

# The Radiative Transfer Equation and Absorption and Emission Spectroscopy

John W Daily



# The Radiative Transfer Equation

- In spectroscopy we typically use focused beams of electromagnetic radiation, looking for how the radiation is absorbed, emitted or scattered.
- We track the propagation of radiation using the radiative transfer equation.
- The radiative transfer equation is essentially a statement of the conservation of radiative energy.



# Characterizing Radiation

- An important radiant property is the irradiance.
- Irradiance is the radiant power per unit area in the direction of propagation. The SI units are  $\text{W}/\text{m}^2$ .
- Spectral irradiance is the irradiance per unit frequency or wavelength. The units are  $\text{Wsec}/\text{m}^2$  or  $\text{W}/\text{nm}\cdot\text{m}^2$ .

# The Radiative Transfer Equation

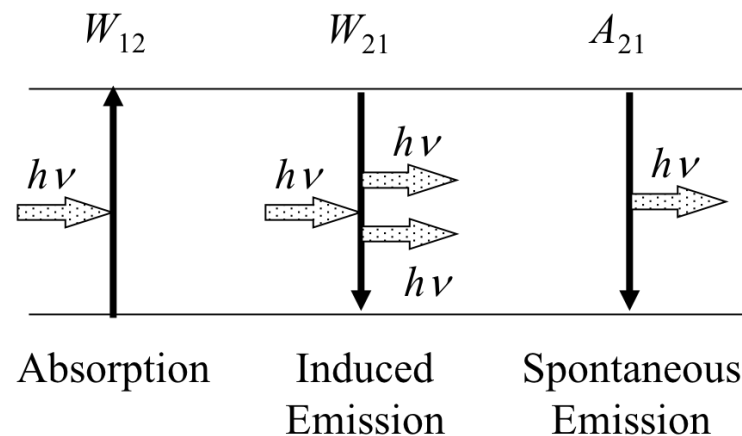
- Equation (Assuming  $E_\nu$  broader than lines)

$$\frac{dE_\nu}{dz} = -h\nu(B_{12}N_1 - B_{21}N_2)\phi(\nu)E_\nu + h\nu\frac{A_{21}}{4\pi}N_2\phi(\nu)$$

- Absorption and emission coefficients

$$\alpha_\nu \equiv h\nu(B_{12}N_1 - B_{21}N_2)\phi(\nu) \quad \epsilon_\nu \equiv h\nu\frac{A_{21}}{4\pi}N_2\phi(\nu)$$

- so  $\frac{dE_\nu}{dz} = \epsilon_\nu - \alpha_\nu E_\nu$



# Line Broadening

- Since the energy difference between two quantum states is a precise value, you might expect that only radiation of frequency  $\nu = E/h$  would be absorbed or emitted.
- However, because of two effects, the Doppler effect, and collisions, the actual absorption/emission line appear to be broader.



# The Doppler Effect

- The doppler effect is the perceived change in frequency of an emitting object due to changes in the relative velocity with respect to the observer.
- This is best known from the change in the tone of a car horn or train whistle as the vehicle passes by.



# The Doppler Effect

- The Doppler linewidth is derived from the Maxwellian velocity distribution:

$$\varphi_D(\nu) = \frac{2\sqrt{\ln 2}}{\Delta\nu_D\sqrt{\pi}} \exp\left(-\left(\frac{2\sqrt{\ln 2}(\nu - \nu_0)}{\Delta\nu_D}\right)^2\right)$$



# Collisional Broadening

- Light is electromagnetic radiation. It is described by Maxwell's equations.
- A simple, coherent, single frequency light wave can be represented as a continuous sine or cosine wave.
- What a detector sees is the Fourier transform of the time dependent wave.
- For a simple wave, the Fourier transform is a delta function.

