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MOLECULAR SPECTROSCOPY: A PHYSICAL CHEMIST'S PERSPECTIVE

PROF. ANINDYA DATTA
DEPARTMENT OF CHEMISTRY,
IIT BOMBAY

LECTURE No. – 2
Schematics of Instrumentation For FD Spectroscopy

Now that the parameters of absorption and emission are well defined, let us go over and try to understand how the actual measurements are made.

To do that let us first draw the schematic of an absorptions spectrophotometer, and the kind of spectrophotometer we are going to describe here is called a split boom spectrophotometer, okay, what do we have? I'm drawing the schematic first, then we will go into a little bit of a detail of some components of the spectrophotometer.

First of all of course you need a light source, which is usually called a lamp. What is the light source that you use? Depends on what kind of energy regime that you want to probe, okay. Usually you want a light source that gives you a wide range of wavelengths as we have discussed the previous day. So you want a source that gives you what we generally call white light, white light means light that contains all possible wavelengths preferably in the same ratio, it should be uniform across the spectrum.

Then we have something called a mono-chromator, the box is too small to write chromator, what is there inside the mono-chromator? What do you have inside the mono-chromator? White light, I want to get specific wavelengths from there, what should I use? A grating right, but not just grating, we'll come to that in a while. So that gives you the colour that you want, let us say the colour of wavelength lambda.

Now if you are doing absorption spectrophotometric you remember we need IT as well as I0 isn't it? What do you want to measure? Absorbance, absorbance is log I0/IT, so one way or either two side ways of doing it actually. One way of doing it is to insert A beam splitter, a beam splitter as a name suggest is an optical component that splits the beam into two parts, meaning it transmits a part of it and reflects a part of it.

Now we are talking about something that reflects, so you can think of it as a partially reflecting mirror, okay, in fact if you take a glass slide, a glass such slide itself can act as a beam splitter, if you make laser light especially wavelength on a glass slide you see most of it has gone through, part of it gets reflected, for glass slide that typical number is 4%, 4% gets reflected, 2% from the front surface, 2% from the back surface, remaining 96% goes through.

In absorption spectrophotometers generally what you use is a 50:50 beam splitter, 50:50 means half of the intensity of the light goes through, half gets reflected, okay, then you have this mirror which produces the parallel arm of the light, here in one of the arms you put it in your sample, in the other arm you put in your reference and then you put in a photo detector, I'll just write D for it which can measure the intensity of the light that reaches it. Now from this detector what is the information that we get, I0 or IT? Louder, IT, right, because this beam passes through the sample, so from here we get IT and from here obviously we get I0 right, generally we want to put in everything except your sample in the reference side, suppose you are working with the solution then we want to put the solvent inside and identical do it on the reference side, but in case there is any absorbance by the solution it gets corrected for, okay, so from here you get IT, from here you get I0 and but then the computer processes the data and gives you an output of absorbance right away, okay, this is the schematic of an absorption spectrophotometer.

What about emissions spectrophotometer? Just a second, now for emission you see what is the difference between an absorption and emission? Absorption means you have two energy levels in the molecule something you say 1 and 2, you shine light of appropriate frequency which matches the energy gap, bold resonance condition delta = H mu and there is a transition from 1 to 2, this is the process you are following when you do absorption spectroscopy.

In emission what happens? You need a particular frequency, I'll call it Mu EX to perform this excitation, and then usually something happens in the excited state, more often they're not the emissive state is not the same as the excited state, okay, so let's say emission takes place from here, and let's say this frequency is Mu EM. If you are more comfortable with lambda you can use lambda, wavelength, okay, so now see it is not enough for me to choose one frequency, I've to choose two, one for excitation, and one for emission, I've to excite the molecule by the proper frequency and I have to record the intensity of the emitted light at the frequency where it emits.

