

# The 8<sup>th</sup> HITRAN Database Conference

*HARVARD-SMITHSONIAN CENTER  
FOR ASTROPHYSICS  
CAMBRIDGE MA, USA*

*16 - 18 JUNE 2004*



“Water, water everywhere, Nor any drop to drink.”

Samuel T. Coleridge (1772-1834)

**16-18 June 2004**  
**Phillips Auditorium**  
**Harvard-Smithsonian Center for Astrophysics**  
**Cambridge MA**

*Wednesday, 16 June*

- 8:30 Registration  
9:00 Welcome ..... Laurence S. Rothman
- SESSION 1: SPECTROSCOPY**  
Chair: Linda Brown
- 9:10 The Atmospheric Chemistry Experiment (ACE): Mission Overview  
..... Peter Bernath
- 9:40 High-resolution Infrared Spectroscopy of Unstable or Reactive Molecules: Line Positions and Intensities..... Johannes Orphal
- 10:10 High-resolution Measurements of Water-vapor Absorption Spectra Using a Frequency-stabilized Cavity Ring-down Spectrometer  
..... Joseph T. Hodges
- 10:30 *Break*
- 11:00 New Information on the Infrared High-Resolution Spectroscopy of  $^{16}\text{O}_3$   
..... Alain Barbe
- 11:30 Photolysis Rate Constants of CFC Molecules through a Spectroscopic Study  
..... Inmaculada Martín
- Noon *Lunch*
- SESSION 2: SPECTROSCOPY**  
Chair: Agnès Perrin
- 2:00 Absolute Absorption Cross Section Measurements of the Schumann-Runge Continuum of  $\text{O}_2$  at 90 K and 295 K..... Kouichi Yoshino
- 2:30 High Temperature Pressure Broadening of Water: Experimental Evidence for Negative Temperature Exponents ..... Manfred Birk
- 3:00 Semi-empirical Calculation of Air-broadened Half-widths and Air-pressure Frequency Shifts of Water-vapor Absorption Lines..... David Jacquemart
- 3:30 Diode Laser Spectroscopic Measurement of  $\text{H}_2\text{O}$  Line Shape in the 822-832 nm Spectral Region..... Pradip N. Ghosh
- 4:00 – 6:00 **POSTER SESSION 1: SPECTROSCOPIC PARAMETERS**

*Thursday, 17 June*

- SESSION 3: SPECTROSCOPIC DATABASES**  
Chair: Jean-Marie Flaud
- 9:00 The 2004 Edition of the HITRAN Compilation.... Laurence S. Rothman
- 9:30 The Cologne Database for Molecular Spectroscopy, CDMS  
..... Holger S.P. Müller
- 10:00 The 2003 Edition of the GEISA Database ..... Nicole Jacquinet-Husson

- 10:30 *Break*
- 11:00 Access to Databases of Atomic and Molecular Data in the Virtual Observatory  
..... Marie-Lise Dubernet-Tuckey
- 11:30 BEAMCAT: a Tool for Accessing and Comparing Spectroscopic Data  
..... Dietrich G. Feist
- 12:00 Assessment of Molecular Line Parameters in the Near-infrared  
..... Linda R. Brown
- 12:30 *Lunch*
- SESSION 4: SPECTROSCOPIC DATABASES**  
Chair: Mary Ann Smith
- 2:00 Validation of the 12- $\mu\text{m}$  Ethane Database, New IR Heterodyne Spectroscopy Intensity Results, Frequency Validation, and Insights into the Construction of the Database ..... William E. Blass
- 2:30 Constructing a Reliable Line List for Water in the Near Infrared and Visible  
..... Jonathan Tennyson
- 3:00 New Cross Sections and Indices of Refraction of Atmospheric Interest  
..... Steve Massie
- 3:30 – 5:00 **POSTER SESSION 2: NEW SPECTROSCOPIC PARAMETERS**
- 6:00 – 9:00 **BANQUET**
- 8:30 Grand Tour of Astronomy Facility (weather permitting)

*Friday, 18 June*

- SESSION 5: REMOTE-SENSING ISSUES**  
Chair: Kelly Chance
- 9:00 Molecular Line Parameters for the “MASTER” (Millimeter wave Acquisition for Stratospheric/ Tropospheric Exchange Research) Database  
..... Agnès Perrin
- 9:30 Infrared Spectroscopy and the MIPAS (Michelson Interferometer for Passive Atmospheric Sounding) Experiment ..... Jean-Marie Flaud
- 10:00  $\text{H}_2\text{O}$   $\nu_2$  Linestrengths and Positions for MIPAS/ENVISAT  
..... Georg Wagner
- 10:30 *Break*
- 11:00 A Case Study of the Retrieval of Tropospheric Water-vapor Profiles from AIRS Radiances ..... Luke L. Chen
- 11:30 Spectroscopy Evaluation using MkIV Balloon Spectra ..... Bhaswar Sen
- 12:00 Atmospheric Chemistry Measurements from the SCIAMACHY Spectrometer on the ESA ENVISAT Satellite: Overview and First Scientific Results  
..... Kelly Chance

## TABLE OF CONTENTS

### SESSION 1: SPECTROSCOPY

THE ATMOSPHERIC CHEMISTRY EXPERIMENT (ACE): MISSION OVERVIEW <u>Peter Bernath</u> , Kaley Walker, Chris Boone, Sean McLeod, and Ray Nassar .....	1
HIGH-RESOLUTION INFRARED SPECTROSCOPY OF UNSTABLE OR REACTIVE MOLECULES: LINE POSITIONS AND INTENSITIES <u>Johannes Orphal</u> , Agnès Perrin, F. Kwabia Tchana, O. Pirali, and Jean-Marie Flaud.....	2
HIGH-RESOLUTION MEASUREMENTS OF WATER-VAPOR ABSORPTION SPECTRA USING A FREQUENCY-STABILIZED CAVITY RING-DOWN SPECTROMETER Joseph T. Hodges.....	3
NEW INFORMATION ON THE INFRARED HIGH-RESOLUTION SPECTROSCOPY OF $^{16}\text{O}_3$ <u>Alain Barbe</u> , Marie-Renée de Backer-Barilly, and Vladimir G. Tyuterev.....	4
PHOTOLYSIS RATE CONSTANTS OF CFC MOLECULES THROUGH A SPECTROSCOPIC STUDY <u>Inmaculada Martín</u> , Ana M. Velasco, and Esteban Mayor .....	5

### SESSION 2: SPECTROSCOPY

ABSOLUTE ABSORPTION CROSS-SECTION MEASUREMENTS OF THE SCHUMANN-RUNGE CONTINUUM OF $\text{O}_2$ AT 90 K AND 295 K <u>Kouichi Yoshino</u> , William H. Parkinson, Kenji Ito, and Takashi Matsui.....	6
HIGH-TEMPERATURE PRESSURE BROADENING OF WATER: EXPERIMENTAL EVIDENCE FOR NEGATIVE TEMPERATURE EXPONENTS <u>Manfred Birk</u> , Georg Wagner, Robert R. Gamache, Jean-Michel Hartmann .....	7
SEMI-EMPIRICAL CALCULATION OF AIR-BROADENED HALF-WIDTHS AND AIR-PRESSURE FREQUENCY SHIFTS OF WATER-VAPOR ABSORPTION LINES <u>David Jacquemart</u> and Laurence S. Rothman .....	8
DIODE LASER SPECTROSCOPIC MEASUREMENT OF $\text{H}_2\text{O}$ LINE SHAPE IN THE 822-832 nm SPECTRAL REGION Ayan Ray, Amitava Bandyopadhyay, Biswajit Ray, Debasish Biswas, and <u>Pradip N. Ghosh</u> .....	9

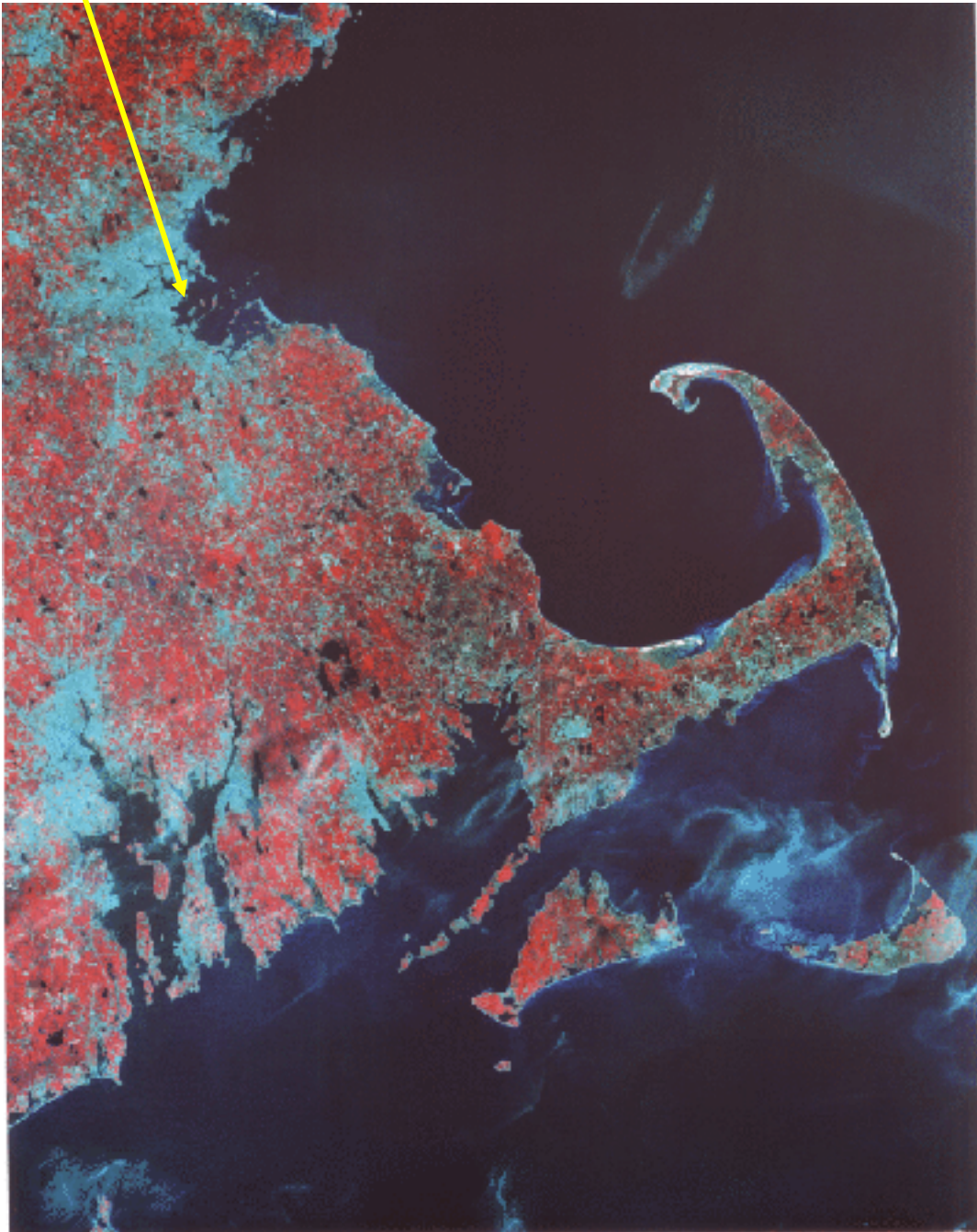
### POSTER SESSION 1: SPECTROSCOPIC PARAMETERS

<b>PW1.</b> THE ABSORPTION SPECTRUM OF $\text{H}_2\text{O}$ IN THE SPECTRAL REGION $4200\text{-}6600\text{ cm}^{-1}$ <u>Alain Jenouvrier</u> , Laurence Régalia-Jarlot, Ludovic Daumont, Vladimir G. Tyuterev, Alain Barbe, Michel Carleer, Pierre-François Coheur, Sophie Fally, Christian Hermans, Anne Carine Vandaele, and Semen N. Mikhailenko ..	10
<b>PW2.</b> COMPARISON OF FAR INFRARED HIGH-RESOLUTION SPECTRA WITH NEW PARAMETERIZATIONS FOR $\text{H}_2\text{O}$ AND OTHER MOLECULES Kenneth Jucks.....	11
<b>PW3.</b> NEAR INFRARED SPECTROSCOPY OF CARBON DIOXIDE <u>Charles E. Miller</u> and Linda R. Brown .....	12
<b>PW4.</b> EINSTEIN-A COEFFICIENTS AND STATISTICAL WEIGHTS IN THE HITRAN 2004 SPECTROSCOPIC DATABASE <u>David Jacquemart</u> , Laurence S. Rothman, Robert R. Gamache, and Aaron Goldman.....	13
<b>PW5.</b> LINE INTENSITIES OF ACETYLENE AT $3\text{ }\mu\text{m}$ <u>David Jacquemart</u> , Victor Dana, Jean-Yves Mandin, Laurence Régalia-Jarlot, Alain Barbe, Valery I. Perevalov, and O.M. Lyulin.....	14

