AEROSOL AND CLOUD PARTICLES IN TROPICAL CIRRUS ANVIL: IMPORTANCE TO RADIATION BALANCE*

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Abstract—With a multi-instrument approach, we determined the particle size spectrum between 20 nm and 1.6 mm diameter in the outflow portions of a convective tropical cloud. The measured particle size spectrum covered ≈12 orders of magnitude particle concentration over ≈5 orders of magnitude particle size. Within this size interval, the particle spectrum revealed three modes: a cirrus haze nucleus mode, a cirrus haze particle mode, and a cirrus ice particle mode. In the optically active size range D > 0.4 μm, the particle population inside the cirrus cloud was enhanced above “background” concentrations by almost 4 orders of magnitude. The prevalence of submicron particles led to the definition of cirrus haze nuclei which can grow along Köhler curves to radiatively important sizes. While cirrus ice particles carried most of the condensate mass, the cirrus haze particles dominated the surface area. Consequently, the presence of cirrus haze particles tripled extinction across the whole (visible and infrared) spectrum, and enhanced the IR single-scatter albedo of the cloud. © 1997 Elsevier Science Ltd

1. INTRODUCTION

Aerosol and cloud particles play significant roles in regulating the earth's energy balance at both solar and thermal wavelengths (Twomey et al., 1984; Charlson et al., 1992). In particular, the presence of high-level cirrus is vital in assessing the overall role of radiation in the global climate. Most importantly, it has been suggested that a mean warming and moistening of the earth's atmosphere may lead to more vigorous convective activities, particularly, in the tropics (Ramanathan and Collins, 1992; Stephens et al., 1990; Ramanathan et al., 1995). This would be associated with greater opacity of cirrus anvils aloft which could feed back to reduce solar radiation absorption and result in a net cooling.

However, climatic effects of cirrus are very complex, depending not only upon cloud microphysics, but also on cloud vertical and horizontal extent, vertical cloud structure, and humidity profiles. Ramaswamy and Ramanathan (1989) found that deep cirrus clouds cause net cooling but that anvil cirrus could cause IR cooling or heating depending upon the atmospheric structure below the cirrus. Small ice crystals can also influence the appearance of cirrus clouds from satellites (Takano et al., 1992) and can be an important component of solar and IR radiative transfer (Platt et al., 1989; Kinne et al., 1992). Heymsfield and Platt (1984) found that as high as 53% of the total visible extinction could be due to particles in the 1–20 μm diameter range as ice crystals of different shape.

Cirrus cloud radiative properties depend on cloud particle optical properties, which in turn depend both on the ice water content and on the ice particle shape and size distribution (Platt and Harshvardhan, 1988; Platt, 1989). To a first approximation, the bulk radiative properties observed by satellite are determined by the size distribution of hydrometeors. Because satellites sense only the clouds at the highest altitude, their physical/optical characteristics may or may not be representative of the bulk cloud properties.

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Changes in the character and occurrence of cirrus clouds result from input of nuclei at the ocean surface (Charlson et al., 1987), from in situ photolytic production (Clarke, 1993; Brock et al., 1995), and/or from volcanic activity (Sassen, 1992; Sassen et al., 1995). We discuss the phase and structure of such small particles later; suffice it to say here that at temperatures below $-40^\circ C$, hygroscopic particles follow the appropriate Köhler curves to grow between water and ice supersaturation, thus, becoming more dilute to nucleate homogeneously at temperatures warmer than $-40^\circ C$ as the freezing point depression becomes smaller than the extent to which the ambient temperature is below $-40^\circ C$. Unucleated particles are spherical, several tenths $\mu m$ in diameter, highly supersaturated particles. We choose to classify this type of particle as a cirrus haze nucleus (CHN) which, at sufficiently high supersaturation, leads to the presence of cirrus haze particles up to several microns diameter. As cloud condensation nuclei (CCN) are a subset of condensation (Aitken) nuclei (CN), determined by the critical supersaturation above water saturation required to activate a nucleus, CHN are a subset of CCN, determined by their solution properties which enable dilution and homogeneous nucleation to take place. The equilibrium freezing point is depressed by $1.86 i M^\circ C$ ($i = $ Van't Hoff factor, $M =$ molality) so that the actual freezing ice nucleation point is lowered to $-(40 + 1.86 i M)^\circ C$. Although $i$ increases slowly with dilution, it approaches an asymptotic limit of the number of ions, whereas $M$ progressively decreases with dilution. Depending on ambient temperature, a condition will always be reached where nucleation takes place as the relative humidity increases. Larger nuclei dilute before smaller ones (the slope of the isomole line is negative) and will therefore be preferred for nucleation. Subsequent ice growth takes place provided there is ice supersaturation which requires a water saturation in excess of some 50% at $-50^\circ C$. This is set by the local vertical velocities and the CCN spectrum. Thus, particles containing a solute will supercool with respect to ice and (at low relative humidities) supersaturate with respect to the solute. Nucleation of either phase will lead to nucleation of the other, since removal of water or solute by crystallization gives increased supersaturation or supercooling, respectively. Once nucleation occurs, ice facets grow from the vapor, with shape depending on supersaturation and temperature. Supersaturation, in turn, depends primarily on ice particle concentration and updraft velocity.

