AFRL-VS-HA-TR-2005-1037

Atmospheric Absorption Parameters for Laser Propagation

Laurence S. Rothman

Smithsonian Astrophysical Observatory
60 Garden Street
Cambridge, MA 02138

15 March 2005

Final Report

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED.

20050629 011

AIR FORCE RESEARCH LABORATORY
Space Vehicles Directorate
29 Randolph Rd
AIR FORCE MATERIEL COMMAND
Hanscom AFB, MA 01731-3010

This technical report has been reviewed and is approved for publication.

/ signed /

Eric Peschell, 1 Lt, USAF
Contract Manager

/ signed /

Robert R. Beland, Chief
Battlespace Surveillance Innovation Center

This report has been reviewed by the ESC Public Affairs Office (PA) and is releasable to the National Technical Information Service (NTIS).

Qualified requestors may obtain additional copies form the Defense Technical Information Center (DTIC). All others should apply to the National Technical Information Service.

If your address has changed, if you wish to be removed from the mailing list, or if the addressee is no longer employed by your organization, please notify AFRL/VSIM, 29 Randolph Rd., Hanscom AFB, MA 01731-3010. This will assist us in maintaining a current mailing list.

Do not return copies of this report unless contractual obligations or notices on a specific document require that it be returned.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*
30-09-2004

2. REPORT TYPE
Scientific, Final

3. DATES COVERED *(From - To)*
30 Sep 2002-30 Sep 2004

4. TITLE AND SUBTITLE
Atmospheric Absorption Parameters for Laser Propagation

5a. CONTRACT NUMBER
F19628-02-C-0085

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
69120G

6. AUTHOR(S)
Laurence S. Rothman

5d. PROJECT NUMBER
1010

5e. TASK NUMBER
0T

5f. WORK UNIT NUMBER
03

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Smithsonian Astrophysical Observatory
Atomic and Molecular Physics Division
60 Garden Street
Cambridge, MA 02138-1516

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Air Force Research Laboratory/VSBYA
29 Randolph Road
Hanscom aFB, MA 01731-3010

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
AFRL-VS-HA-TR-2005-1037

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for Public Release; distribution unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

The ability of high-energy lasers to penetrate the terrestrial atmosphere without loss of energy or focus has been the primary focus of this project. The task developed here has been to improve the line positions, intensities, and air-broadened half-widths of water vapor, carbon dioxide, carbon monoxide, and methane in the spectral regions of candidate high-energy lasers. This effort required acquisition of new high-resolution, high photometric accuracy spectroscopic data, as well as the applications of quantum mechanical theoretical calculations. The results, after validation, evaluation and comparison with current data, have been cast into the format of the HITRAN molecular spectroscopic data base. HITRAN is the input for standardized high-resolution transmission and radiance codes, enabling assessment of laser performance among other applications.

15. SUBJECT TERMS

High-energy lasers	Quantum mechanics
HITRAN	High-resolution transmission

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Eric Peschell, 1Lt, USAF
UNCL	UNCL	UNCL	UNL		19b. TELEPHONE NUMBER *(Include area code)* (781) 377-3068

Standard Form 298 (Rev. 8/98)
Prescribed by ANSI Std. Z39.18

Atmospheric Absorption Parameters for Laser Propagation

Final report for F19628-02-C-0085
Sept. 30, 2002 through Sept. 30, 2004

Dr. Laurence S. Rothman
Principal Investigator
Smithsonian Institution, Astrophysical Observatory
Atomic and Molecular Physics Division
Mail Stop 50, 60 Garden St
Cambridge MA 02138-1516

1. Introduction

Successful propagation of laser radiation through the atmosphere requires detailed knowledge of the absorption properties of the intervening medium. In the infrared and near-IR regions being considered for high-energy lasers, some atmospheric constituents have very significant absorptive properties. In particular, water vapor, carbon dioxide, and methane, although minor constituents in terms of percentage abundance in the atmosphere, possess sizable electric dipole moments which give rise to very significant absorptions. The absorptions form a discrete line spectrum arising in this energy region from the interaction of vibration and rotation of the molecules. In addition, collisional broadening of transitions makes line-wing effects important.

The *HITRAN* database was established to provide an archival database of necessary spectroscopic parameters of molecules to serve as input to high-resolution transmission and radiance codes. It is the international standard database for this purpose. The 1996 edition [1] of *HITRAN* at the conception of this effort contained line-by-line data for 38 molecular species, including their most significant isotopes. The parameters for each transition include: line position, intensity, air- and self-broadened half-widths, lower-state energies, and relevant temperature-dependent coefficients. A good summary of the quantities involved, and how they are applied, is contained in the appendix of Ref. [1].

The development of the *HITRAN* database takes place on two fronts. Ideally, all parameters (especially line positions and intensities) would be calculated from quantum-mechanical formulae. This would ensure a self-consistent set of parameters that would be well characterized and also maintainable. However, this is not practical at this time for many molecular species due in part to the complexity of the problem. Resonances, perturbations, and energy-level mixing are major contributors to the complexity, especially for the shorter wavelength regions where one is dealing with vibrational overtone and combination bands. Thus, to achieve the required accuracy in *HITRAN* for many applications, molecular spectroscopic parameters are often indirectly transcribed from experimental observations. An overwhelming number of the observations are obtained from Fourier transform spectroscopy (FTS), a technology that has matured in several laboratories throughout the world.

The principal goal of this project is to provide improved absorption line parameters for molecules and their isotopologues for the purposes of long-path laser transmission in the terrestrial atmosphere. In particular, the focus was to improve the line positions, intensities, and air-broadened half-widths of water vapor, carbon dioxide, carbon monoxide, and methane in the spectral regions of candidate high-energy lasers. The sections below describe the results of this effort, and some unresolved issues. The original plan of this program was a three-year effort.

2. Enhancements to molecular spectroscopic line parameters

2.1 Water vapor (H_2O)

Of the species to be studied in this effort, by far the most important and most difficult for improvement is water vapor in the near-infrared and visible. Being a "light" molecule, H_2O has spectral lines extended over wide spectral regions. For example, the pure-rotation lines well overlap the fundamental bending mode vibration at 6 μm. The situation gets much more complex in the near-IR and especially the visible, where many combination bands are involved. The lightness of this molecule (low moments of inertia and thus large rotational constants) makes convergence with standard theoretical analysis a serious impediment. The experimental work is also made difficult by blending of lines, adsorption on cell walls, the need for very long-path cells in standard procedures, resonances, perturbations, and a host of other challenges.

We started our research with the study of the different types of lasers likely to be used by the military. We assembled the principal characteristics for each laser (wavelength, tunable or not, etc.) which were essential to target our work. We collected articles about line parameters (frequencies, intensities, air broadening, and air shifting) of water vapor in the different spectral regions of interest. The goal, at the outset, was to compare the different files in the literature with the *HITRAN* database, and then to make assessments concerning the more correct line parameters. We initially examined the 0.532-μm spectral region (YAG laser) with the line list of

Prof. Michel Carleer, Université Libre de Bruxelles (ULB), Belgium). We also researched many other possible new available sources of water-vapor parameters (high-resolution, high-photometric accuracy data) that needed to be assessed.

The post-doc on this program, Dr. David Jacquemart, continued his research on the various sources of water-vapor lines and focused his work on the (0.87-1.25), (1.307-1.515), and (1.6-2.1)-μm spectral regions. His work consisted in doing cross comparisons with the different data obtained from the literature. He began with the study of the 1.307 to 1.515-μm spectral region, which corresponds mainly to the use of the COIL. We also studied the possibility to support the project of a new powerful approach, intracavity laser absorption spectroscopy [2]. This method has the potential to allow the determination of intensities of very weak lines. This project could lead to the recording of water-vapor spectra in the 1.315-micrometer spectral region.

The comparisons in the 0.532-μm region have indicated several discrepancies for the line attributions. For lines that have the same quantum identification (1580 lines of 4610 in *HITRAN* between 13238 and 22656 cm^{-1}), we observed discrepancies of $(0.9\pm4.7)\times10^{-3}$ cm^{-1} for positions, of (5±50)% on intensities, (-9±28)% on air-broadening coefficients, and (-13±58)% on self-broadening coefficients. These results were not definitive; and confirmation was needed from the team of Prof. Michel Carleer.

