Lecture 7

Absorption/emission by atmospheric gases. Solar, IR and microwave spectra of main atmospheric gases .

Objectives:

1. Concept of a spectral line.

2. Basic principles of molecular emission/absorption.

3. Spectral line shapes:

  ➢ Lorentz profile

  ➢ Doppler profile

  ➢ Voigt profile

4. Beer-Bouguer-Lambert law. Gas absorption coefficient.

5. Absorption spectra of radiatively active atmospheric gases.

Required reading:

G 3.1-3.5

Advanced reading:

McCartney E.J. *Absorption and emission by atmospheric gases*. John Wiley&Sons, 1983.
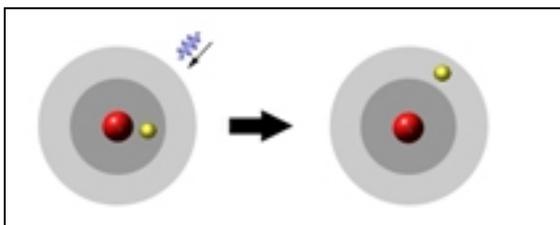
1. Concept of a spectral line.

Atomic Absorption (Emission) Spectrum.
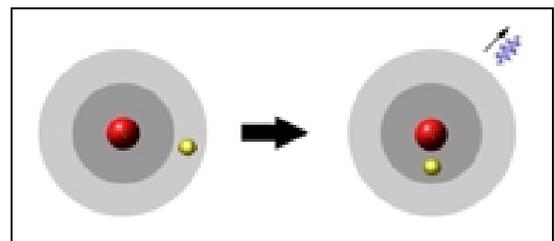
- Radiation emission (absorption) occurs only when an atom makes a transition from one state with energy E_k to a state with lower (higher) energy E_j:

$$\text{for emission:} \qquad E_k - E_j = hc\nu$$

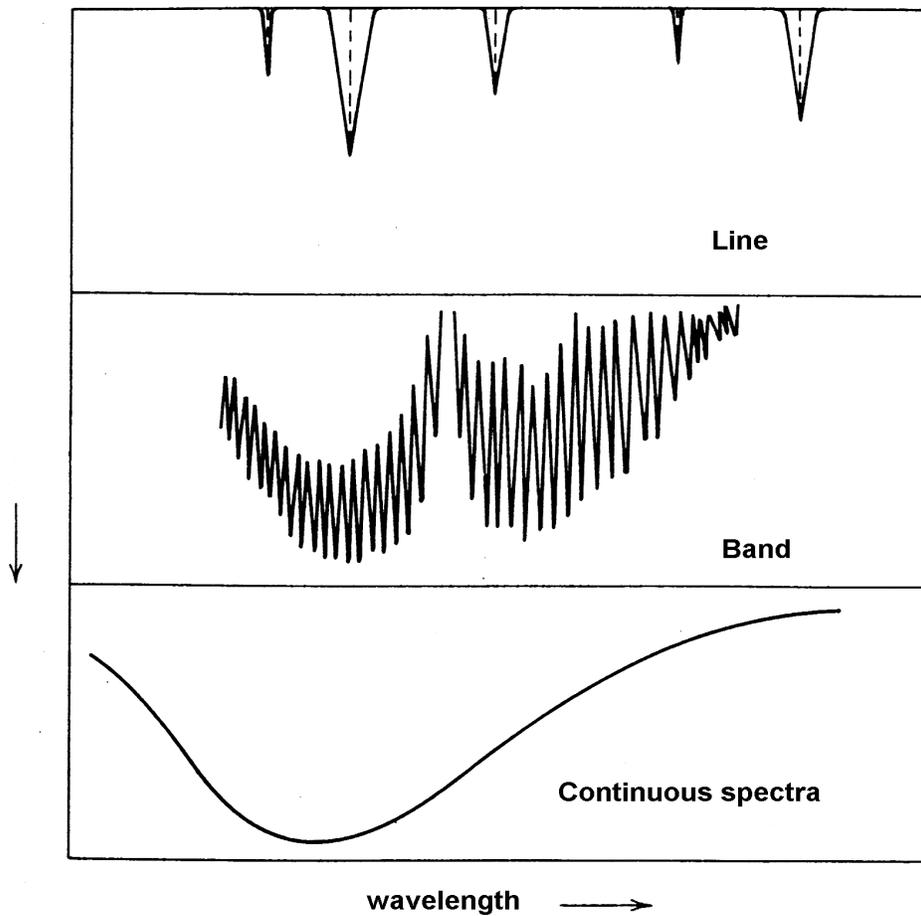Absorption   Emission

Molecular Absorption/Emission Spectra

Molecular absorption spectrum is substantially more complicated than that of an atom because molecules have several forms of internal energy. This is the 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

