Chemistry II: Introduction to Molecular Spectroscopy

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Lecture – 04
Analysis of spectra

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 this are broadly classified into 3 aspects and this 3 aspects are given here in the page.

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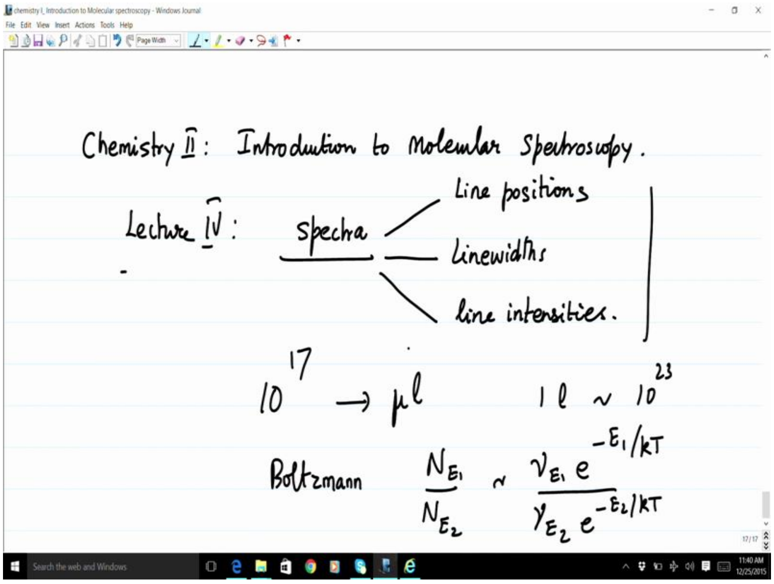

Chemistry II: Introduction to Molecular Spectroscopy.

Lecture IV: spectra — Line positions / Linewidths / line intensities.

$10^{17} \rightarrow \mu l \qquad 1\,l \sim 10^{23}$

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

You can see that spectrum you are always concerned about to the line positions or the frequencies for the transitions to take place between molecular energy levels and molecular energy levels are discreet and therefore, frequency are also discreet, that they do not happen everywhere that only specific energies.

The other important aspect of a spectrum is that each of this line as a line width associated with it, and these are important in that they contain information about the molecule and what about the distribution of energies in the molecule? And the third line widths and the third is, the line intensities. In fact, in the order I would say line positions, line intensities and line width in the order of difficulty of more understanding. So, I would alignments are very difficult to understand. Line intensities are the approximate indicators of the statistical distribution of energies in the molecule. Let us see what this thing is by an example.

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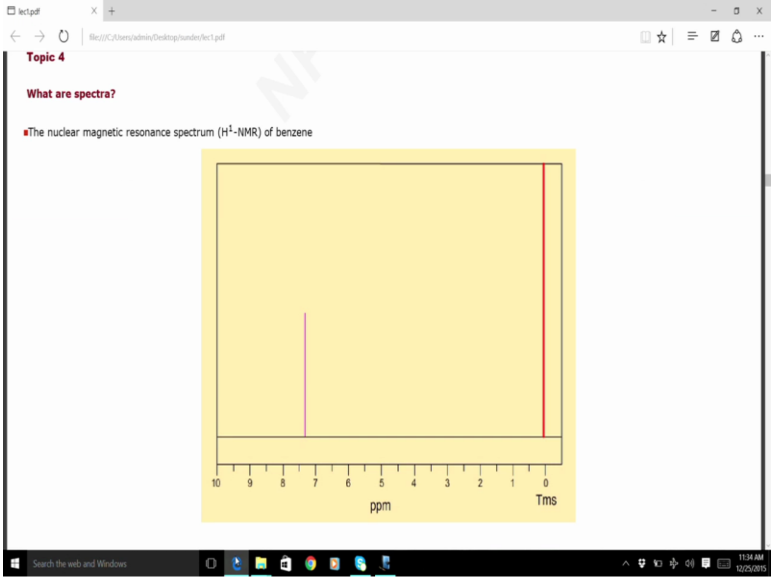

Topic 4

What are spectra?

- The nuclear magnetic resonance spectrum (H^1-NMR) of benzene

Let 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 photon magnetic resonance spectrum of benzene which contains typically only one line. There is only one frequency for the photon n m r for the benzene molecule and this large line is sample reference line due to this solvents that you have. This is a magnetic resonance spectrum, but if you do this under very high resolution even the single line will have small line width associated with that.