Dr. Jacquemart confirmed that in the 0.532-μm spectral region (YAG laser), improvement could be accomplished in *HITRAN* using the line list of ULB. However, it was discovered that their broadening coefficients occasionally had erroneous values. Dr. Rothman met with Pierre-François Coheur of the Belgium group and Jean-Michel Hartmann of the University of Paris on 5 December 2002 in Paris to discuss the ULB line list. We proposed an approach that would set criteria on the original spectra that will substitute calculated values for parameters that are clearly unphysical (the occasional result of fitting of weak lines or blends). For this we have to wait for calculated values (from Prof. Robert Gamache, University of Massachusetts) of self- and air-broadening coefficients. However, this in turn requires correct identifications of these features, and for this process Prof. Jonathan Tennyson of the University of London has agreed to perform a new assignment of lines in the ULB linelist.

A meeting was held with Gamache, Jacquemart and Rothman at the SAO in December 2002. Gamache has some lists that contain quantum assignments, the nitrogen-broadened half-width, temperature-dependence, and the line-shift. The transition-dependent calculations presently include the bands (000-000), (010-000), (010-010), (020-000), (020-010), (020-020), (100-000), (100-010), (100-020), (001-010), (001-020), (030-020). These transitions, however, are in the submillimeter and longwave region. There are completed calculations for the bands (301-000), (221-000) at shorter wavelengths, which include air-broadening coefficients.

The study of the (1.307-1.515)-micrometer spectral region showed that it will be possible to improve positions and intensities of the main isotopologue $H_2{}^{16}O$. Figures 1 and 2 give examples from independent sources [3, 4] showing real problems with some lines presently in *HITRAN*. The improvement will come from Robert A. Toth of JPL. It will also be possible to add into *HITRAN* line positions and intensities for the isotopologues $H_2{}^{17}O$ and $H_2{}^{18}O$ [5]. *HITRAN* did not contain any data for these isotopologues in this region. For the broadening coefficients of these isotopologues, we could use calculated values from Gamache. Dr. Linda Brown of JPL reports that a totally new line list in this region could be made available from Toth (supported by a NASA program), but we propose in the interim to make a reduced updated line list covering the 1.315-µm spectral region.

In parallel to this work, Jacquemart attempted to resurrect and run the programs of the late Richard Wattson. These programs consist of a Direct Numerical Diagonalization of the Hamiltonian. This technique [6] has been developed for use in calculations of atmospheric opacity due to molecular absorption under conditions that cannot be duplicated in an Earth-based laboratory. This technique succeeded for the CO_2 molecule, and should also be applied with success for the H_2O molecule. The major problem with this large suite of program is first to understand their structure: indeed, there is no main program, but many subroutines that were sometimes duplicated in different directories. The suite of subroutines is quite complex, lacking in comments, and many difficulties need to be surmounted, but it seems to be possible to once again use the set of subroutines leading to the Direct Numerical Diagonalization of the Hamiltonian.

Dr. Rothman was invited by the Centre National de Recherche Scientific (CNRS) of France to be part of a committee evaluating research at the University of Reims. This visit allowed him the opportunity to meet with Drs. Guy Guelachvili and Nathalie Picqué of the Laboratoire de

Photophysique Moléculaire, Université Paris-Sud in Orsay. They have developed a very novel technique combining intracavity laser spectroscopy (ICLAS) with time-resolved Fourier Transform spectroscopy that enables one to simulate extremely long path lengths in small cells [2]. This method would be extremely useful for measuring weak line absorption in the near-IR and visible regions. A modest proposal, on the order of $80000, has been submitted. It would be extremely beneficial to this project to be able to support this revolutionary and promising technique.

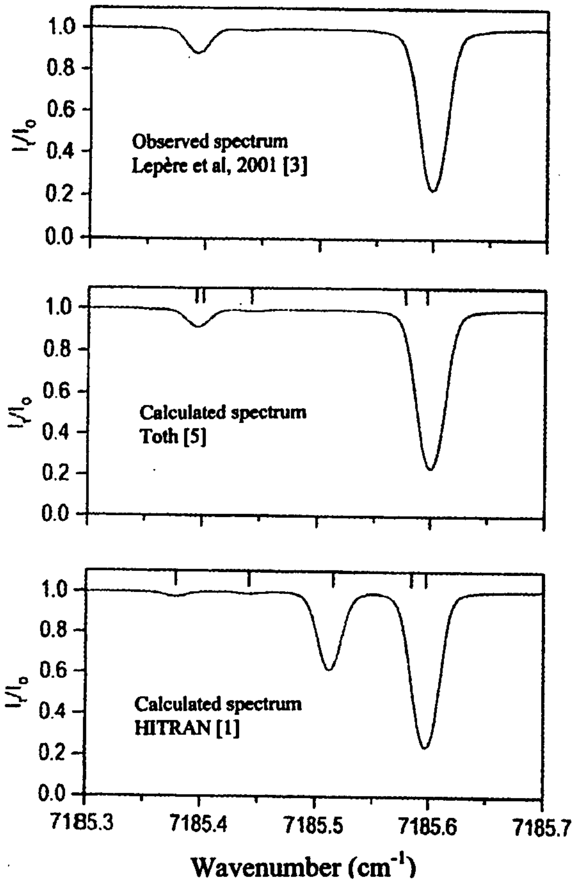

Figure 1 Comparison of Lepère et al [3], Toth [5], and *HITRAN* [1] around 7185 cm^{-1}.

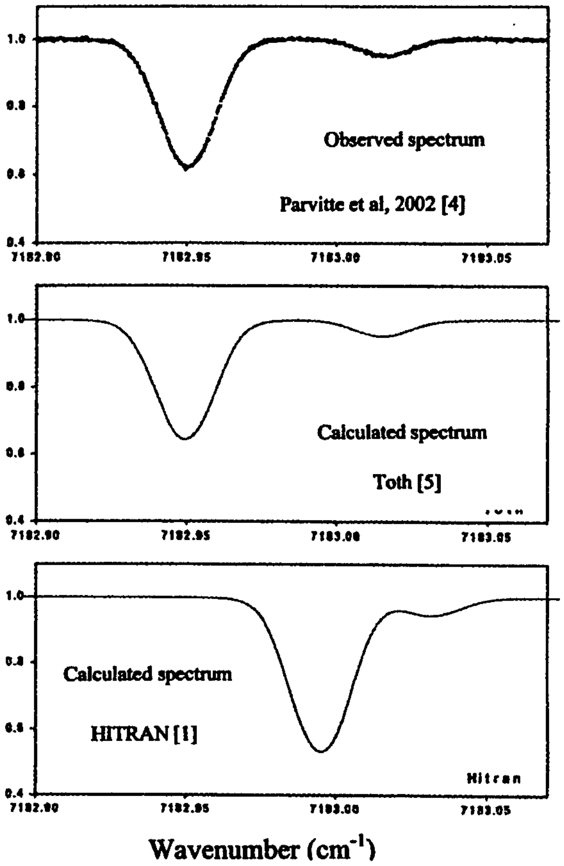

Figure 2. Comparison of Parvitte et al [4], Toth [5], and *HITRAN* [1] around 7183 cm^{-1}.

In the region of the COIL (1.315 μm = 7604.563 cm^{-1}), a preliminary line list in the *HITRAN* format has been created. This line list covers the region from 7603.625 to 7605.796 cm^{-1} for the main isotopologue $H_2{}^{16}O$. The discrepancy between *HITRAN*, and these new values are between

5% and 10%. Moreover, two lines have been added and one has been deleted. Table 1 is a summary of the line position and intensity improvements from Toth [5] in this region.

