Chapter 2

Emission and spectroscopy of the clear atmosphere

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2.1 Introduction

The purpose of this chapter is to review the current state and recent developments in the modelling of microwave absorption by atmospheric gases and in the validation of those models by radiometric measurements. Local thermodynamic equilibrium implies that the absorption coefficient also determines the thermal energy emitted by the clear atmosphere. Absorption models generally consist of (1) a database of line parameters (e.g. transition frequencies, intensities, widths), which may be specific to the model or drawn from a large general-purpose database such as HITRAN or GEISA, (2) shape factors for the lines and (3) ancillary model components such as continuum absorption. In general, the absorption coefficient γ_a at frequency ν due to a particular gas can be written in the form

$$\gamma_{a}(\nu) = N \sum_{i} S_{i} F_{i}(\nu) + \text{continuum terms}$$
(2.1)

where S_i is the intensity (dependent on temperature) of line *i*, $F_i(v)$ is the shape factor for line *i* and *N* is the abundance of the gas, corresponding to the definition of line intensity. In the HITRAN (see Rothman *et al.*, 1998, eq. A5) and GEISA databases, for example, the definition of line intensity requires *N* to be the molecule number density of the absorbing gas (i.e. relative isotopic abundance is contained in S_i); but this definition is not universally followed in the literature. The selection of lines to be included in the summation of (2.1) may require the exercise of some educated judgement on the part of the user who wishes to compare calculations with

a particular set of measurements. The total absorption by a mixture of gases is the sum of absorption coefficients from the individual species under the conditions of pressure, temperature and abundances existing in the mixture. One may combine absorption models for different gases from different sources; hence, the number of possible combinations is large.

The most abundant gases of the atmosphere, H_2O , O_2 and N_2 , have a role in determining atmospheric transmittance over a wide range of frequencies; this makes them necessary components in the modelling of observations of surface phenomena, in addition to their intrinsic interest for measurement of atmospheric water vapour and temperature (the latter being done by observation of oxygen lines).

Hill (1986) devised a test criterion that responds to line shape while being insensitive to width or continuum level. He applied this test to the water-vapour absorption data of Becker and Autler (1946) near 22 GHz and found that the Van Vleck–Weisskopf line shape was an acceptable fit to that line, while the Gross and full Lorentz line shapes were rejected. With higher line centre frequencies, the differences between these shape factors would be reduced, and this experimental test of line shape has apparently not been applied to other water lines. The line shape factor of Van Vleck and Weisskopf is

$$F_{i}(\nu) = \frac{1}{\pi} \left(\frac{\nu}{\nu_{i}}\right)^{2} \left[\frac{w_{i}}{(\nu - \nu_{i} - \delta_{i})^{2} + w_{i}^{2}} + \frac{w_{i}}{(\nu + \nu_{i} + \delta_{i})^{2} + w_{i}^{2}}\right]$$
(2.2)

In the above, v_i is the line frequency, δ_i is the line shift and w_i is the line half-width; w_i and δ_i depend on temperature. Line shifts are typically much smaller than widths of microwave lines, but they may produce a detectable effect in some measurements.

At atmospheric densities (except very low densities where Doppler broadening is significant, see below), both widths and shifts are proportional to pressure, but the broadening or shifting coefficients can be different for different perturbing gases. The total width or shift is the sum of contributions from all gases in the atmosphere. For practical calculations, one needs a coefficient for broadening by dry air and another for broadening by water vapour, the latter being the most significant variable gas in the atmosphere. Calculation of water vapour absorption also requires inclusion of a model for the H_2O continuum, which will be discussed later in this chapter.

Oxygen is unusual in that it absorbs microwaves by means of a magnetic dipole moment rather than an electric dipole moment. Consequently, the molecules exhibit both resonant and non-resonant absorption in the gas phase. For O₂, pressure line shifts appear to be negligible, but calculation of the absorption requires the addition to (2.2) of first-order line-mixing (sometimes called line coupling) parameters Y_i , which are also dependent on temperature and proportional to pressure:

$$F_{i}(\nu) = \frac{1}{\pi} \left(\frac{\nu}{\nu_{i}}\right)^{2} \left[\frac{w_{i} + (\nu - \nu_{i})Y_{i}}{(\nu - \nu_{i})^{2} + w_{i}^{2}} + \frac{w_{i} - (\nu + \nu_{i})Y_{i}}{(\nu + \nu_{i})^{2} + w_{i}^{2}}\right]$$
(2.3)

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Because the Y_i in (2.3) arise through the mixing of lines due to correlation of the molecular state before and after collisions, they have physical meaning only in a summation over lines, such as in (2.1). Correct calculation of the line-mixing effect requires the summation to include all of the terms considered in derivation of the mixing coefficients, including the non-resonant term. It is also necessary to realise that the mixing parameters and widths are associated; thus they should not be obtained from different sources. The non-resonant term has a Debye shape factor:

$$F_0(\nu) = \frac{\nu^2 w_0}{\nu^2 + w_0^2} \tag{2.4}$$

Measured values of the non-resonant broadening parameter w_0 are about half as large as a typical half-width of the resonant O₂ lines. This difference is closely connected with the phenomenon of line mixing, as shown by Gordon (1967). On the wings of the O₂ band, the net effect of line mixing is to reduce absorption, as though molecular collisions were less effective at broadening the lines.

Nitrogen has no microwave lines, but it does exhibit a weak continuum absorption due to collision-induced dipole moments, as do other molecules, including oxygen. Collision-induced absorption is discussed later in the chapter.

Lines of other atmospheric gases are both broad and weak at tropospheric pressures, which makes them difficult to detect against the background of the major gases. However, in the stratosphere, microwave lines of many molecular species are observable. The lines are very narrow in comparison to their centre frequencies. When that condition applies, and the frequency of observation is also close to the line centre, (2.2) reduces to a Lorentz shape factor:

$$F_i(\nu) = \frac{\pi^{-1} w_i}{(\nu - \nu_i - \delta_i)^2 + w_i^2}$$
(2.5)

which is sometimes called the simple Lorentz shape factor when it is necessary to distinguish it from the full Lorentz shape factor, which includes a negative-resonant term. However, if Doppler broadening is significant, which can be easily calculated, then a Voigt lineshape is appropriate. The Voigt shape factor results from the convolution of a Lorentzian function, which accounts for line broadening by collisions, with a Gaussian function having half-width (at half-maximum) of $3.6 \times 10^{-7} (T/M)^{1/2} v_i$, where *T* is the temperature in Kelvin and *M* is the molecular weight in g/mole, which describes the Doppler broadening. Accurate series expansions are available for the Voigt shape factor (see, e.g., Schreier, 1992). Modelling of absorption is then largely concerned with values for line frequency, intensity, width and possibly shift. However, particular effects such as Zeeman splitting also need to be considered for a few gases. A more detailed discussion of these points can be found in Rosenkranz (1993) or Melsheimer *et al.* (2005).

When large quantities of data from a single instrument are processed, a parametrised, or rapid, algorithm may be employed. These models (of which RTTOV is an example) approximate the result of a line-by-line summation, but with significantly less computation. This is achieved by means of coefficients that are

pre-computed, usually for a specific instrument with defined channels and viewing geometry. Errors in approximation of transmittance are generally less than 10^{-2} , and sometimes much less, which is smaller than the uncertainties in the line-by-line models. The accuracy of a transmittance calculation is thus limited by the line-by-line model from which the coefficients are derived.

The next eight sections of this chapter describe recent developments in databases, models, laboratory measurements and theoretical work. Two sections concerned with the accuracy and state of validation of models follow. The chapter concludes with some recommendations for future work.

2.2 HITRAN (high resolution transmission)

A new archival compilation was made available in the summer of 2004. The compilation brings together the HITRAN line-transition parameters, infrared cross-sections, UV line-by-line parameters and cross-sections, aerosol refractive indices and documentation. This compilation, called HAWKS (HITRAN atmospheric workstation), is available on an anonymous ftp-site. Instructions for accessing the database can be found in the HITRAN web-site (cfa-www.harvard.edu/HITRAN). A summary of the data that have been added, modified, or enhanced since the previous update of 2001 (Rothman *et al.* (2003)) is given below. For a complete and detailed description of HITRAN-2004 see Rothman *et al.* (2005).

2.2.1 Line-by-line parameters archive

The line-by-line portion of the database contains spectroscopic parameters for 39 molecules including 93 of their isotopologues. Twelve molecular species, i.e. SO_2 , NH₃, HF, HBr, HI, ClO, H₂CO, N₂, ClONO₂, HOBr, C₂H₄, NO⁺, have been kept identical since the former edition of HITRAN. There is a new entry, namely, the methanol molecule (CH₃OH). For two of the molecules, i.e. SF_6 and ClONO₂, the parameters have been put in a supplemental folder. Details of the updates follow.

H₂**O**: Important updates have been accomplished, especially for the main isotopologue $H_2^{16}O$. In the pure-rotation region, 952 lines of HD¹⁸O have been added. Line positions and intensities derive from the JPL catalog (Pickett *et al.*, 1998). Updates of line positions have been made for $H_2^{17}O$ and $H_2^{18}O$ from 0 to 500 cm⁻¹ based on the work of Toth (1992) and of line intensities for $H_2^{17}O$, $H_2^{18}O$ and $HD^{16}O$ from 0 to 500 cm⁻¹ based on the work of Pearson (1999). For the main isotopologue $H_2^{16}O$ between 0 and 800 cm⁻¹, the calculations of Coudert (1999), Lanquetin *et al.* (2001) and Flaud *et al.* (2003a) have been used to update line positions and line intensities has been done for all water vapour isotopologues between 500 and 8000 cm⁻¹ based on the work of Toth (2005). From 9600 to 11400 cm⁻¹, the line positions and intensities of the isotopologue H_2¹⁷O have been update too. From 12400 to 14518 cm⁻¹, 918 lines of H_2¹⁸O have been incorporated,

from the works of Tanaka *et al.* (2002, 2005). Another significant improvement concerns the 9250–9600 cm⁻¹, 11400–12895 cm⁻¹ and 13184–25000 cm⁻¹ regions for which the line lists generated from the works of Mérienne *et al.* (2003) and of Coheur *et al.* (2002) have been used to replace the former lines of $H_2^{16}O$. Concerning the line-shape parameters, the air-broadened half-widths and line shifts and the self-broadened half-widths, a complete update has been performed for the $H_2^{16}O$, $H_2^{18}O$ and $H_2^{17}O$ isotopologues.

CO₂: The data of the 'Carbon Dioxide Spectroscopic Database at 296 K' (CDSD-296) by Tashkun *et al.* (2003) have been used to update the positions and intensities of the lines of ${}^{12}C^{16}O_2$, ${}^{13}C^{16}O^2$, ${}^{12}C^{16}O^{18}O$ and ${}^{12}C^{16}O^{17}O$ when no high-quality laboratory observed data (i.e. the data of Miller and Brown (2004), in a large range of the infrared, the works of Ding *et al.* (2002) around 9950 cm⁻¹ and of Benner (2003) around 3500 cm⁻¹) were available. Two line lists, from the JPL catalog (Pickett *et al.*, 1998), in the pure-rotational spectral region have been added in this edition for the isotopologues ${}^{16}O^{12}C^{18}O$ and ${}^{16}O^{12}C^{17}O$. Line parameters above 9650 cm⁻¹ have been newly archived from works of Campargue *et al.* (1994) and Lucchesini (2004).

O₃: In the pure-rotation region, the positions, the intensities and the lower-state energies of the transitions have been updated for the isotopologues ${}^{16}O{}^{16}O{}^{17}O$ and ${}^{16}O{}^{17}O{}^{16}O$ from the JPL catalog (Pickett *et al.*, 1998). Using the line list of the MIPAS (Michelson Interferometer for Passive Atmospheric Sounding) database (Flaud *et al.*, 2003a), line positions and intensities have been updated for 49 bands of ${}^{16}O{}_3$ and the ν_1 and ν_3 bands of the ${}^{16}O{}^{16}O{}^{18}O$ and ${}^{16}O{}^{18}O{}^{16}O$ isotopologues. Seventeen bands of ${}^{16}O{}_3$, one band of ${}^{16}O{}^{16}O{}^{18}O$ and ${}^{16}O{}^{16}O{}^{16}O$ and three bands of ${}^{16}O{}^{16}O{}^{17}O$ and ${}^{16}O{}^{17}O{}^{16}O$ have been incorporated. The 14 μ m region has been updated with the work of Wagner *et al.* (2002). A total of 12 bands for ${}^{16}O{}_3$, from the works of Flaud *et al.* (1987, 1989) and Mikhailenko *et al.* (2002), have been added in three spectral regions, i.e. 1613–1903 cm⁻¹ (6 bands), 1872–2288 cm⁻¹ (3 bands) and 2590–3006 cm⁻¹ (3 bands).

 N_2O : The line list has been almost completely revised using the extensive work of Toth (2004) and the results of Daumont *et al.* (2002), Johns *et al.* (1996), Lacome *et al.* (1984) and Nemtchinov *et al.* (2003).

CO: Line intensities have been updated for the first overtone of ${}^{12}C{}^{16}O$, located near 2.4 μ m, using the measurements of Brault *et al.* (2003) and for the second overtone, located around 1.6 μ m, using the calculated values of Sung and Varanasi (2004). Details for the updates of air-broadened half-widths, self-broadened line widths, air-broadening temperature-dependence exponent and air pressure-induced line shifts are given in Rothman *et al.* (2005).

CH₄: Some 48 000 methane parameters were completely replaced by updated line lists of over 240 000 lines. Most of the revisions made in the region from 0 to 6185 cm⁻¹ are described by Brown *et al.* (2003). In the pure-rotation region, a new line list was taken from the JPL catalog (Pickett *et al.*, 1998). In the dyad region, a few of the air pressure-induced line shifts of ¹²CH₄ were revised. The near-infrared

parameters of the lines of CH₄ between 4800 and 9200 cm⁻¹ have been improved, using the measurements of Brown (2004) in the 4800–5500 cm⁻¹ region and high-resolution laboratory spectra recorded with the McMath–Pierce Fourier transform spectrometer between 6180 and 9200 cm⁻¹.

O₂: The A bands of the isotopologues ¹⁸O¹⁶O and ¹⁷O¹⁶O centred at 0.76 μ m have been updated using the work of Camy-Peyret *et al.* (2000).

NO: The calculation by Goldman *et al.* (1998), for line positions and intensities of ${}^{14}N^{16}O$, has been used to replace the previous parameters for line positions and intensities associated with algorithms deduced from Chackerien *et al.* (1998a) and Spencer *et al.* (1994) to update the air-broadened half-widths. The results of Pine *et al.* (1985) and Spencer *et al.* (1997) have been used to update the self-broadened widths and the temperature dependence of the air-broadened widths, respectively.

NO₂: The coding of the rotational quantum numbers N, K_a , K_c , J and F has been standardised according to Perrin *et al.* (1998). The air-broadened half-widths, the air pressure-induced shifts and the temperature dependence of the air-widths were revised throughout the database using empirical expressions and measurements by Benner *et al.* (2004).

HNO₃: The line list for the pure-rotation band which covered the 0–43 cm⁻¹ region has been replaced by the line list of the JPL catalog (Pickett *et al.*, 1998) which extends the spectral coverage to 0–84 cm⁻¹. In the far infrared, two hot bands, $2v_9 - v_9$ and $v_5 - v_9$, have been added. Line positions are from a simulation based on analyses of rotational spectra by Petkie *et al.* (2005). The intensities of the v_5 and $2v_9$ bands have been normalised based on the work of Toth *et al.* (2003). The former individual line intensities of the v_5 and $2v_9$ bands have been multiplied by 0.879. The two hot bands $v_5 + v_9 - v_9$ and $3v_9 - v_9$, located at 885.424 and 830.6 cm⁻¹, respectively, have been updated from the results of Flaud *et al.* (2003a,b) and Perrin *et al.* (1994). Some values of the intensities have been rescaled. The self-broadened half-width has been fixed to the constant value of 0.8 cm⁻¹ atm⁻¹ for all the lines (Zu *et al.*, 2002; Brockman *et al.*, 1978).