<b>PW6.</b> HIGH-RESOLUTION SPECTROSCOPY OF THE METHANE MOLECULE: CH <sub>3</sub> D AND CH <sub>2</sub> D <sub>2</sub> SPECIES <u>Oleg N. Ulenikov</u> , Elena S. Bekhtereva, H. Hollenstein, and M. Quack .....	15
<b>PW7.</b> NEAR-IR METHANE Linda R. Brown.....	16
<b>PW8.</b> NEW ASSIGNMENTS, LINE INTENSITIES, AND HITRAN DATABASE FOR CH <sub>3</sub> OH AT 10 μm Li-Hong Xu, Ronald M. Lees, Peng Wang, <u>Linda R. Brown</u> , Isabelle Kleiner, and John W.C. Johns.....	17
<b>PW9.</b> ACCURATE ROTATIONAL SPECTROSCOPY OF O <sub>2</sub> <sup>3</sup> Σ <sub>g</sub> <sup>-</sup> AND <sup>1</sup> Δ <sub>g</sub> AND OF SO <sub>2</sub> , ν <sub>2</sub> = 0, 1, UP TO 2 THz <u>Holger S.P. Müller</u> , Sandra Brünken, Frank Lewen, Hideta Habara, and Gisbert Winnewisser .....	18
<b>PW10.</b> HCN UPDATE FOR HITRAN <u>Mary Ann H. Smith</u> , David Jacquemart, Laurence S. Rothman, Arthur Maki, V. Malathy Devi, D. Chris Benner, and Curtis P. Rinsland.....	19
<b>PW11.</b> ON THE STUDY OF HIGH-RESOLUTION ROVIBRATIONAL SPECTRUM OF H <sub>2</sub> S IN THE REGION OF 7300 TO 7900 cm <sup>-1</sup> <u>Elena S. Bekhtereva</u> , Oleg N. Ulenikov, A.-W. Liu, L.-Y. Hao, and S.-M. Hu .....	20
<b>PW12.</b> ABSOLUTE LINE INTENSITIES IN THE ν <sub>6</sub> BAND OF <i>TRANS</i> -FORMIC ACID <u>Jean Vander Auwera</u> , K. Didriche, Agnès Perrin, F. Keller, and Jean-Marie Flaud.....	21
<b>PW13.</b> NEW RESULTS ON D <sub>2</sub> : A NEW SPECTROSCOPIC PARAMETERIZATION OF THE BREAKDOWN OF THE BORN-OPPENHEIMER APPROXIMATION <u>John J. Hillman</u> , William E. Blass, Dennis Reuter, and Donald E. Jennings .....	22
<b>PW14.</b> SPECTROSCOPY TO BE REQUIRED FOR GOSAT TRACE GAS MEASUREMENT Makoto Suzuki.....	23
<b>PW15.</b> AEROSOL RESEARCH AT THE RAL MOLECULAR SPECTROSCOPY FACILITY Robert A. McPheat and <u>Kevin M. Smith</u> .....	24
<b>PW16.</b> ABSORPTION CROSS-SECTIONS FOR THE INFRARED BANDS OF PEROXYACETYL NITRATE <u>Grant Allen</u> , John J. Remedios, Kevin M Smith, David A Newnham, and Paul S. Monks .....	25
<b>SESSION 3: SPECTROSCOPIC DATABASES</b>	
THE 2004 EDITION OF THE HITRAN COMPILATION <u>Laurence S. Rothman</u> and David Jacquemart .....	26
THE COLOGNE DATABASE FOR MOLECULAR SPECTROSCOPY, CDMS <u>Holger S.P. Müller</u> , Frank Schlöder, Jürgen. Stutzki, and Gisbert Winnewisser.....	27
THE 2003 EDITION OF THE GEISA DATABASE <u>Nicole Jacquinet-Husson</u> , N.A. Scott, K. Garceran, R. Armante, A. Chédin .....	28
ACCESS TO DATABASES OF ATOMIC AND MOLECULAR DATA IN THE VIRTUAL OBSERVATORY Marie-Lise Dubernet-Tuckey.....	29
BEAMCAT: A TOOL FOR ACCESSING AND COMPARING SPECTROSCOPIC DATA FROM MULTIPLE SPECTROSCOPIC DATABASES Dietrich G. Feist.....	30
ASSESSMENT OF MOLECULAR LINE PARAMETERS IN THE NEAR-INFRARED <u>Linda R. Brown</u> , Pin Chen, Geoffrey C. Toon, and Robert A. Toth.....	31
<b>SESSION 4: SPECTROSCOPIC DATABASES</b>	
VALIDATION OF THE 12-μm ETHANE DATABASE, NEW IR HETERODYNE SPECTROSCOPY INTENSITY RESULTS, FREQUENCY VALIDATION, AND INSIGHTS INTO THE CONSTRUCTION OF THE DATABASE <u>William E. Blass</u> , John J. Hillman, Theodor Kostiuk, Juan Delgado, and Tilak Hewagama .....	32

CONSTRUCTING A RELIABLE LINE LIST FOR WATER IN THE NEAR INFRARED AND VISIBLE Jonathan Tennyson .....	33
NEW CROSS SECTIONS AND INDICES OF REFRACTION OF ATMOSPHERIC INTEREST J. Orlando, G. Tyndall, <u>Steve Massie</u> , and Aaron Goldman .....	34
<b>POSTER SESSION 2: NEW SPECTROSCOPIC PARAMETERS</b>	
<b>PT1.</b> LINE-SHAPE PARAMETERS FOR WATER VAPOR IN THE 3.2-17.76 $\mu\text{m}$ REGION Robert R. Gamache .....	35
<b>PT2.</b> DETERMINING THE PROFILE OF STRONG WATER LINES AT VISIBLE AND NEAR-INFRARED WAVELENGTHS <u>Roman N. Tolchenov</u> and Jonathan Tennyson .....	36
<b>PT3.</b> THE SPECTRAL AND MOLECULAR PROPERTIES OF OZONE (S&MPO) DATABANK Alain Barbe, S.N. Mikhailenko, V.I.G. Tyuterev, and Yu.L. Babikov .....	37
<b>PT4.</b> FT ABSORPTION SPECTRUM OF HDO IN THE VISIBLE AND NEAR-IR Mohamed Bach, Michel Carleer, Pierre-François Coheur, <u>Sophie Fally</u> , Christian Hermans, Alain Jenouvrier, and Anne Carine Vandaele .....	38
<b>PT5.</b> TUNABLE-DIODE LASER ABSORPTION OF H <sub>2</sub> O VAPOR BETWEEN 1355 AND 1441 nm VERSUS <i>T</i> AND <i>P</i> AND COMPARISON TO HITRAN PREDICTIONS <u>Xiang Liu</u> , Jay B. Jeffries, and Ronald K. Hanson .....	39
<b>PT6.</b> INTENSITY AND AIR-BROADENING COEFFICIENTS OF H <sub>2</sub> O AND CO <sub>2</sub> LINES WITH A NEAR- INFRARED SPECTROMETER Virginie Zéninari, Bertrand Parvitte, L. Joly, T. Le Barbu, and Georges Durry .....	40
<b>PT7.</b> LINE STRENGTHS AND HALF-WIDTHS OF CO <sub>2</sub> BANDS IN THE 2.7- $\mu\text{m}$ REGION AT ATMOSPHERIC TEMPERATURES <u>Masashi Fukabori</u> , Tadao Aoki, Tsuyoshi Fujieda, and Takeshi Watanabe .....	41
<b>PT8.</b> SPECTRAL LINE PARAMETERS FOR CO <sub>2</sub> BANDS NEAR 4.8 $\mu\text{m}$ <u>Tomoaki Tanaka</u> , Masashi Fukabori, Hideaki Nakajima, Tatsuya Yokota, and Takeshi Watanabe .....	42
<b>PT9.</b> LINESHAPE STUDIES OF ROTATIONAL TRANSITIONS OF OZONE AND NITRIC ACID <u>Georges Wlodarczak</u> , Bilal Bakri, Jean-Marcel Colmont, Jean Demaison, François Rohart, Gabriele Cazzoli, Luca Dore, Cristina Puzzarini, and Agnès Perrin .....	43
<b>PT10.</b> SELF- AND H <sub>2</sub> -BROADENED WIDTH AND SHIFT COEFFICIENTS IN THE 2 $\leftarrow$ 0 BAND OF <sup>12</sup> C <sup>16</sup> O: REVISITED V. Malathy Devi, <u>Adriana Predoi-Cross</u> , D. Chris Benner, Mary Ann H. Smith, Curtis P. Rinsland, and Arlan W. Mantz .....	44
<b>PT11.</b> CO BROADENING AND SHIFT PARAMETERS FOR TES <u>Mary Ann H. Smith</u> , Linda R. Brown, V. Malathy Devi, and Travis J. Pittman .....	45
<b>PT12.</b> AIR-BROADENING PARAMETERS IN THE $\nu_3$ BAND OF <sup>14</sup> N <sup>16</sup> O <sub>2</sub> USING A MULTISPECTRUM FITTING TECHNIQUE D. Chris Benner, T.A. Blake, <u>Linda R. Brown</u> , V. Malathy Devi, Mary Ann H. Smith, and Robert A. Toth .....	46
<b>PT13.</b> SPECTROSCOPIC BROADENING STUDY OF SO <sub>2</sub> IN SUBMILLIMETER REGION USING A LASER HETERODYNE SPECTROMETER <u>Vinay Kumar</u> , Hemant Dave, and Jayesh Pabari .....	47
<b>PT14.</b> STUDIES OF COLLISION-INDUCED ABSORPTION IN N <sub>2</sub> AND O <sub>2</sub> IN THE TEMPERATURE RANGE 296 TO 363 K <u>Yuri I. Baranov</u> and Walter J. Lafferty .....	48
<b>PT15.</b> PHOTOIONIZATION CROSS SECTIONS FOR ATMOSPHERICALLY AND ASTROPHYSICALLY RELEVANT MOLECULES	

<u>Ana M. Velasco</u> , Inmaculada Martín, C. Lavín, E. Bustos, Esteban Mayor, and J.M. Menéndez.....	49
<b>PT16.</b> INFORMATION SYSTEM FOR CALCULATING THE SPECTRAL CHARACTERISTICS OF INHOMOGENEOUS GASES	
<u>Olga K.Voitsekhovskaya</u> and <u>A. Yu Zapryaygaev</u> .....	50
<b>PT17.</b> N <sub>2</sub> O AND O <sub>3</sub> SOLAR SOURCED ATMOSPHERIC SPECTRA OBSERVED AT KNOXVILLE, TENNESSEE ARE ANALYZED YIELDING CONCENTRATION PROFILES AND TEMPORAL VARIATION RESULTS	
<u>John Stewart Hager</u> , <u>William E. Blass</u> , <u>Forrest Hoffman</u> , and <u>Robert Compton</u> .....	52
 <b>SESSION 5: REMOTE-SENSING ISSUES</b>	
MOLECULAR LINE PARAMETERS FOR THE “MASTER” (MILLIMETER WAVE ACQUISITION FOR STRATOSPHERIC/TROPOSPHERIC EXCHANGE RESEARCH) DATABASE	
<u>Agnès Perrin</u> , <u>Gabriele Cazzoli</u> , <u>Cristina Puzzarini</u> , <u>Jean-Marcel Colmont</u> , <u>Jean Demaison</u> , <u>Georges Wlodarczak</u> , <u>Jean-Marie Flaud</u> , <u>C. Verdes</u> , and <u>S. Bühler</u> .....	53
INFRARED SPECTROSCOPY AND THE MIPAS (MICHELSON INTERFEROMETER FOR PASSIVE ATMOSPHERIC SOUNDING) EXPERIMENT	
<u>Jean-Marie Flaud</u> , <u>C. Piccolo</u> , <u>Bruno Carli</u> , <u>Agnès Perrin</u> , <u>Laurent H. Coudert</u> , <u>Jean-Luc Teffo</u> , and <u>Linda R. Brown</u> .....	54
H <sub>2</sub> O v <sub>2</sub> LINE STRENGTHS AND POSITIONS FOR MIPAS/ENVISAT	
<u>Georg Wagner</u> , <u>Manfred Birk</u> , <u>Laurent H. Coudert</u> , <u>Jean-Marie Flaud</u> .....	55
A CASE STUDY OF THE RETRIEVAL OF TROPOSPHERIC WATER-VAPOR PROFILES FROM AIRS RADIANCES	
<u>Luke L. Chen</u> and <u>Crofton B. Farmer</u> .....	56
SPECTROSCOPY EVALUATION USING MkIV BALLOON SPECTRA	
<u>Bhaswar Sen</u> and <u>Geoffrey C. Toon</u> .....	57
ATMOSPHERIC CHEMISTRY MEASUREMENTS FROM THE SCIAMACHY SPECTROMETER ON THE ESA ENVISAT SATELLITE: OVERVIEW AND FIRST SCIENTIFIC RESULTS	
<u>Kelly Chance</u> , <u>Christopher Sioris</u> , <u>Randall Martin</u> , <u>Thomas Kurosu</u> , and <u>Paul Palmer</u> .....	58
<b>AUTHOR INDEX</b> .....	59





## The Atmospheric Chemistry Experiment (ACE): Mission Overview

**Peter Bernath, Kaley Walker, Chris Boone, Sean McLeod, and Ray Nassar**

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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 ( $0.02\text{ cm}^{-1}$ ) infrared Fourier Transform Spectrometer (FTS) operating from 2 to 13 microns ( $750\text{-}4100\text{ cm}^{-1}$ ) is measuring the vertical distribution of trace gases, and the meteorological variables of temperature and pressure. The ACE concept is derived from the now-retired ATMOS FTS instrument, which flew on the Space Shuttle in 1985, 1992, 1993, 1994.

Climate-chemistry coupling may lead to the formation of an Arctic ozone hole. ACE will provide high quality data to confront these model predictions and will monitor polar chemistry as chlorine levels decline.

Aerosols and clouds will be 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 2-year mission. The commissioning activities and first results will be presented. Spectroscopic data needs for ACE will also be discussed.

## High-resolution Infrared Spectroscopy of Unstable or Reactive Molecules: Line Positions and Intensities

**Johannes Orphal, Agnès Perrin, F. Kwabia Tchana, O. Pirali, and Jean-Marie Flaud**

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For atmospheric remote-sensing and laboratory investigations of chemical kinetics, infrared line positions and intensities are required also for unstable or reactive molecules. For such species, conventional measurement techniques like Fourier-transform spectroscopy or laser absorption spectroscopy can be used as well, but the experimental set-up and procedure have to be modified to take into account possible variations of sample concentration with time.

Furthermore, the determination of sample concentration itself is a challenging task, since in many cases (highly unstable species, radicals) it is impossible to obtain pure samples, so that pressure measurements cannot be used. For this reason, line intensities of such species are difficult to measure. Therefore, alternative pathways for determination of the concentrations of unstable species need to be explored. For example, the combination and comparison of measurements is a possibility which has been used already in the past. The modelling of chemical kinetics or chemical titration of reactive mixtures is another promising approach but has been used until now mainly for spectroscopy in the ultraviolet-visible region.

