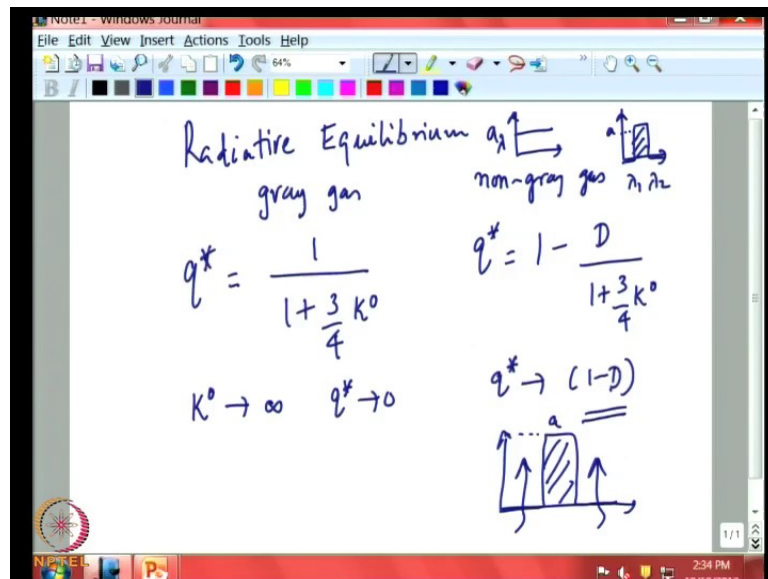**Radiation Heat Transfer**
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Indian Institute of Science, Bangalore

Lecture - 19
Radiation spectroscopy

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In the last lecture, we looked at two solutions to gas in radiative equilibrium. And one was for a gray gas, and the other for non-gray. This non-gray gas was a very simple model in which gas absorbed in a certain wavelength. The gray gas we think about is where the a lambda is a constant. And in a non-gray gas we looked at a lambda at a very simple structure.

In the range from lambda 1 to lambda 2, it was constant value. And outside that, it was not absorbed. It is a very simple model for non-gray gas, and the results we got for flux was, the flux was non-dimensional and was equal to 1 by 1 plus three-fourth the total of that thickness; while in the non-gray gas case, 1 minus D by 1 plus three-fourth kappa 0. These two solutions look similar, but they have fundamental difference. And the difference comes in the limit as kappa 0 becomes very large, in the optically thick limit. In the gray gas case q star tends to 0, here q star tends to 1 minus D. This is a very important result which is worth remembering that in a gray gas as you go to thicker limit, the resistance of the heat transfer is very large. Hence heat flux goes to 0. In a non-gray

gas, there are always regions in the spectrum where the gas is completely transparent. Hence the radiation just goes through it, whatever the thickness of the gas. The 1 minus D is the fraction of the black body radiation lying outside this absorbing region. And so essentially the gas is absorbing only in a narrow region, and so in the transparent region, radiation is always transmitted through the gas. Whatever the value of a, whatever the absorption coefficient of the gas as long as non-gray, there are regions called, these are called windows; where the gas is transparent.

Hence q star can never go to 0; heat flux can never go to 0. In a gray gas it goes to 0. Since, all the real world situations that we encounter are non-gray, we must recognize this important difference between gray and non-gray behavior. This clearly tells us that the gray gas approximation, although very useful to teach certain basic methods and techniques will not be resolved to really deal with a real problem; because the results it will give especially in the thick limit, are not realistic.

We must understand the non-gray behavior of these gasses. Now we go back to basic Physics and try to understand why do gasses behave as non-gray medium with a large variation of the absorption coefficient at different wavelengths. And once we explain this complex behavior, then we will see how to deal with this complex variation of absorption coefficient with wavelength, when we deal with the real life problem. In the final analysis, must remember that as far as the teaching of the subject is concerned, there is not much we can do in the lectures in the class in dealing with complex behavior of real gasses.

Further ultimately, today courses are made to powerful software which incorporates all the complex behavior. Ultimately most results are obtained by running the software. But the purpose of a course like this is to teach you to understand how radiation behaves in the real world. We have to deal with approximation. But at the same time we must recognize the limitation of the approximation. We did with gray gas knowing fully well; it is not a good approximation for real gases. One example we saw just now that in the thick limit, a gray gas will say the flux will go to 0, but in a non-gray gas the flux can be quite large because radiation moves freely through most of the spectrum by the gas is not absorbing at all.

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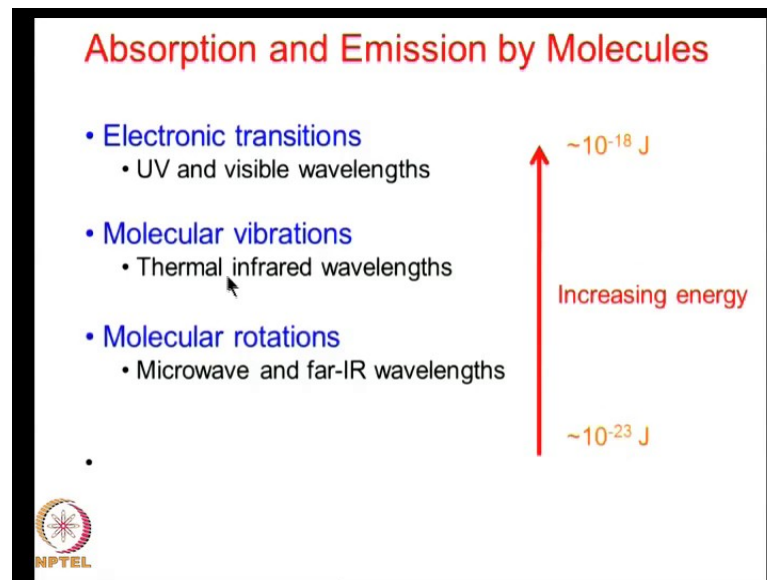
Now let us go next to understand the radiative properties of real gases. Now, all of you know that molecules absorb and emit photons. The absorption of a photon may result in the change in the state of the vibration of the molecules. Molecules vibrate about their center. When a photon is absorbed the molecule may vibrate more rapidly or it may rotate faster or it may undergo an electronic transition.

Electronic transition, where electrons move from one state to another state or the absorption of photon may lead to molecule vibrating more vigorously or it might rotate more vigorously. We can see that as you move from rotation to electronic transition, the energy required is more and more. This requires very little energy; this requires a lot of energy. Hence, only the photons in the microwave and far infrared can really be absorbed and create changes in the rotational state. The photons are little more energetic are in the infrared region; nearer or far infrared. Then it can induce changes in the vibration of the molecule. Finally, if the photons are in visible ultra violet, they can really induce an electron to go from a lower state to an upper state.
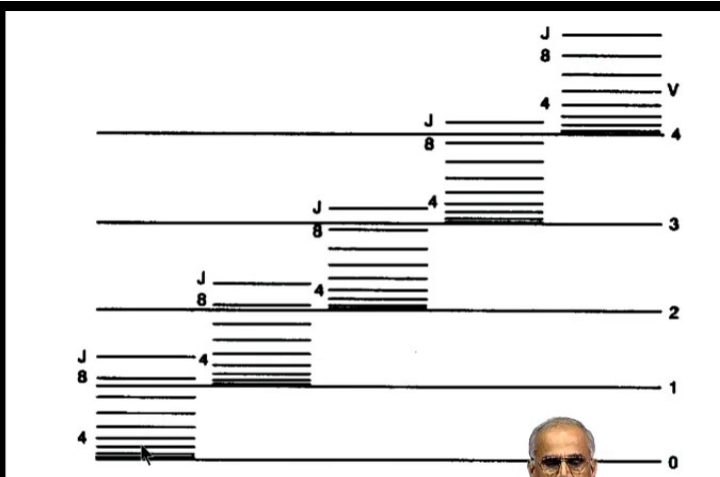
Absorption or emission of photons by molecules cause changes in rotational ,vibrational , or electronic energy of the molecule

•Changes in electronic state result in photons being emitted in the visible or ultraviolet region
•Changes in vibrational state result in photons being emitted in the near to far-infrared regions
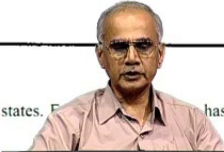•Changes in rotational state result in photons being emitted in the far-infrared to microwave regions

The same thing now is stated clearly. Changes in electronic state result in photons being emitted in the visible or ultraviolet region; while changes in vibrational state cause photons to be emitted in the near to far infrared; while changes in rotation result photons being emitted in the infrared to microwave. As soon as we see a photon in a certain wavelength range, we must be able to guess which transition in the molecule cause this photon to be emitted. So, just by looking at the wavelength of the photon we can make a judgment about, in which part of the molecule the transition occurred; in the electronic part or the vibration part or rotation part.

ch vibrational state has an associated set of rotational states. has roughly e same set of rotational energies. [Kyle Fig. 8.5]

Now here is the pictorial depiction of the different vibrational states of the molecule; 0, 1, 2, 3, 4. This may be called the ground state 0. State 1, where the molecules are vibrating more rapidly and so on. Since the amount of energy to induce a transient vibration is large compared to the energy required to induce a rotational change, so a vibrational state transition will inevitably be accounted by a small change in rotation. Because this is small value; this is a large value.

The analogy can be given to; when you are purchasing something, you have an amount in rupees and you have a small change. When a photon comes and is absorbed by a molecule and it has energy slightly more than what is required to take the photon from this state to this state, what it will do is the additional energy will be used to shift the photon not only from V equal 0 to V equal to 1, also from let us say J equals 0 to J equals 1 here. So, a small change in rotation is also induced, so that the complete photon energy is fully utilized.

 A change in vibration is normally also associated with some change in rotational state. The total change in energy h nu is the combination of change in vibration, change in rotation. But the rotational change, as we can see is one-tenth or one-twentieth of the vibrational change.

