Long-Pathlength Infrared Absorption Measurements of Line and Continuum Features in the 8- to 14-μm Atmospheric Window

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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 μm, 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 ν_2 rovibrational band (at the high-wavenumber boundary of the window) and 2) the water vapor continuum absorption.

The goal of our project is to improve our quantitative and physical understanding of both of these absorption processes. Specifically, our immediate aims are to fill in 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. There are many lines that have not been measured in the laboratory. Similarly, there are many conditions of atmospheric importance under which the continuum absorption has not been determined.

To accomplish our goals, we are making 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 are being made on gas samples contained in a 400-m maximum pathlength Horn Pimentel multipass cell that was designed and constructed for this project. Accomplishments of our project in the past year are summarized in the following sections.

Completion of the Experimental Apparatus

The experimental apparatus used to make our measurements consists of the multipass cell and its chamber, the FTIR spectrometer, the TDLAS system, and the necessary data collection apparatus. This equipment was assembled and the chamber was constructed during the first year of our project. The primary thrust of that effort was to design and fabricate the cell and chamber. Special attention was paid to ensuring the mechanical stability of the optics and the ability of the cell to contain stable water vapor samples.

To meet these goals, the chamber was constructed from polished stainless steel and mounted in a way to mechanically isolate it from the cell optics. For a summary of this design, the reader is referred to the last Science Team proceedings (Kulp and Shinn 1992). At the time of that meeting, the chamber construction had not yet been completed. Since then, we accepted delivery of the chamber and installed it in our lab.

Following this, our efforts were directed toward characterizating the stability of the chamber and of the BOMEM MB100 FTIR spectrometer and our TDLAS system. Attention was also paid to developing our sample handling methods, including heating the cell optical surfaces and filling and evacuating the chamber. These efforts extended through March 1992, whereupon our water vapor absorption experiments began.

Water Vapor Absorption Measurements

During the past year, IR absorption measurements were made using both FTIR spectroscopy and tunable diode laser absorption spectroscopy (TDLAS). The FTIR measurements are targeted toward the measurement of both the lines and the continuum, while the TDLAS measurements are made with the goal of determining line parameters only. Although the FTIR measurements provide line intensity information, they are not made at a sufficient resolution to resolve the lines. Thus, the TDLAS data give information about lineshapes and widths. In the following two sections, progress in both these measurements will be discussed.

FTIR Measurements of Lines and Continuum in the 8- to 14-µm Window

The FTIR measurements made during the past year began with the collection of room temperature spectra of pure water vapor absorption. They have provided information about the window region line intensities (albeit at the 1 cm^{-1} resolution of the MB100) and the self-broadened continuum at room temperature. Measurements were made by coupling the modulated beam from sideport of the MB100 into the chamber and directing the exit radiation from the cell through the MB100 sample area and onto its detector using a set of plane mirrors. Data were collected by first recording a reference spectrum with the chamber evacuated and then filling the chamber with the sample and recording a sample transmission spectrum. These spectra were rationed to determine the water absorption spectrum.

At the present time, data have been collected using water vapor samples at several pressures. Figure 1 contains a representative spectrum of the entire window region, obtained at a pressure of 8.1 torr, a temperature of 297 K and a pathlength of 252 m. It represents an average of four runs (i.e., four different fills of the chamber), each being an average of 150 scans. The spectral resolution is 1 cm^{-1}, apodized, using the BOMEM cosine apodization function. Note the line spectra and the underlying continuum. The scan near zero absorbance is a spectrum in which pure nitrogen was introduced at a pressure of 8.1 torr, rather than water vapor. The purpose was to measure the system (cell + spectrometer) drift during the time of a measurement.

Figures 2a-c contain enlargements of three regions of the spectrum in Figure 1, magnified to better show the line spectra. Figures 3a-c show these regions further magnified to feature the continuum. The nitrogen spectrum is also shown in Figures 2 and 3. The nitrogen spectra in Figures 3a-c shows the baseline drift of the system to be less than 10^{-3} absorbance units.

