

# Measurement of Absorption Characteristics of Water Vapor Near Saturation

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## Introduction

It has been suggested that the significant differences that still persist between the measurements of earth's radiation budget and the predictions are partially due to the inadequacies in the absorption coefficients of water vapor used in the calculations. Water in all its three phases has a profound influence on both the longwave and shortwave streams of radiation, because of its strong absorption over large spectral regions and scattering by the condensed phases. Furthermore, the mixing ratio and the saturation of water vapor can vary over a wide range. Thus, even small errors in the values of absorption properties can have a large influence on the results predicted by atmospheric models. A question that has continued to defy accurate characterization is whether the absorption by water vapor is enhanced when it is close to saturation. These questions are more relevant in the light of observations of anomalously high extinction in fogs or clouds where the partial pressure of the vapor is close to saturation.

A systematic experimental measurement program has recently been initiated by us for determining the absorption linewidths and line strengths of water vapor over a wide range of temperatures and saturations from the under-saturated through saturated to the super-saturated. For these measurements, we will utilize a special diffusion chamber, within which precisely characterized distributions of water vapor with varying levels of saturation are created. A novel photo-acoustic (PA) spectrometer will be built into this diffusion chamber for the absorption coefficient measurements. Additional experiments utilizing a long path absorption cell and Fourier Transform Infrared (FTIR) spectroscopy will be performed to complement the PA spectrometer measurements. Unlike conventional absorption methods, which measure extinction, the PA spectrometer measures absorption directly, thus avoiding the difficult task of separating the extraneous contributions to

extinction, such as molecular and aerosol scattering. In addition, the PA method is much more sensitive and compact. In this paper, we describe the basic design of the experiments and present some preliminary PA water vapor absorption measurements.

## PA Spectrometer

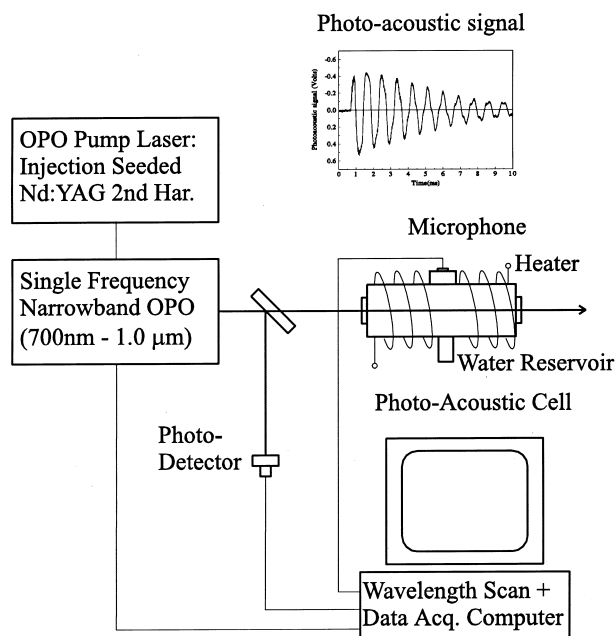
The conventional absorption measurement techniques (FTIR or absorption spectrometers) utilize an absorption cell in conjunction with a monochromatic or a broadband spectral source to determine the extinction of radiation through the absorbing media over a known path length. Because extinction includes both absorption and scattering, contributions from scattering have to be separately determined in order to obtain the absorption coefficient. Although Rayleigh (molecular) scattering that scales as the inverse fourth power of the wavelength is negligible in the infrared (IR), it is significant in the visible, especially at shorter wavelengths. The errors due to scattering become even more important when very long absorption paths are required, as it is in the case of weak absorption lines.

PA spectroscopy (Tam 1983) is a sensitive technique that is utilized for measurements of very low absorptions or low concentrations in a broad range of applications. PA measurements are not affected by scattering because the PA signal is generated by the thermalization of the absorbed energy. Absorption coefficients of the order of  $10^{-10} \text{ cm}^{-1}$  in a 10-cm-long absorption path can be determined by the PA technique. This sensitivity cannot be matched by other conventional techniques which measure extinction, and cannot readily be used to measure absorption coefficients less than  $10^{-3} \text{ cm}^{-1}$ . Although there are other ultra-sensitive spectroscopic techniques with even higher sensitivities, the simplicity and convenience of the PA method makes it suitable for the present application.

The PA effect refers to the generation of acoustic waves due to the absorption of a modulated electromagnetic wave passing through the medium. This effect, which was discovered by Bell in 1880, is normally weak because it is usually applied to situations where a very small fraction of the optical energy is absorbed and converted into acoustic energy. Many reviews of the PA technique (Tam 1983) are available in the literature, and they address not only the underlying theory but also the details of design and construction of PA spectrometers. Both continuous wave (cw) (Ritter and Wilkerson 1987) and pulsed laser sources are suitable for obtaining PA spectra. For measuring the PA spectrum, it is essential to modulate the heat source induced by the radiation. When a cw source is used, the absorption by the gas is modulated either by a chopper, or by dithering the wavelength of the source (Schwemmer et al. 1991), about the absorption line center. With a pulsed laser source, the absorption spectrum is obtained directly.

