Lesson 9:
Quantum Spectroscopy II

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EPS 237: Planetary Radiation and Climate

Full 3D expression:

$$f(v)\, d^3v = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{mv^2}{2kT}}\, d^3v$$

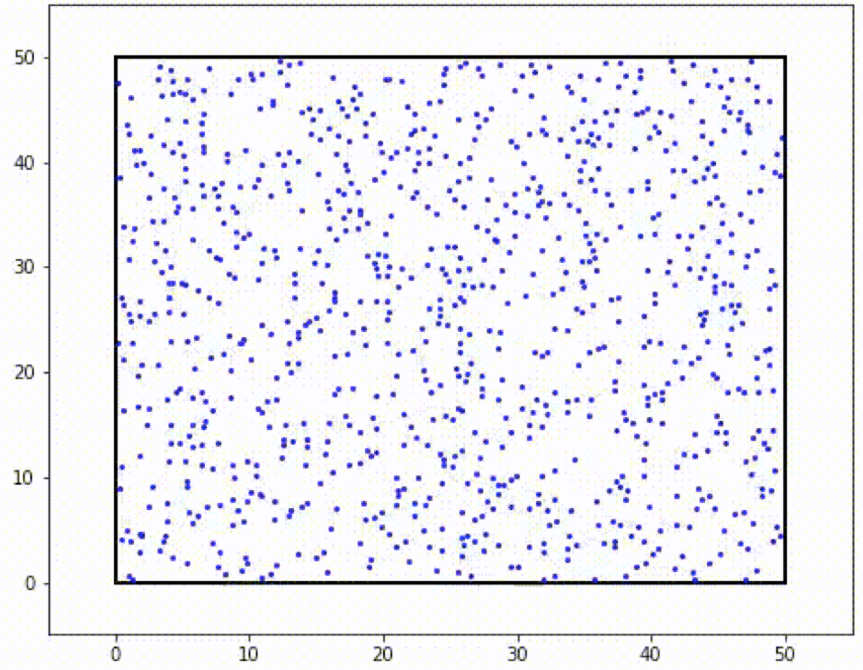
$$d^3v = dv_x\, dv_y\, dv_z$$

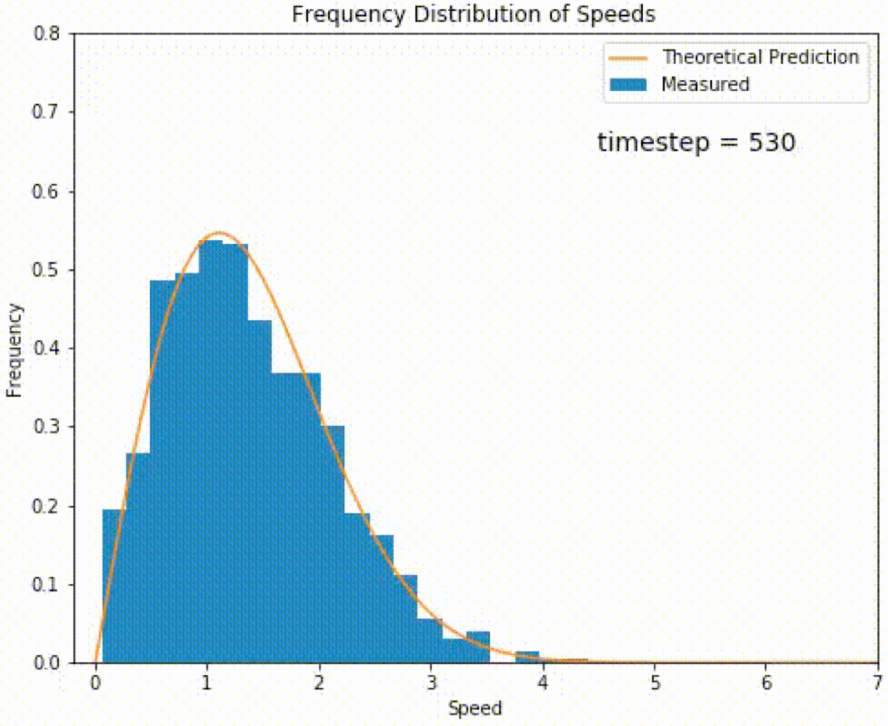
Probability distribution for single velocity component in x-direction:

$$f(v_x)\, dv_x = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-\frac{mv_x^2}{2kT}}\, dv_x$$