1996 *HITRAN* [1]		Toth [5]		Ratio of intensities %
Position (cm^{-1})	Intensity (cm^{-1}/molecule×cm^{-2})	Position (cm^{-1})	Intensity (cm^{-1}/molecule×cm^{-2})	
7603.625030	3.83×10^{-25}	7603.6250	4.11×10^{-25}	-7.3
7603.894020	1.00×10^{-25}	7603.895	1.09×10^{-25}	-9.0
7603.983180	8.56×10^{-26}	7603.983	9.07×10^{-26}	-6.0
7604.251740	2.73×10^{-25}	7604.2515	2.98×10^{-25}	-9.2
		7604.2781	1.64×10^{-26}	—
		7604.3823	1.15×10^{-26}	—
7604.997830	1.34×10^{-23}	7604.99785	1.41×10^{-23}	-5.2
7605.293850	9.68×10^{-26}	7605.294	1.04×10^{-25}	-7.4
7605.504870	4.76×10^{-25}	7605.5045	5.16×10^{-25}	-8.4
7605.698000	2.90×10^{-26}			—
7605.796710	9.49×10^{-24}	7605.79673	1.00×10^{-23}	-5.4

Table 1. Comparison of selected lines of *HITRAN* [1] and Toth [5] in the 1.315-µm region.

Besides the improvement in positions and intensities made possible by the more recent high-resolution, high photometric accuracy intensities throughout the spectrum, one can notice several other problems that occur throughout the *HITRAN* water-vapor list: (1) there are lines in *HITRAN* not found in spectra, and (2) conversely, there are missing lines in the current *HITRAN* database. The *HITRAN* lines in the COIL spectral region came from a combination of preliminary results supplied from JPL over a decade ago, mixed in with some weaker lines that originate from early *HITRAN* editions. The latter have come from early grating spectrometer observations taken at the mountain facility in Jungfraujoch, Switzerland. The more recent data in *HITRAN* are mostly from controlled laboratory studies using Fourier transform spectrometers. We intend to gradually replace all old grating spectrometer data in *HITRAN* with new high-resolution data, or sophisticated quantum-mechanical calculations such as the Direct Numerical Diagonalization (DND) method [6] where laboratory observations are not feasible (due to blended lines, interfering lines, etc.).

David Jacquemart has continued identification and correction of problems in the *HITRAN* database for the H_2O molecule. All regions of the H_2O molecule in *HITRAN* have been considered.

The improvements, which concern laser performance calculations for tactical applications, will affect mostly the region of the COIL laser (1.315 µm), where new results for $H_2{}^{16}O$, $H_2{}^{18}O$, and $H_2{}^{17}O$ [Refs. 5, 7] will be incorporated into *HITRAN*. Other improvements will also apply to the 1.03- and 1.06-µm regions (Yb:YAG and Nd:Yag respectively). These improvements will be of less magnitude since they only pertain to the isotopologue $H_2{}^{17}O$ [Ref. 8]. For the region of the COIL, we have to work with Dr. Robert A. Toth (JPL) to provide us his results in an electronic format in order to create a line list in the *HITRAN* format. A visit to JPL was planned in order to have a meeting with Dr. Linda R. Brown concerning the progress in methane and carbon dioxide parameters. For the region of the YAG lasers, we have good collaboration with Dr. Claude Camy-Peyret (Univ. of Paris) and a line list is going to be prepared. The other region of tactical interest involves the FEL, but few improvements for the positions and intensities have been found. We are maintaining contact with Dr. Guy Guelachvili from the Université de Paris-Sud, who has developed a very sensitive technique [2] to measure positions and intensities of very weak lines. His group recently wanted to change their principal laser in order to do some measurements between 1.3-1.7 µm (a very interesting region since it covers the COIL region and a part of the FEL region).

In the other spectral regions, the improvements are in the 0.40-0.76 µm spectral region (Nd:YAG at 0.532 µm, and LIDAR at 0.7 µm), which will be updated from the work of the team of Prof. Michel Carleer [9, 10] of the Université Libre de Bruxelles (ULB). This team will also provide some interesting results between 0.78 and 0.86 µm [Ref. 11] that we will have to compare with the work of Flaud et al [12, 13]. Between 2.5 and 16.9 µm, Refs. [14-18] will be used to improve the current version of *HITRAN*.

In May 2003, Dr. Jacquemart went to the University of Paris VI, to present an invited seminar on spectroscopic parameters of atmospheric molecules. He met with Dr. Camy-Peyret (Univ. of Paris) in order to set up a line list of $H_2{}^{17}O$ in the YAG spectral region. It is planned to add some weak lines of $H_2{}^{17}O$ in *HITRAN* between 0.87 and 1.25 µm. He also had discussions with Dr. Agnes Perrin (Univ. of Paris-Sud) concerning the structure of the next edition of *HITRAN*.

Dr. Jacquemart completed the line list of $H_2{}^{17}O$ in the YAG spectral region. The number of lines has been increased to 1063 in this region (instead of 370 as in the previous *HITRAN* edition). The isotopologue with oxygen-17 is known to be deficient in *HITRAN*. The positions and line intensities have been adopted from Ref. [19]. The difference between the current *HITRAN* database and the new data is illustrated in Fig. 3. The stick plots are in log scale, created using the HAWKS software.

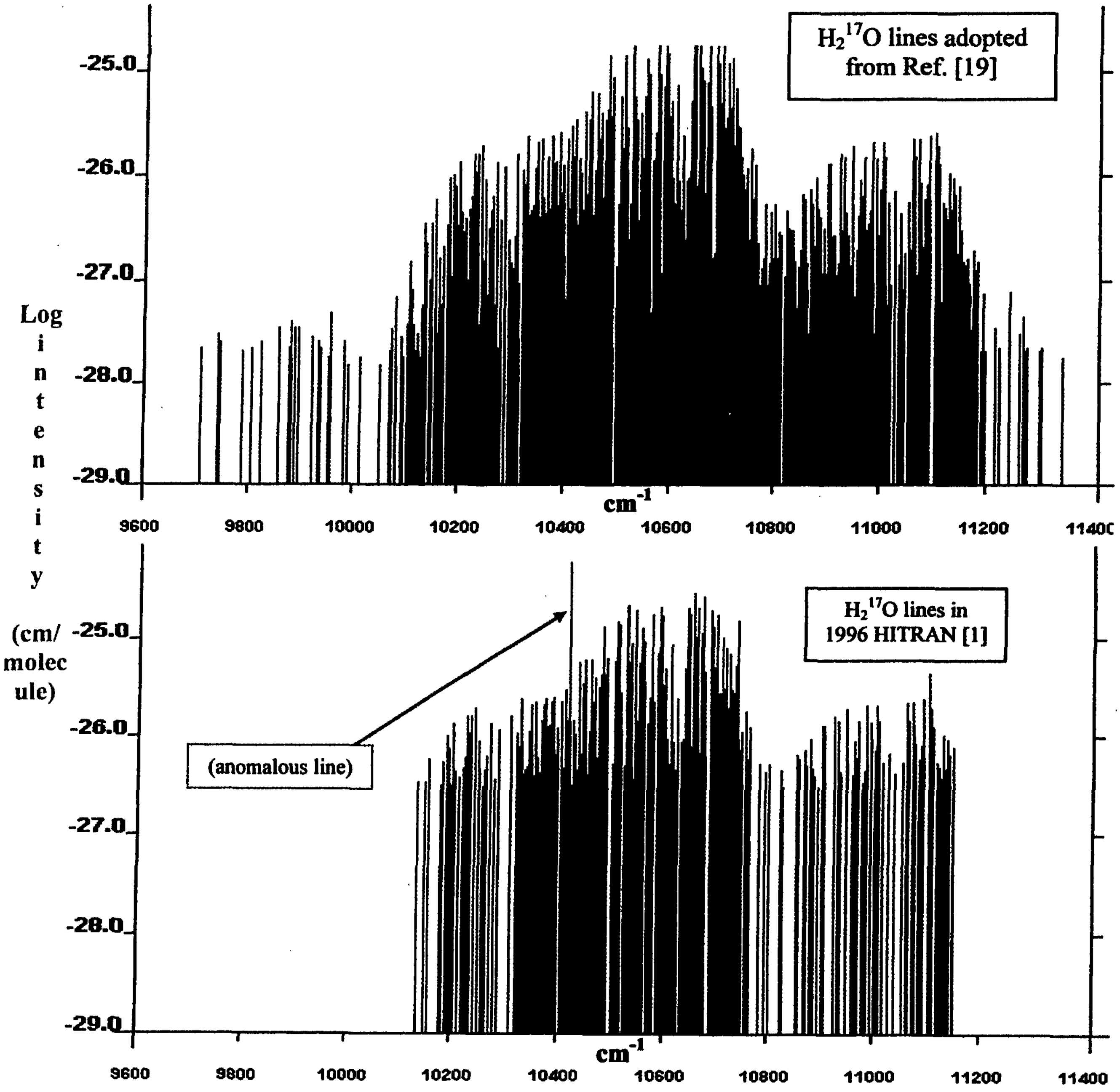

Figure 3. Increase in spectral coverage and dynamic range for $H_2{}^{17}O$ line parameters. Top plot is new data based on Ref [19]. Lower plot is 1996 *HITRAN* data based on old spectra and analysis.

