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MOLECULAR SPECTROSCOPY: A PHYSICAL CHEMIST'S PERSPECTIVE

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LECTURE NO. – 03
Sensitivity Light Collection and Signal to Noise Ratio

Now we'll begin, we'll discuss two topics today, first of all we'll complete our discussion that we have had about frequency domain spectroscopy, then we will move on to time domain spectroscopy.

Now one thing to do whenever you do any measurement, or whenever you do anything is first of all you have to understand how good a measurement that you are performing is. And the second thing that you have to worry about is how much light you collect, so how good and how much? And as we'll see in the next few minutes how good and how much are very often in, don't act in each other's interest, if you try to make a good measurement you have to compromise on the amount, if you want to collect a lot of photons you have to compromise on quality more often than not. So to make a good measurement you have to somewhere strike a balance between these two.

So let us start with how good, how do you make a measurement, what is the meaning of a good measurement when I talk about frequency domain spectroscopy, what would be the meaning of good, accurate, sensitive? What is the meaning of that? I should be able to differentiate between two wavelengths or two frequencies that are very close to each other, that is a precise measurement, see if I can differentiate with confidence between 2,893 centimeter inverse and 2,894 centimeter inverse, right, that is one level of making a good measurement, right.

Suppose now I can make a difference between, well I've forgotten the other two numbers that I cited just now, so I'll make up new numbers, 2,538.5 centimeter inverse and 2,835, I said 2,835.6 centimeter inverse, that requires a greater degree of accuracy, right, so how do you do that? First of all, let us go back to our good old friend Black's law, we know Black's law, lambda = 2d sin theta, why am I writing lambda, not L lambda, because N = 1 is the strongest scattering anyway, so we're only working with the first order scattering. Second order, third order scattering is actually a problem when you make emission measurements, if in case you have recorded fluorescence spectrum sometime you might have come across this problem, okay.

So let us talk about two wavelengths, so lambda 1 = 2d sin theta 1, lambda 2 = 2d sin theta 2. Let's say delta lambda is lambda 1 – lambda 2, let us say delta sin theta is sin theta 1 – sin theta 2, of course it's not very difficult for you to see that delta lambda = 2d delta sin theta, simple, no issue with that, so in other words we can write delta sin theta divided by delta lambda = 1/2d, does this equation give us an idea of what we need to do in order to make a good measurement? Let us for quick a given value of delta lambda for a given value of delta lambda, do you want delta sin theta to be large or do you want it to be small? Small or large? You want it to be large, because you want the thetas to be different so that you can detect better, isn't it, I'll be clear about this, for a given value of delta lambda you want this delta sin theta to be large, because then only you'll be able to differentiate, if this is delta lambda, is it easier to tell between this two, or is it easier to tell between this two if this is delta lambda? This right, so you want this, for a given delta lambda you want this to be large, so if this ratio is to be large is it better to have a larger D, or is it better to have a smaller d? Smaller d, right, so that is the first thing.

Smaller d gives you a better resolution, what is d by the way? Independent distance, right, now there was some questions after the class yesterday but somebody asked me that why do you even need something that is ruled, so suppose you take a crystal, a crystal of salt sodium chloride, right, and you can kind of make a smooth surface out of sodium chloride crystals, right, that would look like a mirror, plane surface no ruling that we can see, but even there you have ions which have some kind of D, and we are now saying that small d is good, so why can't we not use say a mirror made out of sodium chloride as a grating for visible light, the reason is this D also there is some other condition, too good is no good that is something that holds for all kinds of measurements, not only spectroscopic measurements too good is no good.

If D is too small, your D has to be compatible with of the same order of length as lambda, then only you'll get good diffraction, okay, otherwise you lose resolution, but within that limit smaller d is better, okay, that is why the gratings that we use, let us say we are most comfortable with a visible spectroscopy right because that's what we can see, visible spectroscopy has a wavelength of how much, 100s of nanometers, right, how much can you see? Say 400 nanometer to 750 nanometer, if you have very good eyes you can see 800 you can see actually, even I can see 800, so I'm sure anybody can see, so up to 800 nanometer, 100s of nanometers so this separation between the lines on the grating has to be of the order of 100s of nanometers, right, but within that if the gratings has lines that are closer then you'd get a better resolution than in the case where gratings have lines that are further apart, that is the first eco message, okay, so that is about the grating, but just grating is not good enough, if you remember what does the mono-chromator consist of? Tell us, mirror, and grating of course then okay lens actually can be replaced by mirrors, so well some focusing device and what else? Slit, slit is very important right, if you don't have a slit all the ambient light will get in, of course very soon we are going to talk about a situation where we don't use the exit slit, but we'll come to that when we come to that.

