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Authors

Monahan, Daniele M
Whaley-Mayda, Lukas V
Ishizaki, Akihito
et al.

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Interpreting Oscillations in Numerically Exact Simulations of 2D Electronic Spectra

Daniele M. Monahan, Lukas V. Whaley-Mayda, Akihito Ishizaki and Graham R. Fleming

Abstract 2D electronic spectroscopy signals are simulated with accurate hierarchy method treatment of an electronic heterodimer coupled to a bath and local vibrations. We examine the effect of vibrations on the correspondence between exciton and population dynamics.

1 Introduction

The mechanisms of excitation energy transfer (EET) in biological systems depend on the interplay between pigment-pigment and pigment-bath interactions [1]. Strong electronic coupling between pigments creates delocalized excitons, helping to avoid trapping at local energy minima. Fluctuations in coupled pigment or protein nuclear modes act to destroy the site superpositions, localizing the excitation and halting reversible coherent energy transfer. Underdamped intramolecular vibrations also play a role, for example by allowing transfer via resonances in the vibronic energy landscape [2, 3]. In this work, we simulate 2D electronic spectra (2D-ES) of a heterodimer in a quantum environment, to study the correspondence between exciton and spatial dynamics in the intermediate coupling regime.

The lifetime of a superposition of excitons, generated by broadband laser pulses in 2D-ES, measures a system's support for delocalization despite environmental

D.M. Monahan · L.V. Whaley-Mayda · G.R. Fleming (✉)
Department of Chemistry, University of California, Berkeley CA 94720, USA
e-mail: grfleming@lbl.gov

D.M. Monahan · L.V. Whaley-Mayda · G.R. Fleming
Physical Biosciences Division, Lawrence Berkeley National Laboratory,
Berkeley CA 94720, USA

A. Ishizaki
Institute for Molecular Science, National Institutes of Natural Sciences,
Okazaki 444-8585, Japan

fluctuations only if the superposition is a mixture of states with different locations. In molecules with substantial electronic-vibrational coupling, two spectroscopically resolvable excitons may be largely confined on a single pigment [4, 5] (i.e. a vibrationally hot state and a cold state). Population transfer between such localized excitons does not measure the transport of energy through space; similarly, the lifetime of localized coherences cannot probe the localization timescale. We focus on this effect of intramolecular vibrations on our ability to study EET via 2D-ES, and on the EET mechanism. We pay special attention to the case of a vibration that is resonant with the electronic energy gap and the effect of the resulting vibronic resonances.

2 Model

We simulate the spectroscopic response of an electronic heterodimer with site energies 200 cm^{-1} apart and electronic coupling $J = 50\text{ cm}^{-1}$. Each site is coupled to an independent bath of overdamped harmonic oscillators, plus an underdamped vibration that dephases over 2 ps. The bath reorganization energy and correlation time, which describe the magnitude and rapidity of the bath's response to electronic excitation, are 35 cm^{-1} and 50 fs, respectively. The vibrational frequency is chosen near resonance with the gap between electronic eigenstates (e.g. $\omega = 223\text{ cm}^{-1}$ for $J = 50\text{ cm}^{-1}$); the Huang-Rhys parameter, S , describes the strength of the vibrational-electronic coupling. We vary the Huang-Rhys factor, adjusting the bath reorganization energy, λ , to hold the total reorganization energy constant. The dynamics including the dissipation are accurately treated using the hierarchy equations of motion (HEOM) method of Ishizaki and Fleming [6]. We calculate the spectroscopic response in the form of 4-point time correlation functions and Fourier transform over the t_1 and t_3 periods to give simulated 2D-ES spectra as in Fig. 1a.

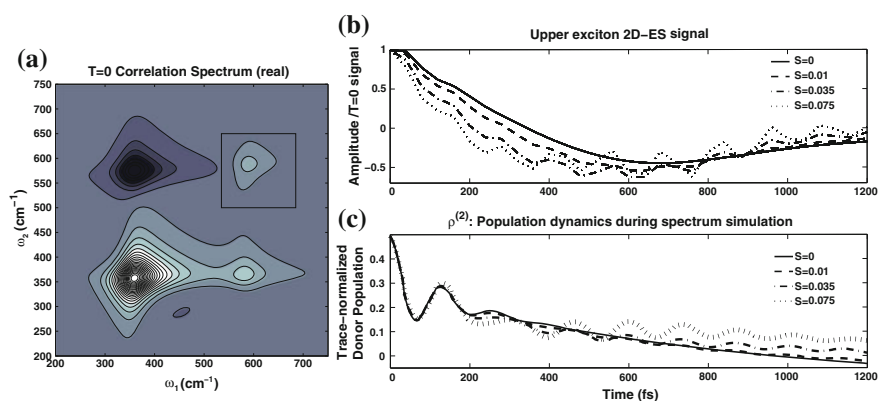


Fig. 1 a 2D-ES spectrum of electronic heterodimer simulated at 77 K, for $t_2 = 0$ fs. b 2D-ES signal integrated over the boxed area (*upper* diagonal peak), as a function of t_2 for given values of S . c diagonal element of $\rho^{(2)}$ corresponding to donor populations in the same simulations

In attempt to compare dynamics measured by these spectra with site population dynamics during the waiting time, we record diagonal elements of

$$\rho^{(2)}(t_2) = \int_0^\infty d\omega_1 \int_{-\infty}^\infty dt_1 e^{-i\omega_1 t_1} G(t_2)[G(t_1)[\rho(0), \mu], \mu]$$

where $G(t_i)$ describes time propagation calculated with the HEOM in the period t_i .

3 Results and Discussion

Our preliminary work on pure population dynamics demonstrates that the bath greatly damps mixed vibrational-electronic coherences, compared to dynamics without dissipation. This implies significant bath-induced energy gap fluctuations are characteristic of the parameter regime described, and that resonance between two vibronic excitons will be fragile. Thus we argue that the accurate quantum-mechanical treatment of dissipation is required to produce the spectroscopic phenomena typical in the intermediate coupling regime. We note that we have not included the low-temperature corrections in the HEOM, leading to breakdown of positivity in the equilibrium populations (though not affecting oscillatory behavior). We accordingly take care to examine only the initial decay rates in Fig. 1.

In the simulated 2D-ES, we note long-lived oscillations that depend on the size of the vibronic coupling *and* are accompanied by oscillatory transfer between pigments (as measured by $\rho^{(2)}$). The long-lived oscillations are significant for simulations with $S > 0.01$. The $\rho^{(2)}$ site dynamics are significantly damped after the first picosecond, but the 2D-ES oscillations persist. Figure 1b shows that increasing S raises the initial rate for exciton relaxation, we have seen a similar effect in site dynamics initialized with pure donor population. We do not observe such a rate enhancement in the initial decay of $\rho^{(2)}$ depicted in Fig. 1c. Future studies will aim to understand this observation.

4 Conclusions

This work illustrates that for most systems with vibrational modes with energy close to the excitonic energy gap, spectral oscillations at late times are the result of localized (vibrational) dynamics, and the lifetime of oscillations in spectra alone cannot indicate the timescale for localization. The environment destroys the mixed-character vibronic coherence (dominating the site dynamics at intermediate times) on a faster timescale than the vibrational dephasing. Under the influence of vibrations, the time for localization is longer than the pure electronic dephasing time, which may be due to vibronic resonances between pigments.

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