

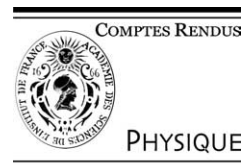


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Gas phase molecular spectroscopy/Spectroscopie moléculaire en phase gazeuse Infrared spectroscopy and the terrestrial atmosphere

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Presented by Guy Laval

Abstract

Fourier transform infrared spectroscopy is an extremely powerful technique for atmospheric remote sensing. In particular, on board a satellite and working in emission in the limb-viewing mode, it allows a global coverage during day and night. Based on this method the MIPAS experiment has been recently launched on ESA's Environmental satellite (ENVISAT). However, accurate retrievals require high quality spectroscopic parameters. It is the goal of this paper to show on a few selected examples the importance of using for the retrievals high quality spectral parameters derived from the best possible experimental and theoretical laboratory methods. *To cite this article: J.-M. Flaud, H. Oelhaf, C. R. Physique 5 (2004).*

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Résumé

Spectroscopie infrarouge et atmosphère terrestre. La spectroscopie par transformée de Fourier est une méthode très puissante pour le sondage atmosphérique. En particulier faire des mesures en émission par sondage au limbe à partir d'un satellite permet d'effectuer une couverture globale aussi bien le jour que la nuit. C'est pourquoi l'expérience MIPAS, basée sur cette technique, a été récemment mise en orbite sur le satellite européen ENVISAT dédié à l'environnement. Cependant la qualité des profils de concentration déduits des spectres atmosphériques est intimement liée à celle des données spectrales utilisées pour le dépouillement. Ce papier a pour but de montrer sur quelques exemples choisis l'importance de disposer pour ce faire de données spectrales de qualité, données obtenues au laboratoire à l'aide des meilleurs outils expérimentaux et théoriques. *Pour citer cet article: J.-M. Flaud, H. Oelhaf, C. R. Physique 5 (2004).*

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Keywords: Molecular spectroscopy; Infrared; Atmospheric sounding; Minor atmospheric constituents retrievals; Stratospheric ozone; Climate research

Mots-clés : Spectroscopie moléculaire ; Infrarouge ; Sondages atmosphériques ; Constituents atmosphériques minoritaires ; Ozone stratosphérique ; Climat

1. Introduction

Molecular spectroscopy, besides its own research themes, represents a powerful tool in a number of fields (atmospheric physics, astrophysics, atmospheres of the planets, combustions, leakage and process control, ...) to probe the medium of interest. It allows one indeed to measure in a non-intrusive way numerous properties of the medium (temperature, pressure, abundance of constituents, ...). As far as atmospheric physics is concerned (see for details [1–3] for example) the past years have seen a noticeable increase of studies aiming at (i) a better understanding of the different phenomena driving the atmospheric

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system and (ii) the prediction of its evolution in the future. In particular, human activities, important since the beginning of the industrial period, are strongly changing the atmospheric composition. One can quote for example the enhanced green house effect due to the emission of gases such as carbon dioxide or methane, or the loss of ozone in the stratosphere clearly observed over the poles (Ozone hole), or even pollution for which overarching issues such as air quality, free tropospheric ozone levels, acidic deposition, natural versus anthropogenic emissions are still open.

These questions are tackled both from the theoretical point of view by developing chemical transport models (CTM) with the intention of simulating the distribution and evolution of trace constituents in the troposphere and/or stratosphere and from the experimental point of view using various platforms (ground networks, balloons, planes, satellites) and different techniques. Among them optical remote sensing methods are widely used [4]. In particular, measurements from space are the only ones able to provide a continental or global view of the atmosphere. This is why a number of satellite experiments using various optical techniques (radiometers, grating spectrometers, Fourier transform interferometers, ...) have been launched. Recently, high quality optical remote sensing instruments working in the middle and thermal infrared such as MIPAS (Michelson Interferometer for Passive Atmospheric Sounding) [5], have been launched on ESA's Environmental satellite (ENVISAT); others will soon be in operation on American satellites, e.g., TES (Tropospheric Emission Spectrometer). In all cases, the analysis of the measurements requires the best possible knowledge of the spectral parameters (line positions, intensities, widths, absorption cross sections, ...) of the measured species and of their variations with temperature and pressure. This is particularly true for the recent instruments which cover wide spectral ranges at rather high spectral resolutions with excellent signal to noise ratios. The spectral parameters are derived from experimental and/or theoretical spectroscopy and, since obviously the accuracy of the retrieved profiles depends highly on the quality of the spectroscopic parameters, given the improved capabilities (higher spectral resolution, better signal to noise ratio, ...) of the new instruments, it is clear that new laboratory studies using the best experimental techniques and/or sophisticated theoretical models are required.

In many cases one has to face the 'classical' problem of laboratory work, i.e., reaching the required accuracy and determining it properly. This is an extremely difficult problem in itself but, in a number of cases, one has to tackle even more challenging questions. Let us quote in particular the difficulty of measuring and/or generating accurate line intensities for 'unstable' molecules or of modeling the spectrum of 'heavy' species.

It is not the goal of this paper to give a complete review of all these questions but rather to show on a few selected examples where up-to-date laboratory spectroscopic methods are required to meet the needs of atmospheric physics. The paper is then organized as follows: after a presentation of the MIPAS remote sensing satellite experiment and its needs, we will concentrate on real examples linked to the 'challenging spectroscopic questions' asked above. The case of the HNO_3 molecule, for which it is only recently that accurate line positions and intensities have been derived, will be described first. Then we shall discuss a case for 'heavy' species. Indeed the absorption of such species appears as a quasi-continuum in the atmospheric spectra and there are two 'schools of thought': either to measure all desired absorption cross sections for the whole range of atmospheric pressures and temperatures or to make some effort to model and generate a synthetic vibration-rotation spectrum. As an example, the case of the ClONO_2 molecule will be described.

2. The MIPAS (Michelson Interferometer for Passive Atmospheric Sounding) satellite experiment

As already stated, the interest in atmospheric research has remained high since the detection of the Antarctic ozone hole. Meanwhile, the Montreal Protocol has been successful in reducing the emission and atmospheric concentration of CFCs. There is a big debate, however, on the question whether and, if at all, by when the ozone layer will return to its pre-ozone hole state. Also, the climate is changing as greenhouse gas concentrations rise and there is a considerable but unexplained increase in stratospheric water vapor, which could have important chemical and climatic impacts. For the understanding of these and many other atmospheric processes, a detailed knowledge of the composition and distribution of trace gas constituents, as well as their evolution with time, is indispensable.

