Biophotonics
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Module 05: LASERs for Biophotonics
Lecture 23: Non-Linear Optical Process

Welcome, we will continue our discussion on various topics of biophotonics, and as per the module number five here.

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We are discussing lasers for biophotonics and you can see my pointer therefore is also the laser pointer, and today we are going to discuss a very interesting but bizarre and truly in the sense weird topic of nonlinear optical processes. Let us discuss what this non-linearity is and how does this help us or this pertains to the domain of biophotonics per se.

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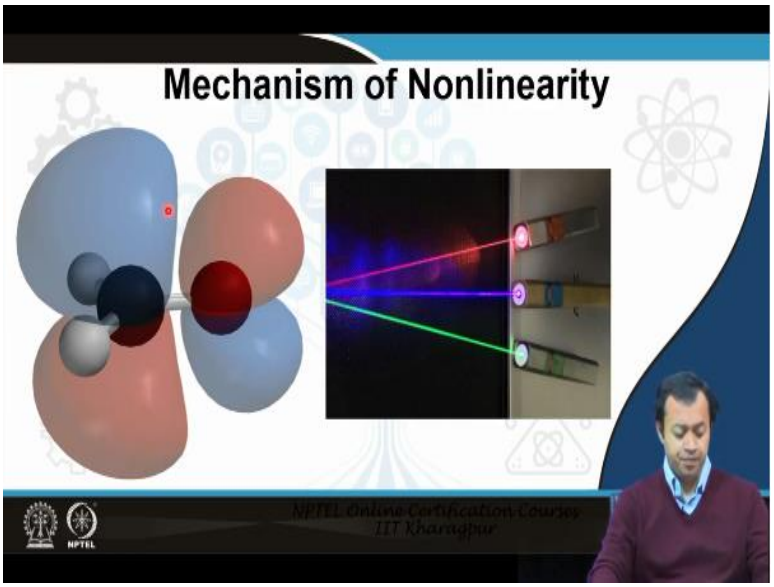

Let us continue, so as we all know that conjugate molecules, bio molecules or molecules which make biological matter are quite complicated in nature, conjugated molecules are quite complicated and they have this non-homogeneous or rather heterogeneous division or heterogeneous distribution of enveloped electronic cloud around it.

The conjugate molecules, the bio molecules are made up of a plethora of different elements, substantial number of them being carbon, hydrogen, oxygen and nitrogen that is the organic compounds, but as we have seen in case of proteins like hemoglobin or similar things other higher atomic number elements can also come in for example, hemoglobin contains iron, hemoglobin may contain iron.

Therefore, the distribution of the electron clouds, so these are the schematic representation of one such conjugated molecule and these are the distribution of the electron clouds. They around it forms a non-homogeneous, non-homogeneous, non-uniform rather heterogeneous cloud, heterogeneous distribution of electrons.

Heterogeneous distribution of electron clouds around the system, around the entire molecule and then you know that these molecules go on being attached with other molecules by non-covalent weak forces such as hydrogen bonds and van der Waals. So, throughout the system, throughout the biological matter, throughout that biological

material, there is a, I cannot state that enough, there is a non-uniform distribution of electron cloud.

Now, when we subject this electron cloud, this uneven, un-uniform heterogeneous weird in that sense, electron cloud to something as intense as a laser light, as intense as a laser light, this is obviously not to scale, these are laser lights and this is much larger in size, but you use your imagination, this will be several thousand million times smaller this entire size and this will be larger.

But nevertheless, if we subject these electron clouds, which are surrounding the molecule to intense laser beams, intense laser light with specific frequency, specific phases, specific energy values, we see somewhat of a redistribution of the electron cloud around the overall molecule.

Now, let me repeat it, first, the electron cloud is uneven, the electron cloud is heterogeneous, and then we are subjecting it to intense optical light sources, i:e laser beams, which has intense coherence, intense intensity, intense energy, phase, velocity all of those things are there, and they upon subjecting to this kind of a complicated and uneven electron cloud further modifies or further bizarrely, further un-uniformly or I would use the term here nonlinearly distribute the electron cloud in to the system.

I told you what does linearity versus non-linearity means. Linearity is direct, X is directly proportional to Y or X is indirectly proportional to Y, so you have a very, very simple relationship between input and output. Non-linearity on the other hand is a very complicated relationship where there is no direct such thing, there is no direct relationship between input and output.

So, we understand that the presence of the laser beam over all redirects or redistributes or remodifies this already existing uneven electron cloud, but there is not a very simple relationship, there is not a very direct relationship between one with respect to other. The overall mechanism what happens because of this intense light beam working on top of electron clouds, the redistribution of electron cloud results in setting up of virtual energy state or virtual quantum states.

