Concepts of Chemistry for Engineering
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Lecture 41
Introduction to molecular spectroscopy

Now we change here, and we start talking about molecular spectroscopy, which is an experimental technique. What we will do in this course is that we will develop the theoretical foundation of spectroscopy. All this time, we have been talking about quantum mechanics.

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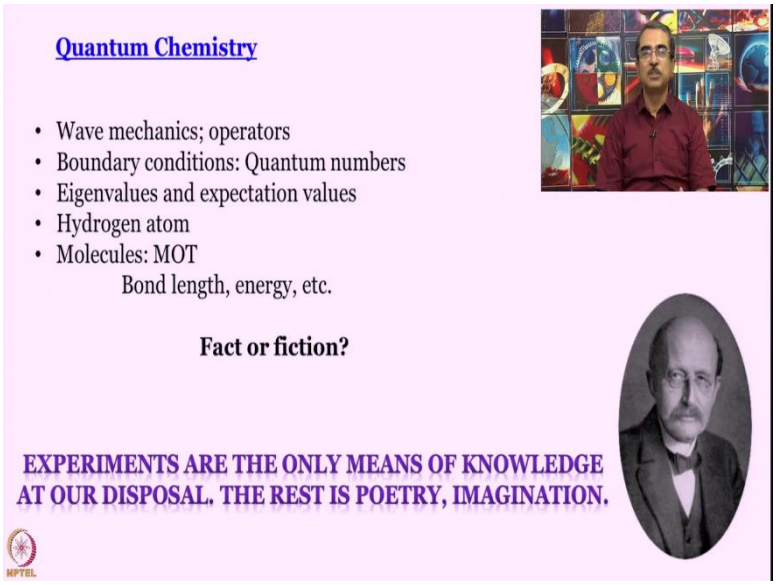

In quantum mechanics, we learnt about wave mechanics, we were introduced to operator algebra, we learned that boundary conditions take us to quantum numbers, we learned about eigenvalues and expectation values, which to use when. We did a, at least preliminary treatment of hydrogen atom, where Schrodinger equation is partially solvable, we solve at least one part of it, and that is going to be handy in our subsequent discussion.

And we arrived at the orbitals, atomic orbitals. And the same atomic orbitals were used to build molecular orbitals, when we try to build a quantum mechanical description of molecules using molecular orbital theory. And from there, we said that we get an idea of bond length, bond energy, so on and so forth. We really did not talk about length so much, but bond energy definitely.

So now, the question that arises is that all these things that we have said, is this true? Is it a fact? Or are we just making things up? Is there anything called wave functions? Well, before going further, I would like to show you a quotation by someone who is a father figure of

quantum mechanics, Max Planck, Max Planck had said, experiments are the only means of knowledge at our disposal. The rest is poetry and imagination, not to undermine poetry and imagination, but in the pursuit of truth, in the pursuit of understanding what everything is about, we must have experiments that will give us insight into the systems actually.

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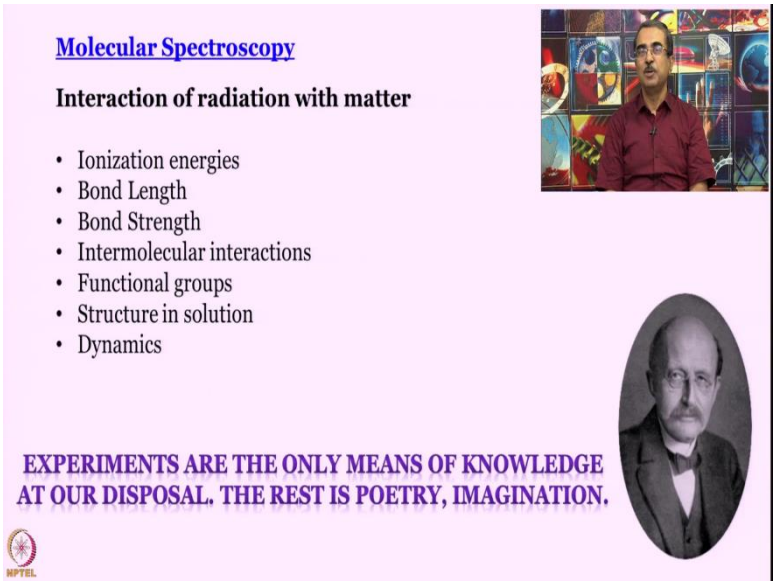

