

## 6.1 Theory Used In Transmission Calculations

This section explains the equations and conversion factors used to calculate the transmission, absorption, and Optical Depth values for the molecular atmosphere in the TRANS program.

### 6.1.1 Beer-Lambert Law, Line Intensity, Lineshapes:

The Transmission of light through a media can be expressed by the Beer-Lambert law as

$$I = I_0 e^{-OD},$$

where  $I_0$  is the initial light intensity,  $I$  is the intensity after passing through the media, and  $OD$  is called the Optical Depth. This can be related to the normal parameters of Transmission,  $T$ , Absorption,  $A$ , and Absorbance,  $AC$ , as:

$$\text{Transmission (T)} \quad T = I / I_0 = e^{-OD}$$

$$\text{Absorption (A)} \quad A = 1 - T$$

$$\text{OpticalDepth (OD)} \quad OD = -\ln(T) = \ln(1/T)$$

$$\text{Absorbance (AC)} \quad AC = -\log_{10}(T) = OD / \ln(10) = 0.434 * OD$$

For the absorption of monochromatic light by one molecular gas in the atmosphere, the Beer-Lambert law becomes

$$I(\nu, L) = I_0 e^{-OD} = I_0 e[-\alpha(\nu) P_a L],$$

where  $\alpha(\nu)$  is the linear absorption coefficient defined in  $\text{cm}^{-1} \text{ atmospheres}^{-1}$ ,  $\nu$  is the frequency in  $\text{cm}^{-1}$ ,  $P_a$  is the partial pressure of the gas in atmospheres (atm.), and  $L$  is the optical pathlength in cm;  $I(\nu, L)$  is the intensity of the monochromatic light at frequency  $\nu$  after transmission through the path length  $L$ . For the case where there are many different gases present in the atmosphere, then the total attenuation or composite transmission is related to the summation of the individual optical depths as

$$OD_{\text{total}} = (P_{a1} \alpha_1(\nu) + P_{a2} \alpha_2(\nu) + \dots) L$$

The absorption coefficient can be related to the molecular line intensity,  $S$ , by

$$\alpha(\nu) = S g(\nu - \nu_0) * N$$

where  $g(\nu - \nu_0)$  is the normalized lineshape function (units of  $\text{cm}^{-1}$ ) and  $\nu_0$  is the frequency at line center in  $\text{cm}^{-1}$ . The molecular line intensity,  $S$ , is given in the HITRAN data base in units of  $\text{cm}^{-1}/(\text{molecule}\cdot\text{cm}^{-2})$  or  $\text{cm} / \text{molecule}$ , and  $N$  is the total number of molecules of absorbing gas per  $\text{cm}^3$  per atmosphere. The value of  $N$  at 296 °K is Loschmidts' number,  $N_L = 2.479 * 10^{19}$  molecules  $\text{cm}^{-3}$  atm $^{-1}$ . At other temperatures,  $N$  is calculated (following the ideal gas law) as

$$N = N_L [296 / T ],$$

where  $T$  is the temperature in Kelvin.

Using the above, the Transmission,  $T$ , of monochromatic light is thus given by

$$T = I(\nu, L) / I_0 = \exp [ - S g(\nu - \nu_0) N P_a L ].$$

As can be seen,  $S g(\nu - \nu_0)$  is the absorption cross section per molecule ( $\text{cm}^2 / \text{molecule}$ ), and  $(N P_a)$  is the absolute density of absorbing molecules in units of molecules /  $\text{cm}^3$ . The Boltzmann population factor is contained within  $S$ . As an aside, although the above expression appears to be valid for each absorbing molecule, the values for  $S$  given in the HITRAN data base have been normalized to one atmosphere of gas and assumes that the composition of the gas contains the natural fractional abundance of each isotopic species. In other words, the value of the isotopic abundances are contained in the  $S$  parameter. As such, it is common to group  $S g(\nu - \nu_0) N$  as the optical line strength per unit atmosphere of gas. Note, however, if the user is conducting laboratory optical spectroscopy using an absorption cell with a sample of gas which contains only one isotope ( or non-standard isotopic mixture) then the value of  $P_a$  used for the transmission calculations should be increased accordingly.

There are three lineshape profiles used in the TRANS program. A Lorentzian lineshape function is available for Pressure Broadening calculations, a Gaussian function is available for Doppler Broadening, and a Voigt profile is used for a composite of both Doppler and Pressure broadening.

