Absorption Line Physics

Topics:
1. Absorption line shapes
2. Absorption line strength
3. Line-by-line models

Reading: Liou 1.3, 4.2.3; Thomas 3.3, 4.4, 4.5

Absorption Line Shapes

Absorption spectrum of a single line is broken into two parts - shape and strength:

\[ k_\nu = S f(\nu - \nu_0) \int k_\nu d\nu = S \]

\( k_\nu \) is absorption coefficient, \( \nu_0 \) is the line center wavenumber, \( f(\nu - \nu_0) \) is the line shape function, and \( S \) is the line strength.

Line shape determined from broadening mechanisms:
1. Natural line width from uncertainty principle is very small.
2. Pressure (collisional) broadening important below stratopause.
3. Doppler broadening important in upper stratosphere and above.

Natural Line Width

Heisenberg uncertainty principle is

\[ \Delta E \Delta t \geq \frac{h}{2\pi} \quad \Delta \nu = \frac{\Delta E}{\hbar c} = \frac{1}{2\pi t_n c} \]

\( t_n \) 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)

Classically, frequency precision depends on number of cycles in wave:

\[ \Delta \tilde{\nu} \sim \tilde{\nu} \frac{1}{N} = \tilde{\nu} \frac{1}{\tilde{\nu} t} = \frac{1}{t} \]
**Collisional Broadening**

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

Estimate collision time:

- Mean velocity $\bar{v} = \sqrt{\frac{8k_bT}{\pi m}} \approx 450 \text{ m/s}$
- Treat molecules as hard spheres of radius $r = 2 \times 10^{-10} \text{ m}$, collides with molecules within $2r$ of flight line.
  - Volume swept is $V = \pi (2r)^2 \bar{v} = 2 \times 10^{-16} \text{ m}^3/\text{s}$
- Number of molecules per 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 halfwidth is $\alpha \approx \frac{1}{2\pi c t_c} = 0.03 \text{ cm}^{-1}$

Typical halfwidth of 15 $\mu$m CO$_2$ line at 296 K at 1013 mb is 0.07 cm$^{-1}$.

Collisional or pressure broadening causes Lorentz line shape

$$f(\nu - \nu_0) = \frac{\alpha/\pi}{(\nu - \nu_0)^2 + \alpha^2}$$

In the microwave the asymmetric *Van Vleck-Weisskopf* shape is used.

Motivate the Lorentz line shape: electric field of emitted wave train

$$E(t) \propto \exp(-t/t_c)e^{2\pi i\tilde{\nu} t}$$

Exponential term from Poisson distribution of collisions.

Fourier transform to get to frequency space

$$E(\tilde{\nu}) \propto \frac{1}{1/t_c + 2\pi i(\tilde{\nu} - \tilde{\nu}_0)}$$

Square to get intensity, so line shape is

$$f(\tilde{\nu} - \tilde{\nu}_0) \propto \frac{1}{(\tilde{\nu} - \tilde{\nu}_0)^2 + 1/(2\pi t_c)^2}$$
Pressure Broadening

Lorentz line shape:

\[ f(\nu - \nu_0) = \frac{\alpha/\pi}{(\nu - \nu_0)^2 + \alpha^2} \]

\(\alpha\) is Lorentz half-width at half max.

Halfwidth is from mean time between collisions \((\alpha = 1/2\pi t_c)\). Halfwidth is proportional to number of collisions per time

\[ \alpha \sim \frac{p}{T}(kT/m)^{1/2} \sim \frac{p}{T^{1/2}} \]

Pressure broadened absorption line halfwidth

\[ \alpha = \alpha_0 \left( \frac{p}{p_0} \right) \left( \frac{T_0}{T} \right)^n \]

\(\alpha_0\) is the line width at a reference temperature \(T_0\) and pressure \(p_0\) \((n\) determined empirically). Line halfwidth is proportional to pressure.

Lorentz line shape profiles for three pressures. A line width of 0.05 cm\(^{-1}\) at a pressure of 1 bar is typical for vibration-rotation bands. [Goody & Yung, Fig. 3.18]
Doppler Broadening

Doppler frequency shift from distribution of molecular velocities causes absorption line broadening. Doppler wavenumber shift is $\nu' = \nu(1 - v/c)$.

Maxwell-Boltzmann distribution of velocities along $x$ is

$$p(v_x) = \frac{1}{\sqrt{\pi v_0}} e^{-v_x^2/v_0^2}$$

where $v_0 = \sqrt{2k_B T/m}$ and $m$ is mass of molecule.

Results in Gaussian line shape for Doppler broadening

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

$$\alpha_D = \nu_0 \sqrt{\frac{2k_B T}{mc^2}}$$

Halfwidth at half max is $\alpha_D \sqrt{\ln 2}$.

Note: Doppler width does not depend on molecular properties other than mass. Width is proportional to wavenumber, so importance depends on frequency.

