Trace and ultra trace analysis of metals Using atomic absorption spectrometry

Dr. J R Mudakavi
Department of Chemical Engineering
Indian Institute of Science, Bangalore

Lecture – 11

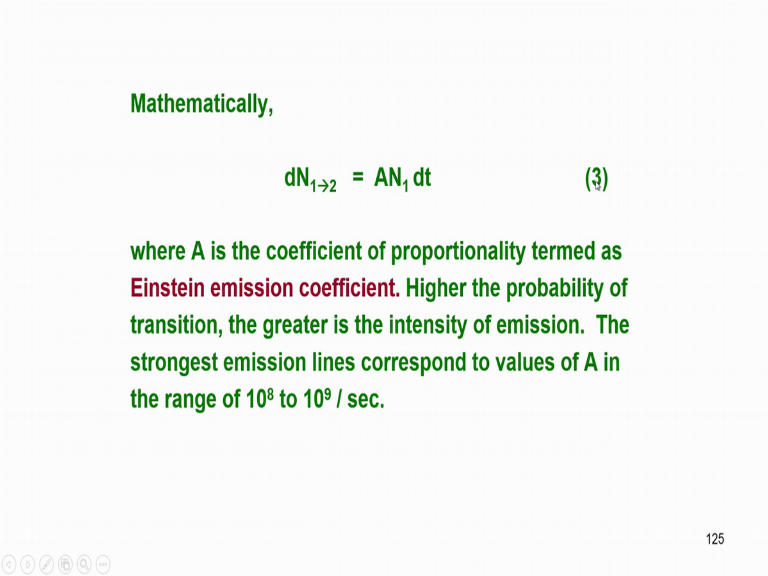
Theoretical basis of AAS II

Greetings to you, we are discussing the emission and absorption when and how they occur. We said that in the ground state most of the atoms are in the ground state at room temperature, only when we introduce the sample in a flame or something like that the temperature will rise and most of the electrons will get excited to higher energy state.

So, when they come down from the excited state to the ground state emission occurs, but when they go to higher energy level absorption of radiation occurs. So, we said for absorption to occur, the maximum number of atoms should be in the ground state; for emission to occur maximum number of atoms must be in the excited state. So, this we have try to quantify the electrons and the characteristic absorption wavelength can be calculated from the Gaussian diagrams, but what happens is every excitation line is not observed all the time, several wavelengths are never observed because of the quantum mechanical restrictions for forbidden transitions.

So, these rules have been developed empirically earlier and then subsequently confirmed by applying quantum mechanical principles to the concept of transition probabilities. So, what is a transition probability, it tells you what is the probability of getting an absorption atomic absorption or emission from the energy level difference what we have seen earlier. So, the probability of a spontaneous emission by transition between 2 energy levels; any 2 energy levels is defined as the number of fraction of atoms they drop to lower level that leading to emission. Similarly, number of electrons that go atoms that go to higher energy level is from fraction of number of atoms that raise to higher energy level.

(Refer Slide Time: 02:43)



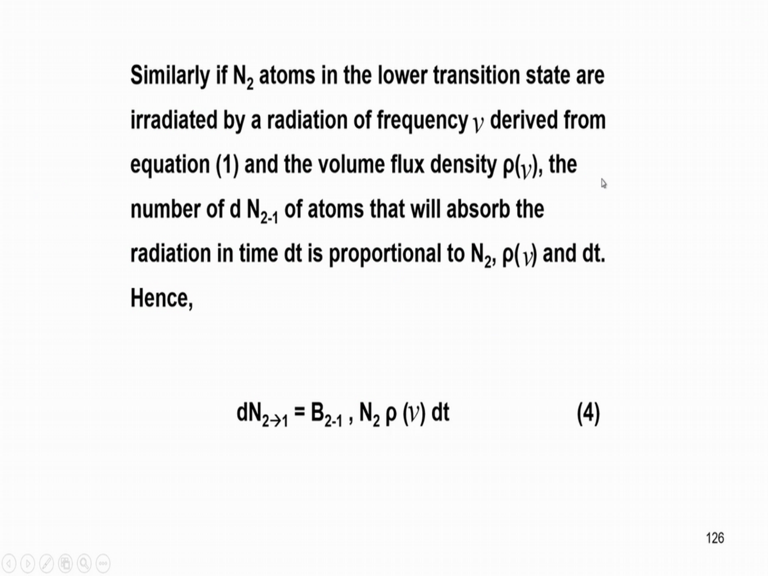
Mathematically,

$$dN_{1\to2} = AN_1\, dt \qquad (3)$$

where A is the coefficient of proportionality termed as **Einstein emission coefficient.** Higher the probability of transition, the greater is the intensity of emission. The strongest emission lines correspond to values of A in the range of 10^8 to 10^9 / sec.

So, mathematically we have decided to formula make a small formulation like this d N 1 is to 2 from one energy level to second energy level is proportional to the a consonantal proportional to the number of atoms and a proportionality constant that is known as Einstein emission coefficient.

(Refer Slide Time: 03:10)

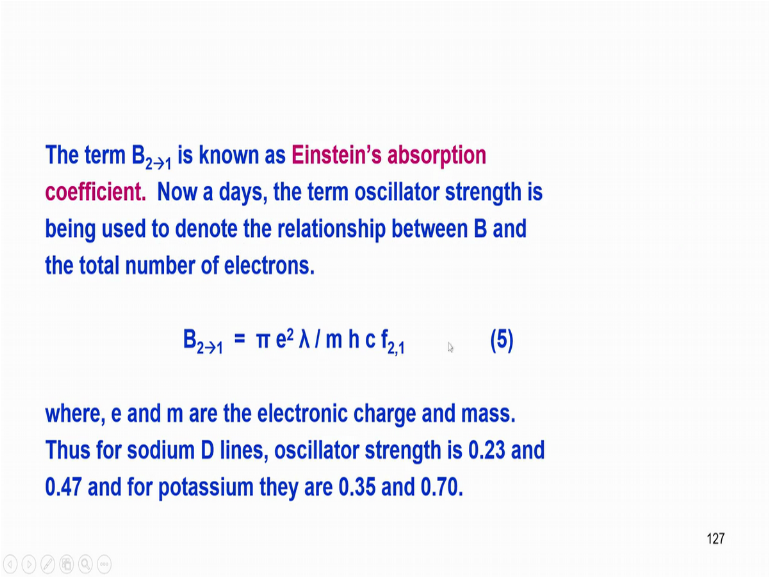


Similarly if N_2 atoms in the lower transition state are irradiated by a radiation of frequency ν derived from equation (1) and the volume flux density $\rho(\nu)$, the number of d $N_{2\text{-}1}$ of atoms that will absorb the radiation in time dt is proportional to N_2, $\rho(\nu)$ and dt. Hence,

$$dN_{2\to1} = B_{2\text{-}1}\, ,\, N_2\, \rho\, (\nu)\, dt \qquad (4)$$

Similarly, for emission we say that it is the total number of atoms that move from higher energy to lower energy level that is from 2 to 1 we define it by another constant proportionality constant B 2 1 and the total number of atoms and rho v. Rho v is the volume flux density that is the number of atoms in a given volume of the system.

