

## Absorption Line Physics

Topics:

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

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

### Absorption Line Shapes

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

$$k_\nu = S f(\nu - \nu_0) \quad \int k_\nu d\nu = S$$

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

Line shape determined from **broadening** mechanisms:

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

### Natural Line Width

Heisenberg uncertainty principle is

$$\Delta E \Delta t \geq h/2\pi \quad \Delta\nu = \frac{\Delta E}{hc} = \frac{1}{2\pi t_n c}$$

$t_n$  is time spent in upper state.

In thermal IR lifetimes of isolated molecules are  $t_n = 0.1$  to 10 sec:

$$\Delta\nu \sim 10^{-11} \text{ cm}^{-1} \text{ (completely negligible)}$$

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

$$\Delta\tilde{\nu} \sim \tilde{\nu} \frac{1}{N} = \tilde{\nu} \frac{1}{\tilde{\nu}t} = \frac{1}{t}$$

## Collisional Broadening

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

Estimate collision time:

$$\text{Mean velocity } \bar{v} = \sqrt{8k_bT/\pi m} \approx 450 \text{ m/s}$$

Treat molecules as hard spheres of radius  $r = 2 \times 10^{-10} \text{ m}$ ,  
collides with molecules within  $2r$  of flight line -

$$\text{Volume swept is } V = \pi(2r)^2\bar{v} = 2 \times 10^{-16} \text{ m}^3/\text{s}$$

Number of molecules per  $\text{m}^3$  at STP is  $n_L = 2.69 \times 10^{25} \text{ m}^{-3}$

Time between collisions  $t_c = 1/(n_L V) = 1.6 \times 10^{-10} \text{ s}$

Line halfwidth is  $\alpha \approx \frac{1}{2\pi t_c} = 0.03 \text{ cm}^{-1}$

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

Collisional or pressure broadening causes Lorentz line shape

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

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

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

$$E(t) \propto \exp(-t/t_c)e^{2\pi i\tilde{\nu}_0 t}$$

Exponential term from Poisson distribution of collisions.

Fourier transform to get to frequency space

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

Square to get intensity, so line shape is

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

## Pressure Broadening

Lorentz line shape:

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

$\alpha$  is Lorentz half-width at half max.

Halfwidth is from mean time between collisions ( $\alpha = 1/2\pi t_c$ ).

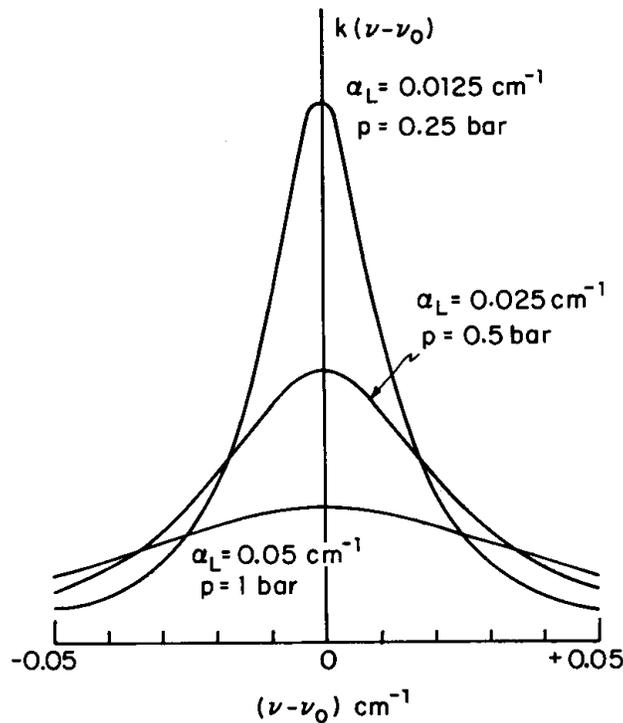
Halfwidth is proportional to number of collisions per time

