Atmospheric Environment Vol. 21, No. 9, pp. 2035–2052, 1987.
Printed in Great Britain.

0004-6981/87 $3.00+0.00
Pergamon Journals Ltd.

EFFICIENT SCAVENGING OF AEROSOL SULFATE BY LIQUID-WATER CLOUDS*

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(*First received* 11 *September* 1986 *and in final form* 8 *December* 1986)

Abstract—Continuous aircraft measurements of aerosol sulfate concentration, [SO_4^{2-}], (flame-photometric detector) and light-scattering coefficient, b_{scat}, (integrating nephelometer) in cloud interstitial air and in associated clear air are reported for several locations in the eastern United States. Measurements were made in situations where, on the basis of other physical and chemical measurements, it can be argued that the cloud air and the clear air have similar history and composition. It is found in cloud interstitial air that [SO_4^{2-}] approaches zero and b_{scat} approaches the Rayleigh scattering coefficient of air. Sulfate concentration and b_{scat} in successive subsaturated regions along a given flight path at a given altitude were frequently nearly constant or slowly varying, the pattern presented appearing to be that of a fairly uniform concentration of sulfate-containing, light-scattering aerosol from which segments had been removed in regions corresponding to the presence of cloud. The strong decrease in both [SO_4^{2-}] and b_{scat} within cloud interstitial air relative to clear air is attributed to nearly complete uptake of sulfate-containing and light-scattering aerosol particles into cloud droplets. From comparison of the in-cloud signal to the non-cloud signal it is possible to set an upper bound to the fraction of unscavenged sulfate aerosol (frequently as low as 0.25) and to b_{scat} (frequently as low as 0.1), although for both quantities the measurements would be consistent with essentially complete scavenging. Additionally, the observation in these situations that no cloud-free regions exhibited the low values of [SO_4^{2-}] and b_{scat} characteristic of the in-cloud regions is indicative of the return of the dissolved material to the air as clear-air aerosol upon cloud evaporation.

Key word index: Clouds, scavenging, aerosol, light-scattering, sulfate, nephelometer, nucleation.

INTRODUCTION

The incorporation of soluble or partially soluble accumulation-mode aerosol particles (0.1–1 μm diameter) into cloudwater by nucleation scavenging at the time of cloud formation is important from two perspectives. Firstly, this process plays a major role in removal of these aerosol particles from the atmosphere since, in the absence of this process, particles in this size range would exhibit a long lifetime against scavenging by pre-existing hydrometeors or against dry deposition (Greenfield, 1957; McDonald, 1964; Twomey, 1977; Williams, 1977; Garland, 1978; Slinn, 1983). This incorporation is thus important for cleansing the atmosphere of its aerosol burden and in turn in controlling atmospheric visibility, since extinction of visible light is dominated by scattering by particles in this size range (e.g. Waggoner *et al.*, 1981). Secondly, the scavenged aerosol particles contribute to the composition of cloud- and rainwater. Particles in the accumulation mode commonly consist largely of sulfuric acid, its ammonia neutralization products and associated water (e.g. Pierson *et al.*, 1980), and dissolution even of rather modest concentrations of aerosol sulfate can result in cloudwater aqueous-phase concentrations that are substantial in the context of acid deposition and potential environmental consequences (Charlson and Rodhe, 1982; Schwartz *et al.*, 1983).

The extent of nucleation scavenging of soluble aerosol particles has been recognized for quite some time to be important to atmospheric chemistry and cloud microphysics. As long ago as the early 1960s Junge (1963, p. 140) argued, from consideration of total number concentrations of cloud droplets and accumulation mode aerosol particles, that "it must be expected that cloud droplets will contain most of the aerosol mass present". Since that time, considerable understanding of nucleation scavenging of aerosol particles has been gained from theoretical and laboratory investigations (Twomey, 1977; Williams, 1977; Pruppacher and Klett, 1978; Slinn, 1983; Jensen and Charlson, 1984; Flossmann *et al.*, 1985; Sarma, 1986) suggestive of highly efficient scavenging of soluble, accumulation-mode aerosol mass at representative cloud supersaturations. However, there have been few measurements that have unambiguously and precisely determined the efficiency of this process in natural

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* Portions of this material were presented at the Third European Symposium on Physico-Chemical Behavior of Atmospheric Pollutants (Varese, Italy, April, 1984; Proceedings edited by B. Versino and G. Angeletti, D. Reidel, Dordrecht, 1984, pp. 356–363) and at the Fall Meeting, American Geophysical Union, San Francisco, CA, December (1986; *Eos* 67, 898, 1986).

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clouds. Previous studies that have addressed this efficiency are briefly examined here.

Scott and Laulainen (1979) compared the concentration of sulfate in cloudwater, multiplied by the cloud liquid water content, to the concentration of aerosol sulfate in what they considered to be pre-cloud air and suggested an incorporation efficiency of 55%. A similar approach was subsequently applied by Hegg *et al.* (1984; Hegg and Hobbs, 1984) and by Leaitch *et al.* (1983, 1986) to consideration of scavenging efficiencies of clouds for aerosol sulfate and nitrate. Reported scavenging efficiencies have ranged broadly from less than 10% to greater than unity. However, the interpretation of such measurements to infer scavenging efficiencies of aerosol particles is subject to question for two reasons. Firstly, this approach relies upon comparison of two quantities of similar magnitude measured by different methods in circumstances for which the argument must be made that the composition is similar except for the presence of the condensed-phase water. Secondly, any conversion of gaseous SO_2 or HNO_3 to cloudwater-dissolved SO_4^{2-} or NO_3^- would confound the interpretation.

An alternative approach to determination of the efficiency of uptake of various species, specifically including SO_4^{2-} and NO_3^-, is to compare the amount of these materials in cloudwater vs that present as unactivated particles in interstitial cloud air. An advantage to such an approach is that one may examine for the presence of non-scavenged aerosol by means of a directly measured quantity rather than as a difference between two comparable signals. Such measurements have been reported for stratiform clouds by Daum *et al.* (1984a), who collected cloudwater and interstitial air samples, the latter for periods of 30 min, and reported apparent uptake efficiencies for sulfate and nitrate frequently approaching 100%, but occasionally well below 50%. However, again the interpretation of such measurements to yield scavenging efficiencies may be compromised, either by uptake of gases to form aqueous SO_4^{2-} or NO_3^- (yielding erroneously high efficiencies) or by contribution from imbedded subsaturated regions to the apparent interstitial aerosol concentration (yielding erroneously low efficiencies), despite precautions taken to assure the absence of subsaturated regions in the period of sample collection.

Jacob *et al.* (1984a) reported measurements of aqueous sulfate and of total sulfate (aqueous plus interstitial) for ground-based fogs. In these measurements the fraction of sulfate present in the fog water was reported to range from 10 to 80%, for measurement periods of ~4 h, suggesting rather low fractional uptake under these circumstances. It might be noted, however, that the liquid-water sampling device in these studies had a fairly high lower size cut (50%) of 20 μm diameter (Jacob *et al.*, 1984b) and that as a consequence any sulfate present in fog droplets below this diameter would not contribute to the fraction reported as scavenged in these studies. Such an approach would also be subject to interference from aerosol present in any imbedded regions of subsaturation as well as to conversion of gaseous precursors to dissolved ionic species.

Another approach to determining efficiency of uptake of aerosol particles into cloudwater is to compare interstitial concentrations to those in subsaturated air below the cloud or in breaks within a cloud layer, provided that it can be argued that such non-cloud air is representative of precursor air to the cloud sampled. Such an approach has been taken in studies (Radke, 1983; Hegg *et al.*, 1984; Hegg and Hobbs, 1984) in which aerosol volume (evaluated from particle size spectra) in interstitial cloud air was compared to that in pre-cloud air or to air in breaks embedded within stratiform clouds. Leaitch *et al.* (1983) and Hegg *et al.* (1984) reported measurements of scavenging efficiencies for isolated cumulus clouds obtained by comparison of cloud interstitial aerosol volume concentration to that of below-cloud inflow air; reported efficiencies ranged from 20 to 90%. Hegg and Hobbs (1986) attempted to infer scavenging efficiencies for aerosol sulfate and nitrate from comparisons of interstitial and below-cloud concentrations determined by filter sampling; however, in almost all cases reported, the stated uncertainties in the concentration measurements preclude drawing any meaningful inferences about scavenging efficiencies (Schwartz, 1987).

In the case of frontal clouds the inflow region of the cloud is difficult to define. However, often breaks are observed in such cloud layers, i.e. zones of subsaturated air interspersed with supersaturated zones. For a well-mixed boundary layer it might be argued that the origin of the air in the subsaturated and supersaturated regions is similar, allowing inferences about scavenging efficiencies to be drawn from comparison of measurements in these two regions. This approach has been taken by Hegg *et al.* (1984), who reported fractional scavenging efficiencies for aerosol volume ranging from as low as 0.2 ± 0.4 to as great as 0.9 ± 0.1.

Sievering *et al.* (1984) reported measurements of the scavenging efficiency of sulfate by low-based clouds from comparison of pre-cloud and interstitial sulfate concentrations measured on a tower. Reported scavenging efficiencies for two case studies were in excess of 80%.

Hudson (1984) has compared the fraction of interstitial cloud condensation nuclei (CCN) relative to total CCN within clouds as a function of supersaturation. These measurements indicate that cloud droplets form preferentially on CCN having lower critical supersaturations, i.e. larger particles containing soluble materials, as has been assumed on theoretical grounds. The fraction of CCN present in interstitial air varied considerably from case to case at a given critical supersaturation but tended, as expected, to decrease with increasing critical supersaturation. The results are frequently indicative of a high fractional scavenging of aerosol particles by cloud droplets, although some exceptions appear to be indicated. Similarly, Knollenberg (1981) has noted that nearly all clouds exhibit low concentrations of particles in the diameter range 1–4 μm relative to cloud droplet concentrations, indicative of highly efficient nucleation scavenging to form cloud droplets.

In summary, the thrust of the several studies cited is that of substantial scavenging of soluble, light-scattering accumulation-mode aerosol particles by liquid-water clouds. However, the uncertainties associated with the measurement approaches taken and the wide range of results reported, as well as the importance of accurate knowledge of the extent of such scavenging, warrant additional study of this phenomenon.

