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Center for Astrophysics | Harvard & Smithsonian, Cambridge, Massachusetts, USA









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SESSION I: Spectroscopy of Earth's atmosphere

I-1. A New Era of Air Quality Monitoring from Space over North America with TEMPO: Commissioning and Early Nominal Operation Results

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We present an overview of the initial data products of TEMPO during its commissioning and early nominal operation and preliminary comparison with correlative satellite and ground-based observations. We also review TEMPO's spectroscopic usage and needs.

TEMPO is NASA's first Earth Venture Instrument and first host payload. It measures hourly daytime atmospheric pollution over North America from Mexico City to the Canadian oil sands, and from the Atlantic to the Pacific, at high spatiotemporal resolution ($\sim 10 \text{ km}^2$ at boresight) from the geostationary orbit. It uses UV/visible spectroscopy (293-493 nm, 538-741 nm) to measure O₃ profiles including lower tropospheric O₃ and columns of NO₂, H₂CO, SO₂, C₂H₂O₂, H₂O, BrO, IO, as well as clouds aerosols, and UVB. TEMPO provides a tropospheric measurement suite that includes the key elements of tropospheric air pollution chemistry and captures the inherent high variability in the diurnal cycle of emissions and chemistry. The TEMPO instrument was built by Ball in 2018. It was integrated into the host commercial communication satellite Intelsat 40e (IS-40e) by Maxar. IS-40e was successfully launched on April 7 by a SpaceX Falcon 9 rocket to the GEO orbit at 91°W. The TEMPO Instrument powered up for the first time in orbit in early June to start its commissioning. After a month of dry out and activation, TEMPO first light of solar and earth measurements occurred on July 31-August 2. Nominal operation started on 19 October 2023 after the commissioning phase and the post-launch acceptance review. Science data products are archived and distributed at NASA's ASDC and were released to the public in February 2024 for L1b and in May 2024 for L2/3. TEMPO is part of a geostationary constellation to measure air quality along with GEMS (launched in Feb. 2020) over Asia and Sentinel-4 (to launch in 2025) over Europe.

I-2. The Atmospheric Chemistry Experiment, ACE: overview and recent results

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ACE is measuring atmospheric composition using the Sun as a light source from low Earth orbit (http://www.ace.uwaterloo.ca/). The primary instrument is an infrared spectrometer (ACE-FTS) that provides atmospheric transmission spectra. ACE-FTS version 5.2 processing yields altitude profiles for the concentrations of 46 molecules as well as spectra of clouds and aerosols. HITRAN2020 is used for these molecular retrievals. After more than 20 years on orbit, ACE data are useful for climate change observations. Topics covered will include measurements of greenhouse gases, gases associated with the Montreal Protocol on Substances that Deplete the Ozone Layer, fire emissions and volcanic eruptions.

I-3. Spectroscopic Needs and the Latest Processing Developments for the Atmospheric Chemistry Experiment (ACE)

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The primary instrument on the Atmospheric Chemistry Experiment (ACE) is a Fourier transform spectrometer (ACE-FTS) operating in the infrared with broad spectral coverage $(750 - 4400 \text{ cm}^{-1})$ and high resolution (0.02 cm^{-1}) . Collecting solar occultation measurements since February 2004, ACE provides over 20 years' worth of atmospheric profiles for pressure, temperature, and the volume mixing ratios of more than 30 molecules, as well as volume mixing ratio profiles for more than 20 subsidiary isotopologues. Updates for the upcoming data processing version will be described, along with areas where improved spectroscopic information could yield better results. In particular, recent work on the infrared spectra of aerosols measured by the ACE-FTS illustrates the need for spectroscopic information for smoke and fuller coverage in the spectroscopy for polar stratospheric clouds.

I-4. Evaluation of the impacts of recent updates to the HITRAN and MT_CKD water vapor models on infrared radiative transfer fluxes

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This study evaluates the effects of recent updates to the High Resolution Transmission (HITRAN) database and the MT_CKD water vapor continuum model on infrared radiative transfer and remote sensing. It focuses on the impact of newer versions of HITRAN (2016 and 2020) and MT_CKD (3.2 and 4.1.1) on clear-sky infrared flux calculations across five atmospheric profiles and simulating satellite infrared channels, particularly those of GOES-ABI. Results show that updates to MT_CKD decrease atmospheric opacity, increasing transmissivity, whereas HITRAN updates generally increase opacity. Significant changes were observed with MT_CKD updates, affecting upward and downward fluxes. These effects vary across the spectrum, atmospheric heights, and profiles, with notable differences in the far-infrared region due to changes in the water vapor continuum. The study also notes significant spectroscopic changes in HITRAN affecting remote sensing, particularly an average temperature decrease in GOES ABI channel 12, highlighting the importance of ongoing updates and assessments of spectroscopic databases and models for enhancing remote sensing accuracy.

I-5. Forward Modeling Telluric Absorption in High-Resolution Stellar Spectra

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Earth's atmosphere contaminates all ground-based astronomical observations, such as high-resolution stellar spectra on which the signatures of Earth's atmosphere (tellurics) are superimposed. Tellurics significantly impact scientific return because they add correlated noise and reduce the spectral range with usable astrophysical information, including contamination of important spectral features (e.g. exoplanet atmospheric probes). This is particularly severe in the infrared where wide swaths of the spectrum contain telluric absorption. Precise spectroscopy necessitates telluric correction, but this is a difficult task requiring expensive calibration observations or reliable atmospheric transmission models and molecular line lists.

We present a method to forward model telluric absorption for the NEID (visible) and HPF (NIR) spectrometers that accounts for their variable instrumental line profiles. We generate a grid of molecular transmission spectra using LBLRTM¹ and the HITRAN line lists², which are then convolved with a parameterization of the instrumental line profiles. We can map the instrumental line profiles using a laser frequency comb, which provides unresolved emission lines regularly spaced across the spectrum. By using a variable kernel convolution, the models accurately represent as-observed telluric spectra.

We highlight the resulting precise telluric corrections, which are often to well-within 1% depending on various factors (e.g. species, line strength, water column). There are remaining structured residuals that need to be addressed. We explore potential causes for these residuals, including the grid's input atmospheric profile, line list inaccuracies, and remaining inadequacies in the line profile parameterization.

¹S. A. Clough, M. W. Shephard, E. J. Mlawer, et al., *JQSRT*, 91, 233 (2005).

²I. E. Gordon, L. S. Rothman, R. J. Hargreaves, et al., *JQSRT*, 277, 107949 (2022).

SESSION II: Lineshapes

II-1. Effect of Finite Collision Duration on Line Shapes

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Most parameterized line profiles used to analyze absorption spectra are derived assuming the impact approximation for which the duration of binary collisions is assumed to be instantaneous. However, Fourier analysis of decoherence in transition moments predicts a broad underlying continuum because of the finite duration of these collisions. Usually this continuum is too weak to be significant and is ignored. Here I discuss recent molecular dynamics simulations and experiments where the intensities of lines are shown to be distributed between two distinct frequency regions: 1) a line core with a width inversely related to the average time between collisions and 2) a broad component with a width scaled by the inverse of the collision duration. The relative contributions to the total intensity of these mechanisms give an overall shape equal to the sum of a core profile plus one or more broad Lorentzian line shapes that depend on the interaction time, rotational quantum number, collisional partners, and temperature. Because these interactions involve binary collisions, the broad component of the spectrum caused by the breakdown of the impact approximation (BIA) is proportional to the square of the density. However, it can be difficult to distinguish this BIA spectrum from other sources of continua such as collision induced absorption (CIA), absorption by dimers and line mixing effects, all of which have the same density-squared dependence. I will discuss experimental results showing evidence of depletion in core intensity with increasing pressure for CO-N₂, O₂-air, O₂-Ar, HCl-N₂, and CO₂-CO₂. Most of these observations are consistent in magnitude with molecular dynamics simulations of the BIA effect, although questions remain about the possible contributions of the other mechanisms.

II-2. Non-impact effects on the measured intensity of HCl lines

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The integrated line shape of an absorption line is widely obtained from fit of laboratorymeasured spectra assuming a line profile model. Such a laboratory-measured intensity is so far assumed to be independent of the pressure. This major assumption is now questioned: to which extent the retrieved integrated line shape is proportional to the absorber density and independent of the total pressure of the gas mixture? In this paper, the pressure dependence of the line intensities retrieved from fits of absorption spectra of HCl are investigated both experimentally and theoretically. The retrieved line intensities reveal large decreases with increasing pressure - up to 3% per atm for pure HCl. We also show that the absorption in between successive P and R transitions are significantly larger than those predicted using the usual Lorentz profile. Requantized classical molecular dynamics simulations have been made in order to predict absorption spectra of HCl matching the experimental conditions. The pressure dependence of the intensities retrieved from the calculated spectra as well as the predicted super-Lorentzian behavior between lines are in good agreement with the measurements. Our analysis shows that these effects are essentially due to incomplete collisions, which govern the dipole autocorrelation function at very short times.

II-3. New spectroscopic database of CO_2 in the 1.6 and 2.0 µm spectral regions for remote sensing

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New FTS measurements of pure, air-, and H₂O-broadened CO₂ in the air pressure range 100-1000 mbar and the temperature range 200-296 K for the 1.6 and 2 µm bands were carried out in the frame of the ESA-funded ISOGG (Improved Spectroscopy for satellite measurements Of Greenhouse Gases) project for the upcoming CO2M mission. The analysis of pure CO_2 in the 1.6 µm band showed intensity depletion in the line cores with increasing pressure and corresponding intensity redistribution to a continuum that varies quadratically with pressure¹. Accurate line intensities with sub-permille uncertainty were determined, as well as air- and H₂O-broadened line profile parameters including speed-dependence and first order Rosenkranz line mixing. The temperature dependence of the air-broadening line profile parameters was also obtained. The temperature dependence of air intensity depletion and the continuum were calculated from second order virial coefficients based on the pure CO_2 results, and line parameters among different bands were compared with HITRAN20. Absorption cross sections were calculated on the ABSCO 5.2 wavenumber, pressure, temperature, and H_2O VMR grids and compared with ABSCO 5.2 by retrieval simulations of TCCON measurements. Continuum and line core intensity depletions were found to be relevant for atmospheric observations.

¹M. Birk, C. Röske, G. Wagner, The pressure dependence of the experimentally-determined line intensity and continuum absorption of pure CO_2 in the 1.6 µm region, submitted to JQSRT, in press.

II-4: On the interest of time domain studies of line-mixing and not impact collisional effects

Jean-Michel Hartmann,^a

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As is well known, line-mixing (LM) and/or non-impact (NI) effects can strongly affect the absorption in the wings of lines and bands, which are regions of interest for remote sensing and radiative transfer in planetary atmospheres. Studying these processes in the spectral domain is often difficults because: (i) One needs to a priori know the spectroscopic parameters of all the (generally very numerous) transitions contributing to the spectrum; (ii) measurements may require long optical paths and/or high pressures. In contrast, using experiments in the time domain, where one tracks the collisional dissipation of the molecular alignment induced by one or two strong laser pulses enables a much more direct look at the influences of both LM and NI effects. Indeed, one only needs to know the molecule rotational constant and short sample cells can be used. We will show that studying the alignment at very short time (a few ps) after the sample excitation clearly reveals both effects. For this, model systems (HCl and CO2, pure or diluted in He) have been retained because the involve very differents sensitivities to LM and NI processes. Comparison between measurements and calculations carried using molecular dynamics simulations demonstrate good agreement and enable a refined analysis of the processes involved.

M-1. The Molecular Orchestra: Sonifying Emission Spectra

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David Ibbett, Ph.D. is a composer, educator and musical advocate for science. Based in Boston, he is a Professor at WPI and directs the Multiverse Concert Series, a project that combines music and science in live performance.

In 2023, David was named the first Resident Composer at the Center for Astrophysics | Harvard & Smithsonian.

SESSION III: Laboratory Spectroscopy for Terrestrial Studies

III-1. Precision spectroscopy of fundamental and hot-band molecular transitions using optical frequency combs

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Optical frequency comb Fourier transform spectroscopy (FTS) allows the measurement of broadband molecular spectra with Doppler-limited and sub-Doppler resolution, and determination of line positions with sub-MHz frequency accuracy. Using mid-infrared direct comb-based FTS, we provided significantly improved line lists of fundamental and hot-band transitions of nitrous oxide (N₂O)⁻¹, methane (CH₄)⁻², and formaldehyde (H₂CO)⁻³ in the 7.2 - 8 μ m range. To measure hot-band transitions in CH₄ from levels not populated at room temperature, we use optical-optical double-resonance spectroscopy. A 3.3 μ m continuous wave pump populates a selected ro-vibrational level in the ν_3 band of methane, and a comb probe tunable between 1.64 - 1.8 μ m measures sub-Doppler transitions from the pumped level to final states in the $3\nu_3$ range^{4–5}. We assign these states using combination differences and by comparison to theoretical prediction. I will discuss the principles and performance of the experimental methods, and how the obtained line lists are used to improve theoretical models of the molecules.

¹A. Hjältén, M. Germann, K. Krzempek, A. Hudzikowski, A. Głuszek, D. Tomaszewska, G. Soboń, A. Foltynowicz, *JQSRT*, 271, 107734 (2021). https://doi.org/10.1016/j.jqsrt.2021.107734.

²M. Germann, A. Hjältén, V. Boudon, C. Richard, et al., *JQSRT*, 288, 108252 (2022). https://doi.org/10.1016/j.jqsrt.2022.108252.

³M. Germann, A. Hjältén, J. Tennyson, S. N. Yurchenko, I. E. Gordon et al., *JQSRT*, 312, 108782 (2024). https://doi.org/10.1016/j.jqsrt.2023.108782.

⁴A. Foltynowicz, L. Rutkowski, I. Silander, A. C. Johansson, et al., *PRL*, 126, 063001 and *PRA* 103, 022810 (2021). https://doi.org/10.1103/PhysRevLett.126.063001, https://doi.org/10.1103/PhysRevA.103.022810.

⁵V. Silva de Oliveira, I. Silander, L. Rutkowski, et al., *Nat. Commun.*, 15, 161 (2024). https://doi.org/10.1038/s41467-023-44417-2.