OH: In the pure-rotation region, line intensities and positions of the two isotopologues 18 OH and OD have been updated based on the JPL catalog (Pickett *et al.*, 1998). For the air-broadened half-widths and their temperature dependence, the data reported in Rothman *et al.* (1998) for 16 OH have been used.

HCl: In the pure-rotation region, the actual line list is a combination of the JPL catalog (Pickett *et al.* (1998)) and of what was in the previous edition of HITRAN Rothman *et al.* (2003).

OCS: In the 3–5 μ m region of the main isotopologue the line intensities have been updated using works of Régalia-Jarlot *et al.* (2002) and Vander Auwera *et al.* (2003). The line intensities of the $\nu_1 + \nu_3$ band located around 2900 cm⁻¹ have been updated according to the work of Régalia-Jarlot *et al.* (2002) and the line intensities in the

 $2\nu_3$ band of ${}^{16}O^{12}C^{32}S$ were also updated according to the work of Bermejo *et al.* (1997).

HOCI: The positions and intensities of the pure rotation lines were updated, and transitions within the (001) level were added according to the work of Flaud *et al.* (1998). The v_2 region from 1178 to 1321 cm^{-1} was updated for both the HO³⁵Cl and the HO³⁷Cl isotopologues according to the results reported in Vander Auwera *et al.* (2000). The air-broadened half-width of all the lines in the v_2 band was set to the average of the measured values reported for two lines by Shorter *et al.* (1997), i.e. $0.1 \text{ cm}^{-1} \text{ atm}^{-1}$. The default value of 0.5 for the temperature dependence of the air-broadened half-widths was replaced by 0.7.

HCN: Line positions and intensities of the three isotopologues present in the purerotation region and in the infrared from 500 to 3425 cm^{-1} have been updated thanks to the works of Maki *et al.* (1996, 2000) and Devi *et al.* (2003). The collision parameters (air and self), the temperature dependence of the air-broadened half-width and the air pressure-induced line shifts have been updated with polynomial expressions based on the works of Devi *et al.* (2003, 2004) and Rinsland *et al.* (2003a).

CH₃Cl: A line list for the v_2 , v_5 and $2v_3$ triad of vibrational bands of methyl chloride covering the 6–8 μ m region has been added based on the works of Chackerian *et al.* (1998b) and Bouanich *et al.* (2001). The pure-rotation bands for the two isotopologues have also been added to the database, using the positions, the intensities and the lower state energy of the JPL catalog (Pickett *et al.* 1998).

 H_2O_2 : A new line list for the pure-rotation region from 0 to 1427 cm⁻¹, prepared by Perrin *et al.* (1996), has been included.

 C_2H_2 : In the 1.5 μ m region (from 6448 to 6686 cm⁻¹), a new line list for the $v_1 + v_3$ bands of ${}^{12}C^{13}CH_2$ and three associated hot bands, based on the works of El Hachtouki and Vander Auwera (2002) and of Kou *et al.* (1994) has been incorporated in the database. The air- and self-broadened half-widths, their temperature dependence and the air pressure-induced line shifts were calculated using the polynomial expansion and the constants reported by Jacquemart *et al.* (2003).

 C_2H_6 : A line list prepared by Pine and Rinsland (1999) in the ν_7 band of ethane has completely replaced the former data.

PH₃: The line list of phosphine has been completely revised and expanded. The line positions and line intensities in the 10 μ m region are from Brown *et al.* (2002b), while those in the 5 μ m region are from Tarrago *et al.* (1992). The air- and self-broadened half-widths from Brown *et al.* (2002b) replace the former default constant values.

COF₂: A new prediction (the number of lines has more than doubled) has been generated by Cohen (2001). A typographical error for the rotational quantum numbers attribution in the 5.1 μ m region has been corrected.

SF₆: An update has been performed for the only band present in the database, the ν_3 band. New positions and intensities by Acef *et al.* (2000) and Boudon *et al.* (2002) have replaced the previous spectroscopic parameters. A constant value for the self-broadened half-width, equal to $0.042 \text{ cm}^{-1} \text{ atm}^{-1}$, based on Tejwani and Fox (1987) has been adopted.

 H_2S : Updates have been made for the air- and self-broadened half-widths and for the air pressure-induced line shift based on the works of Sumpf *et al.* (1996, 1997, 2004), Kissel *et al.* (2002) and Waschull *et al.* (1994).

HCOOH: The spectral parameters of the pure-rotation lines observed between 10 and 100 cm⁻¹ have been updated thanks to the works of Vander Auwera (1992) and Winnewisser *et al.* (2002). The new spectral line parameters (positions and intensities) generated by Perrin *et al.* (1999) were used to update the data on the ν_6 band. The constant values of $0.1 \text{ cm}^{-1} \text{ atm}^{-1}$ and $0.4 \text{ cm}^{-1} \text{ atm}^{-1}$, used, respectively, for the air- and self-broadened half-widths, in the ν_6 band, have been applied to the far-infrared region.

HO₂: The rotational quantum numbers format has been revised.

O: Slight changes have been made for the line positions, intensities and lower-state energies of the two transitions of atomic oxygen thanks to newer values in the JPL catalog (Pickett *et al.* 1998).

CH₃OH: The data on methanol make their debut in HITRAN. In the microwave spectral region, line positions and intensities of the rotational transitions between 0 and 34 cm^{-1} from Müller *et al.* (2001) have been used. A recent work of Xu *et al.* (2004) led to the creation of an empirical line list around 10 μ m that has been used. The air- and self-broadened half-widths have been fixed, respectively, to the assumed values of 0.1 cm⁻¹ atm⁻¹ and 0.4 cm⁻¹ atm⁻¹. The assumed value for the temperature dependence of the widths is taken equal to 0.75.

The format of the parameters for each spectral line (equivalent to a record in the database) is given in Table 2.1 (from Rothman *et al.*, 2005) where the description of the parameters is in the bottom half. The total length of the record is 160 characters, an increase from the 100 bytes adopted in the former editions of HITRAN.

Table 2.2 (from Rothman *et al.*, 2005) is a summary of the molecular species and spectral regions covered in the current edition of HITRAN. In column 1 is the identification code for the molecular species listed in column 2 with their associated isotopologue in column 3 (AFGL notation, Rothman *et al.*, 2005); the two last columns, 4 and 5, give the spectral coverage and the number of lines, respectively, for each isotopologue of column 3.

2.2.2 Infrared cross-sections archive

Many of the infrared cross-sections have been retained from the previous edition of HITRAN (Rothman *et al.*, 2003) and the format has remained the same. New or

Parameter Field length FORTRAN descriptor	M 2 12	/ 1 11	v 12 F12.6	<i>S</i> 10 E10.3	A 10 E10.3	γair 5 F5.4	γ _{self} 5 F5.4	$E^{''}$ 10 F10.4	n _{air} 4 F4.2	δ _{air} 8 F8.6	V' I5 A15	<i>V"</i> I5 A15	$\begin{array}{c} Q' \\ 15 \\ A15 \end{array}$	Q" 15 A15	l _{err} 6 611	I _{ref} 12 612	* (flag) 1 A1	8 7 F7.1	8" 7 F7.1
Parameter	Mean	ing					ъ	nits or cc	mment	ş									
Μ	Mole	cule n	umber				H	ITRAN (chronol	ogical a	ssignm	ent							
I u	Isotol	polog m w	ue numb avenimh	ber Jer			ÖE	rdering v 1	vithin a	molecu	ile by tƙ	errestri£	ıl abund	lance					
S	Intent	sity					5 15 (n ⁻¹ /(mo Rothmar	lecule · 1 <i>et al.</i> (cm ⁻²) (1998) ă	at stand liscuss	lard 29 T depe	6 K ndence)	-					
А	Einste	ein A-	-coeffici	ent			່ິວ			<u>,</u>		-	`						
$\gamma_{ m air}$	Air-b	roade	ned half	E-width (E	(MHW)	at 296 I	ζ cn	n^{-1} atm ⁻											
$\gamma_{ m self}$	Self-t	proade	ened hal	f-width ((MHWH) at 296	K cn	$n^{-1}atm^{-1}$	-										
E″	Lowe	r-stat	e energy				cn	n^{-1}											
nair	Temp	eratui	re-depen	ndence ex	ponent f	for γ_{air}	un	nitless γ_{a} .	$i_{r}(T) =$	$\gamma_{\rm air}(T_0)$	$T(T_0) \times (T_0)$	$_{0/T}$.ч						
δ_{air}	Air pı	ressur	e-induc(ed line sh	uift		cn	n ⁻¹ atm	⁻¹ at 29	96 K									
V' V''	Uppe	r-state	global) و امطمام، م	l' quanta															
> `c	LUWE	a state	c gioua.	u quanta															
0`C	Lowe	r-stati T-stati	e "local"	quanta guanta															
Ierr	Unce	rtainty	y indices				Υ	ccuracy 1	for 6 cri	itical pa	rametei	s(v, S)	$\gamma_{\mathrm{air}}, \gamma$	self, <i>n</i> ai	r, δ_{air})	_			
I_{ref}	Refer	ence	indices				R	eference	s for 6 c	ritical p	aramet	ers $(\nu,$	S, γ_{air} ,	$\gamma_{\rm self}, n$	air, δ_{ai}	r)			
*	Flag						Αı	vailabilit	y of pro	igram ai	nd data	for the	case of	line m	ixing				
مر مر	Statis	tical v	weight o	of the upp	er state														
50	SLALIS	ucar	weigin u	MOI AIII II	'er state														

 Table 2.1
 Format for HITRAN parameters in the line-by-line section, 2004 edition

Mol. ID.	Molecule	Isotopologue	Spectral coverage	Number of
		(AFGL notation)	(cm ⁻¹)	lines
1	H ₂ O	161	0-25233	36114
		181	0-14519	9548
		171	10-11335	6120
		162	0-7514	9628
		182	0-3825	1611
		172	1234–1599	175
2	CO ₂	626	442–9649	27979
		636	497-8105	8836
		628	0-8133	13445
		627	0-6962	7739
		638	567-4947	2312
		637	584-3642	1593
		828	615-3670	721
		728	626–2359	288
3	O ₃	666	0-4061	183785
		668	0–2114	21718
		686	1-2075	8937
		667	0-2122	65106
		676	0-2101	31935
4	N_2O	446	0-5135	33066
		456	5-5086	4222
		546	4-4704	4592
		448	542-4672	4250
		447	550-4430	1705
5	CO	26	3-8465	917
		36	3-6279	780
		28	3-6267	760
		27	3-6339	728
		38	3-6124	712
		37	1807–6197	580
6	CH ₄	211	0–9200	187128
		311	0-6070	28793
		212	7–3307	35519
7	\mathbf{O}_2	66	0-15927	1430
		68	1-15852	671
		67	0–14537	4326
8	NO	46	0-9274	100902
		56	1609-2061	699
		48	1601–2039	679

 Table 2.2
 HITRAN-04 individual lines sub-database detailed content

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Mol. ID.	Molecule	Isotopologue (AFGL notation)	Spectral coverage (cm^{-1})	Number of lines
9	SO ₂	626 646	0–4093 2463–2497	38566 287
10	NO ₂	646	0-3075	104223
11	NH ₃	4111 5111	0–5295 0–5180	27994 1090
12	HNO ₃	146	0-1770	271166
13	ОН	61 81 62	0–19268 0–329 0–332	41166 295 912
14	HF	19	41–11536	107
15	HCl	15 17	20–13458 20–10995	324 289
16	HBr	19 11	16–9759 16–9758	651 642
17	HI	17	12-8488	806
18	CIO	56 76	0–1208 0–1200	3599 3631
19	OCS	622 624 632 623 822	0-4119 0-4116 0-4013 509-4116 0-4042	10553 4186 2283 1802 1096
20	H ₂ CO	126 136 128	0–2999 0–73 0–48	1772 563 367
21	HOCI	165 167	$1-3800 \\ 1-3800$	8877 7399
22	N_2	44	1922–2626	120
23	HCN	124 134 125	0-3424 2-3405 2-3420	2955 652 646
24	CH ₃ Cl	215	0-3173	16411
25	H ₂ O ₂	217 1661	0-3162 0-1500	14708 100781

Table 2.2 (Continued)

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Mol. ID.	Molecule	Isotopologue (AFGL notation)	Spectral coverage (cm^{-1})	Number of lines
26	C_2H_2	1221 1231	604–6686 613–6589	3232 285
27	C_2H_6	1221	720–2978	4749
28	PH ₃	1111	770–2472	11790
29	COF ₂	269	725–2002	70601
30	SF ₆	29	929–964	22901
31	H ₂ S	121 141 131	2-4257 5-4172 5-4099	12330 4894 3564
32	нсоон	126	10–1235	24808
33	HO ₂	166	0-3676	38804
34	0	6	68–159	2
35	CIONO ₂	5646 7646	763–798 765–791	21988 10211
36	NO^+	46	1634–2531	1206
37	HOBr	169 161	0–316 0–316	2177 2181
38	C_2H_4	221 231	701–3243 2947–3181	12967 281
39	СН ₃ ОН	2161	0–1408	19899

Table 2.2 (Continued)

updated data are as follows:

- the cross-sections for chlorine nitrate, ClONO₂, have been totally updated in the 750–1320 cm⁻¹ region from the measurements by Wagner and Birk (2003). In the range 1680–1790 cm⁻¹, data from Ballard *et al.* (1988) have been retained;
- data of Wagner and Birk (2003) also include cross-sections of nitrogen pentoxide, N₂O₅, which have been used to replace entirely the former archived data;
- the cross-sections of HNO₄ (peroxynitric acid, PNA) measured by May and Friedl (1993) at 220 K, using spectral resolution of 0.003 cm⁻¹ in the 780–830 cm⁻¹ region, have been included and they replace the earlier cross-sections;
- absorption cross-sections of SF₅CF₃ (trifluoromethyl sulphur pentafluoride) have been included for the first time. The cross-sections were measured in the 520–6500 cm⁻¹ spectral range, at the Pacific Northwest National Laboratory by Rinsland *et al.* (2003b).

The summary of HITRAN-04 archived cross-sections is given later in Table 2.5, along with those of GEISA.

2.2.3 Ultraviolet datasets

New cross-sections, in the ultraviolet and visible spectral regions, for six molecular species have been implemented in the database:

O₃: Absorption cross-sections in the Hartley–Huggins bands, including their temperature dependence have been included for the spectral range 29 164–40 798 cm⁻¹. The data are adapted from the results of Bass and Paur (1981, 1985a,b), Edlén (1966) and Voigt *et al.* (2001).

NO₃: Cross-sections of nitrogen trioxide at 298 K have been taken from Orphal *et al.* (2003) and www.iup.physik.uni-bremen.de/gruppen/molspec.

BrO: Cross-sections for bromine monoxide at temperatures of 228 and 298 K, at 10 cm^{-1} spectral resolution, are from Wilmouth *et al.* (1999).

OCIO: Chlorine dioxide cross-sections at two spectral resolutions $(1 \text{ cm}^{-1} \text{ and } 20 \text{ cm}^{-1})$ and five temperatures (213 to 293 K) have been taken from Kromminga *et al.* (2003) and www.iup.physik.uni-bremen.de/gruppen/molspec.

 H_2CO : Cross-sections of formaldehyde have been adapted from Cantrell *et al.* (1990).

 O_2-O_2 : Cross-sections for the oxygen collision complex at 296 K have been adapted from Greenblatt *et al.* (1990); they have been corrected from air to vacuum wavelengths using Edlén (1966).

2.2.4 Aerosol refractive indices

Refractive indices of water, ice, aqueous sulphuric and nitric acid, solid hydrates (i.e. nitric acid, mono-, di- and tri- hydrate), organic non-volatile aerosol and crustal material (e.g. quartz, haematite and sand) in the previous version of HITRAN are discussed by Massie and Goldman (2003). Recently, Norman *et al.* (2002) published the real and imaginary refractive indices at 220 K for six different ternary compositions, and these data have been added to the current HITRAN compilation.

2.3 GEISA (Gestion et étude des informations spectroscopiques atmosphériques: Management and study of atmospheric spectroscopic information)

Since its 1997 edition (GEISA-97), the GEISA database, extensively described in Jacquinet-Husson *et al.* (1999), has been updated twice: partially in 2001 (Jacquinet-Husson *et al.* 2003a) and extensively in 2003 (GEISA-03) (Jacquinet-Husson *et al.*, 2003b, 2005).

