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Wednesday Aug. 24, 2016 Program

8:00-8:30	Welcome	
8:30-9:00	Official opening	
Chair : J. Vander Auwera		
9:00-9:35	C. Goldenstein (<i>invited speaker</i>)	p 7
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9:55-10:15	S.T. Melin	p 9
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10:50-11:10	R. Georges	p 10
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12:00-14:00	Lunch	
Chair : P. Rannou		
14:00-14:35	R. Wordsworth (<i>invited speaker</i>)	p 13
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16:35-17:00	Coffee break	
17:00-18:30	Poster session 1	P 23-72

Infrared Laser-Absorption Sensing for Combustion Flows

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Laser-absorption spectroscopy (LAS) sensors have been used to characterize a wide range of combustion systems, including power plants, internal combustion engines, hypersonic propulsion systems, and novel detonation combustors. Such systems demand sensors capable of providing increasingly accurate measurements of temperature and molecular species at extreme temperatures and pressures spanning 500 to 4000 K and 0.5 to 100 atm, respectively. Researchers have employed a variety of light sources (diode, quantum cascade, and hyperspectral lasers) and diagnostic techniques to meet these needs by interrogating the infrared absorption bands of key combustion products, primarily H₂O, CO, CO₂, and NO_x. However, the relative deficit of spectroscopic databases and parameters that are accurate at such extreme thermodynamic conditions continues to limit the accuracy of such sensors. This talk will provide an overview regarding the status of infrared LAS sensors and how they have been applied to study combustion systems. Particular attention will be paid to several recently developed diode- and quantum-cascade-laser-based sensors that were used to characterize detonation combustors [1,2]. Several semi-empirical databases enabling improved modeling of high-*J* H₂O transitions at high-temperatures and -pressures via lineshape models that account for Dicke narrowing and speed-dependent broadening will also be discussed [3-5].

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Recent progress in variational hot spectra calculations

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Accurate knowledge of near infrared intensities of polyatomic molecules is essential for the modeling of various planetary atmospheres, brown dwarfs and for other astrophysical applications. The spectral characterization of such planetary objects relies on the necessity of having adequate and reliable molecular data in extreme conditions (temperature, optical path length, pressure). On the other hand in the modeling of astrophysical opacities, millions of lines are generally involved and the line-by-line extraction is clearly not feasible in laboratory measurements. Though they do not yet reach spectroscopic accuracies, recent global variational calculations based on ab initio surfaces are probably the most suited for providing reliable cold and hot band transitions because they implicitly account for all intramolecular interactions in a wide spectral range.

In the framework of the Reims-Tomsk collaboration, we present the recent advances in hot spectra calculations from normal-mode models, accurate intra-molecular potential energy and dipole moment surfaces and efficient computational methods. We will focus on our updated hot methane, ethylene and phosphine line lists. First results obtained from our new Eckart frame curvilinear model will be also presented.

Sapphire gas cell for collection of reference spectra with validation of H₂O vapor absorption thermometry up to 1723 K

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Our recent work demonstrates a novel static gas cell developed for quantitative spectroscopic studies at temperatures up to 2273K. The gas cell is sealed internally using optically contacted sapphire, allowing it to operate at temperatures beyond that of previously demonstrated static cells. The cell is suitable for studies with a variety of gas species, including CO₂, CO, O₂, OH, H₂O, and NO. Using a wavelength tunable external cavity diode laser, direct absorption spectra for H₂O vapor were recorded in the cell over the 7326-7598 cm⁻¹ range with resolution 0.0001 cm⁻¹ at temperatures from 296-1723K [1] and pressures from 0.0235 – 0.955 bar. Measured spectra were compared to simulated spectra to infer gas temperature [2], consistent with a common use of absorption spectroscopy as a combustion diagnostic. For a cell temperature of 1723 K, the inferred temperature was 1728 K when BT2 was used, and 1688 K when HITEMP was used.

For applications in high speed *in situ* gas thermometry, a high repetition rate (10-100kHz) H₂O vapor absorption thermometer has been built based on a MEMS-VCSEL source [3]. To validate the MEMS-VCSEL sensor, H₂O vapor absorption measurements were performed in the gas cell over the 296-1723K temperature range at atmospheric pressure. The temperature accuracy of this sensor was assessed using the fitting technique of Simms *et al* [4].

Keywords:

High-temperature spectroscopy

Gas cell

Reference spectra

H₂O vapor thermometry

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High-temperature infrared spectroscopy using a high enthalpy source

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High-temperature spectroscopic data of polyatomic molecules are lacking in the mid and near-infrared ranges. They are especially needed for the modelling of brown dwarf and hot Jupiter atmospheres or the circumstellar envelopes of evolved stars. Various experimental approaches, based on the use of subsonic and hypersonic flows produced by a high enthalpy source [1], have been developed in Rennes.

Thus, FTIR emission infrared data of methane have been recorded at about 1400 K in the dyad [2] and pentad regions, under local thermodynamic equilibrium (LTE) conditions. In addition, high-resolution cw-CRDS data have been recorded in the tetradecad region under non-LTE conditions by probing a hypersonic expansion generated by a preheated mixture of argon and methane [3]. A strong decoupling of the molecular internal degrees of freedom has been obtained with rotational and vibrational temperatures of about 10 K and 750 K respectively, producing rotationally cold “hot bands” issued from highly excited vibrational levels. In parallel, cw-CRDS data of methane have been recorded around 1.5 μm by probing the shock layer resulting from the sudden deceleration of the hypersonic flow impacting on a screen, leading to almost equilibrated rotational and vibrational temperatures of about 800 K.

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Empirical line lists and assignments of hot methane and ammonia for the 1-2 μm region

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High resolution transmission spectra (0.02 cm^{-1}) of methane and ammonia have been recorded at elevated temperatures (up to 1000 K) for the 1-2 μm spectral range, using a Fourier transform infrared spectrometer and tube furnace. These transmission spectra have been used to construct empirical line lists that contain line positions, intensities and lower state energies, which are suitable for high temperature applications such as exoplanet and brown dwarf atmospheres as well as combustion environments.

The 1-2 μm spectral region contains a large number of transitions for both molecules, and the spectra become very congested and difficult to assign at elevated temperatures. By comparing our high temperature spectra to the latest state-of-the-art *ab initio* calculations from the University of Reims and the University College London, we are making line assignments for hot bands and higher rotational levels. We will present our empirical line lists and compare our data with the latest predictions.

High temperature line lists for C₂H₂ and NO₂ molecules

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We present the high-resolution, high-temperature line lists for acetylene and nitrogen dioxide molecules. These line lists have been generated on the basis of the global modeling of the line positions and intensities within the framework of the method of effective operators. The line shape parameters were calculated using the semi-empirical approach (NO₂ molecule) or simple empirical equations (C₂H₂ molecule). The reference temperature for the line intensity in both line lists is 296 K and the intensity cutoffs are 10⁻²⁷ cm⁻¹/molecule cm⁻² at 1000 K for C₂H₂ and 10⁻²⁵ cm⁻¹/molecule cm⁻² at 1000 K for NO₂. The C₂H₂ line list covers 50-9900 cm⁻¹ wavenumber region. The NO₂ line list covers 466-4776 cm⁻¹ wavenumber region. The line lists are useful for studying high-temperature radiative properties of C₂H₂ and NO₂ molecules. These line lists will be freely accessible via the Internet site of V.E. Zuev Institute of Atmospheric Optics SB RAS <ftp://ftp.iao.ru/pub/>.

Climate modelling of primitive atmospheres and exoplanets: Progress, problems and key spectroscopic uncertainties

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The rapid growth of exoplanet science over the last 20 years has brought a wealth of new opportunities and challenges in the study of planetary atmospheres. It has also reinvigorated study of exotic climates (past and present) within the Solar System. The need for new spectroscopic data in planetary climate studies is pressing, but the parameter space is vast. In this talk I discuss a few key areas where more accurate spectroscopic data is most needed. In particular, I describe current research frontiers in radiative calculations of the runaway greenhouse effect, hot rocky exoplanet atmospheres, and cold reducing climates. I also present some new results on the early Martian climate that utilize recently calculated collision-induced absorption coefficients for CO₂ in combination with other gases (see also Kalugina et al., this conference). I conclude by discussing ways to increase communication and collaboration between spectroscopists and planetary scientists in order to maximize future progress.

Spectroscopic needs for the Atmospheric Chemistry Experiment (ACE)

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The Atmospheric Chemistry Experiment [1] (ACE) is a satellite mission for remote sensing of the Earth's atmosphere, launched August 2003. The primary instrument on board is a high resolution (25 cm maximum optical path difference) Fourier transform spectrometer (FTS) operating in the infrared (750-4400 cm⁻¹). The current status of the mission will be described, along with summaries of recent results, work on the forthcoming processing version (v4.0), and spectroscopic needs for the mission.