In the present talk, recent examples for such experiments (e. g.  $\text{HNO}_3$ ,  $\text{ClONO}_2$ ,  $\text{HOBr}$ , *cis*- and *trans*-HONO) will be used to illustrate the complexity of the problem, and an overview of current and future experimental activities of the LPPM group in Orsay, related to this area, will be given.

## High-resolution Measurements of Water-vapor Absorption Spectra Using a Frequency-stabilized Cavity Ring-down Spectrometer

Joseph T. Hodges

*National Institute of Standards and Technology  
Chemical Science and Technology Laboratory  
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We present a high-resolution cavity ring-down spectroscopy apparatus that provides absolute intensities and self- and foreign- broadening coefficients of individual transitions, differential pressure shifting of transition pairs, and continuum absorption coefficients for water vapor and other gases [1,2]. This system also enables quantification of departures from Voigt line shapes, thus making it suitable for the investigation of higher-order line-shape effects such as collisional narrowing. The principal feature of the spectrometer is a compact (75-cm long, 0.2-L internal volume) ring-down cavity whose comb of eigenfrequencies is actively stabilized with respect to a tunable, frequency-stabilized reference laser. A tunable, single-mode external cavity diode laser is used as a probe laser to cover the spectral range 917 nm to 940 nm. By using the cavity eigenfrequencies as markers in spectral scans, we achieve a frequency resolution less than 1 MHz. This ring-down technique gives a measurement sensitivity  $\approx 10^{-9} \text{ cm}^{-1}$  for the determination of sample absorption coefficient and enables low-uncertainty measurements of individual transitions with intensities  $\sim 5 \times 10^{-27} \text{ cm}^2 \text{ cm}^{-1} \text{ molec}^{-1}$ . For the system described here, all internal surfaces of the sample volume are composed of electro-polished stainless steel (except for the viewports and cavity mirrors) and the water-vapor concentration is linked directly to primary standards of humidity generation. These two factors reduce common sources of uncertainty in the sample concentration and contribute to the line intensity measurement accuracy. We report room-temperature measurements of water-vapor foreign- and self- broadening coefficients and transition intensities (the latter with standard relative uncertainties below 0.5 %), and we quantify differential pressure shifting and collisional narrowing effects.

1. J.G. Cormier, J.T. Hodges, and J.R. Drummond, "On the Application of Cavity Ringdown Spectroscopy to Measurements of Line Shapes and Continuum Absorption," in SPECTRAL LINE SHAPES: 16th International Conference on Spectral Line Shapes (Volume 12), AIP Conference Proceedings 645, ed. Christina A. Back, pp.401-412, 2002.
2. J.T. Hodges, H.P. Layer, W.M. Miller, and G.E. Scace, "Frequency-stabilized single-mode cavity ring-down apparatus for high-resolution absorption spectroscopy," (in press) *Rev. Sci. Instr.* **75**, (2004).

## **New Information on the Infrared High-Resolution Spectroscopy of $^{16}\text{O}_3$**

**Alain Barbe, Marie-Renée de Backer-Barilly, and Vladimir G. Tyuterev**

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The infrared spectrum of the ozone molecule, main absorber of earth atmosphere must be known, in order to detect other trace gas molecule. A systematic study of this molecule is performed in GSMA (Reims). In 2004, new spectra have been recorded in the range  $4000 - 7000 \text{ cm}^{-1}$ . Very recent improvements of the FTS facilities allow now to record them with a signal/noise ratio better than 7000. This permits to observe for the first time very weak bands, with including  $\Delta v = 7$ , as well numerous hot bands. Part of these results, relevant for the knowledge of potential, dipole moment and then for ozone atlas line list compilation will be presented.

## Photolysis Rate Constants of CFC Molecules through a Spectroscopic Study

**Inmaculada Martín, Ana M. Velasco, and Esteban Mayor**

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In spite of the presently active research in atmospheric chemistry and physics, there are some relevant regions of the Earth's atmosphere that, given to practical difficulties, have not yet received full attention. Such is the case of the Ionosphere, the outermost layer, where the physical and chemical processes are determined by the VUV, EUV and X-ray solar radiation present in the region. Data on the Ionosphere's physical and chemical processes are of fundamental importance for an understanding of the solar activity on the Earth, the variation of its geomagnetic field, and other environmental aspects.

The absorption of high-frequency radiation by CFC compounds present in the Ionosphere, by diffusion from the Stratosphere, leads to a competition between their photoionization and photodissociation. Also, recent studies have concluded that Rydberg states play an essential role in the initiation of photochemical processes. The study of the photoabsorption of CFC molecules, through the allowed Rydberg channels, has been followed by the use of the calculated intensity data, in both bound and continuum spectral regions, to determine photolysis rate constants for the different dissociation pathways. The calculated rate constants have been analyzed as a function of the compound's fluorine content. An extension of the Molecular Quantum Defect Orbital (MQDO) [1,2] approach has been used to supply these data for the first time. No previous measurements nor theoretical calculations on these properties have, to our knowledge, been reported.

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## Absolute Absorption Cross-section Measurements of the Schumann-Runge Continuum of O<sub>2</sub> at 90 K and 295 K

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Laboratory measurements of the absorption cross section of the Schumann-Runge continuum of O<sub>2</sub> at the temperatures 90 K and 295 K have been made in the wavelength region 130 nm to 175 nm. The absolute absorption cross sections at the same temperatures have been measured at several discrete wavelengths through the region. The absolute cross sections of the O<sub>2</sub> continuum have been used to put relative cross sections on a firm absolute basis throughout the region 130 nm to 175 nm. These recalibrated cross sections are available as numerical compilations. In the course of these experiments, we discovered that when using the stainless-steel absorption cell the O<sub>2</sub> gas temperature was not 78 K but was 90 K, because of thermal conduction through the inner tube.

## High-temperature Pressure Broadening of Water: Experimental Evidence for Negative Temperature Exponents

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Fourier transform spectra of H<sub>2</sub>O-air mixtures have been measured at 296, 742, and 980 K for total pressures of 0.5 and 1.0 atm with a H<sub>2</sub>O VMR of 0.5% in the  $\nu_2$  band (range 1550-2300 cm<sup>-1</sup>) at a spectral resolution of 0.01 cm<sup>-1</sup>. These measurements were initially carried out in the frame of two EC projects aiming at a spectroscopic database for non-intrusive aircraft exhaust measurement. A special cell for high temperatures, good temperature homogeneity, 16 cm absorption path, equipped for continuous gas flow, has been developed to be operated stand-alone and inside the evacuated sample compartment of the Bruker IFS 120 HR FT spectrometer. Thermal emission compensation and proper transmittance calculation required high resolution sample and reference spectra for the IR source switched on and off. Temperatures were deduced from CO line intensity measurements. Line positions, linestrengths and Lorentzian halfwidths have been retrieved from the spectra. For the following analysis, only air-broadening for the doublet lines with  $K_c = J$  is considered. From these data and previous experimental determinations, line-broadening parameters  $\gamma(T)$  are obtained at all three temperatures for the doublet lines from  $J = 0$  up to  $J = 16$ . These values are then used to deduce the temperature dependence exponent  $n$ , such that  $\gamma(T) = \gamma(296) \times (296/T)^n$ . The values of  $n$  obtained using the two elevated temperatures are consistent and show that line widths decrease with  $T$  for small  $J$  values ( $n \approx +0.8$ ), are almost temperature independent on  $T$  for  $J \approx 10$ , and increase with  $T$  for high  $J$  lines ( $n \approx -0.3$  for  $J \approx 15$ ). This original result, which confirms theoretical predictions made about fifteen years ago with a semi-classical approach [1], is analyzed here using an improved version of the model.

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## Semi-empirical Calculation of Air-broadened Half-widths and Air-pressure Frequency Shifts of Water-vapor Absorption Lines

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A description of a semi-empirical calculation of the air-broadened half-widths and the air-pressure frequency shifts for the  $\text{H}_2^{16}\text{O}$  isotopologue will be presented. This semi-empirical calculation is based on fits of several recent high-quality experimental measurements and theoretical calculations to a second-order polynomial function of the differences in the upper- and lower-state vibrational quantum numbers. The aim of this work was to obtain a complete set of air-broadened half-widths and air-pressure frequency shifts for all  $\text{H}_2\text{O}$  transitions present in the HITRAN database. For around 700 sets of rotational quantum numbers ( $J'K'_aK'_c \leftarrow J''K''_aK''_c$ ), semi-empirical coefficients describing the vibrational dependence of the air-broadened half-widths and the air-pressure frequency shifts have been obtained directly from the fit of experimental and/or theoretical data. For sets of rotational quantum numbers for which either none or insufficient experimental/theoretical data were available to deduce a vibrational dependence, approximations have been used to obtain a complete set of semi-empirical coefficients. This approach has allowed us to calculate the air-broadened half-widths and the air-pressure frequency shifts for any transition of the main water-vapor isotopologue. This work has been used to update these coefficients of all the assigned transitions of the  $\text{H}_2^{16}\text{O}$ ,  $\text{H}_2^{18}\text{O}$  and  $\text{H}_2^{17}\text{O}$  isotopologues present in the 2004 HITRAN database edition. Recent atmospheric simulations in the pure-rotation region (presented in Poster PW2 at this meeting) show a marked improvement using these new results.



## Diode Laser Spectroscopic Measurement of H<sub>2</sub>O Line Shape in the 822-832 nm Spectral Region

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The line shapes of nine rovibronic components of the (2,1,1) ← (0,0,0) transition have been measured by using a high-resolution tunable semiconductor diode laser spectrometer based on Hitachi GaAlAs diodes. The diodes have standard wavelength ranges within 800 - 850 nm with typical values of 822-832 nm at 25°C. The temperature range used for wavelength scanning is 26 - 15°C. A Coherent wavemeter is employed to get the wavelength readout. An air-spaced etalon from TecOptics with an FSR of 5.00 GHz and a finesse value of 36 is used for single mode selection and relative frequency calibration. Si photodetectors (UDT455) are used for reception of spectral signals. The injection current to the laser diode is sinusoidally modulated at 5 kHz frequency and ±10 μA amplitude. Thermal tuning revealed all the transitions reported in the literature. The ramp voltage of 2V caused a 4 mA change in the laser drive current. All measurements are performed with a fixed absorber pressure of 20 Torr and varied perturber pressure in step up to 230 Torr at room temperature (298 K). Care has been taken to monitor the change of pressure during the measurement. The high sensitivity of the spectrometer enabled us to detect two very weak lines. Previous diode-laser spectroscopic measurements reported line-broadening data for only four transitions.

The first derivative spectrum thus obtained is transformed to the absorption spectrum through numerical integration routine. For simulation of the spectral lines we have used the standard Voigt profile. The Voigt profile is based on the dimensionless parameters  $x$  and  $y$  defined as  $x = (\omega - \omega_0)/\sigma$ ,  $y = \Gamma/\sigma$  and  $A = \sqrt{\pi} S/\sigma$ .  $\Gamma$  is the collisional half width arising from state changing collisions,  $\sigma = \omega_0 \sqrt{(2kT/mc^2)}$  is the calculated Doppler half width at 1/e intensity at temperature  $T$  and  $m$  is the molecular mass of the absorber.  $S$  is the line strength parameter while  $\omega_0$  is the line center frequency. The laser line width and other instrumental contributions are taken into account by using a Lorentzian function. The observed spectra were fitted by using the standard Voigt profiles. The Doppler broadening coefficient is kept constant at the theoretical value calculated for the corresponding temperature. The results obtained for the pressure broadening coefficients and line intensities agree well with the data published in the HITRAN database. The effect of collisional narrowing will also be discussed.

**PW1. The Absorption Spectrum of H<sub>2</sub>O in the Spectral Region 4200-6600 cm<sup>-1</sup>**

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New laboratory absorption spectra of water vapor have been recorded in the spectral region 4200-6600 cm<sup>-1</sup> by Fourier transform spectroscopy at high resolution (0.010 and 0.015 cm<sup>-1</sup>). A small absorption path of 32 m is used to measure the most intense lines ( $I$  up to  $10^{-20}$  cm/molec) while long absorption paths up to 1800 m allow us to obtain the best experimental conditions for the weakest lines ( $I < 10^{-27}$  cm/molec).

The observed lines have been fitted to Voigt line profiles and their parameters have been determined: calibrated line positions, absorption cross-sections, self- and air-broadening coefficients and shifts by air.

Overall, several thousand absorption lines of the H<sub>2</sub><sup>16</sup>O, H<sub>2</sub><sup>17</sup>O, H<sub>2</sub><sup>18</sup>O and HDO species are observed for the first time and identified. Comparisons with the most recent observations and calculations are presented and the improvements of this work to the databases are clearly demonstrated.

**PW2. Comparison of Far Infrared High-resolution Spectra  
with New Parameterizations for H<sub>2</sub>O and other Molecules**

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Using the high-resolution atmospheric spectra from the FIRS-2 balloon-borne interferometer, we will show the improvements in the comparison between forward calculations using the previous versions of HITRAN and recent improvements in parameterizations. FIRS-2 operates over the far-infrared wavelength region from 80 to 1400  $\text{cm}^{-1}$ . The long wavelength part of the band is dominated by the rotational transitions of H<sub>2</sub>O that had not been updated in HITRAN for some time. Recent advancements in the calculation of positions and strengths of these lines improve the calculation of the atmospheric spectra immensely. A new set of calculations for applying the mid-IR widths and pressure shifts to the rotational band also make a big improvement, especially for limb-viewing spectra with tangent altitudes in the upper troposphere. Recent improvements in molecules like HNO<sub>3</sub> are also important for properly modeling this wavelength region.