And the experiments that are most related in this context are of molecular spectroscopy. In molecular spectroscopy, we study the interaction of radiation with matter. We are already exposed to molecular spectroscopy to some extent, because we did talk about photoelectron spectrum. We will talk about some other forms of spectroscopy here. Ionization energies is something that we have already access to.

Now, we are going to learn how do we determine bond length experimentally using spectroscopy? How do we determine bond strength? Can we determine bond strength? Can we talk about intermolecular interactions? We might not go into very deep detail of this, but we will see.

Can we tell which functional group it is? And can we talk about structure in solution? Can we talk about dynamics or processes going on a solution? Unfortunately, will not go into all of these, but at least some of the questions I hope will be answered by the time we are done discussing spectroscopy.

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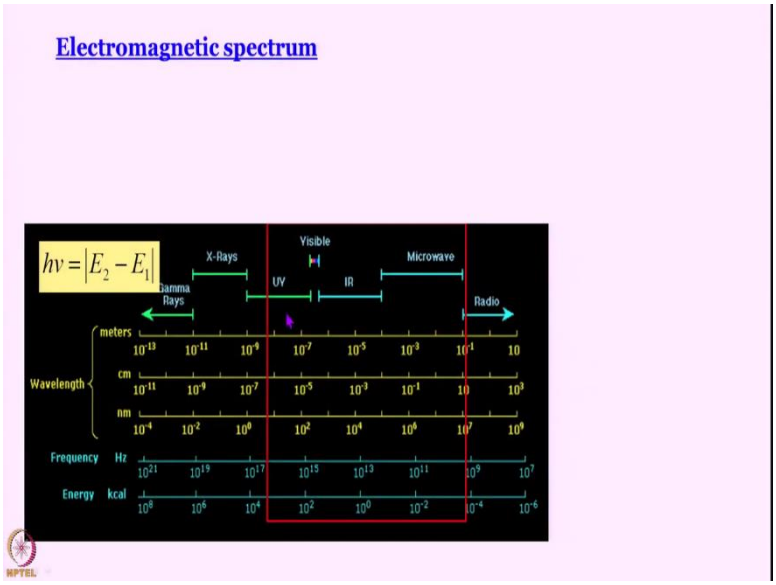

Now, when you do spectroscopy, the most important relationship is this $h\nu = E_2 - E_1$, this is called Bohr resonance condition and this has to be fulfilled for light to be absorbed, energy of a photon must match some energy gap in the molecule, E1 and E2 are the energies of two stationary states in the molecule. And if you look at the electromagnetic spectrum, it spans all the way from gamma rays, very, very high energy to radio waves, very, very low energy.

And there are different regions you have radio waves, microwaves, IR radiation, visible radiation, ultraviolet radiation, x rays and finally gamma rays. Note, how small the visible radiation is. If we talk in terms of say, wavelength, light wavelength spans 10^{3} to 10^{-11} centimeter or visible one is somewhere here 10^{-4} maybe to 10^{-5}, not even that, not even like one order of magnitude.

This very narrow region of electromagnetic spectrum that we can see. But using instruments, we can have access to everything from radio waves to gamma rays. In this course, we are going to focus our attention in this microwave to ultraviolet region. Microwave is what we talk about first, then we will go on to IR, then we will discuss UV visible.

