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2006

The 9th HITRAN Database Conference

HARVARD-SMITHSONIAN CENTER
FOR ASTROPHYSICS
CAMBRIDGE MA, USA

26 -28 June 2006

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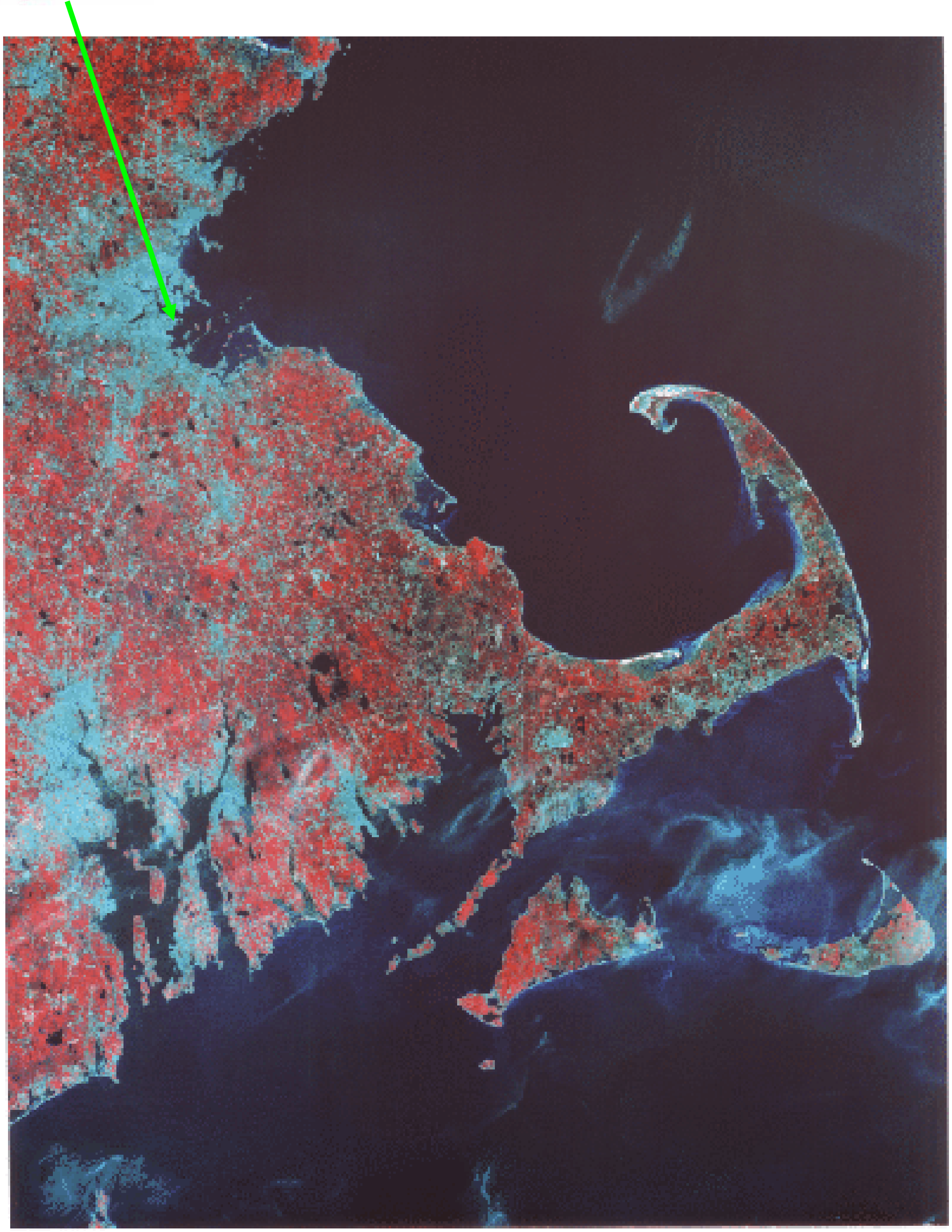

CONFERENCE PROGRAM

DAY 1, Monday 26 June

7:30 Registration

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

9:10 KEYNOTE . . . . Stephen S. Murray

SESSION 1: Laboratory Spectroscopy

9:30 The Quest for Consistency and Accuracy of Spectroscopic Parameters in HITRAN: Bridge between Archive and Application Laurence S. Rothman

10:00 Diode- and Difference-Frequency Laser Studies of Atmospheric Molecules in the Near- and Mid-infrared: H_2O, NO_2, and NH_3 Johannes Orphal

10:30 Water Pressure Broadening: A Never-ending Story . . . . Georg Wagner

11:00 *Coffee Break*

11:15 Analysis of High Resolution Infrared CW-CRDS Spectra of Ozone in the 6000-6750 cm^{-1} Spectral Region . . . . A. Barbe

11:45 Relief is on the Way: Status of the Line Positions and Intensities for Nitric Acid . A. Perrin

12:15 *Lunch Served*

SESSION 2: Theory

13:30 The Water Molecule: Line Position and Line Intensity Analyses up to the Second Triad Laurent H. Coudert

14:00 Global Frequency and Infrared Intensity Analysis of $^{12}CH_4$ Lines in the 900–4800 cm^{-1} Region . . . . V.Boudon

14:30 Temperature Dependence of N_2-, O_2-, and Air-Broadened Half-Widths of Water Vapor Transitions: Insight from Theory and Comparison with Measurement . . . . R. R. Gamache

15:00 Modifications of the Robert-Bonamy Formalism and Further Refinements Required . Q. Ma

15:30 Using Laboratory FT-IR Spectrometer Measurements and HITRAN to Derive the Pure Water Vapour Continuum Between 3000 cm^{-1} and 8000 cm^{-1} . . . . David Paynter

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

19:00 *Dinner, Inn at Harvard*

DAY 2, Tuesday 27 June

SESSION 3: Remote Sensing

9:00 What about the Spectral Parameters when Performing Synergistic Atmospheric Measurements? . . . . J.-M. Flaud

9:30 Linelist Needs for the Atmospheric Chemistry Experiment . . . . C. D. Boone

10:00 CO_2 Spectroscopy Evaluation Using FTS Spectra . . . . B. Sen

10:30 *Coffee Break*

11:00 Infrared Laboratory Spectroscopy of CH_4 and CH_3D for Atmospheric Remote Sensing Linda R. Brown

11:30 Spectroscopic Parameter Requirements for Remote Sensing of Terrestrial Planets Mary Ann H. Smith

12:00 *Lunch Served*

SESSION 4: Laboratory Spectroscopy

13:30 THz Studies of Water Vapor D. F. Plusquellic

14:00 HDO and D_2O Long Path Spectroscopy: On-Going Work of the Brussels-Reims Team L. Daumont

14:30 Air Broadened Ozone Linewidths in the Submillimeter Wavelengths . . . . Brian Drouin

15:00 A complete set of line parameters for CH_3Br in the 10-μm spectral region . . . D. Jacquemart

15:30 High Resolution Assignment of ν_{14} and ν_{16} Bands in the 10 μm for Trans-Acrolein L.-H. Xu

16:00-18:00 **POSTER SESSION 2**

DAY 3, Wednesday 28 June

SESSION 5: Databases

9:00 Recent Developments in the Cologne Database for Molecular Spectroscopy, CDMS, and the Need for Further Laboratory Spectroscopic Data . . . . H. S. P. Müller

9:30 Assessment of the GEISA and GEISA/IASI-03 Spectroscopic Data Quality: through Comparisons with Other Public Database Archives N. Jacquinet-Husson

10:00 A Comprehensive Database for Water Spectra Jonathan Tennyson

10:30 *Coffee Break*

10:45 New Cross Sections, Indices of Refraction, and Reflectance Spectra of Atmospheric Interest S. Massie

11:15 MolExplorer: A New Tool for Computation and Display of Spectra from the HITRAN Database . . . . H. Harde

11:45 First Definition and Implementation of Standards for the Exchange of Atomic and Molecular Data . . . . M.L. Dubernet

DAY 1, Monday 26 June

DAY 2, Tuesday 27 June

DAY 3, Wednesday 28 June

SESSION 1: Laboratory Spectroscopy

The Quest for Consistency and Accuracy of Spectroscopic Parameters in HITRAN: Bridge between Archive and Application

Laurence S. Rothman

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Recent satellite remote-sensing experiments are making unprecedented demands on the spectroscopic databases. The reasons arise from numerous factors, for example high signal-to-noise, broad spectral coverage, long path lengths, and improved retrieval algorithms. The progress of the experiments was highlighted in the workshop, Atmospheric Science from Space using Fourier Transform Spectrometry, held last year in Canada[1].

Among the requirements anticipated by current and future space missions is the need to obtain a global consistency of spectral parameters. For adequate retrievals of the atmospheric state, line intensities will be required to be good to the one-percent level for different bands, within the band, and between different isotopologues. The same is true for the collision-broadened half-widths.

We present some examples of the quest for consistency and the efforts for validation of the HITRAN database archive.

The current effort has been supported by the NASA Earth Observing System (EOS), under grant NAG5-13534.

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[1] Proceedings of the 12th Workshop Atmospheric Science from Space using Fourier Transform Spectrometry (ASSFTS), Quebec City, Canada, 18-20 May 2005.

Diode- and Difference-Frequency Laser Studies of Atmospheric Molecules in the Near- and Mid-infrared: H_2O, NO_2, and NH_3

Johannes Orphal, **Pascale Chelin**, **Pierre-Marie Flaud**, and **Nofal Ibrahim**

Université de Paris-12, Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), Créteil, France

The advantages of using external cavity diode-lasers (ECDL) for quantitative spectroscopy in the laboratory are in particular the absence of any significant instrumental line shape (ECDL have typical emission line widths of 1 MHz i.e. a few 0.00001 cm^{-1}), the fast temporal response and the high signal-to-noise ratio that can be achieved in rather short experiments.

We have used near-infrared ECDL to study line widths and intensities of H_2O around 820 nm and of NH_3 around 1.5 μm. The results are compared with HITRAN and with previous experimental studies. For NH_3 we have also recorded new near-infrared absorption spectra using a Bruker IFS 120 HR Fourier transform spectrometer, to investigate significant discrepancies concerning the line positions and intensities from the available literature.

Recently we have constructed a compact difference frequency (DFG) laser that is operating in the mid-infrared region between $1900 - 3100$ cm^{-1} by mixing a tuneable ECDL ($820 - 880$ nm range) with a cw Nd:YAG laser (1064 nm) using a Periodically Poled Lithium Niobate – PPLN – crystal as non-linear medium. This DFG laser (also 1 MHz linewidth) was used to study line positions and intensities of NO_2 in the 3.5 μm region and in particular to compare the line intensities with the absorption cross-sections of NO_2 in the 400 nm region that are known to within better than 2%. Again the results are compared with the HITRAN database.

We are now moving towards using ECDL for studying unstable species and radicals.

Water Pressure Broadening: A Never-ending Story

Georg Wagner, Manfred Birk

DLR – Remote Sensing Technology Institute, Oberpfaffenhofen, Germany

Numerous papers on pressure broadening of water have been published, however, with differences exceeding stated uncertainties. The present work attempts to initiate a process towards better defined uncertainties.

Self- and airbroadened water vapour spectra were recorded with a Bruker IFS120HR in the range from 1250 to 1750 cm^{-1}. 45 measurements covered the temperature range 208 – 316 K, air pressures from 0 – 1000 mbar, sample pressures 0.0004 – 5 mbar, and absorption paths 0.16 – 84 m. To allow for quality assurance, care was taken to cover most lines by several measurements with different opacity and linewidth. Furthermore, the data cover five orders of magnitude in intensity. Transmittance spectra were corrected for detector non-linearity and channeling. Line-by-line analysis was done on a microwindow basis resulting in positions, linestrengths and linewidths using the Voigt function as monochromatic lineshape. In the line fitting, especially of the 50 mbar measurements, the residual spectra show systematic deviations due to Dicke narrowing which are mostly smaller than 1%. The further data reduction was done with a new software tool which reads the broadening data and fits air and self pressure broadening parameter and temperature exponent. The software compiles the experimental data for each transition and selects the parameters to be fitted. The software also allows for various data quality assessments which are presented in this talk. This quality assessment revealed that 50 mbar measurements had to be excluded from the data analysis due to the Voigt profile being not capable of yielding pressure- and opacity-independent broadening parameters for these measurements.

