Enhanced absorption of solar radiation by cloud droplets containing soot particles in their surface

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(Received 24 January 1991; revised 1 August 1991)

SUMMARY

Laboratory studies show that when soot particles from acetylene combustion are captured by drops of size 0.1 to 1 mm they remain partially submerged in the surface for several hours. The intensity of solar radiation passing through a drop is calculated to be much greater near the surface, and therefore with such particles on the surface will give enhanced absorption compared with the situation in which the particles are uniformly distributed throughout the drop volume. This gives a possible explanation for enhanced cloud absorption when soot particles are present in amounts consistent with field measurements.

1. INTRODUCTION

We draw attention to an effect which could contribute to an increase in absorption of solar radiation by cloud droplets that contain small amounts of absorbing impurity, provided such impurity is located close to the droplet's surface. The recent paper by Stephens and Tsay (1990) reviewed the disparity between observed and calculated values of absorption by clouds, and of cloud albedo, in the visible and near-infrared regions of the electromagnetic spectrum. The authors discussed a variety of effects which could possibly contribute to this discrepancy, such as large droplets (Wiscombe et al. 1984), cloud edge effects (Welch et al. 1980; Ackerman and Cox 1981; Rawlins 1989), water vapour near-infrared continuum hypothesis and aerosol effect (Danielson et al. 1969; Twomey 1972; Chýlek et al. 1984). Although disagreement is not found in all measurements, the reports of an absorption anomaly are sufficiently frequent not to be ignored. Absorption of solar radiation by clouds is a component of the global radiation budget of the earth, and can reduce the solar flux by as much as 10 to 20%, whereas the theoretical estimate of this reduction is less than half these values.

An energy density distribution with enhancement close to the surface of a typical cloud-sized droplet has been reported by Chýlek et al. (1985) who demonstrated the effect theoretically, and subsequently verified it by laboratory experiments. It follows that should there be some means whereby absorbing aerosol particles are concentrated near this interface, they will be much more effective at absorbing radiation than if they were distributed uniformly throughout the droplet. A certain class of aerosol particle, containing a hygroscopic component, acts as a cloud condensation nucleus, leaving the less hygroscopic aerosol particles as interstitial between the cloud drops (Hudson 1984). These aerosol particles may be captured by droplets through inertia or, more likely, through Brownian diffusion and could attach themselves to the outer surface of a drop. Should these particles contain only small amounts of hygroscopic material, they could reside on the droplet surface for a considerable time.

2. EXPERIMENTS

Soot was produced from an acetylene flame with oxygen adjusted to low values to give particles with a maximum size of some 5 μm diameter. Drops with diameter 10 to 20 μm were produced by a 100 kHz ultrasonic nebulizer and allowed to coalesce to a size of 100 μm to 1 mm diameter on a nylon mesh or on a microscope slide covered with a non-wetting polyethylene film. The slide or mesh was then held briefly for one second in the smoke, some 20 cm from the flame, for soot particles to be collected on the drops. The flow rate was adjusted by a fan to be near 4 m s$^{-1}$—the terminal velocity of a 1 mm drop. The soot particles impinged on the drop surface and were subsequently examined under a microscope. The relative humidity was maintained near 100% by enclosure in a small chamber covered with wet filter paper.

It was observed that these particles remained on the surface of the drop for several hours, and were swept to the lee side of the drop by the airflow. Figure 1(a, b) shows particles collected on the lee and upstream sides of a drop, viewed under quiescent conditions in the humidity chamber. Particles of sizes down to at least the limits of resolution (about 1 μm) remained on the
Figure 1. Soot from acetylene combustion on the surface of a water drop suspended on a nylon mesh. Each soot particle is an aggregate of much smaller (<0.1 μm) spheroidal particles. (a) Shows particles collected on the lee side (more) and (b) on the leading surface (less) of the drop from sooty air flowing through the mesh. The microscope is focused on the lower and upper surface, respectively. (c) Shows particles coalesced in a partial surface layer. (d) Shows soot particles part in and part out of the water surface.

surface for a period of several hours—a reasonable upper limit for the lifetime of a droplet in a cloud. At low concentrations the particles remained individually on the surface; under high concentrations they aggregated to form a well-defined surface patch with the larger particles remaining apart (Fig. 1(c)). Figure 1(d) clearly shows large soot particles protruding from the drop surface. Particles of sizes down to about 1 μm were observed to behave in this way. Soot particles of sizes less than 1 μm could not be studied by this technique, as they are beyond the resolution of the microscope. It does however appear that such particles are collected and form into layers (Fig. 1(c)) which appear continuous because of the limits of the optical resolution; from which it is reasonable to suppose that the smaller particles will be retained on the droplet surface for a similar length of time.

