Ultrafast Processes in Chemistry
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Module No # 08
Lecture No # 37
Brief Overview of Nonlinear Optical Phenomena

Now we start next part of our discussion and what we want to talk about really is we have been using and we have demonstrated when we went to the lab and we talk about it we have been using nonlinear optics quite a bit. In the last module we have talked about your amplified laser the laser that we have the next step is the optical parametric amplifier. Now in order to understand optical parametric amplification first of all we need to build little bit of basics of nonlinear optics and as has been the central theme of this course we are not going to try to derive everything perhaps but we will try to understand how things work?

So what we learnt today is this when we showed this femtosecond optical getting experiment we have shown that red light comes falls on non-linear crystal and then when we turned the crystal by using a micrometer screw we see that second harmonic is generated to a greater extent. So today in this module we are going to learn why that happens why is it that you turn the angle of a crystal and you get good second harmonic while you do not get it earlier to do that we have to I am sure many of us know already about nonlinear optical phenomena. So we will discuss the basics and let us see how far we can get.

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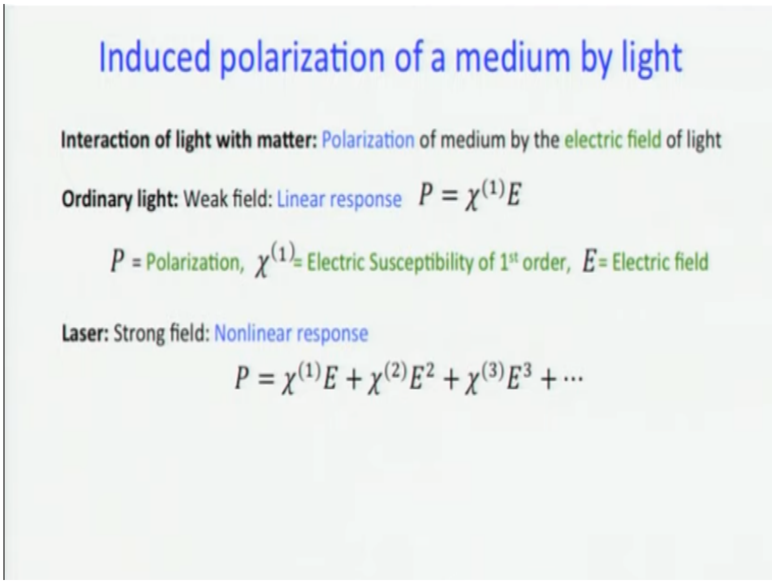

Induced polarization of a medium by light

Interaction of light with matter: Polarization of medium by the electric field of light

Ordinary light: Weak field: Linear response $P = \chi^{(1)}E$

P = Polarization, $\chi^{(1)}$= Electric Susceptibility of 1st order, E= Electric field

Laser: Strong field: Nonlinear response

$$P = \chi^{(1)}E + \chi^{(2)}E^2 + \chi^{(3)}E^3 + \cdots$$

So first of all we have talked about this earlier and I am sure everybody as learnt this in other courses the model of interaction of light with matter is that light induces a polarization in the medium electric the electric field component of light induces the dipole moment electrical dipole moment and that is what interacts with the electric field to give you the radiation matter interaction which is what we are talking about forth. Now if we have ordinary light then you have linear response meaning the polarization is directly proportional to the amplitude of the electric field E.

So you can write it very simplistic manner as P = Chi first order that 1 in superscript in bracket means first order it is not Chi to the power 1 it is not Chi 1 it is Chi first order. So P = Chi first order E now P is polarization first order Chi is electric susceptibility of first order and E is the amplitude of the electric field. But then there is actually more to this then what we have written can someone tell me what more is there what is it that we are actually hiding in this simplistic expression no that even before going to square cube term even in linear response.

Suppose the response is linear I am saying even then in that case this equation that we have written is a tad 2 simplistic this situation is more complicated than that okay hint Raman spectroscopy you learnt in Raman spectroscopy yes not dipole moment susceptibility so let us say alpha lot of Chi first order I will write alpha polarizorabilty let us say. If I write polarizability is that ring a bell. Think of what you learnt in Raman's spectroscopy this expression is actually more complicated then what it is?

