Two-Dimensional Electronic Spectroscopy as Probes of Excitonic Structures and Fluctuations in Molecular Aggregates

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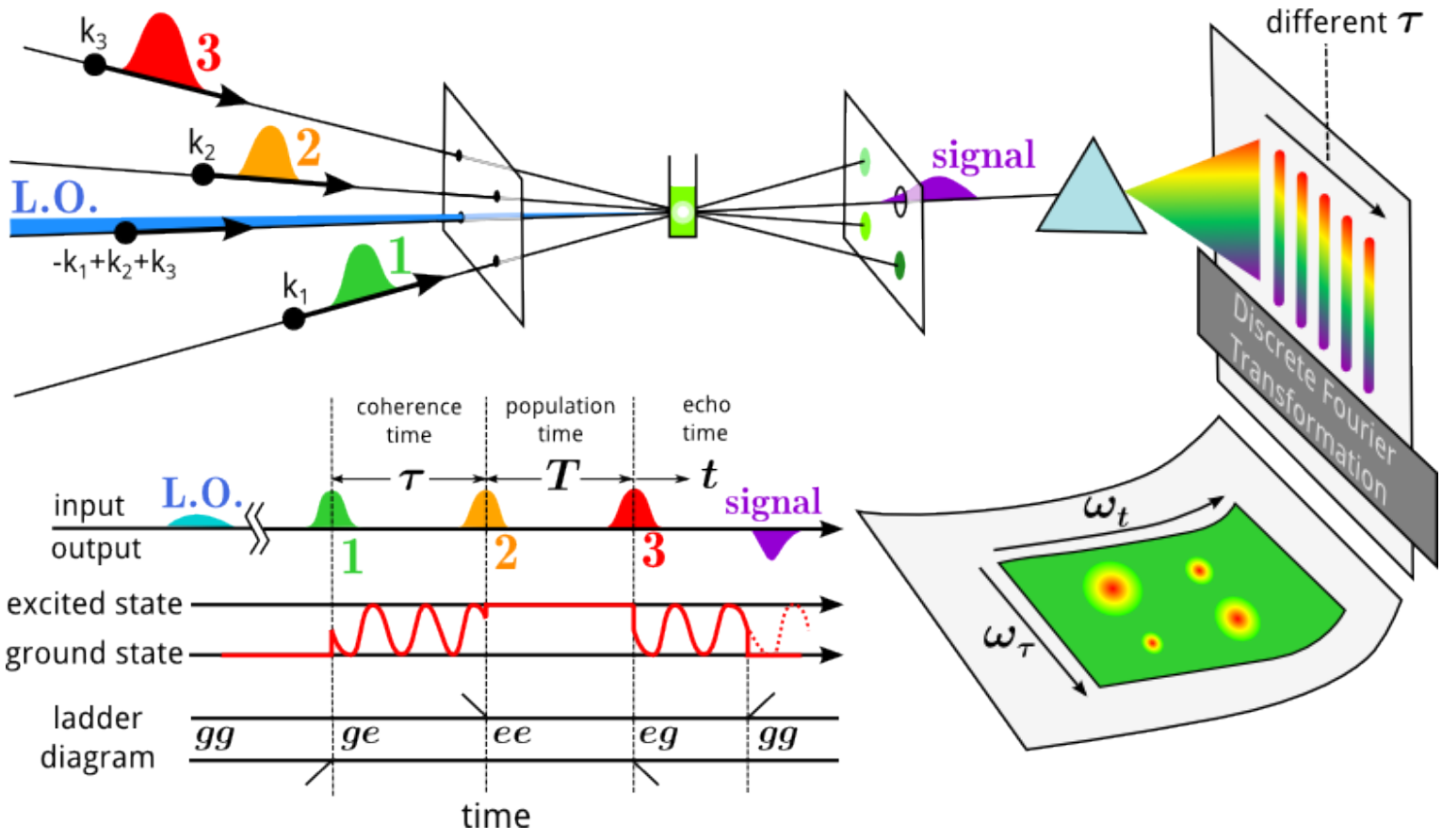
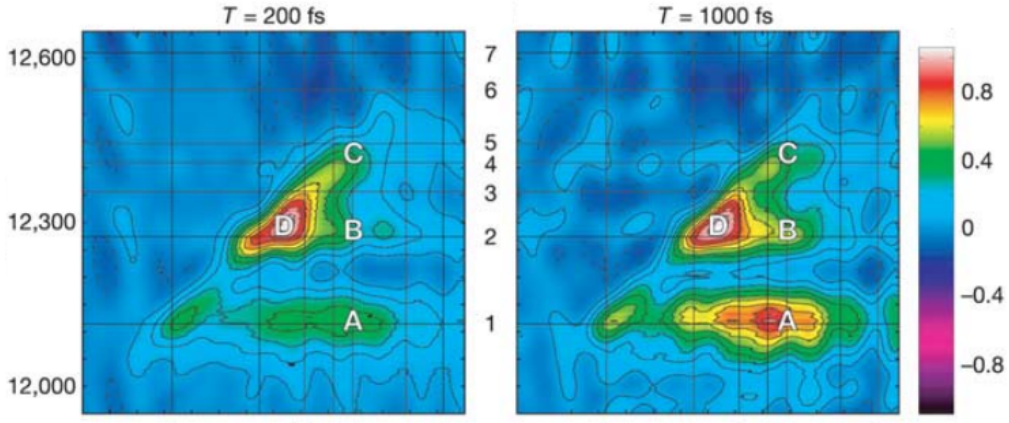
2D Electronic Spectroscopy (2DES)

Introduction

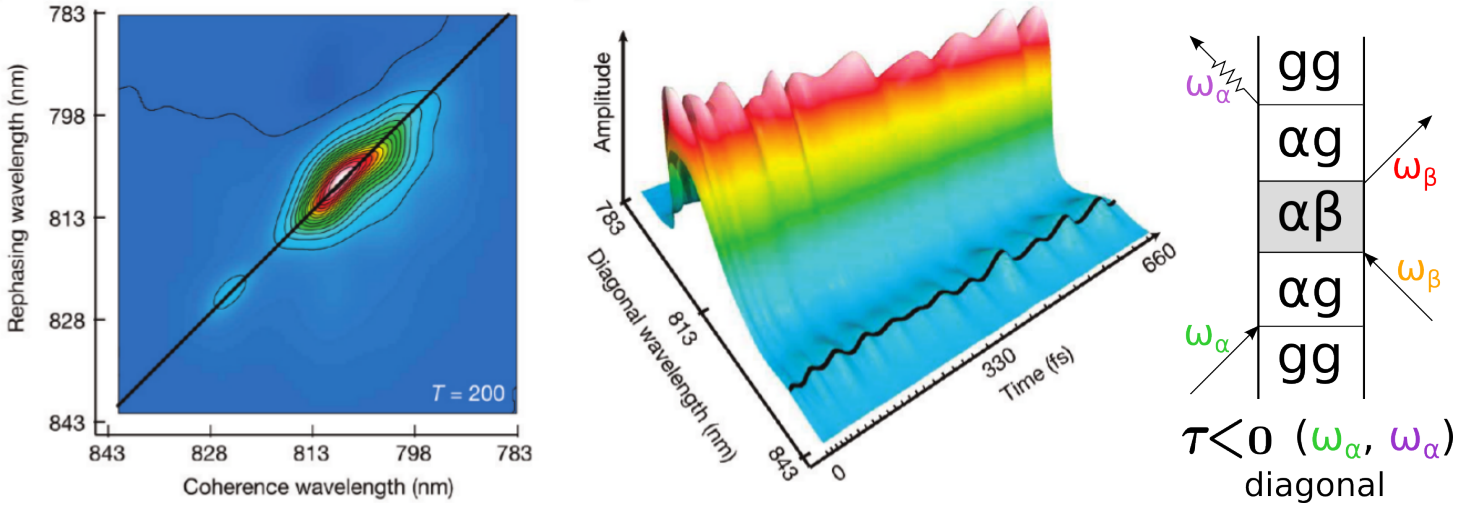


2D Electronic Spectroscopy (2DES)

A Useful Tool for Studying Excitaion Energy Transfer



Brixner, T. et al., 2005. Nature, 434: 625-628.