(a) A comparison of Doppler and Lorentz line shapes. (b) Relationship between atmospheric height and linewidth for a microwave line of $\text{O}_2$ and an infrared line of $\text{CO}_2$. [Stephens, Fig. 3.14]
**Voigt Profile**

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

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

where \( a = \alpha_L/\alpha_D \) and \( x = (\nu - \nu_0)/\alpha_D \).

There is no simple analytical function for the Voigt profiles, so various approximations are used.

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. [Lenoble, Fig. 6.1]
Absorption Line Strength

Line strength is integrated absorption cross section across a line:

\[ S = \int k_\nu d\nu \]

Line strength depends on

1) quantum mechanical transition probability, and
2) the fraction of molecules in the lower state.

Line strength is temperature dependent through population of states.

Boltzmann Distribution of States

In Local Thermodynamic Equilibrium the population of states is determined by

\[ \frac{n_i}{n_t} = \frac{g_i \exp(-E_i/k_B T)}{Q(T)} \]

where \( n_i \) is the number of molecules in energy level \( E_i \),
\( n_t \) is the total number of molecules,
\( k_B T \) is Boltzmann constant times temperature, and
\( g_i \) is the degeneracy of level (number of states with same energy).

\( Q \) is the partition function:  \( Q(T) = \sum_i g_i \exp(-E_i/k_B T) \)

Example: rotational states  \( g_J = 2J + 1 \)  \( E_J = \hbar C B J(J + 1) \)  \( Q_r \approx \frac{k_B T}{\hbar C B} \)

States with energy levels comparable or less than thermal energy \( k_B T \) are populated, but higher energy states much less populated.
The Boltzmann distribution peaks at intermediate $J$ (rotational quantum number). Increasing the temperature moves the peak to higher $J$. [Kyle, Fig. 8.3]

Distribution of rotational energy levels with $J$ for various diatomic molecules at $T=250$ K. The lower mass molecules have a larger rotational constant $B$, and hence the higher $J$ states have higher energy and are less populated. [Thomas & Stamnes, Fig. 4.11]
Two-level Atom Radiative Processes

<table>
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<th>Transition Process</th>
<th>Rate</th>
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<tr>
<td>1. Absorption</td>
<td>$B_{12}n_1\bar{I}$</td>
</tr>
<tr>
<td>2. Spontaneous emission</td>
<td>$A_{21}n_2$</td>
</tr>
<tr>
<td>3. Stimulated emission</td>
<td>$B_{21}n_2\bar{I}$</td>
</tr>
</tbody>
</table>

Stimulated emission: photon with correct energy triggers emission of identical photon from excited molecule.

$n_1$ and $n_2$ are number of molecules in states 1 and 2.

$A_{21}$, $B_{12}$, and $B_{21}$ are Einstein coefficients.

Einstein relations: $A_{21} = \frac{(2\hbar \nu^3/\epsilon^2)}{c^2}B_{21}$, $g_1 B_{12} = g_2 B_{21}$

Non LTE: population of states determined by radiation and collisions.

Illustration of the five radiative and collisional processes involved in the rate of population of energy levels in a two-level atom. [Thomas & Stamnes, Fig. 4.7]
**Line Strength Expressions**

Simulated emission is like negative absorption.

Ratio of stimulated emission to absorption =

\[
\frac{B_{21} n_2}{B_{12} n_1} = \frac{B_{21} g_2 \exp(-E_2/k_B T)}{B_{12} g_1 \exp(-E_1/k_B T)} = \exp(-h \nu_0/k_B T)
\]

Strength of \(i\)'th absorption line is

\[
S_i \propto a_i |R|^2 \frac{n_L}{n_t} [1 - \exp(-h \nu_0/k_B T)]
\]

\(n_L/n_t\) is fraction of molecules in lower state of transition,

\(|R|^2\) is quantum mechanical transition probability,

\(a_i\) is abundance of this isotope (typically built into strength).

Substitute in molecule fraction in lower state to get line strength

\[
S_i \propto a_i |R|^2 \frac{g_i \exp(-h c E_{L,i}/k_B T)}{Q_T(T)} [1 - \exp(-h \nu_0/k_B T)]
\]

\(E_{L,i}\) is lower state energy in \(\text{cm}^{-1}\),

\(Q_T(T)\) is Total Internal Partition function (rotational \(\times\) vibrational)

Spectroscopic databases have line strength at reference temperature \(T_0\).

Temperature dependence of line strength then obtained from

\[
S_i(T) = S_i(T_0) \frac{\exp(-h c E_{L,i}/k_B T)Q_T(T)}{\exp(-h c E_{L,i}/k_B T_0)Q_T(T_0)} \frac{[1 - \exp(-h \nu_0/k_B T)]}{[1 - \exp(-h \nu_0/k_B T_0)]}
\]

The total partition function \(Q_T(T)\) depends on molecule/isotope.
HITRAN Spectroscopic Database

The 2000 HITRAN Database contains over 1,000,000 spectral lines for 36 different molecules. Information and database is at http://www.HITRAN.com/. The 1996 HITRAN Database is available on CD-ROM.

