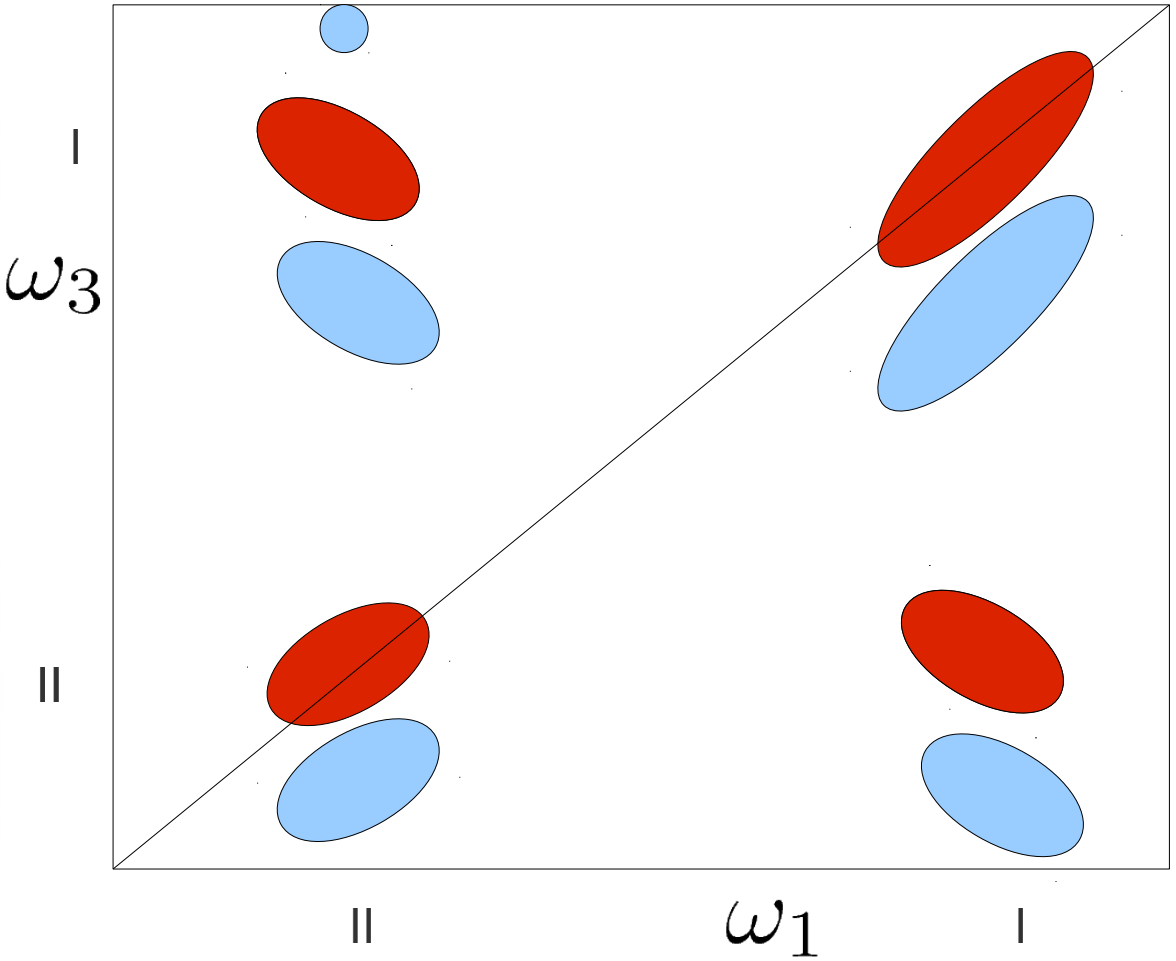
Vibrational dynamics
(nonlinear) spectra

Nonadiabatic and non-Markovian dynamics

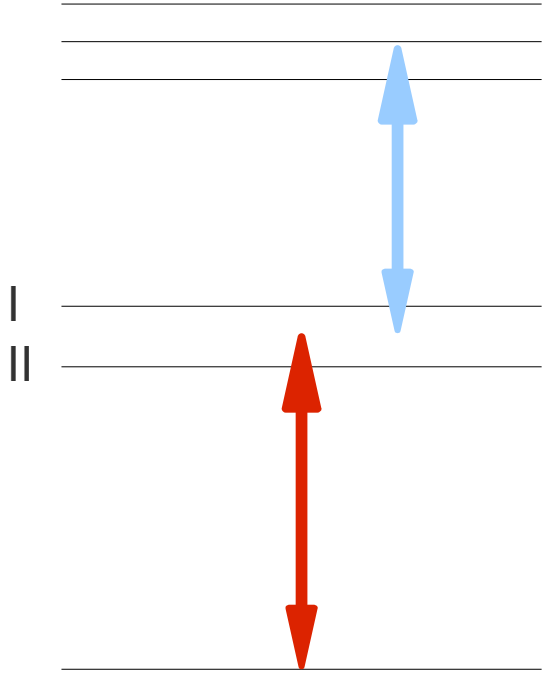
High T; OK for amide I modes, reasonable for amide I + II

2DIR of two coupled vibrations

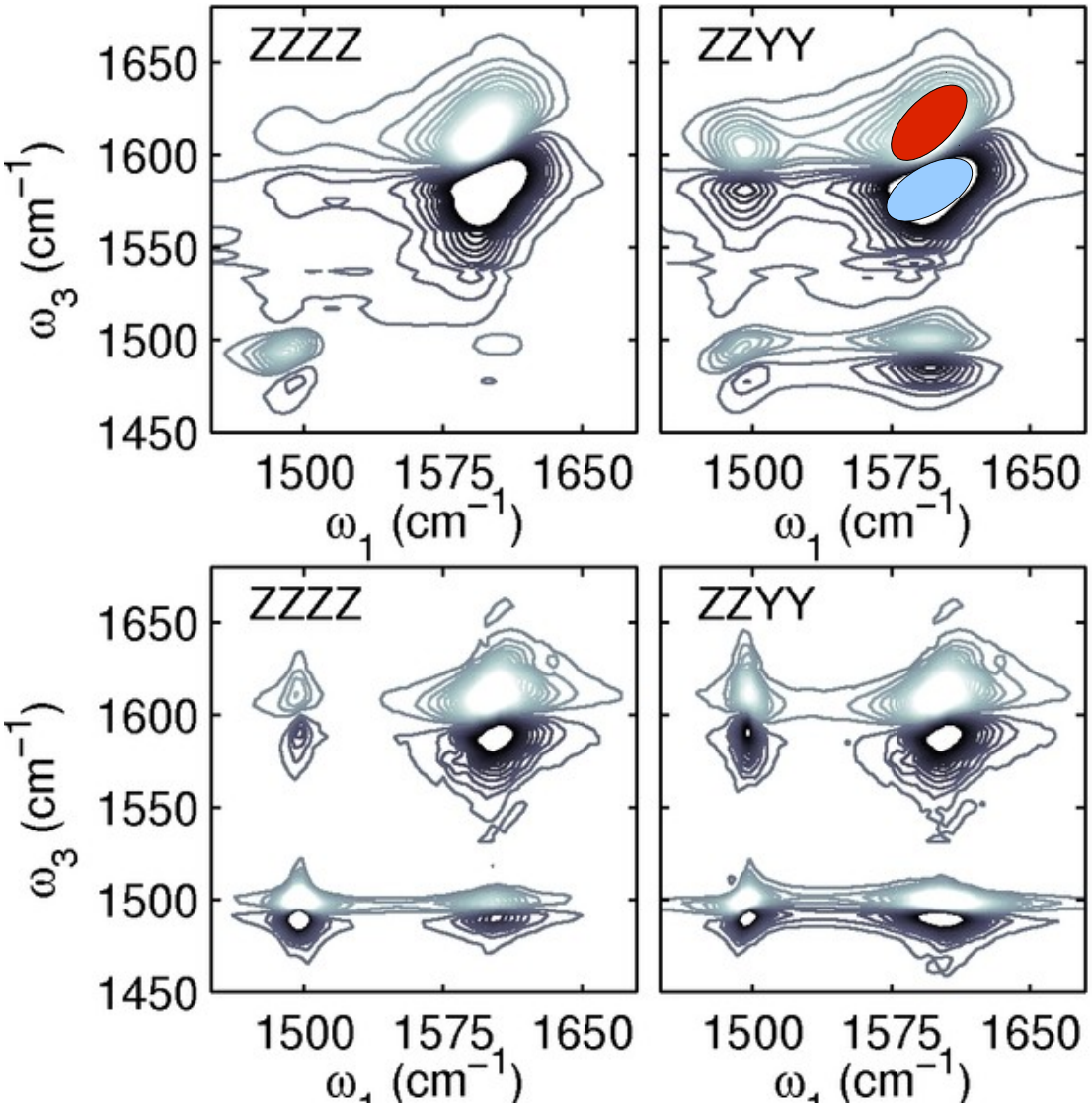
cross peak: mode coupling
(anti-diagonal slant: anti-correlation)



diagonal peak. slant:
inhomogeneous distribution



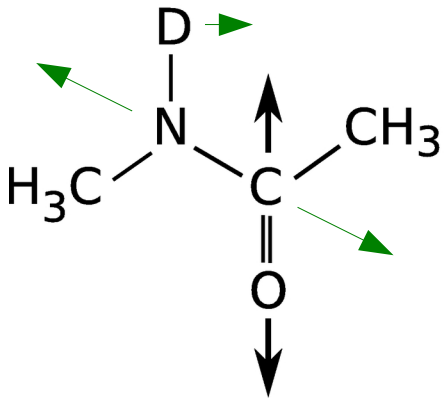
Amide I – II cross peak in NMA-d7



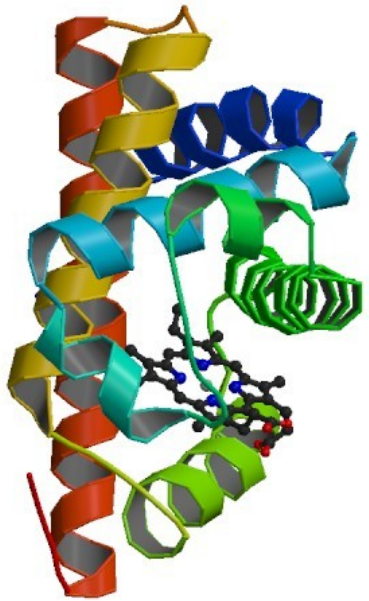
Strong cross peak in ZZYY polarization: perpendicular transition dipoles