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

Pressure broadened absorption line halfwidth

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

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



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

## Doppler Broadening

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

Maxwell-Boltzmann distribution of velocities along  $x$  is

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

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

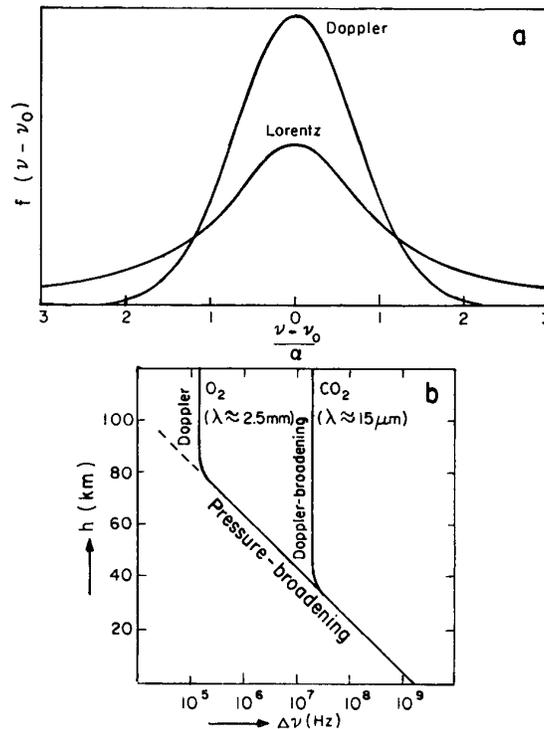
Results in Gaussian line shape for Doppler broadening

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

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

Note: Doppler width does not depend on molecular properties other than mass.

Width is proportional to wavenumber, so importance depends on frequency.



a) A comparison of Doppler and Lorentz line shapes. b) Relationship between atmospheric height and linewidth for a microwave line of  $O_2$  and an infrared line of  $CO_2$ . [Stephens, Fig. 3.14]

## Voigt Profile

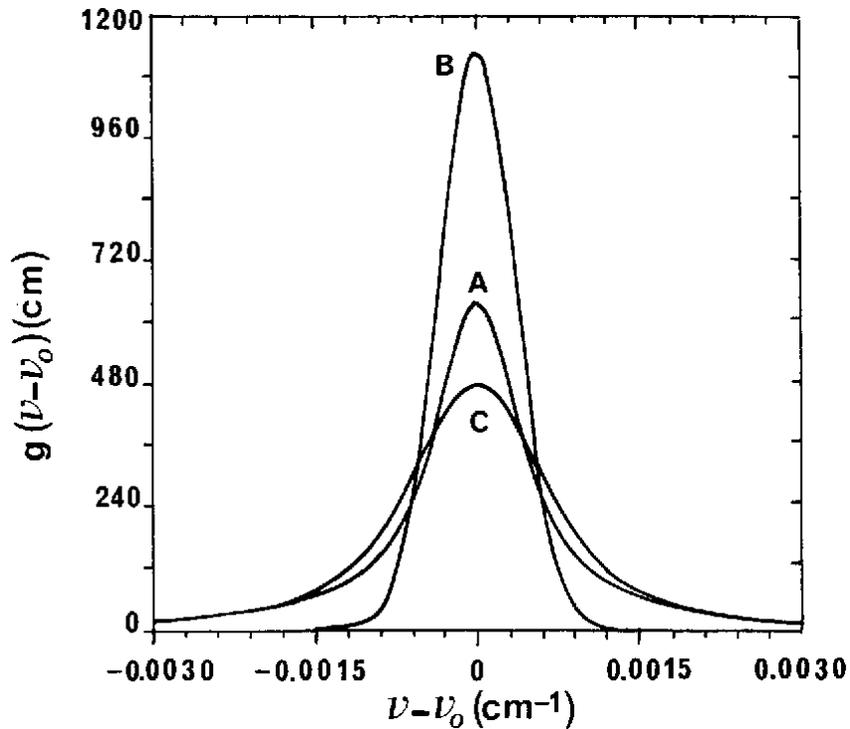
When pressure broadened Lorentz halfwidth becomes comparable to Doppler width, the broadening effects must be convolved to get the Voigt line shape:

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

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

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

In the line wings the Voigt profile has a Lorentz shape. At the line center or core, it has a Doppler behavior.



Line profiles: A is Lorentz, B is Doppler, and C is Voigt profile resulting from convolution of A and B. [Lenoble, Fig. 6.1]

## Absorption Line Strength

Line strength is integrated absorption cross section across a line:

$$S = \int k_\nu d\nu$$

Line strength depends on

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

Line strength is temperature dependent through population of states.

