Ultrafast Processes in Chemistry
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Module No # 09
Lecture No # 42
Optical Parametric Generation and Amplification

So today we are going to talk about how to generate femtosecond pulses of different wavelengths for applications like pump probe spectroscopy. As you have talked about the amplifiers earlier the reason why we want to use amplifiers is that for many applications you want to use a laser pulse that is really very intense. And the way you do it as we have discussed is first you use a seed laser an oscillator.

Feed into another laser which is an amplifier and we have learnt different techniques of elongating the laser pulse feeding it into the cavity of the amplifier by using pockels cell. Then switching it out using another pockel cell, or maybe the same pockels cell and then compressing it once again to get an amplified pulse which is short as well. Now the issue with this chirped pulse amplification method that we have discussed earlier is that you can only get one model wavelength.

Of course you know that femtosecond pulse by itself is brought back. We are not talking about that. But if we think of the model wavelength this no way in which you can tune it because the seed pulse has to have exactly the same frequency as the one that will come out well when I say frequency I mean model frequency as you want that will come out of the amplifier. So if you try to tune the seed then you have to pair round to be amplifier laser cavity and all that and then alignment becomes problematic.

I am not saying that tunable amplifiers are not there, they are there. But alignment there is a nontrivial process. So what one needs to do is one need to work on the pulses post production if you want to generate pulses with different central frequencies. And the way it is done is called optical parametric generation and optical parametric amplification. So these once again are non-linear optical techniques as we are going to see their exactly the opposite of what we have studied earlier second harmonic generation and sum frequency generation sum frequency generation to be more general.

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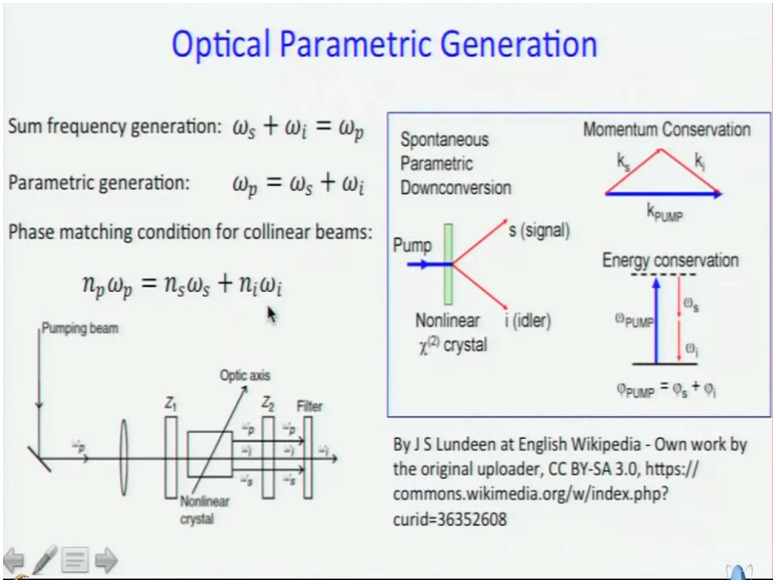

So as you know in sum frequency generation what we do is we take a light of 2 different frequencies and we have in our previous discussion we have developed this concept of signal and idler. We have talked about the relative frequencies of signal idler and pump. And their what we said that the pump is the highest frequencies right. The pulse width highest frequency is called the pump pulse and that time it might have sounded the little counter intuitive because there you are actually producing the pump.

But when we say pump we think of something that is going in right. The reason why we introduce that time is what we are going to use now. So earlier we have studied sum frequency generation not very difficult to understand by considering virtual states we said it is sort of like 2 droplets of water joining up to giving you a droplet of to give you a droplet of bigger mass. Similarly you have 2 photons of smaller energy which join up will give you a single photon of a higher energy.

And what we explained was that you have this material in ground state then let us say omega s comes in the signal frequency it this systems gets promoted to a virtual state and then at the same instance if omega i comes in it will get promoted to higher virtual state frequency of the energy gap between which and the ground state would be a say h omega p where omega p = omega i + omega s.

And then when since this is virtual state is 0 lifetime so when relaxation takes place in within 0 lifetime the light that comes out has frequency of omega p which is omega s + omega i and that is not very difficult to understand right. Omega s + omega i combining to give you omega p what we want to talk about now is whether it is possible to do the reverse? We have omega p which is a higher frequency is it possible to break it down into a 2 photons one with frequency omega p omega s and another with frequency omega i.