Figure 7.1 Concept of a line, band, and continuous spectra

2. Basic principles of molecular emission/absorption.

NOTE: The structure of molecules is important for an understanding of their energy forms (see Lecture 6):

- ✓ Linear molecules (CO_2, N_2O; C_2H_2, all diatomic molecules):
- ✓ Symmetric top molecules (NH_3, CH_3CL):
- ✓ Spherical symmetric top molecules (CH_4):
- ✓ Asymmetric top molecules (H_2O, O_3):

Review of 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:

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

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

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

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

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

- **From $E_{rot} < E_{tr} < E_{vib} < E_{el}$ follows that:**

i) Rotational energy change will accompany a vibrational transition. Therefore, vibration-rotation bands are often formed.

ii) Kinetic collisions, by changing the translation energy, influence rotational levels strongly, vibrational levels slightly, and electronic levels scarcely at all.

- **Energy E_{rot}, E_{vib}, and E_{el} are quantized** and have only discrete values specified by one or more **quantum numbers**. Not all transitions between quantized energy level are allowed - they are subject to selection rules.

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

(recall Table 6.2)

- If charges are distributed symmetrically => no permanent dipole moment => no radiative activity in the far-infrared (i.e., no transitions in rotational energy) Example: homonuclear diatomic molecules (N_2, O_2);

- O_2 has a weak permanent magnetic dipole and thus has a rotational transition in microwave.

- 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

4) Radiative transitions of vibrational energy require a change in the dipole moment (i.e., oscillating moment)

Figure 7.2 Vibrational modes of diatomic and triatomic atmospheric molecules (see also Figure 6.3)

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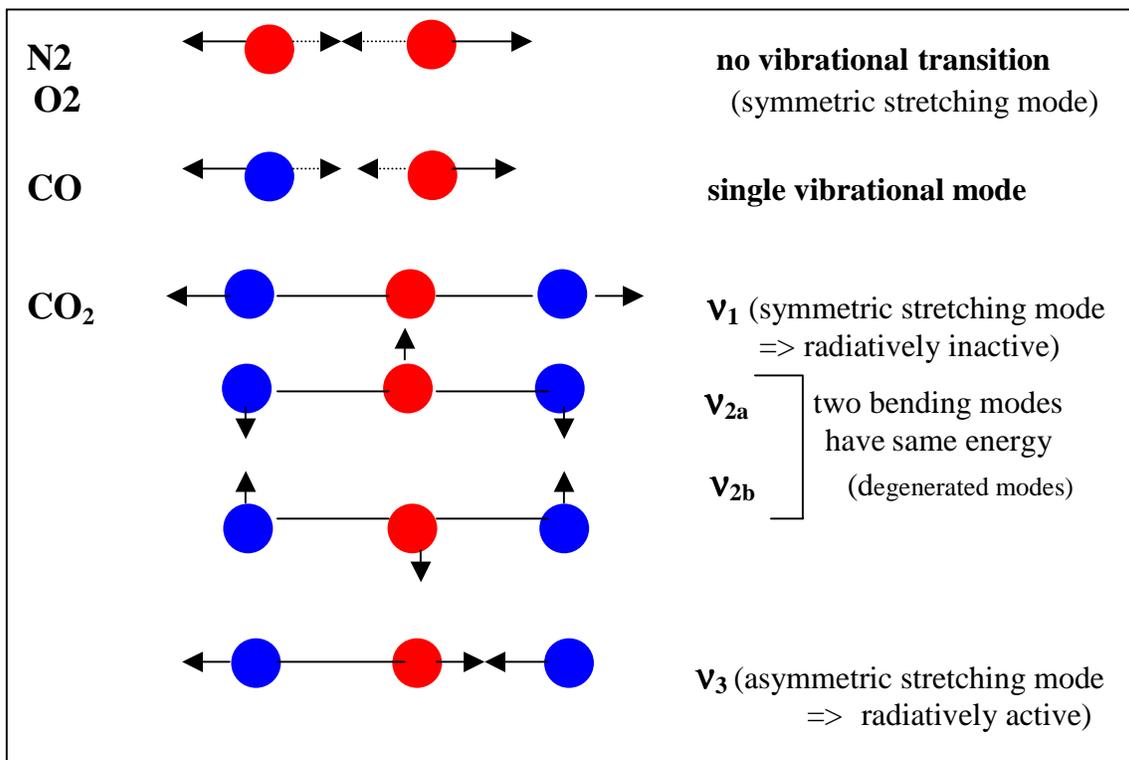
NOTE: Homonuclear diatomic molecules N_2 and O_2 don't have neither rotational nor vibrational transitions (because of their symmetrical structures) => no radiative activity in the infrared. But these molecules become radiatively active in UV.

