

# AOSC400-2015

## October 20, Lecture # 13

### Absorption and Emission by Gas Molecules

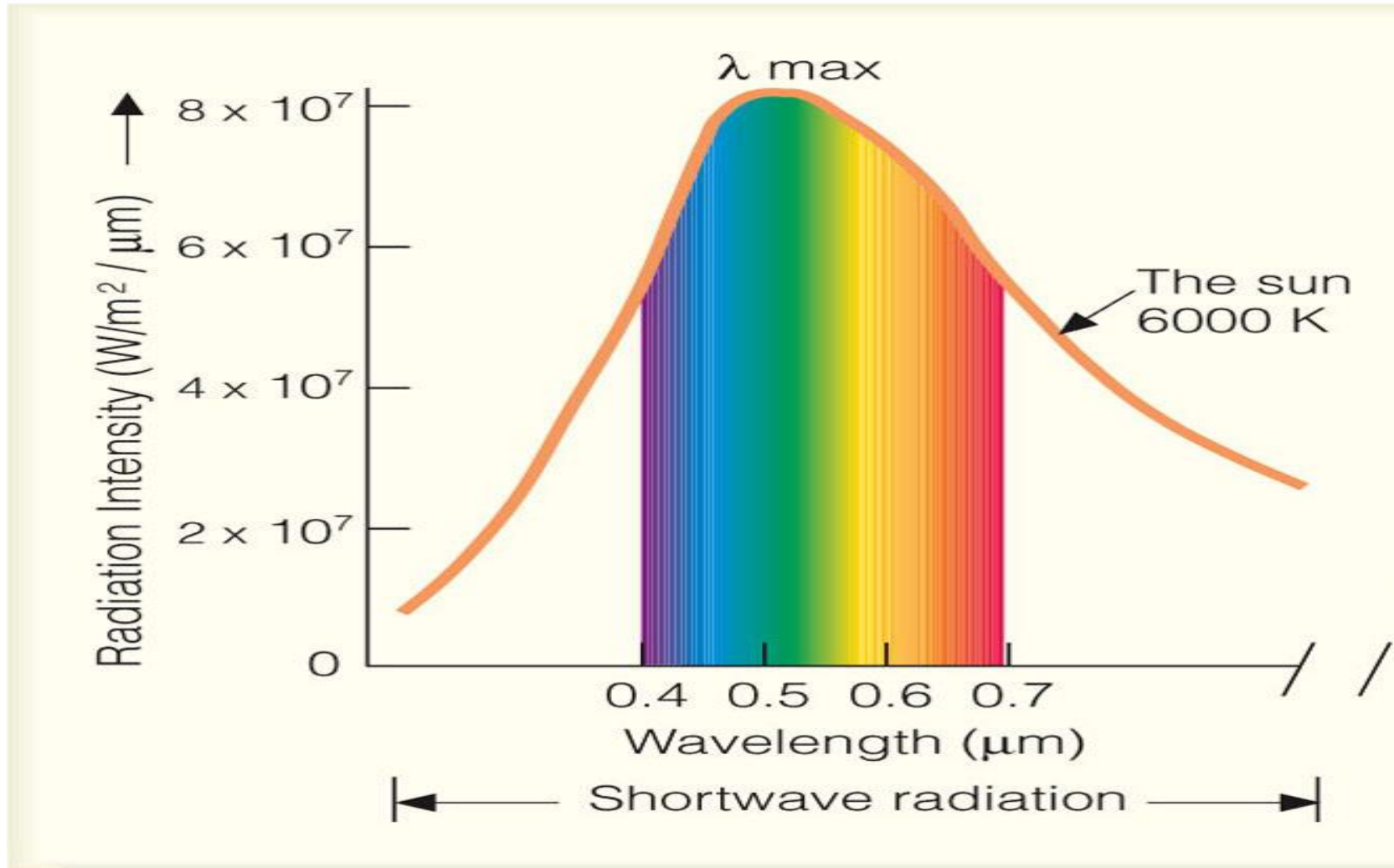
- Basics of atomic and molecular absorption/emission spectra
- Spectral line shapes: Lorentz and Doppler profiles
- Absorption coefficient and transmission function
- The **Schwarzchild's equation**

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\*Sources of information used for this lecture are listed in updated Syllabus.

# Refresher: What is a spectrum? Example of the sun's visible spectrum



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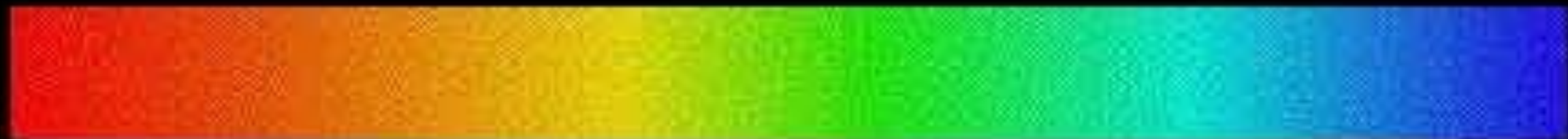
Sir Isaac Newton used a prism to split sunlight into its fundamental colors of the rainbow.

# Continuum, Emission, and Absorption Spectra

## Types of spectra

- Produced in different ways, and can tell us about the physical properties of the materials producing them.
- The three types of spectra are called “a *continuous spectrum*” (or continuum emission), “an *emission line spectrum*” and “an *absorption line spectrum*”. They look like the following:

