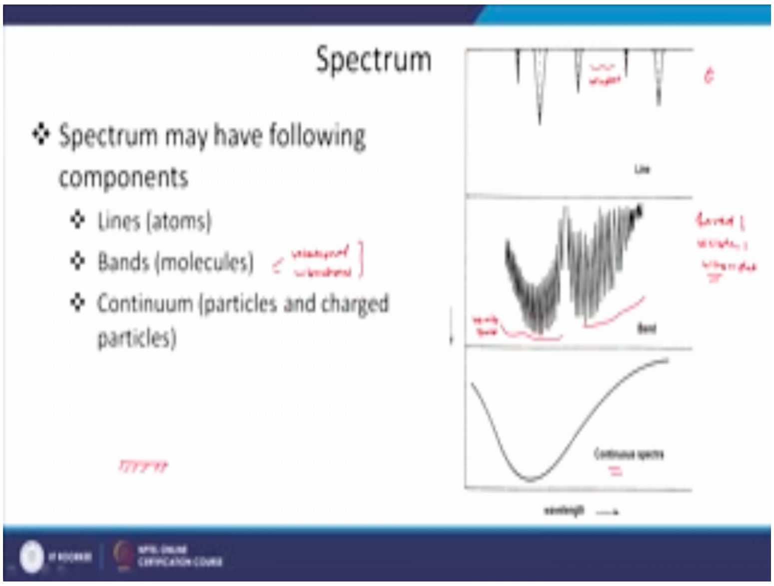
Radiative Heat Transfer
Prof. Ankit Bansal
Department of Mechanical and Industrial Engineering
Indian Institute of Technology - Roorkee

Module - 6
Lecture - 30
Atomic and Molecular Spectra

Hello friends, in the previous lecture we discussed how the atoms and molecules store energy in their electronic states, rotational and vibrational states and how the energy undergoes transition from 1 state to another and results in emission and absorption of photon. In this lecture, we will connect that knowledge to generate spectrum of emission and absorption coefficients for different types of gases.

(Refer Slide Time: 00:58)



Spectrum

- Spectrum may have following components
  - Lines (atoms)
  - Bands (molecules)
  - Continuum (particles and charged particles)

So, first of all, let us understand what is spectrum and how the different spectrums differ from each other. So, normally we see that we have 3 types of spectrum. In the first spectrum, we have lines, isolated lines. That means, radiation is emitted and absorbed along these lines in a very short wavelength region. So, this is typical of atomic gases which we discussed in the previous class also.

So, atoms basically have electronic states that undergoes transition. And as a result of this transition, they emit or absorb a photon. Then, we have bands. So, we have large number of lines grouped in a band. So, let us say this is 1 band, this is another band. So, they have large number of lines forming a band. This is contrast to atoms where we have isolated lines. This is typical of molecules where we have simultaneous rotational and vibrational transitions.

So, molecules have rotational and vibrational transitions. That means, the quantum number associated with rotation and vibration change. And as a result, the energy of the molecule change. And this change is accompanied by emission and absorption of photon. Now, we can have different types of bans, we can have infrared, we may have bands in a visible and we may have bands in ultraviolet as well.

So, ultraviolet has shortest wavelength and infrared and red far infrared has longest wavelength. That means, infrared bands will require least amount of energy for transition. Visible and near infrared bands require medium amount of energy. And ultraviolet bands require largest amount of energy. Ultraviolet bands typically are encountered in high temperature applications, where we have one of the electronic transitions happening simultaneous with vibration and rotational transitions.

Infrared band is accompanied by only rotational transitions. So, far infrared and infrared, we do not have much of vibrational transitions, just we have rotational translations. And the energy change in rotational transition is minimum. And that is why the wavelength is largest. And visible band, visible and near infrared bands are accompanied by medium amount of energy change which is typically governed by vibrational transition together with rotational transitions.

So, rotational and vibrational transitions normally are going together. And we get large number of lines in the form of bands. And this typical band, many times is also called Ro-vibrational band. Ro-vibrational band, because we have lines accompanied by rotational transitions and we have a band which is accompanied by a vibrational transition. Now, we also have third type which is continuous spectra.

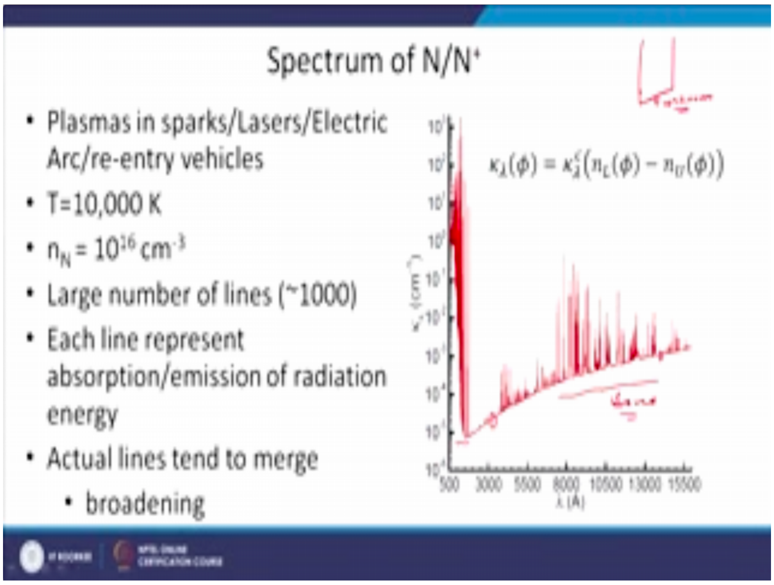
Continuous spectra does not have line structure, we do not have band structure, we have continuous emission of energy, continuous absorption of energy over all wavelengths. This is typical of particles such as soot, such as ash. So, soot, ash, carbon particles, they emit and absorb radiation continuously. We have also seen this in surfaces. So, if you have surface, a flat surface, it emits and absorb radiation continuously.

