# PHY2505S
# Atmospheric Radiative Transfer and Remote Sounding

## Lecture 10

- Width and Shape of Spectral Lines (continued)
- Equivalent Width and Schwarzchild's Equation again

# Infrared Line Shapes

- In order to perform any calculations with an infrared line, we need to define its line shape function (f) and line strength (S).

- These are independent properties of a line.
  - → Line shape is determined by atmospheric broadening mechanisms.
  - → Line strength is determined by quantum mechanical considerations of the strength of the interactions between the molecule and the photon field.

- The absorption coefficient is thus: $k(\bar{\nu}) \propto S\,f(\bar{\nu})$

- The line shape function is also normalized (completely separating the effects of broadening from the line strength):

$$\int_0^\infty f(\bar{\nu})\,d\bar{\nu} = 1 \quad \text{and} \quad S = \int_0^\infty k_{\bar{\nu}}\,d\bar{\nu}$$

# Line-Broadening Processes

Every infrared line has a line width, which results from 3 processes:

**(1)** Natural line broadening due to uncertainties in the energy levels.

→ Only important in the upper stratosphere and mesosphere.

**(2)** Pressure (or Lorentz) broadening due to collisions between molecules which distort them and cause absorption at slightly different frequencies.

→ Most relevant to the lower atmosphere below 40 km.

→ Note: pressure varies by a factor of 3 from the surface to ~40 km

**(3)** Doppler broadening due to the random motion of molecules.

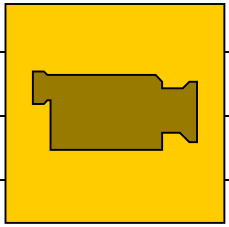
→ If a molecule moves with thermal velocity *V* and emits at $\bar{\nu}_o$:

$$\bar{\nu} = \bar{\nu}_o\left(1 \pm V / c\right) \quad \text{with} \quad V << c$$

→ Most relevant to the atmosphere above about 40 km, becoming comparable to Lorentz broadening at 40 km.

# Width and Shape of Spectral Lines

## … continued from Lecture 9



# Doppler-Broadened Lines

- The line shape function for a Doppler-broadened line is:

$$f_D(\bar{\nu}-\bar{\nu}_o)=\frac{1}{\sqrt{\pi}\alpha_D}\exp\left(-\frac{(\bar{\nu}-\bar{\nu}_o)^2}{\alpha_D^{\ 2}}\right)$$

where

$$\alpha_D(T)=\sqrt{\frac{2k_BT}{M}}\frac{\bar{\nu}_o}{c}$$

→ $\alpha_D$ = Doppler line-width (HWHM / $\sqrt{\ln 2}$)

→ $k_B$ = Boltzmann's constant

→ M = molecular mass

- The absorption coefficient of a Doppler-broadened line is thus:

$$k_a(\bar{\nu})=\frac{S}{\sqrt{\pi}\alpha_D}\exp\left(-\frac{(\bar{\nu}-\bar{\nu}_o)^2}{\alpha_D^{\ 2}}\right)$$

# Lorentz-Broadened Lines

- The line shape function for a Lorentz-broadened line is:

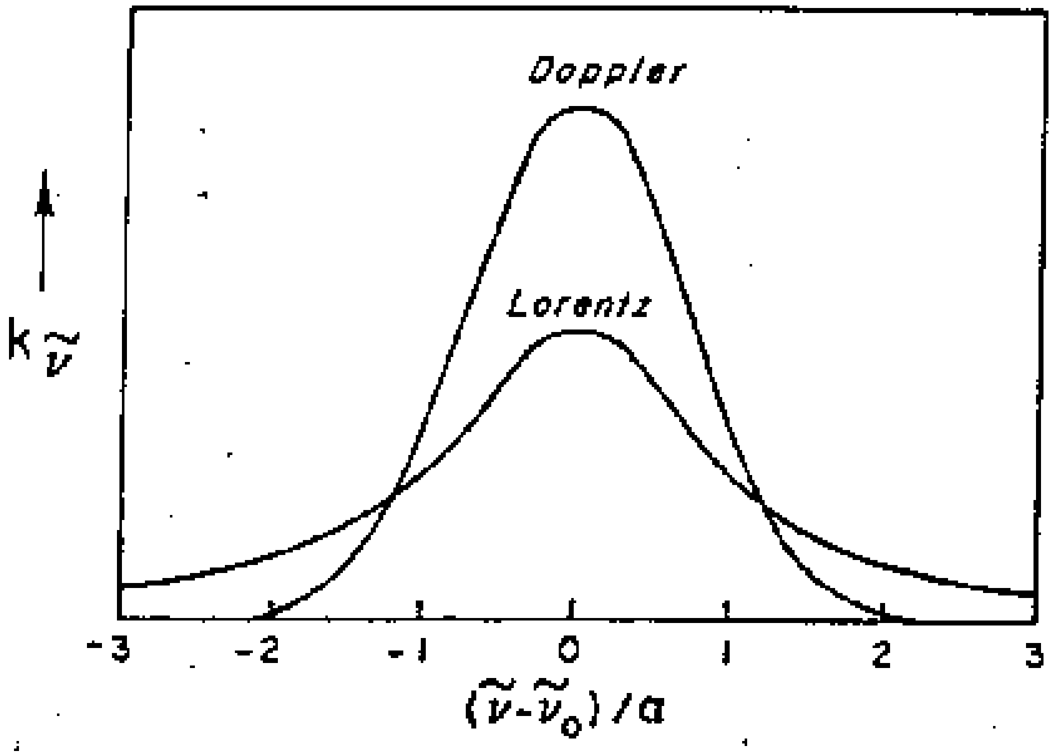
$$f_L(\bar{\nu}-\bar{\nu}_o) = \frac{1}{\pi}\frac{\alpha_L}{(\bar{\nu}-\bar{\nu}_o)^2+\alpha_L^{\ 2}}$$