NOTE: The number of independent vibrational modes of a molecule with N>2 atoms are 3N-6 for non-linear molecules and 3N-5 for a linear molecule. Both H_2O and O_3 have three normal band ν_1, ν_2 and ν_3: all are optically active.
CH_4 has nine normal modes but only ν_3 and ν_4 are active in IR.

5) Electronic transitions

- **Electrons on inner orbits** (close to the atomic nucleus) can be disturbed or dislodged only by photons having the large energies (short-wave UV and X-rays);
- **Electrons on the outermost orbits** can be disturbed by the photons having the energies of UV and visible radiation => these electrons are involved in absorption/emission in the UV and visible.
- Both an atom and a molecule can have the **electronic transitions**. Electronic transitions of a molecule are always accompanied by vibrational and rotational transitions and are governed by numerous selection rules.

2. Spectral line shapes: Lorentz profile, Doppler profile, and Voigt profile.

Three main properties that define an absorption line: central position of the line (e.g., the central frequency $\tilde{\nu}_0$ or wavenumber ν_0), strength of the line (or intensity, S), and shape factor (or profile, f) of the line.

- Each absorption line has a 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**); and 3) the combination of the above processes.

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

$$f_L(\nu - \nu_0) = \frac{\alpha / \pi}{(\nu - \nu_0)^2 + \alpha^2}$$ [7.1]

where $f(\nu - \nu_0)$ is the shape factor of a spectral line;

ν_0 is the wavenumber of a central position of a line;

α is the half-width of a line at the half maximum (in cm^{-1}), (often referred as a **line width**)

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

$$\alpha(P,T) = \alpha_0 \frac{P}{P_0}\left(\frac{T_0}{T}\right)^n$$ [7.2]

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. For most gases n=1/2.

NOTE: 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**) 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.

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

$$f_D(\nu - \nu_0) = \frac{1}{\alpha_D \sqrt{\pi}} \exp\left[-\left(\frac{\nu - \nu_0}{\alpha_D}\right)^2\right]$$ [7.3]

α_D is the **Doppler line width**

$$\alpha_D = \frac{\nu_0}{c}(2k_B T / m)^{1/2}$$ [7.4]

where c is the speed of light; k_B is the Boltzmann's constant, m is the mass of the molecule (for air m = 4.8×10^{-23}).

- The Doppler broadening is important at the altitudes from about 20 to 50 km.

Voigt profile is the combination of the Lorentz and Doppler profiles to characterize broadening under the low-pressure conditions (above about 40 km in the atmosphere). (i.e., it is required because the collisions (pressure broadening) and Doppler effect can not be treated as completely independent processes:

$$f_{Voigt}(\nu - \nu_0) = \int_{-\infty}^{\infty} f_L(\nu' - \nu_0) f_D(\nu - \nu') d\nu' =$$

$$\frac{\alpha}{\alpha_D \pi^{3/2}} \int_{-\infty}^{\infty} \frac{1}{(\nu' - \nu_0')^2 + \alpha^2} \exp\left[-\left(\frac{\nu - \nu'}{\alpha_D}\right)^2\right] d\nu'$$ [7.5]

NOTE: The Voigt profile requires numerical calculations.

