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Spectroscopic tools for remote sensing of greenhouse gases CH₄, CF₄ and SF₆

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Abstract Highly symmetrical molecules such as CH₄, CF₄ or SF₆ are known to be atmospheric pollutants and greenhouse gases. High-resolution spectroscopy in the infrared is particularly suitable for the monitoring of gas concentration and radiative transfers in the earth's atmosphere. This technique requires extensive theoretical studies for the modeling of the spectra of such molecules (positions, intensities and shapes of absorption lines). Here, we have developed powerful tools for the analysis and the simulation of absorption spectra of highly symmetrical molecules. These tools have been implemented in the spherical top data system (STDS) and highly-spherical top data system (HTDS) software available at <http://www.u-bourgogne.fr/LPUB/shTDS.html>. They include a compilation of modeled data obtained during the last 20 years. An overview of our latest results in this domain will be presented.

Keywords Greenhouse gases · Molecular spectroscopy · Simulation · CH₄ · SF₆ · CF₄ · Climate change

Introduction

Among the various gaseous pollutants that are present in the earth's atmosphere, the greenhouse gases require careful monitoring for the global warming survey. These species are very strong absorbers in the infrared region and some of them are chemically "inert" in the sense that they hardly react with other molecules and thus have a long or even extremely long lifetime in the atmosphere. These compounds have various natural or non-natural sources. The most abundant greenhouse gas is carbon

dioxide (CO₂). Nonetheless, several other gases, even if present in much lower quantities, must be taken into account since their absorption is much stronger than that of CO₂. Table 1 shows selected data about important greenhouse gases, and especially their so-called "global warming potential" (GWP). This value compares the ability of a given molecule to trap heat in the atmosphere compared to CO₂ (that has thus a GWP equal to 1). More precisely, the GWP of a greenhouse gas is the ratio of global warming (both direct and indirect), also known as radiative forcing, between one unit mass of a greenhouse gas and one unit mass of carbon dioxide over a period of time.

The quantitative remote sensing of molecular species in the atmosphere is usually done by means of infrared absorption spectroscopy, either from the ground or from balloons (Pieroni et al. 2001) or satellites. It is thus necessary to develop precise models able to reproduce molecular absorption spectra in both frequency and intensity. CH₄, CF₄ and SF₆ are highly symmetrical molecules. Such compounds, also called "spherical-top" molecules have complex vibration – rotation spectra, which require specific theoretical treatment. During the last 40 years, our group has developed models for handling such complex spherical-top spectra (Moret-Bailly 1959, Champion et al. 1992). Spectrum calculations and fitting programs implementing these methods, as well as results from analyses, are available using the STDS (Wenger and Champion 1998) and HTDS (Wenger et al. 2000) software.

The aim of the present paper is to give an overview of what can be done with the STDS and HTDS tools in the field of greenhouse gas spectroscopy. Thus, after recalling a very few basic properties of XY₄ and XY₆ molecules and their spectroscopy, we will review the cases of methane, sulfur hexafluoride and carbon tetrafluoride.

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Table 1 Selected data about important greenhouse gases. Concentration is given in parts per trillion (10^{12}) in volume (pptv)

Gas	Global warming potential	Lifetime (years)	Concentration (pptv)	Annual increase (%)
CO ₂ ^{a, b}	1	~250	0.360×10^9	0.4
CH ₄ ^{a, b}	21	~12	1.720×10^6	1.6
CF ₄ ^{a, b}	6,500	~50,000	75.0	1.0
SF ₆ ^{a, c}	23,900	~3,200	3.8	8.0
SF ₃ CF ₃ ^d	22,200	~3,500	0.12	–

^a <http://www.epa.gov> ^b Khalil 1999 ^c Geller et al. 1997 ^d Sturges et al. 2000

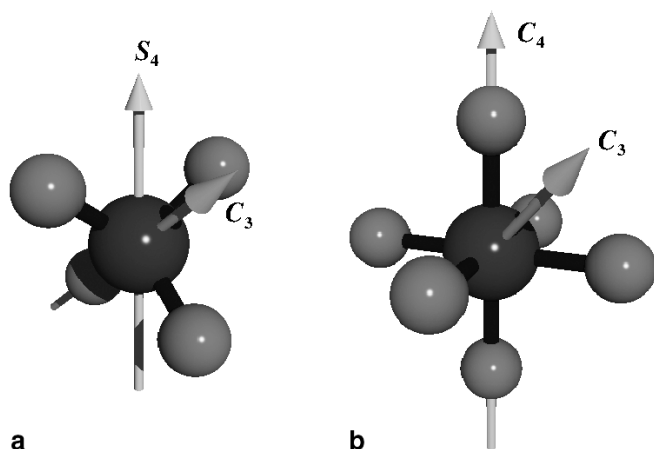


Fig. 1 **a** A tetrahedral molecule like CH₄. **b** An octahedral molecule like SF₆. Examples of symmetry axes are given (C_3 and C_4 are rotations of $2\pi/3$ and $2\pi/4$, respectively, and S_4 is a rotation of $2\pi/4$ combined with an inversion of all coordinates). The spectra strongly depend on these symmetry properties

