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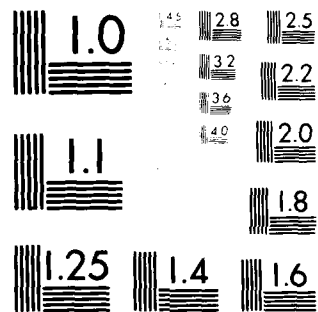
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A STUDY OF CLUSTERING IN WATER VAPOR
AT ULTRAVIOLET WAVELENGTHS.

Final Report for Period 1 December 1979 - 1 November 1980

J. C. Wyss, R. E. Drullinger, E. W. Smith
and J. Cooper

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A device for measuring clusters in water vapor was constructed based on vacuum ultraviolet absorption techniques. Four absorption cells were built with sapphire windows to provide paths lengths of 5.0, 11.0, 76.2, and 284.5 mm. Each cell was held at a constant temperature (180 °C), while the water vapor pressure was varied from 4 - 400 kPa (30 - 3000 Torr). At each pressure, an extinction coefficient was determined by measuring the differential absorption between two cells which were identical except for path length. The ultraviolet light (150 - 175 nm) was produced using a xenon.		

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BLOCK 20, continued:

- 15 kPa continuum lamp and was wavelength selected using an evacuated $\frac{1}{2}$ meter spectrometer. The measured extinction coefficient is observed to have a water vapor density dependence stronger than linear, which may indicate the presence of clusters. Further refinements in the experimental apparatus will be necessary to provide definitive evidence for clustering of water vapor.

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1. Objectives

Water vapor is an ever-present substance whose effects must frequently be taken into account when propagating signals through the atmosphere either for communications, detection, or range/distance measurements. Often, when only opacity is important, accounting for these effects takes the form of simply looking at the known spectrum of pure water vapor in the spectral region of interest and selecting a "window" or blocked region, depending on the intended objective. It has been known for some time, however, that some of the important window regions can sometimes become obscured under actual field conditions. This effect has come to be known as the "anomalous absorption of water vapor," and although much effort has been devoted to its study, there still seems to be no general agreement as to its cause. [1]

It has been suggested that the anomalous absorption is due to the dimer, or small clusters, of water molecules which should exist because of the strong hydrogen bonding in water. However, the experiments aimed at this question have been few and less than conclusive. It is the objective of the present research project, therefore, to develop an independent spectroscopic probe (using ultraviolet rather than infrared light, as is common in water vapor studies) for the presence of these small clusters of water molecules. The probe, which should be capable of measuring the number density of each of several small cluster sizes (e.g., $n = 2-5$), would then have two immediate uses. First, to study the cluster formation kinetics under laboratory equilibrium conditions for subsequent modeling, and secondly, to be used in conjunction with microwave laboratory and field experiments to aid in answering the questions regarding the "anomalous absorption."

The probe is based on a shift in an electronic transition band in the cluster from that in the separated molecules. The first allowed electronic

transition in water gives rise to a broad molecular band in the ultraviolet whose center is observed to shift from 164 nm in the vapor to 147 nm in the liquid. This large shift (17 nm or 7050 cm^{-1}) indicates water vapor should be amenable to kinetic analysis of its clustering by quantitative spectroscopic techniques similar to those already successfully developed by our group for the study of mercury vapor, where clusters up to $n = 3$ were observed and their formation, relaxation, and destruction rates were measured.^[2]

The proposed project was divided into three distinct steps, each about a year in length:

First Year: Measurement of the temperature and density dependence of the bandshape and shift for the lowest energy electronic transition in pure water vapor. This involved the construction of a two-compartment oven and cell, in which the reservoir temperature (and hence, vapor density) could be controlled independently of the temperature of the main cell chamber. This oven was somewhat complicated by the temperature and pressure range of interest (from below to above room temperature and from 0 - 4 atmospheres pressure). The experiments also required the entire optical path be evacuated and a digital recording system that would allow data of sufficient quantity and precision for subsequent analysis.

Second Year: Modeling the data obtained in the first year. This will involve fitting the density dependence of each small λ increment in the band at each temperature. With this data, a bandshape and intensity can be drawn for each cluster size. The temperature dependence of these integrated band intensities will give the binding energies of various

clusters and the change in bandshape with temperature may tell something about the structure and potential curves of the clusters.

