Measurement of the Absorption Characteristics of Water Vapor Near Saturation

P. Varanasi
State University of New York at Stony Brook
Stony Brook, New York

B. Ranganayakamma, S. Mathur, T. Refaat, and C. R. Prasad
Science & Engineering Services, Inc.
Burtonsville, Maryland

Introduction

We report the results of our measurements of the absorption coefficients of water vapor in the near-infrared (IR) (800 nm to 960 nm wavelength range) over a wide range of temperatures and levels of saturation (Varanasi and Prasad 1998). By saturation, we mean here the saturation level of the vapor over the liquid phase as against the saturation of the absorption by spectral lines. A special diffusion cell, within which any super-saturated water vapor distribution can be maintained at a steady state, has been built and serves as the absorption cell for our experiments. For high-sensitivity absorption-coefficient measurements, a novel photo-acoustic sensor has been incorporated into the diffusion cell. Experiments were performed to characterize both the diffusion cell and the photo-acoustic spectrometer, and, subsequently, to measure the spectral absorption by super-saturated water vapor. In this paper, a brief description of the analytical procedure for predicting the super-saturated state of water vapor inside the diffusion cell is given, followed by the results of the experiments characterizing the diffusion cell and the photo-acoustic sensor. Also given are the results of our initial set of measurements of near-IR (at ~ 816 nm) absorption coefficients of supersaturated water vapor.

Distribution of Temperature and Pressure in the Diffusion Cell

A parallel-planar thermal diffusion cell, consisting of a sealed rectangular enclosure (10.75 in. x 4 in. x 2 in.) whose top and bottom surfaces are maintained at precisely regulated temperatures, is used to create the super-saturated states of water vapor. Steady-state diffusion of water vapor through a carrier gas is set up inside the diffusion cell by evaporating water vapor from a saturated warm surface (bottom plate), and condensing it on a cold surface (top plate). A stable convection-free diffusion is achieved by using helium as the buffer gas. The profiles of temperature, partial pressure, super-saturation, and density across the cell from the hot to cold plates can be determined by solving the non-linear differential equations governing heat conduction and mass diffusion simultaneously. The equations are greatly simplified by assuming one-dimensional (1-D) transport, a stagnant buffer gas, the absence of external forces and pressure gradients (Katz et al. 1967), and the vapor to behave as an ideal gas.

The profiles of the partial pressure of the vapor and its temperature in the diffusion cell were obtained by means of an iterative procedure that uses successive relaxation of the 1-D non-linear differential equations for heat conduction and mass diffusion to linear difference equations. The solutions are required to satisfy the boundary conditions which are the temperature T_0 of the vapor on the bottom plate of the cell, the partial pressure of the vapor is equal to equilibrium saturated vapor pressure at T_0; and similarly, the temperature T_1 of the top plate and the equilibrium partial pressure corresponding to T_1. The level of super-saturation is then calculated by taking the ratio of the actual partial pressure to the saturation vapor pressure of water at the temperature at the same location in the cell.

The method of solution consists of defining first a non-dimensional height as the ratio of the actual height to the height of the diffusion cell, and then dividing this *reduced height* interval, extending from 0 to 1, into N equal increments and computing the solution at each of the mesh points using a scheme of iterative linearization of the differential equations (Katz et al. 1975). Initial guesses for the pressure and temperature profiles are obtained by assuming them to be linear functions of *reduced height,* which satisfy the boundary conditions. Improved estimates are obtained at each iteration by solving a set of linearized differential equations, which makes use of the previous estimates and replaces the derivatives with finite differences. Usually 3 to 4 iterations have been found to be sufficient. The calculated distributions of temperature and level of super-saturation are shown in Figures 1 and 2.