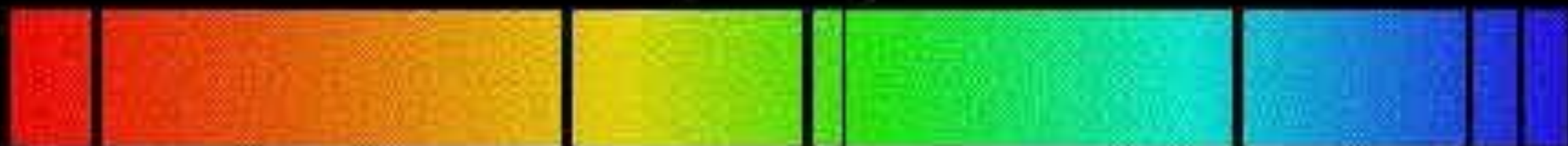
# Continuous Spectrum



# Emission Spectrum



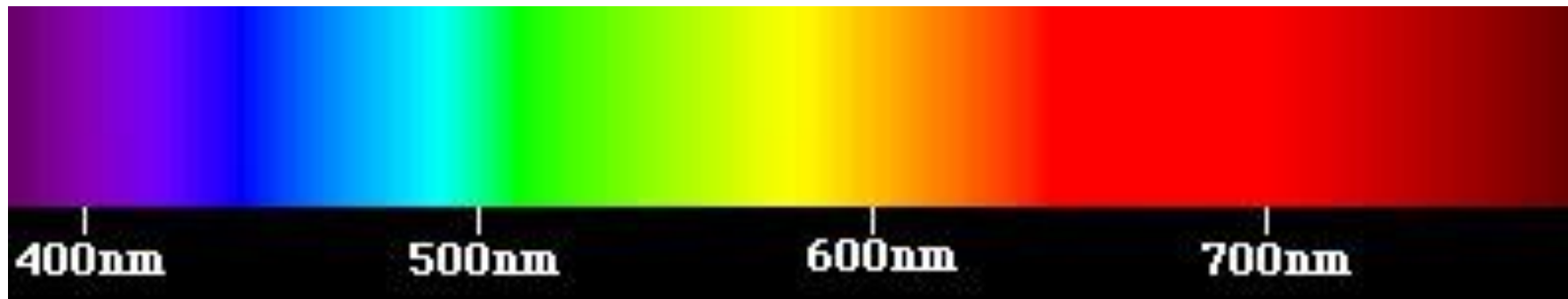
# Absorption Spectrum



# A continuous spectrum

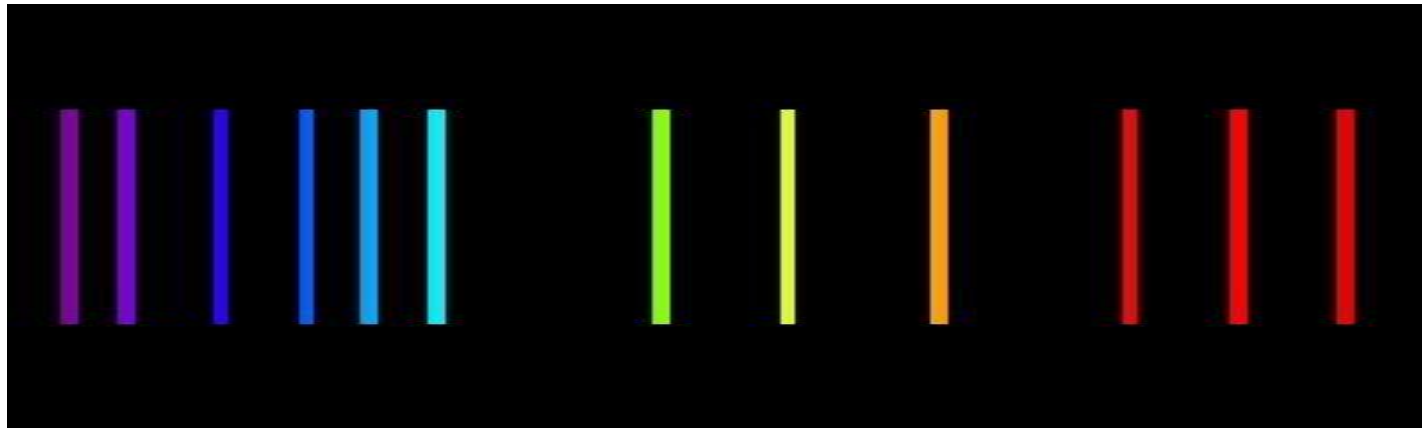
- Light from the Sun or any star, produces a continuous spectrum.
- Light produced by incandescent light bulbs is a continuum spectrum; the filament gets extremely hot from having an electric current passed through it and gives off light.

Note:  $400\text{ nm} = 0.4\ \mu\text{m}$



# An emission line spectrum

The emission spectrum of an object would produce a series of bright lines with a dark background. **Emissivity** at visible and longer wavelengths can thus be described in terms of a *line spectrum* consisting of extremely narrow *emission lines separated* by much wider gaps in which the gas is not emitting.



## An absorption line spectrum

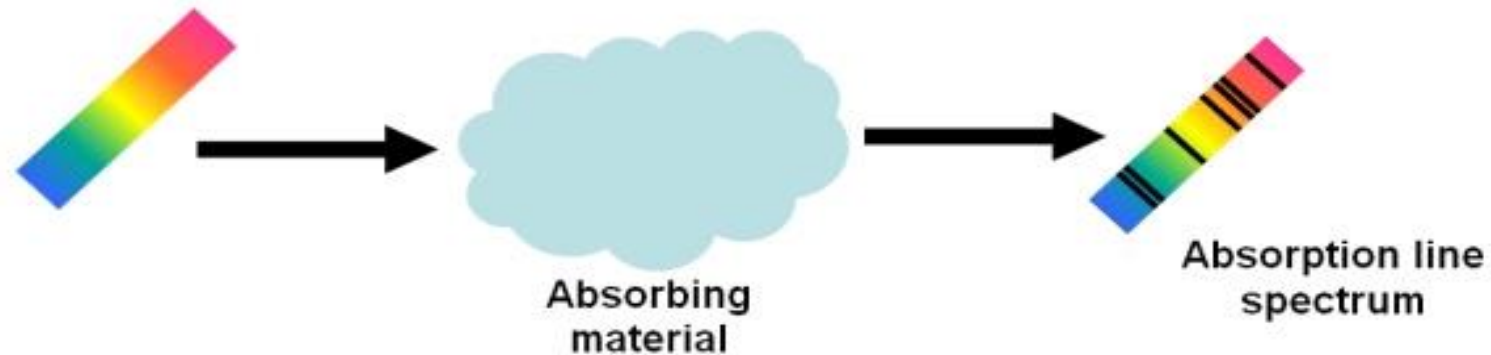
An absorption line spectrum is in some ways the opposite of an emission line spectrum. Instead of seeing a series of bright lines on a dark background, one sees dark lines on a continuous spectrum.



Absorption lines are usually seen as dark lines, or lines of reduced intensity, on a continuous spectrum. This is seen in the spectra of **stars**, where gas (mostly **hydrogen**) in the outer layers of the star absorbs some of the light from the underlying thermal **blackbody** spectrum.

## ABSORPTION LINE

An **absorption line** will appear in a spectrum if an absorbing material is placed between a source and the observer. This material could be the outer layers of a **star**, a cloud of **interstellar gas** or a cloud of **dust**.



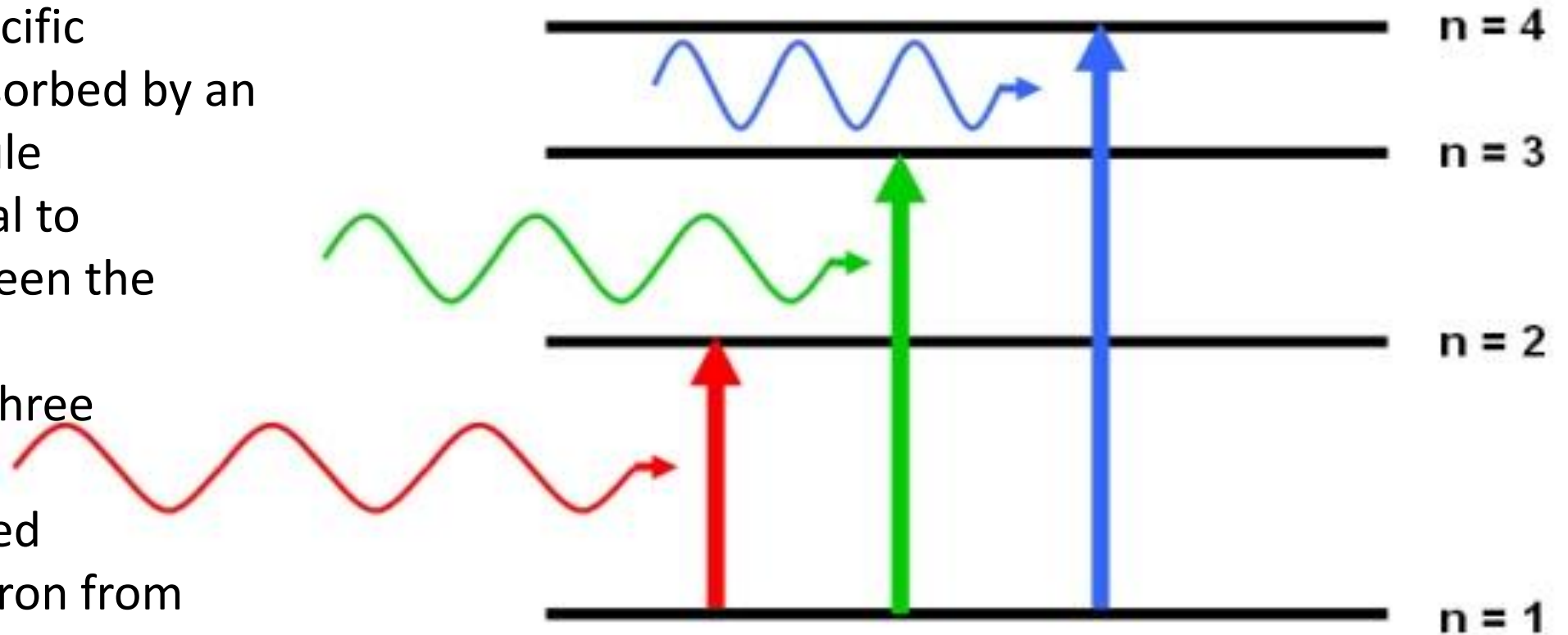
The light that leaves the cloud shows absorption lines in the spectrum at discrete frequencies.



According to **quantum mechanics**, an atom or molecule can absorb photons with energies equal to the difference between two energy states.

- Photons with specific energies will be absorbed by an atom, ion or molecule if this energy is equal to the difference between the energy levels.