Our data are being compared with calculations generated by the Line-by-Line Radiative Transfer Model (LBLRTM) developed by Atmospheric and Environmental Research (AER, Cambridge, Massachusetts). These comparisons are being done in collaboration with Tony Clough of AER. Examples of these calculations are also plotted in Figures 2a-c and 3a-c. The spectrum was calculated by AER assuming a homogeneous horizontal path containing only water vapor under the conditions of our measurement. The line-by-line calculations were convolved with an instrumental response function (assuming the BOMEM cosine apodization) to generate the experimental spectrum.

Using LBLRTM and our data, we were able to generate an empirical self-broadened continuum. This was accomplished by using LBLRTM to calculate the window region lines-only contribution (assuming line wings out to 20 cm^{-1} from line center) and subtracting this from our measured window region spectrum. This is plotted in Figure 4. Also plotted there is the LBLRTM continuum and an empirical self-broadened continuum calculated using the self-broadening coefficients measured by Burch et al. (1981a,b) and Burch and Alt (1984). The Burch values represent an empirical fit to ten data points within the range covered by that curve.

In general, the comparison of calculations and measurements indicate that errors remain in the HITRAN 92 line parameter database We have also compared AERI - LBLRTM simulation residuals (obtained from Tony Clough) with our residual from LBLRTM and were able to correlate line errors in both sets of measurements. This further substantiates the need to correct these lines. The fit to the continuum is fairly good and tends to support the Burch measurements (over other past measurements that differed from his). It should be noted, however, that our data should be considered preliminary at this time and that we are in the process of testing its accuracy. That accomplished, we will move on to the measurement of the foreign-broadened continuum and to measurements at lower temperatures.

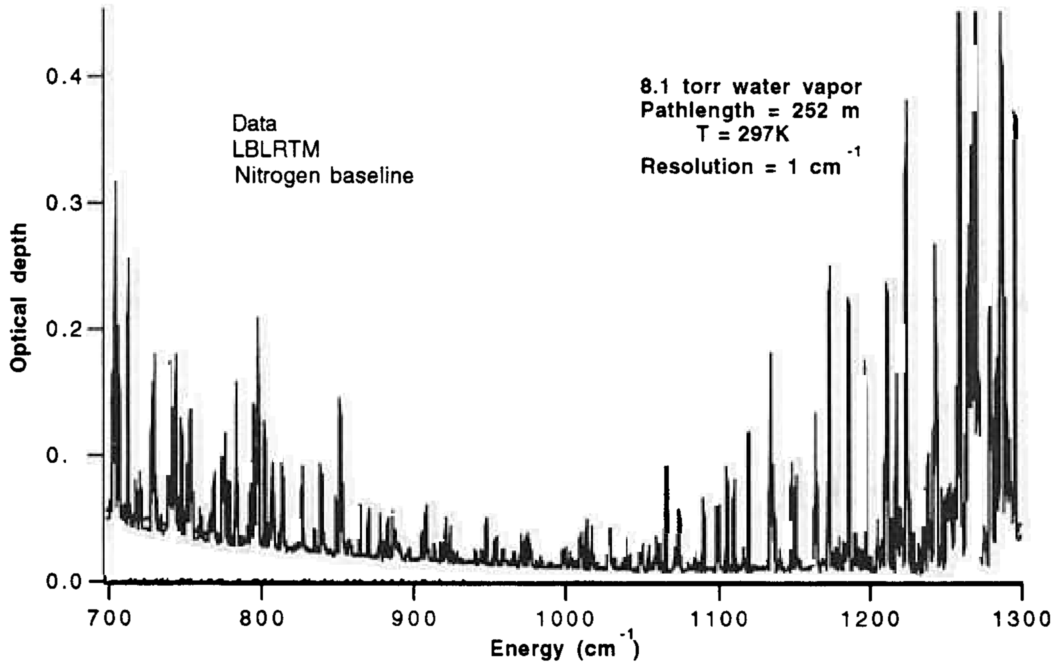

Figure 1. Water vapor spectrum of the window region obtained under conditions indicated, showing entire region between 700 and 1300 cm^{-1} at lowest magnification.

