

Probing aerosol dynamics by interfacing optical tweezing with cavity enhanced droplet spectroscopy

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Introduction

Aerosols play a significant role in many diverse areas of chemistry and physics, spanning from the atmospheric sciences, to plasma physics and combustion science. Despite their wide ranging importance, quantifying and characterising their impact is challenging. Strategies for examining processes in aerosols rely mostly on conventional techniques that provide an ensemble measurement of particle size distribution and composition. Thus, the rates of heterogeneous chemistry and mass transfer are averaged over an ensemble of particles, making it difficult to address the fundamental factors that govern aerosol dynamics.

The strategy outlined here provides an opportunity to characterise in detail the dynamics occurring on a single particle, and to investigate the fundamental factors that govern aerosol particle size and composition in more complex environments. A single liquid aerosol droplet 4-14 μm in diameter is trapped and manipulated with optical tweezers. Spectroscopic techniques can then be used to characterise the trapped droplet. In this work we demonstrate that cavity enhanced Raman scattering can be used to determine the size of the droplet with nanometre accuracy and that the composition of the droplet can also be determined.

Aerosol Optical Tweezing

Particle levitation in a laser beam has been used to levitate an aerosol particle for timescales of hours, with the scattering force finely balancing the gravitational force exerted on a particle. However, such an approach does not allow manipulation of the particle. In addition, the position of the particle must be monitored and the laser power varied to compensate for any change in particle mass by changing the scattering force. In this work, we have demonstrated that an aerosol droplet can be trapped and manipulated in a single-beam gradient-force optical trap¹ (optical tweezers). In contrast to levitation, the gradient force dominates the scattering force and a three-dimensional trap is formed at the focal spot of a tightly focused laser².

A schematic of the tweezing instrument is shown in Figure 1(a). The optical tweezing instrument has been described in detail in an earlier publication³. A mist of aerosol droplets with a size distribution peaking in particle number at $<1 \mu\text{m}$ is generated with an ultrasonic nebuliser. Both decane and water droplets have been trapped directly from a decane or water aerosol mist using the optical tweezers for timescales of hours. Trapping is achieved with either a 63x water immersion objective (NA 1.2) or a 60x oil immersion objective (NA 1.4). Unlike most optical tweezing experiments, trapping is performed with an argon-ion laser operating in the visible at a wavelength of 514.5 nm. This wavelength is chosen as it corresponds to the minimum in the complex refractive index of water⁴, avoiding any droplet heating. In addition, the water droplets are doped with sodium chloride to lower the vapour pressure of the droplet to a value close to the relative humidity that can be achieved in the cell.

The axial trapping efficiency can be estimated by measuring the lowest power at which the droplet is retained in the trap by progressively lowering the laser power until the droplet falls out^{5,6,7}. The dependence of the minimum trapping power on aerosol droplet size is illustrated in Figure 1(b). Water droplets

can be trapped at trapping powers as low as 2 mW, and decane droplets at powers below 1 mW. The axial trapping efficiencies are 0.07 ± 0.02 and 0.1 ± 0.04 for water droplets trapped with the water and oil immersion objectives respectively. An axial trapping efficiency of 0.45 ± 0.12 for decane droplets trapped with the oil immersion objective was determined.

