Probing Anomalous Spectral Diffusion and Exciton Fluctuations by Coherent Multidimensional Spectroscopy

František Šanda[1], and Shaul Mukamel[2]

[1] Charles University, Faculty of Mathematics and Physics, 121 16 Praha, Czech Republic
E-mail: sanda@karlov.mff.cuni.cz
[2] University of California, Department of Chemistry, Irvine, CA, USA

Abstract. Novel signatures of anomalous algebraic spectral relaxation, non Gaussian fluctuations and bath-induced transition dipole moments in two dimensional optical lineshapes of excitonic aggregates are predicted using stochastic models with long algebraic relaxation tails.

1. Introduction

Two dimensional infrared and optical spectroscopy probes exciton dynamics through cross (correlation) peaks extending ideas proven in NMR to the femtosecond timescale.

Multidimensional lineshapes are obtained by the coherent nonlinear response to three laser pulses where three time intervals t_1,t_2 and t_3 are controlled. Frequency-frequency correlation plots in Ω_1, Ω_3, the Fourier conjugates to t_1, t_3, give valuable insights into the pathways and time profiles of bath spectral diffusion dynamics, as observed in the contour shapes of 2D peaks and in the cross peaks dynamics respectively. Virtually all modelling of these signals in molecular aggregates is limited to white noise fluctuations of exciton couplings (Redfield equations) and Gaussian fluctuations of frequencies. These describe multiexponential relaxation decay of correlations. Long algebraic tails of anomalous relaxation are common in many complex systems (Glasses, proteins, quantum dots) [1]. These require different dynamical models such as continuous time random walks (CTRW) characterized by the probability distribution function (WTDF) $\psi(t)$ of waiting times for successive jumps between bath states.

We assume an excitonic Hamiltonian $H = \sum_i \varepsilon_i |i\rangle\langle i| + \sum_{ij} J_{ij} |i\rangle\langle i|$ [2] whose parameters ε_i, J_{ij} depend on stochastic bath variables $\sigma(t)$. All physical observables are related to the weighted average over the ensemble of stochastic paths $\sigma(t)$ of the bath

$$\rho(\mathrm{t}) = \left\langle \mathrm{T} \exp -\mathrm{i} \int_0^{\mathrm{t}} \Lambda(\sigma(\mathrm{t}'))\mathrm{dt}' \right\rangle \qquad \Lambda \equiv \frac{1}{\mathrm{h}}[\mathrm{H}, \ldots] \tag{1}$$

2. Anomalous relaxation and 2D lineshapes

Stochastic quantum dynamics can be computed by a direct generation of random bath paths $\sigma(t)$. More efficient methods are at hand for specific bath models. The key point of the CTRW model, which makes it tractable, is that all memory is erased at the time of jump and the WTDF for the next jump is independent of the history. This is known as renewal. We developed a general algorithm for calculating nonlinear response functions for this model [3,4]. When the asymptotic decay of $\psi(t)$ is fast and all moments of $\psi(t)$ exist the 2D lineshapes show a typical Markovian relaxation pattern (represented by exponential WTDF). A qualitatively different behaviour is observed when the first or the second moments of WTDF diverge $\psi(t) \approx 1/t^{\alpha+1}$.

2.1. Stationary ensembles ($1 < \alpha < 2$).

When the first moment κ_1 of $\psi(t)$ is finite the process is stationary. Stationary ensembles are defined by prescribing special WTDF $\psi'(t) = \kappa_1^{-1} \int_t^\infty \psi(t')dt'$ for the first jump (it may differ from $\psi(t)$ depending on the initial preparation) [3]. In Fig 1 2D absorptive lineshapes are plotted for of a single two level chromophore whose transition frequency $\varepsilon_1 = \pm\omega_0$ is modulated by a two state jump CTRW in slow limit ($\kappa_1\omega_0 >> 1$). Novel signatures of algebraic WTDF seen in Fig 1 are: divergencies $\sim \Omega^{\alpha-3}$ at peaks (-1,-1), (1,1), discontinuity of the first derivatives at fundamental frequencies $\Omega_1 = \pm 1$ and $\Omega_3 = \pm 1$ and algebraic growth $\sim t_2^{1-\alpha}$ of cross peaks.

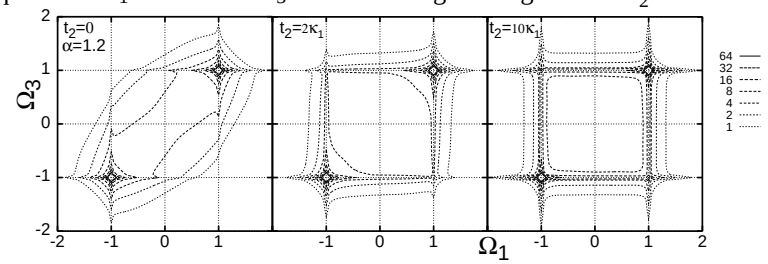

Fig. 1. 2D absorptive lineshape of a single chromophore coupled to two state anomalous spectral CTRW ($\alpha = 1.2, \omega_0 = 1$). Diagonal peaks correspond fundamental frequencies of the bath states; cross-peaks volume gives the fraction of paths that are in different states during intervals t_1, t_3.