The Lorentzian/Pressure broadened profile is given by

$$g_p(\nu - \nu_0) = (\gamma_p / \pi) / [(\nu - \nu_0)^2 + \gamma_p^2 ],$$

where  $\gamma_p$  is the pressure-broadened halfwidth at half-maximum (HWHM) in wavenumbers ( $\text{cm}^{-1}$ ). The pressure broadened halfwidth is related to the air-broadened halfwidth parameter,  $g$ , (contained in the HITRAN data base) as

$$\gamma_p = g (296 \text{ K} / T)^n P_t$$

where  $P_t$  is the total background atmospheric pressure as specified explicitly by the TRANS user. The value of  $g$  is temperature dependent and is scaled to other temperatures using the temperature coefficient parameter for the air-broadened linewidth,  $n$ , which is contained in the HITRAN database. The value for  $g$  is usually on the order of  $0.05 \text{ cm}^{-1} / \text{atmosphere}$ , and the value of  $n$  is on the order of 0.5.

Note that TRANS does not at present use the self-broadening coefficient,  $g_s$ , in these calculations because some of the molecular values for  $g_s$  are missing in the HITRAN92 data base.

The Gaussian or Doppler line profile is expressed as

$$g_D(\nu - \nu_0) = (1/\gamma_D) (\ln 2/\pi)^{.5} \exp [ -\ln 2 (\nu - \nu_0)^2 / \gamma_D^2 ],$$

where  $\gamma_D$  is the Doppler linewidth (HWHM in  $\text{cm}^{-1}$ ) given by

$$\gamma_D = (\nu_0 / c) [ 2 R T \ln 2 / M ]^{.5}$$

where  $R$  is the gas constant,  $T$  is the temperature in Kelvin and  $M$  is the molecular weight of the molecule. The value for the appropriate (isotopic averaged) molecular weight for each molecule is stored in the TRANS program, and is also listed in Appendix 10.

The Voigt profile is an integral over both the Doppler and Pressure profiles, and is used when both broadening mechanisms are present in approximately equal amounts. An approximation to the Voigt profile is used in the TRANS program as reported by E. E. Whiting. The equation used is accurate to within 1 to 2 %, and is given by<sup>4,5</sup>

$$g_V / I_{gVmax} = \{ [1 - (w_l/w_v)] \exp[-2.772(DN/w_v)^2] \} \\ + \{ (w_l/w_v) / [1 + 4 (DN/w_v)^2] \} \\ + \{ 0.016 [1 - (w_l/w_v)] (w_l/w_v) \} \\ \{ \exp[-0.4(DN/w_v)^{2.25}] - [10/(10 + (DN/w_v)^{2.25})] \},$$

where

$$wv = 0.5346 w_l + (0.2166 w_l^2 + w_d^2)^{1/2}$$

is the Voigt linewidth given by Olivero and Longbothum, and

$$I_{gvmax} = 1 / \{ wv * [1.065 + 0.447 (w_l/wv) + 0.058 (w_l/wv)^2] \}$$

is the value of the Voigt profile at line center. In the above equations,  $\Delta\nu$  is the differential frequency from line center,  $(\nu - \nu_0)$ , and  $w_l$ ,  $w_d$ , and  $wv$  are the FWHM linewidths of the Lorentzian, Doppler, and Voigt profiles, respectively. Note that  $w_l$  is the FWHM linewidth, so that  $w_l = 2 \gamma_p$ ; the FWHM values are used in the above equations in order to be consistent with the specified references and for ease of verification of the equations by the user.

Either Pressure, Doppler, or Voigt Lineshape profiles may be used to determine the absorption coefficient in the TRANS program.

For the case of the STICK (Lorentzian Peak) lineshape option used for the fast TRANS plot of the spectrum, only the peak or maximum value of the pressure broadened lineshape is calculated and drawn. In this case,  $g_p \max$  is equal to  $1/(\pi \gamma_p) = .318 / \gamma_p$ . For the STICK(Doppler Peak) option,  $g_D \max$  is  $(\ln 2/\pi)^{.5} / \gamma_D = 0.469 / \gamma_D$ .

### 6.1.2 Temperature Dependence

The temperature dependence of the calculated transmission spectrum in the TRANS program occurs primarily through the parameters,  $S$ ,  $N$ ,  $\gamma_D$ , and  $\gamma_p$ , which are directly temperature dependent, and through the values of  $P_a$  and  $P_t$  if the pressure and temperature altitude profiles of the atmosphere are used to specify  $P_a$  and  $P_t$ . The temperature dependence of these parameters is explained in the following:

#### (a) Calculation of S for Temperatures Not Equal to 296K

The line intensity,  $S$ , is dependent upon several factors, some of which are a function of temperature. The most important of these dependencies can be explained to first order approximately as in the following:

The line intensity,  $S$ , as defined in the HITRAN data base includes the Boltzmann population factor and is, thus, a function of temperature. The Boltzmann population factor can be expressed approximately by

$$P(E') = g_l \exp \{ -E' / kT \} / \sum \exp \{ -E_l / kT \} ,$$

where  $E'$  is the energy of the lower level of the transition (referenced to the ground state of the molecule),  $T$  is the temperature, and the summation is taken over all energy levels,  $E_i$ , of the molecule;  $g_i$  is the degeneracy of the  $E'$  level. The value of  $E'$  for each molecular transition is in the HITRAN database and can be obtained using the SEARCH program.

