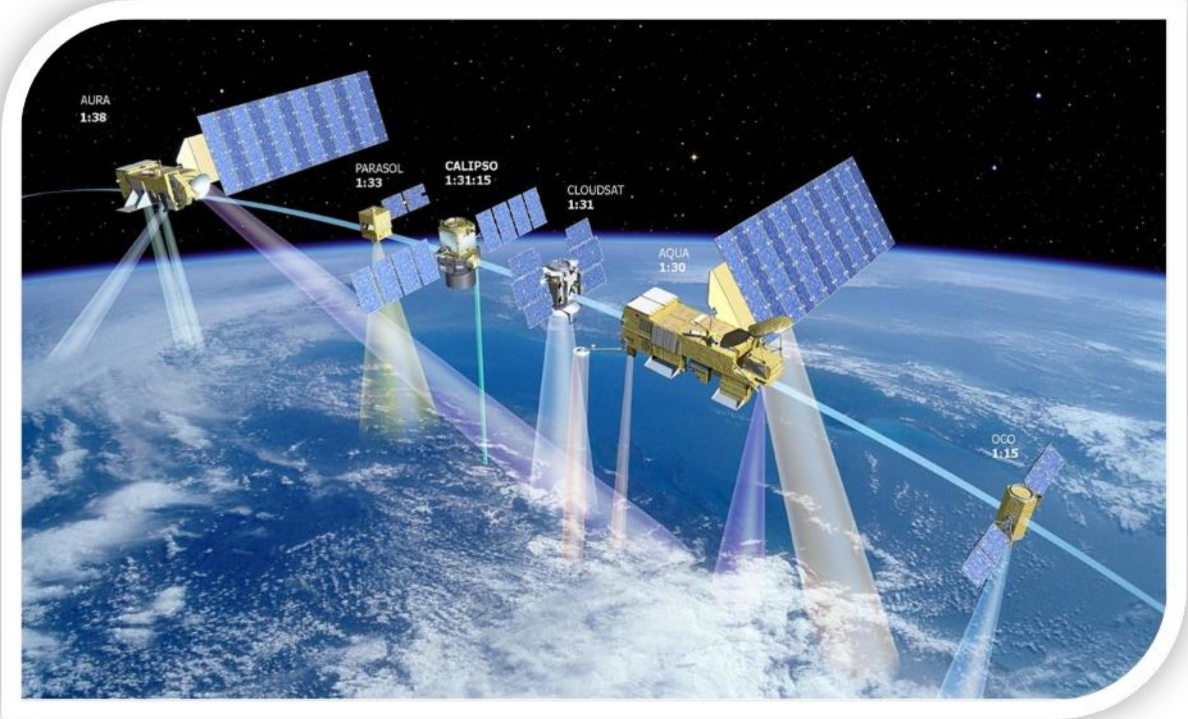
ASA-HITRAN 2016

13th ASA Conference

(united with 14th HITRAN Conference)

University of Reims

Wednesday, 24 August – Friday, 26 August 2016



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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** (*invited speaker*)	p 7
9:35-9:55	M. Rey	p 8
9:55-10:15	S.T. Melin	p 9
10:15-10:50	Coffee break	
10:50-11:10	R. Georges	p 10
11:10-11:30	R.J. Hargreaves	p 11
11:30-11:50	V. Perevalov	p 12
12:00-14:00	Lunch	
	Chair : P. Rannou	
14:00-14:35	**R. Wordsworth** (*invited speaker*)	p 13
14:35-14:55	C.D. Boone	p 14
14:55-15:15	A. Perrin	p 15
15:15-15:35	T. Delahaye	p 16
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15:55-16:15	G. Liuzzi	p 18
16:15-16:35	J. Orphal	p 19
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 H_2O, CO, CO_2, 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 H_2O 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 H_2O 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 CO_2, CO, O_2, OH, H_2O, and NO. Using a wavelength tunable external cavity diode laser, direct absorption spectra for H_2O 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) H_2O vapor absorption thermometer has been built based on a MEMS-VCSEL source [3]. To validate the MEMS-VCSEL sensor, H_2O 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
H_2O vapor thermometry

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High-temperature infrared spectroscopy using a high enthalpy source

Nicolas Suas-David[1], Vinayak Kulkarni[1,2], Robert Georges[1,*], Samir Kassi[3], Abdessamad Benidar[1], Jonathan Thiévin[1], Badr Amyay[4], Vincent Boudon[4], Mickaël Rey[5], Olivier Pirali[6] and Jean Vander Auwera[7]

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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 C_2H_2 and NO_2 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 (NO_2 molecule) or simple empirical equations (C_2H_2 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 C_2H_2 and 10^{-25} cm^{-1}/molecule cm^{-2} at 1000 K for NO_2. The C_2H_2 line list covers 50-9900 cm^{-1} wavenumber region. The NO_2 line list covers 466-4776 cm^{-1} wavenumber region. The line lists are useful for studying high-temperature radiative properties of C_2H_2 and NO_2 molecules. These line lists will be freely accessible via the Internet site of V.E. Zuev Istitute 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 CO_2 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 7.6µm 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 HNO_3 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 HNO_3 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 Deusches 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 (λ=1645.55 nm) between two strong absorption features which belong to the R(6) manifold of the $2\nu_3$ band of $12CH_4$ [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 Spectroscopie 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 nightglow at 1.27μm at low altitudes on Mars with a Doppler Michelson interferometer

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The $O_2(a^1\Delta_g)$ 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, H_2O, HDO, O_3 profiles and average column abundance of CO_2, CO, CH_4, SO_2, N_2O, HNO_3, NH_3, OCS and CF_4. 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 H_2O, CH_4 and CO_2. The H_2O ν_2 spectral region is in general warmer (higher radiance) than observations and the spectroscopy is inconsistent among the IASI bands. The CO_2 ν_2 and N_2O/CO_2 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 CH_4 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 $BrONO_2$ [3] and SO_2 [4] in the stratosphere or NH_3 [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 8-9µm 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, H_2O, HCL, HCN, HNO_3, N_2O, O_3, SO_2) 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 CO_2 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 CO_2 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 SF_6 Absorption in the 10µm atmospheric window

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To model correctly the SF_6 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 SF_6 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 $100 - 3200\ \mathrm{cm}^{-1}$ 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 $\nu 5$, $2\nu_5$ 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 SF_6 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 $^{32}S^{16}O^{18}O$ and $^{32}S^{18}O_2$

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High-resolution Fourier transform spectra of ^{18}O- enriched isotopic samples of sulfur dioxide ($^{32}S^{16}O^{18}O$ and $^{32}S^{18}O_2$) have been recorded at 0.00102cm^{-1} resolution in the 400-620 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 $^{32}S^{16}O^{18}O$ and $^{32}S^{18}O_2$ isotopologues of sulfur dioxide located at 507.36541(1) and 496.59988(1) 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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P1-7

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 $^{12}CH_3I$ [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 v_6=1 energy levels with those from the $v_3 = 2$ and $v_2 = 1$ 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 µm. 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 $v_6 = 1$ and $v_3 = 2$ vibrational states to get the upper state rotational constants and interacting parameters for the $v_6 = 1$ and $v_3 = 2$ states. On the other hand, it proved unnecessary to update the existing hyperfine parameters for the $v_6 = 1$ and $v_3 = 2$ 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 $\alpha_{min} \approx 2\times10^{-10}$ cm^{-1}.

A total of 8671 transitions belonging to 166 bands of eleven CO_2 isotopologues were rovibrationnally 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 ΔP=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 $^{16}O^{12}C^{18}O$ (628) and $^{12}C^{18}O_2$ (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 $^{16}O^{12}C^{18}O$, $^{16}O^{12}C^{17}O$, $^{12}C^{18}O_2$, $^{17}O^{12}C^{18}O$ and $^{13}C^{18}O_2$ isotopologues. A number of inter- and intra- polyad resonance perturbations were identified.

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Far-infrared collision-induced absorption by CO_2-H_2 and CH_4-CO_2 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 CO_2 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 CO_2-H_2 and CH_4-CO_2 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 CO_2-CO_2, H_2-H_2, and CH_4-CH_4 pairs were obtained using Borysow's set of FORTRAN codes [5]. Using our simulated CIA rototranslational spectra for CO_2-H_2 and CH_4-CO_2 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 CO_2 at T = 200 K

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The low temperature (T = 200 K) far-infrared collision-induced spectra of pure CO_2 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 CO_2 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 CO_2 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 $2x10^{-3}$. 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 $2.7x10^{-27}$ 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 O_4, HONO and OClO 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 $1x10^5$ which corresponds to the minimal detectable absorption coefficient of $6x10^{-9}$ 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 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} cm/molecule are confidently measured by the spectrometer. The results of H_2O-N_2 and H_2O-H_2O broadening investigation recorded by a high resolution Fourier-transform spectrometer IFS-125M with LED sources in the region 15500 – 16000 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 $D_2{}^{16}O$ 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 D_2O 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 D_2O 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 D_2O 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 D_2O 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 D_2O 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 $^{13}C^{12}CH_6$ and $^{13}C_2H_6$ in the 3.2 – 3.6 µm region

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Absorption line positions for the ethane isotopologues $^{13}C^{12}CH_6$ and $^{13}C_2H_6$ have been determined in 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 H_2O at 2.3µm

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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 H_2O in the 2.3µm region [1]. We present measurements of absorption line parameters for H_2O 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 H_2O, 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 CO_2 and H_2O 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 CO_2 and H_2O. CO_2 and H_2O 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 CO_2 and H_2O 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 CO_2/H_2O 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 CO_2 and H_2O 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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P1-19

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].

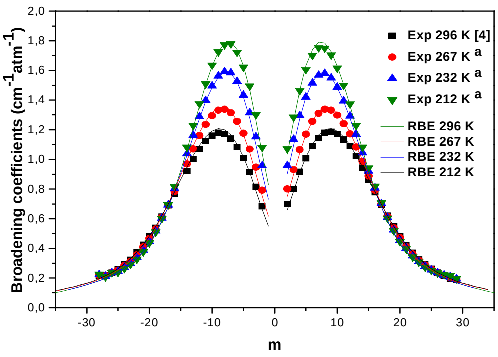

Figure 1. Comparison between measured [4] and theoretical (present work RBE) self-broadening coefficients of the ν_2 band of HCN. (a) : experimental values at temperatures 267 K, 232 K and 212 K deduced from measured values of γ_{HCN} (296) given in the Ref. [4].

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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 CO_2 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 CO_2 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 $H_2{}^{16}O$ 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: H_2 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 H_2 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 H_2 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 H_2 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 H_2 spectra.

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CRDS measurements and *ab initio* calculations of collisional effects in pure D_2

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Recent progress in theoretical calculations of molecular states energies for H_2, HD and D_2 [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 H_2 (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 D_2 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←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[1] used only the Voigt line shape. The line shape models used ~~in~~ 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 HITRAN[4] 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 profiles[6], 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. O_2 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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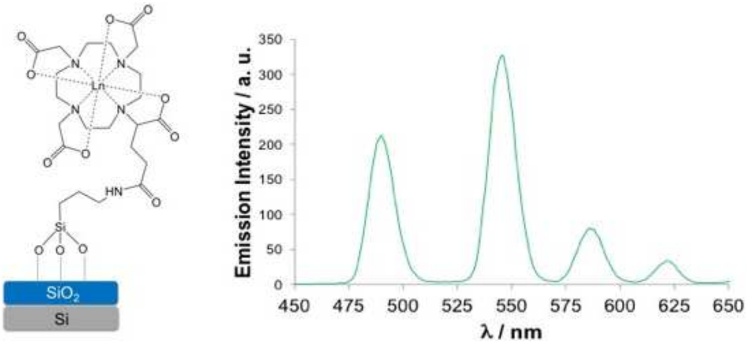
The results of a study concerning the covalent anchoring of luminescent lanthanide complexes onto silicon surfaces will be described. The aim of this work is to design new sensors for gases based on the following principle: an alteration of the optical signal should occur when the analyte is in contact 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 NOx 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 (~ 10 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 µm 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 µm 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 CO_2 laser shot noise. In a second time, the oscillator linewidth is measured from beat note stability between QCL and CO_2 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.

Acknowledgments

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CO_2 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 CO_2 above sparkling liquids such as champagne. The progressive desorption of dissolved CO_2 in champagne is responsible for bubble formation. Moreover, CO_2 may also escape by diffusion at the air-champagne interface. A first step in the understanding of the role of CO_2 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 CO_2 desorption are not well known and interactions between CO_2 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 CO_2 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 CO_2. 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 CO_2 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 CH_4. 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 CO_2 [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 hyperpolarizabilty 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 NO_2 molecule between 6100 and 6200 cm^{-1}

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The high sensitivity CRDS spectrum of the NO_2 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 $^{14}NH_3$ 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 $^{14}NH_3$ have been recorded between 1510 and 1570 nm (6367-6622 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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Line intensity study of water vapor enriched by ^{18}O in the spectral range between 6400 and 9400 cm^{-1}

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This study is a continuation of experimental efforts on the absorption water vapor spectrum analysis in the near infrared. The previous studies [1-3] were focused on water vapor in natural isotopic abundance. Now we are focusing on the ^{18}O water isotopologues. New spectra of water samples enriched by ^{18}O were recorded between 6400 and 9400 cm^{-1} in Reims with the Connes-type Fourier Transform Spectrometer. The spectra were recorded at room temperature with an $H_2{}^{18}O$ abundance enrichment of about 95% and a non apodized resolution of 0.010 cm^{-1}. The pressure is varying from 2 to 13 torr and the absorption path length is from 67 cm to 200 m.

Preliminary results of the spectra analysis below 8000 cm^{-1} will be presented. About 8000 absorption lines were found in the recorded spectra with an absorption path length from 8 to 88 m. Overall, 7845 lines were assigned to 8466 transitions of six water isotopologues ($H_2{}^{16}O$, $H_2{}^{17}O$, $H_2{}^{18}O$, $HD^{16}O$, $HD^{17}O$, and $HD^{18}O$). One hundred forty-seven lines with intensities between 5×10^{-27} and 8×10^{-26} cm/molecule were left unassigned. More than 870 lines of the $H_2{}^{18}O$, $H_2{}^{17}O$ and $HD^{18}O$ were observed for the first time. An overview of the $H_2{}^{18}O$ results is shown on Figure 1 as well as a comparison with previous studies [4-11]. More than 80 rotation-vibration energies of $H_2{}^{18}O$ and $H_2{}^{17}O$ were obtained for the first time.

The line intensity comparison with literature data will be discussed.

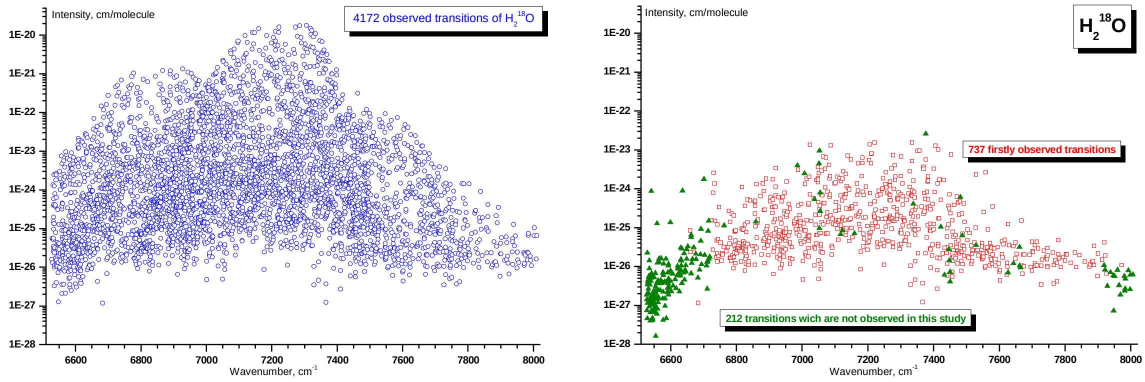

Figure 1: *Left panel*: Overview of observed $H_2{}^{18}O$ transitions between 6425 and 8010 cm^{-1}. *Right panel*: firstly observed transitions (red squares) and not observed transitions in this study which were reported in Refs. [4-11] (olive triangles)

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Line parameters of H_2O in CO_2-rich atmospheres

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Both Venus' and Mars' atmosphere are composed of 95-96% of CO_2. Considering the resolution of the remote instruments nowadays, the line parameters used to perform the retrievals of the spectra should be as accurate as possible. SOIR [1] and NOMAD [2] are spectrometers respectively onboard Venus Express (2008-2014) and ExoMars Trace Gas Orbiter (2016-). These instruments perform solar occultation measurements in the IR region (2.2 – 4.3 µm) with a resolution of 0.15 cm^{-1}. The wavelength range probed by SOIR and NOMAD allows a detailed chemical inventory of the Venus' and Mars' atmosphere at the terminators in the upper mesosphere and lower thermosphere (70 to 170 km) with an emphasis on vertical distribution of the gases (CO_2, CO, H_2O, HCl, HF…).

An initiative led by the GSMA aims to measure line parameters of H_2O broadened by CO_2 in the laboratory using their expertise in the field. They already performed these types of measures twenty years ago [3]. This new study is motivated by the improvement of their Fourier Transform spectrometer and also the software used to retrieve the line parameters.

New spectra have been recorded using the "home-made" FT spectrometer based in Reims. The line parameters will be retrieved using a multi-spectrum fitting software. The usual Voigt profile and the speed dependent Voigt model (see [4] and references therein), taking into account the speed dependences of the line width and shift, will be used to fit the measured spectra. Then these results will be confronted to the calculated values of R.R. Gamache [5].

This study is performed with the aim of improving the spectral parameters used by planetary atmospherists, in particular the Mars' and Venus' communities. Therefore spectra from the SOIR instrument will be used as test-case, in order to be ready to analyse the NOMAD spectra, as soon as the Science Phase will start, in November 2017.