Theoretical considerations

Readers interested in the detailed theory of spherical-top spectra can refer to several of our previous papers (Champion et al. 1992; Cheblal et al. 1999). In this section, we will focus on the specific aspects of the methods developed and used in our group.

In order to determine gas concentrations in the atmosphere, it is necessary to compare in situ or remote spectroscopic measurements with synthetic spectra. This requires the calculation of transition frequencies and intensities. Both depend strongly on the symmetry of the molecule. Here, we consider so-called “spherical-top” molecules (molecules whose ellipsoid of inertia is a sphere), i.e., either tetrahedral molecules of type XY₄ or octahedral molecules of type XY₆. Their symmetry point group is thus either T_d or O_h , respectively. Examples of such molecules with their main symmetry elements are shown in Fig. 1.

Tetrahedral XY₄ molecules possess four fundamental frequencies of vibration, usually labeled by ν_1 , ν_2 , ν_3 and ν_4 . Vibrations ν_1 and ν_3 correspond to stretching motions, while ν_2 and ν_4 correspond to bending motions. It is possible to observe the ν_3 and ν_4 fundamental frequencies in infrared absorption and all four fundamental frequencies using the Raman scattering technique. This can be

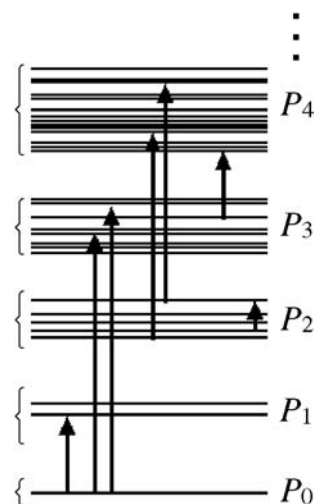


Fig. 2 Vibrational polyads for a molecule and examples of possible absorption transitions. Such a structure results in well-defined absorption windows, as shown in Fig. 3a in the case of methane

explained by symmetry considerations that we will not develop here.

In the same way, octahedral XY₆ molecules have six fundamental frequencies of vibration, usually labeled by ν_1 , ν_2 , ν_3 , ν_4 , ν_5 and ν_6 . Vibrations ν_1 , ν_2 and ν_3 are stretching modes, while ν_4 , ν_5 and ν_6 are bending modes. Only the ν_3 and ν_4 fundamental frequencies can be observed by infrared absorption, while only ν_1 , ν_2 and ν_5 can be observed using Raman scattering. The ν_6 mode is optically inactive. This last point has some consequences that we will discuss later for SF₆.

Each vibrational band has a very complex rotational structure. The specificities of our approach for the analysis and the calculation of rotation-vibration spectra of these species can be summarized as follows:

- The fundamental, harmonic and combination bands of vibration are usually grouped in packets called *polyads*. Figure 2 shows a schematic example of a vibrational polyad scheme of a molecule. The existence of such polyads results in well-defined absorption regions or “windows” in the spectra. Our method consists of a step-by-step study of the different polyads: P_0 (the ground state), P_1 , P_2 , ...

All these techniques are implemented in the programs included in the STDS (Wenger and Champion 1998) and

HTDS (Wenger et al. 2000) packages. Moreover, specific methods have also been developed for the modeling of line shifts and line broadenings that are induced by collisions between molecules. This is essential for the remote sensing of gas mixtures like the earth's atmosphere. This point will be discussed later when dealing with the case of methane.

Methane (CH₄)

Methane is a relatively abundant constituent of planetary atmospheres. It is also one of the major greenhouse gases on earth (Table 1) with many natural, industrial or agricultural sources. As a result, remote sensing applications require good knowledge of its spectroscopic parameters: position, intensity, air-broadened line width, lower-state transition energy, self-broadened line width, temperature dependence of the air-broadened width and the air-broadened pressure shift. In recent years, laboratory studies have resulted in significant revisions of these molecular line parameters in the public databases (Rothman et al. 1992; Rothman et al. 1998; Goldman et al. 2000).

