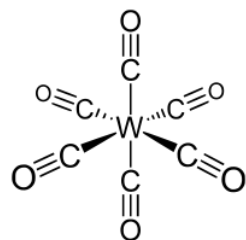


1) Take a mixture of two compounds



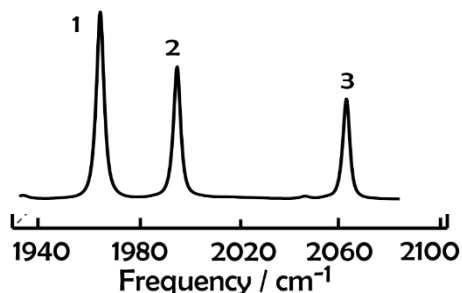
1 IR mode

+



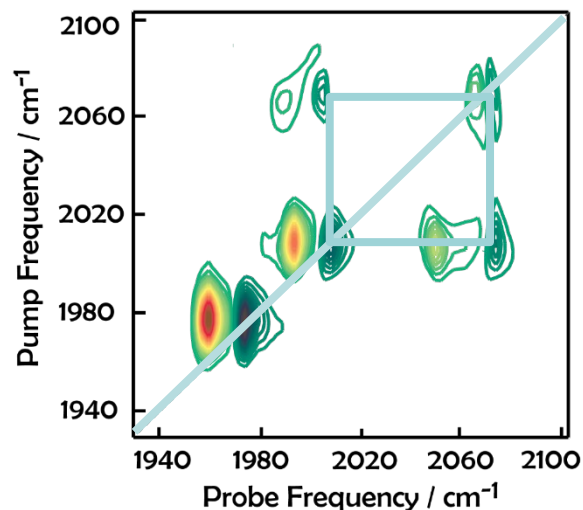
2 IR modes

2) Measure FT-IR >



Three peaks, but which peaks belong to which molecule?

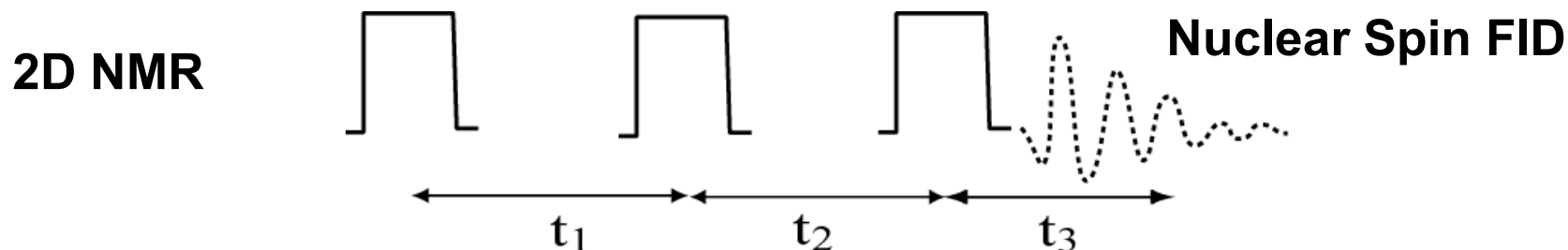
3) Measure 2D IR >



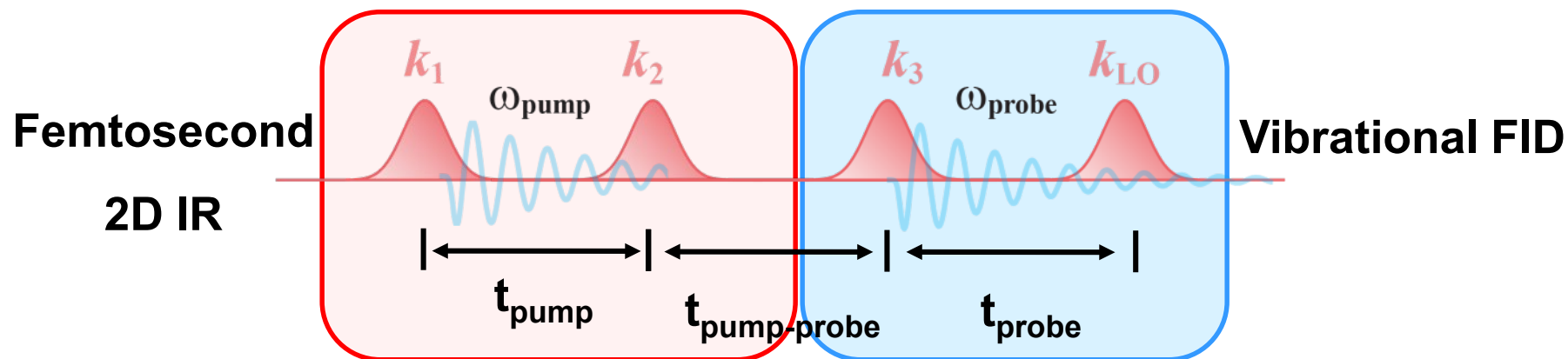
Crosspeaks between vibrations mean they belong to the same molecule