In this communication, we will present the status of the project. The first spectra obtained in Reims will be presented and the current study on the recorded spectra. Examples of water retrievals obtained using the SOIR instrument will be shown as well. This complete study should improve the linelists made available to the planetary community, or at least provide important information on line parameters

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Total carbon monoxide and tropospheric ozone contents over Paris area during winter and summer pollution episodes using the ground-based FTIR station OASIS

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Ground-based Fourier-transform infrared (FTIR) solar absorption spectroscopy is a powerful remote sensing technique providing information on the concentration and vertical distribution of various trace gases. This study reports measurements of two atmospheric components: carbon monoxide (CO) and ozone (O_3) made by OASIS for "Observations of the Atmosphere by Solar absorption Infrared Spectroscopy, an urban ground-based FTIR station over Paris suburbs. Even with mid-resolution (0.06 cm^{-1}) the information provided by OASIS ozone retrievals is clearly relevant to monitor both tropospheric (columns integrated from the surface up to 8 km) and stratospheric ozone amounts [1] and the instrument is also suited for monitoring total columns of CO [2]. Usually used for long-term time series of CO and O_3 vertical columns, temporal variabilities of total columns of CO from OASIS are investigated during two winter pollution events in March 2014 and March 2016 when local emissions of aerosol particles were particularly strong in Paris area. The interrelation of tropospheric ozone columns from OASIS and surface ozone is also investigated, particularly in early July 2015 and comparison was made with data from the chemistry-transport code CHIMERE for 11 ozone pollution events from 2009 to 2015.

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HITRANonline: a new structure and interface for HITRAN line lists and cross sections

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We describe HITRAN*online*, an online interface to the internationally-recognized HITRAN molecular spectroscopic database[1], and outline the structure of its relational database backend[2].

As the amount and complexity of spectroscopic data on molecules used in atmospheric modelling has increased, the existing 160-character, text-based format has become inadequate for its description. For example, line shapes such as the Hartmann-Tran (HT) profile[3] require at least six parameters for their full description (each with uncertainties and references). Data is also available on line-broadening by perturbers other than “air” and “self” and more than the current maximum of 10 isotopologues of some molecules (for example, CO_2) can be important for accurate radiative-transfer modelling. The new relational database structure overcomes all of these limitations. Indeed, parameters describing line broadening and shifts due to the perturbers H_2, He and CO_2 have recently been introduced into the database[4] as well as HT profile parameters for H_2 absorption[5].

To take full advantage of this new database structure, the online interface HITRAN*online*, available at <www.hitran.org>, provides a user-friendly way to make queries of HITRAN data with the option of returning it in a customizable format with user-defined fields and number of significant figures. Binary output formats such as HDF-5 are also supported. In addition to the data, each query also produces its own bibliography (in HTML and BibTeX formats), “README” documentation and interactive graph for easy visualization.

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Modified Complex Robert-Bonamy (MCRB) calculations of H_2O transitions broadened by H_2 for applications to planetary and exoplanet atmospheres atmospheres

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Line shape parameters for hydrogen broadening of water vapor are needed to understand remote sensing measurements of planetary and exoplanet atmospheres. In order to address these needs, semiclassical line shape calculations based on the Modified Complex Robert-Bonamy_(MCRB) formalism [1,2] were made. The intermolecular potential for the calculation is comprised of electrostatic, atom-atom (expanded to order 20 and rank 4), induction, and London dispersion terms. The trajectories were determined by numerical integration of the Hamilton's equations. The average over the Maxwell–Boltzmann distribution of velocities was performed by integration over 35 velocities corresponding to the temperature range 75K – 27000K. The formalism is complex valued yielding the half-width and line shift from a single calculation. The calculations are reported at 7 temperatures from 200 to 700 K. The half-width temperature dependence coefficient *n* was determined using the relation $\gamma(T)=\gamma(T_0)\left[T_0/T\right]^n$ with T_0=296K. It will be shown that H_2O-H_2 is a very off-resonance collision system, which leads to the atom-atom potential having a dominant role. Adjustments to the atom-atom parameters were made to improve the agreement with and structure of the measurements. The calculations are compared with a database of measured H_2O-H_2 line shape parameters. The rotational, vibrational, and temperature structure are discussed.

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P1-44

The use of pair identity and smooth variation rules to check asymmetric rotor molecules on the HITRAN database

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The concept of *families of transitions* was introduced by Brown and Plymate [1] to study the structure of variations in collision-broadened half-widths. Several other studies [2, 3] have used the *families of transitions* and *partner transitions* idea to analyze line shape parameters. In 2011, Ma *et al.* [4] developed theoretically what they termed pair identity and smooth variation rules. These rules were developed for a-type transitions of water vapor and are applicable under certain constraints to the line position, intensity, half-width, line shift, and temperature dependence of the half-width. Here the pair identity and smooth variation rules are extended to consider other types of transitions. These rules are applied to water vapor transitions on the 2012 HITRAN database [5]. The rules are then tested on other asymmetric rotor molecules on HITRAN.

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Measurements of H_2O broadening and shifting coefficients of CO_2, CH_4 and O_2 lines

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Atmospheric observation is mainly based on the solar radiation transmitted by the atmosphere or on the thermal radiation emitted by the Earth surface and by the atmosphere. The analysis of the measured data, mostly done through the so-called "inversion" procedures, requires the knowledge of the intrinsic spectroscopic parameters of absorption lines (positions, intensities...). The collisions between the molecules also have to be considered as their effects yield a modification of the line shape for most of the atmospheric physical conditions (pressure, temperature). Since the amount of water vapor in our atmosphere can be significant at low altitude, spectral line broadening by collisions with water vapor must be taken into account in order to meet the objective of precision of current satellite missions. In this study, H_2O-broadening and shifting coefficients of many lines of methane, carbon dioxide and oxygen in the mid- and near-infrared region were measured. For that, spectra of CH_4, CO_2 and O_2 diluted in water vapor were recorded with a high resolution Fourier Transform spectrometer for various pressures and at 50 and 95°C. Line broadening and shifting were retrieved from the measured spectra through fits using Voigt profiles. Values at room temperature and their temperature dependences were then deduced and compared with those of dry air. The results show that H_2O-broadenings of methane lines are, on average, 34% larger than those for dry air [1]. For CO_2, our result are about 4% lower than the values recommended in a previous study but they confirm the relative variations of the line broadening on the rotational quantum numbers. We also provide the first determination of H_2O-induced line shifts of CO_2 lines [2]. Finally, for O_2 our measurements confirms that H_2O-broadenings of oxygen lines are, on average, 10% larger than those for dry air [3,4].

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HITRAN Application Programming Interface (HAPI): extending HITRAN capabilities

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We present the HITRAN Application Programming Interface (HAPI) [1], a free Python library incorporating a flexible set of tools to work with the most up-to-date spectroscopic data provided by the new information system HITRAN*online*(www.hitran.org) [2,3]. HAPI provides the user with the following features:

- Access to the spectroscopic parameters which are continuously being added to HITRAN*online*. These include, for instance, non-Voigt line profile parameters [4], foreign broadenings and shifts [5], and in the upcoming upgrade line mixing [6].
- Single-layer absorption calculation accounting for an instrument function. HAPI enables complex broadener modeling for atmospheric and astrophysical applications.
- Expert algorithm for the line profile selection for a single-layer radiative transfer calculation
- Extension by custom line, partition sums, instrumental functions, and temperature and pressure dependences.

HAPI applications include spectroscopic data validation and analysis [7] as well as experiment verification and spectroscopic code benchmarking [1]. HAPI can serve as a foundation for building custom radiative-transfer codes [1] and also as a tool for teaching advance courses in spectroscopy.

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An improved line list for the 5 μm spectral region of carbonyl sulfide

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The information available for the 5 μm spectral region (1658.6 – 2153.2 cm^{-1}) of carbonyl sulfide in the HITRAN [1] spectroscopic database originates from an extensive self-consistent line list generated by A. Fayt on the basis of the global analysis developed for this molecule [2] and included in the 2000 edition of HITRAN [3]. Although the intensities of 19 bands were increased by 15.8% in the 2008 edition [4] to match the average of measured intensities reported for the ν_3 band [5,6] and the air- and self-broadening coefficients were corrected in the 2012 edition [1], the spectroscopic information currently available in HITRAN is essentially the same as in HITRAN 2000. It consists in 9314 lines belonging to 52 bands of 5 isotopologues ($^{16}O^{12}C^{32}S$, $^{16}O^{12}C^{34}S$, $^{16}O^{13}C^{32}S$, $^{16}O^{12}C^{33}S$, $^{18}O^{12}C^{32}S$), with a minimum intensity of 1.012×10^{23} cm/molecule at 296 K. Although of a similar origin, the spectroscopic data in the GEISA database [7] consists in 13021 lines belonging to 73 bands of 6 isotopologues ($^{16}O^{13}C^{34}S$ is the additional one), provided in the same spectral range and with the same minimum intensity as in HITRAN.

It was found that the information available in HITRAN does not account for several hundreds of weak lines observed around 5 μm for a sample of OCS in natural abundance [8]. This count is substantially reduced when using GEISA. These missing lines correspond to hot bands of several isotopologues of OCS. Relying on an improved global model of OCS and available experimental line intensities, a new line list was generated. In particular, it includes strong bands of isotopologues less abundant than $^{16}O^{13}C^{34}S$ and hot bands weaker than available in HITRAN and GEISA for the more abundant isotopologues. This new line list will be presented and compared with experimental information, HITRAN and GEISA.

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P1-48

Line shape parameters of helium- and hydrogen-broadened $^{12}C^{16}O$ in the 3→0 overtone transition near 1.57 µm

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Frequency-stabilized cavity ring-down spectroscopy was used to determine helium- and hydrogen- broadened $^{12}C^{16}O$ line shape parameters for eleven lines in the $3 \rightarrow 0$ vibrational overtone band, including helium- and hydrogen-pressure broadening and pressure shifting. We report spectra with excellent signal-to-noise (exceeding 5×10^4), which offer stringent tests of line shape models. These spectra provide evidence of three non-Voight mechanisms affecting line shape: collisional (Dicke) narrowing, speed dependence, and correlations between velocity-changing and phase-changing collisions. This work provides another demonstration that multispectrum fitting of the partially correlated speed dependent Nelkin-Ghatak profile (with the quadratic approximation for speed dependence) is necessary for precise determinations of line shape parameters associated with these three mechanisms [1-3].

The measured line shape are compared to previous work for helium- and hydrogen-broadened CO transitions in the $3 \rightarrow 0$ vibrational band (helium- and hydrogen- broadening coefficients) [4, 5] and in the $1 \rightarrow 0$ fundamental vibrational band (helium- and hydrogen- broadening and shifting coefficients) [6, 7]. The uncertainty of the broadening coefficients are significantly reduced, and the shifting and narrowing parameters are reported for the first time for this transition. Analysis of the spectra at elevated pressure reveals evidence of line mixing with first-order line mixing parameters that are consistent with literature values.

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New investigation of the UV spectra of SO_2 for the validation of the TROPOMI/SENTINEL-5 instrument

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The UV spectra of SO_2 in natural concentration is measured by Fourier Transform Spectrometry in the region 26 000 – 40 000 cm^{-1} at room temperature. The goal is to enhance the cross sections and their associated uncertainty from the work of Vandaele et al [1, 2, 3] which is recommended in the HITRAN database. The new measurements try to meet the TROPOMI requirements for uncertainty and resolution. The spectrometer is the new BRUKER IFS 125HR spectrometer equipped for the UV in an emission configuration. The SO_2 sample is filled in a 20 cm long single pass BRUKER cell. The temperature is fixed by the air conditioning of the room and some tests are made to isolate the cell from small air blows that can arise. Different kind of UV light sources are tested to quantify the effects of the light source on the cross sections (heating of the cell, photodissociation, etc…). They consist in a Xenon arc lamp and two groups of LED from different companies and different power. The spectra are recorded at 8 and 2 cm^{-1} resolution and a higher resolution of 0.1 cm^{-1} was also recorded to check the presence of finer structures that could behave differently in the comparisons of cross sections when dealing with apparatus of different resolution. The results will be presented and analysed. The comparisons to references will be made considering the Edlen correction since our spectrometer is used under vacuum whereas the BRUKER IFS120M used in [1, 2, 3] operates in air.

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High-resolution spectroscopy and analysis of various bands of CF_4 to elucidate its hot band structure

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We have recorded spectra of the $\nu_2 + \nu_3$ combination band of CF_4 under two different physical conditions. i) Jet-cooled spectra with a rotational temperature of *ca*. 50 K, recorded thanks to the Jet-AILES[1] apparatus of the AILES Beamline at the SOLEIL Synchrotron facility. ii) Room-temperature spectra recorded in Reims with a 8 m optical path in a multiple-pass White cell. We could also record high-resolution spectra of the forbidden ν_2 fundamental band and of the $\nu_1 + \nu_3$ combination band.

We present a detailed analysis of these spectra realized thanks to the XTDS software[2]. The assignments are included into a global fit implying several interacting bands previously studied[3]. Our final aim is to obtain a global analysis of all the lower vibrational bands of CF_4 and to simulate its hot bands in the atmospheric absorption region.

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Thursday Aug. 25, 2016 Program

	Chair : H. Tran	
9:00-9:35	**X. Huang** (*invited speaker*)	p 75
9:35-9:55	P. Wcislo	p 76
9:55-10:15	T. Mendaza	p 77
10:15-10:50	Coffee break	
10:50-11:10	M. Ghysels	p 78
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11:30-11:50	A. Pedroi-Cross	p 80
12:00-14:00	Lunch	
	Chair : V. Boudon	
14:00-14:35	**A. Nikitin** (*invited speaker*)	p 81
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Computing highly accurate spectroscopic line lists for characterization of exoplanet atmospheres and assignment of astronomical observations

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Over the last decade, it has become apparent that the most effective approach for determining highly accurate rotational and rovibrational line lists for molecules of interest in planetary atmospheres and other astrophysical environments is through a combination of high-resolution laboratory experiments coupled with state-of-the art *ab initio* quantum chemistry methods. The approach involves computing the most accurate potential energy surface (PES) possible using state-of-the art electronic structure methods, followed by computing rotational and rovibrational energy levels using an exact variational method to solve the nuclear Schrödinger equation. Then, reliable experimental data from high-resolution experiments is used to refine the *ab initio* PES in order to improve the accuracy of the computed energy levels and transition energies. From the refinement step, we have been able to achieve an accuracy of approximately σ_{RMS}= 0.02 cm^{-1} for rovibrational transition energies, and even better for purely rotational transitions. This combined "experiment + theory" approach allows for determination of essentially a complete line list, with hundreds of millions of transitions, and having the transition energies and intensities be highly accurate. Our group has successfully applied this approach to determine highly accurate line lists for NH_3 and CO_2 (and isotopologues), and very recently for SO_2 and isotopologues. Here I will report our latest results for SO_2 isotopologues and updates on CO_2 isotopologues. Comparisons to the available data in HITRAN2012 and other available experimental data will be shown, though we note that our line lists for SO_2 isotopologues are significantly more complete than any other databases. Since it is important to span a large temperature range in order to model the spectral signature of exoplanets, we will also demonstrate how the spectra of CO_2 change on going from low temperatures (100 K) to higher temperatures (500 K to 1500 K).

Shapes of molecular lines from first principles (proposal for constructing line-shape databases from *ab initio* calculations)

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A proper treatment of non-Voigt line-shape effects is crucial to reliably interpret and reconstruct accurate molecular spectra as well as to reduce the systematic errors in atmospheric measurements of the Earth and other planets. This fact has stimulated development of a new structure of modern spectroscopic databases [1-3] and incorporation of an extensive set of new line-shape parameters [4]. It turned out, however, that the most challenging issue is to determine the values of these parameters for a wide range of pressures and temperatures covering all the bands and branches. Currently a set of available experimental data is relatively sparse and even if the experimental data can be reliably fitted and reproduced with the non-Voigt line-shape model then their extrapolations to other transitions and other thermodynamic conditions would result in very large errors [4]. Following [5, 6] we present our proposal for overcoming this difficulty by performing a set of *ab initio* line-shape calculations. We calculate from first principles the phase-/state-changing contribution by full quantum-scattering calculations [7-9] and velocity-changing one from the Boltzmann collisional operator based on the billiard-ball approximation [10, 11]. After validation with experimental spectra for several particular lines we will be able to generate a complete dataset of *ab initio* line-shape parameters for a given molecular system. Finally, they will be projected [4] on a simple structure of the quadratic correlated speed-dependent hard collision profile [12, 13] also called the Hartmann-Tran profile [14], hence making them ready to be included into the new structure [1, 2] of the HITRAN database [15].

To validate our concept, we chose H_2 perturbed by helium which, on one hand, is the simplest possible system for such studies while, on the other hand, it is relevant for the studies of the atmospheres of gas giants and hence required to be stored in the spectral line databases. Our preliminary results for pure rotational and fundamental bands demonstrate that our *ab initio* approach not only well reproduces experimental spectra, but can also be used to validate the potential energy surfaces available in the literature [8]. In the next step we will repeat these calculations for higher H_2 vibrations with an extended version of the recent highly accurate PES [16]. A positive validation of our calculations will open a way for generating the first complete *ab initio* dataset of the line-shape parameters for a particular molecular system. In a long-term perspective we would like to focus on the CO-N_2 system, which is not only relevant for the investigations of Earth's atmosphere but can also be a feasible objective of *ab initio* studies.