When you look at emission, any emission even has to be PC read by excitation, right, and for excitation any wavelength is not good enough, any energy is not good enough, you have to supply light or frequency such that delta = H Mu that condition is fulfilled. If this is delta E, and let us say this is Mu X, H Mu X must be equal to E2 – E1, okay, so there how will I get that Mu X by using some mono-chromator? So I need a mono-chromator to select the excitation light, clear about that, so let us actually start from there. I have a lamp, then I put in a mono-chromator, I'll call this excitation mono-chromator, this chooses the frequency or wavelength whatever you want to say, this chooses Mu X. What determines the choice of Mu X? The energy gap between the state, the ground state and the excited state to which I'm exciting, okay. Now this slide goes and is incident on the sample, and sample let's say MX.

Now usually the light that is emitted has lower energy then light that is used for excitation, in special cases it can higher frequency, higher energy that is called up conversion, but that would involve what is called the two photon excitation, multi-photon excitation, but in the simple case what happens is after you excite generally before the molecule can emit it undergoes some kind of relaxation in the excited state, relaxation causes a decrease in energy, there are different mechanisms of relaxation, I'm not sure whether we'll have time to discuss that in this course, alright, but it undergoes some relaxation, it's not easy for it to go up right, unless you provide more energy, but coming down is not very difficult, right, so it usually comes down to a lower energy state and emits at a lower frequency Mu EM.

I want to now study this emission, okay, Mu EM, how do I do it? I have to, okay, usually this emission is not mono-chromatic, emission is also polychromatic, it is not white but usually the emission has bands, there are several energy levels that can be involved in emission process, from there I have to choose the frequency that I want to work with, so let me not use yellow there, this is your emitted light even that has to go through what I call an emission mono-chromator which allows me to choose the frequency of emission which is then detected.

We need two mono-chromators in an emission spectrometer, I'll clear about that, that is why usual emission instrument cost, well that's one of the reasons why emission instruments cost more than significantly more than absorption instruments, one but not the only reason there are several reasons actually, okay, so these are the schematics. Now one question that we'd like to ask is what is there inside a mono-chromator, we know that there is a grating but it cannot be just a grating.

Let us see what is there in the mono-chromator, maybe we can understand this question better than, what do we have inside a mono-chromator? Of course we have a grating, right, we have discuss this already, a grating disperses the light and breaks it down into its components of different frequency, how? What is Black's law? M Lambda = 2D sin theta right, I'll only work with N = 1, when N = 1 you call it first order diffraction, generally it is more prominent than second order diffraction, second order is more prominent than third order so on and so forth, so I'll just write lambda = 2D sin theta, so for different values of lambda, theta will be different, okay, this is basically the principal, but now the problem is this, I have some light source, okay, can we the lamp, or can we the sample itself, if you are talking about emission, okay, it's always consider to be a point source, okay.

Now if it's a point source in which direction will light be emitted? All direction, right, unless it's a laser we'll talk about lasers later on, but there is a reason why laser have such a highly directional outputs, it's not straight forward, okay, if you just take a simple lamp something like a tube light, then light goes out in all possible directions, okay and here I have my grating, so if lights solves in many different direction then we got a problem, isn't it? Because then all colours will go in all directions, okay, I must have a parallel beam of light falling on the grating, is this point met? I cannot have a divergence source and like from the divergence source falling on the grating directly, is that point met? Have you understood? So what is one way of doing it? I can put in a lens, I can put it in such a way that this light source is exactly at the focus, that is going to give me a parallel beam alright, and then what will happen? If lambda 1, lambda 1 is a particular wavelength, lambda 2 is another particular wavelength, goes in this direction, from this part also it will go in parallel direction, I'll clear about that, just theta has to be same.

What about lambda 2 if I select some other wavelength? Let's say it goes in this direction, this will be parallel, okay, but there is a problem with this arrangement, the problem is if this is the case then my grating has to be exposed right after the lamp, I mean that case ambient light can get it, understand, if my instrument is absolutely open, and if I have just a point source and the grating, then I cannot have anything in between right, then like some tube lights will always have to, will also get in which means we have to always perform the experiment in a dark room like we perform this physics optics experiments, but then who wants to stay in a dark room all day, so one way of avoiding this problem would be, let me draw it again. Let us say this is the situation, this is my grating, one way of stopping external light from getting in, ambient light from getting in would be to put in a slit.