An important quality assessment is the intercomparison with hot cell measurements which were obtained a few years ago using a different cell, beamsplitter, detector, higher air pressure (500, 1000 mbar) and a different flow setup. The line broadening agreed within 1% on average. Finally, the differences of measured and calculated spectra were investigated showing almost pure instrumental noise and thus indicating that the data reduction is not introducing systematic errors.

In total the number of air broadening parameters is 985 (ν_2: 44% $\mathrm{H_2O}$, 17% $\mathrm{H_2^{18}O}$, 10% $\mathrm{H_2^{17}O}$, 12% HDO, $2\nu_2 - \nu_2$ $\mathrm{H_2O}$: 17%) and of temperature exponents is 672. The resulting data show that in contrast to ozone the pressure broadening cannot be expressed in polynomials in the quantum numbers. Intercomparison with HITRAN 2004 and other authors, especially Toth, will be discussed.

Analysis of High Resolution Infrared CW-CRDS Spectra of Ozone in the $6000 - 6750$ cm^{-1} Spectral Region

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

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The fibered Distributed Feed-Back (DFB) diode laser CW-CRDS spectrometer of LSP Grenoble, has been used to record the absorption spectrum of ozone in the 6000-6750 cm^{-1} region with a typical sensitivity of α_{min} ~3×10^{-10}cm^{-1}. Transitions as weak as 1×10^{-27} cm^{-1}/ mol. cm^{-2} (296 K) could be detected. Removing usual impurities as H_2O, CO, CO_2, a total of 5578 transitions have been assigned to 15 bands (9 A type and 6 B type).

We present an overview of this work, in course, and present in detail two specific spectral ranges, where analysis are complete, that is to say $5970 - 6210$ and $6640 - 6830$ cm^{-1}. For these regions, we give: range of assigned quantum numbers, Hamiltonian and transition moment parameters, statistics for positions and intensities and examples of agreement between observations and calculations.

Relief is on the Way: Status of the Line Positions and Intensities for Nitric Acid

A. Perrin,[a] J.-M. Flaud,[a] J. Orphal,[a] F. Mencaraglia,[b] G. Bianchini,[b] A. Boscaleri,[b] B. Carli,[b] S. Ceccherini,[b] P. Raspollini,[b] G. Brizzi,[c] M. Carlotti,[c] and M. Ridolfi[c]

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[b]*Istituto di Fisica Applicata Carrara, Via Panciatichi 64 - 50127 Firenze - Italy*

[c]*Dipartimento di Chimica Fisica e Inorganica, Università di Bologna, Viale del Risorgimento, 4 – 40136 Bologna, Italia*

In this paper, we will make a review of the status of the HNO_3 line parameters.

Using new and accurate experimental results concerning the spectroscopic properties of the HNO_3 molecule in term of line positions, line intensities and line air-broadening parameters as well as improved theoretical methods it has been possible to generate an improved set of line parameters for this molecule both in the broadband spectral region covered by the MIPAS (Michelson Interferometer for Passive Atmospheric Sounding) instrument operating on EnviSAT and in the far infrared spectral region.

The validation of satellite measurements like MIPAS is aimed at identifying possible systematic errors. In order to identify those which are due to the spectroscopic parameters, it is required to perform retrievals using a different instrument operating in a different spectral region. Therefore HNO_3 profiles measured at 11 μm by MIPAS were validated with the IBEX (Infrared Balloon EXperiment) measurements performed in the far infrared region. An agreement of ±5% is obtained between the profiles achieved by these two instruments after significant upgradings of the spectroscopic databases in both spectral regions.

We will describe the updates will have been performed recently since the previous 2004 version of HITRAN. Also some spectral regions need to be improved (in terms of line positions and line intensities), and we will recommend further studies.

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[1] J-.M.Flaud, C.Piccolo, B.Carli, A.Perrin, L.H.Coudert, J.L.Teffo, and L. R.Brown, J. *Atm. and Ocean Optics, 16, (2003) 172-182.*

[2] A.Perrin, C.Puzzarini, J.-M.Colmont, C.Verdes, G.Wlodarczak, G.Cazzoli, S.Buehler, J.-M.Flaud, and J.Demaison, *J. of Atmos. Chemistry 51 (2005) 161-205.*

[3] F. Mencaraglia, G. Bianchini, A. Boscaleri, B. Carli, S. Ceccherini, P. Raspollini, J.-M. Flaud and A. Perrin, *J. Geophys. Res. (in press).*

SESSION 2: Theory

The Water Molecule: Line Position and Line Intensity Analyses up to the Second Triad

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With a view towards building a highly accurate database for the water molecule in the 1000 to 2000 cm^{-1} region, line position and line intensity analyses of a large body of high-resolution data were carried out. For both analyses, the bending-rotation theoretical approach[1] was used. The body of data fitted in the line position analysis consists of experimental energies as well as microwave, FIR, and IR transitions. In the line strength analysis, experimental line intensities were fitted. For both analyses, the data involve the first eight vibrational states of water, that is, all the vibrational states up to the second triad.

In the first part of the paper, the results of the line position analysis will be reported and the inclusion in the data set of the recent microwave measurements of Matsushima *et al.*[2] will be discussed. The second part of the paper we will devoted to the line strength analysis. The results obtained fitting the new measurements of Toth[3], concerning transitions involving one the states of the second triad, will be reported.

Although the results of both the line position and the line intensity analyses are satisfactory, they indicate that there are inconsistencies within and between the various sets of of data. This is certainly the case of the line intensity data for transitions belonging to the ν_2 band, which is the band for which there is the largest amount of data. For this band the measurements reported by Toth[4] are available as well as the recent ones carried out at DLR. Depending on the set of data being considered, the observed minus calculated residuals, in % of the observed strength, do not display the same behavior when the strength increases from 10^{-25} to 10^{-19} $\mathrm{cm}^{-1}/\mathrm{molecule}\cdot\mathrm{cm}^{-2}$. This behavior will be given for the line strengths reported by Toth[4] and for those measured in the present work. Issues addressing the data quality and reasons for the differences of the data sets will be discussed.

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[1] Coudert, *J. Molec. Spectrosc.* **181,** 246 (1997) and Lanquetin, Coudert, and Camy-Peyret, *J. Molec. Spectrosc.* **195,** 54 (1999) and Coudert, Pirali, Vervloet, Lanquetin, and Camy-Peyret, *J. Molec. Spectrosc.* **228,** 471 (2004).

[2] Matsushima, Tomatsu, Nagai, Moriwaki, and Takagi, *J. Molec. Spectrosc.* **235,** 194 (2006).

[3] Toth, *J. Quant. Spectrosc. Rad. Transfer* **94,** 51 (2005).

[4] Toth, *J. Molec. Spectrosc.* **190,** 379 (1998) and Toth, *J. Opt. Soc. Am. B* **10,** 1526 (1993) and Toth, *J. Opt. Soc. Am. B* **10,** 2006 (1993).

Global Frequency and Infrared Intensity Analysis of $^{12}CH_4$ Lines in the 900–4800 cm^{-1} Region

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A new global analysis of methane lines in the 900–4800 cm^{-1} region has been performed thanks to new experimental data for both line positions and intensities. This implies three of the $^{12}CH_4$ polyads, namely the dyad (940–1850 cm^{-1}, 2 vibrational levels, 2 sublevels), the pentad (2150–3350 cm^{-1}, 5 vibrational levels, 9 sublevels) and the octad (3550–4800 cm^{-1}, 8 vibrational levels, 24 sublevels) and some of the associated hot bands. New FTIR spectra of the pentad and octad regions have been recorded with a very high resolution (better than 0.001 cm^{-1} instrumental bandwidth, unapodized) at 78 K using the Bruker IFS 125 HR Zürich prototype (ZP2001) spectrometer[1]. New intensity measurements were performed in the whole region at the Kitt Peak National Observatory. We also used previously recorded high-resolution Raman spectra[2]. The effective Hamiltonian was expanded up to order 6 for the ground state, 6 for the dyad, 5 for the pentad and 5 for the octad. We obtain global root mean square deviations d_{RMS} for line positions $= 1.4\times10^{-4}$ cm^{-1} for the dyad, 6.0×10^{-4} cm^{-1} for the pentad and 3.3×10^{-3} cm^{-1} for the octad. This analysis represents a large improvement over the previous one[3] with $d_{RMS} = 0.041$ cm^{-1} for the octad system.

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[1] S. Albert, K. Albert and M. Quack, *TOPS (Trends in Optics and Photonics Series)* **84**, 177–180 (2003).

[2] D. Bermejo, J. Santos and P. Cancio, *J. Mol. Spectrosc.* **156**, 15–21 (1992) and J.-M. Jouvard, PhD Thesis, Dijon (1991).

[3] J.-C. Hilico, O. Robert, M. Loëte, S. Toumi, A. S. Pine and L. R. Brown, *J. Mol. Spectrosc.* **208**, 1–13 (2001).

Temperature Dependence of N_2-, O_2-, and Air-Broadened Half-Widths of Water Vapor Transitions: Insight from Theory and Comparison with Measurement

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Calculations of N_2-, O_2-broadened half-widths, γ, of water vapor transitions in the 3.2 to 17.76 μm spectral region were made at 225 and 296 K with the mean relative thermal velocity approximation of the complex Robert-Bonamy (CRB) formalism. Five thousand four hundred and forty two transitions belonging to 11 vibrational bands were studied. From these data air-broadened half-widths were determined at the two temperatures and the temperature dependence of the half-width was evaluated using the standard formula

$$\gamma(T) = \gamma(T_0) \left[\frac{T_0}{T}\right]^n$$

For a limited number of transitions CRB calculations doing the velocity integral were made at 7 temperatures in the range 200-980 K. The mechanisms in the broadening process are discussed and the effects on γ and on the temperature dependence of the half-width as a function of the quantum states of the transitions are shown. Where possible this work is compared with measurement. It is shown that the standard temperature dependence model for the half-width is not correct for a number of transitions.

Modifications of the Robert-Bonamy Formalism and Further Refinements Required

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We have made two modifications of the Robert-Bonamy (RB) formalism that has been widely used for calculating Lorentzian spectral line half-widths and shifts for decades. The first one comes from a correction of their derivation where they assumed the cumulant expansion can be used to evaluate the Liouville matrix element <<j2i2|S|j2i2>>. At first sight, their assumption appears to be correct because this matrix element is diagonal in the Liouville space and as a result, it looks like that a basic requirement in applying the cumulant expansion is satisfied. However, by decomposing it into two Hilbert matrix elements associated with S_I and S_F ($\hat{S} = S_I{\cdot}S_F^*$) respectively, we have found neither of these is diagonal in Hilbert space. Therefore, their assumption is not valid and their expressions for the half-widths and shifts are incorrect. We have found by choosing an average over the internal degrees of the bath molecule as the average in the cumulant expansion, one is able to apply this expansion properly and obtain the correct expressions. Numerical calculations show new half-width and shift values differ from previous ones, and the stronger the interaction between two molecules is, the larger these differences are. The second correction is the expression for S_1 (i.e., the first term in the expansion of the S matrix) that is essential in calculating vibration-rotation pressure-broadened shifts that is not correctly given in the RB formalism. In this case, the problem resulted when they considered effects of the vibrational dephasing on S_1; they made the incorrect assumption that the trajectories of interest are vibrationally independent. As a result, the current expression is not applicable in calculating shifts for molecular lines involving vibrational transitions. Based on a vibration-dependent trajectory model, which is physically sound, we derive the correct expression for S_1. In comparison with the original expression, the new formula contains extra terms which represent the contributions from vibration- dependent trajectories. We find for some molecular systems of interest, calculated shifts based on the new formula differ significantly from those calculated using the existing formalism. Beside these corrections, we point out that there are several other assumptions introduced in the RB formalism. Some lack theoretical justifications and others may limit the accuracy of the results. One must address these problems in order to make further refinements of the RB formalism.

Using Laboratory FT-IR Spectrometer Measurements and HITRAN to Derive the Pure Water Vapour Continuum Between 3000 cm^{-1} and 8000 cm^{-1}

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[b] *Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire, UK*

The origin and magnitude of the water vapour continuum has long been a subject of controversy and uncertainty. Pure water vapour FT-IR measurements have been conducted between 3000 cm^{-1} and 8000 cm^{-1} at 0.03 cm^{-1} resolution over a temperature range of 296K-351K and a pressure range of 20 mb - 350 mb using the Molecular Spectroscopy Facility at the Rutherford Appleton Laboratory. The pure water vapour continuum is derived by calculating the difference between the absorption measured and that calculated for the laboratory conditions using the HITRAN 2004 database and a line-by-line model.

