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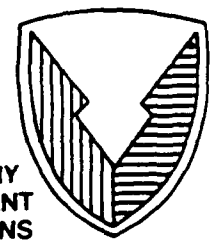
**ION CONTENT AND INFRARED ABSORPTION
OF MOIST ATMOSPHERIC AIR**

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by **Hugh R. Carlon**
RESEARCH DIRECTORATE

October 1987

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19 ABSTRACT (Continue on reverse if necessary and identify by block number) New measurements have been made of anomalous infrared absorption in moist air using a White cell and optical path lengths of 56.4 and 94.0 m. Simultaneous measurements were made of the ion content of the moist air, which was humidified by boiling water in a recirculating system. Data are presented for absorption cross section, self-broadening coefficient, and ion content as functions of humidity. The results show that the infrared absorption is proportional to the ion content of moist air, and that the observed behavior is consistent with the theory that ions are formed by dissociation of huge populations of large neutral clusters that are formed by evaporation, and these are responsible for much of the infrared continuum absorption. Other theoretical aspects and projected work are discussed briefly.					
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PREFACE

The work described in this report was performed under Project No. 1L161101A91A, Independent Laboratory In-House Research (ILIR). This work was started in January 1981 and completed in December 1982.

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This report has been approved for release to the public.

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*The Chemical Systems Laboratory is now known as the U.S. Army Chemical Research, Development and Engineering Center.

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ION CONTENT AND INFRARED ABSORPTION OF
MOIST ATMOSPHERIC AIR

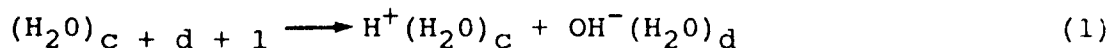
1. INTRODUCTION

Anomalous infrared absorption by water vapor has been studied for nearly two decades at this laboratory.¹⁻¹² The problem is extremely complex, but the following points seem to be reasonably well established by this work.

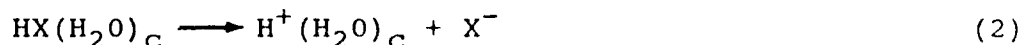
- Water vapor and moist air contain enormous populations of electrically-neutral molecular clusters. They are present in peaked statistical size distributions with typical mean sizes of 10-30 water molecules (monomers) per cluster.^{11,13} The neutral water clusters are formed primarily by the evaporation of liquid water, water solutions, or droplets.

- Intermolecular and rotational modes of these neutral cluster distributions account for much (perhaps most) of the infrared water vapor continuum absorption and can explain the amplitude and wavelength dependencies of this absorption versus temperature and humidity.^{9,13}

- These neutral clusters dissociate to a very small extent to yield ions by reactions that might be represented, e.g. by¹⁴⁻¹⁸



or



where X^- could be a negative ion or an electron. This dissociation can be enhanced by using an ionization source, e.g. a β -emitter.¹¹

- If, and only if, liquid water is in contact with its vapor, it is an essentially closed system.^{17,18} Equilibrium vapor populations of neutral clusters and dissociative ions will be approached that are much larger than those commonly observed in dynamic atmospheres. These equilibria have time constants of minutes to hours.

- High, nonequilibrium populations of neutral clusters can be induced artificially in water vapor in moist air by evaporating water at a higher-than-ambient temperature, e.g. by using steam.⁷ When the higher-temperature evaporation stops, ambient equilibrium is recovered in minutes to hours.

- The presence and nature of neutral water clusters in vapor can be inferred by infrared absorption measurements, but these clusters cannot be measured directly. Neutral water cluster's dissociative ions, however, being present in presumably proportional but much smaller numbers, can be monitored by electrical conductivity^{14,16-18} or by mass spectrometric^{11,13} measurements.

- New experimental results are presented in this report, which seem to support this theoretical model of water vapor. The effects of humidity on infrared absorption and ion content of moist air are examined.

