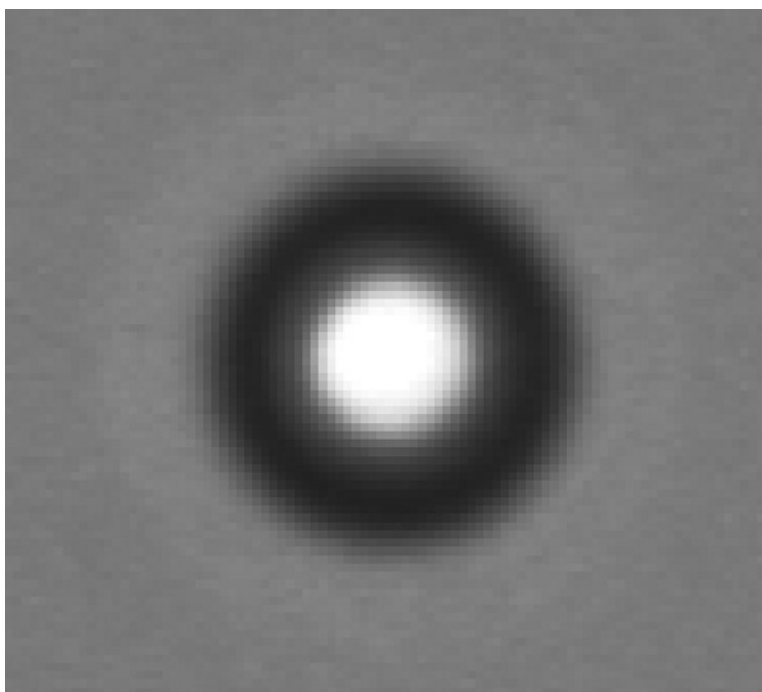Communication

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Laser Tweezers Raman Study of Optically Trapped Aerosol Droplets of Seawater and Oleic Acid Reacting with Ozone: Implications for Cloud-Droplet Properties

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In this communication we report two exciting results: first, the use of laser Raman tweezers to hold a mixed droplet of oleic acid and water at atmospheric pressure for 30 min, oxidize the oleic acid on the droplet, follow the decay of reactants and the growth of chemical products with Raman spectroscopy, and monitor the growth of the droplet size as the droplet becomes more hydrophilic. Second, we demonstrate that the oxidation of organic films on water droplets could have large climatic effects. Organic films can retard cloud-droplet growth and hence prevent cloud condensation nuclei from activating (to become cloud droplets). Chemical oxidation of these films, however, can allow cloud-droplet growth, thus forming a cloud and increasing the albedo of the Earth; in addition, activation reduces cloud albedo by inducing precipitation.

Sea-salt particles, formed following the action of wind on the surface of seawater, affect climate both directly, by scattering radiation, and indirectly, owing both to their ability to form clouds by acting as efficient cloud condensation nuclei and by altering the cloud-droplet spectrum by precipitation.[1] Many authors have suggested that in the atmosphere a significant fraction of these sea-salt particles will initially be coated with a hydrophobic organic layer,[2] a suggestion that has more recently been confirmed by atmospheric measurements.[3] The existence of an organic layer is significant because a hydrophobic organic layer would prevent the particle from taking up water to form a cloud droplet, whereas a hydrophilic organic layer would lower the supersaturation level required to activate a cloud condensation nucleus and form a cloud droplet. In the atmosphere the atmospheric oxidants, OH and NO_3 radicals and ozone, will attack the initially hydrophobic organic layer, forming more water soluble products and potentially destroying the organic film. If chemical oxidation were also to lead to a growth in the size of the particle, then new cloud formation could occur which would increase the albedo (reflectivity) of the planet and may alter the albedo of existing clouds by causing precipitation.