Nature of the Voigt profile:
- At high pressure: the Doppler profile is narrow compare to the Lorentz profile so under these conditions the Voigt profile is the same as Lorentz profile.
- At low pressure: the behavior is more complicated – a kind of hybrid line with a Doppler center but with Lorentz wings.

## 3. Beer-Bouguer-Lambert law. Gas absorption coefficient.

The fundamental law of extinction is the **Beer-Bouguer-Lambert law,** which states that the extinction process is linear in the intensity of radiation and amount of matter, provided that the physical state (i.e., T, P, composition) is held constant.

Consider a small volume ΔV of infinitesimal length ds and unit area ΔA containing optically active matter (gases, aerosols, and/or cloud drops). Thus, the change of intensity along a path ds is proportional to the amount of matter (number concentration) in the path.

For extinction
$$dI_\lambda = -k_{e,\lambda} I_\lambda ds \qquad [7.6]$$

For emission:
$$dI_\lambda = k_{e,\lambda} J_\lambda ds$$
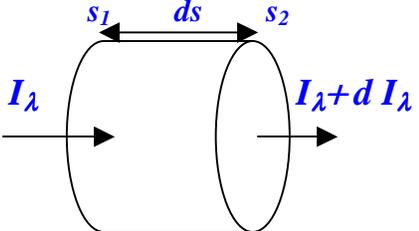
where $\kappa_{e,\lambda}$ is the **volume extinction coefficient** (LENGTH^{-1}) and J_λ is the **source function**.

NOTE: In general, the source function is due to emission and scattering, where as extinction is due to absorption and scattering (see Lecture 3).

Integrating Eq.[7.6], we have

$$I_{s2,\lambda} = I_{s1,\lambda} \exp\left(-\int_{s1}^{s2} k_{e,\lambda}(s)ds\right) = I_{s1,\lambda} \exp(-\tau_\lambda) \qquad [7.7]$$

where $I_{s1,\lambda}$ and $I_{s2,\lambda}$ are the incident and transmitted intensities, respectively.

Optical depth along the path s is defined as

$$\tau_\lambda = \int_{s_1}^{s_2} k_{e,\lambda}(s)ds \qquad [7.8]$$

UNITS: optical depth is unitless.

NOTE: "same name": **optical depth = optical thickness = optical path**

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Transmission function is defined as

$$T_\lambda = \exp(-\tau_\lambda)$$ [7.9]

UNITS: transmission function is unitless (between 0 and 1)

- In general, the extinction coefficient is a sum of the absorption coefficient and scattering coefficient of gases and particulates.

NOTE: scattering by gases and scattering and absorption by particulates will be discussed in Lecture 9.

Absorption coefficient of a gas is defined by the position, strength, and shape of a spectral line:

$$k_{a,\nu} = S f(\nu - \nu_0)$$ [7.10]

where **S** in the line intensity and f is the line profile:

$$S = \int k_{a,\nu} d\nu \qquad \text{and} \qquad \int f(\nu - \nu_0) d\nu = 1$$

*Dependencies***:**

S depends on **T;**

$f(\nu - \nu_0, \alpha)$ depends on the line halfwidth α **(p, T),** which depends on pressure and temperature.

- **Because the amount of an absorbing gas may be expressed in a number of possible ways (e.g., molecules per unit volume, mass of molecules per unit volume, etc.), different kinds of absorption coefficient may be introduced is such a way that the optical depth remains unitless. Introducing a path length (or amount of gas), *u*, we have**

$$\tau_\nu = \int_{u_1}^{u_2} k_{a,\nu} du$$ [7.11]

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Most commonly used absorption coefficients:

$k_{a,v}$ Volume absorption coefficient (in LENGTH^{-1})

$k_{m,a,v}$ Mass absorption coefficient (in LENGTH^2/MASS)

$k_{cs,a,v}$ Absorption cross section (in LENGTH^2)

Mass absorption coefficient = volume absorption coefficient/density

Absorption cross section = volume absorption coefficient/number concentration

Thus, optical depth can be expressed in several ways

$$\tau_v(s_1, s_2) = \int_{s_1}^{s_2} k_{a,v} \, ds = \int_{s_1}^{s_2} \rho k_{m,a,v} \, ds = \int_{s_1}^{s_2} N k_{cs,a,v} \, ds \qquad [7.12]$$

Table 7.1 Units used for path length, absorption coefficient, and line intensity (for Eqs.[7.10] - [7.12])

