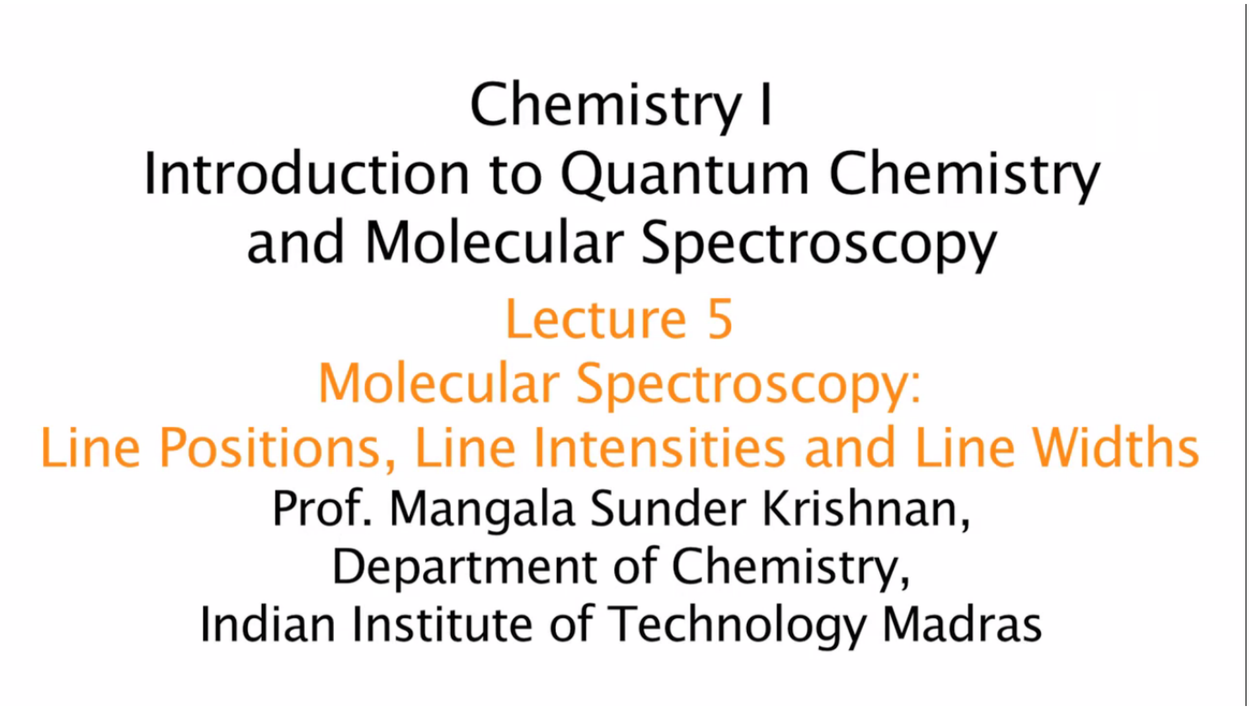

Chemistry I
Introduction to Quantum Chemistry and Molecular Spectroscopy

Lecture 5

Molecular Spectroscopy: Line Positions, Line Intensities and Line Widths

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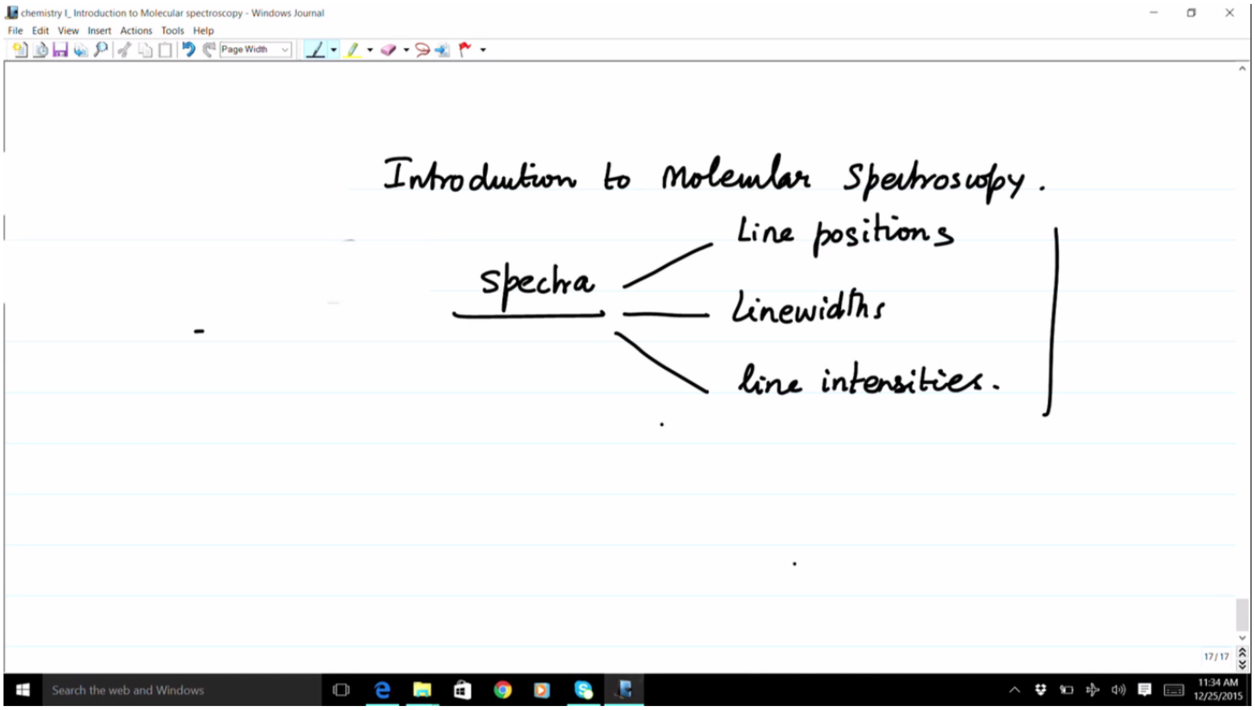
Welcome back to the lectures on molecular spectroscopy at the introductory level. In this lecture we shall look at the specific features that one looks for in a spectrum and these are broadly classified into three aspects and these three aspects are given here in the page. You can see that spectrum we are always concerned about the line positions or the frequencies for the transitions to take place between molecular energy levels and molecular energy levels are discrete and therefore frequencies are also discrete that they don't happen everywhere but only at specific energies. The other important aspect of the spectrum is that each of these line has a line width associated with it and these are important in that they contain information about the molecule and about the distribution of energies in the molecule and the third linewidths and the third is the line intensities in fact in the order I would say line positions line intensities and linewidths in the order of difficulty of more understanding I would say linewidths are very very difficult to understand. Line intensities are the approximate indicators of the statistical distribution of energies in the molecules. So let's see what these things are by an example. Let's start with the spectrum of a single molecule to begin with and what you see in this picture is the nuclear magnetic resonance spectrum. The proton magnetic resonance spectrum of benzene which contains typically will be one line. There is only one frequency for the proton MMR for the benzene molecule and this large line is the sample reference line due to these solvents that you have. This is magnetic resonance spectrum but if you do this under very very high resolution even the single line will have a small line bit associated with that. The same molecule in the infrared region when we worry about molecular vibrational motion of benzene, benzene being C6H6 has many many vibrational degrees of freedom and you can see that the spectrum has several lines. It's quite different from the proton MMR spectrum that you saw and also if you study benzene using UV visible light and I've given you the reference source that I've taken this picture from the National Institute of Science and Technology Chemistry webbook this is a typical visible spectrum of benzene. So the same molecule under three different radiations has three different spectra but all of them have three important things namely specific energies here the specific energies are the absorption peaks that you see here and in this spectrum the specific energies are the positions corresponding to the wavelength wave number. Wave number is inversely proportional to the wavelength. So increasing wave number means this is decreasing numbers therefore it means that decreasing energies. This is the lowest energy vibrational motion and then so on.