2. EXPERIMENTAL PROCEDURE

Visible and infrared absorption/extinction measurements were carried out in a variable-path optical cell (White cell) shown in Figure 1 and represented schematically in Figure 2. The base length of the cell was 4.7 m, but it is shown truncated in the figure. A He:Ne laser beam (wavelength, $\lambda = 0.63 \mu\text{m}$) was reflected from mirror M_1 through a spatial filter consisting of a 50 mm microscope objective O , a precision pinhole P , and a lens L_1 onto a rotatable beamsplitter B_1 . The beam was then focused by viewing a white screen at I , where it was superimposed on the image of the infrared source S reflected from mirror M_2 through beamsplitter B_1 . The distance from I to B_1 was the same as from F_1 to B_1 , via mirror M_3 . Thus, the He:Ne and infrared beams were focused at the first focal point of the White cell (F_1) and passed together through multiple reflections via mirrors $A' B A$ to the exit focal point F_2 and then, via mirror M_4 to beam-splitter B_2 where they were divided between laser detector D_v and the radiometer (described previously⁴), which was focused at F_2 .

Because the visible laser beam was scattered by developing hazes and water fogs, it was used to monitor the onset of such liquid specie formation in measurements at higher humidities, before extinction in the infrared wavelengths was noted. The radiometer continuously scanned at the 3-5 μm and 8-14 μm atmospheric window wavelength regions. The developing fogs could be monitored by observing near-infrared spectra and comparing them with various fog and haze models. Since the

