Two-Color three-pulse Photon Echoes

- IR144 in Methanol
- DTTCI in Methanol
Condensed Phase Dynamics

In an ensemble of chromophores, the dynamics for an individual chromophore \( i \) can be expressed as

\[
\omega_{eg}^i (t) = \langle \omega_{eg} \rangle + \delta \omega_{eg} (t) + \epsilon_i
\]

Full width half maximum of \( f(\epsilon) \) = inhomogeneous width

Optical lineshapes and echo measurements relate to:

\[
M(t) = \frac{\langle \delta \omega(0) \delta \omega(t) \rangle}{\langle \delta \omega^2 \rangle}
\]

\[
\Delta E^i(t_1) = \hbar \omega_{eg}^i(t_1)
\]
Stokes Shift and Solvation Dynamics

Optical Lineshapes

\[ \omega_{eg} = \langle \omega_{eg} \rangle + \delta \omega_i(t) + \varepsilon_i \]

For the \( i \) th chromophore

Optical lineshapes and echo measurements relate to

\[ M(t) = \frac{\langle \delta \omega(0) \delta \omega(t) \rangle}{\langle \delta \omega^2 \rangle} \]
Solvation Dynamics in C343 in Water

Two-Color three-pulse Photon Echoes

IR144 in Methanol

DTTCI in Methanol
**Difference Peak Shift**

For a fixed phase matching direction, i.e., $k_3 + k_2 - k_1$

Type I scan
Echo (Rephasing)
(pulse sequence, 1-2-3)

Type II scan
FID (Non-Rephasing)
(pulse sequence, 2-1-3)

\[
\Delta \tau^*(T) = \tau_I^*(T_I) - \tau_{II}^*(T_{II})
\]

Two Colour Difference Peak Shift

For a fixed phase matching direction, i.e., $k_3 + k_2 - k_1$
IR144 Methanol 750, 750, 800
Experimental Difference Peak Shift Data (downhill)

The Difference Peak Shift starts at a near zero value, then rises to a maximum value in ~ 200 fs and then decays to zero for both IR144 and DTTCI in methanol.

Based on the turnover time, it is suggested that the ultrafast component in methanol is ~ 200 fs.
Two-Color 3PEPS as a Probe of Memory Transfer in Spectral Shift

Two-Color 3PEPS measures correlation dynamics (between transition energies in pumped and probed regions).

\[ \langle d_{pu}(t) d_{pu} \rangle \]
Homogeneous and Inhomogeneous Distributions of Transition Energies

- Homogeneous distribution

$$s_{\text{hom}}(w,j_g) = \hat{a}_{j_e} d\left(w - (E_{j_e} - E_{j_g})\right) |\langle j_e | j_g \rangle|^2$$

A particular nuclear state in the ground electronic state

- Inhomogeneous distribution

$$s(w) = \hat{a}_{j_g} s_{\text{hom}}(w,j_g) P_g(j_g)$$

Statistical probability for a molecule to occupy the nuclear state $j_g$

Two Mechanisms for Existence of Non-Linear Signals of Two-Color Experiments

- Interactions of pump and probe lasers have to be made with the same molecule

  A) Spectral Overlap due to Homogeneous Distribution

  B) Spectral evolution due to Fluctuation of Inhomogeneous Distribution

- These two mechanisms are included in the response function formalism in a complicated way
A Simple ad hoc Model for the Dynamics of Correlation Function

\[ \text{Total Signal} = P_{\text{hom}}(t)R_{\text{hom}}(t) + P_{\text{inhom}}(t)R_{\text{inhom}}(t) \]

**Total Correlation Function**

\[ \langle de_{pr}(t)de_{pu} \rangle = \frac{P_{\text{hom}}(t)}{P_{\text{hom}}(t) + P_{\text{inhom}}(t)} \langle de_{pr}(t)de_{pu} \rangle_{\text{hom}} + \frac{P_{\text{inhom}}(t)}{P_{\text{hom}}(t) + P_{\text{inhom}}(t)} \langle de_{pr}(t)de_{pu} \rangle_{\text{inhom}} \]

