Measurements of the Infrared Spectral Lines of Water Vapor at Atmospheric Temperatures

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Introduction

Water vapor is undoubtedly the most dominant greenhouse gas in the terrestrial atmosphere. In the two facets of Atmospheric Radiation Measurement (ARM) Program research, atmospheric remote sensing (air-borne as well as Cloud and Radiation Testbed [CART] site-based) and modeling of atmospheric radiation, the spectrum of water vapor, ranging from the microwave to the visible wavelengths, plays a significant role. Its spectrum has been the subject of many studies throughout the last century. Therefore, it is natural to presume it should be fairly well established by now. However, the need for a robust infrared (IR) spectroscopic database of this molecule is greater now than ever before, because we are discovering the deficiencies, if not inaccuracies, in the existing databases: high-resolution transmission (HITRAN) database (Rothman et al. 1998) and Gestion et Etude des Informations Spectroscopiques Atmosphériques (GEISA) databank (Jacquinet-Husson et al. 1999). In view of this need our laboratory has been actively engaged in the accurate measurement of the spectral line parameters of water vapor at atmospheric temperatures and spectral regions relevant to the ARM Initiative's observations and modeling endeavors. The line parameters mentioned above are the absolute intensity or the strength, the self-broadened line width, the air-broadened line width of the spectral line, and the dependence of the air-broadened width with temperature. The discrepancies we show here between our data, the entries in the HITRAN-98 database, and the data of Toth may seem small to a climate modeler but it must be emphasized that the current state-of-the-art of IR remote sensing of the atmosphere is such that a precision of 98 percent or higher in the spectral line parameters is indeed demanded.

Experimental Details

The spectra were recorded using a high-resolution (Bruker IFS-120HR) Fourier-transform spectrometer. A globar source, a KBr beam-splitter, and a liquid-nitrogen-cooled mercury-cadmium-telluride detector were used. Using a cryogenically cooled absorption cell, we were able to measure the air-broadened half-widths at 252, 273, and 296 K, and deduce their dependence upon temperature. Our newly developed non-linear least-squares multi-spectral-line-fitting algorithm was used in the retrieval of the spectroscopic parameters from measured spectral transmissivity datasets. An example of this line-fitting procedure is shown in Figure 1. During the simultaneous non-linear least-squares fitting of multiple spectra, the initial estimates or guesses of the parameters were based upon the data available in the HITRAN-98 database.

