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## History and future of the molecular spectroscopic databases

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### Abstract

A brief history and review of the development of some molecular spectroscopic databases is presented. Such databases are compilations of spectroscopic parameters whose principal purpose is to provide the necessary molecular absorption input for transmission and radiance codes. Remote sensing of the terrestrial atmosphere has advanced significantly in recent years, and this has placed greater demands on the compilations in terms of accuracy, additional species, and spectral coverage. This paper discusses current pressing issues, such as the deficiencies in line positions, intensities, and line shape, as well as the directions of future enhancements. **To cite this article:** *L.S. Rothman et al., C. R. Physique 6 (2005).*

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### Résumé

**Histoire et avenir des banques de données spectroscopiques moléculaires.** On présente tout d'abord un bref historique et une revue du développement de quelques banques de données spectroscopiques moléculaires. Il s'agit de compilations des paramètres spectroscopiques nécessaires au calcul du coefficient d'absorption des espèces moléculaires que l'on rencontre dans les codes de transferts radiatifs. Le sondage de l'atmosphère terrestre a, par ailleurs, beaucoup progressé dans les dernières années, avec comme conséquence une demande accrue aux banques de données d'étendre leur couverture, aussi bien en termes d'espèces moléculaires, de domaine spectral mais aussi de précision. On présente dans cet article, quelques problèmes d'actualité illustrant diverses lacunes des banques actuelles (positions des raies, intensités, profils spectraux, ...) ainsi que quelques pistes d'évolutions futures. **Pour citer cet article :** *L.S. Rothman et al., C. R. Physique 6 (2005).*

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**Mots-clés :** Banques de données spectroscopiques ; Spectroscopie moléculaire ; Profil spectral ; Paramètres d'absorption ; Sections efficaces (infrarouge) ; HITRAN ; GEISA ; MIPAS

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## 1. Introduction

Notable progress is often made in sudden large steps when several new technologies are simultaneously developed, and individuals realize the synergism and applications inherent in these technologies. The development of molecular spectroscopic databases is a good example of this phenomenon. At the start of the second half of the twentieth century, several technologies matured: computers, infrared detectors, quantum-mechanical treatments of the molecular Hamiltonian, and high-resolution laboratory facilities.

With these new technologies, it became possible to provide a means of performing rapid long-path atmospheric transmission and radiance calculations for numerous scenarios. The confluence of technologies led to the publication in 1973 of the first standardized spectroscopic database [1] known as *HITRAN* (*HIgh-resolution TRANsmission*). This early database was limited to the strongest infrared absorbers ( $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{O}_3$ ,  $\text{N}_2\text{O}$ ,  $\text{CO}$ ,  $\text{CH}_4$ , and  $\text{O}_2$ ) in the terrestrial atmosphere, and also was focused on the basic parameters for applying the Lambert–Beers–Bouguet law of transmission. The fundamental parameters were the line position  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ), the line intensity  $S$  ( $\text{cm}^{-1}/(\text{cm}^{-2} \times \text{molecule}^{-1})$ ), the air-broadened half-width  $\gamma_{\text{air}}$  ( $\text{cm}^{-1} \text{atm}^{-1}$ ), and the lower-state energy  $E''$  ( $\text{cm}^{-1}$ ) of the transition. A cutoff in intensity was established for the database appropriate for very long-path absorption in the terrestrial atmosphere, although at the time this criterion could not be met for molecules such as ozone or methane due to both the experimental and theoretical difficulty of achieving a description of the ‘weak’ lines. The database, or so-called ‘AFGL tape’, contained approximately 100 000 transitions, with some parameters, such as  $\gamma_{\text{air}}$ , being set to a default value due to lack of experimental or theoretical values at the time. It should be noted that the database contained, and continues to have, a mixture of theoretical and experimental parameters, although the idealized goal is to have a calculated self-consistent set of parameters.

In 1976, a similar effort was started at Laboratoire de météorologie dynamique (LMD) in France, with the development of *GEISA* (*Gestion et étude des informations spectroscopiques atmosphériques*: Management and Study of Spectroscopic Information) [2]. The initial emphasis of these two databases varied slightly. Whereas *HITRAN* was focused on the terrestrial atmosphere, *GEISA* was oriented towards the Jovian planetary atmospheres. The *GEISA* archive included the same seven atmospheric absorbers as in *HITRAN*, with additional species such as  $\text{NO}$ ,  $\text{SO}_2$ ,  $\text{NO}_2$ ,  $\text{NH}_3$ ,  $\text{PH}_3$ , as well as the molecules  $\text{C}_2\text{H}_4$ ,  $\text{GeH}_4$ ,  $\text{C}_3\text{H}_8$ ,  $\text{C}_2\text{H}_2$ ,  $\text{HC}_3\text{N}$ ,  $\text{HCOOH}$ ,  $\text{C}_3\text{H}_4$ .

