Concepts and Methods of 2D Infrared Spectroscopy

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Answer Keys: Chapter 11

Problem 11.1:

In the 3D spectra presented above, 5 "diagonal" peaks are observed both for the 5th-order 2Q and the purely absorptive pulse sequences. Use Feynman diagrams to explain the differences.

Solution: The figure below contains the Feynman diagrams for the diagonal peaks in the 5th-order 2Q spectrum, which is take from Ref. 43,
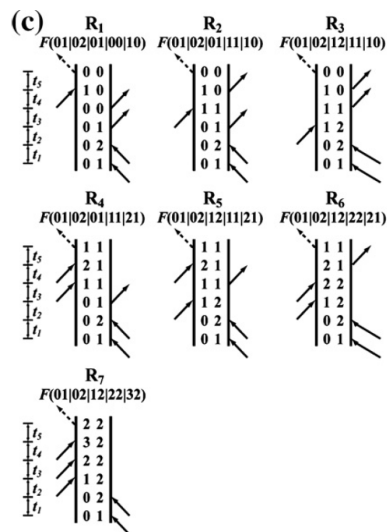

The following Figure shows all Feynman diagrams relevant in a pure absorptive 3D IR spectrum of a 2-level system, taken from Ref. 79 (note that there is an error in Fig. 11.7b, which is supposed to be the same as the first line in the Figure below).
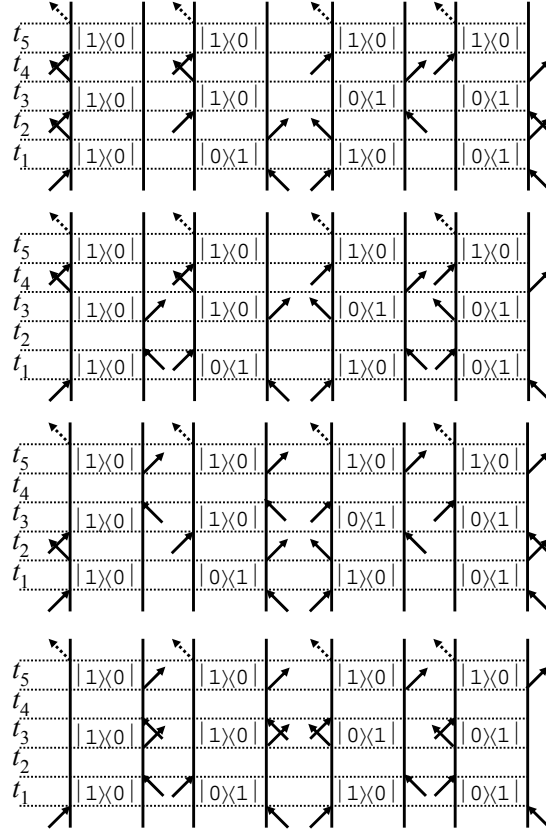
The columns are ordered by the permutations of the coherences during the three coherence times (*left-left-left*, *right-left-left*, *left-right-left* and *right-right-left*). These four measurements are added together to remove the phase twist in the 3D IR spectra. The rows are ordered by the permutations of population states during the population times ($|0\rangle\langle 0| - |0\rangle\langle 0|$, $|1\rangle\langle 1| - |0\rangle\langle 0|$, $|0\rangle\langle 0| - |1\rangle\langle 1|$ and $|1\rangle\langle 1| - |1\rangle\langle 1|$). These are emitted into the same phase matching direction, and thus can not be separated. Furthermore, on the level of Kubo's stochastic theory of lineshapes, they give rise to the same response functions, so the 4 rows just result in a 4 times stronger signal.