The GEISA-03 system comprises three independent sub-databases devoted, respectively, to

- individual line transition spectroscopic parameters (line-by-line archive);
- infrared absorption cross-sections;
- micro-physical and optical properties of atmospheric aerosols.

All the archived data can be handled through general and user friendly GEISA associated management software facilities which are interfaced on the ARA/LMD group web site at www.ara.lmd.polytechnique.fr. They are also accessible at the GEISA restricted free access ftp site www.ara.lmd.polytechnique.fr/ftpgeisa. First, the potential user has to get a login and a password at www.ara.lmd.polytechnique.fr/ registration.

Currently, GEISA is involved in activities related to the assessment of the capabilities of IASI (infrared atmospheric sounding interferometer), as described in Jacquinet-Husson *et al.* (1998).

2.3.1 Subdatabase on line transition parameters

The GEISA-03 subdatabase of line transition parameters involves 42 molecules (98 isotopic species) and contains 1 668 371 entries (321 905 supplementary entries since GEISA-97) in the spectral range from 10^{-6} to 22 656 cm⁻¹. The included molecules are constituents of the atmospheres of earth (major permanent and trace molecules) and of other planets (such as C₂H₄, GeH₄, C₃H₈, C₂N₂, C₄H₂, HC₃N, H₂S, HCOOH and C₃H₄, for the giant planets). It has to be noted that CH₃D is considered as an individual molecule in GEISA and as an isotope of CH4 in HITRAN. Details of the updates follow.

H₂**O**: Three spectral regions have been reinvestigated. In the 500–2850 cm⁻¹ region, the line parameters were replaced with a compilation of 10755 water transitions obtained by Toth (1998a, 1999a,b, 2000) and Toth *et al.* (1998b). Alternative line parameters from Stewart (2003), related to the H₂O archive in the 10 μ m region have been issued as a support study for IASI and archived in GEISA as an alternative file. In the 9650–11 400 cm⁻¹ region, the update comes from empirical line parameters of H₂¹⁶O obtained by Brown *et al.* (2002a). In the 13 000–26 000 cm⁻¹ region the new line parameters are from Carleer *et al.* (1999), Coheur *et al.* (2002) and Fally *et al.* (2003).

 CO_2 : The previous line parameters of the transitions belonging to the four most abundant isotopomers ${}^{12}C^{16}O_2$, ${}^{13}C^{16}O_2$, ${}^{16}O^{12}C^{18}O$ and ${}^{16}O^{12}C^{17}O$ in the 442–2797 cm⁻¹ spectral region have been replaced with 48 627 new ones covering the 436–2826 cm⁻¹ spectral range, based on the results described in Tashkun *et al.* (1998, 2001) and Teffo *et al.* (2002, 2003).

O₃: Updates occur in four spectral regions: in the 600–1232 cm⁻¹ spectral region, there are new and more accurate line parameters for the v_1 and v_3 bands of ${}^{16}O_3$ derived by Wagner *et al.* (2002) and Flaud *et al.* (2003c). A complete new study of the 1300–1500 cm⁻¹ spectral range, related to the $2v_2$, $3v_2 - v_2$, $v_1 + v_3 + v_3 - v_2$

and $2\nu_3 - \nu_2$ bands of ${}^{16}O_3$, has been made by Barbe *et al.* (1998). The 1820–2260 cm⁻¹ ($2\nu_3$, $\nu_1 + \nu_3$ and $2\nu_1 + \nu_3$ interactive bands of ${}^{16}O^{18}O^{16}O$) and the 2600–2900 cm⁻¹ (triad: $\nu_2 + 2\nu_3$, $\nu_1 + \nu_2 + \nu_3$ with $2\nu_1 + \nu_2$) regions have been reinvestigated by De Backer-Barilly *et al.* (2003) and Mikhaïlenko *et al.* (1999, 2002), respectively.

N₂**O**: 279 lines in the spectral region 870–1240 cm⁻¹, recently revisited by Daumont *et al.* (2002), have been substituted in two bands, $v_3 - v_1$ and v_3-2v_2 , the intensities of which were doubtful. In addition, a technical update has removed 118 duplicated lines in the spectral interval 564–629 cm⁻¹.

CH₄ and CH₃D: The CH₄ and CH₃D contents of GEISA have been extensively updated. The spectral range has been extended from 6184.492 cm^{-1} to 9199.285 cm^{-1} and the number of entries increased from $66\,883$ to $216\,196$ (weaker transitions of 12 CH₄ and new bands of 13 CH₄ and CH₃D included). Full details about the revision in the spectral interval from 0.01 to 6184.492 cm^{-1} can be found in a review paper by Brown *et al.* (2003). The new CH₄ near infrared data from 4800 to 5500 cm^{-1} and $6180-10\,000 \text{ cm}^{-1}$ are from an empirical list obtained by Brown (2001, 2002, 2003), from a few selected FTS laboratory spectra.

O₂: The two spectral regions, 7664.726–8064.311 cm⁻¹ and 11483.727–15927.806 cm⁻¹, have been updated with new results by Goldman *et al.* (2003a) and by Brown and Plymate (2000), respectively.

NO: A new line list has been produced by Goldman (2003) in the first overtone region of the main isotopic species ${}^{14}N^{16}O$, i.e. between 3547.318 and 3799.155 cm⁻¹. This calculation has been issued from the experimental data from Mandin *et al.* (1997b, 1998) and theoretical results from Gillis and Goldman (1982).

NO₂: A new line list was set up in the spectral region of the $v_1 + v_3$, $v_1 + 2v_2$ and $v_1 + v_2 + v_3 - v_2$ bands of the ¹⁴N¹⁶O₂ main isotopic species. New line parameters come from the works of Mandin *et al.* (1997a), Dana *et al.* (1997), Devi *et al.* (1982) and May and Webster (1990).

NH₃: The line parameters of the interval $0.058-5294.502 \text{ cm}^{-1}$ have been totally replaced by those issued by Kleiner and Brown (2003) and are described in Kleiner *et al.* (2003).

PH₃: New data from Kleiner and Brown (2003), described in Kleiner *et al.* (2003), have replaced the whole content of the region from 770.877 to 2478.765 cm^{-1} .

OH: Line parameters in the ultraviolet region from 29 808.500 to $35 877.030 \text{ cm}^{-1}$, from Gillis *et al.* (2001) have been added to the GEISA archive.

HBr: New line parameters of H^{79} Br and H^{81} Br, for the spectral regions of the pure rotation band $X^1 \Sigma^+$ (0-0) (16.692–396.474 cm⁻¹) and of the fundamental band (1-0) (2123.812–2790.533 cm⁻¹), have been derived for spectroscopic databases update, as described in Goldman *et al.* (2003b).

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HI: The description of the updates in the spectral regions of the $X^1\Sigma^+$ (0-0) (12.842–319.820 cm⁻¹) and of the (0-1) (1950.689–2403.162 cm⁻¹) bands is given in Goldman *et al.* (2003b).

 C_2H_6 : In the spectral region 2975.331–2977.926 cm⁻¹, a modified list by Rinsland *et al.* (1998), for the ^pQ₃ subbranch in the ν_7 band, has replaced the previously archived line parameters.

 C_2H_2 : The updates of the database concern three spectral regions: the 13.6 and 5 μ m regions, from work performed by Mandin *et al.* (2000) and Jacquemart *et al.* (2001, 2002) and the 7.5 μ m region, from results by Vander Auwera (2000a).

HOCI: A new line list has been created in the spectral interval 1178.673–1320.332 cm⁻¹, corresponding to the v_2 region, on the basis of the works of Flaud *et al.* (1998), Flaud (2002) and Vander Auwera *et al.* (2000).

CH₃Cl: In the spectral region from 1261.562 to 1645.899 cm⁻¹, a list of 8989 transitions of the $[\nu_2, \nu_5, 2\nu_3]$ -vibrational-band triad, prepared by Brown (2001, 2002, 2003) and based upon the work of Chackerian *et al.* (1998b), has been newly archived for CH₃³⁵Cl and CH₃³⁷Cl.

COF₂: An update of the 1856.730–2001.348 cm⁻¹ region has been made thanks to a list generated by Brown (2001, 2002, 2003) based on an unpublished analysis of the line positions.

 HO_2 : Spectroscopic parameters for the ground state have been replaced by those generated on the basis of the work of Chance (1997, 2003).

The line parameters for each transition are stored following the new GEISA format standard with an extended number (from 16 to 30) of the selected line parameters, including associated error estimations. The file structure is presented in Table 2.3; symbolic field names are in the first line and field lengths and format descriptors in lines 2 and 3, respectively. The A–Q fields are similar to those described in Jacquinet-Husson *et al.* (1999) but with some extensions in the field lengths and differences in the format description; these differences are identified by a reminder of the former format in italics. The description of each field is given at the bottom of the table.

A summary of the GEISA-03 line transition parameters subdatabase content is given in Table 2.4. The items listed for each molecular species, given in column 1, are as follows: the identification code (ID codes defined for the GEISA management software), the number of lines, the intensity average (in cm molecule⁻¹), the mean half-width at half maximum (cm⁻¹ atm⁻¹ at 296 K), the identification codes of its various isotopes and for each isotope, the number of lines, the transitions minimum and maximum wavenumbers (in cm⁻¹), and the line intensities minimum and maximum values (in cm molecule⁻¹), in columns 2 to 11, respectively.

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Field name	Α	В	С	D	Е	F	G	I	J	K	L	М	Ν	0	Р	Q
Field length	12	11	6	10	36	4	3	3	1	2	1	10	5	8	3	6
Fortran descriptor	F12.6 (F10.6)	D11.4 (D10.3)	F6.4 (F5.3)	F10.4 (F10.3)	A36	F4.2	13	13	A1 (A3)	I2	I1	E10.3	F5.4	F8.6	13	16

Table 2.3	GEISA-03	line	parameters	record	format
1 4010 2.5	OPIDII 02	11110	parameters	100010	101 111011

1.	R	A'	B'	<i>C'</i>	F'	0'	R'	N'	S	S'	Т	T'	U	U'
	6	10	11	6	4	8	6	5	4	4	8	8	4	4
	F6.4	F10.6	D11.4	F6.4	F4.2	F8.6	F6.4	F5.4	F4.2	F4.2	F8.6	F8.6	F4.2	F4.2

A: Wavenumber (cm⁻¹) of the line

Intensity of the line in $(cm^{-1}/(molecule.cm^{-2})$ at 296 K B:

Air broadening pressure half-width (HWHM) (cm⁻¹atm⁻¹) at 296 K C:

D: Energy of the lower transition level (cm⁻¹)

Transition quantum identifications for the lower and upper state of the transition E:

F: Temperature dependence coefficient n of the air broadening half-width

G: Identification code for isotope as in GEISA

I: Identification code for molecule as in GEISA

J: Internal GEISA code for the data identification

K: Molecule number as in HITRAN

L: Isotope number (1=most abundant. 2=second...etc) as in HITRAN

Transition probability (in debye²) M: Self broadening pressure half-width (HWHM) (cm⁻¹ atm⁻¹) at 296 K (for water) N:

Air pressure shift of the line transition $(cm^{-1}atm^{-1})$ at 296 K 0:

P: Accuracy indices for frequency, intensity and half-width

Q: Indices for lookup of references for frequency, intensity and half-width

R: Temperature dependence coefficient n of the air pressure shift

Estimated accuracy (cm⁻¹) on the line position

A': B': Estimated accuracy on the intensity of the line in $(cm^{-1}/(molecule.cm^{-2}))$

Estimated accuracy on the air collision half-width (HWHM) (cm⁻¹ atm⁻¹) C':

F': Estimated accuracy on the temperature dependence coefficient n of the air broadening half-width

0': Estimated accuracy on the air pressure shift of the line transition (cm⁻¹atm⁻¹) at 296 K R': Estimated accuracy on the temperature dependence coefficient n of the air pressure shift

N': Estimated accuracy on the self broadened (HWHM) (cm⁻¹atm⁻¹) at 296 K (for water)

S: Temperature dependence coefficient n of the self broadening half-width (for water)

S': Estimated accuracy on the temperature dependence coefficient n of the self broadening half-width (for water)

T: Self pressure shift of the line transition (cm⁻¹ atm⁻¹) at 296 K (for water)

T': Estimated accuracy on the self pressure shift of the line transition (cm⁻¹ atm⁻¹) at 296 K (for water)

U: Temperature dependence coefficient n of the self pressure shift (for water) U': Estimated accuracy on the temperature dependence coefficient n of

the self pressure shift (for water)

The GEISA-97 format is recalled, in italic brackets, if different

Fields A to Q common to the former GEISA-97 edition format (Jacquinet-Husson et al. 1999)

> Fields R to U'new for GEISA-03

Fields R to U' added to GEISA/IASI-03 Table 2.4 GEISA-03 individual lines sub-database detailed content

Molecule	Mol. ID.	# lines	Intensity average (cm mol. ⁻¹)	Alpha average (cm ⁻¹ atm. ⁻¹)	Isot. ID	# lines	Minimum frequency (cm ⁻¹)	Maximum frequency (cm ⁻¹)	Minimum intensity (cm mol. ⁻¹)	Maximum intensity (cm mol. ⁻¹)
H ₂ O	-	58726	1.242E – 21	0.0712	161	36701	0.401	25232.004	1.010E-32	2.670E - 18
					181	7406	6.785	11246.170	$1.440 \mathrm{E} - 28$	$5.390 \mathrm{E} - 21$
					171	3874	6.471	11150.790	1.480E - 27	9.830E - 22
					162	10132	0.007	5507.548	$1.240 \mathrm{E} - 32$	$2.700 \mathrm{E} - 22$
					182	438	1173.772	1684.226	2.030E - 27	$5.080 \mathrm{E} - 26$
					172	175	1234.235	1598.765	2.030E - 27	9.320E - 27
CO_2	2	76826	1.470E - 21	0.0713	626	32692	436.123	9648.007	3.440 E - 39	3.530E - 18
					636	11122	494.472	8104.666	1.820E - 39	3.750E - 20
					628	17417	498.933	8132.007	1.390 E - 36	$6.840 \mathrm{E} - 21$
					627	10009	514.430	6961.226	$1.000 \mathrm{E} - 27$	1.250E - 21
					638	2312	567.596	4946.384	3.700E - 27	7.230E - 23
					637	1584	584.754	3641.072	3.710E - 27	1.360E - 23
					828	1107	615.974	3669.609	1.760E - 40	1.310E - 23
					728	288	626.438	2358.226	3.870E - 27	$2.500 \mathrm{E} - 24$
					838	295	2115.685	2276.481	$4.870 \mathrm{E} - 42$	1.760E - 25
03	ю	319248	$5.583 \mathrm{E} - 23$	0.0693	666	190832	0.026	4060.783	$3.904 \mathrm{E} - 29$	4.060E - 20
					668	19147	0.921	1177.493	4.692E - 28	7.760E - 23
					686	22211	1.177	2259.896	9.970E - 29	7.560E - 23
					667	58171	0.289	820.380	5.135E - 31	5.356E - 25
					676	28887	0.213	822.795	1.433 E - 31	5.827E - 25