There are four essential requirements which any instrument dedicated to study atmospheric composition and its evolution with time needs to meet: sensitivity, selectivity, simultaneity and continuity. High sensitivity is needed since many of the relevant atmospheric species are minor constituents with mixing ratios in the ppt and ppb level. Good selectivity is needed in terms of spectral resolution, in order to enable, in the rather dense mid-IR spectrum, discrimination of spectral lines of different species from each other. Simultaneity is required since chemical constituents are highly interrelated by (photo-)chemical reactions. Last but not least, in order to study dynamics and chemistry as well as the atmospheric evolution, the measurements need to be made continuously over the whole globe with a high sampling rate.

One of the very few techniques that is able to meet these requirements is limb sounding with a Fourier-transform spectrometer in the mid infrared spectral region (FTIR). FTIR experiments for remote sensing of atmospheric species in the limb-viewing mode have been used now for almost three decades on stratospheric balloons, aircraft and space platforms [6–13]. Most of these experiments have been performed using the sun as a source of radiation, applying the solar occultation technique.

However, to enable observations with a maximum degree of flexibility in terms of scanning strategy and observation time, spectra need to be taken in emission, independently of any external background radiation source. From spacecraft, the limb emission spectroscopy offers continuous observation on a global scale with high sampling rate. Therefore, the basic decision for all MIPAS instruments has been to design the instruments for thermal limb emission sounding [13] instead of solar occultation. Based on this concept, various versions of airborne MIPAS instruments have been developed and operated in recent years on stratospheric balloon gondolas [14,15] and high altitude aircraft [16]. MIPAS-Balloon has participated successfully in all recent major European field campaigns concerning ozone research and satellite validation programs. In particular, vertical profiles of all relevant molecules belonging to the NO_y -family including the source gas N_2O and the key reservoir species HNO_3 , ClONO_2 and N_2O_5 were measured at different geophysical situations allowing one to tackle important issues related to ozone research such as denitrification [17–19], dehydration [20], nitrogen partitioning [21–24], chlorine activation and ozone loss [25,26], polar stratospheric clouds [27], and satellite validation [28–30]. However, though balloon-borne observations are a powerful technique to obtain precise and accurate measurements for process studies, they suffer from their snapshot character. MIPAS versions tailored to operate on aircraft, as, e.g., [16], allows one to increase the spatial coverage by providing cross sections of trace constituents, but high vertical resolution is limited to areas underneath the aircraft. In fact, global and continuous measurements of the whole stratosphere with a high sampling rate can only be achieved by using this concept on satellites.

Based on the experience achieved with MIPAS-B, a satellite version was proposed to the European Space Agency and accepted by ESA in the late 1980s as a core payload [5] of the environmental research satellite ENVISAT which was launched on 1 March 2002. Fig. 1 presents a general view of the ENVISAT satellite. Among the various experiments three of them are devoted to the observation of the Earth atmosphere. They are GOMOS (The Global Ozone Monitoring by Occultation of Stars) and SCIAMACHY (Scanning Imaging Absorption spectroMeter for Atmospheric CHartographY) working in the ultra-violet, visible and near infrared spectral ranges, and MIPAS working in the thermal infrared. MIPAS on ENVISAT is measuring the emission of the atmosphere in the $4.15\text{--}14.6\ \mu\text{m}$ spectral region where the atmospheric emission is significant. Also it is worth noticing that, besides its capability to provide broadband atmospheric spectra, its resolution ($0.05\ \text{cm}^{-1}$ apodized) is suitable for spectroscopic characterization since it allows one to resolve the spectroscopic features of most atmospheric constituents. A complete high-resolution spectrum is measured within 4 seconds. MIPAS is designed to perform measurements also with a lower spectral resolution in shorter time for special measurement opportunities.

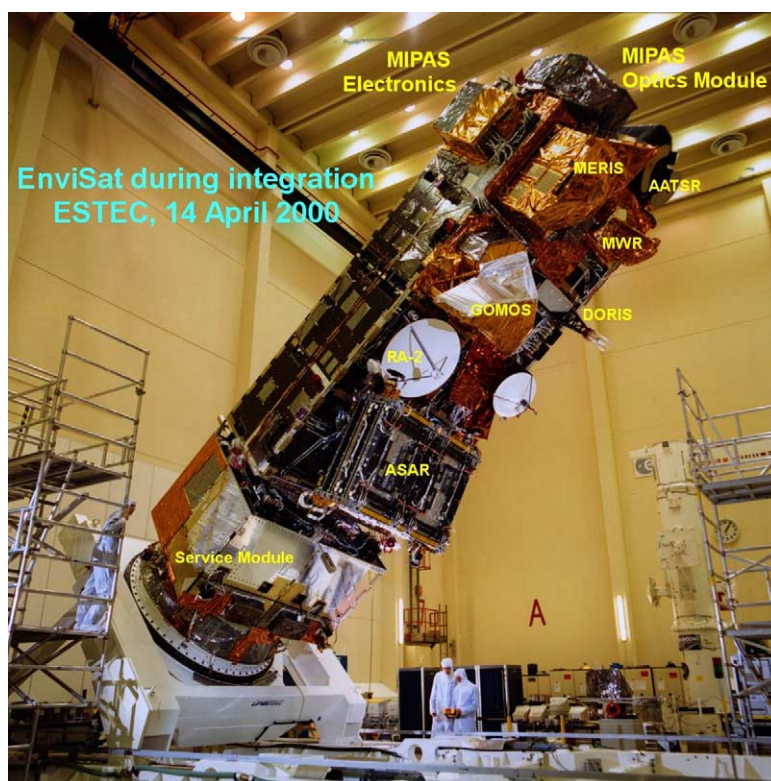


Fig. 1. View of the ENVISAT satellite (courtesy of ESA).

