Concepts and Methods of 2D Infrared Spectroscopy

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Answer Keys: Chapter 9

Problem 9.2: Design a 3D-IR spectrometer.

Solution: There are lots of different answers to this question. The most straightforward answer is that one uses 5 independent beams that each have a unique wavevector, so that phase matching separates as many of the possible Feynman paths as possible. To generate absorptive 3D IR spectra, one then needs to generate 4 separate rephasing/non-rephasing spectra and add them together. This is the method used by Hamm and coworkers as described in Chapt. 11. Alternatively, if one is interested in a subset of Feynman paths, then it may be possible to use fewer excitation pulses, but choose a phase matching condition in which forces one or more of the beams to interact twice with the sample (see Fig. 2.14). This method was used by Zanni to measure 3D IR spectra of the 2Q pulse sequence (see Chapt. 11). So far, these are the only two 3D IR experiments performed at this time. Conceptually they are the simplest to describe, but their implementation can be quite tricky because additional work is required for phase stabilization or post phase correction.

Another way that would be convenient would be to use a pulse shaper. With a pulse shaper, one can just program additional laser pulses without having to add additional optics. For instance, one could use the shaper to create 4 of the pulse and then use a probe pulse, so that the entire experiment would only require two independent laser beams. Phase cycling would be used to separate out the desired Feynman paths. The spectra would be absorptive and automatically phased. The only difficult will be making sure that the pulse shaper is accurate enough to make the complex waveforms necessary. Less complex waveforms and less phase cycling would be required by using two pulse shapers instead of just one, so that each produce a pulse pair. Phase stability and time-zeros would also no longer

be an issue. The experiment would be similar to the original pulse shaping work by Warren Warren [175] in collecting 2D Elec spectra, except that the pump-probe phase matching geometry would allow any absorptive species to be measured rather than just molecules that fluoresce.

Problem 9.2: Imagine you have a purely absorptive real-valued 2D IR spectrum $I(\omega_1, \omega_2)$. Write out the equations to mathematically extract the rephasing and non-rephasing spectra.

Solution: This question arises from the discussion in the last paragraph of Sect. 9.3.2. In that paragraph, it is explained how one can extract the rephasing and non-rephasing spectra from an absorptive 2D IR spectrum by collecting $I(\phi_{12} = 0, \phi_{3,LO} = 0)$ and $I(\phi_{12} = \pi/2, \phi_{3,LO} = 0)$ and using a Fourier transform "trick." But one can actually extract the rephasing and non-rephasing spectrum from the absorptive $I(\phi_{12} = 0, \phi_{3,LO} = 0)$ by itself, by using the "trick" twice, once along each dimension. Each time we use the trick, we enforce causality to go from a real spectrum to a complex spectrum. Thus, we Fourier transform along one dimension, enforce causality by zeroing the negative time delays, and then Fourier transforming back to the frequency domain. We then repeat the procedure along the other dimension.

To demonstrate this, consider the 2D interferogram $\cos(\omega_1 t_1)\cos(\omega_2 t_2)$. If we Fourier transform along ω_1, we get $\frac{1}{2\sqrt{2\pi}}(\delta(t+t_1) + \delta(t-t_1))\cos(\omega_2 t_2)$. We eliminate $\delta(t+t_1)$ and Fourier transform back to get $e^{-i\omega t_1}\cos(\omega_2 t_2)$. We then do the same along the other dimension to get $e^{-i\omega t_1}e^{-i\omega t_3}$. Thus, we get a fully complex spectrum, from which the rephasing and non-rephasing are extracted by the appropriate sums.

Problem 9.3: Think of a phase cycling sequence that separates the two Feynman diagrams of Fig.9.22, assuming k_2 and k_3 are collinear (k_1 is the first pulse in the diagram).

Solution: Since it is the k_2 and k_3 beams that are collinear, we need to use the phase dependence of the signal with respect to these two beams to differentiate between them. I'll call the two Feynman diagrams S_1 and S_2, respectively. The total signal measured will be $S_T = e^{-i(\phi_2-\phi_3)}S_1 + e^{+i(\phi_2-\phi_3)}S_2 \equiv e^{-i\Delta\phi_{23}}S_1 + e^{+i\Delta\phi_{23}}S_2$. Thus, to get S_1, one add the signals

measured for $S_T(\Delta\phi_{23}=0)+iS_T(\Delta\phi_{23}=\pi/2)$ and to get S_2, one subtracts the signals $S_T(\Delta\phi_{23}=0)-iS_T(\Delta\phi_{23}=\pi/2)$.