Other molecular spectroscopic data compilations have been constructed within the past decades, with different emphases. These include, for example:

- (1) the *JPL* catalog of microwave and submillimeter transmission [3];
- (2) the *ATMOS* (Atmospheric Trace Molecule Spectroscopy) [4] Molecular Line-List, compiled for the *ATMOS* experiment [5];
- (3) the Smithsonian Astrophysical Observatory database (*SAO* database) [6];
- (4) the *MIPAS* database [7];
- (5) the spectral line database *BEAMCAT*, for millimeter and submillimeter wave propagation in the Earth’s atmosphere [8];  
and
- (6) the Cologne database for molecular spectroscopy (*CDMS*) [9].

Some of these latter databases are specifically tied to satellite experiments in the Earth’s atmosphere (*ATMOS* and *MIPAS*), some are more in the realm of catalogs for the interstellar medium (*JPL* and *CDMS*), and some are no longer being developed (*ATMOS* and *SAO*).

## 2. Database evolution: examples of *HITRAN* and *GEISA*

Since their initial publications [1,2] there have been periodic releases of new editions of *HITRAN* and *GEISA*. For *HITRAN*, the editions of 1986 [10], 1996 [11], and most recently 2004 [12] marked significant expansions of the scope of the compilation. The contemporary editions have been driven to a large extent by the increasing demands of remote-sensing experiments. In particular, the satellite-based experiments that monitor the atmospheric state have grown in sophistication, robustness, signal-to-noise, and accuracy. Likewise, the algorithms for obtaining retrievals of constituent profiles from the observed spectra have matured. These developments have led to many enhancements in the spectroscopic database: the addition of more spectral parameters for each transition; increased accuracy of the parameters; additional molecules; additional bands and isotopologues for each molecule; extended spectral coverage both towards the long wavelength region and through the visible and ultraviolet. The appendix in [11] presents the units and definitions of the various parameters in the databases.

In recent years, the spectroscopic databases have encompassed molecules that do not readily lend themselves to a line-by-line description. Typical of these species are the chlorofluorocarbons and other trace atmospheric species possessing very dense spectra and numerous low-frequency modes of vibration. The spectroscopic databases have dealt with these species by adding

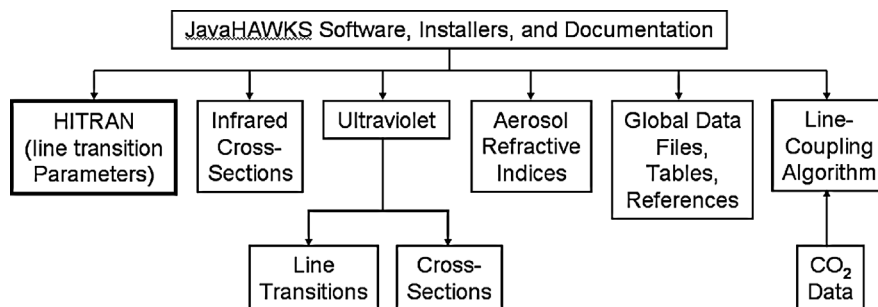


Fig. 1. Structure of the *HITRAN* database compilation.

a folder called ‘IR cross-sections’. The cross-sections are tabulations of spectra taken with very high-resolution spectrometers at representative temperature–pressure sets. Forward calculating simulation programs have been successful in using these data in a quasi-quantitative manner, yielding adequate retrievals of constituent profiles.

The *HITRAN* and *GEISA* databases have also added other features of matter in a quantifiable standardized nature. Fig. 1 illustrates the structure of the current *HITRAN* database. It is anticipated that more phenomena will soon be added as well, such as collision-induced absorption, data on line coupling for more molecules, and additional gas broadeners of the lines (applicable especially for planetary applications). Indeed, spectral line shapes are an area that will be a major focus of future databases, and is discussed in more detail in the next section.