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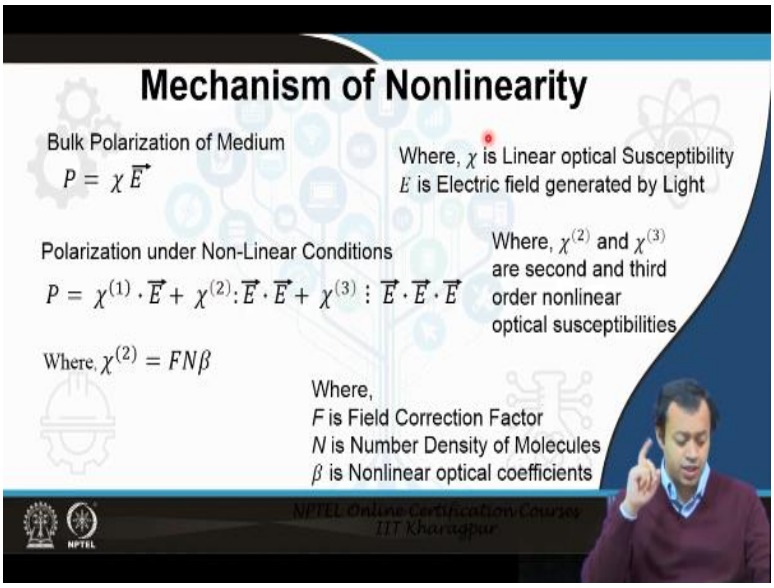

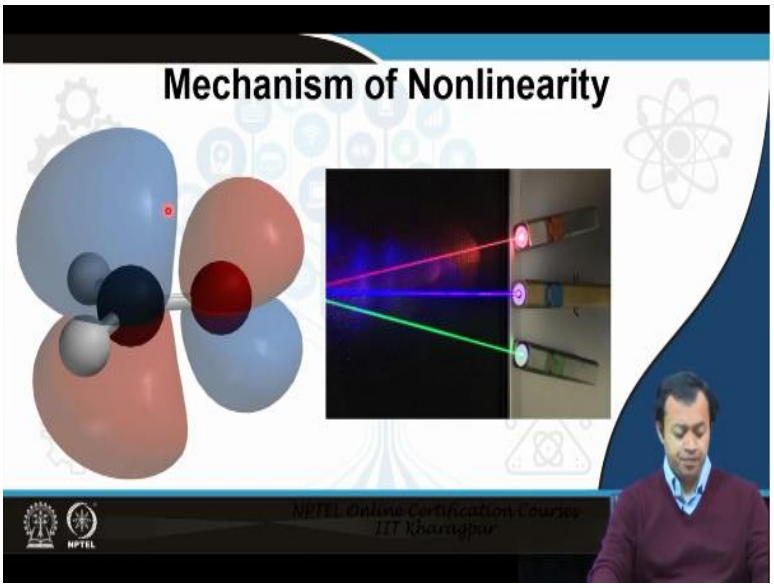

What are they us ask, wait I will let you know. So, what exactly is mechanism of nonlinearity? So, in bulk polarization medium a normal material, you have the polarization given by this particular formula, the polarization of the material distribution or susceptibility or how the material will change, will modify in the presence of a strong electric field is given by this particular formula where X.

Well chi actually is the linear optical susceptibility, susceptible I have used the term susceptible, medical doctors use the term susceptible, some people are more susceptible

to dangerous diseases, than are some people are more susceptible to bad advice and susceptible is someone who are, how to say, quickly comes under the influence, quickly comes under the influence.

So, certain materials according to the electric field quickly redistributes its electron, quickly redistribute its electron cloud, and how quickly or the measure of that redistribution is given by chi, we use the term chi as linear optical susceptibility and overall how quickly, how intensely, how much you get a dipole moment forming, how much is your electron getting modified, very easily in a linear moment, in a linear material is given by this thing, where P is the polarization, chi and E are the electric field and chi the linear optical susceptibility.

But when you have a non-uniform material, a non-uniform or something called anisotropic material, especially optically anisotropic material, where there are different, not a uniform distribution. Remember, biological materials are hardly crystalline like your semiconductor structures, we cannot just use this particular formula, but we have to use this particular formula and expand it as a power series where chi 1, chi 2 and chi 3, you can consider them as power.

These things starts coming into effect where chi 2 and chi 3, especially and this goes on forever because it is an infinite series. Although the accessibility of chi 4, chi 5, chi 10, chi 100, chi n becomes more and more weak, but, but, the time, the point that I am making is for a material where the electron distribution is non-uniform in x, y and z direction, we get this formula expanded on to some kind of a power series where chi 2 and chi 3 are coming into effect.

What are chi 2 and chi 3? These are second and third order nonlinear optical susceptibility, these are second and third order, 2 for second and 3 for third nonlinear optical susceptibilities and chi 2 is given by this formula where you can understand or where you can read what the different terms of the formula mean.