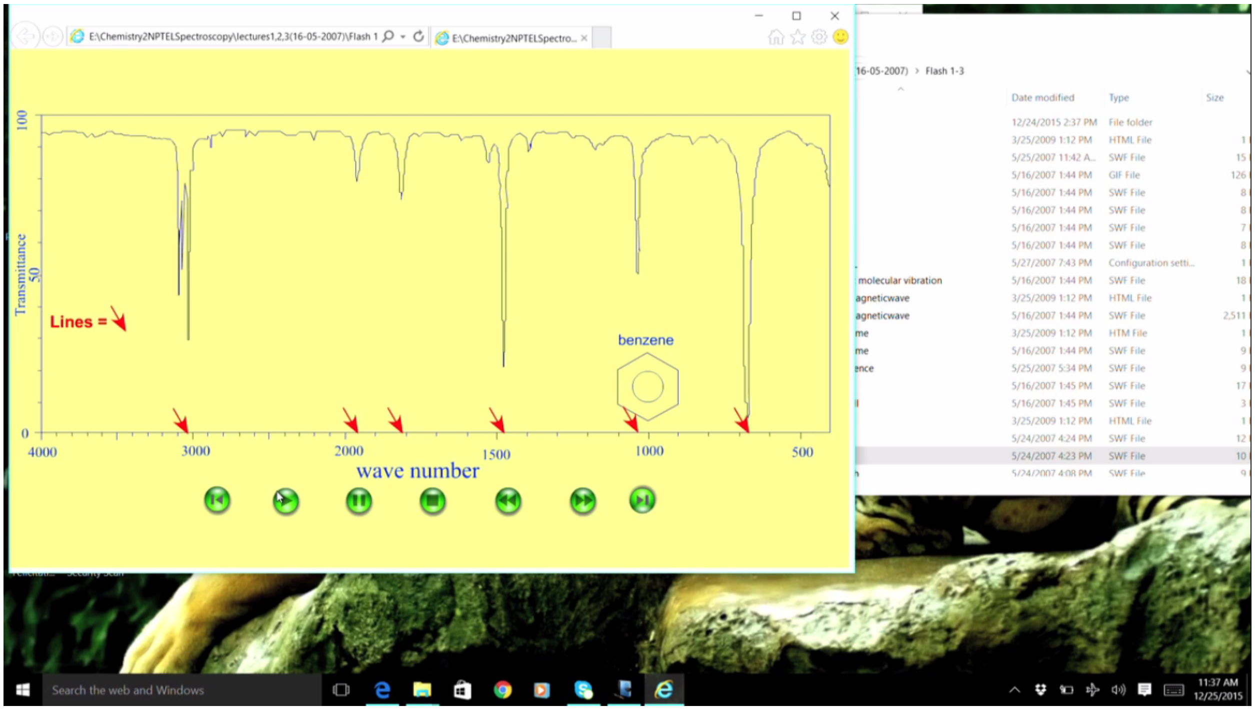


Introduction to Molecular Spectroscopy.

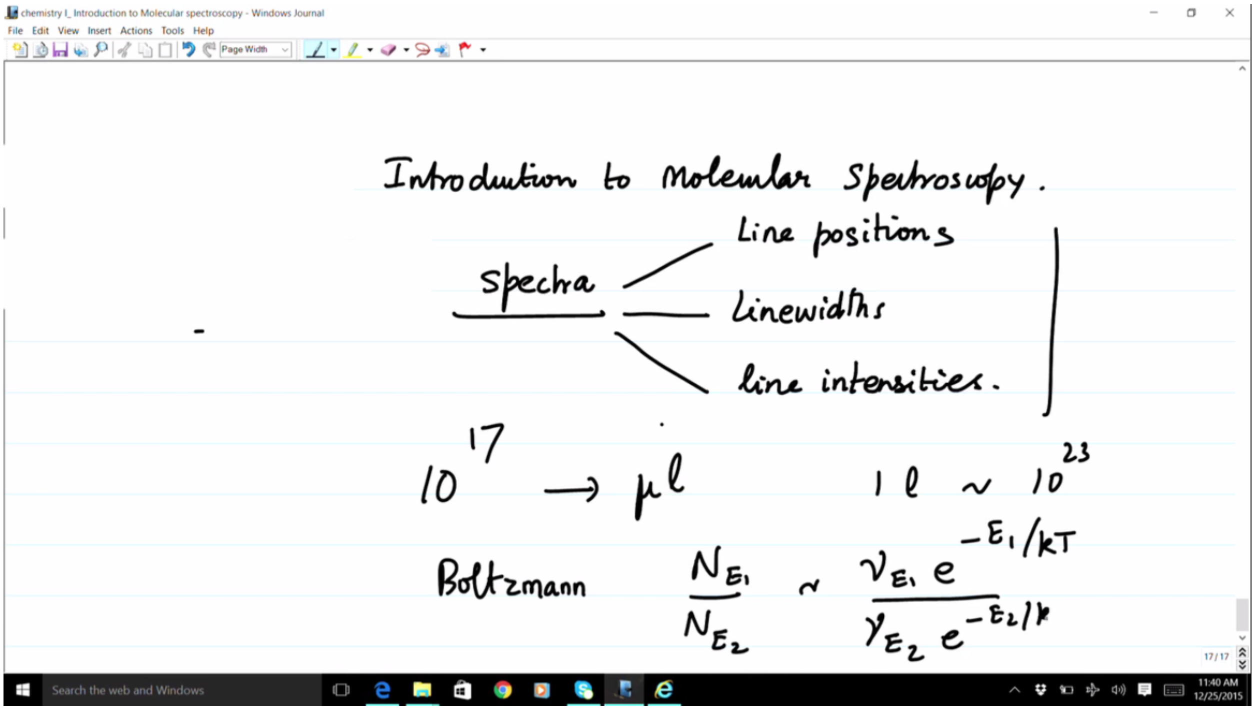
Spectra
- Line positions
- Linewidths
- line intensities.

Now the line positions linewidths and line intensities are seen like this. Let's see that using an animation.