Water Vapor Line Absorption Measurements

TDLAS absorption measurements of a number of weak lines were carried out between March and August of 1992. Table 1 lists the lines of which spectra have been taken and the conditions under which the measurements were made. Spectra of each line were made under a number of nitrogen pressures to determine their nitrogen-broadening coefficients. As with the self-broadened continuum data, we are now preparing a publication on the line data acquired to date. TDLAS line measurements will continue for the remainder of this fiscal year. In the proposed continuation of our work, we hope to accelerate our line measurements using a high resolution FTIR (BOMEM DA8) that will be made available to us and used in concert with the TDLAS system.

Future Work

In our future work, we will continue our line and continuum measurements to expand our understanding of the window region absorption to other atmospheric conditions. In particular, we will begin the foreign-broadened continuum measurements and will also begin lower temperature measurements. Initially, we will use our existing FTIR and TDLAS instruments.

We are also, however, proposing to improve our capabilities in two ways: 1) using a high resolution FTIR (BOMEM DA8) that will be made available to accelerate our line measurements and 2) incorporating a cavity-ringdown spectrometer (CRS) into our apparatus. CRS is a highly sensitive laser-based method (O'Keefe and Deacon 1988; Ramponi et al. 1988) that can measure absorption in relatively small cells with an effective total pathlength of up to 6 km. We propose to use CRS to improve the sensitivity and precision of our continuum measurements, particularly at low temperatures.

Both new approaches will be implemented in our existing chamber in such a way that they can operate simultaneously with the existing approaches. This will allow validation of the new methods against the current ones.

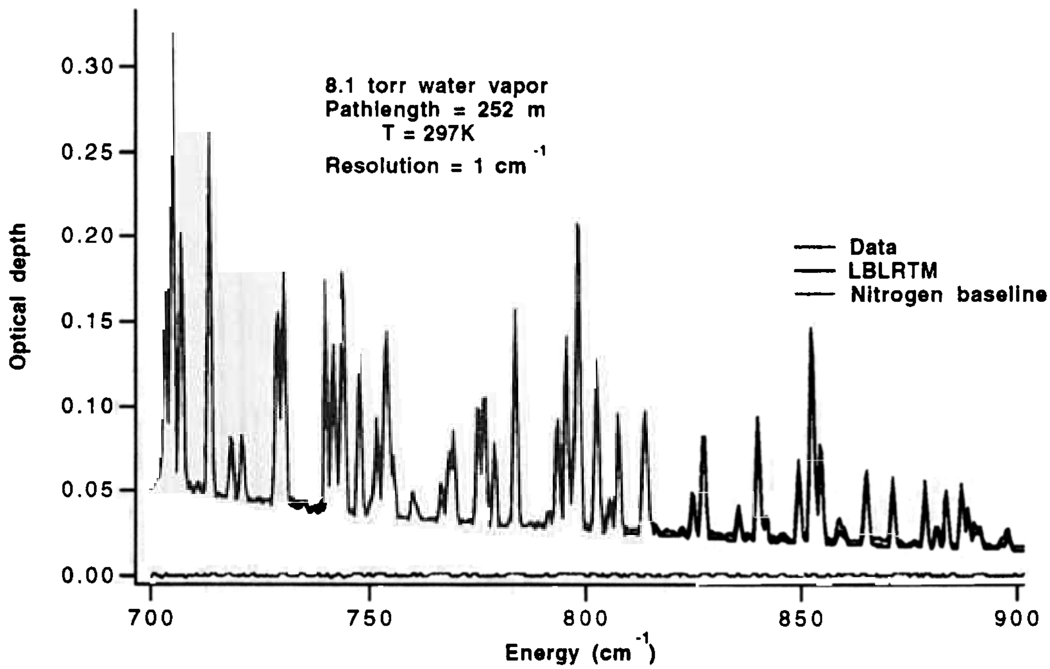

Figure 2a. Portion of the spectrum between 700 and 900 cm^{-1}.