(Refer Slide Time: 03:39)



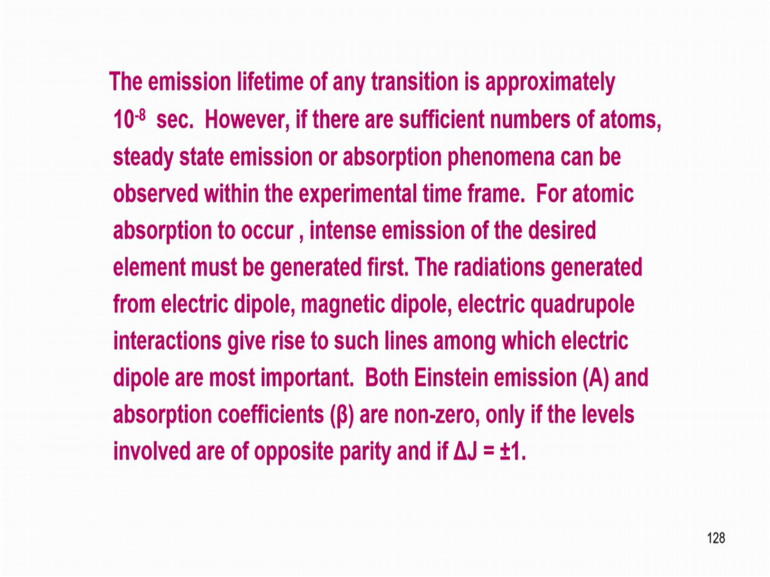
The term $B_{2\to1}$ is known as Einstein's absorption coefficient. Now a days, the term oscillator strength is being used to denote the relationship between B and the total number of electrons.

$$B_{2\to1} = \pi e^2 \lambda / m h c f_{2,1} \qquad (5)$$

where, e and m are the electronic charge and mass. Thus for sodium D lines, oscillator strength is 0.23 and 0.47 and for potassium they are 0.35 and 0.70.

So, the term B 2 to 1 is known as Einstein absorption coefficient. Nowadays, the term oscillator strength is being used have to denote the relationship between B in the number total number of atoms and the expression I have given you yesterday that is this number and the sodium electronic charge and mass. So, for sodium D lines, we can calculate the oscillator strength as 0.23 and 0.47 and for potassium it is like this.

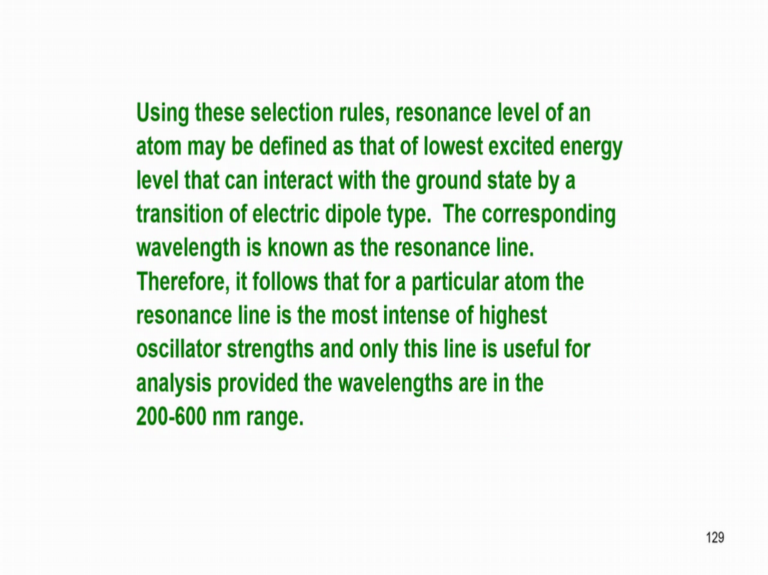
(Refer Slide Time: 04:10)



The emission lifetime of any transition is approximately 10^{-8} sec. However, if there are sufficient numbers of atoms, steady state emission or absorption phenomena can be observed within the experimental time frame. For atomic absorption to occur , intense emission of the desired element must be generated first. The radiations generated from electric dipole, magnetic dipole, electric quadrupole interactions give rise to such lines among which electric dipole are most important. Both Einstein emission (A) and absorption coefficients (β) are non-zero, only if the levels involved are of opposite parity and if $\Delta J = \pm 1$.

Now, the emission lifetime of any transition is approximately 10 raised to minus 8 seconds, but if there are sufficient number of atoms the steady state occurs and you will not see any excitation or emission because the number of excitations will be exactly equal to the number of emissions. So, the radiations generated from electrical dipole, magnetic dipole, electrical dipole interactions give raise to such lines among which electrical dipole are most important to get higher temperature. So, both Einstein emission and absorption coefficients are basically non-0 if the levels involved are of the opposite parity and delta J is equal to plus or minus 1, this is the theoretical background.

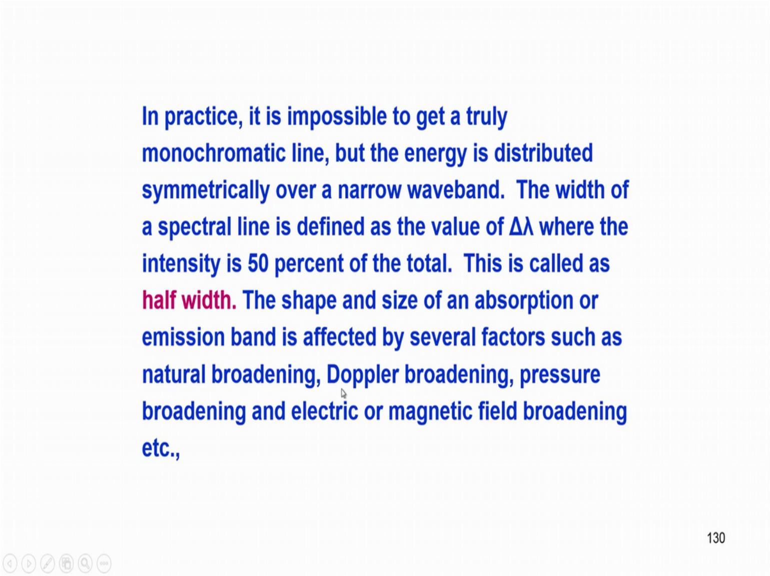
(Refer Slide Time: 05:00)



Using these selection rules, resonance level of an atom may be defined as that of lowest excited energy level that can interact with the ground state by a transition of electric dipole type. The corresponding wavelength is known as the resonance line. Therefore, it follows that for a particular atom the resonance line is the most intense of highest oscillator strengths and only this line is useful for analysis provided the wavelengths are in the 200-600 nm range.