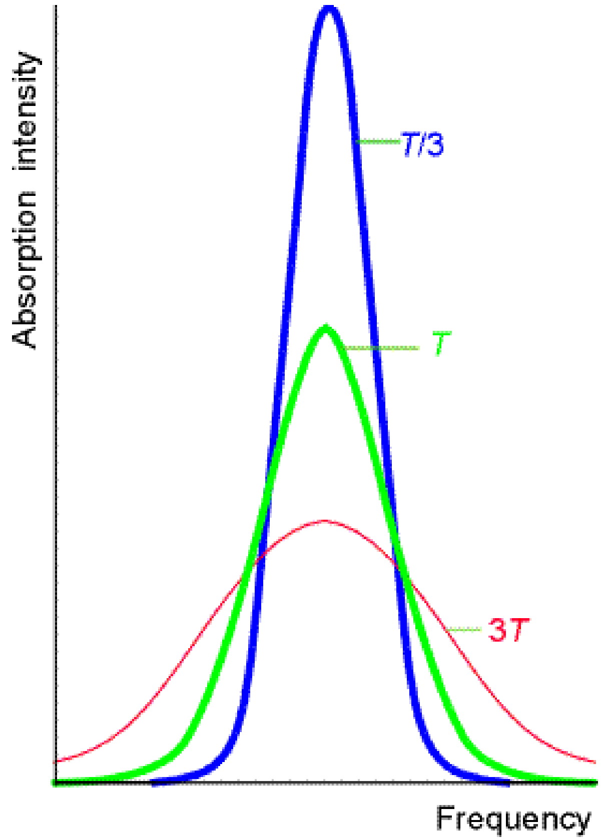
  where
  - → $\bar{\nu}_o$ = central wavenumber
  - → $\alpha_L$ = Lorentz half-width (HW at HM) $\quad \alpha_L(T,p) = \alpha_L^o(T_o,p_o)\frac{p}{p_o}\left(\frac{T_o}{T}\right)^N$
  - → $\alpha_L^0$ ranges from 0.01 to 0.1 cm$^{-1}$ for most gases
  - → $T_o$ and $p_o$ = reference T and p (273.15 K, 1013.25 mbar)
  - → N = exponent of temperature dependence = 0.5 to 1 (usually use 0.5)
- The absorption coefficient of a Lorentz-broadened line is thus:

$$k_a(\bar{\nu}) = \frac{S}{\pi}\frac{\alpha_L}{(\bar{\nu}-\bar{\nu}_o)^2+\alpha_L^{\ 2}}$$

  where
  - → S = line strength, a function of T and lower state energy E"
- Every Lorentz-broadened line can be specified by four parameters: $\bar{\nu}_o$, S, $\alpha_L^o$, E".

# Lorentz and Doppler Lines




Note: Doppler lines are more intense at the centre and weaker in the wings than Lorentz lines.

*From Liou, 1980.*

The shape of a Doppler-broadened line reflects the Maxwell distribution of speeds in the sample at the temperature of the experiment. Notice that the line broadens temperature increases.