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Line-Mixing Relaxation Matrix model for spectroscopic and radiative transfer studies

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We present a new open source and user-friendly model to compute the line-mixing relaxation matrix for linear molecules. The model is based on the previous work [1], and follows the Energy-Corrected Sudden (ECS) approximation/theory [2]. The main innovation of the model is the implementation of a new experimental Basis Transition Rate function that, allows to remove the dependency of fitted parameters to every molecule-perturber system, and to treat customized-combinations within the Infinite Order Sudden (IOS) approximation. The model reads the needed spectroscopic data from the HIgh-resolution TRANsmission molecular absorption (HITRAN) [3]. In this work we present an example of the calculations with our model for the Carbon Dioxide (CO_2) molecule, and a comparison with a previous works. The data produced by our model can be used to characterise the line-mixing effects on ro-vibrational lines of the infrared emitters on Earth or any planetary atmosphere, and to calculate accurate absorption spectra, which are needed in the interpretation of atmospheric spectra, radiative transfer modelling and General Circulation Models (GCM).

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Temperature- and Pressure-Dependence of Line Shape Parameters for (30012) ← (00001) CO_2 Band Transitions

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Measurements of atmospheric carbon from remote sensing platforms such as the Orbiting Carbon Observatory-2 satellite require predictive, line-by-line models of the absorption coefficient of carbon dioxide (CO_2) [1]. These models must account for the pressure- and temperature-dependence of line shapes for isolated transitions and for line mixing effects within the vibrational band. Here we describe a new low-temperature cavity ring-down spectrometer which enables high-precision, laboratory line shape studies over a temperature range that is relevant to remote sensing applications. The ring-down spectrometer consists of a monolithic invar cell and optical resonator assembly inside a low-temperature enclosure. The system has a long-term temperature stability of 5 mK. This configuration yields stable cavity resonances which provide a low-drift spectrum detuning axis with 1-MHz-level uncertainty. The optical cavity is nominally 80 cm long, with a finesse of 15,000 and a 1-s detection limit of 3×10^{-10} cm^{-1}. As an illustration of the system performance, we report measurements of air-broadened (30012) ← (00001) CO_2 band line parameters obtained over a pressure range of 10 hPa to 100 hPa and for temperatures between 220 K and 300 K. Using multispectrum fits of the Hartmann-Tran profile (HTP) [2] (which includes the effects of collisional narrowing and speed-dependent narrowing effects in addition to correlations between velocity-changing and phase-changing collisions) we analyze the measured spectra. These results underscore the importance of modeling spectra with advanced (i.e. non-Voigt) profiles to precisely capture the temperature- and pressure-dependence of the line shape. In particular, we show how the use of the HTP can reduce bias in the measured broadening coefficient, which is relevant to the accurate calculation of distant line wings for saturated features that are typically observed in long-path atmospheric spectra [3].

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Theoretical studies of the relaxation matrix for molecular systems

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The phenomenon of collisional transfer of intensity due to line mixing has an increasing importance for atmospheric monitoring. From a theoretical point of view, all relevant information about the collisional effect on line shapes is contained in the relaxation matrix whose diagonal elements are the half-widths and shifts of individual lines while the off-diagonal elements correspond to line interferences. For simple systems such as those consisting of diatom-atom or diatom-diatom, accurate fully quantum calculations based on sophisticated and realistic interaction potentials are feasible. However, fully quantum calculations become unrealistic for more complex systems. So far, the semi-classical Robert-Bonamy formalism, which has been widely used to calculate half-widths and shifts for decades, fails in calculating the off-diagonal matrix elements resulting from applying the isolated line approximation. As a result, in order to simulate atmospheric spectra where effects from line mixing are important, semi-empirical fitting or scaling laws such as the energy corrected sudden (ECS) and infinite order sudden (IOS) models are commonly used. Recently, we have found that in developing semi-classical line shape theories, to rely on the isolated line approximation is not necessary [1]. By eliminating this assumption, and accurately evaluating matrix elements of the exponential operators, we have developed a more capable formalism that enables one not only to reduce uncertainties of calculated half-widths and shifts, but also to calculate the whole relaxation matrix. Thanks to this progress, one can address the line mixing based on interaction potentials between molecular absorber and molecular perturber. We have applied this formalism for Raman and infrared spectra of linear molecules [1-4] and asymmetric-top molecule [5]. Recently, the method has been extended to symmetric tops with inversion symmetry such as the NH_3 molecule [6,7]. Our calculated half-widths of NH_3 lines in the ν_1 and the pure rotational band match measurements very well. Furthermore, the method has been applied to the calculation of the shape of the Q branch and of some R manifolds, for which an obvious signature of line mixing effects has been experimentally demonstrated. Comparisons with measurements show that predictions from the new formalism accurately match the experimental line shapes.

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Experimental and theoretical line parameters for self- and H_2-broadened transitions in the first overtone band of CO

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In this study we have re-analyzed high-resolution spectra of pure CO and CO broadened by hydrogen recorded in the spectral range of the first overtone band [1]. Self- and H_2-Lorentzian pressure-broadened half-width, pressure-induced shift parameters, line mixing coefficients as well as line centers and intensities were obtained for 48 (P(24) to R(23)) ro-vibrational transitions belonging to the first overtone (2←0) band of $^{12}C^{16}O$ at the ambient temperature (~298 K).

The diffusion constants needed to estimate the narrowing line parameters were calculated theoretically. H_2 was modeled by means of a single united atom force field [2] while CO was described from a three electrostatic sites model [3]. Intermolecular interactions were described by combining electrostatic and van der Waals interactions. The electrostatic contribution was computed using the Ewald sum while the van der Waals interactions were modeled from a Lennard-Jones potential. For CO-H_2 mixtures, five molar fractions were investigated, 0.0, 0.0126, 0.05, 0.5 and 1. Molecular dynamics simulations were carried out using the DLPOLY software [4]. This procedure allowed us to fix the narrowing parameters to the calculated values while fitting the spectra with the Rautian and speed-dependent Rautian profiles.

The spectra were fitted simultaneously within the range 4146 to 4332 cm^{-1} employing four line shape functions: the Voigt, Speed Dependent Voigt, Rautian and Speed Dependent Rautian Profiles. The line coupling effect has been observed and investigated as an asymmetry in the analyzed line profiles. Two semi-empirical methods (Energy Corrected Sudden Approximation, Exponential Power Gap Law) were used to estimate the self-broadening and self-line mixing parameters.
Furthermore, a classical approach [5] was applied to calculate the half-widths of CO absorption lines in CO-H_2 and CO-CO collisions. The calculations utilize simple vibrationally independent intermolecular interaction potential (Tipping-Herman + electrostatic) [6,7]. Both molecules were treated as rigid rotors. The dependences of CO half-widths on rotational quantum number for $J \leq 24$ are computed at room temperature and compared with measured data.

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Modeling and analysis of spectra of 4-, 5- atomic molecules of high symmetry

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Theoretical calculation of spectra of molecules is very useful for spectra analysis and spectra assignment. New full dimensional ab initio potential energy surface (PES) and dipole moment surface (DMS) of 4,- 5- atomic molecules are discussed [1,2,3]. The high precision pure ab initio PES of methane was constructed. It results in significantly better band center predictions even in comparison with best available empirically corrected potential energy surfaces. The issues related to the basis set extrapolation and an additivity of various PES corrections at this level of accuracy is discussed. The problem of energy levels convergence and empirical PES correction are discussed. The intensities calculated from different high order ab initio DMS are compared with available observed data. The state of art of global analysis of methane is discussed. The work is partly supported by French-Russian LIA SAMIA and Tomsk State University Mendeleev program.

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Far-infrared $^{14}NH_3$ line positions and intensities measured with submillimeter-wave and FT-IR spectroscopy

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The vibrational spectrum of ammonia has received an enormous amount of attention due to its potential prevalence in hot exo-planet atmospheres and persistent challenges in assigning and modeling highly excited and often highly perturbed states. Effective Hamiltonian models face challenges due to strong coupling between the large amplitude inversion and the other small amplitude vibrations. To date, only the ground and ν_2 positions could be modeled to experimental accuracy using effective Hamiltonians. Several previous attempts to analyze the $2\nu_2$ and ν_4 energy levels failed to model both the microwave and infrared transitions to experimental accuracy. In this work, we performed extensive experimental frequency measurement and analysis for the $2\nu_2$ and ν_4 inversion-rotation and vibrational transitions. We measured 159 new transition frequencies with microwave precision and assigned 1680 new ones from existing Fourier Transform spectra recorded in Synchrotron SOLEIL. The newly assigned frequencies significantly expand the range of assigned quantum numbers; combined with all the previously published high-resolution data, the $2\nu_2$ and ν_4 states are reproduced to experimental accuracy using a global model. Achieving experimental accuracy required inclusion of a number of terms in the effective Hamiltonian that were neglected in previous work. These terms have also been neglected in the analysis of states higher than $2\nu_2$ and ν_4 suggesting that the inversion-rotation-vibration spectrum of ammonia may be far more tractable to effective Hamiltonians than previously believed.

To evaluate the intensities of Far-IR ammonia transitions from HITRAN2012 and our effective Hamiltonian model, we performed independent measurements of high-resolution (0.00167 cm^{-1}, unapodized) Fourier-transform spectra of high purity (99.5%) normal ammonia sample using the AILES beamline of Synchrotron SOLEIL. The experimental conditions are designed to study numerous transitions with intensities weaker than 1×10^{-22} $cm^{-1}/(molecule\cdot cm^{-2})$ at room temperatures. Line positions and intensities of more than 2830 transitions of $^{14}NH_3$ are measured and compiled after proper quality control; the features from minor isotopologues ($^{15}NH_3$ and NH_2D) and H_2O are identified and removed. Based on the predictions of our effective Hamiltonian model, systematic quantum assignments are made for 2047 transitions from eight bands including four inversion-rotation bands (gs, v_2, $2v_2$, and v_4) and four ro-vibrational bands (v_2 – gs, $2v_2 - v_2$, $v_4 - v_2$, and $2v_2 - v_4$), as well as covering their $\Delta K = 3$ forbidden transitions. The measured line positions for the assigned transitions are in an excellent agreement (typically better than 0.001 cm^{-1}) with our Hamiltonian predictions in a wide range of J and K for all the eight bands. The comparison with the HITRAN 2012 database is also satisfactory, although systematic offsets are seen for transitions with high J and K and those from weak bands. For line positions, greater differences are found for some NH_3 bands in HITRAN 2012 than our effective Hamiltonian model. Also we note that out of the 8 bands, the $2v_2 - v_4$ has not been listed in the HITRAN 2012 database. Differences of 20% are seen between our measured and calculated intensities depending on the bands. Measurements of the individual line positions and intensities are presented for eight bands, and the final spectroscopic line positions and intensities are compiled as an electronic supplement.

CH_4 Spectroscopy at 2.3µm: analysis of ambient and low temperature pure CH_4 measurements

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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, requires high-accuracy spectral reference data for CH_4 in the 2.3 µm region [1]. Retrieval simulations have been performed to specify spectroscopic requirements showing the need for line intensity measurements down to 1e-25 cm^{-1}/(molecule cm^{-2}). Pure CH_4 measurements targeting line intensities have been carried out with a Bruker IFS 125HR Fourier transform spectrometer and a coolable multireflection cell. Eight ambient temperature spectra with CH_4 pressures between 0.4 and 10 mbar and absorption paths between 15 and 168 m and three 193 K spectra with pressures between 1 and 5 mbar and absorption paths between 33 and 168 m were recorded at Doppler limited resolution.

Baseline for the analysis was a line list from Vladimir Tyuterev [2] merged with HITRAN2012 [3]. The eleven spectra were analysed with a multispectrum fitting software developed at DLR [4] using the Voigt profile. The combination of low and ambient temperature measurements allowed fitting/validating lower state energies. It turned out that 2000 new lines had to be added and about 1600 lines were dropped from the initial list due to wrong position or lower state energy. The remaining 3900 fitted Tyuterev/Hitran2012 lines showed an averaged absolute line position difference of 0.0014 cm^{-1} and line intensity difference of 21%. Due to numerous blended lines and misassigned/missing lines with weak intensities the spectra, especially those with larger column amounts, could not be fitted down to the noise level. Therefore, line parameter based uncertainties are not meaningful. An alternative concept called “residual absorption cross sections” was introduced. The impact of the new results on simulated retrievals with TROPOMI together with the application of residual absorption cross sections will be discussed.

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Multispectrum Analysis of the Oxygen A-Band

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Retrievals of atmospheric composition from near-infrared measurements require measurements of airmass to better than the desired precision of the composition. The oxygen bands are obvious choices to quantify airmass since the mixing ratio of oxygen is fixed over the full range of atmospheric conditions. The OCO-2 mission is currently retrieving carbon dioxide concentration using the oxygen A-band for airmass normalization. The 0.25% accuracy desired for the carbon dioxide concentration has pushed the required state-of-the-art for oxygen spectroscopy. To measure O_2 A-band cross-sections with such accuracy through the full range of atmospheric pressure requires a sophisticated line-shape model (Rautian or Speed-Dependent Voigt) with line mixing (LM) and collision induced absorption (CIA). Models of each of these phenomena exist, however, this work presents an integrated self-consistent model developed to ensure the best accuracy.

It is also important to consider multiple sources of spectroscopic data for such a study in order to improve the dynamic range of the model and to minimize effects of instrumentation and associated systematic errors. The techniques of Fourier Transform Spectroscopy (FTS) and Cavity Ring-Down Spectroscopy (CRDS) allow complimentary information for such an analysis. We utilize multispectrum fitting software to generate a comprehensive new database with improved accuracy based on these datasets. The extensive information will be made available as a multi-dimensional cross-section (ABSCO) table and the parameterization will be offered for inclusion in the HITRANonline database.

Global frequency and intensity analysis of the $\nu_{10}/\nu_7/\nu_4/\nu_{12}$ band system of $^{12}C_2H_4$ at 10 µm using the D_{2h} Top Data System

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A global frequency and intensity analysis of the infrared tetrad located in the 600 - 1500 cm^{-1} region was carried out using the tensorial formalism developed in Dijon for X_2Y_4 asymmetric-top molecules [1] and a program suite called D_{2h}TDS (now part of the XTDS/SPVIEW spectroscopic software) [2]. It relies on spectroscopic information available in the literature and retrieved from absorption spectra recorded in Brussels using a Bruker IFS 120 to 125 HR upgraded Fourier transform spectrometer, in the frame of either the present or previous work [3]. In particular, 645 and 131 lines intensities have been respectively measured for the weak ν_{10} and ν_4 bands. Including the Coriolis interactions affecting the upper vibrational levels 10^1, 7^1, 4^1 and 12^1, a total of 10737 line positions and 1645 line intensities have been assigned and fitted with global root mean square deviations of 2.6×10^{-4} cm^{-1} and 2.5 %, respectively. Relying on the results of the present work and available in the literature, a list of parameters for 65420 lines in the ν_{10}, ν_7, ν_4 and ν_{12} bands of $^{12}C_2H_4$ was generated. The present work provides an obvious improvement over HITRAN and GEISA for the ν_{10} band (see figure below), and a marginally better modeling for the ν_7 band (and for the ν_4 band hidden beneath it). To the best of our knowledge, this is the first time that a global intensity analysis is carried out in this range of the ethylene spectrum.

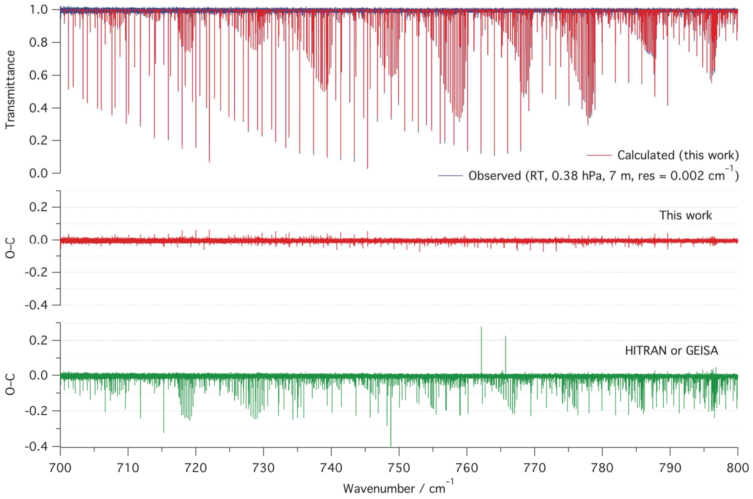

Fig. 1: Comparison of an observed spectrum (blue) of the P branch of the ν_{10} band of ethylene with spectra calculated (red) for $^{12}C_2H_4$ using results of the present analysis.

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Speed dependence, velocity change and line mixing in CO_2 under high pressures in the 30013←00001 band: measurements and test of models

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High-precision measurements of the 30013←00001 *R* branch of pure CO_2 were performed using 3-channel diode laser spectrometer [1] with resolution of $1\cdot10^{-4}$ cm^{-1} and signal-to-noise ratio (S/N) up to 7000. Lines from *R*(12) to *R*(22), that may be treated as isolated, were measured in pressure range from 0.005 to 0.9 atmosphere at a temperature of 296 K. Spectra were analyzed using spectrum-by-spectrum and multispectrum fittings with a variety of up-to-day models including speed dependence, velocity change and line mixing effects. Including in line shape profiles velocity change or Dicke narrowing parameters does not lead to the improvement in obtained residuals and, moreover, results in nonlinear pressure dependences of other collisional line shape parameters i.e., speed dependent narrowing, shifting and line mixing coefficients. It was shown that the quadratic Speed Dependent Voigt Profile with Line Mixing (qSDVP+LM) provides the measured-calculated residual less than 0.02%. All retrieved collisional parameters from spectrum-by-spectrum fitting are linear with pressure. The self-colliding line shape collisional coefficients were determined and presented using spectrum-by-spectrum and multispectrum fittings.

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Poster Session 2

Self-, N_2- and O_2-broadening coefficients of CH_3Br in the ν_2 band

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Methyl bromine is of interest for atmospheric applications, since this molecule is directly involved in the catalytic destruction of ozone in the lower stratosphere. Methyl bromide (CH_3Br) has been identified as the major contributor to stratospheric bromine and the primary organobromine species in the lower atmosphere.