And the answer is yes but this is a not as efficient process as it is inverse. It is much easier to combine omega i and omega s to give you omega p then to take omega p and break it down into omega s and omega i that is point number 1. And we are not going to get into the detailed quantitative treatment of this that itself can be a course. But what we are trying to do here is that we are trying to develop the general idea of how this is done.

Now can you just looking at this expression does it occur to you that there is a potential problem or potential issue or potential feature associated with breaking up omega p into omega s and omega i. That problem is not there when you start with omega s and omega i and produce omega p which is sum of the frequencies. When I want to break down into consequence there is something that should strike us. What is that feature I am thinking about?

See when we do sum frequency you start with omega s and omega i there is sum can be only one quantity there is no problem with that. But you start with omega p there can be in principle infinite for combinations of omega s and omega i right. So there is no predetermined value at least at this moment. We will see later on whether it is possible to bring in some predetermined value. But as of now all that is required is omega p must be omega s + omega i right.

So that reminds me of the story I heard as a child that there was an arithmetic problem in which it was said that 10 pens cost 50 rupees how much does 1 pen cost? And the student wrote we cannot say. And when he was asked why you cannot say he said see in nowhere it is written that all cost the same. So I can buy 1 pen for 5 rupees 1 pen for 10 rupees and I have some kind of combination and there are many different combinations that are possible. Actually that student was right.

So you have to say that there each pen cost the same. Here we cannot say each pen cost the same ok or maybe we can as we will see later right but this is what it is? Now this thing takes place and

it is actually a complicated process when you produce these photons they are correlated and the science of this goes beyond our requirement of producing a light of different frequencies. Actually what you produce here is correlated photons and that opens up a different branch altogether.

In our institute we had this talk by professor Mukamel couple of weeks ago might remember that he did mention about passing correlated photons right. So this is where it starts. Now when you do it let us say we can do it that a pump light gets into a non-linear crystal and gets broken up into signal and idler. First thing that we want to say is you cannot have infinite combination. Little while ago we said at least at that point I could write any value of omega s and any value of omega i as long as I adapt to omega p that is not necessarily correct.

Because not only do you need energy conservation momentum has to be conserved as well as we have discussed for sum frequency generation. The moment you say momentum has to be conserved the number of possibilities goes down right. And also directionality has a role to play now because we are just splitting now I can combine this ks and ki and the vectors sum can be k pump but you can see that if I have longer ks going higher up and I have a longer ki then again you I you can have the same vector sum right if you change the angle.

So once again it is going to depend on the angle at which the photons propagate right. And for a completely collinear geometry the equation that you get is once again you might remember that we have discussed that those polar plots and all and we said that the condition for the production of second harmonic was that the refractive index had to match for the fundamental second harmonic. Here also refractive index multiplied by omega p np multiplied by omega p = ns multiplied by omega s + ni multiplied by omega i is the conservation of momentum condition.

The moment you bring this in is sort of bringing in quantization right not all combinations of omega s and omega i are going to be now allowed but still there will be many okay there can be many. Of course we have already brought in some restriction here remember we are talking about a collinear geometry that is what will restrict thing a little bit. Now why I am not saying that there will be only one combination?

Why am I still saying that there can be several combinations? np omega p = ns omega s + ni omega i. So if np is defined ns is defined and ni is defined then I should think that only one pair of values

of omega s and omega i should satisfy this condition. Why I am still saying there can be several pairs yes what do they depend upon? ns and ni are not constant that is the answer. Even the np may not be constant.

What would they depend upon? Sorry no the wavelength is frequency right omega i omega p they automatically wavelengths are defined it cannot be wavelength something else something simpler. Something you studied when you are younger before you studied wavelength yes maybe but then I am working with the same medium I will not change the medium. So that is one way of course. You change the crystal you can have different kind of optical parametric generation.

Suppose I work with the same medium what can I change to change the refractive indexes? What about temperature? Temperature so you can have temperature control refractive index so therefore using changing temperature as you are going to demonstrate later on. You are you can actually get different combination of omega s and omega i ok. So temperature tuning becomes very important here right ok.

