

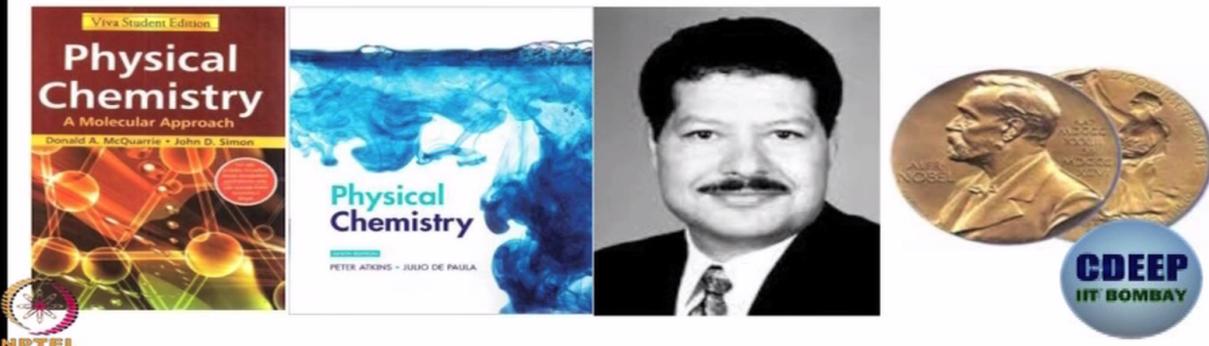
(Foreign language) Knowledge is supreme.

We have discussed the basics of lasers already, now very quickly in the next half an hour, let us go through some applications that laser have in spectroscopy in particular and chemistry in general, okay. To do that first of all, this is what we need to, we will believe actually, because I am not really going to prove this you.