O_2- broadening coefficients of CH_3Br have been retrieved in the ν_2 band at room temperature. Measurements have been performed using Fourier transform infrared spectroscopy. The lines were fitted with a single-spectrum non-linear least squares fitting procedure of Voigt profiles. The experimental results are compared with theoretical values calculated using the Robert and Bonamy formalism [1] which reproduces the measured broadening coefficients.

Recently, self- and N_2- broadening coefficients of CH_3Br have been measured for the P, Q and R branches of the ν_2 fundamental band at room temperature [2]. To complete this study, we have calculated these coefficients. The intermolecular potential used in this work for the CH_3Br-CH_3Br includes the overwhelming electrostatic interactions. For the CH_3Br-O_2 and CH_3Br-N_2, we have added to this potential the induction and dispersion energy contributions. For all studied collisional systems, the comparison between the theoretical and measured results leads to a good agreement.

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P2-2

Numerical issues in the conventional tools for calculating high-overtone ro-vibrational transition probabilities in diatomic molecules

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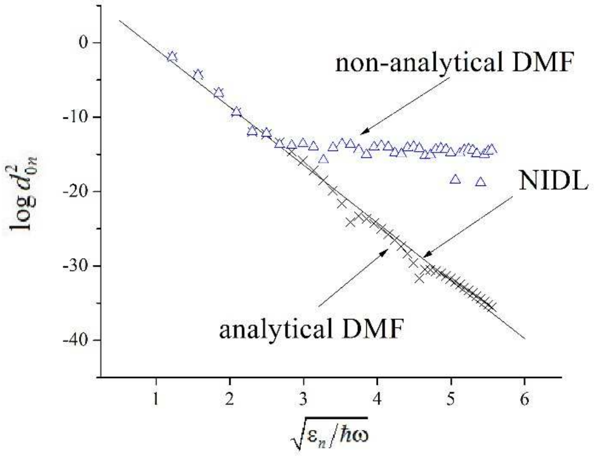
The most efficient and commonly employed method for calculating intensities in the high-temperature line lists of the diatomic molecules is to use one of the publically available computer codes that allow calculating the linelists with an input of the potential energy functions and dipole moment functions in point-wise or functional forms (see [1], for instance, for how this method was carried out for CO). It was found that conventional methods fail to correctly calculate the intensities of the high overtone transitions. The failure manifests itself as flattening (saturation) of the calculated transition probabilities starting at certain Δn, the change in the vibrational quantum number, which depends on both the molecule and the method used. In CO, $\Delta n = 11$ if calculations are performed with double precision [2], and $\Delta n = 7$ [3] if a spline-interpolated ab initio dipole-moment function (DMF) [1] is used (see figure). The flattening is revealed when the calculated intensities are compared with the theoretical NIDL (Normal Intensity Distribution Law) [4] predictions.



The flattening is also observed in SiO [5] (as expected in [6]), LiCl [7], CS (the saturated transitions are excluded in [8]).

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Py4CAtS - PYthon scripts for Computational ATmospheric Spectroscopy

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Line-by-line models have become mandatory for many atmospheric spectroscopy applications. Because of the large computational burden codes developed with Fortran or C/C++ are indispensable for operational processing. In general these codes work as a kind of 'black box' where intermediate quantities such as cross sections are difficult to access. However, script languages such as Python are becoming attractive now because they allow for "rapid prototyping" and codes are easily ported to a variety of platforms [1].

Py4CAtS --- PYthon scripts for Computational ATmospheric Spectroscopy [2] is a Python re-implementation of our Fortran infrared radiative transfer code GARLIC (Generic Atmospheric Radiation Line-by-line Infrared Code, [3]), where compute-intensive code sections utilize the Numeric/Scientific Python modules for highly optimized array-processing. The individual steps of an infrared or microwave radiative transfer computation are implemented in separate scripts to extract lines of relevant molecules in the spectral range of interest, to compute line-by-line cross sections for given pressure(s) and temperature(s), to combine cross sections to absorption coefficients and optical depths, and to integrate along the line-of-sight to transmission and radiance/intensity. Py4CAtS can be used in two ways, from the Unix/Linux (or Windows/Mac) console/terminal or (more flexibly) inside the (i)python interpreter. The basic design of the package (available at http://atmos.eoc.dlr.de/tools/Py4CAtS/), numerical and computational aspects relevant for optimization, and a sketch of the typical workflow are presented.

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Temperature-dependent absorption cross-sections of two fluorinated compounds: HFPO and perfluorodecalin

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We present temperature-dependent absorption cross sections of two fluorinated compounds. The first is 1,1,1,3,3,3-hexafluoro-2-propanol (HFPO), which is a fluorinated liquid commonly used as a speciality solvent for some polar polymers and in organic synthesis. HFPO vapour can be considered a potential greenhouse gas due to being radiatively active in the mid-infrared spectral region.

Experimental absorption cross-sections of HFPO were derived from Fourier transform infrared spectra recorded from 550 to 3400 cm^{-1} with a resolution of 0.1 cm^{-1} over a temperature range of 298 to 360 K. These results were compared to theoretical density functional theory (DFT) calculations and previously published experimental measurements made at room temperature [1].

Theoretical DFT calculations were performed using the B3LYP method and the 6-311G(d,p) basis set. The calculations have determined the optimized geometrical configuration and infrared intensities and wavenumbers of the harmonic frequencies for different ground state configurations for HFPO due to its internal rotors.

Additionally, experimental absorption cross-sections of both cis- and trans-perfluorodecalin were derived from Fourier transform infrared spectra recorded from 560 to 3500 cm^{-1} with a resolution of 0.1 cm^{-1} over a temperature range of 300-340 K. Perfluorodecalin is commonly used in medicine and biology as it can dissolve large amounts of oxygen. Radiative efficiencies and the global warming potential for both species were calculated and compared to previously published values [2].

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Analysis of air-broadened ozone line shapes in the 9.6-µm region

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We have been analyzing air-broadened line shapes in the in the ν_3 fundamental band of $^{16}O_3$ [1] by applying the multispectrum nonlinear least squares fitting technique [2] to a set of 31 high-resolution (0.003-0.005 cm^{-1}) infrared absorption spectra of O_3 previously recorded with the McMath-Pierce Fourier transform spectrometer at the National Solar Observatory on Kitt Peak. Room-temperature and coolable sample cells were used to obtain these spectra at temperatures between 160 and 300 K and total pressures up to 0.3 atm. Since line mixing has been experimentally investigated at higher sample pressures [3] in the ν_3 and other ozone bands, we have also examined selected transitions in our present data set for evidence of line mixing.

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Extent, quality and completness of data in HITRAN2016

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The HITRAN2016 database is scheduled to be released this year. The assembly of this edition (as is the tradition for the HITRAN database) exemplifies the efficiency and necessity of worldwide scientific collaborations. It is a titanic effort of experimentalists, theoreticians and atmospheric scientists, who measure, calculate and validate the HITRAN data.

The line-by-line lists for almost all of the 47 HITRAN molecules were updated in comparison with the previous compilation HITRAN2012 [1], that has been in use, along with some intermediate updates, since 2012. The extent of the updates ranges from updating a few lines of certain molecules to complete replacements of the lists and introduction of new isotopologues. Many new vibrational bands were added to the database, extending the spectral coverage and completeness of the datasets. For several molecules, such as water vapor, CO_2 and CH_4, the extent of the updates is so complex that separate task groups were assembled to make strategic decisions about the choices of sources for different parameters in different spectral regions. These task groups are composed of relevant HITRAN committee members and their close collaborators.

The amount of parameters has also been significantly increased, now incorporating, for instance, non-Voigt line profiles [2]; broadening by gases other than air and "self" [3]; and other phenomena.

In addition, the amount of cross-sectional sets in the database has increased dramatically and includes many recent experiments as well as adaptation of the existing databases that were not in HITRAN previously (for instance data described in the review by Hodnebrog et al [4] and the PNNL database [5]).

The HITRAN2016 edition takes full advantage of the new structure and interface available at www.hitran.org [6] and the HITRAN Application Programming Interface [7] (which are described in separate posters).

This poster will provide a summary of the updates, emphasizing details of some of the most important or drastic improvements.

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Speed-dependent broadening and line-mixing in the 118-GHz oxygen line

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The single 118-GHz, $N = 1-$ line of fine structure transitions of molecular oxygen is of great importance for remote sensing of the Earth's atmosphere. In particular, the line is widely used by airborne and satellite-based instruments for atmospheric temperature and pressure profile recovery. Accuracy and reliability of the recovered information directly depends on how accurately the diagnostic line profile is known. Such information can be obtained only from precise laboratory experiments. Here, we report on the results of laboratory investigations of the shape of the $N = 1-$ oxygen line performed over a very wide range of pressures using two principally different spectrometers having complimentary abilities. The RAD spectrometer [1] was used to record low pressures spectra, spanning the 0.7-2 Torr range, while high pressures data from 250 to 1000 Torr were recorded with a resonator spectrometer [1]. We improved considerably the sensitivity of both instruments for this study. This improvement allowed us to obtain signal to noise ratio at spectra recordings of the order of a few thousands. The spectra analysis enabled the first manifestation of the speed-dependence of the collisional broadening of the line, along with considerable refinement of other parameters of the line, including collisional broadening, line-mixing and integrated intensity.

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Transparency of the 2 µm (5000 cm^{-1}) methane window in Titan's atmosphere

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The study of Titan properties with remote sensing relies on a good knowledge of the atmosphere properties. The in-situ observations made by Huygens combined with recent advances in the definition of methane properties enable to model and interpret observations with a very good accuracy. Thanks to these progresses, we can analyze in this work the observations made at the limb of Titan in order to retrieve information on the haze properties as its vertical profiles and its spectral behaviour along the VIMS/Cassini range (from 0.88 to 5.1 µm - or 2000 to 12000 cm^{-1}). However, for applications to real atmospheres, one need to account for the widening of the spectroscopic lines (e.g., Voigt profile) and apply an empirical cut-off of the far wings. In general, this is a multiplying function of the wavenumber, $f(\nu)$, applied to the Voigt profile that allows a faster decay of the wing profile beyond a given distance from the center of the line $\nu_0 : f(\nu) = 1$ if $|\nu - \nu_0| \leq \Delta\nu$, and $f(\nu) = \exp(-\frac{|\nu-\nu_0|}{\sigma})$ if $|\nu - \nu_0| > \Delta\nu$.

Although the 2-µm window is apparently straitforward to model, it appears that the standard cut-off parameters [1] (that is $\Delta\nu \sim 26$ cm^{-1} and $\sigma \sim 120$ cm^{-1}) which is used for other windows in Titan's atmosphere is not adequat for this window. Other sets of parameter must be used to reproduce Titan spectrum at 2 µm ([2],[3],[4]). However, there is no convergence of the results between these works and a large variety of cut-off parameters are used. Alternatively, it was found that some gas absorptions (ethane and another unknown gas) leave a signature around 2-µm [5] and also affect the transparency in this window. In our study we make an exhaustive investigation on the cut-off parameters to determine which are the best couples of parameters to fit the 2-µm window. We also evaluated how gaseous absorptions can allow to reach a satisfactory agreement and, especially, if it allows to match observations with the standard cut-off. Finally, we investigate the impact of the different solutions (different cut-off, with or without supplementary absorptions) on the retrieved surface albedo.

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Theoretical Self and N_2-broadening coefficients of CH_3Br

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Self and N_2-broadening coefficients have been calculated first at 296 K in the *P*, *Q* and *R* branches of the ν_2 band of $CH_3{}^{79}Br$ and $CH_3{}^{81}Br$ near 7 mm, using a semiclassical theory. Comparisons have then been performed with the extensive set of previous measurements [1]. The intermolecular potential used, includes in addition to the overwhelming electrostatic interactions, induction and dispersion energy contributions which are significant only for low *J* transitions with *K* approaching or equal to *J*. The theoretical results are in satisfactory agreement with the experimental data and the *J* and *K* dependences are reasonably well reproduced.

Keywords: Methyl bromide; Self and N_2-broadening coefficients; Semiclassical formalism

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Room temperature line lists for CO_2 isotopologues with *ab initio* computed intensities

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We report 13 room temperature line lists for all major CO2 isotopologues, covering 0-8000 cm^-1. These line lists are a response to the need for line intensities of high, preferably sub-percent, accuracy by remote sensing experiments. Our scheme encompasses nuclear motion calculations supported by critical reliability analysis of the generated line intensities.

Rotation-vibration wavefunctions and energy levels are computed using DVR3D and a high quality semi-empirical potential energy surface (PES) [1], followed by computation of intensities using a fully *ab initio* dipole moment surface (DMS). Cross comparison of line lists calculated using pairs of high-quality PES's and DMS's is used to assess imperfections in the PES, which lead to unreliable transition intensities between levels involved in resonance interactions. Four line lists are computed for each isotopologue to quantify sensitivity to minor distortions of the PES/DMS. This provides an estimate of the contribution to the overall line intensity error introduced by the underlying PES. Reliable lines are benchmarked against recent state-of-the-art measurements [2] and HITRAN-2012 supporting the claim that the majority of line intensities for strong bands are predicted with sub-percent accuracy [3]. Accurate line positions are generated using an effective Hamiltonian [4]. We recommend use of these line lists for future remote sensing studies and inclusions in databases.

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High-resolution stimulated Raman spectroscopy and analysis of line positions and assignments for the ν_2 and ν_2 bands of $^{13}C_2H_4$

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High resolution stimulated Raman spectra of $^{13}C_2H_4$ in the regions of the ν_2 and ν_3 Raman active modes have been recorded at two temperatures (145 and 296 K) based on the quasi continuous-wave (cw) stimulated Raman spectrometer at Instituto de Estructura de la Materia (CSIC) in Madrid. A tensorial formalism adapted to X_2Y_4 planar asymmetric tops with D_{2h} symmetry has been developed in Dijon [1] and a program suite called D_{2h}TDS (now part of the XTDS/SPVIEW spectroscopic software) [2] was proposed to calculate their high-resolution spectra. The effective Hamiltonian operator, involving a polyad structure, and transition moment (dipole moment and polarizability) operators can be systematically expanded to carry out global analyses of many rovibrational bands. A total of 103 and 51 lines corresponding to ν_2 and ν_3 Raman active modes have been assigned and fitted in frequency with a global root mean square deviation of 0.54×10^{-3} cm^{-1} and 0.36×10^{-3} cm^{-1}, respectively. The figures below shows the stimulated Raman spectrum of the ν_3 and ν_2 bands of $^{13}C_2H_4$, compared to the simulation at 296 K.

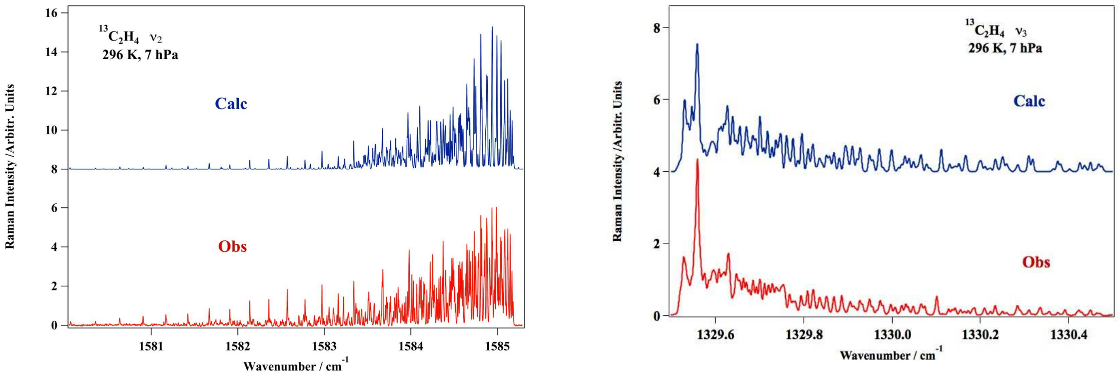

Fig. 1: The stimulated Raman spectrum of the ν_2 and ν_3 bands of $^{13}C_2H_4$ compared to the simulation at 296 K.

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Experimental and theoretical work applied to the research of Titan's and other icy moons' atmospheres and surfaces

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The outer regions of our solar system in particular, including the giant gaseous planets Jupiter and Saturn and their satellites, have recently been the target of space missions such as Cassini-Huygens and several investigations from the ground. A large quantity of observations has been acquired in the Saturnian system in particular since 2004 and the advent of the Cassini-Huygens mission. Spectro-imaging observations play a major role in this type of investigation in particular for the determination of the organic chemistry in the atmospheres and the surface properties [1,2 and references within]. To analyze and exploit these observations, planetary scientists need spectroscopic databases covering wide ranges in wavelength but also in temperature, pressure, pathlength, etc. Titan, the largest moon of Saturn, in particular, offers many similarities with our own planet, among which a dense atmosphere whose major component is dinitrogen at about 95%. Combining with methane (at a few percent) and hydrogen, gives rise to a complex organic chemistry with hydrocarbons and nitriles. Oxygen compounds also exist in Titan's atmosphere. Investigations of Enceladus have also shown the presence of organics in its plumes, along with the water vapour. By studying Titan, we learn about our own planet and our Solar system Solar as a whole. The tenuous atmospheres of Europa and of other icy moons are also of interest to exobiological studies. To properly interpret the Cassini-Huygens data and in anticipation of future missions like ESA's JUICE or other Europa missions to the jovian moons, spectroscopic data are crucially needed. I will discuss recent results on the chemical composition of Titan and other icy moons and the application of theoretical and experimental data on the investigation of these satellites' atmospheres and surface, with emphasis on methane [3,4,5,6].