- In this example, three different photon energies are required to promote an electron from the ground state ( $n=1$ ) to an excited state ( $n=2, 3$  and  $4$ )



# Absorption and Emission by Gas Molecules

When radiation interacts with matter it is absorbed, scattered, or emitted in discrete packets called **photons**. Each photon contains energy

$$E = h\nu = hc/\lambda \quad (4.21)$$

where  $h$  is Planck's constant ( $6.626 \times 10^{-34}$  J s).

The **energy** carried by a **photon** is **inversely proportional to the wavelength of the radiation**.

A molecule may undergo a transition to a **higher energy level** by absorbing electromagnetic radiation and it may **drop to a lower level** by emitting radiation.

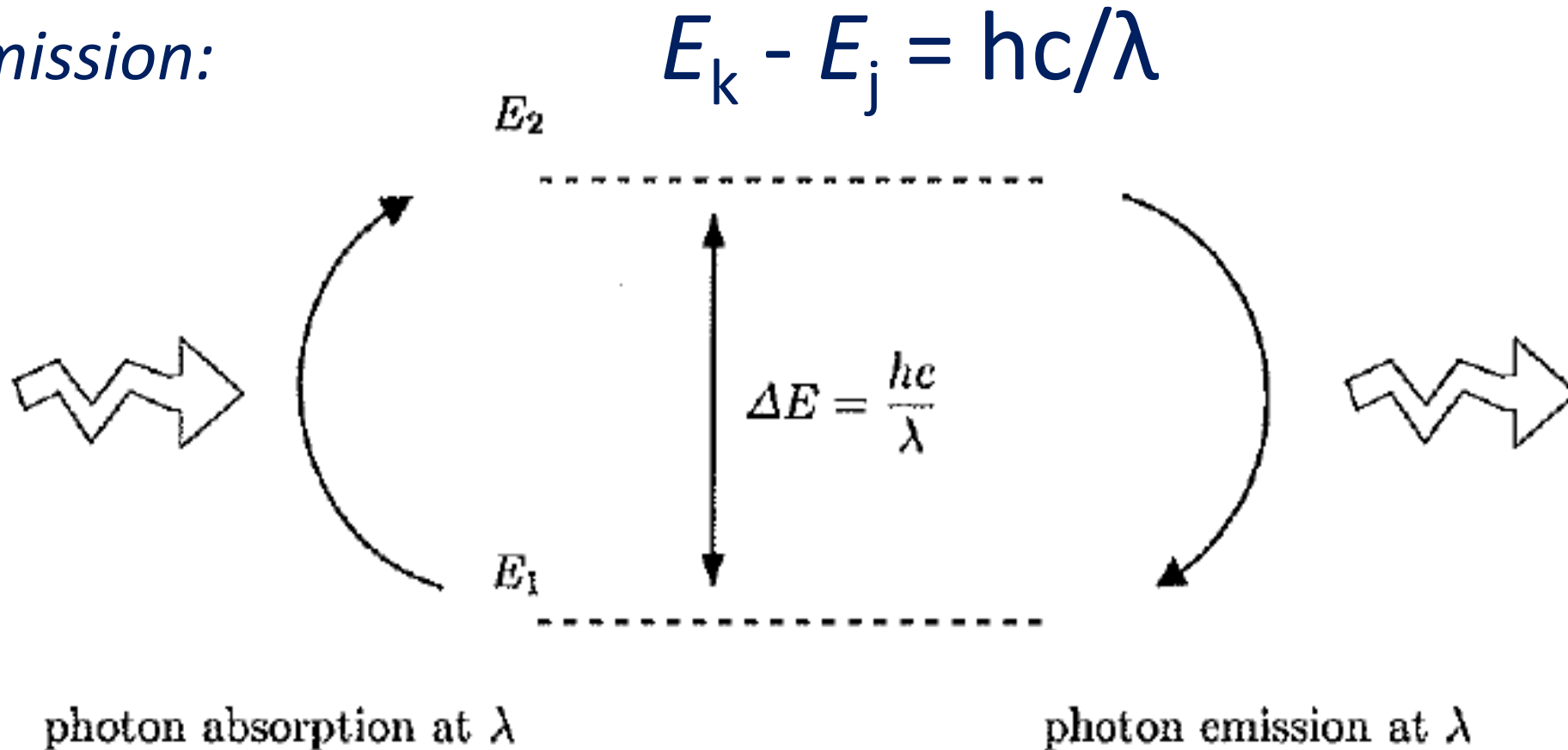
Absorption and emission can occur only in association with discrete changes in energy level  $\Delta E$ . The frequency of the absorbed or emitted radiation is related to the change in energy level through the relation

$$\Delta E = h\nu \quad (4.23)$$

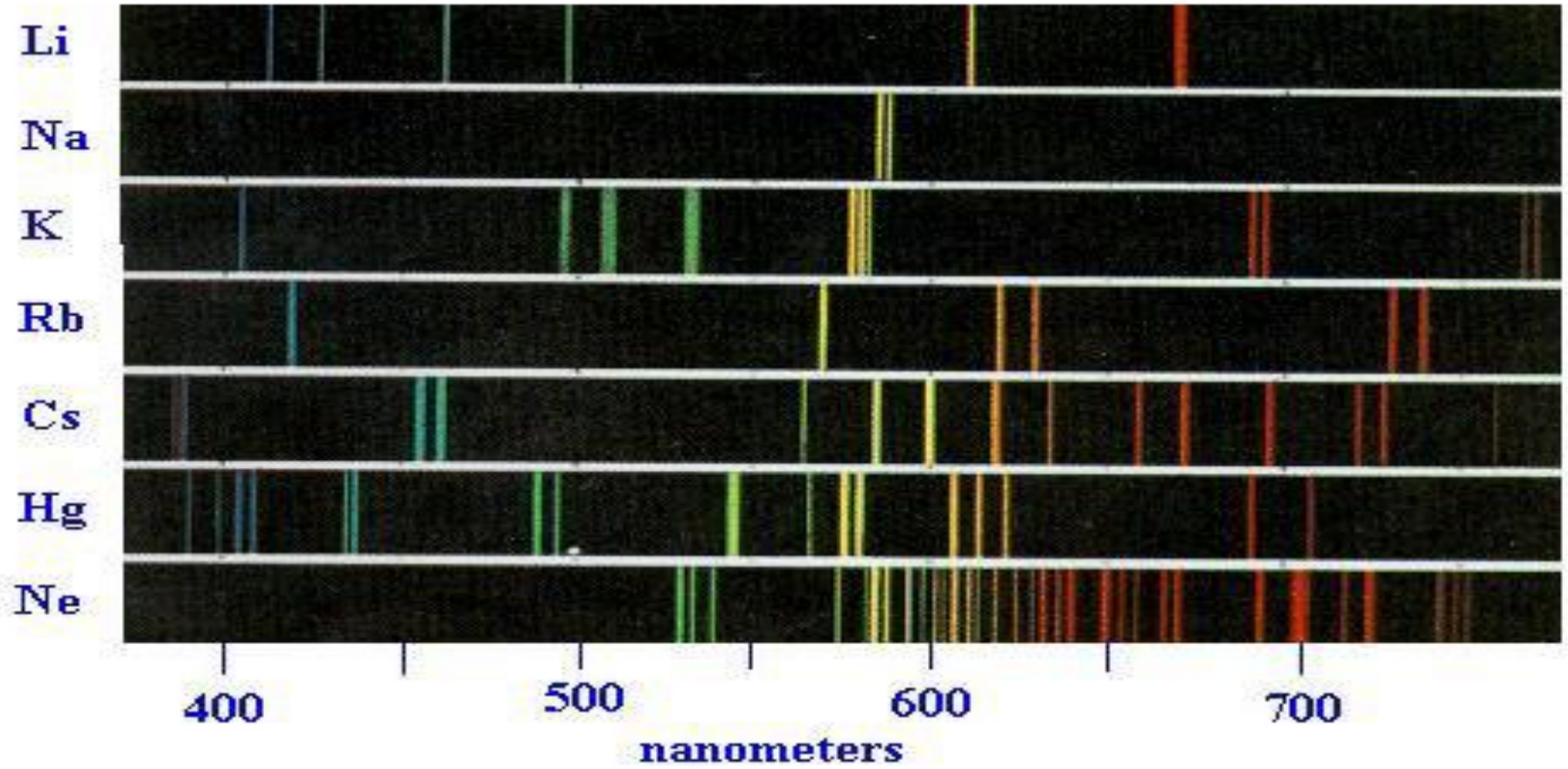
# Atomic absorption/emission spectra:

Radiation emission (absorption) occurs only when an electron makes a transition from one state with energy  $E_k$  to a state with lower (higher) energy  $E_j$ :

*for emission:*



## Black Body



Examples of atomic emission spectra

## Bohr's model of a hydrogen atom:

The energy level is given as

$$E_n = -\frac{R_H hc}{n^2}$$

$n=1,2,3$

where  $R_H$  is the Ryberg constant ( $=1.092 \times 10^5 \text{ cm}^{-1}$  for hydrogen);  $h$  is the Planck's constant, and  $c$  is the speed of light.