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MIPAS database: new HNO₃ line parameters at 7.6 μm validated with MIPAS satellite measurements

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Improved line positions and intensities have been generated for the 7.6 μm spectral region of nitric acid [1]. They were obtained relying on a recent reinvestigation of the nitric acid band system at 7.6 μm [2] and comparisons of HNO₃ volume mixing ratio profiles retrieved from the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) limb emission radiances in the 11 and 7.6 μm domains. This has led to an improved database called MIPAS-2015. Comparisons with available laboratory information (individual line intensities, integrated absorption cross sections, and absorption cross sections) show that MIPAS-2015 provides an improved description of the 7.6 μm region of nitric acid. This work should help to improve HNO₃ satellite retrievals by allowing measurements to be performed simultaneously in the 11 and 7.6 μm spectral domains. In particular, it should allow a better analysis of the existing IASI spectra as well as spectra to be recorded by the forthcoming Infrared Atmospheric Sounding Interferometer – New Generation (IASI-NG) instrument.

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Precise methane absorption measurements for MERLIN: an example of high-resolution spectroscopy application for space-based remote sensing missions

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Methane (CH₄) is the second most important anthropogenic greenhouse gas after carbon dioxide. It is responsible for about 20% of the warming induced by long-lived greenhouse gases. The lack of precise global measurements of atmospheric methane is a major problem which limits our understanding of methane source- and sink-processes, existing surface measurements of methane do not have sufficient spatial coverage to adequately quantify the worldwide distribution of methane emissions. Thus, high-precision space-borne measurement techniques are necessary to obtain global coverage. In order to realize this goal, Centre National d'Etudes Spatiales (CNES) and Deutsches Zentrum für Luft- und Raumfahrt (DLR) proposed the "Methane Remote Sensing Lidar Mission" (MERLIN [1,2]) in 2010 within the framework of a German-French climate-monitoring initiative, based on the integrated-path differential-absorption (IPDA) LIDAR technique. The selected on-line wavelength is situated at the trough ($\lambda=1645.55$ nm) between two strong absorption features which belong to the R(6) manifold of the 2v₃ band of 12CH₄ [1]. The primary objective of the mission is to obtain spatial and temporal gradients of atmospheric methane columns with high precision and unprecedented accuracy on a global scale. Therefore, the temperature-, pressure- and wavelength- dependent absorption cross-sections which describe the attenuation of the radiation by methane have to be known with extremely high accuracy in order to achieve this objective.

Such spectroscopic monitoring of gases in the atmosphere of the Earth requires a precise description of absorption lines shapes that goes beyond the usual Voigt profile (VP). In the case of methane, the differences between the measured profiles and those given by the VP can be very important [3,4], making the VP completely incompatible with the reliable detection of sources and sinks from space. These differences are due to various collisional effects between molecules that are neglected by the VP (line-mixing, Dicke narrowing effect and speed dependence of the collisional broadening and shifting). The consideration of the recently recommended line-shape model, the Hartmann-Tran profile (HTP) [5], along with line-mixing, is then particularly relevant in this context.

This lecture reviews our latest results on the modeling of methane lines broadened by air in the 1.64 μm region and the associated spectroscopic parameters, taking into account the latter collisional effects and their temperature dependence. These results were obtained by simultaneously fitting the model parameters to high sensitivity and high-resolution cavity ring-down spectroscopy (CRDS) spectra recorded at the National Institute of Standards and Technology (NIST) and high-resolution tunable diode laser spectra recorded at the Groupe de Spectrométrie Moléculaire et Atmosphérique (GSMA, Reims), over a wide pressure and temperature range. The influence of collisions involving water vapor will also be discussed. The use of these spectroscopic data and the associated model to calculate the spectrum absorption coefficient to analyze ground-based atmospheric TCCON will finally be presented.

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Snapshot the O₂(a¹Δ_g) nightglow at 1.27μm at low altitudes on Mars with a Doppler Michelson interferometer

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The O₂(a¹Δ_g) nightglow at 1.27μm at low altitudes on Mars has escaped detection up to now due to its low intensity [1], which is only a few tens of kilo-Rayleigh as the models predicted [2-4]. Doppler Michelson Interferometer (DMI) [5] is highly sensitive to weak airglow emissions and therefore well suited for this mission. A new version of DMI is designed to accommodate Martian observations. It is stable as it utilizes glasses only, monolithic with no moving part, field widened with a maximum diameter up to 30°, thermally compensated with optical path difference (OPD) variation lower than 2e-5cmK⁻¹ and portable since both arms are shorter than 13cm. Specifically, four highly reflective right-angle cones are attached to each end of the arms, rendering it simultaneous obtainment of 4 images of airglow and its emission rate, as well as the velocity and temperature structure of the air parcel where the emission forms in a single integration time, i.e. being able to snapshot the atmosphere. The cone radius also serves as an additional degree of freedom for manipulation of OPD. Together with a concave pyramid prism which is designed to eliminate reflection loss, the photon arrival rate at the detector is increased by about one half compared to traditional DMI as our calculation shows. The underlying principles and design details are presented. The retrieval algorithm for the air parcel velocity and temperature is demonstrated and discussed.

Keywords : Mars, Atmospheric measurement, Nightglow, Doppler Michelson interferometer

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Random Projection Method applied to the Physical inversion of the full IASI spectra: Assessment of spectroscopy and forward modelling consistency

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The random projection method have been used to perform the mathematical inversion of spectra observed by the Infrared Atmospheric Sounder Interferometer (IASI). The retrieval analysis have been used to assess the spectral quality and consistency of state-of-art forward modelling and spectroscopic databases for atmospheric gas lines and continuum absorption. The study has considered thousands of IASI spectra acquired over sea surface in the Pacific Ocean close to the Mauna Loa (Hawaii) validation station. We have resorted to dimensionality reduction of the data space and performed a simultaneous retrieval method for surface temperature and emissivity, atmospheric temperature, H₂O, HDO, O₃ profiles and average column abundance of CO₂, CO, CH₄, SO₂, N₂O, HNO₃, NH₃, OCS and CF₄. The random-projection-based retrieval system considers the whole IASI spectrum (all 8461 spectral channels on the range 645 cm⁻¹ to 2760 cm⁻¹) and has the unique characteristic to perform a mathematical inversion with a unified treatment of instrument noise and forward model error, which can be consistently assessed. The analysis of spectral residuals shows that, after inversion, they are generally reduced to within the IASI radiometric noise. However, larger residuals still hold for many of the most abundant gases, namely H₂O, CH₄ and CO₂. The H₂O ν_2 spectral region is in general warmer (higher radiance) than observations and the spectroscopy is inconsistent among the IASI bands. The CO₂ ν_2 and N₂O/CO₂ ν_3 spectral regions now show a consistent behaviour for channels, which are probing the troposphere. On overall, the spectroscopy in IASI band 1 (645 – 1210 cm⁻¹) shows an excellent consistency with IASI observations, with systematic effects confined below 30% of the instrument noise. Instead, updates in CH₄ spectroscopy do not seem to improve residuals. The effect of isotopic fractionation of HDO is evident in the 2500–2760 cm⁻¹ region and in the atmospheric window around 1200 cm⁻¹.

Atmospheric remote-sensing in the mid- and near-infrared: from the circulation of the middle atmosphere to the accurate quantification of greenhouse-gas sources and sinks

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Remote-sensing of the Earth's atmosphere in the mid-infrared has several advantages: first, observations are possible during day and night (in contrast to methods using the ultraviolet and visible regions of the spectrum); second, there are many species that can only be detected in the infrared; third, one can obtain vertical profile information, not only from the observation geometry, but also from the impact of temperature on the molecular spectra. To illustrate this, I will present recent advances at IMK in Karlsruhe, e.g. the detection of circulation changes in the middle atmosphere using tracers [1, 2], first observations of new species such as BrONO₂ [3] and SO₂ [4] in the stratosphere or NH₃ [5] in the Asian monsoon, new technology for air-borne 3D imaging spectroscopy of the upper troposphere and lower stratosphere [6, 7] and mobile ground-based measurements in the near-infrared to quantify the greenhouse-gas emissions of large cities [8]. Finally, a concept for the accurate quantification of greenhouse-gas sources and sinks from geostationary satellite observations [9] is presented.

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Poster Session 1

Analysis of the ν_6 band of CH_3F between 1078 and 1240 cm^{-1} : line positions, intensities and self-broadening coefficients at room temperature

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The 8.5 μm -spectral region of methyl fluoride was studied in terms of line positions, intensities and self-broadening coefficients at room temperature. A multispectrum fitting was used to retrieve from 7 high-resolution Fourier transform spectra line parameters for more than 750 transitions belonging to the ν_6 band between 1078 and 1240 cm^{-1} . The accuracy line intensities and widths measurements were estimated to be around 5 and 5-10% respectively. J - and K -rotational were observed and modeled from the transition dipole moments squared and the self-broadening coefficients retrievals. Comparisons with previous measurements and modeling in the literature were also performed showing good agreement with the present measurements (line positions and intensities). Based on the calculated line positions from Papoušek et al. [1], on the calculated intensities from the work of Lepère et al. [2], and the calculated self-broadening coefficients from this work, a complete line list of almost 1500 transitions was generated for atmospheric or industrial detection of CH_3F in the 8-9 μm spectral region. Moreover an overview of the broadening coefficients obtained for CH_3F , CH_3Cl [3,4,5] and CH_3Br [6] will be presented as well as the results from the semi-empirical model applied to model the J - and K -rotational dependence.

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Brightness temperature and sensitivity analysis of trace gases in the atmosphere based on the limb remote sensing model

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In China, the air pollution has received more and more attention by the government and the public. In the latest Chinese 13th Five-Year Plan, China has proposed coping with serious global climate change positively. China will take effective measures to control greenhouse gas emissions, strengthen the climate change research, build a space-based remote sensing monitoring system and promote international cooperation in the next five years.

