**Ultrafast Processes in Chemistry**
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**Module No # 09**
**Lecture No # 41**
**SFG and SHG with Ultrafast Pulses (Contd.)**

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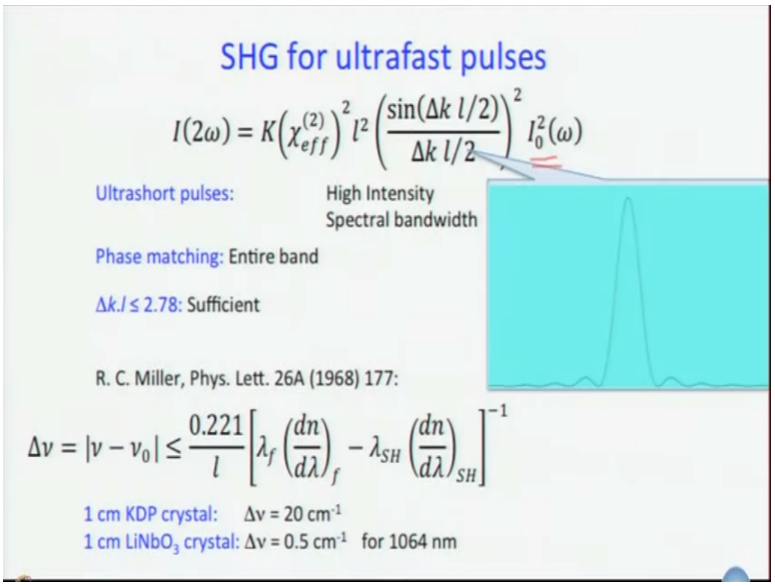


Alright we are back and do have an answer which is better while working with ultra-short pulses is KDP better or is lithium niobite better. KDP is better because see the problem is this what it means is that if delta Nu is more than 20 cm inverse you will not get second harmonic generation for KDP. But if delta Nu is more than 0.5 cm inverse you will not get second harmonic generation for lithium niobite.

And we know very well that the characteristic of ultra-short pulse is a large band width, shorter the pulse bigger the band width right. So if you are going to use a short pulse femtosecond pulse and use lithium niobite to generate second harmonic wavelength what will happen? Your model wavelength is 1061 nanometer for fundamental. So you are going to generate 532 nanometer fine but the bandwidth will be very small yes.

If the bandwidth is very small then we have studied transform limited pulses when width is small then what does that mean? What does that how does that effect the pulse width? Pulse width becomes large right remember the delta Nu multiplied by Del T that would be a constant depending on what shape the pulse is? And the physical reason for that is if this spectral bandwidth is large that means a large number of longitudinal modes have been locked to produce the pulse.

Greater the number of modes locked shorter is the pulse. Why there is the spectrum? So now after second harmonic generation if the spectrum; has become narrow just because your delta Nu is small for the crystal. Then automatically what will mean is that in the second harmonic light very small number of modes are locked right when width is small that means a fewer number of modes would be locked compare to fundamental which would mean that the pulse width would be significantly larger compared to the fundamental right.

Even 20 centimeter inverse is not very large but at least it is much better that 0.5 centimeter inverse. So you want a crystal so that is the first point we are we want to make here you want a crystal for which delta Nu is going to be large as large as possible. So, that your pulse does not become temporarily broadened. Spectrally it will become a narrower but at the same time temporarily it will become broader if delta Nu is small.

See in order to ensure that your ultra-short pulse remain ultra-short even after frequency doubling you want delta Nu to be as large as possible right. And what determines delta Nu? The material so this is a an important point here you want to use a material for which delta Nu is large ok while working with ultra-short pulses ok. So it is a very complicated thing first of all you want a large value of second order non-linear susceptibility right Chi second order.

Then you want the crystal to be birefringence then when you working with ultra-short laser you want the delta Nu to be large as well. So we are getting into more and more restrictions and in fact there will be one more before we complete this discussion. So far we have talked about this bandwidth business next we want to discuss another aspect of ultra-short pulses and that is group delay. We will say what group delay is?

But the central theme of this entire discussion is something that we had discussed several modules earlier the issue is our ultra-short laser is not a single mode laser. Lot of longitudinal modes are actually locked to produce the ultra-short pulse ok. So whatever discussion we had earlier during mode locking that becomes the determinant in the discussion we are going to perform now. So when we do the experiment we do not even think we took this and took that and things happen.

But a lot of effort by many people has gone into the system before we could use it as a toy. And it is important that we understand we do not need to know all the math but we should at least understand the principles otherwise if you have to design experiment if you do not know these we will end up taking out a crystal from anywhere and trying to do second harmonic with ultra-short pulse and it will not work ok so second factor group delay.

