Calculation of molecular spectra with the Spectral Calculator

Understanding observed spectra is the foundation of remote sensing, and more often than not, gas spectra play a significant role. We describe here the methods used by the Spectral Calculator (www.spectralcalc.com) to compute the spectra of molecular gases. These are presented with some brief justification, but mostly without detailed derivations. Gordley et al. (*1994*) described in detail the *LinePak*[TM] algorithms that are used for these calculations. The LinePak[TM] calculations have been extensively compared to other LBL rotational-vibrational calculations (e.g. Gordley 1994, and Kratz 2005). The LinePak[TM] library has served as the radiative transfer calculation engine in the data processing systems for the satellite sensors HALOE and CLAES (on the UARS satellite), SABER (on the TIMED satellite), and SOFIE (on the AIM satellite). The goal here is simply to give users the background needed to correctly apply and interpret the results from the Spectral Calculator.

Line-by-line models

Molecules absorb and emit radiation only at certain discrete frequencies or wavenumbers, corresponding to allowable changes in their quantum energy levels. This produces a unique spectrum for each gas species. To begin a discussion of modeling molecular spectra, it's useful to define several quantities:

v	wavenumber (cm^{-1})	number of waves per cm. $v = f/c = 10^4/\lambda$ where f = frequency (Hz), c = speed of light (cm/s), and λ = wavelength (μm).
τ_v	transmittance	ratio of transmitted radiance to incident radiance at wavenumber v
ε_v	emissivity	ratio of emitted radiance at v to the radiance emitted by a blackbody at the same temperature
α_v	absorptivity	fraction of incident radiance at v that is absorbed

(We adopt the convention of using a subscript v to indicate quantities that have spectral dependence.) Kirchhoff's law equates the absorptivity to emissivity at each wavenumber. Further, in the absence of scattering or reflections, the absorptivity is the compliment of the transmittance:

$$\alpha_v = \varepsilon_v = 1 - \tau_v \quad .$$

Eq. 1

We focus here on calculating the transmittance spectrum of a uniform gas. Fig. 1 shows an example CO_2 transmittance spectrum. Absorption lines appear as dips in the

transmittance. Each line has a certain width and depth, and is centered at a particular wavenumber. The line positions and shapes are determined by the quantum mechanical properties of the molecule, and are affected by macroscopic conditions like pressure and temperature. The spectrum can be calculated from first principles, but for most applications the accuracy attained in this manner is insufficient. Instead, we derive the line parameters by fitting a variety of laboratory spectra, measured over a range of conditions. Each absorption line is thereby characterized by a small set of parameters (e.g., Table 2). With these parameters, an absorption line can be modeled at any given pressure, temperature and gas concentration. The collection of line parameters for a group of absorption lines is called a *line list*. HITRAN is perhaps the most comprehensive and commonly used line list for atmospheric applications. (*Rothman, et al., 2008*)
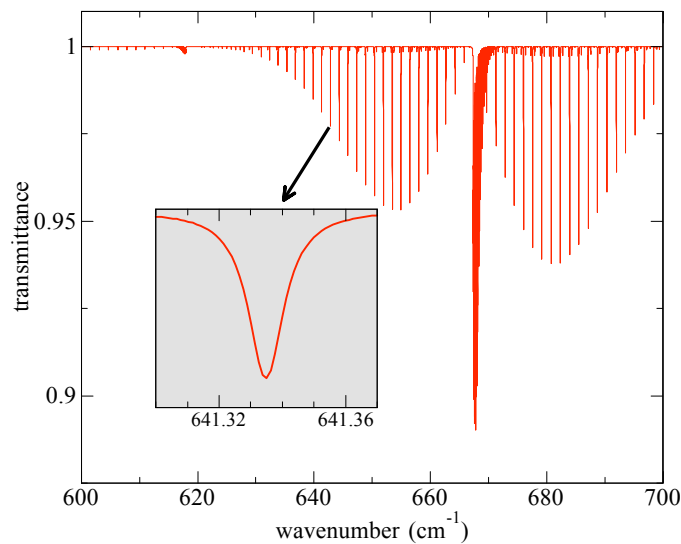