The question now arises how these particles interact with incident radiation and how the degree of absorption varies between particles on the surface and particles uniformly distributed throughout the drop volume. The energy density distribution within the droplet can be represented by the source function, S, defined as \( S = \frac{|\mathbf{E}|^2}{|\mathbf{E}_0|^2} \), where \( \mathbf{E} \) is an electric field vector at a location within or near the surface of the droplet, and \( \mathbf{E}_0 \) is the electric field vector of the incoming radiation. A typical distribution of the source function on the axis of a 7.0 μm diameter droplet is shown in Fig. 2; it changes in detail with drop size, as shown by comparison with the 7.1 μm diameter droplet, but in all cases increases near the drop surface. The details of such calculations
are given by Chýlek et al. 1985. In general, enhancement is higher for larger droplets and for higher refractive indices, although the changes within the refractive index range between 1.25 and 1.50 are only of the order of a few percent. A similar but slightly lower enhancement exists in other directions at all points close to the surface of a droplet, although any directional dependence disappears in the case of diffuse radiation inside the cloud and near the cloud base. If a small absorbing particle is placed in an electromagnetic field its absorption is linearly proportional to the amount of electromagnetic energy incident on it. Consequently, if an absorbing particle is placed close to the surface of a droplet where the electromagnetic energy density is considerably higher than the energy density remote from the droplet, its absorption will be enhanced by a factor approximately equal to the source function at that point. This is true only if the absorbing particle is sufficiently small so that it does not significantly affect the energy distribution corresponding to a homogeneous droplet. A typical submicrometric-sized soot particle attached to the surface or submersed inside a cloud droplet may be supposed to satisfy the above requirement. Consider for example a 0.1 μm sized soot particle (typical of aircraft exhaust) on the surface of a 10 μm diameter droplet. The soot particle occupies only 0.0025% of the droplet's surface area and therefore would appear to be unlikely to affect significantly the fields inside and close to the surface of the droplet.

It is very difficult to investigate experimentally the fields inside a micrometric-sized droplet; according to our knowledge only indirect information can be obtained. One possibility is to investigate the resonance structure in scattering by a large pure droplet and by one containing a small amount of absorbing impurity. For that purpose we performed the following experiment. A single droplet, diameter between 6 and 20 μm, was levitated by the radiation pressure of a laser beam, and the intensity of light scattered at 90 degrees was measured. As the droplet slowly evaporated it passed through a series of resonances which were clearly observed in the scatter pattern. The resonances in the scatter pattern are related to resonances in internal fields. Thus, if for a droplet containing particulate impurities a change in resonance structure is observed, one may expect that there is also a similar change in the internal fields. On the other hand, if for a given amount of absorbing impurities no changes in resonance structure of the scattered field are observed, we can assume that there are also no observable changes in the fields inside the droplet. Our experimental results indicate that the presence of a small amount of absorbing material in 6–20 μm sized droplets does not in fact affect the resonance structure of droplets. This result was demonstrated by levitating droplets from a nebulizer by a laser beam and measuring the intensity of radiation scattered at an angle near 90 degrees. Glycerol (refractive index 1.47) was chosen as the dielectric material to minimize evaporation during the course of the experiment. Submicrometric particles of carbon black were uniformly mixed in the liquid. The transmittance along a cell of length l cm for the bulk suspension within the wavelength band 0.51 μm ≤ λ ≤ 0.52 μm was measured using a Cary 14 spectrophotometer. The imaginary part of an effective refractive index, $n_i$, at the laser wavelength, λ, of 0.514 μm was determined from the relation $n_i = -(λ l)/4πl$ for a range of mixing ratio up to $2 \times 10^{-5}$. Experiments with individual droplets have shown that the presence of the highly-absorbing material within a droplet does not destroy the resonance structure of the electromagnetic field. Figure 3 shows the measured scattered intensity at 90 degrees of pure glycerol (GL) and for two droplets of a glycerol–carbon-black mixture (C1 and C2); the basic resonance structure of the pure glycerol is preserved in the droplets. Additional peaks appearing in the glycerol–carbon mixture are not reproducible and are probably related to the configuration of the carbon-black particles within the droplet. Although a microscopic examination showed that some particles were near the drop surface, nevertheless the main resonances showed very little change in the measurements. This implies that the structure of the electromagnetic field remains essentially unchanged and that therefore the specific absorption of the carbon will be enhanced by a factor approximate equal to the value of the source function at the place where the carbon particle is located (Chýlek et al. 1992). At resonance the source function reaches values of $10^6$ to $10^7$ (Chýlek et al. 1985). However, this resonance enhancement occurs only for a given size of droplet and certain very narrow spectral bands of solar radiation. Consequently, this resonance enhancement will have only a small effect on the absorption of solar radiation by cloud droplets. It is only the enhancement away from the exact resonance state, which is of the order of 10 to 100 (Fig. 2), and which occurs close to the droplet surface at all wavelengths and droplet sizes, that can produce the important enhancement of absorption of solar radiation by clouds. Although our experiment and calculation (Fig. 2) were performed with a glycerol droplet, the same conclusion is valid for droplets of a water and water–carbon-black mixture, as the scatter functions and physical processes are similar. For clouds in which the carbon particles are distributed randomly throughout the droplets, a carbon-to-water mixing ratio of $5 \times 10^{-6}$ is required to reduce the droplet single-scattering albedo, $ω_0$, to 0.999 and to decrease the cloud albedo by 5 to 10% (depending on the cloud type),
Figure 2. Distribution of the source function \( S = |E|^2 / |E_o|^2 \) on the axis of a spherical particle of about 7 \( \mu \)m diameter with refractive index \( m = 1.47 \) (from Chylek et al. 1985). Negative horizontal coordinate represents the irradiated side of the drop; positive . . . the shadow side.

