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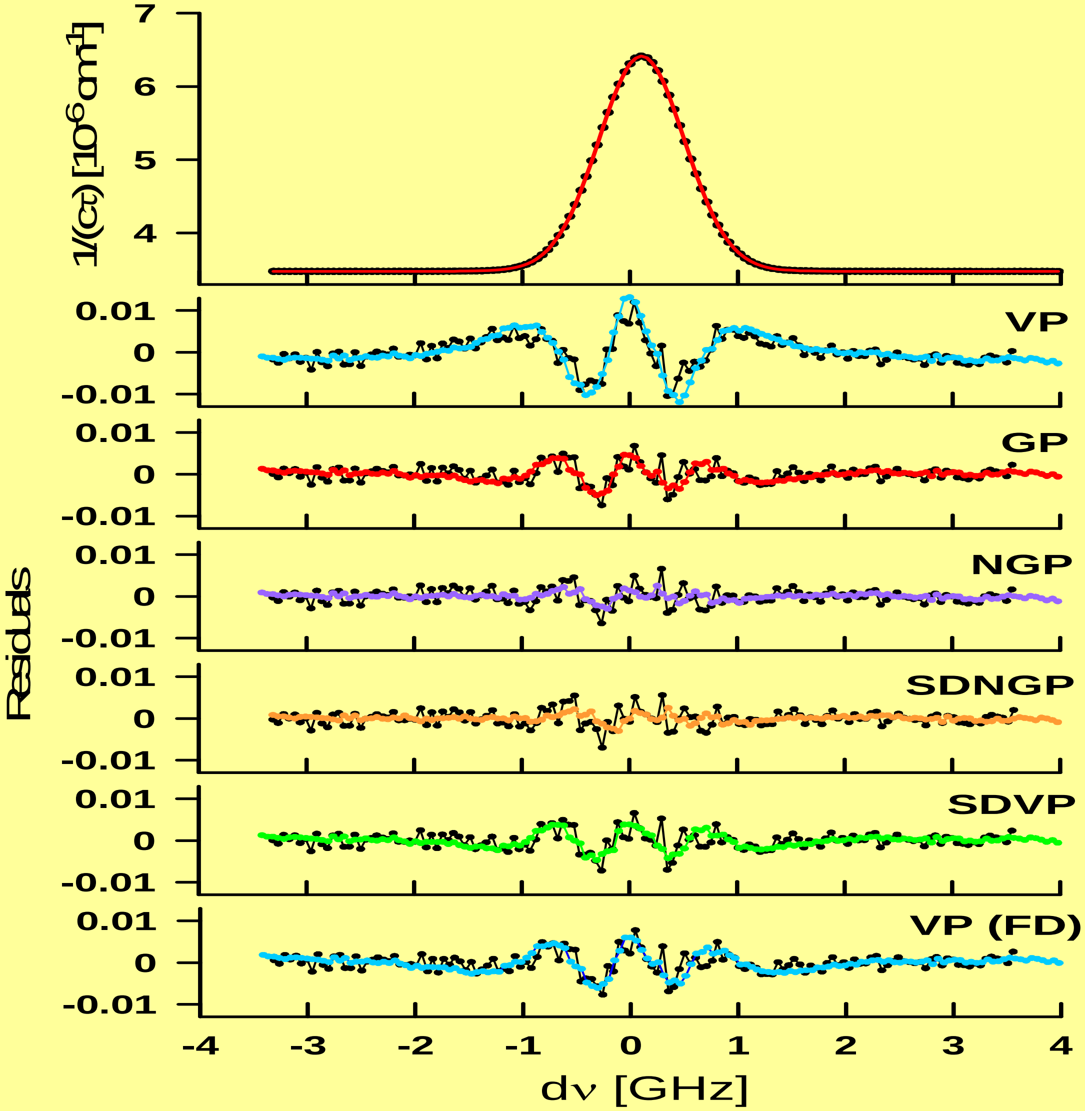

The 11th HITRAN Database Conference

June 16 – June 18, 2010

HITRAN

2010

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Front page: This image shows an example of different fits of line-shape profiles to the oxygen line at 14546.008755 cm^{-1}*, as well as implementation of advanced signal-to-noise reduction techniques. The issue of line shape is one of the salient topics at this year's HITRAN conference. The figure was taken from the poster presented at the 20th International Symposium on Spectral Lineshapes, June 6-11, 2010, Memorial University of Newfoundland by A. Cygan, et al.*

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

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SESSION I: Databases-1

I-1. Spectroscopic Molecular Databases: Evolution and Revolution

Laurence S. Rothman, **Iouli E. Gordon**

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

We first present a brief summary of the status of the current molecular spectroscopic databases, HITRAN[1] and HITEMP[2]. The means of access and the documentation are reviewed, and some successful simulation with the new editions are shown. Remarks on future developments of the content of the databases will be made. These developments naturally include new molecules, more bands, line-shape parameters, and higher accuracy. Finally, the direction for modernizing the structure of the database will be discussed.

The databases are supported by the NASA Earth Observing System (EOS) under the grant NAG5-13534 and the Planetary Atmospheres program under grant NNX10AB94G.

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[1] Rothman LS, Gordon IE, Barbe A, Benner DC, Bernath PF, Birk M, et al. The HITRAN 2008 molecular spectroscopic database. JQSRT 2009;110:533-72.

[2] Rothman LS, Gordon IE, Barber RJ, Dothe H, Gamache RR, Goldman A, Perevalov VI, Tashkun SA, and Tennyson J. HITEMP, the high-temperature molecular spectroscopic database. *JQSRT*, In Press.

I-2. The GEISA Database 2009 Edition: Update Description and Assessment of Spectroscopic Parameters Through Hyperspectral Remote Sensing Applications

N. Jacquinet, L. Crépeau, V. Capelle, N. Scott, R. Armante, A. Chédin

Laboratoire de Météorologie Dynamique, Ecole Polytechnique, 91128 Palaiseau, France,
http://ara.lmd.polytechnique.fr

The updated 2009 edition of GEISA[1] (Gestion et Etude des Informations Spectroscopiques Atmosphriques; Management and Study of Atmospheric Spectroscopic Information), a computer-accessible system comprising three independent sub-databases devoted respectively to: line transition parameters, infrared and ultraviolet/visible absorption cross-sections, microphysical and optical properties of atmospheric aerosols will be summarized. In this edition, 50 molecules are involved in the line transition parameters sub-database, including 111 isotopes, for a total of 3,807,997 entries, in the spectral range from 10^{-6} to 35,877.031 cm^{-1}.
The successful performances of the new generation of hyperspectral sounders depend ultimately on the accuracy to which the spectroscopic parameters of the optically active atmospheric gases are known, since they constitute an essential input to the forward radiative transfer models that are used to interpret their observations. Currently, GEISA is involved in activities related to the assessment of the capabilities of IASI (Infrared Atmospheric Sounding Interferometer on board the METOP European satellite http://earth-sciences.cnes.fr/IASI) through the GEISA/IASI database[2] derived from GEISA. Since the Metop (http://www.eumetsat.int) launch (October 19th 2006), GEISA/IASI is the reference spectroscopic database for the validation of the level-1 IASI data, using the 4A radiative transfer model[3] (4A/LMD http://ara.lmd.polytechnique.fr; 4A/OP co-developed by LMD and Noveltis http://www.noveltis.fr, with the support of CNES).
Also, GEISA is involved in planetary research, i.e.: modelling of Titans atmosphere, in the comparison with observations performed by Voyager, or by ground-based telescopes, and by the instruments on board the Cassini-Huygens mission.
Highlights will be given on a selection of problems that pertains to current status of the line parameters affecting IASI hyperspectral remote sensing applications. A special effort has been given in the validation of the updated parameters and the evaluation of the subsequent impact on radiative transfer simulations. Results of comparisons "calc-obs" based on IASI observations and 4AOP simulations will be presented.

---

[1] Jacquinet-Husson N., N.A. Scott, A. Chédin,L. Crépeau, R. Armante, V. Capelle, J. Orphal, A. Coustenis, C. Boonne, N. Poulet-Crovisier, et al. JQSRT, 109, 1043-1059, 2008.

[2] Jacquinet-Husson N., N.A. Scott, A. Chédin, K. Garceran, R. Armante, et al. JQSRT, 95, 429-67, 2005.

[3] Scott, N.A. and A. Chédin, 1981. J. Appl. Meteor., 20,556-564

GEISA, continuously developed and maintained at LMD (Laboratoire de Météorologie Dynamique, France) since 1976, is implemented on the CNES/CNRS (France) "Ether" Products and Services Centre WEB site (http://ether.ipsl.jussieu.fr), where all archived spectroscopic data can be handled through general and user friendly associated management software facilities. More than 350 researchers are registered for on line use of GEISA.

I-3. Blended HITRAN and other Spectra Databases for Modeling Emission-based LIDAR

Denis Plutov and **Dennis K. Killinger**

University of South Florida, Department of Physics, 4202 East Fowler Ave, PHY 114, Tampa, FL 33620

Emission based lidar is a stand-off laser remote sensing technique that uses the excitation laser to produce a spectral emission signature at a distant target that can be detected and analyzed to determine the concentration and composition of the distant target. Examples of this technique include Laser-Induced-Thermal-Emission (LITE), Laser-Induced-Breakdown Spectroscopy (LIBS), and remote Raman Lidar, all of which are being studied for the remote sensing of a wide range of target substances and chemical species. In order to study and successfully model these atmospheric remote sensing lidar techniques, we have developed a modeling approach used to predict the detected power and S/N as a function of detection range and wavelength which depends upon the use of the HITRAN database augmented by other spectral databases in order to predict the spectral transmission of the emission spectrum back toward the lidar telescope detector system.

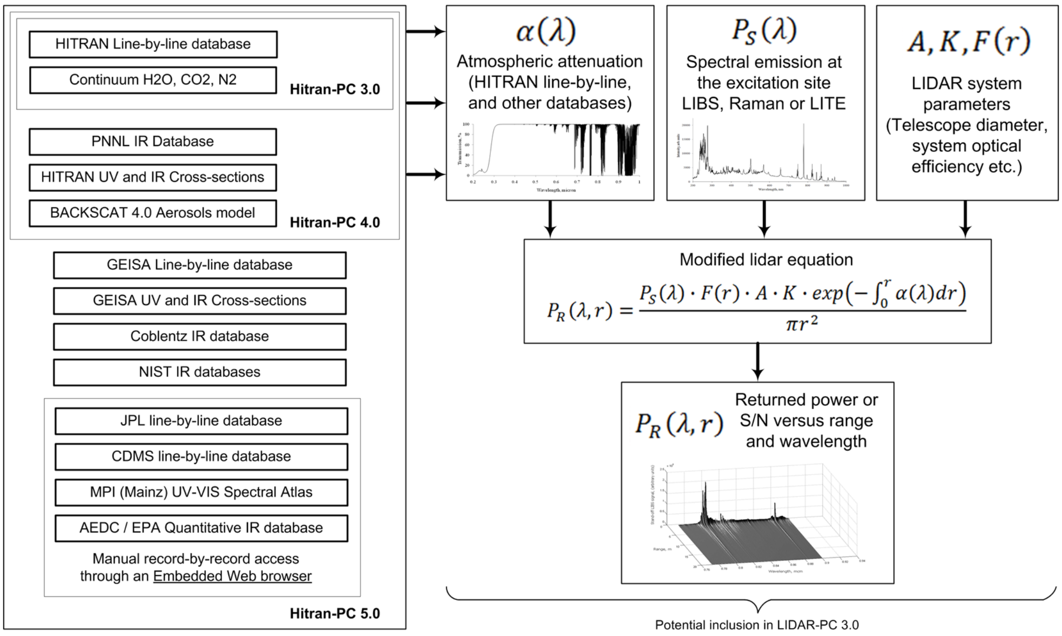

Figure 1. Plans for blending HITRAN and other spectra databases for modeling emission-based lidar.

The modeling approach is summarized in the figure above, and is based on a modified one-way lidar equation that uses the atmospheric transmission spectra obtained with our

Hitran-PC program; it is anticipated that the lidar modeling may be incorporated later into our existing LIDAR-PC (V. 2.0) program, but is as of yet not incorporated. The current HITRAN-PC program (Version 4.1) can calculate the transmission spectrum of the atmosphere using the HITRAN line-by-line and cross section database, augmented by the PNNL hydrocarbon gas database in the mid-IR to model clouds and plumes of gases. Recently, we have started to incorporate additional spectral databases to provide comparisons and extend the spectral range and molecules modeled. These include using the GEISA, Coblentz, and NIST databases. We plan to incorporate several of these augmented databases into HITRAN-PC, as shown in the figure, and hope to release Version 5.0 later this year. Our current Beta version 5.0 allows simultaneous use of a combination of line-by-line and experimental databases to obtain blended transmission spectra derived from different databases which is useful for modeling of atmospheric transmission with various contaminants present in the atmosphere. This also allows one to carry out cross comparisons of spectra derived from various sources such as the real time comparisons of simulation spectra obtained using the HITRAN and GEISA line-by-line databases.

Finally, the development of HITRAN-PC V5.0 is part of our experimental study of emission based lidar. Theoretical calculations and experimental results of LIBS and LITE measurements will be presented, and new capabilities of the Hitran-PC 5.0 program will be outlined.

I-4. Calculating the Spectroscopic Behaviour of Hot Molecules

Jonathan Tennyson

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

Spectroscopic information on hot or highly excited molecules is vital for many application both in our own atmosphere and in astrophysics. Since the number of lines required for modelling the spectrum of a small molecule such as water increases hugely as the temperature rises; it is not possible to obtain all the data necessary from directly from laboratory measurements.

My group is systematically calculating linelists of rotation-vibration transitions for hot molecules. Our BT2 linelist[1] for water forms part of the input for the 2010 edition of HITEMP[2], which also includes data on CO_2, CO, NO and OH. We have recently complete a companion linelist for hot HDO[3].

Our recent focus has been on ammonia for which room temperature[4] and hot[5] linelists have been completed. These data are being used in astrophysical applications particularly to do with extrasolar planets and brown dwarfs. Comparisons with HITRAN for ammonia suggests that the current database has significant omissions, errors and, as is well-known, many unassigned lines. We have started systematically working through these problems and have so far re-assigned some 900 transitions.

A summary of our vibration-rotation data for hot molecules can be found at exomol.com.

---

[1] R. J. Barber, J. Tennyson, G. J. Harris and R. N. Tolchenov, *Mon. Not. R. Astr. Soc.*, **368**, 1087 (2006).

[2] Rothman LS, Gordon IE, Barber RJ, Dothe H, Gamache RR, Goldman A, Perevalov VI, Tashkun SA, and Tennyson J. HITEMP, the high-temperature molecular spectroscopic database. *JQSRT*, In Press.

[3] B.A. Voronin, J. Tennyson, R.N. Tolchenov, A.A. Lugovskoy and S.N. Yurchenko, *Mon. Not. R. astr. Soc.*, **402**, 492 (2010).

[4] S.N. Yurchenko, R.J. Barber, A. Yachmenev, W. Theil, P. Jensen and J. Tennyson, *J. Phys. Chem. A*, **113**, 11845 (2009).

[5] S.N. Yurchenko, R.J. Barber and J. Tennyson, *Mon. Not. R. Astr. Soc.*, to be submitted.

I-5. High-Accuracy Ab Initio Water Line Intensities

L. Lodi

University College London, Department of Physics and Astronomy, London UK

Radiation transport in our atmosphere is dominantly determined by the behaviour of the water molecule. The way water absorbs and emits light is crucial in many other regimes and is surprisingly complex to either measure or model. More specifically, water line intensities vary by 10 orders of magnitude for atmospherically important transitions and have proved difficult to measure with complete reliability.

Rotation-vibrational spectra of molecules may be determined in a completely *ab initio* fashion from the principles of quantum mechanics. This entails solving in two steps for the motions of the electrons and then of the nuclei; for a three-atom system it is the first step that determines the overall accuracy of computed rotational-vibrational line positions and intensities.

We used UCL's supercomputer Legion[1] and the quantum-chemistry package MOLPRO[2] to perform the most extensive and accurate electronic structure calculation on water ever, producing a new, extremely accurate dipole moment surface (DMS) and a companion potential energy surface (PES).

The electronic-structure method used is IC-MRCI+Q (Internally-Contracted Multi-Reference Configuration-Interaction with Davidson correction) in an 8-electron, 10-orbital active space and the aug-cc-pCVnZ, (n=Q,5,6) basis sets. All 10 electrons were correlated. Relativistic corrections were also computed via the Pauli Hamiltonian. The value of the DMS was calculated for a large set of about 2,600 geometries as the derivative of the energy with respect to an external, very weak electric field. This procedure results in a total number of runs which is five times the number of geometries, for a total of ≈13000 runs. On a single workstation the total computation would take more than 25 years, whence the need to use parallel computers.

The purpose of these calculations is twofold. First, we wish to map the water PES all the way to break-up of the molecule. This will allow us to extend our theoretical modelling of novel experiments recently completed in Lausanne[3]. The second major objective is to use our new DMS to determine nearly all medium-to-strong water line intensities ($I \gtrapprox 10^{-24}$ cm/molecule) and about 90% of weaker lines ($10^{-28} \lessapprox I \lessapprox 10^{-24}$)

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[1] The system comprises 1280 Intel Xeon 5160 3 GHz dual-core CPUs (2560 cores total), 11 TB of RAM and 320 TB of storage space.

[2] MOLPRO, version 2009.1, a package of ab initio programs, H.-J. Werner, P. J. Knowles, R. Lindh, F. R. Manby, M. Schütz, and others, see http://www.molpro.net .

[3] M. Grechko, O. V. Boyarkin, T. R. Rizzo *et al.*, State-selective spectroscopy of water up to its first dissociation limit, J. Chem. Phys., 131, 221105 (2009)

with an error better than ±1%. Comparison with recent, ultra-high accuracy experiments[4] indicates that this ambitious objective is achievable. The intensities of some spectroscopic lines, so-called ‘resonances’, are extremely sensitive to the DMS employed and cannot be reliably calculated with the same degree of accuracy. Resonances were identified by comparing line intensities produced using different sets of nuclear-motion wave functions.

Together with experimentally-based line positions and energy levels obtained by the MARVEL strategy[5], our studies hold the promise to significantly improve standard database compilations of water transitions including HITRAN[6].

