

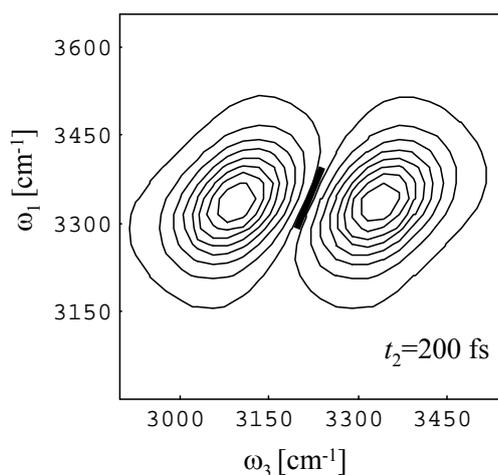
# Concepts and Methods of 2D Infrared Spectroscopy

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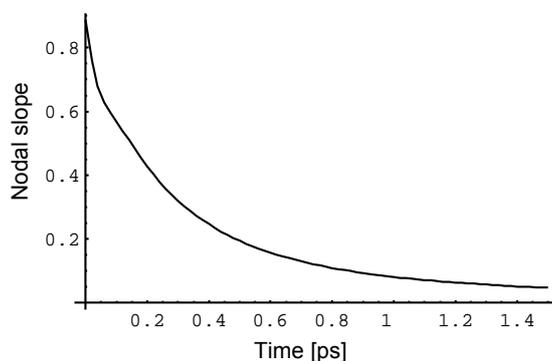
## Answer Keys: Chapter 10

**Problem 10.1:** For Fig. 10.5, explain why the 2D lineshapes change with time. Is the nodal slope consistent with the frequency correlation function from which the spectra were calculated?

**Solution:** The thick line in the figure below is a linear interpolation to the nodal line.



It is constructed by first searching for the  $\omega_1$ -frequency that generates the maximum of the 0-1 signal. Then, the zero-crossing of horizontal cuts through the 2D IR spectrum for  $\omega_1$ -frequency plus/minus a certain frequency around that maximum  $\omega_1$ -frequency is calculated, and the slope is then estimated as linear interpolation. The figure below shows the decay of the nodal slope as a function of  $t_2$ , which closely resembles the (normalized) frequency fluctuation correlation function of Fig. 10.3 c.



**Problem 10.1:** For 10.8, explain why the cross peak are further separated than the diagonal peaks.

**Solution:** The two  $\text{-C}\equiv\text{O}$  local-mode oscillators are identical because of the symmetry of the molecule. Hence, on the level of an exciton model (which would work very well here), the situation is identical to Fig. 6.3c.

**Problem 10.1:** Re-calculate Fig. 10.6 with improved signal-to-noise. (ATTENTION: we meant Fig. 10.6, not 10.5)

**Solution:** The brute force solution would be to run a longer MD simulation. However, as noise reduces only with the square-root of time, this quickly becomes computer-expensive. A improvement of signal-of-noise by a factor 10 would imply a 100 ns trajectory, which runs for about a week on a single processor.

The smarter solution for this particular situation is the following: In the calculation of Fig. 10.6, we used one single water molecule. As we had not explicitly isotope labelled it (this could be done by changing its mass in the topology file, which however would have only a very minor effect), all 1019 waters in the simulation box are identical. With the command:

```
g_traj -f spc.trr -s spc.tpr -ox coord.xvg -of force.xvg -noxvgr
```

one is asked to specify for which group the coordinates and forces are written, and one option is the whole system. The files then become huge, but

contain all water molecules. The response function calculation `2DwaterWithoutCumulant.nb` would have to be rewritten to average over all waters. On the level of Mathematica or Matlab, this will take a very long time, so it should rather be done in Fortran or C.

**Problem 10.1:** Simulate the 2D IR spectrum of the antibiotic ovispirin which has been studied with 2D IR spectroscopy and has a solution NMR structure in the protein data bank (1HU5). Do two simulations. In one simulation, isotope label an end residue, in the other a middle residue and see if they have different lineshapes and cross peaks.

**Solution:** Introductory remark: It turns out that 1HU5 is not the best example. Looking at the pdb structure file with, for example, VMD (see <http://www.ks.uiuc.edu/Research/vmd/>), one finds that it is a bend helix, which implies that some of the hydrogen bonds are extraordinarily strong. Eq. 10.14 strongly overestimates the frequency shift of these hydrogen bonds. This effect can be suppressed by setting the parameter `hydrogenbondshift` to zero in the C-code.

The figure below shows simulated 2D IR spectra for the peptide with no isotope labeling (left), with  $^{13}\text{C}^{18}\text{O}$ -labeling at position 1 (middle), and  $^{13}\text{C}^{18}\text{O}$ -labeling at position 9 (right). The isotope peak is marked by an arrow. Isotope labeling is introduced by inserting e.g.:

```
H1[9][9]=-60;
```

after the line

```
interaction(H1,vxd,vyd,vzd,x,y,z,n,protein);
```

into the C-code. This introduces a frequency shift of the diagonal matrix element of  $-60\text{ cm}^{-1}$  for position 9 (in this case). It is seen that the isotope peak is significantly more pronounced in the center of the helix as compared to the end.

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