At short times, \( P_{\text{hom}}(t) >> P_{\text{inhom}}(t) \) \hspace{1cm} At longer times, \( P_{\text{hom}}(t) << P_{\text{inhom}}(t) \)

Inhomogeneous distribution fluctuates with time due to random fluctuation of the statistical distribution of the nuclear states, which is described by a stochastic approach.

\[ \langle de_{pr}(t)de_{pu} \rangle_{\text{inhom}} = \frac{1}{N(t)} \hat{\partial} dw_1 dw_2 \left( w_2 - \langle w(t) \rangle_{pr} \right) \left( w_1 - \langle w \rangle_{pu} \right) W \left( w_2 \mid E_{pr} \right) P \left( w_2 \mid t \right) W \left( w_1 \mid E_{pu} \right) s_{\text{abs}}(w_1) \]

\[ P(\omega_2 \mid \omega_1) = \frac{1}{\sqrt{2\pi\Delta^2(1-M(t)^2)}} \exp \left\{ -\frac{[(\omega_2 - \langle \omega \rangle) - (\omega_1 - \langle \omega \rangle)M(t)]^2}{2\Delta^2(1-M(t)^2)} \right\} \]

\[ P(\omega_2 \mid 0 \mid \omega_1) = \delta(\omega_2 - \omega_1) \]

Dynamics of Conditional Probability for the Inhomogeneous Distribution

\[ \langle d e_p (t) d e_p \rangle_{inhom} \]

Homogeneous broadening domain

: No common transitions between the pump and the probe
(no rephasing capability)

Rise in Two-Color Difference Peak Shift \( \sim \) Inertial Solvation Dynamics

Uphill and Downhill difference peak shifts should have distinct behavior for systems with a systematic red shift
Model Calculations for Difference Peak Shift (downhill)

Empirical formula:  \( T\big|_{\text{turnover}} \sim \tau_g \{c_1 \Delta \log(c_2 / \lambda) + c_3\} \),

\( \tau_g \) = Gaussian Time Constant, \( \lambda \) = reorganization energy
\( \Delta = \) Frequency difference between the two pulses

Adding exponentials and vibrations does not alter the turnover time significantly. Therefore, we can extract information of the Gaussian parameters from the turnover time.
Simulation model for the Difference Peak Shift

Simulation scheme: Type I and II peak shifts were calculated using a Gaussian (220 fs, $\lambda = 150$ cm$^{-1}$), exponential 1 (2500 fs, $\lambda = 75$ cm$^{-1}$), exponential 2 (9500 fs, 70 cm$^{-1}$), 35 intramolecular modes ($\lambda_{\text{tot}} \sim 400$ cm$^{-1}$).
Two Color Difference Peak Shift for Nile Blue

Experiment

Simulation

Acetonitrile

Ethylene glycol
Two-Color Three-Pulse Photon Echoes

1. Electronic Mixing in Molecular Complexes

Site Representation

Eigen State Representation

2. Correlation between initial and final states e.g. disordered energy transfer system

Energy Transfer system

\[ S = \langle f(G)S(G) \rangle_G \]

\[ \phi(\Gamma) \] phase factor

\[ S(\Gamma) \] population kinetics

\[ \langle \ldots \rangle_G \]

\[ S \gg \langle f(G) \rangle_G < S(k(G)) \rangle_G \]

Ensemble averages over distribution of static energies

Donors and acceptors become correlated via energy transfer (even though initially uncorrelated)
One-color three-pulse photon echo peakshift (1C3PEPS)

Interaction with 1st pulse ▼ ▲

2nd (Population state)

3rd

Strong correlation between the two coherence states (long-lasting memory) \(\rightarrow\) large peakshift
One-color three-pulse photon echo peakshift (1C3PEPS)

