

Lecture 5

Terrestrial infrared radiative processes. Part 1:

Gaseous absorption/emission: Concepts of a spectral line. Line shapes.

Absorption coefficient and transmission function. IR spectra of main atmospheric gases.

Objectives:

1. Concept of a spectral line:
 - Atomic absorption (emission) spectrum.
 - Molecular absorption (emission) spectrum.
2. Spectral line shapes:
 - Lorentz profile
 - Doppler profile
 - Voigt profile
3. Absorption coefficient and transmission function.
4. IR absorption spectra of radiatively active atmospheric gases.

Required reading:

L80: 1.3; 4.1; 4.2;

Recommended/advanced reading:

Le93: 5-8/ G&Y: 3, 5

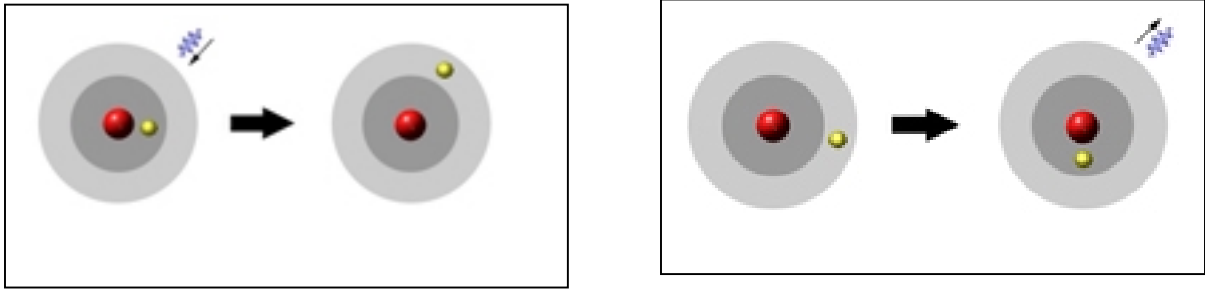
1. Concept of a spectral line.

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 :

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

Figure 5. 1 Absorption/Emission processes



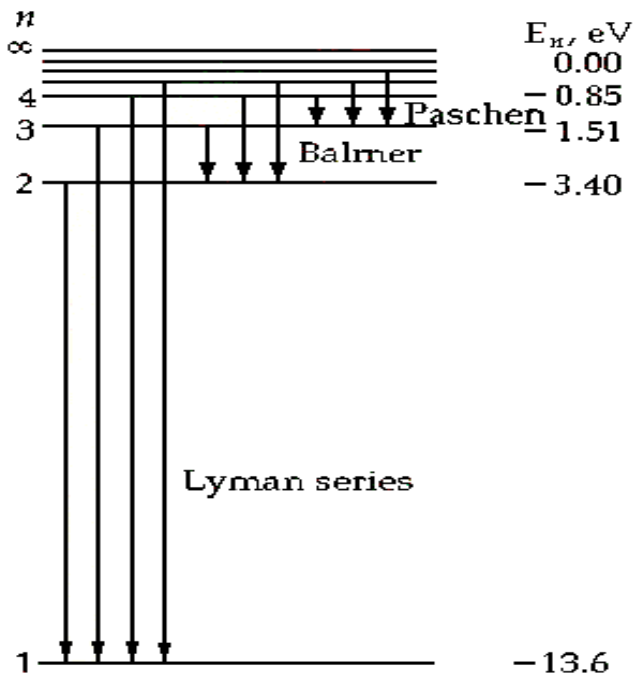
Hydrogen atom:

- The energy level is given as $E_n = - R_H h c / n^2$
 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.

Figure 5.2 Energy level diagram for the hydrogen atom.