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(Continued)	
Table 2.4	

Molecule	Mol. ID.	# lines	Intensity average (cm mol. ⁻¹)	Alpha average (cm ⁻¹ atm. ⁻¹)	Isot. ID	# lines	Minimum frequency (cm^{-1})	Maximum frequency (cm ⁻¹)	Minimum intensity (cm mol. ⁻¹)	Maximum intensity (cm mol. ⁻¹)
PH ₃	12	11740	2.315E – 21	0.0864	131	11740	17.805	2478.765	1.850E - 28	2.520E - 19
HNO ₃	13	171504	$6.879 \mathrm{E} - 22$	0.11	146	171504	0.035	1769.982	$3.490 \mathrm{E} - 27$	$3.020 \mathrm{E} - 20$
НО	14	42866	2.806E – 20	0.044	61 62 81	42711 90 65	0.005 0.010 0.053	35877.031 1.824 6.325	1.500E - 85 2.090E - 31 1.200E - 30	6.450E - 17 5.780E - 29 1.200E - 26
HF	15	107	6.773 E - 19	0.0407	19	107	41.111	11535.570	1.110E - 26	$1.440 { m E} - 17$
HCI	16	533	3.189E – 20	0.0403	15 17	284 249	20.270 20.240	13457.841 10994.721	1.090E - 26 1.010E - 26	$5.030 \mathrm{E} - 19$ $1.610 \mathrm{E} - 19$
HBr	17	1294	4.770E – 21	0.0429	11 19	642 652	16.232 16.237	9757.189 9758.565	1.530E - 32 9.450E - 33	1.180E - 19 1.210E - 19
IH	18	806	1.361E - 21	0.05	17	806	12.509	8487.305	$1.640 \mathrm{E} - 30$	$3.420 \mathrm{E} - 20$
CIO	19	7230	1.605E – 22	0.0873	56 76	3599 3631	0.028 0.015	1207.639 1199.840	1.520E - 29 5.090E - 30	$3.240 \mathrm{E} - 21$ $1.030 \mathrm{E} - 21$
ocs	20	24922	4.659E – 21	0.0896	622 624 637	14500 4764 2403	0.406 0.396 0.404	4118.004 4115.931 4012 467	1.560E - 25 6.400E - 27 1 720F - 27	1.220E - 18 4.720E - 20 1.200E - 20
					623	1802	509.007	4115.588	1.010E - 23	8.430E - 21
					822	1096	0.381	4041.565	2.620E - 28	$2.090 \mathrm{E} - 21$
					634	357	1972.188	2032.039	1.010E - 23	$5.240 \mathrm{E} - 22$

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Table 2.4	(Contin	(pən							
Molecule	Mol. ID.	# lines	Intensity average (cm mol. ⁻¹)	Alpha average (cm ⁻¹ atm. ⁻¹)	Isot. ID	# lines	Minimum frequency (cm ⁻¹)	Maximum frequency (cm ⁻¹)	Minimum intensity (cm mol. ⁻¹)
CH ₃ Cl	34	18344	4.370E – 22	0.0825	215 217	10039 8305	679.050 674.143	3172.927 3161 830	9.050E – 32 4 190F – 26
H_2O_2	35	100781	4.848E – 22	0.1076	166	100781	0.043	1499.487	5.090 E - 29
H_2S	36	20788	2.992E – 22	0.08	121 131 141	12330 3564 4894	2.985 5.601 5.615	4256.547 4098.234 4171.176	$\begin{array}{c} 1.450\mathrm{E}-26\\ 2.020\mathrm{E}-26\\ 2.020\mathrm{E}-26\\ \end{array}$
НСООН	37	3388	5.186E - 21	0.4	261	3388	1060.962	1161.251	2.140E - 22
COF_2	38	83750	2.105E - 21	0.0845	269	83750	725.006	2001.348	4.740 E - 24
SF_6	39	11520	4.551E - 21	0.05	29	11520	940.425	952.238	2.160E - 22
C_3H_4	40	3390	4.277E – 22	(*)	341	3390	290.274	359.995	2.020E - 23
HO_2	41	38804	6.846E - 22	0.1072	166	38804	0.173	3675.819	$1.000\mathrm{E}-26$
CIONO ₂	42	32199	8.768E – 23	0.14	564 764	21988 10211	763.641 765.212	797.741 790.805	1.240E - 24 6.340E - 25
	TOTAL	1668371	LINES						

Maximum intensity (cm mol. -1) (cm mol. -1) 3.540E - 20 5.610E - 20 1.360E - 19 5.990E - 21 1.080E - 21 1.080E - 21 1.080E - 21 3.940E - 20 3.940E - 20 3.940E - 20 3.180E - 21 2.740E - 20 3.180E - 21 2.740E - 20 3.180E - 21 1.500E - 20 3.180E - 20 3.180E - 20 3.180E - 21 1.500E - 20 3.180E - 20 3.180E - 20 3.560E - 2

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2.3.2 Subdatabase on absorption cross-sections

Infrared Cross-Sections: The GEISA-03 archive has been significantly enriched since the GEISA-97 issue. The spectral range has been extended from 200 cm^{-1} to 2000 cm^{-1} (from 556 to 1763 cm⁻¹, previously) and the number of molecules has increased, as well, from 23 to 35. The updated already-archived species are: CFC-11, CFC-12, CFC-14, HCFC-22, HCFC-123, HCFC-124, HFC-125, HFC-134a, HCFC-141b, HCFC-142b, HFC-152a, HCFC-225ca, HCFC-225cb, HFC-32, HFC-143a, HFC-134, N₂O₅, SF₆, ClONO₂. No update has occurred for CFC-13, CFC-113, CFC-114, CFC-115. Twelve molecular species are new for the GEISA-03 archive; these are HFC-143, HCFC-21, CCl4, C₂F₆, C₂H₂, C₂H₄, C₂H₆, C₃H₈, C₄F₈, HNO₄, SF₅CF₃, HCH-365mfc.

A summary of the GEISA-03 subdatabase on absorption cross-sections is given in Table 2.5. The molecular species names are listed in columns 1. In the three following columns (2 to 4) are the experimental conditions associated with the data files, i.e. the spectral range (cm^{-1}), the overall temperature range (K) and the total pressure range (Pa). If the pressure is set to zero, it means that the cross-sections have been measured for a pure vapour (non-air broadened) at different pressures for the same point or that the pure vapour cross-sections were extrapolated to zero pressure from a set of laboratory data. For each file, the number of associated temperature/pressure sets is in column 5 and the related references, in column 6. Reference 'GEISA-97' corresponds to molecules not updated since the archive described in Jacquinet-Husson *et al.* (1999).

Table 2.5 summarises the HITRAN-04 infrared cross-sections content too. GEISA specific molecular species or references are identified by an asterisk. Slant characters are used when references are different in HITRAN and in GEISA, for a common molecular species. Note that the original data for cross-sections contain some negative numbers, which was due to the noise in the recorded spectra. HITRAN made the choice to set all of the negative cross-sections to zero; GEISA made the choice to keep the integrity of the original data provided by their authors.

Ultraviolet and Visible Cross-Sections: In the spectral range 230–1333 nm, 11 molecular species, i.e. O_3 , NO_2 , BrO, OClO, OBrO, SO_2 , H_2CO , O_2 , $O_2 + N_2$, O_4 , CS_2 , have been archived, as summarised in Table 2.6 (organised as Table 2.5, with an extra seventh column giving the number of entries). These represent, as a whole, 164 temperature/pressure sets for a total of 12 958 953 entries. 'Undef' in column 4 corresponds to a missing pressure value.

2.3.3 Subdatabase on microphysical and optical properties of atmospheric aerosols

A GEISA aerosol subdatabase has been recently issued (see Jacquinet-Husson *et al.* 2003a for details). It includes microphysical and optical properties from published aerosol data catalogs from Massie (1994, 2003), Rublev (1994), Hess *et al.* (1998), Köpke *et al.* (1997) and Van de Hulst (1981). The overall content of this archive deals with complex refractive indices data and possibly computed optical related

Molecule	Spectral range (cm ⁻¹)	Temperature range (K)	Pressure range (Pa)	Number of T,P sets	References
CFC-11	210–2000	296	93325		Hurlev (2003): Christidis (1997) *
	500 - 1600	297	0	1	Smith (2003) *
	810-1120	190–296	1000-101325	55	Li and Varanasi(1994); Varanasi (2000)
CFC-12	850-1190	253–287	0	Э	Clerbaux (1993) *
	210 - 2000	296	93325	1	Hurley (2003) *
	800 - 1200	190–296	1000-101392	57	Varanasi and Nemtchinov (1994); Varanasi (2000)
CFC-13	765-1235	203–293	0	3	GEISA97
CFC-14	220 - 2000	296	93325	1	Hurley (2003) *
	1250 - 1290	180 - 296	1005 - 101458	55	Nemtchinov and Varanasi (2003a)
CFC-113	780-1232	203–293	0	9	GEISA97
CFC-114	815-1285	203–293	0	6	GEISA97
CFC-115	955-1260	203–293	0	6	GEISA97
HFC-32	204 - 2000	296	93325	1	Hurley (2003) *; Pinnock (1995) *
	995-1475	203–297	0 - 10000	17	Smith (2003)
HFC-125	700 - 1465	287	0	1	Clerbaux (1993)
	495–1504	203–293	0-80000	16	Di Lonardo (2000) *
	208 - 2000	296	93325	1	Pinnock (1995) *; Hurley (2003) *
HFC-134	210 - 2000	296	93325	1	Hurley (2003) *; Christidis (1997) *
	600 - 1700	203–297	0 - 10000	6	Smith (2003)
HFC-134a	815-1485	253–287	0	ε	Clerbaux (1993)
	203 - 2000	296	93325	1	Pinnock (1995) *; Hurley (2003) *
	600 - 1600	203–296	0 - 10000	15	Smith (2003) *
	1035 - 1340	190-296	2666-101376	33	Nemtchinov and Varanasi (2004)

 Table 2.5
 GEISA-03 and HITRAN-04 infrared cross-sections subdatabase

HFC-143	204 - 2000	296	93325	1	Pinnock (1995) *; Hurley (2003) *
HFC-143a	694 - 1504	203–293	0-800000	19	Di Lonardo (2000) *
	200 - 2000	296	93325	1	Pinnock (1995) *; Hurley (2003) *
	580-1500	203-297	0 - 10000	6	Smith (2003)
HFC-152a	700 - 1600	203–293	0-80000	16	Vander Auwera (2000b) *
	840 - 1490	253–287	0	ю	Clerbaux (1993)
	200 - 2000	296	93325	1	Pinnock (1995) *; Hurley (2003) *
HCFC-21	785 - 840	296	133	1	Massie et al. (1985)
HCFC-22	700-1500	203–293	0-80000	8	Vander Auwera (2003) * Ballard et al. (2000) *
	765-1380	253–287	0	ю	Clerbaux (1993)
	208 - 2000	296	93325	1	Pinnock (1995) *; Hurley (2003) *
	760-1195	181 - 297	2666-101936	51	Varanasi (1994, 2001))
HCFC-123	740–1450	253–287	0	б	Clerbaux (1993)
	204 - 2000	296	93325	1	Pinnock (1995) *; Hurley (2003) *
HCFC-124	675-1425	287	0	1	Clerbaux (1993)
	208 - 2000	296	93325	1	Pinnock (1995) *; Hurley (2003) *
HCFC-141b	209–2000	296	93325	1	Pinnock (1995) *; Hurley (2003) *
	710 - 1470	253–287	0	б	Clerbaux (1993)
HCFC-142b	650-1475	253–287	0	б	Clerbaux (1993)
	200–2000	296	93325	1	Pinnock (1995) *; Hurley (2003) *

Molecule	Spectral range (cm ⁻¹)	Temperature range (K)	Pressure range (Pa)	Number of T,P sets	References
HCFC-225ca	695-1420	253–287 206	0 03375	~~ - ~	Clerbaux (1993) Dimoch (1905), Hunley (2002)
HCFC-225cb	715-1375	253-287	0 20000	- m -	Clerbaux (1993) Clerbaux (1993) Direcole (1005) at IIdor (2003)
N2 05	540-1380	205–293 205–293	0	5	Wagner and Birk (2003) *, Huntey (2003) *
SF_6	650-2000	296	93325	1	Hurley (2003) *
	925–955	180–295	2693-101350	29	Varanasi (1994, 2001))
CIONO ₂	500-1330	190–297	0 - 15580	25	Wagner and Birk (2003)
	1265-1325	201–222	0	e	GEISA97
CC14	750-812	208–297	1070 - 101272	32	Nemtchinov and Varanasi (2003b)
C_2F_6	1061 - 1285	180 - 296	3320-101363	43	Zou et al. (2004)
	210 - 2000	296	93325	1	Highwood (1999) *, Hurley (2003) *
	600-2750	203–293	0-80000	15	Smith (2003) *
C_2H_2*	450–2000	296	93325	1	Highwood (1999) *; Hurley (2003) *
C_2H_{4*}	220–2000	296	93325	1	Highwood (1999) *; Hurley (2003)
C_2H_6*	220–2000	296	93325	1	Highwood (1999) *; Hurley (2003)
$C_{3}H_{8}*$	220–2000	296	93325	1	Highwood (1999) *; Hurley (2003)
C_4F_{8*}	500 - 1600	203–297	0-65000	19	Smith (2003) *
HNO ₄	770-830	268	93	1	Massie et al. (1985)
SF_5CF_3	600 - 2000	296	93325	1	Hurley (2003)
HCH-365mfc*	665–1480	287	0	1	Clerbaux (1993) *

Table 2.5 (Continued)

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Molecule	Spectral range (nm)	Temperature range (K)	Pressure range (hPa)	Number of T,P sets	References	Number of entries
$\overline{O_3}$	231–794	202–293	undef	5	BU	16500
-	230-830	203–293	100-1000	10		200000
	230-1070	203–293	50-900	5		21000
NO ₂	231-794	221-293	undef	4		13600
	230-830	223–293	100-1000	10		1358000
	230-900	203–293	100-150	5		16800
	238-1000	294	0	1	BIRA/IASB	13500
	238-1000	220–294	0-1.33	13		225000
	385-725	220–294	0-1013.23	27		9855000
BrO	300-385	203–298	undef	5	BU	25000
OClO	325-425	213-293	undef	10		132500
	290-460	293	900	1		1200
ObrO	385-616	298	undef	1		40500
SO_2	240-395	203–293	100	5		7000
	250-330	294	undef	2	BIRA/IASB	9600
H ₂ CO	250-400	293	4.10	1	BU	1400
O ₂	235-800	203–293	900–945	6		5990
	627-1290	223-290	100-1000	24	MSF/RAL	390360
	246-266	296	200	5		517495
	240-330	287–289	undef	2	BIRA/IASB	15560
$O_2 + N_2$	1000-1333	132–295	668-1009	12	MSF/RAL	50800
O4	333-666	294	undef	1	BIRA/IASB	12200
	454–667	223–294	1000	8	MSF/RAL	29040
CS_2	290-350	294	undef	1	BIRA/IASB	908

Table 2.6 GEISA-03 ultraviolet/visible cross-sections subdatabase

BU: Bremen University Molecular Spectroscopy and Chemical Kinetics Group (Orphal, 2003; Vandaele et al. 2002).

BIRA/IASB: Belgium Institute for Space Aeronomy (Vandaele et al. 2002).

MSF/RAL: Molecular Spectroscopy Facility/Rutherford Appleton Laboratory (Smith, 2003).

properties, for selected basic aerosol components. Software for data management and user-selected aerosol mixtures elaboration are available from the database too.

2.4 BEAMCAT

The well-known spectroscopic databases like the JPL catalog (Pickett *et al.*, 1998), HITRAN (Rothman *et al.*, 1998) or GEISA (Jacquinet-Husson et al., 1999) provide only part of the information that is necessary for the calculation of atmospheric spectra in the microwave region. The JPL catalog, for example, contains a large collection of molecular species and an exhaustive list of their spectral lines in the millimetre

and submillimetre domain. However, while it lists centre frequency and line strength with good accuracy, it does not contain any line broadening parameters that are also necessary for these calculations. The reason is probably that the target audience for this catalog are radio astronomers and not necessarily atmospheric scientists. The catalogs for atmospheric scientists, like HITRAN or GEISA, list these parameters but miss a lot of the molecular species that are included in the JPL catalog. Even for the common species they list only a fraction of the lines in the millimetre and submillimetre domain that are included in the JPL catalog. Besides that, the accuracy of the listed centre frequencies in the microwave region is limited by the data format in both these catalogs. The reason for that may be that the catalogs were designed with the needs of the infrared remote sensing community in mind.