Okay electric field is it a scalar or a vector? The vector field right whatever polarization scalar or vector yes so now Prajith as remembered the thing is this it is not necessary that if apply an electric field along x direction polarization will be along with x direction only electric field along x direction can produce polarization in other direction as well. So if you write P the component of P Px, Py,Pz let us say write it as column vector column matrix that will be equal to column matrix Ex, Ey, Ez left multiplied by A square matrix right and the component will be something like alpha xx, alpha xy, alpha xz so on and so forth why is it?

That if I apply electric field along a particular direction polarization produced in other direction as well yes I am applying in one direction. So to answer this question the easiest approach is to think like a baby like a kid think of simple analogies it is easier to understand that way. Okay what is the meaning of polarization? Production of dipole moment what is actually happening to the molecule electron right? So electron is it particle wave or what right? So electron cloud and the electron cloud is distributed all over the molecule.

So when you polarize what you do essentially is that you distort the electron cloud is that right so let us say we have spherical electron cloud over the molecule you distort is so that on in one direction the concentration of electron cloud is more in the other direction it is less okay. I like to think of it as a balloon is a entire electron cloud is like the air contain inside a balloon. Now think of holding a balloon and pressing like this well you can pull also but then it is easier to press so this is the field you are applying and the balloon will get depressed in this direction but is it not elongated in the perpendicular direction x and y?

So that is a rough analogy that explains why that when you apply an electric field in a particular direction distortion takes place not only in that direction but also in perpendicular directions all directions that is why it is actually a tensor. For our purpose for now it is okay if you write like this right next we come to what souradip was saying? This expression that we have written in simple form of; or in matrix form this is valid when we have ordinary light.

Light coming out from the electric bulb whether field is weak what happens when you use a laser? A laser is associated with significantly higher electric field right then the response is no longer linear then you have something like this your non-linear response P = Chi first order E + Chi second order E square + Chi third order E cube so on and so forth. The reason why you see this for high values of E and not for low values of E is that first order Chi is much larger usually than second Chi if it is provided this second order Chi is non-zero will come to that.

Second order Chi is generally much larger than third order Chi and so on and so forth so that is why unless this E square term or in some cases E cube term can take over unless the value of E is sufficiently large you do not see the higher order terms okay but when you deal with lasers you can get at least the second order term. Sometimes you can get the third order or forth order term as well. We will see what are the conditions that are required for this higher order terms to be involved okay.

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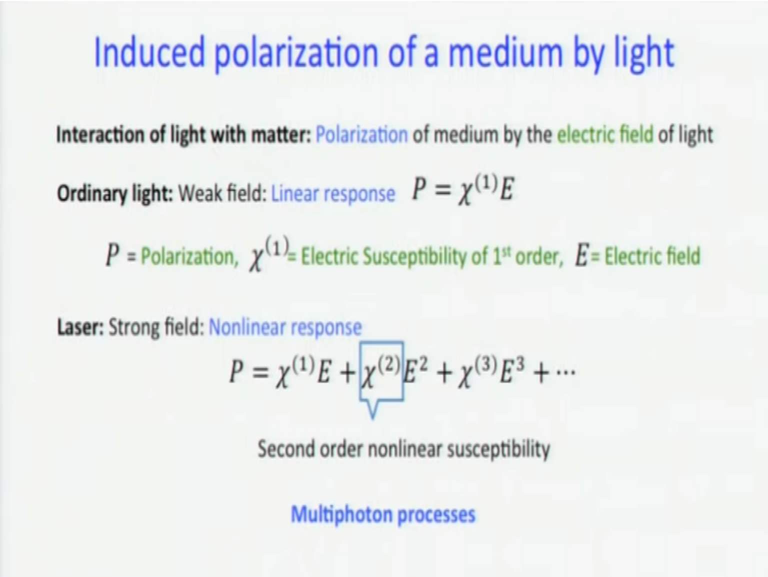

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Second order nonlinear susceptibility

Multiphoton processes

For now let us focus on the second order Chi it is called the second order non-linear susceptibility okay. So this is the beginning of our discussion of multi photon processes 2 photon process of course is the simplest multi photon process one can think of and the second order non-linear susceptibility is responsible for bringing about 2 photon processes. So once again let us remind ourselves of what 2 photon processes are?