III-2. Study of the 1.27 μ m band of O₂ by CRDS in the frame of the *MicroCarb* mission

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The atmospheric band of O_2 near 1.27 μm consists of narrow absorption lines of the $a^1\Delta_g - X^3\Sigma_g^-(0-0)$ transitions superimposed to a broad collision-induced absorption (CIA) structure. This band is now suitable for spaceborne observations thanks to accurate modeling of the strong mesosphere/stratosphere airglow produced by O_3 photodissociation¹. Together with the stronger A-band near 760 nm, the 1.27 µm band is thus used to determine the air mass along the line of sight from atmospheric spectra recorded at ground by the Total Carbon Column Observing Network (TCCON)² or from space. The derivation of the dry air column from the O₂ column is made possible by the fact that the mixing ratio of oxygen is mostly constant (20.95%) in the Earth's atmosphere.

The present work is part of a project dedicated to an improved characterization of this band in support of the satellite mission $MicroCarb^3$, dedicated to the accurate determination of column integrated concentrations of CO₂. After having measured the line profile parameters of the O₂ transitions at room temperature in air in a previous study⁴, we are now characterizing the temperature dependence of these parameters. For this purpose, a cavity ring down spectrometer (CRDS) is coupled to a temperature regulated high-finesse optical cavity. The frequency scale of each spectrum is accurately determined thanks to a referencing to an optical frequency comb. Spectra are recorded at various temperatures and pressures and analyzed using the speed dependent Nelkin-Ghatak model and a multi-spectrum treatment, taken line mixing into account when necessary. The derived line parameters obtained so far will be presented and compared to literature data.

¹K. Sun, I. E. Gordon, C. E. Sioris, X. Liu X, K. Chance, S. C. Wofsy, *GRL*, 45,5779-87 (2018). https://doi.org/10.1029/2018GL077823

²D. Wunch, G. C. Toon, J. F. Blavier, R. A. Washenfelder, J. Notholt, B. J. Connor, *PTRSA*, 369, 2087-2112 (2011). https://doi.org/10.1098/rsta.2010.0240

³https://microcarb.cnes.fr/en

⁴D. D. Tran, H. Tran, S. Vasilchenko, S. Kassi, A. Campargue, D. Mondelain. *JQSRT*, 240, 106673 (2020). https://doi.org/10.1016/j.jqsrt.2019.106673

III-3. Line intensity measurements and far-wing intensity redistribution in the 0.76 μ m O₂ band

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The well-known uniform atmospheric distribution of oxygen has led to frequent use of the near-infrared oxygen molecular absorption bands in remote sensing and satellite missions to measure the airmass of an atmospheric column. Fitting accurate parameterized spectroscopic models describing all relevant physics to laboratory measurements is critical to accurately retrieving the remote sensing target observables and uncertainties. In the Hartmann-Tran line profile, the spectrum is derived assuming that collisions occur instantaneously (impact approximation). When this approximation is not satisfied, the finite duration of collisions leads to a redistribution of the line intensity from the line cores to the far wings- an effect that increases with the pressure.^{1,2,3} While the line intensity is conserved over the line core and far-wing spectral regions, failure to account for this redistribution leads to observable depletion in the core line intensity as a function of pressure. This work reports cavity ring-down spectroscopy measurements of core line intensities and pressure-dependent line intensity redistribution in the 0.76 µm oxygen band. We compare the core intensity depletion magnitude and rotational quantum number dependence to those predicted by renormalized classical molecular dynamics simulations. Additionally, we discuss how including these previously unaccounted-for physics might affect satellite and remote sensing retrievals.

¹Z. D. Reed, et al., *Phys Rev Lett*, 130(14), 143001 (2023)

²H. Tran, et al., J Chem Phys, 158(18), (2023)

³H. Tran, et al., Phys Chem Chem Phys, 25(15), 10343-52 (2023)

III-4. Recent updates on air-broadened O_2 B-band line shapes: pressure- and temperature-dependencies

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Air-broadened O_2 B-band line shapes were recently for the first time measured in high resolution in laboratory conditions, in pressure range up to 27 kPa and nominal temperatures of 288 K, 296 K and 328 K¹. Complete sets of line-shape parameters, including the speed dependence of the collisional broadening and shift, as well as frequency of the velocity-changing collisions were derived. The temperature dependence of collisional broadening and shift was also determined, whereas no significant dependence on temperature of their speed dependence and the frequency of the velocity-changing collisions was observed. We show that based on determination of the speed dependence of collisional broadening in a single temperature, it is possible to estimate the temperature dependence of the pressure broadening. The line intensities determined from this measurement differ by up to 3% from the previously available values. Although only 20 transitions were measured, including the improved line-shape parameters and intensities leads to 5-fold improvement in determination of the vertical column density reducing the difference between retrievals based on A- and B-band lines².

Additionally, preliminary results of the recent measurement of the ¹⁶O¹⁸O B-band lines will be presented. They indicate a systematic difference between measured and presently available line positions having magnitude of approximately 50 MHz.

¹K. Bielska, D. D. Tran. A. A. Balashov, et al., *Spectrochim. Acta A*, 303, 123185 (2023). https://doi.org/10.1016/j.saa.2023.123185

²P. Edinger, Developing an instrumental setup for atmospheric validation of absorption cross-sections for the O_2 A and B band, master thesis under supervision of André Butz, University of Heidelberg 2023

III-5. Recent developments in the MT_CKD water vapor continuum

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^aAtmospheric and Environmental Research ^bNOAA/Global Systems Laboratory ^cJet Propulsion Laboratory, California Institute of Technology ^dUniversity of Oklahoma School of Meteorology ^eLamont-Doherty Earth Observatory, Columbia University

This talk will include details of the two most recent revisions to the MT_CKD water vapor continuum, versions 4.2 and 4.3.

MT_CKD_4.2 was developed based on an analysis of ground-based observations from the AERI interferometer that demonstrated that the water vapor self continuum is significantly weaker than in the previous version of MT_CKD and the foreign continuum is significantly stronger. The combination of both continuum modifications increases the transparency of the infrared window for most precipitable water vapor (PWV) amounts, has a large impact on the radiative budget for high PWV values, and has implications for climate. An additional feature of MT_CKD_4.2 is that it includes two versions of the foreign continuum, one derived directly from the AERI measurements and another that has been modified from the first version to remove the estimated contribution due to aerosols.

MT_CKD_4.3 includes revised foreign continuum coefficients in window regions for wavenumbers greater than 4000 cm-1 that were derived based on a modification to the MT_CKD line shape formalism that was constrained by results from a series of laboratory studies from the U. Grenoble group led by Alain Campargue.

III-6. Calculating collision-induced absorption spectra

T. Karman

Radboud University, Nijmegen, Netherlands

Collision-induced absorption (CIA) leads to broad features in spectra that arise due to absorption during collisions, when the interactions induce a transient dipole moment. CIA can be important for remote sensing and affect the atmospheric heat balance, even for forbidden transitions or if the individual molecules have no dipole moment and hence negligible monomer absorption. In this talk I will discuss the calculation of CIA spectra from first principles, and highlight some atmospherically relevant examples such as molecular nitrogen and oxygen. The theoretical absorption spectra are also useful for parameterizing experimental spectra, for example to constrain fits of experimental data. Calculations can yield spectra for wide frequency and temperature ranges, that could be hard to access experimentally yet be relevant for applications in astrophysics and exoplanetary science. I will outline our strategy to computing such spectra for many molecules and their collision partners.

POSTER SESSION

P-1. Heterodyne dispersion and absorption cavity ring-down spectroscopy

A. Cygan,^a <u>S. Wójtewicz</u>,^a H. Jóźwiak,^a G. Kowzan,^a N. Stolarczyk,^a K. Bielska,^a P. Wcisło,^a R. Ciuryło,^a D. Lisak^a

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We present a new approach to cavity ring-down spectroscopy (CRDS), which enables fast, highly accurate measurement of both absorption and dispersion of a gas sample¹. The dispersion spectrum is retrieved from a heterodyne detection of the cavity ringdowns with the use of a reference optical frequency locked to the same cavity. This approach is characterized by insensitivity to light intensity measurement inaccuracies which usually poses a problem in traditional CRDS systems. Since this scheme does not require fine frequency tuning of the probe laser through the cavity modes, it is much faster than earlier developed cavity mode dispersion spectroscopy (CMDS)². Therefore, this new approach combines the high speed of CRDS with the high accuracy of CMDS³. The heterodyne CRDS can be used as a reference technique in atmospheric studies, optical thermometry, isotope ratio metrology, and the establishment of primary gas pressure standards.

The performance of this new spectroscopic method was demonstrated on the example of precise measurements of line shapes, intensities, and unperturbed frequencies of the R23 line from the CO (3–0) band and P3 line from the HD (2–0) band. In the analysis of molecular hydrogen line shape, strongly influenced by the narrowing effects, we used the speed-dependent billiard-ball profile (SDBB)⁴ supproted by *ab initio* calculated parameters of Dicke narrowing and the speed-dependent collision broadening and shift. We found that obtained line intensities agree with the thoretically predicted values at permille level.

¹A. Cygan, et al., (2024) arXiv:2403.01961 [physics.optics]. https://doi.org/10.48550/arXiv. 2403.01961

²A. Cygan, et al., Opt. Express 23, 14472 (2015). https://doi.org/10.1364/OE.23.014472

³A. Cygan, et al., *Opt. Express* 27, 21810 (2019). https://doi.org/10.1364/OE.27.021810; K. Bielska, et al., *Phys. Rev. Lett.* 129, 043002 (2022). https://doi.org/10.1103/physrevlett. 129.043002

⁴R. Ciuryło, et al., *Phys. Rev. A* 65, 012502 (2002). https://doi.org/10.1103/PhysRevA.65. 012502

P-2. New high-resolution study of combination bands of SiF_4

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Silicon tetrafluoride (SiF₄) is an important gas in semiconductor technology in the electronic and optical industries, as a precursor for the preparation of various siliconbased materials. It is a trace component of fumarole gases on volcanoes and it has also been suggested that it is present on Io, a volcanic moon of Jupiter. Studying the structural and spectroscopic properties of SiF₄ is also interesting in itself, since spectroscopic studies of this molecule in different spectral ranges provides a detailed understanding of its structure (bond lengths and angles) and properties, such as quantum mechanical features, as well as intra- and intermolecular dynamical processes. Therefore, both line positions and ro-vibrational energy values can be of primary importance.

New spectra were recorded on the AILES Beamline of the SOLEIL Synchrotron facility. Due to the presence of many hot bands, a low temperature (160 K) was required. Silicon tetrafluoride in a natural isotopic composition produces complex infrared spectra. Not less than three stable isotopologues exist in natural abundance: ²⁸ SiF₄ (92.23 %), ²⁹ SiF₄ (4.67 %) and ³⁰ SiF₄ (3.10 %). Thus, the $\nu_3 + \nu_4$ fundamental band of SiF₄ could be analyzed for these three isotopologues. In this band we found four sub-bands whose centres are located very close to each other (less than 5 cm^{-1}). This fact, as well as the possible presence of hot bands of weak intensity, complicates the process of assignment of the lines for this band. As a result, for the $\nu_3 + \nu_4$ band it was possible, based on the assignment of about 2200 lines, to fit more than 30 spectroscopic parameters that allow us to reproduce the experimental spectrum with a standard deviation $d_{rms} =$ 0.733×10^{-3} cm⁻¹. Analyzing $\nu_1 + \nu_2$ band was difficult due to its weak intensity and overlap of the P-branch with the strong ν_3 fundamental band. However, despite this, it was possible for the first time to analyse this band up to the value $J_{max} = 50$ with an accuracy of a few 10^{-4} cm⁻¹ and obtain values of the main parameters with an acceptable standard deviation.

P-3. FIR and MIR laboratory spectra of isobutyronitrile and cyanopropyne at room temperature

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The gas phase infrared spectra of pure cyanopropyne (CH₃C₃N) and isobutyronitrile ((CH₃)₂CHCN) have been recorded at room temperature between 160 and 3500 cm⁻¹ (3-60 μ m) using Fourier transform spectrometer. Absorption cross-sections at room temperature have been derived for these two non cyclic organic molecules and will be proposed for the 2024 update of the HITRAN database. Among the various bands observed, the ν_{10} band of cyanopropyne and the ν_{13} band of isobutyronitrile around 500-560 cm⁻¹ (18-20 μ m) are especially interesting to detect and quantify these molecules in astrophysical objects (such as Titan's stratosphere) through the Texas Echelon Cross Echelle Spectrograph (TEXES) for example.

P-4. CaSDa24: Latest Updates to the Dijon Calculated Spectroscopic Databases

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France

^cUniversité Paris-Est Créteil et Université de Paris, Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), UMR 7583 CNRS, Créteil, France ^dSynchrotron SOLEIL, UMR 8233 CNRS-MONARIS and AILES Beamline,

Saint-Aubin, France



In this talk, we present the latest version of our database cluster, which we have decided to call CaSDa24. This is a set of 10 databases, each operating independently and dedicated to a single molecule. It contains data for CH_4 , C_2H_4 , SF_6 , CF_4 , GeH_4 , CH_3Cl , RuO_4 , UF_6 , SiF_4 and SiH_4 . The relational schemas of these databases are equivalent and optimised to enable the better compromise between data retrieval and compatibility with the XSAMS (XML Schema for Atoms, Molecules and Solids) format adopted by the VAMDC project. Several of them have been updated, and others have been added in regard to our last publication in 2020. The polyad structures are reported and the transitions are precisely described by their energy, their intensity and the full description of the lower and upper states involved in the transitions. Calculations and modeling are carried out by the XTDS/SPVIEW tandem developed in the Dijon group. Theses software use a tensorial model originally developed for spherical tops such as methane and now extended to different symmetries. Finally, all the databases are accessible online for free at the following url http://vamdc.icb.cnrs.fr.

P-5. The Near- and mid-infrared Nitrous oxide Observatory (N₂O) project: a sensitivity analysis

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^aDepartment of Civil, Structural and Environmental Engineering, University at Buffalo ^bEnvironmental Defense Fund ^cHarvard John A. Paulson School of Engineering and Applied Sciences, Harvard University ^dAtmospheric and Environmental Research

The Near- and Mid-infrared Nitrous Oxide Observatory (N2O) project is a comprehensive initiative to enhance the detection and monitoring of N₂O, a potent greenhouse gas. For this purpose, we are conducting a sensitivity study to evaluate different infrared bands in order to find an optimal solution for N₂O remote sensing. Smithsonian PLanetary ATmosphere radiative transfer model (SPLAT) is utilized to model the backscattered solar radiance of the 2- μ m band and a customized line-by-line model is used for simulating longwave thermal radiation from the Earth at the 4- μ m and 7- μ m bands.

