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The extinction efficiency of water in the form of vapor, water cloud, and ice cloud per molecule for the 1.27 μm to 4.2 μm region

by

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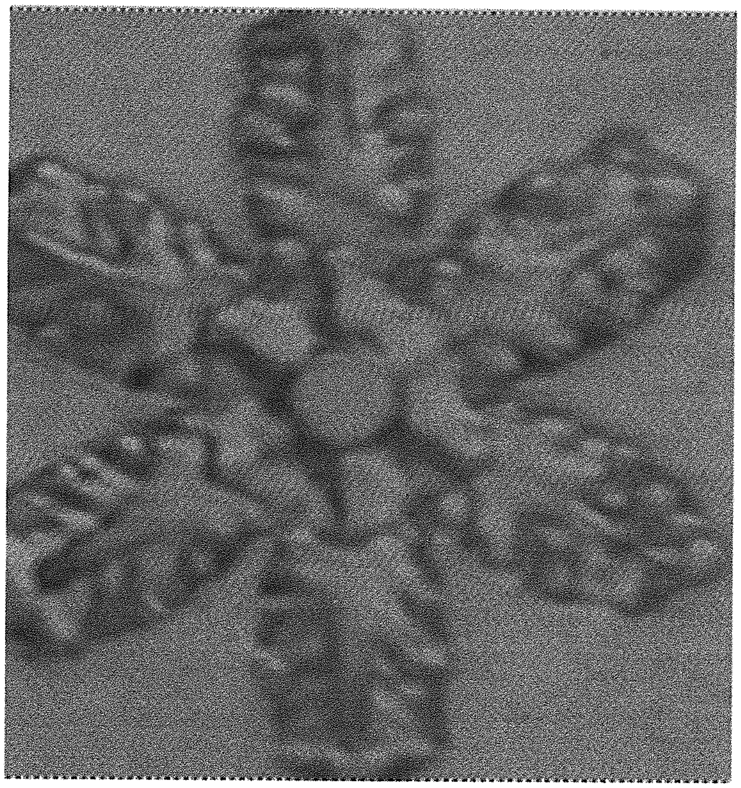


ABSTRACT

Extinction measurements with a laser (0.685 µm) and a Fourier transform infrared spectrometer (1.27-4.2 µm) were performed on the three basic phases of water in a laboratory setting. The extinction efficiency per molecule was calculated for water vapor, water clouds, and ice clouds. For ice clouds, measurements were taken at a variety of temperatures and thus a variety of crystal habits and average projected area. A cloud video microscope was used to measure particle sizes. The IR spectral optical-depth measurements revealed an extinction minimum at 2.75 µm for the water cloud, and 2.84 µm for the ice cloud. Water vapor showed bands of absorption in the same area as well as around 1.8 µm and 1.4 µm. Water clouds had the highest extinction efficiency per molecule over most of the range. Ice clouds had extinction efficiencies about 10% lower. In comparison with the broad spectra of the condensed phases of water, water vapor only had absorption spectra at selected wavelengths. Water and ice IR spectra are interpreted in relation to the bulk refractive indices of each, and applications to Atmospheric Sciences are discussed.

INTRODUCTION

Understanding how radiation is transferred in the atmosphere has many far reaching consequences. Ultraviolet, visible, and IR radiation from the sun are constantly bombarding the planet. The atmosphere is composed of gasses and particles that interact with radiation. Water vapor, and water droplets and ice crystals in clouds are obstacles for solar radiation on its way to warming the planet.

Cirrus clouds regularly cover about 20%-30% of the globe.[1,2] Cirrus clouds are composed of ice crystals because of the cold environment of their surroundings. Cirrus clouds are sufficiently abundant that they can have a large influence on the temperature in the upper troposphere and can play a significant role in the earth's radiation budget.[3] These high clouds can dramatically affect weather. Man-made ice clouds such as contrails can be regularly seen, though the global impact of such clouds is not clear at present.

El Nino (an oceanic warming on the Pacific coast) has been seen to cause dramatic changes in the atmosphere. The surface of the ocean heats up as much as 2-4 K.[4] This causes highly reflective cirrus clouds to form. These clouds are hypothesized to shield the ocean from solar radiation, acting to stabilize warming.[4] Understanding radiative transfer in these clouds could lead to better weather models for the Pacific coast.

A major concern among environmentalists is the global warming caused by the rise in CO_2 concentrations in the atmosphere. Thin cirrus clouds are thought by some to enhance the "greenhouse effect".[5] The relationship between size and shape of ice crystals and the gross radiative properties of cirrus clouds are poorly understood. Their effect on the greenhouse effect cannot be fully understood without knowing more about the make up of these clouds and how radiation is transferred through them.

Studies have shown that cirrus clouds with a large concentration of very small particles (below 50 μm) will actually absorb and scatter more solar radiation than insulate the planet by partially trapping outgoing terrestrial IR radiation.[5] Aircraft studies have indicated that small particles can contribute significantly to and sometimes dominate solar extinction and infrared emission.[6]

Knowing how these clouds work will help us understand global warming better. The composition of cirrus clouds can significantly affect the way radiation is transferred.

A Christiansen filter is similar to filters based on absorption of light in that both types have a passband of wavelengths. A Christiansen filter works by scattering wavelengths not desired and not scattering the desired wavelengths.[7] A simple example of the Christiansen effect that Christiansen filters are based on can be performed by coating a pitted car windshield with a fluid that closely matches the refractive index of the windshield. Filling in the pits with an index matching fluid eliminates nearly all light scattering by the pits. Ice clouds can be used as Christiansen filters. Wavelengths around 2.8 microns (where the real index of refraction for ice is near that of air, unity) will pass through ice clouds with greatly reduced scattering. All other wavelengths where the index of refraction is different from one will experience appreciable scattering. Absorption will still take place at 2.8 microns, since ice has an appreciable imaginary portion of the refractive index, but refraction will be significantly reduced.

Radiation transfer in the atmosphere is complicated significantly by the presence of water. Water is found in three forms in varying amounts throughout the atmosphere. Water vapor accounts for the largest portion of water in our atmosphere. For example, at 20 ^oC there can be approximately 20 grams of water per cubic meter in the form of water vapor. Relatively warm clouds such as cumulus clouds contain approximately 0.02-2 g/m^3 in the form of water drops. Relatively cold clouds like cirrus are composed of ice crystals and only contain about 1-100 mg/m^3.[8]

Extinction is the measure of a particle's ability to remove energy from an incoming beam. An extinction measurement consists of a light source and a detector separated by some distance, with a cloud of particles or gas in between. When the cloud or gas is present some power is removed (or extinguished) from the forward direction by the process of elastic scattering or absorption. Scattering changes the direction of the photon, while an absorbed photon will have its energy converted to heat.