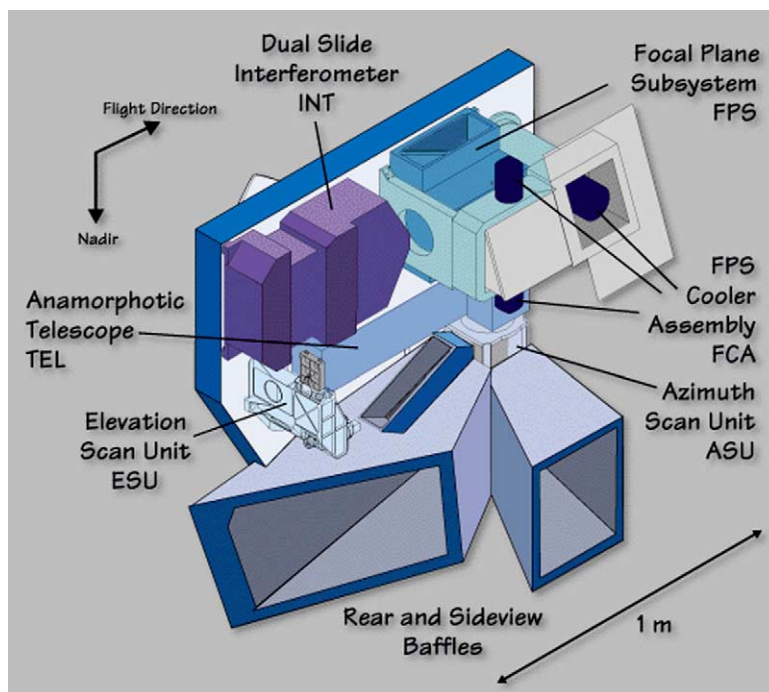


Fig. 2. Three-dimensional view of MIPAS (courtesy of ESA).

A three dimensional scheme of MIPAS including all major subsystems is displayed in Fig. 2. The MIPAS optics module is installed at the anti-sunward side of ENVISAT and has the following major parts: (1) front-end optics consisting of the azimuth scan unit, the elevation scan unit, the receiving telescope, and the calibration blackbody; (2) interferometer; and (3) focal plane subsystem. The optics module is about 1.36 m long (in the flight direction), 1.46 m high (nadir direction) and about 0.74 m deep (cold-space direction). It has a mass of about 170 kg. Additionally, the housing of the optics module carries several radiators: (1) a large radiator to cool all optical components of the instrument to about 205 K to reduce the thermal background of the instrument; (2) two separate radiators to cool the compressor of the Stirling cycle coolers and to precool the focal plane subsystem which keeps the detectors at about 70 K.

Fig. 3 illustrates the schematic layout of the optics module indicating the optical path of MIPAS from the entrance baffle to the detector elements in the cold unit. The optical layout of the major assemblies is clearly visible in the drawing. Not shown are the Stirling cycle coolers that provide the cooling of the detectors to temperatures as low as ~ 70 K which are located above the Focal Plane subsystem.

The radiometric requirements on MIPAS are highly demanding. A good radiometric sensitivity is indeed essential to allow detection of weak atmospheric signals without additional averaging. Radiometric sensitivity is expressed here by the noise equivalent spectral radiance NESR, which characterizes the instrument noise in terms of incident radiance. The required sensitivity must be better than $50 \text{ nW/cm}^2 \text{ sr cm}^{-1}$ at the long wavelength side, decreasing to $4.2 \text{ nW/cm}^2 \text{ sr cm}^{-1}$ at the short wavelength side. The requirement on radiometric accuracy is equally stringent: a calibration accuracy in the 1 to 3% range, which is difficult to achieve even for ground-based instruments, is essential to retrieve the atmospheric temperature of the emitting layer, which is a key parameter in the data retrieval.

Data processing on ground for the operational products T, p, O_3 , N_2O , CH_4 , H_2O , HNO_3 , and NO_2 is provided almost in real time under control of ESA. This dedicated processor has resulted from a number of scientific studies (see [31] and references therein). Other products, such as distributions of minor constituents not defined as operational, cloud properties, non-LTE parameters etc. are processed in a number of European Expert Support Laboratories in Europe.

First calibration, characterization and geophysical validation have proven that MIPAS on ENVISAT is largely compliant to the specifications [32]. Fig. 4 presents an atmospheric spectrum as observed by MIPAS on ENVISAT: Besides the most abundant minor atmospheric constituents such as CO_2 , H_2O , O_3 , CH_4 , ... whose emissions are obvious in the spectra it is worth noticing that, thanks to the broad band coverage and the high spectral resolution, it is also possible to observe a number of less abundant species such as NO , NO_2 , HNO_3 , HNO_4 , ClONO_2 , ... which are involved in the destruction processes of the ozone molecule and whose measurement is crucial to assess the validity of the photochemical atmospheric models. The pointing

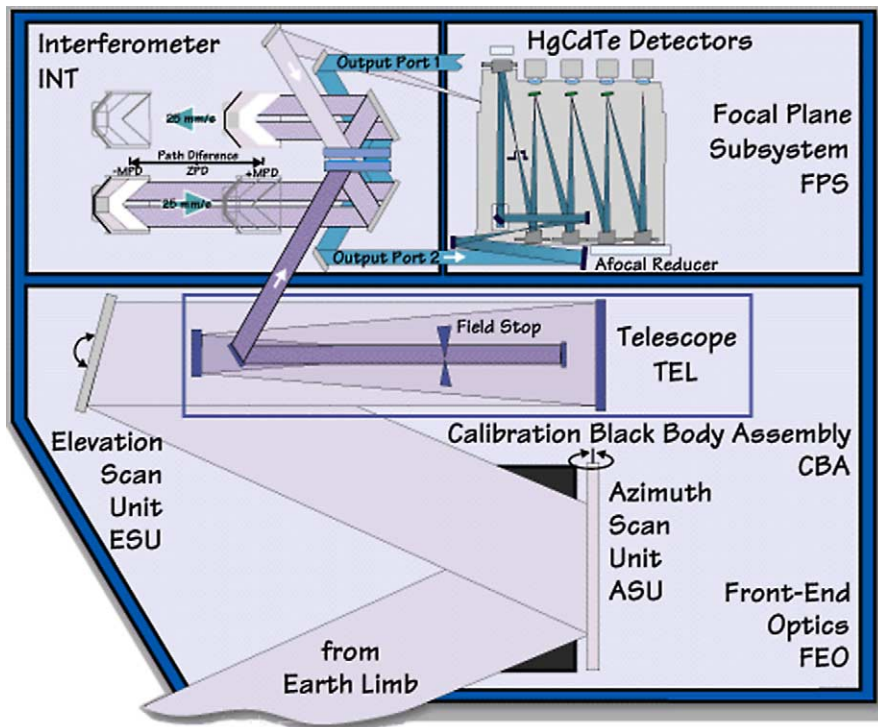


Fig. 3. Schematic layout of the optics module of MIPAS (courtesy of ESA).

