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 the Atmospheric Radiation Measurement (ARM) Program's 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 spectroscopic database of this molecule is greater now than ever before, as 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 database, and the data of Toth may seem small to the modeler, but it must be emphasized that the current state-of-the-art of infrared remote sensing of the atmosphere is such that a precision of 98% 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 K, 273 K, and 296 K, and deduce their dependence on 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 data sets. 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 on the data available in the HITRAN database.

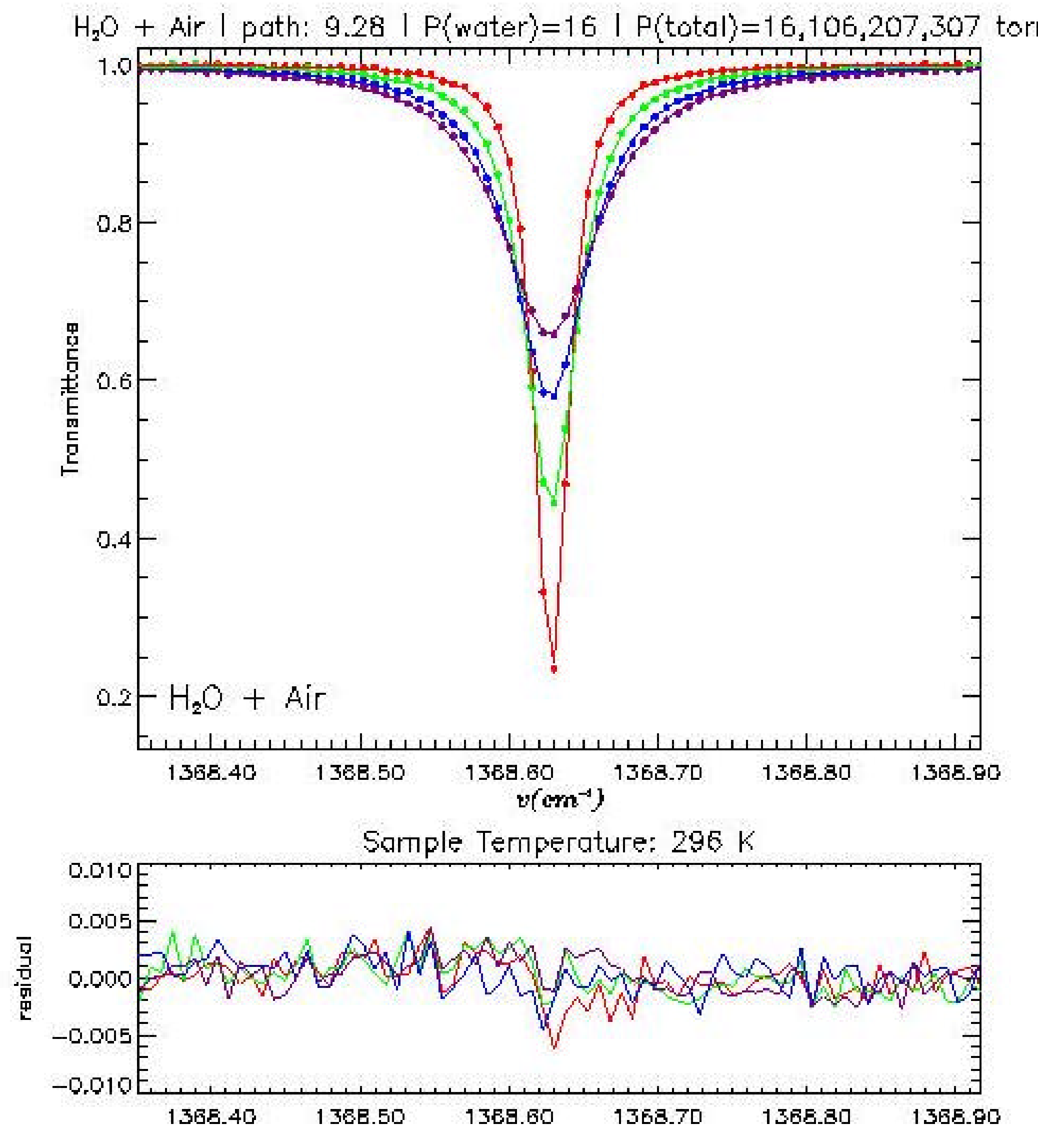


Figure 1.

