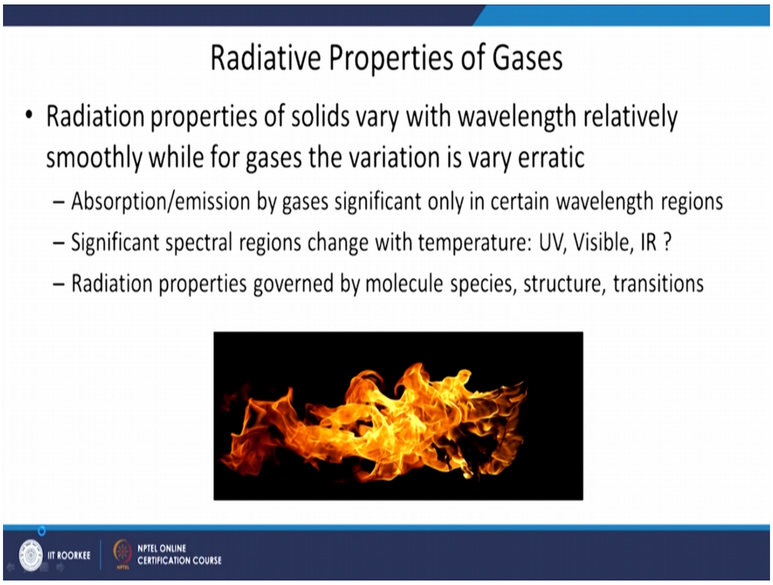
Radiative Heat Transfer
Prof. Ankit Bansal
Department of Mechanical and Industrial Engineering
Indian Institute of Technology - Roorkee

Module - 6
Lecture - 29
Radiative Properties of Gases

Hello friends, so, far in this course we have discussed how to solve radiation problem in enclosures. The enclosures may be bounded by vacuum, that is no participating media or they may be filled with gas with gray absorbing gas. We have assumed in many applications that the properties of the surfaces are either black or gray. We also understood that, when we consider gray or black surfaces, the emittance may vary, either over a wavelength region or it may continuously very.

But, the variation of emittance for either non-conductors or conductors was very smooth. So far, we have an only considered, that the gas within the medium is gray. Here, now we will introduce how the gas properties change over the spectrum. So, unlike the emittance and reflectance of plane surfaces which shows smooth variation over wavelength, the properties of gas varies very erratically.

(Refer Slide Time: 01:37)



Radiative Properties of Gases

- Radiation properties of solids vary with wavelength relatively smoothly while for gases the variation is vary erratic
  - Absorption/emission by gases significant only in certain wavelength regions
  - Significant spectral regions change with temperature: UV, Visible, IR ?
  - Radiation properties governed by molecule species, structure, transitions

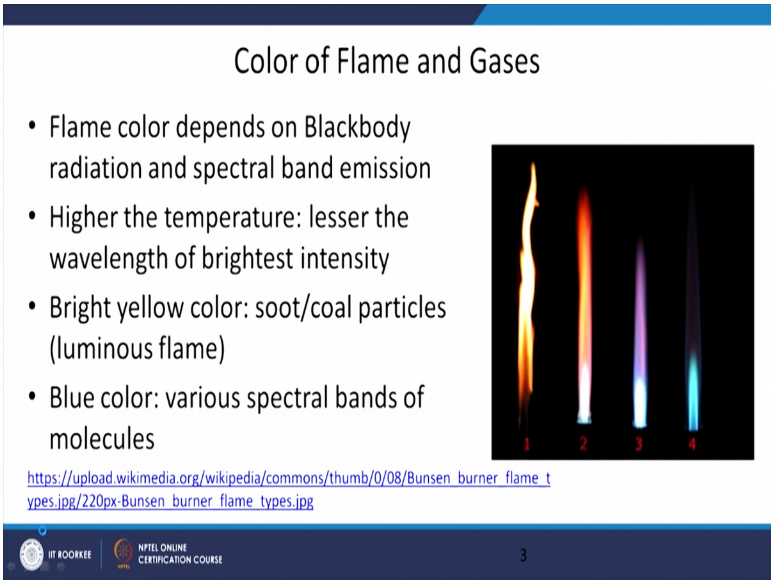
So, we are basically interested in determining how the properties of the gas varies over wavelength; how can we calculate the absorption, emission and scattering of these gases. Now, depending on the temperature and pressure, different gases radiate or absorb radiation in different part of the spectrum. Some gases absorb radiation in ultraviolet region of the spectrum, some gases absorb invisible and others may absorb and emit radiation in infrared.

So, we are interested in how these gases basically absorb and emit radiation; how the wavelength dependence come ins to play; and in what part of the spectrum different gases will absorb and emit radiation. Now, the properties of the gas depends on number of things. It depends on the molecular structure, what kind of molecule we have; whether we have a diatomic molecule, we have a triatomic molecule; whether the molecule has linear structure or it is angular structure;

Whether the molecule has dipole moment or the molecule does not have dipole moment. So, all these things basically decide how the molecule will absorb or emit radiation. There may be a single gas, there may be mixture of gases. As in combustion we have number of gases formed as a result of production of different species of combustion. And these gases undergoes transitions.

Transition here means that the energy of the gas molecule will change as a result of emission or absorption of photons or radiation. So, the mechanism of energy emission or energy absorption in molecules is mainly governed by these transitions. Now, transitions may be associated with different forms of energy that are molecule stores like rotational, vibrational, electronic and so on. So, first we will start with electronic or molecular structure. And then, we will see how this structure basically helps us understand the concept of molecular emission and radiation.

(Refer Slide Time: 03:55)



Color of Flame and Gases

- Flame color depends on Blackbody radiation and spectral band emission
- Higher the temperature: lesser the wavelength of brightest intensity
- Bright yellow color: soot/coal particles (luminous flame)
- Blue color: various spectral bands of molecules

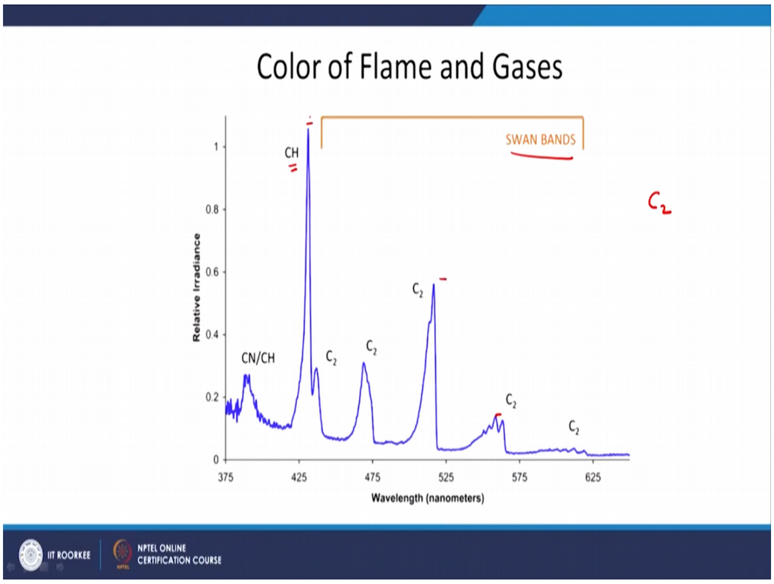
https://upload.wikimedia.org/wikipedia/commons/thumb/0/08/Bunsen_burner_flame_types.jpg/220px-Bunsen_burner_flame_types.jpg

IIT ROORKEE | NPTEL ONLINE CERTIFICATION COURSE

Now, in combustion the flame is identified by colors. Many flames are bright yellow in appearance. Some flames may be reddish, some may be blue, some may have a color of green. Now, these colors depend on what kind of different species gaseous species are present in the flame. Normally, the color yellow is attributed to the particles formed as a result of combustion. These particles may be particles of soot or they may be unburned carbon.

