Development of the HITRAN Compilation
In Support of the NASA Earth Observing System Program

Annual Progress Report for NASA Grant NAG5-13534
15 May 2005

Dr. Laurence S. Rothman
Principal Investigator
Harvard-Smithsonian Center for Astrophysics
Atomic and Molecular Physics Division
Mail Stop 50, 60 Garden Street
Cambridge MA 02138-1516

1. Introduction

The purpose of this project is to develop and enhance the *HITRAN* molecular spectroscopic database and associated software to support the observational programs of the NASA Earth Observing System (**EOS**). In particular, the focus is on the EOS projects: the Atmospheric Infrared Sounder (**AIRS**), the High-Resolution Dynamics Limb Sounder (**HIRDLS**), Measurements of Pollution in the Troposphere (**MOPITT**), the Tropospheric Emission Spectrometer (**TES**), and the Stratospheric Aerosol and Gas Experiment (**SAGE III**). The *HITRAN* program is also involved in the Ozone Monitoring Experiment (**OMI**). The data requirements of these programs in terms of spectroscopy are varied with respect to constituents being observed, required remote-sensing parameters, and spectral coverage. A general requisite is for additional spectral parameters and improvements to existing molecular bands sufficient for the simulation of the observations leading to retrieval of the atmospheric state. In addition, cross-section data for heavier molecular species must be expanded and made amenable to modeling in remote sensing. The effort in the project also includes developing software and distribution to make access, manipulation, and use of *HITRAN* functional to the EOS program.

2. Accomplishments

A new edition of the *HITRAN* compilation was released in September 2004. The format of the section of the database on individual line parameters of *HITRAN* has undergone the most extensive enhancement in almost two decades. It now lists the Einstein *A*-coefficients, statistical weights of the upper and lower levels of the transitions, a better system for the representation of quantum identifications, and enhanced referencing and uncertainty codes. In addition, there is a provision for making corrections to the broadening of line transitions due to line mixing.

The most significant of the improvements featured in this newly updated edition of *HITRAN* relates to the line-by-line parameters. A major improvement was accomplished for water vapor. This update covers the whole spectral range, from microwave through visible, and also for the lesser-abundant isotopologues. The improvements concern line positions, intensities, and half-widths. For air-broadened half-widths and pressure-induced line shifts, we have developed a semi-empirical algorithm that supplies values for all lines. We employed this calculation for lines that did not possess reliable experimental values.

There are numerous independent examples of the improvement of the water-vapor parameters since the last *HITRAN* edition of 2000. Figure 1 shows the improved residuals resulting from the use of the new *HITRAN* in the 1.4-μm region. The observations were carried out by the group of Prof. Hanson at Stanford University.