The main difficulties in modeling the vibration – rotation spectrum of methane arise from the existence of essential degeneracies (induced by symmetry properties), accidental resonances (between stretching and bending vibrational motions) and broad rotational fine structure (large inertia constant).

The accuracy of the modeling of the methane infrared (IR) spectrum is enough to satisfy the needs of atmospheric applications: a few 10^{-3} cm^{-1} for line positions and a few percent for line intensities, including $^{12}\text{CH}_4$, $^{13}\text{CH}_4$ and CH_3D .

The low-resolution overview infrared spectrum of methane plotted in Fig. 3a reflects its polyad structure. Numerous experimental and theoretical studies have been devoted to its analysis over decades. At present, the lower polyads (P_0 : ground state – P_1 : dyad – P_2 : pentad – P_3 : octad) covering the region from 0 to 4,850 cm^{-1} can be considered as well known.

Appropriate effective frequency and intensity models have been developed and applied to analyses of the ground state (Champion et al. 1989a; Roche and Champion 1991), in the range below 10 μm , the dyad (Brown et al. 1989; Champion et al. 1989b; Roche and Champion 1991; Ouardi et al. 1996) from 5 to 10 μm (see Fig. 4), and the pentad (Hilico et al. 1994; Féjard et al. 2000) from 3 to 5 μm . The analysis of the next polyad (octad) observed from 2 to 3 μm has recently been performed (Hilico et al. 2001). The upper polyad (tetradecad, P_4) is only partially analyzed (Robert et al. 2001).

The line parameters of the dyad system (ν_2 and ν_4 interacting bands) are modeled with an accuracy of 0.00006 cm^{-1} for positions and 3% for intensities respectively. For the pentad system (ν_1 , ν_3 , $2\nu_2$, $\nu_2+\nu_4$, $2\nu_4$) around 3 μm , the accuracy achieved is 0.002 cm^{-1} for

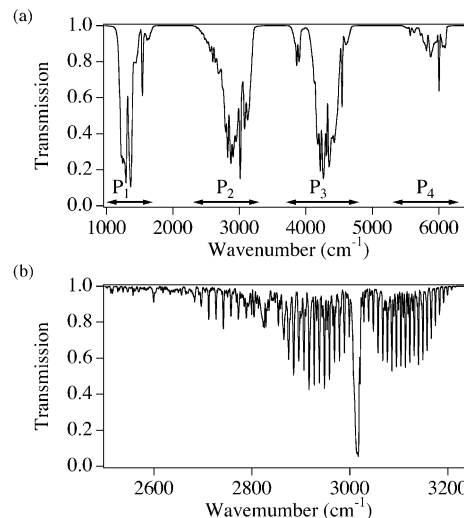


Fig. 3 Simulation of the infrared absorption spectrum of methane at different resolutions. **a** is an overview of the first polyads in the

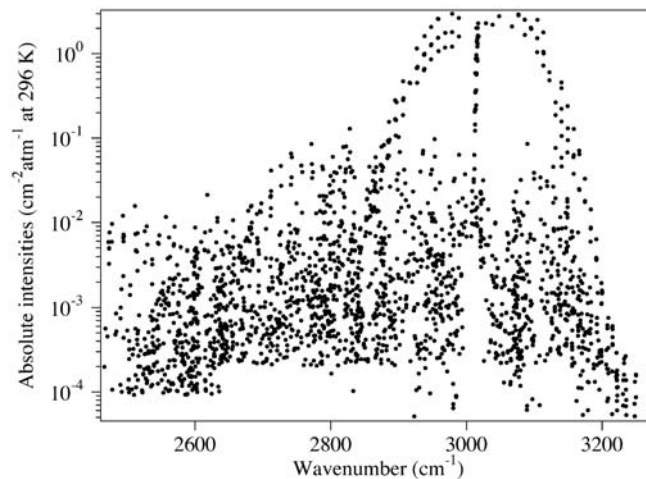


Fig. 4 Distribution of measured line intensities in the region of the ν_3 band of methane. Each dot represents a transition. The intensity scale is logarithmic, showing that strong as well as very weak transitions are considered in the analysis

positions and 3% for intensities (see Fig. 4). Selected transitions from the ν_3 band of CH_4 are proposed as secondary standards with absolute accuracy of 0.002 cm^{-1} for positions and 2% for intensities. Figure 3b shows an overview of the strongest ν_3 band. Of course, all the lines shown on this last figure have their own complex substructure that can be observed at higher resolution.