Fig. 1 – Example transmittance spectrum. The red line is the simulated spectrum of a 10 cm path through 350 ppmv of CO_2 at 0.1 atm. The inset is an expanded view of one absorption line, in which the line shape is apparent. Each line's position, depth and shape are determined by the quantum properties of the molecule, as well as the pressure, temperature and concentration of the gas. Note that the intense absorption feature at 668 cm^{-1} is actually the superposition of many individual overlapping absorption lines. This is a so-called *Q*-branch: a group of transitions that leave quantum angular momentum unchanged. Transitions that decrease or increase the quantum angular momentum by one quantum produce an envelope of absorption lines to the left or right of the *Q* branch, referred to as *P* and *R* branches, respectively.

To simulate the transmittance spectrum of a gas mixture in a given spectral range, the absorption lines of each gas must be calculated. Lines whose centers fall outside the spectral range, but whose wings extend into the range, must be included. The complete spectrum is effectively the product of the individual absorption line spectra. Algorithms that simulate molecular spectra in this way—by accumulating the spectra of each individual absorption line—are known as *line-by-line* models, and provide the most accurate prediction of molecular absorption available. The line-by-line model used by the Spectral Calculator is the LinePak™ library (*Gordley, et al., 1994*). NASA and other international research institutions rely on the LinePak™ software for satellite missions and atmospheric remote sensing projects.

One should be aware that there are other interactions that attenuate light in the atmosphere, in addition to molecular absorption. Some important effects include scattering by small particles (aerosols), molecular (Rayleigh) scattering, and continuum absorption. Here, however, we focus only on the modeling of molecular absorption and emission lines.

Beer-Lambert Law

Transmittance, τ_v, is the ratio of received to incident light intensity (Fig. 2). The transmittance decreases exponentially with distance travelled through a uniform absorber, as expressed by Bouguer's or the Beer-Lambert law:

$$\tau_v = e^{-k_v x} \quad . \qquad\qquad\qquad Eq.\ 2$$
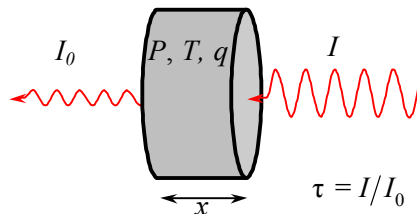

Fig. 2—Transmittance is the fraction of incident radiation at a particular wavenumber, v, that exits the volume. For a uniformly distributed absorber, the transmittance decreases exponentially with path length, x, as $\tau_v = I/I_0 = \exp(-k_v x)$.

Here k_v is the absorption coefficient and x is the path length. As one would expect, k_v is proportional to the number of molecules along the path. For an ideal gas at pressure P, temperature T and volume mixing ratio q, the absorption coefficient can be written

$$k_v = \frac{qP}{kT} \sigma_v \quad .$$ *Eq. 3*

where k is Boltzmann's constant. All spectral dependence is contained in the *cross section*, σ_v (cm^2/molecule). We can then write the Beer-Lambert law as

$$\tau_v = \exp\left(-\frac{qPx}{kT}\sigma_v\right) = \exp\left(-u\,\sigma_v\right),$$ *Eq. 4*

where $u = qPx/kT$ is the *mass path* and gives the number of molecules per cross-sectional area in the path (molecules/cm^2). To further isolate the spectral dependence of the calculation, we write the cross section as the product of a spectrally independent line intensity, S, and a spectral line shape, g_v:

$$\sigma_v = Sg_v \quad .$$ *Eq. 5*

S has units of cm^{-1}/(molecule/cm^2), and g_v has units of 1/cm^{-1}. (It's preferable to keep the units for wavenumber and area separated, rather than writing the result as cm/molecule.) This brings us to our final expression for the spectral transmittance:

$$\tau_v = \exp\left(-\frac{qPx}{kT}S\,g_v\right) \quad .$$ *Eq. 6*

Line Shape

The bulk of the effort in simulating molecular spectra lies in computing the line shape, g_v, for each individual absorption line. First, the position of the line center is determined. The wavenumber of the line center, v_c, increases linearly with pressure from its zero-pressure position, v_c^0:

$$v_c = v_c^0 + \delta\,P/P_0 \quad .$$ *Eq. 7*

The parameters v_c^0 and δ are found in an appropriate line list such as HITRAN.

In Fig. 1 we saw that the absorption from a particular molecular transition is not confined to a single wavenumber, but is spread over a range of wavenumbers. This spreading of the absorption line arises from three mechanisms. First, every spectral line has a natural width arising from the Heisenberg uncertainty principle, but this is almost always negligible in comparison to other broadening effects. Second, thermal motions impart a random Doppler velocity to each molecule, causing the ensemble absorption to be blurred over some range of wavenumbers. Finally, random collisions perturb the energy levels of individual molecules, each slightly differently, and the cumulative effect is known as pressure broadening.

At pressures less than 0.01 atm (altitudes above 30 km), Doppler broadening dominates. This results in a Gaussian line shape with halfwidth given by

$$\alpha_D = \nu_c \sqrt{\frac{2kT}{mc^2}} \quad , \qquad\qquad Eq.\ 8$$

where m is the molecular mass and c is the speed of light.

At pressures over 0.1 atm (altitudes below 16 km), pressure broadening dominates and produces a Lorentz line shape. The amount of broadening depends somewhat on the type of molecules involved in the collisions. Collisions between two molecules of the same species can produce a noticeably different broadening than collisions between a given molecule and an N_2 molecule, so the Lorentz halfwidth, α_L, is computed as the weighted sum of air- and self-broadened halfwidths, $\alpha_{L_a}^0$ and $\alpha_{L_s}^0$, adjusted for pressure and temperature:

$$\alpha_L = \left[(1-q)\alpha_{L_a}^0 + q\alpha_{L_s}^0\right]\left(\frac{P}{P_0}\right)\left(\frac{T_0}{T}\right)^\gamma , \qquad\qquad Eq.\ 9$$

where $T_0 = 296$ K. Note also that we have made the common assumption that the same temperature exponent, γ , applies to both air- and self-broadening. Once again, the parameters $\alpha_{L_a}^0$, $\alpha_{L_s}^0$ and γ are obtained from a line list such as HITRAN. The combination of Doppler and Lorentz broadening yields the more general Voigt profile:

$$f_v = \frac{1}{\sqrt{\pi}\alpha_D} \frac{1}{\pi} \frac{\alpha_L}{\alpha_D} \int_{\pm\infty} \frac{\exp(-t^2)}{\left[(v - v_c)/\alpha_D - t\right]^2 + \left(\alpha_L/\alpha_D\right)^2} dt \quad .$$

Eq. 10

The Voigt profile reduces to the Lorentz line shape at high pressure (α_L ? α_D) and the Doppler or Gaussian line shape at low pressure ($\alpha_L = \alpha_D$). Having calculated the Voigt profile, we make one additional adjustment to the line shape for far-wing effects:

$$g_v = \frac{v}{v_c} \frac{\tanh\left(hcv/2kT\right)}{\tanh\left(hcv_c/2kT\right)} f_v \quad .$$

Eq. 11

While the Voigt profile is accurate enough for most applications, there are cases in which other line shapes are preferred. At very low wavenumbers the Van Vleck-Weisskopf line shape is more appropriate (see Appendix A). The Spectral Calculator uses the Van Vleck-Weiskopf line shape for lines with $v_c <$ 200 cm^{-1}, and the Voigt profile for all others. Other effects such as line-coupling and speed-dependent broadening become important in certain conditions. However, for most situations, the Voigt profile provides acceptable results, and is the obvious choice for a general-purpose utility like the Spectral Calculator.