Now, what exactly from a point of a layman's terms what exactly does that mean, what exactly does that mean? It means, it simply means that when you have a system such as

this, with a non-uniform distribution of electron cloud, different electron cloud attached to your parent nucleus differently.

Obviously when you have hydrogen, the electron cloud or electron just 1 electron enveloping, it will have a different force of attraction, then when you have an electron clouds enveloping iron and everything in between, I am giving two extreme cases, two extreme cases, one have sigma bonding, one have pi bonding, one half different bonding.

So, there are different forces of attraction between different electrons or different electron clouds subjected to different to their respective parent atom which then form the overall complicated molecular structure, meaning, then we cannot use the original formula P is equal to chi E stating that the distribution of the molecule, distribution of the electron cloud upon application of an electric field is going to be uniform.

The electron cloud around the system is itself at the beginning non-uniform. So when you have a single light coming up, when you have a photon coming up with specific energy, specific electric field, specific magnetic field, the redistribution of the electron cloud is also going to be non-uniform. It started non-uniformly, it is going to be more or at least the chaos or the non-uniformity will increase.

So, the formula will obviously change from a simple formula to a power series, where you start seeing higher order, second or third order susceptible terms, second and third order optical susceptibility chi 2 and chi 3 coming up, where chi 2 is given by this particular formula where F is the field correction factor is determines, filed correction factor simply determines the electric field redistribution, electric fields modification at each single atom or each single molecule per se, depending on the individual electron cloud distribution.

N is the number density of molecules, how many are they and beta is of course, the nonlinear optical coefficient, nonlinear optical coefficient, there are several coefficients coming up, and the beta is different in different direction, beta is different in different conditions etcetera.

Moral of the story is the distribution of the electron is non-uniform in x, y and z direction what we in optics called anisotropy, the electrical property or the optical property in x, y and z direction is also going to be different, I told you that at the end of the day refractive index depends on epsilon and mu, but at the end of the day, both refractive index epsilon and mu were vector quantities.

So, if the electric field is different in different direction because the molecule is arranged differently in different direction, then obviously, when you are subjecting the entire molecule to one set of electric optic field, the distribution is also going to be non-uniform.

Now, that is the closest way in which I can understand, make you understand non-linearity, non-linearity means uneven or nonlinear indirect redistribution of the electron cloud around a molecule which is already started which a non-uniform distribution to begin with, which started with the non-uniform distribution to begin with as the previous structure say.

But then, since it is the technology based course, so what, okay, non-linearity has happened, you have bizarre distribution of the electron clouds around, so what? Well several weird things start happening when you have a nonlinear material, when you have a material which is anisotropic which is complex, which is differently complex in different directions and you are subjecting it to one single type of photon, or one single type of laser light.

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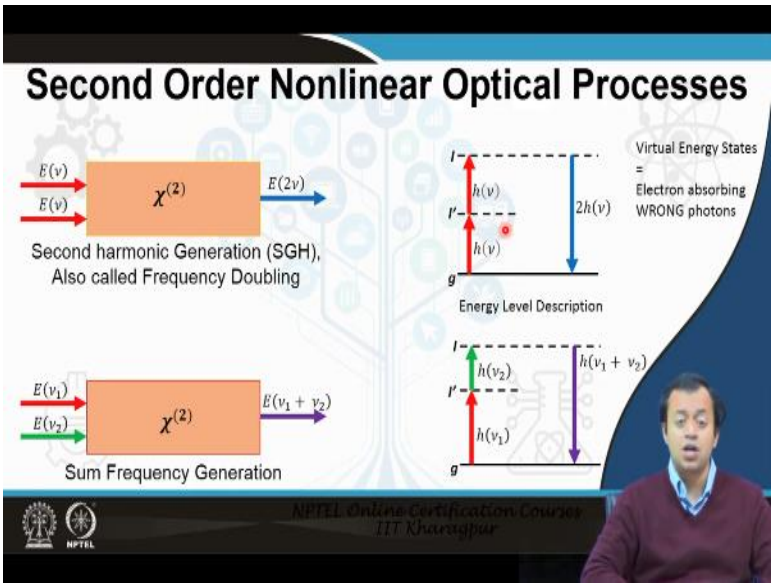

You start seeing this development of second order nonlinear optical processes becoming more and more prominent. The second order nonlinear optical processes, the most famous one of it being the Second Harmonic Generation SGH, in any optical lecture these days you will see people talking about second harmonic generation, second harmonic generation, what does second harmonic generation mean? Second Harmonic Generation distributes the energy level into real and virtual states.

Previously, there were energy levels, lower level, upper level, ground state, higher states and electron absorbs light goes from ground state or goes from lower level to upper level, after some time spontaneous emission returns back, and I have told you that the energy level are quantized, the energy level are quantized.

So this level, this level there is nothing in between, electron cannot exist in between, electronics engineers students knows, electron can only exist in valence band conduction band, no electron, no electron can exist in the bandgap, no electron can exist, this is not a continuous process, these are discrete process.

