Simulating the two-dimensional electronic spectroscopy of vibronic systems with multiple excited states.

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Introduction

In this work, we model the 2D optical spectroscopy of a zinc-porphyrin chromophore with multiple excited states, using two approaches.[1,2] The Multimode Brownian Oscillator (MBO) model calculates the third order molecular response functions using the cumulant expansion.[3,4] Whilst the Equation of Motion-Phase Matching Approach (EOM-PMA) calculates the polarisation in the phase-matched direction from a series of quantum dynamical simulations.[5]

Linear absorption spectrum of zinc-porphyrin chromophore

Figure 1 identifies three singlet states for the zinc-porphyrin chromophore. The first, the Q band, is split into two orthogonal components.

Q_x shows a vibronic absorption at 15545 cm^{-1}, corresponding to a metal-pyrrole breathing mode of 380 cm^{-1}, which has been studied using 2D spectroscopy.[1,2]

Whilst the B band has little influence on these 2D spectra, as the very broad N band is located at twice the frequency of Q_x, excited state absorption (ESA) pathways become involved.

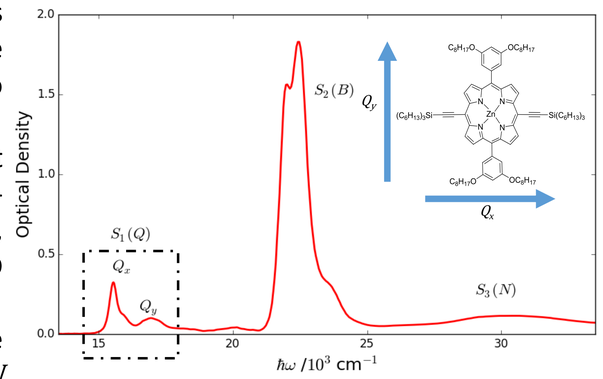

Figure 1: Linear absorption spectrum of the bis-alkynyl zinc-porphyrin chromophore. Inset shows the structure of the chromophore and the directional dipole moments for the Q band, which is highlighted.[2]

3 level displaced Harmonic oscillator model

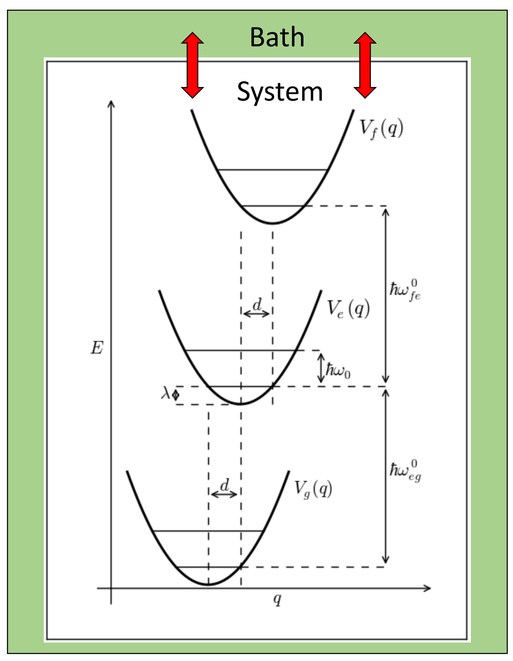

Figure 2: Diagram representing the interaction of the wider bath with the system.

We model the S_0, S_1 and S_3 states of the zinc-porphyrin system by coupling three electronic states $|g\rangle$, $|e\rangle$, and $|f\rangle$ to a single harmonic vibrational mode of frequency ω_0. Each excited state is displaced along the mode coordinate (q) by d resulting in the reorganisation energy, λ.

$$H_S = |g\rangle h_g \langle g| + |e\rangle(h_e + \hbar\omega^0_{eg})\langle e| + |f\rangle(h_f + \hbar\omega^0_{fg})\langle f|$$

$$h_i = \hbar\omega_0\left(b^\dagger b + \frac{1}{2} - \frac{d_i}{\sqrt{2}}(b^\dagger + b)\right) \quad \text{where} \quad i = g, e, f$$

Assumptions

- We limit each excited state to the first two vibrational levels.
- We assume the two transition frequencies and displacements between states to be equal.

$$\omega^0_{fe} = \omega^0_{eg}$$

*This does not account for the full width of the N band, but suitably simplifies the quasi-continuum.