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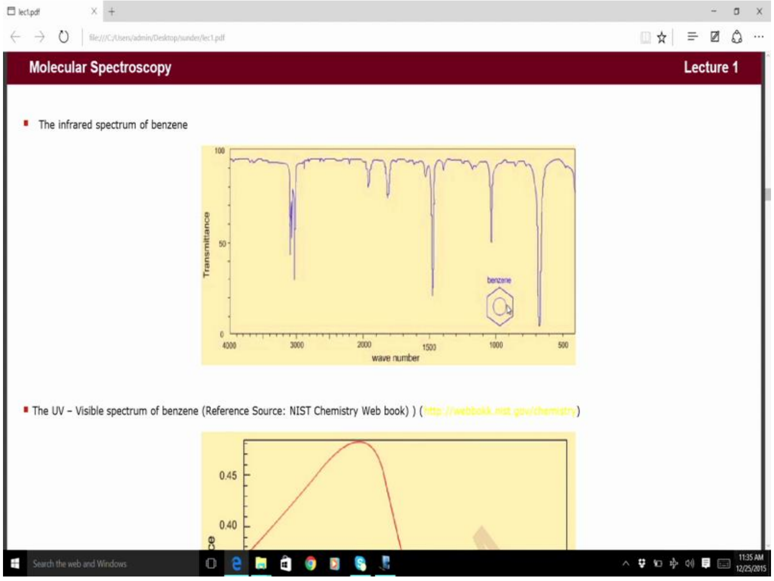

Molecular Spectroscopy

Lecture 1

- The infrared spectrum of benzene

- The UV – Visible spectrum of benzene (Reference Source: NIST Chemistry Web book)) (http://webbook.nist.gov/chemistry)

The same molecule in the infrared region when we worry about molecular vibrational motion of benzene, benzene being 6 as 4 as many vibrational degrees of freedom and you can see that the spectrum as several lines it is quite different from the photon NMR spectrum that you have saw and also if you study benzene using UV visible light and I have given the reference source that I have taken the picture from the national institute technology chemistry web book, this is a typical visible spectrum of benzene.

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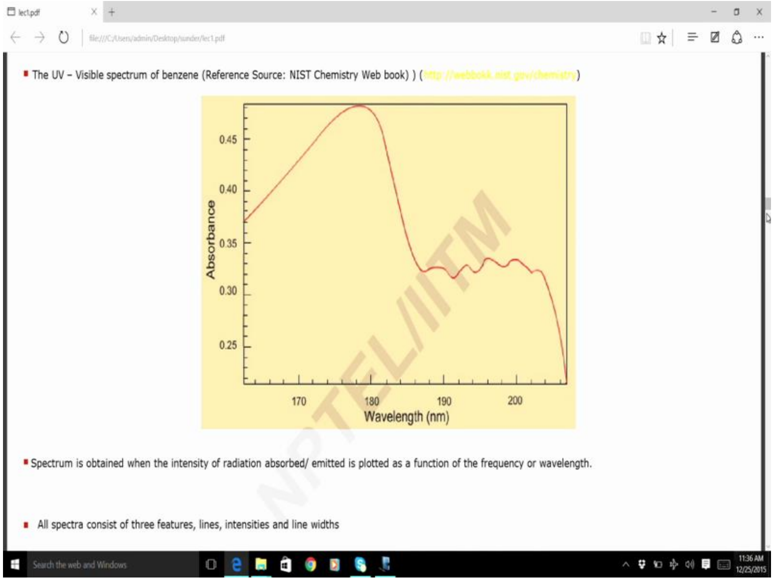

- The UV – Visible spectrum of benzene (Reference Source: NIST Chemistry Web book)) (http://webbook.nist.gov/chemistry)

- Spectrum is obtained when the intensity of radiation absorbed/ emitted is plotted as a function of the frequency or wavelength.

- All spectra consist of three features, lines, intensities and line widths

So, the same molecule and the 3 different radiations plus three different spectrums, but all of them have 3 important things namely specific energies here. The specific energies are you observed from the pics that you see here and in this spectrum in the specific energies are positions corresponding to the wave length, wave number; wave number is inversely proportionally to the wave length. So, increase in wave number means sorry this is decreasing wave number. So, therefore, means decreasing energies this is the lowest energy vibrational motion and then so on.