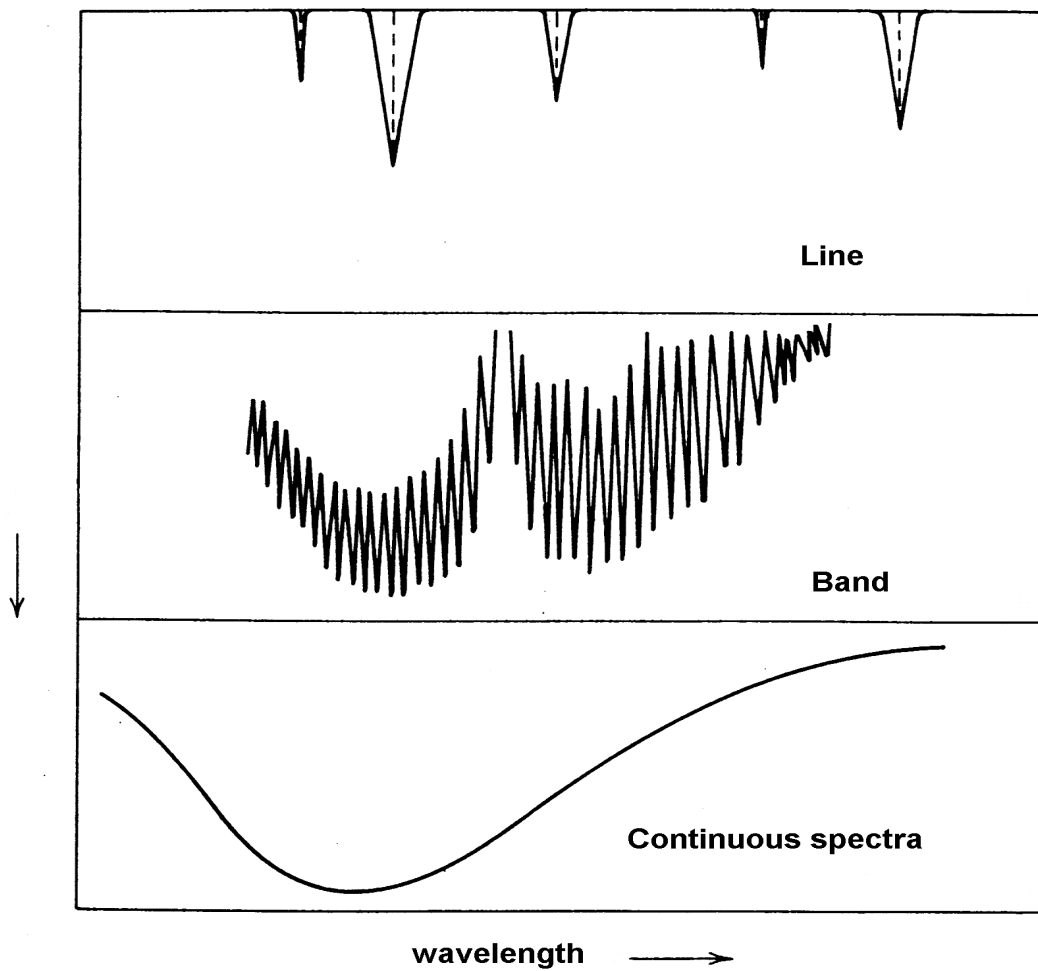
Molecular Absorption/Emission Spectra

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 5.3 Concept of a line, band, and continuous spectra



NOTE: The structure of molecules is important for an understanding of their energy forms:

Linear molecules (CO₂, N₂O; C₂H₂, all diatomic molecules):

Symmetric top molecules (NH₃, CH₃CL):

Spherical symmetric top molecules (CH₄):

Asymmetric top molecules (H₂O, O₃):

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:

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

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 nuclei about their equilibrium positions; about 500 to 10⁴ cm⁻¹ (near- to far-IR)

E_{el} is the electronic energy: potential energy of electron arrangement; about 10⁴-10⁵ 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.

