Chemistry II: Introduction to Molecular Spectroscopy

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Lecture - 25

Review of basic concepts in Molecular Spectroscopy

Welcome back to the lectures on chemistry. This is the last lecture in the course, the short introductory course on molecular spectroscopy that I started giving about 2 months ago and in this particular lecture I want to summarize all the important results. That it would help you in keeping the sub in your studies and also towards the test that you wanted to write in the coming weekend and also the week after wards 1 of the 2 weekends.

Let me first of all tell you that I have enjoyed; obviously, giving the course in public domain and I have had quite lot of interactions with a few students here and there, but unlike a massive open online course, the number of interactions I have had is not that many, hopefully things will improve as you read more and more. Let us get to the topic namely the review of basic concepts, which I hope you would take it as a lesson forward and as a take on lesson, if any for the next course, any advanced activity in molecular spectroscopy, the this is the final lecture of this course that mean the supplementary readings, but they are not parcel of the final examination.

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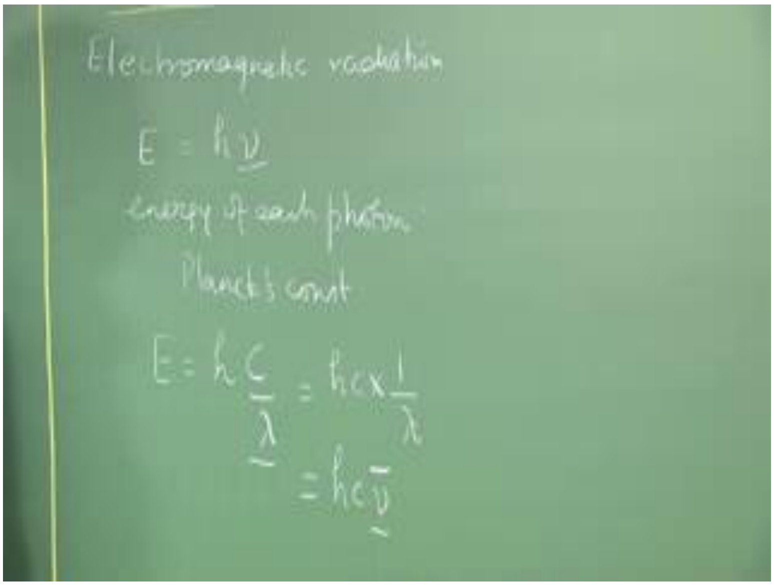

Electromagnetic radiation

$E = h\underline{\nu}$

energy of each photon

Planck's const

$E = h\frac{c}{\underline{\lambda}} = hc \times \frac{1}{\lambda}$

$= hc\underline{\bar{\nu}}$

We started with electromagnetic radiation, as the first object and its interaction with matter was define as the basic area of molecular spectroscopy and if you recall we use to the Einstein relation E is equal to H nu, where this is the Planck constraint and this is the frequency of the radiation that interacts with the substance and the energy of each photon is given by its frequency with the Planck's constant here. This was also written as E is equal to H C by lambda, by lambda is the wave length of the radiation and C is the speed of light in vacuum. We did not do calculations for the wave length or the speed up light in other medium, but we assumed vacuum and the last thing was also to write to the H C into 1 by lambda or equal to H C nu bar. These are the 3 fundamental relation that we need not to use the frequency energy is proportional to that the lambda. The wave length energy is inversely proportional to that and the wave number energy is directly proportional to that with these three things as to 3 properties defining the radiation.

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Radio waves

-cosmic rad.

Microwave.

Infrared.

Then we decided to look at to the electromagnetic spectrum and came up with the radiation, all the way from radio waves to cosmic radiation, that is the whole range of electromagnetic radiation frequencies of the order about 15 orders of magnitude 15 to 20 orders of magnitude and therefore, we saw that the radio waves where important in interacting with the magnetic property of the matter and that let to what is called, thus the magnetic resonance which we did not look in to this course and then microwaves which also interacts with the magnetic properties of the electron to give you, what is called the electron paramagnetic lessons. Those 2 branches, the nuclear magnetic resonance which is the result of the interaction of the radio waves of electromagnetic radiation with the nuclei which or placed in a studying magnetic field to that of the electron in microwave. Both of these were called the magnetic phenomena and then we studied only the optical phenomena namely the interaction of electric component of the radiation with matter and that we studied using 2 branches of spectroscopy microwave and infrared.