Extinction of light in the visible by cloud droplets or ice crystals is related mainly to projected area.[9] At IR wavelengths particles of water or ice deviate from that rule substantially. Laboratory measurements of ice and water clouds are useful to better understand the scattering properties of cirrus clouds.

The extinction efficiency is defined as $\langle Q_{extIR}(\lambda)\rangle = 2(\tau_{IR}/\tau_{vis})$ where $\tau = -\ln(T)$, and T is the transmission measurement for the wavelength in question. $\langle Q_{extIR}(\lambda)\rangle = 2$ when τ_{IR} and τ_{vis} are equal. This paper reports on the measurement $\langle Q_{extIR}(\lambda)\rangle$ for laboratory ice clouds, water clouds, and τ_{IR} for water vapor. This paper also reports on the extinction per molecule for each phases.

EXTINCTION MEASUREMENTS

The experimental arrangement is shown in Fig 1. The cloud region is the interior of a box measuring 1 m high x 1.2 m x 1.2 m. A precooling chamber (a vertical tube with antifreeze circulation around the outside jacket with a diameter of 15 cm and a height of 92 cm) sits above the box to precool water droplets (for the ice cloud measurements only) from an ultrasonic nebulizer. A thin sheet of plastic wrap (generic supermarket brand had less absorption than both more expensive brands and a Mylar sheet) serves as a window to the box for both IR and visible radiation. The plastic wrap served to keep the cloud in the box. A curved mirror of 152.4 cm and diameter of 15.2 cm reflected the visible and IR beams. A resistance heater was placed on the back of the mirror to prevent condensation. The actual path length for both the IR and the visible was 228 cm.

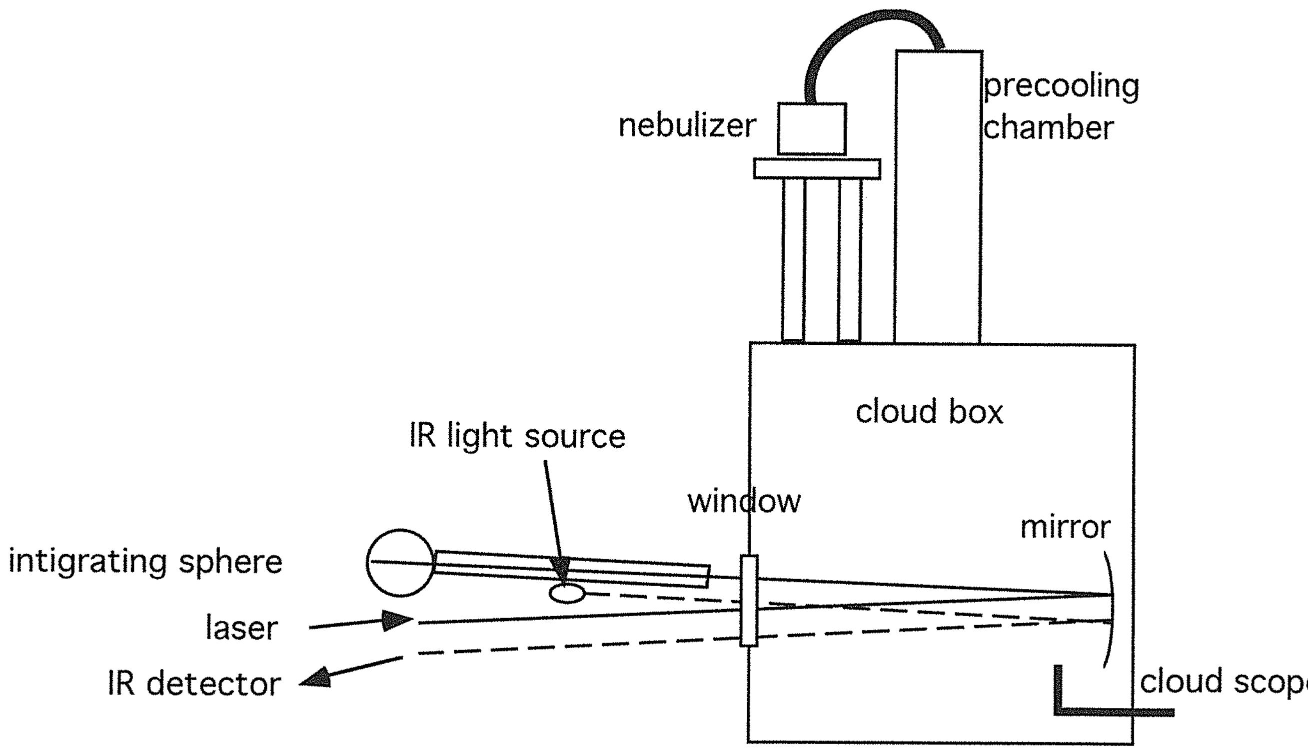


Fig 1. Schematic arrangement for the extinction measurements.

An IR heating lamp was used as the IR source. The blackbody spectrum of the lamp was strong in the 1.27μm to 4.2μm region. The IR was collected by a mercury cadmium telluride IR detector attached to a Fourier Transform Infrared Spectrometer (Bomem manufacture) with a scanning Michelson interferometer. Operation of the spectrometer was controlled by computer that received the detector signal and performed the necessary Fourier transform of the spatial interferogram into the IR wavelength spectrum. Typically 30 scans were averaged over a period of 40 s with a resolution in wave numbers of 4 cm^{-1}.

A visible beam of wavelength 0.685 μm was used to measure the total projected area of particles in the chamber. The laser light was collected in an integrating sphere with an input port diameter of 3.8 cm. The entire unscattered beam was collected by the integrating sphere. The laser light passed through a 1.2m tube stopped down to approximately 2 cm to prevent stray light from entering the integrating sphere. A phototransistor was, on a side port of the integrating sphere, monitored the throughput of the laser. The signal from the phototransistor was recorded on a strip chart recorder.

EXPERIMENTAL PROCEDURES

The typical procedure for an extinction measurement for water vapor was to take a reference measurement in the IR and the visible just before adding water drops to the chamber. The relative humidity of the chamber was also taken just before adding water. Once the measurements were taken the nebulizer was turned on. After about 20 minutes, the visible optical depth was up to about 5. At this point the nebulizer was turned off. When the visible optical depth returned to zero (indicating that no more water drops were present) an IR transmission measurement (equal to the current IR spectrum divided by the reference spectrum) was taken. The relative humidity in the chamber was also taken again.

