Cross-sections of heavy molecules and pseudo-lines

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Abstract: Absorption coefficients of heavy molecules such as CFC-11, CFC-12, CFC-14, CFC-113, CFC-114, HCFC-22, HCFC-123, HCFC-124, HCFC-141b, HCFC-142b, CCl_4, SF_6, $ClONO_2$, N_2O_5, CH_3COCH_3 (acetone), $CH_3CO_3NO_2$ (peroxyacetylnitrate, PAN), CH_3OH (methanol), CH_3CCl_3 (methylchloroform), C_5H_8 (isoprene), C_3H_6 (propene), DMS (dimethylsulfide), H_2CO (formaldehyde), CH_3Br (methylbromide), and C_6H_6 (benzene) are calculated by interpolation of reference cross-section spectra rather than line-by-line calculation. For most species interpolation in pressure and temperature follows a summation of selected reference data weighted by the inverse quadratic distance from the target point in the pressure temperature plane. For $ClONO_2$ two cross-section sources are implemented: for those by *Ballard et al.*[1] no pressure-dependence is considered, and temperature-dependence of the absorption is scaled following an 1/temperature law. Pressure and temperature dependent cross-sections of $ClONO_2$ by *M. Birk (pers. com., 2000)* are also supported. Additionally, for many of the heavy molecules a pseudo-line treatment is implemented in KOPRA.

1 Cross-sections

1.1 Introduction

Heavy molecules give raise to very dense, often continuum-like spectra of which single rotational transitions are generally not resolved. This applies to CFC-11 (CCl_3F), CFC-12 (CCl_2F_2), CFC-14 (CF_4), CFC-113 ($C_2Cl_3F_3$), CFC-114 ($C_2Cl_2F_4$), HCFC-22 ($CHClF_2$), HCFC-123 (CF_3CHCl_2), HCFC-124 (CF_3CHFCl), HCFC-141 ($CFCl_2CH_3$), HCFC-142 (CF_2ClCH_3), CCl_4, SF_6, $ClONO_2$, N_2O_5, acetone (CH_3COCH_3), $CH_3CO_3NO_2$ (peroxyacetylnitrate, PAN), CH_3OH (methanol), CH_3CCl_3 (methylchloroform), C_5H_8 (isoprene), C_3H_6 (propene), DMS (dimethylsulfide), H_2CO (formaldehyde), CH_3Br (methylbromide), and benzene (C_6H_6). Since spectroscopic data are not available for single transitions, and for reasons of efficient computing, absorption coefficients of these species for given pressure and temperature are generated by two-dimensional interpolation of pretabulated reference cross section spectra in pressure and temperature rather than line-by-line calculations.

1.2 Interpolation Procedure

Laboratory measurements of absorption cross sections of CFC's, HCFC's, and other heavy molecules at various pressures and temperatures are provided by *Varanasi et al.*[2, 3, 4, 5, 6], *Li et al.*[7], *Massie et al*[8], *McDaniel et al.*[9], *Clerbaux et al.*[10], *Hanst et al.*[11], and others. They cover typical stratospheric temperatures and pressures (Table 1).

As a first step, the availability of reference spectra in the vicinity of the target pressure and temperature are checked: There are four cases to be distinguished, dependent on how in many quadrants in the pressure temperature plane reference cross section data are available:

(a) **1 Quadrant**: The target pressure and temperature point is ouside the range of both temperatures and pressures covered by reference measurements. See Fig. 1 A.

(b) **2 Quadrants**: The target pressure and temperature point is outside the range of values covered by the reference data either for pressure or for temperature

(c) **3 Quadrants**: The target pressure and temperature point is situated near a concave boundary of the aerea covered by the reference measurements

(d) **4 Quadrants**: The target pressure and temperature point is situated in the aerea covered by reference measurements.

At a next step from each "occupied" quadrant one reference measurement is selected. The selection criterion is

$$d = \sqrt{(T_{ref} - T_{target})^2 + (100 \times \frac{p_{ref} - p_{target}}{p_{target}})^2} = min. \tag{1}$$

The selected reference cross section spectra then are interpolated linearily onto a common wavenumber grid. The interpolation in the pressure and temperature plane is depends on the number of quadrants in the pressure temperature plane where reference spectra are available.

1.2.1 One Quadrant

If reference spectra are available in one quadrant in the pressure temperature plane (see Fig. 1 A), the reference cross-section spectrum selected by means of Eq. 1 is used. No extrapolation is performed. This case applies also to species where only one measurement is available.