In coal combustion, specially we may have particles of ash and coal particles. So, all these particles, they emit radiation which is yellow in appearance and such flames are called luminous flames. So, there are 2 types of flames that we distinguish in radiation, luminous flames and non-luminous flames. Luminous flames are basically having bright yellow appearance and they are attributed by the presence of particles such as coal and soot. The blue and greenish color in the flame is attributed to different species, emission from different species of gases.

(Refer Slide Time: 05:16)



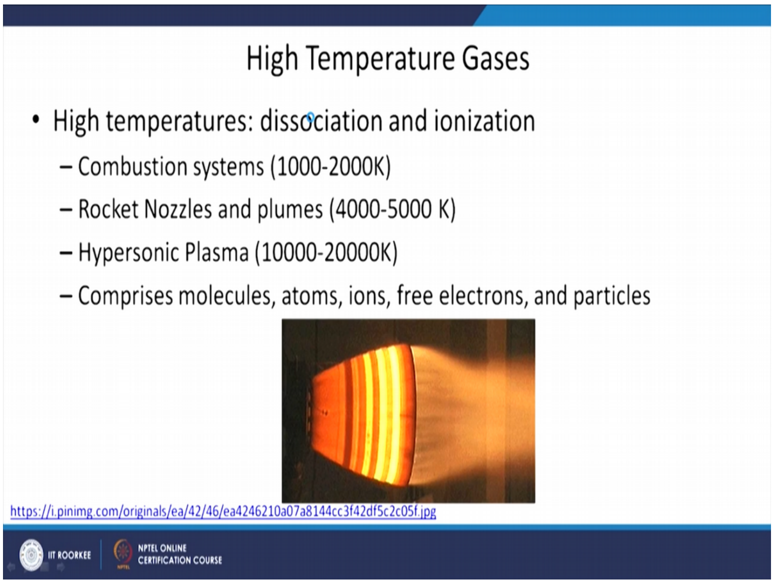
Color of Flame and Gases

So, the color of the flame is basically identified by the presence of many gaseous species that are formed as a result of combustion. As is seen in this spectrum where the irradiance of the flame is plotted versus wavelength, we can identify various gaseous species, especially the C 2. C 2 carbon species has significant emission across its, what we call swan bands. We will discuss what are bands later on in this lecture.

So, this species gives bluish color to the flame. We have also have a strong emission from methane or CH bands. And we may have radiation form CN and other molecular species. These species strongly radiate in combustion flames. And they give rise to what we call band emission and typical color of the flame is identified with these gases. If the soot is present in the flame, the color of the flame is decided by the strong emission from the soot particles which is bright yellow in color.

So, always when soot is present in the flame the color of the flame will be yellow and the flame will be luminous. Only when the soot is not present, you can see the color distinct color of the flame and you can identify different bands. In spectroscopy, we try to identify the concentration of various gases by identifying these band structure. So, the purpose of spectroscopy is that we identify what are the different species different bands are formed. And by measuring the peaks of different bands, we can quantify the concentration of various species in the gas mixture.

(Refer Slide Time: 07:07)



High Temperature Gases

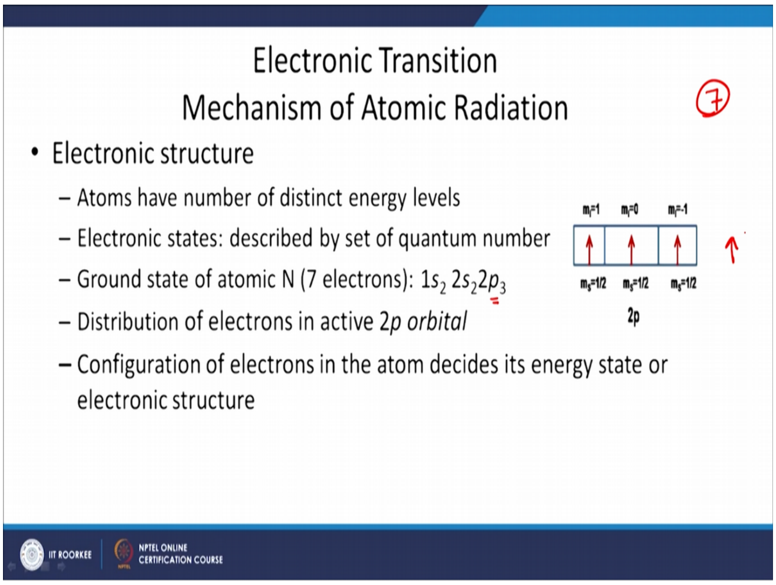
- High temperatures: dissociation and ionization
  - Combustion systems (1000-2000K)
  - Rocket Nozzles and plumes (4000-5000 K)
  - Hypersonic Plasma (10000-20000K)
  - Comprises molecules, atoms, ions, free electrons, and particles

https://i.pinimg.com/originals/ea/42/46/ea4246210a07a8144cc3f42df5c2c05f.jpg

Similarly, so, this was the example of typical combustion of organic fuel that gives rise to different type of flames. In hypersonic application or high temperature gas applications, such as rocket nozzles, rocket plumes, the temperature is very high of the order of 4,000 to 5,000 kelvin. And if you go for hypersonic plasma around a space shuttle, the temperature may be of the order of 10,000 to 20,000 kelvin.

At such high temperatures, we may have radiation even at shorter wavelength. That is in ultraviolet and vacuum ultraviolet regions. And the reason is, in high temperature gases and we call it plasma, because lot of species are ionized and dissociated. So, molecular species may fully dissociate at that high temperature. Some of the atomic species may ionize. So, we may have basically a mixture of diatomic species, atomic species, ion free electrons and so on. And this mixture is called plasma and its radius radiates strong radiation not only in infrared, but also in shorter wavelength regions such as violet, ultraviolet and vacuum ultraviolet.

(Refer Slide Time: 08:19)



Electronic Transition

Mechanism of Atomic Radiation

⑦

- Electronic structure
  - Atoms have number of distinct energy levels
  - Electronic states: described by set of quantum number
  - Ground state of atomic N (7 electrons): $1s_2\,2s_2 2p_3$
  - Distribution of electrons in active 2*p orbital*
  - Configuration of electrons in the atom decides its energy state or electronic structure

IIT ROORKEE

NPTEL ONLINE CERTIFICATION COURSE

So, we will first understand how the atoms basically radiate energy. Understanding of emission and absorption in atoms is relatively easy, because atoms do not have vibration and rotation mode of energy storage. Atoms store energy based on their electronic structure. So, this requires little bit of understanding of the electronic structure that you might have learned in class twelfth.