Error analysis and forward model simulation are conducted using CrIS-retrieved N₂O/temperature profiles and surface temperature/emissivity. CrIS spectra are from level 1 data of the same pixel, located at -90.37689972° lon and 31.99931717° lat on 8/23/2023 having TC of 4.497K. The analysis includes the implementation of a column-averaging kernel to assess the accuracy of the retrieval process across different strata of the atmosphere. The results show that both short and longwave bands are critical for reducing risk and leveraging the strength of solar and thermal signal detection, with the 4- μ m band exhibiting a lower influence level. High thermal contrast plays a pivotal role in reducing the error and increasing sensitivity. Integration of these infrared bands can substantially improve the efficacy of remote sensing methods for N₂O.

P-6. The New ExoMol Photodissociation Database

Q. Ni, S. N Yurchenko, M. Pezzella, J. Tennyson

Department of Physics and Astronomy, University College London

Photodissociation, the process of breaking chemical bonds through photon absorption, plays a crucial role in astrophysics, particularly in understanding the properties of stars and other celestial bodies. However, obtaining accurate photodissociation rates requires integrating flux and cross-section data, posing challenges due to gaps in the photodissociation cross-section database and the strong temperature-dependence of photodissociation rates¹.

To address this issue, ExoMol, a molecular line list library developed by University College London's theoretical molecular physics group², is undertaking a significant expansion of the database to consider processes at ultra violet wavelengths including photodissociaiton. This project aims to compile temperature-dependent photodissociation cross-section data for over 30 small molecules relevant to astrophysics, filling gaps identified in previous literature. By providing a unified format for photodissociation crosssection data, this initiative simplifies the process for physicists to calculate photodissociation rates and characterize stellar physics properties more accurately. Moreover, the expansion of the ExoMol database to include temperature-dependent photodissociation offers researchers enhanced capabilities for further investigations and, particularly, chemical models of photo driven processes such as those in the upper atmospheres of exoplanets.

¹Pezzella, M., Tennyson, J. & Yurchenko, S. N. "ExoMol photodissociation cross-sections–I. HCl and HF." Monthly Notices of the Royal Astronomical Society 514, 4413–4425 (2022)

²Tennyson, J. et al. The 2020 release of the ExoMol database: Molecular line lists for exoplanet and other hot atmospheres. Journal of Quantitative Spectroscopy and Radiative Transfer 255, 107228 (2020)

P-7. Accurate measurements of some rovibrational bands for diacetylene (C_4H_2) and cyanoacetylene (HC_3N) in the infrared region

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The high-resolution infrared spectrum of diacetylene has been detected by FTIR spectroscopy at the AILES beamline of the SOLEIL synchrotron facility (France) in the region of the ν_4 fundamental band, around 3333 cm⁻¹. This new analysis improves the previous investigations in terms of i) total number of observed transitions, ii) correction of misassigned transitions, iii) introduction of resonance terms previously disregarded. The analysis of the first hot band $\nu_4 + \nu_9 - \nu_9$ is also presented. As far as cyanoacetylene is concerned, the $2\nu_5$ overtone band, around 1313 cm⁻¹, has been remeasured by high-resolution FTIR spectroscopy in Bologna (Italy) and at SOLEIL, with different experimental conditions. Also in this case, the analysis shows a general improvement compared to the previous investigations. Moreover, several perturbations have been identified and analysed. For this molecule, the assignment of the hot-bands $\nu_1 + 2\nu_7 - 2\nu_7$, $\nu_2 + 2\nu_7 - 2\nu_7$, $\nu_3 + 2\nu_7 - 2\nu_7$ relative to the stretching modes ν_1 , ν_2 and ν_3 are presented. The studied bands are very important as they are the second most intense transitions in the infrared spectra of both molecules. The data will be included in the HITRAN database.
P-8. Line lists for four isotopologues of ammonia, NH₂D, ¹⁵NH₃, ND₃, and ND₂H.

<u>F. Tamassia</u>,^{*a*} <u>J. Tennyson</u>,^{*b*} E. Cané,^{*a*} S. N. Yurchenko,^{*b*} O. Smola,^{*b*} K. Batrakov^{*b*} and ExoMol Team

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We present theoretical rotation-vibrational line lists for four isotopologues of ammonia, ¹⁵NH₃, NH₂D, ND₂H and ND₃, computed using the variational program TROVE. The spectroscopic model is based on the empirical potential energy surface and *ab initio* dipole moments surfaces developed and used for the production of the ExoMol line list CoYuTe¹ for ¹⁴NH₃. The line lists ranges up to 10 000 cm⁻¹ ($\lambda \ge 1 \mu$ m) and cover the rotational excitations up to J = 30. To improve the accuracy of the line positions, the theoretical energies are replaced with extensive sets of experimentally-derived energy levels, where available, produced using the MARVEL procedure. Comparison with the recent experimental spectra show excellent agreement and illustrate the potential of the line lists in detections and spectroscopic analysis. The line lists in ExoMol format will be made available from www.exomol.com.



¹P.A. Coles, S.N. Yurchenko and J. Tennyson. Mon. Not. Roy. Astron. Soc., 490, 4638 (2019).

P-9. The ExoMol Database: developments and the 2024 data release

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The desire to characterize and model the atmospheres of the many extrasolar planets that have been discovered over the last three decades is a major driver of current astronomy. This goal is impacted by the lack of spectroscopic data for the molecules in question since it requires significant quantities of spectroscopic data, in many cases billions of lines, to accurately reproduce the spectroscopic features of the atmospheres of hot exoplanets.

The ExoMol database www.exomol.com provides molecular data for about 100 molecules plus many more isotopologues. These data are widely used for interpreting spectra and modelling exoplanets and other hot atmospheres. The core of the ExoMol database is comprehensive high-temperature molecular line lists; see the 2024 data release¹. The table summarizes some recent developments in the ExoMol project.

Table 1: Recent developments in the ExoMol database.

- 1 26 extra ExoMol line lists since the 2020 release.
- 2 | The use of the MARVEL procedure to create high accuracy line lists (35 + molecules).
- 3 PyExoCross: a python package to post-process both ExoMol and HITRAN line lists.
- 4 Creation of a new database of temperature-dependent photodissociation cross sections.
- 5 | High-resolution line list database ExoMolHR.
- 6 Ancillary database LiDB: vibronic state radiative lifetimes for plasma processes.
- 7 Adopting IAEA (International Atomic Energy Agency) standards for molecular data.
- 8 Use of JSON format for the line list APIs (Application Programming Interface).
- 9 Extended and improved provision of collisional broadening parameters.
- 10 Extension to UV wavelengths.
- 11 Consideration of predissociation and continuum absorption.

¹J. Tennyson et al. JQSRT (submitted).

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Atmospheric models play a key role in our understanding of planets within our Solar System and exoplanets, and they can be considered as important as observations. Unfortunately, these models are limited by the lack of in situ laboratory data collected at pressures and temperatures like the ones observed in some of these planets. Among others, this lack of data includes measurements of Collision-Induced Absorption (CIA) phenomena of infrared radiation, whose correct parameterization is essential for accurate modeling of planetary atmospheres because of their appreciable contribution to the total absorption of radiation¹. To address this knowledge gap, we present here an experimental Fourier Transform InfraRed (FTIR) spectroscopy study of absorption processes in hot and dense, predominately CO_2 atmospheres, with a focus on the CO_2 - CO_2 CIAs. The experiments have been carried out at the Hot Environments Lab at NASA-GSFC using a short pathlength (3 cm) environmental cell under conditions from ambient temperature and pressure to 1000 Kelvin and 60 bars respectively. In particular, spectra around the $\nu_1/2\nu_2$ Fermi dyad monomer vibrational transition at 7.5 μ m have been systematically collected to investigate the temperature dependence of CIAs up to 500 K. The obtained binary absorption coefficients $(k^{(2)}(\nu))$ show good agreement with the HITRAN catalogue up to the maximum temperature therein (350 K). At higher temperatures, the integrated intensities of the two Fermi dyad bands $(S_{CO_2-CO_2})^2$ show an increase with temperature. In addition, experimental results of CO_2 - CO_2 CIAs at pressure-temperature conditions that simulate a descent in the Venus' atmosphere are presented.

¹Karman, Tijs, et al. "Update of the HITRAN collision-induced absorption section." *Icarus* 328 (2019): 160-175.

²Y. I. Baranov, W. J. Lafferty, and G. T. Fraser. "Infrared spectrum of the continuum and dimer absorption in the vicinity of the O_2 vibrational fundamental in O_2/CO_2 mixtures." Journal of molecular spectroscopy 228.2 (2004): 432-440.

P-11. Updating the CO_2 line list in HITEMP: Demonstrating challenges for theoretical line lists

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The HITEMP database¹ (www.hitran.org/hitemp) provides accurate line-by-line spectroscopic parameters for eight molecules: H_2O , CO_2 , N_2O , CO, CH_4 , NO, NO_2 , and OH. These HITEMP line lists are suitable for high-temperature environments including combustion monitoring or calculating radiative transfer of stellar, brown dwarf, and exoplanetary atmospheres.

Based on evaluations of several sources of data, the CO_2 line list in HITEMP is being updated using the recent AI-3000K infrared line list² as a base. AI-3000K contains over 36 billion transitions for the four most abundant isotopologues (${}^{12}C^{16}O_2$, ${}^{13}C^{16}O_2$, ${}^{16}O^{12}C^{18}O$, ${}^{16}O^{12}C^{17}O$). For HITEMP, an "effective" line methodology has been developed to reduce the total number of lines by two orders of magnitude, thereby making the line list practical to use for typical applications. AI-3000K has been validated against room and high-temperature experimental measurements and provides excellent agreement up to 1770 K for the MIR regime, with a few exceptions. For instance, some bands, especially those that exhibit strong Fermi resonances, require adjusting to experimental values. In addition, there has been evidence³ to indicate that *ab initio* dipole moments or potential energy surfaces can be sensitive to sequences of bands⁴ when predicting weak intensities in the NIR. This poster will present how these challenges are being addressed for the forthcoming HITEMP update.

¹Rothman, et al. *JQSRT*, 111, 2139 (2010). https://doi.org/10.1016/j.jqsrt.2010.05.001

²Huang, et al. *JQSRT*, 392, 111748 (2023). https://doi.org/10.1016/j.jms.2023.111748

³Balashov, et al. *JQSRT*, 320, 108978 (2024). https://doi.org/10.1016/j.jqsrt.2024.108978

⁴Huang, et al. J. Chem. Phys. A, 126, 5940-5964 (2022). https://doi.org/10.1016/j.jms.2023. 111748

P-12. Empirical models of the pressure broadening parameter of methane

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Knowledge of accurate spectral parameters of methane transitions is very important in atmospheric and planetary sciences. With that, the line shape parameters, including line mixing, remain to be the major source of uncertainties. HITRAN¹ database sources its methane line shape parameters from many different sources. Unfortunately, some of them are not well traceable, and as such can present inconsistencies and gaps throughout the spectrum. In an effort to improve HITRAN, the present work aims to provide a simple and consistent solution to model the pressure-induced parameters and predict them at a wide range of rotational quanta. Considering the wealth of data in the ν_3 band, we chose it as a benchmark. For this purpose, we gathered the values from previous experimental and theoretical work focused on methane spectra. Several studies using different collision partners conducted after the year 2000 were included. The parameters were separated according to their rotational symmetry, ranking index, branch, and line profile used and fit to an empirical Padé approximant. We present the results of these fits, the recurring patterns appearing in the broadening, as well as a comparison of the predictions with theoretical calculations. Having a consistent set of parameters per profile allows for better parametrization of line mixing as the next step.

¹I. E. Gordon, L. S. Rothman, R. J. Hargreaves, et al., *JQSRT*, 277, 107949 (2022). https://doi.org/10.1016/j.jqsrt.2021.107949

P-13. MARVEL analysis of high-resolution rovibrational spectra of CO₂ isotopologues

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We present a series of studies, carefully analyzing experimental high resolution rovibrational spectra of CO₂ isotopologues. The MARVEL (measured active rotation vibration energy levels) procedure is used to build sets of empirical ro-vibrational energy levels. Each MARVEL project aims to: 1. Provide a comprehensive quantitative and qualitative review of experimental literature, assessing accuracy indicators, and suggesting corrections such as re-labelling of energy levels, re-assignment of isotopologue identification and re-calibration of frequencies. 2. Build an empirical ro-vibrational energy levels dataset, produced from the compiled experimental frequency data. 3. Provide a qualitative assessment of the theoretical literature (CDSD and Ames), through comparisons with the compiled experimental frequencies and our obtained empirical energy levels dataset. In each case the spectroscopic networks utilize a weighted least-squares refinement to yield an assessment of accuracy and recommended energy levels. So far we have completed projects for ${}^{13}C{}^{16}O{}_{2}{}^{1}$ and ${}^{16}O{}^{12}C{}^{18}O{}^{2}$, while further work on the parent isotopologue ${}^{12}C{}^{16}O{}_{2}$ is nearly complete as is work on a combined study of ${}^{18}O{}^{12}C{}^{18}O{}$, ${}^{17}O{}^{12}C{}^{18}O{}$ and ${}^{18}O{}^{13}C{}^{18}O{}$; the remaining isotopologues will be considered in due course.

¹M. T. I. Ibrahim, D. Alatoom, T. Furtenbacher, A. G. Császár, S. N. Yurchenko, A. A. Azzam, J. Tennyson, *J. Comput. Chem.* 2024, 45, 969.

²D. Alatoom, M. T. I. Ibrahim, T. Furtenbacher, A. G. Császár, M. Alghizzawi, S. N. Yurchenko, A. A. Azzam, J. Tennyson, *J. Comput. Chem.* 2024, in press

P-14. Line Shape Parameters for the CO₂-H₂O Collision System

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Complex Robert-Bonamy-Ma calculations were made for the CO_2 -H₂O collision system using an intermolecular potential comprised of quadrupole-dipole, quadrupole-quadrupole, Lennard-Jones atom-atom, induction, and London dispersion terms. The initial atomatom parameters were obtained using combination rules and the other parameters from taken from the literature. The intermolecular potential was then adjusted to give results that agree with the measurements of Sung *et al.*¹ The final potential results (pot 46) compared with the data of Sung *et al.* have an average percent difference of 0.11 and a standard deviation of 0.993 percent. Calculations were then made for all transitions in the 00011-00001 band with J" from 0 to 120 at 13 temperatures from 200 to 3000 K. The speed dependence of the half-width and line shift were computed for use in more advanced line shape models. The temperature dependence of the half-widths and line shifts were determined using the double power-law (DPL) model of Gamache and Vispoel ².

From these data, a routing to predict γ and δ at the temperatures of this study for any CO₂ transition was developed.

