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Preface

# New visions of spectroscopic databases: An introduction to the special issue

## 1. Introduction

This Special Issue (SI) of the Journal of Molecular Spectroscopy is on "New Visions of Spectroscopic Databases". It stems from the 2014 GEISA Workshop, the purpose of which was to assess the current spectroscopic databases and to reinforce the interactions between experts from various disciplines needed to meet the challenges and requirements of future space observation.

Spectroscopic remote sensing is an indispensable tool of modern meteorology. It is used to investigate climate change and provide an improved understanding of the different phenomena driving an atmospheric system in order to predict its past and future evolution. During the second half of the 20th century, the synergy between the simultaneous development of new technologies (high speed processing with computers, high-resolution laboratory facilities, quantum-mechanical treatment in theoretical spectroscopy, etc.), provided the means to interpret a multitude of long-path atmospheric transmissions by performing radiance calculations for numerous scenarios and initiating notable progress in the development of molecular spectroscopy. The progress in Hamiltonian mechanics led theoreticians to demand more precision and detail in spectra, obtained from laboratory or planetary observations.

Numerous physical phenomena that influence the radiative transfer of a planet can be discerned and often measured from the variation of specific spectral features. As a consequence, spectroscopy is at the root of modern planetology, enabling us to determine the physical properties of planets remotely. From the mid 1960's, various scientific communities (Astrophysics, Atmospheric Physics, Metrology and soon after, Climate and Chemistry) required access to databases detailing the spectral characteristics of atmospheric molecular absorption and atmospheric diffusion. As a result, standardized spectroscopic databases (spectral range from $10^{-6}$ to 35,877.031 cm$^{-1}$), were initiated in the early 1970's, such as, the so-called pioneer "AFGL tape", ancestor of HITRAN (**HI**gh-resolution **TRAN**smission molecular absorption database), at the Air Force Geophysics Laboratory USA, and GEISA (**G**estion et **E**tude des **I**nformations **S**pectroscopiques **A**tmosphériques: Management and Study of Atmospheric Spectroscopic Information), at the Laboratoire de Météorologie Dynamique, in France. Both databases are regularly updated and they not only contain parameters for lines that have been measured in the laboratory but also calculated values for lines that have not been measured. Currently those comprehensive databases can be compared to a number of other spectroscopic databases, such as: MIPAS (**M**ichelson **I**nterferometer for **P**assive **A**tmospheric **S**ounding dedicated database) specifically tied to satellite experiments in the Earth's atmosphere; the JPL Catalog (**J**et **P**ropulsion **L**aboratory Submillimeter, Millimeter and Microwave Spectral line catalog) which mainly contains rotational transitions for a few hundred molecules which can or may be observed in the atmospheres of the Earth or other planets, or in the interstellar- or circum-stellar medium; the CDMS catalog (the **C**ologne **D**atabase for **M**olecular **S**pectroscopy) which mostly contains rotational transitions of molecules, on a similar basis as the JPL catalog, related to interstellar medium studies; ExoMol (high temperature **M**olecular line lists for modelling **E**xoplanet atmospheres) a database of molecular line lists that can be used for spectral characterization and simulation, and as input to atmospheric models of exoplanets, brown dwarfs and cool stars, and other models including those for combustion and sunspots. International cooperation contributed to the establishment of these widely used spectroscopic databases. The present status of these databases is the result of numerous studies performed during the last 50 years in several dedicated spectroscopic laboratories.

