

About Omics Group

OMICS Group International through its Open Access Initiative is committed to make genuine and reliable contributions to the scientific community. OMICS Group hosts over 400 leading-edge peer reviewed Open Access Journals and organize over 300 International Conferences annually all over the world. OMICS Publishing Group journals have over 3 million readers and the fame and success of the same can be attributed to the strong editorial board which contains over 30000 eminent personalities that ensure a rapid, quality and quick review process.

About Omics Group conferences

- [OMICS Group](#) signed an agreement with more than 1000 International Societies to make healthcare information Open Access. [OMICS Group](#) Conferences make the perfect platform for global networking as it brings together renowned speakers and scientists across the globe to a most exciting and memorable scientific event filled with much enlightening interactive sessions, world class exhibitions and poster presentations
- Omics group has organised 500 conferences, workshops and national symposium across the major cities including San Francisco, Omaha, Orlando, Raleigh, Santa Clara, Chicago, Philadelphia, United Kingdom, Baltimore, San Antonio, Dubai, Hyderabad, Bangaluru and Mumbai.

Efficiency of Excitation Dynamics and Regulation Ability in Photosynthetic Light Harvesting

L. Valkunas

Institute of Physics, Center for Physical Sciences and
Technology, Vilnius

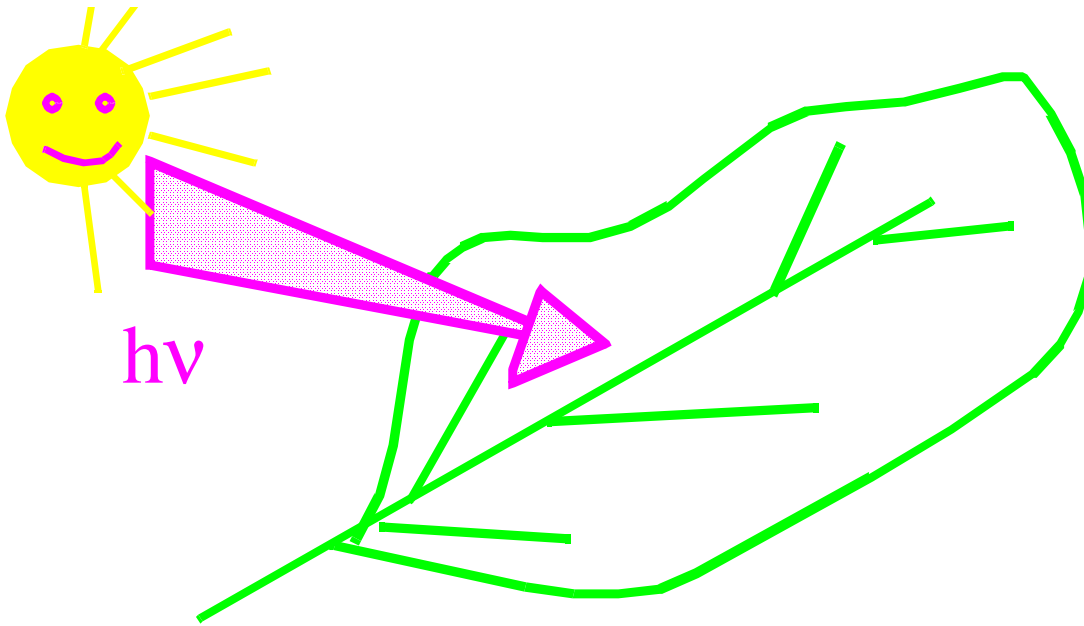
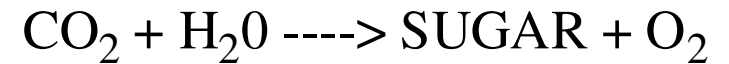
Department of Theoretical Physics, Faculty of Physics,
Vilnius University,
Lithuania



Outline:

- Photosynthesis: introduction
- Sensitivity to the external conditions: NPQ
- Single Molecular Spectroscopy
- Coherences and oscillations in 2D electronic spectroscopy

Photosynthesis



Absorption of Light

Excitation Energy Transfer in the Antenna

Charge Separation in the Reaction Center

10 x World Energy Consumption

SEQUENCE of ULTRAFAST EVENTS

$$k_{\text{loss}} = 10^9 \text{ s}^{-1} \longrightarrow k_{\text{phot}} > 2 \cdot 10^{10} \text{ s}^{-1}$$

or $< 50 \text{ ps}$

Light energy accumulation processes: time scales

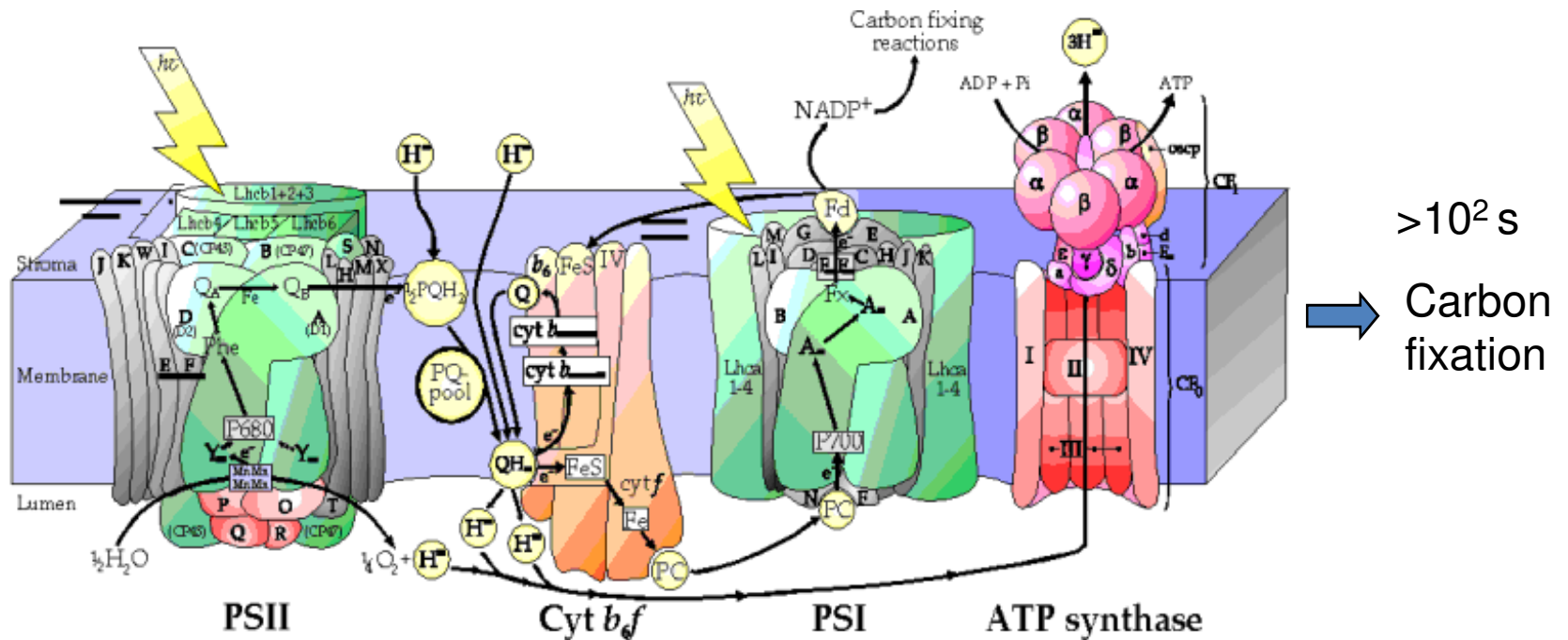
10^{-15} s

10^{-10} s

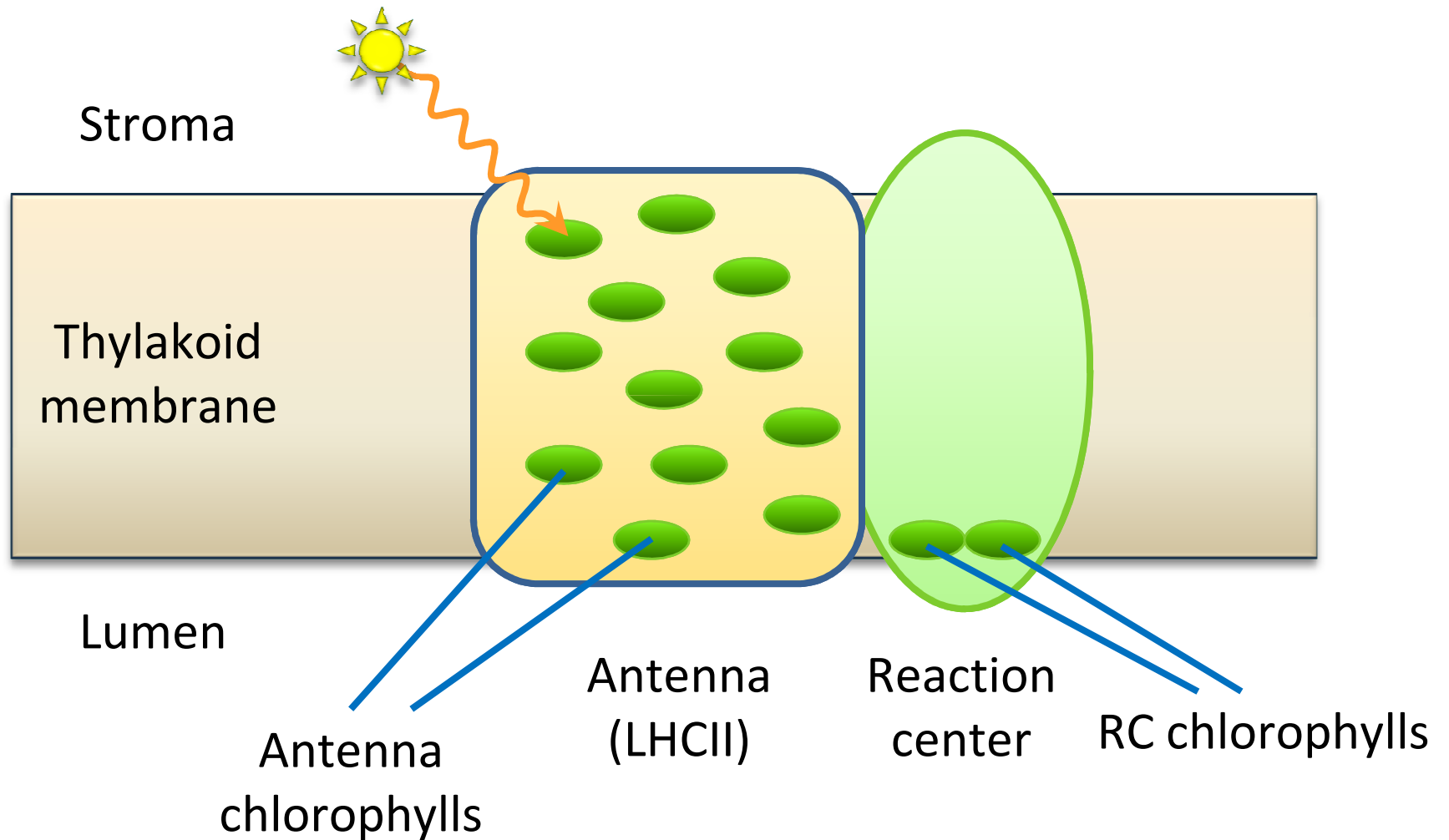
10^{-10} - 10^{-1} s

10^{-3} - 10^1 s

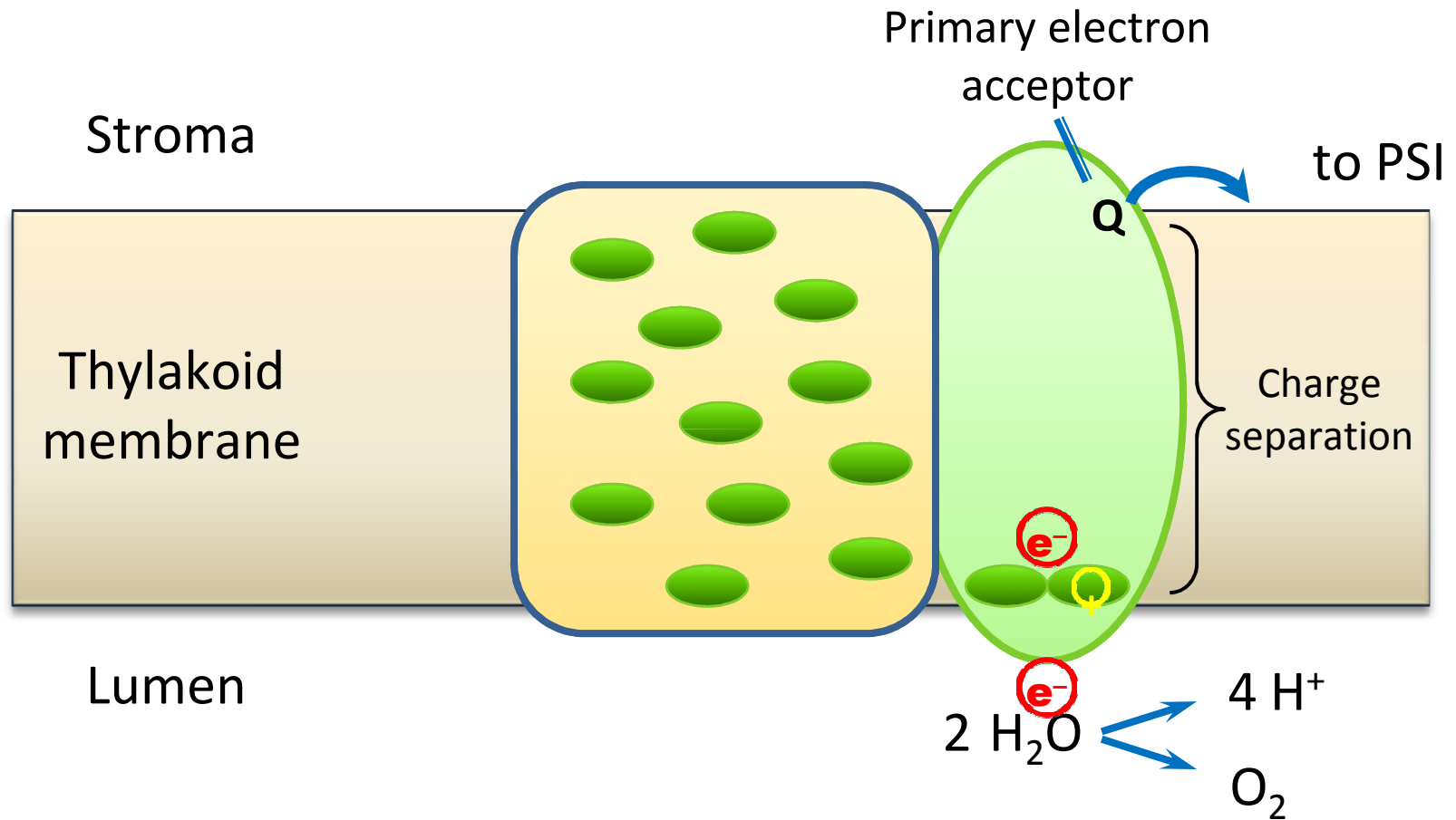
Photon $\longrightarrow$ *Exciton* $\longrightarrow$ *Electron* $\longrightarrow$ *Proton*



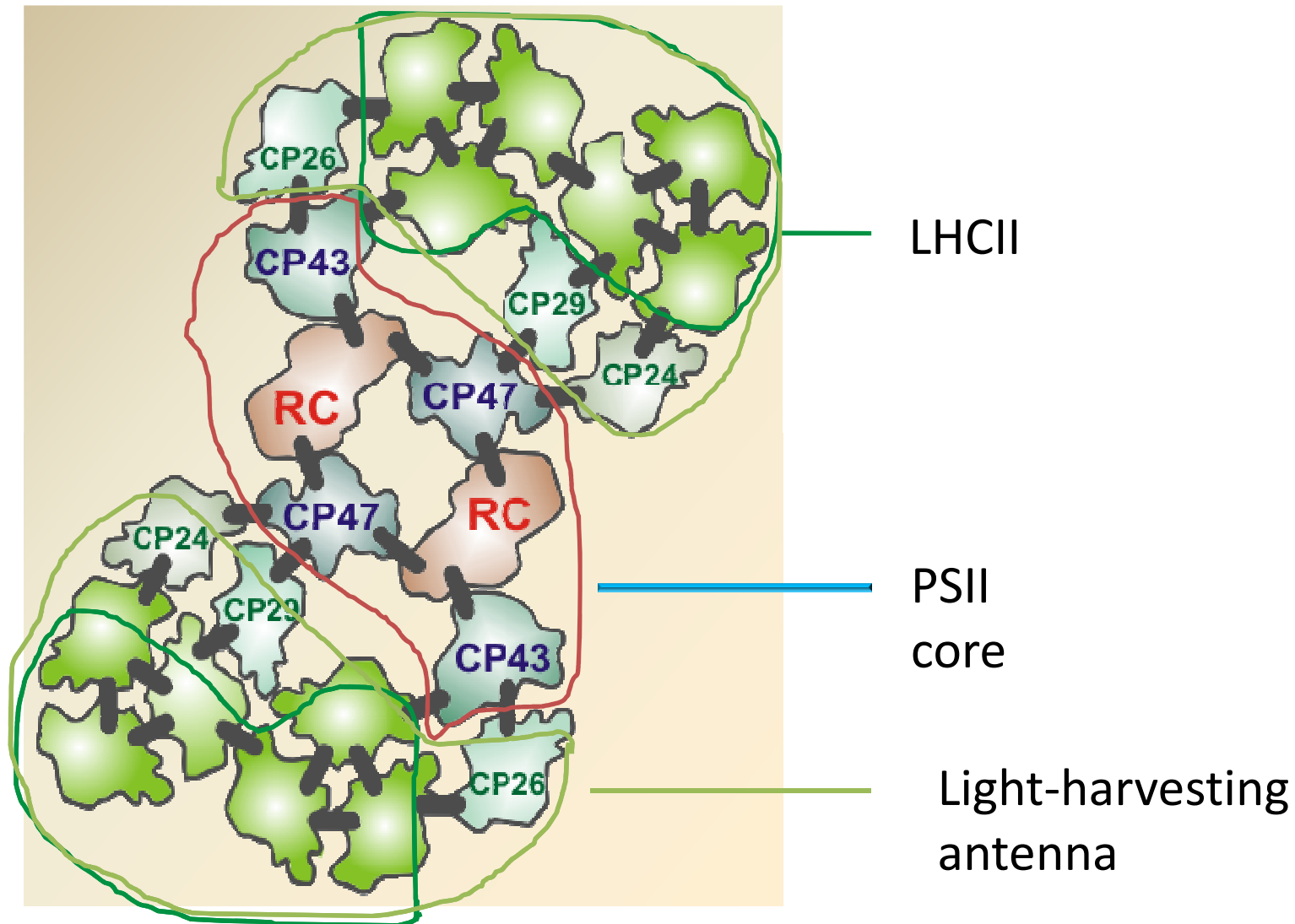
Photosystem II



Photosystem II



PSII



Theory

Balance-type equation

$$\frac{dp_i}{dt} = -kp_i + \sum (p_j W_{ji} - p_i W_{ij}) - \delta_{i,RC} \mathcal{P}_{RC}$$

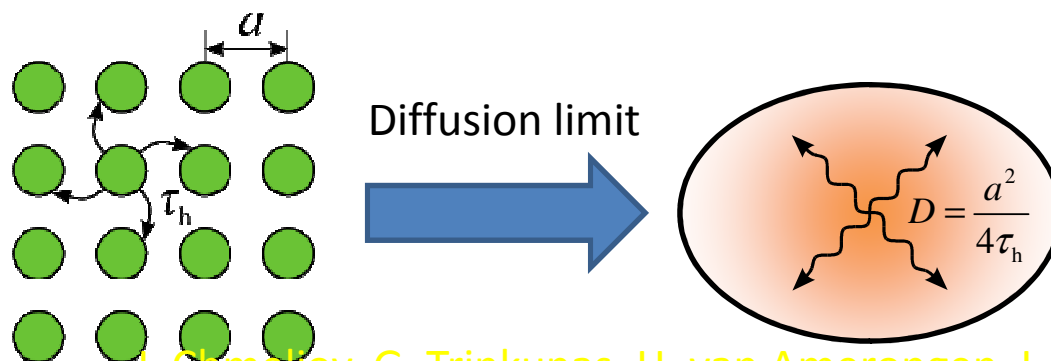
where p_i is the excitation population.

