Radiative Heat Transfer
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Module - 7
Lecture - 31
Line Radiation

Hello friends, in the previous lecture we discussed how the atomic and molecular spectrum is generated. Now, based on the theory of quantum mechanics that we discussed in the previous lectures, the transitions either electronic transitions, vibrational transitions or rotational transitions, they give rise to emission or absorption of photon at a single wavelength. That means, the energy absorbed should be monochromatic, that means at a single wavelength. However, in practice, it has been observed that radiation cannot be emitted or absorbed at a single wavelength. So, let us understand this concept which is called line radiation.

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So, we basically studied that we have a energy level E 1 and we have a energy level E 2. Now, this energy level E 1 and E 2 may be electronic levels as in the case of atoms or it may be vibrational levels or rotational level in the case of molecules. When an energy photon is emitted, then the level drops down E 1 to E 2. So, this gives through photon emission. When a photon is absorbed, the level changes from lower level to higher level and a photon is basically absorbed by the gas.

This is what we have learned in the previous lecture. And what it basically gives you is, if you look at the spectrum and light absorption coefficient or emission coefficient, it should be a single line. That means, a monochromatic line. So, monochromatic means single wavelength. But what is observed in actual practice is that this is a not a single line, but rather it is a spread of line like this. That means, the wavelength is not sharp.

And what basically decides this sharpness is called broadening. So, broadening is a concept related to both atomic and molecular lines. And let us first discuss the nomenclature of this. So, we have let us say a any line we are considering, it may be a rotational line, electronic line or vibrational transition. This line will be not sharp. The intensity, let us say this is s, the wavelength is lambda, it is called s lambda.

So, s lambda is called line strength or the magnitude of the intensity. It is called line strength. Let us call this line strength. Okay. Now, what we see is that this cannot be sharp. Okay. We will see what are the reasons. It cannot be monochromatic. Although, from this we see that E 1 is a fixed value, E 2 is fixed value and lambda is given by E 1 − E 2 upon hc. So, as per this relation, lambda should have a unique value.

Because E 1 and E 2 are unique value. But we also understand that E 1 an E 2 is subjected to uncertainty as per Heisenberg's uncertainty principle. E1 and E2 are not sharp. So, there may be some variation in E 1 and E 2 as well. So, if E 1 and E 2 are subjected to change, then definitely lambda is subjected to change. But that is just 1 cause of uncertainty. There are other causes of line broadening also. That we will discuss.

So, finally the line looks like this. So, this is the sharp line that is theoretically predicted. But actual line looks like this. So, the peak value will be less and the line will be broadened like a typical Gaussian profile. It is Gaussian actually, when we talk about Doppler broadening that we will discuss. And it is Lorentzian in shape, when we talk about collision broadening. So, the line will look like this.
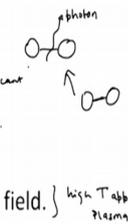
So, a single transition from 1 electronic level to another electronic level will actually lead to wavelengths. Not a single value of wavelength, but over a range of wavelengths. And we represent this just like we represent Gaussian distribution by mean and standard deviation. We represent this line by what we called full width at half maximum. That means, at the

maximum, half of that value and the width of this line. So, we represent the line with what we call full width at half maximum also called broadening width. Okay. So, we will discuss how this is formed.

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So, there are many types of broadening mechanisms that leads to spread of lines. The first one is the uncertainty principle of Heisenberg. It is called natural broadening. So, what uncertainty principle says that, you cannot determine the energy of a state electronic or otherwise sharply. So, there will be always some uncertainty in its energy value. And this energy uncertainty leads to uncertainty in wavelength.

So, this is called natural broadening. That means, a single monochromatic photon will have spread out and line will be broadened. The second one is collision between molecules. It is called collision broadening. When we have molecules, let us say this is the molecule, maybe oxygen or some other molecule. And it is emitting some photon let us say. And in the mechanism, when it is emitting photon, it is collided by another molecule.

Then the collision between these 2 molecules basically leads to change in the wavelength of photon. This is called collision broadening. So, as a result of collision, the photon wavelengths shifts little bit. The third mechanism of broadening is Doppler Shift. You all have observed that the frequency of sound changes when the source, let us say a electric, a railway engine is moving towards or away you from you; that the frequency of sound changes.

Same thing happens in the case of stars. A star that is moving away from you, you will see flicker in its color. That means, the wavelength appears to be changing for that star. So, here, the molecules which are emitting or absorbing radiation, they are also moving. So, they are moving source. So, we expect that there will be a Doppler Shift applied to them. And the amount of radiation emitted from this moving atoms and molecules will be shifted by Doppler broadening.