Relevant quantities in HITRAN database:

- $\nu_0$: Transition frequency (cm$^{-1}$)
- $S$: Strength at $T_0 = 296$ K (cm/molecule)
- $\alpha_{L,\text{air}}^0$: air broadened halfwidth (cm$^{-1}$/atm) at 296 K
- $\alpha_{L,\text{self}}^0$: self broadened halfwidth (cm$^{-1}$/atm) at 296 K
- $E_L$: Lower state energy (cm$^{-1}$)
- $n$: temperature dependence coefficient for halfwidth

Table 6. Example of direct image of line parameters.

| Mol/ Iso | $\nu_0$ | $S$ | $|R|^2$ | $\gamma_{\text{air}}$ | $\gamma_{\text{self}}$ | $E^*$ | $n$ | $\delta$ | $\nu^\prime$, $\nu^\prime\prime$, $Q^\prime$, $Q^\prime\prime$, IER, IREF |
|----------|---------|-----|---------|----------------------|----------------------|--------|-----|---------|---------------------------------|
| 21       | 800.450992 3.199E-26 6.578E-05 0.676E-08 181 2461.5624 78 000000 14 6 | 374 465 1 1 1 |
| 291      | 800.454690 3.242E-22 0.000000 0.845E-175 369 6303 94 000000 9 1341519 | 331419 000 4 4 1 |
| 291      | 800.454690 9.724E-22 0.000000 0.845E-175 369 6303 94 000000 9 1341519 | 331419 000 4 4 1 |
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| 121      | 800.455338 1.037E-22 1.596E-03 1.100E-0000 530 3300 75 000000 32 1446 740 | 45 640 000 4 4 1 |
| 121      | 800.455338 9.190E-23 5.133E-04 6.670E-0000 851 0515 50 000000 2 145 244 | -44 143 -301 3 3 1 |
| 121      | 800.457760 4.726E-23 4.466E-03 1.100E-0000 920 0900 75 000000 32 145028222 | 492722 000 4 4 1 |
| 121      | 800.457760 4.726E-23 4.466E-03 1.100E-0000 920 0900 75 000000 32 145028222 | 492722 000 4 4 1 |
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| 291      | 800.475220 3.199E-22 0.000000 0.845E-175 361 9747 94 000000 9 1341520 | 331420 000 4 4 1 |
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| 121      | 800.485680 5.770E-23 4.232E-02 0.110E-0000 846 9090 75 000000 32 144544 1 4443 1 | 4443 1 00 4 4 1 |
| 121      | 800.485680 5.836E-23 4.262E-02 0.110E-0000 846 9090 75 000000 32 144544 2 4443 2 | 4443 2 00 4 4 1 |
| 121      | 800.491430 6.593E-23 4.056E-02 0.110E-0000 826 9990 75 000000 32 144923277 | 482227 000 4 4 1 |
| 121      | 800.491430 6.593E-23 4.056E-02 0.110E-0000 826 9990 75 000000 32 144923277 | 482227 000 4 4 1 |

The format of the HITRAN 1996 and 2000 database. The HITRAN 2001 format will be the same, except $|R|^2$ is replaced by the Einstein A coefficient and the $\nu^\prime$, $\nu^\prime\prime$, $Q^\prime$, $Q^\prime\prime$, IER, IREF formats are expanded.

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### APPENDIX B. HITRAN Molecules with Associated Indices

<table>
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<th>HITRAN Molecule Number</th>
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The HITRAN numbering scheme for various molecules.
**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:

$$\Delta \tau_\nu(z) = k_\nu(z) \Delta u(z) = \left[ \sum_i S_i(T) f(\nu - \nu_i; \alpha_i) \right] \Delta u(z)$$

Typically, absorption lines within 25 cm$^{-1}$ of $\nu$ are used.

The Lorentz halfwidth is obtained from pressure/temperature scaling:

$$\alpha_i = \alpha_i^0 \left( \frac{p}{p_0} \right) \left( \frac{T_0}{T} \right)^n$$

The foreign and self broadening are added with volume mixing ratio $q$:

$$\alpha_i^0 = (1 - q)\alpha_{L,\text{air}}^0 + q\alpha_{L,\text{self}}^0$$

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

$$\Delta \tau_\nu = \Delta \tau_\nu, H_2O + \Delta \tau_\nu, O_3 + \Delta \tau_\nu, CO_2$$

Integrate optical depth vertically:

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

Integrate monochromatic transmission across spectrum:

$$T_{\Delta \nu} = \int_{\Delta \nu} \exp \left[ -\tau_\nu / \cos \theta \right] d\nu$$

Line-by-line models are accurate but very expensive to run.

Line-by-line models use complex algorithms to speed up computation (e.g. FASCODE and LBLRTM):

- Three functions of different resolutions represent Voigt profile.
- Line centers added to fine grid; line wings to coarse grid.
- After all absorption lines added to grids, then spectral grids interpolated finest grid and added.