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[4] D. Lisak, D. K. Havey and J. T. Hodges, Spectroscopic line parameters of water vapor for rotation-vibration transitions near 7180 cm^{-1}, Phys. Rev. A, 79, 052507 (2009)

[5] J. Tennyson J, P. F. Bernath, L. R. Brown *et al.*, IUPAC critical evaluation of the rotational-vibrational spectra of water vapor. Part I-Energy levels and transition wavenumbers for (H2O)-O-17 and (H2O)-O-18, J. Quant. Spect. Rad. Transf., 110, 573-596 (2009)

[6] L. S. Rothman, I. E. Gordon, A. Barbe *et al.*, The HITRAN 2008 molecular spectroscopic database, J. Quant. Spect. Rad. Transf., 110, 533-572 (2009)

I-6. CDSD-4000: High-Temperature Spectroscopic CO_2 Databank

Sergey A. Tashkun and Varery I. Perevalov

Laboratory of Theoretical Spectroscopy, V.E. Zuev Institute of Atmospheric Optics, 634021, Tomsk, RUSSIA

A high-temperature version of the Carbon Dioxide Spectroscopic Databank called CDSD-4000 is presented. Reference temperature of the bank is 4000 K and an intensity cutoff is 10^{-27} cm/molecule. CDSD-4000 is an enlarged and improved version of the CDSD-1000 databank [1] and it will be included into the HITEMP database [2]. The databank is aimed at industrial and astrophysical applications. A number of comparisons of measured high-temperature spectra with those simulated using CDSD-4000 will be discussed.

This work is supported by a RFBR grant 09-05-93105. SAT acknowledges financial support from a joint RFBR (09-05-92508) and CRDF (RUG1-2954-TO-09) grant.

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[1] S. A. Tashkun, V. I. Perevalov, J. L. Teffo, A. D. Bykov and N. N. Lavrentieva *JQSRT* **82**, 165 (2003)

[2] L. S. Rothman, I. E. Gordon, R. J. Barber, H. Dothe, R. R. Gamache, A. Goldman, V. I. Perevalov, S. A. Tashkun, J. Tennyson *JQSRT*, in press (2010)

SESSION II: Remote Sensing

II-1. Line Parameters and Forward Calculation for Retrieving Carbon Dioxide and Methane from GOSAT Data

Tatsuya Yokota,[a] **Yukio Yoshida,**[a] **Isamu Morino,**[a] **Nobuhiro Kikuchi**[b]

[a] *CGER, National Institute for Environmental Studies (NIES), Tsukuba, 305-8506 Japan*

[b] *Fujitsu FIP Co. @GOSAT DHF, NIES, 305-8506 Japan*

Greenhouse gases Observing SATellite (GOSAT) was successfully launched on January 23, 2009. GOSAT Level 2 data products (versions 00.50 and 00.80) of carbon dioxide and methane have been distributed to general users since February 18, 2010. Column abundances of carbon dioxide from 1.6 micron band are retrieved by using line parameters of HITRAN 2008 database. Column abundances of methane from 1.67 micron band are retrieved by using line parameters of Lyulin et al. (2009). We are now improving the retrieval method by using GOSAT oxygen A-band spectral data as well as carbon dioxide 1.6 and 2.0 micron bands by adopting a line mixing methods developed by J.-M. Hartman's group. GOSAT data retrieval status, known issues, and improvement plan of the retrieval algorithm will be also presented.

II-2. MIPAS: New Results and Spectroscopy Issues

Johannes Orphal, Johannes Plieninger, Michael Hoepfner, Gabriele Stiller, Thomas von Clarmann, Norbert Glatthor, Udo Grabowski, Sylvia Kellmann, Michael Kiefer, and Andrea Linden

Institute for Meteorology and Climate Research (IMK), Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany

The MIPAS instrument on the European ENVISAT satellite was launched in March 2002 and has already produced over 8 years of scientific data. MIPAS is an infrared limb-emission sounder (Fourier-transform spectrometer) covering the spectral range from 4.15 to 14.6 microns with over 50000 spectral elements. The MIPAS data have been used in many scientific studies of atmospheric chemistry and dynamics. Here, we will present results obtained recently at IMK, like the first detection of bromine nitrate ($BrONO_2$) in the stratosphere in 2009, and the discovery of a “tape recorder” effect of isotopic water (HDO) in 2010. We will then discuss some issues related to the quality of spectroscopic reference data.

II-3. The Atmospheric Chemistry Experiment, ACE: Status and Spectroscopic Issues

P. F. Bernath

Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK

The Canadian ACE (Atmospheric Chemistry Experiment) mission has a high resolution (0.02 cm^{-1}) Fourier transform spectrometer (FTS) in low earth orbit. The primary ACE mission goal is the study ozone chemistry in the stratosphere although it is making a wide range of other measurements, for example, of organic molecules in the troposphere. A status report will be presented with an overview of a number of current science topics. For example, the rapid transport of pollution into the upper troposphere and lower stratosphere by the Asian monsoon [Randel et al., Science 328, 611 (2010)] will be discussed. New laboratory measurements of infrared absorption cross sections of organics as well as ACE retrievals will be covered. An ACE solar atlas in the 750–4400 cm^{-1} spectral region [Hase et al., JQSRT 111, 521 (2010), see http://www.ace.uwaterloo.ca/solaratlas.html] has been prepared and a set of 5 high signal-to-noise atmospheric atlases will be described.

II-4. Spectroscopy for the Atmospheric Chemistry Experiment (ACE)

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

[a] *Department of Chemistry, University of Waterloo, 200 University Ave West, Waterloo, Ontario, Canada, N2L 3G1*

[b] *Department of Chemistry, University of York, Heslington, York, UK, YO10 5DD*

The Atmospheric Chemistry Experiment (ACE) is a satellite mission for remote sensing of the Earth's atmosphere. The primary instrument on board is a high resolution (0.02 $\mathrm{cm^{-1}}$) Fourier transform spectrometer (FTS) operating in the infrared (750-4400 $\mathrm{cm^{-1}}$). Launched in August 2003, the mission has been in operation for more than six years. The search for weak spectral signatures in the FTS spectra (e.g., from hydrocarbons or CFCs/HCFCs/HFCs) is often hampered by deviations from the Voigt line shape for molecules such as CH_4 and H_2O. Investigations into line mixing and speed dependence in the line shapes of these molecules from the ACE FTS spectra will be described. Spectroscopic needs for the ACE mission will also be discussed.

II-5. Spectroscopic Issues in the Data Analysis of REFIR-PAD Measurements Performed During the 2009 Ground-Based Campaigns

Giovanni Bianchini, Luca Palchetti

Consiglio Nazionale delle Ricerche, Istituto di Fisica Applicata “Nello Carrara”, Via Madonna del Piano 10, 50019 Sesto Fiorentino, Italy.

The REFIR-PAD (Radiation Explorer in the Far-InfraRed - Prototype for Applications and Development) spectroradiometer is capable to perform spectrally resolved atmospheric radiance measurements in the 100-1400 cm^{-1} spectral range, with a nominal resolution of 0.5 cm^{-1}.

The REFIR-PAD instrument during 2009 took part to two ground-based campaigns: between 22^{nd} and 29^{th} of April, 2009 from the ARM Pagosa Springs Staging Facility (2329 m a.s.l., Colorado, USA), and between August and October 2009 from Cerro Toco, in the Chilean Andes (5383 m a.s.l.). During these campaigns the instrument performed measurements in a widely varying range of atmospheric conditions, with total water vapor column amounts from 0.25 mm to about 1 cm, in clear sky conditions and in presence of thin cirrus clouds.

REFIR-PAD measured downwelling long-wave radiation (DLR) spectra were analyzed through a retrieval code based on the LBLRTM version 11.7 forward model (with AER version 2.4 spectral database) and the MINUIT function minimization routines available from CERN.

The choice of atmospheric variables to be fitted has been optimized keeping into account the sensitivity of zenith-looking radiance spectra to atmospheric physical parameters, obtained from the Jacobian matrices of the DLR. The set of variables obtained with this procedure includes cloud optical depth, and 4 points at selected altitudes for the water vapor and temperature vertical profiles. The atmospheric profiles used in the retrieval are then obtained rescaling the initial guess profile above the higher point, and linearly interpolating the profile between the fitted points.

The main atmospheric parameter that can be retrieved from the DLR spectra is the total precipitable water vapor (PWV), to which the instrument has the maximum sensitivity, with relative errors generally lesser than 10% and typically of the order of 5%. Further information about water vapor distribution with height can be extracted from the 4 fitted levels.

While residuals from a single fit are generally in good agreement with the measurement uncertainty, the averaging of fitting residuals on the timescale of a measurement day (about 20-30 spectra) shows interesting spectral features that are above uncertainty and can be used to refine water vapor continuum model and spectroscopy, in particular in the far-infrared region.

II-6. Polar Mesospheric Clouds and Cosmic Dust: Three Years of SOFIE Measurements

Martin McHugh, Mark Hervig, Larry Gordley, Lance Deaver

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

The Solar Occultation for Ice Experiment (SOFIE), aboard the Aeronomy of Ice in the Mesosphere (AIM) satellite, has been collecting atmospheric transmittance measurements in the polar mesopause region since May 2007. These measurements are used to retrieve vertical profiles of water vapor, ozone, methane, carbon dioxide, nitric oxide, temperature, and polar mesospheric cloud (PMC) extinction. Additionally, SOFIE has provided the first satellite observations of meteoric smoke in the middle atmosphere. This data set has revealed interesting new details about the formation, characteristics and variability of PMCs, with temperature and water vapor identified as critical factors in explaining cloud variability. For example, the unusually early onset of the 2009-2010 cloud season in the southern hemisphere has been linked to colder temperatures and enhanced water vapor concentrations. Also, SOFIE observations of meteoric smoke particles indicate reduced smoke abundance during polar summer when PMCs are present. While the observed smoke variations are in agreement with model predictions, questions remain about the exact connection between PMCs and smoke. In this presentation we describe the SOFIE instrument and the science retrieval algorithms, and highlight some of the recent findings from these data.

II-7. LBL Models: State of the Art and Perspective

B. A. Fomin

Central Aerological Observatory (CAO), 3 Pervomayskaya st., Dolgoprudny, Moscow Region, 141700 RUSSIA

I present the current version of the Fast Line-By-Line Model (FLBLM) aimed at validations of radiation codes for climate models and remote sensing. In this version are used the HITRAN- 2008 database and the MT CKD-2.1 water vapor continuum models and can be taken into account the non-LTE and Line-Mixing effects by means of a pair of independent methods. Then spectroscopic parameters and models required by radiative-transfer modeling as well as effect of their recent improvement on LBL calculation are discussed. Also is considered state of the art of radiative-transfer modeling by means of the latest intercomparisons of radiation codes. Finally perspective of application of the LBL models to remote sensing, climate problems and education is discussed. This work was supported by grants from RFBR (08-01-00024 and 09-01-00071, Russia).

SESSION III: Laboratory Spectroscopy-1

III-1. The Absorption Spectrum of Methane Between 1.27 and 1.71 μm By High Sensitivity CRDS at 80 K and 300 K. Importance of the CH_3D Contribution in the 1.58 μm Transparency Window

Samir Kassi, Le Wang and Alain Campargue

Laboratoire de Spectrométrie Physique (CNRS, UMR 5588), Université Joseph Fourier de Grenoble, BP 87, 38402 Saint-Martin-d'Hères Cedex, France

The high resolution absorption spectrum of methane has been recorded between 1.27 and 1.71 μm by high sensitivity laser absorption spectroscopy at room temperature and at 80 K. In the high absorbing regions surrounding the transparency window at 1.58 μm, the spectra at 80 K were obtained by differential absorption spectroscopy using a specifically designed cryogenic cell and several tens DFB diode lasers [1]. This experimental approach provided a sufficient sensitivity ($\alpha_{min} \sim 10^{-6} cm^{-1}$) in the high energy part of the tetradecad (5850 - 6180 cm^{-1}) [1,2,3] and in the icosad region (6700 - 7700 cm^{-1}) [4,5,6]. In the 1.58 μm transparency window corresponding to the 6165 - 6750 cm^{-1} gap, a much higher sensitivity was achieved by combining the CW-CRDS technique with the same cryogenic cell[7]. The sensitivity achieved at 80 K and room temperature ($\alpha_{min} \sim 3 \times 10^{-10} cm^{-1}$) allowed measuring line intensities as weak as 3×10^{-29} cm/molecule i.e. three orders of magnitude smaller than the intensity cut off of the HITRAN line list of methane. Of importance for planetary applications, is the observed important temperature variation of the transmission in the transparency window [8,9].

A list of more than 28000 transitions with intensity as weak as 1×10^{-29} cm/molecule was constructed from the recordings at 296 and 80 K. The low energy values of the transitions observed both at 80 K and at room temperature were systematically derived from the variation of their line intensities[1-9]. The quality of the obtained empirical low

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[9] A. Campargue, L. Wang, A. W. Liu, S. M. Hu, S. Kassi, Chem. Phys. Submitted

energy values is demonstrated by the marked propensity of the empirical low J values of CH_4 to be close to integers. The line lists associated to the low energy values allow accounting for most of the temperature dependence of methane absorption between these two temperatures.

In the 1.58 μm transparency window, a number of CH_3D transitions were identified by comparison with a spectrum of CH_3D recorded separately by Fourier Transform Spectroscopy. From simulations of the CH_3D and methane spectra at low resolution, the CH_3D isotopologue has be found to contribute by up to 30% of the absorption in the region. In view of future applications, we point out the importance of taking into account the variation of the CH_3D/CH_4 relative abundance according to the studied absorption medium in order to satisfactorily account for the methane transmission in the considered transparency window[8,9].

III-2. The $4\nu_3$ Spectral Region of Methane

D. Chris Benner,[a] **V. Malathy Devi**,[a] **J. J. O'Brien**,[b] **S. Shaji**,[b]
P. T. Spickler,[c] **C. P. Houck**,[c] **J. A. Coakley**,[c] **Kasie J. Haga**[c]

[a] *Department of Physics, College of William and Mary, Williamsburg, VA 23187-8795*

[b] *Department of Chemistry and Biochemistry, University of Missouri - St. Louis, St. Louis, MO 63121-4400*

[c] *Department of Physics, Bridgewater College, Bridgewater, VA 22812*

The near infrared bands of methane were the first observed in the outer planets and Titan. In this spectral region very long paths within the atmospheres of these objects make scattering and pressure and temperature inhomogeneities important. The spectrum is complex, and long absorption paths in the laboratory are difficult to cool to outer solar system temperatures. At room temperature many significant spectral lines appear per Doppler width, so the absorption is usually modeled statistically using unrealistic assumptions. These models generally do not provide transmissions that are multiplicative, so scattering and inhomogeneous atmospheres cannot be properly modeled.

The intracavity laser spectrometer at the University of Missouri-St. Louis was used to obtain low temperature (99-161K), low pressure (0.12-7.13 Torr), long path (3.14-5.65 km) and high resolution (0.01 cm^{-1} HWHM) spectra of methane covering the entire 890nm feature (10925-11500 cm^{-1}), the deepest band in the CCD spectral region. At these temperatures the spectral lines originating from higher energy levels are not visible, and the Doppler width is substantially smaller than at room temperature. The result is a dense, but manageable spectrum from which line positions, intensities and lower state energies are derived on a line by line basis by the College of William and Mary multispectrum nonlinear least squares fitting program[1]. The results allow the simulation of the methane spectrum at infinite resolution at temperatures less than ~160K, even for complex atmospheric paths.[2]

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[2] Support for the work at William and Mary was provided by NASA through grant NNX08AF06G. Support for the work at UM-St. Louis provided by NASA through grant NAG5-12013, from NSF through grant CHE-0213356 and by the University of Missouri Research Board. Partial Support for the work at Bridgewater College was provided from an AAS Small Research Grant.

III-3. Line Strengths and Self-Broadening of Pure Rotational Lines of Carbon Monoxide and Nitrous Oxide Measured by Terahertz Time-Domain Spectroscopy.

W. Aenchbacher[1],[a] **M. Naftaly,**[b] **R. Dudley**[b]

[a]*Drexel University, Dept. of Electrical and Computer Engineering, Philadelphia, PA 19103, USA*

[b]*National Physical Laboratory, Hampton Road, Teddington, Middlesex TW11 0LW, UK*

Terahertz time-domain spectroscopy was used to obtain the line intensities and self-broadening parameters of pure rotational lines of CO and N_2O. The technique yields a direct measurement of an absorption spectrum from 0.2 THz to 3 THz, which is linear in amplitude, therefore allowing the profiles of multiple lines to be observed and quantified. The transitions studied in CO were from $J' = 3 \leftarrow 2$ to $J' = 22 \leftarrow 21$, and in N_2O from $J' = 9 \leftarrow 8$ to $J' = 52 \leftarrow 51$. The gas spectra were measured at elevated pressures in the range of 0.7-5 bar for CO and 0.7-1.7 bar for N_2O. The measured absorption spectra were analyzed assuming a Lorentzian lineshape and using a multiple-peak fitting procedure. The obtained values of the line intensities and self-broadening parameters are in good agreement with the HITRAN database.

III-4. Submillimeter-Wave and Far-Infrared Spectroscopy of High-J Transitions of Ammonia

Shanshan Yu,[a] John C. Pearson,[a] Brian J. Drouin,[a] and Keeyoon Sung[a],
Olivier Pirali,[b] Michel Vervloet,[b] Marie-Aline Martin,[b] Christian P. Endres,[c]
Tetsuro Shiraishi,[d] Kaori Kobayashi,[d] and Fusakazu Matsushima[d]

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

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

[c]*I. Physikalisches Institut, Universität zu Köln, 50937 Köln, Germany*

[d]*Department of Physics, University of Toyama, Gofuku, Toyama 930-8555, Japan*

Ammonia has large-amplitude inversion motion, which makes it particularly non rigid and difficult to model with quantum mechanics. Additionally, the excited inversion states couple strongly to other vibrational modes resulting in a very complex spectrum. Current experimental dataset have been limited to low quantum numbers (J of about 20), and the spectrum of ammonia in many vibrational states has defied analyses to experimental accuracy. The previous attempt at a global analysis of the $v_2 = 2$ and $v_4 = 1$ states ignored the available $2v_2 - v_4$ microwave data and achieved a standard deviation of 0.003 cm^{-1},[1,2] which is an order of magnitude larger than experimental accuracy. There is only one available analysis on the v_1 and v_3 fundamental bands,[3] and the standard deviation of the fit (0.085 cm^{-1}) was about two hundred times larger than the experimental line position uncertainty (about 0.0005 cm^{-1}).

Ammonia has been observed in the interstellar medium up to $J = 18$ and more highly excited transitions are expected to appear in hot exoplanets and brown dwarfs. Modeling exoplanet atmospheres and brown dwarf stars with relatively high temperatures (1000-3000K) requires consideration of ammonia hot bands to model the flux from these objects. As a result, there is a large effort to assign the high J spectrum. There is ongoing ab initio work at NASA Ames and University College London to create a full potential surface. Currently, ab initio calculations are available for levels up to $J = 20$ but these remain untested in $2v_2$ and v_4 above $J = 15$.

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[2] H. Sasada, Y. Endo, E. Hirota, R.L. Poynter, and J.S. Margolis, J. Mol. Spectrosc. 151, 33 (1992).