Strong correlation between the two coherence states (long-lasting memory) $\Rightarrow$ large peakshift
Weak correlation between the two coherence states (quick memory loss) $\Rightarrow$ small peakshift
3PEPS profile closely follows the transition frequency correlation function

$$M(t) = \frac{\langle \Delta \omega(0) \Delta \omega(t) \rangle}{\langle \Delta \omega^2 \rangle}$$
Two-color three-pulse photon echo peakshift (2C3PEPS)

Pulses of two different colors generate photo echo signal associated with correlation between $\Delta \omega_H$ and $\Delta \omega_B$

Energy fluctuation of two excitonically mixed states are correlated due to electronic coupling

Electronic coupling constant ($J$) can be determined by 2C3PEPS without knowing the site energies ($E_h$ and $E_b$) of the two chromophores
One- and two-color three-pulse photon echo peakshift experiment

Photon echo peakshift: coherence time ($\tau$) where a photon echo signal is maximum

<table>
<thead>
<tr>
<th>One-color three-pulse photon echo peakshift (1C3PEPS)</th>
<th>Two-color Three-pulse Photon Echo Peakshift (2C3PEPS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda_1=\lambda_2=\lambda_3$</td>
<td>$\lambda_1=\lambda_2\neq\lambda_3$</td>
</tr>
<tr>
<td>Sensitive to environment around a chromophore and energy transfer process</td>
<td>Sensitive to coupling between two chromophores</td>
</tr>
</tbody>
</table>
Strongly Coupled: Exciton Dimer

$$|1e2e>$$

$$c_1 |1e2g> + c_2 |1g2e>$$

$$|1e>$$

$$c_1 |1e2g> - c_2 |1g2e>$$

$$|1g>$$

$$|1g2g>$$

$$|2g>$$

Molecule 1

Dimer

Molecule 2

Electronic Coupling, $J$, can be extracted from shifts of absorption peaks.

This requires knowledge of original site energies.
Pump Probe Spectroscopy of Bis-Phthalocyanine: Excited State and Wavepacket Dynamics

N. Ishikawa, Chuo University
LuPc$_2$ Dimer

- Absorption spectra shows monomer’s single peak is split in the dimer.

- Inset: Sandwich structure of Lutetium bisphthalocyanine.
Two-Color Echoes on Excitonic Systems: Theory

Mixing between states with site energies $\varepsilon_1$ and $\varepsilon_2$ and coupling $J$ can be quantified by $\theta$.

$$\tan(2\theta) = \frac{2J}{\varepsilon_1^{eq} - \varepsilon_2^{eq}}$$

$$|\mu\rangle \equiv (\cos(\theta) \cdot B_1^+ + \sin(\theta) \cdot B_2^+) |0\rangle \equiv B_\mu^+ |0\rangle$$

$$|\nu\rangle \equiv (-\sin(\theta) \cdot B_1^+ + \cos(\theta) \cdot B_2^+) |0\rangle \equiv B_\nu^+ |0\rangle$$

Energy fluctuations at one monomer shift both exciton states in the same direction; the magnitude depends on the coupling.

Stronger mixing yields stronger correlation.

Coupling strength relates to the renormalization coefficient, $C_{mn}$, for the line broadening function, $g(t)$.

$$C_{\mu\nu} = C_{\nu\mu} = 2 \cdot \sin^2 \theta \cos^2 \theta$$

Dependence of $g(t)$ on coupling causes the one-color and two-color peak shift to increase with increased coupling.

$$C_{\mu\nu} \approx C_{\tau^*}(T) \equiv \frac{\tau^*_{\text{two}}(T)}{\tau^*_{\text{two}}(T) + \tau^*_{\text{one}}(T)}$$

1-and 2-Color (620, 620, 700nm) Photon Echo Peak Shift

- 1-color and 2-color peakshifts of LuPc$_2$ are very similar.