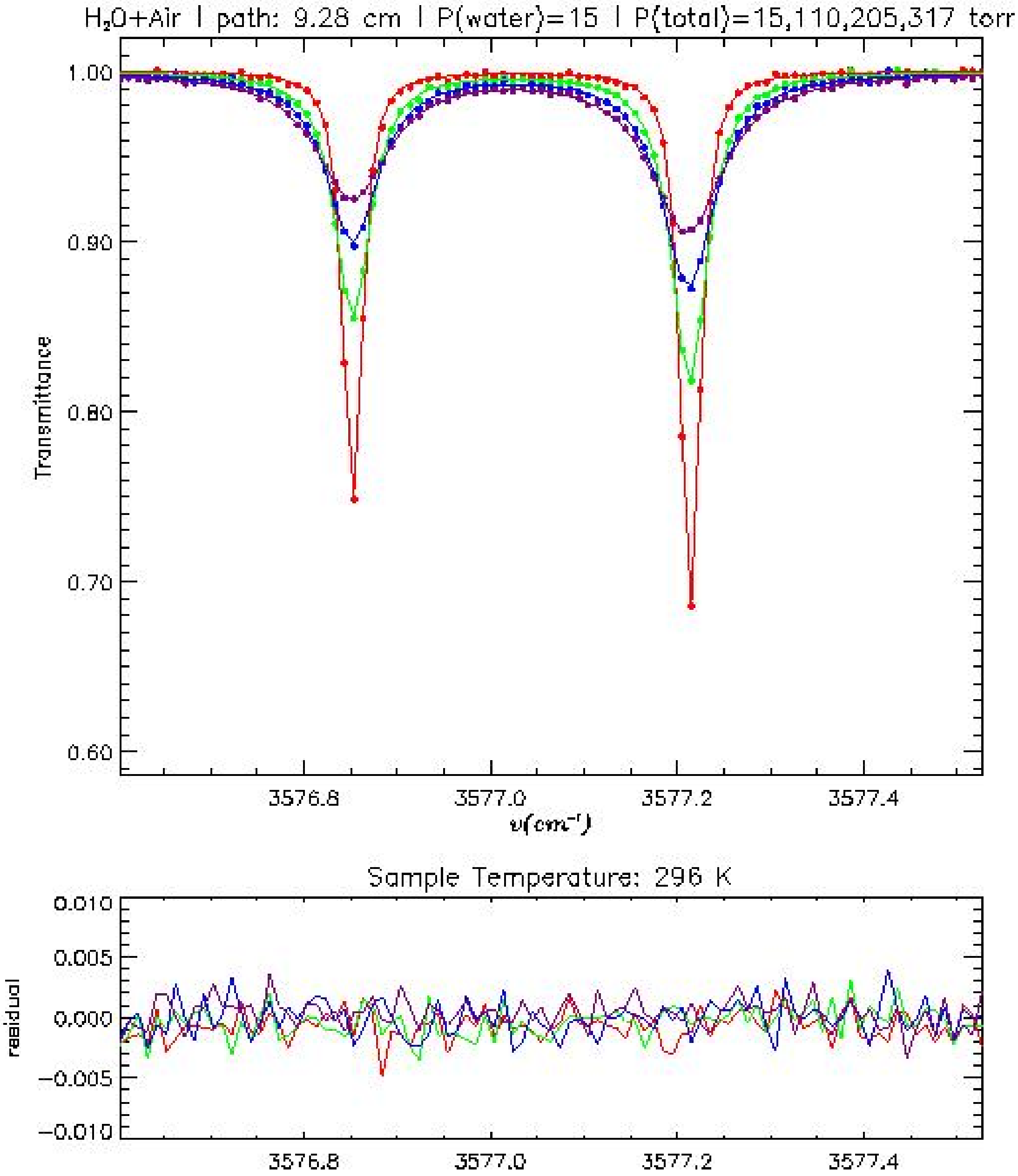
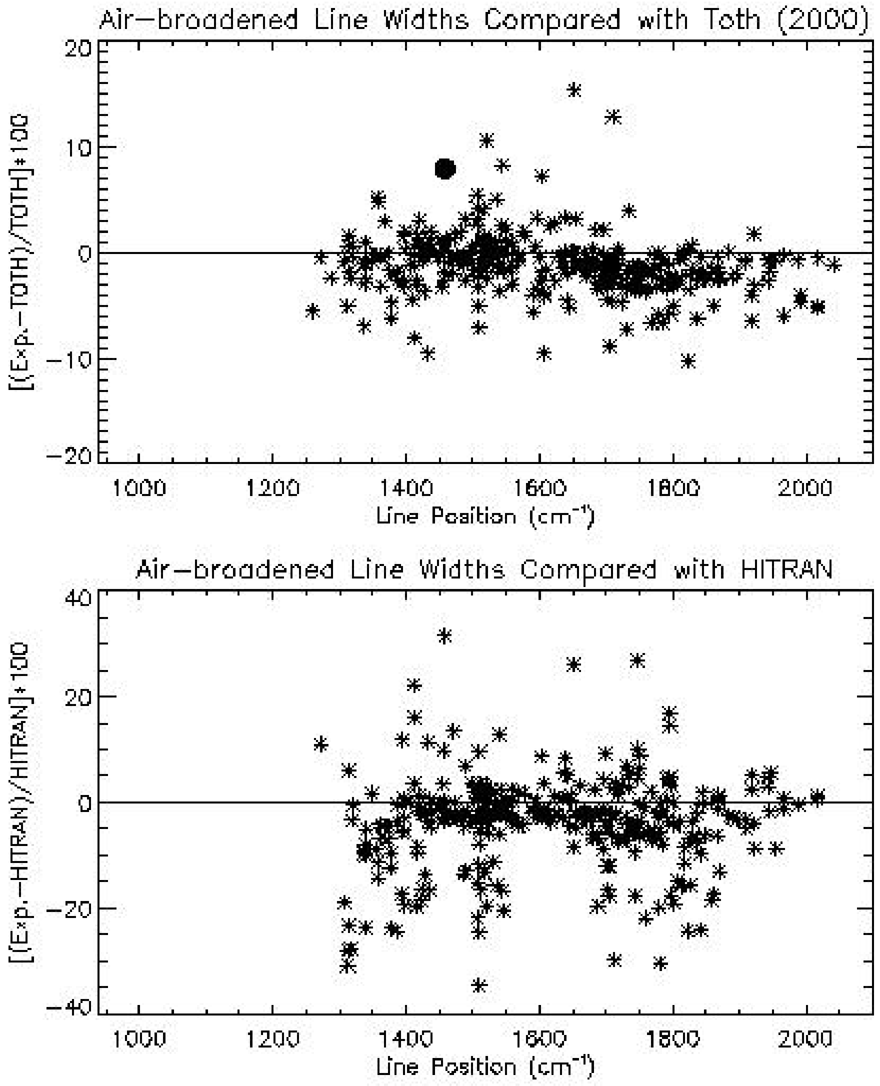


Figure 1. An illustration of the multi-spectral non-linear least-squares fitting procedure. The spectral line shown is an air-broadened line of water vapor at 15 torr of the absorber and several different pressures of the broadener (air).