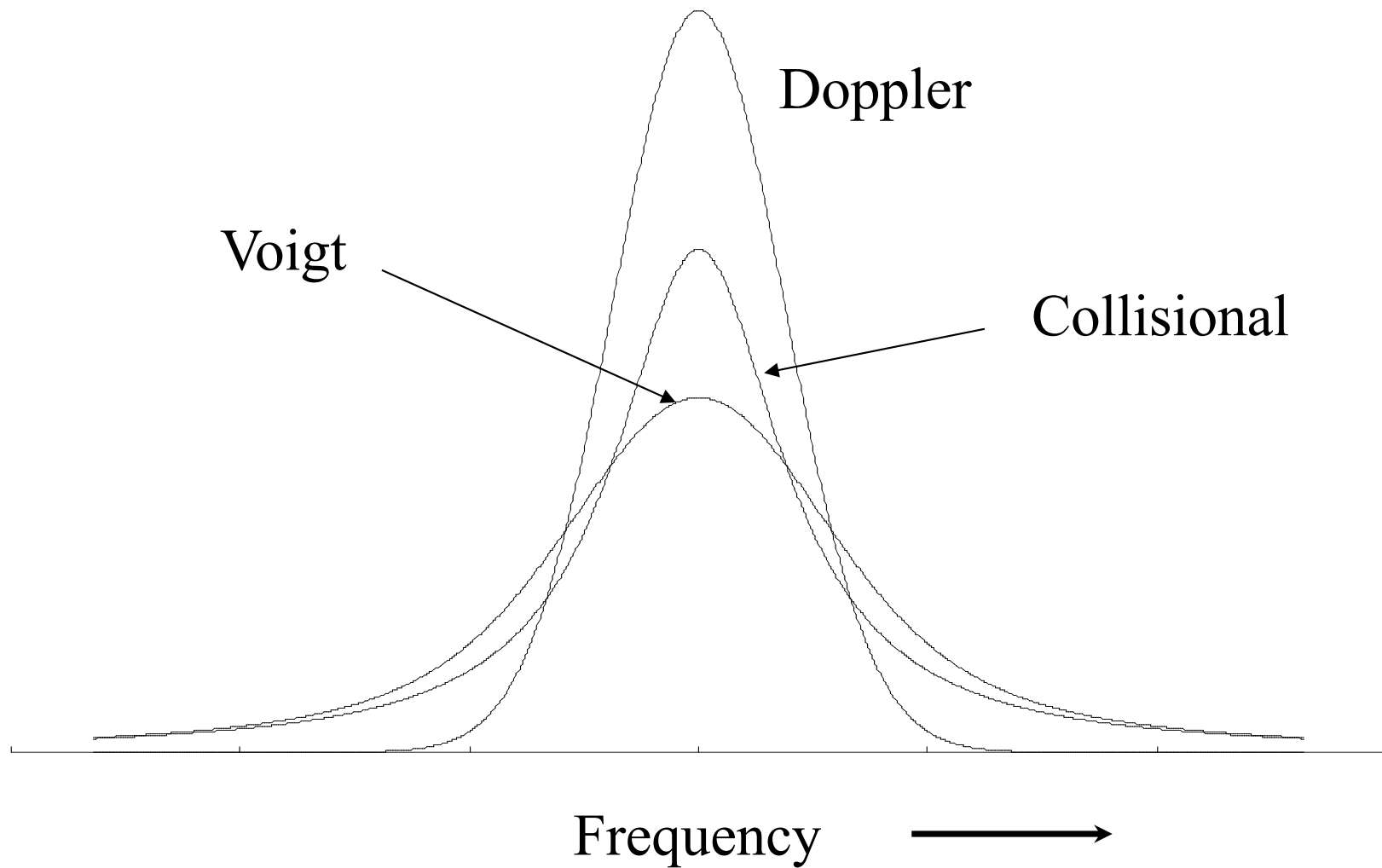


# Collisional Broadening

- However, light is not emitted by atoms and molecules without interruption.
- Collisions will certainly disrupt absorption and emission, and emission will only last the lifetime, or inverse of the A-coefficient.
- One can show that the line shape function is of the form

$$\varphi_L(\nu) = \frac{1}{\pi} \frac{\Delta\nu / 2}{(\nu - \nu_0)^2 + (\Delta\nu / 2)^2}$$