Assignment is clear!

2D NMR spectroscopy uses multiple radio-frequency pulses to generate a nuclear spin signal



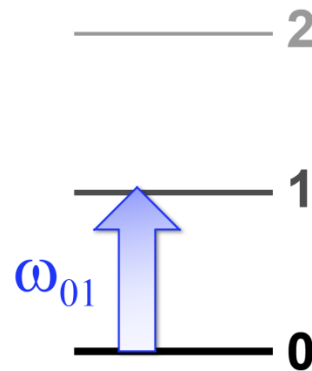
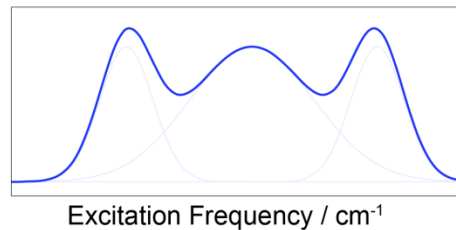
In 2D IR spectroscopy, we use 3 femtosecond pulses to generate a signal that can each be Fourier transformed to give a 2D spectrum.



$k_1$  &  $k_2$  generated from a single pulse by **pulse shaper**

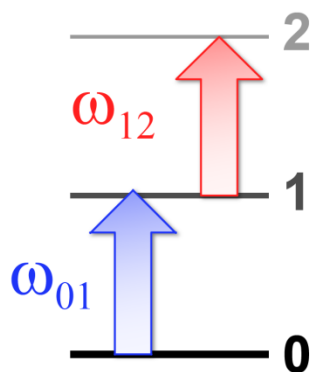
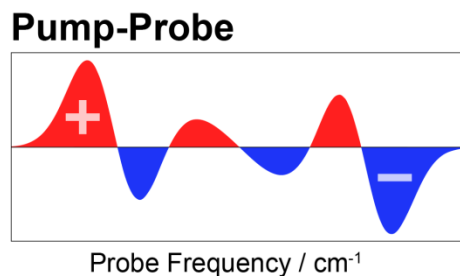
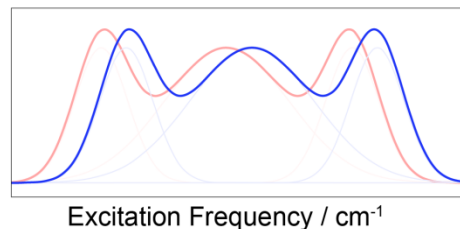
LO generated automatically from  $k_3$

delay, phase and shape is **computer controlled**



Linear IR spectra measure ground-state vibrational frequencies (peak maxima) and distributions (linewidths)