The databases have grown enormously over the past four decades. The first edition of *HITRAN* [1] contained about 100 000 lines for 7 gases with a limited set of parameters. The most recent edition [12] contains over 1 700 000 lines with many parameters for 37 gases (93 distinct isotopologues). Since its first issue [2], the number of archived line transitions in *GEISA* increased in the same manner, from 178 758 (12 gases; 36 distinct isotopologues) to 1 668 371 (42 gases; 98 distinct isotopologues) entries. However, it is the improved accuracy and broader spectral coverage that is most remarkable. Nonetheless, the accuracy and consistency demands of current environmental experiments have put unprecedented demands on the quality of the spectroscopic parameters. Whereas a 5% accuracy in the values of intensities was only recently considered a goal to be obtained for vibration–rotation bands, an accuracy better than 1% is now required for adequate retrievals for several species. This requirement is pushing the technology of laboratory experiments that provide the data, as well as the theoretical and analysis techniques that extract the final parameters.

The next section describes the issues of line shape as relative to the future. Section 4 highlights a selection of problems that pertain to the current status of the line parameters affecting remote-sensing applications.

### 3. Spectral line shapes

It is well known that the accuracy of the line shape description [13–18] is the key to accurate modelling of radiative transfer and remote-sensing studies. Indeed, line shape is becoming a major concern for the future development of spectroscopic databases.

Historically, the line shape used by most of the line-by-line codes was either the Lorentz function (ignoring translational effects), the Doppler function (ignoring collisional effects), or the Voigt profile which is the convolution of the two. A great deal of work has been done to provide accurate Lorentzian widths, shifts, and temperature dependences of the corresponding absorption lines, for most of the gaseous components of the Earth’s atmosphere (and some for other planets). This is clearly illustrated by the recent editions of *HITRAN* [12] and *GEISA* [19]. However, the increasing capability of instrumentation will give rise to a number of new requirements of the database with respect to line shape.

Up to now, the assumption usually made was that the absorption can be calculated by adding the contributions of isolated Voigt-shaped components. Although it is satisfactory for many situations, severe deviations have been observed when lines overlap [20]. These line-mixing effects influence the shape of Q branches and of closely spaced manifolds and also the wings of the vibrational bands. In the far wings, an additional mechanism needs to be taken into account: the finite duration of collisions. Modelling the resulting shape is certainly one of the most difficult and less tractable problems of a spectroscopic character. Here too, the databases have been vastly improved and for instance, the 2004 *HITRAN* compilation [12] provides flexible tools for taking into account line mixing in CO<sub>2</sub> Q branches. However a number of effects remain unaccounted for and need to be included in the near future.

### 3.1. Lorentz profile: pressure broadened widths and shifts

The databases now include temperature-dependent self- and air-broadened widths of reasonable accuracy, even if, of course, numerous data are not always at the required accuracy. Note that, for applications that depend on the precision of the line transitions, the modeller needs to trace the source of the values being used. *HITRAN* provides indices to help in the research of references. Most of the stored widths have been obtained from experiment, when available, or from a combined use of measured and calculated values [21–23]. However, accurate analysis of planetary (other than Earth) spectra will require storage of broadening parameters due to other gases than O<sub>2</sub> and N<sub>2</sub> (H<sub>2</sub>O, H<sub>2</sub>, He, CO<sub>2</sub>, ...), together with their temperature dependences. Two strategies are possible: extension of the existing ‘general’ databases, or generation of ‘ad hoc’ related databases, starting of course from the general ones, in order to meet the need of a given program and of a given instrument.

As atmospheric instruments and experiments are becoming more and more sophisticated, the need for storage of data on self and air (or other perturbers) induced shifts is emerging [12,24]. The use of a strategy similar to that previously used to catalog the widths will be more difficult for various reasons, such as the difficulty of accurate measurements, the significant vibrational dependence of the shifts [22], and so forth. When it becomes necessary to store the  $T$ -dependences of the shifts, a new difficulty will arise. Contrary to the widths for which the  $T$ -dependence may be expressed by assuming, at least within a limited range of temperature values

$$\gamma(T) = \gamma(T_0) \left( \frac{T_0}{T} \right)^n \quad (1)$$

such a simple law which has some physical basis for widths [25], does not seem to be systematically valid for fitting existing shifts [26]. Therefore, an alternative could be, for shift *as well as for width parameters*, a direct storage of numerical values of these parameters for a grid of ‘atmospheric temperatures’ together with a data management program devoted to interpolation procedures (temperature and molecular mixtures, ...).

