

ESCI 340 – Physical Meteorology
Radiation Lesson 3 – Absorption Spectra
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References: *An Introduction to Atmospheric Radiation*, Liou
Radiation and Cloud Processes in the Atmosphere, Liou
Atmospheric Radiation: Theoretical Basis, Goody and Yung
Spectra of Diatomic Molecules, Herzberg
The Spectra and Structure of Simple Free Radicals, Herzberg
A First Course in Atmospheric Radiation, Petty

Reading: Petty, Chapter 9

EMISSION SPECTRUM OF HYDROGEN

- Hydrogen consists of a nucleus with 1 proton, and a shell of 1 electron.
- Through absorption of energy, the electron can take on a higher energy state.
- As the electron transitions back into a lower energy state, the excess energy is emitted as a photon.
- The frequency of the emitted photon is determined by the difference in energy between the initial state (E_i) and the final state (E_f),

$$\nu = (E_f - E_i)/h.$$

- Quantum mechanics predicts (and observations confirm) that for the hydrogen atom the energy level of an electron is given by

$$E_n = -\frac{m_e e^4}{8\epsilon_0^2 h^2} \left(\frac{1}{n^2} \right),$$

where ϵ_0 is the permittivity constant ($8.85 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$).

- n is the *quantum number*, and can only take on positive, integer values ($n = 1, 2, 3, 4, \dots$).
- The *ground state* has $n = 1$, and represents the lowest energy state attainable for the atom.
- The energy transitions that can occur in the hydrogen atom are then

$$\Delta E = E_k - E_j = \frac{m_e e^4}{8\epsilon_0^2 h^2} \left(\frac{1}{j^2} - \frac{1}{k^2} \right),$$

where m_e is the mass of an electron (9.109×10^{-31} kg) and e is the charge on an electron (1.602×10^{-19} C). The frequencies that can be emitted from the hydrogen atom are then given by

$$\nu = \Delta E/h = \frac{m_e e^4}{8\epsilon_0^2 h^3} \left(\frac{1}{j^2} - \frac{1}{k^2} \right).$$

VIBRATIONAL TRANSITIONS

- The energy transitions in an atom are due solely to changes in the energy levels of the electrons.
- For a molecule, there are additional energy transitions possible due to changes in vibrational energy and rotational energy.
- A vibrational transition can only result in emission of radiation if there is a non-zero dipole moment present.
 - A homonucleic molecule such as O₂ or N₂ does not have a dipole moment, and therefore does not emit radiation via vibrational transitions.
- If a diatomic molecule is imagined as being a simple harmonic oscillator, the energy levels are given by

$$E(J_v) = h\nu_{osc} \left(J_v + \frac{1}{2} \right)$$

where ν_{osc} is the frequency of oscillation.

- J_v is the vibrational quantum number, and has values of 0, 1, 2, 3, ...
 - Note: Petty uses slightly different notation. He used ν' instead of ν_{osc} , and ν for the rotational quantum number instead of J_v .
- The lowest energy level does not have zero energy (there is no state of zero vibration).
- The energy levels are fairly evenly spaced.
- Vibrational transitions are associated with radiation in the near IR region.
- A triatomic molecule has three modes of vibration and a more complex form for the energy levels.

ROTATIONAL TRANSITIONS

- A rotational transition can only result in emission of radiation if there is a non-zero dipole moment present.
 - A homonucleic molecule such as O₂ or N₂ does not have a dipole moment, and therefore does not emit radiation via rotational transitions.
- If a diatomic molecule is envisioned as a rotating “dumbbell”, the energy levels are given by

$$E(J_r) = \frac{h^2}{8\pi^2 I} J_r(J_r + 1).$$

- J_r is the rotational quantum number
- Are associated with emission in the far IR and microwave region
- There are three modes (one per axis)

VIBRATIONAL-ROTATIONAL TRANSITIONS

- The formulas for the energy levels given above were for the very simplest cases. In reality, the expressions for energy levels would be more complex.
- More than one type of transition can occur simultaneously, leading to an even larger number of absorption lines, and closer spacing of lines.
 - Vibrational transitions are always associated with rotational transitions, giving rise to a family of absorption lines in the IR.
- Vibrational absorption and emission lines are fairly evenly spaced.

TRANSITION MODES AND EMISSION SPECTRA

- Each type of transition (electronic, vibrational, and rotational) are associated with different parts of the EM spectrum.
- *Electronic transitions are associated with UV and higher frequency radiation.*
- *Vibrational transitions are associated with near IR radiation.*
- *Rotational transitions are associated with far IR and microwave radiation*

SHAPE OF ABSORPTION LINES

- The radiation emitted from a transition between two energy levels in an isolated molecule would theoretically be an infinitely narrow line, but in actuality the “line” has some finite width.
- The parameters of a spectral line are
 - *Position* – The central wavenumber or wavelength corresponding to the peak of the line. The position is given either as a center frequency (ν_0) or center wavenumber ($\tilde{\nu}_0$).
 - *Strength* is how much total absorption the line has, and is denoted as S .
 - *Shape* is what the line looks like, and is expressed as a function of the distance from the center frequency, $f(\nu - \nu_0)$.

