Concepts and Methods of 2D Infrared Spectroscopy

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Answer Keys: Chapter 4

Problem 4.1: Show that a linear absorption spectrum is independent of the phase of the incident light field.

Solution: Lets assume we have a pulse with arbitrary spectral phase $\phi(\omega)$:

$$E(\omega) = E'(\omega)e^{i\phi(\omega)}$$

whose time-domain representation $E(t)$ might be very complicated. Since it is not necessary a short pulse, we have to use the convolution Eq. 3.62 explicitly:

$$E_{sig}(t) = i\int_0^\infty E(t-t_1)R^{(1)}(t_1)dt_1$$

Using the convolution theorem of the Fourier transformation (Appendix A), we obtain for the frequency representation:

$$E_{sig}(\omega_1) = iE(\omega_1)R^{(1)}(\omega_1)$$

This signal is heterodyned by $E(\omega_1)$ which also acts as local oscillator:

$$S(\omega_1) \propto \Re(E(\omega_1)E^*_{sig}(\omega_1)) = \Im(E(\omega_1)E^*(\omega_1)R^{(1)}(\omega_1))$$

The arbitrary phase factor cancels when evaluating $E(\omega_1)E^*(\omega_1)$.

Problem 4.2: For an isolated vibrator, discuss the t_2 dependence of the intensity of the 2D IR peaks if the system undergoes a chemical reaction from the first excited state so that population relaxation does not refill the ground state.

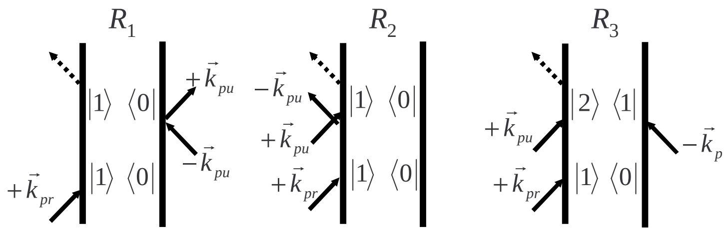
Solution: In this case, response functions R_1, R_3, R_4, and R_6, all of which are in a $|1\rangle\langle 1|$ population state during time period t_2, would include a e^{-t_2/T_1} term, like in Eq. 4.19, but the term is missing in R_2 and R_5, since the ground state is not refilled.

Problem 4.3: Plot the rephasing and non-rephasing spectra of a set of two coupled oscillators for $t_2 = 0$ and t_2 equal to half the interstate coherence times. How could these spectra be used to simplify the absorption spectra?

Solution: Feynman diagrams that are in a $|i\rangle\langle j|$ (with $i \neq j$) interstate coherence state during time t_2 contribute to peaks D,C in the rephasing spectrum (Fig. 4.11), and in particular give rise to the cross peaks" on the diagonal in the non-rephasing spectrum (Fig. 4.13). These diagrams oscillate during time t_2 due to the $e^{-i\omega_{i,j}t_2}$ factor, see Eq. 4.38. The spectrum measured at t_2 equal to half the interstate coherence times will thus have opposite sign, so when adding up both spectra, the diagrams containing interstate coherences will be suppressed, less peaks a re present, and the outcome will be the same as for a frequency-domain 2D IR spectrum (Sect. 4.4)

Problem 4.4: Should pump-probe spectra have signals at negative time-delays? Hint: Consider a frequency resolved pump-probe experiment (Fig. 4.15a) with interchanged time-ordering of pump and probe pulses (i.e. negative delay times). Assume semi-impulsive pulses. Collect the Feynman diagrams that describe this experiment for a slightly anharmonic oscillator, develop the response function and the signal as a function of pump-probe delay time. You will have to take into account that the 3^{rd}-order polarization starts to emit only after the last field-interaction, which is the pump-pulse, and not the probe pulse. As a consequence, probe pulse and 3^{rd}-order polarization have a time lag when they interfere. Show that this leads to characteristic beats at negative delay times, as shown in Fig. 4.18. This effect is called a *perturbed free induction decay.*

Solution: In a pump-probe geometry, the probe pulse acts both as field interaction (the first in this case) and local oscillator, $k_{pr} = k_{LO}$. Thus, the pump pulse interacts with the sample twice, and does so one time with $+k_{pu}$, and the other time with $+k_{pu}$. Thus, the relevant Feynman diagrams are:

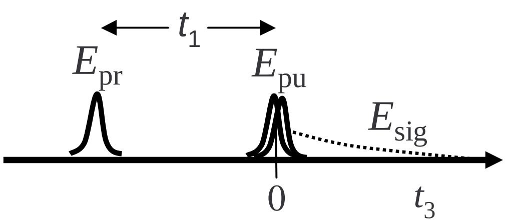


The response functions are:

$$R_1(t_3, t_1) = R_2(t_3, t_1) = -\mu_{01}^4 e^{-i\omega_{01}(t_1+t3)} e^{-(t_1+t_3)/T_2}$$
$$R_3(t_3, t_1) = +\mu_{01}^2 \mu_{12}^2 e^{-i(\omega_{01}t_1+\omega_{12}t3)} e^{-(t_1+t_3)/T_2}$$