The deduced pure water vapour continuum shows good agreement with the MT_CKD continuum between 5000 cm^{-1} and 8000 cm^{-1}. However, it is apparent that the MT_CKD continuum overestimates the size of the continuum between $3950-4150$ cm^{-1}, $5500-5700$ cm^{-1} and $7400-7600$ cm^{-1} at the far edge of each absorption band. This overestimate is also apparent in the Ma and Tipping continuum suggesting that the contribution from far wings absorption could be overestimated by these continuum models.

Features are detected in the continuum around 3200 cm^{-1}, 3600 cm^{-1} and 3700 cm^{-1} that are not predicted by the MT_CKD continuum, but are consistent with theoretically predicted water dimer features of Schofield et al. (2003)[1]. However, the derived dimer line strengths could be smaller than those predicted. The temperature dependence of the dimer is seen to be in excellent agreement with the theoretical predictions of Vigasin (2000)[2].

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[1] D. P. Schofield and H. G. Kjaergaard, Calculated OH-stretching and HOH-bending vibrational transitions in the water dimer, *Phys. Chem. Chem. Phys.*, 2003, **5**, 3100-3105.

[2] A. A. Vigasin, Water vapor continuous absorption in various mixtures: possible role of weakly bound complexes, *J. Quant. Spectrosc. Radiat. Transf.*, 2000, **64**, 25-40.

Poster Session 1

Water Line Parameters from Refitted Spectra Using a New Fitting Technique.

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The accuracy of water line parameters has been an issue of many recent publications and discussions. Here we report out progress on refitting previously recorded near infrared and visible long path length Fourier Transform pure water and water-air spectra[1,2,3] using a new fitting method. This method uses additional information, including assignments and results of theoretical calculations, to constrain parameters which have big statistical errors. These the parameters are particularly associated with very weak and/or blended lines. Use of these constraints is found to significantly improve both the robustness of the fit and the transferability of the parameters between different spectra recorded in the same region.

The procedure allows us to also determine the relative pressure shifts in the pure water spectra. These can be compared with recent calculations.

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[1] R.Schermaul et al, J. Mol. Spectrosc., 208, 32-42 (2001).

[2] R.Schermaul et al, J. Mol. Spectrosc., 211, 169-178 (2002).

[3] P.-F.Coheur et al, JQSRT, 74, 493-510 (2002).

Labeling of $H_2^{16}O$, $H_2^{17}O$ and $H_2^{18}O$ Synthetic Line Lists in the 0 – 26000 cm^{-1} range.

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Programs of variational calculations in general, and DVR3D program suite[1] in particular, assign only rigorous quantum numbers. For H_2O molecule they are the rotational angular momentum, $\boldsymbol{J}$, the rotational parity $\boldsymbol{p}$ and the interchange symmetry between the two H atoms. For use of theoretical line lists in different applications it is usual to label energy levels with approximate vibrational quantum numbers v_1, v_2, v_3 and rotational quantum numbers K_a and K_c.

Spectroscopically determined potential energy surfaces (PES)[2], obtained from high quality *ab initio* PES[3], was used for the calculations. Synthetic line lists of $H_2^{16}O$, $H_2{}^{17}O$ and $H_2{}^{18}O$ isotopologues of water were calculated in the 0 – 26000 cm^{-1}range for temperature 296 K.

The labeling scheme utilized in this work uses smooth dependence of level's energy on vibrational and rotational quantum numbers. Starting from initial set of energy levels with known, for example from experimental studies, approximate quantum numbers we iteratively label levels with higher excitations. During this procedure we check the results using other labeling methods – analysis of wave functions and changes of vibrational energy due to additional terms in PES. The line lists can be downloaded from the server: saga.atmos.appl.sci-nnov.ru/fis3/.

This work was supported by the INTAS foundation, the Russian Fund for Fundamental Studies, DAAD.

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[1] J. Tennyson, M.A. Kostin, P. Barletta, G.J. Harris, O.L. Polyansky, J. Ramanlal, N.F. Zobov, Comp. Phys. Comm., 163, 85-116, (2004).

[2] S.V. Shirin, O.L. Polyansky, N.F. Zobov, A.G. Csaszar and J. Tennyson, J. Mol. Spectrosc., 236, 216-223 (2006).

[3] O.L. Polyansky, A.G. Csaszar, S.V. Shirin, N.F. Zobov, P. Barletta, J. Tennyson, D.W. Schwenke and P.J. Knowles, Science, 299, 539-542 (2003).

The Experimental Investigation of the Water Vapor Discrete and Continuum Absorption in the 8 to 12 μm Region at Temperatures from 311 K to 352 K

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The water vapor continuum absorption in the atmospheric 8 - 12 μm window strongly affects the Earth's outgoing radiation and therefore is of great importance for radiative balance calculations. Quantitative measurements of the water vapor continuum were first made by Burch and coworkers in the early 1980's and published in a number of AFGL reports[1]. At that time many scientific groups in the world used long-base and long-path length cells combined with spectrometers or tunable lasers to get more precise data over an extended range of conditions. Recently a cavity ring-down laser spectroscopy technique was employed to measure water vapor continuum absorption coefficients with a precision of about 1%.[2]

We have performed measurements using a 2 m base length White cell coupled to a BOMEM DA002 FTIR spectrometer. A path length of 84 or 116 m was used in experiments. The continuum is fairly weak in the region studied, and it was necessary to record the spectra of water-vapor samples at elevated temperatures, allowing pressures from 40 to 120 torr (0.05 to 0.16 atm). Under these conditions, the continuum absorbance could be accurately measured. We have recorded more than 150 spectra over the spectral range from 780 to 3500 cm^{-1} at temperatures from 311K to 352K. The resolution was set to 0.1 cm^{-1} to provide an acceptable signal-to-noise ratio within approximately two hours of scanning. The longer integration time required for higher spectral resolution leads to increased errors caused by baseline drift. We have determined binary absorption coefficients at 20 wavenumbers over the spectral range from 820 to 1157 cm^{-1}.

Our data compared with models and data from other laboratories are in reasonable agreement at lower temperature but differ as much as 50% at higher temperatures, depending on the wavenumber. Observed ro-vibrational structure was compared with calculations performed with the HITRAN date base. This comparison showed that intensities for many weak lines over the region 800 to 1250 cm^{-1} need correction.

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[1] See for example, Burch, D. E., Continuum Absorption by H_2O, Rep. AFGL-TR-81-0300, 46pp., Air Force Geophysics Lab., Hanscom AFB, MA, 1982.

[2] J. G. Cormier, J. T. Hodges, and J. R. Drummond. Infrared water vapor continuum absorption at atmospheric temperatures. J. Chem. Phys. 122, 114309, (2005).

Measurement and Analysis of High Resolution Terahertz Spectra of HDO and D_2O

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We present highly accurate laboratory measurements of the deuterated water species HDO and D_2O in selected frequency regions starting from 8 GHz up to 2.5 THz. Around 280 rotational transitions in both the vibrational ground and first excited bending states ($v_2 = 0, 1$) were measured in total, involving energy levels with to date unexcelled high J and K_a rotational quantum numbers. The data give valuable information for the spectroscopic analysis of these molecules. In the case of the light and non-rigid water molecule, standard methods for its analysis are limited due to large centrifugal distortion interactions. Recently, the so-called Euler expansion of the Hamiltonian was introduced by H. Pickett for the analysis of these kind of molecules, and its capability was demonstrated for the main isotopomer of water [1]. Here we present a global analysis of rotational and rovibrational data of the $v_2 = 0$ and 1 state of HDO and D_2O by means of the Euler approach. In addition to the newly measured transitions, around 3800 and 2750 lines have been included from previous work for HDO and D_2O, respectively. It was possible to reproduce the extensive dataset to nearly its experimental uncertainty. The improved predictive capability of the model compared to previous work will be demonstrated.

This analysis yields highly precise transition frequency predictions for both species far into the terahertz region which will be made available to the astronomy community *via* the Cologne Database for Molecular Spectroscopy *www.cdms.de.*[2]

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[1] Pickett, H. M., Pearson, J. C. and Miller, C. E., submitted to *J. Mol. Spectrosc.*, (2005).

[2] Müller, H. S. P., Schlöder, F., Stutzki, J., and Winnewisser, G., *J. Mol. Struct.* **742**, 215 (2005).

A New "Diet" For Air-Broadened Half-Widths of Water Vapor in the HITRAN2004 Compilation

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The half-widths of molecular lines are very important parameters for atmospheric remote sensing. Out of all the molecules represented in HITRAN, the air-broadened half-widths for H_2O have the greatest dynamic range. The HITRAN2004 compilation employs an efficient algorithm for choosing the most accurate values available for these half-widths[1]. Nevertheless some of the values in the HITRAN2004 database were found to be far from ideal.

It was found that the major source of problems was associated with arithmetic averaging of all experimental data available for every transition[2], which is a first step in the algorithm. The available experimental data have been reassessed, and inaccurate measurements were removed from the averaging or replaced by a calculated value. This procedure yields a significant improvement of the air-broadened half-width parameters in the database. Other collision-induced parameters for water vapor will be discussed as well.

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[1] L. S. Rothman et al., JQSRT 96, 139 (2005).

[2] R. R. Gamache and J.-M. Hartmann, Can. J. Chem. 82, 1013 (2004).

High-Precision Measurements of H_2O Line Intensities and Broadening Coefficients Using Frequency-Stabilized Cavity Ring-Down Spectroscopy

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We report room-temperature line intensities and self- and N_2- and air- broadening parameters for selected transitions within the $2\nu_1+ \nu_3$ band of water vapor. We used a frequency-stabilized cavity ring-down spectrometer with a tunable frequency comb to probe water vapor absorption with a frequency resolution of 50 kHz and signal-to-noise ratio approaching 1000:1.[1,2] For the strongest transitions in this band having intensities in the range 2×10^{-22} $\mathrm{cm^2cm^{-1}}$ $\mathrm{molec^{-1}}$ to $6.5\times10^{-22}\mathrm{cm^2cm^{-1}}$ $\mathrm{molec^{-1}}$ we used a steady flow humidity generation scheme to deliver a constant flow of the sample gas mixture to the ring-down cell. The water vapor concentration in the gas mixture was measured using a high-precision transfer-standard hygrometer linked to a NIST-maintained primary thermodynamic humidity standard.[3] Weaker transitions having intensities in the range 2×10^{-27} $\mathrm{cm^2cm^{-1}}$ $\mathrm{molec^{-1}}$ to 1×10^{-24} $\mathrm{cm^2cm^{-1}}$ $\mathrm{molec^{-1}}$ were probed with the ring-down spectrometer using static charges of pure water vapor near saturation conditions. Various line shape profiles accounting for collisional narrowing and speed-dependent effects were fit to the measured spectra. Of these models, the Galatry line shape yielded an adequate representation of the observed line shapes as it gave essentially the same area (within the noise level of the observations) as more complicated profiles.[2] For the strongest transitions, the relative standard uncertainties in line intensity and broadening coefficients were estimated to be less than 0.5 %. The results were compared to current HITRAN database,[4] and disagreement between our line intensity measurements and the corresponding HITRAN values was typically less than 3 %. However, significantly larger discrepancies in line intensities and broadening parameters were observed for the relatively weak transitions in this band.

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[1] J.T. Hodges and R. Ciurylo, Rev. Sci. Instrum., **76**, 023112 (2005).

[2] D. Lisak, J.T. Hodges and R. Ciurylo, Phys. Rev. A., **73,** 012507 (2006).

[3] G.E. Scace and J.T. Hodges, Proc. 8th Intl. Symp. Temp. Therm. Meas. Indust. Sci (TEMP-MEKO 2001) (VDE Verlag GmbH, Berlin, 2002), p. 597.

[4] L. Rothman *et al.*, Jour. Quant. Spect. Radiat. Transf. **96**, 139 (2005).

Line Mixing in Pure CO_2 Absorption at 6348 cm^{-1}

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Using sample pressures up to 900 Torr, we observe line mixing in pure carbon dioxide spectra for P and R branches of the 30012 ← 00001 band at 6347.8 cm^{-1}. We apply multispectrum retrieval techniques to high signal-to-noise, 0.01 cm^{-1} resolution laboratory spectra of CO_2 to demonstrate that introducing line mixing and non-Voigt profiles reduces the RMS residual differences between observed and calculated spectra by a factor of 5, compared to the residuals from using the standard Voigt line shape. Line mixing is required despite the fact that the unperturbed 30012 ← 00001 band contains no Q branch, and the P- and R-branch transitions are ~ 1 cm^{-1} apart. We present both Rosenkranz and off diagonal relaxation matrix element coefficients for this band. We conclude that line mixing will be required to retrieve atmospheric CO_2 abundances better than 1% from remote sensing spectra.