The wavenumber of emission/absorption lines of hydrogen atom:

$$\nu = R_H \left( \frac{1}{j^2} - \frac{1}{k^2} \right)$$

where  $j$  and  $k$  are integers defining the lower and higher energy levels, respectively.

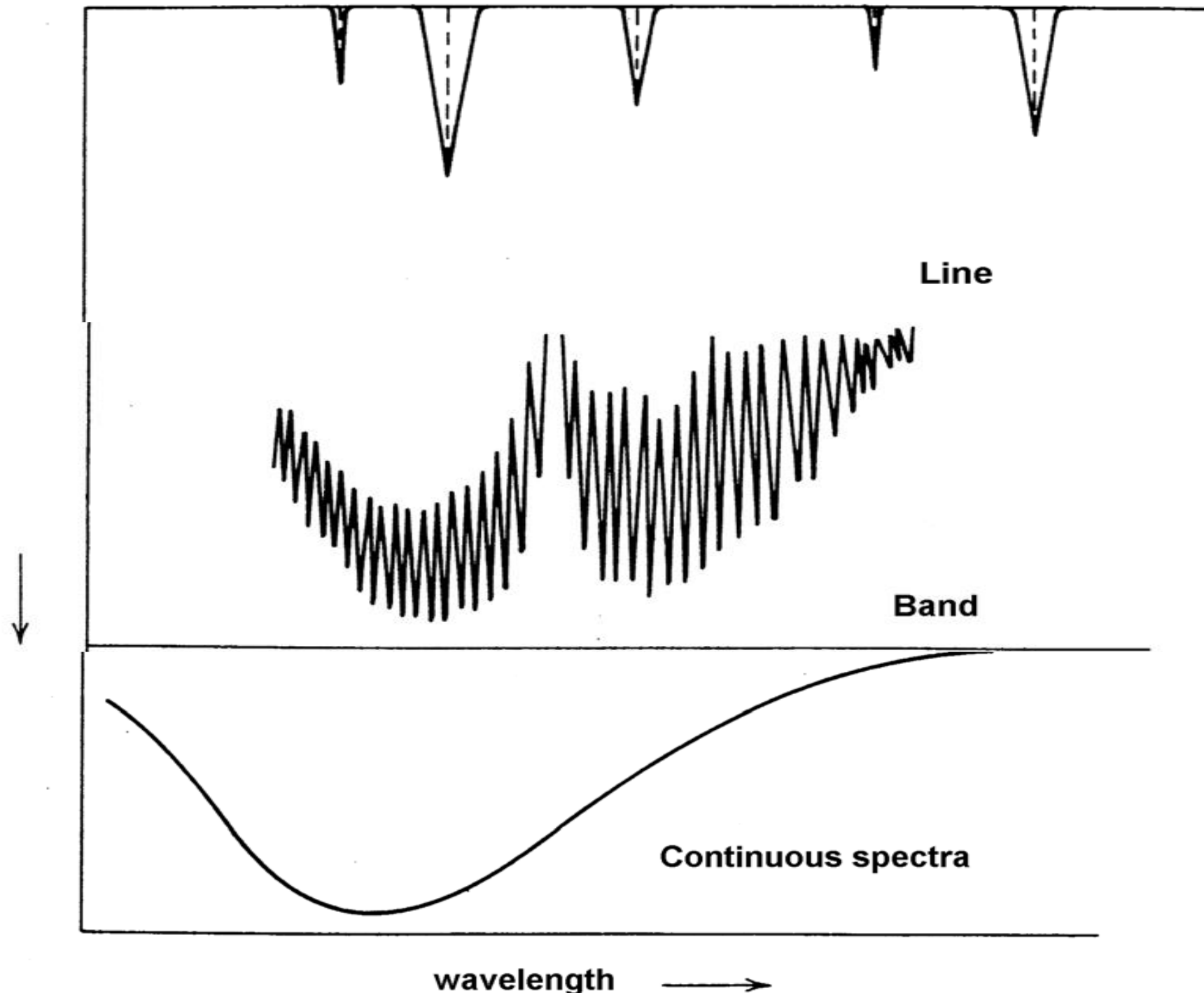
# Molecular Absorption/Emission Spectra

Molecular absorption spectrum is more complicated than that of an atom because molecules have several forms of internal energy. This is a subject of **spectroscopy** and **quantum theory**.

**Three types of absorption/emission spectra:**

- i) Sharp **lines** of finite widths
- ii) Aggregations (series) of lines called **bands**;
- iii) **Spectral continuum** extending over a broad range of wavelengths

Examples  
of the 3  
types of  
spectra





- Main underlying physical principles of molecular absorption/emission:

- 1) The origins of absorption/emission lie in exchanges of energy between gas molecules and electromagnetic field.
- 2) In general, total energy of a molecule can be given as:

$$E = E_{\text{rot}} + E_{\text{vib}} + E_{\text{el}} + E_{\text{tr}}$$

$E_{\text{rot}}$  is the kinetic energy of rotation (energy of the rotation of a molecule as a unit body): about  $1\text{-}500\text{ cm}^{-1}$  (in the far-infrared to microwave region)

$E_{\text{vib}}$  is the kinetic energy of vibration: energy of vibrating nuclei about their equilibrium positions; about  $500$  to  $10^4\text{ cm}^{-1}$  (in the near- to far-IR)

$E_{\text{el}}$  is the electronic energy: potential energy of electron arrangement; about  $10^4\text{-}10^5\text{ cm}^{-1}$  (in the UV and visible)

$E_{\text{tr}}$  is translation energy: exchange of kinetic energy between the molecules during collisions; about  $400\text{ cm}^{-1}$  for  $T = 300\text{ K}$

Quantum mechanics predicts that only certain configurations of electron orbits are permitted within each atom, and only certain vibrational frequencies and amplitudes and only certain rotation rates are permitted for a given molecular species. Each possible combination of electron orbits, vibration, and rotation is characterized by its own energy level, which represents the sum of the three kinds of energy.

The changes in state of molecules that give rise to these absorption lines may involve *orbital, vibrational, or rotational* transitions or combinations thereof.

*Orbital* transitions are associated with absorption lines in the *ultraviolet* and *visible* part of the spectrum; vibrational changes - with *near infrared* and *infrared* wavelengths; and *rotational* lines, which involve the smallest changes in energy, with *infrared* and *microwave* radiation.

The absorption spectra of the dominant species  $O_2$  and  $N_2$  exhibit a sparse population of absorption lines because these molecular species do not possess an electric dipole, even when they are vibrating. In contrast, so-called "greenhouse gases" (notably  $H_2O$ ,  $CO_2$ ,  $O_3$ , and trace species such as  $CH_4$ ,  $N_2O$ ,  $CO$  and chlorocarbons exhibit many closely spaced absorption lines in the infrared region of the spectrum that are due to pure rotational or simultaneous vibrational-rotational transitions.

# Broadening of absorption lines

The absorption lines of molecules are of **finite width** due to the inherent **uncertainty** (*Heisenberg*) in **quantizing** their energy levels, but this "natural broadening" is **small** in comparison to the broadening attributable to the motions and collisions of the gas molecules.