Engel, G. S. et al., 2007. Nature, 446: 782-786.

Element-specific 2D Electronic Spectroscopy

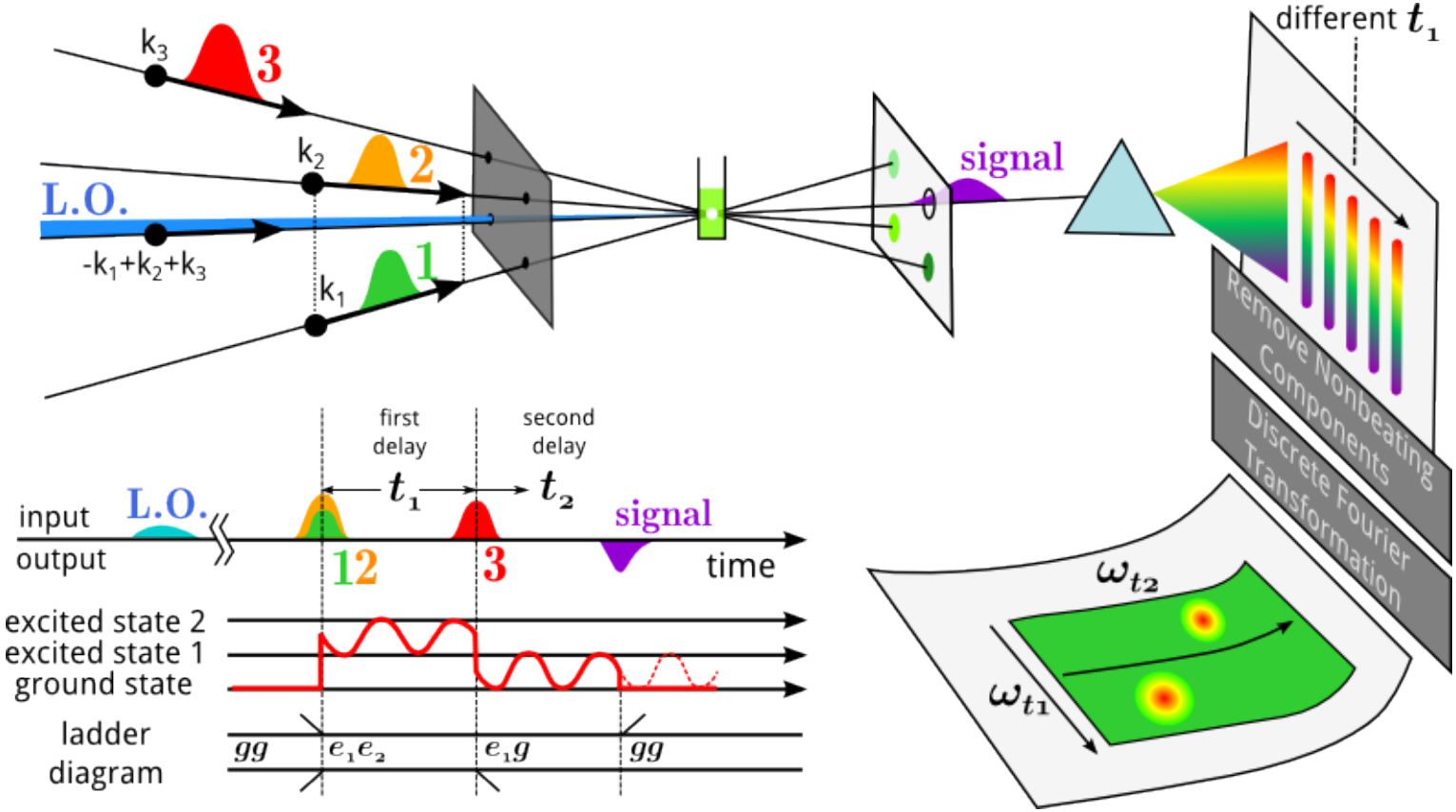
Motivation

To design a spectroscopic tool, which

- is based on (or simplifies) conventional 2DES experiments.
- resolves less convoluted spectra than 2DES.
- focuses on coherence dynamics in molecular aggregates.

Element-specific 2D Electronic Spectroscopy

Proposed Experimental Setup



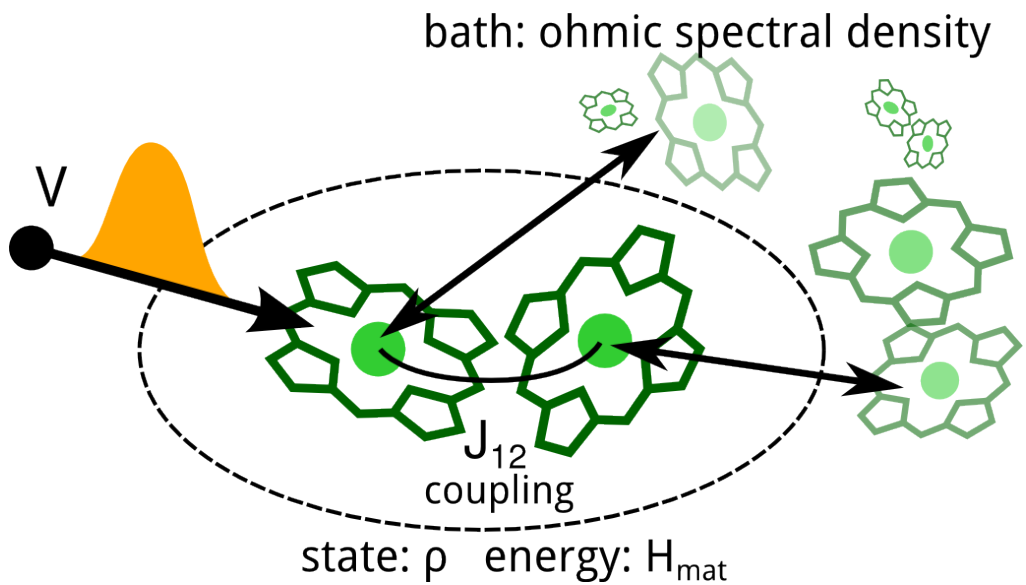
Verification of ES2DES Design

Model and Computational Method

Utilize a time-nonlocal quantum master equation (TNLQME) approach, developed by Meier and Tannor.

$$\frac{d\rho}{dt} = -i\left[H_{\mathrm{mat}} + V, \rho\right] - \int_0^t \kappa(\tau)\rho(t-\tau)\, d\tau$$

Meier, C., Tannor, D. J., 1999. J. Chem. Phys., 111, 3365.



Verification of ES2DES Design

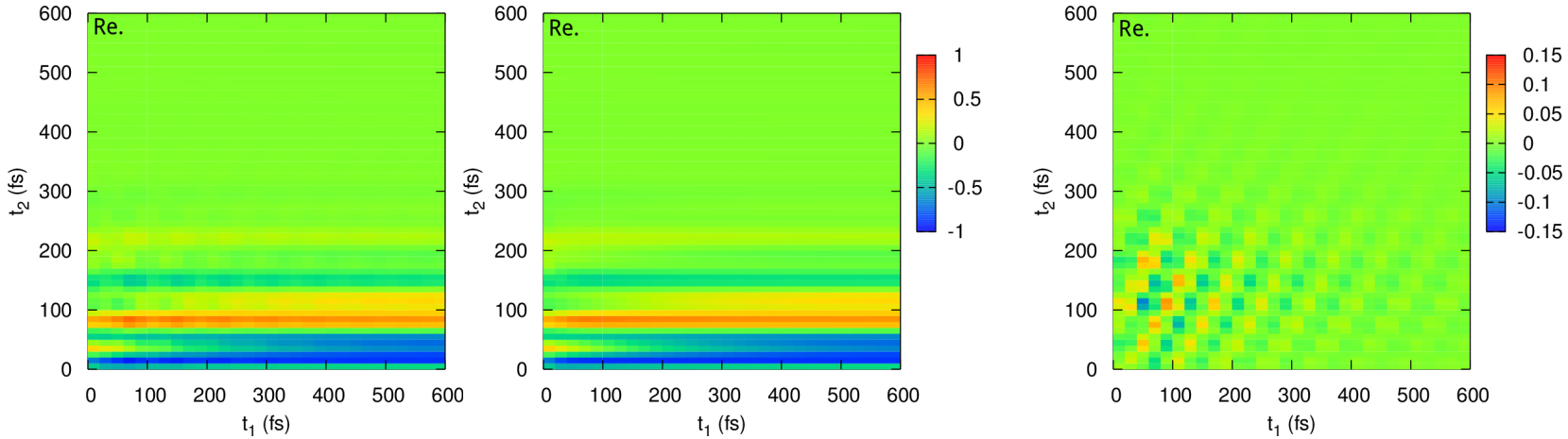
Post-detectional Signal Processing

Model the non-beating components with $f(t_1)$, where

$$\begin{cases} f(t_1) = Ae^{-\lambda t_1} + Be^{-t_1^2/2\sigma^2} + C \\ f(t_1 = t_{1,N}) = 0 \end{cases}.$$

Joo, T. et al., 1996. J. Chem. Phys., 104, 60896108.