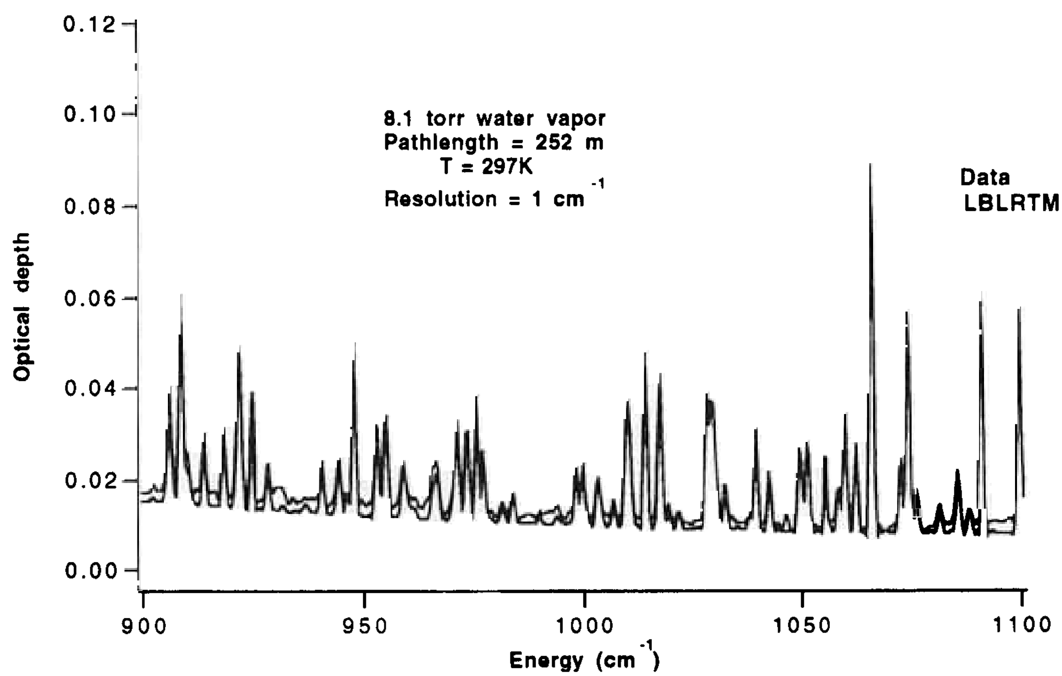

Figure 2b. Portion of the spectrum between 900 and 1100 cm^{-1}

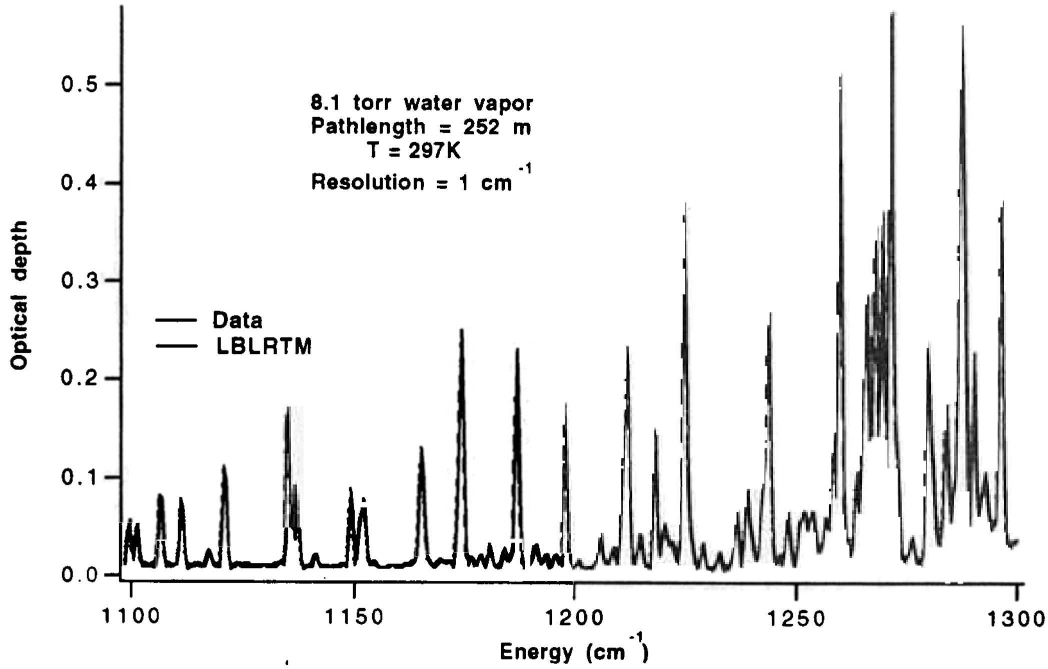

Figure 2c. Portion of the spectrum between 1100 and 1300 cm^{-1}.

