

## Lecture 6

### Basics of gaseous absorption/emission. Line shapes.

1. Basics of atomic and molecular absorption/emission spectra.
2. Spectral line shapes: Lorentz profile, Doppler profile and Voigt profile

#### Required reading:

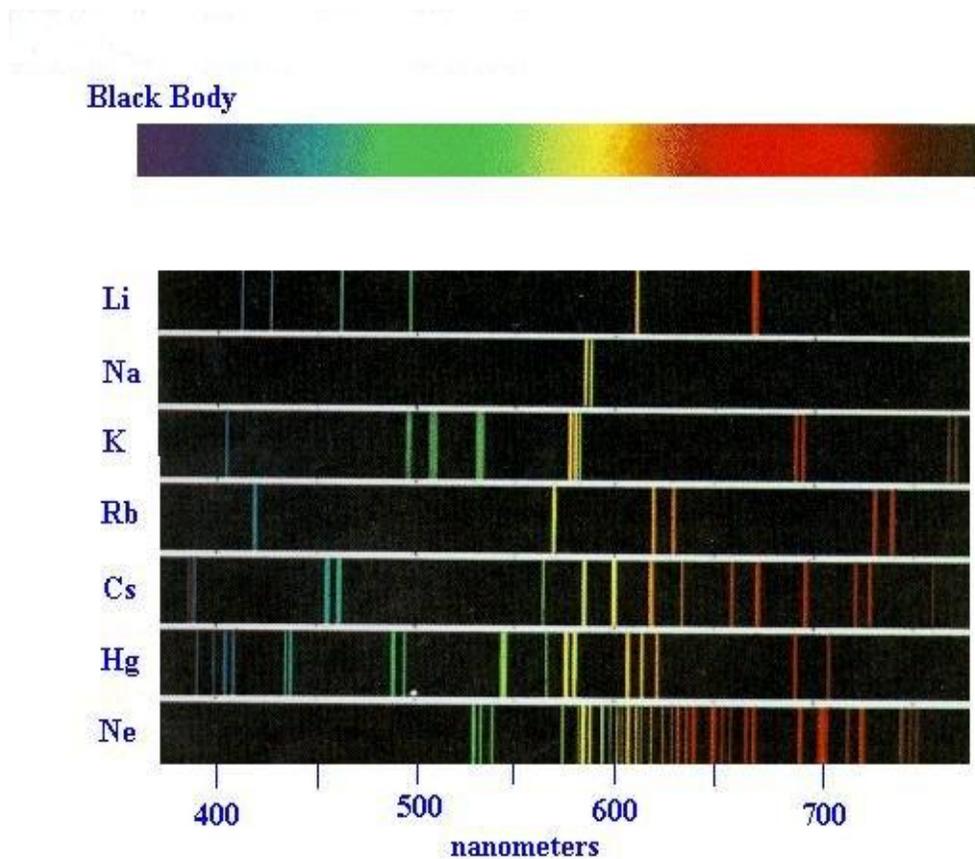
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### 1. Basics of atomic and molecular absorption/emission spectra