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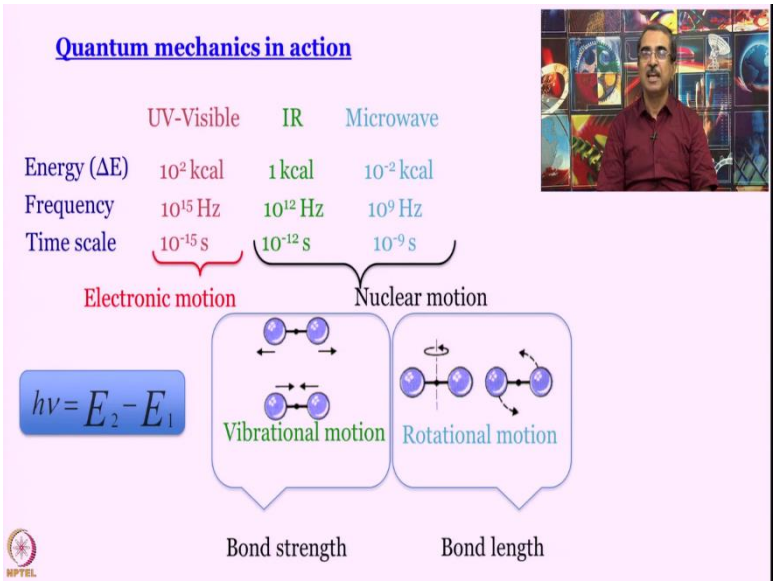

The reason why these different regions are important is that in different regions, you can probe different kinds of energies, if you want to put it that way different kinds of motion within atoms and molecules. This is that we know we are going to talk about as we said, so as you see, energy is 10^2 kilo calorie for UV visible, 1 kilo calorie for IR 10^{-2} kilo calorie for microwave.

In terms of frequency, we are going to span 6 decades, 10^9 hertz for microwave to 10^{-15} hertz for UV visible and in terms of timescale, which may not be important in our discussion, we go from nanosecond to femtosecond. Now, this IR and microwave radiation, these have energies that are more or less comparable to energies of nuclear motion, whereas UV visible light has energy that matches the energy gaps associated with electronic levels.

So, when I say nuclear motion, what do I mean? I mean two kinds of motion; one is rotation and the other is vibration. Rotational energies are associated with lower energy microwave region, vibrational energies are a little higher in IR region. So, these are the 2 regions we are going to talk about, first we start with microwave.

So, if I do microwave spectroscopy, I essentially talk about rotating molecules. If I do IR spectroscopy, infrared spectroscopy, I talk about vibration of molecules and what is the molecular parameters that they lead to we will see and when we talk about UV visible spectroscopy, we are doing electronic spectroscopy which itself is a very, very rich field of study. So, vibrational motion gives us an idea about bond strength as we are going to see.

And rotational motion gives us an idea about bond length. So, even though we have not really discussed yet, see this is sort of a spoiler which is an answer to the question that we asked a

while ago, can we experimentally determine bond length and bond strength? The answer is yes, by doing micro spectroscopy and IR spectroscopy.

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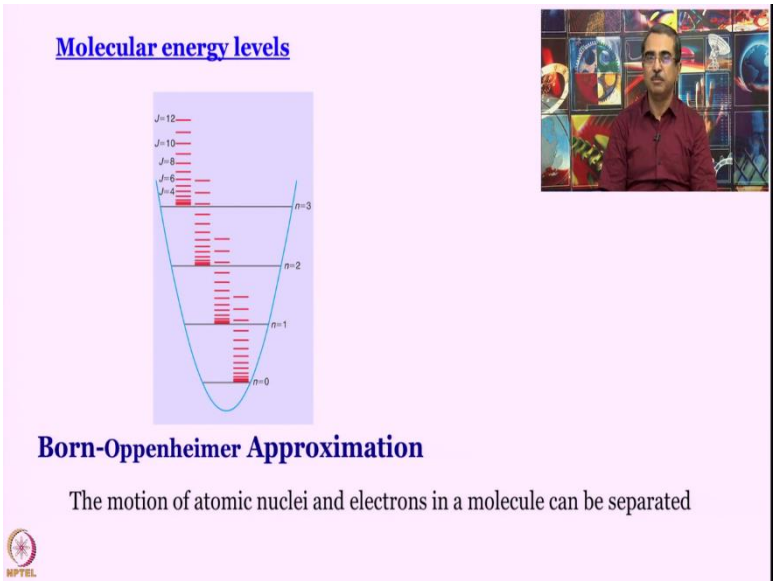

And the reason why we can do it, why we can explore different regions is that, well there are so many different kinds of molecule energy levels, electronic levels, vibrational levels, rotational levels, but Born-Oppenheimer approximation that we encountered earlier tells us essentially that these different kinds of energies can we handle one at a time, atomic motion of nuclei and motion of electrons can be separated, that is what Born-Oppenheimer approximation says in very, very simple terms, we have encountered this earlier also.