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Lasers in Spectroscopy

- Intensity
- Monochromaticity
- Pulsed operation
- Coherence

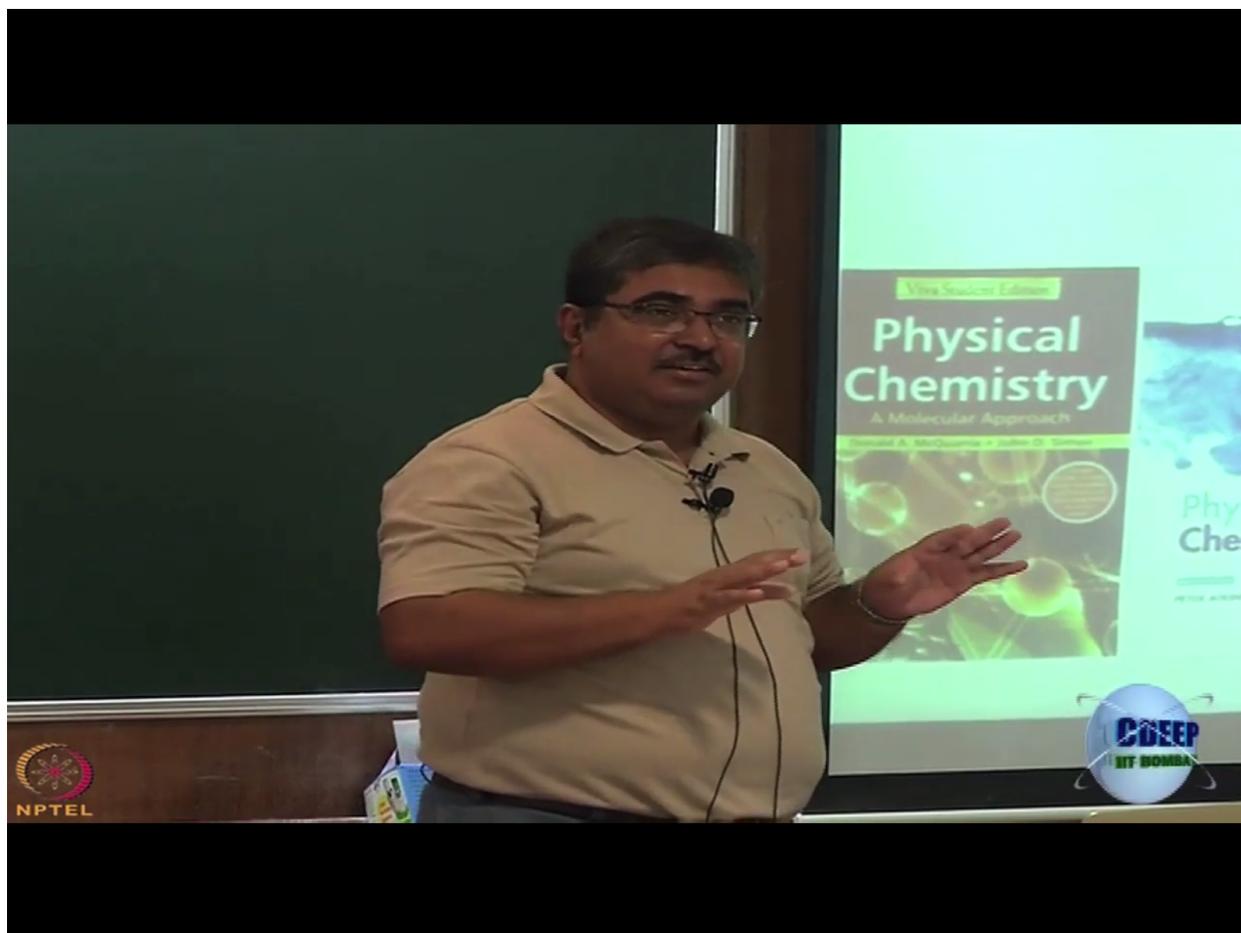


The slide features a collage of images. On the left is the cover of the book 'Physical Chemistry: A Molecular Approach' by Donald A. McQuarrie and John D. Simon. In the center is a portrait of a man with a mustache, likely a professor. To the right is another book cover 'Physical Chemistry' by Peter Atkins and Julio de Paula. Further right are two gold medals, one of which is the CDEEP IIT Bombay award. At the bottom left is the NPTEL logo.

So there is this seminal paper published in 1917, if I remember correctly by Einstein, which deals with this problem of stimulated emission in great detail. So all this comes out of there, but then that will be too much for us. Let us just believe what I say and some of these you can see yourself. So this is your laser light, what is a difference between this laser light and the light that comes off out of these lamps. Firstly you can see its intensity, right, very bright. So the intensity is very-very strong. Second thing also, what is the color of this light that you can see it is too bright actually, what is the color, what is the color of light coming out of this lamp, white. So this is highly monochromatic, that is the second thing. So essentially what happens is, the emitted photon, the photon that comes out as a result of stimulated emission has exactly the same properties as the photon that causes this

