HITRAN

Celebrating the 25th Anniversary of the HITRAN Conferences

The 13th HITRAN Database Conference

HARVARD-SMITHSONIAN CENTER FOR ASTROPHYSICS
CAMBRIDGE MA, USA
June 23 – June 25, 2014

2014

The following companies contributed to the HITRAN 2014 Conference:

Aerodyne Research, Inc.
45 Manning Road
Billerica MA 01821-3976
USA

Port City Instruments, LLC
8209 Market Street, Suite A271
Wilmington NC 28411
USA

Bruker Optics Inc.
19 Fortune Dr
Billerica MA 01821
USA

GATS, Inc.
11864 Canon Blvd, Suite 101
Newport News VA 23606
USA

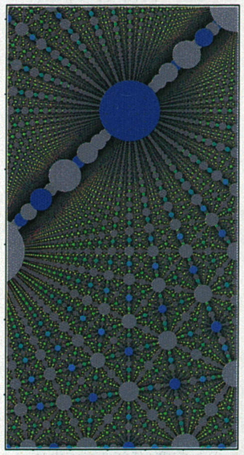
ONTAR Corp.
9 Village Way
North Andover MA 01845
USA

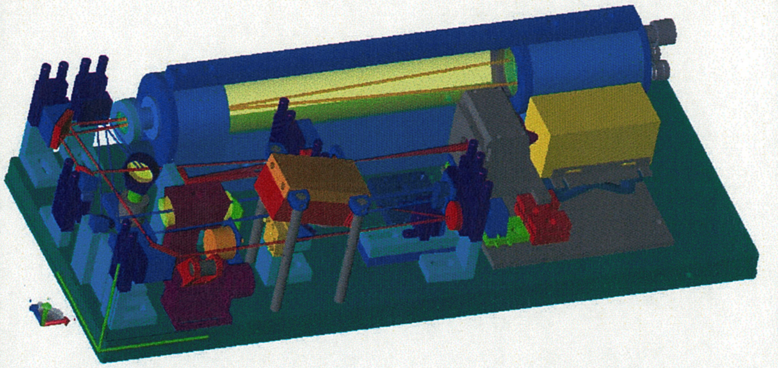
Front page: Group photo of the first HITRAN Conference, held 25 years ago.

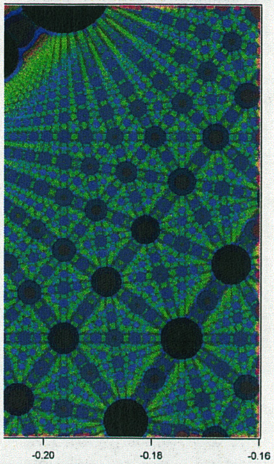
The HITRAN Project has been funded by grants from the National Aeronautics and Space Administration.

AERODYNE RESEARCH, Inc.

Quantum Cascade Laser Trace Gas Monitors







MEASUREMENTS OF ATMOSPHERIC TRACE GASES IN AMBIENT AIR: SENSITIVE, RAPID, HIGHLY SPECIFIC AND CONTINUOUS

QCL Mini Monitor – Compact, low cost

QCL Dual Monitor – More species, more sensitivity

Instrument Configurations

- GHG Monitors: N_2O, CH_4, CO_2, CO and H_2O
- Isotope Monitors: CO_2, CO_2 and H_2O, CH_4, or N_2O
- Ammonia Monitor
- COS, CO_2 Monitor
- Formaldehyde Monitor
- Ethane/Methane Monitor

Many Others:

NO, N_2O, NO_2, NH_3, HONO, HNO_3, CO, CH_4,
C_2H_4, HCHO, CHOOH, SO_2, COS, O_3, HOOH

TDLAS Sweep-Integration & 2f Controller

Port City Instruments, LLC
SINGLE-LINE SPECTROSCOPY SOLUTIONS

The PCI-1E controller drives the external inputs of commercial laser controllers such as those from Arroyo Instruments, ILX, Stanford Research, and others. It provides a variable-amplitude, continuous voltage ramp (linear or quadratic) with superimposed variable-amplitude sine wave for performing direct absorption or second harmonic (2f) spectroscopy. All-digital 2f demodulator based on FPGA. Great for sweep-integration experiments using tunable diode lasers, quantum cascade lasers, or VCSEL lasers. Analog spectrum and trigger outputs (0–5V range).

FEATURES

Output: 0 - 8V ramp, linear or quadratic waveform, programmable amplitude and period

1f Modulation: 31.4 KHz, 0 - 2V amplitude (p-t-p)

2f Demodulation: 62.8 KHz (all digital within FPGA)

Sweep Rate: 0.1 Hz to 100 Hz (2f 0.1 Hz to 20 Hz)

Ext. Preamp Input: 0 - 10V range, 5K input impedance

Temperature Sensor Inputs: NTC thermistors (3)

Pressure Sensor Input: 0 - 5V input range. Stable 5.0V reference provided for ratiometric sensors.

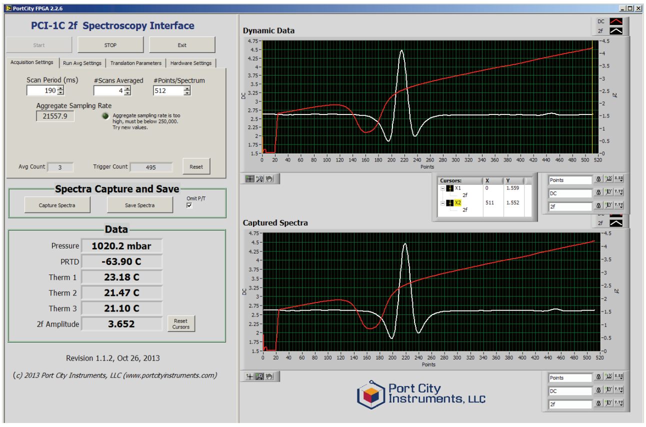
Programming Interface: PC via USB and GUI

Dimensions: 8.5"W x 9.5"D x 3.0"H

Weight: 2.7 lbs (1.2 kg)

Power: +5 VDC, <0.4 A

PCI-1C USER INTERFACE


PortCity FPGA 2.2.6

PCI-1C 2f Spectroscopy Interface

Scan Period (ms): 190
#Scans Averaged: 4
#Points/Spectrum: 512
Aggregate Sampling Rate: 21557.9
Aggregate sampling rate is too high, must be below 250,000. Try new values.
Avg Count: 3
Trigger Count: 495

Data
Pressure: 1020.2 mbar
PRTD: -63.90 C
Therm 1: 23.18 C
Therm 2: 21.47 C
Therm 3: 21.10 C
2f Amplitude: 3.652

Revision 1.1.2, Oct 26, 2013

(c) 2013 Port City Instruments, LLC (www.portcityinstruments.com)

PCI-1C

(GUI shown at left)

PCI-1C data acquisition and display module. Receives analog outputs from PCI-1E or other controller modules and provides real-time spectrum plotting, averaging, capture and storage. Pressure and temperature inputs. See our website for additional details (sold separately from PCI-1E).

10.1m Herriott Cell

General purpose, economical, multipass free-space Herriott cell for laboratory and field use. This gas flow cell provides 10.1m of optical absorption pathlength and is ruggedly constructed with honed and polished interior walls and high-quality protected gold mirrors (HfO_2 overcoat).

Useable over the 1–5 micron wavelength range (mirrors 1–12 μm) and 0.001 to 1.5 Bar pressure range. Replaceable 1" diameter coupling window (mount is compatible with 2–7 mm thickness windows). Cells are electroless nickel plated inside and out for corrosion resistance and a lower "sticking" coefficient for polar gases. Optional items include a thermostatting kit for operation at stable elevated temperatures (to 75°C), and an alignment fixture to aid in correct beam injection.

SPECIFICATIONS	
Optical Pathlength	10.13 m
Cell Volume	0.24 L
Number of passes	34
f-Number	5.2
Entrance Slopes (deg)	2.072
Coupling Hole Diameter	3.25 mm
Max Beam Diameter	3.0 mm
Spot Spacing	4.39 mm
Surface Figure	1/10 wave
Scratch-Dig	20–10
Mirror Coating	Protected Au
Overall Length	13.7"

Remote Sensing

High Performance FT-IR Systems

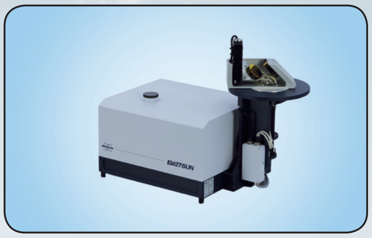
- Identification and Quantification of Pollutants and Hazardous Material
- High-Precision Quantification of Trace Gases
- Cloud Imaging
- Air Quality Monitoring
- Fenceline Monitoring
- Emission Measurement
- Leak Detection
- Atmospheric Gas Determination by Solar Absorption Spectroscopy

Bruker Remote Sensing Systems allow for analysis of gases, liquids, and solids. In addition, HI 90 and SIGIS 2 are imaging spectrometers, adding mapping capabilities.

All systems utilize ruggedized Bruker FT-IR interferometers assuring unsurpassed reliability and accuracy. All systems are available in mobile configurations for field applications.

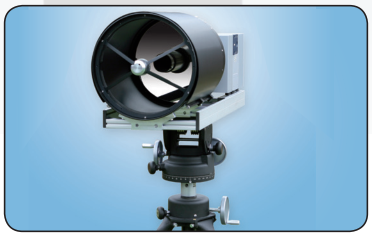
Contact us for more details:
www.BrukerOpenPath.com

HI 90–Hyperspectral Imaging System



EM 27 SUN–Spectrometer with Solar Tracker

SIGIS 2–Scanning Imaging Remote Sensing System



OPS–Open Path Air Monitoring System

DAY 1, Monday 23 June

SESSION I: Remote Sensing and Radiative Transfer 1

SESSION II: Databases-I 15

DAY 2, Tuesday 24 June

DAY 3, Wednesday 25 June

SESSION I: Remote Sensing and Radiative Transfer

I-1. Tropospheric Emissions: Monitoring of Pollution (TEMPO)

Kelly Chance,[a] **Xiong Liu,**[a] **Raid M. Suleiman,**[a] **David E. Flittner,**[b]
Jassim Al–Saadi,[b] **Scott J. Janz**[c]

[a]*Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, United States*

[b]*NASA Langley Research Center, Hampton, VA, United States*

[c]*NASA Goddard Space Flight Center, Greenbelt, MD, United States*

TEMPO, selected by NASA as the first Earth Venture Instrument, will measure atmospheric pollution for greater North America from space using ultraviolet and visible spectroscopy. TEMPO measures from Mexico City to the Canadian oil sands, and from the Atlantic to the Pacific, hourly and at high spatial resolution. TEMPO provides a tropospheric measurement suite that includes the key elements of tropospheric air pollution chemistry. Measurements are from geostationary (GEO) orbit, to capture the inherent high variability in the diurnal cycle of emissions and chemistry. The small product spatial footprint resolves pollution sources at sub-urban scale. Together, this temporal and spatial resolution improves emission inventories, monitors population exposure, and enables effective emission-control strategies.

TEMPO takes advantage of a GEO host spacecraft to provide a modest-cost mission that measures the spectra required to retrieve O_3, NO_2, SO_2, H_2CO, $C_2H_2O_2$, H_2O, aerosols, cloud parameters, and UVB radiation. TEMPO thus measures the major elements, directly or by proxy, in the tropospheric O_3 chemistry cycle. Multi-spectral observations provide sensitivity to O_3 in the lowermost troposphere, reducing uncertainty in air quality predictions by 50 %. TEMPO quantifies and tracks the evolution of aerosol loading. It provides near-real-time air quality products that will be made widely, publicly available.

TEMPO makes the first tropospheric trace gas measurements from GEO, by building on the heritage of five spectrometers flown in low-earth-orbit (LEO). These LEO instruments measure the needed spectra, although at coarse spatial and temporal resolutions, to the precisions required for TEMPO and use retrieval algorithms developed for them by TEMPO Science Team members and currently running in operational environments. This makes TEMPO an innovative use of a well-proven technique, able to produce a revolutionary data set.

TEMPO provides much of the atmospheric measurement capability recommended for GEO-CAPE in the 2007 National Research Council Decadal Survey, Earth Science and Applications from Space: National Imperatives for the Next Decade and Beyond. GEO-CAPE is not planned for implementation this decade. However, instruments from Europe (Sentinel 4) and Asia (GEMS) will form parts of a global GEO constellation for pollution monitoring later this decade, with a major focus on intercontinental pollution transport. TEMPO will launch at a prime time to be a component of this constellation.

I-2. Retrieving CO_2 from Orbiting Carbon Observatory-2 (OCO-2) Spectra

David Crisp, for the OCO-2 Science Team

MS 183-501, Jet Propulsion Laboratory, 4800 Oak Grove Drive, Pasadena, CA, 91109

Fossil fuel combustion, deforestation, and other human activities are currently adding almost 40 billion tons of carbon dioxide (CO_2) to the atmosphere each year. These emissions have increased by roughly a factor of 3 over the past half century and are still growing by more than 2% per year. The developing world is now responsible for the majority (57%) of these emissions and their rapid growth rates. Precise measurements collected by a global network of surface stations show that these emissions have contributed to a 25% increase in the atmospheric CO_2 concentration over the past half century. Surprisingly, comparisons of these measurements with fossil fuel emission inventories indicate that only about half of the CO_2 emitted into the atmosphere by human activities stays there. The rest is apparently being absorbed by natural CO_2 "sinks" at the Earth's surface. Measurements of the pH of the ocean indicate that it absorbs roughly one quarter of these emissions. The remainder has been attributed to the land biosphere, but the identity and location of the land sinks is still unknown. In addition, the fraction of the anthropogenic CO_2 absorbed by these natural sinks has varied dramatically from year to year, but has remained near 1/2 on decadal time scales as the emissions have steadily increased. Uncertainties in the nature, location, and processes controlling these natural sink largely preclude reliable predictions of future atmospheric CO_2 buildup rates.

The existing greenhouse gas monitoring network can accurately track CO_2 changes on hemispheric to global scales, but does not have the resolution or coverage needed to quantify emission sources on regional scales or to identify the natural sinks responsible for absorbing CO_2. One way to improve the measurement density is to retrieve precise, spatially-resolved estimates of the column-averaged CO_2 dry air mole fraction, X_{CO_2}, from satellites. Surface-weighted estimates of X_{CO_2} can be retrieved from measurements of reflected sunlight in near infrared CO_2 and O_2 bands. However, this is among the most challenging space-based remote sensing applications because even the largest CO_2 sources and sinks produce changes in the background X_{CO_2} distribution no larger than 1%, and most are smaller 0.25% (~1 ppm).

This approach was pioneered by the European Space Agency's EnviSat SCIAMACHY and Japanese GOSAT TANSO-FTS instruments. These sensors have provided valuable insights into space based X_{CO_2} measurement techniques, but still do not have the sensitivity, resolution, and coverage needed to quantify CO_2 sources and sinks on regional scales. The Orbiting Carbon Observatory-2 (OCO-2) is the first NASA spacecraft designed to exploit this measurement approach. This spacecraft carries and points a 3-channel, imaging, grating spectrometer that collects high resolution spectra of reflected sunlight in the 765 nm O_2 A-band and in the 1610 and 2060 nm CO_2 bands. Coincident O_2 and CO_2 spectra are combined into "soundings" that are analyzed with a full-physics retrieval algorithm to yield estimates of X_{CO_2}. Each spectrometer channel will collect 24 spectra per second, yielding up to a million soundings per day over the sunlit hemisphere. Between 10 and 30% of these soundings are expected to be sufficiently cloud free to yield full-column estimates of X_{CO_2}.

OCO-2 is currently scheduled for launch from Space Launch Complex 2 at Vandenberg Air Force Base in California on a United Launch Alliance Delta-II 7320-10 Launch Vehicle at 02:56:44 AM PDT (12:56:44 GMT) on 1 July 2014. The nominal spacecraft checkout and orbit raising plan will take about 37 days to insert the observatory into the 705-km Afternoon Constellation (A-Train). This 98.8-minute, sun-synchronous orbit has a 98.2-degree inclination, a 1:36:30 PM mean ascending equator crossing time time, and a 16-day (233 orbit) ground track repeat cycle. Once in the A-Train, the instrument's optical bench and detectors will be cooled to their operating temperatures, and a ∼7-day instrument check-out period will commence. OCO-2 will then start routinely collecting and returning science data.

For routine science operations, the instrument's bore sight will be pointed to the local nadir or at the "glint spot," where sunlight is specularly reflected from the Earth's surface. Nadir observations provide the best spatial resolution and are expected to yield more cloud-free X_{CO_2} soundings over land. Glint observations will have much better signal-to-noise ratios (SNR) over dark, ocean surfaces. As often as once each day, the satellite will target a selected surface calibration and validation site and collect thousands of observations as the spacecraft flies overhead. The instrument's rapid sampling, relatively small (< 3 km^2) sounding footprint, and high SNR, combined with the spacecraft's ability to point the instrument's bore sight toward the glint spot over the entire sunlit hemisphere, are expected to provide more complete coverage of the ocean, cloudy regions, and high latitude continents than earlier CO_2 monitoring spacecraft. The first calibrated, geo-located spectral radiances will be delivered to the NASA Earth Sciences Data and Information Services Center (GES DISC) approximately 90 days after nominal science operations begin. The first X_{CO_2} products will start being delivered 90 days after that.

The OCO-2 mission is required to return estimates of X_{CO_2} with accuracies of 0.3% on regional scales at monthly intervals. To meet this stringent requirement, the OCO-2 team has developed a "full-physics" retrieval algorithm that incorporates a forward radiative-transfer model based on a spectrum-resolving multiple scattering algorithm, an OCO-2 instrument model, and an inverse model based on Optimal Estimation. To yield X_{CO_2} estimates with accuracies of 0.3%, the forward radiative-transfer model must simulate reflected solar radiances with biases no larger than $\sim 0.1\%$. The accuracy of our X_{CO_2} estimates retrieved from spectra collected by the GOSAT TANSO-FTS and the ground based Total Carbon Column Observing Network (TCCON) has improved steadily over the past 5 years, but these retrievals still yield biases as large as 1%. Persistent biases and spectrally-dependent residuals in fits to the O_2 A-band and the two CO_2 bands sampled by OCO-2 indicate that shortcomings in gas absorption cross sections are a leading cause of these errors. To address this issue, the OCO-2 project has supported an ambitious molecular spectroscopy measurement and analysis effort. Laboratory spectra of CO_2 and O_2 collected with cavity ringdown and photoacoustic techniques are being combined with new low-temperature Fourier transform spectra and analyzed with multi-spectral fitting techniques to yield a new, self-consistent description of the line positions, strengths, shapes, and mixing in these bands. This presentation will provide a quick overview of the OCO-2 mission and summarize the recent progress in our molecular spectroscopy effort.

I-3. Spectroscopic Issues for the Atmospheric Chemistry Experiment (ACE)

Chris Boone,[a] **Peter Bernath**[b]

[a] *Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada*

[b] *Department of Chemistry and Biochemistry, Old Dominion University, Norfolk, Virginia, USA*

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

I-4. Remote Sensing of Greenhouse Gases and Their Sources and Sinks

Andre Butz,[a] **Arne Babenhauserheide,**[a] **Marco Bertleff,**[a]
Ramiro Checa-Garcia[a]**, Philipp Hahne,**[a] **Frank Hase,**[a]
Friedrich Klappenbach,[a] **Julian Kostinek,**[a] **Ilse Aben,**[b] **Otto Hasekamp,**[b]
Jochen Landgraf,[b] **Andre Galli,**[c] **Sourish Basu**[d]

[a]*IMK-ASF, Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany*

[b]*Netherlands Institute for Space Research (SRON), Utrecht, The Netherlands*

[c]*Physics Institute, University of Bern, Bern, Switzerland / Netherlands Institute for Space Research (SRON), Utrecht, The Netherlands*

[d]*NOAA ESRL Global Monitoring division, Boulder, Colorado, USA*

The man-made emissions of the greenhouse gases carbon dioxide (CO_2) and methane (CH_4) are considered the main drivers of anthropogenically induced climate change. Major uncertainties persist when it comes to quantifying regional scale surface fluxes of these gases or predicting the evolution of the relevant source/sink processes in a changing climate. Remote sensing of the atmospheric greenhouse gas concentrations from space-borne and ground-based platforms offers the opportunity to significantly advance our knowledge on spatial and temporal scales that are suitable for process attribution and mitigation actions. Overall, the most promising remote-sensing strategy exploits the rotational-vibrational absorption of CO_2 and CH_4 in sunlight penetrating the Earth's atmosphere. Typically, satellite sounders such as GOSAT (Greenhouse Gases Observing Satellite), OCO-2 (Orbiting Carbon Observatory), and S5P (Sentinel-5 precursor) as well as the ground-based spectrometers of the TCCON (Total Carbon Column Observing Network) cover various CO_2, CH_4, and O_2 absorption bands in the near and shortwave infrared spectral range between 0.75 micron ($13400\,\mathrm{cm}^{-1}$) and 2.5 micron ($4000\,\mathrm{cm}^{-1}$). Accuracy of the inferred gas concentrations is contingent on the accuracy of the adopted spectroscopic parameters and spectroscopic models available in these spectral regions.

Here, I will report on recent achievements and challenges within our greenhouse-gas remote-sensing activities mainly focusing on the GOSAT observational record. Since its launch in early 2009, the Fourier Transform Spectrometer onboard GOSAT delivers solar absorption spectra with good spectral resolution and high signal-to-noise. It has been shown that the CO_2 and CH_4 retrievals from these observations can achieve an accuracy on the order of fractions of a percent which makes them suitable for tracking regional scale source/sink processes and their response to climate events. In order to achieve the required accuracy, it is crucial to develop highly accurate radiative-transfer algorithms and to validate the satellite soundings by ground-based observations. I will illustrate some cases where the excellent quality of the absorption spectra collected by

GOSAT reveals spectroscopic deficiencies and inconsistencies among the various absorption bands covered. As such, lessons learned from GOSAT can be used as a feedback to the spectroscopy community. Beyond GOSAT, future satellite missions such as S5P or the planned S5 (Sentinel-5, launch ∼2020) will cover spectral ranges which have not yet been spectroscopically optimized for remote-sensing purposes. In that case, simulations and studies based on ground-based observations show that spectroscopic uncertainties constitute a dominant contribution to the error budget of the retrieved gas concentrations. Therefore, further improvements of spectroscopic parameters and line-shape models is of paramount interest for remote sensing of greenhouse gases.

I-5. Validation of H_2O Continuum Absorption Models in the Wave Number Range 180-600 cm^{-1} with Atmospheric Emitted Spectral Radiance Measured at the Antarctica Dome-C Site.

Giuliano Liuzzi,[a] Guido Masiello,[a] Carmine Serio,[a] Sara Venafra,[a] Maria Grazia Blasi,[a] Luca Palchetti,[b] Giovanni Bianchini[b]

[a]*School of Engineering, Università degli Studi della Basilicata, Via dell'Ateneo Lucano 10, 85100 Potenza (Italy)*

[b]*Istituto Nazionale di Ottica - CNR, largo E. Fermi 6, 50125 Firenze, (Italy)*

We present the results concerning the analysis of a set of atmospheric emitted (down welling) spectral radiance observations in the spectral range 180 to 1100 cm^{-1} acquired at the Dome-C site in Antarctica during an extensive field campaign in 2011-2012. The work has been mainly focused on retrieving and validating the coefficients of the foreign contribution to the water vapour continuum absorption, within a spectral range overlapping the water vapour rotational band. Retrievals have been performed by using a simultaneous physical retrieval procedure for atmospheric and spectroscopic parameters. Both day (summer) and night (winter) spectra have been used in our analysis. This new set of observations in the far infrared range has allowed us to extend validation and verification of state-of-the-art water vapour continuum absorption models down to 180 cm^{-1}. The results show that discrepancies between measurements and models are less than 10% in the interval 350-590 cm^{-1}, while they are slightly larger at wave numbers below 350 cm^{-1}. Overall, our study shows a good consistency between observations and state-of-the-art models and gives evidence for the need of also adjusting line absorption as done in Delamere et al. (2010). Finally, it has been found that there is a good agreement between the coefficients retrieved using either summer or winter spectra, which are acquired in far different meteorological conditions.

I-6. Determination of Near-IR Water Vapor Self Continuum from Observations

Eli Mlawer,[a] Daniel Gombos,[a] Matthew Alvarado,[a] Karen Cady-Pereira,[a] Vivienne Payne,[b] Alison Chase,[c] Joseph Michalsky[d]

[a] *AER, 131 Hartwell Ave., Lexington, MA*

[b] *Jet Propulsion Laboratory, Caltech, Pasadena, CA*

[c] *University of Maine, Orono, ME*

[d] *NOAA ESRL, Boulder, CO*

There is still significant uncertainty in the strength of water vapor continuum absorption in the windows between near-infrared water vapor bands. Many radiation codes obtain their water vapor continuum absorption coefficients from the MT_CKD continuum model, which derives its near-infrared values from a water vapor line-shape function that has been constrained by continuum measurements in other spectral regions. A number of recent laboratory studies have shown that the strength of the near-IR self continuum in the MT_CKD model is too low, but these laboratory studies disagree with each other by more than an order of magnitude. At the high end of the range of measured strengths, the self continuum absorbs a significant amount of solar radiation, so it is crucial that other observational studies are performed to establish the actual strength of this absorption source. We describe here an analysis of measurements from a solar FTS in Lamont, OK, part of the Total Carbon Column Observing Network (TCCON). Thirteen periods on individual days in 2012 were identified as being reasonably stable with respect to aerosol optical depth and precipitable water vapor. For each period, the FTS measurements, coincident measurements from a Normal Incidence Multi-Filter Radiometer (NIMFR) at the DOE ARM site, and calculations from the Line-By-Line Radiative Transfer Model (LBLRTM) were used to obtain aerosol optical depths in window regions from 8000-20000 cm^{-1}, which were then extended to lower wavenumbers through a generalized Angstrom relationship. In windows between 4000-7000 cm^{-1}, these aerosol optical depths, and the LBLRTM optical depths without any self continuum, were subtracted from FTS-derived total optical depths. The self continuum absorption coefficients that were derived from this procedure were at the low end of the recent laboratory studies, but higher than the current version of MT_CKD. The implications of the results of this study with respect to the absorption of solar irradiance will be discussed.

I-7. Atmospheric Radiative Transfer Generalised for Use on Earth and Other Planets: ARTS 2.2

J. Mendrok,[a] A. Perrin,[b] P. Eriksson,[c] S. A. Buehler,[d] O. Lemke[d]

[a]*Department of Computer Science, Electrical and Space Engineering, Luleå University of Technology, Kiruna, Sweden*

[b]*Laboratoire Inter Universitaire des Systemes Atmosphériques, CNRS, Université Paris EST-Créteil, Cedex, France*

[c]*Department of Earth and Space Science, Chalmers University of Technology, Sweden*

[d]*Meteorological Institute, University of Hamburg, Germany*

One of the major differences in radiative-transfer modeling in the atmospheres of Earth and other planets arises from the different composition of the atmospheres. When interested in measuring total abundance or even vertical distribution of atmospheric constituents, knowledge of parameters describing spectrally dependent absorption in dependence of atmospheric state is required. When modeling radiative transfer for different planets, the line shapes are often accounted for by scaling the parameters valid for Earth's "air" or by building a spectroscopic catalogue specific to the planet in question and its main atmospheric composition. This strongly limits applicability of these models. Based on the ARTS model (www.sat.ltu.se/arts), we have developed a toolbox for microwave atmospheric radiative transfer in solar system planets. As part of this, we developed and implemented a more generalized absorption calculation approach that is able to flexibly handle largely different atmospheric compositions. In order to facilitate this approach, we compiled a spectroscopic catalogue for the 0-3 THz spectral range that reports broadening and shift parameters for individual molecular species. Currently it covers the most abundant species in Earth and its neighboring planets (Venus, Mars, Jupiter). All spectroscopic data has been collected from literature (when available) or adapted from the HITRAN, GEISA, or JPL catalogues. Here, we present the generalized approach, introduce the spectroscopic catalogue in more depth, and show example results of absorption calculations for different planets underlining the relevance of our approach. Based on this experience, we recommend the reporting of broadening/shift parameters of individual species in spectroscopic catalogues like HITRAN in the future.