Cross peak means coupling => there must be energy transport

Relaxation rate can be obtained from the cross peak intensity



Vibrations in peptides: classical bath

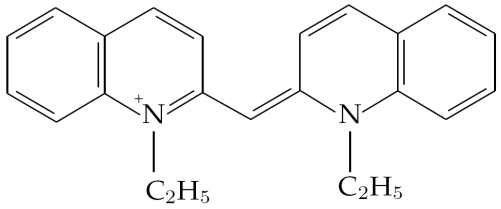


- amide vibrations in peptides: classical fluctuating environment

- no dissipation, all states equally populated in equilibrium

- only good if the system bandwidth is much smaller than the thermal energy

pseudo-isocyanine (PIC)



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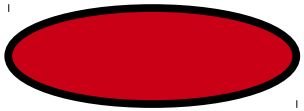
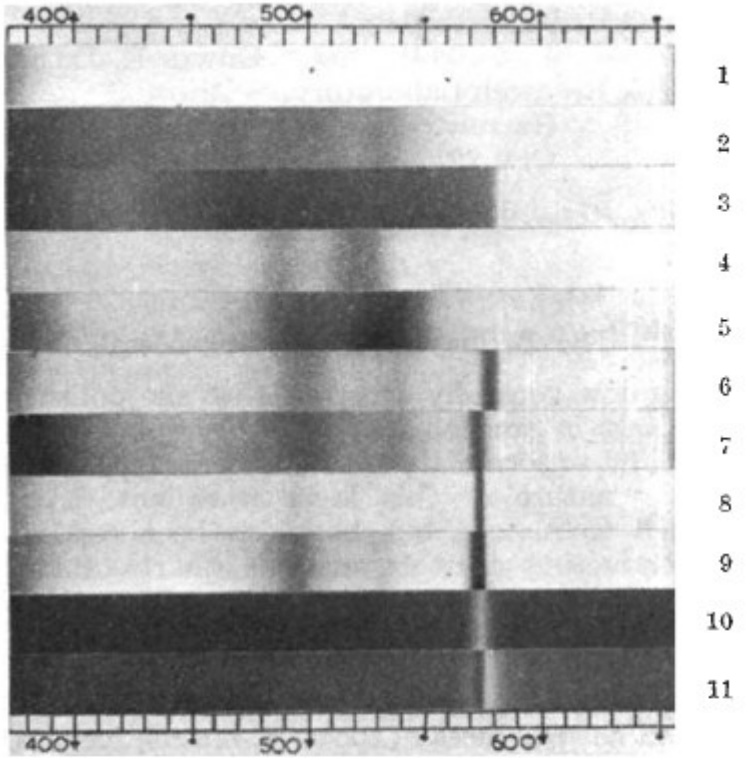
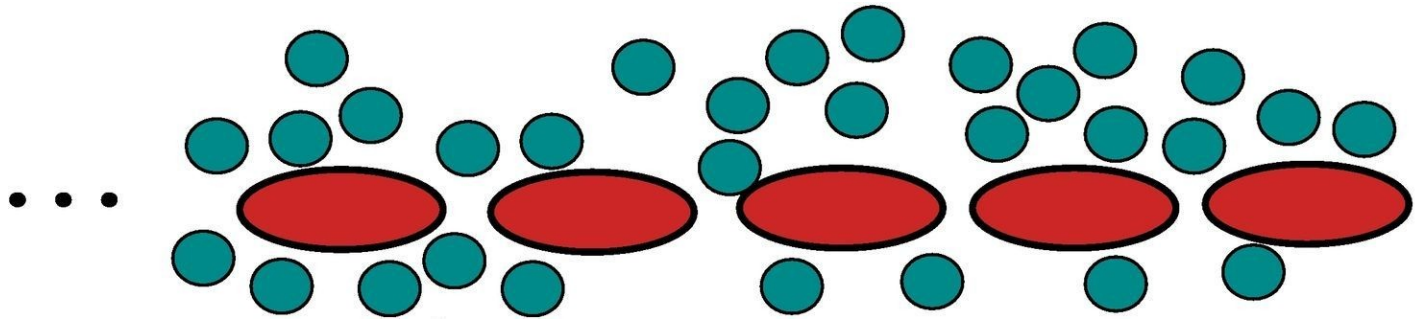




(1) Spectrum of tungsten arc lamp (containing neon).
(2) and (3) The two principal absorptions corresponding to the *X* and *Y* vibration directions of crystals of 1 : 1′ diethyl-ψ-cyanine chloride.
(4) Absorption spectrum of the dye in methyl alcohol.
(5) Absorption spectrum of the dye in nitrobenzene.
(6) Absorption spectrum of a molecular suspension of the dye in toluene.
(7) Absorption spectrum of the dye molecularly dispersed in benzophenone crystals.
(8) and (9) Absorption spectra of two different concentrations of the dye in sodium chloride solution.
(10) Fluorescence spectrum of the dye in sodium chloride solution.
(11) Fluorescence spectrum of the dye in sodium chloride solution. In this case the fluorescent light has been made to traverse a small thickness of unilluminated solution, so that the absorption band is seen superimposed on the fluorescence band. It will be noticed that the two do not exactly correspond.

Jelley (Nature, 1936)

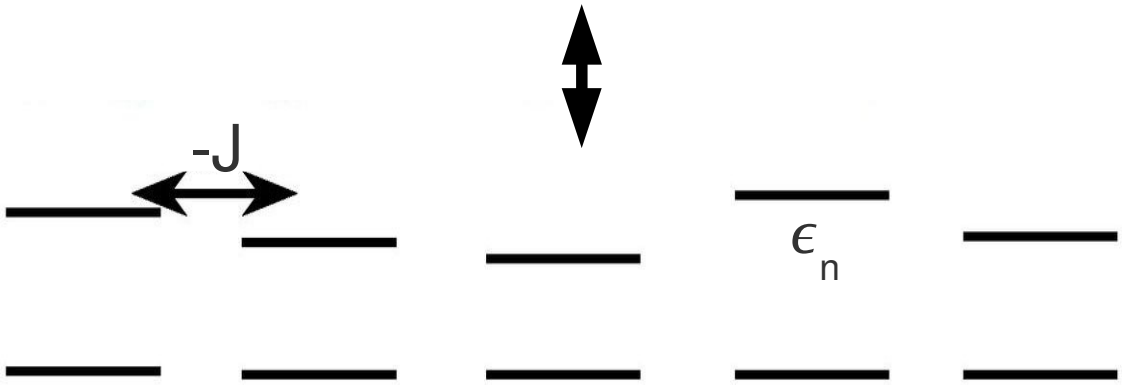
Model at a low temperature (< 5 K)



solvent molecule

chromophore

dipole-dipole interactions



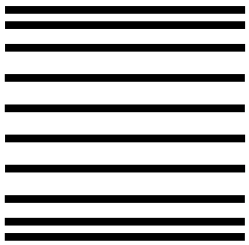
excited state, energy disorder, spread σ