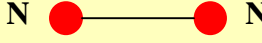
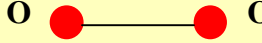
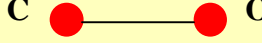
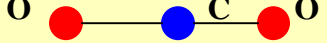

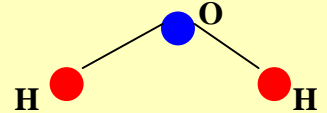
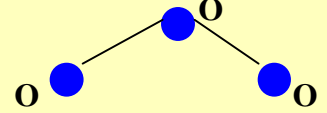
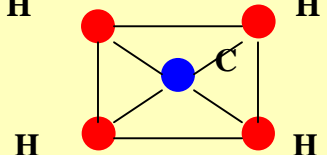
ii) Kinetic collisions, by changing the translation energy, influence rotational levels strongly, vibrational levels slightly, and electronic levels scarcely at all.

• **Energy E_{rot}, E_{vib}, and E_{el} are quantized** and have only discrete values specified by one or more **quantum numbers** (see below). 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.

NOTE: A dipole is represented by centers of positive and negative charges Q separated by a distance d : the dipole moment = $Q d$

Table 5.1 Atmospheric molecule structure and dipole moment status.

Molecule	Structure	Permanent dipole moment	May acquire dipole moment
N ₂		No	No
O ₂		No	No
CO		Yes	Yes
CO ₂		No	Yes (in two vibrational modes)
N ₂ O		Yes	Yes
H ₂ O		Yes	Yes
O ₃		Yes	Yes
CH ₄		No	Yes (in two vibrational modes)

NOTE: If charges are distributed symmetrically => no permanent dipole moment => no radiative activity in the far-infrared (i.e., no transitions in rotational energy)

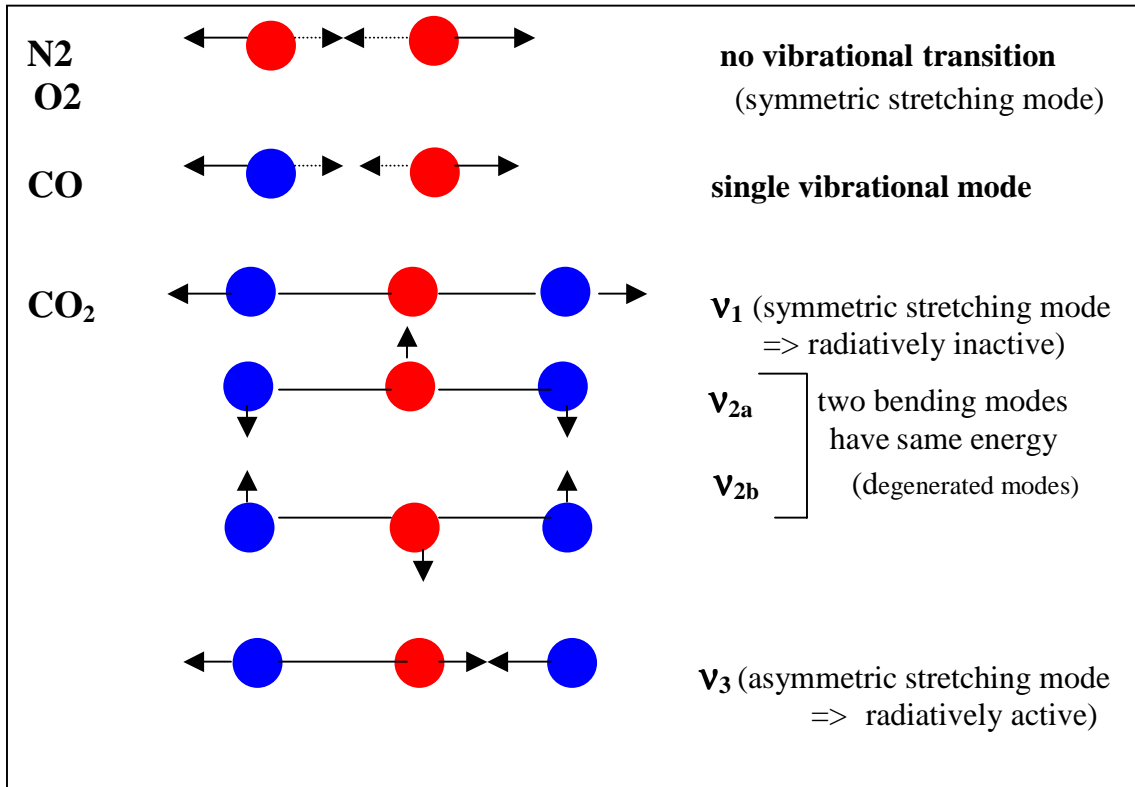
Example: homonuclear diatomic molecules (N₂, O₂);