Experimental Setup

A broadly tunable (400 nm to 2.1 μm) narrow-band (0.02 cm^{-1}) laser source was used to generate the photo-acoustic absorption signal in the diffusion cell. The top and bottom surfaces of the diffusion cell are made of chromium-plated copper plates whose temperatures were maintained constant to better than 0.1° by circulating water from two high precision water baths (Neslab Model RTE111). The body of the

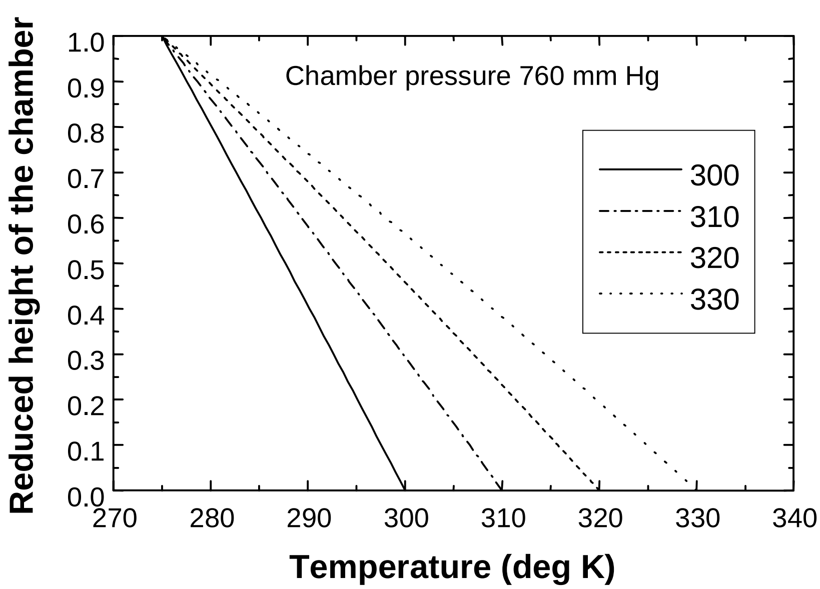

Figure 1. Calculated temperature distributions in a diffusion cell containing a mixture of water vapor and helium, when stable diffusion is established. Top plate temperature = 275 K.

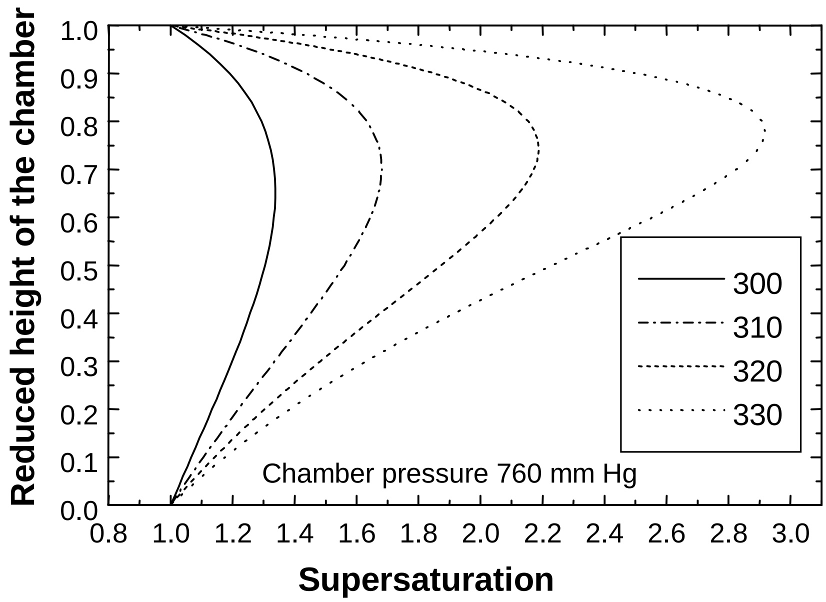

Figure 2. Calculated water vapor super-saturation profiles for stable diffusion within helium-filled diffusion cell. S > 1.4 will not be sustained after the onset of homogeneous nucleation.

cell was made of 1-in. thick Perspex, to provide a non-conducting enclosure. Further insulation was provided all around the cell except for openings for the laser beam input and exit. Two rectangular (1 in. x 3 in.) anti-reflection-coated BK7 windows allowed the laser beam to be positioned at any height across the diffusion cell. An electret condenser microphone supplied by Radio Shack was placed inside the cell for measuring the photo-acoustic signal. Both the microphone and the windows were heated to approximately 40°C to prevent condensation. Heating the microphone keeps its gain constant when the temperature inside the cell is varied. The microphone output was band-pass filtered, amplified and rectified before its digitization using a 12-bit digitizer.