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In this work, numerous spectroscopic techniques were employed to study its high J transitions in the ground, $v_2 = 1, 2$ and $v_4 = 1$ states. Measurements were carried out using a frequency multiplied submillimeter spectrometer at JPL, a tunable far-infrared spectrometer at University of Toyama, and a high resolution Bruker IFS 125 Fourier transform spectrometer at Synchrotron SOLEIL. Highly excited ammonia was observed with a radio frequency discharge and a DC discharge, which allowed assignments of transitions with J up to 35. 177 ground state and $v_2 = 1$ inversion transitions were observed with microwave accuracy in the 0.3-4.7 THz region. Of these, 125 were observed for the first time, including 26 $\Delta K = 3$ transitions. Over 2000 far-infrared transitions were assigned to the ground state and $v_2 = 1$ inversion bands as well as the v_2 fundamental band. Of these, 1912 were assigned for the first time, including 222 $\Delta K = 3$ transitions. The accuracy of these measurements has been estimated to be 0.0003 to 0.0006 cm^{-1}. A reduced RMS of 0.9 was obtained for a global fit of the ground and $v_2 = 1$ states, which includes the lines assigned in this work and the previously available microwave, terahertz, far-infrared and mid-infrared data. A global analysis of the ground, $v_2 = 1, 2$ and $v_4 = 1$ states is still in progress, and we will present the most recent fitting results to date.

Poster Session 1

PI-1. Study of $H_2{}^{16}O$ Line Intensities around 8800 cm^{-1}

C. Oudot,[a] **L. Regalia**,[a] **L. Daumont**,[a] **X. Thomas**,[a] **P. Von Der Heyden**,[a]
D. Decatoire,[a] **Le Wang**[b]

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

[b] *Laboratoire de Spectrométrie Physique 140 Avenue de la Physique- BP87 38 Saint Martin d'Hères-France*

A precise knowledge of spectroscopic parameters for atmospheric molecules is necessary for the control and the modeling of the Earth's atmosphere. The water vapor plays a special role as it participates to the global radiative balance of the atmosphere.

Our laboratory (GSMA) is engaged since many years in the study of $H_2{}^{16}O$ vapor and its isotopologues. The work presented here is a part of a huge work being performed in the range between 6600 and 9300 cm-1 which should complete the systematic study of natural abundance water vapor from 4200 to 26 000 cm^{-1}.[1,2,3]. We focused on the lines around 8800 cm^{-1}. In the HITRAN database, data reported for this region is taken from the work of Mandin (1988)[4,5] and several articles pointed out problems on the line intensities.

Several spectra were recorded with the GSMA Fourier Transform Spectrometer,[6] using sample of water vapor in natural abundance and with absorption path length of 4 m up to 1200 meters.

Our new intensity measurements have been compared to the HITRAN2008[7] database and recent literature data[8].

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PI-2. Line List of $HD^{18}O$ Rotation-Vibration Transitions for Atmospheric Applications

Semen N. Mikhailenko,[a] Olga V. Naumenko,[a] Sergey A. Tashkun,[a]
An-Wen Liu,[b] Shui-Ming Hu[b]

[a] *Laboratory of Theoretical Spectroscopy, V.E. Zuev Institute of Atmospheric Optics, 634021, Tomsk, RUSSIA*

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

The $HD^{18}O$ molecule was detected recently in the upper Earths atmosphere [1]. We present and discuss a line list of $HD^{18}O$ aimed at atmospheric applications. The line list is based on the theoretical line list by Partridge and Schwenke [2, 3] and experimental energy levels [4, 5]. Rotation-vibration spectrum of $HD^{18}O$, taking into account the natural concentration of this molecule ($6.23*10^{-7}$) and intensity cutoff of 10^{-30} cm/molecule at 296 K., covers the 0-14 000 cm^{-1} spectral region.

This study was supported by Grant nos. 06-03-3914 and 10-0591176 of RFBR (Russia) and by Grant nos. 20903085 and 10574124 of NSFC (China). Work of SNM and SAT was also partly supported by CRDF (USA) Grant RUG1-2954-TO-09 and by RFBR. Grant 09-05-92508.

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PI-3. SMPO Line List of $^{16}O_3$ in the Range 6000-7000 cm^{-1}

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M.-R. De Backer-Barilly,[a] **S.N. Mikhailenko,**[b] **A. Campargue,**[c]
Vl. G. Tuyterev,[a] **A. Barbe,**[a] **S. Kassi**[c]

[a] *Groupe de Spectrométrie Moléculaire et Atmosphérique, U.M.R. CNRS 6089, Université de REIMS, Moulin de la Housse, B.P. 1039, 51687 REIMS cedex 2, FRANCE*

[b] *LTS, Institute of Atmospheric Optics, 634055 TOMSK, RUSSIA*

[c] *Laboratoire de Spectrométrie Physique, U.M.R. CNRS 5588, Université Joseph Fourier B.P. 87, 38402 Saint Martin d'Hères cedex, FRANCE*

Since 2004, the high energy levels (>6000 cm^{-1}) of $^{16}O_3$ have been investigated thanks to the CW-CRDS technique developped in Grenoble. The spectra have been analysed in Reims. Up to now, 22 bands have been assigned in the 6000-7000 cm^{-1} spectral range. This represents 7315 observed transitions corresponding to 3863 energy levels. All the studies have been published.

From Hamiltonian and dipole moment models, all the observed transitions are calculated allowing to generate line lists. But the rms of the fits are larger than the experimental accuracy, due to the difficulty of modelling these high energy levels.

In these conditions, the calculated transitions reported in the line lists are replaced by the "calculated ones" replacing the upper state energy levels by those derived from the observations.

The line lists concerned with this spectral range will be introduced in the SMPO database devoted to the ozone molecule.

`This work is financially supported by VAMDC EU Project.`

PI-4. CRDS of $^{16}O_3$ in the Range 7000-8000 cm^{-1} : First Rovibrational Assignments of the ν_1+$2\nu_2$+$5\nu_3$ (7130 cm^{-1}), $6\nu_1$+ν_3 (7442 cm^{-1}), $5\nu_1$+$2\nu_2$+ν_3 (7579 cm^{-1}), and ν_1+$3\nu_2$+$5\nu_3$ (7686 cm^{-1}) Bands.

S. Kassi,[a] **A. Barbe,**[b] **M.-R. De Backer-Barilly,**[b] **Vl. G. Tuyterev,**[b]
A. Campargue[a]

[a]*Laboratoire de Spectrométrie Physique, U.M.R. CNRS 5588, Université Joseph Fourier B.P. 87, 38402 Saint Martin d'Hères cedex, FRANCE*

[b]*Groupe de Spectrométrie Moléculaire et Atmosphérique, U.M.R. CNRS 6089, Université de REIMS, Moulin de la Housse, B.P. 1039, 51687 REIMS cedex 2, FRANCE*

The high resolution CRDS spectra of $^{16}O_3$ have been recorded from 7000 to 7900 cm^{-1}. In this newly investigated spectral range, thousands of lines were detected. Another difficulty of the analysis is the large number of cold bands predicted in this spectral range : sixty two [1] as the dissociation of ozone is low (8000 cm^{-1}), difficulty due to the absence of band intensities predictions. Up to now, we have assigned 4 A-type bands easily recognizable to their shape, with compressed R branch. They are:

ν_1+$2\nu_2$+$5\nu_3$ at 7130 cm^{-1}, 219 transitions assigned, with $Jmax$=29, $K_a max$=8,

$6\nu_1$+ν_3 at 7442 cm^{-1}, 38 transitions assigned, with $Jmax = 17$, $K_a max$= 3,

$5\nu_1$+$2\nu_2$+ν_3 at 7579 cm^{-1}, 138 transitions assigned, with $Jmax = 22$, $K_a max$=4,

ν_1+$3\nu_2$+$5\nu_3$ at 7686 cm^{-1}, 172 transitions assigned, with $Jmax = 26$, $K_a max$=4.

For each of these bands, we present the preliminary results for Hamiltonian and dipole moment parameters, the statistics of the fits, comparisons with theoretical predictions of band centers and rotational constants. We have generated line-lists of calculated transitions, in which calculated energy levels have been replaced by "observed ones". Several examples of agreement between observed spectra and synthetic ones are shown.

`This work is financially supported by VAMDC EU Project.`

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[1] Vl.G. Tyuterev, S.A. Tashkun, H. Seghir, *SPIE Proceedings* , 5311, 164-175, (2004).

PI-5. High Sensitivity CRDS of the $a^1\Delta_g \leftarrow X^3\Sigma_g^-$ Band of Oxygen near 1.27 μm: Magnetic Dipole and Electric Quadrupole Transitions in Different Bands of Six Isotopologues

S. Kassi,[a] O. M. Leshchishina,[a] L. Wang,[a]
I. E. Gordon,[b] L. S. Rothman,[b] A. Campargue[a]

[a] *Université Joseph Fourier/CNRS, Laboratoire de Spectrométrie Physique, 38402 Saint Martin d'Hères, FRANCE*

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

The knowledge of accurate spectroscopic parameters for $a^1\Delta_g \leftarrow X^3\Sigma_g^-$ band of molecular oxygen near 1.27 μm is very important in the field of remote sensing. Although, this band was studied by spectroscopists for over a century a lot of discrepancies still remain in the previously reported line positions and intensities. In this work the CW-Cavity Ring Down Spectroscopy (CW-CRDS) technique has been used to record the high sensitivity absorption spectrum of this band. The spectra were obtained between 7640 and 7917 cm^{-1} with “natural” oxygen and with samples highly enriched in ^{18}O and ^{17}O. They measured transitions belong to the $a^1\Delta_g \leftarrow X^3\Sigma_g^-$ (0-0) bands of $^{16}O_2$, $^{16}O^{18}O$, $^{16}O^{17}O$, $^{17}O^{18}O$, $^{18}O_2$ and $^{17}O_2$. The (0-0) bands of $^{16}O_2$ and $^{18}O_2$ show (previously undetected) electric quadrupole transitions with line intensities ranging from 1×10^{-30} to 1.9×10^{-28} cm/molecule. They are accompanied by the $a^1\Delta_g \leftarrow X^3\Sigma_g^-$ (1-1) hot bands which are also reported for the first time. Lines of the isotopologues containing ^{17}O atom were observed to be plagued with unresolved hyperfine structure, especially in the $^{17}O_2$ spectrum. Accurate spectroscopic parameters for the observed bands were derived from a global fit of the experimental line positions, combined with microwave and Raman measurements available in the literature.

PI-6. First High Resolution Analysis of the $4\nu_1+\nu_3$ Band of Nitrogen Dioxide near 1.5 μm

A. Perrin,[a] **S.Kassi,**[b] **A.Campargue**[b]

[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] *Laboratoire de Spectrométrie Physique (associated with CNRS, UMR 5588), Université Joseph Fourier de Grenoble, B.P. 87, 38402 Saint-Martin-d'Hères Cedex, France*

The high-resolution absorption spectrum of the $4\nu_1+\nu_3$ band of the $^{14}N^{16}O_2$ molecule was recorded by CW-Cavity Ring Down Spectroscopy between 6575 and 6700 cm^{-1}. The assignments involve energy levels of the (4,0,1) vibrational state with rotational quantum numbers up to $K_a = 8$ and $N = 48$. A large majority of the spin-rotation energy levels were reproduced within their experimental uncertainty using a theoretical model which takes explicitly into account the Coriolis interactions between the spin rotational levels of the (4,0,1) vibrational state and those of the (4,2,0) and of (0,9,0) dark states, the anharmonic interactions between the (4,2,0) and (0,9,0) states together with the electron spin-rotation resonances within the (4,0,1), (4,2,0) and (0,9,0) states. Precise vibrational energies, rotational, spin-rotational, and coupling constants were determined for the (4,2,0), (0,9,0), (4,0,1) triad of interacting states. Using these parameters and the value of the transition dipole moment operator determined from a fit of a selection of experimental line intensities, the synthetic spectrum of the $4\nu_1+\nu_3$ band was generated.

PI-7. The COF_2 Rotational Spectrum near 1 THz and the Infrared Spectrum Revisited; Improved Molecular Constants for the Ground and First Excited States of ν_2, ν_3, ν_5, and ν_6

Edward A. Cohen, Brian J. Drouin, and Linda R. Brown

Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109-8099

The rotational spectrum of COF_2 has been observed near 1 THz as part of a continuing program to precisely characterize the spectra of atmospheric molecules. THz spectra of the ground, ν_2, ν_3, ν_5, and ν_6 states have been assigned, combined with other available rotational data and high resolution infrared data, and fit in a single calculation up to $J \approx 90$ for a wide range of K_c. The spectrum of naturally abundant $^{13}COF_2$ in its ground vibrational state has also been observed and fit separately, although the range of quantum states is smaller due to interference from the nearby normal species. Watson $III^l\,S$ or $I^r\,A$ parameters produce essentially the same quality of the fit. These results allow more accurate prediction of high J infrared spectra of the fundamental vibrations below 1000 cm^{-1}. The fits will be described and some examples of rotational and infrared spectra will be shown.

PI-8. Revised Line-Strengths and Peak-Positions for *cis*-HONO at 1660 cm^{-1} Using a New CW-QC TILDAS

Ben H. Lee,[a] **Ezra C. Wood**,[b] **Mark S. Zahniser**,[b] **J. Barry McManus**,[b]
David D. Nelson,[b] **Scott C. Herndon**,[b] **Joanne H. Shorter**,[b]
Joda C. Wormhoudt,[b] **Steven C. Wofsy**,[a] **J. William Munger**[a]

[a]*Harvard University, School of Engineering and Applied Sciences, Cambridge, Ma, U.S.A.*

[b]*Aerodyne Research, Inc., Center for Atmospheric and Environmental Chemistry, Billerica, Ma, U.S.A.*

Nitrous acid, HONO, is a significant source of atmospheric HO_x and the production of HONO may be responsible for the recycling of deposited NO_y back into the atmosphere in active form. Many current techniques rely on wet-chemical extractive methods, but are potentially prone to interferences and have not always shown good agreement with optical techniques[1]. Spectroscopy offers an alternative method with greater specificity, however, the rotational-vibrational transitions of HONO in the mid-infrared region are not well studied. We present results from an experiment using a new tunable continuous-wave quantum cascade laser absorption spectrometer. We measured the *cis*-HONO spectra between 1659 and 1660 cm^{-1} and the *trans*-HONO spectra near 1275 cm^{-1} (both at a resolution of about 0.001 cm^{-1}). Absolute mixing ratios of total HONO were determined by catalytic conversion to NO followed by calibrated absorption spectroscopy. The effective line-strengths for *cis*-HONO near 1660 cm^{-1} were about a factor of 2.5 smaller than those listed in the ATMOS database, but line-strengths for *trans*-HONO around 1275 cm^{-1} agreed well with reported values.

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[1] J. Kleffmann, J. C. Lörzer, P. Wiesen, C. Kern, S. Trick, R. Volkamer, M. Rodenas and K. Wirtz, *Atmospheric Environment*, **40**, March 2006.

PI-9. Detection and Quantification of OH Radical by Emission and Absorption THz Spectroscopy

Arnaud Cuisset,[a] **Sophie Eliet**,[a] **Francis Hindle**,[a] **Gaël Mouret**,[a]
Robin Bocquet,[a] **Olivier Pirali**,[b] **Marie Aline Martin**,[b] **Michel Vervloet**[b]

[a]*Laboratoire de Physico-Chimie de l'Atmosphère, Université du Littoral Côte d'Opale, 189A Ave. Maurice Schumann, 59140 Dunkerque, France*

[b]*Ligne AILES (Advance InfraRed Line Exploited for Spectroscopy), synchrotron SOLEIL, L'Orme des Merisiers, Saint Aubin, BP 48, 91192 Gif-sur-Yvette, France.*

OH radical is an important compound for both atmospherical and astrophysical chemistry. Therefore improving the spectroscopic knowledge of this unstable specie is important to quantify its abundance in different environments. In this study, the results obtained with emission FTIR spectroscopy and continuous-wave THz absorption spectroscopy demonstrate their ability for the measurement of accurate lines positions and intensities of the OH radical . In both experiments, the radical was produced in cold plasma created by an electrodless radio-frequency discharge in a continuous flow of H_2O. The first experiment was performed with the Bruker IFS 125HR Fourier transform interferometer connected to the far infrared AILES beamline at SOLEIL. The high resolution (resolution = 0.004 cm^{-1} , 120 GHz) emission spectrum of OH has been recorded between 1,5 and 18 THz (50 and 600 cm^{-1}). We observed pure rotational transitions of the OH radical in the vibrational states v=0,1,2 with a frequency accuracy better than $4{\cdot}10^{-4}$ cm^{-1} (12 GHz). The emission spectrum permitted to resolve the spin-orbit and the Λ-doubling effects.

The rotational lines absorption of OH radical were recorded in the THz domain at 1.8 and 2.5 THz (60 and 85 cm^{-1}) with a cw-THz spectrometer. The THz radiation was generated by optoelectronic conversion of an optical beatnote of two laser diodes on a photomixer. This high resolution THz technique allowed to study OH at very low pressures close to the Doppler limit and to resolve the hyperfine rotational structure non observed in the FTIR measurements.

This study highlights the complementary between the two techniques for the determination of experimental parameters such as the thermodynamical and rotational temperatures of the plasma which are necessary for an accurate quantification of OH.

PI-10. Far Infrared High Resolution Rovibrational Spectroscopy of Dimethylsulfoxyde

Arnaud Cuisset,[a] **Irina Smirnova**,[a] **Robin Bocquet**,[a] **Francis Hindle**,[a] **Gaël Mouret**,[a] **Dmitrii A. Sadovskii**,[a] **Olivier Pirali**,[b] **Pascale Roy**[b]

[a]*Laboratoire de Physico-Chimie de l'Atmosphère, Université du Littoral Côte d'Opale, 189A Ave. Maurice Schumann, 59140 Dunkerque, France*

[b]*Ligne AILES (Advance InfraRed Line Exploited for Spectroscopy), synchrotron SOLEIL, L'Orme des Merisiers, Saint Aubin, BP 48, 91192 Gif-sur-Yvette, France.*

In addition to its importance for industrial and environmental studies, the monitoring of DiMethylSulfOxyde (DMSO, $(CH_3)_2SO$) concentrations is of considerable interest for civil protection. The existing high resolution gas phase spectroscopic data of DMSO only cover the pure rotational transitions in the ground state.[1] In the Far-IR domain, the low-frequency rovibrational transitions have never previously been resolved.[2] The high brightness of the AILES beamline of the synchrotron SOLEIL and the instrumental sensitivity provided by the multipass cell allowed to measure these transitions for the first time.[3] 1581 A-type and C-type transitions in the ν_{11} band have been assigned and 25 molecular constants of Watson's s-form hamiltonian developed to degree 8 have been fitted within the experimental accuracy.