ground state

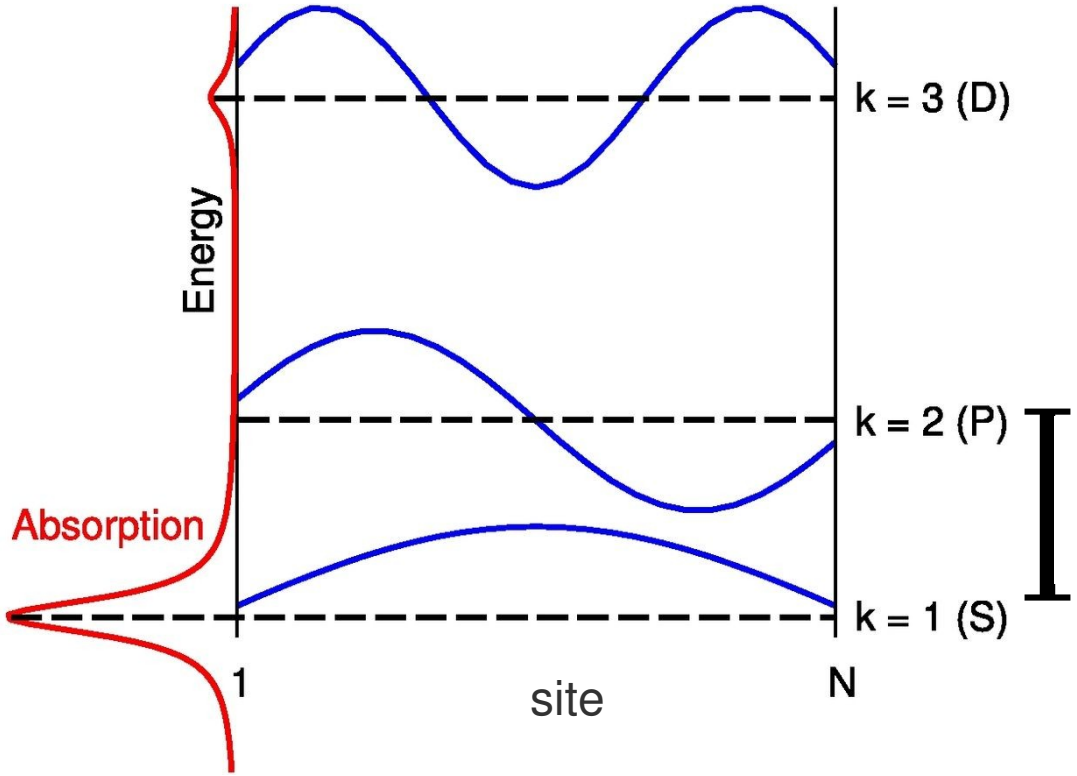
$$H = \sum_n \epsilon_n c_n^\dagger c_n + \sum_{m \neq n} \frac{-J}{|n-m|^3} c_n^\dagger c_m .$$

Excitons: homogeneous aggregates

Simplifications:
- no disorder
- only nearest neighbour interactions



Noninteracting fermions, 2-exciton states as anti-symmetric products



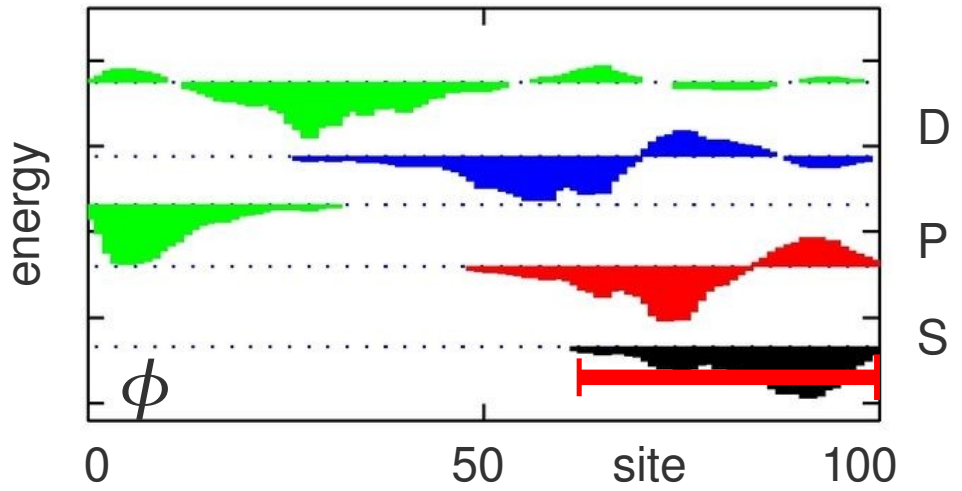
$$E_2 - E_1 \approx \frac{3\pi^2}{(N+1)^2} J$$