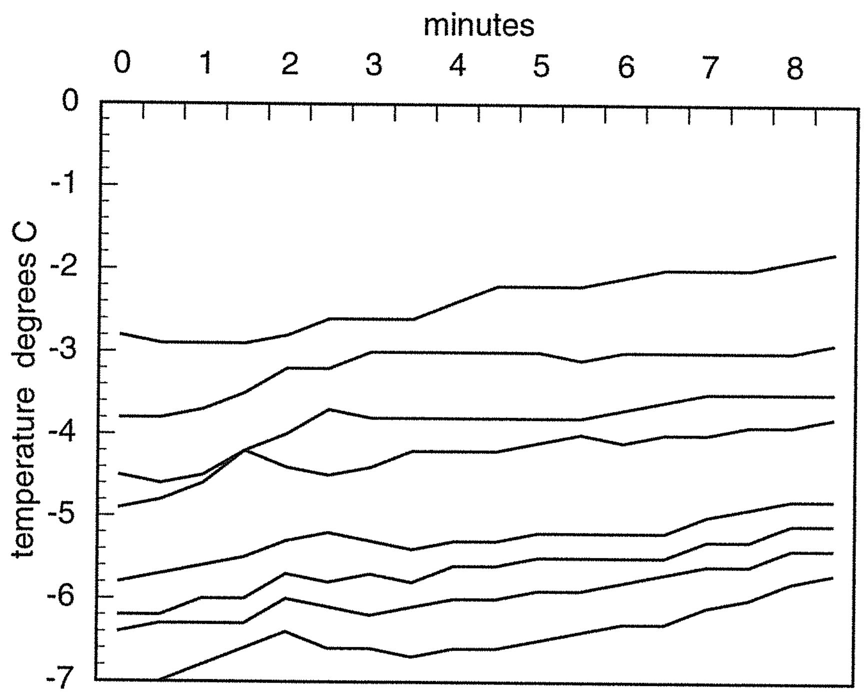


Fig 2. The temperatures at eight different levels in the cloud box during an ice crystal measurement. The lines are (from top to bottom) for 9, 21, 31, 43, 55, 67, 79, and 89 cm from the top of the box.

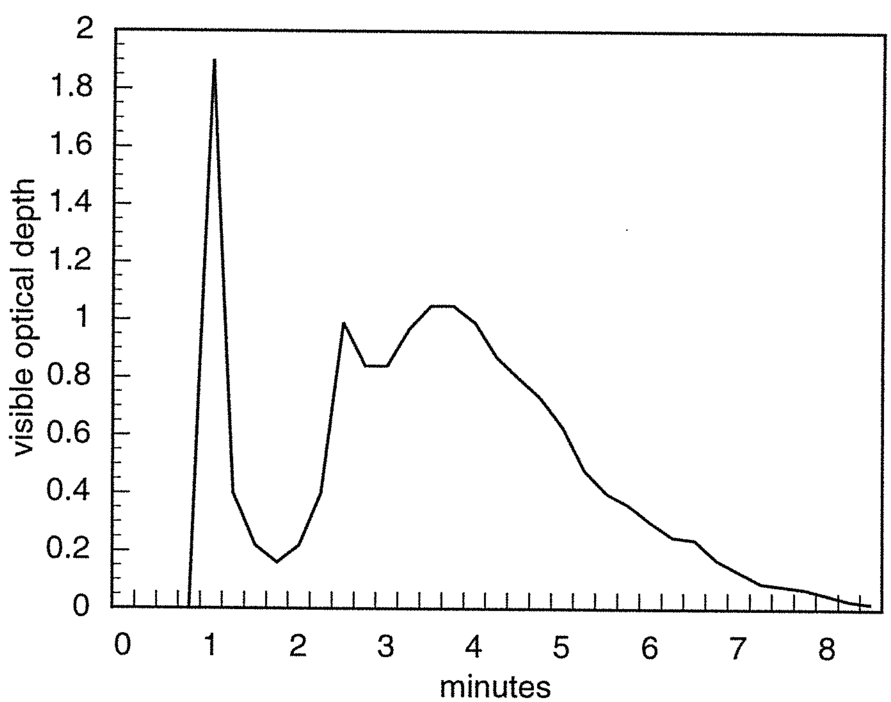


Fig. 3 Visible optical depth for a typical laboratory ice cloud life.

