UMBC_LBL vers 8: An Algorithm to Compute Line-by-Line Spectra

Sergio De Souza-Machado, L. Larrabee Strow,
David Tobin, Howard Motteler and Scott Hannon

Physics Department
University of Maryland Baltimore County
Baltimore, MD 21250 USA

v6 October 27, 2011

Sergio De Souza-Machado: sergio@umbc.edu
L. Larrabee Strow: strow@umbc.edu

Contents

List of Tables

List of Figures

ABSTRACT

We have developed a line-by-line code to compute the spectral lineshapes of gases under varying pressure and temperatures. This code can use the spectral line parameters of a variety of databases such as HITRAN or GEISA. The code ensures that the same lines are used in all layers of an atmosphere, so that the resulting line profiles are smooth. The latest models for CO2 line mixing and in water vapor lineshapes are incorporated in the code. The code is can be used to compute absorption spectra at user specified resolutions, using one of various lineshapes. One of our uses for the code is to generate new versions of the spectroscopic database for kCARTA, which is the reference for the AIRS forward model.

This document is very much a work in progress. Some major omissions include references, significant examples of output, and comparisons of output to GENLN2. These omissions will be rectified in the future. Please give us your feedback on both the code and the documentation!

1 Introduction

This documentation describes a line-by-line code that can be used to compute optical depths for various gases (that appear in the HITRAN database). The code has been written in Matlab, with many of the routines written as FORTRAN-MEX files in the interests of speed. The lineshape database that is used in the computations, is currently the HITRAN 2008 database. Other databases, such as the GEISA or HITRAN92,96,2K,2004 databases, can be merged in and used. With this, we can incorporate the latest lineshape studies and parameters into our computations.

The HITRAN homepage is at http://www.cfa.harvard.edu/hitran/.

This code will be used to generate a new database for kCARTA, our radiative transfer algorithm that is the reference for the AIRS forward model. AIRS is a high resolution infrared instrument due to be launched by NASA in the year 2000. The instrument will be used to make measurements of the gas content and temperatures of the Earth's atmosphere, as well as study the global climate and weather.

For all gases except carbon dioxide and water vapor, the lineshapes of the individual lines are simply added together to give the overall absorption spectrum. To speed things up, the code uses the binning methods of GENLN2, where the lines are divided into near lines, medium-far lines and far lines. The general code to compute the lineshape of this majority of gases is called $run6.m$ Note that we also have code to incorporate the computation of the lineshapes of the cross section gases as well.

For the case of carbon dioxide, we have utilised Dave Tobin's work on linemixing and duration of collisions effects in the 4 μm band, and applied it to the 15 μm band as well. The code to compute the lineshape of carbon dioxide is called $run6co2.m$

For the case of water vapor, we have written two source codes. $run6water.m$ can compute the spectral lineshapes with or without the basement term removed, and add on the user specified continuum (CKD 0,2.1,2.3 or 2.4). In addition, this code also includes Tobin's work on water vapor chi functions. We also have a specialised continuum code $run6watercontinuum.m$ that can output one of the following (a) the completely computed water continuum (b) the self continuum coefficients (c) the foreign continuum coefficients or (d) combinations of the above three.

We begin the documentation by briefly describing how our code computes an optical depths, given the necessary input parameters. This section is divided into three; the first can be used for all gases, while the second and third apply to water vapor and carbon dioxide respectively.

The next sections describe the $UMBC\_LBL$ Version 6 code implemetation. A section on the basic code for most gases, $run8.m$ is then followed by section on $run8water(continuum).m$ and $run8co2.m$. We have improved upon Version 6 by defaulting most parameters to a set of values that are usually used; if the user wants to change these settings, he/she can send in the new value(s) by using a Matlab structure.

This will be the *UMBC_LBL* Version 8 implementation. All the basic physics is the same as version 6.

Theis is followed by sections which describe spectral lineshapes in detail. First is a section on general spectral lineshape theory, where the meaning of terms such as line widths and line broadening is explained. Next are two sections, one on computing water vapor spectra and the other computing carbon dixide spectra. As mentioned in the previous paragraphs, to accurately compute the absorption spectra of these two gases, one needs to use more involved lineshape theories than those for other gases. This is particularly important as these two gases are actively important in the infrared portion of the radiation emitted by the Earth, and so a thorough understanding of their spectra would be beneficial to the remote sensing community.

Finally, a short set of appendices briefly describe the general code to compute partition functions, line widths and line strengths.

2 General algorithm to compute optical depth

For each gas cell or atmopheric layer, the code expects a 1x5 array of inputs
[index P PP T q] =

```
[index    press  part.press  temp  col.density ] =
[integer  real   real        real  real        ]  =
[nounits  atm    atm         K     kmoles/cm2  ]
```

Assume the user wants the optical depth to be computed for a certain gas, using known parameters. These parameters are the total pressure P , partial (self) pressure PS, temperature T and gas amount (column density) U. The gas amount U is related to self pressure, temperature, path cell length (or atmospheric layer thickness) L by the equation

$$U = \frac{CF \times L \times PS}{R \times T}$$

where R is the molar gas constant (8.31 J/mol/K), P, PS are the total and partial pressures in atmospheres (only partial pressure is relevant for gas amount), T is the temperature in Kelvin, and L is the path length in cm. CF is a units conversion factor of1.01325×10^{-4} to give us U in units of $kiloMoles/cm^2$. This equation uses the Ideal Gas Law to calculate molecular density for a unit volume, and then multiplies the density by the path length L to convert density to column density (gas amount).

Knowing for what gas the spectrum is to be computed, and within which frequency interval, the lineshape parameters for that gas need to be read in. These parameters can be obtained from a database such as HITRAN98, and should include the following :

TYPE	DESCRIPTION	USE
gasid	input HITRAN GasID	1=water,2=CO2, etc
iso	list of isotopes	1=most abundant,2=next ...
linct	number of lines in wavenumber interval	
wnum	wavenumbers of the line centers $[cm^{-1}]$	$\nu_0(1), \nu_0(2), ...$
tsp	line center shift due to pressure P [cm-1/atm]	$\nu_0(j) \rightarrow \nu_0(j) + P \times tsp(j)$
stren	line strengths (See Eqn 19)	$S(T) \simeq S(296)Z(296)/Z(T) \times \rho$
	$[cm^{-1}/(molecules cm^{-2})]$	Z are partition functions (Eqn 14)
		$\rho \simeq$ upper/lower state populations
abroad	air broadened half widths HWHM $[cm^{-1}/atm]$	$brd_{air} = (P - PS) \times abroad$
sbroad	self broadened half widths HWHM $[cm^{-1}/atm]$	$brd_{self} = (PS) \times sbroad$
abcoef	temperature dependence of air	$brd = brd_{air} + brd_{self}$
	broadened half width	$brd \rightarrow brd \times (296/T)^{abcoef}$

tprob	transition probabilility [$debyes^2$]	
els	lower state energy [cm^{-1}]	computing S(T)
usgq	Upper state global quanta index	identifying
lsgq	Lower state global quanta index	P,Q,R branches
uslq	Upper State local quanta	local quantum numbers
bslq	Lower State local quanta	local quantum numbers
ai	accuracy indices	
ref	lookup for references	

Note that the *stren* parameter is used in units of $cm^{-1}/(molecules cm^{-2})$ while the gas amounts U are in units of $kiloMoles/cm^2$. To get absorption coefficients and optical depths that are in the correct units, the program eventually multiplies *stren* by 6.023×10^{26}, which is the number of molecules per kilomole (ie Avagadro's Number times 1000).

Having read in these parameters, the code is almost ready to proceed with the computations. Before this, it needs to read in the mass of each of the isotopes of the current gas. In addition, it needs to compute the partition function Z, and thus it needs four parameters a, b, c, d for each isotope (refer to Eqn 14). For the current temperature T , $Z(T)$ is then readily computed as :

$$Z(T) = a + bT + cT^2 + dT^3$$

The partition function is used when computing the line strength, as that term is proportional to the relative populations of the lower and upper levels of the transition.

Using parameter tsp, any shift of the line centers due to the total pressure is then computed, giving the adjusted line centers

$$\nu_0(P) = \nu_0 + P \times tsp(j)$$

The broadening of each line, due to the self component and the foreign component, is then computed.

$$brd_{air} = (P - PS) \times abroad$$

$$brd_{self} = (PS) \times sbroad$$

$$brd = brd_{air} + brd_{self}$$

$$brd \to brd \times (296/T)^{abcoef}$$

With the above information for each line having been determined, the absorption coefficients for the individual lines can now be computed, using the required lineshape

(Lorentz, Doppler, Voigt, etc). Looking at the simplest lineshape equation, the Lorentz lineshape is given by

$$k_L(\nu) = \frac{1}{\pi}\left(\frac{\gamma_L}{(\nu-\nu_0)^2+\gamma_L^2}\right)$$

where γ_L is the linewidth and ν, ν_0 are the wavenumber and line center frequency respectively. This means the units that result from a lineshape computation is cm

The final term required to compute the absorption spectrum is the line strength associated with each line. In the equation below, $S_i(T_{ref})$ is the line strength at the HITRAN reference temperature of $T_{ref} = 296K$, E_i is the lower state energy (given by els) and ν_i is the line center wavenumber :

$$S_i(T) = S_i(T_{ref})\frac{Z(T_{ref})}{Z(T)}\frac{\exp(-hcE_i/kT)}{\exp(-hcE_i/kT_{ref})}\frac{[1-\exp(-hc\nu_i/kT)]}{[1-\exp(-hc\nu_i/kT_{ref})]}$$

With S_i being in units of $cm^{-1}/(moleculescm^{-2})$, when this mutliplies the lineshape, the final abosrption coeficient units are $1/(moleculescm^{-2})$

By summing over the individual lines, the absorption spectra can be computed. However, for purposes of radiative transfer in the atmosphere, it is more convenient to think in terms of optical depths (and transmittances) instead of absorption spectra. With this in mind, and to get the units right, the adjusted line strength is simply multiplied by the gas amount times number of molecules per kilomole : $U(kiloMoles/cm^2) \times 6.023 \times 10^{26}(molecules/kiloMoles)$, from which the optical depth of the line (in dimensionless units) can be computed. By summing over all the individual optical depths, the total optical depth can be computed :

$$k_i^{opticaldepth}(\nu, \nu_0) = S_i(T) \times U \times 6.023E^{26} \times LineShape(P, PS, T, \nu_0(i), \gamma(i), mass(i))$$

$$k(\nu)^{opticaldepth} = \sum_i k_i^{opticaldepth}(\nu, \nu_0)$$

The actual steps described above are summarized in Fig. 2. In the case of water vapor and carbon dioxide, the spectral lineshape that is used for each line can be more complicated than a simple lorentz or voigt shape. This will be discussed in more detail later. For now, let us obtain some order of magnitude estimates for the optical depths of some of the gases in the atmosphere. The gas amounts U come from the AIRS layers. Assume the temperature T is 296 K, so all temperature effects are unimportant. Here we use units $\eta = molecules/cm^2$ for gas amounts U. Following are typical line paramter values obtained from the HITRAN database, in the regions where the optical depths for the individual gases peak in the atmosphere :

gas	wavenumber cm^{-1}	abroad cm^{-1}/atm	sbroad cm^{-1}/atm	S cm^{-1}/η	U η	mix ratio %
water	1500	0.08	0.4	2E-19	5.6E+21	0.77
CO2	2400	0.08	0.1	4E-18	2.2E+20	0.0036
N2	2400	0.05	0.05	4E-28	4.8E+23	78.1
CH4	1320	0.06	0.09	1E-19	1.0E+18	0.00017

The amount of water vapor in the atmosphere varies greatly both in time and space. The mixing ratio of water near the surface might be anywhere between 0.01% and 4%. The amount of CO2 and N2 varies by only a few percent, while CH4 may vary by a factor of two. Note that due to the size and range of variation of the water mixing ratio, as well as the lage difference between air- and self- broadened widths, that the total line widths can vary by upwards of 15amount of water in the atmosphere. That is, the widths of water lines in a dry atmosphere will be noticeably narrower than the widths in a wet atmosphere. This is not true for any of the other important atmospheric gases; their widths are nearly constant. This is because either their mixing ratio is relatively constant, very tiny, or their air- and self-broadened widths are very similar.

The peak absorption coefficent in the lower atmosphere is approximately given by $S/(\pi \times \gamma)$ where γ is the linewidth computed from the self and foreign broadening. Using the values in the previous table, we get the following estimates for the optical depths in the lowest 200 meters of the atmosphere :

gas	total P atm	self P atm	γ $[cm^{-1}]$	peak abs $[1/\eta]$	peak optical depth
water	1.0	9.8E-3	8.8E-2	7.2E-19	4000
CO2	1.0	3.4E-7	8.5E-2	1.5E-17	3000
N2	1.0	8.4E-1	5.5E-2	2.3E-27	0.001
CH4	1.0	1.8E-6	6.4E-2	4.9E-19	0.5

One immediately sees that methane and nitrogen have much smaller peak optical depths than water or carbon dioxide. Most of the other gases in the atmosphere also have maximum optical depths of less than one. Remember that when the spectra are actually computed, there is a sum over the individual lines, so the peak values in the table above are slight underestimates. In addition, the above table is only for the lowest 200m meters of the atmosphere; the total surface-to-space optical depths are typically 50 times larger.

Using typical values from the table above (which use parameters for the lowest layer in the atmosphere), the absorption due to an individual line has decayed by $\frac{\gamma}{25^2+\gamma^2}/\frac{\gamma}{\gamma^2} \simeq$

10^{-5} by the time it is $25cm^{-1}$ away from line center. For most gases except H2O and CO2, this $25cm{-}1$ distance may be used a safe cutoff limit beyond which the contribution of an individual line to the overall spectrum can be considered negligible. The large optical depth of the strong CO2 and water lines means we must go a couple hundred wavenumbers into the wing before the optical depth drops off to a negligible level!

To speed up the code while maintaining accuracy, our algorithm uses a variant of the GENLN2 method of binning the lines while computing the spectra. To compute the absorption spectrum in the chosen interval, the code divides up the interval into bins of width $fstep \simeq 1cm^{-1}$. It then loops through these bins, computing the overall spectra in each bin using three stages. To reinforce the ideas, actual example numbers will be used. Suppose the wavenumber interval being considered is 1005 - 1030 cm^{-1}. There are 25 bins of width $ffin = 1cm^{-1}$ in this interval. Suppose we are considering the $4th$ bin, which is the bin spanning 1008 to 1009 cm^{-1}.

