Introductory Quantum Mechanics and Spectroscopy

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Lecture – 8
Part 2
Introduction to Molecular Spectroscopy
What are the Signatures?

Let us look at what a spectrum that I am mentioning in spectroscopy means and what is common across all the different types of spectroscopy is.

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When we talk about electromagnetic radiation, you are familiar that, electromagnetic radiation from the radio waves, I mean, radio receivers, transmitters that you have to the x-ray that you might have had a reason to visit in the hospital, where an x-ray picture is taken. The order of magnitude of energies that you have from radio waves to x-rays; that order is very large; it is about 12-15 orders of magnitude. And, order of magnitude is ten times what is the previous one. If I have to say it is one order of magnitude more, what it means is that, this is ten times more than the previous one. Now, you are talking about 15 orders of magnitude; that means the frequency or the wave length or the wave number – we will define all these things now of the electromagnetic radiation that we have to deal with in molecular spectroscopy – ranges by about 15 orders. And therefore, you have a very powerful; at the same time, a very complex technique, because the technology that you require to handle radiation of these different orders of magnitude also varies. Before we go into those details, first, let us define what we see common in all these branches of spectroscopy.

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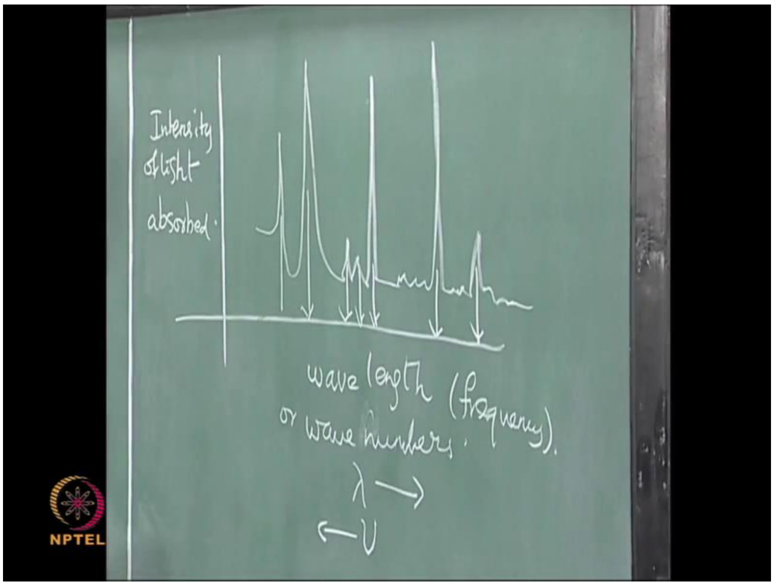

You almost always see the axes – x- and y-axis. This axis is usually called the axis for the wave length or wave numbers or frequency, whichever way. It is a property of light or the electromagnetic radiation that you are showing. And, on this axis, the amount of light that is absorbed or emitted even in the form of an intensity – intensity of light absorbed, for example. Ideally, if the substance absorbs radiation, whatever the radiation on it, then what you should see is that, the absorption takes place at all wavelengths of the radiation. A spectrum almost always looks something like… I am just giving some sketches. What you see is a set of peaks, not everywhere absorption. Absorption seems to take place – absorption of the electromagnetic radiation by the substance that is being studied seems to take place only in certain frequencies as I am not here only for certain wavelengths. If you say wavelength, lambda increases this way, the frequency increases this way. We will see the relation in a few minutes. What you see is that, there are only certain positions – line positions.

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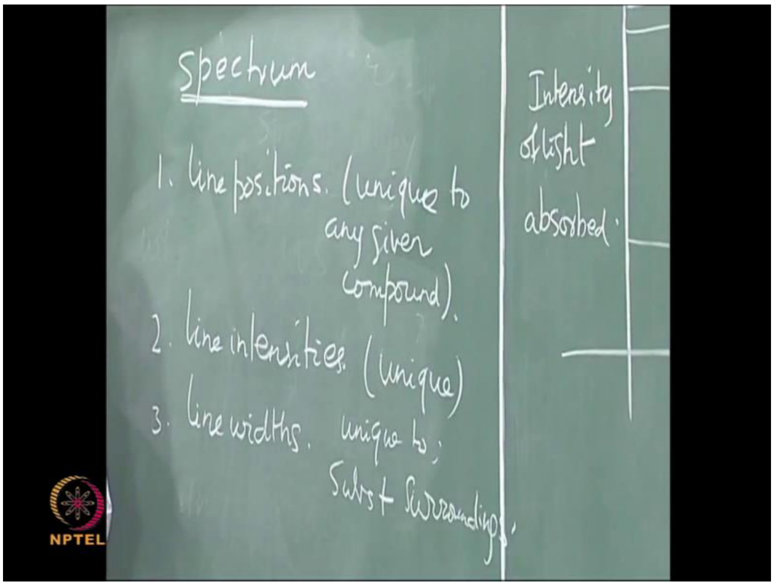