The application and research results show that millimeter/sub-millimeter limb sounding technique has a special significance to the atmospheric environmental monitoring. In order to build an all-weather observation system of trace gases in the atmosphere, it's imperative to develop millimeter/sub-millimeter limb sounder. However, for the sake of design work of key performance parameters for the payload, it's essential to carry out some basic researches and establish forward model. This paper proposes a new forward model for millimeter/sub-millimeter limb sounding based on the "am" program, and reaches some basic conclusions.

To be specific, the "am" atmospheric model, developed by Smithsonian Astrophysical Observatory, was chose as the base of the latter research at first. Then, "am" program was extended to "ame" (atmospheric model extension) program, based on the atmospheric radiative transfer theory and the molecular data from HITRAN2008 database. Much more species of gases which contained in the HITRAN database can be analyzed through the "ame" program. This new program can meet the requirement of following analysis. Then the layer model, established on the basis of the limb viewing geometry, is set up in this paper. The optimum detection frequency of the concerned gas (CLO, CO, H₂O, HCL, HCN, HNO₃, N₂O, O₃, SO₂) can be determined by the simulation of the "ame" program. Compared to the detection frequency of the EOS-MLS, the simulation results are highly consistent which verifies the feasibility of this method. At last, this paper has analyzed the effect of gas content to the detector threshold sensitivity. The value of the payload's sensitivity is put forward in this paper and become the reference during the subsequent development of the millimeter/sub-millimeter limb sounder in China.

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The Line Shape Problem of High-precision Spectra of CO₂ in the Pressure Range between 0.002 and 1 atm: Measurements and Test of Models

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A dual-channel diode laser absorption spectrometer [1] was used to perform a highly accurate study of the shape of CO₂ absorption line in pure gas, belonging to the R4, 30013-00001 combination band, at a temperature of 296 K.

Standard models, including Voigt, Hard-collisional (Rautian), Soft-collisional (Galatry), and quadratic Speed-dependent Voigt (Boone), were applied, tested, and compared in the pressure range between 0.005 and 0.8 atm, in order to prove the spectral line parameters linear pressure dependences.

It was shown an essential effect of small closely spaced lines on shifting, narrowing and broadening spectral coefficients. The usage of Rautian and Galatry lineshape models leads to a significant deviation from linear pressure dependence of the collision velocity change coefficients under pressure increasing. Most appropriate for the common description of whole experimental spectra in wide pressure range (up to 1 atm.) is the quadratic Speed-Dependent (Boone) profile.

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Implementation of the Hartmann-Tran Profile in a multispectrum fitting program

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In its technical report, the IUPAC task group [1] recommended the adoption of the Hartmann–Tran profile (HTP) as the appropriate model for high-resolution spectroscopy. The HITRAN*Online* database now accepts extensible line shape formats compatible with this profile. We have incorporated the HTP model into a multispectrum fitting program, Labfit, initially developed by Chris Benner [2]. This multispectrum fitting program has proved very useful over the years and was used to determine parameters now in the HITRAN data base (see [3] for instance). More recently, the development of the program was transferred to the Jet Propulsion Laboratory to accommodate the needs of the OCO-2 mission. New features were added such as a modern interface and the calculation of the collision-induced absorption (CIA).

We report on the progress and characteristics of the program augmented with the HTP model. Portions of the HTP code are adopted from literature. We have validated these codes and extended the derivatives. This presentation describes the performances of the model for different implementations of the Voigt function upon which the HTP model depends. Ultimately the program will be applied to laboratory spectra of interest to Earth and planetary sciences in general, and, in particular, to oxygen A-band spectra of interest to current and future missions (OCO-2, GOSAT, TROPOMI, CarbonSat and TanSat). We will describe how we intend to test and validate this new program with already available experimental data of the oxygen A-band. High quality laboratory spectra obtained with different techniques in a wide range of pressures across multiple temperatures will allow us to test the HTP model in different regimes.

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New spectroscopic data for modelling SF₆ Absorption in the 10μm atmospheric window

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To model correctly the SF₆ atmospheric absorption requires the knowledge of the spectroscopic parameters of all states involved in the many hot bands in the 10μm atmospheric. Nevertheless, due to their overlapping, a direct analysis of the hot bands near the 10,5 μm absorption of SF₆ in the atmospheric window is not possible. It is necessary to use another strategy, gathering information in the far and mid infrared regions on initial and final states to compute the relevant total absorption.

Here we present new results of an analysis of spectra recorded at the AILES beamline at the SOLEIL Synchrotron facility. For these measurements, we used a IFS125HR interferometer in the 100 – 3200 cm⁻¹ range, coupled to a cryogenic multiple pass cell [1]. The optical path length was varied from 45 to 141 m with temperatures between 223 and 153 K. New information has been obtained on $\nu_2 + \nu_4 - \nu_5$, $2\nu_5 - \nu_6$ and $\nu_3 + \nu_6 - \nu_4$, which allow to derive improved parameters for ν_5 , $2\nu_5$ and $\nu_3 + \nu_6$. This is used to model the more important $\nu_3 + \nu_5 - \nu_5$ and $\nu_3 + \nu_6 - \nu_6$ hot band contributions. Including these new parameters in the XTDS model [2], we substantially improved the previous SF₆ parameters [3]. In addition spectra obtained at lower temperature (120K) have been collected to attempt extracting a line list for the fundamental ν_3 band.

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First far-infrared high resolution analysis of the ν_2 band of sulfur dioxide $^{32}\text{S}^{16}\text{O}^{18}\text{O}$ and $^{32}\text{S}^{18}\text{O}_2$

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High-resolution Fourier transform spectra of ^{18}O -enriched isotopic samples of sulfur dioxide ($^{32}\text{S}^{16}\text{O}^{18}\text{O}$ and $^{32}\text{S}^{18}\text{O}_2$) have been recorded at 0.00102cm^{-1} resolution in the $400\text{--}620\text{cm}^{-1}$ region at synchrotron SOLEIL. These spectra have been recorded at low temperature 185K using a 3.14m optical path length cryogenic cell. This enables the first detailed infrared analysis of the ν_2 bands of the $^{32}\text{S}^{16}\text{O}^{18}\text{O}$ and $^{32}\text{S}^{18}\text{O}_2$ isotopologues of sulfur dioxide located at $507.36541(1)$ and $496.59988(1)\text{cm}^{-1}$, respectively. Using a Watson-type Hamiltonian model to compute the upper and lower state energy levels, it was possible to reproduce the observed transitions. For both species, accurate rotational and centrifugal distortion constants were derived for the upper $(0,1,0)$ vibrational state, while those of the $(0,0,0)$ ground state were significantly updated as compared to those achieved during previous investigations [1,2]. For this task, we combined the results of the present infrared measurements with the available literature microwave data in the $(0,0,0)$ and $(0,1,0)$ vibrational states. Finally, we took the opportunity of this study to compare the quality of the fit using an A- and S-type reduction for the Watson Hamiltonian.

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New analysis of the ν_6 and $2\nu_3$ bands of methyl iodide (CH_3I)

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Methyl iodide, (CH_3I) is emitted in the atmosphere by marine algae and photolyzes with a lifetime of the order of a week [1]. It is also of nuclear interest. However this molecule is still not considered in spectroscopic databases as GEISA or HITRAN. The goal of the present work is to generate a set of accurate line positions for the ν_6 band of $^{12}\text{CH}_3\text{I}$ [2]. The spectrum of this band has been first recorded using the Bruker IFS125HR Fourier transform spectrometer (FTS) at the AILES beamline of the SOLEIL Synchrotron facility and later with the Bruker IFS125HR FTS located at the LISA facility in Créteil. The theoretical model used during this study accounts for the hyperfine structure and for the Coriolis resonances for the C_x ($\Delta\ell = \pm 1; \Delta K = \pm 1$) and α ($\Delta\ell = \mp 1; \Delta K = \pm 2$) types of Coriolis interactions coupling together the $\nu_6=1$ energy levels with those from the $\nu_3 = 2$ and $\nu_2 = 1$ states, respectively. Altogether, about 10000 lines were assigned for the ν_6 and $2\nu_3$ bands up to high quantum numbers ($J \leq 85$ and $K \leq 20$). Because of the large value of the ^{127}I nuclear quadrupole hyperfine constant, a significant portion of these assignments concerns clusters of hyperfine subcomponents, which are easily observable at $11 \mu\text{m}$. Therefore, the infrared data achieved during this work were combined in a least squares fit together with the existing microwave data on rotational transitions within the $\nu_6 = 1$ and $\nu_3 = 2$ vibrational states to get the upper state rotational constants and interacting parameters for the $\nu_6 = 1$ and $\nu_3 = 2$ states. On the other hand, it proved unnecessary to update the existing hyperfine parameters for the $\nu_6 = 1$ and $\nu_3 = 2$ states.

