Chemistry II: Introduction to Molecular Spectroscopy
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Lecture - 03
Introduction to Chemical applications

Welcome back to the lectures on Molecular Spectroscopy. In this lecture let me give you a bit of quantitative assessment of some of the ideas that were presented in the last lecture. If I recall in the last lecture I suggested that electromagnetic radiation with different frequencies, samples, different properties. For example, we looked at molecular rotational motion and molecular structure information being studied by radiation of gigahertz frequencies and known as Microwave Radiation, it is an optical phenomenon electrical property of the molecule being studied by the changing electric field in the electromagnetic radiation and likewise visible infrared spectroscopy sampling the molecular (Refer Time: 01:21) and so on.

We will do a bit of quantitative assessment in this lecture today, with some numbers and this what are called the ball park numbers or they are also known as the back of the envelope calculations. For those of who do not understand what is meant by the back of the envelope calculations I must give an (Refer Time: 01:45) that long before when your (Refer Time: 01:48) internet was not obviously there and even emails were not there only postage and post offices are mail through normally delivery was the order of the day, when scientist declared new results through fellow scientist through postage, very often the new results were checked by the receivers on the back of empty envelope which was attached to them and in that they will do small calculations and try to assess that it is indeed a new result that (Refer Time: 02:23) or there communicator has been declaring.

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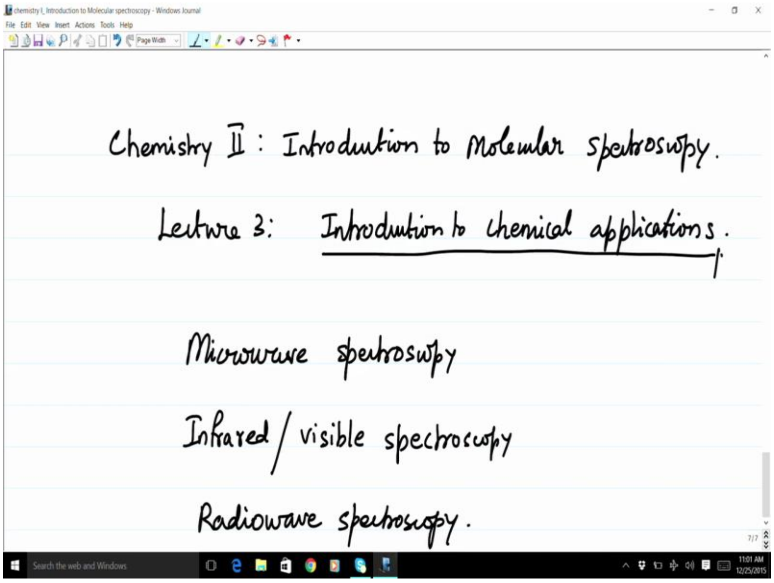

Chemistry II : Introduction to Molecular spectroscopy.

Lecture 3: Introduction to chemical applications.

Microwave spectroscopy

Infrared / visible spectroscopy

Radiowave spectroscopy.

So, if you recall we will just to do something very similar order of magnitude calculations on back of the envelope 2, 3 applications three branches of spectroscopy that you see here namely Microwave Spectroscopy, Infrared visible spectroscopy and Radio Wave Spectroscopy. Let us look at the microwave spectroscopy to begin with.