## Boltzmann Distribution of States

In Local Thermodynamic Equilibrium the population of states is determined by

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

where  $n_i$  is the number of molecules in energy level  $E_i$ ,

$n_t$  is the total number of molecules,

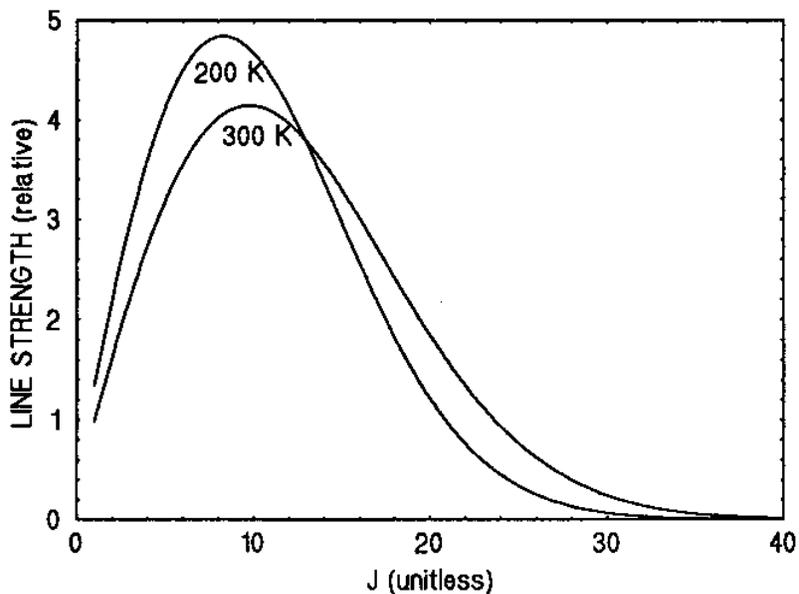
$k_B T$  is Boltzmann constant times temperature, and

$g_i$  is the degeneracy of level (number of states with same energy).

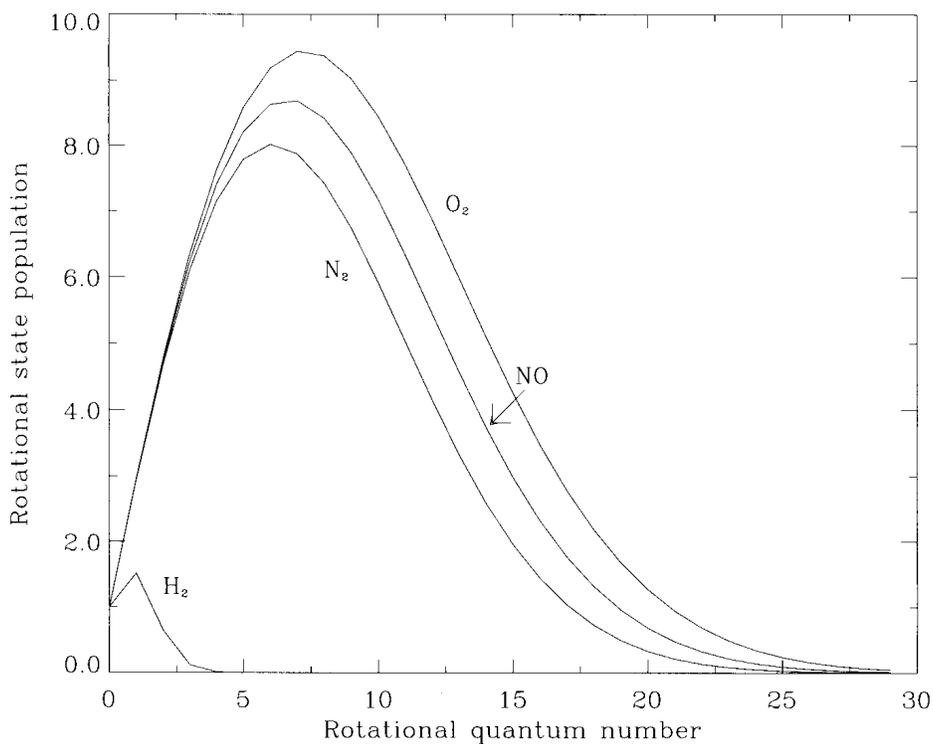
$Q$  is the partition function:  $Q(T) = \sum_i g_i \exp(-E_i/k_B T)$

Example: rotational states  $g_J = 2J + 1$   $E_J = hcBJ(J + 1)$   $Q_r \approx \frac{k_B T}{hcB}$

States with energy levels comparable or less than thermal energy  $k_B T$  are populated, but higher energy states much less populated.