And using the selection rules of quantum mechanics, what we can say is the resonance level of an atom we define it as that of the lowest excited energy level that can interact with the ground state by transition of an electrical dipole type. So, the corresponding wavelength is known as resonance line this is what we always look for in atomic absorption. Therefore, it follows that for a particular atom the resonance line is the most intense line of the highest oscillator strength and only this line is useful for analysis provided the wavelength ranges are in 200 to 600 nanometer range.

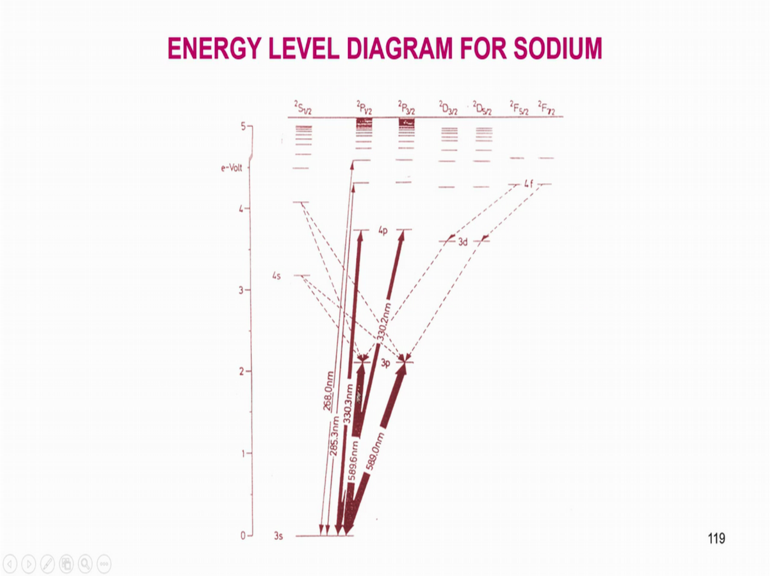
(Refer Slide Time: 05:46)



In practice, it is impossible to get a truly monochromatic line, but the energy is distributed symmetrically over a narrow waveband. The width of a spectral line is defined as the value of Δλ where the intensity is 50 percent of the total. This is called as **half width.** The shape and size of an absorption or emission band is affected by several factors such as natural broadening, Doppler broadening, pressure broadening and electric or magnetic field broadening etc.,

So, what does it mean the resonance lines in the Gaussian diagram are thicker?

(Refer Slide Time: 06:00)



ENERGY LEVEL DIAGRAM FOR SODIUM

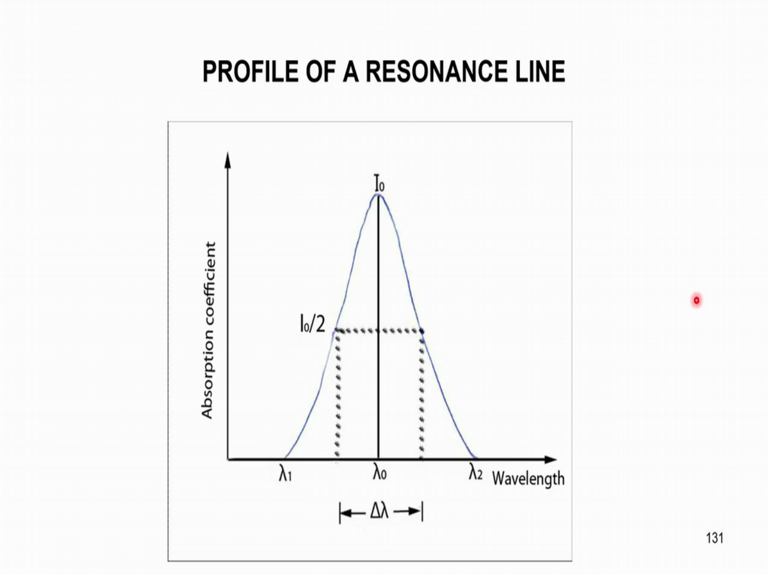
I want to show you this. See the resonance lines are much thicker than the other lines which are non-resonance lines. So, what is the reason that means, the lines are broader in for resonance lines. So, what is the reason for this broadening of the resonance line? So, actually a broadening of a resonance line decreases the purity of the spectrum. For example, if you plot wavelength versus intensity, the particular frequency should be a single line, but here you see the width particular width. And in practice what actually it means is it is impossible to get a truly monochromatic line in a spectrum that means, you cannot isolate a monochromatic line single wavelength frequency, single radiation of one wavelength or one frequency. But whenever you place a straight in front of a prism or a grating, what you do is you pick up a group of frequency where the desired frequency what you want to pull out is flanked by some frequencies on the left side and some frequencies on the longer side shorter side and longer side. So, you pull out a group of frequencies.

So, the width of a spectral line that then the problem comes that how do we define, so what we pull out from a spectrum using a mechanical slate is the group of frequency. And the width of these spectral line it is it appears as a spectral line having a broader width like this broad width instead of a single line. So, because it contains wavelengths corresponding to lower energy as well as higher energy, lower wavelength as well as higher wavelength, lower frequency as well as higher frequency. So, all are all essentially mean the same thing because they are all interlinked by e is equal to h c by lambda frequency wavelength and energy.

So, the width of a spectral what we are getting is a small width of the spectrum whenever you put a slit. So, that width of a spectral line is defined as the value of delta lambda that means any lambda which you want to extract plus or minus certain amount of radiation on the left on the shorter and longer wavelength that is delta lambda, where the intensity is 50 percent of the total. So, this is called as half width. The energy of the extracted wavelength group of wavelengths at 50 percent is known as half width. So, the shape and size of an absorption emission or emission band is affected by several factors, why does it occur by several it appears several factors are there such as natural broadening, Doppler broadening and pressure broadening, electrical or magnetic field broadening etcetera.