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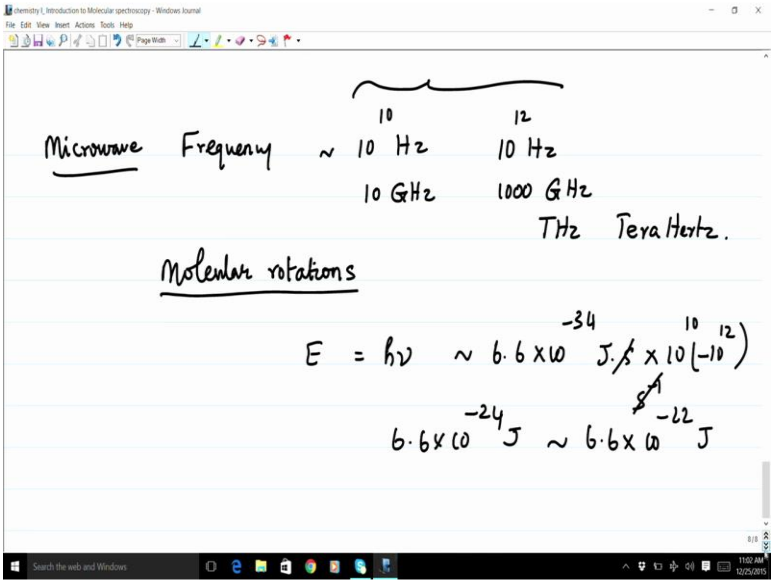

Microwave Frequency $\sim \overbrace{10^{10}\ Hz \quad 10^{12}\ Hz}$

10 GHz 1000 GHz

THz Tera Hertz.

Molecular rotations

$$E = h\nu \sim 6.6\times10^{-34}\ J.\cancel{s} \times 10^{10}(-10^{12})\ \cancel{s}^{-1}$$

$$6.6\times10^{-24}\ J \sim 6.6\times10^{-22}\ J$$

Radiation frequency range, if you remember is 10 to the 10 hertz that is about 10 gigahertz to about 10 to the 12 hertz, which is 1000 gigahertz or a terahertz or a terahertz and this is for microwave and microwave spectroscopy is used to study molecular rotations and through molecular rotations the equilibrium the structure of the molecule. Now that means, molecular rotational energies must be in the range of the frequency that you have here and the energy corresponding to this frequency which is given by E is equal to h nu which if you write approximately 6.6 to the 10 raise to minus 34 joule second times say 10 to the 10, 10 to the 12 hertz either one of this hertz, which is basically second inverse therefore that goes away. So you are looking at the energy ranges between 6.6 into 10 to the minus 24 to 10 to the minus to minus 22 joules.

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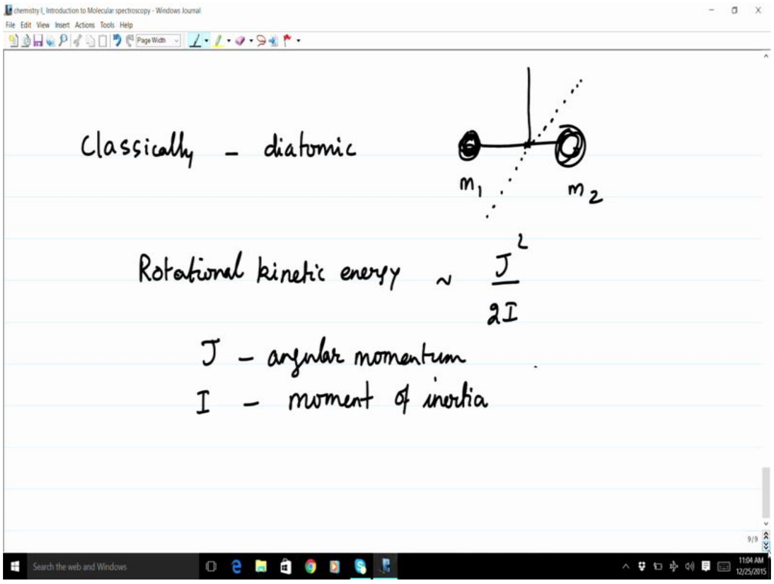

Classically – diatomic

m_1 m_2

Rotational kinetic energy $\sim \frac{J^2}{2I}$

J – angular momentum

I – moment of inertia

Now, let us see the molecular rotations. Classically rotational energy for a by atomic molecule we have to consider about an axis suppose the a atomic molecule is m 1, m 2 and the center mass say about an axis which is perpendicular to the bond because this are the two axis about which the moment of inertia of the molecule is non-zero in the point mass approximation. So, if we do that the molecular rotational kinetic energy is given by a simple expression it is given by J square by 2 I where J is the angular momentum of the molecule which causes the rotation and I is the moment of the inertia of the molecule. We will do this calculation more elaborately when we deal with microwave spectroscopy specially.