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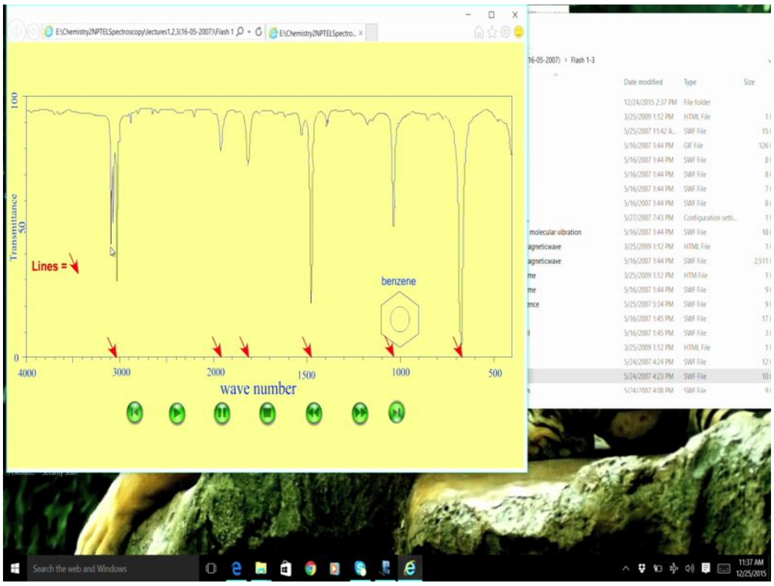

Now, the line positions, line widths and line intensities are seem like this. Let us see that using an animation. So, in this animation you can see that for that same benzene spectrum, lines correspond to specific resonance absorption. So the red arrows indicate the dominant absorption frequencies, which benzene has in the infrared region. They correspond to very specific energies therefore, what do it tell us? They tell us the transition takes 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 (Refer Time: 04:52) equation and (Refer Time: 04:54) equation give us different energy levels and we absorption frequency are the line position tell us which of these energies are seen in the spectrum. Therefore line positions are studied quantum mechanics.

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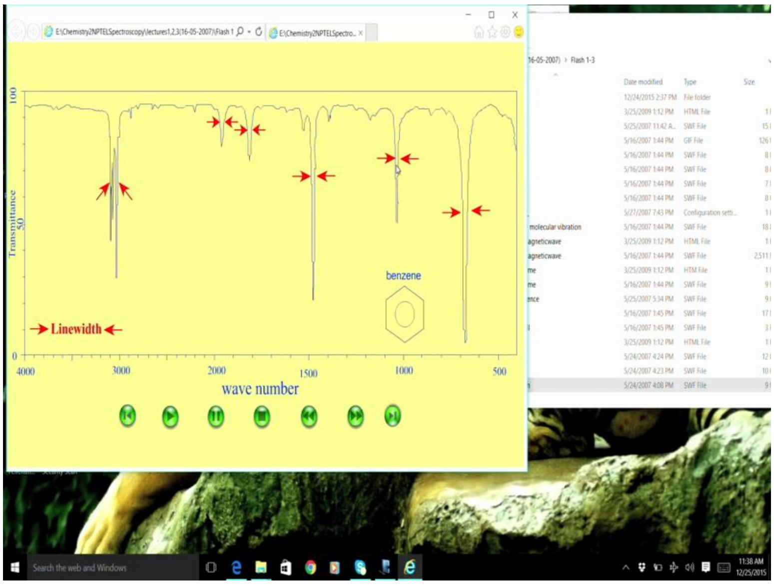

Next if you look at the line width you can see that in this picture, you can see the line widths are different for different energies of absorption, they are not unique form, this is very large line width, this is slightly narrow over and this is extremely narrow therefore, the line width also vary depending 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.