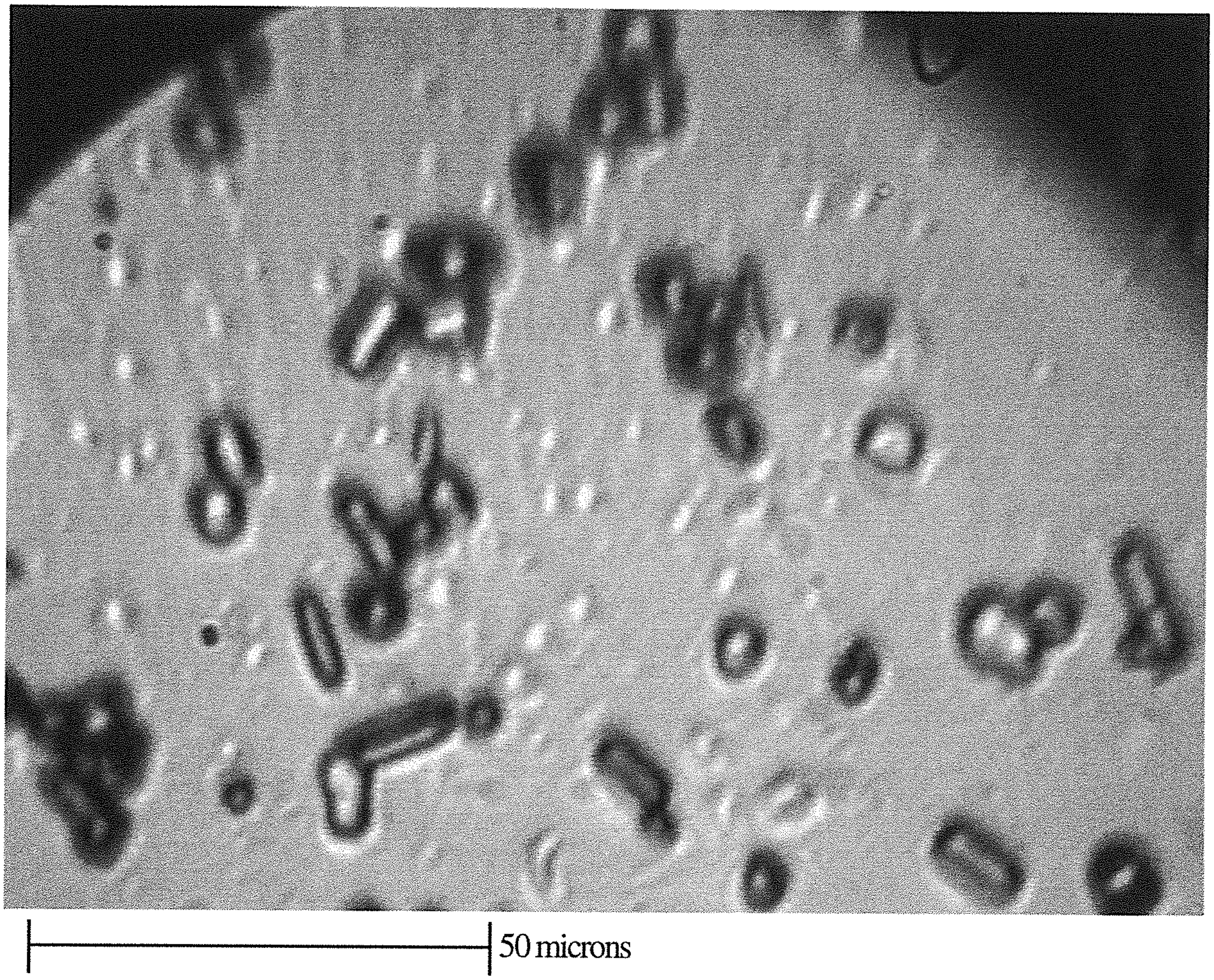


Fig. 10 An example of the typical cloud-scope view during a measurement.

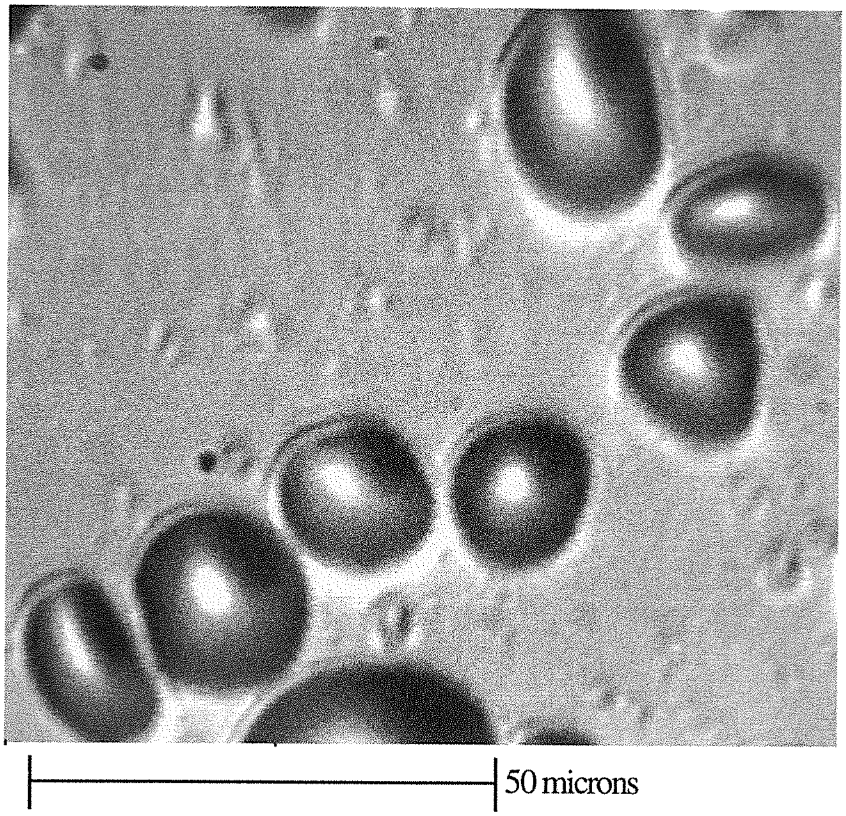


Fig 11 Water drops recorded on the cloud-scope.

RESULTS

Water vapor:

The cloud chamber was at a relative humidity of 35% when the references were taken for the vapor measurements. The optical depth in the IR (after the relative humidity in the chamber had been raised to 80%) is shown in Fig 12.

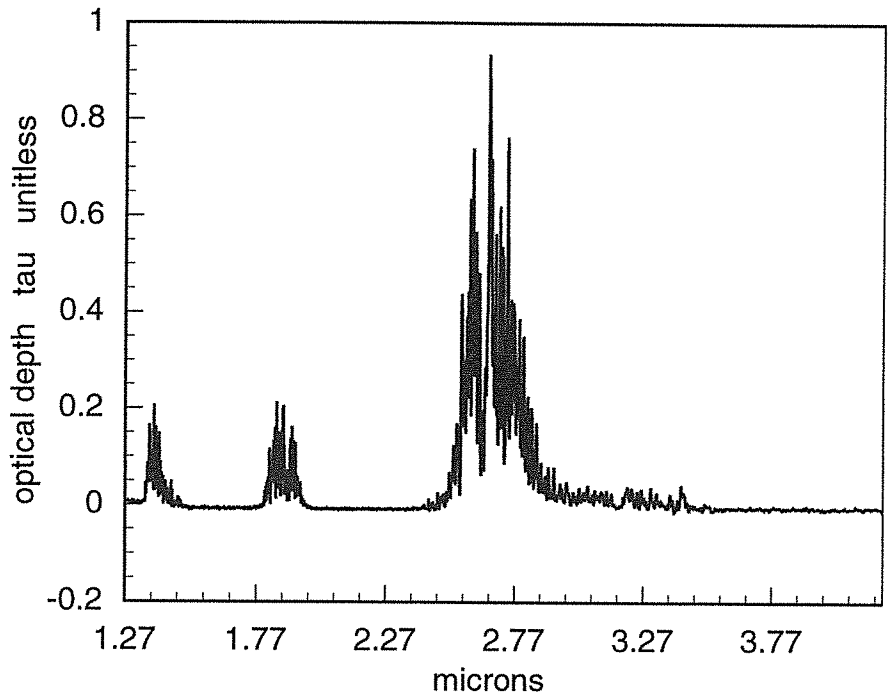


Fig 12 The optical depth of water vapor.

The math for calculating Fig 13 is located in Appendix A. Fig.13 is the extinction efficiency in barns for vapor.

