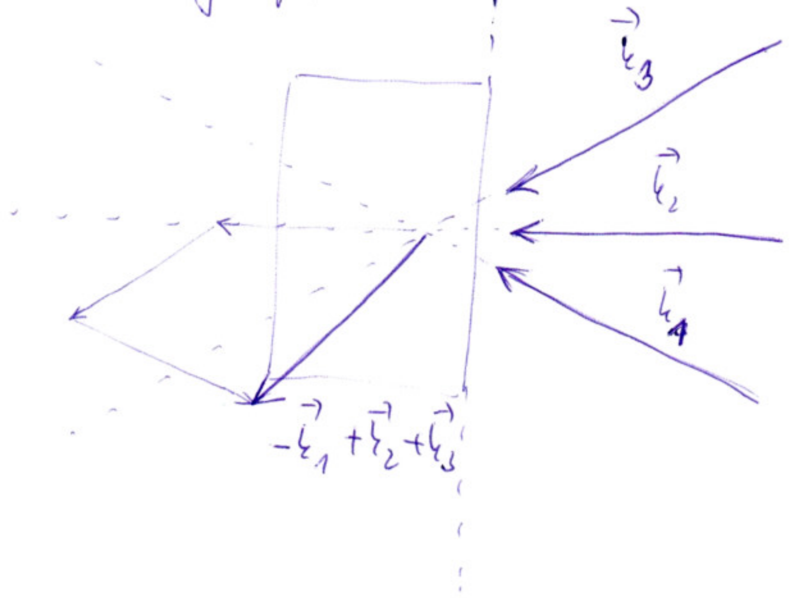
n-wave mixing experiments

n-1 incoming fields generates a non-linear signal



Let us consider the total field in form of a sum

$$\boxed{\vec{E}(\vec{r},t) = \sum_{j=1}^{n} \vec{E}_j(\vec{r},t)\, e^{i\vec{k}_j\cdot\vec{r} - i\omega_j t} + c.c.} \qquad (21)$$

complex conjugated

During integration of Maxwell equations we need to take into account our results for linear response, i.e. refraction and absorption – let us simplify the treatment by assuming that <u>absorption is small</u> $\kappa \sim 0$

$$\Rightarrow \quad \varepsilon(\omega_j) \equiv n_j^2$$ ... only refraction is taken into account

For all the waves ~~we~~ have dispersion relation

$$\boxed{k_j = \frac{\omega_j}{c} n_j} \qquad (22)$$

Maxwell wave equation becomes

$$(23) \qquad \boxed{\nabla \times \nabla \times \vec{E}(\vec{r},t) + \frac{n^2}{c^2}\frac{\partial^2}{\partial t^2}\vec{E}(\vec{r},t) = -\frac{4\pi}{c^2}\frac{\partial^2}{\partial t^2}\vec{P}_{NL}(\vec{r},t)}$$

For $\vec{P}_{NL}(\vec{r},t)$ we take the following ansatz

$$\boxed{\vec{P}_{NL}(\vec{r},t) = \sum_{n=2,3,\ldots} \sum_s P_s^{(n)}(t)\, e^{i\vec{k}_s\cdot\vec{r} - i\omega_s t}} \qquad (24)$$

Here, $\underline{n}$ numbers the order of non-linearity, we start with 2 because 1 (linear) is in already.

$\underline{s}$ numbers possible combinations of k-vectors and frequencies

$$\boxed{\begin{aligned} \vec{k}_s &= \pm\vec{k}_1 \pm \vec{k}_2 \pm \vec{k}_3 \pm \ldots \pm \vec{k}_n \\ \omega_s &= \pm\omega_1 \pm \omega_2 \pm \omega_3 \ldots \pm \omega_n \end{aligned}} \qquad (25)$$

Let us consider material slab as on page $\underline{10}$ and let us take certain direction $\vec{k}_s$ to define z axis. The thickness of the slab along the z direction will be ℓ. We assume $k_s \cdot \ell \gg 1$.