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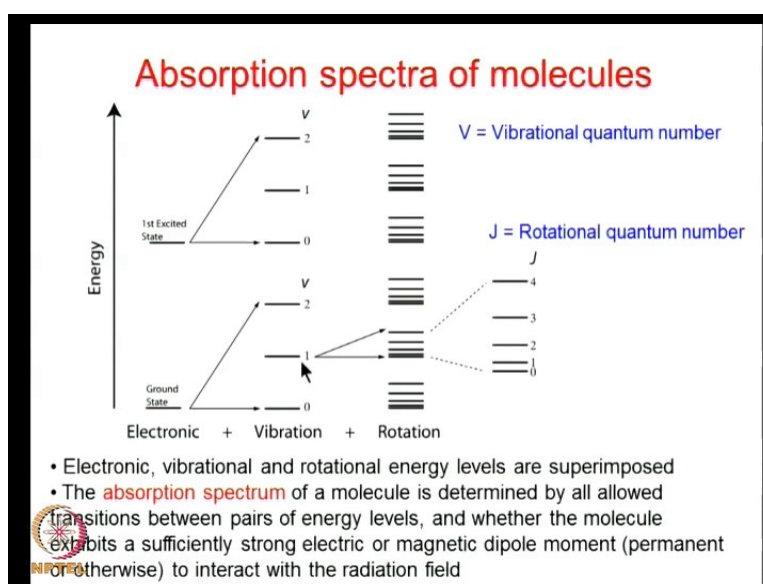
This is shown more pictorially here. This is the ground state, and the molecules can move from the ground state 0 to ground state 1 here or ground state 2 here. This is the

first excited state and these are the electronic transition, these are the vibration transition, this is rotational transition.

Now, let us look at the vibrational-rotational transition. We can have a change of one in vibration, accompanied by also a change in rotation. The molecule can move from V equals 0 to V equal to 1 and J equals 0 to J equals 1 or 2, and thereby absorbing the full energy of the photon.

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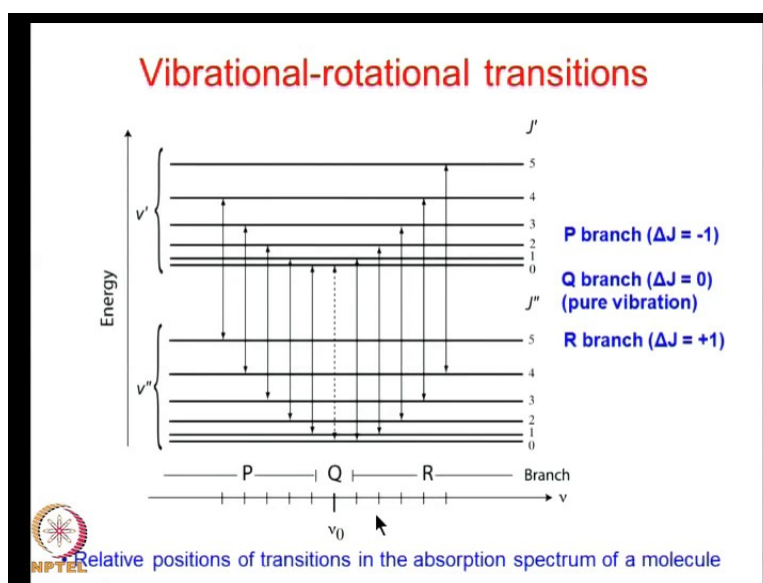
We can also have a situation where the molecules move from the ground state of vibration to the first excited state. But in the case of rotation it moves from the upper state to the lower state. This will mean that the photon that is required to do transition will have slightly less frequency or less energy. These are shown in this picture as a vibrational-rotational spectra of the gas. The Q branch is called the pure vibrational branch; where delta J is 0; no rotational transition, only pure vibration.

Sometimes this does not occur; it is called forbidden transition. To the right and left are transitions in which there is both vibration and rotation. On this side is R branch, whose frequency is higher; which means in addition to the basic vibrational transition, the rotational quantum number also increases. We require more energy. The photons have frequency above nu 0. On the other hand, if the rotational change is negative, that is, the molecules goes from a higher rotational state to lower rotational state, then the frequency

required is little less, and so all these are various transitions possible around a vibrational transition. So, each one of these will be a line of a different frequency.

All of this can occur at the same time because you may absorb photon with this frequency here, to have this transition. The next photon may have slightly higher frequency. It will be shown as transition here. The spectrum you see of vibrational-rotational band of a molecule will show many lines. We will show many examples of that in this lecture.

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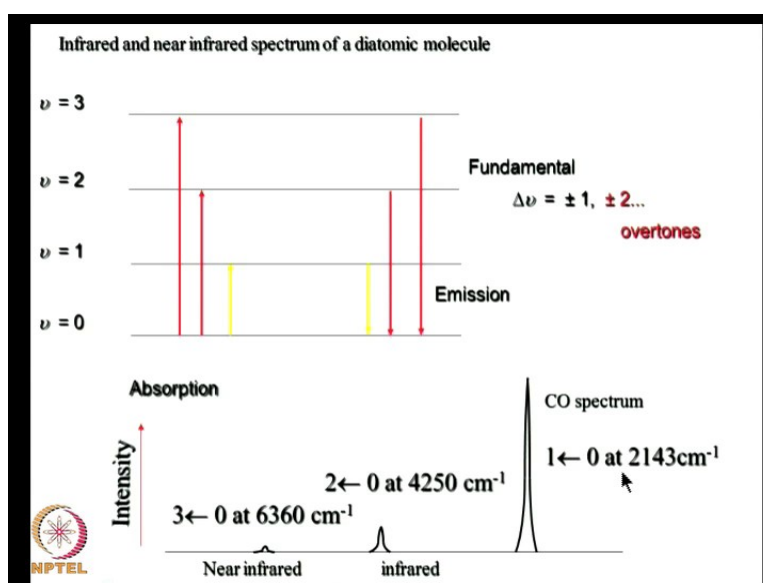
Now, in addition to undergoing a vibrational transition of change unity, it can also jump to two states. They are rare, as you probably know from your basic Physics that the most common transition is one in which the vibration quantum number changes by 1. But occasionally, at high temperatures can also change by 2 or by 3. These are called overtones. They are rare, except for high temperatures.

We can see that, the frequencies will go on increasing and the wave number will decrease. This is the 0 to 1 transition here; it is 0 to 2 will be approximately double the wave number, higher frequency. The ground state to three will be approximately three times this. Our focus should be only on the transition 0 to 1 because that is the most common transition that we observe.

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Vibrational-Rotational Transitions

Vibrational transitions include rotational transitions, giving a band of many absorption lines.

For a linear molecule: P branch ($\Delta J = -1$) is lines below band center (vibrational energy only), Q branch ($\Delta J = 0$) is near band center, R branch ($\Delta J = +1$) is above center.

Compare rotational and vibrational transitions with thermal energy:
Thermal ($k_B T$): $\nu = k_B T/hc = 250\,K/1.44\,K\,cm = 175\,cm^{-1}$
Vibrational transitions: $\sim 600 < \nu < 10000\,cm^{-1}$
Rotational transitions: $\sim 1 < \nu < 500\,cm^{-1}$
Molecules in lowest vibrational state, but many rotational states occupied.

We summarize the fact that the wave numbers of the rotational transitions is in the range of frequency a wave number from 1 to 500 centimeter minus 1; while vibrational transition are typically in the range 600 to 10000 centimeter minus 1. These are much larger than the basic thermal energy of the molecule.

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Rotational Transitions

Rigid rotator model for linear molecules.   Rotational energy for molecule with moment of inertia I is $E = L^2/2I$. Moment of inertia is $I = \sum_i m_i r_i^2$. Angular momentum L is *quantized*, so

$$E_J = \frac{J(J+1)(h/2\pi)^2}{2I}$$

where J is integer rotational quantum number.
Quantum mechanical selection rule (photon has angular momentum $h/2\pi$):

$$\Delta J = \pm 1$$

Therefore the wavenumber of a rotational transition is

$$\nu = \frac{1}{hc}(E_{J+1} - E_J) = 2B(J+1) \quad B = \frac{h}{8\pi^2 cI}$$

B is called the rotational constant (units: cm^{-1})

Now, how are these changes in it calculated. In the case of rotating transition, you have to know the moment of inertia of the molecule. Once we know that, based on the mass and the radius of the various atoms in the molecule, we can calculate the energy in terms

of the moment of inertia and the rotational quantum number. The change in energy due to a change in middle quantum number of 1 will be 2 B into J plus 1. That B is known as the rotational constant; depends on the moment of inertia of the molecule.

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Vibrational Transitions

Three vibrational modes of molecules:

ν_1 symmetric stretch (2.7 μm H_2O)
ν_2 bending mode (15.0 μm CO_2, 6.3 μm H_2O)
ν_3 asymmetric stretch (4.3 μm CO_2, 2.7 μm H_2O)

Vibrating molecule is like quantum mechanical harmonic oscillator:

$$E_n = h\nu = (n + 1/2)\frac{h}{2\pi}\sqrt{\frac{k_{bond}}{m_r}}$$

k_{bond} = spring constant of bond, m_r = reduced mass,
n = vibrational quantum number.
Most infrared absorption bands from the fundamental transition: $n = 0 \rightarrow 1$.
Hot bands are from lower state $n > 0$.
Isotopic bands are from nonstandard isotopes in molecule.
Combination bands are from multiple vibrational mode changes

Similarly, for vibrational transition you treat the molecule as a simple harmonic oscillator with two masses m 1, m 2. We can calculate the vibrational frequency as root K by m, the standard simple harmonic motion. This n plus half comes from quantum mechanical requirements. Here, n or J is the vibration quantum number. Now, one example here is given that of water vapor, carbon dioxide and they undergo different kinds of vibration. It can be stretching of the molecule or bending of the molecule. And we will give examples of this little later.

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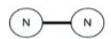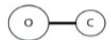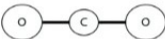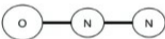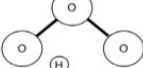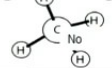

Absorption frequency for a diatomic molecule
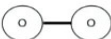
$$v = \frac{1}{2\pi c} \sqrt{\frac{k(m_1 + m_2)A_v}{m_1 m_2}}$$

m_1, m_2 = atomic mass of vibrating atoms
c = speed of light [3×10^8 m s^{-1}]
V = wavenumber [cm^{-1}]
A_v = Avogadro's number [6.023×10^{23} atoms mole^{-1}]
k = force constant (bond strength) [dynes cm^{-1}]

This is the equation, if molecule with two different masses forms a diatomic molecule. Then the effective mass will be m 1 m 2 by m 1 plus m 2. From this we can calculate the vibrational frequency.