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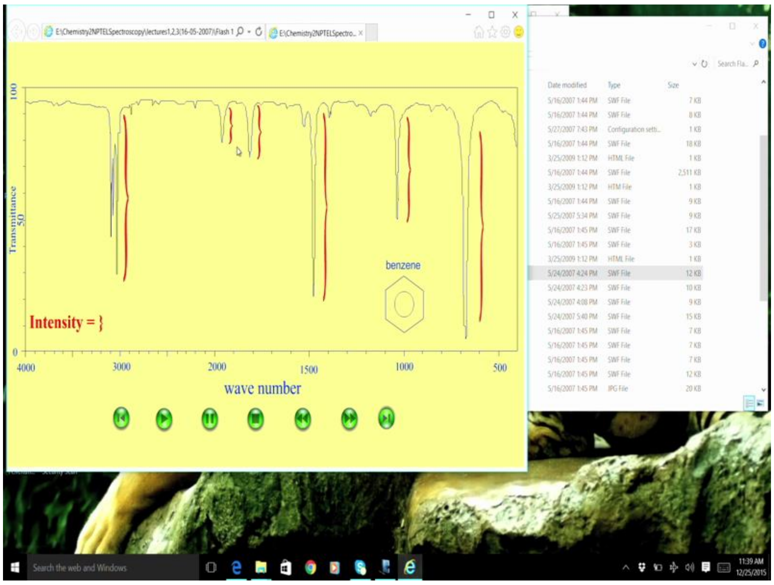

The line intensities are again different for, different absorption frequencies they are not uniform, all of them have do not have same intensity, the line intensities or essentially measures of the number of molecules which undergo absorption at that particular energy of transition. Therefore, it is obvious that molecules all the molecules even though they may given at a temperature, all of them do not have same energy and molecules are distributed in their energy levels and this is something that we are familiar from the eliminatory distribution of molecular velocities in the equilibrium molecules have different energies and different numbers.

So, even if you take a micro litre of a sample and if you assume that one litre approximately contains a Avogadro number of molecules, a micro litre contains 10 to the 17 molecules micro litre assuming that one litre contains 10 to the 23 molecules and that is a huge number of molecules and therefore, not all of them have the same energy it is a distribution and the thermal distribution at equilibrium is given by the Boltzmann formula, the number of molecules in any energy level E 1 to number of molecules in another energy level E 2 is given by the ratio D generousy corresponding to that E 1 times exponential minus E 1 by k T this is molecular energy divided by nu E 2 which is the d genres exponential E 2 by k T, k is the Boltzmann constant and t is the temperature.

And therefore, the intensities give us distribution or what is known as statistical distribution because this is thermal equilibrium. How many molecules are in this energy level? How many are in that energy level? When there is a progressive number decrease as the molecular energy is increase and that increases by this ratio namely the Boltzmann ratio molecular. Line positions are given by pure quantum mechanical energy levels and solutions, where as the intensities are not only given by the quantum mechanics because the energy levels themselves are quantum mechanical, but in addition to that or in top of that the statistical distribution is impose. So, 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 shortly defined the molecules are in constant motion and the molecules are constantly interacting with each other, therefore the energy level are really sharply defined between different molecules and there is a spread of even a given energy state in the molecules to multiple to collection of molecules there is a small spread. Therefore, the absorption does not happen that particular frequency of 1 molecule, but from varies from 1 molecule to 1 molecule and that is the reason why you see this spread here or the spread here or the spread here being different for different energies.

In addition the solvents play a role the surrounding gases play a role therefore, the line widths or very dynamic phenomenon of the molecules actually evolving at any given temperature due to various dynamical motions. 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 a very eliminatory sort of (Refer Time: 09:48) analogy I have to give, take about the population in I mean the planet approximately 6 billion people, not all of them have the same wealth, not all of them have same energies the wealth is distributed in some way there is an average wealth distribution there are poor countries there is a rich countries even there in rich countries there are poor people rich people. So, there is a distribution therefore, you see that the wealth is distributed according to what about the local the conditions are. All of them do not have same wealth and money also does not necessary 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 planks constant. So, you can see that there is a loose association with what we call as molecular behavior with a large statistical behavior of a social of a system, that is there is wealth concentrated in small 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 also in equilibrium, but the radiation the steps are equilibrium and therefore the dynamics that happen is thoroughly understood through spectroscopy if we concentrate on this 3 phenomenon line widths, line intensities and line position each and every branch of spectroscopy, then we are able to map to whole molecule with multiple trees and we would get to know the maximum piece of information about molecular systems. We will see that branch by branch in the next several lectures micro wave to infrared to visible and to roman spectroscopy until then.

Thank you very much.