

## Molecular Absorption

Equation of motion for a harmonic oscillator, mass  $m$ , charge  $e$ , acted on by EM wave

with frequency  $\omega$ : 
$$\frac{d^2 \mathbf{x}}{dt^2} = -\omega_o^2 \mathbf{x} - \gamma \frac{d\mathbf{x}}{dt} + \frac{e}{m} E$$

1<sup>st</sup> term on right side of equation: restoring force

2<sup>nd</sup> term: dissipative force

3<sup>rd</sup> term: Electric-field force

Recall that this is similar to the harmonic oscillator model for scattering without the radiative reaction force.

$\mathbf{x}$  is time harmonic with same frequency as E field:

$$\mathbf{x} = \mathbf{x}_o \exp(-i\omega t); \mathbf{x}_o = \frac{e}{m} \frac{\mathbf{E}_o}{\omega_o^2 - \omega^2 - i\gamma\omega}$$

**Instantaneous** rate at which work is done on oscillator by external field:  $P = e\mathbf{E} \cdot \frac{d\mathbf{x}}{dt}$

Time average of  $P$ : 
$$\langle P \rangle = \frac{e^2}{2m} E_o^2 \frac{\gamma \omega^2}{(\omega_o^2 - \omega^2)^2 + \gamma^2 \omega^2} = W_a$$

Interpretation:  $\langle P \rangle$  is the rate  $W_a$  at which energy is absorbed from the incident EM field by the oscillator.

For isolated molecule illuminated by radiation with irradiance  $F$ , rate of absorption is,

$$W_a = \sigma_a F.$$

Therefore,  $\langle P \rangle / E_o^2$  is the frequency dependent absorption coefficient of the harmonic oscillator and  $\sigma_a$  is the absorption cross section.

Maximum absorption occurs at  $\omega_o$ , the resonant frequency.  $W_a$  (and  $\sigma_a$ ) are proportional to  $1/\gamma$  at  $\omega = \omega_o$ .

Absorption line shape: 
$$\sigma_a = \gamma \sigma_{am} \frac{\gamma \omega^2}{(\omega_o^2 - \omega^2)^2 + \gamma^2 \omega^2}$$

$\sigma_{am}$  is the maximum absorption coefficient.

High frequency limit ( $\omega \gg \omega_o$ ):  $\sigma_a$  decreases as  $1/\omega^2$ .

Low frequency limit ( $\omega \ll \omega_o$ ):  $\sigma_a$  increases as  $\omega^2$ .

Frequencies at which absorption falls to one-half maximum value:

$$\omega_{1/2} = \sqrt{\omega_o^2 + \gamma^2/4} \pm \gamma/2; \text{ line width} = \gamma$$

Often lines are narrow such that  $\gamma \ll \omega_0^2$ :  $\sigma_a = \frac{\gamma \sigma_{am}}{4} \frac{\gamma}{(\omega_0 - \omega)^2 + \gamma^2/4}$  where

$\frac{\gamma}{(\omega_0 - \omega)^2 + \gamma^2/4}$  is called the **Lorentz line shape**.

For the Lorentz line shape,  $\omega_{1/2} = \omega_0 \pm \gamma/2$ .

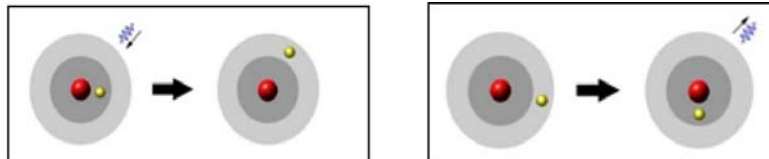
### The classical harmonic oscillator model:

- The simplest description of a vibration is a harmonic oscillator
- A harmonic oscillator is defined by the potential energy being proportional to the square of the distance displaced from an equilibrium position.
- In a classical treatment of a vibrating object, the motion is fastest at the equilibrium position and comes to a complete stop for an instant at the turning points, where all of the energy is potential energy.
- The probability of finding the object is highest at the turning point and lowest at the equilibrium point.

