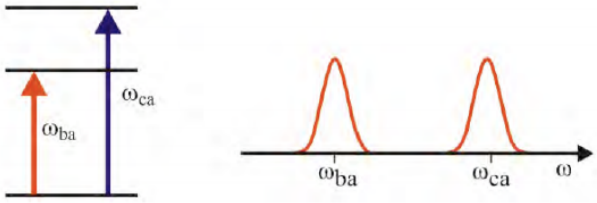
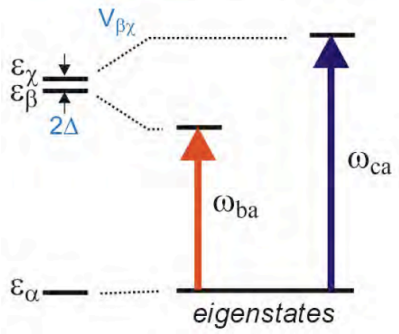
5.1: Two-Dimensional Correlation Spectroscopy

What is two-dimensional spectroscopy? This is a method that will describe the underlying correlations between two spectral features. Our examination of pump-probe experiments indicates that the third-order response reports on the correlation between different spectral features. Let's look at this in more detail using a system with two excited states as an example, for which the absorption spectrum shows two spectral features at ω_{ba} and ω_{ca}.

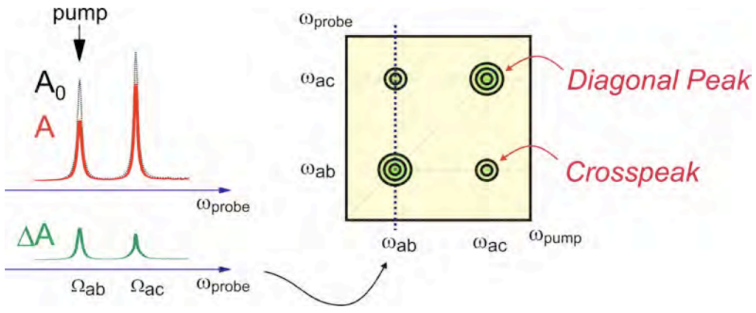


Imagine a double resonance (pump-probe) experiment in which we choose a tunable excitation frequency ω_{pump}, and for each pump frequency we measure changes in the absorption spectrum as a function of ω_{probe}. Generally speaking, we expect resonant excitation to induce a change of absorbance.

The question is: what do we observe if we pump at ω_{ba} and probe at ω_{ca}? If nothing happens, then we can conclude that microscopically, there is no interaction between the degrees of freedom that give rise to the ba and ca transitions. However, a change of absorbance at ω_{ca} indicates that in some manner the excitation of ω_{ba} is correlated with ω_{ca}. Microscopically, there is a coupling or chemical conversion that allows deposited energy to flow between the coordinates. Alternatively, we can say that the observed transitions occur between eigenstates whose character and energy encode molecular interactions between the coupled degrees of freedom (here β and χ):



