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.

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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 *μ*m 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 *μ*m 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 *μ*m 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.

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 $\alpha_{min} \approx 2 \times 10^{-10}$ 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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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 (CH_4) 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 v_2 spectral region is in general warmer (higher radiance) than observations and the spectroscopy is inconsistent among the IASI bands. The CO_2 v_2 and N_2O/CO_2 v_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}.

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 $\sigma_{RMS} = 0.02$ 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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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·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$_2$H$_4$ 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$_2$Y$_4$ 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$_2$H$_4$ 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.
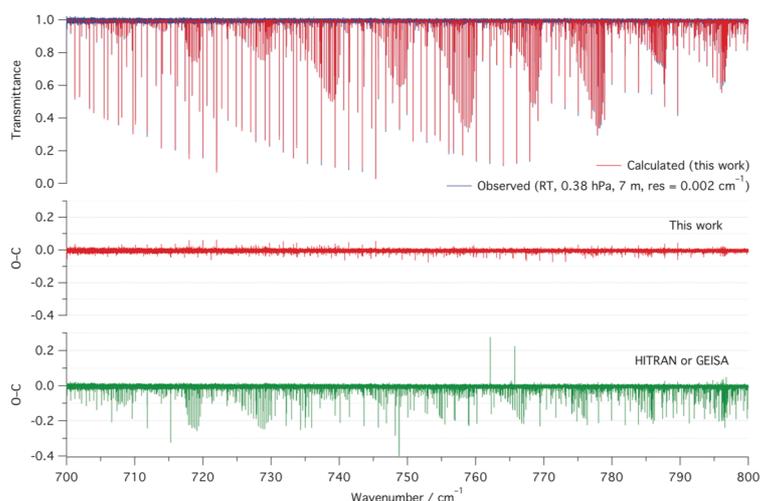

Fig. 1: Comparison of an observed spectrum (blue) of the P branch of the ν_{10} band of ethylene with spectra calculated (red) for ^{12}C$_2$H$_4$ using results of the present analysis.

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Speed dependence, velocity change and line mixing in CO₂ 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 $1 \cdot 10^{-4}$ 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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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.
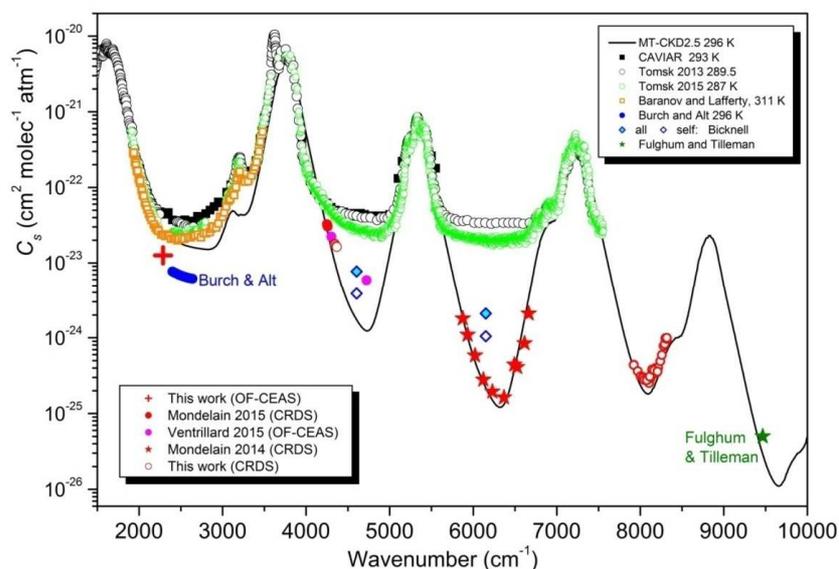
Perfecting methods of metrological traceability of NO using UV absorption spectroscopy

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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 ($3\leftarrow0$) 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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