The use of then synchrotron radiation has opened many possibilities for new spectroscopic studies. Together with several other recent studies, our successful measurement and analysis of DMSO convincingly demonstrates the potential of the AILES beamline for high resolution FIR spectroscopy.

Thus our present work is just at the beginning of unraveling the rovibrational structure of low frequency bending and torsional vibrational states of DMSO and yielding important comprehensive structural and spectroscopic information on this molecule.

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[3] A. Cuisset, L. Nanobashvili, I. Smirnova, R. Bocquet, F. Hindle, G. Mouret, O. Pirali, P. Roy, D. Sadovskii, *Chem. Phys. Lett.*, accepted for publication

PI-11. Simulation of Snow Spectral Albedo at 0.4-2.5 micron: Updated with New Measurement of the Refractive Index of Ice

Jianping Mao,[a] **Bo-Cai Gao**[a,b]

[a] *Goddard Earth Sciences and Technology Center, NASA Goddard Space Flight Center, Greenbelt, MD 20771*

[b] *Remote Sensing Division, Naval Research Laboratory, Washington, DC 20375*

The large uncertainty exists in the previous snow spectral albedo models, especially in the near infrared where snow has strong absorption and direct measurement is hard to achieve due to the interface with water vapor and carbon dioxide absorption bands. This work updated the refractive index of ice in the solar spectra (0.4-2.5 micron) with new lab measurements and developed a physical approach to simulate snow spectral albedo and bi-directional reflectance. New calculations show the general improvement of snow albedo simulation in the near infrared wavelength >1.4 micron and the dramatic reduction of uncertainty peaking at 1.85 micron.

PI-12. Gas Turbine Engine Soot Particle Emissions and Aerosol Interaction in Experimentally Simulated High Altitude Conditions

Moira Hilton,[a] **Michael Antony Welch,**[a] **Mark Peter Johnson**[b]

[a]*J.J.Thomson Physical Laboratory, The University of Reading, Whiteknights, Reading, RG6 6AF, United Kingdom*

[b]*Rolls Royce PLC, P.O.BOX 31, Victory Road, Derby DE24 8BJ, United Kingdom*

To further the understanding of the impact of aviation on the atmosphere the condensation of water vapour on soot particles and aerosols emitted by gas turbine engines in the upper atmosphere was studied under laboratory conditions. Changes in size distribution, morphology and chemical composition of particles /aerosols emitted from gas turbine engine exhausts were monitored when they interacted with a simulated tropopause atmosphere. These laboratory experiments were designed to investigate particulate precursors for cloud formation and the evolution of hydrocarbon species immediately downstream from aircraft engines. Small volume samples of the exhaust emissions of a small gas turbine engine (SGTE) combusting aviation fuel (kerosene) were introduced into the 75 dm^3 volume aerosol chamber at the NERC Molecular Spectroscopy Facility (MSF) in the Rutherford Appleton Laboratory, UK. Before the exhaust sample was injected, the atmosphere inside the aerosol cell was conditioned by filling with dry air at constant, known pressures, humidity and temperatures equivalent to the atmosphere at an altitude of 6km and at 10km. The hot exhaust gases were injected into cell and allowed to interact with the air and water vapour present at different temperatures, and pressure. Vacuum pumps extracted the excess gases inside the aerosol cell and maintained the internal air pressure at nominated values.

A Scanning Mobility Particle Sizer (SMPS) measured particle size distribution and counted particle numbers. Particle size/surface/volume distribution changes with dilution and the growth of cloud condensation nuclei were studied over the size range 10nm to 1000nm. A Bruker IFS 66 FTIR spectrometer was setup to monitor ice formation and hydrocarbon and other contents of the aerosol cell.

Reproducible particle size distributions and FTIR measurements indicated creation of simulated contrails in the aerosol cell. Differences in unburnt hydrocarbon (UHC) concentrations were observed for the same engine operating conditions at different simulated altitudes corresponding to changes in particle size distribution. At higher simulated altitudes the UHCs may be contributing to the growth in numbers at of larger size particles.

PI-13. Improving Radiative Forcing Estimates in GCM Radiation Codes

David Paynter

GFDL, Princeton, NJ, 08540

Nearly all GCM and line by line (LBL) radiation codes make use of the HITRAN database. Collins et al. (2006) compared the forcing estimates of 16 GCM and 5 LBL codes in clear-sky conditions. For each scenario the GCM codes produced a large range of estimates. However, there was good agreement between the different LBL codes. This raises the question of what factors lead to GCM radiation codes performing poorly when estimating radiative forcing. This work has focused on the longwave spectral region, and examines which parameterizations used in GCM band models are most likely to lead to errors in forcing estimates. Particular emphasis is placed upon the approximations made in the GFDL SEA code. However, many of the results are applicable to different GCM radiation codes. The results demonstrate that most errors are due to a mixture of excluding certain spectral regions and improper treatment of the overlap between absorbers.

SESSION IV: Databases-2

IV-1. Error Propagation from Line Parameters to Spectra Simulations. Illustration on High Temperature Methane

Jean Paul Champion and **Christian Wenger**

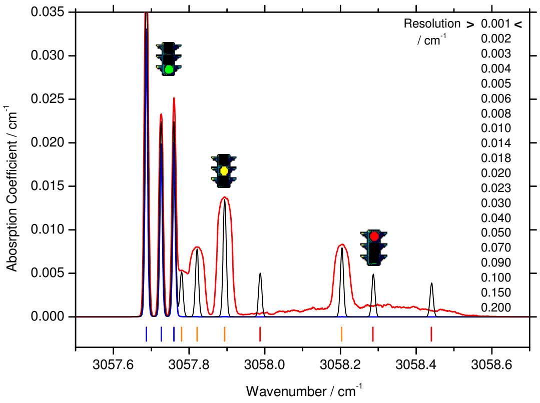
Laboratoire Interdisciplinaire Carnot de Bourgogne (ICB), UMR 5209 CNRS - Universit de Bourgogne, 9 Av. A. Savary, BP 47870, F-21078 DIJON, France.
(jean-paul.champion@u-bourgogne.fr, christian.wenger@u-bourgogne.fr)

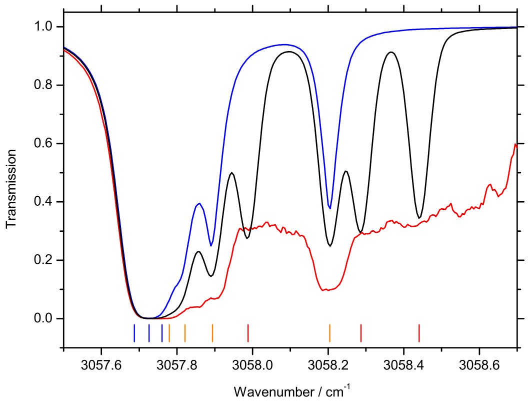
Astrophysical investigations generally need both complete and accurate spectroscopic databases. Despite continuous efforts in experimental and theoretical spectroscopic investigations, the lack of data in some spectral regions of interest is one of the main limitation of the presently available spectroscopic databases. Unfortunately information about missing data relevant to specific experimental conditions is rarely directly accessible from spectroscopic databases (focusing naturally on available data). Such information relies essentially on theoretical investigations which are equally limited to the present state of the art of modelling.

The purpose of the talk is to show how multi-resolution models and rigorous error analyses can help overcoming such deficiencies. Rather than ignoring the spectral regions for which high-resolution line by line modeling is presently inaccessible, low-resolution modeling can be exploited for the sake of exhaustivity which represents a major issue in many astrophysical applications. In parallel, a rigorous quantitative estimation of uncertainties, also essential for applications, represents the second key feature of this approach.

The error propagation from predicted line positions and intensities onto simulated spectra will be described in detail based on multi-resolution global analyses using an effective Hamiltonian approach. The procedure makes extensive use of statistical numerical experiments. It is illustrated on methane which is present in the atmospheres of many astrophysical objects. The modeling of the methane absorption coefficient in the near infrared and/or at high temperature remains a challenge mainly due to the intrinsic complexity of its ro-vibrational spectrum. The extremely large density of levels in highly excited polyads makes it very difficult (if not to say impossible) to envisage line by line modeling above say 10 000 cm^{-1} (http://hal.archives-ouvertes.fr/hal-00277904/fr/). In fact, the present state of the art of high-resolution modeling is limited approximately to the spectral region below around 5 000 cm^{-1}.

The example of methane at high temperature (T_{vib} = 2000 K and T_{rot} = 296 K) will be presented as a typical situation where transitions from several hot band systems with quite different accuracies have to be considered in the same spectral window. Typical confidence bands for the absorption coefficient and transmission signal are plotted in the figures below (details at http://hal.archives-ouvertes.fr/hal-00473611/fr/). Prospects concerning possible improvements of the procedure and its computer implementation will be outlined.





IV-2. High-Lying Rotational Levels of Water Obtained by FIR Emission Spectroscopy

L. H. Coudert,[a] **M.-A. Martin,**[b] **O. Pirali,**[b] **D. Balcon,**[b] **and M. Vervloet**[b]

[a]*LISA, CNRS/Universités Paris Est et Paris Diderot, 61 Avenue du Général de Gaulle, 94010 Créteil, France*

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

In an attempt to compute an accurate linelist for the water molecule, the high resolution emission spectrum of water vapor has been recorded between 50 and 600 cm^{-1} using a Bruker IFS 125HR Fourier transform interferometer and a continuous flow of water vapor rovibrationaly excited by an electrodless radio-frequency discharge.[1] More than 6000 pure rotational lines within the eight first vibrational states were assigned up to $J = 35$. Rotational as well as rovibrational lines were identified for higher lying states belonging to the first hexad. About 1000 pure rotational transitions within vibrational states of the first hexad were assigned for the first time.

The new data, along with a large body of high-resolution data,[2] was fitted using the bending-rotation theoretical approach[3] to compute line positions. In a preliminary analysis, the wavenumbers of 4185 new transitions involving all vibrational states up to the first triad were accounted for up to $J = 27$ with a root mean square value of 0.87×10^{-3} cm^{-1}. Work is still in progress and we are hoping to account for the new data up to the second triad and beyond.

In the paper, the new data will be presented and the results of the line position analysis will be given. The observed minus calculated residuals obtained in the present analysis will be compared to those retrieved using other calculated[4] or experimental[5] rovibrational energies.

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[5] Tennyson, Zobov, Williamson, and Polyansky, *J. Phys. Chem. Ref. Data* **30** (2001) 735.

IV-3. Assignment of the $5\nu_4$ and $\nu_2 + 4\nu_4$ band system of $^{12}CH_4$ in the Region 6287-6550 cm^{-1}.

A. V. Nikitin,[a] X. Thomas,[a] L. Regalia,[a] L. Daumont,[a]
P. Von Der Heyden,[a] Vl. G. Tyuterev,[a] A. Liu,[b] S. Kassi,[b] A. Campargue[b]

[a] *Groupe de Spectromtrie Molculaire et Atmosphrique, UMR CNRS 6089, Universit de Reims, U.F.R. Sciences, B.P. 1039, 51687 Reims Cedex 2, France*

[b] *Laboratoire de Spectromtrie Physique (associated with CNRS, UMR 5588), Universit Joseph Fourier de Grenoble, B.P. 87, 38402 Saint-Martin-dHres Cedex, France.*

This paper reports a first assignment of rovibrational transitions of the $5\nu_4$ and $\nu_2 + 4\nu_4$ $^{12}CH_4$ band systems in the range 6287-6550 cm^{-1} which is usually referred to as a part of the 1.6μm methane transparency window. Five experimental data sources for methane were used for the analyses in this range: two line lists came from the measurements of line positions and line intensities on spectra recorded by Cavity Ring Down Spectroscopy in Grenoble at T= 297 K and 79 K and the other measurements came from the analyses of the three long path Fourier Transform Spectra recorded in Reims (L=1603 m, P= 1-34 mbar). In order to determine the dipole transition moment parameters and quantify the intensity borrowing due to the resonance interactions we had to include in the fitted model also some lines of stronger $\nu_1 + 3\nu_4$ and $\nu_2 + 4\nu_4$ bands. For this purpose we measured additional 180 lines outside this range in FTS spectra though the analysis of these bands is not complete. About 1941 experimental line positions and 1465 line intensities were fitted with RMS standard deviations of 0.003 cm^{-1} and 14%, respectively. A line list of 7877 $^{12}CH_4$ calculated and observed transitions which are considered as dominant ones in the region 6287-6550 cm^{-1} was constructed. This is the first high-resolution analysis and modeling of 5-quanta band systems for a five-atomic molecule close to experimental accuracy. A support from ANR CH4-at-Titan and from GDRI SAMIA collaboration programs is acknowledged.

IV-4. Towards New Line List of Magnetic Dipole and Electric Quadrupole Transitions in the $a^1\Delta_g \leftarrow X^3\Sigma_g^-$ Band of Oxygen

I. E. Gordon,[a] **L. S. Rothman**,[a] **S. Kassi**,[b] **A. Campargue**,[b] **G. C. Toon**[c]

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

[b] *Université Joseph Fourier/CNRS, Laboratoire de Spectrométrie Physique, 38402 Saint Martin d'Hères, FRANCE*

[c] *Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, CA 91109, USA*

The spectroscopic parameters for the $a^1\Delta_g \leftarrow X^3\Sigma_g^-$ band of molecular oxygen near 1.27 μm were given in HITRAN almost since the inception of the database. This band is of fundamental importance in the field of remote sensing. Although, the spectral parameters were updated several times numerous uncertainties have remained. Even the most recent update (November, 2009), that was proven to be superior to previous versions of HITRAN in the atmospheric retrievals [1], leaves room for improvement. This includes not only correction of the existing parameters (for instance the J-dependence of line intensities for $^{16}O^{18}O$) but also accounting for electric quadrupole transitions. The addition of the $\Delta J=\pm2$ electric quadrupole transitions was recently shown to be important [2]. Also one has to evaluate, the correlation between the overlapping $\Delta J=\pm1$, 0 magnetic dipole and electric quadrupole lines. The (1-1) band of $^{16}O_2$ and (0-0) band of $^{16}O^{17}O$ have intensities similar to quadrupole transitions, and therefore the reference spectroscopic data for these species is required. In order to provide accurate input parameters for calculation of line lists the CW-Cavity Ring Down Spectroscopy (CW-CRDS) technique has been used to record the high sensitivity absorption spectrum of this band. The spectra were obtained between 7640 and 7917 cm^{-1} with "natural" oxygen and the absolute intensities of 377 oxygen transitions were measured. They include the $a^1\Delta_g \leftarrow X^3\Sigma_g^-$ (0-0) bands of $^{16}O_2$, $^{16}O^{18}O$ and $^{16}O^{17}O$. The (0-0) bands of $^{16}O_2$ contain electric quadrupole transitions with line intensities ranging from 1×10^{-30} to 1.9×10^{-28} cm/molecule. The lines from (1-1) band were also measured.

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IV-5. Update for Methyl Chloride at 3 μm

C. Bray,[a] A. Perrin,[b] D. Jacquemart,[a] N. Lacome[a]

[a] *Université Pierre et Marie Curie-Paris 6; CNRS; Laboratoire de Dynamique, Interactions et Réactivité (LADIR), UMR 7075, Case Courrier 49, 4 Place Jussieu, 75252 Paris Cedex 05, France*

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

Methyl chloride (CH_3Cl) is one of the most abundant chlorine-containing molecules in the atmosphere. For this reason a recent update was performed in HITRAN for this molecule in the 0-2600 cm^{-1} region by Nikitin et al.[1]. CH_3Cl has a rather strong signature at 3 μm which has been used recently by the Atmospheric Chemistry Experiment (ACE) satellite mission to produce the first study of the global distribution of methyl chloride in the upper troposphere and stratosphere [2]. However it was mentioned that the CH_3Cl line parameters are of very low quality in this spectral region in the HITRAN or GEISA databases [3]. In this work we present a complete update of the line positions and of the (absolute) line intensities for $CH_3{}^{35}Cl$ and $CH_3{}^{37}Cl$ in the 3 μm region. At LADIR about 4000 line positions and 500 line intensities were measured for $CH_3{}^{35}Cl$ and $CH_3{}^{37}Cl$ using new high resolution FTS spectra (Bruker IFS 120) of methyl chloride. The theoretical model accounts for the interactions coupling the ν_1 (l=0), ν_4 (l=1), $2\nu_3+\nu_5$ (l=1), $2\nu_5$ (l=2) and $3\nu_6$ (l=1 and l=3) vibrational states. In addition line shape studies are in progress.

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IV-6. Indices of Refraction of Absorptive Aerosol - Their Importance and Complexity

Steven T. Massie

National Center for Atmospheric Research, PO Box 3000, Boulder, Colorado, 80307

Absorptive indices of refraction of desert dust, black carbon, and fire smoke are important because they produce aerosol effects in which altitude dependent absorption of radiation occurs on regional scales. Atmospheric warming, the lifting of material in the troposphere and stratosphere, perturbations of atmospheric stability, and changes in rainfall rates and drought occurrences, are attributable to the presence of absorptive aerosol. Aerosol properties, however, are very complex. Aerosol is known to evolve in its physical characteristics such as size, optical, and hydroscopic properties. This presentation looks at how well one can specify the indices of refraction of absorptive aerosol, and makes recommendations for improvements in these indices for the HITRAN compilation.

SESSION V: Line Shapes

V-1. The Importance of Being Earnest about Line Shapes

Charles E. Miller and Linda R. Brown

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

Recent advances in theoretical and experimental spectroscopy demonstrate that physical inadequacies in standard Voigt molecular line shape models degrade laboratory and atmospheric spectral curve-fitting retrievals even for state-of-the-art spectrometers. More sophisticated physics associated with molecular collisions (line mixing, speed dependence, narrowing etc.) are generally known, but the atmospheric and laboratory spectroscopy communities lack a comprehensive (validated) software required to compute the very accurate synthetic spectra needed for the retrieval process. For the remote sensing of important greenhouse gases (e.g. CO_2, CH_4 and H_2O), these deficiencies must be corrected in order to achieve abundances with the 0.3% accuracies required for climate change science. We need an international effort to correct this situation.[1]

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[1] The research described in this paper was performed the Jet Propulsion Laboratory, California Institute of Technology, under contracts and cooperative agreements with the National Aeronautics and Space Administration.

V-2. Improvements, Corrections and New Developments in Semiclassical Theories of Collisional Line Broadening

J. Buldyreva

Institut UTINAM, UMR CNRS 6213, Université de Franche-Comté, 16 route de Gray,
25030 Besançon cedex, France

Needs of environment protection and global modeling of terrestrial atmosphere stimulated during last years an active development of international research for non intrusive diagnostics of atmospheric gases by spectroscopic techniques. In order to extract vertical concentration and temperature profiles of atmospheric species, the spectra recorded in infrared, microwave and millimeter spectral regions should be described with high precision. Particularly, not only the intensities and positions of the spectral lines but also their shapes and their overlapping must be perfectly understood.