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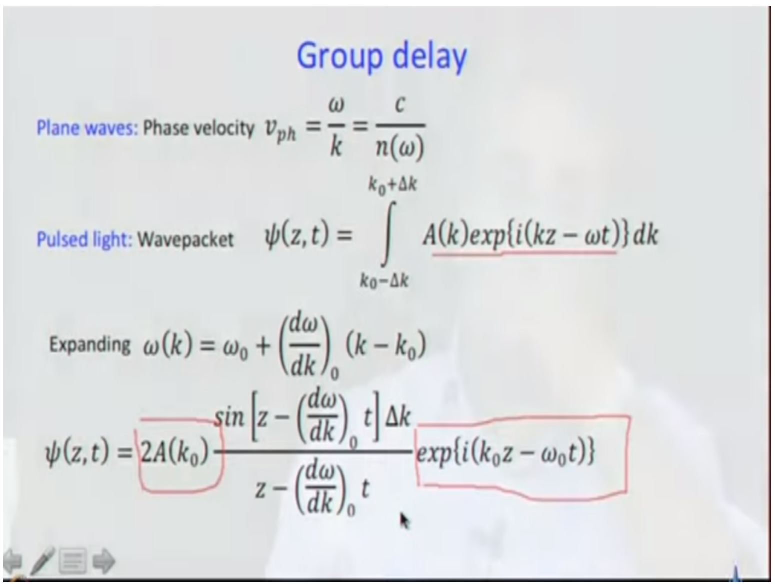


Now see we have discussed earlier that plane waves are characterized by their phase velocity right VPh = Omega / k = c divided by refractive index at that value of Omega. We have talked about this earlier yes so now how do I define pulse light? Pulse light you said is actually not used you did not say anything I said but you know that pulse light is a mixture of many plane waves right.

So the amplitude the wave function of pulse light can be written like this might as well write as summation in if we write as integration because it is easier to arrive at the next step if you do an integration. You can do it numerically as well ok. So let us understand what we have written. Forget about this integral for the moment we will come to that. What is this? A k A at k multiplied by e to the power i / kz - Omega t.

That is the expression of a plane wave we have written there right. And our ultra-short pulse comprise of many such plane waves what we are doing is we are adding up all the fields. So Psi as you know is an amplitude and it depends on z as well as t. What is z? z is the direction of propagation of light ok. So the light goes this direction then this is z direction of propagation of light and of course it is dependent on time as well.

So what we have is Psi at some values of z and some value of t is an integral of this field for a plane wave over the entire range of plane waves. So integral dk and lower limit is k0 - Delta k upper limit is k0 + delta k. So what is k0? K0 is the k value of the model. K0 is the let us just say k0 is the model k value. So delta k on this side and delta k on that side we are working with a symmetric kind of distribution ok.

How do you do it? We are not going to do the entire integration any integration enthusiastic is welcome to do so. I will just tell you how it starts and I will show you what the final answer is. So to workout this integral what is done is omega so as you said earlier every plane wave is characterized by a k vector and an omega right. A characteristic k vector a characteristic omega. So we can pretend as if omega is a characteristic of k.

So you can write omega for a particular k value. That is written as omega 0 again the model omega + d omega dk 0 multiplied by k- k0 does this ring a bell have you encountered an expression like this somewhere in spectroscopy fundamental spectroscopy not in this course where a little louder please very easy question as demonstrated many times I do not ask difficult questions. Where have we encountered why Raman what about vibration?

When you derive the vibrations oscillation rule how do write the dipole movement Mu = Mu 0 + del Mu del x multiplied by x. So that is what it is ok this is the rate of change of omega with respective to k that is multiplied by k - k0 it works because k - k0 is a small quantity ok. This is how it is expanded and then after doing the integration now I will show you the final expression please do not get scared we will demonstrate that it is not very difficult expression.

So this is this the final answer. Nothing to be scared of as you will see Psi at z and t particular value of z, particular value of t turns out to be 2A at k0. A at k0 means amplitude for the model k value k0 neglect this thing for the moment. The last factor is e to the power i k0 z - omega 0 t that is quite simple is not it? What is e to the power i k0z - omega 0 t? That is the same expression you have here instead of z you have written instead of k you have written k0 instead omega you have written omega 0.

So that is the expression for the once again the plane wave at the center of the distribution alright I am talking about this one. Have you shared better control over my figures but I do not alright. This is what I am saying so do you see that this is what comes from the plane wave at the center of the distribution and this ok it is the amplitude comes from the integration. What are we left with here?

