Basics of gaseous absorption/emission. Line shapes.

Absorption coefficient and transmission function.

Objectives:

1. Basics of atomic and molecular absorption/emission spectra.

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

3. Absorption coefficient and transmission function.

Required reading:

L02: 1.3

1. Basics of atomic and molecular absorption/emission spectra.

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:

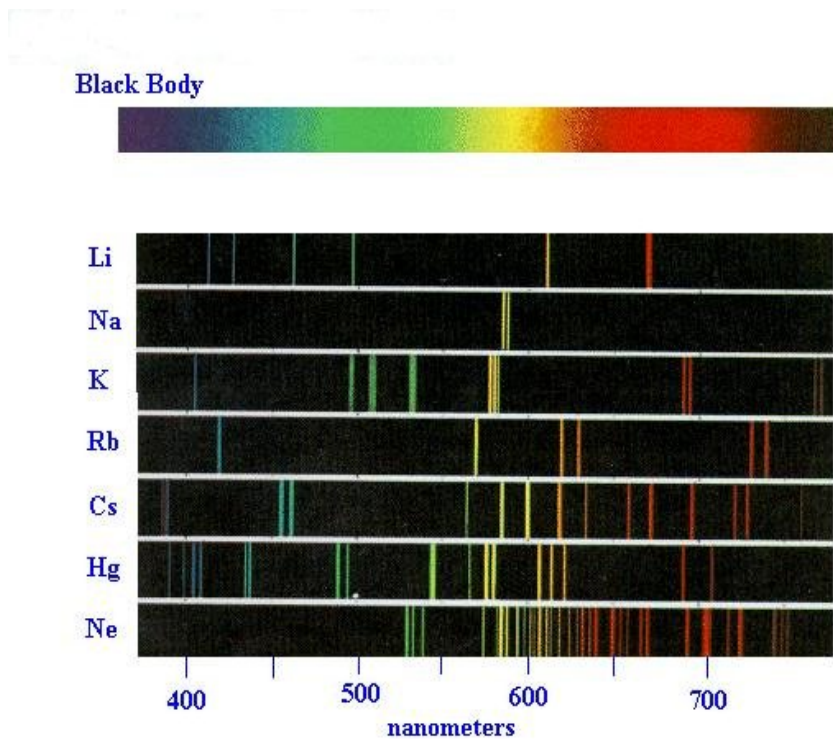$$for\ emission: \quad E_k - E_j = hc\nu$$

Figure 5.1 Examples of atomic emission spectra.

Bohr's model of a hydrogen atom:

The energy level is given as

$$E_n = -\frac{R_H hc}{n^2} \qquad , n=1,2,3\ldots\ldots \qquad [5.1]$$

where R_H is the Ryberg constant ($=1.092\times10^5$ 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:

$$v = R_H \left(\frac{1}{j^2} - \frac{1}{k^2}\right) \qquad [5.2]$$

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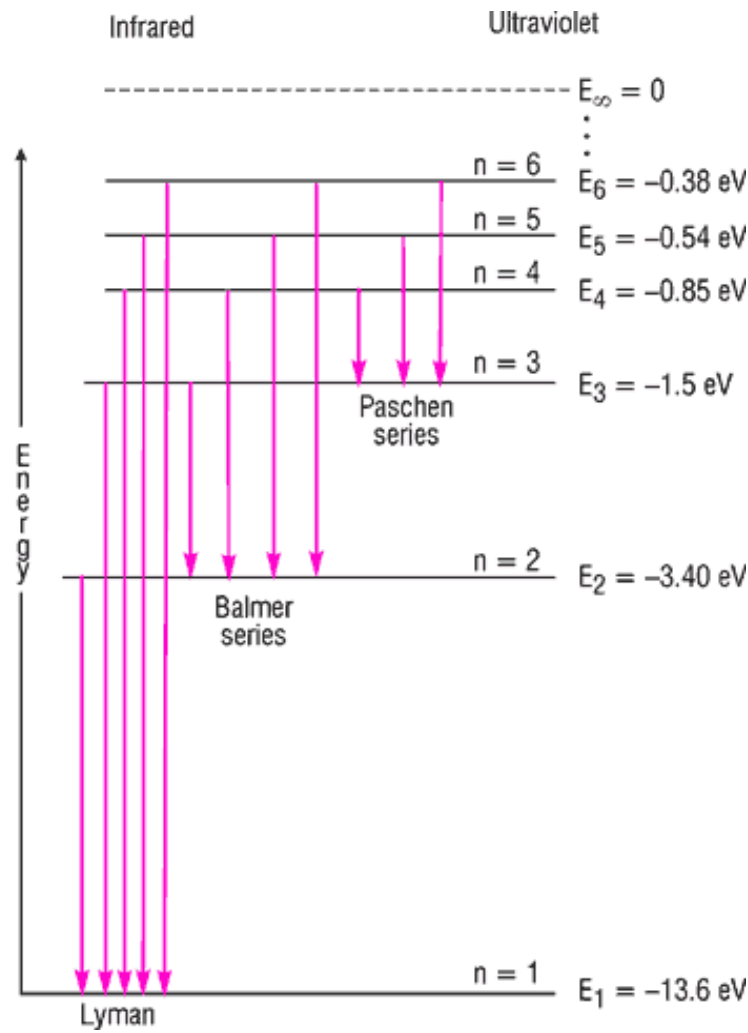