- (a) *fine mesh stage* : lines that are $\pm xnear \simeq 1cm^{-1}$ on either side of the edges of this bin, are used in computing the overall lineshape at this stage, at a very fine resolution of $ffin \simeq 0.0005cm^{-1}$. The results of this computation are then boxcar averaged to the output resolution $nbox \times ffin \simeq 0.0025cm^{-1}$
  Thus the lines that are used in this stage have their centers spanning 1007 to 1010 cm^{-1}.

- (b) *medium mesh stage* : lines that are an additional $xmed - xnear \simeq (2-1) = 1cm^{-1}$ on either side of the edges of this bin, are now used in computing the overall lineshape, at a medium resolution of $fmed \simeq 0.1cm^{-1}$. The results of this computation are then splined onto the output resolution and added onto the running sum from above. Thus the lines that are used in this stage have their centers spanning (1006,1007) and (1010,1011) cm^{-1}.

- (b) *coarse mesh stage* : lines that are an additional $xfar - xmed \simeq (25-2) = 23cm^{-1}$ on either side of the edges of the medium meshes, are now used in computing the overall lineshape, at a coarse resolution of $fcor \simeq 0.5cm^{-1}$. The results of this computation are then splined onto the output resolution and added onto the running sum from above. Thus the lines that are used in this stage have their centers spanning (983,1006) and (1011,1034) cm^{-1}.

The speed up in the code is gained by computing contributions at the medium and coarse resoutions as much as possible, instead of using the fine resolution grid all the time.

As was pointed out above, the strengths of some of the lines sometimes sometimes make it necessary to use lines that could be upto 200 cm^{-1} away (in the coarse part of the computation). Instead of doing this, a common practice is to remain with the 25 cm^{-1} width of the coarse meshes, but include the effects of lines outside these coarse mesh by adding on an extra *continuum*. This is true for oxygen and nitrogen, and in particular water vapor (see below). Carbon dioxide also requires this; however we choose not to use the continuum in this case, but simply use the entire 200 cm^{-1} wide coarse meshes.

Carbon dioxide, like water vapor, is radiatively active in the Earth's atmosphere. Just like water, it is important to accurately compute the absorption spectra using the correct lineshape, as optical depths of these gases vary greately in the atmosphere, allowing one to probe several layers of the atmosphere within a small spectral region. A thorough understanding of the absorption spectra of these two gases is therefore very important for the remote sensing community.

2.1 Computing water vapor absorption coefficients

Almost all that has been said above remains valid when computing the lineshape of water vapor. However, the lineshape far away from line center is sub-Lorentz ($k/k_{lor} \leq 1$), while the lineshape close to line center is super Lorentz ($k/k_{lor} \geq 1$). To account for this behavior, the above algorithm has to be slightly modified. This leads to the water vapor lineshape algorithm to include the following three different modifications, put together :

- Instead of using a lorentz lineshape, a *local lineshape* is used. Upto 25 cm^{-1} away from line cenetr, this is defined as lorentz less the lorentz value $25cm^{-1}$, and zero everywhere else.
- To include the super Lorentz behavior close to the line center, the local lineshape is then multiplied by a chi (χ) function
- To include the sub Lorentz behavior far from the line center, a continuum function is then added on. This is done after the effects of all lines have been used. Another way of thinking of this continuum is to say that the water lines are quite strong, and thus the computational algorithm should not restricted to using only lines that are at most 25 cm^{-1} wavenumbers away from the spectral region under consideration. But instead of individually using lines that could be upto 200 cm^{-1} away (and modelling their sub Lorentz far wing behavior), the far wing effects of these far lines are all lumped into the continuum.

To summarize, when computing a water vapor optical depth, the code proceeds as in the general case described above, except that it uses a *local* lineshape for each line j, multiplied by a χ function. After all the necessary lines have been included, a *continuum* absorption coefficient is also added on :

$$k(\nu) = k_{continuum}(\nu) + \sum_j k_{local}(\nu, \nu_j)\chi(\nu)$$

which can be rewritten, for the individual lines j

$$k_{local}(\nu, \nu_j) = \begin{cases} (k_{lorentz}(\nu, \nu_j) - k_{lorentz}(\nu, 25 + \nu_j))\chi(\nu) & \text{if } |\Delta\nu| \leq 25\text{cm}^{-1} \\ 0 & \text{if } |\Delta\nu| > 25\text{cm}^{-1} \end{cases}$$

where appropriate factors of $\nu \tanh(\beta\nu/2)$ multiply the above coefficients.

The computation for k_{local} proceeds as described in the previous section, *viz.* using fine, medium and coarse meshes.

2.2 Computing carbon dioxide absorption coefficients

Computing the spectral lineshape of carbon dioxide can be quite complicated. There are many bands within which there are lines that are very closely spaced. Collisions have the effect of mixing these lines together, transferring intensity from the line wings to the line centers. Furthermore, the collisions are not instantaneous, but have a finite duration. This also makes the lineshape deviate from Lorentz, especially far from the line centers. Additionally, some of the bands are very strong and have an effect on the absorption spectrum, at quite large distances from their band (line) centers. This third effect can be accounted for by either using a continuum, or by allowing the inclusion of effects of lines that are upto 200 cm^{-1} away from the region of interest.

We currently use full and dirst order line mixing methods of Strow *et al*; we are assessing using Hartmann linemixing coeffs.

3 run8

The Matlab code has four main driver files : $run8.m$, $run8co2.m$ and $run8water.m$ and $run8watercontiunuum.m$.

$run8.m$ is a general code that will work for all gases; however one should run the specialized codes for water and CO2, so as to to utilise the above physics in the computed lineshapes. We describe the $run8.m$ program parameters and algorithm in detail below; in the next two sections, we will discuss the corresponding similarities and differences for the water and carbon dioxide codes.

3.1 input units for run8

The input argument list to all codes also includes the name of a profile file which specifies the layer number, total pressure, gas partial pressures (both in atm), gas temperature (in Kelvin) and gas amount (in $kilomoles cm^{-2}$). The profile should be in a 5 column format, and should be a text file.

3.2 Mex files and HITRAN database

(this is for run8)
If the user wants to change the name of the line database file that is used, he/she will have to go into the run8* files and change the name of the file in the line beginning with the word $fnamePRE$, which is currently set to :

```
fnamePRE='/salsify/scratch4/h98.by.gas/g';
```

(this is for run7)
The default is to use HITRAN2000; if the user wants to change this, all that has to be done is supply an additional input parameters, topt.HITTRAN = xxxx (see below for details!!!)

To speed the code up, a number of loops have been written as fortran MEX files. All these files are in subdirectory FORTRANFILES, and assume input arrays/matrices that are smaller than certain limits. If the user wants to change these limits, he/she will have to edit the file $max.inc$ and recompile the Mex files.

```
c this is max length of arrays that can be used in the Mex Files
c this number came out of
c   200000 = max number of elements in mesh
c               eg (755-655)/0.0005 = 160000
c        4 = number tacked on to arrays so boxint(y,5) can be done
      integer MaxLen
      parameter(MaxLen=200010)
```

```
c assume max number of any of P,Q,R lines = 300
      integer MaxPQR
      parameter(MaxPQR=300)

c assume max number of any of layers = 100
      integer kMaxLayer
      parameter(kMaxLayer=100)
```

To compile the Mex files, the user has to type *makemex1* at the UNIX prompt (if only *run8/7.m* is being used), or type *makemex* (if *run8/7co2.m* will be used). This compiles all the Mex files, and creates symbolic links to these files from the necessary subdirectories.

If the user is going to use *run8/7co2.m*, he/she will also need to go to the C02_COMMON subdirectory, and type *link.sc* so that symbolic links from the CO2 subdirectories to the common files are created.

3.3 Water, nitrogen, oxygen continuum

Through parameter CKD (see below), the user can toggle the continuum calculation on/off for three gases : water, oxygen and nitrogen (gasIDs 1,7,22 respectively).

- Water : CKD can be set to -1 (no continuum), or 0,21,23,24 for CKD versions 0, 2.1, 2.3, 2.4. Note when the first 3 versions of CKD are included, the computation proceeds by using the code which does not require a "local" lineshape. However, CKD 2.4 does require a "local" lineshape.
- Oxygen : CKD can be set to -1 (no continuum), or +1 (continuum)
- Nitrogen : CKD can be set to -1 (no continuum), or +1 (continuum)
- For all other gases, the value of CKD is irrelevant

3.4 run8.m input parameters

A typical call to run8 would involve sending in the following :

$[outwave, outarray] = run8(gasID, fmin, fmax, ffin, fmed, fcor, fstep$ $xnear, xmed, xfar, nbox, strfar, strnear, LVG, CKD, profile)$

where the right hand side variables would be

TYPE	VAR	DESCRIPTION	TYPICAL VALUE

integer	gasID	HITRAN gas ID	3
integer	fmin	minimum freq (cm-1)	605
integer	fmax	maximum freq (cm-1)	630
real	ffin	fine point spacing (cm-1)	0.0005
real	fmed	medium point spacing (cm-1)	0.1
real	fcor	coarse point spacing (cm-1)	0.5
real	fstep	wide mesh width size (cm-1)	1.0
real	xnear	near wing distance(cm-1)	1.0
real	xmed	med wing distance(cm-1)	2.0
real	xfar	far wing distance(cm-1)	25.0
integer	nbox	boxcar sum size (odd integer)	1,5
real	strfar	min line strength for far wing lines	
real	strnear	min line strength for near wing lines	
char	LVG	(L)orentz,Voi(G)t,(V)anHuber	'V'
integer	CKD	continuum no = -1 (most gases) yes for water (0,21,23,24) yes for N2, O2 (gases 7,22)	-1
matrix	profname	Nx5 matrix (gasID,pressure,pp,temp,amt) pressure, partial pressure in atm, T in K gas amount in kilomolecules/cm2	

The HITRAN gasIDs and cross sections can be found at http://www.cfa.harvard.edu/hitran/

The output arguments from the function call are the output wavevector, outwave, and the computed line spectra in outarray. The vector outwave (and thus the output array outarray) spans the wavenumber range from $fmin$ to $fmax - (ffin \times nbox)$, at a resolution of $ffin \times nbox$.

3.5 run7.m input parameters

The same parameters as above are used. However, many of them are now defaulted to preset values, and can be reset by using optional input argument *topts*, where *topts* is a structure.

A typical call to run7 would involve sending in the following :

$[outwave, outarray] = run7(gasID, fmin, fmax, profile, \{topts\})$;

where the required right hand side variables would be

TYPE	REQUIRED	DESCRIPTION	TYPICAL VALUE

integer	gasID	HITRAN gas ID	3
integer	fmin	minimum freq (cm-1)	605
integer	fmax	maximum freq (cm-1)	630
matrix	profname	Nx5 matrix (gasID,pressure,pp,temp,amt) pressure, partial pressure in atm, T in K gas amount in kilomolecules/cm2	

and the optional right hand side arguments would be sent in structure *topts*; the default values are as shown :

TYPE	OPTIONAL	DESCRIPTION	DEFAULT VALUE
real	ffin	fine point spacing (cm-1)	0.0005
real	fmed	medium point spacing (cm-1)	0.1
real	fcor	coarse point spacing (cm-1)	0.5
real	fstep	wide mesh width size (cm-1)	1.0
real	xnear	near wing distance(cm-1)	1.0
real	xmed	med wing distance(cm-1)	2.0
real	xfar	far wing distance(cm-1)	25.0
integer	nbox	boxcar sum size (odd integer)	5
real	strfar	min line strength for far wing lines	0.0
real	strnear	min line strength for near wing lines	0.0
char	LVG	lineshape : (L)orentz,Voi(G)t,(V)anHuber	'V'
string	HITRAN	path to HITRAN database	/asl/data/hitran/h2k.by.gas
integer	CKD	continuum no = -1 (most gases) yes for water (0,21,23,24) yes for N2, O2 (gases 7,22)	-1

The output arguments from the function call are the output wavevector, outwave, and the computed line spectra in outarray. The vector outwave (and thus the output array outarray) spans the wavenumber range from $fmin$ to $fmax - (ffin \times nbox)$, at a resolution of $ffin \times nbox$.

3.6 Detailed description of the input parameters

Two of the input parameters are self-describing. The first parameter, $gasID$ is an integer value specifying which gas you want to compute the line spectra for. This integer value is the same as that used for the HITRAN database; for example gasID=3 corresponds to ozone. LVG is a character parameter that tells the code which lineshape to use for *all* the lines. Of the lineshapes described previously, our code can compute one of the following three - **L**orentz, Voi**G**t or **V**anVleck-Huber. The VanVleck-Huber is computed with a Voigt lineshape, and is the one we recommend; to use this lineshape, LVG is set to 'V'.

When the code starts running, it loads in all lines whose centers lie between $fmin - xfar$ and $fmax + xfar$, and whose database line strength is greater than min(strfar,strnear), as the user assumes these are the lines which will have a discernible effect on the overall spectra. Using these lines, and their associated parameters, the computations are performed on a fine mesh resolution $ffin$ and then boxcar averaged to an output resolution $ffin \times nbox$. The results of the computations are output for a wavector that spans $fmin$ to $fmax - ffin \times nbox$. Internally, the computations are essentially performed on a fine mesh that spans $fmin - (nbox - 1)/2$ to $fmax - ffin \times nbox + (nbox - 1)/2$. In this way, the boxcar averaging can be done on the endpoints.

If this direct method were used, depending in the gasID and wavenumber region chosen, the code could be agonizingly slow. In the interests of speed (and mantaining the accuracy), the code therefore requires some more parameters to be sent in.