For each t_2, subtract a $f(t_1)$ fit from the dataset. This gives descent results on dimer and trimer systems.



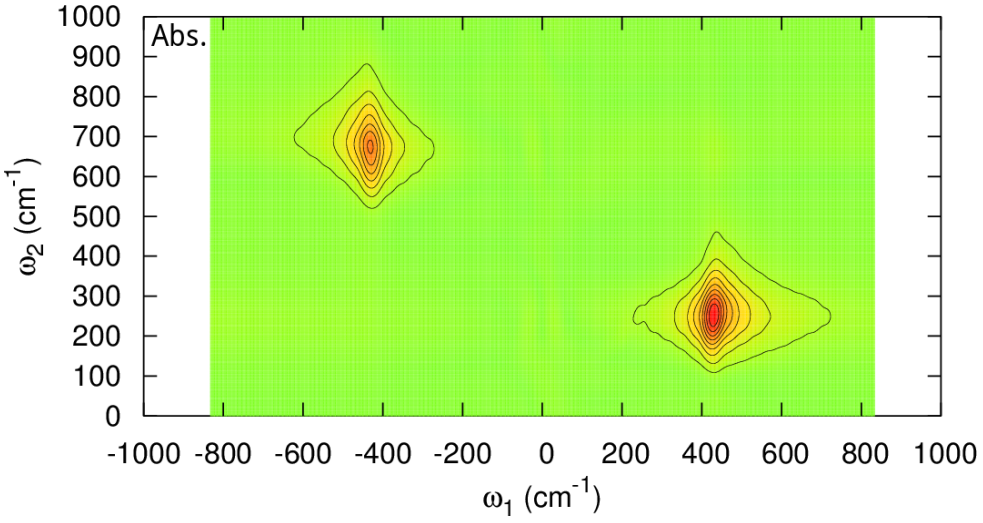
(a) Raw signal. (b) Removed part. (c) After removal.

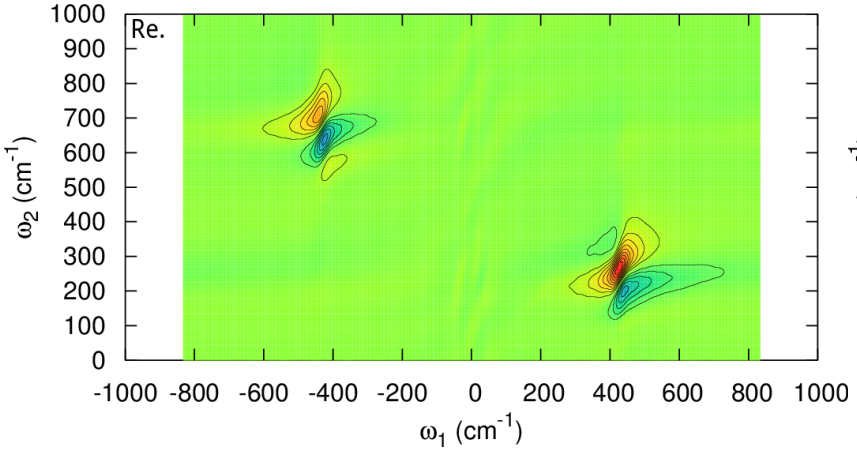
Verification of ES2DES Design

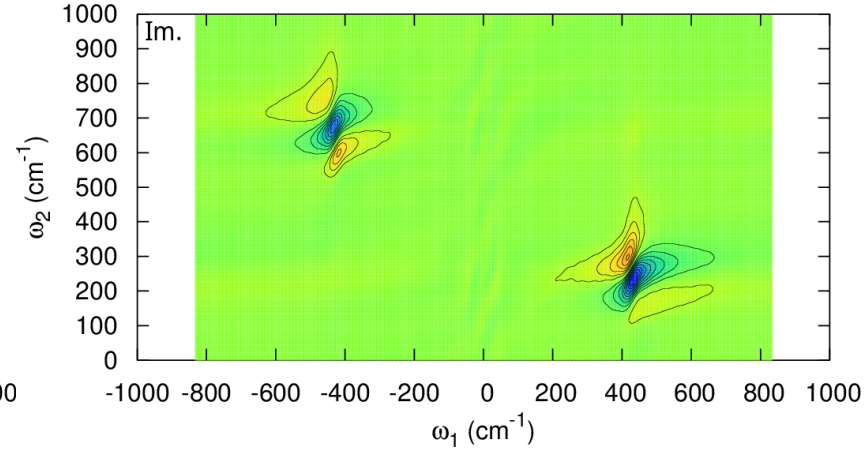
Results – Dimer

Exciton State	Energy (cm^{-1})
$\|\alpha\rangle$	$\omega_\alpha = 243$
$\|\beta\rangle$	$\omega_\beta = 656$

Signal (cm^{-1})	Assignment
$(413, 243)$	$(\omega_{\beta\alpha}, \omega_\alpha)$
$(-413, 656)$	$(-\omega_{\beta\alpha}, \omega_\beta)$





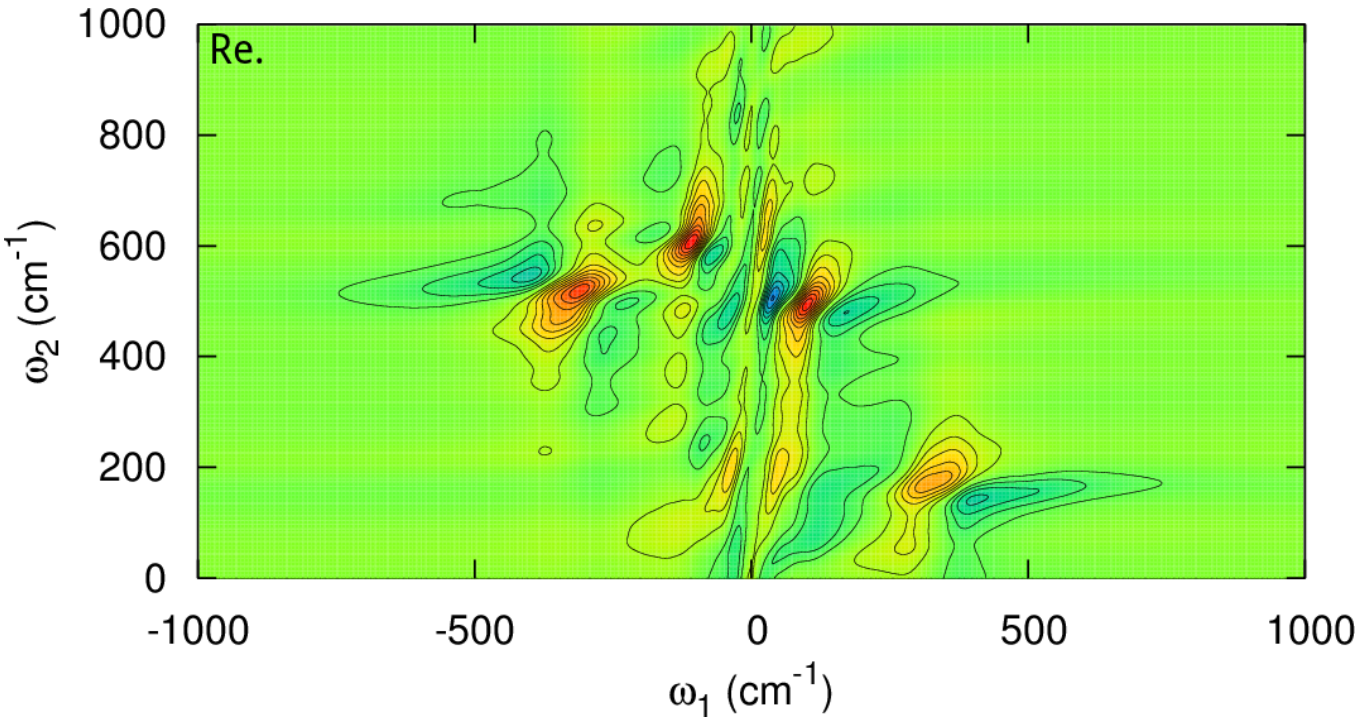


Verification of ES2DES Design

Results – Trimer

Exciton State	Energy (cm^{-1})
$\|\alpha\rangle$	$\omega_\alpha = 169$
$\|\beta\rangle$	$\omega_\beta = 506$
$\|\gamma\rangle$	$\omega_\beta = 624$