The value of the summation in the denominator is called the Internal Partition Sum,  $Q$ . The value of  $Q$  is dependent upon the temperature,  $T$ , of the molecule. The value for  $Q$  is calculated in the HITRAN programs through use of a set of values of  $Q$  for each molecule that is valid for a  $T$  of 296 K, and then applying a 3rd order polynomial expression which describes the variation of  $Q$  with temperature. The coefficients used for the polynomial expression are temperature dependent, so different coefficients are used over different temperature ranges. The coefficients for the current HITRAN database are valid for a temperature from 70 K to 3000K, and are contained in the TRANS program and also listed in Appendix 12.

The above temperature extrapolation is available for all molecules in the 1992 database, except for one molecule ( $O_2$ ) which does not as yet have partition sum values, and those few molecules that the ground state energy of the transition,  $E'$ , is not known (listed in the HITRAN92 data base with  $E = -1$ ).

It should be noted that the partition sums as supplied with the HITRAN database are only valid for a reference temperature of 296 K. If the user uses the SEARCH program to generate another HITRAN92.USF like database using a temperature that is not 296 K, then subsequent use of this new database by the other HITRAN-PC programs is not valid, because the corresponding value of  $Q$  can not be referenced to a temperature of 296 K. As such, all of the HITRAN92.USF databases contain the temperature value for that database and all of the HITRAN-PC programs check for this temperature value.

The value of the line intensity,  $S$ , also contains the effect of the population of the upper level and stimulated emission from that level. This can be seen by expressing the normal definition of the line strength in terms of the upper and lower state populations, as

$$S' = \{h \nu / c\} B [N_l - N_u] ,$$

where  $B$  is the Einstein B coefficient,  $N_l$  is the Boltzmann population of the lower state,  $N_u$  is the population of the upper level in molecules/cm<sup>3</sup>, and  $\nu$  is the transition frequency in cm<sup>-1</sup>. In the above equation, a prime is used (ie.  $S'$ ) since the units of  $S'$  assumes that the populations are given in molecules/cm<sup>3</sup>, while  $S$  involves population units in atmospheres;  $S$  will be related to  $S'$  later in this section.

The population term can be written as

$$[ N_l - N_u ] = N_l [ 1 - \exp ( - h c \nu / k T ) ] .$$

This latter term is also calculated in the HITRAN programs in order to properly scale the value of S as a function of temperature. Note that in terms of the population term used earlier,  $N_l$  is also further dependent upon temperature if expressed in units of atmosphere since

$$N_l = N_L [ 296 / T ] P(E')$$

Using the above equations, the value of the line strength at a temperature T can be referenced to the value of S at a reference temperature  $T_r$  as

$$S(T) = S(T_r) [ Q(T_r) / Q(T) ] \exp\{ 1.439 \nu (T - T_r) / T T_r \} .$$

In the HITRAN data base, the values of Q and S are referenced to a temperature of 296 K.<sup>3</sup> The above equation is valid for the temperature dependence of either S or S'.

The user of the HITRAN database should be aware of the above temperature dependence of S, which is valid for absorption transitions.

For the case of non thermodynamic equilibrium, then one often uses the temperature independent parameter of the transition probability,  $|R|^2 / g_l$ . This term is related to B as

$$B = \{ 8 \pi^2 / 3 h^2 \} |R|^2 / g_l .$$

where again  $g_l$  is the degeneracy of the lower state, and is usually equal to  $2J''+1$  for a basic diatomic molecule.

R is the transition dipole moment and is defined as

$$R = \int \Psi^* \hat{M} \Psi \, d\tau$$

where  $\hat{M}$  is the molecular electric-dipole moment. The transition dipole moment R is usually given in units of Debye and  $1 \text{ Debye} = 10^{-18} \text{ esu-cm}$ . Often R is due to several terms arising from vibrational, rotational, and rotational-vibrational interactions as

$$|R|^2 = |R_{v'v''}|^2 |R_{J'J''}|^2 F(m)$$

where the first term is due to pure vibrational transition probability, the second term due to rotational transitions, and the third term is a rotational-vibrational correction term called the Herman-Wallis factor.  $F(m)$  can be given for a linear diatomic molecule as

$$F(m) = 1 + C_V m + D_V m^2 + \dots$$

where  $2m = J'(J'+1) - J''(J''+1)$ . Here  $J''$  is the rotational quantum number of the lower level and  $J'$  is that for the upper level. For a P-branch transition,  $m = -J''$  and for a R-branch,  $m = J''+1$ . For a simple diatomic molecule like HCl,  $|R_J J''|^2$  is equal to  $|m|$ .