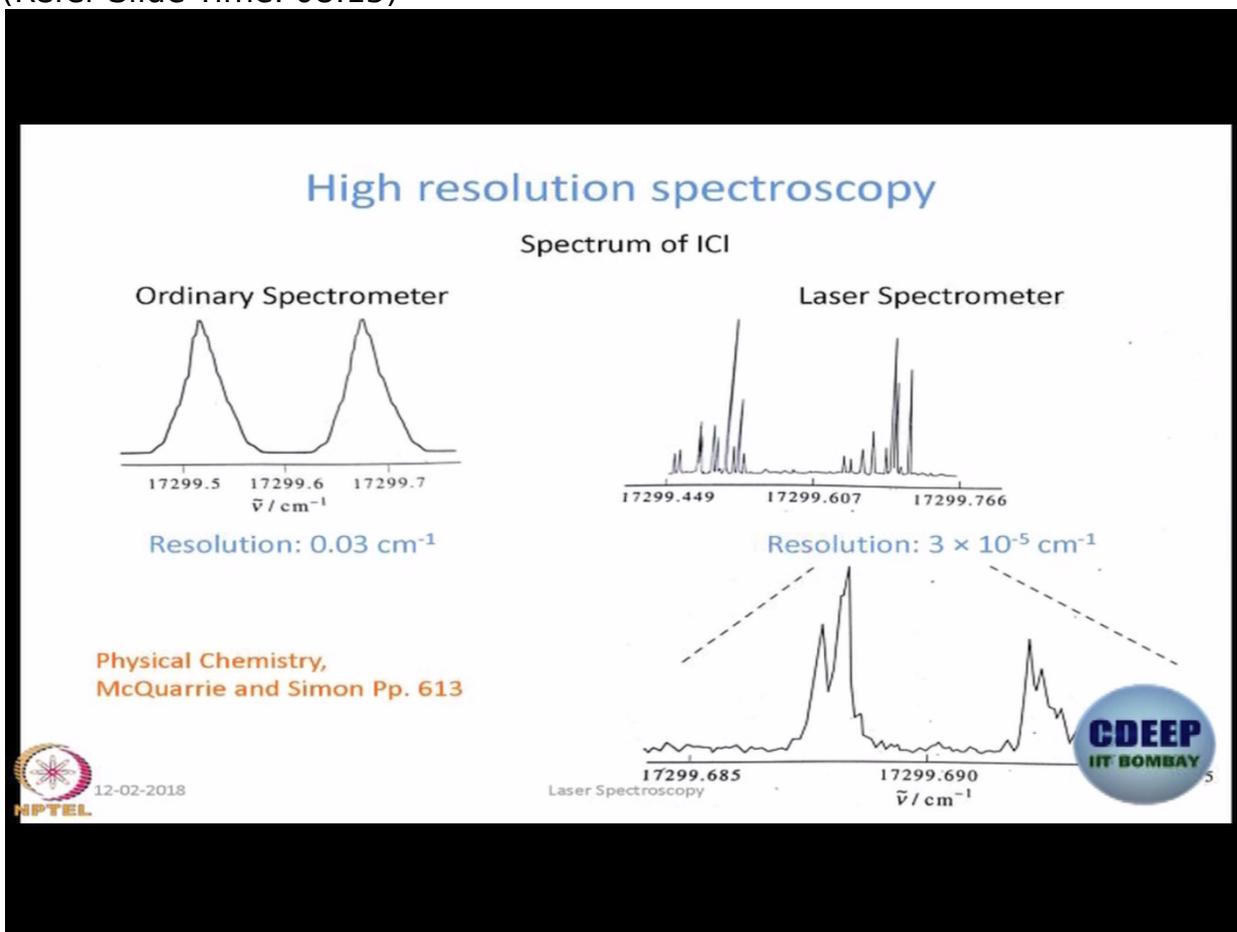
stimulated emission, that is what leads to all these properties. Monochromaticity and then intensity of course because you are building up the gain. First operation, we have discussed already in the previous module and last part is coherence. What is the meaning of coherence? Same frequency is monochromaticity, that's why I asked that question. Same phase. What is the meaning of same phase, that they walk in steps, right. So it's like many photons marching together, why? Because as I said earlier, you have to believe me on this one now, the output photon exactly has the same properties as the photon that comes in. And of course if... and if they are incoherent of course, it would all break down, right. So they are all in phase. And these properties of laser... each of these properties of lasers actually come handy in laser spectroscopy. Now what I don't have on this slide is intensity. Because of intensity what you can perhaps, what you can actually do is, you can especially in... so you can excite many-many molecules in using laser, right that is what intensity does. So what you can do is, for molecules with very feeble emission, you can use the laser and still get a reasonable emission spectrum. There is an application of this in things that are as well apparently far away from the scores, as a cancer detection. See the thing is this, all of us are emissive actually. So take any living tissue, what you have there is, you have collagen, right collagen is emissive. If you take paper and put it in ultraviolet light you can see the emission, that's because of collagen. You also have proteins, right, tryptophan, well collagen is also a kind of protein that is emissive, and you have NADH in your blood, NADH is also emissive. But then the thing is, look at me, emitting light, not exactly. But if I put my finger in laser beam or strong enough light source, which is at say 340 nanometer, UV, then you can see my finger, right. Using that, people have tried to make devices even for cancer detection. One of them is right now installed in Tata Memorial Hospital in Mumbai. But we will talk about something else.

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As we discussed another property of lasers is monochromaticity, okay, you can even see it here, qualitatively it is green and not white. But when we say monochromaticity, it actually goes way beyond, just saying that it is green or blue or red. So the example that we will discuss in the next few minutes, that is what we will try to emphasize, how monochromatic lasers can be. So first I show you a spectrum of ICL and by the way this discussion is available in McQuarrie and Simon's book. I will show you a spectrum of ICL. First on an ordinary spectrometer. Well when I say ordinary spectrometer, I actually... I am not doing justice to the spectrometer, because the resolution is 0.03 cm^{-1} and we are talking about electronic spectroscopy. So this so called ordinary spectrometer of ours is actually extraordinary. Okay so in that spectrometer, which does not use a laser, what we get is this. This is the kind of spectrum that we get, okay. Please look at the X axis, $17,299.5$, $20,299.6 \text{ cm}^{-1}$, it's actually good resolution, okay. But see what happens when I try to record the same spectrum on a laser spectrometer. Here resolution is $C \times 10$ to the power -5 cm^{-1} , that's why we are... we have the audacity to call this an ordinary spectrum, because resolution is a lonely 0.03 cm^{-1} , okay. There if we look at the same range of the spectrum, this is what you will get. So what you see is, these are not bands. Actually each of these bands is made up of