The role of molecular spectroscopy in modern atmospheric research has indeed entered a new phase with the advent of highly sophisticated spectroscopic instruments. Numerous space-based missions continually provide spectral observations which produce new revelations in planetology. The launch of high spectral resolution vertical infrared sounders like the **A**tmospheric **I**nfra**R**ed **S**ounder (AIRS) on board NASA/Aqua satellite since May 2002, or the **I**nfrared **A**tmospheric **S**ounding **I**nterferometer (IASI) on board the European polar satellites Metop since October 2006, have opened new perspectives for remote sensing applications, for numerical weather prediction, atmospheric composition and climate studies. The launching of the **T**hermal **A**nd **N**ear infrared **S**ensor for carbon **O**bservation (TANSO) on board JAXA Greenhouse **G**ases **O**bserving **SAT**ellite (GOSAT) in January 2009 and the NASA **O**rbiting **C**arbon **O**bservatory (OCO-2) in February 2014 have called for the need of improved spectroscopic parameters in the short-wave absorption bands of carbon dioxide ($CO_2$), methane ($CH_4$) and oxygen ($O_2$).

Planetary examples include Mars Express, Venus Express and Cassini-Huygens missions, studying the terrestrial planets and Jupiter, Saturn and Titan respectively. Accurate spectroscopic line parameters are also essential to interpret the planetary and astrophysical spectra observed with Herschel/HIFI, SOFIA/SAFIRE farinfrared spectrometer, ALMA (**A**tacama **L**arge **M**illimeter **A**rray) and JWST (**J**ames **W**ebb **S**pace **T**elescope).

Spectrally highly resolved radiances measured by powerful observational techniques such as ground-, aircraft-, balloon-, or satellite-based sensors enable global monitoring of atmospheres,

providing a wealth of information about its actual state. The exploitation of these remote sensing data requires accurate radiative transfer modelling to simulate (via the computation of the absorption coefficients) radiances and transmittance at high spectral resolution. The so-called line-by-line (LBL) Radiative Transfer Models (RTM's) are mainly used, needing as input the knowledge of the spectroscopic line parameters of the absorption/emission lines associated to all known discrete molecular transitions of each atmospheric molecule.

The infrared line parameters usually come from spectroscopic databases, such as HITRAN and GEISA, which provide information on spectral properties of various molecular species: (i) parameters for the molecules having an IR spectrum which can be described in terms of line spectrum ($CO_2$, $H_2O$, $O_3$, $CH_4$, $N_2O$, $CO$, etc.); (ii) far wing absorption and continuum data for $H_2O$; (iii) far wing absorption and line interference effects data for $CO_2$ or $CH_4$; (iv) cross-section parameters for heavy molecules (such as CFCs) for which line data are typically not available.

The quality of these spectroscopic parameters is of crucial importance for high resolution sounders. The need to improve and consolidate the spectroscopic parameters and the RTM's that use them will become a priority in order to exploit the increased spectral resolution and radiometric accuracy of new atmospheric instruments like IASI-New Generation (IASI-NG), which has been designed to improve by a factor of 2 the spectral resolution and by a factor of 2–4 the radiometric characteristics as compared to IASI.

The 31 publications included in this SI, edited in two volumes (volume II will appear in the next issue of the Journal of Molecular Spectroscopy), have been sorted into 3 classes (T1, T2, T3) evolving from themes issued from the conclusions of the GEISA-2014 workshop and considered as being at the root of new visions of spectroscopic databases. The description of each theme is given below with references to the related SI articles.

## 2. T1: Anticipating the future of molecular spectroscopy

(1) *Assessment of actual constraints imposed by the limited precision/accuracy of available spectroscopic data on studies of Earth and planetary atmospheres, as well as in astrophysics and astronomy.*
(2) *Anticipated evolution of requirements to be met by experimental and theoretical spectroscopic information (molecular species, spectral ranges, pressure and temperature dependencies, gas concentration ranges, evolving selection and accuracy of line parameters...).*

Five publications meet the subjects of this theme, mainly on the second topic and deal with $CO_2$, $O_3$, $D_2$, HD.

In the near infrared spectral region, modern laser spectroscopic techniques like Cavity Ring Down Spectroscopy (CRDS) provide a much higher sensitivity and require a smaller gas quantity than the traditional detection scheme based on a long path multiple pass cell associated with grating spectrographs or Fourier Transform Spectrometers (FTS). This technique, with associated experimental enhancements, is becoming an increasingly important spectroscopic tool, as illustrated by the papers of Mondelain et al. [1] and Vasilchenko et al. [2], on $D_2$ and HD respectively.