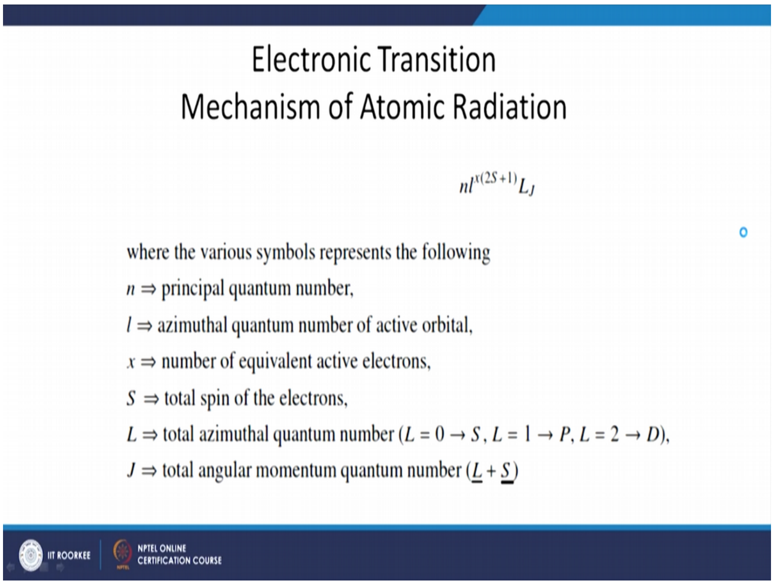
So, we represent the electronic structure of any atom by its quantum numbers. So, for example, here, down state of atomic nitrogen has been taken. So, atomic nitrogen has 7 electrons and the electrons in its outermost shell are total 3 in number. Its electronic configuration can be written as 1 s 2 2 s 2 2 p 3. You might have studied this in twelfth class. So, s 1 s orbital, 2 s orbital and 2 p orbital. And outermost shell the 2 p 3 has 3 electrons.

And all these 3 electrons are unpaired. And they have sim same spin of half. Okay. So, spin is basically the direction of the electrons. In this case, all the electrons are pointing upwards. So, they have same spin half, spin quantum number. And the, all the electrons are unpaired. Now, this is just 1 configuration. And this particular configuration that I have drawn is basically the ground state of nitrogen.

Now, what may happen is this electron, one of the electrons in this outermost shell may change its configuration, either by changing the sign of the spin or one of the electrons may jump from this shell to outer shells, let us say 3 d orbital or 4 s. So, one of electrons may jump from this current ground state to higher states. All these states are called excited states. So, the configuration that I have drawn is basically the ground state.

But when one of the electrons from this configuration jumps into other states, let us say higher orbital or change its spin, all those states are called excited state. So, there is a notation that has been developed to denote the configuration or electronic state of atoms. And this configuration, without going in too much detail, is identified by a number of quantum numbers.

(Refer Slide Time: 10:51)



Electronic Transition
Mechanism of Atomic Radiation

$$nl^{x(2S+1)}L_J$$

where the various symbols represents the following

$n \Rightarrow$ principal quantum number,

$l \Rightarrow$ azimuthal quantum number of active orbital,

$x \Rightarrow$ number of equivalent active electrons,

$S \Rightarrow$ total spin of the electrons,

$L \Rightarrow$ total azimuthal quantum number ($L = 0 \rightarrow S$, $L = 1 \rightarrow P$, $L = 2 \rightarrow D$),

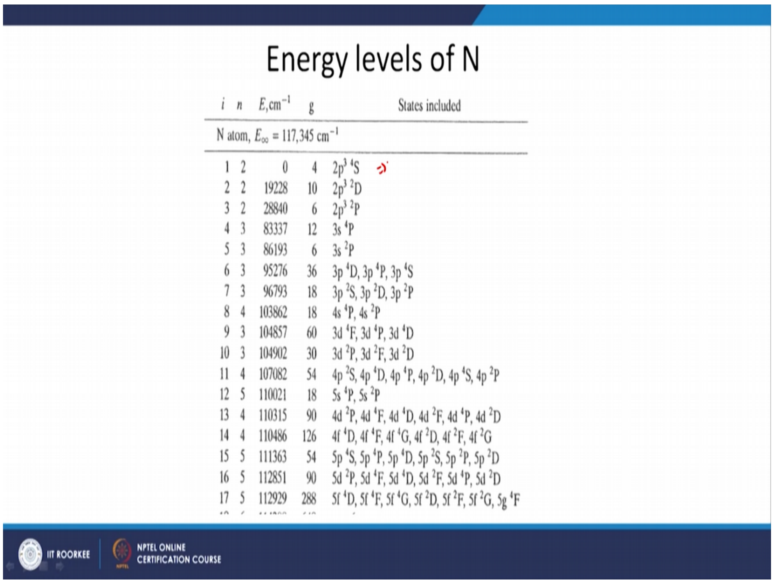
$J \Rightarrow$ total angular momentum quantum number ($\underline{L} + \underline{S}$)

The configuration is written as nl superscript x 2S + 1 capital L subscript j, where these quantities are different quantum numbers. n is called principal quantum number and it is the quantum number of the outermost shell. So, for example, in the previous ground state, 2 was the principal quantum number. Because the outermost shell was 2 p 3. l is the azimuthal quantum number. p is the orbital that the outermost electron is in.

So, we identify l with a p orbital. x is number of equivalent active electrons. So, in this case, number of equivalent active electron is 3. Because in outermost shell we have 3 electrons. s is total spin of the electrons. L is total azimuthal quantum number. And j is total angular momentum. So, we see that there are large number of quantum numbers that define in electronic state.

So, we may not be interested in at this moment how this electronics states are basically decided. But all we need to understand is that atoms do possess different electronic configuration. And this electronic configurations play an important role in radiative heat transfer.

(Refer Slide Time: 12:04)