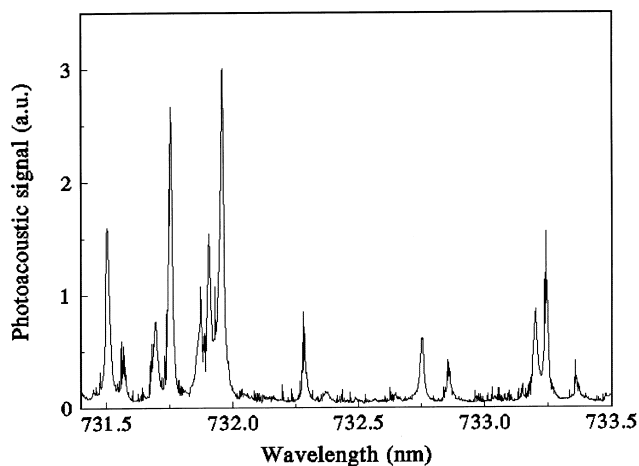
## PA Measurement of Water Vapor Absorption in Near IR

Recently, we constructed a PA spectrometer utilizing a pulsed laser and obtained high-resolution spectra of water vapor in the 730-nm region and oxygen in the 760-nm to 770-nm region. Such measurements are also of great value for the remote sensing of atmospheric parameters such as water vapor mixing ratios (Henderson et al. 1997), pressure and temperature profiles (Korb et al. 1995), using differential absorption lidars. Figure 1 shows the experimental set up used for obtaining the PA water vapor absorption spectrum. A pulsed (5 ns pulse width) broadly tunable (720 nm to 920 nm) narrowband ( $0.01 \text{ cm}^{-1}$ ) laser source was used to generate PA signals in a short 10-cm-long cylindrical heated cell equipped with a microphone. The laser source (Continuum Mirage 800) consisted of a single-frequency KTP (potassium titanyl ortho-phosphate) Optical Parametric Oscillator (OPO) pumped by the frequency doubled output of a Nd:YAG laser, and its output energy was approximately 10 mJ/pulse. The PA cell was connected with a small reservoir of water and the partial pressure of water vapor in the cell was controlled by varying the temperature of the cell. Condensation on the windows of the cell was avoided by keeping them warm. The PA signal detected by the microphone, was amplified, rectified, and digitized using a 12-bit Analog Digital Conversion (ADC) before being stored on a PC. During the experiment, the OPO was operated at 10 Hz and the PA signal as well as the laser pulse energy were measured on shot-by-shot basis. After normalizing the PA signals by the laser energy, they were averaged at each laser wavelength to eliminate random noise contributions. In the results shown here, the laser



**Figure 1.** Schematic of a pulsed laser PA spectrometer used for water vapor absorption.

wavelength was tuned over the 730-nm water vapor band. From the available listings of water vapor line strengths and line widths (Grossman and Browell 1989, Camy-Peyret et al. 1985, Mandin et al. 1985), the absorption spectrum of water vapor was also computed. Figure 2 shows the experimental water vapor spectra over a 2-nm region, which compared very well with the calculated spectrum. For saturated vapor at 293 K, the absorption coefficient is of the order of  $< 0.1 / \text{km}$  ( $< 10^{-6} / \text{cm}$ ) for some of the weaker lines, while it is as large as  $2.5 / \text{km}$  for the stronger lines.



**Figure 2.** PA spectrum of water vapor measured with the tunable laser source.

Some discrepancies between the measured and the calculated spectra were observed, indicating the need for more careful measurements.

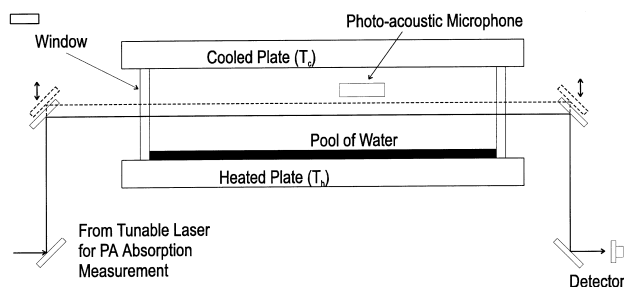
## Design of Absorption Cell

An ability to create a well characterized distribution of water vapor and the ability to vary its level of saturation are the important considerations in the design of the water vapor absorption cell. It is well known that a vapor will condense whenever its partial pressure increases above the saturation pressure, in the presence of its liquid phase. However, when the liquid phase is not present, the vapor can sustain a large degree of supersaturation,  $S$ , (defined as the ratio of actual vapor pressure to the saturation vapor pressure), without condensation, depending on factors such as, cleanliness, wall materials, the presence of ions, and other nucleating factors. Thus, in a dust-free gas, in the absence of walls and ions, condensation does not occur until a certain critical supersaturation is attained, soon after which rapid condensation occurs.