Super-saturated Water Vapor in the Diffusion Cell

The thermal characteristics of the diffusion cell were monitored using five highly accurate ($\delta T < 0.1°C$) thermistors placed inside at fixed locations along a vertical line between the bottom and the top plates. In addition, thermistors were also placed on the plates to monitor their temperatures. In the first set of experiments, the cell was filled first with dry air and then sealed. By measuring the air temperatures with the thermistors, the temperature profiles and convectional stability of the cell were monitored. More insulation was added around the cell until nearly perfect 1-D operation of the cell was achieved. In the second set of experiments, saturated and uniform distribution of water vapor was created by adding water (about 20 ml) to the cell, and making the cell isothermal by maintaining at the same temperature. The thermistor's readings were monitored to ensure a steady state within the cell.

In the absence of external nuclei (such as dust), condensation of water requires homogeneous nucleation, which sets in only when the level S of super-saturation exceeds ~ 1.4. Thus, values of S up to 1.4 can be created, by setting up a steady diffusion of water vapor across the cell by heating the bottom plate and cooling the top plate. Since this leads to a thermally unstable state, helium is added as the buffer gas instead of air to prevent convection. In our experiments, the air in the cell was replaced by helium with a vacuum pump and a gas manifold. The value of S at the beam height depends on the difference of the two plate temperatures, as shown in Figure 2. However, the measurement of temperature by thermistors becomes difficult when the level of super-saturation exceeds a value ~ 1.2, because of condensation that can occur at the surfaces and can cause erroneous readings. Hence, the thermistors were removed from the cell, after using them to determine the temperature profiles in the low super-saturated state to ensure that the cell was thermally stable and its performance corresponded to the predicted levels (Figure 3).

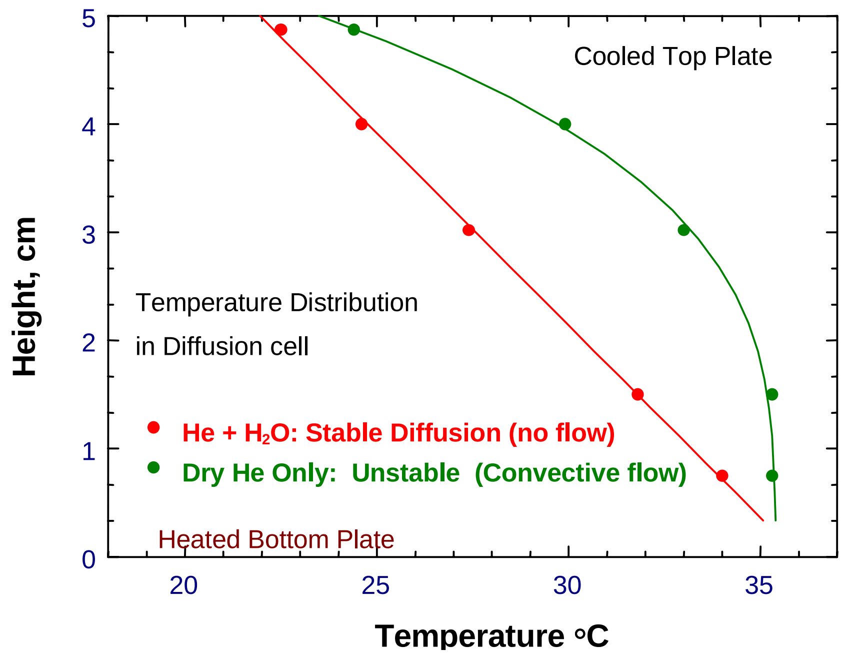

Figure 3. Measured temperature distributions in diffusion cell. With only a single component (dry He) convective flow occurs. Stable diffusion of water vapor is obtained with the two-component mixture of He + water vapor.