Energy levels of N

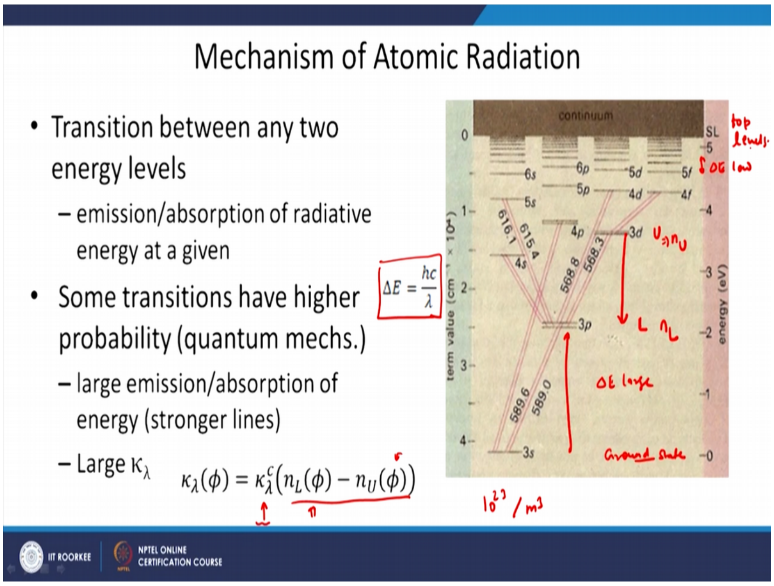
i	n	E,cm^{-1}	g	States included
N atom, $E_\infty = 117{,}345$ cm^{-1}				
1	2	0	4	$2p^3\,^4S$
2	2	19228	10	$2p^3\,^2D$
3	2	28840	6	$2p^3\,^2P$
4	3	83337	12	$3s\,^4P$
5	3	86193	6	$3s\,^2P$
6	3	95276	36	$3p\,^4D$, $3p\,^4P$, $3p\,^4S$
7	3	96793	18	$3p\,^2S$, $3p\,^2D$, $3p\,^2P$
8	4	103862	18	$4s\,^4P$, $4s\,^2P$
9	3	104857	60	$3d\,^4F$, $3d\,^4P$, $3d\,^4D$
10	3	104902	30	$3d\,^2P$, $3d\,^2F$, $3d\,^2D$
11	4	107082	54	$4p\,^2S$, $4p\,^4D$, $4p\,^4P$, $4p\,^2D$, $4p\,^4S$, $4p\,^2P$
12	5	110021	18	$5s\,^4P$, $5s\,^2P$
13	4	110315	90	$4d\,^2P$, $4d\,^4F$, $4d\,^4D$, $4d\,^2F$, $4d\,^4P$, $4d\,^2D$
14	4	110486	126	$4f\,^4D$, $4f\,^4F$, $4f\,^4G$, $4f\,^2D$, $4f\,^2F$, $4f\,^2G$
15	5	111363	54	$5p\,^4S$, $5p\,^4P$, $5p\,^4D$, $5p\,^2S$, $5p\,^2P$, $5p\,^2D$
16	5	112851	90	$5d\,^2P$, $5d\,^4F$, $5d\,^4D$, $5d\,^2F$, $5d\,^4P$, $5d\,^2D$
17	5	112929	288	$5f\,^4D$, $5f\,^4F$, $5f\,^4G$, $5f\,^2D$, $5f\,^2F$, $5f\,^2G$, $5g\,^4F$

On this slide, I have listed some of the energy levels of a atomic nitrogen. Top atomic, top electronic levels, starting from the ground state. So, the first state, the principal quantum number is 2 and the energy is sin 0. This is the ground state of atomic nitrogen with configuration 2 p 3 4 S. The second level has energy, the units of energy are typically given in centimeter inverse.

But it can be converted to any other unit. So, in many applications we write the energy of electronic levels in units of centimeter inverse. But, by multiplying with Planck constant, we can convert it into energy easily. So, this has again principal quantum number as 2. But the active to the term symbol or the configuration of this state is 2 p 3 2 D. So, there are large number of electronic states that are given here.

And these states decides the energy of different atoms. 1 may, atom in the gas mixture, may be in the ground state. Another atom may be in excited state. And at high temperatures, especially in plasmas where temperature is very high, most of the atoms will be in excited states. While at room temperature, normally at room temperature you will not find atomic gases, but even if we have some atomic gas at room temperature, most of its atoms will be in ground state.

(Refer Slide Time: 13:35)



Mechanism of Atomic Radiation

- Transition between any two energy levels
  - emission/absorption of radiative energy at a given
- Some transitions have higher probability (quantum mechs.)
  - large emission/absorption of energy (stronger lines)
  - Large κ_λ

$$\boxed{\Delta E = \frac{hc}{\lambda}}$$

$$\kappa_\lambda(\phi) = \underset{\uparrow}{\kappa_\lambda^c}\underbrace{\left(n_L(\phi) - n_U(\phi)\right)}_{\uparrow}$$

On the chart, these energy levels can be represented in such form. At the bottom we have the ground state. This is the ground state with minimum energy. And at the top, we may have large number of states. This is the top levels. 1 thing you should observe is that the energy gap between lower levels is very large. So, the gap between first 2 levels is very large. The energy difference between the first 2 level is very large.

But as you go on higher levels, the energy gap decreases. And this has significance in radiation. This has significance in the deciding spectrum of atomic nitrogen or any atomic species. The atomic spectrum is generated when 1 atom jumps from 1 excited state to another excited state. That means, if you have an atom in this state and it jumps to a lower state, then a photon is basically emitted.

Similarly, if you have an atom in ground state and it absorbs 1 photon, it will jump to a higher level. So, by changing the levels, by changing the electronic energy between levels, between atoms, photon is emitted or absorbed. Now, some transitions may have higher probability and some transitions may be forbidden. So, this is decided by quantum mechanics. So, quantum mechanics may forbid some transitions.

That from a particular energy level, you cannot jump into another energy level. And this is decided by quantum mechanics. These energy levels are called forbidden transitions. Because you cannot jump from this energy level to another energy level. And they are called forbidden energy level. Or the probability of transition is 0. Similarly, some transitions are favored. That means, they are most likely to happen.

And most of the transitions to ground state are basically favored transitions, because ground state is the equilibrium state and most of the states ultimately fall to the ground state. So, most of the transitions to ground state are favored and they have high probability. And those who have high probability, they depict strong emission or strong radiation. So, the magnitude of intensity originating from those transitions will be very high.

We write absorption coefficient. So, ultimately, we are interested in finding the absorption coefficient of the gas. So, absorption coefficient is basically given by many factors. But I have written here the key factors. So, there is a constant and there is a dependence on the number density or concentration of the gas. So, here kappa lambda C is a constant that comes from quantum mechanics. It basically includes the probability of transition between 2 energy levels.

So, if we have energy level, let us say 1 and 5 and it is favored, then you will have very large value of kappa lambda C. That means, this energy transition is favored and it has high probability. So, the constant value depends on the probability. And it is calculated based on quantum mechanical principle. The other quantity that absorption coefficient depends on is the number density or concentration of the gas in each energy level.

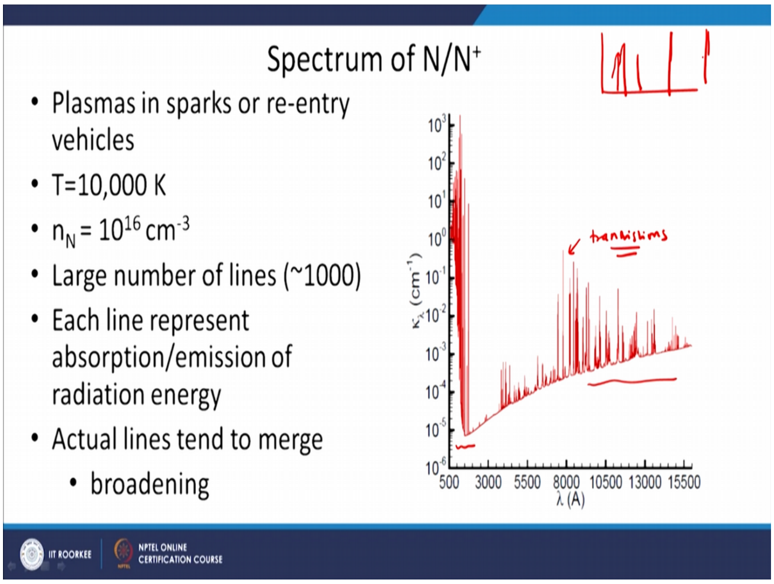
So, total number of atoms, maybe let us say 10 to the power 23 per meter cube. So, the density or number density of the gas may be 10 to the power 23 per meter cube. But out of these total number of atoms, some atoms may be in the ground state, some atoms may be in higher energy state and so on. So, they will be continuously distributed. In equilibrium, this distribution, it is called Boltzmann distribution.