I-8. TAPAS, a web-based service of atmospheric transmission computation for astronomy

Jean-Loup Bertaux,[a] **Rosine Lallement,**[b] **Stephane Ferron,**[c] **Cathy Boonne**[d]

[a]*LATMOS, University of Versailles Saint-Quentin, 11 Boulevard d'Alembert, 78280, Guyancourt*

[b]*GEPI, Observatoire de Paris, 5 Place Jules Janssen, Meudon 92195,France*

[c]*ACRI-ST, Route du Pin Montard, Sofia-Antipolis,France*

[d]*IPSL, Institut Pierre-Simon Laplace, Place Jussieu, Paris 5*

We have developed a web-based service, TAPAS (“Transmissions Atmosphriques Personnalise pour lAStronomie” or Transmissions of the AtmosPhere for AStronomical data, Bertaux et al., Astronomy and Astrophysics, 564,A46, 2014). This service, hosted at ETHER/IPSL in Paris, computes the atmospheric transmission in the line-of-sight (LOS) to the target indicated by the user. The user files a request indicating the time, ground location, and RA/DEC of the target or the Zenith Angle of the LOS. The actual atmospheric profile (temperature, pressure, humidity, ozone content) at that time and place is retrieved from the ETHER atmospheric data base (from a combination of ECMWF meteorological field and other information), and the atmospheric transmission is computed from LBLRTM software and HITRAN data base for a number of gases O_2,H_2O,O_3,CO_2,CH_4,N_2O, and Rayleigh extinction. The first purpose of TAPAS output is to allow identification of observed spectral features as being from atmospheric or astrophysics origin. The returned transmission may also serve for characterizing the spectrometer in wavelength scale and Instrument Line Spectral Function (ILSF) by comparing one observed spectrum of an atmospheric feature to the transmission. Finally, the TOA (Top Of Atmosphere) spectrum is obtained by division of the observed spectrum by the computed atmospheric transmission. We describe briefly the mechanism of computation of the atmospheric transmissions, and we show some results for O_2 and H_2O atmospheric absorption in the range 0.5-1.5 μm. The wavelength range is 500-2500 nm, but may be extended in the future. It is hoped that this service will help many astronomers in their research. The user may also contribute to general knowledge of the atmospheric transmission, if he/she finds systematic discrepancies between synthetic transmissions and the observed spectra. We show an extreme case of a water line at 1507.26 nm whose intensity predicted by HITRAN 2008 is overestimated by a factor 5, while much better estimated with HITRAN 2012. The TAPAS address is http://ether.ipsl.jussieu.fr/tapas/

I-9. The Doppler Wind and Temperature Sounder

Martin McHugh, Dave Fritts, Larry Gordley

Global Atmospheric Technology and Sciences (GATS), Newport News, Virginia, USA

The Doppler Wind and Temperature Sounder (DWTS) is novel sensor concept for measuring global winds and temperatures from cloud-top to the thermosphere. This will significantly improve medium- and long-range weather forecasts and enable more advanced tracking of severe storms. The approach uses the inherent high spectral resolution from gas filter correlation radiometry to simultaneously measure the Doppler shift and linewidth of limb emission spectra as viewed from low-Earth orbit. DWTS images the limb through low-pressure gas cells containing CO_2, NO and NO_2. We describe here how very accurate vector winds and kinetic temperatures can be inferred from these observations. Profiles of temperature and wind can be measured day and night continuously from 15 to over 250 km at intervals of 10 km along-track with less than 2% uncertainty. A constellation of 6-12 DWTS instruments on small satellites would provide unprecedented observations of global atmospheric dynamics from the lower stratosphere into the middle thermosphere, greatly improving weather and storm forecasting. We present the current status and plans to realize this important mission.

SESSION II: Databases-I

II-1. Comparison between HITRAN2012 data and a new experimental line list recently published for water vapor in the spectral region 6450 to 9400 cm^{-1}

S. Mikhailenko,[a] **L. Régalia**[b]

[a] *Laboratory of Theoretical Spectroscopy, V.E. Zuev Institute of Atmospheric Optics, SB, Russian Academy of Science, 1, Akademician Zuev square, 634021 Tomsk, Russia,Mathematical Physics Department, Tomsk Polytechnic University, 30, Lenin av., 634050 Tomsk, Russia*

[b] *Groupe de Spectrométrie Moléculaire et Atmosphérique, UMR 6089, Faculté des sciences, BP 1039, 51687 REIMS CEDEX2, France*

Recently an experimental list of water absorption lines between 6450 and 9400 cm^{-1} has been published by Régalia et al.[1] This paper includes detailed comparison with HITRAN2008[2] and GEISA2009[3] databases. Before the end of the redaction of this article[1], the new version of the HITRAN database[4] was published. Only a short comment on the HITRAN2012 water data has been included in the paper[1].

The aim of this presentation is to continue the comparison of the experimental data[1] versus the HITRAN2012 database[4]. A short description of the HITRAN2012 water content in the 6450 - 9400 cm^{-1} spectral range is given and data are separated into 16 groups according to their origin and independent of the absorption bands. Selected examples of comparison between the observed data[1] and the HITRAN2012 line list[4] will be presented according to those groups.

---

[1] L. Régalia, et al Water vapor line parameters from 6450 to 9400 cm^{-1} *J Quant Spectrosc Radiat Transfer* **136**(119), 2014.

[2] L.S. Rothman et al. The HITRAN 2008 molecular spectroscopic database *J Quant Spectrosc Radiat Transfer* **110**(533), 2009.

[3] N. Jacquinet-Husson, et al. The 2009 edition of the GEISA spectroscopic database *J Quant Spectrosc Radiat Transfer* **112**(2395), 2011.

[4] L.S. Rothman, et al. The HITRAN2012 molecular spectroscopic database *J Quant Spectrosc Radiat Transfer* **130**(4), 2013

II-2. A Comprehensive Catalogue of Absorption Cross-Sections of Halocarbons and Related Molecules

Keith P. Shine,[a] **O. Hodnebrog**,[b] **J. S. Fuglestvedt**,[b] **G. Myhre**,[b]
G. Marston,[c] **C. J. Nielsen**,[d] **T. J. Wallington**[e]

[a]*Department of Meteorology, University of Reading, RG6 6BB, UK*

[b]*Center for International Climate and Environmental Research-Oslo (CICERO), Oslo, Norway*

[c]*Department of Chemistry, University of Reading, Reading, UK*

[d]*Department of Chemistry, University of Oslo, Oslo, Norway*

[e]*Ford Motor Company, Research and Advanced Engineering Department, Dearborn, Michigan, USA*

The collation and applications of a comprehensive database of infrared cross-sections of 200 halocarbons and related molecules is described. The first phase of this research was published by Hodnebrog et al. (Reviews of Geophysics, 2013, doi:10.1002/rog.20013) in which cross-sections were drawn from a wide range of laboratory studies in the published literature and, when these were not available, from ab initio calculations. The criteria for selection of particular cross-section data sets will be described. The primary purpose of the database is for use in the calculation of radiative forcing and climate metrics such as the Global Warming Potential, and illustrations of their usage will be given. The work on the database is intended to be an ongoing exercise and the plan is to revise and expand the database as new data become available.

II-3. New and Improved Infrared Spectroscopy of Halogen-Containing Species for ACE-FTS Retrievals

Jeremy J. Harrison

Department of Chemistry, University of York, York, United Kingdom

The Atmospheric Chemistry Experiment Fourier transform spectrometer (ACE-FTS), onboard the SCISAT-1 satellite, is a high-resolution (0.02 cm^{-1}) instrument covering the 750-4400 cm^{-1} spectral region in solar occultation mode. Launched in August 2003, the ACE-FTS has been taking atmospheric measurements for over ten years. With long atmospheric pathlengths ($\sim$300 km) and the sun as a radiation source, the ACE-FTS provides a low detection threshold for trace species in the atmosphere. In fact, it measures the vertical profiles of more molecules in the atmosphere than any other satellite instrument.

Fluorine- and chlorine-containing molecules in the atmosphere are very strong greenhouse gases, meaning that even small amounts of these gases contribute significantly to the radiative forcing of climate. Chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) are regulated by the 1987 Montreal Protocol because they deplete the ozone layer. Hydrofluorocarbons (HFCs), which do not deplete the ozone layer and are not regulated by the Montreal Protocol, have been introduced as replacements for CFCs and HCFCs. HFCs have global-warming potentials many times greater than carbon dioxide, and are increasing in the atmosphere at a very fast rate.

The quantification of the atmospheric abundances of such molecules from measurements taken by the ACE-FTS and other satellite instruments crucially requires accurate quantitative infrared spectroscopy. HITRAN contains absorption cross section datasets for a number of these species, but many of them have minor deficiencies that introduce systematic errors into satellite retrievals. This talk will focus on new and improved laboratory measurements for a number of important halogenated species.

II-4. New Analysis of the CRDS Spectrum of the Six ^{16}O/^{18}O Isotopologues of Ozone up to 7920 cm^{-1}

Alain Barbe,[a] **M.-R. De Backer**,[a] **Vl. G. Tyuterev**,[a] **D. Mondelain**,[b]
S. Kassi,[b] **A. Campargue**,[b] **E. N. Starikova**[c]

[a]*Groupe de Spectrométrie Moléculaire et Atmosphérique, UMR CNRS 7331, Université de Reims, Moulin de la Housse, B.P. 1039, 51687 Reims cedex 2, France*

[b]*LIPhy Université de Grenoble Alpes, UMR CNRS 5588, 38041 Grenoble, France*

[c]*LTS, V.E. Zuev Institut of Atmospheric Optics SB RAS, 1 Akademician Zuev square, 634021 Tomsk, Russia*

We have extended the analysis of the near infrared absorption spectrum of ozone up to 7920 cm^{-1} i.e. only 7 % below the dissociation energy, D_0. The spectra of $^{16}O_3$ and $^{18}O_3$ and of two ^{18}O enriched samples were recorded at LIPhy-Grenoble by high-sensitivity Cavity Ring Down Spectroscopy between 5850 and 7920 cm^{-1}. In this presentation, we will update the recent review of Refs[1,2] by new analysis for the different isotopologues, in particular the three most excited bands of $^{16}O_3$ reported so far. These results are of particular interest to test and validate the potential energy surface in its ground electronic state with potential impact on non-LTE studies.

Overall, a total of 71 bands were rovibrationally assigned and modelled:

29 bands for 666 (9024 assigned transitions)

7 bands for 668 (3117)

4 bands for 686 (1308)

3 bands for 886 (1849)

6 bands for 868 (1914)

22 bands for 888 (6332)

Total : 23544, leading to the knowledge of 13412 energy levels.

The effective Hamiltonian modelling also includes 69 dark bands in interaction with the observed bright bands. We will illustrate the achieved agreements between observed and calculated spectra. Comparisons between fitted and predicted band centres and rotational constants will be discussed.

---

[1] A. Barbe, S. Mikhailenko, E. Starikova, M.R. De Backer-Barilly, Vl.G. Tyuterev, D. Mondelain, S. Kassi, A. Campargue, C. Janssen, S. Tashkun, R. Kochanov, R. Gamache, J. Orphal, *JQSRT*, 130, 172-190, (2013).

[2] www.ozone.univ-reims.fr and www.ozone.iao.ru

II-5. Measurements and Modeling of $^{16}O^{12}C^{17}O$ Spectroscopic Parameters at 2μm

D. Jacquemart,[a] **K. Sung**,[b] **L. R. Brown**,[b] **M. Coleman**,[b] **A. W. Mantz**,[c]
M. A. H. Smith[d]

[a]*Sorbonne Universités, UPMC Univ Paris 06, UMR 8233, Monaris, Paris, France*

[b]*Jet Propulsion Laboratory, California Institute of Technology, Pasadena, USA*

[c]*Connecticut College, New London, USA*

[d]*NASA Langley Research Center, Hampton, USA*

In the present study, line-intensity measurements for $^{16}O^{12}C^{17}O$ were performed using a high-resolution Fourier transform spectrometer (Bruker IFS-125HR) together with a Herriott cell allowing a 20.956 m absorption path. For this, a ^{17}O-enriched CO_2 gas sample mixture was used. The $^{16}O^{12}C^{17}O$ isotopologue abundance in the sample was determined to be 0.3991 by mass spectrometry. Since a collisional narrowing effect has been observed, the Rautian profile was systematically used instead of the Voigt profile. Finally, around 1000 transitions were studied between 4604 and 5126 cm^{-1} involving 15 bands of the $^{16}O^{12}C^{17}O$ isotopologue. For each of the 15 bands, transition dipole moments and Herman-Wallis factors were derived, which also enabled a global comparison with theoretical calculations and predictions achieved for carbon dioxide. For the measured and calculated line positions, the accuracy is between 0.1 - 1×10^{-3} cm^{-1}. For line intensities, depending on the intensity of the band, accuracies are between 2 - 3 % for 5 cold bands and 2 hot bands and between 6 - 30 % for 8 weaker hot bands. Results from this work are compared to previous works and to HITRAN 2012. Complete line lists were generated to support atmospheric remote sensing for the Earth (e.g. GOSAT, OCO-2 ...), Mars and Venus.

II-6. Line Positions and Intensities of $^{13}C^{12}CH_6$ in the 12.2 μm Region

M. A. H. Smith,[a] **V. Malathy Devi**,[b] **D. Chris Benner**,[b] **K. Sung**,[c]
T. J. Crawford,[c] **A. W. Mantz**[d]

[a]*Science Directorate, NASA Langley Research Center, Hampton, VA 23681*

[b]*Dept. of Physics, The College of William and Mary, Williamsburg, VA 23187*

[c]*Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109*

[d]*Dept. of Physics, Astronomy and Geophysics, Connecticut College, New London, CT 06320*

High-resolution, high signal-to-noise spectra of mono-substituted ^{13}C-ethane ($^{13}C^{12}CH_6$) in the 12.2 μm region have been recorded with a Bruker IFS 125HR Fourier transform spectrometer. Four of these spectra were recorded at three different temperatures between 130 and 208 K using a 99% ^{13}C-enriched ethane sample contained in a 20.38-cm long coolable absorption cell[1]. A multispectrum nonlinear least squares fitting technique[2] was used to fit the same intervals in these four spectra simultaneously to determine line positions and intensities. Similar to our previous analyses of $^{12}C_2H_6$ spectra in this same region[3], constraints were applied to accurately fit each pair of doublet components arising from torsional Coriolis interaction of the excited $\nu_{12} = 1$ state with the nearby torsional $\nu_6 = 3$ state. Line intensities are reported for 1660 ν_{12} absorption lines for which the assignments are known, and integrated intensities are estimated as the summation of the measured values. The measured line positions and intensities are compared with values in recent editions of spectroscopic databases.[4]

---

[1] K. Sung, A. W. Mantz, L. R. Brown, *et al.*, *J. Mol. Spectrosc.* **162** (2010) 124-134.

[2] D. C. Benner, C. P. Rinsland, V. Malathy Devi, M. A. H. Smith and D. Atkins, *JQSRT* **53** (1995) 705-721.

[3] V. Malathy Devi, C. P. Rinsland, D. Chris Benner, *et al.*, *JQSRT* **111** (2010) 1234-1251; V. Malathy Devi, D. Chris Benner, C. P. Rinsland, *et al.*, *JQSRT* **111** (2010) 2481-2504.

[4] Research described in this paper was performed at Connecticut College, the College of William and Mary, NASA Langley Research Center and the Jet Propulsion Laboratory, California Institute of Technology, under contracts and cooperative agreements with the National Aeronautics and Space Administration.

II-7. Are your Spectroscopic Data being used?

Iouli E. Gordon,[a] **Laurence S. Rothman**,[a] **Jonas S. Wilzewski**[b]

[a]*Harvard-Smithsonian Center for Astrophysics, Atomic and Molecular Physics Division, Cambridge MA 02138-1516, USA*

[b]*Fachrichtung Physik, Fakultät Mathematik und Naturwissenschaften, Technische Universität Dresden, Mommsenstraße 11, 01069 Dresden, Germany*

Spectroscopy is an established and indispensable tool in science, industry, agriculture, medicine, surveillance, etc.. The potential user of spectral data which is not available in HITRAN[1] or other databases, searches the spectroscopy publications. After finding the desired publication, the user very often encounters the following problems: 1) They cannot find the data described in the paper. There can be many reasons for this: nothing is provided in the paper itself or supplementary material; the authors are not responding to any requests; the web links provided in the paper have long been broken, etc..
2) The data is presented in a reduced form, for instance through the fitted spectroscopic constants. While this is a long-standing practice among spectroscopists, there are numerous serious problems with this practice, such as users getting different energy and intensity values because of different representations of the solution to the Hamiltonian, or even just despairing of trying to generate usable line lists from the published constants.

Properly providing the data benefits not only users but also the authors of the spectroscopic research. We will show that this increases citations to the spectroscopy papers and visibility of the research groups. We will also address the quite common issue when researchers obtain the data, but do not feel that they have time, interest or resources to write an article describing it. There are modern tools that allow one to make these data available to potential users and still get credit for it. However, this is a worst case scenario recommendation, i.e., publishing the data in a peer-reviewed journal is still the preferred way.

---

[1] L. S. Rothman, I. E. Gordon, et al. "The HITRAN 2012 molecular spectroscopic database," JQSRT 113, 4-50 (2013).

Poster Session I

PI-1. The IUPAC Database of Rotational-Vibrational Energy Levels and Transitions of Water Isotopologues from Experiment and Theory

Attila G. Császár,[a] **T. Furtenbacher,**[a] **Jonathan Tennyson,**[b]
Peter F. Bernath,[c] **Linda R. Brown,**[d] **Alain Campargue,**[e]
Ludovic Daumont,[f] **Robert R. Gamache,**[g] **Joseph T. Hodges,**[h]
Olga V. Naumenko,[i] **Oleg L. Polyansky,**[j] **Laurence S. Rothman,**[k]
Ann Carine Vandaele,[l] **Nikolai F. Zobov**[j]

[a] *MTA-ELTE Research Group on Complex Chemical Systems, H-1518 Budapest, P.O. Box 32, Hungary*

[b] *Department of Physics and Astronomy, University College London, Gower Street, London, WC1E 6BT, U.K.*

[c] *Old Dominion University, Norfolk, VA, USA*

[d] *Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, USA*

[e] *Université Joseph Fourier/CNRS, Grenoble, France*

[f] *Université de Reims Champagne-Ardenne, Reims, France*

[g] *University of Massachusetts, Lowell, MA, USA*

[h] *National Institute of Standards and Technology, Gaithersburg, MD, USA*

[i] *Institute of Atmospheric Optics, Russian Academy of Sciences, Tomsk, Russia*

[j] *Institute of Applied Physics, Russian Academy of Sciences, Nizhny Novgorod, Russia*

[k] *Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, USA*

[l] *Institut d'Aéronomie Spatiale de Belgique, Brussels, Belgium*

The results of an IUPAC Task Group formed in 2004 on "A Database of Water Transitions from Experiment and Theory" (Project No. 2004-035-1-100) are presented. Energy levels and recommended labels involving exact and approximate quantum numbers for the main isotopologues of water in the gas phase, $H_2{}^{16}O$, $H_2{}^{18}O$, $H_2{}^{17}O$, $HD^{16}O$, $HD^{18}O$, $HD^{17}O$, $D_2{}^{16}O$, $D_2{}^{18}O$, and $D_2{}^{17}O$, are determined from measured transition wavenumbers. The transition wavenumbers and energy levels are validated using the MARVEL (measured active rotational–vibrational energy levels) approach and first-principles nuclear motion computations. The extensive data, *e.g.*, more than 200,000 transitions have been handled for $H_2{}^{16}O$, including lines and levels that are required for analysis and synthesis of spectra, thermochemical applications, the construction of theoretical models, and the removal of spectral contamination by ubiquitous water lines. These datasets can also be used to assess where measurements are lacking for each isotopologue and to provide accurate frequencies for many yet-to-be measured transitions. The lack of high-quality frequency calibration standards in the near infrared is identified as an issue that has hindered the determination of high-accuracy energy levels at higher frequencies. The generation of spectra using the MARVEL energy levels combined with transition intensities computed using high accuracy ab initio dipole moment surfaces are discussed.

PI-2. High Temperature Linelists Of Three Major Water Isotopologues

O. L. Polyansky,[a] **A. A. Kyuberis**,[b] **N. F. Zobov**,[b] **J. Tennyson**,[c] **L. Lodi**[c]

[a] *University College London and Russian Academy of Sciences, Nizhny Novgorod*

[b] *Russian Academy of Sciences, Nizhny Novgorod*

[c] *University College London, U.K.*

High-temperature water linelists for three water isotopologues - $H_2{}^{16}O$, $H_2{}^{17}O$ and $H_2{}^{18}O$ are calculated using the newly developed potential energy surfaces (PESs) and the high-quality dipole moment surface (DMS)[1]. For $H_2^{16}O$, a PES accurate up to 40 000 cm^{-1} was developed and the energy levels cutoff up to 40 000 cm^{-1} was used. The lines for all the levels up to J =72 are computed. The accuracy of the PES is an order of magnitude better than the one used for the BT2 linelist[2]. For the two minor isotopologues, less extensive linelists are calculated, which coincide in highest $J \leq 50$ and energy levels up to 30 000 cm^{-1}, with the parameters used for the BT2 linelist. A newly-developed method for calculating the PES of isotopologues is used which gives the same level of accuracy for $H_2{}^{17}O$ and $H_2{}^{18}O$ as obtained for known levels of $\mathrm{H_2{}^{16}O}$ even when these levels are yet unknown experimentally for the minor isotopologue.

---

[1] L. Lodi, J. Tennyson and O.L. Polyansky, 2011, J. Chem. Phys., **135** , 034113

[2] R. J. Barber AND J. Tennyson AND G. J. Harris AND R. N. Tolchenov, 2006, MNRAS, **368**, 1087.

PI-3. Observations of Relative Absorption Strengths of Water Vapour in the Blue Wavelength Range

Johannes Lampel,[a] Denis Pöhler,[a] Jens Tschritter,[a] Udo Frieß,[a]
Ulrich Platt,[a] André Butz[b]

[a] *Inst. of Environmental Physics, Heidelberg University, Germany*

[b] *IMK-ASF, Karlsruhe Institute of Technology Eggenstein-Leopoldshafen, Germany*

In recent updates (2009-2012) of the HITRAN water vapour (H_2O) spectroscopic line-strength compilation in the blue spectral region (394 - 480 nm), significant changes for the absorption bands at 416 nm and 426 nm were reported. In order to study the consistency of the cross sections calculated from these compilations and the BT2 line list, we retrieved relative H_2O absorption strengths from atmospheric Long-path and Multi-Axis - Differential Optical Absorption Spectroscopy (DOAS) measurements for the spectral range from 390-480 nm. We observe a significantly better agreement of the updated HITRAN water vapour absorption cross sections with observation. However we also found that significant correction factors are required to bring the wavelength intervals from 410-434 nm of the water vapour absorption into agreement with observation. These factors (with which the new HITRAN line strengths have to be multiplied to obtain good optimum fit of modeled and measured spectra) range between 0.5 and 2.1 indicating that the HITRAN water vapour absorption compilation still needs significant corrections in the blue spectral region. These improvements of the H_2O line-strength data base would be an important step towards better DOAS measurements of atmospheric species in the blue wavelength range (e.g. of NO_2 or iodine oxide radicals). It is therefore relevant for ground-based and satellite observations.

PI-4. Mid infrared and near infrared spectral data of CO_2, CO and CH_4 measured with high-resolution FTIR-spectroscopy

Jens Brunzendorf, Anne Rausch, Anton Serdyukov, Viktor Werwein, Olav Werhahn, Volker Ebert

Physikalisch-Technische Bundesanstalt, Bundesallee 100, 38116 Braunschweig, Germany

As part of the European EUMETRISPEC project (www.eumetrispec.org), which is a joint effort of the national metrology institutes (NMI) of Germany, Denmark, France, The Netherlands, Slovakia and Finland, PTB, the NMI of Germany, had the task to setup a European high-resolution spectroscopy infrastructure to target measurements of spectral line parameters of the major greenhouse gases traceable to the SI units. This infrastructure, to be validated by the partners traceable high-resolution laser instrumentation, is based on a modified, high-resolution ($0.002\,\mathrm{cm}^{-1}$) Bruker IFS 125 Fourier transform spectrometer which covers in the current development stage the near infrared and mid infrared spectral region. While the project is still ongoing, the FTIR facility has been setup in the meantime and has begun to be used for various high-resolution measurements intended to deliver spectral sample data of greenhouse gases as well as test case molecules like carbon monoxide. In order to enable background-free absolute $CO_2\,/\,H_2O\,/\,CH_4\,/\,N_2O$ measurements the FTIR instruments vacuum system was significantly improved. Now a pressure of 10^{-5} mbar is maintained which is at least two orders of magnitude lower than in the unmodified spectrometer. Furthermore, temperature-controlled, ethanol-cooled FTIR-internal measurement cells are developed in order to allow temperature dependent measurements at least down to 220 K. While N_2O results will be presented in a separate paper by Werwein et al. we present here a first sample set of spectral data covering CO, CH_4 and CO_2. For CO we determined self-broadening coefficients of the R16 to R23 lines in the CO $2\,\nu$ band between $4300 - 4350\,\mathrm{cm}^{-1}$ as well as their temperature-dependence for temperatures between 213 K and room-temperature. In addition, we measured pressure-dependent CH_4 spectra between 20 and 1200 mbar and experimentally derived CH_4 self-broadening coefficients in the tetradecade between $5880\,\mathrm{cm}^{-1}$ and $5900\,\mathrm{cm}^{-1}$, for which currently estimates are available in the HITRAN 2012 database. Finally, we also analyzed pressure-dependent, room-temperature CO_2 spectra and derived self-broadening coefficients of more than 50 rotational lines of the $\nu_1 + 2\nu_2 + \nu_3$ band near $2\,\mu$m. Due to the excellent background vacuum in our new FT facility, we were also able to precisely analyze the strong CO_2 lines without any interferences from CO_2 inside the spectrometer compartment. This presentation will discuss the quality of the raw spectra and the intermediate products as well as the current accuracy levels achieved for the final spectral data products.

These measurements were realized within the framework of the EUMETRISPEC project and the authors acknowledge financial support within the EMRP. The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union.

PI-5. FTS Studies of the ^{17}O-Enriched Isotopologues of CO_2 Toward Creating a Complete and Highly Accurate Reference Standard

Ben M. Elliott, Keeyoon Sung, Charles E. Miller

NASA Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, M/S 233-300, Pasadena, CA 91109

The proliferation and increased abilities of remote-sensing missions for the monitoring of planetary atmospheric gas species has spurred the need for complete and accurate spectroscopic reference standards. As a part of our ongoing effort toward creating a global carbon dioxide (CO_2) frequency reference standard, we report new FTS measurements of the ^{17}O-enriched isotopologues of CO_2. The first measurements were taken in the ν_3 region (2200 - 2450 cm^{-1}, ∼65 - 75 THz), and have absolute calibration accuracies of 100 kHz (3×10^{-6} cm^{-1}), comparable to the uncertainties for typical sub-millimeter/THz spectroscopy. Such high absolute calibration accuracy has become regular procedure for the cases of linear molecules such as CO_2 and CO for FTS measurements at JPL, and enables us to produce measured transition frequencies for entire bands with accuracies that rival those of early heterodyne measurements for individual beat notes. Additionally, by acquiring spectra of multiple carbon dioxide isotopologues simultaneously, we have begun to construct a self-consistent frequency grid based on CO_2 that extends from 20 - 200 THz. These new spectroscopic reference standards are a significant step towards minimizing CO_2 retrieval errors from remote-sensing applications, especially those involving targets with predominantly CO_2 atmospheres such as Mars, Venus and candidate terrestrial exoplanets where minor isotopologues will make significant contributions to the radiance signals.