For molecular species with rotational structure well resolved at atmospheric conditions, the current problem of experimental studies concerns clear departures of experimentally recorded line shapes from the traditionally used Voigt model. Other more sophisticated theoretical profiles should therefore be tested to deduce the collisional line shape parameters containing the information on temperatures and concentrations. Theoretical studies, on their side, must now reproduce the measurements within 1-2% precision in order to be successfully used for estimation of lineshape parameters not yet measured or not accessible experimentally. New substantial developments have been made in the past decade towards such accurate calculations of spectral parameters. The aim of the present work is to describe some of these theoretical approaches and to put them in the general frame of studies concerning the influence of molecular collisions on the spectral lineshape.

For atmospheric applications, the systems of practical interest are polyatomic molecules (linear, symmetric, spherical or asymmetric tops) colliding with diatoms (N_2, O_2, CO, …) or other polyatomic molecules. The considered theoretical approaches are therefore of semiclassical type: the relative molecular motion is described by a classical trajectory governed by the isotropic interaction potential whereas the internal molecular states (vibrations and rotations) are described quantum-mechanically. For active molecules with many vibrational modes and a huge quantity of experimentally observed vibrotational transitions, these computations become very expensive from the viewpoint of CPU time, so that simplified models of semiempirical type are worthy of being attempted. This kind of approaches is briefly considered with examples of asymmetric rotors H_2O and O_3. Moreover, polyatomic but linear molecules for which the rotation-translational decoupling employed by semiclassical approaches is questionable can be treated from a purely classical point of view where the relative trajectory defined by the full anisotropic potential is no more planar and energy transfer between translations and rotations can occur. The efficiency of this method is demonstrated for infrared absorption spectra of C_2H_2 molecule.

V-3. Spectral shapes modeling and remote sensing of greenhouse gases: Toward the OCO and GOSAT experiments and future HITRAN issues

Jean-Michel Hartmann

Laboratoire Interuniversitaire des Systmes Atmosphriques (LISA) CNRS (UMR 7583),
Universits Paris XII et Paris VII Universit Paris XII, 94010 Crteil Cedex, FRANCE;
hartmann@lisa.univ-paris12.fr

Recent advances in the modeling of absorption by oxygen, carbon dioxide, and methane in the regions retained for remote sensing by the Orbiting Carbon Observatory (OCO) and Greenhouse gases Observation SATellite (GOSAT) will be presented. It will be shown that the usual Voigt profile is inadequate and line-mixing and collision induced absorption processes must be properly taken into account for meaningful results concerning the total pressure and species atmospheric amounts. These statements raise the question, which will be discussed, of the evolution of the HITRAN database to include the relevant parameters.

V-4. An Improved Version of the CO_2 Line-mixing Database and Software: Update and Extension

Anne L. Laraia,[a] Julien Lamouroux,[a] Robert R. Gamache,[a] Ha Tran,[b]
Laurence S. Rothman,[c] Iouli E. Gordon,[c] Jean-Michel Hartmann[b]

[a] *University of Massachusetts School of Marine Sciences, Department of Environmental, Earth, and Atmospheric Sciences, One University Avenue,University of Massachusetts Lowell, Lowell, MA 01854-5045,USA*

[b] *Université Paris 12, Lab. Interuniversitaire des Systèmes Atmosphériques, Créteil, FRANCE*

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

In a previous series of studies, a model and the database/software[1] to calculate CO_2-air absorption coefficients taking into account the effect of line-mixing was introduced and tested. Here we present the update recently made[2] to the database and the software. The spectroscopic data were taken from the 2008 version of the HITRAN database[3]. When needed transitions with J" up to 70, or to the J_{max} of HITRAN, were added whenever possible using the CDSD-296[4] database, and the high-temperature CDSD-1000[5] database. The extensions made within the new database by adding the air-induced pressure shifts, the CO_2-H_2O half-widths and their temperature dependence, will also be described. The quality of the new database is demonstrated by the agreement obtained between the calculations and the laboratory spectra measurements in the 1.5-2.3μm region.

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V-5. The Collision-Broadened Line Shape of CO_2 via the Complex Robert-Bonamy Method: The Complexity of Simplicity

Julien Lamouroux, Anne L. Laraia, Robert R. Gamache

University of Massachusetts School of Marine Sciences, Department of Environmental, Earth, and Atmospheric Sciences, One University Avenue, University of Massachusetts Lowell, Lowell, MA 01854-5045, USA

Calculations of the pressure-broadened half-width and pressure-induced line shift are made for CO_2 with N_2, O_2, air, and CO_2 as the buffer gas. It will be shown that the intermolecular potential for these systems is unusually simple, which has lead to many problems and complications in the calculations. The temperature and velocity dependence of the calculations and many of the pitfalls encountered will be discussed. Comparison with measurements of both the half-width and line shift will be shown and the future direction of the work presented.

V-6. Uncertainties Associated with Theoretically Calculated N_2 Broadened Half-Widths of H_2O Lines

Q. Ma,[a] **R. H. Tipping**,[b] **R. R. Gamache**[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]*Department of Physics and Astronomy, University of Alabama, Tuscaloosa, AL 35487*

[c]*Department of Environmental, Earth and Atmospheric Science, University of Mass. Lowell, Lowell, MA 01854*

For many accurate atmospheric applications involving the water vapor molecule, it is desirable to know the half-widths and their temperature dependences better than a 3 % uncertainty for strong lines and 10 % for weaker lines[1]. Unfortunately, of all spectroscopic parameters in HITRAN for H_2O, the self and air half-widths and their temperature dependences contain the largest uncertainties. Recently, in order to improve this situation, the H_2O database in HITRAN has been updated. In developing this updated version, in cases where there are no half-width values to the desired accuracy available in the vast experimental literature, theoretically calculated values have been adopted. For many years researchers have used the Robert-Bonamy (RB) formalism and adopted a realistic potential model to derive these values. Because of the large number of potential matrix elements appearing in these calculations, one is forced to introduce cut-offs that may limit the accuracy attainable. To obviate the necessity of lower cut-offs, we recently reformulated the theory using the coordinate representation[2]. With different choices of the cut-offs used in the theoretical calculations, we have carried out extensive numerical calculations of the N_2-broadend Lorentzian half-widths of the H_2O lines using the modified RB formalism[3]. Based on these results, we are able to thoroughly check the convergence. We find that with lower cut-offs commonly used in the literature, one is able to obtain converged values only for lines with large half-widths. Conversely, for lines with small half-widths much higher cut-offs are necessary to guarantee the convergence. We also analyze uncertainties associated with the calculated half-widths, and these are correlated as above. In general, the smaller the half-widths are, the poorer the convergence and the larger the uncertainty associated with them. For convenience, one can divide all H_2O lines into three categories: large, intermediate, and small according to their half-width values. One can use this division to judge whether the calculated half-widths are converged or not, based on the cut-offs used, and also to estimate how large their uncertainties are. We conclude that with the current RB formalism for lines in category 1, one can achieve the accuracy requirement set by HITRAN while for lines in category 3, it is absolutely impossible to meet this goal.

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V-7. Complex Robert-Bonamy Calculation of H_2O Broadened by N_2, O_2 and Air Made with Realistic Trajectories

Julien Lamouroux,[a] **Anne L. Laraia,**[a] **Robert R. Gamache,**[a] **Qiancheng Ma,**[b]
Richard H. Tipping[c]

[a] *University of Massachusetts School of Marine Sciences, Department of Environmental, Earth, and Atmospheric Sciences, One University Avenue,University of Massachusetts Lowell, Lowell, MA 01854-5045,USA*

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

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

In the present work Complex Robert-Bonamy (CRB) calculations of the pressure-broadened half-width and the pressure induced line shift are made for 1639 transitions in the rotation band of water vapor for N_2 and O_2 as perturbing gases. The half-width and line shift were calculated using the average over the Maxwell-Boltzmann distribution of velocities at seven temperatures in the range 200K - 700K. The air-broadened half widths were determined for each temperature by using the standard formula $\gamma_{air} = 0.79 * \gamma_{N_2} + 0.21 * \gamma_{O_2}$. These calculations employed realistic trajectories determined by solving Hamiltons Equations of motion where the potential is taken as the isotropic part of the atom-atom intermolecular potential expended at 8th order. We present the comparisons of these new calculations with former ones[1] that used the Robert-Bonamy second-order in time trajectory model. The comparisons of both calculations with measurements from the database of measured half-widths[2] updated in 2008[3] and the recent recommended data of Delamere et al.[4] is also discussed. The use of trajectories determined using Hamilton's Equations of motion improved agreement with measurement for almost all transitions. Given the recent work of Ma et al.[5] we expect that the improved agreement for intermediate to narrow lines will only come once the order and rank of the intermolecular potential are increased and a better potential model is used.

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V-8. N_2 Collisional Broadening of Methane in the THz Region Measured at the SOLEIL Synchrotron

V. Boudon,[a] **T. Gabard**,[a] **O. Pirali**,[b] **P. Roy**,[b] **J.-B. Brubach**,[b] **L. Manceron**,[c]
J. Vander Auwera[d]

[a] *Institut Carnot de Bourgogne, UMR 5209 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, France*

[c] *Laboratoire de Dynamique, Interactions et Réactivité, UMR 7075 – Universit Pierre et Marie Curie – CNRS, Case 49, 4 Place Jussieu, F-75252, Paris Cedex, France*

[d] *Service de Chimie Quantique et Photophysique, Université Libre de Bruxelles, CP 160/09, 50 avenue F.D. Roosevelt, B-1050 Brussels, Belgium*

Recently, we recorded the THz centrifugal distortion-induced spectrum of methane using synchrotron radiation at the SOLEIL facility. Intensities of pure rotation lines of CH_4 were precisely measured, from which the induced dipole moment of this weak spectrum, of great interest for planetology, was accurately inferred.[1] This study should in particular help to measure methane concentrations in Titan's atmosphere.[2]

Here, we continue the work by presenting spectra of CH_4/N_2 mixtures, again recorded with a 150 m optical path in a White cell and a Bruker IFS 125 HR FTIR spectrometer at the AILES beamline of SOLEIL. More precisely, the spectra were recorded with 5 % of CH_4 in N_2 at various total pressures (*ca.* 100, 200, 400, 600 and 800 mbar). These spectra will allow to measure collisional broadening and shift coefficients, as well as line-mixing parameters, with N_2 as a perturber (like in Titan's atmosphere).

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V-9. N_2-broadened $^{13}CH_4$ at 80 to 296 K

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

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

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

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

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

High-resolution spectra of the ν_4 fundamental band of $^{13}CH_4$ broadened by N_2 at temperatures relevant to the atmosphere of Titan (80 K to 296 K) have been recorded using new temperature-controlled absorption cells installed in the sample compartment of a Bruker IFS-125HR Fourier Transform spectrometer (FTS) at the Jet Propulsion Laboratory (JPL). Early analysis of these spectra using multispectrum fitting has determined half widths, pressure-induced shifts, line mixing parameters and their temperature dependences for R-branch transitions from R(0) through R(6). The analysis for these J-manifolds examined in detail whether or not the N_2-broadened half width coefficients follow the simple exponential temperature-dependence over the entire temperature range from 80 K to 296 K. The results are compared with other published measurements of N_2- and air-broadened methane parameters.[1]

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[1] 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.

V-10. Formaldehyde Broadening Coefficients: the 5.7μm AND 3.6μm Bands

D. Jacquemart,[a] **N. Lacome**,[a] **A. Laraia**,[b] **R.R. Gamache**,[b] **A. Perrin**,[c]
F. Kwabia Tchana[c]

[a] *Université Pierre et Marie Curie-Paris 6; CNRS; Laboratoire de Dynamique, Interactions et Réactivité (LADIR), UMR 7075, Case Courrier 49, 4 Place Jussieu, 75252 Paris Cedex 05, France*

[b] *University of Mass Lowell, Department of Environmental, Earth and Atmospheric Sciences, Lowell, MA 01854, USA*

[c] *Université Paris 12; CNRS; Laboratoire Inter Universitaire des Systèmes Atmosphériques (LISA), UMR 7583, 61 Av du General de Gaulle, 94010 Créteil Cedex France*

The goal of this study was to achieve absolute line intensities and reliable line broadening parameters for the strong 5.7 μm and 3.6 μm bands of formaldehyde (H_2CO) and to generate, for both spectral regions, a complete linelist for atmospheric applications.

High-resolution Fourier transform spectra were recorded at LADIR for the whole 1600 - 3200 cm^{-1} spectral range and for different path-length-pressure products conditions. Using these spectra, a large set of H_2CO individual line intensities[1] and of self- and N_2-broadening linewidths[2] were measured.

The linelist of positions and intensities based on this work[a] has been included in the HITRAN 2008 database. This presentation will be focused on the retrieved linewidths (self and by N_2). Empirical expansions and theoretical calculations (semi-classical Robert-Bonamy formalism) have been performed and compared to the measurements. Rotational dependences have been studied, and the temperature dependence of the N_2-broadening coefficients has been calculated.

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Poster Session II

PII-1. High Resolution Fourier Transform Spectroscopy in the 1.57 μm Region Using a Frequency Comb Laser Source

Keeyoon Sung, Pin Chen, Timothy J. Crawford

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

A limiting factor to high-resolution Fourier-transform infrared spectrometry (FT-IR) is available photon flux with a conventional light source such as tungsten or Globar lamp. This is particularly problematic when studying weak absorption features requiring long path, multi-pass cells, which have low optical throughput at their maximum path length (often on the order of 20%). We report the implementation of a frequency comb laser with the Bruker 125 HR Fourier transform spectrometer at JPL. The laser (PolarOnyx, Model: Mercury 1000-100-100) generates a frequency comb spanning the 6200 - 6600 cm^{-1} spectral range, with a tooth spacing of 0.0015 cm^{-1} and average output power of 120 mW. The output was attenuated and coupled into the spectrometer via single-mode optical fibers. Instrumental line shape (ILS) function has been investigated with the nominal aperture diameter of 0.1 mm, and compares well against the ILS function for a conventional continuum light source. The CO$_2$ spectrum at the 1.57 μm is used to test the performance of the new system, whose preliminary results are presented along with discussion on potential applications of the laser source for other species in the spectral region.[1]

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[1] The research at the Jet Propulsion Laboratory, California Institute of Technology was performed under contracts and grants with National Aeronautics and Space Administration. In particular, we acknowledge the NASA Planetary Instrument Definition and Development program.

PII-2. Development of an External-Cavity Quantum Cascade Laser Spectrometer

Virginie Zeninari, Dominique Mammez, Julien Cousin, Lilian Joly, Bertrand Parvitte

Groupe de Spectrométrie Moléculaire et Atmosphérique, Université de Reims Champagne-Ardenne, Fac des Sciences, Moulin de la Housse, BP 1039, 51687 Reims Cedex 2, Email : virginie.zeninari@univ-reims.fr

The laser team of GSMA in Reims has previously developed various tunable diode laser spectrometers in the infrared in order to measure spectroscopic parameters. However a tunable diode laser spectrometer is usually limited to the study of less than 10 cm^{-1}. This problem is related to the Distributed FeedBack system integrated on the Fabry-Perot chip laser in order to obtain a single-mode emission. Thus usual spectroscopic parameters retrieved by tunable diode laser spectroscopy cannot significantly contribute to databases such as HITRAN.

In this poster we will present the current developments of an external-cavity quantum cascade laser spectrometer. The main objective is to use the main part of the curve gain of the laser to obtain a single-mode emission (up to 200 cm^{-1}). For that purpose we are working with the Alcatel-Thales III-V lab from Palaiseau (France) which develops the laser chips and the mandatory anti-reflection coatings. First results and tests will be presented.

PII-3. High-Resolution Diode Laser Spectroscopy of C_2H_2, H_2O, CO_2 and their Isotopologues and Application to TDLAS a Tunable Near Infrared Diode Laser Spectrometer for the Martian PHOBOS-GRUNT Space Mission

Virginie Zeninari, Jingsong Li, Julien Cousin, Bertrand Parvitte, Lilian Joly, Georges Durry

Groupe de Spectrométrie Moléculaire et Atmosphérique, Université de Reims Champagne-Ardenne, Fac des Sciences, Moulin de la Housse, BP 1039, 51687 Reims Cedex 2, Email : virginie.zeninari@univ-reims.fr

A near-infrared tunable diode laser spectrometer called TDLAS has been developed that combines telecommunication- type as well as new-generation antimonide laser diodes to measure C_2H_2, H_2O, CO_2 and their isotopologues in the near infrared. This sensor is devoted to the in situ analysis of the soil of the Martian satellite PHOBOS, within the framework of the Russian space mission PHOBOS-GRUNT.

In the first part of the poster, we report accurate spectroscopic measurements of C_2H_2 and $^{13}C^{12}CH_2$ near 1.533 μm, of H_2O and CO_2 at 2.682 μm, of the isotopologues $^{13}C^{16}O_2$ and $^{16}O^{12}C^{18}O$ near 2.041 μm and $H_2{}^{17}O$, $H_2{}^{18}O$ and HDO near 2.642 μm. The achieved line strengths are thoroughly compared to HITRAN data. In the second part of the poster, we describe the TDLAS spectrometer for the PHOBOS-GRUNT mission.

PII-4. Pressure Broadening Coefficients of HCl and DCl for the Venus Atmosphere

T. Földes and J. Vander Auwera

Service de Chimie Quantique et Photophysique, Université Libre de Bruxelles, CP 160/09, 50 avenue F.D. Roosevelt, B-1050 Brussels, Belgium

Recent observations in the 2.2 to 4.3 μm range by the Solar Occultation InfraRed Spectrometer (SOIR) aboard the ESA VENUS EXPRESS spacecraft include the detection of HCl and the first vertical profile of HCl in the atmosphere of Venus.[1] Since precise spectroscopic data of pressure broadened lineshapes of HCl in such an environment are presently missing, we recorded CO_2 broadened spectra of the $1-0$ band of HCl near 2886 cm^{-1} at several pressures between 150 and 700 Torr, using a high-resolution Fourier transform spectrometer. Similarly, we also recorded CO_2 pressure broadened spectra of the $1-0$ band of DCl near 2089 cm^{-1}. Pressure broadening coefficients are extracted by least-squares fitting of Voigt and Rautian-Sobel'man profiles with the Gaussian component and self broadening parameters fixed to the Doppler width and values reported in the literature,[2] respectively. Results will be presented and discussed.