- $f(\nu - \nu_0)$ is called the *line shape function*, and is normalized so that

$$\int_0^{\infty} f(\nu - \nu_0) d\nu = 1.$$

- The *absorption cross-section per molecule* as a function of line shape and strength is

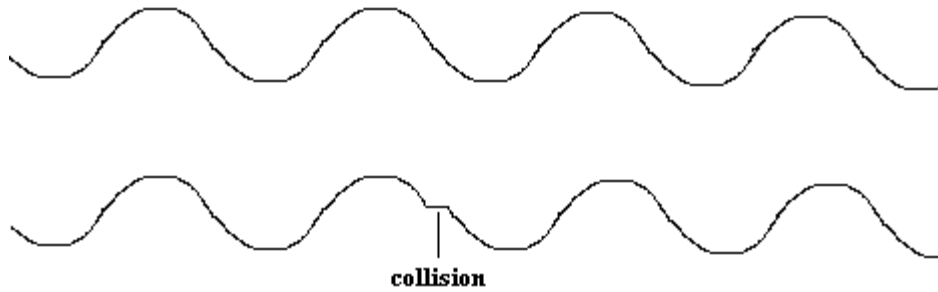
$$\sigma_{\nu} = S f(\nu - \nu_0),$$

and if integrated over all frequencies will yield the line strength,

$$\int_0^{\infty} \sigma_{\nu} d\nu = S,$$

BROADENING OF SPECTRAL LINES

- The shape of the spectral line is broadened by two main factors.
 - Collisions with other molecules (pressure broadening)
 - Doppler effect (Doppler broadening)
- Pressure broadening
 - If a molecule collides with another molecule while it is in the process of emitting a photon, the emission may be temporarily interrupted. The interruption alters the phase of the emitted wave. This discontinuity results in a larger bandwidth of radiation being emitted.



- **The shape of a pressure broadened line is given by**

$$f(\nu - \nu_0) = \frac{\alpha_L}{\pi \left[(\nu - \nu_0)^2 + \alpha_L^2 \right]}$$

where α_L is the half-width of the line and is given by

$$\alpha_L(p, T) = \alpha_0 \left(\frac{p}{p_0} \right) \left(\frac{T_0}{T} \right)^n.$$

where n is an empirically determined constant (the kinetic theory of gasses predicts a value of $1/2$).

- **An increase of pressure increases the half-width, because an increase in pressure results in more collisions.**
- **An increase of temperature decreases the half-width, because an increase in temperature (with pressure constant) decreases density, and results in fewer collisions.**
- **Doppler broadening**
 - **Doppler broadening is the result of the frequency shift of emitted radiation due to the Doppler effect.**
 - **Doppler broadening is only important in the upper atmosphere (above about 20 km) where molecular velocities become significant.**
 - **The Doppler broadened line shape is given by**

$$f(\nu - \nu_0) = \frac{1}{\alpha_D \sqrt{\pi}} \exp \left(- \frac{(\nu - \nu_0)^2}{\alpha_D^2} \right)$$

where

$$\alpha_D = \frac{\nu_0}{c} \sqrt{\frac{2k_B T}{m}}.$$

- The Doppler broadened line-width increases with increasing temperature because increased temperature implies an increased molecular velocity.

ABSORPTION SPECTRA OF ATMOSPHERIC GASES

● Nitrogen

- Molecular nitrogen is a diatomic molecule.
- Since it has no electric dipole moment, we don't expect any vibration-rotation lines, only electronic transition lines.
- It turns out that N_2 , even though vibrational-rotational transitions are prohibited, exhibits what are known as “forbidden” and “pressure-induced” vibrational and rotational transitions. These are weak, and overlap with stronger bands from CO_2 and H_2O . Usually they can be ignored, except in the stratosphere (which is very dry).
- N_2 absorbs in the ultraviolet. Absorption by N_2 is important in the upper atmosphere. It is one of the absorbers that are responsible for the increase of temperature in the thermosphere.
- Atomic nitrogen may also play a role in absorption in the thermosphere.

● Molecular oxygen

- O_2 is a diatomic molecule.
- Like N_2 , it turns out that O_2 exhibits “forbidden” or “pressure-induced” vibrational and rotational transitions. However, these bands are relatively weak.
- Molecular oxygen absorbs strongly in the visible and ultraviolet region.
- Atomic oxygen absorbs in the far UV.

- **Ozone**
 - **Ozone consists of three oxygen atoms (O₃).**
 - **Ozone is a very strong absorber in the UV.**
 - **Ozone also has rotational and vibrational transitions, and absorbs very strongly in the IR in a band centered on 9.6 μm.**

- **Carbon dioxide**
 - **Carbon dioxide is a linear molecule. It has no permanent electric dipole, but as it vibrates a dipole can be created. Thus, it has vibrational-rotational bands, and they are very important for the atmosphere.**
 - **CO₂ bands of most importance are centered at 15 μm and 4.3 μm.**

- **Water vapor**
 - **Water is a bent molecule.**
 - **Water exhibits strong absorption in many bands throughout the IR region.**
 - **Water is also a strong absorber in the microwave region.**

- **Nitrous oxide, methane, and carbon monoxide**
 - **N₂O is a linear, asymmetric molecule.**
 - **Nitrous oxide has a couple of very strong absorption bands in the IR.**
 - **Methane (CH₄) has a couple of strong absorption bands in the IR.**
 - **Carbon monoxide (CO) has one strong band in IR**

EXERCISES

1. Using a computer or graphing calculator, plot on the same set of axes the line shape function, $f(\nu - \nu_0)$ for a pressure broadened spectral line for a temperature of 288 K and pressure of 1013 mb, and for a temperature of 225 K and pressure of 250 mb. Use $p_0 = 1013$ mb, $\alpha_0 = 0.5$ cm⁻¹, $\tilde{\nu}_0 = 1000$ cm⁻¹, $n = 0.75$, and $T_0 = 273$ K.
2. Using a computer or graphing calculator, plot on the same set of axes the line shape function, $f(\nu - \nu_0)$ for a Doppler broadened spectral line for temperatures of 215 K and 360 K. Use $\tilde{\nu}_0 = 1000$ cm⁻¹ and $R' = 462$ J·kg⁻¹·K⁻¹.