#### 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  $E_j$ :

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



**Figure 6. 1** Examples of atomic emission spectra.

**Bohr's model of a hydrogen atom:**

- The energy level is given as

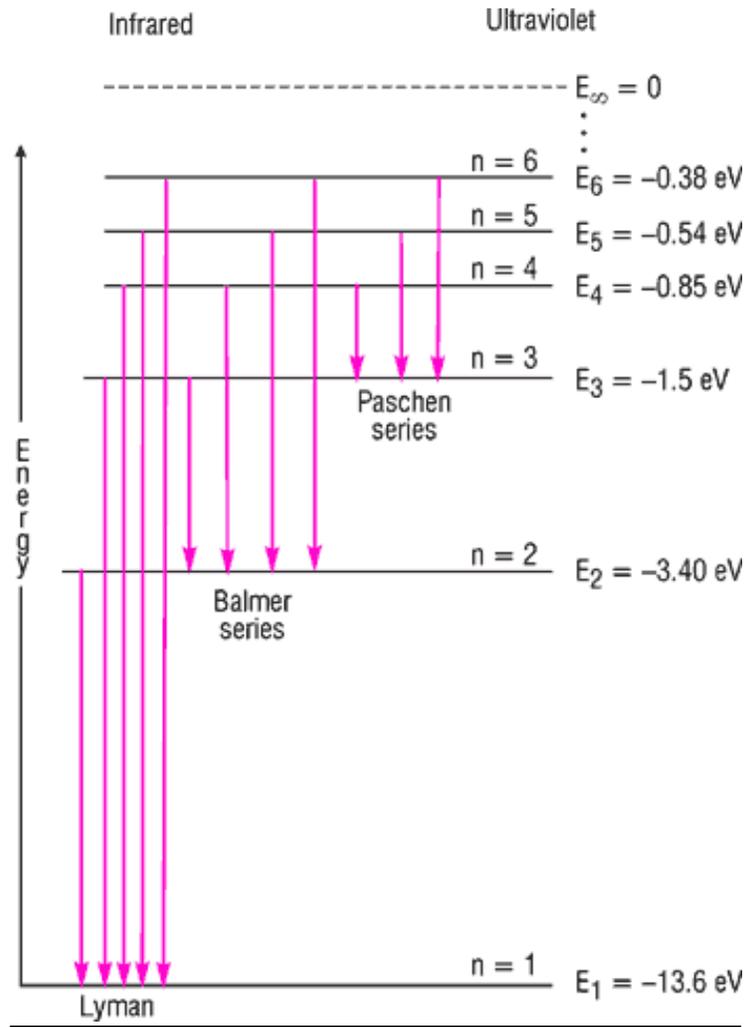