### Quantum mechanical model:

- A quantum mechanical description of a harmonic oscillator uses the same potential energy function, but gives radically different results.
  - There are no turning points.
  - There is some probability of finding the object at any displacement, but that probability becomes very small (decreasing exponentially) at large distances.
  - The energy is quantized, with a quantum number describing each possible energy state and only certain energies possible.
- Very small objects, such as atomic particles behave according to the quantum description.
- Macroscopic objects under a quantum description will have energy spacings that are too close together to measure and a probability distribution that becomes identical to the classical result in the limit of infinite quantum numbers.
- absorption/emission of a photon is due to a transition to a higher quantized energy level in an atom or molecule.
- Frequency of a photon is proportional to energy of transition:

$$E_{\text{upper}} - E_{\text{lower}} = \Delta E = h\nu = hc/\lambda$$



## Molecular Energy Transitions

- **Electronic** transitions cause absorption in visible and ultraviolet.
- Absorption in the microwave and infrared is from two types of molecular transitions: **rotational** and **vibrational**.
- The energy of a molecule can be written as:

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

- $E_{rot}$  is the energy of rotation of molecule around center of mass; about  $1500 \text{ cm}^{-1}$  (microwave to mid-infrared).
- $E_{vib}$  is the energy of vibration of atoms about their equilibrium positions; about  $500\text{-}104 \text{ cm}^{-1}$  (mid-infrared to near-IR).
- $E_{el}$  is the energy of the electron arrangement; about  $104\text{-}105 \text{ cm}^{-1}$  (visible and ultraviolet).
- The different energies of a molecule are quantized and can have only discrete values specified by one or more *quantum numbers*. Not all transitions between quantized energy levels are allowed; there are **selection rules** that specify which transitions are allowed.

Recall:  $\Delta E = h\nu$  so  $\nu = \Delta E/h$ ; lower transition energy, lower frequency of emitted/absorbed photon

## Absorption from a Line

Three main properties that define an absorption line: **central position** of the line (e.g., the central frequency  $\nu_0$ ), **strength** of the line (or intensity,  $S$ ), and **shape** factor (or line profile,  $f$ ) of the line.

$$\tau = \kappa h; \kappa_\nu = S f(\nu - \nu_0); \int f(\nu) d\nu = 1$$

- $\tau$  is optical depth of layer
- $\kappa$  is absorption coefficient (depends on concentration)
- $\nu_0$  is the line center frequency
- $f(\nu)$  is the line shape function
- $S$  is the line strength or intensity.
- Units:  $f(\nu)$  [cm]  $S$  [cm/g] or [cm/molec]

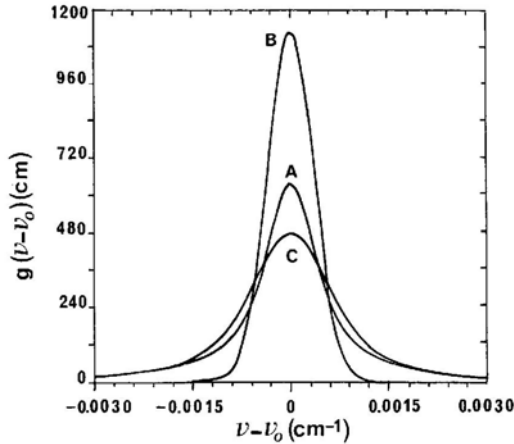
## Line Broadening

Line shape determined from broadening mechanisms:

- Natural line width from uncertainty principle; very small.
- Pressure (collisional) broadening; important below stratopause.
- Doppler broadening; important in upper stratosphere and above.

Molecular collisions in air greatly reduce upper state lifetimes, and hence broaden absorption lines.

Doppler frequency shift from distribution of molecular velocities causes absorption line broadening.