Results and Discussion

The line strengths retrieved from our experiments are compared in Figures 2 and 3 with the recently published data of Toth (1999; 2000) and the entries in the HITRAN-98 database. Figure 2 is for the 950 - 2100 cm^{-1} region, while Figure 3 is for the 3000 - 4050 cm^{-1} region. The ordinate is the percentage difference between our data and the HITRAN-98 database, and the data of Toth, and the


Air–broadened Line Widths Compared with Toth (2000)

Air–broadened Line Widths Compared with HITRAN

Figure 2. Line strengths in the 950 to 2100 cm^{-1} region compared with the results obtained by Toth (2000) and the entries in the HITRAN-98 database.

abscissa is the line strength in cm/molecule units. Clough suggested this choice of presentation, so that the discrepancy between the datasets is gauged in terms of the magnitude of the line strength measured. It is apparent that observable discrepancy can amount up to ± 30 percent in the 950 - 2100 cm^{-1}region, while it lies within ± 20 percent in the 3000 - 4050 cm^{-1} region. Compared to Toth's results, our data in the latter region are, for the most part, smaller by about 4 percent for the lines with strengths larger than 8×10^{-20} cm/molecule, but are larger by about 4 percent for the lines with strengths between 10^{-21} and 3×10^{-20} cm/molecule. The differences with the entries in the HITRAN-98 database are smaller for the strong lines but larger for the weak lines, as shown in the lower panel of Figure 2. When the line strengths of all the lines are added together, Toth's results and the HITRAN-98 database agree with our results within 3 percent and 2 percent, respectively. Figure 3 shows that our results are generally

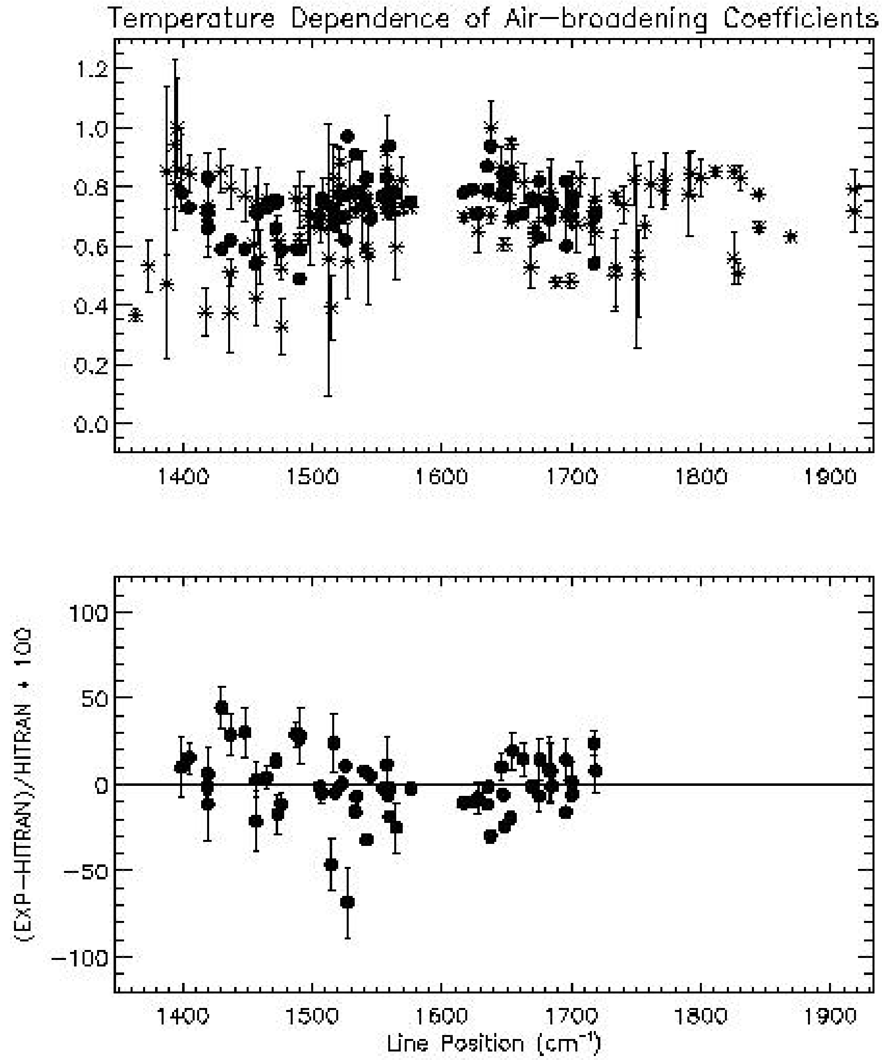


Figure 3. Line strengths in the 3000 to 4050 cm^{-1} region compared with the results obtained by Toth (1999) and the entries in the HITRAN-98 database.