It is not just a mechanical operation, but also something related to the electron behavior in an excited state. So, even if you make the finest slit width you still you will end up with a group of frequency whenever you extract a wavelength. So, the reason for this is not only mechanical, but there is also certain amount of mechanical aspects of the radiation of the behavior of electrons in the excited state, so that is why this kind of broadening occurs you can never get away from that. That means, whenever you use any spectrophotometer or spectrometer or any other instrument which extracts an electromagnetic radiation, you are always burdened with a group of frequencies of shorter and longer wavelengths along with your desired wavelength.

(Refer Slide Time: 11:02)

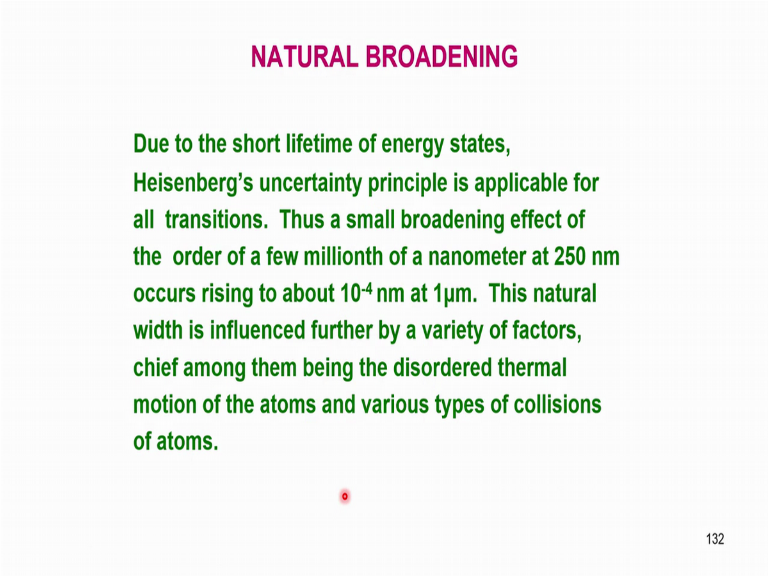


PROFILE OF A RESONANCE LINE

So, what we want to how it looks like is like this. Here I am plotting absorption coefficient, and here it is the delta lambda, here you can see it is lambda 0, this is what I want to extract from a given radiation source using prism or a grating or a filter etcetera. And then what I get is I also put a mechanical slit to pick up the wavelength. So, the combination of this is that I get lambda 0 of maximum intensity which is what I like and also I get lambda 1 of shorter wavelength and lambda 2 of higher wavelength. So, if I choose a smaller slit width, the shape of the curve will remain same, but lambda 1 will move towards the right a little bit, lambda 2 will move towards the left a little bit, so the curve will become sharper, but you will never get a single line. That you should understand very clearly that the group of wavelengths what we extract from a given radiation is always a bundle of energy.

Now, this bundle of energy is a resonance line corresponding to resonance line will become broader. And 50 percent of this height I 0 to; from on the x-axis from here to here I 0, 50 percent of that is I 0 by 2 and if I plot a, if I draw a straight line here and straight line here, this is known as half bandwidth half width. So, this half width is normally quoted in almost all technical literatures of atomic absorption spectrometer, this must be as narrow as possible for our requirement.

(Refer Slide Time: 13:15)



NATURAL BROADENING

Due to the short lifetime of energy states, Heisenberg's uncertainty principle is applicable for all transitions. Thus a small broadening effect of the order of a few millionth of a nanometer at 250 nm occurs rising to about 10^{-4} nm at 1μm. This natural width is influenced further by a variety of factors, chief among them being the disordered thermal motion of the atoms and various types of collisions of atoms.

Now, I said that apart from mechanical slit about which you can do nothing to reduce the broadening, but also you should see that there are other reasons for broadening, and I had explained to you that natural broadening, Doppler effect and several other kinds of electro other kinds of atomic absorption electron behavior at excited states causes broadening. So, due to the lifetime of; and now I am discussing about the natural broadening. So, what is natural broadening? The short lifetime of the energy state, because the moment the go electrons go up they come down to the lower level. So, the lifetime of an excited state is of the order of about 10 raised to minus 8 to 10 raised to minus 9 seconds that we have already covered. And due to the short lifetime Heisenberg's uncertainty principle is applicable for all transitions.

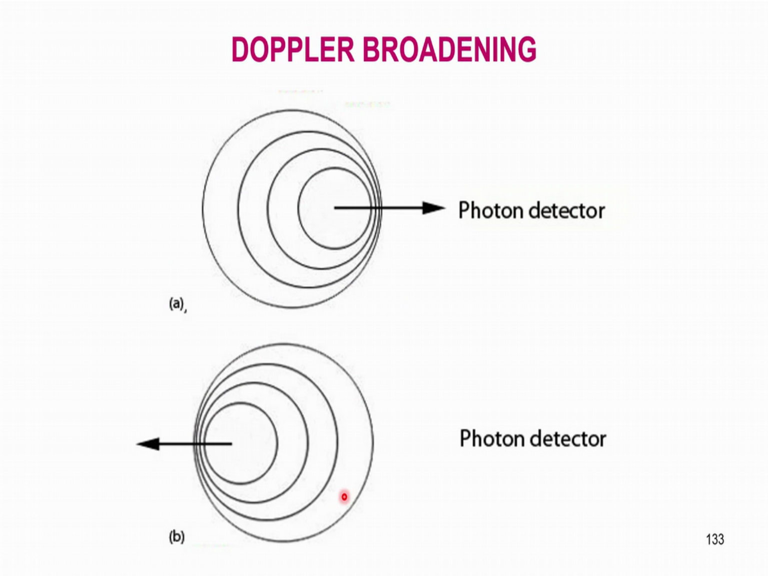
So, what is Heisenberg's uncertainty principle if you want to know the position, we cannot determine the momentum; and if you want to know the momentum, then you cannot determine the position of the atom, so or an electron for that matter.

So, a small broadening by the time you measure position it has moved so somewhere else. By the time you measure if you want to measure the speed, it would have moved a little bit by the position, it would have moved. So, the uncertainty is given by h by pi. So, the small broadening effect of the order of a few millionth of a nanometer, please remember we are talking of the wavelength of the selected radiation. And this natural broadening increases the width of the chosen wavelength by a few millionth of a nanometer. So, if you want to choose 250 nanometer wavelength, natural broadening makes it 250 plus or minus 0.00001, 251, 1 nanometer. So, sometimes it increases.

