Measurement of the Absorption Characteristics of Water Vapor Near Saturation

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Introduction

New results from our measurement program to determine the absorption coefficients of water vapor (WV) in the near-IR (800 - 960 nm) wavelength region over a wide range of temperatures and super saturations (Varanasi and Prasad 1999) are presented. For providing a steady-state distribution of supersaturated WV, a special diffusion cell has been built and serves as the absorption cell for our experiments. A widely tunable narrow-line pulsed laser is used to generate a photo-acoustic absorption signal inside the cell, from which high-sensitivity WV absorption coefficient measurements are made. A microphone incorporated into the diffusion cell permits the measurement of photo-acoustic absorption signal. Earlier we had characterized the performance of the diffusion cell for producing supersaturated WV and also carried out preliminary measurements of near-IR (at ~ 816 nm) absorption coefficients in supersaturated WV (Varanasi et al. 2000). We have extended the absorption measurements further to cover a wider region: 815 - 820 nm and 940 - 950 nm. These experiments indicate the increase in absorption to be linear with increasing concentration of WV, and no anomalous changes in absorption have been observed. The minimum detectable signal for our experimental system was determined to estimate the sensitivity of the experimental setup to detect changes in absorption. In this paper, we describe the results of experiments and the calculation of the system sensitivity. We have also indicated steps to be taken to further increase the sensitivity of the measurement.

Experimental System

Figure 1 shows the setup of the experimental system. The diffusion cell used in our experiments consisted of a well insulated, sealed rectangular perspex enclosure (10.75 in. × 4 in. × 2 in.). The top and bottom plates of the enclosure were made of copper and their temperatures were maintained constant to better than 0.1° by circulating water from two high-precision water baths. A stable, convection-free, steady-state diffusion of WV is set up by filling the cell with helium, and evaporating WV from a saturated warm surface (bottom), and condensing it on a cold surface (top). Two rectangular (1 in. × 3 in.) antireflection-coated BK7 windows allowed the laser beam to be positioned at any

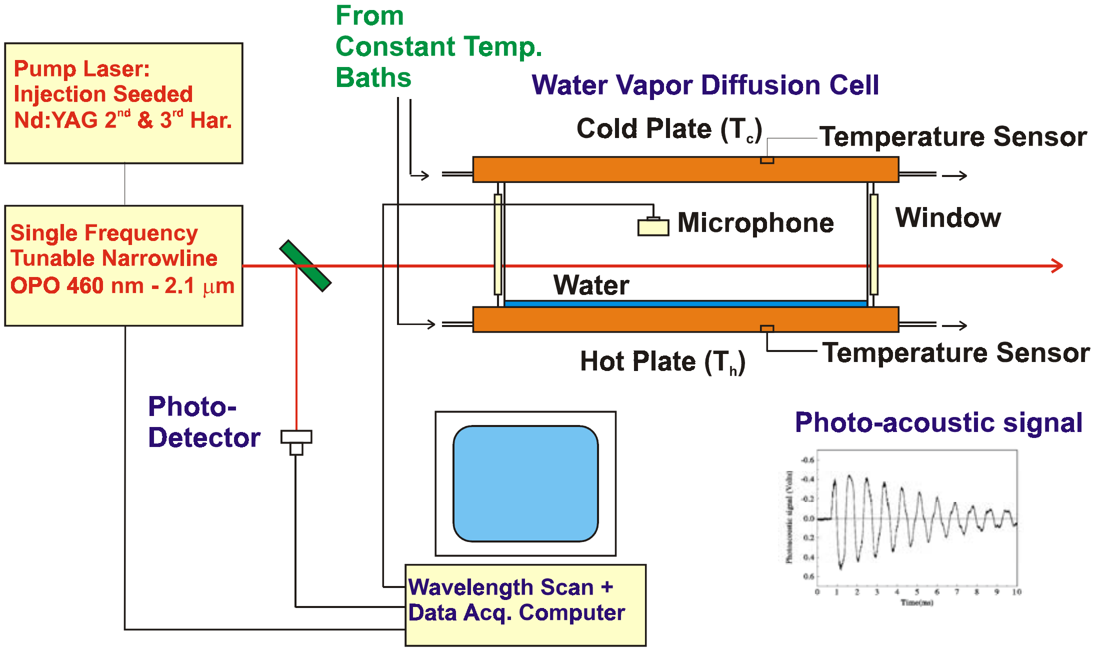

Figure 1. Schematic of the experimental setup. Steady-state distribution of supersaturated WV is produced in the diffusion cell containing a mixture of WV and helium.