But, if thermodynamic equilibrium is not prevailing, then the population distribution among energy levels may not follow Boltzmann distribution. So, we will see how this population is distributed, we will see how the Boltzmann distribution is written. At this point, what we are basically interested in, we should know the value of number of atoms in different energy levels. So, subscript L means, the lower level and subscript U mean the upper level.

So, if we have transition from this upper level to this lower level, we must be having the number of atoms in this level and number of atoms in this level. So, once we have these 2 levels population, we can calculate the absorption coefficient by taking the difference, that is, n L – n U. And multiply by a constant which depends on probability kappa lambda c. And this is how we calculate the absorption coefficient.

So, this will give you a single atomic line or single absorption coefficient line on the spectrum. Now, phi in this case basically is a gas state vector, where we have pressure, temperature and concentration. So, the number of particles, number of atoms in a given level depends on pressure, temperature and concentration of the gas in the mixture.

(Refer Slide Time: 18:49)



Spectrum of N/N⁺

- Plasmas in sparks or re-entry vehicles
- T=10,000 K
- $n_N = 10^{16}\ cm^{-3}$
- Large number of lines (~1000)
- Each line represent absorption/emission of radiation energy
- Actual lines tend to merge
  - broadening

So, this is 1 typical spectrum of atomic nitrogen and a mixture of atomic nitrogen and nitrogen ion. This is calculated for a plasma, air plasma, where we have air at very high temperature of 10,000 kelvin. The number of total atoms of atomic nitrogen is 10 to the power 16 per centimeter cube. Okay. So, we will have a large number of transitions. So, what you see here, the lines, are basically transitions from 1 atomic level to another atomic level, 1 electronic level to another electronic level.

Each transition gives rise to a single line or single absorption coefficient. And there may be different different lines. The wavelength is decided by this relation. The wavelength of transition is decided by this relation. So, delta E is = hc by lambda. This relation you must have studied in twelfth class. So, h is Planck constant, c is speed of light, lambda is the wavelength and delta is the energy difference between upper level and low level.

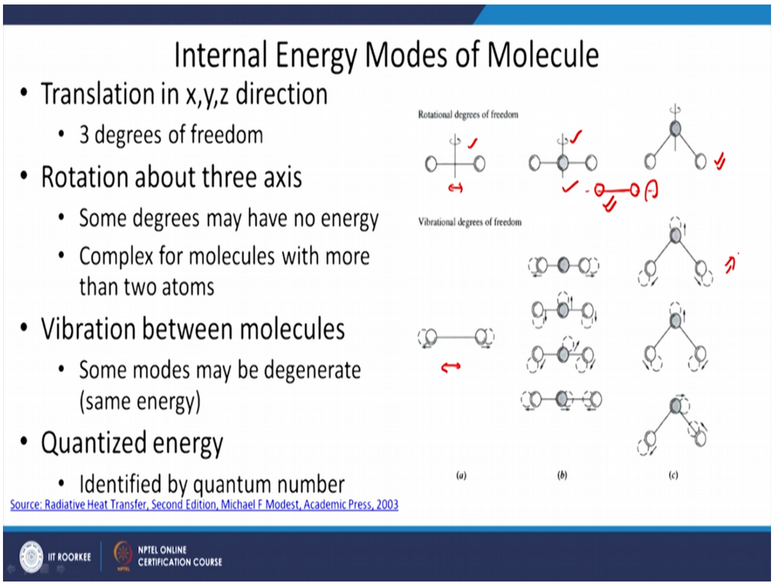
So, energy levels of atomic, electronic states. The difference between the 2 gives you delta E. Larger the delta E, smaller will be the wavelength. That means, transitions with have, which have larger electronic energy difference, they will emit radiation in shorter wavelength region. That is vacuum ultraviolet. While transitions which have small energy difference will have radiation in infinite region.

So, from this, you can conclude that transitions happening in upper levels will give lines in infrared, while transitions happening in lower energy states will give you energy in vacuum ultraviolet or ultraviolet region. Because, the energy gap here is large. So, delta E is large here. So, we will have transitions in ultraviolet and vacuum ultraviolet, while transitions in the upper level delta E is low and we will have lines in the infrared region.

So, there are total number of 1,000 or more lines for atomic nitrogen and each line represents absorption and emission of radiation energy. What you also observe here is that lines tends to merge. So, we should have, ideally, we should have the spectrum look like this, a single line at different different wavelengths. But what you actually observe is that the lines tend to merge together.

That means, 2 lines which are very close to each other, they merge. They merge with each other. And we will call this broadening, which we will study in the next lecture. And this broadening again is a consequence of number of physical phenomena. So, actual spectrum will be continuous. That, you basically see in this image. So, actual spectrum will not be discreet lines, rather actual spectrum will be rather continuous with lines merging together and some other mechanisms of radiation coming together.

(Refer Slide Time: 21:50)



Internal Energy Modes of Molecule

- Translation in x,y,z direction
  - 3 degrees of freedom
- Rotation about three axis
  - Some degrees may have no energy
  - Complex for molecules with more than two atoms
- Vibration between molecules
  - Some modes may be degenerate (same energy)
- Quantized energy
  - Identified by quantum number

Source: Radiative Heat Transfer, Second Edition, Michael F Modest, Academic Press, 2003

So, after the atomic spectrum, we will go for the molecules. Now, molecules, the energy analysis is little complicated. Unlike atoms, molecules have large degrees of freedom in which they can absorb energy. Molecules as atoms, translate in 3-dimensional space. So, they have 3 degrees of freedom in translation, similar to atoms. But more than atoms, they can rotate. They can rotate about x, y and z axis.