Measurements of ice crystal distributions depending on imaging probes alone, with a lower cutoff of some 50 $\mu m$, significantly underestimate the contribution of small particles to the cloud physical and optical properties. Measurements by Heymsfield (1986), using a higher resolution replicator, of cirrus formed in gentle updrafts at the base of the cold tropical tropopause point to an abundance of very small crystals of some 5 $\mu m$ diameter; Arnott et al. (1994) similarly found high concentrations of small crystals in cirrus over Kansas which, on occasions, dominated the radiative properties. Even though data on ice particle characteristics in the tropics are rare, recent observations down to even smaller sizes (0.1–2000 $\mu m$, Knollenberg et al., 1993) revealed that small particles dominated the total population by an order of magnitude or more in the cold tops ($-60^\circ C < T < -90^\circ C$) of tropical cumulonimbus systems. Medium to large size crystals accounted for nearly 90% of the mass whenever present.

This paper provides further evidence of an abundance of relatively small ice crystals and yet smaller haze particles down to the lower detection limit ($\approx 0.4 \mu m$ diameter) of the size-classifying instruments. Inclusion of CN concentration into the data set shows a further increase of particle concentration down to tens of nanometers particle diameter. Further, the paper will demonstrate the importance of these large concentrations of micron to submicron-sized particles to the radiative properties of tropical clouds. Invoking a Mie algorithm to compute the optical properties of the particles we show the spectral extinction, scattering and absorption properties of both classes of cloud particles and document their importance to radiative transfer.

The data were acquired during the Pilot Tropical Cirrus Experiment (PTCE), a component of the TOGA-COARE (Tropical Ocean and the Global Atmosphere-Coupled Ocean/Atmosphere Response Experiment) intensive field campaign in January–March 1993. For this campaign we put together an instrument package for the NASA DC-8
research aircraft that permitted the determination of number concentration, size and shape of high-altitude cloud and aerosol particles between 0.02 and 1,600 μm diameter. In this paper we present the results of measurements at various altitudes, hence, different temperatures of cirrus ice and haze particles in tropical cyclone “Oliver” on 6 and 8 February 1993.

2. METHODOLOGIES

2.1. CN measurements

A TSI model 3010 condensation nuclei particle counter was employed to measure the total number concentration of particles of sizes between 0.02 and 0.2 μm diameter. The lower-size limit is determined by the degree of supersaturation that can be achieved in the instrument’s cloud chamber. The upper-size limit is determined by the loss of particles exceeding 0.2 μm diameter in the air-intake system of the aircraft. Data are acquired by exposing the sample stream to butanol-saturated warm air. After cooling, a supersaturation of several 100% is achieved, whereupon butanol condenses on the particles, thus, growing them to optically detectable sizes. The response time of the instrument is < 5 s, corresponding to a spatial resolution of ≈ 1000 m at a nominal aircraft speed of ≈ 200 m s⁻¹. Within this resolution, the measurement is a continuous record of the total aerosol population in the 0.02 μm < D < 0.2 μm diameter size interval. Particles are counted with a precision of ± 1% mass flow.

2.2. Electro-optical particle sensing

2.2.1. Forward scattering aerosol spectrometer probe (FSSP-300). The Forward Scattering Spectrometer Probe Model 300, manufactured by Particle Measurement Systems of Boulder, Colorado, sizes particles by measuring the light intensity scattered forward at angles between 4° and 12° by cirrus haze and ice particles that pass through a focused laser beam (Knollenberg, 1976). The signal pulses are AC-coupled to a pulse-height analyzer which compares their maximum amplitude with a reference voltage derived from a separate measurement of the DC laser light signal illuminating the particles. Comparison of the voltage outputs from the signal detector and dark detector defines the sample area. The product of sample area with aircraft speed and sampling time determines the sampling volume.