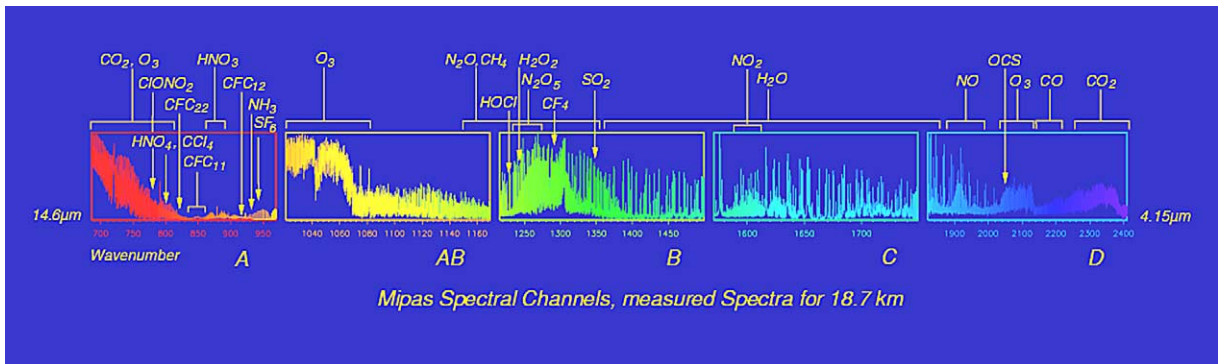


Fig. 4. Sample of atmospheric spectra measured by MIPAS-ENVISAT (plot prepared by U. Grabowski/IMK using calibrated spectra as provided by ESA). The figure shows the various spectral bands recorded by MIPAS at a tangent altitude of about 19 km. The x-scale displays wavenumbers in a linear scale from 685 cm^{-1} to 2410 cm^{-1} (wavelength range from 14.6 to $4.15\text{ }\mu\text{m}$). Also the emission domains of a number of minor atmospheric constituents are indicated.

geometry (see Fig. 5) is dual. The nominal mode is a rear viewing geometry allowing one to record at a vertical resolution of about 3 km spectra covering an altitude range going from about 6 km to about 68 km leading to the determination of well resolved vertical profiles of a large number of species (see Fig. 4). There exists also a distinct mode, the sideways viewing mode, dedicated to the measurement of unexpected events such as volcanic eruptions, to the monitoring of crowded aircraft routes over the Atlantic or Pacific oceans or to the study of day-night transitions of short-lived chemical species. Finally, other special modes are dedicated, e.g., to high altitude physics: The combination of high spectral resolution and broadband coverage allows the studying of non-LTE radiative processes well into the mesosphere or even thermosphere.

Obviously, the analysis of the MIPAS atmospheric spectra and the retrieval of accurate vertical concentration profiles require a precise knowledge of the spectral parameters of a large number of species. As already stressed it is not the goal of this paper to discuss all the problems faced by experimental and theoretical spectroscopy to provide such data but to concentrate on two

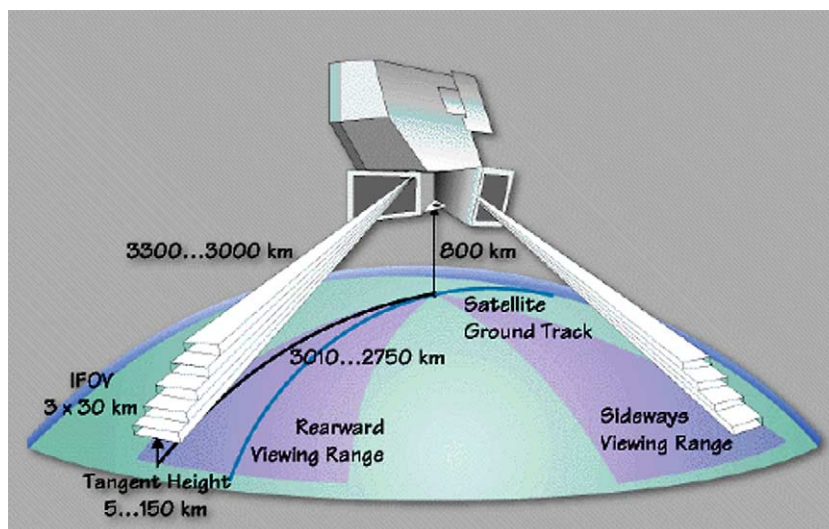


Fig. 5. The various observational modes of MIPAS (courtesy of ESA). The nominal mode is rearward viewing with an adjustable azimuth direction in order to ensure real pole-to-pole coverage of observed air masses. There is also a sideways viewing mode dedicated to the study of specific problems such as a volcano eruption, ... (see text).

characteristic examples, namely the cases of the nitric acid molecule for which it proved very difficult to get the line intensities with the sufficient accuracy and of a heavy species such as ClONO_2 for which a high resolution analysis is a challenge.

3. Line intensities for nitric acid: HNO_3

Nitric acid (HNO_3) plays an important role as a 'reservoir' molecule for the NO_x (nitrogen oxides) and OH_x (hydrogen oxides) species in the stratosphere. These radicals are potentially active contributors to the ozone destruction in the stratosphere through catalytic reactions. In addition, HNO_3 is incorporated in polar stratospheric clouds and in certain cases is removed from stratospheric layers by sedimentation of large ice crystals containing water and HNO_3 . It plays therefore a key role in the understanding of the ozone hole. In spite of this, HNO_3 has been for a long time the abundant atmospheric constituent with the least reliable spectroscopic data, both in terms of absolute intensity and in terms of representation of the interferences of the different cold and hot transitions in the $11 \mu\text{m}$ region. For this reason, HNO_3 has been the subject of numerous spectroscopic studies. The $11 \mu\text{m}$ band, which exhibits a strong signature in a rather clear atmospheric window, is commonly used for the remote sensing of this species from satellites, balloons, e.g., [33–35] or from the ground, e.g., [36]. This spectral region involves mainly the ν_5 and $2\nu_9$ cold bands located at 879.108 and 896.447 cm^{-1} respectively together with two hot bands, namely $\nu_5 + \nu_9 - \nu_9$ which possesses a rather sharp signature at 885.425 cm^{-1} [37] and the much weaker $3\nu_9 - \nu_9$ band at 830.6 cm^{-1} [38].