In addition to $^{12}\text{CH}_4$, the next two main isotopomers ($^{13}\text{CH}_4$ and CH_3D) contribute also significantly to the absorption spectrum. They have motivated several works. In particular, a global analysis of nine interacting bands of CH_3D in the 3 μm region has been published recently (Nikitin et al. 2002). Further details, updates and refer-

ences are available at <http://www.u-bourgogne.fr/LPUB/methane/metspec.htm>

Let us now say a few words about the problem of line shapes which we illustrate with the case of methane. As already explained, the remote sensing and detection of such molecular species as spherical tops in the atmosphere is usually done through the measurements of spectra in the infrared region. In most of the thermodynamic conditions encountered in this medium, a given spectrum cannot be modeled as a simple sum of profiles over all the individual lines. While the line widths do depend on the individual quantum numbers of the lines, the collisional transfers of populations in the lower and upper states of the transitions induce a phenomenon known as “line-mixing”, or collisional coupling of lines (Pieroni et al. 1999, 2000, 2001; Grigoriev et al. 2001). As a consequence, the spectrum of a given vibrational band must be calculated as a whole, to give satisfactory agreement with the measurements.

Sulfur hexafluoride, SF₆

Some new interest in sulfur hexafluoride studies has appeared recently, since this compound has proved to be a species of growing importance in the field of atmospheric physics and chemistry (Reddmann et al. 2001). In fact, it is now recognized as a pollutant that can contribute to the greenhouse effect (Khalil 1999; Dervos and Vassiliou 2000). This molecule is a by-product of electrical industries. Because of its chemical stability and diffusion properties, it is also the “air” in “Nike Air” shoes. At present, the concentration of SF₆ in the earth’s atmosphere is small, but increases at a rate of about 7% per year due to industrial emissions (Geller et al. 1997; Volk et al. 1997). Moreover, its lifetime in the atmosphere is very long, reaching 3,200 years (Geller et al. 1997; Volk et al. 1997) or maybe even more (Reddmann et al. 2001) as shown in Table 1. This molecule is also observed at low altitude, near large urban areas (Ho and Schlosser 2000). The small, but regularly increasing SF₆ concentration is also used to understand gas transport and circulation phenomena in the middle atmosphere (Eklund 1999; Hall et al. 1999; Khalil 1999; Manzini and Feichter 1999; Ray et al. 1999; Kjellström et al. 2000) or to monitor the distribution of other pollutants such as chlorofluorocarbons (CFCs) (Hurst et al. 1997; Wamsley et al. 1998; Romashkin et al. 1999). For all these reasons, correct quantitative measurements and monitoring of SF₆ in the earth’s atmosphere is necessary.

However, as we have shown in Boudon and Pierre (2002) and in earlier papers (Boudon et al. 1998, 2001; Bermejo et al. 2000), that the spectroscopy of this molecule is still not very well known. The present knowledge about SF₆ spectroscopy is very limited compared to methane for instance. In particular, the region of the ν_3 fundamental frequency near 948 cm⁻¹ is of great importance since its very strong absorption is responsible for the huge greenhouse capabilities of SF₆.

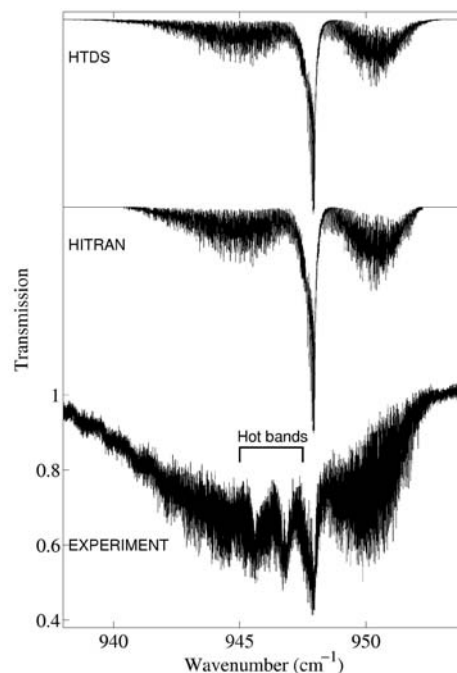


Fig. 5 Comparison between STDS and HITRAN simulations of the ν_3 stretching fundamental of SF₆ with an experimental spectrum from N. Lacombe

Nevertheless, if the $\nu_3=1$ level itself is very well known (Acef et al. 2000), the hot bands in this region, which largely contribute to the absorption (remember that the ground state population is only 30% at 300 K), are very poorly known. The knowledge of these hot bands requires the study of many other vibrational states, especially those with low energy.