The instrument resolves particle’s linear dimensions into 15 size bins. Calibration is provided by comparing the signals due to cirrus haze and ice particles with those of particles of known size, shape and refractive index, usually beads of glass and polystyrene latex. The accuracy of the measurement will be affected by deviations of shape and refractive index of the cirrus haze and ice particles from those of the calibration aerosol. Typically, the accuracy of particle size is ± 1 bin width, and the accuracy of particle number concentration is ± 1.96√N, where N is the particle number per unit volume.

Baumgardner (1983), based on an examination of individual errors associated with various aspects of the FSSP, suggested errors of ± 17% for sizing and ± 17% for concentration, yielding an expected error of ± 34% for surface area calculations, when measuring water droplets of about 10–40 μm diameter. At smaller sizes, where the Mie peaks are more pronounced, uncertainties of 20–25% in sizing have to be reckoned with, leading to uncertainties in particle surface area of ≈ 50% (Baumgardner et al., 1989).

2.2.2. Optical array 2D greyscale probe. In the Optical Array 2D Greyscale Probe (Knollenberg, 1976) manufactured by Particle Measurement Systems of Boulder, Colorado, particle size and shape information is acquired by shadowing part of a 64-element photodiode array while passing through a He–Ne laser beam. Image information representing > 25%, > 50% and > 75% darkness levels are sensed, thereby providing three levels of grey information on the particles from each of 64 elements of the array. If the image is dark
enough on a particular element of the array, the outputs from a comparator will switch and provide output from an amplifier card. The outputs from the amplifier cards are delivered to random access memory chips which are operated in parallel to store the particle-shadow information. In addition to information of the presence of a particle and three levels of grey within each particle image, the output bit stream also encodes particle size and shape information. The calibration is a function of the center-to-center spacing of the diodes of 200 μm and the overall 5 x magnification of the imaging optics resulting in a resolution of 25 μm per array element. Thus, the resolution of the 64-element instrument is 25 μm < D < 1.6 mm with regard to particle size, and between 50 μm and 1.6 mm with regard to particle shape.

2.3. Ice crystal replicator

A thin layer of Formvar resin in chloroform solution is applied to a 16 mm film which is drawn past a 2.5 mm x 7.5 mm slot exposed to the air outside the aircraft boundary layer. Particles carried in the air stream, if they are large enough, cross the stream lines, pass through the slot and deposit on the Formvar solution-coated film. As the Formvar solution dries, a detailed cast of the original ice crystal remains. These replicas were monitored by a standard TV system in flight to provide information on the type of cloud the aircraft penetrates. The replicas were further analyzed on return by standard optical and/or electron microscopy to identify their size and potential ice nuclei morphologically and/or chemically. The detection limit is from a few to several hundred micrometers diameter with an accuracy of ± 15% particle size. The accuracy in number concentration N is ± 1.96√N.

3. RESULTS AND DISCUSSION

3.1. Physical cloud characteristics

Pueschel et al. (1995) presented data on water condensates at three different levels of the stratified portion of tropical cyclone “Oliver” on 8 February 1993. Each of the three cloud-particle size distributions, measured at different times, altitudes and temperatures during an aircraft spiral from 10,000 to 35,000 ft pressure altitude showed an increase in particle concentration with decreasing particle size down to 25 μm diameter, the lower limit of the 2D-Greyprobe instrument with which cloud particle sizes and shapes were determined in PTCE. In this paper we present measurements in one of those clouds of submicron particles D > 0.4 μm utilizing a FSSP300 optical particle counter, and of particles as small as 0.02 μm from a CN particle counter. Both instruments were operated side by side with the 2D-Greyscale probe on 8 February, and with an ice crystal replicator on 6 February while penetrating the outflow portions of “Oliver”. In both instances, the instruments covered a cloud particle size range between 0.02 μm and several hundred μm particle diameter.

Figure 1 shows the particle size distributions of the cloud observed on 8 February 1993 at 30,300 feet pressure altitude and – 25°C ambient temperature. The measurements are those of a 2D-Greyscale probe (shown by open diamonds) and of an FSSP300 (shown as open squares). CN concentration and its variability are indicated by the vertical bar assigned to 0.02 μm particle diameter. It follows from Fig. 1 that the aerosol inside the cloud was the more abundant the smaller the particle size, down to CN particle sizes of the order of 0.02 μm diameter.