Finally, taking into account all of the above equations, one can write

$$S' = \{8 \pi^3 / 3hc\} \nu \{ |R|^2 / g_l \} g_l N_L [296 / T] I_a \times \\ [1 - \exp(-h\nu / kT)] g_l \exp\{-E'/kT\} / Q \times 10^{-36},$$

where  $I_a$  is the isotope fraction and  $g_l$  is the nuclear spin degeneracy of the lower level. The term of  $10^{-36}$  is used to convert the values of Debyes<sup>2</sup> to cgs units. In the above equation, the numerical value of the term  $\{ |R|^2 / g_l \}$  is given in the HITRAN data base in units of Debyes<sup>2</sup> and includes the degeneracy factor as indicated. In the above equation  $I_a$  is the isotopic abundance and these values are listed in Appendix 8.

Finally, the value of  $S'$  can be related to  $S$  as used in the HITRAN database by normalizing  $S$  to 1 atmosphere of pressure as

$$S = S' / \{ N_L [296 / T] \}.$$

A more thorough discussion of the above definition of  $S$  as used in the HITRAN database is contained in Reference 10.

### (b) Atmospheric Density $N$ :

In the TRANS program, the user is also given the option of specifying whether or not  $N$  will depend upon temperature. The usual (default) answer will use  $N$  proportional to  $1/T$ , which follows the ideal gas law.

However, the user can set  $N$  equal to a constant value ( $N_L = 2.479 \times 10^{19}$  molecules/cm<sup>3</sup>) for all temperature values using the "Fixed Value of  $N$ " Option specified during the question/answer start of the TRANS program. This option is offered so that the user can model an absorption experiment in which the gas is contained inside a sealed (enclosed) absorption cell. In this case, the total pressure would increase with the temperature, but the concentration of the gas (ie.  $N P_a$ ) would remain fixed. This can be modeled in the TRANS program by using the "Fixed  $N$ " option which fixes the value of  $N P_a$ . Unfortunately, however, the TRANS program does not change the value of  $P_t$  with this option.

As such, the user must manually increase the value of  $P_t$  in order to model the linear increase of the total pressure with temperature.

(c) The **Doppler linewidths** are calculated using the standard Doppler equation and the molecular weights of the molecules; the molecular weights of the molecules used in the TRANS program are given in an Appendix .

(d) **Temperature Override Option:** The TRANS program allows the user to specify the temperature to be used for the transmission calculations. For temperatures not equal to the HITRAN database reference temperature ( 296 K), then the temperature extrapolation routines are used for all lines, except those few lines for which the temperature extrapolation is not valid ( ie. O<sub>2</sub> and those molecules with  $E = -1$ ). For these latter lines, the TRANS program will just ignore their contribution to the overall transmission spectrum and inform the user that some lines are not being plotted because of this reason. However, the user can override the skipping of these lines by using the temperature override option as specified during the input parameter selection. In this case, these lines are included in the overall transmission calculations, except a temperature of 296 K is used for the determination of the S value; that is, the user specified temperature is used for all molecules except O<sub>2</sub> and those with  $E=-1$ , and a temperature of 296 K is used for O<sub>2</sub> and those molecules with  $E=-1$ . Note, however, that the user specified temperature is used for the calculation of the linewidths ( pressure and Doppler) and the atmospheric density term, N. For example in the case of O<sub>2</sub> lines, if the user specifies a temperature of 1000K and the override option is used, then  $T=1000$  K is used for the linewidth and N calculations, and  $T= 296$ K is used for the S value determination of the O<sub>2</sub> lines. The temperature dependence of N can also be overridden as specified by the user so that a constant value of N is used for all temperatures ( see subsection b above)

### **6.1.3 Slant Path Calculations Using Altitude Profiles**

The total transmission spectrum of the atmosphere along a slant path is modeled in the TRANS program by subdividing the path into multiple layers and assigning the appropriate value of the temperature, total atmospheric pressure, and partial pressure for each gas at the altitude of each layer. The number of layers and the altitude of each layer is specified by the user. The TRANS program performs a linear interpolation of the stored altitude profiles in order to compute the appropriate total pressure, temperature, and partial pressures for each layer. The TRANS program can handle up to 100 layers for these calculations, although such detail will reduce the execution speed of the program. The program uses a spherical earth geometry in that the ending altitude is calculated using this geometry; ie. a long horizontal path will show an increase in altitude at far ranges.

The profiles used are those from one of the U.S. Atmospheric Models and are stored in 34 ASCII data files in the [PRESS\*] subdirectories.<sup>9</sup> The parameter values stored are total pressure (millibars, mb), temperature (K), and mixing ratios ( ppmv, parts per million - volume) for each of the gases. Each data file is a list of altitude values in Km and the parameter value. The altitude