The choice for a microwave remote sensing scientist used to be either a catalog like JPL that lacked line broadening parameters or a catalog like HITRAN or GEISA that missed many molecules and spectral lines and listed centre frequencies only with degraded accuracy. The usual workaround for that problem was to combine data from two or more catalogs and create a merged catalog (Chance *et al.*, 1994; Eriksson and Merino, 1997; Bauer *et al.*, 1998). The ideal merged catalog would list all necessary parameters and provide them from the source with the best quality. However, the process of creating such a merged catalog was anything but trivial and included several pitfalls:

- Line identification. Since the spectral line databases like the JPL catalog, HITRAN or GEISA are huge, the merging process should be completely automatic. However, the different data formats and different philosophies of the catalogs make it very difficult to build an algorithm that can accurately identify lines in several catalogs. In theory, lines should be identified by their quantum numbers. However, while that approach works well for some species it completely fails for others since the catalogs may list different sets of quantum numbers for the same species.
- *Quality selection.* Even if one is able to correctly identify spectral lines within two different catalogs, it is still another problem to automatically decide which catalog lists a certain parameter with better quality. This might be different for each listed line and it might even change over time as new data from various sources are incorporated into the source catalogs.
- *Errors and mismatches.* The merging process would most likely introduce some errors and mismatches. These mismatches could be corrected manually but the corrections would be lost when the merging process has to be repeated.
- *Handling updates*. Updates in the source catalogs would make it necessary to produce a new merged catalog version. However, since this would be a complex task every time, frequent updates would not be possible.
- *Lost information*. All the existing merged catalogs throw away information during the merging process by preferring parameters from one catalog over the corresponding parameters from the other catalog. This lost information cannot be recovered from the merged catalog any more.

An alternative that avoids most of the problems of a merged catalog is a meta catalog. Unlike a merged catalog, a meta catalog does not contain spectral line parameters

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Figure 2.1 Concept of the meta catalog. Unlike a merged spectral line catalog, the meta catalog provides links between identical quantum-mechanical transitions listed in different catalogs (A and B in this case). The meta catalog itself does not contain any spectral parameters. It rather provides an index to where the parameters for a certain spectral line can be found in each of the catalogs A and B. The concept works with any number of catalogs (reprinted from Dietrich G. Feist: The Bernese Atmospheric Multiple Catalog Access Tool (BEAMCAT): a tool for users of popular spectral line catalogs, Journal of Quantitative Spectroscopy and Radiative Transfer, 85(1), pp. 57–97, Copyright (2004), with permission from Elsevier)

itself. Instead, it contains information that describes which spectral line in one catalog corresponds to a spectral line in one or more other spectral line catalogs. In other words, the meta catalog provides links between matching spectral lines in different catalogs. Figure 2.1 illustrates the concept. By following these links, merged spectral line catalogs can be generated from the meta catalog on-the-fly. The pitfalls of merged catalogs do not apply to a meta catalog:

- *Line identification.* For the meta catalog, it is not important how a link between two matching lines was established. Therefore, it is not necessary to build an algorithm that can automatically identify lines in several catalogs. Links could even be created or corrected manually.
- *Quality selection*. There is no need to select the quality of parameters when the links are created.
- *Errors and mismatches.* Errors and mismatches can easily be corrected by removing or changing the link between two mismatched lines.

Handling updates. Updates in the source catalogs only affect the spectral line parameters and not the links between the lines in different catalogs. Only additional lines in the source catalogs would have to be checked after an update. *Lost information.* No information would be lost since all the information is available from the source catalogs.

Besides that, a meta catalog has several additional advantages over a merged catalog:

- the concept is not limited to two catalogs. A meta catalog could contain link information for any number of spectral line catalogs. This solves the problem of how to best combine a small set of good-quality spectral lines with background spectral lines from the large catalogs;
- most data format issues with spectral line databases become irrelevant as merged databases can be created from the meta catalog in arbitrary formats;
- a meta catalog allows different versions of spectral line databases to be used together.

BEAMCAT is a spectral line meta catalog that was developed at the Institute of Applied Physics at the University of Bern (Feist, 2004). It resides on a MySQL database server and can be accessed either through a web interface or directly through a MySQL client on the user's computer. Since MySQL is free software, clients are available for almost any platform and operating system. Interfaces are available for most programming and scripting languages so users can access the BEAMCAT database server directly from their applications.

BEAMCAT is provided as a free service to the scientific community. The website at www.beamcat.org contains information on how to use the catalog. Users can download merged spectral line data directly from the web site or sign up to receive a free user account for the BEAMCAT MySQL server. With a user account, they can access the MySQL server directly through a local MySQL client or through programs in their favourite programming language. Registered users will also be informed about new developments around the BEAMCAT database.

One of the first applications of BEAMCAT was an extensive intercomparison of spectral line data from the JPL catalog and HITRAN (Feist, 2004). This intercomparison between roughly 148 000 spectral lines that exist both in HITRAN and the JPL catalog points out several problems with the spectral line data in those two catalogs. The article also provides detailed information on how BEAMCAT works internally and how the line matching between the JPL catalog and HITRAN was accomplished.

2.5 Atmospheric radiative-transfer simulator

The atmospheric radiative-transfer simulator, ARTS (Buehler *et al.*, 2005b), is a public domain project which was initiated jointly by the University of Bremen, Germany and Chalmers University, Gothenburg, Sweden. The aim was to create a radiative-transfer code that is as general and flexible as possible, while at the same time being

portable and user-friendly. The program itself is written in C^{++} , but is accompanied by interface functions and helper functions in IDL and Matlab. The complete source code, along with extensive documentation, is freely available on the Internet, under www.sat.uni-bremen.de/arts/.

There are two versions of ARTS, a clear-sky version (current version at the time of writing 1-0-173) and a version with scattering (current version at the time of writing 1-1-912). The 1-0-x version simulates scalar radiative transfer (total intensity only) in a one-dimensional spherical atmosphere. The 1-1-y version simulates vector radiative transfer (1 to 4 Stokes components) in a one-dimensional or three-dimensional spherical atmosphere. It is planned that at some time in the future the 1-0-x version will disappear, when the 1-1-y version is considered sufficiently stable for operational work and when all features of absorption calculation that are now available in the 1-0-x version have been ported to the 1-1-y version. The text here describes the 1-0-x version; for information on the 1-1-y version of ARTS see Chapter 3.

The primary vertical coordinate in ARTS is pressure. All other quantities, such as temperature, geometric altitude and trace gas concentrations, are given on pressure grids. The model can be used to simulate measurements for any observation geometry: up looking, down looking or limb looking; and for any sensor position: on the ground, inside the atmosphere or on a satellite. It has been developed having passive emission measurements in mind, but pure transmission measurements are also handled.

ARTS works with arbitrary frequency grids; hence, it can be used both for the simulation of high-resolution sensors and for the simulation of broad frequency ranges. The applicable spectral range is from the microwave up to the thermal infrared, but so far it has been mostly used for the frequency region roughly below 1 THz. In that frequency range, particular care has been taken to make the absorption calculation consistent with state-of-the-art continuum models for water vapour and nitrogen, and with continuum and line mixing models for oxygen.

Absorption coefficients can be calculated in ARTS by a combination of line-byline calculation (using external or built-in spectroscopic data) and various continua. Supported external spectral line catalog formats are JPL (Pickett *et al.*, 1998), HITRAN (Rothman *et al.*, 2003) and MYTRAN (Bauer *et al.*,1998), as well as a native catalog format, as described by Buehler and Eriksson (2000). For the temperature conversion of the line strength, partition functions are calculated from an internal polynomial representation, which is taken from the TIPSdst97 FORTRAN program (Gamache *et al.*, 2000) for those species included in TIPS. For the other species, a polynomial fit to the tabulated partition function values of JPL is used. Where not even that is available for some isotopic species, the partition function from the main isotope is used. For a discussion on the impact of different partition function sources on the forward model and retrieval accuracy see Verdes *et al.* (2005). For a detailed list of the partition function source that is used by ARTS for each species see Buehler *et al.* (2005b).

All standard line shape functions can be used (Lorentz, Doppler, Voigt, Van–Vleck–Weisskopf). The recommended line shape function is a hybrid between Voigt and Van–Vleck–Weisskopf, behaving like the former in the low pressure limit

and like the latter in the high pressure limit. It is discussed in more detail in Buehler *et al.* (2005b). In addition to the line spectrum, ARTS can use any of the following continuum absorption models: MPM (Liebe and Layton, 1987; Liebe, 1989; Liebe *et al.*, 1993), PWR (Rosenkranz, 1993, 1998), CKD (Clough *et al.*, 1989), the model by Ma and Tipping (2002) and the model by Cruz Pol *et al.* (1998). For some of these models it is up to the user to use only the continuum part along with an external line catalog or to also use a model-specific built-in line list. The latter is safer for inexperienced users, since line-by-line calculation and continuum model must fit together in order to give the right total absorption and cannot be combined arbitrarily. For details on the available options see Buehler *et al.* (2005b).

The radiative transfer in ARTS-1-0-x is calculated in equal distance steps along the line of sight, assuming a spherically symmetric atmosphere. The absorption coefficients at line-of-sight grid points are interpolated (linearly in log pressure) from absorption coefficients pre-calculated on a sufficiently fine pressure grid. Besides providing sets of spectra, ARTS can calculate Jacobians for a number of variables. Analytical expressions are used to calculate Jacobians for trace gas concentrations, continuum absorption and ground emissivity. Perturbations are used to calculate Jacobians for pointing and frequency offsets and spectroscopic parameters. For temperature Jacobians, the user can choose between an analytical method, which does not assume hydrostatic equilibrium, and a perturbation method, which does assume hydrostatic equilibrium.

ARTS itself calculates only monochromatic pencil beam radiances; no sensor characteristics are included. The sensor part is covered by a set of Matlab functions that make use of a matrix vector formalism (Eriksson *et al.*, 2005a,b).

Melsheimer et al. (2005) describe an intercomparison of eight clear-sky radiativetransfer models, including ARTS. The aim of the exercise was to compare a number of radiative-transfer models for atmospheric sounding in the millimetre and submillimetre wavelength range and to check their consistency and mutual deviations. The intercomparison dealt with three different aspects of the radiative-transfer models: (1) The inherent physics of gaseous absorption lines and how they are modelled, (2) the calculation of absorption coefficients and (3) the full calculation of radiative transfer for different geometries. The correctness and consistency of the implementations was tested by comparing calculations with pre-defined input such as spectroscopic data, line shape, continuum absorption model and frequency grid. It was found that the absorption coefficients and brightness temperatures calculated by the different models are generally within about 1 per cent of each other. In a second step, the variability or uncertainty of the model results is estimated if – except for the atmospheric scenario – the input such as spectroscopic data, line shape and continuum absorption model was varied. Here, the models deviate from each other by what amounts to about 10 per cent around the centre of major absorption lines. The main sources of such discrepancies are the variability of the reported spectroscopic data for the line absorption and in the continuum absorption model. Further possible causes of discrepancies are different frequency and pressure grids and differences in the corresponding interpolation routines as well as differences in the line shape functions used.

2.6 Atmospheric transmission at microwaves

The atmospheric transmission at microwaves (ATM) model has been in continuous development for 20 years (see the first report, Cernicharo 1985). It was first developed for ground-based astronomy applications and later extended for remote sensing applications. Besides model development, the ATM team has devoted a great effort to validation and measurement of continuum terms (Pardo *et al.*, 2001a, 2005a) in the submillimetre domain. Attention has been paid to modelling the real part of the atmospheric refractivity because of its impact on ground-based interferometry. The ATM model was part of an intercomparison including nine microwave models (Garand *et al.*, 2001). Scattering of atmospheric radiation by hydrometeors has been included in the model and several studies have been conducted (Prigent *et al.*, 2001, 2005; Wiedner *et al.*, 2004).

The gaseous absorption algorithm and its coupling to specific 'cloud' and 'surface' routines in ATM have been programmed in FORTRAN 90. Information on the code can be found at www.damir.iem.csic.es/ATM/atmmain.htm. The executable is available upon request. The gaseous absorption and phase delay in ATM was described in detail in Pardo *et al.* (2001b), whereas the scattering part was presented and used for the first time to study real data in Prigent *et al.* (2001). The potential contribution of the surface, ocean or land, can also be calculated. For the ocean, a geometric optics model is adopted (Guillou *et al.*, 1996) coupled to recent measurements of the sea water dielectric properties (Guillou *et al.*, 1998). The land-surface emissivities between 15 and 200 GHz can be deduced from pre-calculated emissivity atlases derived from satellite observations (Prigent *et al.*, 1997, 2000).

Frequency and pressure grids, geometry and surface type can be fully defined by the user. If due to one or more of these parameters (ocean surface or proximity to Zeeman-affected O_2 lines for example) different polarisations need to be treated separately, the code will use the appropriate transfer equation. Some additional information may then be necessary. For example, geographical location and orientation of the antenna are necessary to use the correct geomagnetic field and its angle with respect to the path for Zeeman calculations near O_2 lines. The description of this part of the code can be found in Pardo *et al.* (1995, 1998, 2002). The line-by-line opacity is calculated as described in this chapter, with Lorentz, Gaussian, Voigt, Van Vleck–Weisskopf and Zhevakin–Naumov line shapes available, and using a line data base created by J. Cernicharo using the most recent Hamiltonians found in the literature (see Table 1 in Pardo *et al.*, 2001a), although for the dominant (in the troposphere) H₂O and O₂ contributions, specific results obtained by the ATM team's ground-based Fourier transform spectroscopy (FTS) experiment (see Pardo *et al.*, 2001a, and Section 2.11.2) have been incorporated.

Due to its primary development for use in opacity estimates and calibration procedures at ground-based millimetre and submillimetre observatories, the ATM team has defined a set of basic atmospheric parameters that can easily be measured or estimated for real-time use at the observatory: ground temperature, ground pressure, ground relative humidity, water vapour scale height, tropospheric temperature lapse rate and water vapour zenith column. Due to the impossibility of measuring vertical

profiles of minor gases in real time and their much smaller impact on the calibration of millimetre and submillimetre astronomical observations, standard profiles for the given latitude are assumed. Based on these parameters, a series of calibration equations have been described (Serabyn *et al.*, 1998; Pardo *et al.*, 2005b) that allow reaching absolute flux calibrations better than 5 per cent in the submillimetre, necessary for future instruments such as the Atacama Large Millimetre Array (see www.alma.nrao.edu). Specific routines have been developed for retrievals of water vapour zenith column from radiometric measurements (Pardo *et al.*, 2004) and its use to predict atmospheric opacities and phase delays over a wide range of frequencies. The phase delay is derived from the real part of the refractivity, which, in turn, is simply obtained from the imaginary part (related to absorption) by applying the Kramers–Kronig theory (see Section 5.1).

The most specific contribution of the ATM team to the current status of atmospheric absorption models has been the study of excess absorption (compared to the resonant or line-by-line absorption), especially at high frequencies (\sim 300– 1600 GHz). Figure 2.2 illustrates real data of the atmospheric spectrum seen from the ground in the 150–1080 GHz frequency range and the different opacity terms that account for the measurements, according to an analysis made with the ATM model.

2.7 RTTOV-8

RTTOV is a radiative-transfer model for very rapid calculations of top-of-atmosphere radiances for a range of space-borne infrared and microwave radiometers as listed in Table 2.7. The original basis for the RTTOV fast computation of transmittances is described by Eyre and Woolf (1988). This was successively modified for later versions of RTTOV by Eyre (1991), Rayer (1995), Saunders and Matricardi (1999) and most recently Matricardi (2003). The recent developments of RTTOV (versions 6–8) have been carried out as part of a collaboration between the Met Office (UK), MétéoFrance and ECMWF in the framework of the EUMETSAT funded NWP Satellite Application Facility. The latest version of RTTOV is RTTOV-8 and was released in mid 2004. In summary RTTOV-8 has the following features:

- It comprises forward, tangent linear, adjoint and K (full Jacobian matrices) versions of the model, the latter three modules for variational assimilation or retrieval applications.
- Top-of-atmosphere radiances, brightness temperatures and layer-to-space plus surface-to-space transmittance for each channel are output for a given input atmospheric profile. There are also other layer-to-space and layer-to-surface radiances output for computing cloudy radiances. In the microwave range, RTTOV-8 approximates the line-by-line models of Liebe (1989) for H₂O absorption and Liebe *et al.* (1992) for O₂ absorption.
- It takes about 0.5 ms to compute radiances for 20 HIRS channels for one profile on a HP workstation.

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Figure 2.2 FTS zenith atmospheric opacity spectra obtained in 2000 from the top of Mauna Kea, HI at 4200 m and opacity contributions (binned to the resolution of the spectra, 0.9 Ghz in 3/18/00 and 0.115 Ghz in 7/16/00) that fit the measurements. Meteorogical data from a weather station at the site and radiosonde data from nearby Hilo airport were used as a priori information for a fit with only one free parameter, the zenith water vapour column. The resulting values from each fit are stated in the figure

- The input profile must have temperature and water vapour concentration. Optionally ozone and carbon dioxide can also be variable gases.
- It can compute sea surface emissivity for each channel internally or use a value provided by the user. For the infrared the ISEM-6 model is used. For the microwave the FASTEM model (see Chapter 4) is used.