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Creation of a line list of HDO transitions broadened by CO_2 in the 1100-4100 cm^{-1} range

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Precise data including line shape parameters and their temperature dependences will be needed to reduce the remote sensing measurements to be made by the ExoMars Trace Gas Orbiter. For that, high-resolution laboratory absorption spectra of HDO in mixture with CO_2 were recorded in the ν_1, ν_2, and ν_3 fundamental bands in the 1100-4100 cm^{-1} region. The spectra were obtained with the Bruker IFS-125HR Fourier transform spectrometer at the Jet Propulsion Laboratory along with two specially built coolable absorption cells with path lengths of 0.2038 m and 20.941 m at various sample gas temperatures (230 - 296 K), pressures and volume mixing ratios. To aid in the analysis of these spectra and to provide line shape data for transitions in the region, modified complex Robert-Bonamy (MCRB) calculations were made. The calculations are compared with the measured line shape parameters determined by a multispectrum nonlinear least squares technique[a]. The line list began with the 6166 HDO transitions form the HITRAN2012 database[b]. The measured positions, intensities, and CO_2-broadened line shape information was added to these transition followed by the MCRB line shape information. Self-broadening of HDO is also included in the line list. The line list was augmented with H_2O and D_2O CO_2-broadened transitions from the line list of Gamache *et al*.[c]

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First pressure shift measurement of ozone molecular lines at 9.54 µm using a tunable quantum cascade laser : implications for the air-shift in the ozone ν_3 band

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Quantum cascade lasers (QCL) represent unique and versatile tools for the study of molecules in the mid-infrared region due to their coverage of the molecular fingerprint spectral region, their large spectral tuning range and their high output power. Using frequency modulated spectroscopy with a free-running distributed-feedback QCL emitting at 9.54 µm, we have measured the pressure shifts of ozone molecular lines. From these shifts we obtain the room temperature pressure shift parameter δ of four intense ro-vibrational transitions in the ν_3 fundamental band of ozone induced by oxygen (O_2), air and the noble gases helium (He), argon (Ar), and xenon (Xe). The high density of transitions in the ν_3 spectral region of ozone makes this region particularly difficult to study with more commonly used techniques such as Fourier transform spectroscopy. The comparatively high spectral resolution of the QCL in the MHz range, on the contrary, allows to measure molecular shifts at relatively low pressures (from 2 to 80 hPa), thus reducing the impact of spectral congestion due to pressure broadening of molecular lines. Except for He, semi-classical calculations using the Robert-Bonamy (CRB) formalism show good agreement with our results.

The comparison of our measurements with published data in the same [1-3], other fundamental [2-4],combination [5, 6] and hot [6] bands shows that presently recommended values [7] for the air-shift are likely too low and should be multiplied by a factor of about 3. A systematic use of our technique covering a larger spectral range could be very useful to investigate the rotational state dependence and to make up for the lack of shift parameters of ozone ν_3 transitions in molecular spectral databases [7-9]. A subsequent stabilization of the QCL onto an optical frequency comb will open up possibilities to perform metrological measurements of Doppler-free molecular lines.

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Circular interferometer for accurate and contact-free measurements of absorption paths

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Accurate path length measurements in absorption cells are recurrent requirements in quantitative molecular absorption spectroscopy [1]. A new twin path laser interferometer for length measurements in a simple direct path absorption geometry is presented, along with a full uncertainty budget. The path in an absorption cell is determined by measuring the optical path length change due to the diminution of the refractive index when the cell originally filled with nitrogen gas is evacuated.

The performance of the instrument based on a stabilized HeNe laser is verified by comparison with the results of direct mechanical length measurements of a roughly 45 mm long, specially designed absorption cell. Due to a resolution of about 1/300 of a HeNe fringe, an expanded (coverage factor $k = 2$) uncertainty of 16 µm in the length measurement is reached, providing a relative uncertainty of 3.6 10^{-4} for the length of our test absorption cell [2]. This value is about eight times lower than what has been reported previously [3].

The instrument will be useful for precision measurements of absorption cross sections of strong absorbers which require short light paths, such as ozone, halogen oxides, sulfur dioxide and volatile organic compounds in the UV [1].

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Line parameter study of ozone at 5 and 10 µm using atmospheric FTIR spectra from the ground: A consistency test of ozone spectral data

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Atmospheric ozone concentration measurements mostly depend on spectroscopic methods that cover different spectral regions. Despite long years of measurement efforts, the uncertainty goal of 1% [1] in absolute line intensities has not yet been reached. Multispectral inter-comparisons using both laboratory and atmospheric studies reveal that important discrepancies exist when ozone columns are retrieved from different spectral regions.

Here, we use ground based FTIR to study the sensitivity of ozone columns on different spectroscopic parameters as a function of individual bands for identifying necessary improvements of the spectroscopic databases. In particular, we examine the degree of consistency that can be reached in ozone retrievals using spectral windows in the 5 and 10 µm bands of ozone. Based on the atmospheric spectra, a detailed database inter-comparison between HITRAN (version 2012) [2], GEISA (version 2011) [3] and S&MPO (as retrieved from the website at the end of 2015) [4] is made.

Data from the 10 µm window are consistent to better than 1%, but there are larger differences when the windows at 5 µm are included [5]. The 5 µm results agree with the results from 10 µm within ±2% for all databases. Recent S&MPO data are even more consistent with the desired level of 1%, but spectroscopic data from HITRAN give about 4% higher ozone columns than those from GEISA. If four sub-windows in the 5 µm band are checked for consistency, retrievals using GEISA or S&MPO parameters show less dispersion than those using HITRAN, where one window in the *P*-branch of the $\nu_1 + \nu_3$ band gives about 2% lower results than the other three. The atmospheric observations are corroborated by a direct comparison of the spectroscopic databases, using a simple statistical analysis based on intensity weighted spectroscopic parameters. The bias introduced by the weighted average approach is investigated and it is negligible if relative differences between databases do not correlate with line intensities. This is the case for the comparison of HITRAN with GEISA in the 10 µm region and the agreement between the simple analysis and the full retrieval is better than 0.1%. At 5 µm biases might be as high as 1.4%, and the proposed method is thus limited to the same level of accuracy. Implications of the new data for database improvements and further studies, in particular in the 5 µm region, are discussed.

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Site-dependent study (Paris, Jungfraujoch and Wollongong) of the seasonal variability of surface and column carbon monoxide between 2009 and 2013: identification of a 2-month time-lag

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Atmospheric carbon monoxide (CO) is a key species due to its toxicity and its impact on the atmospheric oxidizing capacity, both factors affecting air quality. While CO is predominantly lost through reaction with the hydroxyl radical (OH), the major sources of CO are diverse: fuel and energy related industries, heating, motor vehicle transport, biomass burning, and the secondary oxidation of methane and of volatile organic compounds such as isoprene and terpene, which are emitted by plants.

Ground-based high-resolution FTIR remote sensing can be used to validate satellite and atmospheric modeling data, but also to study the seasonal variability of atmospheric trace gases. Here, the seasonality of CO is obtained from total and partial columns, at three different sites: Paris megacity and high mountain Jungfraujoch in the Northern Hemisphere and urban Wollongong in the Southern Hemisphere [1]. The CO total columns show a maximum around March-April and a minimum around September-October in the Northern Hemisphere. In the Southern Hemisphere, the seasonal pattern is shifted by about 6 months. The ground-based FTIR data are compared to satellite data from IASI-MetOp and MOPITT instruments as well as to chemical transport model calculations using GEOS-Chem. Satellite data is consistent with ground-based observations and model results reproduce the observed total CO seasonal variability. Additional in situ surface measurements of CO volume mixing ratios are used to observe the CO surface seasonality of each site. Depending on the magnitude of local emissions, our study shows a significant time shift between surface and total column seasonal variabilities.

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Ozone Bond resonant states near the dissociation threshold

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The new potential energy surface of ozone recently developed[1,2] is used to determine energies of vibrational bound states and predissociation resonances of O_3. For the vibrational state calculations, the hyperspherical coordinates and the methods of slow-variable discretization with a complex absorbing potential are used[3]. Results obtained in this study perfectly agree with previous calculations and reproduce the experimental energies up to the 8000 cm^{-1} region. Coupling between the three potential wells of the ozone molecule is taken into account, which is important for the correct description of excited vibrational levels and resonances. Symmetric and asymmetric isotopologues can be treated. For symmetric isotopologues, levels of all possible irreducible representations have been calculated and widths of the resonances in the region 0-1500 cm^{-1} above dissociation have been determined.

The widths are mostly between 0.1 cm^{-1} and 10 cm^{-1}, depending on the nature of the short-range part of the resonance wave functions : Resonances may differ by the degree of vibrational excitation and also by the relative angular momentum of the dissociating O-O_2 system, which can also be viewed as motion between the three potential wells. Wave functions of the predissociation resonances obtained for asymmetric molecules provide information about the exchange reaction $^{x}O + {}^{y}O^{y}O \rightarrow {}^{y}O + {}^{x}O^{y}O$.

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Absorption cross-sections of CH_3D in the infrared for low-T atmospheric and planetary applications: *ab initio* predictions and experimental validations

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Global calculations of rovibrational spectra and dipole transition intensities of CH_3D using our recent *ab initio* dipole moment and potential surfaces [1-2] are reported. For a full account of symmetry properties, a variational normal-mode tensor formalism is applied, the convergence of high-J calculations being improved using vibrational eigenfunctions with a compressed basis set for solving the rovibrational problem. We report detailed comparisons between the global predictions and our recent high-resolution Fourier Transform room-temperature spectra recorded up to 9000 cm^{-1}. The agreement is good over the whole spectral range.

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First principles calculation of energy levels and rovibrational spectra for CF_4 and SiH_4 molecules

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New potential energy surfaces (PES) and dipole moment surfaces (DMS) of molecules CF_4, SiH_4 were constructed using extended *ab initio* CCSD(T) calculations. The empirical PES [1] correction was applied SiH_4 for to improve the precision of spectra calculation. The dipole moment surfaces (DMS) of molecules SiH_4 and CF_4 were constructed. The PES[1] and DMS[2] analytical representation are determined through an expansion in symmetry adapted products of internal nonlinear coordinates involving parameters up to the 8th order and 6th order. Lower rovibrational levels were calculated and compared with observed values. The calculated spectra of SiH4 were compared with PNNL[4] database and calculated spectra of ref [5].

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Ab initio calculation of ro-vibrational spectra for five isotopologues of GeH_4 molecule

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Improved potential energy surface (PES) of molecule GeH_4 was constructed using extended *ab initio* CCSD(T) calculations. The empirical PES [1] correction was applied to improve the precision of spectra calculation. Calculated energy levels were compared with observed values for five most abundant isotopologues. New dipole moment surface [2] of GeH_4 was calculated up to the 6th order. The spectra calculated for natural abundance of five GeH_4 isotopologues: ^{70}Ge (20.84 %), ^{72}Ge (27.54 %), ^{73}Ge (7.73 %), ^{74}Ge (36.28 %), ^{76}Ge (7.61%) were compared with PNNL [3] database. The work is partly supported by French-Russian LIA SAMIA and Tomsk State University Mendeleev program.

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Isotopic and symmetry breaking effects in phosphine spectra from *ab initio* variational calculations under H → D substitutions

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Isotopic effects in phosphine IR spectra under $H \to D$ substitutions are considered for the sequence of isotopic species PH_3, PH_2D, PHD_2, and PD_3. Particular focus is on the state/polyad and band correspondence for symmetry breaking ($C_{3v} \to C_s$) substitutions. All calculations are based on our *ab initio* potential and dipole moment surfaces [1, 2] using variational normal mode calculations. The effects of this substitution were studied from theoretical considerations throught nonlinear normal mode coordinate transformations and symmetry considerations. Calculated rovibrational line intensities surfaces agree quite well with those available in the literature [3-6]. This work provides the first theoretical predictions of phosphine isotopologue spectra using the variational approach.

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Recent updates in the TheoReTS database

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Knowledge of intensities of rovibrational transitions of various molecules and theirs isotopic species in wide spectral and temperature ranges is essential for the modeling of optical properties of planetary atmospheres, brown dwarfs and for other astrophysical applications. This demonstrates the necessity of having adequate and reliable molecular line lists. The TheoReTS (Theoretical Reims Tomsk Spectra) project [1] aims at providing complete and comprehensive lists of transitions based on accurate *ab initio* and variational calculations for a large variety of highly symmetric molecular species as CH_4, PH_3, C_2H_4, SiH_4, CH_3F including all isotopologues. Predicted hot methane and ethylene line lists are also included. In case of very large high-temperature line lists, a data compression is implemented for fast interactive spectra simulations of a quasi-continual absorption due to big line density. Calculations on new molecular systems are currently in progress (CH_3Cl, CH_3I, GeH_4, CF_4, H_2CO, SO_2F_2, *etc*.).

The information system provides the associated software for spectra simulation including absorption coefficient, absorption and emission cross-sections, transmittance and radiance. The simulations allow Lorentz, Gauss and Voigt line shapes. Rectangular, triangular, Lorentzian, Gaussian, sinc and sinc squared apparatus function can be used with user-defined specifications for broadening parameters and spectral resolution.

The system is freely accessible *via* internet on the two mirror sites: in Reims, France (http://theorets.univ-reims.fr) and in Tomsk, Russia (http://theorets.tsu.ru).

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Closure study between 183.31 GHz passive microwave and in-situ radiosonde measurements of water vapor in the atmosphere

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Water vapor has dense absorption spectrum therefore, it is an important greenhouse gas and has a strong effect on the Earth's Energy balance. There are two principal sources of WV measurements: in-situ radiosonde and remote sensing measurement with radiometers that utilize water vapor absorption line, for example the one at 183.31 GHz. Satellite and radiosonde measurements can not be compared directly because of their different nature. We can use the profiles measured by the radiosondes as an input data for a radiative transfer model and then compare the output of the model with the satellite data [1]. Recently bias at measurements of WV by weather prediction model and radiosondes versus satellite measurements was found [2]. To achieve clearer description of the characteristics of the bias and identify known biases and thus possible sources of uncertainties "Joint workshop on uncertainties at 183 GHz (June 2015, Paris, France) was held. Aftermath paper was published where the summary and recommendations were formulated [3].

Objective of this study is to make a closure study of 183.31 GHz satellite and radiosonde measurements to check the agreement between them. To accomplish this we utilized the Global Climate Observing System (GCOS) Reference Upper-Air Network (GRUAN) processed radiosonde data for 5 stations around the globe. We used data for three microwave sensors the Microwave Humidity Sounder (MHS), Advanced Technology Microwave Sounder (ATMS) and the Sondeur Atmosphérique du Profil d'Humidité Intertropicale par Radiométrie (SAPHIR). We examined data from 2009 to 2015. We used the Atmospheric Radiative Transfer Simulator (ARTS) to simulate radiosonde profiles.

The results indicate that bias found in [2], is present. The magnitude of the bias is smaller than was previously reported. We have used 3 microwave sensors, which have channels on the different distance from the center of the absorption line. With special care we have investigated the effects of known uncertainties in absorption line parameters on the bias – line intensity, self- and air-broadened width of the line as well as uncertainties in water vapor continua. Changing these parameters have significant impact on the bias magnitude.

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Progress towards new “spectroscopic” PES and *ab initio* DMS for $^{14}NH_3$, and measurement of NH_3 around 7180 cm^{-1}

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We present a new “spectroscopic” potential energy surface (PES) and *ab initio* dipole moment surface (DMS) for $^{14}NH_3$, to be used in production of a new high-accuracy linelist. Line intensities calculated using our DMS display significantly less scatter than those of BYTe in the 4700-5000 cm^{-1} and 6300-7000 cm^{-1} regions, when compared to HITRAN. This results in, on average, a 20% improvement on medium lines in the 4700-5000 cm^{-1} region, and a 10% improvement on strong lines in the 6300-7000 cm^{-1} region. We also report a 10% improvement on strong lines in the 7400-8000 cm^{-1} region when compared to the newly assigned Kitt Peak spectra [4]. Further high-accuracy experiment is in progress to provide comparison at 6000 cm^{-1}. Spectral measurements around 7180 cm^{-1} using second-harmonic wavelength modulation spectroscopy are also being recorded, with a view to using the subsequent assignments to further improve our spectroscopic PES. This has been obtained by using the program TROVE [1] to refine the parameters of the recent high-accuracy *ab initio* PES [2] via a least-squares fitting to experimental data [3,4].

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A variationally computed T = 300 K Raman and electric quadrupole line lists for NH_3

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We present the first ever variationally computed non-resonant Raman and electric quadrupole transition line lists for NH_3 in gas-phase. The line lists were generated using the program suite TROVE [1,2], where we have implemented the new module for computing the rovibrational matrix elements and transition moments of electric polarizability and quadrupole moment tensors [3]. We employed the accurate 'spectroscopic' PES of [4], and the newly computed high-level *ab initio* electric quadrupole moment and electric dipole-polarizability surfaces. Our quadrupole transition line list comprises of 84460231 transitions, and our Raman line list comprises of 85794915 scattering probabilities evaluated at 0^o and 90^o to the incident wavevector. These are constructed from 299324 rovibratioal energy levels below 14000 cm^{-1} having J values <=20, and are therefore applicable for use at temperatures up to 300 K.

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Non-adiabatic effects on the high-resolution spectroscopic properties of LiH

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Non-adiabatic vibrational calculations performed with the accuracy of 0.2 cm^{-1} spanning the whole energy spectrum up to the dissociation limit for ^{7}LiH are reported. A so far un- known v = 23 energy level is predicted. A key feature of the approach used in the calculations is a valence-bond (VB) based procedure for determining the effective masses of the two vibrating atoms, which depend on the internuclear distance, R. It is found that all LiH electrons participate in the vibrational motion. The R-dependent masses are obtained from the analysis of the simple VB two-configuration ionic-covalent representation of the electronic wave function. These findings are consistent with an interpretation of the chemical bond in LiH as a quantum mechanical superposition of one-electron ionic and covalent states [1].