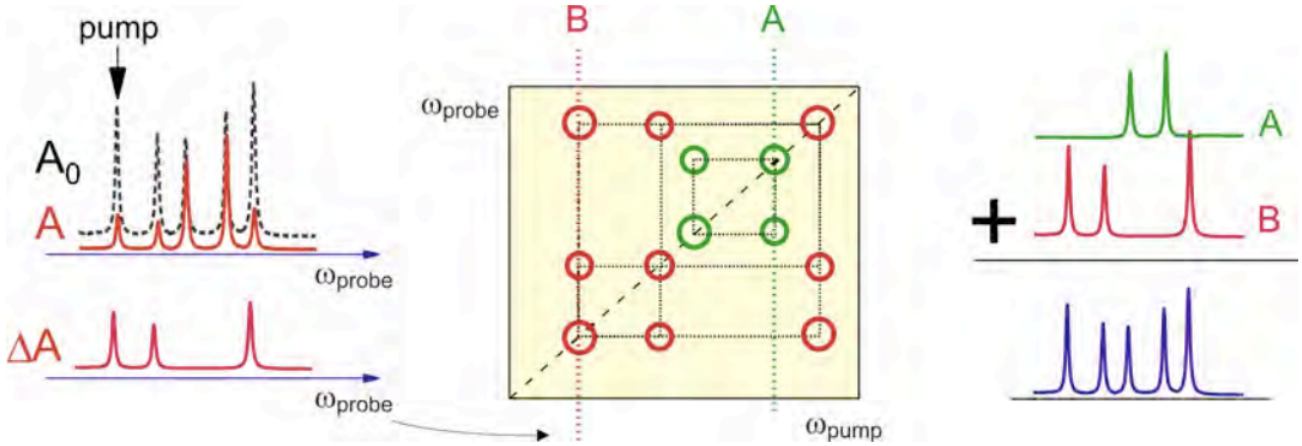
Now imagine that you perform this double resonance experiment measuring the change in absorption for all possible values of ω_{pump} and ω_{probe}, and plot these as a two-dimensional contour plot:[1]



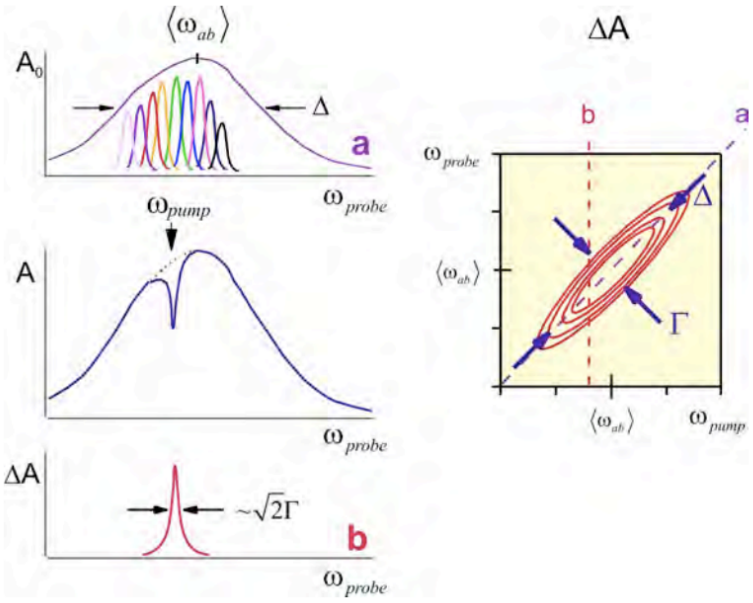
This is a two-dimensional spectrum that reports on the correlation of spectral features observed in the absorption spectrum. Diagonal peaks reflect the case where the same resonance is pumped and probed. Cross peaks indicate a cross-correlation that arises from pumping one feature and observing a change in the other. The principles of correlation spectroscopy in this form were

initially developed in the area of magnetic resonance, but are finding increasing use in the areas of optical and infrared spectroscopy.

Double resonance analogies such as these illustrate the power of a two-dimensional spectrum to visualize the molecular interactions in a complex system with many degrees of freedom. Similarly, we can see how a 2D spectrum can separate components of a mixture through the presence or absence of cross peaks.



Also, it becomes clear how an inhomogeneous lineshape can be decomposed into the distribution of configurations, and the underlying dynamics within the ensemble. Take 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 the same narrow band excitation followed by probing the differential absorption ΔA at all probe frequencies.



Here we observe that the contours of a two-dimensional lineshape report on the inhomogeneous broadening. We observe that the 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.

1. Here we use the right-hand rule convention for the frequency axes, in which the pump or excitation frequency is on the horizontal axis and the probe or detection frequency is on the vertical axis. Different conventions are being used, which does lead to confusion. We note that the first presentations of two-dimensional spectra in the case of 2D Raman and 2D IR spectra used a RHR convention, whereas the first 2D NMR and 2D electronic measurements used the LHR convention.