### 3.2. Line mixing: Q branches, closely spaced manifolds, and near wings

In the 2004 edition of the *HITRAN* data compilation [12], a package of subroutines and input files now allows one to take into account line coupling between the rotational components of any CO<sub>2</sub> Q branches. A similar package [27] is available from the *GEISA* management service, associated with the LMD radiative transfer algorithms in their latest editions (Stransac2000 [28]/4A2000 [29]). The procedure is based on an energy corrected sudden (ECS) approach developed in [30,31]. Schematically, off-diagonal elements of the relaxation matrix coupling the lines have been obtained from various experiments and fitted, according to ECS laws. Then a series of available subroutines computes the CO<sub>2</sub> Q branches profiles. It should be noted that when the line-mixing modelling in the radiative transfer algorithms is based on the approach suggested in [30,31], it is not necessary to include the line-mixing parameters in the line-parameter database itself.

This model has been recently extended by taking into account all types of line coupling such as P–P, P–R, P–Q, etc., and now allows for the calculation of entire CO<sub>2</sub> bands, including their near wings, where important sub-Lorentzian behavior appears [16,17,32]. Comparisons with laboratory as well as atmospheric data have demonstrated the accuracy of the ECS approach. Significant discrepancies only appear in the far wing, for distances from the resonant frequencies of the most populated lines higher than 150 cm<sup>-1</sup>, i.e., when the finite duration of collisions needs to be introduced in the theory. Such a ‘unified’ ECS approach may avoid, in the future, the use of different models: one for the Q branches (ECS model) and a different one for the wings (empirical correcting line shape factor [33]). Since that model is only an extension of what is now implemented in the line-coupling directory of *HITRAN* (see Fig. 1), it will be easy to update that directory in the near future.

Similar models are now under development for CH<sub>4</sub> [34] and N<sub>2</sub>O [35], and some similar results have been recently published for the 60 GHz O<sub>2</sub> band [36] where line-mixing effects are important. Data from these studies may be easily incorporated into future editions of the database compilation.

It must be emphasized that all these models are ‘*database dependent*’: they strongly depend on the version of the databases, since, for instance, the whole relaxation matrix is constructed in two steps. First, off-diagonal elements are computed from stored data. Then the diagonal terms are set to the line broadening parameters available in the database through a renormalization procedure in which the available line intensities play a major role. Since the spectroscopic databases are changing continuously, great care was taken in designing a procedure which facilitates an easy updating of the line shape.

### 3.3. The far wing problem

All the models discussed above have been developed within the sudden impact approximation. Consequently, they cannot provide an accurate description of the far-wing absorption, where the effects of the collision durations are no longer negligible [20]. The importance of an accurate description of the far wings of the strong H<sub>2</sub>O rotational and vibrational bands for atmospheric modelling is a very well-known example.

Although first principles far-wing H<sub>2</sub>O line shapes are available [37–39], both in the millimeter and IR regions, most of the codes that simulate atmospheric radiative transfer use a more empirical approach that is known as the ‘water–vapor continuum’ [18,40]. Schematically, for a given wavenumber  $\tilde{\nu}$ , the absorption is divided into two components: (i) ‘local’ lines centered within  $\pm 25 \text{ cm}^{-1}$  of  $\tilde{\nu}$ , the contributions of which are taken as Lorentzian; (ii) the continuum, defined as the absorption remaining after removing that local absorption from laboratory or atmospheric data. Such an empirical approach avoids any question about the physical origin of the continuum (far wings of vibrational bands and/or absorption by dimers or van der Waals molecules). A widely used example of H<sub>2</sub>O continuum is the CKDV 2.4 model of Clough [41]. Note that the exact definition of that so-called continuum is somewhat arbitrary: it strongly depends on the definition of the ‘local’ absorption (for example the  $\pm 25 \text{ cm}^{-1}$  chosen is arbitrary, if  $30 \text{ cm}^{-1}$  had been chosen, the continuum would be different). More important, it also strongly depends on the version of the spectroscopic database used to remove the local contributions. Consequently, implementation of new spectroscopic parameters in a database may require the derivation of a new continuum. Here too, a package of subroutines and input files could be made available to adapt the continuum to any further improvements of the database.

Finally, let us mention another type of absorption: the collision induced absorptions, such as N<sub>2</sub>–N<sub>2</sub>, N<sub>2</sub>–O<sub>2</sub>, and O<sub>2</sub>–O<sub>2</sub> pairs. By fitting experimental and/or theoretical data, analytical parameterization of normalized absorptions has been proposed [42,43]. However, an alternative exists: a storage, similar to that of the so-called ‘infrared cross-sections’ used for heavy molecules, for a sufficient grid of temperatures, together with data management programs associated with that sub-database. However, the modelling of these spectra is not dependent on any further evolution of the spectroscopic parameters of the spectroscopic database, and consequently may be directly implemented into radiative transfer codes.