Following on from this, we have computed a new dipole moment curve [2] using all-particle explicitly correlated Gaussian functions with shifted centres. The exceptional accuracy of this dipole moment curve as well as of the potential energy curve obtained with the same method, when coupled with the effective vibrational reduced mass approach to handle non-adiabatic effects, permits computation of very accurate Einstein coefficients[2]. Examples are presented at the conference.

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Frequency analysis of the (ν_3,ν_7,ν_9) bending triad of SO_2F_2 using the C_{2v} Top Data System

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A new high-resolution infrared spectrum of the (ν_3, ν_7, ν_9) bending triad of SO_2F_2 in the 550 cm^{-1} region has been recorded at 165 K using a multi-pass cell [1] coupled to a high-resolution Bruker IFS 125 interferometer with a spectral resolution of 0.00102 cm^{-1} located at the AILES beamline of the SOLEIL Synchrotron.

The analysis of the triad has been performed thanks to the $C_{2v}TDS$ program suite based on the tensorial formalism adapted to the case of XY_2Z_2asymmetric-top molecules with C_{2v} symmetry developed by Rotger *et al.* in the $O_3 \supset T_d \supset C_{2v}$ group chain [2]. This approach allows a systematic expansion of the Hamiltonian and dipole moment operators, including all possible interactions for a given rovibrational polyad system.

In this work, we present the first results of our analysis for the (ν_3, ν_7, ν_9) triad. At present a total of 2634 lines have been assigned and fitted in frequency with a global root mean square deviation (RMS) of 0.371×10^{-3} cm^{-1}. This result improves the previous analysis [3].

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Analysis of the ν_2 band of the Quasi-Spherical Top Molecule SO_2F_2

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Sulfuryl fluoride (SO_2F_2) appeared recently as an important atmospheric pollutant [1]. It also presents a fundamental interest due to its nearly tetrahedral symmetry, making it an intermediate case between spherical and asymmetric-top molecules. That is why, modeling the absorption spectrum of SO_2F_2 is essential both for atmospheric concentration measurements and theoretical aspects of spectroscopy.

The infrared spectrum of the ν_2 fundamental band of SO_2F_2 has been recorded with a resolution of 0.00102 cm^{-1} using the FTIR Bruker HR125 at the AILES beamline of the SOLEIL Synchrotron facility. A cryogenic multi-pass cell equipped with diamond windows [2] has been connected to the interferometer. The pressure in the cell was maintained at 1.99×10^{-2} mbar at T = 165 K.

The analysis of the symmetric SF_2 stretching vibration has been performed used a specific model and programs based on tensorial formalism, group theory and vibrational extrapolation method adapted to the case of this molecule [3].

More than 1600 transitions have been assigned and fitted with a standard deviation of about 0.199×10^{-3} cm^{-1}. A set of 7 effective parameters was determined. These results are compared to those obtained with the classical approach [4].

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Fourier transform spectrum of water vapor around 1.07 µm atmospheric transparency window

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About 1000 weak absorption lines of water vapor are recorded at a room temperature between 9100 and 9800 cm^{-1} using Fourier transform spectrometer connected with 30-meter gas cell. The line centers and intensities are retrieved from a line shape fitting assuming a Voigt profile. The uncertainty of the line positions of the isolated lines is estimated to be of 0.001 cm^{-1} and better. The accuracy of measured intensities varies from 3% for isolated lines of medium intensity to 15-20% in case of weaker lines. A sensitivity provided by the experimental set up allows recording the absorption lines as weak as 3-5x10^{-28} cm/molecule.

Detailed comparison of the new recordings with all relevant experimental data, collected and verified in [1], as well as with recent variational calculations is presented. About 160 absorption lines of water vapor were observed for the first time. Forty transitions involving new upper energy levels and mostly belonging to the highly excited $6\nu_2$ band were identified based on the accurate variational calculations. The substantial disagreements between the presently recorded and previously known water vapor line positions and intensities are discussed. As a whole, the new experimental information obtained in this study will help to clarify a weak absorption caused by water vapor in the 9100-9800 cm^{-1} atmospheric transparency window important for a number of applications, e.g. retrieval of the continuum absorption.

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Analysis of line parameters of the H_2O molecule in spectral region 6700 and 7650 cm^{-1}

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We present the measurements of line parameters for rotation-vibration transitions of water vapor in the wave number range of 6700–7650 cm^{-1} using a Bruker IFS 125 HR Fourier transform spectrometer [1]. Room temperature spectra of water vapor have been measured with high signal to noise ratio in a wide range of pressure of hydrogen , helium and argon with spectral resolution of 0.01 cm^{-1}. The signal-to-noise ratio was typically several thousands for the strongest transition. The spectra of each H_2O line have been adjusted using a multi-spectrum fitting procedure with speed-depended line-shape model. The intensities and broadening parameters (self- and foreign- gas broadening and pressure-shift coefficients) for H_2O spectral lines of 5 vibrational bands $2\nu_2+\nu_3$, $2\nu_1$, $\nu_1+2\nu_2$, $2\nu_3$, $\nu_1+\nu_3$ are measured. The data obtained is compared to experimental and theoretical literature ones.

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Precise line-shape investigation of the oxygen B-band transitions

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We present precise line-shape measurements of self-broadened transitions of the oxygen B band near wavelength 689 nm. Data were acquired using the optical frequency comb-assisted Pound-Drever-Hall-locked frequency-stabilized cavity ring-down spectrometer (OFC-assisted PDH-locked FS-CRDS) [1-3]. This technique enables to achieve high spectral resolution (well below 1 MHz) and high signal-to-noise ratio spectra (above 10000:1) of relatively weak B-band transitions. The data analysis was performed with several line-shape models. The multispectrum fitting technique was used to minimize correlation between line-shape parameters. We investigated the limitations of the commonly used Voigt profile and discussed the influence of the spectral line-shape model used in data analysis on determined line-shape parameters. Our results show that for the signal-to-noise ratio of our laboratory data the Voigt profile is insufficient to properly describe measured spectra. The use of the Voigt profile leads to even several percent systematic errors of line-shape parameters. We show that in the line-shape analysis the line narrowing described by velocity-changing collisions or/and the speed dependence of collisional broadening needs to be taken into account. We present the consistent line-shape parameters dataset obtained from the speed-dependent Voigt profile fits [4]. We report line positions with accuracy reaching 150 kHz as well as intensities and the collisional broadening and shifting coefficients with subpercent uncertainties [4]. We compare our results to data available in the literature including HITRAN database.

We also determined absolute frequency of the P7 P7 oxygen B-band transition in reference to the strontium optical atomic clock. The use of ^{88}Sr clock working on $^1S_0 - {}^3P_0$ transition as an optical frequency reference enabled us to avoid systematic errors present in previous measurements [5,6]. The link between the CRDS spectrometer and the clock was made with the OFC. During the line-shape measurements frequency of each point of the spectrum was referenced to the frequency of the clock transition. All necessary equipment used the same 10 MHz reference signal from the hydrogen maser [7] transferred by 330 km fibre link [6,8]. Data analysis showed about one order of magnitude reduction of the line position uncertainty compared to our previous results. This is a proof-of-principle experiment that demonstrates application of the optical atomic clock in the molecular spectroscopy.

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Dispersion and relativistic deformation of the spectral line-shape models

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Modern spectrometers are capable of providing spectra with the ultra-high signal-to-noise-ratio exceeding 10^5. Such precise spectroscopic data require proper analysis in terms of the line-shape models which should be supplemented by neglected so far very subtle physical effects. Here we present the dispersion and relativistic corrections to the line shapes on an example of simple Gaussian and Voigt profiles.

We consider the dispersion corrections including the frequency dependence of the Doppler shifting caused by dispersion [1,2] as well as by light frequency variation over the whole spectral line shape [2]. These effects can have non-negligible influence on the spectral line shape and can affect it even at the level of 10^{-5} [2]. The dispersion correction may influence the determination of the line position at the level of kHz.

Moreover, we developed the relativistic formula describing the Voigt profile in the case of spontaneous emission [3]. We verified that our formula has a proper behavior in two asymptotic cases: the classical Voigt profile and the relativistic Gaussian profile [4]. We presented an alternative expression, which simplify numerical evaluation for the most physically meaningful weak-relativistic regime. We estimated that at room temperature the relativistic correction can be at the level of 10^{-6}.

The presented results are important for the Doppler-width thermometry [1] and precise molecular spectroscopy for fundamental studies [5].

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Implementation of the exact-trajectory model in semi-classical calculations of line-shape parameters for XY_4-A_2 systems: Symbolic computation and source code generation

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Recently, semi-classical calculations of collisional parameters for infrared absorption lines of methane perturbed by the key atmospheric molecules N_2, O_2 and H_2 [1,2] were performed using symbolic computation procedures and object-oriented source-code generation techniques. The theory is consistent with the so-called tetrahedral formalism relevant to high resolution spectral analyses [3]. This approach takes also advantage of the analytical resonance-function expressions resulting from the use of parabolic classical trajectories for the relative molecular motion. Large amounts of transitions, arising from the complex internal dynamics of CH_4, could be handled. These amounts increase rapidly as the wavenumber ranges under consideration become high.

During the last years, the more advanced exact-trajectory model [4] based on the exact solutions of the classical equations of motion in the field of an isotropic potential and requiring in consequence numerical integrations, has proved its efficiency for various molecular systems of atmospheric interest, including absorbing molecules derived from methane: CH_3Cl [5], CH_3D [6], etc. In this context, it appears crucial to implement exact classical trajectories in the semi-classical calculations of methane line-shape parameters required for numerous applications in planetology and astrophysics.

In the present work we outline the general scheme of the computation process which keeps the advantages of the symbolic computation facilities and of the source-code generation techniques and introduces, simultaneously, some specific procedures for the numerical integration with exact trajectories. The connection with necessary input data (methane effective Hamiltonian models, corresponding eigenfunctions and eigenvalues, …) is also described.

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The GEISA-2015 spectroscopic database: context and new release

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A precise knowledge of spectroscopic data appear to be at the root of the investigation of climate change providing an improved understanding of the different phenomena driving the atmospheric system. The already important role of molecular spectroscopy in atmospheric research has entered a new promising perspectives phase for remote sensing applications (meteorology, climatology, chemistry) with the advent of highly sophisticated and resolved instrumentations like AIRS (2002), IASI (2006, 2012 and 2017), TANSO-FTS(2009) and CrIs (2011). In this context, the ARA/ABC(t) group at LMD[1] develops and maintains since 1974, the GEISA database (Gestion et Etude des Informations Spectroscopiques Atmosphériques: Management and Study of Atmospheric Spectroscopic Information[2]. GEISA has been at the heart of state-of-the-art developments in spectroscopy and radiative transfer modelling to meet the needs of the international space agencies, by collecting, archiving and distributing all the necessary inputs for atmospheric radiative transfer models.

The 2015 release of GEISA (J. Mol. Spectr., 2016), which updates the last edition of 2011[2] and celebrates the 40th anniversary[3] of the database, will be presented. Significant updates and additions have been implemented in the three independent sub-databases of GEISA-2015:

- The "line parameters database" contains 52 molecular species (113 isotopologues) and transitions in the spectral range from 10^{-6} to 35,877.031 cm^{-1}, representing 5,059,777 entries, against 3,794,297 in GEISA-2011. Among the previously existing molecules, 20 molecular species have been updated. A new molecule (SO_3) has been added. HDO, isotopologue of H_2O, is now identified as an independent molecular species. Six new isotopologues have been added.

-.The "cross section sub-database" has been enriched by the addition of 43 new molecular species in its infrared part, 4 molecules (ethane, propane, acetone, acetonitrile) are also updated; they represent 3% of the update. A new section is added, in the near-infrared spectral region, involving 7 molecular species: CH_3CN, CH_3I, CH_3O_2, H_2CO, HO_2, HONO, NH_3.

-.The "microphysical and optical properties of atmospheric aerosols sub-database" has been updated for the first time since 2003. It contains more than 40 species originating from NCAR and 20 from the ARIA archive of Oxford University.

As for the previous versions, this new release of GEISA and associated management software facilities are implemented and freely accessible on the AERIS/ESPRI atmospheric chemistry data center website[4]. It is used on-line by more than 300 laboratories working in various domains like atmospheric physics, planetology, astronomy, astrophysics.

GEISA line parameter database is the reference for current or planned TIR SWIR space missions and it is associated with the work in progress in the CNES-MENINGE scientific group for the future of the IASI instruments (IASI-NG).

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Line lists with Duo, a general multi-state program for solving the nuclear motion Schrödinger equation for diatomic molecules

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Although solution of the diatomic nuclear motion problem for a single, uncoupled potential energy curve is standard [1], there appears to be no general rovibronic program available for diatomics characterized by complex interactions between electronic states. We have therefore developed a new computational tool, Duo [2], to fill this gap. Duo is a flexible, user-friendly program capable of solving the Schrödinger equation for the nuclear motion of a general diatomic molecule with an arbitrary number and type of coupling between electronic states. The program allows one to build diatomic 'projects' from a set of pre-defined objects such as potential energy and dipole moment functions, spin-orbit, electronic angular momentum, spin-rotational, Λ-doubling terms etc. From these objects Duo computes energy levels, line positions and line intensities. Duo can refine potential energy and coupling curves to best reproduce reference data such as experimental energy levels or line positions. Duo is currently being used as a diatomic computational tool as part of the ExoMol project [3]. ExoMol aims to produce a comprehensive database of high-temperature line lists for molecules, which may be present in the atmospheres of exoplanets, planetary disks, brown dwarfs and cool stars. Examples include line lists for AlO [4], ScH [5], CaO [6], VO [7], PO, PS, NO, NS, PS and C_2.

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Infrared spectra of the C_s ozone isotopic species $^{16}O^{16}O^{18}O$ in the FTS 1000-5800 cm^{-1} range: Comparison between predictions and observations of band centers and rotational constants

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The high resolution (0.003 cm^{-1}) spectra of ^{18}O enriched isotopic species of ozone have been recorded in the 1000-5800 cm^{-1} domain with the GSMA homemade spectrometer described in [1, 2]. In order to discriminate between the different ^{18}O enriched sample of ozone, several spectra with various mixtures of ^{18}O -^{16} O have been used, as explained in [3, 4]. Analyses were performed using effective Hamiltonians described in [2], and the G.I.P code [5]. A total of 13609 lines have been observed and assigned, corresponding to 27 bands: 17 dark states have in addition been included in these analyses. The comparisons of Hamiltonian parameters (band centers and rotational constants) between the present results of our analyses and their variational predictions [6], are very satisfactorily. The derived parameters (Hamiltonian and transition moments) permitted constructing a full line list of 64500 transitions in the considered spectral range. We also present one particular analysis (Hamiltonian parameters, transition moment, statistics of the fits and comparison between observed and calculated spectrum). The support from Mendeleev funding program of TSU is acknowledged.

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Infrared spectra of the $^{16}O^{16}O^{17}O$ and the $^{16}O^{17}O^{16}O$ ozone isotopic species in the 10 microns spectral range.

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Despite a relatively weak abundance in atmospheric spectra: respectively 0.074 % and 0.037 % for $^{16}O^{16}O^{17}O$ and $^{16}O^{17}O^{16}O$, many lines of the ν_3 band are clearly visible in atmospheric spectra [1]. Very recently, diode laser spectra [2] showed good agreement between 13 lines for $^{16}O^{16}O^{17}O$, but differences on the order of a few 10^{-3} cm^{-1} for 15 transitions of $^{16}O^{17}O^{16}O$, with respect to HITRAN database [3], based on works of references [4, 5].
New spectra have been recorded with the GSMA spectrometer [6], using ozone generated from ^{17}O 70.2 % enriched oxygen atoms.
564 transitions, with J up to 51 and $K_a = 13$ have been fitted, using well known procedure [7], leading to an *rms* of 0.58×10^{-3} cm^{-1}.
The Hamiltonian parameters allow to perform a new line-list, in good agreement with the observations of [2].
We present the experimental conditions, the tables of parameters and some examples of agreements between observed and synthetic spectra.

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Ozone absorption cross-section measurements in the UV-Hartley band

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Ozone is an important minor constituent of the Earth's atmosphere. It plays a significant role in atmospheric radiative transfer and tropospheric chemistry as it is the third largest contributor to greenhouse radiative forcing after CO_2 and CH_4. So, long-term measurements of tropospheric ozone have been performed globally for more than 30 years with UV photometers (ground based instruments as Dobson and/or Brewer and balloons).

In the UV-Visible range, 240–790 nm region, the O_3 absorption cross-sections can be separated into four systems: the Hartley band, the Huggins bands, the Chappuis band, and the Wulf bands.
For all these bands there exists a large number of laboratory measurements using different spectrometers and experimental conditions. Many measurements have been published in the past 20 years (see IGACO website [1] and [2]) and recently, studies have been performed by Viallon et al. [3] and Serdyuchenko et al. [4-5].

As the ozone laboratory data available today do not fill all the requirements of the last ACSO report 2015 [6], this committee recommends continuing the different efforts in measuring Ozone Absorption cross-sections in different laboratories.

For the first time, we have used the DESIRS Beamline of the French SOLEIL synchrotron to record the absorption cross-sections of ozone in the 200-300 nm range.
The results will be presented and comparisons with previous measurements will be discussed.

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Carbon monoxide: subwavenumber accuracy for energy levels and sub percentage accuracy for intensities from *ab initio* theory and experiment

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The *ab initio* calculation of transition intensities and of vibrational and rovibrational levels of CO are presented. These calculations extend up to 30000 cm^{-1} and v=16 for vibrations and 40 000 cm^{-1} and J=116 for rotational levels. Unprecedented accuracy for energy levels is achieved – better than 0.1 cm^{-1}. The *ab initio* accuracy for intensities for bands up to 0-6 at the percent and subpercent level is also achieved.