Equation of Motion-Phase Matching Approach

Theory:

The molecular vibration is included in the system Hamiltonian, H_S. The laser field is introduced by three Gaussian pulses in the interaction Hamiltonian, $V_n(t)$. Separate baths for electronic and vibrational transitions are described by Ohmic spectral densities, $J(\omega)$.

$$V_n(t) = \hat{\mu}\cdot\left(\chi_n E_n(t-\tau_n)\mathrm{e}^{(-i\omega_n t + i\mathbf{k}_n\mathbf{r})}\right) \qquad J(\omega) = \gamma_{el/vib}\,\omega\,\mathrm{e}^{(-\omega/\omega_c)}$$

Seven auxiliary master equations are evolved using Lindblad relaxation dynamics, before being combined to calculate the third order polarisation in the rephasing direction.

$$\dot{\rho}_1(t) = -\frac{i}{\hbar}\left[H_S - V_1(t) - V_2^\dagger(t) - V_3^\dagger(t), \rho_1(t)\right] + \sum_{k=el/vib}\gamma_k\left(A_k\rho(t)A_k^\dagger - \frac{1}{2}\left\{A_k^\dagger A_k, \rho_1(t)\right\}\right)$$

$$P^{(3)}_{\mathbf{k}_s}(\tau, T, t) = \mathrm{e}^{\mathbf{k}_s\mathbf{r}}\langle\hat{\mu}\left(\rho_1(t) - \rho_2(t) - \rho_3(t) + \rho_4(t) - \rho_5(t) + \rho_6(t) + \rho_7(t)\right)\rangle$$

Parameters (at 300 K)

$\omega^0_{eg} = \omega^0_{fe} = 15545$ cm^{-1} $\quad \omega_n = 15545$ cm^{-1} | $\tau_n = 15$ fs

$\omega_0 = 380$ cm^{-1} | $d = 0.8$ $\quad \gamma_{el} = 0.9$ | $\gamma_{vib} = 0.1$ | $\omega_c = 700$ cm^{-1}

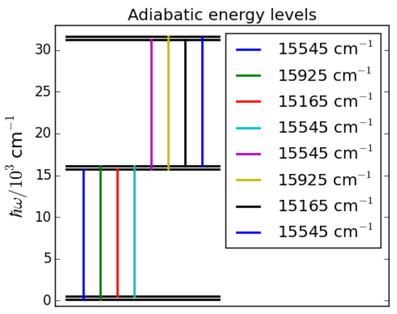

Figure 3: Calculated energy levels with transition frequencies labelled.

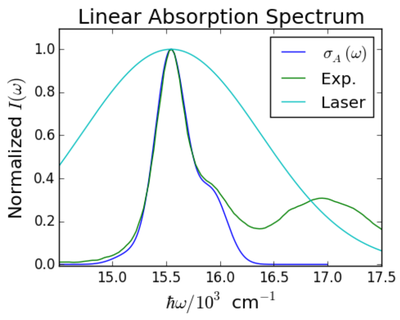

Figure 4: Calculated, $\sigma_A(\omega)$, and experimental, Exp., absorption spectra, with laser spectrum.

Results:

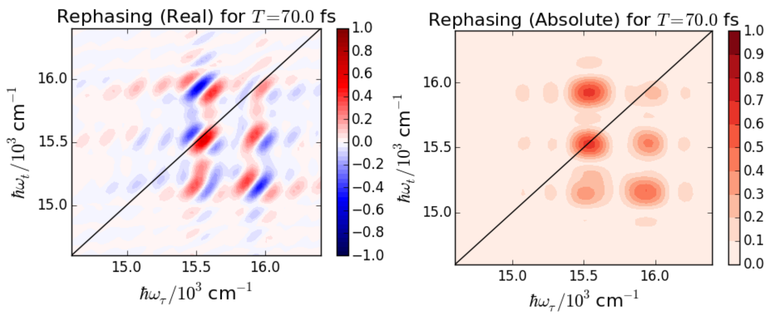

Figure 5: Real (left) and absolute (right) component of calculated rephasing 2D spectrum for a population time of $T = 70$ fs.

The resulting rephasing spectra show the expected 'chair' formation of peaks, but no inhomogeneous broadening due to the use of Markovian dynamics.

Multimode Brownian Oscillator Model

Theory:

The system is defined by the electronic states only, all nuclear motions are incorporated into the spectral density, $C(\omega)$. The intramolecular vibration is described by an underdamped mode, $C_u(\omega)$; intermolecular vibrations for solvent interactions by overdamped modes, $C_o(\omega)$.[3]

$$C_u(\omega) = \frac{2\lambda\omega\omega_0^2\gamma}{(\omega_0^2 - \omega^2)^2 + \gamma^2\omega^2} \qquad C_o(\omega) = 2\lambda\frac{\omega\Lambda}{\omega^2 + \Lambda^2}$$

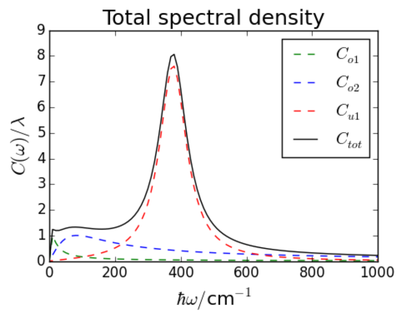

Figure 6: Total spectral density and contributing modes.