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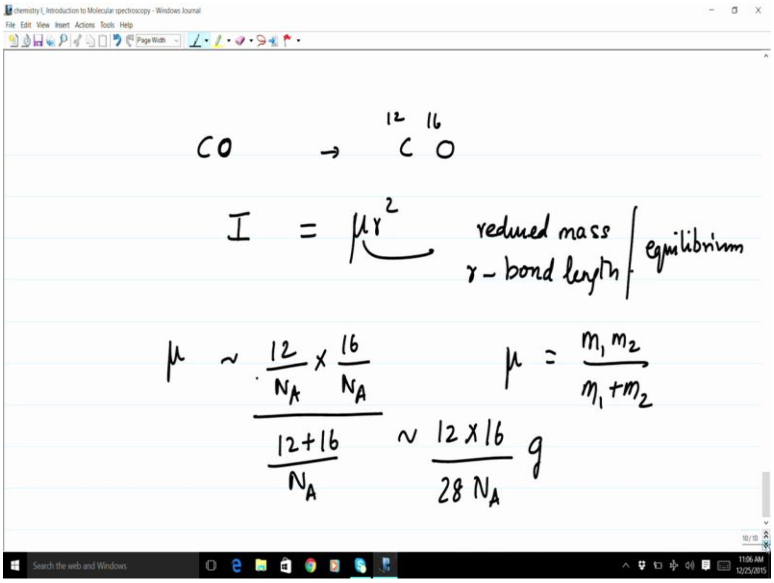

$$CO \rightarrow {}^{12}C\,{}^{16}O$$

$$I = \underbrace{\mu r^2} \quad \text{reduced mass} \quad r - \text{bond length} \quad \Big| \ \text{equilibrium}$$

$$\mu \sim \frac{\frac{12}{N_A} \times \frac{16}{N_A}}{\frac{12+16}{N_A}} \sim \frac{12 \times 16}{28\, N_A}\ g \qquad \mu = \frac{m_1 m_2}{m_1 + m_2}$$

But today’s lecture is to give you roughly the magnitude and the scale. So if you are looking the say for example, carbon monoxide CO the masses are let us do simple calculations, carbon 12 and oxygen 16, then the moment of inertia I is given by mu r square, where mu is the reduced mass of the molecule and r is the bond length the distance between the carbon and oxygen let us assume equilibrium, not very excited state and so on, equilibrium if you do that then approximate masses for carbon monoxide if you want to calculate you do this by 12 grams divided by the Avogadro number which is the atomic mass and 16 oxygen mass divided by Avogadro number please remember reduced mass is m 1 m 2 by m 1 plus m 2, where you have seen m 1 and m 2 are the 2 masses that you have.

So, in this case mu is given by 12 plus 16 by NA. So, you are looking at roughly 12 into 16 divided by 28 Avogadro number this is the gram of course, we use joules and therefore, the s I unit is we have to use mu is approximately 12 times 16 times 10 to the minus 3 divided by 28 into 10 to the minus 10 to the NA is 10 to the 23 into 6 point something. Let us keep it 6.02 it was 6 point. So, let us do simple calculation you have 2 and 2 into 16, 32 by 28 roughly keep it as one we are looking at 10 to the minus 26 kilo gram. Order of magnitude that is what you are looking at and that is mu or let us assume that somewhere between 1 and 1.2 angstrom if we keep 1 angstrom that is 10 to the minus 10 meters.