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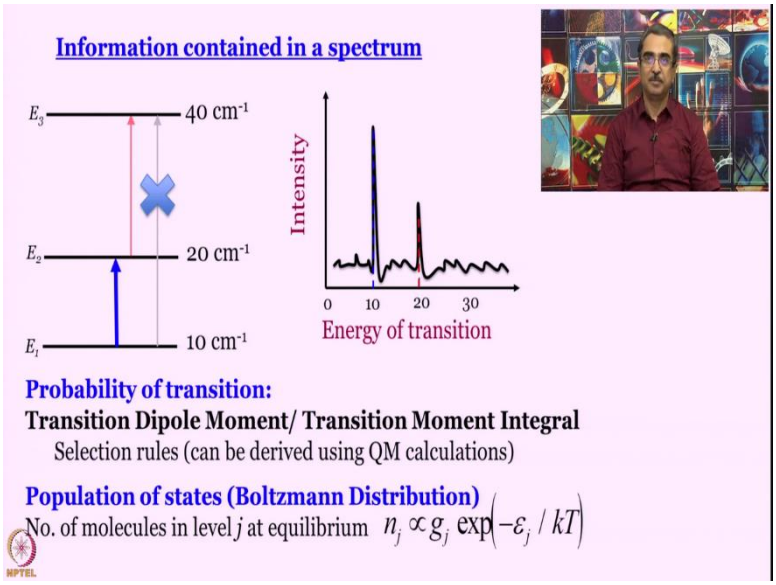

But, let us before starting a discussion on micro spectroscopy or anything there is this thing what is a spectrum and what is the information it contains, let us say I have three levels in a molecule. For now, do not worry about what kind of levels these are, just three levels energies are 10, 20, 40 cm^{-1}. Let us say the transition between E1 and E2, levels one and two is allowed.

In spectroscopy, we are going to encounter these terms allowed transition and forbidden transition. Allowed transitions are those that happen, forbidden transitions the transitions that do not happen, it comes from a little more sophisticated quantum mechanical treatment, time dependent perturbation theoretical treatment of interaction of radiation with matter when we do that, we arrive at a quantity called transition moment in detail.

The essential condition for a transition between two levels to take place is that the transition moment integral must be nonzero. So, let us say in this particular molecule, this first one is allowed. Let us say this one is not allowed, 1 to 3 transition is not allowed. And let us say these 2 to 3 transitions is allowed.

Now, when I try to plot the spectrum, a spectrum is essentially a plot of intensity versus energy in some form it can be wavelength, it can be wave number, it can be energy in electron volt, it can be energy in kilocalorie, it can be Joule, whatever. So, essentially it is a plot of some energy parameter in X axis and intensity in Y axis. Where should I get the lines?

This energy gap is 10 cm^{-1}. So, I should get a line at 10 cm^{-1} and this energy gap between 2 and 3 is 20 cm^{-1}. So, I should get another line at 20 cm^{-1}. And I should not get a line at 30 cm^{-1}, because this transition from 1 to 3 is forbidden. So, that is what takes care of the X axis. What

about Y axis? Is it going to be stronger? The lower energy transition? Is it going to be weaker? Is there a correlation?

We will come to that as well. For now, let us say for whatever reason, the transition for this 1 to 2 is twice as intense as the transition from 2 to 3. What do you expect in the spectrum? We expect two lines like the dotted lines that are shown here, what you get in reality is this. The lines always have some finite width. They are not delta functions, it is not as if they have nonzero value only at a particular value of energy of transition, there is a width spread.