What kind of function is that earlier we have sin square theta by theta is it that or is it something else. If sin theta by theta so what is the difference between sin square theta by theta square by sin theta by theta more or less similar looking functions. But there is a difference yes sin square theta by theta square is always positive. But this goes negative but not too much thing negative but it does go negative so this is the shape ok.

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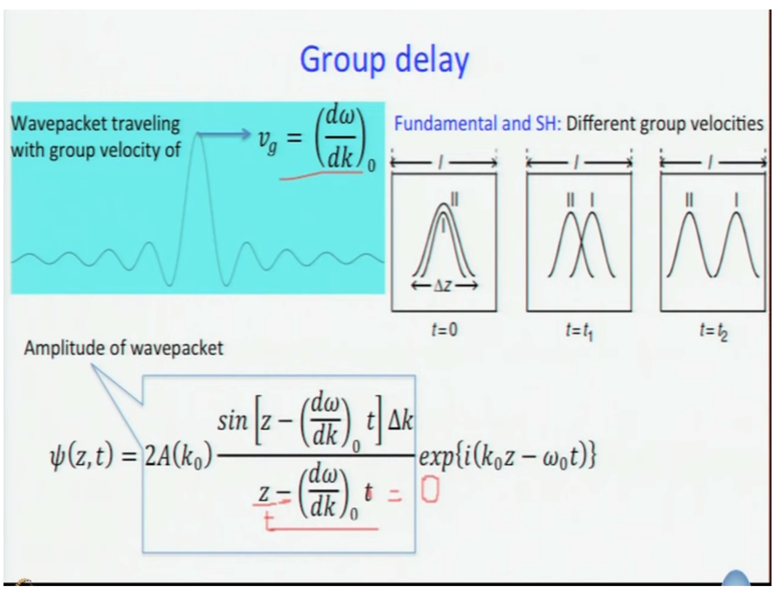


Now this whole thing here is the amplitude of the wave packet. Let the term wave packet not scare you some people write wave packet as 1 word but some people in some books most of the books wave packet is written as 2 words. I prefer to write this things as 1 word always nanoparticle is 1 word for me wave packet is 1 word for me because I am influenced by television series that I saw as a kid that was on bodyline bowling.

You know bodyline Douglas Jardine, Don Bradman so there was a scene where this British reporters is trying to send a message by telegram and he fights with the clerk at the telegraph office because he wrote bodyline which was a new word at that time. There is no such word earlier so the clerk insisted that this is 2 words. So every time you write bodyline you have to pay for 2 words and journalist insisted no it is a new word it is one word. So somehow that got into my head and I like to combine words whenever I can.

So for me the wavepacket is 1 word. You write whatever you want. What is the meaning of wavepacket? What is a wavepacket? My favorite answer to this question sounds almost stupid. A wavepacket is a packet of waves. It is sounds very strange mundane and but actually that is what it means. You combine a lot of waves right that gives you a packet of waves and you combine them in such a way that at one particular point that they all in phase then as you go out on either side they will go out of phase and that is why you get a shape like this ok.

How do you generate a wavepacket? We are going to discuss this later. Suppose once again it is related with that spectral bandwidth of ultrafast pulses ultra-short pulses. Suppose you excite something using a ultra-short pulse. Excitation starts from v = 0 of the lowest of the ground electronic state let us say right. What is the destination? Can you say that we only populates v = 3 v' = 3 of a S1 you cannot because this is a distribution right.

Some molecules will be excited to v dashed = 3 some might be excited to v dashed = 2 some will be excited to v dashed = 4 and so on and so forth. And then that will form a coherent wavepacket. And coherent wavepacket dynamics is an important problem that has been studied for ages in ultrafast spectroscopy we are going to discuss it in this course as well. But for now this is a wavepacket ok ultra-short pulse and this is a shape that you get of the amplitude of the wavepacket.

Now this entire wavepacket is not stationary it is not a standing wave the entire wavepacket moves ok. And it moves with what is called a group velocity given by d omega dk 0. Do you get this significance of d omega dk 0 look at this function? Where will the function be equal to 0? z = z - d w d omega dk 0 t = 0 right that is where this is going to be = 0 is that right? What is z / t so what we are saying essential is that z = d omega dk 0 t ok.

So what is z / t I got d from here and I write t here z / t = d omega dk 0 this. Why do you call that group velocity all of a sudden? What is z? Last letter in English alphabet yes but in this context what is z? You have to speak loudly. It is a big room very few people are there I cannot I am little short of hearing what is z? z is the direction of propagation of light. So what is z / t? Distance covered in direction propagation of light per unit time that is velocity right.