Probability distribution for speed:

$$f(v)\, dv = \left(\frac{m}{2\pi kT}\right)^{3/2} 4\pi v^2 e^{-\frac{mv^2}{2kT}}\, dv$$





Objectives

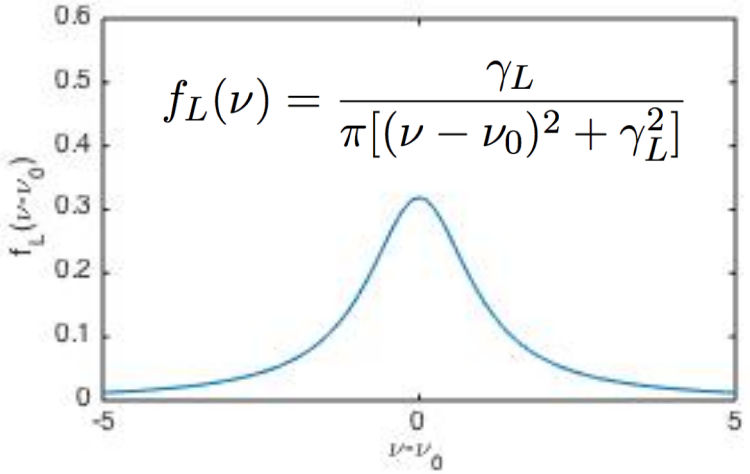
- Discuss physical principles behind line broadening
- Derive the Einstein coefficients linking absorption and emission strength
- Learn how line strengths depend on the quantum mechanical properties of a given transition

Line Broadening

- Spectral line positions in frequency / wavenumber correspond to the *differences* in energy between initial + final molecular state
- Transition most likely when photon frequency matches this value. However, there is also finite probability of transition at nearby frequencies due to:
  - Natural line broadening (Heisenberg uncertainty)
  - Doppler line broadening
  - Collisional line broadening