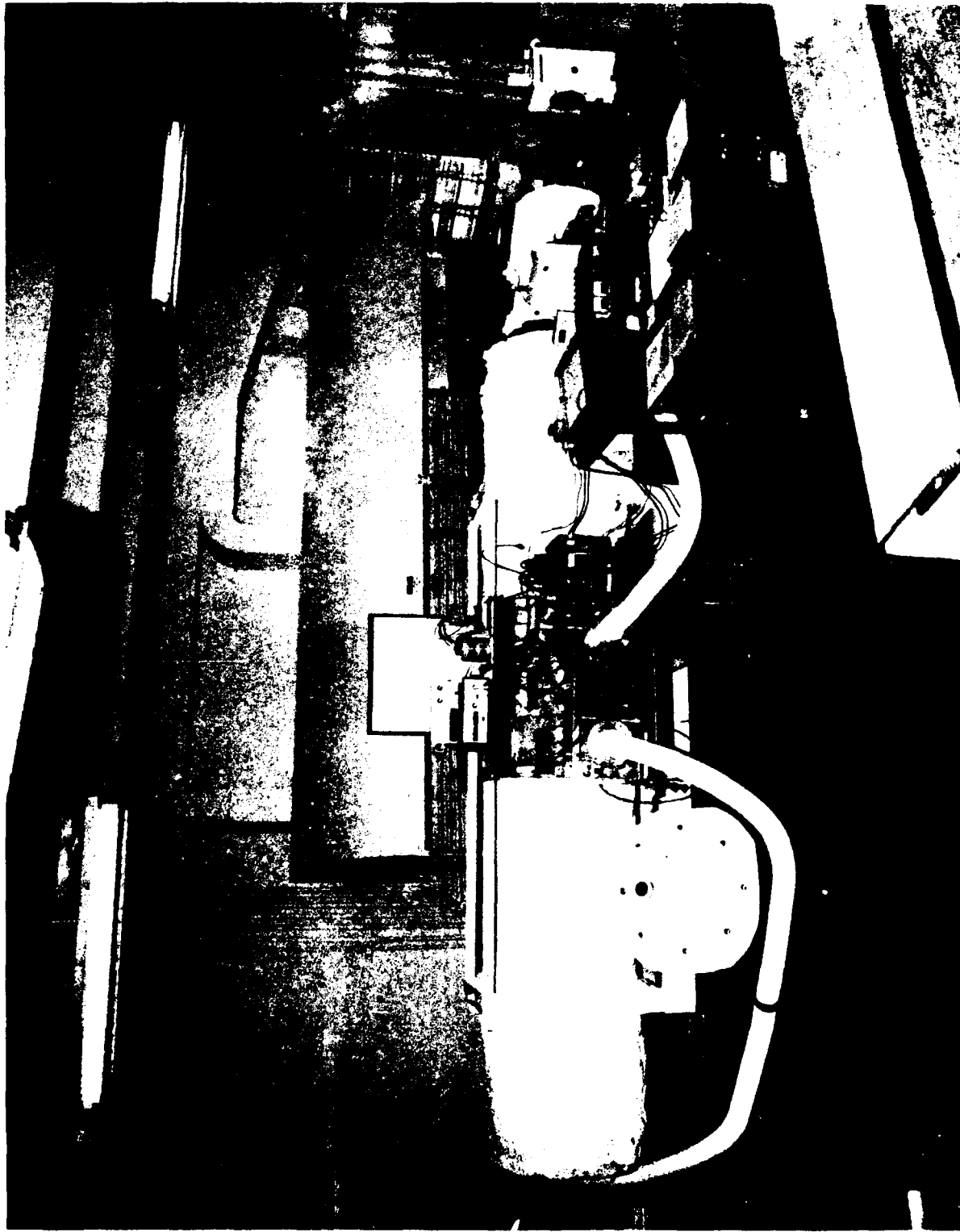


Figure 1. White Cell Used in Spectral Measurements
Described in this Report.