And we can define this surface as gray or even non-gray, where we have mild dependence of emittance on the spectrum or the wavelength. The mechanism of absorption and emission in solids is different. It is basically the lattice vibration that basically leads to emission and absorption on photon. And lattice vibration has continuous spectrum. And that is why solids can emit and absorb radiation continuously.

While the gases cannot. Gases have distinct and quantized vibrational and rotational energy. And they cannot continuously emit and absorb radiation. And this is very significant from the point of view of heat transfer. Because, if you are interested in radiative heat transfer, we must look for transparent window. That means, which part of the spectrum will allow you to do heat transfer and which part of the spectrum will not allow you to transfer heat.

Because, if you have any applications, combustion or otherwise and you have a gas which is absorbing in certain bands, then definitely radiation will be blocked in that part of the spectrum. So, you will look at the spectrum window. So, for example, this is a window, right. Of course, in atomic lines, there are so many windows. But in molecular spectra, there will not be many windows. So, we have to look for windows when we are talking about radiative transfer. So, first we will look at the atomic spectrum we discussed in the previous lecture also.

(Refer Slide Time: 06:33)



Spectrum of N/N⁺

- Plasmas in sparks/Lasers/Electric Arc/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

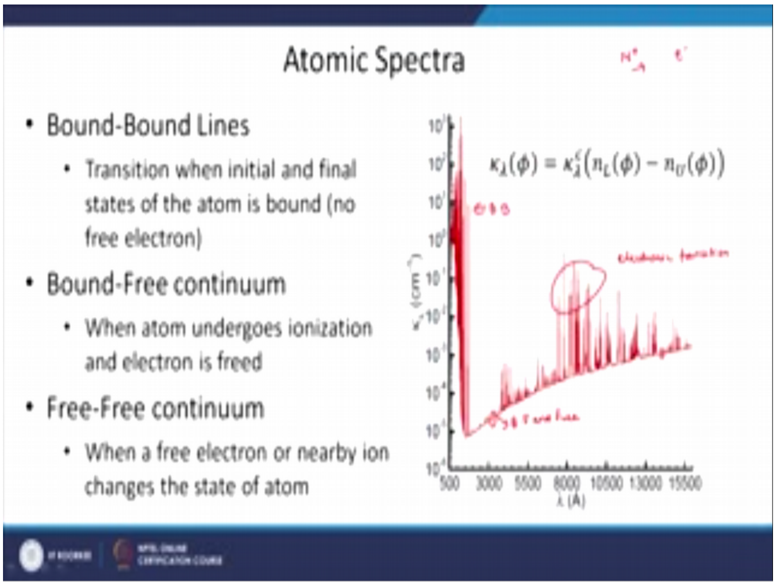
$\kappa_\lambda(\phi) = \kappa_\lambda^c(n_L(\phi) - n_U(\phi))$

I will just emphasize some points here. That points that I emphasize is that, there are lines in a vacuum ultraviolet short wavelength region and there are lines in a infrared region also. So, this is a infrared. Infrared is basically wavelength > 6,000, 7,000 angstrom and vacuum ultraviolet is wavelength 500 to 1,000 angstrom. So, atomic lines of nitrogen and nitrogen + ion, they have continuous presence of lines in the vacuum ultraviolet as well as infrared.

Normally the atomic spectra is obtained only in a high temperature applications such as lasers, electric arcs, reentry vehicles, sparks. So, all these are basically applications where you will have atomic spectrum. And atomic spectrum is not only governed by these lines, but there is also presence of this continuous spectrum. So, you will also observe that we have line, radiating lines, but we also have some continuous spectrum between these 2 lines. Okay.

This is not completely 0 absorption coefficient. So, we have some continuum also. Okay. So, we will understand what is the reason we have this continuum. And the other phenomena that we observe in atomic spectrum is that the lines merge. If we have lines near each other, they tend to merge. I will show a zoomed picture of this slide and you will be able to understand it.

(Refer Slide Time: 24:49)



Atomic Spectra

- Bound-Bound Lines
  - Transition when initial and final states of the atom is bound (no free electron)
- Bound-Free continuum
  - When atom undergoes ionization and electron is freed
- Free-Free continuum
  - When a free electron or nearby ion changes the state of atom

$$\kappa_\lambda(\phi) = \kappa_\lambda^c\left(n_L(\phi) - n_U(\phi)\right)$$

So, atomic spectrum basically has 3 components. So, atoms have 3 components. 1 is bound-bound lines. Bound-bound lines is basically transition from 1 electronic level to another electronic level. We discussed in the previous lecture that atoms have distinct electronic levels decided by their electronic configuration and quantum numbers. So, when an atom changes its electronic state, that means, 1 electron jumps from 1 orbit, orbital to another orbital or changes its one of the quantum numbers, either spin quantum number or magnetic quantum number; then, it changes its energy states and energy is emitted and absorbed.