height across the diffusion cell. An electret-type microphone (Radio Shack Model 270) was placed inside the cell for measuring the photo-acoustic signal. Both the microphone and the windows were heated to prevent condensation.

A broadly tunable (460 - 2.1 µm) narrowband (0.02 cm^{-1}) single longitudinal mode (SLM) laser (Continuum Mirage 500 OPO pumped by a Continuum Powerlite Nd:YAG laser) source was used to generate photo-acoustic absorption signals in the diffusion cell. Its pulse repetition rate was 10 Hz, and its output energy was ~ 10 mJ in most of our experiments. The laser beam was aligned horizontally through the middle of the diffusion cell, and its wavelength was tuned across the absorption lines with a step size of ~1 pm.

The photo-acoustic signal generated by the absorption of the laser beam by the WV is coupled into a large number of standing wave modes within the enclosure. We computed the resonant mode frequencies and chose the 2 - 15-kHz region for our measurements because most of the absorbed energy is contained in these modes. A band pass filter (2 - 15 kHz) and amplifier (Krohn-Hite Model 3886) with a voltage gain of 74 dB was used to condition the signal from the microphone, which was then digitized with a 12-bit ADC card with a 100 kS/s sampling rate and acquired on a personal computer.

Supersaturation S is defined as the ratio of actual partial pressure to the saturation pressure of the WV at the local temperature. In the absence of external nuclei (such as dust, ions, etc.), condensation of water requires homogeneous nucleation, which occurs readily when the supersaturation S reaches ~ 1.4. Thus, values of S up to 1.4 can be created before drop-wise condensation of water sets in. The value of S at the beam height depends on the difference of the two plate temperatures. However, since direct measurement of temperature profile in the cell by sensors (e.g., thermistors) becomes erroneous at high supersaturation because of the condensation that can occur at the surface of the sensor, the temperature profile is found by calculation. The profiles of temperature and supersaturation across the cell were determined by solving the heat conduction and mass diffusion (nonlinear) differential equations simultaneously. The accuracy of the calculated temperature profile was verified by comparing with direct temperature measurements in the cell at several low levels of supersaturation ($S < 1.15$). The calculated temperature profiles were found to agree very closely with the measurements.

A number of absorption measurements were performed wherein the cell was kept isothermal by keeping the top and bottom plate temperature the same but varying its value so as to vary the concentration of WV. Figure 2 shows the photo-acoustic absorption signals for saturated WV in the isothermal cell, as the laser is tuned across the 816.37-nm absorption line. A linear relation was obtained for the measured absorption signal against the calculated absorption of WV whose concentration corresponds to the local temperature. These experiments have served to establish the linearity of photo-acoustic signals with the absorbed energy. To maintain the same photo-acoustic environment for all the experiments, the laser beam height was kept fixed to approximately the middle of the cell. Any desired value of supersaturation was created at the beam location by calculating and setting the top and bottom plate temperatures, which gave a local temperature of 25°C at the beam height, while providing the required value of S (between 1.1 and 1.4).