With these additional parameters, the output wavevector $fmin$ to $fmax - ffin \times nbox$ is divided into equal sized “wide meshes” of size $fstep\ cm^{-1}$. Thus there are N wide meshes, where

$$N = \frac{fmax - fmin}{fstep} \tag{1}$$

Suppose we are considering the ith widemesh, and we denote the start frequency of this widemesh by $f1$, and the stop frequency by $f2$. These two numbers are related to each other and to the other numbers by

$$f1 = fmin + (i - 1) \times fstep - ffin \times (nbox - 1)/2$$

$$f2 = fmin + ii \times fstep - (ffin \times nbox) + ffin \times (nbox - 1)/2 \tag{2}$$

This “finemesh” thus spans $(f1, f2)$ at the fine resolution of $ffin\ cm^{-1}$

Associated with this finemesh is a medium resolution mesh, that spans $(f3, f4)$ at a coarser resolution $fmed$ where

$$f3 = fmin + (i - 1) \times fstep$$

$$f4 = fmin + ii \times fstep \tag{3}$$

In addition there is a coarse resolution mesh, that spans $(f3, f4)$ at a coarsest resolution $fcor$ where $f3, f5$ are the same, as are $f4, f6$:

$$f5 = fmin + (i - 1) \times fstep$$

$$f6 = fmin + ii \times fstep \tag{4}$$

The spectral region of the output wavevector that corresponds to these three meshes is essentially $f3, f4$, adjusted for the last point. In other words, the ith output region $fout(i)$ spans $f3$ to $f4 - nbox \times ffin$, at a resolution of $nbox \times ffin$

For any of the N widemeshes, lines are grouped into three categories, depending where they fall within the three categories defined below :
(a) near lines are those whose line centers lie in the wavenumber interval $(f3 - xnear, f4 + xnear) = (w1, w2)$. All computations using these lines are performed on the fine mesh (spanning $f1, f2$) of point spacing ffin, and then boxcar averaged to the output wavevector $fout(i)$
(b) medium lines are those whose line centers lie in the wavenumber interval $(f3 - xnear - xmed, f3 - xnear) \cup (f4 + xnear, f4 + xnear + xmed) = (w3, w1) \cup (w2, w4)$. All computations using these lines are performed on the medium mesh (spanning $f3, f4$) of point spacing fmed, and then splined to the output wavevector $fout(i)$
(c) far lines are those whose line centers lie in the wavenumber interval $(f3 - xmed, f3 - xfar) \cup (f4 + xmed, f4 + xfar) = (w5, w3) \cup (w4, w6)$. All computations using these lines are performed on the coarse mesh (spanning $f3, f4$) of point spacing fcor, and then splined to the output wavevector $fout(i)$
The cartoon in Figure **??** summarizes the above relationships.

With the above description, the following restrictions on the parameters are now self explanatory :
(1) xnear $\leq$ xmed $\leq$ xfar
(2) xnear $\geq$ fstep
(3) xmed/fmed xnear/fmin fstep/fmed fstep/ffin are integers
(4)fstep/(nbox*ffin) fcor/ffin are integers
(5)(fmax-fmin)/fstep (fmax-fmin)/fcor are integers

A useful rule of thumb is that ffin,fmed,fcor are chosen so that they are all equal to $(1/2)/10^n$ $n \leq 5$, with n chosen as necesary for the three parameters. For example, $n = 3, 1, 0$ gives $ffin = 0.0005, fmed = 0.05, fcor = 0.5cm^{-1}$.

The above algorithm used is almost the same as that used by GENLN2, except that GENLN2 does not currently have the medium resoltion mesh ie the overall lineshape is a sum of boxcar averaged fine mesh contribution and a spline computed coarse mesh contribution.

Other differences found between this LBL code and GENLN2 is that all computations here are in real*8, while GENLN2 mixes bewteen real*8 and real*4. The discrepancies between these two representations is noticeable in computations of eg the partition fucntions. In addition, we believe that the contribution of a line whose center is in the "far line" regime, is incorrectly splined at the last interval $|x_{center} - x| \sim xfar$

3.7 Detailed description of the output parameters

Two parameters are passed out after running the code : a 1d array *outwave* that contains the output wavevector, and a 2d matrix *outarray* that contains the computed lineshapes at the user set atmospheric levels.

3.8 Outline of the algorithm

The code starts out by checking to ensure that the input parameters make sense and that they are self consistent. For example, parameter LVG must be set to one of the allowable line shapes. In addition, the parameters should all be self consistent in that they have to staisfy the restrictions given at the end of the previous subsection.

Having ascertained the self consistency of the parameters sent in by the user, the program loads in the required mass isotopes for the chosen gas. For example ozone has 5 isotopes.

The program then loads in the user specified profile for the gas. Having done this, the program then uses $fmin, fmax, ffin, nbox$ to define the output wave vector. After this, the gas initializes the *qtipts* coefficients that are used to compute the partition functions. This is essentially a GENLN2 subroutine, similar to the program "tips" by R.R.Gamache.

The program is now ready to load in the gas line parameters from the HITRAN database. As described above, it loads in all lines whose centers lie between $fmin - xfar$ and $fmax + xfar$, and whose database line strength is greater than min(strfar,strnear).

At this point, the program is almost ready to start running in earnest. Before doing that, it computes the number of wide meshes N and the number of points in each wide mesh that will be mapped to the output wavevector. If the user loaded in a profile that has more than one layer in it, the program calls subroutine $doUnion2$, that computes the optical depth of each linecenter for the chosen profile conditions; if a line is strong enough to be used in any *one* of the levels, it will be used at *all* levels. This will ensure that the optical depth profiles are smooth. An example of this is the case of ozone, where lines could "turn-on" high in the atmosphere, but have almost no optical depth lower in the atmosphere. The importance of this is when the output from the code is used to generate the kCARTA database using Singular Value Decomposition; the SVD algorithm would work more efficiently with smoothly varying data (achieve better compression).

Figure 5 outlines the above initialisation stages of the algorithm.

The program is now ready to loop over the far,medium and near lines. For each of the wide meshes, the program first defines the fine, medium and coarse meshes (frequencies and indices), as described in the previous section. It then sorts all the lines it has loaded into three bins; near, medium and far, also as described in the previous section.

It then enters a loop over layers. For the current layer, the program uses the gas profile to determine the gas amount, temperature, total and self pressures. For each layer, it first computes the contribution due to the near lines, then the medium lines and finally the far lines. The near line spectrum is computed on the fine mesh, and the results are boxcar averaged and added onto the output array. The medium line spectrum is computed on the medium mesh, spline interpolated onto the output wavevector and added on to the output array.The far line spectrum is computed on the coarse mesh, spline interpolated onto the output wavevector and added on to the output array.

For each of the fine,medium and coarse computations, the code computes the following line parameters, for each of the lines
(a) the partition function, using $qfcn = q(A, B, C, D, G, lines, tempr)$
(b) the line center frequency, taking the pressure of the current layer into account $freq = lines.ZWNUM + press(jj) * lines.ZTSP$
(c) the overall broadening of the line, using the self and foreign broadening contributions $brd = broad(p, ps, 1.0, forbrd, selfbrd, pwr, tempr, gasID)$
(d) the line center line strength, using the necessary layer parameters such as temperature, gas amount and necessary line parameters
$strength = find_stren(qfcn, freq, tempr, energy, s0, GasAmt(jj))$
The above computations are essentially GENLN2 routines.

Figure 6 outlines the loop stage of the algorithm.

4 run8water

run8water.m is a specialised code for H2O, so as to to utilise the above physics, namely local lineshape and the CKD continuum effects in the computed lineshapes. If the user simply wants to do a Lorentz or Voigt computation, then it would behoove him/her to use *run8.m* instead of this special code.

4.1 run8water.m input parameters

A typical call to run8water would involve sending in the following :

$[outwave, outarray] = run8water(gasID, fmin, fmax, ffin, fmed, fcor,$
$fstep, xnear, xmed, xfar, nbox, strfar, strnear, LVF,$
$CKD, selfmult, formult, usetoth, local, profname);$

where the right hand side variables are the same as those for run8 described above; there are 5 new variables on the right side.

TYPE	VAR	DESCRIPTION	TYPICAL VALUE
integer	gasID	HITRAN gas ID	1

integer	fmin	minimum freq (cm-1)	705
integer	fmax	maximum freq (cm-1)	730
real	ffin	fine point spacing (cm-1)	0.0005
real	fmed	medium point spacing (cm-1)	0.1
real	fcor	coarse point spacing (cm-1)	0.5
real	fstep	wide mesh width size (cm-1)	1.0
real	xnear	near wing distance(cm-1)	1.0
real	xmed	med wing distance(cm-1)	2.0
real	xfar	far wing distance(cm-1)	150.0
integer	nbox	boxcar sum size (odd integer)	1,5
real	strfar	min line strength for far wing lines	
real	strnear	min line strength for near wing lines	
char	LVG	(L)orentz,Voi(G)t,(V)anHuber	'V'
integer	CKD	continumm no (-1) yes water : (0,21,23,24)	-1
real	selfmult	multiplier for self part of contiuum	0¡x¡1
	formult	multiplier for for part of contiuum	0¡x¡1
integer	usetoth	use Toth or HITRAN	+1 to use Toth -1 to use HITRAN
integer	local	use local lineshape	+1 to use local*chi defn 0 to use local defn -1 to use run8 defn

The output arguments from the function call are once again the output wavevector, outwave, and the computed line spectra in outarray. The vector outwave (and thus the output array outarray) spans the wavenumber range from $fmin$ to $fmax-(ffin\times nbox)$, at a resolution of $ffin \times nbox$.

4.2 run7water.m input parameters

The same parameters as above are used. However, many of them are now defaulted to preset values, and can be reset by using optional input argument *topts*, where *topts* is a structure.

A typical call to run7 would involve sending in the following :
$[outwave, outarray] = run7water(gasID, fmin, fmax, profile, \{topts\});$
where the required right hand side variables would be

TYPE	REQUIRED	DESCRIPTION	TYPICAL VALUE

integer	gasID	HITRAN gas ID	1
integer	fmin	minimum freq (cm-1)	605
integer	fmax	maximum freq (cm-1)	630
matrix	profname	Nx5 matrix (gasID,pressure,pp,temp,amt) pressure, partial pressure in atm, T in K gas amount in kilomolecules/cm2	

and the optional right hand side arguments would be sent in structure *topts*; the default values are as shown (notice that CKD is defaulted to -1 (OFF) and the lineshape is augmented to "local") :

TYPE	OPTIONAL	DESCRIPTION	DEFAULT VALUE
real	ffin	fine point spacing (cm-1)	0.0005
real	fmed	medium point spacing (cm-1)	0.1
real	fcor	coarse point spacing (cm-1)	0.5
real	fstep	wide mesh width size (cm-1)	1.0
real	xnear	near wing distance(cm-1)	1.0
real	xmed	med wing distance(cm-1)	2.0
real	xfar	far wing distance(cm-1)	25.0
integer	nbox	boxcar sum size (odd integer)	5
real	strfar	min line strength for far wing lines	0.0
real	strnear	min line strength for near wing lines	0.0
char	LVG	lineshape : (L)orentz,Voi(G)t,(V)anHuber	'V'
string	HITRAN	path to HITRAN database	/asl/data/hitran/h2k.by.gas
integer	CKD	continuum no = -1 (most gases) yes for water (0,21,23,24) yes for N2, O2 (gases 7,22)	-1
real	selfmult	multiplier for self contiuum 0¡ x¡ 1	1
real	formult	multiplier for foreign continuum 0¡ x¡ 1	1
integer	local	modification to LVG lineshape +1 to use local*chi lineshape defn 0 to use local lineshape defn -1 to use standard LVG lineshape defn	0

4.3 Detailed description of the input parameters

As mentioned above, most of the input parameters are the same as for *run*8 and a description is not repeated here. However, five of the last six parameters are new, and so will be explained below.

CKD is a integer parameter that tells the code which continuum to use. Note that based on whether or not the "local" lineshape was used, the appropriate CKD lookup tables are used. For CKD 0,21,23 the code can compute the continuum whether or not the local lineshape was used; for CKD24, only the local lineshape can be used.

$selfmult$ is a real parameter between 0 and 1, that is used to scale the "self" contribution to the continuum.

$formult$ is a real parameter between 0 and 1, that is used to scale the "foreign" contribution to the continuum.

usetoth is a integer parameter that tells the code whether or not to use the Toth database.

local is a integer parameter that tells the code whether or not to compute the local lineshape (must be set to "0" or "1" to use CKD2.4)

5 run8watercontinuum

run8watercontinuum.m is a specialised code for H2O, that only computes the CKD continuum. This code is to be used in conjunction with run8water.m

5.1 run8watercontinuum.m input parameters

A typical call to run8watercontinuum would involve sending in the following (note that the 'LVG" parameter has been replaced by "divide") :

$[outwave, outarray] = run8water(gasID, fmin, fmax, ffin, fmed, fcor,$
$fstep, xnear, xmed, xfar, nbox, strfar, strnear, divide,$
$CKD, selfmult, formult, usetoth, local, profname);$

where the right hand side variables are the same as those for run8 described above; there are 5 new variables on the right side.

TYPE	VAR	DESCRIPTION	TYPICAL VALUE
integer	gasID	HITRAN gas ID	1
integer	fmin	minimum freq (cm-1)	705
integer	fmax	maximum freq (cm-1)	730
real	ffin	fine point spacing (cm-1)	0.0005
real	fmed	medium point spacing (cm-1)	0.1
real	fcor	coarse point spacing (cm-1)	0.5
real	fstep	wide mesh width size (cm-1)	1.0
real	xnear	near wing distance(cm-1)	1.0
real	xmed	med wing distance(cm-1)	2.0

real	xfar	far wing distance(cm-1)	150.0
integer	nbox	boxcar sum size (odd integer)	1,5
real	strfar	min line strength for far wing lines	
real	strnear	min line strength for near wing lines	
integer	divide	what is overall computation	-1
integer	CKD	continumm no (-1)	24
		yes water : (0,21,23,24)	
real	selfmult	mult for self part of contiuum	0¡ x¡ 1
	formult	mult for for part of contiuum	0¡ x¡ 1
integer	usetoth	use Toth or HITRAN	+1 to use Toth -1 to use HITRAN
integer	local	use local lineshape	+1 to use local*chi defn 0 to use local defn -1 to use run8 defn

The output arguments from the function call are once again the output wavevector, outwave, and the computed line spectra in outarray. The vector outwave (and thus the output array outarray) spans the wavenumber range from $fmin$ to $fmax-(ffin\times nbox)$, at a resolution of $ffin \times nbox$.

