Ultrafast Processes in Chemistry
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Lecture # 13
Femtosecond Fluorescence Upconversion 3

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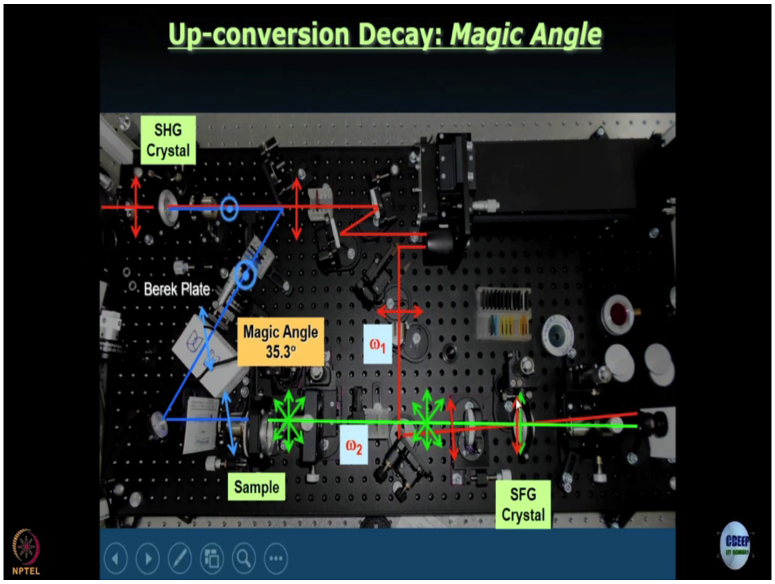

Up-conversion Decay: *Magic Angle*

So this is where we had left off in the previous class with a something called Magic Angle. And what is that? Once again, we want to deal with it briefly because we intend to come back to the issue of polarization of fluorescence in a little more detail later on to keep it very brief. Generally you excite using a linearly polarized light. And you do that because, first of all the laser that you use is usually linearly polarized. If you are talking about a Ti-sapphire laser, it is very nicely linearly polarized.

If you are working with diode laser, of course, you cannot work with diode laser for upconversion, diode laser usually is elliptically polarized, which means there is a mixture of horizontal and vertical polarizations there you put in another polarizer and generate one kind of polarization. So, when you excite with polarized light, then what happens is photo selection for the selection means only molecules that have a component of whose dipole moment has a component along this direction is going to get excited come back to this a little more detail later on but the issue is this.

When you excite and then when florescence takes place, even though you excite with a linearly polarized light this one the fluorescence that comes out is actually depolarized to different extent depending on your sample medium and so on and so forth. And I hope it is not very difficult to understand what these jumping targets are. What it means is that generally not generally always, when light polarized light is incident on a nonlinear medium, then the harmonic that is generated undergoes a 90 degree shift of polarization.

So, what you see here, the red double arrow here the polarization is in the plane of the red road, the blue light has polarization in perpendicular direction. So, the problem is this, you have depolarized florescence coming out but then depolarization can take place by many different mechanisms, rotation of the fluorophore while in the excited state being a major one and that brings something like a risetime in the decay, unless you are careful after all when you excite the molecule has this kind of polarization, where it emits it has say this kind of polarization.

Then this state was not even there, which has grown over time after excitation that can show up as a risetime. In fact, if you measure at 90 degree polarization with respect to the excitation polarization, you do get a risetime distinctly. And then if you measure at parallel polarization, then also you are not safe because this state of state with this kind of polarization undergoes and additional decay because this one is being formed. And that decay is not the decay of the excited state. That decay is just because of rotation of the molecule.

So if you measure a long parallel polarization, then you are going to get a very fast. So crux of the matter is because of rotation of the molecule while in the excited state, you are going to have additional fast decay or rise in your decay in your transient. Rising decay sound foolish? How do we eliminate that? We are going to do the math a little more detail later on. But for now, let me just tell you that there is this angle 54.7 degrees, which is called a magic and you might be wondering why I am saying 54.7 when the magic angle written on the slide is 35.3.

You understand that do a very simple bit of math, subtract 54.7 from 90 degrees, what do you get? You get 35.3. So 35.3 because 35.3 is what you maintain with respect to the fundamental red light, so that the angle with the blue light is 54.7 degree. What happens at this magic angle? So, once again, skipping the math for now, let me just tell you that this rotation thing has a 3 cos square theta - 1 term. And when theta is equal to 54.7 degrees 3 cos square theta - 1 term is 0.