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| Molecule	Structure		Permanent Electric Dipole Moment?
Oxygen	O—O	linear	No (magnetic dipole)
Nitrogen	N—N	linear	No
Carbon Monoxide	O—C	linear	Yes
Carbon Dioxide	O—C—O	linear	No
Nitrous Oxide	O—N—N	linear	Yes
Water		asymmetric top	Yes
Ozone		asymmetric top	Yes
Methane		spherical top	Yes

Here are typical examples of molecules that you encounter in the gasses. The main one is, oxygen and nitrogen. Then we have carbon monoxide, carbon dioxide and nitrous oxide. Notice that, all these are liner molecules. It is a line in a linear way. These two are symmetric. They do not have permanent dipole moment. Hence, they cannot interact

with the electric field. We will not find any strong absorption bands of oxygen or nitrogen because being linear symmetric molecules, they do not have permanent dipole moment.

They do not interact with the electric field. And so no transition of radiation; no foreign absorption takes place in these two molecules. Carbon monoxide, on the other hand is the asymmetric that of molecule. So, when it vibrates there will be change in dipole moment. Hence there is a permanent dipole moment because of the asymmetry. And that will cause absorption and emission of photon. Same is for carbon monoxide. If it vibrates in an asymmetric way, it will have energy transition. But with symmetric, there is no dipole moment there. Nitrous oxide is asymmetric in its very structure. So, any vibration here will create a change in dipole moment and hence cause absorption.

Here is water vapor, molecule and it is non-linear; it is not linear. It is called asymmetric top. Another example is ozone, which is very common in the earth's atmosphere, and finally Methane. These are the typical molecules that you encounter in dealing with heat transfer in both Engineering and Atmospheric Science.

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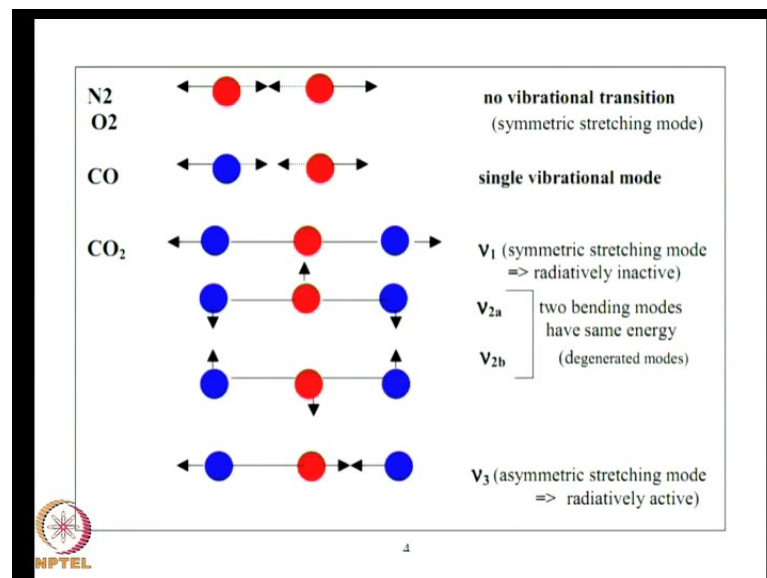
So the information that is given in the last study is again reproduced here. Then you see the different modes of carbon dioxide; a very important gas in combustion. We can say that a symmetric stretching, in which there can be no change in dipole moment. And so it is not radiatively active vibrational mode. But then you have this bending mode where

the molecules in the edges move in a different direction than the molecule in the middle. These two bending, these bending mode either we can bend in the plane of this paper or perpendicular to it.

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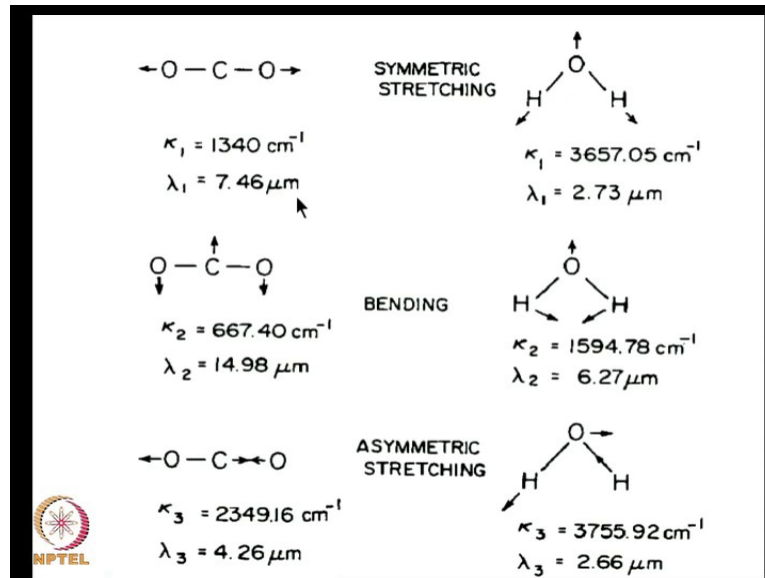
And then you have asymmetric stretching which we will show the examples of a little later. For all these modes, we can identify a wavelength. For example, for carbon dioxide there are absorption bands at 7.5 micron, 15 micron and 4.3 micron; for water vapor there are absorption bands due to symmetric stretching at 2.7 micron, bending at 6.3 micron and asymmetric stretching as this molecules move in different direction at 2.66 micron.

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Methane is a more complicated molecule; so-called spherical top. And of course it has many more number of degrees of freedom. It has nine fundamental modes of vibration. Some of them are similar, so they are degenerate; it has no permanent dipole moment, so no pure rotational spectrum. But there are vibrational modes at 3.3 micron and 7.7 micron.

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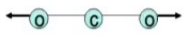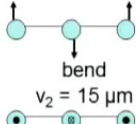
Ozone, a very important molecule in the earth's atmosphere has a symmetric stretching mode at 9 micron, a bending mode at 14 micron and asymmetric stretching mode at 9.6. This is very important band of ozone.

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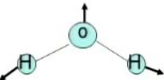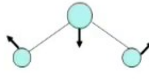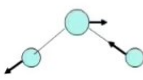Carbon dioxide, we saw it already. We just recapitulation; 7.5 micron, 4.3 micron and 15 micron bands.

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Water vapor, we saw it already; same 2.7, 6.25 and 2.66. This information is provided in a slightly more pictorial way.

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The symmetric stretching, bending are shown here. We will show it in a more animated way little later.

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There is Nitrous oxide, an important in the earth's atmosphere. And you see it has bands; now 7.8, 17, 4.5. You must have noticed that many of these molecules have absorption band very close to 7 and 4 micron; which means, when we deal with problems in the real world we must worry about overlap between these absorption bands. So, absorption band

nitrous oxide will overlap with carbon dioxide and water vapor, This must be accounted for in our calculation.

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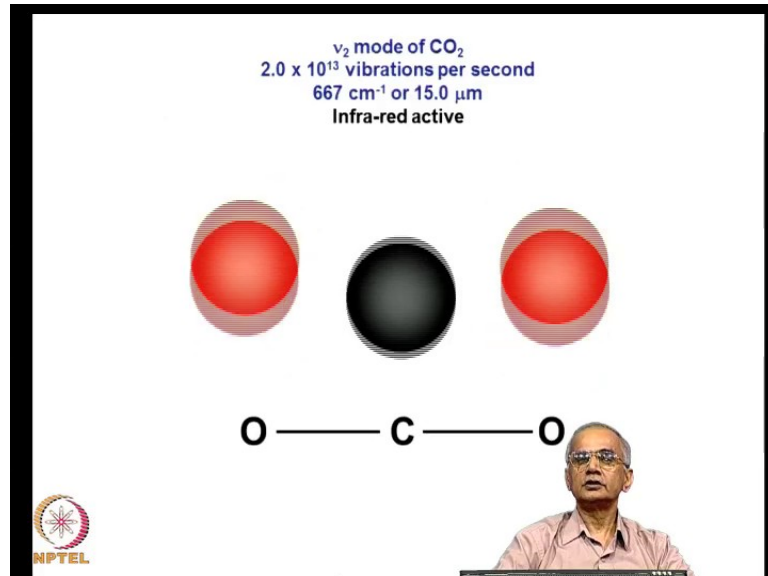
Now, here is the model showing a vibration. This is the one vibrational mode or symmetric stretching mode. It is not active because this mode, there can be no change in dipole moment. The next one is the asymmetric stretching. We can see that the molecules are not moving in the same direction. This mode is very important mode of carbon dioxide at 4.3 micron wavelength very active. The next is bending where the molecules go up and down. We see clearly that this one is occurring around 15 microns. This is a very important absorption band of carbon dioxide because this comes very close to the region, where earth emits maximum radiation.

From the Wien's displacement law, you know that a body at temperature around 300 Kelvin will have the maximum radiation, which is around 10 to 15 micron range. It is this region that carbon dioxide absorbs maximum radiation. Therefore, although carbon dioxide amount in the atmosphere is only now 398 parts per million. Its role in earth's climate is very important; because its absorption band occurs right where the radiation emitted with the earth's surface is maximum. We must remember that the importance of the gas partly depends on where the absorption band of the molecule is with reference to the radiation emitted by a surface.

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We must have noticed that both stretching and bending as we mentioned, for stretching frequencies are higher than the bending frequencies; because to stretch a molecule, it requires much more energy than to bend a molecule. Bending is always easier. We can take a stick and bend it easily. But you try to compress it or stretch it, it is more difficult. So, more energy is required to stretch than to bend Hence the stretching frequencies are usually much larger.