1.2.2 Two Quadrants

If reference spectra are available in two quadrant in the pressure temperature plane, two subcases have to be considered (see Figs. 1 B and E). In the case of occupation of two adjacent quadrants (Fig. 1 B), linear interpolation is performed in the quantity where one value higher and one value lower than the target value is available, while for the other quantity no extrapolation is performed. This typically applies to situations where the reference cross-sections do not cover the pressure or temperature range needed, or species where only temperature but no pressure dependent cross-sections are available (CFC-113, CFC-114, $ClONO_2$, N_2O_5). In the case of occupation of two opposite quadrants (Fig. 1 E), the same scheme as for the case of three or four quadrants is used.

Molecule	Spectral Intervals [cm^{-1}]	Temperatures [K]	Pressures [torr]	References
CFC-11	810–880 1050–1120	201–296 201–296	40–760 40–760	Li and Varanasi, 1994[7]
CFC-12	800–950 1040–1200	216–296 216–296	170–760 170–760	Varanasi and Nemtchinov, 1994[6]
CFC-14	1250–1289	180–296	22–760	Varanasi, 1997 pers. com. Massie et al.,1991[8] McDaniel et al., 1991[9] Husson et al., 1992[12] Husson et al., 1994[13]
CFC-113	780–995 1005.5–1232	203–293 203–293		Husson et al., 1992[12] Husson et al., 1994[13] Massie et al.,1991[8] McDaniel et al., 1991[9]
CFC-114	815–860 870–960 1030–1067 1095–1285	203–293		Husson et al., 1992[12] Husson et al., 1994[13] Massie et al., 1991[8] McDaniel et al., 1991[9]
HCFC-22	750–870 1060–1209 1275–1380	216–294 216–294 216–294	40–760 40–760 40–760	Varanasi et al., 1994[5] Clerbaux et al., 1993[10]
HCFC-123	740–900 1080–1450	253, 270, 287		Clerbaux et al., 1993 [10]
HCFC-124	675–715 790–920 1035–1430	287 (pure vapor)		Clerbaux et al., 1993 [10]
HCFC-141b	710–790 990–1210 1325–1470	253, 270, 287		Clerbaux et al., 1993 [10]
HCFC-142b	650–705 875–1030 1075–1265 1360–1475	253, 270, 287		Clerbaux et al., 1993 [10]
CCl_4	770–810	170–310		Orlando et al., 1992[14]
SF_6	925–956	216–295	25–760	Varanasi et al., 1994[5]
$ClONO_2$	740–840 1240–1340 1680–1790	213 and 296		Ballard et al., 1988[1]
$ClONO_2$	690–1330	190–297	0–113	M. Birk, 2000 pers. com.
N_2O_5	550–600 720–765 1210–1275 1680–1765	233–293		Massie et al., 1985[15]
CH_3COCH_3	700–2000	298		Remedios, 2000 pers. com. from EPA-webside
CH_3COCH_3	500–3700	298	760	Hanst, 2000[11]
C_6H_6	600–1800	295		Remedios, 2000 priv. com. measured by P. Sinclair
$CH_3CO_3NO_2$	531–3653	298	760	Hanst, 2000[11]
CH_3OH	500–3740	298	760	Hanst, 2000[11]
CH_3CCl_3	500–3700	298	760	Hanst, 2000[11]
C_5H_8	500–3700	298	760	Hanst, 2000[11]
C_3H_6	500–3700	298	760	Hanst, 2000[11]
DMS	500–3700	298	760	Hanst, 2000[11]
H_2CO	500–3700	298	760	Hanst, 2000[11]
CH_3Br	500–3700	298	760	Hanst, 2000[11]

Table 1: Molecules handled by tabulated cross section data, and their data sources