So, in maximum of a how much it can increase it can increase up to 10 raise to minus 4 that is 0.0001 nanometer at 1 micrometer though the micrometer range is in infrared, but for atomic absorption we are talking of the a u v and visible range. So, in the u v visible range, it is about a few millionth of a nanometer. This natural width is influenced further by a variety of factors; that means, some other factors tend to increase this width a few millionth of nanometer chief of among them are disordered thermal motions of the atoms and various types of collisions of atoms.

Now, what we are discussing right now is to make absorption and emission occurs, I have to and measure the energy resonance line, I have to choose that resonance line frequency from a given electromagnetic radiation. But you are not able to choose the radiation exactly. Now, there are reasons, mechanical reasons slit and this is the natural broadening. So, the natural broadening is again increased by disordered thermal we said it is a few millionth of a nanometer, now it is going to become bigger due to disordered thermal motion of the atoms and various types of collisions of the atoms.

(Refer Slide Time: 17:49)

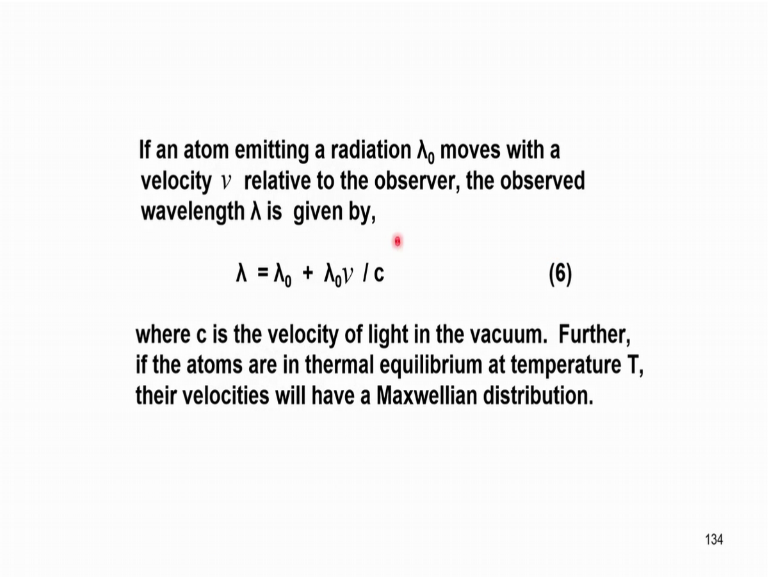


DOPPLER BROADENING

Now, this is the Doppler broadening effect. I think all of you are familiar with this kind of a figure in your physics class. What it means is if there is a disturbance or a sound especially a Doppler broadening is very well known towards in the sound, physics of the sounds. So, if there is a source and the sound is you are moving towards the source then the sound will appear sound is moving towards you, the sound will appear very strong. So, if the sound is moving away then the sound will be very short. For example, if you are on a railway platform when the train is very far, you will hear very less sound, but as the train comes nearer the intensity of the sound increases. So, it has something to do with the distance between the observer and they moving target. So, here the moving target is a train and you are the observer standing on the platform train is moving towards you, you hear. So, the sound is becoming bigger. So, if it is moving away from you the sound will appear weaker.

So, essentially same thing happens in the electromagnetic radiation. We have said if electromagnetic radiation is nothing but a series of photons being thrown towards in a particular direction. So, if I place a detector and then electron keeps on coming towards that there will be a effect similar to sound effect that is Doppler effect. So, as this comes nearer the energy of the electron keeps on increasing and as it goes away this is the Doppler effect. So, same thing happens with the electrons.

(Refer Slide Time: 20:03)



If an atom emitting a radiation λ_0 moves with a velocity v relative to the observer, the observed wavelength λ is given by,

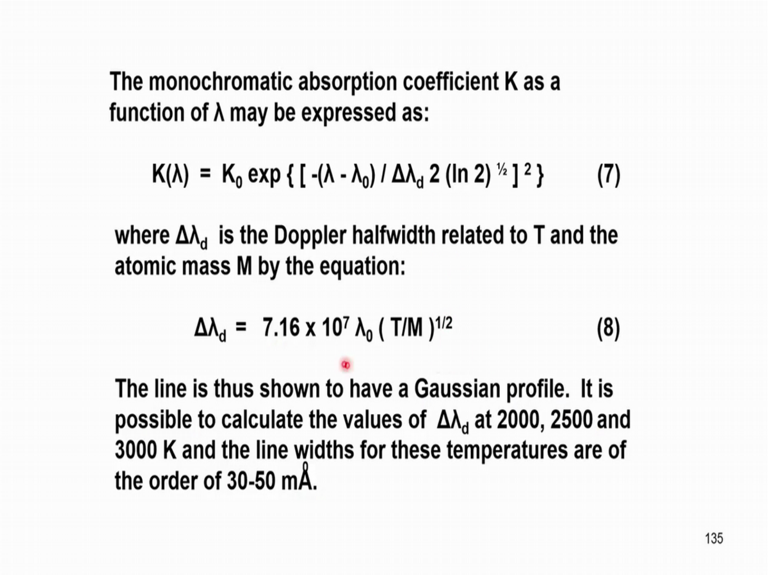
$$\lambda = \lambda_0 + \lambda_0 v / c \qquad (6)$$

where c is the velocity of light in the vacuum. Further, if the atoms are in thermal equilibrium at temperature T, their velocities will have a Maxwellian distribution.

So, if an atom emitting a radiation lambda 0, I am putting the same Doppler effect into an equation now. So, what happens if an atom emitting a radiation, lambda 0 moves with a velocity v relative to the observer, the observed wavelength lambda is given by lambda is equal to lambda 0 that is the actual wavelength plus you will also hear the get the radiation corresponding to wavelength from lambda 0 into mu divided by c. And c is the velocity of the light in the vacuum. Further, if the atoms are in thermal equilibrium at temperature T, their velocities will have a Maxwellian distribution.

Now, the Doppler effect I have already explained to you that the width of this spectral line keeps on increasing. And it is also due to natural broadening as well as Doppler broadening. Doppler broadening, we have given an equation now just now and you also have to assume that the electrons are not stationary, so that is the structure of the atoms and at higher temperature that means, they are moving in a particular space. When I increase the temperature electrons will still be moving but at a higher velocity. So, what we are saying is if the atoms are in thermal equilibrium at temperature at a room temperature, there is a particular velocity with which the electrons will be moving. So, if I increase the temperature to 100 degrees, 500 degrees, 1000 degrees, what happens the same electrons will be moving more and more a faster? So, their velocities will have if you plot velocity of the electrons versus temperature, you will get a curve - a Maxwellian curve.