In the multilevel system of a weakly anharmonic oscillator, we climb up to third excited state. One fundamental set of Feynman diagrams is:
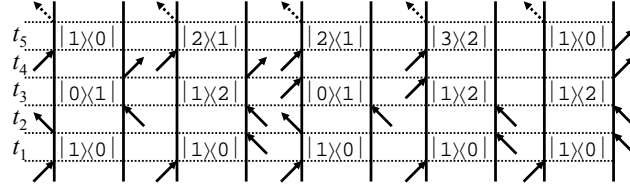
However, we need to keep in mind that one still has the similar possibility of permutations as above. There are 4×4 permutations of the first diagram at frequency $\omega_{01} - \omega_{01} - \omega_{01}$ (as above), 2×4 permutations of the second diagram at frequency $\omega_{01} - \omega_{12} - \omega_{12}$, 2×4 permutations for the third diagram at frequency $\omega_{01} - \omega_{01} - \omega_{12}$, 1×4 permutations for the fourth diagram at frequency $\omega_{01} - \omega_{12} - \omega_{23}$, and 1×4 permutations for the fifth diagram at frequency $\omega_{01} - \omega_{12} - \omega_{01}$. Hence, the total numbers of diagrams is 40!

Problem 11.2: Write the 5th-order response function for the Feynman diagram in Fig. 11.3.

Solution: The answer is

$$R = \mu_{01}\mu_{12}\mu_{01}\mu_{12}\mu_{01}\mu_{01}e^{+i\omega_{01}t_1 + i\omega_{02}t_2 + i\omega_{12}t_3 - i\omega_{01}t_5}e^{-(t_1+t_2+t_3+t_5)/T_2}e^{-t_4/T_1} \qquad (0.1)$$

One can compress the transition dipole strength to μ_{01}^8, since $\mu_{12} = 2\mu_{01}$. We have also approximated the T_2 dephasing time and T_1 population times as equal no matter which states are involved, which is probably not the case.

Problem 11.3: The 2Q 2D IR spectra in Sect. 11.2 are not absorptive. Describe how one could generate an absorptive 2Q spectrum in order to implement our dream experiment in Sect. 11.7.3.

Solution: In order to generate an absorptive 2Q 2D IR spectrum, one would need to collect both a rephasing and a non-rephasing type of 2Q spectrum. Since one can only generate a non-rephasing response with a third-order 2Q pulse sequence (Fig. 11.1), one must go to 5th-order to get both. Thus, we would use a pulse sequence like that for the Feynman diagram in Fig. 11.3, in which the 02-coherence during t_2 has the opposite phase as the 10-coherence during t_5, along with a non-rephasing version, in which the coherences during t_1 and t_5 are in-phase. Therefore, the non-rephasing version would be

something like that show in the figure below (the rephasing 2Q Feynman diagram is also shown). The complete dream experiment is 7th-order, only because we imagine initiating the dynamics with another laser pulse such as an actinic pump which would count as two more interactions.
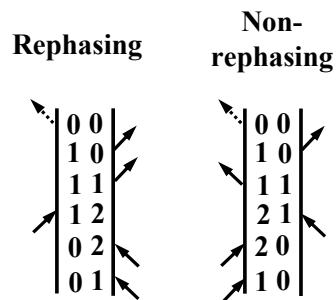
Problem 11.4: Draw the Feynman diagrams and predict the spectrum for a transient 2D IR experiment in which the actinic pump excites the molecule to a stable electronic state. Do the same for a pulse sequence in which the actinic pump appear after k_1 and k_2, but before k_3.

Solution: Shown in the figure below are three hypothetical 2D IR spectra. In (a), a 2D IR spectrum is shown for the molecule in its ground electronic

state. In (b), a transient 2D IR spectrum is shown, which has a new set of coupled 2D IR peaks. The new peaks are what the 2D IR spectrum might look like in the excited electronic state that has a different curvature from the ground state (hence, different frequencies, diagonal and off-diagonal anharmonicities). The phases of the peaks are flipped because the ground state features are now bleached. In this spectrum, one cannot tell *a priori* how the two ground state vibrations are correlated to the excited state features. This information can be ascertained from the spectrum in (c), in which cross peaks appear at frequencies $(\omega_1,\omega_3){=}(\omega_a,\omega_c)$ and $(\omega_1,\omega_3){=}(\omega_b,\omega_d)$. Thus, mode a becomes mode c, and mode b becomes mode d. The ordering could be reversed, which is what Hamm and coworkers found in Ref. [17,18]. The frequency shifts may also not be very dramatic, such as for ω_b, which can lead to destructive interferences between the peaks.