Figure 5.2 Energy level diagram for the hydrogen atom.

➢ **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**;

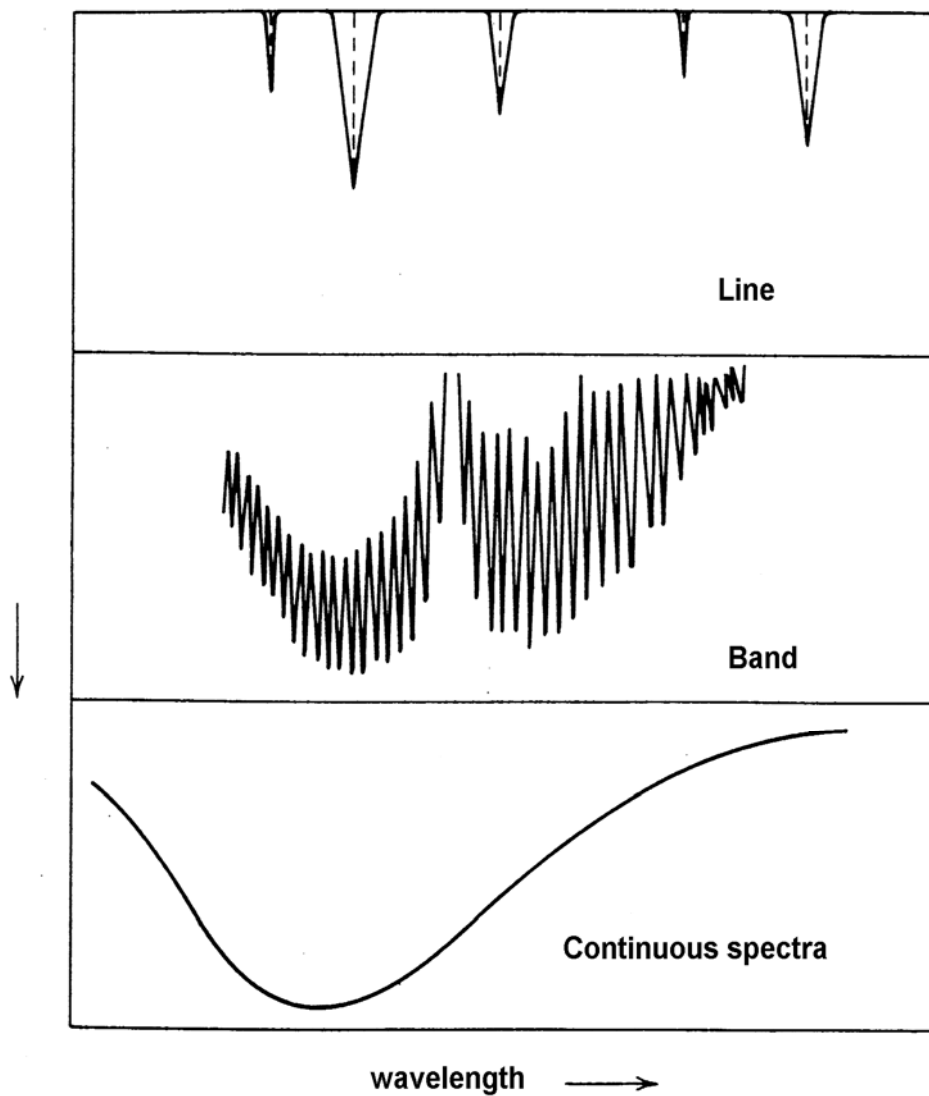   iii)   **Spectral continuum** extending over a broad range of wavelengths