¹K. Sung, L. R. Brown, R. A. Toth, T. J. Crawford, *Can. J. Phys*, 87, 469 (2009). https://doi.org/10.1139/P08-130

²R. R. Gamache, B. Vispoel, *JQSRT*, 217, 440 (2018). https://doi.org/10.1016/j.jqsrt.2018.05.019

P-15. CRBM calculations of Line Shape Parameters for the H₂O-He Collision System

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Complex Robert-Bonamy-Ma (CRBM) calculations were made for the H₂O-He collision system using an intermolecular potential comprised of Lennard-Jones atom-atom, induction, and London dispersion terms. The initial atom-atom parameters were obtained using combination rules and the other parameters from taken from the literature. The intermolecular potential was then adjusted to give results that agree with the measurements of Koshelev *et al.*¹ for the 183 and 380 GHz lines of H₂O. The final potential results (pot 35) compared with the data of Koshelev *et al.* have an average percent differences for γ of 0.83 and -0.63 percent, respectively and differences in δ of 0.000071 and -0.000027 cm⁻¹ atm⁻¹, respectively. Calculations were then made for all unique rotational transitions of H₂O on HITRAN2020². at 13 temperatures from 200 to 3000 K. The speed dependence of the half-width and line shift were computed for use in more advanced line shape models. The temperature dependence of the half-widths and line shifts were determined using the double power-law (DPL) model of Gamache and Vispoel ³ and the standard power law model.

¹Private Communication, 2017

²I. E. Gordon, L. S. Rothman, R. J. Hargreaves, et al., *JQSRT*, 277, 107949 (2022). https://doi.org/10.1016/j.jqsrt.2021.107949

³R. R. Gamache, B. Vispoel, *JQSRT*, 217, 440 (2018). https://doi.org/10.1016/j.jqsrt.2018. 05.019

P-16. High Precision Measurements and CRBM calculations of Line Shape Parameters for the $H_2O-N_2Collision$ System

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Laboratory measurements to H_2O transitions broadened by N_2 were made for three N_2 -mixture spectra in the ν_2 band at room temperature using the high-resolution Fourier transform spectrometer (Bruker IFS-125HR) at the Jet Propulsion Laboratory. The high-precision spectrum fitting package, Labfit, was used to analyze the spectra. The half-widths and pressure shifts were retrieved by fitting all the three spectra simultaneously, and holding their line intensities to the HITRAN values. Combining the N_2 -broadened data with previous results for O_2 -broadening,¹ air-broadened data were determined. Using the pairing rules of Ma *et al.*² transitions were selected with pairs that agree to 1.5 % and air-broadening values that agree with the data of Birk and Wagner³ to better than 1.5 % were selected. This procedure generated 50 lines of exceptional precision. Complex Robert-Bonamy-Ma calculations were made to adjust the H₂O-N₂ intermolecular potential. Results of the final potential fit are presented and calculations will be made to produce air-broadening data for the HITRAN database. Government sponsorship acknowledged.

¹R. R. Gamache, N. G. Orphanos, K. Sung, and G. C. Toon, *Mol. Phys*, e2281592 (2024). https://doi.org/10.1080/00268976.2023.2281592

²Q. Ma, R. H. Tipping, N. N. Lavrentieva, Mol. Phys. 110, 307, 2012, https://doi.org/10.1080/00268976.2011.646333

³M. Birk, G. Wagner, JQSRT. 113, 889, 2012, https://doi.org/10.1016/j.jqsrt.2011.12.013

P-17. Trace and planetary gases in HITRAN2024

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The HITRAN2020 edition¹ features line lists for dozens of trace gases and planetary gases (i.e. those that are not typically abundant in the terrestrial atmosphere, for instance, PH₃ and GeH₄). Some of the line lists, e.g., SO₂, receive very substantial updates and expansions with respect to previous editions. However, many line lists are still limited only to a few selected bands, and the quality of parameters often leaves room for improvement. For example, nitric acid (HNO₃) and diacetylene (C₄H₂) line lists in HITRAN still lack some of very strong bands at 3 μ m. This poster will briefly summarize the work toward improving the spectroscopy of trace and planetary gases in the 2024 edition. This effort includes eliminating some errors found in the 2020 edition, validating and implementing new data, improving and extending parametrization of the spectral properties in the database, as well as improving user experience. The most important aspects of these improvements will be highlighted.

¹I. E. Gordon, L. S. Rothman, R. J. Hargreaves, et al., *JQSRT* 277, 107949 (2022). https://doi.org/10.1016/j.jqsrt.2021.107949

P-18. A new ${}^{13}CH_4$ linelist in the Octad region updated with quantum assignments and lower state energies through a two temperature method

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As part of the JPL Summer Internship project in 2021 and 2022, we made an effort to update quantum identification and lower state energies in existing 13CH4 linelists in the 4000 - 4700 cm⁻¹ region, by using the HITRAN 2020 database, an in-house linelist of the JPL GFIT package (atm.161), and model predictions. Updates were carried out by generating synthetic spectra at two temperatures (296 and 80 K), based on the aforementioned linelists, and evaluating them against laboratory FT-IR spectra at both temperatures. Their corresponding line matching and identification was conducted line-by-line to update any missing fields or inconsistecies from their observed features, resulting in the number of transitions assigned from 761 in the HITRAN 2020 to 3712 in the intership project of 2021 (Broussard+Toon 2021), and further extended to 4673 in that of 2022 (Coy+Broussard+Toon 2022). Since accurate spectroscopy is the cornerstone to atmospheric remote sensing, results from this work are expected to make a significant contribution to the wider community, from (exo)planetary science to Earth science, in support of various NASA science missions. ¹

¹Government sponsorship acknowledged.

P-19. Familiar and foreign pale blue dots - 3D simulations of the Earth as an exoplanet

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The pale blue dot, Voyager capturing the unresolved light of the Earth from a distance of 40 AU, is one of the most humbling astronomical observations. Planned future observatories, such as the Habitable Worlds Observatory, may one day image planets just like ours, but what can we learn from these faint worlds? What are the physical processes that result in the iconic color of our world? In this work, we reproduce several space-based observations of the Earth and study the underlying radiative transfer processes ¹. The 3D interface of the Planetary Spectrum Generator, a tool called GlobES, is used to simulate high spatial resolution (roughly 200x200 km) spectra of the planets' disk, using historic weather data, ground coverage, and molecular abundances². Included in the study are Mie scattering from clouds and aerosols, Rayleigh scattering, oceanic specular reflection, spectral reflectance curves from the five main ground cover types, and the major spectroscopic absorbers in the UV-visible. It is shown that aerosols contribute an important part to the characteristic color of the Earth. We demonstrate that our relatively simple model accurately reproduces the intensity and spectra of the Earth as seen in the DSCOVR/EPIC bands, demonstrating the power of the simulations.

Next, our simulated pale blue dots are studied using telescopic model for a potential configuration of the Habitable Worlds Observatory. The relevance of clouds in the detectability of the major atmospheric signatures, O_2 , O_3 and H_2O , is demonstrated, as they significantly enhance the number of photons returned from a planet. An outlook is given for the implications of the 3D studies for the study of faint exoplanets.

¹Kofman, V., Villanueva, G., Fauchez, T. *et al.*, The pale blue dot: Using the Planetary Spectrum Generator to simulate signals from hyper realistic exo-Earths. PSJ, under review.

²https://psg.gsfc.nasa.gov/

P-20. Isotopologue dependence of γ and δ for the CO₂-air Collision System: ¹³CO₂ vs ¹²CO₂

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Fourteen transitions of the 20012-00001 band of ${}^{13}\text{CO}_2$ in air have been recorded at room temperature using a cavity ring-down spectrometer linked to an optical frequency comb referenced to a GPS-disciplined Rb oscillator. The comb-coherence transfer (CCT) technique was applied to obtain a RF tunable narrow-line laser comb-disciplined source using an external cavity diode laser and a simple electro-optic modulator. For each transition a multi-spectrum fit was used with a speed dependent Nelkin-Ghatak line profile to analyze the high S/N (several thousands) spectra recorded at five pressures from 50 to 750 Torr. The air-broadened half-width and air-induced line shift were retrieved for each transition studied. Measurements of ${}^{12}\text{CO}_2$ in air at total pressures from 75 to 760 Torr were made on the FT spectrometer at DLR, Germany, for transitions in the 30012-00001 and 20012-00001 bands, allowing comparison with the ${}^{13}\text{CO}_2$ data.

A refinement to the simple model proposed in the Appendix of Lamouroux *et al.*¹ was made by assuming that γ is proportional to $v_{rel}(T)$, the thermally averaged relative speed which is proportional to $T^{1/2}$ and $(1/\mu)^{1/2}$ where μ is the reduced mass. From the power law temperature dependence n, one can show that γ is proportional to $v_{rel}(T)^{2-2n}$ and thus to $(1/\mu)^{1-n}$. This approximate but very simple expression allows the determination of $\gamma(^{13}CO_2)$ from $\gamma(^{12}CO_2)$.

Complex Robert-Bonamy-Ma calculations were made for ${}^{12}CO_2$ and ${}^{13}CO_2$ in collision with N₂ and O₂ for J" from 0 to 85 for the 20012-00001 band. The intermolecular potential was optimized to the data of Devi *et al.*² for the 30012-00001 band of ${}^{12}CO_2$. From these data the ${}^{13}CO_2$ -air and ${}^{12}CO_2$ -air half-widths and line shifts can be computed and the isotopologue effect studied.

The agreement between the measurements, model, and calculations will be presented.

¹J. Lamouroux *et al.*, *JQSRT*, textbf111, *2321* (2010). https://doi.org/10.1016/j.jqsrt.2010. 03.006

²V. M. Devi, et al., JQSRT **111**, 2355 (2010). doi:10.1016/j.jqsrt.2010.06.003.

P-21. Laboratory Measurements of the Absorption Cross Sections and Pressure-broadening Coefficients of key Exoplanetary Molecules with High Resolution MIR Spectroscopy

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With the increasing detection of exoplanets and the spectroscopic characterization of their atmospheres, our knowledge of extrasolar systems is expanding significantly. Determining fundamental atmospheric properties and characteristics of chemically diverse exoplanets from spectroscopy measurements necessarily requires a rigorous comparison between atmospheric chemical/radiative transfer models and observations. To accurately model exoplanet atmospheres, opacity data of key molecules (e.g., H_2O , CO, CO_2, CH_4) and background gases at relevant temperatures are required. Incorporating opacity data with inaccurate spectral intensity, line position, and pressure broadening coefficients in radiative transfer modeling could lead to inaccuracies in chemical characterization and inaccurate thermal profile (T[P]). Here, we present preliminary results of high-resolution mid-infrared (MIR) absorption measurements at room temperature of methane broadened through self-broadening and with various background gases $(H_2,$ He, CO_2). The measurements are conducted using a multipass cell (IRsweep 15) with an effective path length of 15 m to allow the measurements of absorbers at very low concentrations. A cw-OPO laser (from Toptica) is used to probe the CH stretching of methane in the 2900-2950 cm^{-1} at 25 MHz resolutions. The broadening coefficients for each of the transition lines are tabulated and compared between the different broadening gases. The implications derived from these preliminary measurements are discussed.

P-22. X-MASS: a script for simultaneous calculations of cross-sections covering a large parameter space for atmospheric applications

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Interpretation of data from high-resolution remote sensing spectrometers that monitor the concentrations of gases in the terrestrial atmosphere essentially requires reliable spectroscopic information, including that provided in the HITRAN database¹. High spectral resolution molecular absorption calculations over a wide spectral range and diverse parameter space using line-by-line models are often considered too slow to be used in operational retrieval algorithms. Using advanced line-shapes and line-mixing parametrizations, which are necessary for accuracy and available in HITRAN for many molecules (e.g. Hashemi *et al.*²), decreases the speed of calculations even further. As an alternative, retrieval codes often rely on massive sets of pre-calculated look-up tables of absorption cross-sections for target molecules that cover a representative set of environmental conditions. For some missions, such as the NASA Orbiting Carbon Observatory (OCO-2/3)³, molecular absorption coefficients are calculated off-line for a range of pressures, temperatures, and H₂O volume mixing ratios and stored in so-called "ABSCO" lookup tables⁴.

The purpose of the Python script called "X-MASS" is to allow calculation of the massive set of ABSCO tables using the HAPI software package⁵ with complete utilization of the parameters' accuracy in HITRAN, including sophisticated line shapes. The outputs in the convenient HDF5 or NetCDF ABSCO formats will be enabled given a user-defined wavenumber step, set of pressures, temperatures, and diluent gas contents. X-MASS will be an open-source code where users can specify parameters for their applications. A sample set of pre-calculated ABSCO tables, corresponding to the work example and covering the spectral range of molecules at a finer grid and resolution will be provided on the HITRAN website. This work will substantially improve the integration of state-of-the-art spectroscopic data into atmospheric radiative transfer codes. In addition, similar calculations are needed for (exo)planetary atmospheres, and although the resolution there is typically larger, but so is the parameter space, which also requires HDF5 representation of look-up tables.

¹Gordon, I. E., et al. JQSRT 277 (2022): 107949.

²Hashemi, R., et al. JQSRT 271 (2021): 107735.

³Crisp, D., et al. Atmospheric Measurement Techniques 10.1 (2017): 59-81.

⁴Payne, V.H., et al. JQSRT 255 (2020): 107217.

⁵Kochanov, R.V., et al. JQSRT 177 (2016): 15-30.

P-23. Simultaneous High-Resolution Dual-Comb Spectroscopy of Rovibrational and Rotational Bands of Ammonia

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The combination of broadband frequency combs achieved through frequency down conversion via optical rectification (intrapulse difference frequency generation) from a femtosecond laser source and electro-optic sampling in the dual frequency comb configuration offers a novel technique for high resolution molecular spectroscopy over an exceptionally broad mid-IR to THz range $(6.6-200\mu m, 50-1500 cm^{-1})$ with frequency scale referenced to a rubidium atomic clock.¹

To demonstrate the capabilities of this powerful technique, the main advantage of which is electro-optic sampling as detection method that does not require cryogenic mid-IR/THz detectors, we performed simultaneous measurement of rovibrational (at 670-1000 cm⁻¹) and rotational (at 85-120 cm⁻¹) spectra of ammonia molecule with approximately 10-MHz spectral resolution. In addition to the high resolution and high precision of the frequency scale, this technique allows a direct comparison between line strengths corresponding to rovibrational and rotational transitions.