Signal (cm^{-1})	Assignment
$(337, 169)$	$(\omega_{\beta\alpha}, \omega_\alpha)$
$(-337, 506)$	$(-\omega_{\beta\alpha}, \omega_\beta)$
$(118, 506)$	$(\omega_{\gamma\beta}, \omega_\beta)$
$(-118, 624)$	$(-\omega_{\gamma\beta}, \omega_\gamma)$



General 3rd-order Response Function

Consider a Hamiltonian with semi-classical light-matter interaction,

$$H = H_{\text{mat}} + V(t) = H_{\text{mat}} - \boldsymbol{\mu} \cdot \mathbf{E}(t).$$

3rd-order nonlinear spectroscopy measures polarization arises from 3 incident light field.

$$\mathbf{P}^{(3)}(t) = \text{Tr}\left\{\boldsymbol{\mu}_{\text{I}}(t)\rho_{\text{I}}^{(3)}(t)\right\},$$

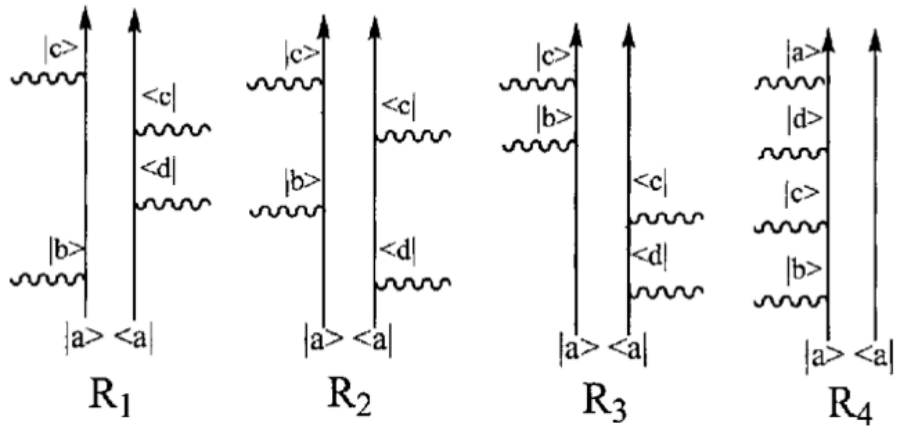
where

$$\begin{aligned}\rho_{\text{I}}^{(3)}(t) &= \left(\frac{-i}{\hbar}\right)^3 \int_{-\infty}^{t} d\tau_3 \int_{-\infty}^{\tau_3} d\tau_2 \int_{-\infty}^{\tau_2} d\tau_1 \left[V_{\text{I}}(\tau_3), [V_{\text{I}}(\tau_2), [V_{\text{I}}(\tau_1), \rho_{\text{eq}}]]\right] \\ &\equiv \left(\frac{-i}{\hbar}\right)^3 \int_{-\infty}^{t} d\tau_3 \int_{-\infty}^{\tau_3} d\tau_2 \int_{-\infty}^{\tau_2} d\tau_1 \, R(\tau_3, \tau_2, \tau_1) E(\tau_3) E(\tau_2) E(\tau_1).\end{aligned}$$

$R(\tau_3, \tau_2, \tau_1)$ is the 3rd-order response function.

Mukamel, S., 1995. "Principles of Nonlinear Spectroscopy."

General 3rd-order Response Function



Cho, M., Fleming, G. R., 2005. J. Chem. Phys. 123, 114506.

$$R(\tau_3,\tau_2,\tau_1) = \left(\frac{i}{\hbar}\right)^3 \Theta(\tau_3)\Theta(\tau_2)\Theta(\tau_1) \sum_{n=1}^{4} \left[R_n(\tau_3,\tau_2,\tau_1) - R_n^*(\tau_3,\tau_2,\tau_1)\right],$$

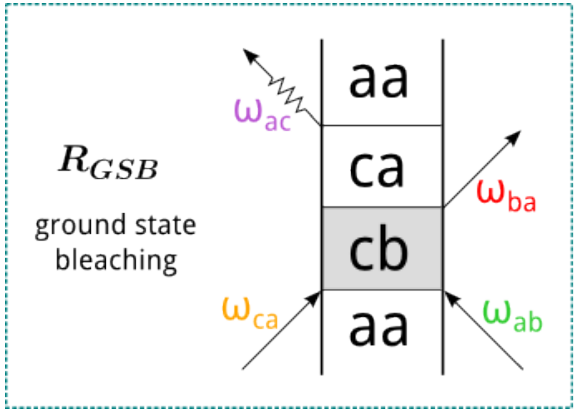
where

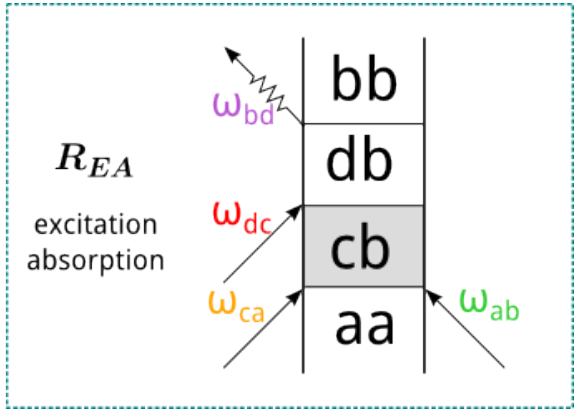
$$\begin{aligned}
R_1(\tau_3,\tau_2,\tau_1) &\equiv \langle \mu(\tau_1)\mu(\tau_1+\tau_2)\mu(\tau_1+\tau_2+\tau_3)\mu(0)\rangle\,,\\
R_2(\tau_3,\tau_2,\tau_1) &\equiv \langle \mu(0)\mu(\tau_1+\tau_2)\mu(\tau_1+\tau_2+\tau_3)\mu(\tau_1)\rangle\,,\\
R_3(\tau_3,\tau_2,\tau_1) &\equiv \langle \mu(0)\mu(\tau_1)\mu(\tau_1+\tau_2+\tau_3)\mu(\tau_1+\tau_2)\rangle\,,\\
R_4(\tau_3,\tau_2,\tau_1) &\equiv \langle \mu(\tau_1+\tau_2+\tau_3)\mu(\tau_1+\tau_2)\mu(\tau_1)\mu(0)\rangle\,.
\end{aligned}$$

Mukamel, S., 1995. "Principles of Nonlinear Spectroscopy."