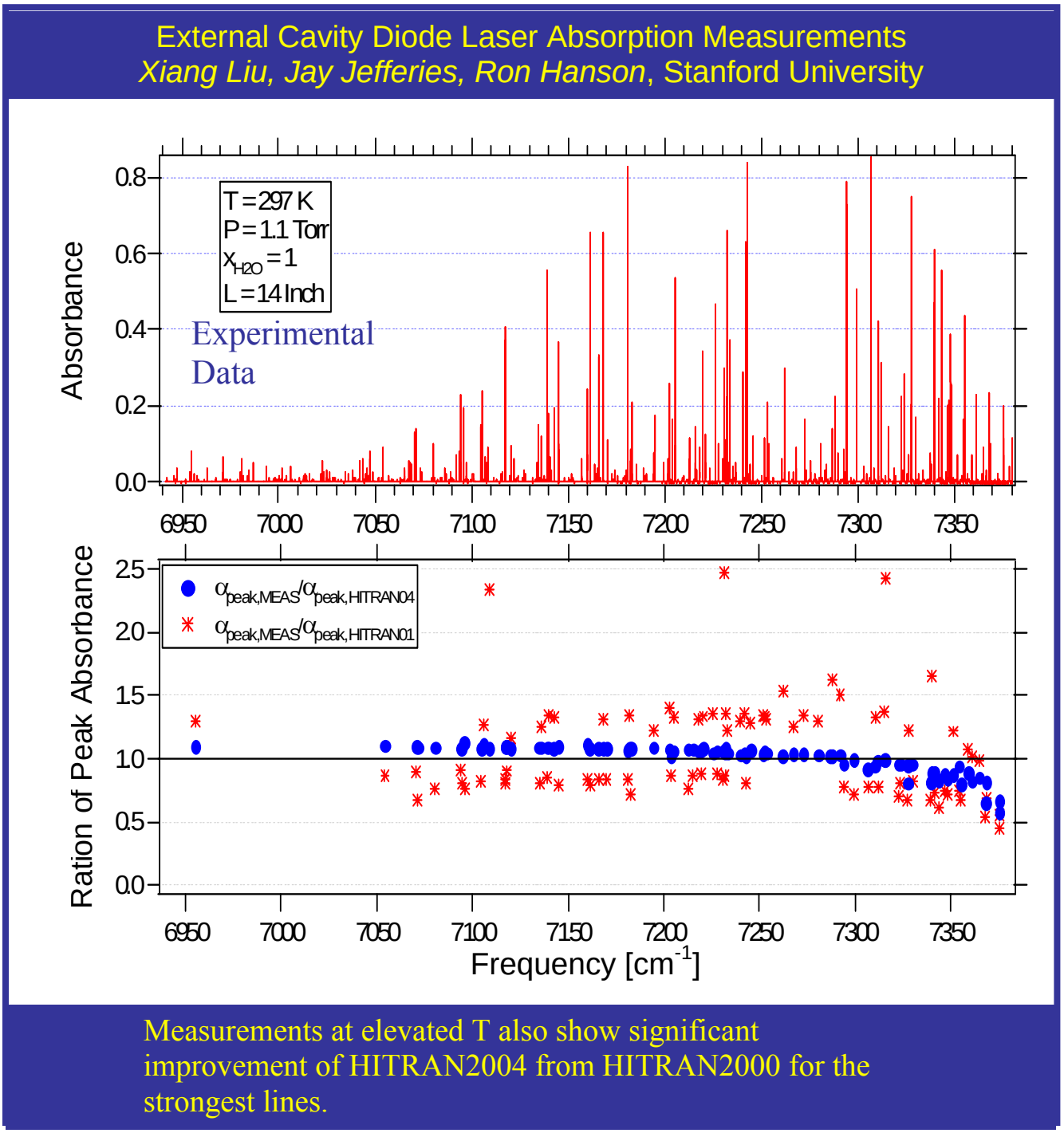

Figure 1. Improvement of H_2O intensities in the 1.4-μm region.

There is an ongoing collaboration with Prof. Tennyson's group at University College London, Prof. Carleer's group at the University of Brussels, and Prof. Barbe's group at the University of Reims to update water-vapor parameters in the near-IR through visible. Analysis is still be performed, but the improvement is nonetheless significant using the preliminary results, as demonstrated in Fig. 2.