Up to now, only one hot band of SF₆ has been analyzed in detail: $\nu_4+\nu_6-\nu_6$ in the ν_4 bending region (Boudon et al. 2001). Several vibrational levels have been analyzed with the aim of understanding the much denser ν_3 region. However, this work is in progress and still requires a lot of effort, from both the experimental and theoretical sides. One important technical difficulty arising when dealing with octahedral molecules like SF₆ is related to the ν_6 bending mode. This vibration, which is the lowest in energy and thus very important for hot band generation, is inactive in both infrared absorption and Raman scattering (see Theoretical considerations). Thus, some of our recent works (Boudon et al. 1998, 2001), although they do not concern the ν_3 region directly, intended to collect indirect information on this mode through the analysis of combination levels associated with this vibration. The final aim of this is the analysis of $\nu_3+\nu_6-\nu_6$.

Figure 5 shows a comparison between data from the existing databases and an actual experimental spectrum of the ν_3 region. While in this case the HTDS simulation and the HITRAN data (Rothman et al. 1992; Rothman et al. 1998) give quite similar results, the lack of hot band data is very clear when compared to the real spectrum. We are presently working on the analysis of the most important

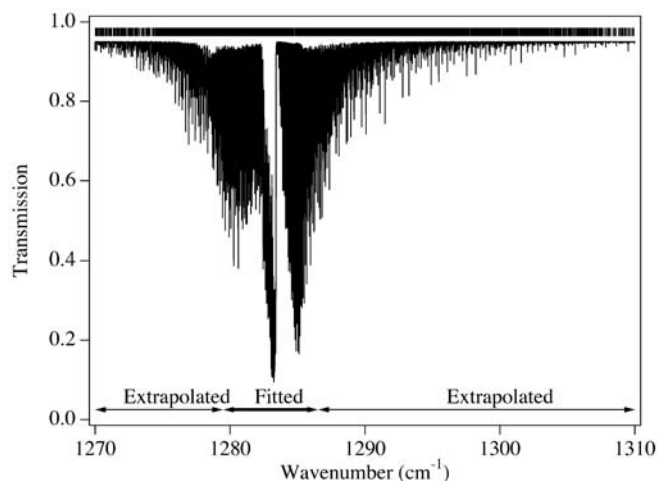


Fig. 6 Absorption spectrum of the ν_3 band of CF_4 at 296 K calculated using STDS. The parameters provided in STDS in this case were obtained through a fit up to $J=40$. Higher J values are extrapolated

hot bands in the region, namely $\nu_3+\nu_6-\nu_6$ and $\nu_3+\nu_5-\nu_5$. The last one should benefit from our recent study of the Raman spectrum of ν_5 (Boudon and Bermejo 2002).

As for methane, the problem of line broadening of SF_6 transitions in an SF_6/N_2 mixture has been treated recently in the case of the ν_3 band (Gamache et al. 2001).

Tetrafluoromethane (CF_4)

The spherical top data system (STDS) and highly-spherical top data system (HTDS) databases contain parameters for several other spherical-top molecules. The most interesting as far as atmospheric absorption is concerned is CF_4 . As for SF_6 , this is an important greenhouse gas with an extremely long lifetime in the atmosphere as shown in Table 1 and in several references (Harnisch et al. 1996; Khalil 1999). Furthermore, CF_4 is one of the most important polyfluorocarbons (PFCs) measured in the earth's atmosphere. It is one of the by-products of aluminum manufacturing. Its concentration is increasing at $\sim 1\%$ per year. However, the CF_4 spectroscopy is even less known than that of SF_6 . Figure 6 shows an example of STDS calculation for the very strongly absorbing ν_3 stretching fundamental (Gabard et al. 1995) and also illustrates how the spectrum calculations can be extrapolated to higher J values than those that were measured experimentally.

Conclusion

We have presented the spherical top data system (STDS) and highly-spherical top data system (HTDS) spectroscopic tools for the simulation of spherical-top spectra. Compared to other classical databases such as HITRAN (high-resolution transmission molecular absorption data-

base; Rothman et al. 1992, 1998; Goldman et al. 2000), these packages offer the advantage that they not only provide computed lists of measured transition frequencies and intensities, but rather programs and parameter files that allow the user to calculate spectra for specific physical conditions. This allows extrapolation to higher temperatures, pressures, or excited levels, within some reasonable limits, of course.

We have discussed the examples of CH_4 , SF_6 and CF_4 . It is clear that, even for the widely studied methane molecule, a lot of work still has to be done for the complete and precise modeling of the absorption spectra. Our group will thus continue its efforts in this direction. At the same time, similar tools will be developed for other types of molecules, which are also of atmospheric interest.

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