### Natural Line Width

$$\Delta E \Delta t \geq h/2\pi$$

$$\Delta \nu = \Delta E/hc = 1/2\pi t_n c \quad (t_n \text{ is time spent in upper state})$$

In thermal IR lifetimes of isolated molecules are  $t_n = 0.1$  to  $10$  sec:  $\Delta \nu \sim 10^{-11} \text{ cm}^{-1}$  (completely negligible)

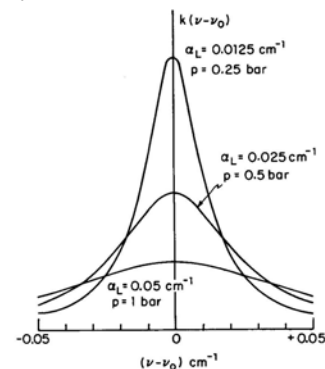
### Collision (Pressure) Broadening

- Molecular collisions in air greatly reduce upper state lifetimes, and hence broaden absorption lines.
- Mean velocity  $v = 8k_b T / \pi m \approx 450 \text{ m/s}$
- Treat molecules as hard spheres of radius  $r = 2 \times 10^{-10} \text{ m}$ , collides with molecules within  $2r$  of trajectory
- Volume swept/time is  $V = \pi(2r)^2 v = 2 \times 10^{-16} \text{ m}^3/\text{s}$
- Number of molecules per  $\text{m}^3$  at STP is  $n_L = 2.69 \times 10^{25} \text{ m}^{-3}$
- Time between collisions  $t_c = 1/(n_L V) = 1.6 \times 10^{-10} \text{ s}$
- Line half-width is  $\gamma \approx 1/2\pi c t_c = 0.03 \text{ cm}^{-1}$

Pressure broadening causes Lorentz line shape: 
$$f(\nu - \nu_0) = \frac{\alpha/\pi}{(\nu - \nu_0)^2 + \alpha^2}$$

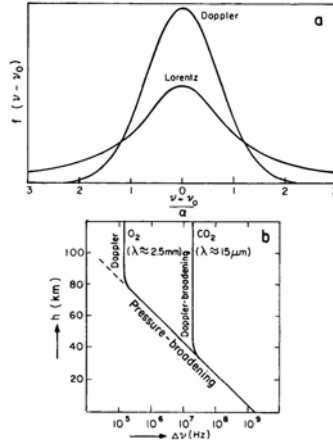
Self broadening: due to collisions between a molecular species and with same molecule; important for high concentrations

Foreign broadening: due to collisions between a molecular species and carrier gas



## Doppler Broadening

Doppler frequency shift from distribution of molecular velocities causes absorption line broadening.

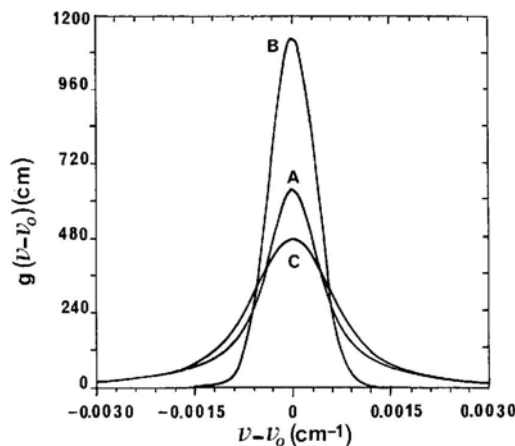


**a) A comparison of Doppler and Lorentz line shapes. b) Relationship between atmospheric height and linewidth for a microwave line of O<sub>2</sub> and an infrared line of CO<sub>2</sub>.**

Voigt Profile: When pressure broadened Lorentz half-width becomes comparable to Doppler width, the broadening effects must be convolved to get the Voigt line shape:

$$f_V(\nu - \nu_0) = \frac{a}{\pi^{3/2} \alpha_D} \int_{-\infty}^{+\infty} \frac{e^{-y^2}}{(x - y)^2 + a^2} dy$$

In the line wings the Voigt profile has a Lorentz shape. At the line center or core, it has a Doppler behavior.



**Line profiles: A is Lorentz, B is Doppler, and C is Voigt profile resulting from convolution of A and B.**

## Line-by-Line Models

Calculate monochromatic optical depth for a layer by summing contribution of all absorption lines, then sum layers vertically, then integrate across spectrum.