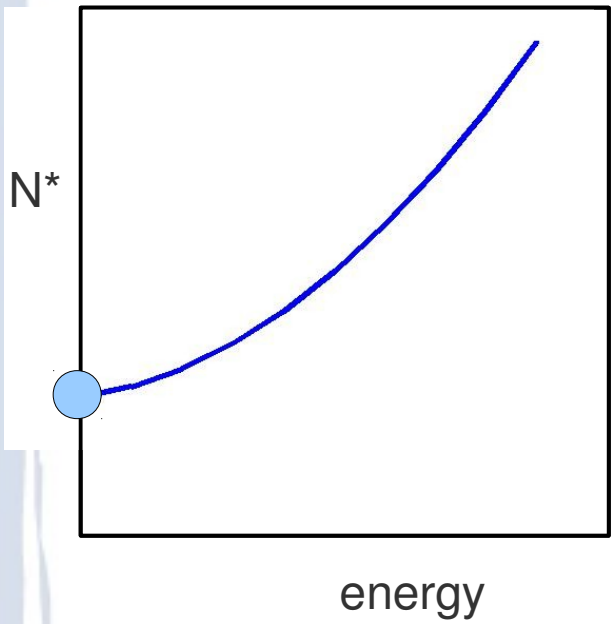
Excitons: disordered aggregate

Full model

- site energy disorder
- long range interactions

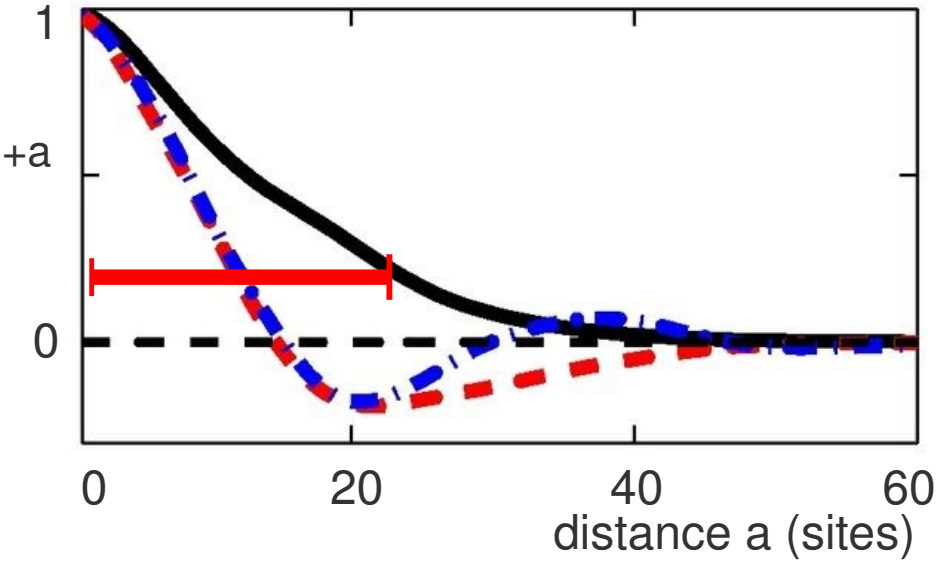
numerical 1- and 2-exciton states



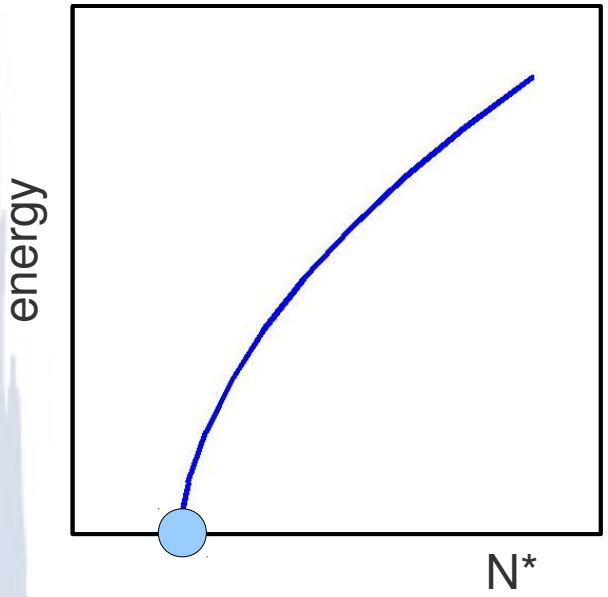


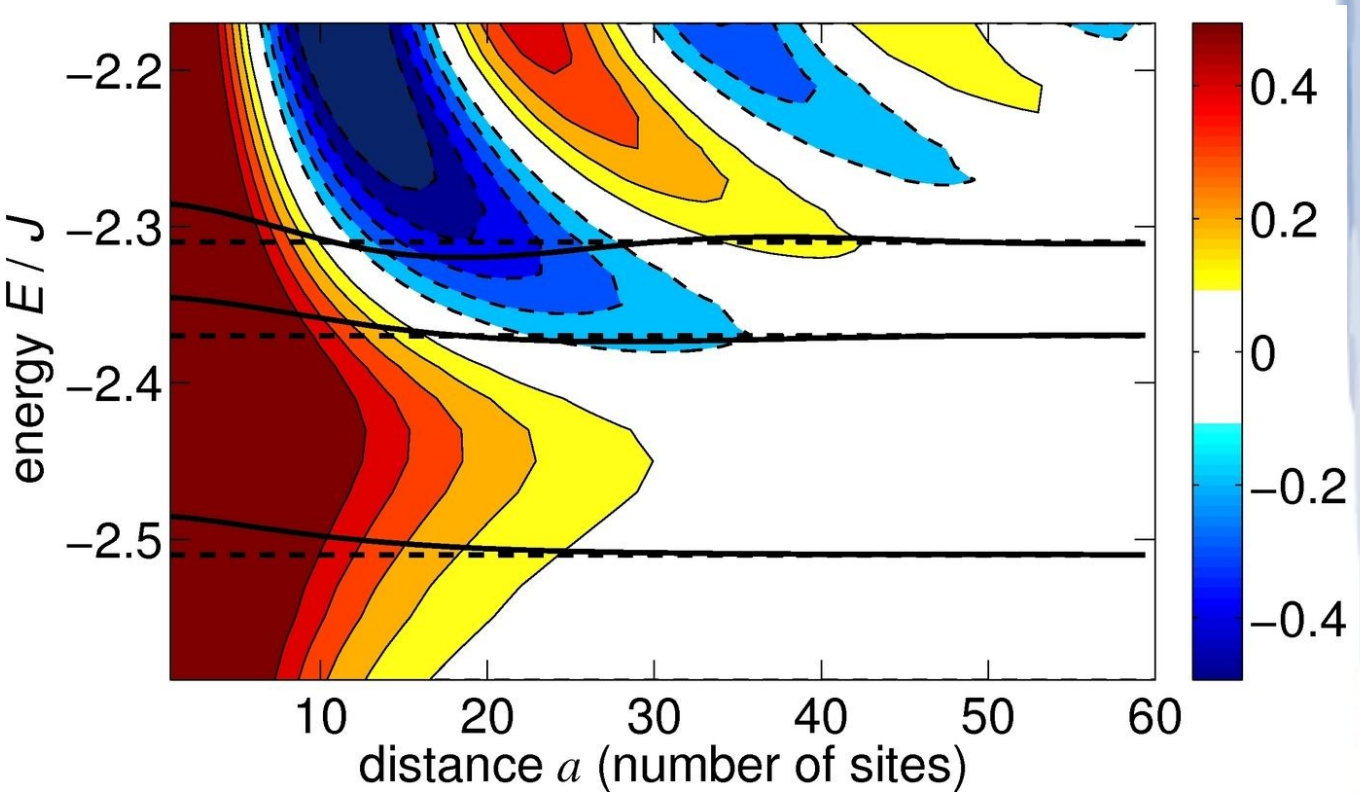
Localization size N*

$\Sigma_n \phi_n \phi_{n+a}$



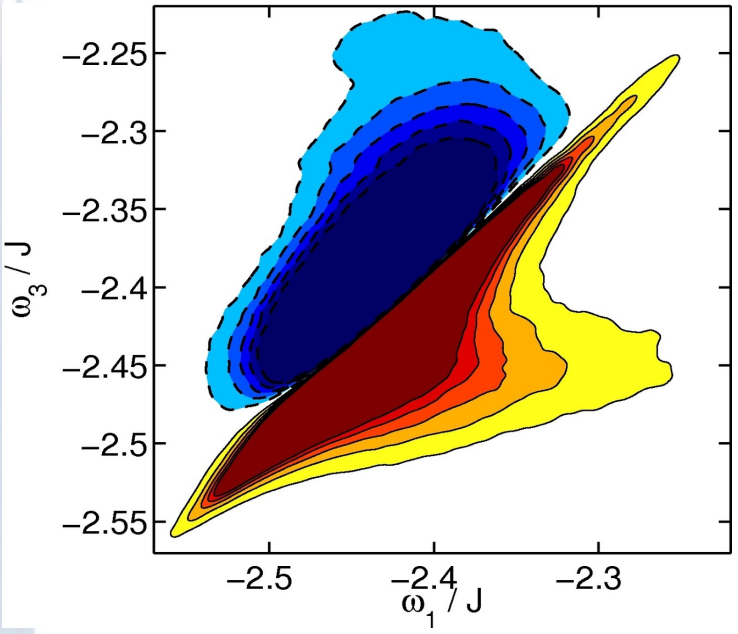
Localization: position correlation function

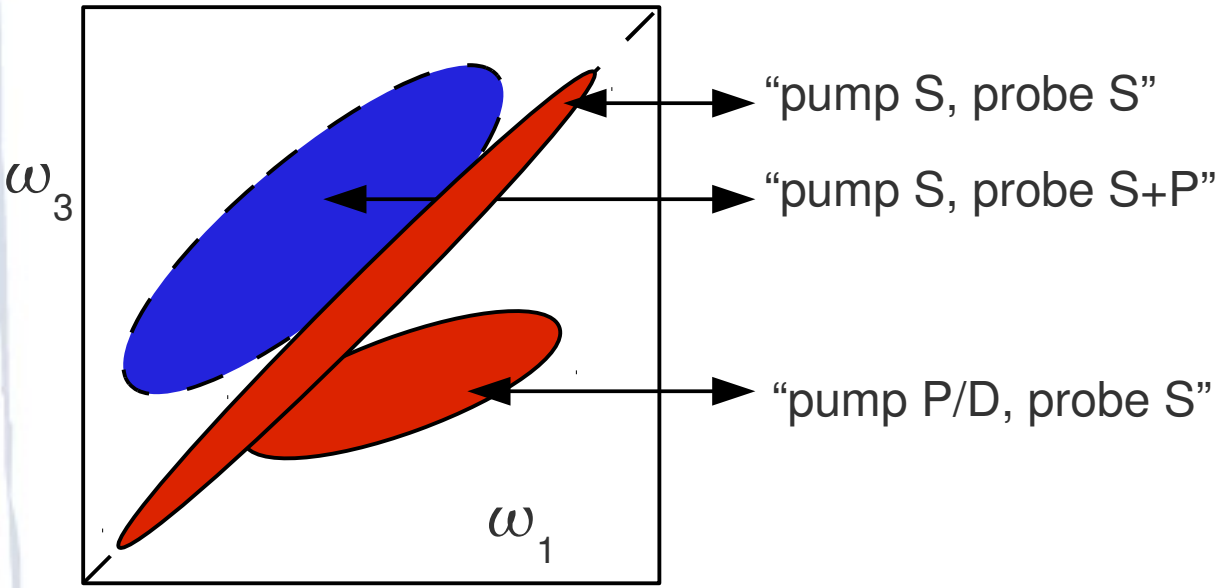


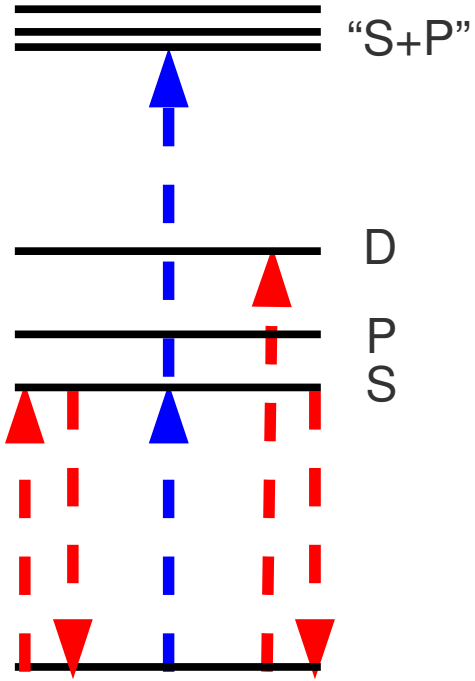


$$C(a;E) = \frac{\langle \sum_k \sum_n \phi_{k,n}\phi_{k,n+a}\delta(E-E_k)\rangle}{\langle \sum_k \delta(E-E_k)\rangle}$$