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PII-5. Recent Collisional Broadening Studies at PhLAM in the Millimeter Range: Temperature Dependencies and Line Shapes Analysis

Georges Wlodarczak and **François Rohart**

Laboratoire de Physique des Lasers, Atomes et Molcules, UMR Lille1-CNRS 8523, Universit de Lille 1 Btiment P5, F-59655 Villeneuve d'Ascq cedex, France; E-mail: georges.wlodarczak@univ-lille1.fr

Remote sensing detection of molecular species of Earth and planetary atmospheres requires a good knowledge of collisional relaxation rates, of their pressure and temperature dependencies as well as of the profiles of considered lines. Since several years, our laboratory has been involved in the study of the influence of molecular collisions on spectral lineshapes. We present a review of our recent results obtained in the millimeter range, namely in the case of atmospheric interest molecules (CO [1, 2], NO [3], N_2O [4, 5], O_3 [6, 7, 8], CH_3Cl [9], CH_3CN [10], HCN [11],). Major results include dependencies of relaxation rates on the temperature and on the K-quantum number, as well as detailed studies of lineshape deviations from the usual Voigt profile. All these experimental results have been confirmed by intercomparisons with measurements from other laboratories and by theoretical calculations.

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PII-6. New Absorption Bands of the Carbon Dioxide Isotopologues in Venus Spectra

S. Robert,[a] **R. Drummond,**[a] **A. Mahieux,**[a] **V. Wilquet,**[a] **A. C. Vandaele,**[a]
J. Vander Auwera,[b] **Yu. Borkov,**[c] **V. I. Perevalov,**[c] **S. A. Tashkun,**[c]
J .- L. Bertaux[d]

[a] *Belgian Institute for Space Aeronomy, 3 Ave Circulaire, 1180 Brussels, Belgium*

[b] *Université Libre de Bruxelles, 50 Ave F.D. Roosevelt, CP 160/09, 1050 Brussels, Belgium*

[c] *V.E. Zuev Institute of Atmospheric Optics SB RAS, 1, Academician Zuev square, Tomsk 634021, Russia.*

[d] *Service d'Aéronomie du CNRS, Verrières-le-Buisson, France; IPSL, Université UVSQ, 78280 Guyancourt, France*

We present new absorption bands of carbon dioxide isotopologues detected by the SOIR instrument on board Venus Express. The SOIR instrument combines an echelle spectrometer and an Acousto-Optical Tunable Filter for order selection. It performs solar occultation measurements in the IR region (2.2 - 4.3 μm) at a resolution of 0.12 – 0.18 cm^{-1}. The wavelength range probed by SOIR allows a detailed chemical inventory of the Venus atmosphere above the cloud layer (65 to 150 km) to be made with emphasis on the vertical distribution of gases.

The sensitivity of the SOIR instrument and the high concentration of CO_2 on Venus, coupled with the long absorption paths sounded during solar occultations, enable us to detect weak absorption bands of rare CO_2 isotopologues.

So far we identified the 20001 – 00001 band of $^{16}O^{13}C^{18}O$ and the 21101 – 01101 band of $^{16}O^{12}C^{18}O$ in the SOIR spectra. Rotational analyses were performed for these two new bands and also for the 01111 – 00001 band of $^{16}O^{12}C^{18}O$, already reported by our group[1].

A systematic study of the recorded spectra is under way and preliminary results will be discussed from a spectroscopical point of view.

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PII-7. A Modified Version of the HITRAN Database for High Temperature Diagnostics and Plume Signature Applications

W. J. Phillips[1] and **D. G. Brown**

1099 Schriever Ave., MS-9013, Arnold AFB, TN, USA 37389-9013

Aerospace ground test facilities capable of simulating hypervelocity flight (>Mach 5) conditions necessarily produce high enthalpy test conditions that can easily result in gas temperatures in excess of 2000K. In such a harsh test environment, one has to rely heavily on optical diagnostics for characterizing the flow. This requirement results in a need for high temperature spectral line parameters of major combustion by-product gases and air constituents, such as O_2, H_2O, CO_2, and CO.

In an attempt to address this need, the extensive 2006 version of BT2 water line list from University of London was merged with the 2008 HITRAN water line listing.[2] Spectral line strengths were determined from the University of London Einstein A coefficients and a crude spectral line broadening half-width correlation with rotational quantum number was utilized to assign broadening half-widths to the University of London line list. The modified line list was vetted for duplicate lines, merged with the HITRAN 2008 water line list, and cast into the HITRAN format. Spectral calculations were conducted for high temperature conditions observed in the exhaust of the liquid hydrogen/oxygen Space Shuttle main engine and compared to signature data acquired with a low resolution spectrometer.

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PII-8. Predicting half-widths and line shifts for water vapor transitions on the HITEMP database

Robert R. Gamache,[a] **Laurence S. Rothman**,[b] **Iouli E. Gordon**[b]

[a] *University of Massachusetts School of Marine Sciences and Department of Environmental, Earth, and Atmospheric Sciences, One University Avenue, University of Massachusetts Lowell, Lowell, MA 01854-5045, USA*

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

The HITEMP database[1] provides molecular spectroscopic parameters for high-temperature modeling of the spectra of molecules in the gas phase. Currently there are 5 molecular species on the database; H_2O, CO_2, CO, NO, OH. For H_2O there are now transitions that have rotational quantum numbers up to J=50 and many transitions where the vibrational quantum numbers and prolate and oblate limit pseudo-quantum numbers (K_a and K_c) are not known. Line shape parameters are not available for most of these transitions. We have developed a method to determine these line shape parameters for the 3 most abundant isotopologues of water based on the Semi-empirical approach of Jacquemart *etal.*[2] and an algorithm that estimates the number of vibrational quanta exchanged in the transition. Thus, vibrational dependence of the line shape parameters, which has been found to be important for H_2O[3], is taken into account for many transitions. When the parameters are not available from this new algorithm, average half-widhts as a function of J" are determined from a polynomial fit of validated calculated data. The results of the new algorithm and the J-averaged half-widths are compared with the values found on the 2008 version of the HITRAN database.

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PII-9. Modelling Water Spectra and their Contribution to the Water Vapour Continuum

Matthew J. Barber, **Ross E. A. Kelly, Jonathan Tennyson**

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

Recent concerns regarding possible climate change have prompted a need for greater analysis of a component of the water vapour spectrum known as the water continuum. Although this can be reasonably modelled by empirical fit, the physical basis for it is not well understood which might hide significant dependencies on variable such as temperature and pressure. Theories regarding its origin include contribution from the far wings of poorly profiled known absorption lines, weak absorption lines, and polymeric water molecules such as dimers, trimers, etc. Assessing the contribution from the water dimer has always been problematic because the size and position of spectral features varies considerably depending on the models used.

Although the HITRAN database contains a comprehensive water line list, this is cut off at a relatively high intensity in many regions. As such, we have produced an enhanced water line list from both theoretical sources, particularly the BT2 line list produced earlier at UCL, and recent experimental measurements particularly in weak regions with little HITRAN data. This extended list allows us to explain some spectral features that cannot be accounted for by the HITRAN database alone.

Additionally, using quantum chemistry models, it is possible to produce an ab initio spectrum for the water dimer, although this is computationally very expensive due to the large number (of the order of billions) of possible states and the even larger number of transitions between them. However, using a Franck-Condon style approach, we can approximate a band spectrum for the water dimer, simulating the rotational structure by other means.

PII-10. Water Vapor Line Measurements to Improve the Continuum Contribution in the THz Region

D. F. Plusquellic,[a] **V. B. Podobedov,**[a] **K. Siegrist,**[a] **G. T. Fraser,**[a]
K. O. Douglass,[a] **E. Gerecht,**[a] **and Q. Ma**[b]

[a] *National Institute of Standards and Technology, Physics Lab, Biophysics Group, Gaithersburg, MD 20899, USA*

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

Experimental THz measurements of the linewidths, integrated intensities, pressure and temperature-induced lineshift parameters for several water vapor lines in the range above the 45 cm^{-1} atmospheric transmittance window are reported. The measurements were performed using a THz photomixer spectrometer in a single-pass absorption cell for pressures from 0.13 kPa to 1 kPa (1 to 8 Torr) H_2O vapor and up to 80 kPa (600 Torr) N_2 or O_2 over a temperature range from 293 to 328 K. The reduced uncertainties associated with the local contributions of these water vapor lines will enable more accurate determinations of the continuum contribution throughout this region. We also report on a new method based on chirped pulse methods [1] that will improve the accuracy of lineshape measurements in the THz region.

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PII-11. High Resolution Investigation of the Ethane Spectrum at 7 micron (1430 cm^{-1})

C. Di Lauro,[a] **F. Lattanzi,**[a] **K. Sung,**[b] **L. R. Brown,**[b] **J. Vander Auwera,**[c]
A. W. Mantz,[d] **M. A. H. Smith**[e]

[a]*Dipartimento di Chimica Farmaceutica e Tossicologia, Università di Napoli Federico II , I-80131 Naples, Italy*

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

[c]*Service de Chimie Quantique et Photophysique, Université Libre de Bruxelles, CP 160/09, 50 avenue F.D. Roosevelt, B-1050 Brussels, Belgium*

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

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

Building upon our previous contributions,[1] we are re-investigating the ethane spectrum between 1330 and 1610 cm^{-1}. For this, spectral data were obtained at room and cold (130 K) temperatures with two Bruker Fourier transform spectrometers (at 0.002 cm^{-1} resolution in Brussels and at 0.003 cm^{-1} resolution in Pasadena). Over 3300 lines were assigned to ν_6, ν_8, $\nu_4 + \nu_{12}$ and $2\nu_4 + \nu_9$ cold bands, and one hot band ($\nu_4 + \nu_8 - \nu_4$). Note that ν_6, ν_8, ν_9, and ν_{12} are near 1379, 1472, 823, and 1195 cm^{-1}, respectively, and ν_4 is the torsional mode near 289 cm^{-1}. Our new analysis includes an improved implementation of the theoretical Hamiltonian needed to interpret the very complex spectral structures caused by numerous interactions between these 5 vibrational modes. From this, an empirical line list of positions and estimated intensities is being generated for planetary applications.

Part of the research described in this paper was performed at the Jet Propulsion Laboratory, California Institute of Technology, Connecticut College, and NASA Langley under contracts and grants with the National Aeronautics and Space Administration.

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PII-12. Calculated Line Intensities for the Deuterated Isotopologues of the Hydrogen Sulphide: Range of Fundamentals and First Polyads

Vladimir G. Tyuterev,[a] Julien Lamouroux,[b] S. A. Tashkun[c]

[a] *G. S. M. A. UMR CNRS 6089, Université de Reims, B.P. 1039, 51687 Reims Cedex 2, France*

[b] *University of Massachusetts School of Marine Sciences, Department of Environmental, Earth, and Atmospheric Sciences, One University Avenue,University of Massachusetts Lowell, Lowell, MA 01854-5045,USA*

[c] *Institute of Atmospheric Optics, RAN, 1, av. Akademicheskii, 634055 Tomsk, Russia*

We study the effect of isotopic substitutions on the line intensities in the hydrogen sulphide molecule. The infrared line intensities were calculated from the *ab initio* dipole moment surfaces using two independent methods : variational calculations[1] and high-order contact transformations[2,3]. Results are compared with experimental FTS measurements made in Reims University[1,4,5]. The theoretical line list in the Hitran format was generated for the D_2S triad bands. A support from IDRIS computer centre of CNRS France and from GDRI SAMIA collaboration program is acknowledged.

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PII-13. Critical Evaluation of the Vibrational-Rotational Transitions of Hydrogen Sulfide and its Isotopologues from 0 to 16500 cm^{-1}

O. V. Naumenko[1],[a] **L.R. Brown**[2],[b] **A. Campargue**[3],[c] **S.-M. Hu**[4],[d]
E. R. Polovtseva,[a] **A. Z. Fazliev**[5],[a] and **S. A. Tashkun**[a]

[a] *V.E. Zuev Institute of Atmospheric Optics SB RAS, Zuev Square, 1, Tomsk 634021, Russia*

[b] *Jet Propulsion Laboratory, California Institute of Technology, Mailstop 183-601, 4800 Oak Grove Drive, Pasadena, CA 91109, USA*

[c] *Laboratoire de Spectrometrie Physique (Associated with CNRS, UMR 5588), Universite Joseph Fourier de Grenoble, B.P. 87, 38402 Saint-Martin-d'Heres Cedex, France*

[d] *Hefei National Laboratory for Physical Sciences at Microscale, Department of Chemical Physics, University of Science and Technology of China, Hefei 230026, China*

More than 30000 rovibrational transitions of the $H_2{}^{32}S$, $H_2{}^{34}S$, $H_2{}^{33}S$, $HD^{32}S$ and $D_2{}^{32}S$ molecules from 35 literature sources have been collected and critically evaluated based on the effective Hamiltonian calculations in the 0-16500 cm^{-1} spectral region. The consistent set of rovibrational energy levels has been derived for each considered isotopologue from the solution of the Rydberg-Ritz system of linear equations using the RITZ computer code. For the main isotope species $H_2{}^{32}S$, more than 7000 precise energy levels and associated uncertainties have been obtained. The (000) energy levels have been modeled with an accuracy close to experimental value using the $generation functions$ approach. Detailed and accurate absorption spectra of the $H_2{}^{32}S$, $H_2{}^{34}S$, and $H_2{}^{33}S$ molecules have been generated in the 2000-7000 cm^{-1} region from the derived sets of the experimental upper and lower energy levels and transitions intensities calculated within the effective Hamiltonian approach using published dipole moment parameters. The numerical information obtained has been deposited in Internet accessible information system W@DIS (http://wadis.saga.iao.ru).

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[1] The supports by RFBR (grant 10-05-91176), and by the Groupement de Recherche International SAMIA between CNRS (France), RFBR (grant 09-05-93105, Russia) and CAS (China) are acknowledged

[2] Part of the research at the Jet Propulsion Laboratory, California Institute of Technology was performed under contracts and grants with National Aeronautics and Space Administration

[3] The support by the Groupement de Recherche International SAMIA between CNRS (France), RFBR (Russia) and CAS (China) is acknowledged

[4] The support by the Groupement de Recherche International SAMIA between CNRS (France), RFBR (Russia) and CAS (China) is acknowledged

[5] The support by RFBR research grant 08-07-00318 is gratefully acknowledged

PII-14. Line Parameters of the $H^{35}Cl$ R(3) Absorption Line in the First Overtone at up to 10 bar

V. Ebert,[a,b,c] **P. Ortwein**,[a,b] **W. Woiwode**,[b] **M. Gisi**,[b] **S. Wagner**[b]

[a]*Physikalisch-Technische Bundesanstalt, Bundesallee 100, 38116 Braunschweig, Germany*

[b]*Institute of Physical Chemistry, University of Heidelberg, INF 253, 69120 Heidelberg, Tel.: +49-6221-545004, volker.ebert@pci.uni-heidelberg.de, www.gasanalysis.org*

[c]*Center of Smart Interfaces, Technische Universitt Darmstadt, Petersenstraße 32, 64287 Darmstadt*

The detection of HCl plays an important role in atmospheric chemistry as well as in combustion and gasification processes. A sensitive HCl measurement especially in gasification processes with high process temperatures and pressures requires a precise knowledge of the spectroscopic line parameters. In particular self and foreign broadening coefficients are of great interest, especially due to the discrepancies in pressure broadening coefficients and line strength between HITRAN 2004 and recent data by De Rosa [1]. Using a new vertical cavity surface emitting laser (VCSEL) at 1.74μm with a wide current tuning range of 10 cm-1 a highly sensitive TDLAS spectrometer was developed to realize an analysis of the $H^{35}Cl$ R(3) absorption line. This high resolution spectrometer was used to determine the line strength $S(T_0)$=12.53(11)$\cdot 10^{-21}$ $cm^{-1}/(molec\cdot cm^{-2})$ and the self broadening coefficient γ^0_{HCl}=0.021787(61) cm^{-1}/atm of the R(3) absorption line in the first overtone (2←0) rovibrational band for $H^{35}Cl$. Furthermore we present the first laser-based high-pressure study on the pressure broadening coefficients of HCl by He, N_2 and O_2 covering pressures of up to 1 MPa ($\gamma^0_{N_2}$=0.07292(5) cm^{-1}/atm, γ^0_{He}=0.02113(1) cm^{-1}/atm, $\gamma^0_{O_2}$=0.03978(6) cm^{-1}/atm). The results are compared to previously available low pressure data. Further comparisons with FT-IR based line parameter studies covering the entire overtone band are in progress.

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SESSION VI: Database Structure

VI-1. Information System to Access HITRAN via the Internet

Yury L. Babikov,[a] **Semen N. Mikhailenko**,[a] **Sergey A. Tashkun**,[a]
Iouli E. Gordon,[b] **Laurence S. Rothman**[b]

[a]*V.E. Zuev Institute of Atmospheric Optics, 634021, Tomsk, RUSSIA*

[b]*Harvard-Smithsonian Center for Astrophysics, Atomic and Molecular Physics Division, Cambridge MA 02318, USA*

We present an information system to access the HITRAN database via the Internet. The system consists of two major components HITRAN/SQL and HITRAN on the Web. HITRAN/SQL is a relational database based on the HITRAN data. Access to the data is controled by the MySQL database management system. HITRAN on the Web is a software engineering tool based on the Model-View-Controller (MVC) architecture. Within the MVC approach the data model of an application, the user interface and the operating logic are considered as separate components so that updating of one of the components has minimum influence on others. A spectroscopic information system SPECTRA [1] developed in V.E. Zuev Institute of Atmospheric Optics SB RAS is a prototype realization of MVC. SPECTRA is available via the site spectra.iao.ru as well as via HITRAN site www.cfa.harvard.edu/hitran/ under menu item 'other lists'. Among functionality of the system we can to note the following:

1 survey of the content of the HITRAN databank;

2 calculation and visualization for a given gas mixture and selected conditions (spectral region, line profile, apparatus function, temperature, pressure, resolution, etc) stick intensity spectra, absorption/transmission coefficients, etc as function of wavenumber or line length;

3 spectra convolution with a given apparatus function;

4 downloading results in various formats on a user's computer and sending them via e-mail;

5 detailed bibliography in an appropriate domain.

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VI-2. New Tools for Storing and Accessing Spectroscopic Data: the Development of an XML Schema for the HITRAN Database

Christian Hill and Jonathan Tennyson

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

HITRAN was designed 40 years ago with a fixed-format suitable for punch-cards. Over time this format has expanded but not fundamentally changed, and its inflexibility is now a major constraint on the information that it can store. A new relational database model for HITRAN and the software tools necessary to query it have been developed and a trial version is available at the URL http://msslsc.mssl.ucl.ac.uk/. The selected data can be returned in various popular formats, including as an ASCII text table, VOTable, and the native 160-byte HITRAN line format. An XML Schema, XSAMS, for representing spectroscopic data, developed as part of the Virtual Atomic and Molecular Data Centre (VAMDC) project, is presented. This EU-funded initiative aims to build a flexible and interoperable e-science environment for the communication of atomic and molecular data. Spectroscopic data represented in XSAMS format carries explicit metadata describing its source and accuracy; this format allows data from different sources to be compared and merged, and has been extended to allow the inclusion of absorption cross section data and relaxation matrix elements for the description of line-mixing effects. XSAMS is currently implemented by several other molecular databases including the CDMS/JPL line list and BASECOL.

