Water Vapor Line Intensity Corrections and Rovibrational Assignment Updates of the Shortwave HITRAN and GEISA Databases

L. P. Giver, C. Chackerian, Jr., and D. W. Schwenke
National Aeronautics and Space Administration
Ames Research Center
Moffett Field, California

R. S. Freedman and M. D. DiRosa
Space Physics Research Institute
Sunnyvale, California

P. Varanasi
Institute for Terrestrial and Planetary Atmospheres
State University of New York at Stony Brook
Stony Brook, New York

R. L. Sams
Pacific Northwest National Laboratory
Richland, Washington

Introduction

While measuring weak water vapor lines in the wings of the 0.94-µm band on spectra obtained with the 25-m base-path White cell and Bomem DA8 Fourier-transform spectrometer (FTS), we compared some of our measured intensity data to those listed in the HIgh resolution TRANsmission molecular absorption (HITRAN-96), Rothman et al. (1996), database, and also to the prior measurements of Chevillard et al. (1988). Our measurements were, on the average, about 20% higher than the entries in HITRAN, but generally compatible with the intensities reported by Chevillard et al. (1988). This was strange, since HITRAN refers to the Chevillard publication as the source data for most of the lines listed in the 9500-cm^{-1} to 11500-cm^{-1} region. We therefore selected over 50 of the best-measured lines from the tables of Chevillard et al. (1988) to compare with the HITRAN values. About half of these lines were previously measured by Giver et al. (1982); each of these prior line measurements agreed with the corresponding Chevillard et al. (1988) measurement within 6%, which was their uncertainty estimate. After making this comparison and finding that the HITRAN intensities did not agree with Chevillard's published values, we made similar comparisons of the experimental data from four other articles reporting the line intensities in the visible and near-infrared that formed the basis for HITRAN lists in the respecive spectral regions. The four articles are by Camy-Peyret et al. (1986), Mandin et al. (1986), Mandin et al. (1988), and Toth (1994b). The measured intensity data are all in the units of cm^{-1}/(cm-atm) at room temperature. All the measurements described in the five mentioned articles are based on FTS spectra obtained with the 6-m base-path White cell at the Kitt Peak solar telescope and they all contain reports of intensities in the units of cm^{-2} atm^{-1}. The unit used in the HITRAN database for the line intensity is cm/molecule at 296. The corrections we refer to here point to several cases of oversight by the creators of the database during the process of converting the measured intensity data reported in the five source papers into the units adapted by the creators of the database. The corrections needed to bring the HITRAN intensities into agreement with the published measurements have been described by Giver et al. (2000). These corrections only apply to assigned lines of the main isotopomer of water reported in the above cited five publications of experimental data, but these lines account for over 97% of the absolute intensity in each of the wavenumber intervals of interest. The corrections are described in detail by Giver et al. (2000). The list of parameters for lines between 8000-cm^{-1} to 25200-cm^{-1}, with the proper intensity revisions, has been posted on the "database updates" page of the HITRAN Internet site: http://www.hitran.com. These corrections affect the Gestion et Etude des Informations Spectroscopiques Atmospheriques (GEISA), Jacquinet-Husson et al. (1999), database as well.

Unassigned Lines in the Databases

There are about 2000 (mostly weak) transitions on the HITRAN and GEISA databases in this shortwave region that do not have rovibrational assignments and thus, the temperature dependence of their intensities is not known. Polyansky et al. (1998) and Carleer et al. (1999) have recently assigned many of these lines in the 13000-cm^{-1} to 16500-cm^{-1} region. We have confirmed most of these assignments and made some additional ones using Partridge and Schwenke's (1997) list of intensities based upon ab initio calculations (Internet site http://ccf.arc.nasa.gov/~dschwenke). We are beginning to assign most of the unassigned lines in the 8000-cm^{-1} to 9500-cm^{-1} region in the same way.

Of the 2000 lines with positions above 8000 cm^{-1} that lack rovibrational assignments, 71 are in the 0.94-μm spectral region. Schwenke (1998) has published rovibrational assignments for many of these unassigned lines, including 58 in the important 0.94-μm band. Using the ab initio line list on Schwenke's Internet site (http://ccf.arc.nasa.gov/~dschwenke), we have included rovibrational assignments on the corrected line list on HITRAN's website for all 71 unassigned lines in the region. Polyansky et al. (1998) have recently assigned over 600 of the unassigned lines in the 13200-cm^{-1} to 16500-cm^{-1} region. Carleer et al. (1999) have also made many new rovibrational assignments in their analysis of new spectra they obtained. There are many disagreements on the complete assignments between these two lists and Schwenke's (1998) assignments. We have been making a detailed comparison of them and Schwenke's website ab initio calculated line list. There is often disagreement among these three articles over the upper state vibrational levels, but we have found agreement among Polyansky, Carleer, and Schwenke's website line list for most lines for the lower state assignment, and thus E", which is of primary importance for atmospheric applications. A line list of "consensus" assignments in the 13200-cm^{-1} to 16500-cm^{-1} region is in preparation for consideration of inclusion on the HITRAN and GEISA databases.