Overview

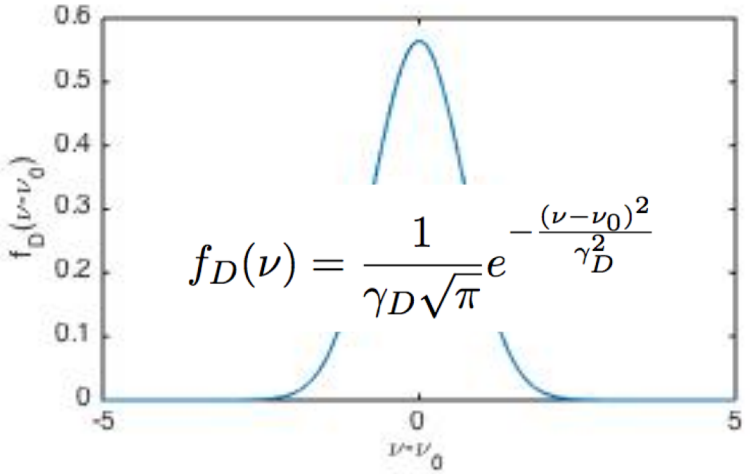
LORENTZIAN



NATURAL BROADENING
Negligible

PRESSURE BROADENING
Dominates in lower atmosphere

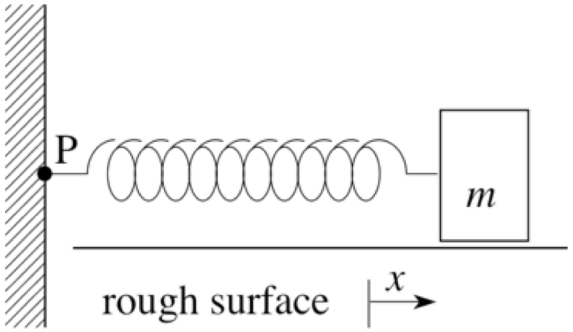
GAUSSIAN



DOPPLER BROADENING
Dominates at high wavenumber and in upper atmosphere

Semi-classical view of collisional broadening: A forced damped oscillator

$$\ddot{x} = -\omega_0^2 x - \alpha\dot{x} + f(t)$$



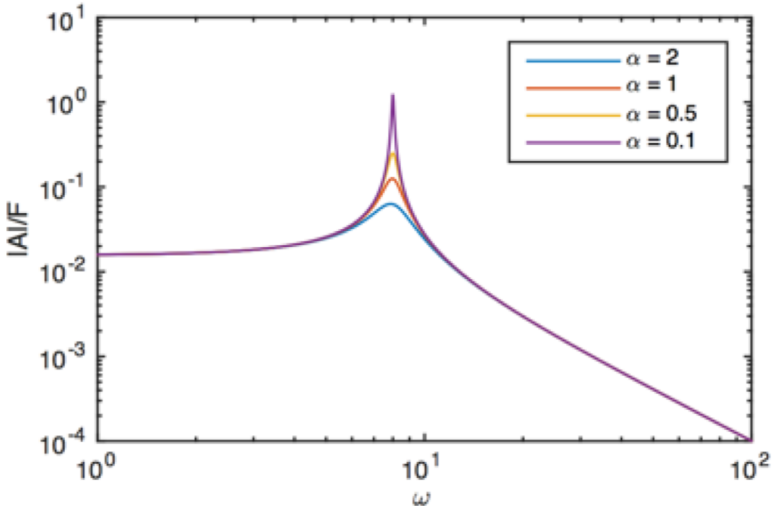
Use complex analysis:

$$f(t) \rightarrow Re[F\mathrm{e}^{i\omega t}], \qquad x \rightarrow z = A\mathrm{e}^{i\omega t}$$

$$x = Re\left[\frac{Fe^{i\omega t}}{\omega_0^2 - \omega^2 + i\alpha\omega}\right]$$

$$|A|^2 = \frac{F^2}{(\omega_0^2 - \omega^2)^2 + \alpha^2\omega^2}$$

$$|A|^2 \approx \frac{1}{4\omega_0^2}\frac{F^2}{(\omega_0 - \omega)^2 + (\alpha^2/2)^2}$$



http://www.met.reading.ac.uk/pplato2/h-flap/phys5_3.html

Calculating Line Widths in Practice

- **Doppler**
  - Just use the formula: $\gamma_D = \frac{\nu_0}{c}\sqrt{2RT}$
- **Pressure**
  - Take the HITRAN values and scale them to the appropriate temperature and pressure. Include self-broadening only if gas is a major constituent.

$$\gamma_L(p,T) = \gamma_L(p_0,T_0)\frac{p}{p_0}\left(\frac{T_0}{T}\right)^n$$

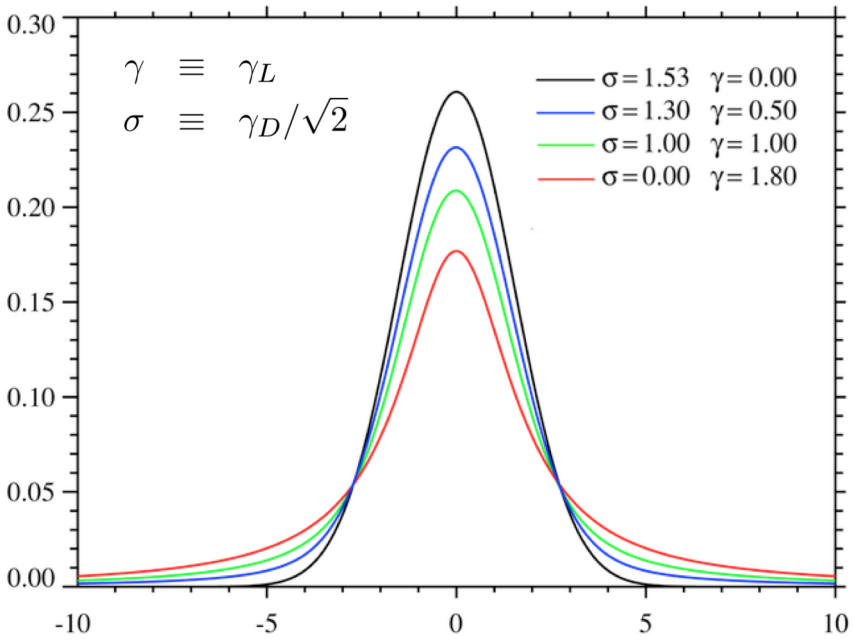
Remember: 'Frequency' in HITRAN is in units of cm^{-1}