And also, you see this vertical up and down jiggly structure, that is noise. When you do any experimental measurement, it is invariably associated with noise. So, this vertical wiggle and jiggle that you see is essentially noise. So, this is what a spectrum would look like for this system. Now, let us think what is it that determines the Y axis, one thing is probability of transition, I talked about transition dipole moment or transition moment integral a little while ago, that is what tells us how probable a transition is.

So, another quantity that is often used for this is oscillator strength, especially for UV visible transition electronic transition. Yet another term that is used very often is well for absorption spectroscopy, absorption cross section, they are all interrelated and they all talk about sort of probability of transition. So, this is an intrinsic quantity, what is a per molecule quantity, take one isolated molecule what is the probability of transition. There is another factor and that factor is population. How are the states populated?

And how they are populated is determined by Boltzmann distribution, where number of molecules in level j at equilibrium is proportional to degeneracy of the state(g_j) multiplied by $e^{-\varepsilon_j/\kappa T}$. So, let us say degeneracy is the same everywhere. You expect the population of the state one to be more than the population of state two, and that is what is reflected in this schematic spectrum that we have shown here. What happens when you have degeneracy of more than one you will see when we talk about microwave spectrum.

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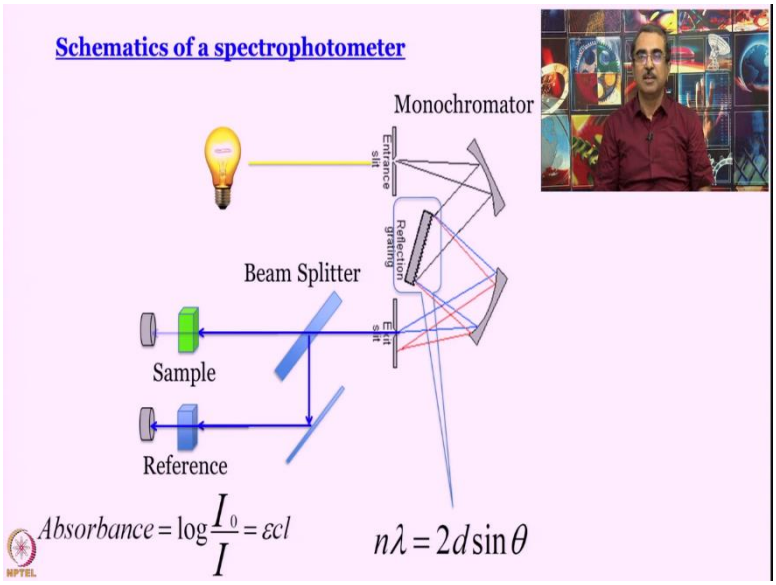

Now, let me introduce you very, very briefly to the schematics of a spectrophotometer and here I am talking about a UV visible spectrophotometer, an instrument on which you record the absorption spectrum. First of all, you have a light source, light source does not really look like a bulb, this is just a schematic remember, most typically for UV's measurements, the light source is a combination of deuterium lamp and tungsten halogen lamp, tungsten halogen lamp gives you light in visible region and the deuterium lamp gives you light in ultraviolet region.

Now, this light is made to go through a monochromator. What is the monochromator? Chroma means colour, mono means one, so monochromator essentially means something that produces one colour. How it does it? We will come to that also. But for now, let us see what happens after the monochromator. So, white light goes in and let us say some coloured light comes out depending on what your monochromatic settings are.

What you do is, let us discuss what is there inside a monochromator. Inside of monochromator you have essentially a reflection grating. We are going to discuss Bragg's law later, Bragg's law essentially says $n\lambda = 2d\ sin\theta$, which means that when light of multiple wavelengths is incident together on a grating, different wavelengths travel in different directions, according to this relationship Bragg's law.

So, when light falls on this grating, you see blue light goes in one direction, red light goes in another direction. So initially, what you have is when light gets into the monochromator there is a slit, and this slit acts as a point source. Then you have a mirror which is placed in such a way that the slit is at its focal point, focal plane.