We choose a single component of the non-linear polarization

$$\boxed{\vec{P}_{NL}(\vec{r},t) = \vec{P}_S(t)\, e^{i\vec{\xi}_S z - i\omega_S t}} \qquad (26)$$

and try to look for a solution

$$\boxed{\vec{E}(\vec{r},t) = E_S(z,t)\, e^{-i\omega_S t + i\vec{\xi}_S{}' \cdot \vec{r}} + c.c.} \qquad (27)$$

with

$$\boxed{\xi_S' \equiv \frac{\omega_S}{c} n_c} \qquad (28)$$

$\vec{\xi}_S$ and $\vec{\xi}_S{}'$ can be different even though their absolute values satisfy the same dispersion relation. Let us assume that $\vec{P}_S(t)$ is a slow envelop, much slower than $e^{i\omega t}$

$$\Rightarrow \quad \left|\frac{\partial}{\partial t} P_S(t)\right| \ll \left|\omega_S P_S(t)\right| \qquad (29)$$

neglecting slowly varying <u>temporal envelop</u> we get

$$\nabla \times \nabla \times E_S(\vec{r},t) - \frac{n_S^2 \omega_S^2}{c^2} E_S(\vec{r},t) = \frac{4\pi \omega_S^2}{c^2} P_S(t)\, e^{i\vec{\xi}_S \cdot \vec{r}} \qquad (30)$$

Now let us do something with $\nabla\times\nabla\times\vec{E}_s(\vec{r},t)$

There is an identity

$$\nabla\times\nabla\times\vec{E}_s(\vec{r},t) = \nabla\cdot(\underbrace{\nabla\cdot\vec{E}_s}_{\substack{\parallel \\ 0 \text{ from Maxwell equations}}}) - \nabla^2\vec{E}_s$$

So we have

$$\nabla\times\nabla\times\vec{E}_s(\vec{r},t) = -\nabla\left((\nabla\vec{E}_s(z,t))e^{i\vec{k}_s'\cdot\vec{r}-i\omega_s t} + i\vec{k}_s'\cdot\vec{E}_s(z,t)e^{i\vec{k}_s'\cdot\vec{r}-i\omega_s t}\right)$$

$$= -(\nabla^2\vec{E}_s(z,t))e^{i\vec{k}_s'\cdot\vec{r}-i\omega_s t} - (\nabla\vec{E}_s(z,t))i\vec{k}_s' e^{i\vec{k}_s'\cdot\vec{r}-i\omega_s t}$$

$$- i\vec{k}_s'(\nabla E_s(z,t))e^{i\vec{k}_s'\cdot\vec{r}-i\omega_s t} - i\vec{k}_s'\cdot(i\vec{k}_s')\vec{E}_s(z,t)e^{i\vec{k}_s'\cdot\vec{r}-i\omega_s t}$$

$$= -(\nabla^2\vec{E}_s(z,t))e^{i\vec{k}_s'\cdot\vec{r}-i\omega_s t} - 2i\vec{k}_s'(\nabla\vec{E}_s(z,t))e^{i\vec{k}_s'\cdot\vec{r}-i\omega_s t}$$

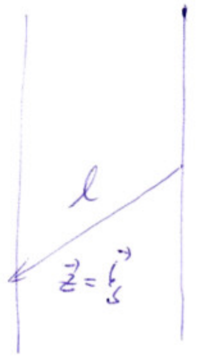
$$+ k_s'^2\vec{E}_s(z,t)e^{i\vec{k}_s'\cdot\vec{r}-i\omega_s t} \qquad (31)$$

Now we use Eq. (28) and neglect the term $\nabla^2\vec{E}_s(z,t)\approx 0$

Inserting our result into Eq. (30) we get $\longrightarrow$

$$\boxed{i k_s' \frac{\partial}{\partial z} E_s(z,t) = -2\pi \frac{\omega_s^2}{c^2} P_s(t)\, e^{i(\vec{k}_s - \vec{k}_s')\cdot z}} \qquad (32)$$

Let us integrate this equation along $\vec{k}_s$ for the distance l



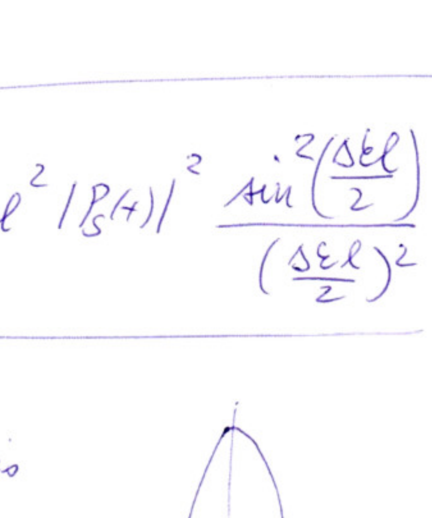
$$\Rightarrow \quad E_s(l,t) = \frac{2\pi i}{n(\omega_s)} \frac{\omega_s}{c} P_s(t) \int_0^l dz\, e^{i\Delta\vec{k}\cdot z}$$

