Molecular Absorption

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1 Introduction

Remote sensing (from ground-, airplane-, balloon-, or satellite-based platforms) is a powerful and versatile tool to estimate profiles of atmospheric temperature, trace gases, etc. and has been established as indispensable for research on climate change, stratospheric ozone depletion etc. An essential prerequisite is the accurate and complete knowledge of the absorption properties of the atmospheric constituents, i.e. the data are mandatory to link the characteristic spectral signature obtained by remote sensing to the trace gas distribution in the atmosphere. Laboratory spectroscopy in support of atmospheric remote sensing has greatly helped to compile several molecular spectroscopic databases of line parameters (i.e., line positions, line strengths, pressure broadening coefficients etc.) or absorption cross sections, e.g., Rothman et al. [2005]; Jacquinet-Husson et al. [2005]; Pickett et al. [1998].

2 Radiative Transfer Basics

Radiation traversing the atmosphere is partially absorbed and scattered at molecules and aerosols. For a thin slab of thickness ds the change of radiation intensity I is proportional to the layer thickness and to the amount of absorbers n.

$$\mathrm{d}I \;=\; -\,I\,k\,n\,\mathrm{d}s\;, \tag{1}$$

where the proportionality constant k is the *cross section.* The solution of this differential equation leads to the Beer–Lambert–Bouguer law [Liou, 1980; Thomas and Stamnes, 1999]

$$\mathcal{T}(\nu;s) \;\equiv\; \frac{I(\nu,s)}{I(\nu,0)} \;=\; \exp\left[-\int_0^s k(\nu,s')\;n(s)\;\mathrm{d}s'\right]\;, \tag{2}$$

For radiation passing through an homogeneous medium (i.e, with constant pressure, temperature, and absorber concentration(s)) this simplifies to

$$\mathcal{T}(\nu) \;=\; e^{-k\,n\,s} \tag{3}$$

Note that the absorption cross section is depending on wavenumber ν (or wavelength $\lambda \sim 1/\nu$) and is also a function of pressure and temperature (i.e., altitude (z) dependant in the atmosphere), but for brevity the condensed notation $k(\nu,s) = k(\nu,p(s),T(s))$ has

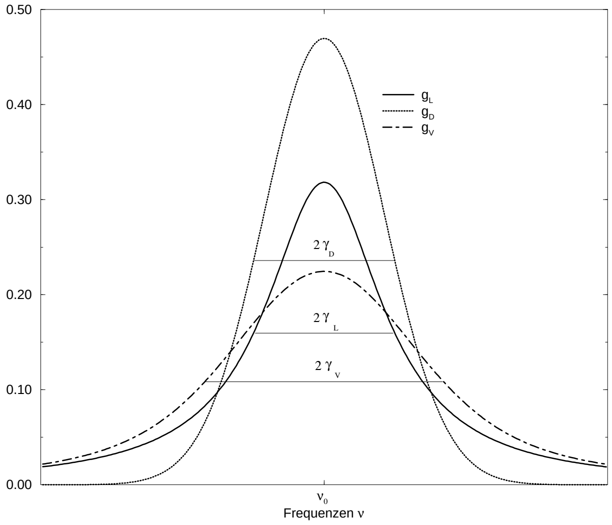

Figure 1: Comparison of Voigt, Lorentz, and Doppler profiles (normalized to 1)

been used. Furthermore different types of absorbers (molecules, aerosols) are contributing to the change of radiation, i.e., Beer's law generalizes to

$$\mathcal{T}(\nu;s) = \exp\left[-\int_0^s \alpha(\nu,s')\,ds'\right] , \tag{4}$$

$$\alpha(\nu;s) = \sum_m k_m(\nu,s)\;n_m(s) + \alpha^{(c)}(\nu,s) \tag{5}$$

where α is the volume absorption coefficient, k_m and n_m are the absorption cross section and density of molecule m, and $\alpha^{(c)}$ is the continuum absorption coefficient [e.g. Clough et al., 1980]. Note that aerosols, scattering and continuum contributions will not be considered in the following.

3 Molecular Absorption Cross Section

In general the molecular absorption cross section is obtained by summing over the contributions from many lines,

$$k_m = \sum_l k_m^{(l)}. \tag{6}$$

For an individual line at position $\hat{\nu}_0$ the cross section is the product of the temperature dependent line strength $S(T)$ and a normalized line shape function $g(\nu)$ describing the broadening mechanism, (the index m will be skipped from now)

$$k(\nu,z) = S(T(z)) \cdot g(\nu, p(z), T(z)) \; . \tag{7}$$

In the atmosphere the combined effect of pressure broadening, corresponding to a Lorentzian line shape (cf. Fig. 1)

$$g_{\mathrm{L}}(\nu) = \frac{\gamma_{\mathrm{L}}/\pi}{(\nu-\hat{\nu}_0)^2 + \gamma_{\mathrm{L}}^2} , \tag{8}$$