- Oscillation, of similar period in both measurements, but approximately $\pi$ out of phase.
The Mixing Coefficient

$C_{\tau^*}$ (experiment)

- Experimental $C_{\tau^*}$ is approximately 0.45
- Dip at longer time due to out-of-phase oscillation between 1- and 2-color

Electronic structure of $\text{Lu}(\text{P}c)_2^-$

Estimating $C_{\mu\nu}$

If all dipole strength comes from $|\text{EX}+\rangle$, the ratio of absorption intensities gives

$$\tan^2(\theta) \Rightarrow C_{\mu\nu} \cong 0.43$$

From wavefunction coefficients of Ishikawa et. al $C_{\mu\nu} \cong 0.40$
Modulation of the Electronic Coupling

\[ \tau_{\text{one}}^*(T) = \frac{(1 - C_{\mu\nu})a(T) + 2C_{\mu\nu}N(T)}{\sqrt{\pi} \left\{ (1 - C_{\mu\nu})C_0 \right\}^{3/2}} \]

\[ \tau_{\text{two}}^*(T) = \frac{(C_{\mu\nu}a(T) - 2C_{\mu\nu}N(T))}{\sqrt{\pi} \left\{ (1 - C_{\mu\nu})C_0 \right\}^{3/2}} \]

\[ N(T) = \frac{1}{\hbar^2} \langle q_{12}(T)q_{12}(0) \rangle \]

\[ = \frac{\langle q_{12}^2 \rangle}{\hbar^2} e^{-\Gamma T} \cos \omega_{\text{vib}} T \]

\[ \frac{\tau_{\text{two}}^*(T)}{\tau_{\text{one}}^*(T) + \tau_{\text{two}}^*(T)} = C_{\mu\nu} \left[ 1 - \frac{2N(T)}{a(T)} \right] \]

Minhaeng Cho

\[ \pi \text{ phase shift} \]

\[ (a(T) = \text{real part of } C(t)) \]
Wavelength resolved pump-probe signals for LuPc$_2$.

The beats on the red side of the high energy band are exactly out of phase with the beats on the red side of the low energy band, but are in phase with the beats on the blue side of the low energy band.
Modulated Electronic Structure

Simple model with a single coordinate, \( x \), coupled linearly to the states \( E_{EX^+} \), \( E_{CR^+} \) and the coupling between these two states \( V_{EX-CR} \)

\[
x(t) = x_o \cos(\omega t) \exp(-t/\tau)
\]
\[
E_{EX^+} = E_{EX^+}^0 + \Delta E_{EX^+} x
\]
\[
E_{CR^+} = E_{CR^+}^0 + \Delta E_{CR^+} x
\]
\[
V_{EX-CR} = V_{EX-CR}^0 + \Delta V_{EX-CR} x
\]

\[\Rightarrow\] Non-Condon effects (modulation of transition moments). If the signs of \( \Delta E_{EX^+} \) and \( \Delta E_{CR^+} \) are opposite the motions of \(|1E^+\rangle\) and \(|2E^+\rangle\) are anti-correlated.

New, time-dependent potential curves for \(|1E^+\rangle\) and \(|2E^+\rangle\)
Physical Origin

Ground State Wave-Packet

\[ \omega_1 \]

\[ \omega_2 \]

Symmetric nitrogen-metal mode; Fluctuating coupling
1C and 2C3PEPS on P-oxidized reaction center of *Rb. Sphaeroides*

<table>
<thead>
<tr>
<th></th>
<th>1C3PEPS</th>
<th>2C3PEPS</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>H band:</strong></td>
<td>$\lambda_1=\lambda_2=\lambda_3=750\text{nm}$</td>
<td>Uphill:</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\lambda_1=\lambda_2=800\text{nm}$, $\lambda_3=750\text{nm}$</td>
</tr>
<tr>
<td><strong>B band:</strong></td>
<td>$\lambda_1=\lambda_2=\lambda_3=800\text{nm}$</td>
<td>Downhill:</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\lambda_1=\lambda_2=750\text{nm}$, $\lambda_3=800\text{nm}$</td>
</tr>
</tbody>
</table>