So this would be the simplest geometry in this case. So what you have here is we have this omega p coming in focused on to Z1 then here we have the non-linear crystal ok here is optical axis. Let us say we do not know what omega i and omega s are at the moment. We only know omega p let us say we have been produce. What you have mixture of omega s omega i omega p ok. And now suppose you want to take idler out. Idler is a typically the lowest frequency.

Lowest frequency means longest wavelength or shortest wavelength? Longest wavelength so use a long pass filter. If you use a long pass filter you can choose to get only the idler out or you could use a long pass filter which will allow the idler and as well as the signal to go out. And then by using a dichroic you can get the idler as well as the signal going in different paths. That is what it is done in a commercial OPO or OPA ok. You can actually generate both I mean generate everything but you can actually use both if you want. What is the problem? So the problem in intensity very small;

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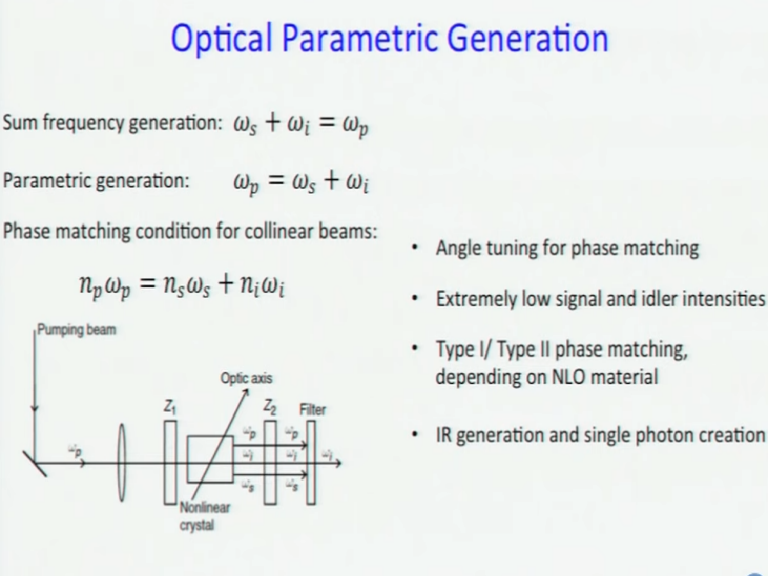

So first of all what you can do is like earlier you can do angle tuning for phase matching that way you can decide omega s omega n you can optimize a the condition by which it is come out. This we have to remember that signals are very low. See even sum frequency we said typical efficiency like 20%. Here typical efficiency would be 2 % or less or 1 % or less depending on what kind of material it is very low.

And then depending on the NLO material you can have type 1 phase matching or type 2 phase matching. Type 1 and type 2 phase matching we have discussed in the previous modules. Now what is the application? The major application in this case is what is the range that is available to us most easily. What is the range of wavelength that is available to us? Suppose you are using Ti-sapphire laser the range of wavelength that is available to us very easily is red right.

From red we have learnt how to create blue or even UV by second or third harmonic generation. Here we have learnt how to create IR right and also how to create single photons. So one application we are not really going to talk about that today but it is a very important application of optical parametric generation is that many times you want to do experiments in which you generate only one photons.

That is done very easily here ok. You can do it by angle tuning you can a do it by modulation of intensity and all that. You do it such a way that in n instance only one photons is produced and then you can do whatever you want to do with it ok. Do you know what is very good detector for

a single photon? Yes our eye. Our eye can actually see a single photon. If you are in a dark room and one photon comes in and it is and if it hits on your eye that will generate the signal. Eye is good enough right.

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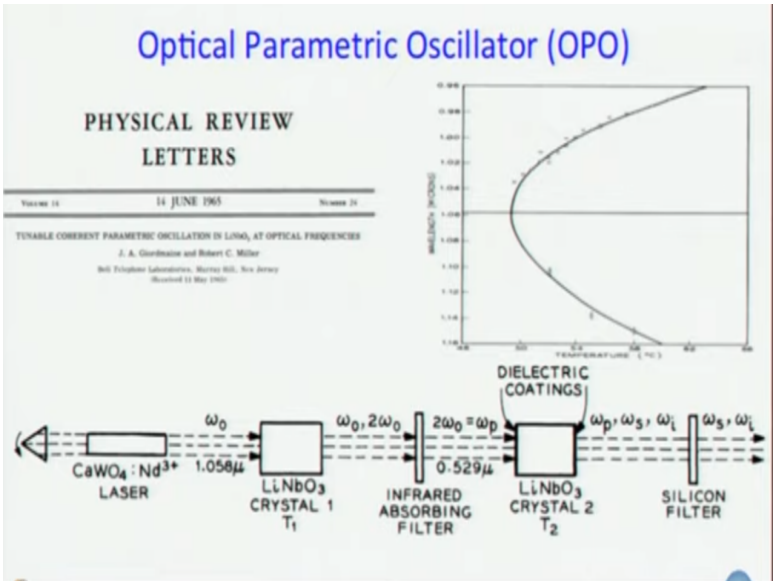