# What is the Heisenberg Uncertainty Principle

The Heisenberg Uncertainty Principle states that you can never simultaneously know the **exact position** and the **exact speed** of an object because everything in the universe behaves like both a particle and a wave at the same time

In **quantum mechanics**, the **uncertainty principle**, also known as **Heisenberg's uncertainty principle**, is any of a variety of mathematical inequalities asserting a fundamental limit to the precision with which certain pairs of physical properties of a particle, known as **complementary** variables, such as **position**  $x$  and **momentum**  $p$ , can be known simultaneously

Introduced first in 1927, by the German physicist Werner Heisenberg, it states that the more precisely the position of some particle is determined, the less precisely its momentum can be known, and vice versa. The formal inequality relates the standard deviation of position  $\sigma_x$  and the standard deviation of momentum  $\sigma_p$  ( $\hbar$  is the reduced Planck constant,  $h / 2\pi$ ).

From Wikipedia

$$\sigma_x \sigma_p \geq \frac{\hbar}{2}$$



# Spectral line shapes: Lorentz profile, Doppler profile

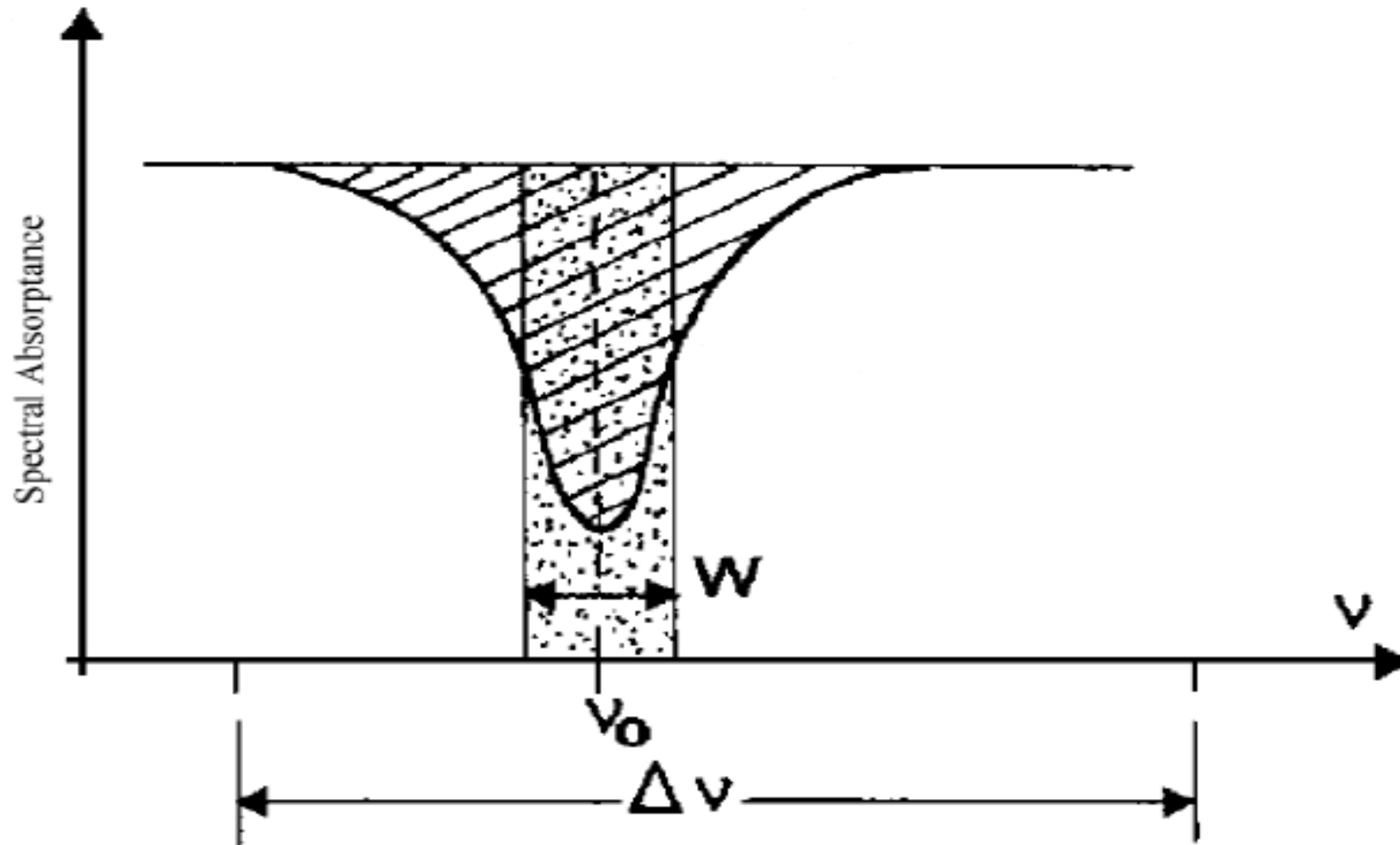
Three main factors define an absorption line: central position of the line, namely, the central frequency or the central wavenumber  $\nu_0$ , strength of the line (or intensity,  $S$ ), and shape factor (or line profile,  $f$ ).

- Each line has a finite width (referred to as **natural broadening of a spectral line**).
- In the atmosphere, several processes may result in an additional broadening of a spectral line of the molecules:
  - 1) collisions between molecules (referred to as the **pressure broadening**);
  - 2) due to the differences in the molecule thermal velocities (referred to as the **Doppler broadening**);
  - 3) the combination of the above processes.

**Lorentz profile** of a spectral line is used to characterize the **pressure broadening** and is defined as:

$$f_L(\nu - \nu_0) = \frac{\alpha / \pi}{(\nu - \nu_0)^2 + \alpha^2}$$

Where  $f(\nu - \nu_0)$  is the shape factor of a spectral line;  
 $\nu_0$  is the wavenumber of a central position of a line;  
 $\alpha$  is the **half-width of a line** at the half maximum (in  $\text{cm}^{-1}$ ),  
(often called the **line width**)



Schematic illustration of the equivalent width. The dotted rectangular area is equal to the hatched area and represents the total energy absorbed in the line.

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

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

where  $\alpha_0$  is the reference half-width for STP:  $T_0 = 273\text{K}$ ;  
 $P=1013 \text{ mb}$ .

$\alpha_0$  is in the range from **about 0.01 to 0.1  $\text{cm}^{-1}$**  for most atmospheric radiatively active gases. For most gases  $n=1/2$

The above **dependence on pressure** is very important because atmospheric pressure varies by an order of 3 from the surface to about 40 km.

- 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**) produce the larger 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.

**Doppler broadening** is the broadening of **spectral lines** due to the **Doppler effect** caused by a distribution of velocities of **atoms** or **molecules**. Different velocities of the **emitting** particles result in different Doppler shifts, the cumulative effect of which is the line broadening. This resulting line profile is known as a **Doppler profile**. A particular case is the **thermal Doppler broadening** due to the **thermal motion** of the particles. Then, the broadening depends only on the **frequency** of the spectral line, the **mass** of the emitting particles, and their **temperature**, and therefore can be used for inferring the temperature of an emitting body.