With respect to the air-broadened half-widths, we took values from equivalent $H_2{}^{16}O$ lines that existed in the *HITRAN* database. We anticipate that our validation will confirm the improvement and that this list will be incorporated into the next edition of *HITRAN*. However, it could be made available in advance for the AF requirements.

We are making validation and comparison tests using the PC version of FASCODE (PcLnWin), and will make runs to examine the consequences of updated water-vapor data. Prof. Robert Gamache, Univ. of Massachusetts Lowell, will be making a decision on what set to use for the updating of collision-broadening parameters of H_2O for *HITRAN*. He has provided a limited set, but is in the process of making a more complete and consistent list as part of the effort for the NASA Earth Observing System (EOS) program. Dr. Brown is the principal investigator of the effort, Infrared Laboratory Spectroscopy for AIRS, TES, and HIRDLS (Atmospheric Infrared Sounder, Tropospheric Emission Spectrometer, and High Resolution Dynamics Limb Sounder), and Gamache and Rothman are collaborators; thus the AF program benefits from this synergism. The calculations by Gamache for the 0.7-µm region [20, 21] and the EOS work use the same methodologies, but the fuller set to come will use a more developed formulation.

We are still waiting for the results of Toth in order to improve the water-vapor line list in the COIL region. Discussions at the Ohio State Symposium on Molecular Spectroscopy in June illuminated a problem that appears for the data of water vapor in the 1.315-micrometer region, which must be updated from the work [5, 7] of Toth (the superiority of these results were again confirmed during a talk in Columbus). It seems to be difficult to obtain these data; we plan to follow up with more communications with Toth.

An article on water vapor in the 1- to 2-µm region by a group in the UK [22], seems to be very interesting for the regions of tactical interest, and consequently will be analyzed carefully. We began a correspondence with Dr. Kevin M. Smith (Rutherford Appleton Laboratory, UK) in order to obtain his data on water-vapor parameters in this region.

2.2 Carbon Dioxide (CO_2)

Carbon dioxide is a trace gas in terms of amount in the terrestrial atmosphere (approximately 360 parts per million and increasing, and uniformly mixed in the atmosphere). However, due to its very strong electric dipole moment, it plays a major role in atmospheric absorption. The molecule is linear in configuration, and has many combination bands and hot bands that must be modeled in atmospheric simulations. The theoretical treatment is generally simpler than for water vapor, but care must be taken with respect to some resonances, perturbations, and also line-shape effects. There are also eight isotopologues to be considered in *HITRAN*, the most of any molecule in the database.

In the second half of this effort, Dr. David Jacquemart worked on the CO_2 line list in *HITRAN*. The last update for line parameters of this molecule and its many isotopologues was made over a decade ago [23]. Jacquemart performed comparisons with CDSD-296 calculations made recently by the group at the Institute of Optics, Tomsk, Russia [24] for all lines in common with *HITRAN*. These comparisons are very interesting, and show occasional significant discrepancies. In order to have an idea about the quality of the results of CDSD calculations and DND calculations [6] (used for *HITRAN* when no experimental results were available), we compared new experimental results of Dr. D. Chris Benner (private communication, College of William and Mary) between 3350 cm^{-1} and 3750 cm^{-1} with the *HITRAN* and CDSD databases. Benner worked with a team from NASA Langley Research Center and acquired high-resolution, good photometric accuracy data for numerous bands in the 3-5 μm region, using the facility at Kitt Peak National Solar Observatory. The results of our tests lead us to believe that the CDSD calculation is better than the DND calculation. This is mainly due to the fact that CDSD incorporated more recent studies into their theory, observations that were not available at the time of the last DND calculation. The data from Benner should be particularly useful for the DF laser (chemical dynamic laser).

In order to improve the CO_2 line parameters in the *HITRAN* database, we decided that it will be better to keep the experimental values for the intensities when available. However, for positions we plan to add the calculation of CDSD for bands that are perturbed or for which coefficients come from DND calculation. We will probably also replace line positions in *HITRAN* that rely on observed Venus spectra [25]. The latter data supplemented more accurate controlled laboratory measurements in *HITRAN*.

For the intensities, we plan to add new high-quality experimental measurements. For this, we have a number of contacts with laboratories using FTS throughout the world. One example is the analysis in progress on the recorded CO_2 spectra from 4000 to 9000 cm^{-1} at Kitt Peak by Dr.

Linda Brown and Prof. Charles Miller (Haverford College) [26]. Moreover, collaboration with Miller will be done in the future in order to recalculate all the CO_2 transitions in the self-consistent method accomplished in Ref. [23].

We have developed a practical strategy to update the carbon-dioxide line parameters in *HITRAN.*

Among the works being considered for the update is the theoretical method of effective operators, advanced by Tashkun et al [24]. They have produced a database in *HITRAN* format. However, we have taken the approach to use experimental results (which are more accurate than the theoretical calculations) whenever available. This applies to both the energy levels and the intensities. First, we retain the *HITRAN* line list based on Refs. [23, 27], but take into account more recent results concerning the line intensities. The works on intensities come from: Mandin et al [28] for the 10012-10001 band of $^{12}C^{16}O_2$ centered at 2225 cm^{-1}; Claveau et al [29] for the fundamental ν_3 and five hot bands of $^{16}O^{12}C^{17}O$ between 2200 and 2400 cm^{-1}; Refs. [30-32] for the laser bands of $^{16}O^{12}C^{17}O$ and $^{16}O^{12}C^{18}O$, for the two bands of the main isotopologue centered at 8294 cm^{-1} and at 8192 cm^{-1} and for the fundamental ν_3 of $^{16}O^{13}C^{17}O$; Henningsen and Simonsen [33] for the $2\nu_1 + 2\nu_2^0 + \nu_3$ band of $^{12}C^{16}O_2$ at 6348 cm^{-1}; Kshirsagar et al [34] for the $2\nu_3$ band of $^{16}O^{12}C^{18}O$ at 4639 cm^{-1}; Ref. [35] for the dyad bands 00031-10001 and 00031-10002 of $^{12}C^{16}O_2$ at 5584 cm^{-1} and 5687 cm^{-1}; Giver et al [36] for five bands of $^{12}C^{16}O_2$ between 5218 cm^{-1} and 5349 cm^{-1}; Devi et al [37] for 33 bands of $^{12}C^{16}O_2$ between 3090-3850 cm^{-1}; and four interacting bands in the 3-μm region acquired from Benner [38].

For positions, we are updating the spectroscopic constants of the triad of levels $2\nu_1 + 3\nu_3$ and the combination level $2\nu_1 + \nu_2 + 3\nu_3$ from the work of Ding et al [39], as recommended in Goldman et al [40]. These updates improve positions of bands in the vicinity of 9600 cm^{-1}. In addition, we decided to improve the positions of the bands of the isotopologues that include the isotopes ^{17}O, ^{18}O, and ^{13}C for which the levels have not been observed. In the 2000 *HITRAN* edition [41], the spectroscopic constants of these levels have been determined using DND constants[6] for $^{12}C^{16}O_2$ and $^{13}C^{16}O_2$, and using the calculations of Rothman and Benedict [42] for the others isotopologues. For the next edition of *HITRAN,* we propose to use the calculated line positions involving these levels from the work of Tashkun et al [24], that is to say from the CDSD-296 database. For the other bands, for which the upper and lower levels have been determined [23, 1] from experimentally observed positions, we prefer keeping these data which are more accurate than calculations (at least up to the highest rotational value measured).