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Simulated high resolution absorption spectrum of a linear molecule. The Q branch ($\Delta J = 0$) is sometimes allowed if there are more than two atoms in the molecule. [Kyle Fig. 9.2]
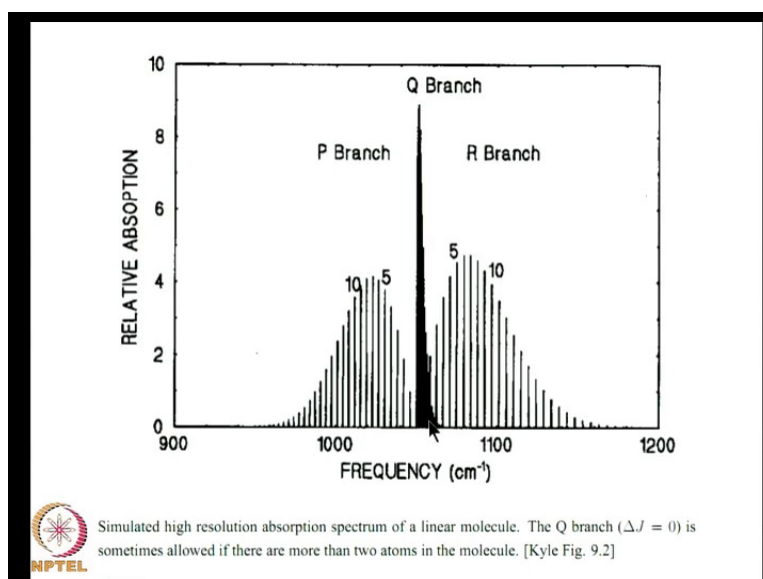
Now, the absorption band of a molecule in the vibrational-rotational spectrum is shown here. This is the relative absorption. It shows the center band called the Q branch, where there is no rotational transition. Sometimes this does not exist. It is not allowed by quantum mechanical rules. But on either side you have the rotational lines, which accompany the vibration; the P branch and R branch and each one is a line.

Now very often, when instruments are used to measure the absorption coefficient of the gas, these lines are not always visible; because these lines are shown as a single frequency or wavelength or wave number. But on account of various processes which we will discuss soon, these lines will get broadened.

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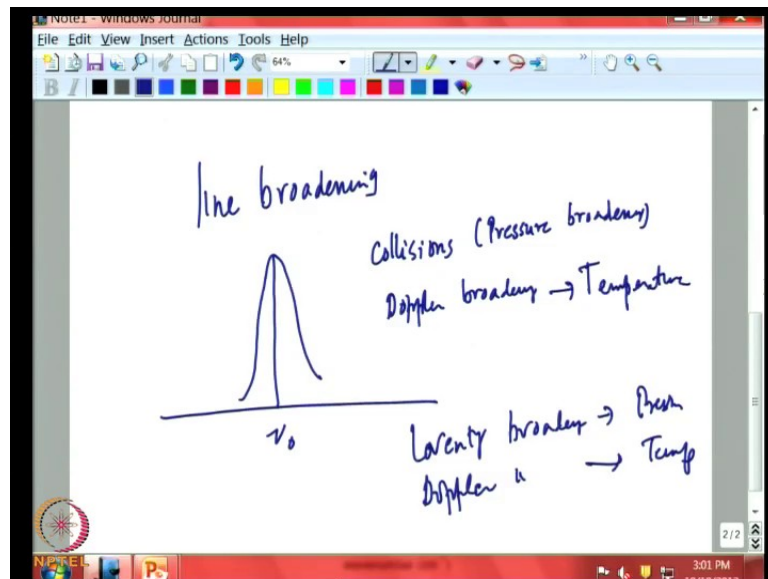
This is called line broadening. That is, what we showed was a single line at a certain frequency, but this line will actually be a shape like this. This broadening of this line can occur fundamentally for all purpose; two ways, due to collisions.

This is called pressure broadening. So, other molecules colliding with the molecule which has absorption band will broaden the range of frequencies in which that molecule gets absorbed. Now, other is called the Doppler broadening. This occurs because the molecules are moving at a fairly high speed. The Doppler Effect will play a role. So, imagine a molecule going away from you and emits a photon, the frequency of photon that is emitted that you will see in the laboratory will be different from the frequency if you are travelling along with the molecule. The frequency changes because the

molecules are moving at a pretty high speed. That alters the frequency of that photon as seen by an observer who is not sitting on a molecule, but sitting outside in the laboratory. So, Doppler broadening depends mainly on temperature because higher the temperature, higher the velocity of the molecules, higher the Doppler effect.

The pressure broadening is also called Lorentz broadening. It was discovered by Lorentz. So, Lorentz broadening depends mainly on pressure, while the Doppler broadening primarily depends on temperature. In most of the situation that we encounter both in Engineering and Atmospheric Sciences, especially near the ground, the Doppler broadening is not that important. More important is the Lorentz broadening, because of the fact that at the earth's surface, the pressure is quite high and so there are lots of collisions, which alter the width of the line. Hence you need to take into account the role of collisions due to high pressure. The Doppler broadening is not that important at the earth's surface, where most Engineering applications are happening. We saw this P branch and R branch, and we said this line ultimately start broadening because of collisions and high temperature.

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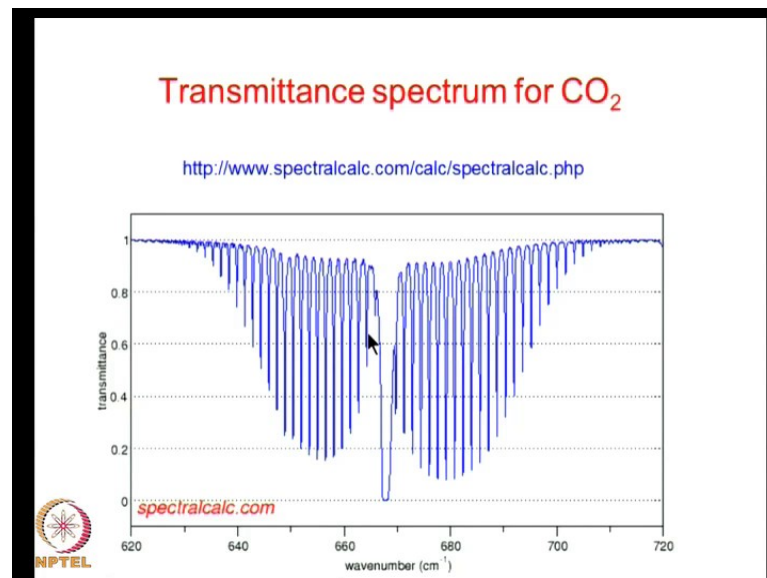
Let us see what it looks like. We can see that in this case is a high resolution spectra of carbon dioxide and it is calculated actually. We can see that, that is the width of the line; this centre line is right here, but the line actually is broadened.

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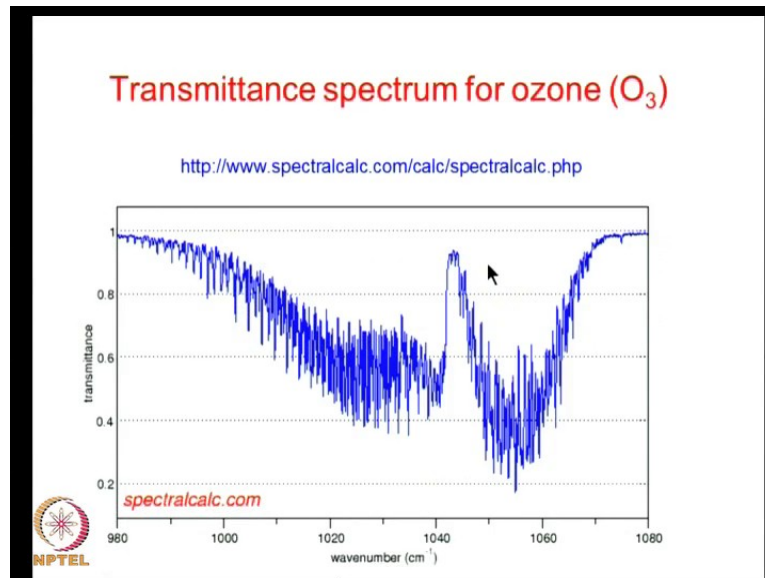
Here is another example and here we can see that there are so many lines here, and we are not able to see the width of each line. This is a challenge you always face in the radiative heat transfer; that in a very small range of wave number, here coming from 980, let us say 1040. There are hundreds of lines and in the center here, absorption is high transmittance is low; while at the edge here, transmittance is high, absorption is low. The radiative transfer calculation has to take into account to high transmissions in the wings here and low transmission at the center of the band. These are difficult calculations one has to do. We can see ideally that, you should integrate over all these features to get accurate estimate of the amount of photon that the gas is absorbing or emitting.

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Table 7.2 The most important vibrational and rotational transitions for H_2O, CO_2, O_3, CH_4, N_2O, and CFCs.

Gas	Center ν (cm^{-1}) ($\lambda(\mu m)$)	Transition	Band interval (cm^{-1})
H₂O	-	pure rotational	0-1000
	1594.8 (6.3)	ν_2; P, R	640-2800
	continuum*	far wings of the strong lines; water vapor dimmers (H₂O)₂	200-1200
CO₂	667 (15)	ν_2; P, R, Q	540-800
	961 (10.4)	overtone and combination	850-1250
	1063.8 (9.4)		
	2349 (4.3)	ν_3; P, R overtone and combination	2100-2400
O₃	1110 (9.01)	ν_1; P, R	950-1200
	1043 (9.59)	ν_3; P, R	600-800
	705 (14.2)	ν_2; P, R	600-800
CH₄	1306.2 (7.6)	ν_4	950-1650
N₂O	1285.6 (7.9)	ν_1	1200-1350
	588.8 (17.0)	ν_2	520-660
	2223.5 (4.5)	ν_3	2120-2270
CFCs			700-1300

*Continuum absorption by water vapor in the region from 800-1200 cm^{-1} remains unexplained. It has been suggested that it results from the accumulated absorption of the

Now, here again is a tabulation of the important absorption bands of the various common gases like water vapor, carbon dioxide, ozone, methane, nitrous oxide, chlorofluorocarbons. We notice that, the regions of the spectra where they absorb and emit photons are very, very similar. Most of them are in the range of 500 to 1000. And so this is a point we have to remember that in any given value of the range, more than one gas can be absorbing the radiation. So, we have to collectively account for the overlap of the absorption bands of different gasses carefully because in most situation we encounter, the gasses which are absorbing are many. Hence their role must be fully recognized.