*From: http://www.raunvis.hi.is/~agust/dopp.htm*

# The Voigt Line Shape

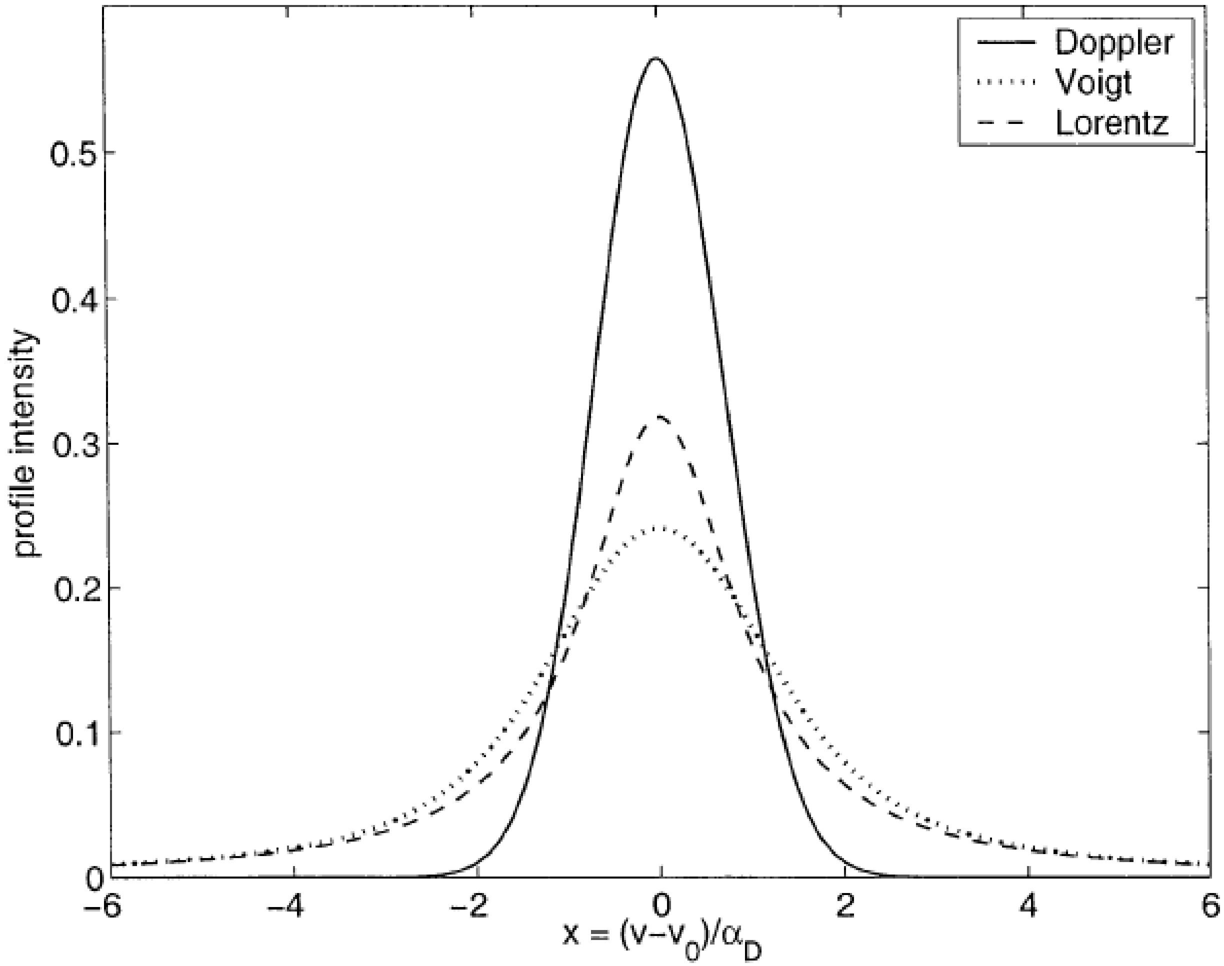
- The influence of Lorentz and Doppler broadening can be combined in a convolution function called the Voigt line shape.
  - → This is useful when both effects are important, e.g., near 40 km in the Earth's atmosphere.
  - → Requires numerical calculations.

$$f_{Voigt}(\tilde{\nu}-\tilde{\nu}_0) = \int_{-\infty}^{\infty} f_L(\tilde{\nu}'-\tilde{\nu}_0) f_D(\tilde{\nu}-\tilde{\nu}') d\nu' =$$

$$\frac{\alpha}{\alpha_D \pi^{3/2}} \int_{-\infty}^{\infty} \frac{1}{(\tilde{\nu}'-\tilde{\nu}_0')^2+\alpha^2} \exp\left[-\left(\frac{\tilde{\nu}-\tilde{\nu}'}{\alpha_D}\right)^2\right] d\nu'$$

- At high pressures: the Doppler profile is narrow compared to the Lorentz → the Voigt profile is the same as the Lorentz profile.
- At low pressures: the Voigt profile is a "hybrid" line with a Doppler center and Lorentz wings.

# The Voigt Line Shape




https://www.researchgate.net/figure/Voigt-profile-is-the-convolution-of-the-Doppler-and-Lorentz-profiles_fig7_305220662.

# Equivalent Width and Schwarzchild's Equation again