Now let me show you these schematics of construction of an optical parametric oscillator. Where does this oscillation thing comes? We have a latest slide where the schematic oscillation is shown briefly. See we have said that the efficient is very less right. So the efficient is less how do you increase the efficiency. One is by amplification which will study later. The other is if you makes sort of laser cavity and if you make the signal beam go around in the cavity several round trips then you can have some amplification right.

So and note the date physical review that is fine but which year was it published 1965 so these experiments started more or less along with the invention of the laser. The moment laser were invented the people started thinking what can you do with them. Perhaps I do not know whether the either thought that we are going to do pump probe spectroscope and all at that time. They just want to create single photons, they wanted to create correlated photon pairs, they wanted to have a mean of tuning the wavelength.

So as far as back as 1965 before any of us here were born this thing was there ok. And here is the schematic again the acting medium here is the niobidium ion the different substrate it gives you 1058 nanometer 1.058 micron that is let us say omega 0. What they did was first of all they put in

lithium niobite crystal they called it T1 crystal and then work of this crystal is actually to do what we have already know to generate the second harmonic 2 omega 0.

Now the moment you create second harmonic you know very well that the efficiency of the conversion is only 20% or 15%, 10%, 8% something like that. So there you have 2 wavelengths already omega 0 and 2 omega 0. Which are more which one is omega p which one is omega s. How have we defined it? What is the highest frequency, what is the largest frequency, what is it called pump signal or idler? No highest frequency. Highest frequency is the pump. So this 2 omega 2 omega 0 is actually = omega p.

That is your pump and omega 0 is the signal of course in this case idler will also have frequency omega 0 if you are going to use it like that. So then here after that there this infrared absorbing filter which one will get removed omega 0 is gone you only have 2 omega 0 here omega p ok. Then they add this second lithium niobite crystal T2 from which you are going to generate omega s and omega i ok.

How can we do it? We have discussed already that if you change temperature then all this refractive index will change. So even for collinear geometry you can get different frequencies for idler different frequency for signal if you simply change the temperature and that is the experiment they actually did. Unfortunately, the 1965 many years ago so that time this drawing graphs and all perhaps did not capture so much of attention like we do now nowadays.

But you can see what is there on the x axis and what is there on the y axis. X axis is temperature degree centigrade right and goes up 46 degrees to 66 degrees about 20 degrees and y axis is what is y axis it is wavelength in micron ok. So what you get is you get 2 branches you see this dots these are the experimental points. The 2 branch is this one is this signal this one is the idler is that right?

Did I say the right thing why not? Idler is longer wavelength look at the y axis shorter values on the top longer values at the bottom. The top one is 0.96 microns, then this is 0.981 and the lowest one is 1.16. In 1965 people used to think different what can it do. So what they have done is they have plotted from the lowest values of wavelength is on the top or you can think like this they have written wavelength that is the issue. Highest value of frequency is on the top right.

So in this parabola that you have the points on the top are this signal. Points on the bottom are the idler ok. And many times you see more points I do not know you can see there. You see their there are more points on the top than in the bottom. So many times it could not even retain the idler. The idler got absorbed or intensity was too small they could not detect something like that. Signal is a little better that is why it is called the signal ok. Lower the frequency more difficult is to detect ok. I have no idea why it is called idler of all things is I mean it is as idle as the signal I guess.

But the signal is little easier to observe ok. So by changing the wavelength sorry changing the temperature here different omega s and omega i were prepared. Of course you understand that for a particular value of omega s frequency of this signal frequency of the idler get automatically determined right because frequency of pump is known that is 2 omega 0. 1058 multiplied by 2 in nanometer right that is of course wavelength the frequency corresponding to that.