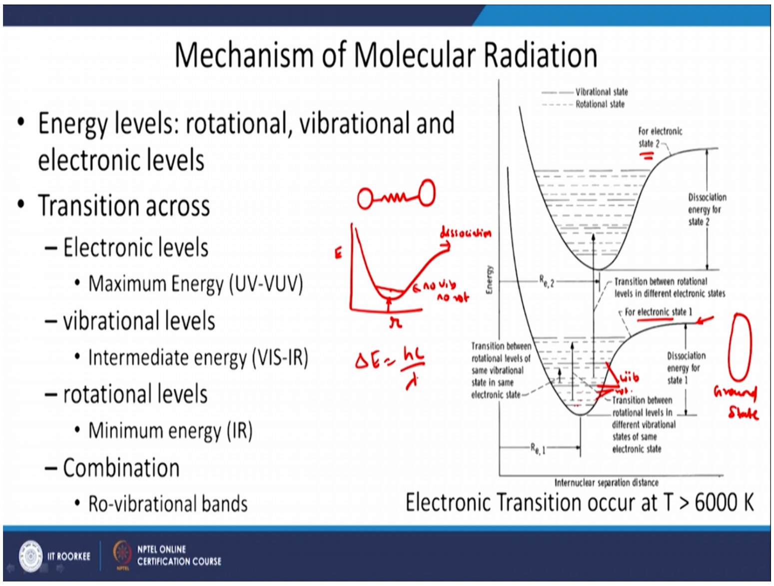
So, this is 1 way of rotation. This is another way of rotation. And if the molecule is not linear, let us say this type of molecule where molecule is not linear, then this type of rotation may be there. So, rotational degree of freedom again depends on what kind of molecule we have. There may be another rotation on axis passing through molecules. But this will not contribute to energy.

So, some degrees may not have any energy contribution. Or the molecules may not absorb or emit energy from those degrees of freedom, such as this. Because, the axis passes through the center of the molecule. So, this does not contribute to any energy storage. While this and this degrees of freedom will contribute to energy storage. So, typically in this diatomic molecule, we have 2 degrees of freedom for rotation.

The triatomic molecule may have more, non-linear molecules may have more. Similar to rotation, molecules also vibrate as is seen here. So, molecules may vibrate. And again, they store energy based on this vibration. A non-linear molecule may have different form of vibration. Now, degrees of freedom of vibration depends on what type of molecule we have. And some of the energy modes may be symmetric or they may be degenerate.

Degeneracy is a term which is used to define states or energy states which are similar, which have same energy. Such energy states are called degenerate. And as per quantum mechanics energy is stored in this rotational and vibrational mode, is not continuous, but rather it is decided by quantum number; the energy is quantized. That means, it is not continuous rather than it is decided by some quantum numbers, rotational and vibrational quantum numbers and the energy is quantized.

(Refer Slide Time: 24:19)



Mechanism of Molecular Radiation

- Energy levels: rotational, vibrational and electronic levels
- Transition across
  - Electronic levels
    - Maximum Energy (UV-VUV)
  - vibrational levels
    - Intermediate energy (VIS-IR)
  - rotational levels
    - Minimum energy (IR)
  - Combination
    - Ro-vibrational bands

Electronic Transition occur at T > 6000 K

IIT ROORKEE | NPTEL ONLINE CERTIFICATION COURSE

So, let us see how the molecules emit and absorb radiation. On this image, what you see is basically, let us say we have; it is a single molecule, connected by 2 atoms. Now, there may be different forms of energy. Now, if the molecule does not rotate, if the molecule does not vibrate, then all it possesses is basically the electronic energy. So, for a molecule which does not rotate or vibrate, the energy can be plotted as a function of interatomic distance.

So, it will have energy storage because of the interatomic forces. And this energy storage can be plotted like this. Where, on the x-axis we have interatomic distance and on the y-axis we have energy. So, this is the plot of energy of this molecule as a function of its interatomic distance. If r is large, then we are basically reaching dissociation limit. So, if the interatomic distance between the atoms is very large, then this molecule is basically approaching the dissociation limit.

While if the r is very small, then the inner energy is going to be very large because of significant amount of repulsion forces, atomic-atomic repulsion forces, when r is very small. So, there may be again more than 1 electronic levels. So, the first shape, this is the lower electronic state. It is called electronic state 1. And there may be another electronic state. So, electronic state 1 and 2 differ not by how their rotation and vibrations are distributed.

But, the difference between electronic state in 1 and 2 is the electronic configuration; how the electrons in the molecules, in the atom of the molecules differ in state 1 and state 2. So, normally, this state does not change unless the temperature is very high. So, if we have temperature typical > 5,000, 6,000 kelvin, then we may think that electrons in the molecules may change their configuration.

But otherwise, this configuration will not change. The electronic configuration will not change. And mostly, molecule will be in this ground level only. So, you may call this as ground state. So, mostly the atoms in the molecule will be in ground state if the temperature is not very high. Now, within this ground state, there may be other energy states. A molecule may vibrate, a molecule may rotate.

So, in that case, this is the curve without no vibration, no rotation. But once the vibration and rotation takes place, the energy will not be given by this curve rather than, we will have energy at same radius more than this value. So, this is the energy with no vibration, no rotation. But once we have vibration, the energy will be higher as is given in this picture. So, we have levels. The solid line represents the vibrational level and the dashed line represents the rotational level.

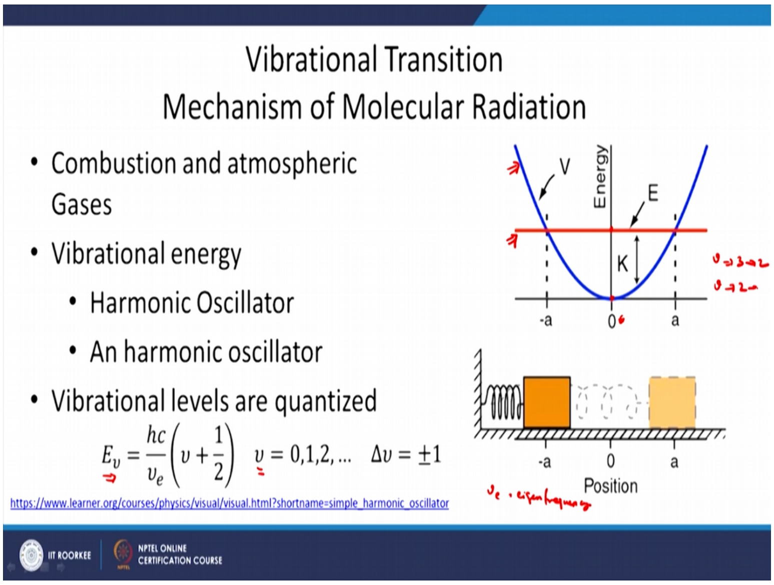
This distance or the separation between vibration level is large compared to rotational distance. So, you see that these 2 lines represents the vibrational and these 2 lines represents the rotational level. So, the distance between vibrational level is large compared to rotational level. And the distance between electronic level is definitely much larger. And this transition takes place only at very high temperature.

So, what it basically means, if molecule undergoes a transition, that means electrons change configuration with within the molecule, then the energy difference is very large, delta E is very large. And as per this relation, the wavelength will be very small because delta is large. So, for molecules that undergoes electronic transitions, the spectrum will be in ultraviolet or vacuum ultraviolet.

If the molecule undergoes only vibrational transitions and no electronic transition, then the energy difference is relatively small compared to electronic transitions. And you will find spectrum typically in visible part of the spectrum and infrared. If the molecule undergoes only rotational transition, that is no vibrational translations, vibrational mode is not changed, only the rotational mode is changed. Then, you will find that the energy will be very very less.