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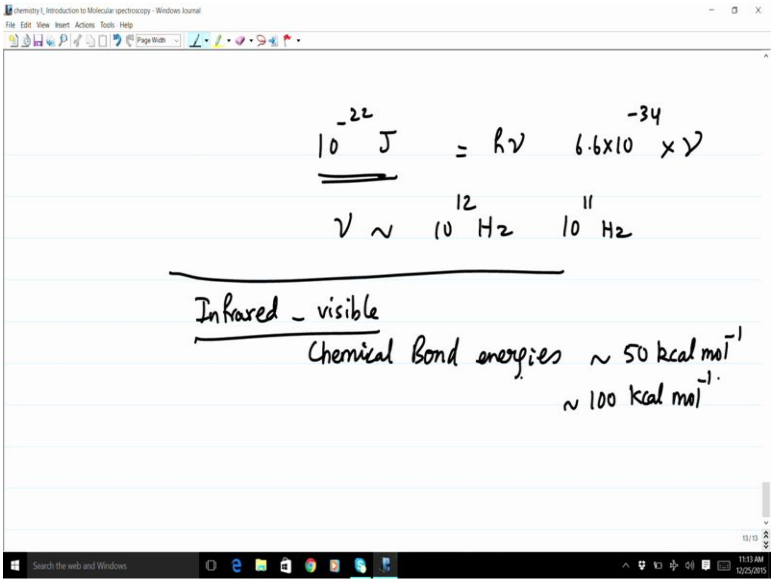

$$10^{-22}\,J = h\nu \quad 6.6\times10^{-34}\times\nu$$

$$\nu \sim 10^{12}\,Hz \quad 10^{11}\,Hz$$

Infrared – visible

Chemical Bond energies $\sim 50\,kcal\,mol^{-1}$

$\sim 100\,kcal\,mol^{-1}$.

Therefore I which is mu r square is approximately 10 to the minus 26 kilo gram times 10 to the minus 10 meter square kilo gram meter square which is about 10 to the minus 46 kilo gram meter square this is the moment of inertia.

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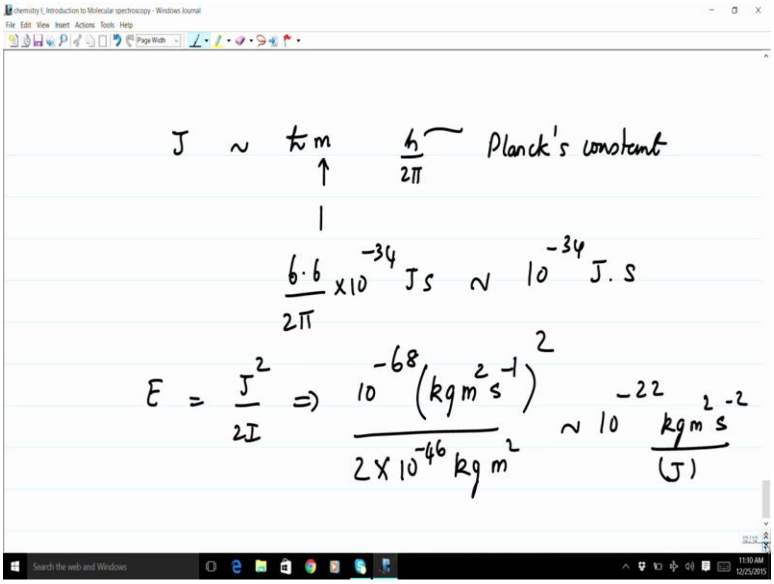

$$J \sim \hbar m \qquad \frac{h}{2\pi} \sim \text{Planck's constant}$$

$$\frac{6.6}{2\pi}\times10^{-34}\,Js \sim 10^{-34}\,J.s$$

$$E = \frac{J^2}{2I} \Rightarrow \frac{10^{-68}\left(kg\,m^2 s^{-1}\right)^2}{2\times10^{-46}\,kg\,m^2} \sim 10^{-22}\,\underline{kg\,m^2 s^{-2}}\,(J)$$