PI-6. Climate Change to the Nuclear Fuel Cycle: Expanding the spectral $^{14}CO_2$ database for non-AMS Field Measurement Systems

B. D. V. Marino, **R. G. Odonnell, D. E. Tolliver**

Planetary Emissions Management, Inc., One Broadway, 14th Floor, Cambridge, MA 02142

Accelerator Mass Spectrometry (AMS) is well known and universally employed for radiocarbon analysis but is not adaptable to in-situ field measurements limiting applications. $^{14}CO_2$ is a key tracer for fossil fuel CO_2 as well as for release of enriched $^{14}CO_2$ characteristic of the nuclear fuel cycle with $\Delta^{14}CO_2$ values ranging from -1000 to $\sim$+500 per mil. However, to exploit the full value of in situ $^{14}CO_2$ data in diverse climate change and nuclear fuel cycle applications, high data rate temporal and spatial field measurement sensors and systems are required. The development of non-AMS methods based on quantum cascade laser, cavity ring down and optogalvanic spectroscopy are emerging applications but not fully developed for field use or widely accepted. Spectral data for lasing transitions for $^{14}CO_2$ are lacking in contrast to HITRAN data available for $^{12}CO_2$ (626) and $^{13}CO_2$ (636) (among other isotopologues 628, 638, etc.) in the spectral databases limiting development and innovation in non-AMS $^{14}CO_2$ sensors and systems. We review the corpus of $^{14}CO_2$ spectral data available in the literature and document grating tuned isotopic lasers (e.g., Freed 1990[1]; Bradley et al., 1986[2]), well suited for expanded spectral studies of $^{14}CO_2$ and inclusion in the HITRAN database. Non-AMS $^{14}CO_2$ approaches are reviewed with suggestions for future work to support field systems for $^{14}CO_2$ measurements. Available isotopic lasers for $^{14}CO_2$ collaborative studies are described.

---

[1] Freed, C., Ultrastable CO_2 Lasers, Lincoln Laboratory Journal, 3, No. 3, 479 (1990).

[2] Bradley, L. C., Soohoo, K. L., & Freed, C. Absolute Frequencies of Lasing Transitions in Nine CO2 Isotopic Species. Quantum, (2), 234267 (1986).

PI-7. S&MPO – an Information System for Ozone Spectroscopy on the Web

Y. Babikov,[a] **S. Mikhailenko,**[a] **A. Barbe,**[b] **V. Tyuterev**[b]

[a] *Tomsk State University; V.E. Zuev Institute of Atmospheric Optics RAN; Tomsk , Russia*

[b] *Groupe de Spectrométrie Moléculaire et Atmosphérique, UMR CNRS 7331, BP 1039, F-51687, Reims Cedex 2, France*

S&MPO ("Spectroscopy and Molecular Properties of Ozone") is an Internet accessible information system[1] devoted to high resolution spectroscopy of the ozone molecule, related properties and data sources. S&MPO contains information on original spectroscopic data (line positions, line intensities, energies, transition moments, spectroscopic parameters) recovered from comprehensive analyses and modeling of experimental spectra (examples in Refs.[2,3,4] and references therein) as well as associated software for data representation written in PHP Java Script, C++ and FORTRAN. The line-by-line list of vibration-rotation transitions and other information are organized as a relational database under control of MySQL database tools. The main S&MPO goal is to provide an access to all available information on vibration-rotation molecular states and transitions under extended conditions based on extrapolations of laboratory measurements using validated theoretical models. Applications for the S&MPO may include: education/training in molecular physics, radiative processes, laser physics; spectroscopic applications (analysis, Fourier transform spectroscopy, atmospheric optics, optical standards, spectroscopic atlases); applications to environment studies and atmospheric physics (remote sensing); data supply for specific databases; and to photochemistry (laser excitation, multiphoton processes). The system is accessible via Internet on two sites: http://smpo.iao.ru and http://smpo.univ-reims.fr. Complementary S&MPO data with respect to HITRAN-2012 database will be discussed.

---

[1] Yu.Babikov, S.Mikhailenko, A.Barbe and V.Tyuterev , JQSRT, in press (2014)

[2] S. Mikhailenko, A. Barbe, V. Tyuterev. J Mol Spectrosc 215,29 (2002)

[3] A. Campargue, M-R. De Backer, A. Barbe, V. Tyuterev, S. Kassi. PCCP, 10,2925(2008)

[4] A. Barbe, S. Mikhailenko, E. Starikova, M-R. De Backer, V.Tyuterev, D. Mondelain, S. Kassi, A. Campargue, C. Janssen, S. Tashkun, R. Kochanov, R. Gamache, J. Orphal JQSRT 130,172 (2013)

PI-8. Ozone 5μm Range Revisited: Accurate Laboratory Measurements and Ab Initio Calculations

V. Tyuterev,[a] **A. Barbe,**[a] **S. Mikhailenko,**[b] **S. Tashkun**[b]

[a] *Groupe de Spectrométrie Moléculaire et Atmosphérique, UMR CNRS 7331, BP 1039, F-51687, Reims Cedex 2, France*

[b] *Tomsk State University; V.E. Zuev Institute of Atmospheric Optics RAN; Tomsk , Russia*

The 5μ range[1] is one of the most important spectral intervals for the retrieval of atmospheric ozone using various remote-sensing techniques. Some inconsistencies in ozone atmospheric column determinations with FTS measurements have been reported[2] when available spectroscopic databases were used simultaneously in the 5μm and 10μm ranges. Our study is a part of a project for an improvement of ozone line intensity determinations in the 5μm range via accurate FTS laboratory measurements and analyses. Comparisons with HITRAN data and with preliminary first-principle intensity predictions using *ab initio* electronic structure calculations[3] will be discussed. A current version of the new line list is included in the last release of the S&MPO database http://smpo.iao.ru and http://smpo.univ-reims.fr [4]. Support from the LEFE Chat program of CNRS is acknowledged.

---

[1] A. Barbe, S. Mikhailenko, E. Starikova, M-R. De Backer, V.Tyuterev, D. Mondelain, S. Kassi, A. Campargue, C. Janssen, S. Tashkun, R. Kochanov, R. Gamache, J. Orphal JQSRT 130, 172 (2013).

[2] C. Janssen and Yao Te, private communication (2013).

[3] V. Tyuterev , R. Kochanov, S.Tashkun, F.Holka, P. Szalay. J Chem Phys 139, 134307 (2013).

[4] Yu.Babikov, S.Mikhailenko, A.Barbe and V.Tyuterev , JQSRT, in press (2014).

PI-9. High Energy States of Ozone Obtained from New Ab Initio Potential Energy Surfaces and from Experimental Spectra Analyses: the "Reef Structure" Puzzle

Roman V. Kochanov,[a] **Vladimir G. Tyuterev,**[b] **Alain Barbe,**[b]
Marie-Renée De Backer,[b] **Evgeniya N. Starikova,**[c] **Alain Campargue,**[d]
Samir Kassi,[d] **Didier Mondelain,**[d] **Peter G. Szalay,**[e] **Sergei A. Tashkun**[f]

[a]*Harvard-Smithsonian Center for Astrophysics Atomic and Molecular Physics Division Cambridge MA 02138, USA; Laboratory of Quantum Mechanics of Molecules and Radiative Processes, Tomsk State University, 36 Lenin Avenue, 634050 Tomsk, Russia*

[b]*Groupe de Spectrométrie Moléculaire et Atmosphérique, UMR CNRS 7331, BP 1039, F-51687, Reims Cedex 2, France*

[c]*Laboratory of Theoretical Spectroscopy, V. E. Zuev Institute of Atmospheric Optics, 1 Academician Zuev square, 634055 Tomsk, Russia; Laboratory of Quantum Mechanics of Molecules and Radiative Processes, Tomsk State University, 36 Lenin Avenue, 634050 Tomsk, Russia*

[d]*Laboratoire Interdisciplinaire de Physique, Université de Grenoble 140 Avenue de la Physique BP 87 38402 Saint Martin dHères, France*

[e]*Institute of Chemistry , Eötvös Loránd University, Pázmány Péter sétány 1/A, 1117 Budapest, Hungary*

[f]*Laboratory of Theoretical Spectroscopy, V. E. Zuev Institute of Atmospheric Optics, 1 Academician Zuev square, 634055 Tomsk, Russia; Laboratory of Quantum Mechanics of Molecules and Radiative Processes, Tomsk State University, 36 Lenin Avenue, 634050 Tomsk, Russia*

High-energy states of ozone $^{16}O_3$ and $^{18}O_3$ isotopologues were predicted from a new *ab initio* potential energy surface[1] and derived from experimental spectra analysis up to 7920 cm^{-1}. A brief outline is given for highly accurate *ab initio*[2] calculations and for new analytical PES modeling. The new analytical PES of ozone takes into account such structural properties of ozone as non-linear minimum energy path and non-additivity of the fragmentation energy. The "reef structure" (activation barrier) problem is investigated as well as its influence on the shifting of harmonic frequencies and vibrational energy levels of ozone. Correction of *ab initio* data was made by accounting

---

[1] Vl. G. Tyuterev, R. V. Kochanov, S. A. Tashkun, F. Holka, P. G. Szalay. JCP, 139(13) ,134307 (2013)

[2] F. Holka, P. G. Szalay, T. Muller, Vl. G. Tyuterev, J. Phys. Chem. A114, 9927 (2010)

for the couplings of many excited electronic states[3]. It is shown that this correction leads to a smoother PES with the ”reef structure” almost vanishing. The PES ”without reef structure” appears to be more precise in terms of spectroscopy: vibration energies are in good agreement with available experimental data[4,5,6] up to 94% of the dissociation energy with an average error of vibrational prediction near 1 cm^{-1}, which is much better than all available calculations that involve the activation barrier on the transition state.

---

[3] R. Dawes, P. Lolur, J. Ma, and H. Guo, J. Chem. Phys. 135, 081102 (2011)

[4] A. Campargue, A. Barbe, M.-R. De Backer et al, PCCP,10, 2925 (2008)

[5] A. Barbe, M.-R. De Backer, Vl. G. Tyuterev et al, J Mol Spectrosc., 269,175 (2011)

[6] A. Barbe, S. N. Mikhailenko, E. N. Starikova, M.-R. De Backer, Vl. G. Tyuterev, D. Mondelain, S. Kassi, A. Campargue, C. Janssen, S. A. Tashkun, R. V. Kochanov, R. Gamache, J. Orphal, JQSRT, 130, 172 (2013)

PI-10. The Impact of Using Different Ozone Cross Sections on Ozone Profile Retrievals from OMI UV Measurements

Cheng Liu, Xiong Liu, Kelly Chance

Atomic and Molecular Physics Division, Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, USA

We compare three datasets of high-resolution O_3 cross sections and evaluate the effects of using these cross sections on O_3 profile retrievals from OMI UV (270-330 nm) measurements. These O_3 cross sections include Brion-Daumont-Malicet (BDM), Bass-Paur (BP) and a new dataset measured by Serdyuchenko et al. (submitted; SGWCB), which is made from measurements at more temperatures and in a wider temperature range than BDM and BP, 193-293 K. Relative to the BDM dataset, the Serdyuchenko data have systematic biases of -2 to +4% for 260-340 nm, and the BP data have smaller biases of 1-2% below 315 nm but larger spiky biases of up to 6% at longer wavelengths. These datasets show distinctly different temperature dependences. Using different cross sections can significantly affect atmospheric retrievals. Using SGWCB data leads to retrieval failure for almost half of the OMI spatial pixels, producing large negative ozone values that cannot be handled by radiative-transfer models and using BP data leads to large fitting residuals over 310-330 nm. Relative to the BDM retrievals, total ozone retrieved using original SGWCB data (with linear temperature interpolation/extrapolation) typically shows negative biases of 5-10 DU; retrieved tropospheric ozone column generally show negative biases of 5 -10 DU and 5 - 20 DU for parameterized and original SGWCB data, respectively. Compared to BDM retrievals, ozone profiles retrieved with BP/SGWCB data on average show large altitude-dependent oscillating differences of up to ±20 - 40 % biases below ~20 km with almost opposite bias patterns. Validation with ozonesonde observations demonstrates that the BDM retrievals agree well with ozonesondes, to typically within 10%, while both BP and SGWCB retrievals consistently show large altitude-dependent biases of up to ±20-70% below 20 km. Therefore, we recommend using the BDM dataset for ozone profile retrievals from UV measurements. Its improved performance is likely due to its better characterization of temperature dependence in the Hartley and Huggins bands.

PI-11. Rovibrational Line Lists for Nine Isotopologues of CO Suitable for Modeling and Interpreting Spectra at Very High Temperatures and Diverse Environments

**G. Li,[a] I. E. Gordon,[a] L. S. Rothman,[a] Y. Tan,[b] S.-M. Hu,[b] S. Kassi,[c]
A. Campargue[c]**

[a] *Harvard-Smithsonian Center for Astrophysics, Atomic and Molecular Physics Division, Cambridge MA 02138-1516, USA*

[b] *Hefei National Laboratory for Sciences at Microscale, University of Science and Technology of China, 230026 Hefei, China*

[c] *Université de Grenoble, CNRS UMR 5588, LIPHY, 38041 Grenoble, France*

In order to improve and extend the existing HITRAN database[1] and HITEMP[2] data for carbon monoxide, the ro-vibrational line lists were computed for all transitions of nine isotopologues of the CO molecule, namely $^{12}C^{16}O$, $^{12}C^{17}O$, $^{12}C^{18}O$, $^{13}C^{16}O$, $^{13}C^{17}O$, $^{13}C^{18}O$, $^{14}C^{16}O$, $^{14}C^{17}O$, and $^{14}C^{18}O$ in the electronic ground state up to $v = 41$ and $J = 150$. Line positions and intensity calculations were carried out using a newly-determined piece-wise dipole moment function (DMF) in conjunction with the wavefunctions calculated from a previous experimentally-determined potential energy function of Coxon and Hajigeorgiou[3]. Ab initio calculations and a direct-fit method which simultaneously fits all the reliable experimental ro-vibrational matrix elements has been used to construct the piecewise dipole moment function.

To provide additional input parameters into the fit, new Cavity Ring Down Spectroscopy experiments were carried out to enable measurements of the lines in the 4-0 band with low uncertainty (Grenoble) as well as the first measurements of lines in the 6-0 band (Hefei). Accurate partition sums have been derived through direct summation for a temperature range from 1 to 9000 Kelvin. A complete set of broadening and shift parameters is also provided and now include parameters induced by CO_2 and H_2 in order to aid planetary applications.

---

[1] L. S. Rothman, I. E. Gordon, et al. "The HITRAN 2012 molecular spectroscopic database," JQSRT 113, 4-50 (2013).

[2] L. S. Rothman, I. E. Gordon, et al. "HITEMP, the high-temperature molecular spectroscopic database," JQSRT 111, 2139-2150 (2010).

[3] J. Coxon and P. Hajigeorgiou. "Direct potential fit analysis of the $X^1\Sigma^+$ ground state of CO," J. Chem. Phys. 121, 2992-3008 (2004).

PI-12. Hypersonic Methane Probed by CRDS

M. Louviot,[a] V. Boudon,[a] N. Suas-David,[b] R. Georges,[b] S. Kassi,[c] M. Rey[d]

[a]*Laboratoire Interdisciplinaire Carnot de Bourgogne, UMR 6303 CNRS/Université de Bourgogne, 9 Avenue Alain Savary, BP 47870, F-21078 Dijon Cedex, France*

[b]*Institut de Physique de Rennes, UMR 6251, Campus de Beaulieu, Bât 11C, Université de Rennes 1/CNRS, F-35042 Rennes Cedex, France*

[c]*Laboratoire Interdisciplinaire de Physique, Université Grenoble 1/CNRS, LIPhy UMR 5588, Grenoble F-38041, France*

[d]*Groupe de Spectrométrie Moléculaire et Atmosphérique, UMR CNRS 6089, Université de Reims, U.F.R. Sciences Exactes et Naturelles, B.P.1039, 51687 Reims Cedex 2, France*

A new cavity ring-down spectroscopy device, designed to study hypersonic gas jets, started to yield encouraging results at the Institut de Physique de Rennes (IPR). In this experiment, two mixtures have been used: first, a mixture of argon and carbon monoxide and second, a mixture of argon and methane. Mixtures were contained at high pressure in a reservoir ($\sim$ 1000 Torr) and heated at very high temperature ($\sim$ 2000 K), thanks to the high enthalpy source developed at IPR[1]. A hypersonic gas expansion was produced in a low-pressure chamber ($\sim$ 0.09 Torr) connected to the reservoir. High-resolution spectra of methane have thus been investigated in the [5920-6030] cm^{-1} spectral range, which corresponds to the Tetradecad region of methane. The CRD spectrometer, developed by the LAME group from the LIPhy laboratory in Grenoble, has been placed perpendicularly to the axis of the jet to record these spectra.

The precise analysis of the CO lines helped to determine the different parameters of the jet: translational, rotational and vibrational temperatures, concentrations of the hot and cold gas. One of the most noteworthy results is the evidence of a strong thermodynamic disequilibrium of CO, with a rotational temperature of 7 K and a vibrational temperature of 2000 K. This confirms the weak vibrational relaxation of the molecules in the jet. Then, the parameters determined for CO gave a starting point for the simulation of the spectrum of methane. Thereupon, they were fitted in order to make the simulation match the experimental results for CH_4. The simulation for CH_4 was obtained from the HITRAN 2012 linelist[2], for the cold bands (Tetradecad-GS), and from a variational calculation from the GSMA laboratory in Reims[3], for the hot bands (Icosad-Dyad). The vibrational temperature is finally about 750 K and the rotational temperature, about 13 K. This rotational simplification is particularly useful for the identification of hot band lines, that is very more difficult in a spectrum at thermal equilibrium.

---

[1] J. F. M. Thiévin *et al.*, *J. Quant. Spectrosc. Radiat. Transfer*, **109**, 2027-2036 (2008).

[2] L. R. Brown *et al.*, *J. Quant. Spectrosc. Radiat. Transfer*, **130**, 201-219 (2013).

[3] M. Rey *et al.*, *Phys.Chem. Chem. Phys*, **15**, 10049 (2013).

PI-13. Improved Spectroscopic Parameters of Methane in the MIR for Atmospheric Remote Sensing

Darko Dubravica,[a] Frank Hase,[a] Manfred Birk,[b] Joep Loos,[b]
Georg Wagner,[b] Mathias Palm,[c] Alireza Sadeghi[c]

[a]*Karlsruhe Institute of Technology (KIT), Institute for Meteorology and Climate Research, Hermann-von-Helmholtz-Platz 1, D-76344 Leopoldshafen, Germany*

[b]*German Aerospace Center (DLR), Remote Sensing Technology Institute, Münchner Straße 20, D-82234 Weßling, Germany*

[c]*University of Bremen, Institute of Environmental Physics, Otto-Hahn-Allee 1, D-28359 Bremen, Germany*

Improved spectroscopic data for methane have been retrieved, covering the spectral range between 2400 and 3000 cm^{-1}. Laboratory molecular absorption spectra at room temperature were recorded with the DLR[1] Bruker IFS125HR FTIR spectrometer in combination with a white cell and an absorption path length of 40 m. The first set of measurements using pure methane and applying low pressures between 0.02 and 5.00 mbar was performed to improve the transition wavenumbers, the line intensities and the self-broadening parameters. The second set of measurements was made with a defined air-methane mixture at total pressures between 30 and 1000 mbar for fitting air-broadening parameters, air-induced pressure shifts and additional parameters for narrowing effects and line mixing. The parameters relevant for atmospheric observations is foreseen to be used within the NDACC (Network for the Detection of Atmospheric Composition Change).

A retrieval software based on the method of least squares has been developed and applied to adjust the spectroscopic parameters using the methane HITRAN 2012 line parameters[2] as a first-guess. A few parts of the energy term scheme resulting from the HITRAN 2012 lower-state energy and the associated transition wavenumber were replaced by values predicted by the MIRS software[3,4] in order to improve the first-guess values. The fitting routine performs multi-spectra fits and handles line parameters of several lines at a time. The spectra and residuals are presented to compare the original HITRAN 2012 values with the modified line list. The fits are based on a speed dependent Voigt lineshape model including line mixing for the adjustment of the Rosenkranz mixing coefficients.

---

[1] German Aerospace Center, Remote Sensing Technology Institute, Oberpfaffenhofen, Germany

[2] http://www.cfa.harvard.edu/hitran/

[3] A. V. Nikitin et al., JQSRT 2003, 82, 239-249

[4] http://xeon.univ-reims.fr/MIRS/

PI-14. Precise Spectroscopy Based on Absorptive Broadening and Dispersive Shift of Cavity Modes

**Agata Cygan, Piotr Wcisło, Szymon Wójtewicz, Piotr Masłowski,
Ryszard S. Trawiński, Roman Ciuryło, Daniel Lisak**

*Institute of Physics, Faculty of Physics, Astronomy, and Informatics, Nicolaus
Copernicus University, Grudziadzka 5, 87-100 Torun, Poland*

Cavity enhanced absorption spectroscopy (CEAS) using high Q-factor optical cavities yielded so far the highest sensitivity of absorption measurements and enabled study of weak molecular spectra with potentially very high resolution and precision. Combination of cavity ring-down spectroscopy (CRDS) with frequency stabilization of cavity modes[1] provided the proper tool for probing the absorption lines with unprecedented precision. Further evolution of this technique including spectral narrowing and frequency stabilization of probing light as well as the use of optical frequency combs[2,3] resulted in the signal-to-noise ratio exceeding 200000[4] and control of the frequency axis with the kilohertz level of accuracy[5], respectively. This created favorable conditions for testing advanced line-shape models and above all it allowed to determine spectral parameters with subpercent accuracy demanded in satellite study of atmosphere[6]. However, the most challenging task in the line-shape analysis of experimental spectra is to distinguish the systematic errors due to experimental imperfections from these caused by the wrong choice of the line-shape model[7]. To solve this problem alternatives to the CRDS method for the measurement of weak spectral lines are being developed.

The photon lifetime in the cavity, commonly measured from the ring-down decays in CRDS, is directly related to the spectral broadening of the cavity resonant modes which also are shifted due to dispersion. This first phenomenon inspires relatively new technique named cavity mode-width spectroscopy (CMWS)[8,9,10] in which absorption information can be retrieved by precise measurements of widths of cavity modes. Qualitative and intuitive comparison of CRDS and CMWS methods reveals their complementarity in the sense that they achieve their best precision in different pressure ranges. For low absorptions the best precision is achieved with the CRDS technique, where the ring-downs are long and hence they can be well determined. In the opposite

---

[1] J. T. Hodges *et al.*, Rev. Sci. Instrum. **75**, 849 (2004)
[2] A. Cygan *et al.*, Rev. Sci. Instrum. **82**, 063107 (2011)
[3] J. Domysławska *et al.*, J. Chem. Phys. **136**, 024201 (2012)
[4] A. Cygan *et al.*, Phys. Rev. A **85**, 022508 (2012)
[5] G.-W. Truong *et al.*, J. Chem. Phys. **138**, 094201 (2013)
[6] P. Wcisło *et al.*, Phys. Rev. A **88**, 012517 (2013)
[7] S. Wójtewicz *et al.*, Phys. Rev. A **84**, 032511 (2011)
[8] K. Nakagawa *et al.*, Opt. Commun. **107**, 369 (1994)
[9] D. A. Long *et al.*, Appl. Phys. B **114**, 489 (2014)
[10] A. Cygan *et al.*, Opt. Express **21**, 29744 (2013)

case, where the absorption is high and hence cavity modes become more broadened, the precision of CMWS is enhanced. On the other hand, measurement of dispersion shift of cavity modes delivers another way for potentially accurate studies of absorption spectra. Direct use of frequency domain quantities to obtain absorption coefficient prevents from nonlinearities of detection system and hence minimizes contribution of systematic instrumental errors in the total shape of investigated spectral lines.

We present a quantitative comparison of three CEAS techniques allowing for precise measurements of molecular spectra, namely CRDS, CMWS and dispersion measurement from the cavity mode spacing. We tested these three methods on the CO rovibrational transitions from the $(3 \leftarrow 0)$ band, measured previously by us with CRDS[11], which are located in the spectral region around 6201 cm^{-1}. Preliminary experimental results and sensitivity comparison of these three independent techniques will be shown.

---

[11] S. Wójtewicz *et al.*, JQSRT **130**, 191 (2013)

PI-15. A cryogenic Herriott cell vacuum-coupled to a FT-IR, JPL Bruker IFS-125HR

Arlan W. Mantz,[a] Keeyoon Sung,[b] Timothy J. Crawford,[b] Linda R. Brown,[b] Mary Ann H. Smith,[c] V. Malathy Devi,[d] D. Chris Benner[d]

[a] *Dept. of Physics, Connecticut College, New London, CT 06320*

[b] *Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Dr.,Pasadena, CA 91109*

[c] *Science Directorate, NASA Langley Research Center, Hampton, VA 23681*

[d] *Dept. of Physics, The College of William and Mary, Williamsburg, VA 23187*

A new cryogenic Herriott cell and associated transfer optics have been designed and fabricated at Connecticut College under contract with NASA Langley Research Center to operate for the first time with the broad-band Bruker IFS-125HR Fourier transform spectrometer at the Jet Propulsion Laboratory (JPL). This 0.375 m base-length optical cavity produces an absorption path length, at 293 K, of 20.941 (± 0.006) m. The Herriott cell, constructed from oxygen-free high conductivity copper, is placed inside its own vacuum enclosure, which is isolated from the transfer optics chamber by one CaF_2 window and separately evacuated. The transfer optics chamber is in turn coupled to the sample compartment of the Bruker 125HR holding another set of transfer optics. The entire spectrometer, including the transfer optics chamber can be evacuated to $\sim$10 mTorr; the cell vacuum enclosure is cryogenically evacuated to pressures below 10^{-6} Torr. A closed-cycle helium refrigerator cools the Herriott cell. Initially tested at Connecticut College for temperatures between 250 and 50 K, the system has successfully been in operation for over two years at JPL. The cell has been used for recording spectra between 75 and 250 K, achieving excellent temperature uniformity (± 0.15 K) and long term stability ($<$ 0.05 K/day). Configured with a single indium-sealed CaF_2 window, it has provided Doppler-limited infrared absorption spectra of a number of molecular species at wavenumbers above 2000 cm^{-1} to investigate detailed spectroscopic properties (e.g. molecular line parameters at temperatures and pressures relevant to planetary atmospheres). The design, performance and detailed characterization of the Herriott cell system are discussed. [1]

---

[1] Research described in this paper was performed at Connecticut College, the Jet Propulsion Laboratory, and California Institute of Technology, NASA Langley Research Center, and the College of William and Mary, under contracts and cooperative agreements with the National Aeronautics and Space Administration. AWM acknowledges Alan Hahn, the science division machinist at Connecticut College, for his skills in precisely machining detailed copper pieces to very tight tolerances. We also thank ITPA/MSRC at Stony Brook University, NY, for generous contribution of the supporting frame and compartment from a retired Bruker 120HR.

PI-16. Three Years of EXOMOL: New Molecular Line Lists for Exoplanet and other Atmospheres

Jonathan Tennyson, **Sergei N. Yurchenko**

Department of Physics and Astronomy, University College London, Gower Street, WC1E 6BT London, UK

Fundamental molecular data play a principal role for spectral characterization of astrophysical objects cool enough to form molecules in their atmospheres (cool stars, extrosolar planets and planetary discs) as well as in a broad range of terrestrial applications. However the laboratory data for a number of key species is absent, inaccurate or incomplete. The ExoMol project aims at providing comprehensive line lists for all molecules likely to be observable in exoplanet atmospheres in the foreseeable future[1]. This is a huge undertaking which will mean providing in excess of tens of billions of spectral lines for a large variety of molecular species[2].