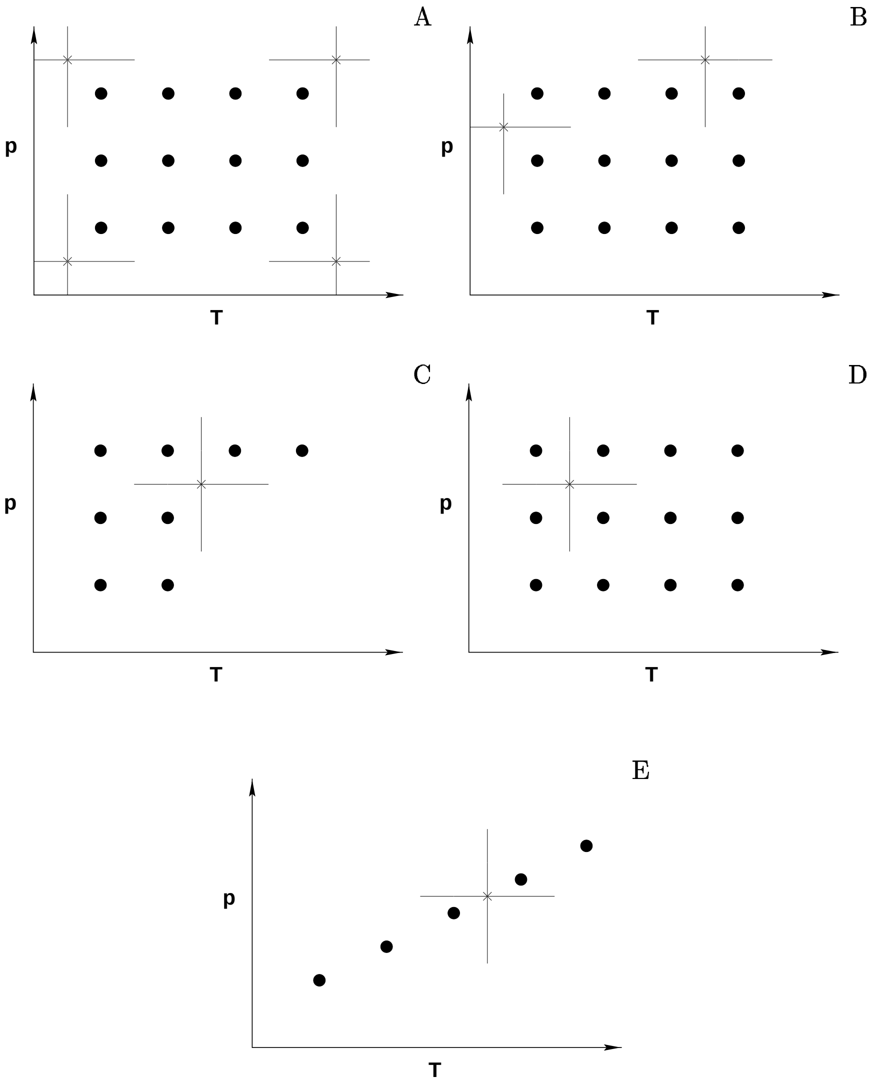

Figure 1: Definition of the cases 1.2(a) to 1.2(d)

1.2.3 Three and Four Quadrants

The interpolation in the pressure temperature plane is performed by summing up the selected reference data from each occupied quadrant weighted by the inverse quadratic distance from the target point. The distance d_n of the target point to the reference point in the pressure temperature plane is defined as

$$d_n = \sqrt{\left(\frac{T_{target} - T_{reference}}{w_T}\right)^2 + \left(\frac{p_{target} - p_{reference}}{p_{target} \times w_p}\right)^2} \qquad (2)$$

where w_T and w_p are factors used for weighting temperature against pressure when transforming both quantities to the dimensionsless, which is necessary, because a scalar distance is not defined for quantities of different dimensions, and the result would depend on the physical units applied. The weighting factor is directly determined from the pressure and temperature dependence of reference laboratory cross-sections. The calculation of cross-section spectrum $X(p_{target}, T_{target})$ is performed as follows:

$$X(p_{target}, T_{target}) = \frac{1}{\sum_{n=1}^{N} \frac{1}{d_n^2}} (\sum \frac{X_n}{d_n^2}) \tag{3}$$

where N is the number of occupied quadrants, and X_n is the cross-section spectrum in the nth occupied quadrant.

1.2.4 Special Case: $ClONO_2$

(a) **Ballard's data:**

Formally $ClONO_2$ cross-sections are handled as described in the standard two-quadrants case. The only difference is that cross-section reference spectra for various temperatures are no lab spectra but have been precalculated from reference data as

$$X_m(T) = \frac{a_m}{T} + b_m \tag{4}$$

where m denotes the spectral gridpoint, and coefficients a_m and b_m have been chosen to fit the reference data provided by *Ballard et al.*[1] for 213 and 296 K.

(b) **Birk's data:**

M. Birk (pers. com., 2000) measured temperature and pressure dependent cross-sections of $ClONO_2$. These were parameterized and delivered together with an p-T interpolation scheme. Making use of this routine the cross-sections were calculated at 7 temperatures between 189K and 297K and at 8 pressures between 0 and 71torr. KOPRA uses these pre-calculated cross-sections to perform it's own 2-d interpolation as described above.