Third Year: Explore the physics and chemistry necessary to develop a two-photon probe for detecting the cluster-shifted electronic transition in atmospheric water vapor. This will involve the use of high-power, near UV lasers to measure the size and density of clusters present in a manner deemed most appropriate, based on the results of steps 1 and 2 of this proposal. The work will probably start with an investigation of the two-photon dissociation of pure water vapor and subsequent detection of the resulting OH fragment. In parallel to this work, a look will have to be taken to determine whether two-photon processes in O_2 , N_2 , and CO_2 exist at these wavelengths. To finally develop the quantitative probe desired here, an auxilliary, tunable UV probe to map out the internal state distribution of the OH photo-fragment will be used.

The initial proposal received funding for the first year of the project. Therefore, this report covers the progress made in the first year to construct a water vapor cell for vacuum ultraviolet absorption measurements and gives the first results which show that clusters can be examined with this technique.

The second and third year portions of this research will be continued as funding becomes available.

II. Progress

Apparatus

The main goal of the first year was to build the system for measuring the absorption of water vapor as a function of water density and temperature

(see Figure 1). Most of the first year was required to complete the design and construction of the system. This report briefly details the challenges and difficulties that were faced. Some data which was taken near the end of the year will be discussed.

The biggest challenge of the project was the construction of an absorption cell that: 1) would not be attacked by hot, high-pressure water vapor; 2) would be transparent from below 150 nm to 170 nm at elevated temperatures and pressures; and 3) would have an optical path-length of 200 μm or less. Selection of window material was complicated by temperatures needed and exposure to hot water vapor. We initially considered sapphire, magnesium fluoride, lithium fluoride, and yttrium lithium fluoride (YLF). Magnesium fluoride and lithium fluoride are transparent over the needed spectral range, but they are attacked by hot water vapor. Sapphire is stable with hot water vapor, but is strongly absorptive below 150 nm. The material YLF is possibly stable with hot water vapor and also is transparent to below 150 nm, but its structural and mechanical properties were unknown. It was therefore decided to use sapphire initially and restrict the data to wavelengths greater than 150 nm.

The next problem was to design a cell using sapphire that could stand 180 °C temperatures and 400 kPa pressures. The first attempt used UV selected sapphire windows that were commercially brazed onto Kovar tubes. The tubes were then welded onto re-entrant flanges such that the spacing of the windows was approximately 100 μm . Unfortunately, in the final welding process, the Kovar tubes were pulled together such that the windows were either too close together or actually touching. The welded designs were abandoned in favor of a flange which was bolted together and had metal O-ring vacuum seals instead of brazed seals. The separation of the windows

was initially maintained with stainless steel shim stock, but unfortunately, when cut, slight discontinuities at the edges of the shims caused the sapphire windows to crack when the flange was bolted together. A new shim was designed which was made by vacuum deposition of silver onto one window. This design worked well with spacings up to 11 μm . No windows were cracked.

For longer spaced cells, new shims were made using Kapton film. The Kapton was more flexible than steel and, hence, was easy to cut without forming lips on the edges which could crack the windows. It was also inert to hot water vapor. Cells were constructed with optical path lengths up to 284.5 μm by stacking Kapton shims between the windows.

Two water absorption cells were constructed and used simultaneously. Each cell was kept at 180 °C and was connected to a single liquid water cell. The liquid cell was used to set the vapor pressure in both absorption cells by varying the temperature of the liquid from 0 °C to 130 °C. The vapor pressure was determined with standard vapor pressure versus temperature curves from the measured liquid temperatures. The two absorption cells thus had the same vapor pressure (both connected together) and same temperature (each temperature controlled). However, they were different in path lengths and, hence, the differential absorption could be measured independent of lamp fluctuations or cell design.

Ultraviolet light from 150 to 175 nm was produced using a xenon, 15 kPa continuum discharge lamp that was built based on a design by Yoshio Tanaka.^[3] It took a number of weeks and new designs to make the lamp work reliably. The main difficulty was with contaminants boiling off the electrodes and quenching the lamp discharge. By repeatedly running the lamp, then baking out while pumping, and then refilling with fresh xenon, stable lamp operation was achieved.

A $\frac{1}{2}$ meter vacuum spectrometer was used to spectrally resolve the lamp output into its different wavelength components. The output of the spectrometer was collimated with a lithium fluoride lens and divided in two by a beam splitter. Each beam illuminated one of the two absorption cells.

A photo-multiplier tube (PMT) was placed behind each cell to gather the light passing through the cells. An amplifier/discriminator was constructed in the housing of each PMT to amplify and detect photon counts. A dual, presettable counter system was built that would count the photon signals coming from each PMT. The counter system was interfaced with and controlled by an existing NBS computer system. The computer system was also modified to set the wavelength on the spectrometer to control the integration times on the PMT's, and to average the data over successive runs.