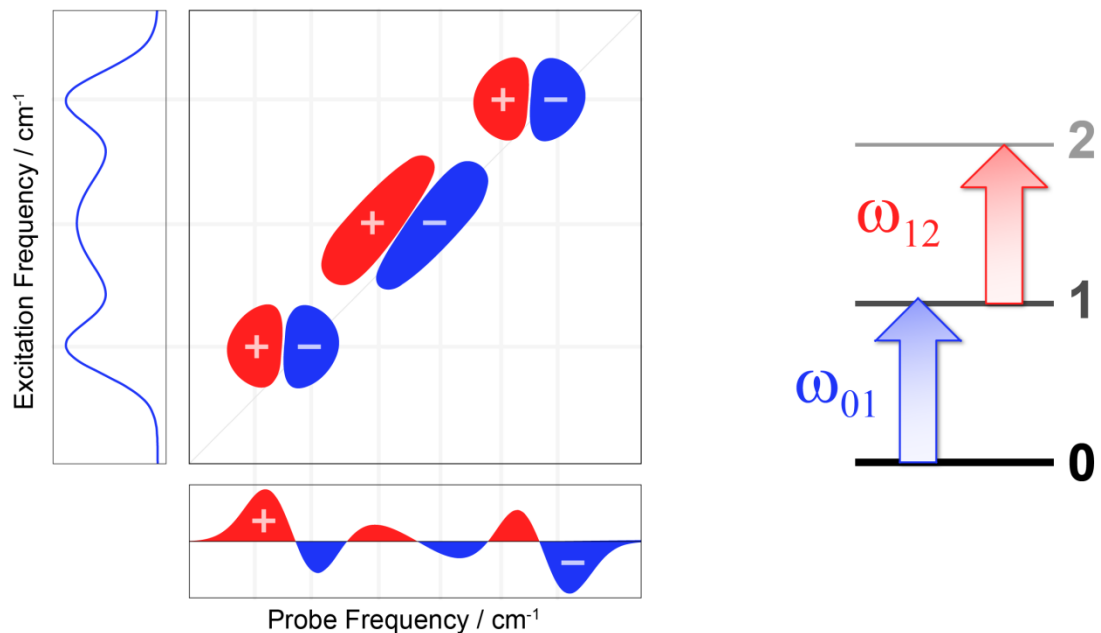
However, for most molecules peaks overlap and greatly complicate analysis



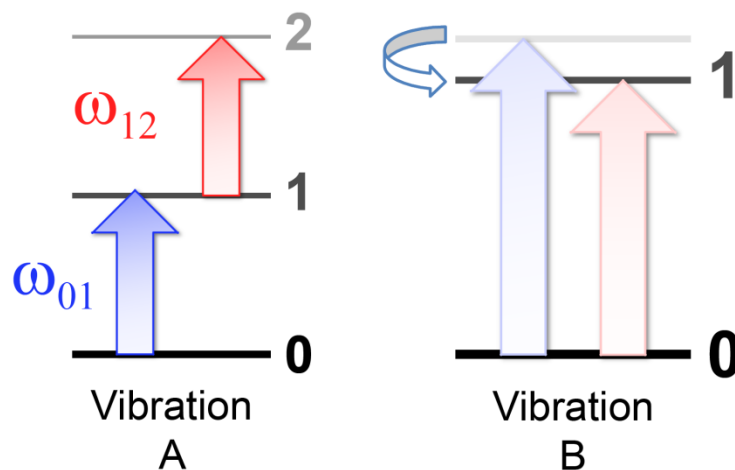
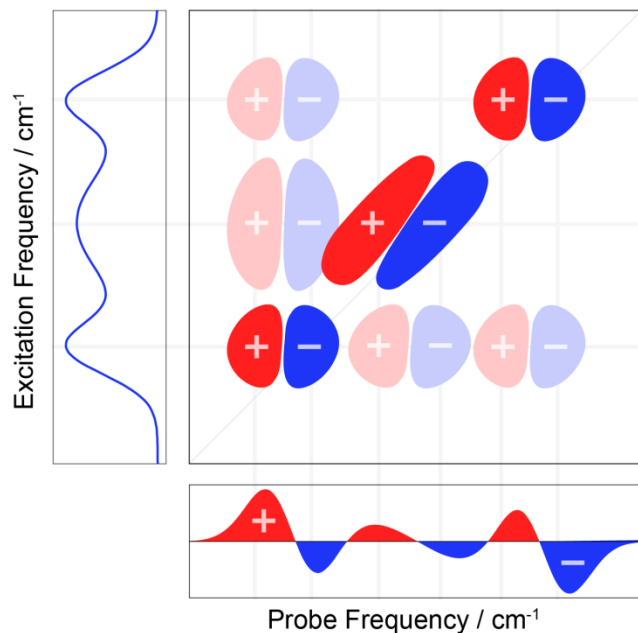
Pump-probe spectra provides more structural information by measuring the anharmonicity of the vibrational potential

However, pump-probe spectra are always measured as excite-state minus ground-state difference spectrum, so peaks interfere

Overlapping peaks makes analysis confusing.