The amount of energy emitted or absorbed by the atom through this mechanism is discrete. That means it is basically in the form of line. So, this is called bound-bound line. So, all these lines are basically result of electronic transitions. Okay. Now, what can also happen is that a photon of very large quantity may be absorbed by atom. So, we have a photon coming which has very large energy.

It may collide with the atom. And what may happen is, one of the electrons may be ejected. That means, the ion, atom becomes ionized as a result of absorption of this photon. So, this is called bound-free continuum. So, 1 part of the spectrum we observe is continuous, in between lines. So, some part is continuous. This is basically a result of continuum radiation which is formed when we have electrons ejected out of the atom as a result of emission or absorption of photons.

So, we have call it free continuum because, the atom is free now. It is no more part of the atom. It has been freed from the atom. Atom has become ionized. Now, this electron that has been ejected out of the atom may have any amount of energy. And that is why there is no quantum limit on the amount of energy this electron can carry; and the spectrum is continuous. While at, when electron is basically bound in a atom, it has quantized limit and the energy is discreet.

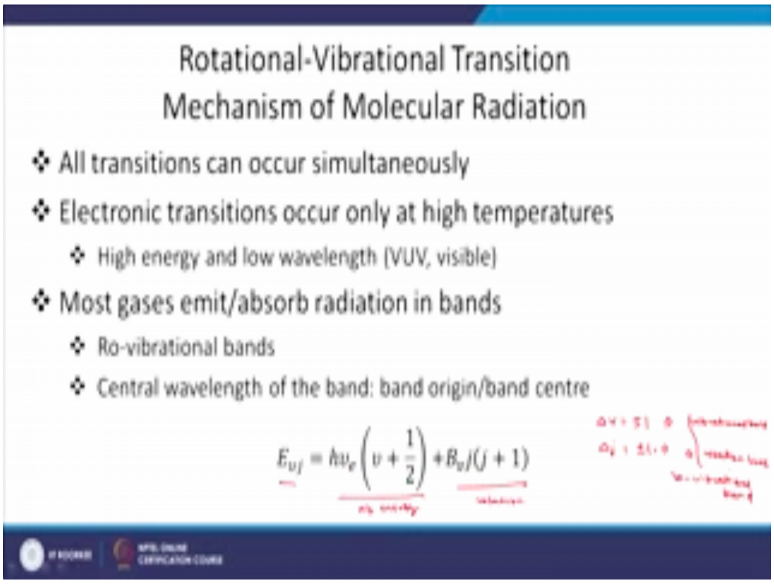
While the free electron does not have any quantum limit and the energy is continuous. And the third is a free-free continuum. That means, free-free continuum radiation. When an electron or any charged particle, let us say come to the vicinity of a 1 ion; let us say we have N + roaming around, an electron comes near this particle, then what may happen is, due to repulsion of this charged particles, the atom may change its energy.

That means, due to the presence of electron, the nitrogen ion may change its energy. Okay. This is called free-free continuum. That means, due to the presence of electric field, due to the presence of electrons, the energies of the atom has changed, atom of the ion has changed. And because there is no limit on the amount of energy that has been exchanged due to this repulsion, we basically have continuous spectra.

So, atoms have 3 mechanisms of emission and absorption of photon. 1 is bound-bound, 1 is bound-free and the last is free-free. In, out of these 3, of course bound-bound line is the most significant. As you see, the absorption coefficient is largest for bound-bound. While bound-free is, bound-free and free-free is not very significant, the magnitude of bound-free and free-free is very less. You see 8 order of magnitude difference.

But, in certain applications, this may be important. So, we have kept it here. So, bound-free and free-free, the magnitude of absorption is very small. But in certain applications, this may be important.

(Refer Slide Time: 12:06)



Rotational-Vibrational Transition
Mechanism of Molecular Radiation

- All transitions can occur simultaneously
- Electronic transitions occur only at high temperatures
  - High energy and low wavelength (VUV, visible)
- Most gases emit/absorb radiation in bands
  - Ro-vibrational bands
  - Central wavelength of the band: band origin/band centre

$$E_{vJ} = h\nu_e\left(v+\frac{1}{2}\right)+B_vJ(J+1)$$

Now, we go for rotational and vibrational transitions. As we discussed, the mechanism of emission and absorption in molecules is governed by rotational and vibrational transitions. And we also discussed that all these transitions can occur simultaneously. So, they can be vibrational transitions together with rotational transitions. They can be electronic transitions together with vibrational and rotational transitions.

Then we have electronic transitions, we have large amount of energy that is exchanged and the spectrum will always be in a vacuum ultraviolet or visible part of the spectrum. When we have only vibrational transitions, no electronic transitions, the spectrum will have medium amount of energy exchange. And the spectrum will be in visible or near infrared. And it is also possible that there is no vibrational transition, no electronic transition, only rotational transition, then the spectrum will have its lines in far infrared region of the spectrum, because that contains least amount of energy.