(Refer Slide Time: 22:12)



The monochromatic absorption coefficient K as a function of λ may be expressed as:

$$K(\lambda) = K_0 \exp \{ [-(\lambda - \lambda_0) / \Delta\lambda_d \, 2 (\ln 2)^{½}]^2 \} \qquad (7)$$

where $\Delta\lambda_d$ is the Doppler halfwidth related to T and the atomic mass M by the equation:

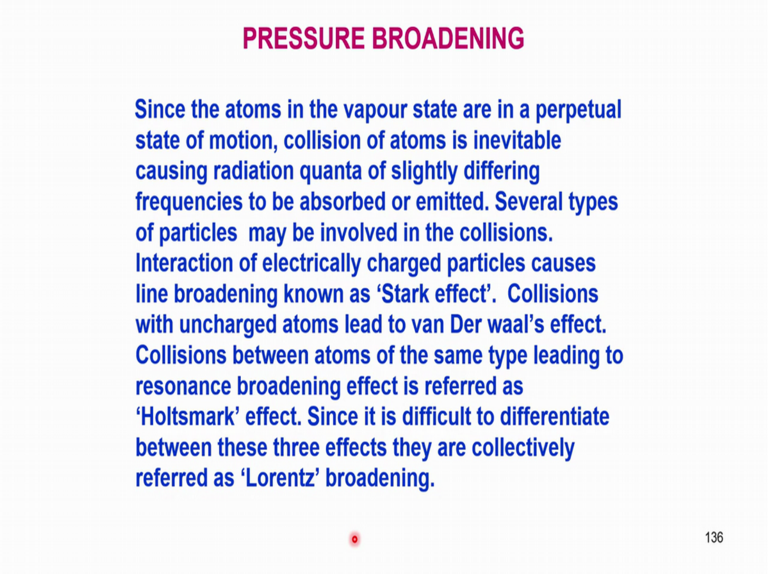
$$\Delta\lambda_d = 7.16 \times 10^7 \lambda_0 (T/M)^{1/2} \qquad (8)$$

The line is thus shown to have a Gaussian profile. It is possible to calculate the values of $\Delta\lambda_d$ at 2000, 2500 and 3000 K and the line widths for these temperatures are of the order of 30-50 mÅ.

So, Maxwellian curve is a something like this only like this; it increase starts increasing and then it falls down, so that is the Maxwellian distribution. And the monochromatic absorption coefficient absorb the absorption coefficient K is a as a function of the lambda may now we want to expand. How does it look it is K lambda is equal to K 0 into exponential of the actual observed lambda minus lambda 0 divided by distance difference between the 2 wavelengths that is lambda d multiplied by 2 log 2 raised to 1 by 2 whole square. So, this is the expression derived for the Maxwellian distribution of the electrons. And delta lambda d is the Doppler half width related to temperature because we are in we trying to include that also.

And the atomic mass for every element atomic mass will be different. And if I want to include the atomic mass and temperature then lambda d this lambda d will change if I put the value of temperature. So, that is 7.16 into 10 raised to 7 lambda 0 into temperature and then atomic mass raised to half. So, this line is thus shown to have a Gaussian profile that means, at extreme left the curve touches 0 and extreme right again it touches 0 in between it reaches a maximum. So, it is possible to calculate the delta lambda d values at different temperatures like 2000 Kelvin, 2500 Kelvin and 3000 Kelvin etcetera. And the line widths of these temperatures are of the order of 30 to 50 micro angstroms.

(Refer Slide Time: 24:29)



PRESSURE BROADENING

Since the atoms in the vapour state are in a perpetual state of motion, collision of atoms is inevitable causing radiation quanta of slightly differing frequencies to be absorbed or emitted. Several types of particles may be involved in the collisions. Interaction of electrically charged particles causes line broadening known as 'Stark effect'. Collisions with uncharged atoms lead to van Der waal's effect. Collisions between atoms of the same type leading to resonance broadening effect is referred as 'Holtsmark' effect. Since it is difficult to differentiate between these three effects they are collectively referred as 'Lorentz' broadening.

136

Now, that is with respect to the wavelength with respect to the movement of the atoms natural movement that is natural broadening then Doppler broadening we had discussed and then with respect to the temperature, again we have added a small correction. So, that also leads to the broadening of the resonance line. Now, there is another kind of broadening that is known as pressure broadening. So, what happens if there is a solid, you apply pressure nothing much happens. If there is a liquid you apply pressure nothing much happens, but if I substances in the gaseous form, and you apply pressure, there will be compression and the available space for the electrons to move around becomes less.

So, if there is a vacuum there will be more space pressure will becomes less and then electrons are free to move in a larger area relatively larger area. So, the atoms in the vapor state are in a perpetual state of motion that is sometimes if the atoms are in a state of perpetual motion, the collision of atoms occurs is it not. If the given a space lot of electrons are moving here and there, and atoms are also moving here and there, if they are in the vapor state then naturally they may collide with each other. So, the collision of atoms is inevitable. So, what happens, it causes the radiation quanta of these slightly different frequencies to be absorbed or emitted because we have said the radiation is always a group of radiation corresponding to lower and higher energy. Now, atoms are colliding with each other in a vapor state. So, in the vapor state the absorption of energy is also associated with the additional frequencies that we are choosing the radiation. So, several types of particles may be involved in the collisions, this is important now.

Now, why there are several types of particles? Now, you can imagine interaction of electrically charged particles causes line broadening known as Stark effect. Now, you can imagine when an electron is in the when an atom is in the vapor state lot of atoms are there, and then neutrons are there, protons are there and then electrons are there. So, the interaction of electrically charged a electrons atoms is a particles, it causes line broadening. Now, I am going to say charged particles are one class there is they make the line broadening more that is known as Stark effect.

Now, are there only charged atoms in the excited state, answer is no, there are uncharged atoms also. So, collisions with uncharged atoms here in the slide collisions with uncharged atoms lead to van Der Waal’s effect why because many of the atoms uncharged they still collide with each other and then that is that leads to van Der Waal’s effect and that also again leads to some sort of broadening of the radiation. So, collisions of between atoms of the same type leading to a resonance effect, this is known as Holtsmark effect.