Time t_1 is the (negative) pump-probe delay time. The spectrometer in Fig. 4.15a performs a Fourier-transform with respect to time t_3, so

$$E_{sig}(\omega_3, t_1) = e^{-i\omega_{01}t_1 - t_1/T_2} \left(\frac{2}{i(\omega_3 - \omega_{12}) - 1/T_2} - \frac{2}{i(\omega_3 - \omega_{01}) - 1/T_2} \right)$$



The signal field interferes with the probe pulse, which also acts as a local oscillator. However, the time-origin of the probe pulse is different from that of the signal field. In the figure above, we have set time $t_3 = 0$ to the point when the signal field starts, but then the probe pulse is peaks at time $t_3 = -t_1$:

$$E_{pr}(t_3) = E_{LO}(t_3) \propto \delta(t_3 + t_1)$$

whose Fourier transform with respect to t_3 is:

$$E_{LO}(\omega_3; t_1) \propto e^{i\omega_3 t_1}$$

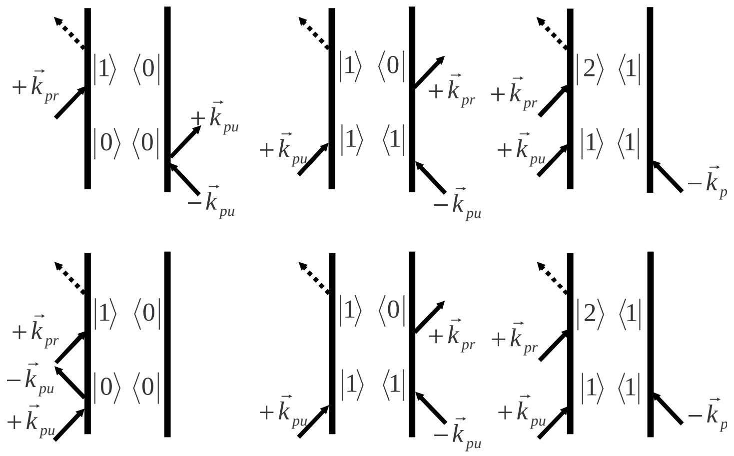
The signal field interferes on the detector with the local oscillator:

$$\Re(E_{LO}(\omega_3) E_{sig}(\omega_3; t_1) = e^{-t_1/T_2} \cdot$$
$$\Re\left(e^{-i(\omega_{01}-\omega_3)t_1} \left(\frac{2}{i(\omega_3 - \omega_{12}) - 1/T_2} - \frac{2}{i(\omega_3 - \omega_{01}) - 1/T_2} \right) \right)$$

We see that this effect gives rise to a signal that decays with the dephasing time T_2 towards negative pump-probe delay times t_1. Evaluating the real part reveals a complicated expression that reflects the oscillatory contribution in Fig. 4.18.

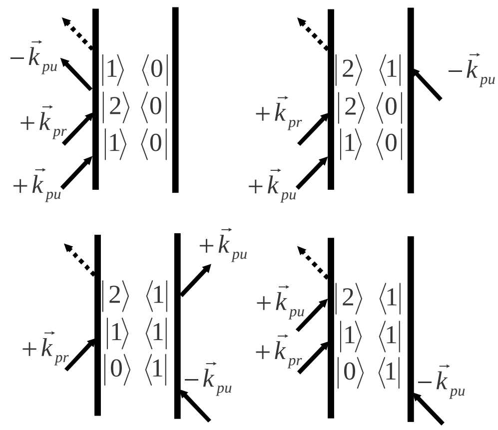
Problem 4.5: Now consider a pump-probe experiment of a vibrational transition with short but finite pump and probe pulses and the pump-probe delay time set to zero. Draw the Feynman diagrams of all possible time-orderings that occur during pulse overlap. The additional Feynman diagrams lead to an effect that is sometimes called *coherence spike* or *coherence artifact*.

Solution: The Feynman diagrams relevant for properly time-ordered pump-probe spectroscopy with the probe arriving after the pump pulse and without pulse overlap are:



Note that we gave the two field interactions from the pump pulse a little bit of time ordering, since the pulses are not exactly delta pulses. The top row is the rephasing diagrams, the bottom row the non-rephasing diagrams, and in total six diagrams contribute.

When pulses start to overlap in time, and we have to explicitly perform the convolution of, e.g. Eq. 2.75. During this integration, all time orderings appear, and one has to switch between set of Feynman diagrams whenever one of the sign of the integration times t_1, t_2 or t_3 change order. For time-ordering *pump − pump − probe*, the normal" six Feynman diagrams shown above are seen, for time-ordering *probe − pump − pump* the Feynman diagrams discussed for problem 4.4, and for *pump − probe − pump* yet another set of Feynman diagrams become relevant:



In simple words, there are just many more Feynman diagrams that play a role during pulse overlap, giving rise to the so-called coherent artifact.