Line Intensity

We now turn our attention to the last remaining term needed for calculating the transmittance given by Eq. 9: the line intensity, *S*. HITRAN and other line lists provide S_0, the line intensity at $T_0 = $ 296 K.[1] To calculate the line intensity at an arbitrary temperature, *T*, we adjust by Boltzmann factors, account for stimulated emission effects, and include vibrational and rotational partition functions, Q_V and Q_R:

$$S(T,P) = S_0 \frac{Q_V(T_0)Q_R(T_0)}{Q_V(T)Q_R(T)} \frac{\exp(hcE_L/kT)}{\exp(hcE_L/kT_0)} \left(\frac{1 - \exp(-hcv_c/kT)}{1 - \exp(-hcv_c/kT_0)}\right) \quad .$$

Eq. 12

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[1] Line intensities for each isotopologue in HITRAN, GEISA and other line lists have been reduced by the isotopologues' natural abundances. See Appendix B for more details. Abundances for each isotopologue can be found at http://www.spectralcalc.com/calc/abundances.php

where E_L is the lower state energy of the transition (also provided by HITRAN). The composite effect of the vibrational and rotational partition functions is found from a tabulation of total internal partition sums (TIPS), parameterized as a function of temperature.

Transmittance spectrum

Up to this point, we have discussed how to compute the transmittance spectrum of a single absorption line. An observed spectrum of a gas mixture will be the product of the spectra of all absorption lines from all gases in or near the spectral region of interest. From Eq. 3, the spectrum of the ith absorption line of the jth gas in the mixture is

$$\tau_v^{i,j} = \exp\left(-u^j \sigma_v^{i,j}\right) \quad , \qquad\qquad \textit{Eq. 13}$$

where the cross section, $\sigma_v^{i,j}$, and mass path, u^j, are computed as prescribed by Eq.s 6-10. The complete spectrum is the product of the transmittance spectra of all lines from all gases:

$$\mathsf{T}_v = \prod_j \prod_i \tau_v^{i,j} = \exp\left(-\sum_j u^j \sum_i \sigma_v^{i,j}\right) \quad . \qquad\qquad \textit{Eq. 14}$$

Strong lines will have significant wings extending far from line center, while weak lines tail off quickly. It is important to carry the calculation of each line sufficiently far from line center. For example, the far wing of a strong line at 1800 cm^{-1} may influence the spectrum in the 2000 to 2010 cm^{-1} region. Depending on the spectral region, there can be many thousands or even millions of significant absorption lines, and the cross section of each must be computed at high enough spectral resolution to fully capture the line shape. For this reason, great effort must be taken to make the computation and accumulation of the cross sections efficient but without loss of accuracy.

Radiance

In general, an observed spectrum will be a combination of both transmitted and emitted radiance. Consider a sensor viewing a blackbody source at temperature T_s through a gas

at temperature T_g. The gas will transmit some of the source radiation, while at the same time emitting some of its own, and the received radiance will be the sum:

$$L_v = \tau_v B_v\left(T_b\right) + \varepsilon_v B_v\left(T_g\right) \quad . \qquad\qquad Eq.\ 15$$

Where $B_v(T)$ is the Planck blackbody function, τ_v is the transmittance of the gas and ε_v is its emissivity. Neglecting scattering effects, $\varepsilon_v = 1 - \tau_v$ (Eq. 1), so

$$L_v = \tau_v \left[B_v\left(T_s\right) - B_v\left(T_g\right)\right] + B_v\left(T_g\right) \quad . \qquad\qquad Eq.\ 16$$