¹D. Konnov, A. Muraviev, S. Vasilyev, K.L. Vodopyanov, APL Photonics 8, 110801 (2023)

SESSION IV: Spectroscopy for Planetary Studies

IV-1. Ab initio computing of collisional properties for spectral lineshapes and intensities

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In astrophysics or planetary sciences, molecular spectral lines are now observed with great precision, thanks in particular to the ALMA and JWST observatories, as well as to several recent planetary probes. Relating the intensity and shapes of such spectral lines to the actual astrophysical/planetary conditions is no trivial task. It has been known for a long that the collisional properties of the gas have to be described in detail, in order to understand intensities, self-absorption, and lineshapes, in the IR or mm spectral ranges¹. The need is becoming pressing, for reliable modeling of the interaction of key molecules $(CO, H_2O, CO_2, CH_4$ to name a few) with the atmospheric background gas molecules $(H_2, He, H_2O, CO_2)^2$, in order to try and lift the degeneracy of atmospheric models.

Theoretical analysis of molecular collisions by quantum dynamical computations is nowadays possible and allows for precise, converged computations of lineshapes and line shifts. We shall present several schemes for such computations, with emphasis on the key H₂O and CO₂ molecules, beginning with *ab initio* potential energy surfaces all the way to the comparisons with experiments³ and to pressure broadening coefficients predictions.

We envision a pipeline of such a quantum dynamical chain of computations, thanks to the the use of massively parallel super-computers and to the scalability of the approach.

 $^{^1 \}rm See$ e.g. Hernández-Gómez, Sahnoun et al., 2019, https://doi.org/10.1093/mnras/sty2971 $^2 \rm Niraula,$ de Wit et al., 2022, https://doi.org/10.1038/s41550-022-01773-1

³Drouin and Wiesenfeld, 2012, https://doi.org/10.1103/PhysRevA.86.022705; Faure, Wiesenfeld *et al.*, 2013, https://doi.org/10.1016/j.jqsrt.2012.09.015

IV-2. Water-Vapor Absorption Database using Dual Comb Spectroscopy from 300-1300 K: Self- and Air-Broadened H₂O, 6600 to 7650 cm⁻¹

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We present broadband dual frequency comb laser absorption measurements of pure H_2O (natural isotopic abundance of 99.7% $H_2^{16}O$) and 2% H_2O in air from 6600-7650 cm⁻¹ (1307-1515 nm) with a spectral point spacing of 0.0068 cm⁻¹. Twenty-nine datasets were collected for each measurement composition at temperatures between 300 and 1300 K (±0.82% average uncertainty) and pressures ranging from 0.5 to 16 Torr for pure H_2O (±0.27%) and 20 to 600 Torr for 2% H_2O in air (±0.25%), with an average residual absorbance noise of 8E-4 across the spectra for all 58 measurements. We fit measurements using a quadratic speed-dependent Voigt profile to determine 24118 spectroscopic line parameters for 5986 individual transitions listed in HITRAN2020¹, using a multispectrum curve-fitting algorithm to secure the best possible consistency among the measurements and line parameters.

The measured parameters include line strength, line center, self-broadening, self-shift, air-broadening, and air-shift, along with their single power law temperature-dependence exponents, and speed-dependent width parameters. Other parameterizations for width and shift temperature-dependence, namely using the double power law equation, are also explored.

In aggregate, the modified database reduces the measured spectra absorbance error to 9E-4, compared to 3E-3 for the HITRAN2020 database, with spectral noise as the dominant remaining residual. We also measured line parameters for an additional 574 features not presently catalogued in the HITRAN2020 database.

¹I. E. Gordon, L. S. Rothman, R. J. Hargreaves, et al., *JQSRT*, 277, 107949 (2022). https://doi.org/10.1016/j.jqsrt.2021.107949

IV-3. New H_2O broadened by CO_2 collisional parameters: from lab to atmospheric retrievals

 $\frac{\acute{\mathbf{E}}. \ \mathbf{Ducreux},^{a,b,c}}{\mathbf{R}. \ \mathbf{R}. \ \mathbf{Gamache},^{d} \ \mathbf{L}. \ \mathbf{R}\acute{\mathbf{e}} \mathbf{galia},^{a} } \mathbf{S}. \ \mathbf{R}\acute{\mathbf{h}} \mathbf{S}. \ \mathbf{S$

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From the lab: To prepare the next missions to Venus, collisional parameters of H_2O broadened by CO_2 need to be known. In continuation of the article published in 2019¹, new spectra were recorded with a high-resolution infrared Fourier transform spectrometer coupled with a 2-meter White cell, in the 2.7 μ m spectral region. The line parameters were then determined with a multispectrum fitting procedure using the Voigt profile, leading to characteristic W-shape residuals. Those have been reduced using beyond-Voigt line shape models: Rautian, speed-dependent Voigt and speed-dependent Rautian profiles. Within the experimental conditions used in this study, our analysis showed that speed dependence effects of the collisional parameters need to be considered to reduce the residuals, resulting in a improvement of the determined line shape parameters. An article has just been accepted for publication².

To atmospheric retrievals: Built using the Modified Complex Robert-Bonamy formalism, a new H₂O broadened by CO₂ collisional parameters linelist combined with the one published in 2019¹ was used to simulate Venus atmospheric spectra. Theoretical retrievals were then performed in the 1.17 μ m and 2.34 μ m spectral regions which will be observed during the future space mission to Venus, EnVision. The impact of the new line parameters was studied and quantified, showing the crucial need of the planetary community for CO₂-collisional parameters of H₂O lines.

¹L. Régalia, E. Cousin, R. R. Gamache, et al., *JQSRT*, 231, 126 (2019). 10.1016/j.jqsrt.2019.04.012

²É. Ducreux, B. Grouiez, S. Robert, et al., *JQSRT*, Accepted (2024). 10.1016/j.jqsrt.2024.109026

IV-4. Pressure broadening of N_2O :He for characterising exoplanetary atmospheres.

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Nitrous oxide (N_2O) is a well studied greenhouse gas present in our atmosphere, it has many known sources on Earth, including production via anaerobic bacteria in soil. N_2O had been observed on Mars and is expected to exist in exoplanets. Due to its biological link, it has been proposed as a potential biomarker. The infrared spectrum of N_2O has been extensively studied and is well documented and accessible in HITRAN, where the line positions and intensities are vital for the identification of this species in Earth's and other planetary atmospheres. Understanding the impact of dominant gases, however, on the trace species at varying temperatures and pressures is required to accurately quantify the molecular abundances. While the impact of air and self-broadening of N_2O has been thoroughly investigated, the impact of other dominant species is still lacking. Over 5000 exoplanets have been observed with varying sizes, temperatures, pressures, and chemical compositions and it is important to be prepared for a range of different environments. A large portion of these observed planets and the focus of recent JWST-based atmospheric measurements are gas-giants, where the dominant species in these atmospheres are H_2 and/or He. Minimal experimental data on the broadening effect of He on N_2O is available in the literature, where the previous work 1,2 is not sufficient to provide a sufficient model. I will, therefore, present on our work to provide the broadening coefficients of N_2O with He using high-resolution infrared spectroscopy to confirm and improve these values.

¹T. Nakayama et al. Chemical Physics, 334.1-3, 196-203 (2007)

²N. Tasinato *et al.* The Journal of Chemical Physics 132.16 (2010)

IV-5 Utilizing Experimental Based Line Positions for Semi-empirical IR Line Lists

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Molecular IR line lists computed from semi-empirically refined *ab initio* potential energy surface and high quality *ab initio* dipole moment surface may have line position accuracy typically within $0.01 - 0.05 \text{ cm}^{-1}$. For high-resolution spectroscopy databases, it is necessary to integrate the computed theoretical IR intensities with the line positions accurately determined from experiments and (or) reliably derived from Effective Hamiltonian models. However, it is not a trivial task, and the choices in reality are heavily contingent upon the coverage, consistency, and accuracy of the data available for a specific molecule or isotopologue. We will present several approaches applied to recent Ames IR line lists of CO_2^1 , N_2O^2 , and OCS to demonstrate how challenging such integration may become, and what we have learned from these projects. Discussions will focus on the relation between each different scenario and the corresponding choice or solution, including their advantages and limits, how the semi-empirical IR line lists can help, and what else may be needed for future improvements. We will emphasize that the "Theory+Experiment" synergy may still play significant role in the determination of the best line positions.

¹X. Huang, R. S. Freedman, S. Tashkun, et al., *J. Mol. Spectrosc.*, 392, 111748 (2023). https://doi.org/10.1016/j.jms.2023.111748

²X. Huang, D. W. Schwenke, and T. J. Lee., *Mol. Phys.*, e2232892 (2023). https://doi.org/10. 1080/00268976.2023.2232892

IV-6 Advances in laboratory studies of high-temperature and high-pressure spectroscopy for planetary atmospheres

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There are noted and significant shortcomings in the availability and accuracy of fundamental gas phase chemistry and spectroscopy input parameters used in the construction of exoplanet atmospheric models and the interpretation of observations.¹ In particular, deficiencies are most prevalent at conditions and compositions that deviate substantially from the atmosphere of Earth, for which the highest-fidelity data are available (such as HITRAN). These shortcomings inherently limit the certainty with which conclusions may be drawn from the remarkable exoplanet spectra presently being collected. Fortuitously, high-temperature and high-pressure gas-phase spectroscopy has been well-studied for its relevance to a number of engineering disciplines, including combustion science, hypersonics, propulsion, and chemical engineering. Although the species of interest within these disciplines may somewhat diverge from those of relevance to the planetary science community, the range of temperatures and pressures have substantial overlap, and the toolsets for laboratory study are broadly applicable. Of particular note are the use of shockwave heating and laser absorption spectroscopy for the determination of temperature- and pressure-dependent fundamental spectroscopic parameters, such as opacities, pressure broadening, line mixing, and collision-induced absorption (CIA). Recent efforts by the authors to adapt these capabilities to knowledge gaps in the interpretation of exoplanet spectra will be discussed. These include improvements to alkali metal lineshapes,² construction of a high-temperature opacity database for large molecules,³ empirical line-mixing models for small molecules⁴, the development of pseudo-line-lists ⁵, and measurements of CIA of homonuclear molecules.

¹Fortney, J. J., et al. (2019) Astro2020 Sci. White Paper; Exoplanet Science Strategy (2018), The Nat. Acad. Press.

²Ding, Y., et al. (2021) JQSRT, 275, 107895; Ding, Y., et al. (2022) JQSRT, 283, 108149

³Strand, C. L., et al. (2019) JQSRT, 222, 122; Ding, Y., et al. (2019) JQSRT, 254, 396; Ding, Y., et al. (2020) JQSRT, 255, 107240

⁴Su, W. W., et al. (2022) JQSRT, 278, 107997; Su, W. W., et al. (2022) J. Mol. Spec., 390, 111699. ⁵Su, W. W., et al. (2024) JQSRT, (submitted).

IV-7. The Ammonia spectrum in the mid-IR region.

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The present contribution is an overview of our recent studies 1,2,3 devoted to the $3900-6350 \text{ cm}^{-1}$ range of the ammonia spectrum and their implications for the upcoming edition of the HITRAN database.

To provide a comprehensive line list based on these datasets, special care was given to (i) verification of the assignments and correction of discrepancies present in the published line lists, (ii) identification of ¹⁵NH₃ transitions with intensity larger than 10^{-23} cm/molecule, (iii) providing the "best possible" line intensities with respect to existing studies and, if possible (iv) extending the line list towards 8000 cm⁻¹ relying on earlier works ^{4,5}.

This research was supported by the Slovak Research and Development Agency (APVV-19-0386) and Scientific Grant Agency (VEGA-1/0710/24).

¹P. Cacciani, P. Čermák, O. Votava, J. Vander Auwera, A. Campargue, *Mol. Phys*, 122, e2256893 (2024). https://doi.org/10.1080/00268976.2023.2256893

²P. Cacciani, P. Čermák, J. Vander Auwera and A. Campargue, *JQRST*, 292, 108350 (2022). https://doi.org/10.1016/j.jqsrt.2022.108350

³P. Cacciani, P. Čermák, J. Vander Auwera and A. Campargue, *JQRST*, 277, 107961 (2022). https://doi.org/10.1016/j.jqsrt.2021.107961

⁴J. El Romh, P. Cacciani, F. Taher, P. Čermák, J. Cosléou, and M. Khelkhal, *J. Mol. Spectrosc.*, 326, 122–129 (2016). https://doi.org/10.1016/j.jms.2016.04.005

⁵T. Földes, T. Vanfleteren, A. Rizopoulos, M. Herman, J. Vander Auwera, *et al.*, *JQRST*, 179, 112-125 (2016). https://doi.org/10.1016/j.jqsrt.2016.03.018

IV-8. High-resolution infrared spectroscopy of molecules of cometary interest

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Comets are small icy bodies that are leftovers of the formation of the Solar system. As they are now located very far from the Sun, their composition have remained pristine, and they are considered fossils of our Solar system, containing crucial information about the conditions that prevailed nearly five billion years ago. The majority of comets observations are made from the ground when comets come closer to the Sun and start sublimating, revealing their inner composition through the formation of a coma.

Among the limited number of space missions dedicated to cometary science, the spacecraft Rosetta launched in 2004 significantly enhanced our understanding of those small bodies, by conducting a two-year study of the comet 67P/Churyumov-Gerasimenko. One of Rosetta's instrument, the mass spectrometer ROSINA, discovered numerous chemical species in the coma that had never before been observed in comets¹. Given the rarity of space missions, these findings must be generalized to ground-based cometary observations to improve our overall understanding of comets.

From high-resolution spectra obtained at the AIMES beamline of the SOLEIL synchrotron facility, positions and intensities of emission lines of three vibrational bands of chloromethane (CH₃Cl) and one vibrational band of cyanogen (C₂N₂) were obtained. Those two cometary molecules detected by ROSINA are yet to be detected from groundbased observations. A cometary fluorescence model for one of the band of chloromethane is currently being developed from our derived parameters. This model will allow us to investigate the presence of this molecule in cometary spectra.

¹Altwegg, K. (2017). Chemical highlights from the Rosetta mission. Proceedings of the International Astronomical Union, 13(S332), 153-162.

IV-9. Cold molecular hydrogen

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Due to its simplicity, H₂ constitutes a perfect tool for testing fundamental physics: testing quantum electrodynamics, determining fundamental constants, or searching for new physics beyond the Standard Model. H₂ has a huge advantage over the other simple calculable systems of having a set of a few hundred ultralong living rovibrational states, which implies the ultimate limit for testing fundamental physics with H₂ at a relative accuracy level of 10^{-24} . The present experiments are far from this limit. I will present our so far results and ongoing projects aimed at exploring this huge potential with cold H₂. I will present our recent H₂ spectra collected with a high-finesse optical cavity cooled down to a deep cryogenic temperature (T = 5 K). I will present our new ongoing project aiming at trapping cold H₂.