For the 0.4 μm < D < 20 μm size range, we also show in Fig. 1 (as closed squares) the particle spectrum that was measured by the FSSP300 particle counter before the aircraft entered the cloud. In comparison with the FSSP300 results from inside the cloud, these data indicate that the concentration of submicron particles inside the cloud was enhanced above “background” concentrations by almost 4 orders of magnitude.
Aerosol and cloud particles in tropical cirrus anvil

Fig. 1. In-cloud particle size distribution between 0.02 and 500 μm particle diameter sampled in tropical cyclone "Oliver" on 8 February, 1993, combining data from a CN counter (upper left-hand bar), an FSSP-300 (open squares) and 2DC greyscale (open diamonds) probe. The FSSP spectrum observed prior to entering the cloud is shown by solid squares. The altitude was 30,300 feet; The temperature was -25°C.

A curve-fit to the data points in Fig. 1, covering ~5 orders of magnitude particle size corresponding to ~12 orders of magnitude particle concentration, reveals three distinguishable modes. From small to large particle sizes we term those modes (1) haze nucleus mode, (2) haze particle mode and (3) ice particle mode, based on physical-chemical arguments presented in the next section. Both the haze and ice particle modes could be resolved with size-classifying electro-optical particle sensors. Particles below the size resolution of the FSSP300 spectrometer probe are probably too small to be radiatively significant in comparison with the cirrus haze and large ice particles.

Lognormal curves

\[
\frac{dN(D)}{dD} = \frac{2N_0}{D \ln \sigma_y \sqrt{2\pi}} \exp \left\{ -\frac{1}{2} \left( \frac{\ln(D/2) - \ln(D_k/2)}{\ln \sigma_y} \right)^2 \right\}
\]  

(1)
Table 1. Physical characteristics of a cirrus cloud measured on 8 February 1993 in the outflow of tropical cyclone “Oliver” at 30,300 feet at -25°C temperature

<table>
<thead>
<tr>
<th>Mode</th>
<th>Cirrus haze nuclei</th>
<th>Cirrus haze particles</th>
<th>Cirrus ice particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (m⁻³)</td>
<td>1.69</td>
<td>1.61</td>
<td>4.65</td>
</tr>
<tr>
<td>Geometric mean diameter (µm)</td>
<td>0.02</td>
<td>5.5</td>
<td>400</td>
</tr>
<tr>
<td>Geometric standard deviation</td>
<td>3.7</td>
<td>2.5</td>
<td>1.3</td>
</tr>
<tr>
<td>Second moment</td>
<td>3.0E-2</td>
<td>4.0E1</td>
<td>4.0E4</td>
</tr>
<tr>
<td>Third moment</td>
<td>2.0E-3</td>
<td>8.4E2</td>
<td>1.1E7</td>
</tr>
<tr>
<td>Surface area (µm² m⁻³)</td>
<td>3.8E7</td>
<td>5.0E9</td>
<td>2.3E9</td>
</tr>
<tr>
<td>Volume (µm³ m⁻³)</td>
<td>8.4E-6</td>
<td>3.5E10</td>
<td>1.8E11</td>
</tr>
<tr>
<td>Effective diameter (µm)</td>
<td></td>
<td>2.4E2</td>
<td></td>
</tr>
<tr>
<td>Liquid water content (g m⁻³)</td>
<td>8.4E-6</td>
<td>3.5E-2</td>
<td>1.8E-1</td>
</tr>
</tbody>
</table>

least-squares fitted to the data points yielded lognormal characteristics of particle concentration N₀ (m⁻³), particle geometric mean diameter Dₑ (µm) and standard deviation aₑ. These parameters permit the computation of the third and second moments of the distributions, viz., \( \mu_i = N_0(D_2/2)^i \exp[(i^2/2)](\ln \sigma^2)\), respectively, with \( i = 2 \) or \( 3 \), cloud particle effective diameter \( D_ₑ = \mu_3/\mu_2 \), and particle volume and surface area, \( V = \frac{4}{3} \pi N_0 \mu_3 \) and \( A = 4\pi N_0 \mu_2 \), respectively (e.g. Herdan, 1960). These results are summarized in Table 1 from which it follows that (a) the volume of condensed water in the clouds was dominated by the large ice particle mode, however, (b) cirrus haze particles contributed significantly to total surface area in the same cloud. Therefore, the presence of cirrus haze in clouds is important for the role clouds play in radiative transfer.