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Cavity Ring Down spectroscopy of ^{18}O enriched carbon dioxide in the 1.43-1.26 μm region

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In this work, we extend our recent works [1-3] devoted to the study of CRDS spectra of ^{18}O enriched carbon dioxide in the 5851–6990 cm^{-1} region to the higher wavenumber range (6977-7918 cm^{-1}). The CW-Cavity Ring Down Spectra (CRDS) of ^{18}O enriched carbon dioxide have been recorded in the 1.43-1.26 μm spectral region at room temperature and pressure 10 Torr with a noise equivalent absorption $\alpha_{\text{min}} \approx 2 \times 10^{-10} \text{ cm}^{-1}$.

A total of 8671 transitions belonging to 166 bands of eleven CO_2 isotopologues were rovibrationally assigned on the basis of the predictions of the effective Hamiltonian models [1-6]. Among the 166 assigned bands 104 were observed for the first time. All identified bands belong to the $\Delta P=9-12$ series of transitions, where $P=2V_1+V_2+3V_3$ is the polyad number (V_i are vibrational quantum numbers). Most of the new observations concern the $^{16}\text{O}^{12}\text{C}^{18}\text{O}$ (628) and $^{12}\text{C}^{18}\text{O}_2$ (828) isotopologues: a total of 45 and 34 bands were assigned for 628 and 828, respectively, while only 8 and 4 bands were observed before.

The spectroscopic parameters have been determined for all newly detected bands from a fit of the measured line positions. The global modeling of the line intensities was performed to refine the corresponding sets of the effective dipole moment parameters for the $^{16}\text{O}^{12}\text{C}^{18}\text{O}$, $^{16}\text{O}^{12}\text{C}^{17}\text{O}$, $^{12}\text{C}^{18}\text{O}_2$, $^{17}\text{O}^{12}\text{C}^{18}\text{O}$ and $^{13}\text{C}^{18}\text{O}_2$ isotopologues. A number of inter- and intra- polyad resonance perturbations were identified.

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Far-infrared collision-induced absorption by CO₂-H₂ and CH₄-CO₂ and applications to modeling of the early Martian atmosphere

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Collision-induced absorption (CIA) in highly symmetrical atmospheric molecules can have significant effects on planetary climate [1-4]. Previous paleoclimate modeling has shown that CO₂ CIA must be modeled correctly for an accurate representation of surface temperatures on early Mars (see e.g. [2]). Exploring possible paleoclimate scenarios requires knowledge of the binary absorption spectra in the far-infrared which is appropriate to various pairs of atmospheric molecules. Presently there exists no conventional procedure to simulate collision-induced spectra of polyatomic molecular pairs. The current paper suggests an affordable procedure that can be used to simulate the CIA spectrum for a dissimilar pair of molecules provided the spectra of similar pairs of each constituent molecule are known. This method requires the knowledge of *ab initio* potential energy (PES) and induced dipole (IDS) surfaces characterising a dissimilar pair. The CIA spectra of CO₂-H₂ and CH₄-CO₂ are taken as an example. First, zero-order spectral moments are evaluated using high-level *ab initio* PES and IDS represented in terms of analytical functions in the space of intermolecular coordinates. Second, the individual CIA spectra are summed and weighted in a way that the integral of this sum matches the *ab initio* calculated spectral moment of a pair. This method is applicable provided that the intermolecular perturbation is so weak that individual rotations of the two molecules in a pair are not suppressed. The CIA spectra of identical CO₂-CO₂, H₂-H₂, and CH₄-CH₄ pairs were obtained using Borysow's set of FORTRAN codes [5]. Using our simulated CIA rototranslational spectra for CO₂-H₂ and CH₄-CO₂ we are evaluating the impact of absorption by these pairs on the early Mars climate. Our analysis shows the importance of detailed knowledge of CIA for dissimilar molecular pairs and its consideration in climate modeling.

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Far-infrared collision-induced absorption in CO₂ at T = 200 K

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The low temperature ($T = 200$ K) far-infrared collision-induced spectra of pure CO₂ have been recorded at the AILES beamline of SOLEIL synchrotron facility using the long-path cryogenic cell [1]. This work is an extension of previous observations (see e.g. [2-4]) to lower temperature. The rototranslational CO₂ band was examined in the spectral range from 25 cm⁻¹ to 400 cm⁻¹ using optical path length of 141 m. The binary absorption coefficient was then derived as a result of an average of the spectra obtained at 400 mbar and 600 mbar CO₂ pressure normalised then to the gas density squared. Our obtained binary absorption coefficient agrees generally well with the calculated values from [5] which are included in the CIA HITRAN data base [6]. Notable deviations are observed, however, among the calculated and experimental band profile. These deviations are qualitatively in agreement but are more significant than those observed in the spectra taken previously at higher gas temperature. Possible origins of these deviations are discussed.

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Detection of water vapour absorption around 363nm (27548 cm⁻¹) in measured atmospheric absorption spectra

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Water vapour is known to absorb radiation from the microwave region to the blue part of the visible spectrum at a decreasing efficiency. Ab-initio approaches to model individual absorption lines of the gaseous water molecule predict absorption lines until its dissociation limit at 243 nm.

We present first evidence of water vapour absorption near 363 nm (27548 cm⁻¹) from field measurements using data from Multi-Axis differential optical absorption spectroscopy (MAX-DOAS) and Longpath (LP)-DOAS measurements. The identification of the absorptions was based on the recent POKAZATEL line list [1].

We observed absorption by water vapour at 363 nm with optical depths of up to 2×10^{-3} . They correlate well with simultaneously measured well-established water vapour absorptions in the blue spectral range from 452-499 nm ($R^2 = 0.89$), but the line intensities are underestimated by a factor of 2.6 ± 0.5 by the ab-initio model. At a spectral resolution of 0.5 nm, we derive a maximum cross-section value of 2.7×10^{-27} cm² molec⁻¹ at 362.3 nm.

The newly found absorption can have a significant impact on the spectral retrieval of absorbing trace-gas species in the spectral range around 363 nm. Its effect on the spectral analysis of O₄, HONO and OCIO is discussed.

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LED-based Fourier transform spectroscopy of water vapour enriched by ^{18}O in the 16,460 – 17,200 cm^{-1} range

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This study is a continuation of our analysis of water vapour spectrum in the visible region [1-3]. The spectrum of water sample enriched by ^{18}O is recorded between 16,460 and 17,200 cm^{-1} by a Fourier transform spectrometer with a spectral resolution of 0.05 cm^{-1} using high luminance LED Cree XPE AMB light source and a 60-cm multipath cell. This is a highest in energy spectral region investigated for the H_2^{18}O molecule so far. Parameters of about 1600 spectral lines are determined from a Voigt line profile fitting. Estimated accuracy of the positions of well isolated lines of strong and medium intensity is about 0.003 cm^{-1} .

The spectrum assignment is based on the accurate variational calculations [4,5] as well as on the known upper energy levels [6]. More than 700 absorption transitions are attributed to the H_2^{18}O molecule, mostly belonging to the 321-000, 401-000, 420-000, and 500-000 vibrational bands. Labeling of the assigned transitions involving the highly excited rotational-vibrational energy levels is established with the help of the effective Hamiltonian calculations.

Previously the H_2^{18}O spectrum in the considered spectral region has been studied in [7] by CRDS technique leading to the assignment of 265 absorption lines approved by the IUPAC TG analysis [6]. The error on the central frequency in [7] was estimated to be 0.01 cm^{-1} . The HITRAN 2012 database [8] includes 683 H_2^{18}O transitions in the considered spectral region of which 290 concern pure variational data without full rotational-vibrational labeling. Then the new experimental data obtained in this study represent an important enlargement and improvement of the information on the H_2^{18}O rotational structure and intramolecular interactions at a high degree of vibrational excitation.

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LED-based Fourier transform spectroscopy of water vapour in the visible range

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The efficiency of LED emitters in high resolution Fourier spectroscopy with small multipass cell has been shown. Using a 2.5 W LED emitter as a light source for the spectrometer with a 60-cm multipass cell during a 24-hour measurement time and by optimizing the passes number in the cell, we have achieved a signal-to-noise ratio of 1×10^5 which corresponds to the minimal detectable absorption coefficient of $6 \times 10^{-9} \text{ cm}^{-1}$.

FT-spectrometer with LED sources was used for the registration of H_2^{16}O , HD^{16}O , D_2^{16}O , and H_2^{18}O absorption spectra in the range of $9000 - 23000 \text{ cm}^{-1}$, determined by the transition to highly excited states of the molecules [2-4]. The frequencies and intensities of weak lines with intensity of 10^{-26} - $10^{-28} \text{ cm/molecule}$ are confidently measured by the spectrometer. The results of $\text{H}_2\text{O-N}_2$ and $\text{H}_2\text{O-H}_2\text{O}$ broadening investigation recorded by a high resolution Fourier-transform spectrometer IFS-125M with LED sources in the region $15500 - 16000 \text{ cm}^{-1}$ are shown. Least-square-fitting algorithm Wxspe was used to retrieve of the spectroscopic parameters from measured spectral data set [5]. Line-broadening and line-shifting coefficients derived from the fitting were compared to calculated data.