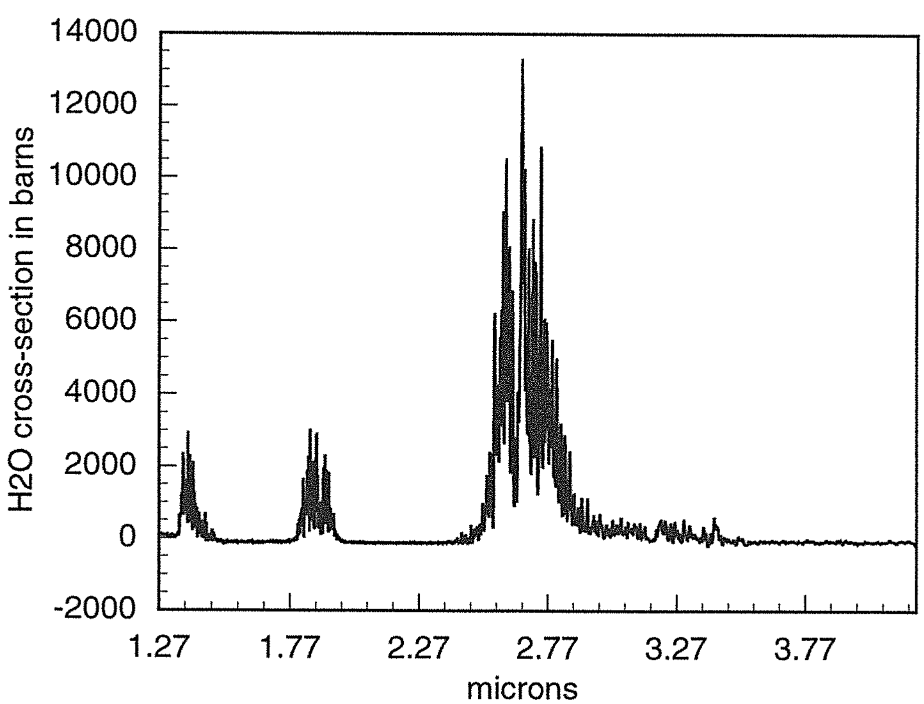


Fig 13. Optical depth in barns for water vapor.

Water clouds:

The water cloud made in the laboratory was very similar to a dense cumulus cloud at low warm elevations. A cumulus cloud has .02 to 2 grams of water in the drop form per cubic meter. The laboratory cloud generally had between 1 and 2 grams per cubic meter.

Figure 14 shows the average extinction efficiency for a water drop cloud over thirty trials. The water cloud extinction efficiency was very easily reproduced.

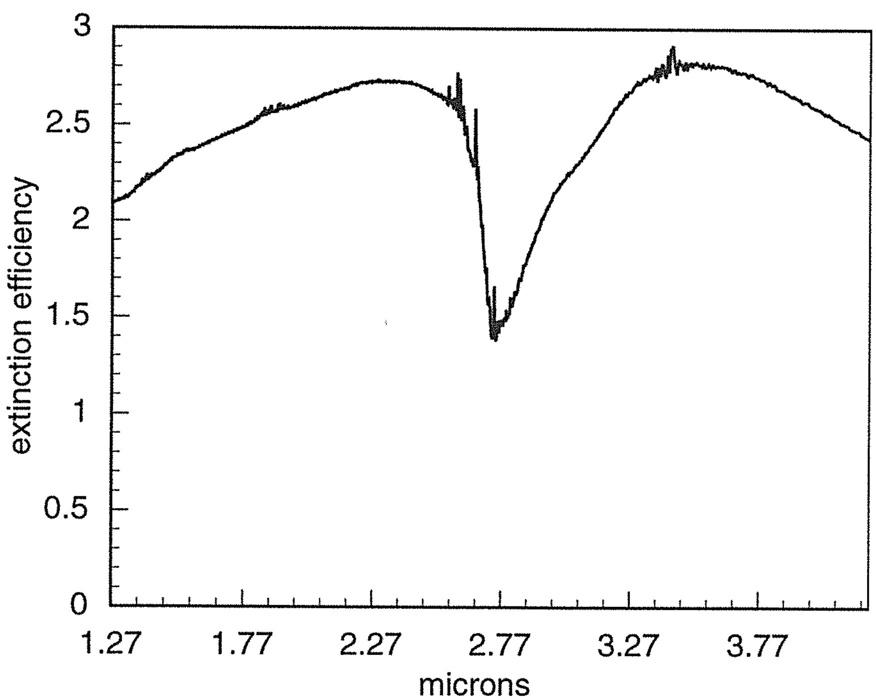


Fig 14 Extinction efficiency for the water drop cloud. $\langle Q_{extIR}(\lambda) \rangle$

The spikes in figure 13 at the 3.35 μm range are due to an absorption band in the plastic wrap. Other spikes in the dip and around 2.6μm were caused by taking the reference spectrum when the chamber was not saturated with water vapor.

Figure 15 shows the distribution of particle diameters normalized for a visible optical depth of one.

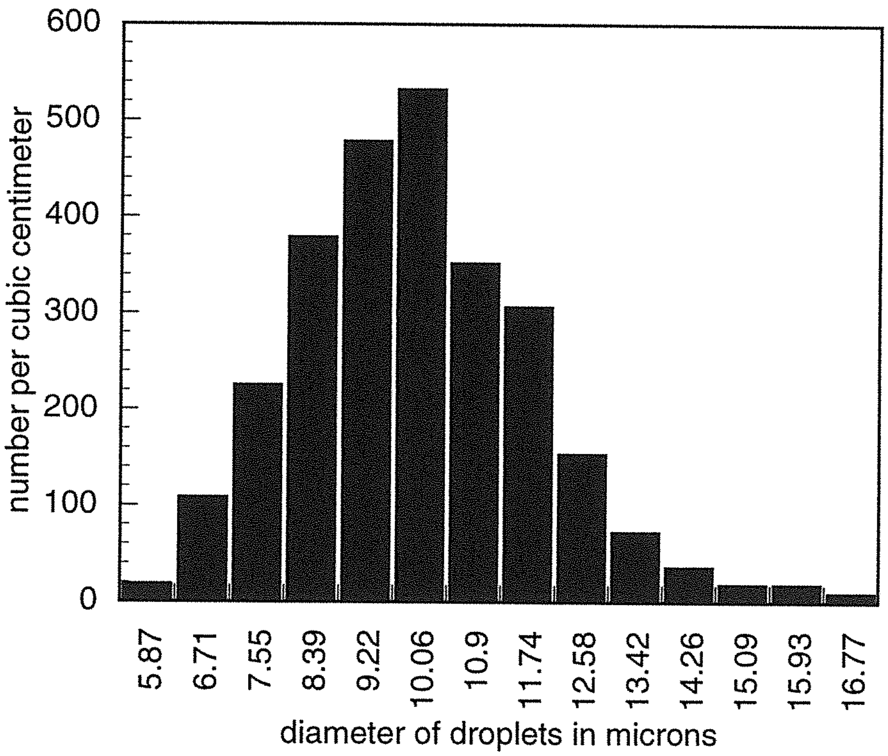


Fig 15 number of droplets per cm^3 for an optical depth of one.