The data from the FSSP300 optical particle counter inside the clouds are somewhat open to interpretation. Gardiner and Hallett (GH, 1985) showed an enhancement of FSSP counts in the presence of ice particles. This observation was interpreted as shape and internal structure of small ice particles causing erroneous counts. Based on the findings in this paper, it is possible also that cirrus haze particles in the cloud investigated by GH caused enhanced FSSP particle counts. GH estimated one order of magnitude increase in total counts. This interpretation would lower the aerosol concentration measured inside the clouds proportionately. It is possible that the GH phenomenon causes the relatively high particle counts at the upper end of the FSSP300-covered size range (10–20 µm diameter), thereby explaining the ≈ one order of magnitude discrepancy between FSSP300 and 2D Greyprobe counts in the overlap range of those two instruments. It would not, however, invalidate our basic conclusion that the haze-enhanced aerosol surface area is similar or greater than those of large ice particles themselves. This conclusion is similar to that of Arnott et al. (1994) for continental cirrus investigated over Kansas. Comparing data from a replicator and a 2D electro-optical cloud particle probe, these authors also showed that cirrus particles which are smaller than can be resolved with 2D cloud particle probes contributed significantly to particle surface area and sometimes dominated both solar extinction and infrared emissions in continental cirrus clouds. We thus believe that an FSSP300 optical particle sensor adequately sizes and counts small ice particles, albeit possibly with reduced accuracy due to the caveats discussed by Gardiner and Hallett (1985), and also due to deviations in shape and refractive index of ice and haze particles from those of the calibration aerosol (Pueschel et al., 1990).

We added credibility to the optical sensor data with simultaneous but independent measurements of ice particles by replication during other flights in PTCE (Foster et al., 1995). The ice particle replicator collected particles through a 3 mm slit in a plastic solution of Formvar to leave permanent casts. Microscopic examination of the replicas showed an increase of ice particle concentration with decreasing particle size down to its limit of detection at several micrometers diameter, analogous to the results in Fig. 1. For example, Fig. 2 compares FSSP300 counts (open squares) with replicator results (open circles and triangles). Both sets of data were acquired simultaneously while penetrating the “Oliver” anvil on 6 February 1993. The replicator data were derived by applying two different
methods to replica counting and sizing of samples. Those analysis methods were optical microscopy (open triangles) and projection of the transparent film strip of replicas onto a screen (open circles). It follows from Fig. 2 that the particle concentration versus size can be approximated by straight lines with a slope of approximately $\Delta N/\Delta D \propto D^{-2}$ for the ($0.4 < D < 20 \mu m$) size range, and a slope of approximately $\Delta N/\Delta D \propto D^{-3}$ for the ($20 < D < 300 \mu m$) size interval. This implies equal surface area for both large and small particles in the ($0.4 < D < 20 \mu m$) size class. Since optical characteristics are proportional to particle surface area (Equation 3, Section 3.3.), this means that both small and large particles carry equal weight in determining cloud optical characteristics. Large particles, however, contain more volume than do small particles, in agreement with the results presented in Table 1.

In combination, Figs. 1 and 2 document a continuous increase of particle concentration with decreasing particle size between 500 $\mu m$ and 0.4 $\mu m$ particle diameter. Condensation
nuclei (CN) were also measured during these flights using a TSI 3010 CN-particle counter. Results showed a general low of 200 cm$^{-3}$ in background air, interspersed by regions of much higher concentrations extending up to 8000 cm$^{-3}$ (Hallett et al., 1996). Those particle densities were converted to $\Delta N/\Delta D$ (m$^{-3}$ $\mu$m$^{-1}$) for the 0.02 to 0.2 $\mu$m diameter interval which was resolved by the TSI 3010 CN particle counter. (The lower cutoff is determined by the supersaturation which the instrument achieves, whereas the upper cutoff is a consequence of the aerosol inlet system which does not allow particles larger than 0.2 $\mu$m to enter the CN particle counter). The CN results, indicated by the left-hand bar in Figs. 1 and 2, indicate that the inverse relationship between particle size and concentration extends down to diameters of the order of nanometers. In the next section we explain this phenomenon by cirrus particle formation mechanisms.

3.2. Mechanisms of aerosol formation inside clouds

Observations of enhanced aerosol concentrations inside clouds have a long history (e.g. Hegg, 1991). Several publications discuss the different mechanisms of particle formation inside clouds. For example, Hegg et al. (1980) explained their observation of enhanced aerosol concentrations in clouds in terms of sulfate production inside cloud drops. Saxena and Hendler (1983) found it necessary to additionally consider shattering of rapidly evaporating salt droplets, as observed in laboratory studies (e.g. Radke and Hegg, 1972). Recently, Hegg et al. (1990) invoked homogeneous, heteromolecular nucleation of H$_2$SO$_4$/H$_2$O droplets to explain measurements of high concentrations of condensation nuclei in the immediate proximity of clouds.