What is a meaning of a slit? This is slit, right, will look like this, right, I can only see her nobody else, right, all other light sources are blocked, so I can put in a slit. What is a problem of putting a slit in this kind of an arrangement? Yes, yeah big time, intensity is decreased means almost no intensity gets through, so your signal is going to be very very small, so one thing is for sure I have to use a slit, in the mono-chromator a grating is not enough a slit is required, but then if I want to get in more light through a slit, if I want to get all the light in through a slit, then what is the only way in which I can do it? I cannot use a parallel beam falling on the mono-chromator slit right, I have to use a focus beam, and the focus should be at the slit, okay. So the light arrangement would be, not this, not this, but something like this, L for lamp, L for light, the correct arrangement would be user lens and focus it like this, and put your slit here.

If I focus tightly then what will happen, all the light gets in through the slit, right, but what is the problem? What is the problem with beam that is focused on to the slit? It's going to be divergent from the slit right. So now see this is called the entrance slit, so now effectively the entrance slit becomes A light source, okay, this is the entrance slit to the monochromated that itself becomes a light source. And one thing I should say is that generally lenses, I'll not say lenses are not used, but it is better to use mirrors, curved mirrors rather than lenses because as we discussed earlier if light goes through anything, then some loss is there, it is better to just reflect from the surface, okay.

So now before it can fall on the grating I have to do something to this light, right, I cannot let a divergent beam fall on the grating, I've to collimate it now, how do you collimate? This is how you collimate. Problem is wait let me make a narrower beam, say something like this, otherwise I'll have to draw a really big mirror. Let's see put a curved mirror here and now you put a curved mirror in such a way, this is your entrance slit here, put your curved mirror in such a way that the entrance slit is exactly at the focus of this curved mirror. Now what do you get? You get a parallel beam of light, parallel beam of white light which retains all the intensity of the light that has been captured by this lens or by the mirror that I've put behind the lamp, clear.

Now I put my grating here, what will happen? Let us say this is lambda 1, lambda 1, I'll just write 1, I get a parallel beam here, what else? Where is my blue chalk? Wavelength number 2, wavelength number 2 another parallel beam, now I have to get the light out right? I've got the light in, white light in, I've to get the individual frequencies out as well, for that I'll need another slit, and now I think you have, you might understand better what we do is you have another curved mirror here, so what this curved mirror would do is that, it would focus all the yellow beams, yellow rays to one point and it would focus all the blue rays to another point. Is this point clear?

Right, the way we have drawn it we have two parallel beams, one yellow and one blue, okay, so focus all the yellow rays at one point, focus all the blue rays at another point.

Now if I put in another slit, and let us say the slit is like this, what will happen? The yellow rays will get through the slit and blue rays will be blocked, okay, now suppose, now I'm trying to answer your question, are you okay so far? Now say, well before that of course what you do is, all you have to do is you put your detector right here, generally you want to put your detector right at the exit slit of the mono-chromator, because that is where all the light energy is focused.

Now suppose I don't want the yellow rays, I want the blue ones, what do I have to do? One thing I can do is I can move the slit, okay, right now I can see only because if I move it like this I can see only Shubna, right, so I can move the slit, but then as I told you we put the detector on the slit, so generally you don't want to move the slit and the detector. What else can we do? Exactly, so what you can do is you can change the tilt of this grating, right, if you change the tilt of this grating depending on the tilt you can choose which frequency will come out, right, so what are fixed? The slits are fixed in position, the concave mirrors are fixed in position, the grating is usually something that you can tilt like this, and depending on the tilt angle of the grating you can get whatever frequency you want to come out of the exit slit, this method is called scanning.

Prof. Sridhar Iyer

NPTEL Principal Investigator
&
Head CDEEP, IIT Bombay

Tushar R. Deshpande
Sr. Project Technical Assistant

Amin B. Shaikh
Sr. Project Technical Assistant

Vijay A. Kedare
Project Technical Assistant

Ravi. D Paswan
Project Attendant

Teaching Assistants

Souradip Das Gupta **Hemen Gogoi**

Bharati Sakpal
Project Manager

Bharati Sarang
Project Research Associate

Nisha Thakur **Vinayak Raut**
Sr. Project Technical Assistant **Project Assistant**