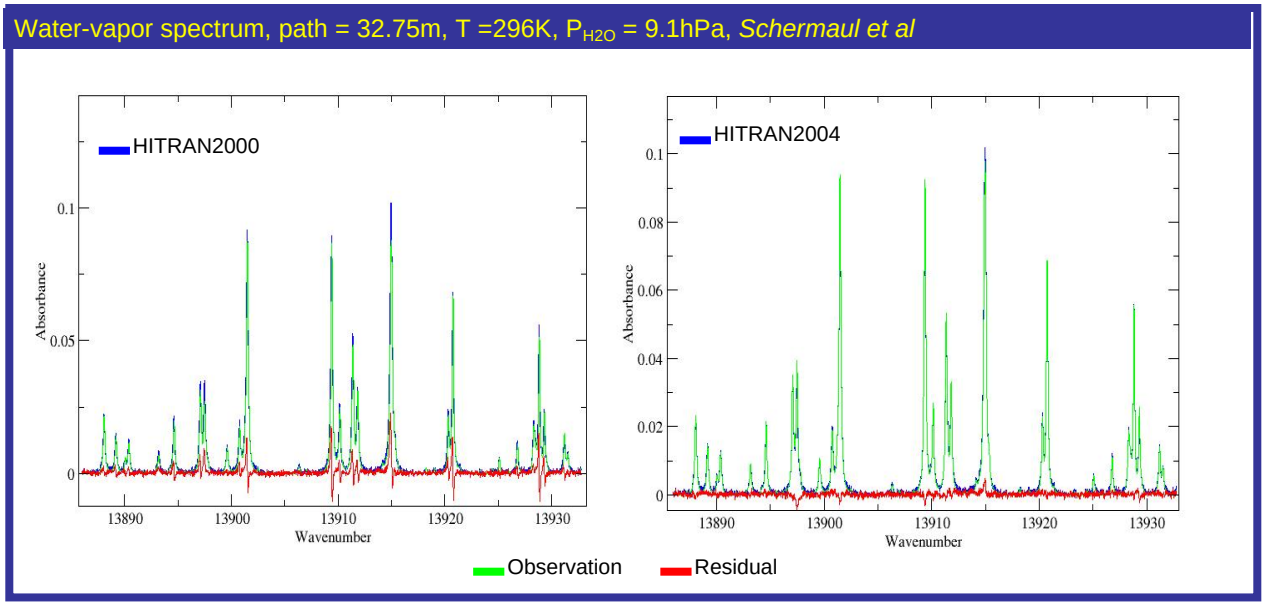

Figure 2. Improvement of H_2O lines in the 0.7-µm region.

Major improvements have similarly been accomplished for many molecular species in *HITRAN* during this period, namely: CO_2, O_3, N_2O, CO, CH_4, O_2, NO, HNO_3, OH, OCS, HOCl, HCN, CH_3Cl, H_2O_2, C_2H_2, C_2H_6, H_2S, HCOOH, and CH_3OH (this latter molecule is a new species for *HITRAN*). Details of the updates are contained in the article describing the latest edition. Of particular interest is the significant improvement made for carbon dioxide by Miller and Brown at JPL. This is part of an ongoing program that is pushing the state-of-the-art in spectroscopy for the upcoming Orbiting Carbon Observatory (**OCO**) mission. Brown has also made significant progress in improving the methane parameters and extending the coverage to shorter wavelengths. Figure 3 shows an example of the improved residuals in the current database. The methane problem is a difficult one due to the many interacting levels as one moves to higher wavenumber. However, the need for accurate line parameters for this molecule extends to many other applications, especially in the shorter wavelength regions.

A major improvement of the *HITRAN* compilation during this period has been the introduction of a generalized, maintainable, and physically realistic approach to handling line coupling. A package of subroutines and input files allows one to take into account line coupling for 306 Q branches of CO_2 isotopologues between 469 and 6935 cm^{-1}. It is hoped that in the future this capability will be expanded to include specific branches of methane, oxygen, water vapor, and other branches of CO_2.