In the present article we report measurement of aerosol sulfate concentration, $[SO_4^{2-}]$, and of light scattering coefficient, b_{scat}, in interstitial cloud air and in subsaturated regions between clouds or, in the case of stratiform clouds, imbedded within these clouds. Measurements were made with real-time continuous instruments having response times (1/*e*) of ~ 20 s and ~ 2 s for $[SO_4^{2-}]$ and b_{scat}, respectively, yielding, for aircraft speed of ~ 50 m s^{-1}, spatial resolution of ~ 1000 m and ~ 100 m, respectively. The suitability of b_{scat} as a surrogate for sulfate aerosol in regions affected by anthropogenic pollution but free of direct emission sources of sub-μm particles is suggested by previously reported correlations (Pierson *et al.*, 1980; Leaderer *et al.*, 1981; Waggoner *et al.*, 1981; Barrie *et al.*, 1981) and is substantiated by further correlations reported here. We present as well continuous measurements of concentrations of O_3 and NO_x, which are not significantly partitioned into cloudwater (Schwartz, 1984), from which inferences may be drawn regarding uniformity of composition of the clouds and adjacent subsaturated regions. The observations indicate essentially complete (> 90 %) uptake of sulfate aerosol and of light scattering aerosol by cloud droplets. The measurements also imply that upon cloud droplet evaporation the dissolved material is once again returned to clear air as light scattering aerosol particles.

EXPERIMENTAL APPROACH

Measurements were made with the Brookhaven National Laboratory Atmospheric Sciences research aircraft, a twin-engine Britten-Norman Islander (BN-2A) equipped with a variety of chemical and meteorological instrumentation for cloud and clear-air chemistry studies. The aircraft, the instrumentation, and the installation and application of this instrumentation have been described in detail elsewhere (Leahy, 1981; Tanner *et al.*, 1983; Daum *et al.*, 1984a, b), so that only a brief description is given here with emphasis on those features especially pertinent to the observations reported here.

Air for measurement of chemical constituents was sampled by means of a 5-cm diameter forward facing tube affixed to the side of the aircraft. Ram air (typical aircraft cruising speed 180 km h^{-1} = 50 m s^{-1}) entering this tube is ducted into the cabin via two shallow (45°) bends past a set of fixed, canted blades (Walters *et al.*, 1983) that impart a swirl to the airstream for the purpose of removing cloud droplets from the airstream by centrifugal impaction to the tube walls where it is collected. The resulting air flow substantially exceeds the requirements of the instruments which are supplied by this inlet system. Previous work by Walters *et al.* (1983) has established that cloud droplets of diameter greater than 5 μm are removed from the airstream with high efficiency. The 'cut' of this inlet system is not well established. However, comparison of concentrations of aerosol and gaseous constituents in air sampled by this inlet system with those in isokinetically sampled air shows close agreement in clear air, establishing the validity of this sampling system for gases and sub-μm aerosol particles. These observations, together with the minimum in number distribution in the size range 1–4 μm characteristic of clouds (Knollenberg, 1981), suggest that the sampling system effectively discriminates between cloud droplets and interstitial aerosol particles.

Continuous real-time measurements of SO_2 and aerosol S were made by means of a two-channel flame photometric detector (FPD) specially modified for enhanced sensitivity and aircraft operation (Garber *et al.*, 1983). SO_2 and any other acidic gaseous S compounds are removed in the aerosol S channel by a diffusion denuder; the SO_2 channel is preceded by a Teflon filter to remove aerosol S. Because of a drift in the baseline, which is exacerbated by changes in altitude, the FPD is periodically zeroed with S-free air (ambient air processed by filter plus denuder). The limit of detection (LOD) of the instrument, which was occasionally as low as *ca* 0.1 ppb, increased under turbulent conditions to *ca* 0.3 ppb. Previous work (Forrest and Newman, 1973, 1977) comparing aerosol sulfate and total aerosol S at locations in the eastern U.S. allows the signal in the aerosol S channel to be ascribed predominately to sulfate. Concentrations of aerosol sulfate are expressed as ppb (mole fraction) equivalent to ppb (volume) for a gaseous constituent: 1 ppb = 4.0 μg SO_4^{2-} (std m^3)$^{-1}$; 1 atm, 20°C.

Nitrogen oxides [$NO_x = NO + NO_2$ + organic nitrates] were determined by a sensitivity-enhanced O_3-chemiluminescence instrument (Tanner *et al.*, 1983; Kelly, 1986); HNO_3 was removed by a nylon filter and is not detected. O_3 was measured by ethylene chemiluminescence (AID, Model 56C). Both instruments were periodically zeroed in flight.

The light scattering coefficient b_{scat} was measured by an integrating nephelometer (MRI, Model 1550) used in its most sensitive mode (10 × 10^{-4} m^{-1} full scale). The 'b_{scat}' signal given by the instrument includes the Rayleigh scatter component of air, $b_R = 0.2$

$\times 10^{-4} m^{-1}$ at 1 atm. The nephelometer, which was calibrated according to standard procedures, was initially operated without use of the pre-heater. Since intake air for the nephelometer was ducted through tubulation having several sharp bends, it is assumed that almost all cloud droplets were removed upon passage through this tubulation. This assumption would appear to be borne out by the observation that even when the nephelometer was operated without heating, b_{scat} was substantially less in clouds than in adjacent subsaturated regions, despite the fact that coefficient of extinction of visible light within clouds is obviously $10^{-2} m^{-1}$ or higher. Further experience with the unheated nephelometer is reported in the Appendix. In later flights the pre-heater upstream of the optical unit was employed to heat and dry the incoming air to a relative humidity of 50% or less; in this way the aerosol was brought to a dry reference state that is relatively insensitive to the ambient humidity.

Measured values of b_{scat} may be converted to mass concentrations by means of the correlation of light scattering and aerosol mass loading m as

$$m = \alpha^{-1} b_{scat}$$

where $\alpha \approx 4 m^2 g^{-1}$ (Pinnick *et al.*, 1980; Waggoner and Weiss, 1980; Waggoner *et al.*, 1981; Lewis, 1981; Dzubay *et al.*, 1982). This conversion, in conjunction with the measured limit of detection of the nephelometer ($5 \times 10^{-6} m^{-1}$ at an instrument response time of ~ 2 s; cf. $2.4 \times 10^{-6} m^{-1}$ reported by Ruby and Wagonner, 1981), yields a value of *ca* 0.6 $\mu g m^{-3}$ for the LOD of the aerosol mass concentration.

Measured values of b_{scat} may also be used as a surrogate for aerosol SO_4^{2-} concentration by the correlation given in the Appendix,

$$[SO_4^{2-}] = \beta^{-1} b_{scat},$$

where $\beta = 0.45 \pm 0.06 \times 10^{-4} m^{-1} ppb^{-1}$ equivalent to $12 \pm 1.4 m^2/g SO_4^{2-}$. This correlation yields 0.11 ppb for the LOD of SO_4^{2-}, as measured by light scattering, comparable to that of the FPD under non-turbulent conditions, but with a response time an order of magnitude lower.

The presence of clouds and the cloud liquid-water content, LWC, were monitored by hot-wire (Johnson-Williams) cloudwater detector (Cloud Technology, Inc., Model LWH; Neel, 1973), which can exhibit an uncertainty of ±50% in LWC (Strapp and Schemenauer, 1982) and a response time of $\lesssim 2$ s. Instrument zero, which depends on air speed, altitude and angle of attack of the aircraft, is obtained by the signal in cloud-free air.

Turbulent energy dissipation rate (epsilon) was determined from RMS pressure fluctuations (MacCready, 1970).

Data from the several instruments were recorded on a Metrodata (Model 640) magnetic tape recorder with sampling frequencies typically 4 Hz, but occasionally 0.2 Hz. In a few instances data records from strip charts (Soltec, Model 6723) are presented to show detail that was lost by the low sampling frequency employed with the magnetic tape recorder on that particular flight.

RESULTS AND INTERPRETATION

Briefly, the observation that comprises the basis of the present article is that of a strong decrease in both aerosol sulfate concentration, $[SO_4^{2-}]$, and light scattering coefficient, b_{scat}, in cloud interstitial air in comparison to the values of these quantities in adjacent subsaturated regions. In the great majority of instances measured values of b_{scat} after subtraction of the Rayleigh scattering signal from air have been close to or below the limit of detection ($\sim 5 \times 10^{-6} m^{-1}$). In the case of aerosol sulfate, the results, while not so unambiguous, in view of longer time constant and baseline drift of the instrument, are nonetheless indicative of substantial or complete decrease in the concentration of sub-μm aerosol sulfate in the presence of cloud liquid water. Observations are documented here in several case studies displaying excerpts from the data records obtained in these flights. These case studies are representative of a substantially larger data set that is summarized below in Table 1.

A further observation that we wish to document is that b_{scat} in successive subsaturated regions along a given flight path at a given altitude was frequently nearly constant or slowly varying, the pattern presented appearing to be that of a fairly uniform concentration of aerosol from which segments had been removed in regions corresponding to the presence of the cloud. A similar pattern was exhibited by aerosol sulfate concentrations.

As noted in the Introduction we consider these observations to be indicative of the highly efficient uptake of sulfate-containing aerosol, as measured either directly or by its surrogate, b_{scat}, by cloud liquid water, and of the return of this material to clear air as aerosol upon cloud evaporation. An alternative explanation of the observations (which we consider unlikely) is that the air present in the clouds examined has derived from different sources than the non-cloud air to which comparison is made, and that the absence of sulfate-containing aerosol within the clouds is a characteristic of the air in which the clouds were formed rather than an indication of efficient scavenging. As evidence against such an alternative explanation we present data records of simultaneously measured concentrations of O_3 and, when available and exhibiting sufficient signal to noise ratio, NO_x. These gases are relatively insoluble and non-reactive in liquid water (Schwartz, 1984), and thus serve as tracers of opportunity by which composition of in-cloud and non-cloud air may be compared. Moreover, as primary or secondary pollutants, the concentrations of these species would be expected to exhibit marked variation if fluctuation in b_{scat} and aerosol sulfate concentration were due to differing sources of subsaturated and cloud air. Consequently the relative constancy of these quantities can be adduced as evidence that the variation in b_{scat} and SO_4^{2-} is not due to difference in air composition between the saturated and subsaturated regions.