---

- **Excitonic Coupling**
- **Energy Levels:** $|b\rangle$, $|B\rangle$, $|H\rangle$, $|g_{b}\rangle$, $|g_{h}\rangle$
- **Wavelengths:**
  - **H band:** $750\text{nm}$
  - **B band:** $800\text{nm}$
Simulation of 3PEPS based on density matrix

\[ \dot{\rho}(t) = -i[H_S + H_{\text{int}}(t), \rho(t)] - R[\rho(t)] \]

Directly simulate \( P^{(3)}_{3\text{PPE}}(t) \) from laser field-driven dynamics:

\[ S(\tau, T) \sim \int_0^\infty dt |P^{(3)}_{3\text{PPE}}(t)|^2 \rightarrow \text{Peakshift} \]

Pros compared to conventional response function formalism:

- Pulse-overlap effects included by considering laser fields explicitly.
- Complete dynamics of the system treated by non-Markovian equations of motion.
Simulation for 1C3PEPS and obtained bath parameters

Most of the dynamics happen in less than 300fs due to the rapid energy transfer (H→B→P+)

Proper inclusion of pulse-overlap effects improved reproduction of the peakshifts measured at small T

Determination of bath parameters for H and B, respectively

<table>
<thead>
<tr>
<th></th>
<th>λ</th>
<th>Ω</th>
<th>Γ</th>
<th>σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>75</td>
<td>100</td>
<td>150</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>1500</td>
<td>220</td>
<td>10</td>
<td>60</td>
</tr>
<tr>
<td>H</td>
<td>250</td>
<td>50</td>
<td>150</td>
<td>60</td>
</tr>
</tbody>
</table>

λ: electron-phonon coupling constant
Ω: characteristic frequency
Γ: damping constant
σ: static disorder
Simulation for 1C3PEPS and obtained bath parameters

Most of the dynamics happen in less than 300fs due to the rapid energy transfer (H→B→P⁺)

Proper inclusion of pulse-overlap effects improved reproduction of the peakshifts measured at small T

Determination of bath parameters for H and B, respectively

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</tr>
</tbody>
</table>

λ: electron-phonon coupling constant
Ω: characteristic frequency
Γ: damping constant
σ: static disorder

Determination of coupling constant J between H & B by 2C3PEPS

J=250 cm⁻¹ gives best fit to both measurements

Negative peakshift due to the rapid dynamics B → P⁺

Nonlinear spectroscopy

incident fields \quad QM \ system \quad signal \ field \quad detection

\sim i \omega P(\omega)

\text{different aspects probed by TA, TG, 3PEPS etc.}

$$\tilde{P}^{(n)}(\omega) = \varepsilon_0 \int_{-\infty}^{\infty} d\omega_1 \cdots \int_{-\infty}^{\infty} d\omega_n \chi^{(n)}(\omega_1, \ldots, \omega_n) |\tilde{E}(\omega_1) \cdots \tilde{E}(\omega_n)\delta(\omega - \omega_s)$$

obtain complete information about system by measuring signal intensity and phase
Third-order spectroscopy

- **coh. time**: \( t_1 \)  
- **pop. time**: \( \tau \)  
- **echo time**: \( T \)  
- **time-domain local oscillator** = 4

