4.2: Energy Gap Fluctuations

How do transition energy gap fluctuations enter into the nonlinear response? As we did in the case of linear experiments, we will make use of the second cumulants approximation to relate dipole correlation functions to the energy gap correlation function $C_{eg}(\tau)$. Remembering that for the case of a system-bath interaction that that linearly couples the system and bath nuclear coordinates, the cumulant expansion allows the linear spectroscopy to be expressed in terms of the lineshape function $g(t)$

$$C_{\mu\mu}(t) = |\mu_{eg}|^2 e^{-i\omega_{eg}t} e^{-g(t)} \tag{4.2.1}$$

$$g(t) = \int_0^t dt'' \int_0^{t''} dt' \underbrace{\frac{1}{\hbar^2}\langle \delta H_{eg}(t')\delta H_{eg}(0)\rangle}_{C_{eg}(t')} \tag{4.2.2}$$

$$C_{eg}(\tau) = \langle \delta\omega_{eg}(\tau)\delta\omega_{eg}(0)\rangle \tag{4.2.3}$$

$g(t)$ is a complex function for which the imaginary components describe nuclear motion modulating or shifting the energy gap, whereas the real part describes the fluctuations and 46 damping that lead to line broadening. When $C_{eg}(\tau)$ takes on an undamped oscillatory form $C_{eg}(\tau) = De^{i\omega_0\tau}$, as we might expect for coupling of the electronic transition to a nuclear mode with frequency ω_0, we recover the expressions that we originally derived for the electronic absorption lineshape in which D is the coupling strength and related to the Frank-Condon factor.

Here we are interested in discerning line-broadening mechanisms, and the time scale of random fluctuations that influence the transition energy gap. Summarizing our earlier results, we can express the lineshape functions for energy gap fluctuations in the homogeneous and inhomogeneous limit as

The Homogeneous Limit

The bath fluctuations are infinitely fast, and only characterized by a magnitude:

$$C_{eg}(\tau) = \Gamma\delta(\tau) \tag{4.2.4}$$

In this limit, we obtain the phenomenological damping result

$$g(t) = \Gamma t \tag{4.2.5}$$

Which leads to homogeneous Lorentzian lineshapes with width Γ.

The Inhomogeneous Limit

The bath fluctuations are infinitely slow, and again characterized by a magnitude, but there is no decay of the correlations

$$C_{eg}(\tau) = \Delta^2 \tag{4.2.6}$$

This limit recovers the Gaussian static limit, and the Gaussian inhomogeneous lineshape where Δ is the distribution of frequencies.

$$g(t) = \frac{1}{2}\Delta^2 t^2 \tag{4.2.7}$$

The intermediate regime

The intermediate regime is when the energy gap fluctuates on the same time scale as the experiment. The simplest description is the stochastic model which describes the loss of correlation with a time scale τ_c

$$C_{eg}(\tau) = \Delta^2 exp(-t/\tau_c) \tag{4.2.8}$$

which leads to

$$g(t) = \Delta^2\tau_c^2\left[exp(-t/\tau_c) + t/\tau_c - 1\right] \tag{4.2.9}$$

For an arbitrary form of the dynamics of the bath, we can construct $g(t)$ as a sum over independent modes $g(t) = \sum_i g_i(t)$. Or for a continuous distribution for modes, we can describe the bath in terms of the spectral density $\rho(\omega)$ that describes the coupled nuclear motions

$$\rho(\omega)=\frac{1}{2\pi\omega^2}Im\left[\tilde{C}_{eg}(\omega)\right] \tag{4.2.10}$$

$$\begin{aligned} g(t) &= \int_{-\infty}^{+\infty} d\omega \frac{1}{2\pi\omega^2}\tilde{C}_{eg}(\omega)\left[exp(-i\omega t)+i\omega t-1\right] \\ &= \int_{-\infty}^{+\infty} d\omega\rho(\omega)\left(\coth\left(\frac{\beta\hbar\omega}{2}\right)(1-\cos\omega t)+i(\sin\omega t-\omega t)\right) \end{aligned}$$

To construct an arbitrary form of the bath, the phenomenological Brownian oscillator model allows us to construct a bath of i damped oscillators,

$$\begin{aligned} C''_{eg}(\omega) &= \sum_i \xi_i C''_i(\omega) \\ C''_i(\omega) &= \frac{\hbar}{m_i}\frac{\omega\Gamma_i}{(\omega_i^2-\omega^2)^2+4\omega^2\Gamma_i^2} \end{aligned}$$

Here ξ_i is the coupling coefficient for oscillator i.