Briefly I lectured a bit about an electronic spectroscopy in 1 of the lecture notes. I believe it is in the lecture 1 of the P D F towards the end of it, where I also talk about the bond (Refer Time: 05:20) approximation and how the electronic transitions are called the Planck content transitions and so on, very, very briefly, I introduce that, but in the lectures I have not given that we spent a lot of time looking at the microwave radiation infrared radiation and also the properties which were responsible for the radiation to absorb in the microwave range and also to absorb in the infrared range. This was the second step, but even before that when we look at the electromagnetic radiation, we looked at a couple of important phenomena called the absorption emission and the stimulated emission.

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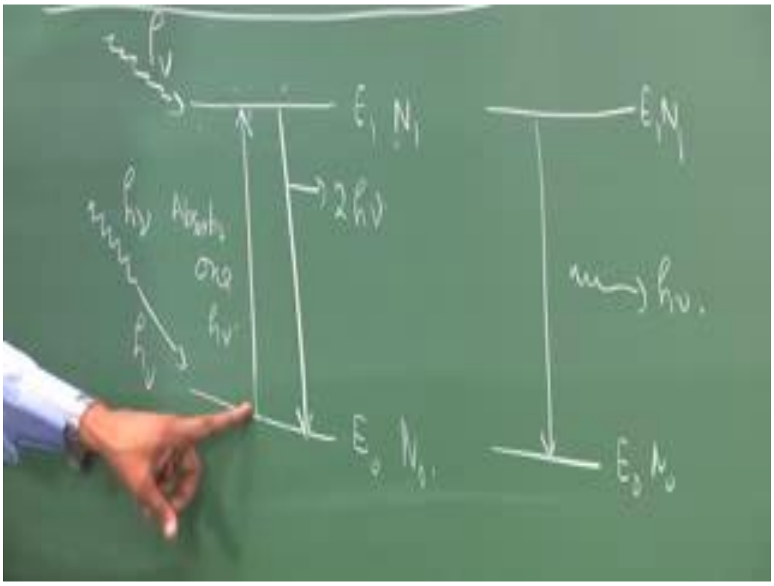

If you recall we had these pictures about the molecular energy levels the lower energy level and the upper energy level and the radiation falling on the molecules in their lower energy level causing them to be excited if the radiation has the frequency H nu which corresponds to the gap between these 2 energy levels. There is a possibility that this radiation will be absorbed and since the radiation in the loss of fall on the excited molecules, it is possible that the radiation will stimulate the emission of molecules on the excited state to the lower energy of the ground state.

The absorption and the stimulated emission, both of which were caused by the radiation were also approximately proportional to the number of molecules in the respective, say and for radiation be used the radiation density rho nu therefore, the absorption process is proportional to both the radiation density and the number of molecules which are in this energy state which allows in the molecule 2 then excited and the stimulated emission is the rate of stimulated emission is proportional to the number of molecules in the excited state and also to the radiation density, but independently there was this process where, molecules which are in the excited state spontaneously decaying to the lower energy state and releasing a quantum of energy when this happens, this releases 2 quantum of energy and this absorbs 1 quantum of energy absorb.

This process was also described to you with the corresponding balance equation of the rates or a system in equilibrium with the radiation, a system in thermal equilibrium and also in equilibrium with the radiation that a given temperature and these rates equations where used along with, what was the known as the max Planck distribution law or the radiation density as a function of the frequencies of light emitted by idealized body such as the black bodies and this led to some relation between the absorption coefficient or the emission coefficients the stimulated emission coefficient both of which are equivalent to the spontaneous emission coefficient. This was the process which was important for us to understand as a semi classical way of understanding why molecules absorb energy and therefore, all the things are happen in the molecules happens as they are.