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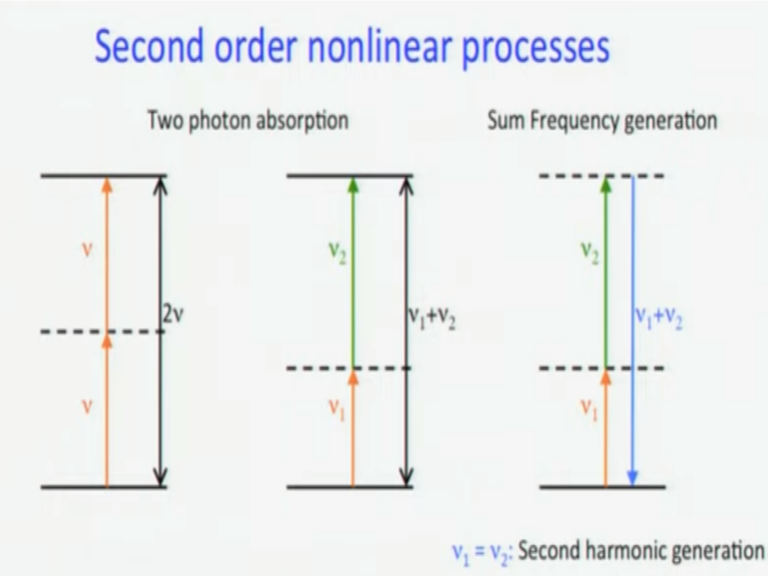
Second order nonlinear processes

Two photon absorption

Sum Frequency generation

$\nu_1 = \nu_2$: Second harmonic generation

So whatever we are discussing now I believe is known to all of us it is just a recapitulation what is the meaning of 2 photon absorption? Let us say we have these 2 energy levels separated by an energy equivalent to frequency of 2 Nu or Nu 1 + Nu 2 depending on whatever we are going to write. So to start with let us say the energy gap is equivalent to frequency of 2 Nu and let us say I excite with laser pulse of or not necessarily pulse laser light of frequency Nu what will happen?

The photon does not have enough energy to cause a transition to the next available stationary state right? But once again cutting a lot of mathematics out and using a little bit of childish analogy the molecule does not know right the molecule does not really the molecule has not studied quantum mechanics so it does not know when the light comes it is not supposed to absorb it.

So what happens is the distortion of the electron cloud starts anyway and then it reaches a virtual stage what is a virtual state? What is the stationary state? What is a virtual state? What is a stationary state? CH107 stationary state is a state in whose energy or whose psi psi star we can say is independent of time okay. So these are states associated with finite life time your molecule can stay there for sometime.

And virtual states are anything in between you can have infinite number of virtual states between any 2 stationary states and the way you generate this virtual states is by taking linear combination of stationary states and the point you remember is that virtual states are associated with lifetime of 0. The molecule cannot stay in the virtual state for any amount of time so the moment it is there it is going to come down. So if your intensity of light is not too much then you will not see any absorption.

You can think like this the electron clouds starts getting distorted this is the shape of electron cloud in the ground state this is the shape in the excited state the starts getting distorted runs out of gas midway and it comes back. However if you use intense laser light then what happens is at the same moment when the molecule or well the let us say the system is promoted to the virtual state there are many other photons around.

So a second photon can cause promotion to a second to this stationary state and if you carefully choose the frequency of this photon you use so that their energy is exactly half of the energy gap between 2 stationary states then you can have what is called 2 photon absorption okay. So this is the very simplistic hand waving way of saying what 2 photon absorption is? And the case we have discussed is the simpler of 2 cases of 2 photon absorption where it is at both the photons are in color same energy same frequency degenerate two photon absorption.

That need not be the case always sometimes what happens is that the energy gap might be equal to the sum of the frequencies of 2 different kinds of photons that you have at your disposal. In that case first photon let us say Nu 1 takes the system to the virtual level and at that instant the large concentration of Nu2 photons are available the molecule is promoted to this next stationary state. Of course all this is just visual thinking we are writing like this to understand.

There is no reason why Nu2 will not be absorb fast we do not know actually which have been absorbed first the other analogy I like is that it is sort of like 2 water droplets joining up together at forming a larger droplets. So, 2 energies of 2 photons are sort of getting added up to give you the promotion that you require okay. So much for 2 photon absorption but then when the absorption, when absorption takes place the energy of the system goes up.

So anything as goes up as to come down, so let us talk about some frequency generation or in some cases 2 photon excited fluorescence's. Let us take the second case where the energy gap is equal to Nu1 + Nu2 non degenerative 2 photon absorption. Now and let us say that the energies of Nu1 and Nu2 are such that Nu1 + Nu2 is not equivalent to any energy gap between 2 stationaries states in that case even after Nu2 is absorbed the system is going to reach some virtual state right.