So at a particular temperature you get omega p is the same at all temperature omega s and omega I value is vary with a condition that omega s and omega i is always equal to omega p that is 2 omega 0. Next that this silicon filters which cuts out visible light and only omega s and omega i are transmitted ok. So this is one of the first examples of optical parametric oscillator that I have not shown the entire diagram here.

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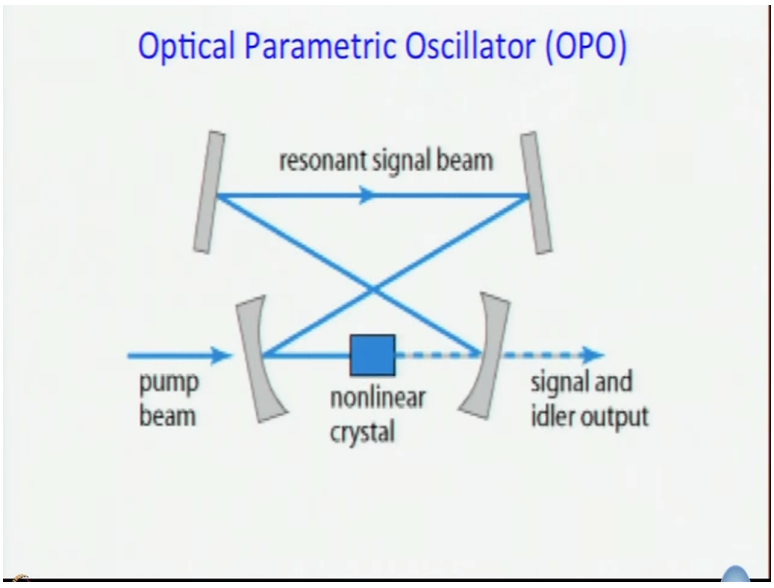

The entire diagram would look something like this where this nonlinear crystal is actually put inside sort of a laser cavity a cavity. So that the resonant signal beam gets amplified little bit and signal and idler output typically travel in same direction and then you can further separate them by using a no there is not that is in next one by using a using a separation optics like a dichroic mirrors ok. So the problem is that the intensity is very small.

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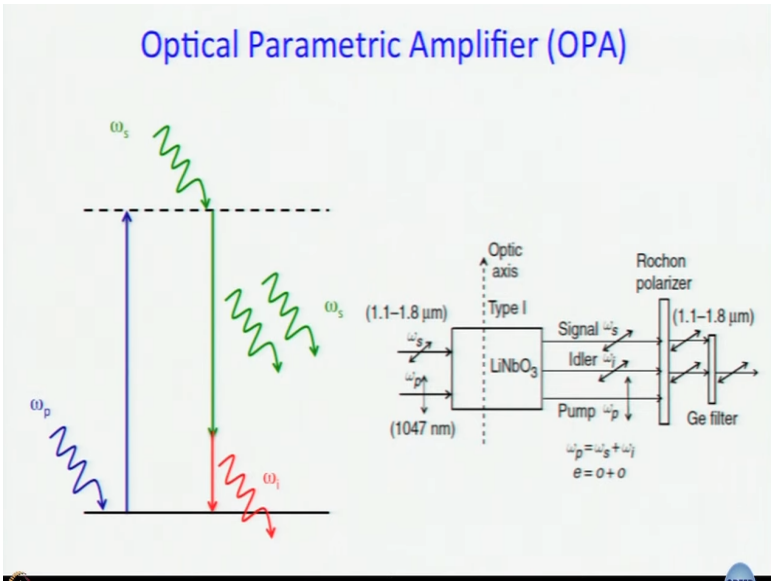

So when intensity is very small you want to amplify it and that brings us to the principle of optical parametric amplifier. And when we discuss optical parametric amplifier actually 2 phenomena come to my mind when we discuss this one is Raman effect the other is stimulated emission. You see why I am saying this. So what you see in this diagram here is you have a stationary state ground state and you have a virtual state at higher energy compare to the ground state ok.

Let us say that the pump frequency promotes the system to this excited this virtual state ok. So omega p takes this system to this virtual state here. Now let us say and that is why this reminds me of the stimulated emission let us say by some means I already have a little bit of omega s in the system ok. Now what will happen? Sort of stimulated emission ok see if you sort of stimulating emission would take this system from this higher energy virtual state to a low energy virtual state difference in energy between which would correspond to the frequency omega s right.