The Boltzmann distribution peaks at intermediate  $J$  (rotational quantum number). Increasing the temperature moves the peak to higher  $J$ . [Kyle, Fig. 8.3]



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

## Two-level Atom Radiative Processes

Transition Process	Rate
1. Absorption	$B_{12}n_1\bar{I}$
2. Spontaneous emission	$A_{21}n_2$
3. Stimulated emission	$B_{21}n_2\bar{I}$

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

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

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

Einstein relations:  $A_{21} = (2h\nu_0^3/c^2)B_{21}$      $g_1B_{12} = g_2B_{21}$

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

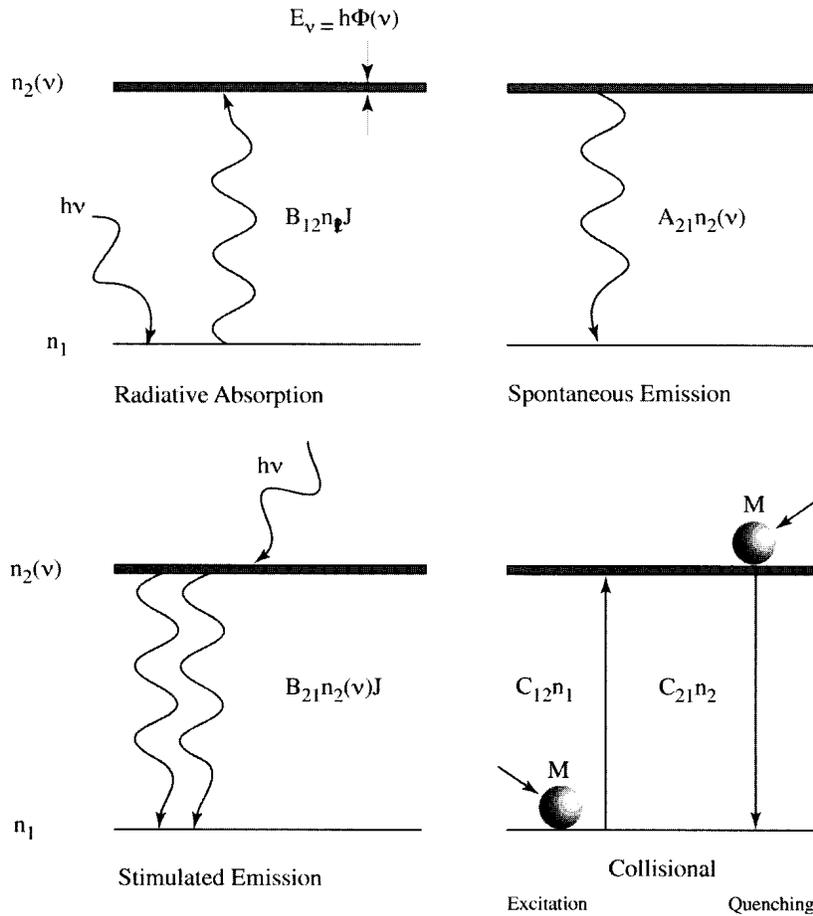


Illustration of the five radiative and collisional processes involved in the rate of population of energy levels in a two-level atom. [Thomas & Stamnes, Fig. 4.7]

## Line Strength Expressions

Simulated emission is like negative absorption.

Ratio of stimulated emission to absorption =

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

Strength of  $i$ 'th absorption line is

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

$n_L/n_t$  is fraction of molecules in lower state of transition,

$|R|^2$  is quantum mechanical transition probability,

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

Substitute in molecule fraction in lower state to get line strength

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

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

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

Spectroscopic databases have line strength at reference temperature  $T_0$ .