and Doppler broadening, corresponding to a Gaussian line shape

$$g_{\mathrm{D}}(\nu) = \frac{1}{\gamma_{\mathrm{D}}}\left(\frac{\ln 2}{\pi}\right)^{1/2} \cdot \exp\left[-\ln 2\left(\frac{\nu-\hat{\nu}_0}{\gamma_{\mathrm{D}}}\right)^2\right] . \tag{9}$$

can be represented by a Voigt line profile [e.g. Armstrong, 1967]

$$g_{\mathrm{V}}(\nu) = g_{\mathrm{L}} \otimes g_{\mathrm{D}}. \tag{10}$$

Pressure broadening and Doppler broadening halfwidths are given by

$$\begin{aligned} \gamma_{\mathrm{L}}(p,T) &= \gamma_{\mathrm{L}}^{(0)} \frac{p}{p_0} \times \left(\frac{T_0}{T}\right)^n , & (11) \\ \gamma_{\mathrm{D}}(T) &= \nu_0 \sqrt{\frac{2\ln 2 \; kT}{mc^2}} . & (12) \end{aligned}$$

where p_0 and T_0 are the reference pressure and temperature of line parameters, respectively, m denotes the molecular mass, and n describes the temperature dependance of pressure broadening (c and k are speed of light and Boltzmann's constant). Typical values (see also Fig. 2) for the pressure broadening line widths are $\gamma_{\mathrm{L}} \approx 0.1p \, [\mathrm{cm}^{-1}/\mathrm{atm}]$ [cf. Tab. 2 in Rothman et al., 1987]. For typical atmospheric molecules ($m \approx 36\,\mathrm{amu}$) one has $\gamma_{\mathrm{D}} \approx 6 \cdot 10^{-8} \, \nu_0 \sqrt{T\,[K]}$.

Note that the line position might be slightly shifted depending on pressure, i.e.,

$$\hat{\nu}_0 \longrightarrow \hat{\nu}_0 + \delta p \tag{13}$$

where δ is the air broadened pressure shift coefficient. Furthermore, in high resolution spectra collisional narrowing effects can be observed, [cf. e.g. Varghese and Hanson, 1984].

4 Atmospheric Remote Sensing Requirements

Combining Eqs. (3) and (7) it becomes obvious that radiative transfer is depending only on the product $S \cdot n$ of line strength and number density; thus any uncertainty in the line strength immediately maps into corresponding uncertainties in the molecular number densities to be retrieved in atmospheric remote sensing. In an extensive sensitivity study for microwave limb sounding Verdes et al. [2005] have shown that uncertainties in the strengths of strong lines give an error of similar magnitude on the retrived species to which this line belongs. Even more seriously they found that uncertainties of strengths of strong lines turns into much higher errors on a retrieved species.

Vertical sounding of altitude dependant temperature or molecular concentration profiles crucially depends on precise knowledge of the pressure broadening parameters γ_L^{ref} and n: For the lower atmosphere where pressure broadening dominates, the line width is directly related to pressure ($\gamma_L \sim p$) and hence altitude, allowing a direct mapping from line center and line wing contributions in the spectrum to upper and lower atmosphere (cf. Fig. 3. Furthermore pressure broadening has been used successfully to retrieve tangent point altitude from limb sounding emission spectra [von Clarmann et al., 2003; Verdes et al., 2002]. As shown by, e.g., Verdes et al. [2005] uncertainties of the air broadening parameters of a few strong lines can dominate the error budget in composition retrievals from limb sounding instruments.

5 Summary

For computation of molecular absorption cross sections and, more generally, radiative transfer in gaseous media like the atmosphere, at least the following set of parameters describing the molecular transitions (lines) is required:

