

DERIVATION OF PSEUDO-LINES FROM LABORATORY CROSS-SECTIONS

G.C.Toon and B.Sen
Jet Propulsion Laboratory

INTRODUCTION

The problem of how best to interpolate/extrapolate laboratory cross-section spectra in temperature and pressure has no simple solution. We have chosen the approach of deriving "pseudo-linelist" to represent the absorption of heavy molecules (e.g. CCl₄, CFC-11, CFC-12, CFC-113, HCFC-22, ClNO₃, HCFC-142b, N₂O₅, CF₄, SF₆) for which only cross-section spectra exist. These pseudo-linelist have been successfully used in the analysis of MkIV balloon spectra (e.g., Toon et al., JGR, 104, 26,779, 1999) and ATMOS Version 3 data (Irion et al., 2002).

This directory contains various pseudo-linelists which were derived at JPL by performing spectral fits to laboratory transmittance spectra. These lab spectra were NOT measured here at JPL, they were from various sources that are tabulated below. The lab transmittance spectra were re-created using the published temperature- and pressure-dependent cross-sections, and knowledge of the ILS of the laboratory FTIR spectrometer, and cell length.

These pseudo-linelists are in the HITRAN format and can be used to compute spectra in the same manner as any other linelist. The directory also contains the file, "isotopomer.dat", of molecular parameters (vibration frequencies, temperature-dependences of the rotational partition function) assumed in the derivation of the pseudo-linelists, along with a FORTRAN program "isotopomer.f" defining the parameters and illustrating how to read them.

Each pseudo-linelist was derived by fitting all of the relevant laboratory transmittance spectra simultaneously while solving for the 296K strength and the Ground State Energy (E'') of each pseudo-line. The pressure-broadened half-width (PBHW) and its temperature dependence were determined "manually", by trying various values and selecting the ones that gave the best overall fit. Generally, for gases without sharp absorption features, the goodness of fit was insensitive to the choice of PBHW, whereas for gases like CFC-12 and HCFC-22 which have sharp Q-branches, the right choice of PBHW is important. Note that for some gases (e.g. CFC-12) the resulting value for the temperature-dependence of the PBHW (0.0) is well outside the normal range (0.5 to 0.8). All lines in a given absorption band were assumed to have the same PBHW and temperature dependence.

The idea of using pseudo-lines to represent broad featureless absorption bands is not new. However, whereas previously workers minimized the number of lines needed by ascribing them an exaggerated PBHW, we achieve the same goal by giving each pseudo-line an exaggerated Doppler width. The advantage of this latter approach is that it allows the correct PBHW to be employed, so that a realistic pressure-dependence can still be simulated, even in cases when all of the laboratory transmittance spectra were measured at low pressure (e.g. CF₄).

These lists are not intended to supplant proper quantum-mechanically-based linelists. They were derived primarily as a convenient means of interpolating (and extrapolating) the laboratory cross-sections to

temperatures and pressures where actual measurements are unavailable (I could not think of a realistic way of doing this directly from the cross-sections). However, in deriving and using these pseudo-linelist, several additional advantages became apparent:

- 1) Since the pseudo-linelist are in the HITRAN format, they can be accessed in exactly the same manner as all the regular gases, avoiding special code to read the raw cross-section spectra and interpolate them to the desired temperatures and pressures.
- 2) Fitting a physically-based function to the laboratory cross-sections also serves as a quality control measure: Since we are typically trying to determine just two unknowns (S & E'') from 4-30 spectra, the problem is over-determined and so performing the fit provides an assessment of the consistency of the various laboratory transmittance spectra. This makes it possible to identify and reject laboratory spectra which are inconsistent with the others, or even to quantify biases between different sets of laboratory spectra, perhaps measured under very different conditions. Furthermore, the retrieval of unphysical (i.e. -ve) values of S and E'' provides a warning that serious problems exist.
- 3) Fitting the laboratory spectra provides an opportunity to remove instrumental artifacts. For example, the laboratory cross-sections will always be convolved with the Instrument Line Shape (ILS) of the laboratory spectrometer. In making a pseudo-linelist, the effects of this ILS is removed, since it is included in the forward model which calculates the cross-sections from the pseudo-lines. This is particularly important if the laboratory transmittance spectra are measured at a worse spectral resolution than the atmospheric spectra. Another example of removal of an instrumental artifact, is that of channel fringes in the laboratory transmittance spectra. If these are properly fitted they cannot propagate into the pseudo-linelist.
- 4) Fitting the laboratory transmittance spectra provides an opportunity to remove absorption lines not belonging to the gas of interest. For example, laboratory spectra acquired over the 1300 to 1900 cm^{-1} region are often contaminated by H_2O absorption lines. However, by fitting H_2O along with the gas of interest, during the analysis of the laboratory spectra, propagation of H_2O artifacts into the pseudo-linelist of the gas of interest will be greatly reduced.
- 5) Several different laboratory data-sets, even with widely different measurement conditions and spectral resolutions, can easily be assimilated into a single pseudo-linelist.
- 6) At the end of the fitting process, the pseudo list can be checked by comparing the forward model calculation (which uses the pseudo-lines) with the laboratory transmittance spectra. Of course, the agreement will not be perfect since the fit was overconstrained, but the differences are usually $<1\%$.
- 7) Absorption spectrum derived from the pseudolines are guaranteed to be continuous and differentiable functions of pressure and temperature (unlike some bivariate interpolation schemes), which helps minimize artifacts in the retrieved vmr profiles.
- 8) Since all the pseudo-lines in a given band are assumed to have the same PBHW and Doppler widths, only one evaluation of the Voigt lineshape per atmospheric level is necessary to compute the absorption spectrum resulting from all the psuedo-lines (provided that this lineshape is stored). Thus, the speed of using the pseudo-linelist is competitive with 2-D interpolation in the raw cross-sections (assuming one knew a good way of doing this).