The influence of water vapor on the reflection coefficient of multilayer mirrors was studied using a gas cell with multiple reflections from the mirrors. A strong increase of the reflection coefficient of the mirrors (up to 0.9%) was found when water vapor under a pressure of 23 mbar was injected into the cell, which was interpreted as a change in the refraction index of the layers of multilayer coatings when water vapor penetrated into the porous coating structure[6]. It can produce both increasing and decreasing reflection coefficient, which is determined by the variation of refraction indices (with water vapor filling) of the materials applied to form a dielectric multilayer mirror. The changes in the reflection coefficient of multilayer dielectric mirrors may lead to major errors in measurements carried out using highly sensitive spectroscopic methods involving high-quality resonators with a mirror reflection coefficient higher than 0.999, such as CRDS and SEAS, especially during measurements of broadband absorption.

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Absorption spectrum of D₂¹⁶O between 10000 and 11400 cm⁻¹ by Light-emitting-diode Fourier-Transform spectroscopy

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Absorption spectrum of dideuterated water has been investigated between 10000 and 11400 cm⁻¹. The set of the D₂O transitions was recorded by IFS-125M interferometer with a spectral resolution of 0.05 cm⁻¹. The bright light emitting diode (LED) EDEI-1LS3-R was used as a radiation source [1, 2]. The spectrometer was coupled to a multipass absorption cell of 60-cm base length. An extensive listing of the D₂O spectroscopic parameters was obtained by fitting more than 470 observed lines to a Voigt line profile convolved by the instrumental function. The line parameters were determined with using a Wxspe software package, which uses pattern recognition methods [3].

A rovibrational assignment was performed on the basis of the variational calculations [4, 5]. Spectral lines of the D₂O molecule in the region of 10000 – 11400 cm⁻¹ are formed by the transitions to highly-excited vibrational - rotational states belonging mostly to the strongest vibrational bands 301-000, 221-000 and 103-000. New experimental information on the D₂O absorption in the 10600-10800 cm⁻¹ spectral region, where 103-000 band is located, was received for the first time. The analysis of the spectrum allowed us to derive a total of the 151 new observed energy levels belonging to (103),(301),(221) vibrational states. The centers of lines determined by analyzing the spectrum agree well with the experimental data of Ref. [6] and with the calculated data of Ref. [5]. The spectral information on the D₂O absorption in the range of the 10000-11400 cm⁻¹ can be used to refine the existing data.

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Absorption spectra and parameters of ethane isotopologues $^{13}\text{C}^{12}\text{CH}_6$ and $^{13}\text{C}_2\text{H}_6$ in the 3.2 – 3.6 μm region

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Absorption line positions for the ethane isotopologues $^{13}\text{C}^{12}\text{CH}_6$ and $^{13}\text{C}_2\text{H}_6$ have been determined in the 3.2 – 3.6 μm spectral region from spectra recorded using an FTIR spectrometer (Newport MIR8025). Results are presented for approximately 1% of ^{13}C -ethane (mixed with nitrogen 5.0) from spectra recorded at 0.5 cm^{-1} resolution at room temperature and atmospheric pressure. For comparison an ethane spectrum with natural isotopologue abundance was obtained under the same conditions. Line positions and line intensities were calibrated using an ethane spectrum taken from The Molecular Spectroscopy Facility, Rutherford Appleton Laboratory [1] and photoacoustic measurements based on a continuous-wave optical parametric oscillator [2].

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Traceable line strength measurements of methane and carbon dioxide in the near infrared wavelength region at 1.65 μm using cavity ring down spectroscopy

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We present the results of accurate line strength measurements of several lines in carbon dioxide and methane in the wavelength region around 1.65 μm . Absorption spectra were recorded using cavity ring down spectroscopy with an optical path length of 1.6 kilometers; this allowed measuring line strength values in the order of 10^{-26} cm/molecule. To obtain traceable values of the line strength specially prepared mixtures were used with well-known mole fractions of carbon dioxide and methane, as well as a calibrated pressure meter. Spectra were recorded at room temperature in the pressure range between 10 and 100 mbar. The analysis of the measured absorption lines was performed using Voigt and Galatry line profiles. The uncertainty budget ($< 1\%$) of the obtained line strength values is discussed and comparison with corresponding data from the literature is presented.

This work was performed within the Researcher Excellence Grants associated with two European Metrology Research Projects ENV06 EUMETRISPEC and ENV52 HIGHGAS aiming at improving the accuracy of atmospheric monitoring based on spectroscopic methods.

Spectroscopic database for TROPOMI/Sentinel-5P: CO and H₂O at 2.3 μ m

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The TROPospheric Monitoring Instrument (TROPOMI) aboard the European Space Agency's Copernicus Sentinel-5 Precursor satellite, to be launched this year, mandates high-accuracy spectral reference data for CO and H₂O in the 2.3 μ m region [1]. We present measurements of absorption line parameters for H₂O and for the 2-0 rovibrational band of CO to be used in TROPOMI atmospheric retrievals. The experiments were carried out on a Bruker IFS 125HR Fourier transform spectrometer and a multispectrum fitting software developed at DLR was used for parameter retrieval [2] using the Hartmann-Tran-Profile [3,4].

In the case of carbon monoxide, we report line intensities, air-broadening and -shift parameters for lines of the 2-0 rovibrational band, which serve as a useful validation of the HITRAN2012 spectral database [5] while our analysis of Dicke narrowing, speed dependence and Rosenkranz line mixing emphasizes the importance of modern line shape functions. Comparisons with previous studies of these non-Voigt parameters (e.g. [6]) show good agreement.

As for H₂O, spectral parameters were measured in the 4190cm⁻¹-4340cm⁻¹ spectral range. Comparisons of measured line intensities of the ν_3 band show remarkable agreement (<1.5% deviation on average) with ab initio values [7,8] and we will present air-broadening, -narrowing and -shift parameters together with their temperature dependences.

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Temperature-dependent absorption cross-sections of CO₂ and H₂O in 110-300 nm

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In gas (non-sooting) flames and post flames UV light absorption in 180-300 nm is dominated by hot CO₂ and H₂O. CO₂ and H₂O are also ones from a long list of other molecules those are of interest for atmospheric chemistry on Earth and other (exo)planets. The exoplanets atmosphere temperature can vary from 200 to 2200C and they are frequently exposed to extremely strong UV radiation from their parent stars. Available UV absorption cross-sections for most molecules are usually limited to ambient or low temperature ranges. The 110-200 nm spectral range (often called as far UV) is extremely important for atmospheric chemistry. It has for example been shown in many publications that the absorption of the UV flux increases substantially at wavelengths above 160 nm together with the temperature [1].

In opposite to IR absorption, the CO₂ and H₂O UV absorption cross-sections are broad-band continua-like structures with weakly pronounced fine structures. On for example Log₁₀-scale the cross sections look like as a straight line in a relatively broad spectra range. The slope of the cross-sections (or its straight line fit) is temperature-dependent and therefore can be used for calculations of gas temperature. Moreover at high temperatures the absorptions cross sections tend to extent to longer wavelengths. Because CO₂/H₂O absorption cross-sections are temperature-dependent and their theoretical calculations are very complicated and nearly impossible with desired accuracy, the only way to build a cross section database is to measure cross sections at well-controlled conditions as for example can be found in a gas cell. We present new UV absorption cross sections for CO₂ and H₂O up to 1500C in 110-300 nm spectral range. The measurements have been performed on a high-end three zones hot flow gas cell with temperature uniformity ± 0.5 C in the central zone, where UV absorption measurements are performed. The results are compared with latest published data Venot *et al* (2013) [2] and the results of Schulz *et al* (2002) [3]. Advantages of UV spectroscopy in the far UV range are discussed.

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Semi-classical calculations of self-broadening coefficients of OCS and HCN for temperatures between 200 and 298 K

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Using the semi classical model of Robert and Bonamy with exact trajectory [1], we have calculated the pressure broadening coefficients of OCS-OCS and HCN-HCN systems for the two ro-vibrational bands ν_1 and ν_2 respectively. We have used the approximation of bi-resonance functions proposed by Starikov [2].

The dependence of broadening coefficients on quantum number up to $J=60$ was studied at various temperatures ranging from 200 to 298 K. The calculated results were compared with previous experimental and theoretical values of broadening coefficients.

The calculations show that the RBE formalism computed the self-broadening coefficients and their temperature dependence exponent better than the semi classical formalism of Robert and Bonamy with parabolic trajectory [3].

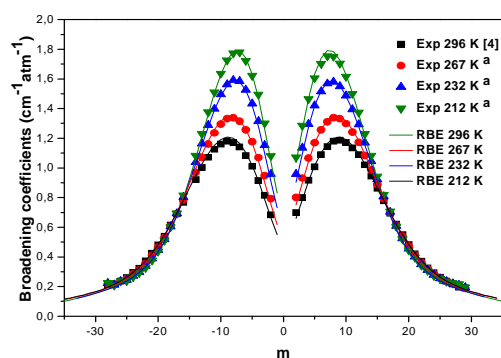


Figure 1. Comparison between measured [4] and theoretical (present work RBE) self-broadening coefficients of the ν_2 band of HCN. (a) : experimental values at temperatures 267 K, 232 K and 212 K deduced from measured values of γ_{HCN} (296) given in the Ref. [4].

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bytran -|- spectral calculations for portable devices using the HITRAN database

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The advances in electronics have made it possible to enable line-by-line calculations performed using the computation power of portable devices. We have developed a free, open-source and cross-platform graphical interface enabled application called bytran targeting portable electronics as well as desktop computers to perform line-by-line calculations using the HITRAN database [1] and based in part on selected HAPI source code [2]. To the best of our knowledge no other user-friendly application for line-by-line calculations deployed on portable electronics exists at the time of this writing.