Theoretical studies of the wet continuum in terahertz windows

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We present a theoretical investigation of the submillimeter wave continuum due to colliding pairs of H_2O-N_2 molecules. It is an extension of our previous study of the millimeter wave foreign continuum based on the Lanczos algorithm. In contrast with the millimeter wave where the frequencies of interest are at the low frequency side of the pure rotational band of H_2O, the terahertz windows are within the band. As a result, the original Lanczos method in which one considers the effect on the absorption from all lines of the band, has to be modified. Because most of strong lines are still at the higher frequency side of the terahertz windows of interest, we can divide the pure rotational band into two parts: the major part consisting of lines whose frequencies are higher than a specified window and a minor part with lower frequency lines. Then, one can apply the Lanczos method to the major part and derive its contribution to the absorption; meanwhile, we treat the minor part as local lines. Based on this idea, we have calculated the continuum due to H_2O-N_2 for four terahertz windows of interest: 1.035, 1.35, 1.5 and 2.518 THz and have derived simple analytical parameterizations for each of these windows. Although our models are preliminary and have rooms to make further refinements, their main features are consistent with physical considerations. One of them (i.e., the increase of the continuum with the frequency f in the terahertz windows becomes less than f^2) has been found by recent measurements.

A Semi-Empirical Adjustment of The Vibrational Dependence of the Polarizability of Ozone for Use in Line Shift Calculations

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Calculation of the line shift of ro-vibrational transitions of ozone via the complex implementation of the formalism of Robert and Bonamy (CRB) is strongly dependent on the vibrational dependence of the polarizability of ozone. The polarizability can be expressed as

$$\alpha = \alpha_0 + C_1\left(v_1 + {}^1\!/_2\right) + C_2\left(v_2 + {}^1\!/_2\right) + C_3\left(v_3 + {}^1\!/_2\right)$$

where α_0 is the vibrationless contribution and C_1, C_2, and C_3, are the coefficients describing the vibrational contributions for the ν_1, ν_2 and ν_3 vibrational states. The coefficients are currently unknown. Employing measured line shift data for the $3\nu_3$, ν_1 and the $\nu_1 + \nu_2 + \nu_3$ bands, the polarizability coefficients were adjusted to fit the measured line shifts. The average absolute percent difference between measurement and theory was used to determine the “best” value of each coefficient. Using these coefficients, line shifts of reasonable accuracy can be calculated within the CRB method. We are currently determining the coefficients via *ab initio* methods and will compare the values determined by the two methods in the future.

Spectroscopic Study of Line Mixing Effects in the $\nu_2 + \nu_3$ Band of Methane

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Room temperature self- and air- off diagonal relaxation matrix coefficients have been measured for transitions in the $\nu_2 + \nu_3$ band of the octad region of methane. These measurements were made by analyzing 21 laboratory absorption spectra recorded at 0.011 cm^{-1} resolution using the McMath–Pierce Fourier transform spectrometer located at the National Solar Observatory on Kitt Peak, Arizona. The spectra were obtained using three absorption cells with path lengths of 2.05, 150 and 1600 cm. The total sample pressures ranged from 2 to 590 torr with CH_4 volume mixing ratios of 0.01 to 0.056 in dry air (in the case of air-broadened spectra). The spectral line parameters were retrieved using a multispectrum nonlinear least squares technique and a speed-dependent Voigt profile with a line mixing component. These results represent the first measurements of line mixing to be reported for the $\nu_2 + \nu_3$ vibrational band.

Measurements and Theoretical Calculations of Self- and Air-Broadening and Shift Coefficients in the ν_2 Band of CH_3D

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Self- and air-broadened widths and pressure-shift coefficients in the ν_2-fundamental band ($\nu_0 \approx 2200$ cm^{-1}) of $^{12}CH_3D$ were measured from spectra recorded at room temperature with the McMath-Pierce Fourier transform spectrometer at the National Solar Observatory on Kitt Peak. Absorption path lengths of 10.2, 25 and 150 cm with the spectral resolution of either 0.0056 or 0.01 cm^{-1}, depending upon the sample pressures, were used in recording the data. All spectra were fitted simultaneously in short segments of a few cm^{-1} wide using a multispectrum nonlinear least squares algorithm. The measurements covered nearly 380 transitions with $J'' = 21$ and $K = 18$, where $K'' = K' \equiv K$ (for a parallel band).

The dependence of the measured broadening and shift parameters on the J'', and K quantum numbers was examined and empirical expressions to describe the broadening coefficients in terms of m ($m = -J''$, J'' and $J'' + 1$ in the ^{Q}P-, ^{Q}Q-, and ^{Q}R-branch, respectively) and Khave been developed.

A semiclassical theory based upon the Robert-Bonamy formalism of interacting linear molecules has been used to calculate the self-broadening and self-induced pressure shift coefficients. Theoretical results for CH_3D-Air were obtained from the calculated results of CH_3D-N_2 (79%) and CH_3D-O_2 (21%). The theoretical and experimental results of the broadening and shift coefficients will be compared and contrasted.

High Accuracy Laboratory Spectroscopy for Atmospheric Applications

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Highly accurate analysis of laboratory spectra is a key requirement for some atmospheric applications. In order to assess the sources and sinks of carbon dioxide in the Earth's atmosphere, the Orbiting Carbon Observatory requires that the absolute amount of gas must be determinable to about 0.3%. This requires laboratory parameters to be determined to better accuracy than has been possible in the past. Each individual contribution to the measurement uncertainty must be kept to no more than $\sim 0.1\%$. The multispectrum nonlinear least squares fitting technique[1] is taken as the starting point for measuring spectra, but careful laboratory techniques are also necessary. Extreme care must be taken to simulate the effects of the spectrometer and the other characteristics of the laboratory setup upon the spectra. Physical parameters must be carefully monitored and the spectra themselves be used to check the precision of parameters such as pressure, mixing ratio and temperature. Uniformity of mixing ratio and temperature is particularly important with not only their effects upon the spectral line parameters, but also in the calculation of the amount of gas in the cell. The analysis technique is modified to take advantage of known relationships among the spectra and among the spectral line parameters. For example, instead of positions of the individual lines within a band, the rovibrational band constants are derived. The line positions can then be determined from the derived constants. This procedure forces the solution into a better physical model and reduces the correlations among determined parameters greatly. The improved zero pressure positions allow for better determination of pressure shifts. The uncertainty in the resulting positions as a function of rotational quantum number is a smooth function. It is not disturbed by blended lines and can be realistically extrapolated to outside the fitted spectral interval to determine the extent to which a simulation remains within guidelines. Similarly, the band intensity and Hermann-Wallis coefficients are determined rather than individual line intensities. Most of the inadequacy of the Voigt profile is corrected by line mixing (even in P and R branches), but speed dependence is also detected. The Van der Waals equation for the pressure of the gas is required and the largest remaining uncertainty is probably the fraction of the molecules in the

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

dimer state. For strong bands there are hints of an additional absorption at the higher pressures which may be attributable to the dimer.

This material is based upon work at the College of William and Mary supported by the National Science Foundation under Grant No. ATM-0338475. Part of the research described here was performed at the Jet Propulsion laboratory, California Institute of Technology, under contracts and cooperative agreements with the National Aeronautics and Space Administration.

Observations of SO_2 Spectra with a Quantum Cascade Laser Spectrometer around 1090 and 1160 cm^{-1}: Comparison with HITRAN Database and Updated Calculations

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Due to its application into atmospheric environment and astrophysics, the infrared spectrum of SO_2 has been the subject of many studies. Since the first realization of a quantum cascade laser (QCL) in 1994, many applications have been studied: communications, detection and quantification of trace gases, and high-resolution spectroscopy. Some years ago we had reported about spectroscopic studies of the ν_1 band of SO_2 using a continuous wave QCL[1] where line intensities and self-broadening coefficients had been measured for 9 isolated lines of SO_2 between 1088 and 1090 cm^{-1}. New spectra recorded in this region have been compared with previous determinations and theoretical predictions. Line positions, line strengths and self-broadening coefficients have shown some discrepancies with those of the HITRAN database. Several lines found in this study were not present in the HITRAN database.

In order to have a complete linelist of transitions of SO_2 appearing into the experimentally recorded spectra at 9 μm, we have performed a new calculation of the ν_1 band of $^{32}SO_2$, the $\nu_1 + \nu_2 - \nu_2$ band of $^{32}SO_2$ and the ν_1 band of $^{34}SO_2$. This new calculation demonstrates a dramatic improvement of the calculations of synthetic spectra of SO_2. These new calculations improve the positions of the ν_1 band of $^{32}SO_2$ with respect to HITRAN database and permit to obtain a complete set of data of the $\nu_1 + \nu_2 - \nu_2$ band of $^{32}SO_2$ and the ν_1 band of $^{34}SO_2$ where the positions and strengths are in excellent agreement with experimental data. This agreement obtained around 1090 cm^{-1} has been confirmed around 1160 cm^{-1} with experimental data obtained with another quantum cascade laser spectrometer.

Acknowledgments : Authors want to thank S. Tashkun and Vl. G. Tyuterev for the use of GIP program.

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[1] Spectroscopic study of the ν_1 band of SO_2 using a continuous wave DFB QCL at 9.1 μm, L. Joly, V. Zéninari, B. Parvitte, D. Weidmann, D. Courtois, Y. Bonetti, T. Aellen, M. Beck, J. Faist, D. Hofstetter, Applied Physics B: Lasers and Optics, **77**, 6-7, pp. 703-706, (2003).

Recent Progress in the Knowledge of C_2H_2 Spectroscopic Parameters in the IR

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The acetylene molecule is important for atmospheric, planetary, and astrophysics applications. In order to improve the knowledge of C_2H_2 spectroscopic parameters, systematic measurements of line parameters have been performed. Two recent works in two different spectral regions will be presented: first, in the 3.8-μm region, where line intensities have been measured for the first time for the 5 strongest bands observed in this region, second, in the 2.5-μm region, where 9 perpendicular bands have been studied, and for which line intensities have been obtained for the first time too. In these two spectral regions, transition dipole moments squared values have been derived from the line intensity measurements, and, for each vibrational band, have been modelled using Herman-Wallis factors.

A complete line list of positions and intensities has been generated for these two spectral regions, and will be proposed to be included in the HITRAN and GEISA databases. A global theoretical treatment of these results is in progress. According to notations adapted to a global treatment, the 3.8-μm spectral domain concerns the series of vibrational transitions $\Delta P = 4$, with P the pseudo-quantum number $P = 5v_1 + 3v_2 + 5v_3 + v_4 + v_5$, where the v_i's are the usual vibrational quantum numbers. This series involved interacting vibrational states belonging to the polyads $\{4\nu_5\}$ through 2 cold bands, and $\{5\nu_5\}$ through 3 hot bands. In the 2.5-μm region, transitions belong to the series $\Delta P = 6$, involving the polyads $\{6\nu_5\}$ through 4 cold bands, and $\{7\nu_5\}$ through 5 hot bands.

Absolute Line Intensities in the ν_2 Band, and Ground-state Electric Dipole Moment, of HOBr

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We measured absolute line intensities in the ν_2 fundamental band near 1165 cm^{-1} of both isotopologues of hypobromous acid HOBr. To obtain the partial pressure of the species in the sample mixture, unavailable through direct measurement since HOBr exists only in equilibrium with its decomposition products H_2O and Br_2O, we relied on known line intensities in the pure rotational far infrared (FIR) spectrum determined from Stark effect measurements, thus following the same procedure as we used for similar measurements for HOCl.[1] The work done involved two separate steps.

We recorded simultaneously the FIR pure rotation spectrum of HOBr using a Bruker IFS120HR spectrometer and the spectrum of a few vibration-rotation lines in the infrared (IR) ν_2 band using a tunable diode laser spectrometer. The FIR lines calculated using the ground state dipole moment derived from Stark effect measurements (see below) were used to derive the abundance of HOBr in the cell allowing one to derive accurate intensities from the diode laser spectra. The absolute intensities of these IR lines thus determined allowed us to "calibrate" the intensities of vibration-rotation lines in the whole band, measured using Fourier transform spectroscopy. The treatment of the data took into account the blackbody emission contribution in the FIR and the evolution of the HOBr amount during the recording of the spectra. The square of the transition dipole moment of the ν_2 band was determined for both isotopologues.