2D spectrum: zero waiting time

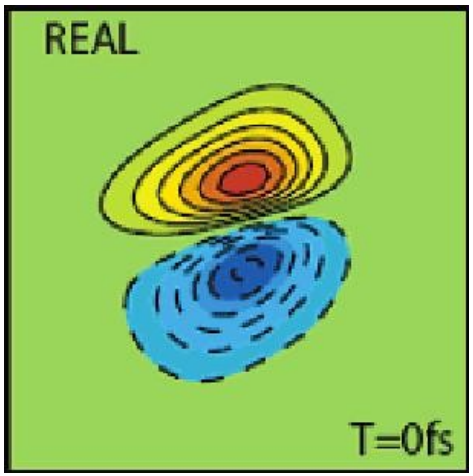




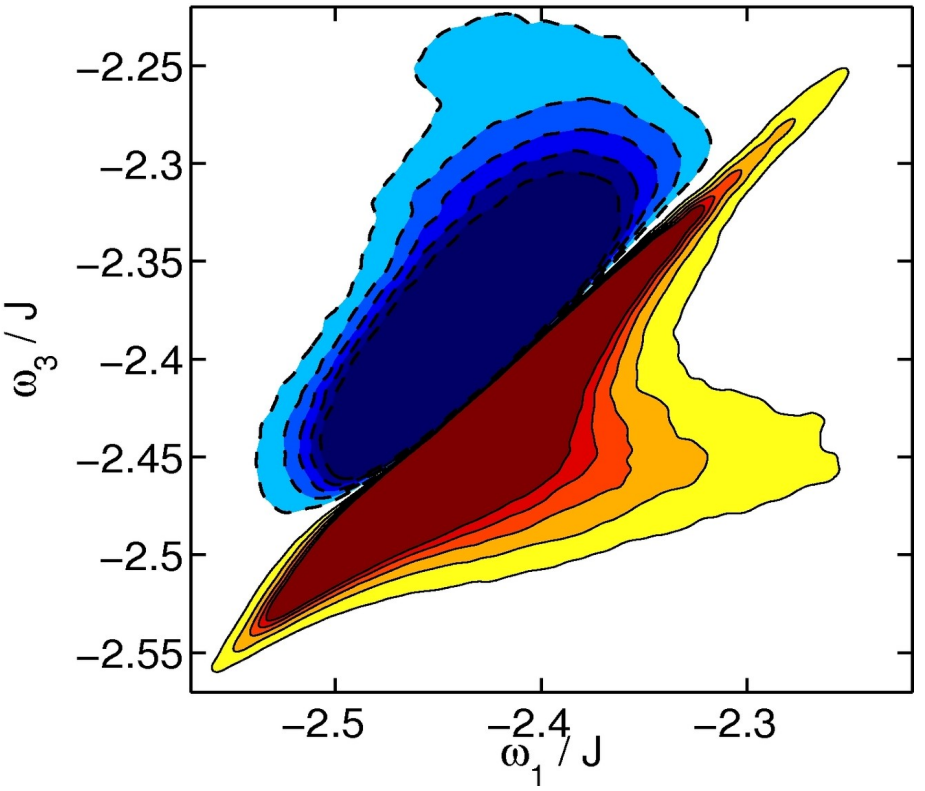


exciton states in localization segment

Low temperature cross peak

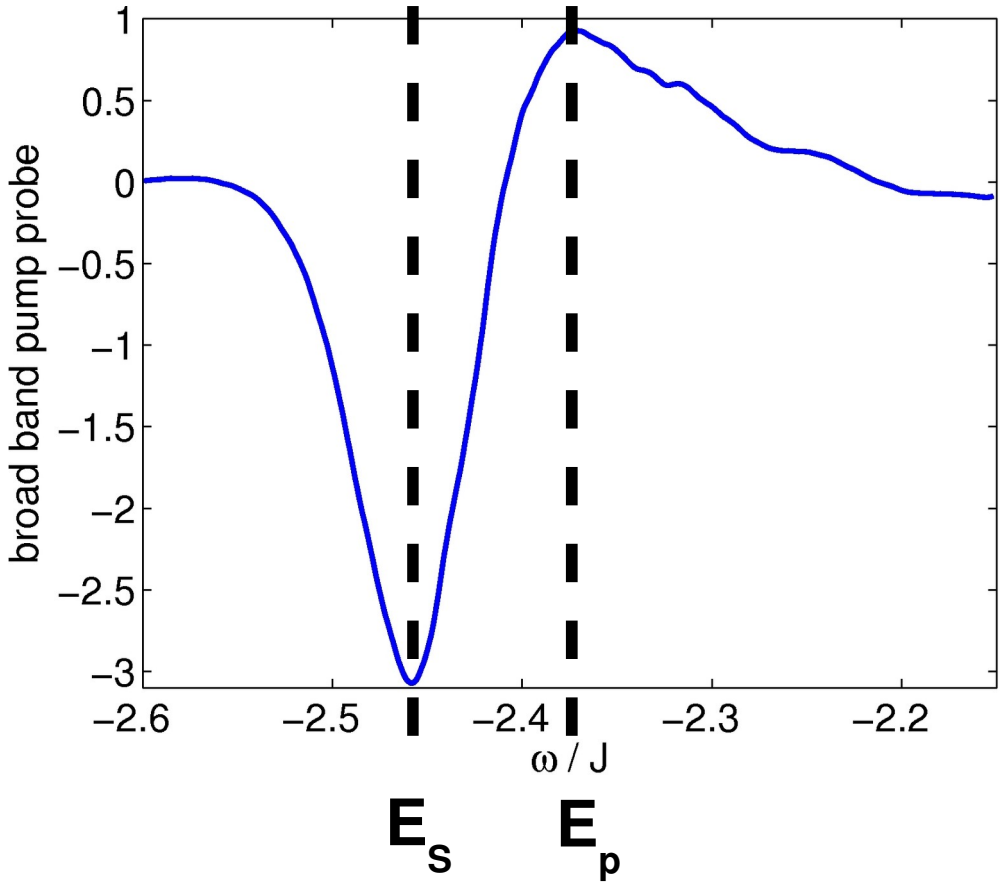


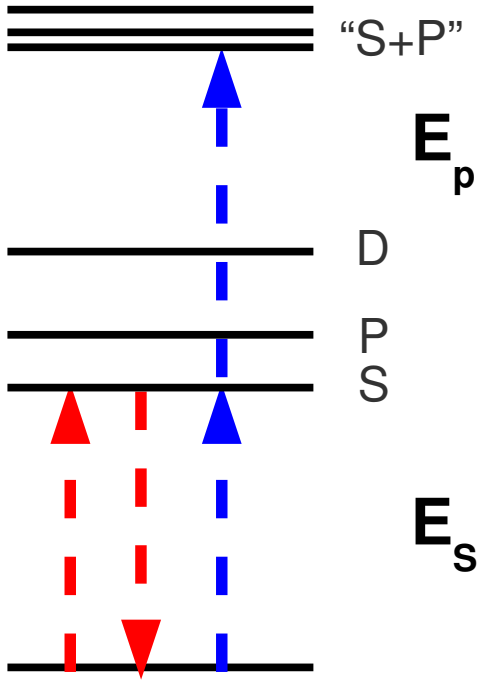
room temperature
(I. Stiopkin et al.
JPCB **110**, 20032
(2006))