So this is what you get instead of one now you get 2 photons. The photons that are part up the virtual state with higher energy and the photon that is generated as a result of lowering the energy

from the high to lower energy virtual state. This is why it remains the stimulate emission. And you can see where amplification comes in here right. One pump photon sorry one signal photon came in and two are produced right.

Now what happens to the remaining energy? Omega p - omega s what would that be equal to omega i idler that would also come out automatically right. This is how this is the very basic principle of optical parametric amplifier. Now if you think a practically where will we get omega s from and then I want a tunable source right. So I might want as many possible values of omega s as possible. The best way of trying to do that is to generate white light.

Now we are familiar with this concept of the white light generation we know that if we focus and intense femtosecond pulse on a substrate like calcium fluorite or your sapphire earlier experiments done by focusing picosecond pulse on water due to mixtures. Then you get something called self phase modulation and white light is generated. Of course white light intensity will be nothing compared to the laser light.

But we do not need a high intensity. We only need some photons that are going to cause this downward transition. So a good strategy of a building an OPA would be you take your light laser light say 800 nanometer light out of an amplified out of an amplifier Ti sapphire amplifier split in into 2 parts. Focus one part on to a some substrate there sapphire filter ok generate white light ok. Then of course you need optics to collimate white light and all.

Then on the nonlinear crystal focus that white light and focus the residual part of the output of the amplifier. Now what will happen output of the amplifier is going to serve as omega p. All the components of white light can be principle contribute can act as omega s. But by a angle tuning the crystal and of course that we are maintaining the same temperature you can select preferentially which of this frequency of white light is going to act as omega s right.

So by angle tuning that is what happens in an OPA by angle tuning you can select the signal frequency. And the idler is generated any way ok. So you have actually generated 2 different colors already. Now you decide whether you want to work with the signal or the idler. Generally we prefer to work with signal sometimes due to some problematic combination of optics and all the signal may not be all that accessible.

And if you are fortunate that the idler frequency idler intensity is that is enough then you might actually end up working with the idler that is point number 1. Point number 2 is sometimes you want to work with idler, when do you want to work with idler what is a output of your Ti sapphire amplifier 800 nanometer model wavelength so that is red. What is the constitution of the white light all visible is not it?

So typically your omega s would be in the visible range. Suppose you want idler light how will you get it? Using all this if you want for some application suppose you want to do an IR probe experiment or suppose you want to do an experiment IR pump and IR probe experiment something like that 2DIR. Then the only hope of generating IR from this essentially visible light giving system is to work with the idler right. So the frequency of the idler is essentially the difference of the frequencies of the pump and signal is not it.

So this process is called optical parametric amplification O OPA it is also called difference frequency generation DFG ok. So what it essentially done is that if you have right optics then in fact it gives you tunability from anywhere to anywhere. What you could do and what is done in commercial amplifier a commercial OPA as might discussed in the next module is that first of all you have nonlinear crystal by which you do second harmonic generation. That give you access to blue and maybe even UV.

You do third harmonic generation 800 / 3 how much is that? Is the magic number you have to know 800 / 3 you neither do arithmetic quickly or you have to know 267 right 266 that is the magic number third harmonic. See third harmonic, second harmonic, fourth harmonic this when you are into lasers this thing will occur to you automatically. 1064 is a magic number is a magic term Nd:YAG fundamental 532 second harmonic then third harmonic of that and fourth harmonic of that all this number will come first automatically. So on one hand by a higher harmonic generation you can access UV right.

And not only that you do not have to be restricted to only the harmonics now you can do this and generate signal in blue or maybe even UV on the other hand if you use the fundamental of the amplifier 800 nanometer as omega p then you can get things in red and the difference frequency can give you IR. So that is why an optical parametric amplifier a single optical parametric amplifier

which is properly a equipped with the right crystal and right optics and in good shape can give you tunability from 200 nanometer all the way to IR.

That is the a strength of this the piece of instrument ok. And the principle if you do not go into a very deep of it the qualitative discussion of the principle is quite simple ok. So again this is an example of one stage of an OPA typically OPA's would have several stages but this is something that is there and this on the usual text book that we use. So let us say this is omega p 1047 nanometer and this is omega s 1.1 to 1.8 micro meter 1.1 micro meter means how many nanometer 1100 nanometer.