5.2 run7watercontinuum.m input parameters

The same parameters as above are used. However, many of them are now defaulted to preset values, and can be reset by using optional input argument *topts*, where *topts* is a structure.

A typical call to run7 would involve sending in the following :
$[outwave, outarray] = run7watercontinuum(gasID, fmin, fmax, profile, \{topts\});$
where the required right hand side variables would be

TYPE	REQUIRED	DESCRIPTION	TYPICAL VALUE
integer	gasID	HITRAN gas ID	1
integer	fmin	minimum freq (cm-1)	605
integer	fmax	maximum freq (cm-1)	630
matrix	profname	Nx5 matrix (gasID,pressure,pp,temp,amt) pressure, partial pressure in atm, T in K gas amount in kilomolecules/cm2	

and the optional right hand side arguments would be sent in structure *topts*; the default values are as shown (as is readily appreciated, most of the run7 input arguments are unnecessary and have been REMOVED; also sice the continuum is smooth, we do not really need 5 point averaging and so nbox is defaulted to +1 instead of +5) :

TYPE	OPTIONAL	DESCRIPTION	DEFAULT VALUE
real	ffin	fine point spacing (cm-1)	0.0025
integer	nbox	boxcar sum size (odd integer)	1
integer	CKD	continuum no = -1 (most gases) yes for water (0,21,23,24)	-1
integer	divide	what is overall computation	-1
real	selfmult	mult for self contiuum 0 ¡ x ¡ 1	1
real	formult	mult for foreign continuum 0 ¡ x ¡ 1	1
integer	local	modification to LVG lineshape +1 to use local*chi lineshape defn 0 to use local lineshape defn -1 to use standard LVG lineshape defn	0

5.3 Detailed description of the input parameters

$ffin \times nbox$ determines the output spacing

CKD is a integer parameter that tells the code which continuum to use. Note that based on whether or not the "local" lineshape was used, the appropriate CKD lookup tables are used. For CKD 0,21,23 the code can compute the continuum whether or not the local lineshape was used; for CKD24, only the local lineshape can be used.

$selfmult$ is a real parameter between 0 and 1, that is used to scale the "self" contribution to the continuum.

$formult$ is a real parameter between 0 and 1, that is used to scale the "foreign" contribution to the continuum.

local is a integer parameter that tells the code whether or not to compute the local lineshape (must be set to "0" or "1" to use CKD2.4)

divide is an IMPORTANT parameter that enables the user to ouput the correct total continuum, or along with $selfmult$, $formult$, just parts of it (such as self or foreign or combination). The effects are described as below

DIVIDE	SELFMULT	FORMULT	DIVIDES BY	RESULT
-1	xx	xx	1.0	q v tanh(c2 v/2T) (296/T) (ps CS + pf CF)
+1	1.0	0.0	q v tanh(c2 v/2T) (296/T) * ps	CS
+1	0.0	1.0	q v tanh(c2 v/2T) (296/T) * (p-ps)	CF
+1	xx	xx	q v tanh(c2 v/2T) (296/T)	(ps CS + pf CF)

6 run8co2

See lbl.pdf for this!

7 General Spectral Lineshape Theory

This section examines the basic lineshape parameters, including line centers, shifts, widths, and strengths. The standard lineshapes for natural and Doppler broadening are then presented, followed by a review of collisional lineshapes. Most of this information is from Dave Tobin's PhD dissertation [1].

7.1 Molecular Absorption and Beer's Law

Molecular absorption occurs when a molecule absorbs light and simultaneously makes a transition to a higher level of internal energy. The absorption of incident photons decreases the outgoing radiation, and a spectral line is produced. The shape or frequency dependence of this absorption is often called the lineshape. Because of various factors, the absorption occurs not only at the resonant frequency of the transition (determined by the difference between the upper and lower energy levels), but over a spread of frequencies. These broadening factors lead to a finite width of the spectral line. While the resonant frequency and the intensity of the absorption are determined primarily by the structure of the molecule, the lineshape is determined by the molecules' environment.

The frequency dependence of the absorption coefficient, $k(\nu)$, determines the shape of a spectral line. Beer's law relates the absorption of radiation through a gaseous medium linearly to the incident radiation (see Figure 7):

$$-dI = k(\nu) I_0 P dl \tag{5}$$

with the absorption coefficient, $k(\nu)$ being the constant of proportionality. $-dI$ is the decrease in radiation flux over a path length of dl through a gas of constant and uniform pressure P. Integrating this equation over a homogeneous path length of L yields the integrated form of Beer's law:

$$T(\nu) = \frac{I_f(\nu)}{I_0(\nu)} = \exp\left(-k(\nu) P L\right). \tag{6}$$

$T(\nu)$ is is the transmission at frequency ν. $I_0(\nu)$ and $I_f(\nu)$ are the initial and final radiation intensities. Thus, the absorption coefficient is related to the observed transmission by

$$k(\nu) = -\frac{1}{PL} \ln\left(T(\nu)\right). \tag{7}$$

It should be noted that deviations from the linear form of Beer's law are only observed at extremely high photon densities. Under atmospheric conditions, however, the linear dependence of the extinction on the amount of absorbing material and incident radiation is valid.

7.2 Line Parameters

The lineshape of a single (non-interacting) transition is commonly characterized by several parameters including the line *center* (ν_0), line *strength* (S), and line *width* (γ). These are illustrated in Figure 8.

Several spectral line databases are available which provide a compilation of the line positions, strengths, and widths as well as several other important parameters such as the lower state energy, pressure induced line center shifts, isotopic abundances, rotational and vibrational quantum indexing, width-temperature exponents, and transition probabilities. HITRAN[2, 3] (the high resolution transmission molecular absorption database) is one such database used in this work which is maintained by the Phillips Laboratory Geophysics Directorate . It currently lists the parameters of over 700,000 rotation and vibration-rotation spectral lines for 31 molecules of atmospheric importance from 0–23,000 cm^{-1}. This database represents the most accurate compilation of line parameters. However, due to its size, it is only updated every two to four years and thus recent state-of-the-art measurements and calculations are not always in the database and must be obtained elsewhere.

7.2.1 Line Centers

The line *center*, or position, of a spectral line is determined by the molecular structure, just as the allowable vibrational-rotational energy levels of the molecule are determined by its structure. Planck's relation:

$$\nu_0 = \frac{\Delta E}{h} \tag{8}$$

relates the transition frequency, ν_0 (cm^{-1}), to the change in internal energy, ΔE, where h is Planck's constant. The line centers are thus determined by the structure and allowed energy levels of the molecule and by transition selection rules.

Since the line centers do not depend critically upon the interactions with other molecules, or upon the population of various states, they do not vary significantly with temperature or pressure. One common exception to this are the very small shifts in line center with increasing pressure. Just as molecular collisions can disturb optical transitions leading to increased line widths (discussed later), these disturbances can also lead to an apparent change in the resonant frequency of the molecule's wave-train. Computationally, the shifted position is given by

$$\nu_0(P) = \nu_0 + P \cdot \delta_\nu \tag{9}$$

where P is the total pressure and δ_ν is the pressure induced frequency shift and is determined either theoretically or experimentally. A more theoretical explanation of line shifts which are due to distant collisions was first given by Lenz and more recently by Breene[4].

7.2.2 Line Strengths

The line *strength* or line intensity is a direct measure of the ability of a molecule to absorb photons corresponding to a given transition. It depends upon both the properties of the single molecule and the relative number of molecules in the upper and lower states. The strength, S, is defined as

$$S = \int k(\nu_0, \nu) d\nu \tag{10}$$

where the integral is over all ν. Experimentally, S can be determined using Equation 10 if $k(\nu_0, \nu)$ is measured. Alternatively, if the functional form of $k(\nu_0, \nu)$ is known, regression techniques can be used to determine S.

By far the strongest interaction between matter and an incident field of electromagnetic radiation involves the molecule's electric dipole moment. The intensity of a dipole transition is proportional to the square of the matrix element of the dipole moment operator M:

$$R_{i,j} = \int \Psi_i^* M \Psi_j dV \tag{11}$$

where dV is a volume element in configuration space and the integral is over all space. Ψ_i and Ψ_j are the wavefunctions of the lower and upper levels of the transition. The wavefunctions are orthogonal and therefore, if M is unchanged during the transition, $R = 0$. Consequently, for a dipole transition to occur, the electric dipole moment must change between the initial and final energy levels of a transition. Otherwise, the molecule is not linked to the incident radiation and no absorption occurs. Weaker transitions can occur, however, for quadrupole transitions even if there is no change in the dipole moment, although these are not considered in this work.

The line strength is also proportional to the relative populations of the upper and lower transition levels. In thermodynamic equilibrium the probability of a molecule being in a specific energy level is given by

$$\frac{N_i}{N} = g_i \exp(-\frac{hc}{kT} E_i)/Z(T) \tag{12}$$

where h is Planck's constant, c is the speed of light, k is Boltzmann's constant, T is the temperature, N is the total number of molecules, N_i is the number of molecules in energy level E_i, g_i is the statistical weight of the level, and $Z(T)$ is the partition function given by:

$$Z(T) = \sum_i g_i \exp(-\frac{hc}{kT} E_i) \tag{13}$$

In this work, the partition functions are computed using Gamache's [5] convenient parameterization:

$$Z(T) = a + bT + cT^2 + dT^3 \tag{14}$$

where a, b, c, and d have been tabulated for most molecules found in the lower atmosphere. Combining Equations 12 and 13, the relative population of the upper and lower energy levels is given by:

$$\frac{N_j - N_i}{N} = \frac{g_j \exp(-\frac{hc}{kT}E_j) - g_i \exp(-\frac{hc}{kT}E_i)}{Z(T)} \tag{15}$$

The line strength is then expressed as

$$S_{i,j} = \sigma_{i,j}\frac{N_j - N_i}{N} \tag{16}$$

where $\sigma_{i,j}$ are integrated absorption cross sections and are given by

$$\sigma_{i,j} = \frac{8\pi^3}{3h}\nu_{i,j}|R_{i,j}|^2. \tag{17}$$

Combining these results yields the full expression for the line strength:

$$S_{i,j} = \frac{8\pi^3}{3h}\nu_{i,j}|R_{i,j}|^2\frac{g_i \exp(-\frac{hc}{kT}E_i)}{Z(T)}[1 - \exp(-\frac{hc}{kT}\nu_{i,j})] \tag{18}$$

Using line strengths determined either theoretically or experimentally at some reference temperature T_{ref}, the strength can be converted to other temperatures using

$$S_i(T) = S_i(T_{ref})\frac{Z(T_{ref})}{Z(T)}\frac{\exp(-hcE_i/kT)}{\exp(-hcE_i/kT_{ref})}\frac{[1 - \exp(-hc\nu_i/kT)]}{[1 - \exp(-hc\nu_i/kT_{ref})]} \tag{19}$$

7.2.3 Line Widths

The line *width*, or halfwidth, is defined as half the frequency interval between ν_0 and the frequency at which $k(\nu)$ has fallen to one half of its maximum value. Values of line widths in the Earth's atmosphere can range from 0.0002 cm^{-1} for conditions where the molecules are isolated to 0.5 cm^{-1} for conditions of extreme pressure broadening. Under pressure broadening conditions, the resulting lineshape near line center is well approximated as a Lorentzian with a nominal line width of

$$\gamma = \frac{2r^2}{m}\frac{P}{R_mT}\left(\frac{3kT}{m}\right)^{\frac{1}{2}}, \tag{20}$$

which has been derived from classical Kinetic theory using the Equipartition theorem and the Ideal gas law. r s the effective radius of the molecule, m is the molecule's mass, P is the total pressure, R_m is the gas constant, and T is the temperature. A typical time between collisions for an atmospheric gas at room temperature and pressure is $\sim 10^{-10}s$, which leads to a Lorentz width of ∼0.05 cm^{-1}. If the line width, γ_0, is determined at a given pressure, temperature combination (P_0, T_0), the line width at other conditions is

$$\gamma = \gamma_0 \left(\frac{T_0}{T}\right)^{\frac{1}{2}} \left(\frac{P}{P_0}\right) \tag{21}$$

Thus, the line width increases linearly with pressure and decreases with temperature. Although this kinetic theory does not result in accurate values of γ_0, the pressure dependence is observed in most cases. More commonly, γ_0 is determined either experimentally or calculated with more realistic theories when accurate measurements are not available. Furthermore, the temperature exponent, $\frac{1}{2}$, is generally replaced with a parameter n, which is also determined experimentally. The accuracy of n was investigated by Lui Zheng and Strow [**?**] for both $CO_2 \leftrightarrow CO_2$ and $CO_2 \leftrightarrow N_2$ collisions: $n \simeq 0.69$ for $CO_2 \leftrightarrow CO_2$ collisions and $n \simeq 0.75$ for $CO_2 \leftrightarrow N_2$ collisions. In general, n can vary with transition for the same molecule. For example, accepted values of n for H_2O range from 0.5 to 1. When n is unknown, default values of 0.64 and 0.68 are generally used.

For mixtures of gases, the total line width is the sum of the individual partial widths:

$$\gamma_{TOT} = \sum_i \gamma_{0,i} P_i \tag{22}$$

From quantum Fourier transform theory calculations, the line width for the $f \leftarrow i$ transition is calculated using [6]

$$\gamma_i = \left(\frac{nv}{2\pi c}\right) \sum_{J_2} \rho(J_2)\sigma_{if,J_2} \tag{23}$$

where n is the perturber density, c is the speed of light, v is the mean relative thermal velocity ($v = \sqrt{8k_B T/\pi\mu}$), μ is the reduced mass of the perturber/absorber system, and $\rho(J_2)$ is the density of the perturber state J_2. σ_{if,J_2} are the absorption cross sections and are dependent upon which type of interactions are dominant. For example, for H_2O-N_2 collisions, the strongest interaction is dipole-quadrupole, yielding

$$\sigma^{DQ}_{if,J_2} = \pi b_0^2 \left(1 + s_{if,J_2}(b_0)\right) \tag{24}$$

where b_0 is an impact parameter related to the minimum distance between absorber and perturber during the interaction and s_{if,J_2} is related to the dipole moment of H_2O, the quadrupole moment of N_2, and the impact parameter. For self-broadened

H_2O, the main interaction is dipole-dipole and similar calculations can be performed. This quantum treatment of line widths represents a large improvement over simple kinetic theory calculations. Such calculations, however, are most often scaled to agree with experimental results to obtain the highest degree of accuracy and are included in spectral line databases whenever accurate measurements are not available or possible.