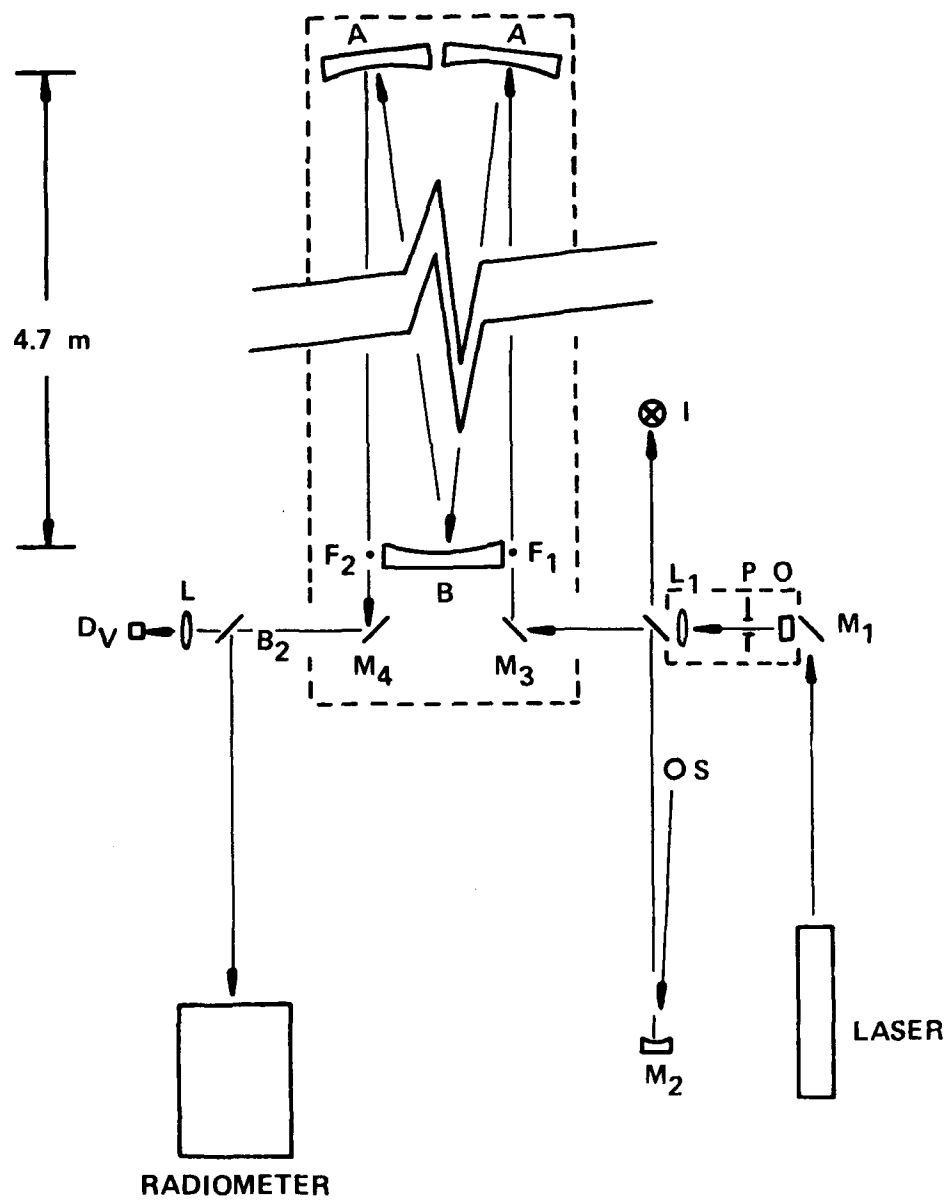


Figure 2. Schematic Representation of Optical Cell (White Cell) Experimental Layout.

8-13 μm wavelengths were the last to be extinguished under high-humidity conditions, most data reported here were taken for these longer wavelengths.

Electrical conductivity of the moist air was monitored by vapor cells of a sensitive new design, described elsewhere.^{10,18} The air was continuously recirculated through the White cell and through a lucite cabinet containing the electrical conductivity cells. The White cell and cabinet were connected by 3-m sections of 10-cm-diameter wire-supported plastic hose. The lucite cabinet included provisions to humidify the recirculating air by boiling water, and to measure relative humidity by wet and dry bulb thermometry. A 10-cm muffin fan recirculated the moist air through the hoses, White cell, and cabinet. While the data reported here were for steam-humidified air, i.e., air humidified by boiling water, recent results¹⁸ have shown that similar results are obtained by simple evaporation of liquid water at ambient temperatures. Thus, although some cluster and ion enhancement resulted by boiling, the results reported here are numerically correct and are extrapolable to ambient air conditions.

Each set of measurements was initiated at ambient room conditions. A "100% line" spectrum was run after all equipment had stabilized. Another reference spectrum was taken at the conclusion of each measurement set to confirm that drift of system components had not occurred. Humidification, using boiling water in a side chamber of the Lucite cabinet, was continuous, and the recirculating air increased steadily in humidity. At desired intervals, infrared spectra were scanned (30-sec scan time) and temperature and humidity were recorded. Within an hour or less, humidities approaching 100% were obtained. As haze and droplet formation occurred, it was noted by a rapid drop in the transmittance of the He:Ne laser beam and near infrared spectra were scanned more slowly to observe droplet growth. Electrical conductivity of the moist air was monitored continuously, and the small ion (ion hydrate) concentrations were thus calculated.¹⁰ Infrared absorption coefficients were calculated from transmittance referenced to the 100% line.

3. EXPERIMENTAL RESULTS

Several kinds of experimental data are shown in Figures 3, 4, and 5. Although it is known that the manner and rate of humidification are important in determining cluster and ion populations and sizes,¹⁸ data taken under all experimental conditions are shown together here because this simulates the