smaller than Toth's by 7 percent for the lines stronger than 2 × 10^{-20} cm/molecule, and that the differences are around 5 percent for the weaker lines. While our results of the strengths of the lines stronger than 3 × 10^{-20} cm/molecule agree fairly well with the HITRAN-98 database, they are about 5 percent larger than the entries in the HITRAN-98 database for the weaker lines. When the line strengths of all the lines in this region are added together, the result from Toth's measurements is larger than ours by 7.2 percent, and the result from the HITRAN-98 database is 1.1 percent smaller than ours.

Figure 4 illustrates the comparison of our air-broadened line-width data with those of Toth (2000) and HITRAN-98 database at 296 K. The dependence of the air-broadening coefficient $\gamma^0(T)$ (cm^{-1} atm^{-1}) on temperature T is described in terms of the commonly used empirical law:

$$\gamma^0(T) / \gamma^0(T_0) = (T_0 / T)^n.$$

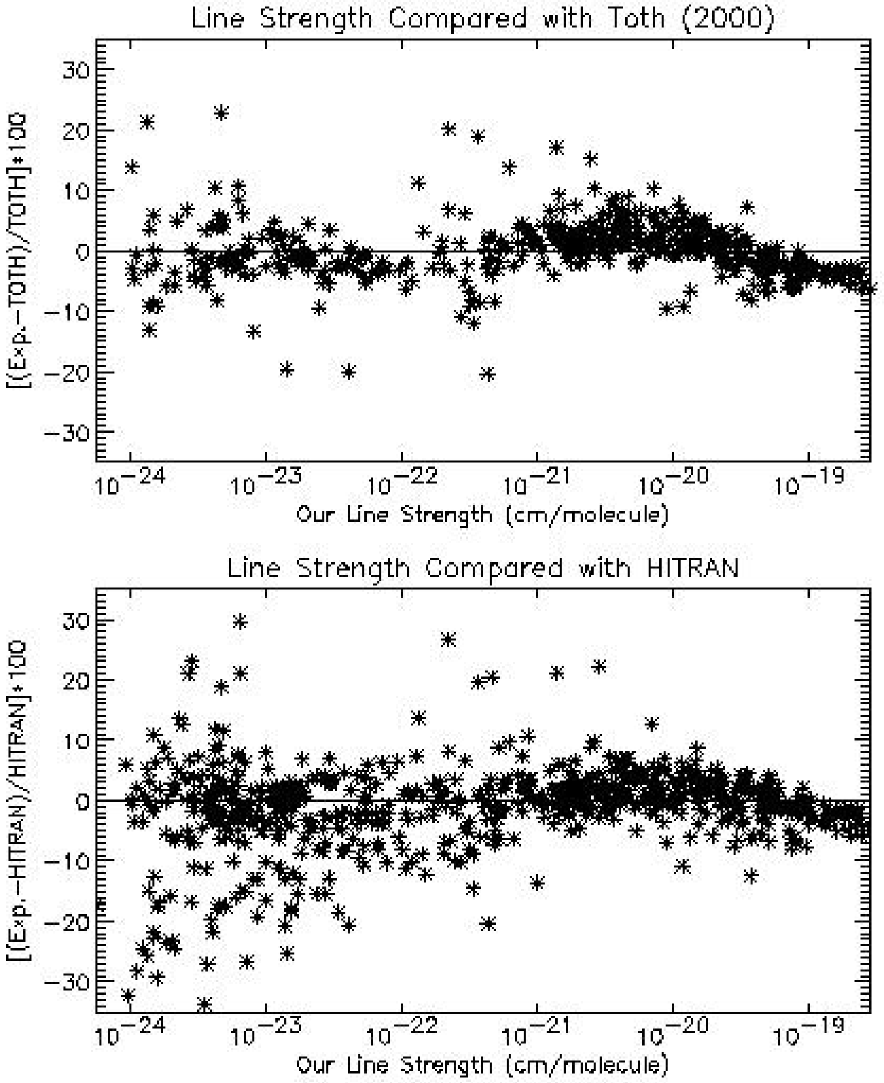


Figure 4. Air-broadened line-widths compared with the results reported by Toth (2000) and the entries in the HITRAN-98 database in the 950 to 2100 cm^{-1} region. When the differences are larger than 40 percent they are divided by a factor of 10 and are shown as big solid dots.