Now, angular momentum for molecules J or usually given in the unit is of h bar namely h by 2 pi and h is planks constant. So, even if we take the lowest value for the angular momentum non 0 value h bar into some value m and so let us choose m to be 1 meaning that (Refer Time: 09:17) really lowest rotational energy if you do that, h by 2 pi is again

6.6 by 2 pi times 10 to the minus 34 joule second is approximately 10 to the minus 34 joule per second, 2 pi is 6.28 or whatever.

So, this about one, let us do the energy calculation now E as J square by 2 I you can see that it is 10 to the minus 48 sorry 10 to the minus 68, it is joules square second square. So, let me write the actual unit kilo gram meter square per second whole square divided by 2 I and if you recall the I, I is about 10 to the minus 46 kilogram meter square. So, it gives you about 10 to the minus 22 kilo gram meter square per second square which is joule.

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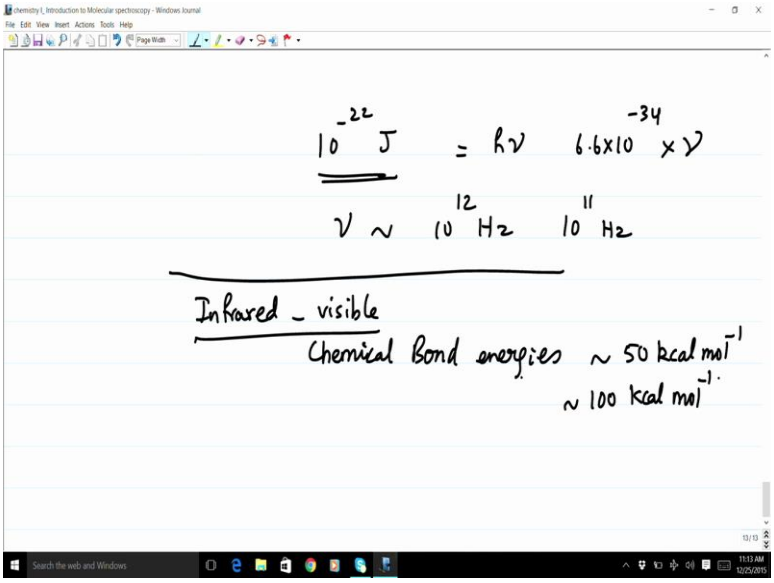

$\underline{10^{-22}\ J} = h\nu \quad 6.6\times10^{-34}\times\nu$

$\nu \sim 10^{12}\ Hz \quad 10^{11}\ Hz$

Infrared – visible

Chemical Bond energies $\sim 50\ kcal\ mol^{-1}$

$\sim 100\ kcal\ mol^{-1}$.

Therefore the rotational energy is of the order for a molecule 10 to the minus 22 joules and if you compare this with the frequency of electromagnetic radiation, that is in this range, you know that h nu and that is 6.6 into 10 to the minus 34 times nu, you see nu immediately falls in to the range of 10 to the 12 hertz, 10 to the 11 hertz. So, the result is that, a simple diatomic molecular rotation for a elementary molecules such as carbon monoxide. The rotational energy levels if they are given by this order namely 10 to the minus 22 joules per molecule.

The transition between the rotational energy is of that order and that corresponds to electromagnetic radiation whose frequency falls in the range of the 10 gigahertz to about 1000 gigahertz. That is the reason why we say microwave spectroscopy probes molecular rotations and molecular rotation is involved the moment of inertia and the moment of inertia is of course, based on mu r square. So, there is bond length information. So, if you extend the triatomic or a polyatomic molecule and you want to study the geometry more in detail or more elaborately, that is the part of microwave spectroscopy which we will look at more carefully, but the ball park figure is gigahertz to 1000 of gigahertz up to in that range you can study the molecular rotations.