We are also planning to incorporate the ongoing high-resolution work of Miller and Brown [26] between 4000 to 9000 cm^{-1}. It should be remarked that some of these aforementioned works will enable us to replace carbon dioxide line positions in *HITRAN* that were derived from observations of Venus by Mandin [25]. The latter values were chosen for many short wave positions in *HITRAN* where no laboratory observations were previously available. The new laboratory high-resolution studies should gradually supersede these lower-resolution results as well as many calculated positions.

This program for improvement to the carbon dioxide parameters is clearly required for many tactical arena problems, but requires some time resources. We will utilize Fortran programs previously developed by Rothman to calculate the line list from the updated energy level spectroscopic constants, band strengths, and Herman-Wallis coefficients. Ideally in the long run, a new consistent least-squares fit of all observed energy levels should be performed in the manner of Ref. [23]. Table 2 is a summary of the data being considered for the *HITRAN* CO_2 update.

Parameters	Spectral region	Source (reference)	Comment on Implementation for HITRAN
ν, S	All	Rothman et al [23]	Retain lines from *HITRAN* database where other information (below) is unavailable
ν, S	All	Tashkun et al [24]	Replace *HITRAN* lines, unless high-resolution observations available
S	4.5 µm	Mandin et al [28]	
S	4.3 µm	Claveau et al [29]	Isotopologues
ν, S	9-10 µm	Claveau et al [30]	Isotopologue 627
S	1.2-1.4 µm	J.-L. Teffo et al [31]	
S	4.3 µm	J.-L. Teffo et al [32]	Isotopologue 637
S	1.6 µm	Henningsen and Simonsen [33]	
S	2.2 µm	Kshirsagar et al [34]	Isotopologue 628
S	1.8 µm	Kshirsagar et al [35]	
S	1.9 µm	Giver et al [36]	
ν, S	2.6-3.2 µm	Devi et al [37]	Many observed bands (ideally should be made self-consistent with other *HITRAN* observations using least-squares fitting)
ν, S	2.6-3.2 µm	Benner [38]	Four interacting bands
ν	1 µm	Ding et al [39]	
ν, S	1.1-2.5 µm	Miller and Brown [26]	Many observed bands (ideally should be made self-consistent with other *HITRAN* observations using least-squares fitting)
ν, S	Sub-mm	Cologne database [43]	Small permanent dipole moment for isotopologues 628 and 627
S	2 µm	Castrillo et al [44]	A few lines
S	1.6 µm	Pouchet et al [45]	~dozen lines (tunable-diode laser work)
γ	1.57 µm	De Rosa et al [46]	A few lines
ν, S, γ, n	All	Multiple sources	Ongoing FTS studies at: SUNY Stony Brook, Battelle Pacific Northwest Laboratory; NASA Langley Research Center

Table 2. Plan for update of carbon dioxide parameters in *HITRAN* (ν, S, γ, n are parameters for position, intensity, half-width, and temperature dependence of half-width).

Figure 4 is an example from Miller and Brown [26] showing the reduction of error in *HITRAN* when applying their work. This is typical of the improvements that will be possible when we incorporate the data of Table 2.

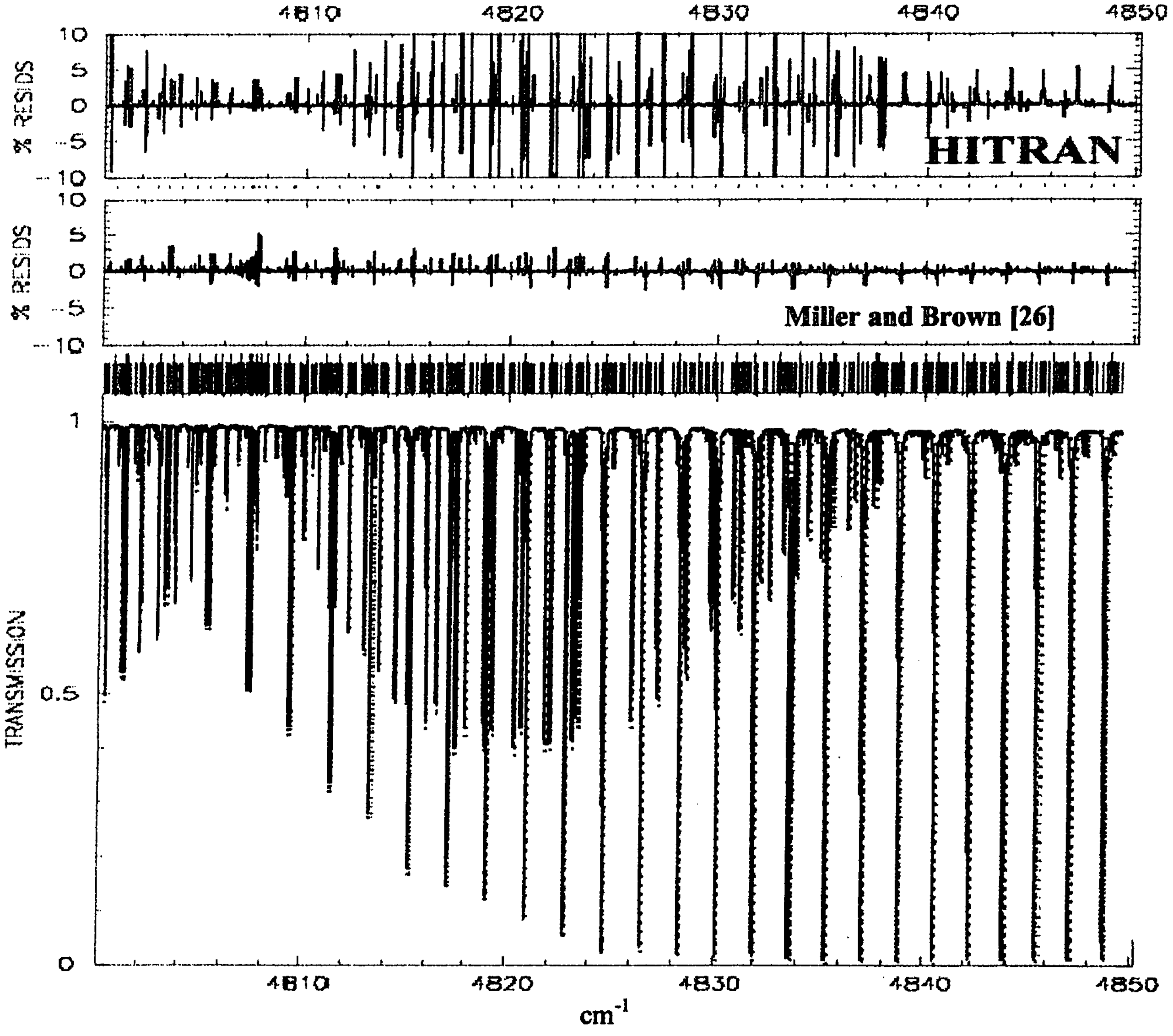

Figure 4. Bottom panel: Experimental (solid line) and simulated (dashed line) CO_2 laboratory spectra in the region of the 20013 ← 00001 band: 30 Torr CO_2 and 25 m path. Top panel: Residuals from simulating the experimental spectrum with the 2000 *HITRAN* database [41]. RMS error = 2.75%. Middle panel: Simulation residuals using the line positions reported in Miller and Brown [26] with unpublished intensity data. RMS error = 0.11%. The remaining residuals are due to small differences in the experimental and simulated intensities.

2.3 Methane (CH_4)

Methane (CH_4, $^{13}CH_4$, and the deuterated isotopologue CH_3D) is a very difficult molecule to make accurate theoretical predictions of spectra in the short wavelength region. The complexity of the interacting bands or polyads becomes one of the true challenges in spectroscopy. The groups that have worked most diligently and for a long time on the problem of methane have been contributing their results for *HITRAN*. Recent achievements in the analysis of the spectra show promise for extending the database.