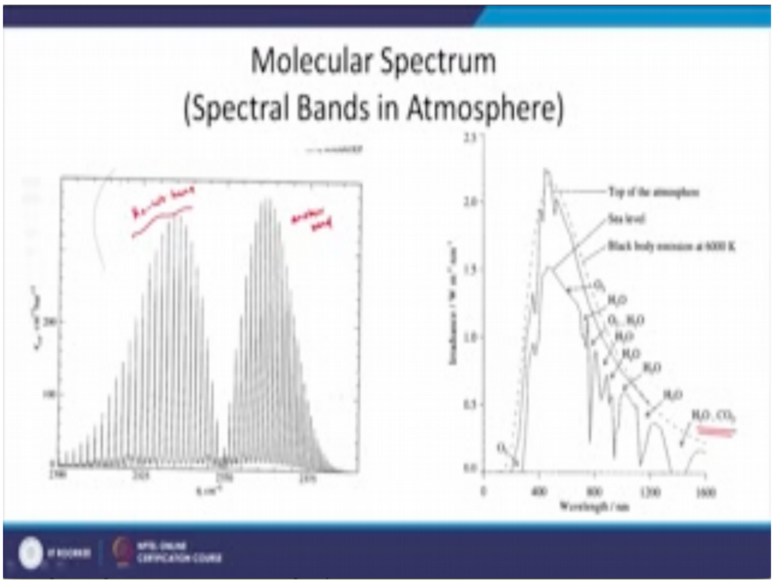
So, here we will consider only rotational and vibrational transition. Because, for combustion application, the electronic transitions are rare. So, we consider only rotational and vibrational transition simultaneously. So, we write, energy stored in a vibrational rotational mode as sum of vibrational energy; this is simple harmonic oscillator model that we have used here. So, this is a vibrational energy.

And we have rotational energy. Again, we have used rigid rotor model. So, we have used simple harmonic oscillator model and we have used rigid rotor model. And with these 2 model, we can write down the energy, total energy in vibrational and rotational mode of a molecule. Now, this will be subjected to transition before, so this will be subjected to transition. So, delta v will be subjected to + – 1.

That means, vibrational transition, vibrational quantum number can change by + – 1. And this will be subjected to rotational transition delta j is = + – 1 or 0. And we discussed in the previous lecture that 0 is only possible when there is delta v of + – 1. If delta v is also 0, well the, there is no vibrational transition. But then, rotational transition must be there. Now, when we have delta v + – 1, we get what we call vibrational band.

This will give you vibrational band. And this will give you; when we have rotational transition, this will give you rotational lines. Okay. And when we combine this 2 together, we get what we call Ro-vibrational band. That means, there is a band and in the band, there are lines. So, let us see how it looks like.

(Refer Slide Time: 15:01)

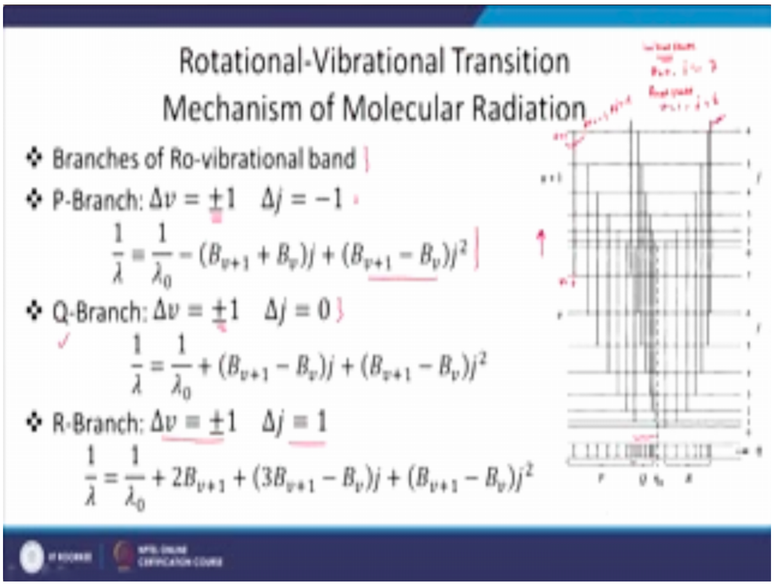


Molecular Spectrum
(Spectral Bands in Atmosphere)

So, this is 1 Ro-vibrational band. This is Ro-vibrational band. Okay. And this is another band. This is another band. So, this will have a delta v, single delta v value. So, 1 band will have only delta, single delta v. Another band will have another delta v. But within that delta v, we can have multiple rotational lines. How these lines basically appear, we will discuss in the next slides. But the point here is that delta v + – 1 gives rise to vibrational band.

And together with rotational transition it gives rise to rotational band. And this is something we observe in our atmosphere also. We see that water molecule and carbon dioxide, they absorb radiation of solar energy. So, solar spectrum we see, lot of energy is absorbed in infrared region, in near infrared region. And the major gases that absorb solar radiation in the form of bands are C O 2 and H 2 O. So, these triatomic gases, they absorb significant amount of radiation. And the major cause of absorption is these 2 gases, the spectral bands of these 2 gases.

(Refer Slide Time: 16:20)



Rotational-Vibrational Transition

Mechanism of Molecular Radiation

- Branches of Ro-vibrational band
- P-Branch: $\Delta v = \pm 1 \quad \Delta j = -1$

$$\frac{1}{\lambda} = \frac{1}{\lambda_0} - (B_{v+1} + B_v)j + (B_{v+1} - B_v)j^2$$

- Q-Branch: $\Delta v = \pm 1 \quad \Delta j = 0$

$$\frac{1}{\lambda} = \frac{1}{\lambda_0} + (B_{v+1} - B_v)j + (B_{v+1} - B_v)j^2$$

- R-Branch: $\Delta v = \pm 1 \quad \Delta j = 1$

$$\frac{1}{\lambda} = \frac{1}{\lambda_0} + 2B_{v+1} + (3B_{v+1} - B_v)j + (B_{v+1} - B_v)j^2$$

Now, how this bands basically are formed. So, now we will make use of this transition and we will derive how the bands are basically formed. So, we have what we called 3 branches of Ro-vibrational band. So, the first branch is delta v + – 1 and delta j is – 1. So, this gives rise to what we call P-branch. The Q-branch has delta v + – 1 and delta j is = 0. This gives you Q-branch. And we have R-branch, delta v is = + – 1 and delta j is = 1.