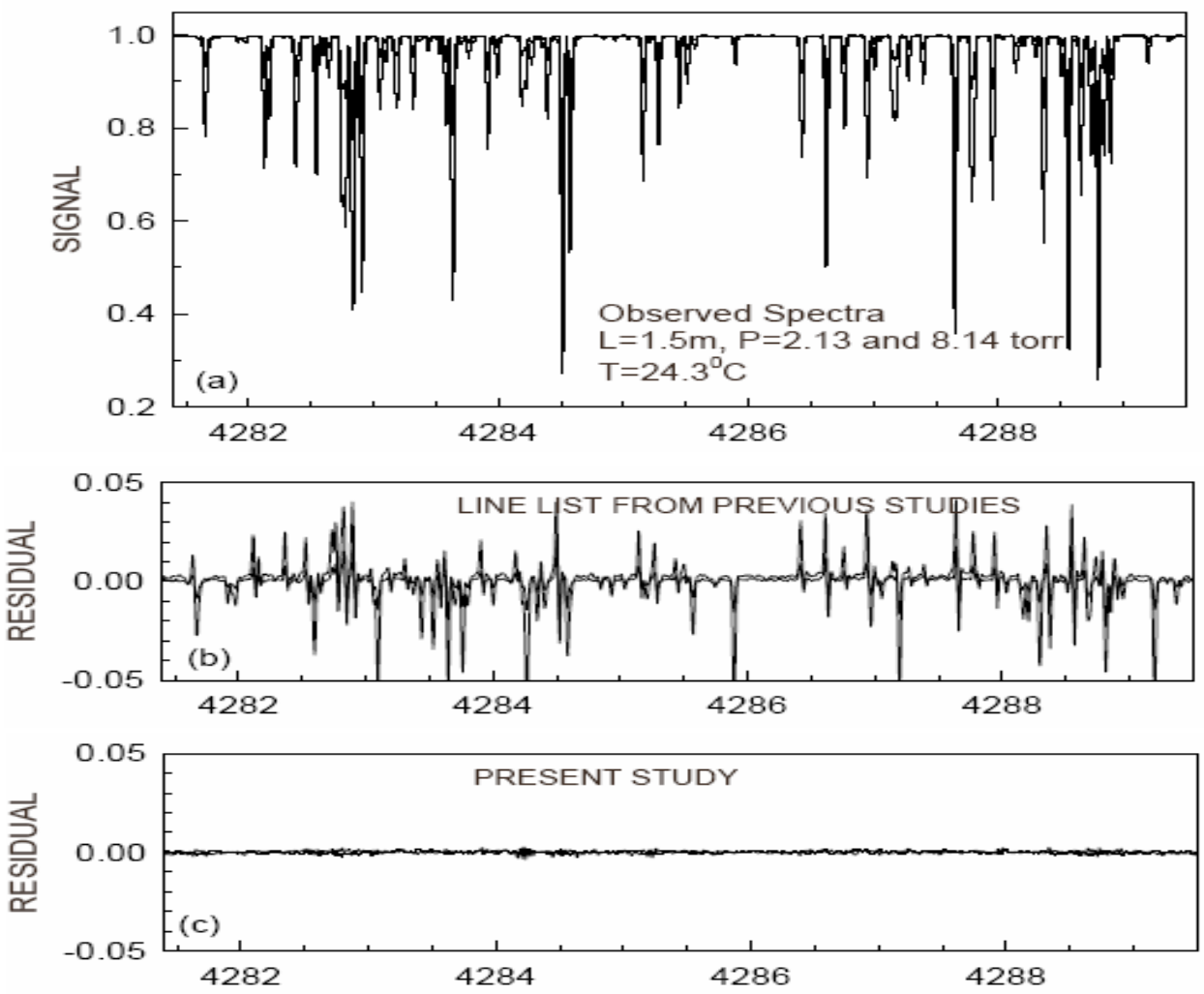

Figure 3. Improvement of CH_4 lines in the 2.3-μm region.

The infrared cross-sections continue to be an essential part of the *HITRAN* compilation. These are high-resolution, experimental values for "heavy" molecular species with dense spectra, such as the chlorofluorocarbons, or molecules with very low vibrational modes, such as chlorine nitrate. Some thirty molecular species are now represented in *HITRAN*, with the most recent additions being SF_5CF_3 (trifluoromethyl sulfur pentafluoride), CH_3CN (methyl cyanide), and PAN (useful for tropospheric studies). To be useful for atmospheric retrievals, the cross-section files should be given at numerous representative pressures and temperatures. At this time only about half the molecules represented by cross-sections in the *HITRAN* compilation have multiple pressure-temperature sets.

The ultraviolet absorption is kept as a separate folder in the *HITRAN* compilation. For the current release, the Hartley-Huggins bands of ozone in the 29,164 - 40,798 cm^{-1} region were added. NO_3, BrO, OClO, and H_2CO UV cross-sections were also added.

There are also data that are applied in a comprehensive or global manner to the line-by-line parameters or cross-sections. These data files include a large table of partition sums at one-degree intervals from 70K to 3000K. A careful study went into the calculation of the approximately 100 isotopologues in *HITRAN*.

3. Interactions with EOS teams

To facilitate communication with **EOS** science teams, this program has weekly communications (e-mail and voice mail) with personnel at JPL and NASA Langley Research Center. In particular, we regularly communicate with Linda Brown, an associate member of the **TES** science team, and Curtis Rinsland and Prof. Aaron Goldman, also members of **TES**. Furthermore, Dr. Brown interacts with regard to the *HITRAN* requirements of the **AIRS** program via Dr. Mike Gunson at JPL. Contact is also maintained between the *HITRAN* program and other EOS personnel, such as Reinhard Beer (JPL), Daniel Jacobs (Harvard Univ.), S.A. Clough (AER), et al.

A salient outcome of these interactions is the new requirement of the EOS missions for improved accuracy of the *HITRAN* parameters. The high signal-to-noise of the satellite-borne instrumentation as well as more sophisticated retrieval algorithms, has made new stringent demands on *HITRAN*. For a number of molecules, the goal for absolute intensities is now in the one-percent range, rather than the previous goal of attempting to achieve 5%. In fact, for carbon dioxide, the requirements for adequate retrieval of the atmospheric state are to achieve intensities to better than 1%. Increased attention to line-shape phenomena has also been emphasized. We are receiving similar input from the European, Canadian, and Japanese satellite programs. These requirements are pushing the technology of laboratory experiments that provide the data, as well as the theoretical and analysis techniques that extract the final parameters.

4. Administration of HITRAN project

During this period, the previous post-doc, Dr. David Jacquemart, returned to a position at the University of Paris. Dr. Marie Šimečková, from Prof. Štepan Urban's group in Prague, became the post-doc on this project in July 2004.