So first of all I do not understand why this is 1047 nanometer and why that is 1.1 micrometer I do not know but we should not think that this is 1000 and that is 1 that is why I want to I wanted to make this. So here in this system that we discussing actually your pump and signal have not very different energies. Now the thing to note is the difference in polarization and that has a role to play later. The pump is vertically polarized the signal is horizontally polarized ok.

And the idler you will produce you are using lithium niobate you remember what we have discussed in earlier once. In $LiNbO_3$ we have e o o kind of situation. If you take pump signal and idler. So the idler that will be produced will have the same polarization as the signal not the pump. So you change the temperature you angle tune it you do whatever you want until you get signal and idler right.

Signal and idler had the same polarization pump has perpendicular polarization. Now it is very easy to take the pump out. Just use the polarizer. Here they use a Rochon polarizer you can look up for a Rochon polarizer that is basically the same as Wollaston polarizer you have calcite or something which is cut into 2 and then joined in the regular stuff that you are studying in organic chemistry rotation of polarization polarimeter that kind of thing.

So first of all when you use the polarizer the pump gets cut out. And then depending on what you want? You want the signal or you want the idler you are going to use a filter. The filter that is shown here is the germanium filter which you will allow the idler to go through this smallest energy. And it will not let the signal to go through ok. You can always use a dichroic mirror to send the idler one way and the signal the other way. That way you have access to both ok.

So this is the principle of optical parametric generator and optical parametric amplifier what we have in our lab is an OPA not an OPO. OPO is generally operated at much higher frequencies similar frequencies as your Ti sapphire oscillators. So OPOs are very good for a thing like up conversion experiments femtosecond up conversion femtosecond optical gating. Thus they can give you a continual tune tunable range of wavelengths at high frequency 80 megahertz.

That is what you need for your fog kind of experiment but in pump probe generally one wants to use OPA because you need higher intensities right. And OPA's once again they are limited by the frequency it goes and the OPA's is also have their own limitation and not all the OPA's are work at all frequencies. Typically you want to use an OPA which can work at the frequency of the output of the amplifier which in our case is 1 kilo hertz right.

So typically OPA's are associated with higher intensities higher number of photons I want to say I do not want to say energy because we will all confused with h Nu higher number of photons let us say and lower frequencies whereas OPO's are usually associated with lower number of photons but higher rep rates ok both have their own advantage both have their own application and both are equally costly. Actually, an OPO is I think more costly than OPA.

As you know amplifier of course is more costly than oscillator because it contains an oscillator it has to cost more. But if you want an OPO that is why we use OPA everywhere OPO's are not all that common because OPO's are actually very expensive. And if you have a shorter enough pulse or a Ti sapphire oscillator with this sealed Ti sapphire oscillator where now have a continuous tunability very often people do not care for OPO anymore.

But some application it might be required ok. So that is what I wanted to say about OPAs in the next module we will briefly discuss the construction of the OPA that we use and then we have discussed instruments for a long time we want to discuss some actual experiments classical experiments that have been done. We will next go on to 2 experiments one is Ahmed Zewail's experiments that got a noble prize in 1999.

How much time does it take for a bond to break and how does the bond breaks? What you called snapshot of bond break we will discuss that in the module. Then I want to talk about a water a little

bit because water is my favorite subject and any case our life is based on water. So 2 things one is solvation dynamics in water flaming's works the other is how a vibration energy is transferred from one mode to the other in associated water molecules.

That is a Eric's nbbering's work perhaps to stop with to stop this section with Eric's nibbering's work on a visible pump higher probe experiments. Then depending on how much time we have I want to tell little bit about pulse shaping and I want to talk about a 2d experiments. If you get time we will talk about terahertz experiment as well. A purpose of this course is that we want to have an overview of all the kinds of different ultrafast experiments that a chemist across the world are doing at the moment.

We are not going to talk about atto-second experiments because until now I believe that there is no chemistry in atto-second it may be a little atrocious statement to make. But then after all the reason why I am saying this is that it takes a hundreds of femtoseconds for a bond to break and chemistry starts with bond breaking. So faster than that there are interesting phenomena they can be state to state dynamics. But at least in this course we are not going to talk about atto-second spectroscopy because that requires a different level of understanding.

But these are the experiments we want to discuss and while doing that we have to come back to instrumentation little bit after this because I want to talk about pulse shape. Because many of you might end up in laboratories where you have to do pulse shaping when you want to do 2d experiment pulse shaping becomes extremely important. So we will talk about that little bit ok. so much for today.