The Voigt Profile

Convolution of Doppler and Lorentz profiles yields the *Voigt* profile:

$$f_V(\nu-\nu_0) = f_D(\nu-\nu_0) \otimes f_L(\nu-\nu_0)$$

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



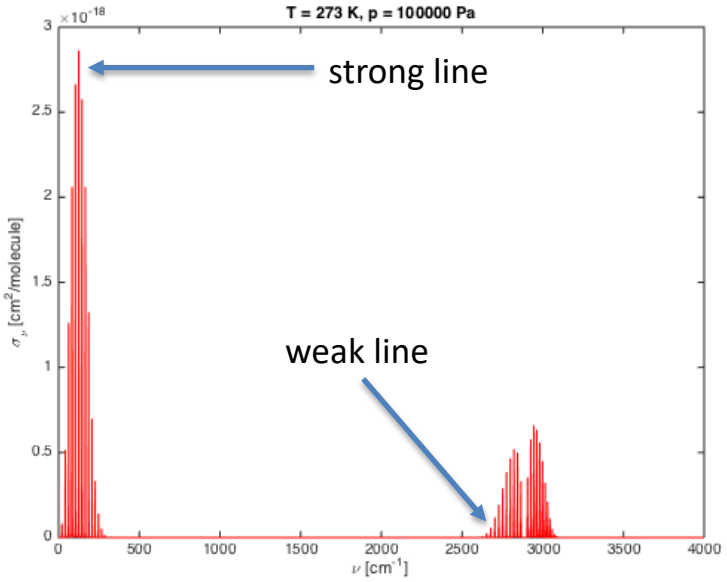
https://en.wikipedia.org/wiki/Voigt_profile

Line Strengths

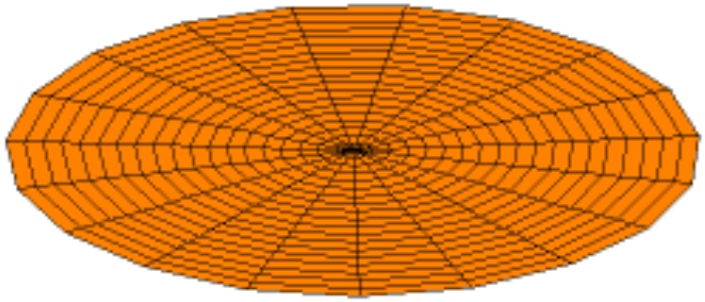
- We now understand the physics behind line locations and line widths
- Final step is to understand what determines overall line strength (line intensity)
- Starting point for this is the time-dependent form of the Schrodinger equation

$$S_{12} \equiv \frac{1}{n} \int_{-\infty}^{+\infty} k_{12}(\nu) d\nu$$

HITRAN UNITS: cm^{-1} / (molecule.cm^{-2})



The time-varying wavefunction



(real part only)