Figure 5 is a comparison of the values of n obtained by us and the 63 entries, which seems to be the few in the HITRAN-98 database that were laboratory measurements (Remedios 1990). So pitiful indeed had been the extent of our knowledge of this important line parameter that we were prompted to extend it to a greater number of lines of interest to ARM and other atmospheric scientists. The actual list of the line parameters measured in our laboratory (Zou 2001) at 296 K and lower temperatures of atmospheric interest is too large for reproduction here. Self-broadened line widths and pressure-induced shifts, both in self-induced and air-induced cases, of lines in moist air of consequence in tropospheric remote-sensing studies and their dependence upon temperature have also been measured by using lean mixtures of water vapor and air. For the sake of brevity they have not been presented here. The data may be obtained by contacting us via e-mail.

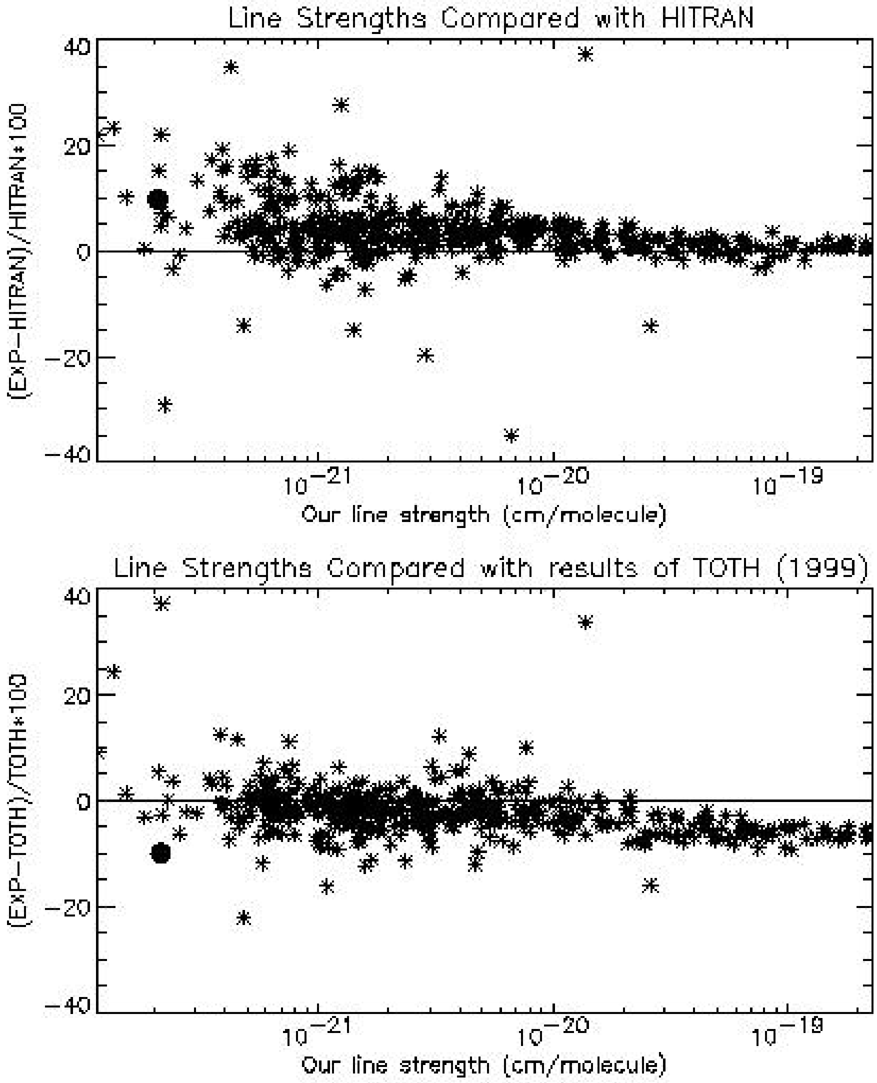


Figure 5. The exponent n for air-broadened line-widths is shown in the top figure, while the discrepancy with the comparable entries in the HITRAN-98 database are shown in the bottom figure. It should be noted that only 63 entries, which are chosen here, in the database are experimentally determined values reported by Remedios (1990).

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