Then we moved on to study the molecular domain with specific properties such as the microwave radiation, absorbing being absorbed by the molecule causing changes in the rotational energy level. We looked at what was known as the rigid rotor model for the rigid rotor model. We used to the rigid body kinetic energy namely E kinetic energy is the square of the angle of momentum divided by twice the moment of inertia.

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And in the case of quanta mechanical systems the angle of momentum being an operator, the Hamiltonian for your rotating system in which the equilibrium configuration did not change. That is why it is called rigid body the molecule remains intact. There is no vibrational emotion of there is no displacement about equilibrium. It is an approximation because molecules no vibrate at even of zero Kelvin, but a rigid molecular approximation means that the molecules the atoms do not move around their equilibrium. they stay remain, they stay rigid and therefore, the moment of inertia does not change for such a system, the Hamiltonian was written as J square by 2 I and for a simple diatonic molecule with a reduced to mass mu given by M 1, M 2 by M 1 plus M 2 where these are the masses of the individual atoms in the diatonic molecule. The momentum of inertia I was written as mu not R nu times R square, where R is inter atomic distance or the bond distance at equilibrium this was used to solve.

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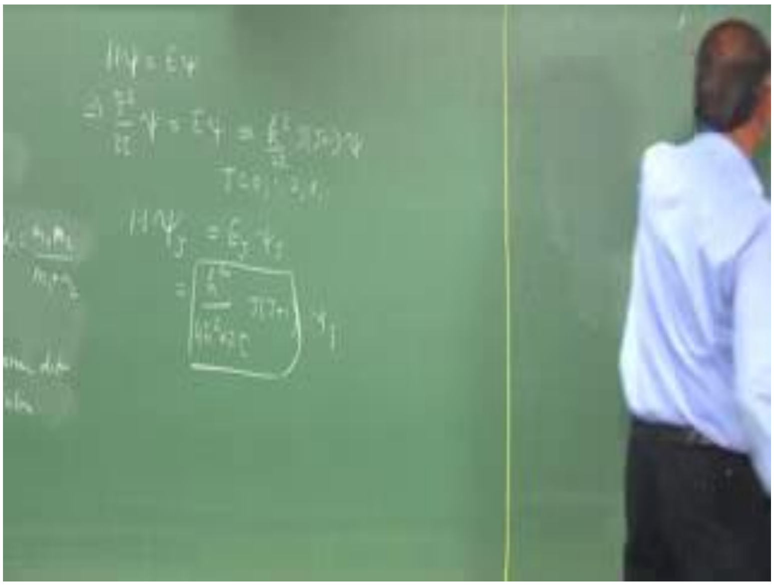

Of course, I gave you the solution and quantum mechanics how to solve this problem by writing the Schrodinger equation H psi is equal to E psi and this gives you J square by 2 I acting on side J being the operator giving you E psi and this E turns out to be H bar square J into J plus 1 a quantum number J where J is 0 1 2 3 etcetera. This was the solution that the head used therefore, what you have is H bar square by 2 I J square by 2. The solution is J square acting on psi gives you H bar square J into J plus 1. Therefore, this by 2, I give you that. This was call the energy E J and the way function corresponding to the was call the psi J and the J later we will find out that the psi J itself is 2 J plus 1 if already generate, but I am get to that in a few minutes. This is E J and E J is given by H bar square which is H square by 4 pi square into 2 I times J into J plus 1 times psi J and this whole quantity, which is called the E J was written as a wave number.