And the spectrum will be in infrared or far infrared. But there is always a possibility of combined transitions. That means, before emission of photon, molecule may have 1 electronic configuration, 1 vibrational configuration, 1 rotational configuration. And after the emission of photon, the electronic configuration, vibrational configuration and rotational configuration, all 3 can change. And that is called combined transition.

(Refer Slide Time: 29:09)



Vibrational Transition

Mechanism of Molecular Radiation

- Combustion and atmospheric Gases
- Vibrational energy
  - Harmonic Oscillator
  - An harmonic oscillator
- Vibrational levels are quantized

$$E_\upsilon = \frac{hc}{\upsilon_e}\left(\upsilon + \frac{1}{2}\right) \quad \upsilon = 0,1,2,\ldots \quad \Delta\upsilon = \pm 1$$

https://www.learner.org/courses/physics/visual/visual.html?shortname=simple_harmonic_oscillator

First, we will understand the vibrational transition. Vibrational transitions in this quantum mechanics can be understood with the help of an example of harmonic oscillator. So, let us say we have a mass spring system. When the mass spring system is not oscillating, the only thing that basically stores energy is given by this curve. So, this is the amount of potential basically it is storing. When it is not vibrating, the blue curve shows the potential of this system.

But once it starts vibrating, then vibrational energy is stored. And as you can see, this can be given by this red line. And this is what, what we show in the previous slides also, that the bottom curve is without any vibration. And once vibration starts, then we have this levels that are basically giving you the vibrational energy. So, same thing is depicted in this harmonic oscillator model also.

Without vibration, the blue curve gives this energy of the system. Once it starts vibrating, then the blue curve does not give you the energy of the system at same location 0. Without vibration, the energy is this. With vibration, the energy is this. So, once the vibration starts taking place, the molecule will absorb more energy in its vibration mode. Now the vibration can be represented by harmonic oscillator.

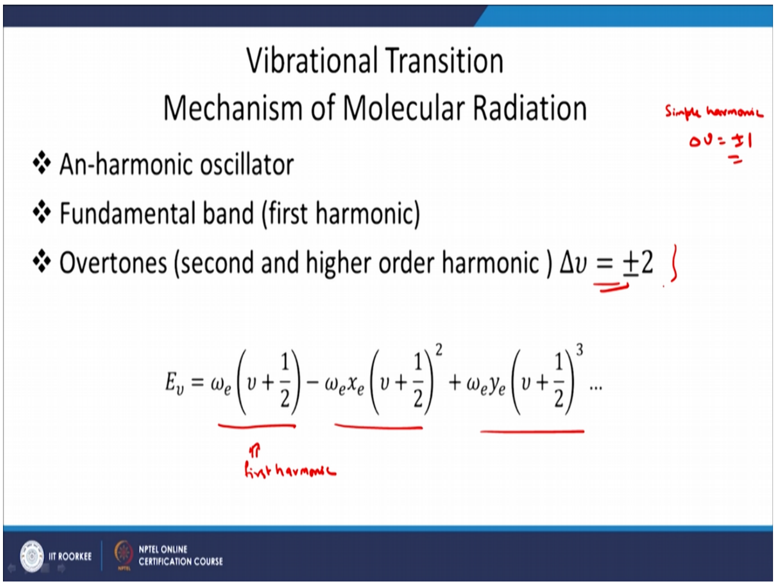
That means, it vibrates like a simple harmonic motion which is the case we take in most of the applications. But, there can be non-harmonic motion also and harmonic oscillator. For harmonic oscillator, the quantum mechanics gives you the solution that energy stored in a vibrational mode E nu or E subscript nu is = hc by nu e multiplied by nu + half, where nu is the vibrational quantum number.

So, new is vibrational quantum number, h is Planck constant, c is speed of light and nu is the frequency or natural frequency of this system. It is called eigenfrequency also. So, nu is basically eigenfrequency which is a constant. And it can be found in literature. So, E nu gives you the energy stored in harmonic oscillator as a function of quantum number, vibrational quantum number.

The vibrational quantum number can take value 0, 1, 2 and so on. Now, what are the translations possible? If this harmonic oscillator changes state by + – 1; that means, before emission of photon, let us say the vibrational quantum number is 2. Then, after emission of photon, the vibrational quantum number will be 1. That means, delta v will be 1. If it absorbs the photon, then delta v will be – 1.

Then delta v will be + 1 rather. And the quantum number will increase by 1 to 3. So, that means, in emission, nu goes from let us say 3 to 2. And in absorption, nu goes from 2 to 3. So, + – 1, this transition is possible as a function of emission and absorption of photon.

(Refer Slide Time: 32:30)



Vibrational Transition

Mechanism of Molecular Radiation

Simple harmonic

$\Delta \upsilon = \pm 1$

- ❖ An-harmonic oscillator
- ❖ Fundamental band (first harmonic)
- ❖ Overtones (second and higher order harmonic) $\Delta \upsilon = \pm 2$

$$E_\upsilon = \underline{\omega_e\left(\upsilon+\frac{1}{2}\right)} - \underline{\omega_e x_e\left(\upsilon+\frac{1}{2}\right)^2} + \underline{\omega_e y_e\left(\upsilon+\frac{1}{2}\right)^3} \ldots$$

↑ first harmonic

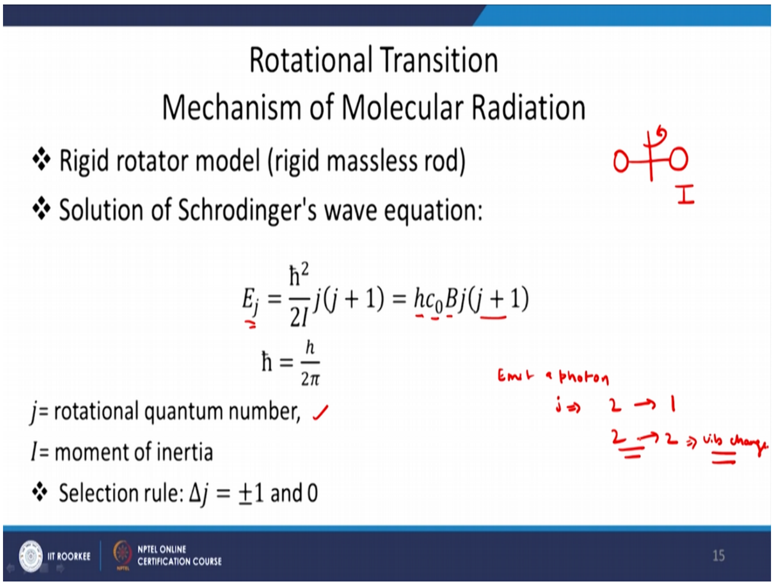
IIT ROORKEE | NPTEL ONLINE CERTIFICATION COURSE

There may be an harmonic oscillator. If there is an harmonic oscillator; normally, for harmonic oscillator, we have only first term. But, if we have oscillator which is not performing simple harmonic motion and many molecules we will see that they do not follow the theory proposed by a simple harmonic motion, we have extra terms that appear in the expression for energy. If we take the first term, it will give you some frequency.