So, now, what we are doing is, we are doing simultaneous vibrational and rotational transition. So, for each vibrational transition, there is a simultaneous rotational translation. And we have grouped these transitions in 3 categories. P-branch, Q-branch and R-branch.

Now, by simple mathematics, the derivation of this energy, we have already calculated. So, in this expression, we will keep the delta v as + – 1 and we will keep delta j as 1 – 1 and 0.

So, when we keep delta v + – 1, we get this expression of wavelength. 1 upon lambda is 1 upon lambda nought – b v + 1 + b v times j. And this b v + 1 – b v times j square. So, this is the expression for wavelength for the P-branch. And we will have lot of wavelengths as you see here. So, P-branch has a number of lines. Some lines, let us say this line. This lines has a vibrational transition.

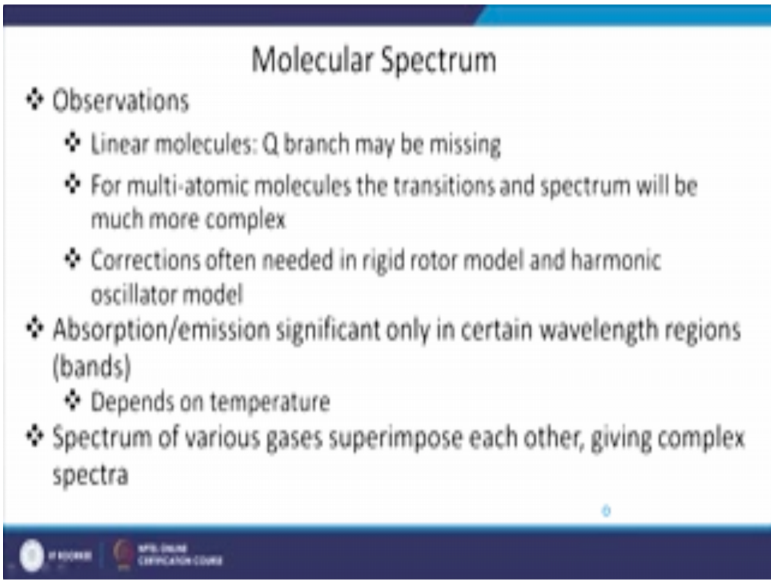
So, this is a v is =, this is v is = let us say 0. And let us say this is v is = 1. So, we have transition, delta v is – 1. So, for this line, delta v is = – 1. So, initially it is 1. And then, it is 0. And the rotational transition is from 7 and this is 6. So, delta j is also – 1. So, delta v is = – 1, delta j is = – 1 for this particular line. The second line, delta v is – 1 again. And delta j is from 5 j 5 to j 6. Again, this is basically delta j is a; so, this is a delta j from here to here.

Again, this is basically – 1. So, this is the P-branch. Okay. So, we are going from this direction to this direction. This is the direction of emission. So, the initial state is, let me write down here. For the first line, so initial state for the first line, just I am giving you; rest of the things are same. So, for the first state, v is = 0. And j is = 7. And the final state is v is = 1 and j is = 6. So, we have delta j is – 1. And delta v is basically = 1.

Delta v is = 1 and delta j is = – 1. So, this gives rise to P-branch. So, there are large number of lines. For different values of j, you can get different type of lines. And this forms a band. Similarly, for the Q-branch we have delta v is = + – 1, but delta j is = 0. So, there are some lines in the Q-branch. And the last is R-branch, where delta j is = + 1. So, the last line, this one, is in the R-branch, where we have j is = 6 to j > 6. So, we have a delta j > 1. Okay.

So, this basically gives you an idea how is the band is basically constructed in a molecule as a result of simultaneous vibrational and rotational transition. So, this complete collection of lines is called a band, a Ro-vibrational band. And it will have 3 branches, P, Q, R and P, Q and R branches. And we can have different gases having different properties.

(Refer Slide Time: 20:21)



Molecular Spectrum

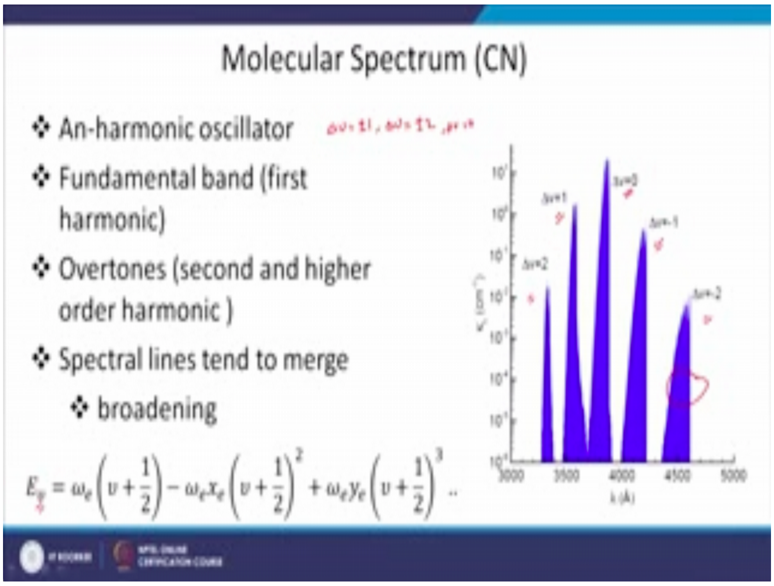
- Observations
  - Linear molecules: Q branch may be missing
  - For multi-atomic molecules the transitions and spectrum will be much more complex
  - Corrections often needed in rigid rotor model and harmonic oscillator model
- Absorption/emission significant only in certain wavelength regions (bands)
  - Depends on temperature
- Spectrum of various gases superimpose each other, giving complex spectra