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

$$f_D(\nu - \nu_0) = \frac{1}{\alpha_D \sqrt{\pi}} \exp\left[-\left(\frac{\nu - \nu_0}{\alpha_D}\right)^2\right]$$

$\alpha_D$  is the **Doppler line width**

$$\alpha_D = \frac{\nu_0}{c} (2k_B T / m)^{1/2}$$



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

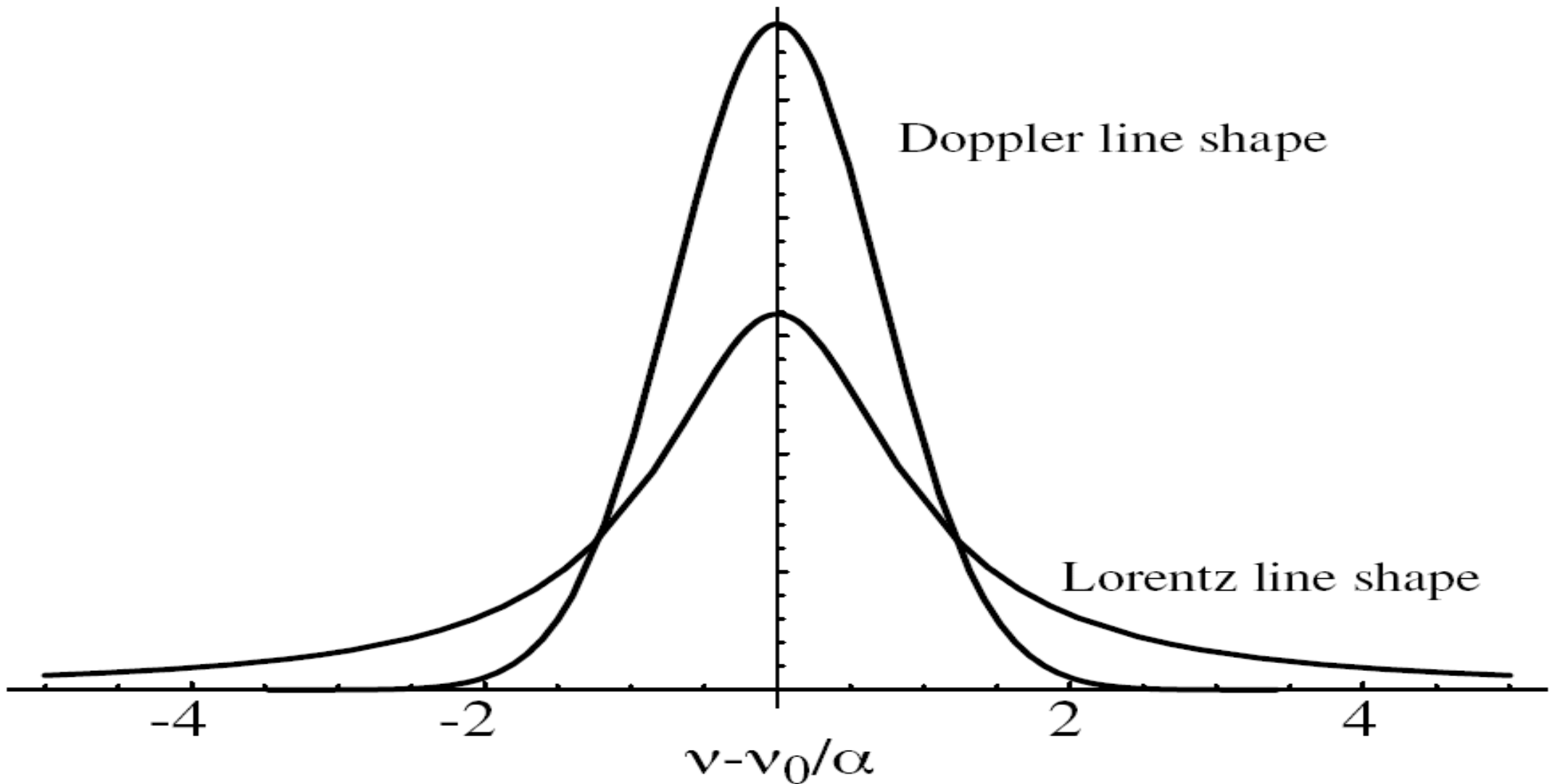
The Doppler half-width at the half maximum is

$$\alpha_D (\ln 2)^{1/2}$$

The Doppler effect comes from random molecular motions. If the molecule moves with the thermal velocity  $V$  and emits at the frequency  $\tilde{\nu}_0$ ,

it would appear that it emits at the frequency

$$\tilde{\nu} = \tilde{\nu}_0 \left( 1 \pm \frac{V}{c} \right)$$

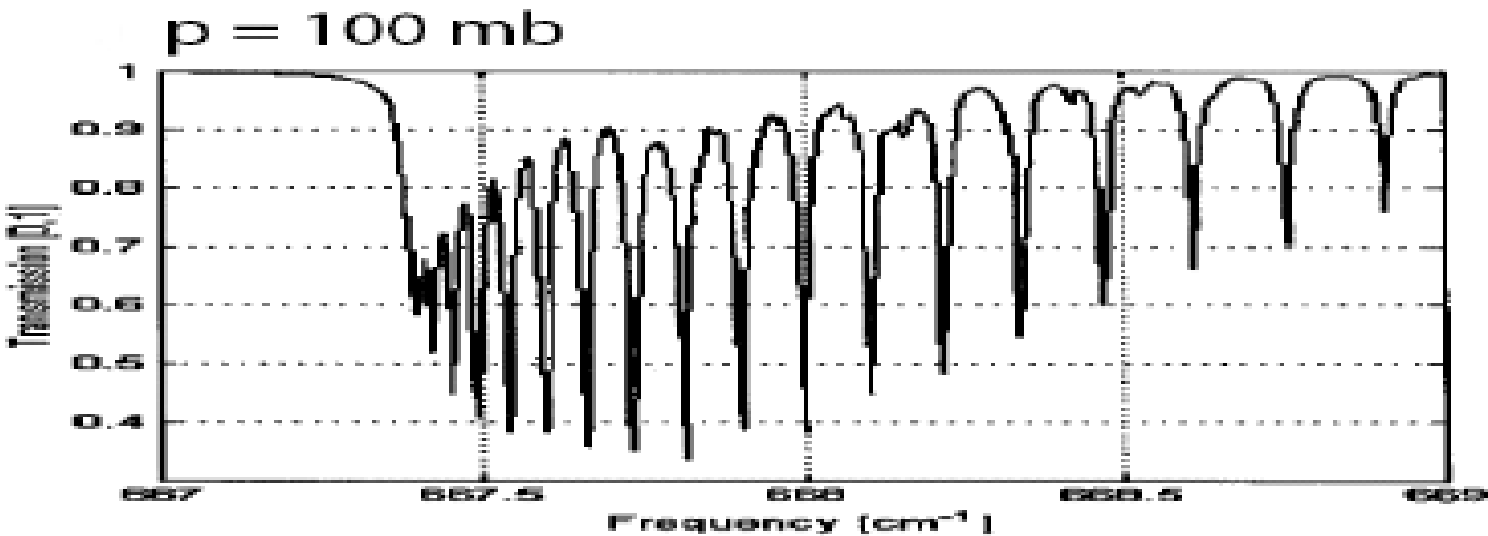
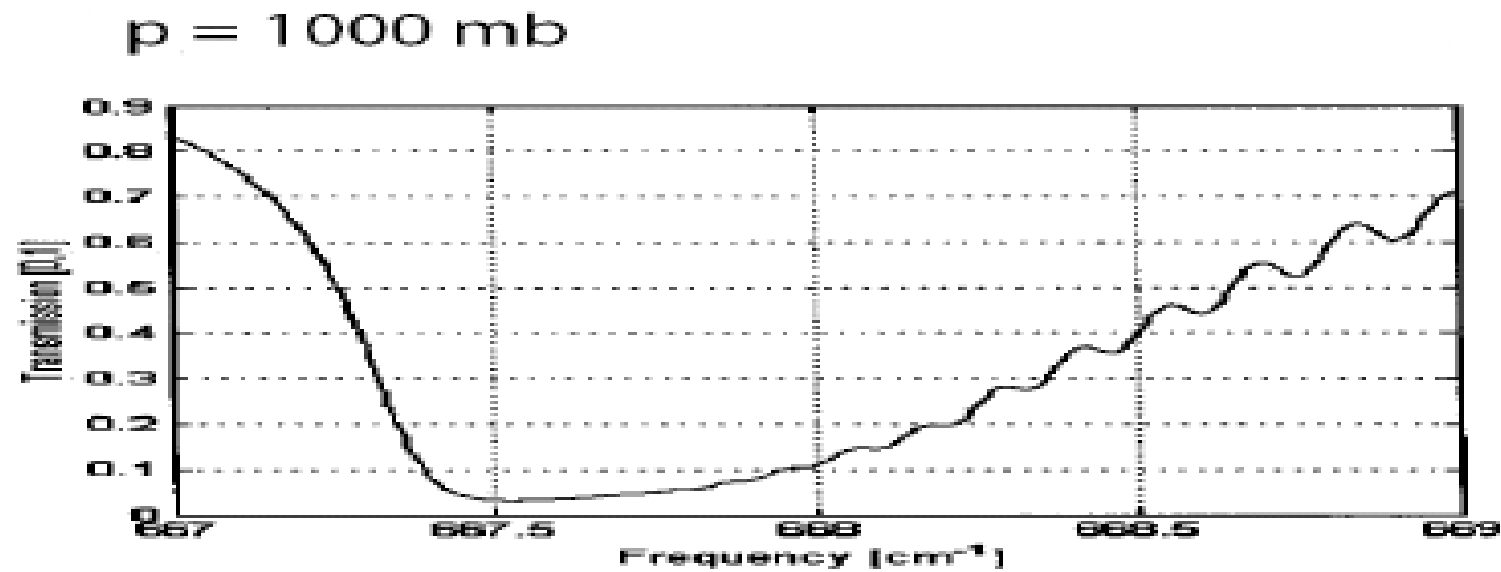