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[1] J. Vander Auwera, J. Kleffmann, J.-M. Flaud, G. Pawelke, H. Bürger, D. Hurtmans, and R. Pétrisse, *J. Mol. Spectrosc.* 204 (2000) 36-47.

Because the electric dipole moment was known for DOBr only,[2] we measured the μ_a and μ_b components of the electric dipole moment of HOBr using millimeterwave Stark measurements on the $K_a = 1 - 0$ transition observed in the 600 GHz region.

The experimental work done and results obtained will be presented.

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[2] Y. Koga, H. Takeo, S. Kondo, M. Sugie, C. Matsumura, G.A. McRae, and E.A. Cohen, *J. Mol. Spectrosc.* 138 (1989) 467-481.

Infrared Absorption Cross Section of CFC-113: Calculations and Measurements

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CFC-113 (CCl_2FCClF_2) is the third most abundant CFC in the atmosphere. Although its emission is now controlled by international regulations, the long lifetime of this compound makes its monitoring essential. Atmospheric measurements of CFC-113 on a global scale have recently become available from the Atmospheric Chemistry Experiment (ACE) satellite mission. However, the uncertainties in the spectroscopic parameters currently available for this molecule compromise the accuracy of the ACE retrievals.

The purpose of this work is to provide self- and air-broadened absorption cross sections of CFC-113 over a range of temperatures and pressures to allow more accurate measurements of its concentration profiles in the atmosphere.

The infrared spectra are investigated with both computational and experimental techniques. The theoretical computation of the harmonic vibrational frequencies and intensities of CFC-113 is performed using the time-dependent density functional theory.

New high resolution infrared cross sections of CFC-113 are measured by Fourier transform spectroscopy using a Bomem DA8 spectrometer equipped with a KBr beam-splitter and a MCT detector. The results show a good agreement between measurements and theory.

Developing a Phenomenological Model of Infrared Emissions from Detonation Fireballs for Explosives Identification

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Classifying battlespace detonations is a challenging problem primarily because of the weak phenomenological understanding of infrared emissions from high-explosives. To address this difficulty, a fast-scanning Fourier-transform spectrometer (FTS) has been deployed in several field experiments to collect time-resolved, moderate resolution spectra of detonation fireballs ($\Delta\tilde{\nu} \simeq 8\,\mathrm{cm}^{-1}$, $\Delta t \simeq 0.05\,\mathrm{s}$ or $\Delta\tilde{\nu} \simeq 2\,\mathrm{cm}^{-1}$, $\Delta t \simeq 0.13\,\mathrm{s}$). The observed spectra have guided the development of a compact, physical description of fireball emissions, which aids classification efforts by reducing dimensionality and providing physically-meaningful features.

The FTS observes a non-static fireball, and while scene-change artifacts are detected, the impact on the observed spectra is shown to be negligible. Fireballs from conventional munitions (CMs) are well-described by a single Planckian distribution (appropriately modified by atmospheric transmittance) with an exponentially decreasing temperature. Initial temperatures are approximately 1800 K and the decay rate is near $1\,\mathrm{s}^{-1}$. A small, systematic residual spanning 2050–2250 cm^{-1} (hot CO and CO_2 emission) is consistently observed shortly after detonation. The temporal behavior of this residual trends with munition type. Enhanced novel explosives (ENEs)—which are uncased charges—initially ($t < 0.2\,\mathrm{s}$) resemble graybody emission, but the spectrum is quickly dominated by selective emission from hot detonation by-products including H_2O, CO_2, and CO. Modeling the fireball as an optically thick (Planckian) core surrounded by an optically thin shell results in a low-dimensional model (8 fit parameters per spectrum) capable of adequately describing both the CM and ENE spectra. The fit parameters provide a kinetic interpretation of detonation spectra and may offer unique information for explosive identification. The high-temperature emission spectra were modeled using Line-By-Line Radiative Transfer Model in conjunction with the HITEMP (H_2O and CO) and CDSD (CO_2) spectral line databases.

Accurate atmospheric compensation is necessary for proper interpretation and robust modeling. A simple method has been developed to decouple the emission features of a rapidly evolving fireball from the absorption effects of a static atmosphere. Given a series of infrared detonation spectra attenuated by a homogenous, isothermal, and isobaric atmosphere, a reasonable estimate of water vapor concentration can be obtained if the temperature, pressure, and distance to target are known. In many cases, additional absorber concentrations (CO_2, N_2O, and CH_4) can also be inferred when a rough estimate of the source emission is obtained.

Rapid And Accurate Calculation of the Voigt Function

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A new algorithm for computation of both the real and imaginary parts of the Voigt (complex error) function is presented. This algorithm sacrifices a small amount of memory space for a considerable gain in speed and accuracy. For Lorentz widths greater than about five times the Doppler width and for points more than about five Doppler widths from the center of the spectral line, Gauss-Hermite quadrature is employed in a manner similar to many published algorithms. For most other cases, a third order Taylor series expansion about the nearest point in a pre-computed table is used. This technique is more efficient than it would seem due to some relationships among the various derivatives. In some cases where the Doppler width is more than an order of magnitude larger than the Lorentz width, Lagrange interpolating polynomials are used with a table of pre-computed points. The accuracy is one part in 106 of the value of the function. In addition, the derivative of the function with respect to the distance from line center and the derivative of the function with respect to the ratio of Lorentz to Doppler halfwidths can be calculated without significant additional computation time. The algorithm is approximately two to four times faster than the Drayson or Humlcek algorithms and about two orders of magnitude more accurate.

This material is based upon work supported by the National Science Foundation under Grant No. ATM-0338475.

SESSION 3: Remote Sensing

What about the Spectral Parameters when Performing Synergistic Atmospheric Measurements?

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Optical measurements of atmospheric minor constituents are performed using spectrometers working in the UV-visible, infrared and microwave spectral ranges. The combined use of nadir viewing UV-visible and thermal infrared spectrometers (such as GOME2 and IASI onboard MetOP) will provide an important improvement of vertical trace gas concentration profiles. The analysis and interpretation of the corresponding atmospheric spectra require good knowledge of the molecular parameters of the species of interest as well as of the interfering species. In particular meaningful comparisons of profiles retrieved by various instruments using different spectral domains require that the spectral parameters are consistent in these spectral domains. To illustrate how this is difficult we will discuss the problems one is facing to achieve this goal in the case of the formaldehyde molecule.

For the measurement of atmospheric formaldehyde concentrations, mid-infrared and ultraviolet absorptions are indeed both used by ground, air or satellite instruments. It is then of the utmost importance to have consistent spectral parameters in these various spectral domains. Consequently the aim of the study performed at LISA was to intercalibrate formaldehyde spectra in the infrared and ultraviolet regions. The experiments were performed by acquiring simultaneously UV and IR spectra at room temperature and atmospheric pressure using a common optical cell. The reactor contains two multiple reflection optical systems interfaced to a Fourier transform infrared spectrometer and to an UV-visible absorption spectrometer. The results of the work will be presented allowing one to point out a much better agreement with one of the various UV absorption cross sections available in the literature. If time permits, problems encountered when comparing the spectral parameters of the ozone molecule in various spectral domains will be discussed.

Linelist Needs for the Atmospheric Chemistry Experiment

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The Atmospheric Chemistry Experiment (ACE) is a satellite mission for remote sensing of the Earth's atmosphere, launched August 2003. The primary instrument on board is a high resolution (± 25 cm maximum optical path difference) Fourier transform spectrometer operating in the infrared ($750 - 4400\ \mathrm{cm}^{-1}$). Forward model calculations employ the HITRAN 2004 linelist. Observations from the mission will be used to illustrate improvements relative to previous versions of the linelist. A wish list for future linelist development will be presented, including molecules that seem to require improvements and molecules of atmospheric interest that we believe should be added to the linelist.

CO_2 Spectroscopy Evaluation Using FTS Spectra

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We evaluated the improvements in successive versions (1996 – 2004) of HITRAN[1] and other molecular line parameter data set[2] to correctly simulate infrared (IR) and near-infrared (NIR) CO_2 transmittance spectra. Understanding the global sources and sinks of CO_2 requires highly accurate measurements ($\leq 0.3\%$) and makes extreme demands on the spectroscopy. We evaluated the line parameter data sets by fitting solar absorption spectra measured by the JPL MkIV FTIR spectrometer[3] and the Caltech FT spectrometer[4]. The JPL spectra cover the entire 650 – 5650 cm^{-1} spectral region simultaneously and were measured during recent balloon flights under conditions that were closely monitored by *in situ* sensors[5]. The Caltech spectra, measured during summer 2004 from Park Falls, WI, cover the entire 4,000 – 11,000 cm^{-1} spectral region simultaneously. The measurements were made under conditions that were also closely monitored by *in situ* sensors (continuous CO_2 monitors, weekly flask sampling and aircraft profiles).[6]

This work benefits the HITRAN user community by documenting and highlighting inadequacies in the data set and quantifying their likely effect on retrieved CO_2 column. The consistency between retrieved column-averaged mole fraction of CO_2 (XCO_2) and measured surface CO_2 is an important demonstration of the adequacy of the spectroscopy. The work provides an objective basis for assessing the adequacy and self-consistency of the existing HITRAN data set and for quantifying the improvements (or otherwise) produced by new CO_2 line parameters. It also helps to prioritize needs for additional laboratory studies.[7]

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[7] The work described here was partly carried out at the Jet Propulsion Laboratory, California Institute of Technology, under contract with the National Aeronautics and Space Administration.

Infrared Laboratory Spectroscopy of CH_4 and CH_3D for Atmospheric Remote Sensing

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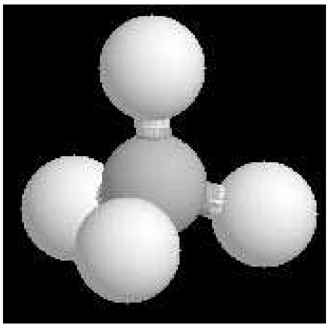
Knowledge of methane spectroscopy is crucial for the interpretation of atmospheric observations, including those of the outer planets. An overview will be given of recent results from high resolution laboratory studies of CH_4 and CH_3D in the 1.6 to 200 micron spectral region. Line intensities and line shape parameters will be emphasized, and methane parameters available from websites and public databases will be discussed.

Finally, future needs for laboratory studies will be summarized.

The research at the Jet Propulsion Laboratory (JPL), California Institute of Technology, was performed under contract with National Aeronautics and Space Administration.



Spectroscopic Parameter Requirements for Remote Sensing of Terrestrial Planets

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Planetary scientists seek to determine the compositions, dynamics, energetics, and chemical behaviors of planetary atmospheres through measurements of atmospheric absorption or emission in a number of wavelength regions. Laboratory studies of molecular spectra are often required to properly interpret telescope and spacecraft observations, particularly for atmospheres of planets such as Mars and Venus that have compositions and temperature and pressure regimes quite different from those in the Earth's atmosphere. While many of the necessary spectroscopic parameters are already available in databases such as HITRAN, updates are needed to meet the changing requirements of terrestrial planetary remote sensing missions. Key issues include (1) expanding line lists to cover near-infrared transitions, (2) adding parameters for isotopologues, (3) lower intensity cutoffs to allow more weak transitions to be listed, and (4) adding parameters for broadening and shifts by gases other than air. Specific requirements, discussed in the recent Chapman Conference on Exploring Venus as a Terrestrial Planet and at the NASA Astrobiology Science Conference, will be reviewed.

SESSION 4: Laboratory Spectroscopy

THz Studies of Water Vapor

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The types of THz absorption studies will be discussed. These include i) measurements of the water-vapor continuum from $12-55$ cm^{-1} ($0.4-1.83$ THz) using a multipass cell coupled to a FIR Fourier transform spectrometer and ii) high resolution THz laser studies of the self-broadened rotational lines of water over a temperature range from $263-340$ K and a pressure range from 30-1400 Pa. For the continuum studies, measurements were made at a room temperature and with water vapor and nitrogen pressures up to 2.2 kPa and 81 kPa, respectively. The effects of the choice of lineshape function and far-wing cut-off factors on the continuum absorption will be discussed. For the high resolution THz studies, the FWHM widths of pure Lorentzian lines were found to vary between $0.67-1.07$ cm^{-1}atm^{-1} and depend on the J, K_a and K_c quantum numbers as well as temperature. The observed pressure induced shifts, $\delta\nu$(P),ranged from $0.013-0.046$ cm^{-1}atm^{-1}. The measured linewidths exhibit the $(\mathrm{T}_0/\mathrm{T})^n$ power law dependence on temperature. The best fit exponent n varied from 0.56 to 0.81 relative to other lines in the set. A decrease in $\delta\nu$(T) with increasing temperature was found to vary between (2-5)$\times 10^{-3}$ cm^{-1}atm^{-1} over the $300-340$ K temperature range. New developments in instrumentation will be discussed with emphasis on coupling the high-resolution THz photomixer source to the long path White cell for proposed measurements on O_2.