So, the general observation is that linear molecules in this category general observation is that linear molecules may have Q-branch missing. So, generally we have P, Q and R branch. But, if you closely examine that we find that linear molecules may have Q-branch missing. For multi-atomic molecules, we may have a much more complicated spectra, not just given by this P, Q and R branch.

Because we have now multi-atomic structure. And we need to have to account that these band has been generated by the assumption of linear harmonic oscillator and rigid rotor model. If the oscillator is not linear, or it is not harmonic, then the spectrum will look different. And we will, I will give you an example how the spectrum will look like. So, this is the spectrum of CN. CN has application in many cases.

CN, normally in combustion we do not find CN forming, but there are large number of applications, specially, many stars have this CN radiation. And this CN is basically not governed by harmonic oscillator.

(Refer Slide Time: 21:28)



Molecular Spectrum (CN)

- An-harmonic oscillator $\Delta v = \pm 1, \Delta v = \pm 2, \ldots$
- Fundamental band (first harmonic)
- Overtones (second and higher order harmonic)
- Spectral lines tend to merge
  - broadening

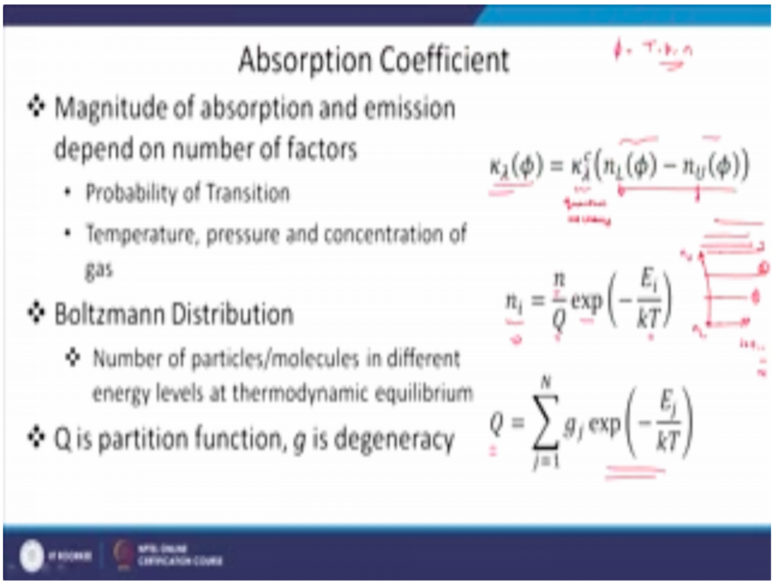
$$E_v = \omega_e\left(v+\frac{1}{2}\right) - \omega_e x_e\left(v+\frac{1}{2}\right)^2 + \omega_e y_e\left(v+\frac{1}{2}\right)^3 \ldots$$

We have to resolve for an harmonic oscillator, where we have many terms in the vibrational energy. And an harmonic oscillator can go delta v, that is change in vibrational quantum number as + – 1, as well as delta v of + – 2 is possible. And delta v of course is 0 is also possible. So, we have this type of configuration for an harmonic oscillator. The first one, delta v is = 0. This is the band, the center band. It is called fundamental band.

Then we have delta v + 1 – 1, delta v is = 2 and delta v is = – 2. So, we get distinct bands. And these bands are called basically the overtones or harmonics. And each band, if we zoom on this each band, you will find there are large number of rotational lines. Okay. So, in this picture, because the resolution of the picture is not fine enough, you are not able to visualize the rotational eyes.

But it is understood that each vibrational band contains number of rotational lines. So, the spectrum becomes very very complicated when we consider gas radiation. Now, how do we calculate the absorption coefficient?

(Refer Slide Time: 22:38)



Absorption Coefficient

ϕ - T, p, n

- Magnitude of absorption and emission depend on number of factors
  - Probability of Transition
  - Temperature, pressure and concentration of gas
- Boltzmann Distribution
  - Number of particles/molecules in different energy levels at thermodynamic equilibrium
- Q is partition function, *g* is degeneracy

$$\kappa_\lambda(\phi) = \kappa_\lambda^c\left(n_L(\phi) - n_U(\phi)\right)$$

$$n_i = \frac{n}{Q}\exp\left(-\frac{E_i}{kT}\right)$$

$$Q = \sum_{j=1}^{N} g_j \exp\left(-\frac{E_j}{kT}\right)$$

We discussed this, that absorption coefficient depends on 2 parameters, the constant which comes from quantum mechanics and it is related to probability. So, this basically depends on wavelength, but it does not depend on the state of the gas. So, it is a constant that comes from quantum mechanics and it basically relates the probability of transition. So, some lines will have large value of kappa lambda c.