Figure 5.3 Concept of a line, band, and continuous spectra

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} (in the far-infrared to microwave region)

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

E_{el} is the electronic energy: potential energy of electron arrangement; about 10^4-10^5 cm^{-1} (in the 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 collision, 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 (see also Table 4.3)

Molecule	Structure	Permanent dipole moment	May acquire dipole moment
N_2	N ● —— ● N	No	No
O_2	O ● —— ● O	No	No
CO	C ● —— ● O	Yes	Yes
CO_2	O ● —— ● C ● O	No	Yes (in two vibrational modes)
N_2O	N ● —— ● N ● O	Yes	Yes
H_2O	O / H ● ● H	Yes	Yes
O_3	O / O ● ● O	Yes	Yes
CH_4	H H ● C ● H H	Yes*	Yes (in two vibrational modes)

*CH4 is an exemption, it has a spherical top configuration and hence no permanent electric dipole but it possesses a transitional dipole moment. Also, it can acquire the oscillating dipole moment in the 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)
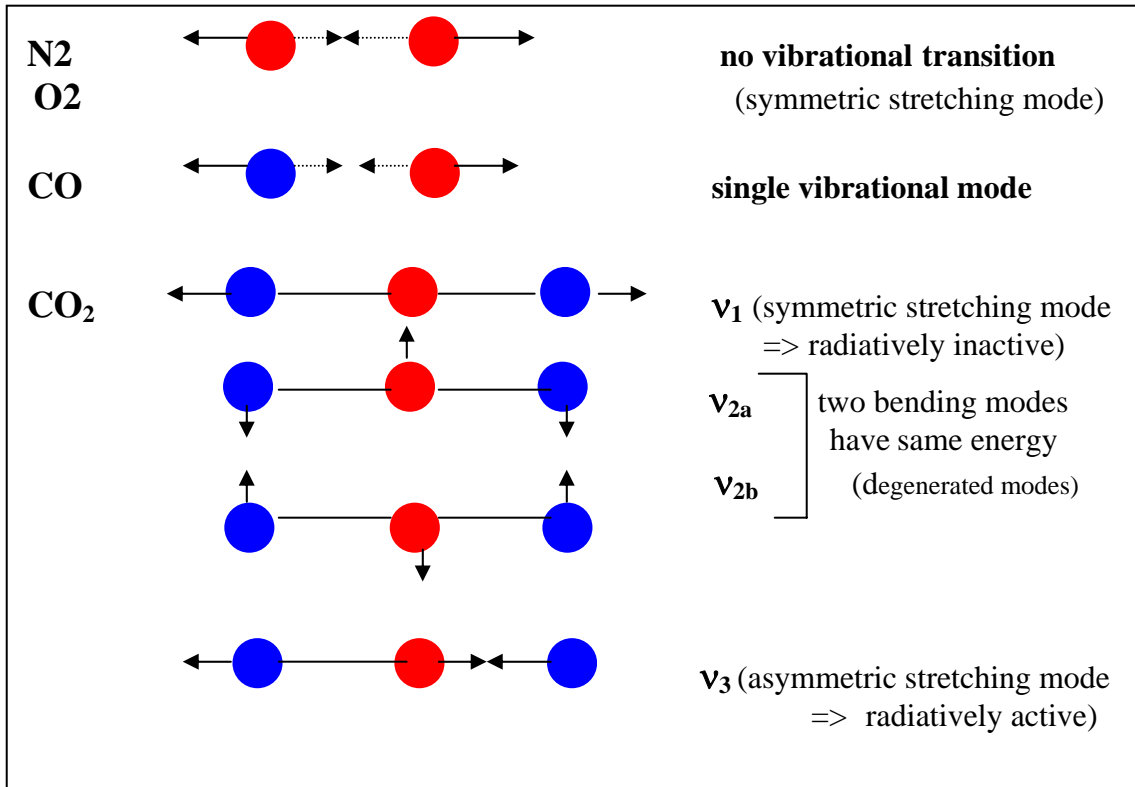
Example: homonuclear diatomic molecules (N_2, O_2);

NOTE: CO, N_2O, H_2O and O_3 exhibit pure rotational spectra.