Now, in second one about Molecular Vibrations and visible spectroscopy namely Infrared Visible Spectroscopy, here we will go back in the reverse direction. Let us assume molecular bond energies chemical bond energies, that weaker bonds namely ionic and covalent bond energies strong bond energies or fully between 50 kilo calories per mole to about 100 kilo calories per mole. When the mole is of course, Avogadro number of molecule.

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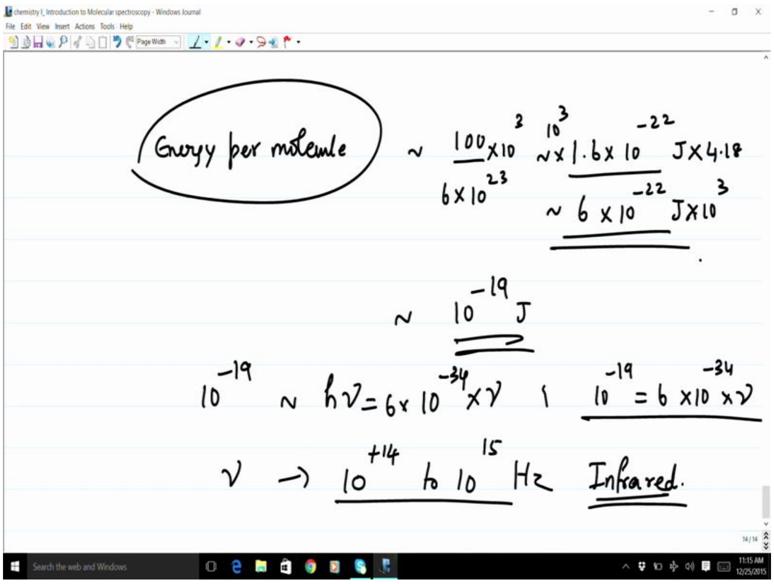

Energy per molecule

$$\sim \frac{100\times10^{3}}{6\times10^{23}} \overset{10^{3}}{\sim\times} \underline{1.6\times10^{-22}}\ J\times4.18$$

$$\sim \underline{\underline{6\times10^{-22}}\ J\times10^{3}}$$

$$\sim \underline{\underline{10^{-19}\ J}}$$

$$10^{-19} \sim h\nu = 6\times10^{-34}\times\nu \quad | \quad \underline{10^{-19} = 6\times10^{-34}\times\nu}$$

$$\nu \rightarrow \underline{10^{+14}\ \text{to}\ 10^{15}}\ Hz \quad \underline{\underline{\text{Infrared}}}.$$

So, if you are looking at energy bond energy per molecule, let us assume 100 and 100 by the Avogadro numbers 6 into 6.022, but 6 into 10 to the 23. So, you are looking at about 16, 1.6 times 10 to the minus 22 joules. This is kilo calories multiplied by 4.18. So, you are looking at approximately 4 into 16. So, it is 6 into 10 to the minus 22 joules. That is for the, that is also a order of magnitude missing it is 100 kilo calories therefore, you multiplied by 10 to the 3. So, you multiply by this 10 to the 3. So, you get about 10 to the minus 19 joules this is the energy per molecule due to the bond length and that much of energy you have to provide, if you want molecular vibrations or molecular energies to lead bond breaking or excitation between different vibration energies it should be a fraction of this.

Now, what is this corresponding to in terms of this spectroscopic energy? So, if this energy 10 to the minus 19 is to be equated to a radiation frequency nu whose energy is h nu then you see immediately that this is 10 to the minus 34 times 6 and, you see that into nu and for nu falls in the range of 10 to the minus plus 14 to 10 to the 15 hertz. You see 10 to the minus 19 is equal to 6 times 10 to the minus 34 times nu. So, you see that nu comes to this order. Therefore molecular bonds or (Refer Time: 15:05) or excitation between vibrational energy states of a molecule can happen, if you are looking at the order of a energies of 10 to 100 kilo calories per mole that corresponds to frequency of radiation of the order of 10 to the 14 to 10 to the 15 hertz and 10 to the 14 hertz is 100 terahertz and 10 to the 15 is 1000 terahertz, that is the range and this frequency is typically the frequency of radiation of infrared light.