Temperature dependence of line strength then obtained from

$$S_i(T) = S_i(T_0) \frac{\exp(-hcE_{L,i}/k_B T) Q_T(T_0) [1 - \exp(-hc\nu_{0,i}/k_B T)]}{\exp(-hcE_{L,i}/k_B T_0) Q_T(T) [1 - \exp(-hc\nu_{0,i}/k_B T_0)]}$$

The total partition function  $Q_T(T)$  depends on molecule/isotope.

## HITRAN Spectroscopic Database

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

Relevant quantities in HITRAN database:

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

Table 6. Example of direct image of line parameters.

Mol/ Iso	$\nu_0$	S	$ R ^2$	$\gamma_{air}$	$\gamma_{self}$	$E''$	n	$\delta$	$v'$	$v''$	$Q'$	$Q''$	IER	IREF
21	800.450992	3.198E-26	6.578E-05	0.0676	0.0818	2481.5624	.78	.000000	14	6		P 37	465	1 1 1
291	800.454690	3.242E-22	0.000E+00	0.0845	1.750	369.6303	.94	.000000	9	1341519	331419	000	4 4 1	
291	800.454690	9.724E-22	0.000E+00	0.0845	1.750	369.6303	.94	.000000	9	1341619	331519	000	4 4 1	
121	800.455380	1.037E-22	1.596E-03	1.100	0.0000	530.3300	.75	.000000	32	1446 740	45 640	000	4 4 1	
121	800.455380	1.037E-22	1.596E-03	1.100	0.0000	530.3300	.75	.000000	32	1446 640	45 540	000	4 4 1	
101	800.456932	5.190E-23	5.133E-04	0.670	0.0000	851.0515	.50	.000000	2	145 244	-44 143	-301	3 3 1	
121	800.457760	4.726E-23	4.446E-03	1.100	0.0000	920.0900	.75	.000000	32	14502822	492722	000	4 4 1	
121	800.457760	4.726E-23	4.446E-03	1.100	0.0000	920.0900	.75	.000000	32	14502922	492822	000	4 4 1	
24	800.465942	9.794E-27	6.064E-04	0.754	1.043	1341.2052	.69	.000000	8	3		R 13	425	1 1 1
121	800.466160	1.061E-22	2.621E-03	1.100	0.0000	632.1200	.75	.000000	32	14471136	461036	000	4 4 1	
121	800.466160	1.061E-22	2.621E-03	1.100	0.0000	632.1200	.75	.000000	32	14471236	461136	000	4 4 1	
101	800.474983	3.650E-23	3.609E-04	0.670	0.0000	851.0117	.50	.000000	2	145 244	+44 143	+301	3 3 1	
31	800.475500	1.680E-24	3.623E-05	0.653	0.890	1092.4340	.76	.000000	2	151 547	50 248	002	1 1 2	
291	800.476220	3.199E-22	0.000E+00	0.0845	1.750	361.9747	.94	.000000	9	1341520	331420	000	4 4 1	
291	800.476220	9.597E-22	0.000E+00	0.0845	1.750	361.9747	.94	.000000	9	1341420	331320	000	4 4 1	
101	800.484407	5.320E-23	6.593E-05	0.670	0.0000	106.0811	.50	.000000	2	1 8 4 4	+ 9 3 7	+301	3 3 1	
121	800.485680	5.770E-23	4.232E-03	1.100	0.0000	846.9900	.75	.000000	32	144544 1	4443 1	000	4 4 1	
121	800.485680	5.838E-23	4.282E-03	1.100	0.0000	846.9900	.75	.000000	32	144544 2	4443 2	000	4 4 1	
121	800.491430	6.593E-23	4.065E-03	1.100	0.0000	828.9900	.75	.000000	32	14492327	482227	000	4 4 1	
121	800.491430	6.593E-23	4.065E-03	1.100	0.0000	828.9900	.75	.000000	32	14492227	482127	000	4 4 1	
291	800.498890	3.146E-22	0.000E+00	0.0845	1.750	353.9254	.94	.000000	9	1341321	331221	000	4 4 1	
291	800.498890	9.440E-22	0.000E+00	0.0845	1.750	353.9254	.94	.000000	9	1341421	331321	000	4 4 1	
271	800.499020	1.580E-22	0.000E+00	1.000	0.0000	2092.3540	.50	.000000	19	14		2 8	000 0 0 0	
271	800.499020	2.940E-23	0.000E+00	1.000	0.0000	2366.1710	.50	.000000	19	14		4 9	000 0 0 0	