$$E_n = -\frac{R_H hc}{n^2}, \quad n=1,2,3,\dots \quad [6.1]$$

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:

$$\nu = R_H \left( \frac{1}{j^2} - \frac{1}{k^2} \right) \quad [6.2]$$

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



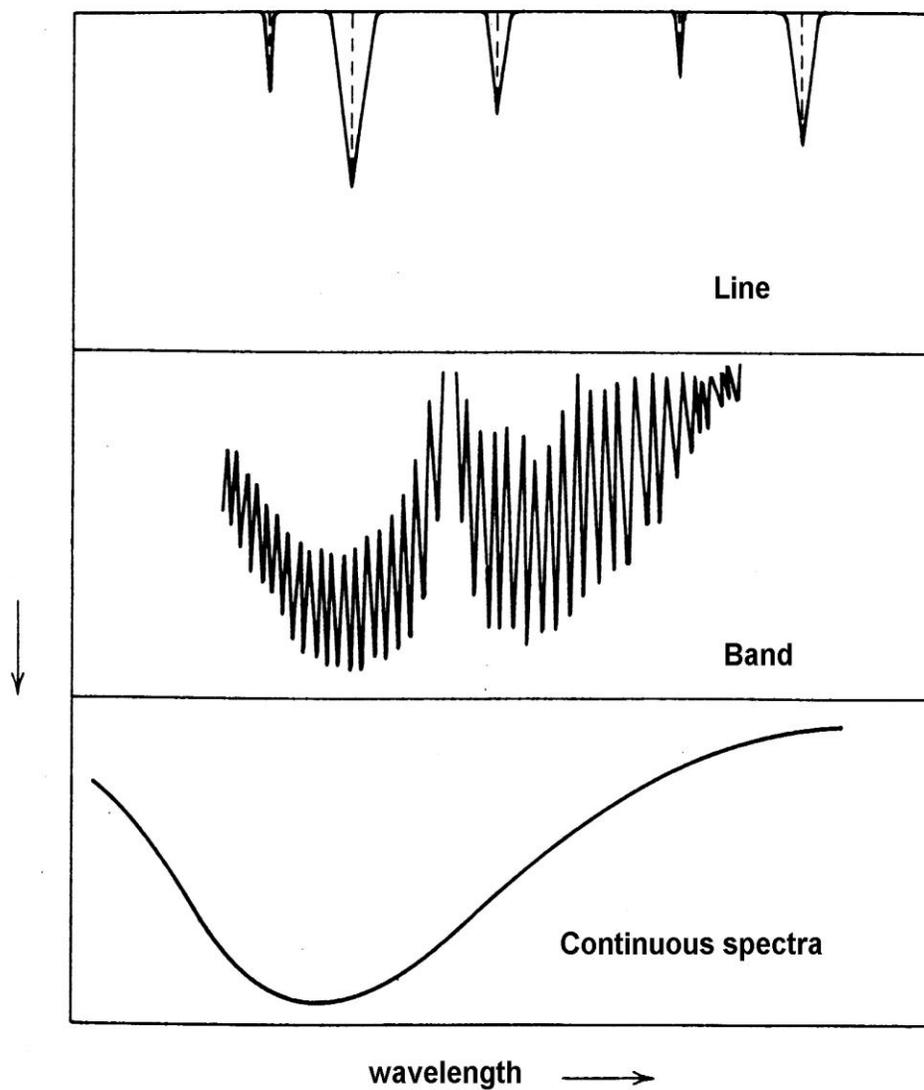
**Figure 6.2** Energy level diagram for the hydrogen atom.