5 *March* 1983, *South Carolina*

We present here in some detail a set of measurements which particularly well illustrates the decrease of b_{scat} and $[SO_4^{2-}]$ in the presence of cloud liquid water and for which there are abundant supporting data that define the physical situation and thereby permit the observed decrease to be attributed to uptake of aerosol particles by cloud droplets. The flight was conducted in the vicinity of Charleston, SC on 5 March 1983 from 1854 to 2145 GMT (1354–1645 EST). The 1800 GMT surface map showed a high-pressure system in the Atlantic Ocean off the east coast of the U.S. and a low-pressure system located in the western section of Oklahoma. A squall line and trough lay in a north–south line through the Mississippi Valley causing widespread rain, rain showers and thunderstorms. Clouds from that system, which were overrunning the back side of the high pressure system, were spreading eastward across the southeastern states including the Charleston area. Figure 1 presents time records giving an overview of the flight between 1954 and 2136 GMT. As may be seen from the figure, the aircraft initially climbed from 1500 to 2700 m above mean sea level (MSL), passing briefly through thin cloud (at 1955) and then through rather dense cloud (1958–2001) into a region of low relative humidity above the cloud. Vertical profiles of several variables derived from this segment of the flight are shown in Fig. 2, from which it may be observed that the cloud extended from about 2100 to 2300 m. Visual observation from above the clouds indicated that the clouds from 2100–2400 m consisted of distinct turreted cumulus clouds separated by breaks.

Information relative to the dynamical situation may be gained from the vertical structure presented in Fig. 2. Attention is called first to a temperature inversion indicated at cloud top and to the lapse rate above cloud, 4.1°C km^{-1}, indicative of a stable above-cloud layer that is decoupled from the cloud layer below. Decoupling of the two layers is supported as well by the observation of low values of epsilon and of relative humidity above the clouds. The nephelometer reading, b_{scat}, was also quite low in the above-cloud region, approaching the value corresponding to the Rayleigh scattering coefficient of air, $b_R \approx 0.2 \times 10^{-4}$ m^{-1}, i.e. indicative of very low aerosol loading. (The sulfate trace is not available in this portion of the flight because of the altitude sensitivity of the instrument.) O_3 concentration above cloud, 43 ppb, was significantly lower than that in the in-cloud and below-cloud regions (50–55 ppb).

Turning to the below-cloud region, we note that also in this region stability against vertical mixing is indicated by the lapse rate (6.9°C km^{-1}, Fig. 2; cf. dry adiabatic lapse rate of 10°C km^{-1}), again as substantiated by the low values of epsilon. However, a comparable lapse rate within the clouds exceeds the wet adiabatic lapse rate (5.3°C km^{-1} at 5°C) suggesting that the latent heat of water condensation could account for enhanced vertical mixing within the clouds. This inference is supported by the relatively high observed values of epsilon.

After completion of the ascent, the aircraft returned to the cloud layer and from 2010 to 2052 GMT attempted to stay within these clouds by circling in level flight at 2100 m. This period was marked by large fluctuations of cloud liquid water content (LWC), b_{scat} and epsilon, Fig. 1. In contrast to these quantities O_3 and NO_x concentrations are seen to have been quite constant in this region. (Here NO_x included any HNO_3 that may have been present; however, average HNO_3 at 2100 m and at 600 m determined by integrated filter sampling downstream of the centrifugal separator was less than LOD of 0.1 ppb.)

Following this period the aircraft descended to 600 m and executed another period of level flight in clear, below-cloud air. From the trace for b_{scat} it may be seen that the aircraft encountered a region of high concentration of light scattering particles during the descent, and that the value of b_{scat} remained higher in the below-cloud region than the envelope corresponding to the in-cloud region. Aerosol sulfate in this region was also relatively high, about 3.3 ppb (13 $\mu g\, SO_4^{2-}\, m^{-3}$). O_3 concentration was 57 ppb. A well-defined plume was encountered at 2116 as evidenced by the positive and negative peaks in NO_x and O_3, respectively.

Figure 3 shows a portion of time records from the level, in-cloud flight (2010–2050 GMT) on an expanded time scale in order to allow examination of these signals in more detail. It is seen that the trace for LWC indicates periods of substantial LWC ($\sim$ 0.5–1 g m^{-3}) interspersed with regions of zero or very low LWC. It is evident moreover that the periods of high LWC exhibit high correlation with periods of high epsilon. Attention is now directed to the upper trace for b_{scat}, which gives the signal as directly received from the instrument. It is seen that this signal is bounded above by a rather smooth envelope of $\sim 1.0 \times 10^{-4}$ m^{-1} and below by the value corresponding to the Rayleigh scatter of air, 0.2×10^{-4} m^{-1}. It may be seen moreover that there is a high degree of negative correlation between the signals for LWC and b_{scat}. More specifically, in almost every instance of non-zero LWC there is a substantial reduction in b_{scat} to or nearly to the Rayleigh scattering coefficient of air.

Also shown in Fig. 3 are traces for aerosol sulfate and, for comparison, b_{scat} displayed with the instrument time response degraded by imposing a 20-s running average on the data points to match the time constant of the sulfate instrument. Comparison of these two traces shows a high degree of positive correlation that we take to be indicative that the same

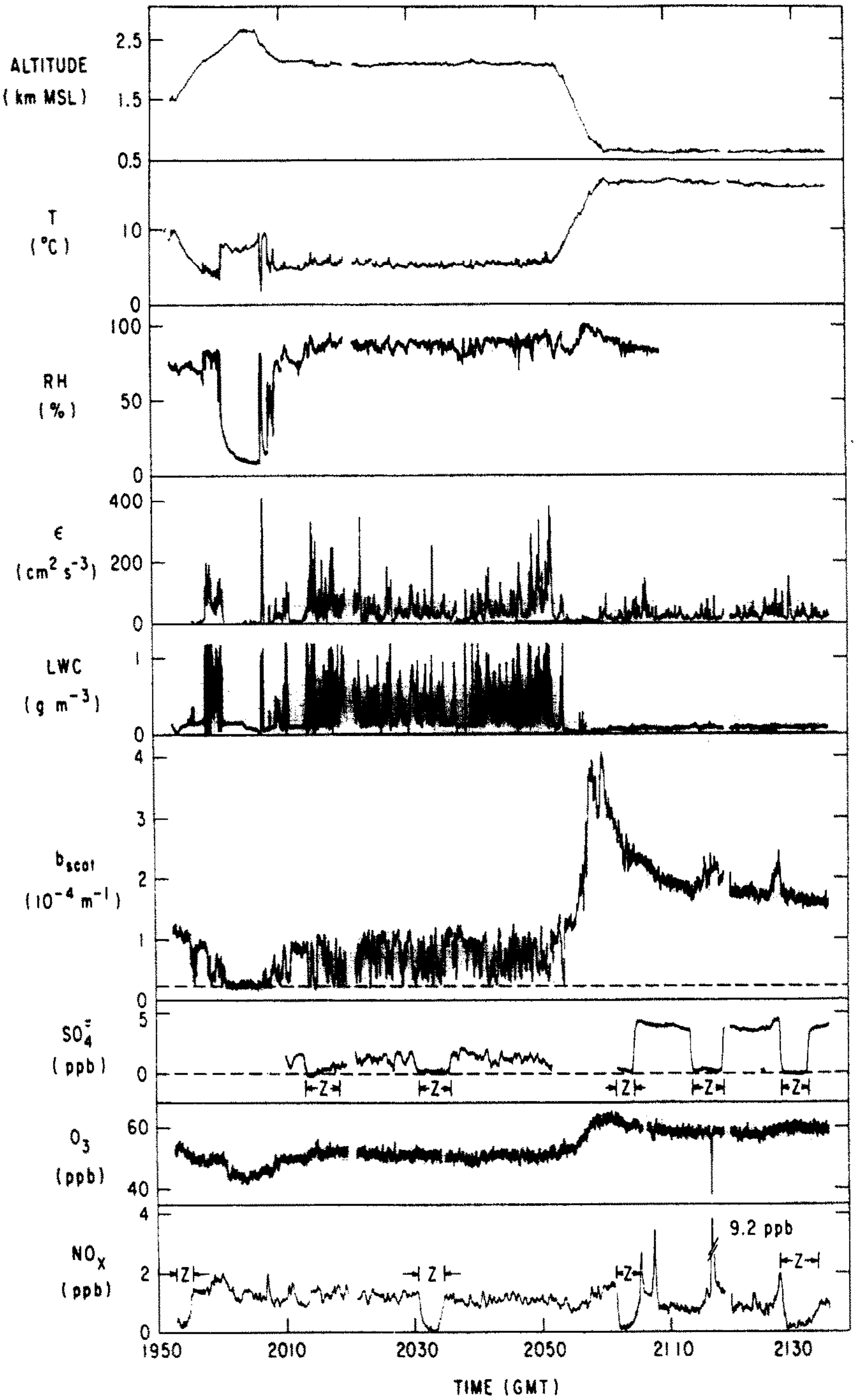

Fig. 1. Time records from flight of 5 March 1983, in vicinity of Charleston, SC. Gaps represent missing data. Periods of zeroing the several instruments are denoted by Z. Zero of trace for cloud liquid water content (LWC) may be inferred from below-cloud signal (2100–2136). Dashed line on b_{scat} trace represents signal from Rayleigh scatter of air, 0.2×10^{-4} m^{-1}.

process is responsible for fluctuations in both quantities. One may infer as well that the modulation depth of the SO_4^{2-} signal would have been comparable to that of the b_{scat} signal had the frequency response of the instrument been sufficient.