Analysis

The overall system was completed near the end of the project year (November 1980) and preliminary data was taken. Data was taken with both cells kept at 180 °C. Two alumel-chromel thermocouples were spot welded to each absorption cell to monitor their temperatures. Heaters were adjusted such that the cell temperatures agreed to ± 0.5 °C. The liquid cell, which controlled the vapor pressure in the absorption cells was either cooled with ice water or heated with a tungsten heater. A temperature controller maintained the temperature of the liquid cell to ± 0.5 °C by varying the voltage on the tungsten wire. By changing the set point of the temperature controller, the temperature of the liquid cell could be changed and, hence, the pressure of the water vapor in the absorption cells could be controlled.

Distilled water, added to the liquid cell and heated gently, was pumped on by an oil diffusion pump with a liquid nitrogen trap until half the water was removed. This was done to remove trapped gases from the liquid water.

The liquid cell was then cooled to produce water vapor of negligible or essentially zero pressure. The xenon lamp was turned on, the spectrometer was set for $\lambda = 155$ nm with 50 μ m slits (0.3 nm resolution), and the rate of photons per second was measured for each cell using the photo-multiplier tubes and counters. This provided a baseline for the absorption measurements. The liquid cell was then heated, increasing the water vapor pressure in the cells. Increasing the water pressure would increase the absorption and, hence, decrease R, the rate of photons passing through the cell per second. The transmission, T, through the cells at total pressure, P_T , and wavelength, λ , is given by:

$$T(P, \lambda) = R(P_T, \lambda) / R(P_T \cong 0, \lambda) \quad (1)$$

where $P_T \cong 0$ is the initial, negligible pressure (less than 0.1 kPa). Assuming the presence of a single gas, the transmission can also be written as:

$$T(P, \lambda) = \exp [-\varepsilon(\lambda) \cdot P \cdot D] \quad (2)$$

where ε is the wavelength-dependent extinction coefficient and D is the cell path length. However, if two gases are present, then T becomes

$$T(P, \lambda) = \exp [-\varepsilon_1(\lambda) \cdot P_1 \cdot D - \varepsilon_2(\lambda) P_2 \cdot D] \quad (3)$$

where the subscripts in this case represent water monomers for 1 and dimers for 2. In static equilibrium P_2 will be equal to:

$$P_2 = K P_1^2 \quad (4)$$

where K is the equilibrium constant. The transmission, T , can then be rewritten as

$$T(P, \lambda) = \exp[(-\epsilon_1(\lambda) \cdot P_1 - \epsilon_2(\lambda) K P_1^2) \cdot D]. \quad (5)$$

The total pressure is just the sum of the partial pressures or

$$P_T = P_1 + P_2, \quad (6)$$

but assuming^[4] that $P_2/P_1 \lesssim 0.014$, the total pressure can be approximated by $P_T \cong P_1$. If T is measured as a function of P_T at a wavelength where ϵ_2 is non-zero (i.e., dimer molecules absorb at that wavelength), then from Eqs. 5 and 6, the natural logarithm of T should have a linear plus quadratic dependence in P_T . Our first set of experiments were designed to show this. It was estimated that the peak of the dimer signal should be at about $\lambda = 155$ nm. The spectrometer was set for 155 nm and T was measured for pressures up to 400 kPa. The observed transmission, as a function of pressure, varied from run to run and was judged unreliable. However, qualitatively the variation was consistent with dimer formation. Our interpretation was that the difficulty occurred in the pressure measurement. The water vapor pressure was inferred from vapor pressure/temperature curves where the temperature of the liquid cell was measured by thermocouples attached to the outside of the glass liquid cell. Because these thermocouples were not in direct contact with the water and the liquid cell was not well-insulated, it is possible the measured temperatures were different from the actual water temperatures. Thus, the inferred pressure values would be in error. This possibility became apparent during analysis after most of the data was taken.

One period of data accumulation was devoted to scanning the wavelength at a fixed, high, constant pressure. The pressure was set at 170 kPa and the spectrometer was scanned from 153 to 170 nm. This scan was then compared with data from Watanabe and Zelikoff,^[5] who measured the absorption of water vapor with pressures from 0.01 to 1.0 kPa using a 4.7 cm long cell. They found no change in the wavelength dependence of the absorption coefficient for their pressure range. When our data is plotted on the same graph as their's (see Fig. 2), it is clear that at 170 kPa there is an increase in the total absorption coefficient ϵ at shorter wavelengths. We attribute this to the presence of dimer molecules whose peak absorption should be shifted to shorter wavelengths and whose concentration only becomes appreciable (compared to monomers) at higher pressures. The two curves were plotted on the same scale by matching their end points near 170 nm, because the absorption on the long wavelength side should be due primarily to monomers and, therefore, the extinction coefficients should be the same at that wavelength.