Photo-Acoustic Absorption Measurements

The laser source used in our measurements was a single longitudinal mode, injection-seeded, continuously tunable (Continuum Mirage 500) OPO laser system, with a pulse repetition rate of 10 Hz, and output energy of ~ 10 mJ to 15 mJ in the 700 nm to 900 nm region. The laser beam is aligned horizontally through the middle of the diffusion cell, and a fraction of the laser is coupled into a power meter to continuously monitor the variation in the laser output. During the course of an experiment, the laser wavelength was tuned across the absorption lines by means of software provided by the manufacturer, with a resolution of 1 pm. When the laser beam is absorbed by the water vapor, a photo-acoustic signal is generated that is coupled into innumerable standing wave modes within the enclosure. The frequency band of the signal is thus a function of the three-dimensional acoustic modes of the diffusion cell. We have computed the resonant mode frequencies and chosen the 2 kHz to 15 kHz band-pass region to obtain adequate signal and signal-to-noise ratio. The signal from the microphone was passed through a 2 kHz to 15 kHz band-pass filter and amplifier (Krohn-Hite Model 3886) with a voltage gain of 74 dB. The amplifier output is digitized with a 12-bit ADC card with a 100 $kS.s^{-1}$ sampling rate and acquired on a PC. Typically, signals from ten laser shots were averaged to generate one data point during the scan. In addition to the acoustic signal, the laser power, and the plate temperatures were also recorded. The data acquisition software also computes the frequency domain values of the signals and displays the acoustic spectrum.

Absorption by water vapor in the 816-nm region was measured by monitoring the photo-acoustic signals as the laser was tuned across the wavelengths of several individual lines. By keeping the cell isothermal and varying its temperature, the concentration of the vapor was changed and absorption measurements were performed to ensure the linearity of the photo-acoustic signal. In order to maintain the same photo-acoustic environment, the height of the laser beam within the cell was fixed. For the super-saturated experiments, the temperatures of the top and bottom plates were chosen to obtain a local temperature of 25.0°C at the beam height, while the level of super-saturation was changed from 1.1 to 1.4.

Results and Discussion

From our thermal characterization tests, it was observed that isothermal conditions near ambient temperature could be established in the cell in a steady state within a short time (~ 30 min). The time taken to establish a steady state when the temperatures of the top and bottom plates differed by 20°C or more required a much longer time (1 to 2 hours). Figure 3 shows the temperature distribution within the cell when the bottom plate was kept at 36°C and the top plate at 21°C. When there is no water inside, this corresponds to a normally unstable situation and convection flow is established within the cell leading to the temperature distribution as shown in Figure 3. But with the addition of water, stable convection-free diffusion of water vapor into helium is established and a nearly linear temperature profile is established as shown in Figure 3. Figure 4 shows the measured temperature gradients for various levels of super-saturations (air and water vapor mixture) while holding the temperature constant (25°C) at the beam location. The calculated temperature profiles are found to agree very closely with the measurements. It may be noted that temperature measurements with thermistors were not done for $S > 1.1$, because of the condensation of water on thermistors that is likely to cause erroneous readings.

Figure 5 shows the photo-acoustic absorption signals for saturated water vapor with air as the buffer gas and an isothermal cell, as the laser is tuned across the 816.37-nm absorption line. It is seen that the photo-acoustic signal increased with temperature, with the increase becoming more rapid as the temperature was increased. This is to be expected because the partial pressure of the water vapor increases exponentially with temperature (Clausius-Clapeyron equation). By plotting the measured absorption signal against the absorption of saturated water vapor calculated for the corresponding temperature, a linear relation was found to exist between the photo-acoustic signal and the absorption. This observation has established the ability of our experimental system for accurate absorption measurement.