**Homodyne detection**: 
\[ |E_{\text{sig}}(\omega)|^2 \]

or even frequency-integrated

**Heterodyne (time domain)**: 
\[ |E_{\text{sig}}(t) + E_{\text{LO}}(t+t_{\text{LO}})|^2 \]

problem: \( t_{\text{LO}} \) needs to be scanned

**Heterodyne (frequency domain)**: 
\[ |E_{\text{sig}}(\omega) + E_{\text{LO}}(\omega) \exp\{-i\omega t_{\text{LO}}\}|^2 \]

multichannel frequency detection

LO-position \( t_{\text{LO}} \) fixed
Two-Dimensional Heterodyne Spectroscopy

coh. pop. echo
time time time
4=LO 1 2 3 sig

diffactive optic (DO)
spectrometer
spherical mirror
sample
OD3

delay 1
delay 2

delay 1

delay 2

2 f
Experimental setup

- diffractive optic (DO)
- spherical mirror
- delay 1
- delay 2
- sample
- lens
Advantages of setup

<table>
<thead>
<tr>
<th>problem</th>
<th>solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>small signals</td>
<td>heterodyne advantage (record signals $&lt; 100$ aJ)</td>
</tr>
<tr>
<td>delay accuracy</td>
<td>small-angled wedges (position repeatability: 5 as)</td>
</tr>
<tr>
<td>phase stability</td>
<td>diffractive-optics-based setup (2D background $&lt; 2%$)</td>
</tr>
<tr>
<td>scattering</td>
<td>subtraction by automated shutter</td>
</tr>
</tbody>
</table>

first implementation of tunable 2D spectroscopy in the visible region
2D data analysis

**step 1a:** slice spectrum (for each $\tau$)

**step 1b:** get $I(\omega)$, $\Phi(\omega)$

**step 2:** FFT$^{-1}$ (along $\tau$)

---

**raw data**

![Graph showing raw data with wavelength on the y-axis and coherence time on the x-axis.](image)

**FFT**

![Graph showing intensity and phase on the y-axis with wavelength on the x-axis.](image)

**cut & FFT$^{-1}$**

![Graph showing intensity with "Fourier" time on the x-axis.](image)
Time-delay accuracy

Nile Blue heterodyned signal recorded within separate scans

lab time:
- 20 min
- 15 min
- 10 min
- 5 min
- 0 min

no shift of fringe pattern:
interferometric stability and reproducibility
Scattering subtraction

Desired heterodyned signal comes from \((E_4 \ast E_{\text{sig}})\)

But heterodyned signal involves scatter \(E_1, \ldots, E_3\):
\[
| E_1 + E_2 + E_3 + E_4 + E_{\text{sig}} |^2
\]
without subtraction

Remove scattering by
\[
| E_1 + E_2 + E_3 + E_4 + E_{\text{sig}} |^2
- | E_3 + E_4 |^2 - | E_1 + E_2 + E_4 |^2
\]
with subtraction
Phasing (PP versus 2D)

Nile Blue in acetonitrile (T = 0 fs)

Positive signal: emission or ground-state bleach

Negative signal: excited-state absorption

Overall phase determines $\text{Re} \{ S_2 \}$: absorption / emission

$\text{Im} \{ S_2 \}$: refraction
2D spectrum

“probability distribution” $S_2(\omega_\tau, T, \omega_t)$

2: wait for population time $T$

3: emit or bleach at frequency $\omega_t$

here: inhomogeneous system “remembers” excitation after time $T$

“homogeneous” linewidth

“inhom.” linewidth

1: excite at frequency $\omega_\tau$
Nile Blue (experiment)

Abs

Re

Pha

Im

$\omega_t / \text{fs}^{-1}$

$\omega_\tau / \text{fs}^{-1}$

$T = 100 \text{ fs}$
Theory of 3-level systems

"regular" energy-gap correlations

correlations between excited states

g(t) has contributions from vibrations: \((\omega_v, \lambda_v, \tau_v)\)
solvent: Gaussian \((\lambda_{sg}, \tau_{sg})\)
Exponential \((\lambda_{se}, \tau_{se})\)

\[
g(t) = \frac{1}{\hbar^2} \int_0^t d\tau \int_0^{\tau} d\tau' C(\tau')
\]

\[
C_{ee}(t) = Tr_{v,s} \{ U_{eg}(t) U_{eg}(0) \rho_{gg} \}
\]

\[
C_{ff}(t) = Tr_{v,s} \{ U_{fg}(t) U_{fg}(0) \rho_{gg} \}
\]

\[
C_{fe}(t) = Tr_{v,s} \{ U_{fg}(t) U_{eg}(0) \rho_{gg} \}
\]
Nile Blue (simulation)