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- Cloud top pressure and effective cloud amount can also be specified for simple single-layer cloudy radiance calculations.
- There is a 'wrapper code' which allows RTTOV to be used to compute more complicated multi-layer cloudy radiances (RTTOV_CLD) with various overlap assumptions.
- There is a new 'wrapper code' which allows RTTOV to be used to compute rain affected microwave radiances (RTTOV_SCATT).
- It can reproduce the results for RTTOV-7 (except for RTTOV_CLD).
- It supports all the sensors given in Table 2.7 for all the platforms the sensor has flown on.
- It is written in Fortran-90 and run under unix or linux.
- It has been tested on a range of platforms including linux PCs.

All the details on the model and how to request a free copy of the software are at www.metoffice.com/research/interproj/nwpsaf/rtm.

2.8 MPM and MonoRTM

A widely cited model for the microwave frequency range is MPM (millimetre-wave propagation model) developed by H. J. Liebe and co-workers (1977–93). The model underwent numerous revisions during the years that Liebe was active and Table 2.8 summarises the major changes with dates of publication. The code includes absorption by N_2 and cloud liquid water/ice, in addition to that of O_2 and H_2O . Zeeman splitting is included in a related but separate code, ZPM (Zeeman propagation model). Rosenkranz (1998) examined the laboratory measurements of H_2O continuum absorption that were available at the time, and recommended a further revision, referred to below as R98, which combines the foreign-broadened component of the H_2O continuum from MPM87 and the self-broadened component of the H_2O continuum from MPM93 with the O_2 line parameters from MPM92.

MonoRTM (Clough *et al.*, 2005) is a code with H_2O continuum based on the modelling work of Clough *et al.* (1989). It thereby achieves self-consistency across the microwave, submillimetre and infrared spectral regions. The code also includes absorption by O_2 , O_3 , N_2 , N_2O , CO, SO_2 , NO_2 , OH and cloud liquid water.

2.9 Laboratory and theoretical work

2.9.1 Line parameters

As a general rule, the large spectroscopic databases contain calculated values of line intensities. Different calculations typically agree to within ~ 1 per cent. Line frequencies are derived from fitting a theoretical model to measured frequencies, which generally yields agreement much better than required for atmospheric applications, often as close as tens of kHz, depending on the molecule. Calculation of
Sensor	RTTOV id	Sensor Channel #	RTTOV-8 Channel #
HIRS	0	1 to 19	1 to 19
MSU	1	1 to 4	1 to 4
SSU	2	1 to 3	1 to 3
AMSU-A	3	1 to 15	1 to 15
AMSU-B	4	1 to 5	1 to 5
AVHRR	5	3b to 5	1 to 3
SSMI	6	1 to 7	1 to 4
VTPR1	7	1 to 8	1 to 8
VTPR2	8	1 to 8	1 to 8
TMI	9	1 to 9	1 to 5
SSMIS	10	1 to 24*	1 to 21
AIRS	11	1 to 2378	1 to 2378
HSB	12	1 to 4	1 to 4
MODIS	13	1 to 17	1 to 17
ATSR	14	1 to 3	1 to 3
MHS	15	1 to 5	1 to 5
IASI	16	1 to 8461	1 to 8461
AMSR	17	1 to 14	1 to 7
MVIRI	20	1 to 2	1 to 2
SEVIRI	21	4 to 11	1 to 8
GOES-Imager	22	1 to 4	1 to 4
GOES-Sounder	23	1 to 18	1 to 18
GMS imager	24	1 to 3	1 to 3
FY2-VISSR	25	1 to 2	1 to 2
FY1-MVISR	26	1 to 3	1 to 3
CriS	27	TBD	TBD
CMISS	28	TBD	TBD
VIIRS	29	TBD	TBD
WINDSAT	30	1 to 10	1 to 5

Table 2.7Instruments supported by RTTOV-8 as of 1 June 2004.
Sensors in italics are not yet supported by RTTOV-8 but
will be in the future

*Channels 19-21 are not simulated accurately.

line widths and shifts involves the interaction between an absorbing molecule and a perturbing molecule and is therefore more complex. Modern calculations often yield agreement with measured widths to within a few per cent, but this depends on the quality of the model for the intermolecular potential. It is probably debatable whether calculations or measurements are more reliable as a source for line width parameters in models. Traditionally modellers have tended to favour measured values when they are available, although calculations have the advantage of being able to yield

Table 2.8	Evolution of O_2 and H_2O line and continuum
	parameters in the millimeter-wave propaga-
	tion model of Liebe (1977–1993). The O_2
	parameters include line-mixing coefficients

Year of publ.	O ₂ parameters	H ₂ O lines	H ₂ O continuum
1977	М	0	0
1978	М	_	_
1981	R	0	_
1984	_	0	М
1987	_	0	Μ
1989	R	0	_
1992	М	_	_
1993	R	0	0

M: new measurements by Liebe and co-workers.

R: revised analysis of earlier measurements by Liebe and co-workers.

O: revision based on measurements by others.

-: no change from previous version.

mutually consistent results for molecules that have numerous lines. The width values actually contained in the large databases come from a variety of sources; in some cases they are merely extrapolated from other lines of the same molecule. Hence, for applications that depend on the precision of line parameters, the modeller needs to trace the source of the values being used. HITRAN and GEISA now provide indices to assist in the lookup of references.

A line-parameter database for selected windows in the 294–626 GHz range was created by Perrin *et al.* (2005), who made an effort to analyse and collect the most reliable values from general-purpose catalogs and the published literature for twenty molecules of interest in a limb-sounding experiment. New measurements of some H₂O, CO, O₃, BrO, ClO, N₂O and HNO₃ lines were also made for this database (Bauer *et al.*, 1998; Demaison *et al.*, 2004).

Table 2.9 compares calculations by Gamache and Fischer (2003) of pressure broadening and shift coefficients for the 183 GHz H₂O line with three recent sets of measurements. The values of the broadening coefficient lie within roughly a 10 per cent range, and the calculated and measured line shifts also show reasonable agreement, considering the difficulty of measuring such small shifts. For air, one would use a (0.79, 0.21) weighted average of the N₂ and O₂ coefficients. Colmont *et al.* (1999) measured N₂- and O₂- pressure-broadening coefficients for the 325 GHz H₂O line, obtaining agreement within 3 per cent with calculated values. However, the relatively small uncertainties associated with their measurement of line widths led to proportionally greater uncertainty in the temperature dependence (represented as T^{-n}) of the widths, e.g. $n = 0.63 \pm 0.22$ for H₂O broadened by N₂. There is a consequent extrapolation uncertainty in modelled absorption when, as in this

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in parentheses are the estimated standard errors in the final digit. HWHM = half-width at half-maximum $T(K) N_2$ -HWHM N_2 -shift O_2 -HWHM O_2 -shift

Recent measurements and calculations of the 183 GHz H_2O line halfwidth and shift, with N_2 and O_2 as perturbing molecules. Values

	I (K)	(MHz/Torr)	(MHz/Torr)	(MHz/Torr)	(MHz/Torr)
Bauer et al. (1989)	300	4.07(7)		2.54(2)	
Goyette and De Lucia (1990)	300	4.19(15)		2.77(10)	
Golubiatnikov (2005)	302	4.230(7)	-0.092(10)	2.580(5)	-0.097(5)
Gamache and Fischer calculated (2003)	296	4.41	-0.140	2.46	-0.099

Note: 1 Torr = 133.322 Pa.

Table 2.9

case, the temperature range of the laboratory measurements does not overlap that of atmospheric temperatures. Pressure-broadening and shift of the 556 GHz H₂O line by N₂ and O₂ was measured by Markov and Krupnov (1995); also, self-broadening and shift parameters were measured by Markov (1994) for the 439 GHz H₂O line and by Podobedov *et al.* (2004) for six strong H₂O lines in the range of 380–1542 GHz.

Tretyakov *et al.* (2005) measured the pressure-broadened widths of oxygen lines near 60 GHz and also obtained revised values for the line-mixing coefficients. Their line widths are 3–4 per cent larger for air broadening than the earlier measurements of corresponding lines by Liebe and Gimmestad (1978) and thus are intermediate between the line-width values used in MPM92 and those in MPM93. Line intensities were also updated to the newer HITRAN values. Neither group of spectroscopists found any measurable pressure-shifting of the O₂ lines, but Tretyakov *et al.* (2004) succeeded in measuring a line-mixing coefficient at 118.75 GHz, where the effect of line mixing is much smaller than in the 60 GHz band. Pressure-broadened widths of the submillimetre lines of O₂ were measured by Golubiatnikov and Krupnov (2003).

2.9.2 Continuum absorption

In the far wings of lines and atmospheric windows, radiative transfer models require a description of what is now known as water-vapour continuum absorption. The continuum is defined as the difference between observed absorption and what can be described by conventional line profiles, such as Van Vleck–Weisskopf. This empirical continuum is dependent on the number of lines considered and their shape, which may or may not incorporate a cutoff; what is not accounted for as line absorption becomes continuum. There is general agreement that the continuum contains two components, one proportional to the square of water-vapour partial pressure and the other proportional to the product of water-vapour and dry-air partial pressures.

However, there are large differences among empirical models for the frequency and temperature dependence of these two components.

Several possible causes of the H_2O continuum have been proposed, among them (1) the inadequacy of analytic line shapes at frequency displacements of hundreds of GHz from the centres of the extremely strong far-infrared lines, (2) a possible spectral contribution from water dimers, clusters of molecules or weakly bound complexes, (3) collision-induced absorption and (4) co-operative absorption by pairs of molecules.

Theoretical work on the continuum has made some progress (e.g. Ma and Tipping, 1990, 2002; Hudis *et al.*, 1991, 1992) but at the present time, theoretical calculations are in the status of being validated by measurements, rather than vice versa, even though the measurements do not present an entirely consistent picture. Working with the far-wing line shape hypothesis for H₂O–H₂O collisions, Ma and Tipping (1990) were able to reproduce the approximate magnitude of the (H₂O vapour)² component in MPM89, but the calculated dependence on frequency and temperature was not separable into a product form, as in MPM. At 239 GHz, their calculation was ~15 per cent less than the absorption measured by Bauer *et al.*(1995). For H₂O–N₂ collisions, Ma and Tipping (2002) calculated absorption intermediate between MPM89 and MPM93, with temperature dependence close to that of MPM93.

Bauer and Godon (2001) measured absorption at 239 GHz by H_2O mixed with N_2 , CO_2 , Ar, CH_4 , C_2H_4 and C_2H_6 and found that the H_2O -dependent absorption is proportional to the square root of the collision-induced absorption by the perturber gas alone. They interpret this result as evidence in favour of the collision-induced hypothesis for the H_2O continuum. However, Brown and Tipping's (2003) theoretical calculation of H_2O-N_2 collision-induced absorption in the range 400–2000 cm⁻¹ is approximately two orders of magnitude less than the observed continuum, implying that the contribution of induced dipole moments is negligible. These computations have not yet been extended to the microwave range.

Kuhn *et al.* (2002) measured absorption at 350 GHz in pure H_2O vapour and in H_2O mixed with N_2 . From these measurements and earlier ones at 153, 213 and 239 GHz, they derived an H_2O continuum model for use with each of several line-parameter databases, with and without cutoff of the line shape function.

Boissoles *et al.* (2003) calculated collision-induced absorption for N_2-N_2 , N_2-O_2 and O_2-O_2 molecular pairs for frequencies up to 12 THz (400 cm⁻¹). They obtained an adjustment factor for air versus pure N_2 that was nearly constant at 1.34 up to \sim 3.6 THz, close to Pardo *et al.*'s (2001a) experimental value of 1.29, which was derived from observations on Mauna Kea, HI.

Calculation of collision-induced absorption is complicated, but Figure 2.3 shows that its frequency dependence can be approximated, up to ~ 2 THz, by an analytic function. The data points in the figure plot absorption divided by (frequency)², calculated from the model of Borosov and Frommhold (1986) for N₂. Including the factor of 1.34 to account for O₂, collision-induced absorption by dry air can be calculated as

$$\gamma_{\rm a}(\nu) = 8.7 \times 10^{-14} p_{\rm dry}^2 \nu^2 \left[0.5 + \frac{0.5}{1 + (\nu/450)^2} \right] (300/T)^{3.6}$$
(2.6)

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Figure 2.3 Absorption in pure N_2 , divided by $(frequency)^2$ and normalised. Asterisks – 296 K; circles – 220 K

where $\gamma_a(\nu)$ is the absorption coefficient in km⁻¹, ν is frequency in GHz (< 2000), p_{drv} is the pressure of the dry-air components in hPa and T is temperature in kelvin.

2.10 Modelling and validation issues

The 22 GHz line of H₂O in the atmosphere is less than opaque at its centre. During the 1990s, several experiments that compared ground-based radiometer measurements in the vicinity of this line with calculations from radiosondes showed that the line appeared to be stronger than calculated. Some modellers (Liebe et al., 1993; Cruz Pol et al., 1998) adjusted the line intensity to reproduce these measured brightness temperatures. Later, it was determined that on a type of radiosonde widely used during this period, the humidity sensor absorbed contamination from the sonde package material during storage and as a result yielded low-biased relative humidities (Wang et al., 2002). Turner et al. (2003) found that correction of radiosonde humidities for this bias resulted in close agreement in the mean with radiometric determination of total precipitable water vapour (PWV), although there remained significant variations of radiosondes within calibration batches. Recent experiments (Cimini et al., 2003) have shown that radiative-transfer calculations using radiosondes of more modern design agree more closely with theory (R98 model). Soden et al. (2004), using satellite-based infrared and ground-based lidar measurements, found that both types of radiosonde underestimated humidity at pressures less than 500 hPa, even when known corrections were applied to the older type; however, even if this

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is true, the results of Cimini *et al.* and Turner *et al.* can be explained by the fact that the upper part of the atmosphere contributes very little to brightness temperatures observed at the ground.

Gamache *et al.* (1994) surveyed and compared ~4000 published infrared and microwave measurements of H₂O line widths broadened by various perturbing gases. They concluded that experimentalists frequently underestimate uncertainties in measurements, sometimes ignoring the possibility of systematic errors. They estimate that as a general rule, most H₂O line widths are uncertain by 10–15 per cent (2 standard deviations) for broadening by dry air components and 20–25 per cent for self-broadening. Although this rather pessimistic conclusion may be justified as a general rule, it does not consider that measurement techniques tend to improve over time. Gamache *et al.* also identified lines, among them those at 22 and 380 GHz, for which the uncertainties were evaluated as less than 5 per cent.

Although H_2O line and continuum absorption are generally treated separately in models, the derivation of the continuum is linked to a line absorption model. The continuum is really an empirical correction added to the line model to obtain agreement with some particular set of measurements. As a consequence of this refitting to data involved in derivation of the continuum, errors in the combination of lines and continuum at window frequencies, where the continuum is dominant, result from the data used and the fitting procedure rather than from the line parameters. The question of cause of the H_2O continuum does not affect the accuracy of these empirical models, except that they usually represent the frequency and temperature dependence of the continuum by separate functions, which may be an oversimplification.

Uncertainties in line and continuum parameters affect calculated brightness temperatures in various ways, depending on frequency, atmospheric state and conditions of observations. For example, an increase in a water line width by x per cent will reduce its opacity at line centre by x per cent but increase the line's opacity in its far wings by x per cent. The latter opacity may be smaller than the continuum contribution, however. Although the greatest sensitivity of upwelling brightness temperature to H₂O opacity occurs in the semi-transparent parts of the spectrum and over an ocean surface, it is also true that for sounding applications, an error in opacity per unit of water translates into an equivalent and opposite error in inferred water vapour at the corresponding sounding altitude.