Some lines will have small value of kappa lambda c. So, those lines which have large value of kappa lambda c, they will see large amount of absorption coefficient. And those lines which have smaller value of kappa lambda c will see that smaller value of absorption coefficient. The other dependence of absorption coefficient is on the gas state phi. So, phi is basically given by temperature, pressure and concentration.

And this is the gas state vector. And the gas state vector basically relates to the number of molecules or number of atoms in a given energy level. And this is governed by temperature and pressure and concentration. In thermodynamic equilibrium, the number of molecules in different energy levels, be it in vibrational modes. So, how many molecules will have vibrational quantum number of 1; how many molecules will have vibration contact number 2 and so on.

How many molecules will have rotational quantum number 0, how many molecules will have rotational quantum number 2 and so on. It is governed by Boltzmann distribution in thermodynamic equilibrium. So, what does Boltzmann distribution says? Now, it is quantized. So, Boltzmann distribution say that, number of molecules or atoms in a given energy level. So, we have energy level, let us say this is ground level, ground state.

We have first state, second state, third state and so on. So, number of molecules in each state i is = 0 to let us say N, where 0 is the ground state. The number of molecules is given by n, where n is total number of molecules in the gas. Q is the partition function, exponential – E i upon kT. E i is the energy level, energy of each level. That means the energy of these levels. k is the Boltzmann constant and T is the temperature.

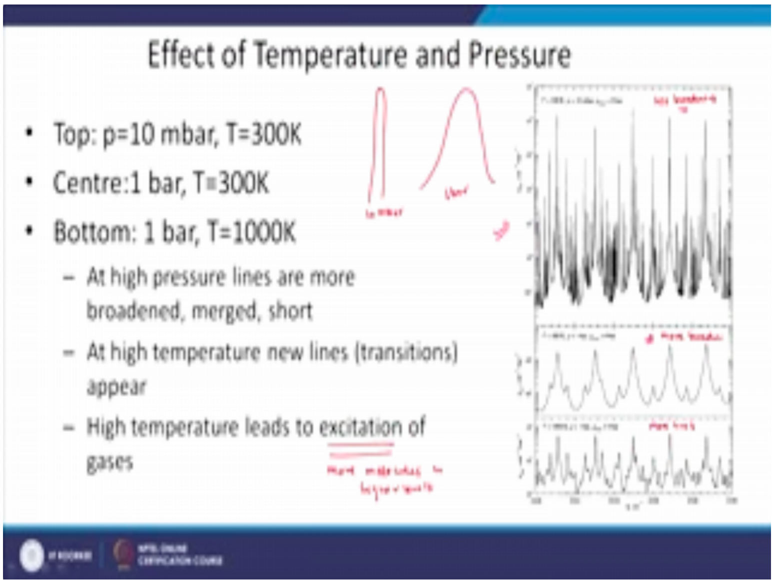
If the thermodynamic equilibrium is not prevalent, then the temperature of each mode may be different. That means, we may have different rotational temperature, we may have different vibrational temperature, we may have different electronic temperature. So, under thermodynamic non-equilibrium, we have to consider different temperatures. If you are interested in finding how much particles are there in different rotational mode, we must use rotational temperature.

If you are interested in finding how many particles are there in each vibrational mode, we must use vibrational temperature, and so on. But under thermodynamic equilibrium, all the temperatures are same. And the number of parts, particles or molecules is given by this Boltzmann distribution. So, this is nothing but a probability distribution which is normalized by partition function Q, where partition function is basically nothing.

Summed over all the levels of g j exponential – E j by kT. Where g j is the degeneracy or all the levels which have same energy. And one which do that, basically what we are doing is, we are normalizing the, this probability distribution by the partition function. So, once we have the population, the absorption coefficient can easily be constructed. So, under this subscript L in this formula means, the lower level and subscript U in this expression gives you upper level.

So, there will be translation. So, when we have absorption, there will be a transition from lower level to higher level. Okay. So, this is, n L is the population here, at the lower level. And n U is the population or number of molecules in the upper level. And the difference basically gives you the idea, how much energy is absorbed. More the number of molecules go from lower level to higher level, more amount of energy is absorbed by the gas.

(Refer Slide Time: 26:33)



Effect of Temperature and Pressure

- Top: p=10 mbar, T=300K
- Centre:1 bar, T=300K
- Bottom: 1 bar, T=1000K
  - At high pressure lines are more broadened, merged, short
  - At high temperature new lines (transitions) appear
  - High temperature leads to excitation of gases

Now, how it affects the temperature. Now, we, if we look at the Boltzmann distribution, it depends on temperature. If we increase the temperature, what will happen is, there will be more number of molecules in higher levels. So, Boltzmann distribution shifts more number of molecules to higher energy levels if the temperature increases. On the other hand, if temperature decreases, more molecules will shift towards the lower levels.

So, this is how the Boltzmann distribution works. We increase the temperature, molecules shift to higher levels. And because at higher temperature molecules are shifted to higher level, we will see that there will be shift in the spectrum. Now, the spectrum shifts like this. At low pressure, this is the spectrum; so, the spectrum looks very very complicated when the pressure is very less.

Let us say, in this case, this is the spectrum of carbon dioxide at a pressure of 10 millibar. The temperature is 300 kelvin. And we see that the spectrum is very complicated. When we increase the pressure, the spectrum becomes relatively smooth. So, here the pressure is 1 bar and temperature is 300 kelvin. And the bottom one is temperature 1,000 kelvin. And the spectrum again becomes complicated.