Comparison of the Doppler and Lorentz profiles  
(Figure 4.21 in textbook)

- Shapes of absorption lines broadened by these two distinctly different processes, are contrasted in Fig. 4.21.
- The "wings" of the absorption lines shaped by pressure broadening (Lorentz) extend out farther from the center of the line than those shaped by Doppler broadening.
- For a water vapor line at  $400 \text{ cm}^{-1}$  and a temperature of 300 K, the Doppler line width is  $7 \times 10^{-4} \text{ cm}^{-1}$ .

A typical water vapor line width for air at the same temperature at the Earth's surface is 100 times wider due to the presence of pressure broadening.

Below 20 km, pressure broadening is the dominant factor in determining the width of absorption lines, whereas above 50 km, where molecular collisions are much less frequent, Doppler broadening is the dominant factor. In the intermediate layer between 20 and 50 km, the line shape is a convolution of the Doppler and Lorentz shapes.



Example of high spectral resolution transmission spectra of a one meter path with typical CO<sub>2</sub> concentration at 1000 mb and 100 mb.

Laboratory measurements of absorption spectra exist for only a very limited sampling of pressures and temperatures.

Through the use of **theoretically derived absorption line information**, climate modelers are able to calculate the absorption spectra for each of the radiatively important atmospheric gases for any specified thermodynamic conditions.

An example showing the excellent agreement between observed and theoretically derived absorption spectra is shown in Fig. 4.22. Note the narrowness of the lines, even when the effects of Doppler and pressure broadening are taken into account. The **greatest uncertainties in theoretically derived absorption spectra are in the so-called "continua" where the superposition of the outermost parts of the wings of many different lines in nearby line clusters produces weak but in some cases significant absorption.**

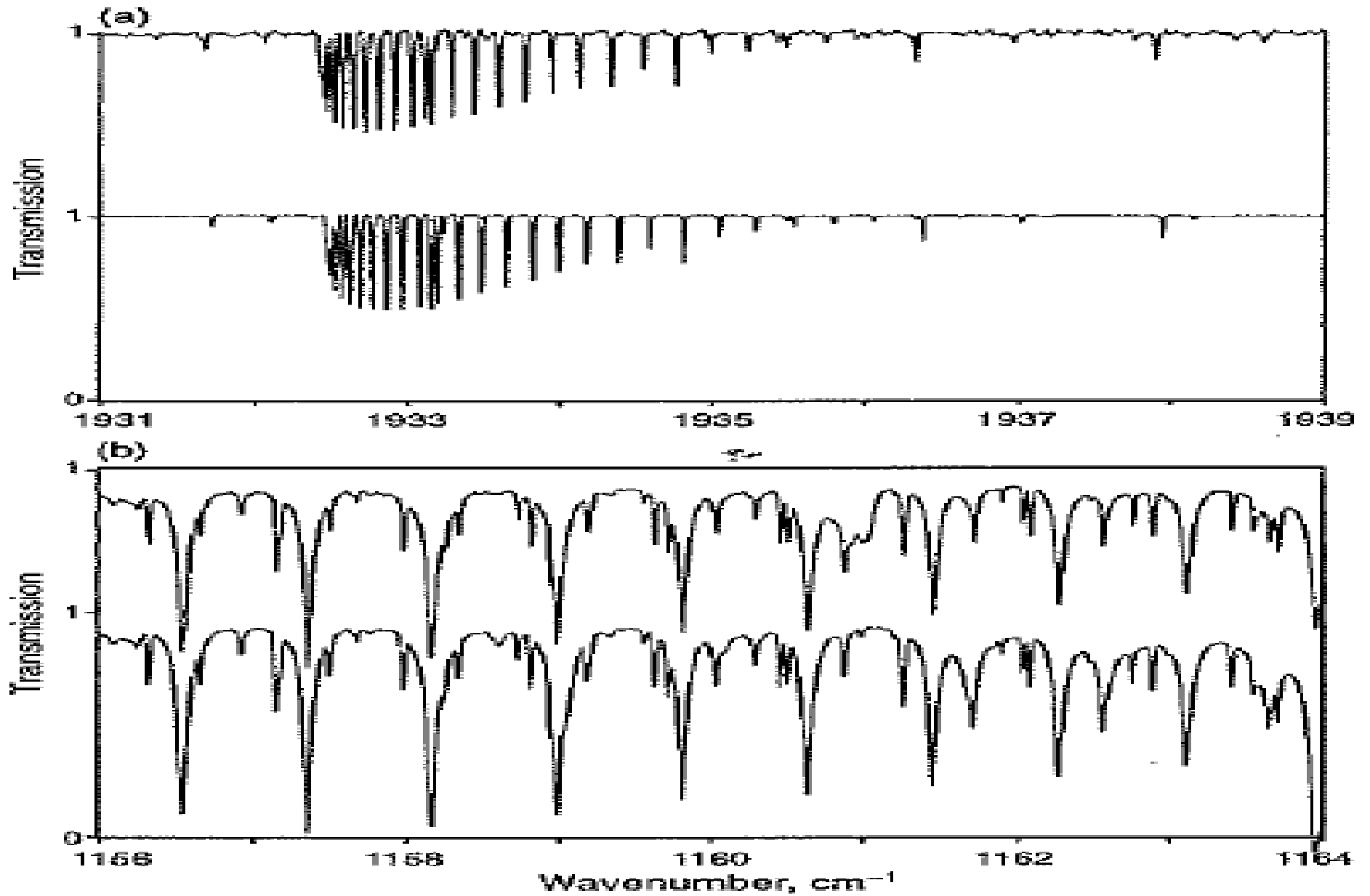


Figure 4.22 in textbook, see legend on next slide.



Fig. 4.22 Comparisons of observed and calculated transmissivity spectra:

(a) Spectral range 1931 to 1939  $\text{cm}^{-1}$  for carbon dioxide and

(b) Spectral range 1156 to 1164  $\text{cm}^{-1}$  for ozone and nitrous oxide.

The upper plot in each panel is the observed spectrum and the lower plot is the calculated spectrum.

From R. M. Goody, R. M. and Y. L. Yung, *Atmospheric Radiation*, 2nd ed., Oxford University Press (1995), p.120. By permission of Oxford University Press, Inc.

# Radiative Transfer in Planetary Atmospheres

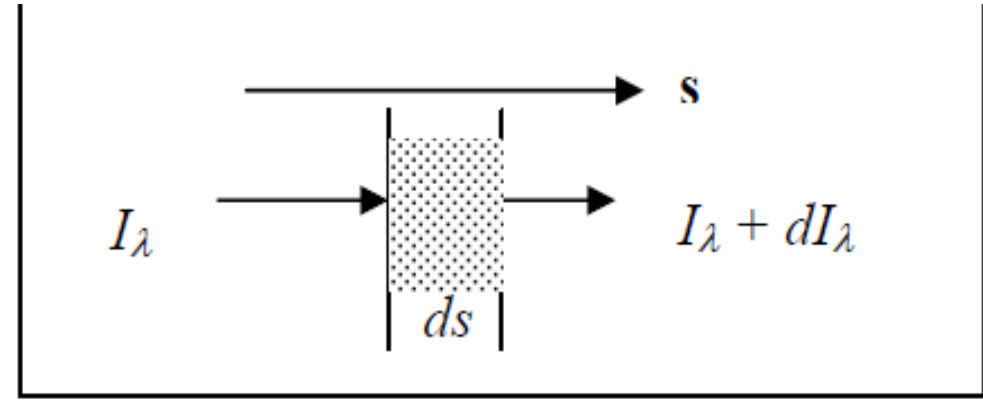
We have already discussed the case for shortwave radiation that led to the Beer's Law. Here, we will add discussion on the transfer of longwave radiation. For completeness (and refresher), we will present the essentials of the shortwave transfer .