2 Pseudo-lines

2.1 Introduction

In order to enable the handling of cross-section in line-by-line codes and to perform the interpolation procedure more 'physically', pseudo-linelists were produced by *G. Toon (pers. com., 1997)*. For this purpose pseudo-lines were made by fitting line-parameters to the laboratory cross-section measurements. In the following we first quote the description of the pseudo-linelists and then describe the implementation into KOPRA.

2.1.1 Pseudo-linelists

The 'readme' file which was distributed together with the pseudo-linelists reads:

> "... Each pseudo-linelist was derived by fitting all of the relevant laboratory 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 have achieved 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 spectra were measured at low pressure (e.g. CF_4).

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-linelists, several additional advantages became apparent:

(a) Since the pseudo-linelists 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.

(b) Fitting a physically-based function to the laboratory spectra 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 spectra. This makes it possible to identify and reject any 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.

(c) The laboratory cross-sections are always 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 atmospheric spectra are measured at a better resolution than the laboratory spectra.

(d) Several different laboratory data-sets, even with widely different measurement conditions and spectral resolutions, can easily be assimilated into a single pseudo-linelist.

(e) 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 measured laboratory spectra. Of course, the agreement will not be perfect since the fit was overconstrained, but the difference are usually $< 1\%$.

(f) 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 is necessary to compute the absorption spectrum from all the psuedo-lines (provided that this lineshape is stored). Thus, the speed of using the pseudo-linelists 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 resolve any structure observed in the laboratory spectra. Typically, the line spacing was chosen to be similar to the resolution of the laboratory spectra. Note that the positions and spacing of the pseudo-lines are completely inde- pendent 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-linelists are spaced at 0.01 cm^{-1}, which is ten times larger than an actual Doppler widths of most heavy gases. While 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 (e.g for $ClONO_2$ it is probably advisable to replaced the 760-798 cm^{-1} section of the pseudo-line list with Bell's linelist). 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 explitly set the Doppler width equal to the line spacing whenever it encounters pseudo-lines, avoiding the need to fudge the molecular weight. This is especially helpful for gases like $ClONO_2$ for which a proper 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:

$$S(T) = S(296)\left(\frac{296}{T}\right)^{tdrpf}\frac{Qvib(T)}{Qvib(296)}\frac{SE(T)}{SE(296)}\exp\left(hcE"(1/296 - 1/T)\right) \tag{5}$$

where $Qvib(T) = \prod[1 - \exp(-hc\nu_j/kT)]$ is the vibrational partition function and the product is performed over all the vibrational frequencies, ν_j. $SE(T) = [1 - \exp(-hc\nu_i/kT)]$ is the correction for the Stimulated Emission, ν_i being the center frequency of the line in question. The term $(296/T)^{tdrpf}$ is commonly known as the rotational partition function and tdrpf is usually (1.0, 1.5, or 2.0).

File	GAS	Interval	Spacing	Lines	Error	Measurer
cf4.h92	CF4	1250-1295	0.005	9001	4%	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	770- 810	0.010	4001	2%	Orlando (omitted 170K)
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
clno3.h92	ClONO2	750- 831	0.00964	8401	0%	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

Table 2: Computed pseudo-linelists

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

Most forward models should already have the code to compute the above expression because they are 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 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.

Finally, we want to make it clear that one should not expect the forward calculation made using these pseudo-lines to agree perfectly (except $ClONO_2$) with individual laboratory 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 2 we summarize the gases and spectral intervals for which we have computed pseudo-linelists. 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.

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2.1.2 KOPRA-implementation of pseudo-linelists

The gas-numbering of the pseudo-line species in KOPRA is actually from 251-260 (see the gas-list in the KOPRA main input file in section 'KOPRA installation' for the detailed numbers).

The pseudo-lines are integrated in the KOPRA spectroscopic line list with their KOPRA numbering (the record length is therefore 101 instead of 100 in the HITRAN case).

In `line_parameters@abco_m` the Doppler width is set to the line-spacing for pseudo-lines.

For calculating the partition functions (vibrational times rotational) KOPRA only uses the polynomial parameterization of the temperature dependence by Gamache. Therefore, for the pseudo-line molecules these coefficients were determined by a fit to the temperature dependence resulting from the explicit formulas as given in the previous section.

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