VI-3. Publishing Tools for a Distributed Information System

A.Z. Fazliev[1], **N.A. Lavrentiev, and A.I. Privezentsev**

V.E. Zuev Institute of Atmospheric Optics SB RAS, Zuev Square, 1, Tomsk 634021, Russia

At present the competitive mechanisms of acquisition, interchange and retrieval of molecular spectroscopy digital data are e-mail, ftp-servers and the information systems based on Internet technologies. The information systems unite their resources by interchanging the data or by executing the queries to the resources of third-party information systems and thus turning into distributed information system[2], or socializing the metadata of these systems, in a virtual data center[3].

The creation of collective use tools requires the unification of resources. In our report some features of publication tools, partially developed by our group in the framework of VAMDC project[4], are discussed. Two of them, namely, data validity and data manipulation, are the main topic of the report.

The verification of formal constraints on the physical quantities published in papers and their information representation in composite data sources is of particular interest in problems of data validity. The following two types of constraints are discussed. The first one is the restrictions on the values of physical quantities derived from the mathematical model of processes, in particular, selection rules. The results of the verification of more than 700 primary data sources related to water spectroscopy are discussed. Another type of restrictions relate to the fact of data publication (existence constraint). The results of the checkup applied to Hitran data for a series of water isotopomers are discussed. These checkups are based on the data collected by IUPAC group[5]. The problem of creation of an information system containing a complete set of published data for a series of atmospheric molecules is discussed. The state of the art of the problem developed in IAO SB RAS is described.

Data manipulation tools are oriented on the data preparation for the solution of inverse problems of spectroscopy and the calculation of spectral functions. The tools provide the data retrieval in DIS, data transformation to different formats, and the execution of a set of binary operations. The tools will provide end-users possibility to develop and correct the composite data sets on the basis of published information. The typical restrictions used in these operations are discussed.

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VI-4. JPL Catalog Upgrades: New Tools, New Formats and New Interfaces

Brian J. Drouin, **Shanshan Yu**, **John C. Pearson**

Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109-8099

A makeover of the JPL Millimeter and Submillimeter Spectral Line Catalog has begun. This process is intended to provide 'single-line-access' to users and virtual astronomy facilities through a server/query interface. In order to provide these users with the maximum amount of reliability and trace-ability, the database format (traditionally ascii-text files on an http/ftp server) has been expanded to include data and data-sources in a format where the measurement data is listed independently of the model predicted line information. This information, although still accessible through the source text-files, is also compiled into a MySQL database. This methodology allows merging of measurement and prediction to be done at the meta-data level and gives the user quick access to the literature source.

Several databases (inlcuding the NIST rest frequencies and CDMS) with common information are each following a common methodology outlined for unified access to users via a 'virtual observatory'. Along with common formats, a special internet protocol, 'Single-Line-Access-Protocol' (SLAP) is to be instituted on the web-servers where these databases reside. This should enable the next generation of spectroscopic tools (i.e. atmospheric and astrophysical models) to be built on a flexible data layer which can access new database additions and changes without the need for localizing the information.

Through the upgrade process we intend to update and improve the current listings of the JPL catalog, with an emphasis on the trace-ability of the data to its source literature. The advent of grand modeling tools that support ever larger projects has the potential of leaving the data sources long forgotten. We intend to vitalize and encourage the linking of spectroscopic observations to the fundamental laboratory spectroscopy that forms the foundation of remote sensing.

VI-5. *SPECTRA*FACTORY.NET: a Database of Molecular Model Spectra for Astronomers

Jan Cami[a] and **Andrew J. Markwick**[b]

[a] *Department of Physics & Astronomy, University of Western Ontario, London, ON N6A 3K7, Canada*

[b] *Jodrell Bank Centre for Astrophysics, School of Physics & Astronomy, University of Manchester, Manchester, UK*

*Spectra*Factory.net is a homogeneous database of synthetic molecular absorption and emission spectra from the optical to mm wavelengths that is aimed at providing observational astronomers with an intuitive tool to identify spectral features of molecular origin. All spectra are calculated in the LTE limit from several molecular line lists (including HITRAN), and are presented at various spectral resolving powers corresponding to several specific astronomical instruments, including various ground-based observatories (e.g. Gemini, ESO-VLT) as well as space-based instruments (e.g. ISO, Spitzer, Herschel). The database is available online at `http://www.spectrafactory.net`, where users can freely browse, search, display and download the spectra. Additional model spectra can be requested for (automatic) calculation and inclusion. The database already contains over half a million model spectra for 39 molecules (96 different isotopologues) over the wavelength range 350nm – 3mm ($\approx 3 - 30000$ cm^{-1}).

*Spectra*Factory contains model spectra for a large range of temperatures and column densities that are relevant for various astrophysical purposes, but in particular for the identification and first-order analysis of molecular bands in spectroscopic astronomical observations. We will show a few examples of how these spectra have been used in various astrophysical contexts, discuss limitations and species on our "wish list", and briefly look at future updates and tools.

VI-6. Representing Scientific Databases Online

A. J. Markwick

Jodrell Bank Centre for Astrophysics, University of Manchester, Manchester, UK

Online offers scientific databases unique opportunities to deliver both data and representations of it. Drawing on practical experience gained over 10 years of deploying web-based such databases, in this talk I will describe what I think the pros and cons of doing so are, using as examples the UMIST Database for Astrochemistry (udfa.net); splatalogue (splatalogue.net); and spectrafactory (spectrafactory.net). I will describe some of the elements of construction of these database 'experiences', highlighting the value that can be added by considering how 'users' use data. I will also discuss some of the (not insignificant) problems that putting a database online can create, for you and for others.

SESSION VII: Planetary Atmospheres

VII-1. Recent Advances in the Spectroscopy of Planetary and Exoplanetary Atmospheres : What is out There?

Pierre Drossart

LESIA, Observatoire de Paris, 5, place Jules Janssen, 92195 Meudon, France

Since the early times of planetary spectroscopy with the detection of CH_4 on Jupiter (Herzberg, 1938), molecular spectroscopy has been essential to planetary atmospheres investigations. Both disciplines have presented a joint development and improvements of the techniques in planetary spectroscopy, together with laboratory and theoretical spectroscopy is an example of a fruitful interdisciplinary co-evolution.

Current questions in planetary atmospheres are now also shifted towards the understanding of exoplanets, where recent detections at low spectral resolution of H_2O, CH_4, CO_2 or CO (Tinetti et al, 2010) raise new questions about planetary evolution. Modeling of exoplanets poses a new challenge to spectroscopists, by requiring models at high temperature and shorter wavelength in the near infrared, implying to analyze hot bands and high-J rotational levels sometimes neglected in previous studies.

Despite a higher complexity in band analysis, with more combination bands and hot bands of simple molecules, or the detection of minor species of heavier molecules, the frontier of extended molecular spectroscopic database has moved towards near-infrared range, giving access to new studies for Venus, Giant Planets or Exoplanets deep atmospheres.

Some examples will be given from recent observations by space probes, including Hershel ESA space telescope.

VII-2. Titan's Neutral Atmospheric Chemistry from the Astronomical Point of View

Athena Coustenis

LESIA, Paris-Meudon Observatory, 5, place Jules Janssen, 92195 Meudon Cedex, France; athena.coustenis@obspm.fr

Our understanding of Titan's atmospheric chemical composition has recently been enhanced by the data returned by the Cassini instruments. Spectra recorded by the Composite Infrared Spectrometer (CIRS) aboard the Cassini spacecraft became available during the Titan flybys spanning three years now since SOI (Flasar et al., 2005;[1] Teanby et al., 2006, 2007;[2] Vinatier et al., 2007;[3] Nixon et al., 2008;[4] Coustenis et al., 2007,2008a[5]). The spectra characterize various regions on Titan with a variety of emission angles, and they pertain to the region between 70 and 500 km in altitude roughly. The 3 CIRS focal planes (covering the 10-1500 cm^{-1} spectral range with apodized resolutions of 2.54 or 0.53 cm^{-1}) give access to the thermal structure and the composition of Titan, containing several signatures of identified molecules: hydrocarbons (CH_4, CH_3D, C_2H_2, C_2HD, C_2H_4, C_2H_6, C_3H_4, C_3H_8, C_4H_2, C_6H_6, nitriles (HCN, HC_3N) and oxygen compounds (H_2O, CO and CO_2). In addition, several isotopes of C, N and O have been detected. The meridional variations of the trace constituents are tied to predictions by dynamical-photochemical models (Crespin et al., 2008;[6] Lavvas et al., 2007[7]). I will review our current understanding of the chemical composition in Titan's stratosphere from space and ground-based observations. The latter concern mainly the near-IR range from 0.8 to 5 micron, where a precise knowledge of the methane opacity is required to be able to infer other parameters, such as the surface composition. Titan studies require more and more precise information on the spectroscopic parameters in order to render models more accurate and performing. In trying to characterize Titans atmosphere from ground-based, ISO (Coustenis et al., 2006) or Cassini data one finds lacks in such parameters for known molecules, but also for the possible candidates predicted by photochemical models and laboratory simulations. I will discuss our current understanding (and lack thereof) of such input and in particular of the methane absorption coefficients in the near-IR and of the spectroscopic parameters for some molecules which could be useful for identifying new molecules in Jupiter, Saturn or Titan data

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[1] Flasar et al., 2005, Science 308, 975.

[2] Teanby et al., 2006, Icarus 181, 243; 2008, Icarus, 193, 595.

[3] Vinatier et al., 2007, Icarus, 188, 120.

[4] Nixon et al., 2008, 195, 778; 2009, Icarus, in press

[5] Coustenis et al., 2006, Icarus 180, 176; 2007, Icarus, 189, 35, 2008; Icarus 197, 539, 2010; Icarus, in press.

[6] Crespin et al., 2008, Icarus, 197, 556.

[7] Lavvas et al., 2008, Plan. Space Sci., 56, 27-99.

VII-3. High-Resolution Analysis of Various Propane Bands: Modeling of Titan's Infrared Spectrum

J.-M. Flaud

Laboratoire Inter Universitaire des Systemes Atmosphériques, CNRS, Université Paris Est et Paris 7, 61 Av du General de Gaulle, 94010 Créteil Cedex France

Optical measurements of atmospheric minor constituents are carried out using spectrometers working in the UV, visible, infrared and microwave spectral ranges. In all cases the quality of the analysis and of the interpretation of the atmospheric spectra requires the best possible knowledge of the molecular parameters of the species of interest. To illustrate this point we will concentrate on recent laboratory studies of propane.

Propane gas, which was first detected in the atmosphere of Titan by the Voyager1 IRIS spectrometer during the 1980 encounter, remains the heaviest saturated hydrocarbon (alkane) found there to date. The Composite Infrared Spectrometer (CIRS) instrument carried on-board the Cassini spacecraft possesses a much improved spectral and spatial resolution, and sensitivity over IRIS showing then clearly for the first time a multitude of propane bands. Thanks to a new line atlas for three bands of propane at shorter wavelengths (6-8 μm) it proved possible to model these weaker bands and to check the measurements made by CIRS using the "usual" 13 μm band alone. We will present the CIRS spectra showing all the visible propane bands and will report on the progress in the modelling of the 6-8 and 13 μm bands, and give an update on the propane abundance in the Titan atmosphere.

SESSION VIII: Laboratory spectroscopy-2

VIII-1. High-Resolution Tunable Diode Laser Spectroscopic Parameters for Atmospheric Applications and Comparisons with HITRAN

Virginie Zeninari, Bertrand Parvitte, Lilian Joly, Georges Durry

Groupe de Spectrométrie Moléculaire et Atmosphérique, Université de Reims Champagne-Ardenne, Fac des Sciences, Moulin de la Housse, BP 1039, 51687 Reims Cedex 2, Email : virginie.zeninari@univ-reims.fr

High resolution laboratory tunable diode laser spectrometers are nowadays commonly used to obtain accurate line rovibrational spectroscopic parameters in the infrared such as line strengths, self- and air-pressure broadening parameters, and their variation with temperature. Such a spectrometer presents the advantage to record one single line at high resolution ($>$ 1000 points/spectrum) in $\approx$10 ms. Thus the thermodynamic parameters (pressure, concentration, temperature) remain stable during the recording. These advantages are combined to a statistical study of the line parameters at various pressures, then parameters given at 296K can be compared to HITRAN.

Several tunable diode laser spectrometers have been developed in the GSMA laser team since approximately ten years. These spectrometers have been applied to several specific line parameters studies for atmospheric applications. Numerous examples will be presented: H_2O in the 1.39 μm region and CO_2 in the 1.60 μm region for the SDLA instrument, H_2O, CO_2 and their isotopologues for the TDLAS instrument, N_2O in the 7.9 μm region for the SPIRALE instrument and CO_2 near 2.05 μm for LIDAR applications. Accurate air pressure-shifts measurements for this region are still in progress. All these results will be thoroughly compared to HITRAN parameters.

To conclude, one can note that high resolution tunable diode laser spectroscopy have the main drawback to study only few lines in front of a whole vibrational band usually obtained with a Fourier-Transform instrument. Thus we currently develop an external-cavity laser to obtain a broadely tunable laser. This type of source will permit to study all ro-vibrational line parameters of an entire band at high resolution includind line shape studies.

VIII-2. Laser Spectroscopic Study of Ozone in the 100⇐000 Band for the SWIFT Instrument

Mickaël Guinet, Didier Mondelain, Christof Janssen and Claude Camy-Peyret

Laboratoire de Physique Molculaire pour l'Atmosphre et l'Astrophysique, UMR 7092, CNRS / UPMC Univ Paris 06, F-75005, Paris, France

A complete spectroscopic study of 15 strong ozone lines in the $1132.5 - 1134.5$ cm^{-1} spectral range has been undertaken in the framework of the development of the Stratospheric Wind Interferometer For Transport studies (SWIFT),[1] led by the Canadian Space Agency. Measurements have been performed with an interferometrically stabilized tunable diode laser spectrometer. Absolute line positions and intensities have been determined with high accuracy (4×10^{-5} cm^{-1} and 1 to 2%, respectively). Self- and air-broadening coefficients at 296 K have been obtained with an accuracy of 1%. The air-shifting coefficient and its temperature dependence have also been measured for unblended lines together with the temperature dependence of the air-broadening. We also performed an absolute measurement of the UV cross section at 253.65 nm. This value is in agreement with the value of Mauersberger [2] and lower (1.4%) than the currently recommended value of Hearn[3]. UV and IR absorption signals have been measured simultaneously. Using our UV value to calibrate the ozone concentration, we find line intensities that are 2.2% higher than HITRAN 2008 and they are higher by 2.6% if we use Mauersbergers UV cross section. This inconsistency of 3.6% between currently recommended IR intensities (HITRAN08) and UV cross sections[3,4] is in support of a previous study [5].

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[1] Guinet M., Mondelain D., Janssen C., Camy-Peyret C. *JQSRT* 11, 961–972, 2010.

[2] Mauersberger K., Hanson D., Barnes J., Morton J. *J. Geophys. Res.* 92, 8480–8482, 1987.

[3] Hearn A. G. *Proc. Phys. Soc.* 78, 932–940, 1961.

[4] Bass A. M., Paur R. J. *Ozone Symposium*, Greece, 1984.

[5] Picquet-Varrault B., Orphal J., Doussin J.-F., Carlier P., Flaud J.-M. *J. Phys. Chem. A* 109, 10081014, 2005.

VIII-3. New Acetone Absorption Cross Sections for ACE Retrievals

N. D. C. Allen, J. J. Harrison, P. F. Bernath

Department of Chemistry, University of York, Heslington, York, YO10 5DD, United Kingdom

ACE (Atmospheric Chemistry Experiment) is a Canadian-led mission on board the satellite SCISAT-1. The satellite has a Fourier Transform Spectrometer (FTS) which collects high resolution spectra in the infrared region of the electromagnetic spectrum (750-4400 cm^{-1}) using the solar occultation technique in order to detect a wide range of trace chemical species. The retrieval of these species relies upon the use of the HITRAN database for spectroscopic line parameters and absorption cross sections.

There is growing scientific interest in the remote detection of Volatile Organic Compounds (VOCs) in the atmosphere and the effect their emissions have on air quality. The significance of these species arises from their participation in a large number of photochemical reactions including the production of tropospheric ozone, which is governed by the mixing ratios of both nitrogen oxides (NO_x) and VOCs.

Acetone (C_3H_6O) is an abundant Oxygenated Volatile Organic Compound (OVOC) with a free tropospheric background concentration of up to 0.5 ppb in clean air at Northern mid-latitudes. Acetone has a large biogenic source including plant growth and decay, as well as oxidation of organic precursors such as terpenes. This tropospheric tracer gas has a lifetime estimated to be between 10 and 20 days and can be used to detect biomass plumes.

The global acetone budget is poorly constrained and, like many larger VOCs, there is insufficient laboratory spectroscopic data. A new set of high resolution acetone infrared absorption cross sections have been recorded and the spectroscopic data will be added to the HITRAN database. A full global distribution of acetone is being retrieved from ACE.

VIII-4. Infrared Absorption Cross Sections of ClOOCl - Laboratory Work and Application in MIPAS-B Measurements

Manfred Birk,[a] **Georg Wagner,**[a] **Hermann Oelhaf,**[b] **Gerald Wetzel**[b]

[a]*Deutsches Zentrum für Luft- und Raumfahrt, Institut für Methodik der Fernerkundung, Wessling, Germany*

[b]*Karlsruhe Institute of Technology, Institute for Meteorology and Climate Research, Karlsruhe, Germany*

Chlorine peroxide, ClOOCl, is involved in the ozone depletion cycle in polar perturbed chemistry (e.g. antarctic ozone hole). Despite its importance there has been no direct detection of this molecule in atmospheric spectra until recently due to the missing spectroscopic database and rather weak spectroscopic features in IR atmospheric spectra superimposed by strong O3 and CO2 lines.

The first part of the present paper will report on laboratory work on mid infrared absorption cross sections of ClOOCl already done in 2000. ClOOCl was produced in a flow reaction of Cl and Cl2O via ClO self reaction below 260 K. Number densities were derived from far infrared measurements utilizing intensities of pure rotational transitions. Measurements were carried out with a high resolution Bruker IFS120HR Fourier-transform spectrometer. A coolable 80 m absorption path multireflexion cell was applied for the subsequent FIR/MIR measurements. Although high resolution structure was partly resolved due to the high complexity (heavy molecule, four isotopologues, internal rotation) absorption cross sections at two different temperatures and total pressures were measured and supplied as spectroscopic database.