The very first lecture, E1, E2, E3, E4 there is no such thing as E1.2 or E1.25, well it seems that I have lied to you, because nonlinearity false on its flat, falls on its face and tells you that whatever, that whatever we have sworn or whatever we have, we have said

that this is the whole truth nothing but the truth, turns out to be not that much truth. Yes, I know, I know, welcome to the world of quantum mechanics, where nothing makes sense, where everything you can say certainty becomes uncertain.

Meaning, in nonlinear optical processes, it is quite possible for two photons of same energy, E nu and E nu that is h nu and h nu combining together to form two h nu, I call them the op-amp, the operational amplifier of optics, where one photon goes towards a virtual energy state I-, the another photon goes to another level, this level, this energy level should not exist, this energy level should not exist, there should not be any energy level between two existing real energy state, it should not, it should not, it should not because if it comes it violates the Heisenberg's Uncertainty Principle.

But guess what, it is there and what are you going to do about it? You are or if you think you are confused, trust me, we all are victims of quantum physics, we all are victims of quantum physics, where it does not make sense, you cannot pinpoint why this is happening, no matter what anybody says, and trust me I have to teach this to you, I have to teach this to you, does that make it any easier for me?

Thus far I have told you that electron only will be absorbing a particular frequency of photon and if that frequency matches that of the bandgap it will go upstairs and then after some time etcetera, etcetera you know the whole detail.

But now, I am asking you, now I am telling you that electron can also absorbed, half an energy of that photon or wrong energy of photon and can go only up, where it can create its own virtual energy state, virtual energy state, an imaginary energy state, virtual energy state or virtual the quantum state, what does that mean?

That means, they are unobservable states, we are only able to understand their presence by theoretical and mathematical calculation, our experimental results fail, our experimental results, thus far has failed to observe it, we do not define it by some kind of an Eigen factor, these exists and without bringing them into our equation, we will not be able to demonstrate, or we will not be able to explain what is happening here.

This is an experimental phenomenon, this is an experimental phenomenon-where you have sent two beams of the exact same frequency, same phase, same velocity and you are seeing the output is a combination of nu 1 and nu 2 a combination, this is like your adder in op-amp, this is like your adder in op-amp, if you have nu 1 and nu 2 equal to nu, as in this case, you have 2 nu in the output, that is the second harmonic generation.

You sent two photons of the same frequency, you get the output as a sum, as an addition of these two and how does that happen? We have come to this explanation, we have come to this explanation that the electron, because of the presence of the photon because of the presence of the intense beam of the light, this is the complex material, this is the material, this is the complex conjugate molecule, this is anisotropic material, this material has an un-uniform distribution of photon around it.

So, I beg your pardon, un-uniform distribution of electrons around it and because of the presence of this photon, the electrons are again redistributed in a far more chaotic manner, the chaotic manner is creating virtual states, imaginary states, imaginary states, just let that sink in. Now what does imaginary energy state means?

It does not mean like Harry Potter or Superman, Batman or Star Wars anything like that. Electrical or electronics engineers students knows that when we talk about the resistance coming from capacitor or inductor, we use the term I, root over minus 1, root over minus 1 that is the imaginary term.

What does that physically means, does it physically means that capacitor or resistor, capacitor or inductor resistance to the flow of current is imaginary. Do they not actually prevents the flow of current or resist the flow of current through them. How do you define in that particular case?

I would like that you utilize the same imagination to explain the imaginary term here, because imaginary states should not exist, imaginary energy states should not exist, they violate the every other fundamental principles by which quantum physicists swore their name on, this is what we are, we are quantum physicists and Heisenberg Uncertainty Principle what governs as, well Heisenberg's Uncertainty Principle is not followed here.

What are you going to do, but you do not have any better explanation. You do not have any better explanation and this is the only explanation, possible explanation that we can come up with to describe the actual phenomenon-that why that when we send two photons we get the output as a sum of the energy, sum of the frequency of the two input photons.

Suspend disbelieved, I do not know how you are going to cope with it. I am still grasping with it and I will let you know a secret, all of us are. This is quantum physics, one single photon can pass through two different slits at the same time, so can be an electron, we can have virtual energy states happening where the electron will absorb the wrong photon, the electron will absorb the wrong photon, go somewhere else, then absorb another photon goes somewhere else and then returned back, giving rise to, giving rise to one single photon which combines the energy of these two photons.

Virtual energy state has come and we have not been able to describe it, or we have not been able to observe it experimentally, there is virtual state spectroscopy coming up, and several new work is being done, but we are still, this is a very short lived state. The idea is that it takes some time for Heisenberg's Uncertainty Principle to kick in before it kicks in this electron has moved or this electron has gone through or gone back. This is somewhat of a hand waving idea that describes the overall non-linearity process.