For now slit focusing element and grating these are the components of the mono-chromator, so it is not just enough to disperse, your slit fit also has to be small enough.

Let us say, let us consider the situation and not draw the grating and all, but since you're already familiar with the diagram I think you can understand that what I am drawing here is that this is one wavelength say lambda 1, this is another wavelength lambda 2, focus at different points on the focal plane of the second concave mirror, right.

Now see suppose my slit width is like this, this is my slit then what will happen? Lambda 1 and lambda 2 will go through the slit together and this is where you detector is, so the detector is going to detect both the wavelengths, so you'll not be able to differentiate between lambda 1 and lambda 2, so even though you might have used a grating in which the lines are very close together so dispersion is good enough, you still don't have A an accurate measurement because your slit width is too much.

What is the way out? How do you solve this problem? By making the slit width smaller, now if I make the slit width small enough something like this, then what will happen? In this situation lambda 2 is blocked, lambda 1 gets through, now you can differentiate between lambda 1 and lambda 2, so in the first situation you spectrum would be something like this, let us say this is lambda 1, this is lambda 2 you'd get something like this, at most like this in the first situation. If you slit width is good enough, small enough then you can expect to see something like this. Are we clear?

It's broad spectrum with maybe a little bit of structure is what you get when you have a large slit width. When you have a smaller slit width then you get more structured accurate spectra, okay, so two things that we've learned so far to get a good detection, one is D has to be small enough, second thing is slit width has to be small enough, okay.

Now let's move on a little bit, as I told you a little bit ago, little while ago too good is no good, right, there is nothing that it can give you perfection if you do too much of it, so you might think that if you make the slit width smaller you make a more accurate measurement, you're right, but there is a limit to that as well.

Now tell me what is the problem with making the slit width smaller, what happens when, what is it that you give up on, what is it that you don't do all that well when you close the slit more and more? Intensity, right, so you collect less amount of light, that's a problem, and if you just let this completely close, then no light gets through at all, okay, so there is always a compromise, okay, so light gathering power that is also an important thing. Let me just call it LGP, how much light, so that is why our heading of the present discussion is not only how good, but also how much, so how much of slit width you'll use, what kind of slit width you'll use depends on not only how accurate a measurement you want to do, but also on the practical consideration what is the minimum amount of light that you need to get what is called a good signal to noise ratio.

Any kind of measurement is associated to the noise, where does noise come from? What is the principal on which this photo detector works? Photoelectric effect, so essentially if you want a photoelectric effect to happen, or what should be the property of the surface on which the photons fall? Work function should be high or low? Now let us that give a hint, the moment you've low work function, don't forget too good is no good, some problem occurs, what is that problem? Yeah, yes, what kind of lower energy?

What is thermionic emission? Thermionic emission is ejection of metals, yeah, electrons from the metal surface due to heat right, now the thing is you perform an experiment you don't always go to south pole and perform the experiment, you want to do it in Bombay, right, and Bombay room temperature right now it's a little pleasant, but even then it is about 26, 27 degree, right, if the work function is low enough, that is what you want to do, right, you want the sensitive detector, you want the low work function of the material, but then if the work function is low then you have the problem of thermionic emission as well, this 26, 27 degree temperature that is good enough to give rise to electrons being ejected from the photocathode even if there is no light, okay, that is one of the sources, one of the major sources of noise.

How can you get rid of that? Yeah, cool the detector, how do you cool the detector? Using, yeah, what would be a suitable coolant? Well, they have many suitable coolants and you can do it without coolants also, very often detectors, so let me just write that down signal to noise ratio, noise mainly from thermionic emission, and the way to get rid of thermionic emission, one is you can decrease the temperature, you can do it in two ways, first is you can use the suitable coolant, and the coolant of choice usually are liquid, sorry dry ice, you don't want to use the ice right, because ice melts and it becomes water and water contains dissolve salt that would conduct and it will give a lot of problem, so dry ice is one suitable choice of detector, if you want to go down further you use liquid nitrogen, liquid nitrogen 77 kelvin, yeah.

