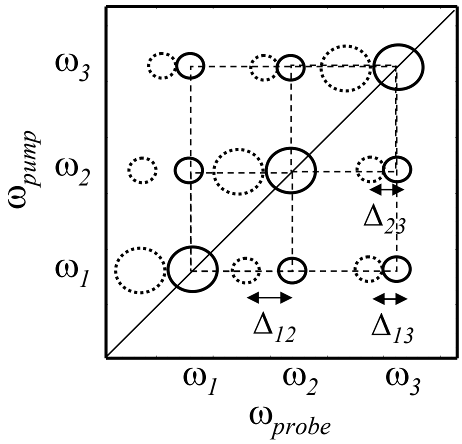
# Concepts and Methods of 2D Infrared Spectroscopy

*Peter Hamm and Martin T. Zanni*

# Answer Keys: Chapter 1

**Problem 1.1:** Draw a 2D IR spectrum of 3 coupled oscillators in which the coupling is quite strong between 1 and 2, weak between 1 and 3, and weak between 2 and 3.

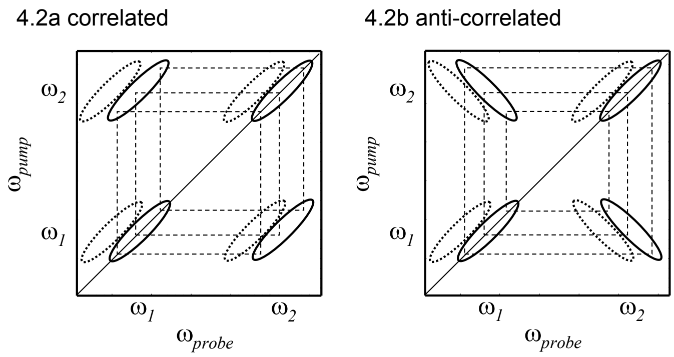
**Solution:** The 2D IR spectrum would look something like




in which $\Delta_{12}$ is larger than $\Delta_{23}$ and $\Delta_{13}$. We have plotted $\Delta_{ii}$ the same for all three modes, but that will not necessarily be the case. It is actually quite unlikely that $\Delta_{ii}$ will be the same for all three modes, because the coupling will change these values as well as their intensities (also not shown).

**Problem 1.2:** Schematically draw the 2D IR spectrum of two coupled oscillators like in Fig. **??**b, except consider the case in which both diagonal peaks are inhomogeneously broadened. (a) Draw one 2D spectrum assuming that the frequency fluctuations of the diagonal modes are correlated. That is, when one mode is at higher frequency, so is the other mode. (Hint: Think of the ensemble 2D IR spectrum as the addition of many 2D IR spectra of individual molecules at different frequencies.) (b) Draw a second 2D IR spectrum in which the two diagonal modes are anti-correlated. That is, when one mode is at a higher frequency, the other is at a lower one. (c) Are the shapes of the cross peaks different in these two situations? [**?** ] (d) Describe two physical processes that could create these types of correlations between coupled modes.

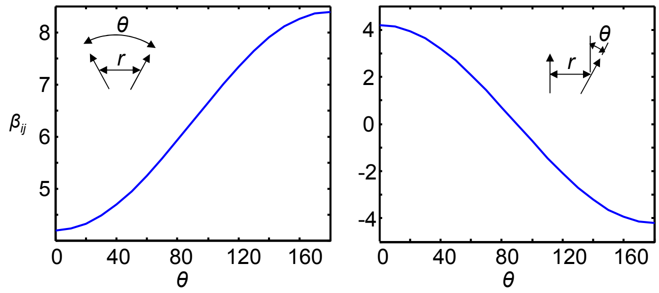
**Solution:** (a) When the frequency fluctuations are correlated, then when the oscillator 1 happens to have a higher or frequency, so will oscillator 2. Thus, the cross peaks will be elongated in a similar fashion to the diagonal peaks. (b) When the frequency fluctuations are anti-correlated, then when oscillator 1 happens to have a high (low) frequency, then oscillator 2 will be low (high). As a result, the cross peaks will oriented perpendicular to the diagonal if the two oscillators have the same amount of inhomogeneous broadening. (c) The shapes of the cross peaks will differ if off-diagonal anharmonicity is smaller than the linewidths, in which case the positive and negative peaks will interfere. The shapes of the cross peaks will also depend on the precise pulse sequence being used to measure the spectrum. (d) A physical process that might created correlated frequency fluctuations is hydrogen bonding, such as between a CO and an NH mode. Anti-correlations could be caused by a distribution of coupling strengths, such as two acetyl groups attached to a benzene ring.




**Problem 1.3:**Plot $\beta_{ij}$ as a function of angle for the two acetone molecules shown in Fig. **??**. Do again, but fix the orientation of one acetone molecule perpendicular to the normal between the two, and rotate the other one. (The

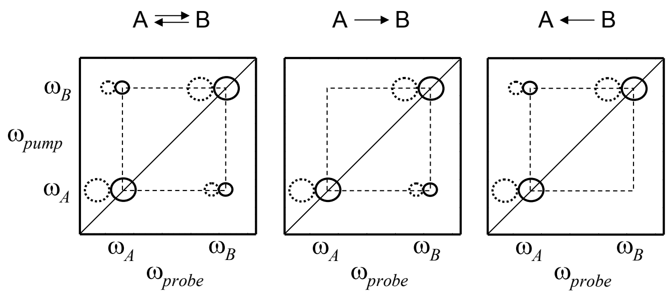
magnitude and sign of the coupling is very important for determining the 2D spectrum, which we will see in the following chapters.)

**Solution:** The magnitude of the couplings will depend on the dipole strength and their relative distance, but the form and sign of the curves should be:




**Problem 1.4:** Plot the intensities of the upper and lower cross peaks as a function of pump-probe time delay for (a) $A \rightleftharpoons B$, (b) $A \rightarrow B$ and (c) $B \rightarrow A$.

**Solution:** (a) Both the upper and lower pairs of cross peaks will increase with time in an equal manner and eventually have intensities that are equal to the diagonal peaks. (b) Only the upper pair will increase in intensity. (c) Only the lower pair will increase in intensity. See figure below.




**Problem 1.5:** In Fig. **??**b, only the peaks arising from allowed transitions are drawn. Draw a 2D IR spectrum that also includes the two missing forbidden transitions.

**Solution:** See Fig. 4.16.