ES2DES Pathways and Responses

Pathways in Coherent States during the First Delay





$$R_{\mathrm{ES2DES}}\left(t_2,t_1\right)=2\left(\frac{i}{\hbar}\right)^3\Theta(t_2)\Theta(t_1)\left[R_{\mathrm{EA}}(t_2,t_1)-R_{\mathrm{GSB}}(t_2,t_1)\right],$$

where

$$R_{\mathrm{EA}}(t_2,t_1)=\sum_{a,b,c,d}\left\langle\mu_{ab}(0)\mu_{bd}(t_1+t_2)\mu_{dc}(t_1)\mu_{ca}(0)\rho_{\mathrm{B}}\right\rangle_{\mathrm{B}},$$

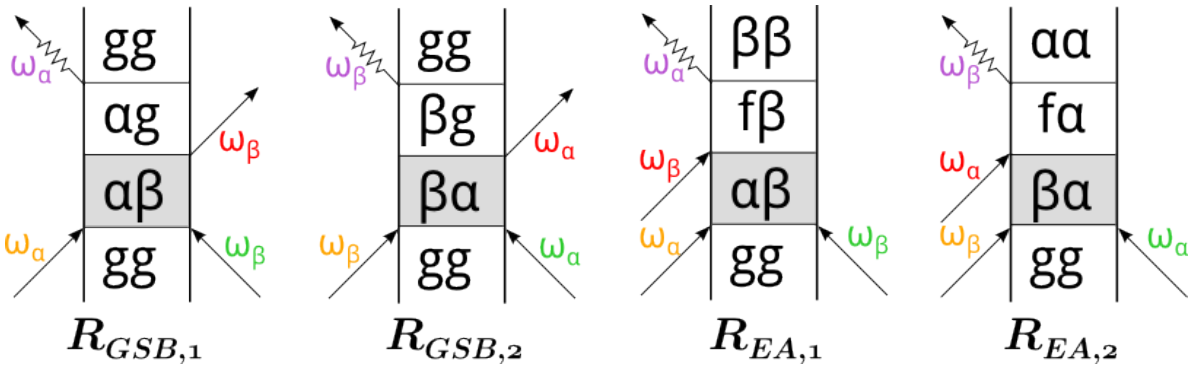
$$R_{\mathrm{GSB}}(t_2,t_1)=\sum_{a,b,c}\left\langle\mu_{ab}(0)\mu_{ba}(t_1)\mu_{ac}(t_1+t_2)\mu_{ca}(0)\rho_{\mathrm{B}}\right\rangle_{\mathrm{B}}.$$

ES2DES Pathways and Responses

A Dimer System with States g, α, β, and f

$$R_{\mathrm{ES2DES}}(t_2,t_1) = 2\left(\frac{i}{\hbar}\right)^3 \Theta(t_2)\Theta(t_1)\left(R_{\mathrm{EA},1}+R_{\mathrm{EA},2}-R_{\mathrm{GSB},1}-R_{\mathrm{GSB},2}\right),$$

$$\begin{aligned}
R_{\mathrm{EA},1} &\equiv \mathrm{Tr}\left\{\mu_{g\beta}(0)\mu_{\beta f}(t_1+t_2)\mu_{f\alpha}(t_1)\mu_{\alpha g}(0)\rho_{\mathrm{B}}\right\},\\
R_{\mathrm{EA},2} &\equiv \mathrm{Tr}\left\{\mu_{g\alpha}(0)\mu_{\alpha f}(t_1+t_2)\mu_{f\beta}(t_1)\mu_{\beta g}(0)\rho_{\mathrm{B}}\right\},\\
R_{\mathrm{GSB},1} &\equiv \mathrm{Tr}\left\{\mu_{g\beta}(0)\mu_{\beta g}(t_1)\mu_{g\alpha}(t_1+t_2)\mu_{\alpha g}(0)\rho_{\mathrm{B}}\right\},\\
R_{\mathrm{GSB},2} &\equiv \mathrm{Tr}\left\{\mu_{g\alpha}(0)\mu_{\alpha g}(t_1)\mu_{g\beta}(t_1+t_2)\mu_{\beta g}(0)\rho_{\mathrm{B}}\right\}.
\end{aligned}$$



Cumulant Expansion Approximation over Bath

$$H_{\text{mat}} = H_{\text{S}} + H_{\text{B}} + H_{\text{SB}}.$$

Expand H_{SB} to the 2^{nd}-order.

$$\begin{aligned} R_{\text{GSB},1} =& \mu_{g\beta}^2 \mu_{g\alpha}^2 \exp\left(-i\omega_{\beta\alpha} t_1 - i\omega_\alpha t_2\right) \cdot \\ & \exp[-g_{\beta\beta}^*(t_1) + g_{\beta\alpha}(t_1) - g_{\beta\alpha}^*(t_2) - g_{\alpha\alpha}(t_1+t_2) + g_{\beta\alpha}^*(t_1+t_2)], \end{aligned}$$

where

$$g_{ab}(t) = \int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 \left\langle q_a(\tau_2) q_b(\tau_1) \right\rangle_{\text{B}}.$$

$R_{\text{GSB},2}$, $R_{\text{EA},1}$ and $R_{\text{EA},2}$ can be similarly evaluated.

Mukamel, S., 1995. "Principles of Nonlinear Spectroscopy."

Short-time Approximation

Assume that t_1 and t_2 are short comparing with correlation time.

$$g_{ab}(t) \approx \frac{C_{ab}}{2} t^2.$$

C_{ab}: the covariance of energy fluctuation between exciton a and b.

Independent Site Fluctuation

Set covariance of energy fluctuation between sites 0.

$$C_{12} = C_{1c} = C_{2c} = 0.$$

Cho, M., Fleming, G. R., 2005. J. Chem. Phys. 123, 114506.

Evaluation of Analytical ES2DES Responses

Final Form

$$R_{\mathrm{ES2DES}}(t_2, t_1) \sim R_{\mathrm{EA},1} + R_{\mathrm{EA},2} - R_{\mathrm{GSB},1} - R_{\mathrm{GSB},2},$$

where

$$R_{\mathrm{GSB},1} = \mu_{g\beta}^2 \mu_{g\alpha}^2 \exp\left(i\omega_{\beta\alpha} t_1 - i\omega_{\alpha} t_2 - \frac{\Delta_1}{2} t_1^2 - \frac{\Delta_2}{2} t_2^2 - \Delta_{12} t_1 t_2 \right),$$

$$R_{\mathrm{GSB},2} = \mu_{g\beta}^2 \mu_{g\alpha}^2 \exp\left(-i\omega_{\beta\alpha} t_1 - i\omega_{\beta} t_2 - \frac{\Delta_1}{2} t_1^2 - \frac{\Delta_2}{2} t_2^2 - \Delta_{12} t_1 t_2 \right),$$

$$R_{\mathrm{EA},1} = \mu_{g\beta} \mu_{\beta f} \mu_{\alpha f} \mu_{g\alpha} \exp\left(i\omega_{\beta\alpha} t_1 - i\omega_{f\beta} t_2 - \frac{\Delta_1}{2} t_1^2 - \frac{\Delta_2}{2} t_2^2 - \Delta_{12} t_1 t_2 \right),$$

$$R_{\mathrm{EA},2} = \mu_{g\beta} \mu_{\beta f} \mu_{\alpha f} \mu_{g\alpha} \exp\left(-i\omega_{\beta\alpha} t_1 - i\omega_{f\alpha} t_2 - \frac{\Delta_1}{2} t_1^2 - \frac{\Delta_2}{2} t_2^2 - \Delta_{12} t_1 t_2 \right),$$