Results and Discussion

The line strengths retrieved from our experiments are compared in Figure 2 with the recently published data of Toth (1998) and the entries in the HITRAN. The ordinate is the percentage difference between our data and the data of Toth and HITRAN and the abscissa is the line position. It is apparent that observable discrepancies exist within ±10%. A similar comparison of self-broadened line widths is presented in Figure 3. The data of Toth et al (1998) were compared with our data. The differences in the self-broadened line widths measured by us and the data in HITRAN are mostly within ±20%. Figure 4 illustrates the comparison of our air-broadened line-width data with those of Toth (2000) and

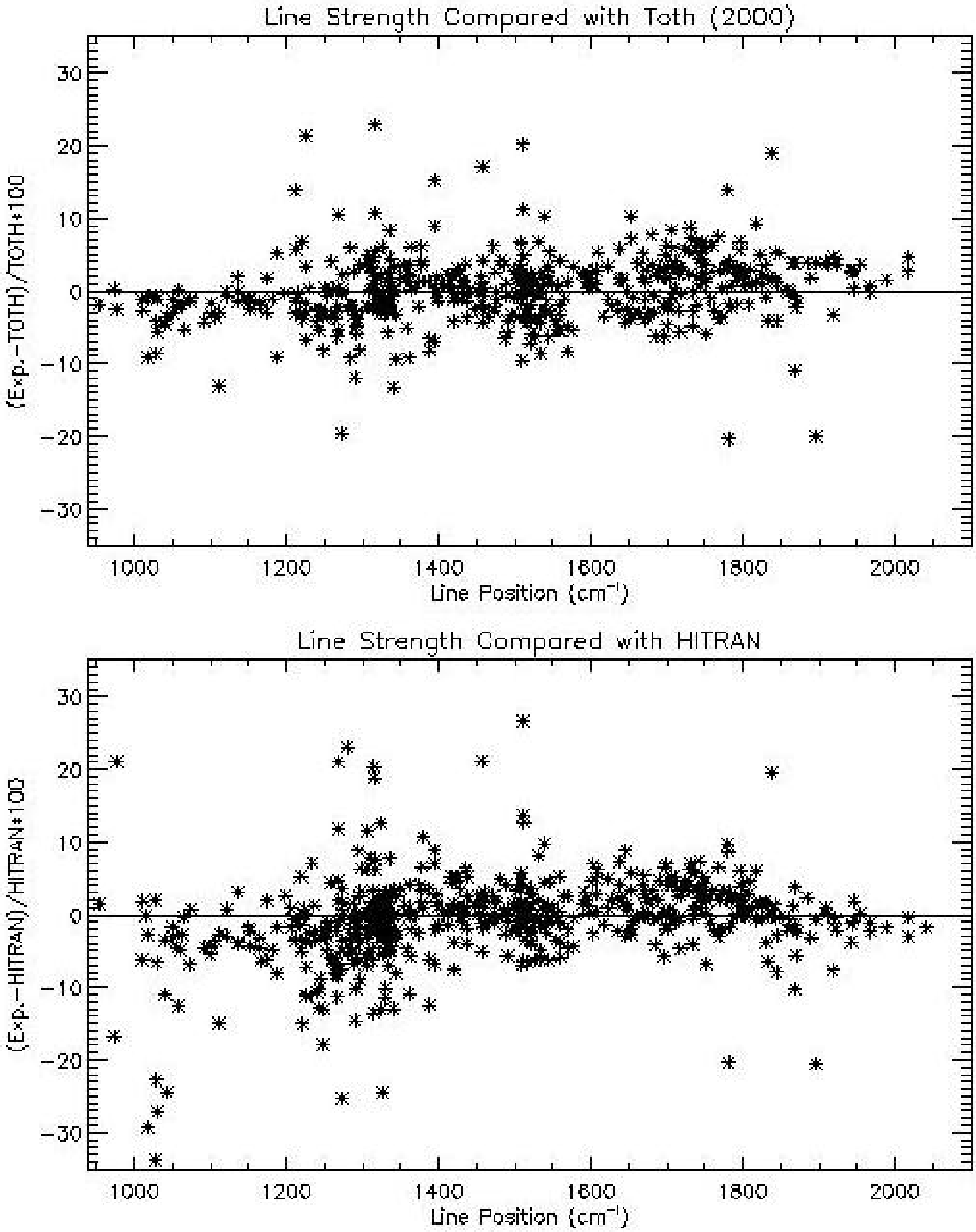
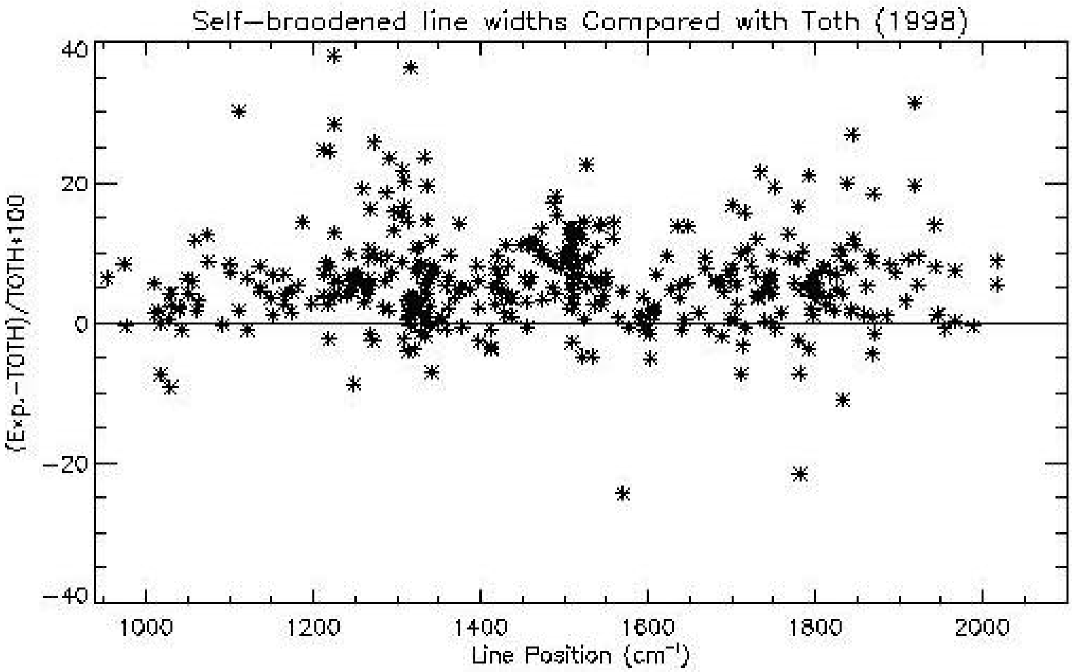