Because of its atmospheric interest, numerous low resolution grating [39–41], high resolution infrared diode laser [42–45], high resolution Fourier transform [37,38,46–49] and microwave [50,51] studies were devoted to the improvement of the line positions or line intensities for the HNO_3 bands at $11 \mu\text{m}$. Also updates of the spectral $11 \mu\text{m}$ line parameters were performed in the last versions of the atmospheric databases [52]. However, they proved not to be of sufficient quality. A good example is the $\nu_5 + \nu_9 - \nu_9$ hot band at 885.425 cm^{-1} which has been the subject of a recent infrared study [37]. As shown by the comparison of Figs. 6 and 7, the new spectroscopic analysis of the hot band has led to a much better agreement between observed and simulated spectra. This results also in an important improvement for HNO_3 retrievals since the spectral region where the Q -branch of the hot band appears is particularly well suited for atmospheric retrievals. Another overarching issue concerning nitric acid is the problem of absolute intensities. As already said there have been a lot of studies devoted to the HNO_3 intensities (see for example [48] for a rather extensive comparison of the various results) with values differing by as much as 30%. This is due to the experimental difficulty of knowing precisely the amount of HNO_3 in the laboratory sample. Fortunately, recent experimental [48,49] and theoretical [53] efforts have been devoted to this problem leading to improved and more consistent line intensities. These new results were introduced in the MIPAS database [54] and used for HNO_3 atmospheric retrievals using MIPAS spectra. Fig. 8 shows the significant improvement achieved for the residuals when using the new spectroscopic parameters. This demonstrates clearly the impact of the quality of the spectral parameters on the retrievals.

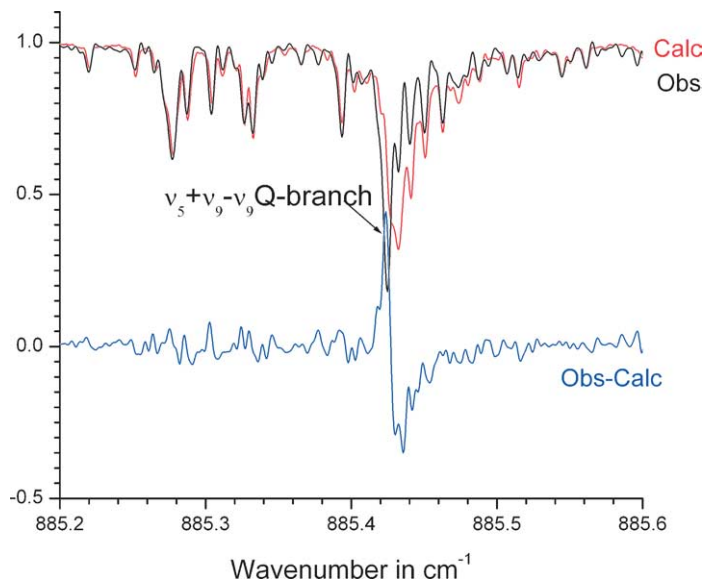


Fig. 6. Simulation of a high resolution FTS laboratory spectrum of HNO_3 , using the HITRAN line parameters [52]. It is clear that both the position and the shape of the Q -branch structure are not well simulated.

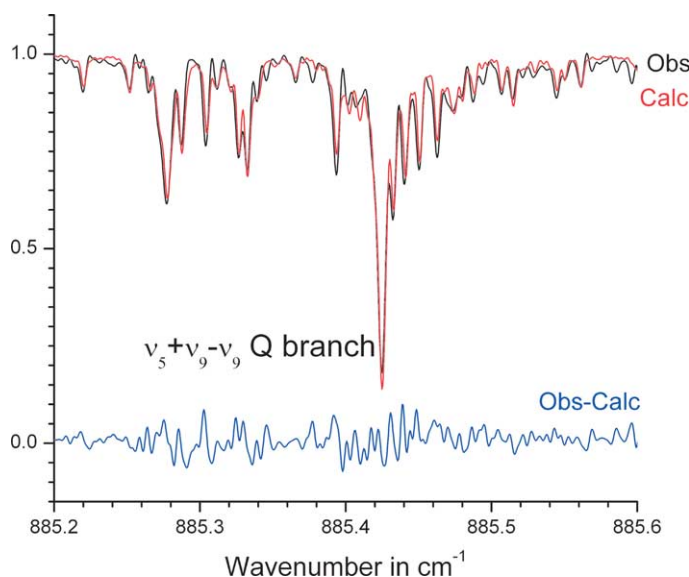


Fig. 7. Simulation of a high resolution FTS laboratory spectrum using the new spectral parameters [37] for the $\nu_5 + \nu_9 - \nu_9$ hot band. The agreement is significantly improved as compared to what is obtained in Fig. 6.

4. Line by line simulation of the spectrum of a heavy molecule: ClONO_2

Chlorine nitrate, ClONO_2 , which serves as a temporary reservoir species for chlorine and nitrogen radicals, plays an important role in stratospheric ozone chemistry. It is produced in the stratosphere as a reaction product of the photolytic break-up of man-made CFCs. It can undergo both gas-phase and photochemical as well as heterogeneous reactions on PSC particles. In the cold polar stratosphere ClONO_2 and HCl react on the surface on PSCs to produce active forms of chlorine which subsequently massively destroy ozone. Therefore, low values of ClONO_2 in the lower polar stratosphere are indicative of active chlorine. Infrared spectroscopy is the almost only and still only reliable technique to measure ClONO_2 in the stratosphere, although quite recently in-situ techniques have become promising, too. It has been detected and measured in the stratosphere in different infrared spectral regions from various platforms (ground, aircraft, balloons, space) using either absorption or emission tech-