Now, what I am going to say one is charged particles like electrons are there. So, electrons interaction leads to broadening effect. And then uncharged atoms there are charged atoms and uncharged atoms. Uncharged atoms also collide with each other leading to van Der Waal’s effect that also causes broadening of the resonance line. Now, there may be some other elements in the vapor state. For example, if you take sodium chloride and heat it into vapor state; in the vapor state, you will not just have sodium ions, you will also have chloride ions. And if you take sodium chloride in water or sodium chloride itself may contain some amount of water of crystallization, so there will be water molecules and then there is atmosphere. So, hydrogen molecules may be there, oxygen molecules also may be there, so hydrogen atoms, oxygen atoms. Similarly there may be number of other elements present in a given sample apart from yours sample which you want to analyze by atomic absorption spectrometry.

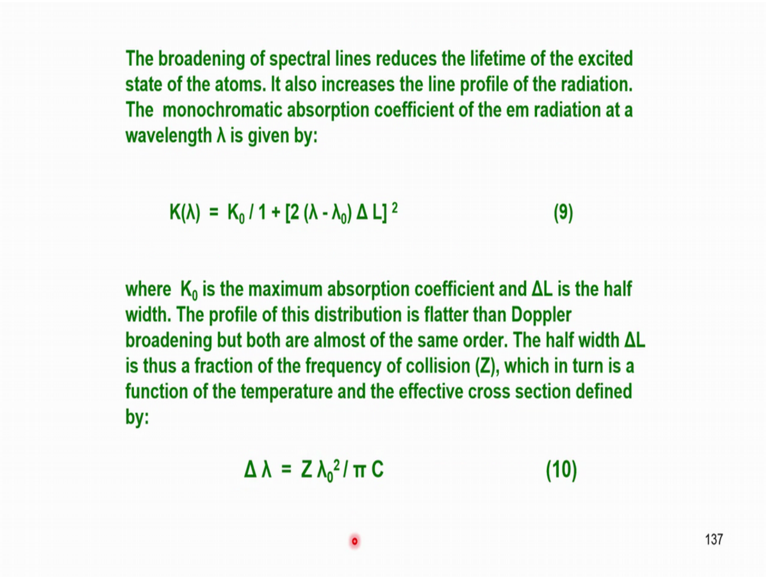
So, the collisions between sodium and sodium atoms leads to one type of transition; collisions between chlorine and chlorine leads to another type of the line broadening. So, atoms of the same type that is sodium and sodium atoms colliding with each other that is known as Holtsmark effect; chloride and chloride again Holtsmark effect. So, what happens in a given system in containing a vapor state of the atoms in the excited state not even excite ground state. Electrons and atoms can be in the ground state even in the vapor state also that you should remember. The you should not imagine that the moment we have something in the vapor state it is all excited state - no, the electrons and atoms will be in the ground state even at higher temperature in the vapor state also.

So, in the vapor state the electrons interaction between electrons and electrons, protons and protons and then and the uncharged atoms, and then atoms of the same kind and atoms of the different kind, all these things will be happening whenever you try to raise the temperature of a given system. Since, it is difficult to differentiate all these things happening so fast simultaneously it is you cannot really pinpoint. So, this is due to uncharged particles, this much of broadening is due to just like what we did for a resonance effect that is a Doppler effect. We cannot say this the amount of broadening occurs due to Stark effect, this of a amount of broadening occurs to uncharged atoms of the this amount of term broadening occurs due to collisions of the same atoms like that it is very difficult to say. So, all in all we refer to it as Holtsmark effect.

So, the Holtsmark effect is the combined effect of broadening due to and charged particles, uncharged particles as well as collisions due to the same kind of atoms uncharged particles and the Holtsmark effect it is due to charge atoms of the same type. So, altogether that is known as Lorentz broadening, Holtsmark effect, Stark effect and all other effects are combined to give you, so Lorentz broadening that we can define Lorentz broadening is so much for a given system at a given temperature. So, you understand now, a natural selection of an natural frequency of an element is does not occur for monochromatic radiation because the monochromatic radiation cannot be chosen. So, you pick up a group of frequencies, the group of frequencies are changing due to the apart from mechanical, it also changes due to natural effects, natural broadening, Doppler effect and then pressure broadening which includes Holtsmark effect, Stark effect and other collisions and this leads to Lorentz broadening. So, there are 3 kinds.

One is natural broadening, one is Doppler effect, another is Lorentz broadening, these 3 broadening systems make a resonance line thicker bigger. The effect of a resonance line bigger means the detection limits, the purity of the spectrum is very less, it becomes less.

(Refer Slide Time: 34:46)



The broadening of spectral lines reduces the lifetime of the excited state of the atoms. It also increases the line profile of the radiation. The monochromatic absorption coefficient of the em radiation at a wavelength λ is given by:

$$K(\lambda) = K_0 / 1 + [2 (\lambda - \lambda_0) \Delta L]^2 \qquad (9)$$

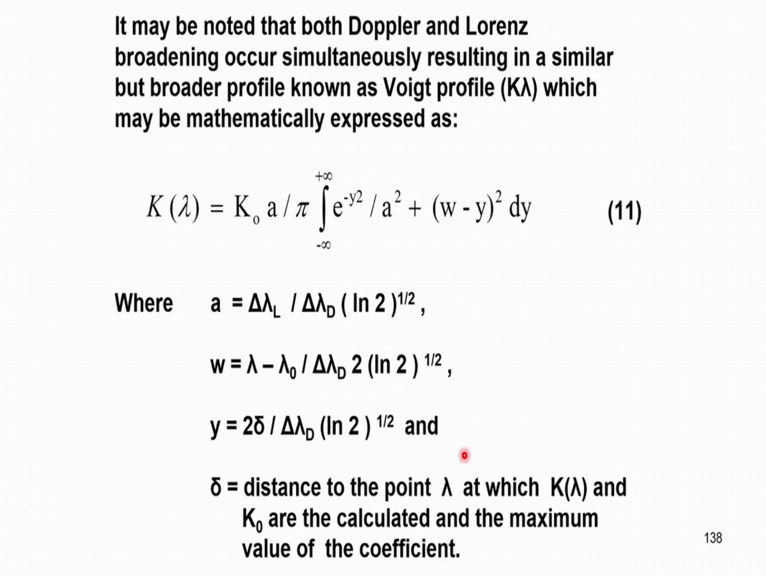
where K_0 is the maximum absorption coefficient and ΔL is the half width. The profile of this distribution is flatter than Doppler broadening but both are almost of the same order. The half width ΔL is thus a fraction of the frequency of collision (Z), which in turn is a function of the temperature and the effective cross section defined by:

$$\Delta \lambda = Z \lambda_0^2 / \pi C \qquad (10)$$

So, the broadening of spectral lines reduces the lifetime of the excited state of atoms that means, you will not get the same amount of intensity for a particular temperature as expected, there will be shorter, it will be less. So, it also increases the line profile of the radiation. And the monochromatic radiation a absorption coefficient of the electromagnetic radiation at a given wavelength lambda, we write it like this K 0 divided by 1 plus 2 lambda minus lambda 0 into delta L whole square. So, here K 0 is the maximum absorption coefficient delta L is the half width. And profile of this distribution is slightly flatter than Doppler broadening, but both have almost of the same order.

