Oxidation of organic films on atmospheric aerosol

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Introduction

In this report we document the use of the laser tweezers to hold (optically levitate) and probe a seawater droplet coated in an organic surfactant (oleic acid) whilst the surfactant is oxidized by gas phase ozone. The chemistry of the droplet is probed with Raman spectroscopy, and the size is monitored with an optical microscope, both in real time. To the authors knowledge this is the first time the laser tweezers techniques has been used to study a heterogeneous gas-particle chemical reaction. For more information on this work the reader is directed to other references[1].

Scientific rationale

Airborne particulate matter plays a crucial role in determining the climate and weather of the Earth[2]. The chemical composition of particulate matter affects climate directly, by scattering and absorbing solar radiation, and indirectly, owing to its ability to act as cloud condensation nuclei, thus leading to an increase in cloud formation and changes to precipitation. Both the direct and indirect effects are influenced by the chemical composition of the aerosol. Organic films on atmospheric aerosol particles can retard cloud droplet growth. Chemical oxidation of these films by the common atmospheric oxidants OH, NO_3 or O_3 could remove this hydrophobic film and activate the particle (particle becomes more hydrophilic) for further growth (depending on the ambient relative humidity). Thus chemical oxidation could lead to cloud formation and the onset of precipitation.

The World's oceans are one of the largest sources of atmospheric aerosol[2] and it has been suggested that particles from this source have a hydrophobic organic coating. Atmospheric measurements confirm this suggestion[3].

Experimental

Marine aerosols were generated by ultrasonically nebulising a solution of oleic acid and synthetic seawater (Tropic Marin® 2 g L^{-1}). Each droplet trapped typically had a mole fraction of oleic acid of 0.2-0.25, corresponding to ~1.4 μm film thickness of oleic acid on each particle. The aerosols were mixed with a humidified stream of oxygen (RH ~95%) and blown into a small aluminum chamber located on the focus stage of an optical microscope. A droplet (3-9 μm) was trapped in the focus of an argon-ion laser (λ=514.5 nm, ~ 7 mW at the point of focus). The remaining particles were flushed from the cell. The scattered laser radiation was collected and analyzed on a spectrometer via a notch filter. Spectra were recorded over 10 second timescales continuously. The particle in the laser trap was illuminated by the microscope light and the optically filtered image was focused onto a CCD using the microscope optics to provide an optical image of the particle. A still image was recorded every 10 second in order to size the droplet. Figure 1 shows a Raman spectrum (in the C=C and C-H stretching region) of bulk oleic acid and of an oleic acid/sea water particle in the optical trap. The Raman spectrum of the droplet includes the start of the water band and morphological resonances[4]. The insert to Figure 1 includes a photograph of the 4 μm droplet.
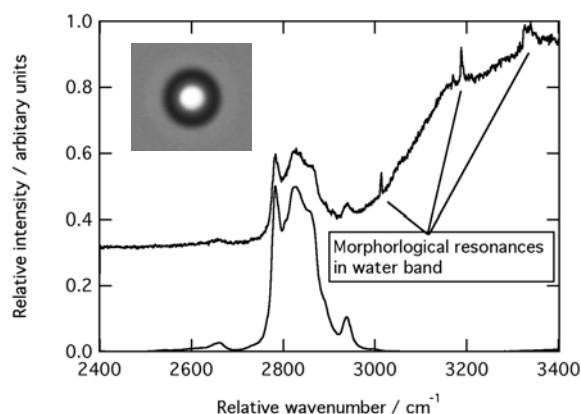

Figure 1. Raman spectra of bulk oleic acid (lower curve) and seawater/oleic acid droplet (upper curve). The upper curve has the water band to the right and the sharp features are morphological resonances[4]. The insert is a picture of a 4 μm droplet.

During a typical experiment the size and Raman signal of the droplet would be monitored for a few minutes and then the oxygen flow would be subjected to light from a mercury pen ray lamp to produce a sub-picomolar concentration of O_3 in the chamber. The reaction was monitored until no oleic acid was detectable in the Raman spectra. Experiments were undertaken without ozone present, and reference spectra were recorded without a particle in the trap and of the reactants and possible products: nonanoic acid, azelaic acid, nonanal.