➤ **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 6.3** 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 expressed 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  $1\text{-}500\text{ cm}^{-1}$  (far-infrared to microwave region)

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

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

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

- **From  $E_{\text{rot}} < E_{\text{tr}} < E_{\text{vib}} < E_{\text{el}}$  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  $E_{\text{rot}}$ ,  $E_{\text{vib}}$ , and  $E_{\text{el}}$  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  $d$ : **dipole moment** =  $Q d$

**Table 6.1** Atmospheric molecule structure and dipole moment status (see also Table 5.3)

<i>Molecule</i>	<i>Structure</i>	<i>Permanent dipole moment</i>	<i>May acquire dipole moment</i>
N <sub>2</sub>		No	No
O <sub>2</sub>		No	No
CO		Yes	Yes
CO <sub>2</sub>		No	Yes (in two vibrational modes)
N <sub>2</sub> O		Yes	Yes
H <sub>2</sub> O		Yes	Yes
O <sub>3</sub>		Yes	Yes
CH <sub>4</sub>		Yes*	Yes (in two vibrational modes)

\*CH<sub>4</sub> 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.

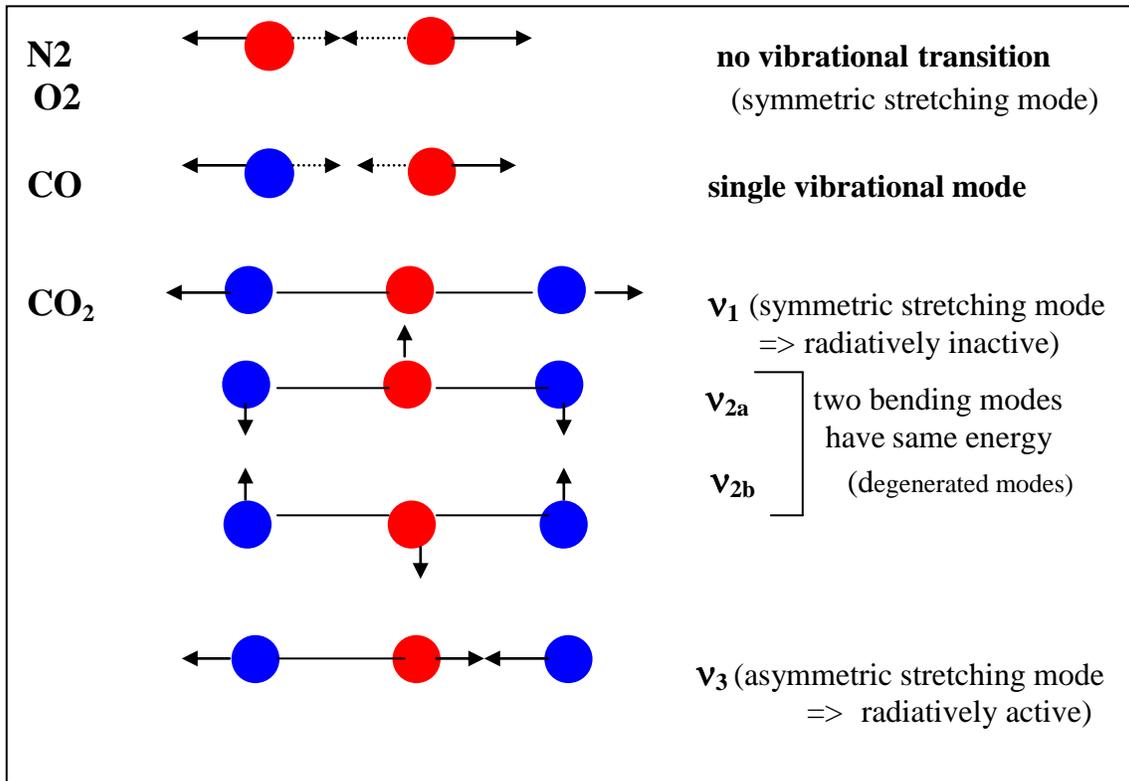
**NOTE:** If charges are distributed symmetrically => no permanent dipole moment => no radiative activity in the far-infrared (i.e., no transitions in rotational energy)

Example: homonuclear diatomic molecules (N<sub>2</sub>, O<sub>2</sub>);

**NOTE:** CO<sub>2</sub> doesn't have permanent dipole moment => no pure rotational transition but it can acquire the oscillating dipole moment in the vibrational modes => has vibration-rotation bands