What is the lifetime of the virtual state? 0 so the moment is reached that virtual state it cannot stay there immediately it has to come down and it comes down with emission of the light that is absorbed. But then there is no memory the system does not remember that I had absorbed Nu1 first and Nu2 second or the other way around. There is no memory so when the emission takes place the emission is of a single photon of frequency Nu1 plus Nu2.

This is how some frequency generation can take place now think of a case where this higher energy state is not a virtual state but rather a stationary state then what will happen? Stationary state is it associated with non-zero lifetime or is a life time 0 generally life time is not 0. So when the molecule gets excited to a stationary state and then the emission takes place from there what is it called? Fluorescence in the simplistic scenario same spin multiplicity so this is something that is used especially in microscopy where you excite where you do a 2 photon excitation and you look at the fluorescence's the problem is this.

Let us say I want to look at some protein under a microscope what are the fluorophores in protein? Generally Tryptophan is the major one anything else Tyrosine anything else phenylalanine this is something that is perhaps the least popular there is a school that as try to promote Tyrosine as a good fluorescence probe and all but generally people followed triptophan emission okay. If I want to follow triptophan emission where do I excite 295 but triptophan absorption maximum is 289 nanometer why do I excite at 295 nanometer?

So as to avoid exciting phenylalanine and Tyrosin okay so that is just a recap not really anything to do with the present discussion. Now the problem is this I want to look at a protein that is inside a cell under a microscope and I want to follow it by triptophan emission then I have to excite by 295 nanometer light 2 issues there. First of all unless you buy a significantly more expensive UV microscope regular microscope optics are all glass.

So 295 light would not even get through secondly even if you use a UV microscope you are looking at cells which is a turbid medium they are going to scatter light scattering efficiency how does it fall off with lambda to the power what? Lambda to the power 4 so these are things we cannot forget we have to remember. So UV light is scattered big time you would not see anything so it is much better in that case to not use 295 nanometer light but rather use some laser which gives you 295 into 2 how much is 295 into 2?

300 into 2 is easier 600. 600 – 10 590 so 590 nanometer laser if you can use intense 590 nanometer laser then you can have 2 photon absorption to a stationary state right and then you can look at the emission of the photon provided that emission is not scattered provided that emission I mean provided your optics that can look at the emission that is a different issues 2 photon excited fluorescence is very popular in biological systems because the problem is this if you use wave length that it is too short that is get scattered.

If you use wavelength that is too long it is absorbed by water so typically when wants to microscopy one wants to work in the therapeutic range of 650 nanometer to 900 nanometer. But then if you excite at 700 nanometer where it will emit it will emit beyond 900. 2 photon excitation followed by fluorescence's is a very popular technique especially in microscopy okay. But here coming back to our present discussion what we have seen here is how you can get sum frequency generation.

So in sum frequency generation there is no delay light is absorbed instantaneously light comes out instantaneously you do not have to wait any time. So if Nu1 + Nu2 is the case we call it some frequency generation and in the special case where Nu1 and Nu2 are equal to each other then we get second harmonic generation that is what we do in inside our millennia laser that is what we do in the fog instrument and in any other place okay. So now with that simplistic background build let us go a little further into understanding second order non-linear phenomena okay.

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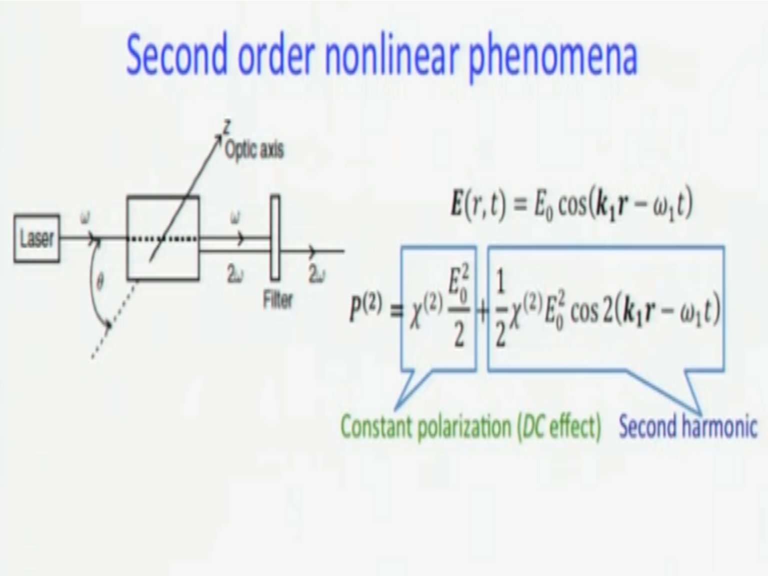