The excitation life-time:

$$\tau = \tau_{mig} + \tau_{del} + \tau_{trap}$$

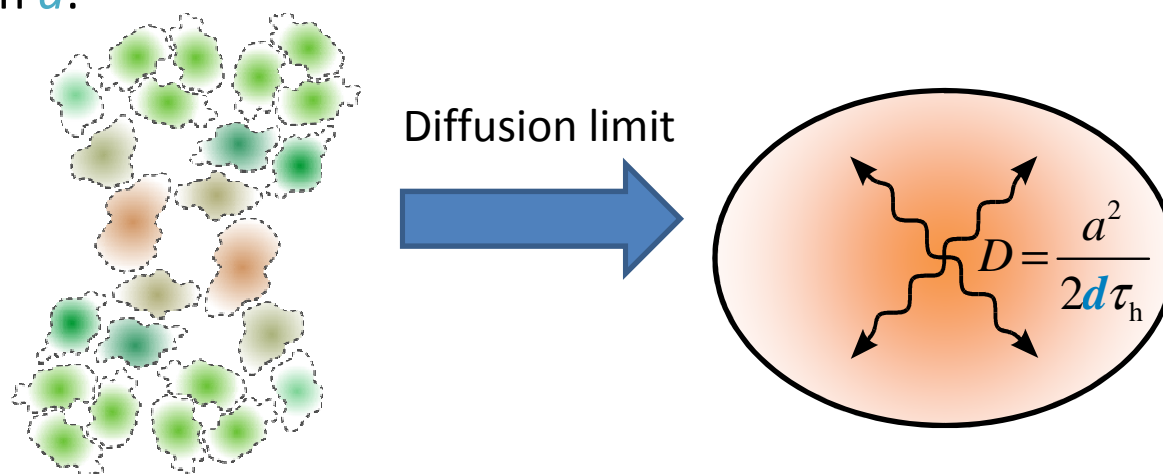
Fluctuating antenna model

- Ideal 2D square lattice:

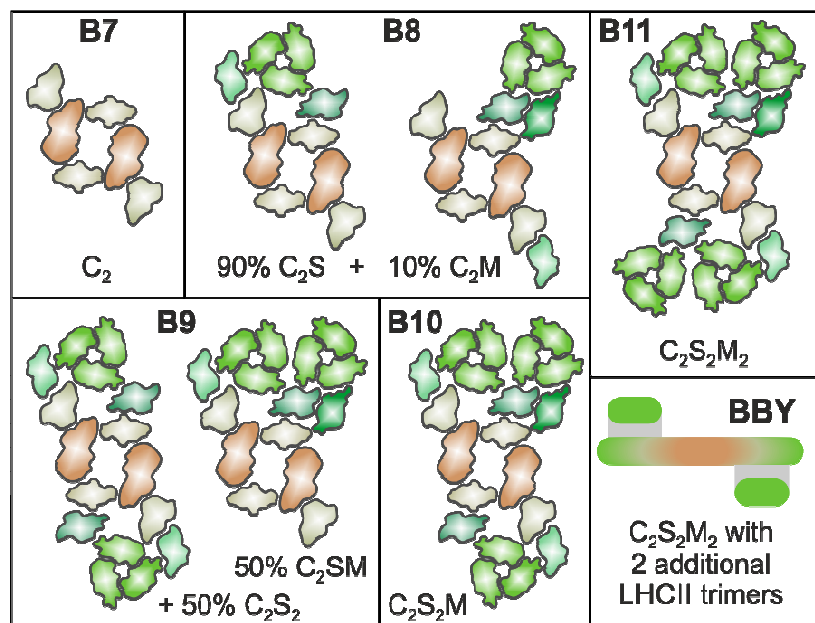
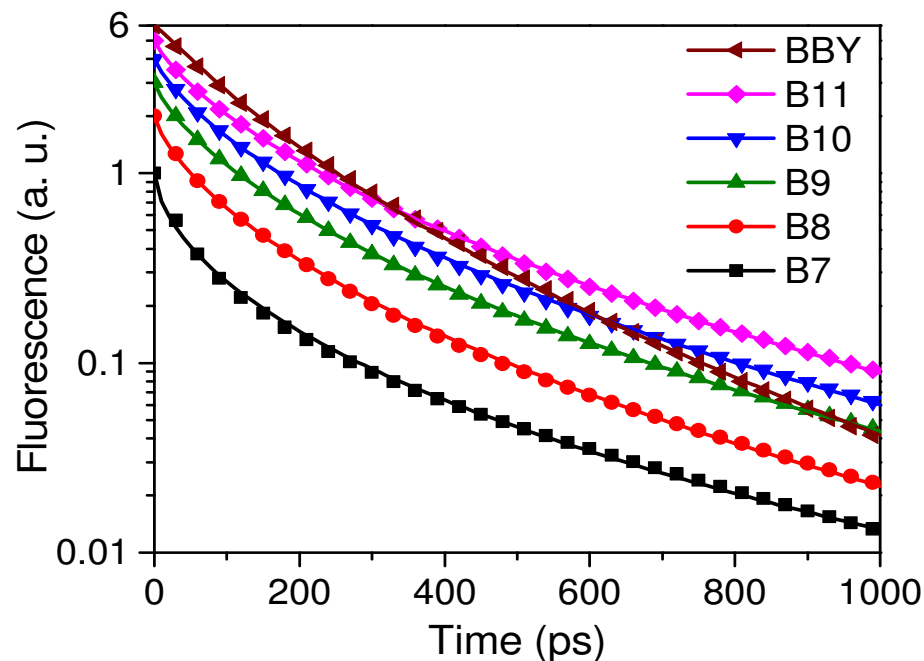


J. Chimeliov, G. Trinkunas, H. van Amerongen, L. Valkunas, *JACS* **136**, 8963-8972, 2014.

- The lack of connectivity at some antenna points may be accounted by *fractional* dimension d :



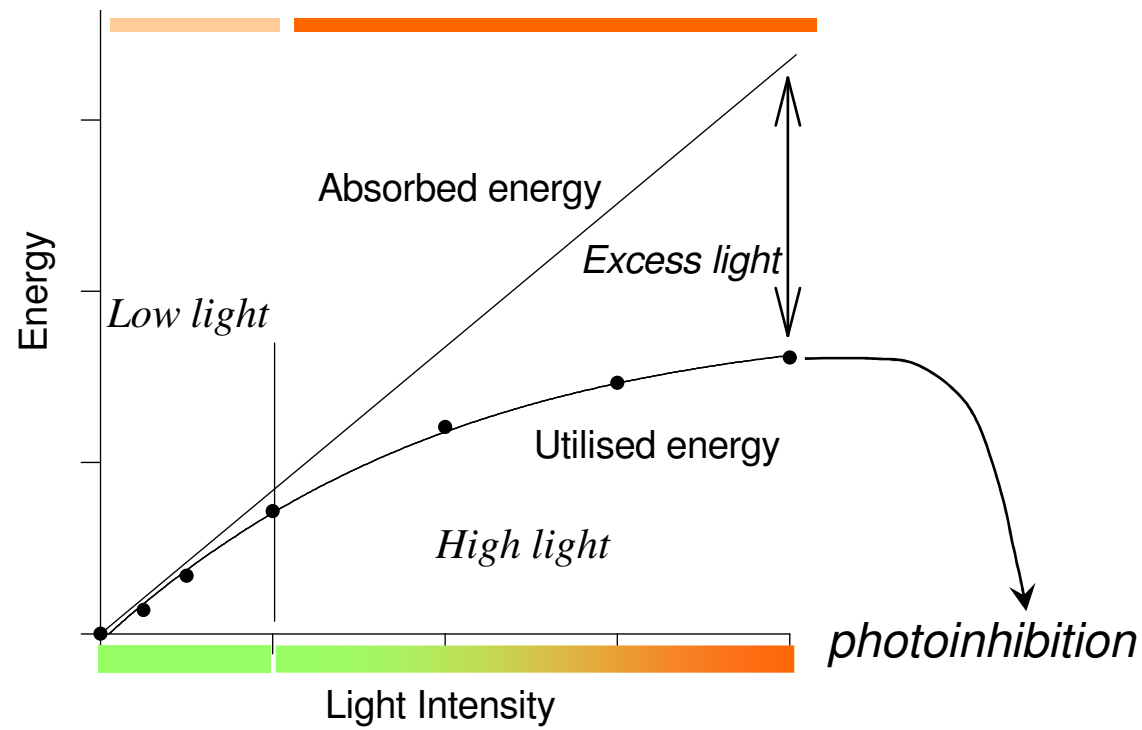
Fluorescence decay kinetics



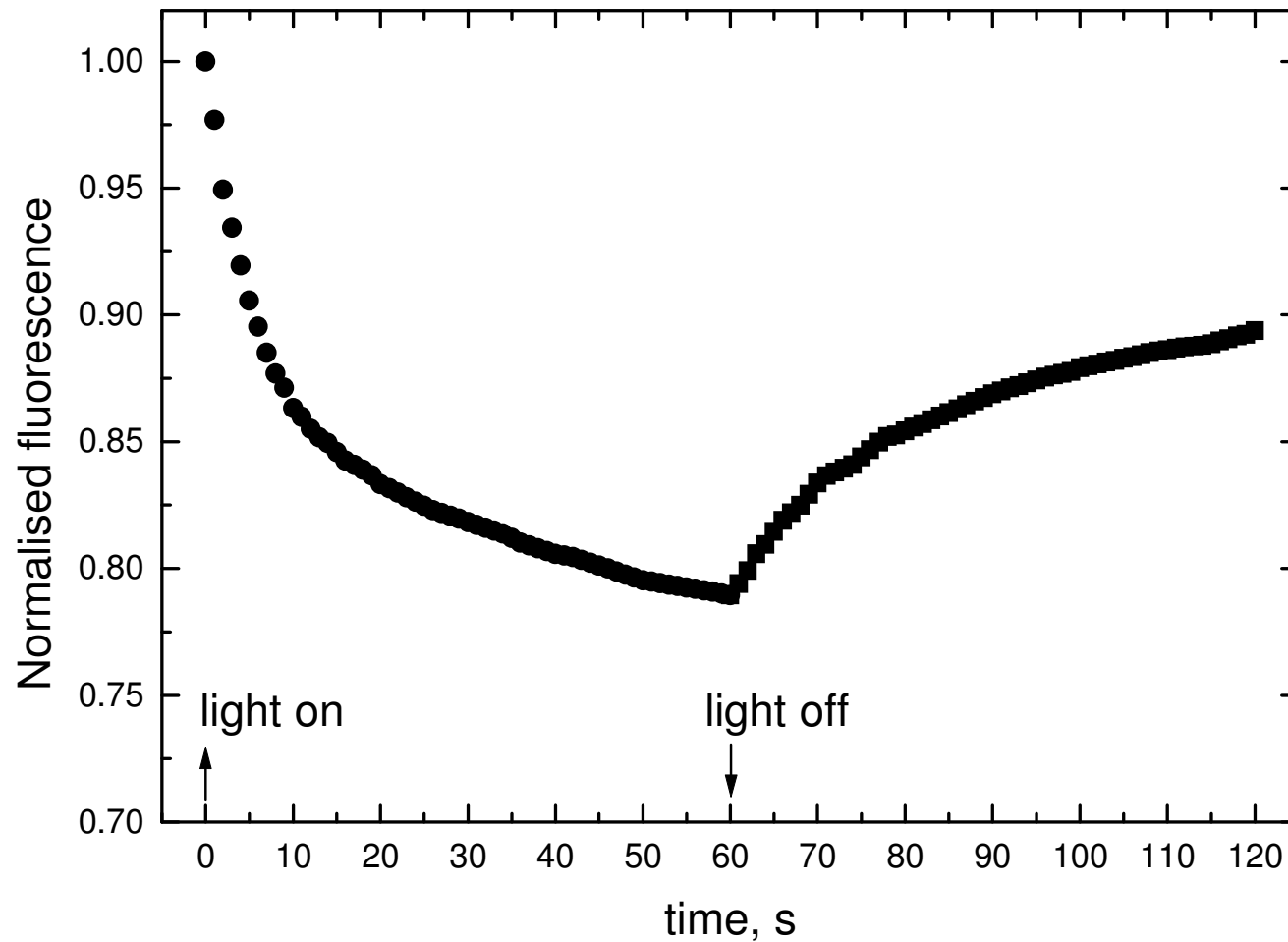
Parameter	B7	B8	B9	B10	B11	BBY
d	1.27	1.57	1.62	1.69	1.69	2.3
$[Dc^{2/d}]^{-1}$ (ms)	0.76	1.17	1.40	1.56	1.66	2.1
$\langle \tau \rangle$ (ps), Model	112	124	142	149	159	147
$\langle \tau \rangle$ (ps), Exper.	109	123	141	148	158	147



The need for photoprotection

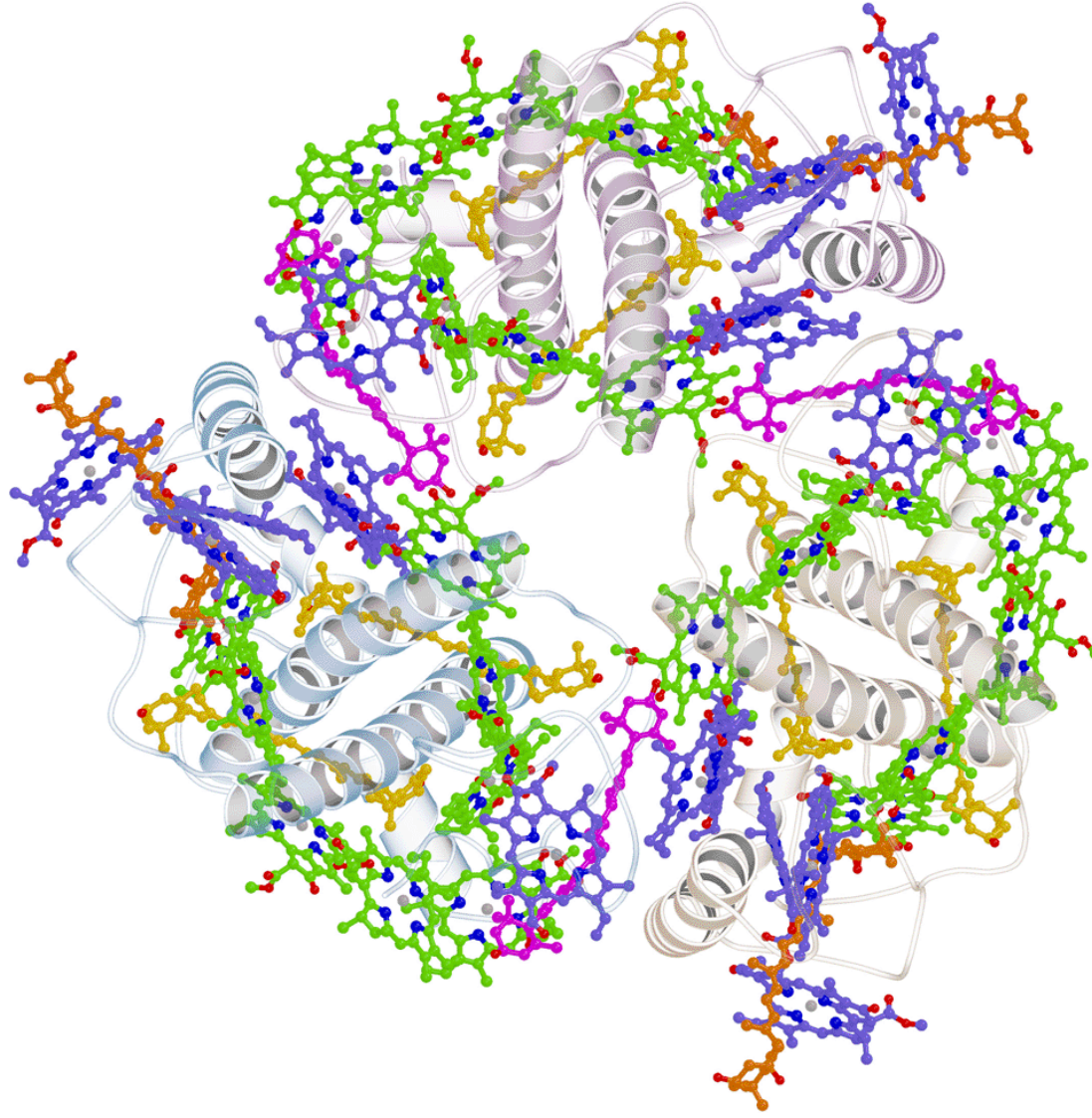


LHCII aggregates

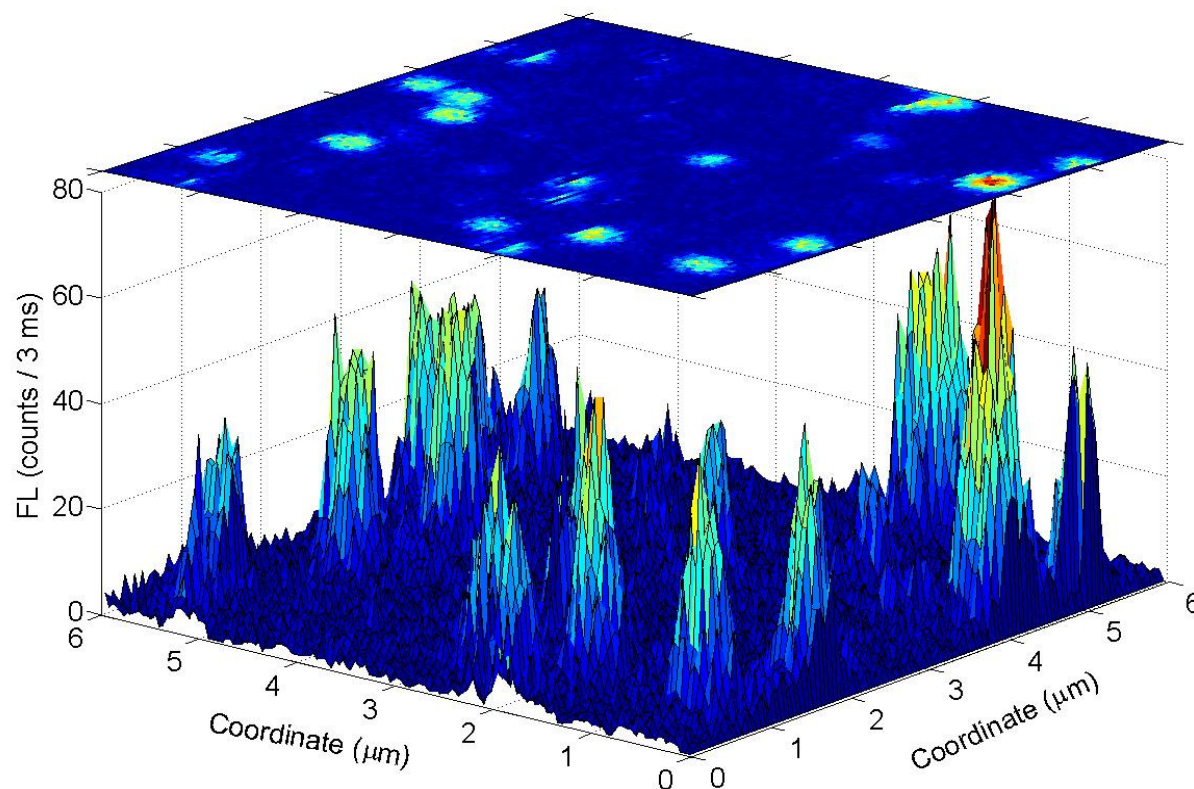


Barzda, V. et al. *Biophys. J.* **2001**, 80, 2409-2421.

LHCII trimer



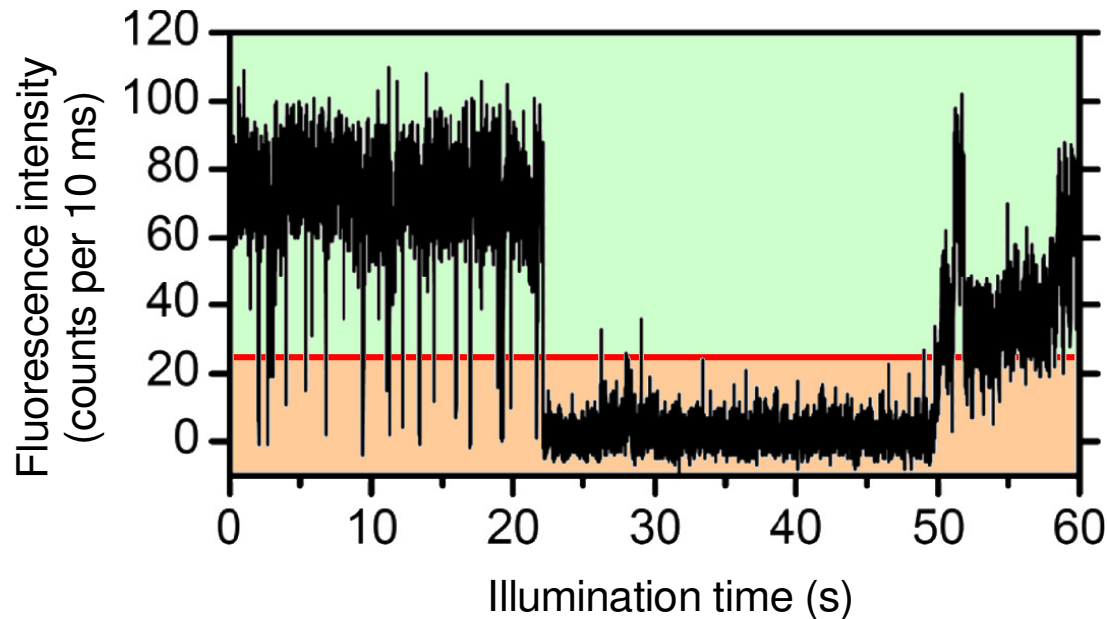
Fluorescence from single LHCII



T.P.J. Krüger, C. Iliaia, and R. van Grondelle, *Fluorescence Intermittency from the Main Plant Light-Harvesting Complex: Resolving Shifts between Intensity Levels*, J. Phys. Chem. B **115**, 5071 (2011).

T.P.J. Krüger, C. Iliaia, L. Valkunas, and R. van Grondelle, *Fluorescence Intermittency from the Main Plant Light-Harvesting Complex: Sensitivity to the Local Environment*, J. Phys. Chem. B **115**, 5083 (2011).