HDO and D_2O Long Path Spectroscopy: On-Going Work of the Brussels-Reims Team

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Laboratory absorption spectra of H_2O–D_2O mixtures have been recorded in the spectral region $8800 - 11500$ cm^{-1} by Fourier transform spectroscopy at high resolution (0.03 cm^{-1}). The 50 m base long cell from Reims was used to record spectra with total pressure × absorption path products of about 6000 torr m. In the continuation of our previous work concerning water vapor[1,2,3,4,5,6,7,8,9,10], the present study deals with the Deuterium enriched spectra. Two spectra with different mixing ratios for H_2O, HDO and D_2O species were recorded. The identification of the HDO and D_2O lines has been made by comparison of ratios between pure and enriched spectra. Partial pressures were carefully determined using (i) $H_2{}^{16}O$ previously determined line intensities, (ii) HDO and D_2O line intensity ratios, and (iii) total pressures. The lines identification was checked through the evolution of the integrated absorption coefficients with the partial pressures. The observed lines have been fitted to Voigt line profiles from which line positions (calibrated afterwards), integrated absorption cross-sections and self-broadening coefficients have been determined. For the two deuterated species the integrated absorption cross sections could be measured down to $5{\cdot}10^{-27}$ cm/molecule. Comparisons with the most recent experimental data and calculations are presented.

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Air Broadened Ozone Linewidths in the Submillimeter Wavelengths

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The submillimeter frequency coverage of the EOS-MLS aboard the Aura spacecraft has necessitated the measurement of a larger data set of air-broadened ozone linewidths at these wavelengths. An automated submillimeter spectrometer that utilizes directly synthesized radiation, programmable mass-flow controllers and a temperature controlled cell was implemented for expedient data collection of 17 different rotational transitions in the $620 - 660$ GHz range. Many previous ozone rotational line-broadening studies have focused on single transitions, typically in the millimeter wavelengths, with the notable exception of a broadband FT-FIR study that characterized the J, K_c dependencies of many higher quanta states. The current measurements lie in a middle range of the previous measurements and allow a more comprehensive picture of the J, K_c dependencies of linewidths over the entire ozone rotational band.

A Complete Set of Line Parameters for CH_3Br in the 10-μm Spectral Region

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Methyl bromine is of interest for atmospheric applications, since this molecule is directly involved in the catalytic destruction of ozone in the lower stratosphere. At the present time no spectroscopic data is available in the atmospheric databases as HITRAN or GEISA.

Using FT spectra (Bruker IFS 120, unapodized FWHM resolution of 0.001 cm^{-1}) of methyl bromide CH_3Br, absolute line positions and intensities, as well as self-and N_2-broadening coefficients have been measured for about 1200 lines between 880 and 1050 cm^{-1} in the ν_6 band of $^{12}CH_3{}^{79}Br$ and $^{12}CH_3{}^{81}Br$. These measurements improve the accuracy on wavenumbers and line intensities previously obtained and lead to a complete set of self- and N_2-broadening coefficients for which clear J-and K-dependences have been observed for the first time. A multispectrum fitting procedure has been used to retrieve simultaneously the line parameters from 6 experimental spectra recorded at different pressures of CH_3Br and N_2. A wavenumber calibration has been performed using the line frequencies of the ν_2 band of NH_3. Average absolute accuracies of the measurements have been estimated around 0.0005 cm^{-1} for line positions, 5% for line intensities, and 5-10% for broadening coefficients. A theoretical treatment of wavenumbers permitted the prediction of assignments and wavenumbers for the whole 10-μm spectral region. Line intensities have been analyzed to deduce the effective vibrational transition moment squared as well as Herman-Wallis coefficients. Self-and N_2-broadening coefficients have been reduced using an empirical polynomial expansion function of $J$and K.

A complete line list containing line positions, intensities, self- and N_2-broadening coefficients has then been generated for atmospheric purposes with all lines from 820 to 1120 cm^{-1} having intensities greater than 10^{-5} $cm^{-2}\cdot atm^{-1}$.

High Resolution Assignment of ν_{14} and ν_{16} Bands in the 10 μm Region for Trans-Acrolein

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Acrolein (CH_2CHCHO) is one of the four (in addition to methanol CH_3OH, Acetaldehyde CH_3CHO, and 1,3-butadiene $CH_2CHCHCH_2$) 2004 target molecules from main- and side-stream (MS and SS) cigarette smoke[1]. The present work is aimed at extending the database of high resolution laboratory spectroscopic information on the molecule in the 10 μm region.

We have obtained 10 μm high resolution spectra from NRC both at room and cooled temperatures at 0.002 cm^{-1} resolution. The spectra cover several vibrational bands including the two dominant ones, the ν_{16} CH_2 out-of-plane rocking and ν_{14} CH2 twisting. Analyses of the ν_{16} and ν_{14} bands are now at advanced stages. More specifically, about 1085 lines have been assigned to the ν_{16} band for transitions to upper state $K'_a = 0$, 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10, and about 800 lines have assigned to the ν_{14} band for transitions to upper state $K'_a = 1$, 2, 3, 4, 5, 6, 7 and 8. We have applied an isolated band model to each band using Maki's asymmetric rotor Hamiltonian in which some assigned transitions were removed from our fits. In our analysis, we have encountered challenges due to high line density as well as perturbations. For the latter, J reduced upper state term values have been obtained and plotted as a function of J, indicating possible interactions among the two states.

For intensity information, we have carried out *ab initio* dipole derivative calculations using the procedure explained in Ref. [2][2] for 1,3-butadiene. A line list with position and intensity has been compiled using this *ab initio* dipole derivative and the rotational constants obtained from the present work.

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Poster Session 2

Analysis of The Accuracy of Line Positions and Intensities of HDO Transitions in HITRAN 2004.

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The HITRAN database is the most popular one for atmospheric applications. The latest version – HITRAN 2004 – contains 9628 transitions identified as belonging to $HD^{16}O$. These data, which lie entirely in the infrared, come from HITRAN 1986 and more recent work by Toth[1]. We analysed this data for errors in line positions and intensity. For this work we used previous variational calculations[2] and our DVR computations. The discrepancies will be discuss at the meeting.

In addition we have analysed a recent long path-length Fourier Transform spectrum of HDO[3]. Results of this analysis, which are being prepared for publication[4], will be reported at the conference.

The authors acknowledges the financial support from the EU framework 6 program via a Marie Curie incoming fellowship for BAV and from the UK NERC.

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Analysis of the Spectrum of Ethylene in the 800–1500 cm^{-1} Region Using Tensorial Formalism: Frequencies and Intensities

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Recently, we have presented a tensorial formalism[1,2] adapted to the spectroscopy of X_2Y_4 molecules. It is based on formalisms already developed in Dijon for spherical-top molecules[3] as well as on the work of Sartakov[4]. This approach has the advantages to allow a systematic development of rovibrational interactions and to make global analyses easier to perform. We have used this tool to perform a re-analysis of the $\nu_{10}/\nu_7/\nu_4/\nu_{12}$ tetrad both in frequencies and intensities in the 800–1500 cm^{-1} region. The effective Hamiltonian was expanded up to order four for the ground state and up to order six for the tetrad. We have used 8943 infrared data in the $\nu_{10}/\nu_7/\nu_4$ region from W. E. Blass' atlas[5] completed by 5420 more recent data in the same range[6] (207 of these having a precision of a few 10^{-6} cm^{-1}) and by 1138 data in the ν_{12} region from a spectrum recorded in Brussels. We obtain a global reduced RMS of 0.54 for line positions, which is comparable to the result of Ref.[6]. Concerning line intensities, the dipole moment was expanded to order 2. We used 9964 data from Blass' atlas, 25 high-precision diode laser data[7] and 182 new data from J. Vander Auwera (Brussels) in the ν_{12} region. This gives a RMS of 1.18 % for ν_{12} and 1.31 % for the $\nu_{10}/\nu_7/\nu_4$ region.

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Improved Line Parameters for the $X^1\Sigma_g^+$ (1-0) IR Quadrupolar Transitions of ^{14}N$_2$

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Re-examination of the ^{14}N$_2$ $X^1\Sigma_g^+$ (1-0) infrared line parameters in the HITRAN database showed that the vibration-rotation interaction effect on the line intensities, which is quite large for N$_2$, has been neglected, and that the halfwidths are not compatible with experimental and theoretical studies. New line parameters have been generated, and tested in retrievals from atmospheric spectra, the ACE occultation spectra and three sets of ground-based spectra taken at NDSC sites. The new line parameters improve the consistency and accuracy in individual N$_2$ line retrievals, but line shape issues remain, and require further studies.

Reinvestigation of the $^{16}O_2$ Atmospheric A Band by High-Resolution Fourier Transform Spectroscopy

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Although the molecule is simple and was intensely investigated in the past years, important spectroscopic issues remain about oxygen [1,2]. Troubles with line strengths and broadening parameters are mentioned among other concerns, like line mixing characterization, lineshape in the far wings, isotopologues spectroscopic parameters.[2]

In view of the need for continuous databases improvements, this work presents experimental line parameters of the $^{16}O_2$ A band located at 13000 cm^{-1} using long absorption path lengths Fourier transform spectroscopy. In particular, line positions, line strengths, self- and air-broadenings, self- and air- pressure-induced shifts are reported at room temperature. Results are compared to recent literature data, in order to assess discrepancies and identify the best quality dataset. Preliminary data of line parameters recorded at 220 K are also presented.

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Assessment of Microwave Line Parameters for oxygen: Comparisons Between Models and Atmospheric Measurements

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Improved spectroscopic parameters for oxygen have recently been published for the 60 GHz band. These parameters are an update of the MPM92 line parameters widely used in the remote sensing community. They include updated line widths, temperature dependence of the widths and line-coupling coefficients.

Here we compare calculated brightness temperatures from a monochromatic radiative transfer model, MonoRTM, with measurements from a twelve-channel ground-based microwave radiometer (MWRP), situated at the Atmospheric Radiation Measurement (ARM) site on the North Slope of Alaska (NSA). The instrument has seven channels in the vicinity of the 60 GHz oxygen band. The dataset spans almost two years. Model calculations have been performed with line parameters from the HITRAN database (using current MonoRTM line-coupling coefficients) and also with the new parameters. Comparisons between measured and modeled brightness temperatures suggest that the HITRAN line widths and temperature dependence of the width should be updated.

Differences between modeled and measured brightness temperatures for both sets of parameters show a dependence on temperature, which suggests that there are issues with the temperature dependence of the parameters. In an attempt to address these issues, spectroscopic parameters have been iteratively adjusted in order to better fit the modeled brightness temperatures to the measurements. The adjusted parameters result in improved model results when compared to the MWRP dataset.

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[1] Tretyakov, M.Yu, M.A. Koshlev, V.V. Dorovskikh, D.S. Marakov and P.W. Rosenkranz, "60-GHz oxygen band: precise broadening and central frequencies of fine-structure lines, absolute absorption at atmospheric pressure, and revision of mixing coefficients". J. Mol. Spec 231, 1-14 (2005)

[2] Boukabara, S.A., S.A. Clough and R.N. Hoffman, "MonoRTM: a monochromatic radiative transfer model for microwave and laser calculation". In Programs and Abstracts: Specialist Meeting on Microwave Remote Sensing, 158, November 2001

Implications for ν_2 and ν_3 CO_2 Spectroscopic Parameters from Atmospheric Remote Sensing

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The new capabilities and improved signal-to-noise ratio of present and future high-resolution passive sensors (e.g. SHIS, AERI, AIRS, ACE, MIPAS, TES, IASI) are placing a greater demand on the accuracy of the atmospheric Forward Model calculations used in the retrievals of atmospheric constituents. In order to improve the residuals and attain the retrieval accuracies of which the present and future sensors are capable, we need to have spectroscopic consistency: (i) for each band; (ii) for all bands of a given species; (ii) for all species for a given observation; and (iii) between observations from multiple instruments that use different spectral regions and techniques (i.e. microwave, thermal infrared, solar occultation, etc).