In conjunction with the line parameters, the computation of the absorption coefficient also requires the specification of the line shape, which should describe the effects of pressure and Doppler line broadening. The Voigt profile molecular line shape commonly used in LBL models is based on the simplified assumption that the collisional parameters are independent from the velocity of the

absorber; this can negatively affect the accuracy of the simulated spectra. There is thus the need for a better representation of the line shape than the Voigt profile. It should be noted that particular attention must be paid to the spectral line shape of species like water vapor and carbon dioxide for which optical depths in the atmosphere can reach very large values. New studies on line shape parameters of $CO_2$ are presented by Delahaye et al. [3] and Benner et al. [4], and go beyond using the Voigt profile by taking into account the speed-dependence and line mixing effects. In addition, Benner et al. [4] use a constrained multispectrum analysis method that minimizes the correlations between line parameters.

In the case of ozone, Janssen et al. [5], present the results of a tentative method for improving the spectroscopic databases, through atmospheric remote sensing studies using the Paris ground-based FTS and multispectral inter-comparisons.

## 3. T2 Improving database contents

(1) *High and very high spectral resolution laboratory measurements.*
(2) *Absorption cross-sections of atmospheric trace constituents (emphasis on potential greenhouse gases).*
(3) *Atmospheric aerosols (microphysical and optical properties, precursors); theoretical spectroscopy (non LTE conditions, line shape models...).*
(4) *Feedback from users, including groups developing remote sensing instrumentation, on latest needs to improve the precision/accuracy of spectroscopic data.*

Thirteen publications participate in the first topic of this theme and one in the second one. A total of 11 molecular species were involved: $H_2O$, $CO_2$, $CO$, $NH_3$, $CH_4$, $C_2H_2$, $C_2H_4$, $CH_3Cl$, $Cl_2CO$, $BrONO_2$, $CD_2HOH$, and some of their isotopologues. Experimental and theoretical approaches were used for the enrichment of spectroscopic databases, deriving new or updated spectroscopic parameters for Earth's or other planetary atmospheres.

The experimental approach included 4 different measurements technics, i.e.:

–   FTS spectroscopy with resulting publications of: Sung et al. [6] ($^{14}NH_3$), Hashemi et al. [7] ($^{12}C^{16}O$), Ben Hassen et al. [8] ($C_2H_4$), Barbouchi Ramchani and Jacquemart [9] ($^{12}CH_3{}^{35}Cl$ and $^{12}CH_3{}^{37}Cl$), Flaud et al. [10] ($Cl_2CO$), Ndao et al. [11] ($^{35}Cl_2CO$ and $^{35}Cl^{37}ClCO$). New infrared absorption cross-sections have been obtained by Wagner and Birk [12] ($BrONO_2$).
–   CRDS spectroscopy with new assignments on $^{12}C_2H_2$ and $^{12}C^{13}C$ $H_2$ described by Kassi et al. [13].
–   CRDS + DAS (Differential Absorption Spectroscopy) used by Campargue et al. [14] ($^{13}CH_4$).
–   External cavity tunable diode laser spectrometer for the investigation of the spectrum of $^{15}NH_3$ by El Romh et al. [15].

The novel approaches make it possible to derive new or updated line lists for implementation in databases, where the experimental data are unavailable. The works of Coudert and Chelin [16] ($H_2{}^{18}O$) and Ndao et al. [17] ($CD_2HOH$), using the bending-rotation approach are suited to Earth's atmosphere studies; planetary atmosphere studies will benefit of the results from Gamache et al. [18] ($H_2O$, all isotopologues); modified Complex Robert-Bonamy (MCRB) for line shape and Polyansky et al. [19] ($NH_3$; *ab initio* potential energy surface).

This first volume includes 17 publications, among the 19 ones sorted in classes T1 and T2, and quoted in sections 2. and 3.; the