FORMAT (I2,I1,F12.6,1P2E10.3,0P2F5.4,F10.4,F4.2,F8.6,2I3,2A9,3I1,3I2) corresponding to:	
Mol	I2- Molecule number
Iso	I1- Isotope number (1= most abundant, 2= second most abundant, etc.)
$\nu_0$	F12.6- Frequency in $\text{cm}^{-1}$
S	E10.3- Intensity in $\text{cm}^{-1}/(\text{molecule}\cdot\text{cm}^{-2})$ @ 296K
$ R ^2$	E10.3- Transition probability-squared in Debye <sup>2</sup>
$\gamma_{air}$	F5.4- Air-broadened halfwidth (HWHM) in $\text{cm}^{-1}/\text{atm}$ @ 296K
$\gamma_{self}$	F5.4- Self-broadened halfwidth (HWHM) in $\text{cm}^{-1}/\text{atm}$ @ 296K
$E''$	F10.4- Lower state energy in $\text{cm}^{-1}$
n	F4.2- Coefficient of temperature dependence of air-broadened halfwidth
$\delta$	F8.6- Air-broadened pressure shift of line transition in $\text{cm}^{-1}/\text{atm}$ @ 296K
$v',v''$	2I3- Upper state global quanta index, lower state global quanta index
$Q',Q''$	2A9- Upper state local quanta, lower state local quanta
IER	3I1- Accuracy indices for frequency, intensity, and air-broadened halfwidth
IREF	3I2- Indices for table of references corresponding to frequency, intensity, and halfwidth

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

**APPENDIX B. HITRAN Molecules with Associated Indices**

HITRAN Molecule Number	Molecule Chemical Symbol	Number of lines	HITRAN Molecule Number	Molecule Chemical Symbol	Number of lines
1	H <sub>2</sub> O	49444	21	HOCl	15565
2	CO <sub>2</sub>	60802	22	N <sub>2</sub>	120
3	O <sub>3</sub>	275133	23	HCN	772
4	N <sub>2</sub> O	26174	24	CH <sub>3</sub> Cl	9355
5	CO	4477	25	H <sub>2</sub> O <sub>2</sub>	5444
6	CH <sub>4</sub>	48032	26	C <sub>2</sub> H <sub>2</sub>	1668
7	O <sub>2</sub>	6292	27	C <sub>2</sub> H <sub>6</sub>	4749
8	NO	15331	28	PH <sub>3</sub>	2886
9	SO <sub>2</sub>	38853	29	COF <sub>2</sub>	54866
10	NO <sub>2</sub>	100680	30	SF <sub>6</sub>	11520
11	NH <sub>3</sub>	11152	31	H <sub>2</sub> S	7151
12	HNO <sub>3</sub>	165426	32	HCOOH	3388
13	OH	8676	33	HO <sub>2</sub>	26963
14	HF	107	34	O	2
15	HCl	533	35	ClONO <sub>2</sub>	32199
16	HB <sub>r</sub>	576	36	NO <sup>+</sup>	1206
17	HI	237	37	HOB <sub>r</sub>	4358
18	ClO	7230			
19	OCS	858			
20	H <sub>2</sub> CO	2702			

The HITRAN numbering scheme for various molecules.

## Line-by-Line Models

Calculate monochromatic optical depth for a layer by summing contribution of all absorption lines, then sum layers vertically, then integrate across spectrum.

Optical depth of layer at height  $z$  due to lines from a particular gas:

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

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

The Lorentz halfwidth is obtained from pressure/temperature scaling:

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

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

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

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

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

Integrate optical depth vertically:

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

Integrate monochromatic transmission across spectrum:

$$\mathcal{T}_{\Delta\nu} = \int_{\Delta\nu} \exp[-\tau_\nu / \cos \theta] d\nu$$

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

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

Three functions of different resolutions represent Voigt profile.

Line centers added to fine grid; line wings to coarse grid.

After all absorption lines added to grids, then spectral grids interpolated finest grid and added.