Figure 2. Water vapor spectrum of Figure 1 magnified to show lines. The spectrum is overlaid with the LBLRTM simulation run for the experimental conditions.

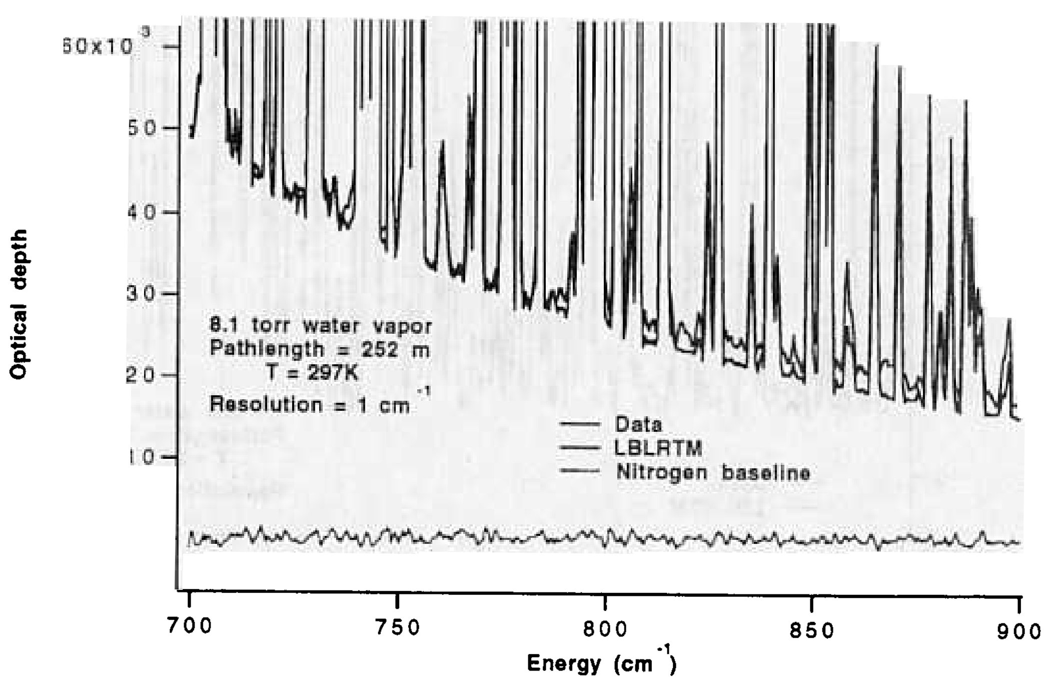

Figure 3a. Portion of the spectrum between 700 and 900 cm^{-1}.