2-level simulation

\[ \text{Re} \quad \text{Im} \]

0 fs

experiment

3-level simulation

\[ \omega_{fe} = \omega_{eg} + 100 \text{ cm}^{-1} \]

\[ g_{fe}(t) = 0 \]

3-level simulation

\[ \omega_{fe} = \omega_{eg} + 100 \text{ cm}^{-1} \]

\[ g_{fe}(t) = g_{ee}(t) \]
Dipole strength and $g_{fe}$

- For $T = 0$ fs:
  - $d_{fe} = d_{eg}$
  - $g_{fe}(t) = 0$
  - $\omega_{fe} = \omega_{eg}$

- For $T = 100$ fs:
  - $d_{fe} = 1.5 \, d_{eg}$
  - $g_{fe}(t) = 0$
  - $\omega_{fe} = \omega_{eg}$

- $d_{fe} = 1.5 \, d_{eg}$
  - $g_{fe}(t) = g_{ee}(t)$
  - $\omega_{fe} = \omega_{eg}$
2D Spectroscopy of Aggregates

MOLECULAR AGGREGATES

WEAKLY COUPLED

STRONGLY COUPLED

Absorption spectra of BIC monomer and J-aggregates

LH2 Complex

Linear chain of 2 level molecules with electrostatic dipole-dipole interaction

Two-exciton Band 2e

One-exciton Band 1e

Ground state g
J-AGGREGATE HAMILTONIAN

**SITE BASIS:**

\[ H(q) = \sum_{n=1}^{N} |n\rangle \varepsilon_{n} \langle n| + \sum_{m,n=1 \atop m \neq n}^{N} |m\rangle J_{mn} \langle n| + \sum_{n=1}^{N} |n\rangle H_{nn}^{el-ph}(q) \langle n| + H_{ph}^{q}(q) \]

**Off-diagonal**
- Electrostatic

**Diagonal**
- Electron-Phonon

**EXCITON BASIS:**

\[ H(q) = \sum_{k=1}^{N} |k\rangle E_{k} \langle k| + \sum_{k=1}^{N} |k\rangle \left[ \sum_{n} |\phi_{kn}|^{2} \cdot H_{nn}^{el-ph}(q) \right] \langle k| + \sum_{k,k'=1 \atop k \neq k'}^{N} |k\rangle \left[ \sum_{n} |\phi_{kn} \cdot \phi_{kn'}^{*}| \cdot H_{nn}^{el-ph}(q) \right] \langle k'| + H_{ph}^{q}(q) \]

**Diagonal Exciton-Phonon**
- Renormalization Factors Cause Exchange Narrowing

**Off-Diagonal Exciton-Phonon**
- Overlap Factors Define Relaxation

**EXCITON WAVEFUNCTIONS**

\[ |k\rangle = \sum_{n=1}^{N} \phi_{kn} \cdot |n\rangle \]

\[ \mu_{k} = \mu_{o} \sum_{n=1}^{N} \phi_{kn} \]

- Higher Exciton States are Strongly Delocalized
- Exchange-Narrowing is Stronger for Higher (More Delocalized) Exciton States
- Relaxation is Faster for Higher Exciton States
BIC J-Aggregates, Real 2D Spectra
Absolute Value 2D Spectra BIC J-Aggregates

Diagonal Elongation: Static Disorder
Width Broadening at Higher Frequencies: Exciton Relaxation
Detailed Width Profile: Frequency-Dependent Dynamics
Absolute Value 2D Plots
BIC J-aggregates

Absolute value of the 2D plots; population periods T=50, 500 fs.