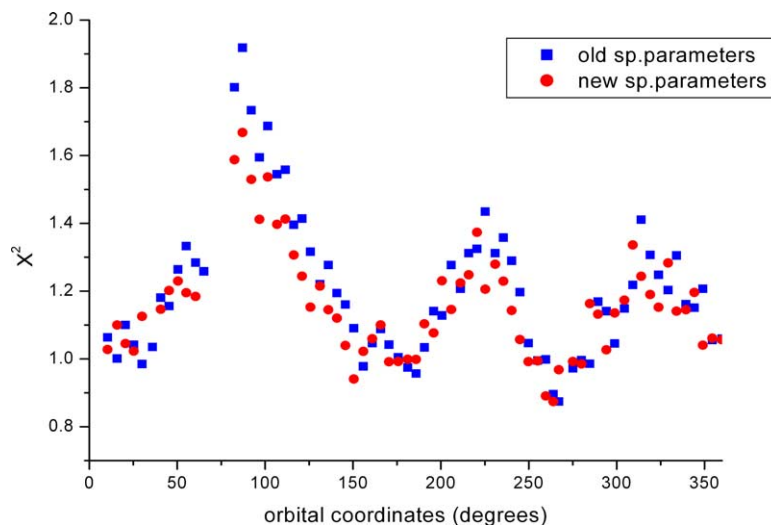


Fig. 8. Residuals versus orbital coordinate obtained for MIPAS HNO_3 retrievals when using the HITRAN [52] and the new [37] spectroscopic parameters (courtesy of P. Raspollini, Istituto di Fisica Applicata Nello Carrara).

niques (e.g., [34]). However, up to now, the analysis of the atmospheric spectra was performed using absorption cross sections since no good line by line spectrum was available. Indeed, at room temperature, even at high resolution, the bands are barely resolved due to the small values of the rotational constants and the overlapping of lines of the two isotopomers (^{35}Cl and ^{37}Cl) as well as from several hot bands. As a consequence, the corresponding absorptions appear as pseudo-continua. One possibility is then, as far as laboratory measurements are concerned, to measure the corresponding cross sections at various temperatures and various air-pressures spanning the atmospheric temperature and pressure ranges. This is an extremely tedious and difficult task. In fact, the measurements are performed for a finite set of temperatures and pressures and the measured cross sections are then interpolated and/or extrapolated for the analysis of the atmospheric spectra. This is not usually totally satisfactory as compared to a line-by-line calculation that allows accounting properly for the temperature and air-pressure variations. However, for all the reasons quoted previously, it is quite a challenge to generate a line list for such a heavy molecule like ClONO_2 .

4.1. High resolution analysis of the ν_4 spectral region of ClONO_2

In fact, as a good starting point for a high resolution spectroscopic analysis of this species, one has to have a fully resolved spectrum. It is only recently that such spectra become available through the use of a molecular beam and of a tunable diode laser spectrometer [55,56]. Indeed the low temperatures ($\sim 7\text{--}30\text{ K}$) obtained in the beam studies greatly simplify the spectrum (the hot bands as well as the transitions involving excited rotational levels vanish almost completely) thus allowing complete ro-vibrational assignment. Are such studies providing enough results to model atmospheric or room temperature spectra? Unfortunately not, since only very low J and K_a levels are observed at the beam temperatures preventing any reliable modeling of the atmospheric spectra. This shows up clearly in Fig. 9 where the Q -branch of the ν_4 band of the ^{35}Cl isotopic variant of chlorine nitrate as recorded by Fourier transform spectroscopy at 190 K [57], denoted 'obs', is not properly modeled using the Hamiltonian constants derived from the analysis of the molecular beam spectra [55]. It proves then essential, in order to make progress, to assign spectra recorded at temperatures much higher than those encountered in a molecular beam. This was done using a spectrum that was recorded at very high resolution (better than 10^{-3} cm^{-1}) and a temperature of 190 K with a Fourier transform spectrometer [57]. However, despite the high resolution, the assignment process proved to be extremely difficult for various reasons:

- given the existence of low-lying vibrational states, a number of hot bands appear in the spectrum even at a temperature of 190 K;
- two isotopomers are absorbing;
- resonance effects perturb the energy level patterns.

It is not the goal of this paper to describe extensively the assignment process but it is important to stress that it was a rather difficult task and that it is only because we use a Hamiltonian model taking into account the relevant vibro-rotational resonances that it was possible to model properly transitions with high J and K_a quantum numbers. This was done for the cold

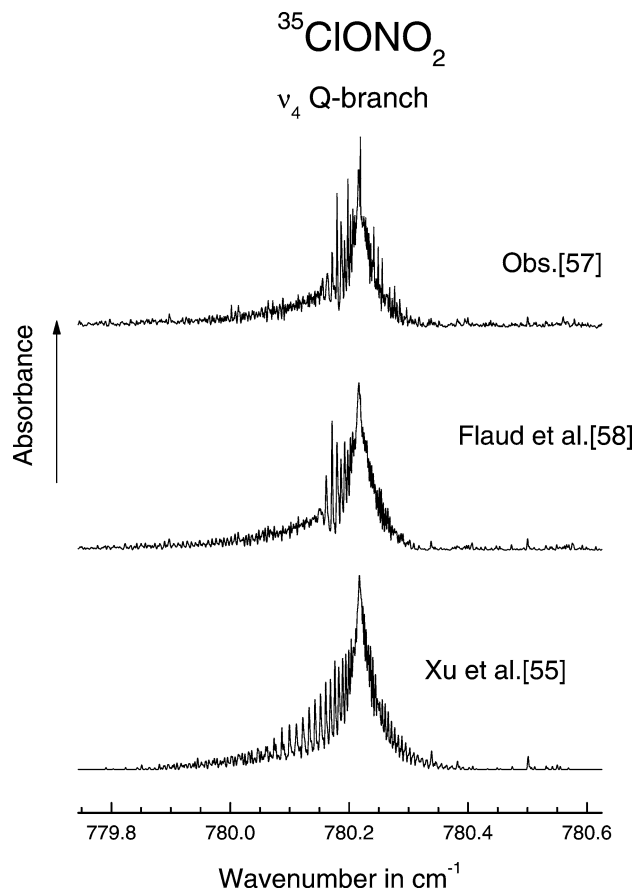


Fig. 9. Comparison of the observed and simulated ν_4 Q -branches of $^{35}\text{ClONO}_2$. The lowest curve is obtained using the Hamiltonian constants which were derived from the analysis of very low temperature beam spectra [55] illustrating the difficulty in extrapolating to stratospheric temperatures. The middle curve shows the improvement obtained by the new analysis [58]. The upper curve displayed the measured lab spectrum [57].