NOTE: CO_2 don't have permanent dipole moment => no pure rotational transitions, but can acquire the oscillating dipole moment in the vibrational modes => has vibration-rotation bands

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 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 the 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 H_2O and O_3 have three normal band ν_1, ν_2 and ν_3: all are optically active.

NOTE: CH_4 has nine normal modes but only ν_3 and ν_4 are active in the IR.

5) Rotational –vibrational transitions:

Pure rotational transitions can be understood by evoking the notion of a rigid quantized rotator.
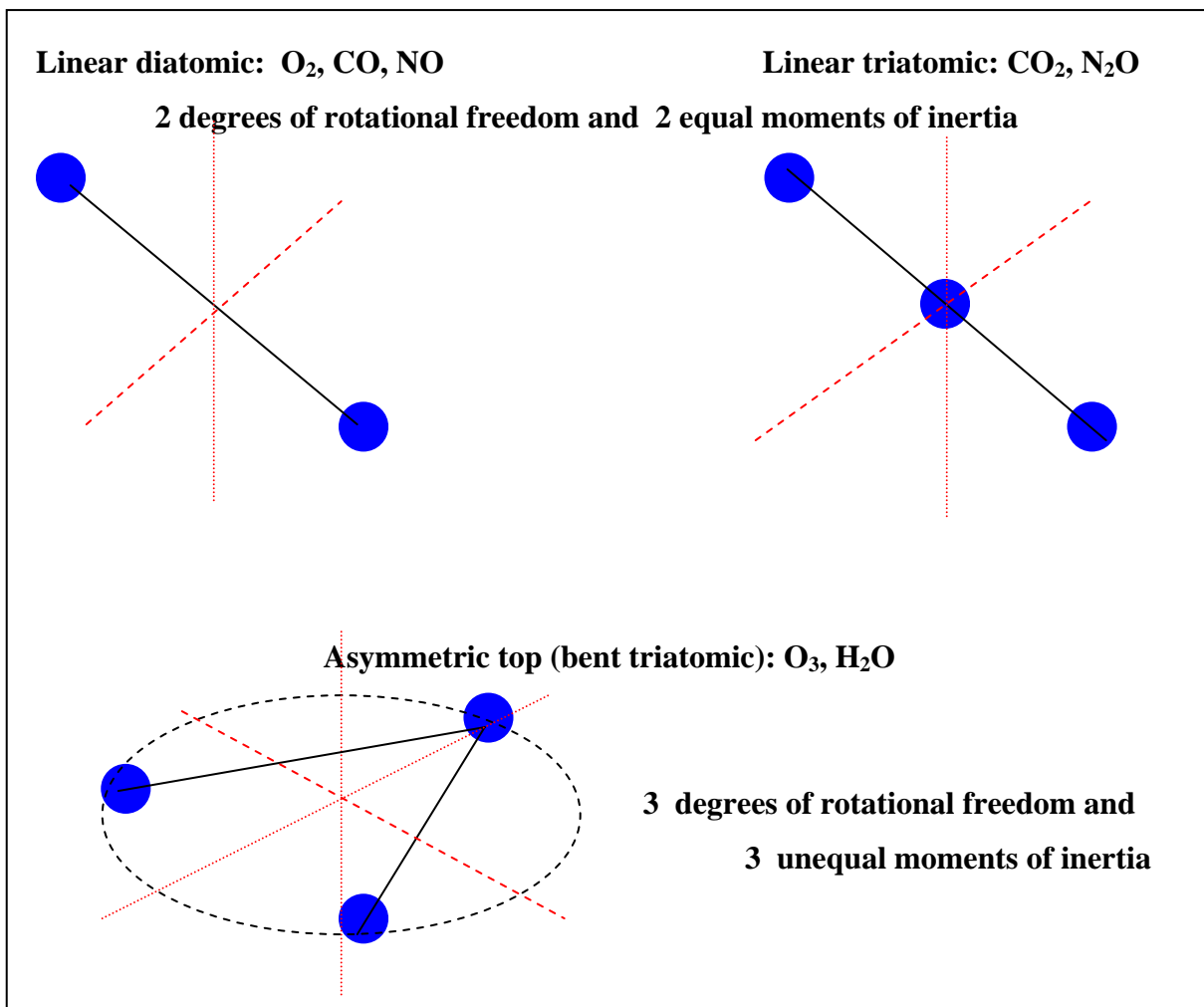

Figure 5.5 Axes of rotational freedom for linear and asymmetric top molecules.