Line Strength Compared with Toth (2000)
(Exp.−TOTH)/TOTH*100
30
20
10
0
−10
−20
−30
1000
1200
1400
1600
1800
2000
Line Position (cm^{-1})
Line Strength Compared with HITRAN
(Exp.−HITRAN)/HITRAN*100
30
20
10
0
−10
−20
−30
1000
1200
1400
1600
1800
2000
Line Position (cm^{-1})

Figure 2.


Self–broadened line widths Compared with Toth (1998)
(Exp.–TOTH)/TOTH*100
Line Position (cm^{-1})

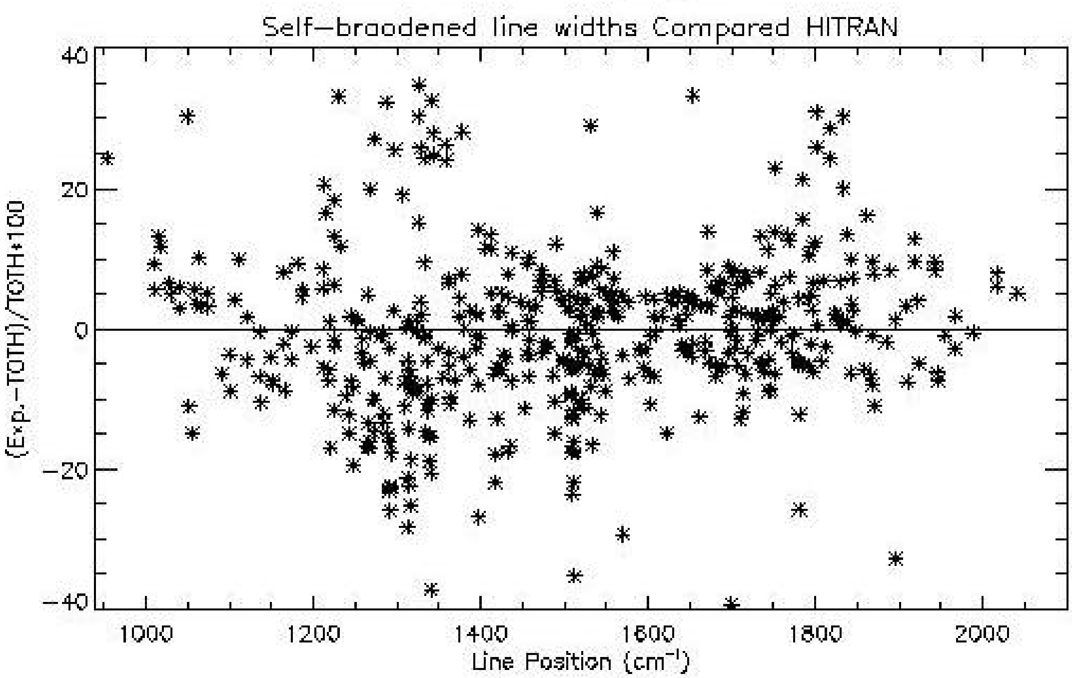

Self–broadened line widths Compared HITRAN
(Exp.–TOTH)/TOTH*100
Line Position (cm^{-1})

Figure 3.