< 5 Kelvin

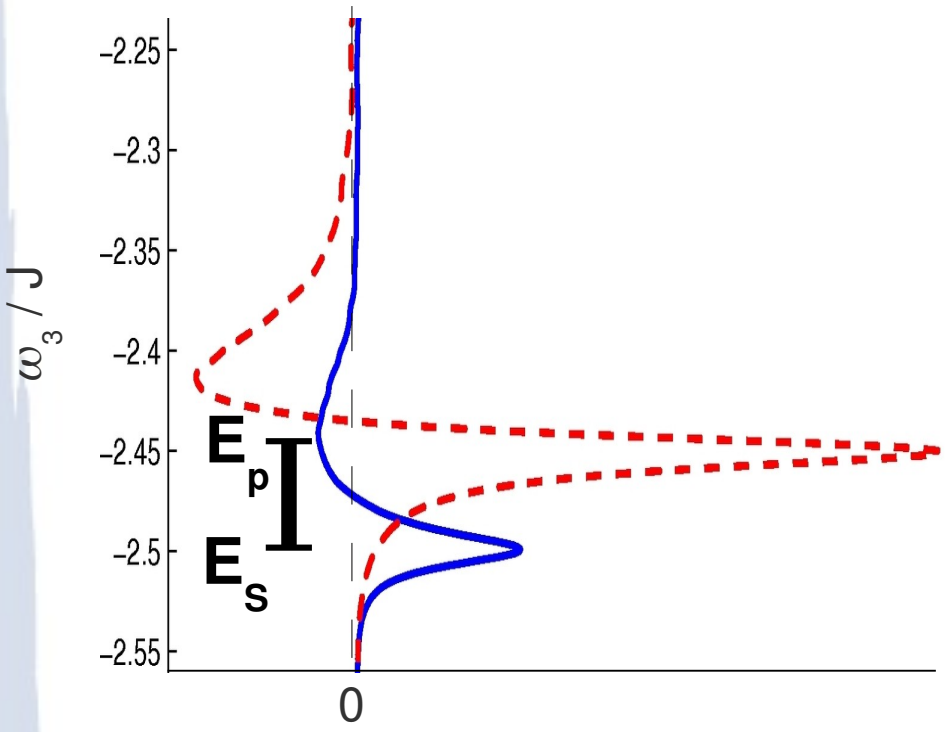
Average localization length

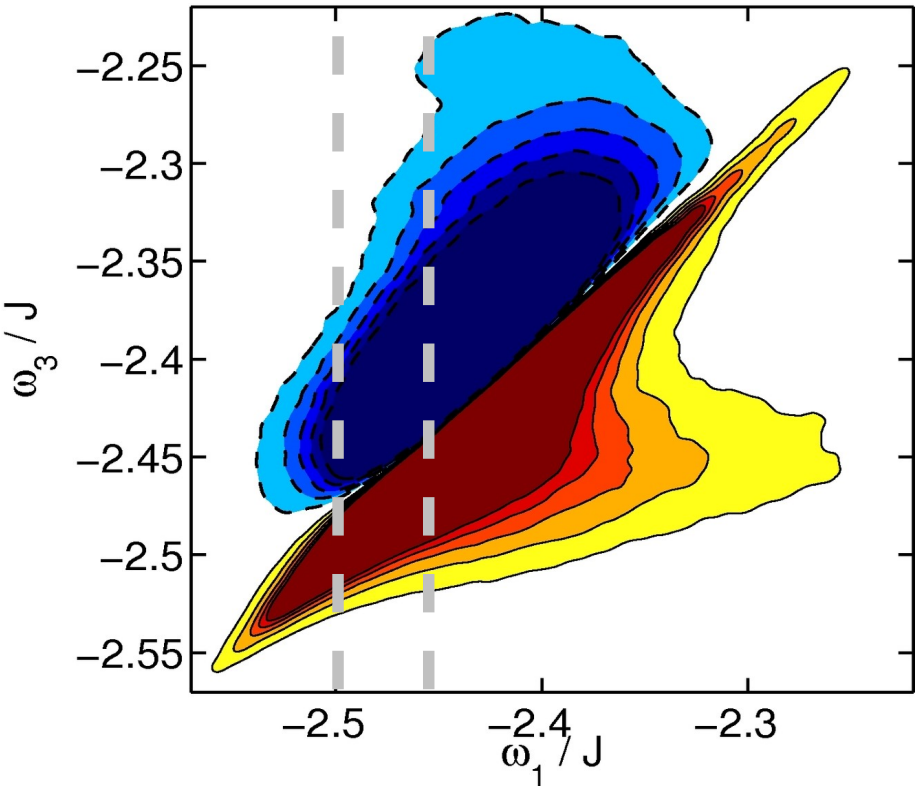




$$E_P - E_S \approx \frac{3\pi^2}{(N^* + 1)^2} J$$

Extraction of localization length



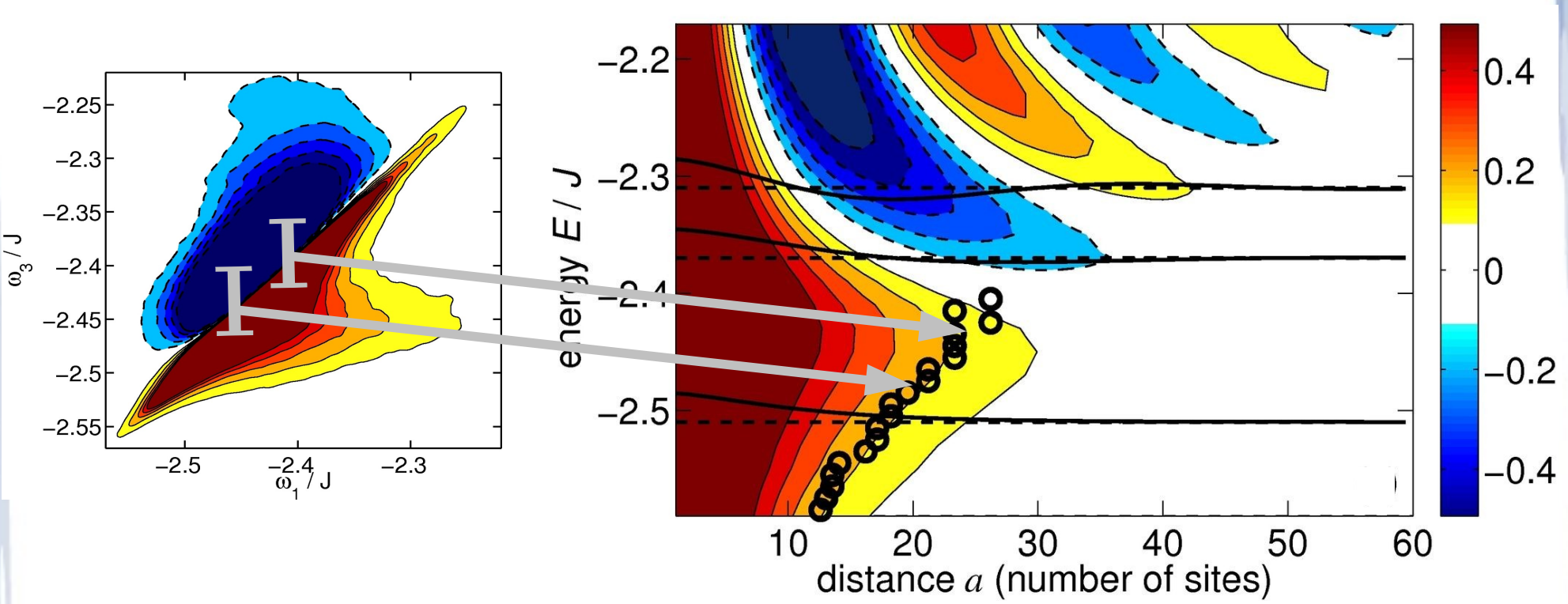


$$E_P - E_S \approx \frac{3\pi^2}{(N^* + 1)^2} J$$

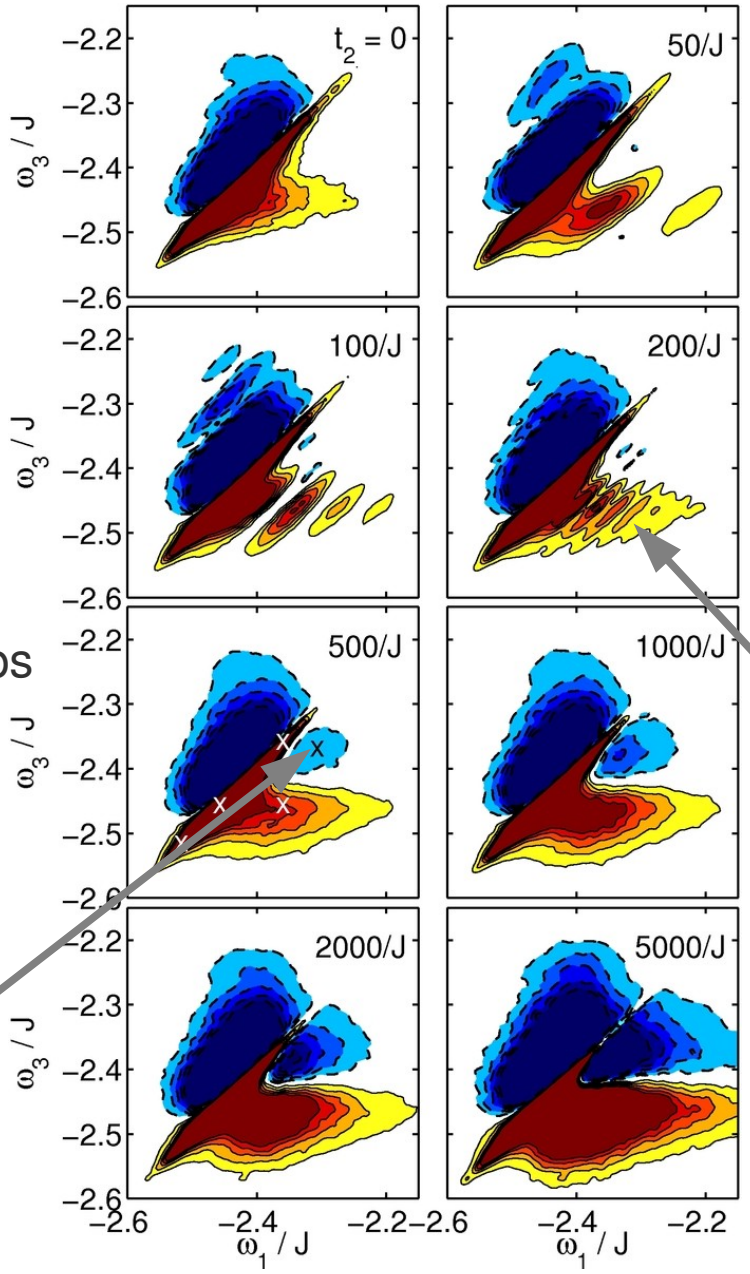
Cross section at fixed ω_1

"excites segments with $E_S = \omega_1$"