The half width delta L is thus a fraction of the frequency of collision, which in turn is a function of the temperature and the effective cross section that is defined by delta lambda is equal to atomic number Z lambda 0 whole square pi and C. All these things are combined into giving you this delta lambda that means; theoretically also you can calculate; what is the half width of a given wavelength for a given system?

(Refer Slide Time: 36:28)



It may be noted that both Doppler and Lorenz broadening occur simultaneously resulting in a similar but broader profile known as Voigt profile (Kλ) which may be mathematically expressed as:

$$K(\lambda) = K_0\, a / \pi \int_{-\infty}^{+\infty} e^{-y^2} / a^2 + (w - y)^2\, dy \qquad \textbf{(11)}$$

Where $a = \Delta\lambda_L / \Delta\lambda_D (\ln 2)^{1/2}$,

$w = \lambda - \lambda_0 / \Delta\lambda_D\, 2 (\ln 2)^{1/2}$,

$y = 2\delta / \Delta\lambda_D (\ln 2)^{1/2}$ **and**

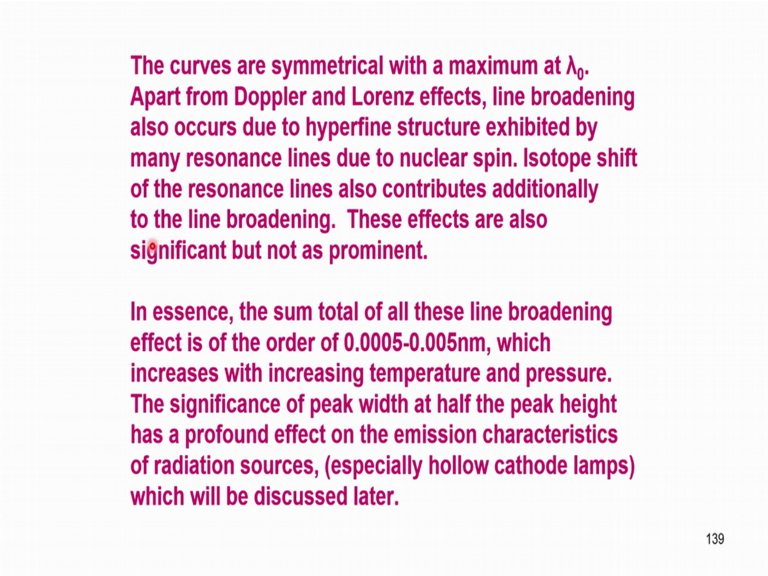
δ = distance to the point λ at which $K(\lambda)$ and K_0 are the calculated and the maximum value of the coefficient.

So, it may be noted that both Doppler and Lorentz broadening occur simultaneously that is the catch. Again it is very difficult to separate Doppler broadening and Lorentz broadening this is due to so much this is so much like that. What you actually see in practical effect is just a simple broadening, but the reasons are many. So, it is again Doppler and Lorentz broadening occur simultaneously resulting in a similar, but broader profile and this profile is known as Voigt profile K lambda that is expressed as a number of as an equation K lambda that is K 0 is the proportionality constant. a is the area cross section and etcetera and that is given by this expression a delta lambda L divided by delta lambda D ln 2 raised to half. You know the other constants pi you know, e you know, a you know, w, y etcetera that we are we going to define now.

And it is the integrated expression that is the sum total of all other broadening the Voigt profile and a is that and w is the lambda minus lambda 0, this w divided by delta lambda D 2 ln 2 raise to half and y is equal to 2 delta and then divided by delta lambda. This you can see that these are mostly common delta lambda ln 2 raised to half. And this delta is nothing but it is the distance to the point lambda at which K lambda and K 0 are calculated and the maximum value of the coefficient.

So, what we are trying to say in this slide is the summation of all our discussion of natural broadening pressure broadening comprising of weight effect comprising of Stark effect, Holtsmark effect and then other natural broadening of the same due to collisions of the same kind and then which is known as Lorentz broadening. And both of the Doppler and Lorentz broadening is known as Voigt profile and Voigt profile is this much that means the broadening of the spectral line can be quantified for a given wavelength lambda in the vapor state.

(Refer Slide Time: 39:14)



The curves are symmetrical with a maximum at λ_0. Apart from Doppler and Lorenz effects, line broadening also occurs due to hyperfine structure exhibited by many resonance lines due to nuclear spin. Isotope shift of the resonance lines also contributes additionally to the line broadening. These effects are also significant but not as prominent.

In essence, the sum total of all these line broadening effect is of the order of 0.0005-0.005nm, which increases with increasing temperature and pressure. The significance of peak width at half the peak height has a profound effect on the emission characteristics of radiation sources, (especially hollow cathode lamps) which will be discussed later.

So, these curves are symmetrical with a maximum at lambda 0 that means, again we go back to this figure in here the broadening occurs and the effect will be similar in all these effects Voigt’s broadening, Lorentz broadening, Doppler effect etcetera. So, we go back. The curves are symmetrical that means, at lambda 0 on shorter wavelength as well as longer wavelength the curves are symmetrical. So, apart from Doppler and Lorentz broadening I also should tell you that there is hyperfine structure in a given spectrum. So, the hyperfine structure is exhibited by several resonance lines due to nuclear spin. So, far we have discussed only about the electronic spin, now why not nuclear structure. So, the hyperfine structure is nothing but line broadening due to several resonance lines due to nucleus spin also. So, a nucleus also keeps on spinning and there may be a certain amount of splitting of the lines that is known as hyperfine splitting of the spectral lines.

So, if you do are not operating in that hyperfine splitting range, what you will see is a bigger resonance line a thick resonance line you will see that means, the frequency of the radiation chosen for measurement in atomic absorption is nothing but a big combination of left and wavelength corresponding to shorter and longer wavelengths. That is all we are discussing in the whole class today. So, isotope shift of the resonance lines also contributes additionally sometimes what happens is the there are several isotopes of the same element, so resonance lines also shifted because of that and these effects are also significant, but not very prominent because most of the time the atomic number is same.