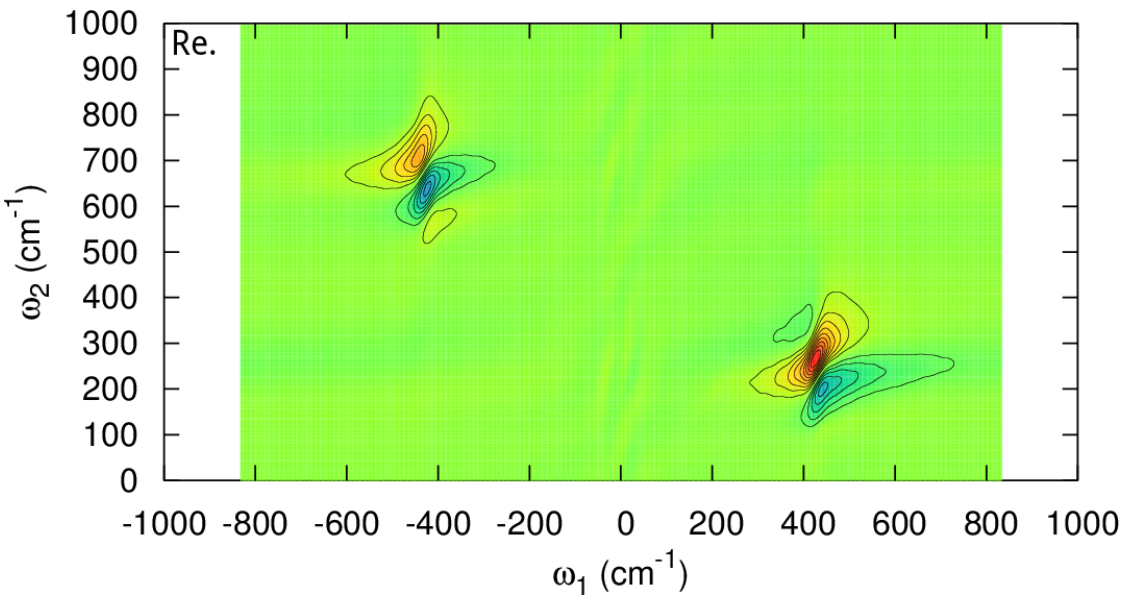
and

$$\begin{aligned}
\Delta_1 &= C_{\alpha\alpha} + C_{\beta\beta} - 2C_{\beta\alpha} &&= \mathrm{Var}(\omega_{\beta\alpha}), \\
\Delta_2 &= C_{\alpha\alpha} &&= \mathrm{Var}(\omega_{\alpha}), \\
\Delta_{12} &= C_{\alpha\alpha} - C_{\beta\alpha} &&= \mathrm{Var}(\omega_{\alpha}) - \mathrm{Cov}(\omega_{\beta\alpha}).
\end{aligned}$$

Evaluation of Analytical ES2DES Responses

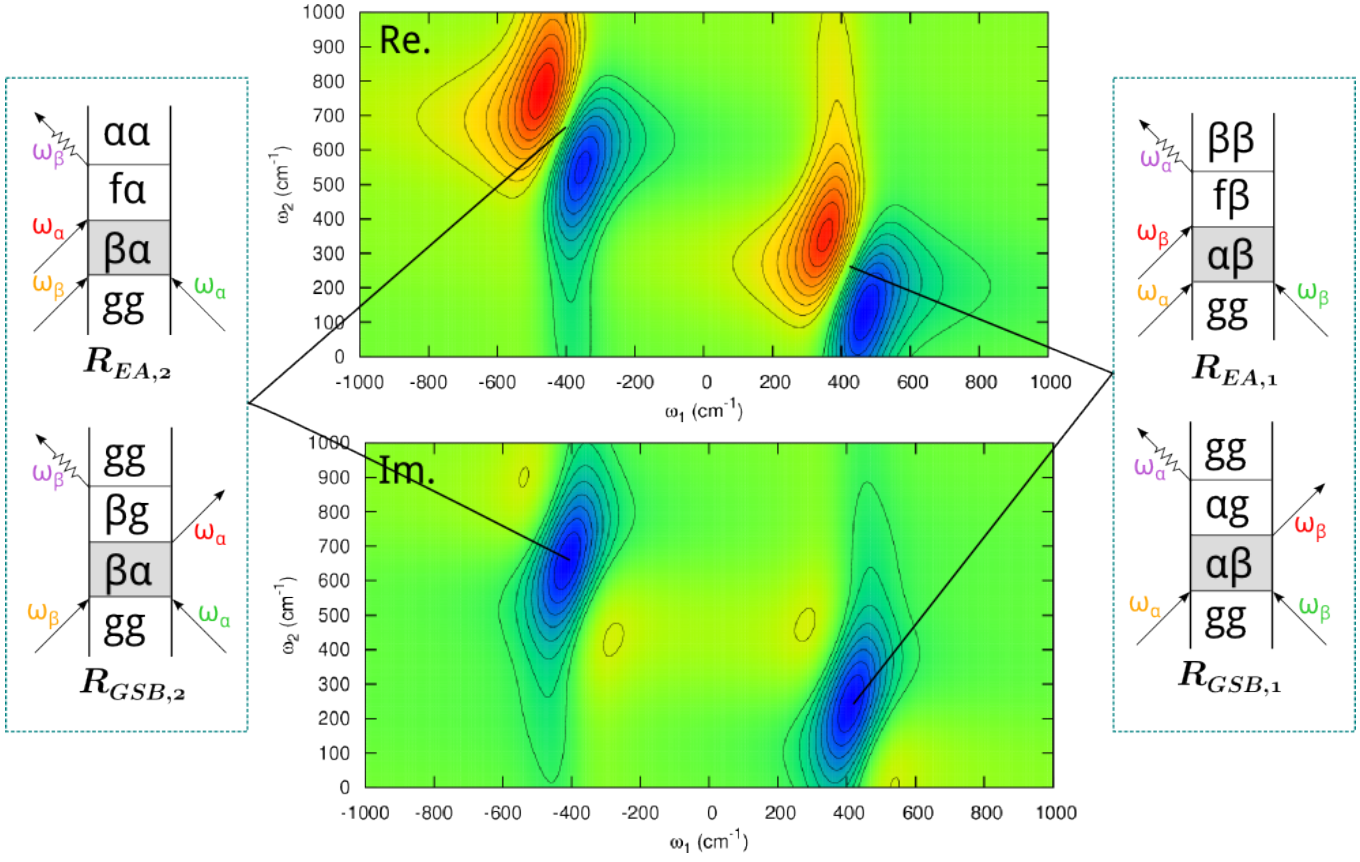
The Model

parameters	default values
ϵ_1	400 (cm^{-1})
ϵ_2	500 (cm^{-1})
J_{12}	200 (cm^{-1})
μ_1	5 (arbitrary unit)
μ_2	1 (arbitrary unit)
C_{11}, C_{22}	34354 (cm^{-2})
C_{cc}	0 (cm^{-2})



Evaluation of Analytical ES2DES Responses

Result

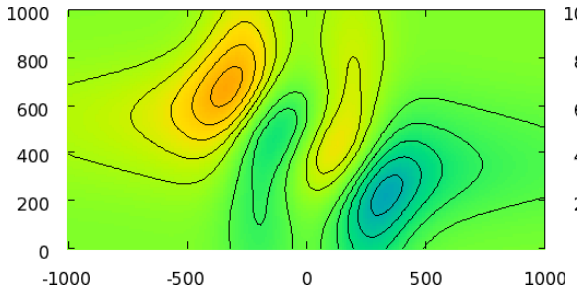


$$R_{\mathrm{ES2DES}} \sim \left(\langle \mu_{g\beta}\mu_{\beta f}\mu_{\alpha f}\mu_{g\alpha}\rangle - \langle \mu_{g\beta}^2\mu_{g\alpha}^2\rangle\right) \exp\left[i\omega_{\beta\alpha}t_1 - i\omega_\alpha t_2 + F(t_1,t_2)\right]$$

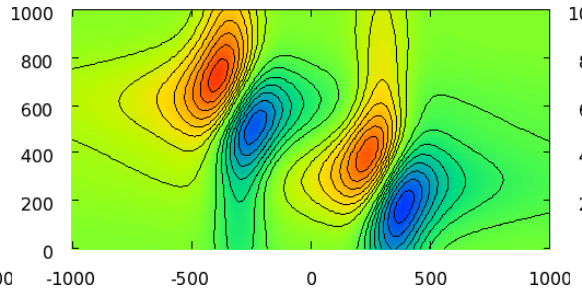
$$S_{\mathrm{ES2DES}} = \mathrm{FT}\left\{iR_{\mathrm{ES2DES}}\right\}$$

Evaluation of Analytical ES2DES Responses

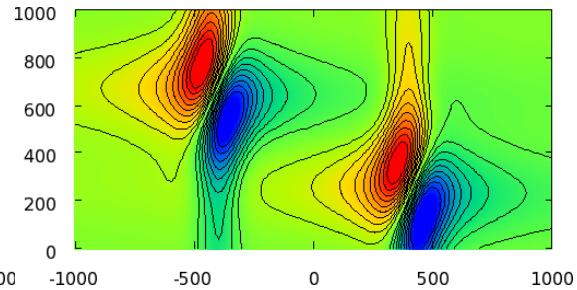
Spectral Variation with Electronic Coupling Constant



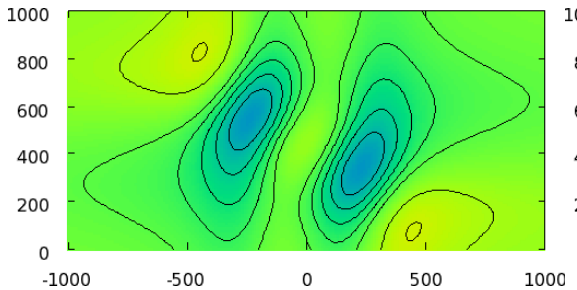
(a) Re., $J_{12} = 100\,\mathrm{cm}^{-1}$.