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IV-10. Fleshing Out Spectral Space

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Ideally, our spectral databases would model the absorption cross-sections for every molecule present in arbitrary-temperature gaseous environments to high accuracy and completeness. However, with finite resources, we need to constrain our models of spectral space and understand the impact of the data we are missing.

The first source of missing data is molecules we don't even consider. Enumerating the chemical space relevant for different atmospheres is a quite open question, with machine learning, molecule generation, and complex chemical models likely to play a role in creating lists of thousands of molecules of interest and ideally their likely abundance in various atmospheres.

From experience, many of these identified molecules will have no spectral data readily searchable. To address this challenge, inspired by the RASCALL approach of Sousa-Silva, my group has recently developed a high-throughput, highly automated method using computational quantum chemistry for predicting vibrational band centres of small organic-like molecules relevant for temperate atmospheres that is being extended to cross-sections and higher temperatures. This approximate data allows shortlisting of molecules of interest for a particular application like identifying unknown spectral lines.

For molecules with known or likely importance, labor-intensive but very successful approaches to produce high quality line lists have been well established and are continually improving, producing, for example, the 55 molecules in the line-by-line section of the HITRAN database and the 95 molecules within the ExoMol database. However, even these datasets have limitations that must be understood. I will focus here on simple general approaches to understand and improve the suitability of a given line list for molecular detection using high-resolution cross-correlation techniques, and identify the experimental data that would most dramatically improve coverage and accuracy.

SESSION V: Needs for Planetary Research

V-1. Atomic and Molecular Databases for the Planetary Community: Access and Challenges

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Atomic and molecular (A&M) data form the foundation of understanding physical and chemical processes within planetary atmospheres. Databases, compilations of spectroscopic parameters, and facility tools are utilized by computer codes to interpret spectroscopic observations and simulate them. In this contribution, we offer insights into two critical aspects essential for advancing our understanding of (exo)planetary atmospheres.

Firstly, we focus on radiative transfer (RT) and inversion codes as powerful tools for characterizing planetary atmospheres. We provide a comprehensive overview of various available codes, equipping researchers with a valuable resource for code selection and application in planetary atmospheric studies¹.

Secondly, the contribution delves into the realm of atomic and molecular (A&M) databases within the (exo)planetary community. We address aspects such as accessibility, organization, limitations, and infrastructures, highlighting their pivotal role in (exo)planetary research².

¹M. Rengel, J. Adamczewski, Front. Astron. Space Sci., Sec. Planetary Science, volume 10, (2023). https://doi.org/10.3389/fspas.2023.1176740

²M. Rengel, *Proceedings of the International Astronomical Union*, vol. 18, no. S371, pp. 87–91, (2022). https://doi.org/10.1017/S1743921323000169

V-2. The Opacity Challenge and Opportunity for Exoplanetary Science

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With an unprecedented influx of JWST observations, atmospheric retrievals are routinely used to extract scientific insights about the exoplanetary atmospheres. Using two cases consisting of a super-Earth and a warm Jupiter synthetic spectra, we performed perturbation tests with nine different versions of cross-sections accounting for various sources of potential uncertainties in the opacity models. This showed opacity-driven limitations lead to an accuracy wall at 0.5-1.0 dex (that is, three- to tenfold) on the reported atmospheric properties, an order of magnitude above the precision targeted by JWST Cycle 1 programs and needed for meaningful C/O-ratio constraints and biosignature identification¹. Fortunately for puffy, hot and high metallicity atmospheres such as WASP-39 b where transmission spectra probe relatively low pressures (< 0.1 bars), the uncertainty of Lorentzian line profiles were below the aforementioned accuracy wall. But observations of temperate sub-Neptunes and super-Earths, where typically higher pressure regimes are probed, the impact of the precision of underlying Lorentzian line profile remains crucial². As for transmission spectroscopy of the metal-rich hot Jupiters, the model inaccuracies are dominated by the incompleteness and inaccuracy of line lists. For all other exoplanets studied in transmission, and for emission spectroscopy studies and climate modeling that depend on deeper parts of a planetary atmosphere, our original findings remain pertinent regarding the need of upgraded broadening and far-wing parametrization. To this end, we suggest a two-tier approach involving cross-retrieval with perturbed opacities and guided improvements in opacity data.

¹P. Niraula et. al "The Impending Opacity Challenge in Exoplanet Atmospheric Characterization," Nature Astronomy, (2022)

²P. Niraula et. al "Origin and extent of the opacity challenge for atmospheric retrievals of WASP-39 b," ApJL, (2023)

V-3. Data needs for the exoplanetary applications: focus on the Ariel space mission

<u>S. Robert</u>,^{*a*} K.L. Chubb,^{*b,c*} C. Sousa-Silva,^{*d*} S.N. Yurchenko,^{*e*}, G. Tinetti,^{*e*} and the Ariel science team

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To fulfil its science requirements, the Ariel space mission¹ has been specifically designed to have a stable payload and satellite platform optimised to provide a broad, instantaneous wavelength coverage to detect many molecular species, probe the thermal structure, identify/characterize clouds and monitor the stellar activity. The chosen wavelength range, from 0.5 to 7.8 μ m, covers all the expected major atmospheric gases from, e.g. H₂O, CO₂, CH₄, NH₃, HCN, H₂S, through to the more exotic metallic compounds, such as TiO, VO, and condensed species.

In the frame of the "Spectral Data and databases" working group, 50+ members of the Ariel science team and colleagues were invited to contribute to a White Paper entitled: "Data availability and requirements relevant for the Ariel space mission and other exoplanet atmosphere applications"².

We identified current data needs related to molecular and atomic line lists, line profiles, computed cross-sections and opacities, collision-induced absorption and other continuum data, optical properties of aerosols and surfaces, atmospheric chemistry and UV photodissociation and photoabsorption cross-sections. Standards in the description and format of such data are also discussed. In this presentation, we will highlight some of the most pressing needs.

In addition, a project on the GitHub platform³ has been created to foster collaboration between the communities. As an open access tool, GitHub provides huge advan-

¹G. Tinetti et al., *ESA Definition Study Report*,(2020) - https://sci.esa.int/documents/34022/ 36216/Ariel_Definition_Study_Report_2020.pdf

²K. L. Chubb, S. Robert, C. Sousa-Silva, S. N. Yurchenko, et al., *RAS Techniques and Instruments*, submitted (2024) - arXiv:2404.02188

³https://github.com/Ariel-data

tages of forming direct dialogues and become a go-to place for both data users and data providers, even for those who are currently not directly involved in the Ariel consortium or in the field of exoplanetary science in general.

V-4. Enabling Cosmic Discoveries: The Vital Role of Laboratory Astrophysics

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This interactive session will be centered around the findings and recommendations of the AAAC Laboratory Astrophysics Task Force report intended to help NSF and NASA address the Astro2020 Recommendation regarding effective support for laboratory astrophysics to enhance the scientific impact and output of astronomical observatories and missions.

V-5. Spectroscopy Needs in the Search for Habitable Worlds

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The Habitable Worlds Observatory (HWO) is a future NASA flagship facility that will revolutionize multiple areas of astrophysics and provide nearly flyby-quality observations of a panoply of solar system targets. While the atmospheres of rocky, temperate planets around M dwarfs are accessible to the James Webb Space Telescope, a next frontier of astronomy and planetary science is to directly image temperate Earth-sized planets in the habitable zones (HZ) of Sun-like stars, measure their spectra, and search for signs of life. HWO will directly image about 25 rocky HZ planets around Sun-like stars, providing the first ever constraints on the occurrence of habitability and life on planets with star-planet evolutionary histories analogous to Earth's. In order to plan for this ambitious facility, we must have a thorough understanding of the spectral features we are looking for, how these features change with fundamental physical parameters such as atmospheric temperature and pressure, and the prospects for biotic and abiotic accumulation of candidate biosignatures to levels that are detectable across interstellar distances. Spectral modeling of exoplanets with biosignatures, biosignature photochemical byproducts, planetary contextual features, and biosignature false positive indicators is a vital part of this process. While the notional HWO wavelength range from the NUV to the NIR highlights the high priority wavelength range for which accurate data is needed to predict observations, longer wavelengths can also be relevant for gases that impact e.g., planetary climate, and shorter UV wavelengths for predicting photochemical processes. For instance, collisional broadening data for CO_2 and H_2 may be relevant for early Earth, but this data is incomplete. Haze may have existed in Archean Earth's atmosphere, but optical properties of Archean-relevant haze over a wide wavelength range are just beginning to be measured. Better measurements and estimates of UV cross-sections at relevant temperatures for key gases (e.g., H_2O , CO_2) are needed. Improved and new spectra of biosignatures beyond the "usual suspects" motivated by the contingent history of the terrestrial atmosphere will help us to anticipate novel biosignatures. The survey of the atmospheric compositions of dozens of potentially habitable worlds will be one of the most challenging goals of any NASA observatory ever flown, demanding the best data possible to help us build a facility maximally capable of to meeting this ambitious goal. This presentation, on behalf of the HWO Living Worlds Working Group, will provide an overview of current thinking on HWO strategies for the search for life outside the solar system and how these strategies may be impacted by current and future spectroscopic measurements and simulations.

SESSION VI: Databases and Tools
VI-1. Empirical Pseudo-Line-Lists derived from laboratory absorption spectra

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We present a method for the automated generation of empirical spectroscopic linelists from laboratory absorption or transmittance spectra. It is based on a forward model (GFIT) that computes a series of spectra based on the known conditions (path length, P, T, and VMR) and an initial linelist. An algorithm then looks at the fitting residuals and adjusts the line intensities and E"-s, perhaps adding new lines. The spectra are then re-fitted. This process is iterated until the spectral fits stop improving. The result is a single linelist that provides the best overall match to all fitted lab spectra. This process can be viewed as a way of interpolating the measured cross-sections in wavenumber, temperature and pressure. We show that the Empirical Pseudo Line List (EPLL) approach has several advantages over the direct use of the measured absorption-cross sections in radiative transfer calculations. EPLLs provide a way of comparing spectra from multiple sets of lab measurements, which helps identify biases, inconsistencies and outliers in the input data. Also, fitting the EPLL to the lab spectra also provide an opportunity to account for artifacts in the lab spectra, such as contaminants (e.g., H₂O), channel fringes, zero-level offsets, and broadening by the ILS of the lab spectrometer.

These empirical "pseudo-linelists" have been developed for over 30 gases and are increasingly being used in atmospheric remote sensing applications, especially for heavy molecules (e.g., N_2O_5 , ClONO₂, CCl₄, CCl₄, CCl₃F, CCl₂F₂, CHClF₂, CHF₃, SF₆, CF₄, NF₃, C₅H₈, C₃H₈, C₃H₆, C₄H₁₀, CH₃COCH₃, C₆H₆, CH₃COOH) for which it is difficult to develop complete and accurate linelists by theoretical approaches. These are available from https://mark4sun.jpl.nasa.gov/pseudo.html.

VI-2. From moons to (exo)planets, simulating observations using NASA's Planetary Spectrum Generator

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The Planetary Spectrum Generator, PSG, is a radiative transfer suite for synthesizing and analyzing planetary spectra of objects ranging from the smallest like asteroids and comets, to moons, rocky planets, and gas giants ¹. It has been widely applied in Solar System, revealing isotopic anomalies both in atmospheres and on surfaces, weather patterns, and constraining strict upper limits providing evolutionary constrains. PSG is also one of the most utilized tool in exoplanetary research, providing a spectral and telescope simulation tool that can be applied to all spectroscopic characterization methods, ranging from transiting hot Jupiters to future direct imaging of Earth-like exoplanets around sun-like stars. Recent development include a detailed comparison of radiative transfer codes, an interface to simulate spectra of 3D objects by ingesting high-spatial resolution global climate models for atmospheres and shape-models for irregularly shaped objects. In this talk, I will highlight a number of science cases studied using the tool, explain its workings (*i.e.* interactions with HITRAN, surface reflectance databases, aerosol scattering), and provide a working example on how to operate PSG.

VI-3. Virtual Planetary Laboratory molecular spectra search engine for the HITRAN molecular spectroscopic database

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The HITRAN database ¹ contains molecular line lists for a wide variety of molecules. While the data in the HITRAN database is very useful for radiative transfer calculations, often it is important to visualize the contents of the HITRAN database. However, the line intensity varies over many orders of magnitude even for narrow wavelength ranges. Hence static plots of line intensity versus wavelength (or wavenumber) for a fixed wavelength range (or wavenumber range) cannot accurately display the variation. It is therefore important to have a tool that can dynamically scale the line intensities based on the wavelength range (or wavenumber range).

We have implemented an online search engine to query the molecular spectroscopic database HITRAN and display plots of line intensity versus wavelength (or wavenumber). The dynamic nature of the search engine allows the user to select narrower and narrower wavelength ranges (or wavenumber ranges) and hence zoom into a specific feature, or features, in the line list. Since the search engine is online, it can be accessed from any device with a browser and the user does not have to install any software.

The search engine can be used in two ways.

(1) Display plots for all molecules active in a given wavelength range (or wavenumber range). There is a separate figure for each molecule.

(2) Display plots for multiple user selected molecules in a given wavelength range (or wavenumber range). The plots for all the molecules are in the same figure. This allows one to compare the line intensity for the difference molecules.

The Virtual Planetary Laboratory (VPL) molecular spectra search engine is at https://vplapps.astro.washington.edu

The search engine has been used in research and in teaching. It has been useful in research for identifying molecules which may be the cause of a feature in an observed spectrum, and in understanding the molecules that may be available in a given instrument-accessible wavelength range. It has also been very useful for students for learning about molecular spectra.

¹I. E. Gordon, L. S. Rothman, R. J. Hargreaves, et al., *JQSRT*, 277, 107949 (2022). https://doi.org/10.1016/j.jqsrt.2021.107949

The search engine has been used by the VPL team and we thank them for their thoughtful feedback on features and functionality, which has allowed us to improve this tool.