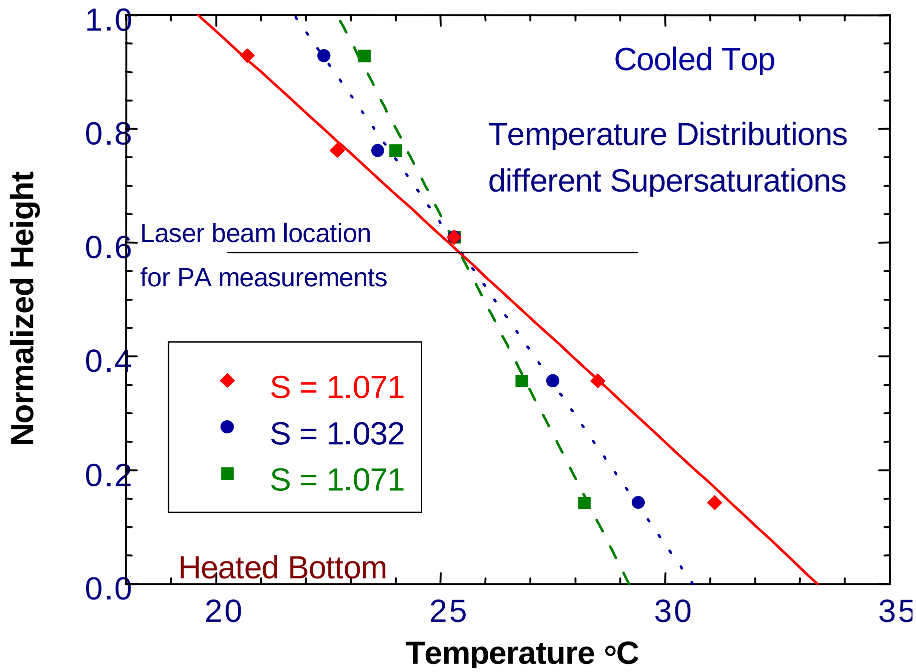

Figure 4. Measured temperature distributions for stable diffusion of water vapor in He. Top and bottom plate temperatures are adjusted to obtain 25°C at center of cell.

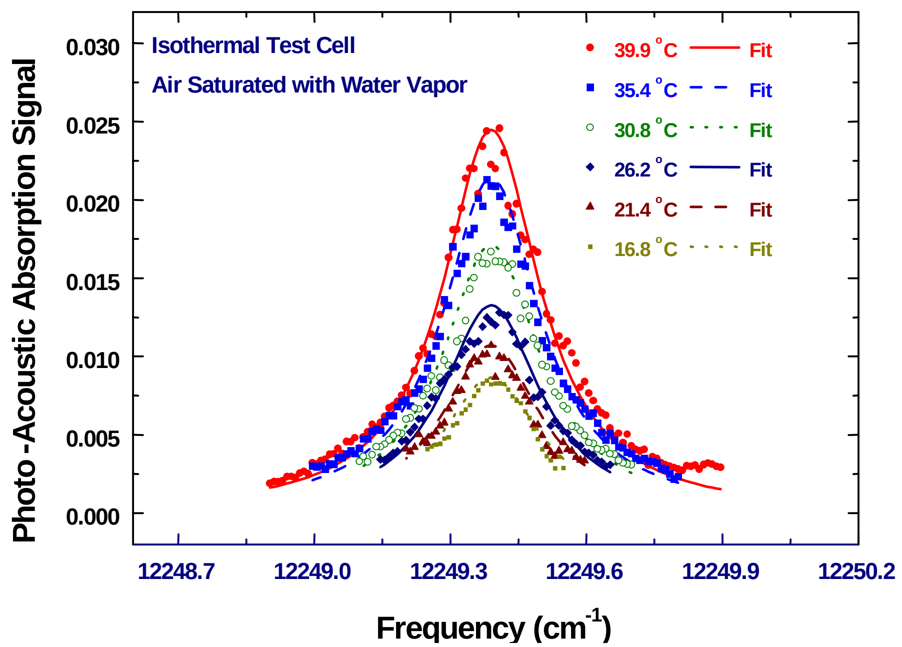

Figure 5. Saturated water vapor absorption line at 816.37 nm measured with photo-acoustic sensor in diffusion cell. Increase in photo-acoustic signal is linear with absorption increase with temperature.