Absorbing gas (path length u)	Absorption coefficient	Line intensity (S)
cm	cm^{-1}	cm^{-2}
g cm^{-2}	cm^2 g^{-1}	cm g^{-1}
cm^{-2}	cm^2	cm
cm atm	(cm atm)$^{-1}$	cm^{-2} atm^{-1}

Units of the line profile, f: LENGTH (often cm)

4. Absorption spectra of main atmospheric gases (H_2O, CO_2, O_3, CH_4, N_2O, CFCs).

- Each atmospheric gas has a specific absorption/emission spectrum – its own radiative signature. HITRAN is a main spectroscopic data base that contains information (e.g., intensity and half-width) for a total of about 1,080,000 spectral lines for 36 different molecules.

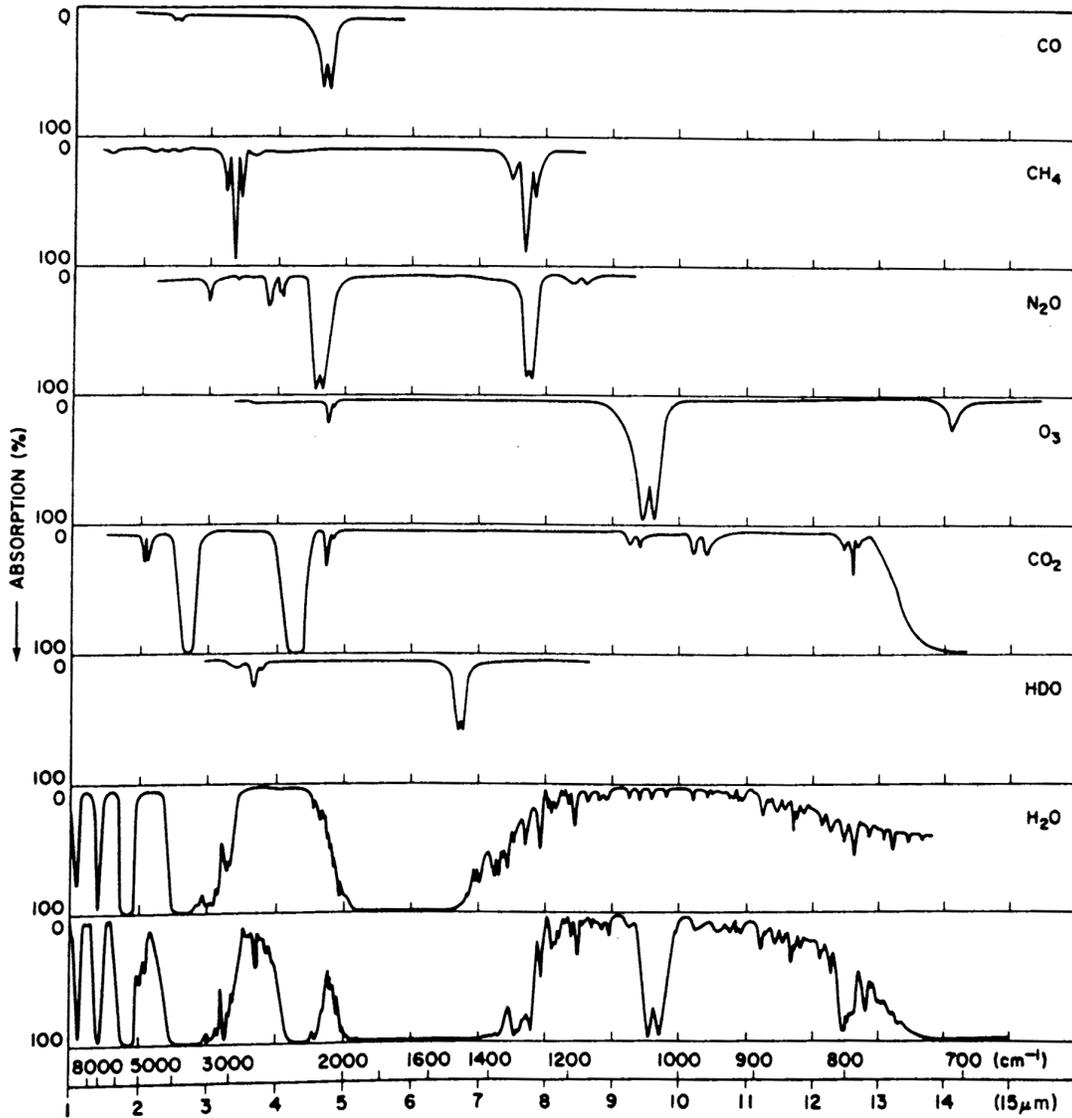| Molecule	Absorption line (Frequency, GHz)
H_2O	22235; 183.3
O_2	about 60; 118.75