bands of the two isotopomers and for the first hot band leading to a much better simulation of the Fourier transform spectrum: see the improvement for the Q -branch (Fig. 9) and see Fig. 10 where one can notice the very good overall agreement between the observed and simulated spectra in the ν_4 Q -branch region [58]. The ultimate goal of a thorough spectroscopic study of the ClONO_2 spectrum would be to generate a complete line listing of all the bands absorbing in the spectral range of interest, i.e., in the 780 cm^{-1} spectral region in this case. Unfortunately, such a goal is nearly out of reach since ClONO_2 possesses several low-lying vibrational states. However, if in a narrow spectral range around the ν_4 Q -branch appropriate for atmospheric retrievals, the absorption can be modeled by a line-by-line calculation plus a pseudo continuum depending only on temperature, then the analysis of the atmospheric spectra and the retrieval of the ClONO_2 abundance would be greatly facilitated. Such an approach proved to be possible by systematically comparing synthetic spectra generated using the Hamiltonian constants derived from the analysis of the Fourier transform spectrum to the recent cross section measurements of [57]. Fig. 11 gives an example of comparison at a temperature of 219 K between observation and calculation [58] in the spectral region $779\text{--}781\text{ cm}^{-1}$ where the ν_4 Q -branch of $^{35}\text{ClONO}_2$, which is widely used in atmospheric retrievals, appears. One can see the excellent agreement achieved.

4.2. ClONO_2 retrievals

As we will see, a significant improvement of the retrievals is obtained when replacing the previously available cross sections by using the line by line calculation obtained from the combination of molecular beam TDL and high resolution lab FTS as described above.

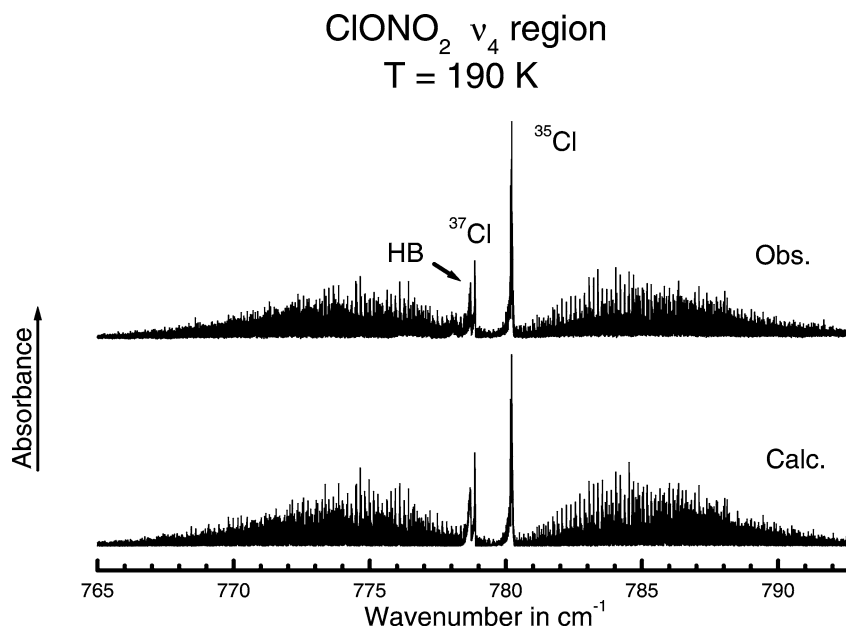


Fig. 10. Simulation of the entire ν_4 band [58] including both isotopic species and the first hot band (HB) of $^{35}\text{ClONO}_2$.

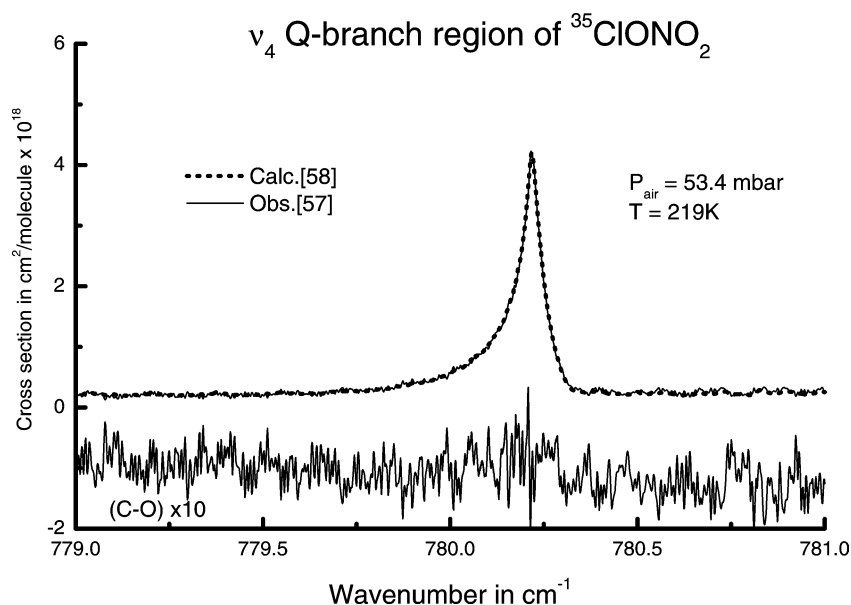


Fig. 11. Modeling of the ν_4 Q-branch region of $^{35}\text{ClONO}_2$ at 219 K. Note the good agreement as shown by the residuals (multiplied by 10) given at the bottom of the figure.