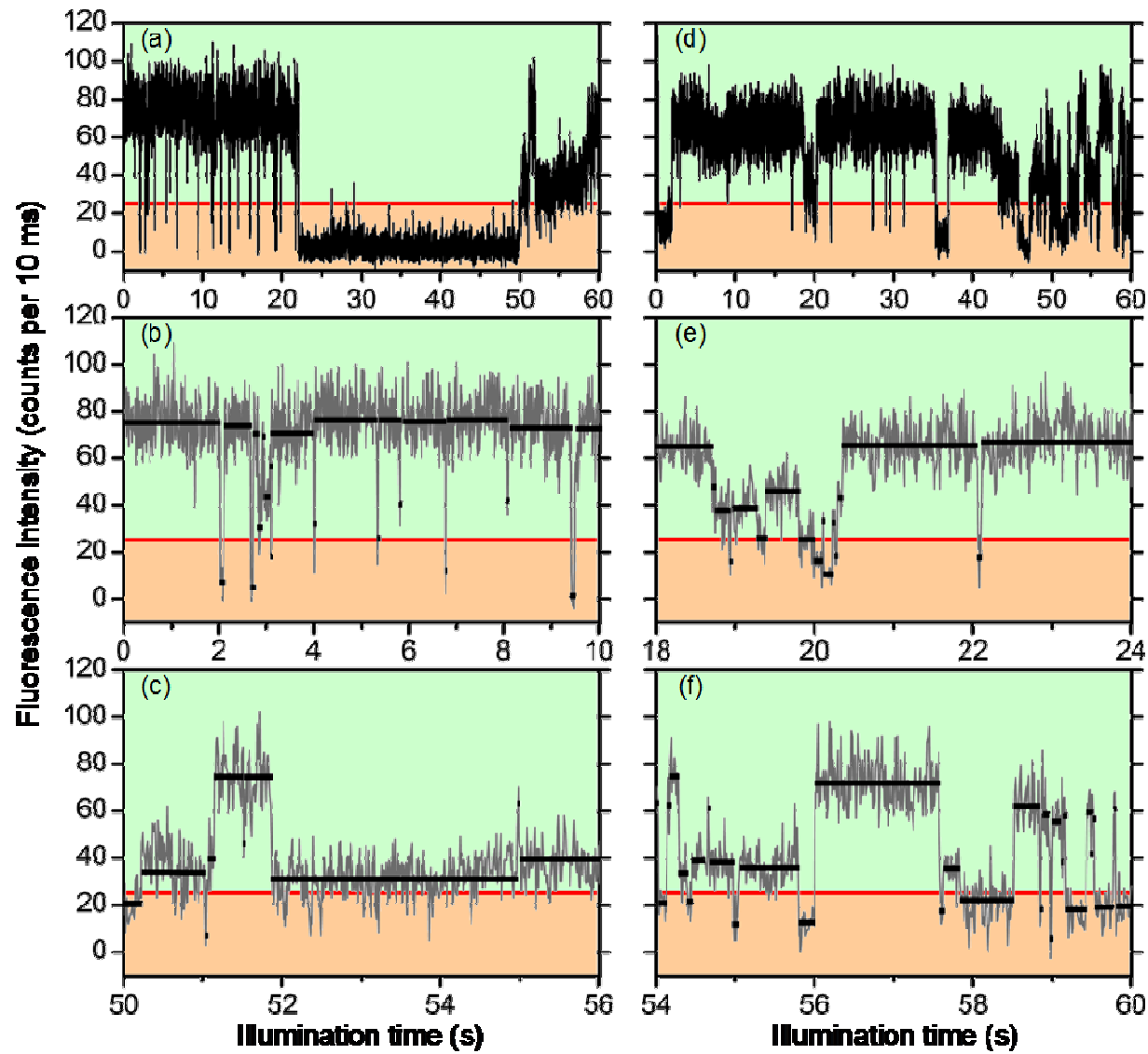
Fluorescence from single LHCII



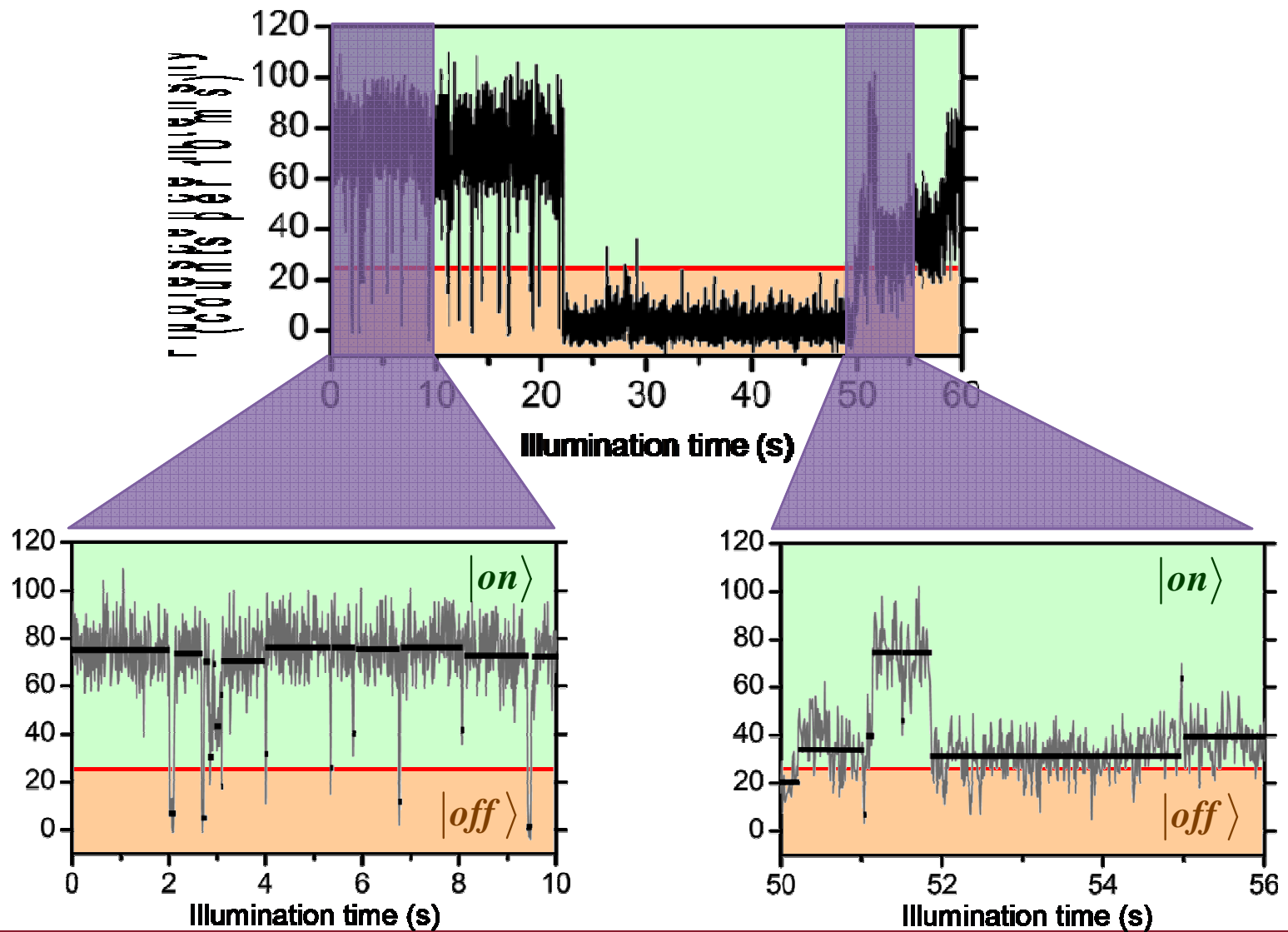
T.P.J. Krüger, C. Iliaia, and R. van Grondelle, *Fluorescence Intermittency from the Main Plant Light-Harvesting Complex: Resolving Shifts between Intensity Levels*, J. Phys. Chem. B **115**, 5071 (2011).

T.P.J. Krüger, C. Iliaia, L. Valkunas, and R. van Grondelle, *Fluorescence Intermittency from the Main Plant Light-Harvesting Complex: Sensitivity to the Local Environment*, J. Phys. Chem. B **115**, 5083 (2011).

Fluorescence traces



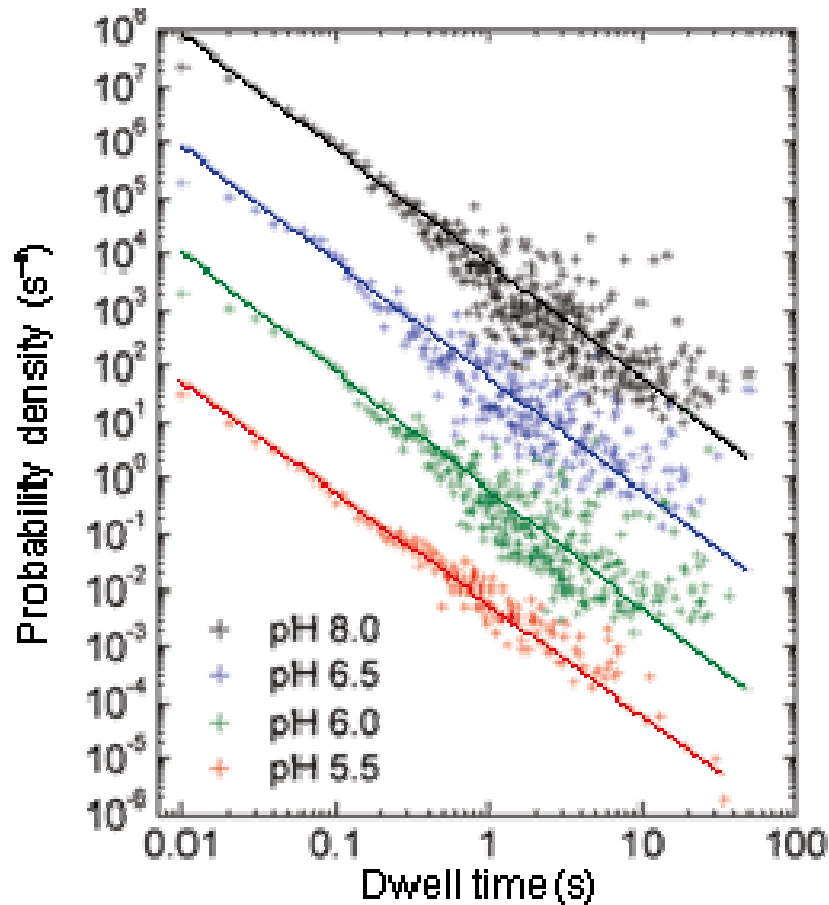
Fluorescence traces



Distributions of the lifetimes

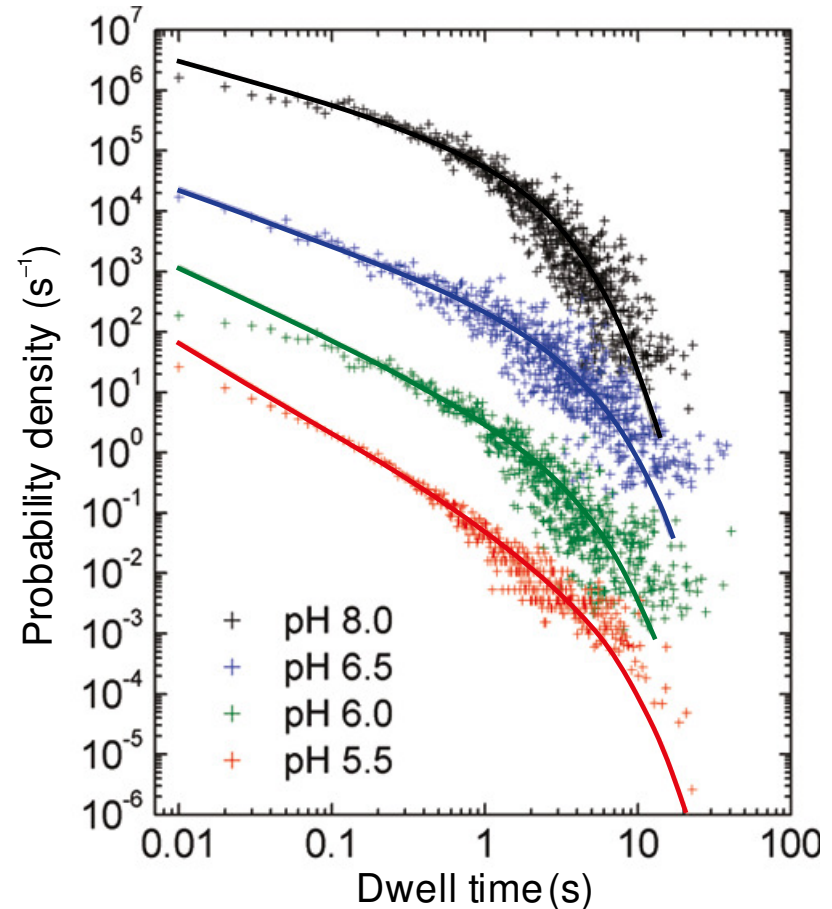
Dark state:

$$P(t_{\text{off}}) \propto t_{\text{off}}^{-m_{\text{off}}}$$

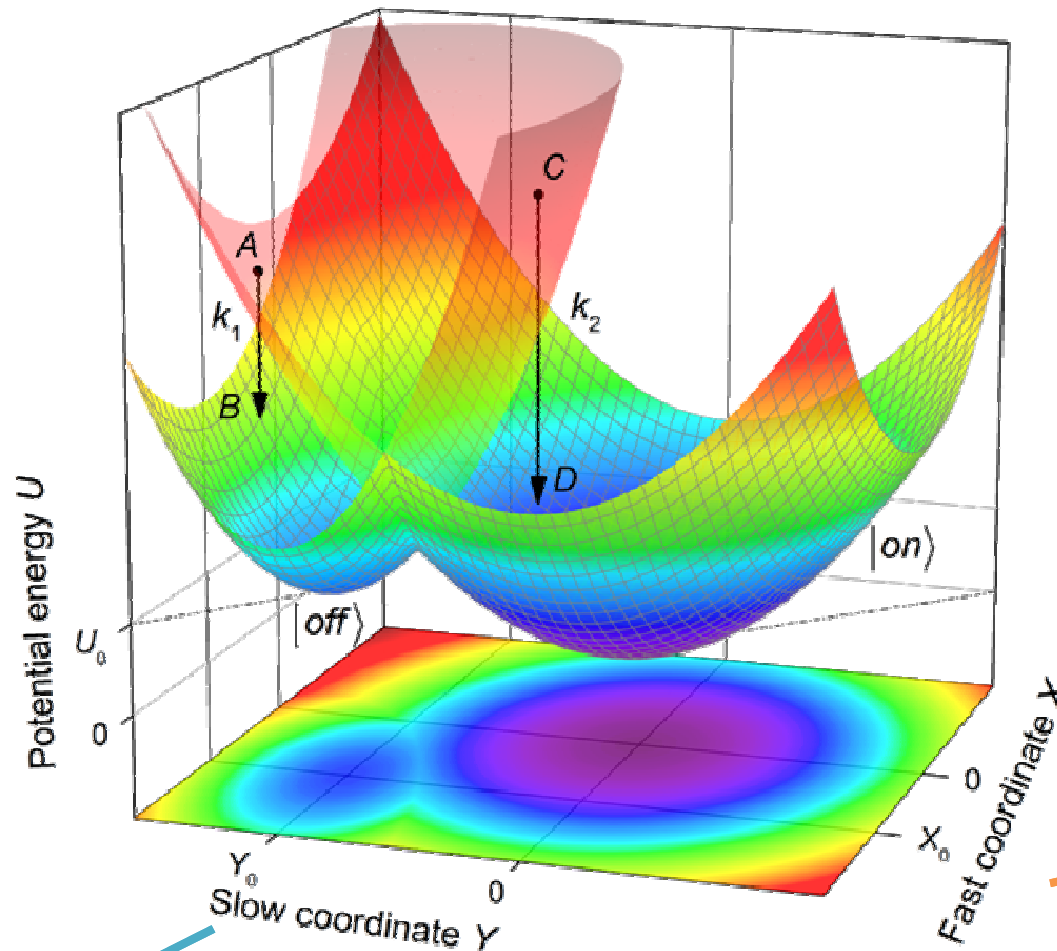


Bright state:

$$P(t_{\text{on}}) \propto t_{\text{on}}^{-m_{\text{on}}} \cdot \exp(-t_{\text{on}}/\tau_{\text{on}})$$



Potential surfaces



Determines slow structural conformations of the protein

$$\begin{cases} A \rightarrow B: & k_1 \\ C \rightarrow D: & k_2 \\ B \rightarrow A: & k_2 \exp\left(-\frac{\Delta U(X_A, Y_A)}{k_B T}\right) \\ D \rightarrow C: & k_1 \exp\left(-\frac{\Delta U(X_C, Y_C)}{k_B T}\right) \end{cases}$$

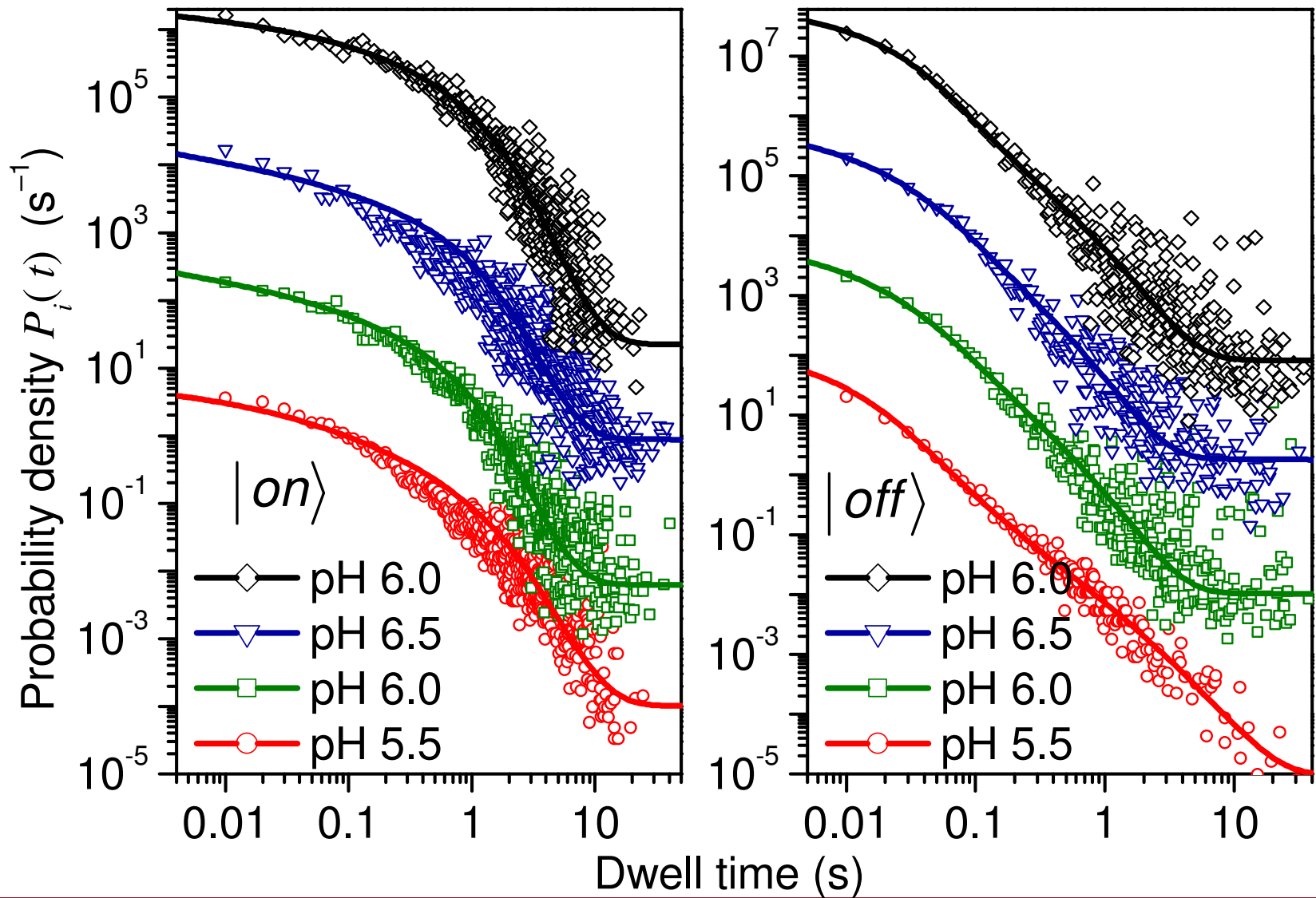
$$k^{(\text{ef})} = k \cdot \exp\left(-\frac{|\Delta U(X, Y)|}{\hbar \omega_0}\right)$$

