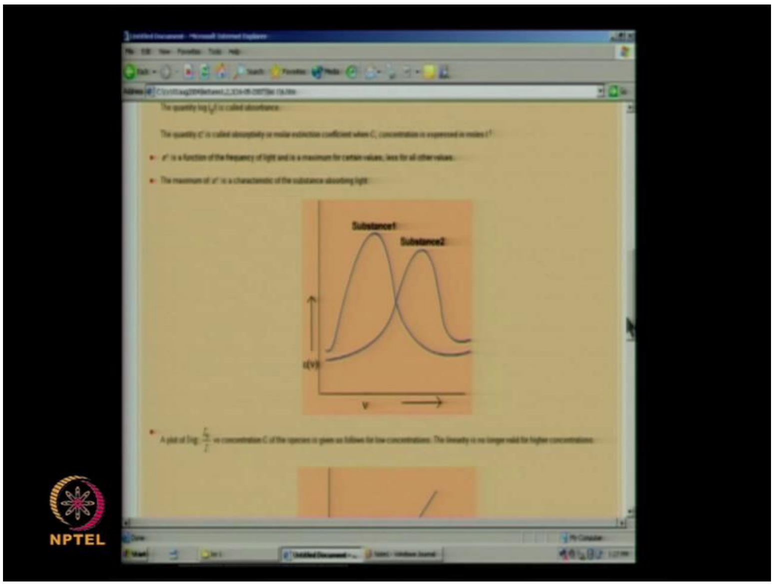
Introductory Quantum Mechanics and Spectroscopy
Prof. Mangala Sunder Krishna
Department of Chemistry
Indian Institute of Technology, Madras

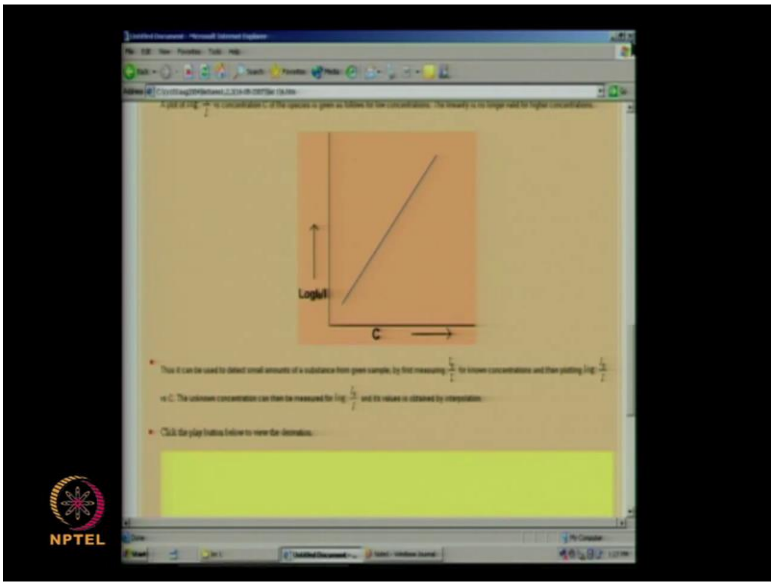
Lecture – 09
Molecular Spectroscopy – Part 3
Elementary Electronic Spectroscopy

Welcome to the lectures on Chemistry. In this module, we have been looking at molecules spectroscopy.

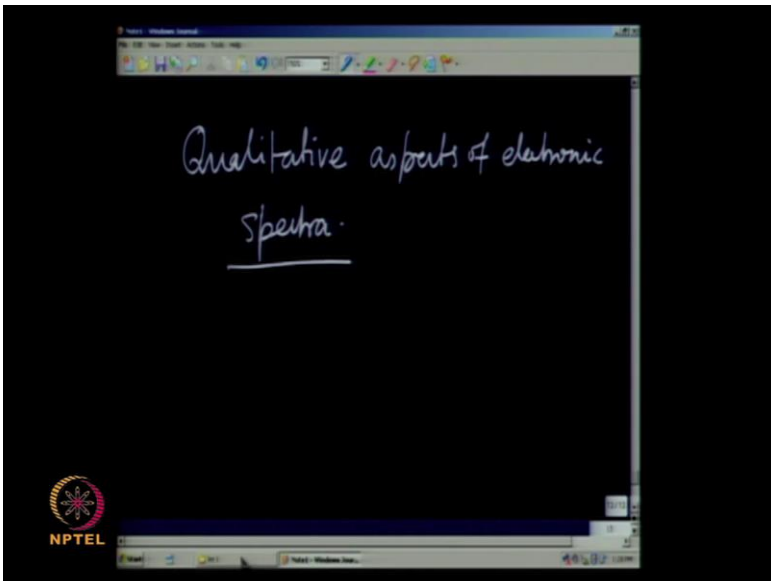
(Refer Slide Time: 00:24)



(Refer Slide Time: 00:26)