**PW3. Near Infrared Spectroscopy of Carbon Dioxide****Charles E. Miller and Linda R. Brown***California Institute of Technology, Jet Propulsion Laboratory  
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High-resolution near-infrared (4000 – 9000  $\text{cm}^{-1}$ ) spectra of carbon dioxide have been recorded using the McMath-Pierce Fourier transform spectrometer at Kitt Peak National Solar Observatory. Calibration by simultaneous use of CO near 4200  $\text{cm}^{-1}$  and  $\text{C}_2\text{H}_2$  near 6500  $\text{cm}^{-1}$  provides absolute line-position accuracies of  $6.0 \times 10^{-5}$   $\text{cm}^{-1}$  (RMS) for strong, isolated transitions throughout the observed range. Some 2500 observed positions have been used to determine spectroscopic constants for 53 different vibrational states of the  $^{16}\text{O}^{12}\text{C}^{16}\text{O}$  isotopologue, including eight vibrational states for which laboratory spectra have not previously been reported. Fits with RMS errors less than  $3.8 \times 10^{-5}$   $\text{cm}^{-1}$  have been obtained for the strongest bands, with RMS errors less than  $5 \times 10^{-4}$   $\text{cm}^{-1}$  for even the weakest fitted bands.

$^{13}\text{C}$ -enriched samples have been used to determine spectroscopic constants for 28 different vibrational states of the  $^{16}\text{O}^{13}\text{C}^{16}\text{O}$  isotopologue from over 1000 positions, the majority of which have previously been observed only in spectra of the Venusian atmosphere [1]. The analysis yielded RMS fitting residuals  $< 1.5 \times 10^{-4}$   $\text{cm}^{-1}$  for the strongest bands and RMS residuals  $< 5 \times 10^{-4}$   $\text{cm}^{-1}$  for most other fitted bands. A 5%  $^{18}\text{O}$ -enrichment in sample enabled us to observe 410 line positions from 5 near-infrared vibrational bands of the  $^{16}\text{O}^{13}\text{C}^{18}\text{O}$  isotopologue, yielding RMS fitting residuals  $< 2 \times 10^{-4}$   $\text{cm}^{-1}$ .

This work reduces  $\text{CO}_2$  near-infrared line-position uncertainties by a factor of 10 or more compared to the HITRAN2000 line list, which had not been modified since the comprehensive work of Rothman et al [2] in 1992. The new line list satisfies the line-position accuracies required for the next generation of  $\text{CO}_2$  remote-sensing instruments, improves the capability of solar-viewing spectrometers to retrieve precise column  $\text{CO}_2$  measurements, and provides a secondary frequency standard in the near infrared.

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PW4. **Einstein-A Coefficients and Statistical Weights  
in the HITRAN 2004 Spectroscopic Database**

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A description of the calculations of the statistical weights and the Einstein-A coefficients for the 39 molecules and their isotopologues present in the line-by-line section of the HITRAN 2004 database will be presented. Calculation of the Einstein-A coefficients has been done for all transitions using the HITRAN line intensities and the appropriate statistical weights. The Einstein-A coefficient and the statistical weights of the upper and lower level of the transition will be added in the new format of the line-by-line section of the 2004 HITRAN edition. Special care was necessary to determine the statistical weights since it has often been the source of errors for the Einstein-A calculation.

## PW5. Line Intensities of Acetylene at 3 $\mu\text{m}$

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The 3- $\mu\text{m}$  spectral region of acetylene is of atmospheric, planetary, and astrophysical interest. Especially, positions of hot bands were intensively studied by Rinsland et al. [1] in view of applications to cool carbon stars. In this spectral region, the HITRAN database contains accurate line positions and intensities for the cold bands  $\nu_3$  and  $\nu_2 + (\nu_4 + \nu_5)_+^0$ , deriving from the work of Vander Auwera et al. [2]. In order to improve the knowledge of the spectrum of  $\text{C}_2\text{H}_2$ , and to complete the database, we have initiated systematic measurements of line parameters in the 3- $\mu\text{m}$  spectral region.

More than 400 absolute line positions and intensities of acetylene have been measured for the two cold bands  $\nu_3$  and  $\nu_2 + (\nu_4 + \nu_5)_+^0$ , and four strong hot bands, from Fourier transform spectra recorded at GSMA (Reims). Accuracies are on the average  $0.0005 \text{ cm}^{-1}$  for line positions and 5 % for line intensities. Comparisons have been made with previous results, and a very good agreement was found with the line intensities measured by Vander Auwera et al. [2], as well as with those that Rinsland et al. obtained for a few lines of the hot bands [1].

Vibrational transition dipole-moment values have been deduced, as well as empirical Herman-Wallis coefficients. For the cold bands, Fermi-type and  $\ell$ -type resonances already observed in Ref. [2], were confirmed by the measurement of a number of new high  $J$  lines. For these bands, the adjustment using Herman-Wallis expansion is worse than the preliminary global fitting performed at Tomsk, using the effective operator approach of Perevalov et al. [3], already used for the  $\text{C}_2\text{H}_2$  molecule [4]. To improve both the database and the theoretical treatment, we plan to continue this work on the other weaker hot bands observable in this spectral region.

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PW6. **High-resolution Spectroscopy of the Methane Molecule:  
CH<sub>3</sub>D and CH<sub>2</sub>D<sub>2</sub> Species**

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High-resolution (instrumental bandwidth  $\Delta\tilde{\nu} = 0.005 \text{ cm}^{-1}$ , FWHM), FTIR spectra of CH<sub>3</sub>D in the regions 3950 - 4600 and 5700 - 6150  $\text{cm}^{-1}$  and of CH<sub>2</sub>D<sub>2</sub> in the region of 900-6400  $\text{cm}^{-1}$  were recorded with the BOMEM DA002 spectrometer in Zürich, using a long-path cell with the different path length sets up to 42 m, and different sample pressures 2-10 mbar.

The assignment of ro-vibrational structures of the recorded spectra was performed by means of ground state combination differences. Totally, more than 2900 transitions were assigned to 15 relatively strong earlier unstudied vibrational bands of the CH<sub>3</sub>D species. The maximum  $J$  value achieved was  $J^{\text{max}} = 12 - 15$  for different bands. Upper state ro-vibrational energies were determined within accuracies of 0.0003 - 0.0005  $\text{cm}^{-1}$ . For the CH<sub>2</sub>D<sub>2</sub> species more than 20 new bands (about 4000 transitions) were observed and analyzed up to  $J^{\text{max}} = 13 - 14$ .

**PW7. Near-IR Methane****Linda R. Brown**

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Over 40,000 line positions and intensities of methane have been measured from 4800-5500 and 6180 to 10000  $\text{cm}^{-1}$ , using two laboratory spectra recorded with the Kitt Peak FTS at room temperatures and at 0.01 and 0.02  $\text{cm}^{-1}$  resolution. Three regions (4800-5500  $\text{cm}^{-1}$ , 7400-7650  $\text{cm}^{-1}$ , and 8960-9160  $\text{cm}^{-1}$ ) were measured from several spectra so that better intensities and positions of the stronger features are often obtained from averaged values.

No new measurements were done for the 5500-6180  $\text{cm}^{-1}$  interval which is already in HITRAN (from Margolis [1,2]). Many weaker lines are still missing in this interval. The new measurements have been submitted for inclusion in the 2004 edition of HITRAN. Less than 2% of the features are assigned.

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The research reported in this paper was performed at the Jet Propulsion Laboratory, California Institute of Technology, under contract with the National Aeronautics and Space Administration.



PW8. **New Assignments, Line Intensities, and HITRAN Database  
for CH<sub>3</sub>OH at 10 μm**

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The Fourier transform spectrum of CH<sub>3</sub>OH in the 10-μm region has been re-examined at higher pressure and path length than heretofore, as part of a program to provide comprehensive CH<sub>3</sub>OH spectral data for astrophysical and atmospheric applications. With the increase in spectral sensitivity, it has been possible to assign new torsionally excited  $\nu_{12} = 1$  and  $\nu_{12} = 2$  subbands plus further high- $K$ ,  $\nu_{12} = 0$  subbands of the  $\nu_8$  CO-stretching band. Upper-state term values have been determined, and have been fitted to  $J(J+1)$  power-series expansions in order to obtain the excited  $\nu_8$  substate origins. A variety of weaker subbands from other modes has also been identified in the 10 μm spectrum including  $\nu_{12} = 0$ , and  $\nu_{12} = 1$  and  $\nu_{12} = 0 \leftarrow 1$  torsional subbands of the  $\nu_7$  in-plane CH<sub>3</sub> rock,  $\nu_{12} = 0 \leftarrow 1$  and  $\nu_{12} = 0 \leftarrow 2$  torsional combination subbands of the  $\nu_6$  OH bend, and  $\nu_{12} = 0 \leftarrow 2$  subbands of the  $\nu_5$  symmetric CH<sub>3</sub> bend. Line intensities have been retrieved line-by-line from the spectra. A large set of “unperturbed”  $\nu_8$  transitions has been modeled using the same type of multi-parameter effective Hamiltonian employed successfully for the ground state, with inclusion of the intensities of a subset of the stronger  $\nu_8$  spectral lines in the fitting in order to obtain appropriate transition dipole terms. Together, a 10-μm methanol database in HITRAN format has been generated.

PW9. **Accurate Rotational Spectroscopy of  $O_2$   $^3\Sigma_g^-$  and  $^1\Delta_g$   
and of  $SO_2$ ,  $\nu_2 = 0, 1$ , up to 2 THz**

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The laboratory spectroscopy group in the physics department of the Cologne university has a long tradition of performing highly accurate measurements of molecules of astrophysical, astrochemical, and planetary interest. Employing Russian backward wave oscillators (BWOs), the entire range between  $\sim 50$  GHz and  $\sim 1$  THz can be investigated. Accuracies of  $10^{-8}$  are achievable routinely for strong, isolated lines. More recently, it has become possible to record spectra with similar relative accuracies in the region of  $\sim 1.75$  to  $2.01$  THz by generating the sum frequency of a FIR laser and a BWO. Recent examples include  $CH_2$ ,  $NH_2$ ,  $PH_2$ ,  $CO$ ,  $HCN$ ,  $HNC$ ,  $H_2CO$ , and  $C_3$ .

The rotational spectra of  $O_2$   $^3\Sigma_g^-$  and  $^1\Delta_g$  in their ground vibrational states have been recorded near 2 THz with additional, selected measurements below 1 THz. The data has been analyzed together with previously reported rotational, rovibrational, and rovibronic data.

The  $\nu_2 = 0, 1$  states of  $SO_2$  have been studied extensively in selected regions below 1 THz with additional measurements near 2 THz reaching highly excited rotational states with  $J$  and  $K_a$  up to 92/81 and 23/21 for the two states. Data from previous rotational studies have been taken into account. For practical purposes, the accuracy of the  $\nu_2 = 1$  state is limited by the accuracy with which its origin is known.

PW10. **HCN Update for HITRAN**

**Mary Ann H. Smith,<sup>a</sup> David Jacquemart,<sup>b</sup> Laurence S. Rothman,<sup>b</sup> Arthur Maki,<sup>c</sup>  
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A new hydrogen cyanide (HCN) linelist has been generated for HITRAN 2004. Line positions and intensities are from the extensive work of Maki and co-workers [1,2]. Self- and air-broadening coefficients and temperature-dependence exponents for air-broadening have been assigned to all transitions based on empirical polynomials fit to available laboratory measurements [3-5]. Air-induced line shift coefficients from recent measurements have been added for the  $\nu_1$  and  $2\nu_2$  band systems. The new HCN linelist contains many more bands than previous HITRAN editions (the last HCN update was in 1986), and the quality of the parameters has been greatly improved.

1. A.G. Maki, G.Ch. Mellau, S. Klee, M. Winnewisser, and W. Quapp, "High-temperature infrared measurements in the region of the bending fundamental of  $\text{H}^{12}\text{C}^{14}\text{N}$ ,  $\text{H}^{12}\text{C}^{15}\text{N}$ , and  $\text{H}^{13}\text{C}^{14}\text{N}$ ," *J. Mol. Spectrosc.* **202**, 67-82 (2000).
2. A.G. Maki, W. Quapp, S. Klee, G.Ch. Mellau, and S. Albert, "Infrared transitions of  $\text{H}^{12}\text{C}^{14}\text{N}$  and  $\text{H}^{12}\text{C}^{15}\text{N}$  between 500 and 10000  $\text{cm}^{-1}$ ," *J. Mol. Spectrosc.* **180**, 323-336 (1996).
3. V. Malathy Devi, D.C. Benner, M.A.H. Smith, C.P. Rinsland, S.W. Sharpe, and R.L. Sams, "A multispectrum analysis of the  $\nu_1$  band of  $\text{H}^{12}\text{C}^{14}\text{N}$ : I. Intensities, self-broadening and self-shift coefficients," *J. Quant. Spectrosc. Radiat. Transfer* **82**, 319-341 (2003).
4. C.P. Rinsland, V. Malathy Devi, M.A.H. Smith, D.C. Benner, S.W. Sharpe, and R.L. Sams, "A multispectrum analysis of the  $\nu_1$  band of  $\text{H}^{12}\text{C}^{14}\text{N}$ : II. Air- and  $\text{N}_2$ -broadening, shifts and their temperature dependences," *J. Quant. Spectrosc. Radiat. Transfer* **82**, 343-362 (2003).
5. V. Malathy Devi, D.C. Benner, M.A.H. Smith, C.P. Rinsland, S.W. Sharpe, and R.L. Sams, "A multispectrum analysis of the  $2\nu_2$  spectral region of  $\text{H}^{12}\text{C}^{14}\text{N}$ : Intensities, broadening and pressure-shift coefficients," *J. Quant. Spectrosc. Radiat. Transfer*, in press (2004).

PW11. **On the Study of High-resolution Rovibrational Spectrum of H<sub>2</sub>S  
in the Region of 7300 to 7900 cm<sup>-1</sup>**

**Elena S. Bekhtereva**,<sup>a</sup> Oleg N. Ulenikov,<sup>a</sup> A.-W. Liu,<sup>b</sup> L.-Y. Hao,<sup>b</sup> and S.-M. Hu<sup>b</sup>

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High-resolution Fourier transform infrared spectrum of H<sub>2</sub>S was recorded and analyzed in the region of the  $\nu = \nu_1 + \nu_2/2 + \nu_3 = 3$  polyad. Experimental transitions were assigned to the  $3\nu_1$ ,  $2\nu_1 + \nu_3$ ,  $\nu_1 + 2\nu_3$ ,  $3\nu_3$ ,  $2\nu_1 + 2\nu_2$ , and  $\nu_1 + 2\nu_2 + \nu_3$  bands with the maximum value of quantum number  $J$  equal to 11, 14, 10, 11, 8, and 11, respectively. The theoretical analysis was fulfilled with the Hamiltonian model which takes into account numerous resonance interactions between all the mentioned vibrational states. The *rms* deviation of the reproduction of 510 upper energy levels (derived from more than 1550 transitions) with 75 parameters was 0.0022 cm<sup>-1</sup>.