And how do you differentiate a virtual state from a natural state, virtual state from an already existing state, it is easy in fluorescence; in fluorescence we have a broad distribution. Remember those emission and absorption curves, they have several broad distribution, they randomly distribute, here it is a very, very sharp spike.

This is a very, very sharp spike in which the electron which occupies a virtual energy state, occupies it for a very, very small instance, so much so that despite our attosecond cameras, femtosecond cameras, we are still unable to capture is, is it true you ask, is this explanation, incomplete explanation is it true enough? I do not know, I am not quantum physicist, but this is the best explanation we have thus far, this is the best explanation we have thus far and we have utilized.

What is the explanation, that because of the presence of intense light beam, the electrons redistribute, the electron cloud redistribute, since there are different electron clouds, they have their own repulsion and attraction among each other because of the different types of atoms that formed this entire material, they create virtual energy states.

And they will behave nonlinearly, they will behave in a bizarre manner, indirect manner, weird manner and when you give two beams of photons of the same energy, same velocity, same phase, we see output coming up and this part, this part is experimentally observable, we saw this experimentally happening.

And then we try to explain it mathematically and there where we got into trouble, and thereby we started setting up of virtual energy state, well virtual energy state have previously been discussed before nonlinear optical process were coming in, but you can understand that it was not very popular at that time but with nonlinear optical forces were experimentally observed. We have to invoke virtual energy state otherwise, it will never get explained.

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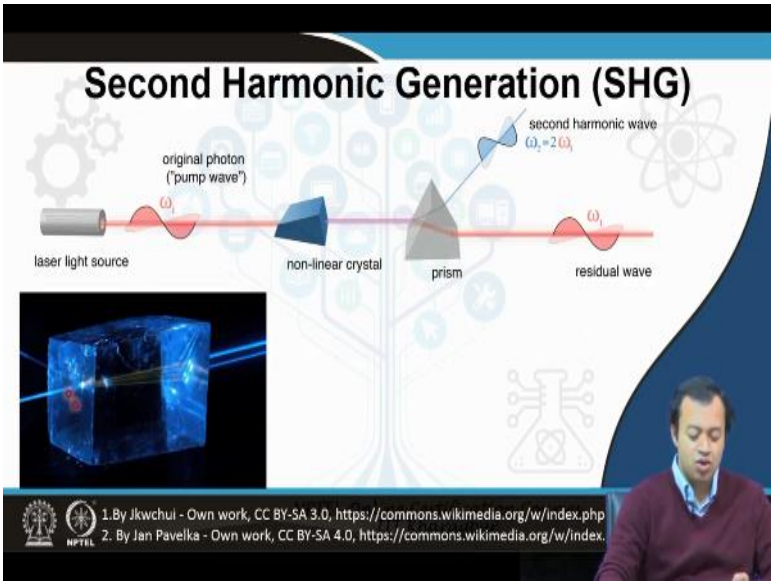

And we see this happening every day in our laboratories, where some kind of a nonlinear crystal, for example, lithium niobate, this complicated crystals, they have different arrangement in different direction, when subjected to beams of light, omega 1 several

sources omega 1, it creates, it generates two omega 1 and omega 1 at the output, this two omega 1 is a combination of omega 1 plus omega 1.

This is not exactly a right picture, this is actually fluorescence, but you can understand that we have been able to measure, we have been able to calculate, we have been able to observe this phenomenon-throughout in our experimental results, throughout in our laboratory, when we try to explain non-linearity we invoke virtual quantum states, virtual quantum states and virtual quantum states, obviously, obviously, bypasses or breaks several existing quantum mechanics rules.

What can you do, you tell me, come up with a better explanation. I ask you to come up with a better explanation, thus far, this is the best explanation we have, yes, I know how incomplete it sounds, but this is the best explanation we have, you can knock yourself out with as many mathematical derivations as you want, but at the end of the day, it still boils down to the fact that virtual energy states makes zero sense, virtual energy states make zero sense and yes, energy state splitting, this, this that, everything is there.

But, explain me any physicist, I am asking you explain me the virtual energy states in a proper manner which does not violate the previous principles that we have, we have discussed. So, where we use them? Again the so what question, well, a very easy thing is we use it for lasers.

We use it to create or tune lasers, think about it, omega 1 maybe the wavelength of light in a laser light at red, two of the red wavelength light, say, around a 800 or 750 or 700 combines together and gives you an output laser, which is twice that of the frequency and thereby you can convert or you can tune a low frequency laser into a high frequency laser, you can tune a low wavelength laser into a high wavelength laser.