The mechanism of cirrus haze formation in tropical clouds is to be inferred from the possible origins of the aerosol and its cirrus haze nuclei (CHN) component found at cirrus levels. The thermal classification technique used by Hallett et al. (1996) suggest that CN are composed of both sulfuric acid and ammonium sulfate/bisulfate. Thus, the nucleus origin could be in situ photolysis (Clarke, 1993; Brock et al., 1995), volcanic (Sassen, 1992; Sassen et al., 1995) or advection from oceanic surface production (Charlson et al., 1987; Hegg et al., 1991). Andranoche et al. (1996) modeled 10$^2$–10$^6$ cm$^{-3}$ ultrafine H$_2$SO$_4$ particles in the nanometer size range in the free atmosphere. Our CN concentrations observed in the cirrus regions of size larger than 0.02 $\mu$m approached 10$^4$ cm$^{-3}$. These small particles could grow by coagulation to optically active particles given times on the order of days. Such particles are well suited for dilution and freezing by homogeneous nucleation under cirrus growth conditions.

This growth to sizes at which particles become optically active and eventually form cloud droplets or ice particles was first explained on thermodynamical grounds by Köhler (1926; see Fig. 3). At very low humidities, hygroscopic aerosol (H$_2$SO$_4$) particles are small. Initially, the optical cross sections of the majority of these particles are too small to be detected by optical particle counters. At water relative humidities beyond some 50% (modest ice supersaturation) at cirrus temperatures particles take up water, although the initial growth in particle size is small. At relative humidities approaching water saturation, however, the particles take up enough water to grow by a factor of 2–3 (Tang et al., 1977). This increase in size could increase the particles' scattering cross section sufficiently to make them detectable by optical particle counters such as an FSSP300. This would explain the common observation of a much higher concentration of optically active aerosols inside a cloud than in the background air outside it. At water supersaturations, the increase in size follows a growth equation based on a combination of Raoult's law and the Kelvin relation for the dependence of vapor pressure of the particle as a function of its radius. For a particle in equilibrium with its environment, the ratio of the actual vapor pressure of the solution droplet, $p$, to the saturated vapor pressure, $p_s$, of water is

$$\frac{p}{p_s} = \left[ \exp\left(\frac{\sigma V}{\rho Tr} \right) \right] \left[ I + \frac{imM_w}{M_\lambda(4/3\pi r^3 p - m)} \right]^{-1},$$

(2)
Fig. 3. Size of sulfuric acid–water droplets with various amounts of solute as function of relative humidity.

where $\sigma$ is the surface tension of a solution droplet, $V$ is the molar volume of the liquid phase, $T$ is the temperature, $r$ is the droplet radius, $i$ is the van't Hoff factor (the average number of moles of dissolved species produced per mole of solute), $m$ is the mass of solute in the droplet, $M_s$ is the molecular weight of solute, $\rho$ is the density of a droplet, and $M_w$ is the molecular weight of water.

Figure 3 shows the growth of $\text{H}_2\text{SO}_4$ particles of various sizes in graphical form. The molality, $M$, was computed along each line. The equilibrium melting point depression is given by $1.86i M^\circ C$. If it is assumed that the solute is fully ionized, then $i = 3$ for sulfuric acid, and a 10 M solution has an equilibrium temperature depression of 56 K. This freezing point depression is in addition to the supercooling by a further 40 K of the pure-water component in the absence of specific nuclei. Therefore, this aerosol could remain liquid at temperatures down to $-96^\circ C$. As the relative humidity increases, the temperature of nucleation lowers $-(40 + 1.86i M)$ K. Thus, it reaches $-45.6^\circ C$ for 1 M and $-40.56^\circ C$ for 0.1 M solutions as the relative humidity over water increases from 50% to 80–90%, depending on ambient temperature and nucleus size. Hence, most particles will nucleate at temperatures a little below $-40^\circ C$ as the relative humidity increases from 50 to 80–90%, depending on ambient temperature and nucleus size. Note that once high ice concentrations have been reached, relative humidity will not rise significantly (a few percent depending on updraft) above ice saturation (60% relative humidity with respect to water at $-40^\circ C$), so that inactivated haze droplets would persist in a supercooled state.