PW12. **Absolute Line Intensities in the  $\nu_6$  Band of *trans*-formic Acid****Jean Vander Auwera,<sup>a</sup> K. Didriche,<sup>a</sup> Agnès Perrin,<sup>b</sup> F. Keller,<sup>b</sup> and Jean-Marie Flaud<sup>b</sup>**

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Formic acid is the simplest carboxylic acid and is found everywhere in the atmosphere, in the vapor and liquid phases. The  $\nu_6$  band of *trans*-HCOOH near  $1105\text{ cm}^{-1}$  is the strongest band of the species and, as it is located in one of the atmospheric windows, it can be used to detect it in the troposphere and lower stratosphere.

We recorded high-resolution Fourier transform spectra of samples of dry formic acid at pressures ranging from 0.11 to 3.0 mbar, using a 19.7-cm long stainless steel cell. The sample temperature was stabilized at 296 K.

Measurements of absolute line intensities require determination of the partial pressure of both the monomer and dimer of formic acid. We achieve this through analysis of the dependence with total pressure of the intensities of isolated lines of the monomer. This work also leads to measurements of pressure self-broadening parameters. Preliminary results will be presented and discussed.

PW13. **New Results on D<sub>2</sub>: A New Spectroscopic Parameterization of the Breakdown of the Born-Oppenheimer Approximation**

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By combining our experimental data with the data of others, these spectra of hydrogen and its isotopic variants will be analyzed simultaneously to obtain a measure of the breakdown of the Born-Oppenheimer approximation. We will employ a variant of the Bunker-Watson extension, which accounts for this breakdown through the nuclear mass dependence of the Dunham coefficients.

The first step in this process is to assemble and confirm accuracy of the data set and to assign appropriate statistical weights. Along these lines we have combined our data with the data of others on D<sub>2</sub> and H<sub>2</sub>. We will report on results of the reanalysis of H<sub>2</sub> and D<sub>2</sub>, show you the state of the entire database to date and provide an update on our progress towards reconfiguring the model matrix elements to be better adapted for the application to the experimental data.

The ultimate goal of this research effort is to obtain a single parameter set which can be used to calculate vibrational-rotational energy levels for H<sub>2</sub> and its isotopic variants D<sub>2</sub>, T<sub>2</sub>, HD, HT and DT in the <sup>1</sup>Σ ground electronic state. This analysis will culminate in the first determination of isotopically invariant vibration-rotation constants for the hydrogen molecule. Such a parameter set does not presently exist to our knowledge. Molecular hydrogen isotopes are of fundamental importance in the molecular sciences, especially molecular astrophysics including stellar, planetary and galactic studies.

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This effort has been funded by the NASA Planetary Atmospheres Program.

PW14. **Spectroscopy to be Required for GOSAT Trace Gas Measurement**

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**Paper Withdrawn**

**PW15. Aerosol Research at the RAL Molecular Spectroscopy Facility****Robert A. McPheat and Kevin M. Smith***CCLRC Rutherford Appleton Laboratory, Space Science & Technology Department  
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The Rutherford Appleton Laboratory (RAL) Molecular Spectroscopy Facility (MSF) provides state-of-the-art laboratories for high-resolution, broadband optical spectroscopy covering the infrared (IR), visible, and ultraviolet (UV) regions (10 to 52,000  $\text{cm}^{-1}$  or 1 mm to 180 nm). Scientific equipment available at the MSF includes Fourier transform, CCD, and diode-array spectrometers providing high spectral resolution (up to 1 part in a million), high-sensitivity, and fast time-resolved measurement capabilities. The spectrometers are interfaced to a wide range of temperature-variable spectroscopic gas cells and sample vessels for optical absorption, emission, reflectance, or scattering measurements on gases, vapours, liquids, solids and aerosols at path-lengths from 1 mm to over 1 km and temperatures of 77 to 350 K.

A 75 litre coolable aerosol cell has been optically and mechanically interfaced to a Fourier transform spectrometer (FTS). A flexible system for generating stable flows of mimic polar stratospheric cloud (PSC) aerosols such as super-cooled ternary solution (STS) and sulphate has been developed and used for a number of experiments. Systems for generating solid aerosols such as Saharan and volcanic dust are under development.

Examples of IR and visible/UV extinction spectra of STS aerosol are given together with complex refractive indices derived from the measurements using a damped harmonic oscillator model. Future developments are described including measurements on other types of PSC (e.g. NAT) and the integration of a scanning mobility particle sizer, optical particle counter and mass spectrometer.



PW16. **Absorption Cross-sections for the Infrared Bands of Peroxyacetyl Nitrate**

**Grant Allen**,<sup>a</sup> **John J. Remedios**,<sup>a</sup> **Kevin M Smith**,<sup>b</sup> **David A Newnham**,<sup>b(\*)</sup> and **Paul S. Monks**<sup>c</sup>

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Infrared absorption cross-sections for peroxyacetyl nitrate (PAN) have been measured using a Fourier transform infrared spectrometer, over the region from 550 to 2200  $\text{cm}^{-1}$ , at spectral resolutions of 0.25 and 0.03  $\text{cm}^{-1}$ . Measurements were recorded of independent PAN samples at nominal temperatures of 250K, 273K and 294K at a range of pressures, both for the pure gas and in an excess nitrogen mix.

The cross-section data will be presented with estimated uncertainties, and comparisons of integrated band strengths with previous work will be made. Uncertainty in the nature of the 1740  $\text{cm}^{-1}$  ( $\nu_{\text{as}}(\text{NO}_2)$ ) PAN absorption band will also be discussed. A description of the application of these new data to infrared remote sensing techniques for the retrieval of trace organic species will be given.

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## The 2004 Edition of the HITRAN Compilation

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The new 2004 edition of the HITRAN compilation represents a major stride forward in several areas. Foremost for the scientific community is an extensive improvement of the parameters for many bands of practically all molecular species on the database. Many of these improvements have been discussed in past workshops and meetings, and have finally come to fruition. This presentation highlights some of the more important of these upgrades. Preliminary comparisons with high-resolution laboratory and field observations indicate substantial improvements in simulations.

The line-by-line portion of the new compilation has undergone its second format revision since the first edition of HITRAN [1]. The line transition now contains the Einstein-A coefficient, statistical weights of the transition, allows for a more explicit and rigorous quantum identification, identifies lines that are subject to a line-coupling algorithm, and increases the number of parameters linked to references and uncertainty codes. The software that comes with the compilation, JavaHAWKS, has also been enhanced.

The distribution continues to be through an anonymous ftp-site, and work is underway to also provide the user with access to a local server to handle most JavaHAWKS functions.

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1. R.A. McClatchey, W.S. Benedict, S.A. Clough, D.E. Burch, R.F. Calfee, K. Fox, L.S. Rothman, and J.S. Garing, "AFCRL Atmospheric Absorption Line Parameters Compilation," AFCRL-TR-0096 (1973).

The current effort has been supported by the NASA Earth Observing System (EOS), under the grant NAG5-13534, funding from the Office of the Secretary of Defense (OSD) High Energy Laser Joint Technology Office, and internal Smithsonian Institution funds.

## The Cologne Database for Molecular Spectroscopy, CDMS

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The CDMS [1] has been around for a few years. One central part is a catalog of (mostly) rotational transition frequencies of atomic and molecular species from the radio frequency to the far-infrared regions (i.e. frequencies up to 18 THz or wavelengths longer than 16.5  $\mu\text{m}$ ). As of February 2004, the catalog contains about 220 species of astrophysical, astrochemical, and planetary interest.

Examples of recent entries such as light hydrides, vibrationally-excited and isotopic data will be given. Several entries are of interest for the atmospheric community, e.g. CO, HCN, H<sub>2</sub>CO, HCOOH, SO<sub>2</sub>. Emphasis is also put on providing accurate line frequencies that are not only important for the study of dynamics of interstellar clouds but that may also be used as secondary standards in the sub-millimeter and far-infrared regions. Finally, the calculation of partition functions will be discussed.

The database 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>.

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1. H.S.P. Müller, S. Thorwirth, D.A. Roth, and G. Winnewisser, *Astron. Astrophys.* **370**, L49--L52 (2002);  
H.S.P. Müller, F. Schlöder, S. Thorwirth, J. Stutzki, and G. Winnewisser; in *Proceedings of the 4th Cologne-Bonn-Zermatt-Symposium* "The Dense Interstellar Medium in Galaxies," Springer Verlag, Heidelberg, 2003, in press.

## The 2003 Edition of the GEISA Database

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The **GEISA** (**G**estion et **E**tude des **I**nformations **S**pectroscopiques **A**tmosphériques: **M**anagement and **S**tudy of Atmospheric Spectroscopic Information) computer accessible database system, in its former 1997 and 2001 versions, has been updated in 2003 (GEISA-03). The GEISA 2003 system comprises three databases with their associated management softwares:

- a database of spectroscopic parameters required to describe adequately the individual spectral lines belonging to 42 molecules (96 isotopic species) and located in a spectral range from the microwave to the limit of the visible. The featured molecules are of interest in studies of the terrestrial as well as the other planetary atmospheres, especially those of the Giant Planets.
- a database of absorption cross-sections of molecules such as chlorofluorocarbons which exhibit unresolvable spectra.
- a database of refractive indices of basic atmospheric aerosol components.

Illustrations will be given of GEISA-03, data archiving method, contents, management softwares and Web access facilities at: <http://ara.lmd.polytechnique.fr>. The performance of instruments like AIRS (Atmospheric Infrared Sounder; <http://www-airs.jpl.nasa.gov>) in the USA, and IASI (Infrared Atmospheric Sounding Interferometer; <http://smc.cnes.fr/IASI/index.htm>) 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, since these are essential input in the forward models used to simulate recorded radiance spectra. For these upcoming atmospheric sounders, the so-called GEISA/IASI sub-database system has been elaborated, from GEISA. Its content, will be described, as well.

This work is ongoing, with the purpose of assessing the IASI measurements capabilities and the spectroscopic information quality, within the 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) Polar System (EPS) project, by simulating high resolution radiances and/or using experimental data. EUMETSAT will implement GEISA/IASI into the EPS ground segment.

The IASI soundings spectroscopic data archive requirements will be discussed in the context of comparisons between recorded and calculated experimental spectra, using the ARA/4A forward line-by-line radiative transfer modelling code in its latest version.

## Access to Databases of Atomic and Molecular Data in the Virtual Observatory

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Numerical and bibliographical Databases in Atomic and Molecular Physics are essential for both the modelling of various astrophysical media and the interpretation of astrophysical spectra provided by ground or space-based telescopes. We report here on our current project concerning the access to Atomic and Molecular Physics Databases within the Virtual Observatories [1], addressing the organization/access of data for specific astrophysical applications and the use of standards for interoperability. This talk aims at informing people about interoperability matters, in order to try to compile efforts which are already started in this domain, evaluate the needs and requirements of the targeted interrelation of atomic and molecular data bases with VO projects, and try to establish collaborations in this domain.

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1. <http://www.ivoa.net>

## **BEAMCAT: a Tool for Accessing and Comparing Spectroscopic Data from Multiple Spectroscopic Databases**

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Users of spectroscopic data bases in the microwave region quickly realize that each existing spectral line catalog provides only part of the information that they would like to have. As a workaround for this problem, several merged spectral line data bases have been created by different groups over the years. However, these merged data bases are usually very specific for a certain application and are difficult to maintain. The BEAMCAT data base takes a totally new approach that makes it possible to generate merged spectral line catalogs from any number of source catalogs in multiple user-defined formats on-the-fly. The current version of BEAMCAT contains the complete JPL and HITRAN catalogs. Other catalogs like GEISA or CDMS are planned to be included in the future.

As a first application of the BEAMCAT data base, a thorough intercomparison of spectral parameters for all the transitions that the JPL catalog and HITRAN have in common was conducted. The intercomparison shows that the spectral parameters in the catalogs are by no means identical. While the difference in center frequency is usually small, the differences in line intensity reach from almost exact match to discrepancies of several orders of magnitude. While it cannot be ruled out that some of the lines were matched incorrectly, this intercomparison might be helpful to identify problems with the original catalogs.

BEAMCAT is not a spectral line catalog itself but a meta-catalog which is a useful tool to handle all kinds of spectral line databases. It uses a modern and free SQL database system that essentially eliminates most of the data-format related problems that many catalogs suffer from. BEAMCAT is provided as a free and open service to the community and all users are welcome to contribute.

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See <http://www.beamcat.org> for more information.

## Assessment of Molecular Line Parameters in the Near-infrared

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The absorption line parameters of the first seven molecules in HITRAN are evaluated between 4000 and 14000  $\text{cm}^{-1}$ . These seven molecules,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{O}_3$ ,  $\text{N}_2\text{O}$ ,  $\text{CO}$ ,  $\text{CH}_4$ , and  $\text{O}_2$ , were the species present in the first published HITRAN [1], chosen because of their significant absorption in the telluric atmosphere due to a convergence of their strong electric dipole moments (magnetic dipole in the case of oxygen) and their concentration in the atmosphere.

This presentation assesses three components: 1) an appraisal of the completeness and uncertainties of parameters in the 2000 edition of the HITRAN database; 2) identification of new results that represent potential improvements in the near term; and 3) recommendations for future laboratory research to remedy serious faults in the database.

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1. R.A. McClatchey, W.S. Benedict, S.A. Clough, D.E. Burch, R.F. Calfee, K. Fox, L.S. Rothman, and J.S. Garing, "AFCRL Atmospheric Absorption Line Parameters Compilation," AFCRL-TR-0096 (1973).