An international advisory committee for the *HITRAN* project has been established. It consists of 12 members, primarily of major contributors to the database, but also has remote-sensing users as well. The first meeting was held just prior to the Biennial *HITRAN* Conference in June 2004. There were two "raconteurs" for NASA present at this meeting. The first meeting was recorded on DVD, which is available on request. Figure 4 shows the members. Linda Brown of JPL chaired the meeting. The purpose of the committee is to: evaluate *HITRAN*, discuss known problems, sources of future improvement, targets for completeness and accuracy of parameters, consistency of parameters, expansion of content, and long-term plans. It should be noted that members are also representatives of both **EOS** programs and the European *MIPAS* experiment.

Figure 4. HITRAN Advisory Council Members.

Top Row: P. Bernath, Univ. Waterloo, Canada; A. Barbe, Univ. Reims, France; M.A.H. Smith, NASA Langley; J-M. Flaud, Univ. Paris, France; A. Goldman, Univ. Denver; A. Perrin, Univ. Paris, France
Second Row: K. Chance, SAO; G. Wagner (alternate), DLR, Germany; J. Orphal, Univ. Paris, France; K. Jucks (NASA raconteur), SAO; J. Vander Auwera, Univ. Brussels, Belgium
Bottom Row: L.R. Brown (chair); JPL, L.S. Rothman, SAO

5. Future Plans

The principal focus will be on updating and correcting the line parameters in the line-by-line portion of the compilation. Among the areas that will be addressed are:

1. Improving water-vapor line parameters in both the long-wave and short-wave regions. The latter involves a collaboration with the UK-Belgium-French consortium mentioned above. We also intend to pursue improving high-temperature parameters for water vapor with the UK and a Russian group; this has benefits for weak line problems in terrestrial retrievals.
2. Improving ozone parameters, and extending coverage to shorter wavelengths. Work with the group at the University of Reims will be key.
3. Extending and improving methane parameters in the near-IR. Investigating line-shape problems for methane.
4. Adding methyl bromide line parameters. A collaboration with our former post-doc will be established.
5. Updating the JavaHAWKS software, and investigating possible new database software methods.

We are interviewing several post-doc candidates for the program, since Dr. Šimečková will be leaving at the end of July. Dr. Šimečková and I will make oral presentations at the June spectroscopy meeting at the Ohio State University. A second meeting of the HITRAN Advisory Council will be held on the weekend prior to the OSU conference in Columbus. Preparations are also being made for the Atmospheric Spectroscopy Applications (ASA) meeting in September in Reims, France. I am co-chair of this meeting. A talk and a poster will be presented. Following that meeting, I will attend the Molecular Spectroscopy Colloquium, to be held in Salamanca, Spain. A poster presentation will be made, and a concurrent meeting will be held of the IUPAC (International Union of Pure and Applied Chemistry) task force on water vapor, of which I am a co-investigator.

6. Publications and Presentations during period

Publications:

"The HITRAN 2004 Molecular Spectroscopic Database," L.S. Rothman, D. Jacquemart, L.R. Brown, M. Carleer, R.R. Gamache, et al, *J. Quant. Spectrosc. and Rad. Transfer* **96,** 139-204 (2005).

"Semi-empirical calculation of air-broadened halfwidths and air pressure-induced frequency shifts of water-vapor absorption lines," D. Jacquemart, R.R. Gamache, and L.S. Rothman, *J. Quant. Spectrosc. and Rad. Transfer* **96,** 205-239 (2005).

"Einstein *A*-coefficients and statistical weights in the HITRAN 2004 spectroscopic database," M. Šimečková, D. Jacquemart, L.S. Rothman, R.R. Gamache, and A. Goldman, in press, *J. Quant. Spectrosc. and Rad. Transfer*.

"History and Future of the Molecular Spectroscopic Databases," L.S. Rothman, N. Jacquinet-Husson, C. Boulet, and A. Perrin, *Comptes Rendus Physique* (submitted).

Presentations:

"The 2004 Edition of the HITRAN Spectroscopic Compilation," The 18th International Conference on High Resolution Infrared Spectroscopy, Prague, Czech Republic (September 2004).

"HITRAN 2004 and Application to Satellite Remote Sounding of the Atmosphere," Workshop: Atmospheric Science from Space using Fourier Transform Spectrometry, Québec City, Canada (May 2005).