$$\Psi(\mathbf{r},t) = \sum_m a_m \psi_m(\mathbf{r}) e^{-iE_m t/\hbar}$$

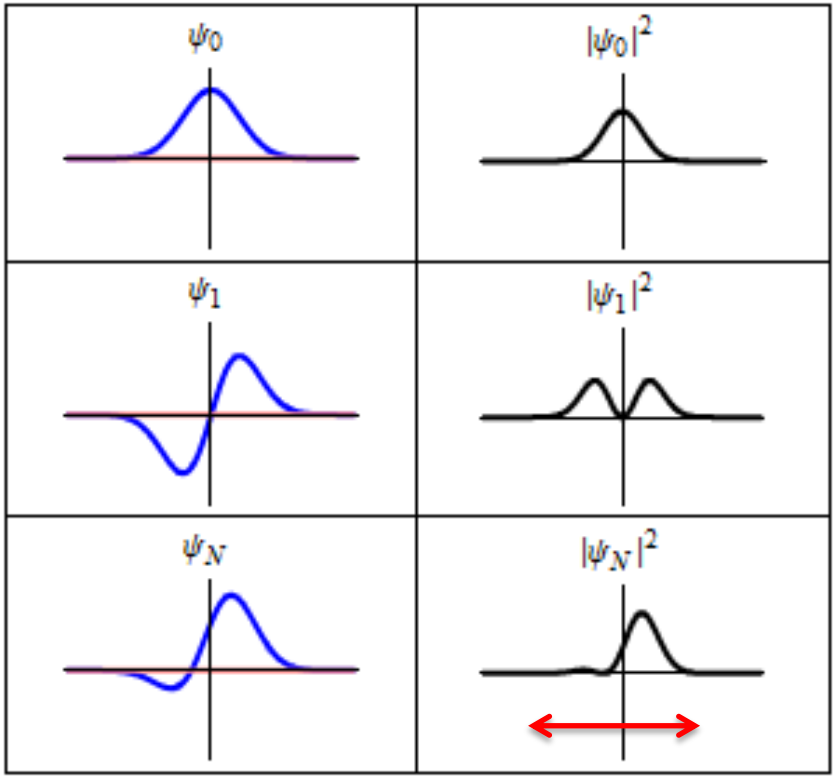
spatially varying part

time varying part

Quantum Transitions

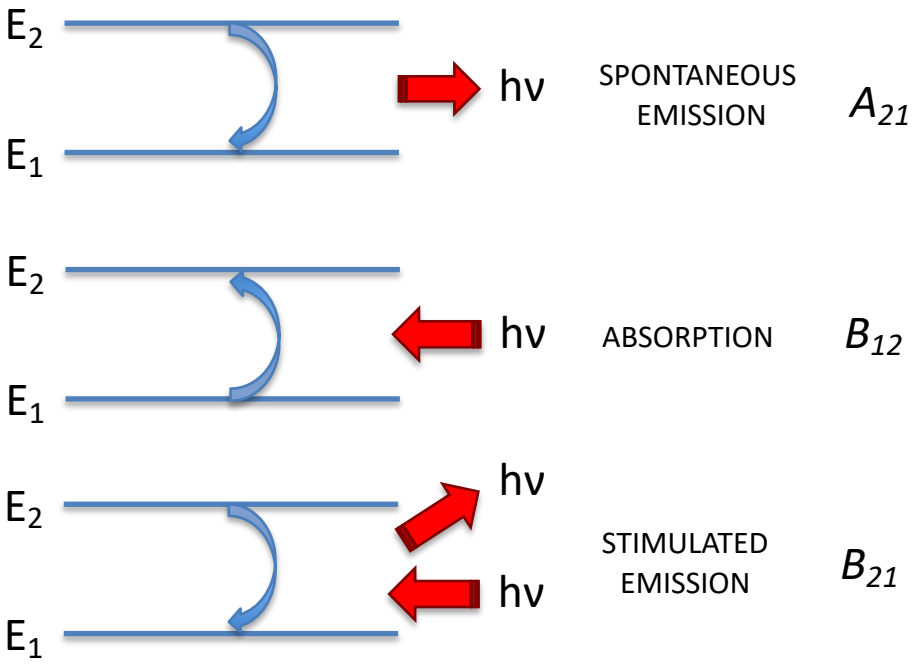
- **Classical picture**: acceleration of charges leads to emission of electromagnetic radiation
- **Quantum picture**: non-zero transition dipole matrix element leads to emission of electromagnetic radiation

Schrödinger equation solutions for a simple harmonic oscillator:



https://en.wikipedia.org/wiki/Transition_dipole_moment#/media/File:StationaryStatesAnimation.gif

Einstein coefficients



$$A_{21} = \frac{8\pi h\nu^3}{c^3} B_{21}$$

$$g_1 B_{12} = g_2 B_{21}$$

statistical weight due to level degeneracy

- Knowledge of any one coefficient allows you to know them all
- True even *out* of thermal equilibrium!

The Transition Dipole Matrix Element

eigenfunction of lower energy state

$$|R_{21}| \equiv \int \psi_2^* p_z \psi_1 d^3\mathbf{r} \equiv \langle \psi_2 | p_z | \psi_1 \rangle$$

eigenfunction of higher energy state

molecule's dipole moment

$$|R_{21}| = |R_{12}|$$

$$B_{12} = \frac{(2\pi)^3 |R_{12}|^2}{h^2}$$

Back to Line Strength

- Line strength depends both on the TDME *and* on occupancy of energy levels
- We already saw this in the shape of the HCl pure rotational band (last lecture)

frequency of transition

frequency of lower energy state

General version:

$$S_{ij} = \frac{8\pi^3}{3hc}\nu_{ij}|R_{ij}|^2\left[1 - e^{-h\nu_{ij}/k_BT}\right]\frac{e^{-h\nu_i/k_BT}}{Z(T)}$$