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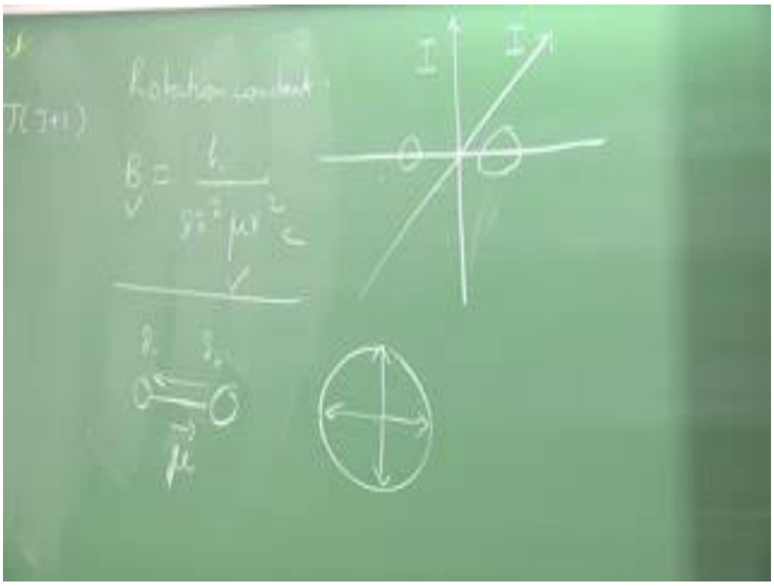

Hence, the appropriate constant namely E J was written as H C times B times J into J plus 1 this B by definition because of H C into B H square by H pi square I, B turns out to be H by 8 pi square I C and the introduction of B was to tell you that spectroscopy is used, this namely wave number unit or measurement of spectroscopy the measurement of distances between the lines and also to identify spectroscopic lines.

By this whole thing is energy H C B is energy and when you divided by H C B becomes what is called the rotation constant and this rotation constant B is; obviously, related to the molecular inter atomic distance 8 5 square times nu or square because of the I times you see and given the molecule you know what the nu is given the experimental data of the splitting between different lines, you know what the B is and therefore, C and H are constant and you can calculate the inter atomic distance or if the atomic space is or substituted by isotopic different isotopes isotopic spaces then isotopic substitution leads a change in the value of B because nu also changes.

These are things which I requested you to do, some manipulations in terms of simple tutorial problems and also in the regular lecture. This is for the diatomic molecule, but then all of this is possible only because, if the diatomic molecule has a dipole movement which is also created in terms of the nu symbol nu, but nu with an arrow meaning the dipole movement having a direction. Suppose the residual approx here and delta minus A due to electoral negativity difference then the nu is given by this direction times that is whatever is the distance bond distance between the 2 atoms times the charge difference namely delta plus or delta minus the delta plus giving you the dipole movement it is dipole movement which under goes oscillations in this course of course, return to goes rotations as the molecule rotates about all the 3 of its axis, but if you look at this axis the movement of whinier here above this axis, is 0 because the mass are concentrated on the line itself on the axis itself.

Therefore, there is no perpendicular distance or from the rebound axis. This I is 0 and this also does not lead to any dipole movement change because the molecule is rotating above its own axis there is no change and this is not a rotational degree of freedom. In fact, this is this does not change anything suppose a diatomic molecule has only 2 rotation degrees of freedom, namely above an axis crossing through the central mass of the molecule and perpendicular to the boned and also another axis perpendicular to the bond again, but also passing through the center mass these are the 2 movements of be next here and both of these are equal therefore, a diatomic molecule is very special case in which draw omens above 2 mutually perpendicular axis if the diatomic molecule is like this 1 axis is this, the other axis is this the third axis which is perpendicular to both of these long. The bond does not contribute to rotational molecule. You have 2 degrees of freedom and the overall angular movement that you talk above is the sum of the 2 degrees of freedom about those 2 axis and with the same movement of inertia.

This is the micro way spectrum for a rigid diatomic molecule and the molecules needed to have dipole movement because during a rotation the dipole movement will be perhaps splitting like this. After some it will rotate and then like this, and then like this if you draw this, the dipole movement rotates about an axis which is perpendicular to that or the dipole movement rotates in an out of the plane dipole movement comes out and then goes into the plane and therefore, it rotates more free axis.

Those two such rotational motions lead to electric charge acceleration, I mean the motion of the eclectic charge dipole movement. Therefore, there will resolute with the electromagnetic radiation of an appropriate recluse, lead into absorbed energy and lead into microwave transitions and the microwave transition had a selection room namely delta J is equal to plus minus 1.