Oxygen line-mixing coefficients in MPM92 were determined by adjusting them to fit the difference between measurements and absorption calculated using the Van Vleck–Weisskopf line shape with previously-measured line widths. MPM92 was based on a much larger set of laboratory measurements than previous versions of MPM. The measurements were estimated to have an accuracy of ± 2 per cent rms for the higher rates of absorption, and in general MPM92 fits the laboratory data to within the experimental scatter; systematic departures of the model from the measurements (by as much as 20 per cent at 50 GHz, though there is considerable scatter in the data at this frequency) are visible in Figures 5 and 6 of Liebe *et al.* (1992), but only at the highest pressure (1013 hPa) and lowest temperature (6°C), consequently the highest density, measured. Some of the atmospheric measurements described in the next section address the question of how well the MPM92 model extrapolates to temperatures lower than 6° C and frequencies outside of 50–70 GHz. In MPM93, the line widths between 50 and 70 GHz were adjusted upward by 5 per cent, with a compensating adjustment of the mixing coefficients; this change slightly improved the fit of the model at low pressures.

There are some anomalies in submillimetre line parameters in MPM. The intensities of H₂O lines at 548, 552 and 923 GHz in MPM93 are stronger than HITRAN values by factors of 10, 82 and 12, respectively, for unknown reasons. In MPM85-93, the intensity of the 774 GHz O₂ line is 17 per cent stronger than in HITRAN, and the temperature dependence of the submillimetre O₂ line widths is $T^{-0.2}$ at constant pressure, compared to $T^{-0.8}$ for the millimetre lines. This temperature dependence was however based on a measurement of the 425 GHz line width by Pickett *et al.* (1981).

2.11 Comparisons of model predictions with atmospheric measurements

Atmospheric absorption models are based on theoretical calculations, approximations and assumptions and laboratory measurements. Laboratory measurements allow the state of a gas to be varied in a controlled way. That makes it easier to isolate the influence of each model input, which is often difficult in nature. As the sampling can be controlled, it is also much easier to ensure that observations of model inputs and outputs are representative in a laboratory environment, though it may not be possible to explore the full range of parameter space that occurs in nature.

Validation experiments, on the other hand, check the predictions of these models against real-world observations. An ideal validation experiment would investigate the model's systematic biases, estimate its accuracy and also check whether it is capable of representing the full range of observed conditions. Validation can be part of an iterative cycle of model development, allowing refinement of certain model parameters, if the validation experiment is designed so as to be able to isolate each mechanism represented in the model.

A well-designed experiment includes *in situ* measurements of all model inputs, together with estimates of their uncertainty. Spatial scales should be sampled at sufficient resolution and coverage to ensure that the observations of model inputs accurately represent them over their full range. The uncertainty introduced by spatial representativeness sometimes dominates the error budget of a validation experiment. The uncertainty in each component of the validation should be analysed – both in terms of random uncertainties, which may be reduced by averaging, and systematic biases, which may not.

2.11.1 Ground-based radiometers

Ground-based radiometer or spectrometer measurements can be used for validation of models, given the *in situ* observations of the model's input variables. When radiosondes provide the *in situ* data, clear sky conditions must be selected as the measurements

Frequency (GHz)	PWV	Average T _B (K)	MPM89	W76
20.7	Low	14.1	+0.38	+0.80
20.7	High	30.0	+0.15	+1.00
22.2	Low	18.8	+0.56	-0.49
22.2	High	45.0	-0.76	-4.30
31.4	Low	13.5	-0.33	+0.31
31.4	High	20.0	-1.10	+0.22

Table 2.10 Calculated minus measured

brightness-temperature differences (K) at Wallops Island, VA from England et al. (1993)*

Low PWV: <1 cm; High PWV: 2.1 cm.

*The original publications present differences with the opposite sign, i.e. measured minus calculated.

are also sensitive to emission from cloud liquid water, which is not measured by the radiosonde sensors. If long-term datasets are available it is possible to validate a model over a wide range of inputs at a single site. Given that both radiometric and in situ observations sample small spatial scales, it is usually not difficult to ensure that the *in situ* data are representative of the scene observed by the radiometer.

England et al. (1993) compared ground-based radiometer measurements from Wallops Island, VA at 20.7, 22.2 and 31.4 GHz with brightness temperatures computed from radiosonde profiles using either MPM89 or the model of Waters (1976), designated W76, for H₂O absorption. In both cases O₂ absorption was calculated from Rosenkranz (1988). The differences between calculated and measured brightness temperatures are listed in Table 2.10. However, the combined uncertainties of radiometers and radiosondes were larger than the differences between absorption models. The radiosondes used for the experiment carried instrument packages made by three different suppliers, and the authors noted significant differences in the relative humidity profiles from different sensors.

Westwater et al. (2003) measured atmospheric emission at 23.8 and 31.4 GHz with radiometers on the island of Nauru (tropical western Pacific) and compared the data with brightness temperatures calculated from radiosondes using MPM87, MPM93 and R98. They applied corrections to the radiosonde humidity measurements which, depending on age of the radiosonde, were as large as 10 per cent. The authors concluded, however, that factors other than age might influence the radiosonde accuracy. After those corrections, they obtained the mean differences listed in Table 2.11.

Marchand et al. (2003) used a different approach to correct radiosonde humidity; they multiplied the moisture profile by a factor so as to bring the calculated brightness temperature at 23.8 GHz into agreement with measured brightness temperature. Brightness temperature at 31.4 GHz was then calculated from the adjusted profile for comparison to measurements at that frequency. In effect, this is a test of model

Table 2.11Calculated minus measured brightness-
temperature differences (K) at Nauru Island
(tropical western Pacific) from Westwater
et al. (2003). Average PWV = 4.7 cm.
The values in parentheses are 99 per cent
confidence intervals for the final digit

Frequency (GHz)	Average $T_{\mathbf{B}}(K)$	MPM87	MPM93	R98
23.8	65	+0.80 (67)	+3.90 (70)	+0.69 (67)
31.4	32	-0.16 (32)	+3.37 (36)	+0.86 (33)

Table 2.12Calculated minus measured 31.4 GHz
brightness-temperature differences (K)
at three sites, from Marchand et al.
(2003)

Location	Average PWV (cm)	MPM87	R98	MonoRTM
Nauru	4.0	-0.35	+0.65	-0.51
Oklahoma	1.0	-0.04	+0.42	+0.05
Alaska	0.7	-0.79	-0.34	-0.84

consistency between the two frequencies, relative to the vertical distribution of moisture determined by the radiosondes. Table 2.12 lists the brightness temperature differences obtained from MPM87, R98 and MonoRTM at three field sites of the Atmospheric Radiation Measurement (ARM) program. Some sign errors in the Nauru differences have been corrected (private communication, R. Marchand, 2004). Radiometer calibration accuracy was estimated to be ± 0.3 K. The authors also noted that differences between individual components of the models (i.e. O₂ absorption, H₂O line absorption, H₂O continuum) were often larger than the differences between total absorption predicted by the three models.

Mattioli *et al.* (2005) compared 23.8 and 31.4 GHz radiometer measurements made at the ARM site in Oklahoma with calculations using the MPM87, MPM93 and R98 models, and also a model by Liljegren *et al.* (2005), denoted L04, which uses the MT-CKD water continuum (Clough *et al.*, 2005) and in which the 22 GHz line width was reduced by 5 per cent compared with R98. A recent update of R98 was also tested, which yielded results very close to R98 at these two frequencies. The *in situ* atmospheric measurements were obtained from radiosondes of a new design that do not suffer from the dry bias described by Wang *et al.* (2002). Three different radiometers and two radiometric calibration methods were employed. Brightness temperatures

covered the range of 12 to 42 K at 23.8 GHz and 11 to 22 K at 31.4 GHz. Table 2.13 lists the mean differences of calculated minus measured brightness temperatures for the C1 radiometer with ARM calibration, followed in brackets by the minimum and maximum values of the difference over the six combinations of radiometer and calibration method. Generally, the C1/ARM value is close to the centre of the ensemble of measurements. Comparison of the 31 GHz results in Table 2.13 with the ones from the same site in Table 2.12 shows that the predictions of R98 are ~0.5 K higher than MPM87 in both cases, but the measurements of Marchand *et al.* are closer to the MPM87 model, while the measurements of Mattioli *et al.* are closer to the R98 model at this frequency. These two papers used different methods to determine water vapour, but the disagreement may also reflect the practically achievable calibration accuracy of radiometric measurements. Table 2.14 lists the slopes obtained by Mattioli *et al.* in a regression of the variability is due to water vapour, so the deviation from unity in slope of the regression line tests the H₂O component of the models.

If we estimate atmospheric emission at a window frequency as the measured downwelling brightness temperature minus 2.7 K from the cosmic background, then the comparisons in Tables 2.10–2.13 indicate that the discrepancies with models are, with some exceptions (e.g. MPM93 tends to over-predict H₂O absorption), often within a few per cent in the 20 to 30 GHz range. There are cases where agreement is within a fraction of a per cent, though not consistently.

Keihm *et al.* (2002) utilised GPS measurements of the atmospheric time delay at the Goldstone Tracking Station in California and the ARM site in Oklahoma for model validation instead of *in situ* atmospheric measurements. The time delay was separated into a hydrostatic part that can be determined directly from surface pressure and a second part termed 'wet delay' which is related to the atmospheric water-vapour profile. Downwelling brightness temperatures measured at 20.7, 22.2, 23.8 and 31.4 GHz were converted to atmospheric opacities using an effective radiating temperature. The measured validation data was then obtained as the slope of the regression line of opacity versus wet delay. This measured quantity was compared with a regression line

Frequency (GHz)	R98	L04	MPM87	MPM93
23.8	-0.44	+0.07	-0.60	+0.65
	[-0.75,+0.03]	[-0.25,+0.55]	[-0.91,-0.12]	[+0.33,+1.13]
31.4	-0.09	+0.11	-0.64	+0.77
	[-0.27,+0.005]	[-0.06,+0.21]	[-0.81,-0.54]	[+0.59,+0.86]

Table 2.13Calculated minus measured brightness-temperature differences (K)
at the Oklahoma ARM site, from Mattioli et al. (2005).* Values
within brackets indicate the range of differences

*The original publications presented differences with the opposite sign, i.e. measured minus calculated.

obtained from calculations based on a database of radiosonde profiles for each of the two sites, using a refraction model for time delay and the MPM87 and R98 models for absorption, as well as two other models with line and continuum parameters that had previously been adjusted to fit atmospheric measurements: one from Cruz-Pol *et al.* (1998), denoted C98 here, and the JPL model (Keihm *et al.*, 1995). The comparison, shown in Table 2.15 as percentage differences in the slopes of the two regressions, is thus between statistics of two ensembles rather than between elements of a single ensemble, as in the validation experiments previously discussed. Hence, there are uncertainties associated both with the measurement of correlation between opacity and wet delay and with the statistical representativeness of the profiles used for the model calculations. The estimates by Keihm *et al.* of those two uncertainties are given in the last two columns of Table 2.15. These results indicate that both MPM87 and R98 under-predict H₂O absorption at all four frequencies, whereas Mattioli *et al.* (2005) found slopes greater than unity (see Table 2.14), implying over-prediction of H₂O absorption by amounts ranging from 0.5 to 3 per cent for these two models.

Table 2.14Slope of modelled versus mea-
sured brightness temperatures at
Oklahoma ARM site, from Mattioli
et al. (2005)

Frequency (GHz)	R98	L04	MPM87	MPM93
23.8	1.0059	1.0247	1.0174	1.0616
31.4	1.0364	1.0079	1.0239	1.1519

Table 2.15Modelled minus measured slopes of opacity versus wet delay,
as percentages of measured slope at two sites, from Keihm
et al. (2002). Uncertainties (%) in measurement and model
calculations are also given

Frequency (GHz)	Location	JPL	C98	MPM87	R98	Meas. error	Modelling error
20.7	Oklahoma	+3.2	+1.7	-2.0	-3.3	2.1	0.4
20.7	California	0.0	-1.0	-5.0	-6.5	1.2	0.4
22.2	Oklahoma	+3.3	-1.8	-1.9	-4.1	1.6	3.5
22.2	California	+3.2	-1.9	-1.9	-4.2	2.2	1.1
23.8	Oklahoma	+3.4	+2.0	-1.9	-3.2	0.7	0.4
31.4	Oklahoma	+1.5	+1.5	-4.9	-4.9	3.2	4.3
31.4	California	-2.0	-1.6	-8.5	-9.0	3.3	4.6

These different conclusions probably result from the differences in technique of the two papers as well as the known statistical uncertainties. Mattioli *et al.* also intercompared PWV derived from radiosondes, GPS and the microwave radiometers (using inversion techniques based on the absorption models). They found biases of a few hundredths of a cm between the three techniques of measurement, which would correspond to a few per cent in the Oklahoma climate.

Hewison *et al.* (2003) used radiosondes and radiative transfer models to validate coincident brightness temperatures measured at twelve frequencies from 22.2 to 58.8 GHz by a ground-based microwave radiometer at Camborne, England. Although the objective was validation of radiometer measurements, the comparison is also sensitive to bias in the models and radiosondes. A bias in channels near the 22 GHz water vapour line was found to be partly explained by a dry bias in the radiosonde sensors. Other biases in the channels close to the centre of the 60 GHz oxygen complex were identified as a calibration problem in the radiometer, allowing this to be rectified. Work is now in progress to analyse the channels between 51 and 53 GHz, which showed biases that depended on brightness temperature and varied from model to model.

Other validation work in progress includes ground-based experiments at 94 and 151 GHz in Switzerland. The 94 GHz measurements were made with a transmitter–receiver link (Martin *et al.*, 2000). At 151 GHz, downwelling atmospheric emission was measured (L. Martin, private communication).

2.11.2 Ground-based FTS

Extensive studies of the atmospheric transmission spectrum as seen from the ground at millimetre and submillimetre wavelengths have been performed with Fourier transform spectrometers (FTS) mounted at high mountain-top sites, potentially interesting for submillimetre astronomy. The earliest attempts were made at 2400 metres above sea level in Tenerife by Hills *et al.* (1978). In recent years, FTS experiments have been mounted at Chajnantor, Chile between 4800 and 5500 m above sea level (see Matsushita *et al.*, 1999; Paine and Blundell, 1999), Mauna Kea, HI at 4200 m above sea level (Serabyn *et al.*, 1998) and the geographic South Pole at 2900 m elevation (Chamberlin *et al.*, 2003). These FTS experiments differ in frequency coverage, resolution and calibration procedures but together have provided valuable data sets for validating and refining atmospheric absorption models from \sim 0.1 to 2 THz, at least for the conditions of the high mountain-top sites. Figure 2.4 shows some of the best spectra obtained with the FTS installed at Mauna Kea. More information can be found at www.damir.iem.csic.es/PARDO/latest fts.html.

Pardo *et al.* (2001a) and Pardo *et al.* (2005a) analysed the line shapes and continuum terms. The results published in Pardo *et al.* (2001a) advise the use of v^2 laws for both the dry and H₂O continuum terms, with coefficients determined in that work from FTS observations under very dry tropospheric conditions extending from 300 to 1100 GHz. Recently, Pardo *et al.* (2005a) have noticed that the H₂O continuum above 1 THz may be following a v^x law with x < 2, which would agree with Ma and Tipping (2002). In the same work the agreement of the measured dry continuum with the result of Boissoles *et al.* (2003) has been well established for



Figure 2.4 Atmospheric transmission data obtained at Mauna Kea under the driest conditions. Windows centred at ~ 1.04 , 1.34 and 1.48 THz are visible. The resolution of the 4/1/98 spectrum (200 MHz) allows separation of the weak and narrow O₃ lines, which get diluted in the 1/21/03 spectrum (1 GHz resolution). These data have allowed separation of the wet- and dry-continuum absorption from the line-by-line absorption at submillimetre wavelengths and therefore their comparison with theory (see Section 2.6 and Pardo et al., 2001a, 2005a)

the full 300–1600 GHz range: The N_2-N_2 collision-induced model of Borisow and Frommhold (1986) has to be multiplied by a factor 1.34 to reproduce all dry collision-induced absorption mechanisms operating in our atmosphere (N_2-N_2 , O_2-O_2 and O_2-N_2).