The 1.38-mm Region

We have investigated the absorption band at 1.38 µm (5750 cm^{-1} to 7965 cm^{-1}) to determine if any similar systematic differences exist between the entries in the databases and published mesurements of intensities. While there are many substantial differences between the latest published measurements by Toth (1994a) and the HITRAN database values, there is no systematic correction that can be applied; the intensity data of the databases require improvements on a line-by-line basis, which is beyond the scope of the present work. This region is similar to the 11610-cm^{-1} to 12861-cm^{-1} region, in that many lines on HITRAN were obtained from preliminary measurements by Toth, which were subsequently completed and published in 1994. However, in the 1.38-µm region, many strong lines on HITRAN-86 were not replaced by Toth's preliminary measurements. In fact, only about 35% of the total intensity of lines in this region are listed as coming from Toth's work. Therefore, when we ratioed Toth's (1994a) measured intensities to HITRAN-96 values, we did not find any systematic trends as was found in the higher wavenumber regions. We have now converted HITRAN intensities to measurement units, sorted the HITRAN lines out as 1986 holdovers or Toth's preliminary entries, and ratioed Toth's (1994a) published measurements to them. Toth's measured values are typically about 75% of the HITRAN intensities for the old 1986 hold-over lines, with some notable exceptions. Also, his final measured intensities are generally larger than the HITRAN values from his own preliminary measurements; some lines are about 40% larger. This is very different from the comparison of Toth's (1994b) published measurements to HITRAN values in the 820 nm region, where Toth's published values were apparently very close to his preliminary values used by HITRAN. There is nothing systematic found in the ratios in the 1.38-µm region.

New spectra have been obtained in the 7250-cm^{-1} region at the Pacific Northwest National Laboratory (PNNL), using a Bruker FTS with spectral resolution better than 0.01 cm^{-1}. These spectra were obtained with a pathlength of 20 cm, and pressures of pure H_2O vapor between 2 and 15 torr. Several lines in these observations were compared to simulations using HITRAN-96 line positions and intensities. Six of these lines were holdovers from HITRAN-86. The compaisons of new spectra with HITRAN simulations demonstrate the need for some improvement in the HITRAN hold-over values of both positions and intensities. But intensities and positions for the strong lines measured on these spectra at PNNL are generally in good agreement with Toth's (1994a) published values.

Summary and Recommendations

For the spectral region above 8000 cm^{-1}, we have determined that unit-conversion errors were made when line intensities originally listed in measurement units were put on the HITRAN and GEISA databases. These findings were published by Giver et al. (2000), and the HITRAN water vapor tables have been corrected and posted on the HITRAN Web site "database updates" page. Also, on this HITRAN update, the 71 lines unassigned on HITRAN in the 10,000-cm^{-1} to 11,500-cm^{-1} region were given rovibrational assignments from Schwenke (1998) and from the line list on Schwenke's Web site.

We have compared the rovibrational assignments of Polyansky et al. (1998), Carleer, et al. (1999), Schwenke (1998), and Schwenke's Web site line list for the more than 700 unassigned HITRAN lines in the 13200-cm^{-1} to 16500-cm^{-1} region. Only 208 lines are in complete agreement between the Polyansky and Schwenke publications. However, a careful search of Schwenke's line list on his Web site confirms at least the lower-level rotational assignments of Polyansky (1998) and Carleer (1999) for most of the lines. We are preparing a list of about 600 lines with "consensus" assignments and lower-level E" values to recommend them for the databases.

For the 1.38-μm band region, we have compared HITRAN intensities with the published measurements of Toth (1994a). We recommend that for the most part, the HITRAN and GEISA databases should be updated using Toth's (1994) finalized measurements of both positions and intensities. For the strongest lines in this region, the new measurements being made at PNNL may be superior, and should be considered for the databases.

The results of incorporating the major corrections to the intensities listed in the database are 14.4% and 8.7% increases in the 9500-cm^{-1} to 11500-cm^{-1} and the 11500-cm^{-1} to 13000-cm^{-1} spectral regions, respectively. The important 0.82-μm and 0.94-μm bands of water vapor are in these regions. The respective intensity corrections to the databases are sufficiently large as to warrant re-analyses of some atmospheric measurements made in these bands. For example, Nedoluha, et al. (2000) have shown that correcting the 0.94-μm water band measurements by the Polar Ozone Atmospheric Measurements (POAM) satellite results in better agreement for POAM III and HALogen Occulation Experiment (HALOE) vapor abundances in the Antarctic lower stratosphere.

Corresponding Author

P. Varanasi, pvaranasi@notes.cc.sunysb.edu.

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