Spectrum

1. line positions. (unique to any given compound).
2. line intensities (unique)
3. line widths. unique to: Subst + surroundings.

So, property number 1 is line positions – unique to any given compound.

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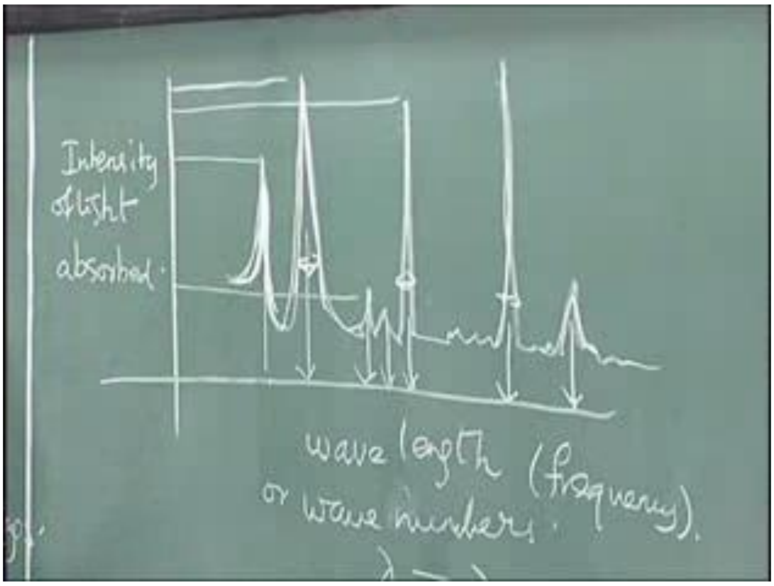

The next property that you see is that, the line intensities or what you call as the heights here or the areas under each curve, there are different waves. But, let us call the intensity as the area under each curve. If you see that, the intensities are not always the same. The intensity of this absorption – energy of absorption corresponding to this energy, the intensity in the picture I have drawn is that; the intensity for this energy is that; and, the intensity for this energy is that; and, the intensity – as you see that, there is again something, which is very small. I have done it purposefully that, what you see is that, not only different line positions, but you also see different line intensities. Again they are unique to any given subscripts.

Third – what you see is also one more pattern. This is if you think about spectroscopy as a pattern identification, you have identified two patterns: one – where the lines occur; and, two – by how much; and, the third – is that, if you see all the lines, do not have. All the lines are not very sharp. Some lines seem to be very sharp. Other lines seem to be very narrow – very bro ad. And then, there is another very broad and there is a line width associated with each one of these lines. The line widths are not only dependent on the substance that you are using the spectrum or taking the spectrum. The line bits are also dependent on the environment in which you take the spectrum – gas phase, liquid phase, solids; same substance in different phases. Whereas, the positions and intensities – the line positions and line intensities may not change that much, but line widths will change. So, it is not only unique to the position – unique to the substance; but, it is also unique to the surroundings.

So, what you have is in any spectrum, whether it is a radio-wave spectrum for the nuclear magnetic resonance spectroscopy or whether it is a microwave spectrum for molecular rotational spectroscopy or whether it is the infrared spectrum of a typical compound in an organic laboratory or the x-ray spectrum of a compound. Irrespective of what the radiation is, every spectrum will have these three distinct features. A feature of the line positions are the energy differences between the levels that the molecule jumps and then the line widths and the line intensities. So, these are the three common characteristics for every substance in every region of spectrum. Let us try and see what the reason is. I will give you a qualitative reason now. But, as we go along, we will see more and more of it.