SPACING OF PSEUDO-LINES

The choice of line spacing for the pseudo-lines was somewhat arbitrary. We tried to make it as wide as possible to minimize the total number of

lines, yet still preserve any structure observed in the laboratory transmittance spectra that would also be apparent in an atmospheric spectrum.

Typically, the line spacing was chosen to be similar to the resolution of the laboratory transmittance spectra. Note that the positions and spacing of the pseudo-lines are completely independent of the spectral frequencies in the laboratory spectra. This fact makes it possible to simultaneously fit different sets of laboratory spectra.

Most of the pseudo-linelist are spaced at 0.01 cm⁻¹, which is ten times larger than an actual Doppler widths of most heavy gases. Although this would not be a problem in the troposphere where the pressure broadening would cause the pseudo-lines to overlap, in the upper stratosphere a high resolution computed spectrum would show narrow lines with large gaps between. To avoid this problem one must artificially increase the Doppler width until it approximately matches the line spacing. A convenient way of doing this is to set the molecular weight to an artificially small value (e.g. 1), however, this has drawbacks if one wants to use pseudo-lines, together with real quantum-mechanical lines, of the same gas in the same interval. Therefore, in all of the pseudo linelists, we have defined the isotope number to be zero. This allows pseudo lines to be easily distinguished from real lines (which have isotope numbers 1-9), and could allow the line-by-line code to explicitly set the Doppler width equal to the pseudo-line spacing whenever it encounters pseudo-lines, avoiding the need to fudge the molecular weight. This is especially helpful for gases like ClNO₃ for which a proper quantum-mechanically derived linelist (requiring the actual molecular weight) exists for the region around the 780 cm⁻¹ Q-branch, but pseudo lines must be used for other regions.

LINE STRENGTH

The following expression for line strength was assumed in the derivation of the pseudo-linelists:

$$S(T) = S(296) \cdot (296/T)^{\text{tdrpf}} \cdot Q_{\text{vib}}(T)/Q_{\text{vib}}(296) \cdot SE(T)/SE(296) \cdot \exp(hcE''(1/296 - 1/T))$$

where S(296) is the line strength (cm⁻¹/molec/cm⁻²) at 296K.

tdrpf is the Temperature Dependence of the Rotational Partition Function, and is commonly denoted by the symbol "Beta".

$Q_{\text{vib}}(T) = \prod [1 - \exp(-h.c.V_j/kT)]^{-G_j}$ is the vibrational partition function and the product is performed over all the vibrational frequencies, V_j , which are read from the file "isotopomer.dat", along with their degeneracies, G_j .

$SE(T) = [1 - \exp(-h.c.V_i/kT)]$ is the correction for the Stimulated Emission, V_i being the center frequency (cm⁻¹) of the line in question.

The term $(296/T)^{\text{tdrpf}}$ is commonly known as the rotational partition function and tdrpf is usually (1.0, 1.5, or 2.0)

The term $\exp(hcE''(1/296 - 1/T))$ is simply the Boltzmann factor, E'' being the ground-state energy (cm⁻¹).

Most forward models should already have the code to compute the above expression because it is needed for the lighter gases. So it should be a simple matter to extend this capability to the heavy gases. Note that the same expression for S(T) was used for the fitting of the laboratory transmittance spectra, so the derived values of S(296) and E'' values will only correctly reproduce the laboratory spectra provided that the user employs the same expressions.