So this is the angle and that is why it is called a magic angle where the fast decay or fast rise due to rotation is not observed. So what you see in your transient is just the time evolution of the electronic excited state irrespective of orientation. That is why when you record lifetime or by a upconversion, you always have to measure at magic angle. Otherwise, you are going to get additional spurious components. And rotation is only one thing if there is homo fret you are going to get a rise. So, magic angle is what you have to maintain.

And magic angle does not mean angle between the beams, it is the angle between polarizations that is usually achieved by something called a Berek plate, once again, will not go into that at the moment later on. If there is time for discussing optics, and a little more detail, we will come back to that. It was just say that berek plate it is something that rotates the polarization and you can rotate it to 35.3 degrees with respect to blue, will you rotate the polarization of the blue light by 35.3 degrees, so that you only look at fluorescence of this polarization. Magic angle to the fundamental.

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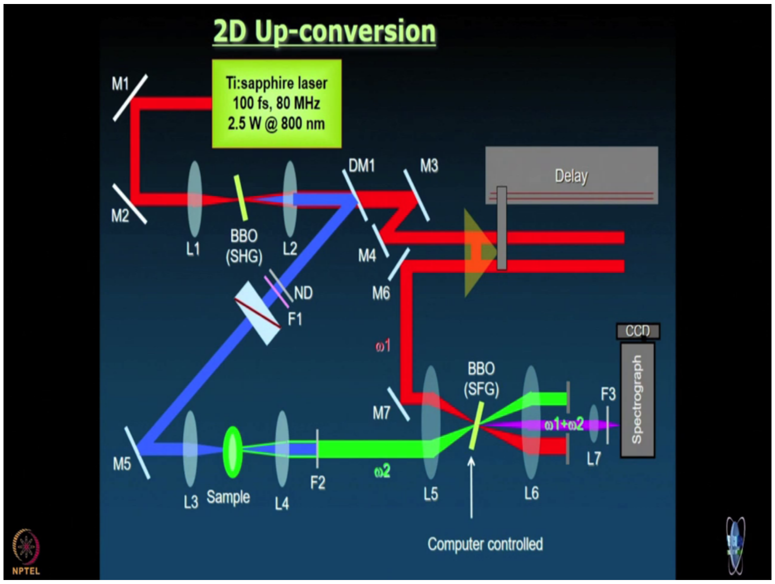

2D Up-conversion

Ti:sapphire laser
100 fs, 80 MHz
2.5 W @ 800 nm

Computer controlled

Next let us move on a little bit and talk about something we did not have in our lab. See in the experiment that we have discussed so far, you have to suppose you want to know how the fluorescence spectrum evolves with time, we have had a discussion of that in the one of the previous modules. So, then you have to go wavelength by wavelength emission wavelength by emission wavelength and every time you have to record a decay stop, then go and change the angle of the SHG crystal start the experiment again.

So, all these can be made a little simpler, if you do what is called 2D upconversion, it also comes in 2 different forms. We are discussing this the simpler form now, if there is time we will talk about the more interesting form later on, but for that will need some knowledge of nonlinear optics. So, we are postponing the discussion. So, especially the group in Switzerland, what they have done is that they have attached a computer control to the sum frequency generation crystal.

So, now, remember the only thing that one thing that changes about the sum frequency generation crystal is that you have to change the angle. So, in this instrument first of all it is calibrated and the angle for all different wavelengths is determined that what is the angle for 600 nanometer what is the angle for 605 nanometer so everything is calibrated and fit into the computer and then the rest is simple. Start the instrument and say that you are going to measure at every position of the BBO crystal for a certain amount of time.

So, understand what is happening first, your computer sets this BBO crystals the SFG crystal at a particular angle, that means your omega 2 is selected omega 1 is constant. Anyway, there, now you scan the delay so you get a transient. Next, you go back and change the position of the BBO crystal. So instead of omega 2 A, your system is tuned for omega 2 B you recorded transient once again for the same amount of time, when I say the same amount of time, I do not mean integration time.