So z / t is essentially is the velocity with which this entire wave packet moves ok d omega dk 0 this is called a group velocity. Not group delay yet, delay comes later when we talk about delay you talk about 2 kinds of light. The 2 kinds of light in this context are fundamental and second harmonic we will come to that. For now what we are able to do is we have been able to define a group velocity of a wave packet.

A group velocity is d omega dk 0 ok; and just for the record fundamental and second harmonic have different group velocities and that creates another problem. One problem we have discussed already is delta Nu. The other problem is that if fundamental and second harmonic travel with different group velocities then this is a situation you get as times passes they move away from each other. So the question is what is the difference in times taken by fundamental and second harmonic to travel the entire length of the crystal ok?

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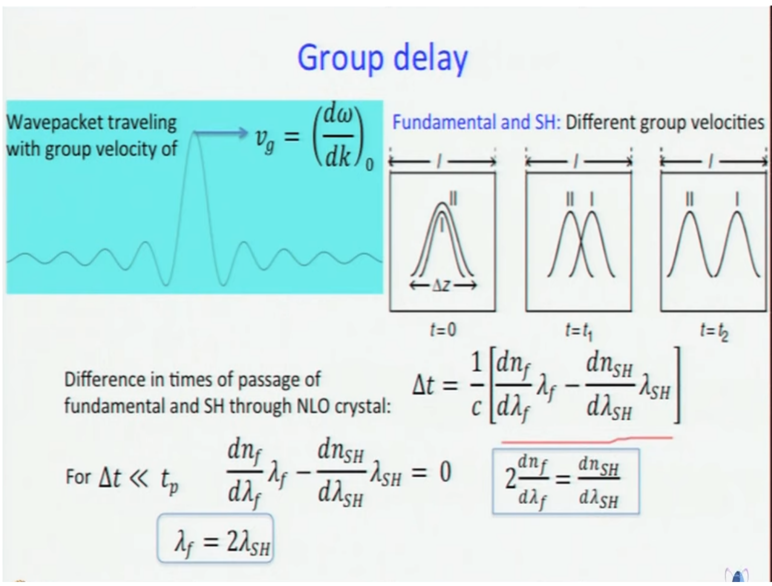


Once again without derivation I will give you the expression this is what it is? Delta t is given by 1 / c dnf d lambda f multiplied by lambda f where f is fundamental equal to dnsH d lambda sH multiplied by lambda sh. I might as well have like the previous slide I might as well have written dn d lambda then put a bracket then written sH subscript. That would have perhaps better ok. So you do not want too much of delta t that is the issue that would travel together for the wave packet to sustain. So now what do you want?

You want the delta t smaller than the laser pulse duration yes. So in other words we can say that delta t should be almost equal to 0. Time required so as long as the within the crystal there should be together the fundamental and second harmonic. So if delta t is to be equal to 0 work with this expression equate that to 0 what do you get? Yes while doing that do not forget something when we equate that to 0 is there some relationship between lambda f and lambda second harmonic and the better would be what is the relationship?

Yes lambda f = 2 multiplied by lambda second harmonic. So putting this expression into this what do you get? You get something like this ok. This is another condition dnd lambda of fundamental should multiplied by 2 should be equal to dnd lambda multiplied dnd lambda of second harmonic dnd lambda right rate of change of refractive index with respective to wavelength for second harmonic should be equal to twice dnd lambda for fundamental ok. That is when your delta t is going to be 0. And delta t should be small in order to get good second harmonic generation using an ultra-short pulse right.

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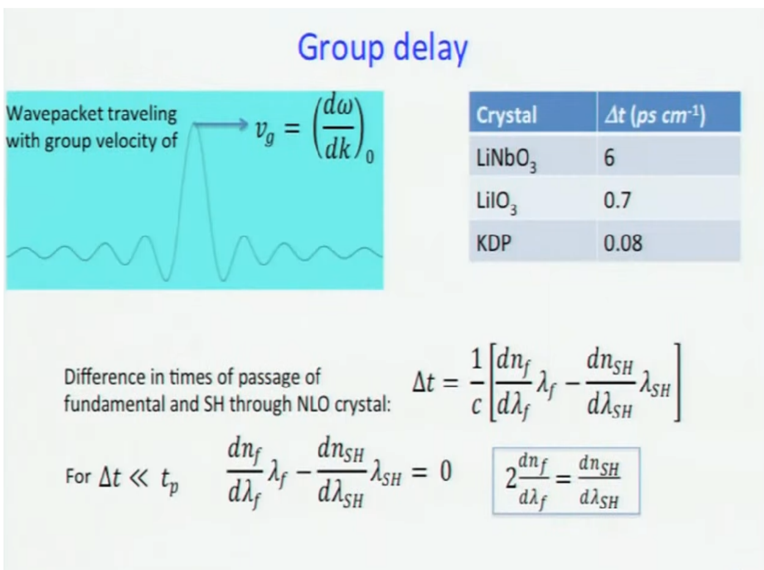