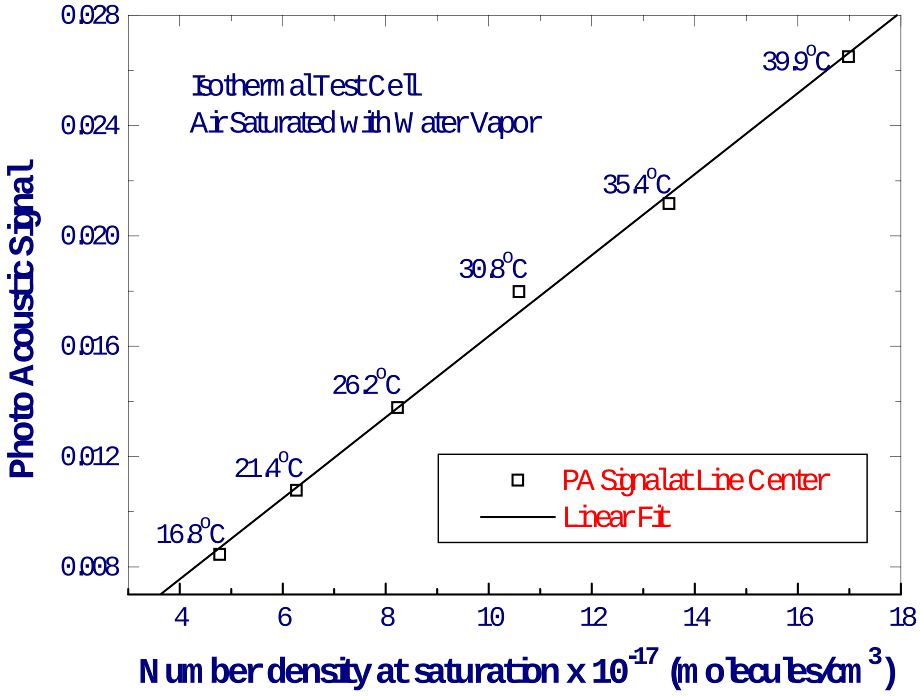

Figure 2. Linearity of photo-acoustic signal with absorption by WV demonstrated by measurements with saturated WV at several temperatures.

Photo-Acoustic Supersaturated WV Absorption Measurements

Water vapor absorption in the 815 - 820-nm and 940 - 950-nm regions were measured by monitoring the photo-acoustic signals as the laser was tuned across several individual lines. Figures 3 and 4 show the absorption line scans. Also shown in the figures are the calculated absorption spectra using the HITRAN listing for saturated WV at 296K at 1 atm pressure and foreign gas broadening by air. In our calculations, we have ignored absorption lines whose cross sections are less than 3 x 10^{-24} cm^2/ molecule. It is seen that the measured absorption spectrum matches very well with the calculated spectrum for the 815 - 820-nm region. In the 940 - 950-nm region, the agreement is very good except for the strongest lines. This is expected to have been caused by the signal saturation at the high signal levels. We are currently modifying the system to allow gain levels to be changed for the signal-conditioning amplifiers.