The CO_2 ν_2 and ν_3 regions are commonly used for the remote sounding of atmospheric temperature profiles. However, spectral residuals between interferometric atmospheric measurements and calculations using a line-by-line radiative transfer model (LBLRTM) in these regions are generally larger than instrument noise. In addition, the residuals show inconsistencies between the 680-800 cm^{-1} spectral region (ν_2 CO_2) and 2150-2450 cm^{-1} spectral regions (ν_3 N_2O; ν_3 CO_2). Here we present efforts to address spectroscopic consistency for CO_2 in these regions. For parameters in which current uncertainties are larger than what is required by atmospheric remote sensing retrievals ($>$ 1-2%), we have developed an approach that involves the fitting of semi-empirical corrections to these spectroscopic parameters. To ensure consistency, parameter corrections are fitted simultaneously. In addition, the form of the corrections is based on the underlying physics. Results are presented in the context of atmospheric temperature retrievals.

Line Strengths and Self-broadening Coefficients of CO_2 from 4600 to 7000 cm^{-1}

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Line positions and strengths are measured for 58 vibrational bands between 4550 and 7000 cm^{-1}. These are retrieved from 42 laboratory spectra recorded using the McMath-Pierce Fourier transform spectrometer located at the National Solar Observatory on Kitt Peak, Arizona. The spectra were recorded using five different absorption cells, with optical path lengths ranging from 0.1 m to 409 m, CO_2 pressures up to 581 Torr and spectral resolutions between 0.01 and 0.013 cm^{-1}. Band strengths in natural abundance range from 3.30×10^{-20} to $2.8 \times 10^{-25} cm^{-1}/(\text{molecule } cm^{-2})$ at 296 K. Comparisons with corresponding values from the literature indicate that absolute accuracies better than 1% and precisions of 0.5% are achieved for the strong bands.

Self-broadened widths (HWHM) are reported in natural abundance for 15 bands, and self-induced pressure shift coefficients are obtained for 13 of these bands:

a) the Fermi triad (20011-00001, 20012-00001, 20013-00001), three hot bands (21111-01101, 21112-01101, 21113-01101), and 01121-00001 (between 4700 and 5400 cm^{-1})

b) the Fermi tetrad (30014-00001, 30013-00001, 30012-00001, 30011-00001), two hot bands (31113-01101, 31112-01101), as well as 00031-00001 and its difference band 01131-01101 (between 6100 and 7000 cm^{-1}).

The experimental width and pressure shift coefficients are well modeled using empirical expressions; for the measured widths, the standard deviations of the fits are less than 1%, while the standard deviations for the pressure-induced shift fits range between 2.3% and 6.7%. Small vibrational and rotational variations are observed in the width coefficients. As expected, pressure-induced shift coefficients vary greatly from region to region, but small differences are also seen from band to band as a function of the rotational quantum number J.

Part of the research described in this paper was performed at the Jet Propulsion Laboratory, California Institute of Technology, and the National Solar Observatory under contracts and cooperative agreements with the National Aeronautics and Space Administration. This material is also based upon work at the College of William and Mary supported by the National Science Foundation under Grant No. ATM-0338475.

The Far Infrared Outgoing Longwave Radiation (OLR) is Finally Observed

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The FIRST instrument was designed and built as a prototype for a space-borne FTS instrument to take daily global maps of the high resolution spectra of the outgoing longwave radiation of the entire Planck curve. All of the previous spectrally resolved space-based radiometers have measured just the short wavelength half the Planck curve, short of 16 microns. Longward of this wavelength, most of the cooling of the middle and upper stratosphere occurs, due to the rotational band of water vapor. The prototype (a collaboration between NASA Langley, Space Dynamics Lab, and the Smithsonian Astrophsyical Observatory) has now been built and has had one observational test flight in a space-like environment (a high altitude balloon). We will recap the experiment, show some early results from this flight, and discuss the spectroscopic issues associated with the project.

The Atmospheric Chemistry Experiment (ACE): Status and Results

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The ACE mission goals are: (1) to measure and to understand the chemical and dynamical processes that control the distribution of ozone in the upper troposphere and stratosphere, with a particular emphasis on the Arctic region; (2) to explore the relationship between atmospheric chemistry and climate change; (3) to study the effects of biomass burning in the free troposphere; and (4) to measure aerosol number density, size distribution and composition in order to reduce the uncertainties in their effects on the global energy balance.

ACE is making a comprehensive set of simultaneous measurements of trace gases, thin clouds, aerosols, and temperature by solar occultation from a satellite in low earth orbit. A high inclination (74 degrees) low earth orbit (650 km) gives ACE coverage of tropical, mid-latitudes and polar regions. A high-resolution (0.02 cm^{-1}) infrared Fourier Transform Spectrometer (FTS) operating from 2 to 13 microns (750-4400 cm^{-1}) is measuring the vertical distribution of trace gases, and the meteorological variables of temperature and pressure. Aerosols and clouds are being monitored using the extinction of solar radiation at 0.525 and 1.02 microns as measured by two filtered imagers as well as by their infrared spectra.

A dual spectrograph called MAESTRO was added to the mission to extend the wavelength coverage to the 280-1000 nm spectral region. The principal investigator for MAESTRO is T. McElroy of the Meteorological Service of Canada. The FTS and imagers have been built by ABB-Bomem in Quebec City, while the satellite bus has been made by Bristol Aerospace in Winnipeg. ACE was selected in the Canadian Space Agency's SCISAT-1 program, and was successfully launched by NASA on August 12, 2003 for a nominal 2-year mission.

The first results of ACE have been presented in a special issue of Geophysics Research Letters (http://www.agu.org/journals/ss/ACECHEM1/) in 2005 and a description of the retrieval methodology used for the ACE Fourier transform spectrometer has also been published[1]. A mission overview and status report will be presented. Science results for a few selected topics including stratospheric fluorine and chlorine budgets as well as the first detection of methanol by remote sensing will be summarized.

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UV Fourier Transform Absorption Cross-Sections of Benzene, Toluene, Ortho-, Meta-, and Para-Xylene

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New measurements of the absorption cross sections of gaseous benzene, toluene, ortho-, meta-, and para-xylene have been performed with a Fourier transform spectrometer BRUKER IFS120M at the resolution of 1 cm^{-1} over the 30000-40000 cm^{-1} spectral range. The recordings were carried out under different pressure and temperature conditions with pure samples and mixtures with dry air.

Preliminary results will be discussed and compared to the available literature data. The effects of low temperature and of the buffer gas on the absorption cross sections will be investigated, given the tropospherical –mostly urban-[1] and astrophysical[2] relevance of these hydrocarbons.

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[1] T. Etzkorn *et al.*, Atmos. Environ. 33, 525-540 (1999).

[2] R. Wu *et al.*, Bull. of Am. Astron. Soc. 32, 1646 (2000).

Global Measurements of OClO, BrO, HCHO, and CHO-CHO from the Ozone Monitoring Instrument on EOS Aura.

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The Ozone Monitoring Instrument (2004 launch on EOS Aura) provides measurements of a number of important tropospheric gases, including O_3, NO_2, HCHO, HCHO, BrO, and CHO-CHO. We present recent advances on the detection of tropospheric BrO released from Salt Lakes and in volcanic plumes, give satellite-based estimates of BrO-to-SO_2 in the plumes, and present updates on the retrievals of HCHO and CHO-CHO. The retrieval algorithm will be discussed briefly, and an overview of the status and availability of OMI data products both, operational (BrO, HCHO, OClO) and scientific (CHO-CHO), derived at the SAO will be given.

The Effect of Different Ozone Cross Sections in the Ultraviolet on Ozone Profile Retrievals from GOME

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The quality of ozone cross sections in the ultraviolet are very important for remote sensing of ozone from space. We investigate the effects of using three different sets of ultraviolet ozone cross sections on ozone profiles retrievals from GOME: Bass and Paur cross sections which are archived in HITRAN and are widely used in the community, cross section by Malicet et al. [1995], and GOME flight model by Burrows et al. (1999). It was found that using the Malicet cross sections not only reduces the fitting residuals by 10-20% over the other two cross sections, but also improves the retrievals in the troposphere.

Temperature Dependence of the O_2 Schumann-Runge Continuum Photoabsorption Cross Section from a Coupled-Channel Perspective

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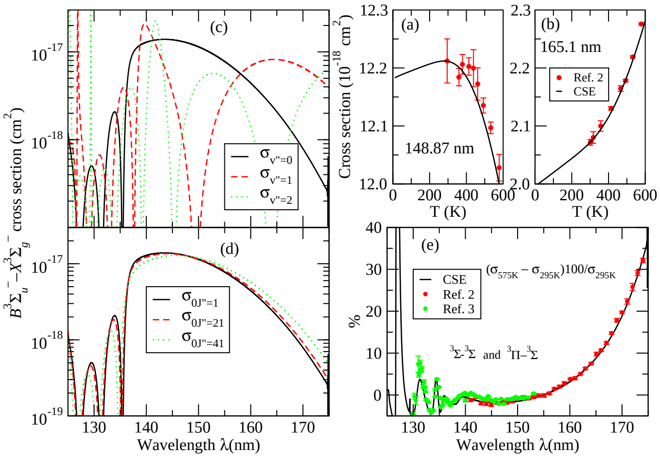
The calculation of diatomic molecular spectra to spectroscopic accuracy in wavelength regions of continua or pseudo continua may only adequately be achieved using a coupled-channel Schrödinger equation (CSE) model.[1] This model provides a physical description of photodissociation at the quantum mechanical level which implicitly characterizes interactions between electronic states to fully describe perturbations (line-shifts), intensity borrowing, resonance widths, and resonance asymmetry.

In the CSE model the apparent complexity of the O_2 photoabsorption spectrum from 115 nm to 175 nm, which includes the Tanaka bands and the Schumann-Runge continuum (SRC), is due to a single Rydberg-valence interaction. This interaction collapses the SRC, near 135 nm, and provides intensity to the Tanaka bands, the rovibrational transitions of which are asymmetric due to the interaction with the residual continuum.

Temperature dependence of the cross section arises from changes to the relative populations of the initial rovibrational levels, weighting each partial cross section, $\sigma_{v''J''}(\lambda)$, according to a Boltzmann summation. There are two main effects: a shift in the position of the partial cross section, due to a change in the energy separation between the initial and final states, and shape differences in the partial rovibrational cross sections. In



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[1] B. R. Lewis, S. T. Gibson,F. T. Hawes, and L. W. Torop, "A new model for the Schumann-Runge bands of O_2", Phys. Chem. Earth(C) **26**, 519 (2001).

particular, variation of the cross section at high temperatures[2,3] (Fig. a,b) arises from the very different v'' cross sections (c), whilst, the similarity of the rotational cross section curves (d) produces only a small effect for low temperatures. This picture places physical limits on the temperature variation which is in contrast to a recent measurement of the 90 K cross section.[4]

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[2] S. T. Gibson, H. P. F. Gies, A. J. Blake, D. G. McCoy, and P. J. Rogers, "Temperature dependence in the Schumann-Runge photoabsorption continuum of oxygen", J. Quant. Spectrosc. Rad. Transfer **30**, 385 (1983).

[3] J. B. Wang, D. G. McCoy, A. J. Blake, and L. Torop, "Effects of the close approach of potential curves in photoabsorption by diatomic-molecules: 2. Temperature-dependence of the O_2 cross-section in the region 130-160 nm", J. Quant. Spectrosc. Rad. Transfer **38**, 19 (1987).

[4] K. Yoshino, W. H. Parkinson, K. Ito, and T. Matsui, "Absolute absorption cross-section measurements of Schumann-Runge continuum of O_2 at 90 and 295 K", J. Mol. Spect. **229**, 238 (2005).

High-Resolution Photoabsorption Cross Section Measurements of SO_2 Between 198 nm and 325 nm

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Accurate photoabsorption cross section data at a range of temperatures are required for the incorporation of sulfur dioxide in atmospheric photochemical models. Our laboratory measurement program focuses on the very congested SO_2 spectrum in the ultraviolet. Using the Imperial College UV Fourier transform spectrometer, we have recorded high-resolution (resolving power $(\lambda/\Delta\lambda) \approx 450,000$) absorption spectra in the 198 – 325 nm region over a range of temperatures from 160 K to 295 K. We have reported absolute photoabsorption cross sections at 295 K (Stark et al., JGR Planets 104, 16585 (1999); Rufus et al. JGR Planets 108, doi:10.1029/2002JE001931,(2003)). Further measurements at 160 K in the 198 – 200 nm region have been recorded, and we are currently measuring the SO_2 spectrum from 220 nm to 325 nm at 200 K.