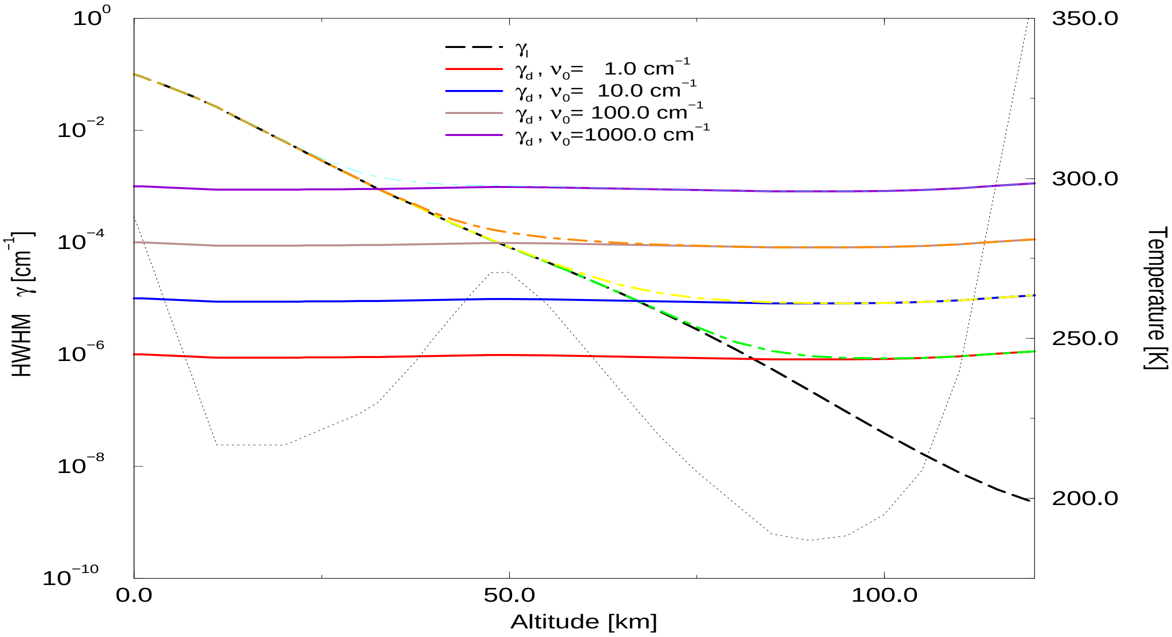

Figure 2: Half width (at half maximum, HWHM) of pressure, Doppler, and Voigt broadening line shapes as a function of altitude for different line positions $\hat{\nu}_0$. The width of the Lorentzian line shape describing pressure broadening is essentially proportional to pressure and therefore decreases exponentially with altitude. Being dependant on the square root of temperature, the Doppler half width changes only weakly with altitude. In the troposphere all lines are pure pressure broadened; the transition to Doppler broadening varies with the spectral region. (Pressure and temperature: US Standard atmosphere, molecular mass $36amu$)

- line position $\hat{\nu}$
- line strength S
- air broadening half width γ_L
- temperature exponent of temperature dependence of pressure broadening n
- lower state energy of transition E (required for temperature conversion of line strength)

Data for million of spectral lines of dozens of molecules relevant for atmospheric spectroscopy are provided in databases like

- Hitran [Rothman et al., 2005];
- Geisa [Jacquinet-Husson et al., 2005];
- JPL [Pickett et al., 1998].

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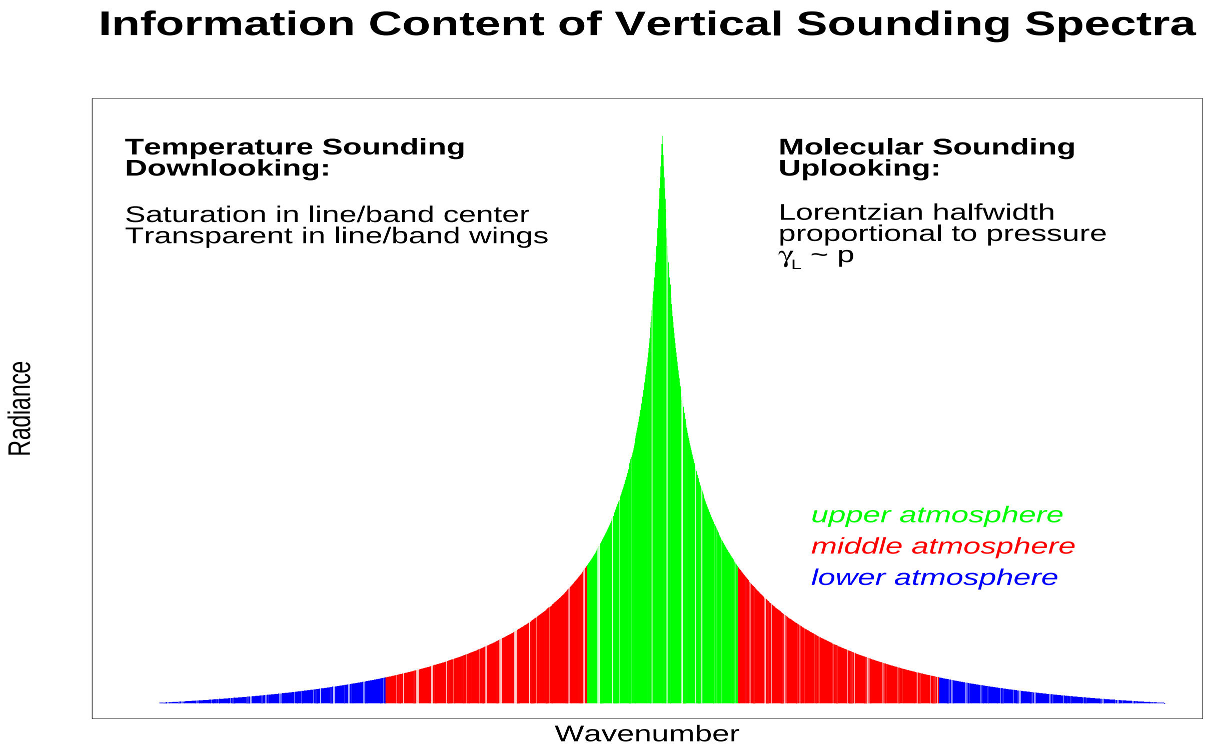

Figure 3: Mapping of line centers and wings to high and low altitudes.

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