NOTE: CO₂ and CH₄ 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

NOTE: CO, N₂O, H₂O and O₃ exhibit pure rotational spectra.

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

Figure 5.4 Vibrational modes of diatomic and triatomic atmospheric molecules.



NOTE: Homonuclear diatomic molecules **N₂** and **O₂** 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 (called **normal modes**) of a molecule with $N > 2$ atoms are $3N - 6$ for non-linear molecules and $3N - 5$ for a linear molecule.

NOTE: Both **H₂O** and **O₃** have three normal band ν_1 , ν_2 and ν_3 : all are optically active.

NOTE: **CH₄** has nine normal modes but only ν_3 and ν_4 are active in IR.

5) Rotational –vibrational transitions:

Pure rotational energy: $E_{rot} = B h c J (J+1)$

where B is the rotational constant (depends on the moments of inertia of a given molecule); h is the Planck's constant.

J is the **rotational quantum number**; $J = 0, 1, 2, 3...$ with a selection rule $\Delta J = +/- 1$

Consider rotational transition between the upper energy level E' and lower energy level E'' . We have for upper level $E' = B h c J' (J'+1)$ and for lower level $E'' = B h c J'' (J''+1)$.

Thus

$$\Delta E_j = B h c (J''+1) = B h c J'$$

- Recalling that $\Delta E_j = n h c$, position of a pure rotational line is given by $n = 2 B J'$ (cm^{-1}) \Rightarrow equally spaced lines because B is constant for a given molecule

Pure vibrational energy: $E_{vib} = h c n_k (v_k + 1/2)$

where n_k is the wavenumber of k -normal vibrational mode;

v_k is the **vibrational quantum number**; $v_k = 0, 1, 2, 3...$

For pure vibrational transition we have $\Delta E = h n_k$

Combine vibrational- rotational energy:

$$E_{j,v} = B h c J (J+1) + h c n_k (v_k + 1/2)$$

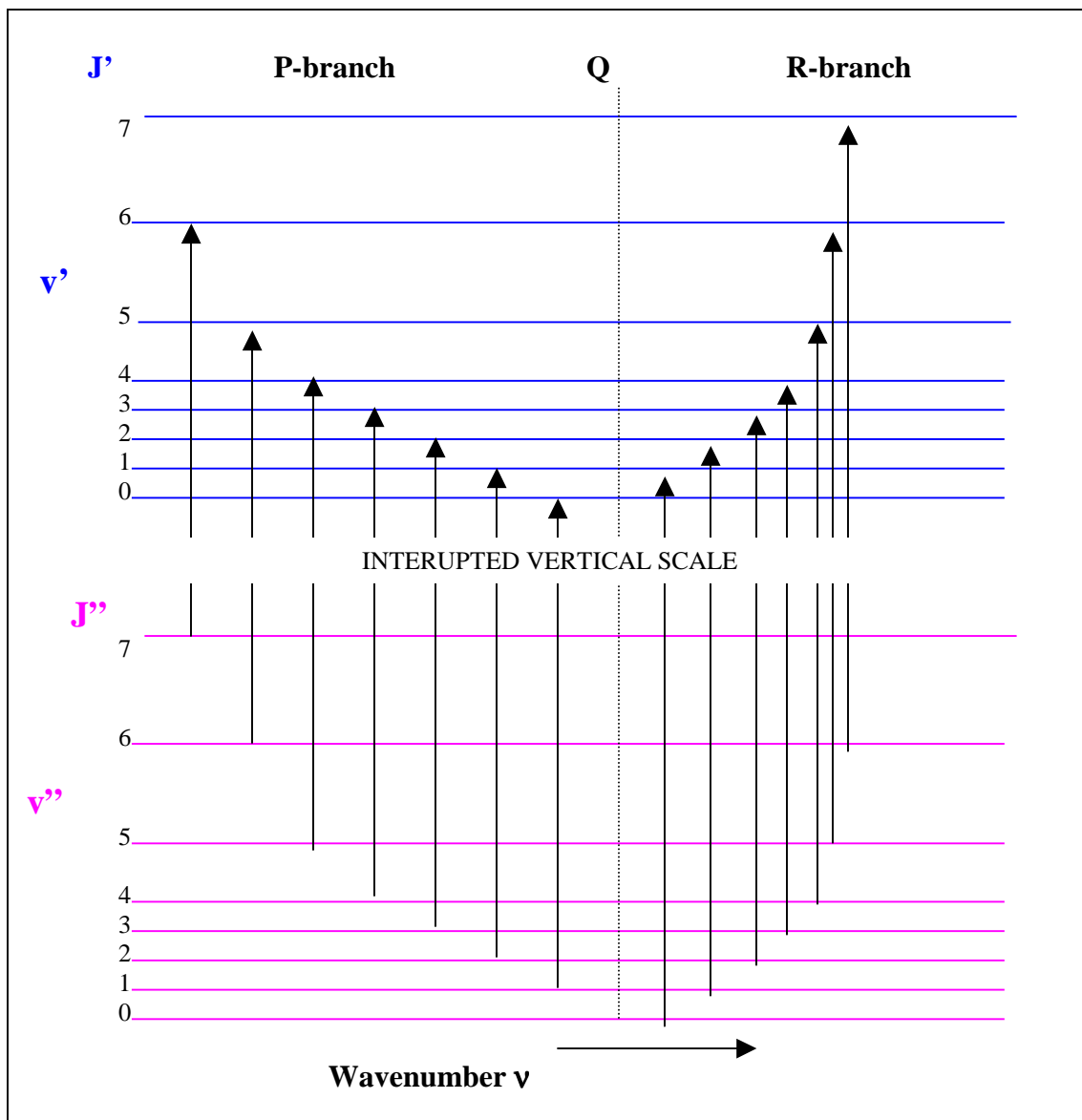
- Because $E_{vib} > E_{rot}$, the spectrum of the combined transitions is a series of rotational lines grouped around the vibrational wavenumber:

For $\Delta J = +1$ we have $n = n_k (2B J')$, $J' = 1, 2, 3...$

For $\Delta J = -1$ we have $n = n_k (-2B (J'+1))$, $J' = 0, 1, 2, 3...$

where J' is the rotational quantum number in the excited vibrational state v_k

Figure 5.5 Simultaneous transitions in vibrational and rotational energies.
 (“ denotes lower energy level and ‘ denotes upper energy level).



NOTE:

P-branch is the rotational transitions following the selection rule $\Delta J = -1$

R-branch is the rotational transitions following the selection rule $\Delta J = +1$

NOTE:

Unequal spacing in R-branch is a result of the increased moment of inertia (or decreased **B**) in higher vibrational levels.

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{n}_0), strength of the line (or intensity, **S**), and shape factor (or profile, **f**) of the line.
- Each line has a final 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:

$$f_L(n - n_0) = \frac{a}{p(n - n_0)^2 + a^2} \quad [5.1]$$

where $f(n - n_0)$ is the shape factor of a spectral line;

n_0 is the wavenumber of a central position of a line;

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

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

$$a(P, T) = a_0 \frac{P}{P_0} \left(\frac{T_0}{T} \right)^{1/2}$$

where a_0 is the reference half-width for STP: $T_0 = 273\text{K}$; $P = 1013 \text{ mb}$.

a_0 is in the range from **about 0.01 to 0.1 cm^{-1}** for most atmospheric radiatively active gases.