The physics of molecular absorptions is complex and varies between different classes of absorbers, which are therefore divided into the following topics (a) diatomic, (b) triatomics, (c) tetratomics, (d) methane and (e) larger molecules. Special techniques are being developed to treat each case. The line lists for a number of key atmospheric species currently available from ExoMol (www.exomol.com) are: NH_3[3], CaH, MgH, BeH[4], SiO[5], HCN/HNC[6], KCl, NaCl[7] and CH_4[8]. The line lists in progress are for PH_3, SO_3, AlH, AlO, C_2, PN, SH, SiH, SO, ScH, TiH, H_2S, HNO_3, H_2CO, and C_2H_4. As an example, we will present a new methane line list generated using a high level of theory, called 10to10, which contains just under 10 billion transitions[8]. This 10to10 line list has the potential to revolutionise the accuracy of models for T-dwarf and other bodies containing hot methane.

---

[1] J. Tennyson and S. N. Yurchenko, *Mon. Not. R. Astron. Soc.*, 2012, **425**, 21.

[2] J. Tennyson and S. N. Yurchenko, *Exp. Astron.*, 2014, in press.

[3] S.N. Yurchenko, R.J. Barber and J. Tennyson, *Mon. Not. R. Astron. Soc.*, 2011, **413**, 1828.

[4] B. Yadin *et al*, *Mon. Not. R. Astron. Soc.*, 2012, **425**, 34.

[5] E.J. Barton, S.N. Yurchenko and J. Tennyson, *Mon. Not. R. Astron. Soc.*, 2013, **434**, 1469.

[6] R.J. Barber *et al*, *Mon. Not. R. Astron. Soc.*, 2014, **437**, 1828.

[7] E.J. Barton *et al*, *Mon. Not. R. Astron. Soc.*, 2014, in press.

[8] S. N. Yurchenko and J. Tennyson, *Mon. Not. R. Astron. Soc.*, 2014 **440**, 1649.

PI-17. Updates to the Virtual Atomic and Molecular Data Centre

Christian Hill,[a] **Jonathan Tennyson**,[a] **Iouli E. Gordon**,[b]
Laurence S. Rothman,[b] **Marie-Lise Dubernet**[c]

[a] *University College London, Gower Street, London WC1E 6BT, UK*

[b] *Harvard-Smithsonian Center for Astrophysics, Atomic and Molecular Physics Division, Cambridge MA 02138-1516, USA*

[c] *Observatory of Paris, 5 Place Jules Janssen, 92195 Meudon, France*

The Virtual Atomic and Molecular Data Centre (VAMDC) has established a set of standards for the storage and transmission of atomic and molecular data and an SQL-based query language (VSS2) for searching online databases, known as *nodes*. The project has also created an online service, the *VAMDC Portal*, through which all of these databases may be searched and their results compared and aggregated.

Since its inception four years ago, the VAMDC e-infrastructure has grown to encompass over 40 databases, including HITRAN, in more than 20 countries and engages actively with scientists in six continents. Associated with the portal are a growing suite of software tools for the transformation of data from its native, XML-based, *XSAMS* format, to a range of more convenient human-readable (such as HTML) and machine-readable (such as CSV) formats.

The relational database for HITRAN[1], created as part of the VAMDC project is a flexible and extensible data model which is able to represent a wider range of parameters than the current fixed-format text-based one. Over the next year, a new online interface to this database will be tested, released and fully documented - this web application, HITRANonline[2], will fully replace the ageing and incomplete JavaHAWKS software suite.

---

[1] C. Hill, I. E. Gordon, L. S. Rothman, J. Tennyson, A new relational database structure and online interface for the HITRAN database, *Journal of Quantitative Spectroscopy and Radiative Transfer* **130**, 51-61 (2013).

[2] http://hitran.org

PI-18. Windows Based Optical Spectra Code (WinOSC)

Bill Phillips

Aerospace Testing Alliance, Arnold Air Force Base, TN 37389-9013

The propulsion, and vehicle, test and evaluation community routinely requires gas diagnostic for measurement of systems-under-test and test facility performance and/or health monitoring. Unlike most atmospheric applications, these require analytical spectral tools capable of modeling high temperature and possibly non-local thermodynamic equilibrium conditions. To that end, WinOSC was written. The goal was to generate a user friendly spectral code with wide applicability and capabilities. WinOSC is designed to run on a Windows operating system platform and is multi-threaded to obtain high execution speed. The computer code is a line-by-line code using HITRAN, HITEMP, or similarly formatted spectral line parameter files as the source of the spectral line parameters. Due to the high temperature modeling requirement, a modified version of the HITRAN database was prepared to include atomic species. The WinOSC can model up to ten layered homogeneous zones each with different concentrations, path lengths, and temperatures. WinOSC calculates spectral optical depth, transmittance, and/or spectral radiance values. The output spectra can be un-convolved or convolved using seven predominant instrument line shape functions associated with Fourier transform spectrometer apodization functions. The graphical user interface displays the calculated spectra and the user has the option of exporting the calculated spectra as ASCII comma delimited or binary GRAMS format files.

This presentation discusses the requirement for WinOSC by the test and evaluation community as well as the capability, limitations, and availability of the computer code. Future enhancements to WinOSC will be presented.

PI-19. Simultaneous Physical Retrieval of Martian Superficial and Atmospheric Parameters Using TES Spectra: the ϕ-MARS Algorithm

**Giuliano Liuzzi,[a] Guido Masiello,[a] Carmine Serio,[a] Sara Venafra,[a]
Maria Grazia Blasi,[a] Sergio Fonti,[b] Francesca Mancarella[b]**

[a]*School of Engineering, Università degli Studi della Basilicata, Via dell'Ateneo Lucano 10, 85100 Potenza, Italy*

[b]*Dept. of Mathematics and Physics, Universitá del Salento, Lecce, Italy*

We present a new and general methodology for the simultaneous retrieval of superficial and atmospheric parameters of Mars. The methodology is essentially based on similar codes implemented for high-resolution instruments looking at Earth (such as IASI) and it has been customized for the Thermal Emission Spectrometer (TES). With minor changes to the forward and inverse modules, it is straightforwardly applicable to any instrument looking at Mars, with particularly effectiveness to high-resolution interferometers.

The forward module is a pseudo-monochromatic radiative transfer model with the capability to calculate genuine analytical jacobians of any geophysical parameter in the RT equation. We describe the general methodology, the optimizations implemented to fit TES data, and its robustness and consistency with the literature.

We focus our attention on some retrieval results referred to surface parameters (temperature and emissivity), temperature profiles, water vapour, dust and ice mixing ratios, on a large dataset covering most of the Martian surface. Furthermore, we briefly investigate the possibility to detect methane with TES data. We will finally analyze the advantages of this approach and compare it to other methods already developed for TES data analysis.

PI-20. Recent Enhancements and Applications of AER's Radiation Models LBLRTM and MonoRTM

Matthew J. Alvarado,[a] **Karen E. Cady-Pereira**,[a] **Pan Liang**[a], **Alan E. Lipton**,[a] **Eli J. Mlawer**,[a] **Jean-Luc Moncet**,[a] **Gennady Uymin**,[a] **Vivienne H. Payne**[b]

[a] *Atmospheric and Environmental Research, Lexington, MA, USA*

[b] *Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, USA*

The radiative transfer models developed at AER are used extensively for a wide range of applications in the atmospheric sciences. In this presentation we will summarize recent enhancements that have been made to these models, present illustrative model applications, and present results of ongoing validation efforts for each model.

AERs line-by-line model LBLRTM is widely regarded as a reference standard within the atmospheric community, with users across a range of disciplines in government agencies, industry, and academia. LBLRTM has been used as the basis of the forward models for the Infrared Atmospheric Sounding Interferometer (IASI) and the NASA Tropospheric Emission Spectrometer (TES). LBLRTM v12.1 calculations in the thermal infrared have been recently validated against a global set of observations from IASI, and we are currently evaluating the HITRAN 2012 line parameters with this dataset and surface data from the Radiative Heating in Underexplored Bands Campaign-II (RHUBC-II).

MonoRTM is used to train the forward models for microwave channels in the Community Radiative Transfer Model (CRTM) and is widely used in the DOE Atmospheric Systems Research (ASR) program. A major upgrade, called MonoRTM_v5.0, has just been developed and released. The model has been upgraded to utilize line parameters from HITRAN 2012, with the exception of certain water vapor lines (e.g., the 22 and 183 GHz lines) for which carefully validated values are used. MonoRTM_v5.0 has also been enhanced to allow the use of additional broadening information (e.g., broadening of O_2 lines by H_2O) and to calculate speed dependent Voigt line shapes.

The AER radiative transfer models LBLRTM and MonoRTM, as well as the associated databases (e.g., line parameters, continua, and molecular cross-sections), are publicly available from AER (http://www.rtweb.aer.com).

PI-PII-21. Field measurements of atmospheric ethane (C_2H_6) using continuous wave 3 micron DFB-TDL and -ICL laser spectroscopy

Tara Yacovitch, Joseph Roscioli, Cody Floerchinger, Ryan McGovern, Scott Herndon, J. Barry McManus, David D. Nelson, Mark S. Zahniser

Aerodyne Research, Inc., 45 Manning Road, Billerica, MA, USA, 01821

Ethane measurements can be useful in determining the sources of methane in studies that aim to assess greenhouse gas emissions for global warming. Ethane is typically 1 to 20% of methane in natural gas emissions from oil and gas wells, natural gas processing, pipeline transmission emissions, and leakage during usage in urban areas. Ethane is minimal or non-existent in biological sources of methane such as cattle, landfill, sewage, swamp, fen, and tundra emissions. Measurements of ethane/methane ratios are therefore valuable in determining the methane source type.

Spectroscopic measurements of ethane are strongest in the 3 micron infrared C-H stretch spectral region. Although measurements in this region had been possible with lead-salt tunable diode lasers, they required liquid nitrogen cooling for both lasers and detectors, making field measurements difficult. DFB-TDL and DFB-ICL lasers from nanoplus are now available which allow near-room temperature, continuous mode absorption for compact, high precision measurements of ethane. Using direct absorption spectroscopy allows absolute mixing ratio measurements with a 1s precision of less than 30 parts-per-trillion in a highly portable instrument developed at Aerodyne Research.

We have made rapid, selective measurements of ethane and methane in Pennsylvania in 2012, urban field sites in Boston during 2012 and 2013, and in the Aerodyne Mobile Laboratory during the studies of natural gas emissions throughout several sectors of the energy industry in 2012 and 2013. The instrument has been demonstrated in flight, on light aircraft studies endeavouring to apportion methane flux measurements between gas production areas and biogenic sources. Demonstration of precision and results of these measurements will be presented.

PI-PII-22. Recent progress in development of infrared laser based instruments for real time ambient measurements of isotopologues of carbon dioxide, water, methane, nitrous oxide and carbon monoxide

David D. Nelson,[a] **J. Barry McManus,**[a] **Mark S. Zahniser,**[a]
Joanne Shorter,[a] **Shuhei Ono**[b]

[a] *Aerodyne Research, Inc., 45 Manning Road, Billerica, MA, USA, 01821*

[b] *Earth Atmospheric and Planetary Sciences, MIT, Cambridge, MA, United States*

The capacity for real time precise in situ measurements of isotopic ratios of a variety of trace gases at ambient concentrations continues to create new opportunities for the study of the exchanges and fluxes of gases in the environment. Aerodyne Research has made rapid progress in laser based instruments since our introduction in 2007 of the first truly field worthy instrument for real time measurements of isotopologues of carbon dioxide. We have focused on two instrument design platforms, with either one or two lasers. Absorption cells with more than 200 meters path length allow precise measurements of trace gases with low ambient concentrations. Most of our systems employ mid infrared quantum cascade lasers. However, recently available 3 micron antimonide based diode lasers are also proving useful for isotopic measurements. By substituting different lasers and detectors, we can simultaneously measure the isotopic composition of a variety of gases, including: H_2O, CO_2, CH_4, N_2O and CO.

Our newest instrument for true simultaneous measurement of isotopologues of CO_2 ($^{12}CO_2$, $^{13}CO_2$, $^{12}C^{18}O^{16}O$) has (1 s) precision better than 0.1 ‰ for both ratios. The availability of 10 Hz measurements allows measurement of isotopic fluxes via eddy correlation. The single laser instrument fits in a 19 inch rack and is only 25 cm tall. A two laser instrument is larger, but with that instrument we can also measure clumped isotopes of CO_2, with 1 second precisions of: 2.3 ‰ for $^{13}C^{18}O^{16}O$, and 6.7 ‰ for $^{13}C17O^{16}O$. The sample size for such a measurement corresponds to 0.2 mole of pure CO_2. Another variation on the two laser instrument simultaneously measures isotopologues of CO_2 ($^{12}CO_2$, $^{13}CO_2$, $^{12}C^{18}O^{16}O$) and H_2O ($H_2{}^{16}O$, $H_2{}^{18}O$, $HD^{16}O$). Preliminary results for water ratio precisions (in 1s) are 0.1 ‰ for $H_2{}^{18}O$ and 0.3 ‰ for $HD^{16}O$, simultaneous (1 s) precisions for isotopologues of CO_2 of ~0.1 ‰.

Methane, nitrous oxide and carbon monoxide have such low ambient concentrations that real time isotopologue measurements are a serious challenge. For these gases, we typically use our 200 m absorption cell. Several of these instruments have already been used for long term field measurements of isotopologues of methane, ($^{12}CH_4$, $^{13}CH_4$), with a demonstrated (1 s) precision of 1.5 ‰. A new version of this instrument operating near 3.3 microns has recently been developed to quantify $^{13}CH_4$ and CH_3D simultaneously. In separate experiments at MIT, using trapped concentrated samples, we have made highly precise measurements of the abundance of the clumped isotope of methane: $^{13}CH_3D$.

We are also developing methods to monitor the isotopic abundance of the isotopes of CO and N_2O. We have achieved a measurement precision for ambient ^{13}CO (1 s) of 1.9 ‰. For the isotopologues of N_2O ($^{14}N_2{}^{16}O$, $^{14}N^{15}N\ {}^{16}O$, $^{15}N^{14}N\ {}^{16}O$, $^{14}N_2{}^{18}O$), we have demonstrated (1 s) precision at ambient levels (320 ppb) of ∼3 ‰. For N_2O, a quasi continuous pre concentrator has been used to give even better precisions (<0.1‰) and one is being developed for CO.

SESSION III: Line Shapes

III-1. Spectral Line-Shape Model to Replace the Voigt Profile in Spectroscopic Databases

Daniel Lisak,[a] **Ngoc Hoa Ngo,**[b] **Ha Tran,**[c] **Jean-Michel Hartmann**[c]

[a]*Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University, Grudziadzka 5, 87-100 Torun, Poland*

[b]*Departement of Physics, Hanoi University of Education, 136 XuanThuy, Hanoi, Vietnam*

[c]*Laboratoire Interuniversitaire des Systèmes Atmosphériques, UMR CNRS 7583, Université Paris Est Créteil, Université Paris Diderot, Institut Pierre-Simon Laplace, 94010 Créteil Cedex, France*

The standard description of molecular line shapes in spectral databases and radiative transfer codes is based on the Voigt profile. It is well known that its simplified assumptions of absorber free motion and independence of collisional parameters from absorber velocity lead to systematic errors in analysis of experimental spectra, and retrieval of gas concentration.

We demonstrate[1,2] that the partially correlated quadratic speed-dependent hard-collision profile[3]. (pCqSDHCP) is a good candidate to replace the Voigt profile in the next generations of spectroscopic databases. This profile takes into account the following physical effects: the Doppler broadening, the pressure broadening and shifting of the line, the velocity-changing collisions, the speed-dependence of pressure broadening and shifting, and correlations between velocity- and phase/state-changing collisions. The speed-dependence of pressure broadening and shifting is incorporated into the pCqSDNGP in the so-called quadratic approximation. The velocity-changing collisions lead to the Dicke narrowing effect; however in many cases correlations between velocity- and phase/state-changing collisions may lead to effective reduction of observed Dicke narrowing. The hard-collision model of velocity-changing collisions is also known as the Nelkin-Ghatak model or Rautian model.

Applicability of the pCqSDHCP for different molecular systems was tested on calculated and experimental spectra of such molecules as H_2, O_2, CO_2, H_2O in a wide span of pressures. For all considered systems, pCqSDHCP is able to describe molecular spectra at least an order of magnitude better than the Voigt profile with all fitted parameters being linear with pressure. In the most cases pCqSDHCP can reproduce the

---

[1] N. H. Ngo, D. Lisak, H. Tran, J.-M. Hartmann, *J. Quant. Spectrosc. Radiat. Transf.* **129**, 89 (2013).

[2] N. H. Ngo, D. Lisak, H. Tran, J.-M. Hartmann, *J. Quant. Spectrosc. Radiat. Transf.* **134**, 105 (2014).

[3] A. S. Pine, *J. Quant. Spectrosc. Radiat. Transf.* **62** 397 (1999).

reference spectra down to 0.2% or better, which fulfills the requirements of the most demanding remote-sensing applications.

An important advantage of pCqSDHCP is that a fast algorithm for its computation was developed^{ab}[4,5] and allows for its calculation only a few times slower than the standard Voigt profile. Moreover, the pCqSDHCP reduces to many simpler models commonly used in experimental spectra analysis simply by setting some parameters to zero, and it can be easily extended to incorporate the line-mixing effect in the first-order approximation.

The idea of using pCqSDHCP as a standard profile to go beyond the Voigt profile for description of H_2O line shapes was recently supported by the IUPAC task group[6] which also recommended to call this profile with fast computation algorithm the HTP profile (for Hartmann-Tran).

---

[4] H. Tran, N. H.. Ngo, J.-M. Hartmann, *J. Quant. Spectrosc. Radiat. Transf.* **129** 199 (2013).

[5] H. Tran, N. H.. Ngo, J.-M. Hartmann, *J. Quant. Spectrosc. Radiat. Transf.* **134** 104 (2014).

[6] J. Tennyson, P. F. Bernath, A. Campargue, A. G. Csaszar, L. Daumont, R. R. Gamache, J. T. Hodges, D. Lisak, O. V. Naumenko, L. S. Rothman, H. Tran, N. F. Zobov, J. Buldyreva, C. D. Boone, M. D. De Vizia, L. Gianfrani, J.-M. Hartmann, R. McPheat, D. Weidmann, J. Murray, N. H. Ngo, O. L. Polyansky, *Pure Appl. Chem.* accepted (2014).

III-2. Line-Parameter Measurements and Stringent Tests of Line-Shape Models Based on Cavity-Enhanced Absorption Spectroscopy

Katarzyna Bielska,[a,b] Adam J. Fleisher,[a] Joseph T. Hodges,[a] Hong Lin,[a,c]
David A. Long,[a] Zachary D. Reed,[a] Vincent Sironneau,[a]
Gar-Wing Truong,[a,d] Szymon Wójtewicz[a,b]

[a] *Chemical Sciences Division, National Institute of Standards and Technology, 100 Bureau Drive, Gaithersburg, Maryland 20899*

[b] *Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University Grudziadzka 5, 87-100 Torun, Poland*

[c] *National Institute of Metrology, Beijing 100013, China*

[d] *Institute for Photonics and Advanced Sensing (IPAS), School of Chemistry and Physics, The University of Adelaide, South Australia, 5005 Australia*

Laser methods that are based on cavity-enhanced absorption spectroscopy (CEAS) are well-suited for measuring molecular line parameters under conditions of low optical density, and as such they are complementary to broadband Fourier-transform spectroscopy (FTS) techniques. Attributes of CEAS include relatively low detection limits, accurate and precise detuning axes and high fidelity measurements of line shape. In many cases these performance criteria are superior to those obtained using direct laser absorption spectroscopy and FTS-based systems.

In this presentation we will survey several examples of frequency-stabilized cavity ring-down spectroscopy (FS-CRDS)[1] measurements obtained with laser spectrometers developed at the National Institute of Standards and Technology (NIST) in Gaithersburg Maryland. These experiments, which are motivated by atmospheric monitoring and remote-sensing applications that require high-precision and accuracy, involve near-infrared transitions of carbon dioxide, water, oxygen and methane. We discuss spectra with signal-to-noise ratios exceeding 10^6, frequency axes with absolute uncertainties in the 10 kHz to 100 kHz range and linked to a Cs clock, line parameters with relative uncertainties at the 0.2 % level and isotopic ratios measured with a precision of 0.03 %. We also present FS-CRDS measurements of CO_2 line intensities which are measured at atmospheric concentration levels and linked to gravimetric standards for CO_2 in air, and we quantify pressure-dependent deviations between various theoretical line profiles and measured line shapes.

Finally we also present recent efforts to increase data throughput and spectral coverage in CEAS experiments. We describe three new high-bandwidth CEAS

---

[1] J. T. Hodges, H. P. Layer, W. W. Miller and G. E. Scace *Rev. Sci. Instrum.* **74**(4), 849 2004.

techniques including frequency-agile, rapid scanning spectroscopy (FARS)[2], which enables continuous-wave measurements of cavity mode linewidth and acquisition of ring-down decays with no dead time during laser frequency tuning, heterodyne-detected cavity ring-down spectroscopy (HD-CRDS)[3,4], which offers shot-noise-limited statistics by interrogating ring-down decays at high frequencies, and finally multi-heterodyne cavity-enhanced spectroscopy (MH-CEAS)[5], which provides wavelength-multiplexed measurements of both the amplitude and phase shift of the transmitted field.

---

[2] G.- W. Truong, K. O. Douglass, S. E. Maxwell, R. D. van Zee, D. F. Plusquellic, J. T. Hodges and D. A. Long *Nat. Phot.* **7**, 532 2013.

[3] J. Ye and J. L. Hall *Phys. Rev. A* **61**(6), 016802 2000.

[4] D. A. Long, A. J. Fleisher, S. Wójtewicz and J. T. Hodges *Appl. Phys. B* **115**, 149 2014.

[5] D. A. Long, A. J. Fleisher, K. O. Douglass, S. E. Maxwell, K. Bielska, J. T. Hodges and D. F. Plusquellic *Opt. Lett.* **39**(9), 2688 2014.

III-3. Narrowing Effects in the $H_2{}^{18}O$ Near-IR Spectrum: Experimental Test of the Partially-Correlated Quadratic-Speed-Dependent Hard-Collision Profile

Maria Domenica De Vizia, **Antonio Castrillo, Pasquale Amodio, Eugenio Fasci, Luigi Moretti, Livio Gianfrani**

Dipartimento di Matematica e Fisica della Seconda Università di Napoli, Viale Lincoln 5, 81100 *Caserta, Italy*

We present the outcomes of a specific study on the quadratic approximation in the partially-Correlated Speed-Dependent Hard-Collision profile (pC-SDHC), which is currently the recommended profile to replace the Voigt convolution for the shape of isolated high-resolution rotational-vibrational transitions, when perturbed by neutral gas-phase molecules. It includes the main effects occurring in the line formation, in particular the Dicke narrowing and the speed-dependent effects, as well as the possible correlation between them. We tested the quadratic (q-) and hypergeometric (hg-) versions for the speed dependence of the pC-SDHC on high quality $H_2{}^{18}O$ absorption spectra, in coincidence with three vibration-rotation transitions of the $\nu_1 + \nu_3$ band, at $1.39\mu m$, looking for possible differences in the retrieved parameters. The absorption spectra were observed in the Doppler regime, with unprecedented spectral fidelity, by using a dual-laser absorption spectrometer, recently developed for the aim of a spectroscopic determination of the Boltzmann constant. The investigated transitions were: $2_{2,1} \rightarrow 2_{2,0}$, $4_{4,1} \rightarrow 4_{4,0}$ and $3_{0,3} \rightarrow 2_{0,2}$. The pC-SDHC profile is found to be quite robust, regardless of the choice of the particular speed dependence, provided that the velocity-changing collision frequency is considered as a free parameter. In particular, the pressure broadening and shifting parameters, retrieved by using the quadratic and hypergeometric versions, were found to be fully consistent. Similarly, the integrated absorbance was found to be completely unaffected by the choice of the speed-dependence, in the whole pressure range that we have explored. It should be said, however, that the velocity-changing collision frequency resulted to be physically meaningful only for the hg-version, but not for the q-version. Therefore, in the quadratic approximation, the collision frequency must be considered just as an indispensable parameter to be included in the fitting procedure for the aims of a successful fit.

III-4. New Multispectrum Fitting Software Used at DLR for Analysis of Laboratory Fourier-Transform Molecular Spectra

Joep Loos, **Manfred Birk**, **Georg Wagner**

German Aerospace Center (DLR), Remote Sensing Technology Institute, Münchner Straße 20, D-82234 Weßling, Germany

A new fitting tool written in IDL for analysis of single or multiple molecular absorption spectra recorded with a Fourier-transform spectrometer will be presented. The software utilizes a microwindow-based line-by-line approach and its capabilities include the choice of numerous different line-shape models, from a simple Voigt to more sophisticated models including e.g. speed-dependence, Dicke narrowing or Rosenkranz line mixing. A comfortable interactive mode as well as a fully automatic mode have been implemented including various quality assessment procedures like the monitoring of correlation coefficients or the supply of useful information e.g. needed for file cuts (single spectrum residuals). Two application examples will be given as illustration of the software's capabilities.

First, the results of a speed-dependent analysis of room temperature water vapor spectra in the 1250-1750 cm^{-1} range are compared to the original results obtained by an analysis based on single spectra fits applying the Voigt procedure. The results of the new approach show significantly reduced residuals and systematically larger broadening parameters. The so far published Voigt broadening parameters are effective parameters being systematically too small since they compensate narrowing. Usually effective Voigt parameters are retrieved from non-opaque lines and should only be used when modelling non-opaque lines.

Second, the results of an analysis of air broadened nitrous oxide spectra in the ν_3 rovibrational band utilizing the pCqSDHC model[1] including first order line mixing will be presented. Speed dependence of the broadening parameter as well as line mixing have to be considered in order to represent the spectral features down to the 0.1 % level.

---

[1] Ngo N, Lisak D, Tran H and Hartmann J-M. J Quant Spectrosc Radiat Transfer 2013;129;89-100.

III-5. Comparisons of Measured and Requantized Classical Molecular Dynamics Calculated Line Shape of Air-Broadened Isolated Transitions of Molecular Oxygen

Julien Lamouroux,[a] **Jean-Michel Hartmann**,[a] **Vincent Sironneau**,[b]
Joseph T. Hodges[b]

[a] *Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA) (UMR CNRS 7583), Universités Paris-Est Créteil et Paris Diderot, Université Paris-Est Créteil, 94010 Créteil Cedex, FRANCE*

[b] *Chemical Sciences Division, National Institute of Standards and Technology, 100 Bureau Drive, Gaithersburg, MD 20899, USA*

The long-term goal of this study is to propose a readily calculable line profile for molecular oxygen. To this end, the present study discussed calculations of isolated air-broadened oxygen lines and the comparison with high-precision absorption spectra acquired on the near-infrared $^1\Delta$ band of O_2 using the frequency-stabilized cavity ring-down spectroscopy (FS-CRDS) technique[1]. Line shapes were calculated based on requantized classical molecular dynamics simulations (rCMDS) for air (20% O_2 + 80% N_2). The comparison of calculated and measured pressure-broadened spectra (through fits using Voigt profiles) demonstrates that the rCMDS can be used to predict subtle but often-observed departures from the Voigt profile. These results illustrate the viability of using the rCMDS method as a benchmark for the development and testing of simpler parameterized line profiles that are suitable for the analysis of underlying physical mechanisms and for atmospheric remote-sensing applications.