Results

Of the numerous experiments performed 8 were studied in detail. Figure 2 demonstrates the results obtained for the reaction of a typical particle. The top pane of Figure 2 shows the size change accompanying the reaction and also shows how the recorded size of a particle held in the trap but not exposed to ozone varied with time. In the case of the particle not exposed to ozone the particles size does not change drastically, however, in the case of the particle exposed to ozone the size of the particle increases rapidly. The rapid increase in size occurs at the same time as the oleic acid is consumed and products (azelaic acid and nonanal) appear, as shown in the lower pane Figure 2. A detailed examination of Figure 2 demonstrates that the increase in the amount of products (nonanoic acid and nonanal) occurs at the same time as the particle uptakes gas-phase water and increases in size, but before the destruction of the oleic acid. This behavior is expected, as the products will make the surface of the particle hydrophobic and uptake water according to Köhler theory. The products nonanal and azelaic acid decay away with time. Nonanal is a volatile product and other workers have reported gas-phase nonanal when studying this reaction[5]. However the disappearance of the other product is thought to be due to radical reactions initiated by the reaction between Br^- in the seawater and the O_3 once the oleic acid film has been removed.
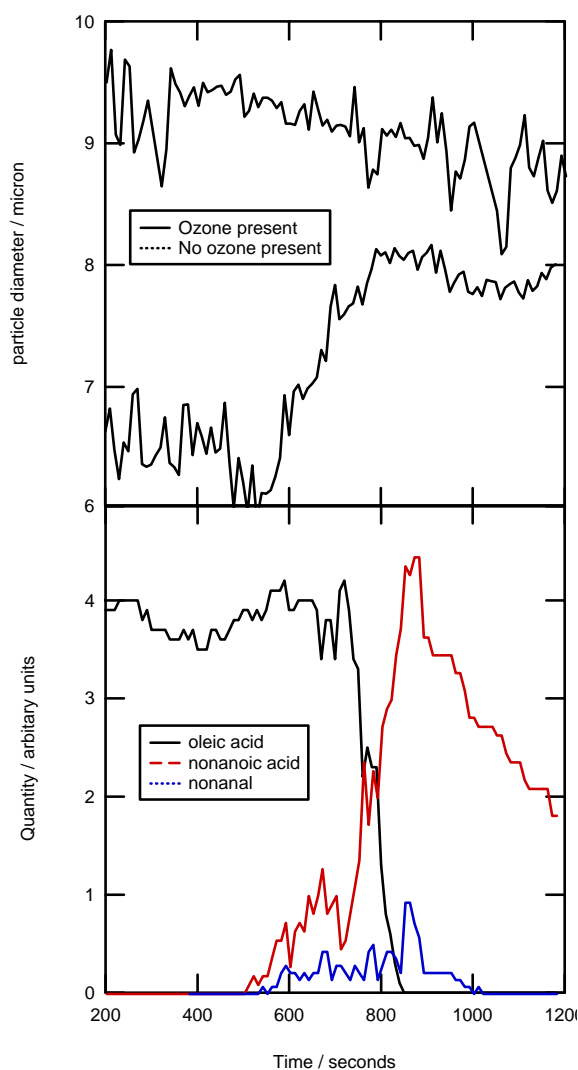
Figure 2. Top pane: Temporal profile for particle diameter for one particle in the presence of ozone (lower trace) and one particle in the absence of ozone (upper trace). Bottom pane: Temporal profile of the quantity of oleic acid, and products azelaic acid and nonanal with time.

The products of the reaction between oleic acid and ozone have been reviewed by Rudich[5]. The products and their abundance appear to depend on the chemical environment present during the collapse of the primary ozonide. Other studies have detected azeliac acid and 9-oxononanoic acid, which were not seen in this study. We view this study as more applicable to the atmosphere owing to the presence of water and transition metals in the seawater droplet, (which will catalyst the primary ozone decomposition) as shown by field studies[6].

Atmospheric and climatic implications

Chemical and size changes in atmospheric aerosol may have large effects for the Earth's climate. First the radiative forcing of clouds over a marine area is -1.4 ± 1.4 W m^{-2} with the uncertainty in cloud albedo. Both Feingold[7] and Han[8] have reported that the cloud albedo decreases with an increase in droplet diameter. Secondly new cloud formation will increase the planetary aldebo, and the oxidation of hydrophobic film on aerosol will activate the particles, to become CCN (cloud condensation nuclei).

Conclusions

- Laser tweezers can be used to hold droplets of aqueous solutions with organic coatings (inverted micelles) in air

for >30 minutes, whilst probing the chemistry in real time with Raman spectroscopy and monitoring the size with optical spectroscopy

- The oxidation of organic films on aerosol droplets will activate the CCN causing droplet growth

- The oxidation of organic films on giant CCN may have two climatic effects: cloud formation increasing the cloud cover and albedo of the planet and increased precipitation in polluted areas.

Acknowledgements

References

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