2.11.3 Airborne radiometers

A radiometer on a research aircraft offers the potential to simultaneously sample the radiative and thermodynamic properties of the atmosphere. With careful experiment design, this can ensure that errors of representativeness are minimised. For example, the aircraft can provide a profile of pressure, temperature and humidity for input to a radiative-transfer model. These calculations can be compared with brightness temperatures measured in clear skies during level runs to validate the absorption models. This is akin to comparing a ground-based radiometer with model calculations from radiosondes, although the analysis can be repeated at different levels in the atmosphere. Errors of representativeness can be further reduced by comparing brightness temperature measurements made *during* an aircraft profile with *in situ* measurements. However, this requires careful control of the radiometer's calibration, which can change with temperature during aircraft ascents/descents.

Measurements of downward-propagating brightness temperatures during ascents and descents of a high-altitude aircraft were made by Schwartz (1998) with two radiometers, one tunable over the range 52.5 to 55.8 GHz and the other having eight fixed double-sideband channels at 0.35 to 2 GHz from the 118.75 GHz O_2 line. The measurements were compared with calculations based on radiosonde profiles using either MPM92 or MPM93. In the 52.5-55.8 GHz band, the measurements agreed within the observational uncertainty of 2 to 5 K with both models, which were indistinguishable at that level of precision. The observational uncertainty corresponds to \sim 2 per cent of zenith atmospheric opacity for the more transparent channels below 54 GHz. Near 118 GHz, discrepancies from the models were as large as 4 K, with uncertainty ± 1.5 K, leading to the conclusion that the width of the 1- line is larger by 5 to 6 per cent in the upper troposphere and stratosphere than given by MPM92 or MPM93. (Both models have the same width coefficients for this line.) That result could be obtained either by increasing the line width by a constant factor at all temperatures or by increasing its temperature exponent from n = 0.8 to 0.97. It should be noted that the later laboratory measurements of Tretyakov et al. (2004) yielded a room-temperature width 2 per cent higher than the value in MPM92/93, which would leave 3 to 4 per cent of Schwartz's recommended increase to be obtained from temperature dependence.

English *et al.* (1994) used an airborne radiometer to test MPM89 and three older H₂O continuum models in the windows at 89 and 157 GHz. They found that all four of the models underestimated downwelling brightness temperatures in the tropics. In subarctic conditions atmospheric emission was overestimated. They proposed a modification to the temperature dependence of the water vapour continuum in MPM89 to match their observations. An improved version of this radiometer was flown by Hewison (unpublished data) to measure downwelling brightness temperatures at 89, 157, 183 ± 1 , 183 ± 3 and 183 ± 7 GHz. Flights took place at various locations with climates ranging from arctic to tropical. Several absorption models are being compared to the measurements; results indicate negative calculation-measurement discrepancies in the window channels for very cold, dry conditions.

2.11.4 Satellite-based radiometers

Satellite observations of model predictands are able to represent their global range. However, in practice, careful data selection is needed to isolate the variable of interest from other factors which may also influence the scene radiance. Usually it is necessary to make some correction for antenna sidelobes, which may receive energy from a different part of the earth or from space. The need for *in situ* measurements of model input variables also imposes stringent selection criteria. This may reduce a huge global dataset to a small number of satellite observations co-located with *in situ* observations, e.g. radiosondes and buoys. Co-location is needed both in space and time. With polarorbiting satellites, this can drastically reduce the data available for comparison. The principal problem in using satellite data to validate radiative-transfer models with *in situ* data is that these observations sample different spatial scales. The co-location

criteria must be chosen by consideration of the spatial and temporal variability of the parameters in question. To minimise errors due to representativeness, it is often necessary to impose criteria on the observations – both spatially for satellite data and temporally for *in situ* data.

Another way to exploit satellite data for model validation is to compare it with numerical weather prediction (NWP) analysis fields in lieu of *in situ* data. Such fields are, by definition, the near-optimal analysis of all current and past observations. They have the advantage of global availability and often lower errors of representativeness, as they are sampled on scales similar to the resolution of space-borne microwave radiometers (tens of km). The NWP field is constructed to be consistent with a diverse set of current and past observations. It is inevitable that this technique includes the observations' and the NWP model's biases as well as those of the radiative-transfer model. Thus, if the observation and analysis biases are unknown or not corrected as part of the assimilation process, they will affect the comparison in a way that may vary with location and time.

The 'observation-background' residuals can be monitored as part of the variational assimilation (Rodgers, 2000) of observations into NWP. This process constructs a best estimate of the model state that is consistent with its own short-range forecast and the observations, taking into account the assumed error characteristics of both. These residuals often show systematic biases, which can be further analysed in multivariate space, e.g. by temperature, humidity, pressure, wind speed, scan angle, etc. This technique is generally believed to be the most effective validation of the consistency of radiometric observations and radiative transfer models. It implies the need to involve NWP centres as partners in the calibration/validation for new instruments. The availability of satellite data often comes late in the development of the model needed to retrieve geophysical parameters from the data, so this technique is most applicable to iterative model development. It is also possible to use NWP analysis fields with ground-based or aircraft-based measurements, but this would re-introduce the problem of representativeness due to different sampling scales.

Meissner and Wentz (2003) tested the R98 and MonoRTM models with satellitebased measurements made by the Special Sensor Microwave Imager. PWV, wind speed and cloud liquid water were first retrieved from the 19, 22 and 37 GHz channels using the algorithm of Wentz (1997). The measurements were screened to find low values of liquid water and wind speed. Then sea surface temperature and water-vapour profiles were obtained from analyses of the National Centre for Environmental Prediction, and the water-vapour density was scaled to match the satellite measurement. Brightness temperatures were calculated for comparison with the 85 GHz measurements, which had not been used for the retrieval of atmospheric parameters, using either R98 or MonoRTM for H₂O and MPM92 for O₂ absorption. The calculation is also dependent on a surface emissivity model but with the best choice for that component, calculated-measured differences at 85.5 GHz were within ± 1.2 K for both models, over the range of 0 to 6 cm PWV. At a given value of PWV, the two models could yield results differing by as much as 1 K. However, both H₂O models were considered to be validated within the estimated uncertainty of 3.3 K in each PWV interval. At this frequency and the 53 degree viewing angle of the instrument, the

sensitivity of vertically-polarised brightness temperature to PWV is approximately 1 K/mm.

Pumphrey and Buehler (2000) examined measurements made by two satellite limb-sounding instruments, the microwave limb sounder (MLS) and the millimetrewave atmospheric sounder (MAS). They found that allowing their retrieval algorithm to solve for a pressure-proportional frequency shift of the 183 GHz H₂O line produced improved agreement with the measurements. Their retrieved values for the shift parameter were equal to -0.19 ± 0.04 MHz/Torr from MLS and -0.27 ± 0.05 MHz/Torr from MAS. These are larger than the laboratory and theoretical values in Table 2.9; however, considering other uncertainties associated with the satellite measurements, this result should be interpreted as consistent with the existence of and the need to model the frequency shift.

Buehler *et al.* (2005a) used data from the up-looking submillimetre wave radiometer ASUR to estimate the pressure shift parameter of the HCl line cluster near 626 GHz. Depending on the assumed temperature dependence of the shift, the HCl pressure shift value consistent with the ASUR data is 0.120 to 0.156 MHz/Torr, instead of the 0.040 MHz/Torr reported in HITRAN. This result is in good agreement with very recent independent laboratory work by Drouin (2003), which suggests a value of 0.147 MHz/Torr for the shift.

Buehler et al. (2004) compared brightness temperatures from the 183.3 \pm 1, ± 3 and ± 7 -GHz channels of the Advanced Microwave Sounding Unit (AMSU-B) with calculations based on radiosonde profiles using ARTS with the R98 absorption model. Comparisons were only made for satellite data within 30 min of the nominal time for radiosondes launched from Lindenberg, Germany and where the sonde drifted by less than 50 km before reaching the tropopause. They also filtered the data to reject dense ice cloud. Brightness temperatures in the three AMSU channels around the water vapour line depend to a good approximation only on atmospheric temperature and humidity; therefore the radiosonde gives all necessary input data. The investigated channels are so close to the line that continuum does not play an important role, resulting in a very simple absorption calculation. The comparison yielded agreement for the two outer channels, but for the channel closest to the line, which is sensitive to the atmospheric state in the upper troposphere, a scatter plot of modelled versus measured brightness temperature showed a slope deviating slightly from unity. The error analysis included contributions from the radiometers, *in situ* observations, radiative-transfer model and uncertainty in the representativeness of the two observations. In the case of the radiative transfer model, the authors tried to reproduce the slope by changing various spectroscopic parameters. They concluded that the most likely explanation for the deviation is a dry bias of the radiosonde humidity sensors under very dry conditions (radiosonde giving 0 per cent relative humidity when the true relative humidity is still 4 per cent), even after correction for the previously known biases. Subsequently, this has been suggested as a method of evaluating the accuracy of different radiosonde observations.

Rosenkranz and Barnet (2006) compared measurements made by the Humidity Sounder for Brazil (HSB), on the Aqua satellite, with calculations based on special

radiosondes launched from the ARM-TWP and SGP sites just before and after the satellite overpass. Profiles from the two sondes were interpolated for the calculation of brightness temperatures with the R98 absorption model. These radiosondes were of the newer design which is not believed to have a dry bias. Also employed, at a variety of sites, were research radiosondes with a chilled-mirror humidity sensor, which is considered to be the most accurate instrumentation for measurement of humidity. The HSB has channels at 150, 183.3 ± 1 , 183.3 ± 3 and 183.3 ± 7 GHz; mean differences between calculations and measurements ranged from 0.1 to 0.8 K. The calculations based on the chilled-mirror sondes were between 0.1 and 0.4 K. For this instrument, no corrections were made for antenna sidelobes, which could account for the measurements being slightly colder than the calculated brightness temperatures. An error of 5 per cent in absorption would correspond to brightness-temperature errors of ~0.5 K for these channels.

In the oxygen band, Rosenkranz (2003) compared measurements from the Advanced Microwave Sounding Unit on the NOAA-15 satellite with brightness temperatures computed from radiosondes using a rapid algorithm based on MPM92, for six channels centred at 52.8, 53.6, 54.4, 54.94, 57.29 and 57.29 ± 0.217 GHz. The measurements were corrected for contributions from sidelobes that miss the earth, although some residual asymmetries indicated that the correction was not perfect. Mean calculated minus measured differences ranged from -0.23 to +0.42 K; all of them were smaller than the instrument's specified 1.5 K accuracy of calibration. Of these channels, 53.6, 54.4 and 54.94 GHz are the most sensitive to atmospheric opacity; an error of 5 per cent in the absorption calculation would have caused brightness temperature errors of 0.7 to 0.9 K. The other channels are less sensitive because of the temperature structure of the atmosphere.

Further validation experiments using aircraft and satellites are described by Wang (2002), Meissner and Wentz (2004) and Ellison *et al.* (2003). Although they were primarily designed to compare water-surface emissivity models, the calculations include modelling of atmospheric absorption and hence test the complete radiative-transfer models, in many cases obtaining agreement of a few degrees Kelvin or less.

2.12 Conclusions and recommendations for future development of models and databases

A careful inspection of the comparisons cited in the previous section does not lead one to identify one particular model as best for all frequencies and atmospheric conditions. More comprehensive testing of models at multiple frequencies and in varied atmospheric conditions is desirable. However, for all measurements in the atmosphere, it is essential to place emphasis on obtaining accurate *in-situ* data for comparison. Especially for water vapour, this is a problem of non-negligible difficulty. Establishment of additional sites with high-accuracy instrumentation in different climates would be useful, particularly in connection with satellite experiments. For the latter, radiosonde launches should be timed to coincide with satellite overpasses, or

slightly earlier to allow for rise time of the sonde. Efforts should be made to distinguish between errors in water-vapour absorption and in dry-air absorption when model calculations are compared with measured brightness temperatures. For example, calculated-measured differences at window frequencies could be plotted versus PWV. The regression-line intercept would be related to the dry-air component of absorption, although it would be necessary to use care in interpreting such a regression, because PWV is correlated with temperature. Involvement of forecasting centres for variational assimilation of observations into NWP models can also be helpful for this purpose.

The most successful theoretical work on the H_2O continuum has calculated absorption due to the permanent dipole moment of H_2O molecules perturbed by collisions, as opposed to permanently-bound dimers or induced dipoles. The calculated temperature and frequency dependence of the continuum, both for pure vapour and for mixtures with foreign gases, should be incorporated into models and tested by comparison with laboratory and atmospheric measurements.

The new generation of atmospheric remote-sensing satellite instruments requires unprecedentedly high accuracies of the molecular spectroscopic parameters. HITRAN's progress in the future will also require the determination of line parameters for systems of bands in the near-infrared, extending the applicability of the parameters at all wavelengths to high temperatures (often tantamount to archiving atmospheric weak lines), addition of collision-induced absorption bands, characterisation of line mixing for more molecules and addition of new molecules that are important for terrestrial, planetary and astrophysical applications.

The pressure-broadened line parameters of greatest utility for atmospheric applications are (1) half-widths and shifts for dry air as a perturber (i.e. weighted sum of N_2 and O_2), (2) half-widths and shifts for H_2O as a perturber and (3) line-mixing coefficients for the 50–70 GHz O_2 band, for both dry air and H_2O as perturbers. Self-broadened half-widths are unnecessary for gases other than H_2O .

Many researchers throughout the world are currently making efforts to ensure the quality of the spectroscopic parameters which are needed as input to atmospheric remote sensing investigation. Several studies, partially overlapping, partially complementary, are currently being undertaken. The regularly updated and evolving spectroscopic databases, such as GEISA, still have their limitations and faults, which have to be corrected or improved upon, in order to meet the requirements of a diverse group of users.

As an example of actual improvement needs, the following list, established in the framework of the ISSWG (IASI Science Sounding Working Group) activities, provides the IASI soundings spectroscopy enhancement requirements.

Quality control of spectroscopic parameters for the most abundant species

 Need to systematically validate the existing databases (HITRAN, GEISA) for the stronger absorbers: H₂O, CO₂, CH₄, O₃, N₂O.

- Intercomparison of existing databases is not sufficient. Comparison with real atmospheric spectra recorded in well-documented conditions is necessary to locate deficiencies.
- Patches and add-ons can degrade the database consistency (duplicates or missing lines).
- Existing and new laboratory data should be combined in a consistent manner using suitable theoretical models for the calculation of line positions, intensities and widths.
- Coding of uncertainties by an index is insufficient for proper use in the forward model variance-covariance matrix. Better and more realistic errors on spectroscopic parameters are required.

Urgent needs

- Water vapour continuum studies (foreign and self) and temperature dependence.
- Perform long path laboratory measurements.
- Perform real atmospheric measurements along horizontal paths in welldocumented conditions.
- Improve existing parametrisations.
- Elaborate new theoretical models.
- Correct known inadequacies observed when modelling high resolution atmospheric spectra (H₂O, CO₂, CH₄) recorded from the ground, balloon or space.

Specific recommendations

H_2O

- Weak lines in the regions 650–1200 cm⁻¹ and 3000–6000 cm⁻¹ especially, still have incorrect positions and intensities. There is a need for both measurements and improved theoretical calculations.
- Widths (foreign and self) have not been validated by enough systematic laboratory work. Very strong variations from line to line exist.
- Temperature dependences of widths are poorly measured or calculated.
- Pressure shifts can be important in the lower troposphere.
- Some lines recorded at high resolution in ground-based solar spectra do show profiles inconsistent with current line shape formalisms.
- More detailed line shape measurements and modelling needed for H_2O (in connection with continuum studies).

CO₂

- Validation of line intensities for the isotopomers in ¹³C, ¹⁸O and ¹⁷O needed.
- New line shape studies needed in the 15 μ m band (laboratory and theoretical).

03

- For lower stratospheric and tropospheric ozone retrievals a better knowledge of the temperature dependence of the line widths is needed.

CH₄

- Intensive laboratory and theoretical work still needed for air-broadened widths.
- Line shape studies needed including line interference effects in multiplets and Q branches.

HNO₃

Work on absolute line intensities is still needed.

Heavy molecules described in terms of cross-section instead of line by line parameters

- Establish a priority list with the known scenarios for man-made species (CFCs, HCFCs, perfluorinated compounds) based on existing cross-section data.
- Perform new measurements and establish smooth parametrisations (as a function of temperature and total pressure) to avoid the use of empirical extrapolations of accurately measured cross-sections as substitutes for unavailable data.

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