so many lines. Where these lines come from, we will not indulge in the discussion of that right now, okay. But the point we are trying to make is that because of this monochromaticity of lasers, so the level of monochromaticity that you can get $C \times 10$ to the power -5 cm^{-1} , right. The way this has been recorded is that they have taken a laser that is tunable. So you remember that $L = N \lambda$ by 2. So if I can change the length a little, what will happen, instead of this λ another λ will come in resonance, that is how tunable lasers are okay and you can tune it so finely that you have resolution of $C \times 10$ to the power -5 cm^{-1} , okay and if you thought this is good, what I will try to now show is, I will ask you to focus on this portion. I am going to blow up this portion and show you, that is what you see. Please read the X axis now, 17,299.685 and 17,299.690 okay, there can be no other line here. So this looks like relatively broad band, from here we have been able to go down here by using a good laser spectrometer, okay. So that is what the monochromaticity of lasers allow us to do in spectrometer, okay second application that we have discussed. First application is laser induced fluorescence that we have talked about already. (Refer Slide Time: 08:15)



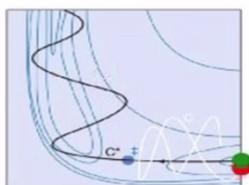
Now let's go over to something else. This is not really spectroscopy, this is dynamics, but then... now what happens is spectroscopy and dynamics kind

of go hand in hand. So one thing that chemist always want to do is, they want to control the reaction path, okay. They want the reaction, as students of chemistry, you have studied that whenever we try to do any reaction, more often than not, we have this side reactions that give us products that are not desired, right. So the challenge of any kind of synthetic chemistry is to get the product, right, to promote the channel that leads to the desired product and to cut out all the side products, undesired impurities, you can call them. Okay so one way of doing it is to do, what we have learned conventionally, what section of chemists and physicists had been wanting to do for a very long time is to have a mind control by which we can try reactions in the pathway that we wanted to go and I will take two very simple examples at this time diagrams familiar to us. Do we know what we have drawn? So these are potential energy substances. You see this contours, so these are three dimensional plots, right. This axis pointing towards you, that is the energy going up and we have reactant on this side and we have product on this side. So since we have not studies this, so thing is that, you have two kinds of potential energy surfaces, one at this point, so this is called the saddle point. So saddle point if it comes very early in the reaction path, then this potential energy surface is called an attractive, one. If it comes very very late, then it is called a repulsive one, and then as you are going to study in that course for an attractive potential energy surface, if the molecule oscillates and vibrates like this, then there is no reaction, it comes back. If the molecule goes straight, then it hits the wall and then comes outer oscillating in the products channel. On the other hand, in the repulsive PS, if the molecule goes straight, then hits the wall and comes back. So it is, you don't even have to think in terms of molecules, think of some kind of a surface and you are rolling a ball up in, okay. In this case, if you... if the wall goes up, wall like this, then it oscillates like this and comes back. If you stand it straight with enough energy, then it can cross the maximum. In that case, where the maximum comes... where saddle point comes late, there what happens is this, if it goes straight, then it comes back. The only hope of getting it through is to make it vibrate like this, okay. So it is... you have to prepare the molecule in a certain state so that it goes towards the reaction site, okay. The only way to do is to use a laser and what is called molecular beam.

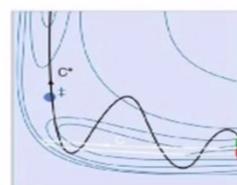
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Control of reaction path

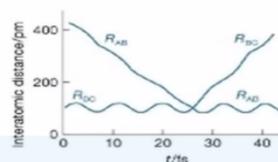
Attractive PES



Repulsive PES



Physical Chemistry,
Atkins and dePaula 10th ed. Pp. 907-913



12-02-2018

Laser Spectroscopy



Now this we can discuss. See when we talk about chemical reactions, many of us have done those experiments by which we have determined the rate constants, haven't we? How have done the reaction? The reaction goes on in some vessel, right. We pipit out 5 ml, 2 ml, 10 ml, whatever, it is, aliquot of the reaction mixture, put it on ice, whereby we create the reaction and then we typed it to see how much of reactant is still left or how much of product is still formed. By that how fast a reaction can you monitor, if you do it like that, what kind of rate constants can you talk about. So this whole process of pipetting out, putting on this ice, that takes a few seconds at least. So typically by those experiments, you can talk about reactions that requires minutes and hours to get complete, but is the fast, what happen... I mean do all the action take place at such slow time scales, or are there faster reactions? There are faster reactions. That brings us to a question, what is the fastest possible reaction, what is the fastest possible chemical process that can take place. And theoretically the answer comes from this equation. Are we familiar with this equation, Eyring equation, well if you have not studied this, you will. Okay, so this is the rate constant k_B is Boltzmann constant, T is absolute temperature, A is everybody knows. What is this tube? Partition function... partition function. Are we familiar with the concept of partition function yet? So this is partition function associated with

