Four-Wave Mixing

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1 Introduction

The goal of this project is to acquire a basic understanding of the pump-probe measurement technique called four-wave mixing in terms of a simple model and interpreting an experimental trace of HgI₂. Pump-probe measurements excite a system with a first 'pump' pulse which is followed by a delayed 'probe' pulse which measures the response of the system to the first pulse. The pump-probe delay $\Delta t$ can be set by the experimentalist, allowing to take the response after many different delay times, leading to a time trace, which can be analyzed. Four-wave mixing is special as it uses two interfering pump pulses, arriving at the same time in the sample but having slightly different directions, and a probe pulse measuring the reaction of the sample. As a consequence of this geometry (which is shown in figure 1), a fourth beam is produced in the sample which can be detected background free on a separate detector, i.e. the background due the three other laser beams present during the measurement does not coincide on the detector. In the first part of the project, a simple analytical approach is pursued in order to understand how four-wave mixing occurs. In the second part, an experimental trace will be analyzed.

Figure 1: Beampaths of a typical four-wave-mixing experiment: The pump pulses $E_a$ and $E_b$ excite a fraction of the sample, which is probed after $\Delta t$ with $E_c$. Due to the geometry of the three beams, the sample emits in a fourth direction, which can be measured without the background of the other beams.
2 Simple Model

Four-wave mixing is difficult to understand, because the response of a system on three incident electric fields is not straight-forward to calculate. The source of an emitted electric field of a system is always its polarization \( \mathbf{P} \), which is usually expanded in terms of the susceptibility \( \chi \)

\[
P_i(t) = \epsilon_0 \left( \sum_{\alpha=a,b,c} \sum_j \chi^{(1)}_{ij} \ast E_{aj} + \sum_{\alpha,\beta=a,b,c} \sum_j \chi^{(2)}_{ijk} \ast E_{aj} \ast E_{bj} + \sum_{\alpha,\beta,\gamma=a,b,c} \sum_{ijkl} \chi^{(3)}_{ijkl} \ast E_{aj} \ast E_{jk} \ast E_{kl} + \ldots \right),
\]

where \( \ast \) denotes the convolution. The susceptibility in which we are interested in is \( \chi^{(3)} \): We want an emission which mixes all three involved electric fields. The problem is the calculation of this quantity, as it has many possible contributing terms (48, if we are only interested in the emission in one direction), and is a third order tensor having 81 entries (although they can be reduced taking the systemic symmetries into account).

Because of this, we will use a simpler model, giving a basic understanding of the four-wave-mixing process. We will try to understand the four wave mixing process step by step: First, we will treat the excitation by the pump pulses, then we will move to the stimulated emission due to the probe pulse.

(a) We model the pump pulses in the focus by two plane waves propagating into slightly different directions \( \mathbf{k} \) with a fixed frequency \( \omega \) and the same amplitude \( A \):

\[
E_{a,b}(r,t) = A \exp( i \cdot (\mathbf{k}_{a,b} \cdot \mathbf{r} - \omega t))
\]

\[
\begin{align*}
\mathbf{k}_a &= N_a \cdot \begin{pmatrix} \sin(\theta/2) \\ \cos(\theta/2) \\ 0 \end{pmatrix} \\
\mathbf{k}_b &= N_b \cdot \begin{pmatrix} -\sin(\theta/2) \\ \cos(\theta/2) \\ 0 \end{pmatrix}
\end{align*}
\]

a) Calculate the scaling factors \( N_a \) and \( N_b \). Explain the meaning of \( \theta \). Hint: What is the length of \( \mathbf{k} \)?

b) Calculate the intensity distribution due to the interference of the two waves.

(b) As a next step, the excitation of the sample is assumed to be linear with respect to the pump intensity. Plot the fraction of excited \( r_e \) and ground state molecules \( r_g \) along the relevant spacial coordinate(s).
(c) After some delay $\Delta t$, the probe pulse will interact with the sample, generating different responses in the excited fraction than in the ground state fraction. We treat this by assuming two different emissions $F_g = A_g \exp(i\varphi_g)$ and $F_e(\Delta t) = A_e(\Delta t) \exp(i\varphi_e(\Delta t))$ of the two populations leading to a total emitted field

$$F_{\text{tot}} = F_g r_g + F_e r_e.$$  

(5)

How does the signal look far away from the source (on the detector) in dependence of $A_g$, $A_e$, $\varphi_g$, and $\varphi_e$? Hint: Read up on fraunhofer diffraction. You will have to fourier-transform equation 5. Remember that a detector measures intensities and not field amplitudes!

(d) Identify the terms in your result of the previous section which could be used to measure a background-free signal. When will this signal be large, when small? What happens if $F_e = F_g$?

(e) Explain in your own words what happens during four wave mixing (in terms of the simple model presented here).
3 Pump Probe Experiment of HgI$_2$

Figure 2 shows a pump-probe trace of HgI$_2$, which was excited non resonantly and probed with the same wavelength. Non-resonant means that the energy delivered by one photon is not equal to any allowed transition in the molecule, which leads (in this case here) to raman-scattering.

(a) Read up on raman scattering. What transitions are possible in a raman process?

(b) Look up the rotational constants and vibrational eigenmodes of HgI$_2$.

(c) At $\Delta t = 0$, when the pump and probe pulses interact at the same time with the sample, there is an additional peak arising in the four wave mixing signal (called coherence peak), which is due to nonlinear processes in the sample. Identify the peak in the trace and subtract it from the signal.

(d) Fourier transform the modified signal and plot the result (with reasonable ordinate units)! What peaks do you see? Determine their positions and uncertainties by fitting Gaussians on them.

(e) Fourier transform the original data and compare it to the result of the modified one.

![Figure 2: Pump-probe trace of HgI$_2$ after non-resonant excitation and probing with the same wavelength.](image-url)