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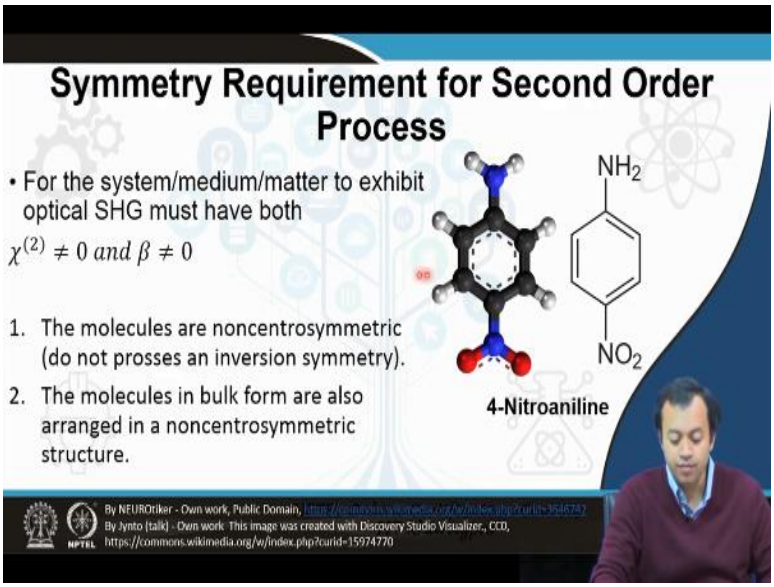

Also, there are certain conditions that needs to be fulfilled to have the second order harmonic generation, it does not happen to any material, I told you it has to be anisotropic, it has to be as they use the term, it is a better term noncentrosymmetric.

You have to, chi 2 is not equal to 0 and beta is not equal to 0, several materials have this thing 0, you do not see this bizarre thing happening in any material, I told you this happens in conjugated materials, but there are far more conditions that the molecules have to be noncentrosymmetric, this is a better term, what does that mean? Meaning it is not symmetric across its center.

Considered the benzene molecule, you remember the benzene molecule is like that, it is like that, if you slice it into half you get equal half, you get equal half, this is a superposition principle that inversion symmetry, if you invert it they are symmetrical to one another, if you invert it, it is symmetrical to one another, consider the benzene molecule, it is symmetric across its center.

However, and if the molecule needs to show second order processes, it needs to be noncentrosymmetric, the molecule in bulk also arranged in noncentrosymmetric structure, it should not be that the molecule is noncentrosymmetric just by itself in the

molecule, the arrangement has to be noncentrosymmetric as well. Now, here, please mark my word, noncentrosymmetric does not mean random.

It does not mean random, it simply means asymmetric, these are two separate words random arrangement is different, random arrangement you take some amount of marbles, throw it away and this is a random arrangement. Noncentrosymmetric is deliberately making it so that the it is not symmetric in x, y and z direction, and you cannot arrange, you cannot get this randomly because in random process, some of them might be similar, some of them somewhere might be similar.

Noncentrosymmetric ascertains, that it is not symmetric across its center, meaning an example is 4-Nitroaniline, this is a stick figure of 4-Nitroaniline, you have NO2 at one hand and NH2 at one hand, this is the amine group, amine, ammonia, the strong smell you get when you enter a lavatory or a laboratory, ammonia, NO2 is the nitrogen dioxide.

And no matter across the center, if you cut it like this or if you are having difficulty cut it in this particular form, you will see that it is asymmetric molecule, there is a different arrangement here, there is a different arrangement here. And if you cut it through this, you will see asymmetry or noncentrosymmetric in one particular direction. There are other molecules.

For example, I do not know, lithium niobate is probably asymmetric in z direction, it is symmetric in x and y direction. So, that matters but there are several complicated molecules, DNA for example, which is, correct me if I am wrong, which is noncentrosymmetric, I might be wrong, just check into it, but you get the point, you get the point that this has to have an asymmetry around it.

These are not randomly arranged, obviously not. These are not randomly arranged and when they combine to be the route other molecules, they are also not randomly arranged. But the fact of matter remains that they are noncentrosymmetric, meaning the electron cloud enveloping them is also noncentrosymmetric.

And when they are subjected to intense light beam like considered my pointer to be light beam, they get redistributed, the redistribution the remodification creates virtual energy

states, the virtual energy states give rise to all these bizarre things that comes up. Not every biological material has noncentrosymmetricity, not every biological or conjugate material has it. However, several of these nitroaniline, certain proteins etcetera does have it.