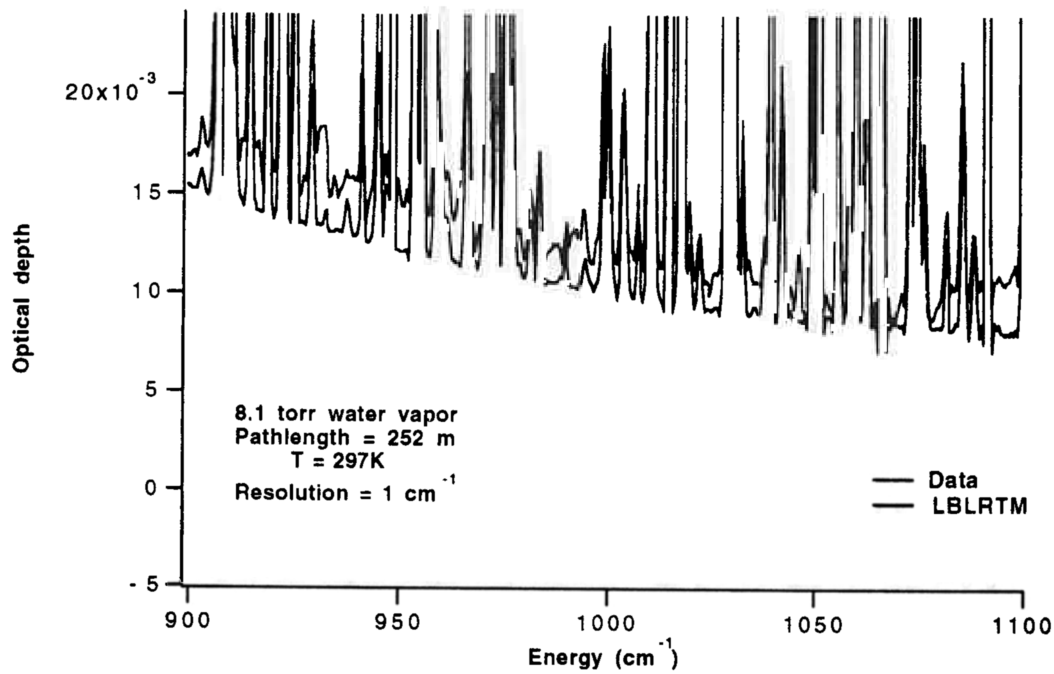

Figure 3b. Portion of the spectrum between 900 and 1100 cm^{-1}.

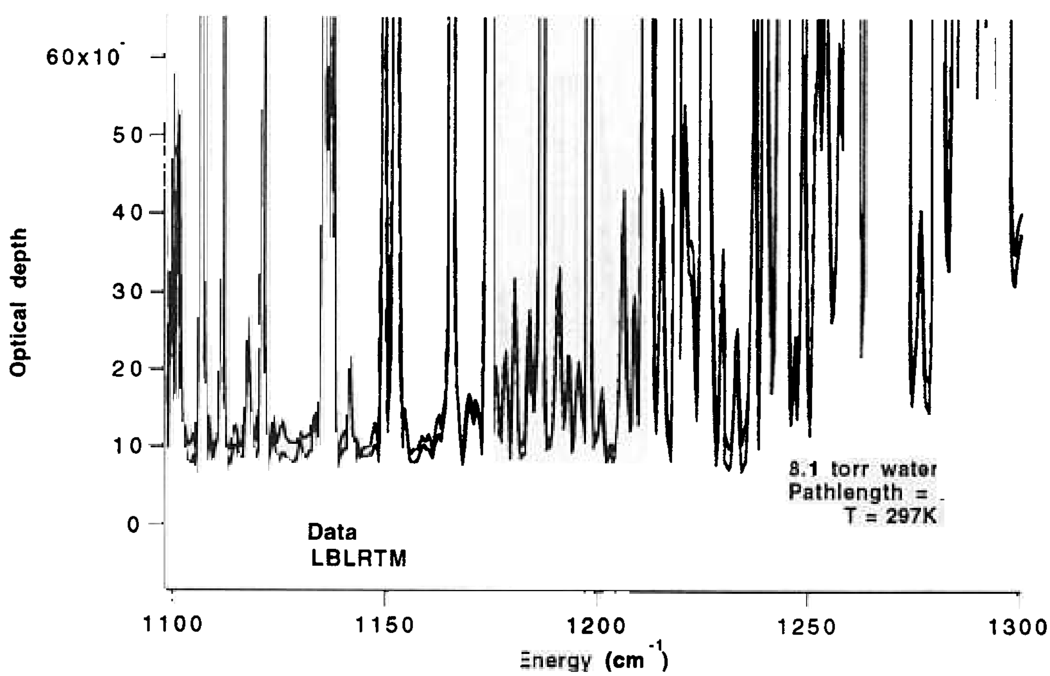

Figure 3c. Portion of the spectrum between 1100 and 1300 cm^{-1}.