**NOTE:** CO, N<sub>2</sub>O, H<sub>2</sub>O and O<sub>3</sub> exhibit pure rotational spectra.

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



**Figure 6.4** 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 UV.

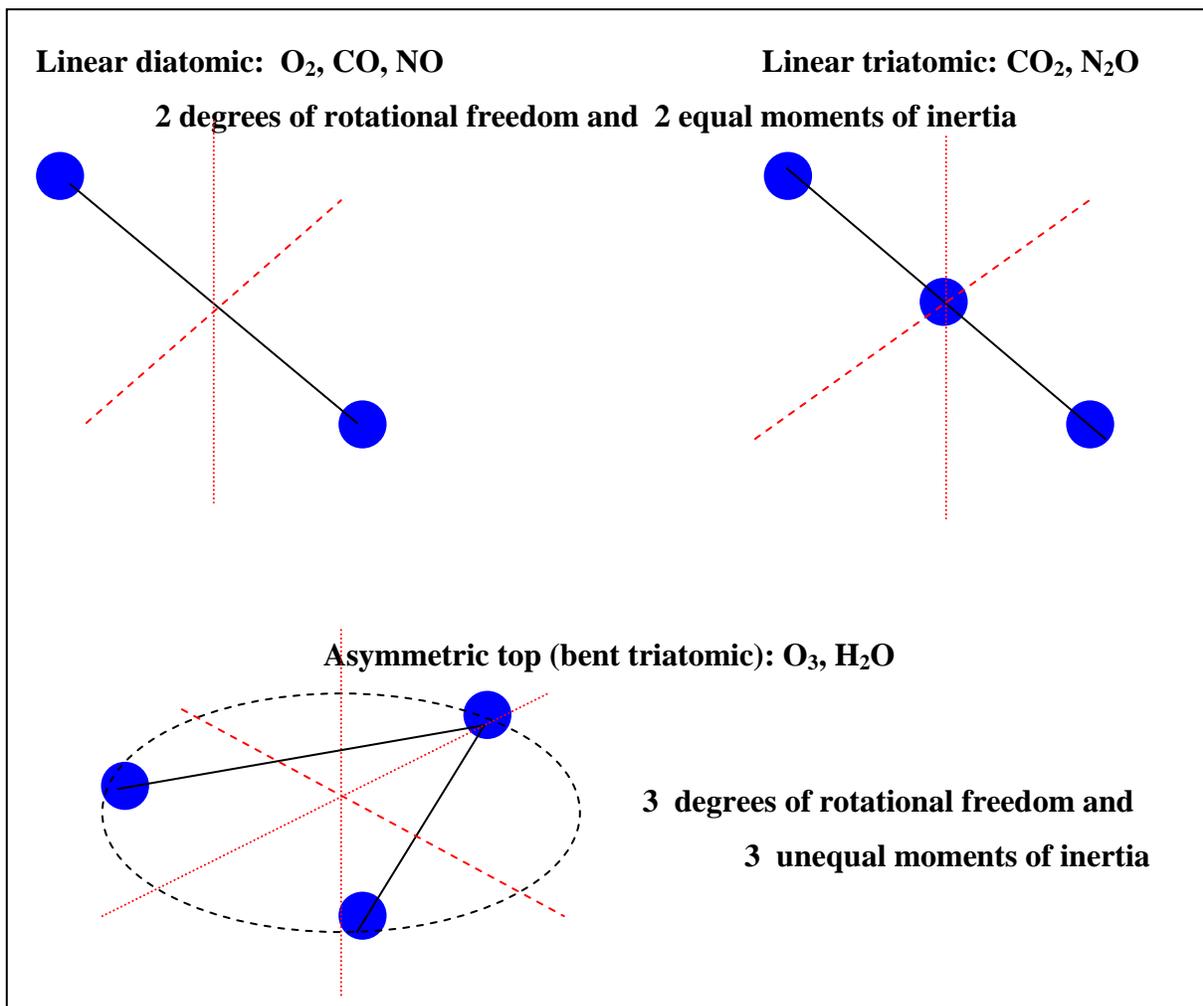
**NOTE:** The number of independent vibrational modes (called **normal modes**) of a molecule with  $N > 2$  atoms are  $3N - 6$  for non-linear molecules and  $3N - 5$  for a linear molecule.

**NOTE:** Both  $H_2O$  and  $O_3$  have three normal band  $\nu_1$ ,  $\nu_2$  and  $\nu_3$ : all are optically active.

**NOTE:**  $CH_4$  has nine normal modes but only  $\nu_3$  and  $\nu_4$  are active in IR.

5) Rotational –vibrational transitions:

Pure rotational transitions can be understood using the analogy of a rigid quantized rotator.



**Figure 6.5** Axes of rotational freedom for linear and asymmetric top molecules.

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

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

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  $\omega$  is the angular velocity (rad sec<sup>-1</sup>)

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 continuous

**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**;  $J = 0, 1, 2, 3, \dots$

$h$  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

$$E_J = B h c J (J+1) \quad [6.3]$$

$B$  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  $B$ :  $\text{LENGTH}^{-1}$

**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

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

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

**NOTE:** The nonlinear molecules  $\text{H}_2\text{O}$  and  $\text{O}_3$ , 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

$$E_{\nu_k} = h c \nu_k (\nu_k + 1/2) \quad [6.4]$$

where  $\nu_k$  is the wavenumber of the k-normal vibrational mode;

