Jyvaskyla Summer School 2013
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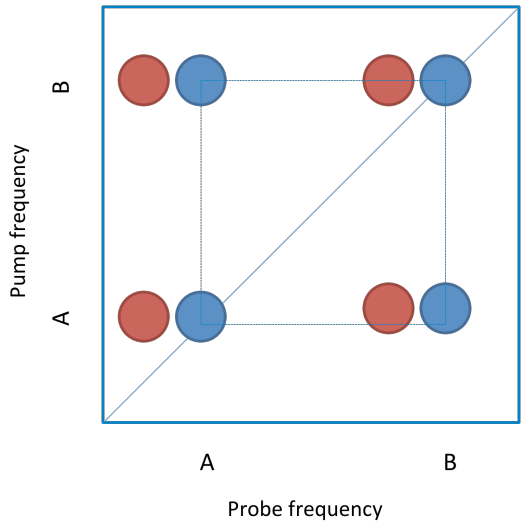
Homework

1) The 2D-IR spectrum of a single-component system, recorded with a waiting time of 5 ps, reveals two sets of diagonal peaks and two pairs of off-diagonal peaks linking the diagonals (see below). The IR absorption spectrum of the sample shows two peaks at frequencies equal to those of the diagonal peaks in the 2D-IR spectrum.

a) Explain, using energy level diagrams, the assignment of each of the observed peaks and two possible reasons for the presence of the off-diagonal modes.

b) Explain what other 2D-IR experiments could be carried out to differentiate between these two possible assignments.



2) a) Explain the term 'spectral diffusion' as applied to 2D-IR spectroscopy

b) During a 2D-IR experiment, the lineshape of the v=0-1 transition of a particular mode is observed to change with waiting time. Using the parameters below, calculate the ellipticity of the peak at each waiting time and plot the dynamics related to the frequency-frequency correlation function (FFCF). By fitting the FFCF dynamics to an appropriate exponential function, quantify the picosecond-timescale dynamics of the system and comment on the values of the ellipticity at T_w = 0 ps and at 20 ps.

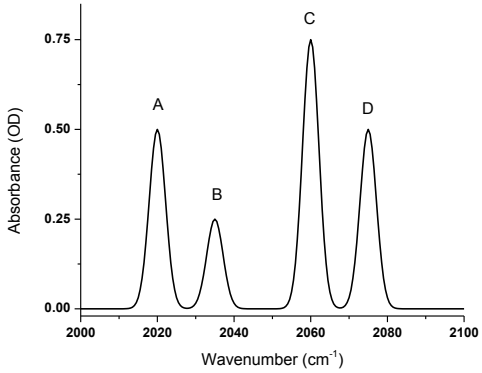
T_w (ps)	Diagonal linewidth (cm^{-1})	Antidiagonal linewidth (cm^{-1})
0	15.00	8.66
1	14.96	9.47
2	14.92	10.14
3	14.88	10.69
4	14.84	11.13
5	14.80	11.50
6	14.76	11.80
7	14.72	12.04
8	14.68	12.23
9	14.64	12.38
10	14.60	12.50
11	14.56	12.59
12	14.52	12.66
13	14.48	12.71
14	14.44	12.74
15	14.40	12.77
16	14.36	12.78
17	14.32	12.78
18	14.28	12.77
19	14.24	12.76
20	14.20	12.75

3) A chemical system exhibits an FTIR spectrum in the 2000-2100 cm^{-1} region as shown below. Assuming each of the following scenarios, describe the 2D-IR spectrum that you would expect to see at short T_w values (close to 0 ps) and, where appropriate, comment on how the spectra would change as T_w increases.

a) The spectrum arises from one molecule. All peaks correspond to modes of this molecule and are coupled to each other.

b) The spectrum is of a mixture of two molecules: Peaks A and C arise from molecule 1. Peaks B and D arise from molecule 2. All modes on a given molecule are coupled.

c) The spectrum is of a mixture of two isomers of a given molecule. Peaks A and B arise from coupled modes of isomer 1. Peaks C and D arise from coupled modes of isomer 2. The isomers are in dynamic equilibrium and exchange on a timescale of 4 ps.



4) Consider a 2D-IR spectrum (T_w ~ 0 ps) of a pair of coupled vibrational modes (see below). Explain, using diagrams, how this will change if the vibrational modes corresponding to the two diagonal peaks are inhomogeneously broadened.

Explain how the shapes of the off-diagonal peaks will change if the frequency fluctuations of the broadened diagonal modes are i) correlated and ii) anticorrelated. Propose a molecular basis for these types of correlation occurring.