Figure 3. Water vapor spectrum of Figure 1 at highest magnification to show continuum. The spectrum is overlaid with the LBLRTM simulation run for the experimental conditions.

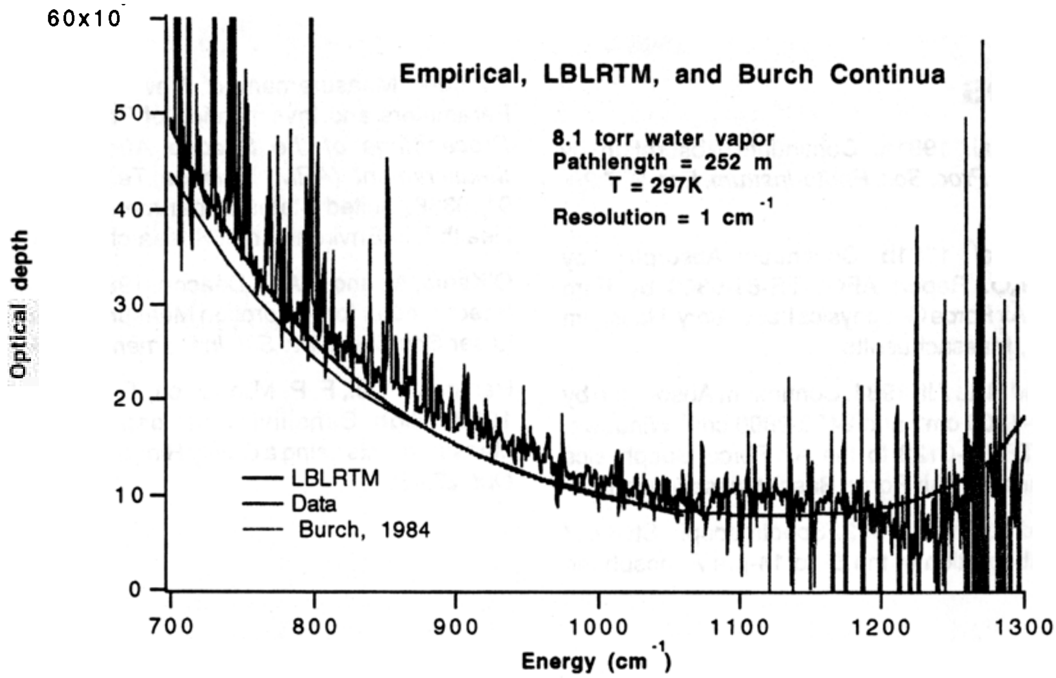

Figure 4. Plot of the empirical continuum derived from the data in Figure 1. Also overlaid on this is the LBLRTM continuum and the continuum derived for these conditions from the data of Burch and Alt (1984).

Table 1. Listing of lines measured during the existing ARM project and the conditions of the measurements.

Energy (cm^{-1})	L (m)	p (N_2, torr)	p (H_2O, torr)	N
922.142	180	0-300	1.20-6.00	8
948.260	108	0-293	2.17-11.07	9
1000.2910	252	0-40	1.49-6.96	8
1003.5673	252	0-90	3.10-7.22	9
1003.6887	252	0-90	3.10-7.22	9
1007.2390	252	0-70	2.04-8.01	11
1010.8132	252	0-400	2.95-6.96	11
1011.6211	252	0-60	1.95-6.11	6
1011.6418	252	0-60	1.95-6.11	6
1014.4751	252	0-400	0.93-4.95	9
1019.6611	252	0-70	1.56-6.99	11
1028.2706	180	0	0.91-7.56	5
1028.3125	180	0	0.91-7.56	5
1028.6842	180	0-200	2.97-9.04	8
1029.4977	180	0-200	1.45-5.17	12
1029.6974	180	0-200	1.45-7.44	14
1032.6844	180	0-80	1.39-9.00	12

L = pathlength; p = pressure; N = number of measurements

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