Currently there are a number of free and subscription based user-friendly online [3-6] line-by-line calculation systems as well as commercial and shareware desktop programs [7-11] relying on HITRAN. These available applications usually have one or more of the following limitations: (1) Closed source code, (2) Commercial distribution, (3) Limited portability. In developing the bytran program we have attempted to address the above limitations.

The bytran program was developed using the Qt/C++ framework which enables write once compile everywhere architecture [12]. As such the bytran source code may be compiled to operate under mobile (Android, iOS, Windows RT), desktop operating systems (Linux, Mac, Windows) as well as a number of embedded Linux-based development boards including the Raspberry Pi [13]. Though the initial software implementation can be compiled to run on desktop computers, its interface was designed to target mobile platforms. As such the mobile specific interface should be modified to look better under desktop environment for better user-experience.

The developed application relies on the HITRAN database downloaded from hitran.org or a complete HITRAN database file manually placed on the mobile device. The initial version is limited to the horizontal path calculation mode with the slant path to be developed. Bytran offers a number standard features commonly offered by line-by-line modeling programs, including the usage of Voigt, Lorentz or Doppler lineshape profiles, instrument functions (ported from HAPI), built-in atmospheric models, sharing the results of the calculations, pinch zoom and several others [2, 14]. Current functionality and performance limitations compared to existing systems include the lack of continuum and aerosol calculations, as well as unavailability of advanced lineshape models.

Bytran may become particularly useful for in-the-field scientific evaluations as well as to university and high-school students and has the potential of further expanding the usage of the HITRAN database. Future improvements will likely include the usage of a range of satellite datasets available from NASA and other agencies for better models. The application is currently available in Beta under Android, Windows, Ubuntu Linux and OS X with iOS and Windows RT releases to follow soon. After the testing phase for all platforms is over the source code will be made available under the terms of the MIT license permitting commercial and/or open-source reuse. More information about the current state of the project is available at www.bytran.org [15].

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Systematization of spectral line parameters for the carbon dioxide molecule

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Databases of considerable current use [1, 2] are intended to provide atmospheric scientists with parameters of spectral lines characterized by a limited number of shapes, while analyses of line shapes available in the scientific literature on the subject employ more than 20 line contours. The problems associated with the systematization of spectral line parameters are discussed, using information system W@DIS as an example. Among the functions of W@DIS are the systematization of the measured spectral line parameters for different types of line shapes and provision of access to this information for researchers and programmable agents along with the representation of data about energy levels, wavenumbers, Einstein coefficients, etc. The carbon dioxide molecule is a good example for testing the systematization at issue. The W@DIS digital library includes 820 publications relevant to the carbon dioxide molecule. A quarter of them contains the parameters of 12 spectral line shapes for 11 CO₂ isotopologues. There are 189 articles incorporating the results obtained from measurements of the spectral line parameters, with 330 data sources being associated with them. Each of the data sources in its turn contains the values of the spectral line parameters measured under the same thermodynamic conditions by one method for one isotopologue, one broadening substance and published in the same information resource. There can be several primary sources in one publication. The data sources and spectral line parameters contained therein are the subject of the systematization developed in this work.

The basic approach to the classification of spectral line shapes involves consistent consideration of the physical mechanisms affecting the formation of line contours. The classification of the line shapes and notation to be used for each of the contours are proposed. Based on the notation set forth here, database tables accumulating solutions to the problems of describing and measuring the spectral line parameters for the CO₂ molecule are presented. The systematization results are available to researchers in information system W@DIS at (<http://wadis.saga.iao.ru/co2/lineprof/comp/>) and are described in detail in an OWL-ontology at (<http://wadis.saga.iao.ru/co2/ontology/>).

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Expert water molecule data quality analysis

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Vacuum wavenumbers of certain isotopologues of the water molecule available in recent versions of the HITRAN and GEISA databases [1,2] are examined. The basis for the analysis is the publishing criterion formulated in [3,4]. Consistency of the data for the water molecule across multiple sources collected in information system W@DIS is reviewed. Lists of spectral lines which fail to meet the publishing criterion are given.

In addition to checking the content of the HITRAN and GEISA expert data according to formal criteria, we have performed a detailed comparison of the datasets with each other, as well as with the reference spectrum and high-accuracy variational calculation. The content of the H₂¹⁶O data was found to exhibit an essential difference in their amount, origin, and quality ever seen in the historical development of the HITRAN and GEISA databases. In particular, the inconsistency of the centers of individual ro-vibrational transitions was revealed: the difference in the wave numbers was far beyond the accuracy range declared in HITRAN.

About 21500 lines from HITRAN and 10000 lines from GEISA fall outside of the set both of the databases have in common. The intensity ratio of the transitions is assumed to vary between 0.3 and 3 even in the case of relatively strong line intensities of (1.0–10.0)*10⁻²⁴ cm/mol. Probable causes for the inconsistency of the HITRAN and GEISA databases are discussed.

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Non-Voigt line-shape parameters for the HITRAN database: H₂ case study

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Non-Voigt line-shape effects, such as Dicke narrowing and speed-dependent effects, have to be considered to reliably represent the shapes of optical resonances in molecular spectra databases. We demonstrate how the line-shape parameters for the case of self-perturbed molecular hydrogen, for which the non-Voigt effects are especially pronounced, can be determined. This work was used as a test case [1] for introducing Hartmann-Tran profile [2] parametrization into the HITRAN database [3] taking advantage of its new relational structure and interface [4, 5].

We performed a detailed analysis of the shapes of the recent high-quality H₂ spectra recorded with cavity ring-down spectrometers [6, 7] and optical feedback cavity-enhanced absorption spectrometer [8]. We showed the possible solutions to the problems of strong numerical correlations between the parameters and their temperature dependences. Previously used line-shape models, which reproduce the H₂ spectra better than the simple phenomenological profiles, appear to be computationally inefficient. We therefore developed, a new technique allowing the Hartmann-Tran profile [2] to be adopted for the H₂ spectra analysis. The results could therefore directly be introduced into the HITRAN database. In order to increase reliability of spectra representation over wide thermodynamic conditions, we introduced four temperature ranges over which all the line-shape parameters are stored separately. Finally we demonstrate the use of the new relational structure of the HITRAN database [4, 5] and the HITRAN Application Programming Interface (HAPI) [9] for the case of H₂ spectra.

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CRDS measurements and *ab initio* calculations of collisional effects in pure D₂

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Recent progress in theoretical calculations of molecular states energies for H₂, HD and D₂ [1–2] gives predictions of the transition frequencies with uncertainty exceeding the level of 10⁻³ cm⁻¹ for the first overtone band (2–0) [3]. Such predictions open a way for testing relativistic and quantum electrodynamics corrections. They give also the opportunity for searching for new physics like additional long-range hadron-hadron interactions [4]. At this level of accuracy the uncertainty of the H₂ (or its isotopologues) line position determination in the Doppler limit becomes considerably affected by the line-shape effects [5] including its asymmetry. Spectral line shapes of D₂ transitions are atypical and difficult to describe. First strategy for overcoming this problem is measuring the spectra at low pressures, where collisional effects are negligible [3]. However, it is experimentally challenging due to exceptionally low intensities of the quadrupole transitions. Another approach is recording them at higher pressures and handling the collisional influence on the spectral line shapes in a more sophisticated way. Here, as an example of the second strategy, we present our preliminary results for very weak S(2) transition of deuterium in the 2-0 band, using *ab initio* calculations. Transition has been measured with the frequency-stabilized cavity ring-down spectroscopy (FS-CRDS) assisted by an optical-frequency comb [6,7], using experimental setup described in Ref. [8]. The line positions at high pressures, up to 1000 Torr, were measured with sub-MHz accuracy.

Furthermore, to validate *ab initio* model, we extended our experiments to a wide range of temperatures. We compare it with *ab initio* quantum scattering calculations, where we obtain the generalized spectroscopic cross sections. The real and imaginary parts provide the speed-dependent collisional broadening $\gamma(v)$ and shifting $\delta(v)$. The velocity-changing collisions, in turn, are described by hard-sphere approximation of the *ab initio* potential. The line shape originating from this approach is called the speed-dependent billiard-ball profile (SDBBP) [9].

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Issues in deriving the near-infrared water vapour continuum from sun-pointing spectrometer measurements

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Measurements of the water vapour continuum in the near-infrared windows are scarce, particularly in atmospheric conditions [1]. We report an analysis of calibrated ground-based sun-pointing Fourier Transform Spectrometer measurements [2], focusing on the continuum in the 1.6 and 2.1 μm windows. Uncertainties in performing such an analysis include instrumental factors and the need for detailed characterisation of the atmospheric state. A less-widely recognised difficulty in the direct use of such observations, is uncertainty in the extra-terrestrial solar spectrum at these wavelengths; recent analyses, using both ground-based and satellite-based techniques, differ by around 7% [3, 4]. The ground-based measurements are used to examine the plausibility of these alternative solar spectra, for a range of assumptions about the error in the assumed atmospheric opacity, and by comparing with Langley analyses of solar spectrum using the same measurements [5]; the most plausible spectra are then used to derive estimates of the opacity and the contribution of the water vapour continuum.