The third effect is Stark effect. In high temperature plasmas, where we have significant amount of electrons, there is the formation of electric field. And this electric field basically perturbs the internal structure of the atom or molecule and leads to what we call Stark broadening. Now, this is only relevant for high temperature applications like plasma. It is not important for the typical combustion applications, while these 2 are important for combustion applications.

Out of this, Doppler broadening is particularly important in low pressure combustion. So, if we have low pressure combustion, this will be particularly important. And natural broadening is mostly insignificant. So, we do not have much importance to natural bonding. So, we will consider only collision broadening and Doppler broadening in this lecture. There are different mathematical functions used to represent it. So, natural broadening, as I explained is based on the principle of Heisenberg uncertainty. It is generally not important. So, we will not discuss this in detail.

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So, the first thing we will discuss is collision broadening. As I explained, if the molecule which is part of a gas mixture is collided with another molecule, the wavelength of transition, the emission or absorption is shifted or spread out. So, we represent absorption coefficient by a function. It is called Lorentz function. We will derive this function in an example. And this is an example of collision broadening.

So, what basically it says is, that if you have a line of line strength S, lambda nought is its center wavelength or and eta nought is wavenumber at the center where lambda nought is predicted as per the theory we discussed. It is sharp. So, we know that this will not be sharp, it will be spread out. The in; the strength of single line without perturbation, without dispersion is S. And due to broadening, this will become like this.

This will be broadened out. Okay. So, this is the coordinate eta. And on this, we have what we called absorption coefficient, kappa eta or kappa lambda. Okay. The expression that I have given is in term of wavenumber eta. And we also understand that the total strength of the lines remain the same. That means, when we integrate, that means the area under this curve should be = S.

So, S is basically nothing but integrated absorption coefficient over the entire width of this line. So, we call this line strength. And the expression b c is basically half-width, line half-width. Okay. So, we define sometimes the line as FWHM. That means, full width at half maximum. So, that means at the half peak we define the full width. And sometimes we define as b c or half width. So, sometimes we define full-width, sometimes we define half-width, just to represents the spread of this line.

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Natural Line Broadening

$$b_c = \frac{2}{\sqrt{\pi}} \frac{D^2 p}{c_0 \sqrt{mkT}} = b_{c0} \left(\frac{p}{p_0}\right) \sqrt{\frac{T_0}{T}} \Rightarrow$$

$$b_c(D, m, p, T)$$
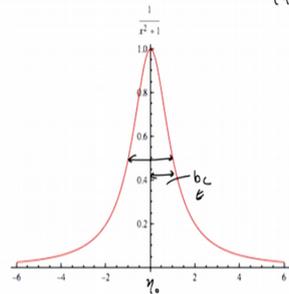
$$f(x) = \frac{1}{1+x^2}$$

D = effective diameter of the molecule

m = mass,

p = total gas pressure

T = absolute temperature

$$\kappa_\eta = \frac{S}{\pi} \frac{b_c}{(\eta - \eta_0)^2 + b_c^2}$$

Now, this is how this Lorentz shape looks like this. It is basically a function which has a form 1 over 1 + x square. So, this function when plotted looks like this. And the broadened line based on collision broadening exactly has the same shape, where the half-width b c is calculated. So, it depends on temperature and pressure. So, the collision width b c; that means, how much wide this line will be.

So, this is full-width and this is half-width. This is the collision width, half-width. So, this collision width, how much the line has broadened depends on number of parameters. It depends on diameter D of the molecule. Depends on the mass of the molecule, pressure and temperature. So, these parameters, this width depend on. We will take 1 example and see how and where this broadening may be important.

And the absorption coefficient as we have already discussed is given by this expression. kappa eta is = S upon pi b c eta – eta nought square + bc square, where eta nought is the center line wavenumber and b c is the collision half-width.

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So, let us do 1 problem. What we are basically interested in is understanding how this Lorentz profile is fitted for this type of problem. Now, this is more of a physics kind of thing. I am just doing this example so that you understand why this mechanism of broadening is coming into picture. So, what we will do is, we will take 2 atoms or a molecule. Let us say we have a molecule. And this molecule is vibrating.

Now, we discussed that molecules should have dipole moment. For example, carbon and oxygen atom tied in this carbon monoxide molecule, they have a dipole moment. Because, number of electron in oxygen is more than the number of electrons in carbon. So, there will be a permanent dipole. While oxygen and oxygen atom will not have a dipole, because same number of electrons in both the atoms, it will not have dipole.