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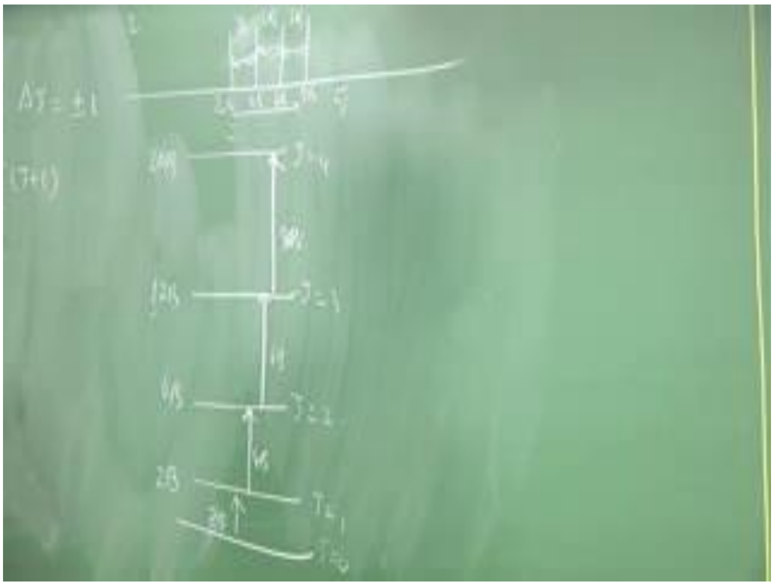

Meaning that if the energies E J or given us H C B J into J plus 1 and E J by H C. If right that then B J into J plus 1 tells you that the energy levels for a diatomic molecule or ranged in this order J is equal to 0 J is equal to 1 and the gap is 2 B, because when J is 1, it is to B and the difference is to B and then it is for 6 B for J is equal to 2 and 12 B for G is equal 2 3 then, T B for J is equal to 4 and so on. You see the successive energy levels differ by 2 B 4 B 6 B 8 B and if all of them appear as spectral transitions there is a transition at 2 B there is a transition at 4 B there is a transition at 6 B. Transition that 8 B and so on. What you see is if this is the increasing a frequency the gap between any fair of successive lines is also 2 B 2 B 2 B because this is. Line of 2 B this is line of 4 B this is line of 6 B; this is line of 8 B and so on.

Therefore, you see the difference between any fair of successive lines in a rigid body microwave gas waves rotations at from is given us to be and from the factor these H by 8 by square mu or square C right away, you can calculate the bound distances. It is possible only if molecule has a permanent dipole movement microwave spectra cannot be obtained for molecules without a permanent dipole movement and this was used in some of the tutorial problems for you to determine which molecules will have a microwave ration spectral and which doubt.

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This was the introduction to microwave spectroscopy with 1 lasting namely the intensity of these lines here I have written these as if you write it, this as nu the if 2 B nu if 2 B is this the next 1 4 B slightly of a higher intensity 6 B of a higher intensity until it reaches upon the intensity maximum and then the intensity is follow or successive transitions and the nu that the reason was due to the fact that the number of molecules in any energy level J prime divided by the number of molecules in any other energy level J double prime is given by the degeneracy of the J energy level J prime, which is 2 J prime plus 1 by the degeneracy of the energy level corresponding to this, which is 2 J double prime cross 1 times exponential minus E J prime minus E J double prime over K B T at any given time temperature and K B is a Bozeman constant.

In this formula was used to calculate the different intensities and the ratios of the intensities from lower to higher to higher and we found out that this whole formula fix into an approximate nu J max. If I have to write, the J max is happening at approximately the number 2 K B T by H C B minus 1 half. This also shown in 1 of the lectures meaning that the intensity of absorption for a rotational spectrum, it has in envelope, this kind and the maximum is given by the corresponding value of B and is also proportional to the square root of T. This is as for as the microwave spectrum is concerned; let me continue with the next short summary of the poly atomic molecular microwave spectroscopy to be in a minute.