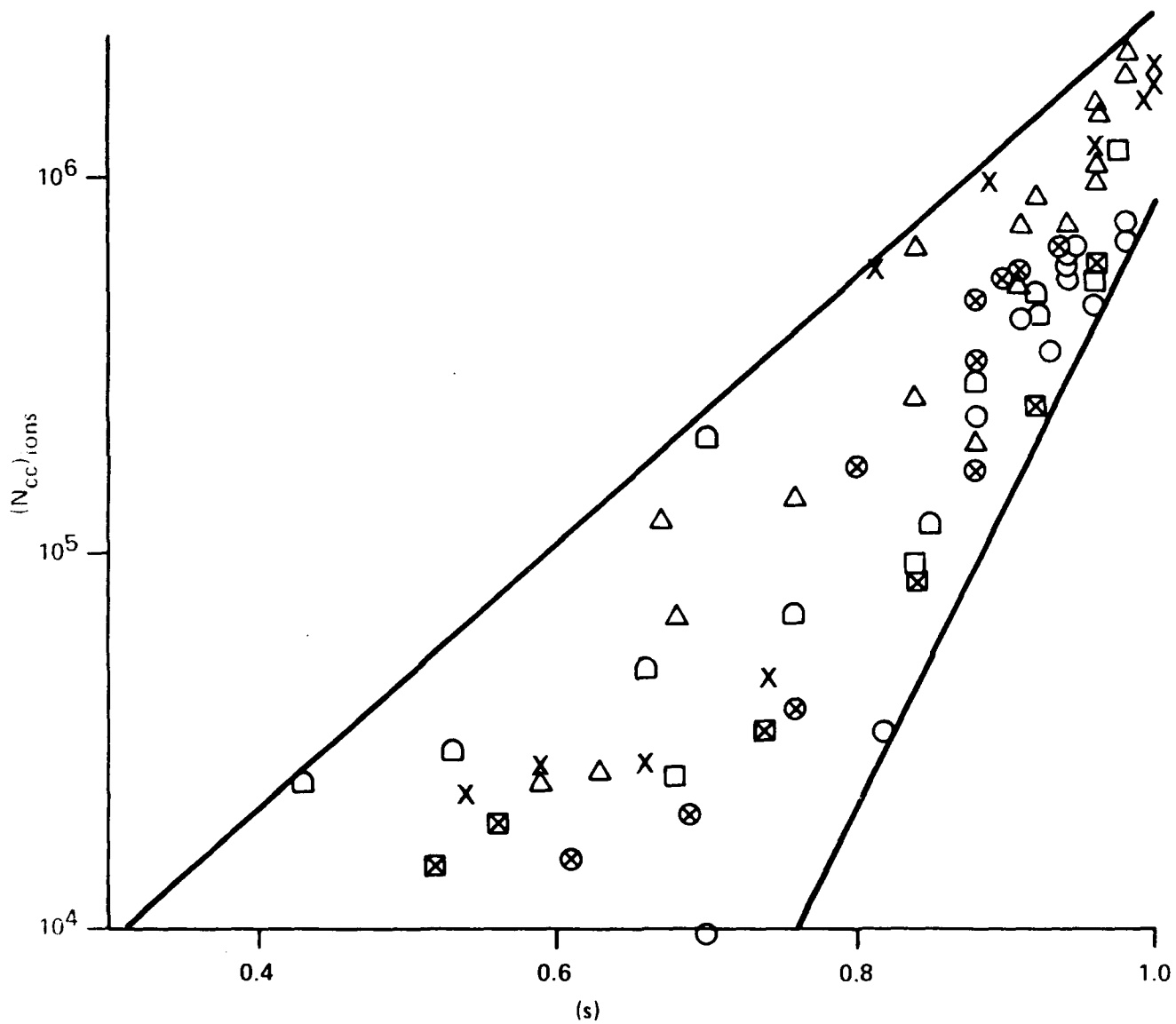


Figure 3. Number of Water Ions/cm³, N_{cc} Measured for the Full Range of Saturation Ratios, $s = \% \text{ R.H.}/100$, Used in the Experiments Summarized in Table 1.