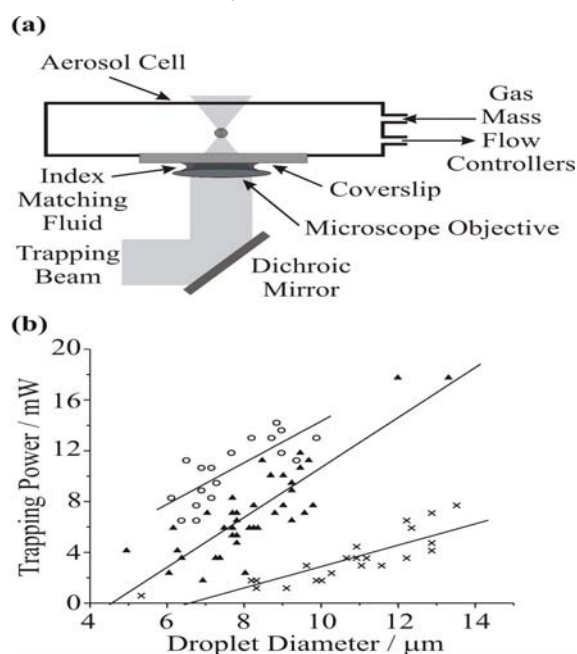


Figure 1. (a) Schematic of the aerosol tweezing instrument. (b) Variation in minimum trapping power with droplet diameter (circles – water droplets trapped with the 63x water immersion objective; triangles – water droplets trapped with the 60x oil immersion objective; crosses – decane droplets trapped with the 60x oil immersion objective) (Phys. Chem. Chem. Phys. 6 4924 (2004) Reproduced by permission of the PCCP Owner Societies).

Cavity Enhanced Raman Scattering

The Raman scattering from the trapped droplet was collected in the backscattered geometry, collimated by the objective lens, passed through a notch filter, and focused onto the entrance slit of a 0.5 m spectrometer (1200 g/mm grating) coupled with a CCD, giving rise to a spectral resolution of 0.05 nm. For the aqueous droplets in the size range studied here, 4-14 μm in diameter, the Raman scattering not only reflects the inelastic scattering process, but also the droplet size through quantum electrodynamics. At discrete wavelengths, referred to below as *whispering gallery modes* (WGMs)⁸, light can undergo total internal reflection each time it encounters the droplet interface. An integer number of wavelengths form a standing wave within the droplet and a cavity quality factor can be defined that determines the lifetime of the light circulating within the droplet. The light can circulate for timescales of nanoseconds, giving rise to metres of path length in a droplet that may be only a few microns in diameter.

WGMs can provide a mechanism for optical feedback, with the simultaneous presence of the Raman light trapped at WGM

wavelengths and the illuminating laser wavelength leading to stimulated Raman scattering. Thus, Raman spectra from water droplets a few microns in diameter reflect both the spontaneous Raman scattering, occurring within the OH stretching band of water, and the stimulated Raman scattering occurring at WGM wavelengths. In a Raman scattering spectrum, stimulated Raman structure appears superimposed on a spontaneous Raman background. An example of this is shown in Figure 2. WGMs are defined in terms of the number of wavelengths of light circulating around the droplet edge (the mode number, n), the polarization of the mode (transverse electric, TE, or transverse magnetic, TM) and the mode order that defines the radial dependence of the mode.

A sequence of three spectra are shown in Figure 2 for water aerosol droplets of radii 5.103, 4.547 and 3.918 μm trapped in the optical tweezers. With decreasing droplet size, the mode structure becomes more separated and less intense. The wavelengths at which the WGMs lead to stimulated Raman scattering can be used to determine the droplet radius with nanometre accuracy by comparing the experimental resonant wavelengths with Mie scattering calculations^{9, 10}.

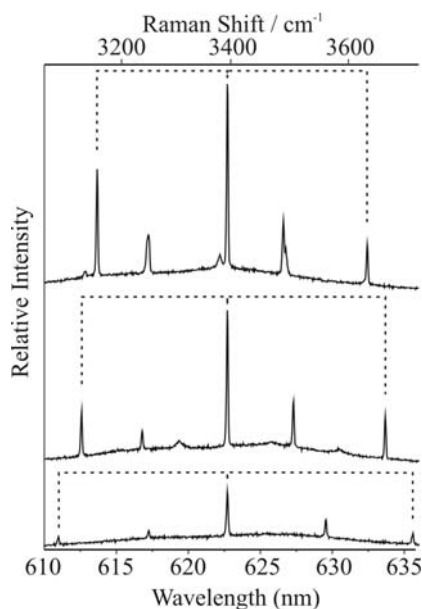


Figure 2. CERS fingerprints of tweezed aqueous droplets of radii 5.103 (top), 4.547 and 3.918 μm (bottom). The underlying continuous spontaneous Raman band is evident, with structure from stimulated Raman scattering at WGM wavelengths superimposed. The wavelengths of the resonances can be used to determine the size of the droplet (Phys. Chem. Chem. Phys. 6 4924 (2004) Reproduced by permission of the PCCP Owner Societies).