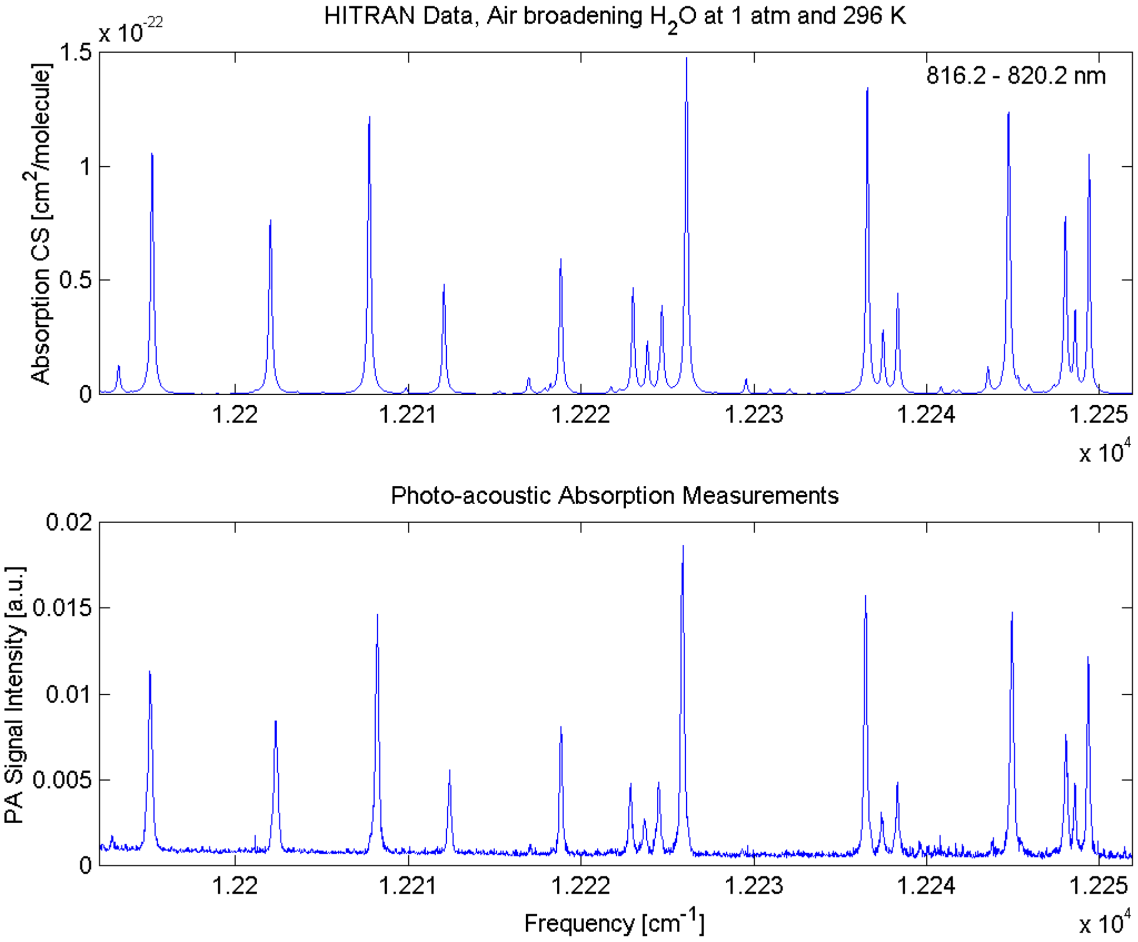

Figure 3. Scan of WV absorption lines in the 815 - 820-nm region. Comparison with calculated HITRAN data shows good agreement. Note that lines with absorption cross sections > 3 x 10^{-24} cm^2/molecule are measured by the photo-acoustic experiment.