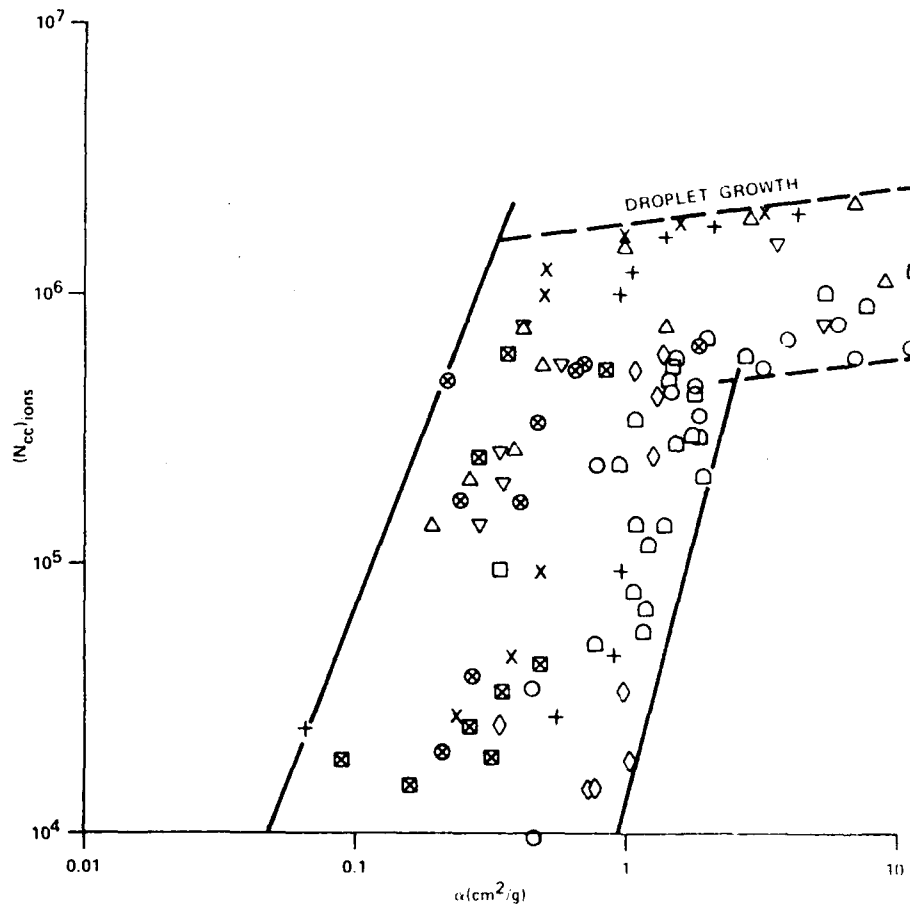


Figure 4. Number of Water Ions/cm³, N_{CC} Measured in Experiments Summarized in Table 1 vs. Measured Values of the Absorption/Extinction Cross-Section, α (cm²/g).

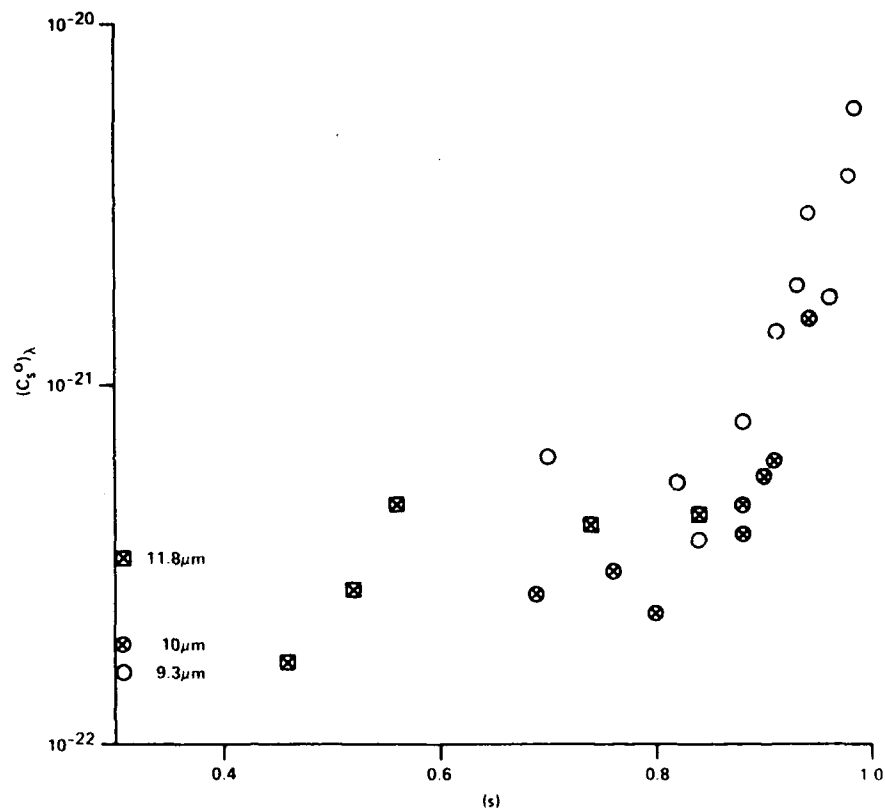


Figure 5. Values of $(C_s^0)_\lambda$, the Self-broadening Coefficient ($\text{cm}^2/\text{molecule-atm}$) vs. Saturation Ratio, $s = \% \text{ R.H.}/100$, for the Experiments Summarized in Table 1; the Three Points Arbitrarily Placed Above $s = 0.31$ Are Expected Values From Reference 19.