The second part will show the first direct atmospheric observations of ClOOCl from MIPAS-B (Michelson Interferometer for Passive Atmospheric Sounding) balloon-based measurements from Kiruna (Sweden) on 11 January 2001 with nighttime values of nearly 1.1 ppbv at 20 km (cf. Wetzel et al., ACP, 10, 931-945, 2010).

VIII-5. Spectral Line Parameters in the ν_9 Band of Ethane

V. Malathy Devi,[a] **D. Chris Benner,**[a] **C. P. Rinsland,**[b] **M. A. H. Smith,**[b]
R. L. Sams,[c] **T. A. Blake,**[c] **J.-M. Flaud,**[d] **K. Sung,**[e] **L. R. Brown,**[e]
A. W. Mantz[f]

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

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

[c] *Pacific Northwest National Laboratory, Richland, WA 99352, U.S.A.*

[d] *Laboratoire Interuniversitaire des Systems Atmospheriques, C.N.R.S., UMR 7583, Universits Paris Est and Paris 7, 94010 Cretiel Cedex, France*

[e] *Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109, U.S.A.*

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

Spectral line parameters, including line center positions, absolute line intensities, self- and N_2-broadened halfwidth coefficients, and the temperature dependences of these halfwidth coefficients, have been measured for more than 1330 transitions in the ν_9 band of ethane (C_2H_6) by applying a multispectrum nonlinear least squares analysis technique.[1] We analyzed a total of 43 high-resolution (0.00156-0.005 cm^{-1}) infrared absorption spectra recorded with two different Bruker Fourier transform spectrometers (at PNNL and at JPL) at various sample path lengths, pressures and temperatures. The ν_9 fundamental of C_2H_6 is the strongest band in the terrestrial spectral window, and it is often used for ethane identification and abundance determination in remote sensing of planetary atmospheres. Torsional splittings are fairly large (dependent upon J, K) and measurable in several ${}^rQ$ and ${}^pQ$ sub-band structures. However, in the case of the ${}^rQ_0$ sub-band the two split components are completely obscured because of the overlap of Doppler-broadened J transitions. The results from the present study[2] will be compared with other published data.

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[1] D. Chris Benner, C. P. Rinsland, V. M. Devi, M. A. H. Smith, and D. A. Atkins, JQSRT 1995;53:705-21.

[2] The spectra were recorded at the Jet Propulsion Laboratory (JPL) and at the W. R. Wiley Environmental Molecular Sciences Laboratory, a national user facility located at Pacific Northwest National Laboratory (PNNL) sponsored by the Department of Energy's Office of Biological and Environment Research. PNNL is operated for the United States Department of Energy by the Battelle Memorial Institute under Contract DE-AC05-76RLO1830. The research at the College of William and Mary, NASA Langley Research Center, Connecticut College and the Jet Propulsion Laboratory, California Institute of Technology, was performed under contracts and cooperative agreements with the National Aeronautics and Space Administration.

VIII-6. A THz Photomixing Synthesizer Based on a Fiber Frequency Comb Dedicated to High Resolution Spectroscopy of Atmospheric Compounds

Arnaud Cuisset, Francis Hindle, Gaël Mouret, Chun Yang, Sophie Eliet, Robin Bocquet

Laboratoire de Physico-Chimie de l'Atmosphère, Université du Littoral Côte d'Opale, 189A Ave. Maurice Schumann, 59140 Dunkerque, France

To date the principal application for photomixing sources has been for high resolution spectroscopy of gases due to the large tuning range and spectral purity. New developments of the opto-electronic THz spectrometer have been performed in order to obtain a powerfull tool for high-resolution spectroscopy. The combination of two extended cavity laser diodes and fast charge carrier lifetime semiconductor materials has allowed a continuous-wave THz spectrometer to be constructed based on optical heterodyning. Unlike many THz sources, this instrument gives access to all frequencies in the range 0.3 to 3.5 THz with a resolution of 1 MHz. Amongst the spectroscopic applications of this spectrometer, precise recording of pure rotational high J line profiles of OCS and HCN have been performed, allowing the determination of new broadening parameters include in HITRAN2008.[1,2] With an improved sensitivity by means of a THz propagation in a multipass cell, the rotational spectra of numerous molecules such as OH, H_2S, H_2CO, HCOOH, NH_3, H_2CCHCl, $SO(CH_3)_2$... have been measured with this spectrometer. One limitation of the THz spectrometer was accuracy with which the generated frequency is known. Recently, this obstacle have been overcome with the construction of a photomixing spectrometer where the two pump lasers are phase locked to two modes of a repetition rate stabilized frequency doubled fiber laser frequency comb.[3] In order to achieve a tuning range in excess to 100 MHz a third cw laser was required in the new configuration of the THz spectrometer. To assess the performance of this instrument, the frequencies of the pure rotational transitions of OCS molecules have been measured beetween 0,8 to 1,2 THz. A rms inferior to 100 kHz, deduced from the fitted frequencies, demonstrates that the accuracy of the THz photomixing synthesizer is now competitive with the accuracy of the microwave and submillimeter techniques.

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[2] C. Yang, J. Buldyreva, I. E. Gordon, F. Rohart, A. Cuisset, G. Mouret, R. Bocquet, F. Hindle,*J. Quant. Spectrosc. Radiat. Transfer*, 2008, **109:** 2857.

[3] G. Mouret, F. Hindle, A. Cuisset, C. Yang, R. Bocquet, M. Lours, D. Rovera, *Opt. Express*, 2009, **17:** 22031.

VIII-7. Toward a Global Model of Low-Lying Vibrational States of CH_3CN: Overview and Interactions in the $v_4 = 1$ State at 920 cm^{-1} with Nearby States

Holger S. P. Müller,[a] B. J. Drouin,[b] J. C. Pearson,[b] L. R. Brown,[b]
I. Kleiner,[c] R. L. Sams[d]

[a]*I. Physikalisches Institut, Universität zu Köln, 50937 Köln*

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

[c]*LISA, Université Paris 12 & Paris 7 & CNRS, 94010 Créteil, France*

[d]*PNNL, Richland, WA 99352, USA*

Methyl cyanide, CH_3CN, is an important interstellar molecule, in particular in hot and dense molecular cores, and it may play a role in the atmospheres of planets or of Titan. Therefore, we have recorded extensive rotational and rovibrational spectra up to ~ 1.6 THz and ~ 1500 cm^{-1}, respectively. The present investigation extends our analysis of states with $v_8 \leq 2$ at vibrational energies below 740 cm^{-1},[1] which will be summarized briefly, and takes into consideration findings from an analysis of the ν_4 band and the higher-lying ν_7 (at ~1042 cm^{-1}) and $3\nu_8^1$ (at ~1078 cm^{-1}) bands.[2] The rotational data extend to $J = 87$ and $K = 15$, infrared assignments currently extend to 55 and 12, respectively. Parameters affecting only $v_7 = 1$ or $v_8 = 3$ as well as some additional interaction parameters were kept fixed to values from (*b*). The largest perturbations of $v_4 = 1$ are caused by a $\Delta k = 0$, $\Delta l = 3$ interaction with $v_8 = 3$ at $K = 8$. Despite the inclusion of the interaction parameter and a centrifugal distortion correction, residuals amount to more than 200 MHz very close to the resonance. Removal of these residuals probably requires explicit inclusion of $v_8 = 3$ data. Several additional perturbations exist at lower as well as higher K with $v_8 = 2$, $v_7 = 1$ and $v_8 = 3$. Higher values of K are difficult to reproduce in spite of an extensive set of distortion parameters which, at highest orders, have rather large magnitudes, possibly indicating unaccounted interactions which would probably occur with states even higher than $v_8 = 3$.

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[2] A.-M. Tolonen et al., *J. Mol. Spectrosc.* **160** (1993) 554−565.

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PI-14. Analysis of spectral line parameters of 1.27 micron band for laser absorption spectrometer based atmospheric oxygen measurements

Narasimha S. Prasad,[a] **and V. Malathi Devi,[b]**

[a]NASA Langley Research Center, 5 N. Dryden St., MS 468, Hampton, VA 23681
[b]Department of Physics, College of William and Mary, Williamsburg,
VA 23187-8795

NASA Langley Research Center is involved in the development of a novel laser absorption spectrometer for oxygen measurements to satisfy requirements of the proposed Active Sensing of CO_2 Emissions over Nights, Days, & Seasons (ASCENDS) mission. The goals of ASCENDS mission is to quantify global spatial distribution of atmospheric CO_2 on scales of weather models as well as terrestrial and oceanic sources and sinks of CO_2 during day/night over all seasons. Enhanced understanding of CO_2 sources and sinks in the global carbon cycle is required for refining climate models. As such, ASCENDS mission is anticipated to provide a scientific basis for future projections of CO_2 sources and sinks through data-driven enhancements of Earth-system process modeling. ASCENDS will deliver laser based remote sensing measurements of CO_2 mixing ratios (XCO_2) day and night, at all latitudes, and during all seasons. The plan is to have several simultaneous measurements to be made that include CO_2 number density tropospheric column and O_2 number density column. O_2 sensing helps in determining surface pressure that is required for converting CO_2 to XCO_2.

Currently, CO_2 column measurements using the 1.57 μm spectral band are being successfully carried out from airborne platforms. The 1.27 micron band has been selected for surface pressure measurements using O_2 Laser Absorption Spectrometer due to architectural advantages and cross-section values. However, lines in this band are being carefully analyzed for optimal design of laser based instrumentation. For precision concentration measurements, the selected O_2 lines have to be highly insensitive to atmospheric parameters while providing optimal SNR values. Accordingly, influence of atmospheric parameters on the measurement of optical depth to select optimal oxygen lines is being investigated.

Accurate measurements of spectral line parameters for the 1.27 μm O_2 band are extremely difficult to make. Neglecting parameters such as line mixing, line narrowing and speed dependence in the spectrum analysis will adversely affect the accuracy of the retrieved parameters and hence will seriously hamper the retrievals of O_2 atmospheric concentration/mixing ratio. At best Voigt profiles can produce parameters that only have meaning at the 1% level even from for less complicated spectra. For high resolution oxygen measurements the situation is worse due to the strong influence of line mixing. The ultimate goal of our ongoing efforts is to be able to retrieve accurate O_2 abundance from atmospheric remote sensing spectra with a high precision of ~0.5% that has not been achieved so far. To achieve this goal, we have undertaken a systematic and careful laboratory analysis of the O_2 spectra in the 1.27 μm and successfully apply its spectroscopic line parameters to atmospheric remote sensing measurements. Accordingly, we are investigating methodologies to collect high resolution O_2 line spectra in the laboratory under carefully controlled pressure and temperature conditions. The various line parameters will be retrieved by fitting all spectra simultaneously. Calibration of the line parameters (including line center positions, absolute intensities, and other important line shape coefficients for Lorentz broadening, pressure-induced shifts, line mixing, speed dependence and/or line narrowing and their temperature dependences) near 1.27 μm to the accuracy required for the O_2 sensor will be carried out. In this paper, preliminary results of sensitivity analysis of oxygen absorption Lines in the 1.27 μm spectral band followed by near term plans for experimental and subsequent spectral analysis will be presented.

VII-4. Mid and Far-Infrared Spectroscopy in Astrophysics

José Cernicharo

CAB. INTA-CSIC. Crta Torrejón Km 4. 28005 Madrid, Spain

The Herschel satellite was launched in May 2009 and is equipped with spectroscopic instruments in the submillimeter and far-IR domains. It the last months it has provided a huge amount of spectroscopic data of interstellar and circumstellar sources. I will present some of these results, together with mid-infrared high spectral resolution observations taken with ground based facilities.

In order to interpret these data, astrophysicists need an important input from the spectroscopic community such as more complete spectroscopic databases in the mid and far infrared domains, line intensities, and collisional rates.

CONFERENCE PROGRAM

DAY 1, Wednesday 16 June

7:30 Registration

9:00 WELCOME .... Laurence S. Rothman

SESSION I: Databases-1

Chair: A. Barbe

9:10 Spectroscopic Molecular Databases: Evolution and Revolution .... L. S. Rothman

9:25 The GEISA Database 2009 Edition: Update Description and Assessment of Spectroscopic Parameters Through Hyperspectral Remote Sensing Applications .... N. Jacquinet

9:40 Blended HITRAN and other Spectra Databases for Modeling Emission-based LIDAR .... D. Plutov

9:55 Calculating the Spectroscopic Behaviour of Hot Molecules .... J. Tennyson

10:25 High-Accuracy *ab initio* Water Line Intensities .... L. Lodi

10:40 CDSD-4000: High-Temperature Spectroscopic CO_2 Databank. S.A. Tashkun

10:55 *Coffee Break*

SESSION II: Remote Sensing

Chair: K. Chance

11:15 Line Parameters and Forward Calculation for Retrieving Carbon Dioxide and Methane from GOSAT data .... T. Yokota

11:45 MIPAS: New Results and Spectroscopy Issues .... J. Orphal

12:00 The Atmospheric Chemistry Experiment, ACE: Status and Spectroscopic Issues .... P. F. Bernath

12:15 Spectroscopy for the Atmospheric Chemistry Experiment (ACE) C. Boone

12:30 *Lunch Served*

13:45 Spectroscopic Issues in the Data Analysis of REFIR-PAD Measurements Performed During the 2009 Ground-Based Campaigns .... G. Bianchini

14:00 Polar Mesospheric Clouds and Cosmic Dust: Three Years of SOFIE Measurements .... M. McHugh

14:15 LBL Models: State of the Art and Perspective .... B. A. Fomin

14:30 *Coffee Break*

SESSION III: Laboratory Spectroscopy-1

Chair: L. R. Brown

14:45 The Absorption Spectrum of Methane Between 1.27 and 1.71 μm by High Sensitivity CRDS at 80 K and 300 K. Importance of the CH_3D Contribution in the 1.58 μm Transparency Window .... A. Campargue

15:15 The $4\nu_3$ Spectral Region of Methane .... D. Chris Benner

15:30 Line Strengths and Self-Broadening of Pure Rotational Lines of Carbon Monoxide and Nitrous Oxide Measured by Terahertz Time-Domain Spectroscopy .... W. Aenchbacher

15:45 Submillimeter-Wave and Far-Infrared Spectroscopy of High-J Transitions of Ammonia .... S. Yu

16:00-18:00 **POSTER SESSION 1**

DAY 2, Thursday 17 June

SESSION IV: Databases-2

Chair: M. A. H. Smith

9:00 Error Propagation from Line Parameters to Spectra Simulations. Illustration on High Temperature Methane .... J.-P. Champion

9:30 High-Lying Rotational Levels of Water Obtained by FIR Emission Spectroscopy .... L. Coudert

9:45 Assignment of the $5\nu_4$ and $\nu_2 + 4\nu_4$ band system of $^{12}CH_4$ in the Region 6287-6550 cm^{-1} .... Vl. G. Tyuterev

10:00 Towards New Line List of Magnetic Dipole and Electric Quadrupole Transitions in the $a^1\Delta_g \leftarrow X^3\Sigma_g^-$ Band of Oxygen .... I. E. Gordon

10:15 Update for Methyl Chloride at 3 μm .... A. Perrin

10:30 Indices of Refraction of Absorptive Aerosol - Their Importance and Complexity .... S. Massie

10:45 *Coffee Break*

SESSION V: Line Shapes

Chair: P. F. Bernath

11:00 The Importance of Being Earnest about Line Shapes .... L. R. Brown

11:10 Improvements, Corrections and New Developments in Semiclassical Theories of Collisional Line Broadening .... J. Buldyreva

11:40 Spectral Shapes Modeling and Remote Sensing of Greenhouse Gases: Toward the OCO and GOSAT Experiments and Future HITRAN Issues .... J.-M. Hartmann

12:10 An Improved Version of the CO_2 Line-mixing Database and Software: Update and Extension .... A. L. Laraia

12:25 *Lunch Served*

Chair: J.-M. Flaud

13:45 The Collision-Broadened Line Shape of CO_2 via the Complex Robert-Bonamy Method: The Complexity of Simplicity .... R. R. Gamache

14:00 Uncertainties Associated with Theoretically Calculated N_2 Broadened Half-Widths of H_2O Lines .... Q. Ma

14:15 Complex Robert-Bonamy Calculation of H_2O Broadened by N_2, O_2 and Air Made with Realistic Trajectories .... J. Lamouroux

14:30 N_2 Collisional Broadening of Methane in the THz Region Measured at the SOLEIL Synchrotron .... V. Boudon

14:45 N_2-broadened $^{13}CH_4$ at 80 to 296 K .... M. A. H. Smith

15:00 Formaldehyde Broadening Coefficients: the 5.7μm and 3.6μm Bands .... D. Jacquemart

15:15-17:15 **POSTER SESSION 2**

18:30 *Banquet*

DAY 3, Friday 18 June

SESSION VI: Database Structure

Chair: I. E. Gordon

9:00 Information System to Access HITRAN via the Internet .... Yu. L. Babikov

9:15 New Tools for Storing and Accessing Spectroscopic Data: the Development of an XML Schema for the HITRAN Database .... C. Hill

9:30 Publishing Tools for a Distributed Information System .... A. Z. Fazliev

9:45 JPL Catalog Upgrades: New Tools, New Formats and New Interfaces .... B. J. Drouin

10:00 *SPECTRA*FACTORY.NET: a Database of Molecular Model Spectra for Astronomers .... J. Cami

10:15 Representing Scientific Databases Online .... A. Markwick

10:30 *Coffee Break*

SESSION VII: Planetary Atmospheres

Chair: J. Vander Auwera

10:45 Recent Advances in the Spectroscopy of Planetary and Exoplanetary Atmospheres : What is out There? .... P. Drossart

11:15 Titan's Neutral Atmospheric Chemistry from the Astronomical Point of View .... A. Coustenis

11:45 High-Resolution Analysis of Various Propane Bands: Modeling of Titan's Infrared Spectrum .... J. -M. Flaud

12:15 *Lunch Served*

SESSION VIII: Laboratory Spectroscopy-2

Chair: D. Jacquemart

13:25 High-Resolution Tunable Diode Laser Spectroscopic Parameters for Atmospheric Applications and Comparisons with HITRAN .... V. Zeninari

13:45 Laser Spectroscopic Study of Ozone in the 100⇐000 Band for the SWIFT Instrument .... M. Guinet

14:00 New Acetone Absorption Cross Sections for ACE Retrievals .... N. Allen

14:15 Infrared Absorption Cross Sections of ClOOCl - Laboratory Work and Application in MIPAS-B Measurements .... M. Birk

14:30 Spectral Line Parameters in the ν_9 Band of Ethane .... V. Malathy Devi

14:45 A THz Photomixing Synthesizer Based on a Fiber Frequency Comb Dedicated to High Resolution Spectroscopy of Atmospheric Compounds .... A. Cuisset

15:00 Toward a Global Model of Low-Lying Vibrational States of CH_3CN: Overview and Interactions in the $v_4 = 1$ State at 920 cm^{-1} with Nearby States .... Holger S. P. M