ASpecT: Active Spectroscopic Tables

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Approaches, and design features of their computational implementations, are reviewed which can actively store (in parallel databases), refine (through statistical approaches), and retrieve (through Java and XML programs) complete spectra obtained from accurate first-principles variational spectral simulations as well as experimentally observed rovibrational spectra. Strategies allowing statistical refinement of energy levels based on a growing number of experimental transitions, with their appropriate error bars, are discussed. The preliminary results concern the water isotopologue $H_2^{17}O$.

Free, Fast and Accurate Online Calculation of Spectral Absorption and Radiance at www.gats-inc.com

Martin McHugh, **Lance Deaver, Ken Beaumont, Kimberly Walls, and Larry Gordley**

GATS Inc, Newport News VA 23606 USA

Calculation of molecular absorption spectra has historically been relegated to research-grade computer codes, available only to researchers in academic or government research programs. Designed to be embedded in complex retrieval algorithms, these codes are unwieldy as stand-alone applications. They are usually tied to specific and often archaic hardware/software configurations. Simulating even simple scenarios requires defining a host of settings, usually in unforgiving and cryptic formats.

To overcome these limitations, we introduce the *GATS Spectral Calculator*, an online tool that quickly and accurately computes molecular absorption and radiance spectra. The *Spectral Calculator* is extremely simple to use and produces research-quality spectra in just seconds. Users can select the pressure, temperature and length of a gas cell, and specify concentrations of up to six gases. Absorption or radiance is computed in any spectral interval up to 500 cm^{-1} wide in the UV, visible or IR—any molecule and spectral region covered by HITRAN 2004. The resulting spectra are displayed online, with high-resolution postscript and plain text data available for download.

The *GATS Spectral Calculator* is powered by the LINEPAK radiative transfer library. Efficient, well tested and accurate, this library is at the heart of the retrieval systems for a number of major NASA satellite remote sensing missions. With the *Spectral Calculator's* easy-to-use online interface, studies that used to take days to set up and analyze can now be completed in minutes, from anywhere. To guide the researcher in the analysis, we also provide a *HITRAN Browser*, which graphically displays the intensities, positions and cross-section data in the complete HITRAN 2004 dataset. These tools and further details are available at www.gats-inc.com.

Use of HITRAN and UVACS Databases for the Task of Precision Ambient Air Control

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Difference between concentration of gas substance calculated using HITRAN database in the infrared spectral region or using UVACS database in the ultraviolet spectral region from one side and concentration of measured standard reference material (gas in this case) from the other side can form several percents. At the same time e.g. accuracy of control of greenhouse gases should be not worse than parts of one percent. National metrological centers under the aegis of the BIPM organize the key comparisons for the purpose to increase the accuracy and to provide the traceability of measurements. Different metrological measures have to be undertaken to increase the accuracy of parameters of HITRAN or/and UVACS databases.

Spectroscopic Needs for NLTE Radiative Transfer Modeling in Planetary Atmospheres

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The principle of atmospheric sounding is based on the assumption that the atmospheric compounds emit according to the Planck function at the local kinetic temperature. However many of the ro-vibrational states of atmospheric constituents responsible for infrared emissions have excitation temperatures that differ from the local kinetic temperature.

These Non Local Thermodynamic Equilibrium (NLTE) emissions must be taken into account in the inversion of infrared measurements taken by space-borne instrumentation. While NLTE situations have been studied extensively for remote sensing of the Earth, a lot of work should be done for the case of other planetary atmospheres. An appropriate modeling of the NLTE in planetary atmospheres is an important task for the accurate analysis of limb emission measurements and for this is crucial a good knowledge of the spectroscopic parameters. In this presentation we will review the specific spectroscopic needs for the modeling of the radiative transfer under NLTE conditions in planetary atmospheres.

SESSION 5: Databases

Recent Developments in the Cologne Database for Molecular Spectroscopy, CDMS, and the Need for Further Laboratory Spectroscopic Data

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The internet browser-accessible Cologne Database for Molecular Spectroscopy, CDMS,[1,2] contains as one main part a catalog of rotational transition frequencies of molecular species that have been or may be identified in the interstellar medium, circumstellar envelopes, or planetary atmospheres. Rovibrational transitions in the far- and mid-infrared regions are currently available to a limited extent, but their importance will likely increase. Separate entries are provided for minor isotopic species or for molecules in excited vibrational states as far as appropriate. The entries have been created by fitting critically evaluated experimental data, mostly from laboratory experiments, to suitable Hamiltonian models to ensure entries as reliable as possible. Particular emphasis has been put on supplying data in the (sub-) millimeter and terahertz regions for telescopes such as APEX and the SMA as well as for the upcoming Herschel mission and ALMA.

The catalog is updated continuously. As of January 2006, the catalog contains more than 350 species of astrophysical, astrochemical, and planetary interest. It is available online free of charge through a link on the KOSMA web-site **http://www.ph1.uni-koeln.de/** or *via* the short-cut **http://www.cdms.de/**.

Transitions of molecules vibrationally or highly rotationally excited are particularly strong toward high-mass star-forming regions where also complex molecules are sought. Further rotational and rovibrational spectroscopic data are needed in order to characterize these states.

The CDMS also includes a web page listing molecules detected in astronomical sources, a help page for fitting rotationally resolved spectra, as well as information on recent changes in the database.

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[1] H. S. P. Müller, S. Thorwirth, D. A. Roth, and G. Winnewisser, *Astron. Astrophys.* **370** (2002) L49–L52

[2] H. S. P. Müller, F. Schlöder, J. Stutzki, and G. Winnewisser, *J. Mol. Struct.* **742** (2005) 215–227

Assessment of the GEISA and GEISA/IASI-03 Spectroscopic Data Quality: through Comparisons with Other Public Database Archives

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The GEISA (Gestion et Etude des Informations Spectroscopiques Atmosphériques; Management and Study of Atmospheric Spectroscopic Information database) has been updated in 2003/2004.

The performances of new atmospheric sounders like AIRS (Advanced InfraRed Sounder), in the USA, and IASI (Infrared Atmospheric Sounder Interferometer) in Europe, which have a better vertical resolution and accuracy, compared to the presently existing satellite infrared vertical sounders, is directly related to the quality of the spectroscopic parameters of the optically active gases. For these instruments, the so-called GEISA /IASI spectroscopic sub-database has been elaborated from the general GEISA spectroscopic database system, with a continuous update from new spectroscopic parameters, when available. The specific purpose of this effort is to assess the capability of measurement by the IASI instrument, within the designated goals of ISSWG (IASI Sounding Science Working Group), in the frame of the CNES (Centre National d'Etudes Spatiales, France) /EUMETSAT (EUropean organization for the exploitation of METeorological SATellites) European Polar System (EPS) preparation. The assessment will be done by simulating either high-resolution radiance spectra or experimental data, or both, as the situation demands.

The purpose of this presentation is to show some selected results of critical comparisons, in terms of spectroscopic line parameter archives (i.e.: HITRAN or MIPAS databases). All the archived spectroscopic data of GEISA and GEISA/IASI can be handled through a user-friendly associated management software, which is posted on the ARA/LMD group web site at: *http://ara.lmd.polytechnique.fr*

A Comprehensive Database for Water Spectra

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Water is molecule number 1 in the HITRAN linelist and the correct treatment of its spectroscopic properties is crucial to the enduring success the database. Recently a task group entitled "A database of water transitions from experiment and theory" has been formed under the auspices of IUPAC to address issues related to the spectroscopy of water not just at cool, atmospheric temperatures, but also at the high temperatures required by many other terrestrial and astronomic applications.

Constructing a reliable, all-temperature database for water is a challenging task. To this end the task group has identified the following sub-topics that need to be addressed: spectra of water at 300 K, database structure, spectra of hot water, line profiles, theory and computation of water spectra, and validation. Progress in this activity will be presented at the meeting.

New Cross Sections, Indices of Refraction, and Reflectance Spectra of Atmospheric Interest

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A brief review is presented of the indices of refraction and cross sections that are on the HITRAN 2004 compilation. New measurements of the refractive indices of ternary ($H_2O/H_2SO_4/HNO_3$) droplets by Myhre[1], and the indices of supercooled water by Wagner[2], are presented and compared to previous data. New infrared, visible, and ultraviolet cross sections of species of atmospheric interest (e.g., the measurements of HFC-125 and HFC-143a of Di Lonardo and Masciarelli[3]) are also discussed.

We finally propose to link to the "other listings" portion of the HITRAN web site several established reflectance data bases, since many current and future remote sensing experiments are influenced by ground emission and reflectance contributions.

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[1] C.E. Lund Myhre, H. Grothe, A. A. Gola, and C. J. Nielsen, J. Phys. Chem. A, 109, 7166-7171, 2005.

[2] R. Wagner, S. Benz, O. Mohler, H. Saathoff, M. Schnaiter, and U. Schurath, J. Phys. Chem. A, 109, 7099-7112, 2005.

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MolExplorer: A New Tool for Computation and Display of Spectra from the HITRAN Database

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We present a program (MolExplorer), which uses the HITRAN04 database to compute and display molecular spectra on a PC Windows platform. Within seconds it provides survey spectra from mm-waves up to the ultraviolet as well as selected parts with highest spectral resolution to model the attenuation of radiation in the atmosphere or under laboratory conditions. The program consists of a graphical user interface and a display area for the calculated spectra. Up to ten molecules or isotopologues can be specified together with their partial pressures or concentrations. Additionally a buffer gas pressure, the temperature, the propagation length and the spectral range (in cm^{-1}, THz or in μm) can be selected on the control panel.

The MolExplorer works in four different display modes: The *Line Strength* modus represents a pure line spectrum indicating the spectral line intensities (or line strengths) as they are stored in the HITRAN database. Each molecule or isotopologue is marked by another color. The *Line Position* modus also shows a pure line spectrum, but the line height reflects the maximum absorption coefficient at the center of a transition. This mode is favorably used to get an overview over a wide spectral range with many narrow lines. The *Absorption* modus displays the absorption coefficient [cm^{-1}] over the selected spectral range. The program automatically determines the collision and Doppler broadening for each individual line and uses the respective lineshape (a Lorentzian for collisions, a Gaussian for Doppler broadening and a Voigt profile in the intermediate case) to calculate the spectral absorption. The T*ransmission* modus displays the transmitted radiation propagating through the atmosphere or a gas cell of specified length.

Together with the *Absorption* and *Transmission* display modes a marker function can be activated, which is identical with the *Line Position* spectrum. The colored markers are helpful to distinguish between different components of a gas mixture and to identify their contributions even under conditions when lines overlap or a limited resolution with only a few pixels across the line causes some rough and arbitrary shape.

A cursor function can be used to determine line positions, to select a spectral range on a magnified scale or to read the absorption coefficient at a desired position.

To compare a new calculation of a spectrum with a previous one or to identify smaller changes in the spectrum, a double plot can be activated.

All relevant data of a transition which are stored in the Hitran04 database may be displayed on the screen. The desired line is marked by the cursor, and the graphic screen changes to a white field in which all data of this line are listed.

The calculated spectrum with up to 32,768 channels can be stored on a separate file, which may be processed by an external plot program. All parameters required for the calculation and the display of a spectrum can also be saved on a parameter file for recurring use.

First Definition and Implementation of Standards for the Exchange of Atomic and Molecular Data

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Numerical and bibliographical Databases in Atomic and Molecular Physics are essential for both the modeling of various astrophysical media and the interpretation of astrophysical spectra provided by ground or space-based telescopes. We report here our latest developments concerning the access to Atomic and Molecular Linelists Databases within the Virtual Observatories[1], addressing the definition of standards through a proposed Data Model[2], an access protocol to linelists[3], and their implementation on customized spectroscopic data from the CDMS/JPL databases. We will present how these new standards allow interoperability between the CDMS/JPL and the BASECOL databases, and between these databases and both a numerical code (PDR code from Meudon) and a spectral analysis software (DALIA). Finally we will show how our standards can be used for the HITRAN database.

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[1] http://www.ivoa.net

[2] M.L. Dubernet, P. Osuna, M. Guainazzi, E. Roueff, J. Salgado, IVOA, **Version 0.5, January 2006**, "Atomic and Molecular Lines Data Model".

[3] J. Salgado, P. Osuna, M. Guainazzi, M.L. Dubernet, IVOA, **Version 0.2, August 2005**, "Simple Line Access Protocol".

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