Experimental studies of line widths can become surprisingly complicated for several reasons. One common complication is due to the overlapping and blending of adjacent spectral lines. Others include excessive experimental noise, badly-characterized instrument functions, incorrect "background" absorptions, and lack of characterization of the optical path. Some of these concerns have been reviewed by Gamache *et.al.*[7]. Furthermore, for some gases such as water vapor, experimental results from different investigators for the same spectral line lie well outside quoted uncertainties. Larger systematic and analysis errors, not inaccurate experimental spectra, are most likely responsible for these disagreements. The case for N_2-broadened water vapor line widths is investigated in detail in section **??**.

7.3 Lineshape Theories

The frequency dependence of the absorption coefficient is determined by the molecule's physical state and its environment. Broadening factors can be divided into three general classes. They are (1) natural broadening, (2) Doppler broadening, and (3) collision broadening. While natural and Doppler broadening can be described with relatively simple theoretical models, providing an accurate generalized collision broadening theory is a very challenging problem. Each of these are addressed below.

Thew HITRAN line parameters can be found at http://www.cfa.harvard.edu/hitran/.

7.3.1 Natural Broadening

The *natural* lineshape is best described by considering a stationary, isolated molecule. If such a molecule is allowed to absorb radiation, undisturbed by any other form, it will eventually make a transition back to a lower level of internal energy. Consequently, the molecule has a limited lifetime at any given energy level. The resulting lineshape is given by

$$k_{nat}(\nu) = \frac{S}{\pi}\left(\frac{\gamma_{nat}}{(\nu-\nu_0)^2+\gamma_{nat}^2}\right) \tag{25}$$

where $\gamma_{nat} = 1/\tau_{nat}$ is the "natural" line width. Due to the relatively long lifetimes of these undisturbed molecules, γ_{nat} is very small, with values on the order of 10^{-5} cm^{-1}. For this reason, natural lineshapes are not observable under atmospheric conditions or with spectrometers of average resolution.

7.3.2 Doppler Broadening

The inhomogeneous *Doppler* lineshape is applicable to conditions encountered in the upper troposphere and stratosphere. In these cases, the temperature is assumed to be high enough to produce molecular motion, but the pressure is low enough so that the molecules experience no collisions; or at least are not subject to *strong* collisions which terminate the dipole moment oscillation. At pressures of about 5 Torr or less, the Doppler lineshape is predominant, with a typical line width of 0.001 cm^{-1} at 296 K. The molecular motion produces an apparent shift in the observed frequencies and such broadening is called Doppler broadening.

The shifted Doppler frequency, ν', for a molecule moving with a speed v_m along the direction of observation, relative to the observer, is given by

$$\nu' = \nu_0 \frac{\sqrt{1-(v_m/c)^2}}{1+v_m/c} \tag{26}$$

where ν_0 is the un-shifted frequency. For $v_m \ll c$, ν' can be approximated with a binomial expansion as

$$\nu' = \nu_0 \left(1 - \frac{v_m}{c}\right) \tag{27}$$

Therefore, for each v_m, there exists a corresponding shifted frequency. Given a Maxwell distribution of velocities within the gas, the density of molecules with velocity v_m is given by

$$dn = N \left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}} \exp\left(-\frac{m}{2kT} v_m^2\right) dv_m \tag{28}$$

N is the total number of molecules, m is the molecular mass, T is the temperature, and k is Boltzmann's constant. The corresponding absorption coefficient, $k_D(\nu)$, like the Boltzmann distribution, has a Gaussian form:

$$k_D(\nu) = \frac{S}{\gamma_D} \sqrt{\frac{\ln 2}{\pi}}\, e^{-\ln 2 \left(\frac{\nu-\nu_0}{\gamma_D}\right)^2} \tag{29}$$

γ_D, the line width of the Doppler lineshape, is given by $\nu_0 \sqrt{\frac{2kT\ln 2}{mc^2}}$. Notice how quickly the Doppler lineshape goes to zero far from the line center due to the negative exponential.

7.3.3 Collision Broadening

At pressures greater than $\sim$ 5 Torr, the collisions between molecules must be addressed. Collisions are the most important phenomenon to contribute to broadening at these higher pressures. In 1906 Lorentz showed that line broadening takes place when absorbing molecules or atoms collide. If one assumes that a collision takes place during the time in which radiation is being absorbed, the coherency of the wave train is interrupted. This interruption results in a broadening of the spectral line. Quantum mechanically, pressure broadening is caused by the broadening of the molecules' energy levels by fields produced by the colliding molecules. This is a complex subject, and exact solutions for the absorption coefficient are found only under certain approximations. The exact treatment of this problem requires the knowledge of the time-dependent quantum mechanical wavefunction of an ensemble of colliding molecules. In general, this has not been achieved to date and therefore the problem is often approached by developing empirical or semi-empirical models which simulate the system. In the following sections, a model leading to the standard Lorentz lineshape is presented, followed by descriptions of more complex techniques of dealing with collisional broadening.

7.3.4 Lorentz Lineshape

In the simplest treatment, the collisional lineshape is that of a Lorentzian. At high pressures, collisions occur often and it is unlikely that a molecule is allowed to oscillate undisturbed for its entire natural lifetime. Instead, the molecule is usually perturbed by many collisions. This model makes several assumptions which lead to a simple solution for the absorption coefficient. The molecule's dipole moment is assumed to be oscillating with frequency ν_0. When a collision occurs at time t, the oscillation terminates instantaneously. No natural damping is included because the time between collisions, t, is much less than the natural lifetime, τ_{nat}. In other words, $\exp(-t/\tau_{nat}) = 1$ for all times considered.

It is important to understand the assumptions which have been made for this model. One of the assumptions is called the *impact approximation*, which assumes that the time between collisions is much greater than the duration of a collision, τ_{dur}, and therefore, the behavior of the dipole moment during the collision is negligible. In this case, τ_{dur} is taken to be zero, corresponding to an instantaneous phase shift in the dipole moment. These types of collisions are also sometimes called *adiabatic* in that the system has no time to react to the collisions. The opposite of the impact approximation is called the *quasi-static* approximation, in which the collision durations are essentially assumed to be much larger than the time between collisions. This point is addressed when statistical lineshapes are discussed. Another assumption made here is that of *strong collisions.* A strong collision is taken to be an interaction which terminates the oscillation, leaving no memory regarding its orientation or other properties before the collision. On the other extreme, *weak* collisions are those which have little or no effect in disturbing the molecule. In this case, collisional effects are only felt as a damping effect after a large number of weaker impacts. Collisions are also assumed to involve only two molecules, and such collisions are referred to as *binary collisions.* One final assumption is that the molecules follow classical straight line trajectories between collisions. So in the Lorentz model, which is often called the billiard-ball model, colliding molecules can be thought of as quickly moving hard spheres which do not interact with one another until they actually touch each other.

Fourier analysis of this model wavetrain leads to a spectral distribution of the form

$$\mid F\{\mu(t)\} \mid^2 = \frac{\sin^2[2\pi(\nu-\nu_0)t/2]}{[2\pi(\nu-\nu_0)]^2} \tag{30}$$

This expression must be averaged over all possible values of t. From the kinetic theory of gases, the distance traveled between collisions, l, by a molecule of average velocity v_m has a Poisson distribution:

$$p(l)dl = \frac{dl}{l_m} e^{-l/l_m} \tag{31}$$

where l_m is the mean free path. Using $dt = \frac{dl}{v_m}$, the distribution for the time between collisions is

$$p(t)dt = \frac{dt}{\tau_{col}} e^{-t/\tau_{col}} \tag{32}$$

where τ_{col} is the mean time between collisions. Using this distribution, the absorption coefficient, $k_L(\nu)$ is found to be

$$k_L(\nu) = \frac{S}{\pi}\left(\frac{\gamma_L}{(\nu-\nu_0)^2+\gamma_L^2}\right) \tag{33}$$

where $\gamma_L = 1/\tau_{col}$ is the Lorentz line width. Within this billiard-ball model, τ_{col} is calculated as l_m/v_m and has an average value of about 1.5×10^{-10} seconds[4]. This corresponds to a Lorentz line width of approximately 0.02 cm^{-1}, which is much larger than a typical Doppler width. Thus, whenever collisions are present, they provide the primary form of broadening.

This absorption coefficient is called the *Lorentz* lineshape. It has the same form as the natural lineshape; the only difference being the value of the line widths. It is useful to compare the Doppler and Lorentz lineshapes. The Doppler model assumes a Boltzmann velocity distribution, which goes smoothly to zero at large velocities. Its corresponding spectral distribution, therefore, also decays quickly in the far-wing (far from line center). This is not the case for the Lorentz model, which assumes instantaneous behavior during collisions. The effect of this unphysical temporal behavior is the placement of extremely high frequency components in the lineshape's spectral distribution. Consequently, $k_L(\nu)$ is too large in the far-wing, and the Lorentz model predicts too much absorption in this region.

Despite the apparent shortcomings of the model used for the Lorentzian line shape, it is very accurate for many applications. The Lorentz lineshape is accurate as long as two conditions are satisfied: (1) the spectral region of interest is not too far removed from the line center where the impact approximation results in the prediction of too much absorption, and (2) there exists no significant overlapping of adjacent spectral lines. The latter of these two conditions arises because the Lorentz theory assumes no transfer of intensity from one spectral line to another (often called "line mixing"). Experimental deviations from the Lorentz lineshape within ∼2–4 γ_0 of line center of isolated lines have not been confirmed for systems of atmospheric interest.

7.3.5 Van Vleck - Weisskopf Lineshape

When describing the procedures used to calculate the Lorentz and natural lineshapes, the assumption that transitions occur at relatively high frequencies (i.e. infrared) was made. When computing the Lorentz lineshape, the Fourier transform of the dipole moment actually yields two terms – one centered about ν_0 and the other about $-\nu_0$. The lineshape should be written as [8]

$$k(\nu) = \frac{S}{\pi}\left(\frac{\gamma}{(\nu-\nu_0)^2+\gamma^2} + \frac{\gamma}{(\nu+\nu_0)^2+\gamma^2}\right). \tag{34}$$

This shape is more often used in the microwave region of the spectrum, where the second term of the sum is not negligible. For molecules active in the infrared region, however, ν_0 is large enough such that $(\nu-\nu_0) \ll (\nu+\nu_0)$ and the resulting lineshape can most often be safely approximated as Lorentzian. An exception is in "window" regions (far from any line centers). Another modification to the Lorentz model involves the behavior of the molecule directly after a collision. In the Lorentz model, we essentially assumed the wave-function experienced *random* phase shifts during collisions and immediately began oscillating again at its resonant frequency. The wave-function, however, does not experience a random reorientation, but should be distributed according to the Boltzmann distribution of the field when the collision occurs[9]. Following this approach leads to a slight modification of Equation 34:

$$k(\nu) = \frac{S}{\pi}\left(\frac{\nu}{\nu_0}\right)^2\left(\frac{\gamma}{(\nu-\nu_0)^2+\gamma^2} + \frac{\gamma}{(\nu+\nu_0)^2+\gamma^2}\right) \tag{35}$$

which is commonly called the *Van Vleck-Weisskopf* lineshape [8]. Equation 35 is an improvement over Equation 34 in that (34) predicts no absorption in the limit of zero resonant frequency, which is not observed experimentally. Equation 35 is also more acceptable in that it agrees with Debye's[9] relaxation theory in the same limit.

7.3.6 Van Vleck - Huber Lineshape

Another similar lineshape which was developed to satisfy the principle of *detailed balance* (discussed below) is[9]

$$k(\nu) = \frac{S}{\pi}\left(\frac{\nu}{\nu_0}\right)\frac{\tanh(hc\nu/2kT)}{\tanh(hc\nu_0/2kT)}\left(\frac{\gamma}{(\nu-\nu_0)^2+\gamma^2}+\frac{\gamma}{(\nu+\nu_0)^2+\gamma^2}\right) \tag{36}$$

which is called the *Van Vleck-Huber* lineshape.

7.3.7 Voigt Lineshape

Before going on to explain more elaborate models, the *Voigt lineshape* should be introduced. It does not introduce any new physical insight into broadening phenomenon, but is very useful computationally. The Voigt lineshape is the convolution of the Doppler and Lorentz lineshapes. For this reason, it assumes Doppler characteristics at low pressure and Lorentz characteristics at higher pressures. Therefore, one single expression for the lineshape can be used throughout a wide range of pressures. The Voigt lineshape, $k_V(\nu)$ is given by

$$k_V(\nu) = \frac{k_0 y}{\pi}\int_{-\infty}^{\infty}\frac{e^{-t^2}}{y^2+(x-t)^2}dt \tag{37}$$

with

$$k_0 = \frac{S}{\gamma_D}, \quad y = \frac{\gamma_L}{\gamma_D}\sqrt{\ln 2}, \quad x = \left(\frac{\nu-\nu_0}{\gamma_D}\right)\sqrt{\ln 2} \tag{38}$$

The Voigt lineshape does assume there is no correlation between collision cross sections and the relative speed of the colloids. Again, for atmospheric systems this approximation appears to be quite accurate.

The VanVleck-Huber lineshape can be computed using the Voigt lineshape instead of the Lorentz lineshape.

7.3.8 General Techniques for Calculating Collisional Lineshapes

The lineshape models have been presented informally in order to provide general physical insight. However, for more advanced approaches, it is useful to understand the more formal techniques in which absorption coefficients are calculated. This is needed to help understand the deviations from Lorentz lineshapes. For more on this, one is refered to Dave Tobin's [1] thesis for a discussion, as well as for more references. In particular, his dissertation describes line mixing for carbon dioxide, as well as intermolecular forces and potentials used in lineshape calculations for water vapor.