I mean total acquisition time, half an hour, 1 hour, 20 minutes, 5 minutes, whatever. So for every angular position of the SFG crystal to record a transient. But the trick is you record the transient for a given amount of time you program it in such a way that all decays are recorded for 5 minutes each or 20 minutes each or something, all of them? So now, some decay will be like this some decay will be bigger depending on the emission wavelength. So now the intensities are believable, since you are recorded for the same amount of time. So now you get this kind of a plot.

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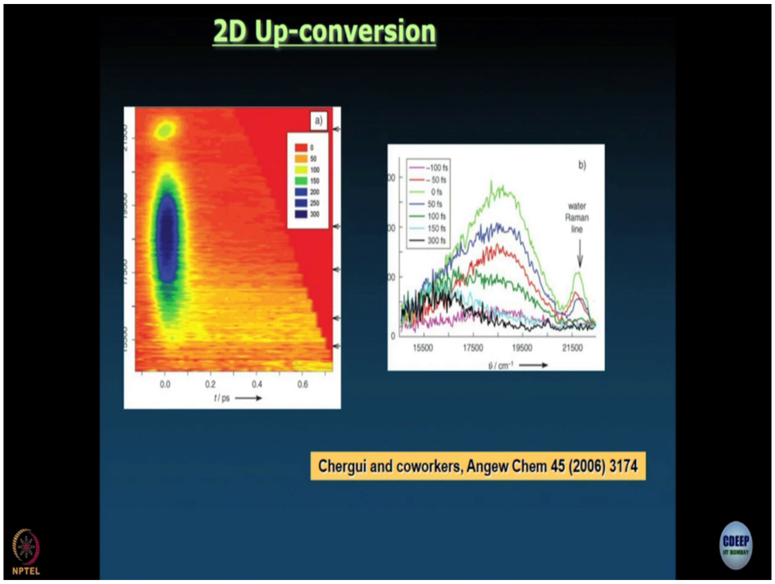

2D Up-conversion

Chergui and coworkers, Angew Chem 45 (2006) 3174

You see this is a 3d plot here it is color coded, X axis is time. Y axis unfortunately is cut, but y axis is wave number, of emission. So if you take a cut along this direction, what do you get? If you get a horizontal cut, then you are keeping the emission frequency constant. And you are looking at time evolution. You get the decay, and that is what you are measuring actually anyway. If you take a vertical cut, then what you get in the spectrum, rating, vertical cut, what am I doing? This is 0 time.

You go from bottom to up, you get these 0 times spectrum. Now when you are at .2 picosecond, you go from bottom to up. You get this spectrum at point 2 femtosecond. So from this plot, you can take this cut or this cut and get either decay at a particular emission wavelength or emission spectrum at a particular time. The problem here of course, is deconvolution. If your pulse is not so small, if it is 300 femtosecond or so, then at least for the first 1 or 2ps, you get a spectrum that is convoluted.

So that is a little bit of an issue. But otherwise, this is a convenient way of doing it. If nothing else, this allows you to get the decays across the entire spectrum. And after that, if you are, if you want to include convolution, you do what we did earlier convolute. Well, de convolute get the lifetimes using the lifetimes and steady state spectrum, generate the time dissolved emission spectrum. And in fact, even the setup we have, or the setups that are there in different labs of India, and in principle, be converted into this 2d upconversion.

It is not such a big deal. You need a Lab view program, which is going to drive this and will interface with the existing program. We you write program for the entire thing. The other way so if you read this paper and you came published in 2006, Mr. Angew Chem by chergui, this is what you see. But then, if you read the work of the terazema and co workers what they do is that they use a very thin sum frequency generation crystal and it is such that this angle tuning is not even required.

So, there you actually record the entire spectrum in 1 shot. You use a spectrograph CCD kind of arrangement to detect the entire spectrum at different positions of delay. That is a smarter way of doing it, but we would like to come back to it later on, if you have gained sufficient understanding of your nonlinear optics. Before concluding this discussion, it is important to understand where we can make mistakes.