An important feature displayed by each growth curve in Fig. 3 is the maximum in the domain of supersaturation above 100% relative humidity. It indicates the degree of supersaturation required for a particle to form a stable cloud droplet. Once a particle has grown just beyond this maximum, it enters a region of instability and must grow further, provided sufficient water supply is in the ambient air. In weak updrafts, nuclei dilute and freeze homogeneously long before activation over the hump in the Köhler curve can occur. The large ice particles may therefore originate in a very early stage of a high vertical velocity.
fluctuation—or more likely from the extreme tail of the CCN spectrum. They may grow, however, to several micrometers diameter to form a cirrus haze particle. This mechanism of particle growth inside clouds would explain the abundance of small particles that we observed in tropical clouds.

Upon decreasing the relative humidity to values below the deliquescence point, the solution may become supersaturated. Recrystallization does not occur as spontaneously as deliquescence, so that the particle size moves along the Köhler curve for a while before it shrinks to a value near the dry radius at low humidities ( < 20%). This hysteresis indicates an important possible mediation of aerosol size by clouds that also has consequences for radiative transfer and atmospheric chemistry. Many cycles of cloud particle condensation/sublimation and evaporation may take place long before the formation of precipitable particles, affecting the size and composition of aerosols downwind of clouds. Thus, a cloud upon evaporation leaves behind an “activated” aerosol particle of a size that is larger than was CCN upon which the droplet initially had formed. The resulting larger surface area renders the particle more active both radiatively and chemically.

3.3. Cloud optical/radiative characteristics

Mie calculations have been used to assess the effects of the cirrus haze particles measured in PTCE on the optical characteristics of tropical cirrus. In these calculations, the particles were assumed to be spherical in shape and the refractive indices for water and ice were taken from Warren (1984). While Takano and Liou (1992) have pointed out that the spherical assumption is inadequate when considering ice particles, this effect is mitigated at cloud optical depths as high as is the case here. In addition, in the IR, absorption is the dominant phenomenon and is controlled by particle mass in some wavelengths (Arnott et al., 1995).

In the Mie calculations, optical characteristics were integrated over the size distributions of the clouds measured using the formula

$$k_{ext} = \frac{\delta_{max}}{\delta_{min}} \frac{\pi D^2}{4} Q_{ext}(X, n) \frac{dN(D)}{dD} dD$$

(3)

to compute extinction coefficients, $k_{ext}$, where $Q_{ext}$ is the optical efficiency for extinction, $X = \pi D/\lambda$ is the particle size parameter and $n$ is the refractive index used in the Mie calculations. The actual measurements were fitted to lognormal distributions, an example of which is shown in Table 1, which were used in the calculations. Calculations were performed for the cirrus ice particle mode only and for both cirrus ice and cirrus haze particles combined.

Figure 4 shows extinction coefficients, single-scatter albedos, and asymmetry parameters for the cloud characterized in Table 1 at selected wavelengths from the visible to the mid-IR. The open circles are for the cirrus ice particle mode only, and the solid circles are for both cirrus ice and cirrus haze modes. Comparing extinction coefficients, we see that the cirrus haze has increased cloud extinction by a factor of three. The increase seems to be independent of wavelength. At solar wavelengths there is little or no effect on the single-scatter albedo and asymmetry parameter. In the near and mid IR, generally, single-scatter albedo has increased and asymmetry parameter decreased with the addition of the cirrus haze to the particle size spectrum. The large increase in extinction coefficient shows that both scattering and absorption have increased with the addition of the cirrus haze but the slight increase in single-scatter albedo shows that the increase in scattering is slightly greater than the increase in absorption.

It must be remembered that these calculations are for a single scattering event. Empirical relations can be used to extend the single-scatter calculations to real cloud emissivities. Following Stephens' work (1978) with water clouds, Griffith et al. (1980) related the effective cloud emissivity ($\varepsilon_{CLD}$) to ice water profiles (IWP)

$$\varepsilon_{CLD} = [1 - \exp(-K \times \text{IWP})] = [1 - \exp(-C_{abs} \times Z)]$$

(4)
Fig. 4. Optical characteristics of a tropical cirrus anvil. From top to bottom: Extinction coefficients (m\(^{-1}\)), single scatter albedo, and asymmetry factor of cirrus ice particles (D > 50 µm) and cirrus ice plus cirrus haze particles (0.4 µm < 1600 µm). The results correspond to the cloud with log-normal characteristics as given in Table 1.