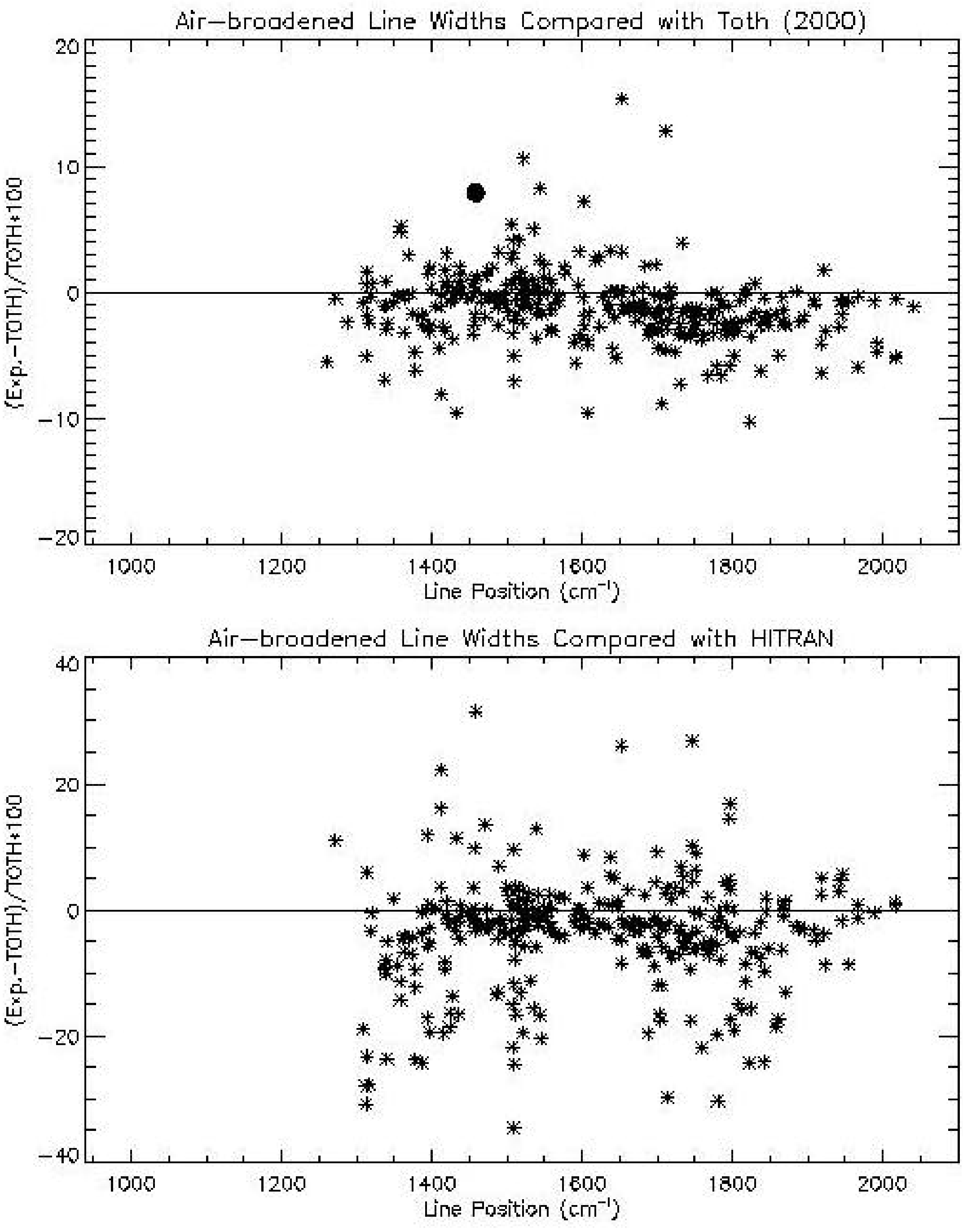

Air—broadened Line Widths Compared with Toth (2000)
(Exp.-TOTH)/TOTH*100
20
10
0
-10
-20
1000
1200
1400
1600
1800
2000
Line Position (cm⁻¹)
Air—broadened Line Widths Compared with HITRAN
(Exp.-TOTH)/TOTH*100
40
20
0
-20
-40
1000
1200
1400
1600
1800
2000
Line Position (cm⁻¹)

Figure 4.

HITRAN. The comparison of the data shown in Figures 2 through 4 is at 296 K. The dependence of the air-broadening coefficient $\tilde{a}^0(T)$ ($cm^{-1}atm^{-1}$) on temperature T is described in terms of the commonly used empirical law:

$$\tilde{a}^0(T) / \tilde{a}^0(T_0) = (T_0 / T)^n .$$

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 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 at 296 K and lower temperatures of atmospheric interest is too large for reproduction here.

The data may be obtained by contacting us via e-mail. Pressure-induced shifts 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. All of the four types of line parameters have been measured the bands in the 2.7 µm region as well and are currently under analysis. The air-induced line-shift data and the 2.7 µm data will be presented at a meeting.

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References

Jacquinet-Husson, N., et al., 1999: The 1997 spectroscopic GEISA databank. *JQSRT*, **62**, 205-254.

Remedios, J. J., 1990: D. Phil Thesis, Oxford University.

Rothman, L. S., et al., 1998: The HITRAN molecular spectroscopic database and HAWKS (HITRAN Atmospheric Workstation): 1996 Edition. *JQSRT*, **60**, 665-710.

Toth, R. A., 1998: Water vapor measurements between 590 and 2582 cm^{-1}; line positions and strengths. *J. Mol. Spectrosc.*, **190**, 379-396.

Toth, R. A., L. R. Brown, and C. Plymate, 1998: Self-broadened and frequency shifts of water vapor lines between 590 and 2400 cm^{-1}. *JQSRT*, **59**, 529-562.

Toth, R. A., 2000: Air- and N_2- broadening parameters of water vapor; 604 to 2271 cm^{-1}. *J. Mol. Spectrosc.*, **201**, 218-243.