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Methane updates in HITRAN 2012 and consequences on terrestrial radiative forcing estimates

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The most recent High-Resolution Transmittance database, HITRAN2012 [1], provides an additional 178,012 methane line parameters compared to HITRAN2008, extends the spectral information from 9200 cm⁻¹ out to the near-infrared at 11500 cm⁻¹, and adjusts over 70% of the line parameters [2]. Furnished with these new updates to methane

to methane lines, we have revisited the methane radiative forcing calculations from the Radiative Transfer Model Intercomparison Project (RTMIP) [3]. Here, radiative the forcing is determined by differencing radiative fluxes associated with terrestrial atmospheric methane mixing ratios set to annually-averaged pre-industrial and present-day values, respectively. We find little variation in radiative forcing associated with the updates since HITRAN2000 [4] and even show that estimates of radiative forcing informed by observations from methane-rich Jovian planetary atmospheres [5] deviate from previous RTMIP results by less than 1%. These findings suggest that line parameters in HITRAN are not contributing to biased radiative forcing calculations from methane. Retrospective terrestrial methane radiative forcing at the top of the model atmosphere, model tropopause, and surface will be presented.

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Experimental and theoretical studies of line-shape parameters and their temperature dependences in the $\nu_1 + \nu_3$ band of $C_2H_2-CO_2$

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Remote sensing of planetary atmospheres with high abundance of carbon dioxide and acetylene traces requires, among others, a precise knowledge of spectroscopic line-shape parameters for the $C_2H_2-CO_2$ system. Not only the positions and intensities of the lines, but also their pressure-broadening and pressure-shift coefficients with their temperature dependences should be well known. Moreover, because of line overlapping appearing at high gas pressures, the line-mixing effects should be accounted for.

The present study continues a series of our works [1–3] on foreign-gas perturbed acetylene absorption in the $\nu_1 + \nu_3$ band, which is a strong combination band often used as a near-infrared frequency calibration standard. As previously, a 3-channel tuneable diode-laser spectrometer has been used to record spectra at different temperatures (216–333 K) and pressures up to 750 Torr. Each set of spectra corresponding to the same temperature has been further analyzed by a non-linear least-squares-fit procedure to retrieve the CO_2 -broadened C_2H_2 line widths and shifts for the *R*- and *P*-branch transitions. The traditional Voigt profile has been employed to model the joint effect of thermal molecular motion and molecular collisions on the observed line shape. Finally, the temperature-dependence exponents and linear temperature-dependence coefficients have been extracted for the line widths and line shifts, respectively.

Pressure-broadening and -shift coefficients have been also evaluated theoretically, with the use of a semi-empirical method [4], developed initially for strongly polar active molecules but, in practice, convenient also for polyatomic colliders with intermediate interaction strength. First, the semi-empirical model parameter was adjusted on some room-temperature *R*-branch line-width measurements and used to calculate the broadening coefficients for 236, 256 and 276 K. Then, the temperature exponents were extracted via a four-point linear-regression analysis of broadening coefficients, and the line widths restored for 216, 316 and 333 K were validated by comparison with our measurements (differences within 0.5% for all lines and all temperatures). The model parameter was further kept fixed for line-shift calculations and required for them but unknown upper-state polarizability was obtained from fits to some experimentally observed line shifts. Both line-broadening and line-shift sets computed semi-empirically compare very favourably with our experimental values and data available in the literature [5].

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Direct measurements and theoretical calculations of CO-He line-shape parameters and their temperature dependences in the fundamental band of CO

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In this presentation we report on direct measurements and theoretical calculations for He-broadened Lorentz half-width, pressure-shift, and line mixing coefficients of 45 carbon monoxide transitions in the $1\leftarrow 0$ band. The spectra analyzed in this study were recorded over a range of temperatures between 296 and 80 K. The He-broadened line parameters and their temperature dependences were retrieved using a multispectrum nonlinear least squares program. A previous analysis of these spectra used only the Voigt line shape. The line shape models used here include Voigt, speed dependent Voigt, Rautian (to take into account confinement narrowing) and Rautian with speed dependence. We were unable to retrieve the temperature dependence of line mixing coefficients. The line mixing coefficients were also derived from the Exponential Power Gap law and the energy corrected sudden approximation. The current measurements and theoretical results are compared with other published results, where appropriate.

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The Oxygen A-Band Revisited: Measurement Results and Theoretical Calculations

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In this study we have re-analyzed high-resolution spectra of pure oxygen recorded in the spectral range of the A-band.¹ Two sets of self-broadened parameters have been retrieved corresponding to two self-calibrations performed with respect to the line positions published by (1) Long et al.², and (2) Drouin et al.³ We compared our line parameters with published results and the entries in HITRAN⁴ database. The data analysis was performed using updated versions of the multispectrum fit software presented in Ref. [5]. The updated analysis software included an algorithm for fast calculation of Voigt profiles⁶, implementation of line mixing^{7,8} and line narrowing^{8,9} effects.

The narrowing parameters were determined using a calculated diffusion constant for the oxygen molecule. O₂ was modelled by means a single united atom force field [1]. Intermolecular interactions were described by only considering van der Waals interactions modelled from Lennard-Jones (LJs) potential. Molecular dynamics simulations were carried out using the DLPOLY software [11].

We have used both the calculated narrowing parameters and the experimental ones from Ref. [2], to fit our data using the Rautian and speed-dependent Rautian profile. Besides, we have fitted our spectra using the Voigt and speed-dependent Voigt profiles. We have taken into account the line mixing effects and compared our results with those published in Refs. [1,3]. For spectra recorded above one atmosphere, we have estimated the collision induced absorption in two ways: (1) using a pseudo-linelist based on fits to the curves in Figure 7 of Ref. [12] and (2) from our high pressure spectra after we removed the contributions from line profiles including the line asymmetries induced by the line mixing.

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Functionalization of silicon surfaces with luminescent lanthanide complexes for the development of NO_x gas sensors

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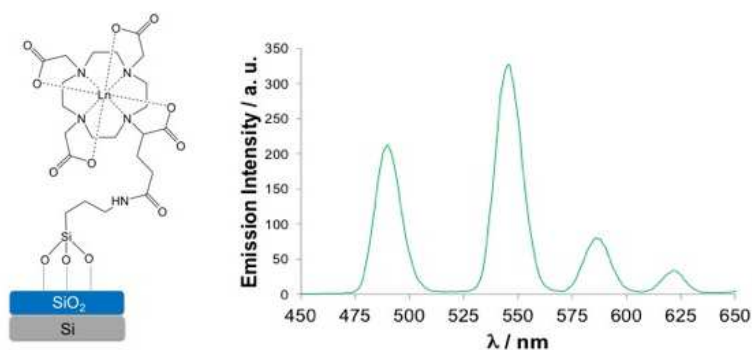
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The results of a study concerning the covalent anchoring of luminescent lanthanide complexes onto silicon surfaces will be described. The aim of this work is to design new sensors for gases based on the following principle: an alteration of the optical signal should occur when the analyte is in contact with the modified solid substrate. Lanthanide complexes were designed in order to show reactivity towards the silica layer that covers the surface of the silicon [1,2,3]. The following figure shows an example of the results obtained with a terbium(III) complex:



The preparation of the surfaces, the synthesis of the ligands and lanthanide complexes, their anchoring onto the surfaces and the first results of the optical study in the presence of NO_x gases will be discussed.

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Quantum Cascade Laser-based sources with broad tunable emission for infrared gas detection

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Laser spectrometers based on tunable diode lasers provide good results for gas sensing in terms of sensibility and selectivity thanks to the characteristics of these sources. Indeed, they commonly deliver power from 1 mW to #100 mW without the need for cryogenic cooling. Distributed feedback (DFB) configuration provides narrow linewidth that enhances selectivity. Finally, the development of quantum cascade lasers enables to reach the fundamental absorption bands of molecules in the mid-infrared region. The main limitation of these sources is their low tuning range ($\sim 10 \text{ cm}^{-1}$) that prevents from monitoring complex species with broad absorption spectra in the infrared region or realizing multi-gas sensing.

To obtain a broader tuning range, one solution is to implement a semiconductor laser in an external cavity system. A commercial external-cavity quantum cascade laser emitting at $10.5 \mu\text{m}$ has been used to demonstrate photoacoustic gas sensing of heavy molecules such as butane [1]. Developments of a lab-made external cavity - quantum cascade laser emitting at $7.5 \mu\text{m}$ and its application to detection of acetone and POCl_3 in gas phase has been demonstrated [2]. The lab-made system is currently used to develop intra-cavity systems for gas detection. Recent results will be presented.

Another solution to obtain a wide tuning range in the mid-infrared is to use commercial quantum cascade laser arrays that permit to develop broadly tunable mid-infrared sources without active mechanical system [3]. One of these sources is currently under study in our lab. Last results will be presented.