Describes fast molecular vibrations

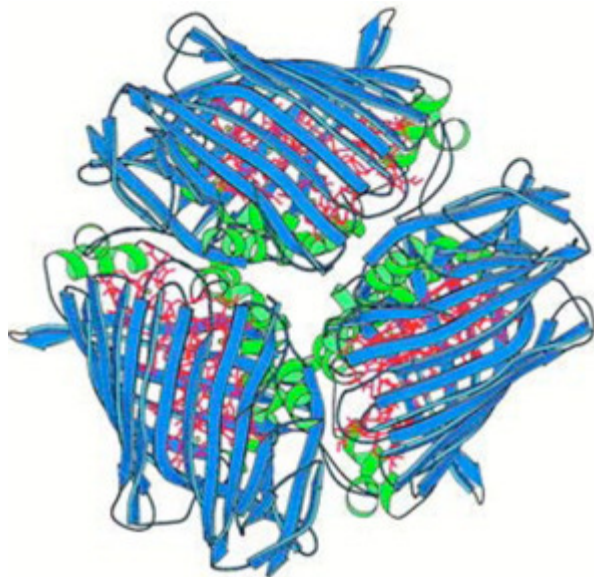
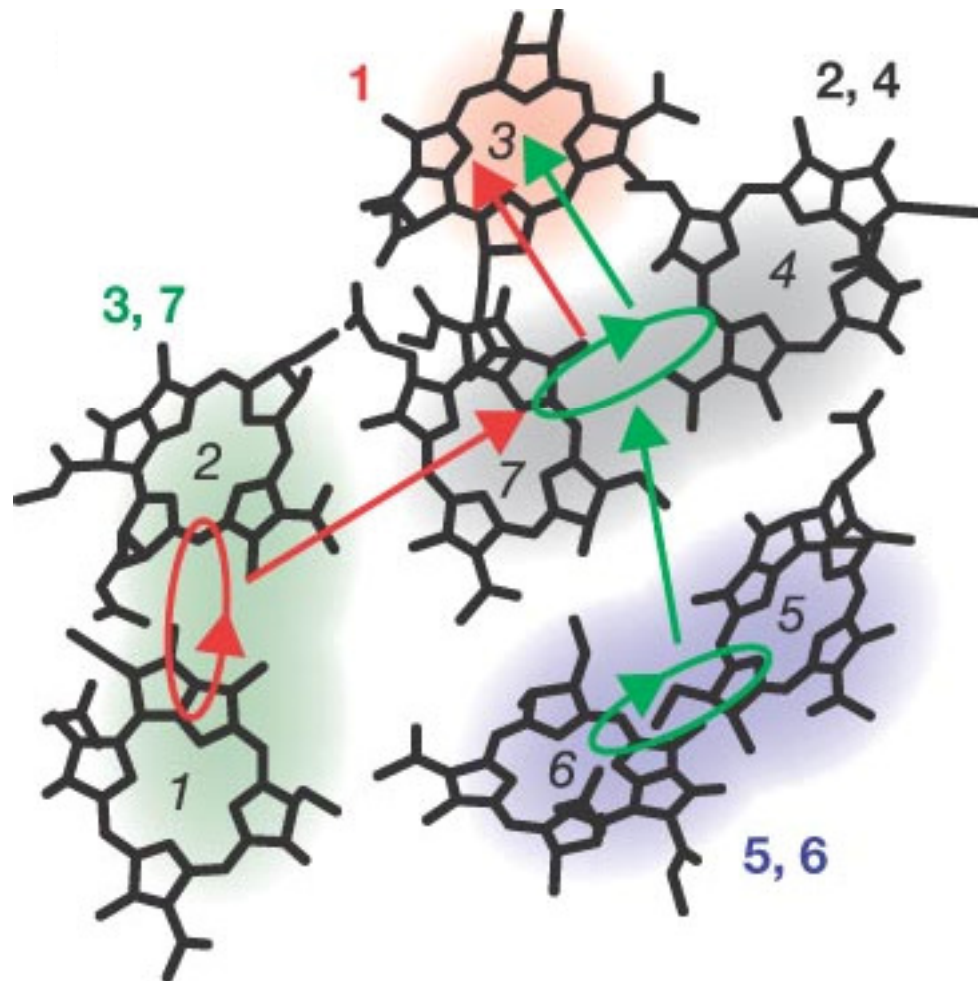
$$U_{|on\rangle}(X, Y) = \frac{1}{2} \lambda_1 X^2 + \frac{1}{2} \gamma_1 Y^2,$$

$$U_{|off\rangle}(X, Y) = \frac{1}{2} \lambda_2 (X - X_0)^2 + \frac{1}{2} \gamma_2 (Y - Y_0)^2 + U_0$$

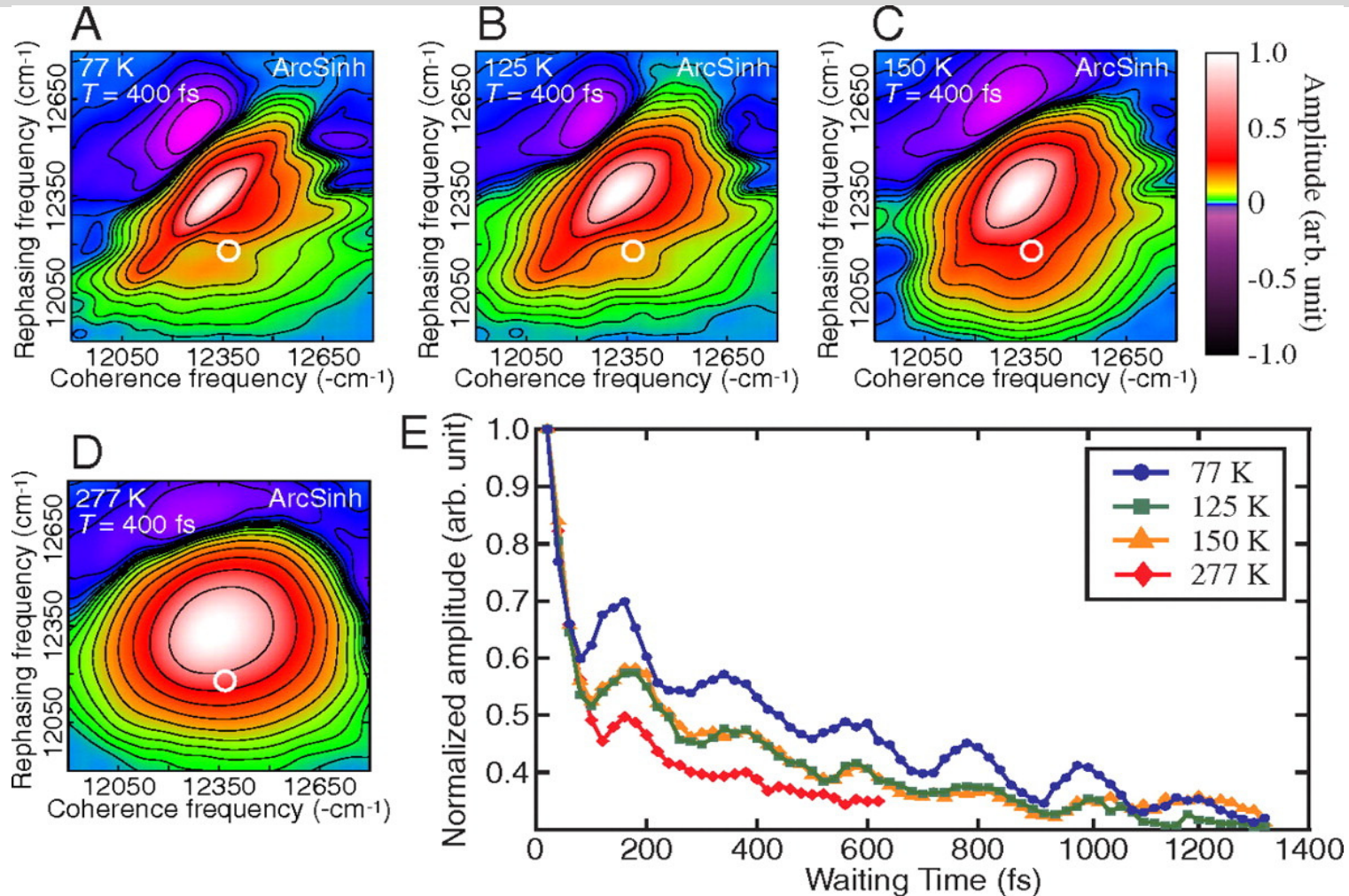
Modeling results



FMO



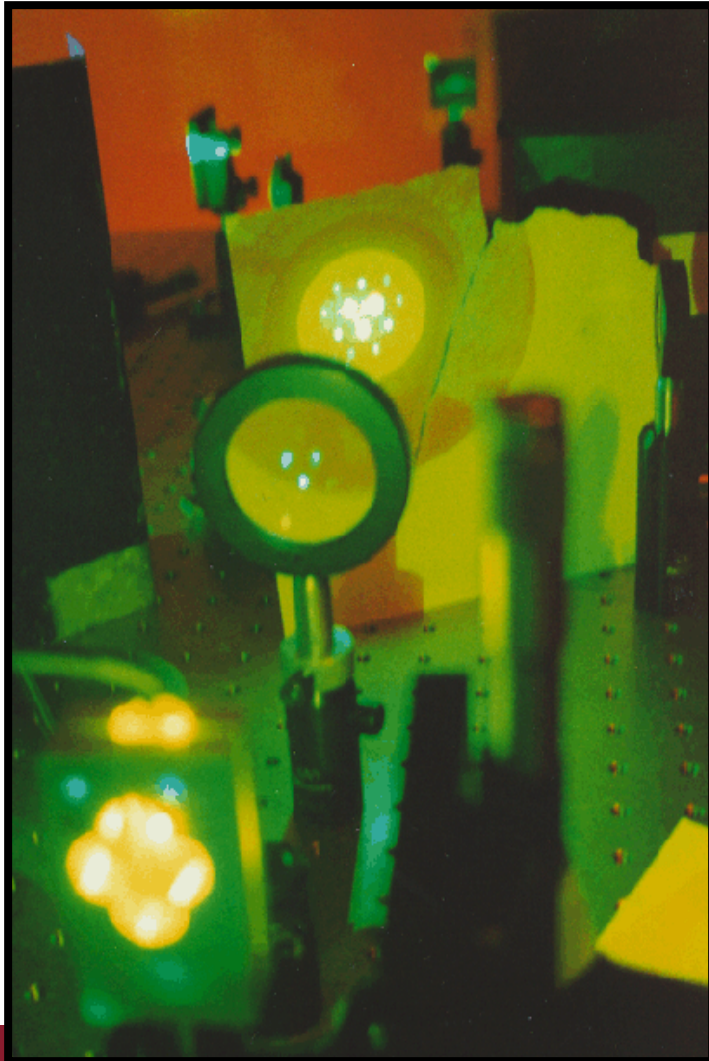
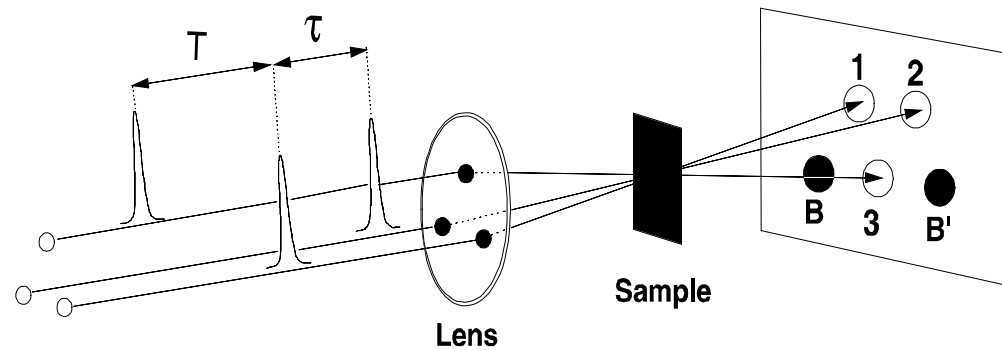
A “must have” slide



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

G. Panitchayangkoon et al. PNAS **107**, 12766-12770 (2010)

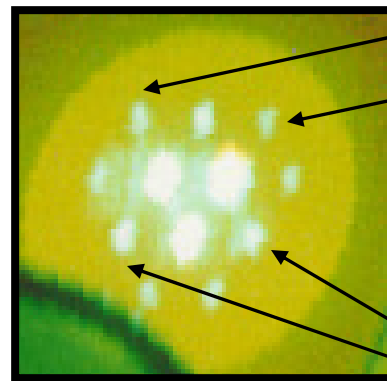
Generating and Measuring Integrated Photon Echo Signals



Two Pulse Echoes:

$$2k_1 - k_2$$

$$k_1 - 2k_2$$

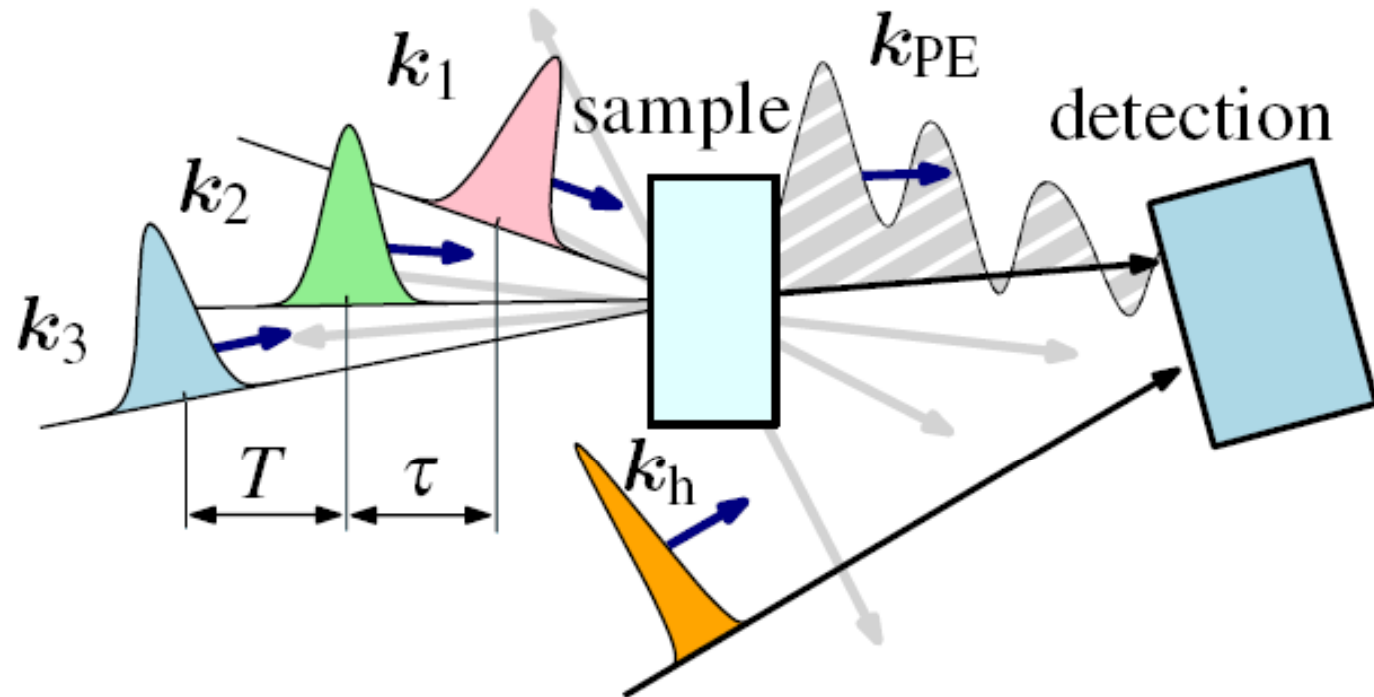


Three Pulse Echoes:

$$k_3 \pm (k_1 - k_2)$$

2D photon echo spectroscopy

Scheme



$$P^{(3)}(\mathbf{r}, t) = \int_0^\infty dt_3 \int_0^\infty dt_2 \int_0^\infty dt_1 S^{(3)}(t_3, t_2, t_1) \times \\ \times E(\mathbf{r}, t - t_3) E(\mathbf{r}, t - t_3 - t_2) E(\mathbf{r}, t - t_3 - t_2 - t_1).$$

Perturbation expansion

- Perturbations of the density matrix

$$i\hbar \frac{d\rho}{dt} = [(\hat{H}_S + H_1(t)), \rho] \equiv L_S \rho + L_1(t) \rho$$
$$\hat{H}' = -\hat{\mu} \cdot \mathbf{E}(\mathbf{r}, t) \Rightarrow L_1(t) = V \cdot E(t)$$

make series expansion for the density matrix

$$\rho = \rho^{(0)} + \rho_t^{(1)} + \dots + \rho_t^{(n)} + \dots$$

calculate expectation values

$$A^{(n)} = \text{Tr}(\hat{A} \rho_t^{(n)})$$

$$\rho^{(n)}(t) = \left(-\frac{i}{\hbar}\right)^n \int_0^t d\tau_n \int_0^{\tau_n} d\tau_{n-1} \dots \int_0^{\tau_2} d\tau_1$$
$$\times G(t - \tau_n) L_1(\tau_n) G(\tau_n - \tau_{n-1}) L_1(\tau_{n-1}) \dots G(\tau_2 - \tau_1) L_1(\tau_1) G(\tau_1) \hat{\rho}(0)$$

Weakly driven quantum dynamics

- Perturbations of the density matrix

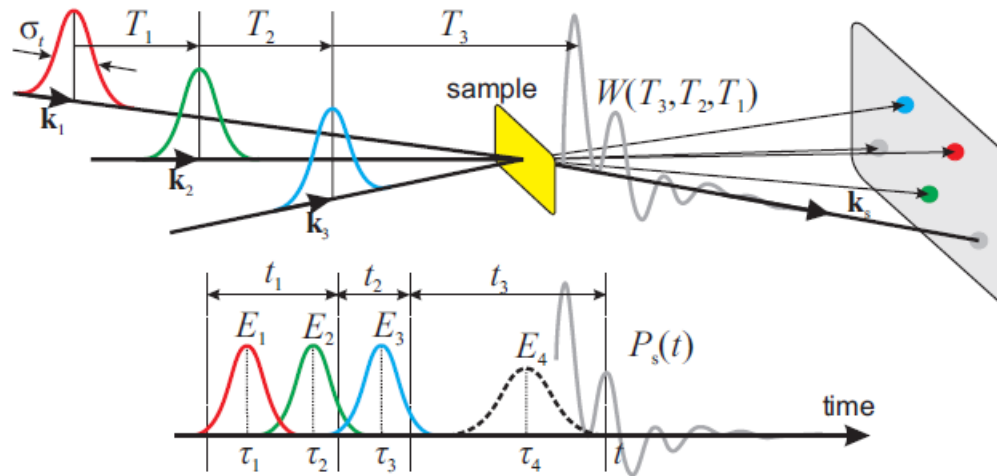
$$\rho = \rho^{(0)} + \rho_t^{(1)} + \dots + \rho_t^{(n)} + \dots$$

$$\begin{aligned} \rho^{(n)}(t) = & \left(-\frac{i}{\hbar}\right)^n \int_0^t d\tau_n \int_0^{\tau_n} d\tau_{n-1} \dots \int_0^{\tau_2} d\tau_1 \\ & \times G(t - \tau_n) L_1(\tau_n) G(\tau_n - \tau_{n-1}) L_1(\tau_{n-1}) \dots G(\tau_2 - \tau_1) L_1(\tau_1) G(\tau_1) \hat{\rho}(0) \end{aligned}$$

- Non-linear response function (optical excitation)

$$\begin{aligned} P^{(n)}(t) = & \int_0^\infty dt_n \int_0^\infty dt_{n-1} \dots \int_0^\infty dt_1 \\ & \times S^{(n)}(t_n, t_{n-1}, \dots, t_2, t_1) \\ & \times E(t - t_n) E(t - t_n - t_{n-1}) \dots E(t - t_n - t_{n-1} - \dots - t_1) \\ S^{(n)}(t_n, t_{n-1}, \dots, t_2, t_1) = & Tr[\mu | G(t_n) V G(t_{n-1}) V \dots G(t_2) V \rho^\infty] \end{aligned}$$

Classification of third order techniques:



Possible phase-matching directions:

$$\mathbf{k}_s = u_1 \mathbf{k}_1 + u_2 \mathbf{k}_2 + u_3 \mathbf{k}_3$$

Assuming that each laser pulse interacts with the system only once, we get 4 linearly independent signals

$$\mathbf{k}_I = -\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3$$

rephasing

non-rephasing

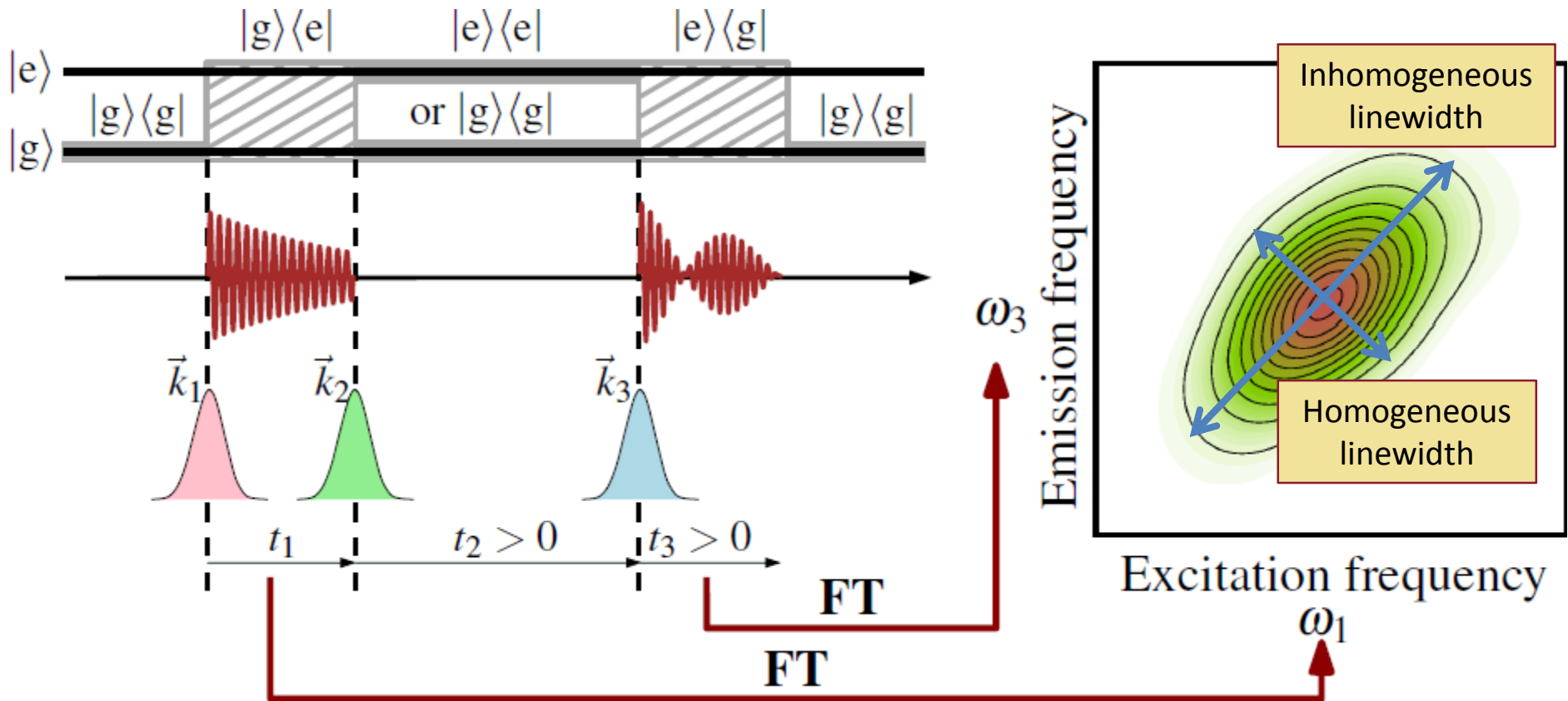
$$\mathbf{k}_{II} = +\mathbf{k}_1 - \mathbf{k}_2 + \mathbf{k}_3$$

double quantum coherence

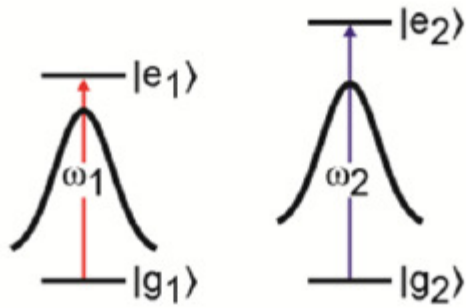
$$\mathbf{k}_{III} = +\mathbf{k}_1 + \mathbf{k}_2 - \mathbf{k}_3$$