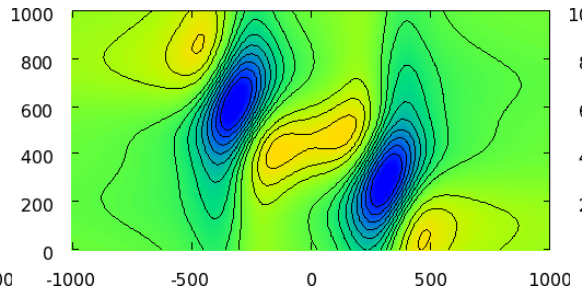
(b) Re., $J_{12} = 150\,\mathrm{cm}^{-1}$.



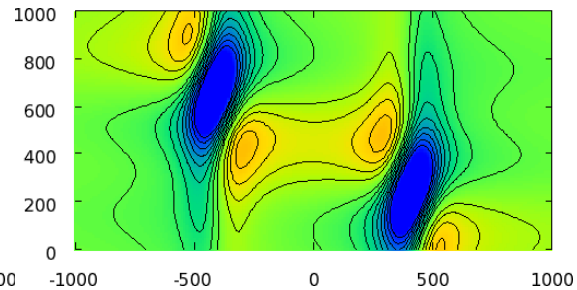
(c) Re., $J_{12} = 200\,\mathrm{cm}^{-1}$.



(d) Im., $J_{12} = 100\,\mathrm{cm}^{-1}$.



(e) Im., $J_{12} = 150\,\mathrm{cm}^{-1}$.



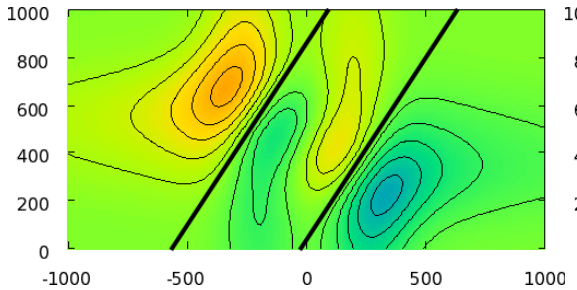
(f) Im., $J_{12} = 200\,\mathrm{cm}^{-1}$.

$$R_{\mathrm{ES2DES}} \sim \left(\langle \mu_{g\beta}\mu_{\beta f}\mu_{\alpha f}\mu_{g\alpha}\rangle - \langle \mu_{g\beta}^2\mu_{g\alpha}^2\rangle\right)\exp\left[i\omega_{\beta\alpha}t_1 - i\omega_{\alpha}t_2 + F(t_1,t_2)\right]$$

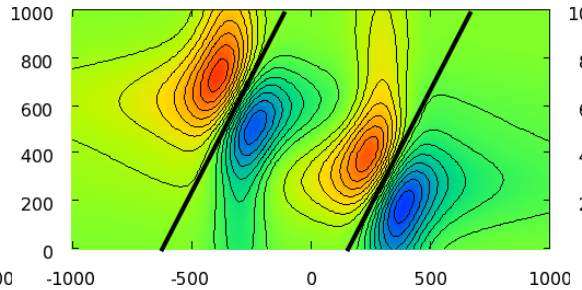
$$S_{\mathrm{ES2DES}} = \mathrm{FT}\left\{iR_{\mathrm{ES2DES}}\right\}$$

Evaluation of Analytical ES2DES Responses

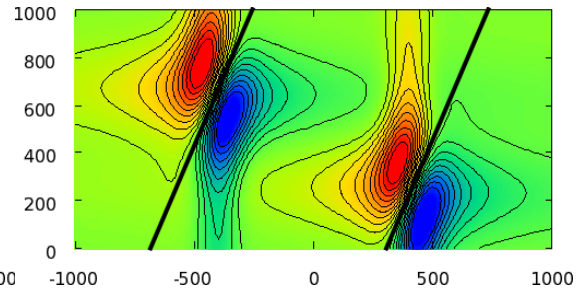
Spectral Variation with Electronic Coupling Constant



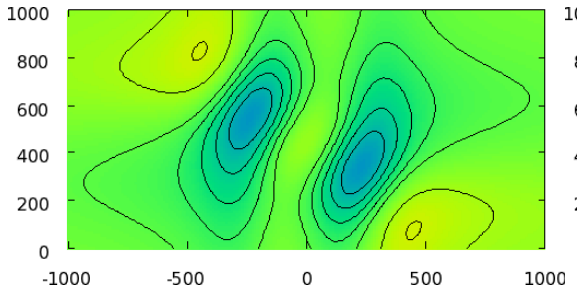
(a) Re., $J_{12} = 100\,\mathrm{cm}^{-1}$.



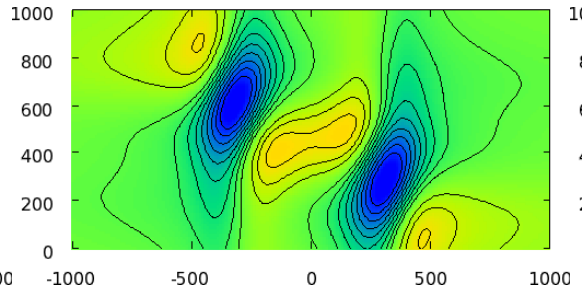
(b) Re., $J_{12} = 150\,\mathrm{cm}^{-1}$.



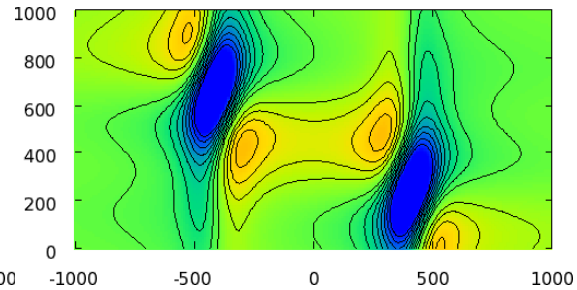
(c) Re., $J_{12} = 200\,\mathrm{cm}^{-1}$.



(d) Im., $J_{12} = 100\,\mathrm{cm}^{-1}$.



(e) Im., $J_{12} = 150\,\mathrm{cm}^{-1}$.



(f) Im., $J_{12} = 200\,\mathrm{cm}^{-1}$.

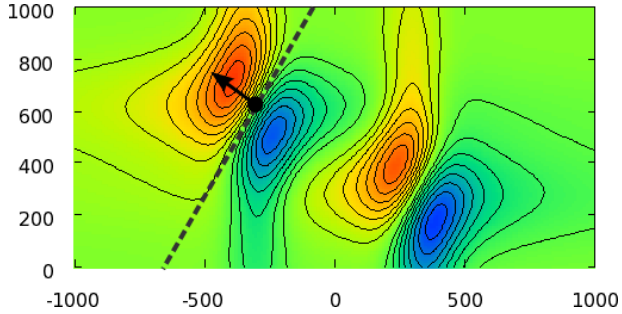
$$R_{\mathrm{ES2DES}} \sim \left(\langle \mu_{g\beta}\mu_{\beta f}\mu_{\alpha f}\mu_{g\alpha}\rangle - \langle \mu_{g\beta}^2\mu_{g\alpha}^2\rangle\right)\exp\left[i\omega_{\beta\alpha}t_1 - i\omega_{\alpha}t_2 + F(t_1,t_2)\right]$$