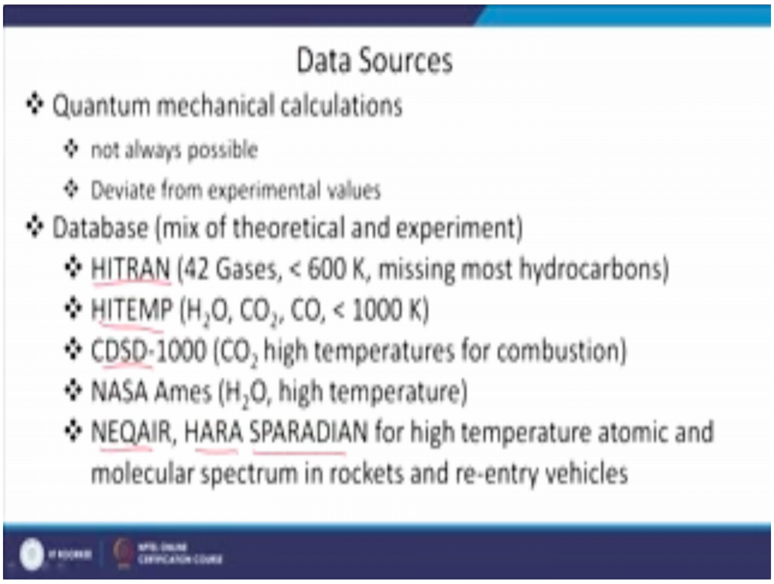
So, the general observation is, by increasing the pressure, the spectrum becomes relatively smooth. By increasing the temperature, the spectrum becomes relatively vibrant or erratic. So, why it is happening? Now, the reason is, when we increase the pressure, the lines become broad. So, if we have a line like this, let us say 10 bar or 10 millibar. If we increase the pressure, the line will become fat or broad at a pressure of 1 bar.

And when the lines become fat or broad at higher pressure, they are basically more broad, they are more broadened. Then lines which are very near to each other, which are very close to each other, they will merge together and the spectrum basically becomes very complicated. So, in this case, the lines merge together. And because of merging of lines the spectrum becomes relatively small.

While in this case, there is less broadening. There is the less broadening and due to this, there are individual lines. And the individual lines do not overlap and the spectrum is very complicated. While here, the there is more broadening and the lines merge together and they form a smooth spectrum. Finally, when we have high temperature, we have more lines because we have more molecules in higher energy level.

So, high temperature leads to excitation. Excitation means, more molecules in higher levels. That is called excited molecules or excitation. With temperature, the excitation increases. The molecules jump into higher energy level, leads to more amount of lines. And in this case, we have more lines. And that is why the spectrum is more complicated.

(Refer Slide Time: 29:30)



Data Sources

- Quantum mechanical calculations
  - not always possible
  - Deviate from experimental values
- Database (mix of theoretical and experiment)
  - HITRAN (42 Gases, < 600 K, missing most hydrocarbons)
  - HITEMP (H_2O, CO_2, CO, < 1000 K)
  - CDSD-1000 (CO_2 high temperatures for combustion)
  - NASA Ames (H_2O, high temperature)
  - NEQAIR, HARA SPARADIAN for high temperature atomic and molecular spectrum in rockets and re-entry vehicles

Now, how do we obtain data? How; these spectrums are basically generated in combustion applications. Many people, they turned to one of the standard data bases for these calculations. While most of the data in this databases is experimental. But some of the data is also generated from quantum mechanics. So, both experimental and theoretical results are available. The problem with quantum mechanical calculation is that, it is not always possible to obtain.

And it is also very difficult to validate with experiments. So, theoretically, you can generate the spectrum, as we have done here based on the transitions of rotational and vibration. But the theory based on rigid rotor model and harmonic oscillator model does not agree with experiments all the time. So, we must rely on experimental data also. Now, experimental data is available from various sources.

And most popular of them are HITRAN and HITEMP. So, HITRAN gives you absorption coefficient data for 42 gases. But this is only valid for temperature < 600 kelvin. That means, if you are doing atmospheric radiation calculation, this data may be good. You can apply this database for atmospheric radiation calculation where the temperature is low and very very significantly < this 600 kelvin.

On the other hand, for combustion application, the temperature is high. And HITRAN database may not be very valid. So, you have to go for HITEMP database which provides data for main species, water, carbon dioxide and carbon monoxide, for temperatures up to 1,000 kelvin. But still, because in combustion applications, the temperature may actually reach beyond 1,000 kelvin. We have high temperature database CDSD for C O 2.

And some data is also available from NASA Ames. Now, all this data is only valid up to 2,000 kelvin. Some of it may not be valid even for 1,000 kelvin. But, if you are interested in doing plasma calculation, for example, reentry vehicles, then we have number of databases. All this data are not validated with experiment. Some of it may be validated from experiment like shock tube experiments.

But most of the data is theoretical in nature. And the database is like NEQAIR, HARA, SPARADIAN, they provide you database along with spectroscopic constant to evaluate absorption coefficient for gases under very high temperature, that is typical in rockets and reentry vehicles. So, I end this lecture here. Thank you. In the next lecture, we will look at the final structure of the spectrum.

So, here we have generated the broader understanding of the spectrum of atomic and molecular gases. In the next lecture, we will look at the fine structure of the spectrum where the lines are broadened and the lines merged together, to form a complicated spectrum. Thank you.