VI-4. Lille Spectroscopic Database for Astrophysically and Atmospherically Relevant Molecules

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The Lille Spectroscopic Database (LSD, https://lsd.univ-lille.fr) was developed in response to a decade of research at the PhLAM laboratory focused on molecules of astrophysical and atmospheric relevance that exhibit large amplitude motions (LAMs). Previously, our spectral data calculated using various codes, including the primary SP-FIT/SPCAT suite (also employed by major databases like CDMS and JPL), were scattered across the supplementary data of different publications or integrated into the Splatalogue database. The Lille Spectroscopic Database aims to consolidate this information into a single, easily accessible repository.

This new database mimics the functionality of existing databases by offering spectral predictions in various formats and units, suitable for different temperatures. It enables users to search the entire database based on specific criteria like frequency range, intensity, or quantum numbers. Additionally, a simple user-friendly API has been developed to facilitate integration with other software systems.

The presentation will also cover essential topics regarding the optimal storage and handling of spectroscopic data. This includes the use of degeneracy factors for molecules with LAMs and calculations of the partition function for deuterated molecules.

VI-5. A Spectral Line Viewer for Online Databases

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Several spectral line list compilations for atmospheric modelling and retrieval, including HITRAN¹, ExoMol² and are available through online, browser-based services, but options for visualizing the lines have been limited by their large size, particularly for heavy molecules and at higher temperatures (for example, there are over 114 million lines for H₂O in the HITEMP³ compilation from 2010.)

This presentation introduces a new visualization tool for such data sets based on the interactive display of binned line strengths at different resolutions for different wavenumber intervals. Pre-calculation of these binned data sets allows for fast data exploration and selection before download.



¹https://hitran.org

²https://exomol.com

³https://hitran.org/hitemp/

SESSION VII: New Waves

VII-1. Transition states and mechanisms of chemical reactions studied with broadband rotational spectroscopy

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The vibrational level structure and the dynamics in the vicinity of a transition state affect the outcome of a chemical reaction and are hard to probe experimentally. In our laboratory, we utilize broadband chirped-pulse Fourier transform millimeter-wave (CP-FTmmW) spectroscopy to probe, with time resolution, the ro-vibrationally excited reaction products exiting a transition state. HCCCN molecules are detected in a variety of bending vibrational states after vinyl cyanide, CH₂CHCN, is photolyzed by a 193 nm laser. The vibrational state-dependent rates of HCCCN formation are observed and analyzed to understand the vibrational energy flow as the CH₂CCN radical dissociates to H + HCCCN. Our second experimental direction focuses on detecting and quantifying the pyrolysis and oxidation intermediates using the CP-FTmmW spectroscopy. The experimentally determined abundances are compared with the results of kinetic modeling and the reaction mechanisms, such as the H-atom substitution reaction in acetone decomposition, are discovered. In those experiments, detection of reaction intermediates at ppb levels of concentration provides rich chemical information, but also puzzles us with plenty of unassigned rotational lines. In our third direction, we turn to machine learning in a quest to automate assignment of rotational spectra and identification of molecular species. The latter task involves solving an inverse problem, and we query whether it is well-posed. Finally, we demonstrate both the artificial neural network and the Bayesian inference approaches to solving the assignment and the identification problems, respectively.

VII-2. Predicting the Rotational Dependence of Line Broadening using Machine Learning

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The ExoMol database is a major producer of molecular line lists for use in the modelling of exoplanetary atmospheres. Exoplanets are expected to have a wide range of atmospheric compositions, where molecules which are uncommon on Earth play a large role in atmospheric processes. Knowing line profiles is essential for simulating spectra in optically thick atmospheres, with pressure broadening being a parameter which is not easy to determine either by measurement or calculation. This is a problem for the many exotic molecules expected in exoplanetary atmospheres. This research has used modern machine learning (ML) methods to mass produce pressure broadening parameters for a large number of molecules in the ExoMol database. Our initial study¹ used empirical air-broadening data from the HITRAN database to train a ML model to predict air-broadening data for 60 molecules that have not been characterised before (see table below). Further work has extended this scheme to predict broadening for an increased number of perturbative species. This is essential for correctly modelling exoplanets which, of course, do not have air-like atmospheres.

			New M	L air bro	oadening	data, γ	air		
MgH	NaH	NiH	AlH	CrH	CaH	BeH	TiH	FeH	LiH
ScH	NH	CH	SiH	\mathbf{SH}	\mathbf{PH}	VO	ALO	YO	MgO
TiO	SiO	CaO	NaO	LaO	ZrO	SO	PO	PN	KCl
NaCl	LiCl	CN	C_2	H_2	CP	\mathbf{PS}	NS	SiS	NaF
AlCl	AlF	\mathbf{KF}	LiF	CaF	MgF	SiN	H_2O_2	SO_3	SiH_4
AsH_3	PF_3	CH_3	$\mathrm{P}_{2}\mathrm{H}_{2}$	H_2CS	CaOH	KOH	NaOH	SiO_2	LiOH

¹E. R. Guest, J. Tennyson, S. N. Yurchenko, Predicting the rotational dependence of line broadening using machine learning, *J. Mol. Spectrosc.*, 401, 111901 (2024), https://doi.org/10.1016/j.jms.2024.111901

VII-3. High-Resolution Dual Frequency Comb Spectroscopy from 1 THz to 1 PHz

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Dual comb spectroscopy (DCS) based on interference of two mutually coherent frequency combs with a slight offset of their comb-line spacing has evolved into a powerful technique that simultaneously provides broad spectral coverage, high spectral resolution, and high data acquisition rate.¹ Our DCS setup, based on a new femtosecond laser platform (mode-locked Cr:ZnS laser operating at 2.4 μ m), covers the whole range from THz to UV. To generate MIR-THz frequency combs we employ subharmonic optical parametric oscillation² or optical rectification techniques³, and for the UV-visible combs generation – high harmonics of the driving laser. In the longwave region of the spectrum $(6.6-200\mu \text{m}, 50-1500 \text{cm}^{-1})$, electro-optic sampling with few-cycle near-IR probing pulses presents a cutting-edge method for molecular spectroscopy with high dynamic range and the ability to access the mid-IR and THz ranges simultaneously. Leveraging this technique, we conducted measurements with 10-MHz resolution of ammonia, ethanol, isoprene, and dimethyl sulfide, revealing previously unexplored Doppler-limited spectroscopic signatures.⁴ In the UV range of 325-412 nm, we performed DCS using a silicon avalanche detector, where we resolved, in a single measurement, close to a million comb lines (spectral data points) spaced by 80 MHz (30-40 fm in wavelength), corresponding to the resolving power of 10^7 . This sets the stage for high-resolution UV spectroscopy of neutral and ionized atoms and molecules with the frequency scale referenced to the atomic clock.

¹N. Picqué and T. W. Hänsch, Nature Photon. 13, 146 (2019).

²A.V. Muraviev, V. O. Smolski, Z. E. Loparo, and K. L. Vodopyanov, Nature Photon. 12, 209 (2018).

³S. Vasilyev, A. Muraviev, D. Konnov, M. Mirov, V. Smolski, I. Moskalev, S. Mirov, and K.L. Vodopyanov, Opt. Lett. 48, 2273-2276 (2023).

⁴D. Konnov, D. Muraviev, S. Vasilyev, K.L. Vodopyanov, APL Photonics 8, 110801 (2023)

VII-4. High-Resolution Dual-Frequency-Comb Laser Spectrometer in the UV Range

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We demonstrate a novel laser spectroscopy method for high-resolution measurements in the UV range. The driving platform of our dual-frequency-comb (multi-heterodyne) UV spectrometer is based on two mutually coherent mode-locked Cr:ZnS lasers with the repetition rate 80 MHz and center wavelength 2350 nm. The spectra of both lasers are up-converted all the way to the UV spectral range (920 THz/325 nm) using high harmonic generation in multi-grating periodically-poled lithium niobate crystals. The spectrum of the 6th harmonic spans 372 - 412 nm and contains close to a million spectrally resolved data points (comb lines) spaced by 80 MHz, while the 7th harmonic spectrum spans 325 - 338 nm with close to 500,000 resolved comb lines. Even without comb tuning, the 80-MHz comb-line spacing provides the wavelength resolution of 30 fm for the 7th harmonic (resolving power 10⁷) - well beyond the resolution of conventional UV spectrometers (20-30 pm).

As a demo experiment, we have measured reflection and transmission spectra of a volume Bragg grating recorded in bulk photosensitive silicate glass (BragGrate[™] Mirror from IPG/OptiGrate) with narrow (180 GHz/95 pm) UV reflection band centered near 390 nm.

To the best of our knowledge, this is the first demonstration of UV spectroscopy with such a high resolution (80 MHz/30 fm), wide-band coverage, and the absolute frequency scale referenced to the atomic clock. This method offers a powerful new approach for high-resolution high-precision spectroscopic studies of neutral and ionized atoms and molecules in the UV spectral range.

VII-5. Looking for position and intensity patterns in the 2OH-stretch band of buffer gas cooled methanol.

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Methanol is a six-atoms asymmetric top molecule presenting internal rotation, and which has a dense and complicated spectral signature. Complexity further increases in the overtone range. Due to these features, this molecule remains poorly known, especially in the near infrared. To simplify its molecular signature, spectroscopy can be performed at cryogenic temperature so that only the states lying low in energy are populated, leading to an important simplification of the measured spectra along with a narrowing of the Doppler-broadened lines. In this talk, I will introduce the experimental development of a buffer gas cooling (BGC) setup combined with a cavity ring-down spectrometer with a detection limit $\alpha_{\min} = 2 \times 10^{-10} \text{cm}^{-1}$ and spectral resolution of few 10^{-4} cm⁻¹. With this instrument, we measured the 2OH stretching band of methanol between 7165 cm⁻¹ and 7230 cm⁻¹ cooled down to 26 ± 12 K in a buffer gas cooling experiment. A total of 350 rovibrational transitions were assigned and 62 rovibrational transitions were tentatively assigned. This assignment was performed by using and extending the pattern recognition method developed by Rakvoský et al.¹. I will explain how we used the relative intensities of the transitions to add one criterion to test the validity of our assignments. Improvements and future outcomes of this approach and of the BGC setup will be discussed.

¹Physical Chemistry Chemical Physics, 2021, 23, 20193-20200

SESSION VIII: Laboratory Spectroscopy for Earth and Planetary atmospheres

VIII-1. Line intensity measurement of CO and H_2 transitions with 0.1% precision

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The frequency accuracy of molecular line positions in the infrared has been improved to the order of 10^{-12} or even 10^{-13} , but a high-accuracy determination of line intensities remains a persistent challenge. Very limited studies have been reported with uncertainties at the level of one-thousandth. Sub-promille precision in line intensities is of great value in various applications, such as planetary atmospheric analysis, trace gas detection, temperature metrology, and pressure standards. Here we report the simultaneous measurement of both cavity-enhanced absorption spectroscopy and cavity-enhanced dispersion spectroscopy of molecules using the same high-finesse cavity. Transitions in the v = 3 - 0 band of carbon monoxide near 1.57 μ m and the first overtone Q(1) line of the H₂ near 1.2 μ m were measured. Both the absorption and dispersion spectra were fitted separately employing the Hartman-Tran profile (HTP), and the results obtained by the two methods are in excellent agreement. The line intensities were determined with uncertainties of around 0.1%, and the deviations from the theoretical results are within 0.2%. The results indicate promising prospects for SI-traceable, high-precision molecular density measurements based on laser spectroscopy.

VIII-2. Line-shape study of carbon monoxide (7–0) band

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Carbon monoxide, an important atmospheric trace gas, is crucial in monitoring pollution in the Earth's atmosphere, e.g. from burning fossil fuels. Being the second most abundant molecule in the universe, CO plays a key role in astrophysical surveys including analysis of the composition of the atmospheres of planets in the Solar System and exoplanets. CO molecule is also an important benchmark system for very accurate, both experimental and theoretical, studies of spectral line intensities¹.

We present the results of line-shape measurements of the CO (7–0) band in the visible range (around 695 nm). The spectra were acquired using the cavity ring-down spectroscopy (CRDS) technique, which is characterized by high sensitivity and stability of the frequency axis². This is the first experimental observation of such high (7–0) and weak (intensities below 2×10^{-29} cm/molecule) overtone spectrum of CO. In the data analysis we took into account the effects that go beyond the commonly used Voigt model. Collisional narrowing of the spectral lines is observed for the first time for such weak transitions and analyzed in terms of speed-dependent effects. The obtained line-shape parameters are mostly characterized by uncertainties of several MHz for the line position and a few percent for the remaining parameters³. Our values of line intensities are on average 100% higher than the HITRAN ones⁴. The line intensities were compared with the results of *ab initio* calculations based on accurate dipole moment curves and semi-empirical potential energy curves. Agreement between theory and experiment

¹K. Bielska, et al., *Phys. Rev. Lett.* 129, 043002, (2022). https://doi.org/10.1103/PhysRevLett. 129.043002

²K. Bielska, et al., JQSRT 276, 107927 (2021). https://doi.org/10.1016/j.jqsrt.2021.107927

³A. A. Balashov, et al., *Spectrochim. Acta A* 312, 124041 (2024). https://doi.org/10.1016/j.saa.2024.124041

⁴I. E. Gordon, et al., *JQSRT*, 277, 107949 (2022). https://doi.org/10.1016/j.jqsrt.2021. 107949

was obtained at the level of several percent, which is comparable to the experimental uncertainties $^{5}.$

⁵A. A. Balashov, et al., *J. Chem. Phys.* 158, 234306 (2023). https://doi.org/10.1063/5.0152996

VIII-3. Multi-laboratory Comparison for Determination of ${}^{12}C^{16}O$ (3-0) Band Absolute Line Intensities

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The band intensity of the ${}^{12}C^{16}O$ (3-0) overtone band was determined through measurements of the line intensities of ten separate lines in five independent laboratories using different linear spectroscopy techniques. The techniques include Fourier transform spectroscopy, performed at DLR and PTB, cavity ring-down spectroscopy at NIM and NIST, and cavity mode-dispersion spectroscopy at NCU.¹ Ten ${}^{12}C^{16}O$ transitions were chosen such that direct comparisons could be made for every determined line intensity across each of the experimental techniques. Molecular transition intensities were determined for each transition using a high-purity carbon monoxide sample at near-natural abundance and near 296K.

The weighted mean experimental results, with sub-permille standard error, agree at the permille level and with previously published theoretically determined intensity values² at the 0.3% level. The determined band intensity differs from the theoretical value by 0.5%. This high level of agreement demonstrates that multi-laboratory coordinated experiments can reduce combined uncertainty from both statistical and systematic effects in determinations of absolute line intensities, enabling accurate determinations at the permille level and below.