Fig 16 is the optical depth in barns as calculated in Appendix B.

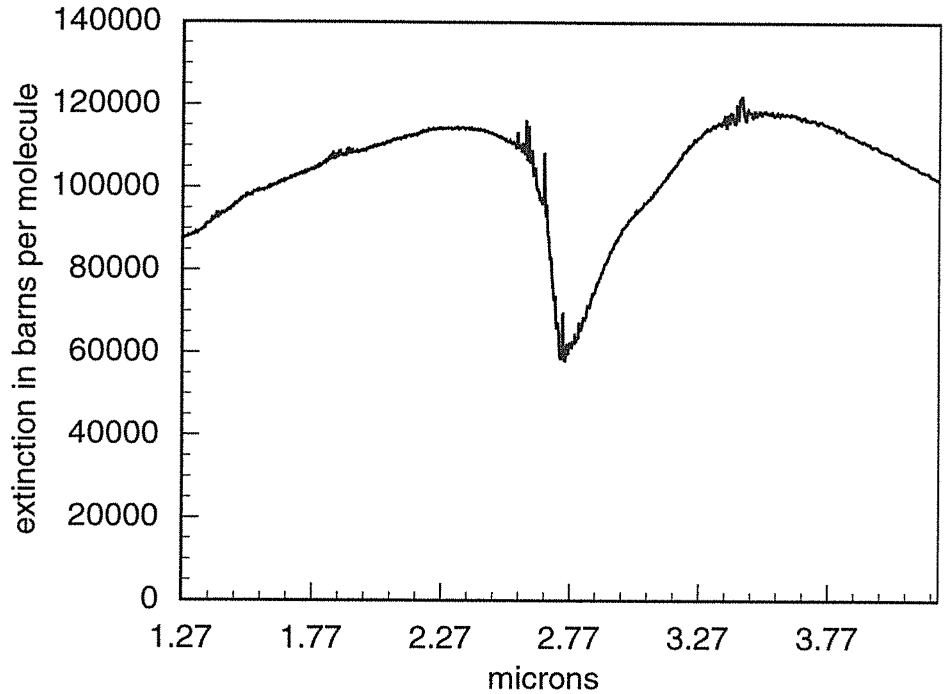
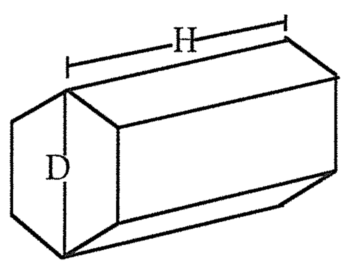


Fig 16 Optical depth in barns for the water drop cloud.

Ice clouds:

The laboratory ice clouds were much more dense than those found in nature. Cirrus clouds generally have 1 to 100 mg/m^3. Laboratory clouds had between 0.5 and 1.5 g/m^3 (from $\Sigma n_i V_i$ in appendex).

For ice crystals the shape of the crystal had to be taken into account.



The c axis of the crystal is referred to as H. D is the maximum dimension across the face of the crystal. When the crystals were mainly columns D and H were easily measured from cloud-scope pictures. For plate crystals H was estimated $H=1.41*D^{0.474}/100$.[9] The following criteria was used to choose good spectra for the ice cloud numbers: The visible optical depth had to be between 0.4 and 1.0 in order to minimize the effects of secondary scattering, and the visible optical depth had to be very steady throughout the 40 second IR reading.

While the spectra were being taken, the cloud-scope was capturing sample crystals. The areas and volumes were calculated for 240 of these crystals. The largest dimension of the ice crystal was measured to produce figure 17. The numbers were normalized to an optical depth of 1.

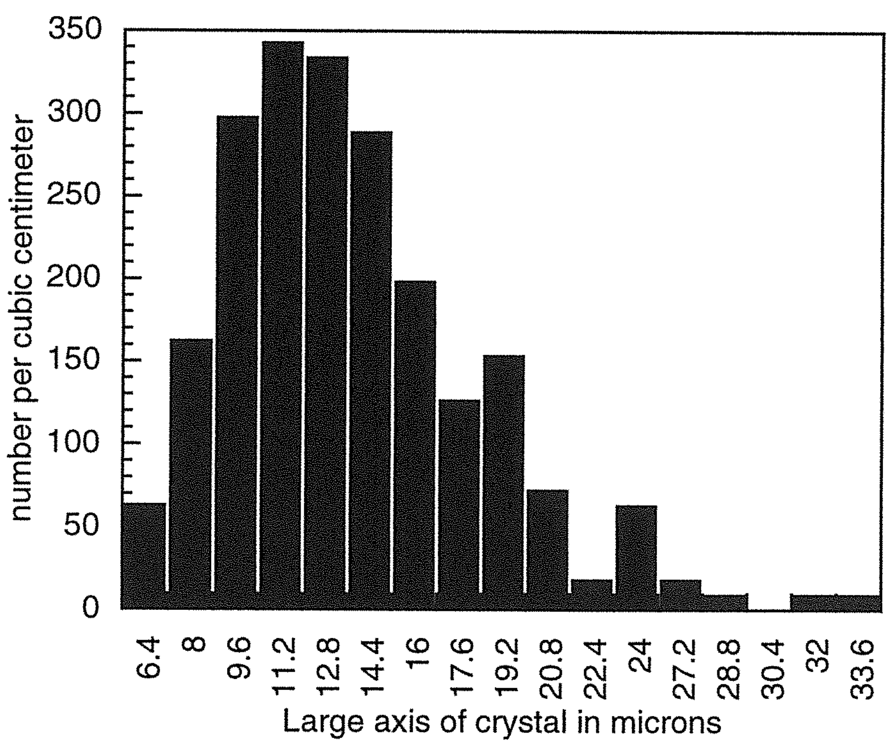


Fig 17. The size distribution of ice crystals normalized to an optical depth of one. The values are per cubic centimeter.

The math involved to calculate the extinction efficiency in barns for ice is in appendix C. The results are in figure 18.