**Validation of the 12- $\mu$ m Ethane Database,  
New IR Heterodyne Spectroscopy Intensity Results,  
Frequency Validation, and Insights into the Construction of the Database**

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Recent questions regarding the HITRAN 12-micrometer ethane frequencies led us to reinvestigate ethane frequencies and intensities which we had published in NASA Technical Memorandum 85108 (The 12 micron band of ethane: a spectral catalog from 765  $\text{cm}^{-1}$  to 900  $\text{cm}^{-1}$ , A.K. Atakan, W.E. Blass, J.W. Brault, G.W. Halsey, D.E. Jennings, D.C. Reuter, and J. Susskind, November 1983). We will present a detailed structural history of the evolution of the database. Many persons are not aware that the published transition frequencies are calculated frequencies. We address questions regarding the value and validity of the database frequencies. Validation of frequencies includes comparison with observations of ethane transition frequencies in the atmospheres of the outer planets and Titan made by the Goddard Space Flight Center infrared heterodyne spectroscopy group using their Infrared Heterodyne Spectrometer and HIPWAC instruments. New intensity measurements carried out at GSFC in the heterodyne spectroscopy laboratory validate the published database intensities – about which there has been some question based on lower resolution observations. We also present a comparison study [1] of the 1996 HITRAN ethane database versus the GSFC-Tennessee database.

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1. UTCSL Technical Report 2003A, James Wicker and Forrest Hoffman, Knoxville, Tennessee 2003. These efforts have been funded by the Department of Physics and Astronomy, The University of Tennessee and the NASA Planetary Atmospheres Program.



## Constructing a Reliable Line List for Water in the Near Infrared and Visible

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Water is molecule number 1 in the HITRAN line list but there remains controversy over whether even some of the most basic properties of water spectra are correctly represented in the HITRAN data base [1]. This is particularly true for the atmospherically critical near infrared and visible region. Our strategy to resolve this problem and hence obtain a reliable and comprehensive linelist is to take data from different sources:

1. Strong line parameters are best determined using laboratory data for water-air spectra recorded at several pathlengths. For these lines accurate fits to the measurements is crucial.

2. Weak line parameters are best determined from long pathlength laboratory spectra of pure water vapour. For weak lines the main problem is obtaining the correct spectral assignments and accurate intensities. Pressure dependent line parameters are of less importance.

3. Isotopomer parameters, particularly for  $\text{H}_2^{18}\text{O}$  and  $\text{H}_2^{17}\text{O}$  can be determined using spectra recorded using isotopically enhanced samples. Such spectra are available from spectra of isotopically enhanced samples recorded in the 1980's and available in the Kitt Peak archive and recently from the group of Ubachs who have used cavity ring down techniques. A new HDO spectrum is available from the Brussels group.

4. Variational line lists are used to aid assignments and to check for the completeness of the data determined experimentally. If necessary, results can be used to fill in gaps in experimental data or to estimate the effect of data (e.g., very weak lines) not observed in the experiments.

Validating any line list against independent data is an important final step in proving its accuracy.

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1. D. Belmiloud, R. Schermaul, K. Smith, N.F. Zobov, J. Brault, R.C.M. Learner, D.A. Newnham, and J. Tennyson, *Geophys. Res. Lett.*, **27**, 3703-3706 (2000).

## **New Cross Sections and Indices of Refraction of Atmospheric Interest**

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New cross sections of species of upper tropospheric interest (e.g. acetone, PAN) have been recently measured at cold temperatures. We discuss the temperature and pressure dependencies of these cross sections, and also comment on the sensitivity of the cross sections to instrument resolution.

A review is presented of the indices of refraction that are on the HITRAN 2001 compilation. Current uncertainties of the indices of refraction and the measurement challenges of current and future satellite sensors are also addressed.

**PT1. Line-shape Parameters for Water Vapor in the 3.2-17.76  $\mu\text{m}$  Region****Robert R. Gamache**

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Several NASA EOS instruments, the Atmospheric Infrared Sounder (AIRS) on Aqua, and the Tropospheric Emission Spectrometer (TES) and the High Resolution Dynamics Limb Sounder (HIRDLS) on AURA, will be measuring water vapor in the earth's atmosphere in the 3.2 to 17.76  $\mu\text{m}$  spectral region. In order to do retrievals of temperature and concentration profiles, the spectral parameters for many thousands of water vapor transitions must be known. Currently the largest uncertainty in these data is associated with the pressure-broadened half-width. To aid in this situation, complex Robert-Bonamy calculations were made to determine  $\text{N}_2$ -,  $\text{O}_2$ -, and air broadened half-widths and line shifts for 5442 transitions of the principal isotopologue of water vapor for the eleven vibrational bands in this region. The formalism is complex valued, thus the half-widths and line shifts are obtained from a single calculation. The application of linked-cluster techniques in the CRB formalism eliminates the awkward cutoff procedure that characterized earlier theories. The intermolecular potential is a sum of electrostatic terms (dipole-quadrupole and quadrupole-quadrupole), isotropic induction and London dispersion terms, and the atom-atom potential expanded to eighth order. The parameters are adjusted as described in Ref.[1]. Calculations were made at 225 and 296 K in order to determine the temperature dependence of the half-widths. When possible, the data are compared with measurements. The average percent difference between the measured and calculated half-widths is -1.97, 2.6, and -1.55 for  $\text{N}_2$ -,  $\text{O}_2$ -, and air-broadening of water vapor, respectively. The agreement for the line shifts is less satisfactory. It is clear that the calculations will benefit from a comprehensive adjustment of the intermolecular potential. The data and comparison plots can be obtained at [http://faculty.uml.edu/Robert\\_Gamache](http://faculty.uml.edu/Robert_Gamache).

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1. R.R. Gamache and J.-M. Hartmann, *J. Quant. Spectrosc. Radiat. Transfer* **83**, 119–47 (2004).

PT2. **Determining the Profile of Strong Water Lines  
at Visible and Near-infrared Wavelengths**

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Parameters which determine the profile of water vapour lines have been measured many times in the visible and near infrared region of the spectrum. HITRAN is probably the most extensive and reliable database containing these parameters which widely used in atmospheric and other applications. But despite recent updates there remain strong indications [1] that HITRAN still underestimates water absorption in the visible and near infrared. On the other hand the database ESA-WVR based on laboratory spectra recorded by Schermaul et al [2] apparently overestimates water line intensities. Believing that the correct answer lies somewhere in between we have performed a systematic reanalysis of the spectra in [2] plus other spectra recorded in same experiment but with different pathlengths and not previously analysed. These accurate comparisons revealed an additional source of systematic errors in the line intensities determination. This has allowed us to remove inconsistencies in the experimental data and hence obtain new, more accurate line parameters. The latest results will be reported at the conference.

1. R.N. Tolchenov et al, *J. Quant. Spectrosc. Radiat. Transfer* **82**, 151-163 (2003).
2. R. Schermaul et al, *J. Molec. Spectrosc.* **208**, 32-42 (2001).

**PT3. The Spectral and Molecular Properties of Ozone (S&MPO) Databank****Alain Barbe,<sup>a</sup> S.N. Mikhailenko,<sup>b</sup> V.I.G. Tyuterev,<sup>a</sup> and Yu.L. Babikov<sup>b</sup>**<sup>a</sup>*Université de Reims**GSMA, BP 1039, 51687 Reims Cedex 2, FRANCE*<sup>d</sup>*Institute of Atmospheric Optics, Siberian Branch, Russian Academy of Sciences  
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Results of recent studies of the ozone molecule are summarized in the interactive graphical information system S&MPO (Spectroscopy and Molecular Properties of Ozone) accessible via Internet. This project is essentially based on experimental and theoretical joint research of laboratories GSMA (Reims) and LTS (Tomsk) supplemented with some results of larger collaborations and with information available in spectroscopic literature. It contains experimental FTS spectra, information on molecular properties, and allows a calculation of a databank of rovibrational line positions and intensities (which is complementary to existing databases as HITRAN or GEISA but contains much more information in 3000 to 6000 cm<sup>-1</sup> range) and absorption/transmittance simulation.

The current version of S&MPO is accessible at two sites: <http://ozone.univ-reims.fr> and <http://ozone.iao.ru>. It has benefited from a large collaboration, in particular contributions from M.-R. Barilly-DeBacker, S. Tashkun, X. Thomas, P. Von Der Heyden, H. Seghir, J.-J. Plateaux, R.R. Gamache, and J.-M. Flaud are gratefully acknowledged. We also thank D. Schwenke for collaborations in global ozone calculations.

The state-of-the-art studies of rovibrational spectra of ozone and its isotopologues in the high-wavenumber range will be discussed.

**PT4. FT Absorption Spectrum of HDO in the Visible and Near-IR****Mohamed Bach,<sup>a</sup> Michel Carleer,<sup>a</sup> Pierre-François Coheur,<sup>a</sup> Sophie Fally,<sup>a</sup>  
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This work presents an extensive listing of HDO spectroscopic parameters in the visible and near-infrared spectral region (20 000 to 11 600 cm<sup>-1</sup>). Absorption spectra of H<sub>2</sub>O:D<sub>2</sub>O:HDO obtained by filling the cell with H<sub>2</sub>O + D<sub>2</sub>O mixtures have been recorded by Fourier transform spectroscopy at high resolution (0.06 cm<sup>-1</sup>) with a long absorption path (600 meters). After a careful removal of the H<sub>2</sub>O and atmospheric O<sub>2</sub> lines and a clear identification of weak D<sub>2</sub>O lines observed in the region 13120-12600 cm<sup>-1</sup>, about 3000 HDO lines belonging to several vibrational bands have been identified and assigned. The lines have then been fitted to Voigt line profiles in order to derive the line parameters. Wavenumber calibrated line positions, absorption cross-sections, nitrogen-broadened widths and shifts are presented. Such experimental data are reported for the first time.

PT5. **Tunable-diode Laser Absorption of H<sub>2</sub>O Vapor  
between 1355 and 1441 nm versus *T* and *P*  
and Comparison to HITRAN Predictions**

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Direct absorption spectra of H<sub>2</sub>O vapor in the 1355-1441 nm (6940-7380 cm<sup>-1</sup>) spectral region were measured as a function of pressure and temperature using an external cavity diode laser (ECDL). The experiments were conducted on gas samples in a static cell placed at the center of a 3-zone tube furnace, where a very uniform temperature distribution can be achieved. Line strength and self-broadening coefficients of 47 selected strong transitions were inferred from Voigt fits to the measured spectra of neat H<sub>2</sub>O vapor at pressures of 1 to 18 Torr and temperatures of 296 to 1000K. Air-broadening coefficients were inferred from measured spectra of H<sub>2</sub>O-air mixtures at pressures of 100 to 600 Torr and temperatures of 296 to 1000K. The measured spectra were compared with predictions by HITRAN2000/HITEMP and the preliminary version of HITRAN2004. The measured linestrengths agree well with HITRAN2004 (average deviation of  $\sigma_{\text{avg}} = 6\%$ ), and poorly with HITRAN2001/HITEMP ( $\sigma_{\text{avg}} = 23\%$ ) for the selected strong lines over the entire temperature range. Measurements of the self-broadening and air-broadening coefficients of those selected transitions have recently been completed. Analysis of these data is underway and results will be available for presentation.

PT6. **Intensity and Air-broadening Coefficients of H<sub>2</sub>O and CO<sub>2</sub> Lines with a Near-infrared Spectrometer**

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A near infrared diode laser spectrometer was used in the laboratory to study H<sub>2</sub>O and CO<sub>2</sub> line intensities and pressure broadening coefficients near 1.39 and 1.60 μm. The spectral region ranging from 7165 to 7186 cm<sup>-1</sup> which is of interest for the in situ monitoring of H<sub>2</sub>O in the middle atmosphere from balloon platforms [1] was studied at first. Twenty-three transitions of ν<sub>1</sub>+ν<sub>3</sub> and 2ν<sub>1</sub> bands have been studied. The results of intensity measurements are carefully compared to previous experimental determinations, *ab initio* calculations and HITRAN database [2]. The broadening coefficients by N<sub>2</sub> and O<sub>2</sub> for the 4 transitions used by the SDLA spectrometer of the Service d'Aéronomie are also reported. The spectral region ranging from 6230 to 6250 cm<sup>-1</sup> which is suitable for the in situ sensing of CO<sub>2</sub> in the lower stratosphere was studied using a commercial telecommunication type diode laser. Thirteen lines of the (30<sup>0</sup>1)<sub>III</sub>←(000) band of CO<sub>2</sub> have been studied. The results of intensity measurements are compared to previous determinations and available databases: HITRAN and CDS (Carbon Dioxide Spectroscopic Databank created using the effective operator approach). Furthermore, the broadening coefficients by N<sub>2</sub> and O<sub>2</sub> for the strongest transitions are also reported [3].

1. G. Durry, A. Hauchecorne, J. Ovarlez, I. Pouchet, V. Zéninari, and B. Parvitte, *J. Atmos. Chem.* **43**, 175 (2002).
2. B. Parvitte, V. Zéninari, I. Pouchet, and G. Durry, *J. Quant. Spectros. Radiat. Transfer* **75**, 493 (2002).
3. I. Pouchet, V. Zéninari, B. Parvitte, and G. Durry, *J. Quant. Spectros. Radiat. Transfer* **83**, 619 (2004).



**PT7. Line Strengths and Half-widths of CO<sub>2</sub> Bands in the 2.7- $\mu$ m Region  
at Atmospheric Temperatures**

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Absorption spectra of the (10011-00001) and (10012-00001) bands of CO<sub>2</sub> were measured with a high-resolution Fourier transform spectrometer at 298K, 240K, and 180K. We used the temperature-variable absorption cell with the path length of 1 cm. The line strengths, N<sub>2</sub>-, and O<sub>2</sub>-broadened half-widths were determined with a nonlinear least-squares fitting technique. The squared transition dipole moments and the coefficients of the Herman-Wallis factors were also determined. The measured line strengths of these bands agreed with the values of the HITRAN databases within the experimental errors. N<sub>2</sub>- and O<sub>2</sub>-broadened half-widths obtained in this study agreed well with the recent high-resolution experiments. The temperature dependence of the half-width was determined assuming the power-law is valid. The exponents of N<sub>2</sub>- and O<sub>2</sub>-broadened half-widths showed the dependence on the rotational quantum number.