compared to pure water clouds. If the carbon particles are located close to the surface of the droplets (within the distance of about 10% of radius inside or outside) then calculations similar to those of Chylek et al. (1984) show that a realistic carbon-to-water mixing ratio of \( 5 \times 10^{-8} \) to \( 5 \times 10^{-7} \) (Twohy et al. 1989) is sufficient to reduce the droplet single-scattering albedo, \( \omega_s \), to 0.099.

The specific absorption of graphitic carbon in the atmosphere has a value normally around 10 \( \text{m}^2 \text{g}^{-1} \). When carbon particles are distributed randomly within a droplet, its specific absorption can be increased by up to 20 to 25 \( \text{m}^2 \text{g}^{-1} \). If the carbon particles are located close to the droplet surface, its specific absorption can reach values considerably higher, enhanced several hundred times, the exact value depending on droplet size. This degree of enhancement, given the measured soot concentration could account adequately for the observed discrepancies.

The location of carbon and other absorbing aerosol particles inside the droplet will depend on the way interstitial particles are scavenged by the droplet, as well as on the dynamical state within the cloud. The cloud-forming ability of particles produced by combustion has been assessed by classifying them on the basis of the ratio of cloud condensation nucleus to total nucleus content (Hallett et al. 1989). With supersaturations inside clouds of 0.5%, typical of most clouds, this ratio is about 0.7 for particles from burning vegetation (such as chaparral) or from forest fires, but is as little as 0.01 for smoke from hydrocarbons such as JP-4 aviation fuels (Pitchford et al. 1991), or 0.1 for sweet (i.e. low-sulphur) crude oil, rising to 0.4 for high-sulphur-content crude oil. These particles are normally about 0.1 \( \mu \)m in diameter and are readily incorporated into clouds downwind from their sources of origin, whether local or distant, such as surface oil fires or aircraft in flight. Particles on a droplet surface can be expected to be swept to the rear of the drop by the air flow over the surface if the surface layer is stable for a large concentration of particles (Fig. 1). Particles on the surface, with dry protruding parts and other parts immersed, lie in those parts of the drop where the field intensity is high, just outside and just inside the water surface. As the drops evaporate, the aggregates cover an ever-increasing fraction of the surface, until, when the humidity becomes very low, they collapse and form a solid soot aggregate. It is of interest to note that soot particles on ice behave in a similar manner, and that such particles are apparently only partly incorporated in the ice as it grows, yet remain on the outside as it evaporates (Oraltay and Hallett 1990).

3. CONCLUSIONS

Soot particles are a variable but important component of the atmospheric aerosol. They were produced in large quantities in the Kuwait oil fires; they have also been observed in snow in
mountain and polar regions (Chylek et al. 1987; Warren and Clarke 1990). This evidence of transport over such long distances demonstrates that clouds, even remote from industry, aircraft routes and ground fires, may contain soot particles, which are potentially capable of increasing the absorption of solar radiation significantly beyond the amount computed for clouds of pure water droplets.

We realize that these considerations add another complexity to the problem of absorption of solar radiation by clouds, namely, that not only is it important to know the total amount of absorbing material within cloud droplets, but it is also important to know the spatial distribution of such material within the droplet. The distribution may vary with time and with location within the cloud and could be very difficult to measure. Nevertheless, the complexity of the problem ought not to be the reason for its being ignored.

ACKNOWLEDGMENTS

These studies were supported by the Lawrence Livermore National Laboratory under Contract # BO48709, and by the National Science Foundation, Washington, D.C., under Contracts ATM-8715636 and ATM-9113908, also by the Atmospheric Environment Service and Natural Sciences and Engineering Research Council of Canada. P.C. thanks R. Pinnick and O. Ngo for the use of their experimental data shown in Fig. 3.

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