Each excited state has a separate spectral density, which are assumed equal so all lineshape functions are equivalent.[4]

The addition of pathways involving the second excited state introduces ESA into the rephasing, R_R, and non-rephasing, R_{NR}, response functions.

$$R_{NR}(t_1,t_2,t_3) = R_{1g}(t_1,t_2,t_3) + R_{4g}(t_1,t_2,t_3) - R^*_{2f}(t_1,t_2,t_3)$$

$$R_R(t_1,t_2,t_3) = R_{2g}(t_1,t_2,t_3) + R_{3g}(t_1,t_2,t_3) - R^*_{1f}(t_1,t_2,t_3)$$

Results:

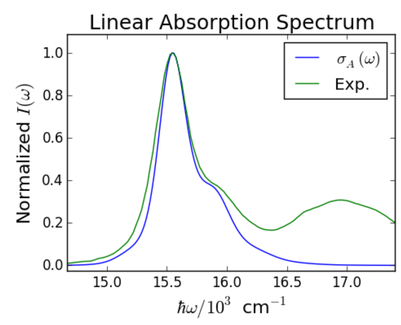

Figure 7: Calculated, $\sigma_A(\omega)$, and experimental, Exp., absorption spectra.

Parameters (at 300 K)

$\omega^0_{eg} = \omega^0_{fe} = 15510$ cm^{-1}

$\omega_0 = 380$ cm^{-1} | $d = 0.8$

	γ (cm^{-1})	λ (cm^{-1})	Λ (cm^{-1})
C_{u1}	100	122	-
C_{o1}	-	19	8.3
C_{o2}	-	21	83.3

Experimental line shape is reproduced correctly, including inhomogeneous broadening effects.

The addition of ESA pathways increases the intensity of negative peaks.

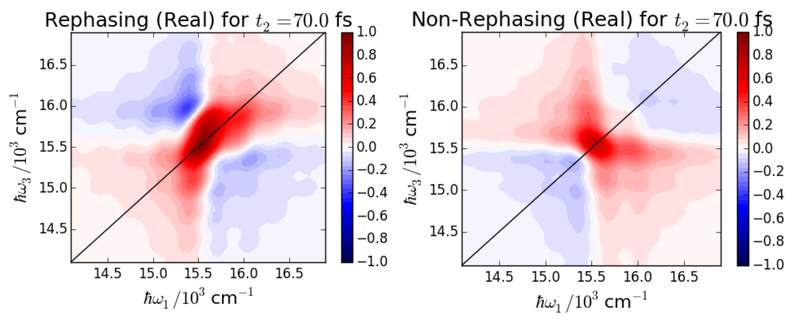

Figure 8: Real component of calculated rephasing (left) and non-rephasing (right) 2D spectra for a population time of $t_2 = 70$ fs.

Experimental 2D Spectra

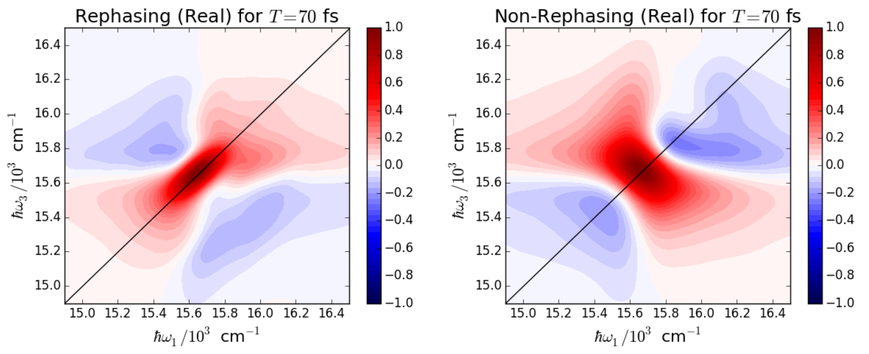

Figure 9: Real component of measured rephasing (left) and non-rephasing (right) 2D spectra for a population time of $T = 70$ fs.[2]

Summary and Objectives

At this stage, both the MBO and EOM-PMA models are producing recognisable 2D spectra for the Q band of the zinc-porphyrin chromophore. Methods have also been identified to expand the system definition to include an additional excited state, representing the N band.

- Improve line shape of EOM-PMA spectra by implementing non-Markovian dynamics.
- Improve representation of the breadth of the *N* band, regarding the use of unequal spectral densities for MBO and efficient incorporation of a vast number of new energy levels in EOM-PMA.
- Explore the influence of variable laser spectra in EOM-PMA vs. impulsive MBO.
- Extend the systems to include additional vibrational modes and/or dimers and larger aggregate structures.

Acknowledgements

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References

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