**PT8. Spectral Line Parameters for CO<sub>2</sub> Bands near 4.8 μm****Tomoaki Tanaka,<sup>a</sup> Masashi Fukabori,<sup>b</sup> Hideaki Nakajima,<sup>a</sup> Tatsuya Yokota,<sup>a</sup>  
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High-resolution spectra of CO<sub>2</sub> bands near the 4.8-μm region were measured by using a Bruker IFS 120HR spectrometer at room temperature (299K). The (11101-00001), (11102-00001), and (20001-01101) bands of CO<sub>2</sub> reveal remarkable contrast in intensity perturbations, i.e. enhancing the P-branch, while reducing R-branch. A nonlinear least-squares fitting procedure is used to determine the line strengths and half-widths of the above bands. As a result of the analysis, the squares of the vibrational dipole moment and the coefficients of the Herman-Wallis factor for these bands are derived. Our data are compared with the values in the HITRAN database.

**PT9. Lineshape Studies of Rotational Transitions of Ozone and Nitric Acid**

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**François Rohart**,<sup>a</sup> **Gabriele Cazzoli**,<sup>b</sup> **Luca Dore**,<sup>b</sup> **Cristina Puzzarini**,<sup>b</sup>  
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In the framework of a contract provided by the European Space Agency, linewidth measurements have been performed on selected rotational lines of ozone and nitric acid, mostly located between 300 and 350 GHz, in the B and C bands of the MASTER platform. Broadening parameters have been determined for O<sub>3</sub> in collision with N<sub>2</sub> and O<sub>2</sub> at five different temperatures in the 190-300K range. For nitric acid, only air broadening coefficients were measured at 296K. The experiments have been performed at LMSB (Bologna) and PhLAM (Lille) by using both different experimental set-ups and different analysis procedures. At PhLAM, the true lineshapes were observed with a video-type spectrometer and compared to Voigt and Galatry theoretical models. At LMSB, a Galatry model has been used to analyse the second derivative of the natural line profiles recorded with a frequency modulation spectrometer. Several lines of ozone and nitric acid were measured in both laboratories. The results of the intercomparison will be discussed.

PT10. **Self- and H<sub>2</sub>-Broadened Width and Shift Coefficients  
in the 2←0 Band of <sup>12</sup>C<sup>16</sup>O: Revisited**

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Room temperature values for self-broadened and hydrogen-broadened Lorentz half width coefficients, and self and hydrogen pressure-induced shift coefficients have been measured for transitions with rotational quantum number  $m$  ranging between  $-24$  and  $24$  in the  $2\leftarrow 0$  band of <sup>12</sup>C<sup>16</sup>O. The spectra were recorded with the McMath-Pierce Fourier transform spectrometer located at the National Solar Observatory on Kitt Peak. The analysis was performed using a multispectrum nonlinear least squares technique. We have compared our results with similar measurements published recently.

PT11. **CO Broadening and Shift Parameters for TES****Mary Ann H. Smith,<sup>a</sup> Linda R. Brown,<sup>b</sup> V. Malathy Devi,<sup>c</sup> and Travis J. Pittman<sup>d</sup>**

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The Tropospheric Emission Spectrometer (TES), an instrument on NASA's EOS-Aura spacecraft to be launched this year, is designed to measure the composition and structure of the earth's lower atmosphere. In response to the TES science team's stated requirements for line parameter accuracies, the quality of the HITRAN 2000 database [1] for CO was evaluated in light of recent laboratory studies. Key problems with the HITRAN 2000 database were its assignment of a too-low constant value for the temperature-dependence of air broadening, and its assumption of a value of zero for all pressure-induced CO line shifts by air. A new CO database incorporating improved line broadening and shift parameters was written for the 5- $\mu\text{m}$  region used by TES. New laboratory results [2,3] were used for the air-broadening, temperature-dependence of air-broadening, and air-shift parameters. Self-broadening coefficients in the new line list are based on more than 15 published studies of the fundamental and first two overtone bands of CO. The TES linelist has been used as the basis for updating all CO broadening and shift parameters for the 2004 edition of HITRAN.

1. L. S. Rothman *et al.*, "The HITRAN molecular spectroscopic database: Edition of 2000 including updates through 2001," *J. Quant. Spectrosc. Radiat. Transfer* **82**, 5-44 (2003).
2. Q. Zou and P. Varanasi, "New laboratory data on the spectral line parameters in the 1-0 and 2-0 bands of  $^{12}\text{C}^{16}\text{O}$  relevant to atmospheric remote sensing," *J. Quant. Spectrosc. Radiat. Transfer* **75**, 63-92 (2002).
3. K. Sung and P. Varanasi, "Intensities, collision-broadened half-widths, and collision-induced line shifts in the second overtone band of  $^{12}\text{C}^{16}\text{O}$ ," *J. Quant. Spectrosc. Radiat. Transfer* **83**, 445-458 (2004).

PT12. **Air-broadening Parameters in the  $\nu_3$  Band of  $^{14}\text{N}^{16}\text{O}_2$   
Using a Multispectrum Fitting Technique**

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Air-broadened line widths, pressure-induced shift coefficients and their temperature dependences were retrieved for over 1000 transitions in the  $\nu_3$  band of  $^{14}\text{N}^{16}\text{O}_2$  at 6  $\mu\text{m}$ . In addition, precise line-center positions and relative intensities were also determined. The results were obtained by fitting simultaneously 27 spectra recorded at high resolution (0.002  $\text{cm}^{-1}$  to 0.006  $\text{cm}^{-1}$ ) with two Fourier transform spectrometers and gas-sample temperatures ranging from 206 K to 298 K. It was necessary to modify the multispectrum fitting software to accommodate constraints on the retrieved parameters of closely-spaced spin-split doublets in order to successfully determine their broadening and shift parameters. The variations of the widths, shifts, and their temperature dependences with the quantum numbers were investigated. Subsets of the observed line widths were reproduced to within 3% using an empirical smoothing function.

**PT13. Spectroscopic Broadening Study of SO<sub>2</sub> in Submillimeter Region  
Using a Laser Heterodyne Spectrometer**

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The detection of the molecular line signals by heterodyne reception is the most powerful experimental method. A submillimeter (SMM) laser heterodyne spectrometer using optically-pumped molecular gas laser as local oscillator and Schottky diode as mixer has been developed at Physical Research Laboratory, Ahmedabad (INDIA).

The structure of the molecular line contains detailed information of the dynamics and temperatures of the investigated region as well as of the abundances of the various species in the space (planets and interstellar) concerned.

The accuracy of the molecular concentration resulting from remote sensing measurements depends to a large extent upon the accuracy of the spectroscopic data available for the molecule concerned. Among the data needed are the line transition frequency, line strengths, foreign gas broadening coefficients, and ground state energies.

In order to interpret the atmospheric absorption signals laboratory measurements of pressure and temperature effects have been made. In this paper we describe the results and technique based on molecular absorption measurements in 500-800 GHz frequency region. A quantitative study of SO<sub>2</sub> (Theoretical and experimental) has been performed in the laboratory. The self and foreign gas (N<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub>O) pressure effects on the SMM wave absorption line profiles have been investigated for SO<sub>2</sub> in 500-800 GHz frequency region. The observed absorption profiles have been fitted with the Voigt function. The obtained pressure broadening coefficients are consistent with the theoretically calculated values.

PT14. **Studies of Collision-induced Absorption in N<sub>2</sub> and O<sub>2</sub>  
in the Temperature Range 296 to 363 K**

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The temperature range of the NIST high-pressure White cell has been extended to cover the range from -80 to 90 °C with a precision of  $\pm 0.3$  °C. The spectra of purified samples of O<sub>2</sub> have been studied using an optical path of 84.05 m with pressures up to 5 atm and with temperatures ranging from -80 to 80 °C. We find, somewhat unexpectedly, that the integrated band intensity of O<sub>2</sub> comes to a minimum at about 280 K and rises on either side of this temperature. The spectra of purified samples of N<sub>2</sub> have also been obtained at elevated temperatures and pressures up to 7 atm. When the data of these measurements are combined with previous lower temperature studies, a similar behavior of the integrated band intensity is observed with the minimum in the band intensity near 280 K.



PT15. **Photoionization Cross Sections for Atmospherically  
and Astrophysically Relevant Molecules**

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Photoabsorption processes are receiving increasing attention both from experimentalists and theoreticians. This may be partly due to their role in atmospheric and interstellar chemistry as these processes are some times followed by photodissociation in many of the compounds that are relevant in these areas. Additionally, many of the state-of-the-art experimental techniques designed to prepare new chemical lasers, including the separation of laser isotopes, are based, in a way or other, on the photofragmentation of simple molecules. A variety of observations are presently being employed to explore the fundamental dynamics of photoionization processes. Photodissociation experiments are also supplying a wealth of data to theoreticians as regards the nature and properties of excited electronic states, in particular those which exhibit a Rydberg character.

In this work, we have undertaken the study of photoionization processes of different molecular species, such as N<sub>2</sub>O, NO, HCl, CH<sub>4</sub> and some CFC's, which are of fundamental importance and find application in a large number of scientific contexts, including aeronomy, astrophysics, planetary sciences, radiation chemistry, physics, and biology. A molecular-adapted version of the Quantum Defect Orbital (MQDO) method, which has proven to yield correct intensities for Rydberg transitions in a large variety of molecular species (see, e.g. Refs.[1-3]), has been adopted in the present calculations. The correctness of our procedure has been assessed with the help of experimental data available in the literature, and by the criterion of continuity of the differential oscillator strength across the ionization threshold, for all the Rydberg series considered.

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2. A.M. Velasco, E. Bustos, I. Martín, and C. Lavín, *J.Phys. Chem. A*, **106**, 6401 (2002).
3. A.M. Velasco, E. Mayor, and I. Martín, *Chem. Phys. Letters* **376**, 159 (2003).

## PT16. **Information System for Calculating the Spectral Characteristics of Inhomogeneous Gases**

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The principles of creation of high resolution spectroscopy information system (HRSIS) are discussed in the report. The system area of spectroscopic characteristics take in spectral line parameters (line center, intensity, level energy, quantum identification and so on), absorption coefficient, emissivity and transmission. There are three subsystems as principal parts: experimental data subsystem; calculation data subsystem and generating recommended data subsystem. The ideology of HRSIS organization was suggested earlier [1-4], but the level of computerization allows to the realization it in fully only at last years.

The general structure of the system is intended for the two kinds of users. First of them are the specialists in molecular spectroscopy and their interests are directed for analysis of molecular and spectroscopic constants, spectral line parameters, and spectral characteristics calculation. Other kind of physicists need to be acquainted only with the purpose, the method of representation of the input-output data and the form of representation of the results.

The structure of this system is next:

- I. The experimental, calculated, recommended spectral line parameters (SLP) databases
- II. The spectroscopic and molecular constants archives
- III .The calculation modules library
- IV. The SLP databases and archives management subsystems
- V. The servicing programs

The functions of subsystems are following:

Data input, structure and format control  
Interaction with the SLP databases and archives  
Search of bibliography

The every subsystem has different structure and string format. The storage of experiment conditions is very important because the interpretation of results due to environmental conditions [5]. The most problem is formalization of formulation of recommended values data. It is supposed the elaboration of criteria based on including the SLP values into database. The disagreement between the numerical SLP values both experimental and calculated can be very large. The same should be note for absorption coefficients and emissivities for the equal environmental conditions.

Before creating the recommended SLP database the first operation is the access to service programs for reduction of all the data in the required frequency interval from the experimental SLP database to wanted conditions (temperature and pressure), default conditions are normal (300K and 1 atm ). The next step is the analysis of the different experimental values for the same parameters and choose the most probable value using the developed criteria. The absent in experimental database values generates by second sybssystem.

The separate block of the system is part "Gas radiation". It's functions allow the calculation of transmissivity, absorption, emissivity and the dependences of the above spectral characteristics from spatial distribution of temperature and gas concentration in gas volume.

The HRSIS modules can use separately and can modify for new system configuration. So, the information system HOTGAS 2.0 is described which allows the parameters of vibrational-

rotational lines of CO, CO<sub>2</sub>, and H<sub>2</sub>O molecules to be calculated in the spectral range 0–8000 cm<sup>-1</sup> and in the temperature range 250–3000 K. A user-friendly system interface allows the data to be displayed in text and graphic formats and has all the advantages of programs written in the Windows environment. The system HOTTGAS 2.0 can be used to calculate the absorption coefficients of individual gases and gaseous mixtures for the optically thin layer model.

The comparison with other databases are fulfilled. The most attention is devoted to comparison between HITEMP and HOTTGAS results. The applied tasks as using describing systems for construction of spatial distribution gas concentration and temperature based on emissivity thermodynamically inhomogeneous gas media are discussed too.

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**PT17. N<sub>2</sub>O and O<sub>3</sub> Solar Sourced Atmospheric Spectra Observed at Knoxville, Tennessee are Analyzed Yielding Concentration Profiles and Temporal Variation Results**

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A high-resolution FTIR Bomem DA8 spectrometer has been installed at the University of Tennessee and has been successfully coupled with a suntracker. Solar absorption spectra were recorded on 75 days in the last 18 months. Both InSb and HgCdTe detectors were used to cover a large spectral range. The high-resolution spectra provide information on the vertical concentration profiles of trace gases in the atmosphere. The HITRAN data base was used along with SFIT2 in order to retrieve concentration profiles of different trace gases. Different computer algorithms were implemented using IDL, to enhance retrieval of concentration profiles. Two main atmospheric trace gases were the main focus of the study.