$\nu_k$  is the **vibrational quantum number**;  $\nu_k = 0, 1, 2, 3, \dots$

For pure vibrational transition, we have  $\Delta E = h c \nu_k \Delta \nu$

**Combine vibrational- rotational energy:**

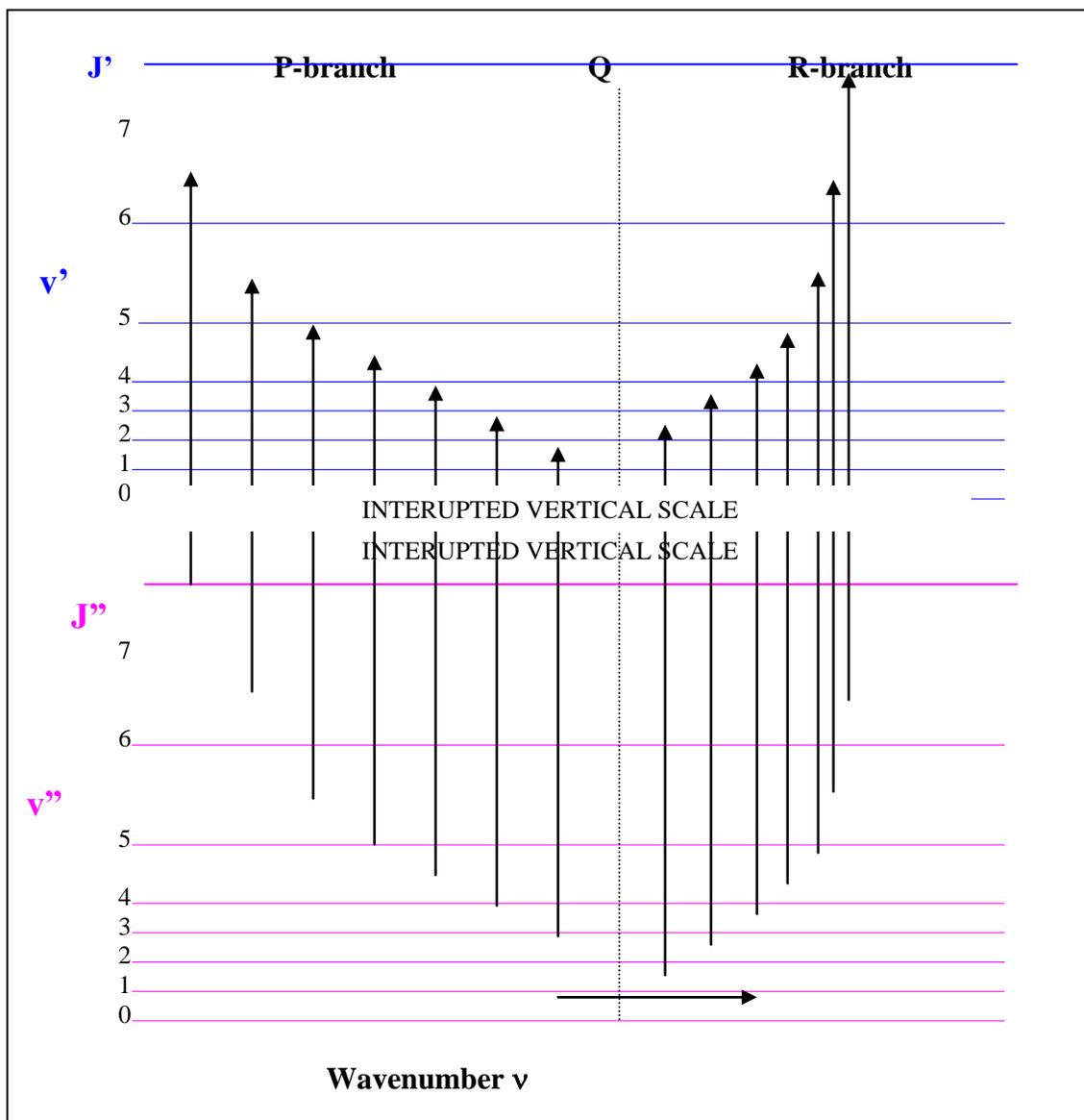
$$E_{j,\nu} = B h c J (J+1) + h c \nu_k (\nu_k + 1/2) \quad [6.5]$$

- 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  $\nu = \nu_k (2B J')$ ,  $J' = 1, 2, 3, \dots$

