MEASUREMENT OF THE ABSORPTION CHARACTERISTICS OF SUPER-SATURATED WATER VAPOR

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There is considerable concern amongst climate modelers, in particular, and atmospheric scientists, in general, that we may have been underestimating the absorption of solar radiation by the atmosphere by as much as 40 Wm⁻². This enhanced absorption, which was recognised by comparing model calculations with satellite-borne radiometric measurements, remains to be explained. Controversial explanations of this newly discovered fact have been offered and debated. A school of thought suggests that the enhanced absorption of the incoming short-wave solar radiation is due to erroneous depiction of the contribution by clouds in the atmosphere. Another school subscribes to the view that the enhanced absorption, which it believes is apparent in the clear-sky case as well, is due to under-estimation of the absorption in the short-wave bands of water vapor. The latter school also wonders if the absorption by water vapor differs from the conventional manner as the substance approaches and exceeds the limit of thermodynamic staturation, a situation not uncommon in the rims of clouds and in highly humid tropics ane equatorial regions. Therefore, in order to examine the nature of the absorption characteristics of water vapor in the short-wave or near-infrared region over a wide range of temperatures and levels of super saturation, we initiated a unique experimental project in 1998.[1]

For providing a steady state distribution of super-saturated water vapor a special diffusion cell has been built and serves as the absorption cell in our experiments. The diffusion cell used in our experiments consisted of a well insulated and sealed rectangular perspex enclosure (10.75" x 4" x 2"). The top and bottom plates of the enclosure were made of copper and were maintained isothermally to better than 0.1° by circulating water from two high precision water baths. A stable, convection-free, steady state diffusion of water vapor is set up by filling the cell with helium, and evaporating water vapor from a saturated warm surface (bottom), and condensing it on a cold surface (top). In a preliminary study [2] we had characterized the performance of the diffusion cell for producing supersaturated water vapor and also carried out preliminary measurements of near-IR (at ~ 816 nm) absorption coefficients in supersaturated water vapor. A broadly tunable (460 nm to 2.1µm) narrowband (0.02 cm⁻¹) single longitudinal mode laser (Continuum Mirage 500 OPO pumped by a Continuum Powerlite Nd:YAG laser) source was used to generate photo-acoustic absorption signal in the diffusion cell. Its pulse repetition rate was 10 Hz, and its output energy was \sim 10 mJ in most of our experiments Two rectangular (1" x 3") antireflection coated BK7 windows allowed the laser beam to be positioned at any 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. . 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.

Super-saturation S, is defined as the ratio of the actual partial pressure to the saturation vapor pressure of water at the temperature of interest. In the absence of foreign nuclei (such as dust, ions, etc), condensation of water is caused by homogeneous nucleation, which occurs readily when the super-saturation 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 the temperature profile in the cell by sensors (e.g. thermistors) becomes erroneous at high super-saturation 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 super-saturation 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 super-saturation (S = 1.15). The calculated temperature profiles were found to agree very closely with the measurements.

Absorption by water vapor in the 815–820 nm and 940–950 regions was measured by monitoring the photo-acoustic signals as the laser was tuned across several individual lines. Figure 1 shows spectral scans of an absorption line of super-saturated water vapor at 816 nm Figure 2 shows the effect of variation of S on water vapor absorption for the supersaturated water vapor with helium buffer gas. The temperature at the height of the beam was maintained at 298 K for all cases. It is seen that there is 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 water vapor monomer molecules due to the formation of polymers and aggregates in the course of homogeneous nucleation.

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Figure 1. Absorption measurements of supersaturated water vapor line at 816.37 nm, and 25C local temperature.



Figure 2. Increase in absorption (for water vapor line at 816.37 nm) is linear for S up to 1.2. For S > 1.2 the signal drops off due to condensation.