So, this will; no permanent dipole. While carbon monoxide will have permanent dipole, nitric oxide will have permanent dipole and so on. So, only a dipole will basically be able to emit and absorb radiation. Based on this analysis, we put some charge q and negative charge on this – q. The mass is m, let us say, in this case we have assumed the mass to be same for both the atoms. It can be different also.

As in the case of carbon monoxide, the mass will be different. In the case of nitric oxide, there will be, mass will be different. But we have simplified the analysis and I have assumed that the masses are same. Now, we write down the harmonic oscillator equation. So, harmonic oscillator equation for this can be written as; now, this coordinate is x. So x, or we can write down this as d square x by dt square.

That means acceleration + gamma times dx by dt. Okay. Now, what basically, I will explain why this gamma is coming in, + omega nought square + x is = 0. Okay. So, this is a modified harmonic oscillator equation. Normally, you will not have this term. The harmonic oscillator equation will be d square x by dt square is = – omega nought square x. This is the harmonic oscillator equation, right.

But, we have added this term. This is basically for damping, when we have damping or capacitance coming into play. So, what happens is, when the molecules are subjected to collision, a damping term basically appears. So, let us put a damper here, between the molecules. So, we have a spring, as we have in simple harmonic motion, we have a spring, mass spring system. But there is a damper here.

So, we define gamma as c by m, where c is the damping coefficient and m is the mass of the molecule. And we define the natural frequency omega nought square as spring constant k by mass m. So, this is something I think you might have studied how to define spring mass system with capacitance or damper and write down the harmonic oscillator equation. Now, we can solve this using any method on differential equation.

This is an ordinary differential equation. We can solve it and the solution can be written as x is = x nought e power – gamma by 2 t e power – i omega nought t. This is a solution of this equation. Okay. Now, we find acceleration x double dot. That is, d square x by dt square is = x nought gamma by 2 + i omega nought square e power – gamma by 2 t e power – omega nought t. So, this is the acceleration of the system of the mass that we have calculated using this solution.

Now, we will do a force balance. So, force balance. So, we can write force as = q times the electric field E. So, we have a dipole. So, it will exert a force which is = q times e, q is the charge and E is the electric field. And we have, force can also be written as mass time acceleration. So, we can also write down force as m x dot. So, this spring system, mass spring system, what is the driving force for this mass spring system?

The dipole is the driving force. So, as we see that it can only vibrate when we have a dipole, permanent dipole. Without permanent dipole, it cannot emit or absorb radiation. So, the driving force for emission and absorption in this is basically the dipole which has electric

field E. The charge is q and electric field E. And this electric field E is related to emission and absorption of photon. And we are interested in finding E because we have already solved for force, which is = mass times acceleration. We can find electric field E as;

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So, E is = m by q x dot is = m by q. We substitute for acceleration expression x nought gamma by 2 + i omega nought square e power – gamma by 2 t e power – i omega nought t. So, this is the expression for the electric field that we have obtained. Now, what we do is, we can just write down this E as E nought. So, we just put it like E nought. This is the magnitude. So, E nought e power – gamma by 2 t e power – i omega nought t.

So, this is the expression for the electric field. Now, we have to find out, what we do is, we apply the Fourier transform. So, what does Fourier transform does? It basically takes you from time to frequency domain. So, we take to frequency domain. We write E omega. Now, E omega is the frequency. So, E omega becomes 1 upon 2 pi. So, some of the steps I am just skipping. So, we apply the Fourier transform.

So, we get 0 to infinity e power i omega t. Okay. So, this is the expression for applying the Fourier transform. And what we get here is, E omega is = E nought upon 2 pi by just substituting the value of E here and integrating. We get E nought upon 2 pi 1 upon 2 omega – omega nought. Sorry, this is i, where i is the root of – 1. And this will be = – gamma by 2. So, this is the expression for electric field in terms of the frequency domain.

Now, line strength S. The line strength is the line strength of emission or absorption is proportional to the electric field square. The magnitude of electric field square. So, we get line strength as proportional to 1 upon omega – omega nought square + gamma by 2. So, this is basically what we call Lorentz profile, that we have discussed earlier also. Omega you can write down in terms of frequency or wavenumber. So, omega is 2 pi the frequency nu.

And we can convert it into wavenumber or wavelength, whatever units we want. So, what we observe here is that the collision broadening, the reason of collision broadening is basically the damping effect that is coming into the harmonic oscillator model. And also, the collision width b c is basically proportional to gamma. Gamma, we have already defined as damping coefficient c by m. So, this damping coefficient is basically leading to what we called broadening due to collision.