Which one are you talking about? Well usually we don't use cool detectors unless you want to make very precise measurements, okay, but there are some detectors that are cool but most of the things that you see are operated room temperature, so there is significant noise.

Now there is another way of doing it, how do you decrease temperature without using a coolant? Peltier effects, seebeck effect, do you know this? Peltier effect, you've got two junctions right, apply a voltage, maintain one at a particular temperature, right, you will develop a particular temperature in the other junction, so peltier cooling is a very popular neat way of doing it, alright, so this is what it is.

Now so we have diagnosed a little bit, but we are saying is you want to make a precise measurement, you want to shut down the slit as far as possible. If you shut down too much then the problem is light gathering is not so good, so you have to always do it at an optimal setting, okay.

Now there is another important issue here, remember what we said in the beginning, all components of mono-chromator have a role to play here, we've talked about the grating, we've talked about slit, but let's not forget there is something else as well, what is that something else, this focusing element, the mirror, right, now see the problem is this, let me erase this one, here is your detector, right, sorry, here is your mirror, and let us say here is your source, when I say source it can be the actual light source, it can be the emitting sample, or can be the slit of the entrance mono-chromated doesn't matter.

Now from here light can go in all directions, can you capture all the light that comes from the source? No, right, what is the solid angle that you can capture? How much light you capture is determine by two things, one is focal length of the mirror, right, if the focal length is long, remember you always have to keep this at the focus, if the focal length is long then you go further away and you capture a smaller solid line. And the other thing is, what is the diameter of the mirror itself, right, small mirror will capture small amount of light, large mirror will capture a larger amount of light, okay, so if focal length divided by let me write small d, diameter, this is called the F number of the mirror, one has to familiar with the F number anyway, do you know F number or not? What is F number? Are you familiar with F number? Have you encountered it somewhere outside the lab? Cameras, you don't have to go as far as cameras, look at yourself in a mirror, you wear glasses, so what is the power of your glasses? It's -7.5, what is that? Isn't that something to do with the F number? Yeah, so F number is important, so actually light gathering power, if I remember correctly is proportional to 1/square of F number, okay, so this is also very important, so as you see all components of mono-chromator have important roles to play in how good a measurement you make, and how much of light you detect? Both are important aspects, a good measurement is a reasonable compromise between the two, alright.

So now we have spoken enough about the mono-chromator, let us quickly talk a little bit about the detector before we end this session and prepare for the next one on the time domain spectroscopy.

But well to talk about the detector once again I need to go back to the mono-chromator, and I need to draw those arrows once again, and use different colour chalks to make it more dramatic, okay, that is dramatic enough. Let us work with this three wavelengths, I want to detect different wavelengths, as we've said one way of doing it is to use an exit slit, as everybody understands what I've drawn here right, this three pairs of lines, pairs of rays of different colours, what do they stand for? They stand for 3 different wavelengths, where do we get it from? After the grating we have put a concave mirror and that concave mirror is focusing different colours at different spots on the focal plane, alright, and we keep the slit on the focal plane depending on where they come, which light falls on the slit we detect that one, that is one way of detecting it. This kind of detector is called a single point detector.

Examples of single point detector are photodiode and what is called photomultiplier tube, in short PMT, now discussion of this how photodiode exactly work, how photomultiplier tube exactly work on interesting, but then if we start engaging in that this will become an instrumentation class rather than spectroscopy class, so we will not try to do that, whoever is interested for starters you can just read, whatever we are discussing now until today, if you are interested in further detail you can read this book on instrumentation by Skoog. Skoog and two other authors but then I forgotten the names of the other authors, the Skoog's book contains all this, if you want you can read it, if you want to discuss you can come and discuss, but of course that's running the syllabus of this course.

So if you put a single point detector, how do you detect then? As we discussed you scan the grating, right, you move the grating, change the tilt, so as you move once yellow light goes through the slit, once blue light goes through the slit and once this is orange right, okay, yes I'm really proud of myself because I could understand that it is orange, so depending on the tilt blue or yellow or orange light goes through, alright, so this method of detection is called detection using a single point detector and what is called a scanning mono-chromator.