These are detected at different directions

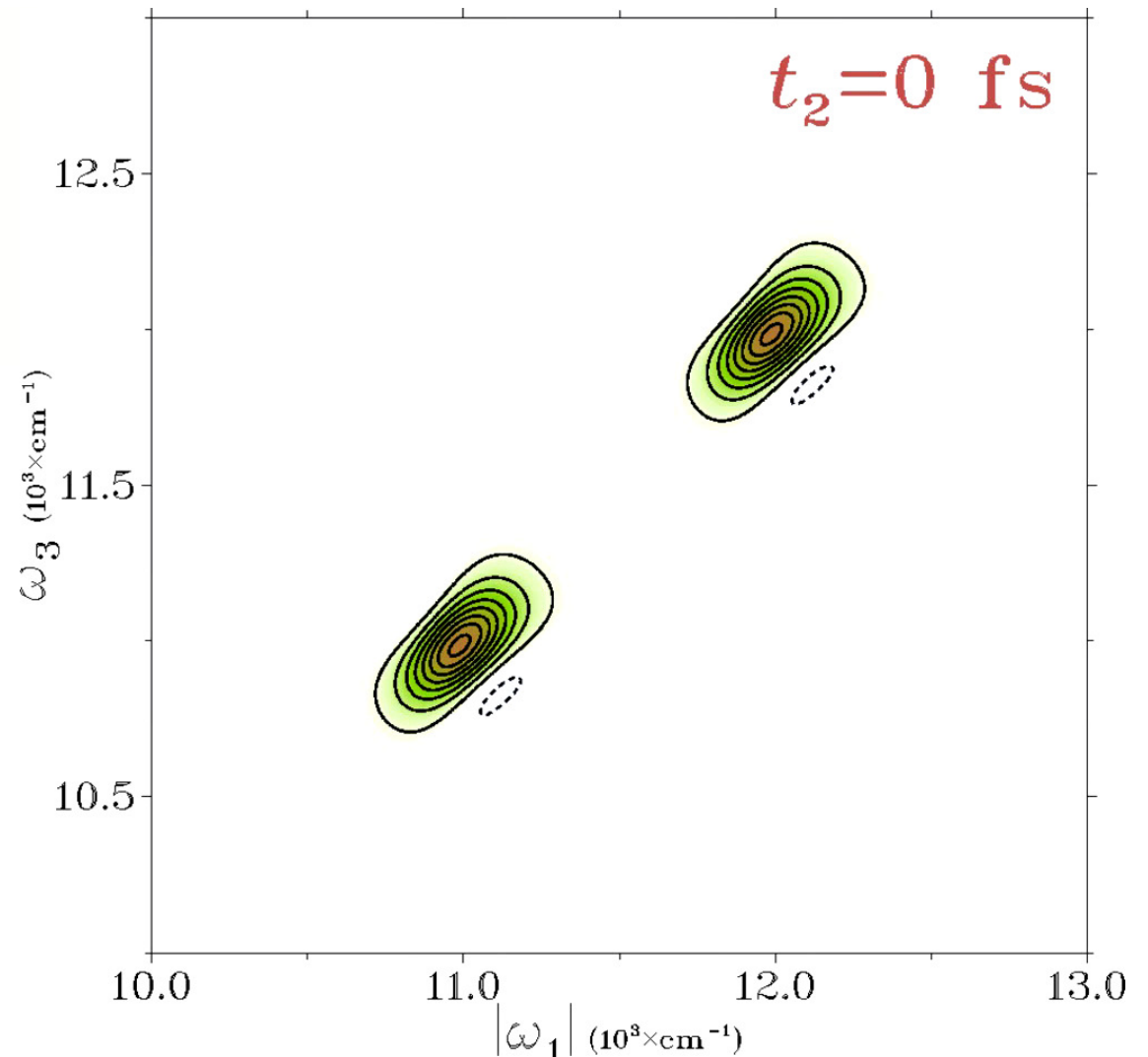
Two-level system



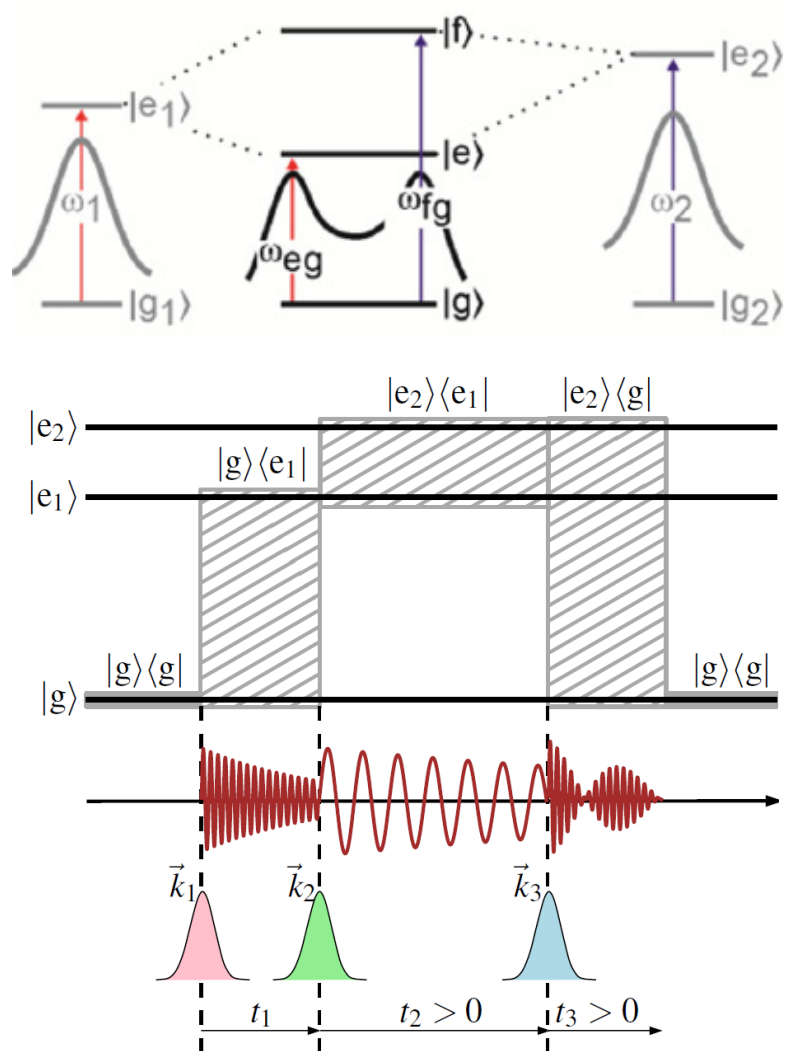
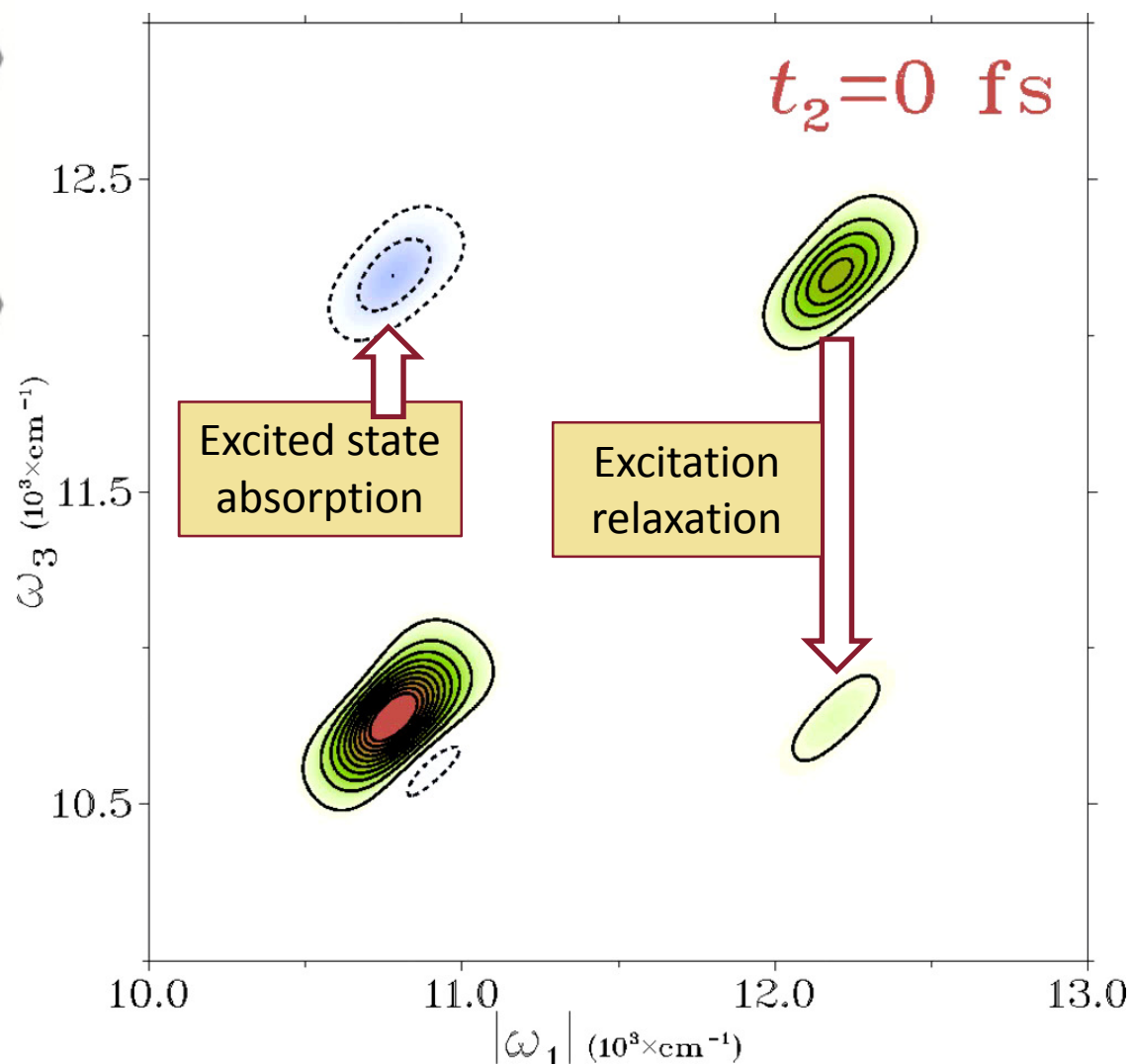
Noninteracting molecules



- Two diagonal peaks present
- Peaks getting round shape due to losing correlation



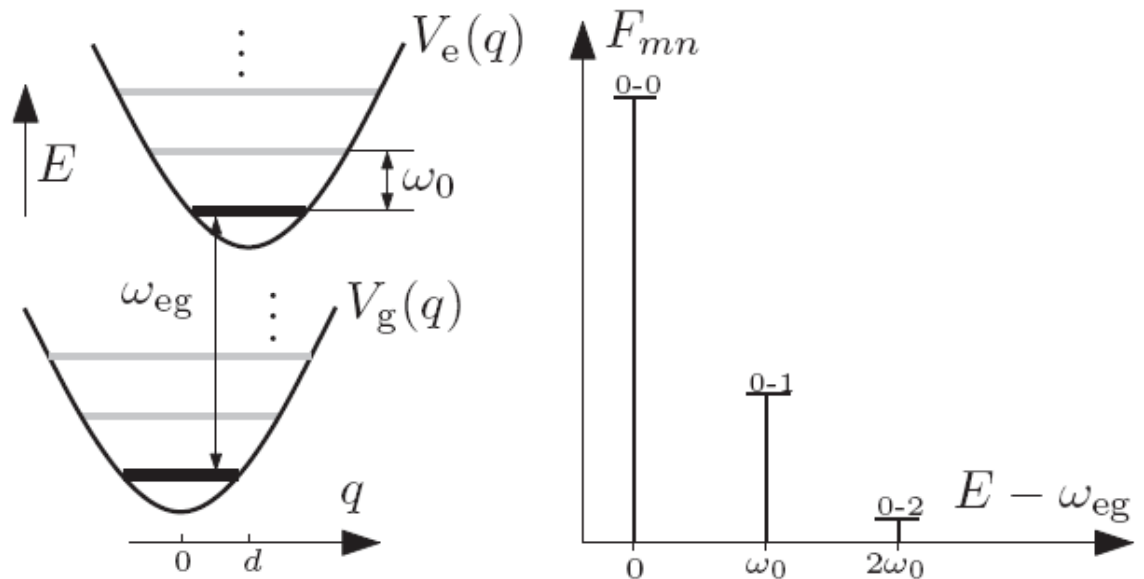
Interacting molecules (a dimer)



Molecule coupled to a phonon bath

Hamiltonian of a single molecule

$$\begin{aligned}\hat{H} = & 0|g\rangle\langle g| + (\omega_{eg} + \lambda)|e\rangle\langle e| \\ & - \sum_{\alpha} \hbar\omega_0^{(\alpha)} \sqrt{s_{\alpha}} (\hat{a}_{\alpha}^{\dagger} + \hat{a}_{\alpha}) |e\rangle\langle e| \\ & + \sum_{\alpha} \hbar\omega_0^{(\alpha)} \left(\hat{a}_{\alpha}^{\dagger} \hat{a}_{\alpha} + \frac{1}{2} \right).\end{aligned}$$



$$d = |\mu_{10}|^2 \sum_{\nu, \nu'} \rho_{\nu} |FC_{\nu\nu'}|^2$$

V. Butkus et al. JCP **137**, 044513 (2012)

Spectral density of harmonic bath

Fluctuating collective bath coordinate

$$Q_e(t) = \sum_{\alpha} \hbar \omega_0^{(\alpha)} \sqrt{s_{\alpha}} \left(\hat{a}_{\alpha}^{\dagger}(t) + \hat{a}_{\alpha}(t) \right)$$

Correlation function $C(t) = \text{Tr}_B \{ Q_e(t) Q_e(0) \rho_{\text{eq}} \}$

$$C(t) = \sum_{\alpha} \hbar^2 (\omega_0^{(\alpha)})^2 s_{\alpha} \left(\coth \frac{\beta \hbar \omega_0^{(\alpha)}}{2} \cos \omega_0^{(\alpha)} t - i \sin \omega_0^{(\alpha)} t \right)$$

$$C(\omega) = \int_{-\infty}^{\infty} e^{i\omega t} C(t) dt = C'(\omega) + C''(\omega)$$

Absorption spectrum

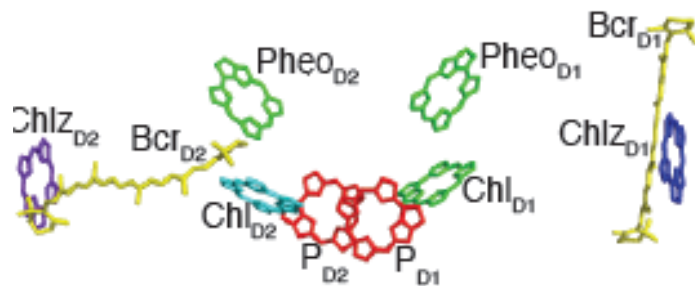
$$\sigma_a(\omega) = \frac{|\mu_{10}|^2}{\pi} \operatorname{Re} \int_0^{\infty} \exp[i(\omega - \omega_e)t - g(t)] dt$$

$$g(t) = \int_0^t dt_1 \int_0^{t_1} d\tau C(\tau) \quad C(\tau) = \langle Q(\tau)Q(0) \rangle$$

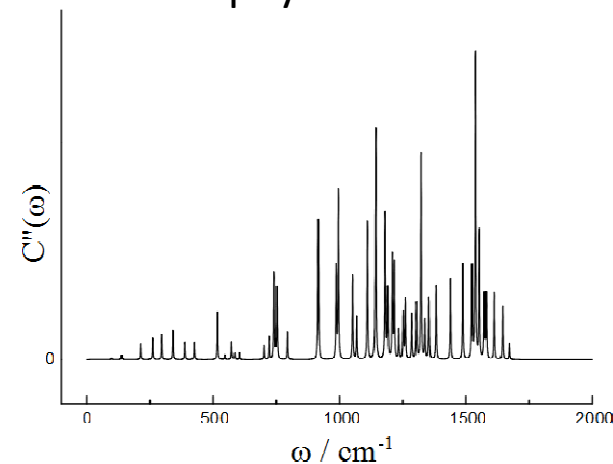
$$C(\omega) = \int_{-\infty}^{\infty} e^{i\omega t} C(t) dt = C'(\omega) + C''(\omega)$$

Nontrivial open quantum system

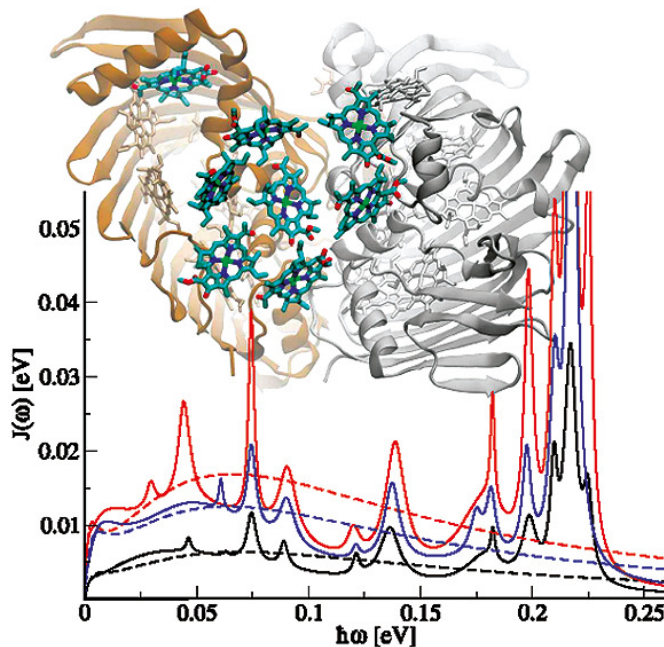
D1-D2 Reaction Center



The spectral density of chlorophyll in PS-II



Novoderezhkin *et al. Biophys. J.* 89, 1464 2005.



$$C''(\omega) = \omega^2 J(\omega)$$

C. Olbrich, *et al. J. Phys. Chem. Lett.*, 2011

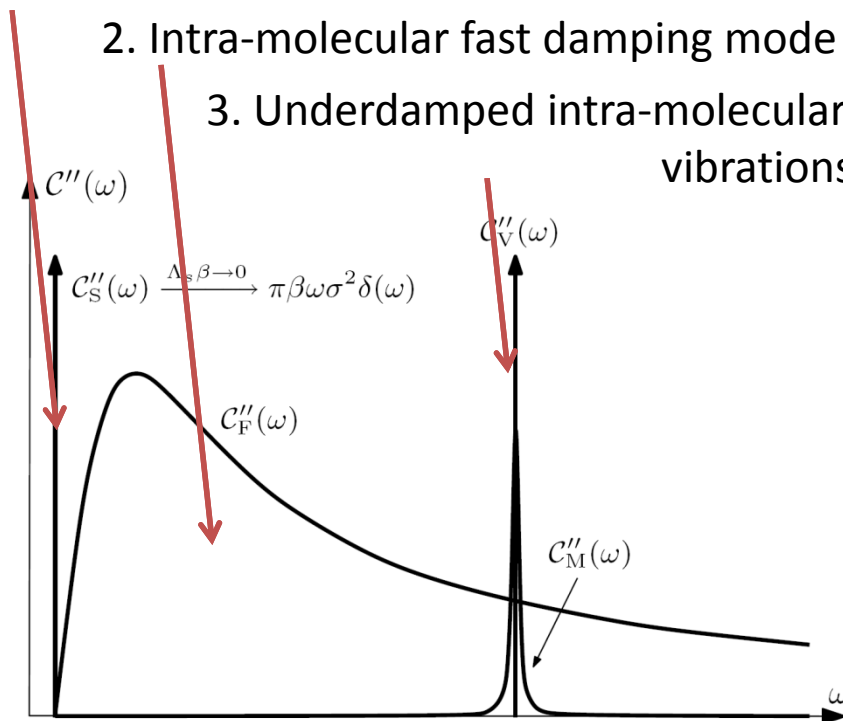
Protein environment is highly structured
This cannot be ignored