Therefore infrared spectroscopy or vibrational spectroscopy is studied using radiation of this order because this order of energy is commensurate to the molecular energy level changes due to vibration of motion or due to electronic excitation, if you have to supply the whole molecular energy it may go towards slightly higher level of energy and that is visible spectroscopy which creates obviously, which leads to what is called bond association and things like that you are familiar with organic chemistry, details of photo chemical process light in disassociation and, visible and infrared spectroscopy fall in this range of 10 to the 14 to 10 to the 18 hertz lead in to molecular bond disassociation.

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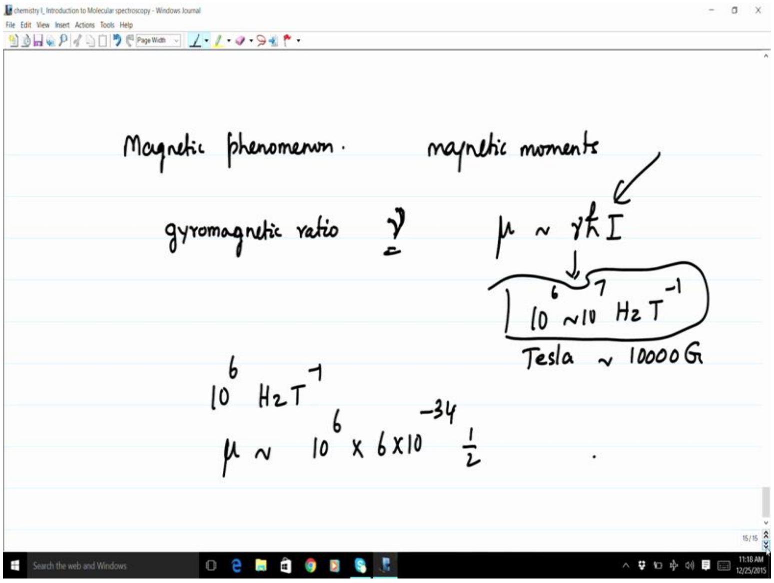

Magnetic phenomenon. magnetic moments

gyromagnetic ratio γ $\mu \sim \gamma \hbar I$

$10^{6} \sim 10^{7}\ Hz\,T^{-1}$

Tesla $\sim$ 10000 G

$10^{6}\ Hz\,T^{-1}$

$\mu \sim 10^{6} \times 6 \times 10^{-34}\ \frac{1}{2}$

Now, last one that you want to look at is a very low energy, but it is a magnetic phenomena. So, magnetic moments of nuclei are tabulated for a large number of molecule and they are given by a factor, a property known as the gyro magnetic ratio and it usually written 10 by a symbol gamma this is gamma not nu and the molecular moment the atomic or nuclei magnetic moment it is given by gamma h bar I, gamma is obviously, of the order of 10 to the 6 to 10 to the 7 hertz per magnetic field, unit magnetic field which is this beautifully reported as per Tesla, T is Tesla and that is 10000 that is the magnetic field, magnetic phenomena are explode by a static magnetic field which allows the magnetic movement to half multiple levels and we will see that more in detail when we study magnetic (Refer Time: 17:52) spectroscopy, but only we are looking at the order of magnitude of what kind of energies are involved.