Once again let me show you some typical values delta t for lithium niobite is 6, delta t for lithium iodate is 0.7 delta t for KDP is 0.08. So which is the best out of 3 from this point of view? Definitely KDP ok so the take home message from a this module and last one is that one needs to be careful about several things before one can think of doing a second harmonic generation or some frequency generation of a using ultra-short pulses.

First of all you have to choose the right material and there is so many parameters right. We are said this once already large value of second order nonlinear susceptibility birefringence, delta t has to be a close to 0 and what else what is the point we just discussed before this delta Nu. Delta Nu has to be as large as possible ok. One more thing that we have not really said explicitly do you want use a crystal that is very large or do you want to use a crystal that is small?

I mean that is not too thick. You want to use a large path length within the crystal? Do you want to use a not so large path length? You want to use a thin crystal because here you are taking about a delta t. Delta t is going to be a longer for a thicker crystal. See delta t here is given in picosecond per centimeter right. So if you use 2 thicker crystal first of all there will be dispersion so your pulse will become broad.

And this delta t is also not going to help. So these are several parameters that one needs to worry about when one wants to do nonlinear optical manipulation using your ultra-short pulses right. So that brings us to the discuss end of the discussion that we intended to do today but let me just give you a preview of what we are going to discuss the next day. See so far we have been talking about some frequency generation right combining 2 photons of small energies to produce a photon of larger energies and that is easily understood.

Is it possible to have a photon of large energy split in to 2 photons of smaller energies in nonlinear optical material? The answer is yes it is just that it is much more difficulty process compare to sum frequency generation. And that splitting into 2 kinds of light with smaller energy longer wavelength that has a name that name is parametric generation or optical parametric generation ok.

So a really very small in one in a million kind of probability and the phenomenon is not easy to understand so far even though we did not do the derivation we more or less understood what we are talking about because we can think of real-life analogy and all. Difference in frequency generation is actually not easy to understand because deals with things like quantum entanglement. In fact parametric generation is used to make what are called correlated photons or single photons or photon pairs.

Not of any use to us as such but they have they are used in sophisticated optics experiments. We are not going to go into that in this course. But the point is it can happen what we want to learn is you are saying is one in million kind of probability for get parametric generation is there any way to increase in intensity? So now see what will happen so far we were dealing with the situation where signal and idler meet at the nonlinear optical crystal and the pump is generated.

In fact when I say it like this it sounds a little strange is not it because when I say pump we think the pump should go in that is what is going to happen in parametric generation. So pump goes in and splits into signal and idler. So signal and idler both have a longer wavelength lesser energies. So this is a good way of generating light of so if you using a visible light it is good way of generating say IR light.

Now the question is how do we get a higher intensity? 2 ways one is do this parametric generation inside a resonator. So if your parametric generator in resonator means a laser cavity right if you do multiple reflection then it happens multiple number of times you are going to get some kinds of increase in the output. The other way is to do what is called optical parametric amplification. That is what we use in our lab right and that is a 2 photon process.

It is not only the pump that goes in into the nonlinear optical crystal. It is pump and signal and what you generate is signal and idler ok that is what we are going to discuss next day. So I think next module is going to be a very sketchy principle of optical parametric generation and optical parametric amplification. You might not talk too much about optical parametric oscillation and module after that will be a discussion of our TOPAS manual.

What is there inside the optical parametric amplifier that we have? How does it work? Those are few were work with TOPAS can you tell me what are the different kinds of light that are there inside? There are several crystals is not it and what do you do? You do second harmonic generation in some crystals. You do something else in some other crystals. What is that? Do not you generate white light? So that white light now by angle tuning and all one particular frequency from that white light well of course is model frequency that gets amplified.

That is our optical parametric amplification works. So that is what we are going to sort of learn in next couple of days and we will perhaps say a few words about so far we are talking about collinear geometry. In fact even our TOPAS has collinear geometry. But there are certain advantages that come if you use non-collinear geometry. And in context of optical parametric amplification that instruments is called as NOPA non-linear optical parametric amplifier.

So if possible in the next couple of module in the next 3 modules this is what we are going to cover let us see whether we can give some brief idea sketchy idea about NOPA as well okay today we stop here.