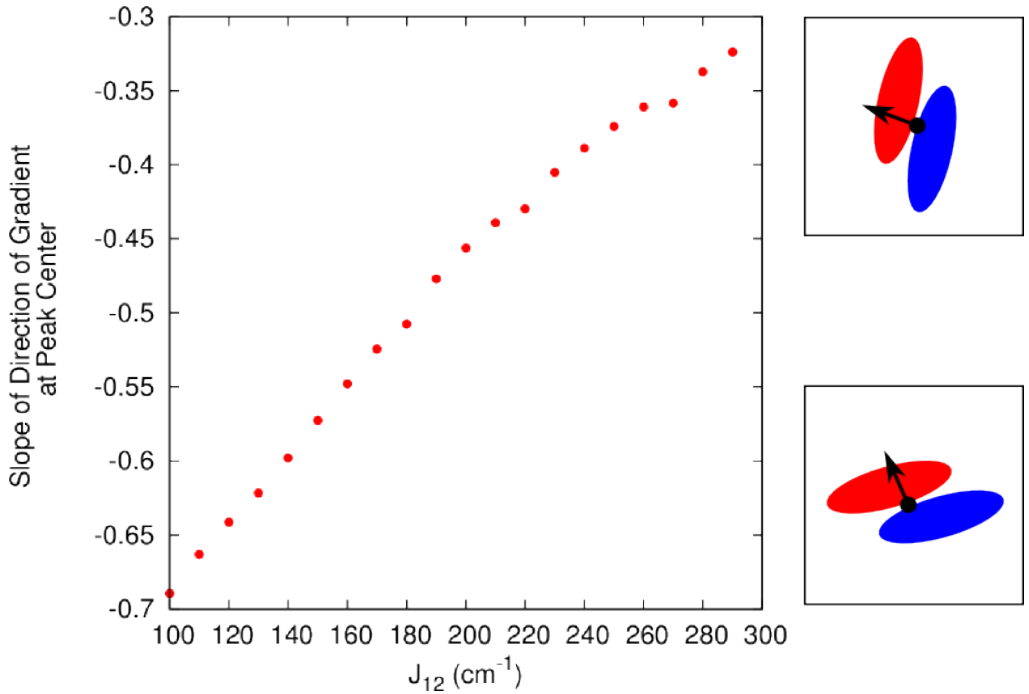
$$S_{\mathrm{ES2DES}} = \mathrm{FT}\left\{iR_{\mathrm{ES2DES}}\right\}$$

Peak Rotation/Elongation

Analysis

We capture the peak rotation/elongation effects with the *direction of gradient* at the center of the peak.





Peak Rotation/Elongation

Analysis

ES2DES Spectrum

$$S_{\mathrm{ES2DES}}(\omega_1, \omega_2) = \int_0^\infty dt_2 \int_0^\infty dt_1 \, iR_{\mathrm{ES2DES}}(t_1, t_2) \exp\left(-i\omega_1 t_1 - i\omega_2 t_2\right).$$

Direction of Gradient at Peak Center

$$\nabla S_{\mathrm{ES2DES}}(\omega_1, \omega_2)|_{(\omega_{\beta\alpha}, -\omega_\alpha)} \propto \left(\sqrt{\Delta_1}\Delta_2 - \sqrt{\Delta_2}\Delta_{12}, \sqrt{\Delta_2}\Delta_1 - \sqrt{\Delta_1}\Delta_{12}\right),$$

where

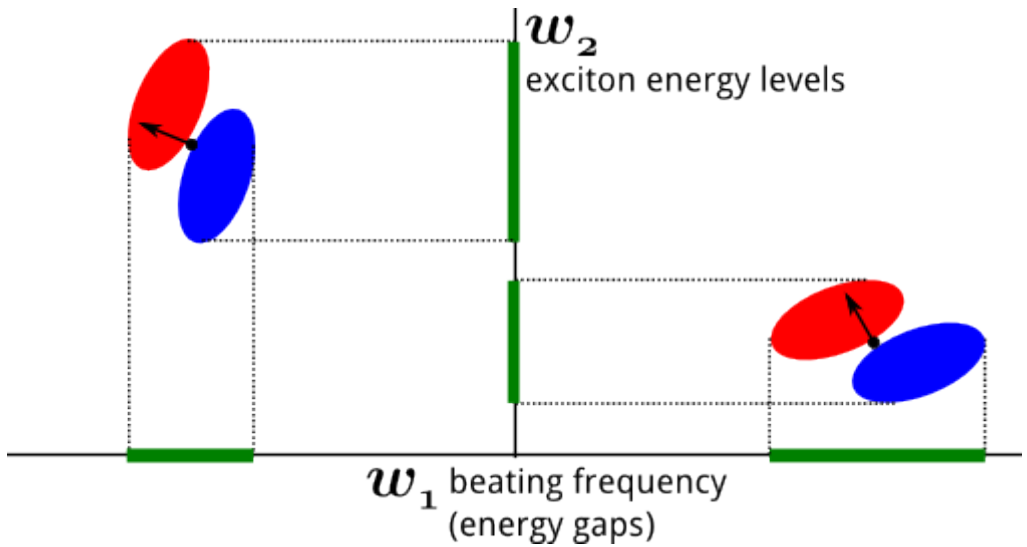
$$\begin{aligned}
\Delta_1 &= C_{\alpha\alpha} + C_{\beta\beta} - 2C_{\beta\alpha} &&= \mathrm{Var}(\omega_{\beta\alpha}), \\
\Delta_2 &= C_{\alpha\alpha} &&= \mathrm{Var}(\omega_\alpha), \\
\Delta_{12} &= C_{\alpha\alpha} - C_{\beta\alpha} &&= \mathrm{Var}(\omega_\alpha) - \mathrm{Cov}(\omega_{\beta\alpha}).
\end{aligned}$$

Peak Rotation/Elongation

Physical Picture

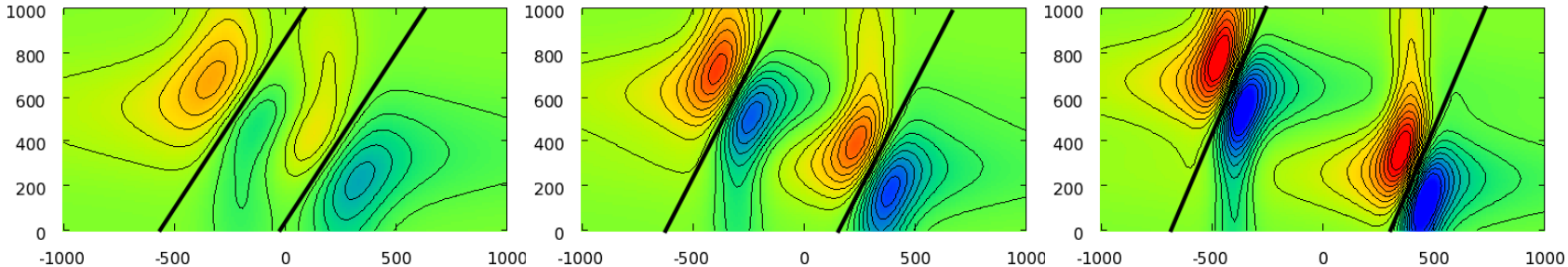
Slope of the Direction of Gradient

$$\left.\frac{\partial S_{\mathrm{ES2DES}}/\partial\omega_2}{\partial S_{\mathrm{ES2DES}}/\partial\omega_1}\right|_{(\omega_{\beta\alpha},-\omega_\alpha)} = \frac{\mathrm{Stdev}(\omega_{\beta\alpha})}{\mathrm{Stdev}(\omega_\alpha)} \equiv \sigma_{\beta\alpha/\alpha}.$$



Peak Rotation/Elongation

Physical Picture



(a) Re., $J_{12} = 100\,\mathrm{cm}^{-1}$. (b) Re., $J_{12} = 150\,\mathrm{cm}^{-1}$. (c) Re., $J_{12} = 200\,\mathrm{cm}^{-1}$.

As J gets larger,

- each exciton gets more delocalized over sites.
- fluctuations of two excitons become correlated.
- ratio of $\omega_{\beta\alpha}$ fluctuaion to ω_α fluctuation decreases.
- peaks get more vertically elongated.
- magnitude of the captured slope gets smaller.

Concluding Remarks

- The design of ES2DES have been verified with time-nonlocal quantum master equation approach on simple Frenkel exciton systems.
- General spectral characterisitics of ES2DES were observed from analytical ES2DES responses under short-time approximation.
- Information of molecular aggregates provided by ES2DES experiments includes
  - maps of exciton energy levels involved in coherence.
  - fluctuation amplitudes and correlations of excitons.

Thanks for your listening.