8 Water vapor lineshape

When computing water wapor spectral lineshapes, the effects of the lines far away from the current region can be included in two ways : by directly individually adding on the far wings of each line to the current region, or just using the lines in the current region, plus a lump sum "continuum" contribution. As the far wings lineshapes might not be lorentz, and also to account for the possibility that the near wing lineshapes might also not be lorentz, a local lineshape definition is preferentially used, along with a continuum contribution.

The local lineshape is defined as the lorentz lineshape out to $\pm 25 cm^{-1}$ minus the lorentz value at $25 cm^{-1}$ away from line center. With this definition, the possibility that the lineshape near linecenter is itself not lorentz, can be modelled by including the effect into the continuum that has to be added on.

Non-Lorentz H_2O lineshapes also have a significant impact *within* the strong pure rotational and vibrational bands. This *in-band* continuum is particularly important for satellite infrared remote sensing of atmospheric H_2O profiles.

For well isolated pressure-broadened water vapor lines in the infrared, the Lorentz lineshape is very accurate near line center. However, if one uses a Lorentz lineshape, this generally overestimate the observed absorption in the far-wing atmospheric window regions and underestimates the absorption within the rotational and vibrational bands. This means that the actual water vapor lineshape is extremely sub-Lorentzian in the far-wing and at least somewhat super-Lorentzian in the intermediate and near-wing. Most experimental studies have focussed on the window regions and so the far-wing lineshape has been studied more than the near-wing (roughly within 5 to 25 cm^{-1} of line center).

Deviations of H_2O spectral lineshapes from Lorentz have been studied extensively for the atmospheric windows at 4 and 10 μm. In general, these deviations are observed to vary slowly with wavenumber and the anomalous absorption has become known as the water vapor continuum.

Several characteristics were found to be common to all window region continuum studies. In general, the continuum absorption [10, 11, for example]: (1) does not change rapidly with wavenumber, (2) decreases rapidly with increasing temperature for pure water vapor, (3) is greater for self-broadening than for foreign broadening, (4) is more significant in regions of weak absorption than in regions of strong absorption, and (5) displays the pressure dependencies associated with gaseous absorption.

It is accepted that the deviations from the impact theory calculations in window regions are due to the non-Lorentz behavior of the far-wings of pure rotational and vibration-rotation water vapor absorption lines.

In the following sections, a review of previous studies of this continuum absorption is presented. These can be separated into two generally different approaches. The first, which is most often adopted in experimental studies, is to express the observed deviations from Lorentzian behavior through the use of *continuum coefficients.* With this method, the cumulative effects of all lines are characterized in a convenient form. The second approach, which provides more information about the shape of individual spectral lines, is used in most theoretical studies. χ-functions are often the end result of this approach.

8.1 A Definition of the Continuum

The definition proposed by Clough is widely used in atmospheric spectroscopy and radiative transfer, particularly in line-by-line codes such as FASCODE[12], GENLN2[13], LINEPAK[14], and LBLRTM. The "local" absorption for a single transition is defined as a Lorentz lineshape out to ±25cm^{-1} from the line center, minus the Lorentz value at 25cm $^{-1}$. For several lines, the local absorption is expressed as[15]

$$k_{local}(\nu) = \nu \tanh(\beta\nu/2)\,\rho_{ref}\frac{T_{ref}}{T}P_{H_2O}L\sum_i \frac{S_i}{\pi}\begin{cases} \frac{\gamma_i}{\Delta\nu^2+\gamma_i^2} - \frac{\gamma_i}{25^2+\gamma_i^2} & \text{if } |\Delta\nu| \le 25\text{cm}^{-1} \\ 0 & \text{if } |\Delta\nu| > 25\text{cm}^{-1} \end{cases} \tag{39}$$

where $T_{ref} = 273.15K$, ρ_{ref} is the absorber number density per atmosphere at T_{ref}, $\beta = hc/kT$, and $\Delta\nu = \nu - \nu_i$. All of the continuum measurements presented in this work are consistent with Equation 39. This is actually a slight modification of Clough's definition[1], which also includes the negative resonance terms ($\frac{\gamma_i}{(\nu+\nu_i)^2+\gamma_i^2}$). In the infrared region (actually for $\nu > 25$ cm^{-1}), the two definitions are equal. *The continuum is then simply defined to be any observed absorption not attributable to the local absorption.* The continuum therefore includes far-wing absorption (beyond 25cm^{-1} from line center), absorption due to any near-wing (within 25cm^{-1}) non-Lorentz behavior, and the Lorentzian value at 25cm^{-1} within ±25cm^{-1} of line center (this is often called the "basement" term). This is illustrated in Figure 10 for a single absorption line. The "basement" term is a relatively minor part of the continuum and is introduced to ensure a smooth continuum for computational reasons.

With this definition of the local absorption, the continuum is always a positive quantity. The basement and far-wing components are certainly always positive. The near-wing component, which represents the difference between the actual lineshape and Lorentz within 25 cm^{-1}, is also positive because water vapor has a super-Lorentzian lineshape in this region. In fact, with this continuum definition, a non-zero continuum exists even for the Lorentz lineshape. A calculation of the total absorption coefficient and the continuum absorption (total minus local) using the Lorentz lineshape for the 0-4000 cm^{-1} region is shown in Figure 11. All of the high frequency components of the

---

[1] Equations 6 through 8 of Reference [15] do not reflect the local lineshape definition used in FASCODE. They actually lead to a χ dependent local lineshape, which is not used in the line-by-line codes.

absorption are contained in k_{local} and the continuum is therefore a smoothly varying function, which can be stored in a look-up table for ease of computation.

In the line-wings, the displacement $\Delta\nu$ is much greater than the halfwidth γ and the Lorentz terms can be approximated as $\frac{\gamma_i}{\Delta\nu^2}$. This leads to a quadratic pressure dependence in the absorption coefficient on P_{H_2O} for self-broadened water vapor and a linear dependence on both P_{H_2O} and the broadening pressure, P_f, for foreign broadened water vapor. Since the continuum is mainly due to line wings, the total continuum absorption coefficient for all lines is formulated as [10, 15]

$$k_{con}(\nu) = \nu \tanh\left(\beta\nu/2\right)\rho_{ref}\frac{T_{ref}}{T}P_{H_2O}L\frac{296}{T}\left(P_{H_2O}C_s^0(\nu,T) + P_fC_f^0(\nu,T)\right) \tag{40}$$

where C_s^0 and C_f^0 are the self- and foreign-broadened continuum coefficients at 296K and 1 atmosphere. To express experimental and theoretical results, the quantities C_f^0 and C_s^0 are often used.

Because absorption in the windows is very weak, all spectra gathering techniques require very long path lengths. The laboratory studies have focussed primarily on self- and nitrogen broadening at room temperature or above, while most atmospheric measurements have naturally looked at air-broadening at room temperature or below. Most of the results from these measurements are in accord with those of Burch *et.al.*, which are discussed in the larger lbl.pdf

References

[1] D. C. Tobin, L. L. Strow, W. J. Lafferty, and Wm. B. Wm. Olson. Experimental investigation of the self- and N_2- broadened continuum within the ν_2 band of water vapor. *Appl. Opt.*, 35:1, 1996.

[2] L. S. Rothman, R. R. Gamache, A. Goldman, L. R. Brown, R. A. Toth, H. M. Pickett, R. L. Poynter, J. M. Flaud, C. C. Peyret, A. Barbe, N. Husson, C. P. Rinsland, and M. A. H. Smith. The HITRAN Database: 1986 edition. *Appl. Opt.*, 26:4058, 1987.

[3] L. S. Rothman, R. R. Gamache, R. H. Tipping, C. P. Rinsland, M. A. H. Smith, D. C Benner, V. M. Devi, J. M. Flaud, C. Camy-Peyret, A. Perrin, A. Goldman, S. T. Massie, L. R. Brown, and R. A. Toth. The HITRAN molecular database: Editions of 1991 and 1992. *J. Quant. Spectrosc. Rad. Trans.*, 48:469–507, 1992.

[4] R. G. Breene. Line width. *Handbuch der Physik*, 27:19, 1956.

[5] R. R. Gamache, R. L. Hawkins, and L. S. Rothman. Total internal partition sums in the temperature range 700-3000 K: Atmospheric linear molecules. *J. Mol. Spectrosc.*, 142:205, 1990.

[6] R. R. Gamache and R. W. Davies. Theoretical calculations of N_2-broadened halfwidths of H_2O using quantum Fourier transform theory. *Appl. Opt.*, 22:4013, 1983.

[7] R. R. Gamache, J. M. Hartmann, and L. Rosenmann. Collisional broadening survey of water vapor lines - I. A survey of experimental results. *J. Quant. Spectrosc. Radiat. Transfer*, 52:481, 1994.

[8] J. H. Van Vleck and V. F. Weisskopf. On the shape of collision-broadened lines. *Rev. Mod. Phys.*, 17:227, 1945.

[9] J. H. Van Vleck and D. L. Huber. Absorption, emission, and linebreadths: A semihistorical perspective. *Rev. Mod. Phys.*, 49:939, 1977.

[10] D. E. Burch. Continuum absorption by atmospheric H_2O. *SPIE Atmospheric Transmission*, 277:28, 1981.

[11] W. B. Grant. Water vapor absorption coefficients in the 8-13μm spectral region: A critical review. *Appl. Opt.*, 29:451, 1990.

[12] S. A. Clough, F. X. Kneizys, L. S. Rothman, and W. O. Gallery. Atmospheric spectra transmittance and radiance: FASCODE1B. *SPIE Atmospheric Transmission*, 277:152, 1981.

[13] D.P. Edwards. The new oxford line–by–line atmospheric transmission model: Genln2. In J. Ballard, editor, *Atmospheric Spectroscopy Applications Workshop*. Rutherford Appleton Lab., UK, RAL–88–009, 1987.

[14] L. L. Gordley, B. T. Marshall, and D. A. Chu. LINEPAK: Algorithms for modeling spectral transmittance and radiance. *J. Quant. Spectrosc. Radiat. Transfer*, 52:563, 1994.

[15] S. A. Clough, F. X. Kneizys, and R. W. Davies. Line shape and the water vapor continuum. *Atmos. Res.*, 23:229–241, 1989.

HITRAN http://www.cfa.harvard.edu/hitran/

The HITRAN Database

HITRAN is an acronym for **hi**gh-resolution **tran**smission molecular absorption database. HITRAN is a compilation of spectroscopic parameters that a variety of computer codes use to predict and simulate the transmission and emission of light in the atmosphere. The database is a long-running project started by the Air Force Cambridge Research Laboratories (AFCRL) in the late 1960's in response to the need for detailed knowledge of the infrared properties of the atmosphere.

For additional background, see Interview.

The HITRAN compilation, a analogous da HITEMP (hig temperature spectroscopic parameters), being develop Atomic and M Physics Divisi Harvard-Smit Center for Ast under the con direction of D S. Rothman.

The current edition of t molecular spectroscopic d associated compilation available on an ftp site lo Smithsonian Astrophysical in Cambridge, USA. U corrections to the compila made available on this we the sub-page HITRAN UPD

In addition to the Mega-line HITRAN2008 database directories containing files of aerosol indices of ref line-by-line and absorption cross-section parameters, extensive IR absorption cross-sections. Supplemental used for line-by-line parameters in cases where mo information may be contained in the corresponding files, and also where we have archived some cross-sectio contain information very similar to newer data.