Let's consider a diatomic molecule with masses m_1 and m_2 at distances r_1 and r_2 from their common center of gravity. The moment of inertia of this two-mass rigid rotator is

$$I_m = m_1 r_1^2 + m_2 r_2^2$$

If **r** is the distance between the atoms, we have

$$r_1 = \frac{m_2}{m_1 + m_2} r \qquad \text{and} \qquad r_2 = \frac{m_1}{m_1 + m_2} r$$

Introducing the reduced mass m' as

$$m' = \frac{m_1 m_2}{m_1 + m_2}$$

we have
$$I_m = \frac{m_1 m_2}{m_1 + m_2} r^2 = m' r^2$$

The angular momentum **L** of a rigid rotator is defined as

$$L = I_m \omega = m' r^2 \omega$$

where ω is the angular velocity (rad sec^{-1})

The kinetic energy of a rotator is equal

$$E_{rot} = \frac{1}{2} L\omega = \frac{1}{2} I_m \omega^2$$

Classic rotator: both angular momentum and rotational kinetic energy are continues.

Quantized rotator: Quantum restrictions on rotational energy as a consequence of the quantum restrictions on angular momentum (which found from a solution of the Schroedinger equation).

The quantum restrictions on angular momentum are

$$I_m \omega = \frac{h}{2\pi} [J(J+1)]^{1/2}$$

J is the **rotational quantum number; J = 0, 1, 2, 3...**

h is the Planck's constant.

Thus we have

$$E_{rot} = \frac{1}{2} I_m \omega^2 = \frac{1}{2} \frac{(I_m \omega)^2}{I_m} = \frac{h^2}{8\pi^2 I_m} J(J+1)$$

or

$$\boxed{E_J = B\, h\, c\, J\,(J+1)}$$ [5.3]

B is the rotational constant and it depends on the moments of inertia I_m of a given molecule as

$$B = \frac{h}{8\pi^2 c I_m}$$

Units of B: LENGTH^{-1}

Selection rules: $\Delta J = 1$ for absorption and $\Delta J = -1$ for emission

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 $\Delta E_j = \nu\, h\, c$, position of a pure rotational line is given by

$$\boxed{\nu = 2\, B\, J'}\ \ (\text{cm}^{-1})$$

=> equally spaced lines because B is constant for a given molecule.

NOTE: The nonlinear molecules H_2O and O_3, asymmetric tops with three moments of inertia, give very complex spectra.

Pure vibrational energy:

Similar to the derivation above, one can introduce a classical vibrator (whose energies are continuous) and then apply the quantum restrictions from the Schroedinger equation. The allowed energy levels are

$$E_{vk} = h \ c \ \nu_k \ (v_k +1/2)$$
[5.4]

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

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

For pure vibrational transition, we have $\Delta E = hc \ \nu_k \ \Delta v$

Combine vibrational- rotational energy:

$$E_{j,v} = B \ h \ c \ J \ (J+1)+ h \ c \ \nu_k \ (v_k +1/2) \ )$$
[5.5]