III. Conclusions

The first version of the apparatus has been completed as proposed, in the first project year. The initial wavelength-dependent data strongly suggests the presence of appreciable cluster densities whose absorptions are shifted to shorter wavelengths as we earlier predicted. The initial pressure-dependent data have shown problems with our pressure measurements that need to be rectified. We are anxious to correct these problems and begin to take more precise quantitative data that will allow a detailed analysis of the cluster concentrations, their absorption bandshapes, and their binding energies.

IV. Participating Scientific Personnel

Dr. J. C. Wyss

Dr. R. E. Drullinger

Dr. E. W. Smith

Dr. J. Cooper

National Bureau of Standards

Boulder Laboratories

V. List of Publications

None

VI. References

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VII. Figure Captions

Figure 1. Schematic diagram of experimental apparatus. Ultraviolet light (150-175 nm) from a xenon discharge lamp is wavelength selected by a $\frac{1}{4}$ meter, evacuated spectrometer. Collimated by a lense, the light from the spectrometer is divided in two by a beam splitter, illuminating two water vapor absorption cells. The light from each cell is detected with photomultiplier tubes (PMT) and is counted using a computer. The two absorption cells are identical except for different optical path lengths.

Figure 2. Extinction coefficient, ϵ , versus wavelength for two separate water vapor pressures. The larger extinction values observed at high pressures near shorter wavelengths are due to the presence of water vapor dimers.