---

[1] D. A. Long, A. Cygan, R. D. van Zee, M. Okumura, C. E. Miller, D. Lisak, and J. T. Hodges, Chem. Phys. Lett. 536, 1 (2012).

III-6. The Use of Ab Initio Wavefunctions in Line-Shape Calculations for Water Vapor

Robert R. Gamache,[a] **Julien Lamouroux**,[b] **David W. Schwenke**[c]

[a] *University of Massachusetts Lowell, Lowell, MA, U.S.A.*

[b] *Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA) (UMR CNRS 7583), Universités Paris-Est Créteil et Paris Diderot, Université Paris-Est Créteil, 94010 Créteil Cedex, FRANCE*

[c] *NAS Facility, NASA Ames Research Center*

In semi-classical line-shape calculations, the internal motions of the colliding pair are treated via quantum mechanics and the collision trajectory is determined by classical dynamics. The quantum mechanical component, i.e. the determination of reduced matrix elements (RME) for the colliding pair, requires the wavefunctions of the radiating and the perturbing molecules be known. Here the reduced matrix elements for collisions in the ground vibrational state of water vapor are calculated by two methods and compared. First, wavefunctions determined by diagonalizing an effective (Watson) Hamiltonian are used to calculate the RMEs and, second, the ab initio wavefunctions of Partridge and Schwenke are used. While the ground vibrational state will yield the best approximation of the wavefunctions from the effective Hamiltonian approach, this study clearly identifies problems for states not included in the fit of the Hamiltonian and for extrapolated states. RMEs determined using ab initio wavefunctions use ∼100000 times more computational time; however, all ro-vibrational interactions are included. Hence, the ab initio approach will yield better RMEs as the number of vibrational quanta exchanged in the optical transition increases, resulting in improvements in calculated half-widths and line shifts. It is important to note that even for pure rotational transitions the use of ab initio wavefunctions will yield improved results.

III-7. Refinement of the Robert-Bonamy Formalism: Taking into Account Contributions from Line Coupling

Q. Ma,[a] **C. Boulet,**[b] **R. H. Tipping**[c]

[a]*NASA/Goddard Institute for Space Studies and Department of Applied Physics and Applied Mathematics, Columbia University, 2880 Broadway, New York, NY 10025*

[b]*Institute des Sciences Moleculaires d'Orsay (ISMO) Universite Paris-Sud 11; Bat. 350, Campus d'ORSAY bureau 52; Rdc 91405 ORAY Cedex; FRANCE*

[c]*Department of Physics and Astronomy, University of Alabama, Tuscaloosa, AL 35487*

The Robert-Bonamy (RB) formalism has been used to calculate half-widths and shifts adopted in HITRAN for years. Besides its success, it contains several approximations whose applicability has not been thoroughly justified. One of them is an assumption that lines of interest are well separated. When these authors developed the formalism, they have relied on this assumption **twice**. First, in calculating the spectral density F(ω), they have only considered the diagonal matrix elements of the relaxation operator. Due to this simplification, effects from line mixing are ignored. Secondly, when they applied the linked cluster theorem to remove the cut-off appearing in Anderson's theory, they have assumed that the operator (-iS_1 - S_2) is diagonal within the linespace so that matrix elements of the operator exp(- iS_1 - S_2) can be replaced by the exponential of the matrix elements of (- iS_1 - S_2). With this replacement, effects on calculated half-widths and shifts from the line coupling are also ignored. Although both these two simplifications relied on the same approximation, their validity criteria are completely different and the latter is more stringent than the former. As a result, in many cases where the line mixing becomes negligible, significant effects from the line coupling have been completely missed. Recently, by abandoning the second simplification and accurately evaluating the matrix elements of exp(- iS_1 - S_2), we have refined the RB formalism such that the line coupling can be taken into account. Our numerical calculations for the Raman Q lines of auto-perturbed N_2, and also the Raman Q lines and the infrared P and R lines of C_2H_2 in a N_2 bath have demonstrated that effects on calculated half-widths from the line coupling are important. In comparison with values derived without the line coupling, new calculated values for these lines are significantly reduced and become closer to measurements.[1] With respect to the H_2O molecule immersed in a N_2 bath, we have found that for most of the H_2O lines, it is unnecessary to consider the line coupling. However, for several dozens of lines, effects on the calculated half-widths from the line coupling are small, but remain noticeable and the reductions due to including the line coupling could reach to 5 %. Meanwhile, effects on the calculated shifts are very significant and the variations could be as large as 25 %.

---

[1] Q. Ma, C. Boulet, and R. H. Tipping, J. Chem. Phys. **139**, 034305 (2013); **140**, 104304 (2014).

III-8. Collisional Line-Shape and Line-Mixing Parameters for CO_2 Absorption near 3340 cm^{-1}: Measurements and Modeling

Jeanna Buldyreva,[a] **Jean Vander Auwera**[b]

[a]*Institut UTINAM UMR CNRS 6213, Université de Franche-Comté, 16 route de Gray, 25030 Besançon, France*

[b]*Service de Chimie Quantique et Photophysique, C.P. 160/09, Université Libre de Bruxelles, 50 avenue F.D. Roosevelt, 1050 Brussels, Belgium*

The present work is focused on the determination of line-shape parameters for one of the $^{12}C^{16}O_2$ bands detectable by the SOIR (Solar Occultation in the InfraRed) instrument onboard the ESA Venus Express spacecraft, namely the $21102 - 00001$ band located near 3340 cm^{-1}. High-resolution Fourier transform spectra of this band have been recorded at sub-atmospheric pressures and analyzed to extract isolated-line intensities and collisional parameters as well as first-order line-mixing coefficients. Voigt, hard-collision Rautian and Sobel'man, and quadratic-speed-dependent Voigt profiles have been used. The retrieved parameters are compared with previous data available in the literature and with theoretical estimates obtained by an Energy-Corrected Sudden approach (generally, non-Markovian) employing a symmetric metric in the Liouville space. The same approach, supplied with additional hypotheses for basic transition rates for the hot bands, has also been used to model the complete band shapes. The need for accounting of line-narrowing effects at sub-atmospheric pressures has been evidenced from comparison with the recorded spectra, and some improvements have been introduced in the relaxation matrix model, leading to a good agreement of calculated and measured absorptions from nearly Doppler pressure regime to nearly atmospheric pressure.

III-9. Ab Initio Computation of Dynamical Properties: Pressure Broadening

Laurent Wiesenfeld,[a] **Brian Drouin**[b]

[a] *UJF-Grenoble 1/CNRS, Institut de Planetologie et d'Astrophysique de Grenoble (IPAG) UMR 5274, Grenoble F-38041, France*

[b] *Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91109-8099, USA*

Rotational spectroscopy of polar molecules is the main observational tool in many areas of astrophysics, for gases of low to medium temperatures ($T \sim 5 - 1000\,\mathrm{K}$), and low densities ($n \sim 10^2 - 10^8\,\mathrm{cm}^{-3}$). Spectral line shapes in astrophysical media are largely dominated by turbulence-induced Doppler effects and natural line broadening are negligible. However line broadening remains an important tool for denser gases, like planetary high atmospheres. Understanding the excitation schemes of polar molecules requires the knowledge of excitation transfer rate due to collisional excitation, between the polar molecule and the ambient gas, usually H_2. Transport properties in ionized media also require a precise knowledge of momentum transfer rates by elastic collisions.

In order to assess the theoretically computed cross section and energy/momentum transfer rates, direct absolute experiments are scarce. The best way is to measure not individual scattering events but rather the global effect of the buffer gas, thanks to the pressure broadening cross sections, whose magnitude can be measured *without* any scaling parameters. At low temperatures, both elastic and inelastic scattering amplitudes are tested. At higher temperature, depending on the interaction strength, only inelastic scattering cross section are shown to play a significant role [1] ,[2].

Thanks to the advances of computer capabilities, it has become practical to compute spectral line parameters from *ab initio* quantum chemistry. In particular, the theory of rotational line broadening is readily incorporated into scattering quantum dynamical theory, like close-coupling schemes. The only approximations used in the computation are the isolated collision/isolated line approximations. We compute the non-binding interaction potential with high precision quantum chemistry and fit the resulting ab initio points onto a suitable functional.

We have recently computed several such systems, for molecules in H_2 buffer gas: H_2O,[3] H_2CO,[4] HCO^+ .[5] Detailed computations taking into account the ortho or para state of H_2 were performed, at temperatures ranging from 10 K to 100K, typically.

---

[1] Baranger 1958, Phys.Rev., 112, 855.

[2] Faure, Wiesenfeld, Drouin, Tennyson, 2013 JQRST, 116, 79.

[3] Wiesenfeld, Faure, 2010, Phys Rev A 82, 040702(R).

[4] Wiesenfeld, Faure, 2013, MNRAS, 432, 2573.

[5] Massó, Wiesenfeld, submitted.

Reliable results are found, that compare favorably to experiments. In particular, the water-molecular hydrogen system has been thoroughly computed and successfully experimentally tested [6].

New projects consider other simple molecules as well as heavier systems, relevant for cometary comae and planetary high atmospheres.

---

[6] Drouin, Wiesenfeld, 2012 Phys.Rev.A , 86, 022705.

III-10. A rapid retrieval methodology based on the spectrally integrated Voigt function for space observation spectral radiance data

Brendan M. Quine,[a] **Sanjar M. Abrarov**,[a] **Raj K. Jagpal**[b]

[a]*Dept. Earth and Space Science and Engineering, York University, 4700 Keele Street, Toronto, Canada, M3J 1P3*

[b]*Dept. Physics and Astronomy, York University, 4700 Keele Street, Toronto, Canada, M3J 1P3*

In our recent publication, we proposed the application of the spectrally integrated Voigt function (SIVF) to a line-by-line (LBL) radiative transfer modelling[1]. We applied the GENSPECT LBL radiative transfer model that utilizes the HITRAN database to generate synthetic spectral data due to thermal or solar radiation of the Earth or planetary atmosphereg[2]. It has been shown that the SIVF methodology enables the computation of a LBL radiative transfer at reduced spectral resolution model without loss in accuracy. In contrast to the traditional method of computation, the SIVF implementation accounts for the area under the Voigt function between adjacent grid points resulting in well-preserved shape of a spectral radiance even at low spectral resolution. This significant advantage of the SIVF methodology can be applied in the rapid retrieval of the space observation data, required for real-time control and decision making in future generation of the Argus[3] remote-sensing micro-spectrometers. The spectrally integrated methodology can be generalized to other line-broadening profiles, such as Galatry, Rautian-Sobelman or speed dependent profiles, to prevent underestimation of the spectral radiance that always occurs at reduced spectral resolution[1] in any LBL radiative transfer model using a traditional method of computation.

---

[1] Quine BM, Abrarov SM, Application of the spectrally integrated Voigt function, J. Spectrosc. Radiat. Transfer 2013;127:37-48. http://dx.doi.org/10.1016/j.jqsrt.2013.04.020.

[2] Quine BM, Drummond JR, GENSPECT: a line-by-line code with selectable interpolation error tolerance. J Quant Spectrosc Radiat Transfer 2002;74:147-65. http://dx.doi.org/10.1016/S0022-4073(01)00193-5

[3] Jagpal RK, Quine BM, Chesser H, Abrarov SM, Lee R, Calibration and in-orbit performance of the Argus 1000 spectrometer - the Canadian pollution monitor, J. Appl. Remote Sens. 2010;4;049501. http://dx.doi.org/10.1117/1.3302405.

SESSION IV: Laboratory Spectroscopy

IV-1. Line Parameters from a Precisely Calibrated Cavity Ring-Down Spectrometer

S.-M. Hu

Hefei National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China, Hefei, 230026 China

Cavity ring-down spectroscopy (CRDS), as a sensitive technique capable of probing weak absorption, now attracts more interests in quantitative studies. Precise line parameters can be retrieved from CRDS spectra, especially for those weak transitions beyond the sensitivity of conventional Fourier-transform spectrometers combined with multi-pass absorption cells. In this talk, we will present some of our recent studies using a CRDS spectrometer calibrated with a set of precise atomic lines. The spectrometer allows us to detect absorptions with a sensitivity of 10^{-11} cm^{-1} and a spectral precision up to 10^{-6} cm^{-1}. Ro-vibrational lines in the second overtone of H_2 have been observed, including the extremely weak $S_3(5)$ line with a line intensity less than 1×10^{-30}cm/molecule, which is among the weakest molecular lines detected by absorption in the gas phase. The absolute line positions of H_2 agree well with the high-level quantum chemical calculations including relativistic and QED corrections, with the deviation being less than 5×10^{-4} cm^{-1}. A quantitative study has also been carried out on the $\nu_1 + 5\nu_3$ band of CO_2. It was the first CO_2 band observed 80 years ago in the spectrum of Venus. We determined the line positions with an accuracy of 3×10^{-5} cm^{-1}, two orders of magnitude better than previous studies. Similar studies have been carried out to determine the line parameters of CO and H_2O in the spectral regions near 0.8 μm. We hope these studies will not only improve our knowledge of the potential energy surfaces and dipole moment surfaces of these molecules, but also provide more reliable line parameters which could be included in the new edition of HITRAN.

WITHDRAWN

IV-2. The Near Infrared Absorption Spectrum of Water by CRDS Between 1.26-1.70 μm:Complete Empirical Line List and Continuum Absorption

Didier Mondelain[a], **Alain Campargue**[a], **Samir Kassi**[a], **Semen Mikhailenko**[b]

[a] *UMR5588 LIPhy, Université Grenoble1/CNRS, Saint Martin D'Hères, France*

[b] *Laboratory of Theoretical Spectroscopy, V.E. Zuev Institute of Atmospheric Optics, SB, Russian Academy of Science, 1, Akademician Zuev square, 634021, Tomsk, Russia and Mathematical Physics Department, Tomsk Polytechnic University 30, Lenin av., 634050, Tomsk, Russia*

Due to the increasing performances of Airborne- and ground-based spectrometers, a more and more accurate characterization of the water vapor absorption is required. This is especially true in the transparency windows, corresponding to low absorption spectral regions widely used for probing the Earth's atmosphere. State-of-the-art experimental developments are required to fulfill the needs in terms of accuracy of the spectroscopic data. For that purpose, we are using high-sensitivity Continuous Wave Cavity Ring Down Spectroscopy (CW-CRDS) allowing reproducing in laboratory conditions comparable to the atmospheric ones in terms of absorption path length (tens of kilometers), temperature and pressure. From extensive analysis of our CRDS spectra, we have constructed an empirical line list for "natural" water vapor at 296 K in the 5850 - 7920 cm^{-1} region including 38 318 transitions of four major water isotopologues (H_2 ^{16}O, $H_2{}^{18}O$, $H_2{}^{17}O$ and $HD^{16}O$) with an intensity cut-off of $1{\cdot}10^{-29}$ cm/molecule. The list is made mostly complete over the whole spectral region by including a large number of unobserved weak lines with positions calculated using experimentally determined energy levels and intensities obtained from variational calculations. In addition, we provide $HD^{18}O$ and HD ^{17}O lists in the same region for transitions with intensities larger than $1{\cdot}10^{-29}$ cm/molecule. The $HD^{18}O$ and $HD^{17}O$ lists (1 972 lines in total) were obtained using empirical energy levels available in the literature and variational intensities. The global list (40 290 transitions) including the contribution of the six major isotopologues has been adopted for the new edition of the GEISA database in the region. The advantages and drawbacks of our list will be discussed in comparison with the list provided for the same region in the 2012 edition of the HITRAN database. Separate experiments were dedicated to the measurement of the water vapor self-continuum cross-sections in the 1.6 μm window by CW-CRDS at different temperatures (from room temperature to 340 K). Due to the weakness of the broadband absorption signal to be measured, very few measurements of the water vapor continuum are available in the NIR windows especially for temperature conditions relevant for our atmosphere. This is in particular the case for the 1.6 μm window where the very few available measurements show a large disagreement. The absorption cross-sections, $C_s(\nu, T)$, were retrieved for different selected wave numbers from a fit of the absorption coefficients measured in real time during pressure ramps, after subtraction of the contributions of the local water monomer lines and of water adsorbed on the CRDS mirrors. The values measured between 5875 and 6665 cm^{-1} range between $1.5{\cdot}10^{-25}$ and $2{\cdot}10^{-24}$ cm^2 molec^{-1} atm^{-1} with a minimum around 6300 cm^{-1}. Overall, our measurements are found in strong disagreement with recent FTS measurements and in a good agreement with the values predicted by the MT_CKD2.5 model, except for the temperature dependence in the center of the window which is found significantly smaller than predicted.

IV-3. Frequency Comb Spectroscopy of CO_2, CH_4, H_2O, and Isotopes Over a 2 km Outdoor Path: Concentration Retrievals Using Different Absorption Models

G. B. Rieker[a], **F. R. Giorgetta**[b], **I. Coddington**[b], **W. C. Swann**[b], **A. M. Zolot**[b], **L. C. Sinclair**[b], **E. Baumann**[b], **C. Cromer**[b], **N. Newbury**[b]

[a]*Department of Mechanical Engineering, University of Colorado, Boulder, National Institute of Standards and Technology, Boulder, CO*

[b]*National Institute of Standards and Technology, Boulder, CO*

A dual frequency comb spectrometer is used to make high signal-to-noise measurements of atmospheric absorption from 5990 to 6260 cm^{-1} with 0.0033 cm^{-1} point spacing and $\sim 4 \cdot 10^{-8}$ cm^{-1} resolution over a 2 km outdoor air path. The spectra, which encompass over 700 absorption features of CO_2, CH_4, and H_2O, are fit with several absorption models to assess the quality of the models and to retrieve the various species concentrations and air temperature. The models tested include the HITRAN 2008 and 2012 spectral databases with Voigt line-shape profiles as well as a recent model for CO_2 that includes the effects of line mixing and speed dependence. Residuals are typically less than 2% of the peak absorbance, except for the HITRAN 2012 CH_4 model, which exhibits larger residuals. Species concentration retrievals using the models are compared with a calibrated point sensor mounted on a tower near the open air path.

IV-4. Frequency Comb-Referenced Spectroscopy in the $\nu_1 + \nu_3$ Region of Acetylene

Matthew J. Cich,[a] **Damien Forthomme,**[b] **Gregory E. Hall,**[b]
Christopher P. Mcraven,[b] **Trevor J. Sears,**[a,b] **Sylvestre Twagirayezu**[b]

[a]*Department of Chemistry, Stony Brook University, Stony Brook, New York 11794*

[b]*Department of Chemistry, Brookhaven National Laboratory, Upton, New York 11973*

By using saturation dip absorption spectroscopy with an extended cavity diode laser locked to a frequency comb, we have measured the rest frequencies of transitions in the $\nu_4 = 1$ and $\nu_5 = 1$ hot bands in the $\nu_1 + \nu_3$ combination band of acetylene. The measured line frequencies are accurate to approximately 20 kHz *i.e.* approximately one part in 10^{11}. Positions of the hot-band lines quoted in the HITRAN database, which are derived from the analysis of high-resolution FTIR spectra, are of the order of 10's of MHz in error. These measurements were undertaken because pressure broadened line-shape measurements of rotational lines in the combination band indicated that weak underlying hot band features were not correctly accounted for on the basis of their previously reported positions. As a result, measured line profiles in the band could not be accurately fit leading to errors of up to 1% in acetylene concentrations derived from the measurements. In addition, the pressure broadened P(11) line in the $\nu_1 + \nu_3$ combination band has been studied as a function of varying concentration of the absorber in nitrogen. Mixture concentrations of 1, 5 and 10% at 296 K and pressures between a few Torr and one atmosphere were made and the measurements analyzed using two different speed-dependent broadening models. These experiments are designed to test the additivity of contributions to pressure broadening and shift in speed-dependent line-shape modeling, *i.e.* whether the lineshape parameters follow partial pressure weighting in the binary mixtures. P(11) is relatively isolated with respect to underlying hot band transitions and neighboring transitions of the same band, but it was found that the accurate positions of underlying hot-band transitions were crucial to the successful modeling of the observed line shapes, even though these lines are typically 100-1000 times weaker than P(11) itself and are many Doppler line widths removed from the line center.

Acknowledgments: Work at Brookhaven National Laboratory was carried out under Contract No. DE-AC02-98CH10886 with the U.S. Department of Energy and supported by its Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences and Biosciences.

IV-5. Spectroscopy for Industrial Applications: High-Temperature Processes

Alexander Fateev[a], **Helge Grosch**[a], **Sonnik Clausen**[a], **Emma J. Barton**[b], **Sergei N. Yurchenko**[b], **Jonathan Tennyson**[b]

[a]*DTU Chemical Engineering, Frederiksborgvej 399, DK-4000, Roskilde, Denmark*

[b]*Department of Physics and Astronomy, University College London, London WC1E 68T, UK*

The continuous development of the spectroscopic databases brings new perspectives in the environmental and industrial on-line process control, monitoring and stimulates further optical sensor developments. This is because no calibration gases are needed and, in general, temperature-dependent spectral absorption features gases of interest for a specific instrument can in principle be calculated by knowing only the gas temperature and pressure in the process under investigation/monitoring. The latest HITRAN-2012 database contains IR/UV spectral data for 47 molecules and it is still growing. However use of HITRAN is limited to low-temperature processes (< 400 K) and therefor can be used for absorption spectra calculations at limited temperature/pressure ranges. For higher temperatures, the HITEMP-2010 database is available. Only a few molecules CO_2, H_2O, CO and NO are those of interest for e.g. various combustion and astronomical applications are included. In the recent few years, several efforts towards a development of hot line lists have been made; those have been implemented in the latest HITRAN-2012 database[1].

High-resolution absorption measurements of NH_3 (IR, 0.1 cm^{-1}) and phenol (UV, 0.019 nm) on a flow gas cell[2] up to 800 K are presented. Molecules are of great interest in various high-temperature environments including exoplanets, combustion and gasification. Measured NH_3 hot lines have been assigned and spectra have been compared with that obtained by calculations based on the BYTe hot line list[1]. High-temperature NH_3 absorption spectra have been used in the analysis of in situ high-resolution IR absorption measurements on the producer gas in low-temperature gasification process on a large scale. High-resolution UV temperature-dependent absorption cross-sections of phenol are reported for the first time. All UV data have been calibrated by relevant GC/MS measurements. Use of the data is demonstrated by the analysis of in situ UV absorption measurements on a small-scale low-temperature gasifier. A comparison between in situ, gas extraction and conventional gas sampling measurements is presented. Overall the presentation shows an example of successful industrial and academic partnerships within the framework of national and international ongoing projects.

---

[1] S.N. Yurchenko, R.J. Barber and J. Tennyson “A variationally computed hot line lists for NH_3”, MNRAS, 413, 1828-1834 (2011).

[2] H. Grosch, A. Fateev, K.L. Nielsen and S. Clausen ”Hot gas cell for optical measurements on reactive gases”, JQSRT, 130, 392-399 (2013).

IV-6. New Development for Terahertz Spectroscopy in Lille

L. Margulès,[a] **R. A. Motiyenko**,[a] **E. A. Alekseev**[b]

[a] *Laboratoire PhLAM, CNRS UMR 8523, Université Lille 1, 59655 Villeneuve d'Ascq Cedex, France*

[b] *Institute of Radio Astronomy of NASU, Chervonopraporna Str., 4, 61002 Kharkov, Ukraine*

Terahertz domain is particularly interesting for spectroscopy of atmospheric species since the rotational spectra of light molecules like water or methanol have their absorption maximum in this range. Up to few years ago the source commonly used in terahertz domain were the backward wave oscillators. These radiation sources provide relatively high output power (several milliwatts) in the frequency range up to 1.2 THz However the BWOs are not easy to handle: they need high voltage supply (2 - 6 kV), water cooling, magnetic field up to 1 Tesla, and a phase locked loop to give accurate frequency measurements.

With the arrival of telescopes working in the THz range, great improvements were achieved in the development of solid state devices based on Schottky diodes. The new spectrometer in Lille take advantage of this development and is now based on a frequency multiplication chain using these devices. The spectrometer covers more than 80% of the frequency range 0.05 - 1.5 THz, and we need about 150 hours to record the spectra in this range with high resolution.

We will present two short-term projects for the spectrometer. The first one is to increase the frequency range up to 1.9 THz in order to have the full coverage of Herschel telescope. The second one is to speed up the experimental setup. Recently we have shown that one can obtain high resolution and high precision broadband spectra with a high recording rate using a DDS synthesizer in the phase-locked loop of a BWO[1]. Such fast-scan spectroscopy is particularly interesting for unstable species[2,3]. Our project is to couple a DDS synthesizer with a 10 - 20 GHz reference synthesizer and a frequency multiplication chain to obtain fast-scan solid state spectrometer.

This work was supported by the CNES and the Action sur Projets de l'INSU, PCMI. This work was also done under Ukrainian-French CNRS-PICS 6051 project

---

[1] Alekseev et al. 2012, Radio Physics and Radio Astronomy, 3, 75

[2] Goubet at al. 2012, J. Phys. Chem. A 116, 5405

[3] Haykal et al. Astrop. 2013, J. 777, 120

Poster Session II

PII-1. Electronic Structure and Spectroscopy Of O_2 and O_2^+

G. J. Vázquez,[a] **H. P. Liebermann,**[b] **H. Lefebvre–Brion**[c]

[a]*Instituto de Ciencias Físicas, Universidad Nacional Autónoma de México (UNAM), Cuernavaca, México 62210*

[b]*Fachbereich C–Mathematik und Naturwissenschaften, Universität Wuppertal, Gaußstraße 20, Wuppertal, Germany D–42119*

[c]*Institut des Sciences Molécularies d'Orsay, Orsay Cedex, France 91405*

We carried out a comprehensive SCF MRD–CI ab initio study of the electronic structure of O_2 and O_2^+. Potential energy curves (PECs) of about 150 electronic states of O_2 (singlets, triplets, quintets, septets) and about 100 of O_2^+ (doublets, quartets, sextets), as well as a number of states of O_2^{++} were computed. The aug–cc–pVQZ basis set was employed for the oxygen atoms and the basis was augmented with seven diffuse functions (three s, three p, one d). Spectroscopic parameters ($T_e, T_v, \omega_e, \omega_e x_e$, B_e, D_e, D_0, μ, IP's, EA, etc.) are reported for several of the bound states and, generally speaking, a good agreement is found with the experimental counterparts. A preliminary sample of the results will be presented. The electronic absorption spectrum of O_2 has proved difficult to analyze/interpret due to the unusually large number of electronic states which arise from the peculiar open–shell structure of both the oxygen atomic fragments and the O_2 molecule. For instance, there are 62 valence molecular electronic states which correlate to the six lowest dissociation limits resulting from the three valence O atom fragment states (^{3}P, ^{1}D, ^{1}S). In addition, there are numerous $ns\lambda$ Rydberg series converging to the $X^2\Pi_g$ ground ionic state and to the lowest two excited states of the cation, $a^4\Pi_{ui}$ and $A^2\Pi_u$. Hence, the energy region below about 16 eV, is rather congested with electronic states. Furthermore, a number of interactions of various types between numerous electronic states result in rovibronic perturbations which manifest themselves, e.g., as irregular vibronic structure, hence severely complicating the assignment of the absorption features and the analysis and interpretation of the spectrum. An overview of the electronic states and spectroscopy of O_2 in the 0–16 eV energy region will be presented.

A chief motivation of this study of O_2 was to try to provide a theoretical insight on the nature, energetic position, shape, and dissociation asymptotes, of electronic states located in the 4 eV energy region encompassed between the O_2^+ ground state $X^2\Pi_g$ (IP= 12.07 eV) and the first excited state of the cation $a^4\Pi_{ui}$ (IP= 16.10 eV). This in order to aid in the interpretation of experimental data related to the mechanism(s) of the neutral dissociation of the O_2^{**} (Rydberg) superexcited states, which compete with autoionization. Figures focusing on the PECs located in the 12–16 eV energy range will be used to visualize possible pathways for the neutral photodissociation of the I, I′ and

I$''$ $^3\Pi_u$ superexcited states of O_2 leading to the O(^{3}P) + O*(^{3}S, ^{5}S) dissociation limits, whereby the electronicaly excited O* fragment has an electron in the 3s Rydberg orbital.