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:

$$f_D(\tilde{\mathbf{n}} - \tilde{\mathbf{n}}_0) = \frac{1}{\mathbf{a}_D \sqrt{\mathbf{p}}} \exp \left[- \left(\frac{\tilde{\mathbf{n}} - \tilde{\mathbf{n}}_0}{\mathbf{a}_D} \right)^2 \right] \quad [5.2]$$

α_D is the **Doppler line width**

$$\mathbf{a}_D = \frac{\tilde{\mathbf{n}}_0}{c} (2k_B T / m)^{1/2}$$

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

NOTE: The Doppler effect comes from random molecular motions. If the molecule moves with the thermal velocity V and emits at the frequency $\tilde{\mathbf{n}}_0$, it would appear that it

emits at the frequency $\tilde{\mathbf{n}} = \tilde{\mathbf{n}}_0 \left(1 \pm \frac{V}{c} \right)$, where c is the speed of light and $V \ll c$.

- 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:

$$f_{Voigt}(\tilde{\mathbf{n}} - \tilde{\mathbf{n}}_0) = \int_{-\infty}^{\infty} f_L(\tilde{\mathbf{n}}' - \tilde{\mathbf{n}}_0) f_D(\tilde{\mathbf{n}} - \tilde{\mathbf{n}}') d\mathbf{n}' = \frac{\mathbf{a}}{\mathbf{a}_D \mathbf{p}^{3/2}} \int_{-\infty}^{\infty} \frac{1}{(\tilde{\mathbf{n}}' - \tilde{\mathbf{n}}_0)^2 + \mathbf{a}^2} \exp\left[-\left(\frac{\tilde{\mathbf{n}} - \tilde{\mathbf{n}}'}{\mathbf{a}_D}\right)^2\right] d\mathbf{n}' \quad [5.3]$$

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. Absorption coefficient and transmission function.

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

$$k_n = \mathbf{S} f(\mathbf{n} - \mathbf{n}_0) \quad [5.4]$$

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

$$S = \int k_n d\mathbf{n} \quad \text{and} \quad \int f(\mathbf{n} - \mathbf{n}_0) d\mathbf{n} = 1$$

Transmission function (or transmittance):

Assuming that the absorption coefficient k_v is independent of path length (i.e., the atmosphere is homogeneous), the **monochromatic transmission function** may be defined as

$$T_n = \exp(-t_n),$$

where

τ_v is the optical depth; $\tau = \int_u^{u_1} k_n du$

and u is the path length defined as $u = \int_{z_1}^{z_2} r(z) dz$

Homogeneous absorption path:

when k_n does not vary along the path and thus $t = k_n u$

Inhomogeneous absorption path:

when k_n varies along the path

NOTE: In general, τ_v depends on both the wavenumber and path length.

Table 5.2 Units used for path length (or amount of absorbing gases); absorption coefficient, and line intensity.

Absorbing gas (path length)	Absorption coefficient	Line intensity
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

4. IR absorption spectra of main atmospheric gases (H₂O, CO₂, O₃, CH₄, N₂O, CFCs).

- Each atmospheric gas has a specific absorption/emission spectrum – its own signature.

Figure 5.5 Low-resolution infrared absorption spectra of the major atmospheric gases.