#### 3.4. From Doppler to the collisional regime

In a recent paper [44], it was shown that the retrieval of HF vertical profile from ground-based FTIR spectra was significantly affected by collision induced narrowing (Dicke effect). However, as is now known from laboratory studies, two different mechanisms may lead to line shapes different from the usual Voigt profile: the Dicke effect itself (molecular confinement, i.e., diffusion due to velocity/speed changing collisions) and the speed dependence (with respect to the active molecule) of the ‘usual’ relaxation matrix. The key point is that it is difficult to discriminate between molecular diffusion and speed dependence of the shift and width parameters: both may play a significant role [45,46].

This example is only an illustration of the problems that will appear in high-resolution sounding of the upper-atmosphere. Even if generalized profiles exist [47] that can be implemented in additional directories, their calculation will require the storage of the line shape parameters at a more detailed level. For instance, the dependence of the width and shift cross-section with respect to the relative kinetic energy  $E_k$  must be available and therefore stored.

### 4. Overview of the status of the line-by-line parameters

In this section we propose some recommendations for possible improvements of the molecular spectroscopic databases in their present form, and we restrict the discussion to problems linked to atmospheric applications. Concerted efforts are currently in place to improve and to validate the existing spectroscopic parameters which are needed as input for atmospheric remote-sensing investigations. However, the databases still have limitations and flaws which are described in some recent and extended review papers [48–50]. These limitations may occur because the parameters do not yet exist in the literature or are not at the required accuracy. Furthermore, there are limited resources at the database manager’s disposal, and the funding source dictates the priorities of additions and updates of the database.

Some directions where efforts should be carried out to improve the quality of the microwave and infrared line-by-line portion of the database are described below. The cases of water, methane, or carbon dioxide for which numerous problems still exist for line positions, intensities and line-broadening parameters are not considered. Rather, examples will be given of deficiencies linked to the line-intensity parameters and to the existence of missing information for some strong infrared bands for supposedly well-documented molecules. We will consider the case of the tropospheric molecules. Finally, we stress the importance of correctly estimating the uncertainties linked to the parameters.

#### 4.1. Line-by-line parameter problems

The line intensities are often not known to the nominal accuracy which is required for the instruments which are performing atmospheric remote sensing. For numerous species, the line-intensity parameters that are implemented in the databases are often inconsistent from one spectral range to the other. This situation can lead to systematic errors when instruments working in different spectral regions retrieve the target molecule simultaneously. The goal of the database is to have *global spectral*

consistency. This takes the form of both relative and absolute accuracy between bands, between different isotopologues, lines within a band itself, and even between different species.

#### 4.1.1. Ozone

From the Envisat-1 satellite, ozone is retrieved simultaneously by the Michelson Interferometer for Passive Atmospheric Sounding (*MIPAS*) instrument in the infrared region (at 10  $\mu\text{m}$ ) and by the SCanning Imaging Absorption SpectroMeter for Atmospheric CHartographY (*SCIAMACHY*) experiment in the UV/VIS region (in the Huggins bands). In order to perform meaningful comparisons of ozone concentration profiles achieved by these two instruments, it is necessary to check the internal coherence of the intensities for the spectroscopic parameters which are used for the retrieval process. For this reason laboratory intercomparisons of the ozone absorption coefficients were performed from simultaneous measurements in the UV/VIS and IR region (10  $\mu\text{m}$ ). Surprisingly, a systematic difference of about 5.5% [51] was achieved between the observed and calculated IR/UV-VIS absorbance ratios when using the recommended and supposedly most accurate and reliable infrared line-intensity parameters [50] and UV/VIS cross-sections [52]. On the other hand, intercomparisons performed by the Atmospheric Chemistry Experiment (ACE) group [53] between the Chappuis bands and the 4.8- $\mu\text{m}$  region lead to an opposite conclusion. It is clear that the problem is not simple at the level of accuracy required by the satellite experiments, and that more studies need to be performed in order to make definitive conclusions about both the relative accuracy of the different bands, and more importantly, their absolute accuracy.