$$= \frac{2\pi i}{n(\omega_s)} \frac{\omega_s}{c} P_s(t)\, l\, \frac{\sin\left(\frac{\Delta k l}{2}\right)}{\left(\frac{\Delta k l}{2}\right)} e^{i\frac{\Delta k l}{2}} \qquad (33)$$

For the intensity of the signal

$$\boxed{I_s(t) = \frac{n_s c}{8\pi} |E_s|^2 = \frac{\pi}{2 n_s} \frac{\omega_s^2}{c} l^2 |P_s(t)|^2 \frac{\sin^2\left(\frac{\Delta k l}{2}\right)}{\left(\frac{\Delta k l}{2}\right)^2}} \qquad (34)$$

Function $\frac{\sin x}{x}$ looks like this



for $l \to \infty$ $\quad \frac{\sin \frac{\Delta k l}{2}}{\left(\frac{\Delta k l}{2}\right)} \to (2\pi)^3 \delta(\Delta k l)$

it is non-zero only for $\Delta k \equiv 0$

Heterodyne detection of signals

One can detect signal directly

$$\underset{E_s(t)}{\rightsquigarrow} \; D_{\text{detector}} \quad \Rightarrow \quad I_s(t) = \frac{n(\omega_s)c}{8\pi} |E_s(t)|^2 \qquad (35)$$

or we can „mix" it with another field usually termed

<u>local oscillator</u> $E_{LO}(t)$.

The total detected intensity is

$$I_T(t) = \frac{n(\omega_s)c}{8\pi} |E_s(t) + E_{LO}(t)|^2 =$$

$$= I_{LO}(t) + I_s(t) + \underbrace{2\frac{n(\omega_s)c}{8\pi} Re\left[E_{LO}^*(t)E_s(t)\right]}_{I_{HET}(t)} \qquad (36)$$

usually $I_{LO}(t) \gg I_s(t)$ $\Rightarrow$ also

$I_{HET}(t) \gg I_s(t)$

$$\boxed{I_{HET}(t) = \frac{n(\omega_s)c}{4\pi} Re\left[E_{LO}^*(t)E_s(t)\right]} \qquad (37)$$

! $I_{HET}(t)$ is linear in $E_s(t)$ and allows easier detection of weak fields

! The detection is phase sensitive, leads to a complete characterization of $E_s(t)$ if $E_{LO}(t)$ is known.

Using Eq. (33) in a simplified form

$$E_S(t) \approx i\omega_S P_S(t)\, l$$

we get

$$\boxed{I_{HET}(t) = \frac{n(\omega_S)c}{4\pi} \mathrm{Re}\left[E_{LO}^{*}(t) E_S(t)\right] \approx -\omega_S l\, \mathrm{Im}\left[E_{LO}^{*}(t) P_S(t)\right]} \tag{38}$$

<u>Absorption of a weak probe</u>

We consider a pump-probe experiment, where pump induces certain dynamics – i.e. $\hat{\rho}(t) \neq$ const. and the ~~pump~~ probe puls gets absorped.

One can look at the problem from both the matter and field perspective – what <u>energy gets added to the matter</u> or what <u>energy gets lost by the field</u>

Matter:

$$\text{Energy} = \langle W(t) \rangle \equiv \mathrm{Tr}\left\{\left(\hat{H}_S + \hat{H}_{SC}(t)\right)\hat{\rho}(t)\right\}$$

$$\frac{\partial}{\partial t}\langle W(t)\rangle = \mathrm{Tr}\left\{\left(\frac{\partial}{\partial t}\hat{H}_{SC}(t)\right)\hat{\rho}(t) + \left(\hat{H}_S + \hat{H}_{SC}(t)\right)\frac{\partial}{\partial t}\hat{\rho}(t)\right\}$$

$$\frac{\partial}{\partial t}\hat{\rho}(t) = -\frac{i}{\hbar}\left[\hat{H}_S + \hat{H}_{SC}(t), \hat{\rho}(t)\right]$$

$$\Rightarrow \frac{\partial}{\partial t}\langle W(t)\rangle = \mathrm{Tr}\left\{\left(\frac{\partial}{\partial t}\hat{H}_{sc}(t)\right)\hat{\rho}(t)\right\}$$

$$+\left(-\frac{i}{\hbar}\right)\mathrm{Tr}\left\{\hat{H}(t)\,\hat{H}(t)\hat{\rho}(t) - \hat{H}(t)\hat{\rho}(t)\,\hat{H}(t)\right\}$$