Spectral density with specific resonances

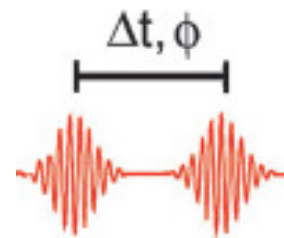
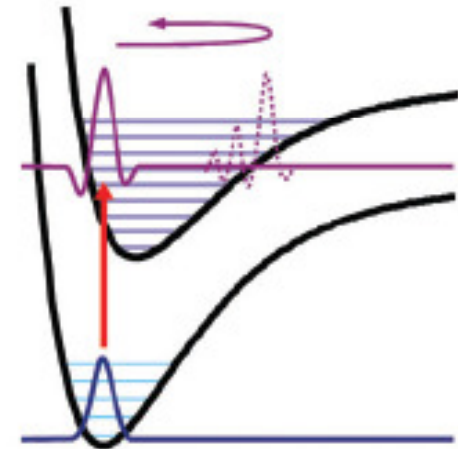
1. Static inter-molecular fluctuations

2. Intra-molecular fast damping mode

3. Underdamped intra-molecular vibrations



colored bath



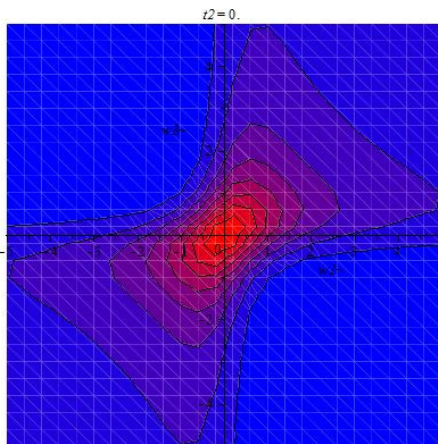
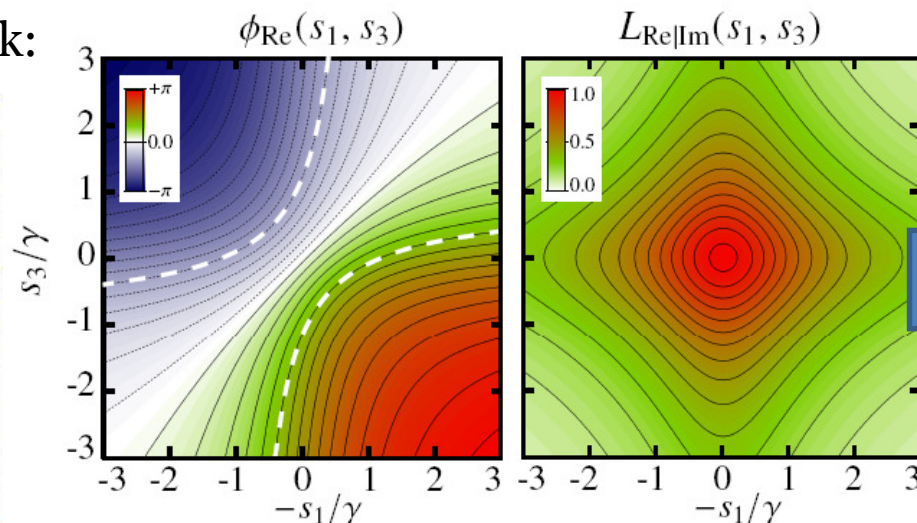
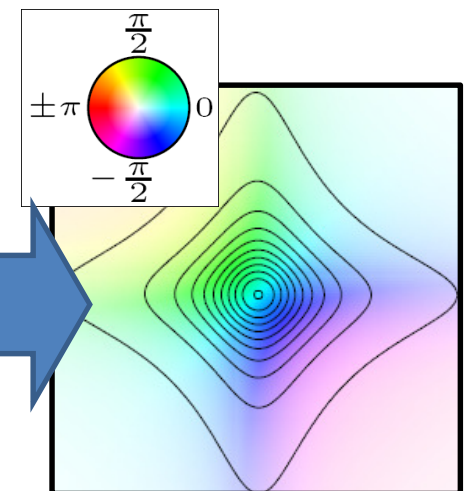
Oscillation Fourier maps

Phase and amplitude of oscillations is obtained by Fourier transform of time-dependent spectra,

$$\phi(\omega_3, \omega_2, \omega_1) = \text{Arg} \left[\int S(\omega_3, t_2, \omega_1) e^{-i\omega_2 t_2} dt_2 \right]$$

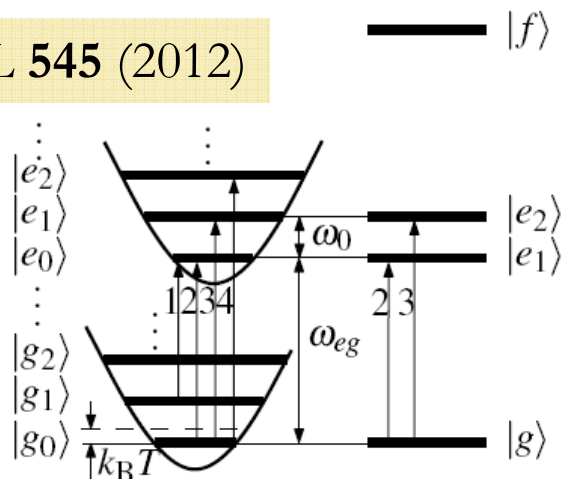
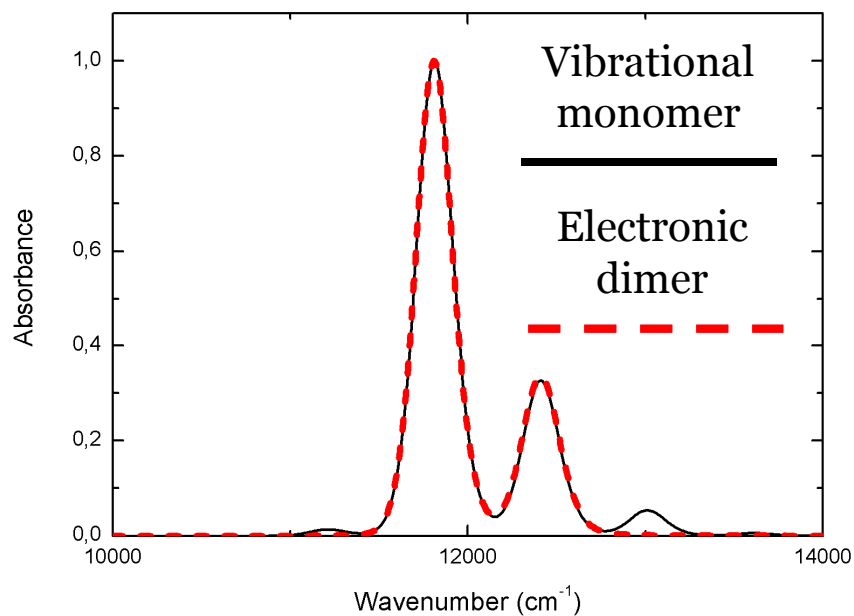
$$L(\omega_3, \omega_2, \omega_1) = \text{Abs} \left[\int S(\omega_3, t_2, \omega_1) e^{-i\omega_2 t_2} dt_2 \right]$$

Oscillating cross-peak:

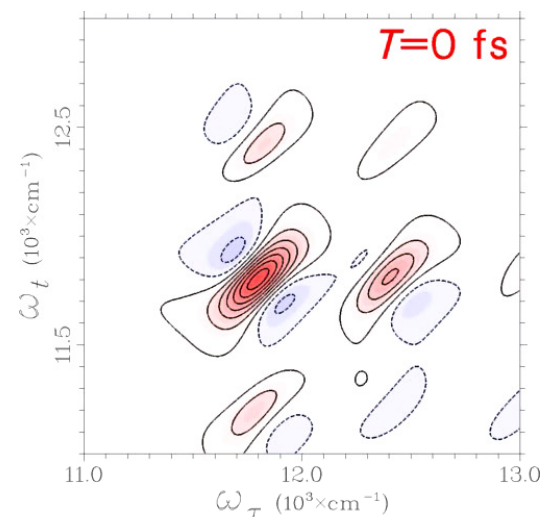


Purely electronic/vibrational systems

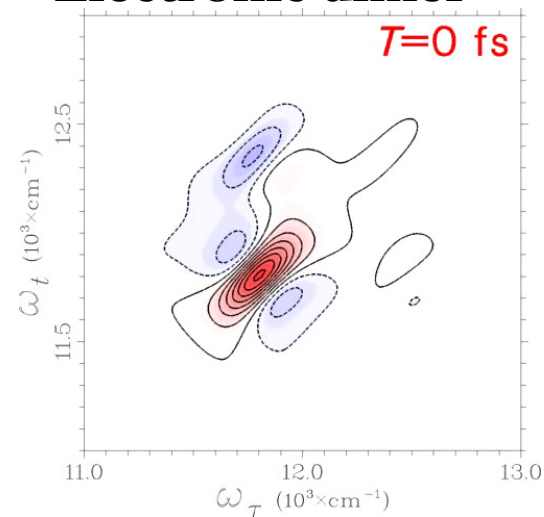
V. Butkus et al. CPL **545** (2012)



Vibrational monomer

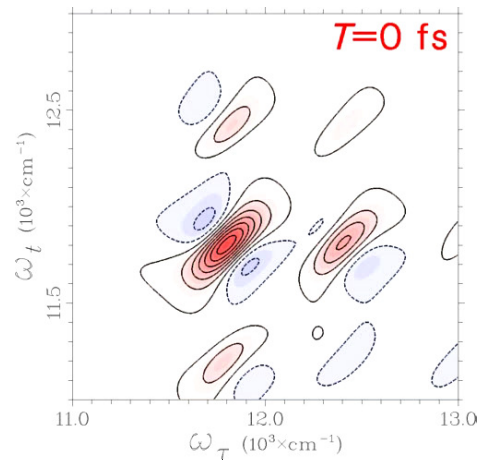
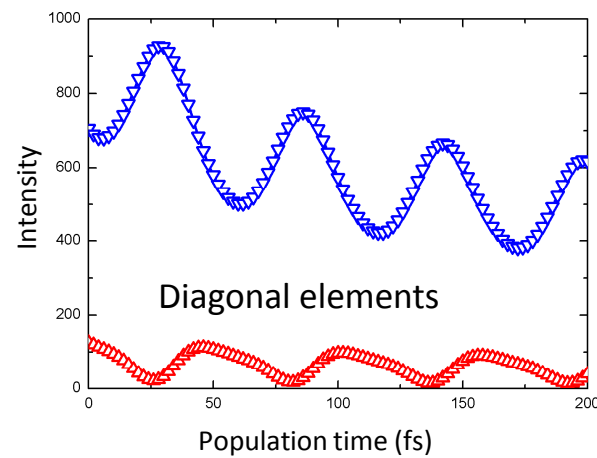
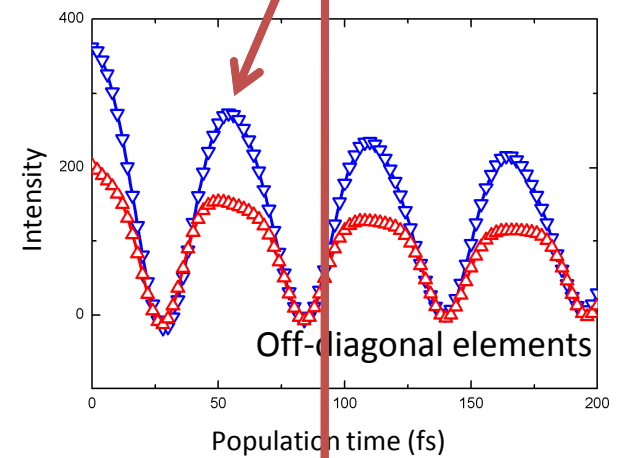
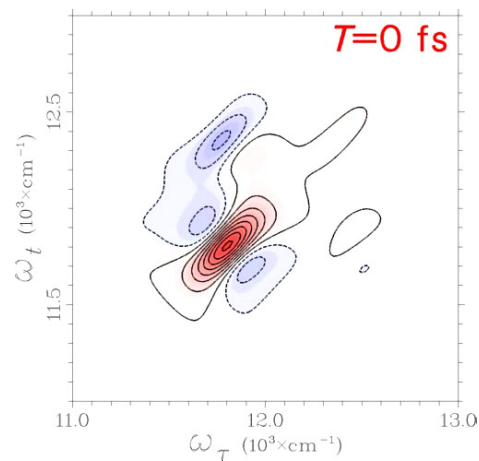
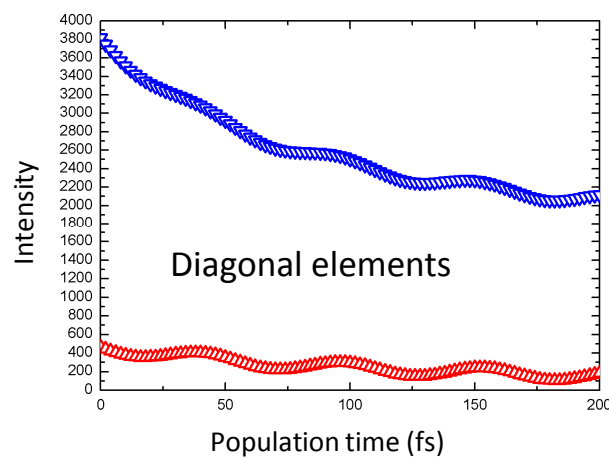
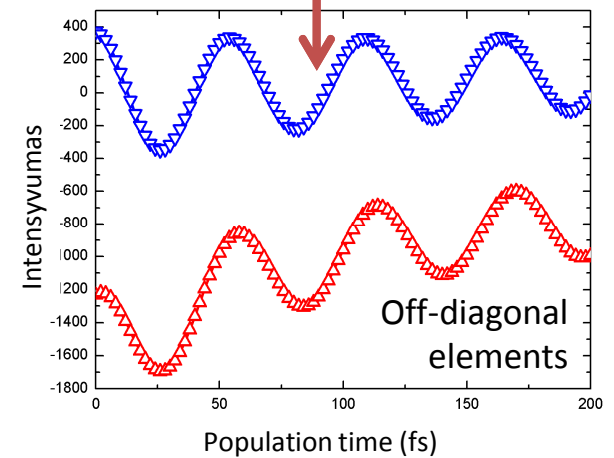


Electronic dimer



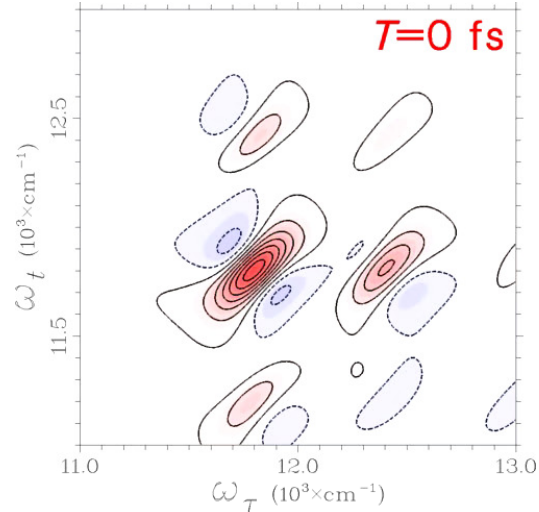
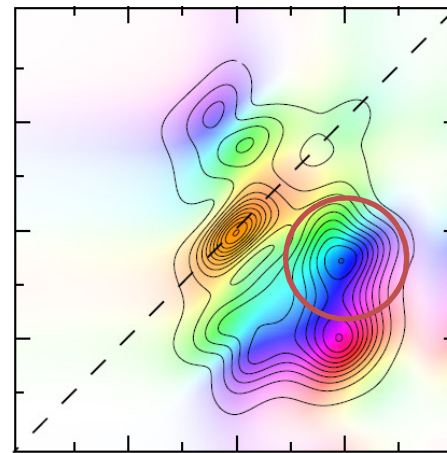
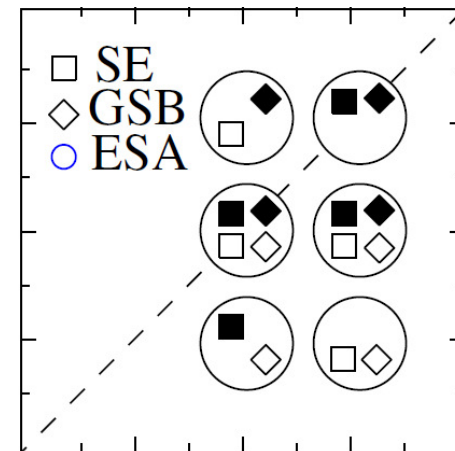
Oscillations in model systems (rephasing signal only)

Cross-peak
oscillations IN PHASE



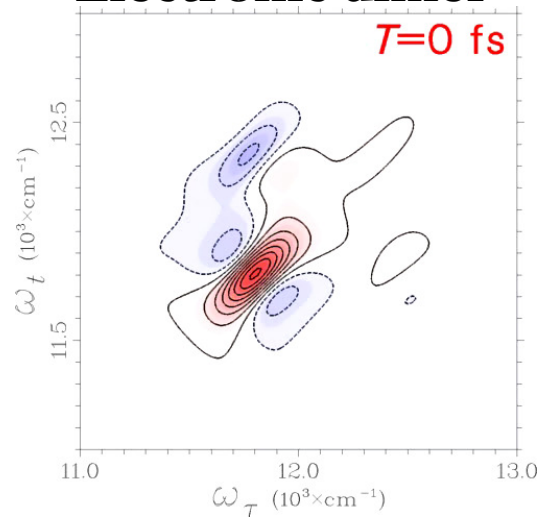
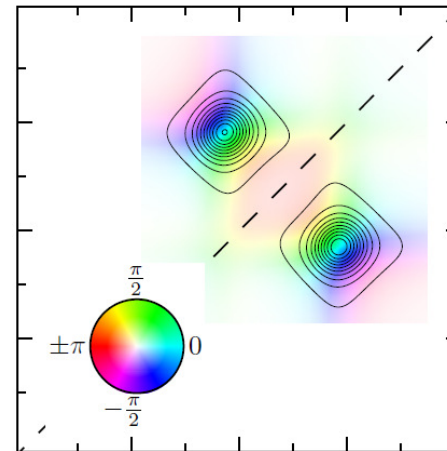
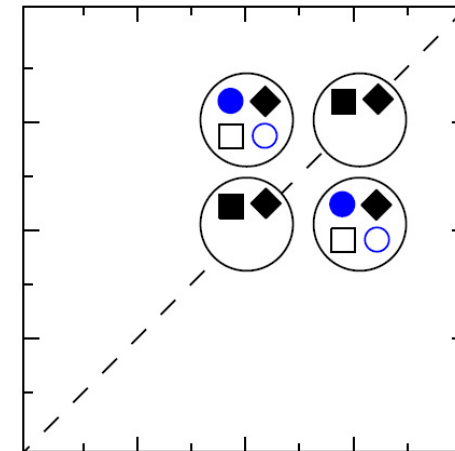
Purely electronic/vibrational systems

Vibrational monomer



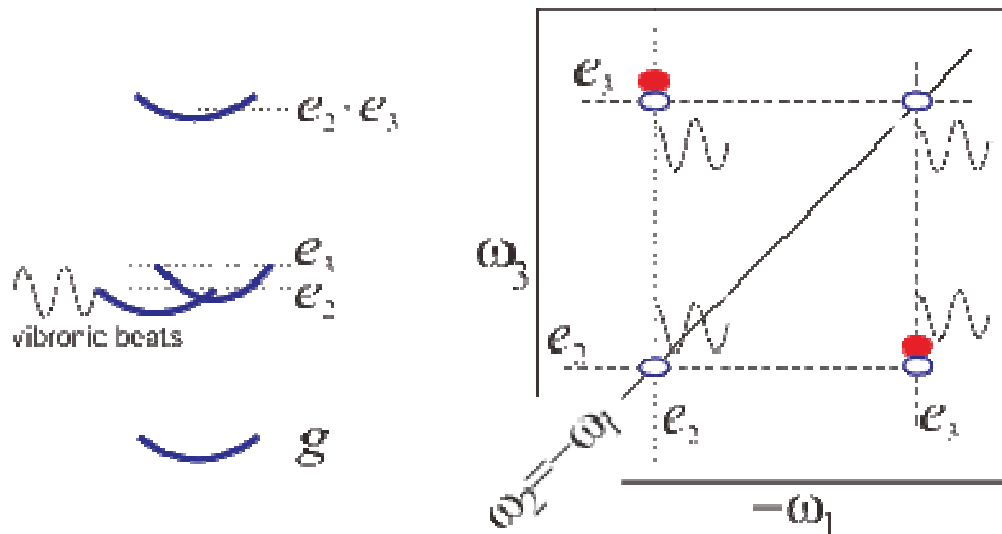
V. Tiwari et al. PNAS 110 (2013)