The limiting cases of this are worth examining. For a completely transparent gas ($\tau_v = 1$), the received radiance is simply the source radiance: $L_v = B_v(T_s)$. If the gas is completely opaque ($\tau_v = 0$), it behaves as a perfect blackbody: $L_v = B_v(T_g)$. If we decrease the background source temperature to zero, we're left with only the emission spectrum of the gas: $L_v = \varepsilon_v B_v(T_g)$. If instead the gas temperature were zero, we would receive only the source radiance modulated by the transmittance spectrum: $L_v = \tau_v B_v(T_g)$. Fig. 3 illustrates these effects by modeling the spectrum of a warm blackbody source viewed through a cooler volume of carbon dioxide. Near 680 cm^{-1}, where the absorption lines are saturated, the radiance spectrum appears identical to a blackbody at the temperature of the cool gas. In regions away from any significant absorption, the warm blackbody spectrum is unattenuated.
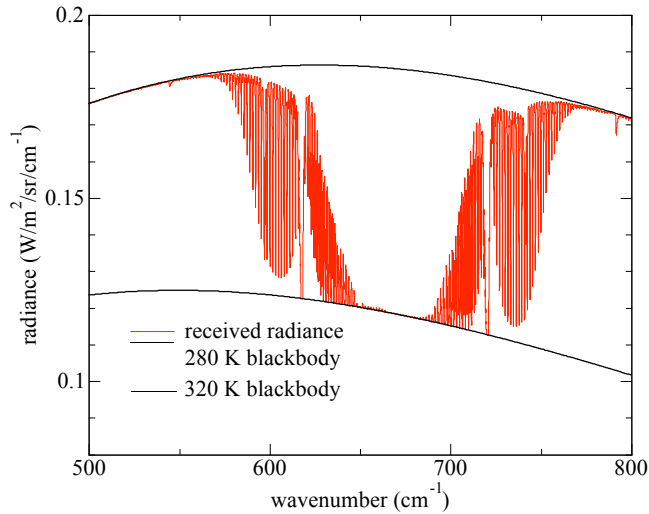
Fig. 3—Radiance spectrum of carbon dioxide in front of a blackbody background. The background is at 320 K, and is viewed through a 1 m path of 10% CO_2 at 280 K. (The remaining gas is assumed transparent.) Where the transmittance is zero, the observed spectrum is identical to a 280 K blackbody; where the transmittance is 1, it is identical to the 320 K source spectrum. If the gas were warmer than the background, the absorption lines would be inverted, becoming emission lines.

Atmospheric paths

To calculate the spectrum of a more complicated path, for example a path through a planetary atmosphere, one can divide the path into segments small enough to be approximated by constant conditions (pressure, temperature and gas concentrations), and apply the techniques described above. This is illustrated in Fig. 4. In LinePak, the effective pressure, temperature and concentration in the segment are determined by mass weighting of the conditions, as described by *Gordley, et al 1994*. The transmittance spectrum of the whole path is the product of the individual spectra of the segments. Long paths can undergo significant refraction, and this must also be accounted for.