¹J.T. Hodges, K. Bielska, M. Birk, et al., International Comparison CCQM-P229, 2024 (in review): ²K. Bielska, A.A. Kyuberis, Z.D. Reed, et al., Phys. Rev. Lett. 129, 043002 (2022).

VIII-4. Molecular Spectroscopy with 10-MHz Resolution over Mid-IR to THz Range Using Dual Frequency Comb Method

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The combination of wideband precision frequency combs obtained by downconverting the frequency of a femtosecond laser source, via optical rectification, and electrooptical sampling as a detection method offers a new tool for high-resolution molecular spectroscopy over an exceptionally wide range from mid-IR to THz (6.6–200 μ m, 50– 1500cm⁻¹) with referencing of the frequency scale to the atomic clock.¹

We discuss spectroscopic applications of this powerful technique, presenting preliminary data and analysis of high S/N Doppler limited spectra in the mid-IR for several molecular species relevant to terrestrial and exoplanetary atmospheres. Specifically, we observe and identify c-type rovibrational bands of isoprene corresponding to out-of-plane methylenic bending in the 800–1200 cm⁻¹ region, a/b/c-type methyl rocking rovibrational bands of dimethylsulfide (900–1100 cm⁻¹), as well as multiple hybrid a/b-type rovibrational bands in ethanol due to asymmetric CO/CC stretching and COH bending vibrations near 1000cm⁻¹. Of special interest is the ability of our system to measure THz spectra simultaneously with mid-IR spectra. As a demo experiment, we performed measurement of rovibrational (at 670–1000cm⁻¹) and rotational (at 85–120cm⁻¹) spectra of ammonia molecule with about 10-MHz spectral resolution.

¹D. Konnov, A. Muraviev, S. Vasilyev, K.L. Vodopyanov, APL Photonics 8, 110801 (2023)

VIII-5. Mid-Infrared Doppler-Free Saturation Absorption Spectroscopy of the Q Branch of CH_4 $\nu_3 = 1$ Band using a Rapid-Scanning Continuous-Wave Optical Parametric Oscillator

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We have developed a mid-infrared Doppler-free saturation absorption spectroscopy apparatus that employs a commercial continuous-wave optical parametric oscillator (CW-OPO), complemented by a home-built automation and wavelength scanning system. Here, we report a comprehensive spectral scan of the Q branch transitions of the $\nu_3 = 1$ band of methane (CH₄) with an average linewidth (FWHM) of 4.5 MHz. The absolute frequency calibration was achieved using previously reported transition frequencies determined using optical frequency combs, while a Fabry-Pérot etalon was used for relative frequency calibration. We report 15 transitions with improved accuracies of 1.13 MHz (3.76×10^{-5} cm⁻¹). The same OPO system and spectroscopic apparatuses have been used to obtain high-resolution spectra of other astrochemical molecules, including acetonitrile. The current project is the first step toward a widely tunable, highresolution, high-frequency-precision mid-infrared spectrometer for studying atmospheric and astrochemical molecules.

VIII-6. New Laboratory Measurements and Spectroscopic Line Parameters of Infrared Carbon Dioxide Bands

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Carbon dioxide (CO_2) is a strong absorber of infrared radiation. Its continuing increase in the Earth's atmosphere is a strong driver of climate change. CO_2 has a range of absorption bands throughout the infrared that are measured in the Earth's atmosphere by satellite-borne atmospheric sounders. These bands are utilised in a range of applications, for example monitoring the concentration of CO_2 in the atmosphere, and determining atmospheric temperature profiles for numerical weather prediction. The motivation for this work is to provide experimental non-Voigt line parameters in order to improve the representation of CO_2 in atmospheric radiative transfer codes. It is recognised that the Voigt profile is inadequate in accurately modelling spectra measured at high signal-to-noise ratio.

Measurements of pure and air-broadened CO_2 spectra at 296 K over a range of pressures and pathlengths were obtained using a Bruker IFS 125 HR spectrometer at the Physikalisch-Technische Bundesanstalt (PTB) in Braunschweig, Germany. The measurements of sample pressure, temperature, and pathlength are all SI-traceable. A multispectrum fitting analysis has been performed using the LabFit program to derive non-Voigt lineshape parameters for various CO_2 bands. Line positions and intensities have been constrained using quantum mechanical expressions. Comparisons between the derived parameters and those from the HITRAN2020 molecular spectroscopic database are made.

VIII-7. Carbon Dioxide Band Intensity Ratio Measurement by Dual Comb Spectroscopy

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The near-infrared bands of carbon dioxide (CO₂) are used in remote sensing to determine atmospheric abundances. Within this atmospheric water window, the $(30012) \leftarrow (00001)$ and $(30013) \leftarrow (00001)$ bands near a wavelength of 1.6 μ m have similar integrated intensities. Low-uncertainty measurements of these intensities by either cavity ring-down spectroscopy (CRDS)¹ or Fourier transform spectroscopy (FTS)² have been reported, along with intensities calculated from quantum chemistry theory.^{3,4} Consensus band intensities for CO₂ near 1.6 μ m were updated in HITRAN2020.⁵

Here we discuss new results from a third experimental technique: dual comb spectroscopy (DCS). After applying tested methods for systematic error evaluation to DCS,⁶ we report broadband measurements of ¹²C-enriched CO₂ samples at a high signal-tonoise ratio over the pressure range of 10 kPa to 21 kPa. Importantly, our DCS experiments were performed in an optically thin regime, with transmittance values of >0.94 for all lines at all pressures. The results constrain the band intensity ratio between the $(30012) \leftarrow (00001)$ and $(30013) \leftarrow (00001)$ bands—aiding in resolving a 0.5 % discrepancy between CRDS and FTS results—and provide new estimates of the self-pressure shifting and self-pressure broadening coefficients for CO₂ in the near-infrared.

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VIII-8. New quantitative measurements and spectroscopic line parameters of ammonia for atmospheric remote sensing

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Ammonia is the most abundant alkaline atmospheric gas. It is emitted by a range of anthropogenic sources, most notably through the use of nitrogen-based fertilizers in agriculture. Ammonia plays a major role in the formation of $PM_{2.5}$, which can significantly affect human health.¹ It also contributes to visibility degradation and to the atmospheric deposition of nitrogen on sensitive ecosystems.

The interpretation of satellite remote sensing measurements to determine the amounts of trace gases such as ammonia in the atmosphere requires accurate radiative transfer calculations. These in turn are heavily reliant on accurate spectroscopic line parameters, which are best derived from high quality laboratory measurements.

The HITRAN 2020 database reports line parameters for ammonia that are derived from both theoretical calculations and laboratory measurements.² In this work, we report the measurement of new, high-resolution infrared spectra of pure and air-broadened ammonia. Using a multispectrum nonlinear least squares fitting approach,³ we determine new spectroscopic line parameters for the NH₃ 0100 00 0 s \leftarrow 0000 00 0 a and 0100 00 0 a \leftarrow 0000 00 0 s bands (using HITRAN notation), including the first reported values of self and foreign pressure-induced shifts.

¹K. E. Wyer et al., J. Environ. Manage. 2022, 323, 116285.

²I. E. Gordon et al., J. Quant. Spectrosc. Radiat. Transfer 2022, 277,107949.

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VIII-9. New high resolution microwave and infrared spectra of isoprene

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Isoprene (2-methyl-1,3-butadiene), emitted by plants, is an unsaturated hydrocarbon of high abundance in Earth's atmosphere. It quickly reacts with the OH radical and is a major source of secondary organic aerosols. Isoprene also affects the oxidative capacity of the atmosphere. It has been suggested to be a biosignature marker for future observations of exoplanet atmosphere. Linelists of frequencies and intensities are highly needed. Here we will present new microwave data for *trans* isoprene using the PARIS spectrometer in resonator mode in the range 4-19 GHz combined with published data¹. Infrared data in the 986-997 cm⁻¹ spectral range recorded with a pulsed jet coupled to a mid-IR tunable quantum cascade laser spectrometer (set-up SPIRALES) allowed new assignments of the ν_{26} band compared to previous work². Fitting of the ground and excited vibrational states using the internal rotor codes XIAM and BELGI will be shown³

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VIII-10. Towards a Global Analysis of the Infrared Spectrum of Formic Acid

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Formic acid and acetic acid are the most abundant organic acids in both Earth's atmosphere and in interstellar molecular clouds. In Earth's atmosphere, formic acid is often remotely sensed in its strongest vibrational band (ν_6), which has a band centre at 1105 cm^{-1} . While the current HITRAN line list of this band is in good agreement with experimental spectra at resolutions that are relevant to remote sensing, at higher resolution, there are inconsistencies.¹ This was evidenced when comparing the line list with high-resolution FTIR spectra that we acquired at the Canadian Light Source. In an effort to improve this situation, we simulated the spectrum of formic acid using the 114 diagonal and 105 off diagonal parameters that were previously determined in a global fit to the heptad of interacting vibrational states near 9 μ m.² Unfortunately, we found that residuals in the line positions are greater than the measurement uncertainty at high K_a values. While the relative intensities are in good agreement for most of the lines, we find poor agreement for many of the lines which are strongly perturbed. It seems the choice of coupling terms used in the Hamiltonian could be improved upon,³ and it is our quest to refine the global fit so that an improved line list of formic acid can be generated in this terrestrial window. The latest progress in this endeavor will be presented.

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VIII-11. Acetylene around 3.8- μ m : new measurements for ${}^{12}C_2H_2$, ${}^{12}C^{13}CH_2$ and ${}^{12}C_2HD$ isotopologues

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Based on natural abundance sample of acetylene and a long absorption path (up to 1 km), Fourier Transform spectra have been recorded and analyzed to measure line positions and intensities of 71 bands of ${}^{12}C_2H_2$, 11 bands of ${}^{12}C^{13}CH_2$ and 6 bands of ${}^{12}C_2HD$ located between 2400 and 2900 cm⁻¹. Line lists have been generated for each isotpologue. For ${}^{12}C_2H_2$ line positions were modeled using set of spectroscopic constants and global effective Hamiltonian model (most of the time rescaled). The intensity calculations with the effective dipole moment operator demonstrated the good agreement with the observation. For ${}^{12}C^{13}CH_2$ and ${}^{12}C_2HD$ the line positions from literature 1,2,3,4 and intensity calculation from vibrational transition dipole moment squared and Herman-Wallis factors have been used. The line lists have been generated in HITRAN format using recommended broadening and shifting parameters 5 .

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VIII-12. Trends in perfluoroalkane band strengths and climate metrics

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Perfluoroalkanes are industrial solvents and cleaning agents. These compounds have millennial-scale atmospheric lifetimes and have infrared absorption features in atmospheric window 800-1200 cm⁻¹. Therefore, perfluoroalkanes can lead to long-term global warming. We have measured the infrared properties of eight perfluoroalkanes at a range of temperatures from 300 to 350 K. In particular, we measured six linear, n-C₃F₈ to n-C₈F₁₈, one cyclic, c-C₄F₈, and one branched, i-C₆F₁₄ molecule. To our knowledge, this is the first measurement of the infrared cross-section of i-C₆F₁₄. We present our cross-sections for i-C₆F₁₄ and summarize results for the total band strength, radiative efficiency, and global warming potential for the perfluoroalkanes. The total band strength increases linearly, while the radiative efficiency increases non-linearly with an increasing number of C-F bonds. Since the global warming potential depends on the radiative efficiency and molecular weight, it increases to a peak at ten C-F bonds and then decreases.

VIII-13. Benchmarking tritiated water species

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The spectroscopy of the water molecule is of high relevance for various terrestrial and extraterrestrial observations. Although of great scientific interest, spectroscopic investigations of water isotopologues with tritium remain sparse due to lack of experimental data or insuperable technological challenges to obtain these.

In order to extend the data base for these isotopologues, we developed two tritiated water vapour samples with a total activity of 1 and 10 GBq⁻¹ from which high-resolution FTIR spectra ranging from 2450 to 6440 cm⁻¹ have been obtained. Assignment of these spectra delivered high-precise line lists of HT¹⁶O, DT¹⁶O and T¹⁶₂O with a total number of 5177 lines and precision up to 5.6×10^{-5} cm⁻¹.

We present an overview of these data 2,3,4,5,6 including its acquisition and validation. A comparison with theoretical predictions from the *SPECTRA* database⁷, based on our assignments, reveals a precision of the vibrational and rotational energies of current theory orders of magnitude lower than the precision of the presented data.

Furthermore, the recorded line list can be utilized to develop laser-based devices to monitor tritiated water species in tritium plants for future DT-fusion reactors.

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⁷www.spectra.iao.ru

VIII-14. Direct Absorption Measurements of Atomic Oxygen at 2.06 THz with a Custom Transmitter / Heterodyne Receiver Pair

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Observation of the atomic oxygen fine structure line at 2.06 terahertz from an orbiting limb sounder serves as a compelling platform for the characterization of neutral winds in the lower thermosphere and E-region ionosphere (LTEI; ~100–140 km). The precision of wind measurements retrieved from this prospective instrument class are directly linked to the rest frequency of this targeted transition as determined from laboratory measurements. This talk will detail recent work at the Jet Propulsion Laboratory to deploy a custom designed transmitter and heterodyne receiver pair optimized for performance at 2.06 THz for use in obtaining high-precision rest frequencies for the oxygen atom ${}^{3}P_{0}$ - ${}^{3}P_{1}$ atomic fine structure splitting. Oxygen atom (${}^{16}O$) is generated by an inductively coupled plasma system with direct absorption measurements obtained by a combined frequency and plasma modulated experimental scheme. Results will be discussed in the context of previous laboratory measurements and the impact on prospective neutral wind measurements in the LTEI.

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HITRAN Anthem

As sang at Larry Rothman's retirement party in May 2017

(Music from "If You're Happy and You Know It")

It's the spectral database - It's called HITRAN It is used from San Francisco to Milan It is used in the US, and in Russia and in France

Everybody use HITRAN, HITRAN, HITRAN

If you want to find a leak in your gas pipe Or you want to find a non-terrestrial life Or check pollution at your plant, that is when you use HITRAN

Everybody use HITRAN, HITRAN, HITRAN

To detect an early cancer in the breath Or to see if someone bakes the crystal meth You should make a proper plan: How to use HITRAN, HITRAN

Everybody use HITRAN, HITRAN, HITRAN

What about that nasty ozone hole? Is it shrinking over the North Pole? You should check the database, against what you see from space

Everybody use HITRAN, HITRAN, HITRAN

Larry Rothman made it so much fun When we use the spectra from HITRAN It is such a useful tool, and we all say big THANK YOU

And we all say big THANK YOU, THANK YOU, THANK YOU