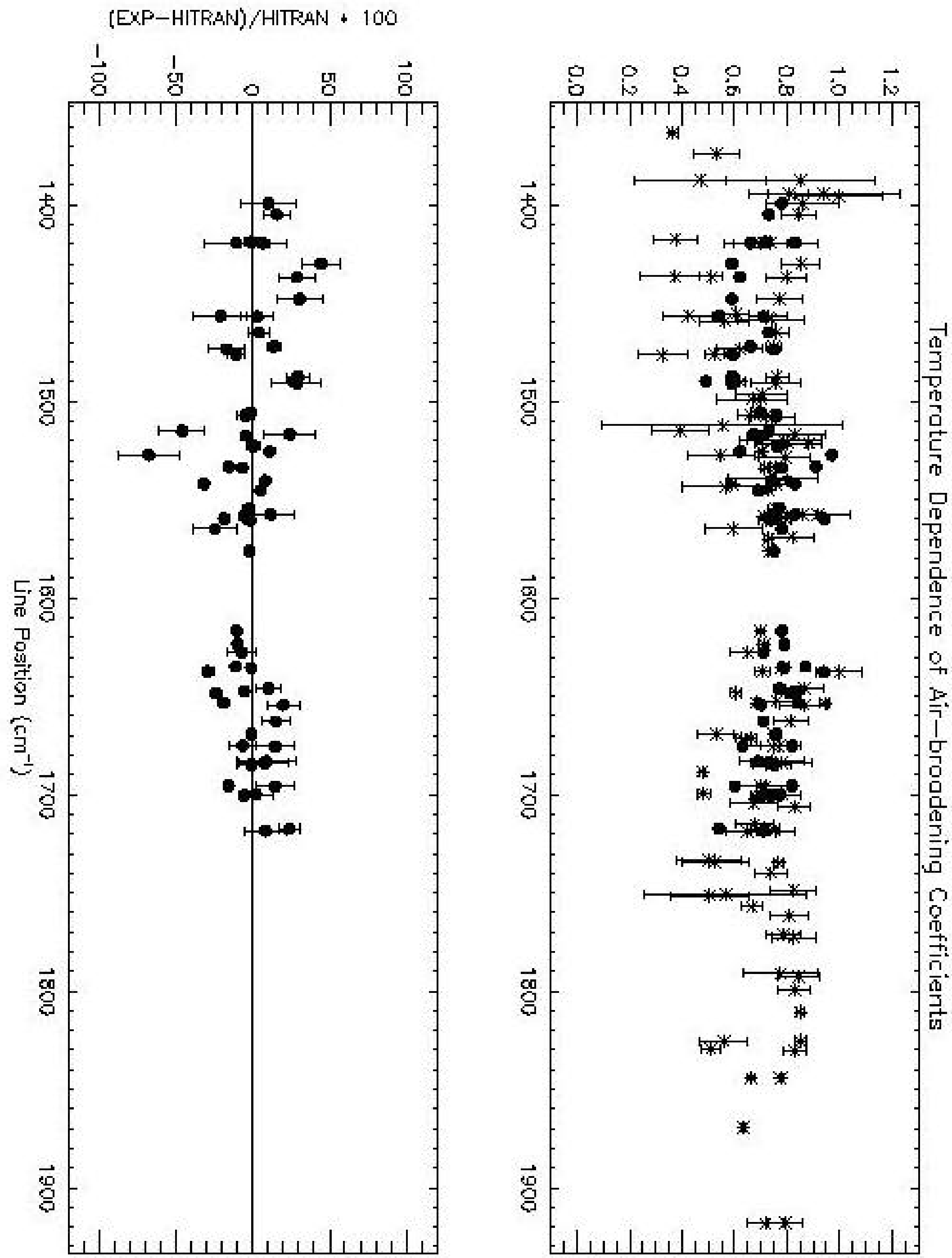
Temperature Dependence of Air–broadening Coefficients
(EXP–HITRAN)/HITRAN * 100
Line Position (cm^{-1})
0.0
0.2
0.4
0.6
0.8
1.0
1.2
-100
-50
0
50
100
1400
1500
1600
1700
1800
1900

Figure 5.