Optical depth of layer at height  $z$  due to lines from a particular gas:

$$\Delta\tau_\nu(z) = \kappa_\nu(z)\Delta u(z) = [\sum S_i f(\nu - \nu_i; \alpha_i)] \Delta u(z)$$

Add up optical depths from all relevant species, e.g.:

$$\Delta\tau_\nu = \Delta\tau_{\nu, H_2O} + \Delta\tau_{\nu, O_3} + \Delta\tau_{\nu, CO_2} + \dots$$

Integrate optical depth vertically:

$$\tau_\nu = \sum \Delta\tau_\nu(z_j)$$

Integrate monochromatic transmission across spectrum:

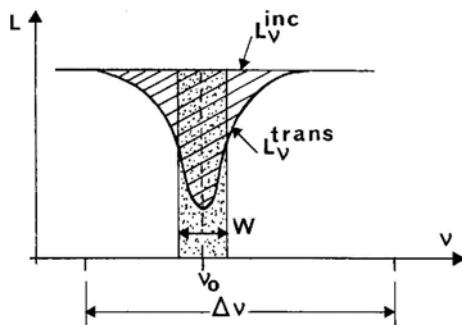
$$t = \int \exp[-\tau_\nu / \cos \theta] d\nu$$

## Band Transmission

- The high spectral detail of molecular absorption lines ( $\sim 0.001 \text{ cm}^{-1}$ ) prevents rapid radiative transfer computations across the spectrum (line-by-line models are very slow)
- Approximate radiative transfer methods divide the spectrum into spectral bands from 10 to  $100 \text{ cm}^{-1}$  wide.
- In each band the Planck function is approximately constant. Longwave radiative transfer can then be formulated in terms of mean transmission between levels. Hence the need for the **mean transmission across a spectral band**:  $\Delta\nu$

## Single Line Transmission

- **Average absorption** across a single line is:  $A_{\Delta\nu}(u) = 1 - t_{\Delta\nu} = \frac{1}{\Delta\nu} \int_{\Delta\nu} (1 - e^{-\kappa u}) d\nu$
- **Equivalent width**:  $W = \Delta\nu A_{\Delta\nu} = \int_{\Delta\nu} (1 - e^{-\kappa u}) d\nu$



- units of spectral interval ( $\text{cm}^{-1}$ )  
 -  $W$  is the equivalent width of a fully absorbing ( $A=1$ ) rectangular line.

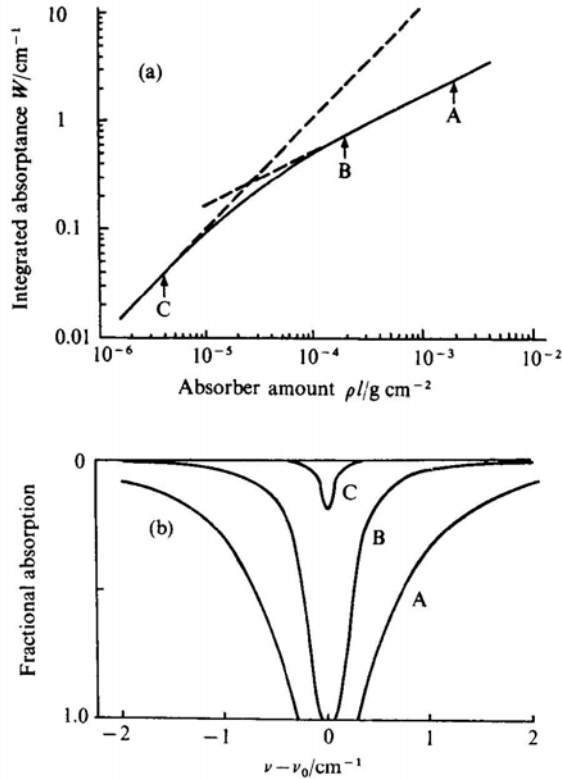
## Equivalent Width of Lorentz Line

Weak line limit,  $\kappa_\nu u \ll 1$ :  $W \approx \int k_\nu u d\nu = Su$

*Linear in absorber amount and line strength.*

Strong line limit:  $\kappa_\nu u \gg 1$   $W = 2\sqrt{Su\alpha}$

*Line center saturates, absorption increases from expanding width.*



*Curve of growth* describes increase in absorption with absorber amount.

## Absorption/emission spectra

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