And this frequency, basically it is called first harmonic or fundamental frequency. If we take delta v is = + – 2, we get overtones. Second and higher order harmonics are also there. So, this, we will discuss in the next lecture. If we have simple harmonic motion. That means, simple harmonic oscillator with it, then delta v, only + – 1 is possible. So, simple harmonic delta v, only + – 1 is possible.

That means, vibrational quantum number can change by only 1 and we get only a fundamental frequency, a single line. But, if we take an harmonic oscillator, the expression of vibrational energy is given by this expression which has more terms. And delta v; that means, the energy state can; the quantum number, vibrational quantum number can change more than 1. It can be + – 2. When it is + – 2, the frequency, the wavelength that we get, it corresponds to overtones or higher order harmonics.

(Refer Slide Time: 34:04)



Rotational Transition

Mechanism of Molecular Radiation

- Rigid rotator model (rigid massless rod)
- Solution of Schrodinger's wave equation:

$$E_j = \frac{\hbar^2}{2I} j(j+1) = hc_0 B j(j+1)$$

$$\hbar = \frac{h}{2\pi}$$

j = rotational quantum number, ✓

I = moment of inertia

- Selection rule: $\Delta j = \pm 1$ and 0

Similar to vibrational transitions, we have rotational transitions. A molecule can store energy in rotational mode. So, in quantum mechanics, the energy storage using rotation is basically model as roter. So, we assume that a molecules or atoms in the molecules are connected by a 2 rigid spheres and they rotate. This is called rigid rotor model. The moment of inertia of this configuration is let us say I. Okay.

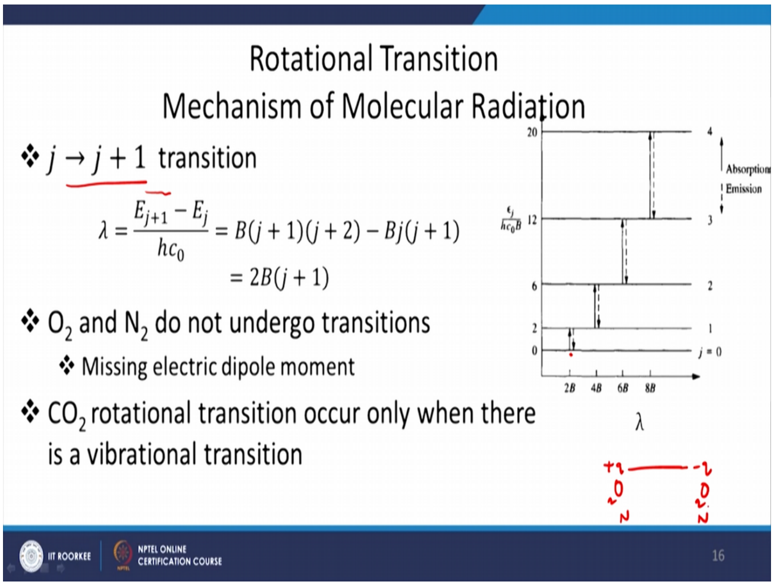
And we apply the principles of quantum mechanics. We solve the Schrodinger equation for this configuration, the rigid rotor model. And the solution gives you the amount of energy stored in this rotor. So, amount of energy stored in this roter is quantized. And the energy is given by this relation h times c nought, where c nought is speed of light, h is the Planck constant, where is a constant B and j times j + 1.

So, this is the expression for the energy for energy storage using the rigid rotor model. So, molecules, they follow this model very closely. So, amount of energy stored inside a molecule based on its rotational degree of freedom can be calculated based on the principle of quantum mechanics. And the relation h c nought Bj j + 1, where j is the rotational quantum number. Now, the transitions can happen; delta j as + – 1 and 0.

That means, if we emit a photon, if an photon is emitted, then j can go from 2 to 1. Or it can go from 2 to 2 itself. Okay. That means, quantum number will decrease either by 1, if the photon is emitted. Or it will not be changing at all. Now, this is possible only when there is a vibrational change. Okay. Because ultimately, the photon is emitted. So, the energy of the molecule should decrease and the energy can only decrease either by rotation or vibration.

So, if the rotation is not changing, then the vibration energy should change. So, this is possible only when there is a vibrational change. So, when vibrational change is there, then the quantum number j for the rotation will not change. So, that means that the energy in the rotational mode is not changing. Only the vibrational change is taking place.

(Refer Slide Time: 36:27)



Rotational Transition
Mechanism of Molecular Radiation

- ❖ $j \rightarrow j+1$ transition

$$\lambda = \frac{E_{j+1} - E_j}{hc_0} = B(j+1)(j+2) - Bj(j+1)$$
$$= 2B(j+1)$$

- ❖ O_2 and N_2 do not undergo transitions
  - ❖ Missing electric dipole moment
- ❖ CO_2 rotational transition occur only when there is a vibrational transition

So, this is the, same thing is represented graphically here. So, if we have a transition from j to j + 1, let us say. That means, we absorb a photon. When we absorb a photon, we jump from lower energy level to higher energy level. So, we represent lambda is = the frequency, the wavelength of the transition as energy in higher state E j + 1 – E j divided by h c nought. So, we substitute for the expression of energy from this relation.

So, it gives you B j + 1 j + 2 – B j j + 1. And this expression reduces to 2B j + 1. So, B is a quantum mechanical constant which is given by quantum mechanics. And for j, you can take j value 0. It gives you 2B. That means, the amount of energy change for quantum number j is 2 times B. If j is = 1, we get 4B. So, what it we observe is that, as we go along higher values of rotational quantum number, the energy jump is increasing.

For j is = 0, the energy jump is 2B. For j is = 1, the energy jump is 4B and so on. Now, there are many molecules that do not exhibit this type of transitions, such as oxygen and nitrogen. We will study this in the next lecture in more detail. Oxygen and nitrogen do not emit or absorb radiation in this form, because they miss electric dipole moment. So, dipole, we know that 2 charges of different sign, separated by some distance is called a dipole.

Now, oxygen, both oxygen atoms are of same type. They have same number of electrons. So, the charge difference is not there. So, they do not form a dipole. Same thing goes with nitrogen. So, oxygen and oxygen, they are same charge. Let us say q and q. Similarly, nitrogen and nitrogen, they do not have opposite charges. So, they have same charges on both ends. So, they do not form dipole.

And that is why they do not exhibit pure rotational transition. Although they can show some transitions if they are accompanied by vibrational and electronic transitions also. Same thing goes for C O 2. So, C O 2 does not show rotational transitions by itself. But when C O 2 undergoes vibrational transitions, it can show rotational transitions. So, we discussed some of the theory in this lecture.

How the interatomic and the molecular structure is used to explain the emission and absorption of photon in atomic and molecular gases. In atomic, it is the electronic structure, the configuration of electron that decides how much energy is emitted or absorbed, at what wavelength. And in molecules it is the electronic configuration as well as vibrational and rotational configuration that decides how much energy is changing as a result of emission and absorption of photon.

In the next lecture, we will connect the theory that we discussed in this lecture to actual spectrum. And we will see how the spectrum of atomic and molecular species is basically generated with the, with this information. Thank you.