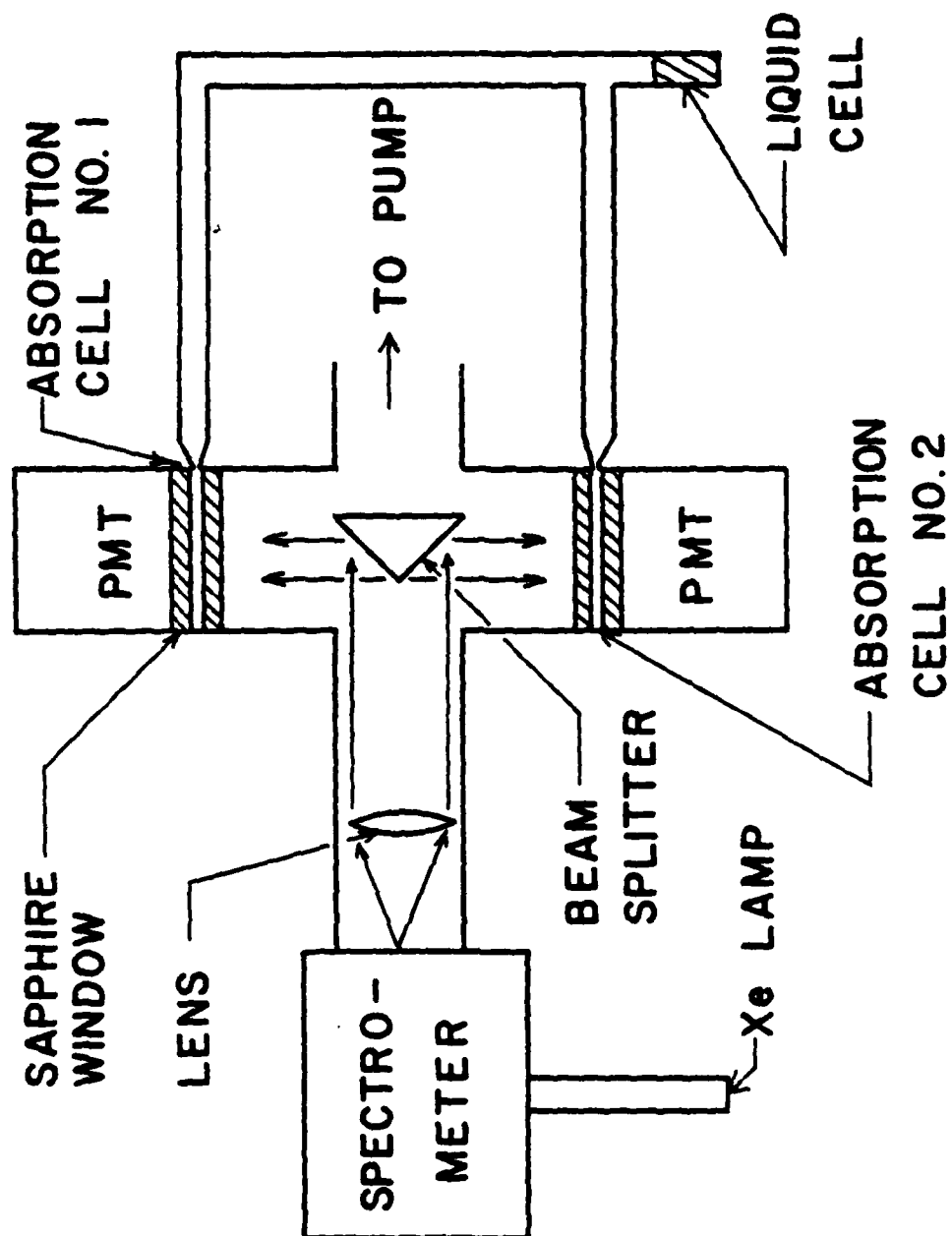


Figure 1.

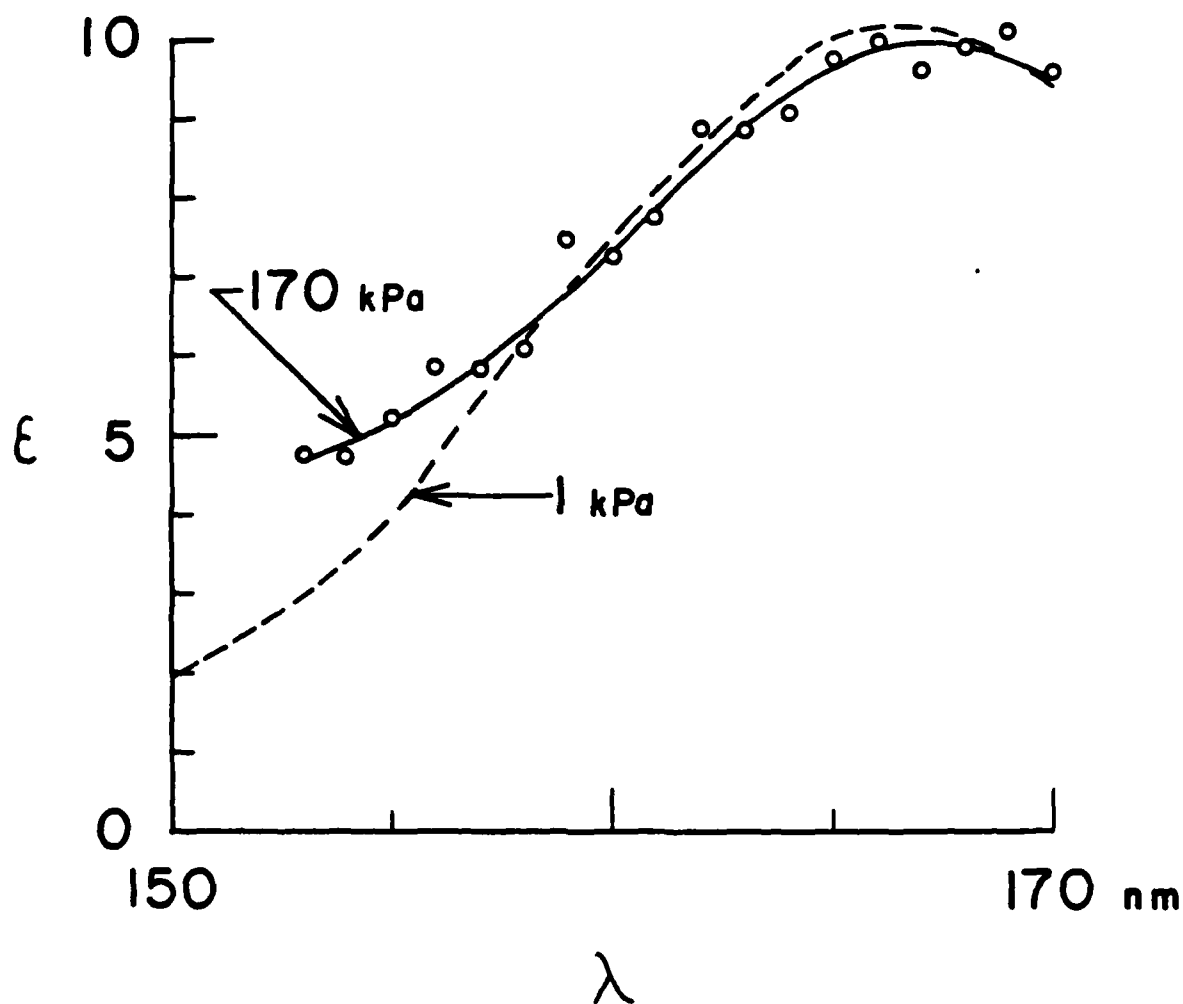


Figure 2.

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