Toward an Accurate Model for the Line Shape Analysis of 2D Correlation Spectra

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Linear & Nonlinear Time-resolved Spectra

Time-resolved emission spectra of dye D149\textsuperscript{1}

\textsuperscript{1} Fakis M.; Hrobárik P.; Stathatos E.; Giannetas V.; Persephonis P. Dyes and Pigments 2013, 96, 304-312

Q-model\textsuperscript{1}

Hamiltonian of the Chromophore

\[ H_i = I_i - C_i q + (\kappa_i/2)q^2 \]

\( q \): the nuclear mode of solvent

Transition Frequency

\[ \hbar \Omega(q) = \hbar \Omega_0 - \Delta C q + (\Delta \kappa/2)q^2 \]

\[ \Delta \kappa = \kappa_e - \kappa_g \]

\[ \Delta \kappa = 0 \quad \text{L-MODEL} \]

\[ \Delta \kappa \neq 0 \quad \text{Q-MODEL} \]

Capturing non-Gaussian features in linear time-resolved spectra

\[ I(\Omega, t) = \langle \delta[\Omega(t) - \omega] \rangle_t \]

\[ I(\Omega, t) = \int_{-\infty}^{\infty} \frac{d\xi}{2\pi} e^{i\xi \omega} e^{F(\xi, t)} \]

Obtain the exact generating function by summing an infinite series of cumulants of the energy gap

Nonlinear Spectroscopy

- At negative times, the sample is in the ground state, described by the density matrix $\rho = |0><0|

- **Pump time** ($0:t_1$):
  - Two pump pulses are used to excite the sample

- **Waiting time** ($T$):
  - The system experiences population relaxation

- **Probe time** (after $t_2$):
  - A third pulse probes the sample

### Third-order Response Function

$$R^{(3)}(t_1, T, t_3)$$

$$\propto \left\langle \exp \left( -i \int_0^{t_1} d\tau \delta \Omega(\tau) \right) \exp \left( i \int_{t_1+T}^{t_1+T+t_3} d\tau \delta \Omega(\tau) \right) \right\rangle$$
2D Lineshapes\(^1\)

L-model:
Determine *correlation functions* from the slope of center line

Q-model:
*No direct determination* from the slope of center line

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1 Dinpajooh, M.; Matyushov, D. M. submitted to *J. Phys. Chem. B*
\[ S_\Omega(t) = S_2(t) \]

Stokes-shift Correlation Function

\[ S_\Omega(t) = \frac{\langle \Omega(t) \rangle - \langle \Omega(\infty) \rangle}{\langle \Omega(0) \rangle - \langle \Omega(\infty) \rangle} \]

Equilibrium Time Correlation Function

\[ S_2(t) = \frac{\langle \delta\Omega(t)\delta\Omega(0) \rangle}{\langle (\delta\Omega)^2 \rangle} \]

**Linear dynamics:**

1. Line width, \( \langle \delta\Omega(t)^2 \rangle \), is constant
2. Equality of Stokes-shift & equilibrium time correlation functions
3. No difference in equilibrium time correlation functions of ground and excited states
Dynamics Predicted by the Q-model

\[ S_\sigma(t) \neq S_\Omega(t) \neq S_2(t) = \chi(t) \]

\[ S_\sigma(t) = \frac{\sigma(t)^2 - \sigma(\infty)^2}{\sigma(0)^2 - \sigma(\infty)^2} \]

\[ S_\Omega(t) = \frac{\langle \Omega(t) \rangle - \langle \Omega(\infty) \rangle}{\langle \Omega(0) \rangle - \langle \Omega(\infty) \rangle} \]

\[ S_2(t) = \frac{\langle \delta \Omega(t) \delta \Omega(0) \rangle}{\langle (\delta \Omega)^2 \rangle} \]

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

Molecular Dynamics Simulations

Transition Frequency

\[ \hbar \Omega(\vec{E}) = \hbar \Omega_0 - \Delta \vec{m}. \vec{E} - (\Delta \alpha/2) \vec{E}^2 \]

Polar-polarizable Chromophore
Normalized Correlation Functions

• Nonlinear character of the dynamics of the transition frequency:

\[ S_\sigma(t) \neq S_\Omega(t) \neq S_2(t) \]

\[ S_2(t) = \chi(t) \]

• Spectroscopy does not directly report on the dynamics of the solvent

\[ S_\Omega(t) \neq \chi(t) \]
Gaussian & Non-Gaussian Dynamics

Skewness Time Correlation Function

\[ S_3(t) = \frac{\langle \delta \Omega(t)^2 \delta \Omega(0) \rangle}{\langle \langle \delta \Omega \rangle^2 \rangle^{3/2}} \]

\[ S_4(t) = \frac{\langle \delta \Omega(t)^2 \delta \Omega(0)^2 \rangle}{\langle \langle \delta \Omega \rangle^4 \rangle} \]

Gaussian Approximation

\[ S_4(t) = \frac{1}{3} + \frac{2}{3} S_2(t)^2 \]

- **Non-Gaussian effects:**
  - Skewness time correlation function is **non-zero**
  - However, \( S_4(t) \) is reduced to the corresponding \( S_2(t) \)