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- Absorption of visible and near IR radiation in the gaseous atmosphere is primarily due to H_2O, O_3, and CO_2.

Table 7.3 Main Visible and near-IR absorption bands of atmospheric gases

Gas	Center ν (cm^{-1}) ($\lambda(\mu m)$)	Band interval (cm^{-1})
H₂O	3703 (2.7)	2500-4500
	5348 (1.87)	4800-6200
	7246 (1.38)	6400-7600
	9090 (1.1)	8200-9400
	10638 (0.94)	10100-11300
	12195 (0.82)	11700-12700
	13888 (0.72)	13400-14600
	visible	15000-22600
CO₂	2526 (4.3)	2000-2400
	3703 (2.7)	3400-3850
	5000 (2.0)	4700-5200
	6250 (1.6)	6100-6450
	7143 (1.4)	6850-7000

Here are more examples of water vapor bands. We can see the water vapor bands starts all the way from 0.72 micron, 0.8 micron, 0.9, all infrared all these; 1.1, 1.38. So, 1, 2, 3, 4, 5, 6, 7, bands are indicated for water vapor here and then there are more than four bands for carbon dioxide; 1.4, 1.6, 2.0, 2.7, 4.3.

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Gas	Center ν (cm^{-1}) (λ(μm))	Band interval (cm^{-1})
O$_3$	2110 (4.74)	2000-2300
	3030 (3.3)	3000-3100
	visible	10600-22600
O$_2$	6329 (1.58)	6300-6350
	7874 (1.27)	7700-8050
	9433 (1.06)	9350-9400
	13158 (0.76)	12850-13200
	14493 (0.69)	14300-14600
	15873 (0.63)	14750-15900
N$_2$O	2222 (4.5)	2100-2300
	2463 (4.06)	2100-2800
	3484 (2.87)	3300-3500
CH$_4$	3030 (3.3)	2500-3200
	4420 (2.20)	4000-4600
	6005 (1.66)	5850-6100
CO	2141 (4.67)	2000-2300
	4273 (2.34)	4150-4350
NO$_2$	visible	14400-50000

In the case of ozone we have two important absorption bands. For oxygen, there are many bands. Although oxygen does not have a permanent dipole moment, it does have week absorption bands in the infrared. Then we have nitrous oxide, methane and carbon monoxide.

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APPENDIX B.   HITRAN Molecules with Associated Indices

HITRAN Molecule Number	Molecule Chemical Symbol	Number of lines	HITRAN Molecule Number	Molecule Chemical Symbol	Number of lines
1	H_2O	49444	21	HOCl	15565
2	CO_2	60802	22	N_2	120
3	O_3	275133	23	HCN	772
4	N_2O	26174	24	CH_3Cl	9355
5	CO	4477	25	H_2O_2	5444
6	CH_4	48032	26	C_2H_2	1668
7	O_2	6292	27	C_2H_6	4749
8	NO	15331	28	PH_3	2886
9	SO_2	38853	29	COF_2	54866
10	NO_2	100680	30	SF_6	11520
11	NH_3	11152	31	H_2S	7151
12	HNO_3	165426	32	HCOOH	3388
13	OH	8676	33	HO_2	26963
14	HF	107	34	O	2
15	HCl	533	35	$ClONO_2$	32199
16	HBr	576	36	NO^+	1206
17	HI	237	37	HOBr	4358
18	ClO	7230			
19	OCS	858			
20	H_2CO	2702			

Here is another tabulation of the various important molecules, relevant to Engineering or Atmospheric science. For example, water vapor according to this HITRAN code has 50,000 lines. Ozone has 2, 75,000 lines; nitric acid has 26,174 lines.

This shows how difficult it is to deal with radiation by these gases because they are absorbed for a large number of lines. At the line center, there is a strong absorption. We can think about doing this calculation only on a computer. There is no other way to do it because we have to correctly deal with all the lines; know where the line begins, where the line ends and what is the peak absorption. We can see this is a quite a tedious task. The people have found various simple short cuts to avoid looking at each line in these complex spectra of the molecules that we encounter every day.

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3) Radiative transitions of purely rotational energy require that a molecule possess a permanent electrical or magnetic dipole moment.

- CO, N_2O, H_2O and O_3 exhibit pure rotational spectra because they all have the permanent dipoles.
- CO_2 and CH_4 don't have permanent dipole moment => no pure rotational transitions. But they can acquire the oscillating dipole moments in their vibrational modes => have vibration-rotation bands
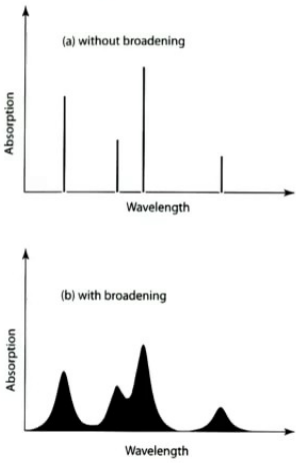
There are also pure rotational transitions, which we will not spend too much time on because that occurs mainly in the microwave. That we will take up a little later.

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Absorption line shapes

- **Doppler broadening:** random translational motions of individual molecules in any gas leads to Doppler shift of absorption and emission wavelengths (important in upper atmosphere)
- **Pressure broadening:** collisions between molecules randomly disrupt natural transitions between energy states, so that absorption and emission occur at wavelengths that deviate from the natural line position (important in troposphere and lower stratosphere)

- Line broadening closes gaps between closely spaced absorption lines, so that the atmosphere becomes opaque over a continuous wavelength range.

(a) without broadening

(b) with broadening

So, our task is to identify the wavelength for each of these lines and then after the line is broadened by a collision how the different line are overlapping here. The two broadening that we discussed. One is due to temperature; other is due to collisions. They broaden the line and lead to a lot of overlap and your account for all this, for you to be able to accurately estimate a radiative heat transfer.

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So proudly speaking, the optical thickness of the gas is absorption coefficient times the path length. The absorption coefficient is some intensity of absorption times the function, which is a function of frequency. And what function to use depends upon, whether in a given situation, the collision broadening is dominating or the broadening due to Doppler, that is, temperature effects.

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Here is an example of the pressure broadening of the Lorentz line. The shape function for this is some constant times nu minus this center frequencies plus some constant a

squared. This is having a simple bell shaped structure. This is the most important broadening mechanism of relevance to Engineering because in Engineering, majority of the time you are dealing with furnaces, whose pressure is close to the that of our atmospheric or some of them are more high pressure, and so all of them will experience this kind of broadening by collisions. Now in this, we saw a constant alpha and that depends on pressure and temperature. This is called the line half-width because this is the place where when alpha equals, this quantity is the center of the line nu 0, This is the width of the line half-width. This is important to know, because it reminds how wide the lines.

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- The **half-width** of the Lorentz line shape is a function of pressure P and temperature T and can be expressed as

$$\alpha(P,T) = \alpha_0 \frac{P}{P_0} \left(\frac{T_0}{T} \right)^{1/2}$$

where α_0 is the reference half-width for STP: $T_0 = 273K$; $P=1013$ mb.

α_0 is in the range from **about 0.01 to 0.1 cm^{-1}** for most atmospheric radiatively active gases.

The **Lorentz profile** is fundamental in the radiative transfer in the lower atmosphere where the pressure is high.

The collisions between like molecules (**self-broadening**) produces the large line-widths than do collisions between unlike molecules (**foreign broadening**). Because radiatively active gases have low concentrations, the **foreign broadening** often dominates in infrared radiative transfer.

And, this half-width depends upon the pressure and temperature of the gas. These are all tabulated for different gases. Now, the broadening by collision has two components; collisions by the other molecules. Suppose, you are dealing with the carbon dioxide molecule and collide nitrogen, oxygen, then the efficiency collision is a certain amount. But on the other hand if the C O 2 molecule collides with another C O 2 molecule, then the energy interaction is more vigorous, because molecules have the same mass. So one has to treat the self-broadening due to collision between like molecules and it is different from foreign-broadening, for a given molecule under goes collision with another molecule. That is more common in our examples because in all our experimentation that we do, nitrogen and oxygen are always there. They may not absorb or emit radiation, but they do play a role.

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Doppler profile is defined in the absence of collision effects (i.e., pressure broadening) as:

$$f_D(\tilde{v} - \tilde{v}_0) = \frac{1}{\alpha_D \sqrt{\pi}} \exp\left[-\left(\frac{\tilde{v} - \tilde{v}_0}{\alpha_D}\right)^2\right] \qquad [7.2]$$

α_D is the **Doppler line width**

$$\alpha_D = \frac{\tilde{v}_0}{c}(2k_B T / m)^{1/2}$$

where c is the speed of light; k_B is the Boltzmann's constant, m is the mass of the molecule.

This is the shape function for the Doppler broadening due to temperature of the gas. That will divide. Look at this function. This function is showing exponential decline in the shape function. This is very different from the function that was seen in the case of Doppler broadening, where the broadening, the line is smoothened to a 1 by 1 plus x squared kind of dependence. We expect that the Doppler broadening will bring down the line absorption very rapidly to 0 because of the exponential character of this function.