variability of atmospheric processes and helps to show why, e.g. measurements of the absorption of water vapor or moist air into the infrared continuum region, show such a wide variability. In Figure 2, the number of water ions per cm^3 N_{CC} is shown versus the fractional relative humidity or saturation ratio, $s = \% \text{ r.h.}/100$, for the full range of experimental data. All points are contained between the two diagonal lines. A key to the points, and those of Figures 3 and 4, is given in Table 1. For these relatively constant temperature data, N_{CC} increases approximately as $(s)^6$ with increasing humidification. Such a sharp dependency is not uncommon.¹⁸ Note in Figure 2 that by the time N_{CC} has reached 10^6 for these experimental conditions, virtually all data points lie above 90% r.h., i.e. $s > 0.9$.

There is little point in continuing most measurements of water vapor absorption beyond $s = 0.9$. This is the domain of very rapid droplet growth, and absorption becomes confused by droplet scattering (extinction). This is shown in Figure 3, where the absorption cross-section α (cm^2/g) is observed to increase gradually (for the same conditions as Figure 2) up to about $N_{\text{CC}} = 10^6$, where as $s \rightarrow 1.0$ (100% r.h.), α obtains very large values due to droplet growth and extinction. This can also be seen if values of the self-broadening coefficient¹⁴ for water vapor, $(C_{\text{S}}^0)_{\lambda}$ in $\text{cm}^2/\text{molecule-atm}$, are calculated from the relationship:

$$(C_{\text{S}}^0)_{\lambda} = \frac{2.28 \times 10^{-20}}{s \cdot p_0} \cdot \alpha \quad (3)$$

where p_0 is the saturation vapor pressure (Torr), and are plotted against s , as is done in Figure 4. The increase in $(C_{\text{S}}^0)_{\lambda}$ where $s > 0.9$, due to droplet growth, is unmistakable. The three points arbitrarily placed above $s = 0.31$ show the values of $(C_{\text{S}}^0)_{\lambda}$ expected from earlier data and modeled by an equation given by Roberts et al.¹⁹ Figure 4 indicates these values are at least of the correct magnitude for lower values of s . The $9.3 \mu\text{m}$ wavelength is troublesome, however, with large values frequently being observed even when $s \sim 0.7-0.8$ or less. Spurious data points also were noted in this wavelength region.¹⁹ Also, it is known that α and $(C_{\text{S}}^0)_{\lambda}$ are dependent, especially at longer wavelengths in the infrared continuum absorption region, upon s for reasons that can be attributed to neutral water cluster activity¹⁴ in vapor. If curves could be fitted accurately through points like those in Figure 4, it is likely that they would not simply descend to the lower left, but would pass through one or more maxima at intermediate values of saturation. Previously it was thought that while the region where $s > 0.9$ in Figure 4 was the domain of droplets, the region where $s < 0.9$ must be that of single water

Table 1. Key to Figures 2-4.

Symbol	Wavelength, λ (μm)	Optical path length, L (m)	Air temp. ($^{\circ}\text{C}$)
○	9.3	56.4	24-26
□	9.3	56.4	24-27
△	11.78	56.4	24-27
▽	4.04	56.4	24-27
⊗	10.00	56.4	27-29
⊠	11.78	96.4	27
◇	13.31	94.0	27
×	11.78	94.0	28-29
+	13.31	94.0	28-29
△	13.31	94.0	28-47

molecules (monomers). Now it is known that for true cluster and ion equilibria to exist, liquid water must be present in the system.¹⁸ These were the conditions for the data presented in this report. Thus, a cluster domain must exist in the region $s > 0.9$ which accomplishes the phase transition between the liquid (droplets) and individual monomers, but this cluster domain apparently extends to values of s far smaller than those shown in Figure 4. For example, some neutral cluster activity is believed to exist even when $s < 0.01$.