Even though O_2 is known to be a difficult molecule to compute accurately by conventional ab initio techniques, particularly the relatively high lying excited states, we feel that the present work provides a significan contribution to the understanding of the electronic spectroscopy of this molecule.

PII-2. Detection of Atmospheric $^{15}NO_2$ Enabled by a New ν_3 Linelist

A. Perrin,[a] **G.Toon**,[b] **J.Orphal**[c]

[a]*Laboratoire Inter Universitaire des Systemes Atmosphériques (LISA), CNRS, Universités Paris Est and Paris 7, 61 Av du Général de Gaulle, 94010 Créteil Cedex France*

[b]*Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California, 91109, USA*

[c]*Karlsruhe Institute of Technology (KIT), Karlsruhe, 76131, Germany*

A reinvestigation of $^{15}NO_2$ -enriched laboratory spectra recorded at 6.2 μm by Fourier transform spectroscopy in 2000 [1] was performed. In this way, an improved set of line positions parameters was achieved for the ν_3 band of $^{15}NO_2$, and using these results, a linelist of line positions, line intensities and line shape parameters was generated for atmospheric studies. This new linelist has been used to detect this isotopologue in the atmosphere for the first time, using balloon-borne solar occultation spectra measured by the JPL MkIV Fourier Transform spectrometer. It is shown that over the 15-35 km altitude range where $^{15}NO_2$ can be detected, the retrieved 15/14 NO_2 ratio is within 5% of the expected value (0.00364), implying that the absolute line intensities in the new linelist are accurate. Over the same altitude range the RMS spectral fitting residuals reduce significantly as a result of including the new $^{15}NO_2$ linelist, improving the accuracy of retrievals of all gases that absorb in the 1550-1650 cm^{-1} region (e.g., $^{14}NO_2$, H_2O, HDO, O_2).

---

[1] Orphal et al. J Mol Spec 2000;204:72-9.

PII-3. Intensity Analysis of the Torsional Band of C_2H_6 at 35 μm

N. Moazzen-Ahmadi,[a] J. Norooz Oliaee,[a] I. Ozier,[b] E. H. Wishnow,[c] K. Sung,[d] T. J. Crawford,[d] L.R. Brown,[d] V.M. Devi[e]

[a] *Dept. of Physics and Astronomy, University of Calgary, Calgary, Alberta, T2N 1N4, Canada*

[b] *Dept. of Physics and Astronomy, University of British Columbia, Vancouver, British Columbia, V6T 1Z1, Canada*

[c] *Space Sciences Lab, University of California, Berkeley, CA 94720, U.S.A.*

[d] *Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Dr., Pasadena, CA 91109, U.S.A.*

[e] *Dept. of Physics, The College of William and Mary, Williamsburg, VA 23187, U.S.A.*

Spectral features of ethane are seen at 35 μm in the CASSINI/CIRS spectra of Titan; thus reliable line intensities are required for accurate characterization of Titan's far-infrared observations. The torsional spectrum of C_2H_6 from 220 to 330 cm^{-1} is presently being investigated to measure the intensity of the fundamental and the first torsional hot band. Several spectra were obtained at resolutions of 0.01 and 0.02 cm^{-1} using a coolable multi-pass absorption cell (with a 52 m path) coupled to the Bruker IFS-125 at the Jet Propulsion Laboratory. Spectra were recorded at temperatures from 293 K to 166 K, with the lower temperatures relevant to the stratosphere of Titan. Because this torsional band is very weak, substantial sample pressures from 35 to 255 Torr were used. Intensities were analyzed by comparing the predicted line positions and intensities from the quantum mechanical model and the observed cold spectrum. Coriolis interaction terms were required to obtain a satisfactory fit. These new results will lead to a better characterization of ethane and in turn an improved understanding of the methane cycle in planetary atmospheres; they will also permit other molecular features in the CIRS spectra to be identified.[1]

---

[1] The research conducted at the University of Calgary is supported by the Canadian Space Agency. Part of the research described in this paper was performed at the Jet Propulsion Laboratory, California Institute of Technology, Connecticut College, and The College of William and Mary, under contracts and cooperative agreements with the National Aeronautics and Space Administration.

PII-4. Analysis of $^{12}CH_3{}^{13}CH_3$ in the 7 μm Region

**Carlo Di Lauro, Franca Lattanzi, Linda R. Brown, Keeyoon Sung,
Arlan W. Mantz, Mary Ann H. Smith**

[a] *Università di Napoli Federico II, 49 via D. Montesano, I-80131 Naples, Italy*

[b] *Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Dr., Pasadena, CA 91109, U.S.A.*

[c] *Dept. of Physics, Astronomy and Geophysics, Connecticut College, New London, CT 06320, U.S.A.*

[d] *Science Directorate, NASA Langley Research Center, Hampton, VA 23681, U.S.A.*

The infrared spectrum of $^{12}CH_3{}^{13}CH_3$ is measured between 1345 and 1550 cm^{-1} using high resolution FT-IR with a ^{13}C-enriched gas sample cooled to 130.3 K. The three fundamentals ν_4, ν_9 and ν_{10} (at 1374, 1470 and 1468 cm^{-1} respectively) and one combination band $\nu_6+\nu_{11}$ at 1473 cm^{-1} are analyzed for the first time. Numerous perturbations are seen. The transitions of ν_{10} (an infrared inactive "g" mode of the ethane) are observed through its resonant coupling with ν_9. Transitions of $\nu_6+\nu_{11}$ are seen due to its strong coupling to ν_9. In general, torsional splitting produces two components (as in normal ethane), but in both ν_9 and ν_{10}, there is an additional small splitting of these components with degenerate torsional symmetry wherever the interacting ν_{10} levels become infrared active. As in normal ethane, a detectable K-doubling occurs in the levels $\Delta k = \pm 2$, $\Delta \ell = \mp 1$ of ν_9, and the parallel band ν_4 shows an intensity bias, with the R-transitions markedly stronger than the P-transitions, due to its x,y-Coriolis coupling with ν_9. The spectrum is analyzed by adopting an appropriate Hamiltonian model, and vibration-rotation-torsion parameters of the four mentioned vibrational states are determined by the least squares process using 1350 observed transition line positions (RMS deviation 0.0032 cm^{-1}). Supplemental linelists provide over 6000 measured positions and intensities at 130.3 K with half of them assigned.[1]

---

[1] Part of the research described in this paper was performed at the Jet Propulsion Laboratory, California Institute of Technology, Connecticut College and the NASA Langley Research Center under contracts and cooperative agreements with the National Aeronautics and Space Administration.

PII-5. Rotational and Vibrational Energy Levels of Ethylene and Isotopologues Calculated from a New Potential Energy Surface

Thibault Delahaye,[a] Michaël Rey,[a] Vladimir Tyuterev,[a] Andrei Nikitin,[b] Péter G. Szalay[c]

[a] *Groupe de Spectrométrie Moléculaire et Atmosphérique, UMR CNRS 7331, BP 1039, F-51687, Reims Cedex 2, France*

[b] *Laboratory of Theoretical Spectroscopy, Institute of Atmospheric Optics, SB RAS, 634055 TOMSK, Russia*

[c] *Institute of Chemistry, Eötvös Loránd University, P.O. Box 32, H-1518 Budapest, Hungary*

Polyatomic molecules such as methane (CH_4), acetylene (C_2H_2) and ethylene (C_2H_4) "carbon chains" are of considerable interest for modeling of planetary atmospheres and other astrophysical applications. Knowledge of rovibrational transitions of hydrocarbons is of primary importance in many fields, as for example for identifying the chemical composition of Titan atmosphere but remains a formidable challenge for the theory and spectral analysis. Several databases aim at collecting the corresponding data but the information about C_2H_4 spectrum present in databases remains limited, only some spectral ranges around 1000, 3000 and 6000 cm^{-1} being available.

We report predictions of vibrationals and rovibrational energy levels of (C_2H_4) using our new ground state potential energy surface obtained from extended ab initio calculations at the CCSD(T)/cc-pVQZ level of theory. A good convergence for variationally-computed vibrational levels of the C_2H_4 molecule was obtained with a RMS(Obs.-Calc.) deviation of 2.6 cm^{-1} for fundamental bands centers and 5.5 cm^{-1} for vibrational bands up to 7800 cm^{-1}. Vibrational calculations for $^{13}C_2H_4$ and $^{12}C_2D_4$ molecules were also performed using this new surface. Empirical optimization of the equilibrium configuration procedure was necessary to reach the accuracy expected in high-resolution spectroscopy applications. Rovibrational calculations using our recent normal mode reduction-truncation procedure previously applied for methane[1,2] as well as comparisons with previous works for the ethylene calculations[3,4] is presented. Additionaly we present a new dipole moment surface for ethylene which has been calculated on the same grid as the PES using the CCSD(T)/cc-pVQZ level of theory. This is the first step towards future analyses of the IR spectra of ethylene and its isotopologues based on this two surfaces.

---

[1] M. Rey, A. V. Nikitin, Vl. G. Tyuterev, J. Chem. Phys. 2012, 136, 244106

[2] M. Rey, A. V. Nikitin, Vl. G. Tyuterev, Phys. Chem. Chem. Phys. 2013, 136, 244106

[3] J. M. L. Martin, T. J. Lee, P. R. Taylor and J.-P. Franois, J. Chem. Phys. 1995, 103, 2589

[4] G. Avila and T. Carrington, J. Phys. Chem. 2011, 135, 064101

PII-6. High Resolution Spectroscopy and Analysis of the ν_3 Band of $^{36}SF_6$ and New Global Fit of $^{32}SF_6$ Parameters Including New $3\nu_3$ Band Data

M. Faye,[a] **V. Boudon,**[a] **L. Manceron,**[b] **F. Kwabia-Tchana**[c]

[a]*Laboratoire Interdisciplinaire Carnot de Bourgogne, UMR 6303 CNRS–Université de Bourgogne, 9 Av. A. Savary, BP 47870, F-21078 Dijon Cedex, France*

[b]*Ligne AILES – Synchrotron SOLEIL, L'Orme des Merisiers, F-91192 Gif-sur-Yvette Cedex, France*

[c]*Laboratoire Interuniversitaire des Systèmes Atmosphériques, UMR CNRS 7583, Université Paris-Est Créteil et Université Paris-Diderot, 61 Avenue du Général de Gaulle, 94010 Créteil Cedex, France*

Aiming a better modeling of sulfur hexafluoride (SF_6) atmospheric absorption, we recently performed new measurements at the AILES beamline of the SOLEIL synchrotron facility near Paris. Thanks to the internal infrared source of the Bruker IFS125 HR coupled to a cryogenic multiple pass cell[1] containing the SF_6 gas, its spectrum has ben recorded in the 800 - 3200 cm^{-1} wavenumber range. The optical path length of the beam light was adjusted to 93 m and the SF_6 gas was cooled down to 150 K with liquid nitrogen. The pressure was 1.25 mbar. We thus identified 17 rovibrational bands of SF_6 in this region with a resolution of 0.0025 cm^{-1}.

These results allowed us to perform in analysis of several of these bands. For the first time, the weak ν_3 band of the $^{36}SF_6$ isotopologue (with 0.02% natural abundance) has been analyzed. We also assigned and fitted the $3\nu_3$ overtone band of the $^{32}SF_6$ main isotopologue. Including these new $3\nu_3$ data in the XTDS model[2], we substantially improved the previous global fit[3] of SF_6 parameters. The analysis of other combination bands is currently underway.

---

[1] F. K. Tchana, F. Willaert, X. Landsheere, J-M. Flaud, L. Lago, M. Chapuis, Ch. Herbeaux, P. Roy and L. Manceron, Review of Scientific Instruments, **84**, 093101 (2013).

[2] Ch. Wenger, V. Boudon, M. Rotger, M. Sanzharov and J-P. Champion, Journal of Molecular Spectroscopy **251**, 102-113 (2008).

[3] M. Faye, A. Le Ven, V. Boudon, L. Manceron, P. Asselin, P. Soulard, F. Kwabia Tchana and P. Roy, Molecular Physics, in press (2014).

PII-7. The BrO A-X Electronic Transition Revisited: Modeling the Absorption Cross-Sections

J. Orphal,[a] **F. Hase,**[a] **C. E. Fellows**[b]

[a]*Institute for Meteorology and Climate Research, Karlsruhe Institute of Technology (KIT), Karlsruhe, 76131, Germany*

[b]*Departamento de Fisica, Universidade Federal Fluminense (UFF), Rio de Janeiro, Brazil*

The well-structured ultraviolet absorption spectrum of the BrO radical is used for its atmospheric detection from ground, airborne platforms and from satellites. Absorption cross-sections of the electronic A-X transition of BrO and their temperature dependence have been measured in the laboratory by several groups, but show significant differences that lead to biases in the atmospheric concentrations. Here we present a theoretical model of the BrO absorption cross-sections including predissociation broadening and compare modelled with different measured spectra.

PII-8. Temperature Dependent Absorption Cross-sections of PFTBA

Paul J. Godin,[a] Stephanie Conway,[a] Angela Hong,[b] Scott Mabury,[b]
Kimberly Strong[a]

[a]*Department of Physics, University of Toronto, 60 St. George St., Toronto, ON, M5S 1A7, Canada*

[b]*Department of Chemistry, University of Toronto, 80 St. George St., Toronto, ON, M5S 3H6, Canada*

We present temperature-dependent absorption cross sections of perfluorotributylamine (PFTBA). PFTBA is a fully-fluorinated liquid commonly used in electronic reliability and quality testing. PFTBA vapour can be considered a potential greenhouse gas due being radiatively active in the mid-IR spectral region and having a long atmospheric lifetime. A recent paper by Hong *et al.*[1] as well as comparisons with previous works for the ethylene calculationsc determined that PFTBA has the highest radiative efficiency of any compound detected in the atmosphere with a detected a mixing ratio of 0.18 parts per trillion by volume over Toronto, ON.

Theoretical density functional theory (DFT) calculations are done using the B3LYP method and the 6-311G(d,p) basis set. The calculations have determined the optimized geometrical configuration and IR intensities and wavenumbers of the harmonic frequencies for both PFBAm (N(CF2CF2CF2CF3)3) and its congener (F3CN(CF2CF2CF2CF3)2).

Experimental cross sections are derived from Fourier transform spectroscopy performed from 600-1450 cm^{-1} at a resolution of 0.02 cm^{-1} for room temperature and above. These experimental results are compared to compared to previous measurements of PFTBA made at room temperature by Young[2].

---

[1] A. C. Hong, C. J. Young, M. D. Hurley, T. J. Wallington, and S. A. Mabury, *Geophys. Res. Lett.*, **40**, 1-6 (2013).

[2] C. J. Young, Ph. D. Thesis, *University of Toronto* (2010).

PII-9. Recommended Isolated-Line Profile for Representing High-Resolution Spectroscoscopic Transitions

J. Tennyson,[a] **P. F. Bernath,**[b] **A. Campargue,**[c] **A. G. Császár,**[d]
L. Daumont,[e] **R. R. Gamache,**[f] **J. T. Hodges,**[g] **D. Lisak,**[h] **O. V. Naumenko,**[i]
L. S. Rothman,[j] **H. Tran,**[k] **J. -M. Hartmann,**[k] **N. F. Zobov,**[l] **J. Buldyreva,**[m]
C. D. Boone,[n] **M. Domenica De Vizia,**[o] **L. Gianfrani,**[o] **R. McPheat,**[p]
D. Weidmann,[p] **J. Murray,**[q] **N. H. Ngo,**[r] **O. L. Polyansky**[a,l]

[a] *University College London, Gower Street, London, WC1E 6BT, U.K.*

[b] *Old Dominion University, Norfolk, VA, USA*

[c] *Université Joseph Fourier/CNRS, Grenoble, France*

[d] *MTA-ELTE Research Group on Complex Chemical Systems, H-1518 Budapest, P.O. Box 32, Hungary*

[e] *Université de Reims Champagne-Ardenne, Reims, France*

[f] *University of Massachusetts, Lowell, MA, USA*

[g] *National Institute of Standards and Technology, Gaithersburg, MD, USA*

[h] *Nicolaus Copernicus University, Grudziadzka 5, 87-100 Torun, Poland*

[i] *Institute of Atmospheric Optics, Russian Academy of Sciences, Tomsk, Russia*

[j] *Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, USA*

[k] *Université Paris Est Créteil, Université Paris Diderot, Institut Pierre-Simon Laplace, 94010 Créteil Cedex, France*

[l] *Institute of Applied Physics, Russian Academy of Sciences, Nizhny Novgorod, Russia*

[m] *Institute UTINAM, University of Franche-Comte, Besancon, France*

[n] *Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada*

[o] *Dipartimento di Matematica e Fisica della Seconda Università di Napoli, Viale Lincoln* 5, 81100 *Caserta, Italy*

[p] *Rutherford Appleton Laboratory, Oxfordshire, UK*

[q] *Imperial College London, UK*

[r] *Hanoi University of Education, 136 XuanThuy, Hanoi, Vietnam*

Recommendations of an IUPAC Task Group, formed in 2011 on “Intensities and line shapes in high-resolution spectra of water isotopologues from experiment and theory”

(Project No. 2011-022-2-100), on line profiles of isolated high-resolution rotational-vibrational transitions perturbed by neutral gas-phase molecules are presented.

The well-documented inadequacies of the Voigt profile, used almost universally by databases and radiative-transfer codes to represent pressure effects and Doppler broadening in isolated vibrational-rotational and pure rotational transitions of the water molecule, have resulted in the development of a variety of alternative line profile models. These models capture more of the physics of the influence of pressure on line shapes but, in general, at the price of greater complexity. The Task Group recommends that the partially-Correlated quadratic-Speed-Dependent Hard-Collision profile should be adopted as the appropriate model for high-resolution spectroscopy. For simplicity this should be called the Hartmann–Tran profile (HTP). This profile is sophisticated enough to capture the various collisional contributions to the isolated line shape, can be computed in a straightforward and rapid manner, and reduces to simpler profiles, including the Voigt profile, under certain simplifying assumptions.

For further details see:
J. Tennyson *et al*, *Pure Appl. Chem.*, 2014, in press.

PII-10. A Global Fitting Approach For Doppler Broadening Thermometry

Pasquale Amodio, Luigi Moretti, Maria Domenica De Vizia, and Livio Gianfrani

Dipartimento di Matematica e Fisica della Seconda Università di Napoli, Viale Lincoln 5, 81100 *Caserta, Italy*

Very recently, a spectroscopic determination of the Boltzmann constant, k_B, has been performed at the Second University of Naples by means of a rather sophisticated implementation of Doppler Broadening Thermometry (DBT)[1]. Performed on a ^{18}O-enriched water sample, at a wavelength of 1.39 μm, the experiment has provided a value for kB with a combined uncertainty of 24 parts over 10^6, which is the best result obtained so far, by using an optical method. In the spectral analysis procedure, the partially correlated speed-dependent hard-collision (pC-SDHC) model was adopted. The uncertainty budget has clearly revealed that the major contributions come from the statistical uncertainty (type A) and from the uncertainty associated to the line-shape model (type B)[2]. In the present work, we present the first results of a theoretical and numerical work aimed at reducing these uncertainty components. It is well known that molecular line shapes exhibit clear deviations from the time honoured Voigt profile. Even in the case of a well isolated spectral line, under the influence of binary collisions, in the Doppler regime, the shape can be quite complicated by the joint occurrence of velocity-change collisions and speed-dependent effects.

The partially correlated speed-dependent Keilson-Storer profile (pC-SDKS) has been recently proposed as a very realistic model, capable of reproducing very accurately the absorption spectra for self-colliding water molecules, in the near infrared[3]. Unfortunately, the model is so complex that it cannot be implemented into a fitting routine for the analysis of experimental spectra. Therefore, we have developed a MATLAB code to simulate a variety of $H_2{}^{18}O$ spectra in thermodynamic conditions identical to the one of our DBT experiment, using the pC-SDKS model. The numerical calculations to determine such a profile have a very large computational cost, resulting from a very sophisticated iterative procedure. Hence, the numerically simulated spectra (with the addition of random noise) have been used to test the validity of simplified line shape models, such as the speed-dependent Galatry (SDG) profile and pC-SDHC model. In particular, we have used the global fitting procedure that is described in Amodio et al[4].

---

[1] L. Moretti, A. Castrillo, E. Fasci, M.D. De Vizia, G. Casa, G. Galzerano, A. Merlone, P. Laporta, and L. Gianfrani, Phys. Rev. L. 111, 060803 (2013).

[2] A. Castrillo, L. Moretti, E. Fasci, M.D. De Vizia, G.Casa and L. Gianfrani J. Mol. Spectrosc. (2014) http://dx.doi.org/10.1016/j.jms.2014.04.001.

[3] N. H. Ngo, H. Tran and R. R. Gamache, J. Chemical Physics 136, 154310 (2012).

[4] P. Amodio, L. Moretti, A. Castrillo and L. Gianfrani, J. Chemical Physics 140, 044310 (2014).

Such a procedure is very effective in reducing the uncertainty resulting from statistical correlation among free parameters. Therefore, the analysis of large amounts of simulated spectra has allowed us to study the influence of the choice of the model and quantify the achievable precision and accuracy levels, at the present value of the signal-to-noise ratio.

PII-11. Explicit Parallelization of Robert-Bonamy Formalism

John M. Styers, **Robert Gamache**

University of Massachusetts Lowell, Lowell, MA, U.S.A.

Robert-Bonamy formalism has long been employed in computational spectroscopy. As a method, it presents a fine balance between accuracy, and computational viability. While within the bounds of present-day computational resources, its calculations still constitute a significant amount of computational overhead. The vast majority of said computational demand, is in the computing of the resonance functions. Major aspects of the calculation of the resonance function are extremely repetitive in nature—presenting a problem which is almost “embarrassingly parallel” in nature. The computation of the resonance functions has been explicitly parallelized, resulting in an order of magnitude speed-up on local Macintosh machines—and multiple orders of magnitude speed-up on two Cray Supercomputers (Darter and MGHPCC). This will facilitate further scientific investigation.

PII-12. Accurate measurements of the N_2O-self-broadening coefficients for the $2\,\nu_3$-band around $2.25\,\mu$m using high resolution FTIR-spectroscopy

Viktor Werwein, **Jens Brunzendorf**, **Anton Serdyukov**, **Volker Ebert**

Physikalisch-Technische Bundesanstalt, Bundesallee 100, 38116 Braunschweig, Germany

Nitrous oxide (N_2O) is an important atmospheric trace gas due to its contribution to global warming[1] and its relevance for the stratospheric chemistry[2]. The self-broadening coefficients of nitrous oxide documented in the latest versions of HITRAN[3] and GEISA[4] originate from Toth[5]. These values were determined through a multi-band fitting procedure of an extensive set of measured lines in the range from 1800 to 2360 cm^{-1} over a pressure range of 87-533 mbar, followed by averaging of the coefficients for the same rotational quantum number and smoothing of the averaged coefficient values. In the HITRAN compilation[3] values from a third-order polynomial fit to Toths data[5] are implemented. Numerous line data were determined solely via interpolation between Toths data. So far, no direct experimental validation of this interpolation process has been reported e.g. for the self-broadening coefficients in parts of the N_2O ν_3-fundamental and particularly the $2\nu_3$-overtone band. For the $2\nu_3$-overtone band, we recently presented first high resolution measurements[6].

Here we report improved measurements of N_2O-self-broadening coefficients in the $2\,\nu_3$-band using a high resolution Fourier transform spectrometer. Infrared spectra were measured from 3800 to 5200 cm^{-1} with a nominal spectral resolution of 0.002 cm^{-1} at a temperature of 296 K. The new data were taken under improved experimental conditions. This includes increased sample purity of 99.999 %, a set of traceably calibrated pressure and temperature sensors, and an improved temperature-stabilized copper cell that compensates temperature fluctuations at room temperature to significantly below 1 K. Compared to Toth the measured pressure range was extended to $50-1020$ mbar. Spectra at eight pressures in this range were taken.

---

[1] Intergovernmental Panel on Climate Change, Third Assessment Report 2007.

[2] A. R. Ravishankara, J. S. Daniel, R. W. Portmann, Science 326, 123, 2009.

[3] L. S. Rothman et al., J. Quant. Spectrosc. Radiat. Transfer, 130, 4, 2013.

[4] N. Jacquinet-Husson et al., J. Quant. Spectrosc. Radiat. Transfer, 112, 2395, 2011.

[5] R. A. Toth, Applied Optics 1993, 32, 7326.

[6] V. Werwein, J. Brunzendorf, A. Rausch, A. Serdyukov, O. Werhahn, V. Ebert, 23rd International Conference on High Resolution Molecular Spectroscopy, 25.-30.08.2013, Budapest.

We report improved N_2O-self-broadening coefficients for the rotational levels of $J = 1$ up to $J = 40$ of the $2\,\nu_3$-band. A thorough investigation of the uncertainty budget is still in progress, the results will be presented at the conference. A preliminary estimation yielded relative uncertainties better than 1.5 % for the confidence level of $k = 1$.

These measurements were realized in the framework of the EUMETRISPEC[7] project, a joint effort of the PTB and other national metrology institutes to establish a European spectroscopy infrastructure enabling measurements of spectral line parameters traceable to the SI units.

---

[7] www.eumetriscpec.org

PII-13. Self- and Air-Broadened Line Shape Parameters of $^{12}CH_4$: 4500-4620 cm^{-1}

V. Malathy Devi,[a] **D. Chris Benner,**[a] **K. Sung,**[b] **L. R. Brown,**[b]
T. J. Crawford,[b] **M. A. H. Smith,**[c] **A. W. Mantz,**[d] **A. Predoi-Cross**[e]

[a] *Dept. of Physics, The College of William and Mary, Williamsburg, VA 23187*

[b] *Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109*

[c] *Science Directorate, NASA Langley Research Center, Hampton, VA 23681*

[d] *Dept. of Physics, Astronomy and Geophysics, Connecticut College, New London, CT 06320*

[e] *Dept. of Physics and Astronomy, University of Lethbridge, Lethbridge, AB, Canada T1K 3M4*

Accurate knowledge of spectral line shape parameters is important for infrared transmission and radiance calculations in the terrestrial atmosphere. We report the self- and air-broadened Lorentz widths, shifts and line mixing coefficients along with their temperature dependencies for methane absorption lines in the 2.2 μm spectral region. For this, we obtained a series of high-resolution, high S/N spectra of 99.99% ^{12}C-enriched samples of pure methane and its dilute mixtures in dry air at cold temperatures down to 150 K using the Bruker IFS 125HR Fourier transform spectrometer at JPL. The coolable absorption cell had an optical path of 20.38 cm and was specially built to reside inside the sample compartment of the Bruker FTS[1]. The 13 spectra used in the analysis consisted of seven pure $^{12}CH_4$ spectra at pressures from 4.5 to 169 Torr and six air-broadened spectra with total sample pressures of 113-300 Torr and methane volume mixing ratios between 4 and 9.7%. These 13 spectra were fit simultaneously using the multispectrum least-squares fitting technique[2]. The results will be compared to existing values reported in the literature.[3]

---

[1] K. Sung, A. W. Mantz, L. R. Brown, *et al.*, *J. Mol. Spectrosc.* **162** (2010) 124-134.

[2] D. C. Benner, C. P. Rinsland, V. Malathy Devi, M. A. H. Smith and D. Atkins, *JQSRT* **53** (1995) 705-721.

[3] Research described in this paper was performed at Connecticut College, the College of William and Mary, NASA Langley Research Center and the Jet Propulsion Laboratory, California Institute of Technology, under contracts and cooperative agreements with the National Aeronautics and Space Administration.