Measurements of water vapor absorption at substantial levels of super-saturation have been measured in the near-IR for the first time. Figure 6 shows the photo-acoustic absorption signals for the super-saturated water vapor with a helium buffer gas. The temperature at the height of the beam was kept at 25.0°C. Three cases are shown, for S = 1 (saturated), 1.1 and 1.2 (super-saturated). It is seen that there is a linear increase of photo-acoustic signal with S. This is again as expected, because the water vapor concentration increases by 10% for S = 1.1 and by 20% for S =1.2 over that for S = 1. However, when S was increased to 1.3 and 1.4, the photo-acoustic signal did not increase linearly. Further investigations are in progress to determine whether this is due to an artifact of the experiment or due to other phenomena.

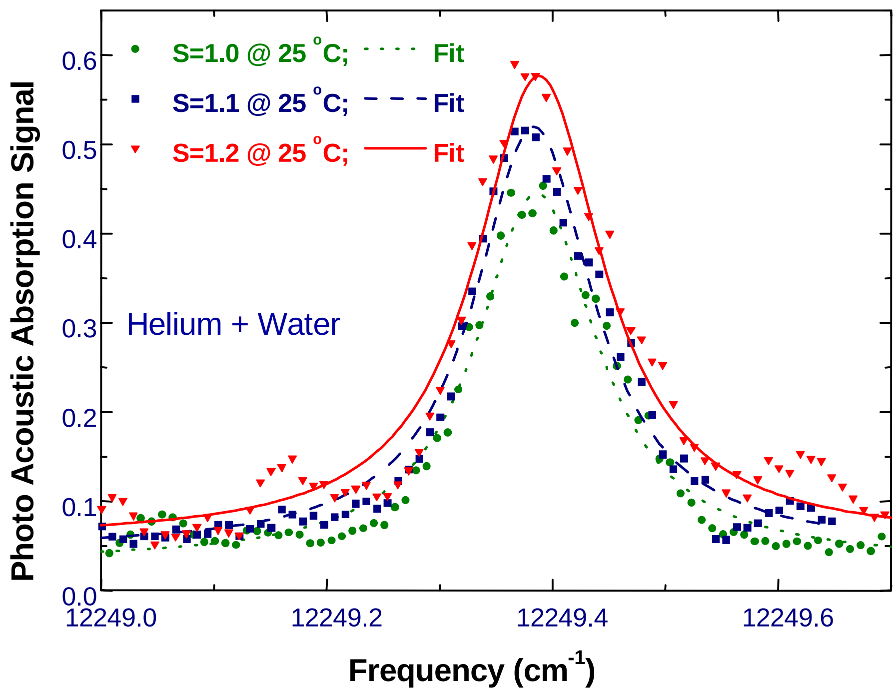

Figure 6. Absorption measurement in supersaturated water vapor line at 816.37 nm, and 25°C local temperature. Increase in absorption is linear with super-saturation.

It is also seen that the helium-broadened line-widths of water vapor are much smaller than the air-broadened line-widths. Measurements of helium-broadened line-widths are in progress and will be reported later.

Corresponding Author

P. Varanasi, pvaranasi@notes.cc.sunysb.edu

References

Katz J. L., and B. J. Ostermier, 1967: Diffusion cloud-chamber investigation of homogeneous nucleation. *J. Chem. Phys.*, **47**(2):478.

Katz, J. L., and P. Mirabel, 1975: Calculation of supersaturatation profiles in thermal diffusion cloud chambers. *J. Atmos. Sci.*, **32**, 646.

Varanasi, P., and C. R. Prasad, 1999: Measurement of the absorption characteristics of water vapor near saturation. In *Proceedings of the Eighth Atmospheric Radiation Measurement (ARM) Science Team Meeting*, DOE/ER-0738. U.S. Department of Energy, Washington, D.C. Available URL: http://www.arm.gov/docs/documents/technical/conf_9803/varanasi-98.pdf