1 of 1 10/27/2011 10:18 AM

Figure 1: HITRAN home page

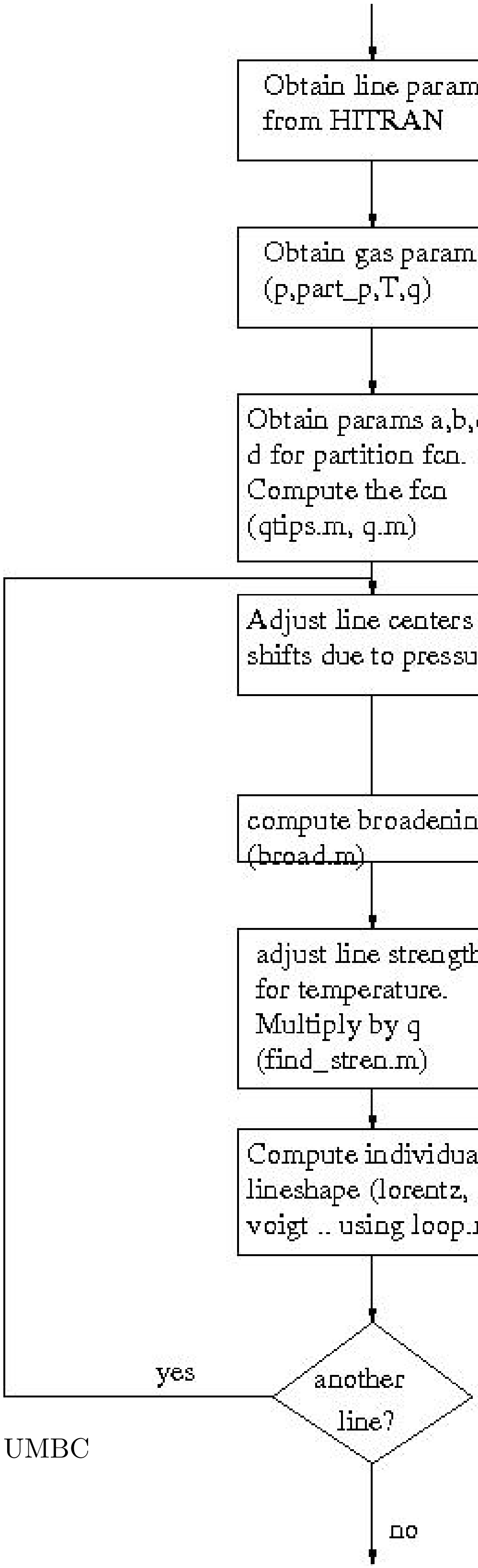
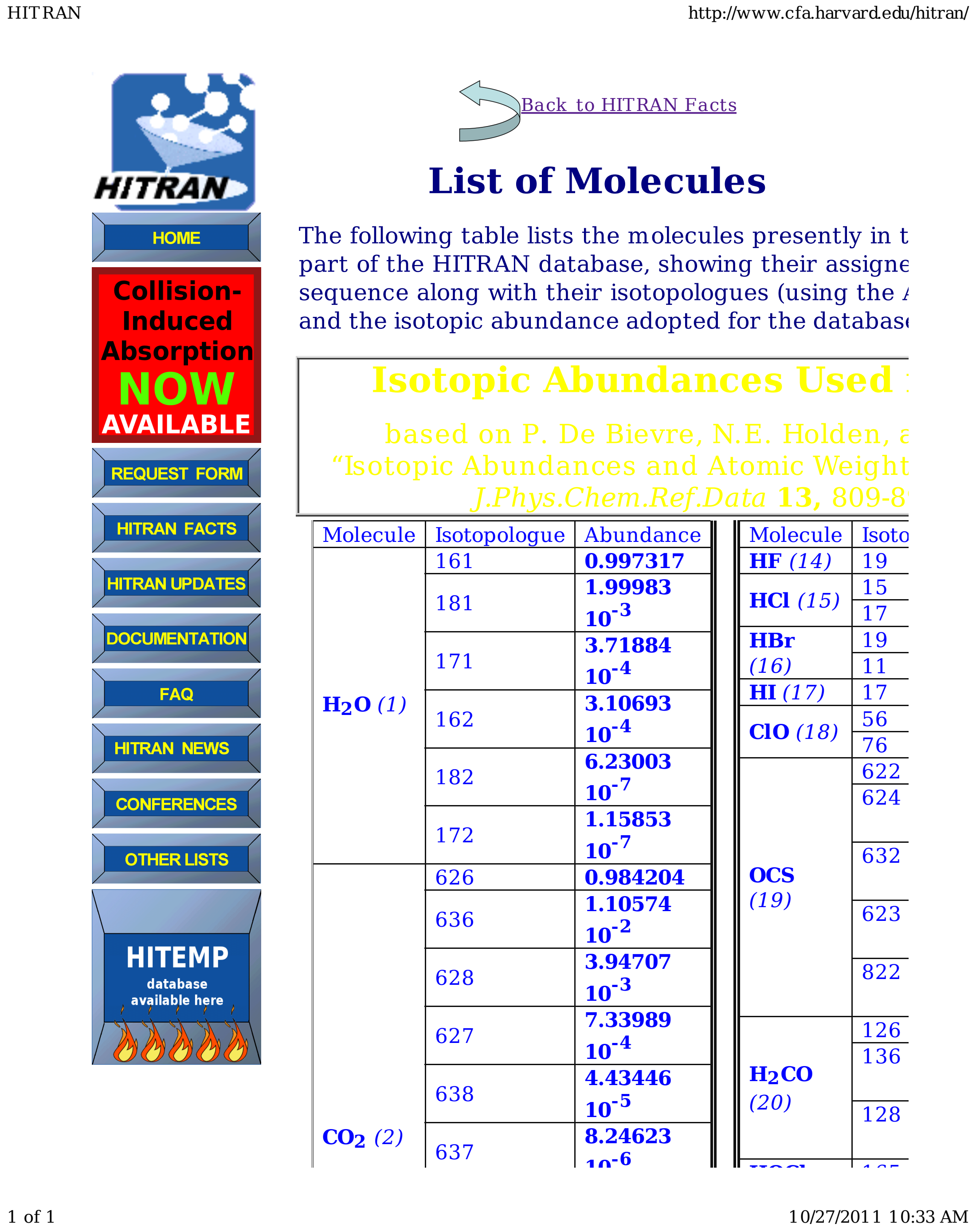


Figure 2: Flow diagram to compute $k(\nu)$


HITRAN http://www.cfa.harvard.edu/hitran/

List of Molecules

The following table lists the molecules presently in t
part of the HITRAN database, showing their assigne
sequence along with their isotopologues (using the A
and the isotopic abundance adopted for the databas

Isotopic Abundances Used
based on P. De Bievre, N.E. Holden, a
"Isotopic Abundances and Atomic Weight
J.Phys.Chem.Ref.Data **13,** 809-8

Molecule	Isotopologue	Abundance
H_2O *(1)*	161	**0.997317**
	181	**1.99983 10^{-3}**
	171	**3.71884 10^{-4}**
	162	**3.10693 10^{-4}**
	182	**6.23003 10^{-7}**
	172	**1.15853 10^{-7}**
CO_2 *(2)*	626	**0.984204**
	636	**1.10574 10^{-2}**
	628	**3.94707 10^{-3}**
	627	**7.33989 10^{-4}**
	638	**4.43446 10^{-5}**
	637	**8.24623 10^{-6}**

Molecule	Isoto
HF *(14)*	19
HCl *(15)*	15
	17
HBr *(16)*	19
	11
HI *(17)*	17
ClO *(18)*	56
	76
OCS *(19)*	622
	624
	632
	623
	822
H_2CO *(20)*	126
	136
	128

1 of 1 10/27/2011 10:33 AM

Figure 3: HITRAN partioal listing of GAS IDs

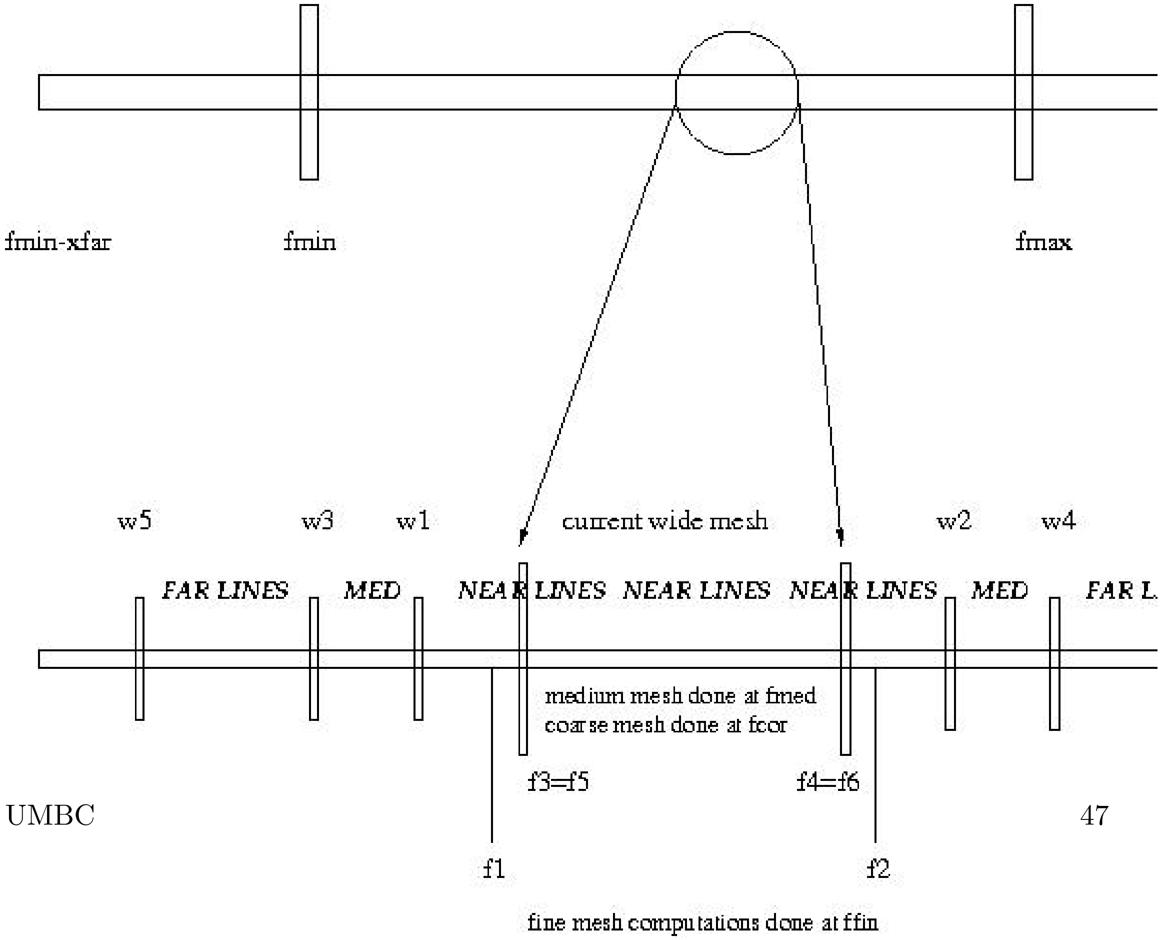

fmin-xfar
fmin
fmax
w5
w3
w1
current wide mesh
w2
w4
FAR LINES
MED
NEAR LINES
NEAR LINES
NEAR LINES
MED
FAR L
medium mesh done at fmed
coarse mesh done at fcor
f3=f5
f4=f6
f1
f2
fine mesh computations done at ffin

Figure 4:

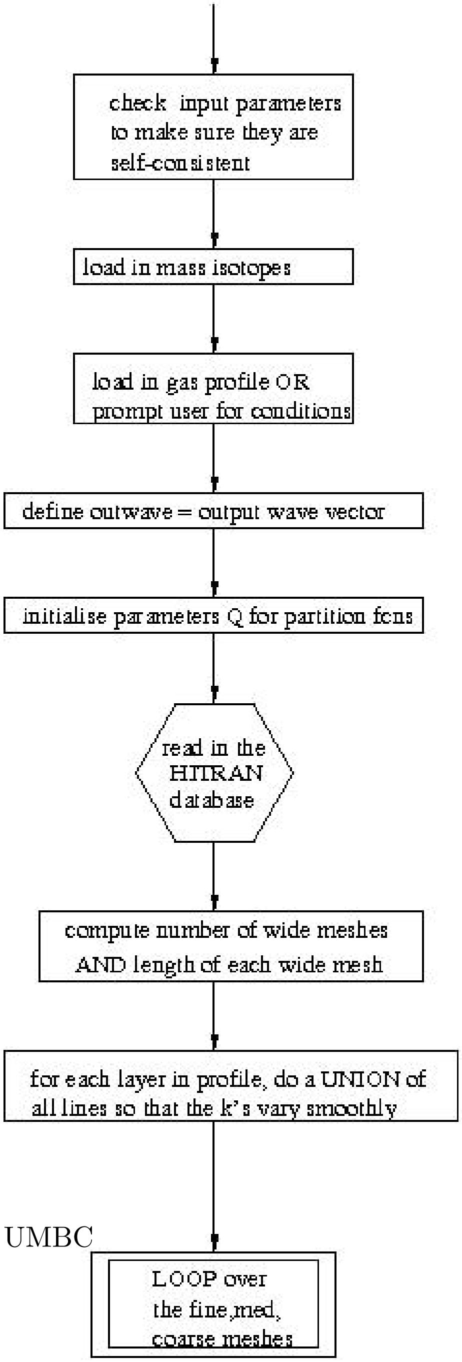

check input parameters to make sure they are self-consistent
load in mass isotopes
load in gas profile OR prompt user for conditions
define outwave = output wave vector
initialise parameters Q for partition fcns
read in the HITRAN database
compute number of wide meshes AND length of each wide mesh
for each layer in profile, do a UNION of all lines so that the k's vary smoothly
LOOP over the fine,med, coarse meshes

Figure 5:

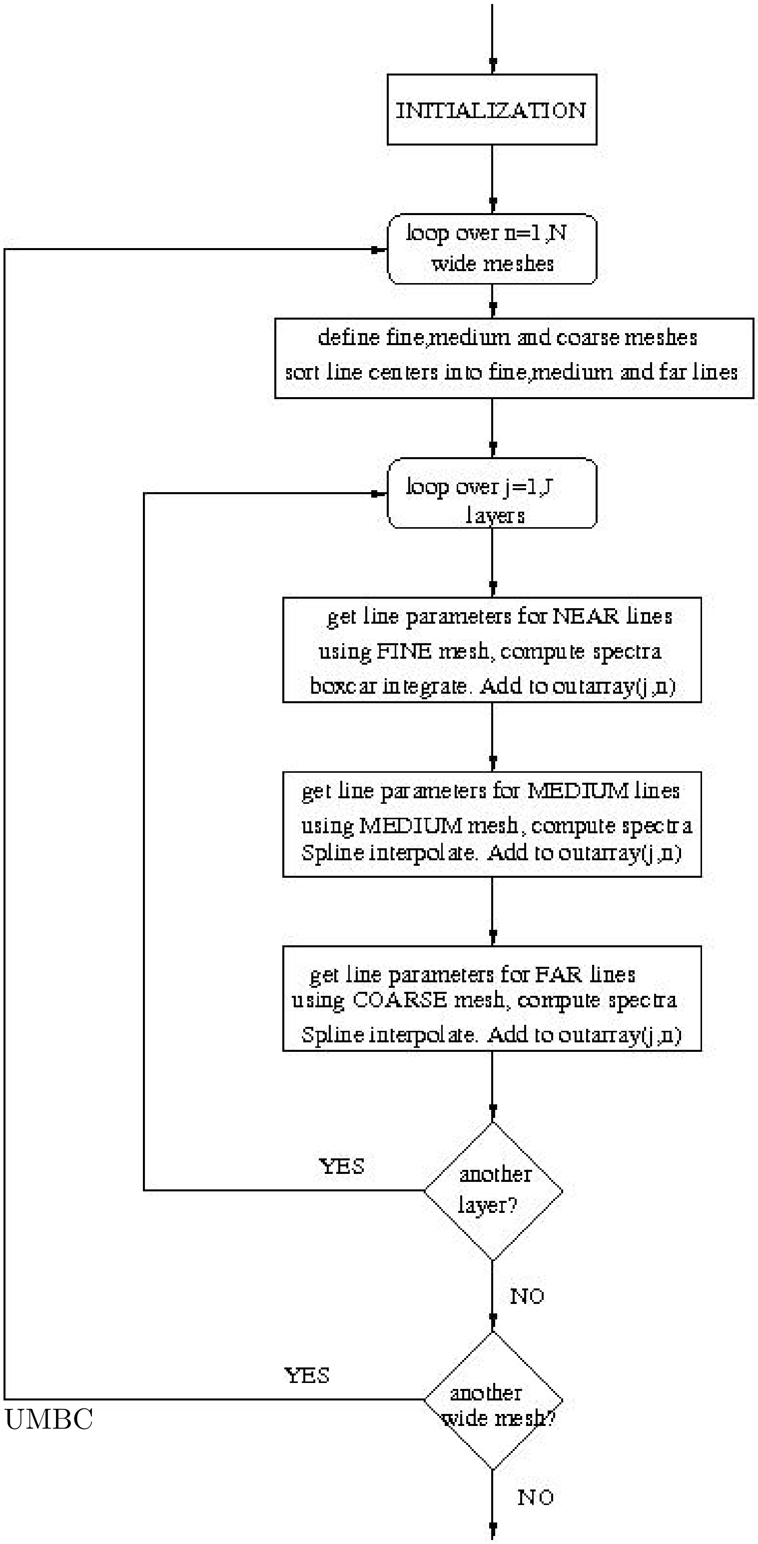

INITIALIZATION
loop over n=1,N wide meshes
define fine,medium and coarse meshes
sort line centers into fine,medium and far lines
loop over j=1,J layers
get line parameters for NEAR lines using FINE mesh, compute spectra boxcar integrate. Add to outarray(j,n)
get line parameters for MEDIUM lines using MEDIUM mesh, compute spectra Spline interpolate. Add to outarray(j,n)
get line parameters for FAR lines using COARSE mesh, compute spectra Spline interpolate. Add to outarray(j,n)
YES
another layer?
NO
YES
another wide mesh?
NO