#### 4.1.2. Nitric acid

Nitric acid ( $\text{HNO}_3$ ) line position and line intensity updates were recently performed in *HITRAN* [12] both in the 11- $\mu\text{m}$  and the far-infrared regions. However, from a subsequent study [54], these line parameters were improved in the far-infrared region and it appears that the  $\text{HNO}_3$  line intensities in *HITRAN* are overestimated by a factor of about 30% for the whole millimeter and far-infrared spectral regions. This was demonstrated later by comparing the  $\text{HNO}_3$  atmospheric concentration profiles achieved by the *MIPAS* experiment in the 11- $\mu\text{m}$  region to those obtained by *IBEX* (Infrared Balloon Experiment) in the far infrared (near 22  $\text{cm}^{-1}$ ). *MIPAS* [55] is a Fourier transform spectrometer on board the Envisat satellite since 2002 that performs measurements of high resolution gaseous emission spectra of the Earth's limb, while *IBEX* [56] is a far infrared interferometer operated in limb mode from a balloon launch in July 2002. The agreement between the  $\text{HNO}_3$  profiles achieved by *MIPAS* and *IBEX* are excellent provided that, for the far infrared region, the parameters given in [54,56] are used instead of those quoted in *HITRAN* [12] or *GEISA* [19].

#### 4.2. Absence of spectroscopic parameters for some strong bands for supposedly well-documented species

Some infrared bands which are strong in atmospheric spectra are still totally absent in the databases even for molecules already well documented in the databases.

For nitric acid, the signature of the  $\nu_1$  band was unambiguously observed at 3551  $\text{cm}^{-1}$  (with about 30% absorption) by the *ATMOS/ATLAS3* experiment [57]. Fig. 2 shows this contribution in the *ATMOSpheric MOlecule trace Spectroscopy (ATMOS)* spectra at 3551  $\text{cm}^{-1}$ . However, parameters for this band are still completely missing in the literature and therefore also in the databases.

#### 4.3. Molecules of tropospheric interest

There have been scarce recent inputs to the *HITRAN* or *GEISA* databases involving molecules of major tropospheric interest, except for water, carbon dioxide, ozone, nitrous oxide, and methane. Species, including carboxyl acids (formic acid ( $\text{HCOOH}$ ), acetic acid ( $\text{CH}_3\text{COOH}$ ), formaldehyde ( $\text{H}_2\text{CO}$ ), ethylene ( $\text{C}_2\text{H}_4$ ), and acetone ( $\text{C}_3\text{H}_6\text{O}$ )), are known to play important roles in tropospheric chemistry [58–60]. For example, in the aqueous phase these species play an important role in the chemistry of clouds [61–63]. These molecules are indicators of pollution in the air of industrial cities [64]. Acetone plays a particular role in the formation of odd hydrogen ( $\text{HO}_x$ ) radicals and peroxyacetyl nitrate (PAN) [65]. Finally, these species are rather abundant during biomass burning [66].

All these species absorb significantly in the mid infrared region and most of them have strong absorption bands in the thermal infrared region [67,68]. To illustrate this point, Fig. 3 gives an overview of the infrared spectrum for acetone [69].

Therefore these infrared signatures may possibly be used to detect these species by the ongoing satellite mission Tropospheric Emission Spectrometer (TES) [70] or the upcoming Infrared Atmospheric Sounding Interferometer (*IASI*) on METOP-1 [19] which will perform emission measurements of the troposphere in the nadir geometry. This is of importance for the definition of the capacities of possible future satellite experiments devoted to tropospheric infrared measurements such as the Tropospheric sounder for Chemistry and climate (*TROC*), or the Geostationary Fourier Imaging Spectrometer (*GeoFIS*) satellite [71].