the transition state, these are with the reactants A and B, multiplied by A to the power minus EA is activation energy, k_B we know and T we know, okay. Just believe me for now, alright, you are going to study this in this course on chemical energetic and dynamics. Now when can K, does K have to be large or small for the reaction to be... okay many per second has to be there. So what is the maximum possible value of K that we can have? What is the maximum possible value of this exponential term that we can have? One, one means what, no activation energy. If there is an activation energy reaction takes longer, if there is no activation energy that we don't have to consider. So for putting EA equals to 0, this term becomes 1. Just believe me now that the best possible scenario is that Q dugger by $Q_A Q_B$ is also equal to 1, so we are left with $k_B T$ by H . Okay this is the rate constant theoretically of the fastest chemical process that can ever take place. If you substitute the value... now everything is known, k_B we know, H we know, T we can use something like 300 Kelvin, room temperature. Substitute those values, the number that comes out is 6×10 to the power 12 per second. 6×10 to the power 12 per second. So if you convert that to time, how do you convert rate constant to time? Remember what we discussed in the last... remember what we discussed last week, when we talked about life time, life time τ is reciprocal of rate constant. So reciprocal of this rate constant turns out to be 170 femtoseconds. So the fastest chemical reaction can take place in theory in about 170 femtoseconds. Anything faster than that is in the domain of physics, we don't worry about it. Now actually it is possible to measure things that are in 10 to the power -18 attoseconds as well, but we don't care about attosecond. Chemist should worry about say 200 femtoseconds or so, if you want to study the fastest process that is there. And what is the chemical process that you can think of? Yeah what reaction? Ionic reaction, acid based reaction, well acid based reaction is tempting, but then I have removed those slides, we will talk about that later if we get time, but the answer I was looking for is more generic actually, more generic than that, breaking of a bond, some bond, I don't know which bond, but breaking of a bond is the most fundamental chemical process, isn't it? right. That should be the fastest one. So can we measure the time required for breaking of a bond. So this is what gave rise to the field called femtochemistry, which started sometime in late 1970s, I believe, 1980s, 1990s, where the golden era of femtochemistry and that culminated in the nobel prize for Amit Goel of Caltech, he is no more, he died last year or year before last, I forgot, I think year before last. But there were many other players in the field also.

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What is the fastest timescale required?

$$k = \frac{k_B T}{h}$$

$$k = 6 \times 10^{12} \text{ s}^{-1}$$

$$\tau = 1/k = 170 \times 10^{-15} \text{ s}$$

Bond breaking

Atomic motion : 1 km s⁻¹

Bond length: 1 Å

Time taken? 100 fs

Ultrafast Dynamics: Femtochemistry



12-02-2018

Ultrafast Dynamics



So we will very briefly discuss what Amit Goel had done. What we need to know, to do that discussion is how do you follow such fast processes. We will do at least qualitative discussion of that today and stop in one minute or two minutes and then we will take it from there in the next... tomorrow. How do you follow something that is so fast, femtoseconds. If you remember our discussion of transformed spectroscopy, time domain spectroscopy that we had in the beginning of this course, we had said, that electronics cannot give you time resolution of more than microseconds or may be some nanoseconds. Okay, how was that problem circumvented in fourier transformed spectroscopy. So what Manthan is saying is moving mirror setup, what fundamentally, what is it that we used to get a resolution that is faster than what electronics can get. Well as I told you, I always look for very simple answers. What I really was looking for right now is we use the fact that light is the fastest thing at our disposal. We use the power of speed of light. So as we will see, we use the power of speed of light in this case as well, and since we are going to start a new discussion tomorrow, tomorrow we... I think we will dedicate the entire class to this, first I will tell you a little bit about the process and then I will tell you about Amit Goel's experiment. If there is time, since you have... me, we will talk about this mechanism of acid based reaction.

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