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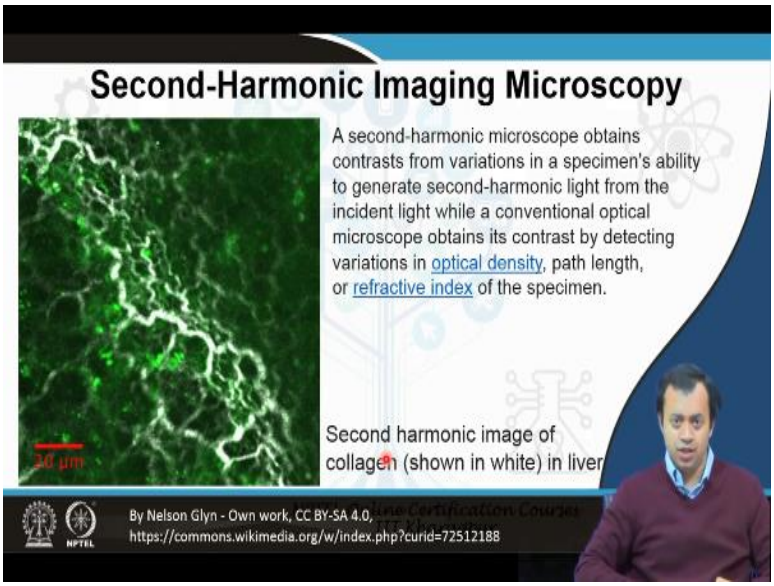

A primary example of where we can utilize it is your second harmonic imaging microscopy. So, you have a material, collagen, for example, is a noncentrosymmetric biological protein. Well, collage, yes, it is kind of a protein, and you know what collagen is for, you have thus far gone through all the courses. Suppose, we want to look into how the collagen is distributed inside the tissue.

We subject, we put it under a microscope slide, we put it under a slide, in a slide put it under a microscope and the microscope gives two strong beam of light, that beam of light when encountering the collagen because of the non-linearity process gets either reflected or transmitted, combine effect a two omega effect, omega 1, omega plus omega gives rise to 2 omega and if you have sufficient filters, sufficient light filters, which can only filter out the 2 omega part in a plethora of tissues.

Say for example, this is looking at the collagen distribution in liver, rest of the areas are not noncentrosymmetric, they are centrosymmetric or they are not producing the

nonlinear effects, thereby they will not emit 2 omega, when they are subjected to omega plus omega, they will not emit 2 omega when they are subjected to beams of omega, they will not emit photon of double the frequencies when they are subjected to single photon frequencies, they will behave normally.

You can therefore identify and locate how the collagen is distributed and if you can identify or locate how the collagen is distributed you can take some, make some inference, make some analytical, make some analysis, at the same time, if you see some kind of a disease happening, if you see some sort of a disease taking place, where the collagen is breaking down or the collagen has some sort of a problem, you might think that the molecule is undergoing some sort of a change.

If the molecule is undergoing some sort of a change, if a pathogen has attacked, if a foreign molecule has come up, something else has happened; maybe the non-linearity will be disturbed. If the non-linearity will be disturbed, 2 omega will not be emitted back, if 2 omega is not emitted back you will see black patches.

So, you compare light with light and you come to a conclusion that this part is probably not alright. So conventional optical microscope deals with optical density, refractive index, path length, the second harmonic microscope only depends on the generation of second harmonic light, second harmonic light omega plus omega, 2 omega, if 2 omega is returning back, you have sent 2 red lights only when you see blue light returning black or green light returning back from a particular specific area.

You know, this area is collagen because collagen is the only nonlinear material there. And this is the distribution of the collagen and from the distribution of the collagen, you are diagnostics, whether the distribution is right or wrong, whether there has been some kind of problem with the distribution etcetera.

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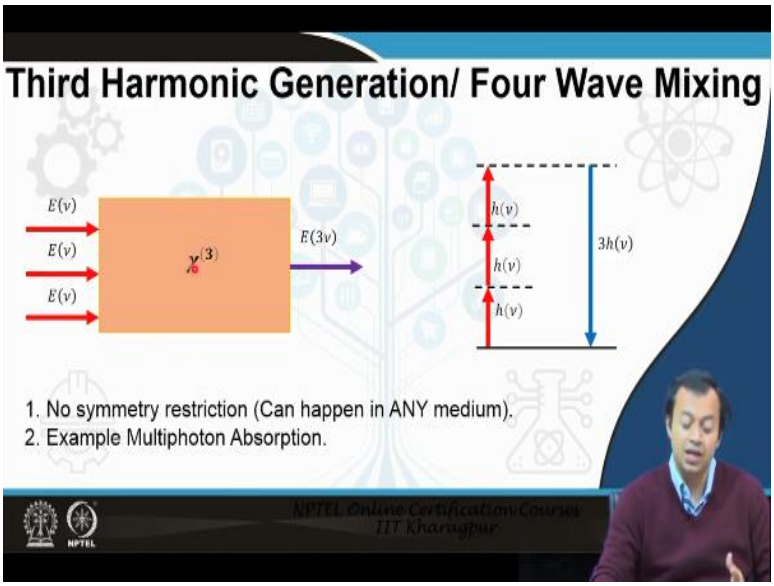

We also see third harmonic generation, yes, I know, it is four wave mixing where photon 1, photon 2, photon 3 combines and you give instead of 2 omega, you give 3 omega, yes, I know, will you be mad if I say that even the top one is also virtual state. Yes, do not hate the messenger, as they say, do not shoot the messenger is the say, I am simply the messenger.