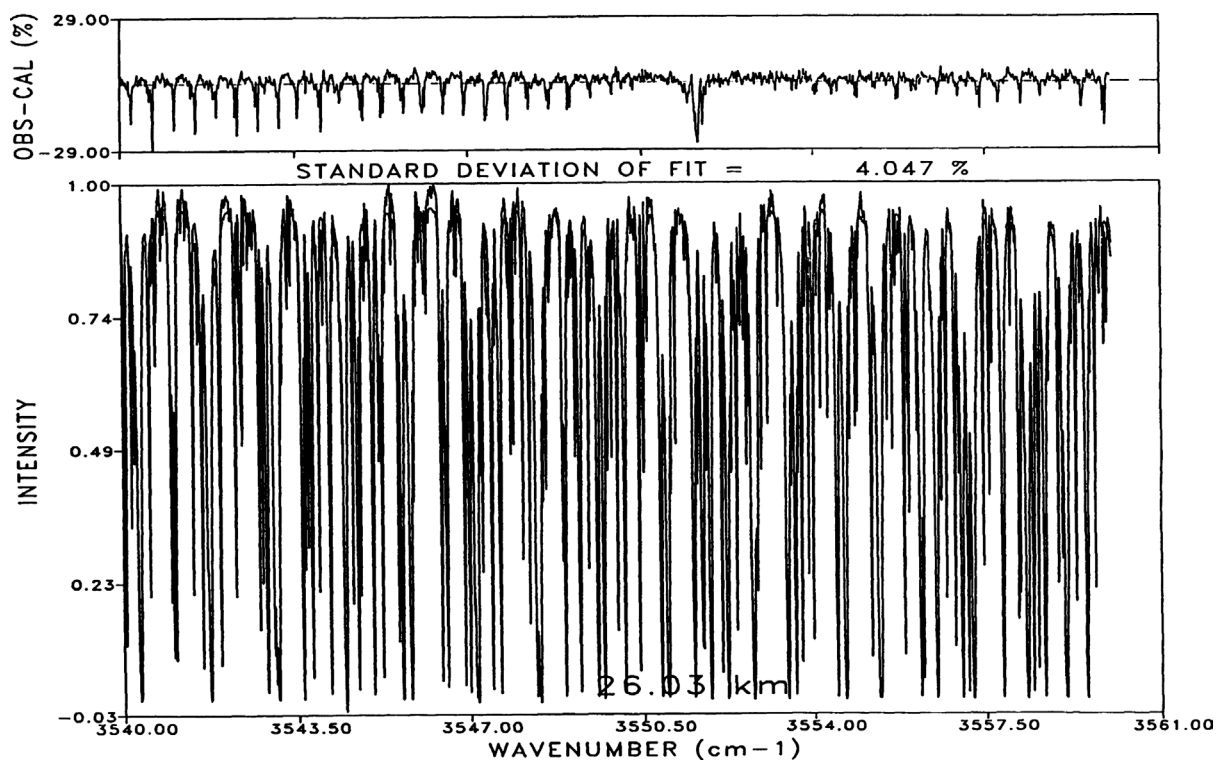


Fig. 2. Spectral least squares fitting to an ATMOS/ATLAS 3 spectrum in the  $3551 \text{ cm}^{-1}$  region. The ATMOS spectrum was recorded with a tangent height of 26.03 km. The spectral lines in this region are mostly due to  $\text{CO}_2$ . The line parameter database still does not include the  $\nu_1$  band of  $\text{HNO}_3$ , which is revealed in the difference spectrum (taken from Goldman et al. [57]).

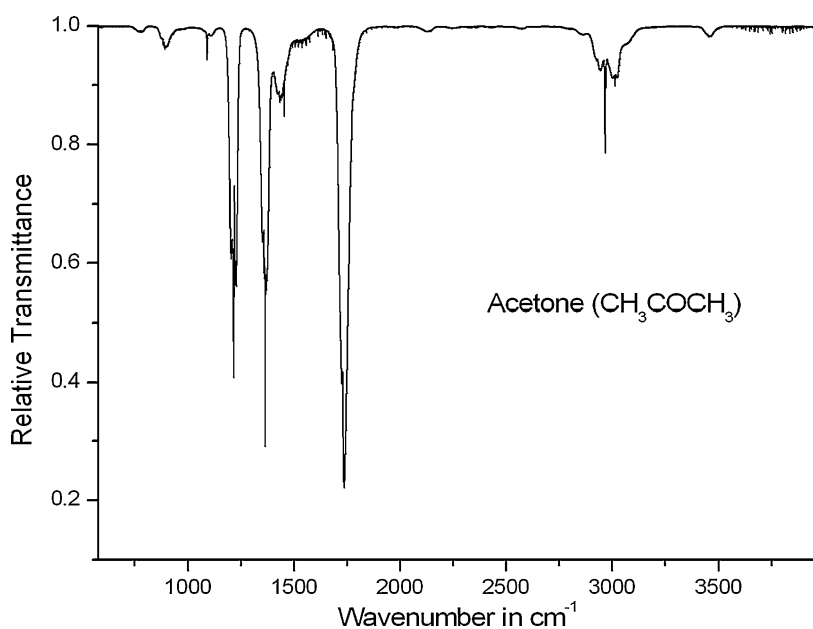


Fig. 3. Overview of the infrared spectrum of acetone (from <http://webbook.nist.gov/chemistry/>). No line-by-line parameters are available for these bands which have only been the subject of some medium resolution cross-section measurements [66,67].

There exist rather few spectroscopic parameters available in the public access databases, e.g., HITRAN and GEISA, to help for these tropospheric retrievals since most of these molecules represent quite a challenge for spectroscopic studies (the analyses are complicated by the existence of strong vibration–rotation interactions, and/or numerous large amplitude effects).