Numerous improvements for methane have been done in the update of *HITRAN* 2001 [47]. These improvements come mainly from calculated positions and intensities of the team of the Laboratory of Physics of the Université de Bourgogne (LPUB) in Dijon (FRANCE). The global treatment of this molecule is continuing to be improved at LPUB especially for octad and tetradecad levels [48, 49]. Collaboration with Drs.Vincent Boudon and Michel Loëte from LPUB has been developed, and a new and complete line list has been furnished to us. A considerable effort has been initiated in order to compare this line list with *HITRAN*. We hope to be able to improve significantly at least two spectral regions of methane: the octad (3350-4950 cm^{-1}) and tetradecad (4900-6300 cm^{-1}) regions. We focused on these two regions that have tactical interests since the Free Electron Laser is susceptible to be efficient at 1.6 μm (6250 cm^{-1}) and 2.1 μm (4760 cm^{-1}). The principal work on methane is coordinated with Dr. Linda Brown of JPL, who is the focal point of methane research in *HITRAN*. We are also investigating the differences in line positions observed by the group of Prof. Sasada of Keio University [50], Yokohama, Japan in the 1.6-μm region to some lines in the current *HITRAN*.

David Jacquemart finished the comparisons for methane between the 2000 *HITRAN* edition and the recent results obtained with the new calculations of positions and intensities of the team of the Laboratory of Physics of the University of Burgundy (LPUB) in Dijon (FRANCE). For the regions of tactical interest (FEL at 1.6 μm, and 2.1 μm), the results in *HITRAN* come from calculation for the 2.1-μm region [48], and from experimental results for the 1.6-μm region [51]. Concerning the 1.6-μm spectral region, comparisons between *HITRAN*, new calculations of Dijon, and results of Prof. Sasada's group [50], showed that the experimental results of *HITRAN* were in good agreement with Ref. [50] (mean discrepancy of 0.0012 ± 0.0005 cm^{-1} for 9 line positions), contrary to recent calculated results of Dijon (mean discrepancy of 0.067 ± 0.053 cm^{-1}

for 9 line positions). The probable explanation of this situation is that, for the moment, the calculation for the tetradecad region is inferior to good observations. So, for this region, it seems that no improvements can be taken from the recent calculation of Dijon. However, for the 2.1-µm spectral region, comparisons between *HITRAN* and new calculations of Dijon showed that numerous discrepancies appear for the line positions and line intensities. The discrepancies for line positions are on the whole between ± 2 cm^{-1}, except for one band for which it can get as large as 12 cm^{-1}. For this band, it really seems that the problem comes from *HITRAN*. For the intensities, the discrepancies are very large, since they can be as much as 4 orders of magnitude (some intensities in *HITRAN* seem to have been overestimated). Thus, in this region, we think we will be able to improve *HITRAN* line positions and intensities.

3. Results and Conclusion

During this effort, we completed the editing of a Special Issue of *HITRAN* for the Journal of Quantitative Spectroscopy and Radiative Transfer (volume 82, 2003). This volume contains the definitive article [41] describing the improvements and enhancements to the 2000 version of the database, as well as including numerous articles on specific topics in *HITRAN*. Of note is the article on methane authored by Brown et al [47] and the series of articles on water vapor by the group of M. Carleer [10, 11, 52].

An algorithm for air-broadened half-widths and the air pressure-induced line shifts was developed during this project. The implementation of this algorithm required David Jacquemart assess each rotational pair of quantum numbers for a transition and plot a combination of available experimental and theoretical data. Outlying points were assessed and removed. It was generally clear where these outliers were coming from: blended, unresolved, weak lines in the short-wave region. The improvement that has been achieved by the implementation of this semi-empirical algorithm has been verified in a couple of spectral regions by independent observations and simulations. A paper on this work [53] has been accepted by the Journal of Quantitative Spectroscopy and Radiative Transfer. We have recently applied this algorithm for all water vapor air-broadened half-widths and shifts in *HITRAN* that did not have either reliable observations or theoretical calculations. Preliminary studies in several spectral regions by independent researchers have confirmed the improvements made possible by our semi-empirical formulation.

As this effort drew to a premature close, a new edition of the HITRAN database [54] was made available in September 2004. The new HITRAN edition features a more comprehensive format, capabilities for line coupling, and improved software for accessing and manipulating the database. But foremost are the substantial improvements for many bands of many molecules. Preliminary validations show marked improvement; we hope to pursue more independent tests to demonstrate the impact of these improvements, as well as discover any further deficiencies. We are also preparing for a HITRAN Special Issue of the Journal of Quantitative Spectroscopy and Radiative Transfer (*JQSRT)* to appear in 2005. This issue will contain Refs. [53 and 54], and a paper [55] on a new parameter throughout the database, namely the Einstein *A*-coefficient with accompanying statistical weights of the levels in a line transition.

In June 2004, the Eighth International Database Conference was held at the Harvard-Smithsonian Center for Astrophysics in Cambridge MA USA. The meeting was chaired by the PI of this contract, and the co-investigator, D. Jacquemart, was on the local committee. Many presentations, both oral and poster, were made, and issues relevant to this contract were discussed. The proceedings of this conference have been placed in the HITRAN web-site, http://cfa-www.harvard.edu/HITRAN. Several presentations outline improvements and validations of the new data incorporated into *HITRAN*. Of particular note is the paper by Liu et al [56] comparing their tunable-diode laser absorption measurements of H_2O in the 1.355 to 1.441 μm region with the latest *HITRAN* results.

We are working with Linda Brown on a paper, "Assessment of Molecular Line Parameters: 0.75 to 2.5 μm" in collaboration with Drs. Pin Chen, Geoffrey Toon, and Robert A. Toth of JPL. This paper should be an excellent guide for evaluating the deficiencies of spectroscopic parameters of the seven most absorbing species (H_2O, CO_2, O_3, N_2O, CO, CH_4, and O_2) in the terrestrial atmosphere from the near-infrared to the visible.

This program for improvement to the carbon dioxide parameters is obviously required for many tactical arena problems, but requires some time resources. The renewal of this contract is clearly necessary to improve the *HITRAN* database in the tactical region. New CO_2 improvements need to be completed as well as for other molecules such as H_2O, CO, N_2O and CH_4. The water-vapor parameter update is very critical to the ABL program and requires a concerted effort of the team. In particular, the near-infrared and visible regions require a concerted effort to evaluate, correct, and merge the best FTS observations being made by our team and several other laboratories. Line-coupling is also expected to be quite relevant for methane, and algorithms for this phenomenon need to be implemented.