In the measurement of absorption by water vapor, it is essential to determine the partial pressure of the vapor accurately. A complicating factor in most of the commonly used experimental systems is that the distribution of the vapor is non-homogeneous, and any local measurement may not be representative of the vapor concentration along the absorption path. Furthermore, when the vapor is saturated, the possibility of condensation and the presence of liquid droplets can lead to significant errors. Hence, a novel design of the absorption cell is proposed that allows accurate characterization of the water vapor concentration.

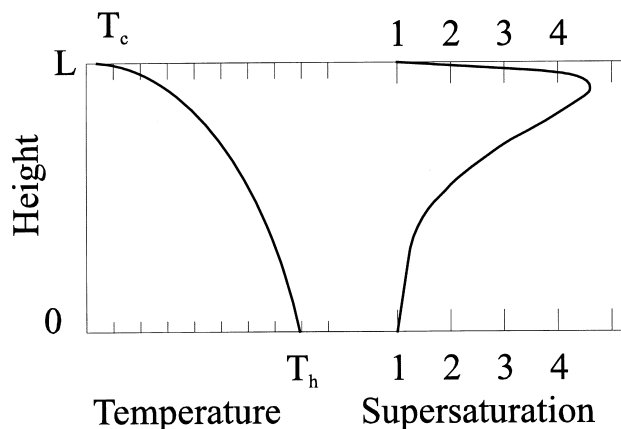
Figure 3 shows the proposed absorption cell in which the distribution of water vapor is uniform in a horizontal plane and can be varied over a large range of saturation values. Such a horizontally homogeneous distribution of vapor allows accurate measurement of absorption at different levels of saturation by simply translating the probe beam up and down. The PA signals caused by the absorption of the probe beam are detected by the microphone placed inside the cell. Condensation on the windows is prevented by heating the window. One of the most useful attributes of this cell is the ability to provide a steady-state distribution of water vapor even in the presence of condensation.

The absorption cell is based on the so-called diffusion cloud chamber, which was used in the past for visualizing the tracks of ionizing radiation and high-energy particles. The diffusion chamber (Katz and Ostermeir 1967) has a liquid pool at the bottom and a metal surface wet by condensate at the top. They provide well-defined surfaces for the accurate



**Figure 3.** Absorption cell for providing uniform distribution of water vapor in any horizontal layer. The vapor is saturated above the water surface and is increasingly supersaturated with height. The probe beam is moved up/down for scanning.

determination of temperature and partial pressures. The basic function of the chamber is to produce a precisely characterized vapor distribution as shown in Figure 4. The vapor is saturated at the bottom surface, and the magnitude of the supersaturation increases continuously until homogeneous nucleation occurs, causing condensation. Direct measurements of the vapor concentration are not feasible, because condensation would occur on any measuring device and destroy the local supersaturated state. On the other hand, the design of the chamber ensures that one-dimensional diffusion takes place through a carrier gas, from a hotter to a cooler layer, the pressure and temperature can be calculated with a high degree of confidence from measurements made outside the cell. The one-dimensional equations for heat conduction and mass diffusion are set up for the given boundary conditions and their solution gives the temperature, density and partial pressure distributions (Epstein and Rosner 1970). Figure 4 shows the distribution of temperature and supersaturation, calculated by taking the ratio of actual pressure of vapor and the equilibrium vapor pressure at any height. By increasing the temperature gradient the supersaturation maximum can be made as large as desired. Because the warm surface is at the bottom of the chamber, convective flow can occur within it unless the density of the gas is reduced. In order to prevent convective flow from setting up inside the chamber, a sufficient amount of a light carrier gas (such as  $H_2$  or  $He$ ) will be added to the chamber such that the density of the gas mixture and the vapor decreases from bottom to top. A steady-state distribution is set up in the cell and condensation occurs only after the critical supersaturation is exceeded within the vapor. If the maximum supersaturation attained is less than the critical supersaturation required for homogeneous nucleation, condensation occurs only on the cooled top surface and no dropwise condensation is present within the chamber. The only drops formed are those due to cosmic rays and other ions coursing through the chamber.



**Figure 4.** Distribution of supersaturation and temperature with height in the absorption cell.

## Absorption Measurements

Using the wavelength tunable OPO source, absorption by water vapor within the diffusion chamber can be measured with the PA detector at conditions corresponding to increasing levels of supersaturation in the three near-IR bands in 730 nm, 813 nm, and 950 nm. Long-path absorption experiments will also be performed for comparison with the PA measurements. Molecular oxygen absorption in the A-band region (760 nm to 770 nm) can also be readily obtained with the same setup.

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