More explicitly, among these species, only ethylene and formic acid were the subject of a recent update in the 10- $\mu\text{m}$  region in the databases, leading to a very significant improvement in terms of line positions and, at least, in terms of relative line intensities. However from a subsequent recent study [72], it seems that for formic acid the absolute line intensities should be significantly revised.

Many of these species (e.g., formic acid, formaldehyde, acetaldehyde, acetic acid, and methyl formate) possess strong absorption bands in the 5.7- $\mu\text{m}$  spectral region, which can be used by quantum cascade laser technology for atmospheric remote sensing of these species. Unfortunately, there exist no parameters for these species at 5.7  $\mu\text{m}$  in the public access spectroscopic databases.

Tropospheric formaldehyde ( $\text{H}_2\text{CO}$ ) is routinely detected in the 3.6- $\mu\text{m}$  region by various techniques like Fourier transform spectroscopy [66,73], Tunable Diode Laser Absorption Spectroscopy (TDLAS) [74], difference-frequency-generation lasers (DFG) [75] and cavity leak-out spectroscopy using CO sideband laser [76]. This is because the 3.6- $\mu\text{m}$  region corresponds to the strongest infrared band of this molecule and to a rather clear window of transparency in the atmosphere. For formaldehyde, the 3.6- $\mu\text{m}$  bands were the subject of an extensive study in 1979 [77]. The experimental line positions and intensities derived there were used as the starting point to generate the  $\text{H}_2\text{CO}$  linelist that is currently implemented in the HITRAN and GEISA databases [12,19]. However, this linelist is highly inadequate since for a significant portion of the strongest lines (actually, most of the blended lines) the intensities are overestimated by a factor of two or three. For this reason it is clearly necessary to improve these parameters.

In discussing application of the database to tropospheric retrievals, particular attention should be given to the part of the HITRAN and GEISA compilations that is rapidly growing: the infrared cross-sections. There are currently over 30 different species represented in the compilations. However, half of these molecules are presently only given at ‘zero’ pressure. While these sets may be adequate for stratospheric simulations, they are insufficient for tropospheric research. In addition, the spectral ranges now available are predominantly in the long-wave region of the spectrum. Clearly new high-resolution laboratory measurements, at representative pressures and temperatures, must be obtained.

#### 4.4. Accuracies of the parameters

In order to estimate the errors associated with the data products (volume mixing ratio of the target species, temperature or humidity profiles in the atmosphere) which may be retrieved from the observed atmospheric spectra, the retrieval codes [78] need as input the errors associated with the spectroscopic parameters together with the spectroscopic parameters themselves. In principle, the uncertainties associated with these parameters are given by code indexes in the HITRAN database. Actually these uncertainties, although of crucial importance for the retrieval codes, are often suspect or even completely absent. In fact an accurate estimation of the uncertainties is a very difficult task that requires a lot of expertise and an extraordinary investment of time for database managers.

This type of sensitive study has only been performed for some specific focused programs, for example the MIPAS experiment [49] and the ‘Millimeter wave Acquisitions for Stratosphere/Troposphere Exchange Research’ (MASTER) [54] during the generation of spectroscopic databases dedicated to these instruments. These expensive studies were coupled with critical analyses of the existing parameters in the literature, with various laboratory measurements and/or theoretical calculations and finally with a selection of the best parameters to be included in an ad hoc database. Thus, the parameters which are finally quoted in these dedicated databases may differ significantly from the ones which are presently available in the public access databases. It is therefore recommended that these line-lists and the results of the associated accuracy studies should be made available as soon as possible.

## 5. Conclusion

The molecular spectroscopic databases have had a vast expansion over the more than three decades since their inception. The proliferation of high-resolution laboratory data of excellent photometric accuracy has been concurrent with this expansion. Whereas in the early days of the compilations decisions of data incorporation were a simple process, it is now often a question of adjudicating between different sets. In addition, due to the expansion of parameters for the line transitions, data must often be merged from separate independent sources. To deal with these and other issues, an international committee of experts has been established that makes recommendations, evaluations, and documentations. It also has the responsibility of looking into the long-term health and continuation of this effort.



While the discussion here has been directed towards applications related to remote sensing of the terrestrial atmosphere, the database has many more applications: environmental monitoring, industrial process control, surveillance, climate modelling, etc. Future directions are planned in order to accommodate planetary atmospheres and high-temperature gaseous phenomena.

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