We used all electron MRCI calculations with the highest available basis set in the MOLPRO package. The aug-cc-pCV6Z results are extrapolated to the complete basis set limit (CBS). First and second order relativistic corrections and adiabatic corrections are also included. The accuracy of the pure rotational energy levels within the first 16 vibrational states is three orders of magnitude better than the best published results.

For calculating intensities we used all electron MRCI calculations with different size extensivity corrections and with the biggest available basis set. These results are significantly better than the previous ab initio calculations, for example for 0-6 band, we provide the sub percentage accuracy using purely ab initio calculations of the dipole moment curve. Comparison with the experimental intensities [1,2] will be presented. New experimental measurements of intensities are made for first three bands 0-1, 0-2, 0-3 of CO. The details of experiment will be presented and their comparison with new ab initio calculations will be given.

The *ab initio* model for CO was used to assist the construction of a high accuracy model for CO_2 intensities [3].

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Global ab initio potential energy surface for the isomerising HCN-HNC system.

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A new global purely *ab initio* potential energy surface for the HCN-HNC isomerising [1] system is presented. We show that this PES is a significant improvement on the previous *ab initio* global PES [2] as well as the global potential fitted to the observed energy levels [3].

This surface was built from 1856 points calculated using MOLPRO with aug-cc-pCV6Z basis set at the all electrons MRCI level of theory. These points were fitted to 272 parameters of analytical form of PES the same as used in [2]. The *ab initio* points were reproduced by this surface with an accuracy of 2.58 cm^{-1}.

The vibrational energy levels were calculated using the DVR3D program suite. At first, a purely BO PES was used for the comparison with experimental energy levels. For HNC vibrational band origins we obtain an order of magnitude improvement comparison with available experimental data, 19 levels were calculated with an accuracy 3.43 cm^{-1} for the energies up to 7200 cm^{-1}. In HCN we obtained 2.25 cm^{-1} accuracy for the energies up to 15000 cm^{-1} (50 levels). When we used BODC and relativistic correction of [1] this standard deviation reduced to 1.6 cm^{-1}.

The comparison with the previous global PES of HCN/HNC [2,3] shows an improvement of one or two orders of magnitude with *ab initio* results [2] and comparable accuracy with the fitted PES of [3] for the low lying energies and an order of magnitude improvement for the energies between 10 000 cm^{-1} and 14 000 cm^{-1} .

Further improvement of the global PES will be presented at the conference. In particular BODC and relativistic surface are now being calculated as well as aug-cc-pCV5Z basis set points for the extrapolation to complete basis set.

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Overview of hot and room T water line lists for $H_2{}^{16}O$, $H_2{}^{17}O$, $H_2{}^{18}O$, D_2O, HDO

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We present here an overview of 5 new water line lists including the main isotopologue and $H_2{}^{17}O$, $H_2{}^{18}O$, D_2O, HDO. All the calculations were performed using DVR3D [1]. For all line lists we used *ab initio* dipole moment surface from (DMS) [2].

The $H_2{}^{16}O$ line list, POKAZATEL, includes all the transitions involving energies up to 40 000 cm^{-1} and J up to 72 and is designed for high temperature applications. We created potential energy surface (PES) using Varandas-type analytical form and using two different data sets. The final PES was obtained by fitting to experimental energy levels up to ~ 40 000cm^{-1} and rotational excitations up to J=5. Extension to rotational quantum numbers up to 72 covers all the bound state rotational excitations. Our PES is the most accurate global water PES available.

This linelist is now complete and involves all the bound states up to dissociation and consists of 15 billion lines [4].

Hot line lists for two isotopologues of water, $H_2{}^{17}O$ and $H_2{}^{18}O$, also are presented. We cover energies up to 30000 cm^{-1} and J up to 50. We fit Born-Oppenheimer (BO) mass-independent PES to the available experimental data for $H_2{}^{16}O$ and fix BO diagonal correction, mass-dependent surface to its ab initio value. For the fit we used data for J=0, 2, 5 rotational states.

We also present new room temperature line lists for D_2O and HDO. These are created using the methodology of Lodi-Tennyson [3] for calculating uncertainties. For the uncertainties characterisation four subsidiary linelists are computed using two PESes and two DMSes. These linelists are suitable for inclusion in HITRAN.

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Absorption spectra of ammonia near 1 micron

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Several NH_3 absorption spectra recorded at room temperature in the region 9000 – 10,000 cm^{-1} are analysed using a variational line list, BYTe [1], and ground state energies determined using the MARVEL procedure [2]. BYTe is used as a starting point to initialise assignments by combination differences and the method of branches [3]. Recently, this technique was successfully applied to study room temperature NH_3 spectra in the region 7400 – 8640 cm^{-1} [4]. The current assignments in the region 9000 – 10,000 cm^{-1} are presented. A recently calculated purely ab initio PES of NH_3 has been used to calculate rovibrational energy levels [5]. Comparison with assigned levels shows better agreement than for BYTe between observed and calculated levels for some bands.

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Analysis of $^{15}NH_3$ absorption spectra in the 2.3 µm atmospheric water window

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The absorption spectra of $^{15}NH_3$ ammonia isotopologue were recorded in the 4275-4355 cm^{-1} spectral range. The experimental conditions covered the temperature range from 180 to 296 K and pressures from 0.4 to 50 mbar in a 7 m path long Herriot cell probed by a Vertical External Cavity Surface Emitting Laser. A Fourier transform spectrum was recorded at 296 K with 28 m path length to complement the room temperature data. These spectra were used to continue our work [1] on $^{15}NH_3$ transitions characterisation (quantum state assignment and line shape parameter determination) in this important atmospheric window, suitable for trace gas measurements. Besides the spectroscopic description of this ammonia isotopologue, the goal of the presented work is to test the improved method for measurements of lower state energies of transitions [2] with datasets from completely independent sources (laser absorption and Fourier transform spectra in this case).

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Introducing the line-mixing effect into the HITRAN database

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It is well known that collisional line-mixing can significantly affect the absorption spectral shapes when lines cannot be considered as collisionally “isolated”, especially when transitions strongly overlap each other for instance, in the molecular band heads. This effect needs to be addressed and accounted for many important atmospheric gases, including CO_2, O_3, N_2O, CO, CH_4, O_2 and NH_3. For CO_2 and CH_4, the two most important anthropogenic greenhouse gases, line-mixing effect needs to be taken into account for accurate retrievals of CO_2 or CH_4 abundances in the atmosphere of the earth but also of other planets. In this presentation, these observations are highlighted and the need to understand atmospheric CO_2 and CH_4 retrievals relevant to several key areas such as climate change, carbon cycle, air quality and remote sensing are recalled. The oxygen A-band, used as a benchmark by these remote sensing missions, being known to have strong line mixing also requires its accurate parametrization.

The HITRAN2012 database[1] has already included the line-mixing parameters for CO and O_2, however without providing guidance or tools for users to implement these parameters in their calculations. The new structure of the HITRAN database[2] and the HITRAN Application Programming Interface (HAPI)[3] allow for the inclusion of line-mixing parameters in the database and provide tools for their implementation. There is a sufficient extent of data for line-mixing in the literature, however, in different formalisms and at different levels of approximation.

The poster will explain the efforts towards accommodating the line-mixing effect for CO_2, N_2O, CO, CH_4 and O_2 in the HITRAN2016 database.

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Preliminary assignment and modeling of cold $^{13}CH_4$ spectrum in the 4970 – 5600 cm^{-1} region

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This work is devoted to the rovibrational assignment and analysis of the $^{13}CH_4$ spectrum in the 4970-5600 cm^{-1} range corresponding to lower part of the Tetradecad. A high resolution spectrum of ^{13}C-enriched CH_4 gas sample was recorded at 80 K using the custom-designed multipass cryogenic Herriott cell [1] configured to a high-resolution Fourier transform spectrometer, Bruker IFS-125HR, at the Jet Propulsion Laboratory. The spectral resolution (unappodized) was 0.0044 cm^{-1} and the sample pressure was 5.12 Torr. The observed line positions are determined through peak-finder with the precision of 0.0003 cm^{-1}.

The initial assignment was made using effective Hamiltonian derived by high-order Contact Transformations (CT) [2] from the *ab initio* potential energy surface [3] and variational calculations [4] using *ab initio* dipole moment surface [5]. A part of the effective Hamiltonian parameters specific to the Tetradecad was previously determined during the analysis of $^{13}CH_4$ laser absorption spectrum in the 5853-6200 cm^{-1} spectral range [6]. At this step of the study about 1900 of 2580 observed lines are rovibrationally assigned belonging to 6 cold bands. The corresponding line list and Obs.-Calc. statistics will be discussed.[&]

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The CO_2 absorption spectrum in the 2.3 µm region by high sensitivity CRDS: Rovibrational lines and continuum

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The absorption of carbon dioxide is very weak near 2.3 µm which makes this spectral window of particular interest to study the lower atmosphere of Venus in the 25–40 km altitude range and measure abundances of carbon monoxide, carbonyl sulfide, water vapor, sulfur dioxide and hydrofluoric acid [1,2]. This implies the accurate characterization of carbon dioxide absorption which is the main source of opacity in the window. This opacity results from the contributions of the local absorption lines absorption due to the rovibrational transitions of the monomer and of the ‘‘continuum’’ absorption.

In this work, we use the Cavity Ring Down Spectroscopy (CRDS) technique for a high sensitivity characterization of the CO_2 absorption spectrum in two spectral intervals of the 2.3 µm window: 4248-4257 and 4295-4380 cm^{-1} which were accessed using a Distributed Feed Back (DFB) diode laser and a Vertical External Cavity Surface Emitting Laser (VECSEL) as light sources, respectively. The achieved sensitivity (noise equivalent absorption, α_{min}, on the order of 5×10^{-10} cm^{-1}) allowed detecting numerous new transitions with intensity values down to 5×10^{-30} cm/molecule. The rovibrational assignments were performed by comparison with available theoretical line lists in particular those obtained at IAO Tomsk using the global effective operator approach. Hot bands of the main isotopologue and $^{16}O^{12}C^{18}O$ bands were found to be missing in the HITRAN database while they contribute importantly to the absorption in the region.

Additional CRDS spectra of a CO_2 sample highly enriched in ^{18}O were recorded in order to improve the spectroscopy of the $^{16}O^{12}C^{18}O$ isotopologue. As a result about 700 lines of $^{16}O^{12}C^{18}O$, $^{16}O^{12}C^{17}O$, $^{17}O^{12}C^{18}O$, $^{12}C^{18}O_2$ and $^{13}C^{18}O_2$ were newly measured.

CO_2 continuum was also determined from in flow CRDS experiments at different pressures between 250 Torr and 750 Torr where pure CO_2 and synthetic air were alternatively passed through the high finesse cell keeping the pressure constant. After subtraction of the monomer contribution, absorption coefficients normalized with density have been retrieved between 4320 and 4380 cm^{-1}. They increase from $\sim2\times10^{-8}$ cm^{-1} $Amagat^{-2}$ near 4330 cm^{-1} to 4.5×10^{-8} cm^{-1} $Amagat^{-2}$ around 4380 cm^{-1} corresponding to the centre of a CIA band. These values show a good agreement with the ones derived from [3] despite big difference in densities.

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Measured and calculated O_2-broadening coefficients of C_2H_4 in the $\nu_7+\nu_8$ band

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Monitoring the abundance and distribution of dominant chemical compounds is critical for understanding the photochemistry and dynamics of planetary and terrestrial atmospheres. Ethylene (C_2H_4) was detected in the atmospheres of the outer solar system bodies including Jupiter [1] and Saturn [2]. This molecule is also observed in the terrestrial atmosphere as a tropospheric pollutant produced by automobiles, forest fires and plant life [3].

We have measured the O_2-broadening coefficients of ethylene in the A-type $\nu_7 + \nu_8$ band at room temperature. These lines are located in the spectral range 1824-1951 cm^{-1}. The lines were fitted with a single-spectrum non-linear least squares fitting procedure of Voigt profiles which appeared to properly model the observed molecular line shapes within the noise level. These coefficients are compared to the results of theoretical calculations based on the semiclassical Robert-Bonamy formalism [4] in which the intermolecular potential includes electrostatic and dispersion energy contributions.

The variation of these coefficients with quantum numbers is examined. The results confirm the typical decrease of the O_2-broadening coefficients with increasing rotational quantum number J. For a given J, these coefficients increase with the quantum number K_a up to a maximum then decrease. The calculated results are generally in satisfactory agreement with experimental data.

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Global analysis of the high temperature infrared emission spectrum of $^{12}CH_4$ in the dyad ν_2/ν_4 region

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We report new assignments of vibration-rotation line positions of methane ($^{12}CH_4$) in the so-called Dyad ν_2/ν_4) region (1000 – 1500 cm^{-1}), and the resulting update of the vibration-rotation effective model of methane, previously reported by Nikitin *et al*. [1], up to and including the Tetradecad. High resolution (0.01 cm^{-1}) emission spectra of methane have been recorded up to about 1400 K using the high-enthalpy source developed at IPR associated with the Fourier transform spectrometer of the SOLEIL synchrotron facility (AILES beamline). Analysis of these spectra allowed extending rotational assignments in the well-known cold band (Dyad–GS) and related hot bands in the Pentad–Dyad system (3000 cm^{-1}) up to $J_{\max} = 30$ and 29, respectively. In addition, 8512 new transitions belonging to the Octad–Pentad (up to $J = 28$) and Tetradecad–Octad (up to $J = 21$) hot band systems were successfully identified. As a result, the MeCaSDa database of methane was significantly improved. The line positions assigned in this work, together with the information available in the literature, were fitted using 1096 effective parameters with a dimensionless standard deviation $\nu = 2.09$. The root mean square deviations d_{RMS} are 3.60×10^{-3} cm^{-1} for Dyad–GS cold band, 4.47×10^{-3} cm^{-1} for the Pentad–Dyad, 5.43×10^{-3} cm^{-1} for the Octad–Pentad and 4.70×10^{-3} cm^{-1} for the Tetradecad–Octad hot bands. The resulting new line list will contribute to improve opacity and radiative transfer models for hot atmospheres, such as those of hot-Jupiter type exoplanets.

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Daniel Cordier

“Aux portes de Saturne: le monde cryogénique de Titan”

Large audience conference
Auditorium de la Villa Douce
(9 boulevard de la Paix, Reims)

Friday Aug. 26, 2016 Program

	Chair : M.-R. De Backer	
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Precision Measurements of Spectroscopic Parameters in Atmospheric Relevant Molecules

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Spectroscopic parameters (namely, line intensity factors, pressure broadening and shifting coefficients) have been accurately determined for atmospheric relevant molecules, in the near-IR portion of the electromagnetic spectrum. Two different approaches were implemented: the former (at the wavelength of 1.4 µm) is based upon the use of a pair of phase-locked extended cavity diode lasers [1-3], while the latter (at the wavelength of 2 µm) makes use of a self-referenced optical frequency comb synthesizer for frequency calibration purposes. In both cases, high spectral fidelity is pursued in recording the absorption line shapes. The spectral analysis procedure, which is another key factor for high-quality determinations, is performed by using a global approach. This latter is applied to fit simultaneously a manifold of experimental profiles across a given range of pressures, sharing a restricted number of unknown parameters [1]. Recent results obtained for H_2O, C_2H_2 and CO_2 molecules will be illustrated. Furthermore, the performance of a variety of semiclassical line shape models will be discussed, with a particular focus on the partially-correlated quadratic speed-dependent hard collision model (the so-called Hartmann-Tran profile, or HTP model), which is currently the recommended profile to replace the Voigt convolution for the shape of an isolated line [4].

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Accurate laser measurements of the water vapor self-continuum absorption in four near infrared atmospheric windows: A test of the MT_CKD model

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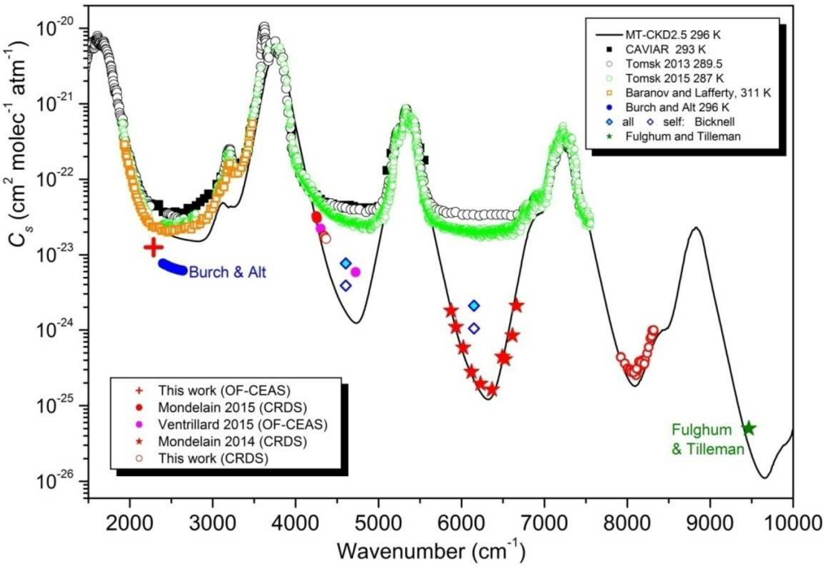
The semi empirical MT_CKD model of the absorption continuum of water vapor is widely used in atmospheric radiative transfer codes of the atmosphere of Earth and exoplanets but lacks of experimental validation in the atmospheric windows. Recent laboratory measurements by Fourier transform Spectroscopy have led to self-continuum cross-sections much larger than the MT_CKD values in the near infrared transparency windows.

