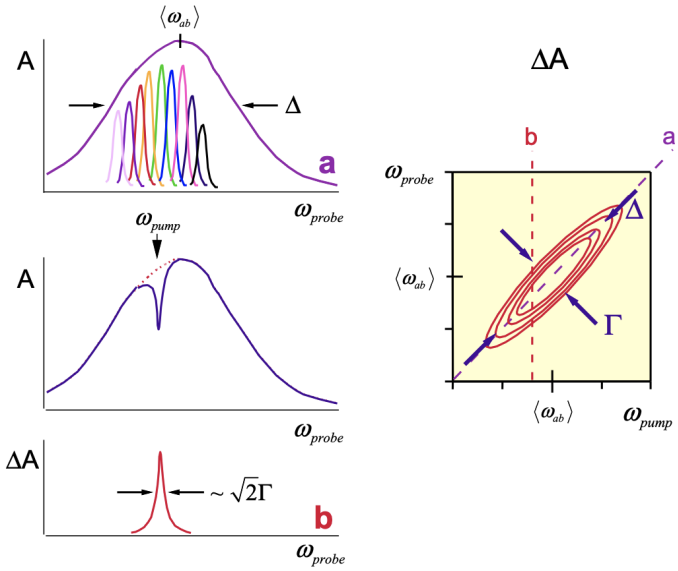
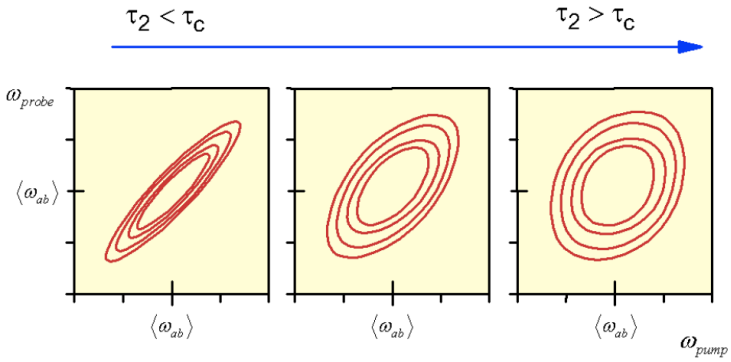
5.5: Two-dimensional spectroscopy to characterize spectral diffusion

A more intuitive, albeit difficult, approach to characterizing spectral diffusion is with a twodimensional correlation technique. Returning to our example of a double resonance experiment, let's describe the response from an inhomogeneous lineshape with width Δ and mean frequency $\langle\omega_{ab}\rangle$, which is composed of a distribution of homogeneous transitions of width Γ. We will now subject the system to excitation by a narrow band pump field, and probe the differential absorption ΔA at all probe frequencies. We then repeat this for all pump frequencies:



In constructing a two-dimensional representation of this correlation spectrum, we observe that the observed lineshape is elongated along the diagonal axis $(\omega_1 = \omega_3)$. The diagonal linewidth is related to the inhomogeneous width Δ whereas the antidiagonal width $[\omega_1 + \omega_3 = \langle\omega_{ab}\rangle/2]$ is determined by the homogeneous linewidth Γ.

For the system exhibiting spectral diffusion, we recognize that we can introduce a waiting time τ_2 between excitation and detection, which provides a controlled period over which the system can evolve. One can see that when τ_2 varies from much less to much greater than the correlation time, τ_c, that the lineshape will gradually become symmetric.

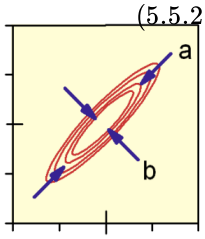


This reflects the fact that at long times the system excited at any one frequency can be observed at any other with equilibrium probability. That is, the correlation between excitation and detection frequencies vanishes.

$$\begin{aligned} &\sum_{ij} \left\langle \delta\left(\omega_1 - \omega_{eg}^{(i)}\right) \delta\left(\omega_3 - \omega_{eg}^{(j)}\right) \right\rangle \\ &\rightarrow \sum_{ij} \left\langle \delta\left(\omega_1 - \omega_{eg}^{(i)}\right) \right\rangle \left\langle \delta\left(\omega_3 - \omega_{eg}^{(j)}\right) \right\rangle \end{aligned} \tag{5.5.1}$$