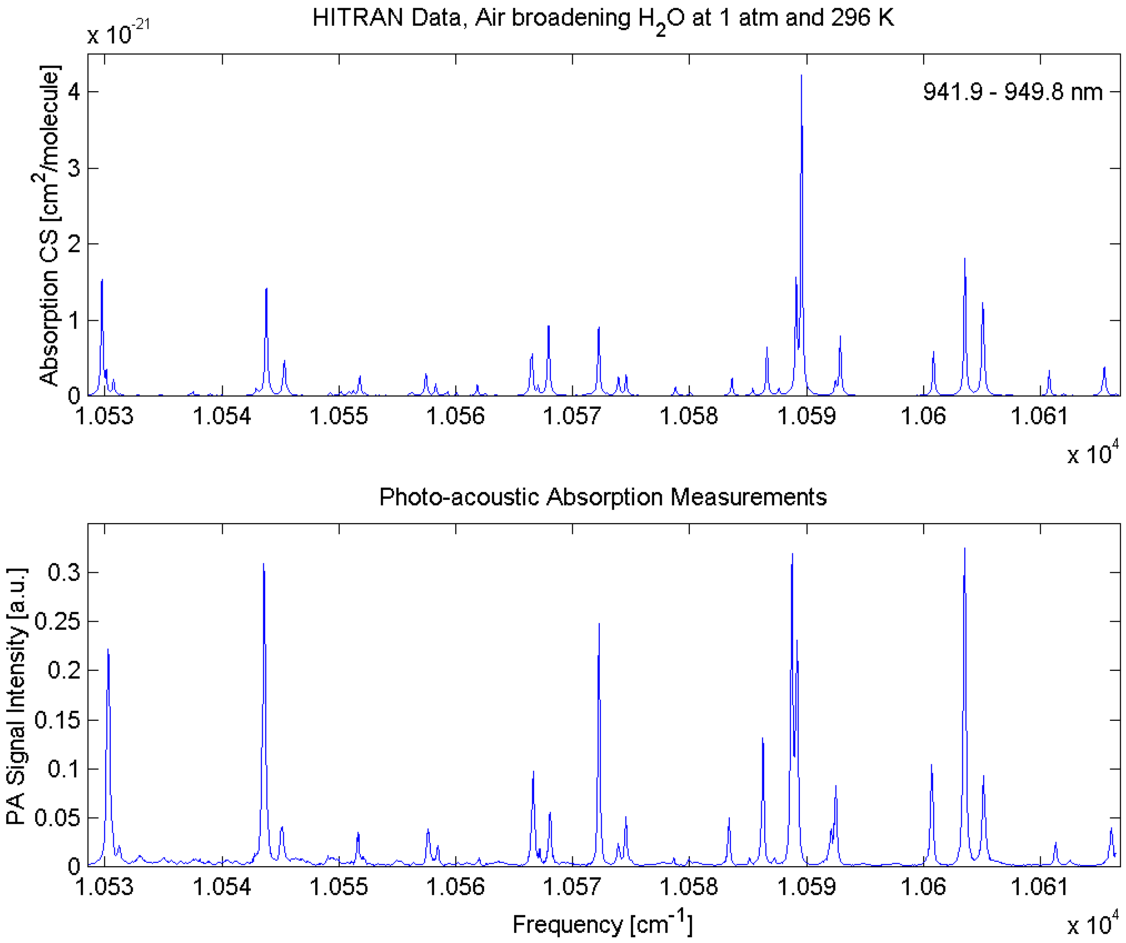

Figure 4. Scan of WV absorption lines in the 940 - 950-nm region, where the absorption cross sections are larger. Comparison with calculated HITRAN data shows good agreement. Absorption cross sections > 3×10^{-24} cm^2/molecule are measured by the photo-acoustic experiment. Onset of signal saturation has caused the strongest lines to be clipped.

Figure 5 shows the effect of variation of S on WV absorption for the supersaturated WV with helium buffer gas. The temperature at the height of the beam was maintained at 25°C for all cases. Figure 6 shows a linear increase of photo-acoustic signal with S for values up to 1.2, when the concentration of vapor is 1.2 times that for saturated vapor. For S > 1.2 the signal is seen to begin to drop off. This decrease is caused by several phenomena that become important: condensation on surfaces, and also the depletion of WV monomer molecules because of the formation of polymers and aggregates in the course of homogeneous nucleation.

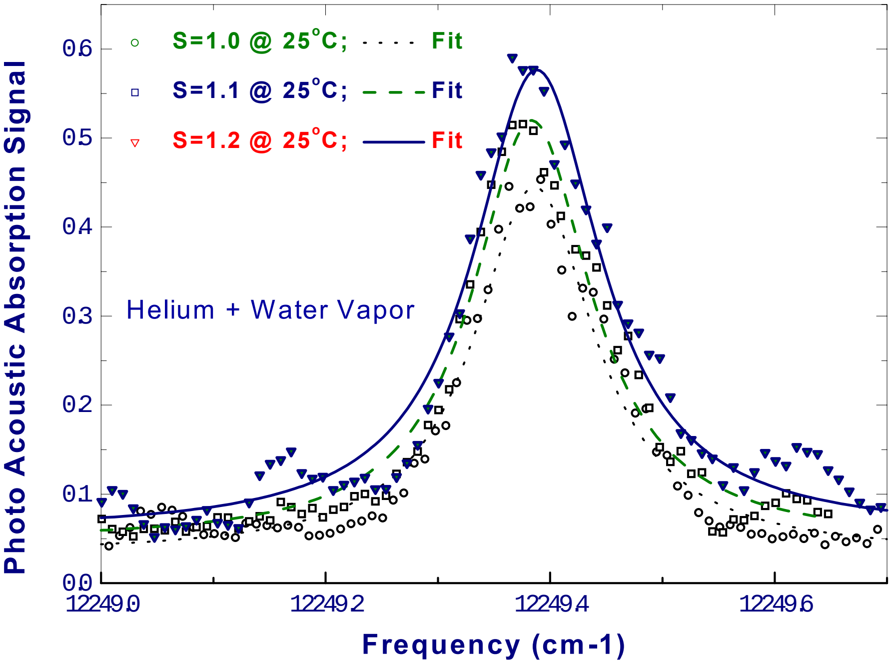

Figure 5. Absorption measurements of supersaturated WV line at 816.37 nm, and 25°C local temperature.