We present here the results of a study of the reaction of ozone with individually optically levitated droplets of oleic acid and aqueous sea salt. To the best of our knowledge this represents the first time that the optical levitation technique has been employed to study a heterogeneous gas-particle chemical reaction; the limited number of other chemical studies have looked at homogeneous reactions.[4] As the size and geometry of a droplet influences its thermodynamic stability (Köhler Theory) and kinetics of growth, the optical levitation technique (laser tweezers)[5] is ideal as it allows us to study the kinetics and size change of individual droplets associated with water uptake from the atmosphere (cloud-droplet
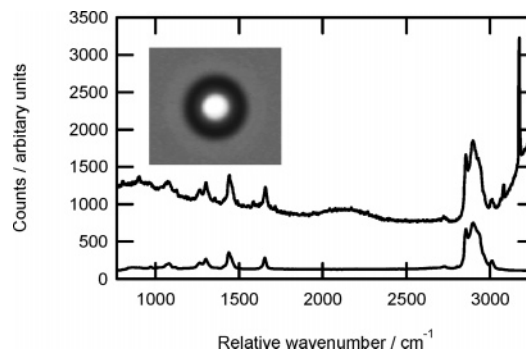

Figure 1. Raman spectrum of bulk phase oleic acid (lower trace) and a 3.1 μm oleic acid/aqueous sea-salt droplet (upper trace). The sharp feature above 3000 cm^{-1} in the droplet spectrum is a morphological resonace.[6]

formation) as an organic species is oxidized without experimental morphological constraints.

Solutions of oleic acid and synthetic seawater (Tropic Marine, 2 g L^{-1}) were nebulized and introduced into a small metal chamber using a gentle flow of oxygen that had been bubbling through pure water at ambient temperature to give a relative humidity of above 95%. A droplet of 5−9 μm was trapped in the focused beam of an Ar-ion laser (λ = 514.5 nm, ∼7 mW at point of focus). The other particles were removed from the system by collisions with the walls of the chamber or blown through the cell by the oxygen stream. The droplet was illuminated using the microscope light and the image focused onto a CCD camera. The scattered light from the laser beam was collected and fed through a notch filter, and the Raman scattered light was analyzed using a spectrometer. Raman signals were collected over 10-s time spans and recorded continuously during an experiment. Wavelength calibration was obtained by recording the Raman spectrum of bulk toluene. A Raman spectrum, showing peaks (assigned to oleic acid and water) and morphological resonances[6] (associated with the water peak) is shown in Figure 1. The insert in Figure 1 contains an image of a droplet held in the optical trap. The droplet size was monitored by recording an image every 10 s.

After 3−5 min of observing a constant Raman signal for a trapped droplet, a small portion of the oxygen flow (upstream of the water bubbler) was exposed to the light from a mercury pen ray lamp, thus producing a dilute (subpicomolar) concentration of ozone in the cell. The droplet was monitored until the Raman signals for oleic acid and its oxidation products were no longer observed, leaving a Raman spectrum of water only. The droplet was ejected from the optical trap and a background spectrum recorded.

The Raman spectra obtained were fitted to bulk spectra for oleic acid, nonanoic acid, azelaic acid, nonanal, nonanol, and water using fitting and subtraction programs. Referencing of reactant and

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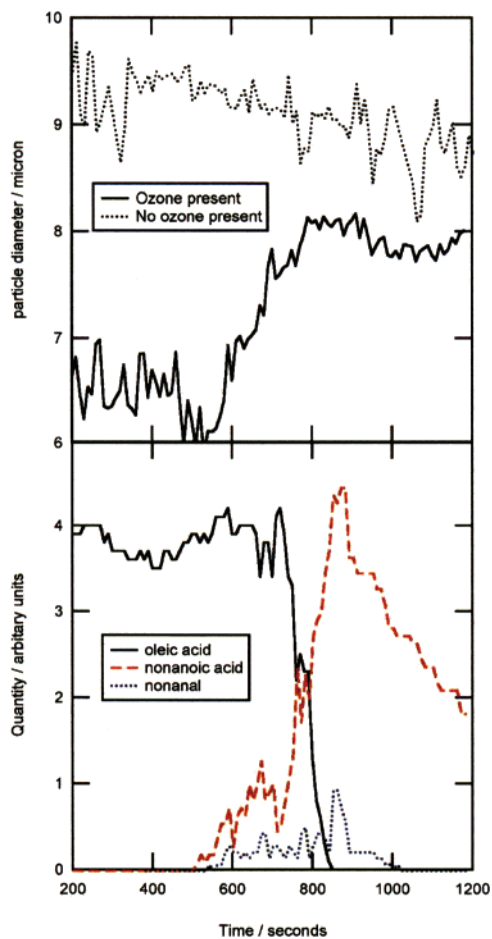[§] Rutherford Appleton Laboratory.