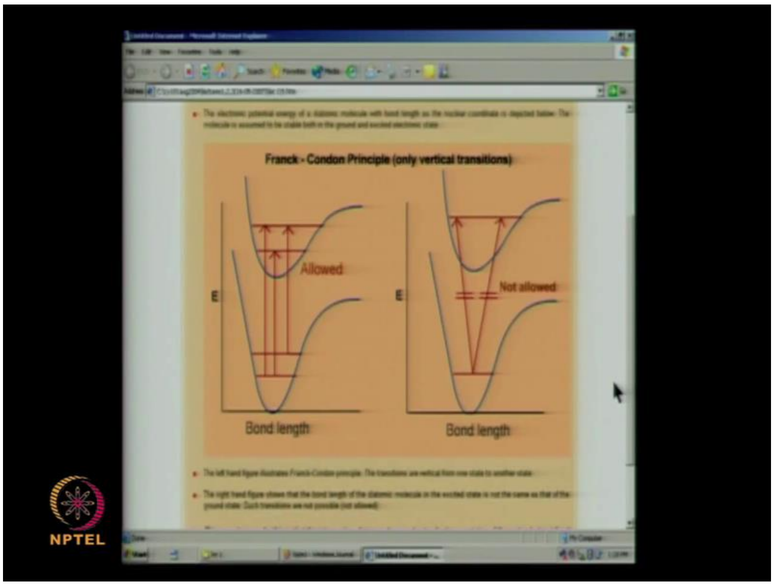
(Refer Slide Time: 00:28)



Qualitative aspects of electronic spectra.

Now let us get to the last part very quickly namely, qualitative electronics spectrum, aspects of electronics spectrum.

(Refer Slide Time: 00:47)

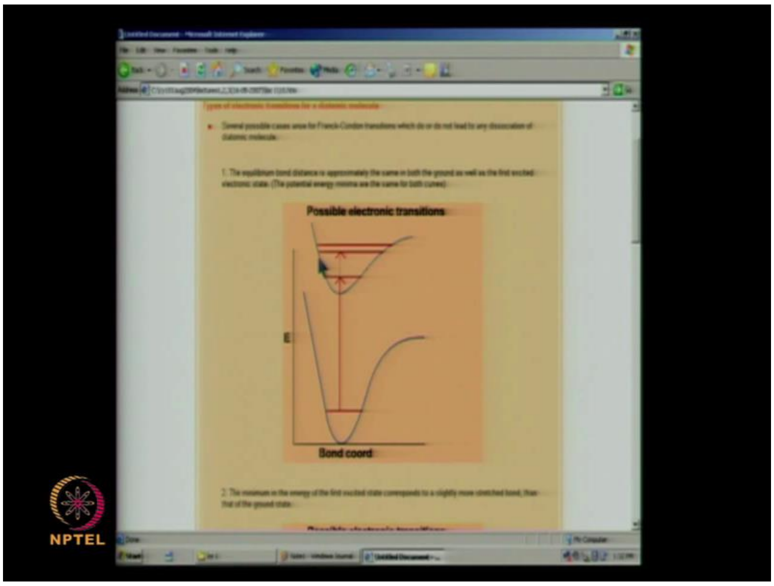


Franck - Condon Principle (only vertical transitions)

The most important part that, I would like you to be familiar in the electronic spectra is the following that is on the screen called the Franck-Condon principle. Pease recall that electronic transition requires a lot of energy we need visible to uv light. Vibrational motion of the molecule, if you remember is in the infrared range and the rotations of the molecule takes place in the change the geometrical rotation of the molecule is even at much lower energy. One of the most important principles in electronic spectroscopy is that, when a molecule is electronically excited from one state to the other, there is very little time for a molecular geometry to change during the transition. You recall the geometry changes in the molecule require molecular displacement relative to each other or orientations relative to each other.