We ~~remaind~~ remind ourselfs that $\mathrm{Tr}\{\hat{A}\hat{B}\hat{C}\} = \mathrm{Tr}\{\hat{C}\hat{A}\hat{B}\} = \mathrm{Tr}\{\hat{B}\hat{C}\hat{A}\}$

and consequently the last term $\equiv 0$

Therefore the change in energy is

$$\boxed{\frac{\partial}{\partial t}\langle W(t)\rangle = \mathrm{Tr}\left\{\left(\frac{\partial}{\partial t}\hat{H}_{sc}(t)\right)\hat{\rho}(t)\right\}} \qquad (39)$$

at this point we have to specify the form of $\hat{H}_{sc}(t)$

The general derivation is difficult, ~~and~~ leads to an expression

$$\boxed{\hat{H}_{sc}(t) = -\int d\vec{r}\ \underbrace{\vec{P}(\vec{r})}_{\text{polarization density}}\cdot\vec{E}(\vec{r},t)} \qquad (40)$$

$\leftarrow$ energy density (we integrate to get energy)

This leads to

$$\boxed{\frac{\partial}{\partial t}\langle W(t)\rangle = -\int d\vec{r}\left(\frac{\partial}{\partial t}\vec{E}(\vec{r},t)\right)\underbrace{\mathrm{Tr}\left\{\vec{P}(\vec{r})\hat{\rho}(t)\right\}}_{\vec{P}(\vec{r},t)}} \qquad (41)$$

Let us assume the probe field with a given frequency ω and a slowly varying envelope

$$\vec{E}(\vec{r},t) = \vec{E}(t)\, e^{-i\omega t + i\vec{\xi}\cdot\vec{r}} + \vec{E}^{*}(t)\, e^{i\omega t - i\vec{\xi}\cdot\vec{r}}$$

$$\frac{\partial}{\partial t}\vec{E}(\vec{r},t) = \frac{\partial}{\partial t}\vec{E}(t)\, e^{-i\omega t + i\vec{\xi}\cdot\vec{r}} - i\omega \vec{E}(t)\, e^{-i\omega t + i\vec{\xi}\cdot\vec{r}}$$

$$+ \text{c.c.}$$

slowly varying condition

$$\left|\frac{\partial}{\partial t}\vec{E}(t)\right| \ll \left|\omega \vec{E}(t)\right| \Rightarrow$$

$\Rightarrow$ $\qquad a+ib - (a-ib) = 2ib$

$$\frac{\partial}{\partial t}\vec{E}(\vec{r},t) = -i\omega\left[\vec{E}(t)\, e^{i\vec{\xi}\cdot\vec{r} - i\omega t} - \vec{E}^{*}(t)\, e^{-i\vec{\xi}\cdot\vec{r} + i\omega t}\right] \qquad (42)$$

$$= -(i)^2\omega\, 2\,\mathrm{Im}\left[\vec{E}(t)\, e^{i\vec{\xi}\cdot\vec{r} - i\omega t}\right]$$

What about polarization?

$$\vec{P}(\vec{r},t) = P_s(t)\, e^{i\vec{\xi}_s\cdot\vec{r} - i\omega_s t} + \text{c.c.}$$

The very same arguments and the same slow varying approximation $\rightarrow$ we obtain

$$\frac{\partial}{\partial t}\langle W(t)\rangle = -i\omega\left[\vec{E}(t)\, e^{i(\vec{\xi}+\vec{\xi}_s)\cdot\vec{r} - i(\omega+\omega_s)t} P_s(t)\right.$$

$$+ \vec{E}^{*}(t) P_s^{*}(t)\, e^{-i(\vec{\xi}+\vec{\xi}_s)\vec{r} + i(\omega+\omega_s)t}$$

$$+$$

$$+ E^*(t) P_s(t)\, e^{i(\vec{k}-\vec{k}_s)\vec{r} - i(\omega-\omega_s)t}$$

$$+ E(t) P_s^*(t)\, e^{-i(\vec{k}-\vec{k}_s)\vec{r} + i(\omega-\omega_s)t} \Big] \qquad (43)$$