Electronic dimer

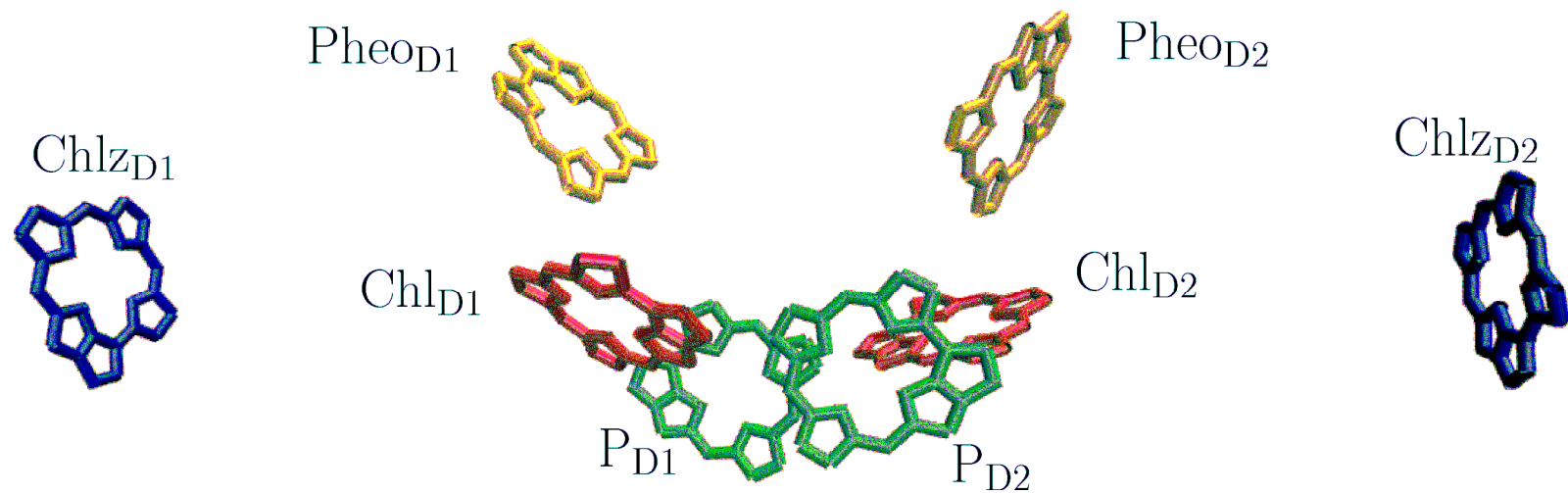


Time-resolved phenomena

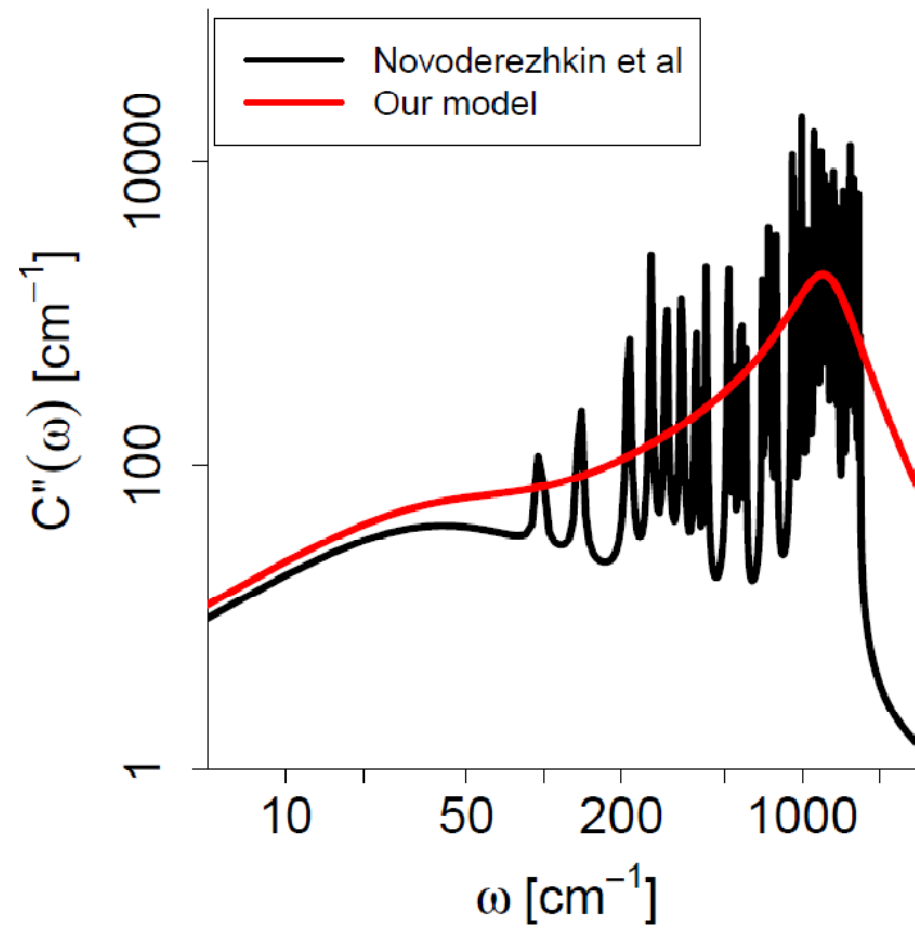
- Coherent beats of vibrational degrees of freedom (internal structure of excitons)