Under the assumption that the decrease in b_{scat} in the presence of cloud is due to scavenging of aerosol particles by cloud droplets, and under the further assumption that b_{scat} in the absence of liquid water would have been given by the envelope of the liquid-water-free values, then these measurements may be used to derive an efficiency for such scavenging. In many of the instances in Fig. 3, the b_{scat} trace approaches sufficiently close to the Rayleigh scattering

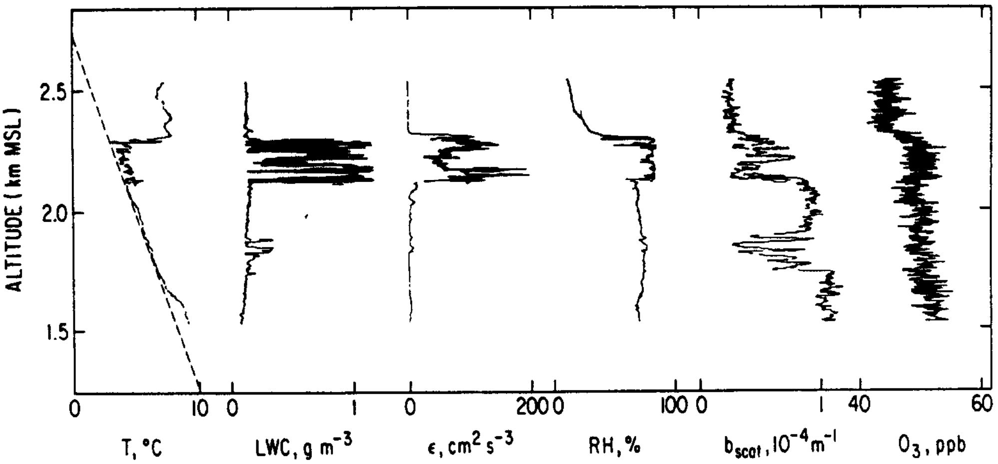

Fig. 2. Altitude dependence of temperature, liquid-water content, turbulent energy dissipation rate, relative humidity, b_{scat} and ozone concentration obtained during the ascent from 1954 to 2003 GMT, 5 March 1983. Dashed line on temperature profile represents a lapse rate of 6.90°C km^{-1}.

coefficient of air that this scavenging efficiency may be considered 100%, with an uncertainty of perhaps 10%. A few instances would appear to be exceptions, e.g. 2016.2, 2022.8, 2024.0, 2026.2, 2031.0, 2938.4, 2044.0–2044.5, 2049.5–2050. In some of these instances, e.g. 2038.4, the argument can be made that the time response of the nephelometer as governed by volume and flow rate, ~ 2 s, is insufficient to follow the rapid fluctuations that might be expected from the rapid fluctuation in LWC, although, in a few instances, e.g. 2044.0–2044.5, it would appear that as much as 30% of the aerosol remained unscavenged. However, the apparent magnitude of such unscavenged aerosol may be overestimated because of enhanced b_{scat} per dry aerosol mass at high relative humidities, as discussed in the Appendix. Additionally, it should be noted that even this residual 'unscavenged' aerosol may represent material in subsaturated regions of such small scale that they are not resolved by the liquid-water indicator.

We now address the alternative hypothesis for these observations, namely that the low values of b_{scat} in supersaturated regions of the clouds are the result of mixing processes rather than scavenging. Specifically this hypothesis would require that the source of air in supersaturated regions be characterized by a low value of b_{scat} distinct from that in non-cloud regions. The possibility of enhanced transport associated with the supersaturated regions would be consistent with the observations of enhanced values of epsilon associated with cloud liquid water. However, this alternative explanation would not be consistent with other observations that have been presented. The only region of low b_{scat} that might serve as a source of the low-b_{scat} air in the cloud is above the cloud layer, but as already noted this air has very low relative humidity, and could thus not be the source of air in the supersaturated cloud regions. In any event the above-cloud region is decoupled from the in-cloud region by the strong temperature inversion at cloud top. The in-cloud O_3 concentrations (which did not exhibit fluctuations coherent with fluctuations in LWC) are also distinctly different from the O_3 concentrations above the cloud layer, providing further evidence against transport of low-b_{scat} air from above as the source of the low-b_{scat} air in the clouds. We thus conclude that the low values of b_{scat} and $[SO_4^{2-}]$ in the supersaturated cloud regions are due to the scavenging of light-scattering aerosol particles and of sulfate-containing aerosol particles by cloud droplets present in these regions.

A further point regarding present measurements concerns the observation that not only were regions of cloud associated with low concentrations of light-scattering aerosol, but also that the converse holds, viz. that subsaturated regions within the cloud layer invariably exhibited a fairly uniform value of b_{scat} with no indication of regions of low b_{scat} in subsaturated air. Insofar as it appears likely that the air present in such subsaturated regions within the cloud layer had experienced one or more cycles of condensation and evaporation, these observations suggest that upon cloud evaporation material that had been scavenged into cloud droplets was released as light scattering aerosol, i.e. that the process of uptake of aerosol particles by cloud droplets is reversible. Additionally, this observation may be taken as evidence against the picture (suggested for example by Carmichael *et al.*, 1983) of clouds as active filters removing soluble materials from air as it flows through. We have previously argued against such a picture on the basis that concentrations of cloudwater-dissolved constituents are comparable to clear-air concentrations (Daum *et al.*, 1984b).

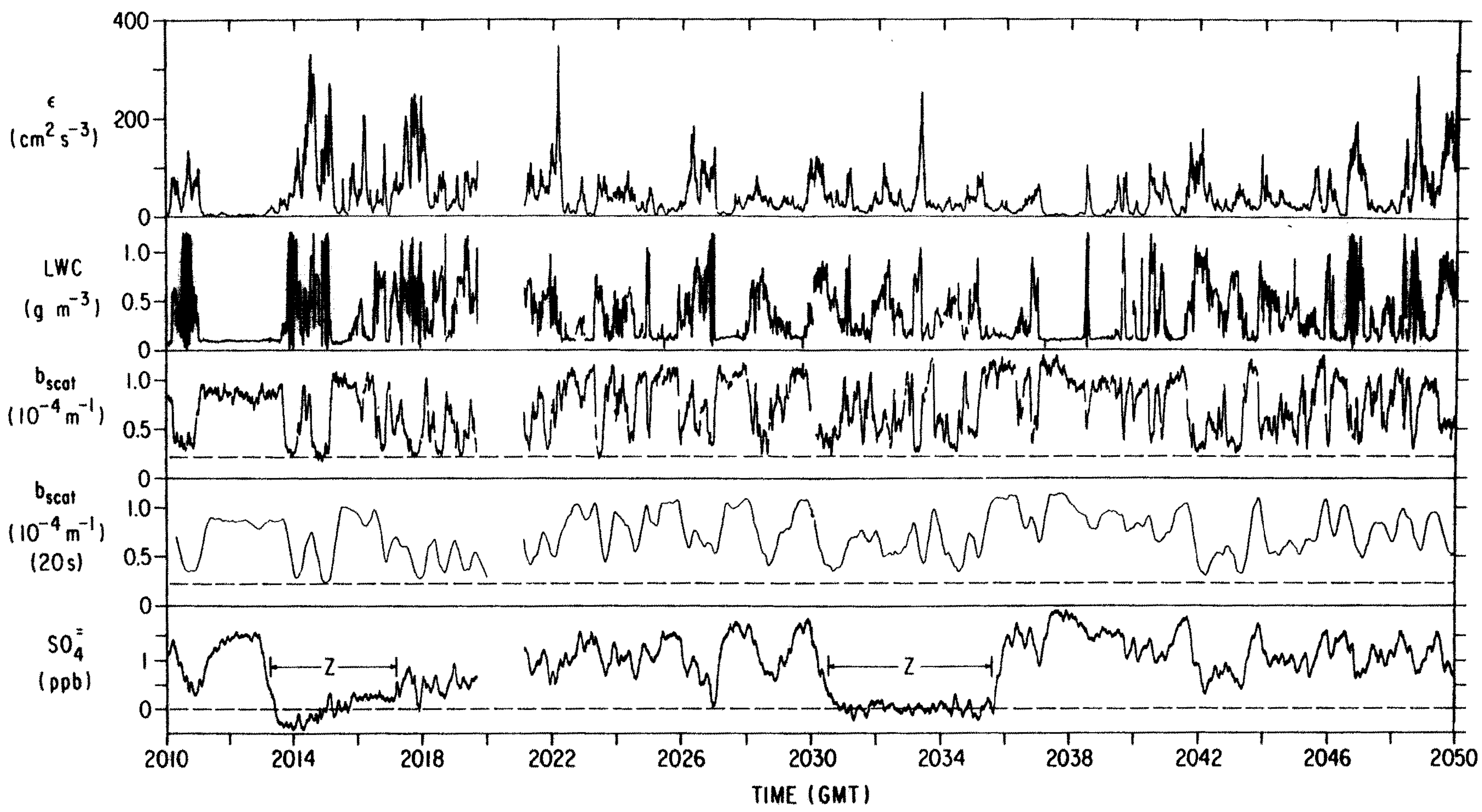

Fig. 3. Time records from a portion of the flight of 5 March 1983. Note periods of instrument zeroing for [SO_4^{2-}] signal. Zero in trace for LWC may be inferred from signal in cloud-free regions, e.g. 2011–2013. Dashed lines on b_{scat} traces represent Rayleigh scatter of air, $0.2 \times 10^{-4}\ m^{-1}$. Lower trace for b_{scat} represents a 20-s running average of upper trace.

17 *November* 1982, *Alabama*

As a second case study we present a set of measurements made in broken stratocumulus and nimbostratus clouds in the vicinity of Birmingham, AL on 17 November 1982 from 1240 to 1506 GMT (0640–0906 CST). The clouds in question were associated with a low pressure system that had formed in the Gulf of Mexico off the Texas coast and had spread through the southeastern states the preceding night. The cloud structure was not solid but exhibited considerable layering as well as breaks at any given altitude. Drizzle to light rain was experienced during much of the flight.