Now when you record the spectrum what do you do? You say record from this wavelength to that wavelength, right, and then what happens? The spectrum gets built point by point, and while the spectrum is getting built if you listen carefully and if you don't talk to each other then you'll hear the sound, have you heard that? What is that sound? And I'm not asking you to imitate the sound but you hear the continuous sound right, it's like something is moving, isn't it? That's actually the grating moving. The sound that you hear while recording this electronic absorption or florescence is the grating tanning on its access, right.

And what it does is it goes to a particular position, stops for a while you record and that is the intensity at that particular wavelength, that is how the spectrum is built point by point, scanning. There is another way of doing it, the other way of doing it is remove the exit slit, I mean you still have a slit, but the slit is like this, very big, and instead of using one detector you use an array of detectors, so instead of a single point detector you use array detectors.

Well, we live in the state of solid state electronics and it is not at all difficult to make thousands of detectors fuse together one after the other to make an array detector, has anybody ever seen or used an array detector? Outside lab of course, no? Nobody has used an array detector ever? Yes or no, you have to say either yes or no, no? Sure, that is the right answer you have used, and if I tell you what you've used you'll kind of, I don't know what you'll be, yeah, exactly, you've never taken a selfie, how does that photograph come? Is it magic? There is a lens there which captures the image, but how is it recorded? What you have behind the lens is actually a two dimensional array detector, okay, we don't have to get into a discussion of what exactly the array is, but there also you actually have an array detector, you have different kinds of digital photography is the order of the day, nobody uses films anymore, right, and when you use digital photography don't you talk about 2 megapixel, 5 megapixel, 20 megapixel, right so each pixel is actually detector, alright. So it is not very difficult to understand what array detector is, for scientific measurements you use two kinds of array detectors usually, well you can say 3, one is A photodiode array, PD means photodiode, or you can use what is called, this is not the popular coffee shop, CCD means charge coupled device, okay.

How charge coupled device works? We don't need to know at this moment, and sometimes if you want to detects very low amounts of light you have to use what is called an intensified CCD or an ICCD, alright, there are advantages, there are disadvantages of both.

What would be the advantage of this array detection? Yes, exactly so you measure all the wavelengths at the same time so your measurement is very quick. So imagine you are trying to take a photograph, if you have to take a photograph point by point, how much time would it take? Long time, right, the one reason why you can take a photograph conveniently is because the entire image is recorded at one shot, so here also the entire spectrum is recorded at one shot, that is what the advantage is, but again recording theme of today is, yes too good is no good, so what would the disadvantage be? What is the disadvantage of array detector? Disadvantage is resolution, see the point is the detector cannot be very, very large, right, so separation between arrays is how much? Actually 0, they are like this, and then when you focus light the smallest size of the focus lights, smallest diameter is lambda/2, so you are working with visible wavelength, say 600 nanometers, smallest part size will be of diameter 300 nanometer, right, so little bit of it can go to the next detector also, so spectral resolution is usually a problem, how can you beat spectral resolution in array detection? By using larger number of points, right, that makes it more expensive, so once again you have to strike a balance all way, alright.

Last point here is signal to noise ratio, now this is something that I'll have to just tell you, when you count photons like what we are projecting that we are doing, then the noise in the measurement is equal to square root of the signal, this comes out of a poissonian noise model, if the noise model is different, of course it will be different, but this is what is usually there when you do what is called photon counting, okay.

So let's do a quick maths, when you measure, what are you doing essentially? Is it one measurement, see what we discussed that you record the spectrum point by point, in each point is it only one measurement, actually it is not. If you look at the frequency, usually you will see that maybe 10,000 or 1,00,000 measurements are being done per second, and what you see there is an average of this thousands or lakhs of measurement, okay, so computer averaging is very important to get a signal to noise ratio, why? Let us say and well every measurement gives you a count, okay, it's like that.

So let us say your signal is say 100 counts, what will the noise be? 10, what is signal to noise ratio? Yeah, 10, now let us say you count not 100, but 10 to the power 4, 10,000, what will noise be? Yes, 100, which is more than 10 of course, but what is signal to noise ratio? What is signal to noise ratio now? 100, which one is better measurement? This is the better measurement, because you see absolute value of noise does not matter, what really matters is the ratio between signal and noise, okay, signal to noise ratio is what is important not the absolute value of noise, since your noise is square root of signal, what happens if you measure more signal, noise also goes up but it doesn't go up as much as the signal, so the ratio becomes better if you measure more, alright, so this is a very brief introduction to signal to noise ratio, okay, that brings us to the end of this session of the discussion.

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