To get the total energy loss we have to integrate over space and average over optical period. In such a averaging both terms with $\omega+\omega_s$ and $\vec{k}+\vec{k}_s$ vanish, and the terms with $\omega-\omega_s$ and $\vec{k}-\vec{k}_s$ give non-zero if $\omega \equiv \omega_s$ and $\vec{k}=\vec{k}_s$. The gained energy is

$$S_A(\omega, t) = 2\omega\, \mathrm{Im}\left[E^*(t) P_s(t) \right] \qquad (44)$$

This can be rewritten as

$$S_A(\omega, t) = 2\omega\, \mathrm{Im}\left[E(t)E^*(t)\; P_s(t) \,/\, E(t) \right] =$$

$$= 2\omega\, |E(t)|^2\, \mathrm{Im}\left[P_s(t)/E(t) \right] \qquad (45)$$

We now integrate over all times (over the duration of the ~~probe~~ puls - at least), and devide by the incoming energy

$$I = \frac{c\, n(\omega)}{2\pi} \int_{-\infty}^{\infty} dt\, |E(t)|^2$$

$$\overset{?}{\;} |E(\vec{r}, t)|^2 = | E(t)\, e^{i\vec{k}\cdot\vec{r} - i\omega t} + E^* \dots |^2 = \underbrace{2E(t)E^*(t)}_{=2|E(t)|^2} + E(t)E(t)\, e^{2i\vec{k}\cdot\vec{r} - 2i\omega t} + E^*(t)E^*(t)\, e^{-i2\vec{k}\cdot\vec{r} + i2\omega t}$$

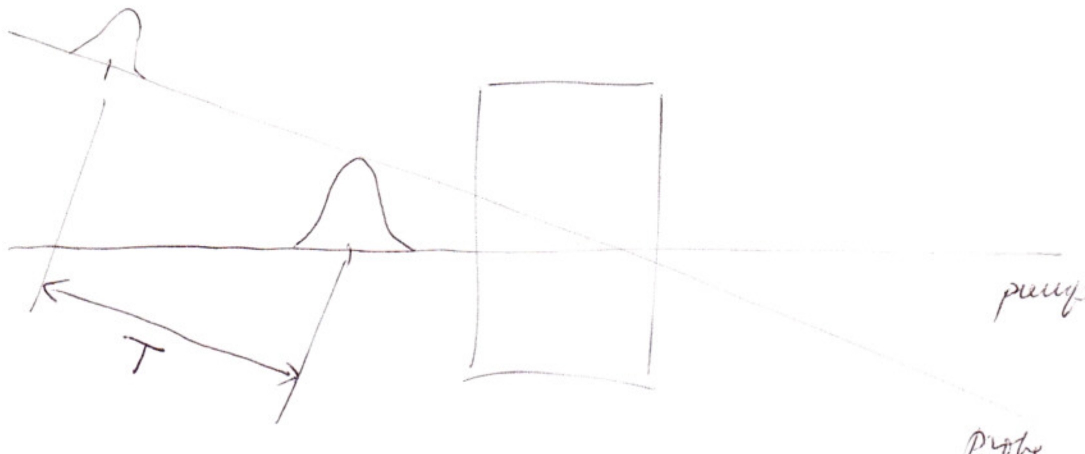
$$I(\vec{r}, t) = \frac{cn}{4\pi} |E(\vec{r}, t)|^2 = \frac{cn}{4\pi} |B(\vec{r}, t)|^2$$

Finaly, absorption signal ⟹

$$S_A(\omega) = \frac{4\pi\omega}{c\,n(\omega)}\, \mathrm{Im} \int_{-\infty}^{\infty} dt\, E^*(t) P_s(t) \Big/ \int_{-\infty}^{\infty} dt\, |E(t)|^2 \qquad (46)$$

There is now time, here, but we claimed that such ~~integrated (~~ pump-probe spectrum is time dependent. Where is that time?