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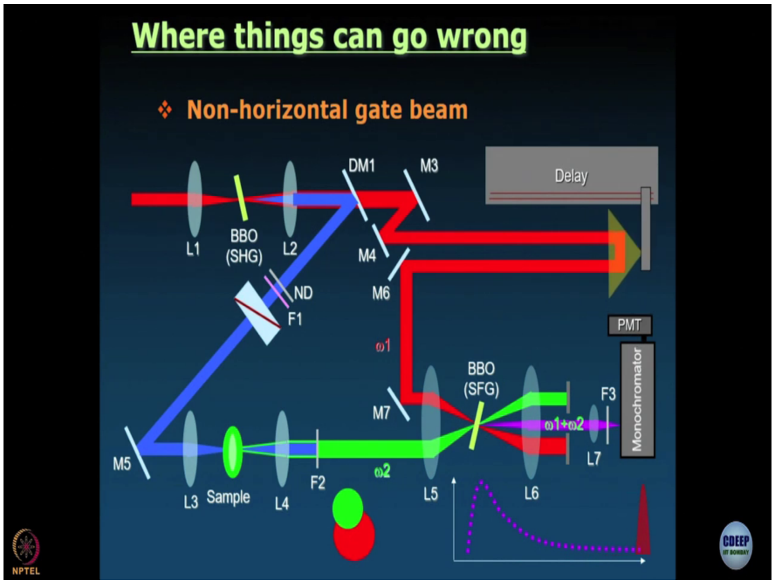
Where things can go wrong

- Non-horizontal gate beam

First mistake that can come and this is something that one needs to be very worried about is if the gate beam is not horizontal. Let us go back to the schematic. Remember, this decay that you are generating this map of the fluorescence decay is actually raw values of intensity. It is not a relative value anything and remember what we said earlier that this intensity of sum frequency is sort of product of intensities of omega 1 and omega 2 beams.

One thing that we have not bought into the discussion so far and now we should is that we do not need to worry about the actual spots on the BBO crystal of course, is showing you a very enlarged picture here, but let us say that this red circle is the spot of omega 1 on the BBO crystal and let us say that this one is omega 2. Here the way I have drawn it the spatial overlap is perfect. All of the intensity of omega 2 is in a region where omega one intensity is there.

And of course, these spots are usually if you think spatially they are gaussian which means that the intensity would be maximum in the center and fall off to the sides. Now let us see, this is the situation or if you understood what went on, I will go back. Let us say that this is omega 2 beam, this is omega 1 beam that is coming in instead of coming horizontally let us say it comes like this, what will happen? As I change the path length, this is what will happen. If it is horizontal, it does not matter, let us say the pulse is here, well for the sake of discussion, lets say I am talking about 1 pulse which is here.

It does not matter moves like this, then what will happen? Spatial overlap will get worse? That is what we are shown here, you start with perfect spatial overlap, but let us say omega 1 is not coming like this, it is not horizontal, and then as it moves the overlap will become poorer and poorer. So, effectively intensity of omega 1 does not remain constant. And effectively always, unless you start from a very bad spatial overlap, always what will happen is that as the stage moves, the special will overlap will become bad. It will go from bad to worse.

So, what does that mean? Suppose you are recording for 0 time to sometime time t dash, spatial overlap keeps on getting worse at every step. So you can think that intensity of omega 1 is decreasing for every measurement. So that adds another spurious component to the decay of the sum frequency intensity, you are going to get always. So your decay is always going to look faster than it what it should look and it is not essential that you are going to be able to resolve it, it is not essential that it is very fast compared to what you are looking for it may be something that is close and that is the most dangerous situation.

You would not even know it, but you are not going to get the correct result. So it is absolutely important to ensure that what we say the stage is flat which means this omega 1 light beam is flat. How do you do that and that is where the role of M3 and M4 is coming. All mirrors have 2 controls horizontal and vertical. If you touch 1, the beam moves horizontally if you touch the other the beam most vertically. So what you do is by playing around with the controls of M3 and M4 for you ensure that the beam is horizontal.

How do you ensure the beam is horizontal? The crude measurement is user ruler and ensure that it is at the same height from the baseplate everywhere. That is what you should do first. Secondly, what you can do is you can put an additional mirror somewhere here and take your beam to a distance and put it on a wall and then move this delay forward and backward. Look at the spot on the wall. See if it is moving vertically or not. It should not you should keep on playing around with M3 and M4 until, for delay being here at the minimum position and here at the maximum position, your spot on the wall does not move.

That is the best way and the most strenuous way of doing it and bigger the stage you work with worse it becomes. Now let me ask you a question. This spurious fast component I am talking about, does it show up for smaller times, or longer times? Shorter times longer times? Definitely longer times. So it is a long component that is going to be affected. If it OK is that you work within 2 picosecond if your decay gets over into picosecond, of course the other problem for a decay that gets sold 2 picosecond is that they will be hardly an intensity that is a different issue.