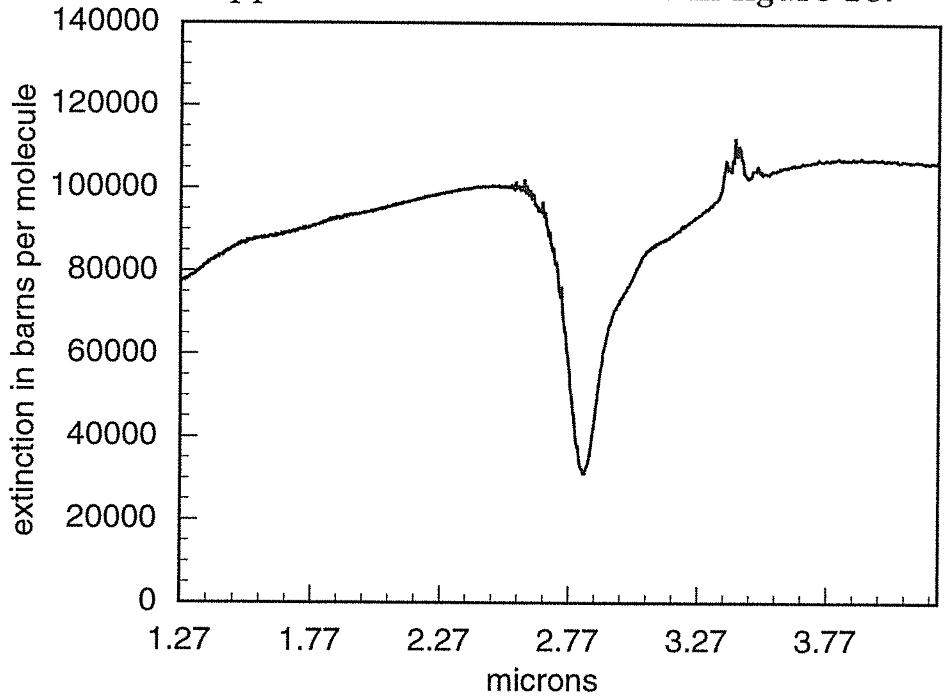


Fig 18 The extinction efficiency in barns for the ice clouds

DISCUSSION

Water vapor:

Water in the vapor form consists of single molecules in among the other gases in the atmosphere. The experimental data strongly suggests that water molecules only absorb photons of selected wavelengths. In the region studied, water vapor absorbed photons around 2.8, 1.9, and 1.4 microns. Studying the index of refraction for water it is noted that the imaginary part of the index of refraction increases rapidly at each of those wavelength areas. The multiple spikes at each area represent the transition of more than one state of the molecule. The 2.8 region, for example, is caused by O-H stretching in the water molecule. The multiple spikes indicate that a number of vibrational states exist. The lines in the water vapor spectrum are due to absorption only. Scattering (which would take place at a continuum of wavelengths) appears to not have played a role, because of the small size of the water molecule compared with the wavelength.

Water and ice clouds:

Solid State Physics teaches us that solids have energy bands (energy levels that will absorb a continuum of energies). Water vapor only absorbed at discrete energy levels. Water and Ice, because they have neighbors, do have energy bands and therefore absorb a wide range of energies.

When short wavelength photons hit a cloud of large particles (with respect to the wavelength) the extinction efficiency should normalize to two. This appears to be true of extinction efficiencies measured. They tend to stay somewhat near two when not in the Christiansen band. The reason the extinction efficiency goes to two is as follows. When a light beam hits a particle geometric optics says that the particle blocks out the amount of energy that is incident upon the particle. Common sense would indicate that this is correct, yet we see twice as much energy removed from the beam. A particle and a mask with a cut-out of the particle's shape will have the same diffraction pattern. Therefore we can replace the particle with a mask and observe its diffraction pattern. The amount of light diffracted by the mask is equal to the amount incident on the aperture. 10

The real and imaginary part of the index of refraction for bulk water and bulk ice can be used to analyze the curves. Graphs for both indices and the curves are displayed in figure 19.

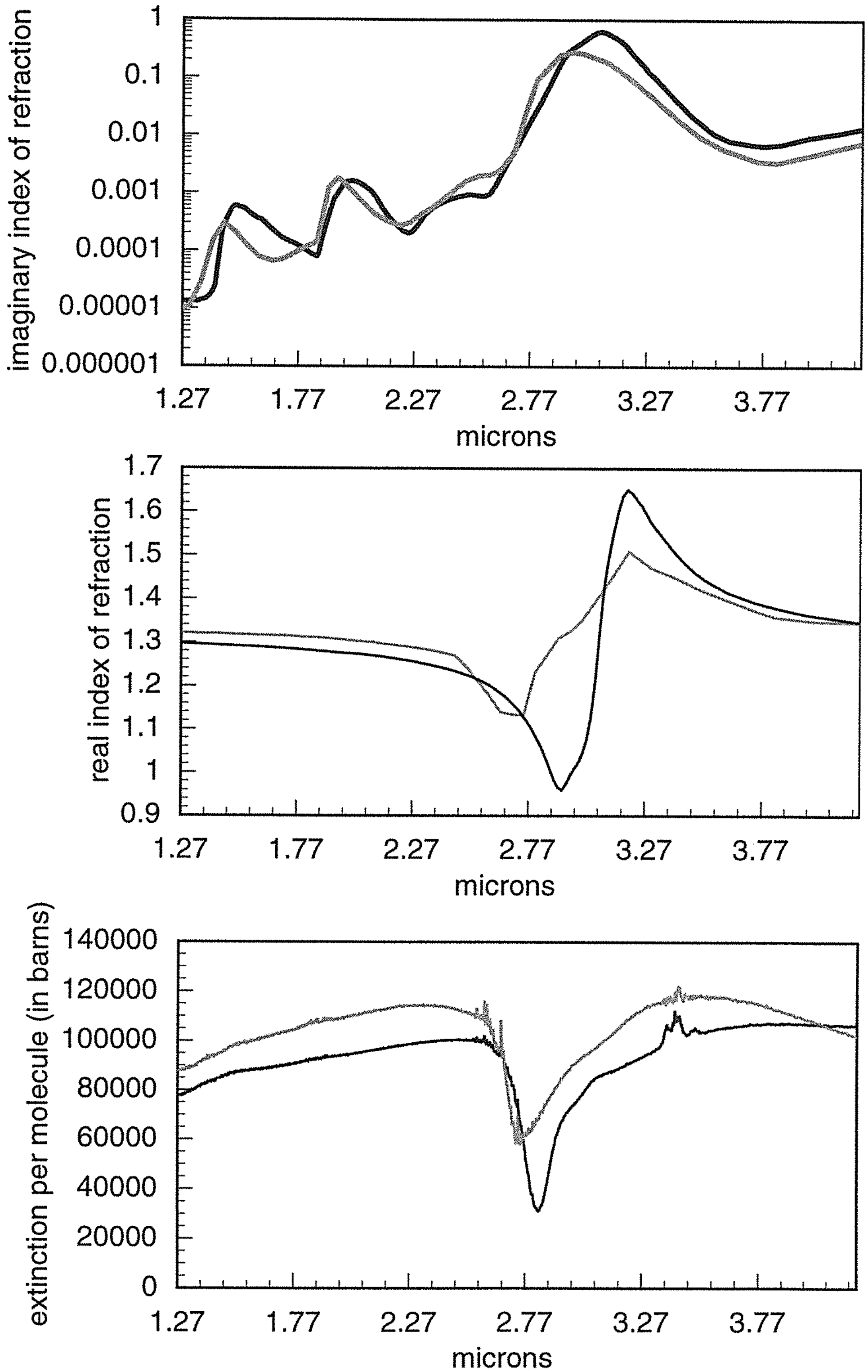


Fig 19 Imaginary, and real part of the index of refraction as well as the spectra for water and ice. The dark lines are ice, light lines are water.