Figures 4 and 5 present time records obtained during this flight. Figure 4 gives an overview of the

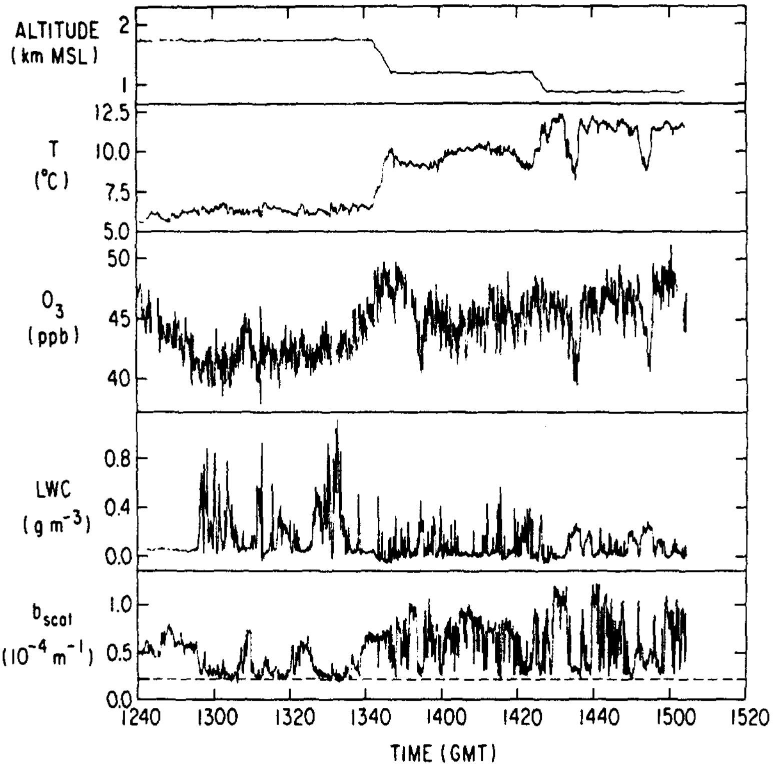

Fig. 4. Time records from flight on 17 November 1982, in vicinity of Birmingham, AL. Zero of trace for LWC may be inferred from measurements in cloud-free air (1240–1256). Dashed line on b_{scat} trace represents signal from Rayleigh scatter of air, 0.2 × 10^{-4} m^{-1}.

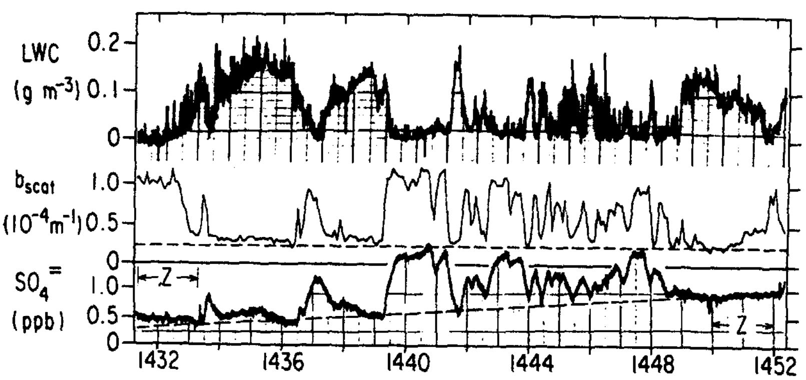

Fig. 5. Time records from a portion of the flight of 17 November 1982. Note periods of instrument zeroing for [SO_4^{2-}] signal denoted by Z; dashed line connecting regions of successive zeroing accounts for slow instrument drift. Dashed line on b_{scat} trace represents Rayleigh scatter of air, 0.2 × 10^{-4} m^{-1}. Zero of LWC trace has been inferred from cloud free regions at 1431.5–1432 and 1439.6–1441.2.

flight, and Fig. 5 presents a portion of the record in greater detail. As may be seen in Fig. 4, the flight consisted of three segments of level flight, at altitudes 1730, 1190 and 860 m MSL. We note that at each altitude liquid water content exhibited considerable fluctuation, indicative of regions containing substantial liquid water interspersed with regions of cloud-free air. It may be discerned as well at each of the three altitudes that values of high liquid water content were associated with low values of b_{scat} (approaching b_R) and vice versa. (This feature of the data is exhibited more clearly in Fig. 5.) It may also be discerned that at each of the altitudes the values of b_{scat} are confined within an envelope of maximum values of *ca* 0.8, 1.0 and 1.2 $\times 10^{-4}\,m^{-1}$, respectively. Thus again the picture presented is one of a concentration of light-scattering aerosol characteristic of a given altitude which has been depleted in the presence of cloudwater.

An interesting feature depicted in Fig. 4 is the indication, from the traces for temperature and O_3 at 1435 and 1454 GMT, of the presence at 860 m of air that is characteristic of the air sampled at the higher altitudes. In both cases this air was associated with relatively high values of LWC, although comparably high values of LWC were observed also in air that does not appear to have been transported from above. While in the present instance the indication of transport does not invalidate the argument that the low observed values of b_{scat} are due to scavenging—since the encounter with transported air was sporadic and since in any event the cloud-free air at higher elevations exhibited substantial levels of b_{scat}—these observations nonetheless establish the utility of temperature and O_3 concentrations as tracers by which such transport may be discerned.

Figure 5 presents a portion of the data record at 860 m with expansion of the time scale in order more clearly to establish the degree of reduction in $[SO_4^{2-}]$ and b_{scat} associated with the presence of cloudwater and in order also to examine the correlation of b_{scat} and SO_4^{2-} concentration. Here the traces for LWC and $[SO_4^{2-}]$ are reproductions of strip chart records since the sampling frequency employed with the magnetic tape data recorder, 0.2 Hz, was insufficient to record the high frequency components of the signal. (As noted above the flame photometric instrument for aerosol sulfate exhibits a characteristic slow zero drift, which is indicated in Fig. 5 by the dashed line connecting regions of successive zeroing of the instrument.) In the case of b_{scat} only the magnetic tape record is available.

Examination of the trace for $[SO_4^{2-}]$ in Fig. 5 shows values of ~ 1 ppb in the absence of cloud with substantial decrease where cloudwater was present. Similarly, despite the limited sampling frequency, great reduction in b_{scat} is indicated in regions of significant LWC. From the comparison of b_{scat}–b_R in regions of continuous LWC, e.g. 1438–1439, 1440.5, 1444, 1446, 1448, 1449–1451, with values in adjacent low LWC regions one may infer scavenging efficiencies consistently greater than 80% and mostly 90–100%. (In view of the indication of vertical transport at 1435 we do not attempt to infer an efficiency from the value of b_{scat} here; nonetheless the low values of b_{scat} are entirely consistent with essentially complete scavenging in this region as well.) It may be noted as well that this essentially complete uptake of light-scattering aerosol is observed even for the rather low values of LWC characterizing the clouds at this altitude, 0.1–0.2 $g\,m^{-3}$.

Comparison of the signal for b_{scat}–b_R with that for $[SO_4^{2-}]$ reveals the high correlation between these signals, indicative that the fluctuations in these two signals are attributable to the same phenomenon, namely the scavenging by cloud droplets of light-scattering sulfate-containing aerosol particles. From the ratio of the magnitudes of the two signals in a plateau region, e.g. at 1440.8, one infers a value for $\beta = b_{scat}/[SO_4^{2-}]$ of $0.85 \pm 0.1 \times 10^{-4}\,m^{-1}\,ppb^{-1}$ ($23 \pm 3\,m^2\,g^{-1}$ SO_4^{2-}). This value is a factor of two higher than has generally been obtained in clear-air studies (cf. Experimental Section and Appendix) and almost certainly reflects enhanced light scattering that is a consequence of the high relative humidity and the fact that the nephelometer was used without the preheater.

10 *March* 1983, *Virginia*

Measurements were made in a system of broken stratus clouds (1.0–1.2 km MSL) in the vicinity of Norfolk, VA. The 1800 GMT surface weather map showed a complex low pressure system along the east coast of the U.S. with a major center located east of Long Island and a second, weaker center in North Carolina. A weak trough connecting these centers caused low clouds and areas of scattered rain in the North Carolina–Virginia area. Clouds were patchy and consisted of more or less well defined layers separated by clear air. Blue sky and/or the surface were frequently visible. In contrast to the flight of 5 March 1983, these clouds exhibited little if any turreting, appearing quite stratified or fog-like. Liquid water content was rather low, varying between 0 and 0.4 $g\,m^{-3}$, as indicated in Figs 6 and 7. Turbulence was also quite low ($\varepsilon \lesssim 15\,cm^2\,s^{-3}$ between 2005 and 2025).

Figures 6 and 7 illustrate the relation between b_{scat} and cloud liquid-water content observed on this flight, namely that the presence of cloudwater was invariably associated with values of b_{scat} much lower than in adjacent subsaturated air and approaching the Rayleigh scattering coefficient of air. This association holds even for rather low values of LWC. Thus, for the periods 1905–1910 and 1915–1926, which were characterized by what appear to be unbroken periods of cloud (LWC $\lesssim 0.2\,g\,m^{-3}$), one sees a decrease of ~ 80% in the average value of b_{scat}, relative to the non-cloud envelope value. Even quite low values of LWC resulted in substantial decreases in b_{scat}. Attention is called for example to the data for 1904 and 1913, where patches of LWC $\lesssim 0.1\,g\,m^{-3}$ resulted in a decrease of b_{scat} by as much as an order of magnitude. This relation is seen to hold even for patches of cloud of quite small extent,

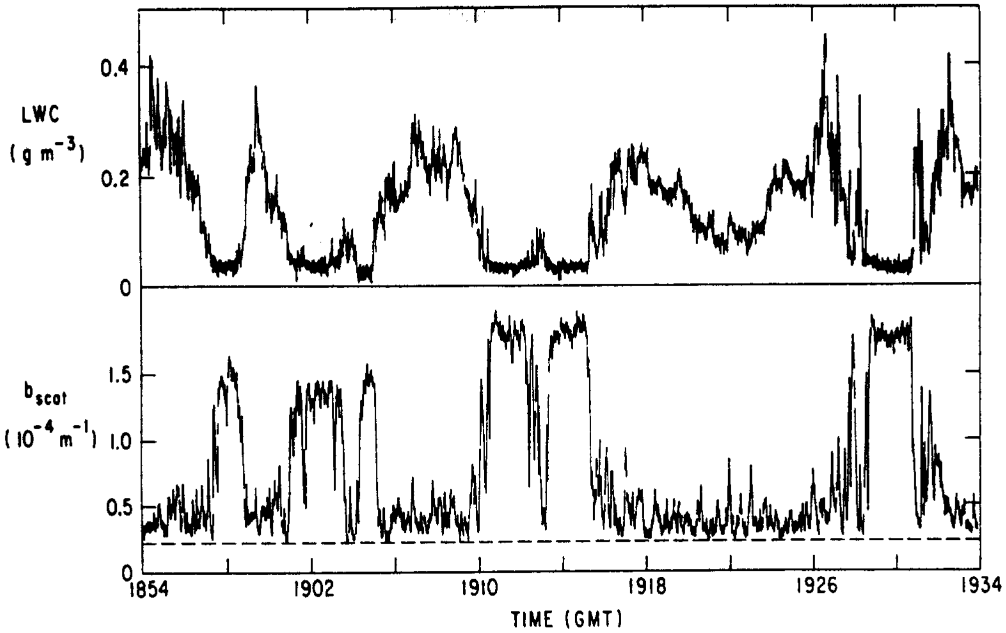

Fig. 6. Time records of LWC and b_{scat} from a portion of the flight of 10 March 1983, in vicinity of Norfolk, VA. Altitude, 1.0 km MSL.