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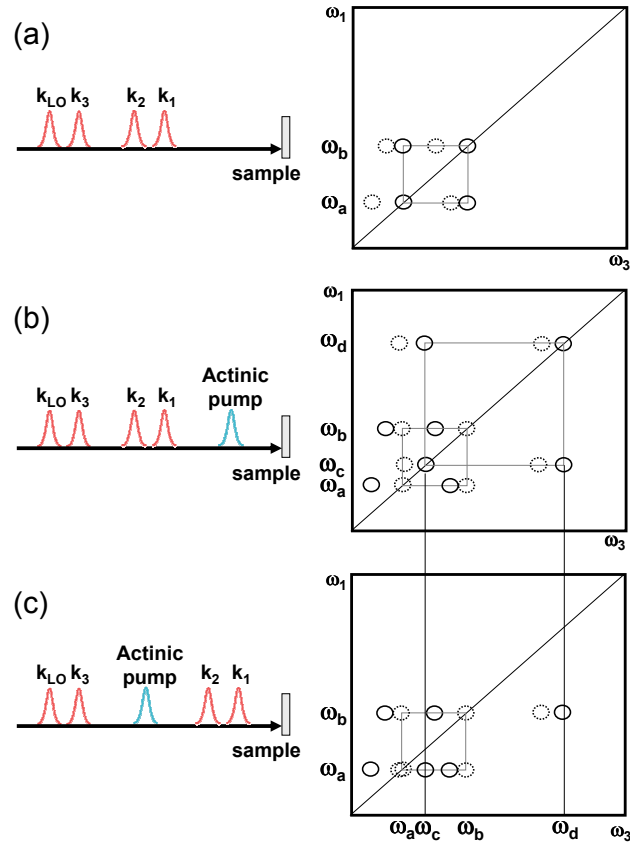
Problem 11.5: Draw all possible Feynman diagrams for sequential and parallel 3rd-order cascading signals for (a) 2-quantum 3D IR spectroscopy and (b) purely absorptive 3D IR spectroscopy. A sequential cascade is one in which the first three pulses emit a 3rd-order field that is reabsorbed by the sample. A parallel cascade is one in which both 3rd-order signals evolve simultaneously.

Solution: (a) Representative sequential and parallel cascading signals are shown below, take from Ref. 59.
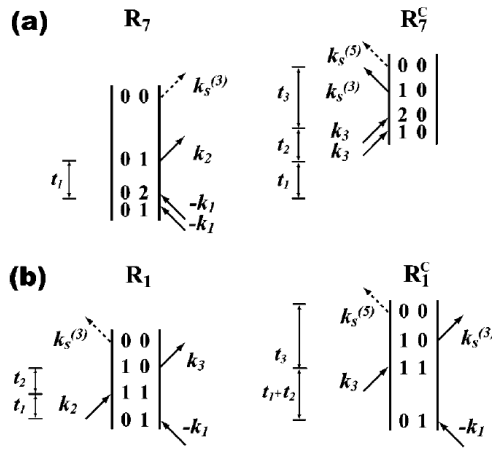

FIG. 11. Representative examples of Feynman diagrams responsible for (a) sequential and (b) parallel cascades in the $k_s^{(5)}$ phase matching direction. The left diagrams generate a third-order response along $k_s^{(3)}$ that is reabsorbed by the sample to act as an excitation pulse for the right diagrams.

Problem 11.6: Draw the Feynman diagrams for a 5th-order Raman experiment, as well as those of two cascaded 3rd-order Raman processes. Verify that a forbidden two-quantum transition is necessary for the 5th-order Raman process, but not for the 3rd-order cascading process, which is why it is very difficult to measure the 5th-order signal in the Raman case. Contrast this to the IR case.