It should be noted that the index of refraction for water is relatively old data and could be unreliable.[9]

At the strong absorption feature near $\lambda = 3$ μm the real part of the index of refraction dips below one for ice and nearly to one for water. This causes what is known as the Christiansen effect. The Christiansen effect is easy to visualize. Imagine putting some solid particles with an index of refraction of 1.33 into water (which has the same index of refraction). The particles would disappear because no scattering would take place at the surface of those particles.

The index of refraction for ice reaches one and for water comes close to one. At these regions the water or ice particles become nearly invisible to the electromagnetic waves. Particles remove energy from a beam through diffraction, refraction, and absorption. At these regions where the index of refraction is close to one, refraction is weak. Absorption (as we see on the vapor graph however) is at its highest for the region.

The dip in the real part of the index of refraction for both ice and water correspond to the dip locations in the extinction graphs. The ice spectra's dip corresponds to where the real part of the index of refraction for ice first drops below one. The real part of the index of refraction for water is higher than for ice in the shorter part of the wavelength range. The water cloud spectrum is higher there also. This does not hold on the longer wavelength side of the dip though.

The sun puts out 1380 watts per m^2 total. Over the interval 1.27μm to 4.2μm the sun puts out 218.9 watts per m^2. Calculations indicate that the each water molecule in the vapor form will absorb $9.62 * 10^{-24}$ watts. The extinction for molecules in the ice form will be 2.00 * 10^{-21} watts. The extinction for molecules in the water droplet form will be 2.28 * 10^{-21} watts. Considering how many water molecules there are in each form in the atmosphere, water takes a lot of energy from this sun light range.

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Appendix A

The mathematics involved to solve the water vapor problem.

The value of τ is the unitless quantity of optical depth and is what we see graphed in Fig.12.

$\tau = \sigma L$ Eq (1)

σ (a cross-section) has units 1/m. L is the length of the chamber and therefore has units m.

$\tau = \alpha N L$ Eq (2)

because $\sigma = \alpha L$. α is in m^2/molecule. N is molecules/m^3.

$\sigma L = \alpha N L$ Eq (3)

by substituting in Eq (1).

$\sigma = \alpha N$ Eq (4)

by canceling the L.

$\alpha = \sigma / N$ Eq (5)

by rearranging things

$\alpha = \tau / NL$ Eq (6)

from Eq vap1.

We need to find N in order to proceed with the per molecule calculation.

$N = \rho$ * 1/18 (moles / gram) * $6.022 X 10^{23}$ (molecules /mole)

ρ is in grams per meter^3 added between spectrum measurements.

$\rho = e_{s(T)} (0.8-0.35)/R_v * T$

0.35 and 0.8 are the relative humidities before and after the vapor was added.

$\rho = 9.12$ g/m^3

therefore,

$N=3.05 X 10^{23}$ molecules/m^3

therefore,

$\alpha = \tau/6.96X10^{23}$ or $\alpha = \tau^*(1.44 \text{ X } 10^4$ barns/molecule) Figure 13 is the result.

Appendix B

The mathematics necessary to calculate the barns per molecule for the water cloud.

$<Q_{extIR}(\lambda)> = 2\tau_{IR} / \tau_{vis}$ Eq (7)

Eq (7) is the definition of $<Q_{extIR}(\lambda)>$. The 2 is due to the extinction paradox mentioned in the text.

$\alpha = \tau_{IRmeas}/LN$ Eq (6)

$\alpha = \tau_{vis} <Q_{extIR}(\lambda)>/2LN$ Eq (8)

by combining Eq (7) and Eq (6).

In order to normalize things we set $\tau_{vis}=1$.

$\tau_{vis} = 2\Sigma P_i N_i L$ Eq (9)

As particles get small their visible optical depth is exactly their surface area.[11] The two is there because the beam goes through the chamber once in each direction. Where P_i is the area of a particle and N_i is the number of particles that size in the cloud. L is the path length in the chamber.

$P_i = \pi (D_i/2)^2$ for water drops Eq (10)

Next set $N_i = N_o n_i$ Eq (11)

N_o is a scaling factor to multiply the experimental cloud particle size distribution by to normalize $\tau_{vis} = 1$.

$N = N_o \Sigma n_i V_i (1/18)(6.022*10^{23})$ Eq (12)

N is the number of molecules/m^3. V_i is the volume of each particular drop size.

$V_i = \pi (4/3)(D_i/2)^3$ for water drops Eq (13)

The quantity in Eq (7) is in the graph above.

The total projection area of all 300 drops $\Sigma P_i N_i L = 24328\ \mu m^2$

$N_o = 9.014*10^{-6}/(\mu m^2\ m)$

$\Sigma n_i V_i = 173404\ \mu m^3$

$N = 5.229*10^{22}$ molecules/m^3

Plugging N back into Eq (8). and multiplying by 10^{28} barns/m^3.

$\alpha = \langle Q_{extIR}(\lambda) \rangle *(41936)$

The resulting graph is Fig 16.

Appendix C

The calculations for ice clouds.

$P_i = D*3/4\ (D\sqrt{3}/4 + H)$ Eq (14)

The average projection area for a randomly tumbling ice crystal is equal to its surface area divided by four.[11]

$V_i = (H3\sqrt{3}\ D^2)/8$ Eq (15)

$N = \Sigma N_o n_i V_i \rho_{ice}$ (1/18) (moles/gram)*($6.022X10^{23}$) (molecules/mole)

$\rho_{ice} = 0.9$

From these crystals the following data was calculated.

The total projection area of all 240 crystals $\Sigma P_i N_i L = 34021\ \mu m^2$

$N_o = 6.445*10^{-6}/(\mu m^2\ m)$

$\Sigma n_i V_i = 255171\ \mu m^3$

$N = 4.952*10^{22}$ molecules/m^3

Plugging N back into Eq H2O2 (which works for ice too) and multiplying by 10^{28} barns/m^3.

$\alpha = \langle Q_{extIR}(\lambda) \rangle *(41936)$

Figure 18 is the result.