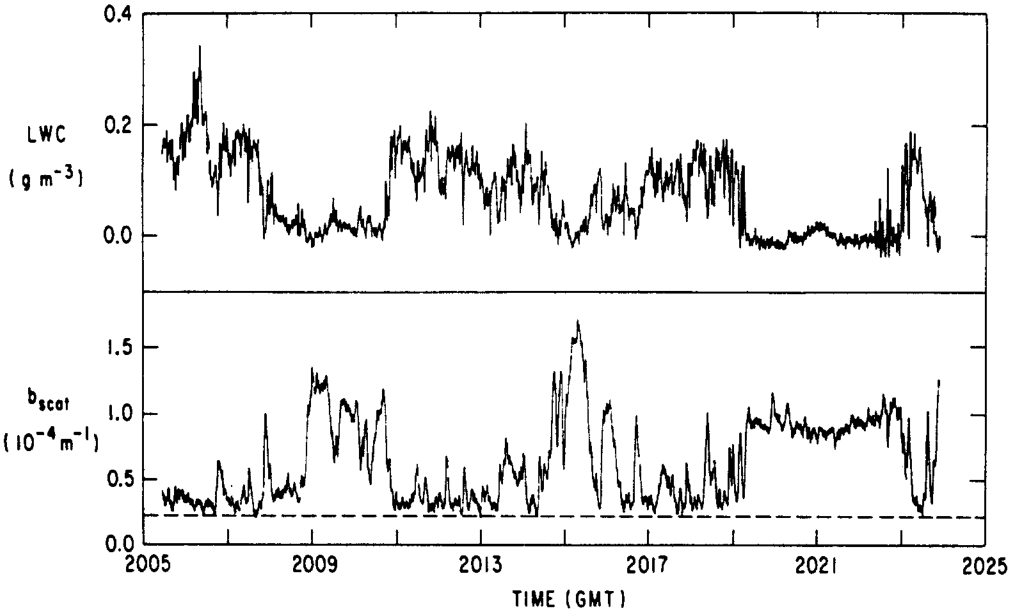

Fig. 7. Time records of LWC and b_{scat} from a portion of the flight of 10 March 1983. Altitude, 1.2 km MSL.

approaching the resolution of our measurements (~ 2 s ≈ 100 m). Thus, one notes a sharp decrease in b_{scat} associated with very short regions of low LWC, e.g. 1901.7 and 1903.3. Examples may be seen also of the converse observation, namely that periods of zero or near-zero LWC of very brief extent may be associated with sharp positive excursions of b_{scat}, e.g. 2008.2 and 2016.8. These observations give further support to our interpretation of highly efficient and reversible scavenging of light-scattering aerosol particles by cloud droplets.

While the foregoing observations are consistent with the picture of nearly complete scavenging of light-scattering aerosol particles by cloud droplets, close examination of the data in Fig. 6 reveals a number of instances that appear to be counter-examples of this phenomenon. Thus, there appear to be numerous examples of brief regions of significant b_{scat} within regions of apparently continuous cloud, e.g. 1907.0, 1908.0, 1922.0, 1923.1, 1926.0, 2006.8, 2017.1–2017.3, 2018.4–2018.6, that might represent significant unscavenged light-scattering aerosol particle concentration within cloud regions. An alternative explanation, which we consider more likely, is that these signals are representative of small-scale structure in the clouds, i.e. imbedded subsaturated regions, that are not resolved by the liquid-water indicator. In support of this we note that the trace for LWC exhibited rather large fluctuations throughout this flight and that many of the peaks in b_{scat} within clouds were associated with negative deflections in LWC, which we take to be an indication of patchy subsaturation even if the LWC trace did not actually reach zero.

12 *August* 1983, *Long Island*, *NY*

The surface weather map showed a low pressure cell centered in central New Jersey and a warm front extending on an E–W line S of Long Island. Measurements were made over Long Island in broken, low-level stratus clouds associated with the front. Although areas of scattered heavy showers were reported in the area, surface observations during the time of the flight indicated relatively little precipitation at the time of the measurements reported here. Figure 8 shows a series of measurements made in and out of patchy clouds at 1.7 km MSL. Liquid-water content was fairly high within clouds, exhibiting strong gradients at the cloud boundaries. Light-scattering coefficient, b_{scat}, which was measured using the nephelometer pre-heater, mirrored the sharp features of the liquid-water content, the b_{scat} trace approaching the Rayleigh scattering coefficient of air in the presence of cloudwater; residual in-cloud b_{scat} is less than 10% of the non-cloud values. As was noted in the examples above, even small patches of low LWC clouds were found to result in large decreases in b_{scat}, e.g. 1857.1 and 1857.5. These observations hold even at the moderate

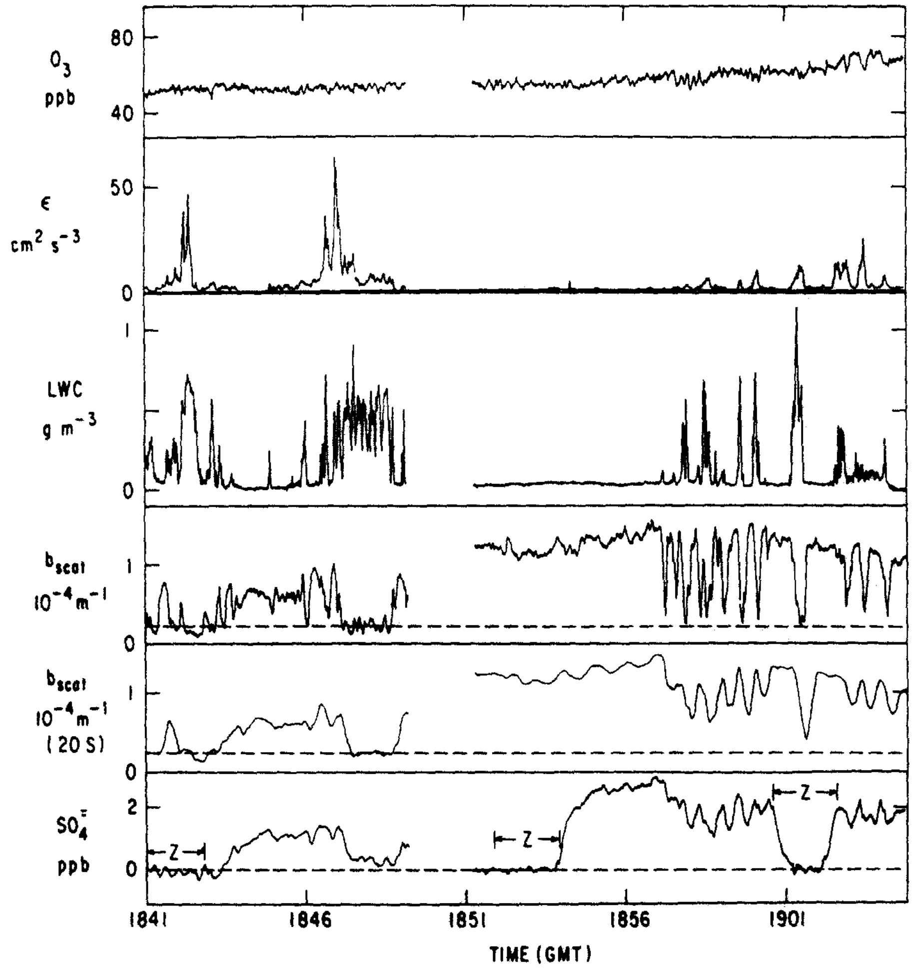

Fig. 8. Time records from a portion of the flight of 12 August 1983, Long Island, New York. Gaps represent missing data. Note periods of instrument zeroing for [SO_4^{2-}] signal. Zero of trace for LWC may be inferred from values in cloud-free air. Dashed lines on b_{scat} traces represent Rayleigh scatter of air, $0.2 \times 10^{-4}\ m^{-1}$. Lower trace for b_{scat} represents a 20-s running average of upper trace. Altitude, 1.7 km MSL.

to extremely low values of epsilon encountered in this flight, indicating that turbulent mixing plays little role in the scavenging phenomenon.

Also shown in Fig. 8 are the trace for $[SO_4^{2-}]$ and, for comparison, the b_{scat} trace degraded by running average to a 20-s time constant. The similarity in the traces substantiates the close correlation between the two quantities, consistent with the interpretation that the same mechanism is responsible for scavenging of the sulfate aerosol and the light-scattering aerosol. The ratio of b_{scat} to sulfate concentration derived from these measurements is $0.55 \pm 0.04 \times 10^{-4}\,m^{-1}\,ppb^{-1}$ ($14.1 \pm 1\,m^2\,g^{-1}\,SO_4^{2-}$). This value is substantially lower than values obtained for b_{scat} measurements without the pre-heater ($23 \pm 3\,m^2 g^{-1}$, data of 17 November 1982) but is comparable to values obtained in low relative humidities and/or with the nephelometer pre-heater in a variety of locations, as noted in the Appendix. Residual in-cloud sulfate concentration during extended periods of cloud (1848) can be confidently stated to be less than 30% of the non-cloud value. However, comparison of the 20-s b_{scat} trace with the sulfate trace at 1857–1901 suggests that the scavenging efficiency for sulfate may in fact be as great as that for b_{scat}, i.e. 90% or more.