Extracted localization length



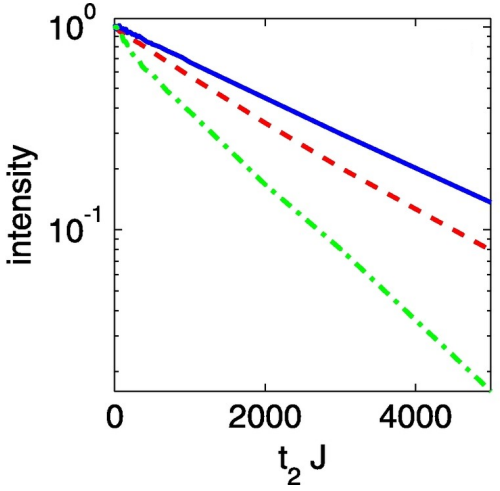
Dynamics: 2D spectra

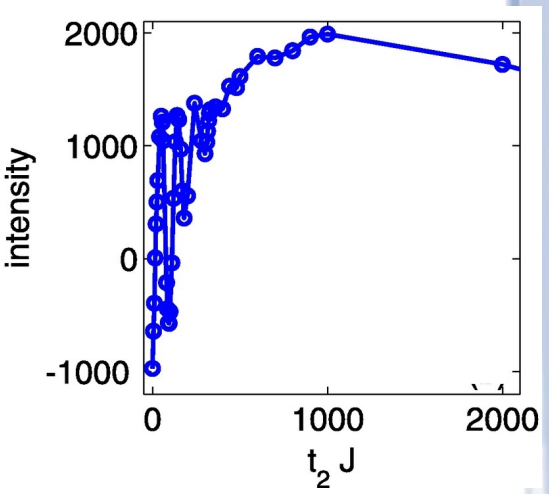


500/J ~ 33 ps

SP	S
S	S
D	D
0	D

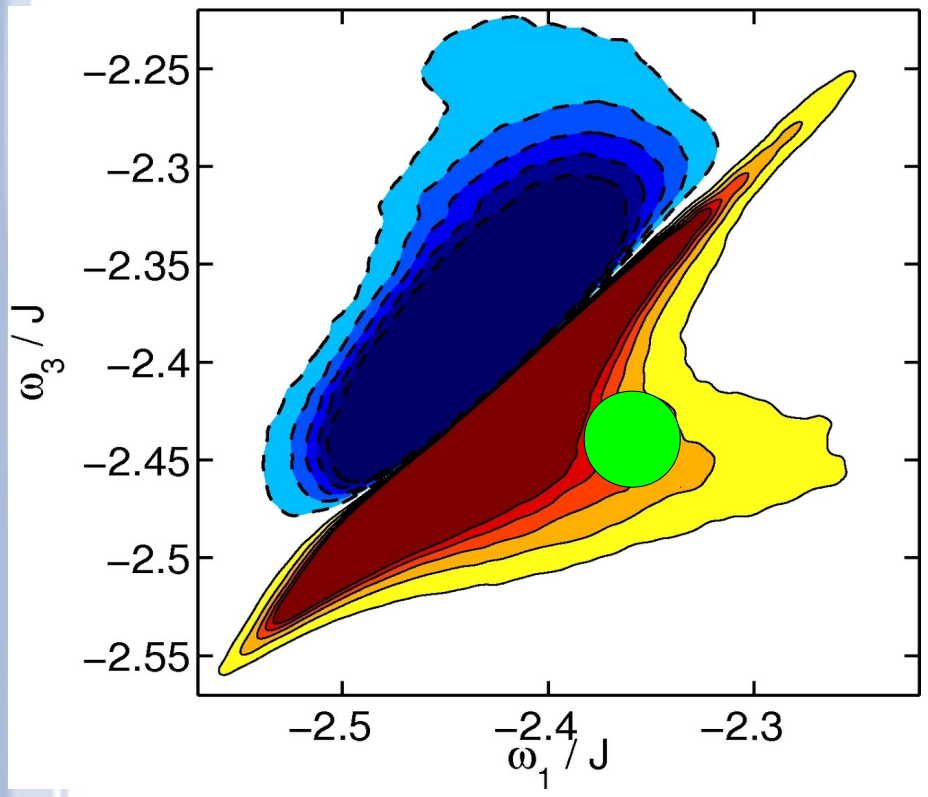
S	0
S	P
0	P

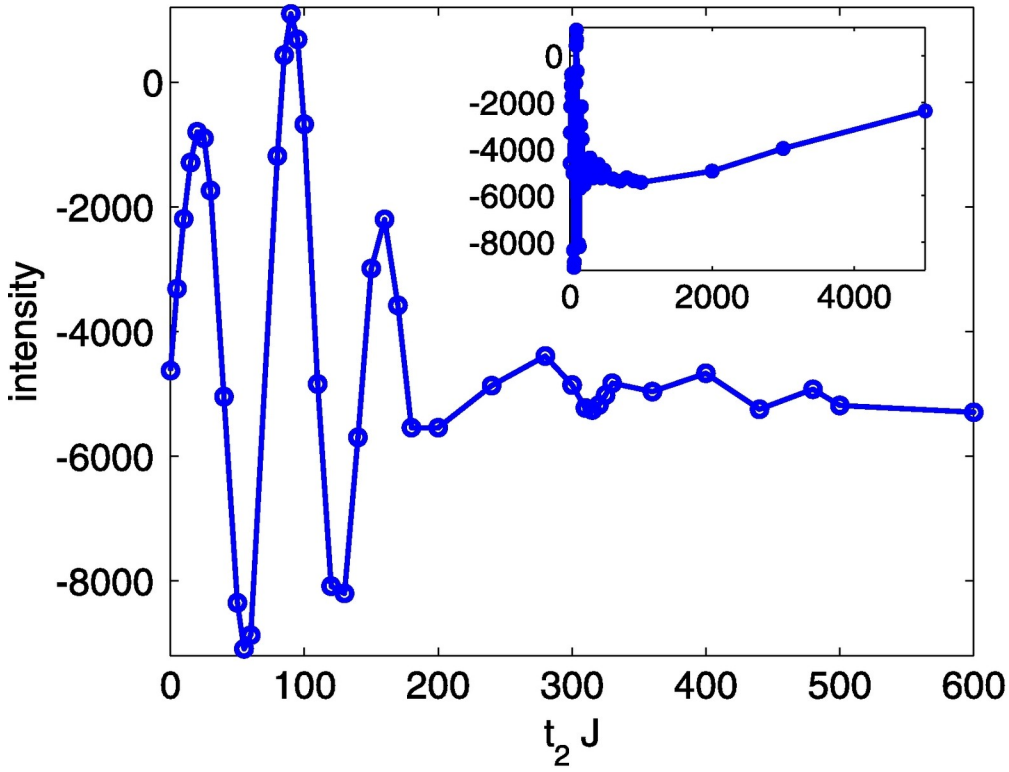




$$e^{-i(E_S-E_P)t_2} = e^{-i(\omega_3-\omega_1)t_2}$$

Coherent oscillations





"long-lived coherent oscillations"

A.G. Dijkstra, T.l.C. Jansen and J. Knoester, J. Chem. Phys. 128, 164511 (2008)

Aggregates – static bath

- Molecular aggregates at low temperature: static bath (no dissipation)
- Response from sum over states
- Dynamics due to remaining fast degrees of freedom
- Fast bath modes described using Redfield theory

Quantum and slow bath

$$H = H_S + H_B + H_{SB}$$

$$H_B = \sum_{\alpha} \left(p_\alpha^2 / 2m_\alpha + m_\alpha \omega_\alpha^2 x_\alpha^2 / 2 \right)$$

$$H_{SB} = -\sum_{n=1}^{N} \sum_{i \in \{A,T\}} \sum_{\alpha} g_{ni,\alpha} V_{ni} x_\alpha \qquad V_{ni} = c_{ni}^\dagger c_{ni}$$

bath time scale

$$\mathcal{J}_{ni,mj}(\omega) = \sum_{\alpha} \frac{g_{ni,\alpha} g_{mj,\alpha}}{2 m_\alpha \omega_\alpha} \delta(\omega - \omega_\alpha) = 2\lambda_{ni,mj} \gamma_{ni,mj} \frac{\omega \gamma_{ni,mj}}{\gamma_{ni,mj}^2 + \omega^2}$$

- Common approximations:
  - Bath dynamics much faster than system dynamics
  - Factorized initial state $\rho_{\text{system+bath}}(t=0) = \rho_{\text{system}}(t=0) \otimes \rho_{\text{bath}}(t=0)$
- Break down for a slow bath and low temperature
- To treat a slow quantum bath: hierarchy of equations of motion method

  (Y. Tanimura, J. Phys. Soc. Jpn. 2006)

Hierarchy of equations of motion

- In the high temperature limit

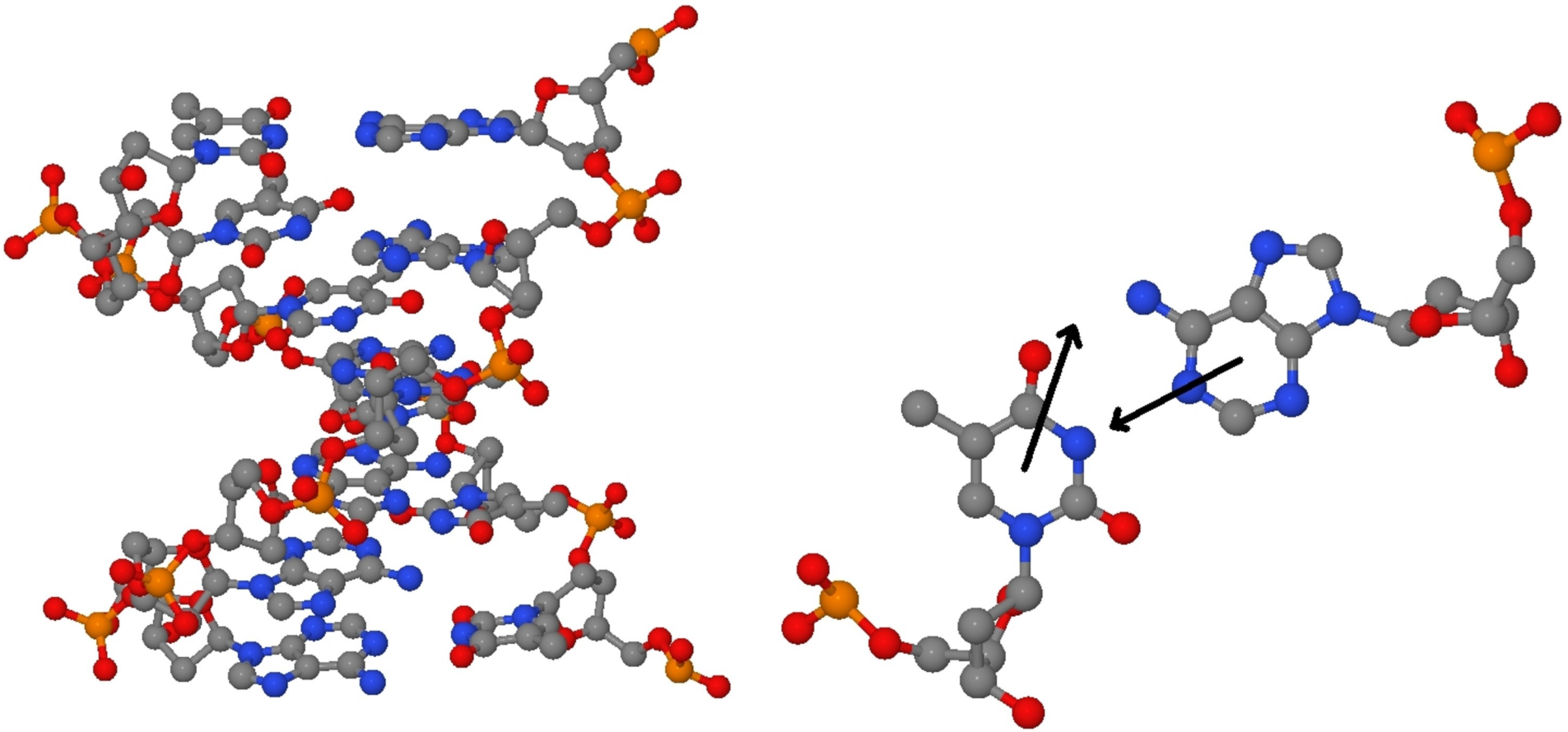
$$L_{ni,mj}(t) = c_{ni,mj} e^{-\gamma_{ni,mj}|t|} \qquad c_{ni,mj} = \lambda_{ni,mj}(-i\gamma_{ni,mj} + \frac{2}{\beta})$$