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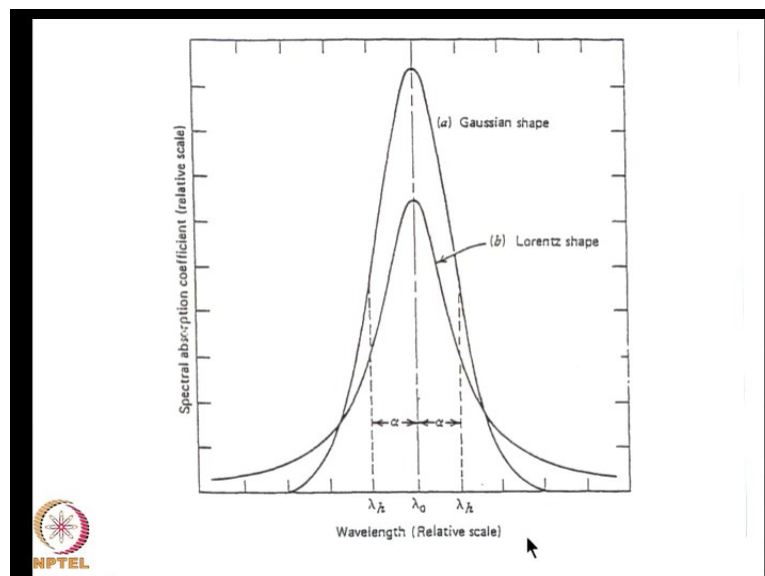
That showed clearly in this picture, we have the pressure broadening of Lorentz line and the Doppler broadening Gaussian shape. And we can see that as you go away from the center of the absorption line, the Gaussian, the exponential function shows the rapid decline. So, after a certain distance the Doppler line is not important and the pressure broadening allowed Doppler broadening is not important and the pressure broadening is not important because that goes as 1 by 1 plus x square. There are situations where you must take into account the Doppler broadening in the center part of this curve and the pressure broadening at the edge of the curve. This is called the white line V O I G T, which is the hybrid of Doppler and pressure broadening.

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Lorentz line shape profiles for three pressures. A line width of 0.05 cm⁻¹ at a pressure of 1 bar is typical for vibration-rotation bands. [Goody & Yung, Fig. 3.18]
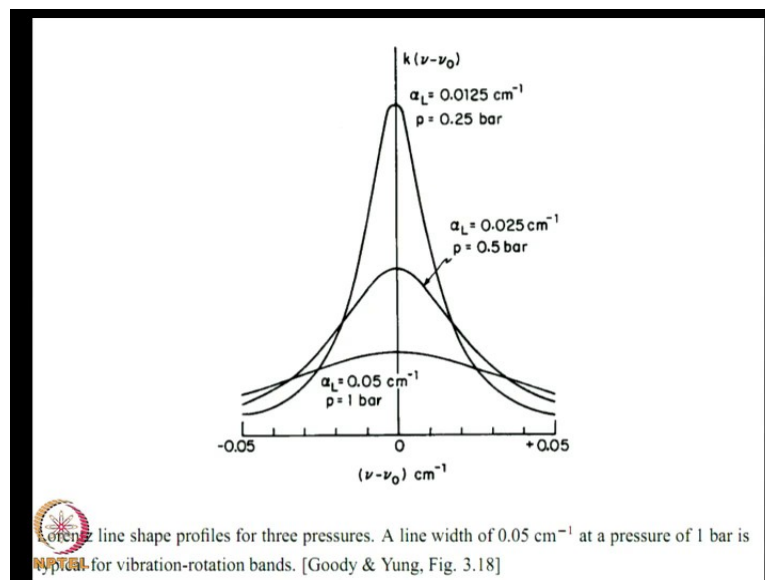
Here, what is shown clearly is the effect of pressure. We can see that the pressure broadening, which is influenced by pressure. When the pressure is one bar like the earth's surface, the line is broadened tremendously; while as you go to low level pressure like half of a bar or 0.25 bar, then the line is much more sharper. Line is very flat at high pressure and not so flat at low pressure. In the earth's atmosphere the surface pressure is close to one bar. While you go to the height over 10 to 20 kilo meters, the pressure would have dropped substantially; at about 15 kilo meter, pressure will be one-tenth of this surface. We expect that the lines at tropopause will look very different from the absorption lines at the earth's surface. At the earth's surface, the adjacent lines will all be absorbed.

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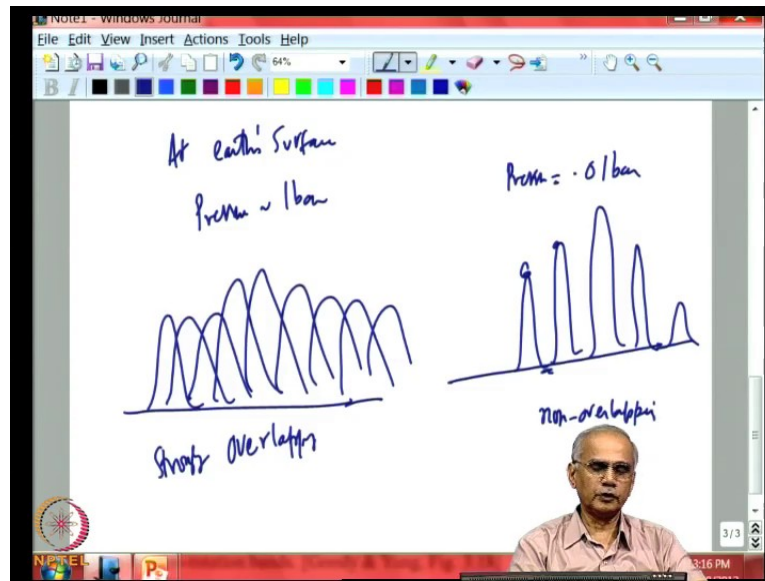
So, let us illustrate that by an example here. At the earth's surface, where the pressure is of the order of one bar, the lines may be all based on the overlapping because of the pressure. The same gas, if we reduce the pressure to 0.01 bar, then you will see the same gas will have distinct absorption lines. These lines are now non-overlapping, while here they are strongly overlapping.

This is very important to know because if it is strongly overlapping lines, then it will remove this complicated structure that you will normally see and you will be able to fit a very simple function to this. On the other hand if the lines are non-overlapping, you will have great difficulty in integrating the equation because between the lines there is no absorption, then suddenly absorption will catch a very high value. But this does occur with many gases that, there is a strong variation of the absorption coefficient with wavelength. But this is unavoidable condition that we have to deal with all the time.

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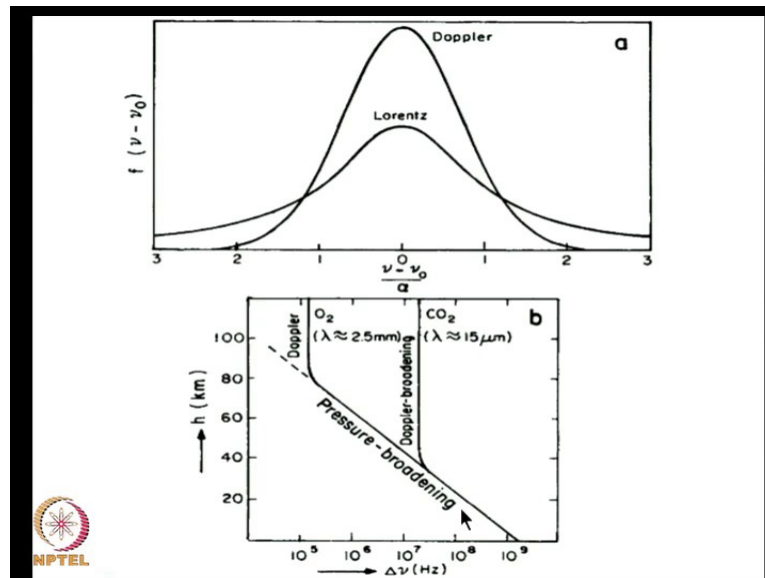
Now, here is one more illustration again of the difference between Doppler broadening by temperature, Lorentz broadening by pressure. Again we are showing here the line width in frequency coordinate as a function of the height above the earth's surface. If you go to very high level, the half width frequency will be very, very low. But if we come close to atmospheric pressure that is near the ground, it will be much higher.

We can see that there is a difference of ten thousand here; width difference. This is very important effect of pressure broadening. But Doppler broadening, which is not that much influenced by a pressure, but it is important at higher altitudes we can see that beyond a certain height, pressure broadening is not important only Doppler broadening dominates. That is at upper atmosphere. This is a discussion you have to remember between the kind of line, which will get in the upper part of the atmosphere; where Doppler broadening versus the kind of pressure, kind of line structure you will see near the ground because of the spinning of the lines.

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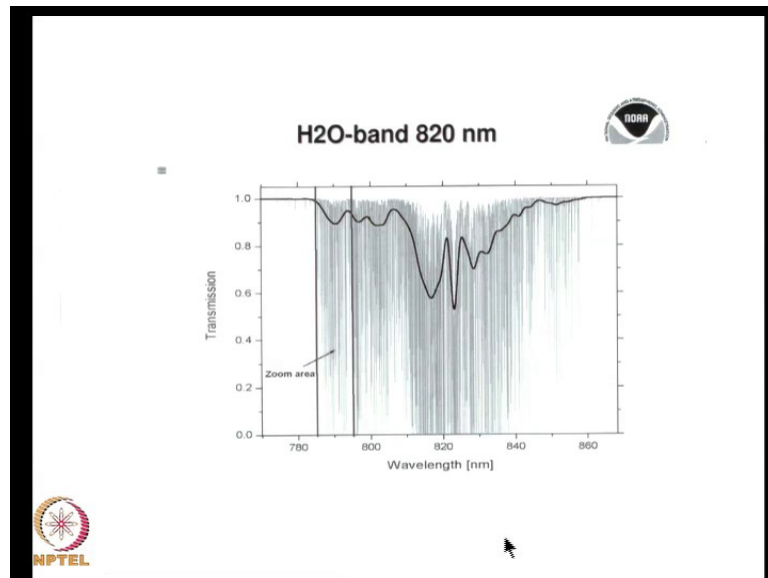
Now to illustrate this further, we are showing the water vapor band at 820 nanometers. Notice that, there are large number of lines here, huge number of them, thousands of them. If you do not want to account for all these details, we can smoothen it and we will get this black curve. But of course, if we calculate your radiation transfer based on this black curve which is very highly average, we will make errors because these are large amount of lines. Between the lines, there is a gap. And in that gap radiation can escape. That will be completely missed out if we use a very smooth function for this. To make this point clear, let us show few more pictures of the same spectra. This went from 780 to 860 about 80 nanometers.