Further observations

The observations reported for the several case studies of large, essentially complete decrease of b_{scat} within clouds are representative of a substantially larger set of data that we have obtained in aircraft flights over the past several years. A number of these measurements are summarized in Table 1 for situations where comparison could be made between in-cloud and cloud-free regions, permitting estimation of the residual b_{scat} within the clouds. This residual b_{scat} is given in the table as $R_{b_{scat}}$, representing an upper limit to the fraction of non-cloud b_{scat} present in the cloud regions, averaged over the duration of in-cloud periods. This quantity is considered to represent an upper limit to the amount of light-scattering aerosol that is not incorporated into cloud droplets, reflecting both the limits of our ability to distinguish the in-cloud measured b_{scat} from the background Rayleigh scattering of air and the inevitable possibility of imbedded regions of subsaturation within the clouds that are not

Table 1. Summary of comparisons of non-cloud and in-cloud light scattering coefficient and sulfate concentrations

Date	Location	Time (GMT)	Altitude (km, MSL)	LWC* ($g\,m^{-3}$)	b_{scat}† ($10^{-4}\,m^{-1}$)	$R_{b_{scat}}$ ≤‡	$[SO_4^{2-}]$† (ppb)	$R_{SO_4^{2-}}$ ≤‡	Figure
11-08-82	LI	1830–1900	0.75	0.3–0.5	0.4	0.4			
23-08-82	LI	1830–1905	1.2	0.1–0.4	1.8	0.1	~ 2	~ 0.5	
25-08-82	LI	1415–1420	0.9 → 1.2	0.1	1.8 → 0.8	0.1			
		1445–1525	1.8	0.5–0.8	1.8	0.1	~ 1.5	~ 0.7	
30-09-82	LI	1530–1555	0.9	0.15	0.3	0.4	< 0.3		
		2200–2220	0.6	0.4–0.6	0.2	0.5	< 0.2		
		2330–2400	0.6	0.2–0.3	0.3	0.4	< 0.3		
17-11-82	AL	1235–1330	1.8	0.8-1	0.3	0.2			4
		1345–1420	1.2	0.4	0.7	0.1	0.9 ± 0.3	0.3	4
		1430–1505	0.9	0.2	0.9	0.1	1.2 ± 0.2	0.2	4,5
19-11-82	AL	1705–1715	2 → 0.75	0.1–0.3	0.4 → 0.95	0.1			
		1715–1735	0.75	0.25 §	1.2	0.1	1.4 ± 0.4	0.25	
		1840–1845	0.75	0.1–0.2	0.3	0.4	< 0.3		
05-03-83	SC	1955–2010	1.5 → 2.6 → 2.1	1.3	0.9 → 0 → 0.75	0.1			1,2
		2010–2050	2.1	1.3	0.85	0.1	1.4 ± 0.4	0.5	1,3
10-03-83	VA	1850–1940	1.05	0.2–0.4	1.7	0.15	1.5 ± 0.4	0.25	6
		2000–2025	1.2	0.2–0.3	0.7–1.5	0.2	1.1 ± 0.5	0.5	7
24-04-83	LI	1300–1325	0.6	0.35 §	1.8	0.1	1.2 ± 0.5	0.5	
		1505–1530	1.8 → 0.9	0.45 §	0.35	0.3			
25-04-83	LI	1600–1700	0.5	0.55	1.2	0.2			
16-05-83	LI	1305–1330	0.75	0.1–0.5	0.4	0.2	< 0.2		
		1930–1955	0.75	0.2	0.2	0.5	< 0.2		
29-06-83	DE-MD	1335–1530	0.5	0.2–0.7	0.4	0.2	~ 0.3		
		1715–1745	0.6	0.3–0.5	0.2	0.4			
		1750–1840	0.6	‖	0.4	0.3	~ 0.3		
12-08-83	LI	1100–1245	0.9	0.9	0.5 ¶	0.1	0.6 ± 0.2	0.3	
		1735–1840	1.5	0.4–0.6	0.7 ¶	0.1			
		1840–1905	1.7	0.6	1.2 ¶	0.1	2.5 ± 0.4	0.25	8
29-08-83	NJ	1900–1910	1.5	0.15	3.8	0.1			

* Envelope of liquid-water content in cloud regions.

† Envelope of values in cloud free regions; for b_{scat}, after correction for Rayleigh scatter of air.

‡ Upper bound of residual b_{scat} (after correction for Rayleigh scatter of air) or SO_4^{2-} concentration, expressed as fraction of cloud-free values.

§ Heavy rain present.

‖ Liquid-water content indicator inoperative.

¶ Heated nephelometer inlet.

resolved by the liquid-water indicator. Thus, in all cases we would consider the observations to be consistent with essentially complete uptake of light-scattering aerosol by cloud droplets, although the possibility of average residual b_{scat} up to the values shown cannot be excluded.

Also included in Table 1, where available, are the values of sulfate concentration (as determined from FPD measurements) and an estimated upper limit to the fractional residual unscavenged sulfate concentration, $R_{SO_4^{2-}}$. As with $R_{b_{scat}}$, this quantity is an upper limit, consistent with high, essentially complete uptake of sulfate by cloud droplets, but not precluding the possibility of unscavenged sulfate to the extent indicated. The less stringent bound compared to that for b_{scat} is a consequence of the reduced sensitivity and time response of the FPD relative to the nephelometer, and should not be considered to be an indication of lower actual scavenging efficiency.

DISCUSSION

The concentration of sulfate aerosol and the coefficient of light scattering are found to be quite low in interstitial cloud air, i.e. at or below the limits of detection, viz. 0.1–0.3 ppb for $[SO_4^{2-}]$ and $5 \times 10^{-6}\ m^{-1}$ for b_{scat}. These measurements, together with measurements of these quantities in non-cloud air, allow inferences to be drawn of the efficiency of uptake of sulfate-containing, light-scattering aerosol particles into cloud droplets. From considerations of limits of detection lower bounds on this scavenging efficiency are frequently as great as 75% (based on measurement of $[SO_4^{2-}]$) or 90% (based on measurement of b_{scat}), but both measurements would be consistent with essentially complete uptake into cloud droplets.

The high scavenging efficiencies reported here and the rather high bounds placed on these efficiencies contrast, in some cases markedly, with results of previous studies cited in the Introduction. We feel that the present approach to determination of scavenging efficiencies constitutes a more sensitive and reliable approach than other approaches previously employed. The reasons for this are briefly outlined here.

1. *Direct measurement.* The signals corresponding to residual (non-scavenged) interstitial aerosol, i.e. $[SO_4^{2-}]$ and b_{scat}, are measured directly and with the same instruments as the non-cloud quantities. This approach thus contrasts with the approach of comparing measurements by two different techniques, e.g. clear-air sulfate concentration vs concentration in collected cloudwater samples multiplied by liquid-water content, for which comparison cloudwater collection efficiency and cloud liquid water content must be accurately known. Also, since the unscavenged fraction is small, the fractional uncertainty in this quantity would necessarily be large if it were to be obtained as the difference of two numbers of comparable magnitude.

2. *Rapid time response.* Use of rapid response instruments minimizes the possibility encountered with filter collection over tens of minutes, of contamination of in-cloud signal by regions of subsaturated air imbedded within the cloud. (We note here that instances of low scavenging efficiencies reported in our own previous work (Daum *et al.*, 1984a) may be attributable to such contamination.) The use of rapid-time-response instruments also allows frequent comparison of in-cloud and non-cloud measurements in situations such as broken clouds where these two regions exhibit similar history and composition.

3. *Specificity.* Measurement of aerosol sulfate concentration is chemically specific and, as well, is not subject to interference by in-cloud reaction, as would be the case for methods involving cloudwater collection. Measurement by b_{scat}, while not chemically specific, is a robust surrogate for aerosol particle mass or sulfate concentration. This approach thus contrasts with approaches based on measurement of aerosol particle number concentrations and size distributions, which require additional interpretation to yield unscavenged volume or mass, and, in any event, are not chemically specific.

We feel that these considerations support the interpretation of the present measurements as indicative of highly efficient scavenging by cloud droplets of sulfate-containing and light-scattering aerosol particles. Moreover, based on the observations reported here, we suggest that the phenomenon of highly efficient scavenging of soluble or partially soluble accumulation-mode particles by liquid-water clouds is probably quite generally the case.

Comparison with theory

Recent numerical studies (Jensen and Charlson, 1984; Flossmann *et al.*, 1985; Leaitch *et al.*, 1987) as well as earlier studies referred to in the Introduction have examined the efficiency of nucleation scavenging for various assumed sets of initial conditions (aerosol particle number and mass concentration; aerosol particle solubility) and supersaturation histories (rate of increase and maximum of supersaturation). The thrust of these calculations, as well as of the earlier studies, is that nucleation scavenging will result in the incorporation of a large fraction of soluble, accumulation-mode aerosol mass into cloud droplets soon (~ 100 s) after the onset of supersaturation. Within this generalization, however, there remain some areas of departure among cases treated by a single study or between studies. Notably, Flossmann *et al.* (1985) suggest that interstitial aerosol particle mass will be reduced via nucleation scavenging by several orders of magnitude compared to non-cloud aerosol mass. The generalization was found to hold even for particles consisting of as little as 1% soluble salt. In contrast, Jensen and Charlson (1984) find, depending on updraft speed and total aerosol mass loading, that a substantial fraction of aerosol mass may remain unactivated. Thus, for their 'clean continental background' case ($1.5\ \mu g\ m^{-3}$

NH_4HSO_4 equivalent to 0.3 ppb) the unscavenged aerosol was calculated to be less than 10% for all updraft velocities studied (2–500 cm s^{-1}), whereas for their 'urban average' case (38.4 $\mu g\,m^{-3}$ = 8 ppb) the fraction unscavenged was indicated to be a strong function of updraft velocity, decreasing from 75% (2 cm s^{-1}) to 55% (10 cm s^{-1}) to 5% (100 cm s^{-1}). A similar decrease in nucleation scavenging efficiency with increasing pre-cloud aerosol particle number density has been exhibited in the calculations of Leaitch *et al.* (1986).