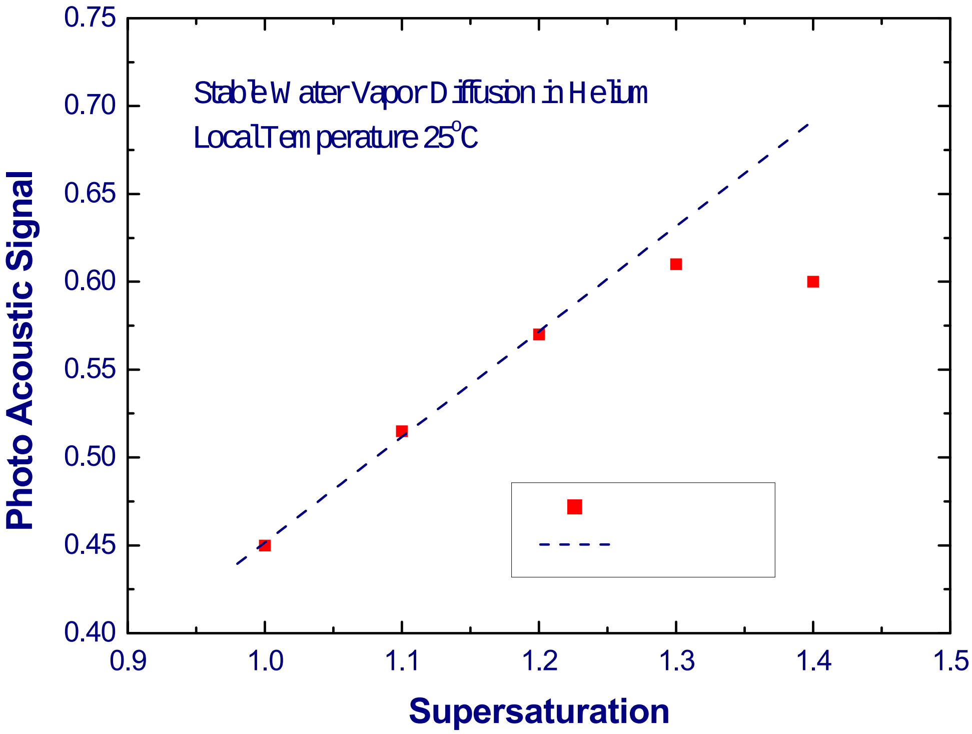

Figure 6. Increase in absorption (for WV line at 816.37 nm) is linear for S up to 1.2. For S > 1.2 the signal drops off due to condensation.

Results and Discussion

The sensitivity and accuracy achievable with our experimental system have been estimated to establish the limits of measurement. From a determination of the noise in our detection system, the signal-to-noise ratio (SNR) was found. For the strongest lines in the 815 - 820-nm region, the SNR was about 140, and is about 20 times larger for the 940 - 950-nm region. The smallest measurable line absorption cross section corresponds to 3×10^{-24} cm^2/molecule. Alternatively, the smallest measurable change in concentration is about 1 percent for the strong lines in the 815 - 820-nm region. In the 940 - 950-nm region, where the absorption cross sections are much larger, the performance is much improved. The signal is saturated for the strong lines in the 940-nm region, and the smallest measurable change in concentration is about 0.1 percent.

Measurements on several strong absorption lines in the 815 - 820-nm region were done and the behavior in all cases was similar; i.e., a linear increase in signal with S up to 1.2 and a deviation from linear behavior with $S > 1.2$. Further, anomalous absorption behavior was not observed either in the case of the weaker lines or in the troughs between lines within the limits of our experimental accuracy. We have currently started to modify the laser for stable SLM operation in the 940-nm region and to improve our experimental system's SNR. A systematic study of absorption lines and regions in between lines will be undertaken in the 940 - 950-nm region.

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