Remember, Schrodinger said that I am sorry I have anything to do with quantum physics, I have not developed quantum physics, not at all, heavens forbid, but I have to teach and I am already apologizing.

So those of you who want to go into this direction, you know what you have to tread with. So, third harmonic generation, the more you go further, the more bizarre it happens, one saving grace is that these things are in relatively few compounds, not in a everyday compounds are can be considered as chi 3 or chi 2, well, depends what you use in a everyday basis, silicone shows chi 3, so a semiconductor physicists can talk about chi 3.

But the farther it goes chi 3, chi 4 it becomes weaker, the effects become permanently weaker, but nowadays we are utilizing different types of laser beam to enhance chi 2, chi 3 effect. For chi 3 you do not even require a symmetry restriction, can happen in any medium, can happen in any medium, so no one is safe, and the multiphoton absorption,

read a bit about multiphoton absorption this is related to the Raman scattering, multiphoton absorption we will use some several different.

So, this is multiphoton absorption, three different types of photons are getting absorbed and the emission is a combination of all three giving rise to bizarre things happening.

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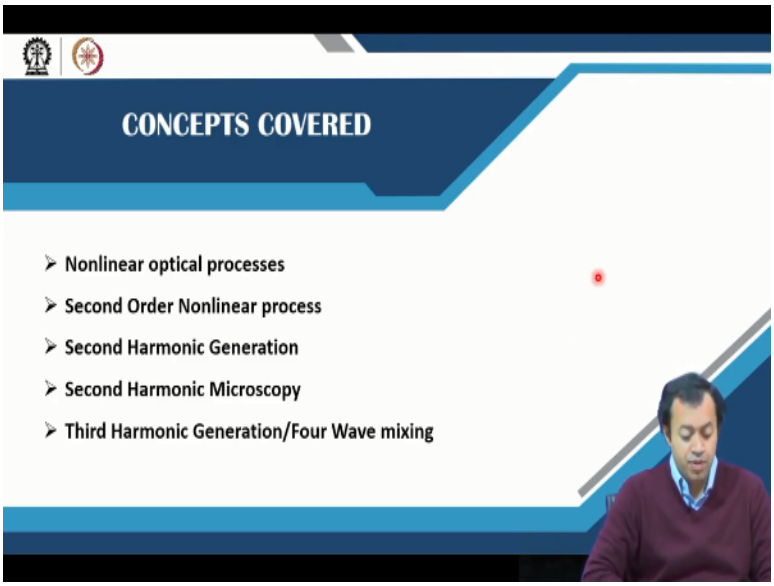

So, this is thus far the topics that we covered for today. Nonlinear optical processes, second harmonic generation, and the third harmonic generation, I did not discuss too much of third harmonic generation because it will take us into the deepest and darkest side of the woods, let us stick to second harmonic microscopy, it is a special kind of microscopy that is specific to our biophotonics, biophotonics is also utilizing third harmonic generation, four wave mixing which is Raman scattering.

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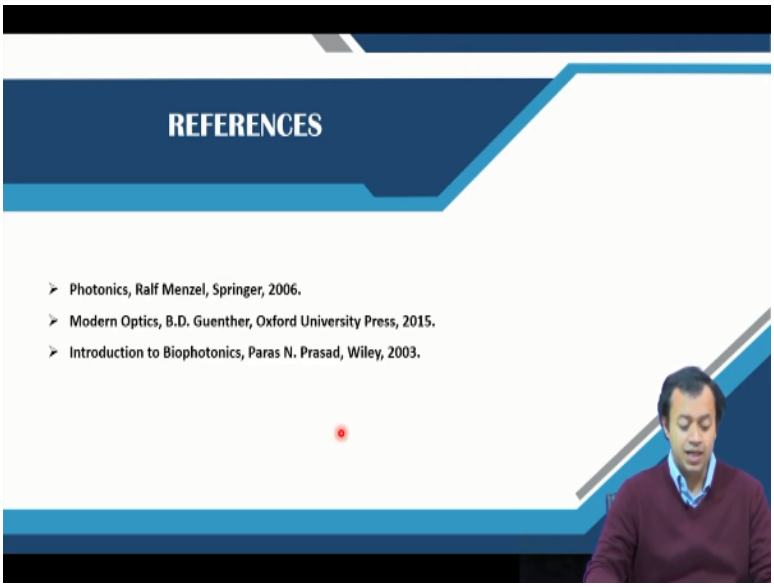

And if you are more interested on to knowing nonlinearities, the bizarreness in quantum physics try reading photonics part, chapter number four or chapter number five, by Ralf Menzel, very, very good book, try to see if you can get it from the library. And of course, the other books are our constant companion. So, thank you. I hope you survive this. Thank you very much.