The volume below  $\Delta v$  is of length  $\Delta s$  and area  $\Delta a$ . Previously, we have allowed only extinction in this volume represented as:

$$dI_\lambda = -\beta_{e,\lambda} I_\lambda ds$$

Now we allow also emission from the volume:

$$dI_\lambda = \beta_{e,\lambda} J_\lambda ds$$



Where  $\beta_{e,\lambda}$  is the volume extinction coefficient ( $\text{length}^{-1}$ ) and  $J_\lambda$  is the source function.

Extinction coefficient = absorption coefficient + scattering coefficient

$$\beta_{e,\lambda} = \beta_{a,\lambda} + \beta_{s,\lambda}$$

If  $\rho$  is the density (mass concentration) of given type of molecules, then:

$$\beta_{e,\lambda} = \rho k_{e,\lambda}$$

$$\beta_{s,\lambda} = \rho k_{s,\lambda}$$

$$\beta_{a,\lambda} = \rho k_{a,\lambda}$$

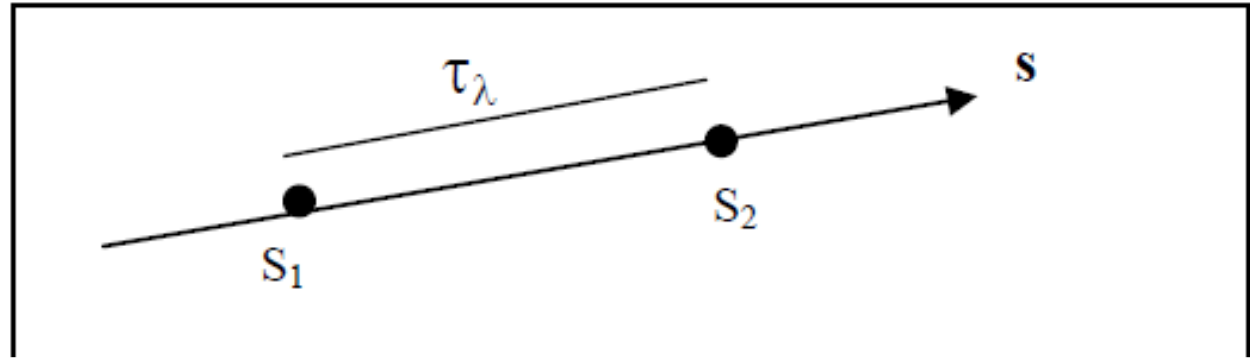
Using the mass extinction coefficient, the Beer law is given as:

$$dI_\lambda = -\rho k_{e,\lambda} I_\lambda ds$$

$$dI_\lambda = \rho k_{e,\lambda} J_\lambda ds$$

Optical depth of a medium between two points is:

$$\tau_{\lambda}(s_2; s_1) = \int_{s_1}^{s_2} \beta_{e,\lambda}(s) ds$$



If  $\beta_{e,\lambda}(s)$  does not depend on position then:

$$\beta_{e,\lambda}(s) = \beta_{e,\lambda} \text{ and } \tau_{\lambda}(s_2; s_1) = \beta_{e,\lambda}(s_2 - s_1) = \beta_{e,\lambda} s$$

and the Extinction Law (Beer's Law) becomes:

$$I_{\lambda} = I_0 \exp(-\tau) = I_0 \exp(-\beta_{e,\lambda} s)$$

## Differential form of the radiative transfer equation-the Schwarzschild's equation

Consider volume  $\Delta v$  of length  $\Delta s$  and area  $\Delta a$ . Previously, we have allowed only extinction in this volume and now we allow also emission, namely:

$$dI_\lambda = -\beta_{e,\lambda} I_\lambda ds + \beta_{e,\lambda} J_\lambda ds$$

dividing by  $\beta_{e,\lambda}(s)$ , we get:

$$\frac{dI_\lambda}{\beta_{e,\lambda} ds} = -I_\lambda + J_\lambda$$

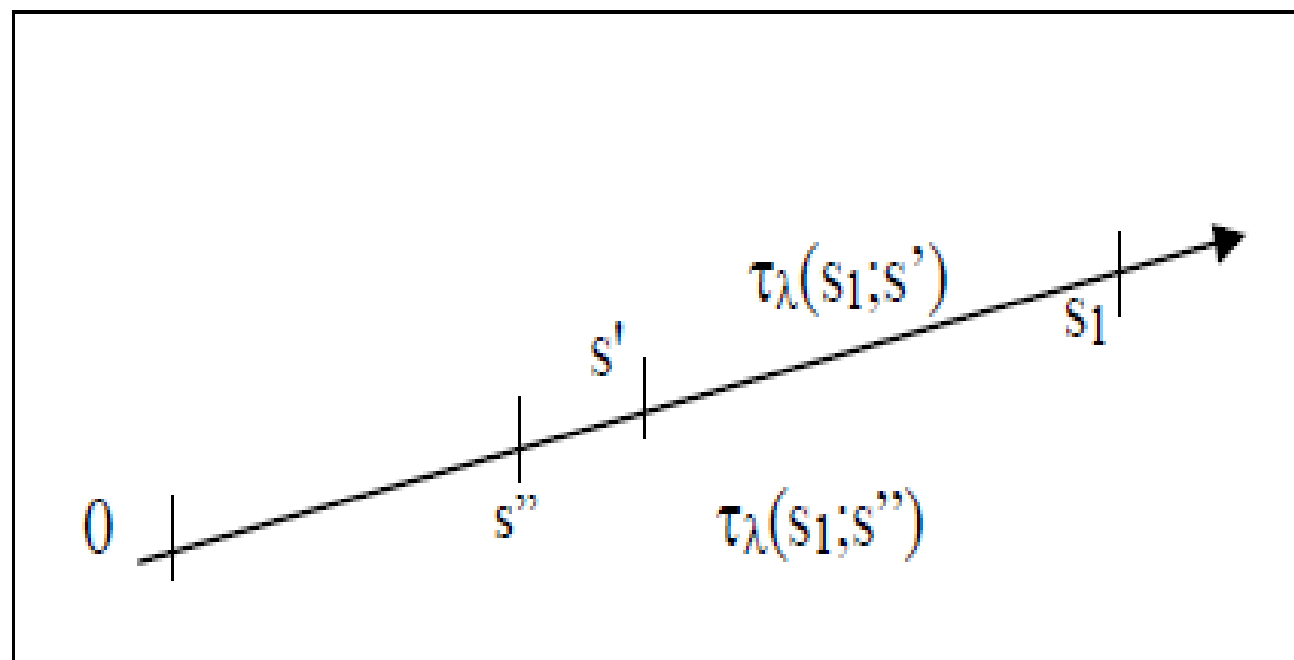
(1)

The optical depth is

$$\tau_{\lambda}(s_1; s) = \int_s^{s_1} \beta_{e,\lambda}(s) ds$$

Thus

$$d\tau_{\lambda} = -\beta_{e,\lambda}(s) ds$$



Using the above expression for the optical depth, we get:

After several manipulations of this equation, we get  
the **Schwarzchild's equation**

$$-\frac{dI_\lambda}{d\tau_\lambda} = -I_\lambda + J_\lambda$$

or as

$$\frac{dI_\lambda}{d\tau_\lambda} = I_\lambda - J_\lambda$$

(2)

$$I_\lambda(s_1) = I_\lambda(0) \exp(-\tau_\lambda(s_1; 0)) + \int_0^{s_1} \exp(-\tau_\lambda(s_1; s)) J_\lambda \beta_{e,\lambda} ds$$

Guidelines will be provided in homework # 3 how to get to this final format of the equation.