Second order nonlinear phenomena

$$\mathbf{E}(r,t) = E_0\cos(\mathbf{k}_1\mathbf{r} - \omega_1 t)$$

$$P^{(2)} = \boxed{\chi^{(2)}\frac{E_0^2}{2}} + \boxed{\frac{1}{2}\chi^{(2)}E_0^2\cos 2(\mathbf{k}_1\mathbf{r} - \omega_1 t)}$$

Constant polarization (DC effect) Second harmonic

So once again we are following this or usual text book Helena now think of what you have in the entrance side of the fog spectrometer we have light from a laser here we have written with frequency of omega it falls on some non-linear crystal will talk about what optic is in a little while and then you get omega and 2 omega out and then you use a long pass filter to get 2 omega out and block omega or do something in our case what we do is we transmit omega and reflect 2 omega fine what you have to use is the dichroic.

Here once again we proceed in the simple with the simple description of the system electric field of light is a function of position as well as time that r we have written anything that is written bold is actually a vector electric field is a function of position and time. And it is given by E0 multiplied by Cos of k1r - omega 1 t what is omega 1? There is no need to write omega 1 here actually I could have written omega but later on I have talked about omega 2 and all that is why here omega 1 is there.

What is omega? The answer is there in the projection omega is the angular frequency of light incident light okay what will be angular frequency of the second harmonic? 2 omega remember okay. What is r? R is in bold so it is a vector what is that r? There are very few things for which we use r and vector at that what is r? Okay I will just tell you what do you r for? Distance right an r vector does that ring the bell distance from where is the position vector distance from origin.

You have some point xyz you draw an arrow from the origin to that point that arrow denotes the position vector r is that same position vector nothing else. What is k1? k1 once again is the vector it is called the k vector is there another name that you know? Wave vector so what is k that is something that we should say and then we can stop this module and then go to the next one we will come back to that. But first of all suppose this is E and for this expression of E I want to write the expression for this second order polarization what will it be?

Just a second order term not the first order remember what it was? P = Chi first order multiplied by E by Chi + Chi second order multiplied by E square. So what will be the second order term for polarization? Chi second order multiplied by well E square what is E square here? E = E0 Cos k1r – omega t omega 1t so what is E square? E0 square that is the good beginning then Cos square k1r – omega1t is very simple so as I have said many times many different fluoride never asked difficult questions Cos square term but now I want to ask you question let us see if you remember our higher secondary trigonometry how do we write Cos square theta?

Cos square theta is equal to well in terms of Cos since your writing Cos will stick to Cos 1 + Cos 2 theta divided by 2 right 1 + Cos 2 theta divided by 2 what is theta here? k1r – omega 1t right so can you work out the expression? E0 square do it in terms of theta E0 square Cos square theta what does it become in terms of Cos 2 theta E0 Square Cos square theta if I want to write it in terms of Cos of 2 theta Cosine of 2 theta what do I get? E0 square by 2 + you taken 2 common + there is a half as well and do not forget second order Chi I might have forgotten to say it okay.

So well okay that will come later fine E0 square / 2 + Cos 2 theta divided by 2 okay that is E square now to get second order term for polarization this term as to be multiplied this factor as to be multiplied by second order Chi second order susceptibility so this is the answer second order term for polarization is given by second order non-linear susceptibility multiplied by E0 square /2 + half second order non-linear susceptibility multiplied by E0 square Cos 2 theta were theta is k1r – omega t okay.

What is the frequency of this associated with the second term? What is the frequency angular frequency associated with this second term this one? 2 omega 1 that is right. So look at the first term the first term is a constant polarization is not it there is nothing in t there it is just second order non-linear susceptibility multiplied by E0 square / 2 E0 is constant of time constant of space constant of everything right.

So this is called constant polarization or DC effect this part is used to measure the power second one is actually the second harmonic term there you have A polarization that is modulated by a frequency of 2 omega 1. So this is the term that is responsible for second harmonic generation okay then we take a break here and in the next module we start right here.