Commonly, the ν_4 Q-branch feature at 780.19 cm^{-1} is used for ClONO_2 retrievals in the mid-IR since this feature is the most prominent and least contaminated one. A first retrieval was performed using the cross sections provided by [59] that were at the time the only available data: it was found that the retrieved ClONO_2 peak mixing ratios in the Arctic appeared to be unrealistically high when using this data set. Also the observed spectrum is not well modeled (see Fig. 12). Such a bad situation can be ascribed to the fact that the spectral parameters were not of sufficient quality: in particular the cross sections had been measured only at 2 temperatures (213 and 296 K) and no variation of the absorption profiles with respect to pressure was provided. Fortunately, a new set of ClONO_2 absorption cross-sections was recently produced that takes into account the pressure and temperature dependence of the absorption at high spectral resolution [57]. A significant improvement of the retrievals [60]

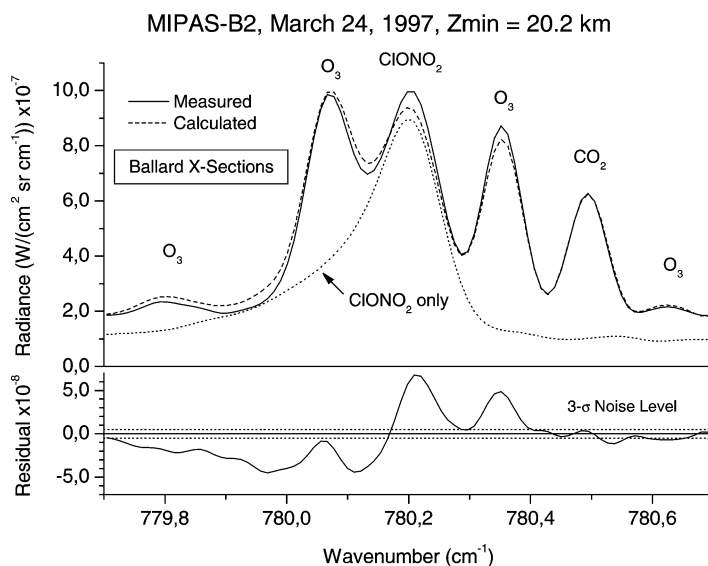


Fig. 12. Simulation of an atmospheric spectrum using the ClONO_2 cross sections of [59]. The rather poor agreement is due to the fact that the spectral parameters are not of sufficient quality (see text).

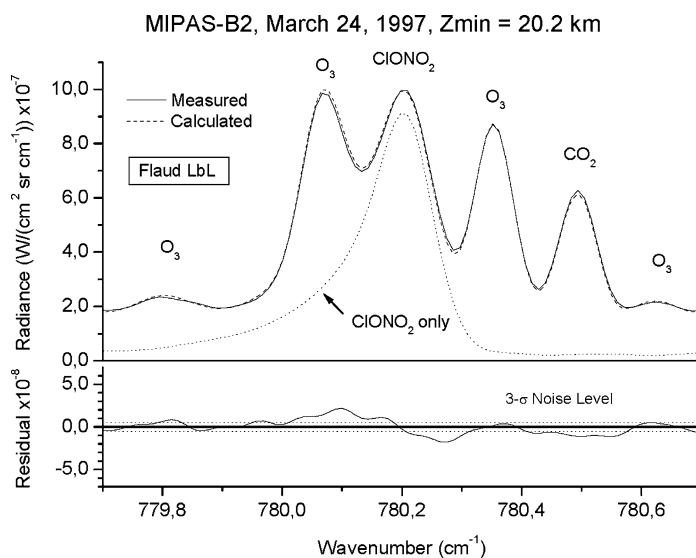


Fig. 13. Line by line simulation of the $\text{ClONO}_2 \nu_4 Q$ -branch absorption in the atmosphere. The line-by-line calculation allows one to account properly for the pressure and temperature ranges encountered along the line of sight.

is obtained when using the new absorption cross section data set. A step further was made using for the ν_4 spectral region the line-by-line parameters. As compared to the results obtained using the previous cross-sections [59] the use of the individual line parameters leads to an excellent simulation of the observed spectrum (Fig. 13) and accordingly to a more precisely retrieved profile. In particular, the significantly modified intensity and shape of the $\nu_4 Q$ -branch at low temperatures results in a lowering of the ClONO_2 volume mixing ratios of up to 35% compared to those resulting from retrievals with the previously available cross sections [59].

Such an example shows that mixing up-to-date high resolution experimental techniques (molecular beam + tunable diode laser spectroscopy, high resolution Fourier transform spectroscopy) with sophisticated theoretical models taking into account the various resonances proves to be extremely efficient since it allows an excellent modeling of the pseudo-continuum exhibited by a heavy molecule through a line by line calculation. It has also a strong atmospheric impact: in 1997 the total chlorine $[\text{Cl}_{\text{tot}}]$ in the stratosphere was about $3.6 (\pm 0.1)$ ppbv [61,62]. MIPAS-B ClONO_2 observations and fairly well collocated HALOE HCl observations inside the late polar vortex were combined to calculate $[\text{ClONO}_2 + \text{HCl}]$ which can be regarded as proxy for

the total reactive chlorine $[Cl_y]$ which becomes close to the total chlorine $[Cl_{tot}]$ in the middle and upper stratosphere. When taking the $ClONO_2$ VMR as retrieved using the 1988 cross sections [59], $[Cl_y]$ is significantly overestimated. With the new spectral parameters the retrieved proxy for total chlorine is consistent to within the error bars with total chlorine as derived from independent measurements [61,62].

5. Conclusion

It has not been the goal of this paper to give a complete overview of the infrared spectroscopy applied to atmospheric measurements or of the various techniques used to probe the atmosphere but rather to show on a few selected examples recent progress, both experimental and theoretical, achieved by modern molecular spectroscopy and atmospheric remote sensing. Indeed it was shown that IR limb emission spectroscopy from highflying carriers offers a great potential for atmospheric research addressing a variety of scientific and social issues such as the ozone problem and the ozone-greenhouse coupling. Furthermore, it was demonstrated that accurate spectral parameters are a prerequisite to obtain reliable distributions of atmospheric parameters from the analysis of atmospheric spectra. For that, it is necessary to use, in the laboratory, the best experimental techniques and/or sophisticated theoretical models. Two examples of studies in which the authors were involved, were chosen. First, the HNO_3 molecule for which it was demonstrated that new careful line intensity measurements combined with spectroscopic sophisticated theoretical models leads to a significant improvement in the quality of the retrieved profiles of this atmospheric important molecule. Second, the heavy $ClONO_2$ molecule for which it was possible, using high resolution experimental techniques coupled to a molecular beam and an appropriate theoretical model, to generate a synthetic line spectrum able to model the pseudo-continuum absorption observed in normal conditions for this molecule.

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