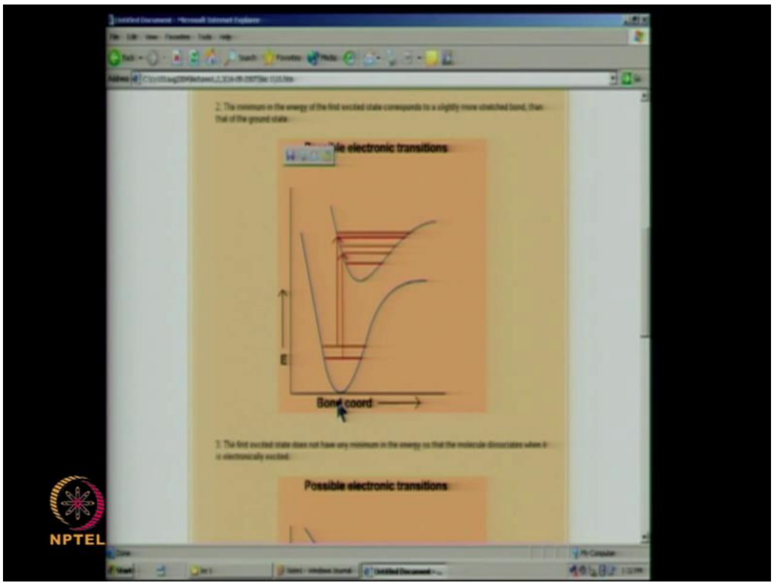
All of these things require a much lower energy take a much longer amount of time. In fact, the frequency when you take about is a measure of the rate at which the processes takes place. So, if you say in the infrared region, molecular bounding I mean the vibration take place the frequency of the infrared light gives you also the times scale. In fact, the inverse of the frequency if you remember has a time unit frequency itself is a time inverse unit. One by frequency tells you the times scale within which the changes the place. Therefore, if the frequency is very high the times scale in which things happen is very, very small, very narrow. Electronic transition takes place at very high frequencies compared to the electronic the molecular motion in vibration and rotations. Therefore, the time scale in which the electronic transition takes place is so much less compared to the time scale of molecular motion. What you see here is a typical diatomic potential energy turn what I have plotted is molecular potential energy as a function of the bond length for a diatomic molecule for the ground state, and for the first excited state that you see here. What happens is the electric transition from the ground state to the excited state takes place vertically that is no changing the bond length of the molecule during this transition. And if you look at the corresponding graph here, you see these two lines which correspond to non-vertical transitions. If you look at this this is the molecular bound the bond length here and here is a slightly different bond length, such transitions are not allowed. The principle is known as one of the cornerstones in electronic spectroscopy, the principle is based on I mean is after two individual who discovered this James Franck and also E U Condon. And it is known as a Franck-Condon principle by which electronic transitions are expected to take place in such a short time scale that what you have is only electronic transition, which are vertical, we will see more of this later. But as a result of this you see there are several different possibilities for the molecular electronic citation which I shall summaries in the next minute.

(Refer Slide Time: 04:18)



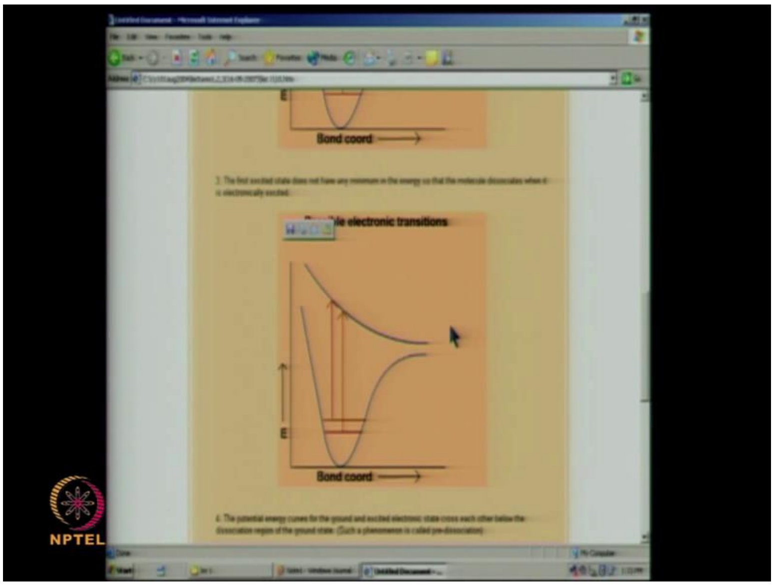
If the potential energy of the ground state of the molecule and the potential energy of the excited state of the molecule both support bound states, you see that molecule gets excited to a higher energy state. It is table here, molecule is trapped in the bound state and therefore, it can emit light and reach the ground state is a process called florescence. And if takes a little while to go from one state to the other and then emits light, light that is emitted is the different frequency it is called a (04:53), different possibilities exists here.

(Refer Slide Time: 04:57)



Whereas, for example, if you have the potential energy of the molecular electronic state in the following way namely, the ground state potential energy the bond length, the excited state bond length or slightly different equilibrium bond length on the excited state is here, the equilibrium bond length of the ground state is here that is the molecular geometries are different between these two different state then a transition may lead to dissociation.. If for example, the molecule is excited the energy level as you see in the next graph or a molecule excited in this graft to a higher energy level like this, this can lead to a transition in one vibrational motion to decomposition

(Refer Slide Time: 05:39)



There are also molecular transition such that, the excited states do not have any bound state for the molecule, no vibrationally bound state, such excitation electronically lead to dissociation of molecule. So, there are various possibilities in electronic spectra we will look at it more after we have done microwave and infrared spectroscopy. Because electronic spectrum is far richer than any other and also it is much more difficult to understand.

We looked at three things namely, the three processes that take place in the molecule called emission, spontaneous emission, absorption in the presence of radiation and stimulated emission. And we quantified a relationship between these three processes following Albert Einstein's model. The semi classical model for the radiation processes and also arrived at a relation between the radiation processes and the molecule property namely dipole moment. The second was to look at the absorption as a quantitative phenomenon in relating to the concentration of the molecular species the Beer-Lamberts law is a very useful quantitative law valid for small concentration. And also gives you coefficient which are characteristics of the substance as well as the light which the substance absorbs. So, a property that can be useful for further studies is the Beer-Lambert law and thirdly we looked at very, very preliminary qualitative aspect of the electronic spectroscopy .