Growth and coagulation of aqueous aerosol droplets studied by cavity enhanced droplet spectroscopy

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Introduction

In an earlier report, we demonstrated that a single-beam gradient force optical trap (optical tweezers) can be used to trap and manipulate single decane or water aerosol droplets 4-14 μm in diameter for timescales of minutes and hours[1]. In addition, by recording spontaneous and stimulated Raman spectra from the trapped droplet, a unique fingerprint of droplet size and composition can be acquired[2-4]. This can allow the evolution in droplet size and composition to be monitored with high time resolution. The combination of optical tweezing and spectroscopy provides a powerful new strategy for examining dynamics of aerosols on a single droplet basis, allowing the fundamental factors that govern the chemical and physical transformation of the droplet to be addressed.

In this report, we illustrate that this approach can be used to monitor the growth of an aqueous aerosol droplet as ethanol is adsorbed at the droplet-gas interface. We also demonstrate that by trapping two droplets simultaneously in two optical traps, the coagulation of aerosol droplets can be investigated. Studies of these two processes could lead to a more detailed understanding of the factors that govern droplet size in complex environments, such as in the atmosphere.

Optical Tweezing and Cavity Enhanced Raman Scattering

Aqueous aerosol droplets are trapped from a nebulised mist of droplets generated with an Omron NE-U07 Ultrasonic Nebuliser in a purpose constructed aerosol cell, which permits the introduction of the aerosol flow and a regulated flow of humidified nitrogen or ethanol vapour. Trapping is achieved with a cw argon ion laser operating at 514.5 nm. The laser beam is passed through two sets of beam expansion optics, reflected from a holographic notch filter (HSPF-514.5, Kaiser Optical Systems) and directed into a Leica DM IRB microscope. A 60× oil immersion objective (NA of 1.4) is used to generate the optical trap in this work. The Raman scatter from the trapped droplet is collected in the backscattered direction by the objective lens, passed through the notch filter, and imaged into a 0.5 m spectrograph (1200 g/mm grating) coupled with a CCD, with a spectral resolution of 0.05 nm. The trapped droplet is imaged onto a CCD camera using conventional brightfield microscopy.

The Raman spectra acquired from a trapped aqueous droplet show a continuous band at Stokes Raman shifts corresponding to excitation of the OH stretching vibration at 3000-3500 cm^{-1}. This results from spontaneous Raman scattering from the droplet, as illustrated in Figure 1. Resonant structure arising from stimulated Raman scattering at wavelengths commensurate with *whispering gallery modes* (WGMs)[5] is evident superimposed on the continuous band. At these wavelengths, the Raman scattered light is coupled into WGMs with lifetimes on the order of nanoseconds. The Raman scattered light circulates in the WGM near the droplet circumference forming a standing wave with an integer number of wavelengths. This provides a mechanism for optical feedback and leads to stimulated Raman scattering at WGM wavelengths, also referred to as cavity enhanced Raman scattering (CERS). By comparing the wavelengths of the WGMs with Mie scattering calculations, the size of the droplet can be determined with nanometer accuracy[2,3].

Aqueous Droplet Growth in Ethanol Vapour

Knowledge of the kinetics of droplet growth or evaporation is crucial to understand the evolution of aerosol size distributions in the atmosphere and in combustion. The rate of mass transfer of a trace non-reactive gas across the interface between the gas and condensed phases is governed by a number of fundamental processes: gas diffusion to the droplet, mass accommodation at the interface, and diffusion into the bulk of the droplet[6,7]. Eventually, the rate of uptake of the trace gas will be balanced by the rate of evaporation of the trace species back into the gas phase and a Henry's law saturation limit is reached. Although the rates of gas and liquid phase diffusion can be routinely calculated, the factors that govern the transition of the trace molecule from the gas phase to the liquid phase in the interfacial region are poorly understood and quantified. It is the aim of the studies presented here to develop a new strategy for probing the mass transfer process. With the ability to measure the evolution in droplet size with nanometer accuracy and with a time resolution of ~ 1 s, the interfacial accommodation can be studied on trapped droplets directly.

To demonstrate the feasibility of this strategy, aqueous droplets were exposed to a nitrogen flow saturated with ethanol vapour and the size of the droplets monitored for timescales as long as 1 hour. During this time period, not only can the CERS technique probe the evolution in droplet size, but the appearance and growth in the CH stretching band at Raman shifts below 3000 cm^{-1} can be used to monitor the evolving composition of the droplet during the growth process. A sequence of three spectra is shown in Figure 1, with the change in wavelength spacing of the resonant modes reflecting the growth of the droplet from 3.84 to 4.56 μm. The growth of the CH stretching band is also evident. In Figure 2, we show that the evolution in droplet size and composition can be followed, with the ratio in the Raman intensities from the CH and OH time is evident. The arrows indicate that the WGM spacing becomes smaller as time progresses and the droplet grows.