# Line Broadening

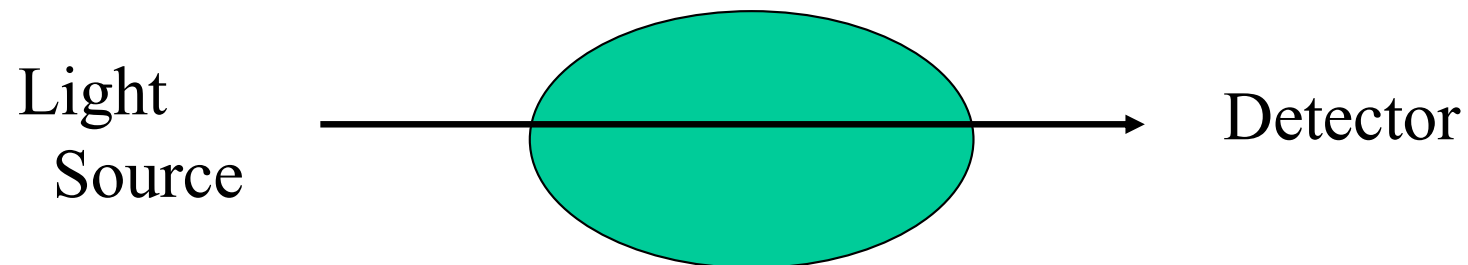


# Absorption Spectroscopy

- Typically,  $N_2 \ll N_1$ , so that

$$E_\nu(z) = E_\nu(0)\exp(-\alpha_\nu z)$$

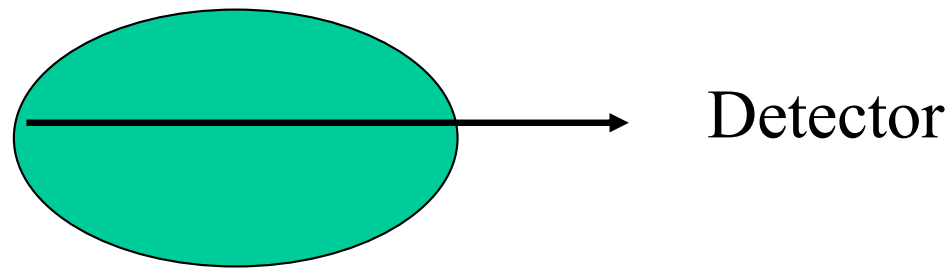
- This is called Beer's Law



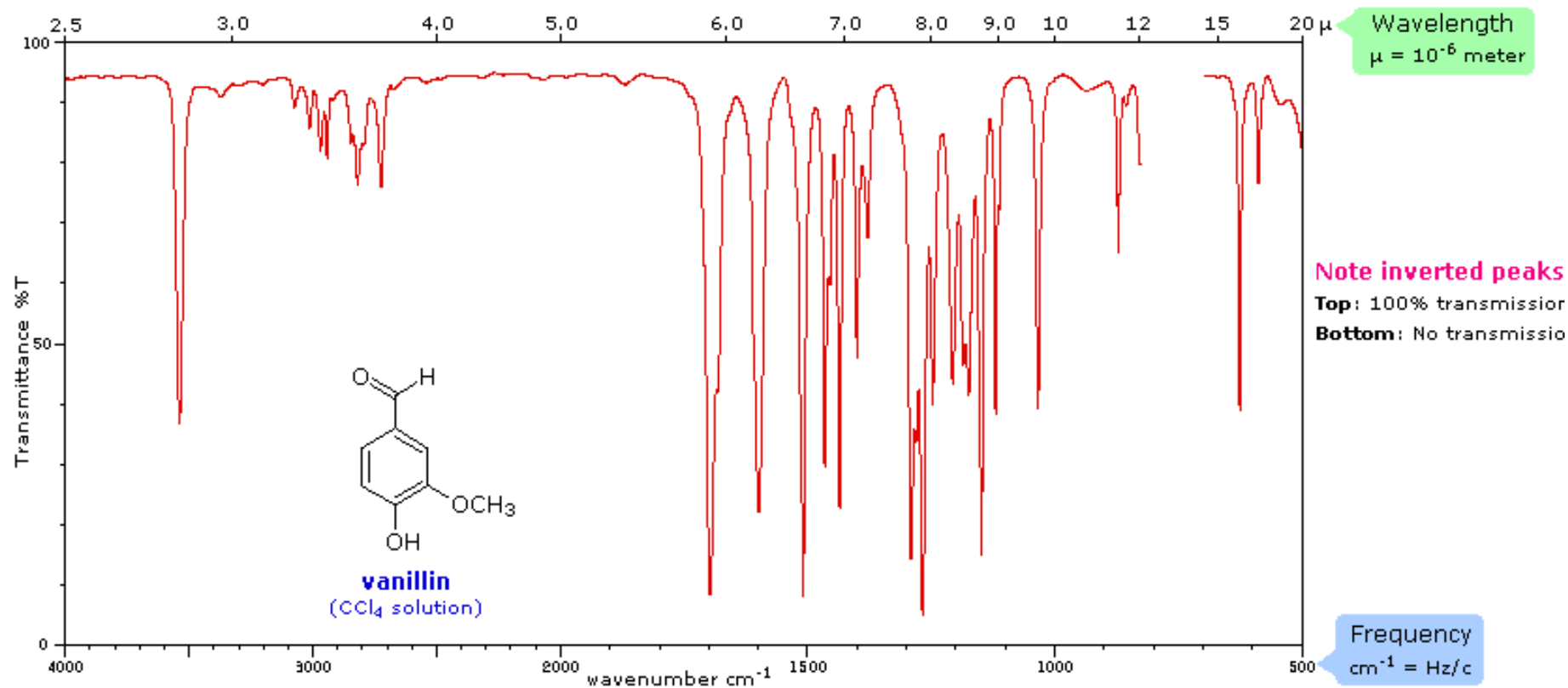
# Emission Spectroscopy

- Here we observe radiation from the atom or molecule

$$E_v(z) = \varepsilon_v z$$



# Example Absorption Spectrum



<https://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/Spectrpy/InfraRed/infrared.htm>

