

# Long-Pathlength Infrared Absorption Measurements in the 8- to 14- $\mu\text{m}$ Atmospheric Window: Self-Broadening Coefficient Data

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## Introduction

The accurate characterization of the latent infrared (IR) absorption in the atmospheric window regions continues to be an area of research interest for the global climate modeling community. In the window between 8 and 14  $\mu\text{m}$ , this absorption can be attributed primarily to water vapor. It consists of 1) weak lines originating from the edge of the water vapor pure rotational band (at low wavenumbers) and the trailing P-branch of the  $\nu_2$  rovibrational band (at the high-wavenumber boundary of the window); and 2) the water vapor continuum absorption.

The goal of our project has been to improve our quantitative and physical understanding of both of these absorption processes. Specifically, our immediate aims are to fill gaps in the experimental radiative transfer databases pertaining to the line parameters (i.e., line intensities and broadening coefficients) and to the self- and foreign-broadened water vapor continuum.

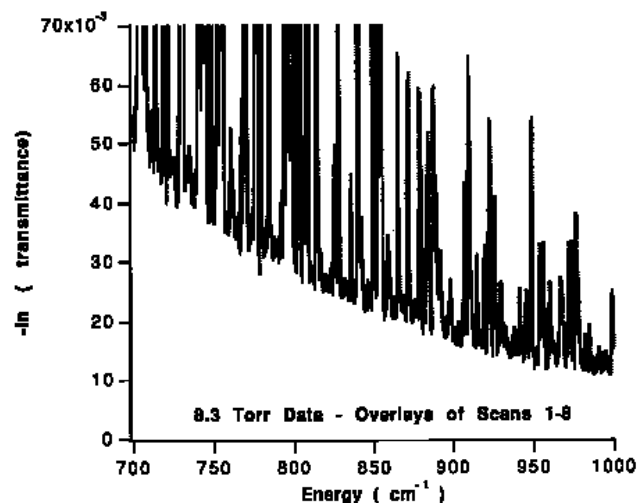
To accomplish our goals, we have made long-pathlength absorption measurements using a Fourier transform infrared spectrometer (FTIR) (for the continuum and line measurements, at low resolution) and a tunable diode laser absorption spectrometer (TDLAS) (for the line measurements, at high resolution). These measurements were made on gas samples contained in a 400-m maximum pathlength Horn Pimentel multipass cell designed and constructed for this project.

## Self-Broadened Continuum Measurements

Between March and September of 1993, efforts were made to improve the accuracy and reproducibility of our measurements of the self-broadened continuum absorption and to make measurements over a broader range of pressures. Run-to-run variability in the past data was found to arise from residual turbulence in the cell that followed the introduction of water vapor samples. This turbulence was corrected by employing a longer settling period before collecting a spectrum. To ensure that conditions were stable, a second spectrum was collected following the completion of the first. Both were ratioed to the same open-cell reference spectrum (collected before the first scan). Comparisons of these scans indicated that the conditions were constant, within experimental uncertainty, over the time period of both scans (about 40 min). Additionally, increased heating of the cell mirrors was used to improve stability by reducing the likelihood of adhesion by water vapor.

Figure 1 contains an overlay of 8 different spectra collected during individual runs and, in some cases, on different days. Each run involves a separate fill of the chamber, and each spectrum represents the average of 100 co-added scans of the FTIR. The standard deviation of the continuum absorption is about 3% in the stronger region of the

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**Figure 1.** Overlaid plots of 8 different window region spectra (plotted between 700 and 1000  $\text{cm}^{-1}$ ) to show representative variance between runs. Each spectrum represents a different run, in which the chamber was refilled with a new water vapor sample. Some spectra were taken on different days. The spectra were collected using a 252-m pathlength, 8.3 torr pure water vapor,  $T=297\text{K}$ .

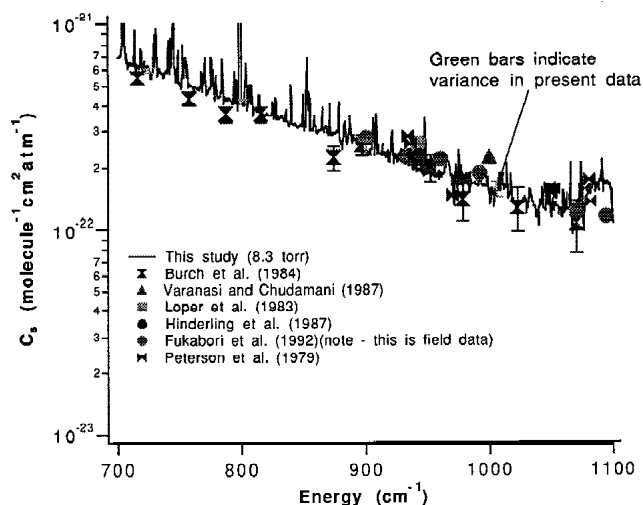
continuum absorption (near 700  $\text{cm}^{-1}$ ) and 8% in the weaker region (near 1000  $\text{cm}^{-1}$ ). This is about a factor of 4 improvement in the variance that was obtained previously.