Figure 6:

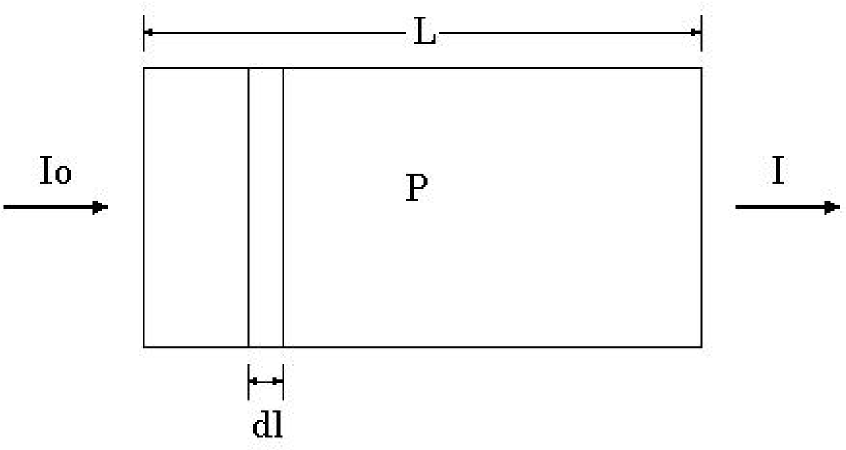


Figure 7: A gas cell of pressure P and length L with incident radiation, I_0, from the left. The amount of absorption at frequency ν is determined by the magnitude of the

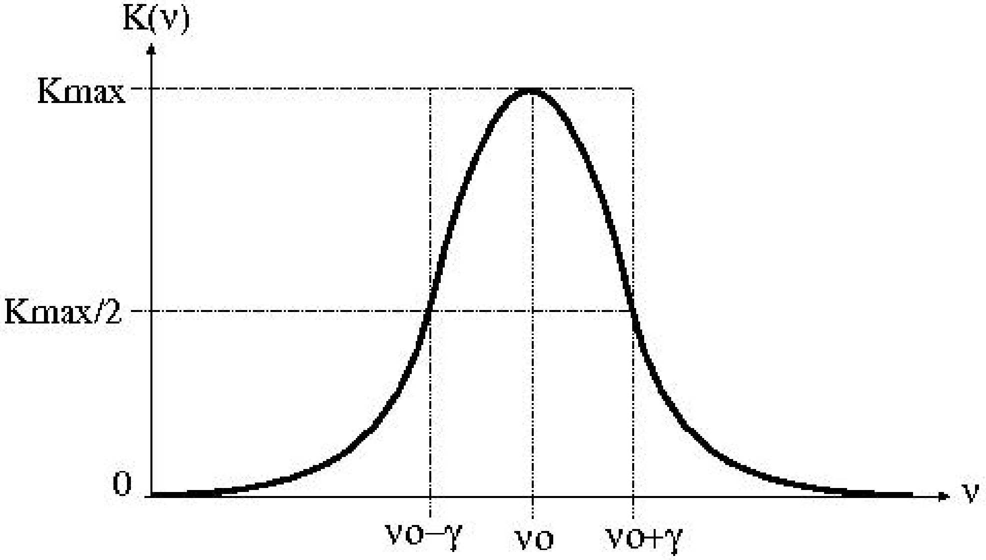
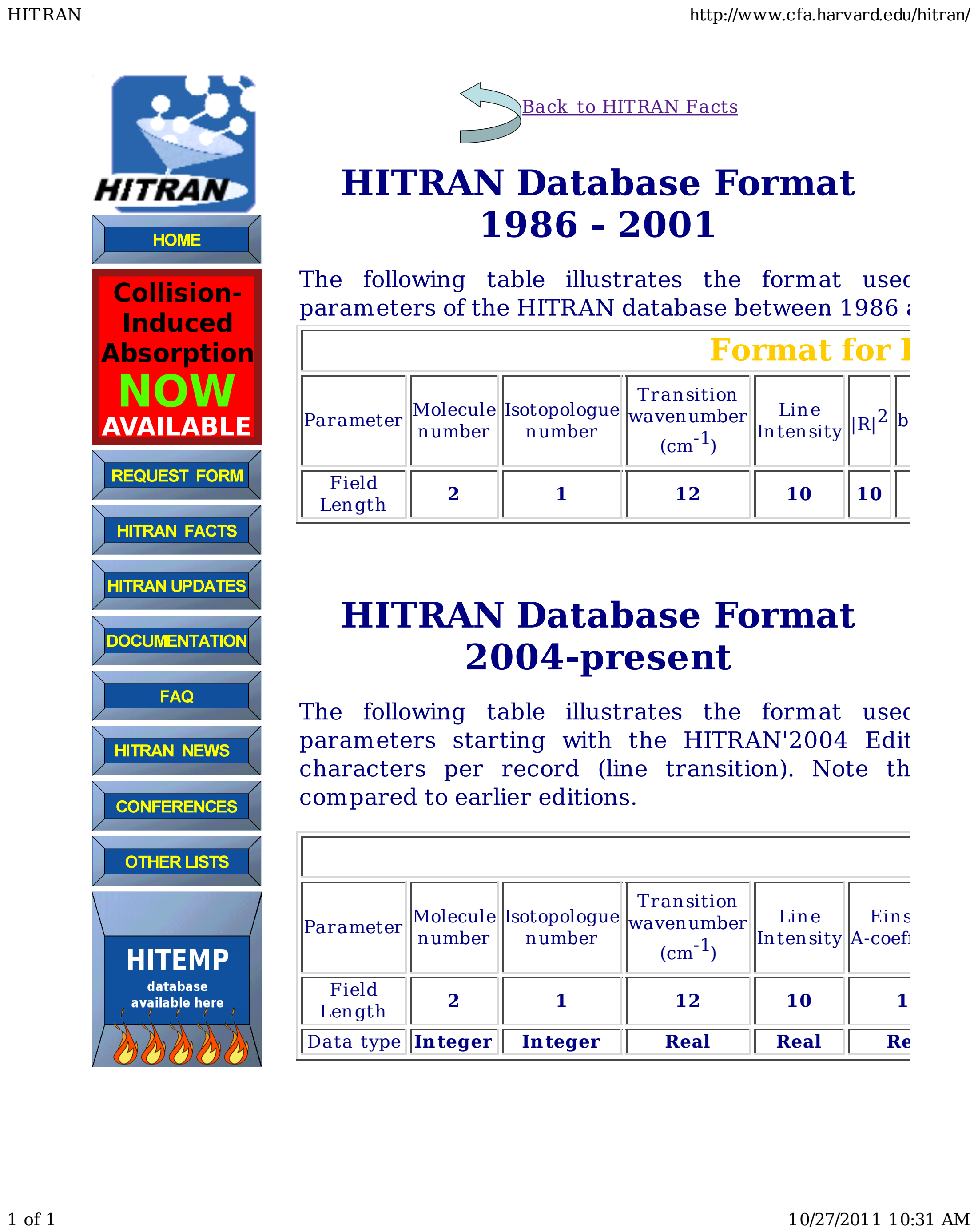


Figure 8: A spectral line depicting the line center, ν_0, and half-width, γ. The line strength, S, is the absorption coefficient, $k(\nu)$, integrated over all wavenumbers ν.



HITRAN http://www.cfa.harvard.edu/hitran/

HITRAN Database Format 1986 - 2001

The following table illustrates the format usec parameters of the HITRAN database between 1986 a

Format for I						
Parameter	Molecule number	Isotopologue number	Transition wavenumber (cm^{-1})	Line Intensity	$\|R\|^2$	b
Field Length	**2**	**1**	**12**	**10**	**10**	

HITRAN Database Format 2004-present

The following table illustrates the format usec parameters starting with the HITRAN'2004 Edit characters per record (line transition). Note th compared to earlier editions.

Parameter	Molecule number	Isotopologue number	Transition wavenumber (cm^{-1})	Line Intensity	Eins A-coeffi
Field Length	**2**	**1**	**12**	**10**	**1**
Data type	**Integer**	**Integer**	**Real**	**Real**	**Re**

1 of 1 10/27/2011 10:31 AM

Figure 9: HITRAN format

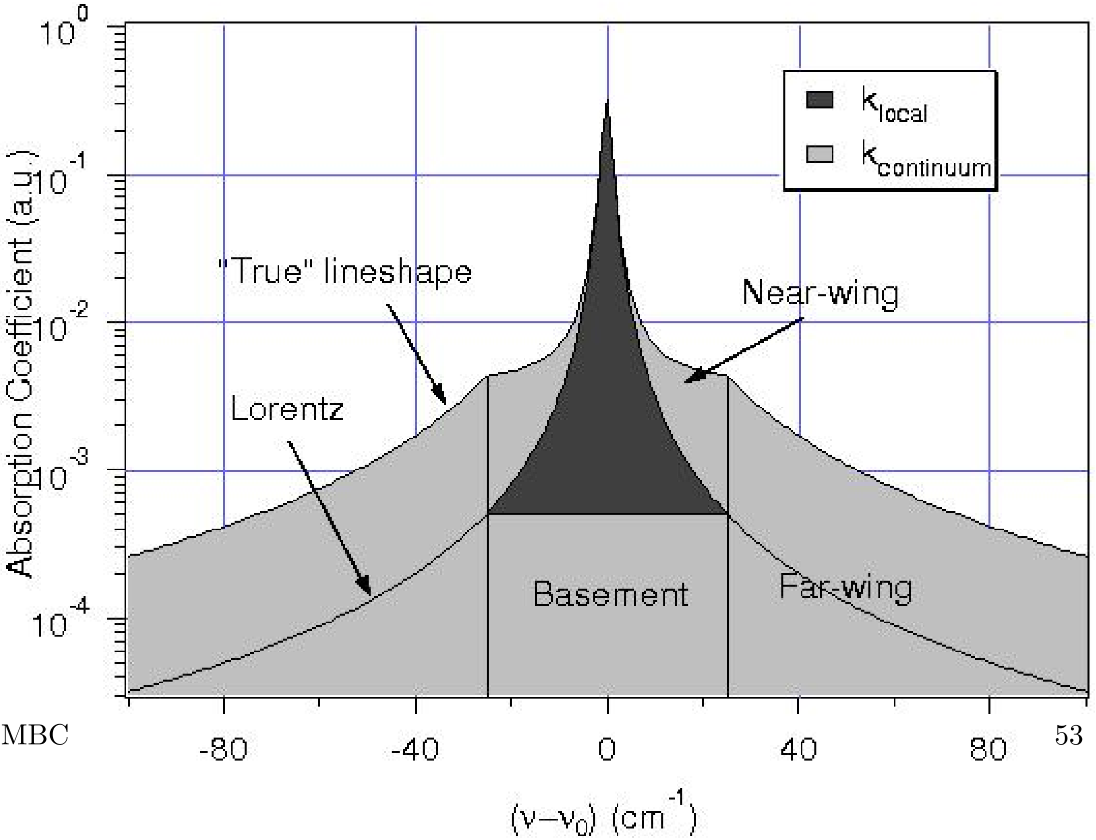


Figure 10: The local lineshape definition used in this work. The far-wing (beyond 25 cm^{-1}), near-wing (within 25 cm^{-1}), and basement components of the continuum are

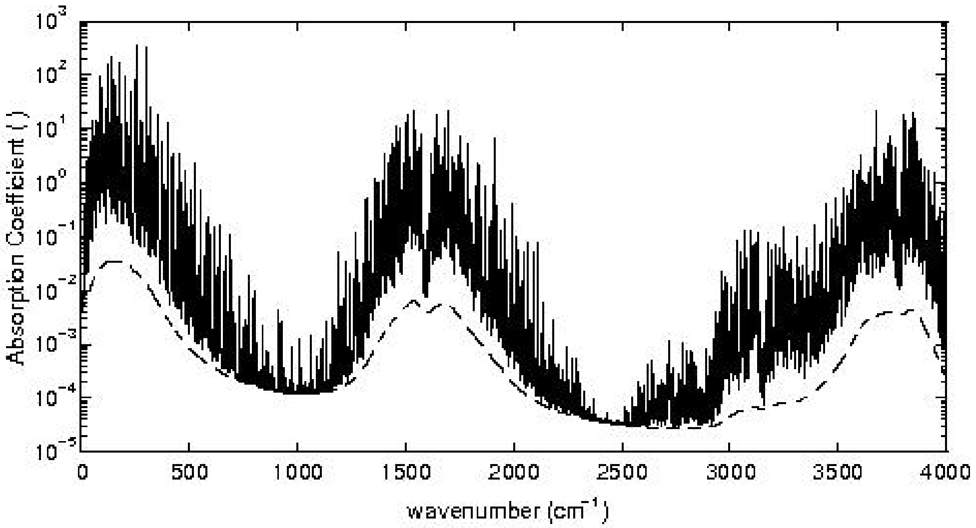


Figure 11: Absorption coefficient calculations using the Lorentz lineshape for 0-4000 cm^{-1} at ~2 cm^{-1} resolution. The total (solid curve) and continuum (dashed curve, as