The aerosol mass loadings and sulfate concentrations employed in the calculations of Jensen and Charlson (1984) may be compared to those observed in the present study via the data in Table 1. These data indicate for cases in which sulfate was directly measured a range of < 0.2–2 ppb. Alternatively if we take the values of b_{scat}, which are available for all of the cases, as a surrogate for sulfate, a range of 0.4–4 ppb is indicated, i.e. in at least one instance approaching the value employed in the calculations of Jensen and Charlson for their 'urban average' case. In none of the situations that we have examined have we found evidence of significant residual unscavenged light-scattering aerosol that would lend support to Jensen and Charlson's predictions of reduced scavenging efficiencies in situations of high aerosol loading and low vertical velocities. Indeed, if anything, we are more confident in estimating a low value for residual fractional unscavenged b_{scat} in cases of high non-cloud b_{scat} because of the larger value of b_{scat} to which the in-cloud signal is referenced. In fairness, we must qualify the comparison of the present observations to the model calculations of Jensen and Charlson by the fact that measurements of vertical velocities are not available. We do note, however, that the present generalization of no significant in-cloud b_{scat} continues to hold in situations of distinct stratus clouds with low values of epsilon that are suggestive of low vertical velocities.

Fate of scavenged aerosol

We have observed that along a given flight path at a given altitude in and out of clouds, not only is cloud interstitial air characterized by low b_{scat} but also the non-cloud air is invariably characterized by non-zero values of b_{scat} that exhibit a relatively smooth, slowly varying profile, i.e. that regions of low b_{scat} characteristic of cloud interstitial air are not found in cloud-free air. We have taken this observation to indicate that upon cloud evaporation, previously scavenged aerosol constituents are returned to clear air as light-scattering aerosol particles. It therefore follows that the fate of the dissolved aerosol constituents is the same as the fate of the water in which they are dissolved, i.e. release to clear air on cloud evaporation or delivery to the surface in precipitation. Since most clouds evaporate, rather than precipitate, one concludes that in similar proportion the dissolved material is returned to clear air. Pruppacher and Klett (1978, p. 349) have argued on the basis of cloud lifetimes, average global cloudwater burden, and precipitation rates that the average number of cloud evaporation–condensation cycles prior to precipitation is of order ten. There appears to be no mechanism that can effect spatial separation of aerosol materials from the associated water, either when the system consists of sub-μm aerosol particles plus water vapor or when the system consists of cloud droplets containing scavenged particles. Consequently, except for possible slight removal of accumulation-mode aerosol particles by dry deposition to the surface (Garland, 1978; Slinn, 1983), it would appear that these particles must, on average, undergo a similar number of excursions between clear-air aerosol and cloud droplet as water undergoes condensation cycles prior to removal in precipitation, i.e. of order ten. Such numerous excursions, together with any scavenging by cloud droplets of nuclei-mode (~ 0.01 μm diameter) aerosol particles or of gases by dissolution and reaction, would provide ample opportunity for production of internally mixed aerosol particles. Such an in-cloud mechanism has been recently proposed also for the production of internal mixtures in 1.5–4 μm remote marine silicate aerosol particles (Andreae *et al.*, 1986).

The finding of high efficiency for cloud scavenging of sulfate-containing accumulation-mode aerosol particles supports the early estimates of Junge (1963, p. 300), using assumed scavenging efficiency of unity, of average atmospheric residence times of such particles of order 2–10 days. This finding also provides support for the suggestion of Slinn (1974, 1983) that the rate-limiting step in the removal of such particles is the removal of cloud droplets by falling precipitation and not nucleation scavenging.

SUMMARY AND CONCLUSIONS

Continuous aircraft measurements are reported of aerosol sulfate concentration, $[SO_4^{2-}]$, and light-scattering coefficient, b_{scat}, in interstitial cloud air and in associated subsaturated air under circumstances where, except for the formation of cloud, the composition and history of the cloud air and the clear air have been similar. In essentially all situations of continuous cloud, $[SO_4^{2-}]$ approached zero and b_{scat} approached the Rayleigh scattering coefficient of air within the sensitivity of the measurements, indicative of highly efficient scavenging of light-scattering and sulfate-containing accumulation-mode aerosol particles. Instances of apparent unscavenged light-scattering aerosol may have been associated with unresolved subsaturated regions within the clouds or may represent a small fraction of unscavenged light-scattering aerosol. The maximum fractional unscavenged light-scattering aerosol, based upon the uncertainty of the measurements, was in many instances established to be as low as 0.1. Similarly the maximum fractional unscavenged aerosol sulfate concentration was established to be as low as 0.25. For both quantities the measurements are consistent with complete scavenging by cloud droplets. Additionally, the observation that $[SO_4^{2-}]$ and b_{scat} exhibited a relatively smooth profile, with low values only in the presence of clouds, is indicative of the reversibility of the scavenging process, i.e. that the dissolved material once again becomes clear-air aerosol upon cloud evaporation.

Acknowledgements—We thank Daniel Leahy, Robert Brown and Seymour Fink for their contributions to the aircraft measurements, and Joyce Tichler and Kathy Norden for assistance in data handling and preparation of the figures. One of the authors (HMtB) expresses his special thanks to Daniel Leahy for the way he was introduced into the complicated field of cloud measurements. We thank Mark Hjelmfelt (NCAR) for valuable discussion. This work was supported in part by the Electric Power Research Institute (RP2023-1) and was conducted under the auspices of the U.S. Department of Energy under Contract No. DE-AC02-76CH00016.

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APPENDIX: RELATION OF b_{scat} AND AEROSOL SULFATE CONCENTRATION WITH AN UNHEATED NEPHELOMETER

As noted in the experimental section, several previous investigators have pointed out the correlation between b_{scat} and sulfate concentration, viz.

$$b_{scat} = \beta [SO_4^{2-}],$$

where reported values of the coefficient β have ranged rather narrowly, as summarized in Table A1. In Fig. A1 are shown a number of simultaneous measurements of b_{scat} and $[SO_4^{2-}]$ obtained with an unheated nephelometer in aircraft flights in clear air at low relative humidities, typically 50%, which give a value of $\beta = 12.0 \pm 1.4\ m^2\ g^{-1}$ in good agreement with results of previous investigators using a heated nephelometer.

The rather narrow range of values obtained for β would, on face, appear to be rather surprising, since numerous variables other than SO_4^{2-} concentration, including aerosol composition and size distribution, are expected to influence this relation (e.g. Sloane and Wolff, 1985; White, 1986). The relative constancy of β would seem to reflect first the observation that the ratio of light scattering coefficient to

Table A1. Relation between b_{scat} and aerosol sulfate concentration

Location	β m^2/gSO_4^{2-}	Comments	Reference
Southwestern Pennsylvania	13.9 ± 1.2	With heater	Pierson *et al.* (1980)
Rural Arkansas	10	With heater	Waggoner *et al.* (1981)
New York City	8.8 ± 0.5	With heater	Leaderer *et al.* (1981)
Canadian Arctic	11 ± 3	Excess SO_4^{2-} only, with heater	Barrie *et al.* (1981)
Canadian Arctic	10.9 ± 1.1	With heater	Barrie and Hoff (1985)
France, Italy industrial regions	14–24	High r.h., no heater	Payrissat *et al.* (1984)
Maryland, Long Island aircraft measurements	12.0 ± 1.4	r.h. ~ 50%, no heater	Present study

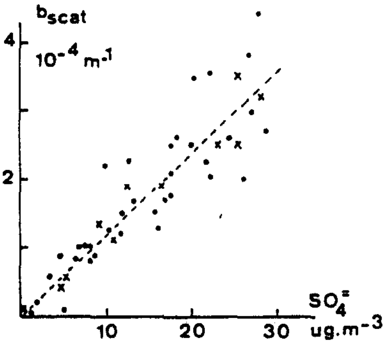

Fig. A1. Correspondence between sulfate aerosol concentration (30-min filter pack) and light scattering coefficient, $b_{scat}-b_R$ (average over time of filter sampling) in clear-air flights. Dots indicate flights over Maryland (1980). Crosses indicate flights over Long Island (1982, 1983).

aerosol particle volume is approximately independent of the size distribution of the aerosol for particle radii comparable to the wavelength of light employed (Pinnick *et al.*, 1980; Waggoner *et al.*, 1981; Lewis, 1981), and second, an apparent circumstance that sulfate anion and other associated species constitute a fairly uniform fraction by volume of sub-μm aerosol in the ambient atmosphere. With respect to the latter circumstance much attention has been given to the variable amount of liquid water associated with hygroscopic or deliquescent substances (such as sulfates) in aerosol particles, especially at high relative humidities as suggested by theoretical and laboratory studies (Garland, 1969; Charlson *et al.*, 1978; Tang, 1980). With respect to field measurements, Weiss *et al.*, (1982) showed an increase of a factor of two in b_{scat} as relative humidity was increased from 60 to nearly 100% that undoubtedly reflects an increased volume of light-scattering particles with increasing r.h. Such influence can be substantially reduced by use of the nephelometer pre-heater (Ruby and Waggoner, 1981).

With respect to the present investigation, liquid water associated with hygroscopic or deliquescent aerosol might be expected to exert a large influence on β, in view of the high relative humidities and in view of the fact that the nephelometer was generally employed without preheating of the airstream. The effect of relative humidity is evidenced in the present results by the ratio of b_{scat} to SO_4^{2-} concentration, e.g. in Fig. 5, for which $\beta = 23 \pm 3$ m^2 g^{-1}, i.e. a factor of two greater than at low r.h.

The dependence of β on relative humidity indicated in these measurements suggests that hygroscopic or deliquescent interstitial in-cloud aerosol particles would, as a consequence of water accretion, exhibit an enhancement in the ratio of b_{scat} to amount of unscavenged solute mass in comparison to that which the same particles would exhibit in clear air. Consequently any inferences of efficiency of scavenging of aerosol particles by cloud droplets drawn from comparison of in-cloud and clear-air values of b_{scat} obtained with the unheated nephelometer must be considered to be lower bounds to the actual efficiency. Similarly, one may note as well that comparison of particle concentrations within and outside of clouds by means of *in situ* probes to infer scavenging efficiencies as a function of particle size (e.g. Leaitch *et al.*, 1983) should be interpreted with caution.