Atmospheric nitrous oxide (N<sub>2</sub>O) is a very long-lived trace gas with a lifetime of about 150 years, and it is an important greenhouse gas as well as a destroyer of stratospheric ozone, through the nitric oxide catalytic cycle. Sources of N<sub>2</sub>O are thought to be oceans, soils, fossil-fuel combustion, biomass burning, and nitrate and ammonium fertilizers. Man-made fertilizers are thought to be a major contributor to atmospheric N<sub>2</sub>O. Studies with open-path ground-level IR spectroscopy have shown a sharp increase in the release of N<sub>2</sub>O after a rain fall in fertilized fields. While many solar spectra observations of N<sub>2</sub>O have been done in dryer climates, this study is done in a heavy agricultural area with large annual rainfall amounts. Analysis of temporal variation of N<sub>2</sub>O will be presented in this study.

Tropospheric ozone in the Knoxville area is rated as the worst in the nation by the American Lung Association. Motor-vehicle exhaust and industrial emissions, gasoline vapors, and chemical solvents are some of the major sources of NO<sub>x</sub> and VOC that help to form ozone. Sunlight and hot weather cause ground-level ozone to form in harmful concentrations in the air. A spike in O<sub>3</sub> concentration was observed in an episode on August 25, 2003. Analysis of this data will be presented in this study.

**Molecular Line Parameters for the “MASTER”  
(Millimeter wave Acquisition for Stratospheric/  
Tropospheric Exchange Research) Database**

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The European Space Agency (ESA/ESTEC) is considering the opportunity of developing the spaceborne limb-sounding millimeter sensor “MASTER” (Millimeter wave Acquisitions for Stratosphere/Troposphere Exchange Research) and in parallel, is developing the “MARSCHAL” (Millimeter-wave Airborne Receiver for Spectroscopic CHAracterization of Atmospheric Limb - Sounding) airborne instrument. The present paper describes the line-by-line database which was generated mainly for the target species for these instruments (BrO, CH<sub>3</sub>Cl, CO, ClO, HCl, HNO<sub>3</sub>, N<sub>2</sub>O, O<sub>2</sub>, O<sub>3</sub> and H<sub>2</sub>O) in the 294-305 GHz, 316-325 GHz, 342-348 GHz, 497-506 GHz and 624-626 GHz spectral microwindows. The line-position, line-intensity, line-broadening, and line-shift parameters were derived depending on their estimated accuracy, (i) from a combination of spectral parameters coming from the JPL and HITRAN catalogs (ii) from data taken from the literature or (iii) using data obtained through experimental measurements (and/or) calculations performed during the present study. The available line-position parameters are almost always well characterized for the MASTER uses. As expected, the existing air-broadening parameters were not always existing at the required accuracy in the literature, and measurements had to be performed at Bologna and Lille. However surprisingly enough, the line intensities had to be re-computed for some of the species under study because of strong deficiencies in the public access databases.

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## **Infrared Spectroscopy and the MIPAS (Michelson Interferometer for Passive Atmospheric Sounding) Experiment**

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The Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) experiment is operating on board the ENVISAT satellite and uses a Fourier-transform spectrometer to acquire for the first time high spectral resolution middle infrared emission limb sounding spectra of the Earth atmosphere from space. The measurement capabilities make it possible to determine every 75 s the vertical profile of several atmospheric trace constituents, during both day and night with an almost full coverage of the globe. In a quasi-operational mode, atmospheric vertical profiles of temperature and pressure, as well as of concentrations of O<sub>3</sub>, H<sub>2</sub>O, CH<sub>4</sub>, HNO<sub>3</sub>, N<sub>2</sub>O, and NO<sub>2</sub>, are retrieved in the altitude range from 12 to 68 km. The analysis and interpretation of the limb spectra require good knowledge of the molecular parameters of these species as well as of the interfering species. In this talk, after a brief presentation of the MIPAS instrument and its capabilities, we will describe the spectroscopic line parameter database compiled for the MIPAS experiment and we will give some examples of improvements.

## **H<sub>2</sub>O $\nu_2$ Line Strengths and Positions for MIPAS/ENVISAT**

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As a first step towards the improvement of the spectroscopic database of water for the MIPAS satellite instrument, linestrengths and line positions have been measured in the range 1250 – 1750 cm<sup>-1</sup>. Pure water vapour was measured at ambient temperature with a Bruker IFS 120 HR at a spectral resolution of 0.0027 cm<sup>-1</sup>, pressures ranging from 0.2 to 5 hPa, and absorption paths from 0.25 to 80 m. In case of the short cell measurements (0.25 m absorption path) high-resolution reference measurements were taken while for the White cell measurements (20 and 80 m) low resolution reference spectra were sufficient. The White cell required a continuous flow of water while for the short cell static filling with a gas reservoir attached was sufficient. Pressures were measured with capacitance manometers for number density determination. Spectra were corrected for non-linearity and thermal self emission. Spectral calibration was performed by means of N<sub>2</sub>O measurements with NIST heterodyne line positions as reference. The field stop diameter was fitted from N<sub>2</sub>O and water lines. In total nine spectra were analyzed. Self broadening was obtained from measurements at 1 and 5 hPa. Merged pressure broadening data were then used as input for line position and linestrength determination of all data sets. Linestrengths with reasonable uncertainties (<10%) were obtained for  $2 \times 10^{-25} < S < 1 \times 10^{-19}$ . The large redundancy among the data allowed for extensive quality checks concerning linestrengths. Averaged linestrength ratios for different measurements revealed some peculiarities which will be discussed. The status of the quantum mechanical analysis will be reported too.

## **A Case Study of the Retrieval of Tropospheric Water-vapor Profiles from AIRS Radiances**

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The Atmospheric InfraRed Sounder (AIRS) is a very precise, medium-resolution spectrometer on EOS Aqua spacecraft. Outgoing radiances measured by AIRS from a selected case of a cloud-free nighttime observation, for a single AIRS footprint over the Chesapeake Bay, have been compared with calculated radiances derived from simultaneous radiosonde temperature and water vapor profiles. The residual differences between the calculated and observed radiances were used iteratively to modify the water vapor distribution in a manner that provides a best fit to the observed outgoing radiances while preserving the major structural features of the measured profile at lower altitudes. This process resulted in reduction of the peak-to-peak differences between observed and calculated brightness temperatures from 3K to less 1K. In the limit, the residuals closely mimic the shape of the radiance spectrum, independent of the altitude of the peak opacity of the source function from which they originate. The accuracy and repeatability of the AIRS data suggest that further improvement of the fit between observed and calculated radiances may require reevaluation of the  $\nu_2$  water vapor spectral parameters – in particular the pressure broadened halfwidths and/or the shapes of the lines in the near wings – before any additional reduction in the magnitude of the residuals can be expected.



## Spectroscopy Evaluation using MkIV Balloon Spectra

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We have evaluated the adequacy of the HITRAN database [1] to correctly simulate infrared limb transmittance spectra. This was done by fitting solar absorption spectra measured by the JPL MkIV interferometer [2]. These spectra cover the entire 650 to 5650  $\text{cm}^{-1}$  spectral region simultaneously and were measured during recent balloon flights under conditions that were closely monitored by *in situ* sensors [3].

This work will benefit the HITRAN user community by documenting and highlighting inadequacies in the database and quantifying their likely effect on retrieved vmr profiles. Future additions or amendments to the database will be tested in terms of their ability to improve the fits to the measured spectra. Checks will be performed of their consistency with previous linelist versions and with lines/bands of the same gas. This work will provide an objective basis for assessing the adequacy and self-consistency of the existing HITRAN database in various spectral regions and for quantifying the improvements (or otherwise) produced by new linelists. It will also help to prioritize needs for additional laboratory studies.

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## **Atmospheric Chemistry Measurements from the SCIAMACHY Spectrometer on the ESA ENVISAT Satellite: Overview and First Scientific Results**

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The Scanning Imaging Absorption Spectrometer for Atmospheric Chartography (SCIAMACHY) was launched on board the European Space Agency Envisat satellite March 1, 2002. SCIAMACHY measures the Earth's atmosphere in the spectral range 240-2400 nm. Measurements are primarily made in the nadir and limb scattering geometries, with additional, limited, occultation measurements.

We present preliminary atmospheric results obtained by fitting spectra from the SCIAMACHY Validation Master Set of data products. The results include profiles of stratospheric BrO, OClO, NO<sub>2</sub>, and O<sub>3</sub>, and tropospheric abundances of NO<sub>2</sub> and HCHO. Tropospheric CO abundances will be presented if they are available in time.

## AUTHOR INDEX

### A

Allen, G. ....	25
Aoki, T. ....	41
Armante, R. ....	28

### B

Babikov, Yu.L. ....	37
Bach, M. ....	38
Bakri, B. ....	43
Bandyopadhyay, A. ....	9
Baranov, Y.I. ....	48
Barbe, A. ....	4, 10, 14, 37
Bekhtereva, E. ....	15, 20
Benner, D.C. ....	19, 44, 46
Bernath, P. ....	1
Birk, M. ....	7, 55
Biswas, D. ....	9
Blake, T.A. ....	46
Blass, W.E. ....	22, 32, 52
Boone, C. ....	1
Brown, L.R. ....	12, 16, 17, 31, 45, 46, 54
Brünken, S. ....	18
Bühler, S. ....	53
Bustos, E. ....	49

### C

Carleer, M. ....	10, 38
Carli, B. ....	54
Cazzoli, G. ....	43, 53
Chance, K. ....	58
Chédin, A. ....	28
Chen, L.L. ....	56
Chen, P. ....	31
Coheur, P.-F. ....	10, 38
Colmont, J.-M. ....	43, 53
Compton, R. ....	52
Coudert, L.H. ....	54, 55

### D

Dana, V. ....	14
Daumont, L. ....	10
Dave, H. ....	47
de Backer-Barilly, M.-R. ....	4
Delgado, J. ....	32
Demaison, J. ....	43, 53
Devi, V.Malathy ....	19, 44, 45, 46
Didriche, K. ....	21
Dore, L. ....	43
Durry, G. ....	40

### F

Fally, S. ....	10, 38
Farmer, C.B. ....	56
Feist, D.G. ....	30

Flaud, J.-M. ....	2, 21, 53, 54, 55
Fujieda, T. ....	41
Fukabori, M. ....	41, 42

### G

Gamache, R.R. ....	7, 13, 35
Garceran, K. ....	28
Ghosh, P.N. ....	9
Goldman, A. ....	13, 34

### H

Habara, H. ....	18
Hager, J.S. ....	52
Hanson, R.K. ....	39
Hao, L.-Y. ....	20
Hartman, J.-M. ....	7
Hermans, C. ....	10, 38
Hewagama, T. ....	32
Hillman, J.J. ....	22, 32
Hodges, J.T. ....	3
Hoffman, F. ....	52
Hollenstein, H. ....	15
Hu, S.-M. ....	20

### I

Ito, K. ....	6
--------------	---

### J

Jacquemart, D. ....	8, 13, 14, 19, 26
Jacquinet-Husson, N. ....	28
Jeffries, J.B. ....	39
Jennings, D.E. ....	22
Jenouvrier, A. ....	10, 38
Johns, J.W.C. ....	17
Joly, L. ....	40
Jucks, K. ....	11

### K

Keller, F. ....	21
Kleiner, I. ....	17
Kumar, V. ....	47
Kurosu, T. ....	58
Kwabia Tchana, F. ....	2

### L

Lafferty, W.J. ....	48
Lavín, C. ....	49
Le Barbu, T. ....	40
Lees, R.M. ....	17
Lewen, F. ....	18
Liu, A.-W. ....	20
Liu, X. ....	39
Lyulin, O.M. ....	14

**M**

Maki, A.....	19
Mandin, J.-Y.....	14
Mantz, A.W.....	44
Martín, I.....	5, 49
Martin, R.....	58
Massie, S.....	34
Matsui, T.....	6
Mayor, E.....	5, 49
McLeod, S.....	1
McPheat, R.A.....	24
Menéndez, J.M.....	49
Mikhailenko, S.N.....	10, 37
Miller, C.E.....	12
Monks, P.S.....	25
Müller, S.P.....	18, 27

**N**

Nakajima, H.....	42
Nassar, R.....	1
Newnham, D.A.....	25

**O**

Orlando, J.....	34
Orphal, J.....	2

**P**

Pabari, J.....	47
Palmer, P.....	58
Parkinson, W.H.....	6
Parvitte, B.....	40
Perevalov, V.I.....	14
Perrin, A.....	2, 21, 43, 53, 54
Piccolo, C.....	54
Pirali, O.....	2
Pittman, T.J.....	45
Predoi-Cross, A.....	44
Puzzarini, C.....	43, 53

**Q**

Quack, M.....	15
---------------	----

**R**

Ray, A.....	9
Ray, B.....	9
Régalia-Jarlot, L.....	10, 14
Remedios, J.J.....	25
Reuter, D.....	22
Rinsland, C.P.....	19, 44
Rohart, F.....	43
Rothman, L.S.....	8, 13, 19, 26

**S**

Schlöder, F.....	27
Scott, N.....	28
Sen, B.....	57
Sioris, C.....	58
Smith, K.M.....	24, 25
Smith, M.A.H.....	19, 44, 45, 46
Stutzki, J.....	27
Suzuki, M.....	23

**T**

Tanaka, T.....	42
Teffo, J.-L.....	54
Tennyson, J.....	33, 36
Tolchenov, R.N.....	36
Toon, G.C.....	31, 57
Toth, R.A.....	31, 46
Tyndall, G.....	34
Tyuterev, V.I.G.....	4, 10, 37

**U**

Ulenikov, O.N.....	15, 20
--------------------	--------

**V**

Vandaele, A.C.....	10, 38
Vander Auwera, J.....	21
Velasco, A.M.....	5, 49
Verdes, C.....	53
Voitsekhovskaya, O.K.....	51

**W**

Wagner, G.....	7, 55
Walker, K.....	1
Wang, P.....	17
Watanabe, T.....	41, 42
Winnewisser, G.....	18, 27
Włodarczak, G.....	43, 53

**X**

Xu, L.-H.....	17
---------------	----

**Y**

Yokota, T.....	42
Yoshino, K.....	6

**Z**

Zapryaygaev, A.Yu.....	51
Zéninari, V.....	40

## Notes

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