Probing Evolving Droplet Sizes

With cavity enhanced Raman scattering providing an accurate method for determining droplet size, the dependence of droplet composition and size on the gas-phase conditions surrounding the droplet can be probed in detail for a single droplet. For example, Figure 3 illustrates the variation in size of a trapped aqueous droplet over a period of approximately 40 seconds. As the local relative humidity around the droplet varies, the equilibrium size of the droplet varies according to Kohler theory. In this sequence of spectra variations in droplet radius as low as 9 nm can be probed. This will provide a rigorous method for investigating the thermodynamic properties of aerosol droplets and for testing the equilibrium droplet sizes predicted by present theories.

To explore the droplet dynamics in detail, it is essential that the possibility of droplet heating is avoided. In detailed studies, we

have demonstrated that the temperature of the droplet is perturbed by $\ll 1$ K during the course of a measurement. Thus, droplet heating can be ignored.

In ongoing work, we have also demonstrated that the uptake of ethanol and water on aqueous droplets can be studied with high temporal resolution and over timescales of minutes. This work takes advantage of our ability to determine the size with high accuracy, and growth rates as low as 0.1 nm/s have been measured.

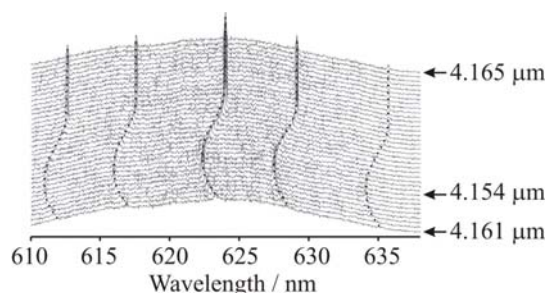


Figure 3. Evolution in the CERS fingerprint over a period of 40s reflects the varying size of the droplet as it responds to local changes in relative humidity. A size change as small as 9 nm in radius is clearly evident (Phys. Chem. Chem. Phys. 6 4924 (2004) Reproduced by permission of the PCCP Owner Societies).

Conclusions and Future Work

By coupling aerosol optical tweezing with cavity enhanced Raman scattering, we can control and manipulate aerosol droplets and probe their evolving size with nanometre accuracy. This can provide a novel combination of techniques for characterising the fundamental factors that govern the dynamics of a single aerosol droplet¹¹. Ongoing work is applying this technique to the uptake of trace gases and the coagulation dynamics of micron sized liquid aerosol droplets.

References

1. A Ashkin, J M Dziedzic, J E Bjorkholm and S Chu, *Opt. Lett.* 11 288 (1986)
2. J E Molloy and M J Padgett, *Contemp. Phys.* 43 241 (2002)
3. J M Sanderson and A D Ward, *Chem. Commun.* 9 1120 (2004)
4. J H Seinfeld and S N Pandis, *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, John Wiley & Sons, New York City (1998)
5. R Omori, T Kobayashi and A Suzuki, *Opt. Lett.*, 22 816 (1997)
6. N Magome, M I Kohira, E Hayata, S Mukai, K Yoshikawa, *J. Phys. Chem. B*, 107 3988 (2003)
7. W H Wright, G J Sonek and M W Berns, *Appl. Phys. Lett.* 63 715 (1993)
8. S C Hill and R E Benner, *Optical Effects Associated with Small Particles*, ed. P W Barber and R K Chang, World Scientific, Singapore (1988)
9. R Symes, R M Sayer and J P Reid, *Phys. Chem. Chem. Phys.* 6 474 (2004)
10. R M Sayer, R D B Gatherer, R Gilham and J P Reid, *Phys. Chem. Chem. Phys.* 5 3732 (2003)
11. R J Hopkins, L Mitchem, A D Ward and J P Reid, *Phys. Chem. Chem. Phys.* 6 4924 (2004).