References

1. L.S. Rothman, C.P. Rinsland, A. Goldman, S.T. Massie, D.P. Edwards, J.-M. Flaud, A. Perrin, C. Camy-Peyret, V. Dana, J.-Y. Mandin, J. Schroeder, A. McCann, R.R. Gamache, R.B. Wattson, K. Yoshino, K.V. Chance, K.W. Jucks, L.R. Brown, V. Nemtchinov, and P. Varanasi, "The HITRAN Molecular Spectroscopic Database and HAWKS (HITRAN Atmospheric Workstation): 1996 Edition," *JQSRT* **60,** 665-710 (1998).
2. N. Picqué, G. Guelachvili, D. Jacquemart, V. Dana, and J.-Y. Mandin, "ICLAS – Time Resolved FTS Intensity Measurements by Multispectrum Fitting Approach. First Tests on H_2O with Absorption Paths up to 130km," Poster PT6, Proceedings of the 7th HITRAN Database Conference, Cambridge MA, June 2002.
3. M. Lepère, A. Henry, A. Valentin, and C. Camy-Peyret, "Diode-Laser Spectroscopy: Line Profiles of H_2O in the Region of 1.39μm," *J. Mol. Spectrosc.* **208,** 25-31 (2001).
4. B. Parvitte, V. Zéninari, I. Pouchet, and G. Durry, "Diode laser spectroscopy of H_2O in the 7165-7185 cm^{-1} range for atmospheric applications," *JQSRT* **75,** 493-505 (2002).
5. R.A. Toth, "Extensive measurements of $H_2{}^{16}O$ line frequencies and strengths: 5750-7965 cm^{-1}," *Appl. Opt.* **33,** 4851-4967 (1994).
6. R.B. Wattson and L.S. Rothman, "Direct Numerical Diagonalization: Wave of the Future," *JQSRT* **48,** 763-780 (1992).
7. R.A. Toth, "Transition frequencies and strengths of $H_2{}^{17}O$ and $H_2{}^{18}O$: 5750-7965 cm^{-1}," *Appl. Opt.* **33,** 4868-4879 (1994).
8. C. Camy-Peyret, J.-M. Flaud, J.-Y. Mandin, A. Bykov, O. Naumenko, L. Sinitsa, and B. Voronin, "Fourier-transform absorption spectrum of the $H_2{}^{17}O$ molecule in the 9711-11 335 cm^{-1} spectral region: the first decade of resonating states," *JQSRT* **61,** 795-812 (1999).
9. P.F. Coheur, S. Fally, M. Carleer, C. Clerbaux, R. Colin, A. Jenouvrier, M.-F. Mérienne, C. Hermans, and A.C. Vandaele, "New water vapor line parameters in the 26000-13000 cm^{-1} region," *JQSRT* **74,** 493-510 (2002).
10. S. Fally, P.F. Coheur, M. Carleer, C. Clerbaux, R. Colin, A. Jenouvrier, M.-F. Mérienne, C. Hermans, and A.C. Vandaele, "Water vapor line broadening and shifting by air in the 26,000-13,000 cm^{-1} region," *JQSRT* **82,** 119-131 (2003).
11. M.-F. Mérienne, A. Jenouvrier, C. Hermans, A.C. Vandaele, M. Carleer, P.F. Coheur, R. Colin, S. Fally, and M. Bach, "Water vapor line parameters in the 13 000-9250 cm^{-1} region," *JQSRT* **82,** 99-117 (2003).
12. J.-M. Flaud, C. Camy-Peyret, A. Bykov, O. Naumenko, T. Petrova, A. Scherbakov, and L. Sinitsa, "The Water Vapor Linestrengths between 11600 and 12750 cm^{-1}," *J. Mol. Spectrosc.* **185,** 211-221 (1997).
13. J.-M. Flaud, C. Camy-Peyret, A. Bykov, O. Naumenko, T. Petrova, A. Scherbakov, and L. Sinitsa, "The High-Resolution Spectrum of Water Vapor between 11600 and 12750 cm^{-1}," *J. Mol. Spectrosc.* **183,** 300-309 (1997).

14. R.A. Toth, "Air- and N_2-Broadening parameters of water vapor: 604 to 2271 cm^{-1}," *J. Mol. Spectrosc.* **201,** 218-243 (2000).
15. R.A. Toth, "Water vapor measurements between 590 and 2582 cm^{-1}: Line positions and strengths," *J. Mol. Spectrosc.* **190,** 379-396 (1998).
16. R.A. Toth, "Analysis of line positions and strengths of $H_2{}^{16}O$ ground and hot bands connecting to interacting upper states: (020), (100), and (001)," *J. Mol. Spectrosc.* **194,** 28-42 (1999).
17. R.A. Toth, L.R. Brown, and C. Plymate, "Self-broadened widths and frequency shifts of water vapor lines between 590 and 2400 cm^{-1}," *JQSRT* **59,** 529-562 (1998).
18. Q. Zou, and P. Varanasi, "Laboratory Measurement of the Spectroscopic Line Parameters of Water Vapor in the 610 – 2100 and 3000 – 4050 cm^{-1} Regions at Tropospheric Temperatures," *JQSRT* **82,** 45-98 (2003).
19. C. Camy-Peyret, J.-M. Flaud, J.-Y. Mandin, A. Bykov, O. Naumenko, L. Sinitsa, and B. Voronin, "Fourier-transform absorption spectrum of the $H_2{}^{17}O$ molecule in the 9711-11 335 cm^{-1} spectral region: the first decade of resonating states," *JQSRT* **61,** 795-812 (1999).
20. R.R. Gamache and J. Fischer, "Half-widths of $H_2{}^{16}O$, $H_2{}^{18}O$, $H_2{}^{17}O$, $HD^{16}O$, and $D_2{}^{16}O$: I Comparison between Isotopomers," *JQSRT* **78,** 289-304 (2003).
21. R.R. Gamache and J. Fischer, "Half-widths of $H_2{}^{16}O$, $H_2{}^{18}O$, $H_2{}^{17}O$, $HD^{16}O$, and $D_2{}^{16}O$: II Comparison with Measurements," *JQSRT* **78,** 305-318 (2003).
22. K.M. Smith, I. Ptashnik, D.A. Newnham, and K.P. Shine, "Absorption by water vapour in the 1 to 2 μm region" *JQSRT* **83,** 735-749 (2004).
23. L.S. Rothman, R.L. Hawkins, R.B. Wattson, and R.R. Gamache, "Energy Levels, Intensities, and Linewidths of Atmsopheric Carbon Dioxide Bands," *JQSRT* **48,** 537-566 (1992).
24. S.A. Tashkun, V.I. Perevalov, J-L. Teffo, A.D. Bykov, and N.N. Lavrentieva, "CDSD-1000, the high-temperature carbon dioxide spectroscopic databank," *JQSRT* **82,** 165-196 (2003).
25. J.-Y. Mandin, "Interpretation of the CO_2 Absorption Bands Observed in the Venus Infrared Spectrum between 1 and 2.5 μm," *J. Molec. Spectrosc.* **67,** 304-321 (1977).
26. C.E. Miller and L.R. Brown, "Near Infrared Spectroscopy of Carbon Dioxide: $^{16}O^{12}C^{16}O$ Line Positions," paper MG08, Proceedings of the Ohio State University International Symposium on Molecular Spectroscopy, Columbus Ohio June 16-20, 2003; C.E. Miller and L.R. Brown, "Near Infrared Spectroscopy of Carbon Dioxide I. $^{16}O^{12}C^{16}O$ Line Positions," in press, *J. Molec. Spectrosc.* (2004).
27. L.S. Rothman, "Infrared energy levels and intensities of carbon dioxide. Part 3," *Appl. Opt.* **25,** 1795-1816 (1986).
28. J.-Y. Mandin, V. Dana, J.-Y. Allout, L. Régalia, A. Barbe, and J.-J. Plateaux, "Line Intensities and Self-Broadening Coefficients in the 10012-10001 Band of $^{12}C^{16}O_2$ Centered at 2224.657 cm^{-1}," *J. Molec. Spectrosc.* **170,** 604-607 (1995).
29. C. Claveau, J.-L. Teffo, D. Hurtmans, and A. Valentin, "Infrared Fundamental and First Hot Bands of $O^{12}C^{17}O$ Isotopic Variants of Carbon Dioxide," *J. Molec. Spectrosc.* **189,** 153-195 (1998).
30. C. Claveau, J.-L. Teffo, D. Hurtmans, A. Valentin, and R.R. Gamache, "Line Positions and Absolute Intensities in the Laser Bands of Carbon-12 Oxygen-17 Isotopic Species of Carbon Dioxide," *J. Molec. Spectrosc.* **193,** 15-32 (1999).