Figure 2. Particle diameter (upper plot) and quantity (lower plot) versus time profiles obtained when an optically trapped aerosol particle initially containing oleic acid and aqueous sea salt was exposed to a dilute flow of humidified ozone in oxygen. The nonanoic acid signal decayed to zero at longer reaction times. Assuming an inverted micelle structure, the oleic acid would initially exist as a 1.4 μm film on an aqueous salt core.

product spectra to the bulk spectra also allowed us to determine relative concentrations. Initially each droplet had an approximate mole fraction of oleic acid in the sea-salt aerosol of 0.20−0.25, as calculated from the Raman spectra.

In total, eight droplets were studied in detail, and all droplets demonstrated a rapid size change once oxidation of the droplet had begun. Figure 2 demonstrates the size (top panel) and relative quantity (bottom panel) versus time profiles during the oxidation of an oleic acid/sea salt droplet. No azelaic acid or nonanol were detected. For comparison the top panel of Figure 2 also includes size data for a similar oleic acid/sea-salt droplet that was not subjected to ozone. The abrupt appearance of the product nonanoic acid coincides and tracks with the increase in the size of the particle as it becomes more hydrophilic and absorbs more water vapor. The growth ends with the disappearance of the oleic acid. A small amount of the volatile species nonanal was detected in the particle. The Raman system is not sensitive to gas-phase species. The decay in the Raman signal of nonanoic acid and nonanal after 900 s is attributed to radical chemistry initiated by the reaction between Br⁻ and O$_3$ in the droplet,[7] a reaction thought to be initially hindered by oleic acid retarding transport of the O$_3$ to the salt core of the droplet.

This is the first study where the size and chemical composition of a mixed aqueous/organic droplet has been followed during oxidation. Previous groups have studied the oxidation of oleic acid;[8]

however, only two of these involved experiments on particles, and in both cases the aim of the experiments was to study the kinetics of ozone uptake and the final products of the reaction.

Products of the oleic acid and ozone reactions are discussed in the review by Rudich.[8] The major products that have previously been detected are nonanoic acid, nonanal, azelaic acid, and 9-oxononanoic acid. In this study we detected nonanoic acid and nonanal; azelaic acid was not detected, and 9-oxononanoic acid was not investigated. The difference between the product distributions observed in this compared to those of other studies can be rationalized because we have studied the reaction under conditions of high relative humidity and in the presence of trace metal ions found in seawater (that can convert the ozonide formed to generate carboxylic acids).

During the oxidation of the oleic acid the droplet changed size from 6.5 to 8 μm. There are two climatic effects that may be a consequence of this size change. First, the modeling work of Feingold[9] on warm marine stratoform clouds demonstrated that albedo may decrease following an increase in sea-salt aerosol diameter owing to the onset of precipitation. Similar evidence was given by Han[10] who also noticed that the albedo of optically thick warm marine- and land-based clouds increases as droplet size decreases. It should be noted that the radiative forcing over a marine area is −1.4 ± 1.4 W m⁻² with nearly all the uncertainty in the cloud albedo.[1] Second, the increase in size of our oxidized particle is due to lowering the relative humidity required for droplet growth caused by a change in the hydrophobicity of the particle. Thus, the oxidation of organic films on sea salt droplets may be important in new cloud growth by activating previously inert cloud condensation nuclei.

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