Solution: Two examples of 5th-order Raman pathways are shown on the left. In both cases, a forbidden transition is required with either a $0 \rightarrow 2$ transition or an $a \rightarrow b$ transition. No such forbidden transition is necessary in the cascaded situation. This is one factor that makes the cascades very intense as compared to the desired 5th-order signal. In the IR, forbidden transitions are not required for either the normal or cascaded pathways. Thus, the rel-

ative ratio of signal to cascade is determined by other factors, including the concentration. At concentrations used in typical IR experiments (mM), cascading should be small.

Two possible 5th-order Raman Pathways

A sequential Cascade
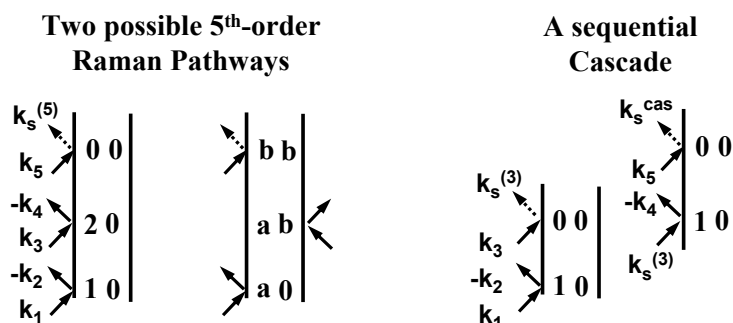
Problem 11.7: Visible dyes absorbed to semiconductor surfaces are often used in solar cells because when they absorb light they inject an electron into the semiconductor that is collected to make electricity. The efficiency at which they inject electrons is related to the coupling of the electronic orbitals of the dye to the semiconductor, among other factors. Strong coupling sometimes manifests itself as a shift in the electronic absorption spectrum. In a recent 2D IR experiment, it was found that one particular dye appears to bind to the surface in 3 different conformations because it exhibits 3 infrared bands when there is normally just one. Moreover, each band has a different electron transfer rate, as measured with transient 2D IR spectroscopy that excites the dye with 400 nm light. Design a 2D Vis/IR experiment that measures the electronic absorption bands of these three conformations that might reveal why the electron transfer rates differ.

Solution: This problem is based on recent experiments by Zanni and coworkers in which they observed three different dye conformations on a TiO_2 nanocrystallin substrate.[196] To extract the Vis absorption spectra of the individual dyes, one could do a mixed IR-Vis 2D experiment. For instance, by using infrared pulses for k_1 and k_2 and a visible pulse for k_3, one could correlate the vibrational frequencies of the dyes to the electronic transition. That is, the cross peaks would be the absorption spectra. One would also want to consider using visible pulses for k_1 and k_2 and an infrared pulse for k_3, which will produce cross peaks on the opposite side of the diagonal. Due to overlap, the cross peaks may be better resolved on one side of the diagonal than the other.
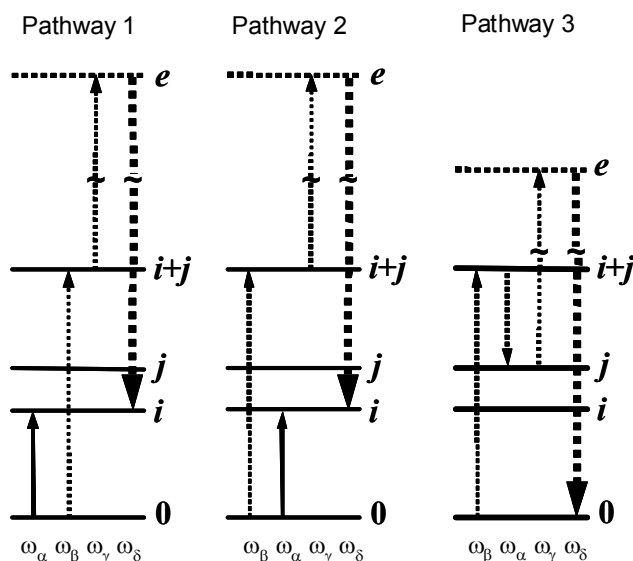
Problem 11.8: The shaped pump pulse in Fig. 11.10 optimizes the population of the ν=2 state as compared to ν=1. Explain how a shaped pulse might be used to optimize the signal strength of a 2Q experiment.