dissipation

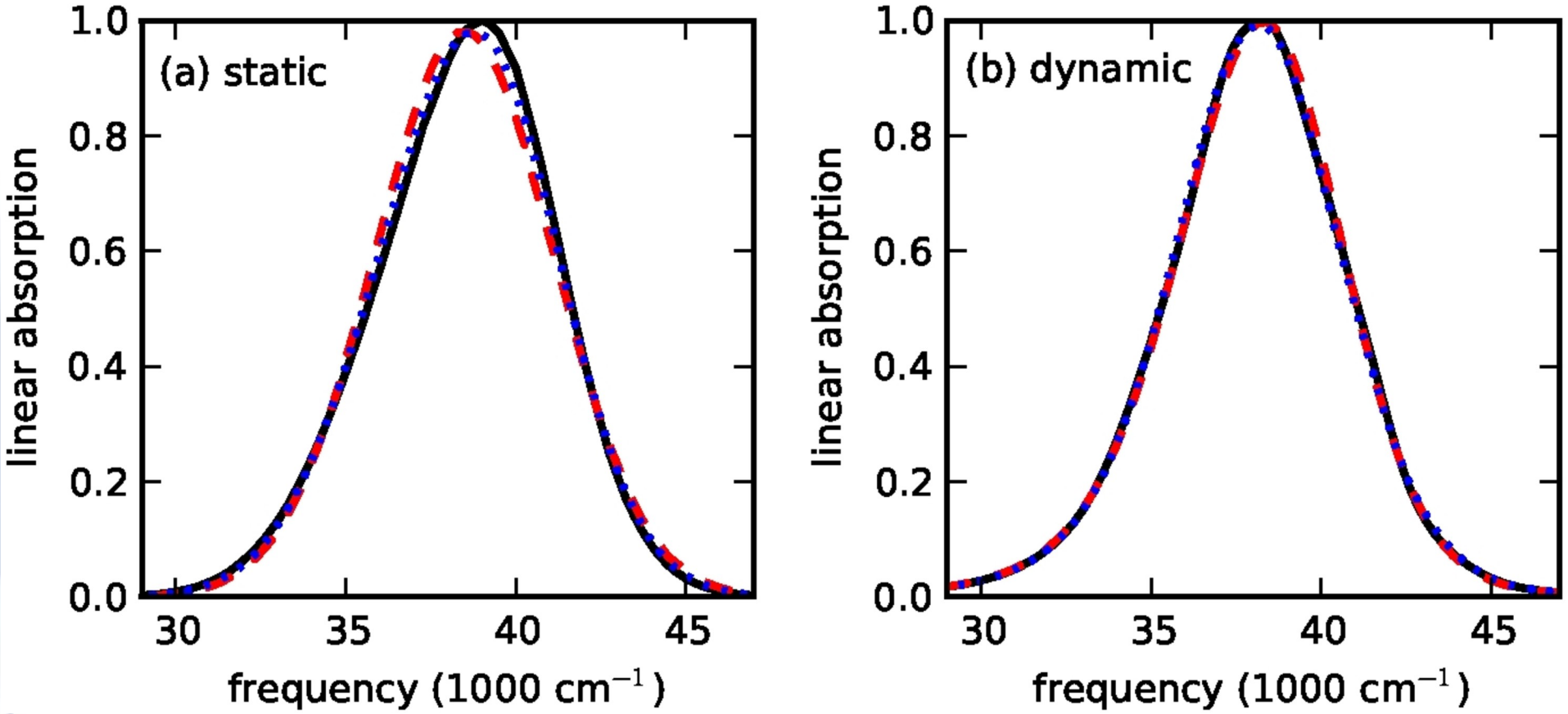
- Equations of motion

$$\dot{\rho}^{\{n\}}(t) = -\left(iH_S^{\times} + \sum_s n_s \gamma\right)\rho^{\{n\}}(t)$$
$$-i\sum_s n_s \left(cV_s\rho^{n_s^-} - c^*\rho^{n_s^-}V_s\right) - i\sum_s V_s^{\times}\rho^{n_s^+}$$

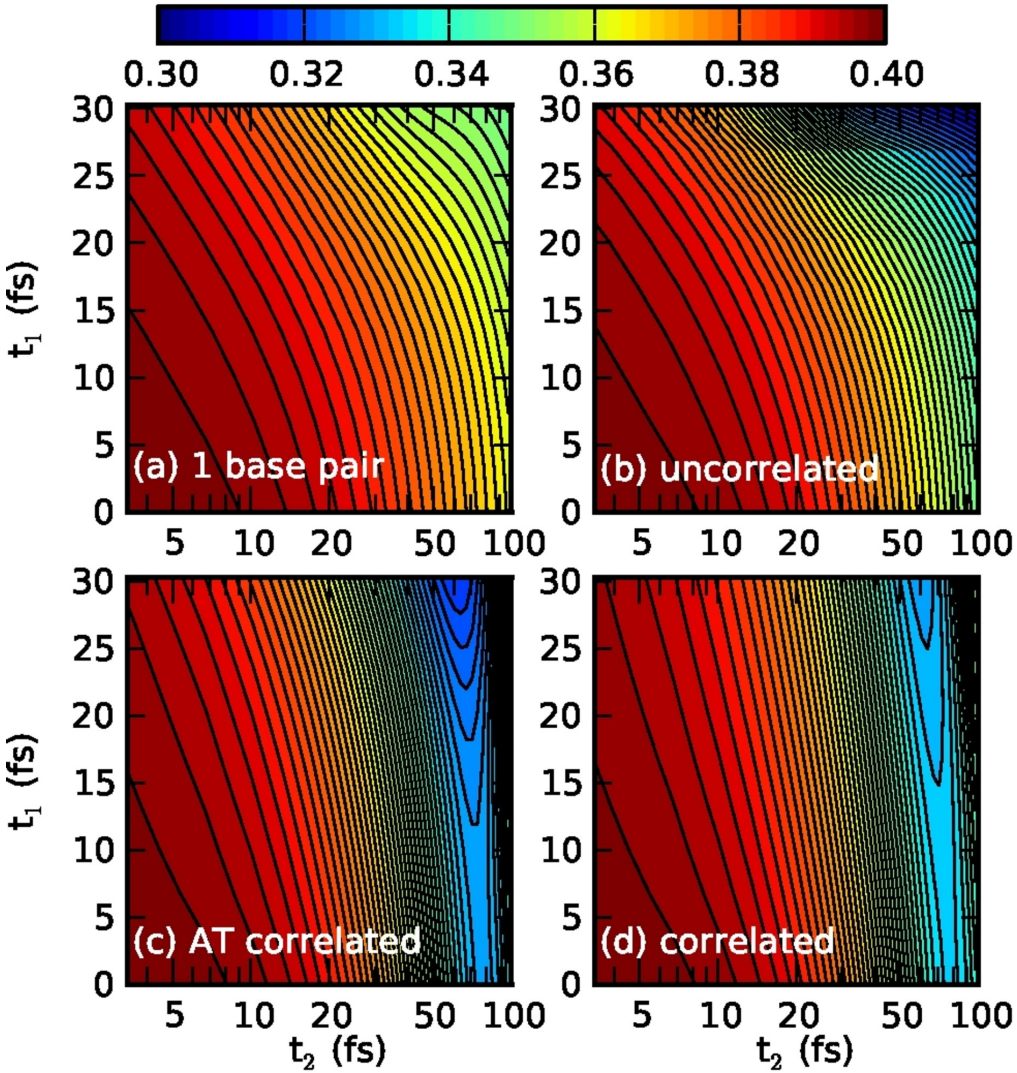
Application: excitons in B-DNA



Linear response



Two-time anisotropy



Conclusions

- Dynamics of coupled oscillators
- Environment
  - Vibrations in peptides: classical environment
  - Low temperature excitons: static environment
  - Room temperature: hierarchy of EOM
- Calculate nonlinear optical observables