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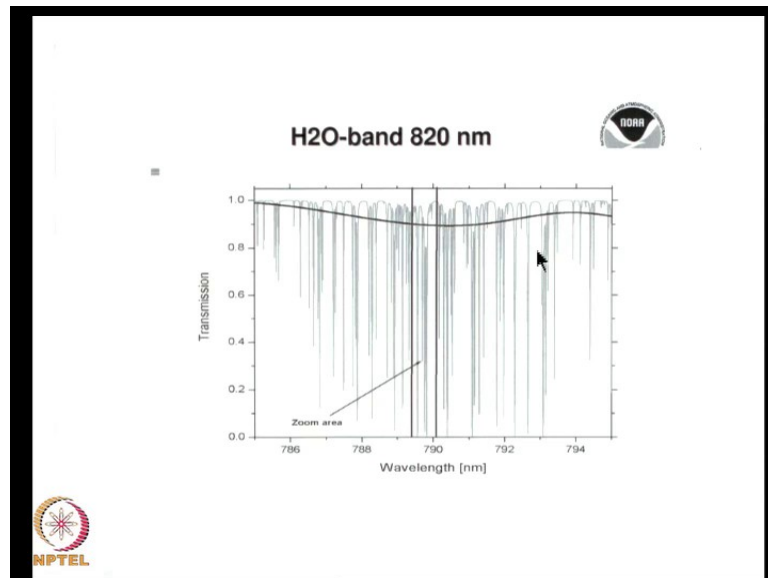
Now, we take a close up and look at 6 nanometers. We are beginning to see the line and there is in between; after this there is no absorption above 0, transmission is one. We have to tackle this high absorption at the center line along with adjacent wavelength that is having the absorption. This is the challenge of calculation in radiative heat transfer is that the absorption of the gas varies strongly with wavelength and small change in wavelength or wave number or frequency cause a large change in the radiative flux. Now, in the same graph this is now 77, only 8 nanometers.

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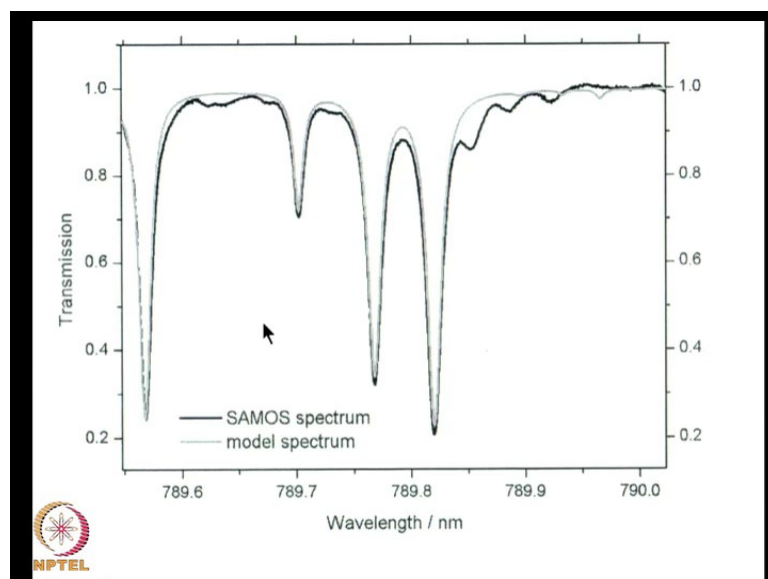
We go further up. This is now only 0.4 nanometers; same spectra. Here, we can see we are able to resolve everything. We see, here there are three major lines which absorbs strongly. In between region there is hardly many absorption. And so you have to get this close to the spectra. That is, variation with 0.1 to 0.2 nanometer, before We can really resolve the shape of these lines.

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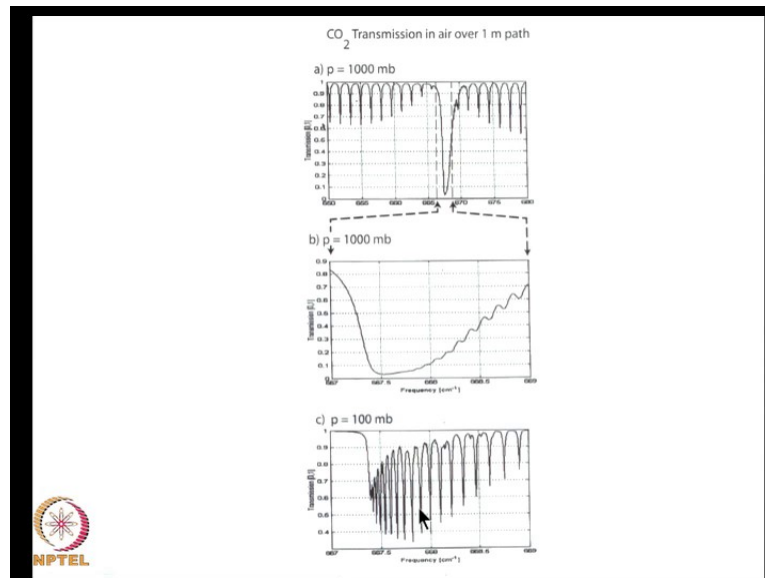
Now, this point is further illustrated in this graph, where the transfer of carbon dioxide through one meter depth of the gas is shown for surface pressure, where we will see large number of lines with the center region there. Now, if we want to know what happens when the same gas is looked at, we will take this portion, the 665 and 670, and expand it.

We can see that right in this slope region, there are beginnings of the line structure visible at one bar. But take the same gas and find the spectra at 100 milli bar; that is about height of 10 kilometers or 12 kilometers. We can see that these lines which were hardly visible here, are actually distinct lines. Here they cannot overlap. At the earth's surface they cannot overlap. But once we bring the molecule to a higher elevation, all this will come out. This has to be remembered that the actual shape of the line depends upon the absorption spectra of the molecule.

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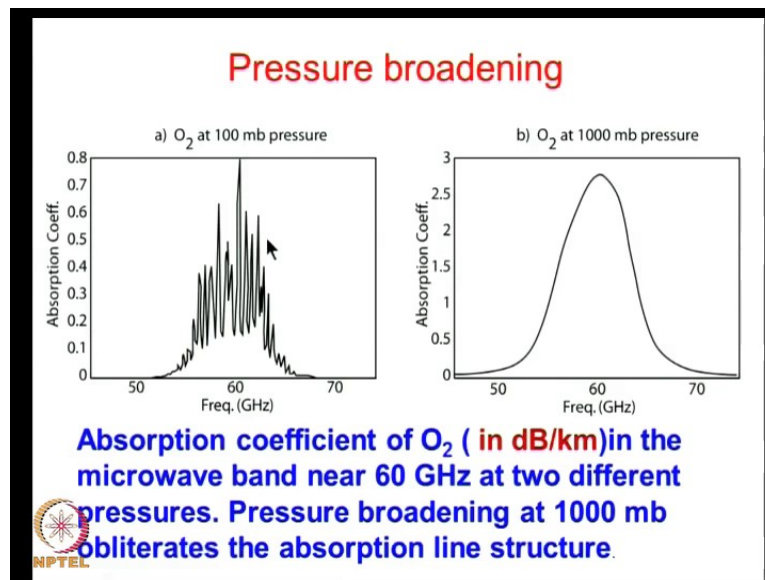
One more illustration here is the oxygen absorption of the microwave. We can see that at 100 milli bar pressure, very low pressure, each line is distinctly visible. But as soon as we go to surface pressure all this is smeared out and we are only getting a smooth curve. Any calculation using this will be very crude and very tedious. But at the end of the day, it will give you very valuable data on C O 2 absorption and emission.

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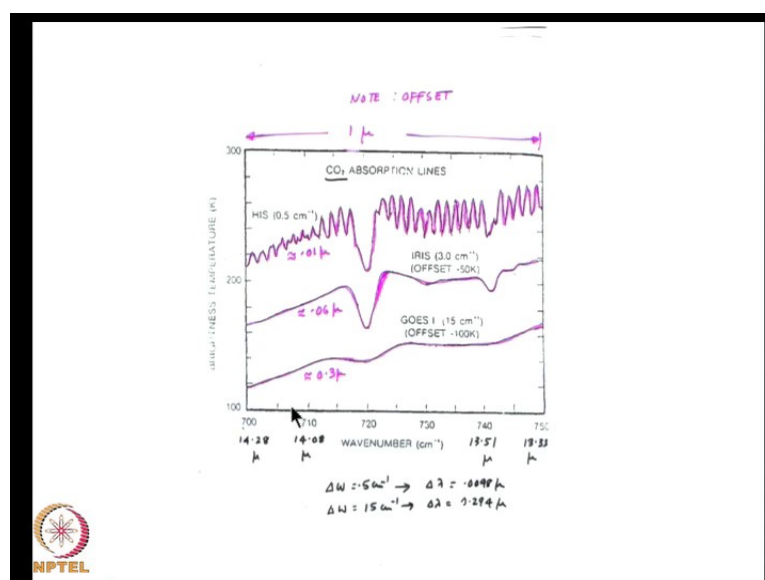
Now, this is further illustrated from satellite data we have shown three different satellites, flux as calculated based on the concept of brightness temperature. So, brightness

temperature is that temperature at which the black body emits the same intensity as actual emission we saw at a given angle at a given wavelength.

Now, this carbon dioxide band is shown by the three different satellites. In the older satellite it goes which had a very poor wavelength resolution. We get a very smooth curve. On the other hand, you look at other satellites like Iris or high resolution high infrared, we can see that the high resolution spectra here shows the line structure, which is just above visible here is almost gone in the case of the older satellite. As we move from older to newer satellite, the resolution is appearing continuously; so newer satellite giving a much more structure, which has some value for interpretation.