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Development of a Quantum Cascade Laser heterodyne spectrometer for remote gas detection

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Heterodyne sensing consists in mixing an unknown signal with the signal from a local oscillator. This superimposition creates a beat note in the RF range. The analysis of this phenomenon enables to determine the spectrum of the unknown source. This type of setup may be developed for atmospheric gas remote sensing [1]. In this work, the local oscillator is a quantum cascade laser (QCL). Its characteristics directly impact the sensitivity of the sensor. Some tests were realized to determine the QCL characteristics that directly impact the spectrometer specifications. First, the impact of the power supply on the QCL intensity noise was assessed by comparing it to CO₂ laser shot noise. In a second time, the oscillator linewidth is measured from beat note stability between QCL and CO₂ laser. In this case, the power supply stability is again decisive. Indeed, the driver current noise increases the QCL frequency noise and then so broadens its linewidth [2].

During this work, a solar tracker was entirely developed and constructed in order to be adapted to the heterodyne spectrometer and develop atmospheric measurements. Details of the characteristics of the instrument will be presented. Finally, we will show the various heterodyne spectrometers developed:

- The first one is based on lenses;
- The second one is based on off-axis parabolic mirrors;
- The third one is based on mid-infrared optical fibers.

First results will be presented.

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CO₂ measurements above sparkling liquids by diode laser spectrometry: Applications to Champagne wines

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The Groupe de Spectrométrie Moléculaire et Atmosphérique (GSMA, Reims, France) has developed a lot of various laser spectrometers using direct-absorption, heterodyne, or photoacoustic spectroscopy for the study of the atmospheres [1]. These spectrometers use different types of infrared lasers such as telecom-type near-infrared diode lasers, multi-quantum wells diode lasers and quantum cascade lasers. Based on this technology we developed the same type of instrument for enological applications. The work consisted in the conception and the optimization of a laser detection system for the measurements of CO₂ above sparkling liquids such as champagne. The progressive desorption of dissolved CO₂ in champagne is responsible for bubble formation. Moreover, CO₂ may also escape by diffusion at the air-champagne interface. A first step in the understanding of the role of CO₂ was to precisely measure its concentration above champagne glasses, under standard tasting conditions [2,3].

We will present the improvements of the instrument adapted to oenological measurements. Details on kinetics of CO₂ desorption are not well known and interactions between CO₂ and aromatic molecules during tasting have never been studied. To address this purpose and to improve the previous set-up [2], many optimizations have been realized. First the original 2,68 μm diode laser is now coupled to an optical fiber. It helps to prevent from atmospheric CO₂ interferences when measuring the carbon dioxide desorbing from champagne. The second main improvement was to adapt a second laser emitting around 2 μm to realize measurements with large concentrations of CO₂. At this wavelength the absorption coefficient is lower and permit to obtain non-saturated measurements. Finally, the whole set-up is driven by a LabView ® program in order to automatically obtain the CO₂ concentration with time.

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Simulation and design of miniaturized Helmholtz photoacoustic cells for atmospheric gas sensing

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Photoacoustic (PA) spectroscopy is a well-established technique and numerous gas sensors designs have been imagined and implemented. The mass deployment of PA gas sensors is often hampered by the systems' overall size and weight but the technique also possesses favourable detection characteristics when the system dimensions are scaled to a micro-system design. In the framework of the ANR project MIRIADE, the favourable downscaling behaviour of PA cells is explored by the miniaturization of PA sensors [1]. Before achievement of this microscopic-size cell goal, GSMA has developed compact versions of Differential Helmholtz Resonator previously used [2].

In order to optimize the miniaturized PA sensor, one must be able to accurately predict the frequency response which can be obtained analytically only for simple cell geometries. For more complex cells, electric analogy can also be used to investigate the cell response but finite element method (FEM) presents the ease of use of a computational calculation and has already demonstrated its capabilities for the simulation of PA cell characteristics. In a previous work we have already shown that the resolution of the equations of pressure acoustics using FEM software allows the accurate determination of the frequency response (resonant frequency, quality factor and peak amplitude at resonance) of a macroscopic Helmholtz resonant PA cell [3-5] thus to quantitatively predict the gas detection limits for gas detection knowing the laser used and gas absorption characteristics.

This paper will present a comparative study between experimental characterizations and FEM simulations using Comsol Multiphysics® that has been carried on two PA cells decreasing in size. This study will show that, as expected, the equations of pressure acoustics are not accurate enough for small resonant cells. A more complex description based on thermoacoustics must be used. The "Thermoacoustics" module of Comsol Multiphysics® especially designed for small elements is used and simulations show a satisfactory agreement with experimental data for compact cells. The influence of several parameters such as mesh quality will be demonstrated.

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Measurements of high-resolution spectroscopic parameters on the R(6) multicomponent of methane around 6077 cm⁻¹ for the MERLIN mission

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Climate change is one of the greatest challenges presently facing mankind, and methane is one of the most powerful anthropogenic greenhouse gases. For a better understanding of future climate trends, it is necessary to apply precise space-based measurements in order to obtain a global view on the complex processes that control atmospheric methane concentration. In this context, a satellite dedicated to the measurements of atmospheric methane is under joint development by the French and German space research centers (CNES and DLR). The so-called MERLIN mission (MEthane Remote LIdar missioN, 2019) aims at providing global information on atmospheric methane concentration (methane column density) with a relative uncertainty less than 2% and with a spatial resolution of 50 km along the measurement track under cloudy and variable-solar illumination conditions. The main data product will be the column-weighted dry-air mixing ratio of CH₄. MERLIN is based on Differential Absorption LIDAR (DIAL) measurements. The DIAL instrument for MERLIN works around 1.64 μm for the methane measurement. λ_{ON} lies in the R(6) multicomponent absorption at 6077 cm⁻¹. In order to reach the needed precision and accuracy, one must have an excellent knowledge of the spectroscopic parameters of the chosen ro-vibrational transition: strength of the line, broadening and shift coefficients and their variations with temperature [1].

In this work, we will present the tunable diode laser spectrometer specially developed for high-resolution measurements of spectroscopic methane parameters previously tested on CO₂ [2-3]. We will also present results on the modeling of methane lines in the 1.64 μm region and the associated spectroscopic parameters taking into account refined collisional effects [4,5]. These results are obtained by simultaneously fitting the model parameters to high-resolution tunable diode laser spectra. For pure methane, the study concerns the intensity measurements of the 6 lines of the R(6) multi-component. These measurements are completed by self-broadening and self-shift coefficients. For methane-air mixtures, the study concerns the air-broadening and air-shift coefficients. These experiments are done in a first step at ambient temperature and then at various lower temperatures in order to reproduce the atmospheric conditions and to obtain the coefficients of variation of air-broadening and air-shift values with temperature.

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The Spectroscopic, Molecular Structure And Electrostatic Potential, Polarizability, Hyperpolarizability, And HOMO–LUMO Analysis Of Monomeric And Dimeric Structures Of N-(3-Methylphenyl)-2-Nitrobenzenesulfonamide

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The monomer and dimer structures of the title molecule have been obtained from density functional theory (DFT) B3LYP method with 6-31G (d,p) as basis set calculations. The optimized geometrical parameters obtained by B3LYP/6-31G (d,p) method show good agreement with experimental X-ray data. The polarizability and first order hyperpolarizability of the title molecule were calculated and interpreted. The intermolecular N–H···O hydrogen bonds are discussed in dimer structure of the molecule. The vibrational wave numbers and their assignments were examined theoretically using the Gaussian 03 set of quantum chemistry codes. The predicted frontier molecular orbital energies at B3LYP/6-31G(d,p) method set show that charge transfer occurs within the molecule. The frontier molecular orbital calculations clearly show the inverse relationship of HOMO–LUMO gap with the total static hyperpolarizability. The results also show that N-(3-Methylphenyl)-2-nitrobenzenesulfonamide [1] molecule may have nonlinear optical (NLO) comportment with non-zero values [2].

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CRDS spectrum of NO₂ molecule between 6100 and 6200 cm⁻¹

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The high sensitivity CRDS spectrum of the NO₂ molecule is recorded for the first time between 6100 and 6200 cm⁻¹. The spectrum is formed by rotational - vibrational transitions belonging to the 311-000 band and the very weak 023-000 band at 6155.85 and 6183.92 cm⁻¹, respectively. In total, about 1700 rotational-vibrational transitions were assigned. Upper energy levels with rotational quantum numbers J and K_a as high as 42 and 8, and 30 and 2 were derived for the 311 and 023 vibrational states, respectively. Experimental line positions were modeled within an *rms* deviation of 0.0033 cm⁻¹ using the effective Hamiltonian approach which takes explicitly into account the spin rotational interaction. Interpolyad resonance coupling between the 311 and 023 states as well as interaction involving the 311 state and two dark states - 330 and 042 - were taken into account. The main parameters in the transition moment series were determined for the 311 and 023 states from a fitting of experimental intensities and the detailed synthetic spectrum was generated in the considered spectral region.

The low energy range of the infrared absorption spectrum of $^{14}\text{NH}_3$ between 6367 and 6580 cm^{-1} : coupling temperature dependence and GSCD technique

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Completing our previous work between 1470 and 1510 nm [1], the infrared spectrum of $^{14}\text{NH}_3$ have been recorded between 1510 and 1570 nm ($6367\text{-}6622\text{ cm}^{-1}$) at different temperatures from 150K to 296K allowing to derive information on the lower state energy of each transition. Compared to previous work [2], 520 new transitions have been detected in this energy range. Taking advantage of the resolution of laser spectroscopy, some attempts have been performed to assign new bands with the help of both GSCD (Ground State Combination Difference) technique [3] and variational calculations [4].

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