PII-14. Measured and Theoretical Self- and N_2-Broadened Line Parameters in the ν_6 Band of CH_3D

V. Malathy Devi,[a] D. Chris Benner,[a] Keeyoon Sung,[b]
Adriana Predoi-Cross,[c] Mary Ann H. Smith,[d] Arlan W. Mantz,[e]
Tatyana Sinyakova,[f] Jeanna Buldyreva[f]

[a]*Department of Physics, College of William and Mary, Williamsburg, VA, USA*

[b]*Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, USA*

[c] *Department of Physics and Astronomy, University of Lethbridge, Lethbridge, AB, Canada*

[d] *Science Directorate, NASA Langley Research Center, Hampton, VA, USA*

[e]*Department of Physics, Connecticut College, New London, CT, USA*

[f]*Institute UTINAM, University of Franche-Comte, Besancon, France*

Monodeuterated methane (CH_3D) is a constituent trace species in several planetary atmospheres, and its spectrum is often used in determinations of atmospheric H/D ratios. Methane plays an important role in terrestrial atmospheric chemistry. It is the most abundant hydrocarbon in our atmosphere and as an IR active gas makes an important contribution to the enhanced greenhouse effect. Methane is increasing in the Earth's atmosphere at a rate of about 1% per year. The current knowledge of its sources and sinks are not sufficient to isolate the cause of the observed changes in the mixing ratio and global distribution. As a result, the infrared spectrum of methane and its isotopomers is continually being investigated in order to obtain improved spectroscopic line parameters needed to interpret remote sensing observations. Remote sensing instruments require laboratory data sets based on measurements of very high accuracy.

The primary objective of this study is to enhance our spectroscopic knowledge of monodeuterated methane in the ν_6 band located at 6.8 microns. We present measurement results for self- and N_2-broadened line parameters from room temperature down to about 80 K. A total of 23 high-resolution, high S/N spectra recorded with two Fourier transform spectrometers: a) the McMath-Pierce FTS located on Kitt Peak and b) a Bruker IFS-125HR FTS at the Jet Propulsion Laboratory (JPL)[1] were fit simultaneously in a multispectrum approach.[2] The set included both pure CH_3D and dilute mixtures of CH_3D in research grade nitrogen. The variations in the measured

---

[1] K. Sung et al., *J. Mol. Spec.* **262** 122-134 (2010).

[2] D. Chris Benner et al., *JQSRT* **53** 705-721 (1995).

line parameters with the symmetry species, the rotational quantum numbers and with temperature are reported and discussed in comparison with earlier measurements.

For the case of nitrogen-broadening, we also provide semi-classical calculations based on a rigorous treatment of the active molecule as a symmetric top, a model intermolecular potential comprising both short- and long-range interactions, and exact classical trajectories. These calculations are done for various temperatures and for wide ranges of rotational quantum numbers. The role of the various high-order multipoles in the line-broadening at low, middle and high values of the rotational quantum number J is investigated. Main features of the K-dependences are also analyzed. These theoretical values are included in the general comparison of our new experimental and already available in the literature results.[3]

---

[3] Research described in this work was performed at the College of William and Mary, Jet Propulsion Laboratory, California Institute of Technology, Connecticut College and NASA Langley Research Center under contracts and cooperative agreements with the National Aeronautics and Space Administration. A. Predoi-Cross was funded by NSERC, Canada.

PII-15. Recent Line-Shape and Doppler Thermometry Studies Involving Transitions in the $\nu_1 + \nu_3$ Band of Acetylene

Robab Hashemi, Hoimonti Rozario, Chad Povey, Jolene Garber, Mark Derksen, Adriana Predoi-Cross

Department of Physics and Astronomy, University of Lethbridge, Lethbridge, AB, Canada

The line positions for transitions in the $\nu_1 + \nu_3$ band are often used as a frequency standard by the telecom industry and also needed for planetary atmospheric studies. Four relevant studies have been recently carried out in our group and will be discussed briefly below. (1) N_2-broadened line widths and N_2-pressure induced line shifts have been measured for transitions in the $\nu_1 + \nu_3$ band of acetylene at seven temperatures in the range 213333K to obtain the temperature dependences of broadening and shift coefficients. The Voigt and hard-collision line profile models were used to retrieve the line parameters. This study has been published in Molecular Physics, 110 Issue 21/22 (2012) 2645-2663. (2) Six nitrogen perturbed transitions of acetylene within the $\nu_1 + \nu_3$ absorption band have been recorded using a 3-channel diode laser spectrometer. We have examined C_2H_2 spectra using a hard collision (Rautian) profile over a range of five temperatures (213 K-333 K). From these fits we have obtained the N_2-broadening and narrowing coefficients of C_2H_2 and examined their temperature dependence. The experimentally measured narrowing coefficients have been used to estimate the nitrogen diffusion coefficients. The broadening coefficients and corresponding temperature dependence exponents have also been compared to that of calculations completed using a classical impact approach on an ab initio potential energy surface. We have observed a good agreement between our theoretical and experimental results. This study was published in Canadian Journal of Physics 91(11) 896-905 (2013). (3) An extension of the previous study was to analyze the room temperature for the same six transitions using the Voigt, Rautian, Galatry, RautianGalatry and Correlated Rautian profiles. For the entire pressure range, we have tested the applicability of these line-shape models. Except for Voigt profile, Dicke narrowing effect has been considered in all mentioned line-shape models. The experimental results for the narrowing parameters have been compared with calculated values based on the theory of diffusion. This study is in press in press in the Journal of Quantitative Spectroscopy and Radiative Transfer. (4) In this paper we present accurate measurements of the fundamental Boltzmann constant based on a line-shape analysis of acetylene spectra in the $\nu_1 + \nu_3$ band recorded using a tunable diode laser. Experimental spectra recorded at low pressures have been analyzed using both the Voigt model and the Speed Dependent Voigt model that takes into account the molecular speed dependence effects. These line-shape models reproduces the experimental data with high accuracy and allow us to determine precise line-shape parameters for the transitions used, the Doppler-width and then determined the Boltzmann constant, k_B. This study has been submitted for publication in the Journal of Chemical Physics. [1]

---

[1] Research described in this work was funded by NSERC, Canada.

PII-16. Spectral line shapes of P-branch transitions of oxygen B-band

Szymon Wójtewicz, Agata Cygan, Piotr Masłowski, Jolanta Domysławska, Piotr Wcisło, Mikołaj Zaborowski, Daniel Lisak, Ryszard S. Trawiński, and Roman Ciuryło

Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University, Grudziadzka 5, 87-100 Torun, Poland

The precise line-shape measurements of self- and foreign-broadened P-branch transitions of the oxygen B band near 689 nm are presented. Data were obtained using the Pound–Drever–Hall-locked frequency-stabilized cavity ring-down spectrometer assisted by the optical frequency comb.[1,2] This technique enables us to achieve high spectral resolution (about 1 MHz) and high signal-to-noise ratio spectra (above 10000:1) of weak transitions.[3,4] It is showed that the inclusion of the line-narrowing effects (Dicke narrowing or the speed dependence of collisional broadening) is necessary to properly model measured line shapes. The multispectrum fitting technique is used to minimize correlation between line-shape parameters. Relations between the line narrowing obtained from different line-shape models in the low pressure limit (below 5 kPa) were verified experimentally. Line positions with uncertainties of about 170 kHz, intensities and the collisional broadening coefficients with uncertainties of about 0.5% are reported and compared to data available in the literature.[5]

The research is part of the program of the National Laboratory FAMO in Toruń, Poland, and is supported by the Polish National Science Centre Projects no. DEC-2011/01/B/ST2/00491 and UMO-2012/05/N/ST2/02717. The research is also supported by the Foundation for Polish Science TEAM and HOMING PLUS Projects co-financed by the EU European Regional Development Fund. A. Cygan is partially supported by the Foundation for Polish Science START Project.

---

[1] J. Domysławska, S. Wójtewicz, A. Cygan, K. Bielska, D. Lisak, P. Masłowski, R. S. Trawiński, and R. Ciuryło, J. Chem. Phys. **139**, 194312 (2013).

[2] A. Cygan, S. Wójtewicz, J. Domysławska, P. Masłowski, K. Bielska, M. Piwiński, K. Stec, R. S. Trawiński, F. Ozimek, C. Radzewicz, H. Abe, T. Ido, J. T. Hodges, D. Lisak, and R. Ciuryło, Eur. Phys. J.-Spec. Top. **222**, 2119 (2013).

[3] D. A. Long, A. Cygan, R. D. van Zee, M. Okumura, C. E. Miller, D. Lisak, and J. T. Hodges, J. Chem. Phys. **536**, 1 (2012).

[4] A. Cygan, D. Lisak, S. Wójtewicz, J. Domysławska, J. T. Hodges, R. S. Trawiński, and R. Ciuryło, Phys. Rev. A **85**, 022508 (2012).

[5] S. Wójtewicz, A. Cygan, P. Masłowski, J. Domysławska, D. Lisak, R. S. Trawiński, and R. Ciuryło, J. Quant. Spectrosc. Radiat. Transfer **144**, 36 (2014).

PII-17. H_2-, $He-$ and CO_2-**line broadening coefficients and pressure shifts for the HITRAN database**

Jonas Wilzewski,[a,b] **Iouli E. Gordon,**[b] **Laurence S. Rothman**[b]

[a] *Physics Department, Technische Universität Dresden, Germany*

[b] *Atomic and Molecular Physics, Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, USA*

To increase the potential of the HITRAN database in astronomy, experimental and theoretical line broadening coefficients and line shifts of molecules of planetary interest broadened by H_2, He, and CO_2 have been assembled from available peer-reviewed sources. Since H_2 and He are major constituents in the atmospheres of gas giants, and CO_2 predominates in atmospheres of some rocky planets with volcanic activity, these spectroscopic data are important for studying planetary atmospheres. The collected data were used to create semi-empirical models for complete data sets from the microwave to the UV part of the spectrum of the studied molecules. The presented work will help identify the need for further investigations of broadening and shifting of spectral lines.

PII-18. Terahertz Spectrum of the SO Radical

M.-A. Martin-Drumel,[a] **A. Cuisset**,[a] **S. Eliet**,[a] **G. Mouret**,[a] **F. Hindle**[a], **J. Cernicharo**[b]

[a] *Laboratoire de Physico-Chimie de l'Atmosphère, EA 4493, Université du Littoral Côte d'Opale, 59140 Dunkerque, France*

[b] *Dept. Astrophys., Lab. Mol. Astrophys., Ctr. Astrobiol. CSIC INTA, E-28850 Madrid, Spain*

The THz absorption spectrum (up to 2.5 THz) of sulfur monoxide has been investigated using cw-THz photomixing. SO radical was produced in a radiofrequency discharge of flowing air in a cell containing pure sulfur. Together with the strong absorption signal of the main isotopologue, transitions of ^{34}SO (^{34}S: 4.21 %) and ^{33}SO (^{33}S: 0.75 %) were observed in natural abundance. The newly observed transitions constitute an extension of the observed rotational quantum numbers of the molecule towards higher N values, allowing an improvement of the molecular parameters for the three species. An isotopically invariant fit have been performed based on all available pure rotation and ro-vibration transitions of SO isotopologues.

SESSION V: Astronomy and Astrophysics

V-1. Combining Theory and Experiment to Compute Highly Accurate Line Lists for Stable Molecules

Timothy J. Lee,[a] **Xinchuan Huang,**[a] **David W. Schwenke**[b]

[a] *Space Science and Astrobiology Division, NASA Ames Research Center* [b] *NAS Facility, NASA Ames Research Center*

Theoretical chemists have been computing vibrational and rovibrational spectra of small molecules for more than 40 years, but over the last decade the interest in this application has grown significantly. The increased interest in computing accurate rotational and rovibrational spectra for small molecules could not come at a better time, as NASA and ESA have acquired a mountain of high-resolution spectra from the Herschel mission, and soon will from the SOFIA and JWST missions. In addition, the ground-based telescope, ALMA, has begun to acquire high-resolution spectra in the same time frame. Hence the need for highly-accurate line lists for many small molecules, including their minor isotopologues, will only continue to increase. Over the last six years, our group has published a set of limited transition energies for the NH_3 and $^{15}NH_3$ molecules, and more complete line lists for CO_2 and SO_2, and more recently we have computed line lists for the isotopologues of CO_2 and the symmetric isotopologues of SO_2. I will present the latest developments from our group on using the Best Theory + High-Resolution Experimental Data strategy to compute highly-accurate rotational and rovibrational spectra for small molecules, with emphasis on SO_2 and CO_2 and their isotopologues.

V-2. Accurate First-Principles Spectra Predictions for Planetological and Astrophysical Applications at Various T-Conditions

M. Rey[a], A. V. Nikitin,[b,c] V. Tyuterev[a]

[a] *Groupe de Spectrométrie Moléculaire et Atmosphérique, UMR CNRS 7331, BP 1039, F-51687, Reims Cedex 2, France*

[b] *Laboratory of Theoretical Spectroscopy, Institute of Atmospheric Optics, SB RAS, 634055 TOMSK, Russia*

[c] *Tomsk State University, 36 Lenin Avenue, 634050 Tomsk, Russia*

Knowledge of near infrared intensities of rovibrational transitions of polyatomic molecules is essential for the modeling of various planetary atmospheres, brown dwarfs and for other astrophysical applications [1,2,3]. For example, to analyze exoplanets, atmospheric models have been developed, thus making the need to provide accurate spectroscopic data. Consequently, the spectral characterization of such planetary objects relies on the necessity of having adequate and reliable molecular data in extreme conditions (temperature, optical path length, pressure). On the other hand, in the modeling of astrophysical opacities, millions of lines are generally involved and the line-by-line extraction is clearly not feasible in laboratory measurements. It is thus suggested that this large amount of data could be interpreted only by reliable theoretical predictions. There exists essentially two theoretical approaches for the computation and prediction of spectra. The first one is based on empirically-fitted effective spectroscopic models. Another way for computing energies, line positions and intensities is based on global variational calculations using *ab initio* surfaces. They do not yet reach the spectroscopic accuracy *stricto sensu* but implicitly account for all intramolecular interactions including resonance couplings in a wide spectral range.

The final aim of this work is to provide reliable predictions which could be quantitatively accurate with respect to the precision of available observations and as complete as possible. All this thus requires extensive first-principles quantum mechanical calculations essentially based on three necessary ingredients which are (*i*) accurate intramolecular potential energy surface and dipole moment surface components well-defined in a large range of vibrational displacements and (*ii*) efficient computational methods combined with suitable choices of coordinates to account for molecular symmetry properties and to achieve a good numerical convergence. Because high-resolution *ab initio* spectra predictions for systems with N>4 atoms is a very challenging task, the

---

[1] Tinetti, G., Vidal Madjar, A., Liang, D., Beaulieu, J.-P., et al., Nature, 448, 169 (2007)

[2] Swain, M. S. Vasisht, G., Tinetti, G., et al., ApJ, 690, L114 (2009)

[3] Tinetti, G., Encrenaz, T., Coustenis, A. Astron Astrophys Rev, 21, 63 (2013)

major issue is to minimize the cost of computations and the loss of accuracy during calculations. To this end, a truncation-reduction technique for the Hamiltonian operator as well as an extraction-compression procedure for the basis set functions will be introduced and discussed in detail.

We will give a review on the recent progress in computational methods as well as on existing experimental and theoretical databases [4,5,6,7,8,9]. This presentation will be focused on highly symmetric molecules such as methane and phosphine, with the corresponding applications at low-T in relation with Titan's atmosphere and at high-T with the production of theoretical line lists for astrophysical opacity calculations[10]. The study of isotopic H→D and ^{12}C→^{13}C substitutions will be also addressed and carried out by means of symmetry and coordinate transformations[11]. Finally we hope this work will help refining studies of currently available analyses which are not yet finalized. The modeling of non-LTE emissions accounting for contribution of many fundamental and hot bands could also be possible.

Support from PNP (French CNRS national planetology program) is acknowledged.

---

[4] Rothman, L. S., Gordon, I. E., Babikov, Y. et al., J. Quant. Spectrosc. Radiat. Transfer, 130, 4 (2013)

[5] Hargreaves, R. J., Beale, C. A., Michaux, L., Irfan, M. and Bernath, P. F., ApJ, 774 (2013)

[6] Huang, X., Schwenke, D. W. and Lee, T. J., J. Chem. Phys., 134, 044320 (2011)

[7] Tennyson, J. and Yurchenko, S. N., Mon. Not. R. Astron. Soc., 425, 21 (2012)

[8] Warmbier, R., Scheider, R., Sharma, A. R., et al., A&A, 495, 665 (2009)

[9] Thiévin, J., Georges, R., Carles, S., et al., J. Quant. Spectrosc. Radiat. Transfer, 109, 2027 (2008)

[10] Rey, M, Nikitin, A. N; and Tyuterev, V. ApJ, In press

[11] Rey, M, Nikitin, A. N; and Tyuterev, V., Submitted

V-3. Spectroscopy for Cool Astronomical Objects

P. F. Bernath,[a] **J. S. A. Brooke**,[b] **R. S. Ram**,[b] **C. Sneden**[c]

[a]*Department of Chemistry & Biochemistry, Old Dominion University, Norfolk, VA, USA*

[b]*Department of Chemistry, University of York, York, United Kingdom*

[c]*Department of Astronomy, The University of Texas at Austin, Austin, Texas, USA*

For cool stellar and substellar objects including brown dwarfs and exoplanets, atomic lines weaken and detailed elemental and isotopic abundances are often derived from molecular absorption features. We have embarked on a project to provide molecular line lists based on combining experimental observations for line positions and ab initio calculations for line strengths. So far we have results for MgH (A-X and B-X transitions)[1,2], C_2 (Swan system)[3,4], CN (red and violet systems)[5], CP (A-X transition)[6], NH (vibration-rotation bands) and OH (Meinel system). This talk will briefly describe the new line lists. Applications to the spectra of carbon-enhanced metal-poor stars, the K giant Arcturus, the metal-rich open cluster NGC 6791, the Sun and comets will be presented.

---

[1] E. GharibNezhad, A. Shayesteh and P.F. Bernath, Mon. Notices R. Astro. Soc. 432, 2043(2013)

[2] K.H. Hinkle, L. Wallace, R.S. Ram, P.F. Bernath, C. Sneden and S. Lucatello, Astrophys. J. Suppl. 207, 26 (2013)

[3] J.S.A. Brooke, P.F. Bernath, T.W. Schmidt and G.B. Bacskay, J. Quant. Spectrosc. Rad. Trans. 124, 11 (2013)

[4] R.S. Ram, J.S.A. Brooke, P.F. Bernath, C. Sneden and S. Lucatello, Astrophys. J. Suppl. 211, 5 (2014)

[5] J.S.A. Brooke, R.S. Ram, C.M. Western, G. Li, D.W. Schwenke and P.F. Bernath, Astrophys. J. Suppl. 210, 23 (2014)

[6] R.S. Ram, J.S.A. Brooke, C.M. Western and P.F. Bernath, J. Quant. Spectrosc. Rad. Transfer 138, 107 (2014)

V-4. No Photon Left Behind: How Billions of Spectral Lines are Transforming Planetary Sciences

Geronimo L. Villanueva

Solar System Exploration Division, NASA Goddard Space Flight Center / CUA,
Greenbelt, MD 20771.

With the advent of realistic potential energy surface (PES) and dipole moment surface (DMS) descriptions, theoretically computed linelists can now synthesize accurate spectral parameters for billions of spectral lines sampling the untamed high-energy molecular domain. Being the initial driver for these databases the characterization of stellar spectra, these theoretical databases, in combination with decades of precise experimental studies (nicely compiled in community databases such as HITRAN and GEISA), are leading to unprecedented precisions in the characterization of planetary atmospheres.

Cometary sciences are among the most affected by this spectroscopic revolution. Even though comets are relatively cold bodies (T∼100 K), their infrared molecular emission is mainly defined by non-LTE solar fluorescence induced by a high-energy source (Sun, T∼5600 K). In order to interpret high-resolution spectra of comets acquired with extremely powerful telescopes (e.g., Keck, VLT, NASA-IRTF), we have developed advanced non-LTE fluorescence models that integrate the high-energy dynamic range of ab-initio databases (e.g., BT2, VTT, HPT2, BYTe, TROVE) and the precision of laboratory and semi-empirical compilations (e.g., HITRAN, GEISA, CDMS, WKMC, SELP, IUPAC). These new models allow us to calculate realistic non-LTE pumps, cascades, branching-ratios, and emission rates for a broad range of excitation regimes for H_2O, HDO, HCN, HNC and NH_3 (see Figure 1). We have implemented elements of these compilations to the study of Mars spectra, and we are now exploring its application to modeling non-LTE emission in exoplanets.

In this presentation, we present application of these advanced models to interpret high-resolution spectra of comets, Mars and exoplanets.

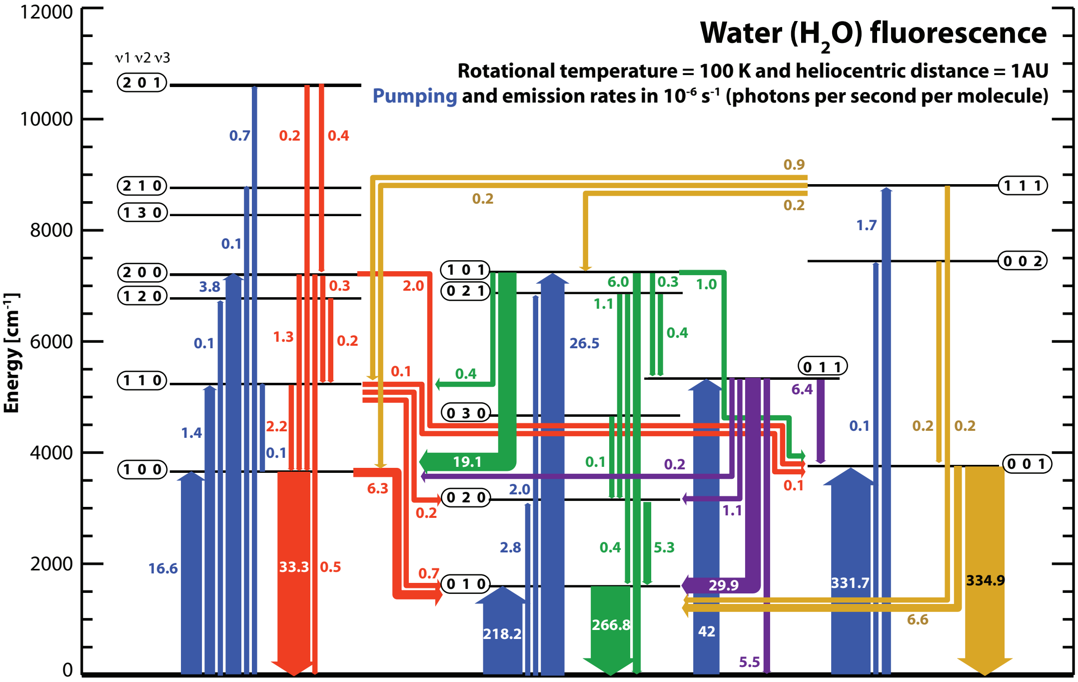


Figure 1. Diagram showing full non resonance fluorescence for H_2O in a comet at 1 Astronomical Unit (AU) and with a rotational temperature of 100 K. The pumping rates (shown in blue) were calculated considering a realistic Solar model, and the emission rates (shown in red/green/purple/yellow colors) were calculated by subsequent cascade down to the ground vibrational level and considering line by line and level by level branching ratios which take into account all 500 million transitions.

V-5. SOIR and NOMAD: Characterization of Planetary Atmospheres

S. Robert, S. Chamberlain, A. Mahieux, I. Thomas, V. Wilquet, A. C. Vandaele

Belgian Institute for Space Aeronomy, Brussels, Belgium

The Belgian Institute for Space Aeronomy is involved in the Venus Express mission (VeX), launched in 2006 and in the ExoMars Trace Gas Orbiter mission (TGO), due for launch in 2016. BISA is responsible for one instrument in each mission, SOIR onboard VeX and NOMAD onboard TGO respectively.

The SOIR instrument onboard Venus Express allows observations of trace gases in the Venus atmosphere, at the terminator for both the morning and evening sides of the planet and for almost all latitudes. It has been designed to measure spectra in the IR region (2.2 – 4.3 μm) of the Venus atmosphere using the solar occultation technique[1]. This method derives unique information on the vertical composition and structure of the mesosphere and lower thermosphere[2][3][4][5]. It is unique in terms of spectral coverage and spectral resolution (0.15 cm^{-1}), and is ideally designed to probe the Venus atmosphere for CO_2 as well as trace gases, such as H_2O, CO, HCl and HF.

SOIR is capable of (1) providing vertical information on a broad series of species, such as CO_2, CO, H_2O, HCl, HF, SO_2[6] and aerosols[7], covering the so far sparsely-known region located above the clouds, (2) contributing to a better understanding of the dynamics and stability of the atmosphere by delivering total density and kinetic temperature profiles at the terminator, an up-to-now still unchartered region, and (3) detecting weak absorption bands of rare CO_2 isotopologues[8], due to the sensitivity of SOIR, the high concentration of CO_2 on Venus and the long absorption paths sounded during solar occultations.

The NOMAD instrument consists of three spectrometers for measuring the atmosphere of Mars in the infrared, visible and ultraviolet. Through observations in solar occultation, limb and nadir modes, it will be able to detect a wide range of

---

[1] Nevejans, D. et al., Applied Optics 45 (2006) 5191-5206

[2] Fedorova, A. et al., J.Geophys.Res. 113 (2008) E00B22

[3] Vandaele, A.C., et al., J.Geophys.Res. 113 (2008) E00B23

[4] Mahieux, A. et al., J.Geophys.Res. 115 (2010) E12014

[5] Mahieux A. et al., J.Geophys.Res. 117 (2012) E07001

[6] Belyaev, D., et al., Icarus 217(2) (2012) 740-751

[7] Wilquet, V., et al., Icarus 217(2) (2012) 875-881

[8] Robert, S., et al., J. Quant. Spectrosc. Radiat. Transfer 114 (2013) 29-41

atmospheric trace gases, many of which are important markers of geophysical and/or biogenic activity[9].
During the two-year mission, NOMAD will investigate the sources and sinks of trace gas species to determine the nature of the processes involved, by mapping trace gases involved in the water, carbon and other atmospheric cycles occurring in the atmosphere of Mars. NOMAD has an order-of-magnitude increase in spectral resolution over previous instruments orbiting Mars: this will allow measurement of isotopic ratios of the major constituents of the atmosphere, in addition to optical properties and particle size distributions of dust and ice aerosols.

One channel of NOMAD is SOIR-like and we will benefit from our experience with SOIR to study the Martian atmosphere. Potential improvements in existing retrieval techniques are under investigation in preparation for this new mission. These include, for example: improvements in spectroscopy, or the use of synergies, where measurements from multiple spectral regions and/or instruments are combined. Most of the new techniques were applied to the detection of CO (for which vertical information is the next scientific objective) and CH_4 (to increase the probability of detection if present), but could be expanded to other atmospheric constituents, such as water (vertical information) or isotopologues (increase detection ability) in the future.

Both instruments' capabilities will be discussed, as the latest results obtained with SOIR and in the frame of the scientific preparation of NOMAD.