4. DISCUSSION

Even the simplest water cluster models suggest that for "loose ends" of hydrogen-bonded water molecule clusters, the approximate wavelength of resonance is given by:^{8,9}

$$\lambda = 6.4 \sqrt{c} \quad (4)$$

where c is the cluster size. The constant 6.4 was evaluated from steam spectra⁹ for the special case of ion clusters, but for any two bonded molecules one could take $c = 2$ so that Equation (4) yields $\lambda = 9.05 \mu\text{m}$, which is close to the wavelengths of spurious spectral activity noted in the discussions of Figure 4 and literature reference 19. Measurements of infrared emission of water fogs that are produced by saturated steam and that are allowed to cool and to dissipate show that: (1) about equal amounts of

emission can be attributed to droplets and to clusters; and (2) when the droplets finally evaporate, the cluster emissions also fall abruptly to much lower values.⁷ Reference 7 also discusses many other kinds of evidence for cluster activity in cooling, steam-generated fogs. Thus, it seems highly likely that in the presence of liquid water, especially in droplet form, neutral cluster activity in the vapor is greatly enhanced. Evaporation, in fact, seems to be the primary mechanism for the formation of these clusters; they do not need to grow from dimers, trimers, etc.¹³ Even water droplets formed on soluble condensation nuclei eventually evaporate to leave behind reusable nuclei as the water is distilled off in drier air. This, to a large extent, is a statistical process, i.e., with nearly-dry salts being characterized by specific numbers of 'waters of hydration' (molecules) arranged in specific crystalline forms not unlike neutral water clusters themselves. There is no prima facie reason why those water molecules that escape from droplet/vapor interfaces cannot escape as homogeneous water clusters rather than monomers. Although their final shapes and sizes might be determined in the interfacial boundary layer by processes that are yet unconsidered, they could be described by existing kinetic theory.

In a typical atmospheric case, the ion populations (N_{CC}) shown in Figures 2 and 3 would not be present in moist air because the equilibria and cluster enhancement elements of these experiments would not exist. Rather, the ion cluster populations typically would be 10^2 - $10^3/\text{cm}^3$, and these would be dissociative products of a proportionately lower neutral cluster population. Optical paths many times longer than those used here would be needed to measure comparable levels of water vapor absorption. Conversely, in a fog formed from cooling steam,⁷ a path length of only 3 m is sufficient to give strong infrared absorption/emission comparable to that obtained using path lengths of 56-94 m in the present work (Table 1).

5. CONCLUSIONS

The preliminary measurements briefly reported here have shown that:

- The absorption cross-section (cm^2/g) and the self-broadening coefficient, $(C_S^0)_\lambda$ ($\text{cm}^2/\text{molecule-atm}$) of water vapor are proportional to the ion content per cm^3 , N_{CC} , of water vapor, up to humidities such that droplet growth and extinction (scattering) become significant.

- The function $(C_S^0)_\lambda$ versus saturation ratio s (Figure 4) is not necessarily continuous and smooth, although measurements at lower s tend to approach accepted values, except for wavelengths near $\lambda = 9.3 \mu\text{m}$.

- The observed behavior is compatible with the theory that ions are formed by the dissociation of huge populations of large neutral clusters in water vapor, and with other points of theory raised in the Introduction.

- Under conditions of cluster enrichment, e.g. using steam humidification of air as in the work reported here, accurate measurements of $(C_S^0)_\lambda$ can be obtained over much shorter optical path lengths than would be required in the atmosphere. Measurements, of the kind reported here, will be continued in the coming months at specific wavelengths where unusual activity has been noted, e.g. at $\lambda = 9.3 \mu\text{m}$. Results of interest will be communicated subsequently. Also, a theoretical development will be undertaken to explain neutral cluster formation at the liquid/vapor interface during evaporation.

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