So, if you are looking at nuclei with gyro magnetic ratio of this order 10 to the 6 for example hertz for Tesla then the magnetic moments are approximately this multiplied by the 6 into the 10 to the 30 minus 34 joules and quantum number I is usually 0, 1 half 0 is not useful to us 1 half 1 half to be halves 2 and so on. These properties we will study, even if we assume one half as the spin quantum number associated with the nucleolus you are looking at energy ranges between energy levels which corresponds to half configuration and the minus half configuration.

So, you are looking at energy delta E of the order of gamma h bar h naught which is the field, because the magnetic moment will interact with the field to have a certain energy and that energy is either corresponding to the half quantum number orientation of photon nucleus or minus half orientation of photon nucleus therefore you are looking at energy of this order gamma h bar h naught.

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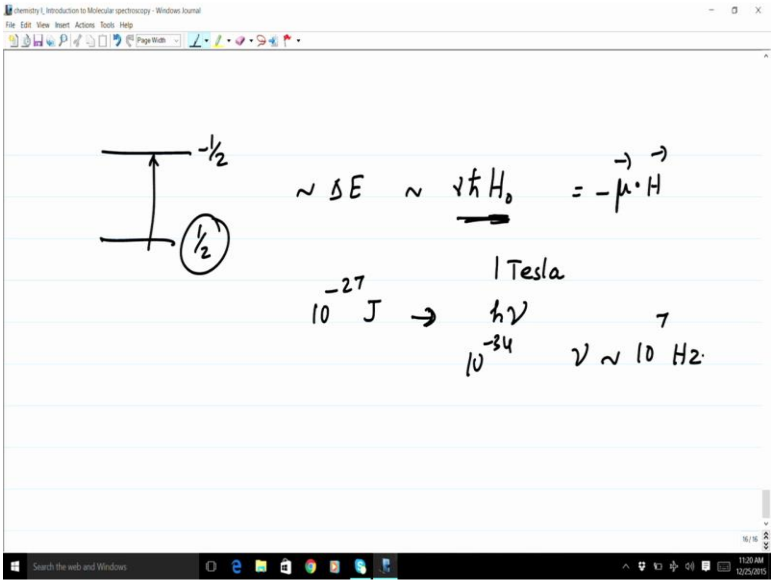

So, if you have a 1 Tesla field and your previous values of gamma h bar h naught is approximately 10 to the 6 into 6 to 10 to the minus 34. So, you are about minus 10 to the minus 27 joules I believe this is hertz per Tesla h is that. So, the energy is order of that 10 to the minus 27 joules and this obviously corresponds to a frequency h nu, the energy is h nu frequency nu in this 10 to the minus 34. So, you see nu is order of 10 to the 7 hertz ok.

Therefore magnetic phenomena, magnetic moments and the detection of nuclear magnetic moments and transitions that happening in the nuclear energy levels due to the energy levels of the nucleus in an magnetic field is of the order of a mega hertz 10 to 100 mega hertz for a field of a about 1 Tesla therefore, radio wave frequency, radio wave have that kind of frequency mega hertz frequency, radio waves are obviously the appropriate tools and to the magnetic the oscillating magnetic field of the radio waves corresponds to frequencies of this order.

So, when you talk about chemical applications of spectroscopy to various fields one must have a prior some information and some knowledge about what see honor of magnitude energies involved. So, I given this only by giving you three simple examples, but as we see more and more individual techniques of spectroscopy, we will see this things in detail and also much more quantitatively, but you have to have an appreciation of which phenomena that you would be normally interested in when you study certain type of spectroscopy.

This was categorized in the previous lecture, but now with a bit of elementary details, I also demonstrated that micro wave spectroscopy study is rotational motion, vibration spectroscopy study bond extent bond information and magnetic (Refer Time: 21:37) spectroscopy studies magnetic moments of nuclei and therefore the chemical phenomena which are relevant to that. With this we will see in the next lecture 3 general phenomena of a spectrum that we should look into for detail. Practically every spectrum will need those 3 and they are lie in positions, lie in widths and lie in in10sities and in the next lecture we will see them until then.

Thank you very much