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

where  $J'$  is the rotational quantum number in the excited vibrational state  $\nu_k$ ,



**Figure 6.6** 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  $\nu_0$ ), strength of the line (or intensity, S), and shape factor (or line profile,  $f$ ) of the line.**

- 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:

$$f_L(\nu - \nu_0) = \frac{\alpha / \pi}{(\nu - \nu_0)^2 + \alpha^2} \quad [6.6]$$

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

$\nu_0$  is the wavenumber of the central position of the line;

$\alpha$  is the half-width of the line at the half maximum (in  $\text{cm}^{-1}$ ), (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

$$\alpha(P, T) = \alpha_0 \frac{P}{P_0} \left( \frac{T_0}{T} \right)^n \quad [6.6a]$$

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 is about 0.5, but it varies among different gases and lines.

**NOTE:** The **dependence of the line width on pressure** is very important because atmospheric pressure varies, for instance, on Earth 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:

$$f_D(\nu - \nu_0) = \frac{1}{\alpha_D \sqrt{\pi}} \exp \left[ - \left( \frac{\nu - \nu_0}{\alpha_D} \right)^2 \right] \quad [6.7]$$

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

$$\alpha_D = \frac{V_0}{c} (2k_B T / m)^{1/2}$$

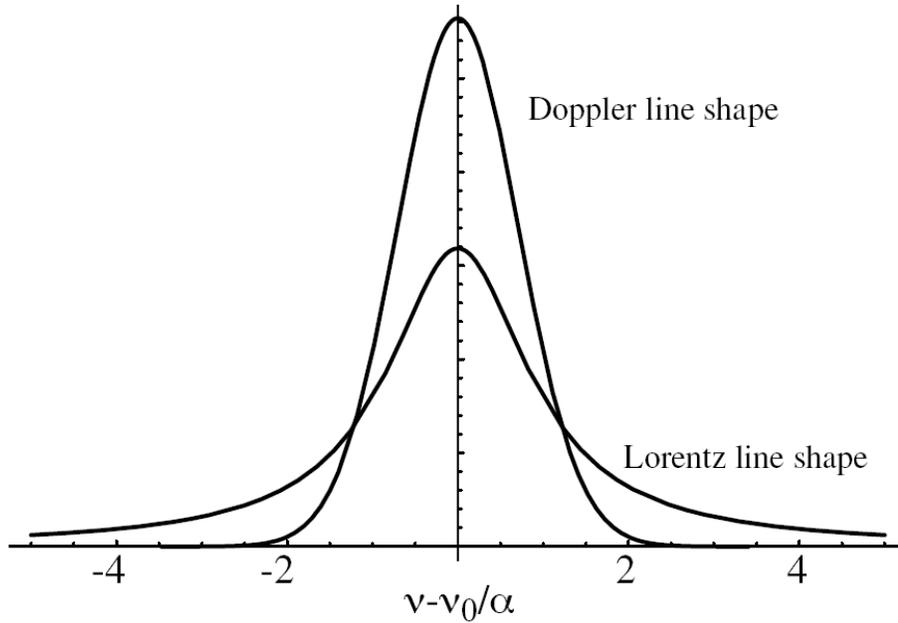
where  $c$  is the speed of light;  $k_B$  is the Boltzmann's constant,  $m$  is the mass of the molecule.

The Doppler half-width at the half maximum is  $\alpha_D (1n2)^{1/2}$

**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  $V \ll c$ .

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



**Figure 6.7** 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:

$$f_{\text{Voigt}}(v - v_0) = \int_{-\infty}^{\infty} f_L(v' - v_0) f_D(v - v') dv' = \frac{\alpha}{\alpha_D \pi^{3/2}} \int_{-\infty}^{\infty} \frac{1}{(v' - v_0')^2 + \alpha^2} \exp\left[-\left(\frac{v - v'}{\alpha_D}\right)^2\right] dv' \quad [6.8]$$

**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.