Pseudo-linelists for collision induced absorption are given for foreign-

collision induced absorption (fcia) and self-collision induced absorption (scia). They contain pseudo-lines for O2 and N2 with the line strength units (cm-1/molec2/cm-5). Note that in the case of CIA calculations, the scia absorption coefficients derived from the pseudolines must be multiplied by the number density times the volume mixing ratio of the considered gas, and the fcia absorption coefficients must be multiplied by the number density times (1 - volume mixing ratio). The sum of both contributions can then be used to calculate optical thicknesses or transmittances.

Finally, we want to make it clear that one should not expect the forward calculation made using these pseudo-lines to agree perfectly with individual laboratory transmittance spectra, since the pseudo-lines were derived from an over-determined fit to ALL of the laboratory spectra. Differences will arise from noise on the laboratory spectra, and uncertainties in the measurement conditions (T,P,vmr), in addition to inadequacies in the pseudo-line approach.

In the table below we summarize the gases and spectral intervals for which we have computed pseudo-linelist. We estimated the maximum error in absorber found in re-fitting the laboratory spectra using the final pseudo-linelist. Note that at specific frequencies, the error in the computed absorption coefficient may well exceed these tabulated values.

File	GAS	Interval	Spacing	Lines	Error	Measurer
cf4.h92	CF4	1250 - 1290	0.0025	16093	4%	Nemtchinov & Varanasi
f12.h92	CFC-12	850 - 950	0.010	10000	2%	Varanasi
	CFC-12	1050 - 1200	0.010	15000	1%	Varanasi
f11.h92	CFC-11	810 - 880	0.010	7000	7%	Varanasi
	CFC-11	1050 - 1120	0.010	7000	6%	Varanasi
ccl4.h92	CCl4	750 - 812	0.010	6201	3%	Varanasi & Nemtchinov
f22.h92	CHF2Cl	776 - 850	0.00742	9977	5%	Varanasi & McDaniel
	CHF2Cl	1080 - 1150	0.010	7001	2%	McDaniel
	CHF2Cl	1290 - 1335	0.010	4501	2%	McDaniel
f113.h92	CFC-113	786 - 990	0.500	408	8%	McDaniel (omitted 203K)
sf6.h92	SF6	925 - 955	0.010	3001	2%	Varanasi
f142b.h92	HCFC-142b	870 - 1270	0.010	40000	4%	Newnham
c1no3.h92	ClNO3	690 - 880	0.01	19000	2%	Birk & Wagner
	ClNO3	965 - 1005	0.01	4000	4%	Birk & Wagner
	ClNO3	1090 - 1130	0.01	4000	4%	Birk & Wagner
	ClNO3	1215 - 1330	0.01	11500	3%	Birk & Wagner
	ClNO3	1680 - 1790	0.07142	1540	?	Ballard (only 2 spectra)
n2o5.h92	N2O5	547 - 610	0.160	373	4%	NCAR
	N2O5	709 - 775	0.210	315	2%	NCAR
	N2O5	1194 - 1281	0.350	266	2%	NCAR
	N2O5	1663 - 1793	0.480	271	2%	NCAR
c2h6.101	C2H6	1350 - 1496	0.0025	58401	1%	Sharpe (PNNL), Brown (JPL)
ch3cn.101	CH3CN	870 - 1650	0.05	15601	1%	Rinsland et al.(2005)

pan.101	PAN	760 - 870	0.1	1101	1%	Allen et al.(2005)
		1110 - 1340	0.1	2301	1%	Allen et al.(2005)
		1700 - 1780	0.1	801	1%	Allen et al.(2005)
ch3cho.101	CH3CHO	1000 - 1900	0.05	18001	2%	Sharpe (PNNL)
		2600 - 2900	0.005	60001	6%	Sharpe (PNNL), Wennberg

(CIT)

=====

COLLISION INDUCED ABSORPTION LINELISTS:

Files: fcia_20060420.101, scia_20060420.101

GAS	Interval	Spacing	Lines	Measurer
02	1275 - 1905	1.0	631	Thibault et al.(1997)
N2	2030 - 2705	1.0	676	Lafferty et al.(1996)
N2	4330 - 4930	1.0	601	Shapiro and Gush (1966)
02	7100 - 10100	1.0	3001	Smith and Newnham (2000)
02	12751 - 13750	1.0	1000	Tran et al.

Please direct any questions or comments to:

	Geoff Toon	818 354 8259	Geoffrey.C.Toon@jpl.nasa.gov
or	Bhaswar Sen	818 354 1165	Bhaswar.Sen@jpl.nasa.gov