(see Figure 3.4)

➢ **Thermal IR region**

Figure 7.3 Low-resolution IR absorption spectra of the major atmospheric gases.

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})
H_2O	-	pure rotational	0-1000
	1594.8 (6.3)	ν_2; P, R	640-2800
	continuum*	far wings of the strong lines; water vapor dimmers $(H_2O)_2$	200-1200
CO_2	667 (15)	ν_2; P, R, Q	540-800
	961 (10.4)	overtone and	850-1250
	1063.8 (9.4)	combination	
	2349 (4.3)	ν_3; P, R overtone and combination	2100-2400
O_3	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
CH_4	1306.2 (7.6)	ν_4	950-1650
N_2O	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 distant wings of lines in the far infrared. This absorption is caused by collision broadening between H_2O molecules (called **self-broadening**) and between H_2O and non-absorbing molecules (N2) (called **foreign broadening**).

➤ **Near-IR and visible regions**

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

NOTE: Atmospheric gases absorb only a small fraction of visible radiation.
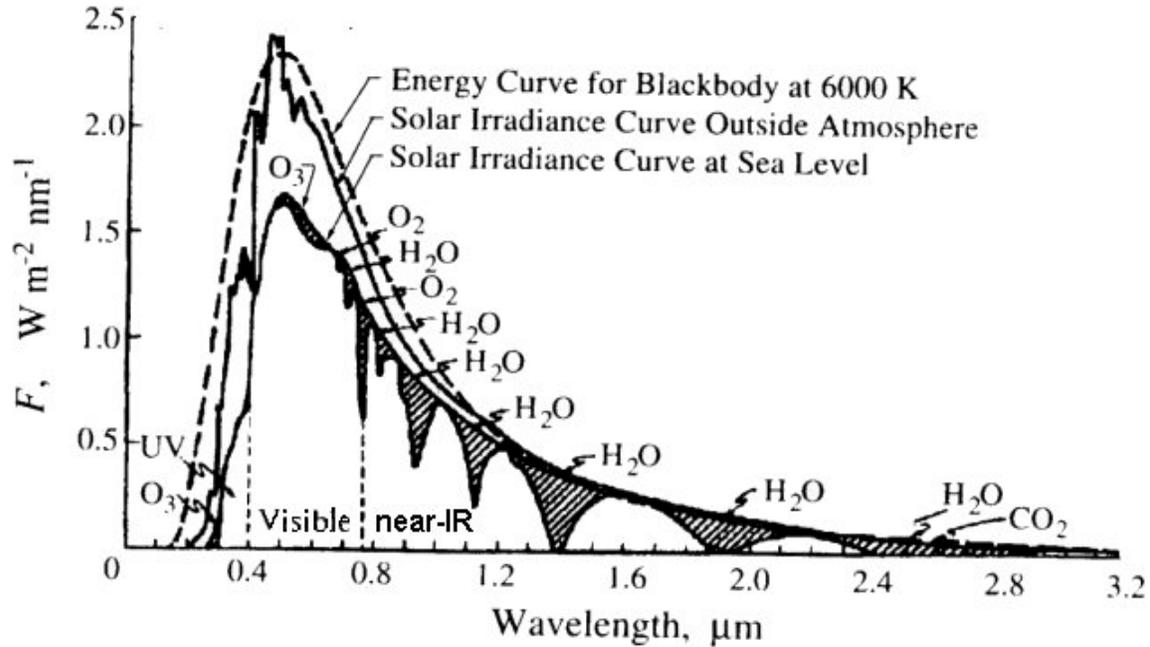

Figure 7.4 Solar spectral irradiance (flux) at the top of the atmosphere and at the surface.