31. J.-L. Teffo, C. Claveau, Q. Kou, G. Guelachvili, A. Ubelmann, V.I. Perevalov, and S.A. Tashkun, "Line Intensities of $^{12}C^{16}O_2$ in the 1.2-1.4 μm Spectral Region," *J. Molec. Spectrosc.* **201,** 249-255 (2000).
32. J.-L. Teffo, C. Claveau, and A. Valentin, "Infrared Fundamental Bands of $O^{13}C^{17}O$ Isotopic Variants of Carbon Dioxide," *JQSRT* **59,** 151-164 (1998).
33. J. Henningsen and H. Simonsen, "The (22^01-00^00) Band of CO_2 at 6348 cm^{-1}: Linestrengths, Broadening Parameters, and Pressure Shifts," *J. Molec. Spectrosc.* **203,** 16-27 (2000).
34. R.J. Kshirsagar, L.P. Giver, C. Chackerian Jr, and L.R. Brown, "The Rovibrational Intensities of the $2\nu_3$ Band of $^{16}O^{12}C^{18}O$ at 4639 cm^{-1}," *JQSRT* **61,** 695-701 (1999).
35. R.J. Kshirsagar, L.P. Giver, and C. Chackerian Jr, "Rovibrational Intensities of the $(00^03) \leftarrow (10^00)$ Dyad Absorption Bands of $^{12}C^{16}O_2$," *J. Molec. Spectrosc.* **199,** 230-235 (2000).
36. L.P. Giver, L.R. Brown, C. Chackerian Jr, and R.S. Freedman, "The rovibrational intensities of five bands of $^{12}C^{16}O_2$ between 5218 and 5349 cm^{-1}," *JQSRT* **78,** 417-436 (2003).
37. V. Malathy Devi, D.C. Benner, C.P. Rinsland, and M.A.H. Smith, "Absolute Rovibrational Intensities of $^{12}C^{16}O_2$ Absorption Bands in the 3090-3850 cm^{-1} Spectral Region," *JQSRT* **60,** 741-770 (1998).
38. D. Chris Benner, College of William and Mary, private communication (2003).
39. Y. Ding, E. Bertseva, and A. Campargue, "The $2\nu_1 + 2\nu_3$ Triad of $^{12}CO_2$," *J. Molec. Spectrosc.* **212,** 219-222 (2002).
40. A. Goldman, T.M. Stephen, L.S. Rothman, L.P. Giver, J.-Y. Mandin, R.R. Gamache, C.P. Rinsland, and F.J. Murcray, "The 1-μm CO_2 bands and the O_2 (0-1) $X^3\Sigma_g^- - a^1\Delta_g$ and (1-0) $X^3\Sigma_g^- - b^1\Sigma_g^+$ bands in the Earth atmosphere," *JQSRT* **82,** 197-205 (2003).
41. L.S. Rothman, A. Barbe, D.Chris Benner, L.R. Brown, C. Camy-Peyret, M.R. Carleer, K. Chance, C. Clerbaux, V. Dana, V.M. Devi, A. Fayt, J.-M. Flaud, R.R. Gamache, A. Goldman, D. Jacquemart, K.W. Jucks, W.J. Lafferty, J.-Y. Mandin, S.T. Massie, V. Nemtchinov, D.A. Newnham, A. Perrin, C.P. Rinsland, J. Schroeder, K.M. Smith, M.A.H. Smith, K. Tang, R.A. Toth, J. Vander Auwera, P. Varanasi, and K. Yoshino, "The HITRAN molecular spectroscopic database: edition of 2000 including updates through 2001," *JQSRT* **82,** 5-44 (2003).
42. L.S. Rothman and W.S. Benedict, "Infrared energy levels and intensities of carbon dioxide," *Appl. Opt.* **17,** 2605-2611 (1978).
43. H.S.P. Müller, S. Thorwirth, D.A. Roth, and G. Winnewisser, "The Cologne Database for Molecular Spectroscopy, CDMS," *Astronomy & Astrophysics* **370,** L49-L52 (2001).
44. A. Castrillo, G. Gagliardi, G. Casa, and L. Gianfrani, "Combined interferometric and absorption-spectroscopic technique for determining molecular line strengths: Applications to CO_2," *Phys. Rev. A* **67,** (2003).
45. I. Pouchet, V. Zéninari, B. Parvitte, and G. Durry, "Diode laser spectroscopy of CO_2 in the 1.6 μm region for the in situ sensing of the middle atmosphere," *JQSRT* **83,** 619-628 (2004).
46. M. De Rosa, C. Corsi, M. Gabrysch, and F. D'Amato, "Collisional broadening and shift of lines in the $2\nu_1 + 2\nu_2 + \nu_3$ band of CO_2," *JQSRT* **61,** 97-104 (1999).
47. L.R. Brown, D. Chris Benner, J.-P. Champion, V.M. Devi, L. Fejard, R.R. Gamache, T. Gabard, J.C. Hilico, B. Lavorel, M. Loëte, G.Ch. Mellau, A. Nikitin, A.S. Pine,

A. Predoi-Cross, C.P. Rinsland, O. Robert, R.L. Sams, M.A.H. Smith, S.A. Tashkun and Vl.G. Tyuterev, "Methane line parameters in HITRAN," *JQRST* **82,** 219-238 (2003).

48. J.C. Hilico, O. Robert, M. Loëte, S. Toumi, S.A. Pine, and L.R. Brown, "Analysis of the interacting octad system of $^{12}CH_4$," *J. Mol. Spectrosc.* **208,** 1-13 (2001).
49. O. Robert, J.C. Hilico, J.P Champion, and L.R. Brown, "First assignment and line strengths of the $4\nu_4$ band of $^{12}CH_4$ near 1.9 μm," *J. Mol. Spectrosc.* **209,** 14-23 (2001).
50. C. Ishibashi, M. Kourogi, K. Imai, B. Widiyatmoko, A. Onae, and H. Sasada, "Absolute frequency measurement of the saturated absorption lines of methane in the 1.66 micron region," *Optics Communications* **161,** 223-226 (1999).
51. J.S. Margolis, "Measured line positions and strengths of methane between 5500 and 6180 cm^{-1}," *Appl.Opt.* **27,** 4038-4051 (1988); J.S. Margolis, "Empirical values of the ground state energies for methane transitions between 5500 and 6150 cm^{-1}," *Appl. Opt.* **29,** 2295-2302 (1990).
52. P. Coheur, C. Clerbaux, M. Carleer, S. Fally, D. Hurtmans, R. Colin, C. Hermans, A.C. Vandaele, B. Barret, M. De Mazière, and H. De Backer," Retrieval of atmospheric water vapor columns from FT visible solar absorption spectra and evaluation of spectroscopic databases," *JQRST* **82,** 133-150 (2003).
53. D. Jacquemart, R.R. Gamache, and L.S. Rothman, "Semi-empirical calculation of air-broadened halfwidths and air pressure-induced frequency shifts of water-vapor absorption lines," in press, *JQSRT* (2004).
54. L.S. Rothman, D. Jacquemart, L.R. Brown, M. Carleer, R.R. Gamache, et al, "The *HITRAN* 2004 Molecular Spectroscopic Database," in press, *JQSRT* (2004).
55. D. Jacquemart, L.S. Rothman, R.R. Gamache, and A. Goldman, "Einstein *A*-coefficients and statistical weights in the *HITRAN* 2004 spectroscopic database," in press, *JQSRT* (2004).
56. X. Liu, J.B. Jeffries, and R.K. Hanson, "Tunable-diode Laser Absorption of H_2O Vapor between 1355 and 1441 nm versus *T* and *P* and Comparison to HITRAN Predictions," The Eighth HITRAN Database Conference, Cambridge MA, 16-18 June 2004.

Presentations during contract period

"Millenium HITRAN Compilation," The 18th Colloquium on High Resolution Molecular Spectroscopy, Dijon, France (September 2003).

"The HITRAN Quest for Accurate Long-path Atmospheric Transmission in Tactical Arenas," 26th AF Annual Review of Atmospheric Transmission Models, Lexington, Massachusetts (September 2003). (Invited)

"Recent Advances in the HITRAN Spectroscopic Database for Atmospheric and Environmental Modeling," Ninth Topical Meeting, Laser Applications to Chemical and Environmental Analysis (LACEA), Annapolis, Maryland (February 2004). (Invited)

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

Publications during contract period

"The 1-μm CO_2 bands and the O_2 (0-1) $X^3\Sigma_g^- - a^1\Delta_g$ and (1-0) $X^3\Sigma_g^- - b^1\Sigma_g^+$ bands in the Earth atmosphere," A. Goldman, T.M. Stephen, L.S. Rothman, L.P. Giver, J.-Y. Mandin, R.R. Gamache, C.P. Rinsland, and F.J. Murcray, *J. Quant. Spectrosc. and Rad. Transfer* **82,** 197-205 (2003).

"The IR acetylene spectrum in HITRAN: update and new results," D. Jacquemart, J.-Y. Mandin, V. Dana, C. Claveau, J. Vander Auwera, L.S. Rothman, L. Régalia-Jarlot, and A. Barbe, *J. Quant. Spectrosc. and Rad. Transfer* **82,** 363-382 (2003).

"Total Internal Partition Sums for Molecular Species in the 2000 edition of the HITRAN database," J. Fischer, R.R. Gamache, A. Goldman, L.S. Rothman, and A. Perrin, *J. Quant. Spectrosc. and Rad. Transfer* **82,** 401-412 (2003).

"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, in press, *J. Quant. Spectrosc. and Rad. Transfer* (2004).

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

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