Spectral scans of the infrared window region were collected between 700 and 1300  $\text{cm}^{-1}$  on pure water vapor samples at room temperature (297K), a 252-m pathlength, and pressures of 3.2, 6.2, and 8.3 torr. These data were processed to generate measurements of the water vapor continuum self-broadening coefficient. This was accomplished by subtracting a calculated lines-only spectrum (generated using the Line-by-Line Radiative Transfer Model [LBLRTM, from AER, Inc, Cambridge, Massachusetts]) from the total absorption spectra and transforming the data according to

$$C_s = -\ln T / (L p^2)$$

where  $T$  is the transmittance,  $L$  is the pathlength, and  $p$  is the water vapor pressure.

Figure 2 contains a plot of the spectrally continuous self-broadening coefficient obtained in this manner for the



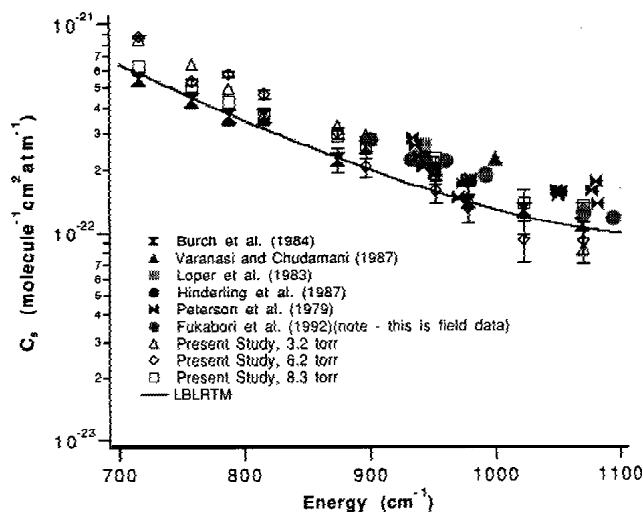
**Figure 2.** Plot of the spectrally continuous self-broadening coefficients obtained from the 8.3 torr data of Figure 1. Also shown are results obtained by past investigators.

8.3 torr measurements. The data represent an average of the runs plotted in Figure 1. The error bars on that graph indicate the variance observed between individual data runs. To our knowledge, there are no spectrally continuous laboratory measurements of the self-broadening coefficients at room temperature reported in the literature.

Also plotted in Figure 2 are previously reported data. The most extensive data set is that by Burch (1982) and Burch and Alt (1984). Figure 2 contains the coefficients reported in the latter report, as they were 15% to 20% lower than those of the previous report, a difference the authors attribute to improved sample handling techniques.

Figure 2 also contains data reported by Loper et al. (1983), Peterson et al. (1979), Hinderling et al. (1987), Varanasi and Chudamani (1987), and Fukabori et al. (1992). The Loper and Hinderling data represent photoacoustic measurements made with a  $\text{CO}_2$  laser, the Peterson data were collected with a  $\text{CO}_2$  laser and a White cell, the data point reported by Varanasi and Chudamani was collected with a grating spectrograph, and the data of Fukabori et al. were derived from field measurements.

Figure 3 contains a plot of the self-broadening coefficients derived from our data at all three of the pressures measured.



**Figure 3.** Plot of the self-broadening coefficients obtained from the 3.2, 6.2, and 8.3 torr water spectra, plotted at the same frequencies used by Burch and Alt (1984). Also shown are results by past investigators and the LBLRTM continuum.

To simplify viewing, the data are plotted only at the frequencies at which data were reported by Burch and Alt. The error bars indicate the variance in the 8.3 torr data. Also plotted are the same past data shown in Figure 2 and the continuum used by LBLRTM.

Comparison of the results in Figures 2 and 3 indicates that, in general, the 1984 data set of Burch and Alt shows somewhat lower attenuation than do the results of past investigators. Our results are within error of the Burch results at energies above 800  $\text{cm}^{-1}$ , but appear consistently higher than those results between 700 and 800  $\text{cm}^{-1}$ , indicating that it may be appropriate to increase the value of the self-broadened continuum there. It is notable that the

spectrally continuous continuum of Figure 2 does not show the “bump” present in the Burch results at  $\sim 897$  and  $953 \text{ cm}^{-1}$ . It is also notable that Burch’s earlier results (1982) agree better with our results in the low wave-number region.

## References

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