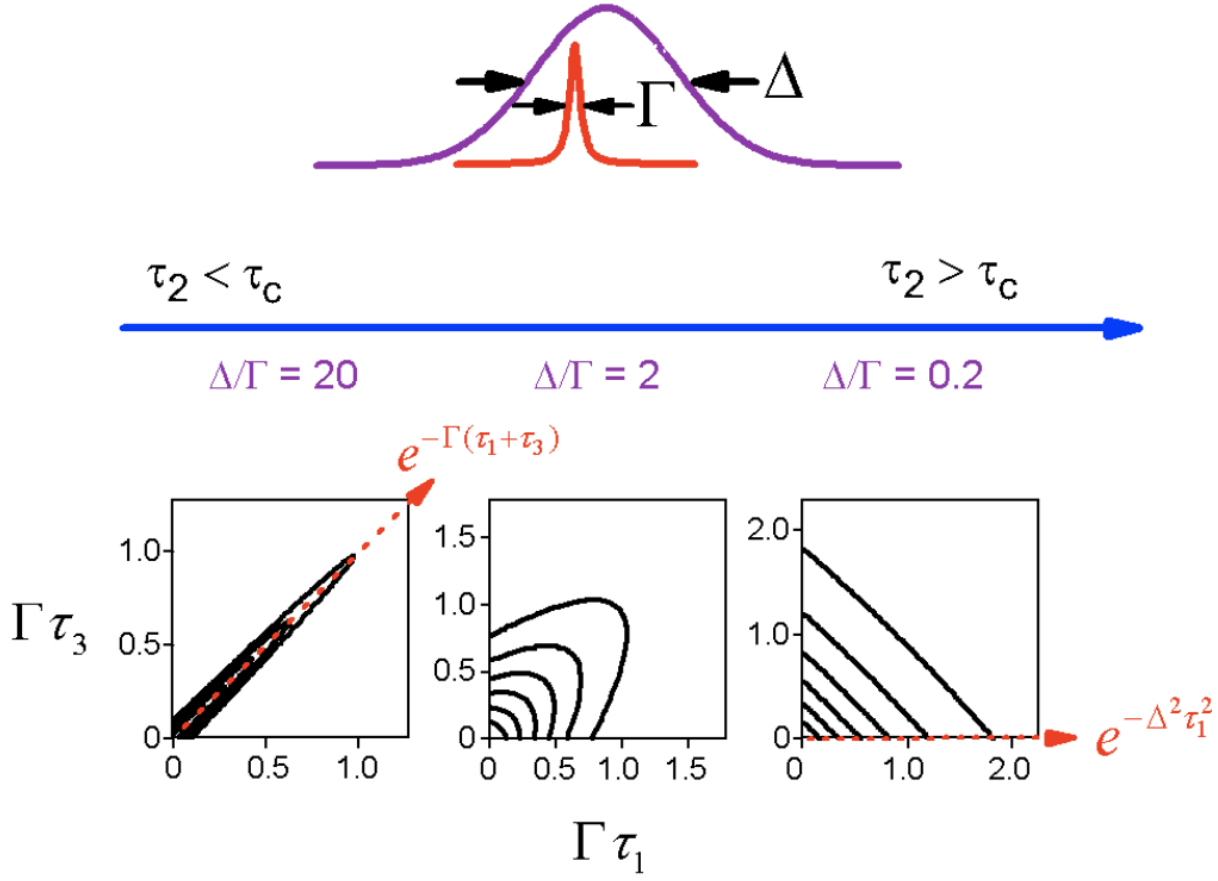
To characterize the energy gap correlation function, we choose a metric that describes the change as a function of τ_2. For instance, the ellipticity

$$E(\tau_2) = \frac{a^2 - b^2}{a^2 + b^2} \tag{5.5.2}$$



is directly proportional to $C_{eg}(\tau)$.

The photon echo experiment is the time domain version of this double-resonance or hole burning experiment. If we examine R_2 in the inhomogeneous and homogeneous limits, we can plot the polarization envelope as a function of τ_1 and τ_3.



In the inhomogeneous limit, an echo ridge decaying as $e^{-\Gamma t}$ extends along $\tau_1 = \tau_3$. It decays with the inhomogeneous distribution in the perpendicular direction. In the homogeneous limit, the response is symmetric in the two time variables. Fourier transformation allows these envelopes to be expressed as the lineshapes above. Here again τ_2 is a control variable to allow us to characterize $C_{eg}(\tau)$ through the change in echo profile or lineshape.