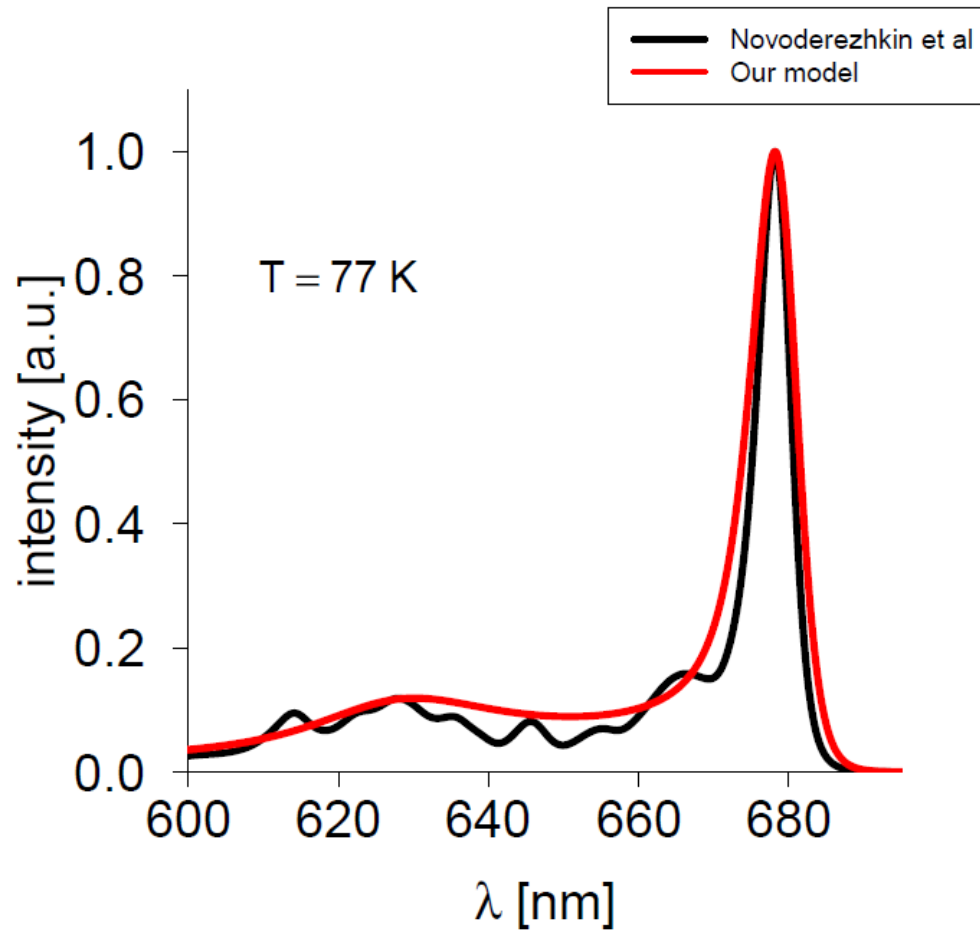
PSII RC



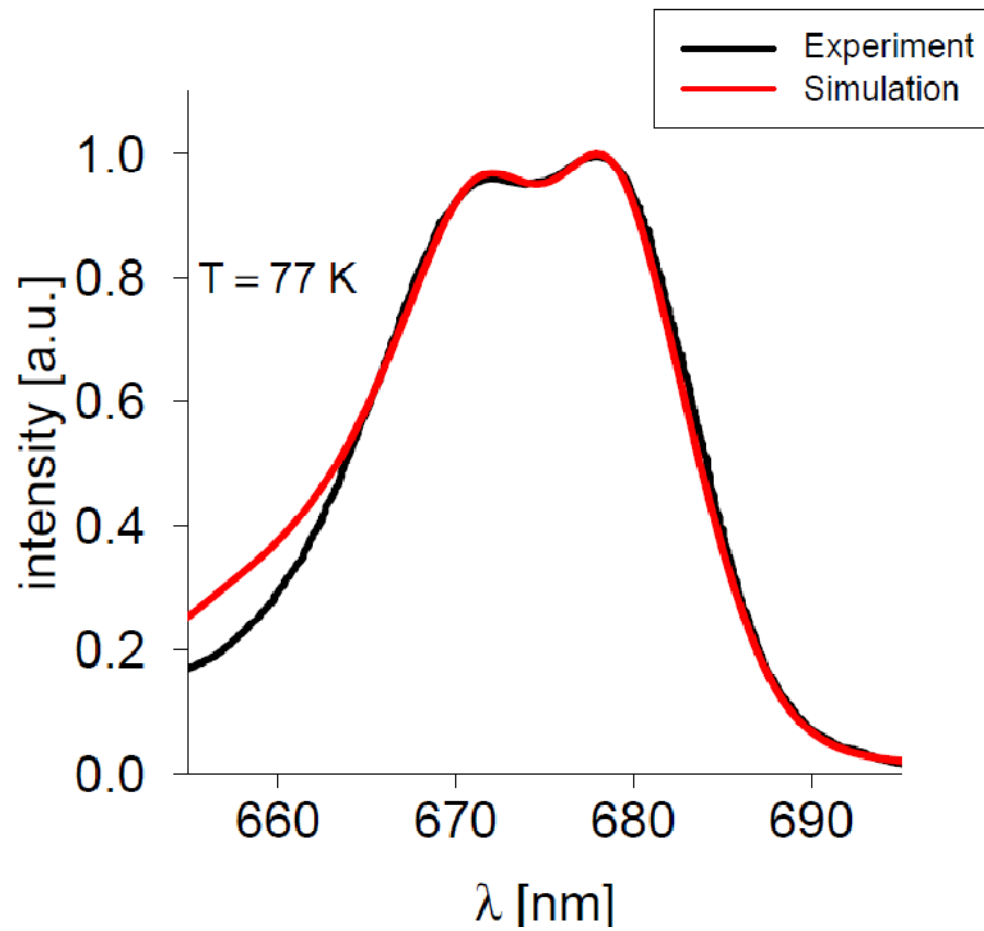
Spectral density



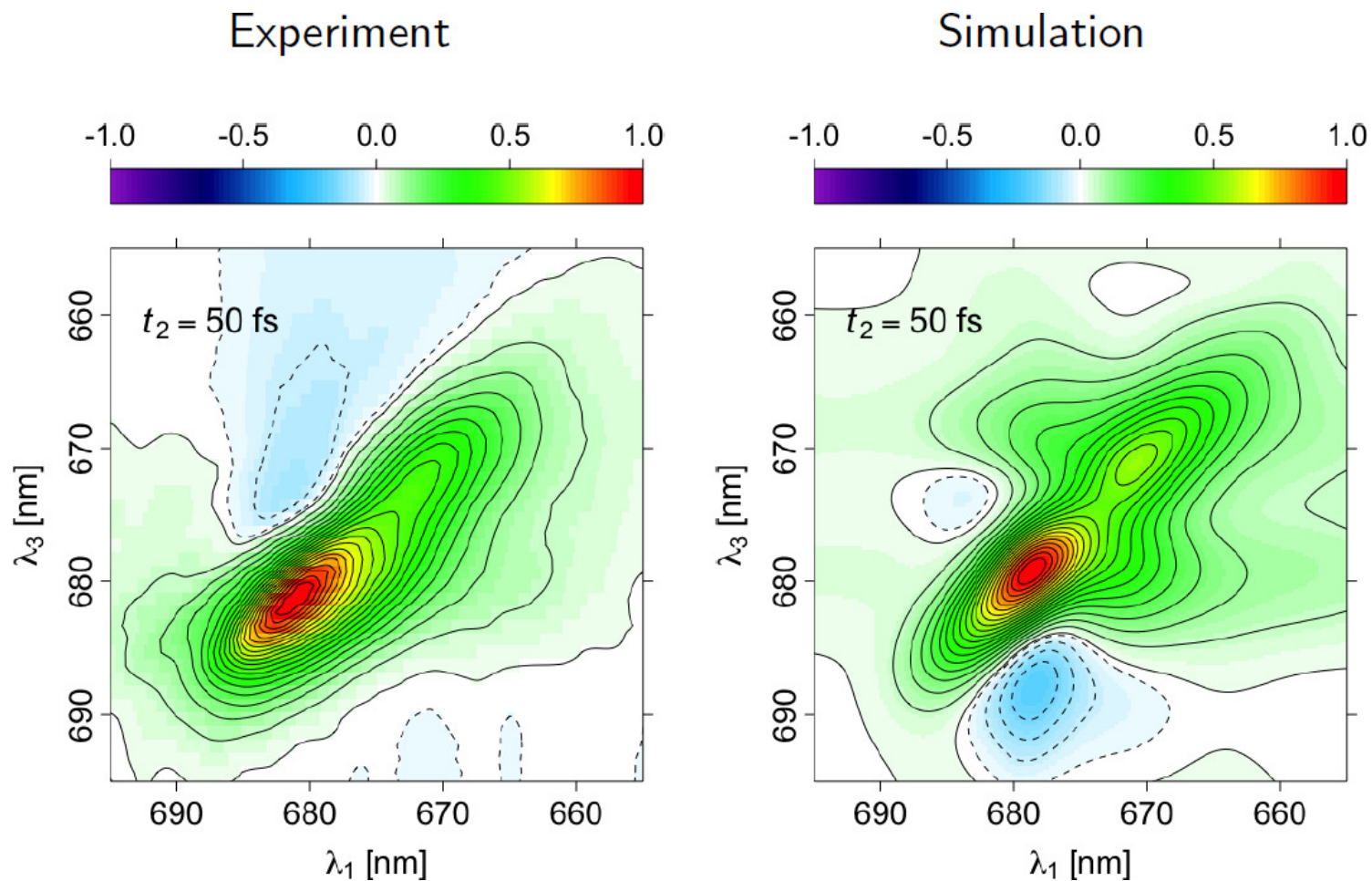
Monomer absorption



Absorption of PSII RC

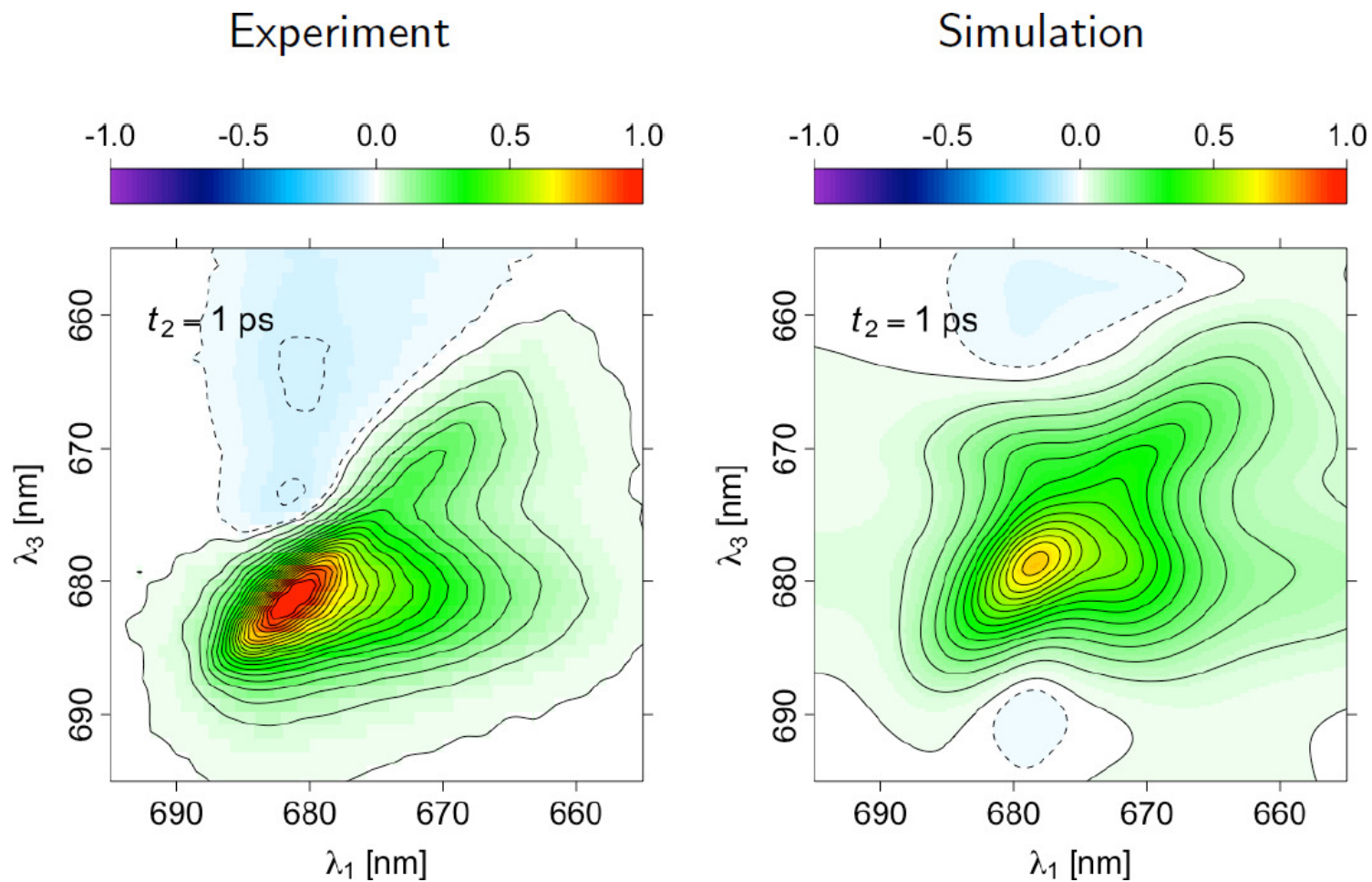


PSII RC 2D at 77 K

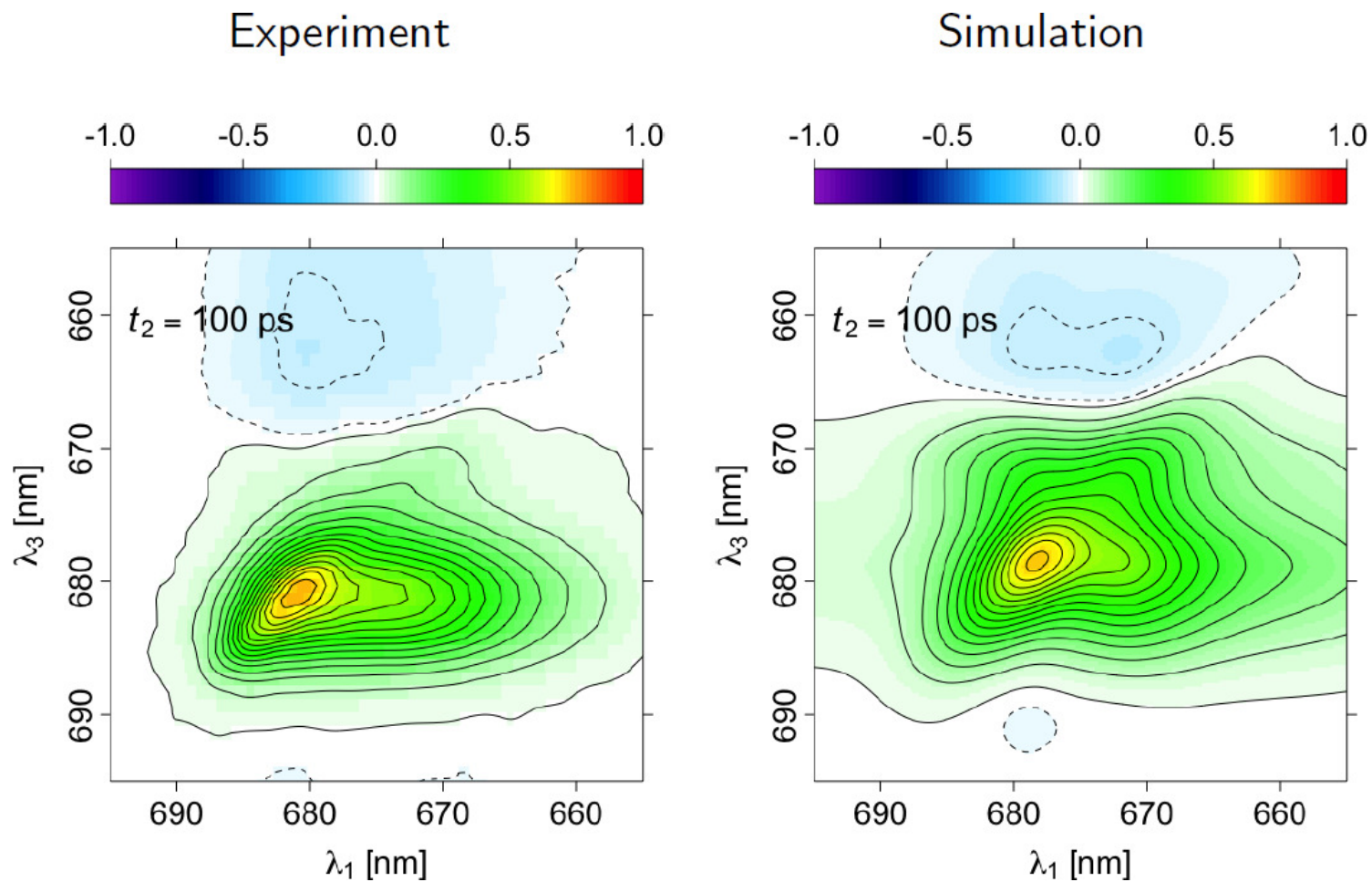


A. Gelzinis et al. New J. Phys. **15**, 075013 (2013)

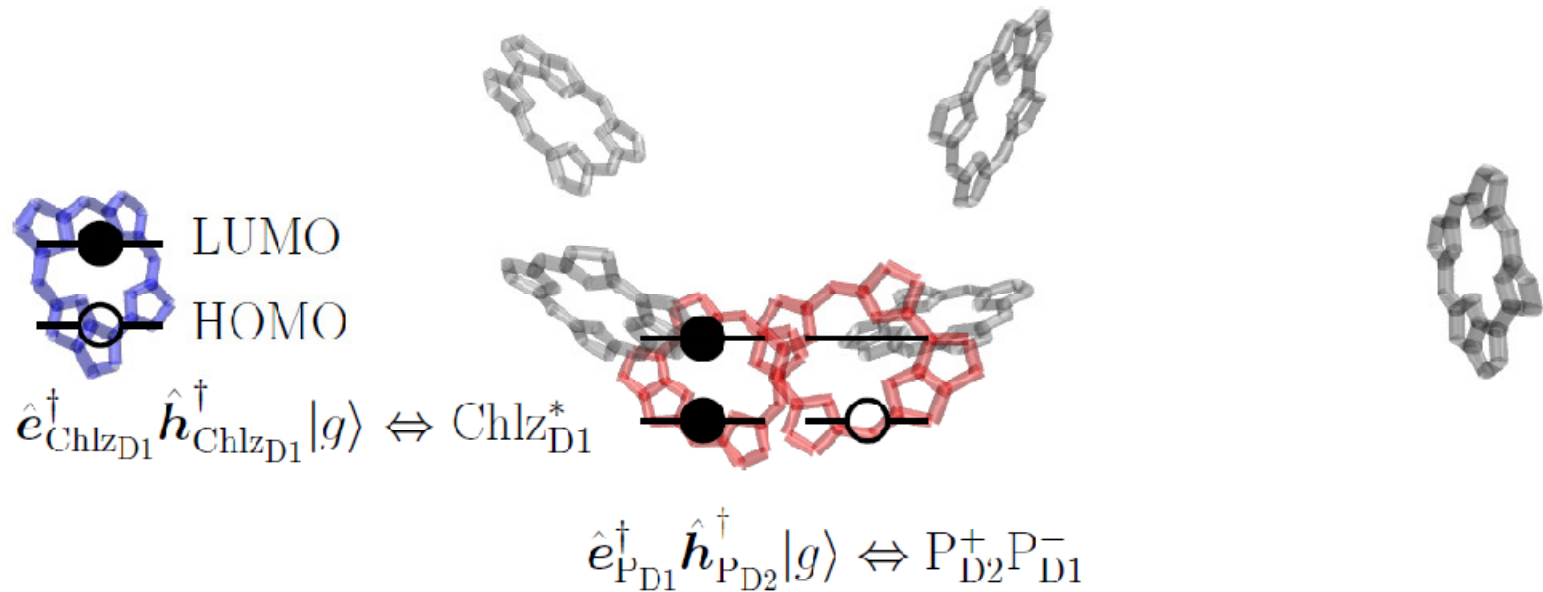
PSII RC 2D at 77 K



PSII RC 2D at 77 K

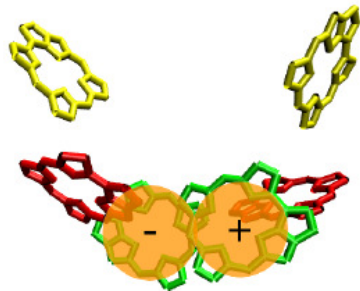
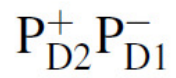
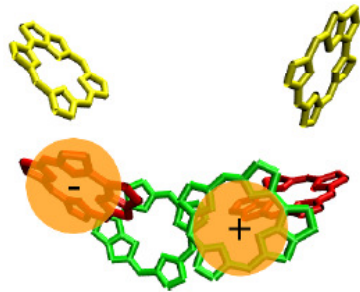
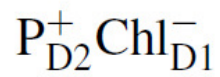
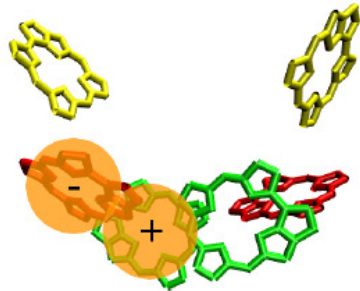
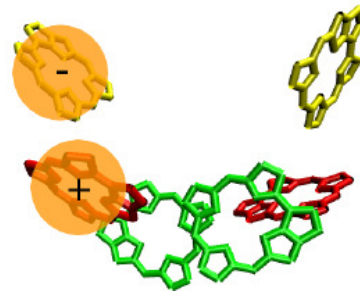
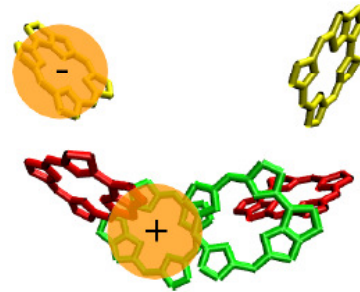


Tight binding hamiltonian



- Frenkel excitonic (FE) states $m^* \Leftrightarrow \hat{e}_m^\dagger \hat{h}_m^\dagger |g\rangle$.
- Charge transfer (CT) states $n^+ m^- \Leftrightarrow \hat{e}_m^\dagger \hat{h}_n^\dagger |g\rangle$.

CT states



CT pathways

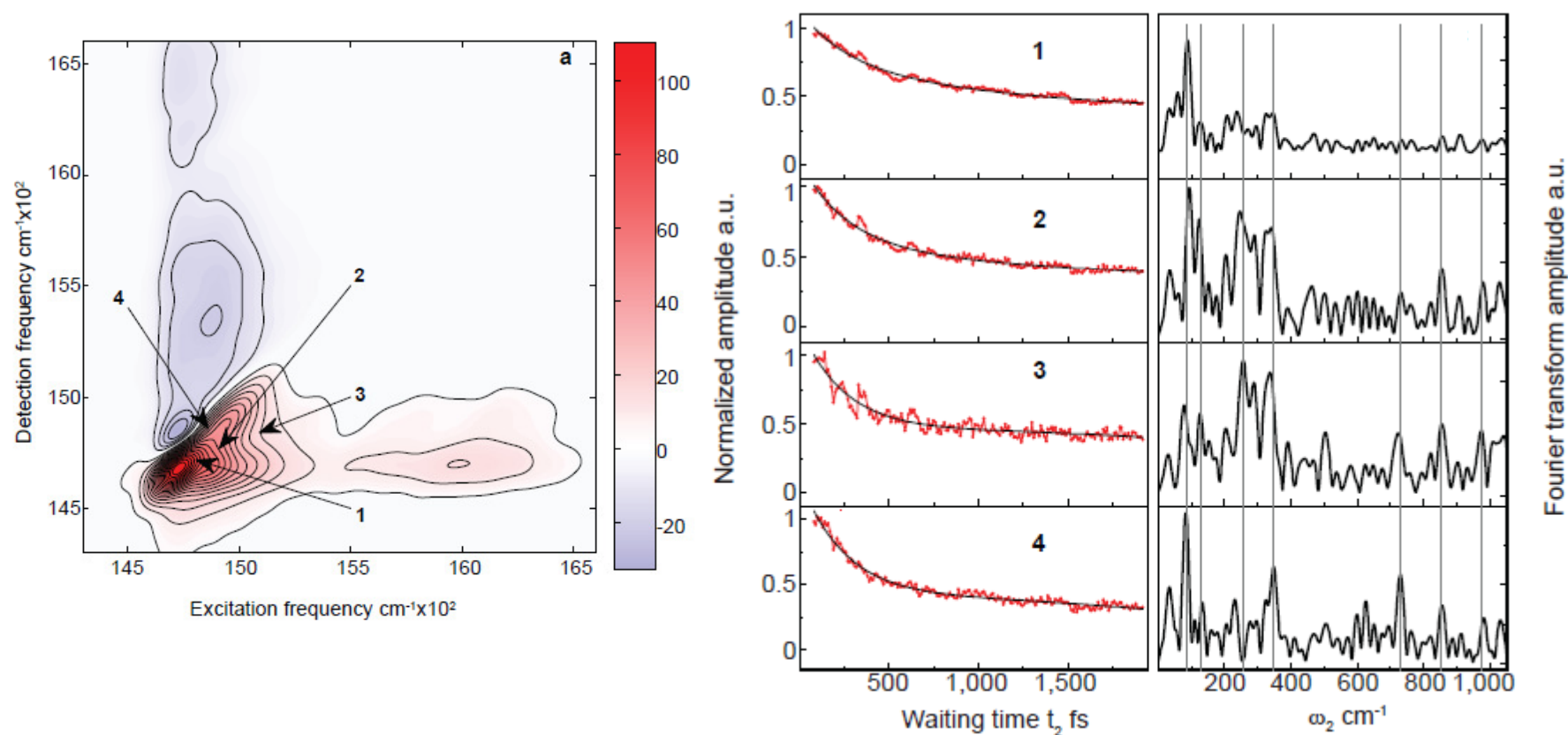
Chl_{D1} pathway



Special pair pathway

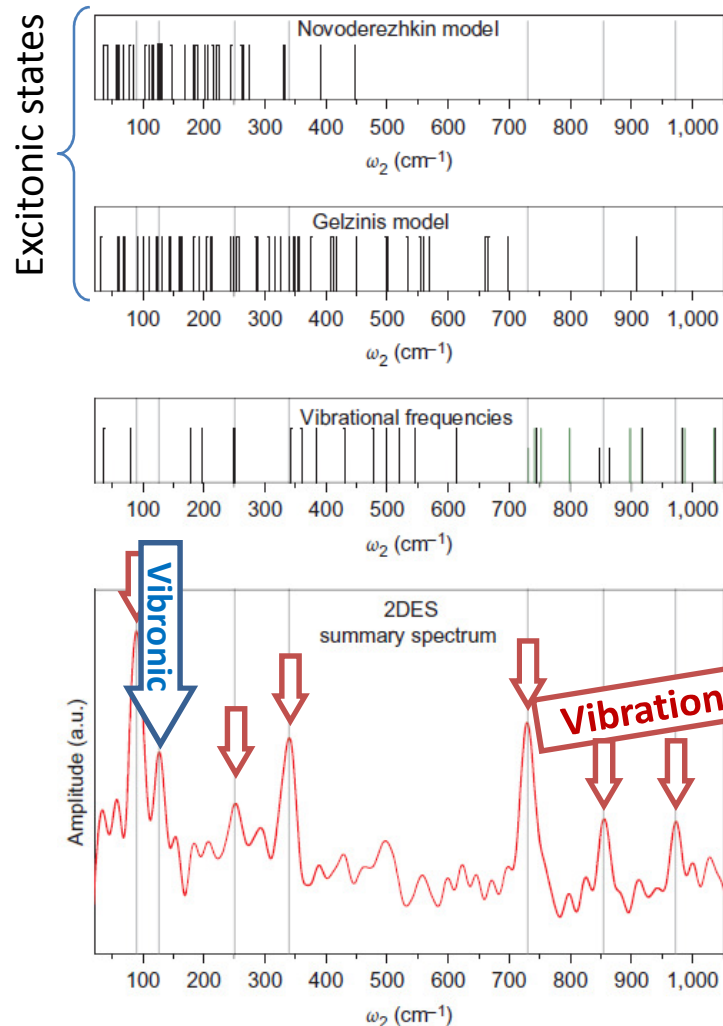
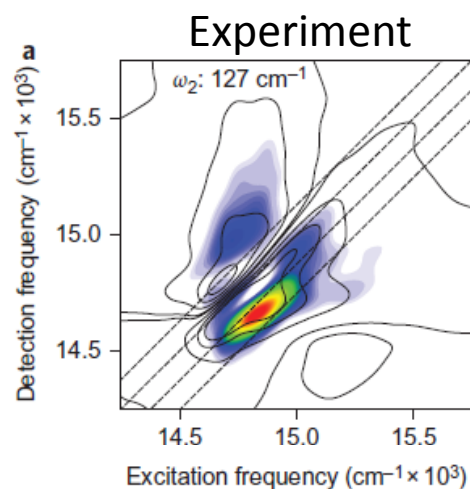
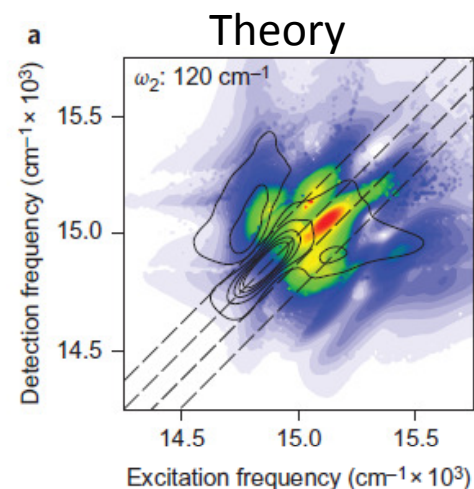
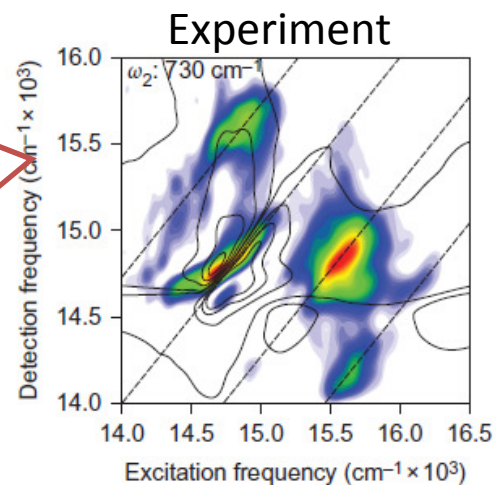
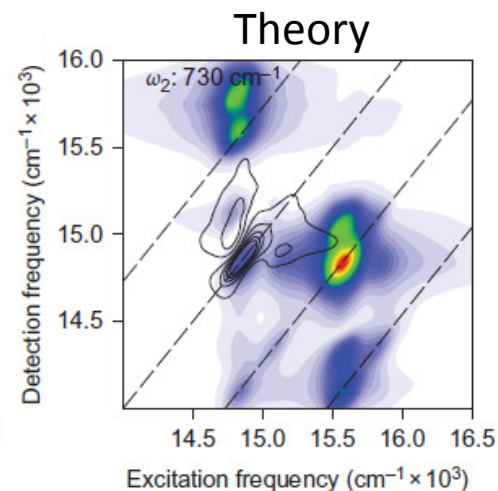


2D spectrum of the PSII RC at 77K at a waiting time of 170 fs.

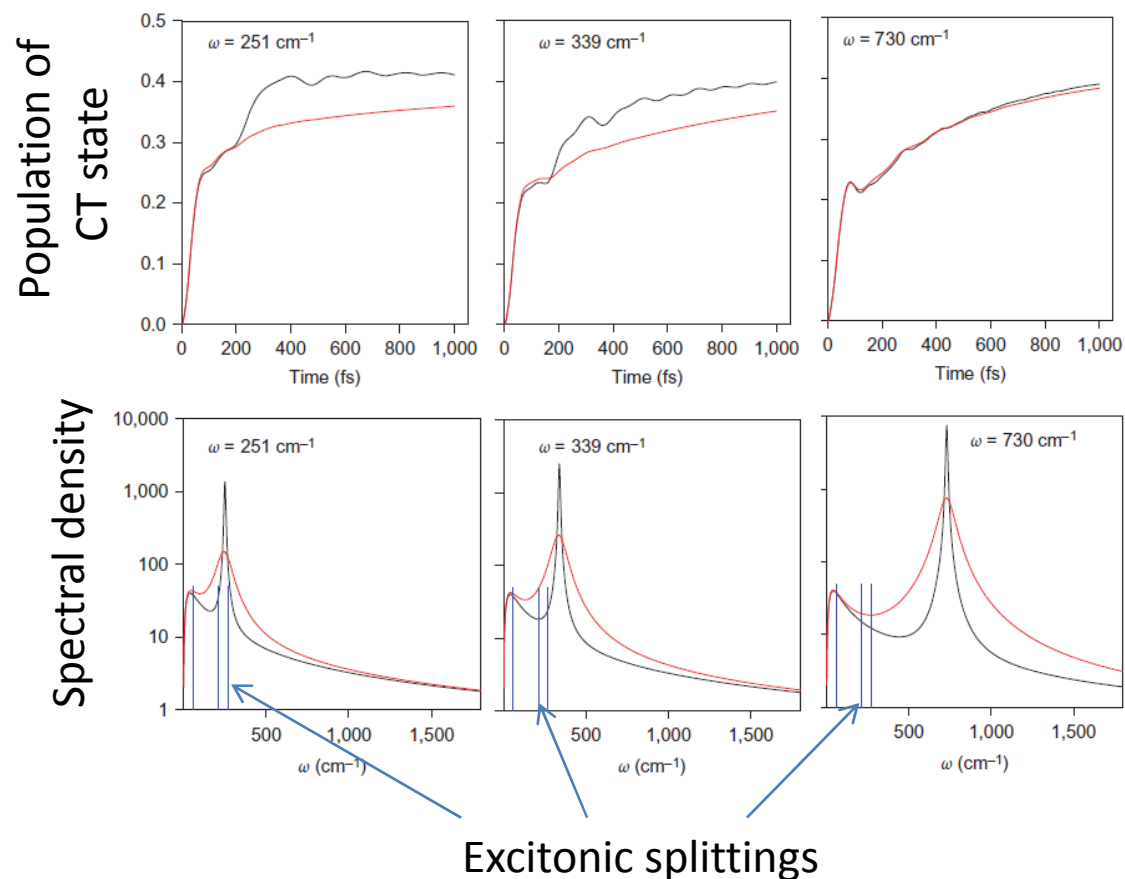
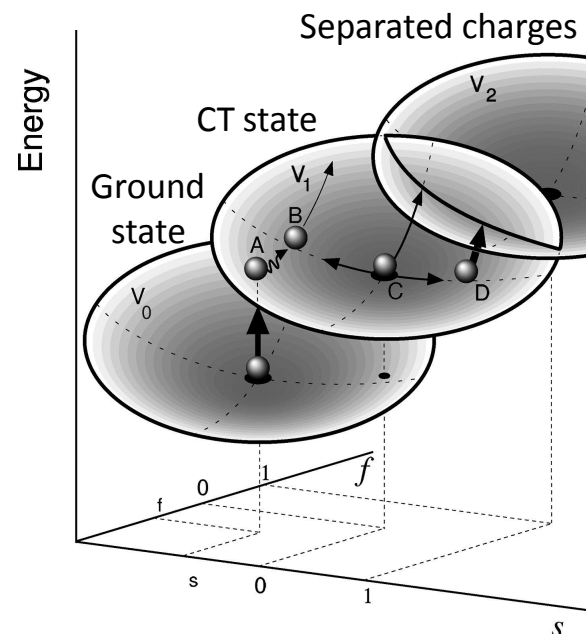


F. D. Fuller, J. Pan, A. Gelzinis, V. Butkus, S. S. Senlik, D. E. Wilcox, C. E. Yocum, L. Valkunas, D. Abramavicius, J. P. Ogilvie. *Nature Chemistry* 6, 706 (2014)

Physical origin of coherences



Enhancement of the charge transfer



After the excitation, the electron appears in the initial state A. The transition along overdamped and underdamped coordinates are indicated as states B, C and D. The charge transfer may take place at any time while the most probable event happens in the state D.

D. Abramavicius et al. Acceleration of charge separation by oscillations of the environment polarization. *Chem Phys Lett* **368** (2003)

F. D. Fuller, J. Pan, A. Gelzinis, V. Butkus, S. S. Senlik, D. E. Wilcox, C. E. Yocum, L. Valkunas, D. Abramavicius, J. P. Ogilvie. *Nature Chemistry* **6**, 706 (2014)

Conclusions

- Fluorescence intermittency in single LHCII is probably related to NPQ and can be explained by considering equilibrium between $|on\rangle$ and $|off\rangle$ states in a dynamic self-organisation model.
- Adverse environment enforce LHCII to switch to the non-fluorescing dark state.
- 2D spectral oscillations come either from electronic coherencies or vibrational resonances of the bath. For this purpose the Fourier maps are useful by analyzing the 2D electronic spectra.
- Inhomogeneous disorder makes different effect of on electronic/vibronic coherences.
- Vibrational coherences evolving in the ground state and vibronic coherences in the excited state are equally significant.

Acknowledgements

Vilnius:

- D. Abramavicius
- V. Butkus
- A. Gelzinis
- R. Augulis
- E. Songaila
- J. Chmeliov

Lund:

D. Zigmantas

Frankfurt:

C. Büchel

Gif sur Yvette:

B. Robert

A. Gall

Ann Arbor:

J. P. Ogilvie

F. D. Fuller

Amsterdam:

R. van Grondelle

T. P. J. Krüger

C. Iliaia

LSC grant no:

VP1-3.1-ŠMM-07-K-01-007.



Let Us Meet Again

We welcome all to our future group conferences of
Omics group international

Please visit:

www.omicsgroup.com

www.Conferenceseries.com

<http://optics.conferenceseries.com/>