where \(K(\text{m}^2 \text{g}^{-1})\) is the broad-band grey-body mass absorption coefficient and IWC \(\times Z = IWP\) is the integrated column ice water profile (with \(\text{IWC(}\text{g m}^{-3}\) \(\equiv\) ice water content) over the altitude range \(Z(\text{m})\) from cloud top, or base, to the level in question. The measurements made in PTCE permit the determination of ice water content directly (Table 1) by integrating over the measured particle size distributions like the one shown in Fig. 1. This approach does not require any assumptions about ice water content and its distribution with altitude. Thus, the absorption cross section, \(k_{\text{abs}} = K \times \text{IWC(}\text{m}^{-1}\)\), can be computed directly (equation (3)) using the measured cloud particle size distributions. The absorption and scattering cross sections can be derived by replacing the extinction efficiency with the corresponding efficiencies, or can be obtained using the single-scatter albedo,

\[
\omega = k_{\text{sec}}/k_{\text{ext}}.
\]

Table 2 lists absorption coefficients, IR emissivities, and the ratios of these quantities for both haze and ice particles, and ice particles only. Thus, it follows that the absorptivity and emissivity of the clouds were enhanced many times for the case of both modes compared to the large ice particle mode for the clouds investigated on 8 February 1993. In conclusion, the measured IR emissivity and optical depth of these clouds were much greater than one
Table 2. IR Absorptivities and emissivities (for 100 m thick cloud) of both (haze and ice) and ice particle modes

<table>
<thead>
<tr>
<th>Wavelength</th>
<th>Ice particles</th>
<th>Ice plus haze particles</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C_\text{abs}</td>
<td>\epsilon</td>
</tr>
<tr>
<td>3.0</td>
<td>5.04E-04</td>
<td>1.71E-03</td>
</tr>
<tr>
<td>3.0</td>
<td>4.92E-02</td>
<td>1.57E-01</td>
</tr>
<tr>
<td>10</td>
<td>5.69E-04</td>
<td>1.55E-03</td>
</tr>
<tr>
<td>10</td>
<td>5.53E-02</td>
<td>1.44E-01</td>
</tr>
<tr>
<td>C_\text{both}/C_\text{ice}</td>
<td>3.0</td>
<td>3.4</td>
</tr>
<tr>
<td>\epsilon_\text{both}/\epsilon_\text{ice}</td>
<td>3.0</td>
<td>3.2</td>
</tr>
<tr>
<td>C_\text{both}/C_\text{ice}</td>
<td>10</td>
<td>2.7</td>
</tr>
<tr>
<td>\epsilon_\text{both}/\epsilon_\text{ice}</td>
<td>10</td>
<td>2.6</td>
</tr>
</tbody>
</table>

would expect from calculations based upon 2D cloudprobe large particle measurements alone.

Because of the complex relationship between cirrus and climate, optical characteristics alone cannot determine the climatic effects of the haze particles observed in this study. More complicated and detailed calculations are needed to make this determination. It is apparent, however, that attention must be given to cirrus haze that co-exists with cirrus ice particles when considering the effects of clouds on radiative transfer.

4. SUMMARY

Cirrus haze results from condensation of water vapor on hygroscopic nuclei which, at temperatures below \((40 + 1.86 i M) \text{C}\), (\(i \equiv \text{Van't Hoff factor; } M \equiv \text{molality}\)) freeze homogeneously as they dilute. At melting point depression temperatures, some of those particles may freeze and grow to cirrus cloud particle size. The nuclei for these particles may originate in the ocean, result from volcanic emissions, or be generated photolytically in situ.

At relative humidities in excess of ice saturation, the originally small cirrus haze particles take up enough water to grow to optically detectable sizes. As a consequence, the concentration of micron-sized cirrus haze particles inside tropical cirrus can be enhanced above background by nearly 4 orders of magnitude. Once grown to optically active size, cirrus haze particles can play a significant role in radiative transfer. Thus, the combined aerosol-cloud spectrum has to be measured, in order to assess the optical-radiative characteristics of clouds.

While most of the condensate mass of tropical clouds is concentrated in cirrus ice particles of several hundred micrometers diameter, the abundance of micron-sized haze particles contributes significantly to the total surface area of cloud particles. As a consequence, (a) light extinction is enhanced threefold inside a cloud across the whole spectrum from visible to thermal infrared wavelengths; and (b) single-scatter albedo is increased between 10 and 20% in the infrared at wavelengths larger than 4 \(\mu\)m.

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REFERENCES