So, light from a focal point coming and being incident on a concave mirror becomes parallel after reflection, that is very important otherwise you will still get a mixture of colours. Now, you see you get two kinds of beams in the scheme that I have shown; one beam of parallel blue light, one beam of parallel red light. Of course, you have many different colours between and beyond them.

Now what happens, now since these blue light rays are all parallel, they are going to be focused at some point because this is also concave mirror. Red lights, red light beams, they are also parallel, they will be focused to some other point and all these points are going to be on the focal plane. So, what you do is you keep a slit here and keep the slit in such a way that if the focal plane is like this, the focal plane is like this, the slit is like this.

So, what happens is red light is focused here, blue light is focused here, yellow right is focused here, in this position, if this is a slit only yellow light would go through. Now, if you turn the grating a little bit, turn this grating a little bit what will happen, this was the situation, yellow light was going through. Now, this entire thing will move and maybe blue light or red light will go through depending on in which direction you have turned the grating, this is how you have point by point collection of different wavelengths.

Of course, there is always a spreading, this is how monochromator works. So, after the monochromatic light comes out of monochromator, you place a beam splitter, beam splitter is essentially a piece of glass upwards, which in this case divides the beam into two equal halves, 50-50 beam splitter is what is typically used in spectrophotometers. So, one part goes straight the other arm is deflected by another plane mirror and made parallel to the original direction.

Now, one of these goes through the sample the other goes to the reference and then they are detected by some detector like photodiode or photomultiplier. These detectors what they do is that when light falls on the detector, it generates the photocurrent and this photocurrent can tell you how much of light has fallen on the detector. It gives you an idea about the intensity of light that impinges upon the detector.

From here you calculate absorbance (A), $\log \frac{I_0}{I}$ and according to Beer-Lamberst's law, this $\log \frac{I_0}{I}$ absorbance is equal to εcl, where c is the concentration in moles per litre, l is the length and epsilon is called molar extinction coefficient or molar absorption coefficient. Your homework is to find out what is the unit of molar absorption coefficient. So, this is how a spectrophotometer roughly works.

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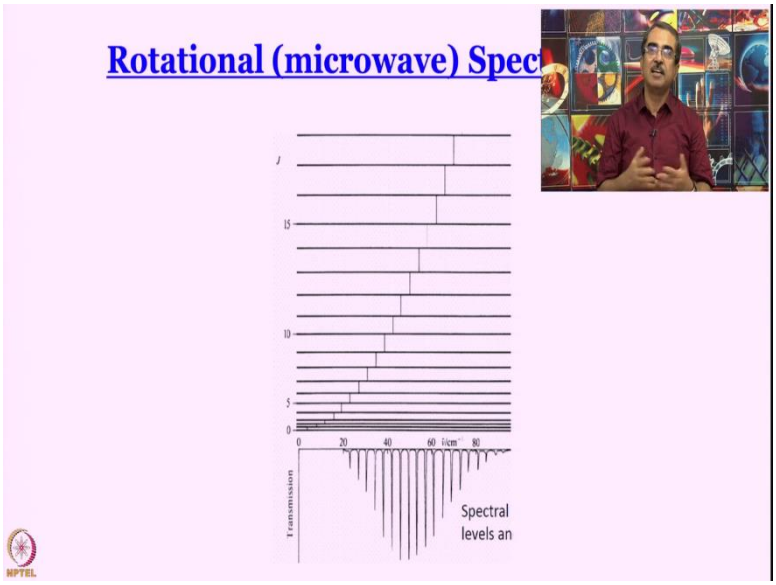

This is the introduction that we wanted to provide to spectroscopy. With this background, we are going to discuss rotational spectroscopy with a caveat. Usually, rotational spectroscopy is not performed using this monochromator, there is some other technique called Fourier transformation which we are not going to discuss here, but you hear about it all the time, if you actually do research involving spectroscopy, you keep hearing about FT-NMR, and FT-IR and FT-Raman, microwave spectroscopy, so that is what is usually used.

So, we need not think that it is the same spectrometer that is used here. But we are not even going to get into that. We are going to talk about the very fundamentals of microwave spectroscopy.