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

  For ΔJ = +1 we have $\nu = \nu_k \ (2B \ J')$, J' = 1, 2, 3…

  For ΔJ = -1 we have $\nu = \nu_k \ (-2B \ (J'+1))$, J' = 0,1, 2, 3…

  where *J'* is the rotational quantum number in the excited vibrational state v_k'
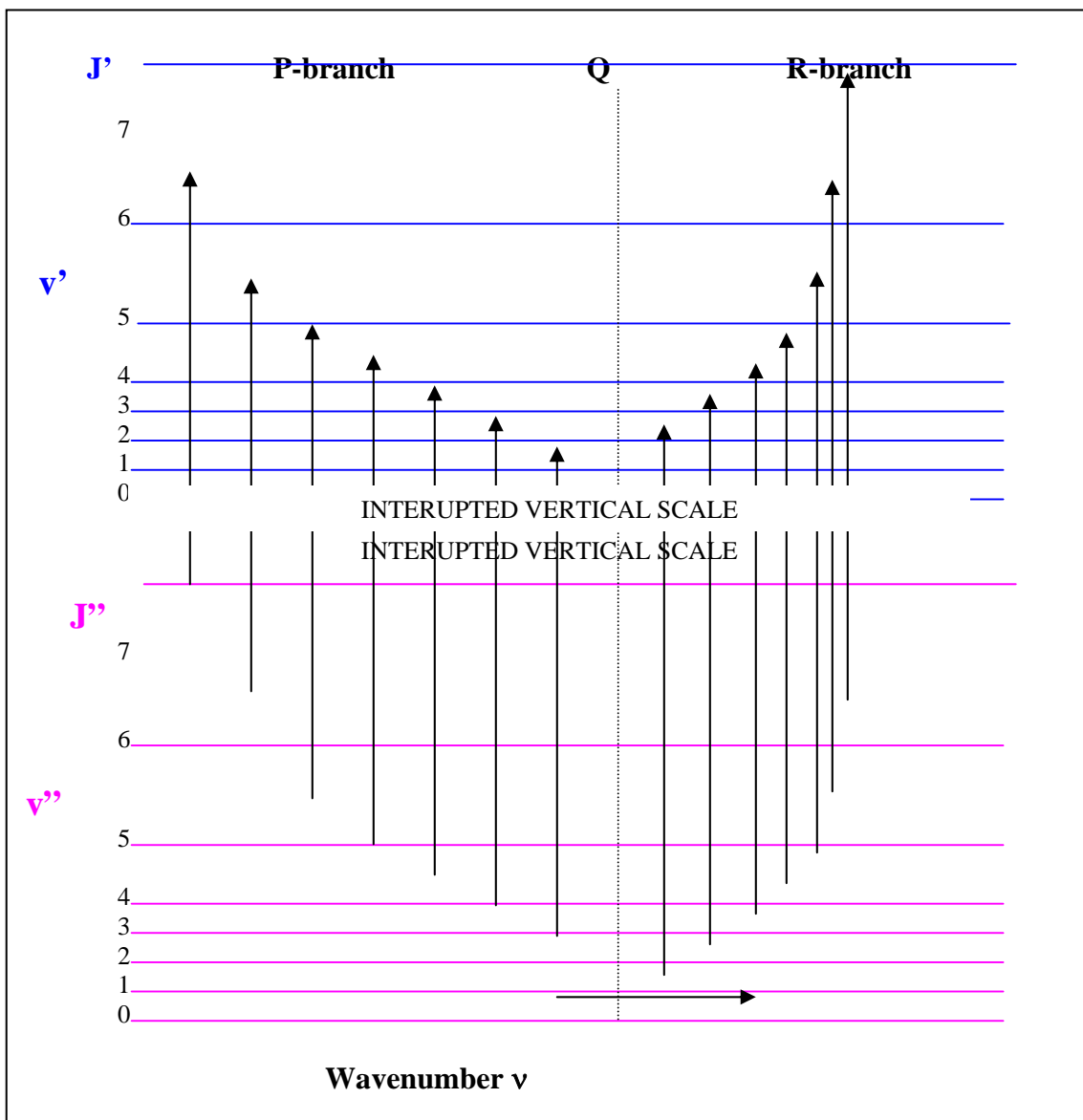
Figure 5.6 Simultaneous transitions in vibrational and rotational energies.
(**"** denotes lower energy level and **'** denotes upper energy level).

NOTE:

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

Q-branch is the rotational transitions following the selection rule $\Delta J = 0$

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

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

> **Three main factors that define an absorption line: central position of the line (e.g., the central frequency $\tilde{\nu}_0$ or the central wavenumber ν_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**); 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:

$$f_L(\nu - \nu_0) = \frac{\alpha / \pi}{(\nu - \nu_0)^2 + \alpha^2}$$ [5.6]

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 called the **line width**)

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

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

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**) produce 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:

$$f_D(\nu - \nu_0) = \frac{1}{\alpha_D \sqrt{\pi}} \exp\left[-\left(\frac{\nu - \nu_0}{\alpha_D} \right)^2 \right]$$ [5.7]