But suppose it gets over in 2 picosecond then even if it is a little away from the alignment, it will not matter. But if you have to move your delay line over a length of 15 centimeter 15 centimeter is 1 nanosecond, then it is simple. So in my opinion, the best way of doing it is to put it on the wall. But now, with the advent of technology, you can do other things. What you could do is remove this BBO crystal or if you are scared to remove the BBO crystal, at least put a lens we put a mirror here and use a webcam put this of course before putting it on the webcam, if you value it with a lot of neutral density filter so their intensity is as low as possible.

You are working with the laser. So just put it on a webcam look at the output. Good thing about this method is that if you put a spot how what is the thickness of the spot? Millimeter less, about a millimeter let us say that spot, if you use a webcam on your computer screen will look this big. So you look at the spot it look like a white spot, white circular sport and move the delay line and see whether the spot is going up and down.

Since your spot is the magnified so much there is no need to put it on the wall. The reason why you put it on the wall is that remember this l equal to r theta. The distance that you see if this is an arc, the length of the arc is equal to radius multiplied by theta. So we need a long distance. So as to have a observable value of l. it is like lamp and scale, arrangement galvanameters that you might have used during a BSc or something in physics labs, but you might as well use a webcam, it is not advisable to use your iPhone you can use your mobile phone actually.

But then we are using a laser, one phone camera might go bad. So just exercise caution, but no matter what you do you have to ensure always that the beam is horizontal. And you cannot think that I saw it always on that it is horizontal today. Therefore it is going to remain horizontal one year later. You do not have to be so paranoid as to check every day or once every two weeks is good practice. You have to ensure that this gate light beam is horizontal. Otherwise, all your measurements are going to be wrong.

Especially when you are talking about longer times so that is the biggest thing. That can give you a wrong result non horizontal gateway. Second thing is magic angle and if you magic angle is not setting properly and setting the magic angle is a bit of a bother because berek waveplate is a little tricky thing. But you have to learn it and you have to do it because if it is not at magic angle now which component will be affected, the short component has to. third thing is something that usually we do not have a problem with is laser stability and power.

Generally Ti-sapphire laser of the present generation are extremely stable in their output. If you keep them on for 3 days, the output does not change. But if your laser is fluctuating then you actually cannot do the experiment. It is very important that your laser is stable throughout the experiment because do not forget you are working with actual intensity not relative intensities. So that is it that completes our discussion of femtosecond optical gating.

We have talked about this TCSPC already there is a go between there is something called streak camera which gives you time resolution which is better than this TCSPC but not as good as a upconversion it is very expensive but very convenient. Unfortunately, we do not have 1 in IIT Bombay, but there is 1 in IISER PUNE. So next day, what we do is we briefly talk about how the camera works and maybe we leave it for a little later.

Next day, let us go back a little bit to the basics. There is all this while we are saying that we are going to use a laser that has hundred femtosecond pulse and so on and so forth. How does one produce 100 femtosecond pulse or 6 femtosecond pulse? That is what we need to learn. To do that we have to go back even further to the basics, it is always good to start at the very beginning. So, in the next module, we start talking about the absolute basics of lasers will start with Einstein's formulation of the problem of absorption and stimulated emission and spontaneous emission.

And from there, we will try to see what are the components required to make a laser and what kind of systems can give you lasing after that, we are going to learn about what are called modes of lasers. The 2 kinds of modes, transverse modes and longitudinal modes, we learn about the modes. And then we will learn how one can lock the modes together to produce pulses. So there is a theory.

Then we are going to learn about pieces of equipment that can actually do this mode looking for us. Actually, for femtosecond lasers, you need nothing. They get modelocked by themselves because of a magical phenomenon called thermal lensing kerr effect. But if you want pico second process, you have to work a little harder will learn and you have to do what is called active mode locking will learn active mode locking, because there are some devices that use which are used later on when you talk about amplified lasers.

So we learned about things called mode lockers and q switches when we are done with all this. Then we come back and talk about what is there inside the titanium Sapphire oscillator. And how do you amplify pulses? Then we hope to go on to optical parametric amplification. So that is quite a bit of work cut out for us. But before we do all that next step is to go to our lab and have a look at this femtosecond optical gating instrument that we have there. That is what the next module will be about, we are done for today. Thank you very much.