Table 7.3 Wavelengths of absorption in the solar spectrum (UV + visible) by several atmospheric gases

Gas	Absorption wavelengths (μm)
N_2	< 0.1
O_2	< 0.245
O_3	0.17-0.35
	0.45-0.75
H_2O	< 0.21
	0.6-0.72
H_2O_2 hydrogen peroxide	< 0.35
NO_2 nitrogen oxide	< 0.6*
N_2O	< 0.24
NO_3 nitrate radical	0.41-0.67
HONO nitrous acid	< 0.4
HNO_3 nitric acid	< 0.33
CH_3Br methyl bromide	< 0.26
$CFCl_3$ (CFC11)	< 0.23
HCHO formaldehyde	0.25-0.36

* **NO_2** absorb at $\lambda < 0.6$ μm, but photodissociate at $\lambda < 0.4$ μm

➢ **UV region**

Absorption of UV radiation in the gaseous atmosphere is primarily due molecular oxygen O_2 and ozone O_3.
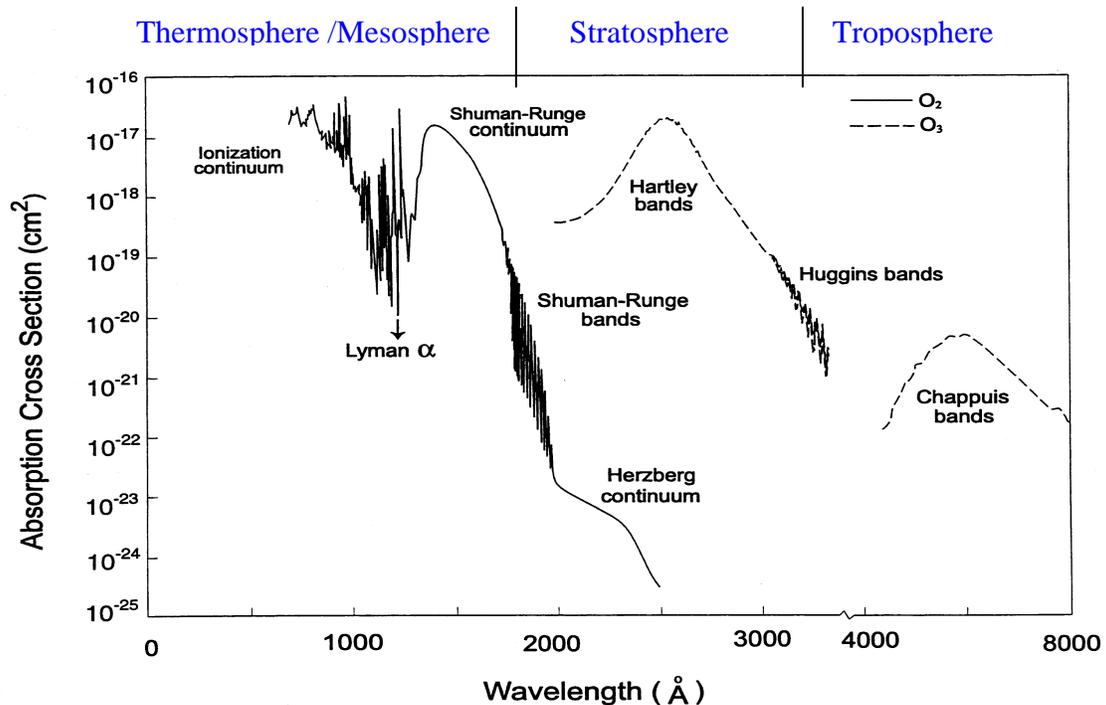

Figure 7.5 Spectral absorption cross-sections of O_2 and O_3

NOTE:

a) Bands of O_2 and O_3 at wavelengths < 1 μm are electronic transitions.

b) These absorption bands are relatively uncomplicated continua because practically all absorption results in dissociation of the molecule (so the upper state is not quantized);

c) Despite the small amount of O_3, no solar radiation penetrates to the lower atmosphere at wavelengths < 310 nm (because of large absorption cross-sections of O_3);

- To avoid very complicated calculations of electronic transitions, numerous measurements of the **absorption cross-sections** of the atmospheric atoms and molecules absorbing in the UV and visible have been performed in laboratory experiments. In general, the absorption cross section varies with temperature.