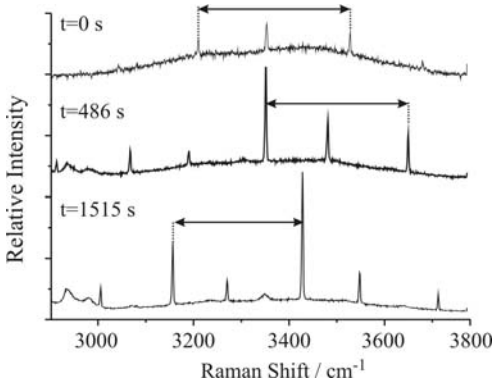

Figure 1. Three spectra at various times after a flow of ethanol vapour is introduced to the aerosol cell. Stimulated Raman scattering is observed superimposed on the spontaneous OH stretching band. The growth of the CH stretching band with stretching vibrations provides a quantitative measure of the evolving droplet composition.

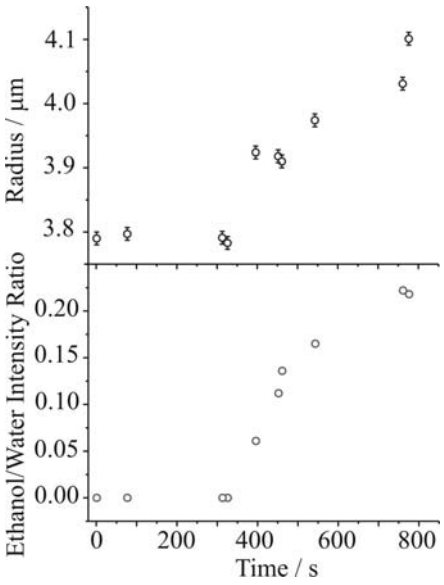

Figure 2. An example of the change in droplet radius and composition with time as a single trapped water droplet is exposed to ethanol vapour.

In addition to probing the growth of aqueous droplets in an ethanol vapour, we have looked at the response of a water droplet to variations in relative humidity. The relative humidity is controlled by flowing water vapour into the cell from two different water bubblers. In one bubbler, a saturated aqueous solution of NaCl produces a water partial pressure of 1.8 kPa. The trapped droplet is first stabilized at this relative humidity, acquiring an equilibrium size governed by Kohler theory. The saturated water vapour flow from a second bubbler containing pure water is then introduced to the aerosol cell, raising the partial pressure of water in the cell to 2.3 kPa. The droplet size responds to this increase in relative humidity, taking up water and growing, a process that is monitored by CERS.

The Coagulation of Water Droplets

By using a beam splitter to divide the trapping beam into two, two traps can be formed and two droplets can be controlled independently. This allows us to study the coagulation of aerosol droplets directly. A sequence of three images is shown in Figure 3, illustrating the control that can be achieved. Two water droplets are translated from a separation of ~10 μm to a point at which they coalesce.

The size of the water droplets can be determined before and after coagulation by CERS, as illustrated in Figure 4. The spectrum from the left droplet is first recorded, followed by the spectrum of the two separated droplets, and finally the spectrum of the coagulated droplet. Prior to coagulation the right and left droplets are 3.014 μm and 4.038 μm, respectively. The final coagulated droplet has a radius of 4.533 μm, and the combined volume before and the volume after coagulation is in agreement to within $\pm 3 \times 10^{-19}$ m^3. Although this would clearly be expected for the coagulation of two water droplets, this provides a powerful new approach for studying coagulation events.

Conclusions and Future Work

We have demonstrated that the combination of aerosol optical tweezers and cavity enhanced Raman scattering can be used to investigate the uptake of trace gas phase species onto water droplets and the response of the droplet size to changes in relative humidity. This can be achieved by monitoring both changes in droplet size and composition. We have also shown that the control provided by optical tweezers can enable the factors influencing the coagulation of aerosol droplets to be studied. Future work will exploit these two types of study to investigate fundamental processes governing aerosol droplet size distributions.

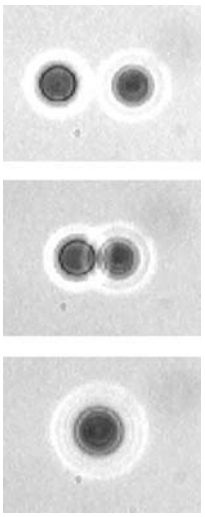

Figure 3. A sequence of images that show the controlled coagulation of two water droplets simultaneously trapped in two optical traps (Phys. Chem. Chem. Phys. 6 4924 (2004). Reproduced by permission of the PCCP Owner Societies).

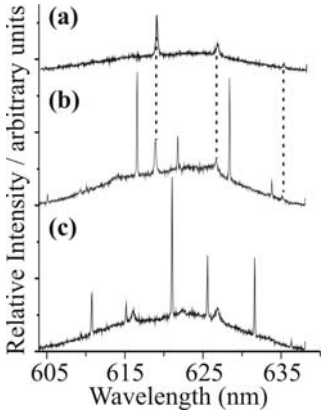

Figure 4. CERS fingerprints for (a) the right hand droplet prior to coagulation; (b) both droplets prior to coagulation and (c) the coagulated droplet (Phys. Chem. Chem. Phys. 6 4924 (2004). Reproduced by permission of the PCCP Owner Societies).

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