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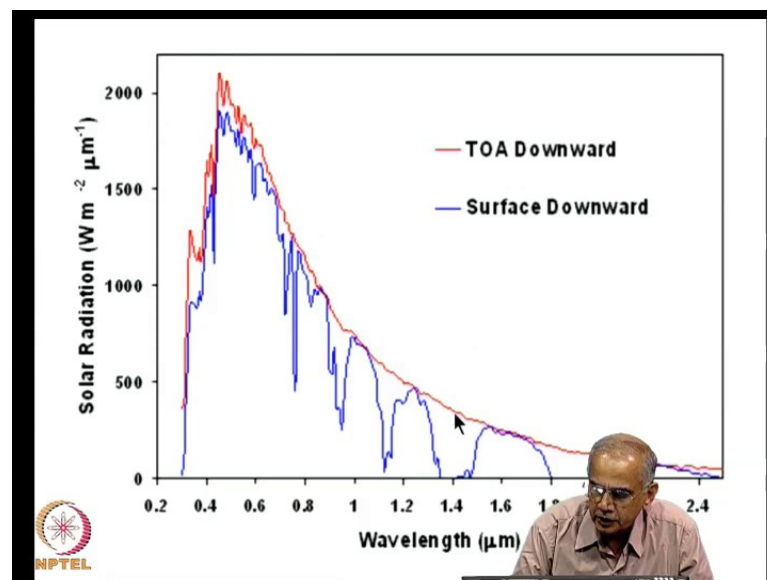
Now because of all this absorption, all of us know that the radiation as coming from the sun behaves close to that of a black body, that is, the orange line. By the time, the radiation goes to the atmosphere is absorbed by various constituents. At the earth's surface, the radiation is lower. There are clear cut absorption bands of carbon dioxide and water vapor which we see here, which has removed the black body radiation that was being emitted by the sun. So blue is the spectra observed at the earth's surface; while orange is the spectra at the top of the atmosphere.
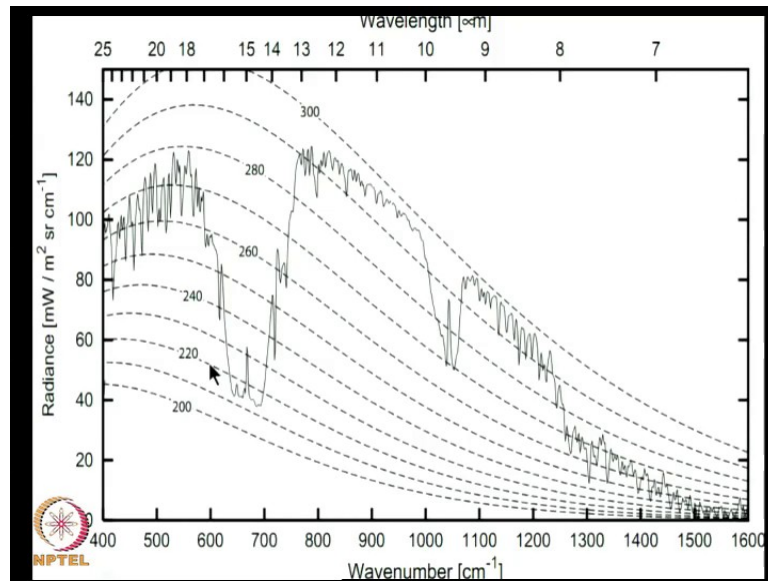
Wherever these two differ is due to absorption by molecules. Now, here is another spectra as obtained from satellite over the Sahara region. We see very clearly the strong absorption by carbon dioxide in the 14 to 16 micron band. Carbon dioxide absorbs radiation of the earth very efficiently and reemits it at a temperature corresponding to the pure tops. Hence the temperature that you notice when you measure it will be very low here. This is ozone. The ozone and C O 2 are all is always sitting there in these locations and they will absorb. Anyhow that, the earth's black body spectrum maximize somewhere around this region. That is why carbon dioxide is playing; without carbon dioxide, the earth's emission would have been like this. With carbon dioxide, now there is a big dip here; which is the role of carbon dioxide. This is at ozone. Water vapor plays important role here, much larger wave number which we will see later.
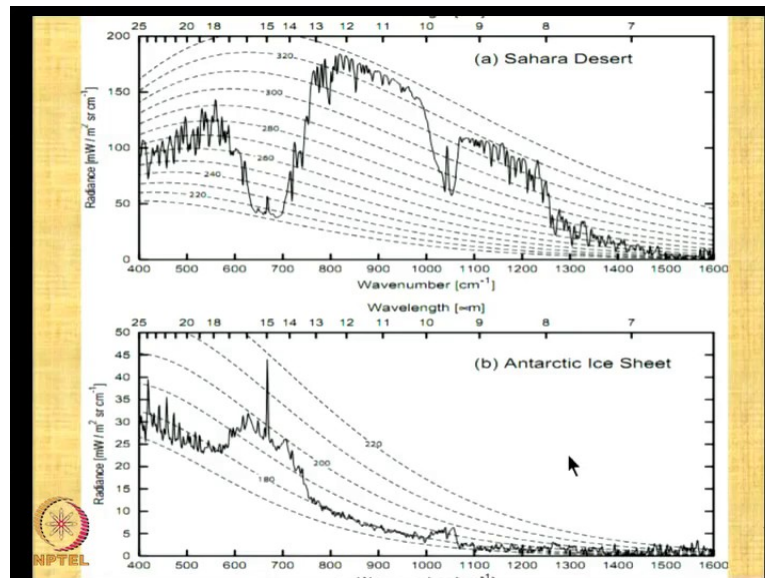
Here are more examples of spectra from Antarctic and Sahara. We are showing this that to show the huge difference between the Sahara and Antarctic. In the case of Antarctic, there is an inversion near the surface, which leads to such a peculiar spectra. It is very different from the Antarctic, where water vapor absorption dominates in Sahara.
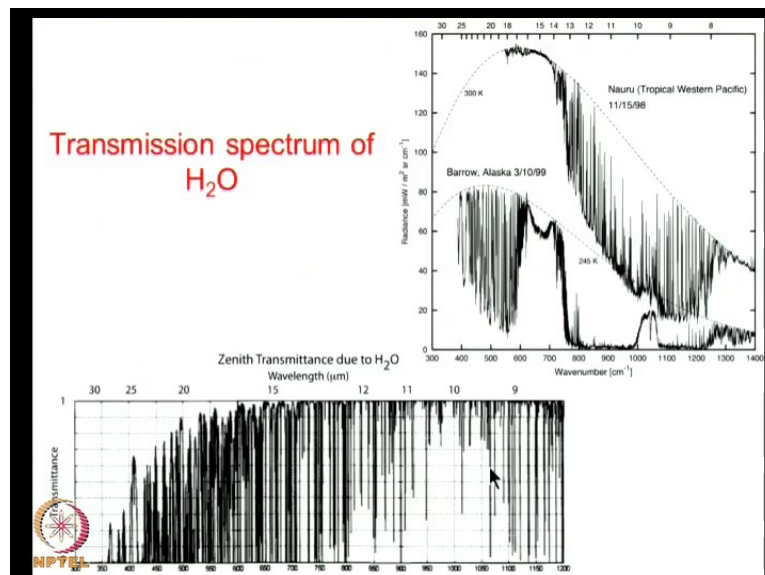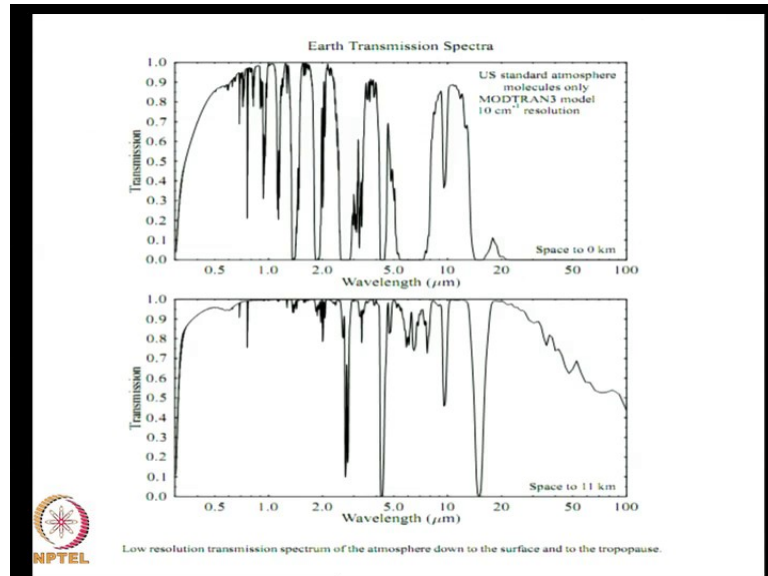
Here are more examples of spectra of water vapor. We can see difference between Nauru in western Pacific and Barrow in Alaska. It is a cold place; this a warm place. In the

warm place the atmosphere emits radiation at more vigorously. In both the cases the presence of gas will reduce the emission spectra substantially.

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Now, here is example of transmission from surface to eleven kilometers and surface to space. If we take to surface of space, then we are taking into account all gases that are there in the earth's atmosphere, all the way from the ground to may be 100 kilometers. But if we compare the spectra of atmosphere layer from surface to 0 kilometers, this is also asked to look at the corresponding spectra from space. Space will be anywhere around 15 kilometers or so.

We see that this spectra differs substantially between what we do for the total integral spectra up to the top of the atmosphere and the one in which you look at only at the tropopause. We can see that the widths have changed because in this example of this region which is the high transfer, it became a highly absorbing region. This is peculiar to radiative transfer.

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Table 7.1 Units used for path length (or amount of absorbing gases), absorption coefficient, and line intensity.

Amount of absorbing gas (path length)	Absorption coefficient	Line intensity
cm	cm^{-1} (volume absorption coefficient)	cm^{-2}
$g\ cm^{-2}$	$cm^2\ g^{-1}$ (mass absorption coefficient)	$cm\ g^{-1}$
cm^{-2}	cm^2	cm
cm atm	$(cm\ atm)^{-1}$	$cm^{-2}\ atm^{-1}$

NOTE: mass absorption coefficient = volume absorption coefficient / density of the gas

Now, let us also get some definitions going. In the next lecture, we will define the absorption coefficient and the amount of absorber and go along to depict these values in real situations.

Thank you.