---

[9] Daerden, F. (2011) EPSC-DPS Joint Meeting 2011, 6, 1300-1

V-6. Ubiquitous Argonium, ArH^+, in the Diffuse Interstellar Medium

P. Schilke,[a] **H. S. P. Müller,**[a] **C. Comito,**[a] **A. Sanchez-Monge,**[a]
D. A. Neufeld,[b] **N. Indriolo,**[b] **E. Bergin,**[c] **D. C. Lis,**[d] **M. Gerin,**[e]
J. H. Black,[f] **M. G. Wolfire,**[g] **J. Pearson,**[h] **K. Menten,**[i] **B. Winkel**[i]

[a]*I. Phys. Institut, Universität zu Köln, Germany*

[b]*Johns Hopkins University, Baltimore, MD, USA*

[c]*University of Michigan, Ann Arbor, MI, USA*

[d]*Caltech, Pasadena, CA, USA*

[e]*LERMA, Observatoire de Paris, France*

[f]*Chalmers University of Technology, Onsala, Sweden*

[g]*University of Maryland, College Park, MD, USA*

[h]*JPL, Pasadena, CA, USA*

[i]*MPIfR, Bonn, Germany*

ArH^+ is isoelectronic with HCl. The $J = 1 - 0$ and $2 - 1$ transitions of $^{36}ArH^+$ near 617.5 and 1234.6 GHz, respectively, have been identified very recently as emission lines in spectra obtained with *Herschel* toward the Crab Nebula supernova remnant.[1] On Earth, ^{40}Ar is by far the most abundant isotope, being almost exclusively formed by the radioactive decay of ^{40}K. However, ^{36}Ar is the dominant isotope in the Universe.

In the course of unbiased line surveys of the massive and very luminous Galactic Center star-forming regions Sagittarius B2(M) and (N) with the high-resolution instrument HIFI on board of *Herschel*, we detected the $J = 1-0$ transition of $^{36}ArH^+$ as a moderately strong absorption line initially associated with an unidentified carrier.[2] In both cases, the absorption feature is unique in its appearance at all velocity components associated with diffuse foreground molecular clouds, together with its conspicuous absence at velocities related to the denser sources themselves. Model calculations are able to reproduce the derived ArH^+ column densities and suggest that argonium resides in the largely atomic, diffuse interstellar medium with a molecular fraction of no more than $\sim 10^{-3}$. The $^{38}ArH^+$ isotopologue was also detected.

Subsequent observations toward the continuum sources W51, W49, W31C, and G34.3+0.1 resulted in unequivocal detections of $^{36}ArH^+$ absorption. Hence, argonium is a good probe of the transition zone between atomic and molecular gas, in particular

---

[1] M. J. Barlow et al., *Science* **342** (2013) 1343.

[2] H. S. P. Müller et al., Proceedings of the IAU Symposium 297, 2013, "The Diffuse Interstellar Bands", Eds. J. Cami & N. Cox.

in combination with OH^+ and H_2O^+, whose abundances peak at a molecular fraction of $\sim$0.1. Moreover, argonium is a good indicator of an enhanced cosmic ray ionization rate. Therefore, it may be prominent toward, e.g., active galactic nuclei (AGNs) in addition to supernova remnants.

V-7. HITRAN and HITEMP Modeling of the Infrared Spectra of Circumstellar Gas around Young and Evolved Stars

B. Sargent,[a] W. Forrest,[b] Dan M. Watson[b],N. Calvet,[c] E. Furlan,[d],
K.-H. Kim,[e] J. Green,[f] K. Pontoppidan,[g] I. Richter,[h] C. Tayrien,[i]
J. Kastner,[j] X. Yu,[j] G. C. Sloan[k]

[a] *Center for Imaging Science and Laboratory for Multiwavelength Astrophysics, Rochester Institute of Technology, 54 Lomb Memorial Drive, Rochester, NY 14623, USA; Space Telescope Science Institute, 3700 San Martin Drive, Baltimore, MD 21218, USA*

[b] *Department of Physics and Astronomy, University of Rochester, Rochester, NY 14627*

[c] *Department of Astronomy, The University of Michigan, 500 Church Street, 830 Dennison Building, Ann Arbor, MI 48109, USA*

[d] *National Optical Astronomy Observatory, 950 North Cherry Avenue, Tucson, AZ 85719, USA; Visitor at the Infrared Processing and Analysis Center, Caltech, 770 South Wilson Avenue, Pasadena, CA 91125, USA*

[e] *Korea Astronomy and Space Science Institute, 776, Daedeokdae-ro, Yuseong-gu, Daejeon, 305-348, Republic of Korea*

[f] *Department of Astronomy, University of Texas, 1 University Station, Austin, TX 78712, USA*

[g] *Space Telescope Science Institute, 3700 San Martin Drive, Baltimore, MD 21218, USA*

[h] *Department of Physics and Astronomy, University of Rochester, Rochester, NY 14627*

[i] *Department of Physics and Astronomy, University of Rochester, Rochester, NY 14627; Department of Computer Science, Rochester Institute of Technology, 102 Lomb Memorial Drive, Rochester, NY 14623, USA*

[j] *Center for Imaging Science and Laboratory for Multiwavelength Astrophysics, Rochester Institute of Technology, 54 Lomb Memorial Drive, Rochester, NY 14623, USA*

[k] *Department of Astronomy, Cornell University, Ithaca, NY 14853, USA*

Using the HITEMP 2010 line list, we model *Spitzer Space Telescope* low spectral resolution (R $\sim$ 90) Infrared Spectrograph (IRS) 5–7.5 μm spectra of T Tauri stars (TTSs), young stars with planet-forming circumstellar gas and dust disks, and identify emission from water vapor (H_2O). Using the HITRAN 2008 line list for formic acid

(HCOOH) and the HITRAN 2012 line list for formaldehyde (H_2CO), we generate absorption models of *Spitzer*-IRS spectra of TTSs suggesting the presence of these gases in the stars' disks. The formic acid HITRAN line list does not include the ν_1 (2.8 μm), ν_2 (3.4 μm), and ν_7 and ν_9 ($\sim$16 μm) bands that would allow independent confirmation of this molecule. *Spitzer*-IRS and *Infrared Space Observatory* (ISO) Short-Wavelength Spectrometer (SWS) low-resolution infrared spectra of evolved stars known as asymptotic giant branch (AGB) stars show absorption from circumstellar acetylene (C_2H_2). Overall, the models using the acetylene HITRAN 2012 line list match the observed 12–16 μm absorption bands in spectra of LMC carbon stars acceptably, though the region around the Q branch ($\sim$ 13.7 μm) does not match in detail. Similarly, the 7.5 μm band in these spectra is also fit acceptably overall, though there are problems matching the band's wings. Milky Way AGB star spectral models of acetylene are more difficult to evaluate, due to increased absorption from other molecules like HCN and CS at these wavelengths. We advocate for more complete HITRAN line lists for formic acid and acetylene.

V-8. Modeling Non-LTE Methane Limb Emissions of Titan's Atmosphere in the IR and Near IR Range

L. Rezac,[a] A. A. Kutepov,[b] A. Feofilov,[c] A. Nikitin,[d] M. Rey,[e] V. Tyuterev[e]

[a] *Max-Planck-Institut für Sonnensystemforschung, Göttingen, Germany*

[b] *Physics Department, The Catholic University of America, Wasington, DC, and NASA Goddrad Space Flight Center, Greenbelt, MD*

[c] *Ecole Polytechnique, Antony, France*

[d] *LTS, V. E. Zuev Institute of Atmospheric Optics, RAN, Tomsk, Russia*

[e] *GSMA, UMR CNRS 7331, Université de Reims, France*

CIRS and VIMS instruments on Cassini provided a large volume of the IR and near IR limb scans of Titan's, Saturn's and Jupiter's atmospheres which are used for retrieving pressure/temperature and trace gas destinies in these atmospheres. We applied the ALI-ARMS code[1] for modeling the non-LTE methane limb emissions of Titan's atmosphere in the altitude region of 300-800 km with accounting for contribution of many fundamental and hot bands. We compare modeled spectra for the CH_4 spectroscopic inputs extracted from HITRAN-2008, HITRAN-2012 as well as from the recent theoretical Reims-Tomsk methane database developed using accurate ab initio calculations[2]. Implications for the diagnostics of CIRS and VIMS/Cassini observations are discussed.

---

[1] A. G. Feofilov and A. A. Kutepov *Surv. Geophys.* **33**, 1231 (2012), doi:10.1007s10712-012-9204-0.

[2] M. Rey, A. Nikitin, and V. Tyuterev, *PCCP* **15**, 10049 (2013), *Astrophys. J*, in press (2014)

SESSION VI: Databases-II

VI-1. Status of the HITRAN and HITEMP databases

L. S. Rothman, **I. E. Gordon**

Harvard-Smithsonian Center for Astrophysics, Atomic and Molecular Physics Division, Cambridge MA 02138-1516, USA

HITRAN2012[1] is the current official release of the database. In HITRAN2012, the line-by-line lists for almost all of the 42 HITRAN molecules were updated with respect to the previous compilation (HITRAN2008[2]). The scope of the updates ranges from corrections to the representations of quantum assignments to complete replacements of the lists and introduction of new isotopologues. Five new molecules and their isotopologues were added to the database, namely: HC_3N, C_4H_2, H_2, CS and SO_3. Some of the most important updates, relevant to the studies of the terrestrial atmosphere such as for water vapor, CO_2, molecular oxygen, etc, will be presented in more detail. Examples of definite improvements of the quality and extent of the spectral parameters will be demonstrated with respect to applications. Some remaining problems will also be shown. In addition, new as well as improved sets of cross-section data have been added. Finally, collision-induced absorption (CIA) parameters were introduced into the database for the first time, and this initiative already has received very positive feedback from the community.

The immediate plans for updates to the existing spectral parameters will be presented. The status and future plans for the HITEMP database[3] will also be discussed. The project for adapting a relational structure of the database with a dynamic and user-friendly web interface will be described. The new structure will enable introduction of a generalized line-shape formalism and parameters as well as many other advantages.

The HITRAN database is supported by the NASA Earth Observing System (EOS) under the grant NNX11AF91G, and by the NASA Planetary Atmospheres program under grant NNX13AI59G.

---

[1] L. S. Rothman, I. E. Gordon, et al. "The HITRAN 2012 molecular spectroscopic database," JQSRT 130, 4-50 (2013).

[2] L. S. Rothman, I. E. Gordon, et al. "The HITRAN 2008 molecular spectroscopic database," JQSRT 110, 532-572 (2009).

[3] L. S. Rothman, I. E. Gordon, et al. "HITEMP, the high-temperature molecular spectroscopic database," JQSRT 111, 2139-50 (2010).

VI-2. Evaluation of HITRAN 2012 H_2O linelist

Geoffrey C. Toon

Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109

The HITRAN 2012 H_2O linelist has been evaluated in spectral regions used for ground-based remote sensing, such as the NDACC and TCCON networks. Both atmospheric and laboratory spectra have been used in the evaluation, which covers selected regions in the mid-IR and Near-IR. Results are compared with some other linelists.

VI-3. High-Accuracy CO and CO_2 Line Intensities from Ab Initio Calculations and Measurements

O. L. Polyansky, L. Lodi, J. Tennyson, N. F. Zobov, K. Bielska, J. T. Hodges

[a]*Department of Physics and Astronomy, University College London, Gower Street, London, WC1E 6BT, U.K.*

[b]*Institute of Applied Physics, Russian Academy of Sciences, Nizhny Novgorod, Russia*

[c]*National Institute of Standards and Technology, Gaithersburg, MD, USA*

[d]*Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University, Grudziadzka 5, 87-100 Torun, Poland*

CO_2 and CO are listed as molecules 2 and 5, respectively, in the HITRAN database, with the former being the most important greenhouse gas in the Earth's atmosphere and the latter being the second most common molecule in the Universe after H_2. Thus knowing the line intensities of both CO_2 and CO with low uncertainty has wide-ranging scientific importance. Until recently only the effective Hamiltonian and Dipole Moment Surfaces (DMS) were used to calculate line positions and intensities of these molecules. However, there is a theoretical line list based on variational calculations using a fitted potential energy surface (PES) and an *ab initio* DMS which has been determined recently[1] and which gives CO_2 line intensities that are accurate to within a few percent. In this work we attempt to improve and experimentally validate the accuracy of the predicted CO_2 line intensities at the sub-percent level. However, only a few lines belonging to four CO_2 bands have thus far been measured at this level of uncertainty.

We performed *ab initio* calculations of the PES and DMS of CO_2 at the all-electron MRCI level of theory using MOLPRO and an aug-cc-pcQz basis set. Values for about 2000 geometries were calculated with energies up to 20 000 cm^{-1} above the minimum. We fitted an analytical surface to these DMS points and calculated intensities using the excellent PES of Ref. 1 and our DMS using the variational triatomic nuclear motion program DVR3D[2]. We will present a comparison of our calculated line intensities with several measured lines in the four above-mentioned bands. This comparison between theory and experiments demonstrates that sub-percent relative uncertainty in the predicted intensities of CO_2 lines has been achieved. The results of similarly accurate calculations on CO will also be presented.

---

[1] X.C. Huang, R.S. Freedman, S.A. Tashkun, D.W. Schwenke and T.J. Lee, 2013, JQSRT, **130** , 134.

[2] J. Tennyson, M.A. Kostin, P. Barletta, G.J.Harris, O.L. Polyansky, J.Ramanlal, N.F. Zobov, 2004, Comput Phys Commun **163**, 85.

VI-4. New Approach for Spectroscopic Data Reduction Using Ab Initio Calculations and Experimental Lines: Application to Methane

V. Tyuterev,[a] **M. Rey,**[a] **T. Delahaye,**[a] **S. Tashkun,**[b] **A. V. Nikitin,**[b] **R. Kochanov**[b]

[a] *Groupe de Spectrométrie Moléculaire et Atmosphérique, UMR CNRS 7331, BP 1039, F-51687, Reims Cedex 2, France.*

[b] *Laboratory of Theoretical Spectroscopy, Institute of Atmospheric Optics, SB RAS, 634055 TOMSK, Russia; Tomsk State University, 36 Lenin Avenue, 634050 Tomsk, Russia.*

Our aim is to address the question: how to generate line lists for molecular spectra containing line positions determined within experimental accuracy and predicted ab initio intensities in a consistent way for atmospheric, planetological and astrophysical applications? In this work we have developed a new combined spectroscopic model[1] for methane vibrational polyads which involves all resonance terms very accurately derived from the molecular potential energy surface[2] *via* high-order contact transformation (CT) method[1]. A subsequent "fine tuning" of the diagonal parameters allows achieving experimental accuracy for about 6000 Dyad and Pentad line positions whereas all resonance coupling parameters were held fixed to *ab initio* values. For determination of dipole transition moment parameters, we have applied two complementary methods. Initial values for the effective dipole moment were first computed from *ab initio* dipole moment surface (DMS)[2], then the final parameters were fitted to selected ab initio line strengths previously computed[3] from the same DMS by variational method. The new polyad model allows generating a spectral line list for the Dyad and Pentad bands with the accuracy $\sim 10^{-3}$ cm^{-1} for line positions combined with *ab initio* predictions for line intensities. Future prospectives for an application of this approach to other molecules will be discussed.

---

[1] Vl.G. Tyuterev, S.A. Tashkun, M. Rey, R.V. Kochanov, A.V. Nikitin, T.Delahaye, J. Phys. Chem. A., 117,13770-13805 (2013)

[2] A.V. Nikitin, M. Rey, Vl.G. Tyuterev, Chem. Phys. Lett. 501, 179, (2011); 565, 5 (2013)

[3] M. Rey, A.V. Nikitin, Vl.G. Tyuterev, Phys. Chem. Chem. Phys. 15, 10049-10061 (2013) ; ApJ , in press (2014)

VI-5. CH_4, C_2H_4, SF_6 and CF_4 Calculated Spectroscopic Databases for the Virtual Atomic and Molecular Data Centre

V. Boudon,[a] **Ch. Wenger,**[a] **R. Surleau,**[a] **M. Louviot,**[a] **M. Faye,**[a] **M. Rotger,**[b] **L. Daumont,**[b] **D. A. Bonhommeau,**[b] **Vl. G. Tyuterev,**[b] **Y. A. Ba,**[c] **M.-L. Dubernet**[c]

[a]*Laboratoire Interdisciplinaire Carnot de Bourgogne, UMR 6303 CNRS–Université de Bourgogne, 9 Av. A. Savary, BP 47870, F-21078 Dijon Cedex, France*

[b]*Groupe de Spectrométrie Moléculaire et Atmosphérique (GSMA), CNRS UMR7 331, Université de Reims Champagne-Ardenne,Moulin de la Housse, B.P.1039, F-51687 Reims Cedex 2, France*

[c]*LERMA2, CNRS UMR8812, Observatoire de Paris, 5 Place Janssen, 92195 Meudon, France*

Two spectroscopic relational databases, denoted MeCaSDa and ECaSDa, have been implemented for methane and ethene, and included in the VAMDC (Virtual Atomic and Molecular Data Centre, http://portal.vamdc.eu/vamdc_portal/home.seam)[1]. These databases collect calculated spectroscopic data from the accurate analyses previously performed for the electronic ground state of methane, ethene, and some of their isotopologues: $^{12}CH_4$, $^{13}CH_4$, and $^{12}C_2H_4$ [2]. Both infrared absorption and Raman scattering lines are included. 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.

Very recently, we also built on the same model two new databases, named SHeCaSDa and TFMeCaSDa for the SF_6 and CF_4 greenhouse gas molecules, respectively.

The relational schemas of these four databases are equivalent and optimized to enable the better compromise between data retrieval and compatibility with the XSAMS (XML Schema for Atoms, Molecules, and Solids) format adopted within the VAMDC European project.

---

[1] Y. A. Ba, Ch. Wenger *et al.*, *J. Quant. Spectrosc. Radiat. Transfer*, **130**, 62 (2013).

[2] M.-L. Dubernet, V. Boudon *et al.*, *J. Quant. Spectrosc. Radiat. Transfer*, **111**, 2151 (2010).

VI-6. O_2 Energy Levels, Band Constants, Potentials, Franck-Condon Factors and Linelists Involving The $X^3\Sigma_g^-$, $a^1\Delta_g$ and $b^1\Sigma_g^+$ States

Shanshan Yu,[a] Brian J. Drouin,[a] Charles E. Miller,[a] Iouli Gordon[b]

[a] *Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109-8099* [b] *Harvard-Smithsonian Center for Astrophysics, Atomic and Molecular Physics Division, Cambridge, MA 02138, USA*

The isotopically invariant Dunham fit of O_2 was updated with newly reported literature transitions to derive (1) the energy levels, band-by-band molecular constants and RKR potentials for the $X^3\Sigma_g^-$, $a^1\Delta_g$ and $b^1\Sigma_g^+$ states of the six O_2 isotopologues, $^{16}O^{16}O$, $^{16}O^{17}O$, $^{16}O^{18}O$, $^{17}O^{17}O$, $^{17}O^{18}O$ and $^{18}O^{18}O$; (2) the line positions and Franck-Condon factors for their $a^1\Delta_g - X^3\Sigma_g^-$, $b^1\Sigma_g^+ - X^3\Sigma_g^-$ and $a^1\Delta_g - b^1\Sigma_g^+$ band systems. Experimental measurements and theoretical calculations on the intensities of lines involving the $X^3\Sigma_g^-$, $a^1\Delta_g$ and $b^1\Sigma_g^+$ states were critically reviewed and a systematic intensity calculation was carried out. The newly calculated positions and intensities are combined to provide HITRAN-format linelists.

VI-7. Simple Molecules as Complex Systems

Attila G. Császár,[a] **T. Furtenbacher**,[a] **Péter Árendás**,[b] **Georg Mellau**[c]

[a] *MTA-ELTE Research Group on Complex Chemical Systems, H-1518 Budapest, P.O. Box 32, Hungary*

[b] *Department of Algebra and Number Theory, Institute of Mathematics, Eötvös Loránd University, H-1518 Budapest 112, P.O. Box 120, Hungary*

[c] *Physikalisch-Chemisches Institut, Justus-Liebig-Universität Gießen, Heinrich-Buff-Ring 58, D-35392 Gießen, Germany*

For individual molecules quantum mechanics (QM) offers a simple, natural and elegant way to build large-scale complex networks: quantized energy levels are the nodes, allowed transitions among the levels are the links, and transition intensities supply the weights. QM networks are intrinsic properties of molecules and they are characterized experimentally via spectroscopy; thus, realizations of QM networks are called spectroscopic networks (SN). As demonstrated for the rovibrational states of $H_2{}^{16}O$, the molecule governing the greenhouse effect on earth through hundreds of millions of its spectroscopic transitions (links), both the measured and first-principles computed one-photon absorption SNs containing experimentally accessible transitions appear to have heavy-tailed degree distributions. The proposed novel view of high-resolution spectroscopy and the observed degree distributions have important implications: appearance of a core of highly interconnected hubs among the nodes, a generally disassortative connection preference, considerable robustness and error tolerance, and an "ultra-small-world" property. The network-theoretical view of spectroscopy offers a data reduction facility via a minimum-weight spanning tree approach, which can assist high-resolution spectroscopists to improve the efficiency of the assignment of their measured spectra.

Author Index

CONFERENCE PROGRAM

DAY 1, Monday 23 June

7:30 Registration

8:45 WELCOME .... Laurence S. Rothman

8:55 Institutional Welcome .... Michael McCarthy

SESSION I: Remote Sensing and Radiative Transfer

Chair: P. F. Bernath

9:05 Tropospheric Emissions: Monitoring of Pollution (TEMPO) . **Kelly Chance**

9:45 Retrieving CO_2 from Orbiting Carbon Observatory-2 (OCO-2) Spectra .... **David Crisp**

10:25 Spectroscopic Issues for the Atmospheric Chemistry Experiment (ACE) .... C. Boone

10:40 *Coffee Break*

10:55 Remote Sensing of Greenhouse Gases and Their Sources and Sinks **A. Butz**

11:35 Validation of H_2O Continuum Absorption Models in the Wave Number Range 180-600 cm^{-1} with Atmospheric Emitted Spectral Radiance Measured at the Antarctica Dome-C Site .... G. Liuzzi

11:50 Determination of Near-IR Water Vapor Self Continuum from Observations .... E. Mlawer

12:05 Atmospheric Radiative Transfer Generalised for Use on Earth and Other Planets: ARTS 2.2 .... A. Perrin

12:20 TAPAS, a Web-Based Service of Atmospheric Transmission Computation for Astronomy .... J.-L. Bertaux

12:35 The Doppler Wind and Temperature Sounder .... M. McHugh

12:50 *Lunch Served*

SESSION II: Databases-I

Chair: V. Boudon

14:00 Comparison between HITRAN2012 data and a new experimental line list recently published for water vapor in the spectral region 6450 to 9400 cm^{-1} .... L. Regalia

14:15 A Comprehensive Catalogue of Absorption Cross-Sections of Halocarbons and Related Molecules .... K. Shine

14:30 New and Improved Infrared Spectroscopy of Halogen-Containing Species for ACE-FTS Retrievals .... J. J. Harrison

14:45 New Analysis of the CRDS Spectrum of the Six $^{16}O/^{18}O$ Isotopologues of Ozone up to 7920 cm^{-1} .... A. Barbe

15:00 Measurements and Modeling of $^{16}O^{12}C^{17}O$ Spectroscopic Parameters at 2 μm .... D. Jacquemart

15:15 Line Positions and Intensities of $^{13}C^{12}CH_6$ in the 12.2 μm region .... M. A. H. Smith

15:30 Are Your Spectroscopic Data Being Used? .... I. E. Gordon

16:00-18:00 **POSTER SESSION I**

DAY 2, Tuesday 24 June

SESSION III: Line Shapes

Chair: B. J. Drouin

9:00 Spectral Line Shape Model to Replace the Voigt Profile in Spectroscopic Databases .... **D. Lisak**

9:40 Line Parameter Measurements and Stringent Tests of Line Shape Models Based on Cavity-Enhanced Absorption Spectroscopy .... **J. Hodges**

10:20 Narrowing Effects in the $H_2{}^{18}O$ Near-IR Spectrum: Experimental Test of the Partially-Correlated Quadratic-Speed-Dependent Hard-Collision Profile .... M. D. De Vizia

10:35 *Coffee Break*

10:50 New Multispectrum Fitting Software Used at DLR for Analysis of Laboratory Fourier-Transform Molecular Spectra .... J. Loos

11:05 Comparisons of Measured and Requantized Classical Molecular Dynamics Calculated Line Shape of Air-Broadened Isolated Transitions of Molecular Oxygen .... J. Lamouroux

11:20 The Use of Ab Initio Wavefunctions in Line Shape Calculations for Water Vapor .... R. R. Gamache

11:35 Refinement of the Robert-Bonamy Formalism: Taking Into Account of Contributions From the Line Coupling .... Q. Ma

11:50 Collisional Line-Shape and Line-Mixing Parameters for CO_2 Absorption near 3340 cm^{-1}: measurements and modeling .... J. Buldyreva

12:05 Ab Initio Computation of Dynamical Properties: Pressure Broadening .... L. Wiesenfeld

12:20 A rapid retrieval methodology based on the spectrally integrated Voigt function for space observation spectral radiance data .... S. Abrarov

12:35 *Lunch Served + Group Photo*

SESSION IV: Laboratory and Field Measurements

Chair: M. A. H. Smith

14:00 The Near Infrared Absorption Spectrum of Water by CRDS Between 1.26-1.70 μm: Complete Empirical Line List and Continuum Absorption .... D. Mondelain

14:15 Frequency Comb Spectroscopy of CO_2, CH_4, H_2O, and Isotopes Over a 2 km Outdoor Path: Concentration Retrievals Using Different Absorption Models .... G. B. Rieker

14:30 Frequency Comb-Referenced Spectroscopy in the $\nu_1 + \nu_3$ Region of Acetylene .... S. Twagirayezu

14:45 Spectroscopy for Industrial Applications: High-Temperature Processes .... A. Fateev

15:00 New Developments for the Terahertz Spectroscopy in Lille ... L. Margulès

15:15-17:15 **POSTER SESSION II**

18:00 *Banquet at Knafel Center, Radcliffe Yard*

DAY 3, Wednesday 25 June

SESSION V: Astrophysics and Astronomy

Chair: J. Tennyson

9:00 Combining Theory and Experiment to Compute Highly Accurate Line Lists for Stable Molecules .... **T. J. Lee**

9:40 Accurate First-Principles Spectra Predictions for Planetological and Astrophysical Applications at Various T-Conditions .... **M. Rey**

10:20 Spectroscopy for Cool Astronomical Objects .... P. F. Bernath

10:35 *Coffee Break*

10:50 No Photon Left Behind: How Billions of Spectral Lines are Transforming Planetary Sciences .... **G. L. Villanueva**

11:30 SOIR and NOMAD: Characterization of Planetary Atmospheres **S. Robert**

12:10 *Lunch Served*

13:20 Ubiquitous Argonium, ArH^+, in the Diffuse Interstellar Medium .... H. S. P. Müller

13:35 HITRAN and HITEMP Modeling of the Infrared Spectra of Circumstellar Gas around Young and Evolved Stars .... B. Sargent

13:50 Modeling Non-LTE Methane Limb Emissions of Titan's Atmosphere in the IR and Near IR Range .... A. A. Kutepov

14:05 *Coffee Break*

SESSION VI: Databases-2

Chair: J. M. Flaud

14:20 Status of the HITRAN and HITEMP databases .... L. S. Rothman

14:35 Evaluation of HITRAN 2012 H_2O linelist .... G. C. Toon

14:50 High Accuracy CO and CO_2 Line Intensities from Ab Initio Calculations and Measurements .... O. L. Polyansky

15:05 New Approach for Spectroscopic Data Reduction Using Ab Initio Calculations and Experimental Lines: Application to Methane . V. Tyuterev

15:20 CH_4, C_2H_4, SF_6 and CF_4 Calculated Spectroscopic Databases for the Virtual Atomic and Molecular Data Centre .... V. Boudon

15:35 Energy Levels, Band Constants, Potentials, Franck-Condon Factors and Linelists Involving the $X^3\Sigma_g^-$, $a^1\Delta_g$ and $b^1\Sigma_g^+$ States .... B. J. Drouin

15:50 Simple Molecules as Complex Systems .... A. G. Császár