! The time t concerns the time running during the experiment, the "absolute" time, but $P_s(t)$ depends on another time parameter T, the delay between the pulses



The correct expression would read

$$\boxed{S_A(\omega, T) = \frac{4\pi\omega}{c\,n(\omega)}\, \mathrm{Im} \int_{-\infty}^{\infty} dt\, E^*(t) P_s(t, T) \Big/ \int_{-\infty}^{\infty} dt\, |E(t)|^2} \qquad (47)$$

Looking at the problem from the field perspective leads to the same result – everything is consistent.

Two points towards interpretation of the result

1) S_A is proportional $Im\left[E^*(t)P_S(t)\right]$ which reminds very much of the heterodyne detection. The pump-probe signal can be interpreted as „self-heterodyned" measurement. No extra local oscillator is provided, but the signal mixes with the incoming field.

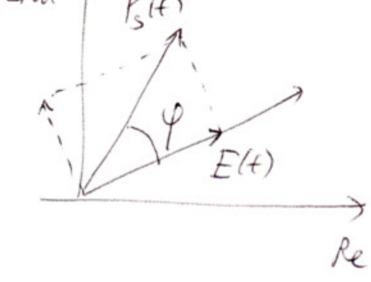
2) Let us assume

$$E(t) = E_0(t)e^{i\omega t} + E_0(t)e^{-i\omega t} \qquad (48)$$

i.e. we assume a real envelop

$$P_S(t) = P_0(t)e^{i\varphi}e^{i\omega t} + P_0(t)e^{-i\varphi}e^{-i\omega t} \qquad (49)$$

where $P_0(t)$ is real again



We split $P_S(t)$ into an in-phase and out-of-phase components

In-phase $P_0(t)\cos\varphi$

Out-of-phase $P_0(t)\sin\varphi$

$$P_S(t) = 2P_0(t)\cos\varphi\cos\omega t - 2P_0(t)\sin\varphi\sin\omega t \qquad (50)$$

Inserting Eq (49) into the definition of $S_A(\omega)$ we get

$$S_A(\omega) \approx \mathrm{Im}\int_{-\infty}^{\infty} dt\, E_0(t)\, P_0(t)\, e^{i\varphi} =$$

$$= \mathrm{Im}\int_{-\infty}^{\infty} dt\, E_0(t)\, P_0(t)\, (\cos\varphi + i\sin\varphi)$$

$$= \int_{-\infty}^{\infty} dt\, E_0(t)\, P_0(t) \sin\varphi \qquad (51)$$

Pump-probe signal is related to the out-of-phase part of the polarization.

↑ This will be important when interpreting multi-dimentional spectra.

The pump-probe signal can be also measured frequency dependent, so that

$$S_A(\omega) = \int_{-\infty}^{\infty} d\omega'\, \underbrace{S_{disp}}_{\text{dispersed}}(\omega') \qquad (52)$$

and

$$\boxed{S_{disp}(\omega') = \frac{4\pi\omega\; \mathrm{Im}\, E^*(\omega')\, P_s(\omega')}{c\, n(\omega) \int d\omega' |E_j(\omega)|^2}} \qquad (53)$$

To show that it is the same thing we need to proof that

$$\int d\omega\, \mathrm{Im}[E^*(\omega) P(\omega)] = \int dt\, \mathrm{Im}[E^*(t) P(t)]$$

$$\parallel$$

$$\int d\omega \frac{1}{2\pi} \mathrm{Im} \int dt'\, E^*(t') e^{-i\omega t'} \int dt''\, P(t'') e^{i\omega t''} = \mathrm{Im}\int dt' \int dt''\, E^*(t') P(t'') \frac{1}{2\pi}\int d\omega\, e^{i\omega(t''-t')}$$

$$= \int dt' \int dt''\, \mathrm{Im}\, E^*(t') P(t'')\, \delta(t'-t'') = \int dt'\, \mathrm{Im}[E^*(t') P(t')] \quad \text{QED}$$

Summary

In all cases it is polarization density $P(t)$ or its Fourier transfor that needs to be calculated in order to calculate spectra. For linear absorption, we transformed the problem of calculating $P^{(1)}(t)$ into calculating $S^{(1)}(t)$ or $\chi^{(1)}(t)$. Similarly, our next attemped will be to continue such a program with higher order spectroscopies.