α_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 $\alpha_D (ln2)^{1/2}$

NOTE: 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 $\tilde{\nu} = \tilde{\nu}_0 \left(1 \pm \frac{V}{c} \right)$, 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.
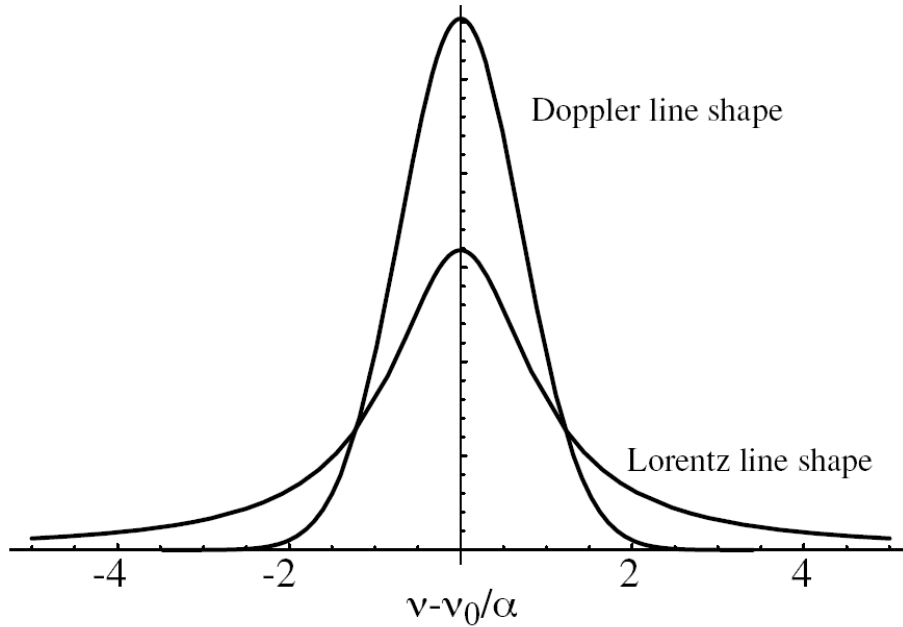
Doppler line shape

Lorentz line shape

$\nu-\nu_0/\alpha$

Figure 5.7 Comparison of the Doppler and Lorentz profiles for equivalent line strengths and widths.

NOTE: Line wings are more strongly affected by pressure than Doppler broadening.

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:

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

$$\frac{\alpha}{\alpha_D \pi^{3/2}} \int_{-\infty}^{\infty} \frac{1}{(\nu' - \nu_0')^2 + \alpha^2} \exp\left[-\left(\frac{\nu - \nu'}{\alpha_D}\right)^2\right] d\nu' \qquad [5.8]$$

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:

$$\boxed{k_{a,\nu} = S f(\nu - \nu_0)} \qquad\qquad [5.9]$$

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

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

Intensity (line strength) gives total absorption associated with the line.

Line shape (line profile) gives the distribution of absorption about the center of the line.

Units of the line profile, f: LENGTH (often cm); *Units of absorption coefficient and intensity* – see Table 5.2 (below)

Dependencies:

S depends on **T;**

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

- ✓ **Path length** (or **path**) is defined as the amount of an absorber along the path. Since the amount of the absorbing gas can be expressed in different ways (see Lecture 4) the different measures of path length are used.

For instance, if the amount of an absorber is given in terms of mass density, then **mass path length** (also called **optical mass)** is

$$u = \int_{s_1}^{s_2} \rho(s)ds$$

Homogeneous absorption path:

when $k_{a,v}$ does not vary along the path $\Rightarrow$ optical depth is $\tau = k_{a,v}u$

Inhomogeneous absorption path: when k_v varies along the path, then

$$\tau = \int_{u_1}^{u_2} k_{a,v}\,du$$

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

NOTE: The product of the absorption coefficients and path length (=optical depth) should be unitless.

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

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}
molecule cm^{-2}	cm^2/molecule	cm/molecule
cm atm	(cm atm)$^{-1}$	cm^{-2} atm^{-1}

Monochromatic transmittance T$_v$ and absorbance A$_v$ of radiance along the path are defined as

$$T_v = \exp(-\tau_v) \qquad A_v = 1 - T_v = 1 - \exp(-\tau_v) \qquad [5.10]$$

NOTE: same name: Transmission function = Transmittance