2D IR provides the pump-probe spectrum as a function of the excitation frequency, improving the spectral separation between peaks

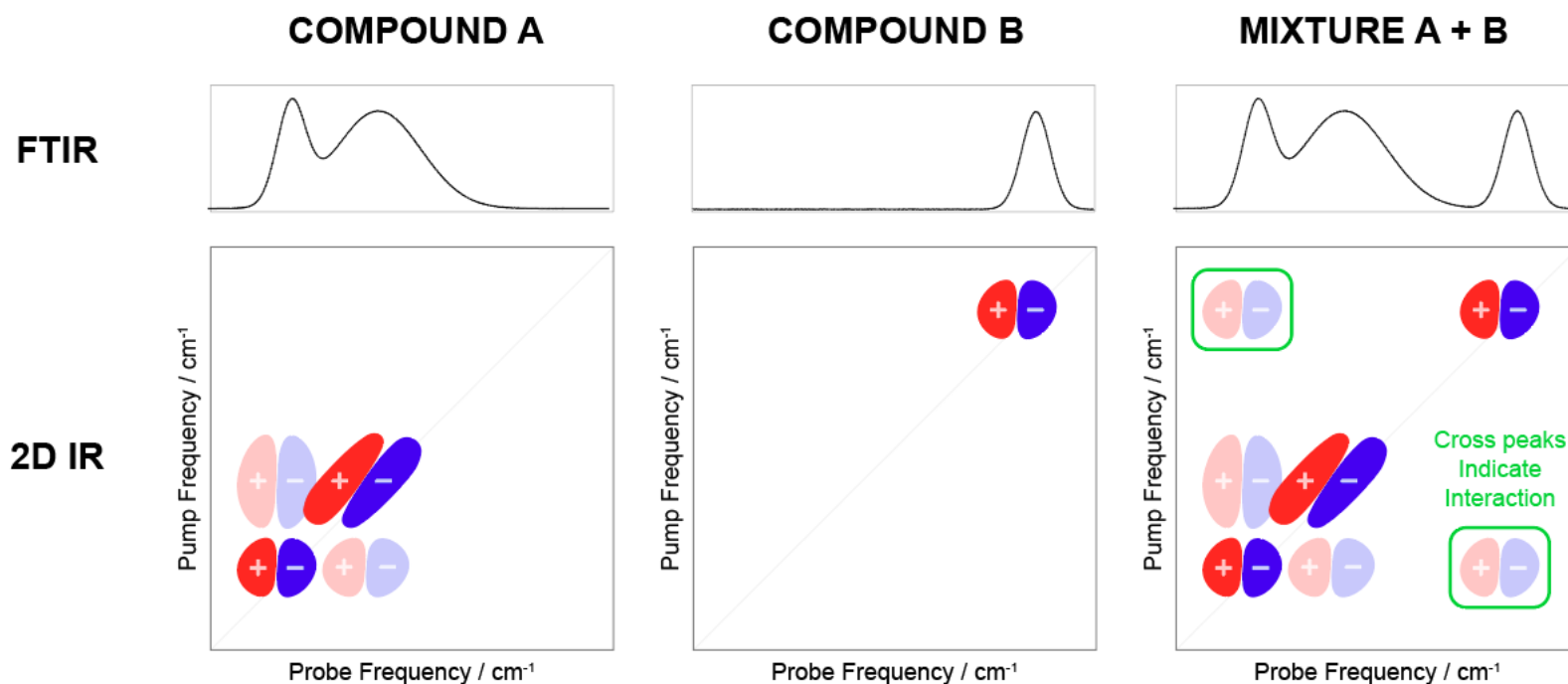


2D IR provides the pump-probe spectrum as a function of the excitation frequency, improving the spectral separation between peaks

Crosspeaks are revealed when excitation of one vibration alters the frequency of a different vibration – the vibrations are coupled

The spacing, shape and intensity of the off diagonal peaks are directly related to the degree of coupling and spatial orientation of the vibrational modes

Crosspeaks arise via through-bond interactions, through-space interactions or chemical exchange – but all required interaction / proximity of two parts of a molecule or species



Interactions between two vibrations can also create frequency or linewidth changes in FTIR spectra, but generally these changes will be small and not nearly as direct as the presence of a cross peak.