2.2. Aging ; spectral diffusion with ($0 < \alpha < 1$).

Random walks with a diverging first moment of $\psi(t)$ retain their memory and never equilibrate. They represent nonstationary ensembles depending on choice of $\psi'(t)$. Usually it is assumed that all allowed bath paths have a jump at some fixed time, where the random walk is started (and $\psi'(t) = \psi(t)$). The mobility of particles will vanish at long times since more random paths $\sigma(t)$ will be trapped due to the long tails of $\psi(t)$.

The nonlinear optical response shows the dependence on the time t_0 elapsed from the start of the random walks to the first laser pulse. (For Markovian relaxation this memory is lost at long t_0.) The 2D lineshapes displayed in Fig 2 interpolate between motional narrowing limit of fast fluctuations at short t_0 (this is similar to Markovian case). However, the static peaks at (-1,-1) and (1,1) which grow with t_0 represent the "trapped" paths (Fig 2). Both types of peaks coexist for anomalous diffusion, what may not be described by master equations with time-dependent rates [4].

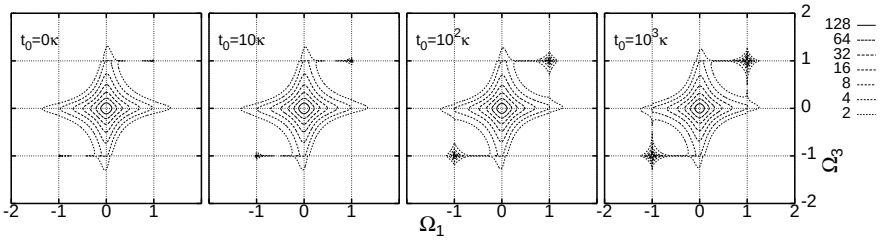

Fig. 2. Aging in 2D absorptive lineshape for nonstationary CTRW spectral diffusion $\psi(t) \sim (\kappa/t)^{\alpha-1}$ ($\alpha = 0.98$, $t_2 = 0$) on single chromophore. Peaks at -1 and 1 show up as the static fraction of particles trapped in long tails of WTDF is developed with t_0. The central motional narrowing peak is consequence of fast jumps and (very) slowly decays with t_0.

3. Peaks induced by slow bath fluctuations

For Markovian random walks the full information is contained in the density matrix in the joint space of the system and the bath. The evolution of the joint density matrix may be described by the Stochastic Liouville equations, which combine the Liouville-von Neumann equation with the master equation for Markovian stochastic variable σ (described by L^{σ}).

$$\frac{\mathrm{d}\rho(\sigma,\mathrm{t})}{\mathrm{dt}} = -\mathrm{i}\Lambda(\sigma,\mathrm{t})\rho(\mathrm{t}) + \mathrm{L}^{\sigma}\rho(\sigma,\mathrm{t}) \tag{2}$$

The third order response functions now factorize into products of Green's functions for the free evolution between pulses and the dipole moment elements that describe the action of the laser pulses. Fast $\sigma(t)$ modulation agrees with the Redfield equations, since all memory effects of the fast bath variables are erased.

New effects which cannot be described by the Redfield equations (where the bath is formally eliminated) are expected for slow or intermediate bath timescales. We consider a homo-dimer with parallel dipole moments. One exciton state carries all oscillator strength and the other is dark. Due to slow Gaussian-Markovian fluctuations of the site frequencies, the σ dependent dark state acquires a transient dipole moment, and additional diagonal peak at (-1,-1) is observed in Fig 3 for the delay times during bath equilibration, but not longer.

The cross peaks (-1,1) and (1,-1) appear at all delay times, because these are induced by the transient dipole moments at either t_1 or t_3 intervals.

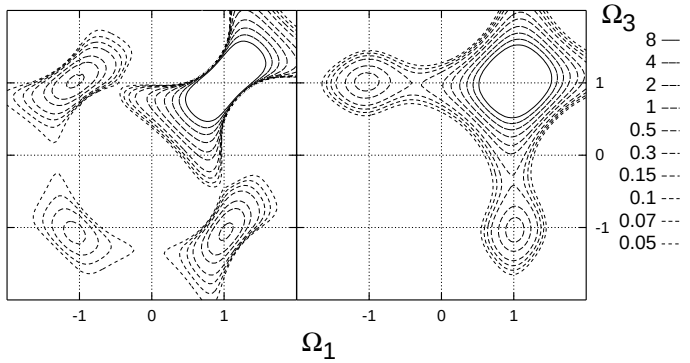

Fig. 3. 2D absorptive lineshape of two coupled chromophores ($J_{12} = 1$) with slow Gaussian-Markovian spectral difussion (of ε_1 and ε_2) with various delay times t_2, shorter and larger then the bath autocorrelation time. The lower transient peak correspond to antibonding orbital, which is dark at equilibrium, but carries transient dipolemoment induced by slow spectral diffusion.

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