As one would expect, such calculations can quickly become computationally intensive. The LinePak™ library used by the Spectral Calculator was carefully designed to maximize efficiency, so that such complex atmospheric spectra can be calculated as quickly as possible, without loss of accuracy.
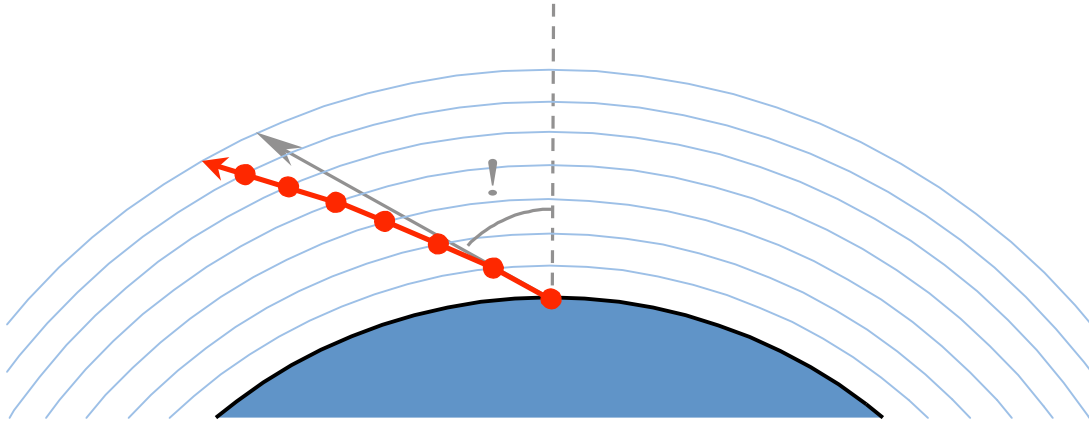
Fig 4—Segmenting of an atmospheric path. SpectralCalc (using the LinePak[TM] algorithms) models a ray through a planetary atmosphere (red line) as a series of segments through concentric atmospheric shells. Shell thicknesses are chosen so that the layers are well approximated with uniform, mass-weighted conditions. Contrary to this illustration, the layering scheme is not constant. Thinner layers are used at lower altitudes, where the atmospheric density is greatest. For a path traversing the whole atmosphere, thirty or more layers may be used to adequately capture the significant effects from all altitudes. Refraction effects become increasingly significant at lower altitudes. A ray path is specified by its apparent direction, as indicated by the straight grey arrow. LinePak accurately calculates the refracted path, shown in red.

Tables

Table 1—Summary of Formulas

Name	Symbol	Formula, Units
wavenumber	v	$10000/\lambda(\mu m)$, cm^{-1}
pressure	P	Pa (P_0 = 1 atm = 101,325 Pa = 1013.25 mbar)
temperature	T	K (T_0 = 298 K, T_{STP} = 273.15 K)
volume mixing ratio	q	dimensionless
molecular mass	m	kg
transmittance	τ_v	$e^{-k_v x}$, $e^{-u\sigma_v}$, $\tau_v = \varepsilon_v = 1 - \tau_v$, dimensionless
emissivity	ε_v	$\alpha_v = \varepsilon_v = 1 - \tau_v$, dimensionless
absorptivity	α_v	$\alpha_v = \varepsilon_v = 1 - \tau_v$, dimensionless
absorption coefficient	k_v	$\dfrac{qP}{kT}\sigma_v$, molecules / cm
cross section	σ_v	$S\,g_v$, cm^2 / molecule
mass path	u	$\dfrac{qPx}{kT}$, molecules / cm^2
Voigt line shape	$f(v,T,P)$	$f_v = \dfrac{1}{\sqrt{\pi}\alpha_D}\dfrac{1}{\pi}\dfrac{\alpha_L}{\alpha_D}\displaystyle\int_{-\infty}^{+\infty}\dfrac{\exp(-t^2)}{\left[(v-v_c)/\alpha_D - t\right]^2 + (\alpha_L/\alpha_D)^2}\,dt$, 1/cm^{-1}
adjusted line shape	$g(v,T,P)$	$g_v = \dfrac{v}{v_c}\dfrac{\tanh(hcv/2kT)}{\tanh(hcv_c/2kT)}f_v$, 1 / cm^{-1}
line intensity	$S(T,P)$	$S(T,P) = S_0\,\dfrac{Q_V(T_0)Q_R(T_0)}{Q_V(T)Q_R(T)}\dfrac{\exp(hcE_L/kT)}{\exp(hcE_L/kT_0)}\left(\dfrac{1-\exp(-hcv_c/kT)}{1-\exp(-hcv_c/kT_0)}\right)$ cm^{-1}/(molecules/cm^2)
line center wavenumber	v_c	$v_c^0 + \delta\left(P/P_0\right)$, cm^{-1}
Doppler halfwidth	α_D	$v_c\sqrt{2kT/mc^2}$, cm^{-1}
Lorentz halfwidth	α_L	$\left[(1-q)\alpha_{L_f}^0 + q\alpha_{L_s}^0\right]\dfrac{P}{P_0}\left(\dfrac{T_0}{T}\right)^{\gamma}$, cm^{-1}