In the present work, we report on accurate water vapor absorption continuum measurements by Cavity Ring Down Spectroscopy (CRDS) and Optical-Feedback-Cavity Enhanced Laser Spectroscopy (OF-CEAS) at selected spectral points of the transparency windows centered around 4.0, 2.1 and 1.25 µm. The temperature dependence of the absorption continuum at 4.38 µm is measured in the 23-39 °C range. The self-continuum water vapor absorption is derived either from the baseline variation of spectra recorded for a series of pressure values over a small spectral interval or from baseline monitoring at fixed laser frequency, during pressure ramps. In order to avoid possible bias approaching the water saturation pressure, the maximum pressure value was limited to about 16 Torr, corresponding to a 75% humidity rate.

After subtraction of the local water monomer lines contribution, self-continuum cross-sections, C_S, were determined with a few % accuracy from the pressure squared dependence of the spectra base line measured for a series of pressure values up to about 15 Torr.

Together with our previous CRDS and OF-CEAS measurements in the 2.1 and 1.6 µm windows, the derived water vapor self-continuum provides a unique set of water vapor self-continuum cross-sections for a test of the MT_CKD model in four transparency windows. A review of the previous experimental results will be presented together with a comparison to the MT_CKD model (See Fig. below). Although showing some important deviations of the absolute values (up to a factor of 4 at the center of the 2.1 µm window), our accurate measurements validate the overall frequency dependence of the MT_CKD2.5 model.



Perfecting methods of metrological traceability of NO using UV absorption spectroscopy

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There are no modern metrologically assured data of the absorption cross-sections for nitrogen oxide in the known spectroscopic databases (DB) of the gas components [1-4]. All publicly available data are presented with too large a step in the spectrum, which limits their practical use.

It is difficult to interpret available data of the absorption cross-section for NO in the UV spectral region. E.g. in [5] there is no indication on the used spectral resolution of the used spectrophotometer etc. Modern reliable data on the absorption cross sections of NO do not exist in publicly available DBs for the UV region of the spectrum.

DB of the Jet propulsion Laboratory [3] and DB of the Max Planck Institute [4] are essentially a kind of an improved version of a list of works of various authors in the Internet with an extremely rare recommendations. Also it can be said that the authors presented in DBs [3, 4] worked on different equipment, by different methods and such work is not consistent in metrological sense.

Thus, for the purposes of metrological traceability of measurement of the concentration of NO was necessary to carry out own measurements of the spectra of NO at the wavelength of 226,2 nm. These measurements were made on equipment that is part of the National Primary Measurement Standard of Mole Fraction and Mass Concentration of Components in Gas Media (GET 154-2011) in Russia.

Results of the measurements were used for development of new certification procedures by UV spectroscopy for transfer of units from the GET 154-2011 to working standards used for calibration of measuring instruments [6].

In our presentation we discuss the features of the methods of metrological traceability of NO using UV absorption spectroscopy.

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HITRAN Spectroscopy Evaluation using Atmospheric Spectra

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High resolution FTIR solar occultation spectra, acquired by the JPL MkIV Fourier transform spectrometer from balloon, covering 650 to 5650 cm^{-1} at 0.01 cm^{-1} resolution, are systematically analyzed using the last four versions of the HITRAN linelist (2000, 2004, 2008, 2012). The rms spectral fitting residuals are used to assess the quality and adequacy of the linelists as a function of wavenumber and altitude. Although there have been substantial overall improvements with each successive version of HITRAN, there are nevertheless a few spectral regions where the latest HITRAN version (2012) has regressed, or produces residuals that far exceed the noise level. A few of these instances are investigated further and their causes identified. We emphasize that fitting atmospheric spectra, in addition to laboratory spectra, should be part of the quality assurance for any new linelist before public release.

High resolution photoacoustic spectroscopy of the oxygen A-band

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NASA's Orbiting Carbon Observatory missions require spectroscopic parameterization of the Oxygen A-Band absorption (757-775 nm) with unprecedented detail to meet the objective of delivering space-based column CO_2 measurements with an accuracy of better than 1 ppm, and spectroscopic parameters with accuracies at the 0.1% level. To achieve this it is necessary for line shape models to include deviations from the Voigt line shape, including the collisional effects of speed-dependence, line mixing (LM), and collision-induced absorption (CIA). LM and CIA have been difficult to quantify in FTIR and CRDS spectra which have been limited to lower pressure measurements. A photoacoustic spectrometer has been designed to study the pressure- dependence of the spectral line shape up to pressures of 5 atm, where LM and CIA contribute significantly to the A-Band absorption. This spectrometer has a high signal-to-noise (S/N) of about 10,000 and frequency accuracy of 2 MHz. In addition, temperature-dependent effects on the line shape are studied using a PID-controlled cooled nitrogen flow/ heater system. The latest acquired spectra and multispectrum analyses are reported here.

Absolute molecular transitions frequencies measured by cavity-enhanced absorption and dispersion spectroscopy techniques

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We present absolute frequencies of unperturbed $^{12}C^{16}O$ transitions from the near-infrared (3←0) band measured with uncertainties five-fold lower than previously available data [1]. The line positions of the Doppler-broadened R24 and R28 lines were obtained with relative uncertainties at the level of 10^{-10}. The pressure shifting coefficients were measured and the influence of the line asymmetry on unperturbed line positions was analyzed.

The measurements were done with three different cavity enhanced absorption and dispersion spectroscopic methods: a well-established frequency-stabilized cavity ring-down spectroscopy (FS-CRDS) [2], the cavity mode-width spectroscopy (CMWS) [3], and the novel one-dimensional cavity mode-dispersion spectroscopy (1D-CMDS) [4]. Two last techniques are based on measurement of half-widths and shifts of resonance modes of the high-finesse optical cavity, respectively. Moreover, the 1D-CMDS method depends solely on the measurement of frequencies or their differences and is insensitive to systematic instrumental errors of the detection system. It has the potential to become the most accurate of all absorptive and dispersive spectroscopic methods and can have significant impact in the future high-accuracy line-shape studies.

We used a unique experimental setup enabling the simultaneous measurement of the spectra by these three cavity-enhanced techniques. We present a detailed comparison between the FS-CRDS and 1D-CMDS methods [5]. The absorptive (FS-CRDS) and dispersive (1D-CMDS) spectra were simultaneously included in the complex-fit line-shape analysis [5]. The limitations of the FS-CRDS technique are mentioned. The frequency axis of spectra was linked to the primary frequency standard – UTC(AOS) (Coordinated Universal Time from the Astro-Geodynamic Observatory in Borowiec, Poland) having long-term relative stability of 10^{-15} [6]. Three different spectroscopic methods and various approaches to data analysis were used to estimate potential systematic instrumental errors in all of them. Presented dispersion line shapes [1] are the highest quality dispersion line-shape measurements in optical spectroscopy demonstrated so far. Our dispersion spectra are the first demonstration of molecular spectroscopy with both axes of the spectra directly linked to the primary frequency standard.

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HITRAN2016: Innovative structure, new data, extra parameters

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A new HITRAN edition is scheduled to be released this year. It will replace the current edition, HITRAN2012 [1], that has been in use, along with some intermediate updates, since 2012.

As usual, we have added, revised, and improved many transitions and bands of molecular species and their isotopologues. This particularly applies to the traditional line-by-line portion of HITRAN. However, there has been a necessity to expand the parameter scope of HITRAN, particularly because of the needs of highly-accurate, terrestrial remote-sensing missions, for example OCO-2 [2], etc.

To accomplish this expansion, the whole database has been reorganized into a relational database structure and presented to the user by means of a very powerful, easy-to-use internet program called HITRAN*online* [3] accessible at <www.hitran.org>. This interface allows the user many queries in standard and user-defined formats. In addition, we have developed a powerful application called HAPI (HITRAN Application Programing Interface) [4] that allows much more functionality for the user. HAPI is meant to work on the user's own computer and thus frees up the server of HITRAN*online* from normally heavy duty calculations including absorption and radiance. We present examples of some of the features of these new programs.

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ExoMol: New molecular linelists for exoplanets and other hot atmospheres

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Fundamental molecular data play a key role for spectral characterization of astrophysical objects cool enough to form molecules in their atmospheres (cool stars, extrosolar planets and planetary discs) as well as in a broad range terrestrial applications. However, at elevated temperatures, the laboratory data for a number of key species is absent, inaccurate or incomplete. The ExoMol project is providing comprehensive line lists for all molecules likely to be observable in exoplanet atmospheres in the foreseeable future [1]; a huge undertaking which will mean providing in excess of a hundred of billions of spectral lines for a large variety of molecular species. The line lists for a number of key atmospheric species currently available from ExoMol (www.exomol.com): CaH, MgH, BeH [2], SiO [3], HCN/HNC [4], CH_4 [5], KCl, NaCl [6], PN [7], PH_3 [8], H_2CO [9], AlO [10], NaH [11], CS [12], HNO_3 [13], CaO [14], SO_2 [15], H_2S [16], HOOH [17], SO_3 [18] and VO [19]. The line lists currently being constructed include those for AlH, C_2, C_3, PO, PS, PH, SH, SiH, CrH,TiH, C_2H_4, CH_3Cl and C_2H_2. We will present examples of molecular spectra computed using the ExoMol line lists.

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Reims-Tomsk information systems TheoReTS and S&MPO: spectra simulations and validation of *ab initio* predictions

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Two interactive web accessible information systems [1,2] have been developed and maintained in collaboration of Reims and Tomsk spectroscopic teams. First one is S&MPO ("Spectroscopy and Molecular Properties of Ozone") [1] devoted to high resolution spectroscopy of the ozone molecule, related properties and data sources. S&MPO contains information on original spectroscopic ozone data (line positions, line intensities, energies, transition moments, spectroscopic parameters) recovered from analyses and modeling of experimental spectra as well as associated software for data representation.

A more recent one is TheoReTS [2] – an information system for theoretical spectra based on variational predictions from molecular potential energy and dipole moment surfaces for various molecular species of interest for planetology and astrophysical applications[#)]. The current TheoReTS implementation contains information on four-to-six atomic molecules, including phosphine, methane, ethylene, silane, methyl-fluoride, and their isotopic species $^{13}CH_4$, $^{12}CH_3D$, $^{12}CH_2D_2$, $^{12}CD_4$, $^{13}C_2H_4$. Predicted hot methane line lists up to T = 2000 K are included. Recent updated of the TheoReTS database will be presented in the Poster [3].

Both information systems provide associated software for spectra simulation including absorption coefficient, absorption and emission cross-sections, transmittance and radiance. The simulations allow Lorentz, Gauss and Voight line shapes. Rectangular, triangular, Lorentzian, Gaussian, sinc and sinc squared apparatus function can be used with user-defined specifications for broadening parameters and spectral resolution. All information is organized as a relational database with the user-friendly graphical interface

The validations of recent ab initio predictions for rotationally resolved spectra of related molecules included in S&MPO and TheoReTS with respect to high-resolution experimental data, low resolution records (PNNL experimental library) and comparisons with HITRAN and GEISA databases will be discussed.

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Evaluation of the GEISA 2015 spectroscopic database using satellite observations

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The accuracy of molecular spectroscopy in atmospheric research has entered in a new phase in the frame of remote sensing applications (meteorology, climatology, chemistry) with the advent of highly sophisticated and resolved instrumentations.

The historical background, actual context of management and contents of GEISA (2015 version) are independently presented in a poster by N. Jacquinet et al. In the frame of a necessary new vision for public spectroscopic databases content management, and following the findings of the GEISA workshop (June 2014, Paris, France),we have undertaken a feasibility study on new appropriate methods to bring an added value to GEISA. Besides, one important conclusion of the GEISA work-shop was the necessity of a closest feedback between spectroscopy research laboratories and responsible managers of public spectroscopic databases (such as GEISA and HITRAN), to assess and monitor suitably the archived spectroscopic parameter values traceability and precision.

Based on a strong experience in CAL/VAL activities at LMD, we have developed a chain of validation, the SPARTE chain (Armante et al, J. Mol. Spectr., 2016), aiming to compare the differences between results of model simulations and satellite observations remote data. The simulations are made with the radiative transfer algorithm 4AOP developed and validated at LMD. In the thermal infrared, instead of laboratory measurements, we have used the richness of the observation data provided by space born satellite instruments like AIRS (2002) and IASI (2006, 2012), TANSO-FTS (2009), CrIs (2011). We are now planning to consider IASI (2017), as well as new generation of higher resolved instruments such as IASI-NG (2021).

In the near infrared, we have used all the potential of one the highest resolved instruments TCCON. In this presentation, we will present results of validations of the GEISA 2015 version, according to IASI and TCCON and how it could prepare a coming new version. Comparisons with other databases like HITRAN 2012 will be given, showing how both databases like HITRAN and GEISA are complementary

Spectroscopic database for water vapour between 5850 and 8340 cm^{-1}

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An empirical spectroscopic database is constructed for natural water in the near infrared region between 5850 and 8340 cm^{-1}. The list includes more than 46500 transitions of the six isotopologues ($H_2{}^{16}O$, $H_2{}^{18}O$, $H_2{}^{17}O$, $HD^{16}O$, $HD^{18}O$, $HD^{17}O$) with intensity cut off of 1×10^{-29} cm/molecule in natural isotopic abundance. The line positions were obtained by difference of empirical energy terms. These empirical determinations are mostly based on extensive investigations of water spectra by high sensitivity CRDS [1-9] complemented with literature data. The empirical line positions were completed by experimental intensities from the literature obtained by FTS for the strong lines and CRDS for weaker lines. The list is made mostly complete by including a large number of weak transitions not yet detected, with empirical positions and variational intensities. Air- and self-broadening coefficients have been added to each transition using the most recent version of the algorithm used for the HITRAN and GEISA databases [10-16]. Examples of comparison of CRDS spectra to simulations based on the HITRAN2012 list [17] illustrate the advantages of presented database.

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Infrared absorption cross sections of halogenated species

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Fluorine- and chlorine-containing molecules in the atmosphere are very strong greenhouse gases. Additionally many of these, in particular chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs), deplete stratospheric ozone and are regulated by the 1987 Montreal Protocol. The quantification of the atmospheric abundances of such molecules using remote-sensing techniques crucially requires accurate quantitative infrared spectroscopy. HITRAN contains cross-section datasets for all the main halogen species, but many of these have deficiencies which introduce systematic errors when used in retrievals.

This talk will focus on recent laboratory measurements for important halogenated species. A number of new cross-section datasets have been created, some of which are now published and will be included in the HITRAN 2016 compilation. A number of these datasets have been validated using solar occultation spectra measured through the Earth's atmospheric by the Atmospheric Chemistry Experiment Fourier transform spectrometer (ACE-FTS), and will be used in the upcoming version 4.0 processing of ACE-FTS data. The ACE-FTS measures atmospheric profiles for many halogenated species, including CCl_4 (CFC-10), CCl_3F (CFC-11), CCl_2F_2 (CFC-12), CHF_2Cl (HCFC-22), CHF_3 (HFC-23), CF_4 (CFC-14) CF_3CH_2F (HFC-134a), and SF_6.

Keywords: infrared absorption cross sections, laboratory measurements, satellite remote sensing, greenhouse gases, ozone-depleting substances

List of authors

ASA HITRAN 2016 – Program

Wednesday Aug. 24, 2016	**Thursday Aug. 25, 2016**	**Friday Aug. 26, 2016**
8h30 – 9h00 : Official opening		
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9:35 – 9 :55 : M Rey p.8	9:35 – 9:55 : P. Wcislo p.76	9:35 – 9:55 : A. Campargue p.144
9:55 – 10:15 : S.T. Melin p.9	9:55 – 10:15 : T. Mendaza p.77	9:55 – 10:15 : V. Belodorodov p.145
10:15 – 10:50 : Coffee break	10:15 – 10:50 : Coffee break	10:15 – 10:50 : Coffee break
10:50 – 11:10 : R. Georges p.10	10:50 – 11:10 : M. Ghysels p.78	10:50 – 11:10 : G.C. Toon p.146
11:10 – 11:30 : R.J. Hargreaves p.11	11:10 – 11:30 : Q. Ma p.79	11:10 – 11:30 : M.J. Cich p.147
11:30 – 11:50 : V. Perevalov p.12	11:30 – 11:50 : A. Predoi-Cross p.80	11:30 – 11:50 : S. Wojtewicz p.148
12:00 – 14:00 : lunch time	12:00 – 14:00 : lunch time	12:00 – 14:00 : lunch time
Chairman: P. Rannou	Chairman: V. Boudon	Chairman: J. Buldyreva
14:00 – 14:35 : **R. Wordsworth** p.13	14:00 – 14:35 : **A. Nikitin** p.81	14:00 – 14:35 : **L. Rothman** p.149
14:35 – 14 :55 : C.D. Boone p.14	14:35 – 14:55 : S. Yu p.82	14:35 – 14:55 : J. Tennyson p.150
14:55 – 15:15 : A. Perrin p.15	14:55 – 15:15 : M. Birk p.83	14:55 – 15:15 : Vl.G. Tyuterev p.151
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15:35 – 15:55 : R. Zhang p.17	15:35 – 15:55 : A. Alkadrou p.85	15:35 – 15:55 : S.N. Mikhailenko p.153
15:55 – 16:15 : G. Liuzzi p.18	15:55 – 16:15 : Yu. Ponomarev p.86	15:55 – 16:15 : J.J. Harrison p.154
16:15 – 16:35 : J. Orphal p.19	16:15 – 16:45 : Coffee break	16:15 – 16:45 : Coffee break
16:35 – 17:00 : Coffee break	16:45 – 18:00 : Poster session p.89-137	16:45 – 19:30 : LIA meeting (invited people)
17:00 – 18:30 : Poster session p.23-72	18:30 – 19:30 : **D. Cordier** (Villa Douce) p.139	
19:30 – **Banquet Brasserie Le Flo**		