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So, the, so this was the collision broadening. The other mechanism of broadening is the Doppler broadening. We discussed that when a sound producing source is coming towards you or going away from you, you observe a change in frequency. So, same thing goes with the light when we have a light source or a source that is emitting or absorbing photon is moving, then we observe a different wavelength or different frequency.

And this change or observed frequency or wavelength can be written. It depends on the velocity of the source. That is, the molecule that is basically emitting, so velocity of the source. And s is basically the direction in which the photon is emitted. We have already discussed this many times that emission is a directional property. So, s is the direction of

emission. So, with this, we can find out observed frequency, wavenumber or wavelength of the photon. And this is leads to what we call broadening.

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Doppler Broadening

$$b_D = \frac{\eta_0}{c_0} \sqrt{\frac{2kT}{m} \ln 2}$$

$$\kappa_\eta = \sqrt{\frac{\ln 2}{\pi}} \left(\frac{S}{b_D}\right) \exp\left[-(\ln 2)\left(\frac{\eta - \eta_0}{b_D}\right)^2\right]$$

Gaussian in nature

b_D = Doppler line half-width
η_0 = wavenumber at line center

The Doppler broadening depends on temperature. And the profile is Gaussian in nature. This is Gaussian in nature. And we can plot the profile, the broadened profile of the line which depends on line strength, Doppler width and Gaussian profile. So, this is Gaussian profile of the Doppler broadening.
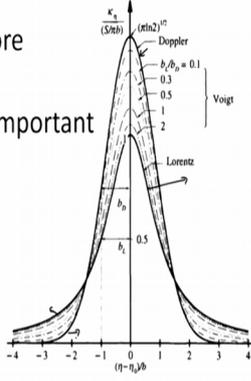
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Combined Effects

❖ At low pressure: Doppler broadening more important
❖ At high pressures: Collision broadening important

$$\kappa_\eta = \frac{Sb_L}{\pi^{3/2}} \int_{-\infty}^{+\infty} \frac{e^{-x^2} dx}{\left(\eta - \eta_0 - \frac{xb_D}{\sqrt{\ln 2}}\right)^2 + b_L^2}$$

$$x = v\sqrt{\frac{m}{2kT}}$$

Now, this picture basically explains everything. If we have a what we called Lorentz profile, this is the Lorentz profile. When we add both Lorentz and Doppler, what we get Doppler void profile. So, pure Doppler, this is pure Doppler. This is pure Lorentz. And if we have both

Doppler broadening and collision broadening taking place in our example or in our problem, we get a combination of Doppler broadening and collision broadening.

That is a combination of Doppler which is Gaussian. And combination of collision broadening which is Lorentzian. The combined profile can be represented with a mathematical function given by void. This is called void profile. And the void profile is given by this integral relation which is very difficult to evaluate. But it is available in books. So, one can use this to find out the profile.

So, the this profile is void profile and this profile is Doppler. And the combination between the 2 is Lorentzian, sorry void profile, which is a sum of Gaussian function and Lorentzian function. A combined function is called void function.

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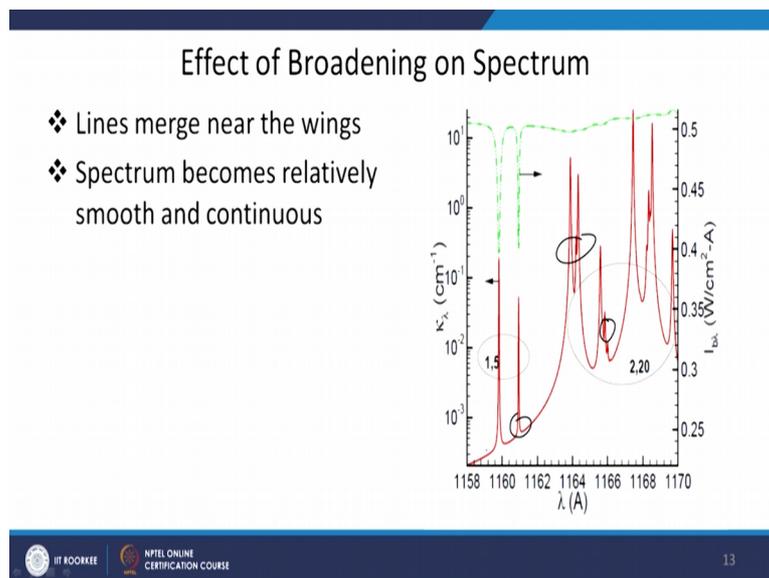
Now, what is the effect of this broadening on the spectrum? We discussed this. So, if we have no broadening, lines will be discreet at a single wavelength. But due to broadening, lines tends to merge, as we have seen here in this picture. This is a spectrum of atomic nitrogen that I showed you earlier also. I have taken a small part of that spectrum, only 10 to 12 angstrom wide.