Table 2—HITRAN line parameters

Name	Symbol	Units
zero-pressure line center	ν_c^0	cm^{-1}
foreign (air) broadened Lorentz halfwidth	$\alpha_{L_f}^0$	cm^{-1} / atm @ T_0
self broadened Lorentz halfwidth	$\alpha_{L_s}^0$	cm^{-1} / atm @ T_0
lower state energy	E_L	cm^{-1}
intensity at STP	S_0	cm^{-1} / (molecule cm^{-2}) @ T_0
pressure shift coefficient	δ	cm^{-1} atm @ T_0
temperature dependence of halfwidth	γ	dimensionless

Table 3—Constants

Name	Symbol	Units
STP temperature	T_{STP}	273.15 K
reference temperature	T_0	296 K
reference pressure	P_0	1 atm = 1013.25 mbar
Boltzmann's constant	k	1.3806489 x 10^{-23} J/K
Planck's constant	h	6.62606957 x 10^{-34} J s
speed of light	c	2.99792458 x 10^8 m/s

Appendix A: Van Vleck-Weisskopf lineshape

The Lorentz, Doppler (Gaussian) and Voigt line shapes are symmetric, with wings that gradually decrease away from line center, v_c. In practice, we simply truncate the line at some distance from v_c, far enough that the contribution has fallen to a negligible value. This leads to problems, however, when v_c is very close to zero. In this regime, we expect a non-symmetric profile that will vanish in the limit $v \to 0$. For these low wavenumber transitions, the Van Vleck-Weisskopf line shape is the appropriate line shape to use:

$$f_v = \frac{a_L}{\pi} \frac{v}{v_c} \left[\frac{1}{\left(v - v_c\right)^2 + a_L^2} + \frac{1}{\left(v + v_c\right)^2 + a_L^2} \right] \quad . \qquad \textit{Eq. A1}$$

This is essentially a correction to the Lorentz profile, which includes negative resonances in the collision effects. In the Spectral Calculator, we use the Van Vleck-Weisskopf line shape for all lines with $v_c < 200 \text{ cm}^{-1}$, and the Voigt profile otherwise.

Appendix B: Isotopic Abundances

The intensities in HITRAN, GEISA and other commonly used line lists have been pre-adjusted by the natural abundance of each isotopologue. For example, ~0.2% of all water molecules in the atmosphere are $H_2^{18}O$, the second most common water isotopologue. The line intensities for $H_2^{18}O$ in HITRAN have therefore been reduced by this factor. This makes simulating a natural atmospheric path simple, because one can simply specify the overall water vapor concentration, and partitioning into the various isotopologues is automatically accounted for by the scaled intensities. However, if a user wishes to simulate a single isotopologue rather than the naturally occurring mix of all isotopologues, he or she will need to "undo" this scaling. The simplest way to do this is by increasing the vmr by the same factor. For example, to simulate the spectrum of 5 parts per million (vmr of 5×10^{-6}) of $H_2^{18}O$, the user should specify an "effective" vmr of $5 \times 10^{-6} / 0.002 = 2.5 \times 10^{-3}$. Abundances for each isotopologue can be found here:

http://www.spectralcalc.com/calc/abundances.php

Using an "effective" vmr will accommodate any vmr up to the natural abundance of the isotopologue. For higher concentrations, the effective vmr will exceed 1 and will not be accepted by the Spectral Calculator. In these cases, one can scale the path-length instead of the vmr. There may be some slight differences in broadening effects when using this approach, but these will likely be negligible. Nonetheless, it is recommended that comparisons be done between the two approaches to see if any significant differences arise for a particular scenario. In simulations involving an individual isotopologue in a mixture of other gases, one may need to use separate cells, one containing the individual isotopologue with an "effective" length, and another containing the remaining gases.

References

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