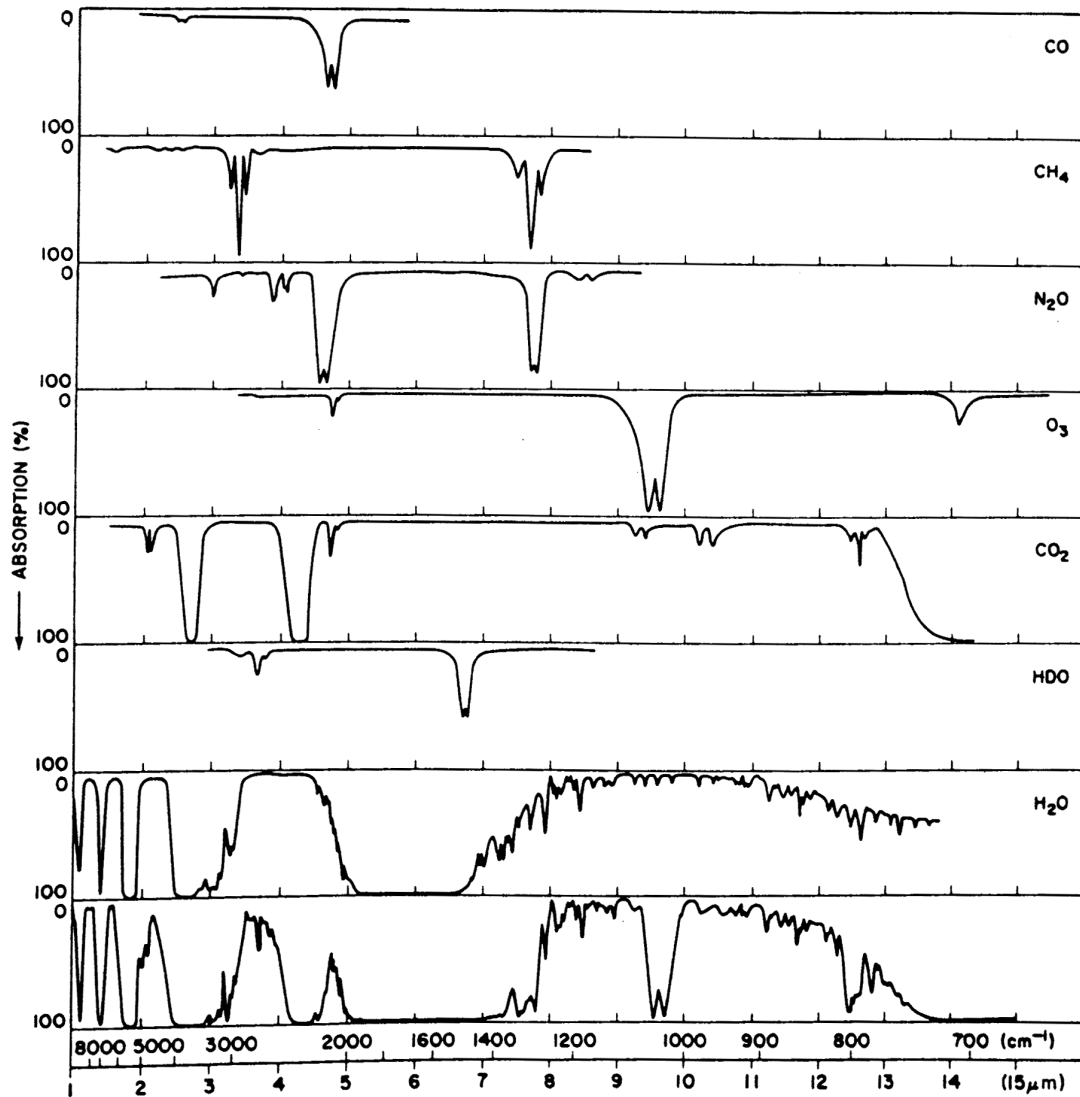


Table 5.3 The most important vibrational and rotational transitions for H₂O, CO₂, O₃, CH₄, N₂O, and CFCs.

Gas	Center ν (cm ⁻¹) (λ (μ 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 (H ₂ O) ₂	200-1200
CO₂	667 (15)] ν_2 ; P, R, Q overtone and combination	540-800
	961 (10.4)		850-1250
	1063.8 (9.4)	ν_3 ; P, R overtone and combination	2100-2400
	2349 (4.3)		
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 distant wings of lines in the far infrared. This absorption is caused by collision broadening between H₂O molecules (called **self-broadening**) and between H₂O and non-absorbing molecules (N₂) (called **foreign broadening**). See Lectures 6-7 and Labs 5-6 for further details.

NOTE: There are several databases providing detailed information on gaseous spectra (e.g. HITRAN). See Lab 3 for further details.