And you see that lines, lot of lines have merged together due to broadening. So, they have merged into each other due to the effect of this Doppler and collision broadening. And the spectrum becomes relatively smooth. So, this is a smooth part of the spectrum between the

lines. Otherwise the lines are very erratic. And you see that, the calculation of absorption coefficient is very difficult for this type of lines.

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Finally, I will take 1 more problem where we will compare the broadening for different type of applications. So, discuss the importance of various broadening mechanism, that is collision broadening and Doppler broadening that we are mainly interested in, in various type of applications. So, the first example is a temperature of 300 kelvin. And we have pressure which is = 1 atmosphere.

Now, at 300 kelvin and pressure is 1 atmosphere, we expect that the pressure is reasonably high. We expect collision broadening will be important. Now, temperature is low. We know Doppler broadening basically takes place mainly it, mainly at high temperature. So, in this type of problem, we expect that the collision broadening will be important. So, the width, the collision width for this can be calculated as the collision width.

And these are rough calculations only. The collision width broadening is calculated as 0.1 centimeter inverse. This is in wavenumber. So, the collision width is in 0.1 centimeter inverse and the Doppler width for this problem is 0.04 centimeter inverse. Okay. So, we see that the Doppler width is less than the collision width. So, the collision broadening is important for this application. Although, the Doppler width, Doppler broadening is not negligible.

So, if you have an application where temperature is of the order of 300 kelvin and pressure is 1 atmosphere; so, this example is from atmospheric radiation. So, atmospheric solar radiation,

both Doppler broadening and collision broadening may be important. Albeit, collision broadening will be more important than Doppler broadening. The second example is, so this was the application where we have; now, we will take another example, temperature is 2700 kelvin and the pressure is 1 atmospheric pressure. Okay.

So, I will take a now 2 cases. Case 1 at wavelength of around 600 nanometer. So, this will be roughly 60 angstrom or 6000 angstrom. Now, this is possible with electronic transition. Now, for this particular case, the Doppler broadening b d comes out to be 0.1 centimeter inverse. Roughly, Doppler broadening comes out to be 0.1 centimeter inverse. And the collision broadening comes out to be 0.03 centimeter inverse.

So, what we see here is that, for this type of application, when we are talking about electronic transitions and the wavelength range is in visible or vacuum ultraviolet, the temperature is high. Both Doppler and collision broadening are important, but the Doppler broadening is more important than collision broadening. The b part is basically vibrational rotational spectrum. That means, in the wavelength region of 6 micron, which is 60,000 angstrom.

That is far infrared. In far infrared, we have Doppler broadening which is = 0.01 centimeter inverse, same temperature and pressure. Temperature is 2700 kelvin, pressure is 1 atmosphere, so Doppler broadening is 0.01 centimeter inverse and collision broadening for this case comes out to be 0.03 centimeter inverse. So, that means collision broadening does not change much or in this case, has not changed with the wavelength.

But, Doppler broadening has reduced. So, where we have now almost similar magnitude of the 2 broadening. Although, now in this case, collision broadening has a slightly less value than the Doppler broadening. And the final example that I will take is vibrational rotational transition at lambda is again 60,000 angstrom. That means, far infrared. Now, the temperature is 300 kelvin and pressure is 1 atmosphere.

So, that means atmospheric radiation but far infrared we are considering. So, Doppler broadening here is 0.004 centimeter inverse. And collision broadening is 0.1 centimeter inverse. So, here Doppler broadening not important. So, Doppler broadening is not important. So, what are the gases here? If you have this first application, the first application where again this is 6,000 angstrom.

The first application atmospheric radiation 6,000 angstrom is the application where we have basically ozone and some amount of absorption by H_2O. We may have to consider both Doppler broadening and collision broadening. But in this case, we have far infrared. So, some CO_2 is absorbing. So, we have only collision broadening. So, this is CO_2, which is mainly collision broadening.

So, we may neglect Doppler broadening in this particular example. So, this is basically the end of topic on this line radiation. So, we have found how to construct the spectrum of various atomic and molecular gases based on the theory of quantum mechanics of rotational and vibrational transition using Boltzmann distribution of molecular species or population and applying the broadening mechanism such as Doppler and void profile for collision broadening.

The lines becomes broad, the spectrum becomes complicated and the lines are spread out over a range of wavelength. Next, we will consider approximate methods to deal with this complicated spectrum.