Solution: In the 2Q experiment, the signal strength depends on size of the 0-2 coherence that is generated. The data shown in Fig. 11.10 demonstrates that the ν=2 state can be populated much better by using a shaped laser pulse. This suggests that one should also be able to generate a much larger 0-2 coherence as well. So, if the shaped pulse is cut into two halves, one half would presumably create a strong coherence, and the remaining half would then create the population. Thus, the two halves would be the k_1 and k_2 pulses. In NMR spectroscopy, one creates the optimum $\pi/2$ pulse by making the best π pulse by increasing the pulse duration until the spin population is completely inverted. Half that duration is then what is used for the $\pi/2$ pulse. So, one could imagine a similar procedure for 2D IR experiments. However, it is not apparent if the best $\pi/2$ pulse is indeed half the π pulse, since the optimized pulse shapes in the Fig. 11.10 experiment are not so simple.

Problem 11.9: It is more common in the EVV/DOVE 2D IR community to use so-called Wave Mixing Energy Level (WMEL) diagrams instead of Feynman diagrams to visualize various pathways [57]. WMEL diagrams depict the field interactions with energy levels of the system in a similar (but not identical) manner to the arrows used in Fig.4.9. For a WMEL diagram, the interaction ordering goes from left to right. Bra side transitions have solid arrows and ket side transitions have dotted arrows. The inward (outward) arrows of a Feynman diagram are represented as upward (downward) arrows on a WMEL diagram. Using these rules, translate the Feynman diagrams of Fig. 11.11.

Solution:

Let's take for this example a 2D-IR cross peak involving a fundamental band i and combination band $i + j$. The relevant energy levels are shown in Figure 11.11 (a). Following the recipe outlined above, we can translate the 'res'Feynman diagrams of Figure 11.11 (b) into the following WMEL diagrams:

Pathway 1   Pathway 2   Pathway 3

$$\omega_\alpha\ \omega_\beta\ \omega_\gamma\ \omega_\delta \qquad \omega_\beta\ \omega_\alpha\ \omega_\gamma\ \omega_\delta \qquad \omega_\beta\ \omega_\alpha\ \omega_\gamma\ \omega_\delta$$

It is common to use a thick or wavy line to depict the radiating nonlinear polarisation. In the literature, the complex conjugates of these diagrams are usually shown, as they contain fewer dotted lines and therefore appear neater. This is of course also achieved if you use the convention that Bra side transitions have dotted arrows and ket side transitions have solid arrows. Beware, as both conventions are in use and it is easy to make mistakes! See if you can also spot the error in one of the diagrams of reference [57]! The 'anti res' diagrams of Figure 11.11 (b) are constructed by drawing the ω_γ arrow downwards, terminating below the groundstate with the ω_δ arrow pointing upwards to terminate on the appropriate final state.

Problem 11.10: Demonstrate that compared with pathways 1 and 2, pathway 3 cross peaks are lower in frequency along ω_α by the mechanical anharmonic shift of the state k.

Solution:
Figure 11.11 (b) shows that pathways 1 and 2 both contain 0 to i transitions. Thus to detect a cross peak, ω_α must be tuned to ω_i. Pathway 3 is different. If you look at the ket side of its Feynman diagram in Figure 11.11 (b), the second interaction drives a downwards k to j transition. Here $k = i+j$ and $\omega_k = \omega_i + \omega_j - \delta$, where δ is the mechanical anharmonic shift of the band (for the case of an overtone take $i = j$). The value of ω_α required

to drive this transition is $\omega_k - \omega_j$, which is equal to $\omega_i - \delta$. For the usual case where we take δ as positive, this gives pathway 3 crosspeaks lower in frequency along the ω_α axis of a 2D spectrum compared with pathways 1 and 2.