So in this animation you can see that for the same benzene spectrum lines correspond to specific resonance absorption. So the red arrows indicate the dominant absorption frequencies that benzene has in the infrared region. They correspond to very specific energies. Therefore what do they tell us. they tell us the transition that take place between a given pair of energy levels therefore the information is directly associated to our understanding of the molecular energy levels through quantum mechanics because molecular energy levels are not studied using classical mechanics. We have to solve the Schrodinger equation and the Schrodinger equation gives us different energy levels and the absorption frequencies or the line positions tell us which of these energies are seen in the spectrum. Therefore, line positions are studied using quantum mechanics.



Next if you look at the line width you can see that in this picture you can see that the line widths are different for different energies of absorption. They are not uniform. This is a very very large line width. This is slightly narrower and this is extremely narrow. Therefore the line widths also vary depending on the energies that you have and the third important factor that you have to study is the line intensities which you can see in this picture. The line intensities are again different for different absorption frequencies. They are not uniform. All of them do not have the same intensity. So the line intensities are essentially measures of the number of molecules which undergo absorption at that particular energy of transition. Therefore it's obvious that molecules, all the molecules even though they may be at a given temperature all of them do not have the same energy and molecules are distributed in their energy levels and this is something that we are very familiar from the elementary Boltzmann distribution of molecular velocities in thermal equilibrium molecules of different energies and different numbers. So even if you take a microliter of a sample and if you assume that one liter approx contains an Avogadro number of molecules a microliter contains 10 to the 17 molecules microliter assuming that one liter contains 10 to the 23 molecules and that's a huge number of molecules and therefore not all of them have the same energy. There is a distribution and the thermal distribution at equilibrium is given by the Boltzmann formula that the number of molecules in any energy level E1 to number of molecules in another energy level E2 is given by the ratio the degeneracy corresponding to that E1 times exponential minus E1 by KT if this is molecular energy divided by nu E2 which is the degeneracy exponential minus E2 by KT. K is the Boltzmann constant and T is the temperature. Therefore the intensities give us a distribution or what is known as a statistical distribution because this is thermal equilibrium, how many molecules are in this energy level, how many are in that energy level and there is a progressive number decrease as the molecular energies increase and that decrease is given by this ratio namely the Boltzmann ratio.



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$10^{17} \rightarrow \mu l$

$1\,l \sim 10^{23}$

Boltzmann $\frac{N_{E_1}}{N_{E_2}} \sim \frac{\nu_{E_1} e^{-E_1/kT}}{\nu_{E_2} e^{-E_2/k}}$

Molecular line positions are given by pure quantum mechanical energy levels and solutions whereas the intensities are not only given by the quantum mechanics because the energy levels themselves are quantum mechanical but in addition to that or on top of that the statistical distribution is imposed therefore, it is given by quantum statistical mechanics. What about line widths? Line widths refer to the fact that even though the energy levels are sharply defined the molecules are in constant motion and the molecules are constantly interacting with each other. Therefore, the energy levels are not really sharply defined between different molecules and that is a spread even given energy state in the molecules to multiple to a collection of molecules there is a small spread therefore the absorption does not happen at that particular frequency of one molecule but it varies from molecule to molecule and that's the reason why you see the spread here or the spread here or the spread here being different for different energies. In addition the solvents play. The the surrounding gases play a role. Therefore the line widths are very very dynamic phenomenon of the molecules actually evolving at any given temperature due to various dynamical moments. Therefore the line widths not only have spectroscopy and the quantum mechanics and statistical mechanics but also the time dynamics of molecular interactions with the surroundings they are more difficult and more complex to understand.

So every elementary sort of an anecdotal I mean analogy if I have to give take about – take the population in I mean on the planet approximately six billion people. Not all of them have the same wealth not all of them have the same energy. The wealth is distributed in some way. There is an average wealth distribution. There are poor countries. There are rich countries and even in rich countries there are poor people and rich people. So there is a distribution. Therefore, you see that the wealth is distributed according to whatever the local the conditions are. All of them do not have the same wealth and money also doesn't necessarily stay with the same person all the time. There is a constant migration of it and you can associate that this transaction of this energy also happens with the minimal currency which varies for different countries and here the currency for the energy transaction is given by the Planck's constant. So you can see that there is a loose association with whatever we call as a molecular behavior with a large statistical behavior of associate of a system that there is wealth concentrated in smaller pockets and then there is dynamics between the concentration of the wealth moving between different pockets and also statistical distribution the number of people having a certain amount of wealth is also different for different amounts. So in that sense molecular distribution this is all in equilibrium but the radiation disturbs that equilibrium and therefore the dynamics that happen is thoroughly understood through spectroscopy if we concentrate on these three phenomena line widths, line intensities and line positions for each and every branch of spectroscopy then we are able to map the whole molecule with multiple pieces and we would get to know the maximum piece of information about molecular systems. We will see that branch by branch in several lectures from microwave to infra red to visible and to [Indiscernible] [00:11:52] spectroscopy until then thank you very much.