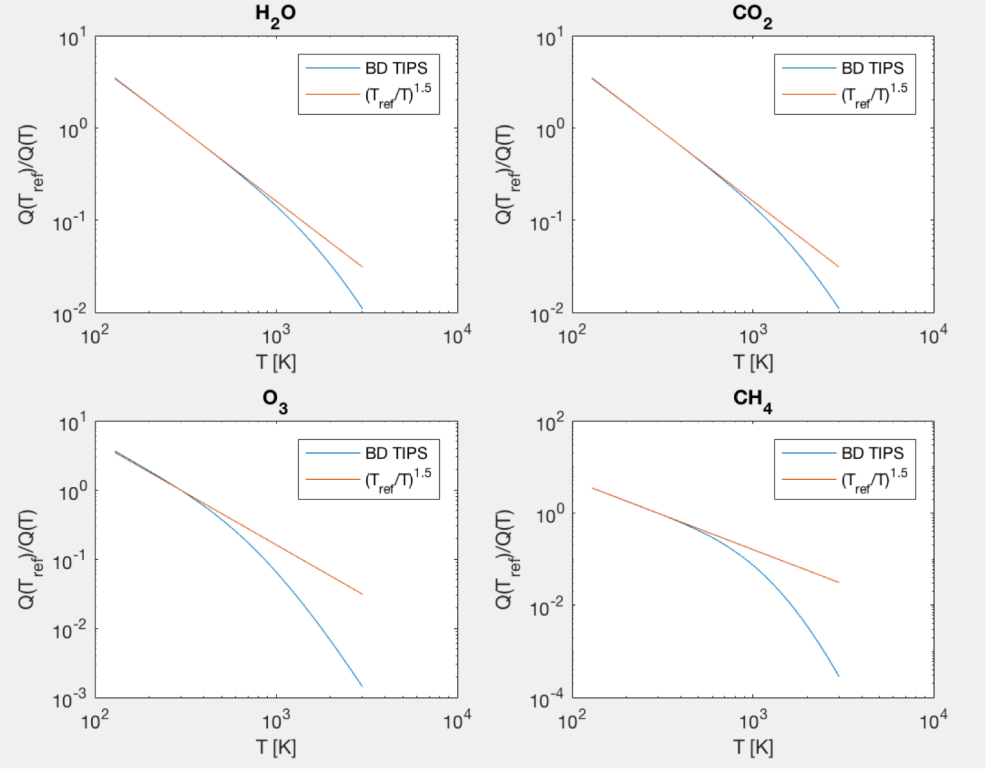
partition function (Q in HITRAN notation)

HITRAN version:

$$S_{ij}(T) = S_{ij}(T_0)\frac{Z(T_0)}{Z(T)}\frac{1 - e^{-h\nu_{ij}/k_BT}}{1 - e^{-h\nu_{ij}/k_BT_0}}\frac{e^{-h\nu_i/k_BT}}{e^{-h\nu_i/k_BT_0}}$$

Calculating the partition function

- Line strength scaling with temperature depends on partition sum $Z(T)$ [$Q(T)$ in HITRAN notation]
- In PSet 5 you can ignore this, but to compute it in later homework exercises and the final project, you have two possibilities:
  1. You can use the full TIPS approach described on the HITRAN website
  2. You can use the simple formula $Q(T_{ref})/Q(T) \approx (T_{ref}/T)^{1.5}$, which is a fair approximation for many gases below 1000 K



Line strength, cross-section and mass absorption coefficient

Cross-section [cm^2/molecule OR m^2/molecule]:

Line strength for transition from state *i* to state *j* [cm^{-1} . cm^2/molecule]

$$\sigma_{ij} = S_{ij} f(\nu, \nu_{ij}, T, p)$$

Line shape function [1 / cm^{-1}]

We sum over all lines to get a complete absorption spectrum

Mass absorption cross-section [m^2/kg]:

$$\kappa = \sigma / m$$

molecular mass [kg / molecule]

Mass absorption cross-section for multiple species (from Lecture 5):

$$\kappa(\nu, p, T) = \sum_{k=0}^{n} \kappa_k(\nu, p, T) q_k(p)$$

Calculating absorption spectra: A suggested numerical approach

1. Define pressure, temperature and composition of the gas
2. Load the HITRAN linelist for the gas (or gases) in question, over the wavenumber range of interest
3. Calculate Doppler and collisional linewidths for all spectral lines
4. Calculate line strengths at the temperature of interest for all spectral lines, scaling with gas abundance as necessary
5. Assume that each line follows a Voigt profile. Create an array of wavenumber points with fixed spacing. At each point, compute absorption cross-section as the summed contribution of each line with line center closer than a fixed distance (e.g., 25 cm^{-1}) to the gridpoint center
6. Repeat Step 5 for all gridpoints

Summary

- Spectral lines have characteristic shape + width depending on background conditions
  - Pressure broadening (Lorentzian profile) dominates in the lower atmosphere and at lower wavenumbers
  - Doppler broadening (Gaussian profile) dominates in the upper atmosphere and at higher wavenumbers
- Line strengths are determined by the transition dipole matrix, and by level occupancy (which is strongly temperature dependent)