Evolution of the 2D plots is mostly determined by the exciton relaxation during the population period.
**Frequency-Dependent Exciton Relaxation**

- **Fast Mode, no Relaxation**: Small Changes with T, Minimum Width at Higher Frequencies

- **Simulation with relaxation & Experiment**:
  - Minimum width to the lower Frequency of 2D Peak & Asymmetric Shape:
    Relaxation induced “Life-Time Broadening” is stronger at Higher Frequency
  - Increased Width: Exciton Relaxation in Population Period
  - Reduced Width: No Exciton Relaxation
J-Aggregate Hamiltonian

**SITE BASIS:**

\[ H(q) = \sum_{n=1}^{N} \langle n | \mathcal{E}_n | n \rangle + \sum_{m,n=1}^{N, m \neq n} | m \rangle J_{mn} \langle n | + \sum_{n=1}^{N} | n \rangle H_{nn}^{el-ph}(q) \langle n | + H^{ph}(q) \]

- Off-diagonal Electrostatic
- Diagonal Electron-Phonon

**EXCITON BASIS:**

\[ |k\rangle = \sum_{n=1}^{N} \phi_{kn} \cdot |n\rangle \]

- Diagonal Exciton-Phonon
- Off-Diagonal Exciton-Phonon

\[ H(q) = \sum_{k=1}^{N} |k\rangle E_k \langle k| + \sum_{k=1}^{N} \langle k| \left[ \sum_{n} \left| \phi_{kn} \right|^2 \cdot H_{nn}^{el-ph}(q) \right] \langle k| + \sum_{k,k'=1}^{N} \langle k| \left[ \sum_{n} \left[ \phi_{kn} \phi_{kn}'^* \right] \cdot H_{nn}^{el-ph}(q) \right] \langle k'| + H^{ph}(q) \]

- Exchange Narrowing: Reduction of the Fluctuation Amplitude
- Relaxation: Hopping Between States

**FREQUENCY-DEPENDENT DYNAMICS**

\[ |n\rangle - \text{monomer } \#n \text{ is excited} \]
Experimental 2D Spectrum

2D Spectra From J-Aggregates for T=50fs and T=500fs

Broadening of Higher Frequency Part is Due to Exciton Relaxation
Discrimination of Fluctuational and Relaxational Dynamics

EXPERIMENT
SIMULATION without RELAXATION
a) fast mode
b) slower mode

SIMULATION with RELAXATION
Relaxation *Broadens*
High Frequency Part

Fluctuation Only Dynamics
High Frequency Part *Shrinks*
Frequency-Dependent Delocalization, Relaxation and Exchange-Narrowing

- Delocalization Varies from 5 to 30 monomers across the Absorption Band of J-aggregates
- Relaxation is Increased at Higher Frequencies
- Dynamic Fluctuations are Reduced at Higher Frequencies by Exchange-Narrowing
**Best Fit: Experiment & Simulations**

- Experiment is Reproduced Theoretically **over Complete R**

- Model Parameters (only 1 independent):
  - *Disorder*: $\sigma = 250 \text{ cm}^{-1}$
  - *Gaussian Mode Correlation Function*: $\lambda = 250 \text{ cm}^{-1}$, $\tau = 50 \text{ fs}$ (liquid water: 30…70fs)
  - *Coupling*: $J = 1080 \text{ cm}^{-1}$ (from absorption)
    - (σ & λ determine absorption spectrum width)
  - *Frequency-Dependent Dynamics is Correctly Reproduced*

- Monomer Static Disorder and the Approximate Correlation Function are Retrieved

- Dynamics of One and Two Exciton Contributions are Correctly Reproduced

**Solid lines are plotted at +10,20,…% and dashed at -10,20,…% of the absolute 2D spectrum maximum [at given time T]**