That the molecule absorbs only at specific energies is something you are familiar from hydrogen atom. The Lyman series, the Balmer series, the Paschen series, the Brackett series and so on that you have studied tell you that, the electron in the hydrogen atom jumps from certain levels to certain other levels from the elementary Niels Bohr quantum mechanical model that you had contact with the earlier. And also, the quantum mechanics of harmonic oscillator is the hydrogen atom, etcetera that you had in the series of lectures that, atoms consist of energy levels. And therefore, the transition between different energy levels will lead to different frequencies or energy differences. And, what you see here as a wave number is one that corresponds to the difference between the initial energy level before electromagnetic radiation falls on it and the final level to which the molecule jumps. So, this is the frequency corresponding to different energy differences. And, since the energy levels are discrete, the absorption also takes place only at discrete wavelengths, not everywhere. The second… So, therefore, that is the quantum mechanics of the molecule. If we understand how to obtain the energy level spectrum of the molecule through quantum mechanics, we can verify through the spectrum, whether those energy level descriptions are correct.

The next is of course the line intensities, which are different. This tells you that, not all molecules have the same energy level; some molecules have… or, at certain energy levels; some other molecules are excited. And, this is not again an uncommon phenomenon for you, because you are familiar with the thermal distribution of molecular velocities from high school from kinetic theory of gases that, molecular velocities is distributed with most molecules having an average velocity and some with a higher velocity and the others with a lower velocity. And that, such a distribution follows the Maxwell-Boltzmann distribution law; that is, there is a distribution of molecular energies – molecular velocities in the case of kinetic theory. But, in general, in terms of molecular energies, certain number of molecules are in certain energy levels and the others has certain energies and so on. And therefore, the number of molecules which are in different starting energy levels is different leading to a population distribution. Therefore, the intensities correspond to the population distribution of molecules in various energy levels. That is explained to buy the statistics of the problem.

If you think of the energy positions as being explained by the quantum mechanics of the problem, the populations, the number at various energy levels, is described by statistical methods or statistical mechanics. The interplay of these two is what you see in the dynamics, which is in the line widths for various spectral lines. The line widths correspond is a signature; the line widths are a signature of the fact that, the molecular energies are not sharply defined, because the molecular are constantly exchanging energies through collision, through interaction with the medium around them, through various other means. And therefore, the molecular energies are not sharply defined. And therefore, the absorption, which is supposed to take place at one particular energy, is slightly distributed over, because the uncertainty associated with the energy at that particular, for example, for this energy, the uncertainty associated with that is given by the width of that.

This uncertainty can be to do various reasons. If molecules are colliding when they emit energy, a speeding molecule emits a slightly different energy than a slower molecule. A Doppler effect is something that you are familiar with. So, there are various reasons. There is collision broadening; there is pressure broadening; there is Doppler broadening; and then, there is of course, the fundamental inherent unavoidable natural line width or natural broadening due to the Heisenberg's uncertainty principle and so on. Therefore, you see that, the dynamics that the molecules undergo during the process of observation, the interactions with this is sort of reflected in the line widths. And therefore, the study of the line widths corresponds to the interplay of the molecular dynamics with the molecular energy levels and depopulation distribution. So, if one wants to understand what is meant by a spectrum for a molecule, one has to understand these three things, no matter what branch of spectroscopy that they want to study. Whether you want to study microwave spectroscopy or whether they want to study x-ray spectroscopy, these are all signatures of the molecule.

In each energy range, the signatures will have different meaning. The properties associated with that particular energy range will have different interpretation. But, these are the three important signatures that one looks or in understanding what is the molecular spectrum. And, as you see it, a molecular spectrum for the same molecule; for example, we talk about the line positions, intensities and line widths for say benzene molecule; if we look at the benzene molecule in the microwave region, we will get a certain spectrum. If we look at the benzene in the infrared region, we will get a certain other spectrum in the electronic absorption and we will get different spectrum. Therefore, the signatures are also different for the same molecules in different regions. But, each one is a clear finger print of that molecule in that region; which means that, if you take microwave spectra of 1000 molecules, you can easily distinguish between them by looking at the spectrum that, disk is that of this molecule, this is that of is molecule. Therefore, you see that, it is unique to the region for the molecule as well as it is unique between the different branches of spectroscopy.